MINISTRY OF SCIENCE AND HIGHER EDUCATION OF THE RUSSIAN FEDERATION
RUDN UNIVERSITY

ADVANCES IN SYNTHESIS AND COMPLEXING

Book of abstracts

The Sixth International Scientific Conference

Organic Chemistry
Inorganic and Coordination chemistry
Physical and Colloidal Chemistry

26–30 September 2022
Moscow, RUDN University

Moscow
2022

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Успехи синтеза и комплексообразования = Advances in synthesis and complexing : сборник тезисов шестой Международной научной конференции : Москва, РУДН, 26–30 сентября 2022 г. – Москва : РУДН, 2022.
ISBN

The book of abstracts of the Sixth International Scientific Conference: «Advances in Synthesis and Complexing» which was held from 26 to 30 September 2022 based on chemical departments of Faculty of Science of RUDN University includes abstracts of lectures of plenary, key-note and invited speakers, oral reports and poster session.

The present publication was designed to popularize scientific research activity in the field of chemistry and to discuss modern chemical problems on the international level. The digest is intended for scientists, students, postgraduates and for wide range of readers interested in problems in chemistry.

ISBN

Dear Colleagues,

For the sixth time, Peoples' Friendship University of Russia brings leading chemists together at the conference "Advances in Synthesis and Complexing". Scientists from Armenia, Belarus, Great Britain, India, Spain, Mexico, Portugal, USA, Turkey, Japan and Russia will present the results of their research.

I'd like to personally welcome each of you to the 6 - th International conference "Advances in Synthesis and Complexing". Series of conferences "Advances in Synthesis and Complexing" has attracted many leading scientists. I am sincerely grateful to all the scientists who decided to take part in our conference. Throughout this conference, I ask you to stay engaged, proactive and help us shape the future of RUDN University. I hope that you will find your participation in the 6-th International Conference "Advances in Synthesis and Complexing" intellectually stimulating and enjoyable, and this conference will become a valuable platform for promoting cooperation between people who share scientific interests in the field of organic, inorganic and physical chemistry, as well as interdisciplinary research.

The conference "Advances in Synthesis and Complexing" in 2022 is dedicated to the 100th anniversary of the birth of Academician Vladimir Mikhailovich Gryaznov, who founded the Department of Physical and Colloidal Chemistry at the RUDN University, and also made a number of world-class discoveries.

Best regards,

Prof. Dr. Leonid G. Voskressensky, Chair of the organizing committee,
Dean of the Science Faculty, RUDN University

ON THE 100TH ANNIVERSARY OF ACADEMICIAN VLADIMIR MIKHAILOVICH GRYAZNOV

Academician Vladimir Mikhailovich Gryaznov was engaged in research in the field of heterogeneous catalysis. Vladimir Mikhailovich elucidated the mechanism of hydrogen redistribution in cycloolefins and discovered the property of two-dimensional metal vapor to catalyze certain organic reactions with assistance of graduate students Viktor Dmitrievich Yagodovsky and Vladislav Ildifonsovich Shimulis. This phenomenon was registered as a discovery (priority 09/16/1960 diploma No. 312).

A logical continuation of studies of the catalytic properties of metals in the presence of hydrogen was a series of works that formed a new direction in physical chemistry - membrane catalysis. In 1964, Vladimir Mikhailovich theoretically substantiated and experimentally confirmed the thermodynamic, energy and kinetic advantages of carrying out catalytic reactions with the selective introduction or removal of a substance through a membrane. The phenomenon of conjugation of reactions on membrane catalysts was also recorded as discovery by Vladimir Mikhailovich Gryaznov (priority 06/12/1964, diploma No. 97). The terms "membrane catalysis" and "composite membrane catalyst" were first introduced into scientific research by Academician Gryaznov.

Of great practical importance are his studies on the development of theoretical foundations for the creation of materials for the production of membrane catalysts and reactors for their industrial application. In these experiments, composite membranes with an active metal layer on a solid polymer or porous inorganic base were developed.

In 1962, Vladimir Mikhailovich, at the invitation of Sergei Vasilyevich Rumyantsev, the first rector of the Patrice Lumumba Peoples' Friendship University (now the Peoples' Friendship University of Russia, RUDN University) began to create the Department of Physical and Colloidal Chemistry at the Science Faculty of the University, head of which he was until the end of his life - from 1962 to 2001.

The team of the scientific school "Perspective membrane-catalytic and catalytic systems for the petrochemical industry", created by Academician Gryaznov at the Department of Physical and Colloidal Chemistry, has developed more than 20,000 new catalysts and catalytic systems, received about 100 copyright certificates and patents, has trained hundreds of professionals in the field of physical and colloid chemistry.

At the Peoples' Friendship University, Vladimir Mikhailovich Gryaznov prepared course programs and lectured on physical chemistry, the structure of matter, catalysis, the history of chemistry and the methodology of scientific creativity. In 1989, Vladimir Mikhailovich Gryaznov and Natalya Vsevolodovna Orekhova published a book titled “Catalysis by noble metals. Dynamic Features”. His monograph "Methodology of Scientific Creativity" was published in 2000 and recommended by the Ministry of Education as a textbook for higher educational institutions.

During his creative activity, Academician Gryaznov published more than 500 scientific articles and works. Vladimir Mikhailovich Gryaznov was the editor-in-chief of the Journal of Physical Chemistry for almost 20 years, a member of the editorial boards of the international journals Catalysis Letters, Catalysis Today, and chairman of the Council on Petrochemistry of the Russian Academy of Sciences. He was repeatedly invited to give lecture courses in the USA, in Europe, Africa and Latin America. Academician V.M. Gryaznov was the author of the script for the popular science film The Secret of Substance, which received an award at the Karlovy Vary Film Festival.

In memory of Academician Gryaznov, RUDN University approved his nominal scholarship, which is annually awarded to the most deserving students of the chemical direction of the Science Faculty.

BIOGRAPHY OF ACADEMICIAN GRYAZNOV

Vladimir Mikhailovich Gryaznov was born in Moscow on July 17, 1922 in a family of employees.

1939 - graduated with honors from secondary school № 73 and enrolled in Faculty of Chemistry of Moscow State University.

Since July 1941, after the second year at the university, he took part in the World War II (Eastern Front) as part of the fighter battalion of the Krasnopresnensky district. Participated in the construction of the Northern Defense Sector of Moscow. In December 1941 he was demobilized for health reasons.

From February 1942 he continued his studies at Moscow State University. Vladimir Mikhailovich Gryaznov began his first scientific research under the guidance of Professor Andrei Vladimirovich Frost, who headed the Department of Physical Chemistry at Moscow State University.

In 1944, Vladimir Mikhailovich Gryaznov graduated with honors from the Faculty of Chemistry of Moscow State University, having defended his thesis "The nature of the active centers of aluminosilicate catalysts." Went to graduate school. In 1945, the results of his graduation research were published in the journal «Reports of the Academy of Sciences of the USSR».

Vladimir Mikhailovich began his pedagogical activity in 1945 while still studying in graduate school and continued as an assistant since 1947.

In 1948 he defended his dissertation for the PhD degree in Chemistry.

In 1949 he published jointly with Professor Frost a monograph on statistical calculation methods in thermodynamics - the first such book in the USSR, which for many years was used in institutions of higher education.

In December 1950 he received the academic title of Associate Professor.

In 1962, Vladimir Mikhailovich Gryaznov defended his dissertation for the degree of Doctor of Chemical Sciences on the topic "Study of the kinetics and mechanism of transformations of some hydrocarbons on metals".

In 1962, Vladimir Mikhailovich, at the invitation of the first rector of RUDN University S.V. Rumyantsev began to create the Department of Physical and Colloidal Chemistry at the Faculty of Sciences of the Peoples' Friendship University of Russia, the head of which he was until the end of his life from 1962 to 2001.

In 1963 he was approved for the degree of Doctor of Chemical Sciences and the academic title of professor.

In 1964, Vladimir Mikhailovich organized a membrane catalysis laboratory at the Institute of Combustible Fossils of the USSR Academy of Sciences (today A. V. Topchiev Institute of Petrochemical Synthesis), which he headed until 2001. Under the leadership of V.M. Gryaznov at RUDN University and at A. V. Topchiev Institute of Petrochemical Synthesis were defended about 40 Ph.D. dissertations and 6 doctoral dissertations.

In 1978, Vladimir Mikhailovich Gryaznov became the "Honored Worker of Science and Technology of the RSFSR" for his work in the field of industrial catalysis.

In 1981 he was elected a corresponding member of the USSR Academy of Sciences (now the Russian Academy of Sciences, RAS).

In 1990, Vladimir Mikhailovich Gryaznov was elected an academician of the USSR Academy of Sciences.

May 19, 2001 - the last day of the life of Academician Vladimir Mikhailovich Gryaznov.

MEMORIES ABOUT ACADEMICIAN GRYAZNOV

In 1969, Reports of the Academy of Sciences of the USSR published an article by Vladimir Mikhailovich Gryaznov "Catalysis on membranes with selective permeability", which marked the emergence of a new scientific direction in chemistry, "membrane catalysis".

Conducted by V.M. Gryaznov and his collaborators, the studies have shown that the obtained catalysts and the proposed technologies for their application are significantly superior to the results of foreign scientists. Among the received titles of protection were not only USSR author's certificates, but also patents from Great Britain, Germany, Italy, the USA, France and Japan. And discoveries made by Vladimir Mikhailovich and his collaborators of the phenomenon of conjugation of reactions on membrane catalysts and the properties of two-dimensional metal vapor to catalyze the reactions of organic compounds finally confirmed the leading role of Soviet and Russian science in this field of knowledge.

Academician of the Russian Academy of Sciences, Prof. Dr., Yulia Germanovna Gorbunova

Scientific achievements, the brilliant talent of a scientist, and a huge capacity for work earned Vladimir Mikhailovich Gryaznov a well-deserved authority in international scientific circles. In 1993, in France, Vladimir Mikhailovich opened the work of the First European Congress on Catalysis with a plenary report "Catalysis on membranes", and in 1996 in Italy he made a report for the UN Economic Commission on the catalysts developed at RUDN University, which allow solving problems of ecology and climate change. In 1994, I had the opportunity to speak in The Hague with the widow of a prominent chemist, Jan Hendrik de Boer. In the bookcase I saw his book "The Dynamic Character of Adsorption" in Russian, edited by Vladimir Mikhailovich Gryaznov. After reviewing it, I found Vladimir Mikhailovich's signature as a keepsake for the author.

Leading Researcher, Zelinsky Institute of Organic Chemistry, Prof. Dr., Margarita Aleksandrovna Ryashentseva

In the biography of Vladimir Mikhailovich Gryaznov there was a place for a feat when he went to war as a volunteer, and for great scientific achievements, discoveries made, and success in pedagogical activity. He never wasted time on trifles and therefore managed to do a lot. The work begun by academician Gryaznov is continued today by his numerous students.

Chairman of the All-Union Chemical Society named after D.I. Mendeleev, Academician of RAS, Prof. Dr., Aslan Yusupovich Tsivadze

In the life of Vladimir Mikhailovich Gryaznov there were a lot of important events that influenced the formation of his personality as a scientist and a person. Member of the World War II, excellent student of the Faculty of Chemistry of Moscow State University, who is interested in science, teacher and recognized world-class scientist, who has gone from assistant to professor, Doctor of Chemical Sciences, head of department and academician. It talks about the great diligence, attention to people and the highest professionalism of Vladimir Mikhailovich. It was precisely these qualities that Vladimir Mikhailovich brought up in his numerous students. Everyone who comes to study or work at the Department of Physical and Colloidal Chemistry, RUDN University, founded by him, invisibly feels his attention and support.

Head of the Department of Physical and Colloidal Chemistry, RUDN University from 2017 to the present, Dr., Alexander Genrikhovich Cherednichenko

Remembering Academician Gryaznov, it must be noted that he was not only a well-known scientist and teacher, but also very educated, sensitive, and attentive person. Despite his high status, every time he came to the department he, first of all, went around all the laboratories and asked each employee, teacher, graduate student and student if there were any problems, if his help was needed. After listening to the interlocutor, Vladimir Mikhailovich always found the right words and helped in solving work and personal problems. He had the ability to see the essence of even the most confusing situation and immediately determine what actions are needed to be taken to solve it. At a difficult, turning point in my life, he believed in me, my abilities, and strengths, helped me get the necessary knowledge, become a professor and Doctor of Science.

Professor of the Department of Physical and Colloid Chemistry of the RUDN University, Head of the Department from 2001 to 2016, Dr., Yuri Mikhailovich Serov

For me, Vladimir Mikhailovich Gryaznov is not only a Great Scientist, Academician, but, above all, a Teacher! A teacher in science, a teacher in a profession, a teacher in life. He surprisingly combined a variety of virtues: strength of character with worldly wisdom, unusual approaches to making global decisions with the ability to find an approach to each interlocutor, high demands and organization with benevolence and warmth. I am grateful to Vladimir Mikhailovich for wise advice, for the knowledge gained, for my small and big achievements. It is a great honor for me to be a student of Vladimir Mikhailovich Gryaznov!

Associate Professor of the Department of Physical and Colloidal Chemistry of RUDN University, Acting head of the department in 2016-2017, Ph.D. Tatyana Fedorovna Sheshko

The reason for my acquaintance with Vladimir Mikhailovich Gryaznov was the proposed trip to Italy to study the results obtained at D. Mendeleev University of Chemical Technology of Russia catalytic membranes. However, there were problems during the travel arrangements. Then Vladimir Mikhailovich suggested that we can conduct experiments at the facilities of the Department of Physical and Colloidal Chemistry of RUDN University. It was the joint work with Academician Gryaznov that determined the direction of our research for many years. The then-established research group at D. Mendeleev University of Chemical Technology of Russia continues to work successfully at the present time.

Professor D. Mendeleev University of Chemical Technology of Russia, Dr., Vladimir Vsevolodovich Skudin

AWARDS

1978 - for scientific achievements, Vladimir Mikhailovich Gryaznov became an Honored Worker of Science and Technology of the Russian Federation, received the Gold Medal of VDNKh of the USSR.

1981 - elected as corresponding member, and in 1990 - an academician of the Academy of Sciences of the USSR (now - the Russian Academy of Sciences).

1995 - for success in creating new materials for membranes, he received the RF Prize in the field of science and technology.

1998 - The Presidium of the Russian Academy of Sciences awarded Academician Gryaznov the A.A. Balandin prize for a series of works in the field of catalysis.

Among the awards of Vladimir Mikhailovich Gryaznov:

- Medal "For the Defense of Moscow",
- The order of Lenin,
- Order of the Badge of Honor,
- Order of the October Revolution.

Plenary Lectures

Progress in the development of the universal theory of catalysis

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The development of a new generation of efficient catalysts based on platinum group metals and, above all, palladium catalysts, determined the progress in modern organic synthesis. According to recent studies, the dynamic nature and relationship between homogeneous and heterogeneous catalysis has been established for C–C cross-coupling reactions [1]. The participation of dynamic catalysis was experimentally proven for C-S bond formation earlier earlier [2]. Catalytic pathways that go beyond the generally accepted assumptions have been found for C-H functionalization reactions and hydrosilylation reactions.

The dual nature of carbon groups and the participation of carbene centers have been shown for the catalytic trimerization of acetylene [3]. The use of artificial intelligence methods for the analysis of catalysis experiments identified highly active catalytic centers with TON ~ 10^9 and led to the discovery of the concept of Totally defined catalysis [4] and the creation of new methods for understanding the nature of homogeneous catalysis [5].

Recent results and cutting-edge progress in the field of fine organic synthesis will be presented and discussed in view of development of a universal theory of catalysis.

The author thanks Scientific Schools grant NSh-5199.2022.1.3 for the support

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Metal-ligand synergy in coordination chemistry

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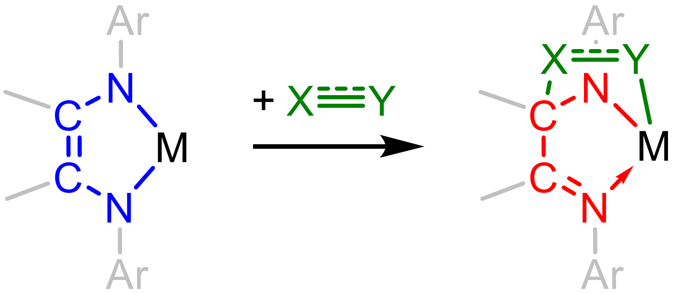
A remarkable π delocalization of an electron density within metalacycles in metal complexes of chelating ligands results in *metalols* whose reactivity is rather different of *classical Werner chelates*. Chemical transformations of *metalols* involve usually several chemical bonds including those of the central metal atom. A *synergy* between the metal and the ligand (organic part of metalacycle) becomes evident in the course of the reactions of *metalols* with unsaturated substrates. To bind the substrates *metalols* offer metal's vacant orbitals, while the ligand and the substrate provide for the electrons for the formation of new chemical bonds.



This work has been supported by the Russian Science Foundation (project № 19-13-00336P)

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Advances in synthesis and material chemistry of tetrapyrrolic compounds

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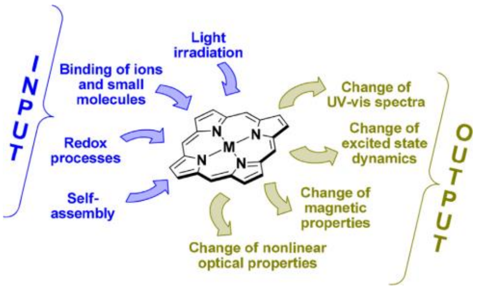
Functional properties of macrocyclic tetrapyrrolic ligands are widely exploited in natural and artificial systems. The molecular structure of free base porphyrins and their complexes can be precisely adapted to the target function and the operating environment by varying the substituents on the macrocycle. Another tool widely used by Nature to increase the functional performance of tetrapyrroles is the coordination and supramolecular chemistry approaches. Such approaches lead to wide range of application of synthetic porphyrinoids [1].

From the other side, the possibility to control and tune the properties of a single molecule attracts scientists from ancient times to our days. This is well confirmed by the Nobel Prize in Chemistry in 2016 that was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa "For the design and synthesis of molecular machines". High sensitivity of physical-chemical properties of porphyrinoids to external influence paved them the way to the area of molecular switches with various types of actions. From this viewpoint, porphyrinoids can be regarded as information processing systems, which convert input physical-chemical data into output signals (Figure) [2].



This report is summarized the recent results on the synthetic and material chemistry of tetrapyrrolic compounds including the results of our scientific group [3-17].

This work was supported by the Russian Science Foundation (project No 19-13-00410P)

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Hydrogen-mediated C-C bond formation

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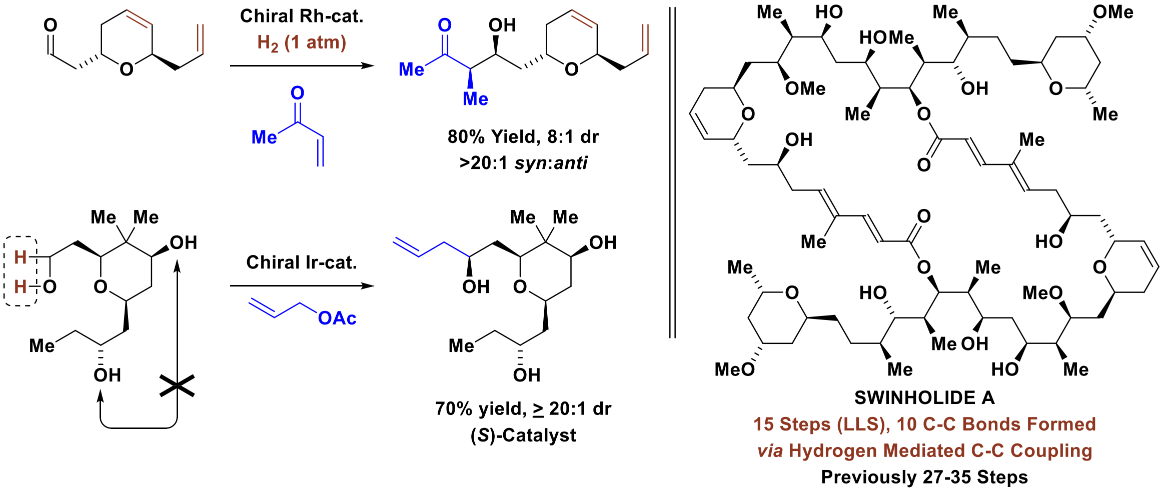
Stereo- and site-selective methods for the modification of unprotected organic compounds via addition or redistribution of hydrogen are natural endpoints in the advancement of methods for chemical synthesis.[1] Our laboratory has developed a broad, new family of reductive C-C couplings that merge the characteristics of catalytic hydrogenation and carbonyl addition. Hydrogenation or transfer hydrogenation of abundant π-unsaturated feedstocks in the presence of C=X (X = O, NR) bonds delivers products of carbonyl or imine addition. In related hydrogen auto-transfer reactions, alcohols served dually as reductants and carbonyl proelectrophiles, enabling direct conversion of lower alcohols to higher alcohols. Such hydrogen-mediated C=X additions bypass non-native structural elements (e.g. premetalated reagents, directing/protecting groups and chiral auxiliaries) for greener and more scalable chemical synthesis.[1-4]



This work was supported by the Robert A. Welch Foundation (F-0038) and the NIH-NIGMS (RO1-GM093905 & RO1-GM069445)

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Organic Chemistry Section Key-note Speakers

Fluorinated pyridinylthio-fragment as a redox active group in photocatalysis

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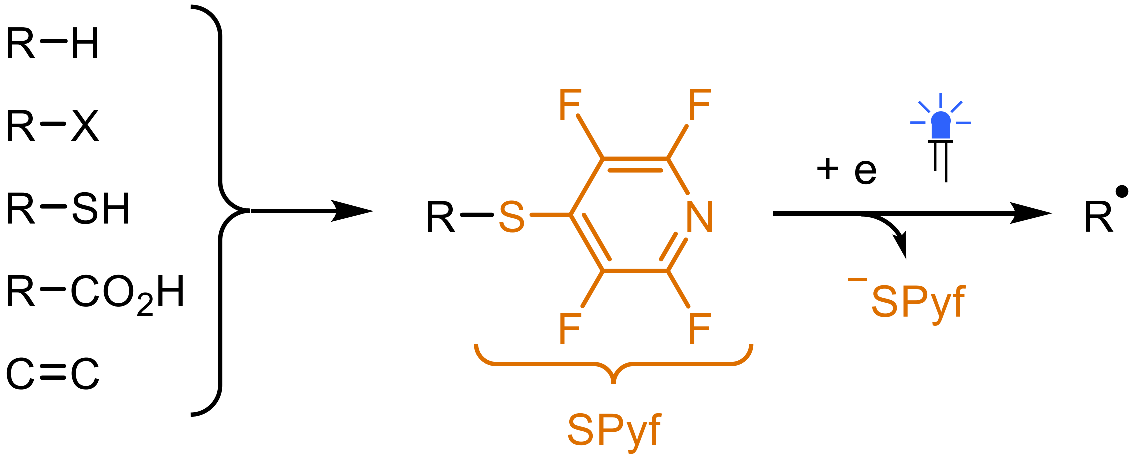
Fluorinated pyridinylthio-fragment (PyfS) serves as efficient leaving group for the generation of alkyl radicals under photoredox conditions. Compounds bearing this group can be easily obtained by variety of methods such as C-H activation, nucleophilic substitution, hydrothiolation of alkenes, and decarboxylative thiolation reaction. Readily available pentafluoropyridine serves as a starting compound for the PyfS auxiliary group.



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Selective inhibitors of BET-proteins as epigenetic strategy in oncology

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BET proteins have multiple functions, including the initiation and elongation of transcription and cell cycle regulation. BET inhibitors provide a novel approach to epigenetic anticancer therapy. These inhibitors exhibit selectivity for tumor cells by preferentially binding to regions of DNA critical for the transcription of genes that determine a cell's identity.

Using the combination of different computational and experimental methods: virtual screening and FRET-methodologies, organic and diversity-oriented target-focused synthesis (DOTS), as well as crystallographical and biochemical approaches, several inhibitors of human BET-proteins with unforeseen selectivity profiles were identified. The hit-compounds contain xanthine, triazolopyrimidinyl and tetrahydrobenzazepine scaffolds and are able to bind preferentially to Brd4(BD1) and Brds(BD1) sites of BET-proteins and to provide the dose-response downregulation of c-Myc levels.

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Functional supramolecular systems using light as an energy source

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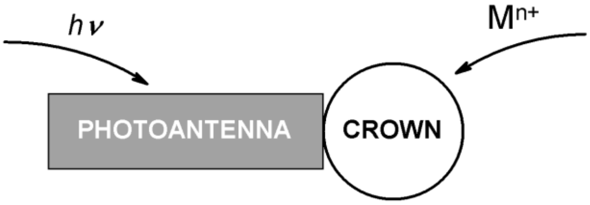
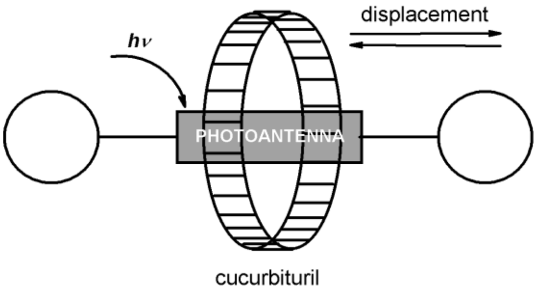
We propose a new unique class of polyfunctional photoactive compounds: unsaturated dyes functioning as photochromes, fluorophores and ionophores [1]. A large body of research has been performed for their synthesis, determination of their spatial structures, study of self-assembly features to give supramolecular systems, and also study of fluorescent, photochemical and complexing properties.

Resulting from the research, we elaborated for the first time universal supramolecular meccano, allowing one to accomplish building-up, with using a limited number of complementary compounds with participation of metal cations and hydrogen bonds, photoactive supramolecular systems of varied architecture with adjusted properties [2]. Within the same class of compounds one can construct in solution, solid and at the air-water interface new types of photoswitchable supramolecular devices, photocontrolled supramolecular machines, photoactive monolayers and monocrystals susceptible to all of the key photoprocesses.



supramolecular devices



supramolecular machines

The high practical value of these studies deserves attention. They provide a new strategy for the design of materials for supramolecular and nanophotonics, which was demonstrated, first of all, by the creation of practically important sensor [3] and photochromic materials [4-6].

This work was supported by the Russian Science Foundation (grant No. 22-13-00064)

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Synthesis of Layered double hydroxides (LDHs) for environmental remediation

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The increased globalization of industries and anthropogenic activities has put environmental ecosystems and human health at serious risk from rising concentrations of diverse pollutants. Layered double hydroxides (LDHs) are 2D hydrotalcite-like compounds containing brucite-like cationic layers, with exchangeable anions between layers and water molecules holding the layered structures. By virtue of their unique structures, they have exceptional anion exchange capacity, superior thermal stability, an abundance of active sites, and amazing recyclability. Owing to their highly tunable composition and structures, they have been applied in a wide range of fields. In the case of environmental remediation, LDHs have been widely used as catalysts, catalyst precursors, or catalyst supports in advanced oxidation processes (AOPs) to decompose organic pollutants in water. LDHs have been applied in processes such as heterogeneous Fenton-like processes, sulfate radical-based AOPs, photocatalysis, sonocatalysis, adsorption, and membrane modification, and coupled processes such as photo-assisted electrochemical, Sono-photocatalytic, and electro-Fenton processes. The type of water pollutants that have been effectively removed by LDHs from water environments include pharmaceuticals, organic dyes, inorganic anions, heavy metals, etc. Combining LDHs with other materials is a common practice to enhance surface properties and catalytic performances. The doping of cations into the lattice of LDH creates adsorption sites and induces lattice defects. Synergistic effects can be obtained after hybrid formation and new properties can arise from this combination. Thermal treatment of LDHs produces metal oxides called layered double oxide (LDO) with narrow bandgap and high surface areas. Finally, future research in LDH-based catalysts should focus on developing green and efficient synthetic methods, optimizing material design, and promoting their practical application, based on the current challenges.

I would like to thank the Scientific and Technical Research Council of Turkey for funding the research project (TUBITAK, Project Number: 120Y350)

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Development of 1,2-azaborine-fused heterocycles and their novel functionalization

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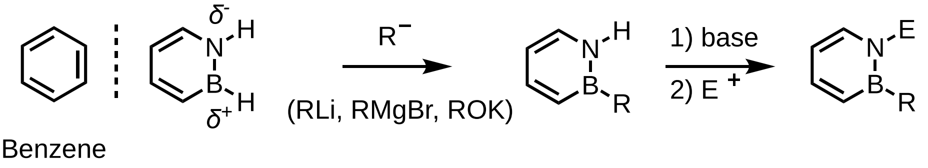
Heterocycles containing boron and nitrogen atoms in their ring systems, the so-called BN heterocycles, have attracted immense interest in various research fields. The structure of azaborines are isoelectronic to that of benzene, and much attention has been paid to the synthetic chemistry of azaborines and their π-extended molecules. Recent synthetic studies have not only generated numerous BN heterocycles but also elucidated their significant utilities in material science, ligand chemistry, and medicinal chemistry as well.

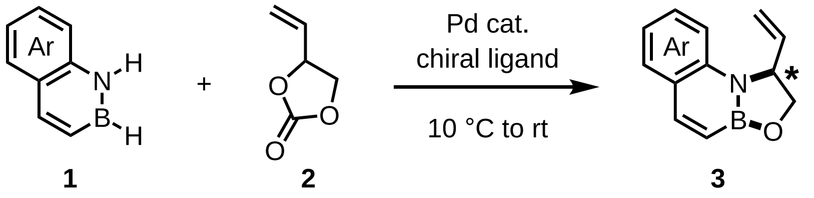
Owing to the unique structures and widespread application of BN heterocycles, direct functionalization of these compounds, especially 1,2-azaborines has been vigorously invetigated in the last decade. However, due to a lack of understanding of their unique reactivity, synthetic methodologies for a range of functionalized azaborines have not been well developed. Indeed, current methods for N-H or B-H substitution require stoichiometric amount of strong bases, which resulted in limited structural diversity of these hetero atoms. In addition, asymmetric synthesis of BN heterocycles has scarcely been explored. To further expand the complexity of 1,2-azaborines, it is highly required to develop catalytic asymmetric N-H or B-H functionalization methods under mild conditions.

In this work, we have developed a palladium-catalyzed N-H/B-H double functionalization of 1,2-benzazaborines **1** via cycloaddition with vinylethylene carbonate **2**. The reaction proceeded smoothly under room temperature to produce novel polycyclic oxazaborolidines **3** with good functional group tolerance. Moreover, highly enantioselective cycloaddition was successfully demonstrated by employing the chiral phosphoramidite ligand, which is the first report of the catalytic asymmetric direct functionalization of 1,2-azaborines. Further derivatization of a cycloaddition product via transition-metal catalyzed transformation of the vinyl group afforded various functionalized BN heterocycles with retension of configuration.

(a) Functionalization of 1,2-azaborine as a benzene isostere



(b) This work: Pd-cat. enantioselective N-H/B-H double activation of 1,2-azaborines **1**



1 **2** **3**

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Dichlorodiazadienes - new building blocks for heterocyclizations

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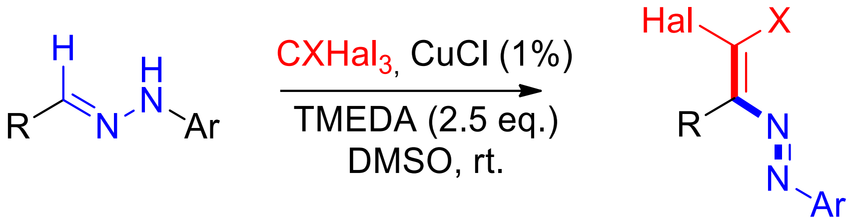
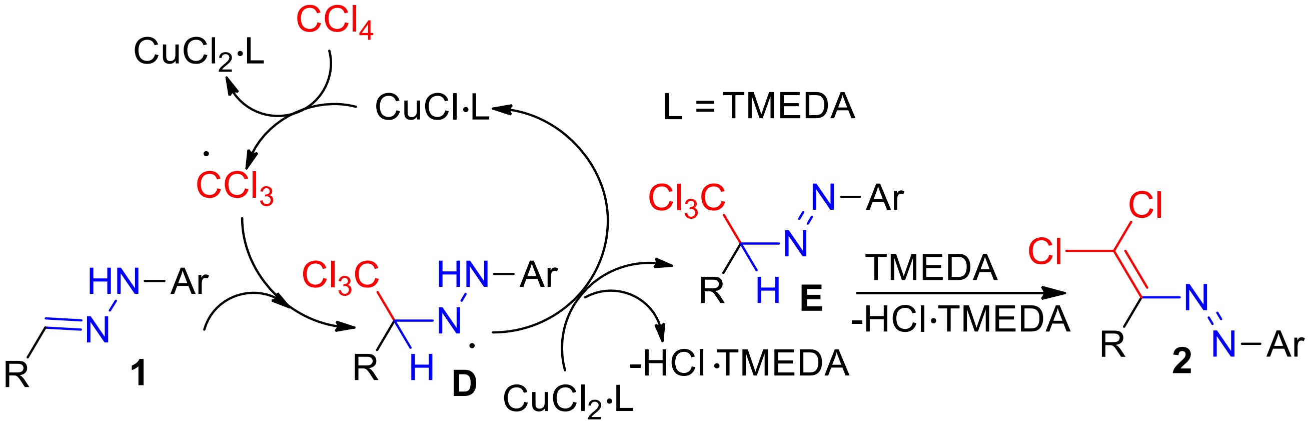
Recently, we found that the reaction with hydrazones catalyzed by copper salts is of a general nature, and N-substituted hydrazones can participate in it. As a result, based on the interaction of N-monosubstituted hydrazones with polyhaloalkanes, we developed a new reaction for creating carbon-carbon bonds with the formation of 1,2-diazabut-1,3-dienes. This high-efficiency copper-catalyzed conversion has broad synthetic capabilities and allows the process to be carried out in a convenient one-pot mode, starting from readily available aldehydes and hydrazines.



Hal = Cl, Br; X = Cl, Br, CN, CO_2Et, CF_3 37 examples, up to 97 %

The synthetic significance of the obtained halogenated azadienes was demonstrated in reactions with O-, N-, S-, and C-nucleophiles, which opened up access to a number of valuable acyclic and heterocyclic products. Mechanistic studies have shown that this copper-catalyzed transformation occurs with the participation of radical intermediates. Currently, our laboratory is conducting further research on the synthetic application of the halogenated azadienes.



Isothiazoles in the design and synthesis of biologically active substances and ligands for metal complexes

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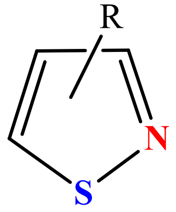
Isothiazoles are 1,2-azoles, with two heteroatoms in a five-membered heterocycle (sulfur and nitrogen). They are widely utilized in medicinal chemistry and organic synthesis due to unique properties.

Isothiazole itself was first synthesized in 1956 when other 1,2-azoles were already well studied. But its benzannelated derivative – saccharin has been known since 1879, when it was isolated from the oxidation products of 2-toluene sulfonamide. Interest in isothiazoles is constantly growing, and the published data are regularly systematized and summarized in monographs and reviews including our own [1,2].

Among natural bioregulators, isothiazole-containing compounds are presented in few examples: phytoalexins, prostaglandin release inhibitor pronkodin A, and cytotoxin aulosirazol. However, this does not impede the use of the isothiazole nucleus in the creation of a wide variety of bioactive substances. All practically useful derivatives of isothiazole are obtained synthetically.

We presented a brief analysis of the properties of isothiazoles and main characteristics of isothiazole core, summarize the most common approaches to their synthesis, and also present our own results on the chemistry of isothiazole derivatives and their unusual biological action Particular attention will be paid to potentiation effects with drugs and pesticides and to transition metal complexes with isothiazole ligands, including the unique catalytic activity of palladium complexes in cross-coupling reactions under environmentally friendly Green Chemistry conditions. Examples of the synthesis of practically valuable products in an aqueous and aqueous-alcoholic medium with the participation of palladium catalysts with isothiazole ligands are presented.



isothiazole

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Asymmetric organocatalysis: from breakthrough methodology to sustainable catalysts and processes

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In 2021 the Nobel Prize in chemistry was awarded to professors B. List and D.W.C. MacMillan "for the development of asymmetric organocatalysis", a method that uses small organic molecules as catalysts instead of enzymes or metals. This innovation in molecular construction has led to organocatalysts that are convenient in handling and environmentally friendly (green chemistry). They enable facile preparation of massive libraries of enantiomerically enriched compounds for drug design under simple experimental conditions [1].

However, in spite of amazing achievements in this area of research, asymmetric organocatalysis has not been overwhelmingly adopted by the pharmaceutical industry. A majority of primary- or secondary amine-derived organocatalysts are prone to lose their activity over catalytic reaction due to irreversible by-side transformations of intermediate enamines and iminium ions. Tertiary amine-based organocatalysts, which activate reagents via the formation of hydrogen bonds, generally provide inferior stereoinduction in environment friendly media (H_2O, alcohols). Furthermore, column chromatography undesirable for industrial applications is commonly needed to separate chiral organic product and organocatalyst.

We propose useful approach to design sustainable organocatalysts based on incorporation of auxiliary ionic groups in the form of *N*-alkylated or protonated nitrogen heterocycles (imidazole, pyridine, quinolone or piperidine). These structural fragments reduce solubility of the catalyst in reaction media (make it "heterogenic") and facilitate its recovery. They make transition states of catalytic reactions more rigid due to Coulombic interactions and the formation of hydrogen bonds with reagents thus improving the reactions rate and selectivity. Moreover, simple variation of anion and/or cation structure allows regulate phase composition of the catalytic system to attain maximal efficiency and sustainability of the catalytic process. Useful synthetic applications of the proposed approach in asymmetric aldol, conjugate addition and domino reactions widely used for enantioselective synthesis of biologically active compounds are remonstrated [2-6].

This work was supported by the Russian Foundation for Basic Research
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Organic Chemistry
Section
Invited Lectures

Design of novel chemical transformations utilizing nitro-olefins as 1.4-dipoles, and their application to access biologically active materials

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Development of synthetic approaches towards alkaloid analogs containing indolyl fragment is one of the central topics of modern synthetic and medicinal chemistry. We have recently reported on investigations of assuring antitumor properties for 2-aryl-2-(3-indolyl)acetohydroxamic acids, which demonstrated significant cytotoxicity against glioma, melanoma, esophagus cancer and many other cancer cell lines inherently resistant to induction of apoptosis and poorly responding to the treatment with proapoptotic medicines. Expanding the search, we stumbled upon the need for elaboration of novel approaches towards analogous structures non-accessible by standard methods. To this end, during the first stage of the project, an efficient method for activation of 3-(2-nitroethyl)-1H-indoles towards spirocyclization and subsequent rearrangement into 2-(1H-indol-2-yl)acetonitriles was developed. These compounds serve as key precursors for the entire project.

It was proposed that the mechanism of this activation involves stabilization of reactive tautomeric nitronate species in a form of phosphorylated mixed anhydride, formed upon interaction of poorly reactive nitroalkane with phosphoryl chloride in the presence of a base.

Biological activity of these novel 2-(1H-indol-2-yl)acetonitriles was investigated. It was found, that a number of these compounds showed micromolar activity (about 10 μм) against seven cancer cell lines: A549, A549, U373n, HS683, HeLa, HS683, and B16F10.

Reactivity of 2-(1*H*-indol-2-yl)acetonitriles and their immediate precursors 4’H-spiro[indole-3,5’-isoxazoles] in the presence of various nucleophiles under various conditions was investigated. Preparation of alkaloid-like structures employing this approach should be specially mentioned.

This work was supported by grants from the Russian Science Foundation
(Grant number 21-73-20051)

4-Cyanoketones as universal precursors for efficient cascade transformations

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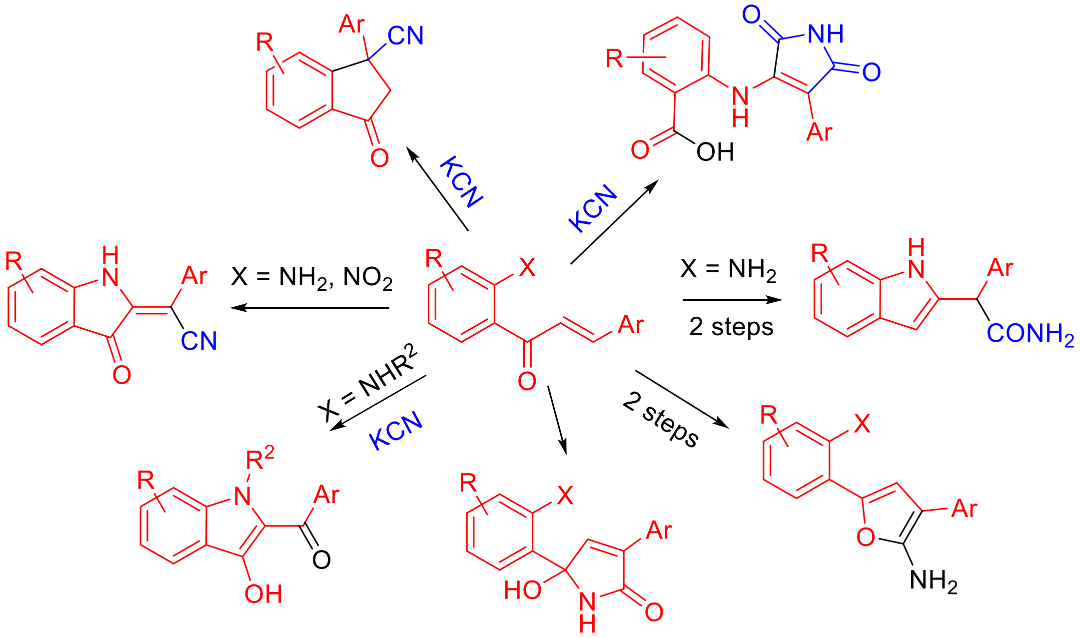
One of the most important tasks of organic chemistry is the constant search for more efficient synthetic methods. Efficient and environmentally friendly synthesis methods, characterized by high yields, a small number of stages, and the use of available reagents, began to take the first place. Cascade transformations are one of the most effective approaches, since they eliminate the intermediate isolation of reaction products, reducing the process time, which translates into less resource consumption and less influence of the human factor.

In the course of our recent studies, we have shown efficient cascade and one-pot transformations based on the reactions of aliphatic nitro compounds in the PPA medium. This made it possible to obtain a number of compounds with high anticancer activity against MDR cells.

The high density of functional groups in 3-cyanoketones has made these compounds another universal platform for the development of cascade transformations. The use of this chemistry in practice makes it possible to carry out a number of unexpected transformations with the formation of previously unknown and hard-to-reach compounds with promising properties.



The study was supported by the Russian Science Foundation (grant № 21-73-10029)

Palladium-catalyzed amination in the synthesis of fluorescent enantioselective detectors

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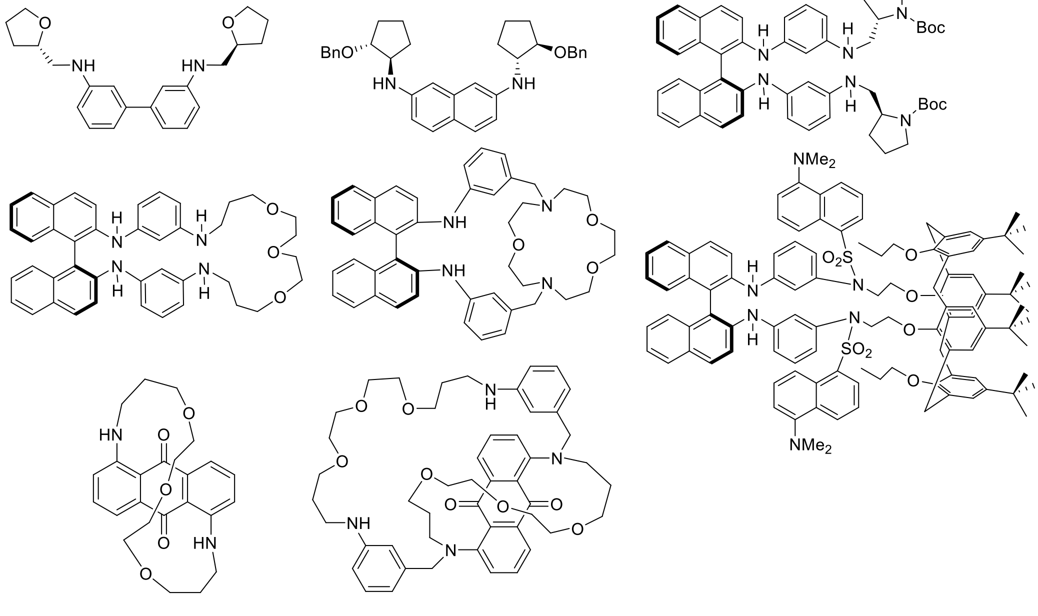
The application of the fluorescent spectroscopy to gain the analytical signal is the most important direction for the development of various molecular chemosensors. Our approach to enantioselective fluorescent detectors utilizes a general method, i.e. Pd-catalyzed amination reactions, allowing to widely vary structures of the compounds which could serve for this purpose. It helps to combine various chiral and fluorophore moieties and to obtain different series of potential detectors comprising various receptor and signal units [1, 2]. Thus we have obtained several families of such compounds based on 3,3'-disubstituted biphenyl, 2,7-disubstituted naphthalene, derivatives of 2,2'-diamino-1,1'-binaphthalene (BINAM). Among these compounds many possess macrocyclic moieties which allow to increase the number of donor N and O atoms participating in analytes binding *via* hydrogen bonds. Compounds of cryptand type were synthesized using derivatives of diazacrown ethers and tetraazamacrocycles. A special case consitute planar-chiral macrocycles – derivatives of 1,5-disubstituted anthracene and anthraquinone. The investigation of the detecting abilities of these compounds has been carried out using 8 pairs of individual enantiomers of amino alcohols, and many of them proved to recognize enantiomers by changing fluorescence in the presence of these analytes (quenching or enhancement, in some cases with the shift of the emission maxima). Also the compounds have been investigated for fluorescent detection of metal cations and some of them were found to be selective towards Cu(II), Hg(II), Pb(II), Zn(II), In(III), Ga(III).



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Novel mesoionic heterocycles and the search of global mesoionic criteria

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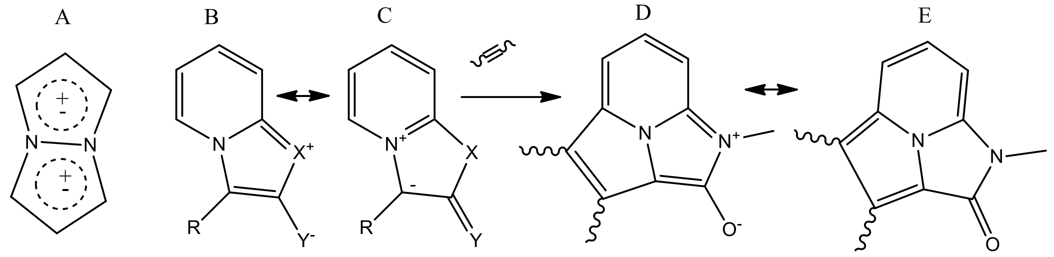
We are working on mesoionic structures for many years [1, 2]. In this communication the synthesis of mesoionic diazapentalenes A and azolo-pyridinium olates (thiolates, imidates) B (C) is presented, Electronic and structural features (based on X-ray and NMR ^{1}H and ^{13}C data, as well as quantum chemistry calculations) are reviewed, giving the choice between resonance structures B and C.



X = S, NR. O; Y = S, NR, O X = NMe.; Y = O

In one case cycloaddition of imidazo-pyridinium olates gave the dipolar structure D (E) which appeared to exist as the covalent molecule E rather than mesoionic structure D [2].
To understand the origin of this phenomena, global analysis of the mesoionicity was undertaken. The concept based on conjugation of (+) and (–) charges in the Kekule- and non-Kekule-like structures was formulated as a rigorous criterion for covalent or mesoionic feature. Four types of mesoionic patterns (given below) based on six-membered rings as the prototypes were analyzed and the theorems (based on removal of special groups from such patterns leading to Kekule or non-Kekule structures) were formulated. More details are given in Ref. [3] and another abstract of the authors in this book.

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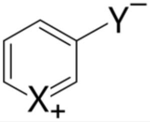	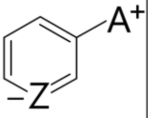	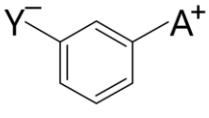	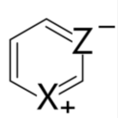

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Catalytic and thermal cycloaddition reactions of heterocyclic azides

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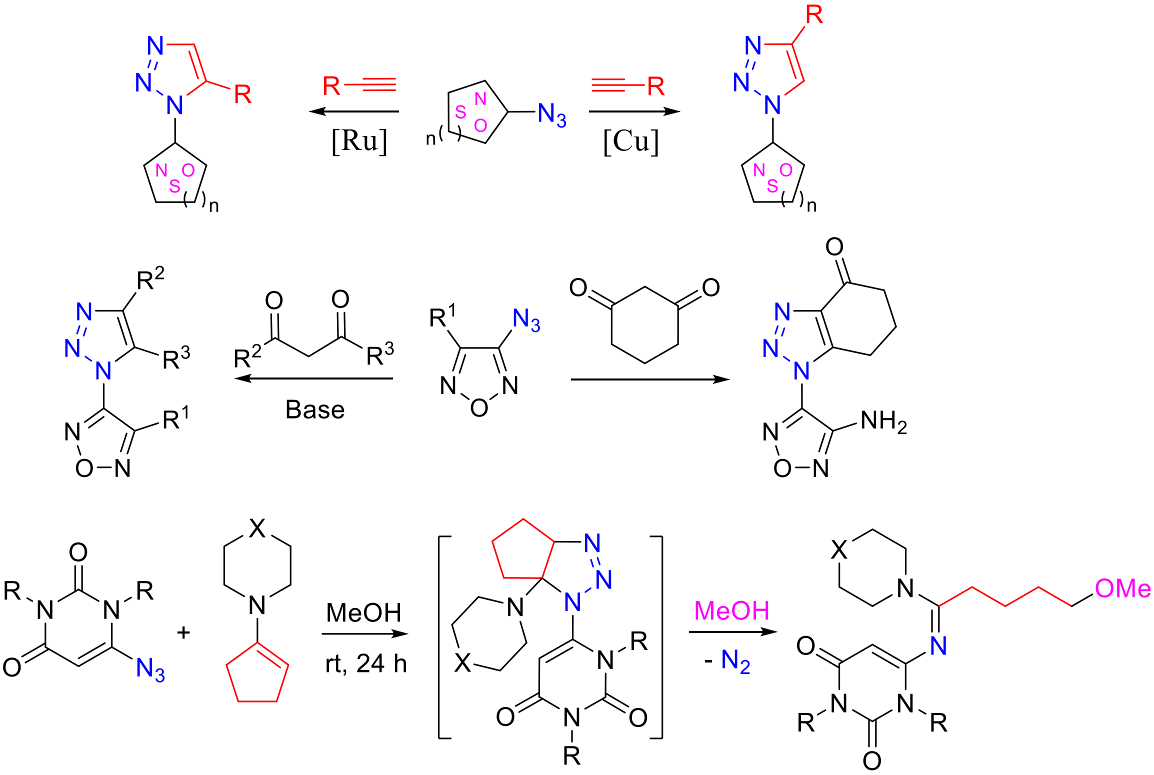
The data of a review on the synthesis and reactions of heterocyclic azides with acetylene and acetonitrile derivatives, alkenes, enamines and dicarbonyl compounds will be presented. Application of these reactions to the synthesis of mono-, bi- and tricyclic compounds and ensembles of various heterocycles (e.g. azines and azoles including 1,2,3-triazole derivatives and nonaromatic 1,2,3-triazolines), amidines and diazo compounds will be also shown.

Furthermore, methods for the synthesis of supramolecular structures, coordination compounds, ligands, bioconjugates and biologically active compounds based on reactions with heterocyclic azides will be considered. The review describes the use of these transformations in biological chemistry to study processes in living systems, as well as in materials chemistry for the production of luminophores and sensors for metals. Original studies published mainly over the past 15 years will be discussed [1].



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A convenient and effective approach to dehydrohalogenation reactions through a diffusion mixing of reagents

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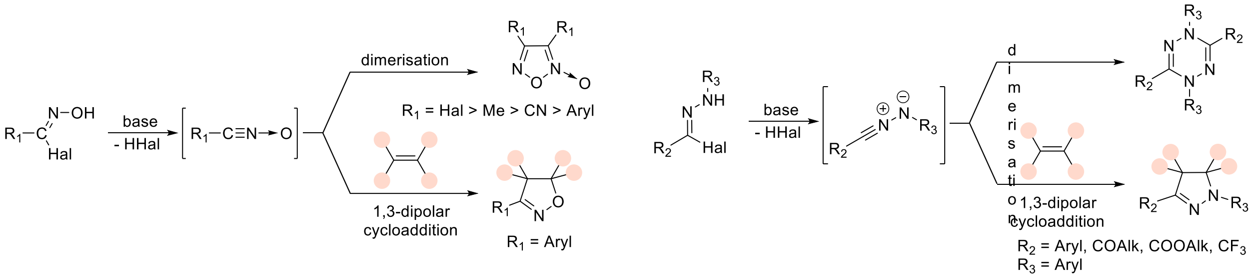
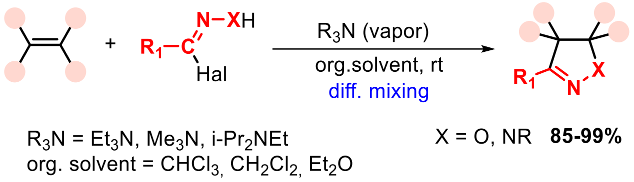
1,3-Dipolar cycloaddition is an important class of organic reactions that make it possible to obtain five-membered cycles of various structural types with high atom economy and chemoselectivity. Among the known 1,3-dipoles, nitrile oxides and nitrilimines are widely used intermediates in the synthesis of functionalized five-membered heterocycles. The best known and most used methods for the generation of nitrile oxides and nitrilimines base on dehydrohalogenation of the corresponding oxime and hydrazone derivatives. However, dipoles formed *in situ* in this way are prone to dimerization, which significantly limits the range of target heterocycles, which are often obtained in unsatisfactory yields even in the case of stabilized dipoles:



Spontaneous diffusion of a volatile reagent vapors into a solution, containing a stabile precursor of an unstable reactive intermediate, may be the simplest method for carrying out some organic reactions, including 1,3-dipolar cycloaddition. This technique was applied to generate nitrilimines and nitrile oxides for the subsequent reactions with dipolarophiles from hydrazonyl halogenides or N-hydroxyimidoyl halogenides by the action of volatile tertiary amines (Et3N, as well as Me3N or DIPEA):



Generation of highly reactive intermediates as a result of a tertiary amine vapors diffusion into reaction mixture makes it possible to obtain the products of 1,3-dipolar cycloaddition reactions in high yields and without the side products formation due to the created conditions of "dipole starvation". The proposed method of diffusion reagents mixing allows to carry out 1,3-dipolar cycloaddition reactions with low-stable and easily dimerizing nitrile oxides and nitrilimines in high yields and is incredibly easy experimentally. In fact, 1,3-dipolesare obtained by this method "molecule-by-molecule", which prevents their unwanted side transformations.

This work was supported by the Russian Science Foundation (grant № 21-13-00023)

N-heterocyclic carbene (NHC)-catalyzed synthesis of C-N and N-N axially chiral molecules

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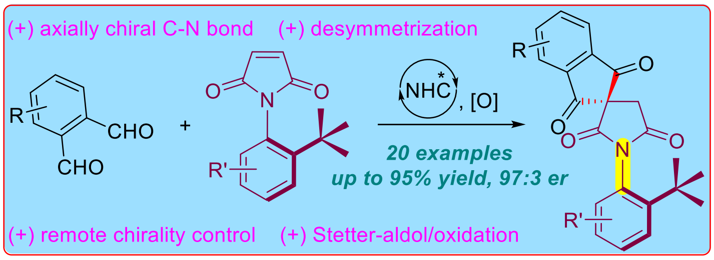
N-Heterocyclic carbene (NHC)-catalyzed umpolung of aldehydes is widely used for the unconventional access to target molecules.[1] Although the assembly of axially chiral C-C bonds leading to the atroposelective synthesis of biaryls and related compounds are well-known, the analogous synthesis of compounds bearing axially chiral C-N bonds are relatively rare. We have recently reported the NHC-catalyzed atroposelective synthesis of N-aryl succinimides having an axially chiral C-N bond via the desymmetrization of N-aryl maleimides.[2] The NHC involved intermolecular Stetter-aldol cascade of dialdehydes with prochiral N-aryl maleimides followed by oxidation afforded N-aryl succinimides in good yields and ee values. Preliminary studies on rotation barrier for the C-N bond, the temperature dependence, and detailed mechanistic studies are also being presented. Moreover, very recent studies on kinetic resolution of amino substituted N-aryl maleimides will be presented.[3] Furthermore, NHC-catalyzed route for the synthesis of compounds containing axially chiral N-N bond also will be discussed.[4]



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Straightforward access to high-performance organometallic catalysts by fluoride activation

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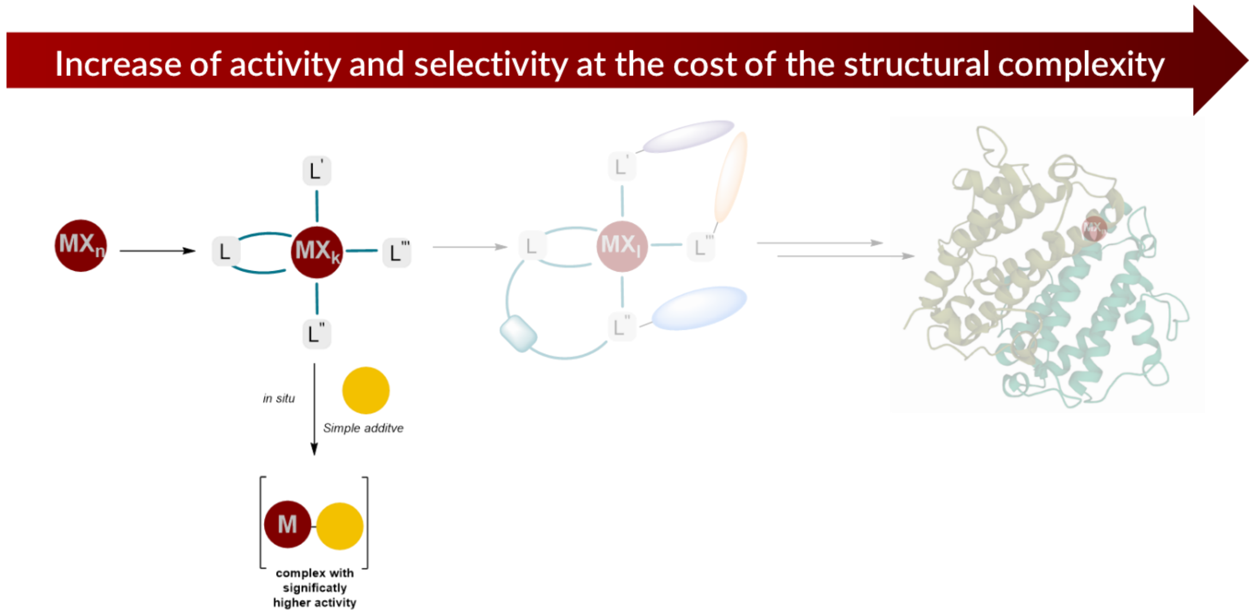
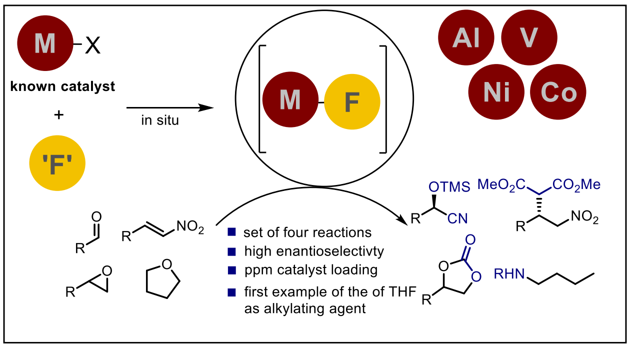
Catalysis plays a key role in a wide variety of chemical transformations in both academic and industrial settings. The development of active and selective catalytic systems is therefore an important research topic; however, the increasing structural complexity of emerging catalysts, together with the poor stability and difficult isolation of the most active catalytic species, emphasize the need for alternative strategies based on the *in situ* activation of well-established and relatively simple systems. The addition of active fluoride additive might provide an effective means for improving the performance of some existing catalysts. We demonstrated the effectiveness of this approach on four transformations.





This work was supported by the Russian Science Foundation (Grant No. 21-13-00157)

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Regioselectivity of isotopic exchange and alkylation in substituted azolo[1,5-a]pyrimidines

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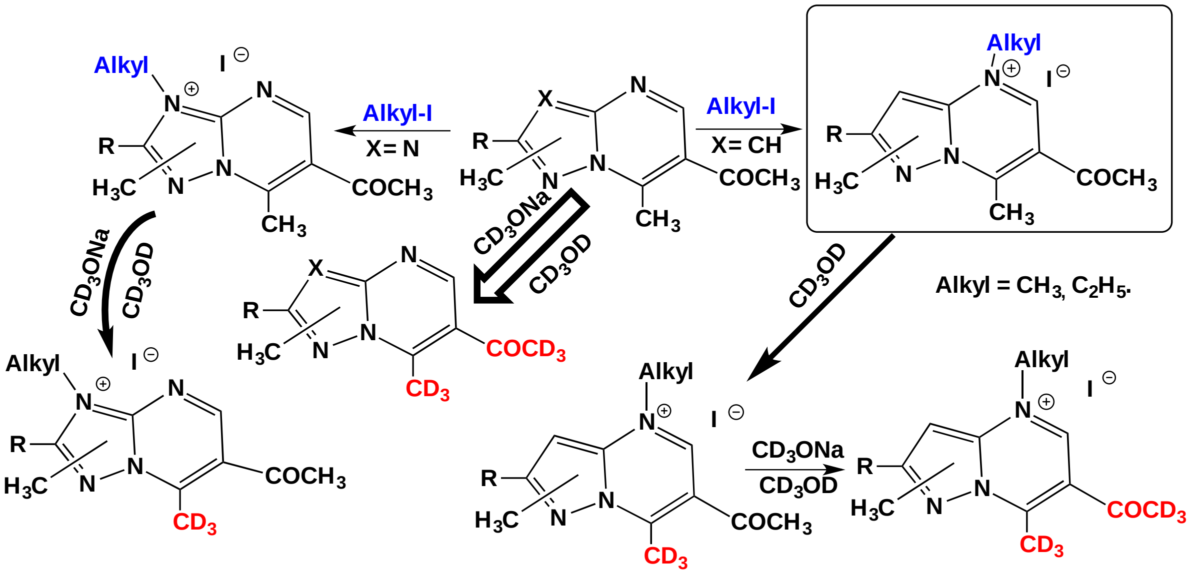
The report will present the results of studies on the alkylation of fused (fused) pyrimidine systems with alkyl halides. ^{1}H NMR spectral (NOESY method) proved that the regioselectivity of alkylation of azolo[1,5-a]pyrimidines depends on the type of azole (pyrazole or 1,2,4-triazole) attached to the pyrimidine ring.

The isotopic exchange of hydrogen atoms in the synthesized azolopyrimidines and their alkylation products was studied using NMR spectroscopy and mass spectrometry. It has been proven that hydrogen atoms of C-methyl groups located in the pyrimidine ring undergo deuterium exchange. It was noted that the dynamics of the deuterium exchange process (the rate of exchange) and its regioselectivity depend on the structure of azolo[1,5-a]pyrimidine.



This work was carried out with the financial support of the State Committee on Science of the Republic of Armenia and the Russian Foundation for Basic Research (project 20RF-138 / 20-53-05010 Arm_a /), as well as within the framework of the grant of the Ministry of Education and Science of the Russian Federation for scientific research of the Russian-Armenian University.

Heterocyclic NO-donors: synthesis, reactivity and properties

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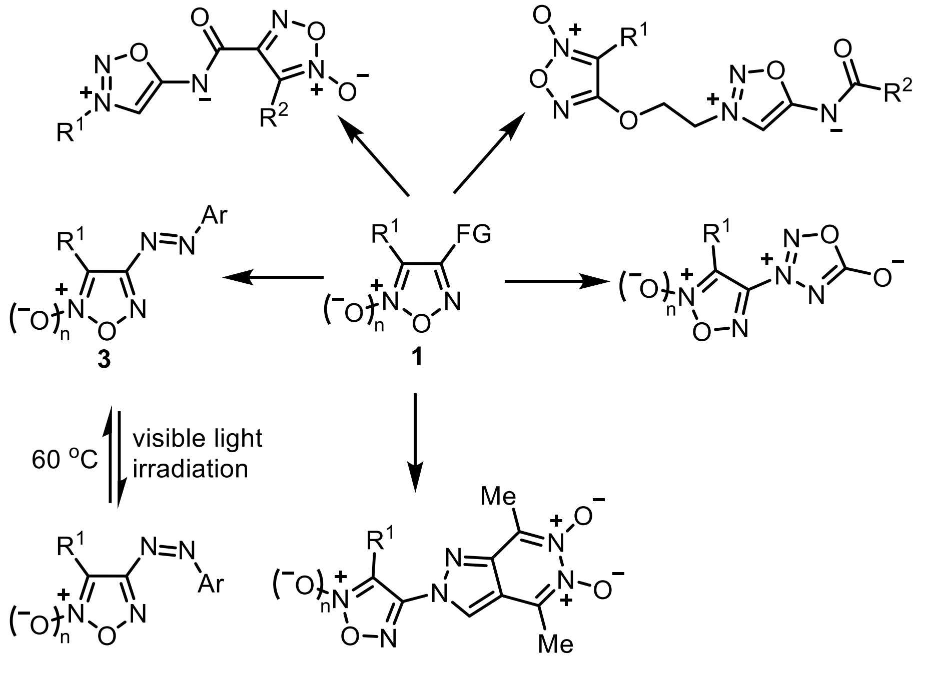
Nitric oxide (NO) is one of the most versatile signaling molecules in animal and human biology with diverse roles in both physiology and pathophysiology. NO exhibits vasodilating activity, inhibits platelet adhesion and aggregation and has other anti-inflammatory properties. Although glyceryl trinitrate (GTN) is a widely known NO-donor clinically used for years, it has serious side effects. As a convenient alternative to GTN, heterocyclic NO-donors are mainly considered because of their hydrolytic stability, safer storage and absence of tolerance. Therefore, the creation of synthetic methodologies for the construction of heterocyclic NO-donors became one of the rapidly developing fields in organic and medicinal chemistry [1,2].

There are several known heterocyclic NO-donors: furoxans, azasydnones, sydnone imines, pyridazine dioxides. Each heterocyclic subclass has its own advantages and their pharmacological profiles are slightly different, while methods for their synthesis differ significantly. In addition, a combination of two structurally diverse heterocyclic NO-donor scaffolds in one molecule may contribute to an improvement of pharmacological properties of the resulting hybrids. Herein, recent achievements of our research group in the synthesis of novel hybrid heterocyclic NO-donor compounds along with an evaluation of their NO-donor ability and antiaggregant activity are summarized.



This work was supported by the Russian Science Foundation (grant № 21-73-10109)

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Reactions of aminoacetal derivatives: simple access to nitrogen heterocycles

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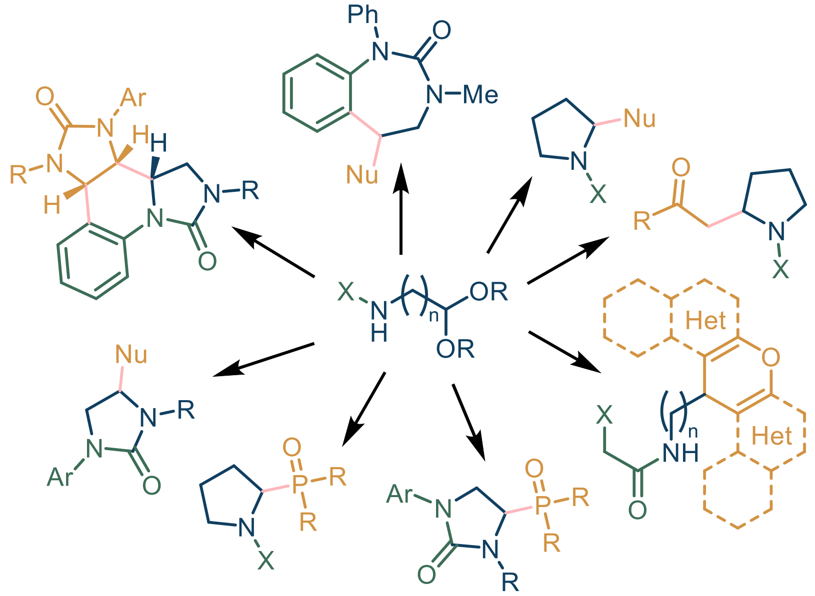
Nitrogen heterocycles play an essential role in both medicinal and organic chemistry due to their usefulness as versatile synthetic intermediates and biological importance. More than 75% of drugs currently available in the market are nitrogen-containing heterocyclic moieties and the number of novel *N*-heterocycles with promising applications is ever-growing. Thus, it is of no surprise that a lot of efforts are devoted to the development of novel approaches to these compounds.

Herein we summarize the results of our studies of acid-catalyzed cascade reactions of nitrogen-containing acetals various *C*- and *P*-nucleophiles and demonstrate their considerable potential in the synthesis of various classes of new heterocyclic compounds [1-3]. Additionally, the application of these reactions to the synthesis of functionalized xanthene derivatives is considered.



The research was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2022-1128)

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Mechanism of the chiral induction of the soai autoamplifying reaction by 1- and 2-aza[6]helicenes

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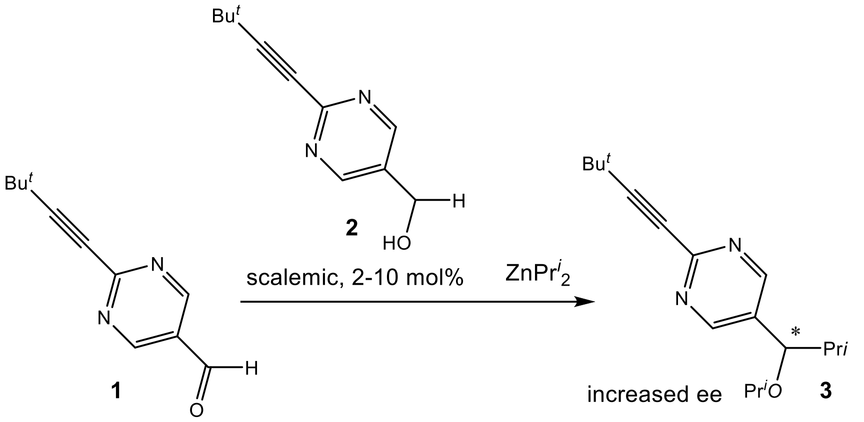
Autoamplifying Soai reaction (Scheme 1) is a transformation capable for the effective increase of the own chirality of a catalyst [1]. Besides the catalytic spontaneous chirality generation [3-5] and chirality generation induced by various chiral inductors [6] are known.



Scheme 1. AutoamplifyingSoai reaction

When applied as inductors, 1- and 2-aza[6]helicenes were reported to trigger the formation of the chiral product with opposite handedness [7]. In this talk the results of DFT computations revealing the corresponding mechanisms of chirality generation will be reported.

This research was financially supported by Russian Science Foundation through Grant 22-13-00275

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Asymmetric organocatalysis and mechanochemistry, two emerging areas in the chemistry of the XXI century

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In the area of asymmetric organocatalysis, significant effort has been dedicated during the last decade to improve the performance of emblematic catalysts such as (*S*)-proline, as well as to carry out organocatalytic reactions under more sustainable conditions.[1] The present lecture summarizes recent developments aiming to satisfy such goals. In particular, the design and evaluation of diamine analogs of privileged (*S*)-prolinols as organocatalysts is discussed. Furthermore, the remarkable influence of solvate ionic liquids as well as the usage of other types of ionic liquids that results in a significant improvement of the catalytic activity of (*S*)-proline is described. A central part of the present lecture is dedicated to report on the organocatalytic activity of □,□- and □,□-dipeptide derivatives of (*S*)-proline, and an additional section describes the preparation and evaluation of several chiral heterocycle-containing (*S*)-proline derivatives.[2]

Among the most successful strategies to achieve ‘‘greener” organocatalyzed processes are (1) the elimination of solvent from reaction media, and (2) the use of alternative activation energies such as solvent-free mechanochemistry in high-speed ball mills. In recent years we have stepped up efforts in the pursuit of organocatalysts and biocatalysts that allow reactions to take place in the absence of solvent and under mechanochemical activation. In this lecture I present the application of small dipeptides as chiral organocatalysts under solvent-free and high-speed ball milling conditions, with focus on the asymmetric aldol addition reaction. Finally, we report on recent results using supported enzymes for the resolution of racemic b-amino acids and amines, under mechanochemical conditions.[3]

This work was supported by Consejo Nacional de Ciencia y Tecnología, Mexico (grant № A1-S-44097)

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Wagner-Meerwein rearrangement in cage compounds

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Aspects of the use of carbocationic rearrangements for the construction of compounds of a sufficiently high degree of molecular complexity and diversity are considered on the example of transformations of framework structures: adamantane, protoadamantane, homoadamantane.

Stereospecific processes in the course of alkyl shifts lead to the formation of polyfunctionalized cage compounds, as well as new types of heterocyclic systems annelated with a polycyclic framework.

This work was supported by the Russian Science Foundation (grant № ***21-73-20103)***

Hydrated imidazoline ring expansion (HIRE) as a facile entry into medium-Sized Heterocyclic Scaffolds

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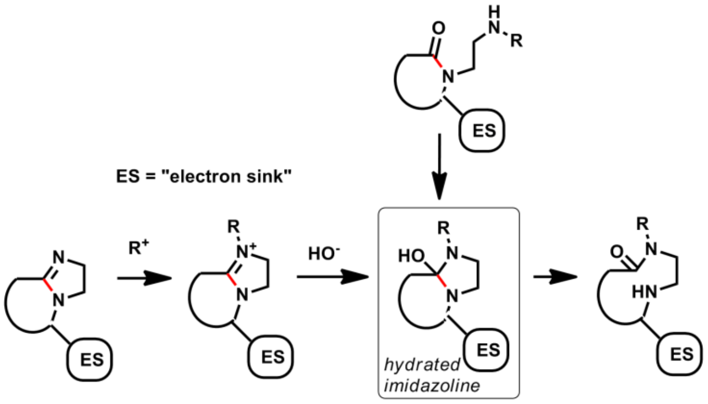
A novel strategy toward medium-sized (10-12-membered) heterocyclic frameworks has been developed which involves the rupture of the central bond in a postulated "hydrated imidazoline" intermediate. The approach appears to possess sufficient generality and can be consider a method of choice when n+3 ring expansion of a lactam framework is required. In this case, elaboration of imidazoline nucleus followed by electrophilic activation and hydrolytic ring expansion can be employed. Alternatively, the same "hydrated imidazoline" intermediate can be re-constructed via 2-aminoethyl side chain addition onto the lactam carbonyl group.



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Asymmetric metal-templated synthesis of challenging α-amino acids

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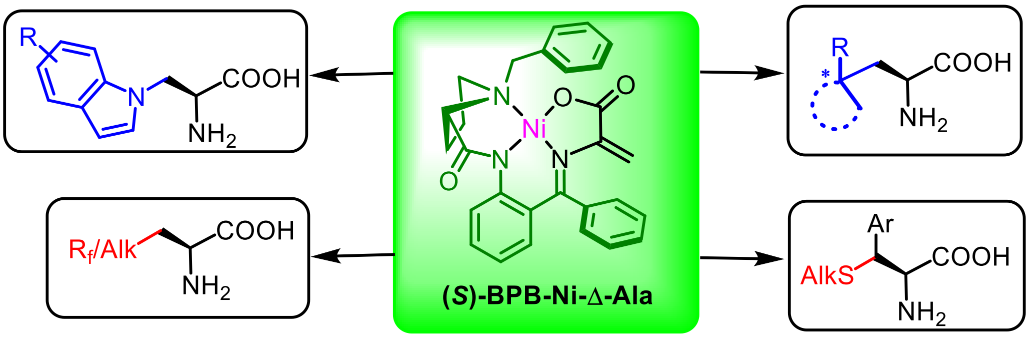
To date, synthetic non-proteinogenic (or unnatural) complex amino acids (AAs) have a considerable interest in biochemistry and pharmaceutical industry. They are very often used in the development of new drugs and modified peptides. In most cases, such molecules can only be obtained using radical coupling reactions. [1] The attractiveness of the approach is provided by the generation of radicals under mild conditions and the functional group tolerance.



Recently, we have developed several reliable and practically useful protocols for the asymmetric synthesis of hard-to-reach amino acids through classical ionic and radical intermediates. [2-6] Using of Belokon's chiral nickel(II) complex we could synthesize several important classes of AAs, some of which were produced for the first time (Scheme). In particular, enantiomerically pure unnatural α-AAs with γ-tertiary and quaternary carbon centers, alkyl and perfluoroalkylated α-AAs and cysteine derivatives have been obtained.

This work was supported by the Russian Foundation for Basic Research (grant Nos. 20-03-00783 and 20-53-05002)

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Electrochemical synthesis: from hydrocarboxylation of alkenes to coupling of arenes

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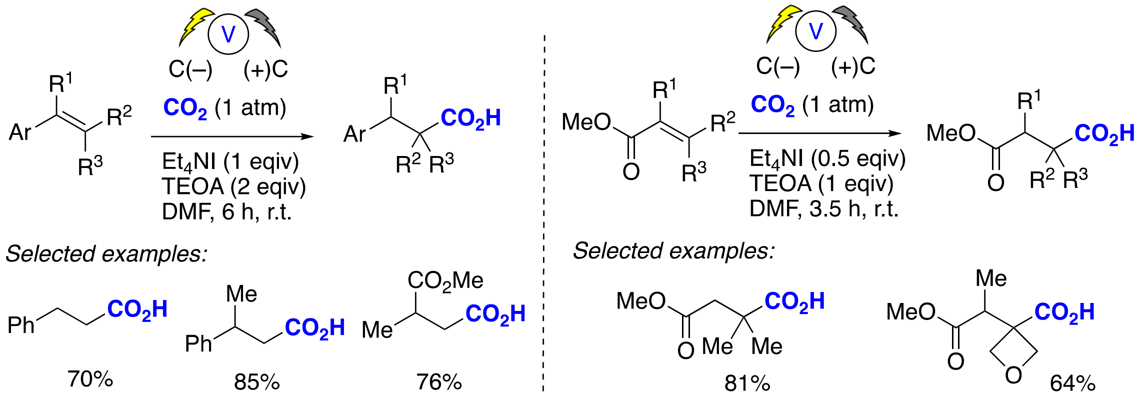
Electrosynthesis has been widely studied within the electrochemical community, but represents an underused tool, with great potential for synthesis.[1] Currently, there are only a few processes at the industrial or pilot-plant scale for the electrosynthesis of organic molecules. Herein we report a new electrosynthetic approach to the selective hydrocarboxylation of alkenes,[2] dienes,[3] and esters.[4] The method allows direct access to carboxylic acids derived from the terminal*,* *di*- and *tri*-substituted alkenes, as well as conjugated dienes and unsaturated esters, in a highly regioselective manner. A plausible reaction mechanism will be discussed.

A wider electrochemical methodology will be showcased by the asymmetric total synthesis of *N*-acetylcolchinol where all the redox processes, except for the asymmetric reduction, were carried out in an electrochemical cell.



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Rearrangements of quinoxalinones in the synthesis of biheterocyclic systems

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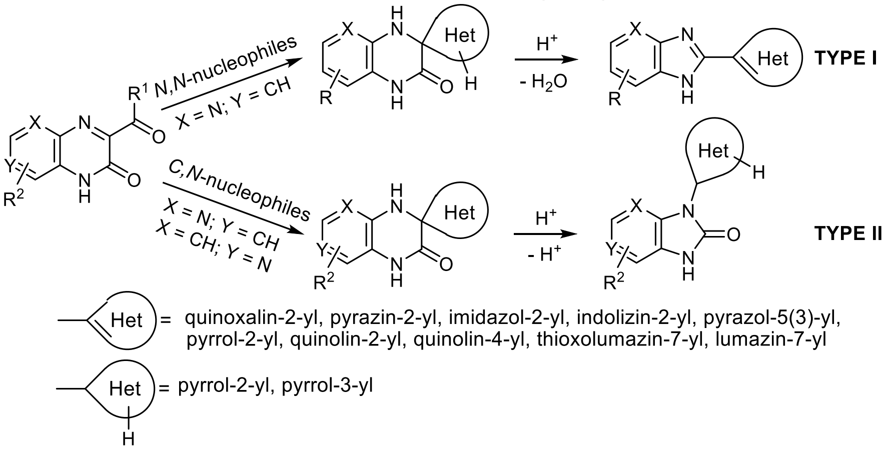
Two types of acid-catalyzed rearrangement of quinoxalin-2(1*H*)-ones into 1-hetarylbenzimidazoles or 2-hetarylbenzimidazolones, proceeding when exposed to various *N,N*[1-6]- and *C,N*-nucleophilic[6-9] reagents *via* spiro-derivatives of quinoxalinones with a mobile hydrogen atom (TYPE I) and without it (TYPE II) in the spiro-forming fragment is discussed.



The possibility of synthesizing a wide variety of 3-substituted derivatives of quinoxalin-2(1*H*)-ones and the availability of a number of nucleophilic reagents indicate the broad possibilities of TYPE I and TYPE II rearrangements. Rearrangements are also applicable for aza-analogues of quinoxalin-2(1*H*)-ones, which significantly expands their synthetic potential.

This work was supported in part by the Russian Science Foundation
(grant № 18-13-00315-p)

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Reactions of heterocumulenes as a method for constructing heterocyclic systems

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The pericyclic transformations of polycarbonyl compounds, dioxoheterocycles and heterocumulenes based on them, including Diels-Alder reactions and dipolar cycloaddition, have been studied. New approaches to the construction of biologically similar heterocyclic systems have been developed.

It was previously shown that thermal decarbonylation of furan-2,3-diones and N-substituted 1H-pyrrole-2,3-diones, including those annelated with various heterocycles on the [e] side, gives heterocumulenes (aroylketenes and imidoylketenes). Chemical behavior imidoylketenes largely depends on the nature of the substituent at N-1.

It has been found that N-(diphenyleneamino)pyrroldiones undergo mild CO extrusion at elevated temperatures, resulting in the formation of zwitterionic azomethineimines (dihydropyrazolones), which can be represented by the enolate-iminium 1,4-dipole resonance form. In the absence of dipolarophiles, [4+4]-cyclodimerization products, bis(pyrazolo)dioxadiazocines, were formed in high yields. Dipyrazolodioxadiazocines are storage-stable "ready-to-use" precursors for the in situ production of iminium enolate 1,4-dipoles.

The generation of heterocumulenes and azomethine imines in the presence of alkyl vinyl ethers, aldehydes, ketones, ketenes, nitriles, and isocyanides leads to the formation of the corresponding cycloaddition and dipolar cycloaddition products, respectively.

Next, we dwelled in detail on the development of various synthetic schemes, including the cycloaddition of aroyl ketones, imidoyl ketenes, and 1,4-dipoles.

Heterocyclizations of heterocumulenes represent new directions in the construction of previously inaccessible and hardly accessible carbonyl derivatives of heterocycles and fused heterocyclic systems.

The toxicity, antimicrobial, anti-inflammatory, analgesic, antihypoxic, psychotropic and other types of biological activity of the representatives of the synthesized compounds have been studied. Most of the studied compounds are derivatives of acylpyruvic acids, structurally close to the natural metabolites of a living organism, which justifies the search for biologically active substances among the synthesis products.

The report presents the results of more than 40 published articles and more than 10 received RF Patents for synthesis methods and physiological activity for 2020-2022.

This work was supported by the Russian Ministry of Education and Science (grantt № FSNF-2020-0008), the Russian Foundation for Basic Research and the Perm Territory (grant № 20-43-596008)

Expanded-ring N-heterocyclic carbenes, utilization in late transition metal catalysis

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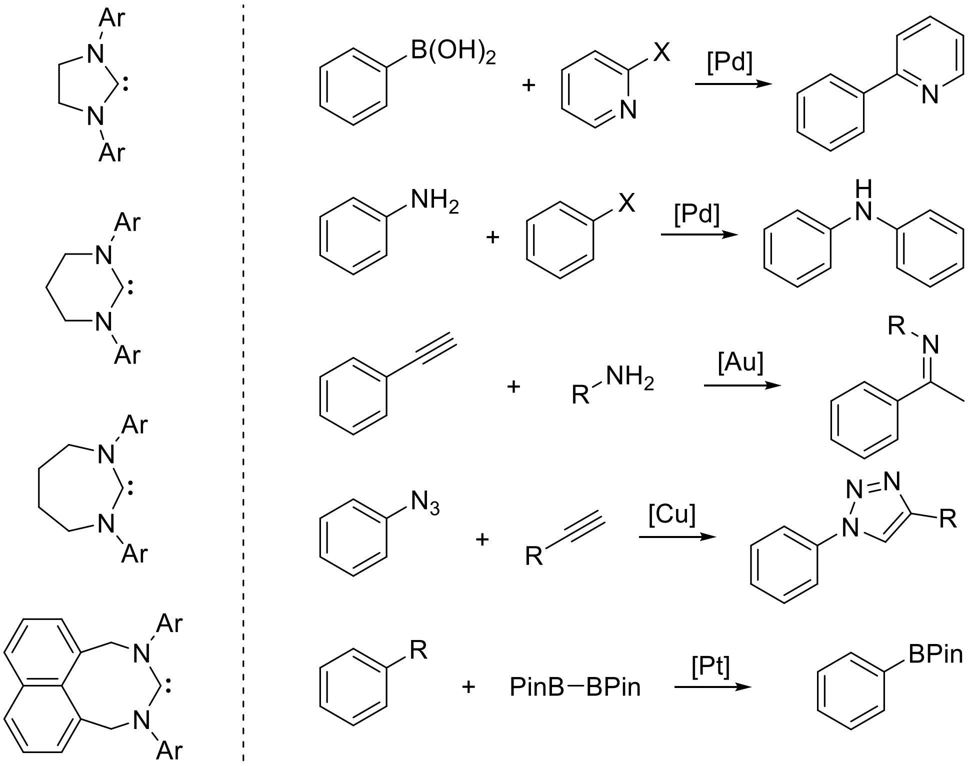
Variation of the ring size in N-heterocyclic carbenes is a powerful tool for tuning of stereoelectronic properties in a wide range. In this contribution we report on efficient synthesis of 6-, 7- and 8-membered ring diaminocarbenes and their complexes with late transition metals (Cu, Ag, Au, Pd, Pt). Complexes supported with strongly donating bulky er-NHSs mediate important catalytic transformations such as C-C and C-N coupling, addition of nucleophiles to acetylenes, CuAAC, aromatic C-H borylation. The developed catalytic processes are highly productive, scalable, and robust. In many cases we were able to show that the ring size in carbene is the key factor that governs catalytic activity and selectivity of the catalysts.



Haloazirine strategy for the synthesis of 5−6-membered nitrogen heterocycles

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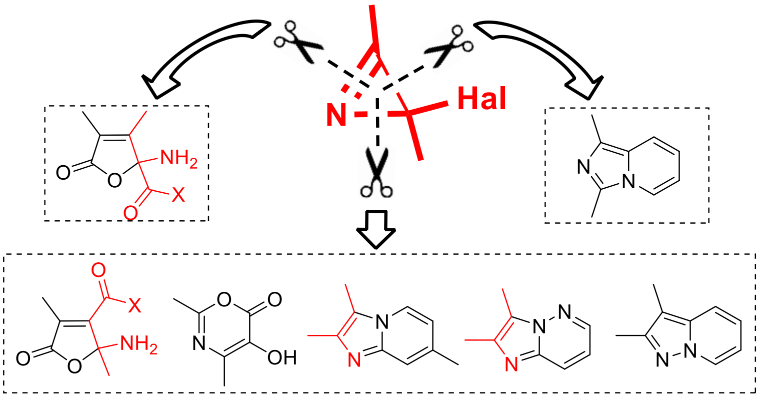
The three-membered ring enlargement of 2*H*-azirines is one of the powerful strategies for the construction of numerous nitrogen 4-7-membered heterocycles, and for some of them it is still the only way to obtain [1]. The most flexible and, at the same time, currently accessible azirine-containing building blocks are 2-haloazirines, which have at least three reaction centers in the molecule.

In this report, we discuss new methods for the selective ring enlargement of 2-halo-substituted azirines in the synthesis of 5−6-membered heterocycles including some aza-analogs of indene [2, 3]. Particular attention will be paid to those methods, which open access to different regioisomeric heterocyclic systems due to the selective cleavage of different bonds of the same azirine substrate. The reaction mechanisms are discussed using the results of quantum chemical calculations.



This work was supported by the Russian Science Foundation (project № 20-13-00044).
This research used recourses of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Computing Centre, Centre for X-ray Diffraction Studies, and Centre for Innovative Technologies of Composite Nanomaterials of St. Petersburg State University.

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Synthesis, structure, affinity to benzodiazepine receptors, and pharmacological properties of 3-arylidene-, heterylydene-1,4-benzodiazepines

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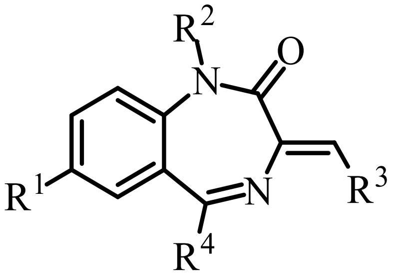
Derivatives of 1,4-benzodiazepine have been widely used in medical practice since the 1960s, mainly as psychotropic, anticonvulsant, hypnotic, anxiolytic, and other types of drugs. Currently, more than 50 original compounds are used in medical practice as pharmaceutical substances. Basically, they are ligands of central or peripheral benzodiazepine receptors. Also, among these compounds are ligands of CCK_1 and CCK_2 receptors, antagonists of bradykinin.

As a result, they have the properties of anorexigenic and orexigenic (affecting food intake) [1-3], or analgesic and anti-inflammatory drugs [4, 5].

A number of derivatives of 3-arylidene-, heterylidene-1,4-benzodiazepines of general formula **I** were synthesized, their structure, affinity to benzodiazepine receptors, and pharmacological properties were investigated.



R^1 = H, Br; R^2 = H, Alkyl; R^3 = Ar, HetAr;
R^4 = Ar, HetAr, VinilAr, VinilHetAr

I

This work was supported by the Tomsk Polytechnic University Development Program (Project Priority-2030-NIP/IZ-009-0000-2022)

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Chiral poison for asymmetric catalysis by racemic rhodium complexes

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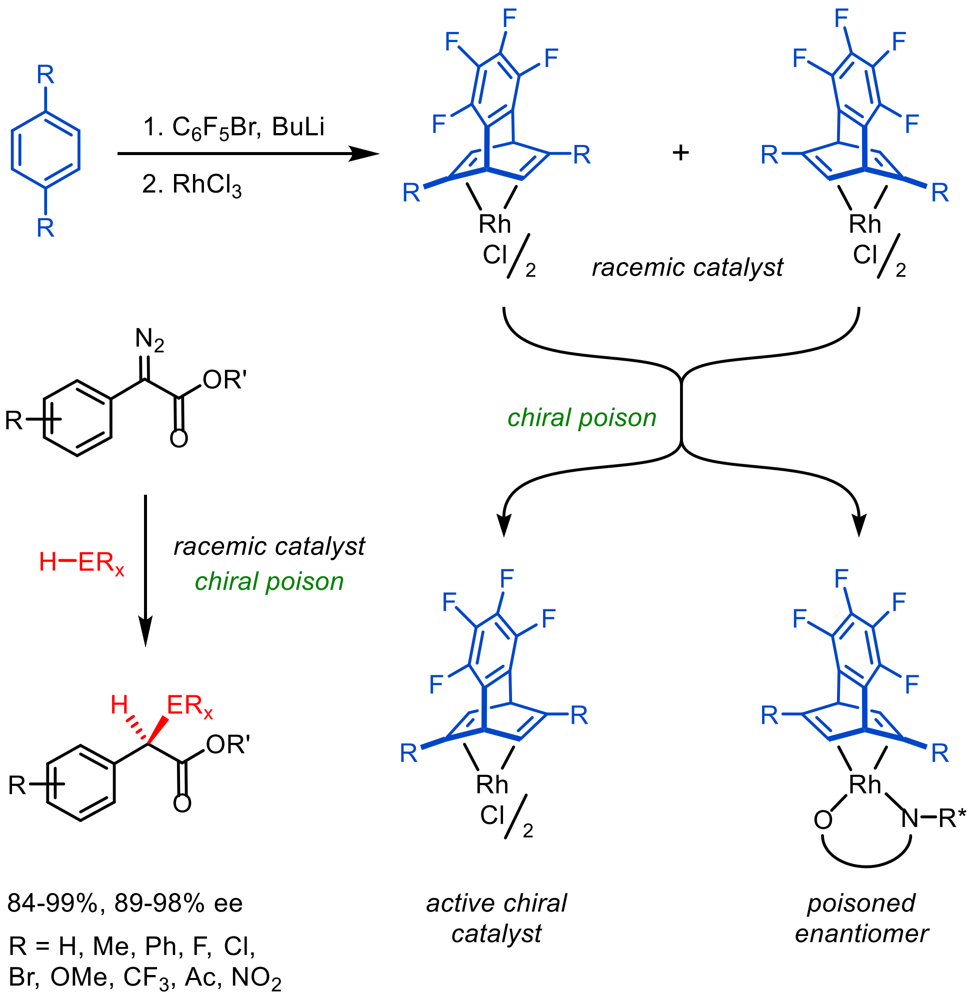
Asymmetric catalysis typically relies on chiral metal complexes. Herein, we show that it can be carried out using more readily available *racemic* complexes in combination with a “chiral poison”, that is a special ligand, which captures and inhibits one of the enantiomers of the catalyst [1]. In particular, this approach allowed us to use rhodium complexes with racemic dienes for asymmetric insertion of diazo esters into B−H bonds to obtain chiral boranes with 89-98% ee [2].



This work was supported by the Russian Science Foundation (grant № 17-73-20144)

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Ethynylation of imines in superbasic media: new reaction and unexpected possibilities

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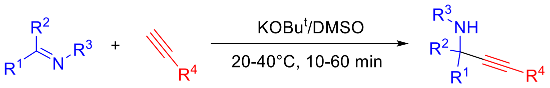
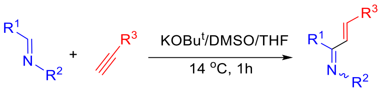
The superbase-mediated C=N bond ethynylation (*aza*-analog of the Favorsky ethynylation) and its divergent development are discussed:

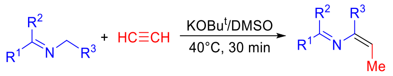
•synthesis of terminal and internal propargylamines from ketimines and acetylenes



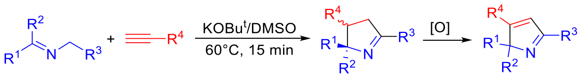
•synthesis of 1-azadienes from aldimines and arylacetylenes



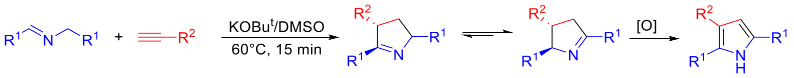
•2-azadienes from *N*-benzyl ketimines and acetylene gas



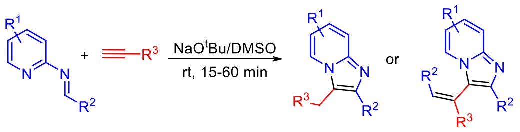
•1-pyrrolines and 2*H*-pyrroles from *N*-benzyl ketimines and arylacetylenes



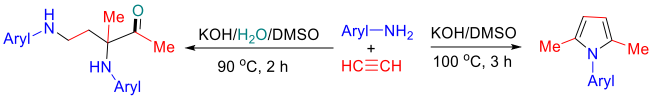
•1-pyrrolines and 1*H*-pyrroles from *N*-benzyl aldimine and arylacetylenes



•imidazopyridines from 2-iminopyridines and arylacetylenes



Self-assemblies of *N*-arylpyrroles and 1,3-bis(arylamines) with the participation of several molecules of acetylene and aromatic amines are discussed. These reactions involve the formation of imines and addition of acetylene to the C=N bond (*aza*-Favorsky reaction).



This work was supported by the Russian Science Foundation (grant no. 19-13-00052)

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Oxidative strategies for the synthesis of N-heterocycles

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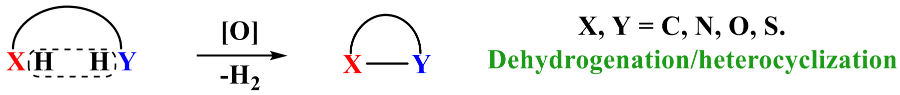
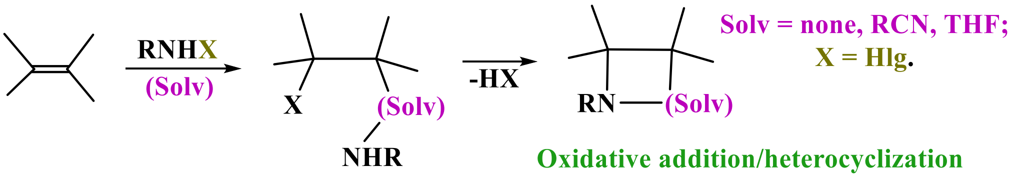
The lecture will summarize the last years progress in the design of various N-heterocycles including those containing O, S, Si, Se, Te heteroatoms via oxidative intramolecular cyclization using different catalysts, oxidants, and reaction conditions. The interest to N-heterocycles and methods of their synthesis is due to high biological activity and the possibility of further transformations by introduction of biologically active moieties. Two main strategies under consideration include dehydrogenative C–C, C–N, C–O, N–N, or N–S bond coupling accompanied by cyclization, and two-step oxidative amination followed by dehydrohalogenative cyclization. A variety of methods includes different metal-catalyzed or catalyst-free protocols, the use of various MW, UV, visible light-assisted syntheses, diverse oxidants and reaction conditions, allowing preparation of the target compounds in good yields and selectivity. A large family of the resulting heterocycles includes aziridines, pyrroles, diazoles, thiazoles, 1,2,4-triazoles, tetrazoles, 1,2,4- and 1,3,4-thiadiazoles, indazoles, benzodiazepines, quinazolines, selenazolines, and various mono- and polycyclic Si,N-heterocycles, some of which were obtained for the first time.





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Development of ligands targeted quadruplexes

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The non-canonical structures of nucleic acids such as four-stranded guanidine-rich (G-quadruplexe, G4) or cytosine-rich quadruplexe (I-motif) elements of the secondary structure of nucleic acids have been discovered in the telomeric regions of DNA, promoter regions of oncogenes and in untranslated mRNA sequences. Low-molecular weight compounds which can bind with quadruplexes inhibited or dysregulated of important biological process including gene transcription or the cell proliferation. Ligands which can stabilize G-quadruplexes or I-motifs considered as promising candidates for the anticancer drug development.

Based on linear heteroareneanthracenediones we have designed and prepared series ligands with high affinity for different G4s of DNA or RNA. Firstly, an original bisguanidine derivative of anthra[2,3-b]thiophene-5,10-dione, which has a high affinity for telomeric quadruplex and G4 from promoters of oncogenes was discovered [1]. The side chains optimization, via a replacement of guanidine groups with the chloroacetamidine groups, lead to G4-ligands with significant improved penetration in tumor cells [2]. Strong stabilization of G4 hras-2 (form hRAS promoter) with selected ligands caused a decreasing of the accumulation of the p21hRAS protein (the product of translation of hRAS oncogene) in T24 bladder cancer cells and induced apoptosis in tumor cells. The introduction in the heterocyclic moiety of an additional side chain with guanidine group lead to discovery of «tri-armed» G4-ligands which have a higher affinity for telomeric G4 and a significantly higher selectivity [3]. As part of the screening of G4 RNA ligands, it was found that derivative of 4,11-diaminoanthrafurandione has a high affinity for the G4 from 5′-untranslated region of the KRAS oncogene mRNA [4].

Based of tetra(4-pyridinyl)porphyrin scaffold we have obtained photoactivated G4-ligands which capable efficiently penetrating into tumor cells [5, 6]. These cationic porphyrins in nanomolar concentrations after irradiation (660 nm) cause ROS-induced degradation of G4s in untranslated region of KRAS mRNA that lead to block KRAS synthesis in tumor cells. The effectiveness of these ligands as a new antitumor photosensitizer was confirmed in the model of pancreatic cancer xenografts Panc-1.

Finally, we have developed an original method for the introduction of aminoalkylamino-groups into poliketide antibiotic heliomycin [7]. This modification of the heliomycin can modulate their affinity to different DNA secondary structures, including G4s and I-motifs. Moreover, we identified one derivative (7-deoxy-7-(2-aminoethyl)amino-10-*O*-methylheliomycin) demonstrated strong affinity, stabilization potential and good selectivity towards i-motif-forming DNA sequences over duplex and G4s.

Thus, some promising directions in the development of ligands of quadruplexes have been developed.

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Progress in the chemistry of 4-pyrones

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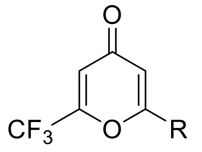
γ-Pyrones belong to the most important class of oxygen-containing heterocycles, but despite the fact that they are widely distributed in nature and their derivatives are highly reactive substrates and exhibit various types of biological activity, many substituted γ-pyrones are still among the little-studied molecules. The report will be devoted to the development of new methods for the preparation of various di- and trisubstituted derivatives of 4-pyrone with useful properties and the study of their chemical properties.



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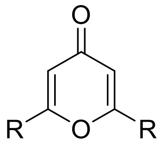
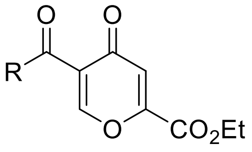


R = Me, CO_2Et, $CONH_2$, CN



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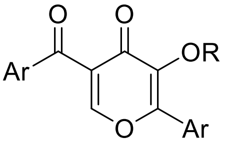
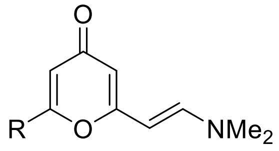


R = H, Ph, Bn, Me



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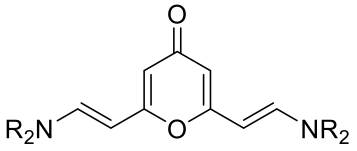

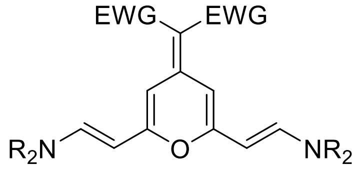

This work was supported by the Russian Science Foundation (grant no. 18-03-00186)

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A renewed "isoxazoline route" to pharmaceutically relevant molecules

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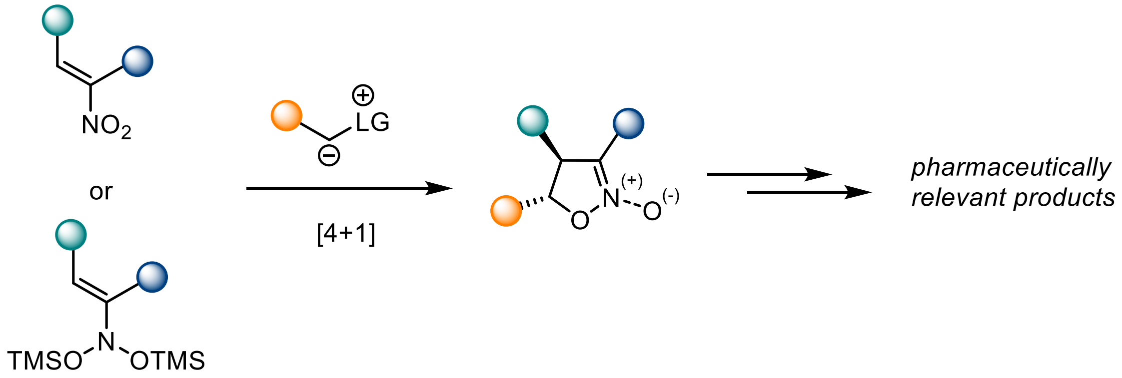
Isoxazolines are classical intermediates in the stereoselective assembly of aldols and 1,3-aminoalcohols, which are widely used in the synthesis of natural products and pharmaceutical ingredients [1]. However, a common approach to the construction of isoxazolines by the [3+2]-cycloaddition of nitrile oxides to alkenes has limitations associated with regioselectivity issues. A solution to this problem may be the use of [4+1]-annulation methodology to assemble the isoxazoline ring.

This talk will outline our latest research toward the development of new [4+1]-annulations leading to isoxazolines and isoxazoline-*N*-oxides, as well as subsequent transformations of these products into pharmaceutically relevant products through metal-free C–H functionalizations, reductive recyclizations and Nef-like reactions [2-4].



Theoretical and experimental studies discussed in this talk were supported by the Russian Science Foundation (grants № 22-13-00230 and 22-23-00289)

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Compounds combining adamantane and monoterpene fragments: synthesis and biological activity

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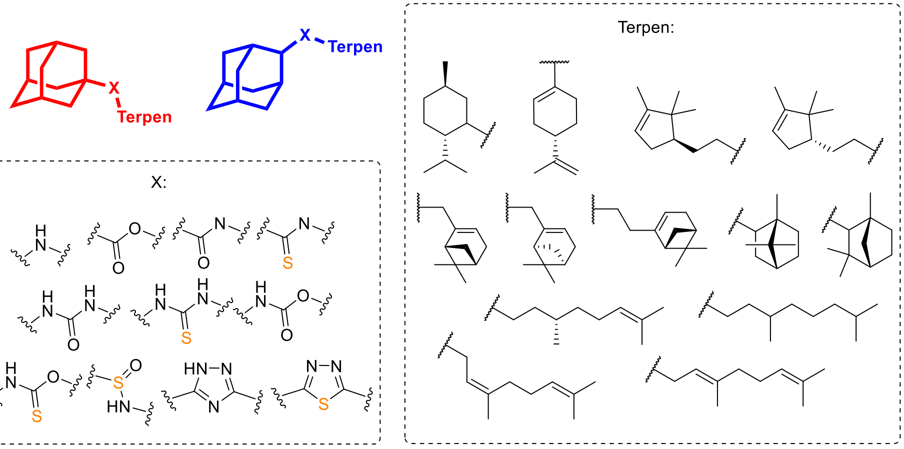
Structural modification of natural metabolites with diverse biological activity, such as monoterpenoids, is currently widely used to develop new drugs [1]. Another approach is the use of compounds containing known pharmacophore groups in their structure, for example, such an adamantane fragment [2], etc.

The aim of our work was to obtain compounds combining adamantane and monoterpenoid fragments connected through various intermediate groups for further study of their biological activity.

We have synthesized a wide library of such compounds: secondary amines, esters, amides, ureas, urethanes and, in some cases, their thioanalogues. We also obtained compounds containing 1,2,4-triazole and 1,3,4-thiazole fragments and combining adamantyl and monoterpenoid fragments.



The synthesized substances showed their inhibitory activity against rimantadine-resistant strains of the influenza virus, vaccinia, cow and mouse pox, as well as against the DNA repair enzyme Tdp1, which is a promising target for antitumor therapy.

This work has been supported by the grants the Russian Science Foundation (№ 19-13-00040 П)

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Decomposition of tetrazoles

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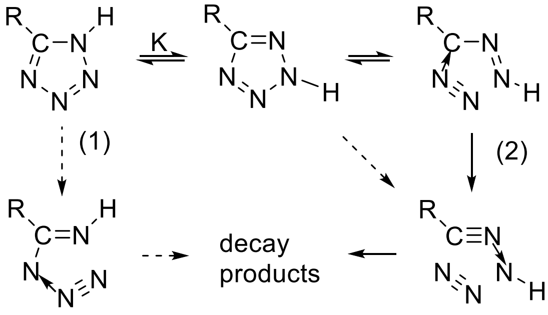
The decomposition of tetrazoles is used in various fields of technology, as it is accompanied by the release of a significant amount of energy and molecular nitrogen [1].

The publications are summarized and the results of new studies of the decomposition of regioisomeric N^1,N^2 and NH-unsubstituted C^5-substituted tetrazoles under the action of a thermal pulse (pyrolysis), electromagnetic radiation (photolysis), radiation (radiolysis), as well as fragmentations detected by high resolution mass spectroscopy are presented.



Routes of decomposition (destruction, fragmentation) of NH-unsubstituted and regioisomeric N-substituted tetrazoles are proposed; analogies and differences in the schemes of the mechanisms of tetrazole decomposition initiated by the energy sources listed above were revealed. Attention is paid to the accompanying problems of tetrazole ring stability, including the metabolic stability of tetrazoles in living systems.

This work was supported by the Russian Foundation for Basic Research
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(Het)arene-annulated azepines from donor-acceptor cyclopropanes

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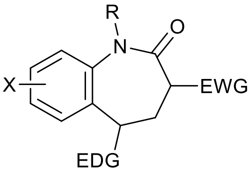
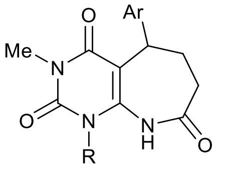
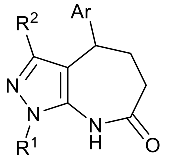
Donor-acceptor (DA) cyclopropanes serves as excellent building blocks for the construction of a broad variety of acyclic, alicyclic and heterocyclic products, including azaheterocycles with diverse size of ring. Nevertheless, their transformations to seven-membered rings are underexplored. In general, there are two major approaches to realize such transformations. The first one is the use of (3+4)-cycloadditions wherein DA cyclopropanes demonstrate their typical reactivity as synthons of 1,3-dipole, and their reaction partners are the appropriate 1,3-dienes [1,2]. Another one is based on reactions of DA cyclopropanes as 1,4-dielectrophiles with 1,3-dinucleophiles. We used this approach for the synthesis of (het)arene-annulated azepines from anilines and their heteroanalogues.

From anilines, we synthesized 2-aryl(alkenyl)-1-*N*-alkyl-*N*-arylcarbamoylcyclopropanecarboxylates and realized their recyclization to benzazepines. We demonstrated that this reaction proceeds with the inversion of the absolute configuration of the electrophilic C(2) atom of cyclopropane, *i.e.*, is a first example of *endo-tet* cyclization providing 7-membered ring *via* cyclic transition state consisting of formally 6 atoms only [3]. The reaction of DA cyclopropanes with 6-amino-1,3-disubstituted uracils afforded exclusively products of the C(5) atom alkylation. Further coupling of 6-amino- and ester groups followed by decarboxylation produced 6,7-dihydro-1*H*-pyrimido[4,5-*b*]azepine-2,4,8-triones [4]. On the other hand, 5-aminopyrazoles react with DA cycliopropanes as typical ambident nucleophiles yielding products of either amino group or the C(4) atom alkylation. *C*-Alkylation products underwent cyclization to pyrazolo[3,4-*b*]azepines.







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Reactions of multicentered electrophiles generated from conjugated unsaturated compounds under superelectrophilic activation

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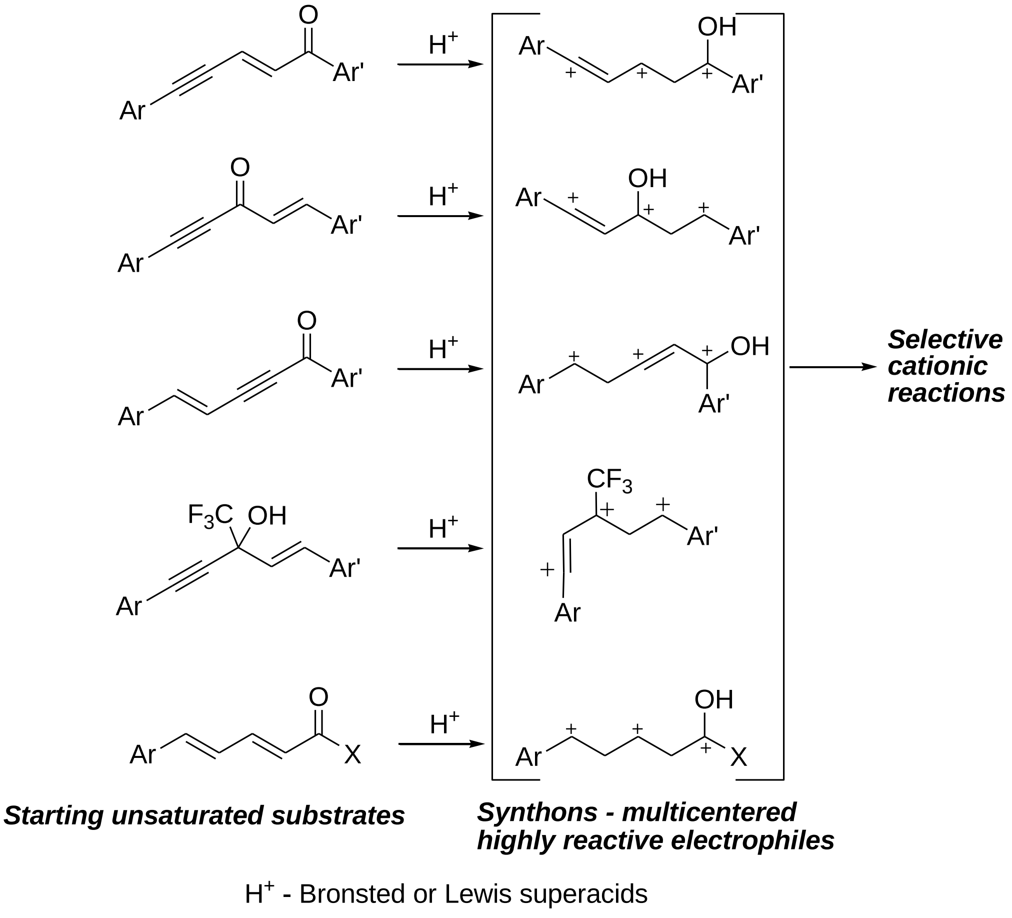
Protonation (or coordination) of carbon-carbon double and triple bonds, along with carbonyl or hydroxyl groups, of conjugated unsaturated compounds under the action of Bronsted superacids (CF_3SO_3H, FSO_3H, etc.) or strong Lewies acids ($AlCl_3$, $AlBr_3$) give rise to multicentered electrophilic cationic species. Reactions of these species lead to the formation of various carbocyclic and heterocyclic substances [1-3].



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How and why to break the chemical bond?

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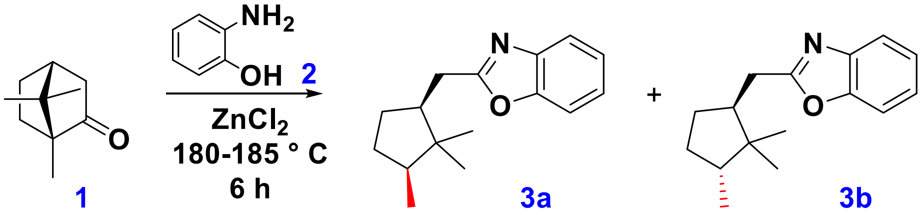
The energy of ordinary chemical bond vary from dozens to hundred of kcal/mol. In general, C-C bond requires about 90 kcal/mol to be broken homolytically. Some structural and/or electronic factor may shift this value to 17 kcal/mol (hexaphenylethane is taken as an example [1]).

In general synthetic chemistry, we deal with creation of chemical bond, rather than with breaking it. At the same time, there are examples of successive synthetic sequences, which include the stage of bond break. To be mentioned are, for example, fragmentation reactions in the synthesis of macrocycles or multiple cases of “retro” reactions [2].

In our work on the simply looking synthesis of imines of camphor and its congeners, we faced to the previously unknown reaction, which include virtually a break of C-C bond of the norbonane core [3] (Scheme).



In the lecture the examples of successive bond break will be discussed [3, 4] together with some general principles that affect and govern these types of transformations. The differencies in the conditions required for the homo- and heterolytic processes will be emphasized.

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How to create a new antiseptic?

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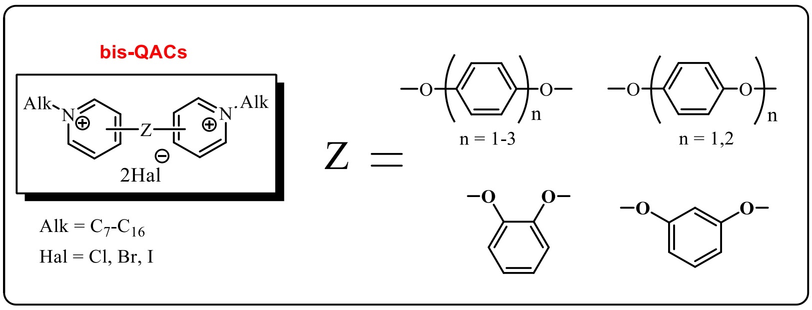
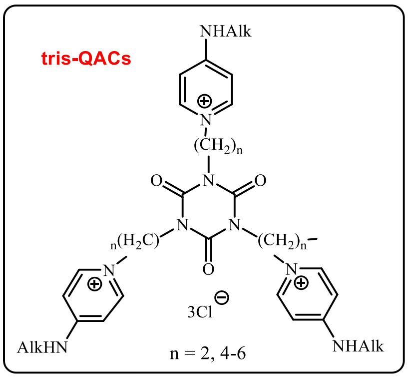
Currently, on the Russian market of medical devices, a significant part of antiseptics is made on the basis of quaternary ammonium compounds (QACs). The most famous and effective antiseptics based on mono-QAC are benzalkonium chloride, cetylpyridinium chloride, miramistin, based on bis-QAC – chlorhexidine, alexidine, octenisept, mestamidin. Various strains of bacteria, including pathogens, are known to develop resistance to antimicrobial drugs over time [1,2].

In this work, we propose an original approach to the synthesis of several new types of QACs based on pyridinium salts. By varying the linker between pyridinium nuclei, bis- and tris-QACs were obtained, which have antibacterial and antifungal activity against a wide range of highly resistant pathogenic bacteria (both gram-positive and gram-negative) and fungi, surpassing the activity of known antiseptics. Of particular note, the new QACs have been successfully tested against highly resistant clinical strains isolated from clinical specimens during the investigation of infections in 2016-2018.





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Design of new biologically active compounds based on monoterpenes

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Terpenes are natural compounds that can be formally considered as isoprene derivatives. Terpenes are present large amounts in coniferous plants and essential oils. The most common form is monoterpenes consisting of two isoprene fragments. Their oxygen-containing derivatives are called monoterpenoids. Although monoterpenoids often demonstrate biological activity [1], the role of these compounds in the development of new drugs currently is not great. This is mainly caused by difficulties arising during chemical transformations of monoterpenoids often containing a number of functional groups with similar reactivity and several asymmetric centers.

We have developed synthetic approaches that make it possible to obtain new compounds of various structural types from monoterpenoids. Among the synthesized compounds, agents demonstrating promising antitumor, antiparkinsonian, antiviral or analgesic activity were found [2, 3]. Antiparkinsonian agent found by us successfully passed stage I of clinical trials.

It was demonstrated that the use of various types of heterogeneous catalysts (zeolites, modified clays, halloysite nanotubes and so on) allowed us to increase selectivity to target products [4, 5].

This work was supported by the Russian Science Foundation (grant 19-13-00040)

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Reactions of phosphinic chlorides with amines and elemental sulfur in the synthesis of organophosphorus compounds

Volkova Y.,[1] Kozlov M.,[1] Komkov A.,[1] Gorbatov S.,[1] Gracheva S.,[1] Salnikova D.,[2] Andreeva O.,[2] Scherbakov A.,[2] Zavarzin I.[1]

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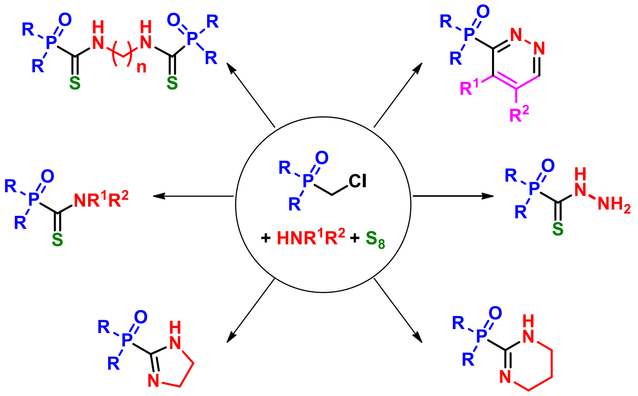
Organophosphorus compounds are of great interest due to their wide occurrence in numerous natural products, various biologically active compounds, fine chemicals, metal ligands and materials.[1] In particular, pyridazines, 1,3,4-thiadiazoles and thioamides with phosphoryl substituents are lead compounds for neuroprotective, anti-inflammatory and anticancer agents. Organophosphorus compounds have received significant attention from the synthetic community, but practical and convenient synthetic tools for their preparation are still lacking.

Our group has disclosed the Willgerodt-type three-component reaction of phosphinic chlorides with amines and sulfur as a highly efficient approach to phosphoryl thioamides, 2-imidazolines, and 1,4,5,6-tetrahydropyrimidines.[2] Moreover, we propose that using of readily available hydrazides of phosphorylthioformic acid in the reactions with carbonyl compounds is an efficient tool for the construction of phosphoryl-substituted *S*- and *N*-containing heterocycles. Namely, we have elaborated flexible synthetic approaches towards unknown POR$_2$ functionalysed 1,3,4-thiadiazoles and pyridazines with chemoselective control of heterocyclization patterns. It was shown that some reactions are efficient for synthesis of phosphoryl substituted heterosteroids with potent antiproliferative activity.



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From white to black: important intermediates and new materials based on element phosphorus

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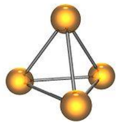
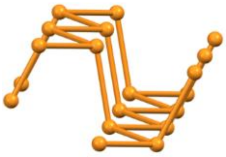
The development of modern chemistry proceeds in various priority directions focused on creation and design of new ecologically friendly methods for preparation of different compounds and materials bearing practically useful chemical and physical properties [1]. White (P_4) and black (BP) phosphorus are main important allotropes of element phosphorus which allow access to practically important phosphorus derivatives including the ligands for transition metal catalysts, biologically active materials, drugs and the components for microelectronics.



White phosphorus (P_4)



Black phosphorus (BP)

Transition-metal mediated white phosphorus activation is of high interest as an ecological alternative to P_4 chlorination pathway to the practically useful phosphorus products [2,3]. Herein, we report facile approaches for P_4 activation, transformation and subsequent functionalization in the coordination sphere of transition metal complexes describing the mechanism of the process and the structure and properties of the formed intermediates bearing coordinated intact and transformed P_4 molecule. The elaborated methods for chemical modification and functionalization of P_4, BP and some polyphosphorus compounds, including cyclic organic polyphosphines and few-layer black phosphorus (FLBP) towards new high reactive phosphorus intermediates, transition metal clusters and metal-free catalysts are also discussed [4,5].

This work is financially supported by the grant of the President of the Russian Federation for supporting of the Leading Scientific Schools (project no. 4078.2022.1.3) and by the Kazan Federal University Strategic Academic Leadership Program ("PRIORITY-2030").

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How to make effective antiviral agents from the available terpenoids? Easy and fun

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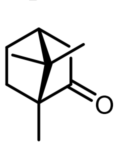
The current pandemic caused by the SARS-CoV-2 virus has clearly demonstrated that the development of effective antiviral agents is one of the most important tasks of medicinal chemistry. The use of terpene compounds as starting objects allowed us to create libraries of new substances with a wide spectrum of antiviral activity [1].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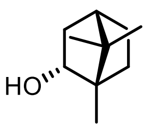
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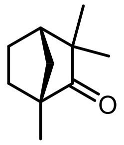
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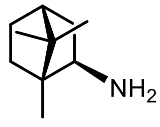
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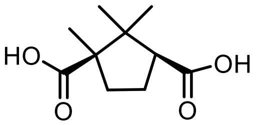
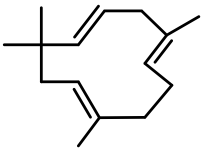
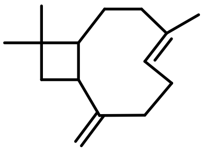
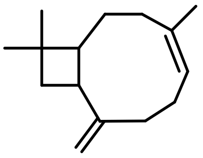

(+)-Camphoric acid


a-Humulene


Caryophyllene


Isocaryophyllene

We have shown that mono- and sesquiterpene derivatives exhibit activity against SARS-CoV-2 viruses, influenza, Hantaan viruses, variola viruses, respiratory syncytial virus and filoviruses [2-7]. It is important to note that the synthesis of target compounds does not exceed four stages and is well scaled.

This work was supported by a grant from the Russian Science Foundation (grant № 22-23-00618)

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Preparation and application of novel organohypervalent halogen compounds

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Organohypervalent iodine compounds are very common reagents, widely used in chemistry area and biology [V. V. Zhdankin, *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Application of Polyvalent Iodine Compounds*, John Wiley & Sons Ltd, 2014]. However, organic hypervalent compounds of other halogens such as bromine, chlorine, and fluorine remain essentially unknown and no significant progress in this area has been reported in recent literature [G. Cavallo, J. S. Murray, P. Politzer, T. Pilati, M. Ursini and G. Resnati, *IUCrJ*, 2017, **4**, 411-419; Halogen bonding in hypervalent iodine and bromine derivatives: halonium salts]. The main reason for the lack of success is that bromine, chlorine, and fluorine have higher electronegativity than iodine and therefore, these elements have higher oxidation potential than iodine.

Aryl compounds are very useful in various synthons, bioactive compounds, or synthetic resins. The proposed diarylhalonium reagents can be utilized as powerful electrophilic aryl transfer reagent for various nucleophiles or substances resulting in the formation of respective carbon-carbon or carbon-heteroatom compounds. Among the other hypervalent halogen(III) compounds, the chemistry of cyclic halonium compounds is potentially important research area.

This work was supported by a research grant from the Russian Science Foundation (RSF-21-73-20031)

Organic Chemistry Section Oral Reports

Di(pyridin-2-yl)amino-1,10-phenanthrolines and their binuclear complexes: synthesis and application in photocatalysis

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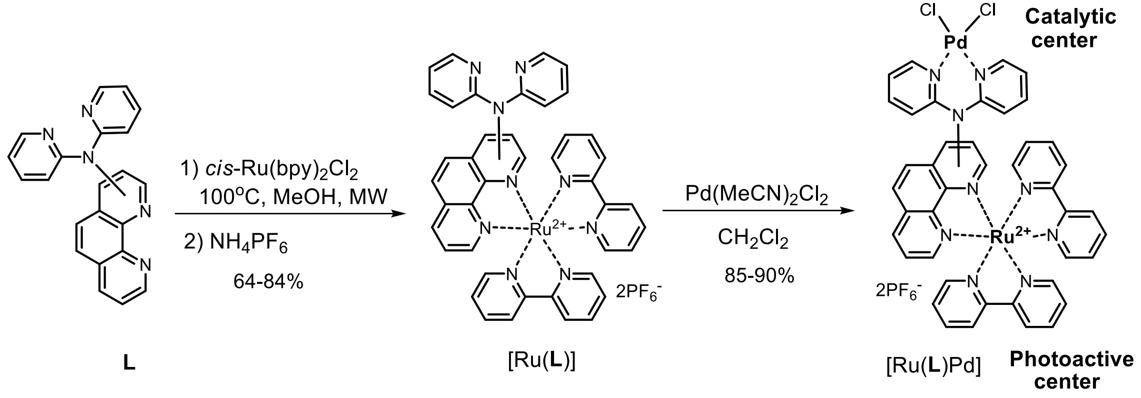
The use of visible light as an energy source is considered to be a promising direction in the development of environmentally friendly and energy-saving chemical processes. However, this approach is limited by the weak ability of most organic compounds to absorb visible light, and the use of higher energy UV-radiation leads to side reactions. The introduction of photosensitizers and dyes into the reaction, which go into an excited state under the action of visible light and transfer energy to the reacting substrates is called photocatalysis. Photocatalysis is actively used to carry out various chemical transformations, allowing them to be conducted under mild conditions. In recent years, dual catalysis has been intensively developed, it uses both a photoactive catalyst and a metal complex catalyst [1]. The key factor determining the efficiency of catalytic systems in such reactions is energy or electron transfer from the photocatalyst to the metal complex catalyst. A promising direction in the development of new catalytic systems in this area is the combination of photoactive and metal complex blocks in one molecule to provide their best interaction.

In this work, we synthesized a series of ditopic ligands based on di(pyridin-2-yl)amino-1,10-phenanthrolines (**L**) differing in the position of the dipyridylamine substituent in the phenanthroline core. These ligands are shown to be a convenient platform for the selective synthesis of binuclear complexes. Thus, [Ru(**L**)] and [Ru(**L**)Pd] complexes were synthesized; the structure of the resulting complexes was confirmed by NMR and X-ray diffraction. [Ru(**L**)Pd] complexes contain Ru-based photoactive block and Pd-based catalytic center.



The [Ru(**L**)Pd] complexes were studied as catalysts in the photoenhanced Sonogashira reaction. The influence of the structure of the ditopic ligand on the activity of the catalyst was studied. An increased activity of binuclear complexes compared to a two-component catalytic system under similar conditions was demonstrated.

This work was supported by the Russian Science Foundation (grant № 22-73-00031)

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Metallo-Drug design of complexes with O- and N-polydentate ligands: synthesis and *in vitro* biomedical evaluation

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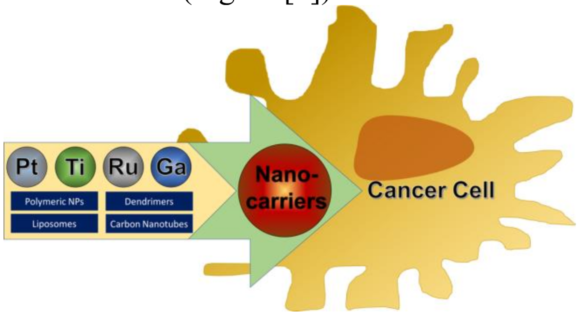
Currently, there is a significant interest in the field of medicinal chemistry in the development of drugs based on metal complexes with unique therapeutic properties. Thus, medicinal metal complexes containing in the molecule **Pt** (an antitumor drug cisplatin), **Au** (auranofin, a drug used in rheumatoid arthritis), **Tc**, **Re** (radiopharmaceuticals for radiation therapy), **Ru** (an anticancer agent), **Gd**, **Co**, **Li**, **Bi**, **Fe**, **Ca**, **Rh**, **Cu**, **Ag**, **Zn**, **Al**, **Lu**, **V**, **Ti**, **Mn** and etc. (antimicrobials, broad-spectrum antibiotics) are successfully used [1].

Especially metallo-drugs have arisen as an important class of cytotoxic agents. Many metallodrugs, such as platinum, titanium, ruthenium, gallium, tin, gold, and copper-based complexes have been found to have anticancer activities (Figure [2]):



When designing metal-containing drugs, it is important to rely on stable ligands with pharmacological properties, which include rigid aromatic and heteroaromatic scaffolds with O- and N-polydentate sites.

With this concept in mind, we developed a drag design of mono- and binuclear complexes of Pd, Pt, and Cu with O-, S-, and N-containing ligands obtained by modifying pharmacologically significant scaffolds such as pyrazole [3], phenol, naphthol [4], and quinalinol.

The strategy of the synthesis of metal complexes and their biomedical properties will be discussed in this report.

The work was carried out within the framework of the state assignment (FMRS-2022-0074 and FMRS-2022-0079) as well as with financial support from the Stipend of the President of the Russian Federation to young scientists and graduate students (SP-1691.2022.4)

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Use of 4-oxo-2,4-diarylbutanenitriles for the preparation of cyclic analogs of indolylacetamides

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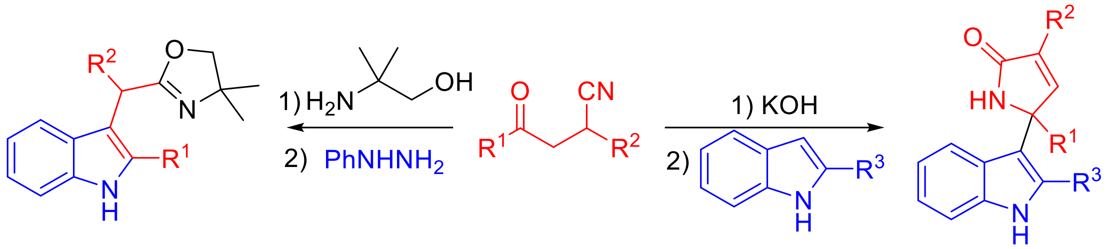
Compounds containing (indole-3-acetamide fragment) have great potential in synthetic chemistry and in the development of biologically active compounds. As an example, we have previously discovered 2-aryl-2-(3-indolyl)acetamides, which have high anticancer activity.

In our laboratory, the possibility of obtaining 3,5-disubstituted-5-(1H-indol-3-yl)-1,5-dihydro-2H-pyrrol-2-ones and 4,4-dimethyl-(1H-indol- 3-yl) 4,5-dihydrooxazoles from 4-oxo-2,4-diarylbutanenitriles. These transformations make it possible to obtain inaccessible compounds, which can also show high biological activity, since they are cyclic analogues of indolylacetamides.



Also, these transformations on the one hand of the compound from glycation, and on the other hand, support enhanced biological activity. Not least, such compounds can easily occur in unsubstituted amides, for example, by dehydration.

This work was supported by the Russian Science Foundation № 21-73-00044

Photoactive supramolecular system based on crown-containing unsaturated compounds and cavitands

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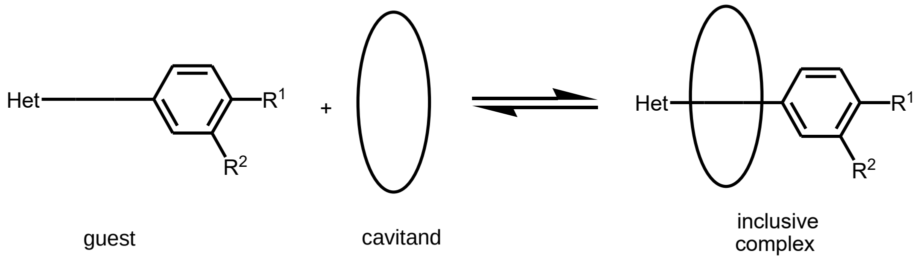
Unsaturated crown-containing and methoxy-substituted styrylheterocycles of the 4-pyridine and 4-quinoline series were synthesized by condensation of methyl-substituted heterocycles with benzaldehydes in the presence of base. Synthesis of 18-crown-6-containing styrylpyridine by condensation of the reagents in Ac_2O was developed [1]. A simple and efficient method for the preparation of crown-containing and methoxy-substituted hetarylphenylacetylenes by the bromination followed by dehydrobromination reactions of the corresponding styrylheterocycles [2].



Complex formation of styrylheterocycles and hetarylphenylacetylenes with macroheterocyclic compounds (cavitands) – β-cyclodextrins and cucurbit[7]uril – was studied by electronic and ^{1}H NMR spectroscopy methods. It was established pseudorotaxane structure and stability constants of the inclusive complexes of the “host–guest” type.

*This work was supported by the RFBR (project № 18-03-00214) and the
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Thiocyanate-containing triple-role protic ionic liquids as surrogates of (iso)thiocyanic acid

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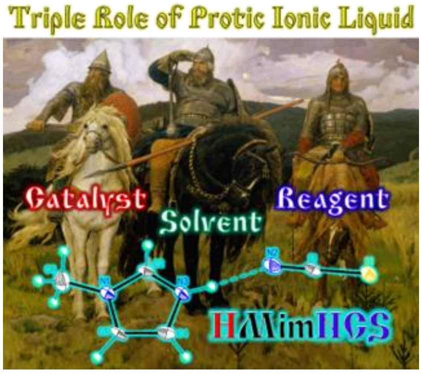
The search for physiologically active small molecules that serve as starting points on the way to modern drugs is one of the most important tasks at the intersection of organic and medicinal chemistry. Although the current state of the art in organic synthesis allows solving problems of a high degree of complexity, the development of new effective synthetic methodologies that satisfy both the growing needs of public health and the principles of "green chemistry" remains in demand.



In order to develop new approaches to the synthesis of bioactive azaheterocycles, we proposed a fundamentally new concept of using protic ionic liquids (PILs, salts of organic bases and Brønsted acids – B: HNu, melting below 100 °C), which perform three functions in concert: 1) recyclable reaction medium; 2) process initiator – Brønsted acid (proton source); 3) nucleophilic reagent [1].

The developed strategy was approved in the ring-opening reaction of DA (donor–acceptor) cyclopropanes with thiocyanate ion. When using 1-methylimidazolium thiocyanate (HMimNCS) or triethylammonium thiocyanate (Et_3N HNCS) as a protic ionic liquid for this process, an unusual chemoselectivity of the ambident thiocyanate ion was found: a formal attack by a nitrogen atom (rather than sulfur, as in the case of Lewis acid catalysis [2]) on the activated three-membered ring led to the formation of alkylisothiocyanate, which underwent immediate cyclization with the formation of 3,5-disubstituted pyrrolidine-2-thiones – the formal [3+2]-cycloaddition products of DA cyclopropanes to isothiocyanic acid. The proposed methodology has been successfully demonstrated on a wide range of DA cyclopropanes.

The developed procedure was successfully scaled-up. In addition, it was demonstrated that multiple (up to 4 times) regenerations of protic ionic liquids do not significantly affect the transformation efficiency. Triple-role PILs were also employed in other reactions leading to synthetically valuable classes of organic compounds [1, 3].

This work was supported by the Russian Science Foundation (grant № 21-73-10212)

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New aspects of the synthesis of thioglycolurils and their derivatives

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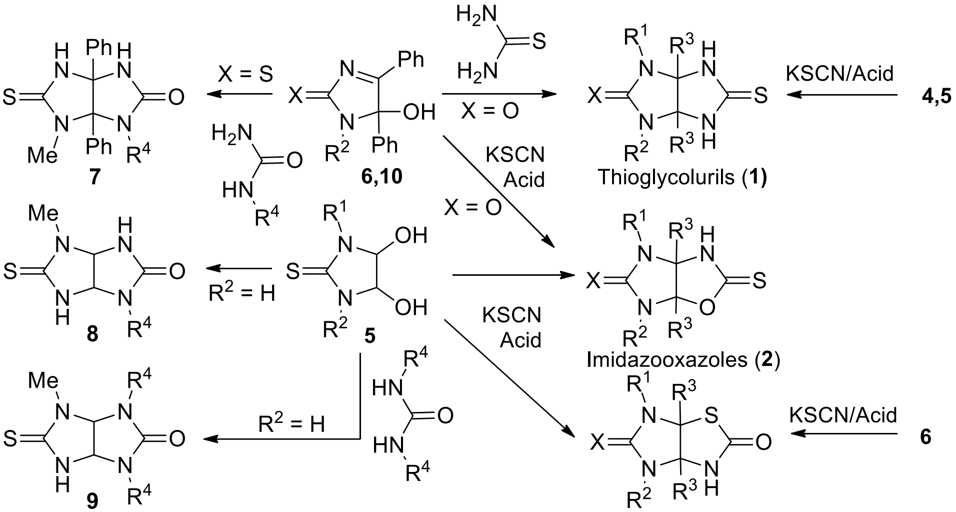
It is known that glycolurils have a wide range of applications and are used as drugs, nitrogen fertilizers, high-energy compounds, starting compounds for the preparation of various annelated, hybrid polyheterocyclic compounds. However, thio- and heteroanalogues of glycolurils are less available and not studied enough, but no less promising.

Syntheses of thioglycolurils (**1**), imidazooxazoles (**2**) and imidazothiazoles (**3**) are the area of our scientific interests. An original approach to the preparation of individual representatives of products **1**,**3** based on interactions KSCN/acid with 4,5-dihydroxyimidazolidin-2-ones (thiones) DHI **4** (DHIT **5**) and 1-alkyl-5-hydroxy-4,5-diphenyl-1*H*-imidazole-2(5*H*)-ones (imidazolones) **6**, respectively, was developed by us earlier [1,2]. This work expanding the boundaries of these reactions to obtain target products **1-3** and developing a new approach to the synthesis of compounds **1**,**3**,**7-9** using thiourea and alkylureas in condensations with DHIT **5**, imidazolones **6** or imidazolthione **10**.



1,2,3 X = O, S; **4,6** X = O; **5,10** X = S

Thioglycolurils **1**,**7** were obtained by condensation of imidazolones **6** with thiourea or by the reaction of 1-methylimidazolthione **10** with 1-alkylureas for the first time. For the synthesis of imidazooxazolones **2**, reactions of imidazolone **6** with KSCN/acid were used. Imidazooxazoles (thiazoles) **2**,**3** were synthesized by the interaction of DHIT **5** with KSCN/acid. Synthesis of unknown trialkylthioglycolurils **9** were carried out by condensation of DHIT **5** with 1,3-dialkylureas.

This work was supported by the Russian Science Foundation
(Project RSF 22-23-00769, https://rscf.ru/project/22-23-00769/)

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3D Hybrid O,N ligands: synthesis and coordination properties

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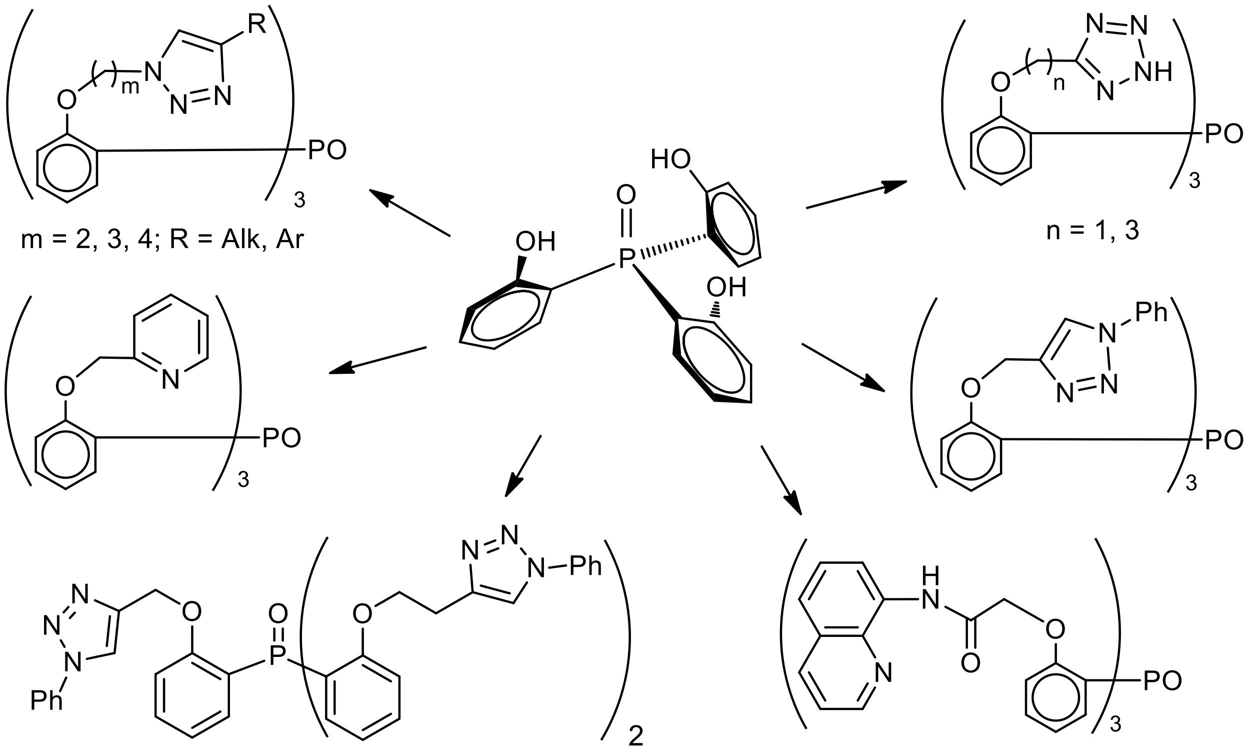
Methods for the synthesis of new hybrid tripodal phosphine oxides modified by triazole, tetrazole, pyridine, and quinoline functional groups have been developed:



Complexes of the obtained ligands with *d*- and *f*-block elements were prepared. The structure of the ligands and their complexes was studied by multinuclear (^{1}H, ^{13}C, ^{31}P) NMR, IR, and Raman spectroscopy and X-ray diffraction.

This work was financially supported by the Russian Science Foundation (project no. 20–13–00329). X-ray diffraction and spectral studies were supported by the Ministry of Science and Higher Education using equipment of the Center for Molecular Structure Studies, Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

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Chemical interactions of imidazolium cation with lignin

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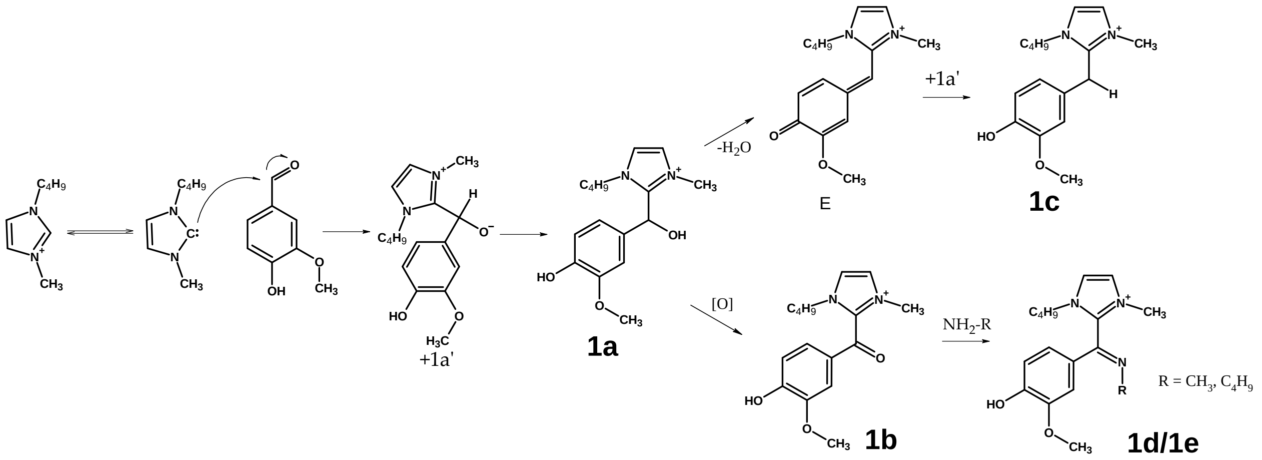
Lignin is the second most common renewable biopolymer after cellulose. Dissolution of lignin during biomass processing is very challenging due to its rigid structure provided by C-C or C-O-C covalent bonding between the structural units. Fractionation of lignocellulosic biomass using ionic liquids (ILs) is one of the most promising approaches for chemical processing of renewable raw plant materials, corresponding to the principles of green chemistry.

It is well known that ILs can actively interact with lignin, causing its chemical transformation. The isolation of lignin with the use of 1-butyl-3-methylimidazolium acetate is accompanied by the formation of a considerable variety of nitrogen-containing oligomers. The formation of these compounds leads to the detection of up to 6.5% nitrogen in isolated samples, but the mechanism of their formation is currently poorly studied.

For this reason, the aim of this study was to investigate the chemical transformations of model lignin compounds with 1-butyl-3-methylimidazolium acetate. As model lignin compounds were chosen compounds bearing aldehyde-group (vanillin, veratraldehyde and syringaldehyde), ketone-group (acetovanillon and acetosyringone), hydroxyl-group (vanillin alcohol), and double C=C bond (eugenol and isoeugenol). The structure as well as quantities of the formed adducts were studied using high-performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS).



It was shown that treatment of model lignin compounds with 1-butyl-3-methylimidazolium acetate leads to their chemical modification due to nucleophilic addition of imidazolium carbene to electron-deficient units. The reactivity of the model compounds with respect to the cation, based on the obtained data, decreases in the series of aldehydes, compounds with C=C double bond, compounds with aliphatic alcohol groups and ketones.

This work was supported by the Russian Science Foundation (grant No. 21-73-20275) and the Russian Foundation for Basic Research (grant № 20-33-90153-asp)

Nucleophilic ring-opening of donor-acceptor cyclopropanes in the synthesis of γ-lactam derivatives

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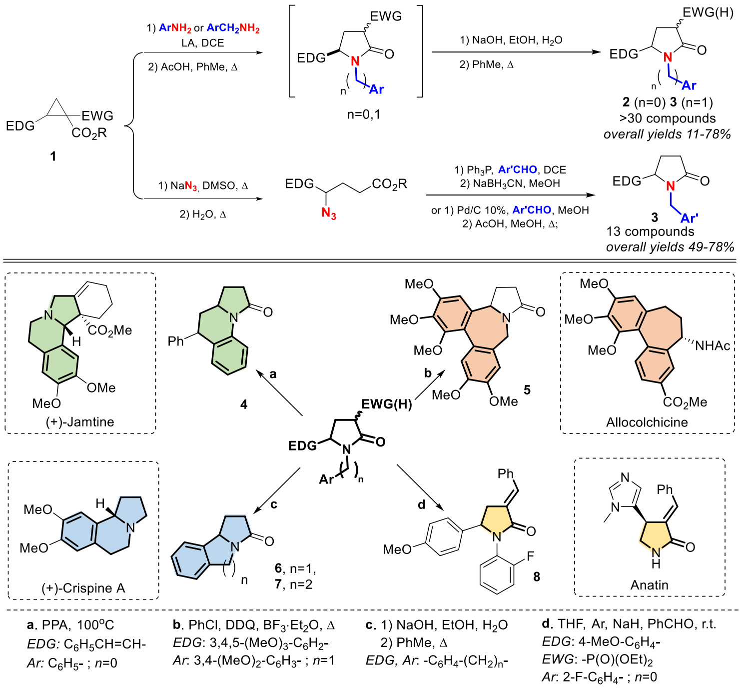
The γ-pyrrolidone based skeletons is a constituent of many biologically active molecules, both natural and synthetic, and a key component of clinically relevant entities [1]. In this work two effective and simple synthetic approaches to polysubstituted pyrrolidin-2-ones **2**,**3** from donor-acceptor cyclopropanes **1**, bearing the ester group as the one of acceptor substituents, and azide [2] or amines were developed. In addition, polysubstituted γ-pyrrolidones are advanced precursors for the development of original and efficient transformations of such compounds into a wide diversity of azaheterocycles with monocyclic, bicyclic and polycyclic skeleton. On basis of simple transformations of synthesized γ-pyrrolidones we developed straightforward and efficient approaches to tetrahydropyrrolo[1,2-*a*]quinolin-1(2*H*)-one **4**, dibenzo[*c,e*]pyrrolo[1,2-*a*]azepines **5**, tetrahydro-3*H*-pyrrolo[2,1-*a*]isoindol-3-one **6**, hexahydropyrrolo[2,1-*a*]isoquinoline **7**.



This work was supported by the Russian Science Foundation (grant № 21-13-00395)

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Phosphonium ylides in the multicomponent synthesis of pyrrolidines

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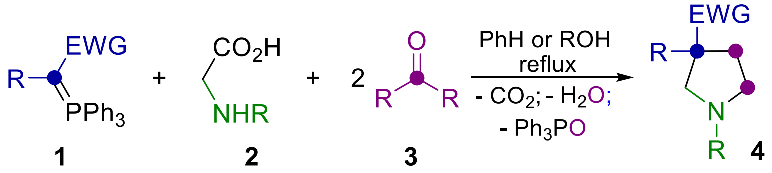
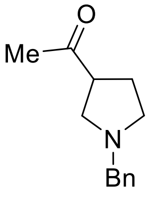
Wittig reaction is a powerful tool for the stereospecific construction of double carbon-carbon bonds in organic chemistry [1]. It also provides a convenient method for the in situ generation of olefin with subsequent reactions at the C=C double bond, for example domino Wittig-Diels-Alder reaction. Nevertheless, only rare examples of tandem Wittig-Huisgen reaction are found in literature [2].

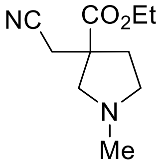
In this work we focused our efforts on the implementation of such tandem reaction and the synthesis of pyrrolidines via in situ generation of alkenes and their reaction with azomethine ylides. Thus, a pseudo-four component reaction of phosphonium ylide **1**, *N*-alkylglycine **2** and two equivalents of carbonyl compound **3** resulting in pyrrolidines **4** in 37–87% ylides was performed. In this process carbonyl compound is involved in two simultaneous reactions: Wittig reaction and formation of azomethine ylide. The subsequent [3+2] cycloaddition reaction of the formed ylide and alkene gives rise to a pyrrolidine core **4**. Both nonstabilized and stabilized types of azomethine ylides were applied, allowing the formation of 3-monosubstituted **4a** as well as 2,3-dispirosubstituted pyrrolidines **4c**,**d**.



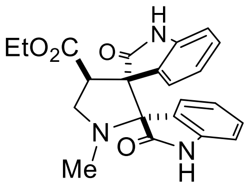
Selected examples:



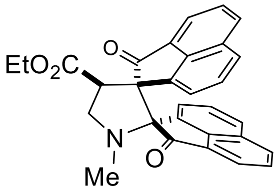
4a (67%)



4b (48%)



4c (87%)



4d (67%)

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University project within the Priority-2030 Program) is gratefully acknowledged

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Investigation of photochemical transformations using electrospray ionization mass spectrometry

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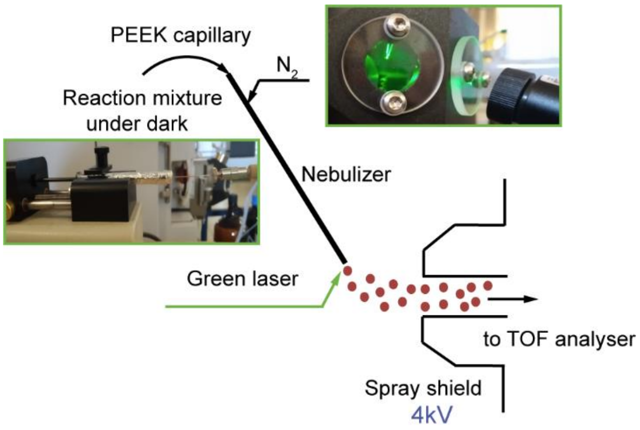
High resolution mass spectrometry is one of the widespread techiqies to study the composition and structure of chemical compounds [1]. High speed of analysis, sensitivity and accuracy are undeniable advantages of this method. So, mass spectrometry is a reliable and effective approach for the reaction mechanism investigation [2]. The development of new techniques and adaptation of existing approaches is the current task for researcher.

Nowadays, photochemical transformations are one of powerful strategies for fine organic synthesis. Visible-light-promoted reactions have significantly changed the field of organic chemistry in recent decades. Investigation of reaction mechanism and revealing the intermediates structure are the key points for understanding the reaction pathways.



In our laboratory we focused on investigation of photochemical transformations and studying the reaction mechanisms [3], [4]. For this purpose, we carried out online monitoring of photochemical transformations by coupling of electrospray ionization mass spectrometer with laser light source. The designed setups were optimized for each studied reaction.

This work was supported by the Russian Science Foundation (grant № 21-13-00193)

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Synthesis of novel benzofuroxan derivatives with wide spectrum of biological action

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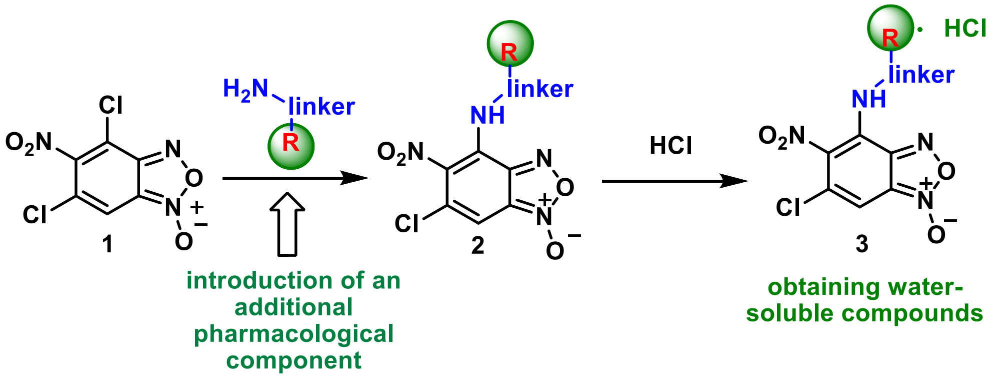
Currently, oncological diseases are one of the most serious problems of humanity, which requires the development of new drugs and methods of treatment. Cases of improving methods of therapy for oncological diseases, leading to a dramatic improvement in treatment results, are extremely rare, and most of the drugs used to treat cancer are toxic to the body as a whole.

The synthesis of amine-containing derivatives of benzofuroxan is of interest due to the possibility of their use as anti-inflammatory and antitumor drugs [1]. At the same time, the use of benzofuroxan derivatives in medicine, despite their wide range of biological activity, is limited due to their low solubility in water, which narrows the range of their potential dosage forms.



As a result of the studies carried out, not only a wide range of hybrid compounds **2** were obtained that showed various types of biological activity [2,3], but also water-soluble salts **3** were obtained for the first time, which are of interest as potential antitumor agents.

The publication of the scientific conference materials was carried out with the financial support of the Russian Science Foundation and the Cabinet of Ministers of the Republic of Tatarstan within the framework of the scientific project № 22-23-20015, https://rscf.ru/en/project/22-23-20015/

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Synthesis and photophysical properties of new borondipyrromethenes containing heterocyclic or aroyl fragments in positions 1 and 7

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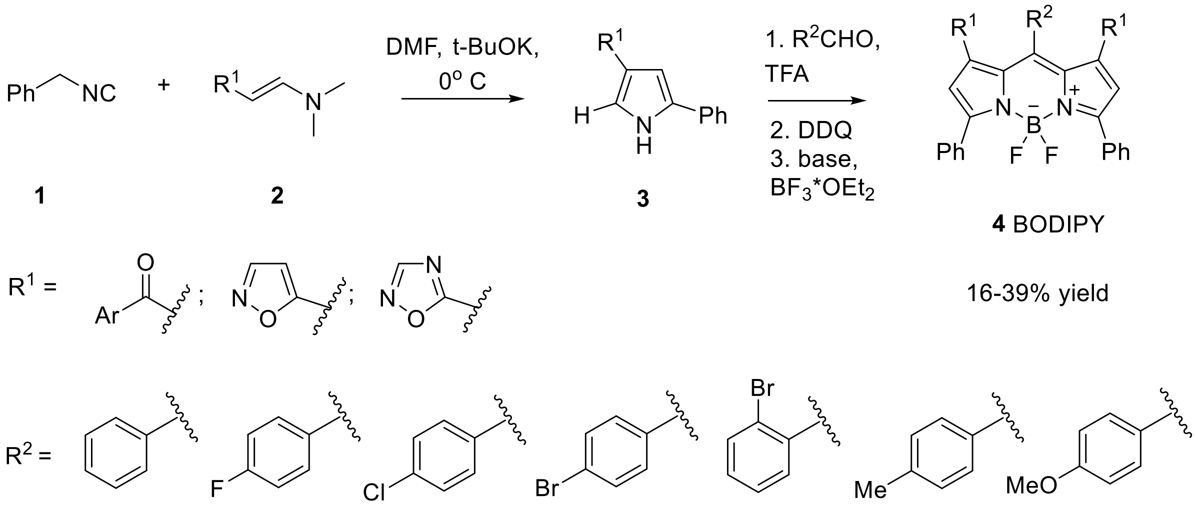
The report presents a strategy for the synthesis of borondipyrromethenes containing 1,2,4-oxadiazole, isoxazole or aroyl substituents. Previously, we have developed a new method for the synthesis of NH-unsubstituted pyrroles with a free alpha position. The resulting pyrroles **3** were used in the synthesis of new BODIPY **4**. The study of the photophysical properties of the obtained compounds showed that the absorption maximum is in the region of 580 nm, the emission maximum is in the region of 630 nm. In addition, it has been shown that the introduction of electron-donating substituents into the phenyl ring at the meso position of BODIPY significantly reduces the fluorescence quantum yield (QY) (up to 12%). At the same time, the introduction of an acceptor substituent increases QY to 96%.



The reported study was funded by RFBR, project number 19-33- 60036 and 21-33-70029 and supported by the RUDN University Strategic Academic Leadership Program

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Synthesis of novel spiro derivatives of hydantoins and thiohydantoins by reaction of 1,3-dipolar cycloaddition of nitrilimines

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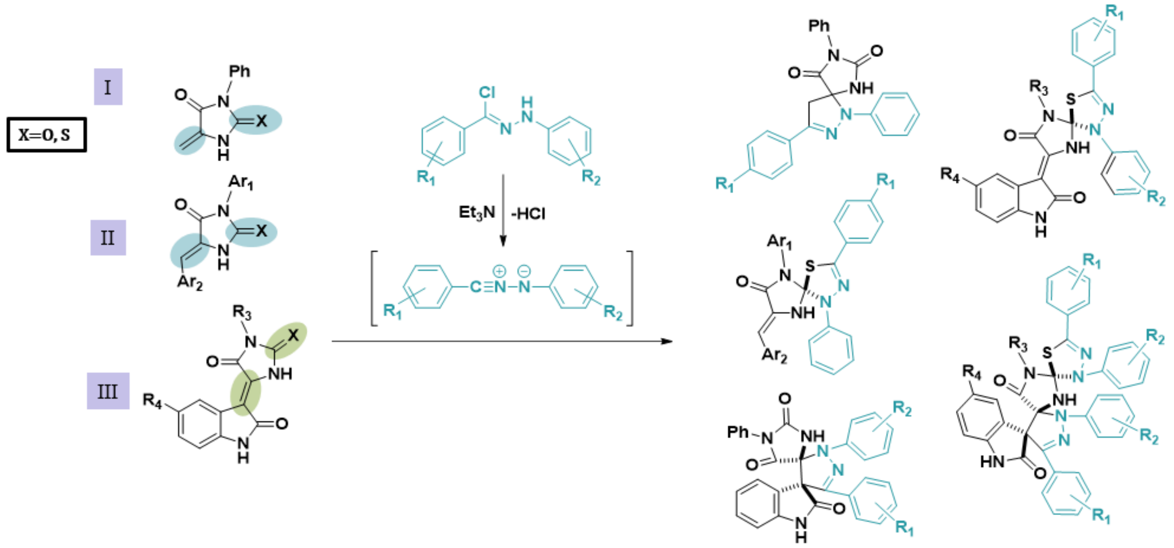
The creation of molecular complexity and diversity from common starting materials in potential drug candidates and biologically important molecules is a challenge in modern organic and medical chemistry from both academic and industrial viewpoints. Nitrile imines, generally prepared from hydrazonyl halides, are important transient 1,3-dipolar species and have been utilized as useful synthons of spiroheterocycles in organic synthesis[1].

These dipoles have a wide range of reactivity with different dipolarophiles, containing carbon-carbon and carbon-heteroatom double and triple bonds[2,3]. In this work we used 1,3-dipolar cycloaddition reaction of nitrile imines with hydantoins and thiohydantoins derivatives, containing carbon-carbon double bond in the 5th position of the cycle, as a new synthetic route to form molecules with two, three and four spiro fused heterocycles.



Using cycloaddition reaction in this work, a study of the reactivity of nitrile imines in reactions with di-, tri- and tetrasubstituted double bonds in the 5th position of the hydantoin and thiohydantoin cycles was carried out (I, II, III). As a result, we were able to develop effective approaches to the synthesis of structures, containing two, three, and four spiro-linked heterocyclic fragments.

This work was supported by grant № MK-3748.2022.1.3

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Imidazo[4,5-*e*]-1,2,4-triazine-3-thiones as precursors in the synthesis of N-, S-, and O-containing heterocycles

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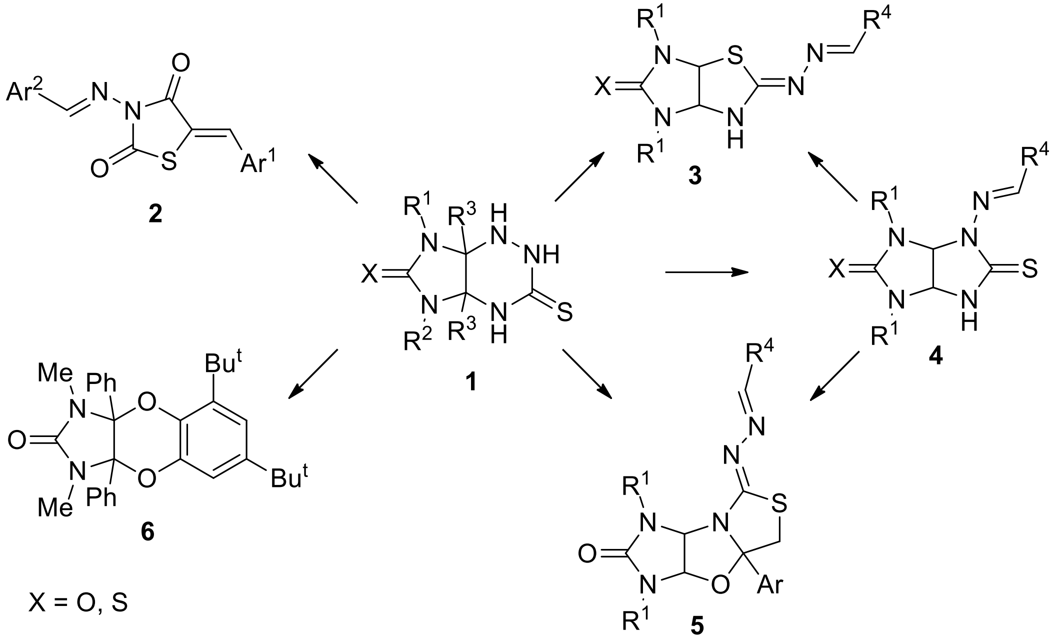
1,2,4-Triazines are a promising class of heterocyclic compounds to search for biologically active substances, agrochemicals, and dyes based on them. Due to their diverse reactivity, 1,2,4-triazines, including heteroannelated examples of such compounds, can be used to produce other heterocyclic compounds: pyridine, pyrimidine, triazole, imidazole derivatives [1].

To synthesize new heterocyclic compounds with potential biological activity, the reactions of imidazo[4,5-*e*]-1,2,4-triazine-3-thiones **1** proceeding with contraction, rearrangement or decomposition of triazine ring are considered in this work.



Thiazolidines **2** were prepared from imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazin-7-ones synthesized by the reaction of compounds **1** with bromoacetic acid upon treatment with aromatic aldehydes. Imidazothiazoles **3** were synthesized via Dimroth-type N/S-interchange of N-aminothioglycolurils **4**. The latter, in turn, were obtained through reaction of compounds **1** with aromatic aldehydes or 3-phenylacroleines. Alkylation of thioglycolurils **4** with bromoacetophenones accompanied with a cascade of intramolecular rearrangements leading to imidazo[4,5-*d*]thiazolo[4,3-*b*]oxazole derivatives **5**. Condensation of S-methylderivative of compound **1** with 3,5-di-*tert*-butyl-1,2-benzoquinone resulted in tricyclic compound **6**.

Target compounds **2**, **3** and **4** possessed antiproliferative activity towards human cancer cell lines.

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Synthesis of 6-halogen-4-hydroxyquinoline-2(*1H*)-ones derivatives, potential antibacterial agents

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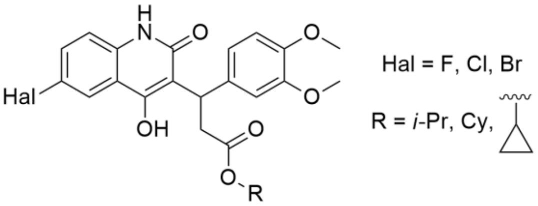
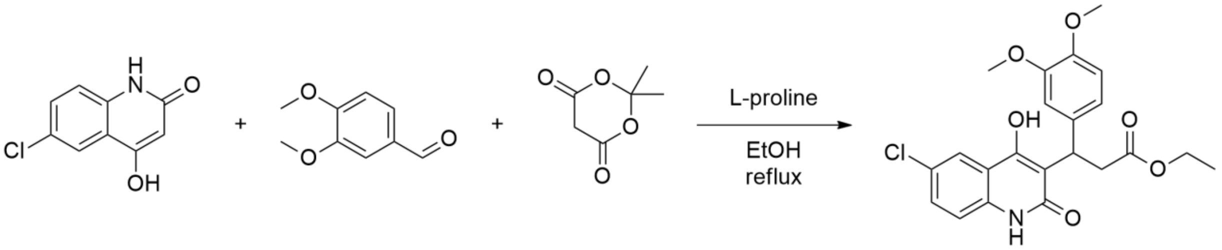
Compounds based on 4-hydroxyquinoline-2(1*H*)-ones have already established themselves as substances that exhibit a variety of pharmacological activity. Among them there are those that have shown themselves to be potential antitumor, antifungal, antiviral, as well as antibacterial agents [1]. The possibility of using these compounds as promising antibiotics is one of the areas of scientific activity of our laboratory.

Previously, we have developed synthetic schemes for the production of compounds based on 6-halogen-4-hydroxyquinoline-2(*1H*)-ones, potentially exhibiting antibacterial activity, whose structures were obtained using computational chemistry methods. At the moment, the synthesis of these substances is being carried out. This paper discusses the implementation of both previously proposed synthetic schemes and those that have recently been used to obtain finite structures.





In particular, we have discovered a very elegant, effective and easy-to-implement method for functionalizing the third position of the heterocyclic substrate used in synthesis. This three-component reaction makes it possible to obtain structures, the subsequent transesterification of which leads to compounds potentially possessing antibacterial properties.

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New D–A–π–A'-type sensitizers with a 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole donor building block

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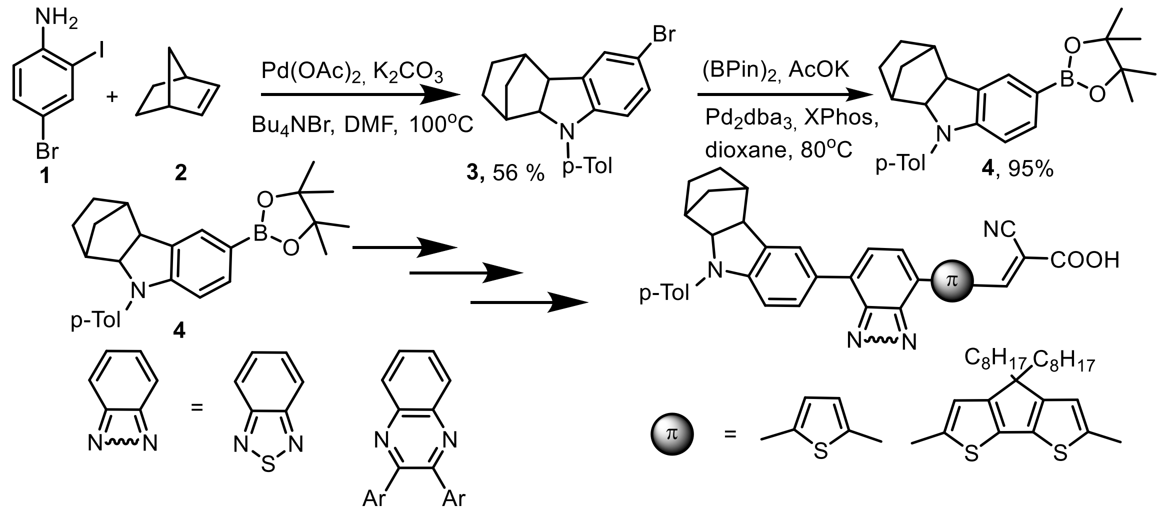
Electron-donating building blocks based on carbazole and related compounds are precursors for the synthesis of sensitizers, which are widely used in OLED-technologies,[1] in thin-film transistors (TFT),[2] in dye-sensitized solar cells (DSSCs)[3]. Varying the structure of these compounds has a significant effect on the characteristics of the target devices, so the study of the molecular design of the dyes is very important.

In this work, we synthesized a new branched non-planar donor block with a rigid structure hexahydro-1*H*-1,4-methanocarbazole building block **3** by the reaction of 4-bromo-2-iodoaniline **1** with norbornene **2**. The reactive group of the boronic ester **4** was introduced into this heterocyclic system by palladium-catalyzed Miyaura reaction with 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) $(BPin)_2$ under optimized conditions in almost quantitative yield. Based on this donor **4**, four new sensitizers of the D-A-π-A' design were obtained by successive cross-coupling reactions. Benzo[*c*][1,2,5]thiadiazole and its quinoxaline analogues as internal acceptors (A), thiophene and dialkyl-substituted cyclopenta[2,1-*b*:3,4-*b*']dithiophene as π-spacers, and cyanoacrylic acid as anchor acceptor A' were used.



On the basis of the obtained dyes, dye-sensitized solar cells were created and PCE value of 5.68% was achieved using CDCA as a co-adsorbent for a dye based on unsubstituted 2,3-diphenylquinoxaline and thiophene π-spacer, which PCE value is higher than efficiency of DSSCs with the known dye **WS-2**.

This work was supported by the Ministry of Education and Science of the Russian Federation, grant number FENU-2020-0019 (2020073GZ)

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A lead-compound for polyphenol oxidases inhibition

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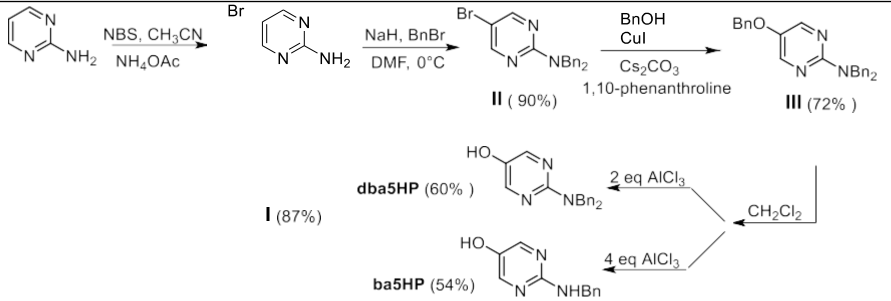
Polyphenol oxidases (PPOs) catalyze o-hydroxylation of monophenols into their corresponding o-diphenols. They also oxidize o-diphenols to the corresponding o-quinones using molecular oxygen. Due to the high chemical activity, o-quinones participate in further chemical reactions and form macromolecules known as melanin which are the core substances of natural pigment of skin, eyes, and hair. Hyper activity of tyrosinase (a famous PPO) causes various dermatological disorders. PPOs are also responsible for unfavorable enzymatic browning of plant-derived phenolic compounds that causes economic loss of agricultural products. Based on tyrosinase inhibition science, two pyrimidine derivatives were designed and studied. Docking of 2-dibenzylamine-5-hydroxy pyrimidine (dba5HP) and 2-benzylamino-5-hydroxy pyrimidine (ba5HP) on mushroom tyrosinase (MT) showed that the former could not occupy MT active site pocket (PAs) while ba5HP could do so (Moldock score = −63.95). MD simulation revealed that the complex of ba5HP-MT reached stability <30 ns. In-silico biocompatibility examinations predicted high permeability, good bioavailability, low toxicity, and synthetic accessibility of 1.59 for ba5HP with high probability for CYP-mediated metabolism. Subsequently, both compounds were synthesized in good yields. Kinetics studies proved that, unlike dba5HP, ba5HP could strongly inhibit MT competitively (IC50 = 32.28, Ki = 11.32 µM). Considering the facile synthesis, potential for structural modifications, and passing most of the lead-likeness filters, it seems likely that ba5HP plays key roles in the syntheses of novel depigmentation medicines as well as more specific inhibitors for various tyrosinases and PPOs. this study has synthesized 2-amino-5-hydroxy pyrimidine derivatives as novel analogues of tyrosinase substrate with inhibitory activity.

Scheme 1. The designed synthetic route to **ba5HP** and **dba5HP**



Ring expansions of donor-acceptor cyclopropanes in the synthesis of carbo- and heterocycles

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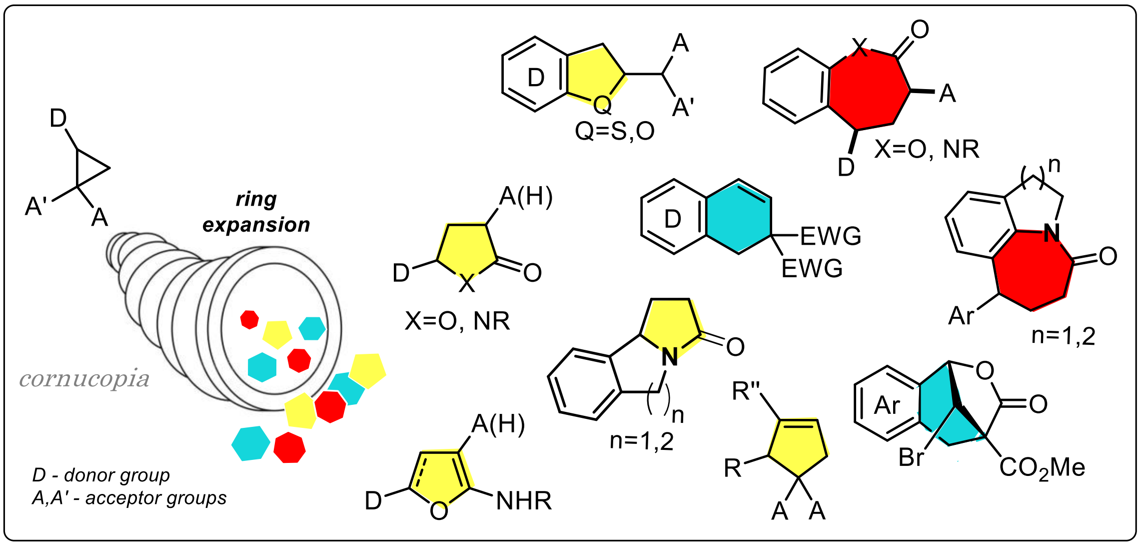
Donor–acceptor (D–A) cyclopropanes are a unique class of substrates which have been proved to be useful building blocks for the synthesis of a broad diversity of cyclic systems. Under the activation with Lewis or Brönsted acid, they undergo three-membered ring opening that can be accompanied by diverse other processes including the participation of multiple reaction centers in D–A cyclopropane molecules. As a result, a broad spectrum of atom-economic processes leading to the significant increase of the molecular complexity has been developed. Herein, we demonstrated several Lewis acid-induced isomerizations including ring enlargement processes producing a large diversity of carbo- and heterocycles, from simple ones to complex polycyclic systems [1-4]. These transformations are promising routes to the synthesis of various bioactive compounds. The process chemo- and stereoselectivities are controlled by the reaction conditions, primarily by the Lewis acid applied, as well as by the nature of donor substituent. Densely functionalized DA cyclopropanes *as horn of plenty* of synthetic opportunities provide rapid accesses to various cyclic systems by means of ring expansions of three-membered ring.



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Molecular interactions in gas–liquid systems of organic compounds

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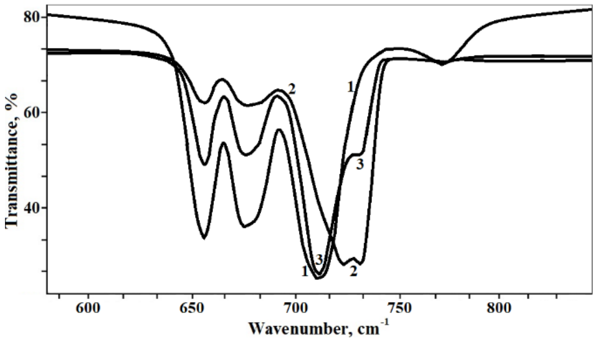
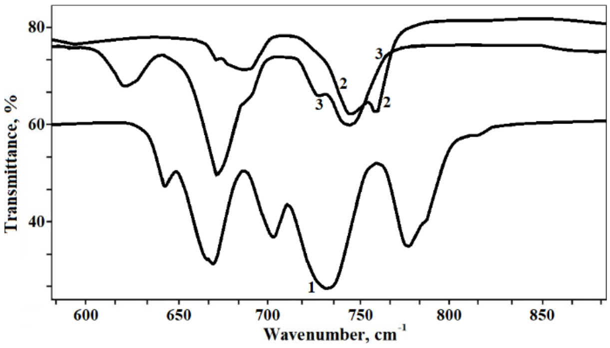
The present research considers the IR spectral study of molecular interactions leading to a transient fluid-like state formation in gas–liquid thin-layered systems of acetonitrile, acetone, bromoform, carbinol, *1,2*-dichloroethane and *1,1,2*-trichloroethane on a solid surface. A similar phase state was previously studied for methane halides by isothermal compression-expansion method described in [1]. The method presented below, in contrast, is not based on varying the pressure, but on changing the temperature according to the following scheme: 1) the sample was put on a KBr optical window under a 1-mm-thickness Teflon gasket; 2) the gasket was covered by another window; 3) all items were clamped in a holder; 4) the holder was placed in the device for *in situ operando* IR spectroscopy; 5) the sample was heated at the selected temperature for a certain time until the intensity of the IR bands stopped changing; 6) the sample was cooled (to room temperature); 7) after one hour, the cell was heated and cooled again.

The experiment showed the reproducibility of the previously obtained results [1] under a different method which means that the transitional phase state can be generated in various ways, since it is formed due to the initiation of molecular interactions in gas–liquid systems of organic compounds. As an example, below are the spectra recorded for *1,2*-dichloroethane (left) and *1,1,2*-trichloroethane (right); **1** – at the stage 5), **2** – at the stage 6), **3** – at the stage 7).





In both cases, sp. **1** corresponds to the liquid spectrum of the substance, sp. **2** – to the gas spectrum, and sp. **3** – to the intermediate state. It can be seen that the spectrum of the transitional state combines the separate characteristic bands of the gas and liquid spectra [1]. Spectra of the transient phase state were obtained for other samples as well. All spectra demonstrate a correlation between a molecular binding and changes of spatial arrangement that combines both the original and transformed structures. The suggested models of transformations consider hyperconjugation, conformational isomerism and intermolecular hydrogen bond [2,3].

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Non-chelate-assisted double C-H activation of arenes via Rh(III) complexes: a simple way for the creation of naphthalene framework

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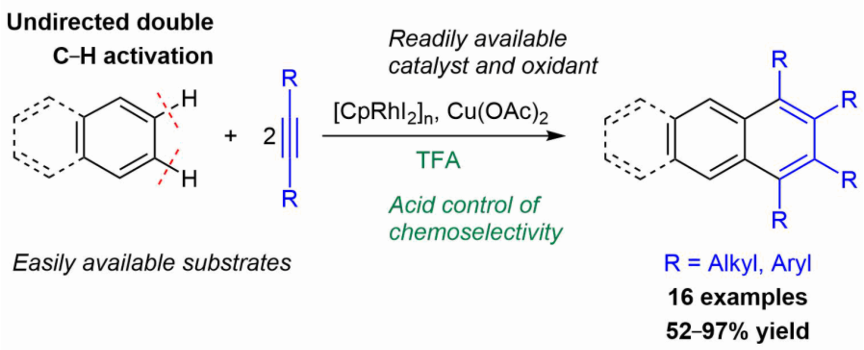
The polycyclic aromatic hydrocarbons (PAHs) are well known to be of particular interest for the construction of organic light-emitting diodes because of their strong luminescence and charge mobility [1,2]. Extended π-conjugated derivatives (such as tetracene and pyrene) demonstrate very rich photophysical properties due to the high delocalization of electron density in them. Therefore, the development of efficient methods for the homologation of benzene derivatives to higher acenes is an important task of modern organic chemistry.

Conventional methods of the construction of PAHs require the presence of directing or leaving groups (such as iodo, boronyl or carboxyl substituents) [1,3]. The main drawbacks of these methods are low atom and step economy. To overcome this problem, double CH activation of arenes seems to be helpful [4].

In the present work we report an efficient protocol for the homologation of arenes with both dialkyl- and diarylacetylenes, using complex $[CpRhI_2]_n$ as a catalyst, the readily available $Cu(OAc)_2$ as an oxidant, and trifluoroacetic acid (TFA) as an additive (Scheme 1) [5]. The reaction proceeds through double undirected C-H activation with tolerance to different functional groups. The reaction mechanism and the role of the TFA additive that increase catalyst activity and determine the direction of the reaction pathway, was also explored.



Scheme 1. Rh(III)-catalyzed arene homologation

This work was supported by the Russian Science Foundation (Grant No. 17-73-30036)

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Reactions of 2-(1'-Me_3SiO-1'-trifluoromethylated)thiophenes and furans in CF_3SO_3H

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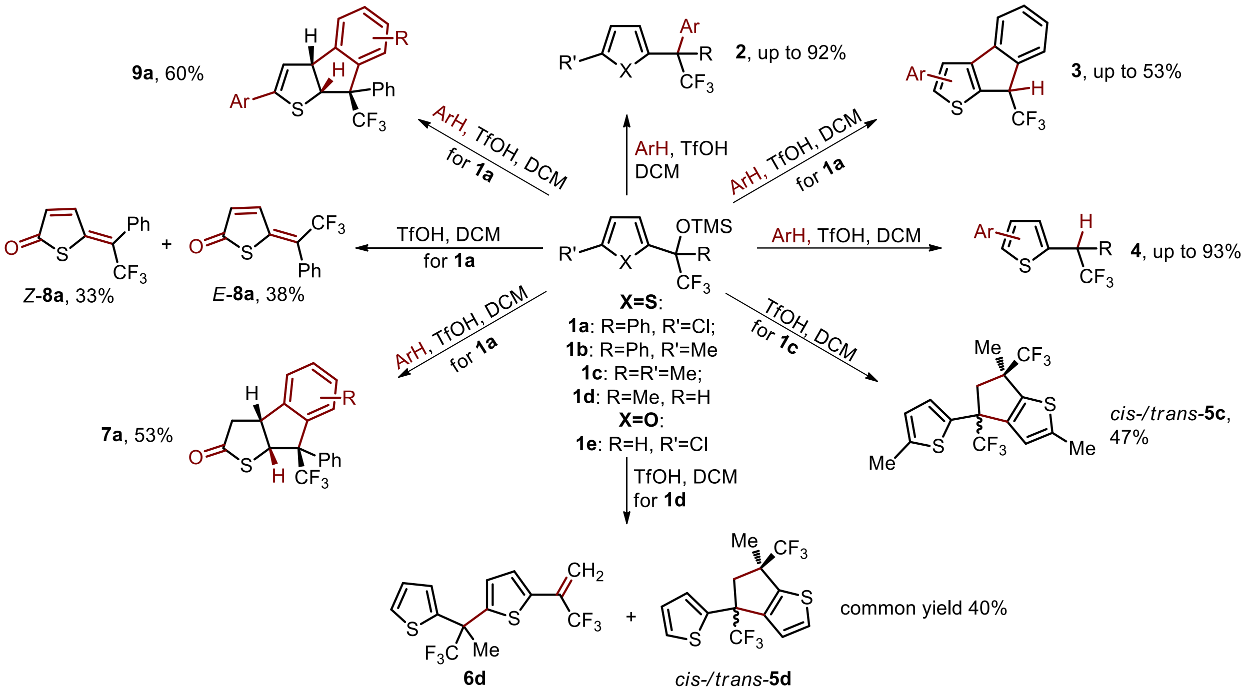
Ubiquitous in Nature, five-membered heterocyclic compounds are part of numerous drugs in therapeutic domains, including the most prominent cardiovascular and metabolic diseases, central nervous system disorders, *etc* [1]. At the same time, fluorinated compounds are getting increasing and widespread applications in medicinal, agrochemical and material sciences, and especially in drug discovery [2,3]. Accordingly, the development of new methods for the synthesis of novel fluoroorganics of the thiophene and furan families is a current issue of organic chemistry.

We have found that 2-(1'-Me_3SiO-1'-trifluoromethylated)heterocycles **1** are convenient building block to construct more complex fluorinated compounds via a formation of new C-C, C-O and C-H bonds. The TfOH mediated multichannel transformations of the heterocycles **1** lead to the formation of novel fluoroorganics of the thiophene and furan families, including thiophenones **7**,**8**, "dimeric" structures as indane-like molecules **5** and alkene **6**, as well as various arylated heterocycles **2-4**, **9**. Significant diastereoselectivity in products formation is observed.



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New reducing systems for reductive amination

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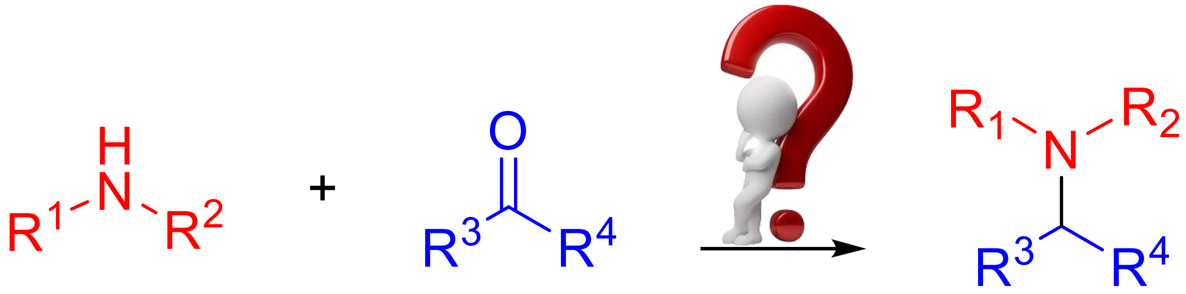
Reductive amination plays a key role in pharmaceutical and medicinal chemistry owing to its synthetic merits and ubiquitous presence of amines among biologically active compounds. Nitrogen-containing compounds play an important role in different fields of chemistry. Various reducing agents for the reductive amination are known. The main problem of common reducing agents is a balance between activity and selectivity. For example, one of the most selective reagents, sodium triacetoxyborohydride, can reduce starting carbonyl compounds to alcohols, thus lowering the yield of the target amines. Small numbers of functional groups are survivable using typical reducing agents.

We developed new methods and upgraded known protocols for effective and selective reductive amination[1,2].



- ★ **CO/[M] activation by phosphines**
- ★ **CO surrogates**
- ★ **something new**

This work was financially supported by the Russian Science Foundation (grant 22-73-00275)

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Intermolecular photocatalytic chemo-, stereo- and regioselective Thiol–Yne–Ene coupling reaction

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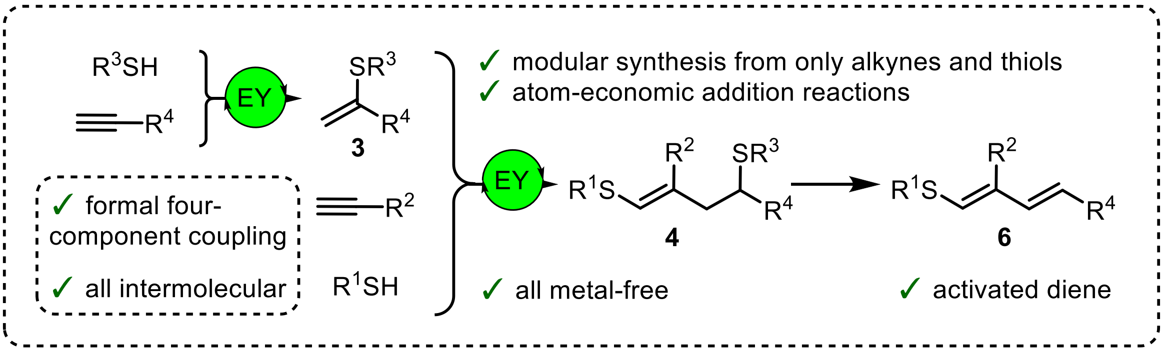
Alkynes and alkenes are widely used substrates in organic synthesis due to their excess energy, concealed in multiple bonds. Coupling of alkynes with other alkynes or alkenes with specific selectivity is a challenging task, which can be overcame by transition metal catalysis. However, this approach requires usage of substrates with directing groups, which can not be easily removed after the synthesis. This problem also has not been solved yet by radical reactions.

In this study novel metal-free photocatalytic approach to the yne-ene coupling is considered. Products **4** are obtained with yields up to 81% [1, 2]. Thiol-yne-ene reaction can be carried out with preliminary one-pot photocatalytic synthesis of α-vinilylsulfide **3** from alkyne and thiol [3]. Ease of elimination of thiol, implemented on the first step allows consider this sequence as a thiol-yne-yne coupling strategy with obtaining of activated diene **6**. Proposal of the mechanism of thiol-yne-ene reaction is made on the basis of investigation of intermediates by combination of EPR, UHRMS and NMR experiments.



This work was supported by the Russian Science Foundation (RSF grant № 21-13-00193)

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Highly accepting halogenacetylenes - new valuable reagents in organic synthesis

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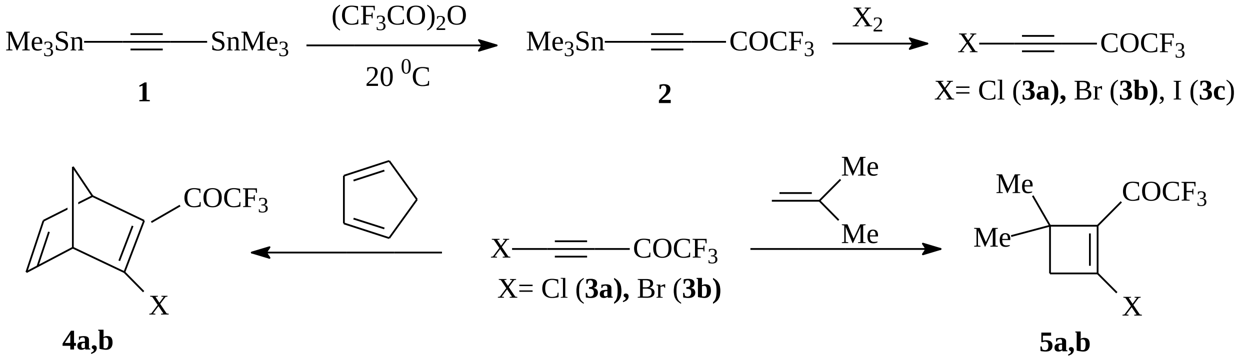
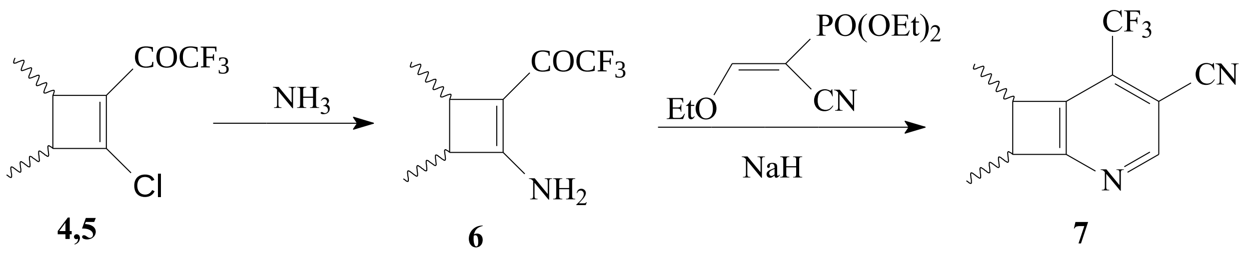
Although a trifluoroacetyl group belongs to the strongest mesomeric acceptors and is extremely promising for further transformation of the cycloadducts, only very few examples of the Diels-Alder reactions of trifluoroacetylacetylenes have been reported up to date. Herein, we describe the simple preparation of 1-trifluoroacetyl-2-halogenoacetylenes and some sorts of their cycloaddition reactions. The unsaturated trifluoromethyl ketones delivering by these reactions appeared to be the useful starting materials for the preparations of complex fluorinated fused heterocyclic compounds.

The first thing we disclosed, the available bis(trimethylstannyl)acetylene **1** easily reacts with trifluoroacetic anhydride to afford the monoacylated alkyne **2,** which in turn can be quantitavely halogenated to form 1-trifluoroacetyl-2-halogen acetylenes **3a-c**. The compounds **2a-b** exhibited the properties of the strongest dienophiles in the Diels-Alder reactions. Furthermore, they entered the unusual orbitally forbidden [2+2]-cycloadditions with simple alkenes under very mild conditions.



$$\underset{\mathbf{1}}{Me_3Sn{-}{\equiv}{-}SnMe_3} \xrightarrow[20\ ^0C]{(CF_3CO)_2O} \underset{\mathbf{2}}{Me_3Sn{-}{\equiv}{-}COCF_3} \xrightarrow{X_2} X{-}{\equiv}{-}COCF_3$$

The cycloadducts **4, 5** thus obtained were found to be the valuable versatile reagents for the preparation of a variety of fluorinated heterocycles fused with the strained carbocyclic moieties. For example, they smoothly react with ammonia to give the corresponding enaminoketones **6,** which serve as a source of trifluoromethylated pyridines **7**.



This work was supported by the Russian Science Foundation (grant № 22-23-00887)

Study of crown-containing styryl dyes and peculiarities of their photoreactions

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Photochemical reactions contribute significantly to carbon-carbon bond formation reactions. They can be used to produce exceptional molecular structures that cannot be formed in the usual way. The [2+2] photocycloaddition reaction is one of the most important reactions in photochemistry: it can produce cyclobutane derivatives that are virtually impossible or very difficult to obtain by other means [1]. Styryl dyes are a class of organic photosensitive compounds with various applications in science, engineering and medicine. Styryl dyes containing the crown ether fragment are promising ligands for creating new functional materials, sensory devices, fluorescent markers, etc. [2]. These systems are also promising for incorporation into polymers [3].

The ionophoric analogues of styryl dyes are considered in this work and their ability to form homo- and hetero containing dimeric structures as well as to participate in the [2+2] photocycloaddition reaction in various media is studied. The ability of styryl dyes containing a crown ether fragment to form stable complexes with cucurbit[8]uril and γ cyclodextrin in water, to undergo E/Z photoisomerization and stereoselective [2+2] photocycloaddition reactions is studied.

Depending on the solution and the pre-organization of molecules in the dimer, the process of the photo-cycloaddition reaction can be controlled. In polycrystalline films, the PCA reaction proceeds in successfully pre-organized pseudo dimers regardless of their heterostructure and counterion. For compounds with donor nitrogen as part of the chromophore, the PCA reaction becomes pH-controlled (Fig. 1). In aqueous solutions, the type of cavitand affects the type of dimer formed and the final photoproduct.

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A predictive model for substrate reactivity in transition metal free borrowing hydrogen amination

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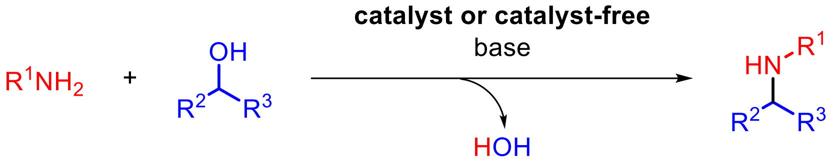
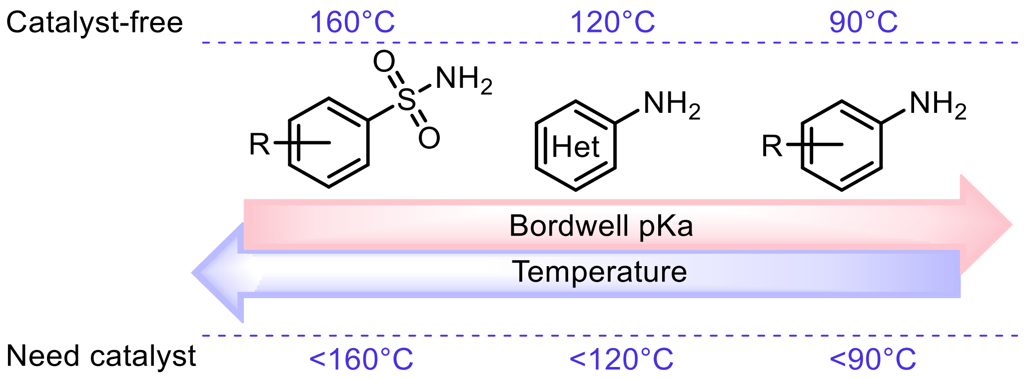
Borrowing hydrogen (BH) is a general, useful, and green method for C–N bond formation.

In contrast to a common opinion, this process can be carried out without transition metal catalysts under basic conditions at a rather low temperature. However, the new transition metal (TM) free BH amination has received considerably less attention. Currently there is no understanding of its potential and limits. Thus a lot of researchers continue to develop new TM catalysts for BH amination with many of these catalysts are reported to work under high temperatures that could allow the reactions to proceed without any catalyst at all. [1]



Herein, we formulated the borderlines, which divide the substrates into the ones requiring a TM catalyst, and the ones that could be prepared via the TM free protocol. We also constructed the general model based on Bordwell's acidity scale to predict the optimal TM free conditions for particular substrates.



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Synthesis of novel water-soluble fullerene derivatives with promising biological activity

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Water-soluble fullerene derivatives are promising candidates for biomedical applications due to their pronounced antiviral, antioxidant, antitumor, neuroprotective and antiamyloid properties.

Recently we have developed efficient and selective methods for the synthesis of a wide range of water-soluble fullerene derivatives [1-4], thus decreasing costs of these compounds and making them available for various biological studies. We will summarize our results on the new synthetic routes for conversion of chlorofullerenes $C_{60}Cl_6$ and $C_{70}Cl_8$ precursors to a variety of water-soluble fullerene derivatives bearing up to 16 carboxylic groups in their molecular structure.

Designed compounds revealed low toxicity *in vitro* and *in vivo* in combination with a pronounced antiviral activity against Influenza, HIV, CMV, and HSV; antitumor; antioxidant and myogenic properties, which makes them promising candidates for the development of novel fullerene-based drugs.

Olga A. Kraevaya acknowledges the support from the Stipend of
the President of Russian Federation (SP-2022)

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Electron-deficient N-oxyl radicals as redox-organocatalysts and reagents in selective CH-functionalization

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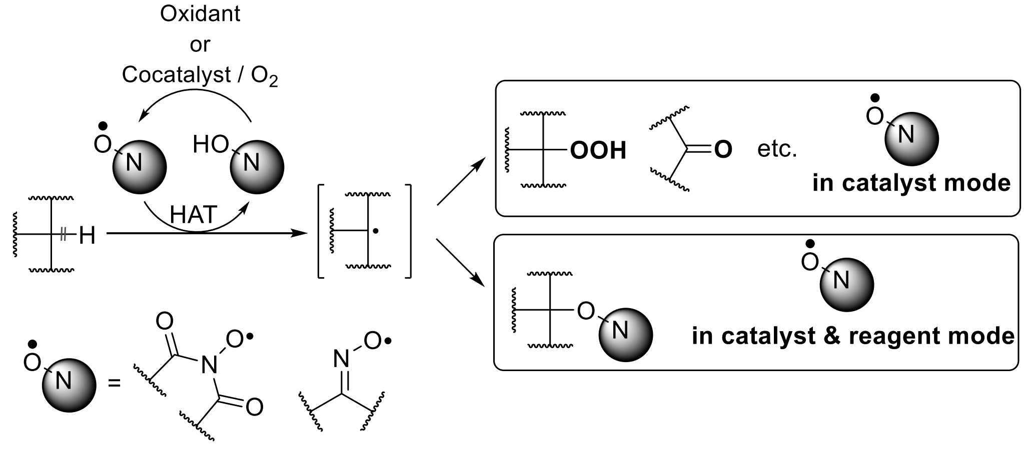
Oxidative CH-functionalization of organic molecules, i.e. the introduction of new functional groups into organic substrates as a result of oxidative C–H bond cleavage is one of the major trends in the development of modern organic synthesis methodology. These processes make it possible to minimize the number of stages in the synthesis of target products and avoid unwanted waste by direct introduction of target functional groups into available starting molecules. N-Oxyl radicals occupy a special place in organic chemistry due to the outstanding stability of the NO radical fragment and the wide variety of structures and properties of such radicals. N-oxyls are used in the development of sensors, spin labels, contrast reagents, organic battaries, mediators of living polymerization, organic magnetic materials, as well as in organic synthesis as redox-organocatalysts [1]. The present report will be focused on new applications of N-oxyl radicals in selective CH-functionalization. Electron-deficient N-oxyl radicals possess balanced properties making them versatile agents for these processes: relatively slow self-decay and high activity in hydrogen atom abstraction. Depending on reaction conditions, N-oxyl radicals play the role of redox-organocatalysts [2] or combine the catalytic role with the role of reagent for oxidative coupling [3–5].



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How to study ionic compounds using NMR spectroscopy?

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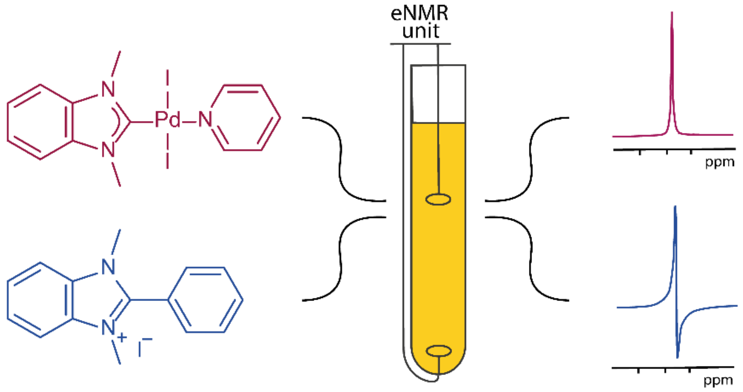
The electrophoretic mobility of ionic compounds in solution can be used to distinguish ions by their characteristic drift velocities in an electric field. Electrophoretic NMR (eNMR) can be used to obtain electrophoretic mobility and other parameters such as charge, transference numbers, and others.[1] The literature describes examples of the successful application of this method to the study of supramolecular objects, for example, to assess the binding of ions to crown ethers. There is a series of articles about the study of the properties of an ionic liquid using the eNMR technique. The result of the experiment is highly dependent on the pH of the sample, which makes this method promising in the field of metabolomics and drug research.

We have shown the opportunity of using electrophoretic NMR for studying catalytic reactions and for observing the changes in the catalyst nature. Pd/NHC complexes are very popular in the field of catalysis. Pd/NHC complexes are able to evolve with the formation of products R-NHC, O-NHC, H-NHC and N-NHC coupling.[2]

The Mizoroki-Heck reaction between iodobenzene and butyl acrylate in DMF-d_7 and triethylamine as the base was studied by electrophoretic NMR. Phase modulation is observed for the signals of charged compounds in the eNMR spectra. The appearance of a set of signals characteristic for the coupling product was observed after the Mizoroki-Heck reaction in ^{1}H NMR spectrum. The specific form of these signals in ^{1}H eNMR spectrum indicates that it ionic compound. The appearance of the R-NHC coupling product is considered evidence of the nanoscale catalytic system formation.[3]



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Mesoionic dioxolenes

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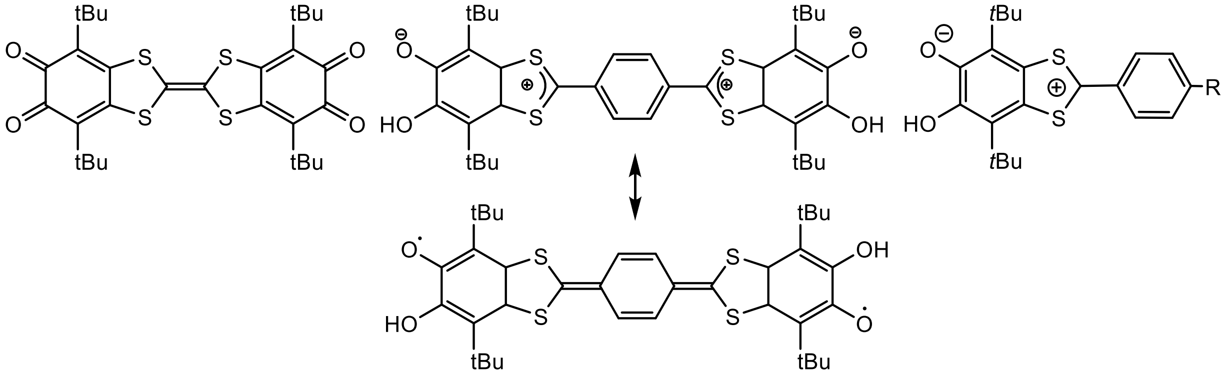
The idea to implement the construction of addressable and readable electronic devices to the molecular level is a challenging task for many chemists and physicists. From this viewpoint coordination compounds exhibiting bi(poly)stable behavior seems to be prominent objects.

o-Quinones are well-known dioxolene ligands that could be bound to the metal ions as o-quinone itself, semiquinone or catecholate depending on various factors, moreover the redox state of such dioxolene ligand could be changed directly in the coordination sphere. Sometimes this redox process is accompanied by spin-crossover or even macro effects resulting in reversible bending of crystals of complex.

In this work we present a new class of o-quinone-type dioxolene ligands bearing mesoionic structure. The synthesis of these species is based on the annulation of 4,5-dithiole-2-substituted ring to 4,5-positions of o-quinone molecule. Bicyclic structure fragment provides a rigid and almost flat structure to the molecule that taking into account zwitter-ionic charge distribution is promising for self-ordering in the crystal phase, molecular conductivity as well as for tuning the redox state of such a ligand in the coordination sphere of complex.

Using these compounds as a ligand for binding to lanthanides we succeeded in preparation of switchable single molecule magnets.[1] The synthesis and properties of this new class of dioxolene compounds will be presented.



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Calcium carbide in the synthesis of labeled compounds

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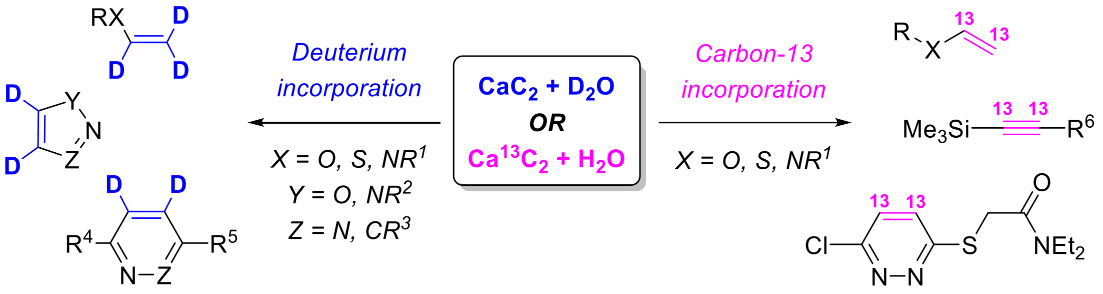
Calcium carbide is a versatile reagent for organic synthesis. Reacting with water, it gives acetylene; and a wide variety of synthetic procedures is based on this chemical property of calcium carbide. In this way, a range of vinyl derivatives, substituted alkynes, pyrroles, pyrazoles, benzofurans, and other heterocyclic compounds was successfully synthesized [1-7].

In our work, a number of D- and ^{13}C-labeled compounds was synthesized from calcium carbide: CaC_2-D_2O mixture was applied as a source of dideuteroacetylene in the synthesis of deuterated vinyl derivatives and D-labeled heterocycles; $Ca^{13}C_2$-H_2O was used for the generation of $^{13}C_2$-acetylene, a key molecule for the construction of $^{13}C_2$-labeled compounds. So, a number of deuterated and $^{13}C_2$-labeled vinyl derivatives was obtained;[1,2] deuterated pyrazoles,[3] isoxazoles,[4] triazoles and pyridazines,[5,6] $^{13}C_2$-alkynes were synthesized; and $^{13}C_2$-labeling of a choleretic drug azintamide was performed.[1]



This work was supported by the Grant Council of the President of the Russian Federation (grant number MK-2615.2021.1.3)

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Piperazine-1,4-diol (PipzDiol) – a novel piperazine-based synthon for the design of crystalline H-bonded architectures

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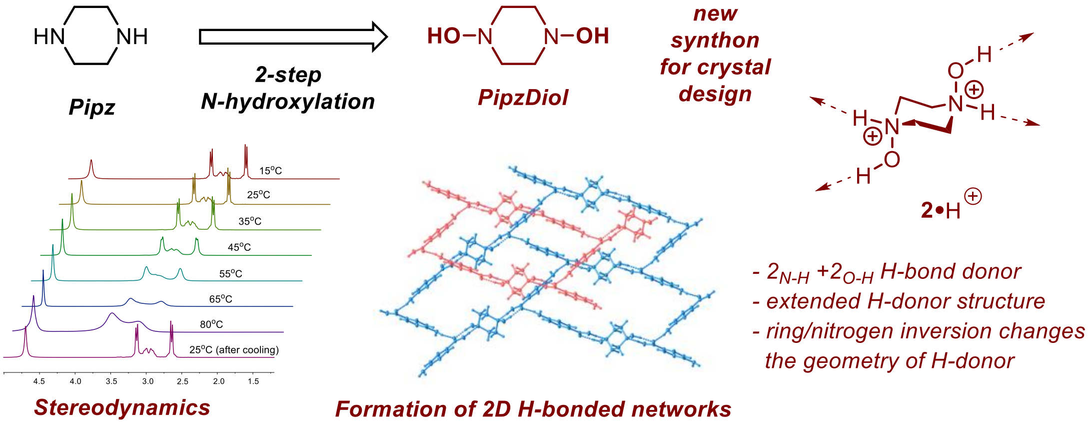
Piperazine (Pipz) and its derivatives are widely used as building blocks in different fields of chemistry and linkers in the crystal design of organic and metal-organic supramolecular architectures. Here, piperazine-1,4-diol (PipzDiol) has been suggested as a novel piperazine-based synthon for the design of crystalline H-bonded architectures with an extended H-bond donor geometry. Despite of a structural simplicity of PipzDiol, no any information on its synthesis or characterization data is available in scientific or patent literature.

We have developed a gram-scalable two-steps synthesis of PipzDiol using organic acyl peroxides as oxidants. Using this method, the target product was prepared in 51% overall yield from piperazine. NMR and DFT studies of stereodynamics showed that the structure of PipzDiol is flexible and undergoes relatively fast inversion of nitrogen atoms and ring flipping under normal conditions. Due to this, PipzDiol exists as a dynamic mixture of conformers/invertomers.



To explore the potential of PipzDiol in the design of crystalline H-bonded networks, adducts (salts) with sulfuric acid, oxalic acid (OxH2) and *para*-aminobenzoic acid (PABA) were prepared. Their XRD structures were compared with the corresponding adducts of piperazine known from the literature. Piperazine and PipzDiol were found to form distinct supramolecular H-bonded networks with topologically different H-bonded motifs. In crystalline adducts with mentioned acids, piperazine forms 3D H-bonded networks, while with PipzDiol 2D layers are assembled. Notably, the equilibrium of invertomers of PipzDiol shifts with a preferable selection of one stereoisomeric form depending on the nature of the acid.

Overall, piperazine-1,4-diol exhibits its own unique H-bond donor/acceptor behavior. A remarkable feature of PipzDiol is its ability to switch between diaxial and diequatorial conformations upon changing the protonation state. Thus, PipzDiol give rise to a larger variety of H-bonded supramolecular structures than the unsubstituted piperazine.

Removing the barriers for application of heterogeneous photocatalysis in organic synthesis: new selective processes in NHPI-TiO₂ system

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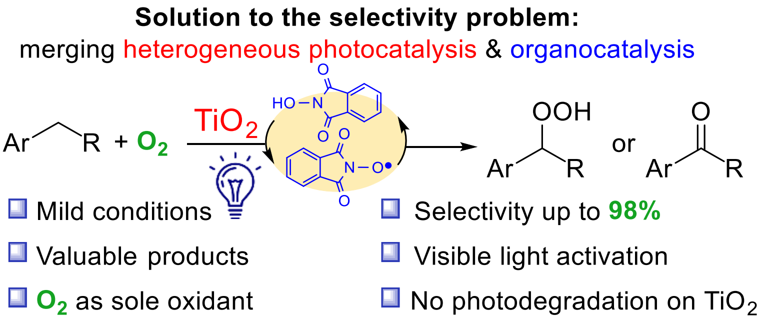
To this day the use of heterogeneous photocatalysis in organic synthesis presents major difficulties due to the lack of selectivity and low efficiency [1]. Most common heterogeneous photocatalysts, such as TiO_2, WO_3, ZnO etc., tend to oxidize and degrade the whole molecules non-selectively due to the strong oxidative power of valence bond holes. In our work, we have managed to control aggressive nature of TiO_2 and switch its reactivity from photodegradation of aromatic substrates to the mild oxidation allowing the synthesis of such easily oxidizable products as hydroperoxides.



The main finding of this work is the novel photocatalytic system N-hydroxyphthalimide-TiO_2 with the distinct features, which were absent in the starting materials: 1) absorption in visible light region, 2) enhanced efficiency due to the free-radical chain NHPI-mediated oxidation in solution, initiated by one catalytic cycle on the surface TiO_2, 3) ability to control the selectivity by changing NHPI/TiO_2 ratio [2]. NHPI favors the free-radical chain oxidation of alkylarene to hydroperoxide and only tiny amounts of TiO_2 are needed for the photoinitiation of this process. The increase of TiO_2 loading favors the heterogeneous process of further conversion of hydroperoxide to ketone. The key intermediates in these processes are the C-centered radicals which can serve as a starting point for the development of new processes in the NHPI/TiO_2 system with radical scavenging by such reagents as electron-deficient heteroarenes and azodicarboxylates.

This work was supported by the Russian Science Foundation (grant № 21-13-00205)

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Thiopyrano[4,3-*b*]indole-3(5*H*)-thiones and their rearrangement in reaction with dimethyl acetylenedicarboxylate

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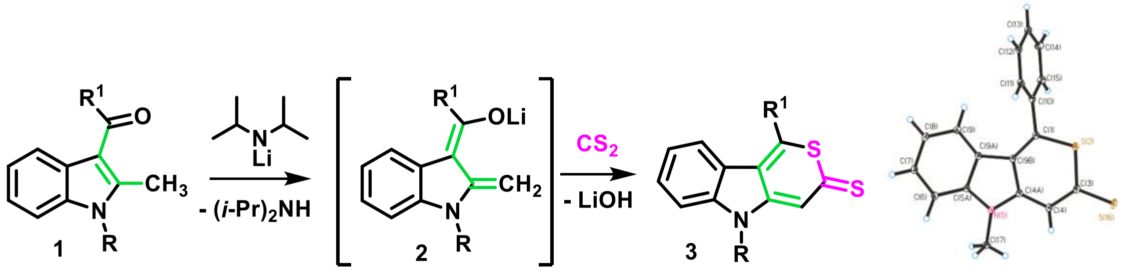
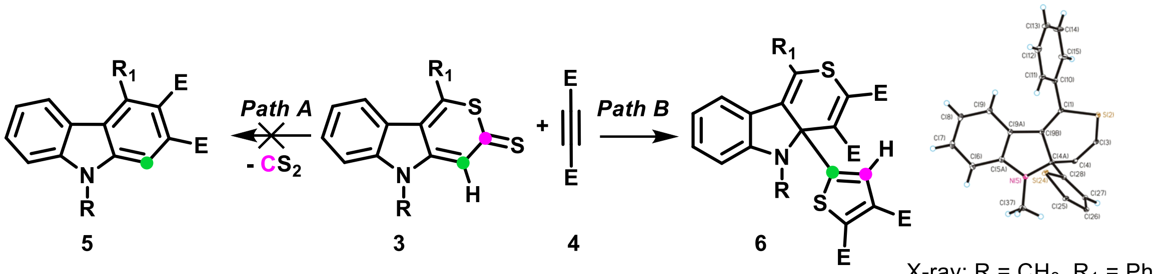
Projects aimed at fostering the preparative methods for the synthesis of heterocycles through new one-pot domino processes are relevant [1] since it paves the ways to the construction of new hard-to-reach structures, possessing high importance for medicine [2].

We developed a new approach for the annulation of thiopyrane ring to the indole core. Treating 2-methyl-3-acylindoles **1** with lithium diisopropylamide leads to the formation of lithium indole-2,3-dienolates **2** which react with CS$_2$ to give the corresponding thiopyrano[4,3-*b*]indole-3(5*H*)-thiones **3**.



X-ray: R = CH$_3$, R$_1$ = Ph

We surprisingly found that thiopyrano[*b*]indoles **3** do not react with dimethyl acetylenedicarboxylate **4** *via* a (4+2) cycloaddition mechanism with the formation of carbazoles **5** [3]. But instead, the alkyne–thiocarbonyl metathesis pathway has been found. Further transformation involves a novel rearrangement including the thiopyrane ring opening and the thiophene ring closure. Structure **6** was determined by X-ray analysis.



E = COOCH$_3$

X-ray: R = CH$_3$, R$_1$ = Ph
without COOCH$_3$ groups

The research was supported by the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030")

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Flexible synthesis of Nitro-substituted heterosteroids

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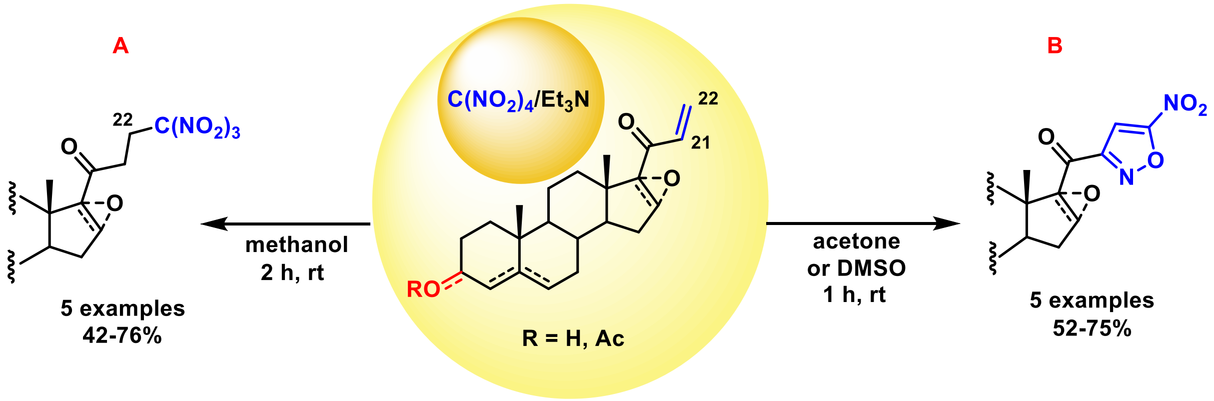
Heterosteroids, over the years, have been considered to be privileged scaffolds for drug discovery. Thus, synthetic azasteroids encompass a wide range of compounds with various biological activities, e.g., antitumor, antiviral, antibacterial, antimicrobial, antifungal, antioxidant, and insecticidal.[1,2] Therefore, the development of efficient methods for the synthesis of novel potent azasteroids is of high interest for the scientific community.[3]

Herein, a solvent-controlled flexible strategy towards trinitro- **A** and 5'-nitroisoxazoles **B** D-ring modified steroidal derivatives was proposed. We found that $\Delta^{21,22}$-androsta(e)nes react with tetranitromethane under basic conditions with formation of two types of products. 20-Isoxazole-substituted steroids were obtained in aprotic solvents, such as acetone or DMSO. The reactions in protic solvent - methanol, resulted in 22-trinitromethyl derivatives – products of the addition of the *in-situ* generated trinitromethane at the steroid $\Delta^{21,22}$-double bond. The reaction scope was quite general with respect to $\Delta^{21,22}$-androsta(e)nes. Triethylamine was found to be the most efficient base to promote both the heterocyclization and addition pathways.[4] The yields of the products were in the range of 42-76% for **A** and 52-75% for **B**.



The research is supported by the Russian Science Foundation (grant No. 22-13-00161)

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Interrupted Nef reaction: a yellow brick road to functionalized nitroso compounds

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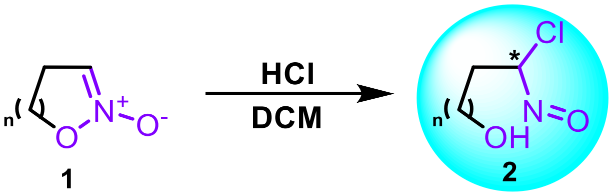
Interrupted reaction occurs when a chemical process is redirected to obtain new end product. This new process may take place with significant selectivity and conversion, therefore be applicable not only in mechanistic investigations of parent reaction but also as a reliable tool in organic synthesis.

Classical Nef reaction (nitro to carbonyl conversion) was discovered in 1894 by Swiss chemist J. U. Nef. The mechanism of this transformation involves deprotonation of primary or secondary nitroalkane to form a nitronate anione, which undergoes O-protonation, followed by a nucleophilic addition of water to the C=N bond. Elimination of HNO from the resulting intermediate leads to the carbonyl compound. In this work, we report an interrupted variant of Nef reaction, namely a reaction of cyclic esters of nitronic acid **1** with hydrochloric acid leading to α-halonitroso compounds **2**. The nature of this transformation resides in a nucleophilic addition of the chloride anion to the C=N double bond with simultaneous heterolytic cleavage of the N-O bond.



1

n = 1,2

2

17 examples

- *** Switchable diastereoselectivity**
- *** Elevated stability**
- *** Mild conditions**
- *** Up to 99% yield**

α-Halonitroso compounds possess a unique bifunctional moiety, which grants them unusual ambiphilic character and high reactivity towards nucleophilic, electrophilic and radical species. In particular, these compounds are involved in nitroso Diels–Alder, nitroso ene, nitrosoaldol and photochemical reactions. On the other hand, reliable synthetic procedures allowing access to α-halonitroso compounds are almost exclusively limited to electrophilic chlorination of oximes, which does not tolerate oxidation-labile groups. The reported transformation allows to alleviate this disadvantage, offering a mild non-oxidative approach to the diastereoselective synthesis of α-halonitroso compounds bearing a free hydroxyl group.

Mechanistic insights into the diastereoselectivity of this transformation, as well as reasons behind the enhanced stability of products **2**, were also considered employing UV-vis spectroscopy, molecular orbital and DFT theory.

This work was supported by Russian Science Foundation (grant № 22-13-00230)

Rare-earth anthracenide complexes: structures and their catalytic activity in ethylene polymerization

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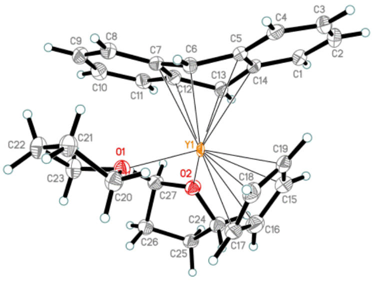
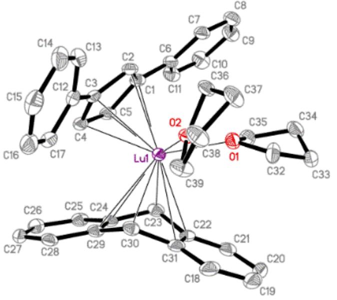
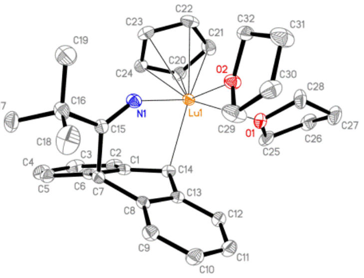
Organolanthanides bearing dianions of aromatic hydrocarbons such as naphthalene, anthracene, biphenyl, *etc.*, are virtually unstudied, and their structures are mainly limited by the $[Ln^{3+}X^{-}{}_2]_2L^{2-}$ type. Less studied systems $[X^{-}Ln^{3+}L^{2-}]$ are of much greater interest, since they form substantially covalent Ln^{3+}-L^{2-} bond [1], mimic frustrated Lewis pairs, and therefore may provide extraordinary reactivity, *e.g.*, activation of multiple C-C bonds. Although, non-classical dianions with predominantly two-center HOMO localization ensure the kinetic stability of the corresponding complexes, a very few examples of mononuclear rare-earth anthracenides have been published up to date [1-6].

A convenient method has been developed for the synthesis of rare-earth anthracenide complexes of type (η^5-Cp')Ln(η^2-Ant) (Cp' = C_5H_5, 1,3-$Ph_2C_5H_3$, 1,2,4-$Ph_3C_5H_2$; Ln=Y, Nd, Lu; Ant= $C_{14}H_{10}$, 2,6-${}^tBu_2C_{14}H_8$) *via* reduction of anthracene with KC_8 in the presence of $Cp'LnCl_2$. For the first time, it has been demonstrated that the complexes may serve as catalysts in coordination polymerization of ethylene and co-polymerization ethylene with α-olefins. The structures of polymerization products formed under various conditions were confirmed by NMR and FD MS methods. The initiation step of ethylene polymerization was modelled by using reactions of the complexes with pivalonitrile. Key complexes have been structurally studied.







This work was supported by the Russian Science Foundation (grant № 22-23-00711)

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Synthesis of liver cells-targeted delivery agents based on quinoline-4-carboxylic acids

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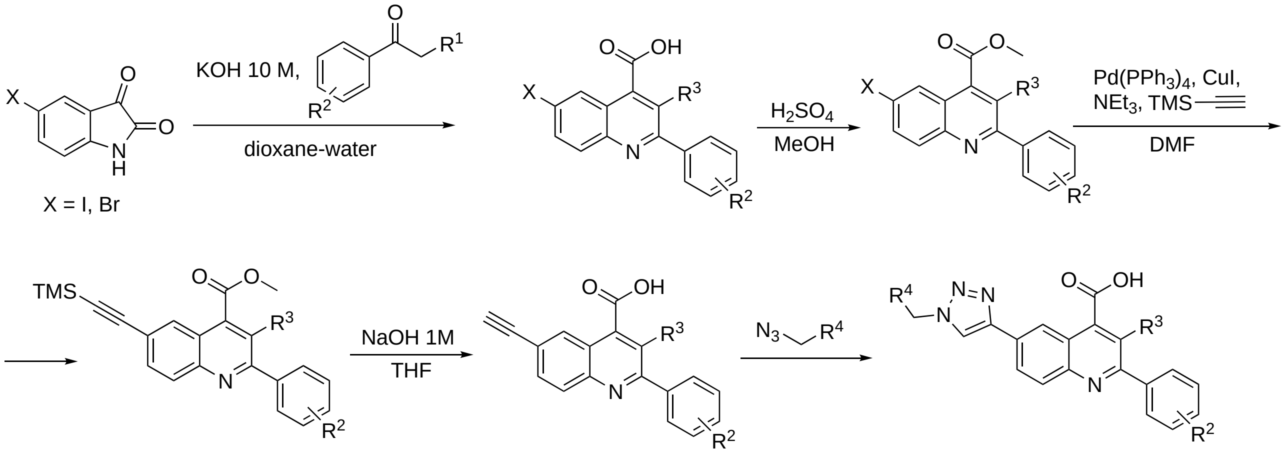
The asialoglycoprotein receptor (ASGPR) is a transmembrane protein highly expressed on the surface of hepatocytes and human hepatocellular carcinoma cells [1]. Since the receptor minimally present on the membranes of other, extrahepatic cells, ASGPR is widely used as a biological target for targeted drug delivery to liver cells [2]. It was found in our laboratory that besides galactose, *N*-galactosamine and their derivatives, some quinoline-4-carboxylic acids are able to interact effectively with the asialoglycoprotein receptor [3].

Therefore, we proposed the following scheme for the synthesis of derivatives of quinolinecarboxylic acids:



where R^1 = H, Br, OAc; R^2 = 4-OMe, H;
R^3 = H, OH; R^4 = COOEt, $(CH_2)_2NHBoc$

The key step in the synthetic scheme is the Sonogashira reaction, which makes the further modification of the molecule possible. It is necessary for connection with the transferred substance.

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Synthesis of quinazoline chromophores for application in optoelectronics

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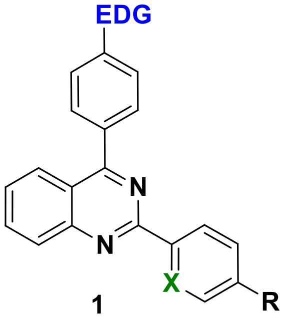
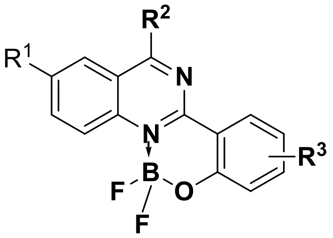
The pyrimidinyl (1,3-diazinyl) fragment has been widely used as attracting part in push-pull structures. Pyrimidine-based chromophores have found key applications as fluorescent sensors, in optoelectronics, particularly for photovoltaism, organic field effect transistors (OFETs) and in organic light emitting diodes (OLEDs) [1]. The quinazolinyl moiety can be considered as stronger electron-withdrawing part than the corresponding pyrimidinyl group due to the possibility of extra electron delocalization into the fused benzene ring [2].

We performed the directed design of push-pull derivatives of quinazoline **1** and obtained molecules with a tunable absorption, emission range and Stokes shift. Multiple studies of photophysical properties were carried out under conditions close to potential application (concentrated phase, aggregated state). We modified the previously developed scaffolds (2,4-diarylquinazoline **1** [3, 4], 2-hydroxyphenylquinazoline **2** [5] and 2-thienylquinazoline **3** [6]), and created new fluorophores containing substituents, spacers and fragments with different numbers and types of heteroatoms with diverse electronic and spatial effect.



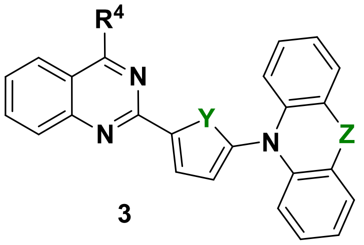
1

X = CH, N; R = H, CN, CF_3
EDG = NEt_2; NPh_2; 9*H*-carbazol-9-yl



2

R^1 = H, Cl; R^2 = OH, Ar;
R^3 = H, di-*t*Bu, diBr, etc.



3

R^4 = CN, OMe;
Y; S, CH=CH;
Z = CMe_2, O, S

We proposed new heterocyclic fluorophores with AIE and TADF effect; we studied halochromic behavior of some samples by switching the donor fragment to acceptor one upon the protonation, as well as the ability to reversible ON-OFF-ON switching in the presence of certain analytes.

This work was supported by the Russian Scientific Foundation (grant № 22-23-00006)

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The selectivity of platinum catalyzed hydrosilylation from the catalysis type perspective

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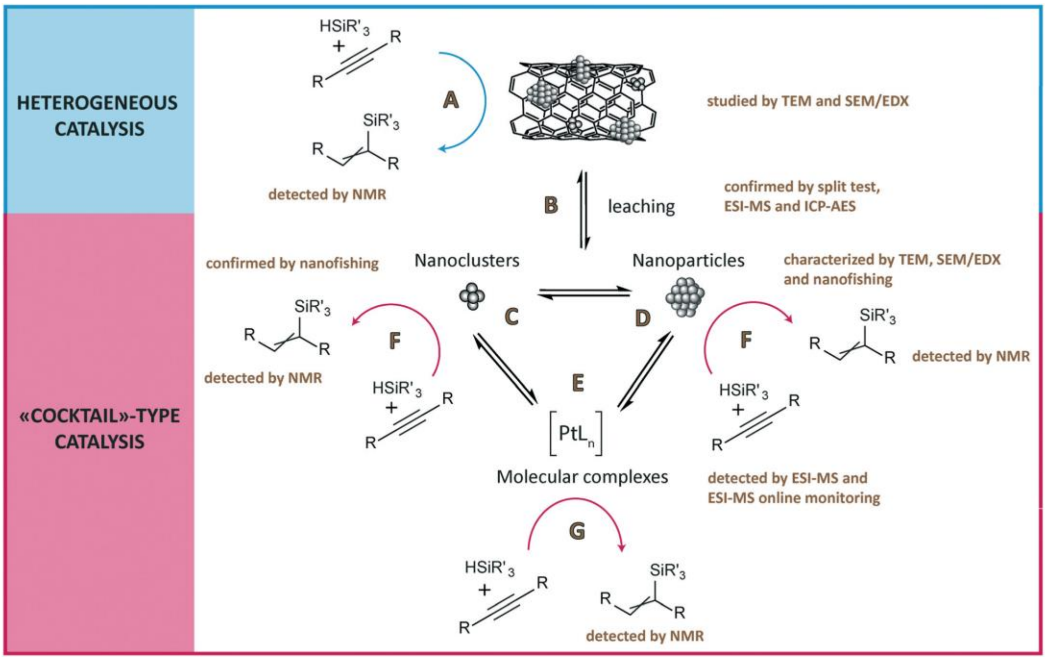
The hydrosilylation reaction is known to have difficulties in controlling reaction selectivity [1]. Many catalysts are in development to address this problem. Acknowledged platinum catalysed hydrosilylation is widely-used in laboratories and industries. Therefore, the mechanism of reaction was a subject of various studies [2].

The “cocktail” or dynamic type of systems is a new mechanistic concept on transition metal catalysis [3]. It implies the formation of metal complexes, and metal nanoparticles, and clusters during a reaction. The dynamic nature of alkene and alkyne hydrosilylation reaction catalyzed by Pt/MWCNT (multi-walled carbon nanotubes) was discovered and studied by use of combination of analytic methods [4].



It was shown that platinum particles leached out into the solution, possibly, giving rise to another catalytic cycles in the solution and variety of by-products. An examination of the reaction's selectivity on various substrates suggested access to the α-isomer as a result of the clusters' catalytic activity.

The authors thanks Scientific Schools grant NSh-5199.2022.1.3 for the support

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Synthesis, characterization and catalytic properties of Pd/NHC complexes with acceptor substituents

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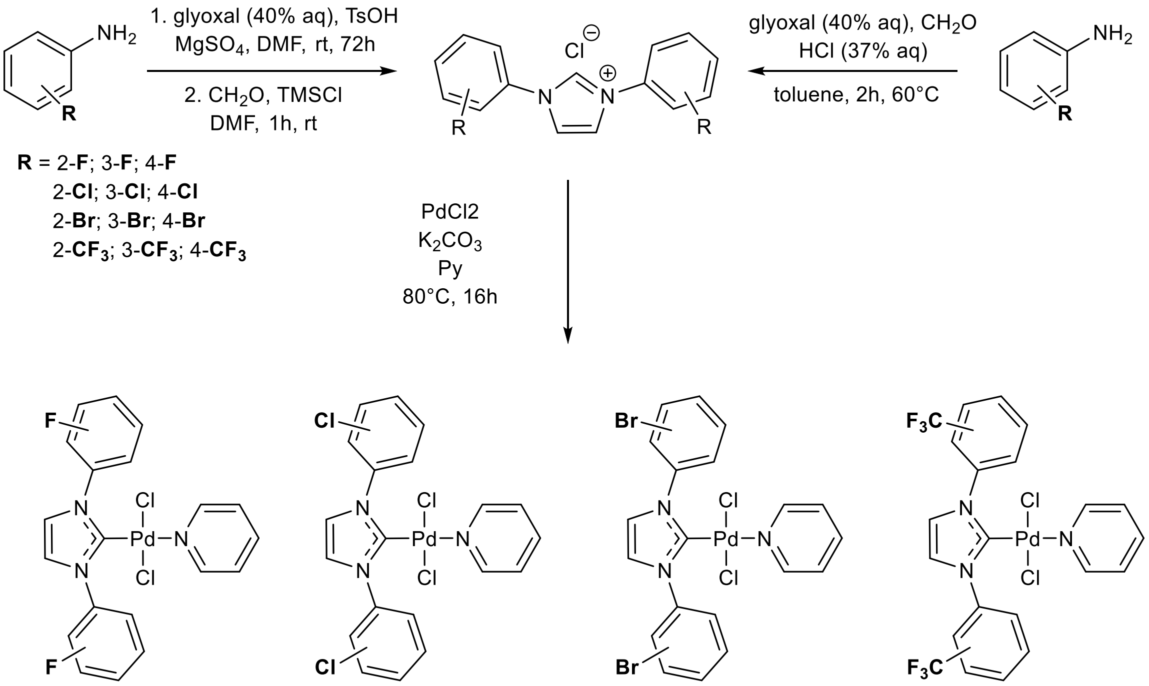
Bulkiness and high donor properties are well-known requirements for the structure and electronic properties of Pd/NHC complexes used in cross-coupling reactions. However, there are only a limited number of Pd/NHC complexes with acceptor substituents [1]. In this work, a series of new Pd/NHC complexes with F, Cl, Br and CF_3 substituents was obtained. Catalytic activity in Heck and Buchwald-Hartwig reactions was tested for all obtained complexes.



The main obstacle in the synthesis of Pd/NHC complexes is the preparation of imidazolium salts NHC*HCl. The paper proposes optimal methods for obtaining acceptor-substituted NHC*HCl, which facilitate the preparation of target catalysts.

The authors thanks Scientific Schools grant NSh-5199.2022.1.3 for the support

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Rh(III)-Catalysed C-H activation/annulation for the synthesis of isoquinolone- and isoquinoline-containing α-trifluoromethyle-α-amino acids

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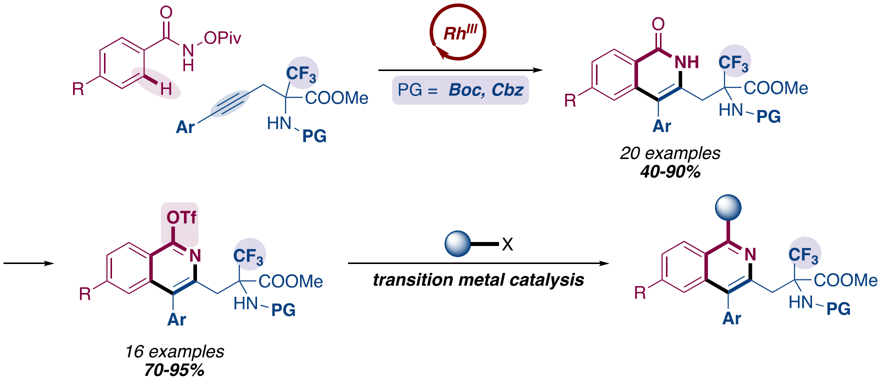
The chemistry of fluorine compounds has considerably evolved over the last decades and become an important area of multidisciplinary research, including biology and medicine. The remarkable properties of such substances are due to the uniqueness of the fluorine atom which can drastically influence biological activity [1]. In the area of peptides α-trifluoromethyl-α-amino acids have gained a prominent place because of their ability to inhibit pyridoxal phosphate-dependent enzymes exhibiting a range of interesting biological properties. On the other hand, heterocyclic cores are frequently found in the majority of natural compounds. In particular, isoquinolones and their relatives are the principal scaffolds in DPP-4 inhibitors, tumour necrosis factor inhibitors, Doravirine medication, and others. Combining this moiety with an α-fluoromethyl-α-amino acidic group within a single molecule might well lead to a substance with potentially useful properties and biological activity [2]. Therefore, the development of methods for the synthesis of new representatives of the isoquinolone-containing α-fluoromethyl-α-amino acids is of great interest [2].

Metal-catalysed tandem C-H activation/annulation of aromatic amides with alkynes under the chelation control of an appropriate directing group has become a powerful strategy for constructing isoquinolone skeletons from cheap starting materials in a step- and atom-economical manner [3]. We have employed this methodology for the synthesis of the novel α-CF_3-α-amino acids decorated with the pharmacophore isoquinolone core [4].



The advantageous property of isoquinolones is the ability to be easily transformed into triflates that are the perfect substances for the transition metal catalysed reactions. This feature grants many approaches for fine-tuning the structure and varying the properties of target molecules.

This work was supported by the Russian Science Foundation (project No. 21-13-00328)

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Syngas *vs* Hydrogen in reductive addition processes

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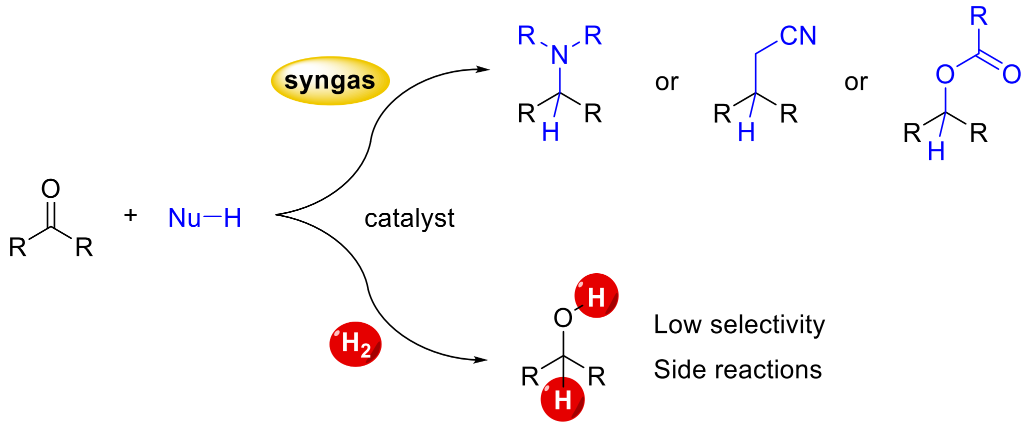
Catalytic reduction reactions have a great impact on modern chemistry and are often based on hydrogen gas as a reducing agent. Reductive addition reactions such as reductive amination [1] are a highly important class of reductive processes. While active molecular hydrogen often leads to over-reduction and functional groups destruction using simple hydrogenation catalysts, carbon monoxide shows high selectivity in reductive reactions without an external hydrogen source [2]. Therefore, we envisioned that utilization of the mixture CO/H_2 known as syngas can allow us to reach a balance between activity and selectivity.

This work [3] confirmed that reductive amination on commercially available Rh-catalysts proceeded more efficiently using syngas, than each of its components. Catalyst loading was decreased to 25 ppm and TON 29648 was achieved. Stoichiometric amounts of syngas were used to successfully scale up the reaction. Control experiments shed the light on the roles of carbon monoxide and molecular hydrogen in reductive amination.

In order to evaluate generality of the elaborated approach, we carried out tandem CH-alkylation-hydrolysis-decarboxylation reaction using syngas. Addition of methyl cyanoacetate to various aromatic and aliphatic aldehydes accompanied by decarboxylation furnished the products of the formal addition of acetonitrile to carbonyl compounds in 69-94% yields (TON 3503-4772).

Application of the catalyst based on Ru instead of Rh to conduct one more process, reductive esterification, illustrated the opportunity to reduce the cost of developed approach, and universal ability of syngas to balance high activity and selectivity in reductive addition processes.



This work was supported by the Russian Science Foundation (grant № 19-73-20212)

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Synthesis of well-defined NHC precatalysts

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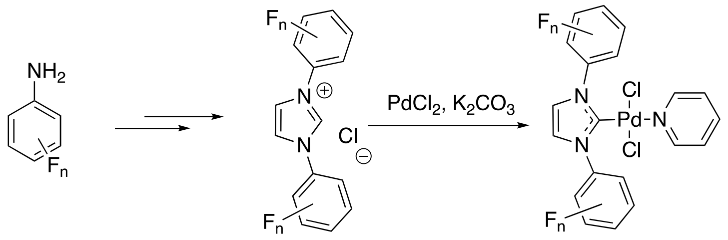
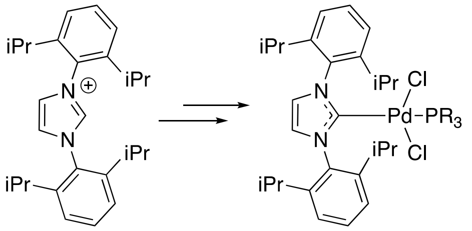
The use of M/NHC complexes has become an attractive practice in catalytic reactions thanks to their wide catalytic possibilities in synthetic methodologies such as Mizoroki–Heck, Suzuki–Miyaura, Negishi, Buchwald–Hartwig, C–H activation, and many others [1]. The dependence of the catalytic properties on the ligand structure has inspired researchers to explore modifications of the NHC ligands to increase the efficiency or selectivity.

These ligands display a wide coordination versatility; in fact, they can coordinate practically to any transition metal. In addition, they are well known for being strong σ-donors, affording electron rich metal centers with a strong C(carbene)–M bonds. Also, they are easily functionalized, generating a plethora of different scaffolds that has led to a better understanding of the relationship between the stereoelectronic character and catalytic properties.

The most common strategy to tune the electronic properties consists of changing, at least, one of the N– substituents present in the heterocycle. In this sense, the presence of different numbers of fluorine atoms in one N–substituent may allow fine–tuning or enhancing the catalytic efficiency. This being especially true when the N–substituent is an aryl group and the fluorine atoms are attached to it [2].

Another strategy is to use the influence of the leaving ligand in the precatalyst.





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Electrochemical generation of copper catalyst for “click”-synthesis of triazoles

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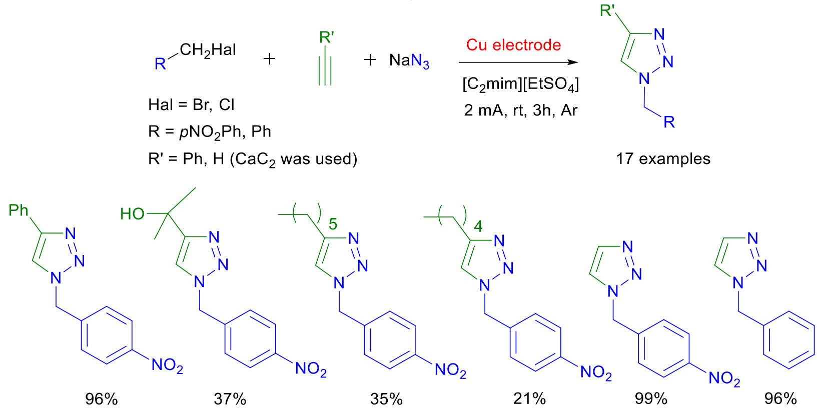
Electrochemistry provides an excellent opportunity to generate metal catalysts *in situ*.[1] A common approach involves metal ore mining, extracting and oxidizing, followed by reduction to metal nanoparticles. After a reaction, metal catalysts are usually not recovered due to challenging procedures and low amounts in a reaction mixture. Therefore, metal complexes are highly expensive. In fact, a metal undergoes a series of successive stages of oxidation-reduction. Thus, the development of efficient method for the regeneration of metal catalysts are in highly demand in organic synthetic procedures.

Here, the possibility of generation and recovering of a copper catalyst was demonstrated using [3+2] dipolar cycloaddition of azides to alkynes. Initially, a catalytically active solution of copper catalyst was obtained using electric current as an initiator and ionic liquids as an electrolyte. Metal species transferred from the surface of the copper electrode to a solution. The process was controlled by voltammetry, and weight loss of the electrode. After that, the reagents were added and the reaction started. The resulted triazoles were extracted and analyzed.



Interestingly, the cycloaddition proceeded well even under *in situ* generation of copper catalyst after addition of all the components. The mechanism of the transformation was studied by X-ray, XRD, ESI-MS, etc., and some intermediates were isolated and characterized.[2]

After the extraction of the products the polarity of electrodes was changed resulted in copper deposition on the surface of the electrode in complete manner. At the same time, the solvent (ionic liquids) was also regenerated and purified and was ready to next run. Thus, the reaction was performed several times using the same electrodes and ionic liquid.

The developed strategy allows to generate and recover copper catalyst for the cycloaddition reaction.

This work was supported by the RFBR (grant № 19-29-08020)

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Regiospecific way for N9-alkylated purines

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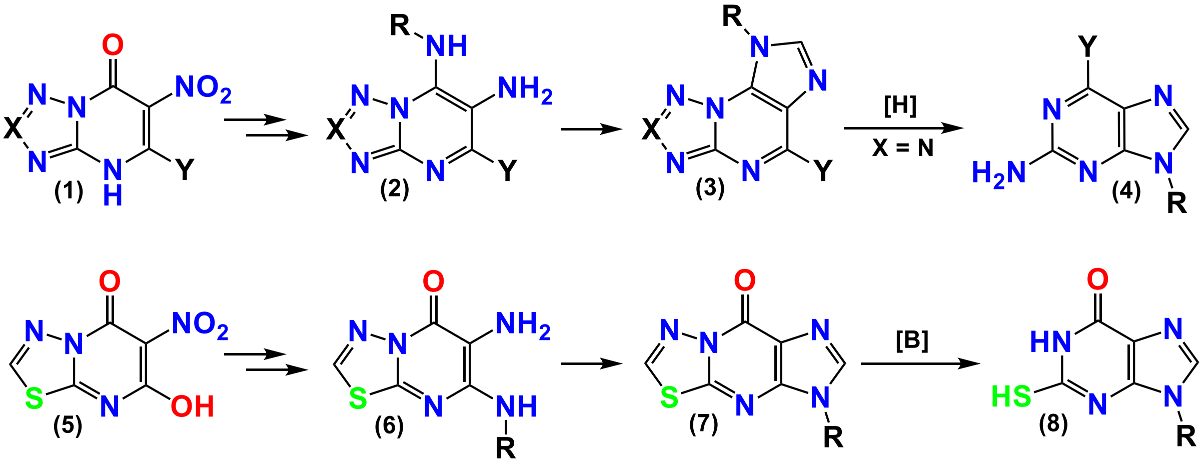
Abnormal purine nucleosides and related structures are a special class of heterocycles in medicinal chemistry due to their close similarity with natural purines, which are part of key energy and information intracellular processes. Abnormal nucleosides as structural analogues of natural purines replace the latter in the key vital processes of viruses or tumor cells, thus leading to pathogen degradation [1,2]. N9-alkylated purines with pseudo-riboside moiety are used widely as antiviral drugs and synthesis of these heterocycles based on alkylation of the purine heterocycle yielded to desired N9-isomer and side N7-product [3]. Isolation of target N9-nucleoside from undesired N7-isomer is the main disadvantage of the most synthetic methodologies towards abnormal nucleosides to date.

We proposed a regiospecific scheme for the synthesis of abnormal N9-nucleosides based on a novel destructive methodology. It is started from readily available nitrotetrazolo- **1** and nitrothiadiazolo-pyrimidines **5** which can be converted to vicinal diaminoheterocycles **2** and **6** in a few steps. Annulation of the imidazole cycle based on the two vicinal amino groups results in tricyclic azolopurines **3** and **7**. The destruction of the thiadiazole fragment in thiadiazolopurines **7** to form thioxanthines **8** is observed under basic conditions, while reduction of the tetrazole cycle leads to the formation of purines **4**.



We obtained a library of the corresponding N9-alkylpurines **4** and a new class of abnormal nucleosides, N9-alkylthioxanthines **8**, by this methodology. These synthesized heterocycles can act as potential antivirals or antimetabolites and their biological properties will be investigated further.

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University project within the Priority-2030 Program) is gratefully acknowledged.

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Methodology of electrochemical oxidative coupling using phthalimide-N-oxyl radical

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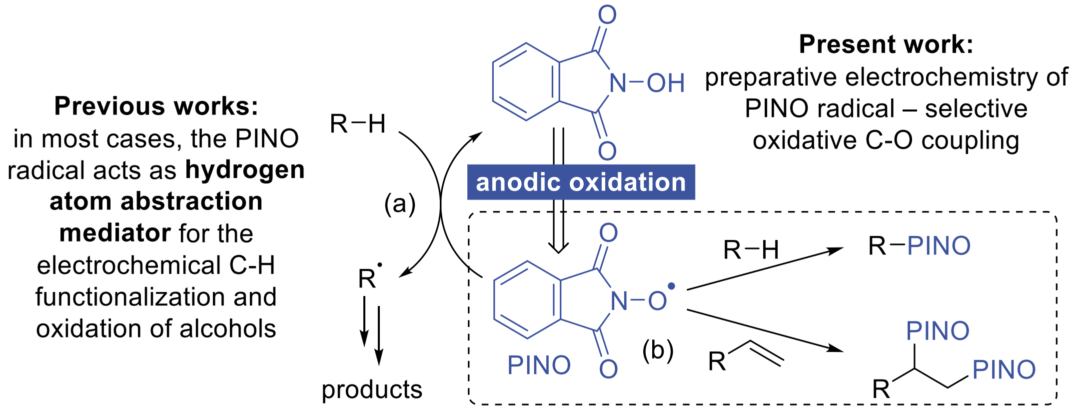
Currently, electroorganic synthesis is one of the most actively developing areas of modern organic chemistry. Much attention is paid to electrochemical C-H functionalization, oxidative coupling and difunctionalization of alkenes. Such processes are often accompanied by the formation of active C-, O-, N-, and S-centered radicals.

The preparative electrochemistry of O-centered N-oxyl radicals remains a poorly studied and complex topic. Imide-N-oxyl radicals are widely presented in many processes of C-O coupling and difunctionalization of alkenes, but in electro-organic synthesis they are used to a limited extent as mediators of C-H functionalization and oxidation of alcohols (Scheme 1, a).



Scheme 1. Present work is in the context of the electrochemical applicability of the phthalimide-N-oxyl radical

In this work, phthalimide-N-oxyl (PINO) radicals anodically generated from N-hydroxyphthalimide are used for radical oxidative coupling in new reactions of C-H functionalization and difunctionalization of alkenes (Scheme 1, b)

This work was supported by the Russian Science Foundation (grant № 21-13-00205)

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Synthesis of novel polycyclic compounds based on phosphorinines and their antitumor activity

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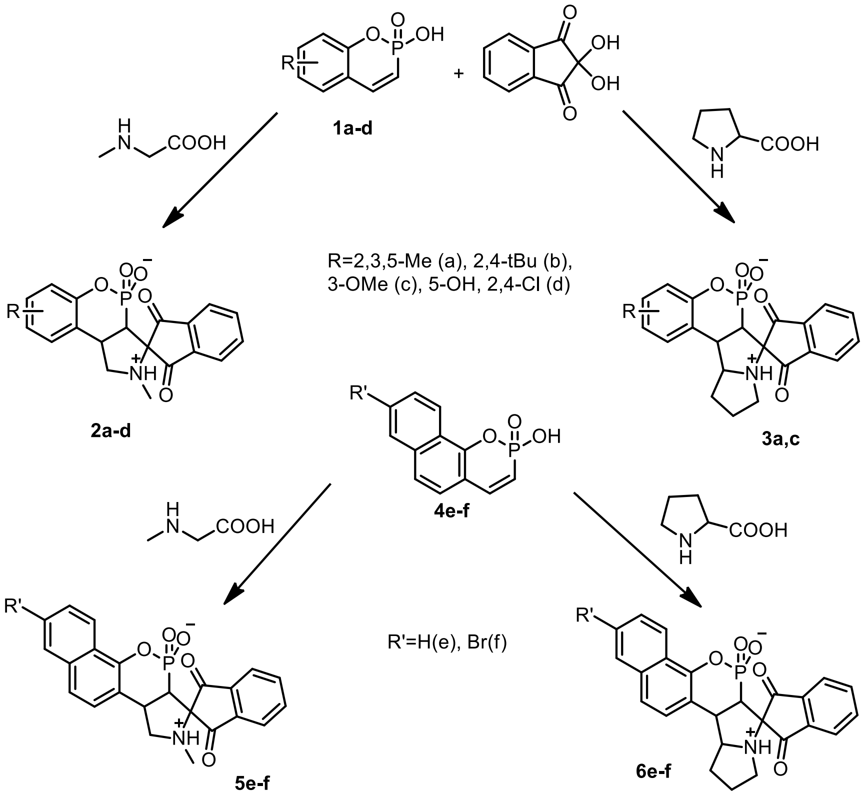
Spiro heterocyclics are proven to be potent pharmalogically active scaffolds[1]. The 1,3-dipolar cycloaddition is frequently exploited towards the synthesis of these compounds.

On the other hand, phosphorinines **1** are the structural phosphorus counterparts of coumarins and α-chromene, many derivatives of which have a wide spectrum of biological activity[2].

Herein, we report phosphorinines as dipolarophile in 1,3-dipolar cycloaddition reactions. The obtained hybrid structures possess antitumor activities and may be of interest as potential drugs for the treatment of different types of cancer.



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Polyvariant modification of calixresorcin[4]arenes and 1,1’-dinaphthylmethanes. The formation of hybrid receptor and dendrimer-like structures

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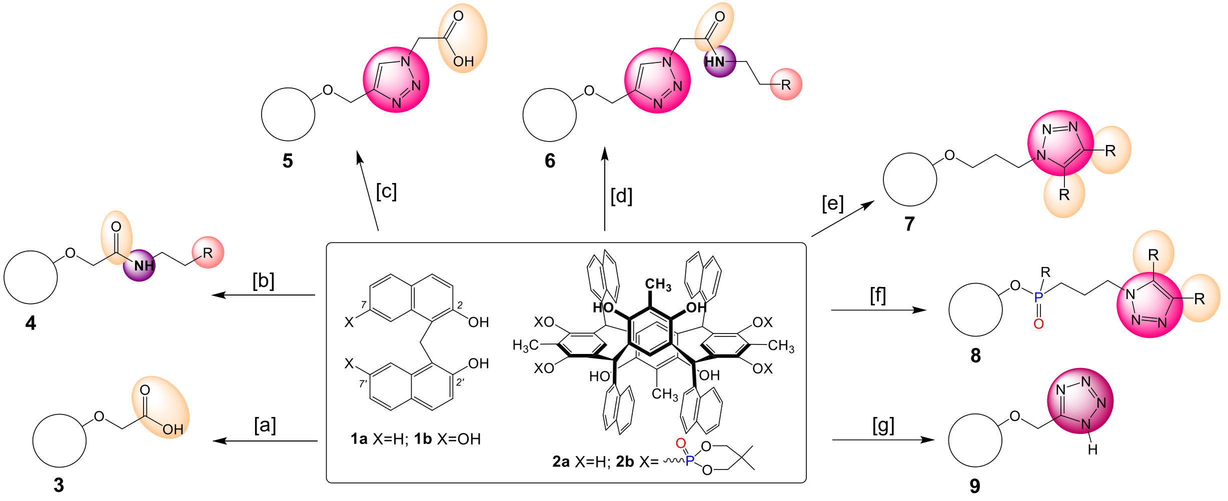
In order to design dendrimer-like polytope receptor systems, routes for sequential modification of 1,1'-dinaphthylmethanes **1** and rctt-resorcinarenes **2**, including alkylation with bifunctional reagents and catalytic cycloaddition in various combinations as the main reactions, were developed.

Series of new polyheterofunctionalized derivatives **3-9** containing active terminal groups capable of further transformation were obtained. The synthesized compounds differ in the structure of the polycyclic frame, the number (2,4,8) and the arrangement of functionalized branches, the length and composition of spacers between the polycyclic core and peripheral terminal groups, the nature of functional sites and terminal fragments [1-3].



[a] = 1) $BrCH_2COOEt$; 2) H_2O, KOH; **[b]** = 1) $BrCH_2COOEt$; 2) $H_2NCH_2CH_2R$; **[c]** = 1) $BrCH_2C\equiv CH$; 2) N_3CH_2COOEt; 3) H_2O, KOH; **[d]** = 1) $BrCH_2C\equiv CH$; 2) N_3CH_2COOEt; 3) $H_2NCH_2CH_2R$;
[e] = 1) $ClCH_2CH_2CH_2Br$; 2) NaN_3; 3) $R—C\equiv C—R$; **[f]** = 1) Et_2N-DOF; 2) RHal, MW; 3) NaN_3; 4) $R—C\equiv C—R$; **[g]** = 1) $BrCH_2C\equiv N$; 2) NaN_3

By the interaction of the carboxylic acids **3,5** with biologically active amines (ethanolamine, benzylamine, phenethylamine, tyramine, tryptamine), the amine-containing derivatives of various types were obtained. Dinaphthylmethane acids formed ammonium salts with all of the used amines; in the case of resorcinarene acids, the outcome of the reaction depended on the combination of reactants: either salts or supramolecular systems were obtained. Irrespective of the structure of molecular platform, all ethanolamine salts and some dinaphthylmethane and resorcinarene salts of benzylamine, phenethylamine, and tyramine were readily soluble in water. Amides of carboxylic acids **4,6** demonstrated the ability to accept and bind cations of s-, p-, d-, f-elements.

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Rhodium-catalyzed C-H Functionalization/N-annulation of 1-pyrrolines with alkynes: a convenient synthesis of fused isoquinolinium salts and beyond

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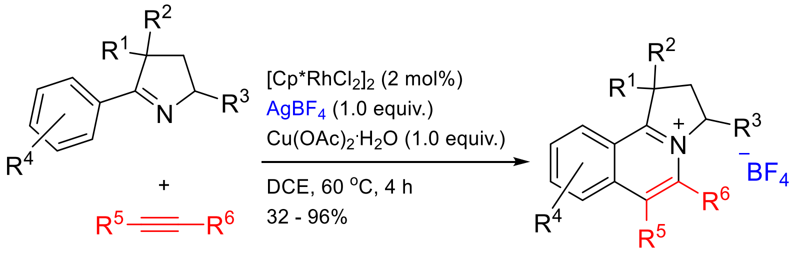
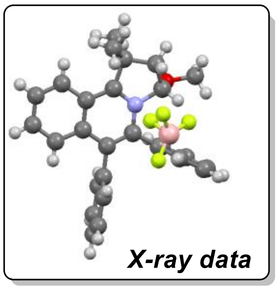
One of the important milestones that completely changed the methodology of organic synthesis was the emergence of homogeneous metal complex catalysis. Today, urgent problems for the chemical community in this direction are the search for new highly selective, resource- and energy-saving chemical transformations of simple substrates into complex molecular systems, proceeding in the presence of "stable" (tolerant to the presence of air, moisture and trace inhibitors in the feedstock) metal complexes under mild and environmentally friendly conditions.

Over the past decades, homogeneous catalysis involving rhodium species has received increasing attention from synthetic community as a versatile tool for diverse chemical transformations [1]. As a part of our continuing studies on the synthesis and reactivity of rare aza-heterocycles [2], herein we report our observations on the rhodium-catalyzed oxidative coupling of 1-pyrrolines with alkynes for generation of fused isoquinolinium salts *via* a C-H bond activation reaction.





$R^1 = R^2 = Me$ or R^1-$R^2 = (CH_2)_5$;
$R^3 = OH, OMe, OBu, OBn, OCy, SPr$;
$R^4 = H$, 4-Me;
$R^5 = R^6 = Et$, Ph, 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-AcC_6H_4, 4-$NO_2C_6H_4$, 2-thienyl

This work was supported by a grant of Russian Science Foundation (Project No. 21-73-00008), https://rscf.ru/project/21-73-00008/

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Tandem electrocyclization/hydrolysis approach for the synthesis of N-aminotetrazoles

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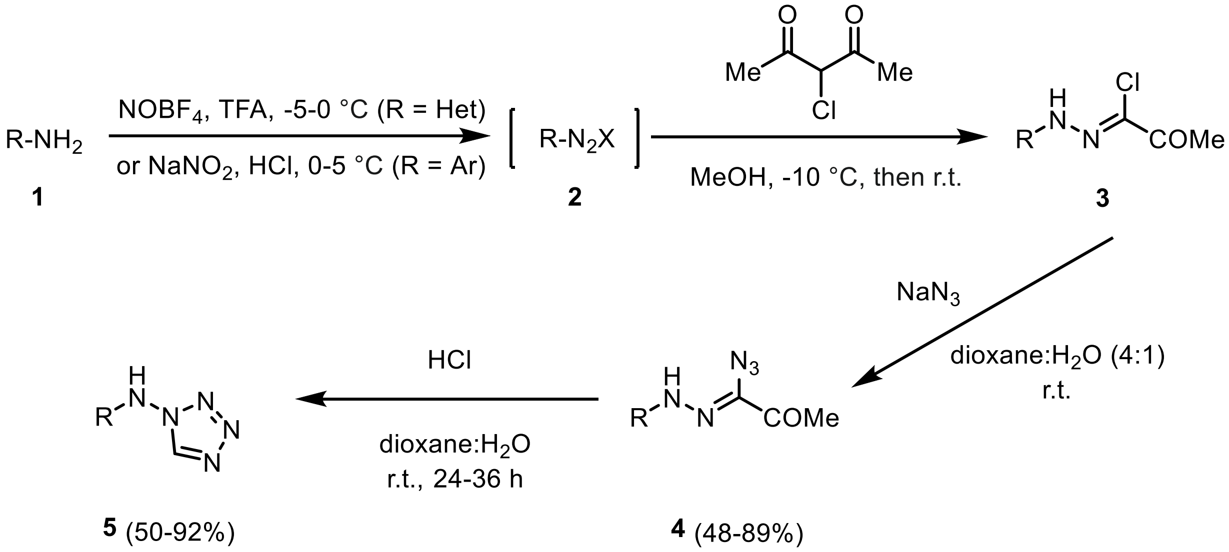
Tetrazoles are an important subclass of polynitrogen heterocycles with myriads of applications in medicinal chemistry and materials science. Tetrazole motif is present in a number of FDA approved medications due to their metabolic stability to many of the biochemical transformations.

In a series of nitrogen-enriched heterocyclic systems, 1,2,5-oxadiazoles (furazans) and their *N*-oxides (furoxans) became emergent pharmacologically oriented scaffolds. Furoxans are capable of an exogenous release of an important signaling molecule – nitric oxide (NO), which justify their wide range of biological activities. In this regard, structures containing both tetrazole and oxadiazole fragments may have potential as pharmacologically active NO donors.

In this work, an approach to the synthesis of *N*-(1,2,5-oxadiazolyl)aminotetrazoles based on the tandem electrocyclization/hydrolysis of azidohydrazones was developed. Diazonium salts **2** were obtained from readily available aminooxadiazoles, the following condensation with chloroacetylacetone led to chlorohydrazones **3**. Azidohydrazones **4**, obtained by nucleophilic substitution of the chlorine atom by azide group, underwent intramolecular electrocyclization in an acidic medium, followed by hydrolysis of the acetyl fragment.



Overall, we have developed a direct one-pot approach to the synthesis of *N*-(heteroaryl)- and *N*-(aryl)aminotetrazoles based on the electrocyclization/hydrolysis tandem reactions of azidohydrazones. A wide array of target aminotetrazoles (22 examples, up to 92% yield) was prepared under mild conditions. A combination of the facile synthesis and useful properties of *N*-(heteroaryl)- and *N*-(aryl)aminotetrazoles enable their application potential for future design of functional materials and pharmaceuticals

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Synthesis 2,4-disubstituted furans from prop-2-yn-1-ones

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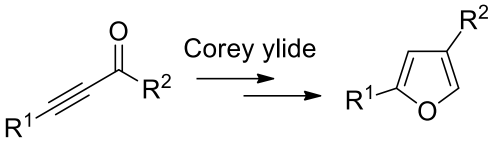
Furans play an important role in modern organic and medicinal chemistry. They exhibit versatile reactivity and are used as multifunctional building blocks for the synthesis of various organic compounds.

Previously, we proposed to introduce the concept of an extended version of Corey-Chaykovsky. This innovation implies the use of the key three-membered rings as intermediate products, not final ones [1]. Despite of the well-known methods for the synthesis of 2,4-disubstituted furans, they use expensive catalysts, reagents, and specific conditions. In this regard, we have developed a simple and efficient method for the synthesis of substituted furans, according to the extended Corey-Chaykovsky reaction.



The report will consider the features of the key transformations; the influence of reaction conditions, steric and electronic factors on the efficiency of cyclization reactions and the yields of target products.

This work was supported by Russian Science Foundation (project № 21-73-10063)

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Switching factors in photocatalytic thiol-yne reactions: comprehensive mechanistic studies and selectivity rationalization

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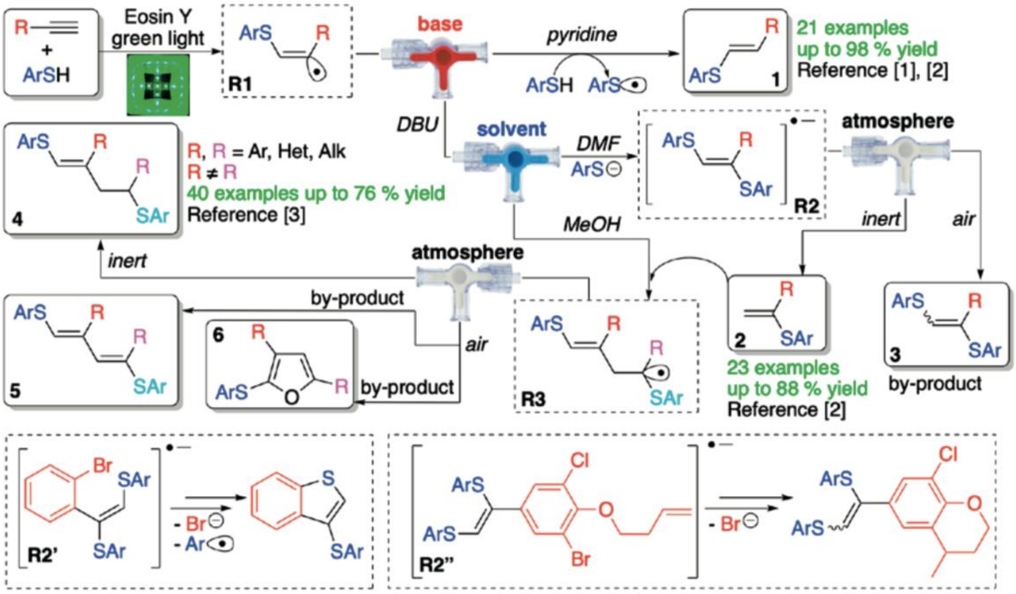
The main problem of thiol-yne coupling reactions is chemo- and regioselectivity. To solve this problem a variety of catalytic systems have been developed. In this work we propose a universal photocatalytic system, in which by regulating a number of factors (base, solvent, reagents ratio, atmosphere, etc.) it is possible to control the chemo- and regioselectivity. On the basis of the proposed scheme synthetic methods were developed that allow regioselective preparation of vinyl sulfides **1** or **2** as well as the product of tandem thiol-yne-ene coupling **4**.

By virtue of of ESI-MS on-line monitoring data some evidences of the main radical intermediates (**R1**, **R2**, and **R3**) formation were detected and mechanistic schemes were proposed to explain the influence of each key factor on selectivity switching. These hypotheses were supported by DFT calculations, by measurements of the reactions quantum yield and through the characterization of the by-products (for example, **3**, **5** and **6**).

Our studies of the **R2** radical-anion chemistry merit special attention. This particle forms via associative electron upconversion. Such an extremely reactive specie is prone to alternative mesolytic dissociation pathways, which leads to the formation of some interesting products (see the transformations of **R2'** and **R2''**).



Thus, a detailed study of the photocatalytic thiol-yne coupling reaction mechanism makes it possible not only to obtain the corresponding vinyl sulfides selectively, but also opens the way to new unusual reactions.

This work was supported by the Russian Science Foundation (RSF grant № 21-13-00193)

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The extended Corey-Chaykovsky reaction: double methylene transfer to activated Knoevenagel adducts

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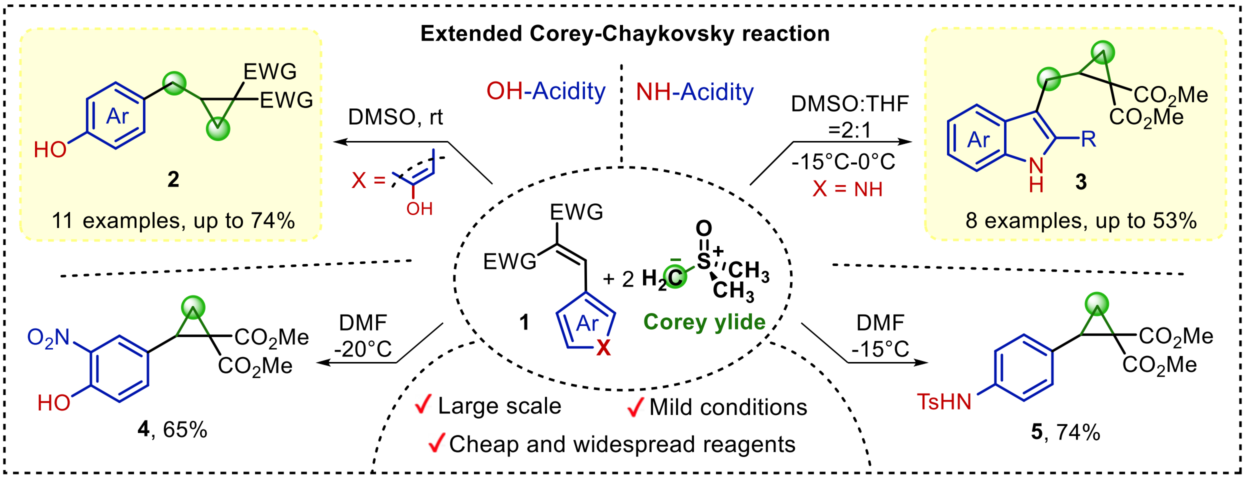
The Corey-Chaykovsky reaction, celebrating this year its sixtieth anniversary, has been developed as a powerful approach to three-membered carbo- and heterocycles *via methylene group transfer* to aldehydes, imines and electrophilic alkenes [1]. With the excess of Corey ylide, the formed oxiranes and aziridines can undergo ring expansion to 4- and even 5-membered rings, while alkenes often produced primary products, *i.e.*, donor-acceptor (DA) cyclopropanes, chemistry of which has been actively developing in recent years [2]. In general, the applicability of the approach is usually limited to Knoevenagel condensation substrates obtained from commercially available aldehydes, most often aromatic ones. This route cannot be used to obtain (hetero)arylmethyl cyclopropanes, which are a promising and uninvestigated subclass of DA cyclopropanes.

In this work we present *extended* [3] *Corey-Chaykovsky reaction* as a versatile approach for synthesis of benzylcyclopropanes **2** and their analogs **3** *via* reaction of the excess of Corey ylide with readily available 4-hydroxyphenyl- and 1*H*- or 1-*p*-tosyl 3-indolyl-substituted alkenes **1**. This reaction proceeds as *double methylene transfer* from Corey ylide to activated Knoevenagel adducts. Investigation of mechanism, including studies of deuterium labelled Corey ylide, allowed us to conclude that the presence of electron releasing groups in (het)aryl substituent and ability to *ipso* attack play a crucial role for the realization of this domino process. Oppositely, common cyclopropanes **4**,**5** were obtained using substrates bearing 3-nitro- or 4-TsNH groups.



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Activated enynes as modern powerful synthons

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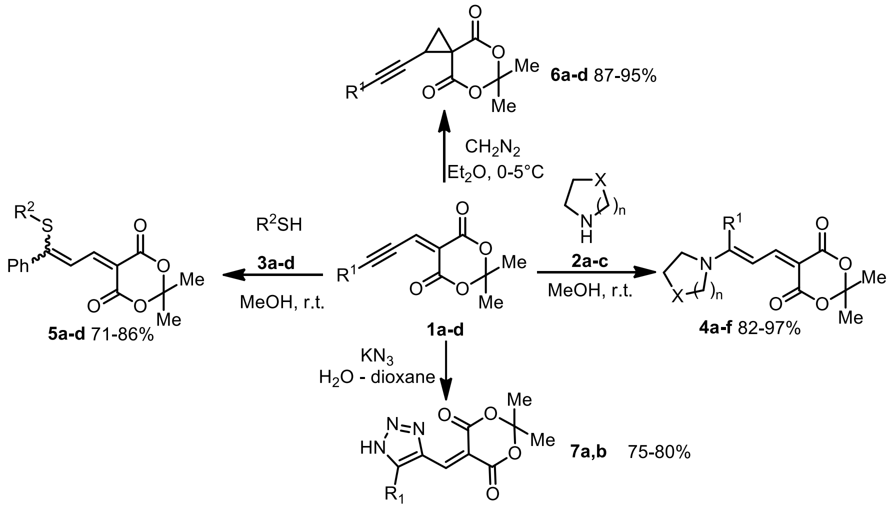
Modern reviews show, that electron-deficient 1,3-enynes has emerged as a powerful synthon in recent years for the efficient synthesis of enantioenriched furans, allenes, 4-H-pyrans, and 4-isoxazolines, which are privileged scaffolds in bioactive compounds and natural products [1]. Unfortunately, there are not many data in the literature on the reactions of 1,3-enynes containing a residue of Meldrum's acid **1**.

Thus, by the method of competing reactions, it was shown that the reactivity of such enines when amines **2** and thiols **3** significantly exceeds the reactivity of structurally similar enynones (in some cases 100:1). The resulting push-pull dienes **4** and **5**, due to the strong polarization of the π-system, exhibit fluorescent and solvatochromic properties [2].

Due to the polarization effect of CO groups, enynes **1** easily react with diazomethane solution, specifically at double C=C bonds with no catalyst resulting the cyclopropane derivative **6** with a high yields.

Meldrum acid derivatives **1** can also be used for the synthesis of heterocyclic structures, for example, the reaction involving potassium azide proceeds selectively at the triple C≡C bond and leads to the formation of the corresponding triazoles **7**.



1,6: R^1 = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), Me_3Si (**d**); **2:** X = CH_2, n = 1 (**a**), X = CH_2, n = 2 (**b**), X = O, n = 2 (**c**);
3,5: R^2 = Ph (**a**), CH_2Ph (**b**); Benzo[*d*]thiazole-2-yl (**c**); 4-Phenyl-1*H*-imidazole-2-yl (**d**)
4: R = Ph, X = CH_2, n = 2 (**a**), R = 4-MeC_6H_4, X = CH_2, n = 2 (**b**), R = 4-ClC_6H_4, X = CH_2, n = 2 (**c**), R = Ph, X = CH_2, n = 1 (**d**), R = Ph, X = O, n = 2 (**e**), R = 4-MeC_6H_4, X = O, n = 2 (**f**); **7**: R^1 = Ph (**a**), Me_3Si (**b**);

The study was funded by a grant Russian Science Foundation, No. 22-13-00185, https://rscf.ru/en/project/22-13-00185/

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Synthesis of estrone-based difluoroboron complexes as versatile precursors

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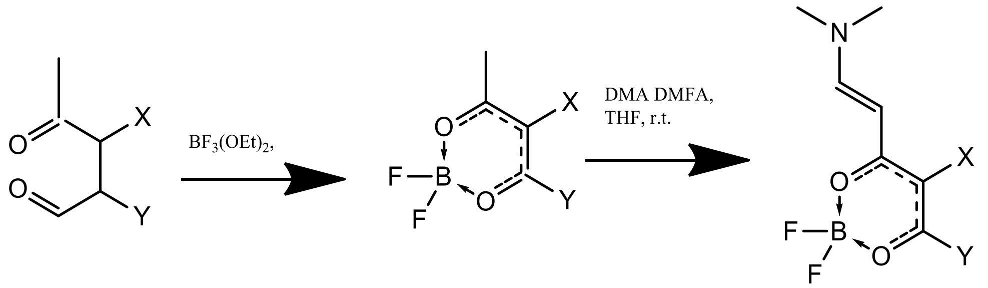
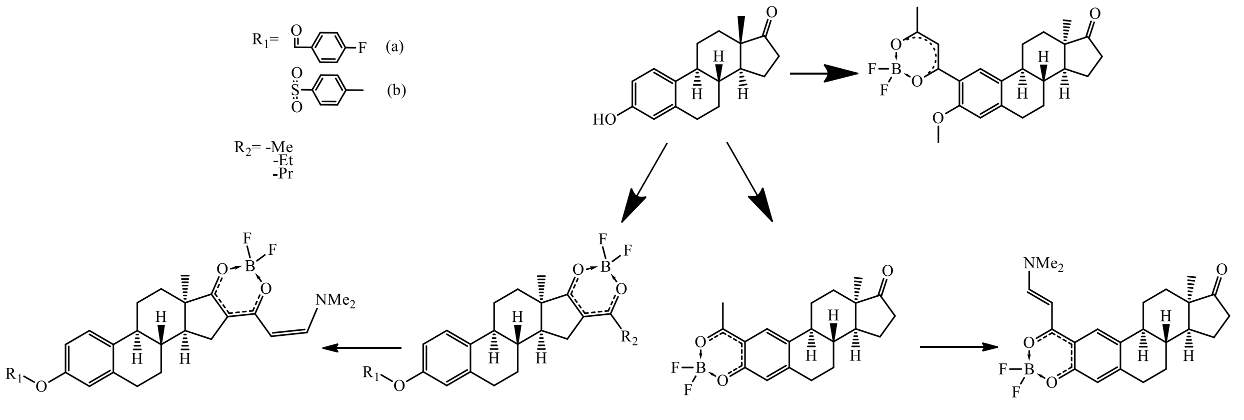
Boron-chelate complexes of β-diketones using in the synthesis of heterocyclic structures are expanded synthetic potential of initial substrate. The most approachable among such complexes are stable difluoroboron chelates obtained from etherates of boron trifluoride and β-dicarbonyl compounds.



Known, any modification of steroid structure leads to changes in their biological activity. We suggest a new path to the functionalization of steroids through the formation of difluoroboron complexes.

Previously, synthesis of difluoroboron complexes of steroids was used as an intermediate step in the 2-position acylation.

We successful to obtain a number of difluoroboron complexes based on estrone, which are appropriate intermediates for further heterocyclizations.



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Synthesis and anti-aggregation activity of 2-substituted imidazolines

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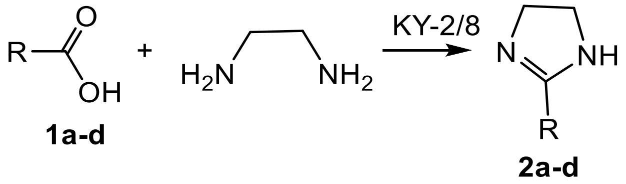
The imidazoline ring is a structural fragment of biologically active natural and synthetic substances [1-3]. These compounds demonstrate high antifungal, antitumor, hypotensive, antiglycemic activity, and are also effective for the treatment of Parkinson's and Alzheimer's diseases.

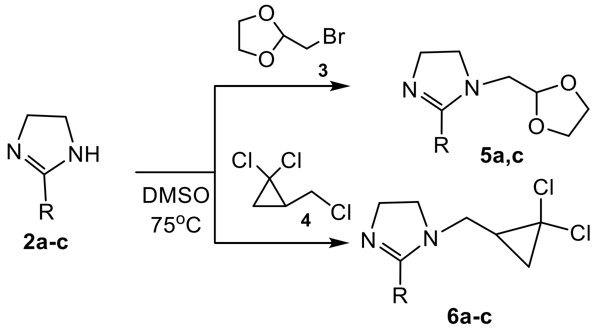
In this work, we present the results of the synthesis studies of 4,5-dihydro-1H-imidazole new derivatives containing gem-dichlorocyclopropane and 1,3-dioxolane fragments and study their anticoagulant and anti-aggregation activity.

Target 2-alkylimidazolines **2a-d** were synthesized by condensation of carboxylic acids with ethylenediamine in the presence of cation-exchange resin KU-2-8 (toluene, 100-110°C, 10-12 h). Benzoic **1a**, salicylic **1b**, phenoxyacetic **1c**, and 2,4-dichlorophenoxyacetic **1d** acids were used as starting compounds.



R = Ph **(1a,2a),** 2-(OH)Ph **(1b,2b),** Ph-O-CH_2 **(1c,2c),** 2,4-(diCl)Ph **(1d,2d)**

New derivatives of 2-substituted 4,5-dihydro-1H-imidazoles containing 1,3-dioxolane or gem-dichlorocyclopropane fragments (**5a,c** and **6a-c**) were obtained during alkylation of imidazolines **2a-c** with 2-bromomethyl-1,3-dioxolane **3** or 2-chloromethyl-gem-dichlorocyclopropane **4** (DMSO, 75-100°C, 8-10 h).



The anti-aggregation and anticoagulation activity of the obtained compounds was studied. It was found that substituted 4,5-dihydro-1H-imidazoles have anti-aggregation activity at the level of acetylsalicylic acid.

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Condensation reaction of chloromethylbenzyl ether with chloro(bromo)substituted benzaldehydes

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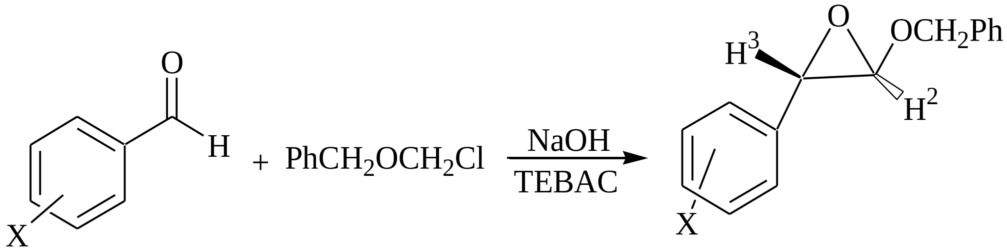
Oxiranes are an important class of organic compounds that are actively used in targeted organic synthesis of various biologically active drugs [1]. Substituted oxiranes containing functional groups are of great interest. Among the most studied of such substituted oxiranes are glycidic esters obtained by the condensation of aromatic aldehydes with chloroacetic acid esters in the presence of bases (the Darzens reaction) [2]. In recent years, we have been studying various condensation reactions occurring in presence of chloromethyl propargyl ether [3-5]. In [6], we first carried out similar condensation of propargylchloromethyl ether with aromatic aldehydes (ketones) and obtained 2-aryl-1-propargyloxiranes.

We expanded the range of studying reagents of condensation and improved the experimental technique, and during the interaction of chloro(bromo)-substituted benzaldehydes **1–6** with chloromethylbenzyl ether in an aqueous medium in the presence of a interphase catalyst triethylbenzylammonium chloride (TEBAC), we obtained *trans*-isomers — 3-haloaryl-2-benzyloxyoxiranes **7-12** with a satisfactory yield (62.1–69.7%).



1-6

X= 2-Cl (1,7), 3-Cl (2,8), 4-Cl (3,9),
2-Br (4,10), 3-Br (5,11), 4-Br (6,12)

7-12

An experimental feature of this work is the use of the method of the process of interphase alkaline catalysis. In this case, it is possible to avoid the use of organic solvents and strong bases (for example, sodium alcoholate), which prevents the destruction processes of the initial reaction products. The mechanism of condensation is similar to the Darzens reaction [2] and includes the formation of the anion and ether at the aqueous and organic phase boundary. Next, the anion is transferred to the organic phase by the aid of TEBAC catalyst and the anion reacts with the aldehyde forming the reaction product.

The yields of bromoderivatives (**10-12**) are higher than yields of the chlorine analogues (**7-9**).

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Synthesis and photophysical studies of perylene-substituted 2,2’-bipyridines push-pull fluorophores

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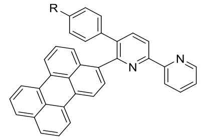
Catacondensed π-electron systems such as polycyclic aromatic hydrocarbons (PAHs) derivatives as electron donor (D) group and 2,2’-bipyridine acceptor (A) groups forming chromophores of the type D-A may display photoinduced intramolecular charge transfer (ICT) processes[1]. In these systems, it is possible to easily perform chemical assembly of fragments to change the energy of frontier orbitals (HOMO-LUMO), the band gap and packing in the solid state, as well as to modulate the structural features of optoelectronic chromophores[2].

We have mentioned already that the inverse demand Diels-Alder reaction in 1,2,4-triazine precursors is one of the promising ways for obtaining asymmetrically substituted aryl-bipyridines [3]. Based on this strategy, our group have developed an effective method for the synthesis of 5-(perylen-3-yl)aryl-substituted 2,2’-bipyridines *via* the interaction of 6-phenyl substituted 3-(pyridin-2-yl)-1,2,4-triazine with lithium perylen followed by oxidative aromatization of the intermediate adduct and conversion of 1,2,4-triazine precursor under the action of 2,5-norbornadiene.

Based on the obtained results of spectroscopic studies, unlike common ICT processes all perylene-substituted 2,2’-bipyridines as D-A type fluorophores demonstrate the excellent solvent polarity dependent fluorescence properties *via* exhibiting a gradual increase in Φ_f with increasing solvent polarity (for example, for 1 32% in toluene, 47% in THF and 67% in MeCN) (Table 1).

Table 1 Data of photophysical properties of perylene-substituted 2,2’-bipyridines

 R = F,OMe,Me 1-3	#	Solvent	λ_{abs}, nm	λ_{em}, nm	Φ_f
	1	MeCN	418, 443	460, 486	0.67
		THF	305,398,421,447	537	0.47
		Toluene	306,400,423,449	539	0.32
	2	MeCN	418, 443	461, 488	0.41
	3	MeCN	417, 443	460, 486	0.54

This work was supported by the Russian Scientific Foundation (grant № 19-73-10144-P) and by the Ministry of Science and high Education of the Russian Federation (MEGAGRANT, contract No 075-15-2022-1118 dd.29.06.2022)

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Synthesis of oxaheterocycles through extended Corey–Chaykovsky reaction

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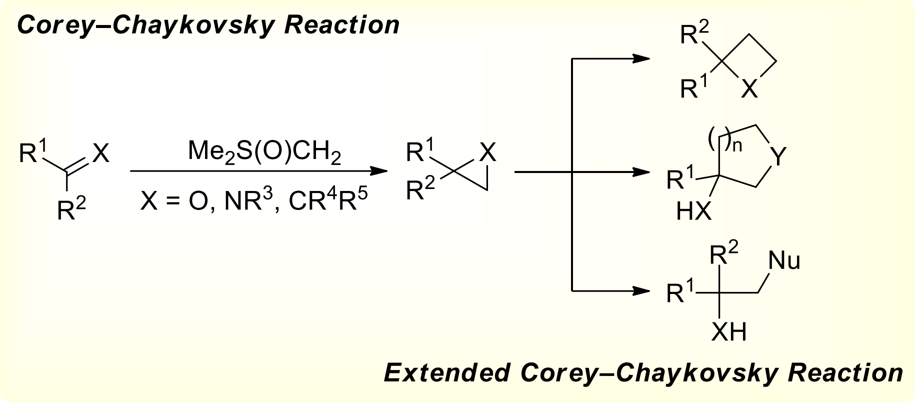
In 1962, Corey and Chaykovsky introduced dimethylsulfoxonium methylide into synthetic practice as a reagent for the simple and efficient construction of three-membered rings from the corresponding carbonyl compounds, their imines and acceptor alkenes.

Among huge diversity of examples of Corey–Chaykovsky reactions, processes wherein three-membered rings are formed as intermediates attract particular attention. For them, we propose to use the term "extended Corey-Chaykovsky reactions" [1].



This report will present examples of extended Corey-Chaykovsky reactions, consider the influence of reaction conditions and the structure of the starting compounds on the efficiency of ongoing processes.

This work was supported by Russian Science Foundation (project № 21-73-10063)

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Aromaticity in the low-lying electronic states of metallocenothiaporphyrins

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The aromaticity and electronic delocalization in the low-lying electronic states of the metallocenothiaporphyrins with the transition metal is V^+, Cr, Mn^+, Fe [1], Co^+, Ni, Mo, Tc^+, Ru [2], or Rh^+ have been studied by using magnetic criterion of aromaticity. The magnetically induced current densities were calculated at the density functional theory (DFT/B3LYP/def2-TZVP) level using the gauge including magnetically induced current method (GIMIC) [3].

Most of the studied metallocenothiaporphyrins are paramagnetic and their ground states have largely the same spin state as the corresponding metallocenes. The low energy barrier between different spin states (1.69-30.48 kcal/mol) allows using metallocenothiaporphyrins as molecular switches.

It was shown that the studied molecules have pronounced character of aromaticity, which is confirmed by none-zero ring-current strength (nA/T). This is a consequence of the transmission of π-electron conjugation across a d-electron metallocene resulting in formation of the united three-dimensional π-d conjugation and metallomacrocyclic aromaticity. Current density calculations reveal helical flow at the metallocene moiety, whose chirality is the same for both the aromatic and antiaromatic species.

Metallocenothiaporphyrins with isoelectronic structure have the same aromatic character and close values of the ring-current strength. This indicates that the nature and degree of aromaticity of the compounds are largely determined by the metal d-electrons. The addition of 2 hydrogen atoms to the porphyrinoid part leads to the reversal of the aromaticity which can be explained by electronic counting and the Hückel aromaticity rule (4n/4n+2).

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Study of stereoselectivity of the [3+2] cycloaddition reaction of carboxymethylideneimidazothiazolotriazines with azomethine ylides

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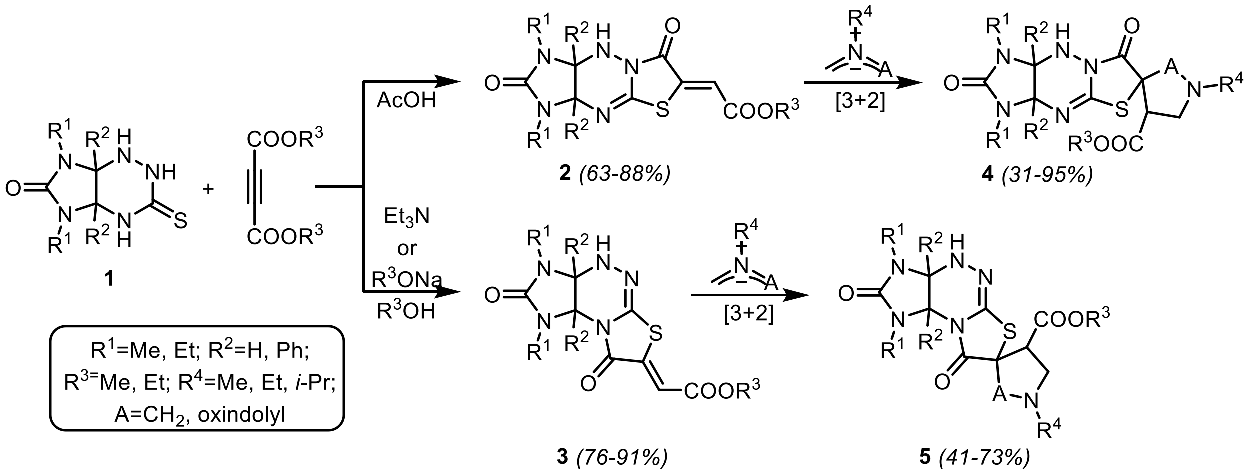
In medicinal chemistry, researchers are of particular interest to spirocyclic derivatives of oxindole due to their highly selective action with respect to a number of biological targets. Methods for the preparation of such compounds primarily include [3+2]-cycloaddition reactions [1]. This method makes it possible to obtain the corresponding spirocyclic products in the form of various stereoisomers.

As substrates for dipolar cycloaddition reactions, we can use the obtained imidazothiazolotriazines, which are formed in the reactions of imidazo[4,5-e]triazinethiones **1** with dialkylacetylenedicarboxylates [2]. Due to the presence of several nucleophilic centers in the structure of imidazo[4,5-e]triazinethiones **1**, this reaction can proceed with the formation of linear and angular imidazothiazolotriazines **2** and **3** respectively.



The resulting compounds enter into (1,3)-dipolar cycloaddition reactions of azomethine ylides generated in situ from amino acids and carbonyl compounds (paraform and isatins). The main issue of this work is to elucidate the factors that determine the stereoselectivity of cyclocondensation. It was found that the selectivity of reactions is affected by both the structure of the substrate and azomethine ylide. The obtained compounds **4** and **5** were characterized by a set of spectral studies, including X-ray diffraction data.

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Unexpected result of the reaction of thioglycolurils derivatives with bromoacetophenone

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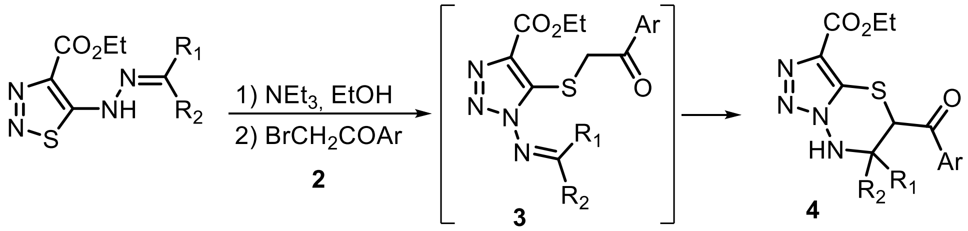
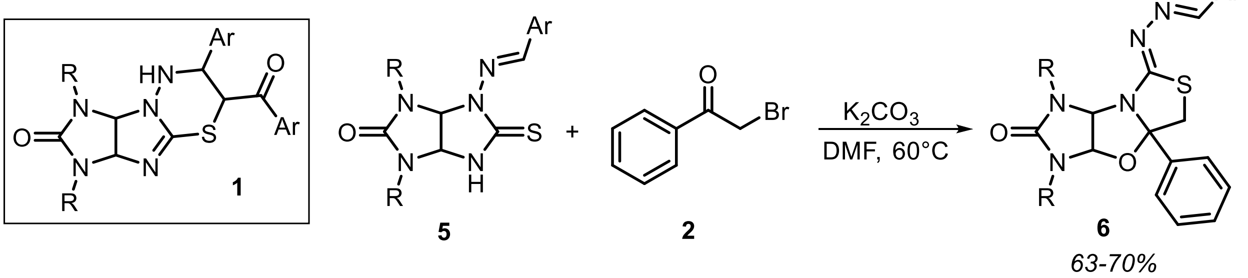
Nitrogen- and sulfur-containing annelated heterocyclic compounds have attracted researchers for many years, since such compounds are contained in a large number of biologically active compounds [1]. However, the existing methods for the synthesis of such heterocyclic structures are not universal and have many limitations. Therefore, the search for new approaches to the synthesis of fused heterocyclic frameworks is an urgent problem in modern organic chemistry.

In this investigation, we focused on the synthesis of structures **1** from thioglycolurils derivatives **5** previously obtained in our laboratory. Such heterocyclic systems have not been previously described, but several synthetic examples of the 1,3,4-thiadiazine system are known [2], which involve the interaction of the hydrazone fragment with substituted bromoacetophenones **2**. Using a slightly modified technique, we got a very unexpected result. Instead of the supposed imidazo[2,1-*b*][1,3,4]thiadiazine system **1**, we obtained an absolutely new heterocyclic system, imidazo[4,5-*d*]thiazolo[4,3-*b*]oxazole **6**.

Previous work:



Current work:



The formation of such a tricyclic condensed structure **6** probably begins with the formation of an S-alkylated derivative of thioglycoluril, which then undergoes a cascade of intramolecular rearrangements. The structure of the compounds **6** was proved by a complex of spectral methods, as well as by the X-ray diffraction method.

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Synthesis of (*S*)-3-(1-benzylpyrrolidin-2-yl)-5-(substitutedthio)-4-phenyl-4*H*-1,2,4-triazoles as a potential asymmetric catalysts for Sulfa-Michael reaction

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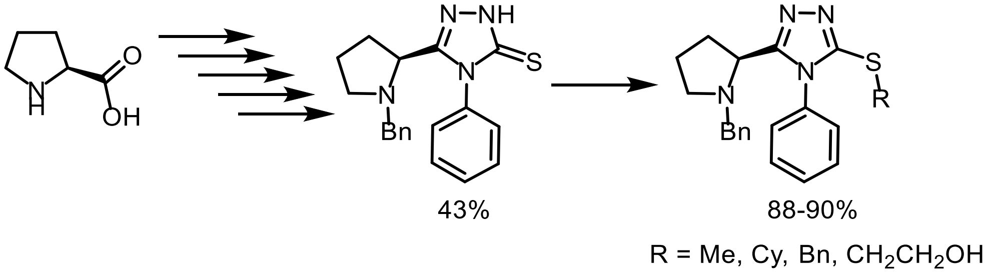
The synthesis of optically pure organic compounds is very important for pharmacy, especially in drug synthesis. Asymmetric catalysis is the most effective way of reaching this optical purity. Modeling and synthesis of new optically active catalysts which can bring to high yields and high enantioselectivity are very important for this field.

It is known that proline derivatives are very good enantioselective catalysts in a huge variety of reactions. Their presence, even in a small amount, determines the high enantioselectivity of the reaction [1]. On the other hand, the 1,2,4-triazole ring can be used as a good linker to combine different groups with the pyrrolidine ring and form new 3D structures. The other advantage of 1,2,4-triazole derivatives is that they are easily synthesizable [2].

As a catalyst for Sulfa-Michael reaction we suggest (*S*)-3-(1-substitutedpyrrolidin-2-yl)-5-(substitutedthio)-4-phenyl-4*H*-1,2,4-triazoles because of their 3D structure.

The synthesis scheme of compounds is shown.



Compounds and their purity are identified be NMR and X-ray spectroscopy. There are also determinates physical properties like melting point and $[\alpha]_D$.

The work was supported by the Science Committee of RA, in the frames of the research projects (grants № 21SCG-1D005 and 21T-1D320)

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Charge-transfer complexes of bis(aza-18-crown-6)-containing dienone with diammoniopropyl derivatives of viologen and dipyridylethylene

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In recent years, there has been extensive development and research into organic donor-acceptor complexes due to their usefulness in a wide range of applications in biological photosystems, photoredox catalysis, analytical probes, molecular sensors, organic light emitting diodes and photovoltaic cells. Particularly, bis(azacrown)-containing dienones, which combine chromophore and ionophore fragments in their structure, are of great interest.

In order to study the features of its' complexation with Ca^{2+} cations, tetraperchlorate diammoniopropyl derivatives of viologen and dipyridylethylene and diperchlorates of alkanediammonium of various chain length, bis(aza-18-crown-6)-containing dienone of the cyclopentanone series **1** was synthesized.

a

b

Structures of pseudocyclic complexes of dienone with the tetraperchlorates diammoniopropyl derivatives of viologen and dipyridylethylene (a). Most probable conformation of the pseudocyclic complex with the diammoniopropyl viologen derivative, according to DFT calculations (b).

The structure of the synthesized dienone **1** was determined by complex of independent methods (NMR, IR, electron spectroscopy, elemental analysis data).

Spectral properties of model supramolecular systems based on dienone **1** with alkanediammonium salts were studied. The complexation of bis(azacrown)dienone **1** with a diammoniopropyl derivative of bipyridylethylene and Ca^{2+} cations was studied by electron and ^1H NMR spectroscopy. It was found that **1** forms stable 1:1 and 1:2 complexes with Ca^{2+} cations, and pseudocyclic 1:1 complex with a diammoniopropyl derivative of dipyridylethylene. The complexation of **1** with a dipyridylethylene derivative is accompanied by quenching of the emission of **1**, which indicates the formation of a charge transfer complex [1]; the addition of Ca^{2+} cations leads to the destruction of the charge transfer complex and accompanied by fluorescence enhancement of **1**. Stability constants of the resulting complexes were determined by spectrophotometric and fluorescence titration methods.

Supramolecular systems based on such bis(azacrown)-containing dienones could be used to determine the presence of different metal ions and organic cations in the environment and biological fluids. This opens up opportunities for their use for analytical purposes.

This work was supported by the Russian Science Foundation (grant № 22-13-00064)

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Organic Chemistry Section Poster Session

Pd-/solvent-free preparation of new phenazine-based functional polymers

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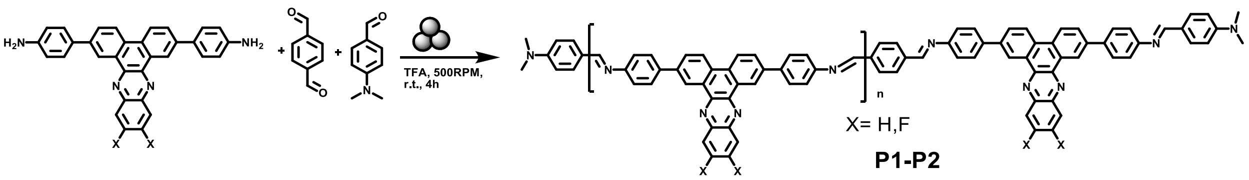
Mechanosynthesis have recently proven to be successful solvent-free synthetic methodology, especially in polymer chemistry[1] due to it being simple and fast, as well as its minimum or no consumption of solvents. In last decades there is growing interest to the organic polymers based on polycyclic (hetero)aromatic (including diazines), ethylene/azamethyne untits etc., for the applications in plastic electronics [2] , energy storage, high redox-active materials, as well as for the colorimetric / fluorogenic analysis [3]

In this communication we wish to report the synthesis of dibenzophenazine/azamethyne based polymers **P1-P2**. These polymers were prepared for the first time via Pd-free and solvent-free condensation reaction between diamino-substituted dibenzophenazines, terephthalaldehyde and 4-(dimethylamino)benzaldehyde as a chain-capping unit under ball-milling conditions (Scheme 1).

The phtophysical, electrochemical and coordination properties of **P1-P2** will be presented.



Scheme 1. Mechanochemical synthesis of polymers P1-P2

This work was supported by the Grants Council of the President of the Russian Federation (NSh-1223.2022.1.3) and Ministry of Higher Education and Science of the Russian Federation (Agreement No. 075-15-2022-1118)

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Synthesis of pyrrolo[2,3-c]quinolines via the Fischer reaction

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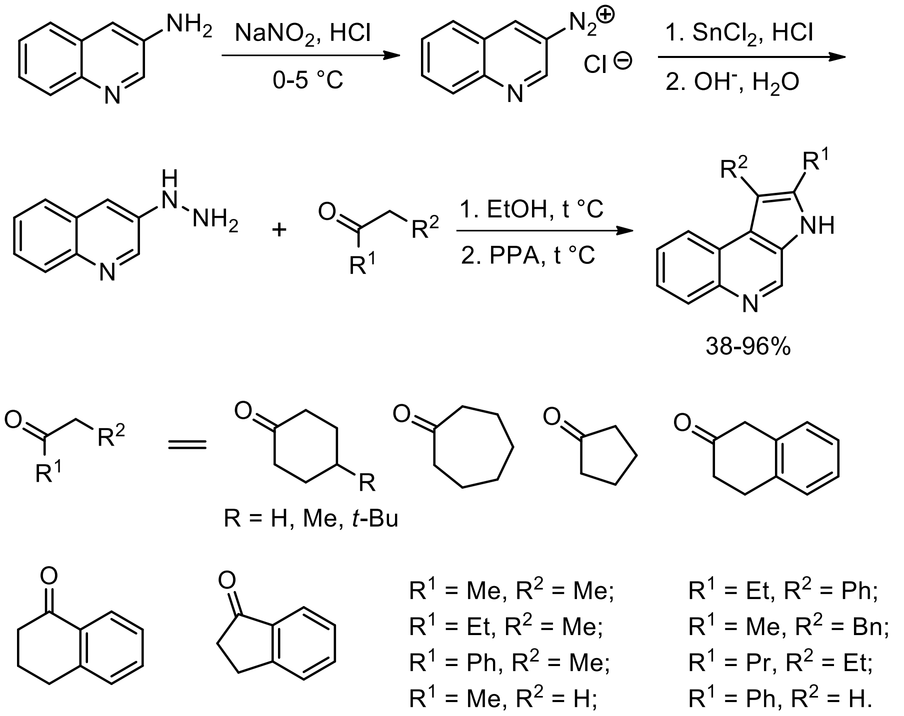
Heterocyclic compounds containing a pyrrolo[2,3-c]quinoline tricyclic system, such as marinoquinolines, have attracted much attention due to their wide spectrum of biological activity. Methods for the synthesis of 3H-pyrrolo[2,3-c]quinolines can be conventionally divided into three categories depending on which cycle is closed at the final stage, which were considered in detail by us [1]. At the moment, there are few publications describing the synthesis of such compounds using the Fischer reaction, so this work is devoted to the preparation of such heterocycles by the Fischer reaction by cyclization of the corresponding hydrazones in polyphosphoric acid (PPA) at 180-200 °C for 5 minutes with a yield of 38-96 % depending on the structure of the corresponding carbonyl compound.

The general synthesis scheme is as follows:



As a result of the experiments, 16 samples of the corresponding pyrrolo[2,3-c]quinolines were obtained, which demonstrates the possibility of obtaining the pyrrolo[2,3-c]quinoline skeleton *via* the Fisher reaction.

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Synthesis and catalytic activity of the Hoveyda-Grubbs type catalysts with the chalcogen-Ru coordination bond in a six-membered chelate ring

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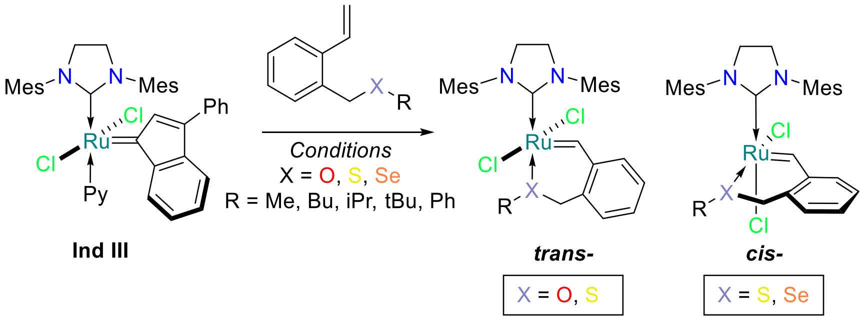
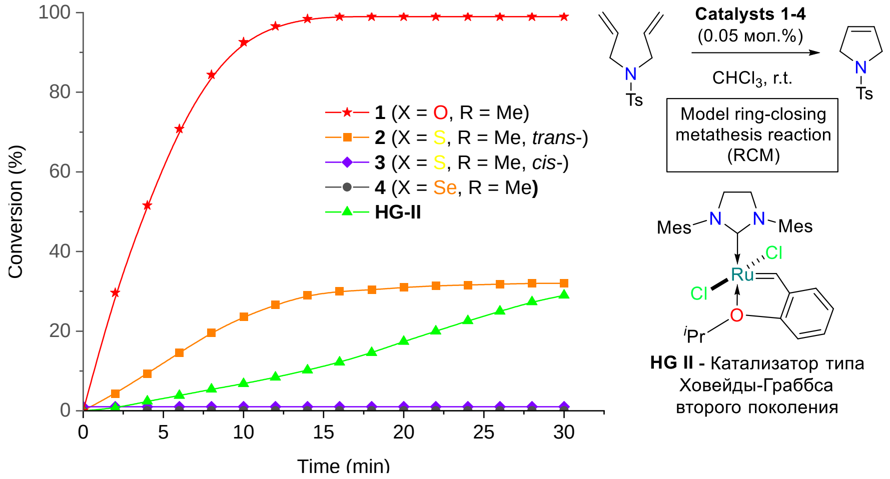
In recent decades catalytic olefin metathesis has become a powerful tool in the hands of researchers. The goal of this work is obtaining ruthenium catalysts containing a six-membered chelate cycle with various halcogens. This stage of the study included both the synthesis of benzylidene ligands and the preparation of target ruthenium complexes. It is interesting to note that oxygen chelates were formed exclusively in the form of one *trans*-isomer, sulfur-containing chelates were formed in the form of both *cis*- and *trans*-isomers, and selenium-containing complexes are formed in only *cis*-form.



Further catalytic experiments were carried out. In the absence of activation, as expected, only oxygen- and *trans*-sulfur-containing complexes showed activity, demonstrating even higher efficiency than the popular commercially available second-generation Hoveyda-Grubbs catalyst (see *Figure* below). At the same time, as expected, the *cis*-isomeric complexes (both S- and Se-containing chelates) were completely inactive under these conditions. Therefore, catalytic properties of cis-complexes were studied under thermal or UV-activation conditions.



The research was funded by the Russian Science Foundation (project No. 22-23-00490)

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Synthesis of non-natural α-amino acids containing 2*H*-isoquinolin-1-one moiety using chiral Ni(II) complexes

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Synthesis of new physiologically active non-natural amino acids is an actual scientific task because of their application for replacement of one of the proteinogenic amino acids in a physiologically active peptide molecules to change their properties and bioactivity [1].

Herein we report the optimized and efficient protocol for the asymmetric synthesis of the non-natural α-amino acids with 2*H*-isoquinolin-1-one moiety via rhodium-catalyzed C-H activation of O-protected aromatic hydroxamic acids with Belokon's chiral α-propargylglycine Ni(II) complexes (Figure 1) [2]. The mild conditions and the presence of an internal oxidants (ether groups) allowed us to use terminal alkynes into the catalytic aromatic C-H bond functionalization reaction, which is impossible in the presence of silver or copper salts as an oxidants, since they can promote dimerization or oligomerization of alkynes [3]. This approach has high regioselectivity to give only 3-substituted isoquinolone derivatives.

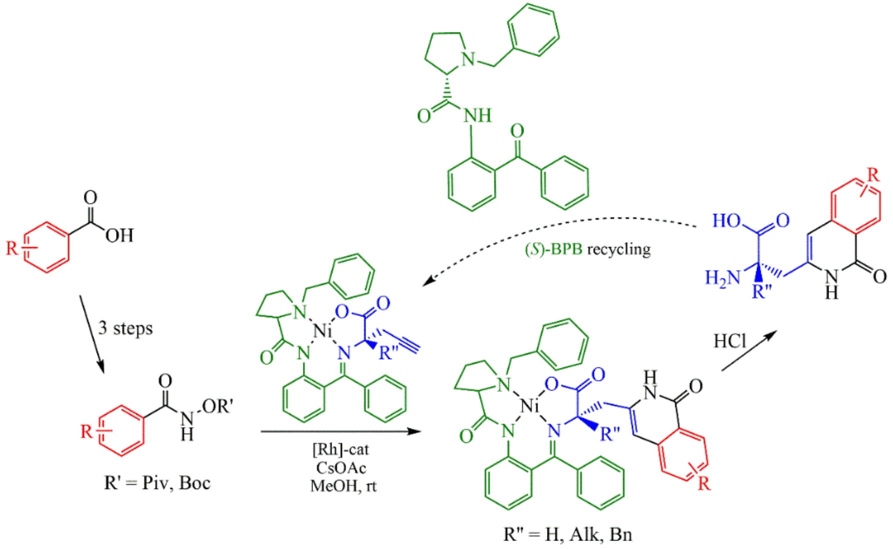

Figure 1. Efficient protocol for synthesis of α-substituted isoquinolone-containing amino acids.

Thus, we developed easy way for the synthesis of a number of nickel (II) complexes with α-amino acid derivatives with various aromatic fragments and substituents in the α-position, from which we can isolate enantiomeric pure α-amino acids with high yields.

This work was supported by the Russian Science Foundation (grant № 22-23-00779)

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Investigation of the complexation of the interaction of nickel (II) with 1- (2-pyridylazo) -2-hydroxy-4-mercaptophenol and aminophenols

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Among organic reagents successfully used in analytical chemistry, azooxy compounds should be mentioned. In the search for more advanced reagents for the determination of metals with an ionic radius of the order of 0.07−0.08 nm (Cu, Ni, Co), 1-(2-pyridylazo)-2-hydroxy-4-mercaptophenol (L) was investigated.

The aim of this work is to study the complexation of nickel (II) with L and aminophenols (AP). From AF used 2-(N,N-dimethylaminomethyl)-4-methylphenol (AF_1), 2-(N,N-dimethylaminomethyl)-4-bromophenol (AF_2).

L is a crystalline substance of dark green color, poorly soluble in water, in acids, partially soluble in alkalis, acetone, well soluble in chloroform. Depending on the acidity of the medium, L can exist in three forms: H_2L, HL^-, HL^{2-}. The first proton of the –SH group is cleaved off at pH> 2.75; the second proton of the –OH group — at pH> 8.5. The light absorption curves of molecular and ionic forms differ markedly from each other. The dissociation constants of the reagent found by the isobestic point method, by calculation and graphical methods at $\mu = 0.1$ and a chloroform concentration of 40% by volume, agree well with each other.

When nickel (II) interacts with L, colored complexes are formed that are insoluble in non-polar organic solvents. When AF is introduced into the system, the transition of anionic complexes to the organic phase is observed in the form of a mixed-ligand complex (MLC). The optimum acidity range, at which the optical density is maximum and constant, is at pH. 3.2−5.5 (pH 2.2−8.7). The extractability of the complexes was assessed by the distribution coefficient and the degree of extraction (R,%). The degree of extraction increases in the series $C_6H_{14} < C_6H_{12} < CCl_4 = C_6H_6 < C_6H_5\text{-}CH_3 < C_6H_5Cl < C_2H_4Cl_2 < CHCl_3$. Further studies were carried out with chloroform (R = 97.6−98.4%). The maximum analytical signal during complexation is noticeable at 625–645 nm. L absorb maximum at 530 nm. Colored chloroform extracts of L-AF associates absorb maximum light at 550−580 nm. For the formation and extraction of MLC, the following solution concentrations are required: $(1.2-1.5) \times 10^{-3}$ M L and $(2.4-2.6)\times10^{-3}$ M AF. The maximum optical density is reached within 15 min. Compliance with Beer's law is observed in the nickel concentration range of 0.5−18 μg/ml. The stoichiometry of the complexes under study was established by the methods of equilibrium shift and relative yield: Ni:L:AF = 1: 2: 2. In this case, the number of protons displaced by it from one H2L molecule turned out to be equal to 2. The composition of the extracted complexes can be represented by the formula $[NiL_2](APH^+)_2$. MLCs in the organic phase do not polymerize and are in the monomeric form ($\gamma = 0.91-1.02$).

The method of coordination of nickel with ligands was established using IR spectroscopy. L is a tridentate ligand coordinated with Ni^{2+} through the nitrogen atom of the azo group ($\nu_{N=N} = 1395$ cm^{-1}), near-bottom nitrogen ($\nu_{C\text{-}N} = 1290$ cm^{-1}; $\nu_{C\text{-}N} = 1170$ cm^{-1}) and oxygen atom ($\delta_{C\text{-}O} = 1250$ cm^{-1}). The detection of absorption bands at 1370 cm^{-1} indicates the presence of a protonated AF. A decrease in the intensity of the band at 2580 cm^{-1} observed in the L spectrum indicates that the –SH group is involved in the formation of the complex in the ionized state.

It was found that the colored complexes with L are also formed by the ions V (IV), Cu (II), Mo (VI), Fe (II), Pt (II), Pd (II), Ti (IV), and Co (II). The selectivity of the determination increases significantly in the presence of masking reagents or when the pH of the medium changes.

The results of studying the equilibria of complexation and extraction were used to develop methods for the determination of nickel in waters obtained by pumping oil (0.79 ± 0.015 μg/ml, $S_r = 0.028$).

Synthesis of first representatives of imidazo[4',5':4,5]imidazo[2,1-b]thiazole heterocyclic system based on thioglycoluril scaffold

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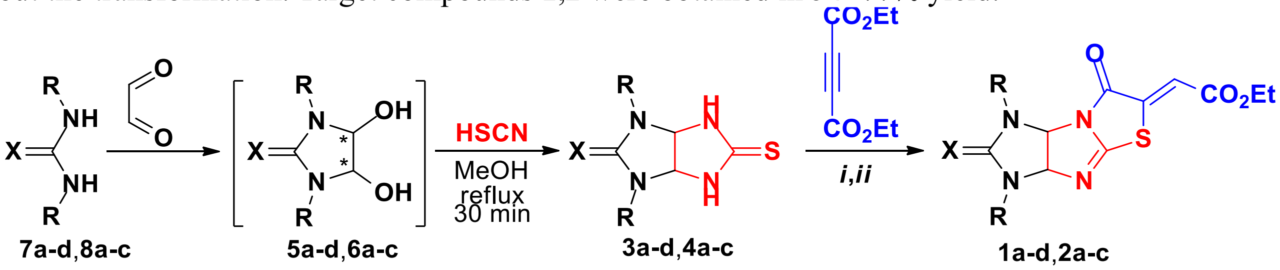
Glycolurils are highly interested heterocycles to study for chemists. The high interest in this class of compounds is due to the wide range of possibilities of using these bicycles. Also thiazole is important fragment in medicinal chemistry as it part of drug molecules. After that it is worth to be concluded that current theme is perspective and new synthetic routes should be investigated.

Here we describe the firs synthesis of 1,3-disubstituted ethyl 2-(7-oxo-3,3a-dihydro-1*H*-imidazo[4',5':4,5]imidazo[2,1-*b*]thiazol-6(2*H*,7*H*,8a*H*)-ylidene)acetates **1**, **2**.

Thioglycolurils **3**, **4** were obtained by the original reaction which is two-stage one-pot condensation. Diols **5**, **6** were synthesized by reacting ureas **7**, **8** with glyoxal, which then were condensed with HSCN without isolation and purification.[1,2]

Target compounds **1**,**2** were obtained in using annulation reactions of the thiazolidine to the imidazolidine with use of acetylenedicarboxylic acid. A synthetic protocol was developed to carry out the transformation. Target compounds **1**,**2** were obtained in 54−77% yield.



1,**3**,**5**,**7** X = O; R = H (**a**), Me (**b**), Et (**c**), Pr (**d**);
2,**4**,**6**,**8** X = S; R = Me (**a**), Et (**b**), Ph (**c**);
i : EtOH, r.t. 30 min;
ii : EtOH, reflux 2h;

The compounds **1**,**2** obtained will be sent to leading scientific organizations to study their biological activity.

This work was supported by the Russian Science Foundation (Project RSF 22-23-00769, https://rscf.ru/project/22-23-00769/)

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Sulfonamidation of trivinyl- and tetravinylsilanes in the presence of NBS

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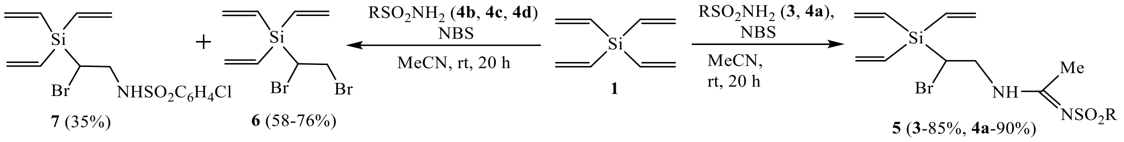
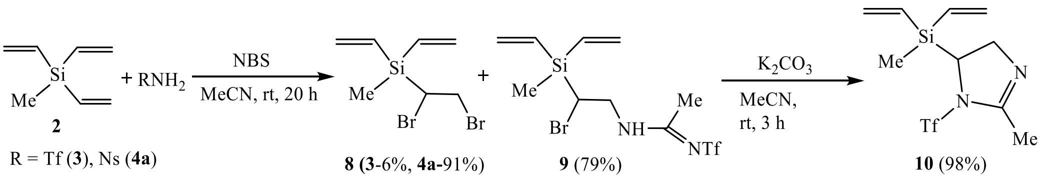
In a series of our works devoted to oxidative sulfamination of mono and divinyl silanes in the presence of different oxidants [1-7], we have synthesized a large family of new organosilicon *N*-heterocycles with pharmacophore sulfonamide and organosilicon groups in the molecule. These include *N*-sulfonylaziridines, products of mono- or bis-aziridination, aminohalogenation, substituted 1,4-azasilinanes, amidines. All products of oxidative amination undergo base-induced heterocyclization to imidazolines, 1,4-oxazocanes or 1,3,5-diazasilinanes, the hitherto unknown Si,N-heterocycles in practically quantitative yield.

Thus, the reactions of tetravinylsilane **1** and methyl(trivinyl)silane **2** with triflamide (TfNH$_2$, **3**) and arenesulfonamides (**4**, *p*-RC$_6$H$_4$SO$_2$NH$_2$, R=NO$_2$ (a), Cl (b), Br (c), Me (d)) were studied in the presence of *N*-bromosuccinimide (NBS) in acetonitrile.

With triflamide **3** and nosylamide **4a**, tetravinylsilane **1** in MeCN gives the corresponding amidines **5**, and with sulfonamides **4b**, **4c**, and **4d**, (1,2-dibromoethyl)trivinylsilane **6** and a minor product of bromosulfamidation **7** are formed. It is worth noting that, in the case of sulfonamide **4b**, no solvent interception (MeCN) was observed.



The reaction of methyl(trivinyl)silane **2** with **3** leads to a Ritter-type bromosulfonamidation product **9**, while with sulfonamide **4a** only dibromide **8** similar to product **6** is formed. *N*-[2-Bromo-2-(methyldivinylsilyl)ethyl]-*N'*-(triflyl)acetamidine **9** with excess K$_2$CO$_3$ in acetonitrile in 3 h was practically quantitatively converted into 2-methyl-5-(methyldivinylsilyl)-1-triflyl-4,5-dihydro-1*H*-imidazole **10**.



This work was supported by the Russian Science Foundation (project 22-13-00036)

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Rapid access to molecular complexity from bioderived 5-HMF derivatives via cascade cycloadditions

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The rapid generation of molecular diversity from easily available and simple starting molecules is a highly demanding goal in organic synthesis [1]. Based on this strategy, new chemotypes and polycyclic scaffolds, which are necessary for the synthesis of natural compounds and their analogues, as well as for the drug discovery, have been created. Within this advanced synthetic framework, the ability of furans to undergo cycloaddition reaction can broaden the scope of renewable 5-HMF derivatives with more complex structures.

Cycloaddition reactions of unsubstituted furan and its simple derivatives are well-known in organic synthesis. In contrast, cycloaddition of biomass-derived 2,5-substituted furans, such as 5-HMF derivatives, represents a challenge [2]. The appearance of two substituents significantly changes the reactivity, affecting steric hindrance, the HOMO energy of the furan cycle, its electrostatic potential, and even influencing aromaticity [3]. The negative influence is more pronounced in the case of electron-withdrawing substituents in positions 2 and/or 5, since the overall reactivity of furans as dienes noticeably drops in Diels-Alder reactions.

In this work, transformation of 5-HMF derivatives succeeded in a cascade cycloaddition reaction leading to a drastic (4-5-fold) increase in the molecular complexity based on the bio-based core as a result of one synthetic step. A new approach to the use of plant biomass in organic synthesis using cascade Diels-Alder reaction of 5-HMF dimer derivatives with different dienophiles has been developed. This reaction proceeds under thermodynamic control, diastereoselectively and regioselectively, providing rapid access to compounds of high molecular complexity with the same synthetic availability as previously obtained regular cycloadducts. As a concept illustration, under conditions of kinetic control, cycloadditions of two molecules of dienophiles are realized, and the resulting products, when heated, rearranged into thermodynamically more favorable cascade products. Reaction pathways were studied in details using quantum chemical calculations for revealing major factors influencing the selectivity of the process.

This work was supported by the Russian Foundation for Basic Research (grant № 20-33-90227)

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Synthesis of Taraxacine-A natural product and analogues

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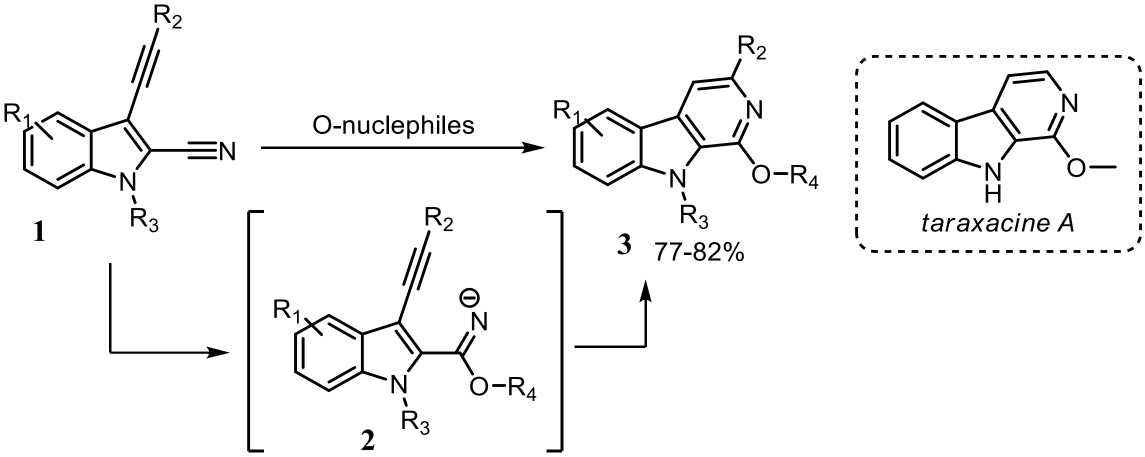
Taraxacine-A, isolated from *Taraxacum formosanum* [1], whose crude extracts have been found to possess interesting pharmacological properties including diuretic, anti-inflammatory, bacteriocidal effect against *Staphylococcus aureus* and inhibitory effect against *Mycobacterium tuberculosis* and *Leptospira* [2]. Still, no biological activity tests have been reported on Taraxacine-A itself and its derivatives.

Alkynyl-nitriles have been found to react with oxygen nucleophiles via *in situ* alkyne-imidate **2** cyclisation in a domino manner.[3] The base-catalyzed alkyne-imidate domino sequence reaction has been exploited for this work using the 3-alkynyl-indole-2-carbonitriles **1** to realize the 1-oxo-*β*-carboline **3** core with yields of 77-82%. We have implored this substrate against varying oxygen nucleophiles in good to excellent yields in an atom economic fashion.



This work is supported by the Russian Science Foundation
(grant № 22-13-00038, https://rscf.ru/project/22-13-00038/)

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Synthesis and reactions of adamantane-containing 5-hydroxymethyloxazolidin-2-ones

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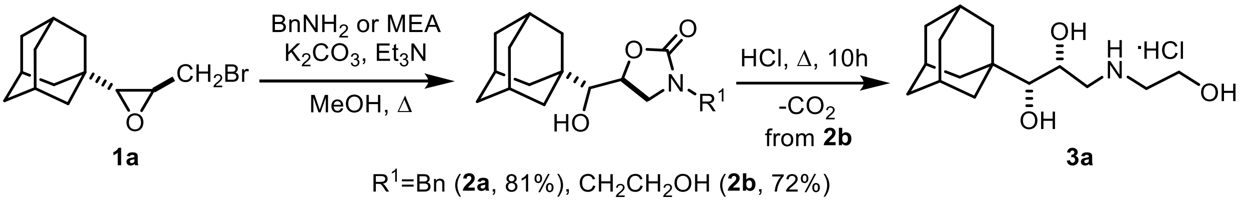
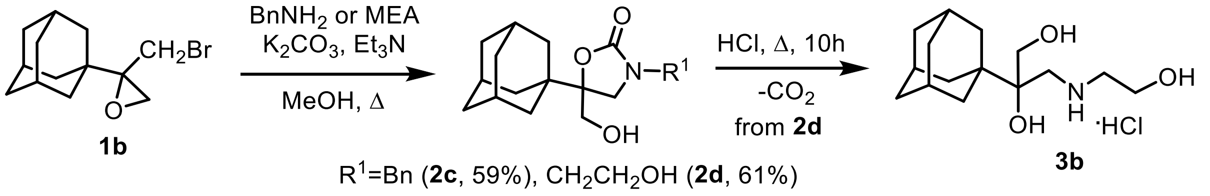
Oxygen-containing heterocycles are among the most common types of heterocycles that are found as structural components of many pharmaceuticals [1]. Some oxazolidinone derivatives represent a new class of synthetic antibacterial agents - linezolid, tedizolid. Oxazolidinones are used as precursors of natural amino alcohols and amino acids as well as chiral excipients in asymmetric synthesis [2].

Transformations of the substituted epoxides can lead to a variety of heterocyclic structures (from four- to nine-membered), differing in the number and type of heteroatoms present in the heterocycle [3]. The reaction of bromomethyloxiranes **1a,b** with benzylamine or monoethanolamine (MEA) in the presence of K_2CO_3 and triethylamine leads to 5-hydroxymethyloxazolidin-2-ones **2a-d** in good yields (59-81%).



R¹=Bn (**2a**, 81%), CH₂CH₂OH (**2b**, 72%)



R¹=Bn (**2c**, 59%), CH₂CH₂OH (**2d**, 61%)

It should be noted that reactions of *trans*-bromomethyloxirane **1a** lead to the formation of individual diastereomers of oxazolidinones **2a** and **2b** with the (*R**,*S**)-configuration. The vicinal coupling constant in ^{1}H NMR spectra of compounds **2a** and **b** were determined as 2.5 and 1.8 Hz respectively. Acid hydrolysis of 5-hydroxymethyloxazolidin-2-ones **2a,b** obtained the corresponding aminotriols, isolated as hydrochlorides **3a,b** with a good yields (60-73%).

These compounds are of interest as potential antiviral agents due to the presence of a highly lipophilic adamantane moiety. In the future, we plan to study the antiviral activity of synthesized oxazolidin-2-ones and amino alcohols against influenza virus and SARS-CoV2.

The work was financially supported by the Russian Science Foundation (project № 21-73-20103)

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Design of 7-substituted 3-azabicyclo[3.3.1]non-6-enes based on allylboron-acetylene condensation

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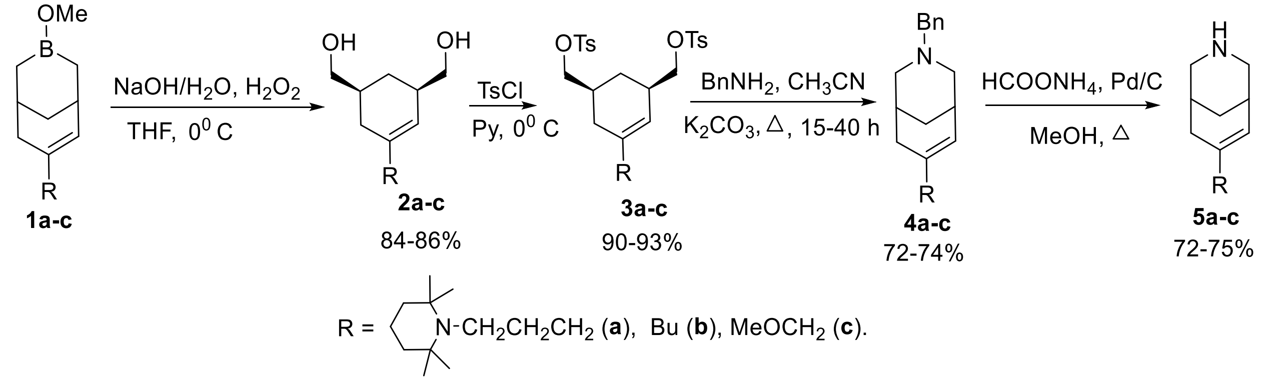
3-Azabicyclo[3.3.1]nonanes and their derivatives have been the subject of constant attention of researchers for more than half a century as compounds with a wide spectrum of biological activity. In addition, a highly efficient new generation drug for the treatment of nicotine addiction, varenicline, a derivative of 3-azabicyclo[3.3.1]non-6-ene with nitrogen-containing substituents at positions 6 and 7 was obtained [1].

An efficient method for the construction of 3-azabicyclo[3.3.1]non-6-ene derivatives from 7-substituted 3-borabicyclo[3.3.1]non-6-enes **1**, the products of a well-known reaction of allylboron-acetylene condensation, which formally consists in replacing the boron atom in the bicycle with a nitrogen atom, was developed [2]. The method includes a sequence of known reactions: the oxidation of 3-borabicyclononenes **1** to the corresponding *cis*-diols **2**, their conversion to *bis*-tosylates **3**, and the reaction of the latter with benzylamine forming *N*-benzyl derivatives **4**.



Unsubstituted at the nitrogen atom 7-substituted 3-azabicyclo[3.3.1]non-6-enes **5a-c** were obtained by *N*-debenzylation of compounds **4a-c** by the reaction with ammonium formate in the presence of Pd/C as a catalyst. These conditions provide a selective removal of the benzyl group, with the C(6)=C(7) double bond present in the bicyclic molecule remaining unaffected.

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Application of “boron” methodology in the lignanes precursors synthesis

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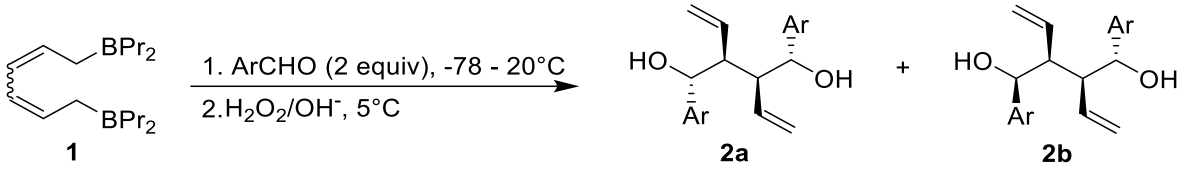
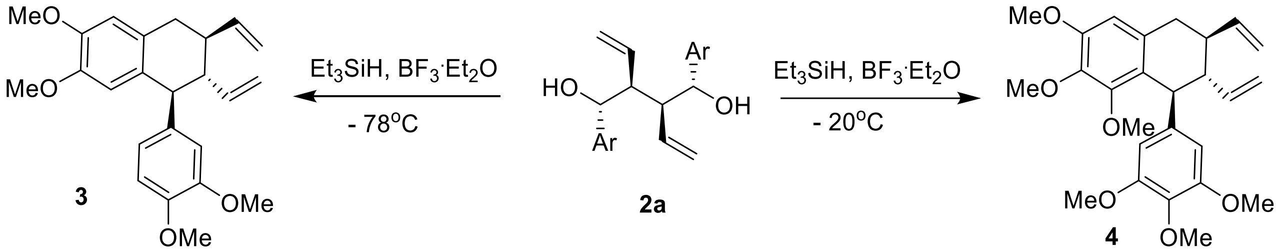
Lignans are a large class of natural substances that combines the plant origin metabolites containing phenyl propanoid fragment [1]. The diversity of biological activity of lignans made them very attractive synthetic targets during the last decades.

Here we developed the application of “boron” methodology for the preparation of lingans groups, based on the stereoselective reaction of 1,6-bis(dipropilboryl)-2,4-hexadiene (**1**) with aromatic aldehydes resulting in **2a** and **2b** isomeric diols [2,3]:

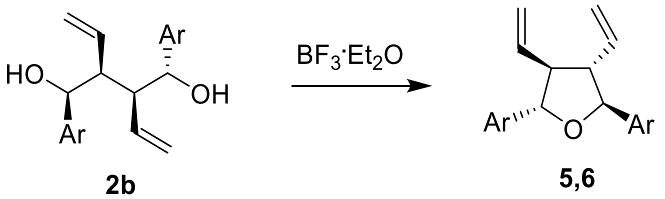


Both of diastereoisomers **2a** and **2b** were easily separated by column chromatography. The interaction of **2a** with Et_3SiH and $BF_3•OEt_2$ leads to the formation of compounds **3** and **4** containing the cyclohexane unit:



Ar = 3,4-$(MeO)_2$-C_6H_3, 3,4,5-$(MeO)_3$-C_6H_3

Further we found that diol **2b** under the action of BF3•OEt_2 unlike **2a** undergoes cyclization into furan derivative **5**:



Ar = 3,4-$(MeO)_2$-C_6H_3, 3,4,5-$(MeO)_3$-C_6H_3

Compounds **3,4** and **5,6** are structural fragments of the aryltetralin and 2,5-diaryltetrahydrofuran lignans series, respectively.

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Electrocyclic opening of triazoles as a route to fused heterocycles

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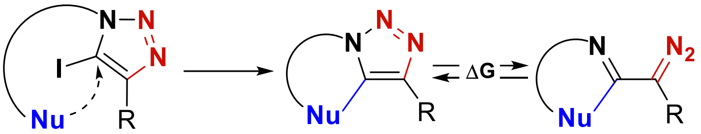
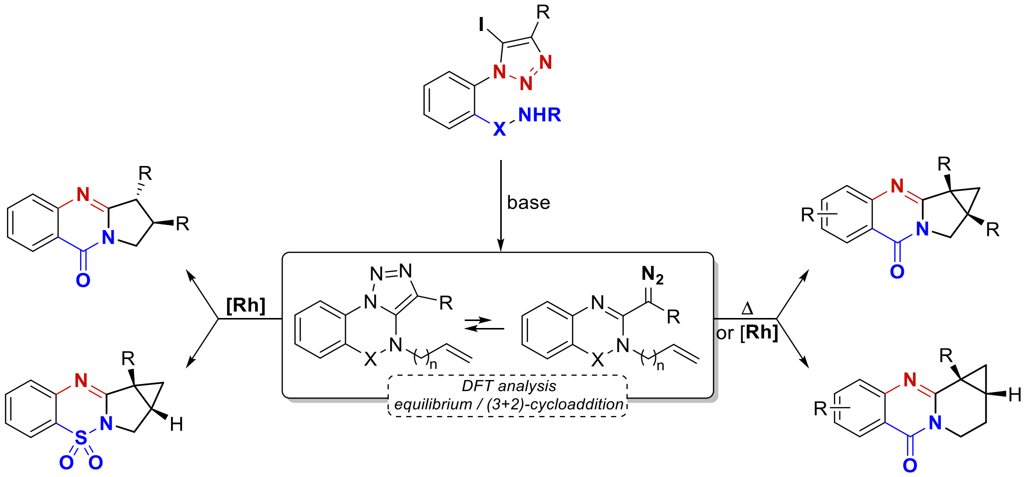
The development of approaches to various fused heterocycles is a very important challenge of modern organic chemistry due to the high utility of such compounds: they open the way to drugs and other biomolecules. Diazoimines are good precursors for this purposes as they are ambifunctional substrates. They can be easy obtained from annulated triazoles by electrocyclic ring opening [1-4].



Herein we have applied base-induced cyclization of 2-(5-iodotriazolyl)benzamides to produce either bicyclo[N.1.0]alkane or triazoloquinazolinone derivatives depending on the position of double bond in the molecule. It has been shown that the efficiency of non-catalytic cyclopropanation depends on the size of the resulting ring and the nature of the nucleophile. A series of desired products were obtained in moderate to good yields. Inactive substrates can be involved in the (2+1)-cycloaddition via rhodium catalysis.

Triazoloquinazolinones containing hydrogen in β-C(sp^3) position were shown to participate in Rh(II)-catalyzed intramolecular C-H insertion reactions with no cyclopropanation product observed.



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Tetraphosphorus decasulfide in thionation of lactams with phenolic moieties

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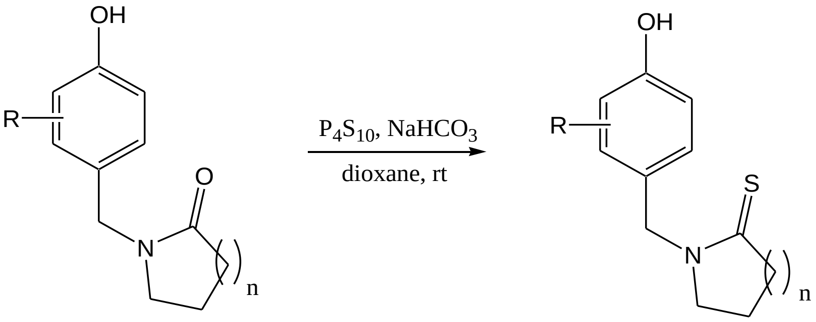
Thioamides and thiolactams, in particular, are important synthones in organic chemistry and possess themselves various kinds of bioactivity [1].

One of the most general method of synthesis of thiolactams is the thionation of the correspondent lactams. The most frequent thionation reagent is Lawesson's reagent; however, tetraphosphorus decasulfide is also used due to its cheapness and efficacy [2].

According to literally known data [3], we suggested the method for thionation of N-substituted lactams, bearing phenolic moieties, with P_4S_{10} [4]. Application of dioxane as a solvent allows to minimize side reactions.

Derivatives of several alkylphenols with thiobutyrolactam, thiovalerolactam and thiocaprolactam were obtained with yields up to 90%. Noteworthy, that lactamomethyl derivatives of polyphenols [5] didn't produce the target componds under these conditions.



R: -Me, -^{i}Pr, -^{t}Bu;
n=1-3

Structures of the synthesized compounds were studied with IR- and NMR-spectroscopy. Peak assignment was performed using Gaussian and VEDA quantum-chemical calculations. Composition of the target compounds was proved by elemental analysis. In preliminary tests on antioxidant activity it was shown that target compounds possess significant activity.

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Synthesis of tridentate selenium-containing compounds based on bis(2-chloroethyl) ether

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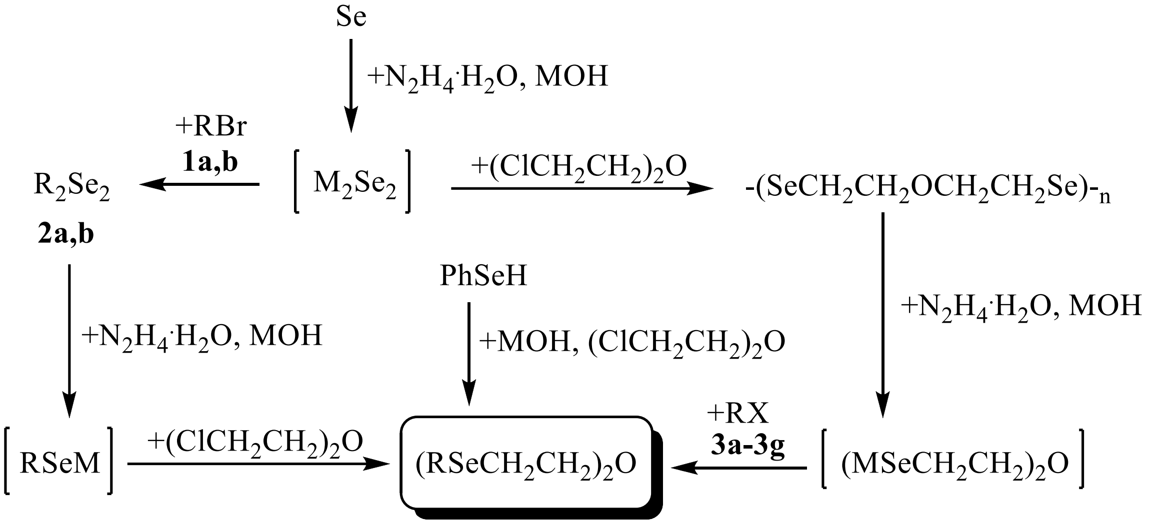
There are a number of different approaches in the literature for the preparation of organochalcogen derivatives of bis(2-chloroethyl) ether. In this work, we synthesized a number of new organoelement polydentate selenium-containing compounds corresponding to the composition $(RSeCH_2CH_2)_2O$, where R = Me, Et, Pr, *i*-Pr, Bu, *i*-Bu, C_6H_{13}, Cy, Ph, and Bn, using various approaches presented in the scheme.



4a,b
5a-5g
6a

M = Na, K
1,2: R = Cy (a), Bn (b)
3: R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *i*-Bu (**f**), C_6H_{13} (**g**)
4: R = Cy (**a**, 41%), Bn (**b**, 70%)
5: R = Me (**a**, 26%), Et (**b**, 28%), Pr (**c**, 24%), *i*-Pr (**d**, 28%), Bu (**e**, 31%), *i*-Bu (**f**, 29%), C_6H_{13} (**g**, 22%)
6: R = Ph (**a**, 75%)

The resulting compounds **4a**, **4b**, **5a-5g** and **6a** were characterized by ^1H, ^{13}C and ^{77}Se NMR and IR spectroscopy, and elemental analysis was performed.

Despite the fact that the use of the corresponding selenols makes it possible to obtain target products in high yields, their use is hampered by high volatility and toxicity. The most optimal approach is based on the use of diorganyl diselenides, which makes it possible to obtain target products in yields from 40 to 70%.

This work was supported by the Government Assignment for Scientific Research from the Ministry of Science and Higher Education of the Russian Federation
(agreement no. 075-03-2020-176/3; project code in Parus 8: FZZE-2020-0022)

Synthesis and antiviral activity of novel C_1-symmetric water-soluble fullerene derivatives with three types of aromatic addends

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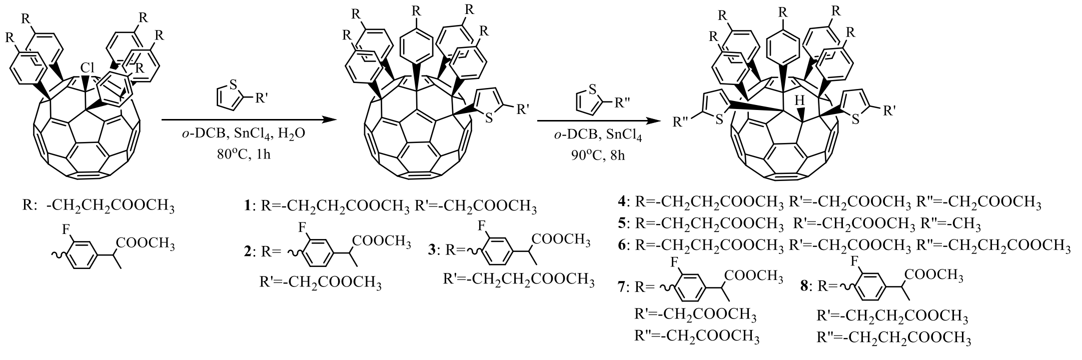
Fullerenes have found application in many areas of science and life, including medicine, due to their antiviral, antioxidant, neuroprotective, antitumor properties. However, they are not able to dissolve in water without prior functionalization. Currently, there are a lot of approaches of covalent functionalization of the fullerene cage, and one of the most effective among them is Friedel-Crafts arylation reaction of chlorofullerene C_s-$C_{60}Cl_6$ with aromatic esters or acids. One of the disadvantages of this method is the formation of C_s-$C_{60}Ar_5Cl$ fullerene derivatives with only one type of functional addends. In order to solve this problem, we have developed a new procedure for the regioselective preparation of fullerene derivatives with two types of aromatic addends [1]. The synthesis of individual fullerene derivatives with three different types of functional addends has remained an unsolved problem until recently.

As part of this work, we will discuss the reaction of addition of thiophene derivatives to the 5-6 double bond of compounds with the general formula C_s-$C_{60}Ar_5Th$, which leads to the formation of previously unknown fullerene derivatives C_1-$C_{60}Ar_5ThTh'H$ with three different types of addends. The composition and structure of all obtained compounds were confirmed using mass spectrometry and NMR spectroscopy. Hydrolysis of ester groups in the structure of compounds **1-8** allowed to obtain the corresponding carboxylic acids, and then potassium salts that were soluble in aqueous media. Several compounds have demonstrated pronounced antiviral activity against influenza virus A/Puerto Rico/8/34 (H1N1) and human immunodeficiency virus (HIV-1 NL4.3 and HIV-2 ROD).



This work was supported by the Russian Science Foundation (project № 19-13-00411-P)

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Three-component azo-coupling of indoles

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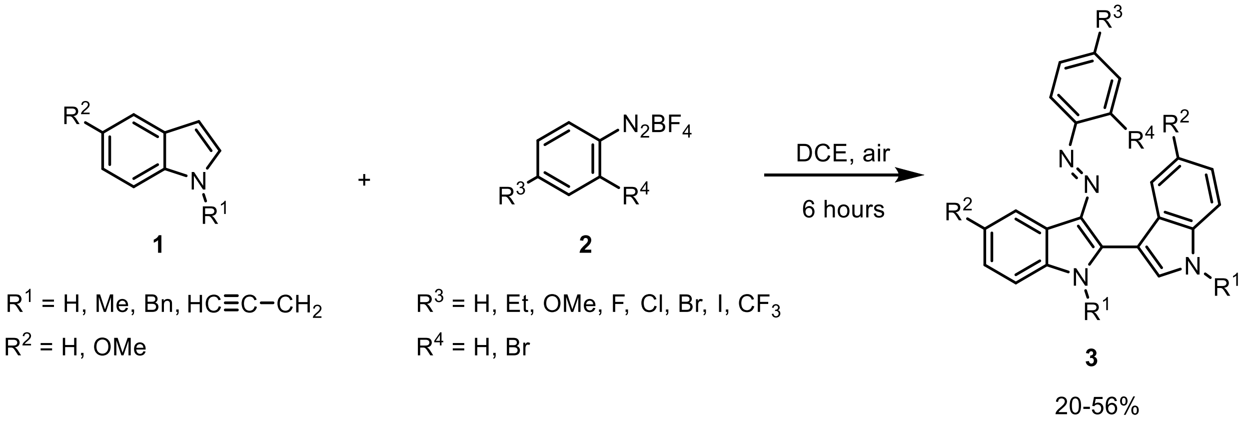
To date, the synthesis of molecular switches – compounds, capable of undergoing reversible isomerization under the influence of external stimulus, is rapidly developing field of research. Azo dyes are well-known class of photoswitches with numerous applications. Recently, heterocyclic azo compounds, especially indoles, have attracted much attention due to opportunity of fine-tuning the properties.[1]

Azo-coupling of indoles has been known for 40 years, but only recently optimal conditions for two-component reaction between indoles and *para*-substituted aryldiazonium salts have been reported [2]. However, we discovered a previously unknown reaction of indoles with aryldiazonium salts, proceeding as a three-component process.



R^1 = H, Me, Bn, HC≡C−CH_2
R^2 = H, OMe

R^3 = H, Et, OMe, F, Cl, Br, I, CF_3
R^4 = H, Br

This work was supported by the Russian Foundation for Basic Research (grant № 21-33-70007)

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Double ɣ-C(sp^3)–H functionalization of internal alkynes in reactions with 1,2-zwitterionic Ga complexes of DACs

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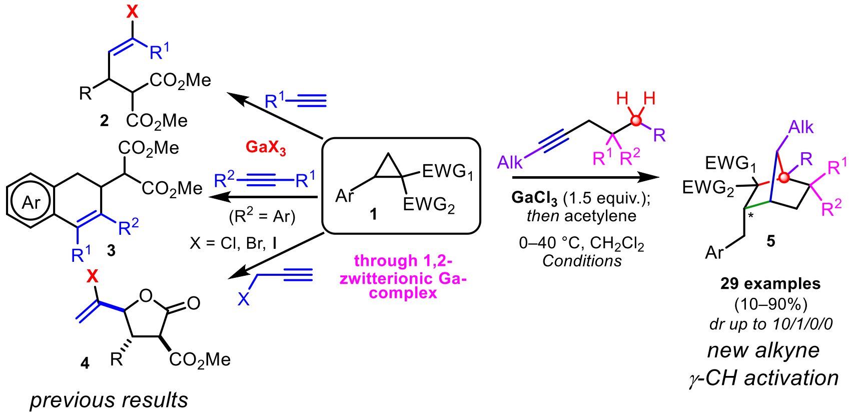
Donor-acceptor cyclopropanes **1** (DACs) are a broad class of substituted three-membered carbocycles. They are known for their capability to undergo small ring opening to act as 1,3-zwitterionic synthons. Our group developed a quiet different type of reactivity of DAC – the use of 2-arylcyclopropane-1,1-dicarboxylates (ACDC, **1**) as sources for generation of 1,2-zwitterions in the presence of $GaCl_3$ [1]. We carefully studied the interactions of DACs with acetylenes in the presence of $GaCl_3$ and developed the selective routes for the synthesis of compounds **2-4** in our previous works [2-4].

Herein we designed a new family of processes that allow one to perform an unprecedented double ɣ-C(sp^3)–H functionalization of inert aliphatic CH_2 groups in an alkyl chain to form a quaternary carbon stereocenter. Our methodology is based on the very rare concerted C–H insertion of vinyl carbocations into C(sp^3)–H bonds, with control by cooperative action of Ga(III) salts & $GaHal_4^-$ anions. The main synthetic implementation was made as a cascade of reactions of alkyl acetylenes with activated cyclopropanes to give the norbornane frame **5** with extensive scopes and good yields and diastereoselectivity.



It should be noted that the norbornane fragment is included in the structure of natural compounds, in particular, terpenoids [5]. It is also worth noting that norbornanes, especially those with alkyl tails, are promising as androgen receptor inhibitors and are steroid mimetics.

This work was supported by the Russian Science Foundation (grant № 22-13-00418)

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Evaluation of fucoidan extracts from *Ascophyllum nodosum* for further studies of its emulsifying properties

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Fucoidan is a term utilized for a class of sulfated, fucose-rich, polysaccharides found in the fibrillar cell walls and intercellular spaces of brown seaweeds (kelp) [1,2]. Consequently, the polysaccharide was named as "fucoidin" when it was first isolated from marine brown algae by Kylin in 1913 [3] but presently, it is named "fucoidan" as per IUPAC rules, yet it is also called fucan, fucosan, or sulfated fucan [4]. Fundamentally, the term fucoidan refers to various heparin-like polysaccharides, which contain significant level of L-fucose, sulfated ester groups, and another sugar including D-xylose, D-galactose, D-mannose, and glucuronic acid [1,2].

Although, the most accessible source of fucoidan in Russia is Ascophyllum nodosum which is predominantly cultivated in the White and Barents Seas. It is widely used in cosmetic preparations and as a food additive. One of the promising directions for the use of this algae is in the production of emulsifiers based on it.

This work is devoted to the relationship between the composition of the polysaccharide, the extraction method, and the emulsifying properties of the extract. Nevertheless, water extraction of fucoidan from *Ascophyllum nodosum* was carried out using various reagents (Citric acid, Acetic acid, Oxalic acid and NaOH), varying their concentration, temperature (80 °C and 100 °C) and extraction time. The resulting extracts were then purified by dialysis and evaporated to dryness. Analysis carried out on each sample included moisture content of extract, total solids, sulphate content, protein content, antioxidant activity, total phenolic content, fucose content. Nuclear magnetic resonance (NMR) analysis was used to determine the composition of sugars.

However, to determine the emulsifying properties, a series of emulsions were obtained using organic solvents (toluene, dichloromethane) as well as vegetable oils. Hence, very stable emulsions that did not separate for several weeks were obtained using samples of fucoidan with a concentration of up to 1.5 g/l. Thus, it was demonstrated that the stabilization of emulsions occurs due to the formation of submicron particles with sizes of 150−400 nm according to the principle of Pickering emulsions. Factors affecting the severity of the emulsifying properties of fucoidan have been identified.

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Synthesis of BKM-120 analogues: the core morpholine replacement strategy is efficient for future conjugation in the synthesis of PROTAC

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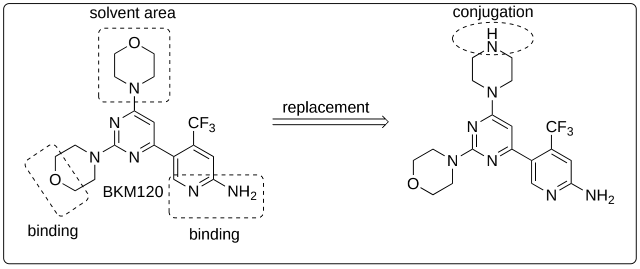
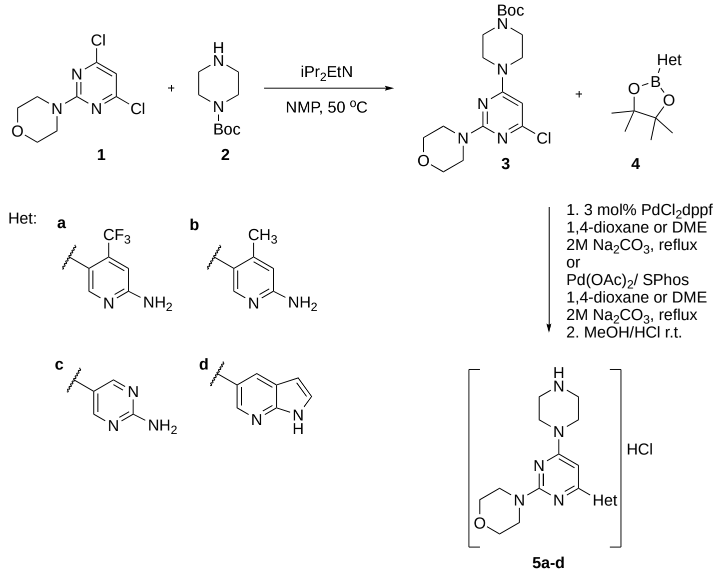
Phosphatidylinositol-3-kinases (PI3Ks) are a family of intracellular lipid kinases, that perform a number of crucial functions in the survival, proliferation, growth, differentiation, and migration of cells. Proteolysis-targeting chimeras (PROTACs) are heterobifunctional compounds, which consist of two recruiting ligands connected by a linker. One ligand binds specific to the protein of interest (POI), while the other one recruits an E3 ligase. By hijacking the E3 ligase around target protein, this strategy can selectively knock down the level of POI.

This work discusses the results of the synthesis of analogues of the pan-PI3K inhibitor BKM-120. It has been shown that the replacement of the morpholine core at position 4 of pyrimidine with a piperazine fragment leads to a slight loss of inhibitory activity (kinase activity and antiproliferative activity). The synthesized analogs **5a-d** can be easily conjugated with an E3 ligase-oriented warhead (CRBN or VHL). In the near future we are planning to synthesize PROTAC on their basis.





This work was supported by the Russian Science Foundation (grant № 22-23-00850)

Synthesis of 5,7-diaryl-6-nitroazolo[1,5-*a*]pyrimidines by the Povarov-type reaction and their potent bioactivity

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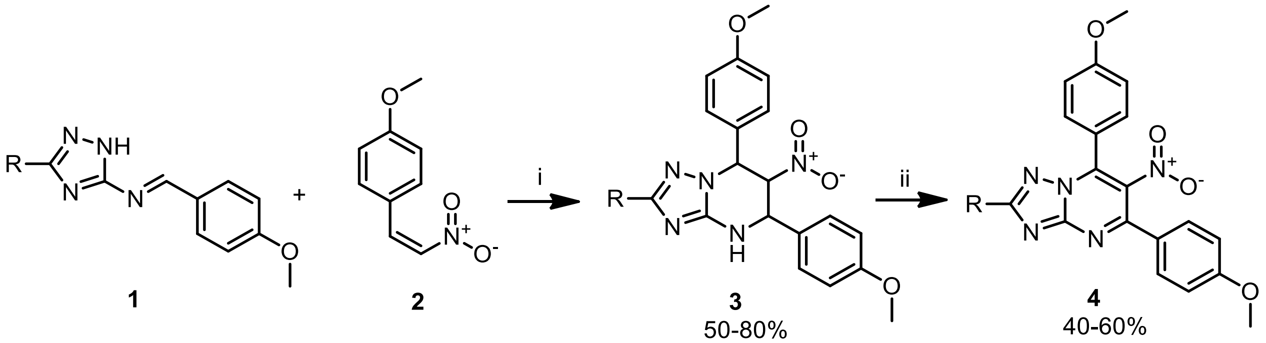
Azolo[1,5-a]pyrimidines are a well-known class of compounds many of which have proven to be effective antitumor, anti-inflammatory, and neuroprotective agents [1].

In this work, we have proposed a method for the preparation of 5,7-diaryl-6-nitroazolo[1,5-a]pyrimidines **4** based on a Povarov-type reaction [2] with *base catalysis* between 4-methoxy-beta-nitrostyrene **2** and substituted N-arylidene-1,2,4-triazoles **1** followed by oxidation formed 4,5,6,7-tetrahydro derivatives **3**.



R:
a) H, b) CH_3, c) CF_3, d) SMe, e) SEt, f) SPr, g) SBn,
h) thien-2-yl, i) furan-2-yl, j) pyridin-3-yl

Scheme 1 – Reagents and conditions: i) MeCN, TEA (1eq.), reflux, 3-10h; ii) MnO_2 (5 eq.), DMF, reflux, 30h

It should be noted that the highest yields were achieved using 1 equivalent of a triethylamine instead of the traditional boron trifluoride as a catalyst for Povarov-type reactions.

The search for biological targets for oxidized derivatives **4** using the SwissTargetPrediction service, depending on substituents in the azole cycle, shows potential activity against kinase targets of anticancer agents (CDK-family, FAK1), neuroprotective and sedative agents (GABA-A receptor subunits, Adenosine A_{2a} receptor, Dopamine D_2 receptor). Molecular docking studies also shows good affinity of **4f** and **4g** compounds to CDK2 and CK2.

In the near future, a study of the cytotoxic effect on cancer cell lines will be carried out for oxidized derivatives **4**, as well as a study of the reaction for obtaining their precursors **3**.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, State Contract no FEUZ-2020-0058 (H687.42B.223/20)

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N-arylidene-substituted 1,2,4-triazoles. Synthesis and in silico modeling of biological activity

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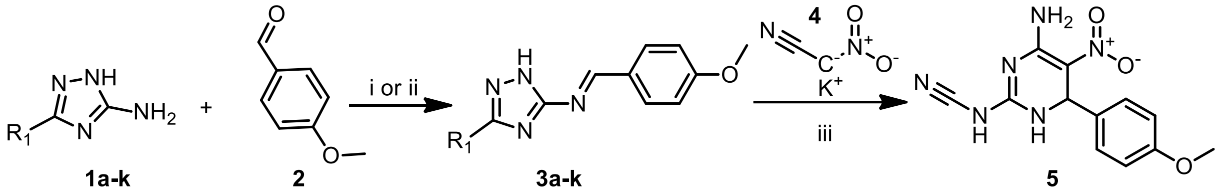
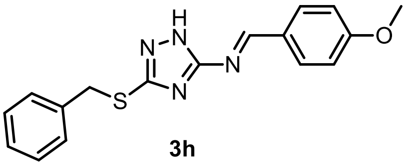
Currently, a few biologically active imines containing aryl and 1,2,4-triazole moieties are known. Using the molecular docking method, it was shown that compounds of this class may have high affinity both for CDK2 and CK2 proteins - targets of anticancer agents, and for viral endonuclease.

A number of the corresponding imines, including the most promising compounds after docking studies (**3h**), were obtained both by the well-known method [1] by heating aminoazoles and p-methoxybenzaldehyde in iPrOH, and by fusing reagents, which made it possible in some cases to increase the yields of target products **3**.



No	R_1	Yields, % i	Yields, % ii
1a	H	63	x
1b	Me	29	87
1c	CF_3	7	88
1d	SMe	65	67
1e	SEt	81	83
1f	SPr	23	50
1g	prop-2-yn-1-ylthio	72	52
1h	benzylthio	83	74
1i	furan-2-yl	22	51
1j	thien-2-yl	63	35
1k	pyridin-3-yl	70	84



3h

$\Delta G_{endoH1N1}$(4ZI0) = -11,73 kcal/mol
ΔG_{CDK2}(3WBL) = -11,09 kcal/mol
ΔG_{CK2}(3H30) = -11,97 kcal/mol

Scheme 1 – Reagents and conditions for imines obtaining and their reactivity:
i) iPrOH, reflux, 2-10h; ii) solvent free, 150 °C, 3h; iii) Pyridine, reflux, 5h

During the study of reactivity, it was found that in the reaction between imines and a nucleophile, the potassium salt of nitroacetonitrile [2], dihydropyridine compound 5 is formed, instead of the expected 7-amino-5-aryl-6-nitro[1,2,4]triazolo[1,5-a]pyrimidine derivatives.

In the near future, a more detailed study of the reactivity of imines 3 with nucleophiles is planned, as well as a study of the cytotoxic effect on cancer cell lines.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, State Contract no FEUZ-2020-0058 (H687.42B.223/20)

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Synthesis of novel purine conjugates with 6-substituted 3,4-dihydro-3-methyl-4-(6-aminohexanoyl)-2*H*-[1,4]benzoxazines

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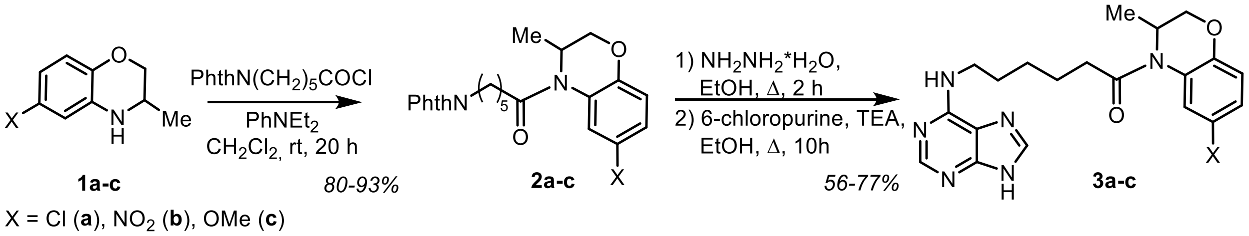
The most urgent task of organic synthesis is the development of methods for obtaining new bioactive compounds as the basis for drug design. One of the ways to solve this problem is the chemical modification of analogues of natural compounds, in particular, purine.

Previously, we have developed the methods for the synthesis of purine conjugates with heterocyclic amines, among which 7,8-difluoro-3,4-dihydro-3-methyl-4-[6-(purin-6-ylamino)hexanoyl]-2*H*-[1,4]benzoxazine has been identified as the lead compound with high anti-herpesvirus activity [1].

In this work, we synthesized new conjugates of purine with 6-substituted benzoxazines linked via a 6-aminohexanoyl fragment and studied their anti-herpesvirus activity.



At the first step, 6-substituted benzoxazines **1a-c** were acylated with 6-phthalimidohexanoyl chloride in dichloromethane in the presence of $PhNEt_2$ to afford phthalimido derivatives **2a-c**. Hydrazinolysis of compounds **2a-c** in refluxing ethanol led to the removal of the *N*-phthaloyl group and the formation of the corresponding amines, the subsequent reaction of which with 6-chloropurine led to the target conjugates **3a-c** in good yields.

The antiviral activity of the synthesized compounds **3a-c** was studied against the reference strain of herpes simplex virus type 1 (HSV-1) and the acyclovir-resistant strain HSV-1/L2/R in the Vero E6 cells. It has been shown that nitro derivative **3b** exhibits the highest anti-herpesvirus activity ($IC_{50} = 2.3$ μM) among the studied compounds.

The work was financially supported by the Russian Science Foundation (grant 19-13-00231-P)

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Syntheses based on substituted 2-benzyl-4-hydrazinopyrimidines

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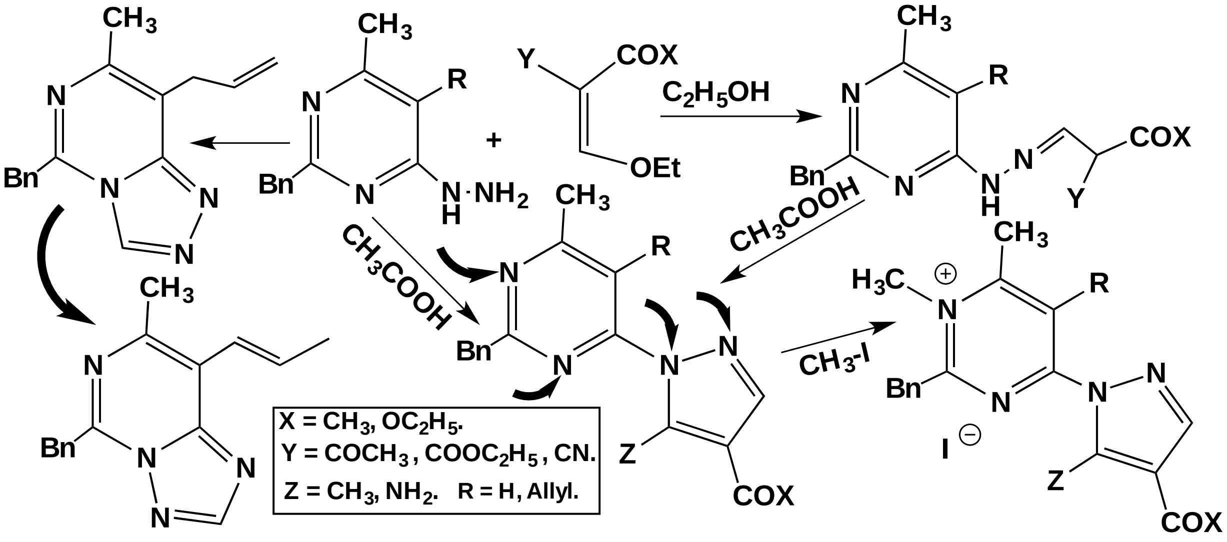
It is known that unannelated pyrazolylpyrimidines are good ligands that easily form metal complexes. The latter have luminescent properties and have found practical application. By reactions of ethoxymethylidene derivatives of acetoacetic and cyanoacetic esters, as well as acetylacetone, we synthesized new 4-(1*H*-pyrazol-1-yl)pyrimidines. It is shown that the condensation begins with the attack of the ethoxymethylidene fragment of the reagent at the terminal amine group and leads to the formation of a pyrazole ring.

The alkylation of the synthesized systems has been studied. NOESY NMR ^{1}H spectroscopy proved the regioselectivity of methylation. It has been shown that alkylation occurs at the N-3 nitrogen atom of the pyrimidine ring.

Based on 4-hydrazinopyrimidines, fused pyrimidines containing an azole ring have also been synthesized.



This work was carried out with the financial support of the State Committee on Science of the Republic of Armenia and the Russian Foundation for Basic Research (project 20RF-138 / 20-53-05010 Arm_a /), as well as within the framework of the grant of the Ministry of Education and Science of the Russian Federation for scientific research of the Russian-Armenian University

The c–c coupling of [1,2,5]oxadiazolo[3,4-b]pyrazines with imidazo[1,2-a]pyridines

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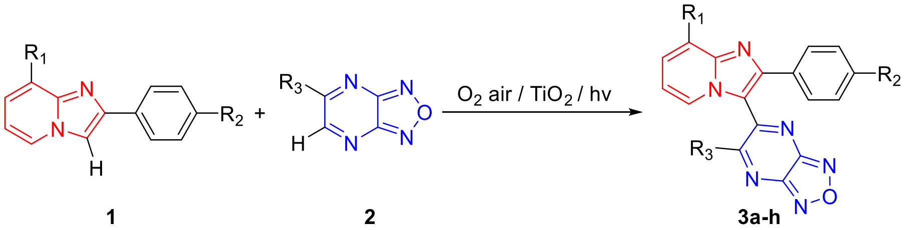
Interest in the synthesis of imidazo[1,2-*a*]pyridine derivatives is due to their broad biological activity and optical properties. Compounds containing an imidazo[1,2-*a*]pyridine scaffold have shown good anticancer [1], antiulcer [2], antiviral [3] and antibacterial [4] properties. In addition, imidazo[1,2-*a*]pyridine derivatives are used as fluorescent probes, for example, to detect sulfur dioxide in the cells of organisms [5], and luminescent sensors to monitor the kinetics of cationic photopolymerisation of monomers [6].

We carried out the direct C–C coupling of 5-substituted [1,2,5]oxadiazolo[3,4-*b*]pyrazines **1** with imidazo[1,2-*a*]pyridines **2** under aerobic oxidation conditions using nanocrystalline TiO_2 as a photocatalyst and UV irradiation. The reaction mixture was stirred at reflux in acetic acid for 6 h.



1 **2** **3a-h**

3a: R_1 = H; R_2 = H; R_3 = Ph
3b: R_1 = H; R_2 = H; R_3 = thiophene
3c: R_1 = H; R_2 = H; R_3 = p-nitrobenzene
3d: R_1 = H; R_2 = F; R_3 = Ph
3e: R_1 = CH_3; R_2 = H; R_3 = Ph
3f: R_1= CH_3; R_2 = H; R_3 = thiophene
3j: R_1 = CH_3; R_2 = H; R_3 = p-nitrobenzene
3h: R_1 = Br; R_2 = H; R_3 = thiophene

As a result, previously unknown imidazo[1,2-*a*]pyridine derivatives **3a–h** were obtained. The synthesized compounds are promising objects for studies of biological activity.

This work was supported by the Russian Science Foundation (grant № 22-13-00298)

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1,2,4-Oxadiazole-based arylidenesulfonamides as potential carbonic anhydrase inhibitors: synthesis in the superbasic *t*-BuONa/DMAA medium

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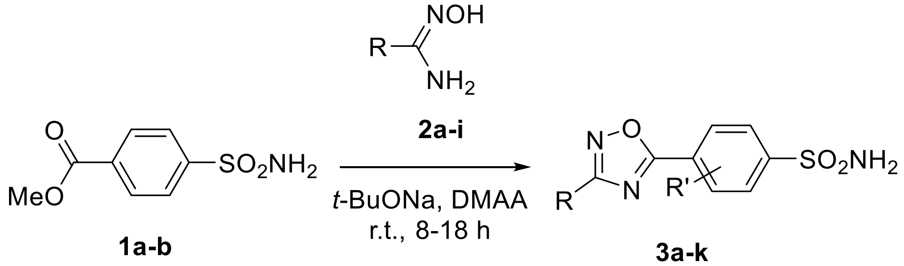
Our previous studies have shown that 1,2,4-oxadiazoles containing a primary sulfonamide fragment can act as selective inhibitors of human carbonic anhydrase (hCA) I, II, IX, XII isoforms, which allows us to consider them as drug candidates for the treatment of cancer and glaucoma [1].

The previously developed method for the synthesis of target 1,2,4-oxadiazoles, which involves the reaction in the superbasic NaOH / DMSO medium, has a number of disadvantages [2]. The improved synthesis technique includes the interaction of amidoximes with carboxylic acid esters in the *t*-BuONa / DMAA medium. The advantages of this method are the ability to carry out the reaction over a wide temperature range (by replacing the solvent from DMSO with DMAA), as well as the absence of side hydrolysis processes for sensitive substrates. The series of 3,5-disubstituted-1,2,4-oxadiazoles synthesized in good yields (35-89%) is interesting for medicinal chemistry and can be useful as antiglaucoma and anticancer agents by inhibiting the enzyme hCA I, II, IX, XII isoforms. It is planned to study the biological properties of the synthesized compounds on cellular and animal models of glaucoma.



3a: R = 2-ClPh, R' = 2-OMe, 60%; **3b**: R = 3-$C_2H_5C(O)NH$-Ph, R' = 2-OMe, 65%; **3c**: R = iPr, R' = 2-OMe, 35%; **3d**: R = Ph, R' = 2-OMe, 75%; **3e**: R = 2-thiophene, R' = 2-OMe, 73%; **3f**: R = 5-Me-2-thiophene, R' = 2-OMe, 68%; **3g**: R = 4-OMe-Ph, R' = H, 82%; **3h**: 3-$C_2H_5C(O)NH$-Ph, R' = H, 74%; **3i**: R = 2-Py, 2-OMe, 64%; **3j**: R = 2-tolyl, 2-OMe, 84%; **3k**: 4-OMe-Ph, R' = 2-OMe, 89%.

This research was supported by the Ministry of Education of the Russian Federation (government contract 073-00077-21-02 "Development of an innovative glaucoma drug based on selective inhibition of carbonic anhydrase II", registry number 730000Ф.99.1.БВ10АА00006)

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Synthesis of 1,2,4-triazol-5-yl derivatives of D-secoestrone from 13α-hydroxy-3-methoxy-13,17-secoestra-1,3,5(10)-trien-17-oic acid hydrazide

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In a continuation of our research on the synthesis of semi-synthetic steroids and evaluation of their antitumor activity, we focused on the derivatives of D-secosteroids to obtain new classes of promising anticancer agents. Recently, we have developed the simple and convenient regioselective method for the synthesis of 17a-oxa-17a-homoestra-1,3,5(10)-trien-17-ones in gram quantities by lactonization of estrone derivatives with H_2O_2/BF_3 [1]. This finding allows us to design an approach to novel derivatives of secosteroids to explore the structure-activity relationships potentially arising from ring D opening by hydrazines and subsequent modification of hydrazide moiety [2].

Now we report the two-stage (**A**) and one-pot (**B**) cyclization of 13α-hydroxy-3-methoxy-13,17-secoestra-1,3,5(10)-trien-17-oic acid hydrazide **1** into 2,4-dihydro-3*H*-1,2,4-triazole-3-thiones **3** with D-secosteroidal fragment in 5 position of 1,2,4-triazole:

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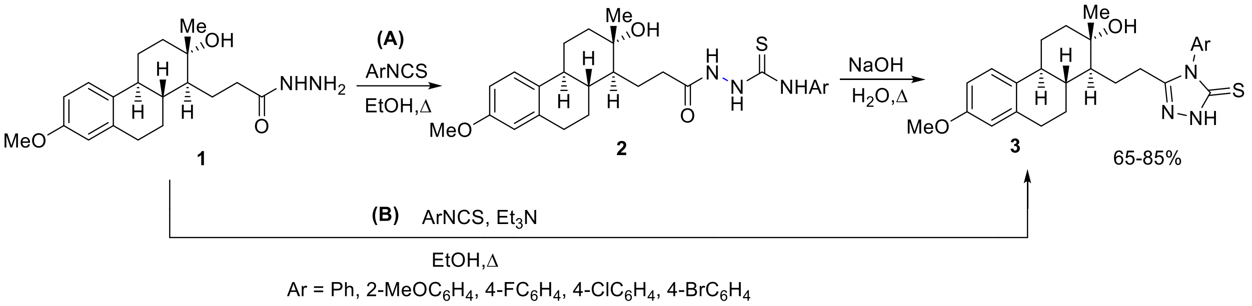

The obtained 1,2,4-triazol-3-thiones **3** and intermediate carbothiaamides **2** were evaluated for their cytotoxicity against the MCF-7 breast cancer cell line and show significant cytotoxic effect comparable to that for reference drug cisplatin.

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Synthetic strategy toward photoactive heterostyrenes on furan- and benzofuran-based matrices

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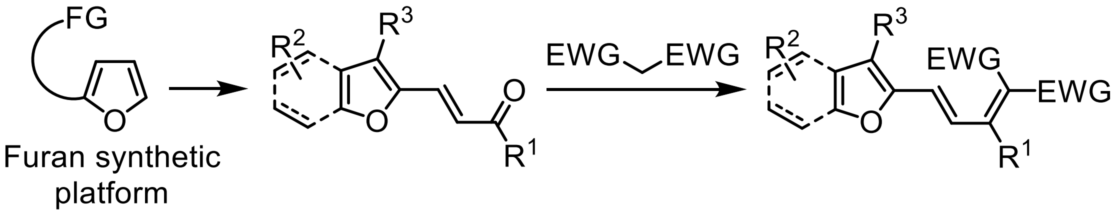
Push-pull chromophores belong to the class of functional molecules that are actively exploited as components in dye-sensitized solar cells.

In our ongoing research project aiming at developing straightforward synthetic protocols toward potential push-pull chromophores based on the heterocyclic products obtained via dearomatization of accessible furan platform molecules we engage an alkanone fragment into oxidation/condensation transformation sequence in order to get a set of compounds with high molar extinction coefficients.



Synthetic details as well as physicochemical, optical, and electrochemical properties of the obtained products will be discussed.

This work was supported by Russian Science Foundation (project 22-23-00505)

Dimerization of stagonolide A by the new type of Baylis–Hillman reaction

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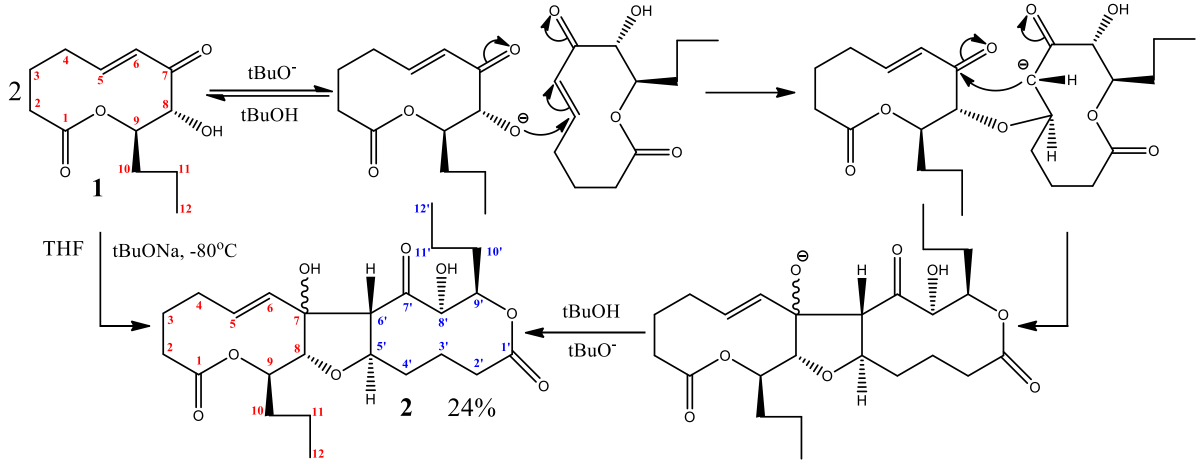
Toxic secondary metabolites of phytopathogenic microorganisms are promising candidates for development of biorational pesticides. Among such compounds 10-membered lactones (nonenolides) represent significant potential as models for the development of pesticides with mechanisms of action different from widely used agrochemicals. Stagonolide A (**1**) produced by *S.cirsii* S-47 is a member of this large family and has a relatively simple structure, but at the same time has a wide spectrum of non-selective biological activity [1]. For that reason, compound **1** could be considered as a mycotoxin. Yet its chemical properties remain unexplored. Our recent study showed that conjugation of keto group and carbon-carbon double bound is responsible for non-target toxicity. Our attempt to break the conjugation therefore to swap functional groups at positions C7 and C8 by α-ketol rearrangement led to the unexpected product **2**.



The synthesis was carried out using a fourfold excess of sodium tert-butoxide in a dry THF solution at a reduced temperature. Based on chromatographic and spectral data, it was found that compound 2 was formed in 24% yield as the only reaction product.

The proposed reaction mechanism is similar to the Baylis-Hillman reaction. In contrast to the typical course of the reaction it is the OH group at C8 that gives rise to a nucleophilic addition to a second molecule of the lactone **1** followed by intramolecular entrapment of the enolate at the C7 position. This process does not regenerate the initial enone so it keeps the furan moiety.

A broad assessment of the biological activity of compound **2** exhibits selective cytotoxic activity on Sf9 insect cells with IC_{50} at a concentration 75 μg/ml.

This work was supported by the Russian Foundation for Basic Research
(grant № 22-16-00038)

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Synthesis of *β*-carbolines from tryptamines, furyl- and thienylacroleins and maleic anhydride

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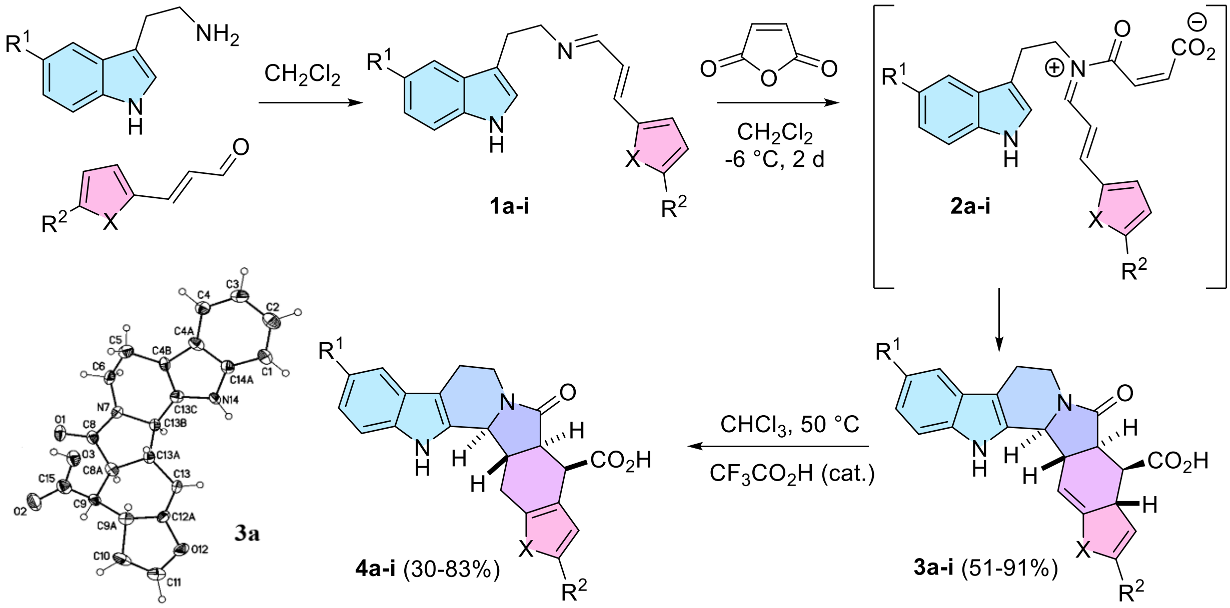
The Pictet-Spengler reaction is one of the methods for obtaining a *β*-carboline core, while the IMDAV reaction can be used to form an isoindole fragment [1]. We assumed that it would be possible to synthesize a *β*-carboline core condensed with an isoindole fragment by combining the special reaction centers in one molecule. In a series of experiments, we have shown that after the addition of maleic anhydride to imines **1** a precipitate of adducts **3** with a non-aromatic five-membered ring is formed. Adducts **3** turn into aromatic products **4** by heating in chloroform at 50 °C.



	R¹	R²	X	Yield **3**, %[1]	Yield **4**, %[2]
a	H	H	O	64	74
b	Me	H	O	66	65
c	MeO	H	O	83	60
d	F	H	O	67	82
e	H	Me	O	30	81
f	MeO	Me	O	62	93
g	H	H	S	70	51[1]
h	MeO	H	S	64	77
i	Me	H	S	36	91

[1] after recrystallization

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Amino derivatives of quinoline and isoquinoline in fluorescent detection of metal cations and chiral molecules

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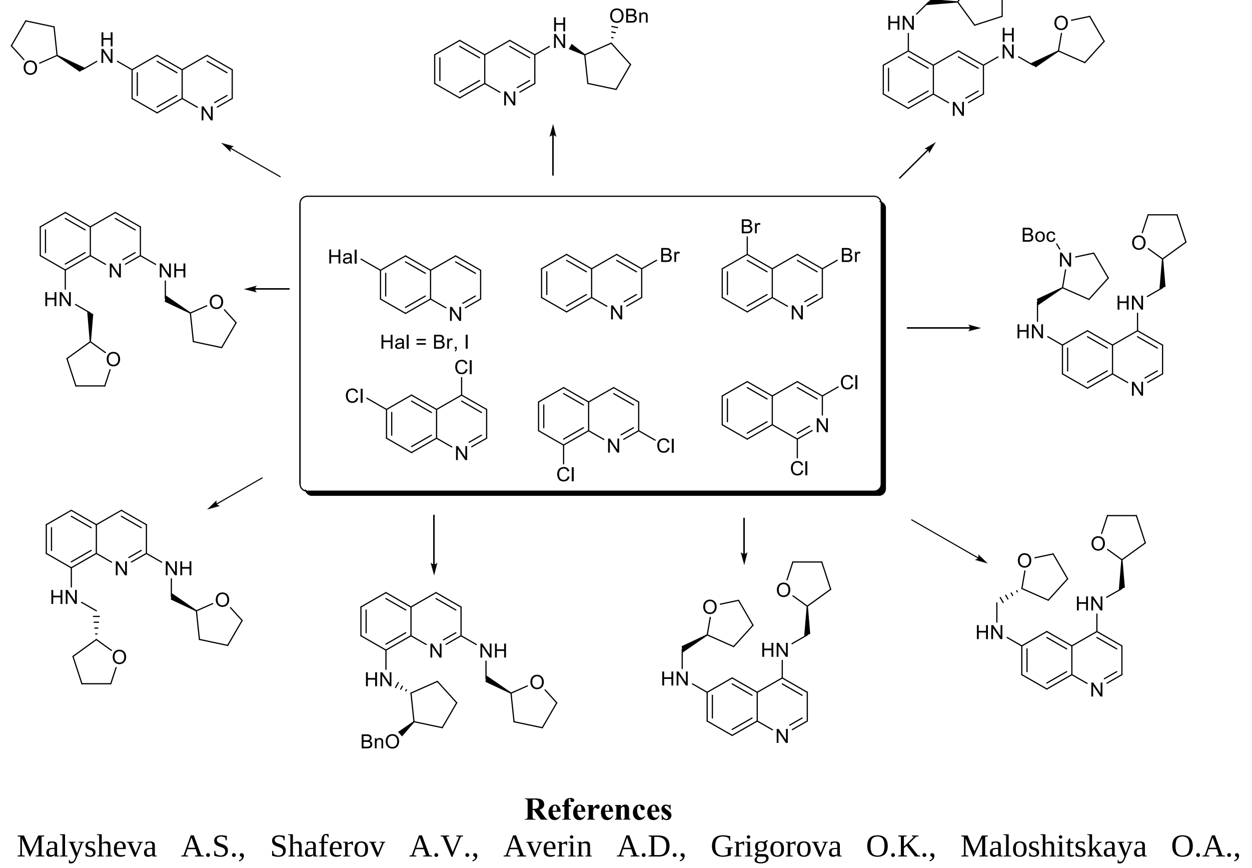
The development of the chemistry of fluorescent detectors is important for a quick search for efficient, selective and enough simple compounds able to recognize metal cations, and in the case of the presence of chiral elements ion their structure, to serve as enantioselective detectors of chiral organic analytes. Previously, we have shown that the derivatives of 3,3'-disubstittued biphenyl and 2,7-disubstituted naphthalene can act as fluorescent enantioselective sensors, however, their efficiency was found to be quite moderate [1]. In the present investigation, we have synthesized a series of quinoline derivatives possessing chiral substituents at various positions of the heteroaromatic structure. Thus, the compounds under investigation differ by the number and nature of such chiral N-containing groups, their reciprocal position and arrangement in the heteroaromatic system. The synthesis was mainly carried out using metal-catalyzed rections of halogenosubstituted quinolines with chiral amines. E.g., the substitution at positions 3 and 6 can be achieved using Cu-catalyzed reactions (in both homogeneous and heterogeneous versions), while the substitution at positions 5 and 8 demands application of catalysis by Pd(0). On the other hand, Cl can be easily substituted under catalyst-free conditions at position 2 of quinoline and at position 1 of isoquinoline. The spectral studies of thus substituted quinolines in the prersence of metal cataions and model chiral amino alcohols demonstrate strong dependence of their sensing abilities on the structure.



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A series of trifluoromethylpyrazolyl-substituted (hetero)aromatic sulfonamide carbonic anhydrase inhibitors: synthesis and convenient prioritization workflow for further in vivo studies

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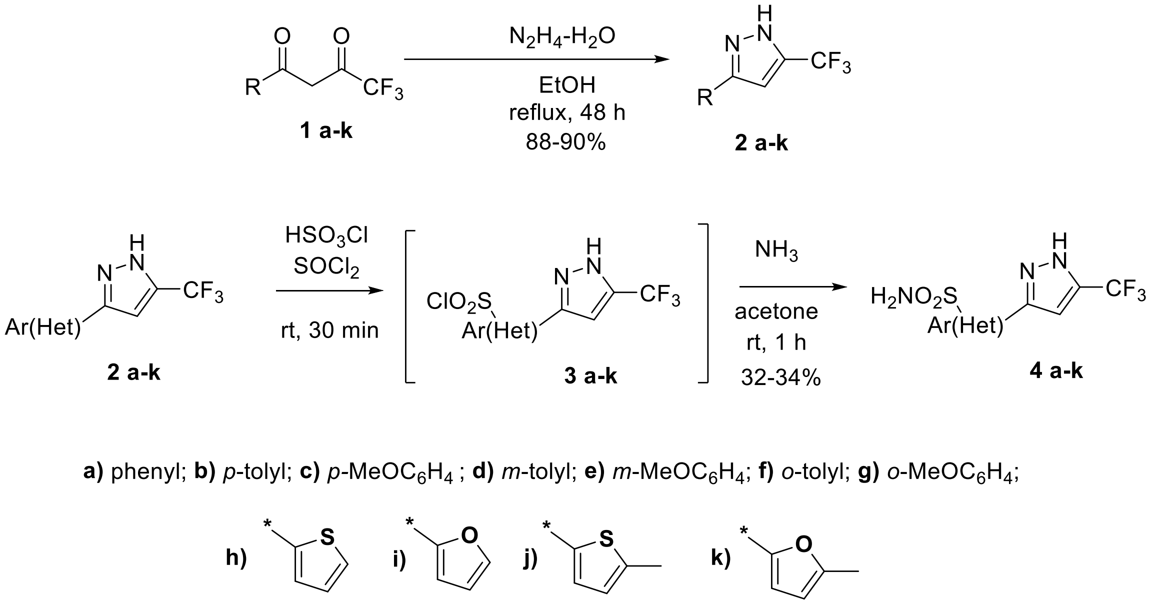
Carbonic anhydrase (CA) inhibitors gain significant attention in the context of drug discovery research for glaucoma, hypoxic malignancies and bacterial infections[1]. In previous works [2], we have successfully used direct sulfochlorination approach to develop diverse heterocyclic primary sulfonamides with remarkable activity and selectivity against therapeutically relevant CA isoforms. Herein we report a synthesis and investigation of the CA inhibitory properties of novel trifluoromethylpyrazolyl substituted (hetero)aromatic sulfonamides. The obtained compounds were evaluated for their potential to block the catalytic activity of CA II which is a popular target for the development of new glaucoma treatments.



a) phenyl; **b)** *p*-tolyl; **c)** *p*-$MeOC_6H_4$; **d)** *m*-tolyl; **e)** *m*-$MeOC_6H_4$; **f)** *o*-tolyl; **g)** *o*-$MeOC_6H_4$;

Compounds based on the pyrazole core showed significant inhibition of the esterase activity of *b*CA II. Inhibitors capable of blocking the esterase activity of *b*CA by 90% or more were selected for further characterization.

This research was supported by the Ministry of Education of the Russian Federation (government contract 073-00077-21-02 "Development of an innovative glaucoma drug based on selective inhibition of carbonic anhydrase II", registry number 730000Ф.99.1.БВ10АА00006)

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Synthesis and biological evaluation of novel diarylmethylphosphonates derivatives containing sterically hindered phenols and urea moieties as potential anticancer agents

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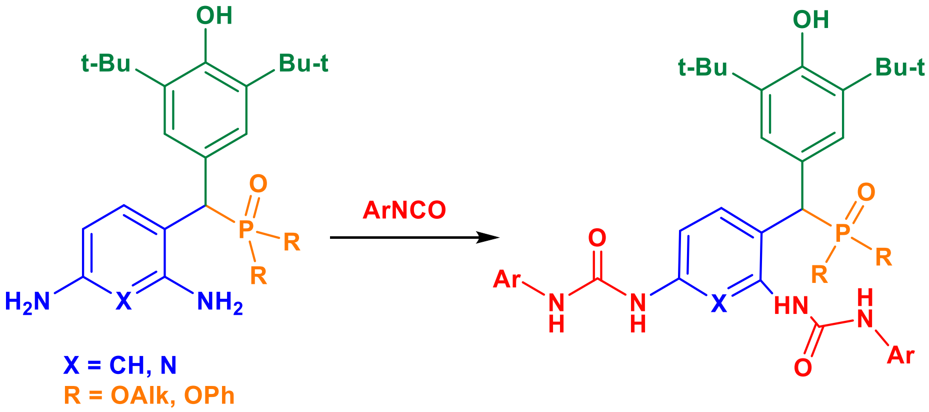
Urea derivatives, especially bis-aryl ureas, have a central role in medicinal chemistry and drug development due to their ability to form stable hydrogen bonds with proteins and target receptors.

In recent years, evidence has accumulated in favor of the hypothesis suggesting that during the growth of tumors and a number of other diseases, there is an excessive formation of reactive oxygen species, which leads to damage to DNA and other biomolecules. With this in mind, sterically hindered phenols (SHP) can be considered as effective tools for the treatment and prevention of tumor diseases. Therefore, it is quite expected that the molecular systems of this class of compounds, which have different functional groups can be considered as new anticancer drugs. Previously developed by our research group the synthesis of new diarylmethylphosphonates containing SHP fragment and terminal amino groups opens up wide possibilities for additional modifications.

In this study, we designed and synthesized urea derivatives by the reaction the primary amino groups of derivatives diarylmethylphosphonates with aryl isocyanates containing electron-donating and electron-withdrawing substituents. As a result, a series of novel urea derivatives was obtained in 50-90% yields.



The biological activity of the obtained compounds was studied, among them the lead-compounds with antioxidant, antitumor activity and low toxicity were found.

The research was supported by the Ministry of Science and Higher Education of the Russian Federation at FRC Kazan Scientific Center (grant No. 075-15-2022-1128)

Synthesis and optical properties of dyes based on 4-(4-oxothiazolidine-2-ylidene)pyrrolidine-2,3,5-trione

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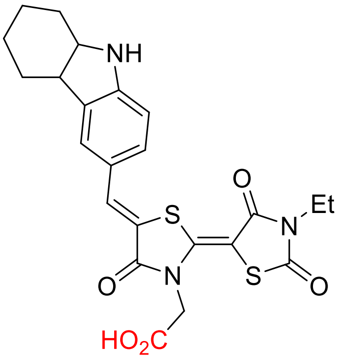
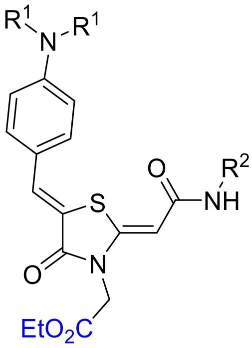
Interest in 1,3-thiazolidine derivatives is due to a wide range of their biological activity, as well as electrochemical and photophysical properties. In recent years, the synthesis of heterocyclic assemblies in which the 1,3-thiazolidine ring is connected by a double C=C bond with another heterocyclic ring has been actively developed. Dyes with a bisrhodonine fragment in their structure received the greatest interest. For example, the dye **ZMB741** is used for *in vivo* fluorescent imaging of blood-brain barrier disruption in animal models [1].

The aim of this work was to develop dyes containing a structural analogue of the bisrhodonin fragment, thiazolidine-4-trioxopyrrolidine, as an electron-withdrawing group. We have developed a method for the synthesis of starting 5-benzylidene-4-oxothiazolidines **1** and target 4-(4-oxothiazolidine-2-ylidene)pyrrolidine-2,3,5-triones containing donor 5-benzylidene groups **2**,**3**.



ZMB741



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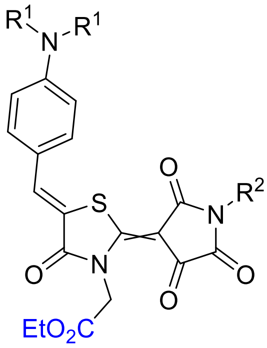

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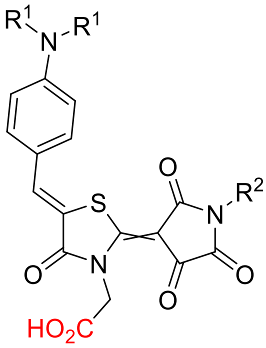

3

Data	Compound 1	Compound 2	Compound 3
Substitutes R^1, R^2	R^1 = Me; R^2 = Oct	R^1 = Me; R^2 = Oct	R^1 = Me; R^2 = Oct
λ_{max}, nm (lg ε)	424 (4,620)	357 (4,307); 519 (4,652)	357 (4,433); 518 (4,666)
Substitutes R^1, R^2	R^1 = Ph; R^2 = Oct	R^1 = Ph; R^2 = Oct	R^1 = Ph; R^2 = Oct
λ_{max}, nm (lg ε)	426 (4,687)	362 (4,281); 509 (4,618)	360 (4,464); 511 (4,648)
Substitutes R^1, R^2	R^1 = Ph; R^2 = Bn	R^1 = Ph; R^2 = Bn	R^1 = Ph; R^2 = Bn
λ_{max}, nm (lg ε)	428 (4,567)	357 (4,350); 522 (4,714)	357 (4,431); 521 (4,794)

In the electronic spectra of bicyclic derivatives **2** and **3**, an absorption band is observed in the region of 509–522 nm, which was absent in monocyclic derivatives **1**. In this work, optimization of the method for the synthesis of compounds **2** and **3**, their structural features, and also their optical properties will be discussed.

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University Program of Development within the Priority-2030 Program) is gratefully acknowledged

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Synthesis of p-Nitrotetrazolium Violet

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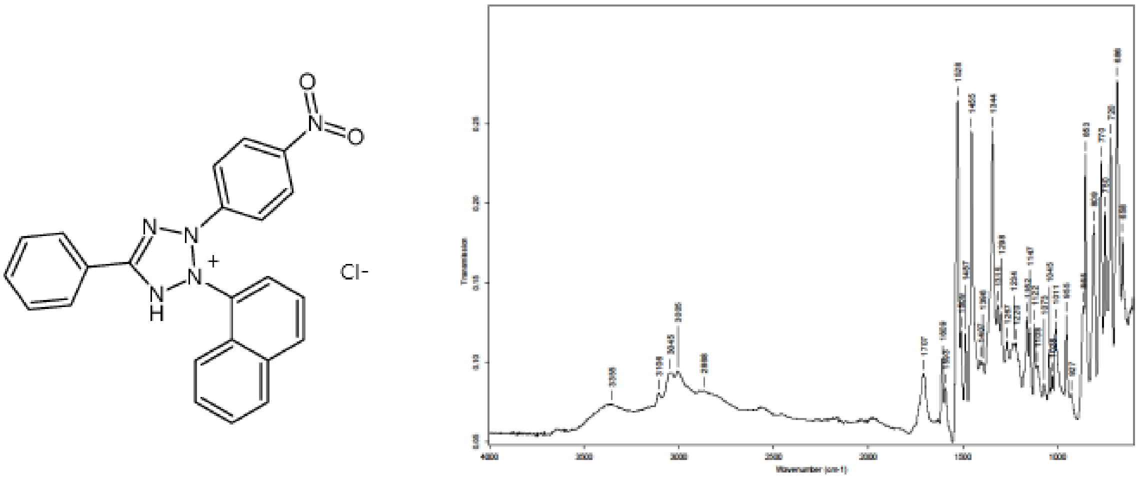
Among the latest developments in modern medical science, one of the most significant places is occupied by the emergence of a field called mitochondrial medicine [1]. One of the main achievements of medical mitochondriology was the creation of effective diagnostic tools to assess polysystem disorders of cellular energy exchange [2],

It is known that multidentate formazanes are effective reagents for the photometric analysis of a number of metals, but, as it was found, their tetrazolium salts proved promising for the express study of objects of medical clinical diagnostics. The p-nitrotetrazolium violet synthesized by us showed high activity when used in diagnostic kits for the determination of intracellular enzymes by the method of Prof. R.P.Narcissov.



Structural formula and IR spectrum of p-nitrotetrazolium violet

Analytical research was done using equipment of NRC "Kurchatov Institute" — IREA Shared Knowledge Center under project's financial support by the Russian Federation, represented by The Ministry of Science and Higher Education of the Russian Federation, Agreement No. 075-11-2021-070 dd. 19.08.2021.

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Domino reactions of 2-imidazolines and electron-deficient alkynes

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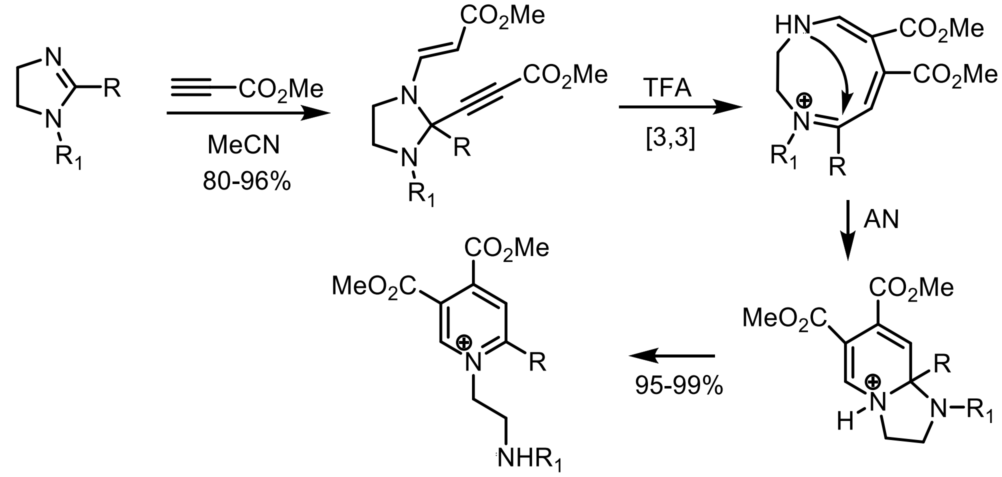
Pyridinium salts containing various functional groups both on the pyridine ring and on the nitrogen atom are fairly well-known chemical structures and have been used in various industries and in everyday life for quite a long time. If initially they were considered only as bactericides, later pyridinium salts were found in many natural substances and began to be used as part of bioactive pharmaceuticals.

This work discloses our latest results concerning the pseudo three-component reaction of cyclic amidines and electron-deficient terminal alkynes with the formation of tetrasubstituted imidazolidines capable of undergoing further transformations [1,2]. As convenient starting compounds, we consider 1,2-disubstituted 2-imidazolines, which are readily available due to recently discovered preparative synthesis methods.



The resulting adducts contain in their structure an amino ester fragment, a cyclic amine fragment and an electron-deficient triple bond; such a concentrated set of reaction centers makes it possible to rely on a high synthetic potential of these compounds. This may be of interest both for studying the mechanism of ongoing reactions and for synthesis aimed at expanding molecular diversity. It turned out that in the presence of protic acids, the adducts can undergo a [3,3]-sigmatropic rearrangement with the formation of a 9-membered cyclic allene followed by a nucleophilic attack and opening of the imidazopyridine system.

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Synthesis of azole-fused anthraquinone derivatives

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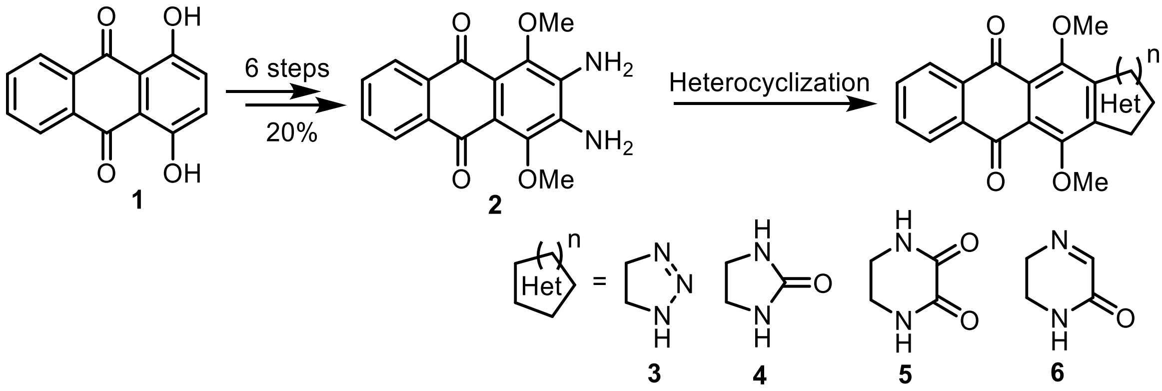
Heteroaren-fused anthraquinone derivatives inhibit the growth of tumor cells and are able to act on various intracellular targets, including topoisomerases 1, 2, deacetylase Sirt1, duplex and quadruplexes of DNA [1,2]. Aza-heterocyclic fragments can be found in many natural products and drugs. This stimulated us to annelate such heterocyclic motif to anthraquinone derivatives for further evaluation of biological properties.

Initially, we developed a new scheme for the synthesis of 2,3-diamino-1,4-dimethoxyanthraquinone (**2**) in 6 steps with a total yield of 20% from commercially available quinizarine **1**. Diamine **2** was used for further heterocyclization resulted in various five- and six-membered heteroarene-fused anthraquinone derivatives **3-6**.

Structures of all new compounds have been proven by NMR and HRMS spectra. Chemical modification of obtained derivatives and synthesis of other aza-heterocyclic anthraquinone derivatives are underway.



This study was funded by the grants Council of the President of the Russian Federation for State support to young scientists of Russia (grant MK-222.2021.1.3)

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Multicomponent approach to the synthesis of bicyclic azaheterocycles

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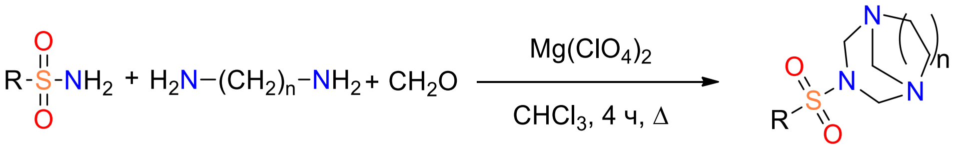
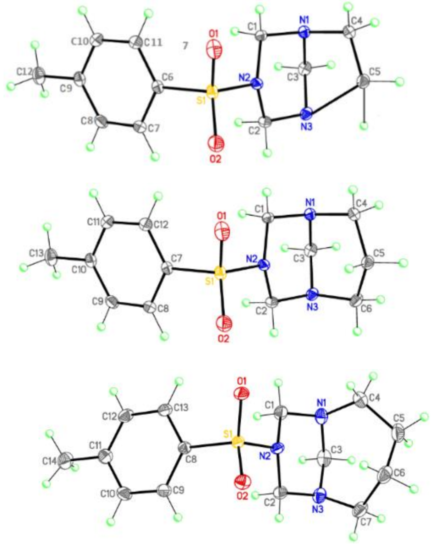
Nitrogen-containing frameworks are promising structural units for the design of various compounds. Such motifs can be discovered in the composition of biologically active natural alkaloids, substances for the agrochemical industry, as well as pharmaceuticals. Therefore, many synthetic approaches have been already developed for the synthesis of such compounds. Despite this the development of effective and conceptually new universal methods for obtaining a variety of nitrogen-containing molecules from easily accessible starting materials, including using a multicomponent approach, remains an urgent task of modern synthetic organic chemistry.[1,2]
In this work we proposed a new available and affordable method for the synthesis of substituted azaheterocyclic compounds with good yields based on a multicomponent approach:



R	n = 2	n = 3	n = 4
	Yield	Yield	Yield
Phenyl	57%	55%	49%
4-CH$_3$-C$_6$H$_4$	78%	66%	72%
4-F-C$_6$H$_4$	43%	60%	62%
4-I-C$_6$H$_4$	38%	56%	54%
4-CH$_3$O-C$_6$H$_4$	53%	44%	43%
4-NO$_2$-C$_6$H$_4$	65%	61%	72%
4-Cl-3-CF$_3$-C$_6$H$_4$	31%	34%	35%
Naphtyl	55%	50%	48%



Also in this work we have established that the best catalyst for the synthesis of such azaheterocycles is Mg(ClO$_4$)$_2$. Besides, we estimate that this approach will found wide application for the construction of various nitrogen-containing compounds and, what is more, these azaheterocycles could be use in organic synthesis, for example as stable and readily available formaldimines precursors [3].

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Synthesis of new enantiopure amino acids with a 3-spiropyrrolidine oxindole core via a selective three-component 1,3-dipolar addition

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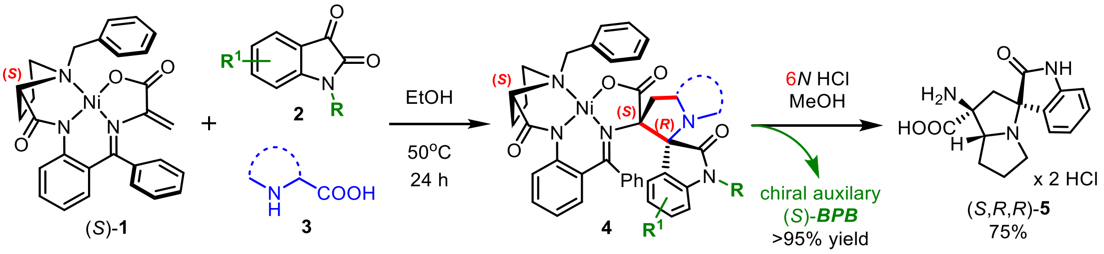
Chiral unnatural amino acids (AAs) are important intermediates in pharmaceutical industry and biochemistry. [1] Among them, AAs featuring heterocyclic cores have a considerable interest, [2] in particular, a 3-spiropyrrolidine oxindole skeletal is presented in various biologically active compounds with pronounced therapeutic properties. [3]



We recently developed a useful protocol for the asymmetric synthesis of artificial AAs comprising a 3-spiropyrrolidine oxindole skeletal with continuous tetrasubstituted carbon stereocenters by a 1,3-dipolar cycloaddition reaction of in situ generated azomethine ylides with a chiral dehydroalanine Ni(II) complex **1**. [4] A three-component reaction of the Ni(II) complex with various isatins **2** and AAs **3** in ethanol provided a series of diastereomeric complexes **4** with high *dr* (>20:1) in 40–86% yields. The acidic decomposition of the obtained Ni(II) complexes led to the target unnatural AAs with a 3-spiropyrrolidine oxindole core **5**.

This work was supported by the Russian Science Foundation (RSF grant No. 22-33-00050)

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Macrocycles and macrobicycles containing structural fragments of anthracene and anthraquinone

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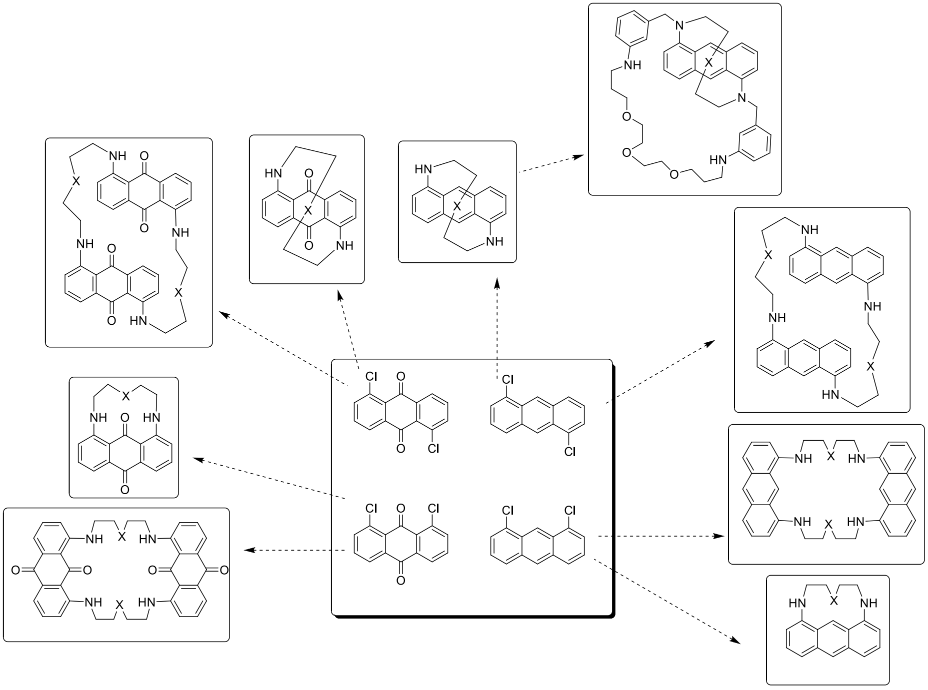
One of the actual problems of modern chemistry is the creation of highly sensitive and reliable methods for the detection of various objects, such as metal cations, organic and inorganic anions, small organic molecules, enantiomers of chiral compounds.

In this work, various macrocyclic compounds based on 1,5- and 1,8-derivatives of anthracene and anthraquinone containing fragments of various diamines, oxadiamines, and polyamines were synthesized using the Pd(0)-catalyzed amination reaction at the macrocyclization step. The dependence of macrocycles yields on the structure of oxadiamines and polyamines has been established; the most efficient reactions took place with long-chain dioxa- and trioxadiamines. Macrocycles which include one structural fragment of 1,5-disubstituted anthracene or anthraquinone and one oxadiamine or polyamine chain are planar-chiral compounds. The use of the chiral phosphine ligand Josiphos for macrocyclization makes it possible to obtain planar-chiral macrocycles with an enantiomeric excess of up to 60%. Starting from these macrocycles, it is possible to obtain macrobicyclic cryptands with elements of planar chirality. The second macrocyclization step is also the Pd(0)-catalyzed amination reaction

The resulting compounds were studied as fluorescent detectors for 21 metal cations and individual enantiomers of 7 model amino alcohols. A number of compounds obtained showed high efficiency in the recognition of copper, gallium, aluminum cations, as well as in the determination of individual enantiomers of some amino alcohols. In the presence of these analytes considerable changes in the fluorescent spectra were observed.



Synthesis, structure and solid-state photoluminescence of novel organic anion of cyano-substituted 2,2'-bipyridine series

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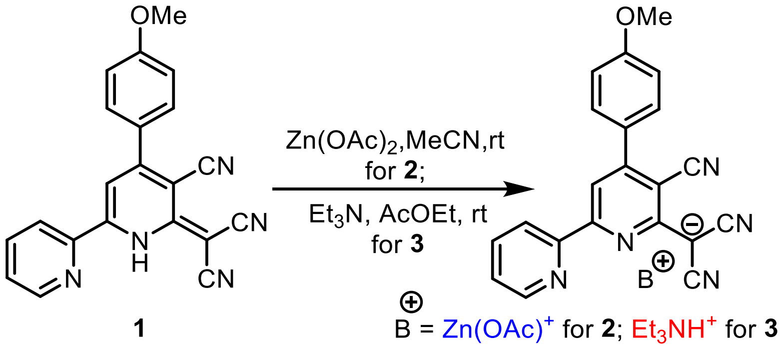
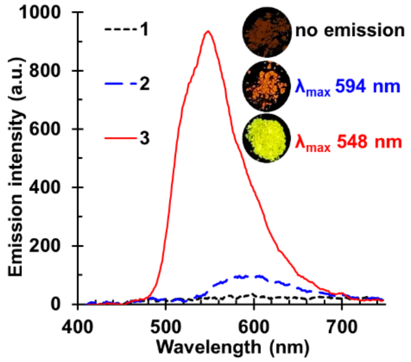
Novel organic luminescent materials are very important for modern science and technology. They found application as efficient light sources in OLED-technology, as real-time sensors for detection of hazardous compounds, as promising labels for bioimaging and many else.

Using previously obtained cyano-substituted 2,2'-bipyridine derivative **1** [1,2] we synthesized novel stable organic salts **2** and **3** showing yellow-orange photoluminescence. Their chemical structure was supported with modern spectral methods as IR, ^{1}H, ^{13}C NMR-spectroscopy and mass-spectrometry. Wavenumbers of cyano group vibrational bands in IR-spectra were decreased from 2189-2222 cm^{-1} for starting bipyridine **1** to 2170-2219 cm^{-1} for complex **2** and to 2149-2207 cm^{-1} for salt **3**. It evidenced about localization of negative charge on a tricarbonitrile moiety participating in coordination with zinc(II) or triethylammonium cation. NMR spectra of compounds **2** and **3** included up-fielded chemical shifts of signals in comparison with starting material **1**, showing that complexes **2** and **3** were also stable enough in DMSO solution.





Powder of starting compound **1** was found almost non-fluorescent upon excitation by 365 nm at room temperature. In the same conditions, powders of the obtained salts **2** and **3** showed a photoluminescence with maxima at 594 nm and 548 nm respectively. It is important to note, that emission intensity for triethylammonium salt **3** is about 9 times higher than for zinc-organic compound **2**. A crystal structure of compound **3** was additionally studied by X-Ray diffraction analysis. It showed that bipyridine anions form stacks with distances between layers of 3.6 Å

The obtained results demonstrated that cyano-substituted 2,2'-bipyridine **1** could be used for fluorescent «turn-on» sensing of metal ions and amines in solutions or in the air of working area.

The study was supported financially by the Grants Council of the President of the Russian Federation for the State support of young Russian scientists (project MK-708.2021.1.3, agreement No. 075-15-2021-082)

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Merging Johnson-Claisen/Aromatic claisen rearrangements for synthesis of densely functionalized phenols

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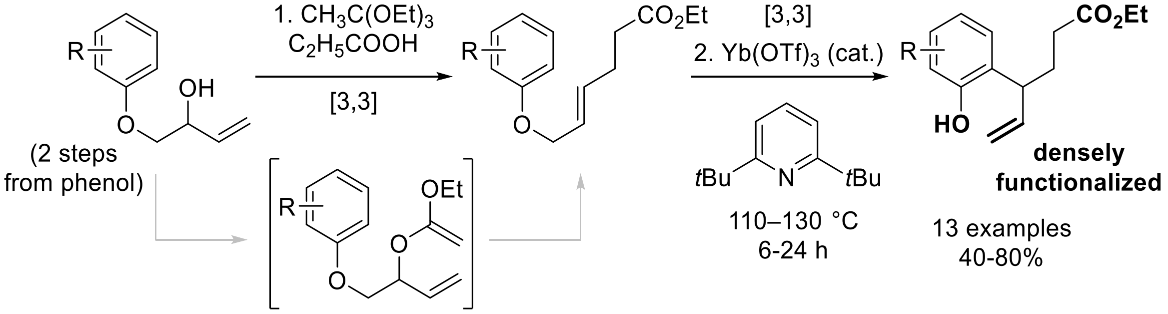
Tandem and cascade transformations have been recognized as the most efficient and elegant in the field of the organic chemistry, at least since the report on synthesis of tropinone made by Robinson.[1] Such reactions allow to carry out a global modification of the molecule in a minimal number of technical stages, which values in the fields of total synthesis and medicinal chemistry.[2]

Meanwhile, [3,3]-sigmatropic rearrangements, and Claisen rearrangement, in particular, are extremely powerful tools for creating C–C bonds.[3] In this regard, the extension of reaction's compatibility with different functional groups, as well as its use in tandem with other reactions, will progress in creation of complex molecular systems in a minimum number of stages.

In this work we studied tandem Johnson-Claisen/Claisen rearrangement, which is almost unprecedented in literature.[4] It was shown, that although the initial hypothesis of the compatibility of the conditions of these two reactions did not succeed, the sequence could be easily performed in *one-pot* manner with solvent exchange. For the last and the most delicate step – Claisen rearrangement, we were able to significantly mitigate the conditions *via* rare-earth metal (III) triflate catalysis in the presence of 2,6-di-*tert*-butylpyridine and establish the key regularities.

The products created in this tandem carry a number of functionalities, such as double bond, ester and phenol, which can be used for creating complicated molecular architectures of natural products in fast and efficient manner.



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The synthesis of luminescent 5-(1,5-diaryl-4,5-dihydro-1h-pyrazol-3-yl)-3-arylisoxazoles

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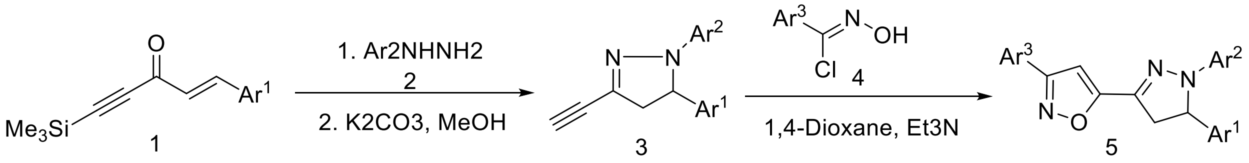
During the last decades, there were many fundamental research experiments performed with a purpose of development of the synthesis methods for novel photoactive materials with a wide range of applications (for instance, in biology, engineering, medical science). It is a well-known fact that the derivatives of pyrazolines1, pyrazoles2 and oxazoles3 possess fluorescent abilities. There were reports about fluorescent characteristics of the isoxazoles4 derivatives also.

A certain method for modification of biologically active and fluorescent substances is the conjunction of several pharmacophoric or fluorophoric fragments in a molecule. Our object was the synthesis of novel compounds, the derivatives of heterocycles that contain pyrazoline and isoxazole rings and possess high Stokes shifts and quantum yields.

For obtaining of such derivatives, quite perspective initial compounds appeared to be the conjugated enynones **1** containing three reaction centers, i.e. a carbon-carbon double bond, a carbon-carbon triple one and a keto group. By the interaction of these substrates with arylhydrazines **2**, with further desilylation, there were 3-ethynylpyrazolines **3** obtained. They are involved easily into 1,3-dipolar cycloaddition reaction with nitriloxides, generated in situ from corresponding chlorobenzaldoximes **4**, with the selectively formed main structures **5** as result.



Ar1 = Ph, 4-MeC6H4, 4-ClC6H4; Ar2 = Ph, 4-MeC6H4, 4-FC6H4, 4-BrC6H4; Ar3 = Ph, 4-MeC6H4,4-MeOC6H4, 4-FC6H4, 3-BrC6H4, 4-BrC6H4, Thiophen-2-yl

There were composition and structure for the obtained compounds approved by the data from elemental microanalysis, ^{1}H, ^{13}C, ^{19}F NMR spectroscopy, X-ray structural analysis.

Compounds **5** possess strongly marked visible luminescent properties (with quantum yield up to 45%) and can be examined and applied as fluorescent probes in biological research, as well as in analytical quantitative determination of metal ions.

This work was supported by the Russian Science Foundation (grant № 22-13-00185)

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Synthesis and nucleophulic dearomatization of methyl [1,2,5]thia- and selenadiazolo[3,4-b]pyridine-6-carboxylates

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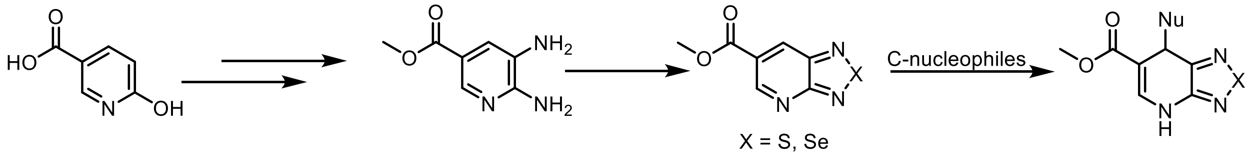
Recently, there has been a rapid development of approaches to the synthesis of condensed pyridines with various types of useful applications. Among the derivatives of pyridine, it is especially worth highlighting – dihydropyridines. The dihydropyridine core is part of a representative range of natural and synthetic compounds, many of which exhibit biological activity [1,2]. One of the most popular methods for the synthesis of dihydropyridine derivatives is the dearomatization of various functionalized pyridines [3].

The aim of this work is the synthesis of pyridines fused with π-deficient heterocycles: thia- and selenadiazoles and study their reactivity toward C-nucleophiles. A new thia- and selenadiazolo[3,4-b]pyridines have been synthesized on the basis of commercially available 6-hydroxynicotinic acid. We found that the resulting π-deficient thiadiazoles and selenadiazoles fused with pyridine ring easily react with C-nucleophiles (such as β-dicarbonyl compounds, π- excessive (het)arenes etc.). Reactions proceed under mild conditions: room temperature without using of a base or a catalyst. Reactions of thia- and selenadiazolo[3,4-*b*]pyridines with nucleophiles gave carbon-bonded 1,4-adducts – 1,4-dihydropyridines fused with azole ring.



Thus, methods for the synthesis of new methyl [1,2,5]thiadiazolo[3,4-b]pyridine-6-carboxylate and methyl [1,2,5]selenadiazolo[3,4-b]pyridine-6-carboxylate were developed and their reactions with C-nucleophiles have been studied.

This work was supported by the Russian Science Foundation (grant № 19-73-20259)

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Synthesis of 3-(furan-2-yl)prop-2-en-1-ones and their reactions with arenes in the superacid CF_3SO_3H

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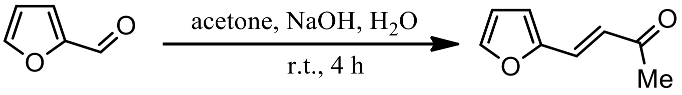
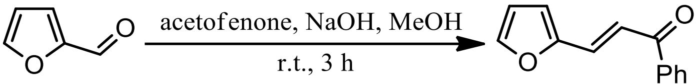
Furans are important class of heterocyclic compounds actively used for synthesis of biopolymers, drugs, biofuels, and other practically valuable compounds. Furans are a good, convenient and affordable platform for synthesis of new compounds with various chemical and physical properties.

In this work, 3-(furan-2-yl)prop-2-en-1-one **1** and 3-(furan-2-yl)-1-phenylprop-2-en-1-one **2** were synthesized from furfural.

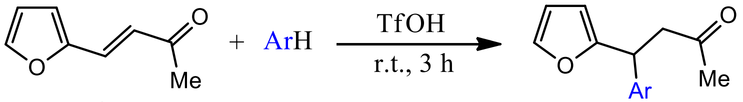


1 (89%)



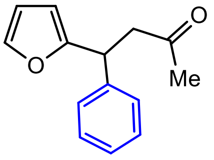
2 (82%)

Reactions of compound **1** with arenes (benzene, toluene, o-, m-, p-xylene, mesitylene, anisole) under the action of trifluoromethane sulfonic acid CF_3SO_3H (TfOH) afford compounds **3-10** as products of hydroarylation of the carbon-carbon double bond.

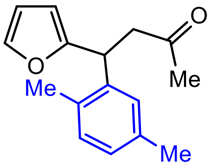


1

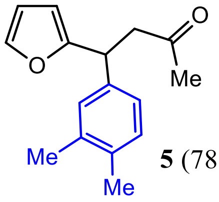
3-10 (4-82%)



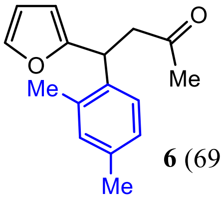
3 (64%)



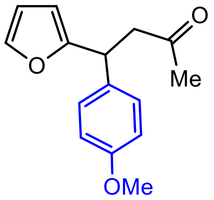
4 (70%)



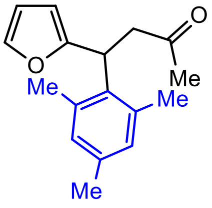
5 (78%)



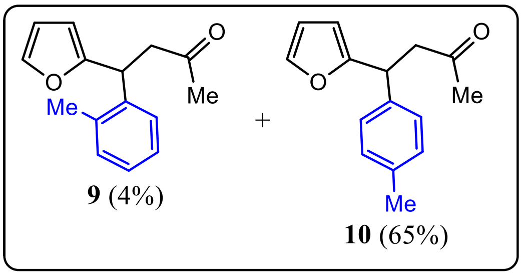
6 (69%)



7 (82%)



8 (74%)



9 (4%)

10 (65%)

This work was supported by the Russian Scientific Foundation (grant № 21-13-00006)

A new route to polyarylated isoxazoles via selective Suzuki aryation of 4,5-dibromoisoxazoles

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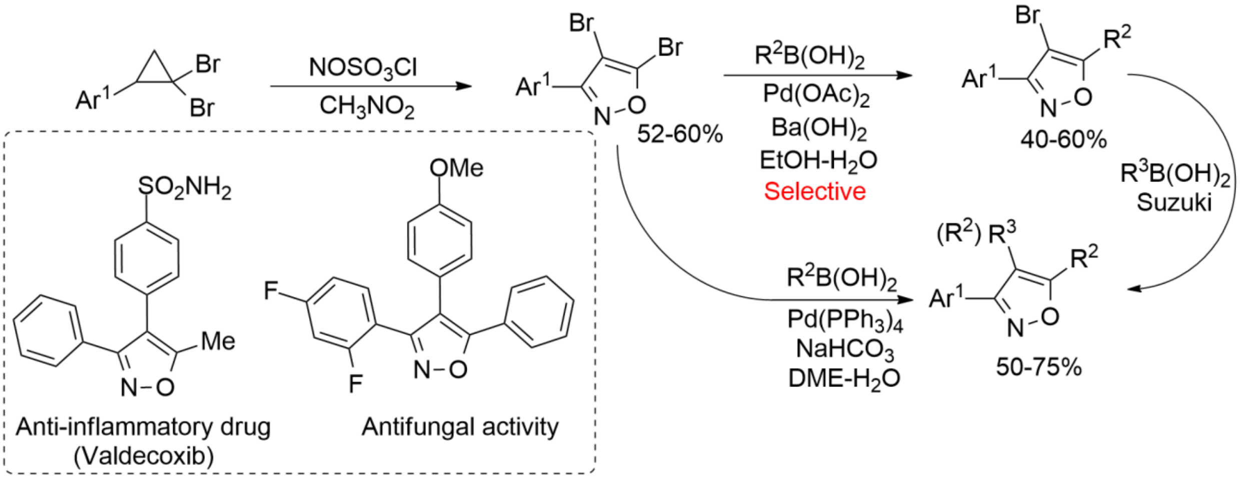
Isoxazole ring is a basic scaffold for many biologically active compounds and so is of great interest. Many drugs used in medicine contain an isoxazole ring (Risperidone, Sulfafurazole, Valdecoxib, etc.). Therefore, at present, new methods and approaches are being developed for the preparation of isoxazole derivatives [1]. Among them haloisoxazoles are convenient base structures for further functionalization of the molecule and the introduction of pharmacophore fragments [2].

We have developed a new convenient route to polyarylated isoxazoles from 2-aryl-1,1-dibromocyclopropanes via nitrozation/Suzuki arylation sequence with excellent selectivity at all stages.



This work was supported by the Russian Foundation for Basic Research (grant № 20-33-90030)

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Function-oriented synthesis of 12-(acylamino)indolo[1,2-c]quinazolin-6(5H)-ones

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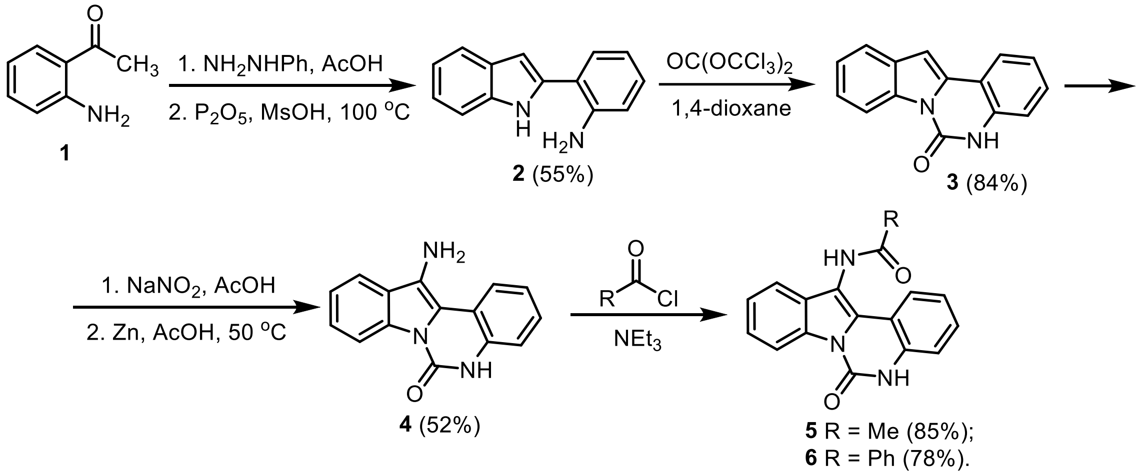
Quinazoline fragment includes many different natural products and pharmaceuticals [1]. Quinazolinones annelated to indole core represent not only synthetical interest for the design of new polyaromatic derivatives: these compounds have valuable biological activities, e.g. antibacterial, anticancer and antiviral [2,3]. To estimate the potency of indolo[1,2-c]quinazolines we synthesized 12-aminoindolo[1,2-c]quinazolin-6(5H)-one and performed acylation reactions of the primary amino group.

Fisher indole synthesis which is based on condensation of *o*-aminoacetophenone (**1**) with phenylhydrazone followed by heterocyclization in Eaton's reagent(P_2O_5 in MsOH) resulted in 2-(*o*-aminophenyl)indole (**2**). Treatment of **2** with triphosgene lead to formation of indolo[1,2-*c*]quinazolin-6(5H)-one (**3**). Introduction of the amino group at the 3 position of indole moiety of compound **3** was done by nitrosation and subsequent reduction of nitroso group by the zinc in AcOH yielding 12-aminoindolo[1,2-c]quinazolin-6(5H)-one (**4**). Acylation of the amino group of **4** with acyl and benzoyl chlorides gave derivatives of 12-(acylamino)indolo[1,2-c]quinazolin-6(5H)-ones **5** and **6** with high yields.

Structures of all new compounds have been proven by NMR and HRMS spectra. Synthesis of other derivatives and biological studies of obtained compounds are underway.



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One-pot synthesis and photophysical studies of 5-aryl-2,2'-bipyridines containing alicyclic amines

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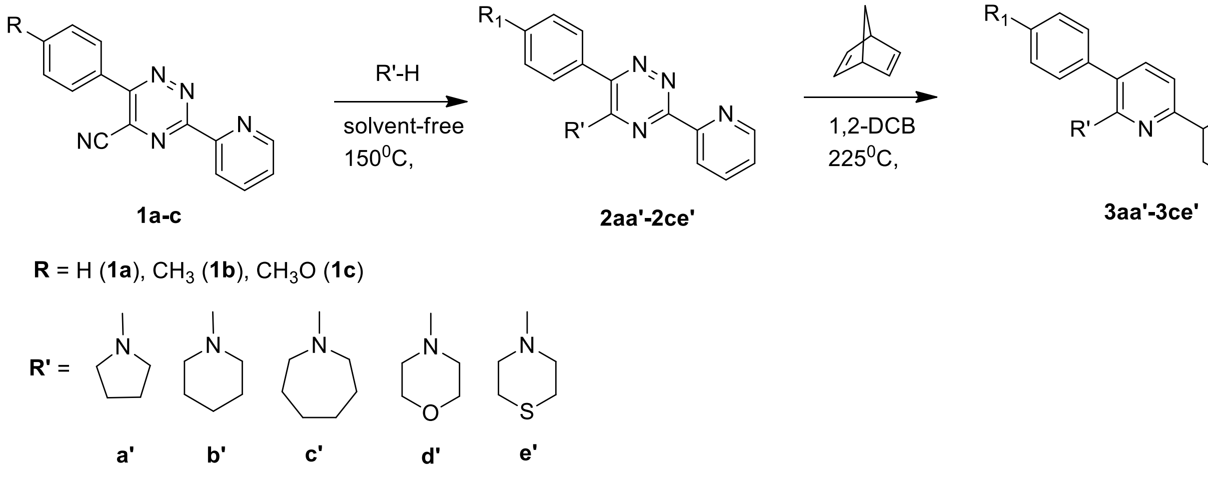
Fragments of alicyclic amines play a versatile role in the composition of heterocyclic compounds. They act as pharmacophore units in many drugs and are widely used as pesticides, herbicides, antifungal agents, etc. Aliphatic cyclic amines have found significant application in the synthesis of luminescent molecules, especially in donor-acceptor systems.

Previously, we proposed a method for introducing fragments of various amines into the 2,2'-bipyridine derivatives by using 1,2,4-triazine methodology [1] and investigated its applicability to various aniline derivatives [2].

In this work, we extend this methodology by using alicyclic amines and one-pot approach. Photophysical studies were carried out for the resulted 2,2'-bipyridines **3aa'-3ce'**.



This work was supported by the Russian Science Foundation (Grant № 19-73-10144-P) and by the Ministry of Science and Higher Education of the Russian Federation (MEGA-GRANT № 075-15-2022-1118)

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A weak base route to bis(N-heterocyclic carbene) complex of Ni(II)

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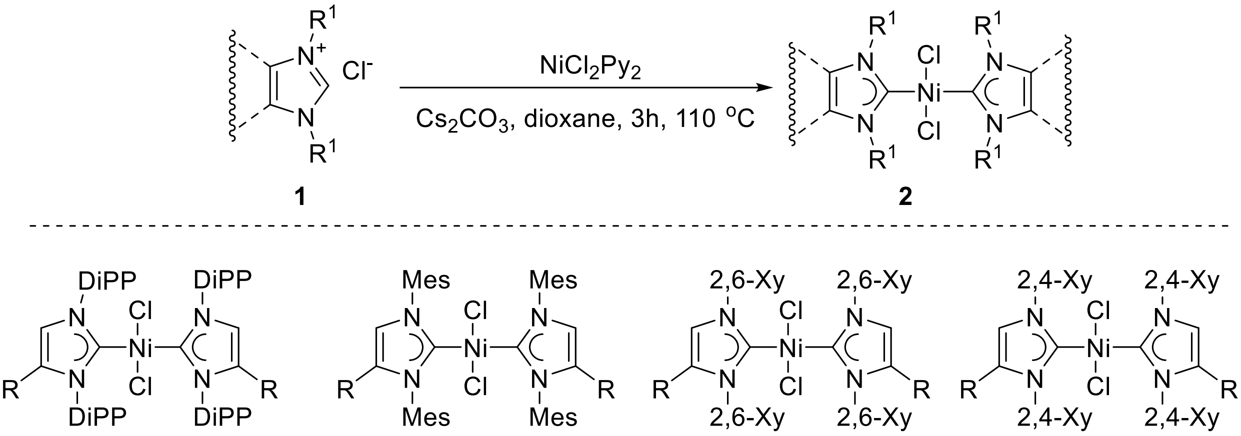
Complexes of N-heterocyclic carbenes (NHC) with Ni have ubiquitous application in catalysis science due to high stability of Ni-NHC bond and variability of steric and electronic parameters of NHC-ligands [1]. Therefore, sustainable routes for the synthesis of Ni/NHC catalysts are highly desirable.

We report a new efficient method for synthesis of Ni/NHC complexes with aryl substitutes on nitrogen atom NHC ligands in one step. The main benefit of the method is use of a weak base, under aerobic conditions. This method enables access to a series of Ni/NHC complexes with moderate to good yields. All described complexes were isolated as air-stabile bright red crystals.



1 **2**

2a, R = H, 49%
2b, R = SBu, 41%
2c, R = SPh, 56%
2d, R = S(4-MePh), 55%
2e, R = S(3-MeOPh), 61%

2f, R = H, 87%
2g, R = SBu, 64%
2h, R = SPh, 76%
2i, R = S(4-MePh), 79%
2j, R = S(3-MeOPh), 73%

2k, R = H, 91%
2l, R = SBu, 54%
2m, R = SPh, 69%
2n, R = S(4-MePh), 76%
2o, R = S(3-MeOPh), 75%

2p, R = H, 82%

This work was supported by the Russian Science Foundation (grant № 22-23-00308)

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Synthesis of a functional derivative of 9,10-diphenylanthracene and its grafting onto siloxane matrices

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Organic luminophores based on functional derivatives of 9,10-diphenylanthracene (DPA) has attracted considerable attention in recent years for applications in organic light-emitting diodes (OLEDs) [1], metal–organic frameworks (MOFs) [2], photocatalytic and biological fields [3]. In addition, derivatives of DPA are used as emitters in systems with up-conversion fluorescence [4]. Such a wide range of applications is due to their optical properties: photostability, high quantum yield and high extinction coefficient.

In this work we obtained a potential emitter for up-conversion systems based on the functional derivative of 9,10-diphenylanthracene containing allyl group **1** (Allyl-DPA). After that, monofunctional derivative Allyl-DPA **1** was grafted onto various siloxane matrices **2-4**: difunctional hexamethyltrisiloxane **2** and polymers with chain-distributed hydride groups **3-4** (Fig.1).

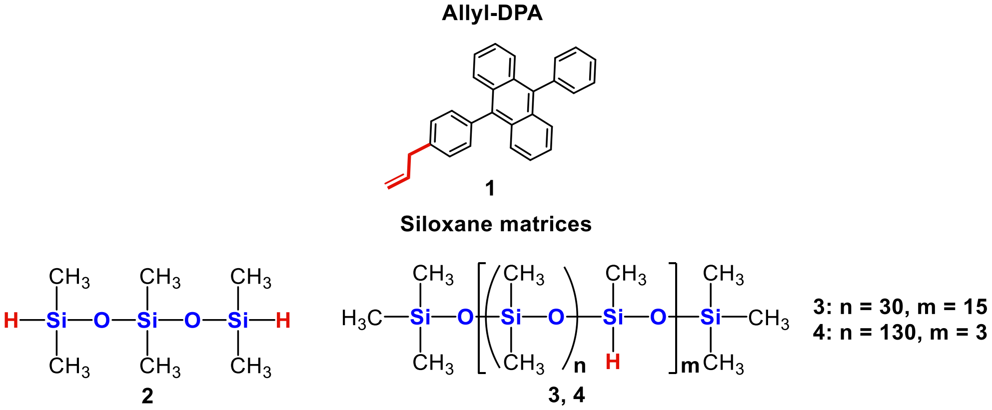

Figure 1. Functional Allyl-DPA derivative **1** and siloxane matrices **2-4**.

The structure of the obtained compounds was confirmed by ^{1}H, ^{13}C, ^{29}Si NMR-, IR-spectroscopy, mass spectrometry (ESI), and their photophysical properties in solutions of various solvents were studied.

This work was supported by the Russian Science Foundation (grant № 18-73-10152)

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The development of methods for the synthesis of pyrrolo[2,1-a][2]benzazepines

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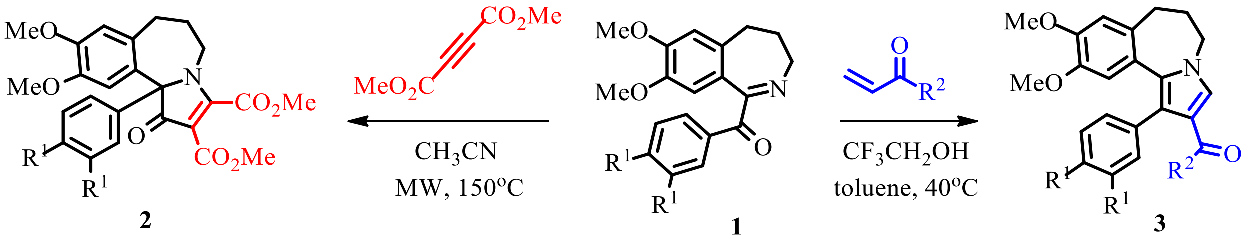
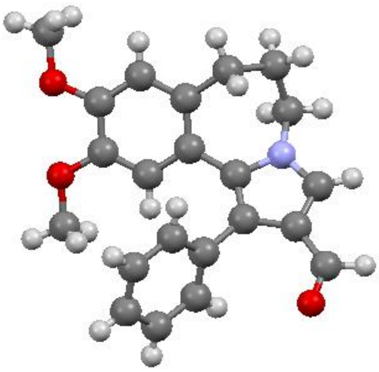
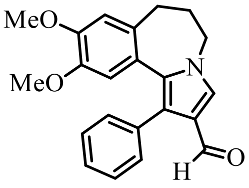
The development of methods for the synthesis of biologically active heterocyclic compounds is an urgent task of modern organic chemistry.

It has been established that domino reactions of 1-aroyl-4,5-dihydro-3H-benzo[*c*]azepines **1** with the participation of electron-deficient alkenes (acrolein, methyl vinyl ketone, *p*-nitrophenyl acrylate) and, as an alkyne, dimethylacetylenedicarboxylate, successfully lead to the synthesis of the expected 6, 7-dihydro-5H-pyrrolo[2,1-*a*][2]benzazepines **2**,**3** in high yields. It was established that the presence of the imino-ketone fragment in all substrates makes it possible to form a five-membered nitrogen-containing cycle and obtain derivatives of pyrrolo[2,1-*a*][2]benzazepines. It has been shown that the transformations of 1-aroylbenzoazepine **1** with the participation of alkynes proceed with the formation of rearrangement products with the transfer of the aryl group, pyrrolo[2,1-*a*][2]benzazepines **2**.



R^1 = H, OMe; R^2 = H, Me, C_6H_4-*p*-NO_2





This paper has been supported by the RUDN University Strategic Academic Leadership Program

Synthesis of metacyclophanes with disturbed planarity of the benzene ring

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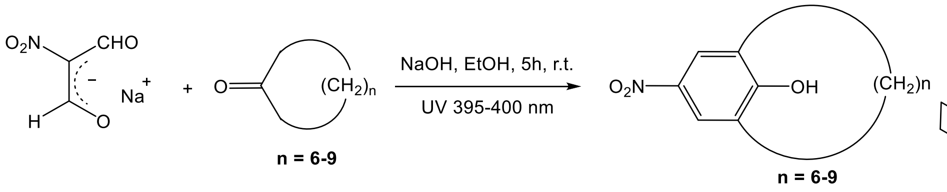
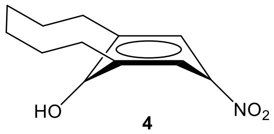
Interest in the synthesis, study of the structure and properties of small, strained molecules ($n \leq 7$) meta- and ($n \leq 8$) paracyclophanes is due to the further development of the fundamental theory of aromaticity. It has been established that the benzene ring of meta- and paracyclophanes with different lengths of the polymethylene chain can be bent without loss of aromaticity **4**. These diatropic compounds do not have alternating lengths of double and single C-C bonds. [1,2]

In 1947, Nobel laureate Vladimir Prelog was the first to synthesize strained [5-8]metacyclophanes by cyclocondensation of nitromalonic dialdehyde with cyclic ketones. [3,4] One-step method for the synthesis of Prelog had one drawback - a low yield of metacyclophanes.

We carried out the synthesis of [6-8]metacyclophanes under modified conditions of the Prelog reaction, adding irradiation with ultraviolet light (395-400 nm), which made it possible to reduce the reaction time to 5 hours and significantly increase the yields of metacyclophanes.





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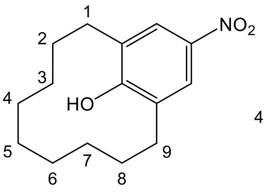

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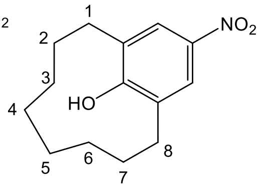
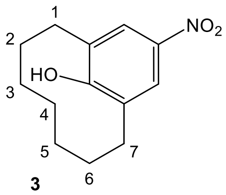


2



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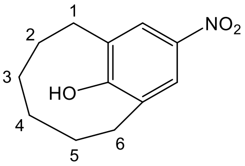

4

№	[n]	Yield, % (under Prelog reaction conditions, t = 2-7 days, 1947.)	Yield,% (under modified Prelog reaction conditions using UV irradiation (395-400nm), t = 5h, OmSU)
2	9	26	78
3	8	2	73
4	7	6	20
5	6	50	52

The efficiency and simplicity of the synthesis of the metacyclophanes obtained by us [6–9] makes it possible to use them as available precursors in the synthesis of retinoids, indolophanes, and carbazolophanes.

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A new approach to the synthesis of 2-substituted 6-nitro-[1,2,4]triazolo[1,5-a]pyrimidine-7-amines

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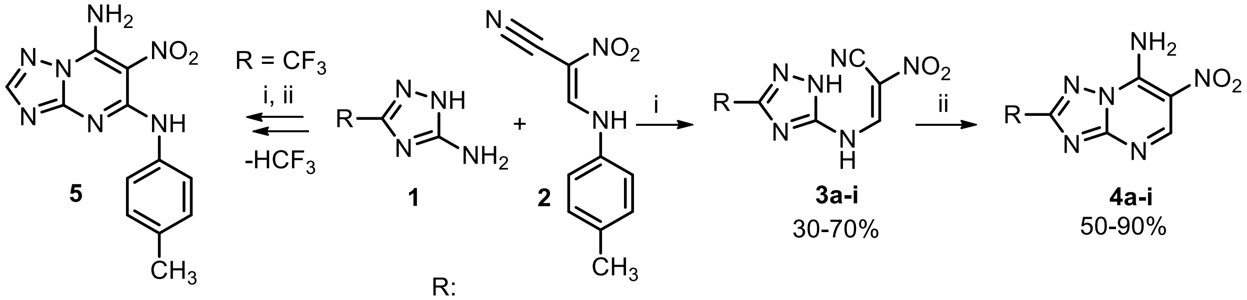
The development of new effective drugs remains an urgent task of organic chemistry. Among the many heterocyclic compounds, azolo[1,5-*a*]pyrimidine derivatives attract special attention due to their well-known wide range of bioactivity, including anti-inflammatory, antiviral, antitumor and others.

Despite the fact that 6-nitro-[1,2,4]triazolo[1,5-a]pyrimidine-7-amines are known, their preparation was previously carried out only by direct nitration of 6-nitro-[1,2,4]triazolo[1, 5-a]pyrimidine-7-amines [1]. In this work,we expand the series of these compounds and propose an alternative method for their preparation by the condensation of 5-substituted [1,2,4]triazolo-3-amines with 2-nitro-3-p-toluidyl acrylonitrile under Michael reaction conditions followed by cyclization. It should be noted that derivative **2** can also be considered as a more stable and cheaper analogue of ethoxymethylenenitroacetonitrile.



R:
a) H, b) SMe, c) SEt, d) SPr, e) SBn, f) prop-2-yn-1-ylthio, g)pyridin-2-yl, h) furan-2-yl, i) thien-2-yl

Scheme 1 – Reagents and conditions: i) iPrOH, reflux, 1-5h; ii) H_2O, reflux, 1h

It is interesting that carrying out this reaction with 3-trifluoromethyl-5-amino-1,2,4-triazole leads already to the elimination of the fluoroform with the formation of 7-amino-6-nitro-5-N-tolyl-[1,2,4] azolo[1,5-a]pyrimidine **5**.

Using virtual screening methods [2], we have established high in silico activity of compounds **4a-i** and **5** and their structure similarity to known adenosine A2a receptor antagonists, which will be experimentally verified by us later.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, Grant No. 075-15-2020-777

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Synthesis of N-(arylamino)substituted 1,2,4-oxadiazol-5(4H)-ones

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[b] Russian State University named after A.N. Kosygin (Technology. Design. Art),
119071, Moscow, Malaya Kaluzhskaya str. 1
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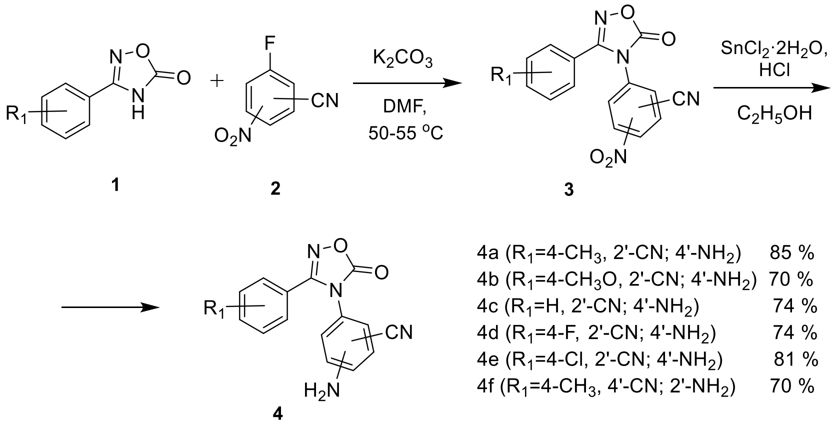
Aniline-containing derivatives of 1,2,4-oxadiazol-5(4*H*)-ones are promising candidates for the role of new organic phosphors class due to the peculiarities of their electronic structure. Moreover, the study of these objects in medicinal chemistry as antibacterial, antiviral and antiglaucomic agents is relevant.

In the work of our scientific group, the process of *N*-arylation of 1,2,4-oxadiazol-5(4*H*)-ones was previously studied, corresponding *N*-aryl derivatives were synthesized in 60–90% yields under conditions of catalytic and classical activated nucleophilic substitution [1]. Intermediate nitro derivatives **3** were obtained via the reaction of 1,2,4-oxadiazol-5(4*H*)-ones **1** with nitro, cyano-group containing fluorarenes **2** in the K_2CO_3/DMF system at the reaction temperature 50-55 °C. In this work, we have developed the method for selective reduction of resulting *N*-(nitroaryl) derivatives **3** at the nitro group to amines **4**.



4a (R_1=4-CH_3, 2'-CN; 4'-NH_2) 85 %
4b (R_1=4-CH_3O, 2'-CN; 4'-NH_2) 70 %
4c (R_1=H, 2'-CN; 4'-NH_2) 74 %
4d (R_1=4-F, 2'-CN; 4'-NH_2) 74 %
4e (R_1=4-Cl, 2'-CN; 4'-NH_2) 81 %
4f (R_1=4-CH_3, 4'-CN; 2'-NH_2) 70 %

In the course of our investigation, it has been found that catalytic reduction of nitro derivatives using H_2 gas on 10% Pd/C does not proceed chemoselectively. It leads to 1,2,4-oxadiazolone ring opening and to the formation of a difficult mixture of side-products. The best results in terms of purity and yield of target amines **4** (at the level of 70–85%) are achieved when compounds **3** are reduced in the $SnCl_2$/HCl/ethanol system. It should be noted that the reduction reaction of **3** at the nitro group in the 4'-position of the *N*-phenyl fragment proceeds easily than 2'-position isomers and requires the room temperature. While reduction of the nitro group in the 2'-position should be conducted at 50-55 °C.

This work was financially supported by the Ministry of Education of the Russian Federation (state contract 073-00077-21-02 "Development of the innovative drug for the treatment of glaucoma based on selective inhibition of carbonic anhydrase II", registration number 730000Ф.99.1.БВ10АА00006)

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The first example of cine-substitution in 1,3-dinitropyrazoles

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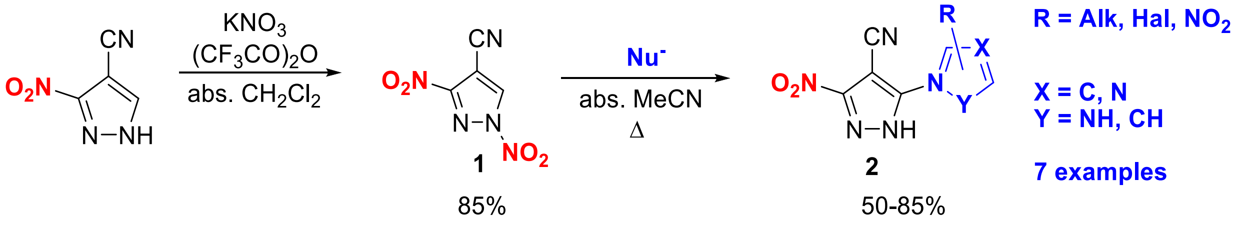
Pyrazole derivatives are of great interest to researchers due to their wide application as biologically active compounds, components of dyes and energetic materials. One of the significant chemical properties of pyrazoles, which fundamentally distinguishes them from other NH-azoles, is the ability to form stable N-nitro derivatives, which often act as key synthons for obtaining new compounds with necessary properties [1]. The main synthetic methods of such substrates from N-nitropyrazoles are thermal sigmatropic rearrangement of the nitro group and *cine*-substitution reactions of the N-nitro group. The analysis of the references has shown that only 1,4-dinitropyrazoles go into *cine*-substitution reactions, whereas in 1,3-dinitropyrazoles denitration of the N-nitro group occurs [2]. Using 4-cyano-1,3-dinitro-1*H*-pyrazole **1** as an example, we have demonstrated for the first time the possibility of *cine*-substitution of the N-nitro group in the series of 1,3-dinitropyrazoles.

N-nitro derivative **1** was obtained by preparative synthetic method that was developed by us from 4-cyano-3-nitro-1*H*-pyrazole. Salts of various NH-azoles, such as pyrazoles, imidazoles, and triazoles, were used as nucleophiles for *cine*-substitution reactions. We have found that refluxing dinitropyrazole **1** with nucleophiles in absolute MeCN leads to *cine*-substitution of the N-nitro group with the formation of bicyclic C-N-bonded pyrazolylazoles **2** in high yields.



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Chan-Lam amination in the synthesis of N,N’-diaryl derivatives of diamines and oxadiamines

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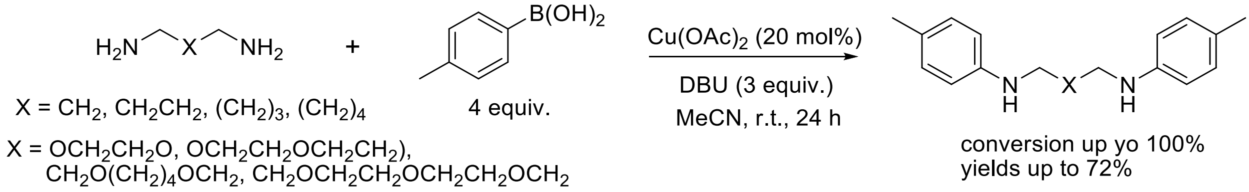
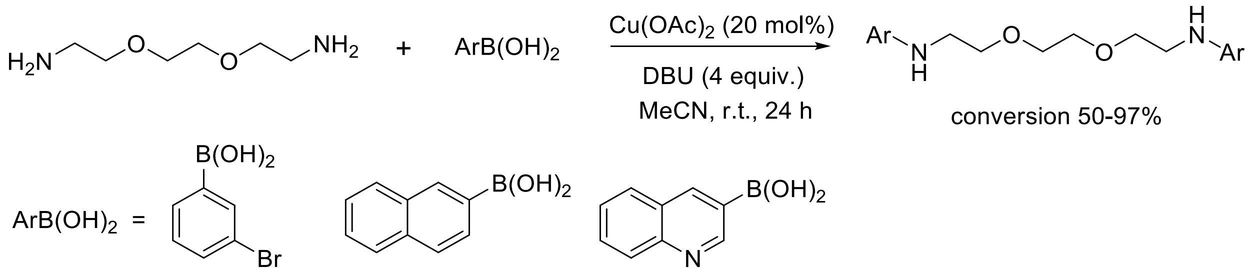
The importance of the development of the convenient synthetic approaches to the formation of C(sp^2)-N bonds gave rise to several alternative catalyitc methods among which most important are Pd(0)-catalyzed amination of aryl halides (Buchwald-Hartwig reaction), catalytic amination using less expensive Cu(I) catalysis and the amination of aryl boronic acids mediated by Cu(II) salts (Chan-Lam reaction) [1]. Previously we thoroughly investigated Pd(0)- and Cu(I)-catalyzed reactions for the synthesis of N,N’-di(hetero)aryl derivatives of various diamines, oxadiamines and polyamines which are interesting from the point of view of their coordination towards metal cations and possibility of their application as fluorescent detectors provided fluorophore groups are introduced in their structure by means of above mentioned reactions. In the present research we have focused on the application of the Chan-Lam reaction for the synthesis of various N,N’-diaryl derivatives of the diamines and oxadiamines as it allows to carry out the arylation at room temperature using very cheap Cu(II) salts without ligands. It was found out that the crucial factor of successful N,N’-diarylation with the model *p*-tolyl boronic acid was the application of DBU as a base taken in appropriate excess (3-4 equiv.) together with a certan excess (2.5-4 equiv.) of *p*-tolyl boronic acid (Scheme 1). Other bases like Et_3N, DIPEA, DBN, pyridine, K_3PO_4, KF were substantially less efficient. MeCN proved to be the best solvent and sufficient volume of the flask (50 ml per 0.1 mmol diamine) was found to be equally important to provide enough oxygen for the catalytic cycle. The reaction can be equally used for the introdution of other aryl and heteroaryl substituents (Scheme 2).



Scheme 1.



Scheme 2.

This work was supported by the Russian Science Foundation (grant № 22-23-00518)

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Synthesis of five-membered heterocycles with an exocyclic methylidene component

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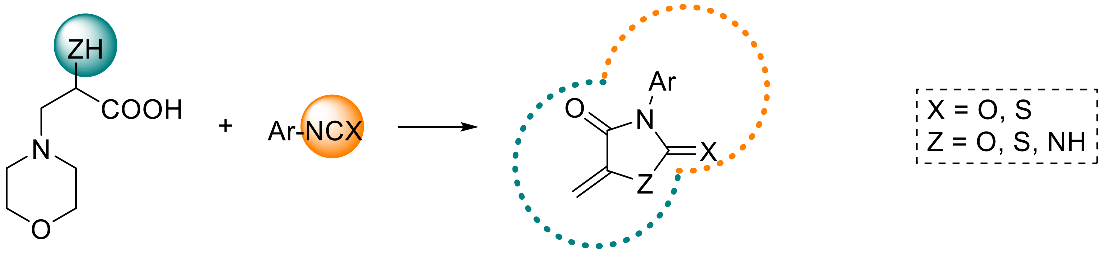
Five-membered heterocycles containing several heteroatoms are known as compounds providing a broad spectrum of pharmacological and biological activities. [1]. The introduction of such fragments into the composition of more complex structures also ensures their bioactivity. The presence of an exocyclic double bond in the heterocycle significantly expands the synthetic possibilities of using these molecules, allowing them to be introduced into Diels-Alder reaction and 1,3-dipolar cycloaddition and others.

Whereas general methods for the preparation of five-membered heterocycles containing 5-arylidene component is known and is widely used in synthetic practice, the methods for obtaining similar compounds with a 5-methylidene fragment are laborious and proceed with low yields [2].



Common preparative procedure for the synthesis of 3-aryl-5-methylidene-2-thiohydantoins have been recently developed in our laboratory [3]. At the current work, we investigate approaches for the synthesis of 5-methylidene derivatives of imidazolidine, thiazolidine and oxazolidine by reaction of 2-amino, 2-mercapto- and 2-hydroxy-3-morpholinopropionic acid, respectively, with aryl isocyanates or aryl isothiocyanates.

This work was supported by the grant MK-3748.2022.1.3

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An efficient synthesis of push-pull fluorophores based on (2-fluoroaryl)-1,2,3-triazoles

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Organic push-pull fluorophores are known to be formed by a π-conjugated system containing both electron-donating groups (EDG) and electron-withdrawing groups (EWG). These molecules are usually based on either an aromatic or heteroaromatic scaffold. The latter framework is now considered as one of the most attractive building blocks due to its diverse chemical properties and wider possibilities to versatile functionalization instead of the aromatic ones. It is worth noting that compounds based on triazoles are widely used in the design of OLEDs, NLO materials, chemosensors, and fluorescent probes. Despite the deep investigations of photophysical properties and numerous examples of similar fluorophores in the literature, the application of the fluoroaromatic fragments in push-pull systems as EWG has not been studied extensively so far.

In this work, we wish to discuss the synthesis of push-pull fluorophores based on N(2)-substituted-1,2,3-triazoles containing both a fluoroaromatic scaffold as an EWG and carbazole or tertiary amines as an EDG of the π-conjugated system.

The synthesis of the desired N(2)-aryl substituted 1,2,3-triazoles was carried out in 5 steps starting from the condensation between arylhydrazines **1a,b** and 2-oxopropanal oxime to obtain intermediates **2a,b,** to be cyclized subsequently in the presence of copper sulfate in pyridine to give triazole-N-oxides **3a,b** in 45-60% two step yields. Further bromination was shown to proceed regioselectively at C(5) carbon atoms in 96-97% yields. Then the Suzuki-Miyaura cross-coupling reaction in the presence of Pd(Ph$_3$)$_4$, K_3PO_4, and boronic acid was utilized to construct the push-pull system. At the last step, the N-oxide group was removed by the action of zinc dust in the presence of NH_4Cl (saturated) to obtain the targeted novel N(2)-aryl-1,2,3-triazole based fluorophores **6a-f** in 98-99% yields.

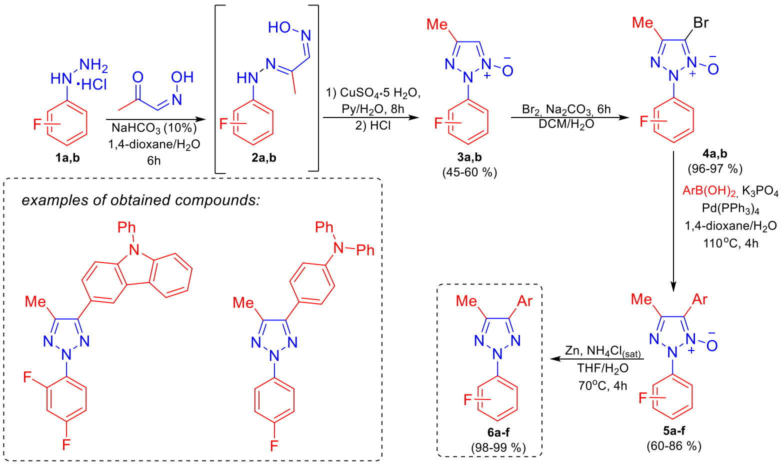

Figure 1. Synthesis of push-pull fluorophores based on (2-Fluoroaryl)-1,2,3-triazoles.

The research was financially supported by the Russian Science Foundation (Project No. 20-73-10077)

Synthesis of 1,2,3,4-Tetrahydrochromeno[3,2-c]pyridin-10-ones derivatives

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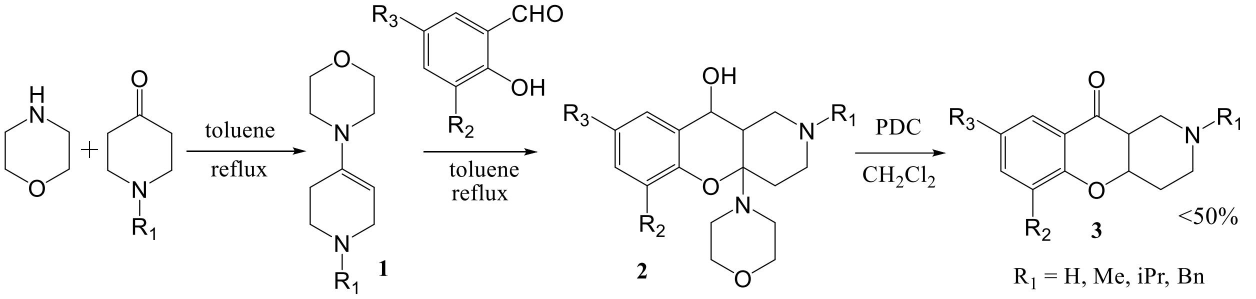
Derivatives of 1,2,3,4-tetrahydro-10H-chromeno[3,2-c]pyridine-10-one combine two widely used heterocycles – chromone and pyridine, which makes them a promising class of heterocyclic compounds with a great biological activity.

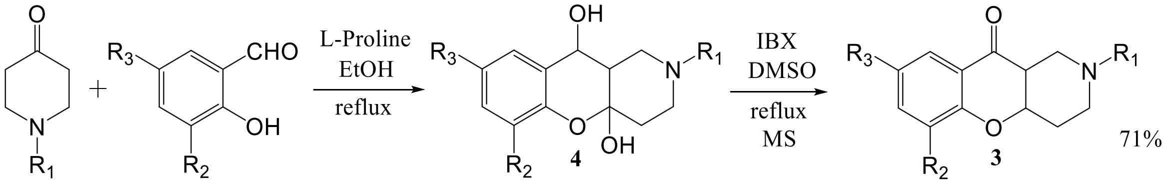
Thus, when two fragments merge, a new class of the chromenopyridines appears, which is of great interest for studying as drugs due to showed high inhibitory activity against various targets involved in the onset and progression of Alzheimer's disease, such as AChE and BchE. The development of new and effective methods for the synthesis of compounds with the chromenopyridine structure is a complicated task of synthetic and pharmaceutical chemistry.

The three-stage method for the synthesis of substituted 1,2,3,4-tetrahydro-10H-chromeno[3,2-c]pyridine-10-one **3** has already been reported [1]. It includes condensation of piperidine with morpholine, cyclization of the obtained enamine with salicylaldehyde and subsequent oxidation of the intermediate **2** with pyridinium dichromate to the product **3** obtained in low yields (less than 50%).



R_1 = H, Me, iPr, Bn
R_2 = H, OEt
R_3 = H, Br

The new method has only two stages, which significantly reduces the costs of the reactants and solvents, the reaction time, and is also less time-consuming compared to the first method. First, piperidine is condensed directly with salicylaldehyde. The reaction is catalyzed by L-proline and refluxed. Then the intermediate **4** is oxidized with iodoxybenzoic acid to the product **3** obtained in excellent yields (71%).



R_1 = Me, Bn
R_2 = H, I
R_3 = Cl, I

The results of the research have great potential, so we are going to explore new synthesis methods and improve chromenopyridine derivatives for even greater biological activity directed towards relevant Alzheimer's targets.

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Catalytic system "$GaCl_3$+$AgBF_4$" as the replacement of gallium salts equimolar amounts in the reaction between *β*-styrylmalonates and aromatic aldehydes

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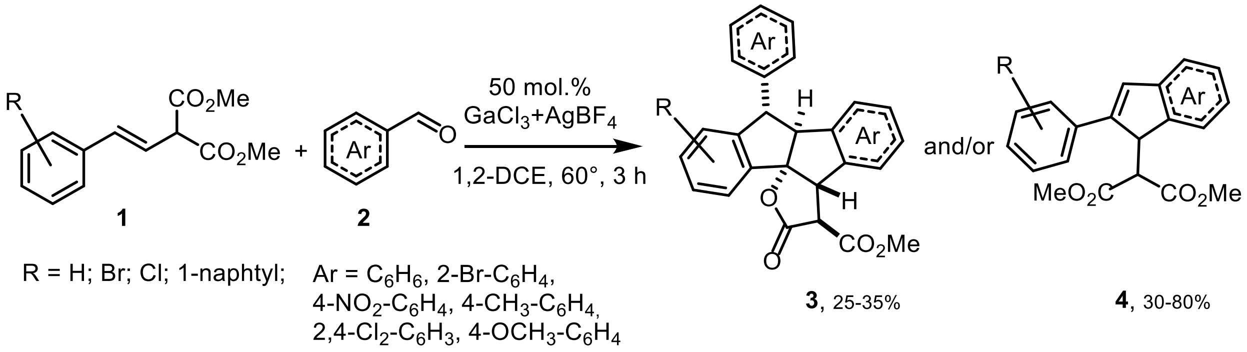
Donor-acceptor cyclopropanes (DAC) have attracted researchers attention for quite a long time, while their synthetic equivalents *β*-styrylmalonates have been studied to a much lesser extent, partly because of the small number of examples of such compounds. Due to study of our group a universal method for the synthesis of this class of compounds was developed [1]. Previously, we has already shown that the new pathways for the transformation of DAC and their isomers are opened in the presence of gallium trichloride: the occurrence of these processes is associated with the ability of donor-acceptor substrates to form 1,2-zwitterionic intermediates [2]. Typically, the generation of the intermediates requires the presence of equimolar amounts of gallium salts; therefore, the development of catalytic versions of such transformations is an urgent task.

This work presents the developed catalytic system based on gallium trichloride and silver tetrafluoroborate, which turned out to be efficient in the reaction between styrylmalonate **1** and aromatic aldehyde **2**. It should be noted that earlier similar processes proceeded with the use of 1–2.5 *equiv.* $GaCl_3$ [3].



As a result we managed to obtain several new representatives of the classes of indenes **3** and pentacyclic lactones **4** with yields from moderate to good (25-80%) and retry the previously known compounds yields, moreover significantly reduce the amount of gallium trichloride introduced into the reaction, due to the new catalytic system "$GaCl_3$+$AgBF_4$".

This work was supported by the Grants of the President of the Russian Federation
(grant № MK-4609.2022.1.3)

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Recyclable polymers based on biomass and calcium carbide

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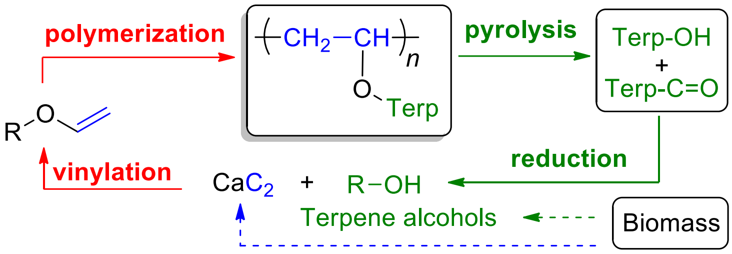
Calcium carbide is a cheap, available and renewable raw material for the production of many substances [1]. Frequently, calcium carbide use as an *in situ* source of acetylene in nucleophilic addition, in particular, reaction of vinylation [2]. At the same time, terpene alcohols, which are also a renewable resource, since they are isolated from biomass, can be used in this reaction. The resulting vinyl ethers can be easily polymerized using boron trifluoride etherate as an initiator. Thus, access to a polymer based on biomass is opened (Scheme, red arrows).



In our work [3], we have obtained several vinyl ethers from calcium carbide and terpene alcohols in super basic conditions with yields up to 93%. The resulting monomers were then undergone to cationic polymerization with yields of the desired polymers up to 82%. A remarkable property of these polymers is that during pyrolysis at 300–450 °C, in most cases, the main products are the initial terpene alcohol and the corresponding aldehyde or ketone (Scheme, green arrows). In the case of primary starting alcohols, an aldehyde is formed, and in the case of secondary ones, a ketone. The most outstanding results have been achieved using polymers based on menthol, borneol and rosafen, where the total content of the alcohol and aldehyde/ketone reached 95-100%. It is noteworthy that reducing the mixture formed as a result of pyrolysis provide to obtain exclusively the original terpene alcohol. We proved the possibility of reuse of the forming alcohol on the example of borneol. Thus, using borneol and calcium carbide, we obtained the corresponding vinyl ether, which was then polymerized. The resulting polymer was pyrolyzed in a quartz tube in an argon atmosphere at 350 °C. The pyrolysis products were washed out of the tube, reduced and re-introduced into the polymer production process. The resulting polymer was characterized by NMR and GPC, and its characteristics were found to be the same as for the polymer obtained for the first time.

In conclusion, we have developed a procedure for obtaining recyclable polymers based on terpene alcohols and calcium carbide.

This work was supported by the Russian Science Foundation (grant № 21-73-20003)

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Development of a method for the synthesis of 5-R-aminoazolo[1,5-*a*]pyrimidin-7-ones and mechanistic insights

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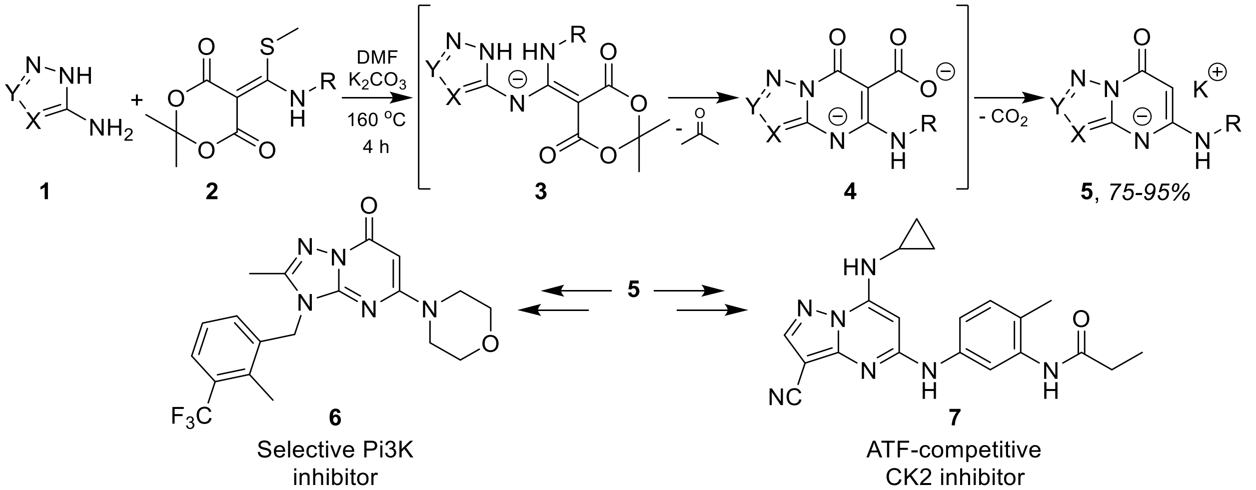
Azolo[1,5-*a*]pyrimidines are an extremely versatile group of heterocycles with applications in various fields of organic synthesis. One of these areas is the search for new drugs. The starting point indicating the adequacy of this search is the fact that these heterocycles are isosters of natural purines. Today, the antitumor activity of azolo[1,5-*a*]pyrimidines is a promising but understudied topic. Despite numerous synthetic approaches to obtaining this series of heterocycles, 5-amino-substituted derivatives of **6**, **7** are obtained in extremely low yields and with a large number of stages, and always require the use of chlorodeoxygenating reagents and often subsequent hydrolysis of the halide. Therefore, we developed a new method based on heterocyclization with a modified Meldrum acid derivative **2**.



It was shown that heating aminoazoles **1** with substrate **2** in DMF in the presence of potassium carbonate leads to the formation of the corresponding salts of 5-R-aminoazolo[1,5-*a*]pyrimidin-7-ones **5** in high yields. It is assumed that initially the methylthiogroup is replaced by a heterocyclic amine to form salt **3**, which is further heterocyclized to dipotassium salt **4**. Intermediate **4** decarboxylates upon heating to form products **5**. Despite the apparent simplicity of the process, only the isolation of intermediate **4** in its pure form made it possible to propose this reaction pathway, since it was previously noted in the literature that substitution of the second methylthiogroup in substrate **2** was possible only at certain pH values [1], and also that substrate **2** was capable of releasing acetone and carbon dioxide molecules upon heating [2].

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University project within the Priority-2030 Program) is gratefully acknowledged

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Synthetic strategy toward photoactive heterostyrenes on pyrrole-, and indole-based matrices

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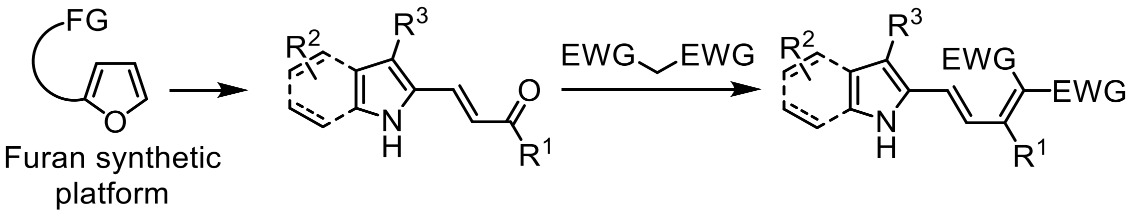
Push-pull chromophores have been studied as light-absorbing compounds in dye-sensitized solar cells as an alternative to inorganic materials due to lower cost and manufacturing simplicity.

In our research project aiming at developing convenient synthetic methods toward potential push-pull chromophores based on the indole and pyrrole matrices obtained via furan dearomatization strategy we utilize an alkanone fragment as a masked linker connecting donor and acceptor units via oxidation/condensation transformation sequence.



Synthetic details as well as physicochemical, optical, and electrochemical properties of the obtained products will be discussed.

This work was supported by Russian Science Foundation (project 22-23-00505)

Water-soluble fluorescent label based on BODIPY derivative: synthesis and photophysical properties

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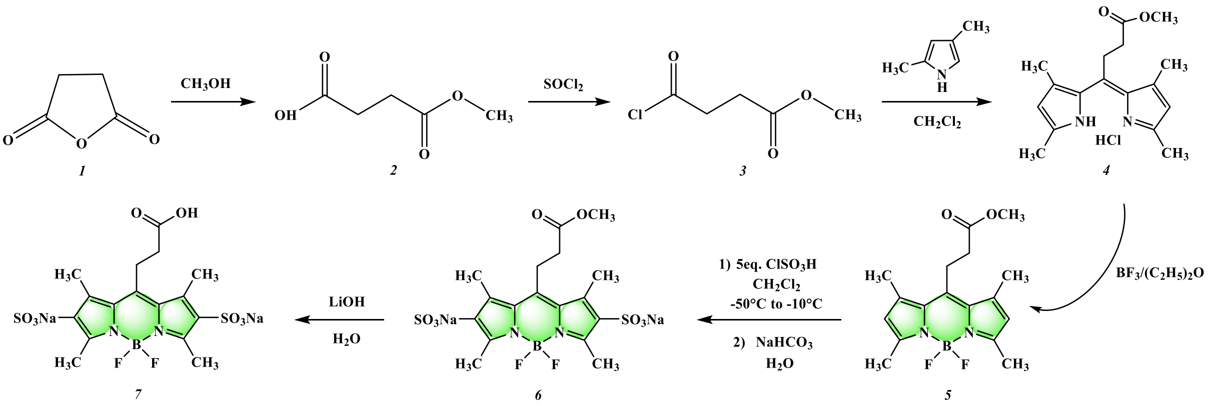
Imaging methods based on fluorescence are widely used in studies of cells and living organisms, as they are highly sensitive and able to provide information of the biochemical interactions at the molecular level. Borondifluorodipyrromethene derivatives (BODIPY) have a number of valuable properties such as low toxity, photostability, high quantum yield and spectral diversity. It makes them promising candidate for use as fluorescent labels. However, a large number of BODIPY derivatives exhibit significant hydrophobicity, therefore, they are subjected to aggregation quenching in the aqueous environment, which leads to decrease in quantum yield and limits the use of these dyes as fluorescent probes in biological systems. Thus, development of modified water-soluble derivatives of BODIPY containing hydrophilic substituents is an urgent task, since wide opportunities are revealed for their use in cell imaging. It should be noted, that the presence of a carboxyl group in the *meso*-position of BODIPY allows it to be conjugated with target biological objects caused by activated esters.



In this work, water-soluble functional derivatives of BODIPY with sulfo-groups in *2*- and *6*-positions were synthesized. The structures of all obtained compounds were confirmed by NMR-, IR-spectroscopy and Mass spectrometry. Absorption and fluorescence spectra in polar solvents were observed, the extinction coefficient and quantum yield were determined and the effect of pH on fluorescent properties were studied. In addition, the protocol for labeling biomolecules with synthesized dyes was developed.

This work was supported by the Russian Science Foundation (grant № 19-73-20194)

Self-oscillating gel based on new catalyst for the Belousov–Zhabotinsky reaction

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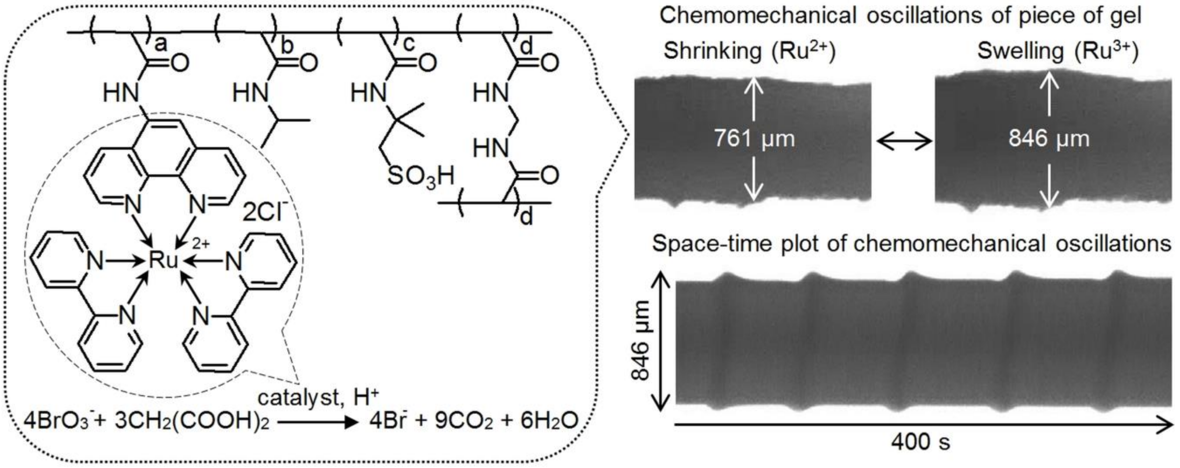
The synthesis of new self-oscillating gels driven by the oscillatory Belousov–Zhabotinsky (BZ) reaction is an actively developing research direction. Such gels have potential application in the design of soft robots and artificial muscles (actuators). To synthesize the gels, most researchers use derivatives of tris(2,2'-bipyridyl)ruthenium(II) complex, Ru(bpy)$_3$, which they covalently bind to polymer materials. When such gels are immersed in an aqueous catalyst-free BZ solution (CFBZ), the oscillatory BZ reaction starts inside the gels generating autonomous periodic redox transitions of the Ru(bpy)$_3$. These transitions induce in their turn the periodic changes in the volume of the gel, i.e., mechanical oscillations. Before our work, complexes of bis(2,2'-bipyridine)(1,10-phenanthroline)ruthenium(II) have not been used as catalysts for the BZ reaction and self-oscillating gels based on them were not created.

We have synthesized bis(2,2'-bipyridine)(1,10-phenanthroline)ruthenium(II) chloride and its derivative bis(2,2'-bipyridine)(5-acrylamide-1,10-phenanthroline)ruthenium(II) chloride, Ru(bpy)$_2$(5-acphen). Both complexes exhibit catalytic activity in the BZ reaction. Complex Ru(bpy)$_2$(5-acphen) is copolymerized with 2-acrylamido-2-methylpropanesulfonic acid (AMPS), N-isopropylacrylamide (NIPA), and N,N-methylenebisacrylamide (MBA). As a result, we have synthesized a gel in which Ru(bpy)$_2$(5-acphen) serves as the catalytic fragment, NIPA as a monomer forming a polymer chain, AMPS as a monomer creating a microstructure, and MBA as the cross-linker.

In the aqueous CFBZ solution, the gel exhibits oscillatory behavior [1]. A piece of the gel swells when Ru(bpy)$_2$(5-acphen) exists in the oxidized state and shrinks when it is in the reduced state. The mechanical oscillations of the gel coincide with the chemical ones. The changes of the linear size of the piece of the gel are about 10%.



This research was supported from the Russian Federal Academic Leadership Program Priority 2030 at the Immanuel Kant Baltic Federal University

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Tuning the detection abilities of BINAM derivatives by structure modifications

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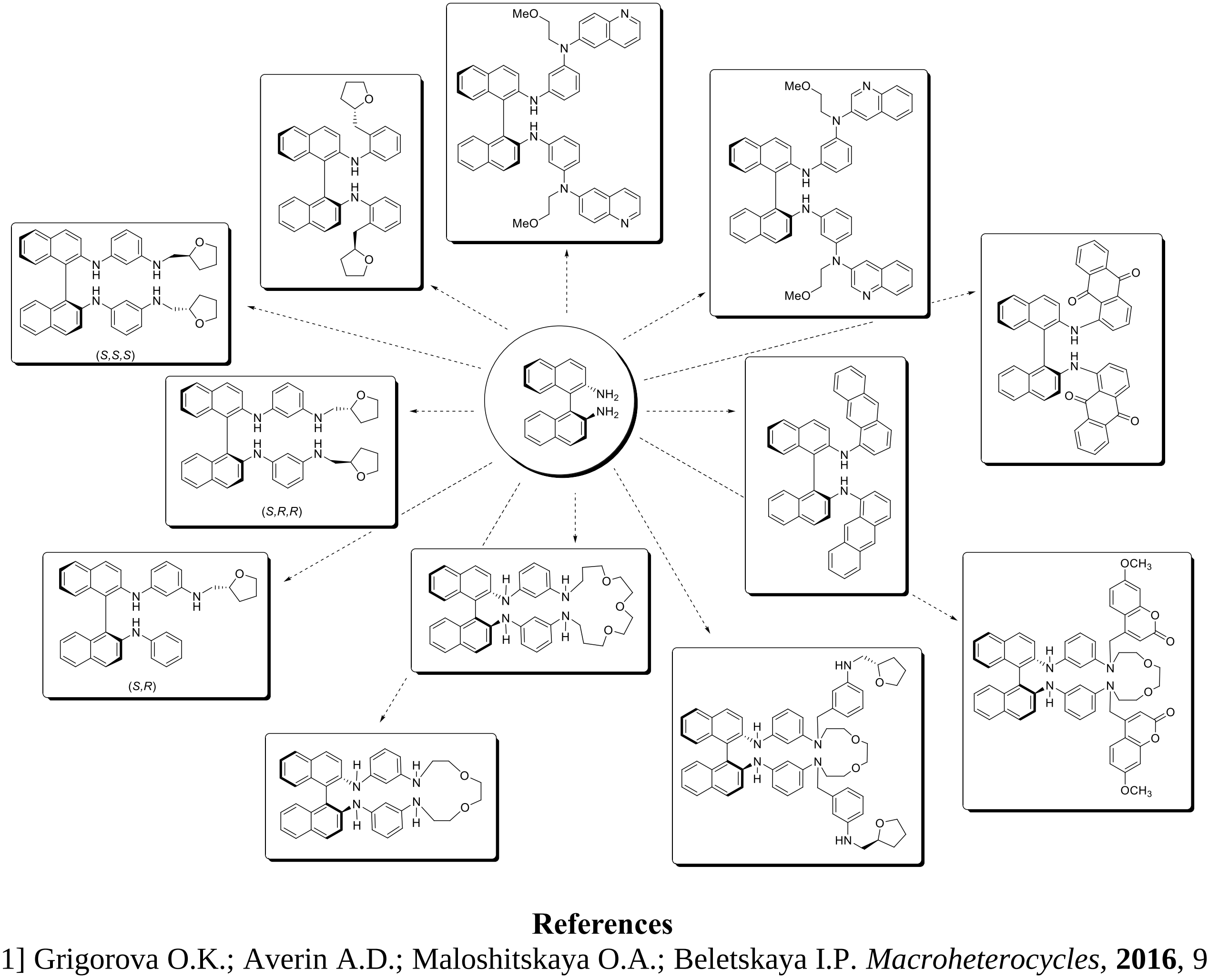
The detection of enantiomers of optically active organic compounds is an important task in the analysis of various natural objects, in the production of modern pharmacological preparations and agrochemicals, in the development of catalysts, and in other areas. Recently we have begun successful investigation of the chiral macrocyclic compounds with endocyclic (S)-2,2’-diamino-1,1’-binaphthalene (BINAM) fragment as fluorescent chemosensors for the selective fluorescent detection of model chiral amino alcohols [1, 2]. In this work a novel series of BINAM derivatives has been synthesized using Pd-catalyzed amination reactions. The detectors thus obtained differ by the nature and number of chiral substituents, presence of the macrocyclic moiety in the structure of the compound, type of the additional fluorophore group and 1,2- or 1,3-disubstitution in the the phenylene spacer. It has shown that even small changes in the structures of these compounds lead to substantial changes in the detecting ability.



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Synthesis of furanones via cyclization of esters of allenecarboxylic acids in triflic acid CF_3SO_3H

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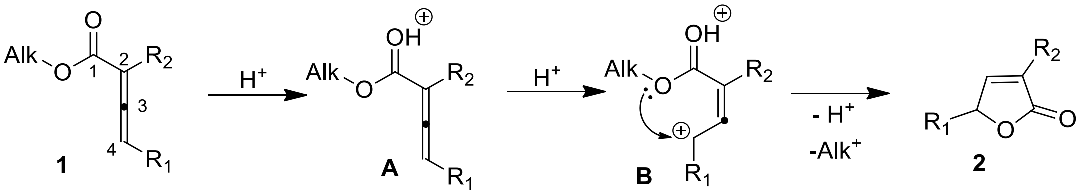
Allenes are widely used in organic synthesis, because of theirs high reactivity and selectivity [1−3]. In this regard, many compounds containing the allene group attracted our attention in the result of their transformations under superelectrophilic activation by Bronsted and Lewis superacids [4−6]. A number of methods were developed in our research group for the synthesis of organic compounds based on the transformation of allenes containing electron-withdrawing substituents under the action of electrophilic reagents: (super) Brønsted and Lewis acids, acid zeolites, etc.

It was shown that, alkyl esters of allenecarboxylic acids **1** are cyclized into furanones **2** in the Bronsted superacid CF_3SO_3H (triflic acid, TfOH) at 60 °C for 45 min in yields of 10−71%. The reaction proceeds through consequent protonation of the carbonyl oxygen and the central carbon of the allene triad leading to cations **A** and **B** correspondingly. The latter is cyclized into furanone **2** at the last stage of the reaction.



H^+ = superacid TfOH
R_1= 4-MeC_6H_4,4-ClC_6H_4,CH_2CH_3, $(CH_2)_3CH_3$
R_2= Me, H

2a: R_1=4-MeC_6H_4, R_2=H, 65%
2b: R_1=4-ClC_6H_4, R_2=H, 10%
2c: R_1=CH_2CH_3, R_2=Me, 71%
2d: R_1=$(CH_2)_3CH_3$, R_2=Me, 25%

In conclusion, a novel method for the synthesis of furanones has been developed based on electrophilic cyclization of esters of allenecarboxylic acids in TfOH.

This work was supported by the Russian Scientific Foundation (grant № 21-13-00006)

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A new method for the synthesis of imidazolidine-2-ones, based on the reaction 1-(2,2-dimethoxyethyl)ureas with *P*-nucleophiles

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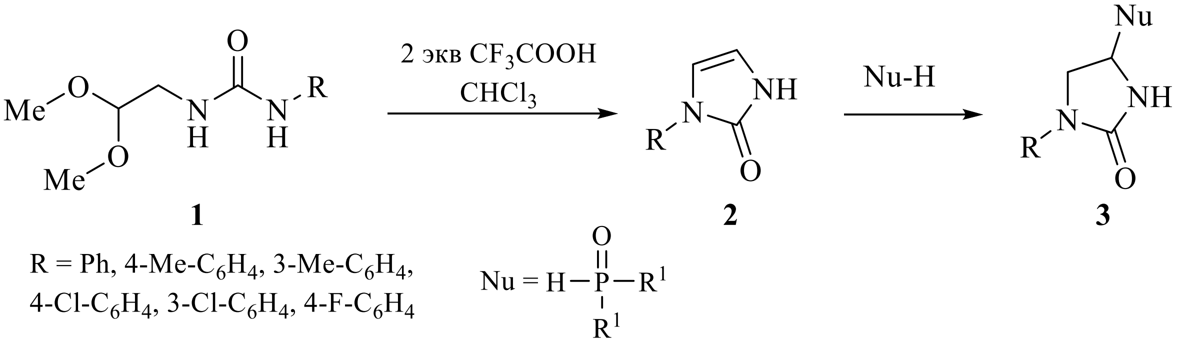
Cyclic urea is widely used in medical chemistry. Of particular interest are derivatives of imidazolidin-2-one **2**, which are part of the antibiotic Azlocillin, used to treat anxiety disorders of Emiserfont, etc. Therefore, it is not surprising that the development of methods for the synthesis of imidazolidines is an urgent task.

We have developed a regioselective method for the synthesis of imidazolidin-2-oh derivatives **3**, based on the acid-catalyzed reaction 1-(2,2-dimethoxyethyl)urea **1** with *P*-nucleophiles. The proposed method does not require strict conditions and allows for wide variation of substituents in the fourth position of the heterocycle.



This work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant № 22-075-64781-1-0001)

IMDAF approach in the synthesis of epoxyisoindoles containing (Thio,seleno)urea moiety

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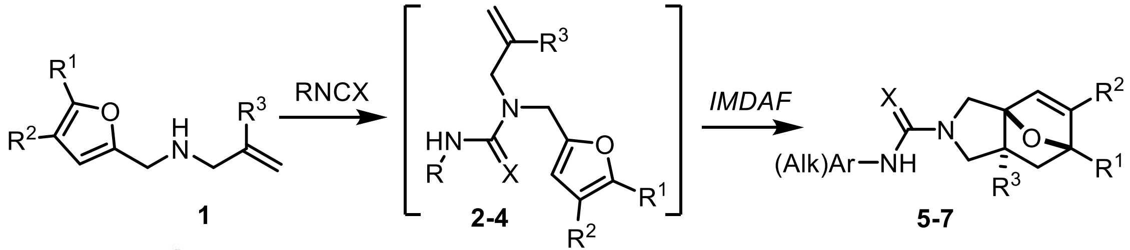
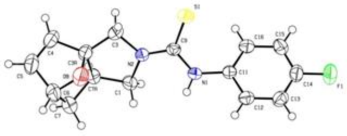
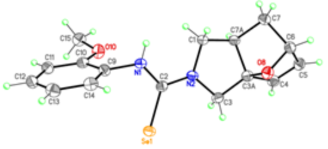
Research in the field of derivatives of urea, thiourea, selenourea occupy a huge niche in organic, pharmaceutical and medicinal chemistry, since a huge number of drugs, dietary supplements, auxiliary compounds used in industry containing the skeletons of these molecules are known. A simple literature analysis shows that since 1990 the number of publications on the synthesis, study of the properties and use of urea, thiourea, selenoureasteadily increasing. The (thio,seleno)ureas attract attention due to their high antitumor activity and, at the same time, acceptably low cytotoxicity. They are used as broad spectrum antimicrobial and antibacterialagents. Thio- and selenoureas are effective scavengers of superoxide radicals, selenoureas act as effective antioxidants, showing low cytotoxicity for some human cells. The importance of (thio)ureas as pesticides, fungicides and bactericides has long been known. In particular, 1,1-dimethyl-3-arylureas such as fenuron, isoproturon, chlorotoluron, methoxuron, monouron and diuron are known as urea herbicides widely used in agricultural practice.

The proposed project is based on the tandem reaction of nucleophilic addition / intramolecular [4+2]-cycloaddition of furylallylamines [1]under the action of alkyl- and aryl- isocyanates, isothiocyanates and isoselenocyanates.





R = Ar, Alk; R^1 = H, Alkyl, Ar,Hal; R^2 = H, Me, Br
R^3 = H, Alkyl, Hal; X = O, S, Se



Itwasshownthatrefluxing allylfurfurylamines**1** with the corresponding alkyl- and aryl-isocyanates, isothiocyanates and isoselenocyanates in benzene or toluene for 6-8 hours leads to the formation of epoxyisoindolyl(thio,seleno)ureas**5-7** in moderate to high yields (49-93%).The *exo*-cycloaddition reaction proceeded stereoselectively with the retention of the substituent R^3 configuration in products **5-7**.

This work was supported by the Russian Science Foundation (RSF) (project №. 22-73-00127)

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Pseudo four-component synthesis of 5,6-dihydroindolo[2,1-*a*]isoquinolines

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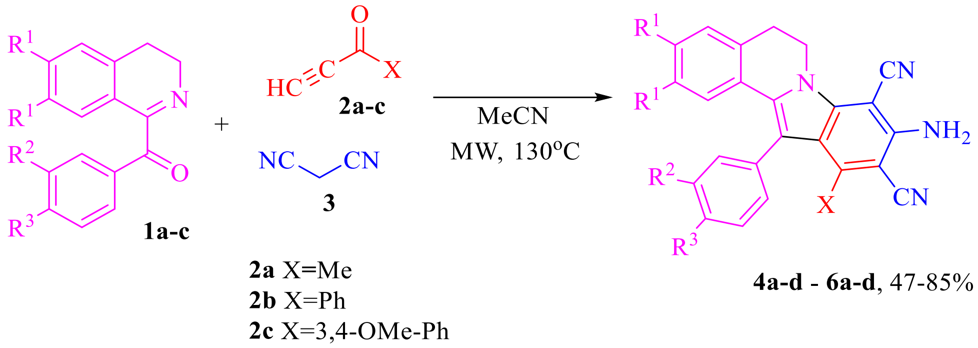
Indolo[2,1-*a*]isoquinolines represent an important class of compounds containing N-fused heterocycles and are the key structural frameworks of many pharmaceuticals and active natural products. Recently our group described the three-component synthesis of 5,6-dihydropyrrolo[2,1-*a*]isoquinolines from 1-aroyl-3,4-dihydroisoquinolines, methyl propiolate and malononitrile.[1] However, the replacement of methyl propiolate with acetylacetylene in reactions with malononitrile leads to pseudo four-component transformation products - 5,6-dihydroindolo[2,1-*a*]isoquinolines **4a-d – 6a-d**. The expected products of the three-component transformation were not isolated even with a significant reduction in the amount of added malononitrile. The reactions were carried out in dry acetonitrile under microwave irradiation at 130°C. The reaction time ranged from 10 to 15 minutes.



All synthesized compounds are yellow crystalline solids, solutions of which exhibit bright fluorescence under UV irradiation. The luminescent properties of the synthesized molecules **4a-d – 5a-d** have been studied in a DCM solution. All compounds showed high emission in the violet-blue region of light. According to the spectra, the photoluminescence maximum is observed at 450 nm. The excitation of molecules is most effective in the near UV region with the maximum at 382 nm (Fig. 1). The measured values of the absolute quantum yield (QY) are shown in Table 1.

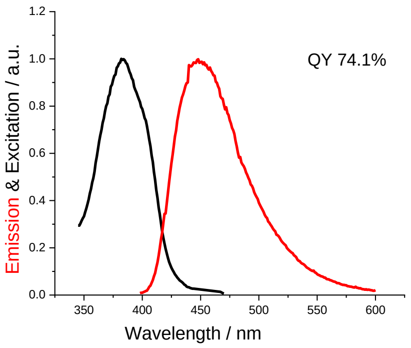


Fig. 1. Excitation (black lines) and emission (red lines) spectra of the **4d** compound.

Compound	R^1	R^2	R^3	X	QY %
4a	OMe	H	H	Me	72%
4b	OMe	F	H	Me	72%
4c	OMe	Cl	H	Me	68%
4d	OEt	OEt	OEt	Me	74%
5a	OMe	H	H	Ph	71%
5b	OMe	F	H	Ph	72%
5c	OMe	Cl	H	Ph	63%
5d	OEt	OEt	OEt	Ph	63%

Table 1. The measured quantum yield (QY)

References

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Synthesis of rearranged angucyclinones

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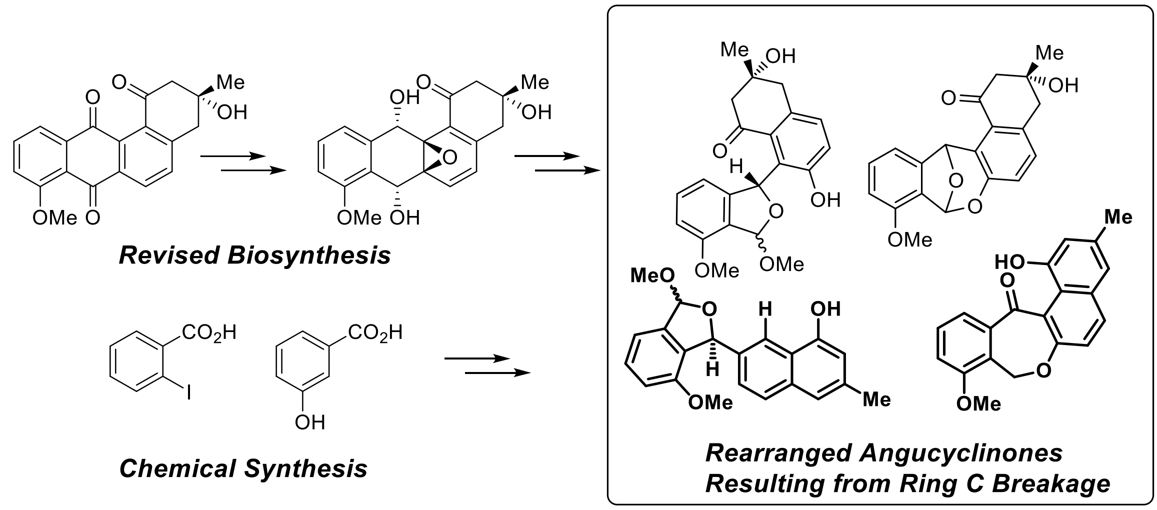
Angucyclines represent a largest family of bacterial metabolites, synthesized by PKS-II.[1] They attracted large attention due to specific antibacterial and anticancer properties, which, however, have never resulted in clinical applications.

Growing bacterial resistance is driving search for potent antibiotics with novel mechanisms of action. In this view, angucyclines are recognized as promising objects due to the diversity of structures, governed by numerous oxidative post-PKS modifications, and well-studied modes of activity. The main obstacles on this way are their poor solubility and several side-effects.



In our work we focused on the recently discovered subgroup of angucycline derivatives – angucyclinones, in which quinone ring C is broken and rearranged by the action of tailoring enzymes. These compounds exhibit better solubility, although significantly lower activity. We revised their biosynthesis in a view that such derivatives could be considered as degradation products and identified their key biosynthetic precursor.[2]

As a part of this work, we focused on chemical synthesis of the selected derivatives to design libraries of the compounds and identify structural motifs responsible for antibiotic activities. The report will address our progress in synthesis[3] and perspective directions.

This work was supported by the grant of the President of the Russian Federation
(Grant № MK-736.2021.1.3)

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Photoinduced assembly of 3,4,4a,7a-tetrahydro-1*H*-cyclopenta[*b*]pyridine-2,7-dione core on the basis of allomaltol derivatives

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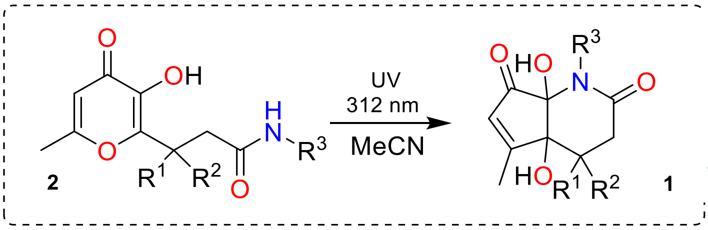
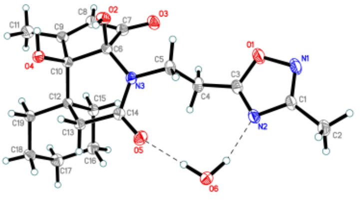
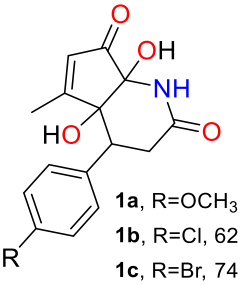
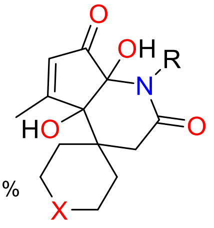
In recent years, photochemical processes are attracting increasing attention of researchers due to the wide use in various fields of organic chemistry. An important area of photochemistry is the study of the behavior of heterocyclic compounds under UV irradiation. Among the vast variety of heterocyclic systems, phototransformations of 4-pyranone derivatives attract considerable attention.

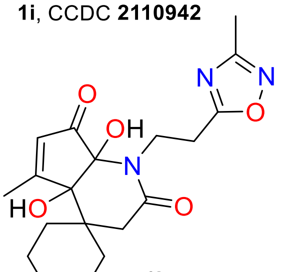
In present study we elaborated novel one-step photochemical method for the synthesis of 4a,7a-dihydroxy- 5-methyl-3,4,4a,7a-tetrahydro-1*H*-cyclopenta[*b*]pyridine-2,7- diones **1** from 3-hydroxypyran-4-one derivatives containing a propionylamide fragment **2**. The suggested approach based on cascade process including initial photoinduced contraction of 4-pyranone ring followed by intramolecular cyclization leading to the final six-membered tetrahydropyridine core. A distinctive feature of the considered approach is the use of the side chain amide function as a trapping element for the final cyclization with photogenerated α-hydroxy-1,2-diketone units. The advantages of the presented synthetic method are good yields, mild reaction conditions, atom economy and easy workup procedure. The structures of two synthesized 4a,7a-dihydroxy- 5-methyl-3,4,4a,7a-tetrahydro-1*H*-cyclopenta[*b*]pyridine-2,7- diones (**1c**, **1i**) were determined by X-Ray diffraction.

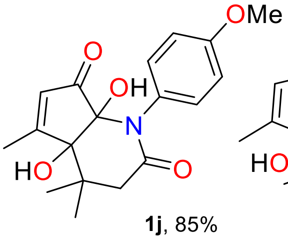


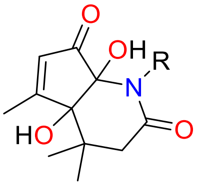

1i, CCDC **2110942**

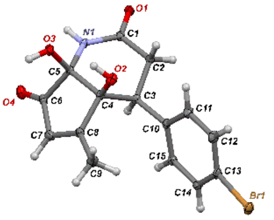

1a, R=OCH$_3$, 56%
1b, R=Cl, 62%
1c, R=Br, 74%


X = O
1d, R=H, 86%
1e, R= (CH$_2$)$_3$OCH$_3$, 70%
X = CH$_2$
1f, R=H, 73%
1g, R=(CH$_2$)$_3$OCH$_3$, 63%
1h, R=CH$_2$C$_6$H$_5$, 67%


1i, 78%


1j, 85%


1k, R=NH$_2$, 71%
1l, R=(CH$_2$)$_3$OCH$_3$, 56%
1m, R=CH$_2$C$_6$H$_5$, 62%
1n, R=(CH$_2$)$_2$C$_6$H$_5$, 59%
1o, R=(CH$_2$)$_2$C$_6$H$_5$, 59%


1c, CCDC **2110941**

This work was supported by the Russian Science Foundation (Project № 18-13-00308-P)

Regiodivergent metal-controlled synthesis of heterocyclic phosphonates from phosphoryl-substituted ynones

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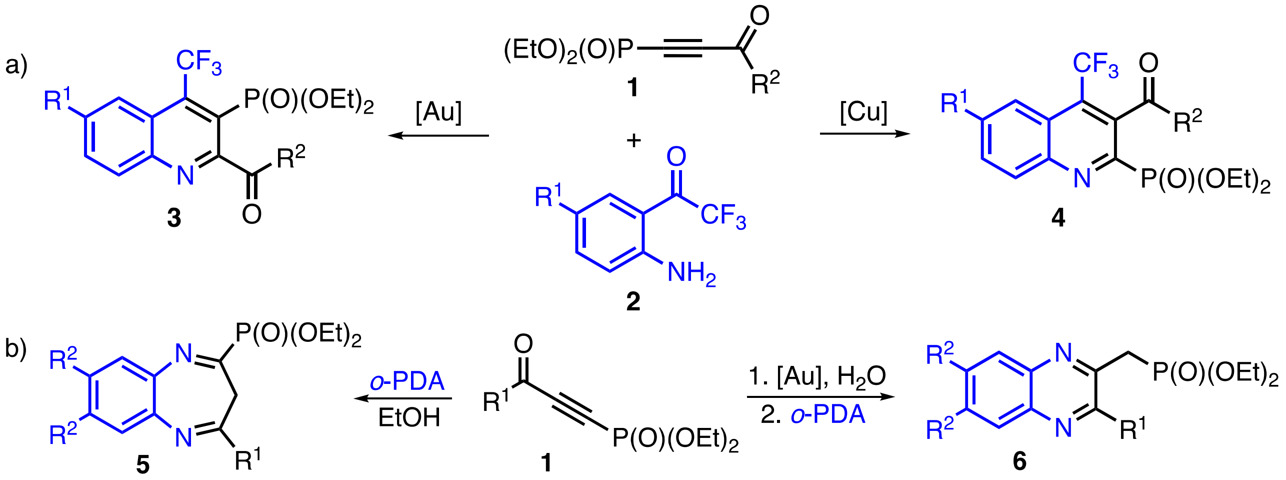
Phosphonic acids and their derivatives found a wide application in organic synthesis, biochemistry, pharmaceutical chemistry, agrochemistry, and material science [1-3]. The synthesis of phosphorylated heterocycles is among the particularly important procedures, as the presence of organophosphorus functionality could often improve the physical and biological reactivity of the parent heterocycles.

Alkynylphosphonates are compounds studied extensively because their triple bond can be easily modified, resulting in new organophosphonates using domino reactions, which is important for the atom economy synthesis of new heterocyclic compounds. These reactions are carried out often divergently depending on conditions or catalysts [4,5]. Here, we present the regiodivergent synthesis of various heterocyclic phosphonates from 3-oxoprop-1-yn-1-ylphosphonates **1**. Using the metal-catalyzed reaction of **1** with 1-(2-aminophenyl)-2,2,2-trifluoroethan-1-ones **2**, a series of new trifluromethylated quinolin-3-ylphosphonates **3** and quinolin-2-ylphosphonates **4** were prepared in good yields. In addition, the reaction of ynones **1** with *o*-phenylenediamines provides a series of phosphoryl-substituted 1,5-benzodiazepines **5** or quinoxalines **6** in high yields.



This work was supported by the Russian Science Foundation (RSF, grant No. 21-73-00147)

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Using the click methodology for the synthesis of PEG-substituted polyaromatic chemosensors for the detection of nitroaromatic compounds

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Zyryanov G.V. [1,2], Charushin V.N. [1,2], Ranu B.C. [1,3]

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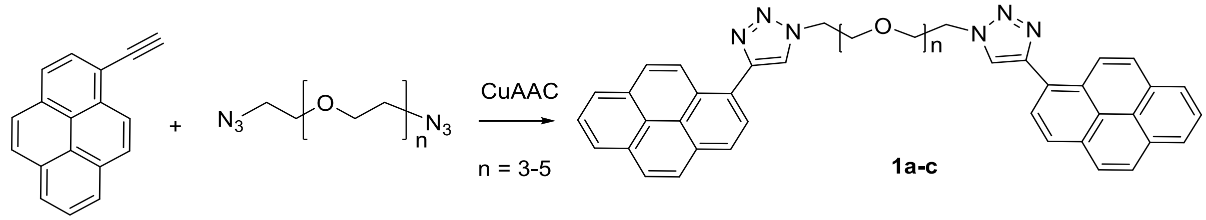
Polyaromatic compounds are effective chemosensors for the fluorescence "turn-off" detection of nitroaromatic compounds (explosives), as well as other electron-deficient/charged analytes.

Using the CuAAC procedure [1], we synthesized PEG-containing polyaromatic chemosensors 1a-c (Fig. 1). In aqueous acetonitrile in the presence of nitroaromatic compounds, intense fluorescence quenching is observed. In the case of chemosensor 1a (n = 3), the value of the quenching constant (Stern-Volmer constant) for 2,4,6-trinitrotoluene (TNT) was calculated to reach 1.39×105 M-1 (Fig. 2).



1a-c

Figure 1. Synthesis of chemosensors **1a-c** using click-methodology

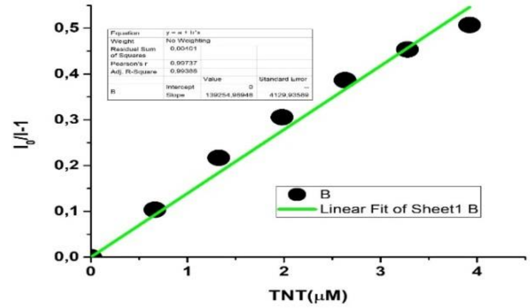


Figure 2. Calculation of the quenching constant for the chemosensor **1a** in case of TNT

This work was supported by the Russian Science Foundation (Grant no. 19-73-10144-P) and the Ministry of Science and Higher Education of the Russian Federation (Agreement no. 075-15-2022-1118, June 29, 2022)

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The combination of the key structural features of Triazavirin and Remdesivir in the development of azoloazine C-nucleosides

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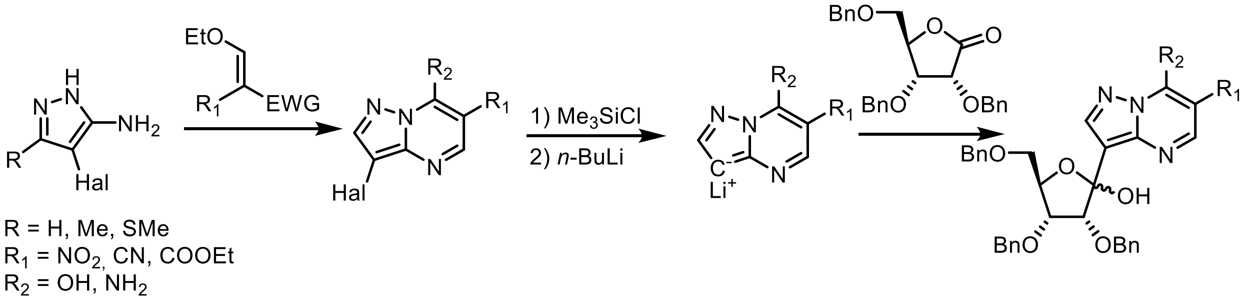
Currently, a decrease of COVID-19 infection cases is an undeniable achievement of global vaccination. However, there are patients with severe form of coronavirus infection who need emergency care as well as further mutations of this virus has to be expected. Accordingly, the search for new generation of antiviral drugs as therapeutic tool for COVID-19 remains an urgent task.

Remdesivir, a nucleotide analogue, has demonstrated promising antiviral activity and was approved by FDA to treatment patients with COVID-19 [1]. Unfortunately, a number of side effects manifested during this treatment [2]. The second drug that showed activity against SARS-COV-2 virus *in vitro* and positive therapeutic feedback is Triazavirin [3]. Negative side effects during clinical trials were not registered in this case.

We decided to combine the key structural features of both Triazavirin and Remdesivir to synthesize a series of novel C-nucleoside analogues with potential antiviral activity.



R = H, Me, SMe
R_1 = NO_2, CN, COOEt
R_2 = OH, NH_2

Based on this strategy, we synthesized a series of bromo- and iodo-containing azoloazine derivatives. This approach was accompanied by novel *one-pot* method for the synthesis of 3H-pyrazolo[1,5-*a*]pyrimidines which are precursors for bromination and iodination. Additionally, a critical review of the C-nucleosides synthetic methods was performed and promising strategies have been highlighted.

This work was supported by RSF (grant № 22-23-00282)

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Copper nanoparticles for C-N and C-S bonds formation

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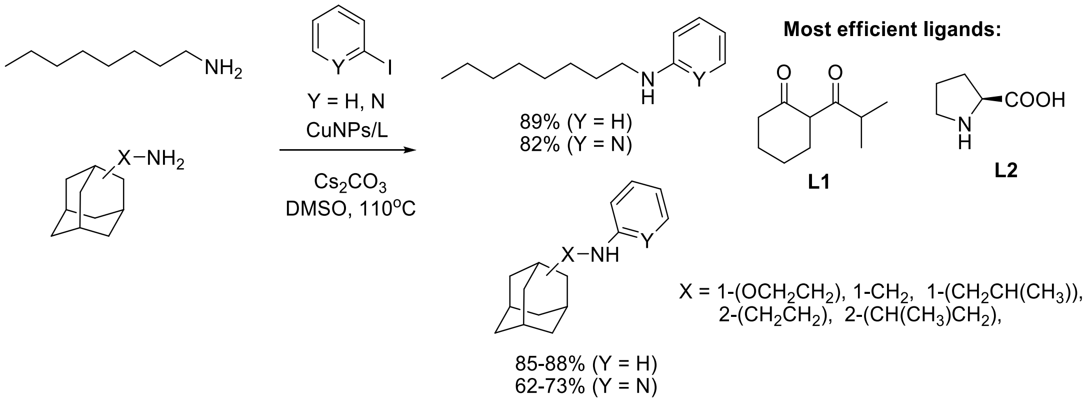
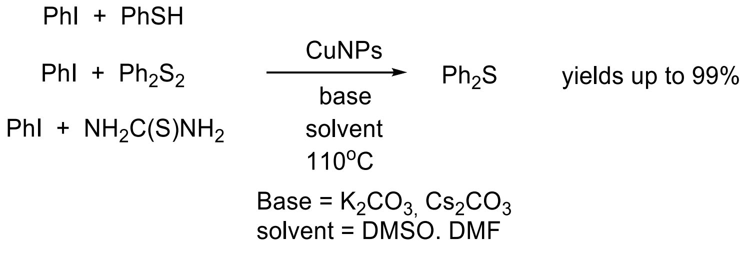
The development of the copper catalysis for the construction of C(sp^2)-N and C(sp^2)-S bonds is associated with the use of copper nanoparticles (CuNPs) due to many advantages of their performance like possibility of separation and multiple use of the catalyst, low catalyst loadings and other favorable features. We have focused on the application of free CuNPs without any support which are commercially available. It was found out that in the model reactions of *n*-octylamine with iodobenzene and 2-iodopyridine CuNPs of the average size 25 nm were quite efficient in the presence of the ligands L1 and L2 (Scheme 1) providing high yields of N-aryl derivatives [1]. DMSO at 110°C proved to be the best solvent in this process. It was shown that various adamantane-containing amines gave high yields of the corresponding N-phenyl derivatives while the yields of their N-pyridyl derivatives were somewhat lower due to side reactions. Reuse of the catalyst was demonstrated to be possible up to 8 cycles without loss of its performance.

CuNPs were very efficient on the formation of C(sp^2)-S bond with thiophenol, diphenyl disulfide and thiourea (Scheme 2). These reactions did not demand the use of additional ligands and ran equally smooth in DMSO and DMF. The possbility of application of various substituted iodobenzenes was shown.



Scheme 1.



Scheme 2.

This work was supported by the Russian Science Foundation (grant № 19-23-00223P)

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Synthesis of carborane-graphene dyads

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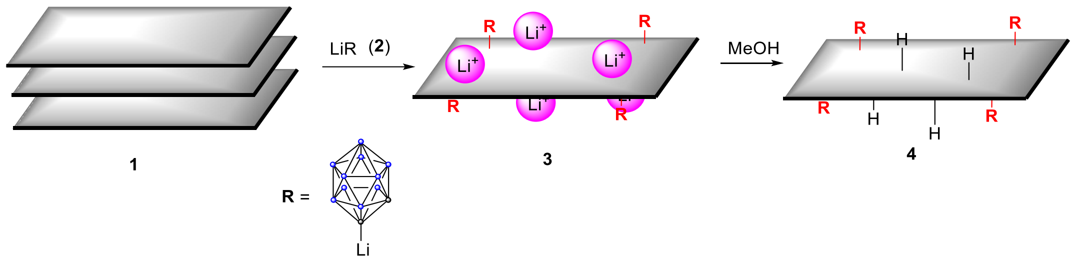
Chemical doping is known to influence electronic structures and redistribution of charge density [1]. Boron atoms, which are covalently doped in the structures of graphene, enable electron deficiency for p-type doping. Introduction of boron into carbon materials can shift their Fermi level and modify the electronic structures of graphene [2].

The strategy for graphene transformation by *closo*-carborane is a simple *one-pot* method (Scheme 1). The first step is the reaction of graphene with organolithium compound. The addition of carboranyl lithium **2** in dry THF to graphene afford graphenide **3** (Scheme 1), thus changing color of the reaction mixture from dark gray to light gray and giving a more homogeneous suspension. The second step is the quenching by methanol.



Sheme 1. The covalent functionalization of graphene by *closo*-carborane.

The structure of carborane-graphene dyad was verified by complex of modern physicochemical analyses methods (the Raman spectroscopy, FTIR, XPS, SEM and TGA analyses) (Figure 1).

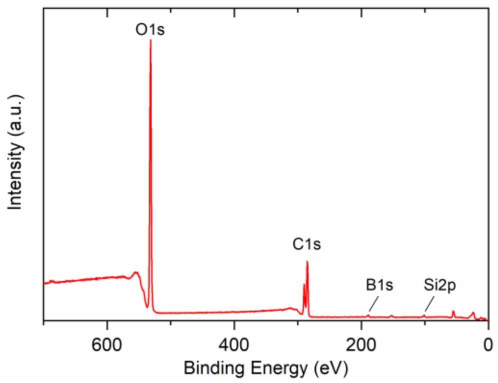


Figure 1. XPS survey spectra of graphene **4**.

This work was supported by the Russian Science Foundation (grant № 22-13-00298)

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Synthesis of 2,4-disubstituted furans by extended Corey-Chaykovsky reaction

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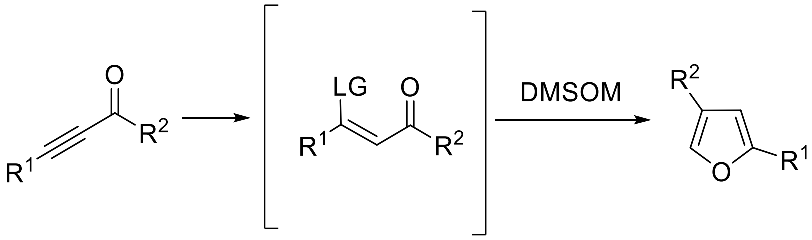
Furans are an important class of heterocyclic compounds with versatile reactivity, biological activity, and useful physicochemical properties. Currently, there is no simple and effective protocol for the synthesis of 2,4-disubstituted furans despite the fact that today many methods for the synthesis of furans are known. We proposed that 2,4-disubstituted furans are promising building blocks for organic synthesis, medicinal chemistry, and materials.

Corey-Chaykovsky reaction it is the process of forming three-membered rings from carbonyl compounds, their imines and activated alkenes through interaction with a sulphur ylide. Previously, extended version of this reaction was developed [1]. The oxirane ring opens to form a new product, unlike the original reaction where it is the final product. In this work, we present a method for the synthesis of 2,4-disubstituted furans based on an extended version of the Corey-Chaykovsky reaction.



Obtained products, limitations of the developed method and its scope will be discussed in this report.

This work was supported by Russian Science Foundation (project № 21-73-10063)

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X-Ray structural analysis and crystallographic study of coordination compounds of 3d-metals with nitrosyl radicals

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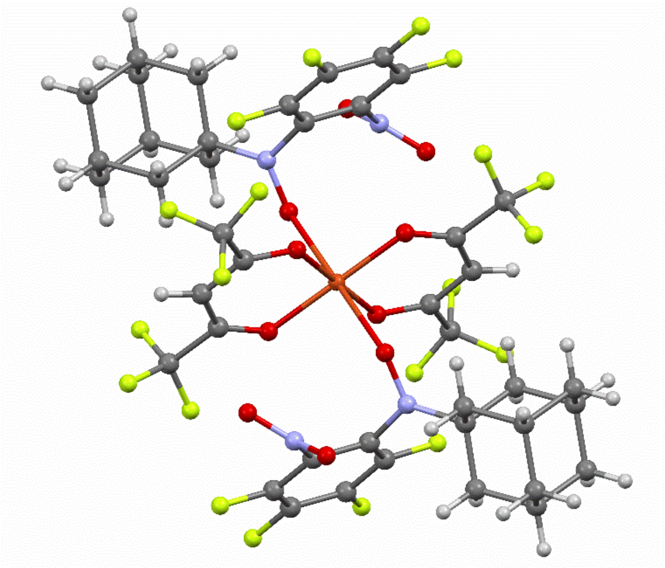
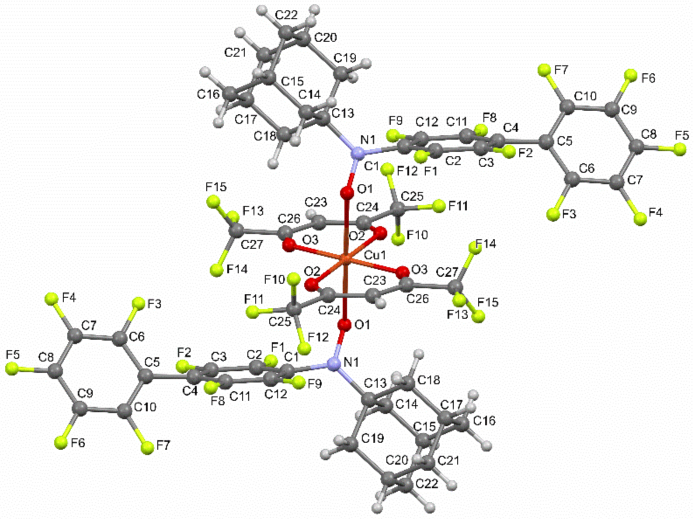
The complex formation of metal ions with conjugated nitroxides with the formation of heterospin systems has opened up a new direction in the field of molecular design of magnets [1, 2], which has been intensively developed in recent years [3].

In the framework of this work, X-ray diffraction analysis of single-crystal samples of coordination compounds of copper (II), manganese (II), cobalt (II), and nickel (II) with nitrosyl mono- and biradicals was carried out. The report will present the results of X-ray diffraction analysis, including features of the geometry of molecules, the nature of their packing in crystalline phases, and short contacts, including those involving paramagnetic centers.





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Glyphosate binding by peptidomimetics based on pillar[5]arene for DNA protection

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About 1.8 billion people around the world are engaged in agriculture and most of them use pesticides to protect crops. In addition, pesticides are used for professional (public health programs) and commercial purposes, as well as for the treatment of lawns and gardens, the home and the surrounding area. However, the use of pesticides inevitably causes serious harm to both human health and the ecosystem. Most of the pesticides used in agriculture do not reach cultivated plants, which is largely due to the dispersion of pesticides into the environment due to degradation, photolysis, and volatilization of pesticides. Research conducted mainly in industrialized countries has established health effects of pesticide exposure, including reproductive health effects and cancer incidence.

Nowadays supramolecular encapsulation by macrocyclic compounds (cyclodextrin, calixarene, cucurbituril, and others) has become one of the approaches for removing toxic substances from the environment, which has significantly reduced unwanted side effects on living systems. The application of the achievements of supramolecular chemistry in agriculture will solve the problem of food security by reducing the pollution of the ecosystem and reducing the toxicity to animals and humans. Among all the variety of macrocyclic compounds, pillar[n]arenes attract special attention. Pillar[n]arenes have become in demand in host-guest chemistry and supramolecular chemistry due to their unique architecture and physicochemical properties. The possibility of regioselective functionalization of pillararenes makes it possible to preorganize a macrocyclic molecule, which significantly expands the possibility of their application. A number of polyfunctional derivatives of pillar[n]arenes have good water solubility, low toxicity, and selective binding to guest molecules, which makes it possible to create macrocyclic antidotes on their basis.

Thus, novel water-soluble derivatives of pillar[5]arene containing *L*-Phe residues were synthesized. It was found that the synthesized macrocycles form stable aggregates with an average hydrodynamic diameter of 138-179 nm, which was confirmed by dynamic light scattering and transmission electron microscopy. It was shown that the synthesized pillar[5]arene derivatives do not interact with the herbicide glyphosate, while glyphosate is able to bind DNA from salmon sperm with $\lg K_{ass} = 4.9$. It was also found that the betaine derivative of pillar[5]arene containing fragments of *L*-Phe binds DNA with $\lg K_{ass}=5.2$. The study of the interaction of the pillar[5]arene-DNA associate with glyphosate showed that the interaction of glyphosate with DNA is inhibited. Competition between the macrocycle and glyphosate for interaction with DNA would potentially protect DNA molecules from the effects of herbicides.

This work was supported by the Russian Science Foundation
(grant № 21-73-00093, https://rscf.ru/project/21-73-00093/)

Synthesis of N,O-heterobiaryl ligands and their tetracoordinate boron complexes

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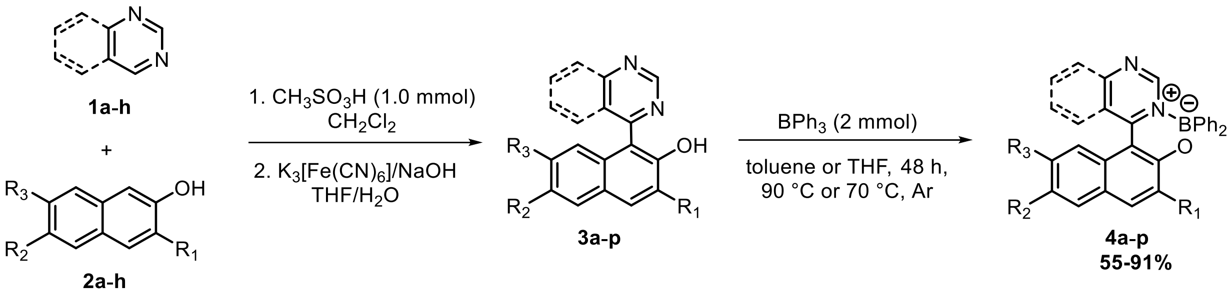
The development of effective methods for the synthesis of promising azine containing ligands is a challenging task of synthetic and material chemistry. Heterobiaryl, containing -OCCCN-chelating unit, are attractive scaffolds for metal complexes.

On the one hand the discovery of tri-(8-hydroxyquinolate)aluminum as a highly efficient electron transport and emitting material, but less stable than its boron derivatives, contributed to an active search for new practically suitable boron-based compounds. On the other hand 2-pyridylphenols form stable 6-membered photoactive boron complexes showing a broad spectrum of fluorescence from deep blue to green.

It was shown that 1,3-diazines interact with 2-naphthols in the presence of Brønsted acid to compounds **3a-p** (Scheme 1) [1]. Tetracoordinated boron luminophores **4a-p** were synthesized by treatment formed N,O-ligands with BPh_3 either in toluene or THF for 48 h. Photophysical investigations of complexes were carried out both for a solid state and a solution.



R_1 = OMe, CN;
R_2 = Br, OMe, CN, carbazolyl;
R_3 = Br, OMe

Structure of compounds **4a-p** have been confirmed by X-ray analysis, NMR, IR, ES-MS and elemental analysis.

This work was supported by the Russian Science Foundation (grant № 22-13-00298)

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Polyelectrolyte complexes based on natural polysaccharides for controlling ciprofloxacin release

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The preparation of polymeric bioactive compounds has a special medical and chemical potential. It is realized by the methods of modern polymer chemistry and medicinal chemistry. The use of chitin, chitosan and hyaluronic acid derivatives for this purpose is particular interesting, since these polymers are biocompatible, biodegradable and non-toxic [1].

The high biocompatibility of polyelectrolyte complexes based on the mentioned polymers is combined with their high mechanical strength, physicochemical stability and stability of the suspension for a long time, as well as the possibility of including antibiotics in the complex [2].

In this study, we elaborated polyelectrolyte complexes based on the cationic chitosan derivative (chitosan-GTMA) and sodium hyaluronate as a polyanion. We obtained polyelectrolyte complexes, both empty and loaded with ciprofloxacin. We used the ratio of initial polymers 1:1, the concentration of initial solutions 0.4 mg/ml and the degree of loading of the antibiotic into the complex 66%.

The synthesized complexes were characterized by XRD, IR and TGA methods. We evaluated the hydrodynamic radii and ζ potentials of the obtained particles, and also the kinetics of ciprofloxacin release from the resulting system [3]. The percentage of antibiotic release was 99.74% of the total weight of the initial ciprofloxacin in 20 hours.

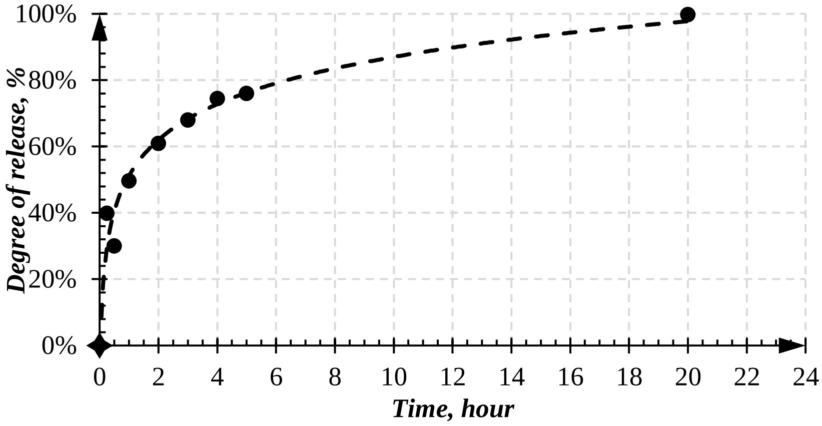

Figure 1. Kinetics of ciprofloxacin release

We plan to use the obtained PECs for targeted drug delivery of fluoroquinolone antibiotics and elaborate long-acting dosage forms of fluoroquinolones. Thus, this project is now underway in our group.

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Transformations of 1-carbomethoxyalkynyl-2-carbomethoxyvinylisoquinolines under the action of nucleophiles

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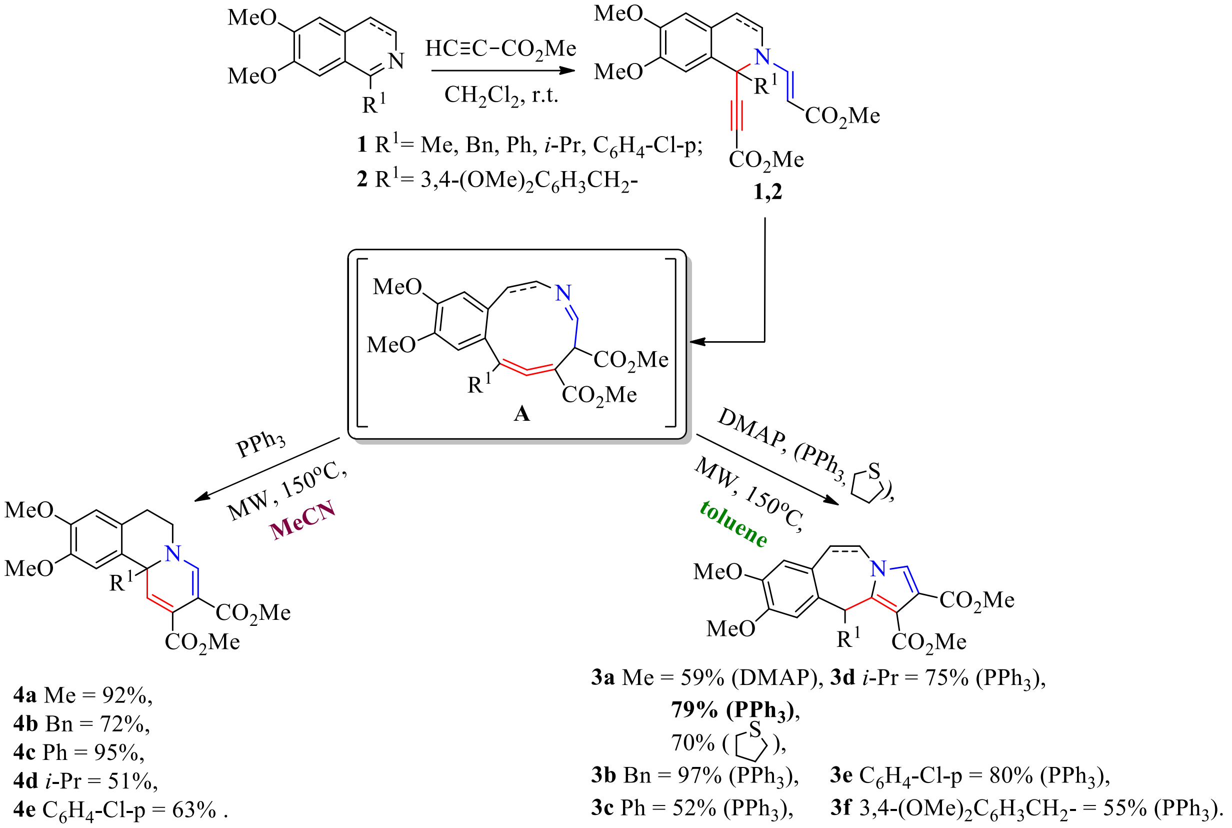
[3,3]-Sigmatropic rearrangements are a convenient method for obtaining various heterocyclic systems [1]. In this work, we report a new approach to the synthesis of pyrrolo[2,1-*b*][3]benzazepines and pyrido[2,1-*a*]isoquinolines based on the [3,3]-transformation of substituted isoquinolines. Starting compounds **1** and **2** containing methoxycarbonylethynyl and methoxycarbonylvinyl groups in positions 1 and 2 were obtained by the reaction of 1-R^1-6,7-dimethoxy-3,4-dihydroisoquinolines and papaverine with an excess of methyl propiolate.



1 R^1= Me, Bn, Ph, *i*-Pr, C_6H_4-Cl-p;
2 R^1= 3,4-$(OMe)_2C_6H_3CH_2$-

1,2

A

4a Me = 92%,
4b Bn = 72%,
4c Ph = 95%,
4d *i*-Pr = 51%,
4e C_6H_4-Cl-p = 63% .

3a Me = 59% (DMAP), **3d** *i*-Pr = 75% (PPh_3),
79% (PPh_3),
70% (S),
3b Bn = 97% (PPh_3), **3e** C_6H_4-Cl-p = 80% (PPh_3),
3c Ph = 52% (PPh_3), **3f** 3,4-$(OMe)_2C_6H_3CH_2$- = 55% (PPh_3).

It was shown that pyrrolo[2,1-*b*][3]benzazepines **3a-f** are formed in toluene, while pyrido[2,1-*a*]isoquinolines **4a-e** are formed in the more polar acetonitrile. The reaction was carried out at 150°C and microwave activation. In our opinion, under the action of nucleophiles (DMAP, triphenylphosphine and tetrahydrothiophene), the formation of intermediate benzazecines **A** with an allene fragment occurs. We suppose that the solvent polarity determines the attack direction of the nitrogen atom in benzazecine **A** on the allene fragment. This explains obtaining two different types of heterocycles.

References

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Evaluation of the ability of mides 2-(2-hydroxyphenylthio)acetic acid containing pyrrolidine fragment to act as free radical scavengers

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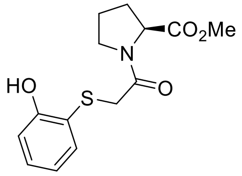
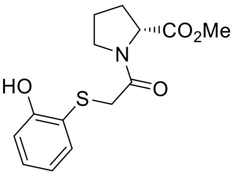
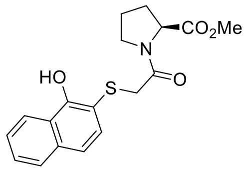
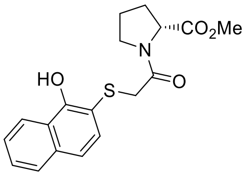
The alkaloids are widespread in nature, which are derivatives of proline and pyrrolidine and have a certain biological and physiological activity [1]. Phenolic compounds provide a relatively stable free radical after losing a hydrogen atom and so have extensively studied as antioxidants [2]. Currently, the most relevant work is the synthesis and study of the biological activity of sterically hindered phenol derivatives, containing a fragment of proline and pyrrolidine, since these compounds can potentially exhibit high antioxidant activity [3]. In this work, the possibility of amides 2-(2-hydroxyphenylthio)acetic acid containing pyrrolidine fragment **1-4** interaction with stable radicals (DPPH, $ABTS^{\bullet+}$ and $NO^{\bullet}$) was investigated.

% of inhibition	 **1**	 **2**	 **3**	 **4**
DPPH, 100 μM	32.84 ± 1.38	38.33 ± 1.20	89.63 ± 1.20	88.60 ± 0.95
$ABTS^{\bullet+}$, 25 μM	23.62 ± 1.13	15.32 ± 0.75	31.90 ± 1.23	21.88 ± 0.95
NO•, 125 μM	17.55 ± 0.57	17.22 ± 0.84	17.73 ± 0.83	14.97 ± 0.46

Potential antioxidants must be easily release electrons or hydrogen atoms and form more stable radicals. The compounds **1–4** to interact with the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH), the 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) cationic radical ($ABTS^{\bullet+}$) and nitric oxide ($NO^{\bullet}$). It is interesting to note that compounds **1** and **2**, like compounds **3** and **4**, are enantiomers. Despite the significant similarity of the structures of the studied compounds, the highest antiradical activity is characteristic of enantiomers **3** and **4** (≈ 90% inhibition). The compounds show the same activity in relation to the $NO^{\bullet}$ radical (15-18% inhibition). In the $ABTS^{\bullet+}$ assay compound **2** exhibits the least activity, and compound **3** exhibits the highest activity, in contrast to its optical antipodes **1** and **4**. Only with respect to the DPPH radical, optical antipodes **1** and **2**, as well as antipodes **3** and **4**, exhibit the same activity, while the α-naphthol derivatives are 2 times more active than phenol derivatives. Among the studied compounds, the highest antiradical activity was found for methyl ether (L)-1-(2-((1-hydroxynaphthalen-2-yl)thio)acetyl)pyrrolidine-2-carboxylic acid (**3**). Additional studies on the antioxidant activity of derivatives **1-4** will make it possible to identify a leading substance for practical use.

This work was supported by the Russian Science Foundation (grant № 22-16-00095)

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Amide derivatives of 1,1'-dinaphthylmethane and *rctt* calix[4]resorcinarene: synthesis, ability to recognize and bind ecotoxic metals cations

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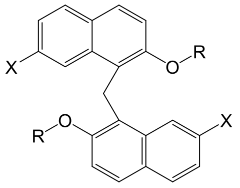
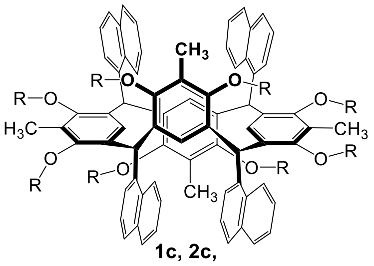
In order to find new receptor systems, series of amid-containing compounds, differing in the structure of the polycyclic core, the number and orientation of functional sites, the nature of amide fragments, and the composition and the size of spacers binding the amide group to the molecular frame were synthesized.

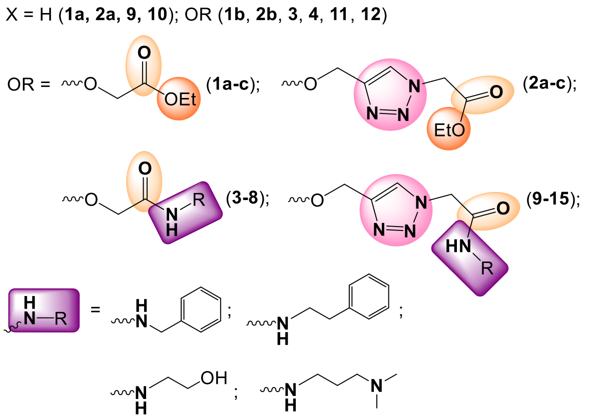
By the aminolysis of ester derivatives of conformationally flexible 1,1'-dinaphthylmethane (**1a**,**b**, **2a**,**b**) [1] and rigid *rctt* C-napthyl-calix[4]resorcinarene (**1c**, **2c**) [2,3] with benzyl-, phenethyl-, ethanol-amines and N,N-dimethyl-1,3-diamine we obtained ligands **3-15** with 2, 4, 8 terminal amide groups in the molecule, linked to the core by short methylene (**3-8**) or longer triazole-containing (**9-15**) spacers.



1a,b, 2a,b,
3, 4, 9-12



1c, 2c,
5-8, 13-15



Using the liquid extraction method, the influence of ligand structural features on its ability to recognize and bind of metal cations was investigated. Amides with short methylene spacer exhibited low activity towards the probed cations. The exception was resorcinarene, containing 8 amide-amine fragments and demonstrating activity and selectivity towards Tb^{3+} and Yb^{3+}. The introduction of triazole ring into the ligand molecule led to increase in the extraction efficiency of Ag^{+}, Hg^{2+}, Cd^{2+} and Pb^{2+} cations, regardless of the polycyclic core nature.

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Synthesis of supramolecular Guest-Host complexes formed by 1,4-benzodiazepin-2-one derivatives with β- and γ-cyclodextrins

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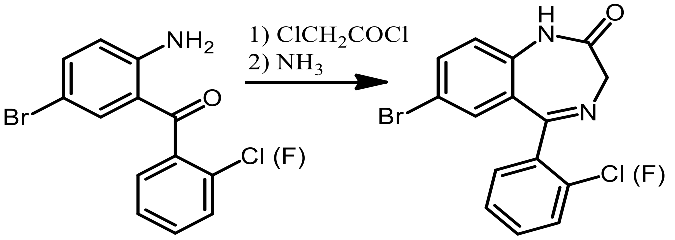
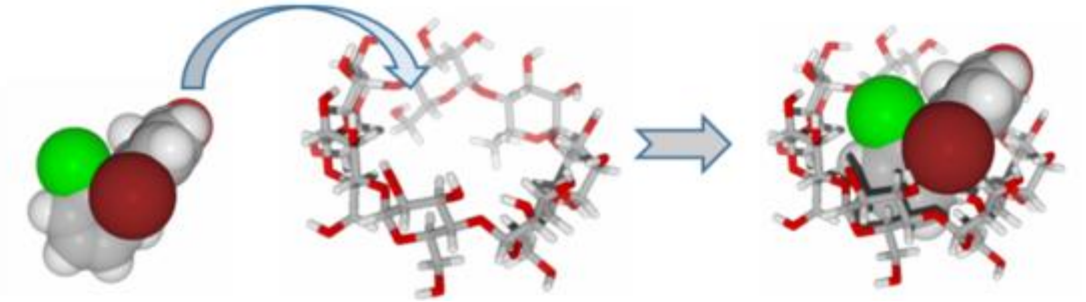
It is known that derivatives of 1,4-benzodiazepines have hypnotic, anxiolytic, anticonvulsant, anorexigenic, orexigenic, analgesic, and other pharmacological properties [1]. At the same time, one of the main indicators of the effectiveness of a drug is its bioavailability, which is directly related to the solubility of the main active substance.

The design of new effective drugs is often hampered by the low bioavailability of the resulting biologically active compounds. In such cases, the development of special delivery systems based on various carriers is required, or the use of higher doses of the drug, which leads to a decrease in its effectiveness and an increase in the toxic load on an organism [2].

To purposefully obtain complexes with optimal thermodynamic characteristics, good solubility, and high biological activity, a molecular modelling of 1,4-benzodiazepine derivatives and their complexes with cyclodextrins was performed using molecular docking, quantum chemical calculations, and the molecular dynamics methods.

Supramolecular complexes of phenazepam and fluorobromazepam with β- and γ-cyclodextrins were synthesized to study the characteristics of bioavailability and pharmacodynamics.





This work was supported by the Tomsk Polytechnic University Development Program (Project Priority-2030-NIP/IZ-009-0000-2022)

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Synthesis of 1,2,4-triazolo[4,3-a]azines as potential HSF1 inductors

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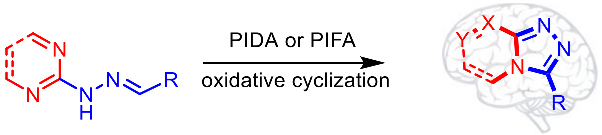
Conformational neurodegenerative pathologies such as Alzheimer's disease, Parkinson's disease, and Huntington's disease develop due to defects in structure of certain proteins specific for each pathology. Molecular chaperones, mostly related to heat shock protein families (HSPs), guide polypeptides through conformational changes, such as de novo folding, assembly and disassembly, transport, and targeting for degradation. The expression of the molecular chaperones is controlled by specific heat shock transcription factor 1 (HSF1). Since an activation of the HSF1 causes elevated synthesis of molecular chaperones, it appears to be a novel strategy for the treatment of the most common neurodegenerative conditions for which no effective treatment currently exists.

In this research, the oxidative cross-dehydrogenative cyclization was demonstrated for the synthesis of 1,2,4-triazolo[4,3-*a*]azines from corresponding azinylhydrazones in the presence of hypervalent iodine(III) (Scheme 1). So, the new 1,2,4-triazolo[4,3-*a*]azines containing both heterocyclic and metallocene fragments have been synthesized [1].



R = thiophen-2-yl, thiophen-3-yl,
5-bromothiophen-2-yl,
ferrocenyl, cymantrenyl

- 24 products with yields 30-98%
- HSF1 inductors
- Compounds can be potentially applied as a protective factor for brain diseases.

Scheme 1

1,2,4-Triazolo[4,3-*a*]azines are able to induce the Hsp70 expression and decrease the mutated huntingtin protein (mHTT) aggregate formation. Taking into account the low toxicity and the highest capacity to suppress HTT aggregation we suggest that these compounds can be potentially applied as a protective factor for brain diseases.

This work was supported by the Russian Science Foundation (grant № 22-13-00298)

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Features of the interaction of ethyl 3-bromo-3-nitroacrylate with dimethyl propanedioate

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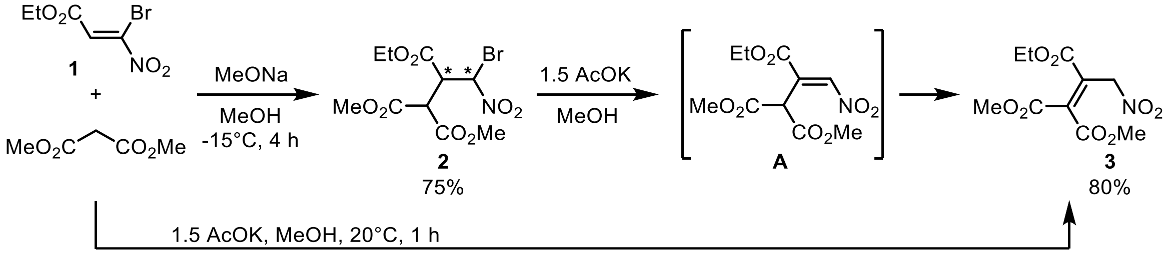
Alkyl 3-bromo-3-nitroacrylates are effective substrates in reactions with cyclic CH-acids leading to the formation of fused furan-3-carboxylates [1, 2]. In the case of the reaction with 2,2-dimethyl-1,3-dioxane-4,6-dione and 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one spiro-fused nitrocyclopropanecarboxylates are formed [3]. It is interesting to study the reactivity of 3-bromo-3-nitroacrylates with acyclic CH-acids. Previously it was shown that the reactions of 3-bromo-3-nitroacrylates with pentane-2,4-dione and methyl 3-oxobutanoate lead to the formation of furan-3-carboxylates [4].

We have studied the interaction of ethyl 3-bromo-3-nitroacrylate **1** with acyclic CH-acid – dimethyl propanedioate. It turned out the reaction in the presence of sodium methoxide (the ratio of bromonitroacrylate : CH-acid : MeONa = 1 : 1 : 1) upon cooling to –15°C in anhydrous methanol for 4 h, the reaction is completed with the formation of the Michael adduct – 2-ethyl 1,1-dimethyl 3-bromo-3-nitropropane-1,1,2-tricarboxylate **2** in 75% yield. Bromonitropropane tricarboxylate **2** undergoes dehydrobromination and subsequent isomerization of the C=C bond of intermediate **A** under the action of fused potassium acetate, turning into 2-ethyl 1,1-dimethyl 3-nitroprop-1-ene-1,1,2-tricarboxylate **3** with the yield 80%. At the same time, carrying out the reaction in the *one pot* mode in the presence of fused potassium acetate also ends with the formation of nitropropene **3**.



Thus, it has been shown that, in contrast to reactions with cyclic enolizable CH-acids, the reaction of 3-bromo-3-nitroacrylates with acyclic CH-acid, dimethyl propanedioate, proceeds along the path of formation of the Michael adduct, which eliminates HBr under basic conditions with the formation of 3-nitroprop-1-en-1,1,2-tricarboxylate.

This work was financially support by the Ministry of Education of Russia (project no. FSZN-2020-0026)

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Ligand-free Cu^0-catalyzed S-arylation of 1,2,4-triazole-3-thioles

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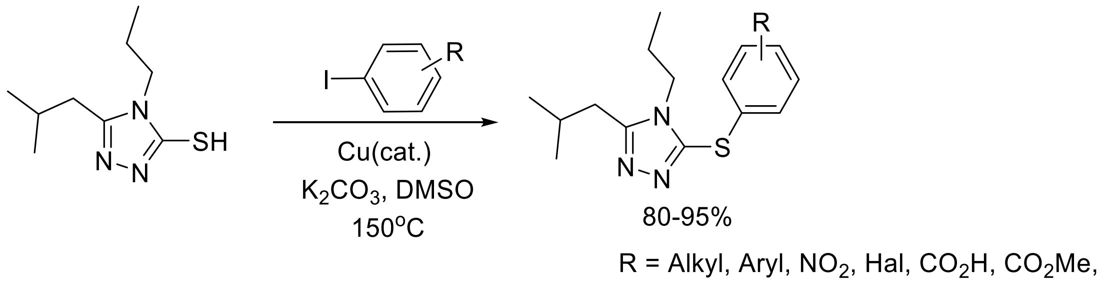
The formation of S-C_{aryl} bonds is a key step in synthesis of many molecules that are biological, pharmaceutical, and material interest. These reactions are not facile and require hard conditions. The S-aryl-1,2,4-triazole-3-thioles can be predominantly found in compounds with antiviral, antiinflammatory, antibacterial, and antitumor properties.

Considering the above facts, the cross-coupling reaction of 1,2,4-triazole-3-thioles and aryl halides was optimized.

As a model reaction, the coupling between 5-isobutyl-4-propyl-4*H*-1,2,4-triazole-3-thiol and phenyl iodide was chosen. Copper was used as a catalyst, due to its availability and practicality in such reactions [1]. Optimal conditions for the reaction, including the best base and solvent were developed. The chosen conditions bring an excellent yield(90%) of reaction. Further the impact of substituent and it's position in aromatic ring on reaction was researched which is shown in scheme.



R = Alkyl, Aryl, NO_2, Hal, CO_2H, CO_2Me,

The influence of some parameters [2] of the catalyst copper, such as the size and area of the clusters and the method of obtaining this copper, was investigated.

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Development and synthesis of novel targeted delivery systems based on ASGPR triantennary ligands

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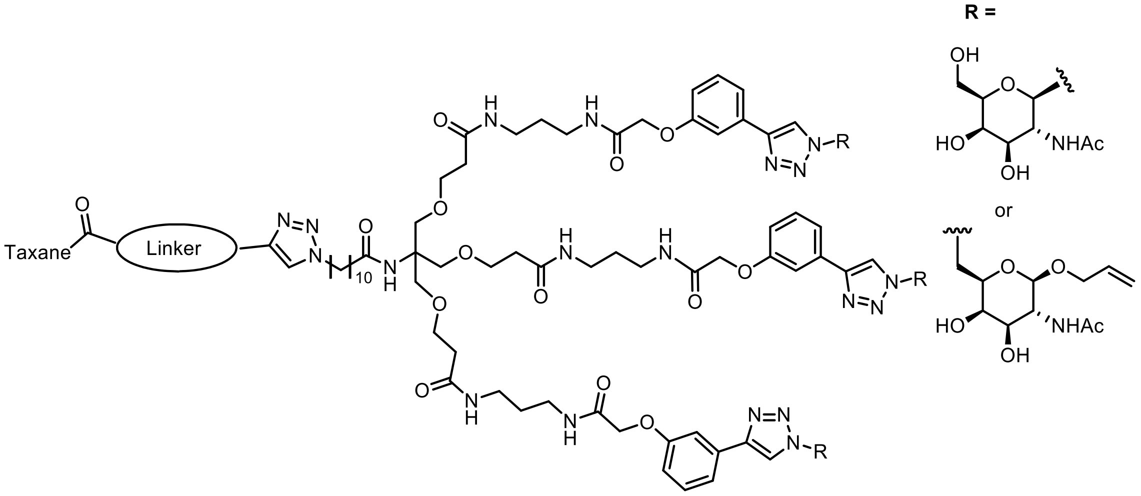
According to WHO, hepatocellular carcinoma (HCC) ranks third in terms of mortality among oncological diseases [1]. Modern drugs used for chemotherapy have a number of serious drawbacks that can be corrected using targeted delivery systems.



A promising target for targeted delivery to hepatocytes is the ASGP receptor, which selectively recognizes galactose derivatives [2]. Due to the structural features of the receptor and the possibility of a cumulative effect of binding several galactose residues [3], we synthesized trivalent ligands of the structure shown in the figure above, which have a higher affinity for the receptor than the native ligand (for the synthesized ligands, the dissociation constant of the receptor-ligand complex per 5-6 orders of magnitude lower). The ligands will be subsequently conjugated with clinically used anticancer agents, docetaxel and paclitaxel.

This work was supported by Russian Science Foundation (grant №. 21-73-00106)

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Antiradical and reducing activity of aromatic thiols

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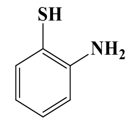
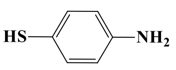
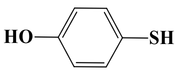
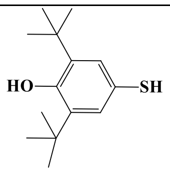
Among antioxidants the compounds containing a thiol group are of great importance, since thiol antioxidants can act as radical scavengers, metal chelators and substrates for specific redox reactions [1]. The free radical scavenging activity of aromatic thiols **1-4** using the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) and the nitric oxide (NO•) radical was evaluated . The reducing ability of compounds **1-4** in CUPRAC- and FRAP-tests also was investigated.

	 **1**	 **2**	 **3**	 **4**
DPPH, % of inhibition	41.80 ± 0.05	38.85 ± 0.03	28.08 ± 0.02	37.51 ± 0.05
NO•, % of inhibition	-18.45 ± 0.09	-10.23 ± 0.08	-12.46 ± 0.11	63.97 ± 0.05
TEAC$_{CUPRAC}$	0.48 ± 0.08	0.54 ± 0.05	0.88 ± 0.08	0.74 ± 0.04
TEAC$_{FRAP}$	1.07 ± 0.13	1.58 ± 0.13	1.06 ± 0.07	0.84 ± 0.06

All the studied thiol compounds showed moderate antiradical activity in reaction with a stable DPPH radical, decreased its concentration in solution by 28-42%. Nitric oxide is a one of the reactive oxygen species which at low concentrations plays an effective role in biological activities, however, high levels of NO• can be toxicity. Aromatic thiols **1-3** promote the formation of the NO• in sodium nitroprusside solution in comparison with the control sample. Only compound **4** reduces the concentration of the NO• due to the presence of a hindered phenol fragment in the structure.

The reducing activity of aromatic thiols **1-4** was studied in CUPRAC- and FRAP-tests based on the ability of the compounds to act as electron donors. The results were presented in Trolox equivalents (Trolox Equivalent Antioxidant Capacity, TEAC). In the CUPRAC-test, all the studied compounds show activity lower than for the Trolox standard. Compounds **1** and **3** in the FRAP-test exhibit a reducing activity approximately equal to 1. At the same time, the activity of compound **2** is 1.58 times higher than the activity of Trolox, despite the similarity of structures with compound **1**.

Thus, the antiradical and reducing activity of aromatic thiols with redox active groups (*HO*- and NH_2-) has been studied. The presence of a hydroxyl or amino group slightly changes the antioxidant activity of the studied thiols. The greatest activity is characteristic of spatially shielded mercaptophenol. The investigated aromatic thiols can be used as pharmacophores in the synthesis of polyfunctional antioxidants with directed action.

This work was supported by the Russian Science Foundation (grant № 20-13-00084)

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Structure and properties of hydrazide-chelate of the Hoveyda-Grubbs type catalysts

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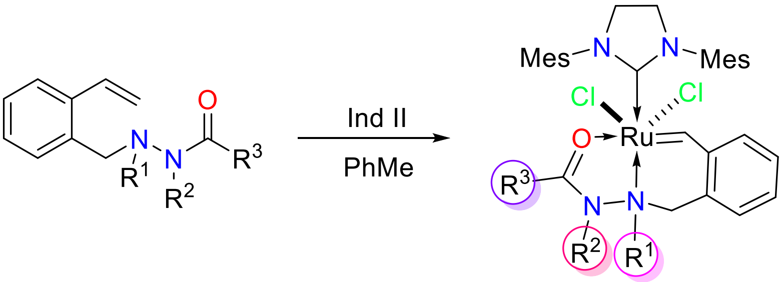
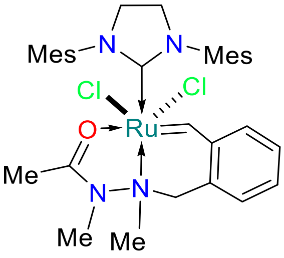
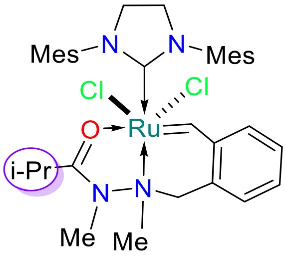
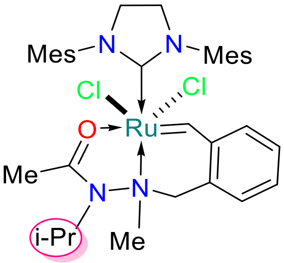
This work is a continuation of our research team's study of new catalysts for olefin metathesis, which examines the effect of chelate ring expansion in Hoveyda-Grubbs-type catalysts. It is aimed at developing methods for obtaining new hydrazide-containing ligands with various substituents and target ruthenium complexes based on them, as well as studying their structure and properties, as well as revealing the dependence that describes the change in catalytic activity with varying substituents (R^1, R^2, R^3) at each of the modification sites present.

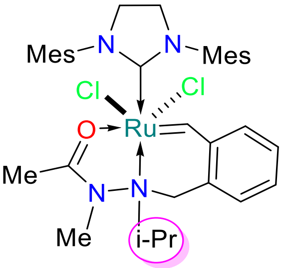


As a result of the work, hydrazide-containing benzylidene lignads and ruthenium complexes were obtained.









However, the most important quality of the complexes is their almost complete tolerance to traces of moisture and even the absence of an inert atmosphere, which contrasts with the pronounced sensitivity of the second-generation Hoveyda-Grubbs-type catalyst to these factors.

The research was funded by the Russian Science Foundation (project No. 22-23-00490)

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New effective surfactants based on framework carbocyclic derivatives

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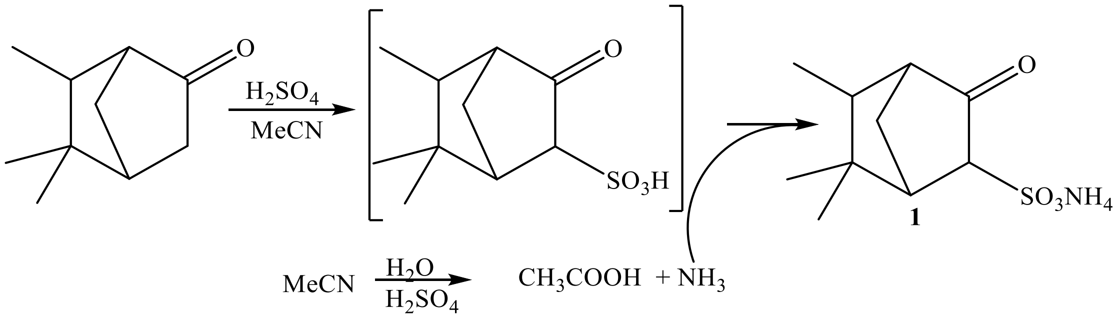
The colloidal chemical properties of surfactants and their flotation characteristics largely depend on the nature and length of the hydrocarbon radical and functional groups. Aliphatic surfactants are the most well studied, while bicyclic and framework analogs are much less studied. However, the bulky hydrophobic carbocyclic radical allows to count on the manifestation of interesting colloid-chemical and flotation properties by such compounds.

In our previous studies, we carried out the synthesis of anionic and cationic surfactants based on isocamphanon and adamantane. The ammonium salt of 5,5,6-trimethylbicyclo-[2,2,1]-heptan-2-one-3-exosulfonic acid (**1**) and 3-(1-adamantyl)-3-chloro-2-propenylamine hydrochloride (**2**) were synthesized. The synthesis routes includes sequential, easily scalable transformations using available reagents.



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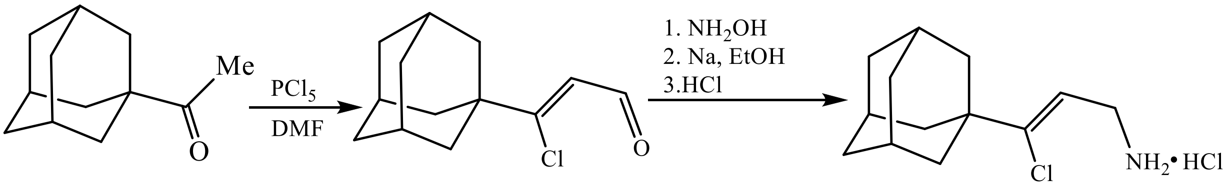

2

The synthesized compounds (**1,2**) were found to have high surface activity. They are effective flotation reagents and can be used in the processes of flotation enrichment of sylvinite ores. They provide both a high recovery of KCl and a high content of KCl in the concentrate. In addition, in the case of compound (**1**), high quality and quantity flotation indicators were achieved during the enrichment of highly clay potash ores without preliminary depression of clay sludges.

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Catalytic N-diphosphonomethylation of amino alkanols and bisamino alkanes using tris(trimethylsilyl) phosphite

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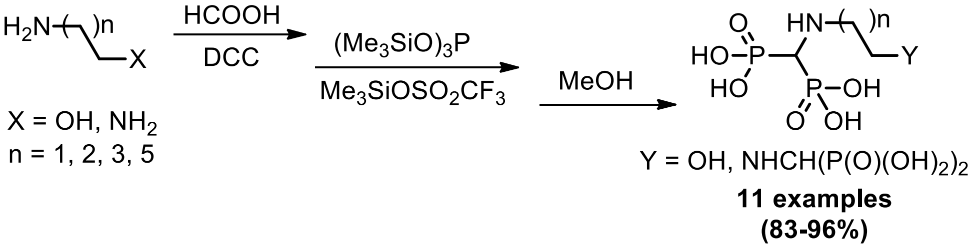
Functionalized methylenebisphosphonic acids with hydroxyl and amino groups are widely investigated among bisphosphoryl compounds due to their great synthetic and biological significance, and some of these substances are found in living systems. These compounds are intensively used as promising polydentate ligands and organophosphorus biomimetics of natural pyrophosphates and hydroxyl or amino acids with multifactorial activity, so they demonstrate the properties of herbicides, pesticides, antibiotics, antiviral and antitumor agents and enzyme inhibitors. Undoubtedly, the diverse biological activity of these acids is firstly determined by a favorable combination of methylenebisphosphonates, hydroxyl and amine moieties. The new bis(aminomethylenediphosphonic) acids are synthesized for the first time via unique reaction of tris(trimethylsilyl) phosphite and various *N*-formyl amino alkanols or bis(*N*-formyl amino) alkanes at the presence of effective catalyst – trimethylsilyl triflate under mild conditions. The further treatment of initially formed trimethylsilyl intermediates with the methanol excess resulted in the crystalline mono- and bis(aminomethylenediphosphonic) acids in high yields (83-96%). The catalytic scheme of target substances formation is proposed and discussed in detail [1].



The resulting compounds are the perspective biologically active substances and polydentate ligands with versatile properties as well as the promising precursors for multitarget drug discovery.

This work was supported by Russian Science Foundation (grant № 19-73-00245)

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Synthesis of new non-proteinogenic amino acids with methylenebisphosphonic acids moieties via a convenient catalytic silicon-assisted route

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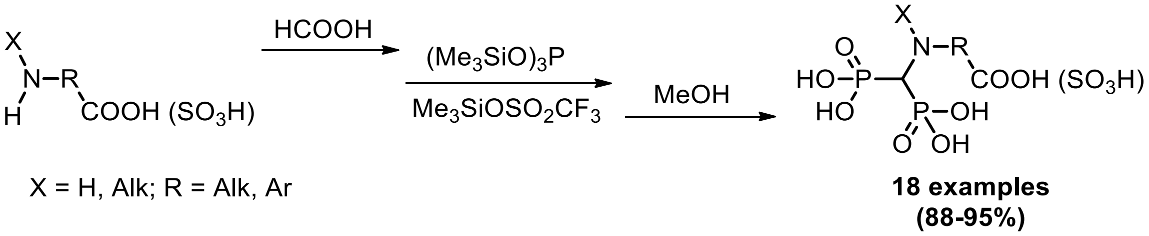
The synthesis of new useful compounds containing several bioactive groups and the organophosphorus moieties currently is a modern trend of bioorganophosphorus chemistry. The functionalized organophosphorus derivatives of aminocarboxylic acids are the perspective organophosphorus biomimetics of natural amino acids and phosphates. These compounds are well known structural components of cells such as lipids and proteins. Many of these substances including non-hydrolysable P-C bonds interfere with various biochemical processes and possess a variety of biological activities. The new non-proteinogenic amino acids with methylenebisphosphonic acids moieties are synthesized for the first time *via* unique reaction of tris(trimethylsilyl) phosphite and various *N*-formyl amino acids at the presence of effective catalyst – trimethylsilyl triflate under mild conditions. The further treatment of initially formed trimethylsilyl intermediates with the methanol excess resulted in the water-soluble non-proteinogenic amino acids with methylenebisphosphonic acids moieties in high yields (88-95%) [1].



The resulting compounds are of great interest as perspective synthons for preparation of organophosphorus substituted peptides, promising bioactive substances with versatile properties and effective polydentate ligands. Our general procedure can be successfully applied to another amino acids for the preparation of biologically relevant amino acids with methylenebisphosphonic acids moieties. The biological evaluation of synthesized compounds is an area of active study.

This work was supported by Russian Science Foundation (grant № 19-73-00245)

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Condensation of diethylmalonate and substituted 5-acyl-1,3-dioxanes under microwave irradiation

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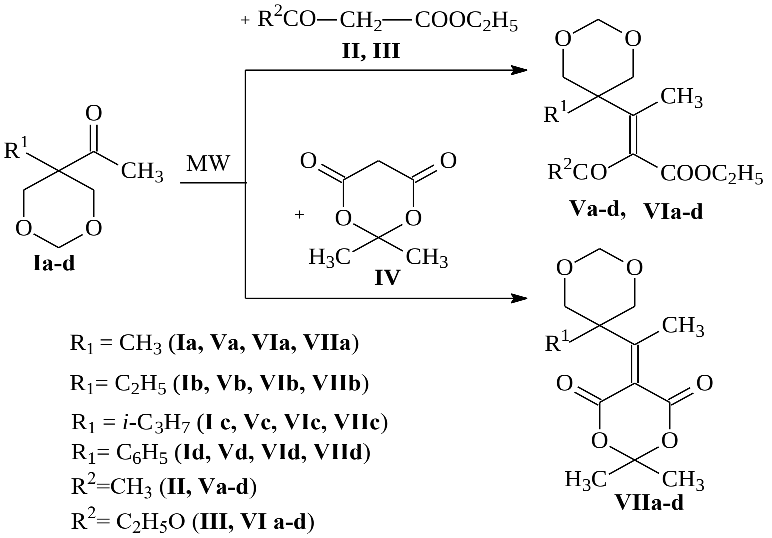
The condensation of diethyl malonate with various structures aldehydes proceeds in the presence of pyridinium acetate with the formation of alkylidene malonates – perspective compounds that can be used for the synthesis of biologically active substances [1, 2].

In this work, we studied the condensation of heterocyclic ketones **Ia-d** (previously synthesized by us [3]) with *CH*-acids **II-IV** under microwave radiation conditions (30-50°C, 3-5 h, radiation power 1000 W).



$R_1 = CH_3$ (**Ia, Va, VIa, VIIa**)

$R_1 = C_2H_5$ (**Ib, Vb, VIb, VIIb**)

$R_1 = i\text{-}C_3H_7$ (**I c, Vc, VIc, VIIc**)

$R_1 = C_6H_5$ (**Id, Vd, VId, VIId**)

$R^2 = CH_3$ (**II, Va-d**)

$R^2 = C_2H_5O$ (**III, VI a-d**)

The best results (yield of compounds **VIIa-d** 70-80%) were obtained using Meldrum's acid **IV**. In the case of using acetoacetic **II** or malonic **III** esters, the reaction proceeds with the formation of compounds **Va-d** and **VIa-d** with 30-60% yields, respectively.

Note that the substituents in the 5th position practically do not affect the course of the reaction. Under conditions of thermal heating (80°C), an acceptable yield of adduct **VIIa** (15–20%) is achieved by condensation of ketone **Ia** with cyclic *CH*-acid **IV** in 20-25 h.

The synthesized compounds **Va-d** – **VIIa-d** demonstrate high cytotoxic activity against HEK293, SH-SY5Y, MCF-7, and A549 cell lines (IC50 < 100 μM), which makes them perspective for use in medicinal chemistry.

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4-(Dimethylamino)pyridinium azide as a convenient source of hydrazoic acid

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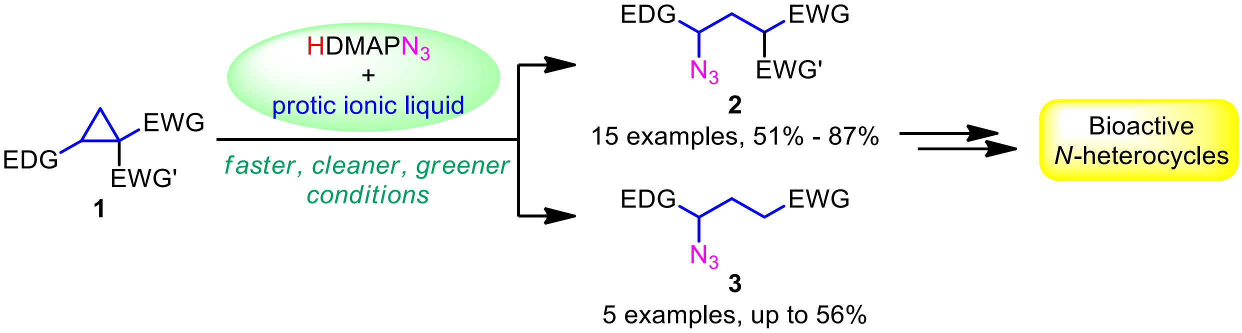
Modern demands of synthetic organic chemistry require the application of reaction conditions which both provide high yields of the target products and meet the principles of green chemistry. One of the ways to solve these problems is the use of protic ionic liquids (PILs), i.e., low-melting salts of Brønsted acid and base. Recently, we proposed a new concept of the triple role of PILs containing nucleophilic anions in organic synthesis: thiocyanate-based PIL served cooperatively as a regenerable reaction medium, an acid initiator of the reaction, and a reagent – a source of a nucleophile. The efficiency of this strategy was demonstrated in the ring-opening of donor–acceptor (D–A) cyclopropanes with thiocyanate ion [1].

We expanded this strategy to the ring-opening of D–A cyclopropanes **1** with azide ion since the known procedures of synthesis of compounds **2** and **3** exhibit some disadvantages, such as problems with scaling and environmental foe properties of DMF used as a solvent in these processes [2].

4-(Dimethylamino)pyridinium azide (HDMAPN$_3$) was employed as a source of azide ion. Its combination with a protic ionic liquid is the efficient system for D–A cyclopropanes **1** opening providing a facile access to a wide range of (2-azido-2-arylethyl)malonates **2** and 4-azido-4-arylbutyrates **3** depending on the choice of the PIL medium. HDMAPN$_3$ – a novel reagent acting as a stable organic soluble equivalent of both hydrazoic acid and N$_3$-anion – found further applications within other conventional organic transformations such as nucleophilic substitution, epoxide ring-opening, (3+2)-cycloaddition reactions, *etc.*



This work was supported by the Russian Science Foundation (grant № 21-73-10212)

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Obtaining nanostructured silicon sol-gel materials and production of antibacterial coatings based on them

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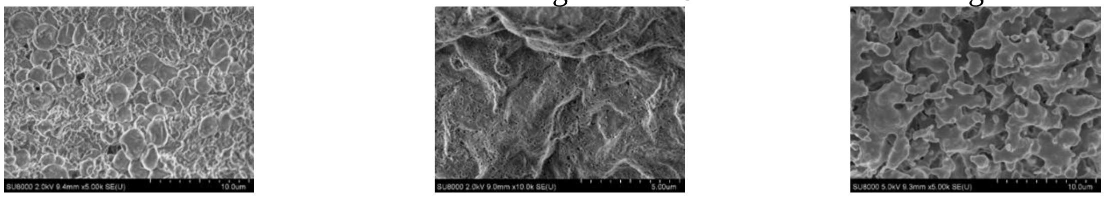
The increased demand for antiseptics and disinfectants over the past few years may lead to a significant decrease in their effectiveness. So today, a significant increase in bacterial resistance has already been registered throughout the world [1, 2]. In addition, serious concern is caused by the ability of microorganisms to form colonies in a polymer matrix — biofilms. In this form, the virulence of microorganisms is significantly increased, as well as their resistance to various environmental factors, including biocides. One of the most effective methods of combating the emergence of bacterial colonies is the application of long-acting antimicrobial coatings.

In this research the synthesis of antibacterial coatings was carried out. Such materials are able to prevent the development of biofilms on the surface due to the gradual long-term release of octenidine. For this purpose, a series of biohybrid organosilicon materials were synthesized using different ratios of silane precursors and various strains of yeast and bacteria as templates. Subsequently, the bacterial component was burned out at different temperatures to form a series of porous materials. Structure and morphology of the resulting silica nanoparticles were studied using a complex of physicochemical methods, such as scanning electron microscopy (SEM) (Figure 1), transmission electron microscopy, IR-spectroscopy. In a next step the study of the processes of sorption / desorption of octenidine dihydrochloride in the obtained porous materials was carried out. It was shown that the best materials demonstrate a gradual release of the substance with a slight loss of concentration even after 10 dilutions (525 hours of experiment).



Before heat treatment   Annealing at 600 °C   Annealing at 1200 °C

Figure 1. Scanning electron microscopy (SEM) data of a sample with a ratio of TEOS/MTES power precursors of 15 vol. %/85 vol. % and with encapsulated yeast cells.

This research was funded by the Ministry of Science and Higher Education of the Russian Federation within the framework of a state assignment on the topic "Synthesis of targeted biologically active ionic compounds and new biocomposite materials" (FEWG-2021-0011)

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The reactivity of azoles bearing a diazo function to β-thiadiazolyl enamines. Novel non-aromatic azolo[5,1-*c*][1,2,4]triazines: synthesis, mechanistic insight and fluorescent properties

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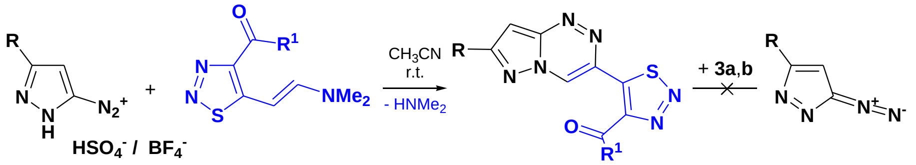
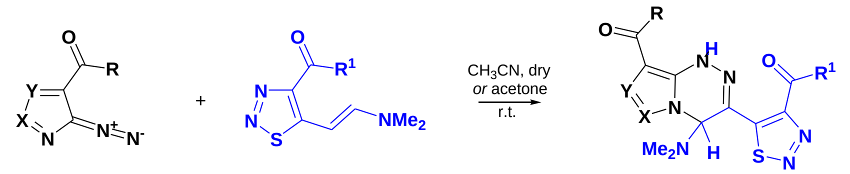
Diazoazoles and azole diazonium salts have demonstrated high potential for the synthesis of practically useful polynitrogen compounds [1]. However, despite the broad synthetic applications of azoles bearing a diazo motif in their structure, many experimental studies do not specify the exact form of these compounds in reactions, complicating systematic analysis and the prediction of the outcome of subsequent synthetic strategies. Earlier we have shown [2, 3] that modern spectral methods are a convenient tool for identifying each of these forms.

In this report we present the results our investigation which deals with interaction of β-1,2,3-thiadiazolyl enamines with azoles containing a diazo function. It is established that azole-5-diazonium salts **1** and 5-diazoazoles **5** have different reactivities, which leads to the formation of aromatic **4** or non-aromatic **6** heterocyclic systems. These reactions were investigated with the NMR technique and it allowed us to shed light on their mechanisms.



1a-e **3a,b** **4a-e** **2a-e**

1,2 a R = 4-Cl-C_6H_4; **1,2b** R = 4-Me-C_6H_4; **1,2c** R = 4-MeO-C_6H_4; **1,2d** R = Ph; **1,2e** R = Me;
4a R = 4-Cl-C_6H_4, R^1 = OEt; **4b** R = 4-Me-C_6H_4, R^1 = OEt; **4c** R = 4-MeO-C_6H_4, R^1 = OEt;
4d R = Ph, R^1 = OEt; **4e** R = Me, R^1 = OMe



5a-e **3a-d** **6a-i**

5a X = N, Y = CH, R = OEt; **5b-e** X = CH, Y = N, **5b** R = OEt, **5c** R = OMe, **5d** R = NH_2, **5e** R = NHMe;
3a R^1 = OMe, **3b** R^1 = OEt, **3c** R^1 = NH_2, **3d** R^1 = Me; **6a** X = N, Y = CH, R = OEt, R^1 = OMe;
6b-i X = CH, Y = N, **6b** R = OEt, R^1 = OMe; **6c** R = OEt, R^1 = OEt; **6d** R = OEt, R^1 = NH_2; **6e** R = OEt, R^1 = Me;
6f R = OMe, R^1 = Me; **6g** R = NH_2, R^1 = OEt, R^1 = Me; **6h** R = NH_2, R^1 = OMe; **6i** R = NHMe, R^1 = Me

Thus in addition to the reaction mechanism established, an efficient PASE approach to the preparation of various 1,4-dihydroazolo[5,1-*c*][1,2,4]triazines **6** was developed as a result of this work. The structure and photophysical properties of the synthesized compounds were examined, the peculiarity of their absorption and emission revealed and the preliminary direction of their applications as sensors outlined.

This work was supported by the Russian Science Foundation (grants № 18-13-00161-P, 20-13-00089) and the Ministry of science and higher education of the Russian Federation (federal academic leadership program "Priority 2030")

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Synthesis and photophysical studies of α,ω-disubstituted with polycyclic aromatic hydrocarbon moieties pentanes

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Alkanes **1a-b** α,ω-disubstituted with polycyclic aromatic hydrocarbons (PAHs) (Fig. 1C) are well-known fluorophores with promising photophysical properties, including tendency for intramolecular excimer formation in organic solvents [1]. However, classic route of their synthesis based on Huang–Minlon reduction of corresponding unsaturated ketones is three-stage, have harsh reaction conditions and low yields (~16%) [2]. Also, photophysical properties of such alkanes weren't studied in aqueous media. Our modification of Clemmensen reaction conditions allowed us to reduce the number of synthetic stages to two and increase the yield up to 41 and 66% (for **1a** and **1b** respectively).

Spectroscopic studies of fluorophores **1a-b** in DMSO:H_2O systems of various ratio of organic solvent revealed some interesting correlations between photophysical properties, nature of PAH and DMSO content (Fig. 1A, 1B). Thus, the absolute quantum yield (QY) values of compounds **1a-b** in pure DMSO exceed those for non-substituted anthracene and pyrene (29% and 55% respectively) probably due to the possible σ–π conjugation [3]. A drastic decrease of the QY in solvent systems containing 50% of DMSO and less (Fig. 1C) probably associated with aggregation-caused quenching (ACQ). It also should be mentioned, that whereas for the anthracene-containing pentane **1a** the QY almost drops to zero after aggregation that occurs in DMSO:H_2O [50:50 (v/v)] and continues to decrease with decrease of DMSO content, the QY of the pyrene-based pentane **1b** decreases only by half upon aggregation, and further shows somehow mixed ACQ-AIE (aggregation-induced emission) character, the nature of which is still unknown.

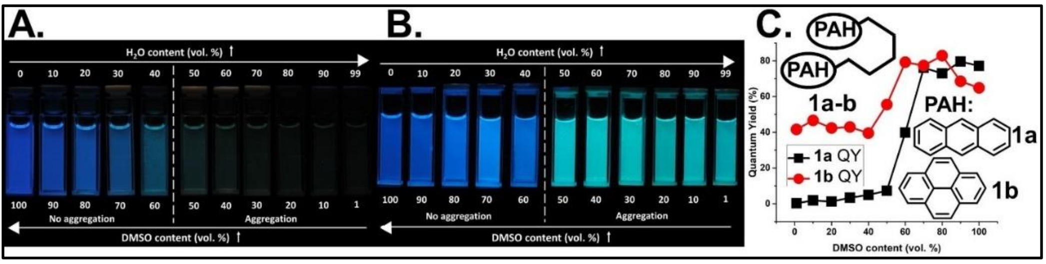

Figure 1. Photographs of the emission of compounds **1a** (A) and **1b** (B) upon irradiation under a UV lamp (λ_{Ex} = 365 nm) in various DMSO:H_2O solvent systems; I_{Ex}/I_M ratio and the absolute quantum yield of fluorescence of the compounds **1a-b** *vs* DMSO content (vol. %) graph (C).

This work was supported by the Russian Scientific Foundation (grant № 19-73-10144-P) and by the Ministry of Science and high Education of the Russian Federation (MEGAGRANT, contract No 075-15-2022-1118 dd.29.06.2022)

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Novel isoxazole containing BF2-complexes: synthesis and fluorescent properties

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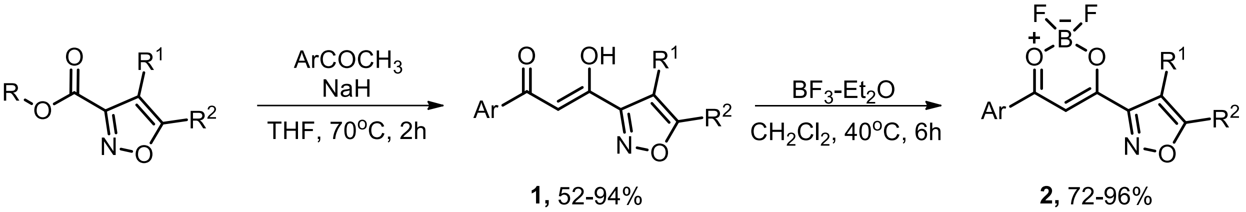
Difluoroboron 1,3-diketonate complexes are well-known type of fluorophores with strong fluorescence, large extinction coefficients and high quantum yield [1, 2]. Although BF_2-complexes of dipyrrole diketones are extensively investigated, the analogues with other heterocyclic or aryl moieties are scarcely researched. In this work we propose the synthesis of previously unknown isoxazole-containing BF_2-complexes and studied their photophysical properties.

A large series of isoxazole-containing 1,3-diketones **1** were obtained using the ester condensation of isoxazole-containing esters and aryl methyl ketones. The subsequent reaction of compounds **1** with $BF_3{*}Et_2O$ resulted in difluoroboron complexes **2** in good yields.



R = Me, Et
R¹ = H, Br, I, 4-Cl-C_6H_4
R² = Me, ^{t}Bu, 1-Ad, 4-Cl-C_6H_4, 4-MeO-C_6H_4, OEt, NEt_2, morph, $NHCH_2Ph$
Ar = 4-MeO-C_6H_4, 3,5-^{t}Bu$_2$-4-MeO-C_6H_2, 3,4,5-(MeO)$_3$-C_6H_2, 4-MeS-C_6H_4, 4-CF_3-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, C_6H_5, 1-Nf, 4-Ph-C_6H_4

Photophysical properties of the obtained compounds **2** were studied and the influence of the electronic nature of the substituents in aryl and isoxazole cycles on the absorption and emission spectra was investigated. For the studied compounds **2**, the longest wavelength absorption maxima are in the visible region at 355–418 nm, the emission maxima are in the range of 388–527 nm, compounds **2** are characterized by large extinction coefficients (up to 54600 $M^{-1}\cdot cm^{-1}$) and high quantum yield (up to 99.9%).

This work was supported by the Russian Science Foundation (grant № 22-73-00058)

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Structural evaluation of the complex of copper (II) acetate with (4-aminobenzo-15-crown-5)-4-pyridinecarboxalimine

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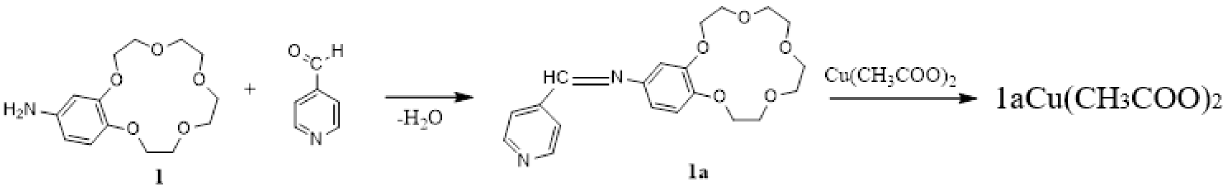
X-ray diffraction analysis is not always possible due to precipitation of an amorphous powder. In this regard, the prediction of the existence of a particular structure can be estimated using the methods of quantum chemistry. This work is devoted to studying and predicting the geometry of the synthesized compounds and assessing the fundamental possibility of forming copper complexes of azomethine derivatives.

We synthesized new Schiff bases by the condensation of 4-pyridinecarboxaldehyde. The copper complex was obtained by adding an equimolar amount of copper (II) acetate to the corresponding azomethine.



At the first stage, the comparative thermodynamic stability of structures with different coordination of the crown ether ligand on the copper atom was estimated. The evaluation was carried out with respect to the total free energy of (4-aminobenzo-15-crown-5)-4-pyridinecarboxalimine (substance 1a) and monomeric copper (II) acetate $Cu(AcO)_2$.

The calculation was carried out by the DFT method in the Priroda 20 program with the PBE exchange-correlation functional and the 3z basis. We also calculated the structures of dimeric copper complexes with bridging acetate ligands and molecules 1a, $(1a)_2[Cu_2(\mu\text{-}AcO)_4]$ apically coordinated through the pyridine fragment, and with the same ligands, but coordinated through the imine nitrogen atom, $(1a')_2[Cu_2(\mu\text{-}AcO)_4]$, as well as a complex with ligands 1a with mixed coordination $(1a)(1a')[Cu_2(\mu\text{-}AcO)_4]$. The singlet and triplet ground states of these complexes were also studied.

Analytical research was done using equipment of NRC "Kurchatov Institute" — IREA Shared Knowledge Center under project's financial support by the Russian Federation, represented by The Ministry of Science and Higher Education of the Russian Federation, Agreement No. 075-11-2021-070 dd. 19.08.2021.

Polymorphism induced by the conformation of a solvent molecule

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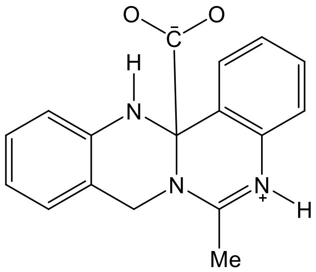
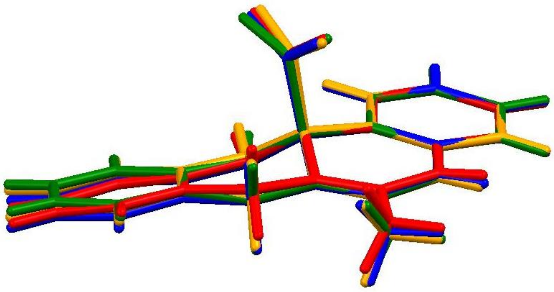
Polymorphism is an important phenomenon for molecular crystals. Many organic compounds exist in two or more crystalline forms, which differ in conformation of the molecule and/or crystal packing. The crystallization of a certain form is usually defined by crystallization conditions, including the interactions with solvent molecules during crystallization. Polymorphism is known not only for pure compounds, but also for multi-component structures such as co-crystals of solvates. It is important that in case of crystal solvates, the crystal packing is mainly defined by interaction of the parent compound, as solvent molecules are usually much smaller. For a flexible solvent, it is possible that differences in its conformation cause polymorphism; however, such cases are unusual and require detailed consideration.

Compound (**1**) 8*H*-6-methyl-13a-carboxy-quinazolino[3,4-*b*]quinazolin-5-ium crystallizes in two polymorphic forms of acid crystal solvate with a stoichiometric ratio of 1:1, **1a** (sp. gr. $P2_1/c$, Z'=1) and **1b** (sp. gr. $P2_1/c$, Z'=3). Despite certain similarity of the unit cell parameters, molecular geometry and supramolecular organization of the main compound, the structures are very different in conformation and crystal packing of the solvent molecules. Thus, in **1a** the acetic acid molecule in *trans*-conformation (which is itself not very typical), while in **1b** two symmetry independent molecules are in *trans*- and one is in *cis*-conformation. As a result, instead of infinite H-bonded chains in **1a**, in **1b** the solvent molecules form only a trimeric associate that is additionally bonded to the main compound.

The features of the supramolecular organization, the results of the quantum-chemical calculations of the associates and crystal structures are reported; and possible reasons leading to the observed polymorphism are discussed.





This work was supported by the Russian scientific foundation (grant № 22-23-00570)

Design and synthesis of y-shaped fluorophores based on n(2)-aryl-1,2,3 triazoles

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Organic fluorophores are the π-conjugated system, containing both an electron-donating group (EDG or D) and electron-withdrawing group (EWG or A). These molecules are finding many applications in the fields of science and technology, namely, (chemo)sensors, OLED, NLO, and biochemistry (for example, bio-imaging, etc.). One of the most interesting types of fluorophores in the view of photophysical properties is the Y-shaped molecules. The structure of these molecules makes it possible to develop such systems as D-D-A, and D-A-D, which are widely known in the literature as effective luminescent materials, in particular, chemosensors for the determination of nitroanalytes. However, the synthesis of these molecules is a non-trivial task for organic synthesis and only several examples are presented in the literature. Thus, this work deals with the development of an efficient synthetic scheme to obtain the Y-shaped fluorophores based on 1,2,3-triazoles.

The synthesis consists of 5 stages. In the first stage, a condensation reaction was carried out between *para*-methoxyarylhydrazine **1** and 2-oxopropanal oxime. As a result, an intermediate product **2** was obtained, which was then cyclized using copper sulfate in pyridine to obtain *para*-meteroxyaryl-1,2,3-triazole **3** with a yield of 65%. Further bromination leads to disubstitution product **4** in *ortho*-position to the methoxygroup in a yield of 96%. A key step was to perform the Suzuki-Miyaura reaction in the presence of $Pd(Ph_3)_4$, K_3PO_4, and boronic acids, which led to the target products **5a-c** in yields of 60%-70%. At the final stage, the N-oxide group was removed by the action of Zn(dust) and NH_4Cl (saturated) from the molecules to form compounds **6a-c** in yields of 98%-99%.

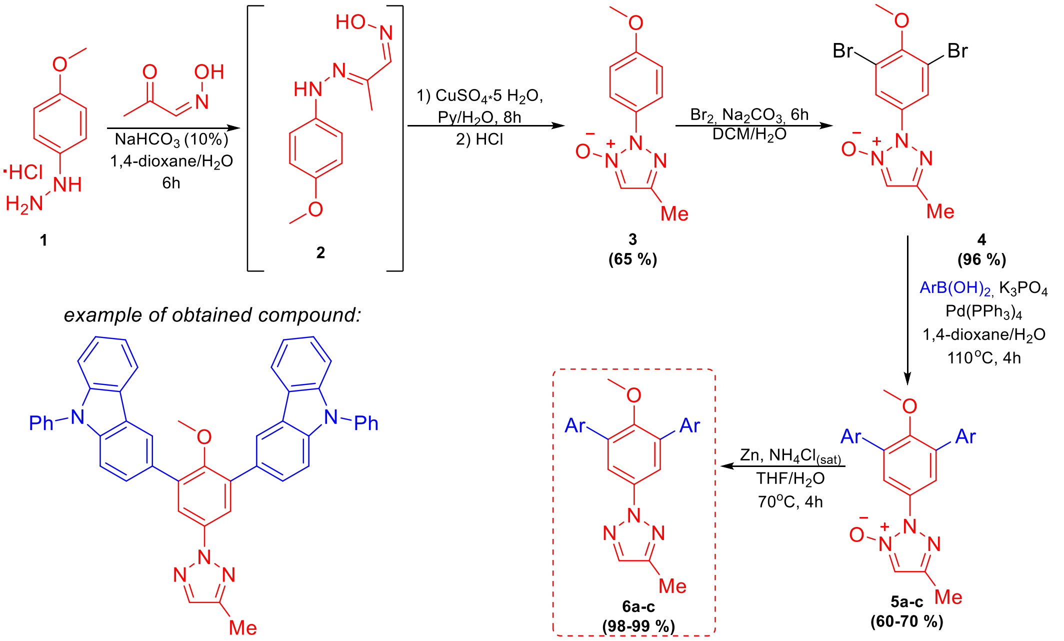

Figure 1. Synthesis of Y-shaped fluorophores based on 1,2,3-triazoles

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University project within the Priority-2030 Program) is gratefully acknowledged

Synthesis of chiral cyclopalladated complexes of azinylferrocenes

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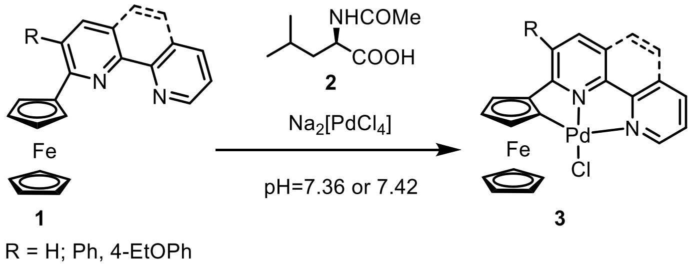
Cyclopalladated complexes of ferrocene derivatives, including enantiomerically enriched ones, are of interest as catalysts for asymmetric synthesis, OLED and biologically active compounds. Currently, two main approaches have been described for obtaining planar chiral cyclopalladated ferrocene derivatives: the first is based on reactions of cyclomercuration of ferrocene and subsequent transmetalation, and the second is direct complexation with palladium salts with the general formula M_2PdCl_4 (M = Li, Na, K) in the presence of bases.

The starting azinylferrocenes **1** have been obtained to the C-C coupling of azines with ferrocenes is the direct C-H functionalization of aromatic compounds through the nucleophilic substitution of hydrogen in π-deficient azines by lithioferrocene. Then we performed asymmetric cyclopalladation of compounds **1** in methanol under pH control catalyzed by an *N*-acetyl-*D*-leucine salt **2** and obtained palladium bicyclic compounds **3** in high yields [1].



The complexes 3 are promising catalysts for the Suzuki reaction, the Heck reaction, the Buchwald–Hartwig cross-coupling et al.

This work was supported by the Russian Science Foundation (grant № 22-13-00298)

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Novel multicationic QACs cyanuric acid-based an effective way to combat bacterial resistance

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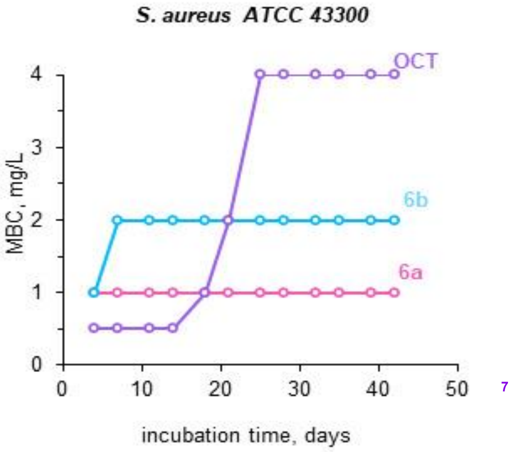
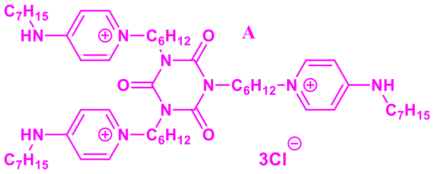
Infections caused by drug-resistant pathogens are becoming a global public health problem. There is an urgent need for new effective therapeutics to address the threat of the spread of drug-resistant pathogens.

Quaternary ammonium compounds (QACs) have been one of the most well-known and effective classes of biocides for almost a century. Recent advances in this field have shown that multicationic compounds are more active than mono-QAS and are less likely to induce bacterial resistance [1].

Trimeric QAS based on cyanuric acid were obtained in this work. The effectiveness of the obtained compounds was studied on reference and clinical bacterial strains *in vitro*, as well as on the fungus *Candida albicans*. For the leading compounds, bacterial resistance development was studied.

The research results show that the MBC* of compounds **A** and **B** is lower compared to the best commercial antiseptic octenidine **OCT**. Substance **1** after 42 days of incubation to *Staphylococcus aureus* does not develop resistance (the cessation of development of resistance by microorganisms corresponds to the plateau on the graph). The compounds also showed great results against *Pseudomonas aeruginosa* and *Escherichia coli*.





A

* MBC-minimum bactericidal concentrations

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Synthesis and preliminary biological activity assessment of novel 1,3,5-triazine derivatives

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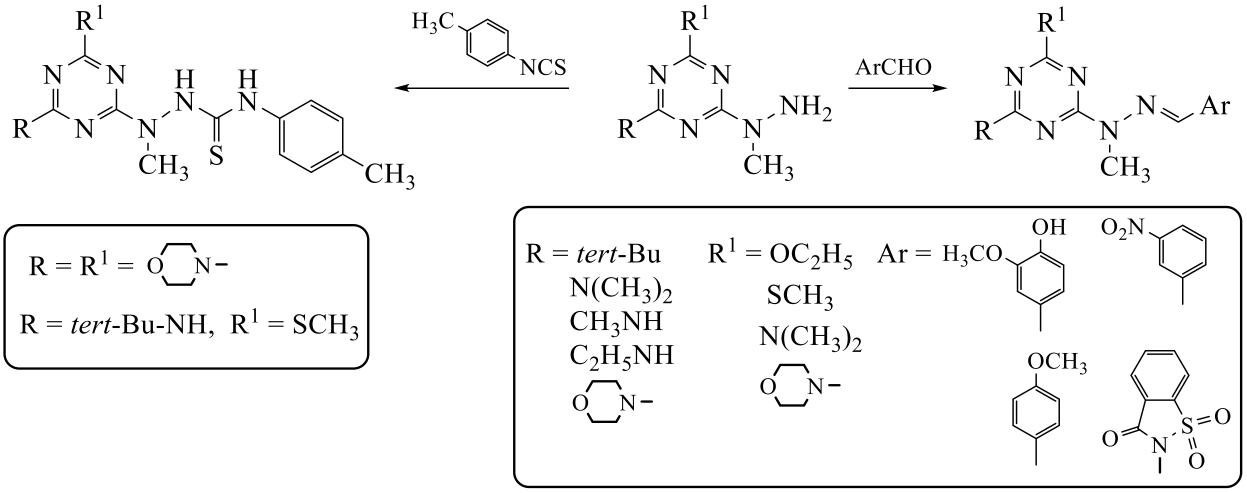
Heterocyclic compounds containing a symmetrical 1,3,5-triazine moiety are an important class of compounds with a wide spectrum of biological activity. In medical practice, a number of drugs are used: almitrin (duxil), altretamine (hexalen), dioxadet, tretamine, irsogladin, isocyuronium bromide, melarsen oxide, melarsomine, cycloguanil [1]. *Sim*-triazine derivatives are also used in various fields of industry and agriculture, mainly as herbicides [2], in particular, a series of sulfurons, in the molecules of which the 1,3,5-triazine ring is linked to other heterocycles or an aryl residue through the sulfonylurea group. In recent years, studies have appeared that describe new derivatives of 1,3,5-triazine, which showed a stimulating effect on plant growth in the experiment [2].

The foregoing shows that 1,3,5-triazine derivatives are widely used both in medicine and in agriculture. However, over time, harmful organisms and pathogens acquire resistance to the substances used, which makes it necessary to systematically replenish their assortment with new compounds, having different mechanisms of action. For this reason, the targeted synthesis of new compounds based on 1,3,5-triazine can lead to such biologically active derivatives, in relation to which the indicated resistance has not yet been formed.



The reaction of starting 2,4-substituted 6-(1-methylhydrazinyl)-1,3,5-triazine with various arylaldehydes and aryl isocyanate, afforded a large number of new *sym*-triazine derivatives with different sets of substituents in the heterocycle. As a result of biological screening, compounds with a pronounced stimulating effect on plant growth were identified among them. The most active drugs have been selected for deeper research and further field trials.

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Ru(II)/NHC catalyzed C(3)-H arylation of biomass-derived furancarboxaldehyde imines

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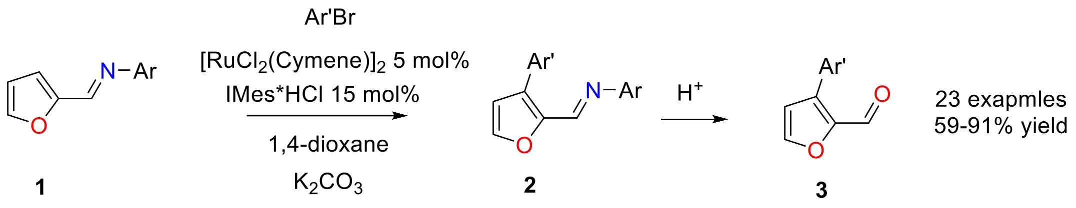
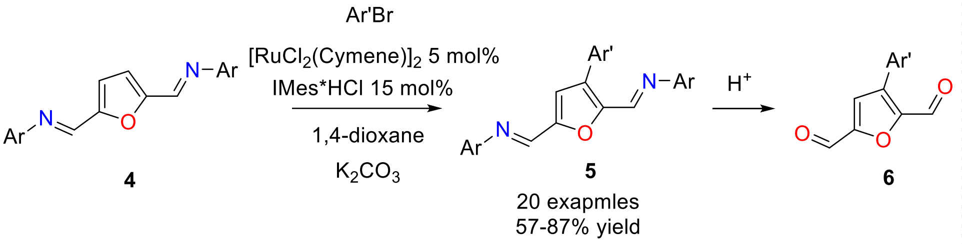
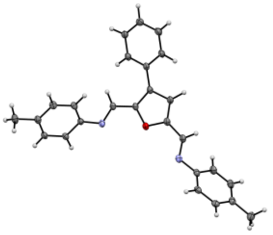
Bio-derived furans obtained from plant biomass, including wastes, are of great interest as renewable displacement for fossil feedstock [1, 2]. Selective C-H arylation of bio-based furan at more active 2 and 5 positions is well known, whereas C-3 arylation require remains poorly explored [3]. Approaches based on directing groups represent a usable way to obtain C-3(4)-functionalized furans [3]. In this way reaction of the C-H activation catalyzed by ruthenium attract attention of researchers last years.

In this study, we demonstrated first Ru(II)/NHC for C(3)-H arylation of imines derived from aldehydes of furan-series. Arylated furfural imines **2**, which were obtained with good to excellent yields, could be easily hydrolyzed to corresponding aldehydes **3** in acidic media.



We also showed that imines **4** derived from 2,5-diformylfuran (DFF) were also suitable substrates for arylation. Using developed catalytic system series of arylated DFF imines were obtained with good yields. It is worth noting that diarylation did not occurred during reaction.





This work was supported by the Russian Foundation for Basic Research (grant № 21-73-00058) and grant of the President of the Russian Federation no. MK-171.2022.1.3

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Ferrocenylalkylation of thio derivatives of sydnones and sydnone imines

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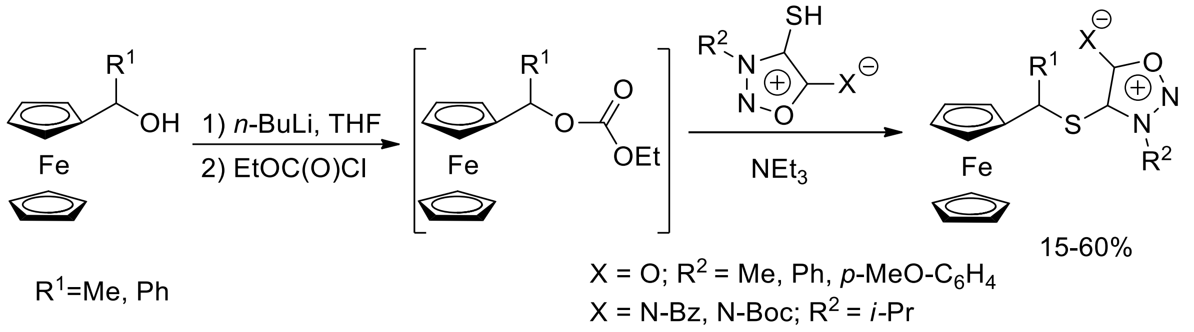
The introduction of a ferrocenyl moiety into biologically active molecules can improve their properties, for example, to decrease toxicity, improve stability in biological media, and facilitate the transport of modified compounds through the cell membranes [1]. Sydnones and sydnone imines, the mesoionic compounds exibiting a wide spectrum of biological activity [2], are among the promising substrates for conjugation with ferrocene. In particular, sydnones and sydnone imine derivatives have been disclosed to show plant growth regulating activity on corn at ultra low doses [3].

The aim of this work is to create a general approach to the preparation of *S*-ferrocenylalkylated of 4-mercaptosydnones and 4-mercaptosydnone imines, a new family of sydnone and sydnone imine derivatives. These compounds can combine the useful properties of the both biologically active fragments, which makes them promising objects for study as the plant growth regulators.



Herein, we report on the ferrocenylalkylation at the SH-group in both 4-mercaptosydnones bearing methyl, phenyl, or *p*-methoxyphenyl substituents at position 3 of the sydnone ring and N$_6$-benzoyl- or N$_6$-*tert*-butoxycarbonyl-3-isopropyl-4-mercaptosydnone imines. We used (*α*-ferrocenylalkyl)carbonates generated *in situ* from easily available ferrocenylcarbinols as the ferrocenylalkylating reagent, which make it possible to carry out the ferrocenylalkylation reactions under mild conditions. The products were characterized by NMR spectra and elemental analysis and the structure of 4-(1-ferrocenylethyl)thio-3-phenyl-sydnone was proved by X-ray diffraction data. At the moment, the studies are underway to elucidate the growth regulating activity of the obtained compounds.

This work was supported by the Russian Science Foundation (grant № 22-23-00726)

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Electrosynthesis of adamantane thioderivatives by direct and indirect activation of hydrogen sulfides

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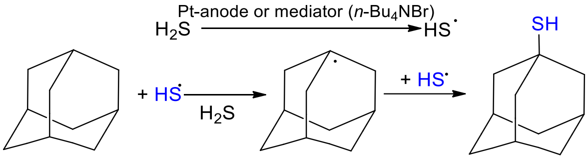
Recently, developments in the field of synthetic organic chemistry have been aimed at finding new available methods for obtaining biologically active substances. Electrosynthesis, especially indirect methods of activation of inert compounds, makes it possible to increase the efficiency of the process, its environmental safety, and reduce energy costs for its implementation. In addition, electrosynthesis is characterized by the ability to control and regulate the composition and ratio of the obtained target compounds.

Adamantane derivatives are of particular interest, as they have the potential of chemotherapeutic, antifungal and anti-inflammatory agents. The adamantane nucleus was found to be important constituent in many antiviral and antibacterial drugs [1, 2]. The introduction of a sulfur atom into the structure of an organic compound enhances its biological activity. However, there are no examples of adamantane sulfidation under mild conditions with the participation of hydrogen sulfide as a cheap and available reagent.

In this work methods of direct (redox-) and indirect (with the use of a mediator) activation of H_2S (1,7 B) in reactions with adamantane are studied. The interaction was carried out on Pt-electrodes, in CH_2Cl_2 with an excess of the reagent in relation to the substrate (1:5).



We used n-Bu_4NBr (0,9 B) in catalytic quantities as a oxidation mediator of H_2S. In this case, the yield of adamantane thiolation reaction products increased noticeably, and the anode overvoltage decreased by 0.8 V. As a result of the electrochemical reaction of adamantane with H_2S, a mixture of sulfur-containing products of the same composition was obtained, regardless of the reagent activation method (Table).

Table – Dependence of the yield of sulfur-containing reaction products on the H_2S activation method (CH_2Cl_2, Pt-anode, 0.15M n-Bu_4NClO_4, Ag/AgCl), molar ratio substrate/reagent = 1:5

Method of H_2S activation	Yield of reaction products, %			
	RSH	**R_2S_2**	**R_2S_3**	**Σ**
Pt-anode	12,3	5,5	10,7	28,5
Mediator	30,7	7,2	10,5	48,4

Thus, the efficiency of mediator synthesis is due to the cyclicity of the electrochemical process and the increase in the rate of generation of thiyl radicals with a decrease in energy consumption compared to direct oxidative activation of H_2S.

This work was supported by the Russian Science Foundation (grant № 20-13-00084)

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Synthesis of enamino-substituted 4-methylene-4*H*-pyrans and their chemical properties

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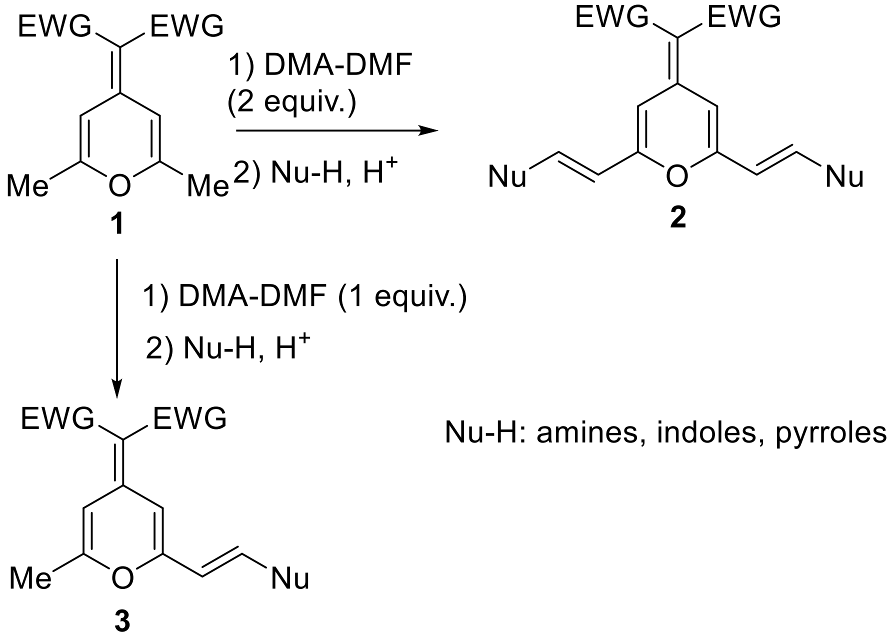
4-Methylene-4*H*-pyrans are attractive push-pull conjugated structures actively explored for various practical applications in laser dyes, in dopants or hosts for organic light-emitting diode, fluorescent chemosensors, solar cells, nonlinear optic materials, and bioimaging [1]. The general method of their preparation includes the condensation of aldehydes with methyl substituted pyrans.

This work is devoted to a new strategy for the functionalization of 4-methylene-4*H*-pyrans based on enamination with DMA-DMF and subsequent 1,8-conjugate addition of C- or N-nucleophiles with substitution of the dimethylamino group. 2,6-Dimethylpyrans **1** can undergo the transformations at two Me-groups, which gives access to symmetrical structures **2**. We also found convenient conditions for the selective modification of only one methyl group leading to pyrans **3**.

Thus, the method of functionalization of 4-methylene-4*H*-pyran opens access to new class of pyran fluorophores, their photophysical properties will be given in detail in the report.



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Unusual reactions of α-aminoenals with arylacetylenes

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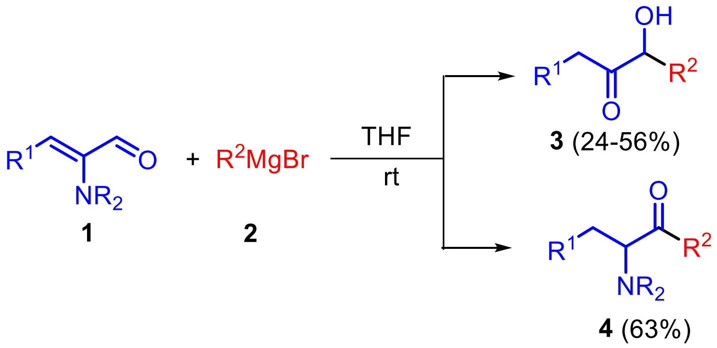
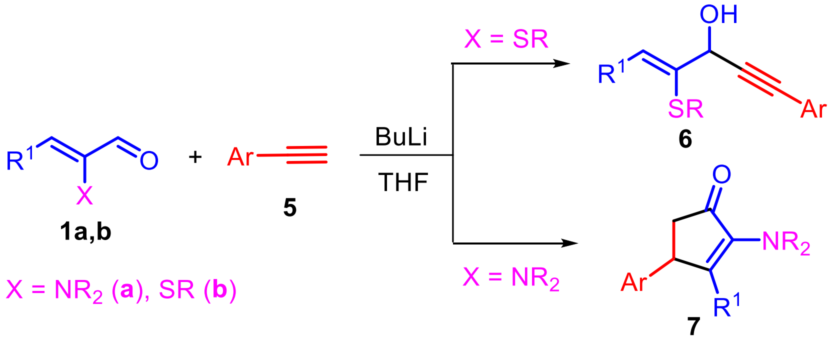
The α,β-unsaturated carbonyl compounds are important building blocks in organic synthesis. [1] Among them, the α-functionally substituted enals became very interesting starting materials for the *de novo* preparation of a wide ring of bioactive compounds. [2] Earlier the reaction of α-aminoenals **1** with Grignard reagents **2** (as C-nucleophiles) was studied. [3] The conditions for the selective formation of α-hydroxy- or α-amino ketones **3** or **4** were determined.



Herein the research results of the reactions of the same aminoenals **1** with other C-nucleophiles (namely, terminal arylacetylenes **5**) are discussed. It was found that the reaction proceeded chemoselectively on the formyl moiety only: no 1,4-adducts were observed in all cases.

The comparison α-aminoenals and their sulfur-bearing analogs in nucleophilic reactions with the same C-nucleophiles showed that secondary amino group plays a vital role in the observed non-trivial domino-transformations: in the case of thioenals **1b** the reaction stoped at the stage of the formation of 1,2-adducts **6**, while the aminoenals **1a** underwent further transformations to give cyclopentenones **7** (Scheme 2). The mechanism of the reaction including 1,2-nucleophilic addition followed by unusual acetylene – allene rearrangement and intramolecular Michael addition is discussed.

Scheme 2.



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How to draw all mesoionic structures

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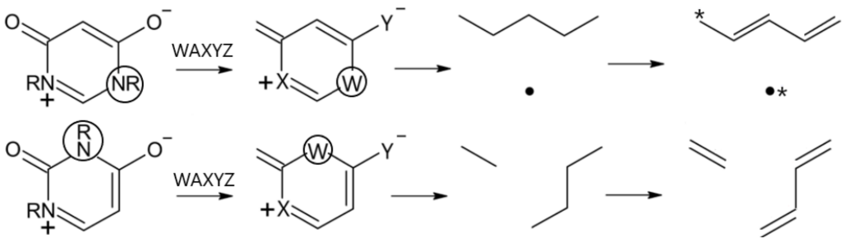
Mesomeric betaines (or mesoionic compounds) are heterocyclic molecules carrying not compensated positive and negative π-charges conjugated in one π-electronic system. Such structures are used in dipolar cycloaddition reactions and have large application and potential for organic synthesis. Moreover, some mesomeric betaines have already used as drugs (mesocarb for instance). However before now there was not a full approach to design of all mesoionic formulas. Such approach is presented.

The core of this work is theorem that we call *mesoionic criterion*. For formulation of its we must introduce WAXYZ-notation. In this notation we replace not participating in formation of multiple bond neutral 2π- or 0π-heteroatom with a symbol W. Carbocationic centers are replaces by a symbol A$^+$. Groups that are similar -C=N$^+$- are denoted as -C=X$^+$-. Anionic centers, like –O$^-$, are Y$^-$ type of atoms. Finally, we replace the four-coordination boron and its analogues with Z$^-$. It is also necessary that all aza-, phospha- and other substitutions in dipolar structures must be replaces by carbon atoms. Example of redrawing of a structure with WAXYZ-notation in a figure.

Mesoionic criterion: Let M be a dipolar structure in WAXYZ-notation and S is a simple graph (it means 'without multiple bonds') corresponding to the molecular structure M from which all W, X$^+$, Z$^-$ type atoms have been removed. The structure M is mesoionic if and only if the graph S is non-Kekule.

A rigorous proof and motivation to formulation of this theorem can be find in [1].



The structure is non-Kekule
Therefore, the
structure is mesoionic

The structure is Kekule
Therefore, the structure has
the covalent form

Mesoionic criterion opens the opportunity to list all mesoionic structures on the given graph using computer. It is because, directed adjacency matrix of non-Kekule structures has a zero determinant. (Kasteleyn [2]) Enumerating all possible pairs of positions for positive and negative charges and calculating the determinant each time, we wrote the computer program and found all mesoionic structures for small structures containing not more 7 atoms. Among these structures some unknown molecules were predicted.

Internal technical discussion of the criterion and algorithms of the computer program are required other important concept such as *π-perfect structures*. However, they are not necessary to formulate the main results (they also are introduced in [1].

As a conclusion, we note that at the mathematical level of rigor, it is shown that the pair of concepts "covalence – mesoionicity" correlates in the same way as the pair "kekulenes – non-kekuleness". It allows to build a library of all mesomeric betaines.

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New example of isocyanides as halogen bond acceptors: Five-center Tetrafurcated (Halogen)4···C/N Bonding

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Halogen bonding (HaB) is the object of growing attention of scientific community. This statement can be proved by a great number of publications that came out last years. These works reveal importance of HaB in crystal engineering[1], HaB-involving noncovalent catalysis[2], synthetic coordination chemistry[3], polymer chemistry[4].

We could find that cocrystallization of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1,4-FBB) with mesitylisocyanide (CNMes) results in formation two bonding patterns. First – expectable pattern includes trimers where one 1,4-FBB has contacts with two CNMes molecules. Second – rare and more complex where we were able to identify five-center tetrafurcated HaBs. Structural features of the HaBs were explored on the base of experimental data (XRD) as well as theoretical considerations such as DFT. In the heterohexamers (Figure 1), one Br atom of 1,4-FBB simultaneously form four contacts with two C and two Br atoms of neighboring molecules. Based on the geometric parameters and the theoretical data these contacts were formulated as five-center tetrafurcated μ_4-Br···(C,Br,C,Br)HaBs.

Although the deviation of the geometric parameters from those observed for two-center HaB and the low energies of some individual contacts (e.g., Br···Br), this aggregation leads to a stable energetically favorable systems (the interaction energies are –33.3 and –32.5 kcal/mol). The π-stacking between CNMes/NCMes and 1,4-FBB and two-center I···N/C HaBs make a significant contribution to the stabilization of these heterohexamers.

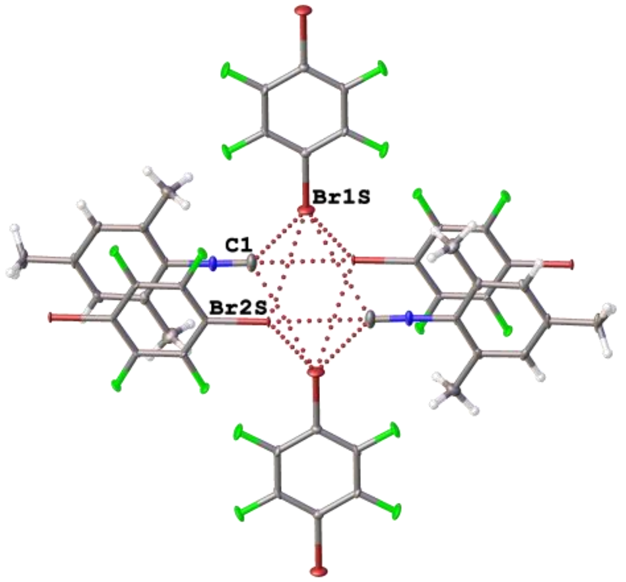

Figure 1. Fragment of the supramolecular structure of (CNMes)·1,4-FBB showing the heterohexamers

This work was supported by the Russian Science Foundation (grant № 22-23-00307). Scientific research were performed at the Research park of St.Petersburg State University «Center for Magnetic Resonance», «Center for X-ray Diffraction Studies»

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New synthesis of 4-arylimidazoles via Ritter reaction

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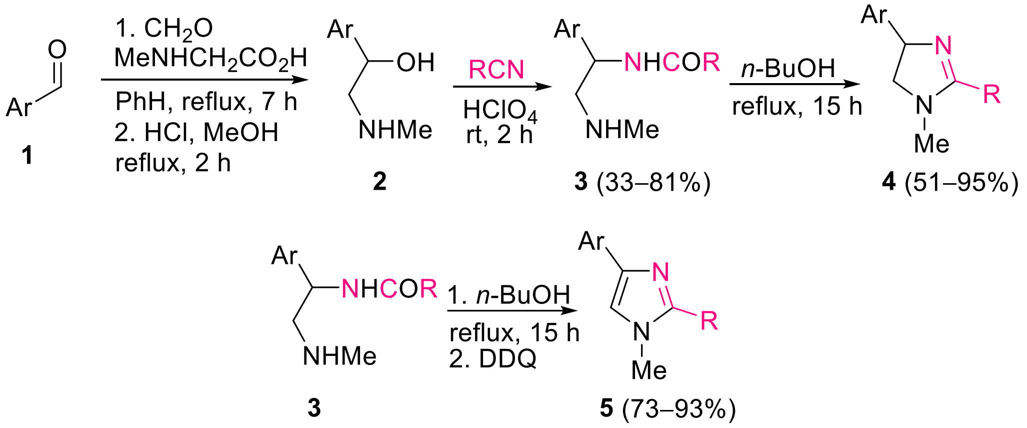
Imidazole core is a popular moiety in organic and pharmaceutical chemistry. Herein, we propose a straightforward method for the synthesis of 1,2-aminoadmides **3**, 2,4-disubstituted imidazolines **4**, and 2,4-disubstituted imidazoles **5** from readily available aromatic aldehydes **1**. The key step in this synthesis is the Ritter reaction of arylethanolamines **2** with nitriles promoted by perchloric acid and resulting in 1,2-diamines **3**. The latter aminoamides were readily cyclized to imidazolines via simple healting in *n*-butanol. The final oxidation provides 2,4-diarylimidazoles **5** in 44–49% total yields starting from aldehyde **1**.



This work was financially supported by the Russian Science Foundation (grant № 22-73-10008)

Synthesis of tetracyclic condensed azaheterocycles from *ortho*-amino ester

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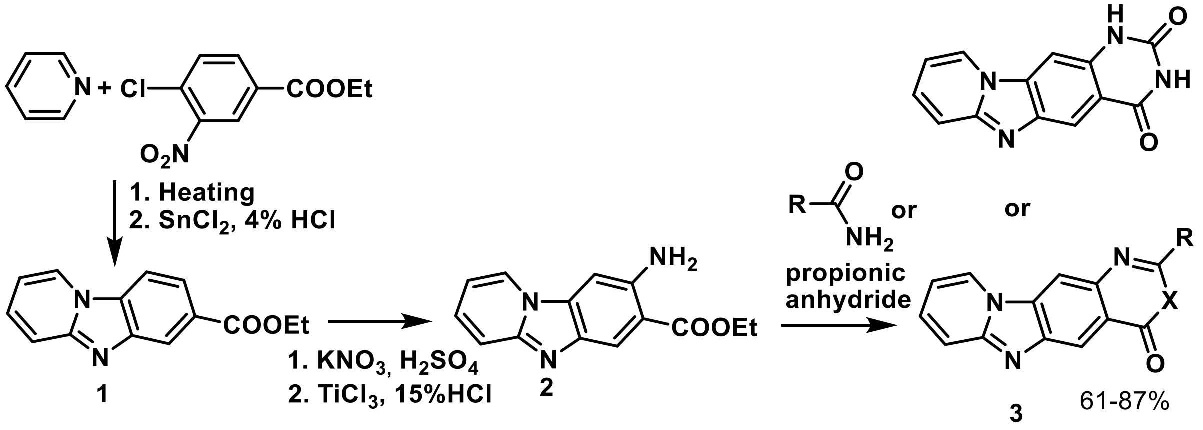
Pyrido[1,2-*a*]benzimidazoles (PBI) are valuable class of bioactive condensed heterocycles, having promising antitumor properties [1-2]. The synthesis of derivatives of these compounds with annulation of new cyclic fragments opens opportunities to develop effective anticancer drugs. To achieve this goal PBI, containing ester group with amino group in *ortho* position was prepared. First, ethyl pyrido[1,2-*a*]benzimidazole-7-carboxylate (**1**) was synthesized using pyridine and 4-chloro-3-nitrobenzoic acid ethyl ester as starting materials.

Ethyl pyrido[1,2-*a*]benzimidazole-7-carboxylate was functionalized in the nitration reaction with KNO_3 in concentrated sulfuric acid. The process proceeded with high regioselectively with the formation of ethyl 8-nitropyrido[1,2-*a*]benzimidazole-7-carboxylate as the only product in 94% yield. Further amino derivative **2** was prepared by chemical reduction with titanium chloride (III). Ethyl 8-aminopyrido[1,2-*a*]benzimidazole-7-carboxylate (**2**) is a building block for annulation of additional fragments to the heterocyclic core. The synthesized substances were studied using NMR spectroscopy and high-resolution mass spectrometry.



, where X=N or O, R=H, Me, Ph, NH_2

Annulation of new cycles to the core was achieved by heating **2** with different carbonyl containing compounds: amides or propionic anhydride within 10-12 hours. Yields of **3** were from moderate to good. In the future, it is planned to study the antitumor activity of the obtained compounds.

This work was carried out with the financial support of grant No MK-3459.2022.1.3 from the President of the Russian Federation for state support of young Russian scientists - candidates of science

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Theoretical investigation of the structure and photophysics of homological series of bis(aryliden)cycloalkanones

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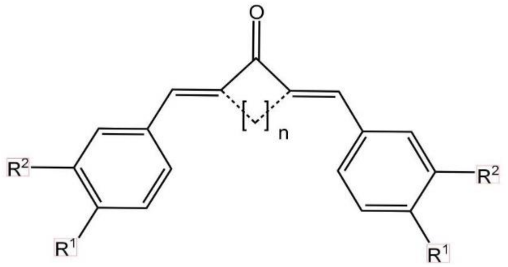
α,α'-Bisarylidene derivatives of cyclic ketones (dienones of cycloalkanone series) are famous for their photochromic and fluorescent properties, which make them applicable as fluorescent probes and photosensitizers in biology [1-2].

Here, we have found theoretically the stable structures of dienons with various electron donating groups in the ground and lower excited states. Main regularities of transitions between the states and excitation relaxation pathways were investigated. The calculated data were used to explain the results of photophysical experiments [3-4].



R^1 = H, OMe, SMe, NMe_2, NEt_2; R^2 = H, OMe;
n = 1-3

Quantum chemical calculations were performed using DFT and TDDFT methods with the PBE0 functional in the 6-31+G(d,p) basis in the Firefly software. Solvent effect was taken into consideration using continuum model.

The influence of conformation, central cycle size and substituent type on the position of absorption and emission maxima in the calculated spectra of substances under question were analyzed. The processes of light absorption, fluorescence and nonradiative relaxation by internal rotation around exocyclic double bonds were considered. The calculation results were in good accordance with the experiment [3-4] and made it possible to explain observed patterns in the spectral and photophysical properties of molecules.

This work was supported by the Russian Science Foundation (grant No. 22-13-00064)

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Synthesis and antioxidant properties of thiadiazolines with hindered phenol moieties

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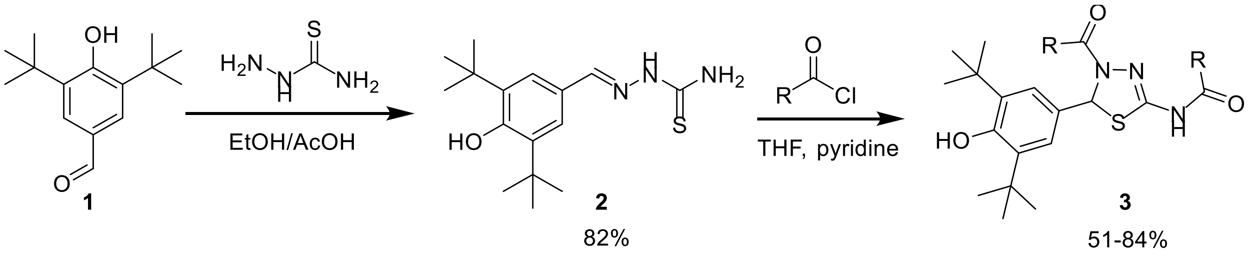
Phenol derivatives are the most common antioxidants used in the food, petrochemical and medical industries. One of the most effective antioxidants is BHT – 4-methyl-2,6-di-tert-butylphenol, which, in addition to antioxidant activity, also has antibacterial properties [1]. Various substituted thiadiazolines also exhibit biological behavior [2,3]. Therefore, interest in the syntheses of thiadiazoline derivatives is significant. Thus, synthesis of phenols with a thiadiazolinyl group by a convenient method is an important part of developing new and potentially biological active compounds.

In this work, a number of thiadiazolines with a 2,6-di-tert-butylphenol moiety were synthesized. At the first stage, the interaction of aldehyde **1** with thiosemicarbazide was carried out to obtain thiosemicarbazone **2**. Next, the reaction of thiosemicarbazone with anhydrides of acetic and propionic acids and a number of acid chlorides was carried out, during which thiadiazolines **3** were obtained in yields of 51-84%. The best yields were achieved by refluxing the starting thiosemicarbazone with an excess of acid chlorides in tetrahydrofuran in the presence of pyridine. In the course of the reaction, a precipitate of acylpyridiniumcloride precipitated, and the target reaction products were isolated from the filtrate.



R = Me; Et; Ph; Ph-CH=CH-; 4-NO$_2$-C$_6$H$_4$-; 4-NO$_2$-C$_4$H$_6$-CH=CH-; 3-cumaryl;

Analysis of the antioxidant activity of the obtained substances showed their high antiradical activity and Fe-reducing capacity.

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Extraction and characterization of crude fiber from khimp (leptadenia pyrotechnica) and date palm tree (phoenix dactyliferal.) and screening their phytochemicals

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Phytochemicals can be extracted by conventional technique (using hexane, acetone, methanol, ethanol. etc.) and carried out generally at atmospheric pressure while new techniques using pressure and/or elevated temperatures(1,2).

Three samples of the plant (khimp, date palm tree leaves, and fiber) were studied to extract the crude fiber and phytochemicals. The study employed ordinary laboratory equipment together with Fourier Transformation Infrared (FTIR) spectroscopy and Ultra Violate – visible(UV-Vis) spectrophotometer. The results obtained showed that the fiber contents were 57.8%, 73.6 %, and 83.3 % for date palm tree leave, khimp, and date palm tree fiber respectively. 12 phytochemicals in all extracts were screened. The structure showed that the three samples contain cellulose, hemicelluloses, and lignin.

It is concluded that the differential extraction method is valuable for the extraction of plant fiber and phytochemicals simultaneously.

Table (1) Components of lignocellulosic materials under investigation. Component

Components		Entity	
	Sample one	Sample two	Sample three
Extractive	16.4 %	17 %	5.6 %
Hemicelluloses	12.5 %	12.2 %	18.8 %
cellulose	55.376 %	56.8 %	62.95 %
Lignin	15 %	11%	10.94 %
Ash	0.724 %	3. %	1.71 %
total	100 %	100 %	100 %

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Photoactive precursor of N-heterocycling carbene complexes for bond-forming photocatalysis

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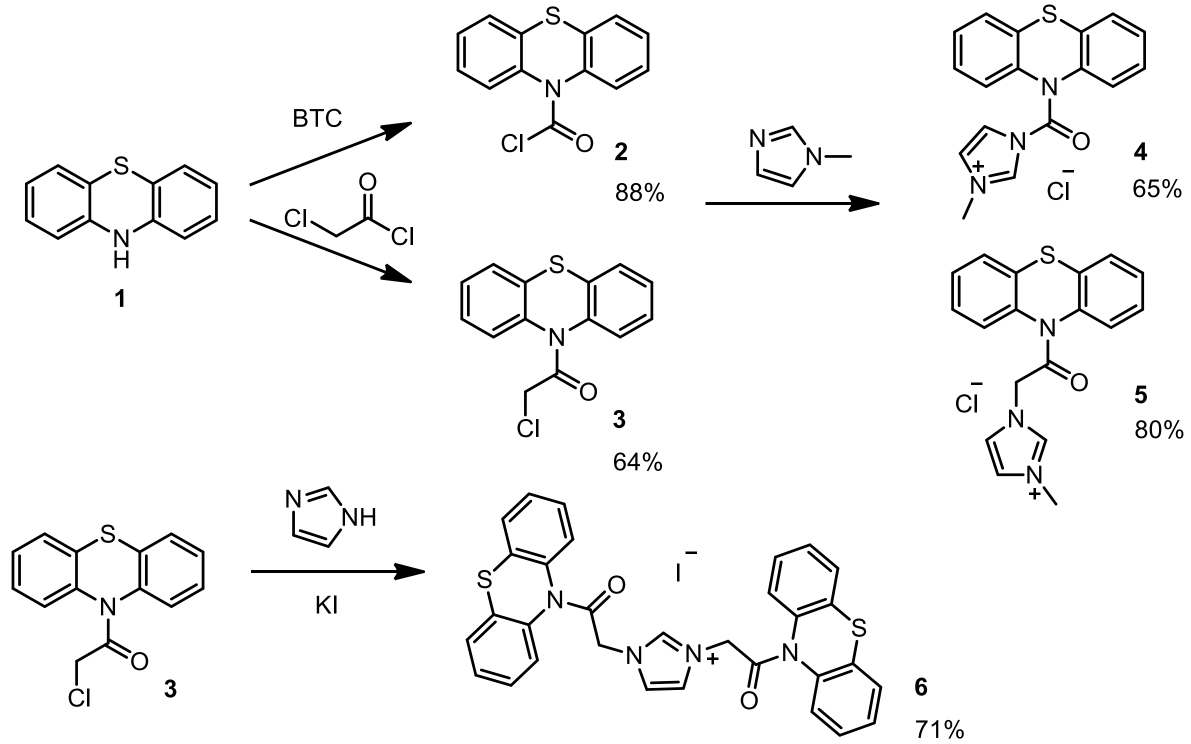
Photoredox catalysis is a powerful tool for chemical transformations under mild eco-friendly conditions. However, controlling stereo- and regioselectivity in photocatalytic reactions is a challenge for chemists because of the high reactivity of free radicals. One of the solutions this problem is the merger of photoredox and transition metal catalysis. Metallaphotocatalysis has recently evolved into a versatile platform for accessing different activation modes, allowing the development of reactions through entirely new mechanistic paradigms [1].

Phenothiazine, due to its easy oxidation and easy functionalization, is an attractive building block from which to construct highly reducing organic photoredox catalysts [2]. N-heterocyclic carbenes (NHC), which have shown to be favorable coordinating ligands, were chosen as a bridge for binding phenothiazine to transition metals.

In this work, phenothiazine was functionalized with a chlorine derivative (**2** and **3**). Its further interaction with imidazole or 1-methylimidazole gave the target precursor of photoactive NHC complexes (**4**, **5** and **6**).



Acknowledgement. The authors thanks Scientific Schools grant NSh-5199.2022.1.3 for the support

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External oxidant free and transition metal free synthesis of 5-amino-1,2,4-thiadiazoles as promising antibacterial against ESKAPE pathogen strains

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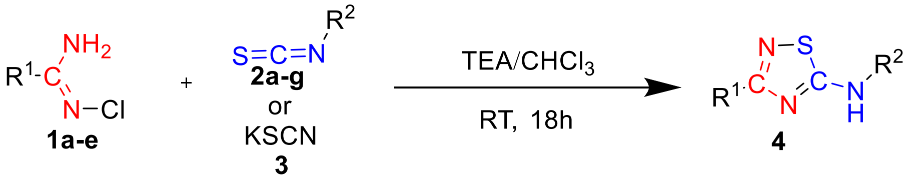
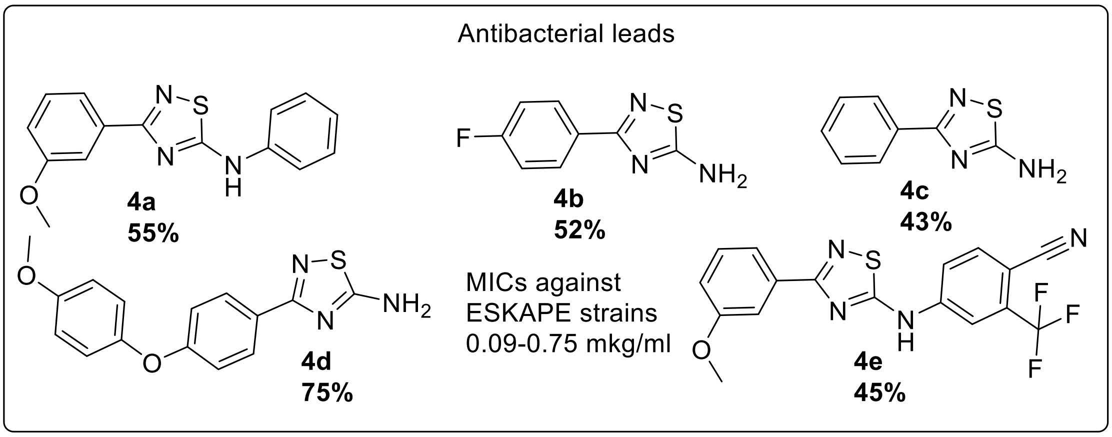
A new route to 5-amino-1,2,4-thiadiazole derivatives via reaction of *N*-chloroamidines with isothiocyanates has been proposed. The advantages of this method are high product yields (up to 93%), the column chromatography-free work-up procedure, scalability, and the absence of additive oxidizing agents or transition metal catalysts [1].





The 28 examples of 5-amino-1,2,4-thiadiazole derivatives obtaining via the proposing protocol were evaluated *in vitro* against ESKAPE pathogens strains (*Enterococcus faecium*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, *Enterobacter cloacae*). It was found that compounds **4a**, **4b**, **4c**, **4d** and **4e** have potent antibacterial activity (MIC values 0.09–1.5 µg mL^{-1}), which is superior to the activity of commercial antibiotics such as Pefloxacin (MIC 4–8 µg mL^{-1}) and Streptomycin (MIC 2–32 µg mL^{-1}). The additional cytotoxic assay of hit-compounds on PANC-1 cell line demonstrated the low or non-cytotoxicity activity at the same level of concentrations. Thus, these 5 compounds are promising starting point for further antimicrobial drug development.

This work was supported by the Russian Foundation for Basic Research (grant № 19-33-60064)

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Photocatalyzed friedel-crafts double addition of indole to aromatic aldehydes by diarylethene

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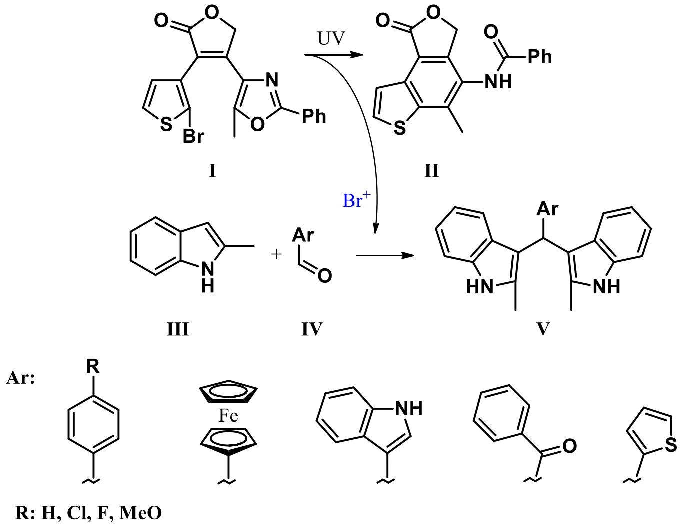
Photochemical reactions are widely used in organic synthesis not only to design various poly(hetero)aromatic systems, but also to develop new smart materials and devices for various purposes. Among them, a special place is occupied by photoacid generators (PAGs), compounds capable of generating acids under the action of light. Substances of this kind are of great interest both for microlithography (microelectronics)[1] and for cationic polymerization.[2] We have recently studied the photocyclization of diarylethene **I** and it was found that the skeletal photorearrangement reaction is accompanied by the release of a bromine cation.[3]



The aim of this work was to study the scope and limitations of the application of neutral diarylethene **I** as PAG for catalysis of electrophilic reactions. The Friedel-Crafts double addition of indole to aryl(hetaryl)aldehydes catalyzed by the bromide cation released under UV light has been studied.

This work was supported by the Russian Science Foundation grant no. 18-13-00308P

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Synthesis of *N*-(3,4-dimethoxyphenylethyl) - benzamide and 3,4-dihydroisoquinoline derivatives

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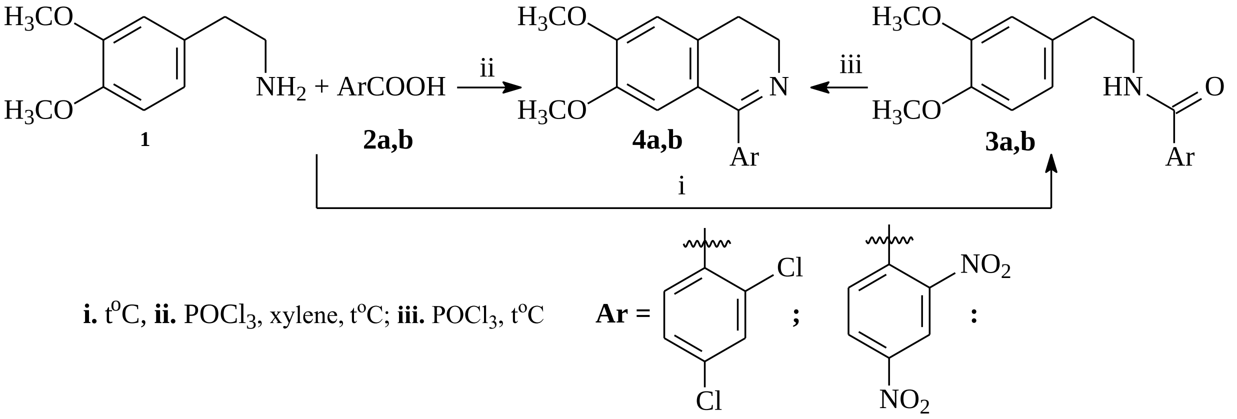
The synthesis of condensed heterocycles containing nitrogen is of great interest in organic chemists. Among them, the alkaloids of isoquinoline series and their analogues have particular significance. Isoquinoline alkaloids have unique pharmacological activity: anticonvulsant, antiepileptic agent, neuroleptic, cardioprotector, antiarrhythmic, analgesic, cytotoxic, antibacterial and anti-fungal, antioxidant. Studying the synthesis of such structural substances and their structure by modern physico-chemical methods, determination of chemical and biological properties is one of the actual problems.

As a continuation of our previous works, the first stage of amidation reaction was carried out thermally by heating aromatic carbonic acid (**2a–d**) and homoveratrilamine (**1**) for 4 hours in an oil bath at 178°C, and as a result of amidation of N-(3,4-dimethoxyphenylethyl)-benzamide (**3a**,**b**) derivatives were synthesized.

The second cyclic stage was carried out on the method of Bishler-Napiralsky reaction by adding **3a**,**b** $POCl_3$ to acid amide and heating the mixture for 4-6 hours under reflux. As a result 3,4-dihydroisoquinolines (**4a**,**b**) are formed.

The reaction takes place according to the following scheme:



i. t°C, **ii.** $POCl_3$, xylene, t°C; **iii.** $POCl_3$, t°C

For the Bischler-Napieralski reaction, one phase synthesis of dihydroisoquinoline derivatives was carried out using microwave heating and without microwave heating. In this case the cyclization reaction of aromatic carbonic acids (**3a**,**b**) in the presence of homoverrilamine (**1**) and $POCl_3$ was carried out by boiling for 6 hours in xylene medium in a laboratory condition and dihydroisoquinoline (**4a**,**b**) derivatives have been prepared.

The structure of resulting *n*-(3,4-dimethoxyphenylethyl)-benzamide and 3,4 - dihydroisoquinoline was proved on the basis of IR and PMR spectrum data.

Study of the cytotoxicity of biologically active 1,2,3,4-tetrahydrobenzo[b]pyridines

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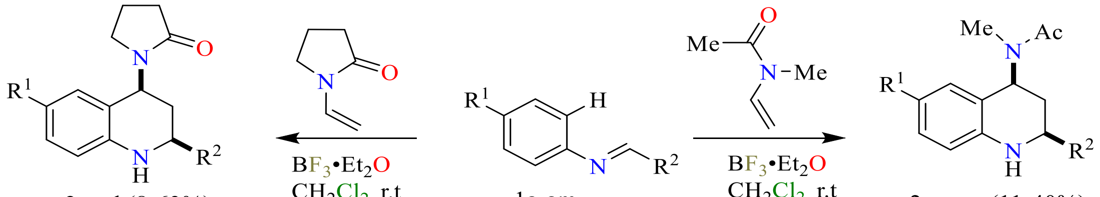
This work is devoted to the synthesis of series of 1,2,3,4-tetrahydrobenzo[b]pyridines and the evaluation of their biological activity. This class of heterocycles is of growing interest to biochemists, since among the derivatives of hydrogenated quinoline, many drugs are known. [1,2,3].

The substances were tested for cytotoxicity against selected cancer cell lines (A375 - melanoma, A431 - epidermoid carcinoma, RT4 - bladder cancer, HepG2 - hepatocarcinoma, BT474 - breast cancer. The table lists the compounds that have shown cytotoxic activity.

According to NCI guidelines, compounds are considered promising if the survival rate is less than 32%.

In this work compounds 2i and 2l showed the highest activity against the A375 and RT4 cell lines, showing a survival efficiency of 1.7% and 1.9% respectively.

It is necessary to emphasize the selective cytotoxic activity of some compounds depending on their structure in relation to certain tested cell lines, which could justify further studies of the relationship between the structure and activity of substances.

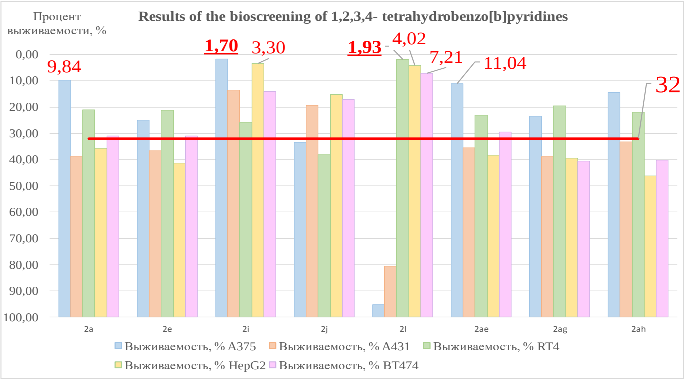


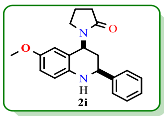
2a-ad (8-63%)

1a-am

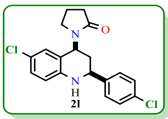
2ae-am (11-40%)

2a: R^1=Cl,R^2=Ph; 2e: R^1=Me,R^2=Ph; 2i: R^1=Cl,R^2=4-Cl-Ph; 2j: R^1=Me,R^2=4-Cl-Ph;
2l: R^1=OMe,R^2=Ph; 2ae: R^1=Cl,R^2=Ph; 2ag: R^1=OMe,R^2=Ph; 2ah: R^1=Me,R^2=4-F-Ph.





2i



2l

	Выживаемость, %				
	A375	A431	RT4	HepG2	BT474
2a	9.84	38.62	21.00	35.58	31.03
2e	24.92	36.62	21.26	41.34	30.91
2i	**1.70**	13.54	25.84	3.30	14.06
2j	33.35	19.38	38.07	15.24	17.05
2l	95.26	80.57	**1.93**	4.02	7.21
2ae	11.04	35.49	23.12	38.30	29.50
2ag	23.49	38.87	19.51	39.47	40.57
2ah	14.49	33.30	21.94	46.25	40.11

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Obtaining grafted polymers based on fish collagen and acrylates

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The creation of new composite materials based on biodegradable collagen copolymers and vinyl monomers for tissue engineering with biomimetic properties is of considerable interest for regenerative medicine: there are no commercially available domestic materials with biomimetic properties in the Russian Federation that can provide an effective regenerative process of soft tissues or act as carrier matrices for cells.

The urgency of the problem is confirmed by both the market demand and the need to create materials for widespread use in regenerative medicine from relatively inexpensive components and using simple technological schemes.

The basic component of the new material is collagen obtained from food waste - the skins of commercial fish. Fish collagen is increasingly replacing the collagen of terrestrial animals due to the fact that it is hypoallergenic, because it is 96% identical to human protein, is not a carrier of infectious animal diseases transmitted to humans and has proven itself well in such materials.

The aim of the work was the synthesis and characterization of grafted polymers based on cod collagen and acrylates of different nature, which can act as the basis of composite materials for regenerative medicine.

The preparation of new materials was carried out by varying the synthesis conditions (temperature, initiator, ratio and nature of components, duration of reactions, etc.). To obtain the characteristics of the grafted copolymer, preparative and physico-chemical methods of analysis were used: elemental analysis, gel-penetrating chromatography, scanning electron microscopy, etc.

Studies have shown that when using the initiator of azoisobutyric acid dinitrile in a suspension of collagen with acrylates (methyl methacrylate, acrylic acid, etc.), grafted copolymers of acrylates on collagen containing ~ 15-20 % of the synthetic fragment are formed.

Depending on the initial composition and the ratio of the synthesis components, different morphology of the surface of lyophilically dried grafted copolymers of acrylates on collagen was revealed. The figure shows the morphology of one of the samples with a pronounced system of interconnected pores characteristic of materials intended for regenerative medicine (magnification 200).

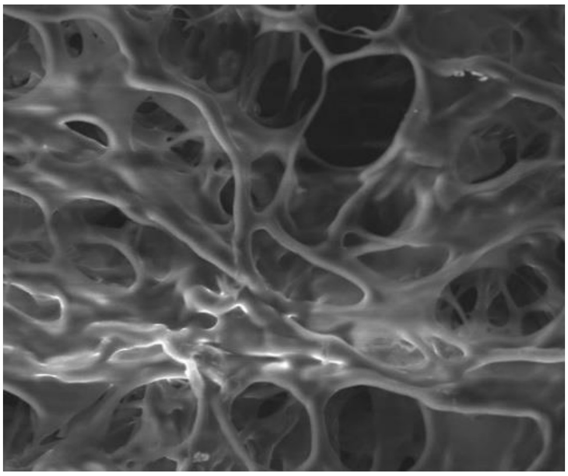

Fig. Morphology of the sponge surface of the grafted copolymer.

The work was carried out within the framework of the consortium "Technologies of regenerative medicine for the treatment of socially-significant diseases" for the implementation of the strategic project "TRANSLATIONAL REGENERATIVE MEDICINE" in the implementation of the program "PRIORITY-2030" using the equipment of the Collective Use Center "New materials and resource-saving technologies" of the Research Institute of Chemistry Nizhny Novgorod State University

New α-(N-diphenyl)-substituted 2,2'-bipyridine push-pull fluorophores: Synthesis and photophysical studies

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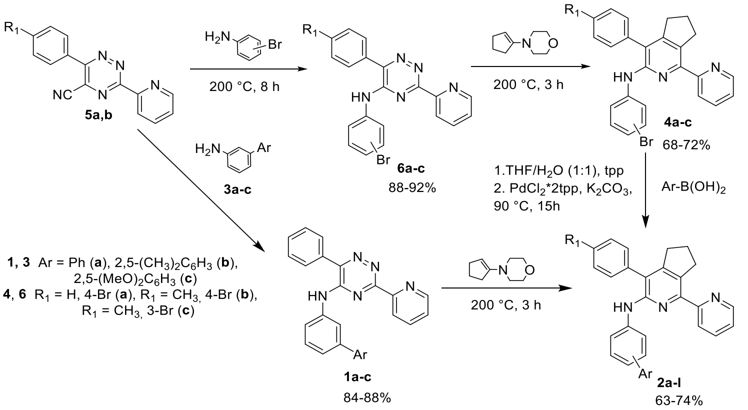
Compounds based on α-arylamino-2,2'-bipyridines and their fused analogs have already found a wide variety of practical applications. In particular, they are promising fluorophores, ligands and drug candidates. Some of *N*-aryl-substituted 2,2'-bipyridines found application in various electroluminescent devices and OLED systems.

Recently, we reported a rational methodology for the preparation of α-arylamino-2,2'-bipyridines. As a first step, according to a previously described procedure [1] *N*-(biphenyl-3-yl)-1,2,4-triazines **1a-c** were prepared in 84-88% yields. And the following *aza*-Diels-Alder reaction afforded cyclopentane-fused 2,2'-bipyridines **2a-c** in 67-74% yields.



However, we were unable to introduce residues of [1,1'-biphenyl]-4-amines **3a,b** into 1,2,4-triazine core. In this regard, we developed an alternative approach to α-arylamino-2,2'-bipyridines **2a-l**, which involves the use of commercially available 3- and 4-bromoanilines. As a result of the *ipso*-substitution of the C5-cyanogroup in 1,2,4-triazines and followed by *aza*-Diels-Alder reaction, bromoarene-substituted 2,2'-bipyridines **4a-c** were readily obtained in 68-72% yields. And the subsequent Suzuki cross-coupling reaction between 2,2’-bipyridines **4a-c** and phenylboronic acid resulted in the formation of the corresponding arylated products.

Photophysical properties, including the phenomenon of solvatochromism and AIE, were investigated for the obtained 2,2'-bipyridines **2a-l**. These compounds exhibited an intense blue to green fluorescence with emission maxima in the range of 443–505 nm and fluorescence quantum yields up to 49.1% in THF solutions.

This work was supported by the Russian Scientific Foundation (grant № 19-73-10144-P) and by the Grants Council of the President of the Russian Federation (grant № NSh-1223.2022.1.3)

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Dual photoredox and nickel catalyzed arylation and alkenylation of cyclopropanols

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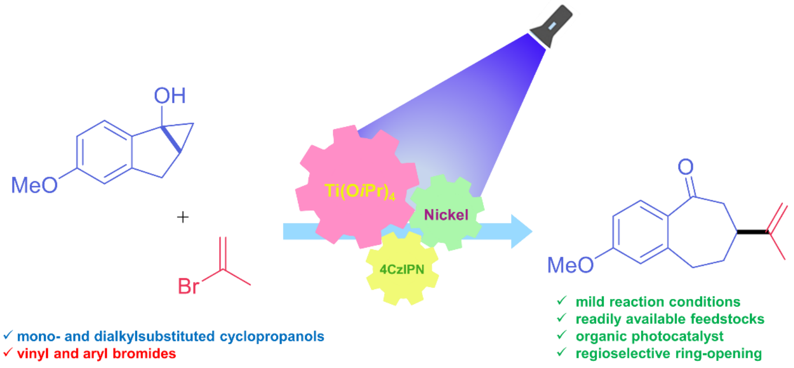
The discovery of new synthetic methods is a crucial task of modern organic chemistry. Especially, there is a great need for new methods of C–C bond construction. Over the last 8 years, nickel/photoredox catalyzed cross-coupling has become a powerful platform for the development of such approaches. In these reactions, two catalytic cycles are combined: the photoredox catalytic cycle and the nickel catalytic cycle. The radical particle formed in the photoredox catalytic cycle is then involved in the nickel catalytic cycle, where it undergoes cross-coupling with an organic halide [1]. One of the attractive radical precursors for these reactions is cyclopropanols which one-electron oxidation delivers valuable β-ketoradicals. However, the typical conditions of nickel/photoredox catalyzed cross-coupling are relatively mild to initiate this oxidation step. Consequently, only limited examples of cyclopropanols were reported to undergo such a reaction [2].

In this work, a general protocol for the photoredox and nickel dual catalyzed arylation and alkenylation of cyclopropanols was developed. The use of titanium isopropoxide as an additive allowed us to overcome the limitations in the scope of reaction. Diverse mono- and disubstituted cyclopropanols with various functional groups in the side chain underwent smooth cross-coupling with *ortho*- or *para*-substituted aryl bromides and mono- or disubstituted vinyl halides. The reaction conditions were mild enough for the preparation of ketones bearing a sensitive α-stereocenter [3].



The authors are grateful for the financial support from the Belarusian Foundation for Fundamental Research (Projects X20M-036 and X20PTI-008)

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Palladium-catalyzed intramolecular furan-yne reaction for the synthesis of functionalized dihydropyrroles and dihydrofurans

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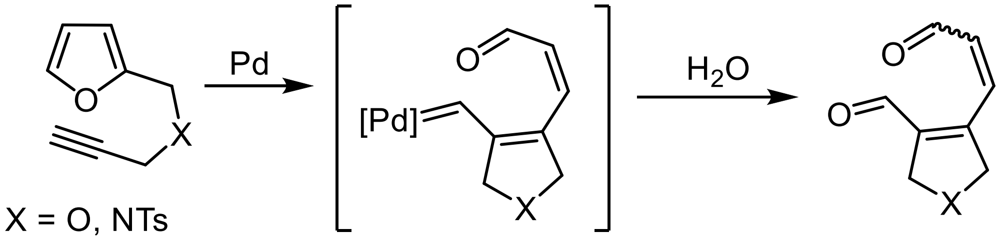
Among the synthetic methods toward heterocycles, dearomatization of the furan ring has proved to be a relatively effective strategy [1]. The homogeneous metal-complex catalysis plays a crucial role in this field as a proper tuning of a catalytic system as well as smart design of a starting material could lead to the formation of a highly complex functionalized product within a single synthetic operation [2].

In early 2000, groups of Hashmi and Echavarren intensively studied a transition metal-catalyzed intramolecular furan-yne cyclization, which yielded densely substituted phenols formed upon a peculiar cascade of transformations. The formation of one of the key intermediates, a metal-carbene, was indirectly detected by the formation of a corresponding dicarbonyl by-product formed via water addition to the carbene center in trace amounts [3,4].

Driven by the hypothesis that such highly functionalyzed compounds can have high synthetic potential as building blocks in organic chemistry, we explored the process in detail, found optimal reaction conditions toward their selective formation and studied some of their chemical properties.



Scheme 1. Synthesis of dicarbonyl compounds

Details of the optimization studies, scope and limitation of the developed synthetic method as well as further synthetic prospects of the obtained products will be discussed.

This work was supported by Russian Science Foundation (project 21-73-10063)

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Influence of ligand surrounding in Hoveyda-Grubbs complexes at increasing catalytic activity

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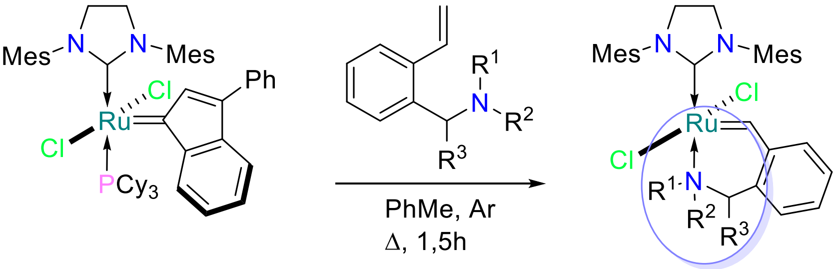
The development of effective methods for the synthesis of new metal complexes of the Hoveyda-Grubbs type with a known ligand environment for studying their catalytic activity in the olefin metathesis reaction.

To obtain α-substituted styrenes as a precursor of 1-alkyl-3,4-dihydroisoquinoline, which was assisted by the reaction rate required for the synthesis of 1-substituted-3,4-dihydroquinolines, and included acyl phenethylamine with fast cycling of the resulting amide according to the Bischler-Napiralski reaction. The product was alkylated followed by Hoffmann digestion [1].

To “assemble” metal complexes, styrenes obtained in the first part of the work were introduced into reactions with an indenylidene complex, referred to in the literature as **Ind II**, which is one of the most common starting materials for the preparation of Hoveyda–Grubbs type catalysts [2]. All syntheses were carried out in an inert atmosphere by heating in absolute degassed toluene.



Ind II

R^1, R^2, R^3 = Alkyl

The final stage of the work was the study of the catalytic activity of metal complexes. To do this, the resulting complexes were introduced into a model metathesis reaction with the formation of a cycle using N,N-diallyltosylamide as an example. When the reaction was carried out in dichloromethane at room temperature (25°C) for an hour, conversions of 80-99% were obtained (according to NMR). thus, complexes with a methyl group at the a-position exhibit superior efficacy even in the absence of activation.

The research was funded by the Russian Science Foundation (project No. 22-23-00490)

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Designer's ionic liquids with an active pharmaceutical ingredient: main regularities on the example of cinnamic acid

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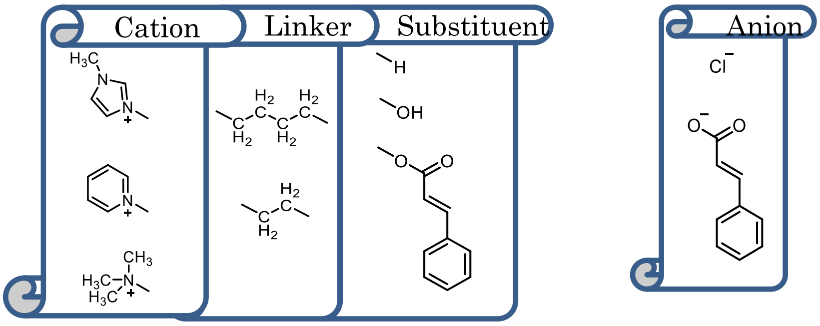
Throughout the history of mankind, many medicinal compounds have been discovered and created. Most of them are bulky molecules containing many functional groups with poor solubility in aqueous media. Low solubility leads to the problems with bioavailability, as an unattainable effective concentration, difficult targeted delivery, high dependency of drug efficiency on polymorphic modifications and the powder fineness.

The often used method of an increasing solubility of pharmaceutical ingredients (APIs) is preparation of their salts through the protonation of basic groups or neutralization of acidic ones. However, such salts are not always highly soluble and their stability strongly depends on the pH of the medium. A more modern and reliable method is the conversion of API into ionic liquids (API-ILs). It allows to affect their solubility, stability and bioavailability by modifying the structure of cations and anions.



In this work API-ILs, containing cinnamic acid moiety in their cations and/or anions were synthesized. Cinnamic acid was chosen as a model poorly soluble API. Trends in physical, physicochemical, and biological properties, depending on the cationic center, the type of API binding to the cationic center, and the length of the covalent linker were found [1].

This work was supported by the Russian Sience Foundation (RSF Project #21-73-10262)

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Selective isolation of oleic acid from rapeseed oil in the hydrothermal process

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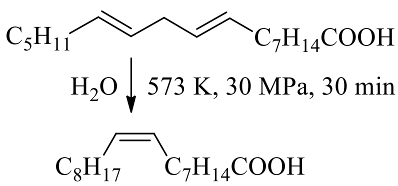
Oleic acid (OA) is the most common monounsaturated fatty acid in nature. It is in demand by chemical production as a base compound in the synthesis of azelaic acid, esters of which are components of modern high-quality lubricants.

Technical OA is obtained by catalytic hydrolysis of rapeseed oil with an OA content of 65-67%. The release of OA from hydrolysate is a labor-intensive energy-consuming process, accompanied by the formation of a significant amount of polluted effluents.

To eliminate such shortcomings in organic processes, alternative supercritical fluid (SCF) techniques are proposed. For hydrolytic transformations, water is of particular interest in the conditions of its SCF formation (T_{cr}=647.1 K, P_{cr}=22.06 MPa). Our experiments on the hydrolysis of rapeseed oil in SCF-water in order to isolate individual OA indicate the obvious advantages of the hydrothermal process in comparison with the traditional one. SCF hydrolysis was carried out without the use of catalysts, special mixing, in the temperature range corresponding to the formation of sub- and supercritical fluids at T=573 K, 623 K and 653 K, with ratios oil : water 1:1 and 1:2 (vol.).

The experimentally established optimal process time is 30 min. The work was carried out on the installation designed and implemented at the Kazan National Research Technological University [1].

The obtained SCF hydrolysates are two-phase systems. The compositions of the light fatty acids phase were studied by chromatography-mass spectrometry. In all experiments, an excess of the content of OA in comparison with its content in the original oil was found. In the process with parameters T=573 K, the ratio of oil : water 1:2 the content of OA in the hydrolysate reaches 95%. The increase of OA content corresponds to the decrease in the content of linoleic acids, which is naturally associated with its transformation into OA as a result of hydrogenation of one of the double bonds by SCF-water.



The found result is an additional factor in favor of the hydrothermal process, in which rapeseed oil becomes a high-level source of OA.

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Rh(III)-catalyzed C-H activation/annulation of indoles with CF_3-containing α-propargyl α-amino carboxylic and α-amino phosphonic acid derivatives

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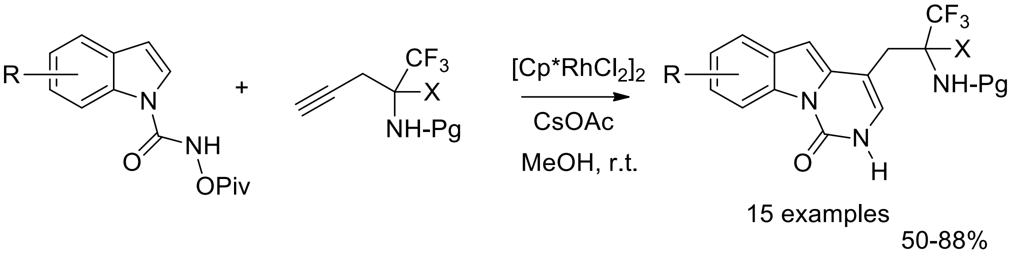
Polycyclic indole-fused heterocycles are an integral part of many biologically active natural and synthetic compounds, including currently used pharmaceutical agents. Usually the construction of these molecules either requires multi-step synthesis, or suffers from narrow substrate scope [1]. At the same time, the significant impact of fluorine functionalities on the modern drug discovery process is well recognized and has been the subject of numerous publications [2]. Therefore, the development of new synthetic approaches that allow rapid assembly of indolic structures, particularly containing fluorine atoms, in simple operation from readily available precursors is of great interest. In this context, the transition-metal-catalyzed functionalization of the C-H bond that emerged as one of the most important strategies in terms atom-economy and efficiency to construct diverse organic molecules from readily available starting materials [3] can be considered as effective tool to access the desired indole-based systems.

Recently we have reported the synthesis of isoquinolone-containing α-CF_3-substituted α-amino acid derivatives *via* C-H activation/annulation reaction of the aryl hydroxamates with the α-propargyl-α-CF_3-α-amino acid derivatives under Rh(III) catalysis [4]. In continuation of the investigation in this field now we wish to disclose our results on the Rh(III)-catalyzed C-H activation/annulation of the indoles with the propargyl-containing α-amino acid derivatives and their phosphorus analogues.



R = H, 3-Me, 4-Me, 6-Me, 6-Cl; X = CO_2Me, $P(O)(OEt)_2$; PG = Boc, Cbz

This work was supported by the Russian Science Foundation (grant № 21-13-00328)

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Photoswitchable complexation of crown-containing styryl dyes bearing ammoniohexyl substituent with metal ions

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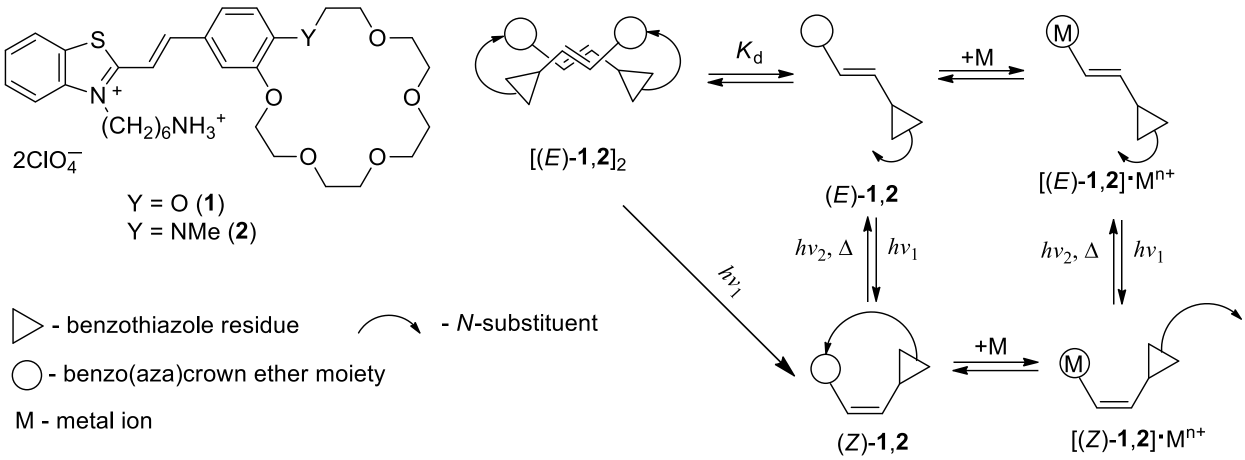
Photoswitchable or photocontrolable ionophores are compounds bearing both photochromic and macrocyclic moieties, the latter can accommodate selectively metal cations or other species. The molecular system should be designed in such a way that structural changes arising in the photochromic fragment have an appreciable influence on the receptor properties of the macrocycle. Such compounds may be used in photocontrolled ion transport, ion extraction and separation [1], and design of photoswitchable nanoelectronic devices [2].

It was shown that *E* isomers of styryl dyes **1** and **2** form dimeric complexes in MeCN due to hydrogen-bonding self-assembly. The stability constants of complexes (*E*)-**1**,**2** and (*Z*)-**1**,**2** with metal cations, as well as the dimerization constants and the quantum yields of reversible *E*–*Z* photoisomerization of the free dyes were measured using spectrophotometry. It was found that the photogenerated *Z* isomers of compounds **1**,**2** have a pseudocyclic structure, which leads to differences in the stability constants of complexes of different isomers of these dyes with metal cations.



This work was supported by the Russian Science Foundation (№ 22-13-00064)

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2-(2-nitrobenzyl)furans: synthesis and reactivity

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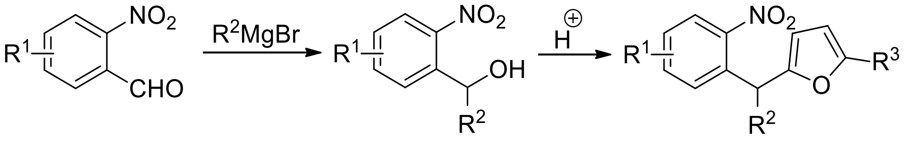
The use of compounds of the "*furan platform molecules*" as starting compounds makes it possible to synthesis a wide range of various complex heterocycles. Among the variety of possible derivatives of furan, a special place is occupied by substrates containing in their structure an additional functional group capable of entering into a various cyclization reaction. This type of furans includes substituted 2-(2-nitrobenzyl)furans, which are difficult to access, however have high synthetic potential.



The report will consider methods for the synthesis of 2-(2-nitrobenzyl)furans containing various substituents; the scope and limitations of the proposed synthetic methods are shown. In addition, the reactivity of 2-(2-nitrobenzyl)furans will be discussed.

This work was supported by Russian Science Foundation, project № 21-73-10063

Synthesis of cyclofuroisoindolones by the IMDAV reaction

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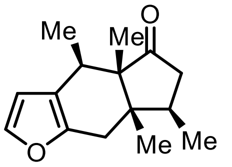
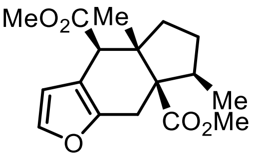
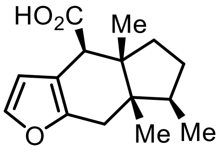
Previously, our scientific group established that the interaction of (3-furyl)allylamines with maleic anhydrides leads to the formation of furo[2,3-*f*]isoindoles – the aza-analogs of pinguisane-type sesquiterpenes [1,2].



Pinguisone

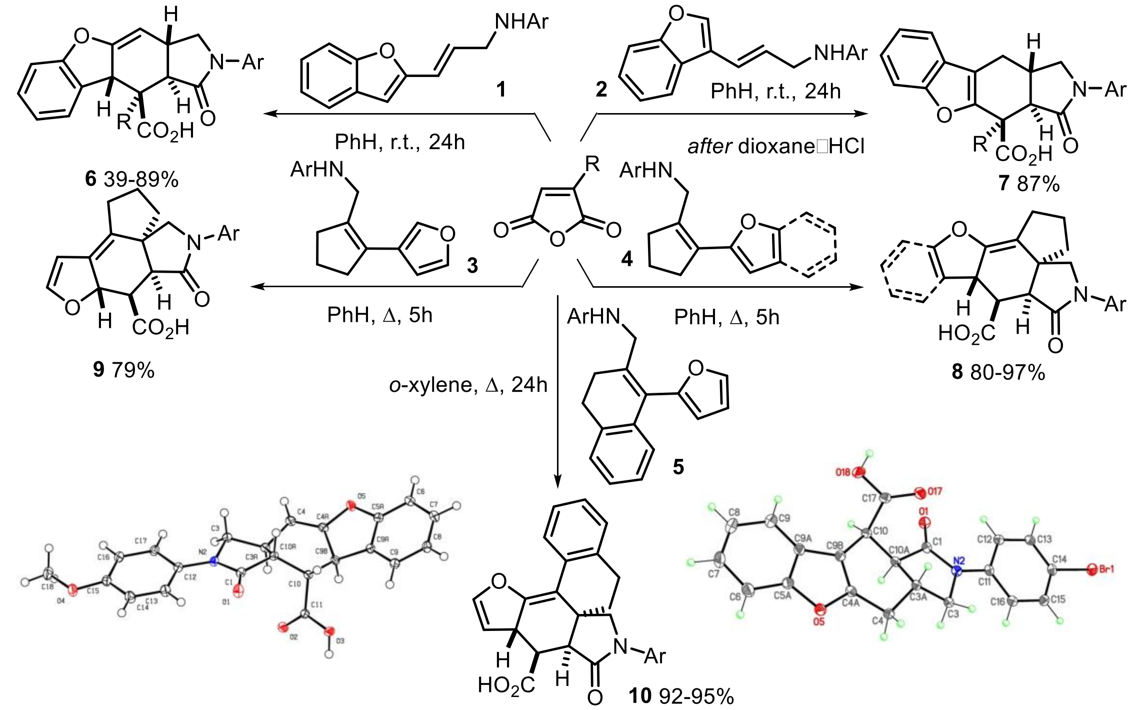


Bryopterin B



Deoxopinguison-15-oic acid

This research was aimed to study cyclosubstituted furylallylamines **1-5**, readily available in two steps from corresponding furylacroleins and primary arylamines, in the tandem *N*-acylation / intramolecular [4+2]-cycloaddition reaction with maleic anhydride and its derivatives. By using a domino reaction of furylallylamines **1-5** and α,β-unsaturated acid anhydrides under mild conditions, various furoisoindolecarboxylic acids **6-10** were obtained with high yields. The domino sequence includes two steps: an acylation of the nitrogen atom in furylallylamines **1-5**, the intramolecular Diels–Alder cycloaddition in the resulting *N*-acyl vinylfurans (IMDAV reaction), and a forced prototropic shift in some cases (*for* **7**) in the adducts **6-10** followed by the recovery of the furan nucleus aromaticity.



This work was supported by the Russian Science Foundation (RSF) (project №. 22-23-00179)

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N,N'-diphenyl substituted diamines and oxadiamines and BINOL-containing macrocyclic derivatives of oxadiamines in fluorescent detection

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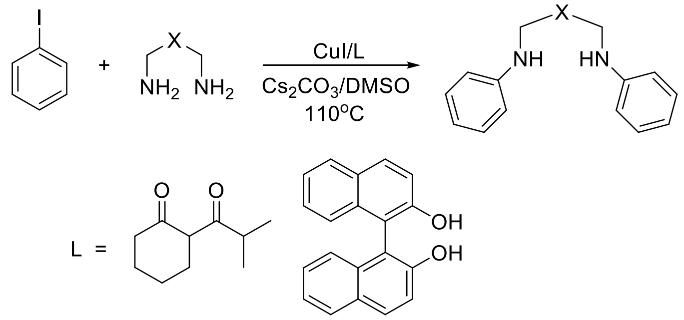
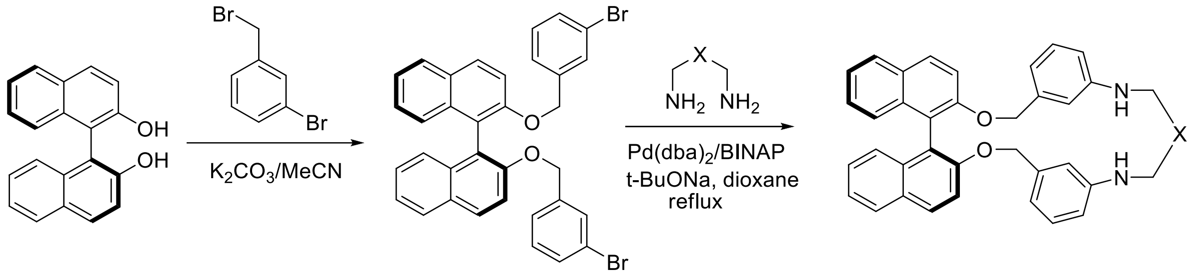
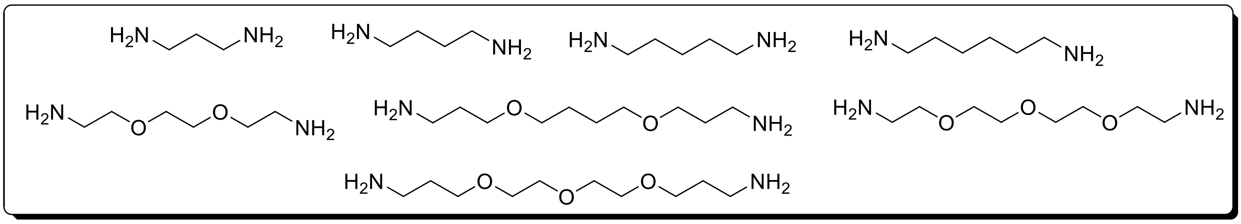
Design and synthesis of efficient UV and fluorescent chemosensors is an important task of the modern organic and analytical chemistry. Our approach utilizes the metal-catalyzed reactions for the construction of C-N bonds for this purpose. In the present investigation we decided to compare the possibilities of the spectrophotometric and spectrofluorimetric detection of metal cations with simple linear *N,N'*-diphenylsubstituted oxadiamines and their cyclic analogues comprising BINOL moiety in order to find out dependence of the efficiency of the recognition on the cyclic/linear structure of the potential detector, the length of the chain and the number of donor oxygen atoms in it.





Diamines and oxadiamines under investigation:



The synthesis of linear *N,N'*-diphenyl derivatives of the diamines and oxadiamines was carried out in the presence of CuI in DMSO at 110°C; two ligands, 2-isobutyrylcyclohexanone and *rac*-BINOL proved to be almost equally efficient providing high yields of the target compounds. The transformation of (*S*)-BINOL into corresponding macrocycles employed a standard Pd(0)-catalyzed macrocyclization step with 4 oxadiamines. The detecting properties of the compounds thus obtained were studied using a panel of 21 metal salts (perchlorates and nitrates) by means of UV and fluorescent spectroscopy.

This work was supported by the RSF grant № 22-23-00518

Chemoselective divergent transformations of N-(propargyl)indole-2-carbonitriles with nitrogen nucleophiles: alkyne hydroamination or domino cyclizations

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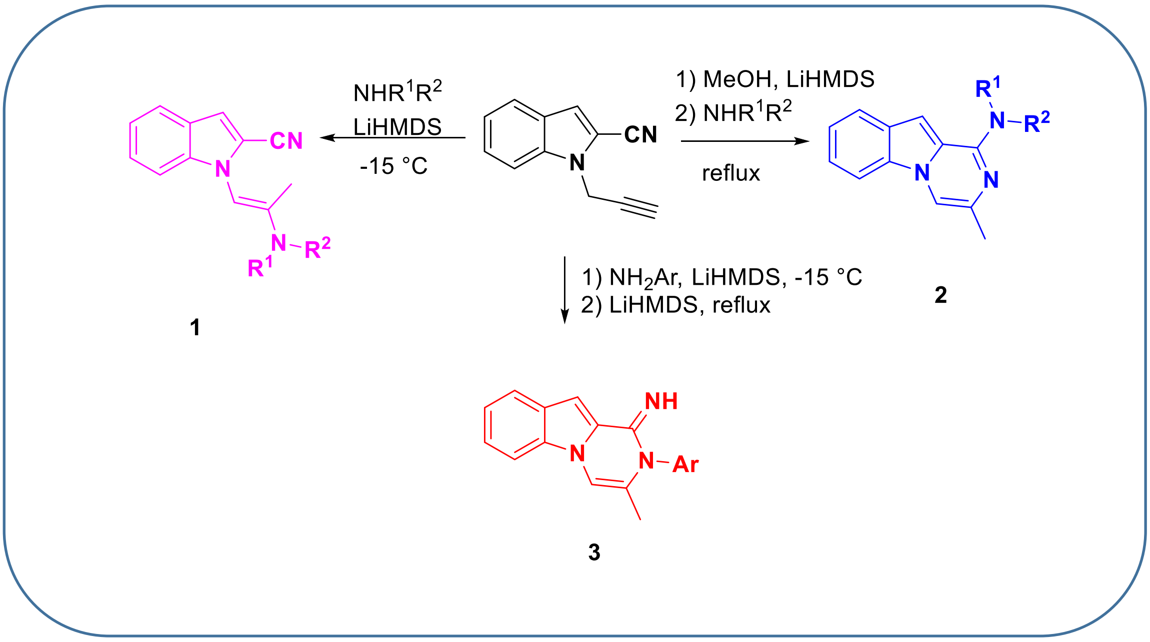
Interactions of *N*-(propargyl)indole-2-carbonitriles with nitrogen nucleophiles were studied. It was found that LiHMDS-promoted reactions lead to the mixture of two product types, originating from an initial attack onto CC or CN triple bonds. Performing the reaction at reduced temperature and in the presence of catalytic amounts of LiHMDS delivered alkyne hydroamination products exclusively. On the contrary, one-pot reaction of *N*-(propargyl)indole-2-carbonitriles with methanol and LiHMDS on heating, followed by addition of nitrogen nucleophile, allowed a selective domino cyclization sequence towards 1-aminopyrazino[1,2-*a*]indoles. Anilines and nitrogen heterocycles could be employed as nucleophiles to obtain products of both types. Moreover, an alternative one-pot route towards third product type has been developed. When *N*-(propargyl)indole-2-carbonitrile was firstly combined with aniline and LiHMDS at reduced temperature, further heating of the *in situ* generated hydroamination product led to the intramolecular cyclization into 1-imino-2-phenylpyrazino[1,2-*a*]indoles. Thus, chemodivergent transformations of the same starting material into three compound classes were investigated. The possible reaction routes were studied, and *N*-(allenyl)indole-2-carbonitrile was identified as a key intermediate. Acyclic and cyclic products are exhibiting fluorescence emission in blue to green.

N-(propargyl)indole-2-carbonitriles - Three product types



This work was supported by the Russian Foundation for Basic Research grant № 21-33-70007 (Festa, A.A)

Asymmetric synthesis of optically active phosphonates with the participation of *P,S*-bidentate ligands based on (*R,R*)-TADDOL

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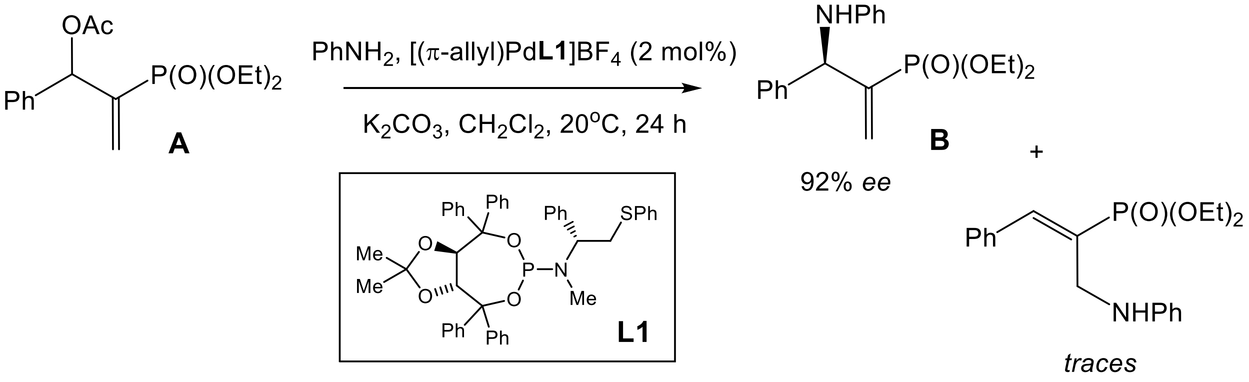
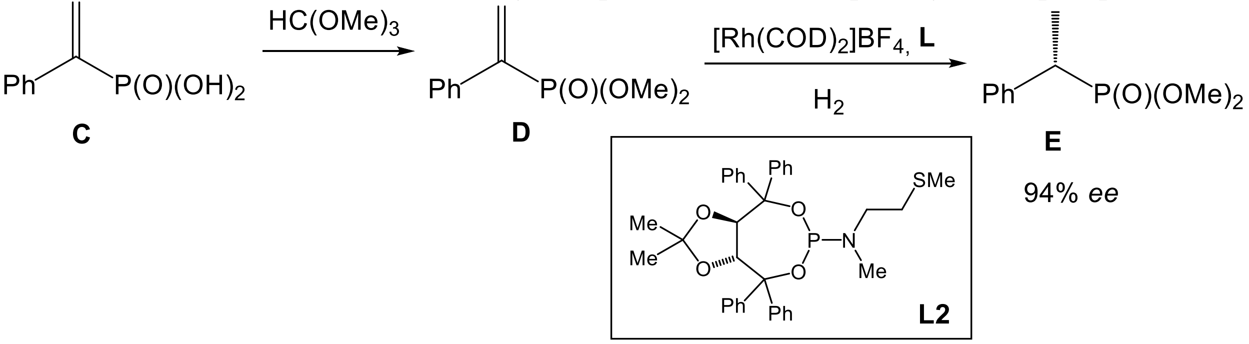
Obtaining optically pure biologically active substances, in particular phosphonates, is an urgent task of modern organic chemistry.

To obtain optically active β-aminophosphonate **B**, we used the previously described technique [1], including the preparation of its precursor **A**, and its further Pd-catalyzed allylation. At the final stage, a palladium(II) cationic π-allyl complex with an amidophosphite type **L1** ligand was tested in the reaction of allyl amination of **A** with aniline.



To obtain optically active phosphonate **E**, we first synthesized vinylphosphonic acid **C** according to the previously described method [2]. Esterification under the action of trimethyl orthoformate made it possible to obtain unsaturated phosphonate **D**, hydrogenation of which under the action of the $[Rh(COD)_2]BF_4$ + **L2** system provided the final optically active phosphonate.



This work was supported by the Russian Science Foundation (project No. 19-13-00197)

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Novel approaches to the synthesis of indolizino[8,7-b]indole and pyrido[1,2-a:3,4-b']diindole derivatives

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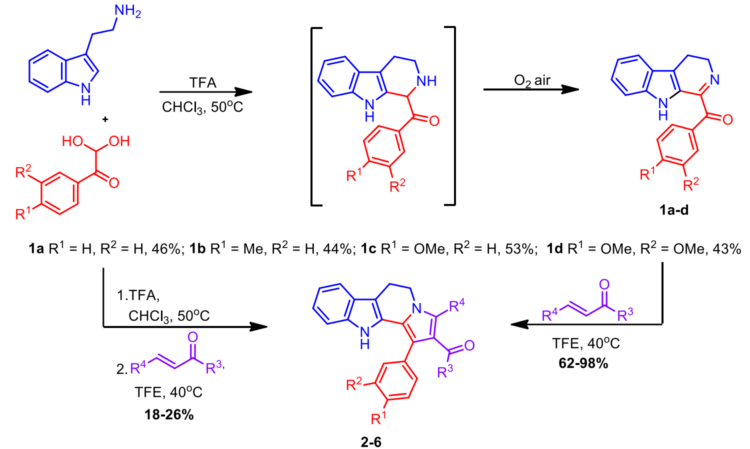
Indolizinoindole derivatives have high biological activity, which provides a large number of publications, including a volume of patents. The indolizino[8,7-*b*]indole skeleton is observed in natural bioactive substances, such as (±)-*Harmicine*, *Fascaplysine, Homofacaplysine B and C*, which have significant analgesic, antitumor and antidiabetic effects[1,2].

In order to reveal the potential possibilities of domino reactions of heterocyclic compounds containing an imino-ketone fragment with the participation of electron-deficient alkenes several approaches were used.

First, a convenient procedure was developed for the synthesis of compounds **1a-d** by the Pictet-Spengler reaction without isolation of the 1,2,3,4-tetrahydro-*β*–carbolines derivatives. Next 1-aroyl-3,4-dihydro-*β*-carbolines **1a-d** were dissolved in 2,2,2-trifluoroethanol (TFE), and the appropriate amount of alkene was added. Indolo[8,7-*b*]indolizine derivatives **2-6** were obtained in yields 62-98% and crystallized from the reaction mixture.

Next a one-pot approach to the synthesis of the corresponding indolizino[8,7-*b*]indole derivatives **2-6** was investigated. So, after reaction between tryptamine and phenylglyoxal monohydrate in chloroform was completed, solvent was replaced by 2,2,2-trifluoroethanol and the required amount of alkene was added. The conversion time did not change, but indolo[8,7-b]indolizine derivatives **2-6** required further purification by column chromatography. Compounds **2-6** were isolated in 18-26% overall (in several steps) yield as crystalline substances.



1a R^1 = H, R^2 = H, 46%; **1b** R^1 = Me, R^2 = H, 44%; **1c** R^1 = OMe, R^2 = H, 53%; **1d** R^1 = OMe, R^2 = OMe, 43%

2 R^3 = R^4 = H; **3** R^3 = H, R^4 =CH_3; **4** R^3 = H, R^4 = Ph; **5** R^3 = CH_3; R^4 = H; **6** R^3 + R^4 = $CO(CH_2)_3$

The first approach with the isolation of carboline derivatives **1a–d** turned out to be more convenient; the absence of reagent residues from previous transformations eliminates side processes at the final stage. But the second approach certainly could also be used, because it was noted that subsequent dehydrogenation of compounds **1a–d** is possible when standing in air, which required the immediate introduction of the starting materials into further transformations. It was shown that the reaction proceeds faster with acrolein, while the reaction with cinnamic aldehyde requires more time.

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Synthesis and biological activity of vinylferrocene derivatives

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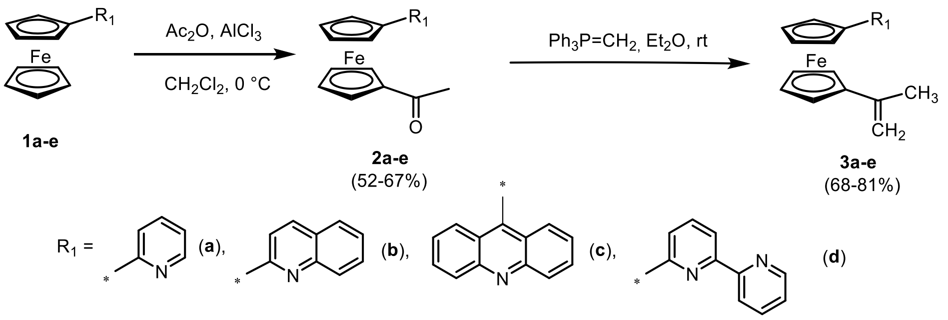
Ferrocene derivatives are attractive molecular systems due to their stability, redox properties and low cytotoxicity, because iron is a natural participant in intracellular metabolism. The introduction of a ferrocene fragment into the structure of azines makes it possible to modulate both the molecular characteristics of the resulting derivatives (solubility, hydrophobicity/lipophilicity) and the biological properties [1].

Previously, it was shown that Friedel-Crafts acetylation of monosubstituted azinylferrocenes occurred regioselectively at the 1'-position of the ferrocene ring with $Ac_2O/AlCl_3$ mixture. Acetylated derivatives **2a-e** entered to the Wittig reaction with $Ph_3P=CH_2$ to form 1-azinyl-1'-isopropenyl-ferrocenes **3a-e** under mild conditions [2].



It was found that the obtained vinylferrocenes exhibited high inhibitory activity against butyrylcholinesterase (BChE), high radical-scavenging activity in the ABTS test, which exceeds that of Trolox. All of the above allows us to consider these substances for further research as drugs for the treatment of Alzheimer's disease.

This work was supported by the Russian Science Foundation (grant № 22-13-00298)

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Inorganic and Coordination chemistry Section Key-note Speakers

Luminescent bio-medical materials based on d^{10}-metall complexes of heterocyclic phosphines

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The growing interest in artificial luminescent compounds is due to the widespread use of various emitting devices in people's daily lives, the use of luminescent compounds as sensors for measuring temperature, pH or the detection of certain chemicals, and as contrast agents for microscopy. Transition metal complexes are most suitable for creating luminescent sensors due to relatively high PLOY values, long service life, and sensitivity of their phosphorescence to changes in the coordination sphere [1]. Phosphinopyridines and other phosphines with chromophore functional groups play a special role among the ligands that are effectively used to create such complexes. For example, their mono-, poly-, and heteropolynuclear complexes of d10-metals demonstrate not only effective radiation in a wide range, but also thermo-, vapo-, and solvochromism [2].

Recently, our laboratory proposed the use of heterocyclic phosphines with exocyclic chromophore groups to create luminescent coordination compounds [3]. A wide range of bi-, tetra- and hexa-, homo- and heteronuclear complexes of gold (I) and copper (I) was obtained based on such ligands. For these compounds, phosphorescence is observed in a wide range of wavelengths, including the infrared range [4] and a rare two-band white emission [5, 6]. The possibility of using both the complexes themselves and materials created by immobilization of their nano-sized collloids on a polyelectrolyte matrix as sensors for pH, temperature [7, 8], the presence of organic solvents [9], biothiols [10], as well as for illuminating cell organelles has been demonstrated by confocal microscopy [11,12]. This makes the presented complexes promising building blocks for the design of luminescent materials for analytical and biomedical applications.

This work was supported by the Russian Science Foundation (grant № 22-13-00147)

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Selected topics towards sustainable Redox and Lewis acid catalysis

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Catalysis is involved in a diversity of areas that are well aligned with the United Nations Sustainable Development Goals 2030 Agenda (*e.g.*, Goals 12 and 9, of significance to this lecture).

Selected catalysis topics within the author´s research group are addressed, namely towards the synthesis of added value functionalized compounds under mild and sustainable conditions. They include, *e.g.*, C-H bond activation of alkanes, oxidation of VOCs (volatile organic compounds), C-C coupling reactions and water splitting.

These topics are illustrated by recent studies according to approaches that have been pursed including the application of metal-organic frameworks (MOFs), catalysts heterogenization, assistance of microwave or ultrasound radiation, single-pot and tandem methods.

This work was supported by Fundação para a Ciência e Tecnologia (project UIDB/00100/2020 of Centro de Química Estrutural) and RUDN University Strategic Academic Leadership Program. Co-authors cited in the references are also gratefully acknowledged

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From white to black: important intermediates and new materials based on element phosphorus

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The development of modern chemistry proceeds in various priority directions focused on creation and design of new ecologically friendly methods for preparation of different compounds and materials bearing practically useful chemical and physical properties [1]. White (P_4) and black (BP) phosphorus are main important allotropes of element phosphorus which allow access to practically important phosphorus derivatives including the ligands for transition metal catalysts, biologically active materials, drugs and the components for microelectronics.

White phosphorus (P_4) Black phosphorus (BP)

Transition-metal mediated white phosphorus activation is of high interest as an ecological alternative to P_4 chlorination pathway to the practically useful phosphorus products [2,3]. Herein, we report facile approaches for P_4 activation, transformation and subsequent functionalization in the coordination sphere of transition metal complexes describing the mechanism of the process and the structure and properties of the formed intermediates bearing coordinated intact and transformed P_4 molecule. The elaborated methods for chemical modification and functionalization of P_4, BP and some polyphosphorus compounds, including cyclic organic polyphosphines and few-layer black phosphorus (FLBP) towards new high reactive phosphorus intermediates, transition metal clusters and metal-free catalysts are also discussed [4,5].

This work is financially supported by the grant of the President of the Russian Federation for supporting of the Leading Scientific Schools (project no. 4078.2022.1.3) and by the Kazan Federal University Strategic Academic Leadership Program ("PRIORITY-2030")

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Inorganic and Coordination chemistry Section Invited Speakers

Metallo-Drug design of complexes with O- and N-polydentate ligands: synthesis and *in vitro* biomedical evaluation

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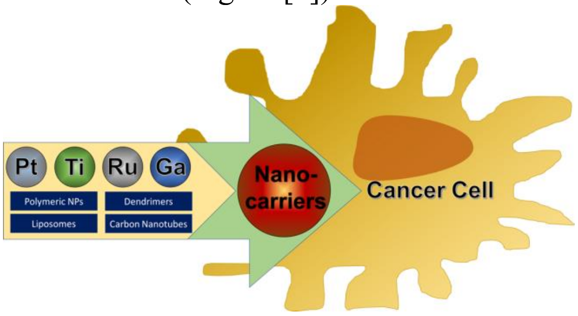
Currently, there is a significant interest in the field of medicinal chemistry in the development of drugs based on metal complexes with unique therapeutic properties. Thus, medicinal metal complexes containing in the molecule **Pt** (an antitumor drug cisplatin), **Au** (auranofin, a drug used in rheumatoid arthritis), **Tc**, **Re** (radiopharmaceuticals for radiation therapy), **Ru** (an anticancer agent), **Gd**, **Co**, **Li**, **Bi**, **Fe**, **Ca**, **Rh**, **Cu**, **Ag**, **Zn**, **Al**, **Lu**, **V**, **Ti**, **Mn** and etc. (antimicrobials, broad-spectrum antibiotics) are successfully used [1].

Especially metallo-drugs have arisen as an important class of cytotoxic agents. Many metallodrugs, such as platinum, titanium, ruthenium, gallium, tin, gold, and copper-based complexes have been found to have anticancer activities (Figure [2]):



When designing metal-containing drugs, it is important to rely on stable ligands with pharmacological properties, which include rigid aromatic and heteroaromatic scaffolds with O- and N-polydentate sites.

With this concept in mind, we developed a drag design of mono- and binuclear complexes of Pd, Pt, and Cu with O-, S-, and N-containing ligands obtained by modifying pharmacologically significant scaffolds such as pyrazole [3], phenol, naphthol [4], and quinalinol.

The strategy of the synthesis of metal complexes and their biomedical properties will be discussed in this report.

The work was carried out within the framework of the state assignment (FMRS-2022-0074 and FMRS-2022-0079) as well as with financial support from the Stipend of the President of the Russian Federation to young scientists and graduate students (SP-1691.2022.4)

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Silver nanoclusters

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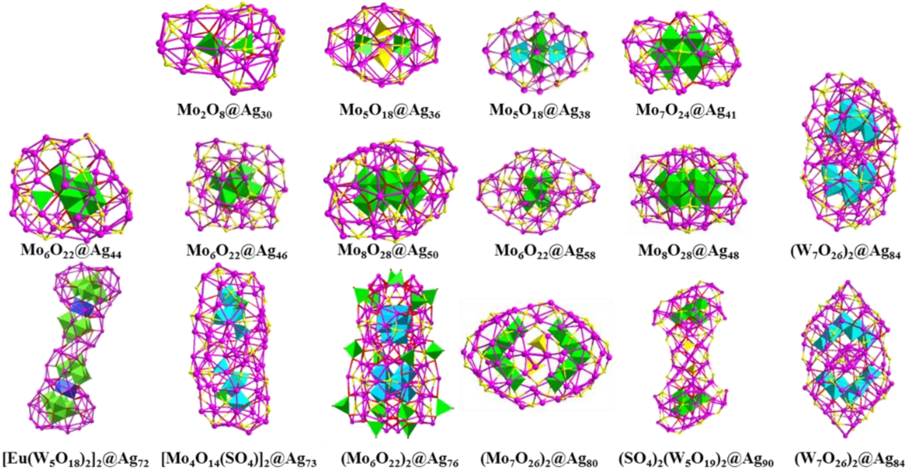
Over recent years, research on the ligand-protected silver clusters have gained significant interest owing to their unique potential applications in catalysis, organic optoelectronics, and luminescent materials. However, the synthesis of structurally precise silver nanoclusters and their assembly mechanism are still challenging and become one of the prime interests of chemists. The controllable synthesis of high-nuclearity silver nanoclusters involves the ingenious use of capping ligands or/and templating agents. Thereinto, the main role of the templating agents is to promote the order arrangement of silver ions around them to form discrete molecules. Our lab has performed comprehensive studies on the ligand-protected silver clusters including silver(I) clusters and silver(I/0) clusters in the past eight years. Furthermore, some interesting photo- and electrochemical properties revealed by silver clusters including luminescent thermochromism and electrical conductivity are quite interesting.



$Mo_2O_8@Ag_{30}$ $Mo_5O_{18}@Ag_{36}$ $Mo_5O_{18}@Ag_{38}$ $Mo_7O_{24}@Ag_{41}$

$Mo_6O_{22}@Ag_{44}$ $Mo_6O_{22}@Ag_{46}$ $Mo_8O_{28}@Ag_{50}$ $Mo_6O_{22}@Ag_{58}$ $Mo_8O_{28}@Ag_{48}$ $(W_7O_{26})_2@Ag_{84}$

$[Eu(W_5O_{18})_2]_2@Ag_{72}$ $[Mo_4O_{14}(SO_4)]_2@Ag_{73}$ $(Mo_6O_{22})_2@Ag_{76}$ $(Mo_7O_{26})_2@Ag_{80}$ $(SO_4)_2(W_5O_{19})_2@Ag_{90}$ $(W_7O_{26})_2@Ag_{84}$

Fig.1 The family of POMs templated silver nanoclusters.

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Theoretical studies and computer modeling of supramolecular chemical systems: structure, properties and reactivity

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Computational chemistry and computer modeling are powerful tools for conducting scientific research in chemistry, biochemistry and materials science, which can help experimentalists with establishing the structure and studying the reactivity of various substances.

I am a computational chemist and have a lot of experience in application of advanced quantum chemical methods as well as some special techniques (e.g., QTAIM, NCI, NBO, CDA, HSAB principle theoretical model, Hirshfeld surface analysis, etc.). Previously, I was involved in studies of catalytic reactions and organic transformations assisted by metal complexes, e.g. oxidation of hydrocarbons, nucleophilic addition and cycloaddition processes (mechanisms, driving forces, kinetics and thermodynamics), as well as properties of coordination and organometallic compounds (e.g. conformational isomerism and rotational barriers, properties of chemical bonds, orbital and charge factors). My current research interests are mainly focused on supramolecular chemistry (in particular, involving coordination and organometallic compounds) and theoretical studies of unusual non-covalent interactions (e.g., hydrogen, halogen and chalcogen bonding, stacking, anagostic and metallophilic interactions, etc.). The obtained results are potentially useful for biochemistry, medicine, and chemical industry/technology.

My studies are interdisciplinary in nature and lie at the junction of computer modeling with such natural science disciplines as chemistry, physics, crystallography, biology and medicine, and also have a direct bearing on the materials science and nanotechnology.

This talk is consisting of the results of my research (Scopus ID: 50262902200), published in more than 230 articles in reputable international scientific journals (including Nat. Commun., J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Commun., Chem. Eur. J., Chem. Asian J., J. Catal, RSC Catal. Sci. Tech., Inorg. Chem., J. Org. Chem., Organometallics, J. Phys. Chem. Lett., Phys. Chem. Chem. Phys., Dalton Trans., Org. Biomol. Chem., Cryst. Growth Des., CrystEngComm, J. Comput. Chem., etc.) in the following areas: properties of coordination, organometallic and organic compounds, their reactivity and catalysis.

The focus will be on the following topics:

- Cycloaddition and nucleophilic addition reactions, their mechanisms, driving forces, kinetics and thermodynamics (development of the fundamentals of the synthesis of valuable compounds for the needs of pharmaceutical industry);
- Consideration of the catalysis of hydrocarbons oxidation processes and their conversion to alcohols, ethers, aldehydes, ketones and carboxylic acids (this topic is promising for the oil and gas industry);
- Investigations of various non-covalent interactions (hydrogen, halogen and chalcogen bonds, stacking and metallophilic interactions, etc.) – a paradigm of supramolecular chemistry and crystal growth and design.

This paper has been supported by the RUDN University Strategic Academic Leadership Program (R.3-2022)

(Thia)calix[4]arenes as a versatile molecular building blocks for functional crystalline materials formation

Ovsyannikov A.S. [1], Kniazeva M.V.[1], Islamov D.R. [1,2], Samigullina A.I. [1], Gubaidullin A.T.[1], Dorovatovskii P.V. [3], Solovieva S.E.[2], Antipin I.S. [1,2]

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Supramolecular chemistry, as a chemistry beyond the molecule, is a powerful tool to design the functional molecular materials formed due to molecular recognition between the complementary building blocks [1]. (Thia)calix[4]arenes represent universal molecular platform for the creation of supramolecular structures in the crystalline phase. When fixed in one of two symmetric conformations (*cone* or *1,3-alternate*), they can bind metal cations leading to formation of either cluster type discrete coordination compounds or coordination polymers (Figure 1) [2–6]. It is worth noting that the control on the self-assembly of (thia)calix[4]arene based coordination supramolecular systems can be achieved by rational design macrocyclic molecular building blocks both with auxiliary ligands, thus leading to control the structure / properties correlation of the resulting solid-state compounds.

In this work, we present synthesis and rational design of new (thia)calix[4]arene based coordination supramolecular assemblies in the crystalline phase exhibiting the tunable functions (especially luminescence, magnetism and porosity).

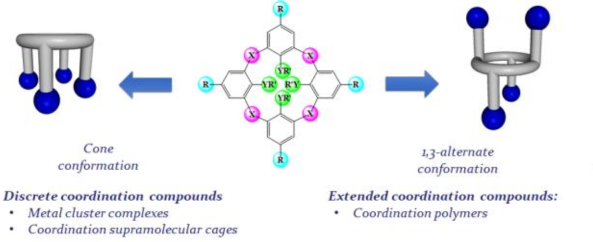

Figure 1. (Thia)calix[4]arenes (X=CH_2, S, SO_2) adopted in *cone* or *1,3-alternate* conformations.

This work was supported by the Russian Science Foundation (grant № 22-73-10139)

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Rare-earth complexes with polyarylcyclopentadienyl ligands, synthesis, structure and luminescence

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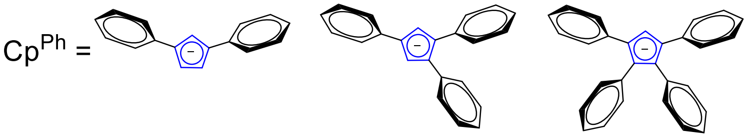
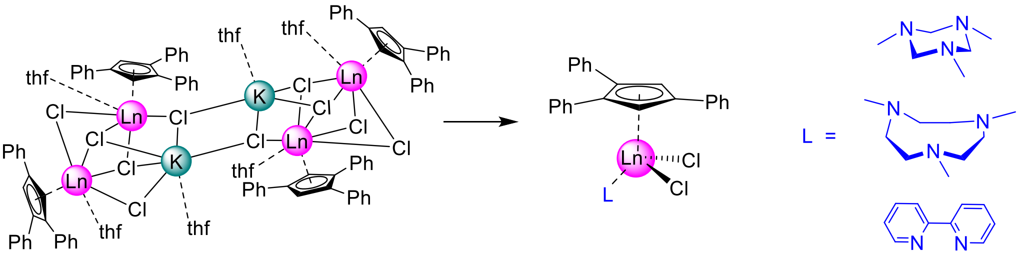
Different substituted cyclopentadienyl ligands are widely used to stabilize heteroleptic rare earth complexes. We have performed an attempt of systematical study of mono-, bis-and tris-phenylcyclopentadienyl lanthanide complexes of Nd, Gd, Tb and Dy. Synthetic routes to these compounds have been developed along with the investigaton of their structures and luminescent properties. We have also examined their use as precursors of catalytic ethylene oligomerization systems. A series of di-, tri-, and tetraphenylcyclopentadienyl complexes has been obtained [1-2].

$$LnCl_3(THF)_3 + Cp^{Ph}K \rightarrow [(Cp^{Ph})_nLnCl_{3-n}(KCl)_x(THF)_y],\quad Ln = Nd, Gd, Tb, Dy$$



Mono- and bis- cyclopentadienyl complexes of this type are mostly bi- or tetranuclear *ate*-complexes like $[\{Cp^{Phn}Ln(THF)\}_2(\mu\text{-}Cl)_5K(THF)_x]_2$ and $[Cp^{Phn}{}_2Ln(\mu\text{-}Cl)_2K(THF)_x]_2$, or even coordination polymers. We were managed to find an efficient route of converting these complexes into well-defined mononuclear complexes not burdened by additional intra- and inter-molecular interactions [3].



The use of arylsubstituted Cp ligands with bulky aryl allowed us to obtain new structural types of complexes [4]. Synthesis, structural diversity and photophysical properties of polyaryl-substituted cyclopentadienyl complexes of Nd, Gd, Tb, Dy will be discussed in the presentation.

This work was supported by the Russian Science Foundation (grant № 22-13-00312)

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P-Amino-cyclopentadienylidene-phosphoranes – synthesis, mechanistic studies and complexing

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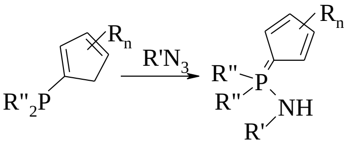
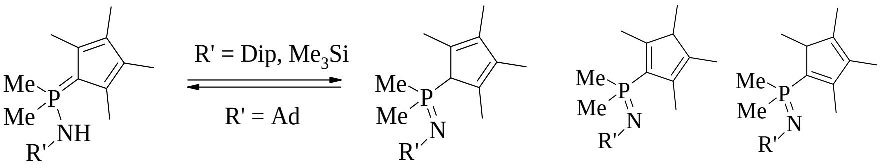


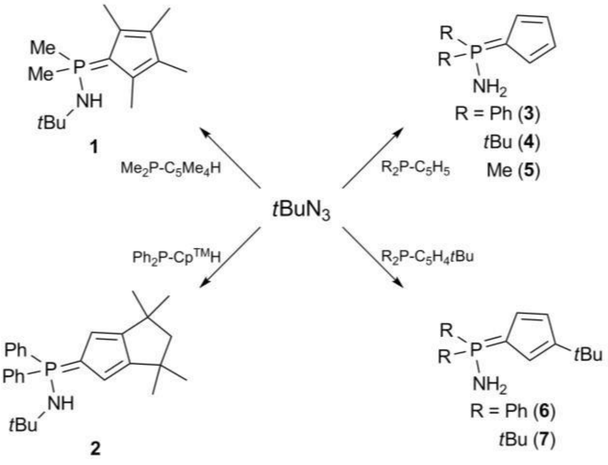
In the course of systematic investigations of ambident organophosphorus(V) donor ligands of the general type [$R_2P(X)Z]^-$ (X, Z = CHR', {Cp}, Ind, Flu, NR') synthesis of a new compound class *P*-amino-cyclopentadienylidene-phosphoranes (***CpPN***) was developed.

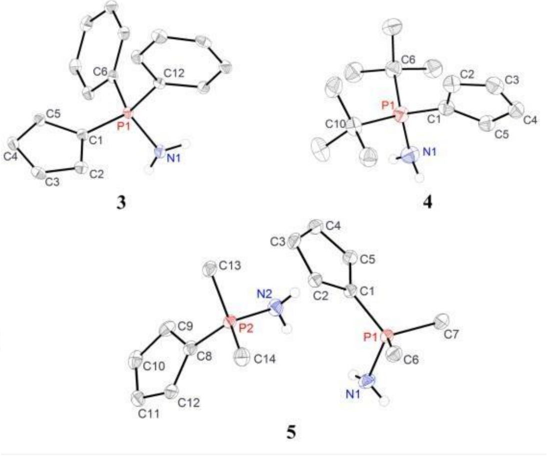
The synthesis was carried out by the Staudinger reaction of an appropriate Cp-phosphane with organic azide. Relative Brønstead acidity of the (R)$_n$Cp–*H* and R'N–*H* protons is responsible for occurrence of ***CpPN*** in one of their two possible tautomeric forms: *P*-amino-cyclopentadienylidene-phosphorane or *P*-cyclopentadienyl-iminophosphorane:



Main isomer Minor isomers (< 5 %)

Formerly we reported on the reactivity of 3,4-disubstituted and *tetra*-methyl-substituted Cp-phosphanes with *t*BuN$_3$, that led to the regular products exclusively as *P*-amino- phosphorane tautomers Me$_2$P(=C$_5$Me$_4$)NH*t*Bu (**1**) and Ph$_2$P(=Cp^{TM})NH*t*Bu (**2**).





Unexpectedly, we have found that the reaction product of *t*BuN$_3$ with ring-unsubstituted Ph$_2$P-C$_5$H$_5$ reveal no resonances of *t*Bu-group. Instead, ^{1}H NMR showed broadened resonance at 2.84 ppm close to the range of the NH-protons of **1** and **2**, but with 2*H* overall integral intensity. Further ^{13}C-NMR, HRMS and elemental analyses revealed that this product refers to *P*-NH$_2$-cyclopentadienylidene-phosphorane **3** (Scheme 2). Similarly, *t*Bu$_2$P–Cp and Me$_2$P–Cp give *P*-NH$_2$-phosphoranes **4** and **5** also characterized by an X-ray structure analysis.

Next, mechanistic studies to ascertain the role of substituents in the Cp-moiety in formation of *P*–NH$_2$-cyclopentadienylidene-phosphoranes **3**–**7** will be discussed.

Organometallic chemistry of ***CpPN*** ligand precursors will be presented and discussed.

Inorganic and Coordination chemistry Section Oral Reports

Novel carbazole-fused porphyrazine complexes: Synthesis and optical properties

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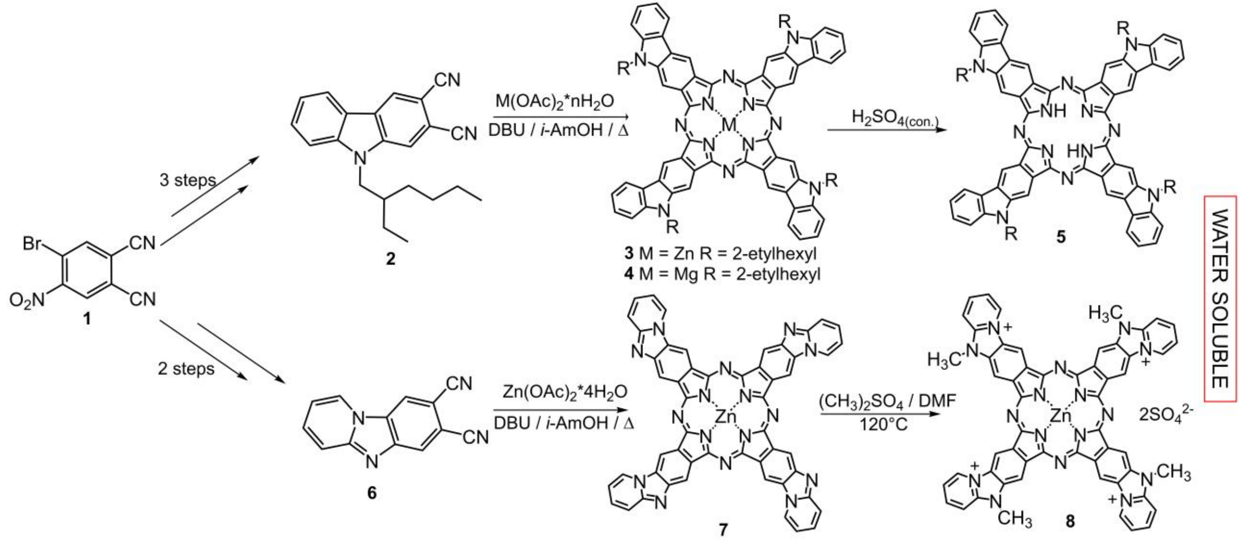
Carbazolocyanines – tetracarbazoloannulated porphyrazine analogs which attract significant research interest due to the strong electron-donating effect of carbazole moiety combined with overall extension of π-electron conjugation system. Their synthesis was first established in the pioneering work of Kimura et. al [1]. Carbazolocyanines were shown to be promising for application in photoelectronic devices [1].

Herein, we report a synthetic approach towards novel carbazolocyanines **3-5** and, for the first time, their azo-analogs - pyrido[1,2-a]benzimidazole-fused porphyrazines **7-8**.

Firstly, N-substituted carbazole dinitrile **2** was obtained by a three-step approach starting from 4-bromo-5-nitrophthalonitrile **1**. The subsequent template condensation reaction led to the target zinc and magnesium complexes **3, 4**. In addition, demetallation of the corresponding magnesium complex successfully yielded free carbazolocyanine ligand **5**, the important building block, crucial for the synthesis of multi-decker sandwich type complexes.

In order to further explore the field of carbazolocyanines, carbazole-like pyrido[1,2-a]benzimidazole dicarbonitrile **6** was synthesized from 4-bromo-5-nitrophthalonitrile **1**. Then, utilizing the analogous template synthetic protocol we managed to obtain zinc complex **7**, the first example of pyrido[1,2-a]benzimidazole-fused porphyrazine class. The presence of an extra basic nitrogen atom at each annulated moiety allowed quaternization resulting in a water soluble complex **8**.

For the obtained carbazolocyanines and their azo-analogs the extension of porphyrazine conjugation system resulted in the absorption maxima shift to the near-IR region up to 775 nm. In addition, photophysical properties of the novel complexes have been studied.



This work was supported by the Russian Science Foundation (grant № 21-73-00162)

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Design, synthesis and study of cyclometalated iridium(III) complexes with heterocyclic nitrogen-donor ligands

Bezzubov S.I.[1], Tatarin S.V.[1,2], Smirnov D.E.[1,2], Kalle P.[1], Zakharov A.Y.[1], Kiseleva M.A.[1,2], Koptyaeva A.G.[1,3], Mesheryakova E.A.[1,2], Zharova A.O.[1,2], Nykhrikova E.V.[1,2]

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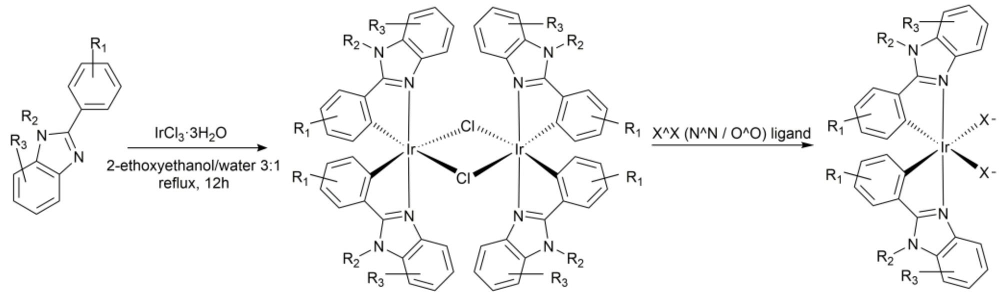
A growing interest in the chemistry of cyclometalated iridium(III) complexes is based on the fact that, unlike complexes of many other transition metals, these compounds can play opposing roles of an effective phosphor or photosensitizer, depending on the ligand environment. Although in a number of cases a successful (and actually random) combination of ligands led to iridium(III) complexes with excellent electroluminescent or light-harvesting characteristics, a systematic approach (based on the rational design of ligands) to the synthesis of cyclometalated iridium(III) complexes could be more useful for solving modern high-tech problems. Synthesis of effective luminophores or photosensitizers based on iridium(III) complexes is hardly possible without a clear understanding of how exactly specific modifications of ligands affect the target properties of the complexes. It is important to assess how the mutual spatial arrangement of cyclometalated and ancillary ligands, the degree of distortion of the iridium polyhedron, as well as steric hindrance of the ligands, and, finally, the presence of electron-donating, electron-withdrawing and linker substituents in the ligand structures affect the optical and electrochemical properties of cyclometalated iridium(III) complexes.

This study aims to create an integrated experimental and theoretical approach towards stable iridium (III) complexes possessing finely tunable properties for various practical tasks of photo/electroluminescence or photosensitization by rational design of the structure of cyclometalated ligands and judicious selection of an appropriate ancillary ligand.



In this work, a library of 85 cyclometalated and ancillary ligands as well as more than 120 novel iridium(III) complexes were synthesized and comprehensively studied including the crystal structure elucidation of ~100 new compounds. Analysis of structural and spectroscopic data supported by DFT calculations revealed several “structure-property” correlations for iridium(III) complexes. It was also found that the dependencies of properties on the electron-donating/withdrawing ability of ligands have a monotonic character only for a limited set of substituents while the presence of nitro- or dimethylamino-groups caused anomalies in properties. Similarly, the use of ligands having extremely large conjugated π-system resulted in iridium(III) complexes possessing non-typical geometry and unexpected properties. Particular attention was given to the study of these edge cases.

Novel substituted boron subphthalocyanines: synthesis, optical properties and photodynamic activity

Dubinina T.V.,[1] Burtsev I.D.,[2] Agranat A.S.,[1] Kosov A.D.,[1] Sizov L.R.,[3]
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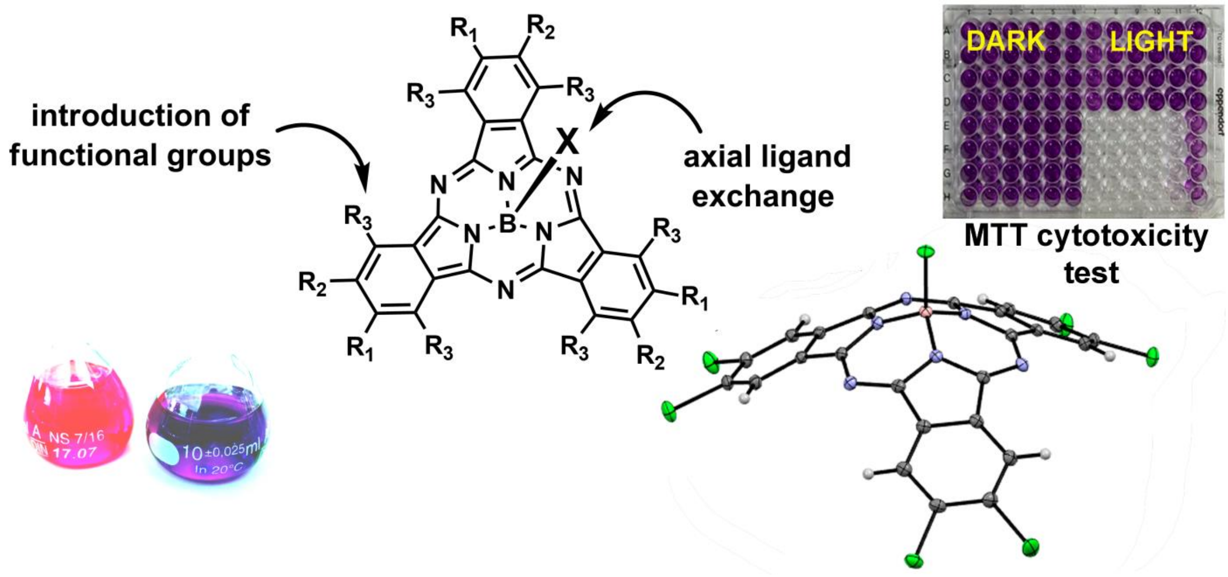
Boron subphthalocyanines are prospective photosensitizers for theranostics of cancer diseases. These coordination compounds demonstrate bright fluorescence and high yields of singlet oxygen generation. To tune optical properties, various functional groups can be introduced into the peripheral or axial positions of subphthalocyanine.

In this study, we have obtained and identified novel subphthalocyanines bearing both electron-releasing (alkyl, aryloxy, aryl) and electron-withdrawing (halogen) substituents. The axial position was successfully decorated by aryloxy-groups via two-step procedure using triflate as the leaving group. For hexachloro-substituted subphthalocyanine the X-ray data confirm the cone-shaped structure of the molecule. Target compounds show intense fluorescence in the visible region (500-600 nm) with Φ_f values up to 0.51. At the same time the high values of singlet oxygen quantum yields (Φ_Δ=0.50÷0.85) indicate the possibility of using these compounds as photosensitizers for the purposes of photodynamic therapy.



Investigation of dark and photoinduced cytotoxicity allows choosing two lead compounds (*tert*-butyl- and iodo-substituted boron subphthalocyaniunes) with high phototoxicity (IC_{50}=1.2 and 7 μM respectively) and low dark cytotoxicity.

We thank RFBR 21-33-70004 mol_a_mos for financial support

Crystal structure and magnetic properties of Cu(II), Co(II), Ni(II) and Mn(II) coordination compounds based on bis-4’,6’-R-pyrimidilhydrazones of 2,6-diformylphenol

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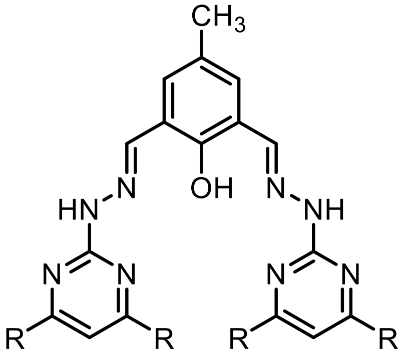
The investigation of magneto-structural correlations in transition metals coordination compounds is one of significant aspects in novel magnetic materials molecular design. The most appropriate substances for that kind of study are 2,6-diformyl-4-R-phenol complex compounds with different types of substituents. In this case, complexes with heteroaromatic substituents are studied much less, than with aliphatic ones.

Thus, in the current research there were synthesized new types of ligand systems based on 2,6-diformyl-4-methylphenol with 2-hydrazino-4,6-dimethylpyrimidine (**1**) [1] and 2-hydrazino-4,6-diphenylpyrimidine (**2**), respectively. The structure of both substances was studied with IR and NMR methods.



R = CH_3 (**1**), C_6H_5 (**2**)

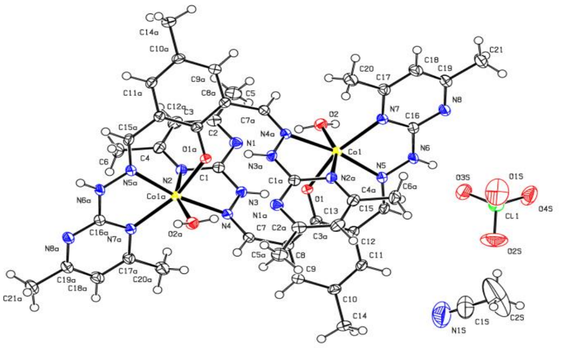


Figure 1. Molecular structure of Co(II) complex

By reaction with different transition metal salts there were synthesized 2 series of coordination compounds: Cu(II), Co(II), Ni(II) and Mn(II) complexes with bis-hydrazone **1** and Cu(II) complexes with bis-hydrazone **2**.

The structure of the first series of compounds were investigated with X-Ray analysis. There was discovered that for Cu(II) complexes ligand:metal ratio is 1:2 and for Co(II), Ni(II) and Mn(II) complexes this ratio is 2:2, which causes quite extended exchange pathway (Fig. 1), and these coordination compounds could possess interesting magnetic properties.

Studies of the magnetic properties of Co(II) and Mn(II) complexes in an alternating magnetic field have shown that these compounds exhibit a slow relaxation of magnetic susceptibility and in zero external magnetic field in the 2 K region, which indicates that these metallohelates exhibit the properties of single molecule magnets.

For all complexes the magnetic properties were modelled with «broken symmetry» approach (B3LYP/6-311G(d), level of theory).

This work was supported by the Russian Foundation for Basic Research (grant № 20-33-90173)

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Molybdenum complexes with cyclic polyphosphorus ligand modified by insertion of carbonyl compounds into P–P bond

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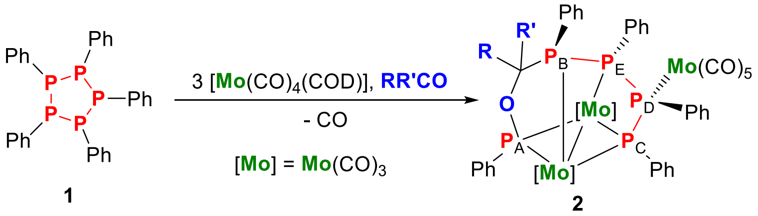
Complexing of transition metals with polyphosphorus compounds can lead to unexpected structures with a vast diversity of bonding situations [1,2]. Transition metal-mediated opening of polyphosphorus cycles followed by the insertion of unsaturated organic substrates is a relatively less known type of reactions [3].

The insertion of carbonyl compounds (acetone, methyl ethyl ketone, cyclopentanone, cyclooctanone and 4-brombenzaldehyde) into the P–P bond of *cyclo*-(P_5Ph_5) **1** in the presence of a molybdenum tetracarbonyl complex $[Mo(CO)_4(COD)]$ (COD = cycloocta-1,5-diene) was observed. This reaction leads to trinuclear complexes with novel bis-phosphanido ligands $(PPhPPh\text{-}PPh\text{-}PPh\text{-}CRR'\text{–}O\text{-}PPh)^{2-}$ **2a-e** connected to the Mo–Mo bond and $Mo(CO)_5$ fragment attached to one free P_D atom.



R = R' = Me (**a**); R = Me, R' = C_2H_5 (**b**); RR' = $-(CH_2)_4-$ (**c**); $-(CH_2)_7-$ (**d**);
R = H, R' = 4-Br-C_6H_4 (**e**);

The products obtained from ketones **2a-d** were studied by various physico-chemical methods including differential scanning calorimetry and fast scanning calorimetry and by the single crystal X-Ray analysis. Comparing to ketones, aldehydes are far less reactive with the polyphosphorus ligand **1** in the presence of $[Mo(CO)_4(COD)]$. However, we also managed to separate crystals of **2e** in this reaction.

The obtained complexes may have a potential for a systematic investigation of the correlations between composition, structure and physico-chemical properties.

This work is carried out in accordance with the Strategic Academic Leadership Program "Priority 2030" and the grant of the President of the Russian Federation for supporting of the Leading Scientific Schools (project no. 4078.2022.1.3). E.G. thanks the DAAD (project no. 57381410, 2018/19) for supporting of the postdoc stay in Leipzig

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Cadmium(II) halide complexes with guanidine: structure, spectral and biological studies

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Guanidine derivatives are widely used in farmacy as they show antineoplastic (by blocking tumor-induced angiogenesis), antidiabetic and antibacterial activity [1]. Cadmium(II) sulphate complex with guanidinium has drawn attention due to its interesting optical properties [2]. Cadmium complexes with N- and S-donor atoms show significant anticancer activity [3]. However, cadmium(II) halide complexes with this ligand were not described yet. The aim of the present work consists in the synthesis and studies of cadmium(II) complexes with guanidine.

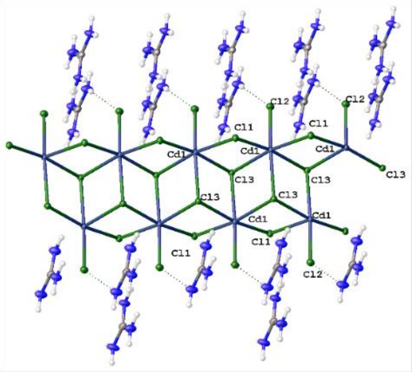

Fig.1. Structure of the complex (**1**).

A number of complex compounds such as [GuaH][$CdCl_3$] (**1**), [GuaH][$CdBr_3$] (**2**), [Cd_2(Gua)Br_4] (**3**), [GuaH][CdI_3] (**4**), [Cd_2(Gua)I_4] (**5**) were prepared in aqueous solutions from $CdX_2{\cdot}nH_2O$ (X = Cl, n = 2.5; Br, n = 4; I, n = 0) and guanidine taken in the molar ratio CdX_2: Gua = 1:1 for (**3**), (**5**) and CdX_2: Gua = 1:(2-3) for (**1**), (**2**), (**4**). The prepared compounds were characterized by elemental analysis, powder- and single crystal X-ray diffraction, IR- and ESI-mass spectra studies. Complex (**1**) (Fig.1) consists of polymeric chains built from $[CdCl_3]^-$ units which alternate with guanidinium cations (monoclinic system, space group $P2_1/c$, a = 3.7911(2), b = 18.9289(10), c = 10.4139(5) Å, $\alpha = \gamma = 90°$, $\beta = 91.315(2)°$, Z = 4). Complexes (**1**), (**2**) and (**4**) are evidently isostructural ones. Guanidine coordination and protonation were confirmed by IR spectra studies: absorption band at 1631 cm^{-1} for uncoordinated ligand (ν(C=N) stretching vibration) is shifted to lower frequencies for all complexes. Mass spectra demonstrate formation of clusters and cadmium halide containing species.

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Copper(II) and zinc(II) acetate complexes with nicotinamide: synthesis, properties and cytotoxicity

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The present work is a continuation of our studies in the area of transition metal complexes with bioactive ligands [1, 2].

Complex compounds $[M_2(Nia)_2(\mu_2\text{-}OAc)_4]\cdot 2H_2O$ (M=Zn (**1**); Cu (**2**); Nia – nicotinamide) were synthesized in aqueous medium from Zn(II)- or Cu(II) acetates and nicotinamide taken in the molar ratio M^{II}:Nia = 1:2.

The compounds obtained were identified by different physicochemical methods (elemental analyses, powder- and single crystal XRD, IR–, ESI-MS spectra studies). Structures of complexes (**1**) and (**2**) are similar: four acetate bidentate bridging groups and two axial N-coordinated nicotinamide molecules form inner coordination sphere.

Cytotoxicity of compounds (MTT assay [3, 4], the postnatal human dental pulp stem cells (DPSC) and the MCF-7 breast cancer cell line) demonstrates the dose-dependent behavior in the concentration range $c = 5\cdot10^{-5} – 5\cdot10^{-4}$ mol$\cdot$L^{-1}. Cytotoxic activities of **(1)** and **(2)** are similar in their action on the MCF-7 cell line, cytotoxicity of **(2)** (survivability 66.05±3.63 %) being slightly higher than that of **(1)** (survivability 77.54±7.03%) for the stem cells ($c = 1\cdot10^{-4}$ mol$\cdot$L^{-1}).

Studies on the cytotoxic activity of the prepared compound on the A549 lung adenocarcinoma, PC3 prostate cancer, JURCAT acute T–cell leukemia, HCT-116 human colon cancer cell lines show higher toxicity of (**2**) for A549, PC3 and JURCAT cells (survivability below 50%) and promise for further investigations.

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Metalla-N-heterocyclic carbene complexes as visible light photocatalysts of hydrosilylation reaction

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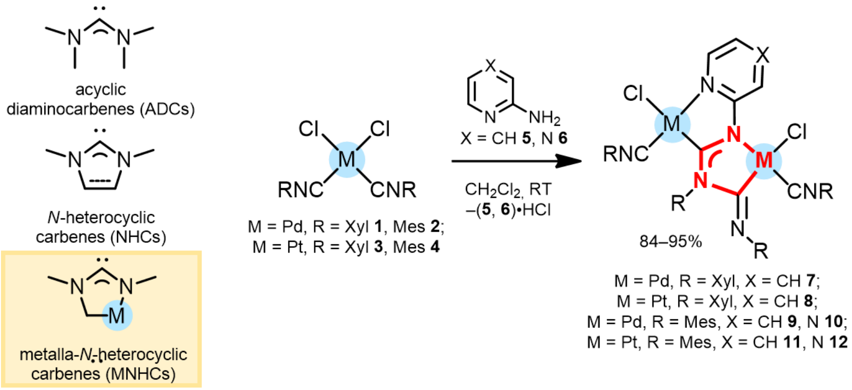
N-heterocyclic (NHC) and acyclic diaminocarbene (ADC) complexes are the most powerful catalysts of the C–C and C–N coupling reactions, due to the strong σ-donor and a weak π-acceptor properties of NHC and ADC ligands.[1] *Metalla-N-heterocyclic carbenes (MNHC)*, ligands with a metal atom within the NHC skeleton, exhibit stronger electron-donor character by comparison with classical NHC analogies, but the catalytic properties of MNHC complexes were reported only in one work by our research group.[2]

A series of Pd(II)- and Pt(II)-MNHC complexes (**7**–**12**) were prepared via metal-mediated coupling between *cis*-[$MCl_2(CNR)_2$] (**1**–**4**, R = Xyl, Mes) and 2-aminoazaheterocycles (**5**, **6**). The **7**–**12** are yellow or yellowish solids, so they demonstrate light absorption up to 450 nm, which are in visible light range. According to the TD DFT calculations and FMO analysis, the absorption characteristics are assigned to ^{1}L'LCT/^{1}ILCT transitions, and are governed by the nature of the azaheterocycle substituent of MNHC fragment: **10** and **12** with pyrazine ring show 20–40 nm red-shifted bands relative to pyridine counterparts **7**–**9** and **11**.



Taking into account the light absorption data, the Pt(II)-MNHC **8**, **11**–**12** were evaluated as visible light photocatalysts for the reaction of diphenylacetylene with triethylsilane affording 1,2-(diphenylvinyl)triethylsilane. The catalytic system operates blue LED irradiation for 6–12 h with a typical catalyst loading of 0.1 mol %. In this catalytic reaction the Pt(II)–MNHC catalysts serve as a light-absorbing species and a transition metal catalyst enabling the catalytic process. The highest catalytic efficiency was achieved with photocatalyst **11** (R = Mes, X = CH), allowing almost quantitative conversion with yields up to 98% and also indicating the effect of R substituent on the catalytic process.[3]

This work was supported by the Russian Science Foundation (project 22-23-00621). Measurements were performed in the Research Park at St. Petersburg University (the resource centres CMR, CXDS, CCAMR, CLMR, DCE and CC)

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Complexes of heavy alkali metal hexafluoroacetylacetonates with 18-crown-6 ether: synthesis, structures and thermal properties

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Volatile alkali metal complexes are of interest for the preparation of functional materials by gas-phase methods. However, such complexes are difficult to obtain since polymer structures with strong interactions are usually formed due to high coordination numbers of alkali metals. Obtaining mixed-ligand complexes by adding a neutral ligand that breaks polymer chains is effective in this case [1, 2]. However, there are no examples of volatile of mixed-ligand fluorinated complexes of heavy alkali metals in the literature. In this work, we have studied the complexes of K, Rb and Cs hexafluoroacetylacetonates (hfac) with 18-crown-6 ether (18C6).

The target mixed-ligand complexes were obtained by two synthetic strategies: *in situ* assembly and the usage of a pre-synthesized M(hfac), M = K, Rb, Cs. The complexes were characterized by various methods (elemental analysis, SXRD, PXRD, IR-spectroscopy, TGA). Also M(CF_3COO)(18C6), M = K, Rb, were found as by-products. Using cesium as an example, the effects of the solvent and the stoichiometry of the reagents were shown. In particular, the different products Cs(hfac)$(18C6)_X$, X = 0.5, 1, 1.5, were obtained at the appropriate M(hfac):18C6 stoichiometries in polar solvents. Moreover, ethylacetate can be coordinated with cesium to form a complex Cs(hfac)(18C6)(EtOAc), while toluene is included as solvate molecules thus changing the structural unit to a dimer in $[Cs(hfac)(18C6)]_2\cdot$PhMe complex.

The complexes with an included solvent and $Cs_2(hfac)_2(18C6)_3$ have an isolated island structures. In the $Cs_2(hfac)_2(18C6)$ complex, linear chains are formed due to the bridging functions of all oxygen atoms of the crown ether. Both M(hfac)(18C6) (M = K [3], Rb) complexes has a chain structure formed by M…F contacts in the a-direction. Oppositely, the chains in the structures of the corresponding M(CF_3COO)(18C6) complexes are formed by M…O_{18C6} contacts. Probably, the M...O_{18C6} contact is realized due to the lower steric hindrance in the case of CF_3COO^-.

For the complexes of M:18C6 stoichiometry = 1:1, no strong intermolecular contacts other than those described have been found analyzing the Hirschfeld surfaces. For M(hfac)(18C6) (M = K, Rb), the unit cell parameters and volume increased anisotropically with increasing temperature within the range of 100–400 K. The greatest thermal expansion was observed along the axis a. Using the sublattice method, a pseudo-hexagonal stacking pattern of M^+ cations in the layers of the M(hfac)(18C6) structure was shown in bc plane.

The melting points of M(hfac)(18C6) (M = K, Rb) were similar (~180°C) due isostructural complexes. The melting point of Cs(hfac)(18C6) was lower and the influence of 18C6 on this parameter was nonmonotonic: Cs(hfac)(18C6) (150°C) < $Cs_2(hfac)_2(18C6)_3$ (162°C) << $Cs_2(hfac)_2(18C6)$ (220°C). Under TGA conditions (He flow), all the complexes decomposed, except for M(hfac)(18C6) (M = K, Rb), where the partial evaporation was observed.

Using K(hfac)(18C6), the molecular layers were prepared by low-pressure physical vapor deposition (PVD). According to the X-Ray analysis in the Bragg-Brentano and 2D GIXD geometries, the molecules were oriented perpendicularly [100].

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New reactions of rhodium complexes with alkynes

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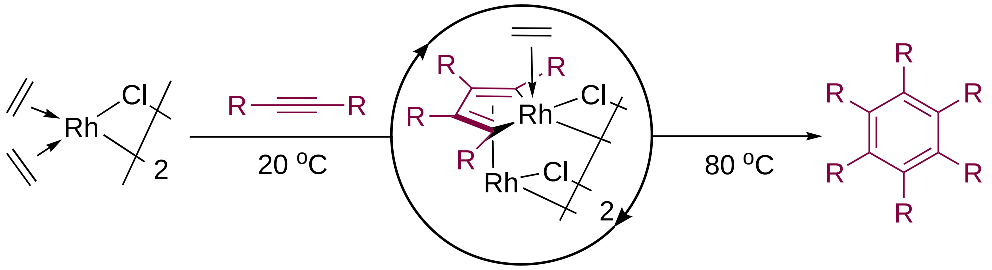
Rhodium compounds are widely used for catalytic transformations of alkynes. The study of intermediates of such processes is of great interest [1, 2]. We found that the simplest rhodium ethylene complex **1** trimerizes alkynes to benzene derivatives. Stoichiometric reactions of **1** with internal alkynes terminates at the stage of intermediate metallocycles of type **2**. Their further interaction with CpTl gives cyclopentadienyl derivatives **3**, which have a filled electron shell and are no longer able to enter into catalytic transformations. Further reactions of these metallocenes with $[CpRhI_2]_2$ and $AgPF_4$ lead to the unique triple-decker complexes **4** with a metal in the central ring. The structures of all three types of complexes have been established by X-ray diffraction.

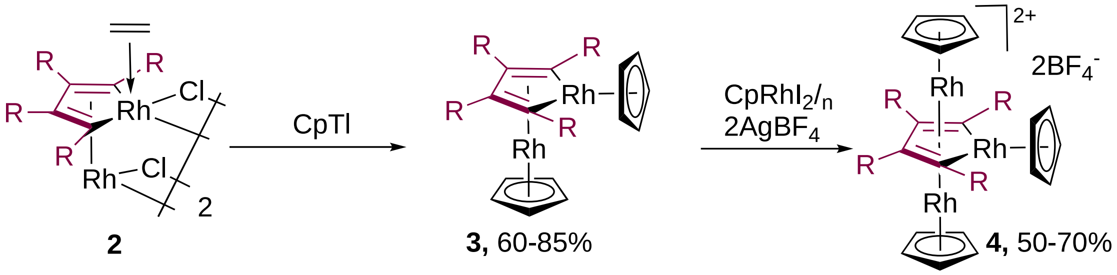
We suggest that binuclear complexes like **2** and **3** are typical intermediates of the reactions of Rh(I) species with alkynes.



1

Intermediate
2, 50-95%

60-95%



2

3, 60-85%

4, 50-70%

This work was supported by the Russian Science Foundation (grant № 17-73-30036)

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Rare-earth anthracenide complexes: structures and their catalytic activity in ethylene polymerization

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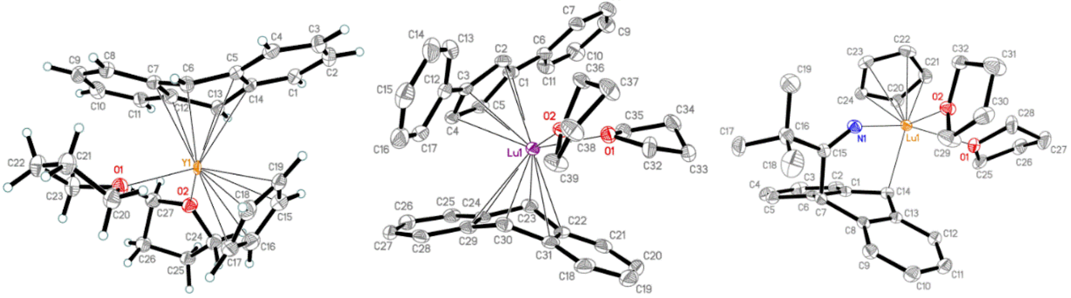
Organolanthanides bearing dianions of aromatic hydrocarbons such as naphthalene, anthracene, biphenyl, *etc*., are virtually unstudied, and their structures are mainly limited by the $[Ln^{3+}X^{-}_{2}]_2L^{2-}$ type. Less studied systems $[X^{-}Ln^{3+}L^{2-}]$ are of much greater interest, since they form substantially covalent Ln^{3+}-L^{2-} bond [1], mimic frustrated Lewis pairs, and therefore may provide extraordinary reactivity, *e.g.*, activation of multiple C-C bonds. Although, non-classical dianions with predominantly two-center HOMO localization ensure the kinetic stability of the corresponding complexes, a very few examples of mononuclear rare-earth anthracenides have been published up to date [1-6].

A convenient method has been developed for the synthesis of rare-earth anthracenide complexes of type $(\eta^5\text{-Cp}')Ln(\eta^2\text{-Ant})$ (Cp' = C_5H_5, 1,3-$Ph_2C_5H_3$, 1,2,4-$Ph_3C_5H_2$; Ln=Y, Nd, Lu; Ant= $C_{14}H_{10}$, 2,6-$^{t}Bu_2C_{14}H_8$) *via* reduction of anthracene with KC_8 in the presence of $Cp'LnCl_2$. For the first time, it has been demonstrated that the complexes may serve as catalysts in coordination polymerization of ethylene and co-polymerization ethylene with α-olefins. The structures of polymerization products formed under various conditions were confirmed by NMR and FD MS methods. The initiation step of ethylene polymerization was modelled by using reactions of the complexes with pivalonitrile. Key complexes have been structurally studied.



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Synthesis and photophysical properties of silanediamido complexes of lanthanides

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A wide range of various stabilizing ligands is applied in the metalloorganic chemistry of lanthanides, which suits to the different aims. Depending on the nature of the ligand, coordination type, steric bulkiness, presence of redox active or chromophore groups, lanthanide complexes with them can be applied in material science, catalysis, they are of interest from the point of view of magnetic and luminescent properties. Thus, constructing and development of new ligands are of current interest even nowadays.

Amidinates $\mathrm{RC(NR')_2^-}$ are one of the most frequently used families of ligands in lanthanide-organic chemistry, side by side with the famous cyclopentadienyls. A closely related group of silanediamido ligands $\mathrm{R_2Si(NR')_2^{2-}}$ is known along them, but much less investigated due to a somewhat more complicated synthesis and a restricted air stability of silanediamines. Nevertheless, their higher negative charge (2–) and a heavier central Si arom replacing the C(R) fragment could be useful for the functional lanthanide complexes

We investigated known silanediamides of type $\mathrm{H_2(^{Ar}\mathbf{NSiN})} = \mathrm{SiMe_2(HNAr)_2}$ (Ar = Dipp, Mes), and supplemented them with new ones bearing chromophore groups (Ar = Pbt, Btd; Pbt = *o*-phenylbenzotiazole, Btd = 2,1,3-benzotiadiazole). By their deprotonation followed by the salt metathesis with lanthanide(III) halides we obtained series of the complexes with lanthanides of the different ionic radii. For Dipp- and Mes- substituted ligands, the binuclear complexes $[\{\mathrm{Ln}(^{\mathrm{Ar}}\mathbf{NSiN})(\mathrm{thf})_2\}_2(\mu\text{-}\mathrm{Cl})_2]$ were synthesized; also, a mononuclear complex $[\mathrm{Y}(^{\mathrm{Dipp}}\mathbf{NSiN})\mathrm{Cl}(\mathrm{thf})_3]$ and ate-complexes $[\{\mathrm{Ln}(^{\mathrm{Dipp}}\mathbf{NSiN})(\mu\text{-}\mathrm{Cl})(\mathrm{thf})(\mathrm{Li}(\mathrm{thf})_3)\}_2(\mu\text{-}\mathrm{Cl})_2]$ (Ln = Y, Tb) were structurally characterized. Pbt- and Btd- substituted ligands have a tendency to the formation of bis-ligand anionic complexes $[\mathrm{Ln}(^{\mathrm{Ar}}\mathbf{NSiN})_2]^-$ because of the additional donor atoms of substituents, and the synthesis of mono-ligand complexes in this case appears challenging.

The energy of the triplet levels of the ligands were experimentally determined by measuring the emission of the Gd complexes at 77 K. Dipp- and Mes- substituted ligands were found to exhibit a suitable antenna effect for the sensitization of the $\mathrm{Tb^{3+}}$ luminescence in the visible range with the energies of $2.05 \cdot 10^4$ and $2.63 \cdot 10^4$ $\mathrm{cm^{-1}}$, respectively. Pbt-substituted ligand, despite the promising bright emission of $\mathrm{NH_2Pbt}$, has a lower energy insufficient for the sensitization of the lanthanides emitting in the visible region, but may be suitable for the NIR region. Further studies are in progress.

This work was supported by the Russian Science Foundation (project No. 21-13-00287) and the Ministry of Science and Higher Education of the Russian Federation (No. 121031700313-8 and No. 121031700321-3)

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Study of complex formation reactions between heterocyclic phosphine oxides and lanthanide nitrates

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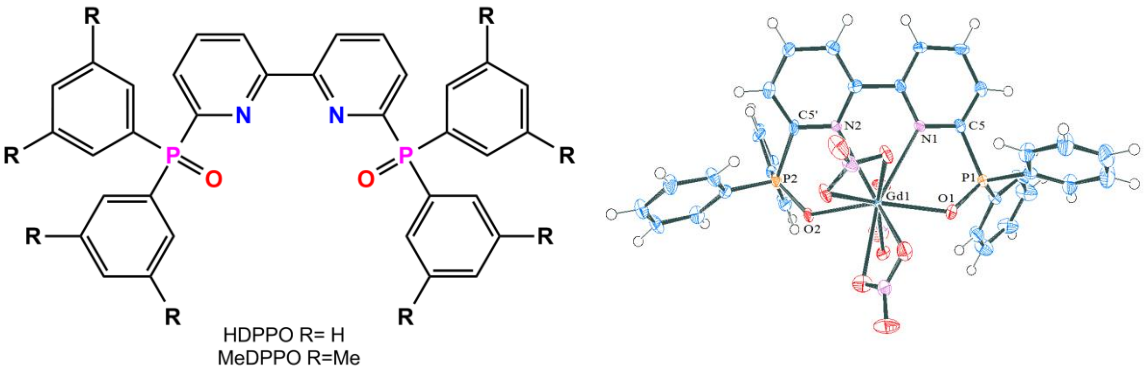
Nowadays, one of the urgent problems of radiochemistry is the disposal of nuclear fuel waste enriched with f-elements. Selective recovery is facilitated by N,O-type heterocyclic ligands. Various thermodynamic characteristics are used to evaluate the efficiency of binding rare-earth metal ions into a complex. The stability constant is one of the most important characteristics of complex formation reactions. The aim of this work was to study complex formation reactions between Ln^{3+} lanthanide salts and heterocyclic phosphine oxides (HDPPO and MeDPPO) in ethanol and acetonitrile as solvents.



Structure 2,2'-bipyrydil-6,6'-il-bis(di-3,5-R-phenylphosphinoxide) (left)
X-ray of complex (right) [1]

The composition of the complexes was studied by the Job method. The complexes have a metal:ligand composition of 1:1. The stability constants of the complex formation reaction were determined by the method of spectrophotometric titration. The HypSpec2014 program was used to process the results. For complexes containing the HDPPO ligand, the stability constants vary from 6.5 to 8.0; and from 5.5 to 7.5 for complexes of MeDPPO. The data obtained indicate the dependence of the stability constants on the structure of the ligand, and also established the effect of the ionic radius of the metal on the stability of these complexes.

This work was supported by the RSF grant no. 21-73-20138

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Variety of structures of acetylurea complexes with rare-earth bromides

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The development of effective methods for separation of rare-earth elements is a challenging task of inorganic and material chemistry. Rare-earth elements often form isostructural compounds for the whole row or two series of isostructural compounds for light and heavy lanthanides, preventing separations of these elements from one another and identification of neighboring lanthanides.

However, acetylurea (AcUr) complexes with rare-earth bromides show surprising structural variability. In this work, we describe earlier reported [1–3] and new non-isostructural compounds in the series of acetylurea complexes with rare-earth bromides.

Complexes $[Ln(AcUr)_2(H_2O)_5]Br_3$ (Ln = La, Pr, Nd, Sm), $[Ln(AcUr)_2(H_2O)_5]Br_3 \cdot H_2O$ (Ln = Gd, Tb), $[Ln(AcUr)_2(H_2O)_{4.5}][Ln(AcUr)_2(H_2O)_4]Br_6 \cdot 2H_2O$ (Ln = Y, Dy, Ho) and $[Ln(AcUr)_2(H_2O)_4]Br_3$ (Ln = Er, Tm), were studied by X-ray diffraction.

The complexes with Ln = La–Sm (except Ce) contain complex cations $[Ln(AcUr)_2(H_2O)_5]^{3+}$ (coordination number 9); halide ions are outer-sphere. They are isostructural at room temperature; on cooling down to 100 K, their structures change. Complex cations of Gd and Tb also include two bidentate acetylurea molecules and five inner-sphere water molecules (coordination number 9), however, these compounds contain additional outer-sphere water molecule. Compounds of Y, Dy and Ho contain two types of complex cations $[Ln(AcUr)_2(H_2O)_4]^{3+}$ (coordination number 8) and $[Ln(AcUr)_2(H_2O)_5]^{3+}$ (coordination number 9) in the 3 : 1 ratio. Complex cations of Er and Tm contain four water molecules along with the acetylurea molecules (coordination number 8).

The most interesting results are the rare coexistence of two different coordination numbers in the compounds of Y, Dy and Ho and the existence of polymorphs for the complexes of light lanthanides at different temperatures.

Slight decrease of Ln atomic radius when going from Ln to Tm results in smooth reduction of coordination number from 9 to 8. As a results, four different types of complexes form in the lanthanide row. Formation of non-isostructural complexes for adjacent rare-earth elements can be used for their separation by the crystallization method.

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Photochemistry of the light-activated dirodium anticancer complex

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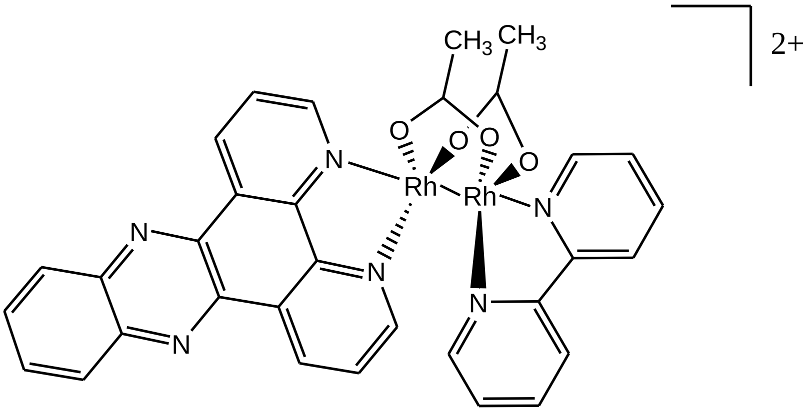
Photochemotherapy (PCT) is one of the most promising methods of anticancer treatment based on the photochemistry of platinum metal complexes. Compared to traditional photodynamic therapy based on triplet sensitizers and formation of singlet oxygen, PCT does not require dissolved oxygen. This is important because many tumors are hypoxic. Several complexes of platinum metals are considered as prospective for PCT; however, their fundamental photophysics and photochemistry are not studied in detail[1].



Complex **1**.

Here we present a case study of photophysics and photochemistry of light-activated anti-cancer complex **1** (cis-[$Rh_2(\mu\text{-}O_2CCH_3)_2(bpy)(dppz)]^{2+}$, where dppz is dipyrido[3,2-a:2',3'-c]phenazine and bpy is bipyridine). Complex **1** exhibits light-induced cytotoxicity both in the absence and in the presence of dissolved oxygen induced by visible irradiation[2]. Irradiation of **1** in the near UV and visible spectral regions (corresponding to π-π* transitions of dppz) does not cause decomposition of **1**. In laser photolysis experiments (355 nm) an intermediate with an oxygen-dependent lifetime was detected, the spectrum of which resembles the spectrum of the dppz ligand triplet state. The lifetime of its formation is about 3 ps. We believe that the cytotoxicity of **1** mainly caused by singlet oxygen. In the absence of dissolved oxygen, the lowest excited state of **1** seems to be the only possible reactive species.

The work was supported by the Russian Science Foundation (Grant № 22-33-00248)

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Molecular design and synthesis of cyclometallated iridium(III) complexes with *N*-benzylbenzimidazoles as photosensitizers

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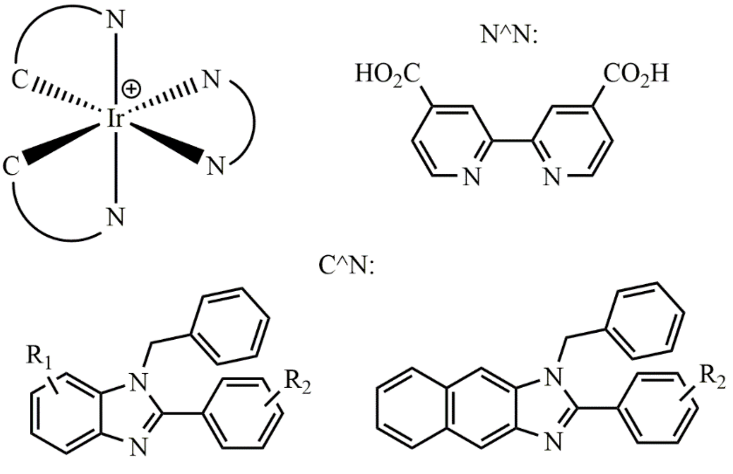
Cyclometallated Ir(III) complexes can be considered as a stable replacement for Ru(II) complexes and organic dyes in dye-sensitized solar cells (DSSC). However, low extinction coefficients of Ir(III) compounds in the visible area obstruct their widespread using in DSSC. N-benzyl-benzimidazoles were chosen as cyclometalated (C^N or `antenna`) ligands. This type of ligands appears as a convenient scaffold for design and synthesis of virtually unlimited set of cyclometalated ligands possessing diverse functionalities. In order to expand variability of iridum(III) complexes, ligands with both the aryl and benzimidazole substituted fragments have been exploited in this work. 2,2′-bipyridine based ligands were chosen as ancillary (N^N) ligands because of their successful application synthesis of ruthenium(II) dyes for DSSC.

The experimental part was carried out in 4 stages. First, C^N ligands were synthesized in 2 steps and characterized by ^{1}H and ^{13}C NMR spectroscopy. After that, dimeric neutral complexes $[Ir(C^\wedge N)_2Cl]_2$ were obtained from iridium(III) chloride hydrate, from which heteroleptic cyclometallated iridium complexes $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ were synthesized.

The resulting complexes were characterized by ^{1}H NMR, HRMS, CV, absorption and luminescence spectroscopy. For most of the complexes, single crystals were obtained and studied by X-ray diffraction. Analysis of the experimental data revealed clear correlations between the Ir coordination environment and properties of the complexes, which can be useful in creation of effective photosensitizers based on cyclometallated iridium(III) complexes.



R_1=3,4-H, 3,4-CH_3, 3,4-Cl, 3,4-F, 3,4-NO_2
R_2=4-H, 4-Cl, 4-*t*-Bu, 3,4-OMe

This work was supported by the Russian Science Foundation (grant № 22-23-01171)

Synthesis of labile transitional metal complexes on the base of *nido*-carborane

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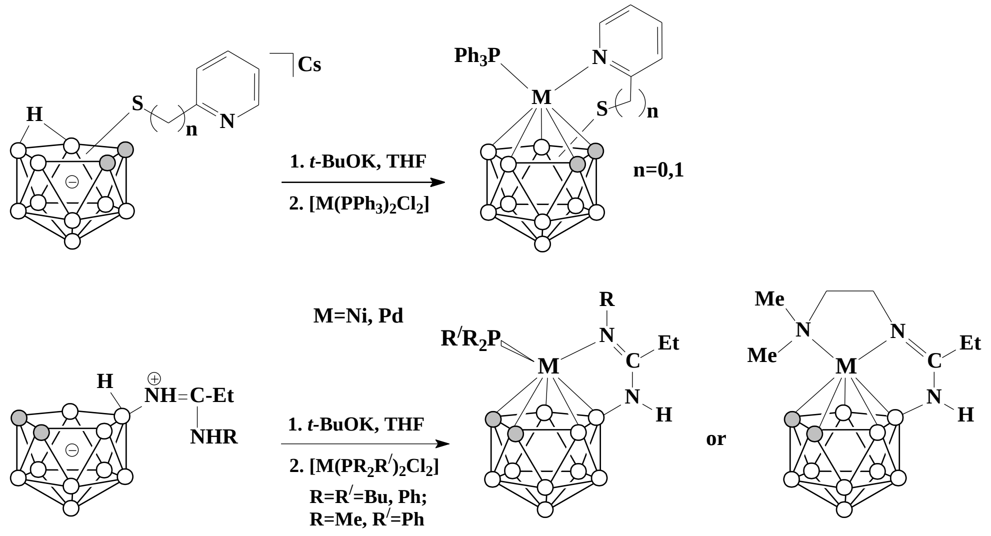
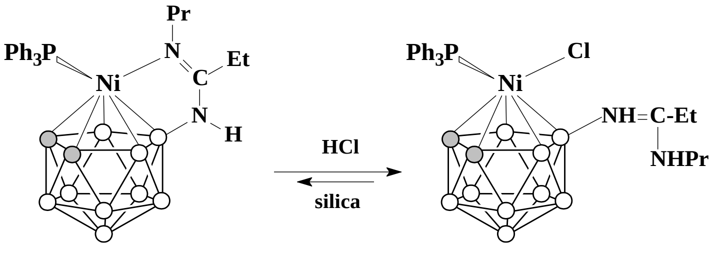
nido-Carborane and its derivatives, due to their unusual properties and three-dimensional structure, are promising ligands for the synthesis of metal complexes that can be used in catalysis [1,2]. In this work, we focused on obtaining *nido*-carborane based bifunctional labile metal complexes, which provide "hard" and "soft" binding with a complexing metal, due to the side substituent on *nido*-carborane cage that can participate in the complexation reaction.

Using different approaches, a series of carbon and boron substituted *nido*-carborane derivatives with a side substituent containing additional *N*-donor group was prepared. The synthesized derivatives were used as ligands in the complexation reactions with various phosphine complexes of nickel(II) and palladium(II). As a result, the *nido*-carborane based half-sandwich complexes with different types of coordination of ligand with metal center were obtained.



It has been shown that under certain conditions the side substituent can be reversibly discoordinated from the metal center.



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Tuning the composition, structure, reactivity and photophysical properties of iridium(III) complexes by variation of ligands steric hindrance

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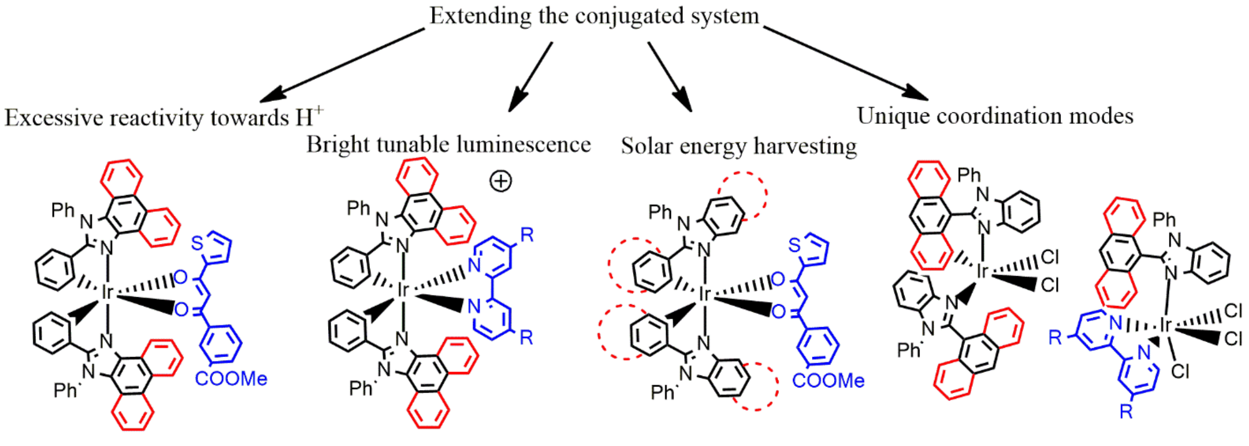
The extension of the conjugated π-system of ligands is usually considered to be an effective tool for improving optical properties of iridium(III) complexes. However, the increase of the steric pressure exerted by bulky cyclometalated ligands results in change of the geometry and, hence, properties of the complexes.

Recently we have shown that the use of cyclometalated 2-aryl-*N*-phenylphenanthro[9,10-d]imidazoles in combination with aromatic β-diketones dramatically enhanced the reactivity of the corresponding iridium(III) complexes[1]. The involvement of 2,2′-bipyridines as ancillary ligands to the same cyclometalated core led to partial release of steric tension and formation of the complexes possessing bright tunable emission. Tailoring the π-system of the cyclometalated ligands allowed the creation of stable strongly absorbing diketonate complexes which were successfully tested as photosensitizers in solar cells and demonstrated efficiency comparable to that of the commercial photosensitizers.

Moreover, it was shown that the involvement of rigid 2-(9-anthracenyl)-*N*-phenylbenzimidazole into iridium(III) chemistry (with appropriate optimisation of reaction conditions and variation of additional ligand environment) yielded a straightforward way to both an unprecedented *mono*-cyclometalated square pyramidal Ir(III) complex and an interesting *non*-cyclometalated species stabilized by intramolecular π-stacking. The latter compound was unexpectedly inert, even in the presence of silver triflate we observed formation of the trinuclear complex with an $Ir(\mu\text{-}Cl)_3Ag(\mu\text{-}Cl)_3Ir$ framework instead of the chloride substitution. These compounds go beyond standard iridium(III) chemistry being interesting not only from the crystallographic point of view, but also as a basis to create complexes of new composition and structure with potentially new properties.



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Volatile magnesium complexes based on fluorinated β-diketonates for MOCVD purposes: synthesis, structure, thermal properties

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Magnesium fluoride films are in demand as antireflection layers for solar energy converting devices in the aspect of reducing primary incident light losses. Metal-organic chemical vapor Deposition (MOCVD) and related methods could provide a quality and affordable alternative to produce such films without the use of harsh chemicals (compared to sol-gel technology where HF is commonly used) or high vacuum equipment (compared to physical vapor deposition). To realize this potential, the effective volatile magnesium compounds that provide the formation of MgF_2 directly in the deposition process or using traditional co-reagents (O_2, H_2O) are required.

Thus, this work is aimed at developing a new class of magnesium MOCVD precursors based on fluorinated β-diketonates (RC(O)CHC(O)R') and N-donor neutral ligands. The goal is to study the effect of both types of ligands on the synthesis features, structure, and thermal properties of such complexes. In particular, with a fixed neutral ligand (*tmeda* = N,N,N',N'-tetramethylethylenediamine), a series of β-diketonates were used, varying the main types of terminal substituents (R = CF_3, R' = CF_3, Me, ^{t}Bu, Ph) including the length extension of fluorinated group (R = CF_2CF_3, R' = Me). With a fixed anionic ligand, the focus of research was on increasing the carbon chain of the bidentate ligand (*tmpda* = N,N,N',N'-tetramethylpropylenediamine), switching to aromatic heterocycles (*bipy* = 2,2'-bipyridyl, *phen* = 1,10-phenanthroline) or to monodentate ligands (pyridine derivatives).

In this work, eight complexes of this class were synthesized, including four new ones. The compounds were characterized by including elemental analysis, IR and NMR spectroscopy, powder XRD. The presence of several by-products has been established. It was shown that substitution of aqua-ligands in the corresponding magnesium β-diketonate complexes is an efficient and versatile approach to obtain the target complexes. The exception is *tmpda* ligand, when the corresponding adduct was directly formed, and the diamine entered the coordination sphere only upon its subsequent sublimation. The structures of seven mixed-ligand complexes and the new adduct were determined by single-crystal XRD. Monodentate ligands were shown to be able to coordinate both in the *cis*- (pyridine, Py) and in the *trans*-positions (4-methylpyridine).

The thermal properties of all compounds were studied by TGA and DSC. The introduction of aromatic bidentate heterocycles significantly increases the melting points and reduces volatility. However, the replacement of *bipy* with two monodentate pyridine derivatives leads to a significant increase in volatility. The latter complexes appear to be more volatile than the aliphatic counterpart *tmeda*. A similar noticeable increase in volatility is observed with an increase in the fluorinated substituent in the β-diketonate, whereas a Ph group reduces not only volatility, but also the thermal stability of the complex. For five compounds, the vaporization processes were also studied by tensimetry methods. The thermodynamic parameters of sublimation/evaporation were calculated. Quantitative data on volatility shows that the replacement of the neutral ligand from *tmeda* to *bipy*/*phen* leads to a decrease in vapor pressure by 3/3.5 orders. The decrease in vapor pressure when the CF_3 substituent is replaced by the ^{t}Bu and Me groups is half an order of magnitude. It has been shown that the effect of β-diketonate-ligand on the decomposition start temperatures is not pronounced, and the introduction of aromatic heterocycles increases the thermal stability.

This work was supported by the Russian Scientific Foundation (project № 21-73-00252)

A new insight into rare-earth lactates: synthesis and functional properties

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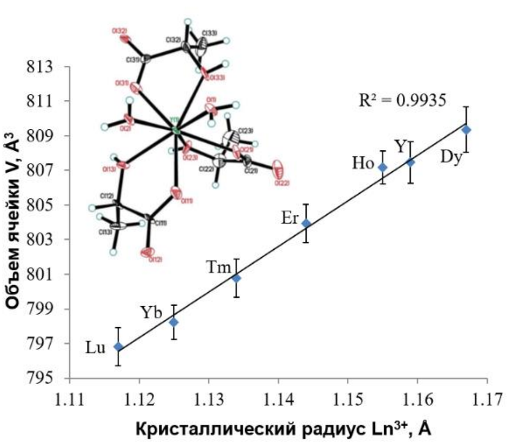
Structural information on crystalline rare-earth lactates was virtually not reported despite the thermodynamic properties of rare-earth lactate complexes in aqueous solutions have been thoroughly studied since the 1960s [1]. Lactate belongs to the class of α-hydroxycarboxylates which have a great variety of coordination modes to metal centers. α-Hydroxycarboxylates (and lactates in particular) have potentially higher denticity in comparison with carboxylates. Moreover, they can form interligand hydrogen bonds. These features along with high coordination numbers of the rare earths make it difficult to obtain crystalline rare earth lactates. On the other hand, recent advances in the prediction and modeling of rare-earth lactate molecular complexes indicated that they could be obtained in the crystalline state [2].

In view of practical applications, rare-earth lactates are definitely of interest for the design of new luminescent and magnetic materials including biosensors or diluted magnets. Until recently, only few rare-earth lactate structures were solved, including $[LnNa(rac\text{-}Lac)_4]\cdot 2H_2O$ (Ln = Sm, Eu) and $[Ln(L\text{-}Lac)_2](H_2O)_2\cdot ClO_4$ (Ln = Eu, Tb), which possessed explicit luminescent and multiferroic properties being promising for creating sources of circularly polarized light, asymmetric catalysis, enantiomer-selective sensorics, and sorption [3].

In our report, a series of isostructural crystalline Y, Dy–Lu lactates as well as new nanocrystalline Y, Eu-Lu basic lactates were obtained using hydrothermal method. The compositions were for crystalline yttrium lactate as $Y(C_3H_5O_3)_3\cdot 2H_2O$ and for nanocrystalline yttrium basic lactate as $Y_4(OH)_5(C_3H_5O_3)_7\cdot 6H_2O$. The unit cell volume of crystalline rare-earth lactates showed a linear dependence on the radius of a rare-earth cation. The nanocrystalline Y, Eu–Lu basic lactates have synthesized in the form of fibrous gels, the drying of these gels resulted in either corresponding aerogels or paper-like materials with essentially different microstructure as assessed using small-angle neutron scattering technique. The paper-like fibrous europium- and terbium-doped yttrium basic lactates have pronounced luminescent properties and can be used for the detection of benzene carboxylate anions or transition metal cations in aqueous media.



This work was supported by Russian Science Foundation (grant № 22-73-00041)

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Crystal growth and design of cationic cyclometallated iridium(III) complexes with various polyiodide anions

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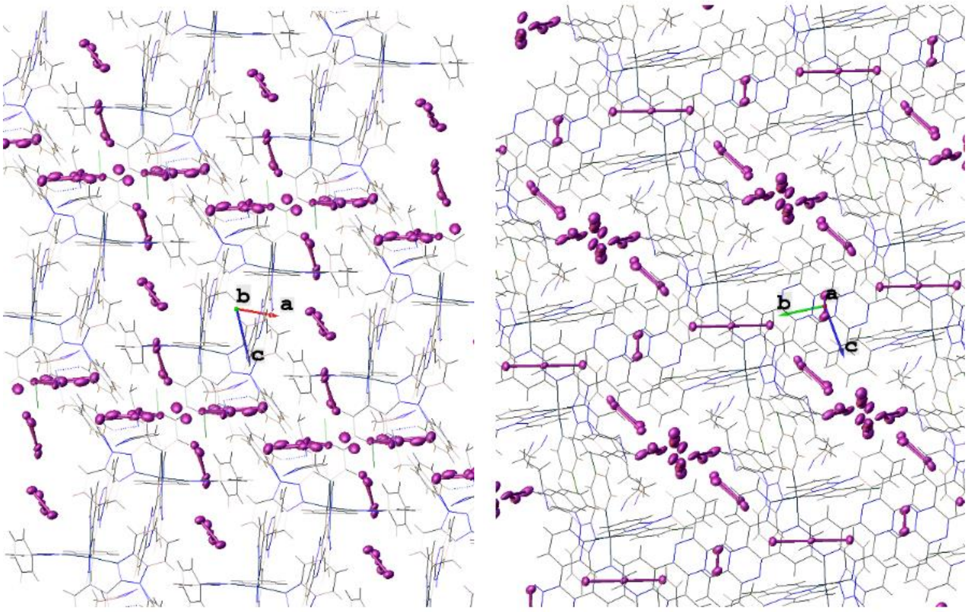
One of the effective technologies of solar energy harvesting is a dye-sensitized solar cell (DSSC). The development and production of stable and efficient devices requires deep understanding of fundamental processes occurring in the cell. One of such processes is the reduction of the oxidized dye (the Ir^{III} complex) by the mediator (I^{3-}/I^- pair). However, there are some side processes in the cell: one of the most harmful is a recombination of electron from the excited photosensitizer with the iodide-anion. To investigate such side processes of electron transfer between the dye and the mediator models with charge separation are needed. The examination of these systems in the solution is rather complicated due to particles mobility, so we consider co-crystals of cationic complexes of a dye with mediator anions as a satisfactory model system. In this case, the essence of the processes occurring in the cell is preserved, and the close packing additionally facilitates the electron transfer.

Our recent investigations have shown that cyclometallated complexes with ancillary N^N ligands containing carboxyl groups form package stabilized by H-bonds. However, in real device these groups link to the surface of semiconductor, so weak interactions such as I-π, π- π, VdW, etc. become crucial. Based on these premises, we changed N^N ligand for neutral dipyridophenazine. 4 different phenyl-benzimidazoles containing various halogens (Cl, Br), located in two different positions were chosen as cyclometallated C^N ligands. Such differences allow to trace possible halogen contacts and to evaluate influence of halogen nature at crystal packing. Depending on the initial iodine concentration, various polyiodide architectures were obtained in the resulting crystals, from insular tri- or pentaiodides to infinite polyiodide chains and polyiodide layers. Obtained objects were systematically studied by X-ray diffraction analysis. Concise correlations between type of the cyclometallated ligand and number of possible structures were disclosed.



Crystal packing formed by polyiodide grid.

Inorganic and Coordination chemistry Section Poster Session

Structural features of rhenium phtalocyanine complexes

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The development of effective original methods for the synthesis of metal complexes with bioactive lygands on the basis of metalporphyrines and metalphtalocyanines is an essential task of synthetic chemistry.

In this work, rhenium phthalocyanines were synthesized by the reaction of tert-butylphthalodinitrile with ammonium perrhenate and the structural features of the resulting complexes were studied. The UV/visible spectra of the resulting complexes show characteristic absorption for metal phthalocyanine. The EPR of benzene solutions of the isolated products was characterized by two main bands at ~370 and ~700 nm. Satellites at 630 and 670 nm are well resolved, which is typical for monomeric forms of phthalocyanines. Band Q at max. ~ 700 nm refers to allowed (π-π^* transition). There is also a second allowed π-π^* transition (B band) around 340 nm extending to the blue of the visible spectrum. Shoulders at max. ~ 670 nm and 630 nm - electronic-vibrational transitions. The intense Q band arises from a doubtly degenerate transition between the A1g ground state and the first excited singlet state with Eu symmetry. The splitting of the Q band can be explained by the lower symmetry of the molecules in the complexes. This can lead to different interactions of dipole moments between the Pc macrocycle and the Re = O axial ligand and, as a consequence, to a smaller degeneracy of the first excited state. IR absorptions common to the spectra of the main Pc fragment were observed, such as (C=Carom) at 1608 cm^{-1}. New bands, which are not observed in the spectra of PcH2, were observed in the spectra of PcReO. These new vibrations, highlighted in the IR data of the obtained complexes, include vibrations (C=O) at (1675-1690 cm^{-1}). Other new signals are also observed with different values in the range of fingerprint spectra (800-1400 cm^{-1}). However, it cannot be assumed that the Re = O bond in the complexes is unambiguously related to stretching because of the well-known multiplicity of IR absorption Pcs in this region. One of the important features of the IR spectra of the obtained complexes is the presence of a band at 945 cm^{-1}, corresponding to the Re = O bond. The absence of bands in the range of 3100–3700 cm^{-1} indicates the absence of OH groups in the complexes.

The EPR spectra of the complexes isolated from benzene solutions exhibit a narrow, slightly asymmetric signal with a g factor of 2.004 and a width of ΔH ~ 0.8 mT, which is characteristic of phthalocyanine molecules. No signals characteristic of separated powders of paramagnetic complexes with the Re = O bond and their benzene solutions were found. The absence of EPR signals for rhenium complexes with the Re = O bond indicates, first of all, the diamagnetism of the resulting complexes.

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On the interaction of nickel(II) with 1-(2-pyridylazo)-2-hydroxy-4-mercaptophenol and aminophenols

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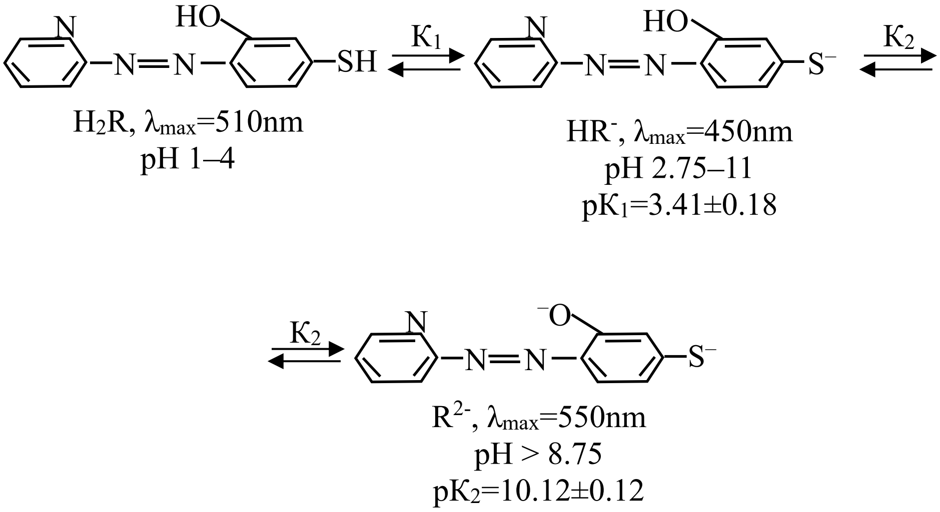
In the search for more advanced reagents for the determination of nickel, 1-(2-pyridylazo)-2-hydroxy-4-mercaptophenol (PAGMP) was investigated. The purpose of this work is to study the complexation of nickel (II) with PAGMP and aminophenols (AP) {2- (N, N-dimethylaminomethyl)-4-methylphenol and 2-(N,N-dimethylaminomethyl)-4-chlorophenol}.

PAGMP is a crystalline substance of dark green color, poorly soluble in water, in acids, partially soluble in alkalis, acetone, well soluble in chloroform. Depending on the acidity of the medium, PAGMP can exist in three forms: H_2R, HR^-, HR^{2-}.



H_2R, λ_{max}=510nm
pH 1–4

HR^-, λ_{max}=450nm
pH 2.75–11
pK_1=3.41±0.18

R^{2-}, λ_{max}=550nm
pH > 8.75
pK_2=10.12±0.12

The optimum acidity range, at which the optical density is maximum and constant, is at pH 3.5-6.5. The optimal condition for the formation and extraction of these compounds is the concentration $(1.2\text{-}1.5)\times10^{-3}$ M PAGMP and $(2.4\text{-}2.6)\times10^{-3}$ M AP. The maximum optical density is reached within 15 min, and the extracts of the complexes obey Beer's law at cobalt concentrations of 0.5–18 μg/ml. The molar absorption coefficient is $\varepsilon_{620\text{-}650} = (3.22\text{-}3.51)\times10^4$.

The stoichiometry of the complexes under study was established by the methods of equilibrium shift and relative yield (Ni:PAGMP:AP=1:2:2). PAGMP is a tridentate ligand coordinated with Ni^{2+} through the nitrogen atom of the azo group ($\upsilon_{N=N}$ = 1395 cm^{-1}), near-bottom nitrogen ($\upsilon_{C\text{-}N}$ = 1290 cm^{-1}; $\upsilon_{C\text{-}N}$ = 1170 cm^{-1}) and oxygen atom ($\delta_{C\text{-}O}$ = 1250 cm^{-1}). The detection of absorption bands at 1370 cm^{-1} indicates the presence of protonated AP.

Large amounts of alkaline, alkaline-earth elements, and REE do not interfere with the determination of nickel.

The developed technique was applied to determine nickel in water [0.175 μg/L Ni] and in soil [2.607×10^{-3}% Ni].

Synthesis of new chromium(III) complex compounds with chalcogen-containing ligands obtained from bis(2-chloroethyl) ether or bis(2-bromoethyl)sulfide

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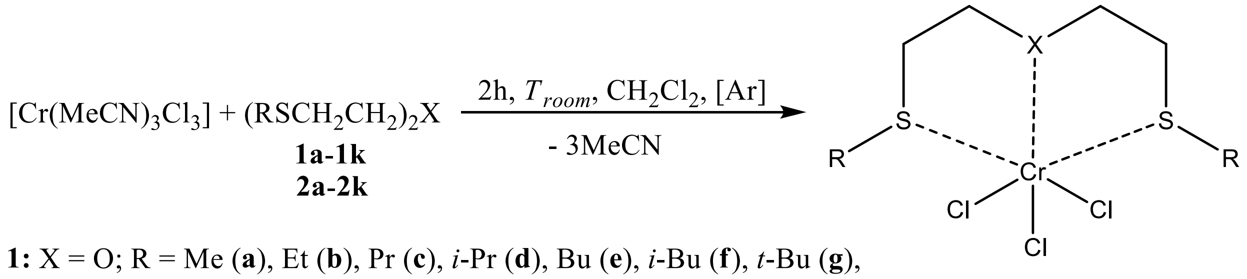
Chromium(III) complex compounds stabilized with various organic ligands are widely used in the catalytic conversion of ethylene. For this reason, the preparation of new complex compounds is an important task of modern coordination chemistry. This paper presents data on the preparation of a number of new chromium(III) complex compounds of the composition $[Cr\{(RSCH_2CH_2)_2X\}Cl_3]$, where X = O or S; R = Me, Et, Pr, *i*-Pr, *i*-Bu, *t*-Bu, Cy and Ph with chalcogen-containing ligands synthesized by known methods [1-3].



$$[Cr(MeCN)_3Cl_3] + (RSCH_2CH_2)_2X \xrightarrow[\text{- 3MeCN}]{\text{2h, } T_{room}\text{, } CH_2Cl_2\text{, [Ar]}}$$

1a-1k
2a-2k

3a-3h
4a-4h

1: X = O; R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *i*-Bu (**f**), *t*-Bu (**g**), C_6H_{13} (**h**), Cy (**i**), Ph (**j**), Bn (**k**)
2: X= S; R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *i*-Bu (**f**), *t*-Bu (**g**), C_6H_{13} (**h**), Cy (**i**), Ph (**j**), Bn (**k**)
3: X = O; R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), *i*-Bu (**e**), *t*-Bu (**f**), Cy (**g**), Ph (**h**)
4: X = S; R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), *i*-Bu (**e**), *t*-Bu (**f**), Cy (**g**), Ph (**h**)

Complex compounds with ligands **1e**, **1h, 1k**, **2e**, **2h** and **2k** could not be isolated individually. In all cases, when these ligands are used, a glassy mass is formed as a result of the reaction, while the remaining compounds can be isolated in the form of powders.

The obtained compounds **3a-3h** and **4a-4h** were characterized by a complex of physicochemical methods, elemental and mass-spectrometric analysis was performed. X-ray diffraction data were obtained for compound **3b**.

The reported study was funded by RFBR, project number 20-33-70139. This work was supported by the Government Assignment for Scientific Research from the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-03-2020-176/3; project code in Parus 8: FZZE-2020-0022)

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Synthesis and ESR study of Pd(II) and Pt(II) binuclear complexes with bridged *electron-rich* 1,10-phenanthrocyanine ligands (*soft colloidal glasses*) – DNA complexones and potential cytostatics

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Coordination compounds Pd(II), as well as earlier Pt(II), have recently attracted increased interest as potential (less toxic) antitumor agents. One of the mechanisms of antitumor action of these complexes is the inhibition of protein synthesis, in particular, due to changes or damage to the matrix properties of DNA macromolecules. Depending on the composition and structure of the complexes, they are capable to various variants (modes) of binding to DNA macromolecules. Including covalent – by *cis*-positions of halide ligands of complexes (as is the case, for example, for *cis*-[Pt(NH$_3$)$_2$Cl$_2$]) or intercalation – embedding of planar heterocyclic ligands of complexes between double turns of DNA helices.

The paper presents data on the synthesis of the Pd(II) and Pt(II) binuclear complexes with bridget electron-rich 1,10-phenanthrocyanine ligands (*dihydro*-bi-1,10-phenanthrolines) [Ln**Pd^{2+} (μ-2,9-Me$_2$-phencyanineH)Pd^{2+}**Ln]X$_4$ (**1**) (*soft colloidal glass)* and [Ln**Pt^{2+}(μ-phencyanine$^-$) Pt^{2+}**Ln]X$_3$ (L–amines, X –halide anions) (*DNA complexones*). The compounds were obtained based on the methodology of *metal-assisted nondehydrogenative* C(sp^2)*H* coupling of coordina-ted 1,10-phenanthrolines [1]. This coupling includes, as one of the main stages, the processes of *heteroaromatic nucleophilic substitution of hydro-gen* **S$_N$^{H}** [2]. Pd(II) complexes were synthesi-zed in melts of [PdCl$_2$]n– 2,9-dimethyl-1,10-phenanthro-line, and Pt(II) compounds were syn-thesized in solutions of [Pt(phen)L$_2$]X$_2$, as a result of activation by single electron transfer (***SET***).

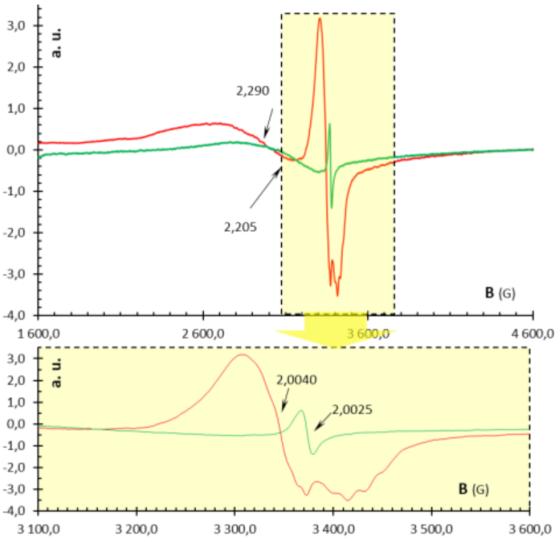

Fig. ESR spectra (X-Band, T = 300 K) of compounds **(1)** (green trend) and **(2)** (red trend)

The obtained compounds were investigated by ESR spectroscopy. Signals (with a nonstoichiometric concentration of paramagnetic centers) with a comp-lex contour were detected in the ESR spectra (Fig.), which we interpreted as the result of the interaction (or superposition) of temperature-accessible low-energy triplet biradicals in the ground electronic state of bridged 1,10-phenanthrocyanines **μ-2,9-Me$_2$-phencyanineH** or **μ-phencyanine$^-$** and **Pd$^{\cdot+}$** or **Pt$^{\cdot+}$** radical states.

The ESR study of the complexes was carried out at the Resource Center for Magnetic Resonan-ce Research Methods of the St. Petersburg State University Science Park

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Cerium oxide nanofiller improve physical and biological properties of chitosan

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Polymeric nanocomposite systems containing inorganic nano-sized fillers such as metal oxides have great potential for the development of tissue-engineered matrices because they affect the structure and properties of polymeric materials and can regulate cell proliferation and differentiation. Cerium oxide is widely used for biomedical application, including tissue engineering. In this work, we incorporated citrate-stabilized cerium oxide nanoparticles (CeONPs) [1] into chitosan (CS) film to improve cell culture due to the redox properties of the cerium oxide [2]. The initial CeONPs with a negative ζ-potential (-25.0 mV) were precoated with CS to obtain positively charged particles (+20.3 mV) and prevent aggregation of the composite solution. The resulting films were prepared using a dry cast process in salt and basic form (the basic form was obtained by treating with a 2% ammonia solution in ethanol). According to scanning electron microscopy data and energy dispersive elemental analysis, the obtained composite films based on CS and CeONPs (CS–CeONP) in both salt and basic forms were characterized by high adhesion of filler to the polymer matrix and a uniform distribution of CeONPs. The introduction of CeONPs into the initial salt form of CS increased the stiffness of the material (a 13 % increase in the Young's modulus and a 22 % increase in the yield point were registered). The conversion of the CS–CeONP film to the basic form significantly decreased (two to three times) both the Young's modulus and the yield point of the composite material compared with both the salt form of the CS–CeONP film and both forms of the CS films. The redox activity of cerium oxide in the CS–CeONP film composition as a result of $Ce^{4+} \rightleftharpoons Ce^{3+}$ transformation was proved by thermal oxidative degradation. Additionally, in vitro cultivation of mesenchymal stem cells showed that CS–CeONP film has good biocompatibility, and in vivo experiments demonstrated its impressive regenerative potential.

This work was financially supported by the Russian Science Foundation (project 22-13-00068)

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Diphenylgermanium (IV) complexes with O,N,O'- donor redox-active ligands: synthesis and electrochemical transformations

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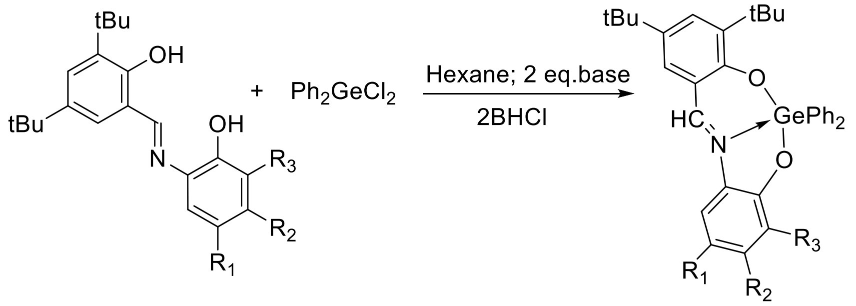
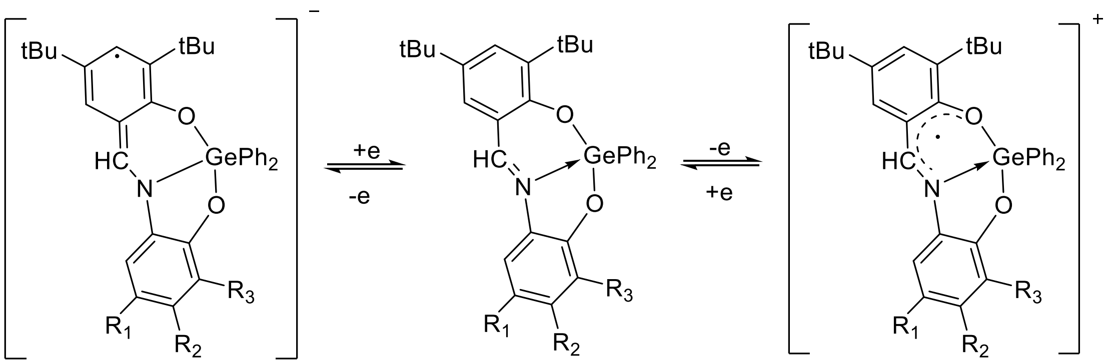
In contrast to tin or lead compounds, coordination and organometallic derivatives of germanium (IV) are characterized by greater chemical stability and less toxicity. These properties contribute to attracting attention to germanium compounds for the development of new functional materials based on supramolecular structures or lithium-ion batteries, as well as physiologically active compounds. In this work, we have obtained new complexes of diphenylgermanium(IV) with redox-active O,N,O'-donor Schiff bases **1-4** (16-87%).



Ph_2GeL^1 (1) L^1H_2: R_1 = t-Bu; R_2 = R_3 = H
Ph_2GeL^2 (2) L^2H_2: R_1 = R_3 = t-Bu; R_2 = H
Ph_2GeL^3 (3) L^3H_2: R_1 = R_3 = Cl; R_2 = Me
Ph_2GeL^4 (4) L^4H_2: R_1 = Cl; R_2 = H; R_3 = NO_2

The ability of redox-active ligands to reversibly change the oxidation state in the coordination sphere of a metal causes the particular interest for the chemistry of non-transition elements. The electrochemical studies of complexes **1-4** by cyclic voltammetry showed that these compounds are possessed by reversible one-electron transitions, both in the anodic and cathodic area of the potential sweep.



The most stable oxidized forms were found for compounds **2** and **3**, while monoanionic electrogenerated species were more stable for complexes **1** and **2**. Based on the electrochemical and spectral data, the differences in the boundary redox orbitals (ΔE) were determined, which varied in the range from 2.44 to 2.52 eV.

This work was supported by the Russian Science Foundation (grant № 22-13-00118)

Mixed isocyanide-phosphine complexes of palladium(II) dihalides

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Isocyanide ligands in platinum metal complexes exhibit strong σ-donor and weak π-acceptor properties, due to which such compounds are used as catalysts in important organic processes and in design of luminescent materials [1]. Of particular interest are mixed-ligand complexes containing, along with the isocyanide ligands, additional auxiliary neutral ligands, such as phosphines: appealing such approach, one can finely adapt the electronic and steric characteristics to target parameters [2, 3].

The complexes *cis*-[PdCl$_2$(CNR)(PPh$_3$)] (R = Mes **1**, Xyl **2**, ^{t}Bu **3**) were prepared by the bridge-splitting reaction of the dimer [PdCl$_2$(PPh$_3$)]$_2$ with corresponding isocyanides. The *cis*-[PdBr$_2$(CNR)(PPh$_3$)] (R = Mes **4**, Xyl **5**, ^{t}Bu **6**) were synthesized employing **1**–**3** and excess KBr in acetone at RT for ca. 4 d. These complexes are obtained as yellowish air- and moisture-stable solids and characterized by CHN elemental analyses, high-resolution mass spectrometry (ESI$^+$-HRMS), FT-IR, and ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopy. The structures of **1** and **4**–**6** were established by single-crystal X-ray diffraction. All **1**–**6** are not subject to isomerization and are isomerically pure in the solid state and in CDCl$_3$ solution (*cis* configuration). The ligand metathesis reaction of **1**–**3** and KI in acetone at RT for approximately 3 h affords mixtures *cis/trans*-[PdI$_2$(CNR)(PPh$_3$)], *trans*-[PdI$_2$(CNR)$_2$)] and *trans*-[PdI$_2$(PPh$_3$)$_2$)].

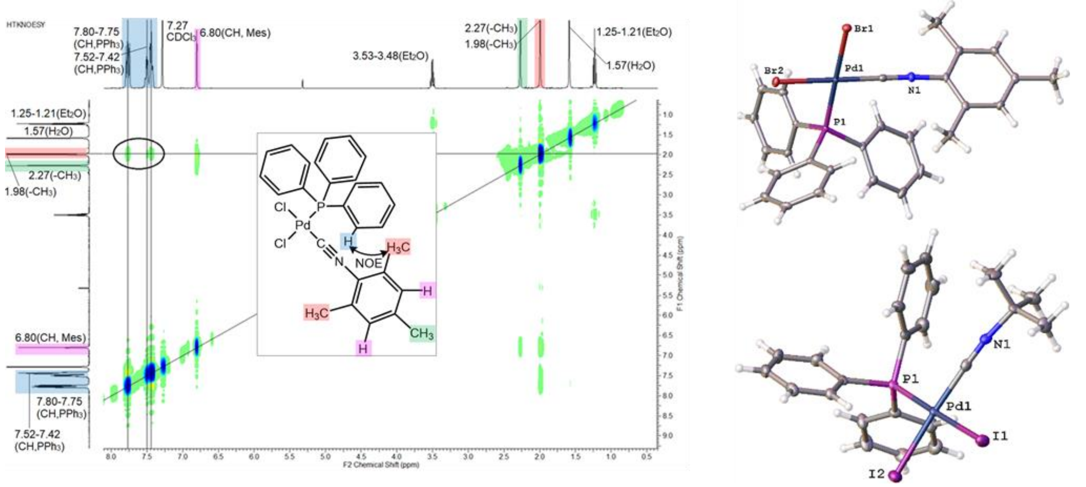

Fig. ^{1}H-^{1}H NOESY spectrum of **1** with indicated cross-peaks between protons of the CNMes and PPh$_3$ ligands (left) and X-ray molecular structures of **4** and *cis*-[PdI$_2$(CN^{t}Bu)(PPh$_3$)] (right).

This study was financially supported by the Russian Science Foundation (project no. 21-73-10083). Measurements were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research and Chemistry Educational Centre (all in St Petersburg University)

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Synthesis and catalytic properties of rhodium and iridium-containing chitosan films

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Despite all the unique properties of chitosan, its use is limited, since it is insoluble in water, has a high viscosity and tends to coagulate with proteins at high pH. To solve this problem, many studies have been carried out, one of which included the creation of composites and nanocomposites of chitosan and its derivatives with platinum metal cations, which exhibit new properties as a result of the interaction between the components.

The aldol reaction is a powerful tool for the formation of C–C bonds in organic synthesis [1]. Aldol structural units have been found in many important natural and synthetic compounds [1, 2]. Investigating the catalytic activity of transition metals, such as: Co-, Pt-, Pd-, Ni-, Cu-, Ir- and Rh-, the coordination compounds Rh, Ir and Cu are the most effective [4].

In the framework of the presented study, chitosan films, containing Rh^{3+} and Ir^{4+}-cations, were obtained. The resulting compounds were characterized by IR-spectroscopy, SEM, DTA, and XPA.

The films are heterogeneous membrane catalysts for the reaction of aldol condensation.

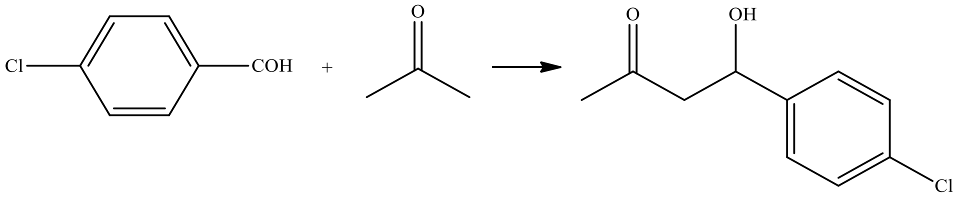

Fig.1 Model aldol reaction

As a result, it was found that in the residue obtained from the reaction mixture, which passed through the BCh3GlyIr0.5:1 film, only the aldol was contained (yield 93%), while in the case of using the BCh3GlyRh0.5:1 film, the residue consisted of 27% of the original aldehyde and 73% aldol. Thus, the VKh3GlyIr0.5:1 film is an efficient membrane catalyst for the aldol reaction based on the natural polymer chitosan.

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Synthesis, structure and magnetic properties of erbium(III) complexes based on halogenated ligands

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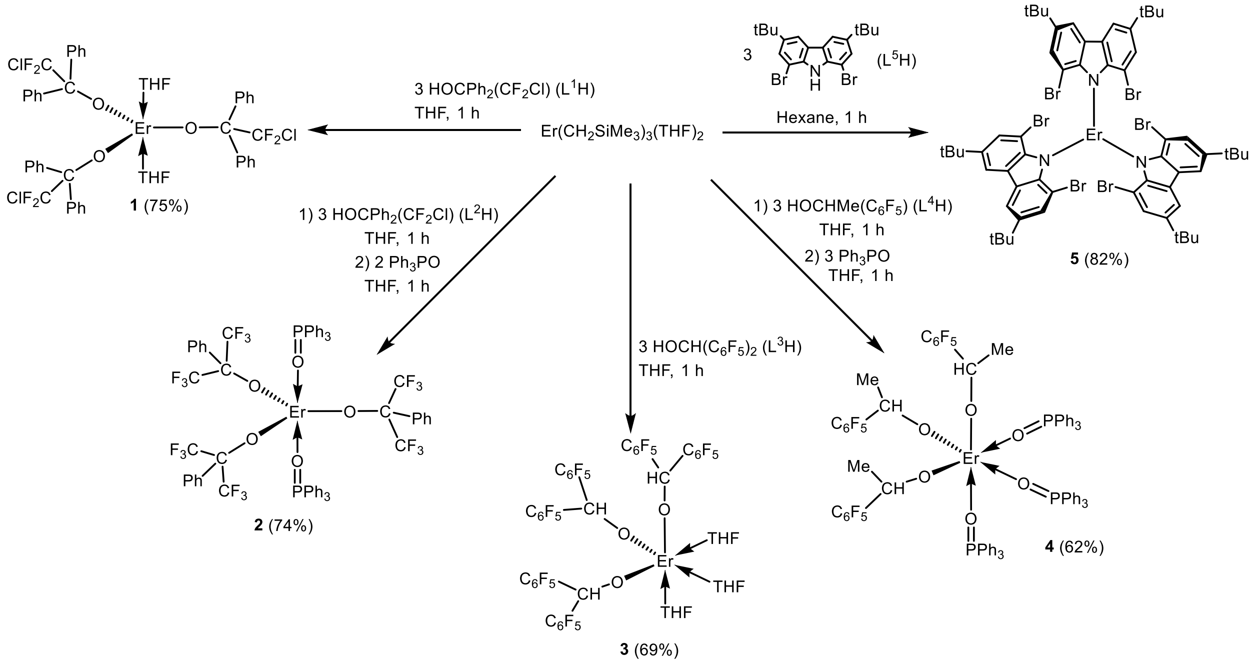
Recently, lanthanide complexes have attracted increasing attention due to their unique magnetic properties, such as high magnetic anisotropy and slow relaxation of the magnetization at the molecular scale. Nevertheless, there are no extensive studies of the structure dependence of the magnetic properties of neutral erbium(III) complexes with an equatorial crystal-field.

In this work, we have synthesized a series of neutral erbium complexes of general formula $[Er(L^x)_3Y_n]$ based on different halogenated L^{1-5} ligands. All obtained compounds have been characterized by the X-ray diffraction, NMR, and IR spectroscopy, and their magnetic properties have been investigated.



In accordance with the steric hindrances created by ligands, complexes **3** and **4** have a *fac* octahedral geometry, while less steric demanding ligands afford the trigonal bipyramidal complexes **1** and **2**. On the other hand, **5** is low-coordinated and has an unusual triangular geometry. A zero-field slow relaxation of the magnetization could be only evidenced for the complex **5**, as a consequence of its predominant equatorial crystal field, although low anisotropy barrier has been observed.

This work was supported by the Russian Science Foundation (project № 17-73-30036-П)

The direct band gap for EuCeCuSe3 and regularities in EuLnCuSe3 sequence

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The compounds $EuLnCuSe_3$ are used as optical materials, thermoelectric materials and considered as potential catalysts in the processing of gaseous hydrocarbons.

Experimental value of direct bandgap for $EuCeCuSe_3$ extracted from modified Kubelka-Munk function is equal to 1.36 eV (fig.1, left). New data on $EuCeCuSe_3$ bandgap are an important addition (fig.1, right) to the data for $EuLnCuSe_3$ reported in [1]. The narrowest bandgap among $EuLnCuSe_3$ compounds is exhibited for Ln=Ce and Ln=Yb. Ce^{3+} ion possesses f^1 electron configuration while Yb^{3+} ion possesses mirror electron configuration to Ce^{3+}, that is, f^{13}. However, the reasons for the narrowing of the bandgaps may be different for these two compounds.

Direct bandgap in Eu^{2+}-containing compounds must be determined by transitions between valence band including *4f* orbitals of Eu^{2+} ion and conduction band including *5d* orbitals of the same ion. Europium-free $SrCeCuS_3$ crystal demonstrates 2.20 eV direct bandgap that is smaller than 2.33 eV direct bandgap of $SrScCuS_3$ [2]. The latter result indicates that *4f* and *5d* orbitals of Ce^{3+} play role in narrowing of $SrCeCuS_3$ bandgap. Similarly, narrower bandgap of $EuCeCuSe_3$ (1.36 eV) with respect to $EuLaCuSe_3$ (1.54 eV) can be ascribed to *4f* and *5d* orbitals of both Ce^{3+} and Eu^{2+}. Additionally, we deduce that crystal field at Eu sites in $EuCeCuS_3$ and $EuCeCuSe_3$, to explain their narrower bandgap, must be higher in comparison with $EuScCuS_3$ with its 1.63 eV bandgap. Oppositely, narrowing of $EuYbCuSe_3$ bandgap is due to charge transfer band of Yb ion.

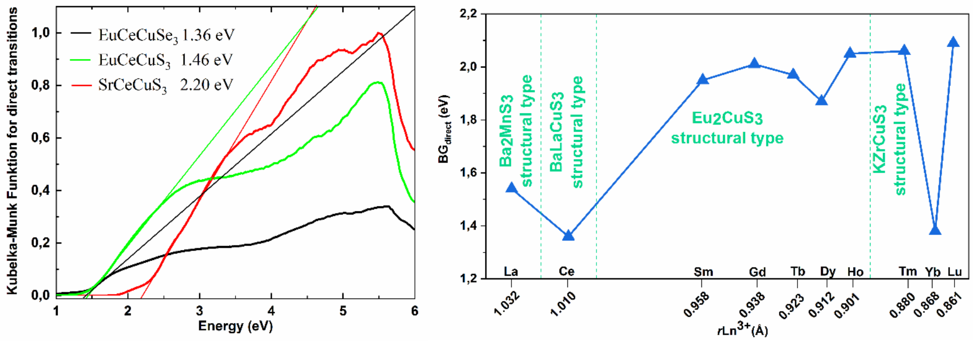

Figure 1. Kubelka-Munk Functions modified for direct bandgap determination for $EuLnCuSe_3$ (left), dependence of the direct band gap on the radius REE (right)

This research was funded by the Tyumen Oblast Government, as part of the West-Siberian Interregional Science and Education Center's project No. 89-DON (3)

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J. Solid State Chem., **2021**, *296(10),* 121926

Synthesis of new cytotoxic conjugates of titanocene with NSAIDs, stable in aqueous media

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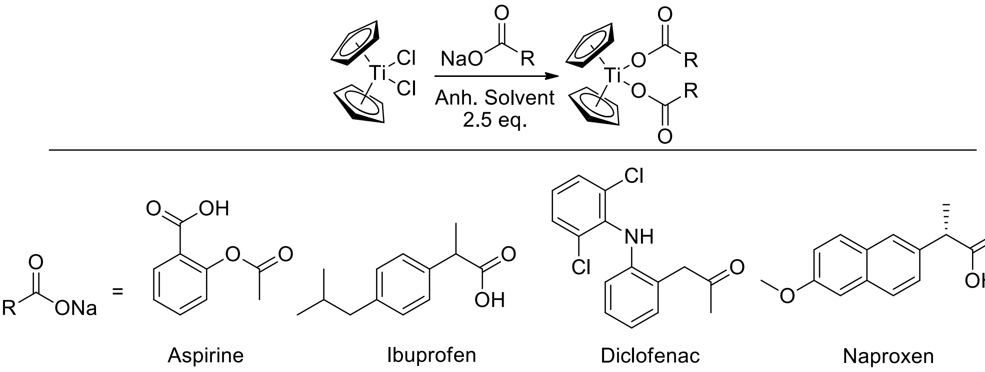
One of the possible solutions to the fundamental problem of high general toxicity and serious side effects of anticancer drugs based on platinum can be the search for coordination compounds based on biogenic metals, which also have high cytotoxic activity on cancer cells.

One of the most promising analogues of cisplatin, containing a biogenic metal atom in its structure, is titanocene dichloride, which has a number of advantages: high cytotoxicity on tumor cells, a mechanism of action similar to cisplatin, and the absence of toxic hydrolysis products.

The only drawback that did not allow titanocene dichloride to successfully complete clinical trials as a drug for the treatment of breast adenocarcinoma is the relatively low resistance of Ti – Cl bonds to hydrolysis in physiological media[1].

In the framework of this study, we propose the synthesis of analogs of titanocene dichloride by replacing the labile Ti – Cl bond with a more stable Ti – O bond. This approach not only improves the hydrolytic stability of coordination compounds based on titanocene, but also allows the introduction of the additional physiologically active ligands into the molecule, in this case the derivatives of non-steroidal anti-inflammatory drugs (NSAIDs).



The choice of NSAIDs as ligands is due to the fact that it was previously shown [2] that coordination compounds based on cisplatin and NSAIDs have increased cytotoxicity on breast adenocarcinoma cell lines and are predominantly localized in the nucleus and mitochondria of the cell.

Thus, the obtained results open a synthetic route to a new generation of cytotoxic coordination compounds based on titanocene with the possibility of tuning properties due to the rational design of carboxylate-containing ligands.

This work was supported by the grant of the Russian Science Foundation, RSF № 22-73-00004

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Study of the reaction of complexation of nickel(II) with aminophenols

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It is of interest to study the interaction of nickel with aminophenols (AF): 2-piperidinomethyl-4- (1-methylcyclopentyl) phenol (AF_1), 2-piperidinomethyl-4- (1-methylcyclohexyl)phenol (AF_2), 2-piperidinomethyl-4- (3-methylcyclohexyl) phenol (AF_3).

The charge of the complexes was established by the method of ion electromigration and by the method of electrophoresis on paper. When studying the electromigration of this complex, the movement of the orange-colored complexes not to the cathode and not to the anode was observed, on the basis of which it was concluded that the colored complexes are neutral. The optimum acidity range, at which the optical density is maximum and constant, is at pH 3.0-5.0. The extractability of the complexes was assessed by the values of the distribution coefficients and the degree of extraction (R,%). The studies were carried out with chloroform (R = 97.6–98.0%). The nickel content in the organic phase was determined photometrically - with dimethylgloxime after reextraction, and in the aqueous phase - by difference. The optimal condition for the formation and extraction of AF is 0.8×10^{-3} M. The maximum optical density is reached within 5 min. The molar absorption coefficients are $(3.56\text{-}3.96)\times10^4$ at 470-476 nm. The stoichiometry of the complexes under study was established by the methods of equilibrium shift and relative yield: Ni:AF = 1:2. The complexing ion of nickel is the doubly charged cation Ni^{2+}. Complexes in the organic phase are in the monomeric form (γ=1.04-1.07). The equilibrium constants of the reaction Kp, calculated by the formula lgKp = lgD – 2lg[AF], are given in table.

Table. Characterization of complexes of nickel with AF

Compound	pH	λ,nm	$\varepsilon\times10^{-4}$	$\lg\beta_s$	$\lg K_{eq}$	$\lg K_{ex}$	Working range, μg/ml
Ni –AF_1	3.3-4.8	476	3.14	9.17	7.89	12.57	0.5-16
Ni –AF_2	3.6-5.0	470	3.36	9.39	7.95	12.74	0.5-18
Ni –AF_3	3.0-4.5	472	3.48	9.68	7.98	12.93	0.5-20

Thermogravimetric study of the Ni-AF_1 complex showed that the thermal decomposition of the complex proceeds in two stages: at 60–120°C water is lost, at 490–510°C AF. The final product of the complex thermolysis is NiO. In the IR spectra of the Ni-AF_1 complex in the region of 950-960 cm^{-1}, an intense absorption band appears, which is absent in the spectra of the reagent, which is due to the stretching vibration of the metal-ligand bond. The disappearance of the band at 3200-3600 cm^{-1} with a maximum at 3460 cm^{-1} indicates that the -OH group is involved in the formation of the complex.

Alkaline, alkaline earth elements, REE do not interfere with the determination of nickel. The interfering effect of Fe(III) was eliminated with ascorbic acid, Ti(IV) - ascorbic acid, Cu(II) - iodide ion, Nb(V) - oxalate ion, and W(VI) - citric acid. When using 0.01M EDTA solution, V(IV), Nb(V), Ta(V), and Fe(III) do not interfere with the determination. The interfering effect of Hg (II) was eliminated by reduction using $S_2O_3^{2-}$ ions.

The developed technique was applied for the determination of nickel in magnesium materials [(Found: $(7.652\ 0.01)\times10^{-4}$); Introduced: 0.001; Found: $(1.17653\ 0.02)\times10^{-3}$; (Sr = 0.014); ($n$ = 6; p = 0.95),%] and in the rock - carnallite [(Found: $(1.8710\ 0.01)\times10^{-4}$); Introduced: 0.001; Found: $(1.18720\ 0.02)\times10^{-3}$; ($S_r$ = 0.013); (n = 6; p = 0.95),%].

Extractıon-spectrophotometrıc determınatıon of copper(II) usıng 2-(pıperıdınomethyl)-4-(1-methylcyclopentyl)phenol

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The control of the mass concentration of copper in waters is a particularly important and urgent task. The development of industry leads to pollution of natural waters, and Cu(II) is one of the main industrial pollutants belonging to the group of toxic metals with a wide spectrum of toxic effects. In drinking water, the concentration of Cu (II) ions may exceed the established maximum permissible concentration (MAC) [1] due to erosion of pipe materials.

This work is devoted to studying the possibility of spectrophotometric determination of Cu(II) using 2-(piperidinomethyl)-4-(1-methylcyclopentyl)phenol (L). L is one of the most sensitive and selective reagents for Cu (II) and is applicable for its extraction-spectrophotometric determination in various objects. When determining Cu(II) with L, the acidity of the analyzed solution has a noticeable effect on the magnitude of the analytical signal. L with Cu(II) at pH 3-8 forms an intracomplex compound. With a single extraction with chloroform, 97.6% of copper is extracted in the form of a complex. The complex absorbs light at λmax = 454 nm. The molar absorption coefficient is 3.11×10^4. The stoichiometry of the studied complex was established by the methods of equilibrium shift, relative yield, and straight line [2]. The Cu:L ratio is 1:2. The interfering effect of K^+, Na^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ni^{2+}, Fe^{3+}, Cl^-, NO^{3-} and SO_4^{2-} most frequently found in waters on the determination of Cu(II) has been studied. The relative deviation of the analytical signal in the presence of an external component is calculated by the formula δ (%) = [(Ai –A) /A]·100, where A and Ai are the optical density of the complex in the absence and in the presence of a foreign component, respectively. The components introduced into the solution do not have a significant interfering effect on the determination of Cu(II). The developed method was tested in the analysis of drinking water for the content of Cu(II): For drinking water [0.22 ± 0.06 mg/l, Sr = 11%]; For tap water [2.51 ± 0.06 mg/l, Sr =11%].

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Spectral study of the dioxygen and carbonyl adducts of ferrous porphyrins ligated by P-donor ligand

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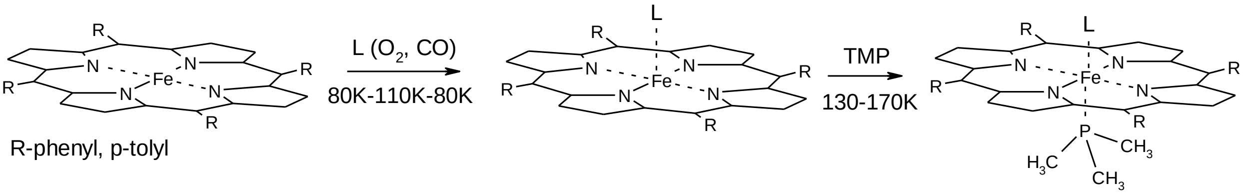
Interaction of diatomic molecules (such as O_2 and CO) with hemoglobin and myoglobin are of great interest and has been extensive studied over the past several decades. Six-coordinate iron porphyrin complexes have been investigated mostly with N- and S-donor ligands as the models of globins and cytochrome P-450 [1-3]. Previous studies have shown that metal tetra-aryl-porphyrinats, sublimed onto a low temperature substrate, form amorphous microporous layers. The reaction of sublimated metallo porphyrins with additional ligands allows one to construct different 5- and 6-coordinate complexes, which can be easily characterized by UV-visible and infrared spectroscopy without solvent interference [4]. Here we present new six-coordinate dioxygen and carbonyl complex of iron porphyrins bearing *trans* P-donor ligand (trimethylphosphine, TMP). Formation of the six-coordinate adducts supported by using FTIR and UV-Vis spectroscopy. The oxy– and carbonyl-hemoglobin models of the general formula (TMP)Fe(Por)(O_2) and (TMP)Fe(Por)(CO) (Por – *meso*–tetra–phenyl or *meso*–tetra–*p*-tolylporphyrinato dianions) were constructed by sequential low temperature interaction of the microporous layers of Fe–porphyrins with O_2 (CO) and TMP at low temperatures.



Upon addition of the ligand vapors to a cryostat containing Fe(Por)(CO) or Fe(Por)(O_2) at temperature range 130-170K, the spectral changes were observed that are consistent with ligand binding in axial position *trans* to the CO (O_2) and formation of the six-coordinate adducts. The $\nu(O_2)$, $\nu(CO)$ shifts upon coordination of TMP are largest in comparison with known N- and S-donor ligands, that is in consistence with the highest basicity. These six-coordinate adducts are stable only at low temperature and dissociate upon warming. The 6-coordinated complexes are characterized by FT-IR spectroscopy using isotopically labeled $^{18}O_2$, ^{13}CO and $C^{18}O$ species.

This work was supported by the State Committee of Science RA (Project 21AG-1D040)

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Photolysis of palladium(II) complexes with diamines and monoethanolamine

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Palladium nanoparticles with well controlled sizes and shape are of great scientific interest in catalysis, for example they exhibit strong catalytic activity for the organic reactions of Suzuki, Heck and Stille couplings. The palladium(II) complexes photochemical reduction is one of the promising methods for the synthesis of palladium nanoparticles, due to the possibility of controlling the process of formation of nanosized particles.

In this regard, the purpose of this work is the synthesis of photosensitive palladium(II) complexes with diamines and aminoethanol, the study of their composition and the possibility of using them as precursors in the photochemical synthesis of palladium nanoparticles both in the bulk of the photolite and on the surface of semiconductors.

Photosensitive complex compounds of palladium (II) with ethylenediamine – en, 1,2-propylenediamine – 1,2-pn, 1,3-propylenediamine – 1,3-pn, and monoethanolamine – (MEA): $[Pden_2]Cl_2$, $[Pd(1,2\text{-}pn)_2]Cl_2$, $[Pd(1,3\text{-}pn)_2]Cl_2$, $[Pden_2](BPh_4)_2$, $[Pd(1,2\text{-}pn)_2](BPh_4)_2$, $[Pd(1,3\text{-}pn)_2](BPh_4)_2$, $[PdMEA_2]$ were used as initial compounds for the palladium nanoparticles synthesis. The composition of the obtained complexes was proved by IR and NMR 1H, 13C{1H} spectroscopy.

The palladium complexes photolysis was carried out by monochromatic light from a lamp with an excitation wavelength λ_{exc} 254 nm in aqueous solutions. It is shown that irradiation of $[PdMEA_2]$ solutions for 90 minutes leads to a decrease in the optical density at 290-310 nm, which characterizes the ligand → metal charge transfer band, and an increase in its values in the visible range of the spectrum, which is more the formation of palladium particles is accompanied by a significant induction period (25 minutes). Analysis of X-ray diffraction patterns of the powder obtained by repeated centrifugation of the colloidal solution and washing of the precipitate shows the presence of low-intensity diffraction peaks at $2\theta^o$, equal to 39.94° and 46.58°, corresponding to the face-centered cubic palladium lattice. According to the results of EDX analysis of samples obtained by photochemical deposition of palladium on the surface of CeO_2 from an aqueous solution of $[PdMEA_2]$, it was revealed that the percentage of palladium varies from 1.5 to 2.5 at.%. and depends both on the duration of photolysis and on the concentration of the complex.

The replacement of monoethanolamine by diamines as ligands ($[Pden_2]Cl_2$, $[Pd(1,2\text{-}pn)_2]Cl_2$, $[Pd(1,3\text{-}pn)_2]Cl_2$) does not lead to the formation of palladium nanoparticles either in aqueous solution or on the surface of semiconductors during the same irradiation period, which is probably due to the lower donor ability of the nitrogen atom in diamines compared to oxygen in $[PdMEA_2]$.

To increase the photosensitivity of palladium(II) diamine complexes, tetraphenylborate ions were introduced into the outer sphere. We propose the following reaction mechanism:

$[Pd^{2+}en_2](BPh_4)_2 \xrightarrow{h\nu} [Pd^{+}en_2]BPh_4 + BPh_3 + Ph^{\bullet}$ (1); $Ph^{\bullet} + S \rightarrow S^{\bullet} + Ph$(2)

$S^{\bullet} + [Pd^{+}en_2]BPh_4 \rightarrow Pd^{o} + BPh_3 + 2en + S + Ph$ (3) S – solvent (alcohol, DMF, etc.)

The $[Pden_2](BPh_4)_2$ $[Pd(1,3\text{-}pn)_2](BPh_4)_2$, $[Pd(1,2\text{-}pn)_2](BPh_4)_2$ complexes photolysis in DMF during 60 minutes led to the formation of thin films on the surface of quartz without an induction period and was characterized by sufficiently high initial rate, the values of which for the above-described palladium complexes are very close. For the above complexes a decrease in the rate of formation of palladium nanoparticles by 1.6 times was observed as a result of diluting the initial solution of the complex by 2 times. The highest initial rate of nanoparticle formation is observed upon photolysis of the $[Pden_2](BPh_4)_2$ complex; it is 1.7–1.5 times higher than upon irradiation of palladium complexes with 1,2-pn and 1,3-pn.

Synthesis of deprotonated Pt(IV)-ADC complexes via MeI oxidative addition

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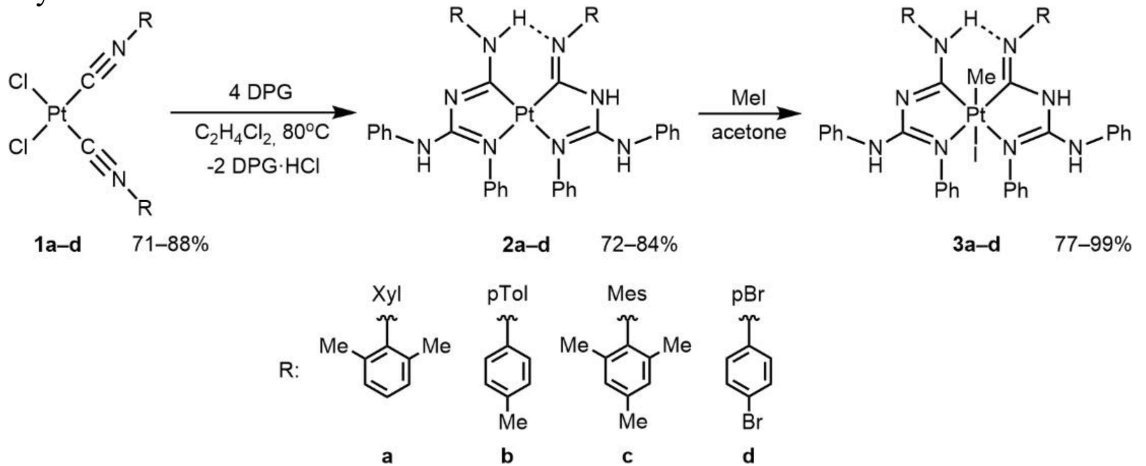
The Pt(IV) compounds, which can be activated in cancer cell by reduction to cytotoxic Pt(II), exhibit attractive properties in plenty fields of modern science In particularly, tunable ligands create opportunities for design of Pt(IV) prodrugs, while inert d^6 octahedral configuration minimizes undesirable reactions with biological molecules. Furthermore, numerous Pt transformations commence with oxidative addition/reductive elimination step which became an integral part of Pt chemistry [1].

The Pt(IV) complexes can be readily obtained under mild conditions in oxidative addition reactions of alkyl halides to Pt(II) centers [2]. In this case, cyclometalated Pt(II) complexes with deprotonated acyclic diaminocarbene ligands (ADC) are appropriate substrates for oxidative addition of MeI. These complexes exhibit square planar cyclometallated geometry and are gently obtained in metal-promoted nucleophilic addition of NH-nucleophiles to isocyanide ligands [3].

For this study, a series of deprotonated Pt(II)-ADC complexes [Pt{C(N(H)R)(NC(N(H)Ph)N(Ph)}$_2$] **2a–d** were obtained *via* the metal-mediated nucleophilic addition of 1,3-diphenilguanidine (DPG) to Pt(II) isocyanide complexes [$PtCl_2(CNR)_2$] **1a–d**. Then these species were exposed to oxidative addition of MeI in acetone at RT for *ca*. 1 h resulting in the formation of Pt(IV) complexes [PtI(Me){C(N(H)R)(NC(N(H)Ph)N(Ph)}$_2$] **3a–d** in good (77–99%) isolated yields.



The resulting species were isolated and characterized by ESI-MS$^+$, NMR (^{1}H, ^{13}C{^{1}H}, ^{195}Pt{^{1}H}) and IR spectroscopies and by X-ray diffraction.

This work was supported by the Russian Science Foundation (grant № 21-73-10083) and performed using the equipment of the SPbU Resource Centers: Center for Magnetic Resonance, Center for X-ray Diffraction Studies and Center for Chemical Analysis and Materials Research

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A new approach to design of the biocompatible luminescent rhenium(I) compounds

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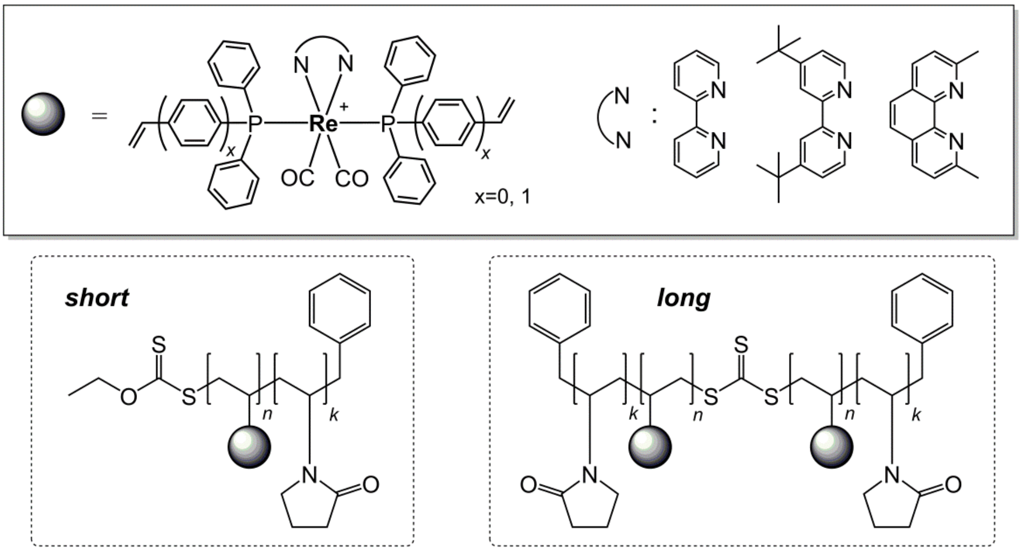
The current enormous interest in exploiting transition metal complexes as emitters stems from their various application prospects in life science and technology areas [1]. Development of novel complexes with efficient luminescence and good biocompatibility for diagnostics and therapy becomes challenging and meaningful [2]. Carbonyl rhenium(I) complexes are among the most fascinating candidates for luminescent materials suitable for biomedical applications [3].

The research presented herein relies on the incorporation of the auxiliary phosphine ligands with the alkenyl groups into the highly emissive rhenium-based core $\{Re(CO)_2(NN)\}$ (Scheme 1, top), with an aim to attain the desired physico-chemical and optical properties.



Scheme 1. Top: the family of the novel rhenium(I) complexes with the alkenyl groups. Bottom: two types of the polymers with different chain lengths containing the rhenium(I) fragments.

The presence of the vinyl or styrene functions allows the rhenium(I) complexes to be polymerized with the formation of the water-soluble, remarkable stable, low toxic luminescent polymers (Scheme 1, bottom).

This work has been supported by the Russian Presidential scholarship № СП-2466.2022.4

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Interactions of cyclometalated iridium(III) complexes with iodine

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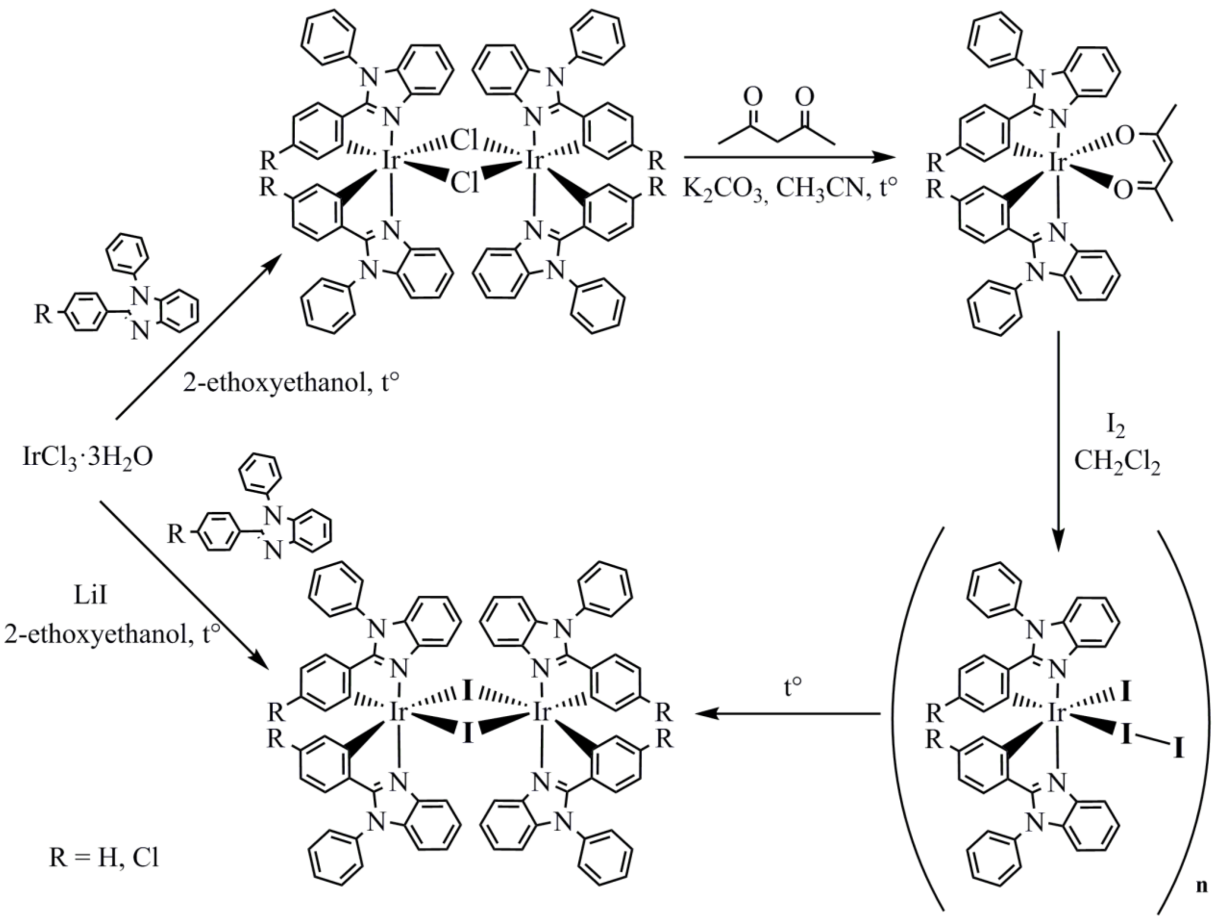
Octahedral *bis*-cyclometalated iridium(III) complexes with ancillary β-diketonate ligands are chemically stable and possess high phosphorescence quantum yields, which determine their application in light-emitting diodes, photodynamic therapy, bioimaging, and as photosensitizing dyes in solar cells. During the operation of the solar cell the iridium dye contacts with an iodine-containing mediator (redox pair I_3^-/I^-), so it is important to understand the nature of these interactions.

This work aims to study in detail the interactions of β-diketonate cyclometalated iridium(III) complexes with various iodine species. Two 1,2-diphenylbenzimidazole-based iridium(III) complexes with acetylacetone were chosen as model compounds, synthesized and characterized. It was shown that both model complexes underwent a quantitative iodine-induced transformation accompanied by the detachment of the diketonate with the formation of either a unique 1D coordination polymer or a dimeric complex with bridging iodine atoms (Scheme); the compounds were characterized by ^1H, ^{13}C NMR, powder and single-crystal XRD, TGA/DSC.



Solvent-induced solid-state transformation of 1D zigzag chains based on clusters of sulfonylcalix[4]arene

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The design, synthesis and study of new supramolecular metal-organic assemblies still attracts a growing interest due to their unique functional properties derived from their electronic and geometrical structure [1]. Many discrete complexes and coordination polymers (CPs) exhibiting the single molecule magnetism, luminescence and adsorption properties are described in the literature [2-4].

(Thia)calix[4]arenes and tetrasulfonylcalix[4]arenes are macrocyclic compounds, possessing of a pre-organized coordination cavities, are especially suitable for the formation of a large variety of coordination compounds in the crystalline phase with adjustable supramolecular architecture and specific functions [5].

In this work three 1D zigzag coordination polymers (CPs) were generated using sulfonylcalix[4]arene, metal M^{2+} cations (M = Co or Zn) and rigid planar N-shaped linkers (stilbene-4,4'-dicarboxylic acid or azobenzene-4,4-dicarboxylic acid) by solvothermal synthesis.

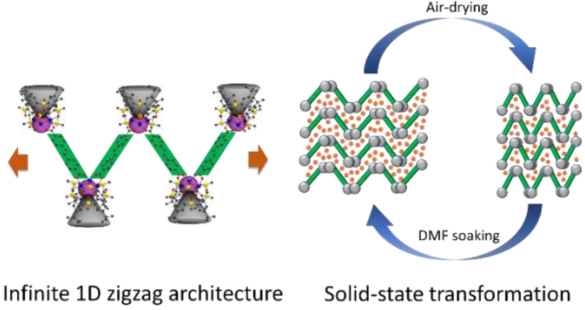

Figure 1. Geometry and solid-state transformation of CPs.

The structure of obtained coordination compounds was studied using X-ray diffraction methods (XRD and PXRD) and it was shown that flexibility of crystal packing of the formed infinite zigzag chains allowed to observe dynamic reversible solid-state transformation upon the release/uptake of solvent DMSO molecules (Fig. 1).

This work was supported by the Russian Science Foundation (grant № 19-73-20035)

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Structural features of volatile fluorinated magnesium complexes based on β-diketonates and neutral N^N-ligands

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Volatile fluorinated magnesium complexes are of interest as precursors in chemical vapor deposition (MOCVD) and related technologies. Effective design of such compounds requires an understanding of the effect of the ligands on the structure and thermal properties of the complexes.

Following this idea, we have perfomed here a systematic study of the structure of a promising class of volatile magnesium precursors based on fluorinated β-diketonates (RC(O)CHC(O)R') ensuring the stability and bidentate N^N-ligands ensuring the formation of mononuclear molecular complexes as the most volatile. The studied series included the model complex [Mg(tmeda)(hfac)$_2$] (R = R' = CF$_3$, tmeda = N,N,N'N'-tetramethylethylenediamine) and related compounds varying:

(1) neutral ligands: [Mg(Q)(hfac)$_2$], Q = tmpda (N,N,N'N'- tetramethylpropylenediamine), phen (1,10-phenanthroline), and bipy (2,2'-bipyridine);

(2) terminal groups in β-diketonates: [Mg(tmeda)(L)$_2$], R = CF$_3$, R' = CH$_3$ (tfac), C(CH$_3$)$_3$ (ptac), C$_6$H$_5$ (btfac), R = C$_2$F$_5$, R' = CH$_3$ (pfpac).

The structures of six studied complexes were established by single-crystal XRD for the first time, including new ones (L = pfpac, btfac or Q = tmpda). The formation of polymorphic modifications was shown for the β-diketonates contained a methyl group (L = tfac, pfpac).

In all the complexes, magnesium in a slightly distorted coordination environment. The geometric parameters of these octahedrons are similar, except for the NMgN angle, which is determined by the neutral ligand (phen/bipy < tmeda < tmpda). The greatest deviations of the conjugated metallocycle from the plane appear in crystals of complexes with aromatic ligands (phen/bipy) due to the presence of stacking contacts. A noticeable deformation of the metallocycle is also caused by the introduction of a ^{t}Bu or Ph group into the β-diketonate ligand.

Intermolecular contacts were visualized using Hirschfeld surface analysis (Crystal Explorer, Tonto). The structure of the model [Mg(tmeda)(hfac)$_2$] complex contains shortened "antibonding" F…F contacts. The growth of the diamine carbon bridge (tmpda) or the transition to aromatic neutral ligands (phen/bipy) lead to the appearance of "bonding" interactions: weak C–F…H contacts and stacking (only phen/bipy). When the CF$_3$ group in β-diketonate is replaced by C(CH$_3$)$_3$ (L = ptac), the F…F contacts are lost, while in the case of C$_6$H$_5$ (L = btfac), the C–F…H contacts appear additionally. The effect of introducing a CH$_3$ (L = tfac) group is ambiguous due to polymorphs where two type of contacts (F…F + C–F…H) or the absence of close contacts are observed. An increase in the fluorinated group (L = pfpac, 1C$_2$F$_5$ vs. hfac, 2CF$_3$) leads to an increase in the number of F…F contacts per molecule and to the appearance of C–F…H contacts.

The crystal lattice energies were calculated using the CrystalExplorer program using the "cluster" approach and the B3LYP/6-31G(d,p) basis. The highest values are achieved for the complexes with aromatic fragments, even in the absence of stacking interactions (L = btfac).

This work was supported by the Russian Scientific Foundation (project № 21-73-00252)

Novel lanthanide complexes with 2-quinolinecarboxylic acid: structural variety, magnetism and thermolysis

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The study of rare earth carboxylates remains an essential part of the coordination chemistry of these metals [1]. One of the common problems in the synthesis of lanthanide carboxylates is the insolubility of the resulting product, which complicates the formation of well-formed crystals or even of a single-phase product. In order to provide the homogeneity of the reaction media, the hydrothermal method is often used. However, it requires the use of special equipment, high temperature, and pressure. Earlier, we have obtained crystalline rare earth carboxylates under mild conditions, and the homogeneity of the reaction medium was achieved by using aqueous-organic mixtures, the organic component of which was slowly evaporating at room temperature [2]. Due to this, the growth of the crystals proceeded under conditions close to equilibrium.

By means of reaction of lanthanide chlorides with 2-quinolinecarboxylic acid (HQA) in an aqueous-organic medium in the presence of pyridine (py), under conditions of slow evaporation of the reaction medium, the following complexes were obtained: the known binuclear one $[Nd_2(QA)_6(H_2O)_6]\cdot 3H_2O$ (**1**) [3], the novel unusual complexes built of binuclear cationic and mononuclear anionic moieties $[Ln_2(QA)_4(H_2O)_4]^{2+}[Ln(QA)_4(H_2O)]^{-}{}_2\cdot 2EtOH\cdot 6H_2O$ (Ln = Gd (**2**), Dy (**3**), Er (**4**), Yb (**5**); Figure 1), and the new anionic mononuclear complex, $[Hpy_2]^{+}[Er(QA)_4]^{-}\cdot 4H_2O$ (**6**). The complexes **2**-**5** were characterized by dc and ac magnetic measurements.

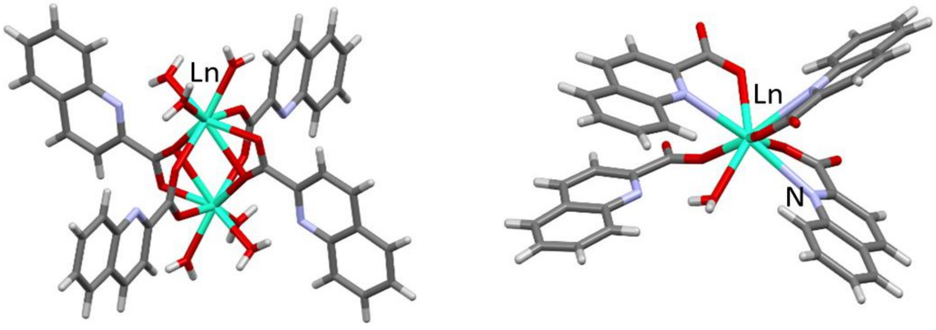

Figure 1. The structure of the complexes **2**-**5** (left: the cationic moiety; right: the anionic part).

The magnetic properties of complexes **2**-**5**, in particular, their ability to serve as single-molecule magnets, as well as their thermal stability, are discussed.

This work was supported by the Russian Science Foundation (grant no. 22-23-00574)

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Extraction-spectrophotometric determination of cobalt(II) with 5-(2-bromo-5-methoxyphenyl)-2,4-thiazolidinedione

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We have studied the possibility of using 5-(2-bromo-5-methoxyphenyl)-2,4-thiazolidinedione (L) for the photometric determination of cobalt(II). Cobalt(II) with 5-(2-bromo-5-methoxyphenyl)-2,4-thiazolidine-2,4-dione forms a colored complex, which dissolves well in non-polar organic solvents. The best extractants were chloroform, dichloroethane and carbon tetrachloride. With a single extraction with chloroform, 99.4% of cobalt is recovered in the form of a complex.

The cobalt(II) complex is extracted into chloroform in the pH range 6.4-7.2. Extraction decreases both with decreasing and with increasing pH of the aqueous phase. The yield of the complex is maximum at a concentration of 8.0×10^{-4} mol/l R. The complex of cobalt with R is stable in aqueous and organic solvents and does not decompose for two days, and after extraction for more than a month.

The maximum optical density is reached within 5 minutes. The complex is stable when heated to 80°C. The maximum analytical signal during the complexation of cobalt with L is observed at 522 nm. The molar absorption coefficient is 2.05×10^4.

The disappearance of a pronounced band at 3280 cm^{-1} in the spectra of the Co(II)-R complex means that the -NH- group is involved in the formation of the complex. The shift of the band at 1690 cm^{-1} to the short-frequency region (1665 cm^{-1}) indicates the participation of the C=O group in the formation of a coordination bond with the Co(II) ion.

The stoichiometry of the studied complex was determined by the methods of equilibrium shift, relative yield, and straight line. All methods showed that the ratio of components in the complex is 1:2.

It was established by the Nazarenko method that Co^{2+} is the complexing form of cobalt. In this case, the number of hydrogen atoms displaced by it from one R molecule turned out to be equal to 1. The results of EPR studies showed that the complex in the organic phase is in the monomeric form.

The extract of the cobalt complex obeys the basic law of light absorption at a concentration of 0.4 - 14 μg/ml. The data obtained for the construction of the calibration graph were processed by the least squares method. The calibration curve equation is $y=0.055+0.0668x$. Based on the calibration curve equation, the limit of photometric detection (0.018 $\mu g/cm^3$) and the limit of quantitative determination of cobalt (0.062 $\mu g/cm^3$) were calculated.

It was found that Fe(III), V(IV), Cu(II), Ni(II) , Mo(VI), Pt(II), Pd(II) and ions also form colored complexes with L. The selectivity of the determination increases significantly in the presence of masking reagents or when the pH of the medium changes.

Based on the results of a spectrophotometric study of cobalt(II) with L, methods have been developed for the determination of cobalt in various natural and industrial objects.

Study of the interaction of copper(II) with 2,6-dithiol-4-methylphenol and heterocyclic diamines

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This work is devoted to studying the interaction of copper(II) with 2,6-dithiol-4-methylphenol (DTMP) in the presence of heterocyclic diamines (Am). Of the heterocyclic diamines, phenanthroline (Phen), bathophenanthroline (BPhen) and 2,2'-dipyridyl (Dip) were used. DTMP form colored complexes with copper, which are insoluble in nonpolar organic solvents. With a single extraction with chloroform, 98.2-98.8% of copper(II) is extracted in the form of mixed-ligand complex (MLC). The optimal acidity range, at which the optical density is maximum and constant, is at pH 5.8-8.5. The optimal conditions for the formation and extraction of these compounds are $0.8\cdot10^{-3}$ mol/l and $1.0\cdot10^{-3}$ mol/l concentrations of DTMP and Am, respectively. MLC of copper with DTMP and Am are stable in aqueous and organic solvents and do not decompose within three days, and after extraction - more than a month. The maximum optical density is reached within 5 minutes.

The maximum analytical signal during the complexation of copper with dithiophenols and Am is observed at 629–640 nm. The molar absorption coefficients are $(3.28\text{-}4.82)\times10^4$. The ratio of components in MLC is Cu : DTMP : Am = 1:1:1. The complexing form of copper is Cu^{2+}. The number of protons displaced by Cu^{2+} from one dithiolphenol molecule turned out to be 1. The disappearance of a pronounced band at 2580 cm^{-1} observed in the spectrum of DTMP and the appearance in the IR spectra of the complex of two absorption bands, one of which is shifted towards lower frequencies, indicates that one of the –SH groups is involved in the formation of the complex. The disappearance of the absorption band in the region of 3200-3600 cm^{-1} with a maximum at 3460 cm^{-1} shows that the hydroxyl group takes part in the formation of a bond with the metal. The detection of absorption bands at 1370 cm^{-1} indicates the presence of coordinated phenanthroline.

A thermogravimetric study of the Cu(DTMP)Phen complex showed that its thermal decomposition proceeds in three stages: at 60–120°C, water escapes (mass loss 4.16%), at 340–390°C, Phen decomposes (mass loss 41.7%), and at 490-510ºC-DTMP (weight loss 39.35%). The final product of thermolysis of the complex is CuO. A single crystal of the complex with DTMP and Phen was studied by X-ray diffraction analysis. The complex is monomeric and the central atom is coordinated by 5 donor atoms. The donor environment of copper in the complex under study consists of 2 nitrogen atoms, 2 oxygen atoms, and a sulfur atom (CuN_2O_2S). According to XRD data, the coordination polyhedron of the central copper atom has the shape of a distorted square pyramid. Based on the equations of the calibration curves, the limit of photometric detection and the limit of quantitative determination of copper in the form of mixed ligand complexes were calculated.

Highly sensitive, selective techniques for the extraction-photometric determination of copper have been developed. The methods were applied to determine copper in food products: beans, wheat bran, gelatin, as well as in steels of various grades.

Study of the interaction of vanadium(IV) with dimercaptophenols in the presence of heterocyclic diamines

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The real work is devoted to studying of reaction of a complex formation of vanadium(IV) with 2,6-dimercaptophenol (DMP), 2,6-dimercapto-4-methylphenol (DMMP) and 2,6-mercapto-4-ethylphenol (DMEP) in the presence of hydrophobic amines (Am). As hydrophobic amine 1,10-phenantroline (Phen) and batophenantroline (BPhen) were used. V(IV) reacts with DP gives a bluish green colored complexes. These complexes are insoluble in non-polar solvents. When hidrophob amins were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. It was found that the spectrophotometric characteristics of the MLC of vanadium(IV) and vanadium(V) were identica, i.e., in the interaction with DP, V(V) was reduced to V(IV) and VO^{2+} was the complex producing form. This fact was also confirmed by EPR spectrometry. The absorbance was found to be maximum in the pH range 5.0-7.9. V(IV) reacts with DP and gives a blue colored complexes. These complexes are in soluble in non-polar solvents. When hidrophob amins were introduced into the system, the extraction of these compounds into the organic phase as a MLC was observed. Chloroform was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. After a single extraction with chloroform, 98.6-99.5% of vanadium was extracted as an mixed-ligand complex.

V(IV)-DP-Am complexes has maximum absorbance at 610-630 nm. The molar coefficient of light absorption is $(2.95\text{-}3.85)\times10^{4}$ L mol^{-1} cm^{-1}. For the formation of mixed-ligand complex V(IV-DP-Am, the concentration of 1.0×10^{-3} M of DP and 8.0×10^{-4} M of Am in the solution is required. Unlike single-ligand complexes, mixed-ligand complexes of vanadium(IV,V) with DP and Am were stable in aqueous and organic solvents and did not decompose for 48 hours, or over a month after extraction. The ratio of components in the complex corresponds to V(IV) : DP : Am = 1:1:1. It was found using the Nazarenko method that V(IV) in the complexes was present in the form of VO^{2+}.

İn IR spectra of the metal complexes the disappearance of the pronounced absorption bands in the 3250-3620 cm^{-1} with a maximum at 3475 cm^{-1} observed in the spectrum of DMMP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2570 sm^{-1} shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1380 cm^{-1} indicates the presence of a coordinated phenantroline.

^{1}H NMR spectra of the complex (for V(V)) were recorded in $CDCl_3$. In the spectrum of the singlet complex at 1.25 ppm refers to the protons of the methyl group. The signal intensity observed at 3.28 ppm associated with the mercapto group –SH is halved and is somewhat shifted to a stronger field (3.41 ppm). This confirms that one mercapto group is involved in complexation. The singlet observed in the spectrum of the DMMP ligand at 5.48 ppm associated with the -OH phenol group disappears. This clearly indicates that the -OH group is involved in complexation. Doublet at 7.28 ppm caused by aromatic protons of the benzene ring DMMP (2H). Multiplet in the area of 7.61-8.95 ppm (8H; aromatic protons) is associated with the protons of the aromatic ring of phenanthroline.

Thermogravimetric study of the complex V(IV)-DMEP-Phen shows that the rapid expansion of the complex starts at 480°C. wherein the mass loss of 49.1% (calculated 49.7 %), which corresponds to the removal phenanthroline. At 510-650 °C stands DMEP mass loss of 39.1% (calculated 39.7%). Further, when heated to 675°C formed V_2O_5.

The stability constant of V(IV)-DP-Am complexes was calculated by method of crossing of curves and found to be $\lg\beta = 9.58\text{-}10.95$ at room temperature. Sandell's sensitivity: 1.3-1.7 ng cm^{-2}.
A calibration graph drawn between absorbance and the metal ion concentration indicates that V(IV) can be determined in the concentration range 0.2 to 18.0 μg mL^{-1}. The proposed method has been applied for the determination of vanadium(IV) in plants, water and soil samples.

Features of solid state synthesis of Dion-Jacobson phases $ABi_2Ti_2NbO_{10}$ ($A=K^+$, Rb^+) and their properties

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Dion-Jacobson phases are layered perovskite-like compounds with general formula $A'[A_{m-1}B_mO_{3m+1}]$, where A' is A^+, A is A^{2+} or A^{3+}, B is a transition metal ion, and $m = 2÷6$ indicates the number of layers within the perovskite-like block. A layer of alkali metal cations is placed between blocks in the structure of these compounds. Layered perovskites have a wide range of applications including photocatalysis, solar cells, storage devices, sensors, thermal detectors, phosphors and semiconductors [1, 2].

The most convenient method to obtain layered perovskite-like compounds is solid state synthesis due to its simplicity. It is noted that the initial components containing alkali metal ions (usually nitrates, carbonates or oxalates) are taken in excess 25–50%, that is associated with the volatilization of the components [3-5]. Then these samples can be used in ion exchange reactions to obtain new compounds with various properties that are important for application in modern industry [6].

Samples $ABi_2Ti_2NbO_{10}$ ($A=K^+$, Rb^+) were obtained by standard ceramic technology in three stages (T_1=800°C, T_2=900°C, T_3=1000°C). Rubidium nitrate, potassium carbonate, and bismuth(III), titanium(IV) and niobium(V) oxides were selected as initial compounds.

According to XRD results, it was revealed that the 50% excess of potassium carbonate significantly affects the formation of single-phase $KBi_2Ti_2NbO_{10}$ with the Dion-Jacobson structure. By using the over stoichiometric amount of initial potassium carbonate, the target layered perovskite-like compound was already obtained at T_2=900°C. Increasing the heat treatment temperature (T_3=1000°C) is accompanied by densification of ceramic but does not change the phase composition. While the introduction of a stoichiometric quantity of K_2CO_3, leads to the pyrochlore phase formation at T_2 = 900°C. This phase is fixed as the main one in the sample at all following stages of synthesis.

Phase formation of $RbBi_2Ti_2NbO_{10}$ does not depend on the excess of initial rubidium nitrate. Single phase samples with layered perovskite-like structure were obtained at T_2=900°C by using both stoichiometric amount and excess of rubidium nitrate. In the last case the increase in the density of $RbBi_2Ti_2NbO_{10}$ ceramics were revealed.

The samples with the Dion-Jacobson structure have an orthorhombic distortion of the unit cell, while the sample with the pyrochlore structure is cubic.

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Nanocomposites of copper, nickel, and cobalt trimesinates with graphene oxide as sorbents for the solid-phase extraction of organic dyes

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In recent decades, the attention of scientists has been focused on a class of polyfunctional materials called organometallic frameworks (MOFs), which can be used as solid-state adsorbents for organic dyes [1]. They are characterized by a high chemical resistance and a significant specific internal surface, hundreds of times higher than carbon materials (up to 10,000 m^2/g). However, MOFs have some limitations associated with low selectivity, easily lose their adsorption activity in a humid atmosphere, and are poorly amenable to postsynthetic functionalization. To expand the practical application of MOFs, a promising direction is the creation of their composites with other materials, in particular with graphene oxide (GO), which makes it possible to obtain polyfunctional materials with improved technological properties. Nanocomposites, in addition to the physical sorption provided by the network structure of MOFs, can retain adsorbate molecules through chemisorption processes. In these materials, separated and functionalized graphene sheets will increase dispersion interactions, and MOFs will increase their pore space in which adsorbates can be stored [2].

The aim of this work was to obtain nanocomposite materials based on copper, nickel, or cobalt trimesinates and GO and to study the possibilities of such a material for solid-phase extraction of organic dyes. The objectives of the study were the synthesis of hybrid composite materials based on metal trimesinates and GO, the selection of the MOF:GO ratio to obtain the most effective material, the study of the ability of the obtained materials for solid-phase extraction of model pollutants, and the study of the influence of various variables (pH, initial dye concentration, temperature and contact time) on the process of solid-phase extraction.

Nanocomposites based on GO and copper, nickel, or cobalt trimesinates were obtained by the *in situ* method. The samples have permanent porosity and a microporous structure with a large surface area corresponding to adsorption type I. The study of the adsorption properties of the obtained composites with respect to organic dyes (malachite green, indigo carmine, brilliant green, Bengal rose, crystal violet) showed that adsorption largely depends on the content of GO in the composites. The complexes are effective sorbents for the extraction of cationic and neutral organic dyes when the content of GO in the nanocomposite is 20% of the calculated metal trimesinates due to electrostatic forces of interaction. For anionic dyes, the maximum adsorption is achieved when using a composite containing 5% GO due to the predominance of physical sorption. Experimental results show that the obtained sorbents can be used for extraction in a wide pH range, which indicates the excellent pH window offered by this adsorbent. The kinetic data were properly fitted to the pseudo-second-order model. The equilibrium data correlated best with the Freundlich model. The process was endothermic and spontaneous in nature. The composites make it possible to achieve a maximum sorption of 393 mg/g, which is a sufficiently high value for the absorption of dyes.

This work was supported by the Russian Science Foundation (grant № 22-13-00260)

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Kinetics of extraction of molybden-containing components from the worked hydrotreatment catalyst by HNO_3 and Na_2CO_3 containing solutions

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Despite the periodic regeneration, the life of the hydrotreating catalysts is short. In the technological process, catalysts are used that represent a system of oxide compounds of molybdenum, cobalt or nickel deposited on an alumina support. After a certain time, the activity of the components decreases and spent catalysts that cannot be restored usually become toxic waste. According to various researchers, the highest degree of extraction of molybdenum by the hydrometallurgical method reaches from 80 to 95%. For "wet" leaching, inorganic strong acids, aqueous solutions of ammonia or soda ash are used. However, the literature provides conflicting information on the carbonate extraction of molybdenum.

In this investigation the study of the leaching kinetics of the Mo-containing catalyst was carried out with solutions of nitric acid and sodium carbonate under isothermal conditions by sampling. Based on the results of the experimental data, the fraction of dissolved molybdenum trioxide MoO_3 (α) was calculated according to the equation:

$$\alpha = \frac{C_1 \cdot V}{m \cdot C} \qquad (1)$$

C_1 – concentration of molybdenum (VI) in solution; V – volume of solution in the reactor, cm^3; m – weight of the spent catalyst, g; C – metal content in the spent catalyst, wt. fraction.

The experimental data were presented in the form of the dependence of the degree of conversion of the solute (α) on time (τ) $\alpha = f(\tau)$ and described by the equation of the chain mechanism. This equation takes into account the formation of active centers (crystal lattice defects) on the surface of particles during dissolution (Fig. 1 (a; b)):

$$\alpha = 1 - \exp(- A \cdot \mathrm{sh}(W_i \cdot \tau) \qquad (2)$$

α – the proportion of dissolved molybdenum (VI) oxide; A – a constant proportional to the average number of active centers (the number of crystal lattice defects) on the surface of one particle of the spent catalyst; W_i – dissolution rate constant, min^{-1}; τ – time, min.

The results of processing the experimental data according to equation (2) are presented in Table 1, which shows the values of the constant dissolution rate W_i.

Table 1

The rate constant of dissolution (W_i) in solutions of nitric acid and sodium carbonate, calculated according to equation (2), A = 5

T, K	C (HNO_3), mol / l	W_i, min^{-1}	C (Na_2CO_3), mol / l	W_i, min^{-1}
338	1,67	0,005	0,498	0,0070
	3,54	0,008	1,064	0,0070
	5,62	0,010	1,658	0,0075
368	1,67	0,010	0,498	0,0130
	3,54	0,010	1,064	0,0380
	5,62	0,019	1,658	0,0880

Based on the experimental results obtained on the solubility of molybdenum (VI) oxide in solutions with different pH values and kinetic data, the conclusion was clarified that in alkaline media, in comparison with acidic media, the dissolution of molybdenum (VI) oxide occurs deeper at lower concentrations of reagents.

This publication was supported by the RUDN University Strategic Academic Leadership Program

Synthesis, crystal structure, and Hirshfeld surface analysis of new imidazole-containing Tc(V) complexes

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Organic Tc(V) complexes are used in nuclear medicine as ^{99m}Tc radiopharmaceuticals. In the present work, a number of new Tc(V) compounds with imidazole (Im) and methylimidazole (MeIm) were prepared. The synthesis was carried out by dissolving thiourea, imidazole (methylimidazole) in methanol with the addition of concentrated HCl (HBr) and $HTcO_4$ to the resulting solution. The solutions, first deep red and pink after 5 hours, were left at room temperature until crystals formed. X-ray diffraction study of crystals at 100 K was carried out.

Crystallographic data:
$[TcO_2Im_4]Br\cdot 2H_2O$ (**I**): $a = 13.0113(11)$, $b = 11.3064(9)$, $c = 14.2554(16)$ Å, $\beta = 114.312(4)°$, $Z = 4$, sp. gr. *Cc*, $R1 = 0.0223$;
$[TcO_2(MeIm)_4]Cl\cdot 2H_2O$ (**II**): $a = 8.2324(7)$, $b = 9.4890(8)$, $c = 15.2946(13)$ Å, $\alpha = 107.160(3)$, $\beta = 95.947(3)$, $\gamma = 96.731(3)$ °, $Z = 2$, sp. gr. *P*-1, $R1 = 0.0487$;
$[TcO_2(MeIm)_4]TcO_4$ (**III**): $a = 14.8088(9)$, $b = 13.1343(8)$, $c = 12.9484(8)$ Å, $\beta = 115.911(2)°$, $Z = 4$, sp. gr. *C2/c*, $R1 = 0.0320$.

All compounds contain $[TcO_2L_4]^+$ cationic complexes, in which the Im (MeIm) molecules are coordinated to the Tc atom by the N atom. In the case of MeIm, the average Tc–N distances (2.134–2.136 Å) are somewhat longer than those with Im (2.130 Å). The Tc=O distances in the complexes vary from 1.743 to 1.763 Å. These small bond elongations may be due to the different participation of the complexes in the hydrogen bond system. There is a π-stacking interaction in **I** and **II**. The crystal packing in all complexes can be represented as layered, where the molecules of the complexes form layers, between which there are molecules of anions and water. The $[TcO_2Im_4]Cl\ 2H_2O$ structure described earlier [1] in the centrosymmetric space group C2/c with disordering of the chloride ion and water molecules is, in fact, probably not centrosymmetric and similar to **I**. In the future, we plan to prove this.

An analysis of the nonvalent interactions of the obtained complexes showed that the main contribution to the crystal packing is made by van der Waals interactions of the type H···H (42.5–55.1%) and H···C/C···H (17.7–21.3%). A significant contribution to intermolecular interactions is made by hydrogen bonds, which are responsible for contacts of the O···H/H···O and Hal···H/H···Hal types, which contribute 15.7–25.3% in total.

This work was supported by the RUDN University Strategic Academic Leadership Program and by the Ministry of Science and Higher Education of the Russian Federation (program no. 122011300061-3)

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Synthesis of platinum-based heterometallic complexes and their thermal transformation

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Study and chemical modification of heterometallic coordination compounds of platinum and precious metals in general are of interest due to the potential application of the obtained compounds as precursors of supported catalysts. Previously the possibility of synthesizing ferrocenecarboxylate complexes of platinum [1] and palladium [2] was shown.

A new approach has been developed for the synthesis of chlorine-free platinum-based complexes *via* platinum(II) tetrapyridine using potassium tetrachloroplatinite $K_2[PtCl_4]$ as starting compound by precipitation of the intermediate – *cis*-$[PtPy_2](Cl)_2$, substitution of chloride anion by pyridine ligands, and subsequent exchange of chloride anions for acetate anions to obtain cation–anion complexes [1]. The interaction of acetate complexes with ferrocenecarboxylic acid under various conditions yielded to a number of heterometallic structures with different coordination type of ferrocenecarboxylate anions (Fig. 1, Fig. 2).

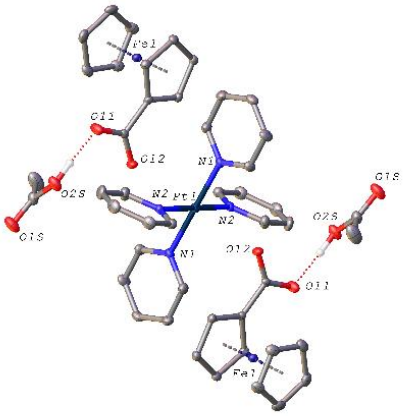

Fig. 1 – Molecular structure $[PtPy_4](FcCOO)_2 \cdot 2MeCOOH$

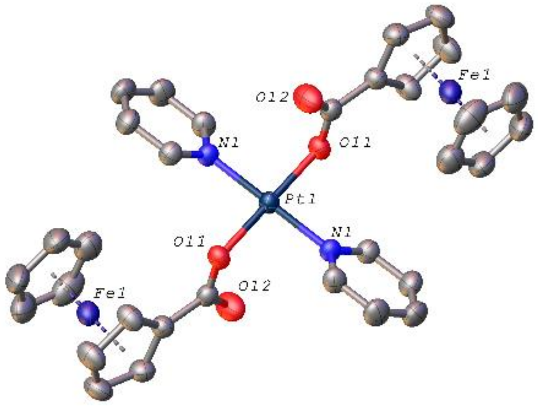

Fig. 2 – Molecular structure *trans*-$[PtPy_2(FcCOO)_2]$

This study was supported by the Russian Science Foundation (project № 18-73-10206-P)

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Binuclear Cu(II) complex as an efficient photocatalyst for N-alkylation of aromatic amines

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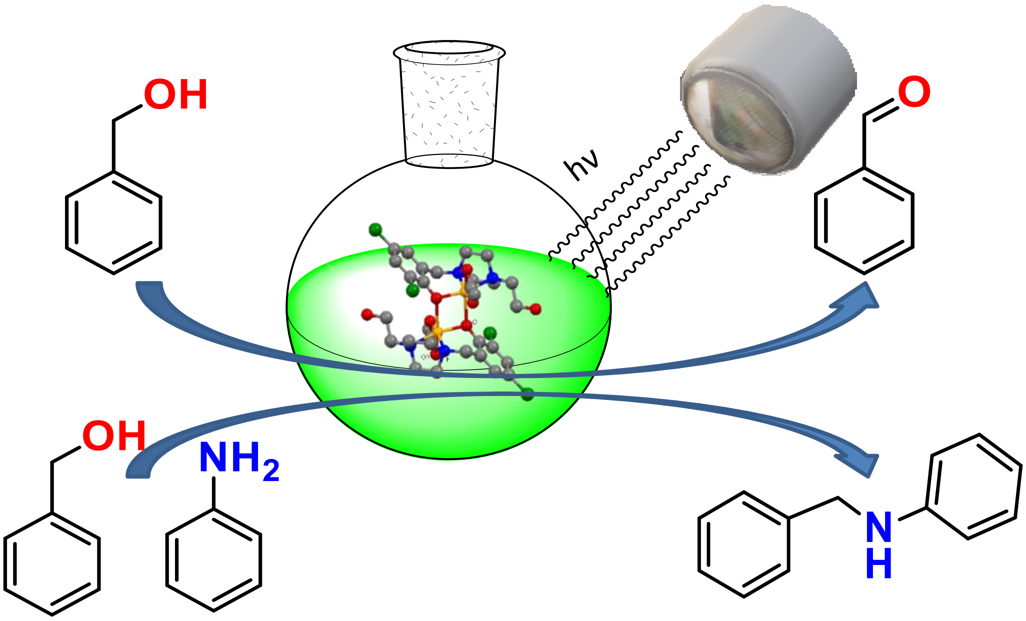
Visible-light driven photoreactions using transition metal complexes as catalysts are currently a research hotspot in developing environmentally friendly sustainable processes. To develop potential copper-based photo-catalyst, a binuclear Cu(II) complex has been synthesized by using a Mannich base ligand viz. 2,4-dichloro-6-((4-(2-hydroxyethyl)piperazin-1-yl)methyl)phenol (**H_2L**). The photo-catalyst has been characterized by ESI-MS and single crystal X-ray diffraction. Under the irradiation of visible light, the catalyst can catalyze the hydrogen auto-transfer in N-alkylated amine formation and benzyl alcohols oxidation reactions with excellent conversion. A plausible mechanistic pathway for catalytic reactions has been explored through ESI-MS spectrometric, UV-Vis spectroscopic study and computational study.



Structural evaluation of the complex of copper(II) acetate with (4-aminobenzo-15-crown-5)-4-pyridinecarboxalimine

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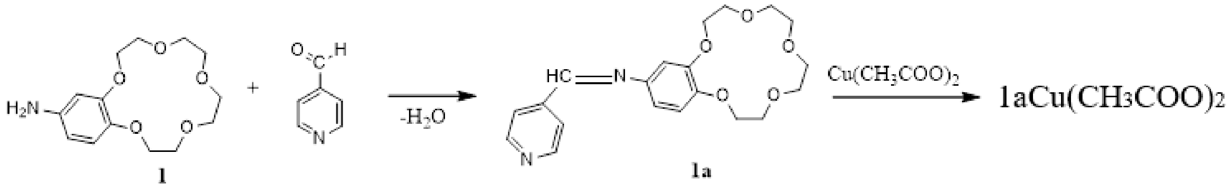
X-ray diffraction analysis is not always possible due to precipitation of an amorphous powder. In this regard, the prediction of the existence of a particular structure can be estimated using the methods of quantum chemistry. This work is devoted to studying and predicting the geometry of the synthesized compounds and assessing the fundamental possibility of forming copper complexes of azomethine derivatives.

We synthesized new Schiff bases by the condensation of 4-pyridinecarboxaldehyde. The copper complex was obtained by adding an equimolar amount of copper (II) acetate to the corresponding azomethine.



At the first stage, the comparative thermodynamic stability of structures with different coordination of the crown ether ligand on the copper atom was estimated. The evaluation was carried out with respect to the total free energy of (4-aminobenzo-15-crown-5)-4-pyridinecarboxalimine (substance 1a) and monomeric copper (II) acetate $Cu(AcO)_2$.

The calculation was carried out by the DFT method in the Priroda 20 program with the PBE exchange-correlation functional and the 3z basis. We also calculated the structures of dimeric copper complexes with bridging acetate ligands and molecules 1a, $(1a)_2[Cu_2(\mu\text{-}AcO)_4]$ apically coordinated through the pyridine fragment, and with the same ligands, but coordinated through the imine nitrogen atom, $(1a')_2[Cu_2(\mu\text{-}AcO)_4]$, as well as a complex with ligands 1a with mixed coordination $(1a)(1a')[Cu_2(\mu\text{-}AcO)_4]$. The singlet and triplet ground states of these complexes were also studied.

Analytical research was done using equipment of NRC "Kurchatov Institute" — IREA Shared Knowledge Center under project's financial support by the Russian Federation, represented by The Ministry of Science and Higher Education of the Russian Federation, Agreement No. 075-11-2021-070 dd. 19.08.2021

π-Stabilized *bis*-ylide organophosphorus (V) ligands for organometallic chemistry

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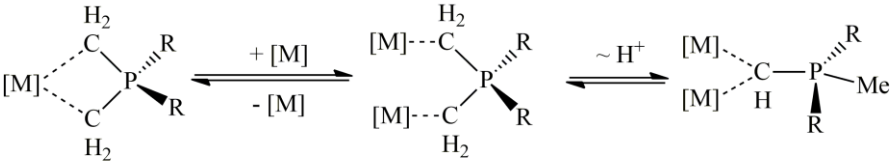
Coordination chemistry of organophosphorus(V) ylides is one of the most studied areas of organometallic chemistry [1]. For the first time this class of compounds was fobtained by Staudinger [2] in the 1920s, and later was developed by Wittig and colleagues [3, 4] in the 1940s and 1950s [5]. Since the 1970s, many types *bis*-ylide ligands have been studied in metal complexing. Initially, *bis*-ylide ligands are considered as 2e-donor chelate systems.

The coordination of *bis*-ylide ligands with metals depends not only on the metal itself (oxidation state, ion size), but also on intermolecular and intramolecular prototropic and metallotropic exchange processes. Thus, three main coordination types can be distinguished: chelate (**A**), μ^1-bridged (**B**) and μ^2-bridged (**C**).



A **B** **C**

However, if electronic density of the ylide carbanion is delocalized by conjugation with π-electron system, the stability of both ylide ligands and the organometallic complexes therefrom can be enhanced. Thus, for example, by replacing of the (CH_2)-group(s) with Cp-, Ind- or Flu-groups, various η-coordination metal-to-ligand modes can be wan leading to an increase in the π-donor ability of ligands and stability of corresponding metal complexes.

$R_2P(X)Y$	**(CH_2)**	**[CHR]**	**{Cp}**	**(Ind)**	**(Flu)**
(CH_2)	$R_2P(CH_2)_2$	$R_2P[CHR]CH_2$	$R_2P\{Cp\}CH_2$	$R_2P(Ind)CH_2$	$R_2P(Flu)CH_2$
[CHR]		$R_2P[CHR]_2$	$R_2P\{Cp\}CHR$	$R_2P(Ind)CHR$	$R_2P(Flu)CHR$
{Cp}			$R_2P\{Cp\}_2$	$R_2P(Ind)\{Cp\}$	$R_2P(Flu)\{Cp\}$
Ind				$R_2P(Ind)_2$	$R_2P(Flu)Ind$
Flu					$R_2P(Flu)_2$

Novel achievements to the chemistry of π-stabilized *bis*-ylide organophosphorus (V) ligands and their main-group and rare-earth organometallic complexes will be presented and discussed.

A.V.S. thanks I. Kant Baltic Federal University for post-graduate fellowship (grant № 877)

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New example of isocyanides as halogen bond acceptors: Five-center Tetrafurcated (Halogen)$_4$···C/N Bonding

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Halogen bonding (HaB) is the object of growing attention of scientific community. This statement can be proved by a great number of publications that came out last years. These works reveal importance of HaB in crystal engineering[1], HaB-involving noncovalent catalysis[2], synthetic coordination chemistry[3], polymer chemistry[4].

We could find that cocrystallization of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1,4-FBB) with mesitylisocyanide (CNMes) results in formation two bonding patterns. First – expectable pattern includes trimers where one 1,4-FBB has contacts with two CNMes molecules. Second – rare and more complex where we were able to identify five-center tetrafurcated HaBs. Structural features of the HaBs were explored on the base of experimental data (XRD) as well as theoretical considerations such as DFT. In the heterohexamers (Figure 1), one Br atom of 1,4-FBB simultaneously form four contacts with two C and two Br atoms of neighboring molecules. Based on the geometric parameters and the theoretical data these contacts were formulated as five-center tetrafurcated μ_4-Br···(C,Br,C,Br)HaBs.

Although the deviation of the geometric parameters from those observed for two-center HaB and the low energies of some individual contacts (e.g., Br···Br), this aggregation leads to a stable energetically favorable systems (the interaction energies are –33.3 and –32.5 kcal/mol). The π-stacking between CNMes/NCMes and 1,4-FBB and two-center I···N/C HaBs make a significant contribution to the stabilization of these heterohexamers.

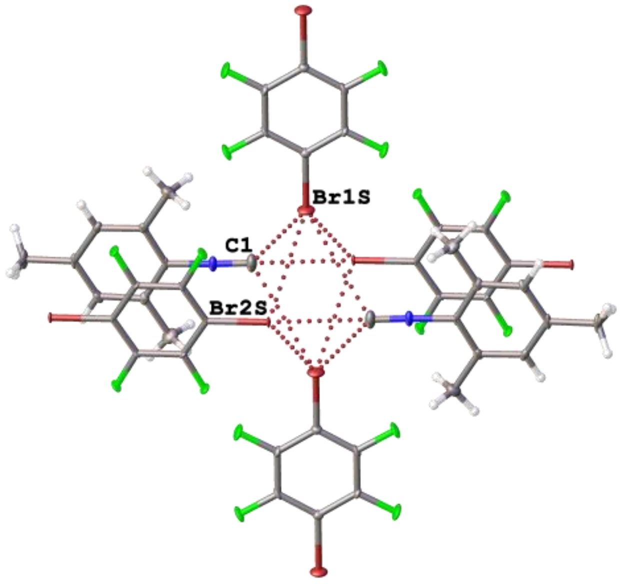

Figure 1. Fragment of the supramolecular structure of (CNMes)·1,4-FBB showing the heterohexamers

This work was supported by the Russian Science Foundation (grant № 22-23-00307). Scientific research were performed at the Research park of St.Petersburg State University «Center for Magnetic Resonance», «Center for X-ray Diffraction Studies»

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Heteroligand α-diimine-Zn(II) complexes with O,N,O'- donor redox-active Schiff bases: synthesis, structure and electrochemical properties

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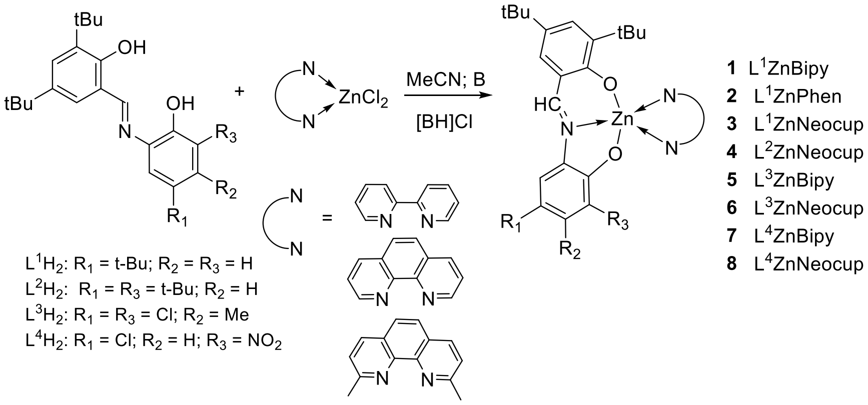
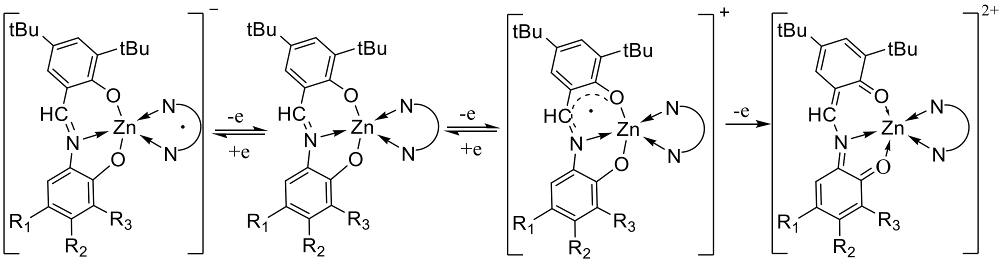
Schiff bases, neutral nitrogen-containing and salen types ligands are widely used to construct zinc(II) complexes with luminescent and fluorescent properties, as well as these compounds have a pronounced bioactivity, in particular, high cytotoxicity against cancer cells. To design polyfunctional zinc(II) complexes, we propose to use a combination of neutral N,N'-chelating ligands such as 2,2'-bipyridine (Bipy), phenanthroline (Phen), neocuproine (Neocup) and tridentate O,N,O'-donor redox-active Schiff bases.



L^1H_2: R_1 = t-Bu; R_2 = R_3 = H
L^2H_2: R_1 = R_3 = t-Bu; R_2 = H
L^3H_2: R_1 = R_3 = Cl; R_2 = Me
L^4H_2: R_1 = Cl; R_2 = H; R_3 = NO_2

1 L^1ZnBipy
2 L^1ZnPhen
3 L^1ZnNeocup
4 L^2ZnNeocup
5 L^3ZnBipy
6 L^3ZnNeocup
7 L^4ZnBipy
8 L^4ZnNeocup

The yield of complexes **1** – **8** varied from 18 to 60%. The structure of the compounds was confirmed by the data of ^{1}H and ^{13}C NMR, IR spectroscopy, mass spectrometry. The molecular structure of complexes **4**, **5** was confirmed by X-ray diffraction. The electrochemical studies of complexes **1-8** by cyclic voltammetry showed that the several compounds (**1-6**) are possessed by reversible one-electron transitions, both in the anodic and cathodic area of the potential sweep.



The second anodic process for complex **4** is also quasi-reversible and leads to the formation of a relatively stable dication. In the case of compounds **7** and **8**, several weakly resolved peaks are observed in the cathodic area, which correspond to the reduction of both the nitro-group and the α,α'-diimine ligand.

This work was supported by the Russian Science Foundation (grant № 22-13-00118)

Synthesis and chemical modification of binuclear palladium(II) complexes

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Preparation of new palladium heterometallic carboxylate complexes with transition 3d metals is promising area of coordination chemistry and catalysis. For example, PdZn nanoparticles synthesised from Pd(OAc)4Zn are catalytically active [1].

In this work we found that the reaction of heterometallic carboxylate complexes Pd(OAc)4M (M = Mn, Ni) with N-donor ligands (L), L = 1,10-phenantroline and 5-nitro-1-10-phenantroline produce complexes with different Pd:M ratios and different modes of ligand coordination.

The crystals of the pivalate carboxylate complex Pd(OPiv)4Mn(OPiv)2 were obtained according to the method [2]. It was found that the replacement of carboxylate bridges is possible in compounds in which a ligand is coordinated to the additional metal atom.

In the reactions between Pd(OAc)4Mn and 1,10-phenantroline, the ligand is coordinated to the transition metal atom without destruction of the «paddlewheel» structure (fig 1). However, when Pd(OAc)4Ni reacts with phenanthroline, the three-core compound of a polymer structure is formed (fig 2).

Pivalate-bridged heterometallic complex PdMn with 5-nitro-1-10-phenantroline was obtained for the first time. The ligand is coordinated in the complex by analogy with 1,10-phenantroline.

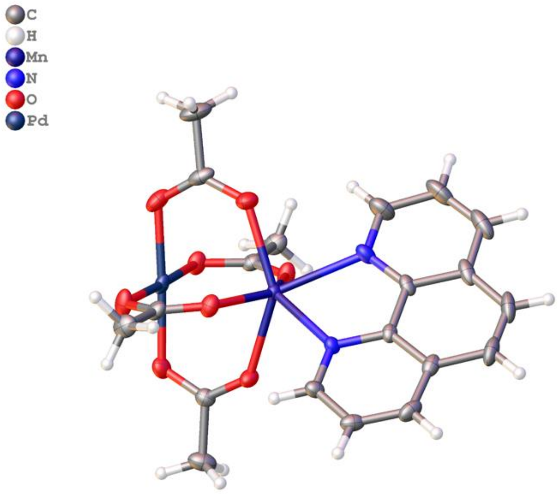

Fig 1. Crystal stucture of Pd(OAc)4Mn(phen)

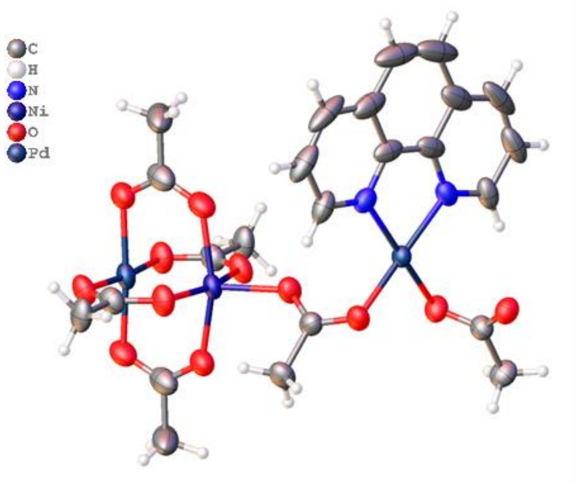

Fig 2. Crystal structure of Pd(OAc)4Ni(Pd(OAc)2(phen))

This research was performed using the equipment of the JRC PMR IGIC RAS

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Synthesis and characterization of the hydrated acid hexamolybdochromate(III) complex with pyridine-3-carboxylic acid of composition $(H_3O)_3[CrMo_6(OH)_6O_{18}]{\cdot}(C_6H_5NO_2)_2{\cdot}5H_2O$

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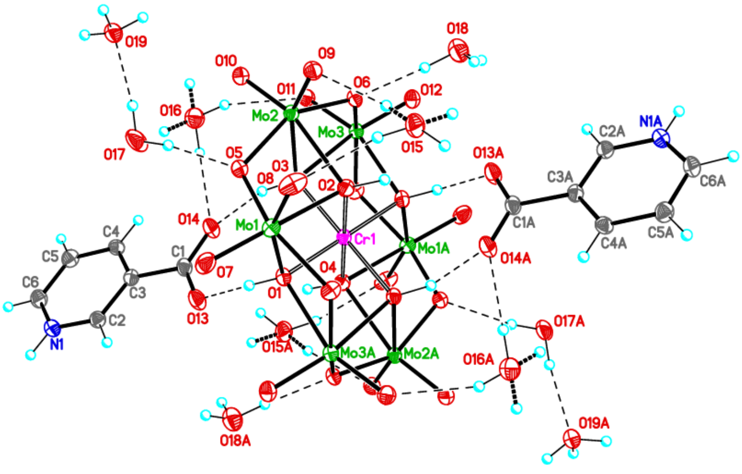
The synthesis of new polyoxometalate complexes is topical due to the wide range of practical applications of these compounds as new generation catalysts and new structural materials [1-2].

The hydrated acid hexamolybdochromate (III) complex with pyridine-3-carboxylic acid of composition $(H_3O)_3[CrMo_6(OH)_6O_{18}]{\cdot}(C_6H_5NO_2)_2{\cdot}5H_2O$ was synthesized. The structure of the new complex was established by single-crystal X-ray diffraction. The synthesized complex belongs to the Perloff - type structural. Nicotinic acid is a zwitterion with a positive charge localized on the ─NH3 group and a negative charge delocalized on the ─COO fragment, and is linked to the complex polyanion by strong hydrogen bonds. The negative charge of the polyanion is compensated by the presence of oxonium ions in the molecule. The complex crystallizes in the triclinic syngony, sp. gr. R-1. Unit cell parameters: a=9.164, b=10.644, c=10.824 (Å), α=95.968°, β=109.864°, γ=105.059°, V=937.2Å^3, d_{calc}=2.500 г/см^3, Z=1.



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New salen-type (THIA)calix[4]arene schiff bases: synthesis,crystal structure and coordination ability towards Fe (III),Ni(II) and Pd(II)

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Islamov D.R.,[1] Gubaydullin A.T.,[1] Litvinov I.A.,[1] Dorovatovskii P.V.,[3] Lazarenko V.A.,[3]
Solovieva S.E.,[1,2] Antipin I.S.[1,2]

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Design and synthesis of supramolecular architectures in the crystalline phase as materials with desired structure/functional properties relationship based on macrocyclic compounds attracted a growing interest in recent decades. The interest for this class of solid-state molecular materials is related with their potential application in catalysis, separation and storage for example. Moreover, depending on the nature of molecular components these solids may exhibit smart luminescence, single molecule magnetism, semiconduction etc. [1-3].

The exploiting of calix[4]arenes for the design of new functional supramolecular systems is determined by their particular ability to adopt different conformations (*cone*, *partial cone, 1,2-Alternate and 1,3-Alternate*) by appending up to eight or more coordinating sites *via* functionalization of the lower and/or upper rims and also by varying –CH_2– or –S- bridges between the phenolic units. The use of salen-type of ligand allows to obtain *d*- and *f*- complexes, which may exhibit some useful properties such as catalysis (synthesis of olefines, cross-coupling reactions etc.) [5].

This work reports on the synthesis of new polydentate salen-type (thia)calixarene Schiff bases and their complexes with Fe (III), Ni(II) and Pd(II). Structures of the obtained ligands are studied in the solution and solid state as well. Their complexes with Pd(II) were characterized by X-ray diffraction analysis. The interplay between the length of alkyl spacer, the nature of used cation with complex structure will be discussed.

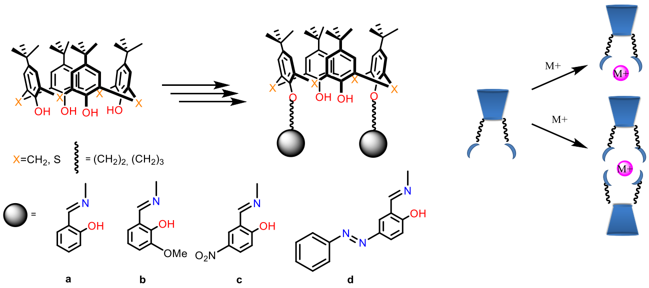

Figure 1. Synthesis of (tia)calix[4]arenes compounds and structural motif of their complexes with *d*-metals.

This work was supported by the Russian Foundation for Basic Research (grant № 22-73-10139)

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Amazing reactions of cymantrene derivatives

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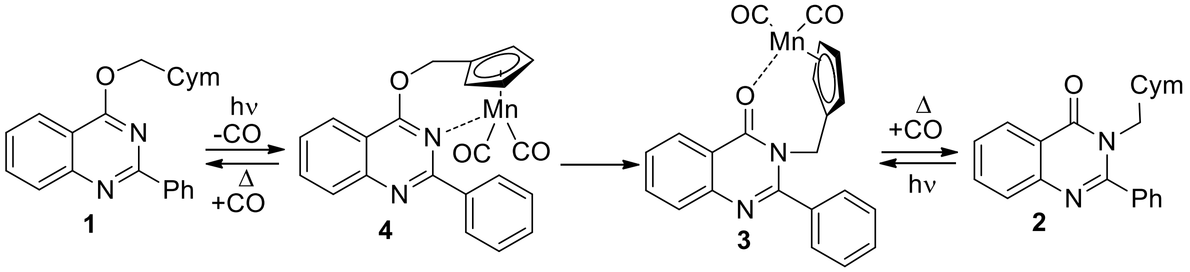
The reactions of derivatives of cyclopentadienylmanganese tricarbonyl (cymantrene) can proceed both at the cyclopentadienyl ring and at the manganese atom. Such chemical behavior has recently attracted attention for the creation of catalytic systems or auxiliary reagents based on cymantrene derivatives. For example, its derivatives have been tested as catalysts for the activation of CH bonds in (de)hydrogenation, hydrosilylation, boronation, CO_2 reduction and in electrochemical hydrogen production processes [1].

We have found that some reactions can proceed only when a cymantrenyl fragment is introduced into the substrate molecule. It was shown that the substituent migration and transalkylation reactions in the triazole ring proceed during the alkylation of 1-cymatrenalkyltriazoles due to an increase in the stability of the carbocation, which is associated with a partial redistribution of the charge on the manganese atom.

Another interesting example is the hydrolysis of isothiouronium salts in the presence of alkalis. In the case of organic analogues, the reaction proceeds with the formation of only thiols, while in the case of cymantrene derivatives, the main reaction products are sulfides and disulfides. The reaction of forming a new bond S-S proceeds due to the coordination of the sulfur atom on manganese.

Monitoring of photolysis of O-alkylated quinazolin-4-one **1** showed that unexpected N-substituted tricarbonyl complex **2** and chelate complex **3** were formed during the reaction. A detailed study of the reaction mechanism by IR, UV, and NMR spectroscopy and quantum chemical calculations showed that the reaction proceeds through the formation of chelate **4** after the removal of CO ligand, which isomerizes into complex **3**, followed by the addition of the CO ligand and the formation of compound **2**. It should be noted that the reaction rate is affected by the rate of CO removal from the “solvent cage” after breaking bond Mn - CO in the starting compound **1**.



Thus, it has been shown that the manganese atom can radically influence the reaction mechanisms.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation

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Chemical evolution of $[H(dmso)_2]_2[IrCl_6]$ in hydrochloric acid

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In the case of kinetically stable Pt(IV), Os(IV), and Ir(IV) hexahalides, the incorporation of DMSO molecules into the coordination sphere of the platinum metal proceeds quite slowly and thus $[H(dmso)_2]_2[M^{IV}X_6]$ complexes (M = Pt, Os, Ir) with intact metal hexahalide anions can be isolated as solid crystalline products [1].

The resulting compound $[H(dmso)_2]_2[IrCl_6]$ was characterized by various physico-chemical methods: spectroscopy, IR, Powder X-ray diffraction studies, X-ray crystal structure determination, EPR.

The UV-Vis spectra of $[IrCl_6]^{2-}$ dianions are characterized by intense absorption maxima in the visible part of the spectra (λ_{max} = 304, 434, 489 nm) assigned to the ligand-to-metal charge transfer (LMCT) bands [2].

In hydrochloric acid solutions a slow evolution of UV-Vis spectra is observed, which is displayed as a gradual decrease in the intensity of these bands at general retention of the spectral shapes and relative component intensities. This strongly assumes that no prominent changes in the coordination sphere of iridium occurs (Fig. 1). And there is a slow recovery to degree of oxidation + 3.

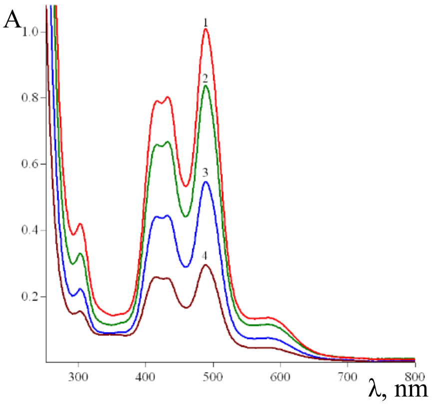

Fig.1. Time evolution of UV-Vis spectra of solution in 6 M HCl.
$C_{Ir} = 2{,}64 \cdot 10^{-4}$ M; l=1,0 cm; τ = 2 min (1), 24 h (2), 15 days (3), 28 days (4).

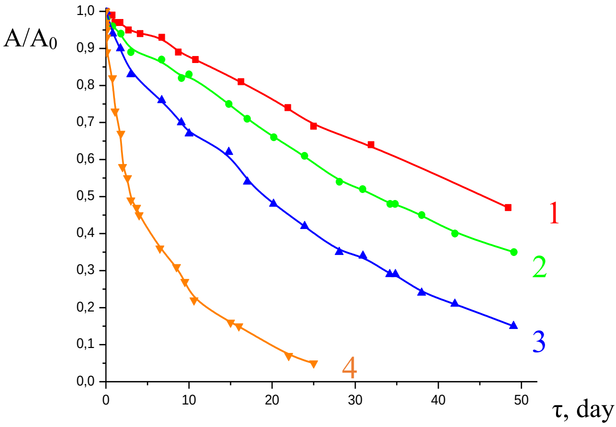

Fig 2. Conversion degrees of Ir reduction from IV to III as a function of time for different solutions of **1** in 0.5 M HCl (1); in water (2); in acetone (3); in 10 M HCl (4). $C_{Ir} \sim 2 \cdot 10^{-3}$ M.

In the case of hydrochloric acid as a solvent, the reduction rate demonstrates dependence on both the iridium concentration and acid concentration with the latter being more pronounced (Fig.2). The UV-Vis spectrum of aged solution of $[H(dmso)_2]_2[IrCl_6]$ in 10 M HCl reveled bands at λ_{max} = 355, 408, and 540 nm typiczal of $[IrCl_6]^{3-}$ [3].

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Complexes of unsaturated silver carboxylates with 1,10-phenanthroline asnew monomers for frontal polymerization

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In recent years, the object of increased attention of researchers has been metal-containing monomers (MCMs) containing a metal complex and unsaturated bonds for various polymerization transformations. They are effective precursors of polymeric metal complexes in which a metal ion is contained in each monomer unit in a given spatial architecture. One of the effective methods for obtaining polymers is frontal polymerization (FP), which consists in carrying out the polymerization process in a localized reaction zone and in the frontal (autowave) mode of its propagation throughout the volume.

In the 1990s, the phenomenon of FP of MCMs was first discovered in our laboratory using the example of acrylamide complexes of transition metal nitrates and was limited to MCMs of this type for a long time. Recently [1], we reported on the synthesis of mixed-ligand MCMs for FP based on copper(II) cinnamate and various chelating N-heterocycles: 2,2'-bipyridine, 1,10-phenanthroline, 4'-phenyl-2,2':6',2''-terpyridine. In continuation of these studies, in this work we synthesized new mixed-ligand complexes of unsaturated silver carboxylates (silver acrylate, cinnamate, and itaconate) with 1,10-phenanthroline and used them as new MCMs for FP. The silver ion coordination node contains a chelating N-heterocycle, a monodentate carboxylate anion,and solvent molecules.

The study of the thermal properties of the obtained MCMs made it possible to determine the temperature regimes of FP. FP of the obtained MCMs proceeds at atmospheric pressure and thermal initiation in the absence of any chemical activators and catalysts. The MCM pellet can be used in various ways to carry out FT: it can be placed in a vacuum ampoule or in a glass reactor that provides heat exchange and hang freely on a bracket. However, studies have shown that the design of MCM pellets does not have a significant effect on the kinetic patterns of FP. All kinetic data were obtained from a series of experiments in air.

Under the conditions of propagation of a stationary reaction front, FP occurs in a small temperature range characteristic of each individual MCM. The initiation of FP was carried out by introducing a short-term (~15 s) thermal perturbation ("ignition") to the bottom of the MCM pellet. In this case, the color of MCM changes, as well as the appearance and growth of a meltingzone associated with first-order phase transitions. To measure the FP velocity, a thermocouple placed along the sample was used, or the time of change in the color position of the growing reaction front was recorded. The optimal temperature conditions for the FP processes of the studiedMCMs were found. Below the indicated temperature range, the front of the polymer slowly formedand due to heat loss (heat dissipation) the front movement did not occur. Above these temperatures,the reaction proceeded rapidly and was accompanied by significant degradation of substances, which makes it impossible to visually establish a clear boundary of the front and track time interval. Kinetic curves have two zones corresponding the stationary and non-stationary modes. Depending on the initial temperature, the values of the FP velocity under stationary conditions canbe higher or lower than the stationary velocity of propagation of the reaction front.

This work was supported by the Russian Science Foundation (grant № 22-13-00260)

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Physical and Colloidal Chemistry
Key-note Speakers

The use of vanadites and vanadates of rare earth metals for the processing of plastic waste

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The growth of industrial production has created conditions for increasing the consumption of various products made of plastics and polymer materials. As a result, the amount of plastic waste that needs to be recycled to solve serious social and environmental problems has increased dramatically [1]. Plastics provide a fundamental contribution to all main daily activities: building materials; agriculture; packing; automobile industry; electricity and electronics. As only a small amount of waste plastic is recycled and most plastics are not biodegradable, all these activities have led to the generation of an increased amount of plastic waste. The measures must be implemented to reduce their negative impact on the environment [2]. The plastic waste can be classified as industrial and municipal plastic waste (MPW) according to their origins; these groups have different qualities and properties and are subjected to different recycling strategies. Incineration of plastic waste to produce heat may be a possibility, but its organic content would totally be destroyed and converted only into carbon dioxide and water.

In this work, a study of catalytic pyrolysis of polymer compounds on the systems $MeVO_3$ and $MeVO_4$ (Me=La, Gd) and compare the obtained results with the non-catalytic process. Previously, we had experience with vanadites ($MeVO_3$) and vanadates ($MeVO_4$) rare earth metals in the study of catalytic cracking of propane [3]. The pyrolysis experiments were carried out in a quartz tube (reactor) with height 250.0 mm. Catalyst and plastic was mixed and then placed into the quartz reactor in the amount of 2.00 g and pyrolyzed in the quartz tube in nitrogen stream.

Vanadites and vanadates of gadolinium and lanthanum as catalysts were used in the catalytic pyrolysis of PE and PP. The influence of the catalyst structure on the yield of gaseous hydrocarbons during catalytic and non-catalytic pyrolysis of polyethylene is presented.

The $LaVO_x$ catalyst contributes to an increase in gas yield and the content of light olefins (ethylene and propylene) in the reaction products. When using $GdVO_x$, similar results were obtained. A similar result was obtained with catalytic and non-catalytic pyrolysis of polypropylene.

The municipal plastic waste PE and PP may be converted into gaseous and liquid hydrocarbons by catalytic pyrolysis processes. Most of the resulting gaseous and liquid products are ideal for further processing into valuable chemical products, with some of the gases can be used as fuel. The use of catalysts based on vanadites and vanadates of REM significantly increases the yield of gaseous pyrolysis products compared to known catalysts (ZSM-5, bentonite clay, kaolin and others), and also has a positive effect on the composition of the reaction products.

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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Active sites evolution and regeneration of CrO_x-ZrO_2-SiO_2 catalysts with low chromium content in non-oxidative propane dehydrogenation

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Catalytic dehydrogenation of light paraffins, including propane, is one of the most promising methods for olefins production. Difficulties of the propane dehydrogenation reaction are associated with some factors: high endothermic effect, the decrease of equilibrium conversion with an increase in partial pressure of propane, and coke formation. The development of effective catalysts that are stable at high temperatures is urgent task. The highly dispersed amorphous Cr_2O_3 particles demonstrate the high activity in this reaction. A promising way to increase the activity of chromium catalysts in PDH is the co-existence of CrO_x and coordinatively unsaturated Zr^{4+} sites.

A series of CrO_x-ZrO_2-SiO_2 (CrZrSi) catalysts with high specific surface area using the one-pot template-assisted evaporation-induced self-assembly process was synthesized. The chromium content was varied from 4 to 9 wt.% assuming Cr_2O_3 stoichiometry. The catalysts were investigated by XRD, SEM-EDX, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR-H_2). The catalysts were tested in non-oxidative propane dehydrogenation at 500–600°C using flow-type fixed-bed reactor.

Silica acted both as a textural promoter that increased the specific surface area of the catalysts and as a stabilizer that prevented crystallization of Cr_2O_3 and ZrO_2. High dispersion of zirconia resulted from the formation of Si−O−Zr bonds during co-precipitation. The action of reaction medium was simulated by treatment by H_2. Raman spectroscopy and XPS revealed that Cr^{6+} species reduces under reaction conditions. The reduction of Cr^{6+} species under X-ray radiation was observed during XPS spectra acquisition. The possibility of Cr^{6+} reduction also agreed with TPR-H_2 results. Raman spectra before and after H_2 treatment confirmed that Cr^{6+} transformation to Cr^{3+} doesn't accompanied by sintering or crystallization of the catalysts.

The 9CrZrSi catalyst initially contained only highly dispersed Cr^{3+} species showed the highest efficiency at 500°C. Cr^{6+} species initially presented in 4CrZrSi and 7CrZrSi were reduced under reaction conditions forming poorly dispersed Cr^{3+} species inactive in PDH. The highest initial propane conversion rate (1.25 mmol(C_3H_6)/(g min)) observed for 9CrZrSi at 550°C. This value is higher than that of 1.05 mmol(C_3H_6)/(g min) achieved in [1] under the same conditions for the commercial catalyst K-CrOx/Al_2O_3 (19.7 wt. % of Cr_2O_3).

The possibility of catalysts regeneration was also investigated. The DSC-TG analysis of the catalysts after 200 min of the test revealed 5–6 mass. % of coke in the catalysts. Analysis of kinetic curves showed that the propane dehydrogenation into propylene and its cracking into CH_4 and C_2H_4 proceeded simultaneously. Further oligomerization and cyclization results in coke formation. Ethane was formed via hydrogenation of C_2H_4. Regeneration of the catalysts was successively performed by 30 min air treatment at 550°C. Both propane conversion and propylene selectivity were recovered.

This work was supported by the Russian Science Foundation, project number 22–23–00445. The authors acknowledge support from Lomonosov Moscow State University Program of Devel-opment for providing access to the XPS instrument

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First-principles study of the defect-activity and optical properties of FAPbCl$_3$

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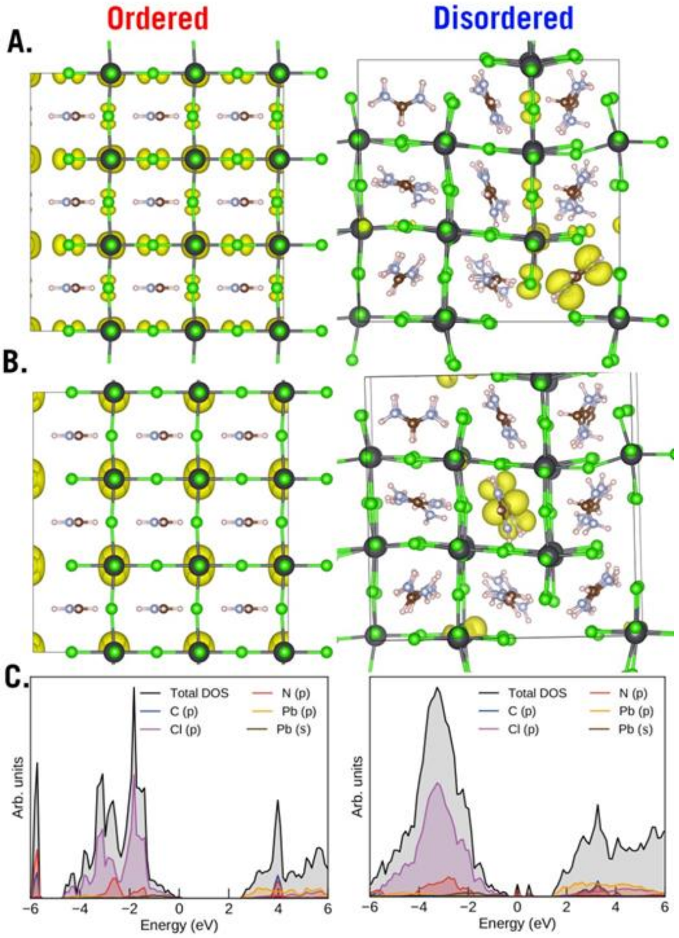
Organic-inorganic lead halide perovskites belong to a novel and rapidly developing class of semiconducting materials. Unlike its well-investigated iodide counterparts, which primarily show promise as solar elements, formamidinium lead chloride (FAPbCl3) is a significantly less studied perovskite that shows superior stability and excellent sensor properties: it detects certain gas analytes with a high selectivity and sensitivity. The origin of the sensing ability of this perovskite material can be traced to its high defect tolerance and the existence of some defects which act as the "lock" to a certain gas analyte's "key". In this talk, I give an overview of how this mechanism was identified and our recent work where we deepened our understanding of this proven perovskite sensor through first-principles computational study of its defect formation energies, charge transition energies, and optical properties. Additionally, we also considered experimental conditions and the effect of temperature on electron screening in the simulations, which demonstrates that screening is particularly important when considering high oxidation states of the defects. We also note the importance of antisites in the Fermi Pinning as well as the importance of FA disorder, which are previously unreported insights.



Use of aqueous solutions of titanium tetrachloride for the synthesis of the Ziegler-Natta catalyst

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The development of new types of catalysts, as well as the improvement of technologies for the production of well-proven products, is an important and extremely urgent task.

The Ziegler-Natta catalyst is an indispensable reagent to produce polymeric materials, while the main component, titanium trichloride, is also widely used in analytical chemistry, the production of titanium dioxide nanoparticles, and even in wastewater treatment processes [1].

For industrial purposes, titanium trichloride is obtained by high-temperature reduction of titanium tetrachloride vapors with various metals, however, due to the specific properties of the reagent, this process is both environmentally and industrially unsafe.

As part of preliminary experiments, it was established that titanium trichloride can be obtained by reacting metallic aluminum, iron, or titanium with aqueous solutions of titanium tetrachloride [2].

The main purpose of this work is to describe the mechanism of the reduction reaction of aqueous solutions of titanium tetrachloride with metallic aluminum. This reaction can proceed both spontaneously at room temperature (low rate) and at elevated temperature (acceleration of the process by 5–10 times), as well as in the process of electrochemical (anodic) dissolution of aluminum.

According to the data on potentially possible reactions occurring in the presence of titanium tetrachloride, two priority reaction mechanisms were proposed:

By hydrolytic direction

$$TiCl_4 + 4\ H_2O \rightarrow 4\ HCl\uparrow + Ti(OH)_4\downarrow \tag{1}$$

$$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2\uparrow \tag{2}$$

By exchange direction

$$3\ TiCl_4 + Al \rightarrow 3\ TiCl_3 + AlCl_3 \tag{3}$$

Based on the data on the change in the color of the solution towards bright purple (characteristic of titanium (III) chloride), it was found that the most priority is the exchange mechanism, with the initial titanium tetrachloride released during the partial hydrolysis (reaction 1) and freshly synthesized titanium trichloride (reaction 4) enters into the reactions of formation of aluminum chloride, which is confirmed by the over-stoichiometric consumption of aluminum, calculated according to reaction 3.

$$TiCl_3 + 3\ H_2O \rightarrow 3\ HCl\uparrow + Ti(OH)_3\downarrow \tag{4}$$

The presence of reactions of hydrolysis and decomposition of titanium chlorides is accompanied by a color change from violet to white, which in turn indicates the formation of ortho- and metatitanic acids.

The possibility of using titanium tetrachloride water absorbers will not only reduce energy costs to produce titanium trichloride, but also significantly increase the environmental friendliness of the process.

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$PdFe/Al_2O_3$ catalysts in hydrodechlorination of diclofenac in aqueous solutions: the influence of iron content, preparation method and reduction conditions

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An important task is the development of environmentally friendly methods of water purification from microecopollutants. Diclofenac (DCF) is widely used as a non-steroidal inflammatory agent; at the same time, it is known as a very persistent chlorinated water pollutant [1]. Catalytic hydrodechlorination (HDC) converts DCF to the much less toxic 2-anilinophenylacetate and is the preferred disposal method. The development of efficient and stable catalysts for this reaction is strongly needed.

This work compares bimetallic catalysts, comprising 1 wt.% Pd and 0.5 or 10% of Fe, supported on alumina by sequential (denoted -s, first by iron then by palladium nitrate), or co-impregnation (denoted -c). The precursor of $PdFe(0.5)/Al_2O_3$-s was calcined, $PdFe(10)/Al_2O_3$-s – not calcined before impregnation with Pd salt. The catalysts (0.05 g) were preliminary reduced 2 h with H_2 in harsh (320°C) or mild (30°C, water suspension) conditions and then tested in HDC of DCF (150 mg/L) at 30°C in water in batch system. It is seen that the catalysts were active even after mild reduction (Fig. 1). The initial reaction rate depends much on the way of catalyst preparation (co-impregnation was preferred), and on the iron content. Mild and harsh reduction provide comparable efficiency. Detailed study by TPR-H_2, DRIFT-CO, XRD, SEM-EDX, and XPS after in-situ and ex-situ reduction provides explanation for the observed features.

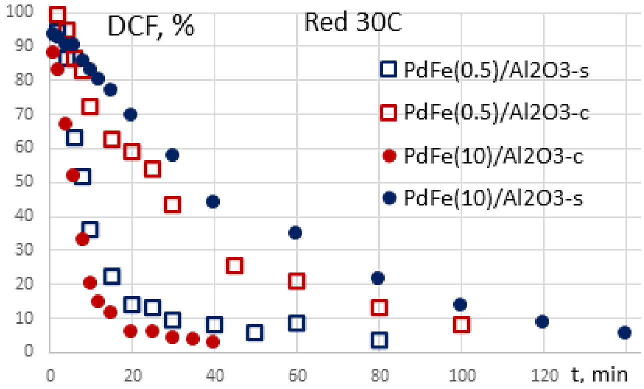

Fig. 1. HDC of DCF (150 mg/L) in batch system on the catalysts (0.05 g) reduced by H_2 at 30°C

According to XPS and TPR-H_2, only iron oxides were presented on the surface of all catalysts after both types of reduction treatement, but Pd was partially (during mild reduction) and nearly totally (during harsh reduction) transferred to Pd^0.

Energy-efficient mild reduction makes it possible to reduce up to 50% of Pd^{2+}, but the degree of reduction and the extent of encapsulation of Pd with alumina (estimated from Al:Pd ratio) depend on the method of catalyst preparation: more active catalysts $PdFe(10)/Al_2O_3$-c and $PdFe(0.5)/Al_2O_3$-s contained more Pd^0 on the surface (48 and 55 at.%), than $PdFe(10)/Al_2O_3$-s and $PdFe(0.5)/Al_2O_3$-c (only 19-20 at.%) and had much lower Al:Pd ratios. TPR-H_2, XPS and DRIFT-CO studies confirm strong interaction between Pd and Fe to form Pd-Fe-O species and even small amounts of PdFe alloys at the points of contact.

The catalysts demonstrated stability in flow-type system (0.1 g of catalyst, C_0(DCF)=75 mg/L) even after mild reduction.

This work was supported by the Russian Foundation for Basic Research (grant № 20-53-10005)

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Nanoheterogeneous catalysis in petrochemicals

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The use of nanoheterogeneous catalysts in oil refining processes is one of the main directions for increasing their efficiency [1].

The report describes in detail the methods of synthesis of heterogeneous catalysts and their practical use in oil refining processes.

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Thermal transpiration is a key factor in the intensification of gas-phase reactions in a reactor with a membrane catalyst

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When determining the intensification of catalytic processes, the reference standard for a membrane reactor is a conventional reactor with a fixed catalyst bed. To characterize the intensification of the catalytic process, the most objective assessment is the specific rate constant or the ratio of these constants when comparing reactors.

For many high temperature reactions, the main problems that arise in a traditional catalytic reactor are associated with the so-called kinetic limitations and maintaining the catalytic activity of known (industrial) catalysts. Both of these problems can be observed in the process of Dry Reforming of Methane (DRM), which in recent decades has attracted the attention of researchers due to the economics of producing syngas and the possibility of simultaneously utilizing two greenhouse gases.

The traditional mechanism of intensification of high-temperature catalytic processes in pores is associated with an increase in convection. Convection, as a phenomenon, can occur only in continuous media and is absolutely impossible in rarefied media in macro and mesopores under normal external conditions. Therefore, under the conditions of Knudsen diffusion, which most often occurs in the pore media of catalysts (including membrane ones), one should consider other mass transfer mechanisms that are possible in rarefied media.

In most studies of heterogeneous gas reactions in membrane reactors, many authors neglect the influence of thermal effects of reactions, which in pore media create conditions for the occurrence of mass transfer phenomena caused by a temperature gradient. A special place among the phenomena of mass transfer caused by a temperature gradient is occupied by thermal transpiration, the occurrence of which experimentally established in our kinetic studies of the DRM in a reactor with a membrane catalyst.

In recent decades, the theory of this phenomenon has received significant development in connection with creating devices of various micro-electromechanical systems (MEMS). Among these devices, the Knudsen compressor stands out, which is constructively, (structurally) closest to the reactor with a membrane catalyst. Mass transfer of gases in the channels of the porous structures of these devices occurs in the absence of mechanical elements that induce movement. And when stationary conditions are established in both devices, microcirculation circuits are formed in the pore channels of these diaphragms (membranes). Micro circulation circuits are initiated in the pore channels by a tangential temperature gradient The application of the kinetic approach to membrane catalysts in combination with the theory of thermal transpiration made it possible to explain the advantages of a membrane catalyst: an increase in the TOF of the methane dissociation reaction by an order of magnitude compared to a traditional catalyst; a significant reduction in the reaction temperature and loss of flow pressure in the DRM reactor in the contactor mode. The use of reactors with a membrane catalyst will make it possible to create economical and small-sized plants for the production of syngas and hydrogen and the processing of various gas mixtures.

Transition metal deposited on schungite as catalysts for biomass processing

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The catalyst development plays an important role in the biomass processing. The catalyst needs to be characterized by the high activity and selectivity to the required products. Also, catalyst stability is an important factor. Some catalysts used in biomass conversion into hydrocarbons tend to be deactivated due to the active phase leaching and surface coking. For this reason, the choice of catalyst support is an urgent task [1].

Schungite is a fullerene-like natural material. It is one of the carbon allotropic modifications. Schungite is a natural carbon-reach material that has high sorption ability and high reductive properties. The main properties of this material are the following: density 2.1-2.4 g/cm^3, compressive strength 100-200 MPa, electrical conductivity 1500 Sm/m, thermal conductivity 3.8 Wt/m, adsorption capacity 20 m^2/g. Such properties make this material suitable for catalyst support [2].

In the current work, novel schungite-based catalysts were developed for the liquefaction of hardwood biomass. The catalyst synthesis was carried out using the hydrothermal deposition method [3]. The study of the porous structure, elemental composition, composition of the surface was carried out for the synthesized schungite-based catalysts. The isotherms obtained for the initial schungite, schungite after the treatment in synthesis conditions, and the catalysts are characterized by the form of type VI with the hysteresis loop of H4 type. Such isotherms are typical for the mesoporous materials with ink-bottle-type of the pores. When the schungite was treated under the catalyst synthesis conditions, the surface area of the support was found to be increased by almost 2 times. This can be explained by the leaching of some compounds (i.e. alkali metal oxides, silica, and alumina) from the support that was confirmed by the elemental analysis. It should be noted that the active phase deposition did not lead to changes in the porous structure in comparison with the treated schungite. This indicates that the metal precursor salt does not affect the catalyst textural properties and the hydrothermal conditions play an important role in the formation of catalyst porosity.

The catalytic activity of the developed systems was studied in the deoxygenation of stearic acid and anisole. Testing of the synthesized catalysts in the deoxygenation of model compounds of vegetable oil and bio-oil showed its high activity and selectivity. For example, the 10%-Ni/Schungite catalyst provided over 90 % of oxygen-containing compound conversion for 1 hour of the deoxygenation process in the medium of supercritical hexane. The yield of hydrocarbons in both stearic acid and guaiacol deoxygenation was found to be over 95 %

This work was supported by the Russian Science Foundation (grant № 22-79-10096)

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Synthesis and application of cyclic organic peroxides

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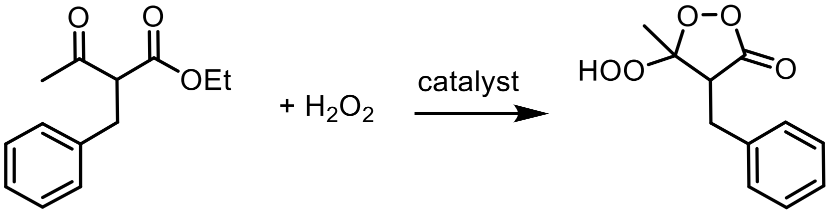
The development of new approaches to the synthesis of cyclic organic peroxides is one of the central problems of modern organic and medical chemistry. Such interest is because these compounds exhibit a wide spectrum of biological activity, in particular, antimalarial, fungicide and antiviral activities [1].

One of the interesting directions of peroxides synthesis is the oxidation of ketones with hydrogen peroxide, which has several significant advantages over other oxidizing agents. We have found that the treatment of β-ketoesters with hydrogen peroxide under acid catalysis conditions leads to the formation of β-hydroperoxy-β-peroxylactones. The reaction proceeds selectively under mild conditions and allows to obtain the corresponding peroxides with good yields (30-96%) [2,3].



To get a deeper inside in the peroxidation of acetoacetic esters, we have studied the effect of acid type and its amount on the process. Thus, the reaction does not proceed in the presence of an equimolar amount of $BF_3 \cdot Et_2O$. Contrariwise, raising the excess of $BF_3 \cdot Et_2O$ to 10 equivalents leads to an increase of the target cyclic peroxide yield to 92%. Using of concentrated H_2SO_4 as a catalyst resulted in desired peroxides with good yields (67-78%).

The work was carried out with the support of the RNF, grant № 21-13-00205

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Physical and Colloidal Chemistry
Invited Lectures

Regularities and periodicity of the properties of metal-organic frameworks: D.I. Mendeleev Periodic System in Action

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Metal-organic frameworks (MOFs) represent just a part of the world of coordination polymers. Twenty years ago this term did not exist as well as the mere class of these compounds. These are periodic frameworks constructed from inorganic units (usually metal ions) and organic linkers connecting the inorganic units. MOF represents an organic zeolite. Starting from 2000-2002, the number of publications on these materials grows like an avalanche. The lecture will present recent trends in the synthesis of metal-organic frameworks and will give an analysis of the structural diversity of MOFs from the point of view of D.I. Mendeleev Periodic Law. Presently 69666 compounds of such coordination polymers with established structures have been synthesized and they contain 78 elements of the Periodic Table. Noteworthy, the number of combinations of inorganic units and organic linkers can be estimated as 10^{20}. Metal-organic frameworks may be 1-dimensional, 2-dimensional or 3-dimensional (porous), with their specific surface area reaching 5000-10000 m^2/g, and the pore volume – 2-3 cm^3/g, which is an order of magnitude larger than the corresponding values for conventional zeolites (500-600 m^2/g, 0.3-0.4 cm^3/g). The fields of their applications are unlimited as well. Except for the well explored areas (catalysis, adsorbents, sensors, membranes), quite non-traditional areas are developed (non-linear optics, storage of odors, drug delivery etc.). The overwhelming majority of the reported structures of MOFs – over 90% of all the known materials – were synthesized with such elements as Al, Cr, Eu and other rare-earth metals, Fe, Mg, Ti, Zn, Zr.

Membrane catalysts for modern energetic

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Fast growth in energy demand is one of the main problems of modern civilization. However, at present, the struggle of mankind to improve the environmental situation is significantly changing the face of modern energy. Renewable energy sources such as solar panels and wind turbines are coming to the fore. However, the stochasticity of their work makes it necessary to use energy storage devices in parallel. If we are talking about seasonal energy fluctuations, the hydrogen cycle will be used to offset them [1].

One of the main problems is associated with the fuel cells production for the efficient generation of energy from the oxidation of hydrogen. In addition, since hydrogen does not exist in nature in its pure form, it must be obtained. All currently existing methods for hydrogen producing produce many by-products, the main of which are carbon oxides. At the same time, carbon monoxide poisons the platinum catalysts of the most common low-temperature fuel cells [2]. Thus, hydrogen needs deep purification. An excellent opportunity to combine the production of hydrogen and its purification is membrane catalysis, proposed by Academician Gryaznov [3]. The operation of the fuel cell is also based on membrane catalysis.

The main goal of this report is the consideration of some membrane catalytic processes for hydrogen production, novel membranes and catalysts for low temperature fuel cells.

The main advantages of membrane catalytic dehydrogenation on the base of palladium alloys is high selectivity of hydrogen transfer (close to 100%) and high catalytic activity in reactions involving hydrogen.

At the industry level, methane is the main source for hydrogen production. Its steam reforming and partial oxidation are widely used. At the same time, it is important to produce hydrogen from renewable sources, such as biomass, wood, the processing products of which are alcohols, primarily ethanol and methanol. The advantage of their reforming is low process temperatures, which minimizes CO impurities. For these processes, membranes based on palladium alloys are used. To increase their productivity, the surface is cleaned and composite membranes are obtained. These processes use catalysts based on noble or transition metals on oxide or carbon carriers [4].

The main problem of fuel cells is the high cost of platinum catalysts and perfluorinated membranes such as Nafion or Aquivion. An important task is to obtain cheaper materials that provide high performance. In terms of catalysts, we are talking about platinum alloys and core-in-shell particles production. Polybenzimidazoles, hybrid materials with embedded nanoparticles, and grafted membranes based on polymer films with grafted polymers containing functional groups are considered as promising membranes for fuel cells [5].

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Physical and Colloidal Chemistry
Oral Reports

Modern technologies of wastewater treatment of electroplating industries

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The transition of mankind to sustainable development is impossible without the development and implementation of various green technologies. Metallurgical enterprises (including electrical engineering, mechanical engineering, etc. related industries) have already moved to the minimum level of waste generation and the maximum degree of waste involvement in technological processes [1].

The most polluting for the environment is the production of electrical products and electrochemical production (electroplating). During the production or operation of systems based on galvanic cells, huge volumes of wastewater are formed, which differ significantly in their composition. Considering the heterogeneity of the composition, wastewater is separated by streams and sent to the appropriate purification processes. For example, wastewater containing cyanide is sent for oxidation of cyanide to thiocyanate, followed by post-treatment on adsorption filters or when using biological purification. Acid-base wastewater with a high content of heavy metals is sent to the stage of neutralization and precipitation of metals in the form of poorly soluble metal hydroxides or sulfides.

Wastewater treatment containing chromium (VI) ions and complex compounds of heavy metals is a much more complex task. Considering the peculiarities of the composition, heavy metals in the composition of wastewater cannot be converted into an insoluble form and precipitated similarly to metals in the composition of acid-base wastewater. For the purification of chromium-containing effluents, the processes of reagent reduction and precipitation, the processes of membrane or electrochemical purification are used. As typical reagents, iron (II) salts can be used - simultaneous reduction of chromium (VI) compounds to the state of chromium (III) and coagulation of colloidal particles.

Wastewater treatment from complex electrolytes has several features. For example, coagulants based on iron compounds cannot be used to purify such effluents, since the latter ions are also capable of forming highly soluble complexes with organic ligands, making this method of purification practically ineffective. Membrane and electrochemical processes, reverse osmosis, oxidation, and adsorption are used to purify such effluents.

To synthesize a sample of a titanium-containing coagulant, a suspension of metallic iron was dissolved in an aqueous solution of titanium tetrachloride. The content of active components in the solution was: 12.3% $TiCl_3$; 16.7% $FeCl_2$. Determination of the content of dissolved forms of metals was carried out on an atomic emission spectrometer with microwave plasma «SpectroScay» in accordance with a specially developed technique.

The acid-base drain was a sample of highly mineralized water with low heavy metal contents. For wastewater treatment, it was proposed to use a titanium-containing coagulant, which has shown high efficiency in wastewater treatment processes of various origins. The choice in favor of a titanium-containing coagulant was because, compared with coagulants based on iron compounds, titanium-containing reagents have less corrosion activity, require less reagent consumption, and the resulting coagulation sludge has a high filtration rate. It has been shown that samples of a complex titanium-containing coagulant can effectively remove chromium compounds from water at a lower consumption compared to iron salts. This phenomenon is primarily due to the high reactivity of titanium (III) compounds that are part of the complex reagent. Aluminum compounds were ineffective in this case.

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Study of synthetic approaches for producing modified CdTe quantum dots with programmable optical properties in aqueous solutions

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Stability and wide range of fluorescence of quantum dots (QDs) make them very promising for application in various fields.

We had to develop a technology for producing high quality CdTe QD samples in aqueous solutions, modified by various ligands, in order to develop protocols for the selective labeling of various recombinant target proteins, containing a hexahistidine tag. The following hydrothermal synthesis variations of CdTe QDs are commonly described in literature: a) generating the precursor of Te^{2-} – hydrogen telluride (H_2Te) solution *in situ* from Al_2Te_3 / H_2SO_4 system, b) generating the precursor of Te^{2-} – NaHTe solution *in situ* from Te / $NaBH_4$ system, c) generating the precursor of Te^{2-} *in situ* from Me_2TeO_3 by reduction with $NaBH_4$. Among other methods we have chosen and substantially modified the hydrothermal method for obtaining preparations of water-soluble CdTe quantum dots stabilized with sulfur-containing ligands, as shown below:

$$4\mathrm{TeO_3^{2-}} + 3\mathrm{BH_4^-} \rightarrow 4\mathrm{Te^{2-}} + 3\mathrm{BO_2^-} + 6\mathrm{H_2O}$$

$$\mathrm{CdCl_2} + \mathrm{Te^{2-}} + \mathrm{MPA} \rightarrow \mathrm{Cd{-}(MPA)}_x\mathrm{Te}_y + 2\mathrm{Cl^-}$$

$$\mathrm{Cd{-}(MPA)}_x\mathrm{Te}_y \overset{\Delta}{\rightarrow} \mathrm{CdTe}$$

We selected the most accessible Cd and Te salts as the initial precursors. The pilot experiments made it possible to select and optimize the following process parameters: the order of reagent addition, their ratios, the temperature and the pH of the main reaction (pH values range from 9 to 12); the choice of sulfur-containing ligands and the reducing agent; temperature parameters and the duration of reflux of the reaction mixture; the solvent for size-selective sedimentation procedure; centrifugation speed and duration. A number of different sulfur-containing ligands with a terminal polar carboxyl group were tested (among them, 3-mercaptopropionic acid appeared to be the most optimal ligand). The spectral properties of synthesized CdTe preparations stabilized with 3-mercaptopropionic acid are presented in table 1.

Table 1. Physical-chemical properties of CdTe QDs.

	pH 9	pH 12
Wavelength of main fluorescence band maximum, nm	520	642
Full width at half maximum (FWHM) of main fluorescence band, nm	45	70
First exciton absorption maximum, nm	488 (±3)	610 (±10)
Nanoparticle diameter, nm	1,9 (±0,2)	3,7 (±0,2)
Molar extinction coefficient, ε ($l\cdot mol^{-1}\cdot cm^{-1}$)	$4,3(\pm0,9)\cdot10^4$	$1,6(\pm0,2)\cdot10^5$

Therefore, we have developed and successfully tested a technology for preparation a range of CdTe QDs samples with programmed optical properties.

The reported study was funded by RFBR (project number 20-03-00139)

Complex Gd-Fe-Co oxides: physicochemical and catalytic properties

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Converting carbon dioxide and methane into chemicals and fuels is a valuable way to conserve renewable energy and achieve zero CO_2 production. The dry reforming of methane is one of the most promising and feasible strategies for using carbon dioxide and methane to produce synthesis gas (a mixture of CO and H_2) in a ratio of 1:1, which can then be used to obtain a wide range of products using the carbon monoxide hydrogenation [1]. CO hydrogenation, in turn, is a promising method for the production of light olefins (key chemicals that are mainly obtained in the petrochemical industry) from alternative sources, the need for which has increased due to limited oil resources [2].

The study is devoted to the study of the physicochemical and catalytic properties of systems with perovskite structure $GdCo_{1-x}Fe_xO_3$ (x = 0; 0,2; 0,5; 0,8; 1) in reactions of hydrogenation of carbon monoxide and dry reforming of methane (DRM). The main purpose of this work was to study the catalytic activity of systems based on perovskite-type iron- and cobalt-containing complex oxides in the process of dry reforming of methane and hydrogenation of carbon monoxide, to establish a relationship between the physicochemical properties of complex oxides and their catalytic characteristics. A series of samples was prepared by the sol-gel method and characterized by a complex of physicochemical analyzes: XRD, BET, DSC, TG, SEM, EDX, and XPS.

The experimental data made it possible to establish a correlation between the amount of cobalt in the composition of gadolinium ferrite and the activity of perovskite in the processes of DRM and CO hydrogenation. A correlation has been established between the state of iron and cobalt atoms, the fractions of surface and lattice oxygen, and catalytic characteristics. It has been established that the formation of catalytically active centers occurs under the action of the reaction medium. It is assumed that Gd_2O_3 (A-position) is responsible for the adsorption of CO and CO_2 with the formation of carbonate complexes, while transition metal ions (B-position, B = Fe, Co) are responsible for the adsorption of hydrogen and the formation of its atomic forms. It has been established that varying the composition of $GdCo_xFe_{1-x}O_3$ complex oxides leads to a change in the oxygen-metal binding energy in Gd-O-Me, the ratio of metals in various oxidation states, the amount of surface and lattice oxygen, which affects the adsorption and catalytic characteristics of complex oxides.

This publication has been supported by the RUDN University Scientific Projects Grant System, project № 021521-2-174 and the scholarship of the President of the Russian Federation (№ СП-686.2021.1)

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Exchange interactions of Mo with transition metals in complexes with dithiooxamide

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We carried out calculations of the complexes $[(L)_2M1^{3+}(L)M2^{2+}(L)_2]^{5-}$ (I) ($M1^{3+}$ is the Mo ion in the oxidation state +3; $M2^{2+}$ is the 3d and 4d transition-metal (Fe, Ru, Rh, Pd) ion in the oxidation state +2; and L is the dithiooxamide ligand) to search for pairs of metals corresponding to the maximum value of the exchange coupling constant J.

The molecular structures of the complex anions I were calculated in the B3LYP/LANL2DZ approximation with geometry optimization for the high-spin ground state using the GAUSSIAN-09 program [1]. Earlier, it was shown that the round-state energy and geometry calculations of the complexes in question require optimization of only nine key structural parameters [2]. Then, the J constants and the spin densities for these complex anions were calculated using optimized geometry in the B3LYP/TZV approximation using the ORCA program [3]. The J constants were obtained using the broken symmetry approach [4].

It was shown that replacement of 3d transition-metal ions in the oxidation state +2 by 4d transition-metal ions in the oxidation state +2 leads to higher J values. One can expect that going from the 4d metal ions in the oxidation state +2 to the same-group 5d metal ions in the oxidation state +2 will be accompanied by further strengthening of ferromagnetic exchange interaction in this type of complexes. The higher the degree of spin density redistribution from one metal ion to the other upon complexation, the higher the J constant. This clarifies the physical meaning of the exchange coupling constant. Finally, the trends revealed allow one to give recommendations to synthetic chemists on how to choose the magnetic sublattice components characterized by the strongest ferromagnetic exchange interaction.

This work was carried out within the framework of the State Assignment
No. AAAA-A19-119092390079-8 to the Institute of Problems of Chemical Physics,
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Transformations of supported metal catalysts and their interaction with carbon substrate

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Materials with supported metal particles are rather specific type of catalysts. Their active use has made a lot of potential supports, in particular, carbon materials, widespread in modern heterogeneous catalysis. In this regard, an important task is to predict the properties of new materials. Defectiveness is one of the possible criteria to evaluate these properties. It affects not only the physical and chemical properties of the carbon material, but also the distribution of deposited particles on the surface. [1] This, in turn, changes the catalytic activity, but at the same time visualizes active centers, making it possible to automate their search on SEM image by neural network technology. [2]

In addition, the study of processes in dynamic systems becomes an urgent task in heterogeneous catalysis, and when the study of liquid state systems has already yielded the concepts of catalytic cocktail and dynamic transformations, [3] substrates are still considered to be inert.

In this work, systematic study on the interaction of metal-containing nanoparticles and their mixtures with graphite with MW radiation was carried out, using several tens of metal compound types. It was proved that under MW radiation treatment, which is actively used for the preparation of catalysts, metal nanoparticles can interact with the support, thereby changing the resulting catalytic activity.

Technique for the qualitative study of changes in palladium particles distribution on support was developed. In addition, a database of SEM images with ordered and disordered metal particles distribution on the surface was created, and a method was developed to automate the marking of defects on support.

This work was supported by the Russian Science Foundation (project No 19-73-20124)

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Role of catalyst supports and active phase composition for synthesis of oxygenated hydrocarbons from ethanol over (K)(Co)MoS$_2$ catalysts

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Effects of catalytic supports and active phase composition on the synthesis of oxygenated hydrocarbons from ethanol over monometallic, bimetallic, and trimetallic (K)(Co)MoS$_2$-based catalysts supported by activated carbon have been studied. The effect of catalytic supports (alumina, CCA, and two commercial ACs, i.e., AG-3 and BAW) on trimetallic KCoMoS$_2$ ethanol catalysts was studied (**Figure 1.a**). The catalysts were synthesized using the incipient wetness impregnation method and sulfidized with H$_2$S. Transmission electron microscopy (TEM) revealed well-defined metal particles with an average MoS$_2$ phase size of 5.0 to 10.6 nm and an average stacking number of 1.7 to 2.0. AC-supported catalysts displayed more activity than Al$_2$O$_3$ and CCA, which seems to be the consequence of improved KCoMoS$_2$ stacking and possibly the presence of micropores and a low quantity of mesopores. The highest catalyst activity was observed under He atmosphere, compared to H$_2$ atmospheres. The turnover frequency (TOF) in each of the studied reactions increased both with an increase in average length ($\bar{L}$) and a reduction in dispersion (D).

Active phase composition (MoS$_2$/C$_{AG-3}$, KMoS$_2$/C$_{AG-3}$, CoMoS$_2$/C$_{AG-3}$, and KCoMoS$_2$/C$_{AG-3}$) influenced catalyst activity (**Figure 1.b**). K and Co alter sulfide catalysts' physical-chemical properties, activity, and selectivity. Adding K to MoS$_2$/C$_{AG-3}$ and CoMoS$_2$/C$_{AG-3}$ lowered catalytic activity. Co and K inhibited ethanol dehydration (to ethene) and intermolecular dehydration (into diethyl ether). K incorporation promotes active sites for higher alcohol synthesis (HAS) and other oxygenates, including (aldol-) condensation and coupling reactions, and increases the liquid-to-hydrocarbon ratio. Acidity had a proportionate impact on product dispersion but no direct effect on total conversion. Ethanol was transformed into ethyl acetate, ethyl acetoacetate, acetaldehyde, butonal-1, and propanol-1, as well as short-chain hydrocarbons.

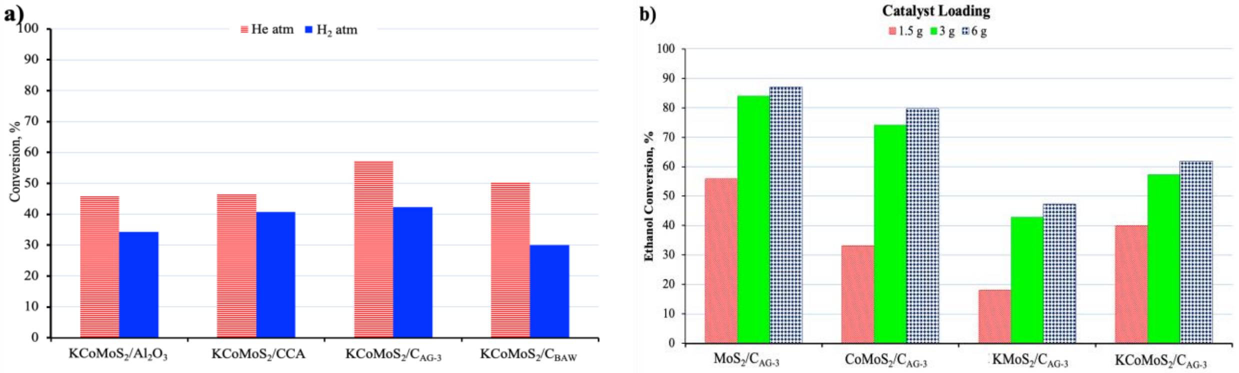

Fig. 1: Ethanol conversion over (K)(Co)MoS$_2$ supported catalysts; **a)** effect of catalyst support; **b)** effect of active phase composition. Standard reaction conditions: (GWSV= 760 L·h^{-1}·(kg·cat)$^{-1}$; catalyst loadings = 1.5 g (3 g and 6 g); feed volume = 30 ml ethanol; ethanol flow rate = 0.3 ml/min; T = 320ºC; P = 2.5 MPa).

Assembly of supramolecular systems based on octaphosphonate-substituted porphyrin and its metal complexes on the surface of liquid and solid substrates

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Porphyrins and their metal complexes are able to form supramolecular systems with different structures, depending on the composition of peripheral groups and the nature of the metal center. Porphyrins decorated by phosphonate-containing functional groups are of particular interest due to their tendency to form strong hydrogen bonds, as well as different coordination ability, which in combination with the nature of the metal center can significantly affect the structure of materials and, as a consequence, their optical properties.

In this work, an approach for design and synthesis of a new *β*-octa[(4-diethoxyphosphoryl)phenyl]porphyrin (**OPPP**) and its metal complexes (**NiOPPP**, **ZnOPPP** and **CuOPPP**) for assembling of organized nanoscale structures at the air/water interface with subsequent immobilization onto solid substrates is proposed. This approach makes it possible to control the molecules orientation at the initial stage of assembly - the formation of precursors - Langmuir monolayers on the air/water interface, followed by their transfer onto solid substrates by Langmuir-Blodgett techniques to obtain organized planar systems with given structural and optical characteristics. Structure, aggregation behavior, and physicochemical properties of porphyrins in Langmuir monolayers at the air/water interface were investigated. The dependence of the optical properties of porphyrins in a Langmuir monolayer on the molecular packing parameters specified by lateral compression were studied. It was found, that structure of supramolecular systems preorganized at air/water interface as well as their optical properties were preserved upon transfer of monolayers onto solid substrates by Langmuir-Blodgett technique, which was confirmed by *in situ* UV-vis absorption spectroscopy, Brewster angle microscopy and atomic-force microscopy (Fig. 1).

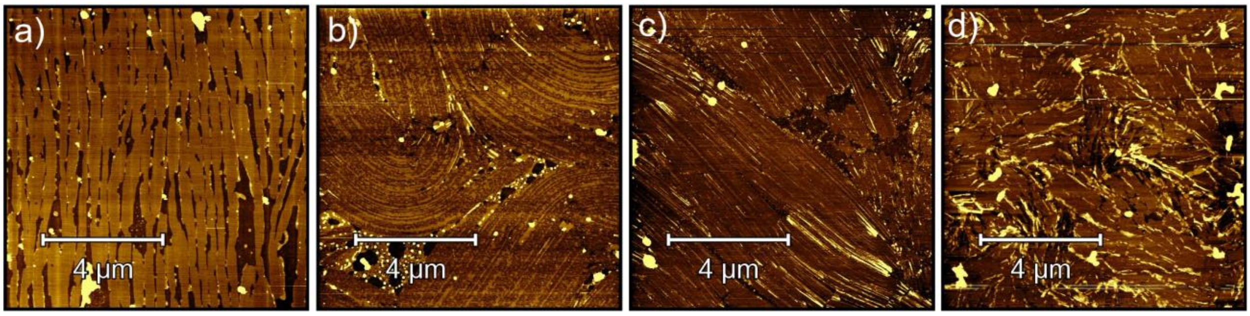

Fig. 1. AFM images of one-layer Langmuir-Blodgett films of **OPPP** (a), **NiOPPP** (b), **ZnOPPP** (c), and **CuOPPP** (d) transferred onto mica substrate at 18 mN m^{-1}.

This work was supported by the Russian Science Foundation (grant № 21-73-00020)

Biodegradation of crude oil by a biocomposition based on humic acids under abiotic stresses

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Oil pollution in terms of scale and toxicity is a global hazard due to the wide, ubiquitous impact of petroleum substances on all forms of life. In high concentrations, the hydrocarbon molecules that make up crude oil and petroleum products are highly toxic to all organisms [1]. So, it is important to create modern biocomplexes containing bacteria that decompose oil hydrocarbons and sorbents of natural origin, which can not only bind oil pollutants into non-toxic complexes, but also have a stimulating effect on both introduced microorganisms and on native microflora.

The purpose of this work is to study the emulsifying activity of biocompositions based on humic acids (HAs) and oil-degrading microorganisms of the genus *Rhodococcus* in the relation to crude oil under abiotic stresses (low temperature (10°C) and high salinity (5% NaCl)). The objects of the study are humic acids of reed fen peat (RFP) [2]; bacteria strains *Rhodococcus erythropolis S67*, *Rhodococcus erythropolis X5*. Model pollutant: crude oil from the refinery of GAZPROMNEFT JSC. The ratio of HAs to microorganisms: 5 : 3.

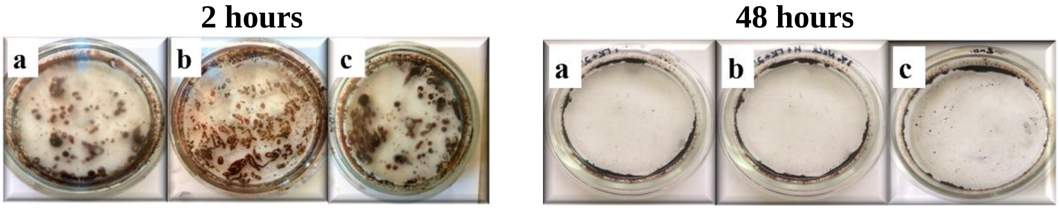

Fig. 1. Influence of biocomposition on the state of oil films: a – room temperature; b – increased salinity; c - low temperature.

It was found, that regardless of abiotic conditions, after 2 hours, almost complete destruction of the oil film by the biocomposition occurs, so even small oil drops are absent on the water surface. In this case unstructured ensembles are observed, consisting of HAs, solubilized oil residues, and a biofilm of microorganisms. Complete utilization of oil hydrocarbons occurs after 47 hours. HAs molecules capture heavy and light oil fractions with their hydrophobic sites and bind them into non-toxic complexes, while heavy oil fractions bind to aromatic fragments of HA, and light ones to peripheral part of the hydrophobic fragments-residues of hydrocarbon radicals, the addition of oil-degrading microorganisms is able to utilize oil products that have not reacted with HAs, as well as oxidize available organic pollutants on the surface of HAs.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of a state assignment on the topic "Synthesis of targeted biologically active ionic compounds and new biocomposite materials" (FEWG-2021-0011)

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Multipurpose strategy for fabrication of ultrathin hybrid films from graphene oxide and chromophores for organic electronics

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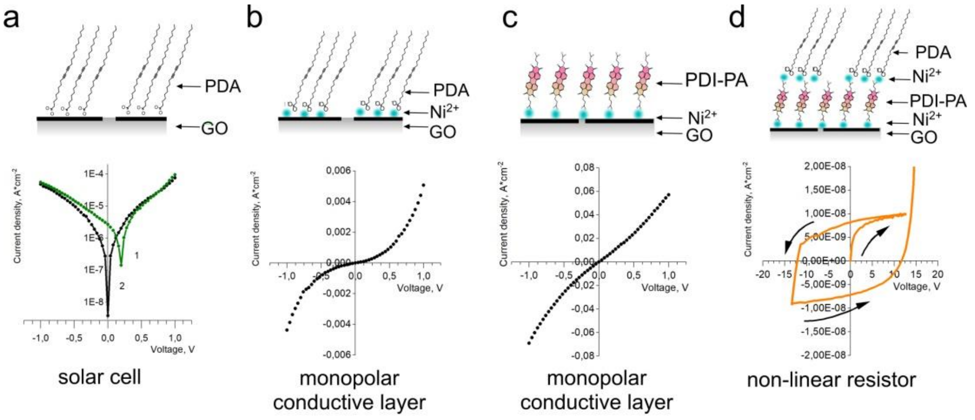
Graphene-based hybrid films represent an extensively developing class of nanostructures, which are broadly used for catalysis, sensorics, optoelectronics, and photovoltaics. In this work a combinatorial interfacial assembly method was developed for fabrication functionally different 2D hybrids by using the same starting set of components comprising graphene oxide, perylene chromophore (PDI-PA), polydiacetylene surfactant (PDA) and nickel nitrate as a source of divalent ions. The components were assembled through either hydrogen or coordination bonds into layered nanofilms with a thickness 8-20 nm to integrate them into conventional ITO-based solar cells. Depending on their composition, the hybrids provide the resulting devices with different operational characteristics. The combination of graphene oxide with the light-absorbing polymer PDA led to a decrease in contact resistance in the GO sublayer through "healing" the gaps between the GO nanosheets. The separation of electron-hole pairs at the PDA/GO interface under applied electric field leads to a doping-free enhancement of the in-plane surface conductivity by 6 orders of magnitude up to 46.4 $S\cdot cm^{-1}$ with respect to those of individual components [1].

We have demonstrated that combining graphene oxide with the PDA polymer in a single electron cell provides photovoltaic properties, whereas the adding of nickel transforms the hybrid into the monopolar conductive layers. The combination of two chromophores (PDA and PDI-PA) gives a multipurpose nanoelement, which performs as either non-linear resistor, diode or photodiode (Fig.1). This strategy can be easily extended to other combinations of chemical tools for the design of various hybrid nanofilms with desirable functional properties for organic electronics.



solar cell monopolar conductive layer monopolar conductive layer non-linear resistor

Fig.1. Schematically illustrated structure and current-voltage dependences of the hybrid cells.

This work was supported by the Russian Science Foundation (project № 20-13-00279)

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Evaluation of the effectiveness of tetracycline photooxidation in the presence of a graphite-like carbon nitride catalyst

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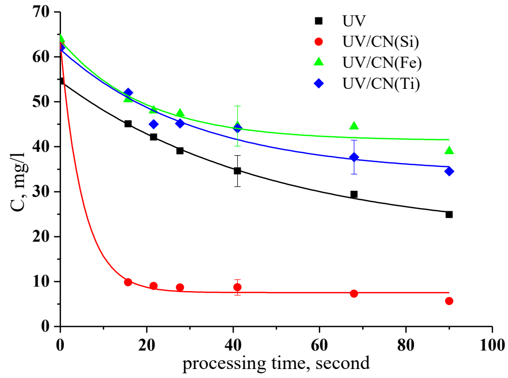
With the growth of the pharmaceutical industry, the state of the environment is deteriorating. There is a high need to create a localized wastewater treatment system at each enterprise before it is discharged into the city sewer system, as well as a regulated procedure for the proper disposal of expired or unused medicines in hospital and veterinary points.

The use of various chemical catalysts together with energy sources, in particular UV-radiation, contribute to the accelerated destruction of complex organic compounds. Based on the analysis of scientific papers, this type of cleaning is also not only environmentally safe and effective, but also economically profitable, compared with other cleaning methods. In recent decades, the field of new, innovative catalysts has been actively developing, which in turn are radically different from metal oxide catalysts.

The purpose and objective of this work was to evaluate the possibility of using graphite–like carbon nitride for photo-oxidation of an aqueous solution of tetracycline.

Samples of heterogeneous carbon nitride (CN) catalysts with the inclusion of silicon oxide (SiO_2), iron (III), titanium (TiO_2) were obtained in the laboratory of the Department of Industrial Ecology of the Mendeleev Russian State Technical University. The method of preparation consisted in dissolving salt in water, followed by dispersion of technical melamine into the resulting solution and heating the mixture to 500 ° C for 4 hours (heating speed 3 °C/min) in a tightly closed bux in a muffle furnace, followed by gradual cooling. The resulting catalyst was ground in an agate mortar immediately before being introduced into the solution [1]. The efficiency of the obtained catalysts was evaluated using a UV installation described in detail in with respect to tetracycline photooxidation. The initial concentration (C) of tetracycline in water was 50-65 mg/l, the catalyst weight was 0.48 g/l.

The graph shows the kinetics of photocatalytic oxidation of tetracycline in the presence of carbon nitride with various inclusions. It is determined that the most effective catalyst for photooxidation of tetracycline is carbon nitride with the inclusion of silicon. The photooxidation efficiency was 92%. It should be noted that the use of catalysts based on iron and titanium oxides did not show their photocatalytic properties in comparison with pure photooxidation within the experimental error.



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Supramolecular self-assembly of functional hybrid materials

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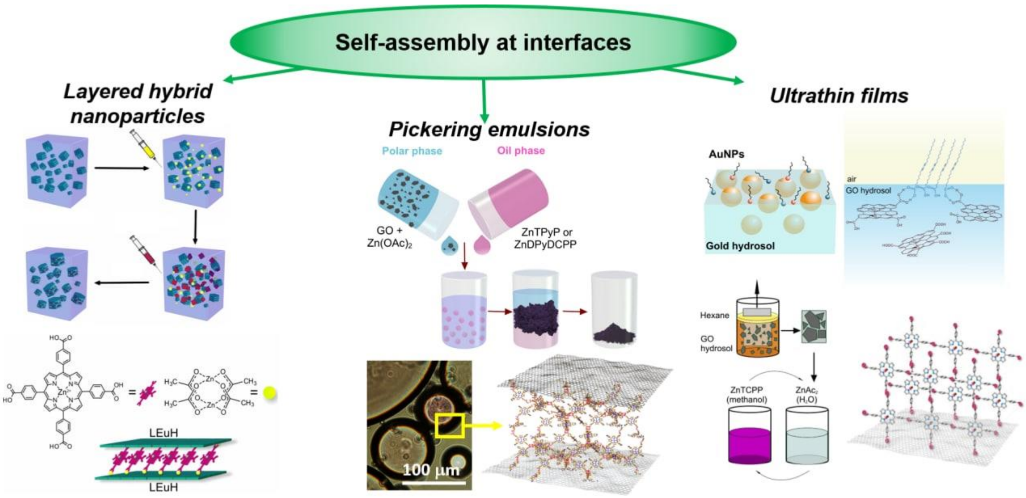
Hybrid materials is a class of nanostructures comprising the advantages of organic compounds with their chemical and functional diversities in combination with mechanical stability, optical and electrophysical properties of inorganic substances [1]. The synergy of interactions between organic and inorganic components due to the charge/energy exchange processes in hybrid structures may lead to the enhancement of properties or even to the emergence of new physical and chemical effects in these materials. Supramolecular self-assembly at interfaces is a powerful tool for integrating organic and inorganic compounds into hybrid nanostructures for a number of potentially useful applications such as sensing membranes, photoactive surface coatings, charge transferring layers, catalysis and photocatalysis etc.

Several interfacial self-assembly strategies rationalizing the design of planar and porous dispersed nanohybrids will be discussed. One-step integration at the air-water interface as well as liquid-interface epitaxy method are applied for fabrication of multifunctional ultrathin planar hybrids and surface-attached SUROMFs for photovoltaic applications (see Figure). Colloidal synthesis in hydrosols and Pickering emulsions is a tool for structuring new hybrid catalysts comprising potent chromophores such as porphyrins. Integration of zinc porphyrins with layered rare earth hydroxides gives symbimetic (i.e., mimicking symbiotic behavior) catalysts as artificial enzymes [2], whereas their hybrids with graphene oxide exhibit the ambivalent photocatalytic properties in aqueous media [3]. These strategies are broadly useful for advancing fabrication of hybrid nanomaterials toward ecology friendly and resource-saving technologies.



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Non-oxidative propane dehydrogenation on CrO_x/ZrO_2-SiO_2 catalysts: the influence of preparation method

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Olefins are the main feedstock for the wide range of polymer materials and valuable chemicals. However, is a difficult industrial task. The prospective production method of alkenes is catalytic dehydrogenation of light paraffins, for instance propane (propane dehydrogenation – PDH). Commercial dehydrogenation catalysts consist of Pt or CrO_x particles supported on different stable oxide materials. Platinum-based systems are quite expensive and short-lived, and high chromium content in catalysts can pose risk to human health due to the possible presence of toxic Cr^{6+} compounds [1]. Therefore, recent studies focus on the development of new catalytic systems with a reduced content of precious metals and chromium.

This work compares catalytic properties of ZrO_2-SiO_2 systems prepared using cetyltrimethylammonium bromide (CTAB) as a template and modified by low amounts of CrO_x thought different techniques: “one-pot” co-precipitation and two-step method with impregnation of the previously synthesized ZrO_2-SiO_2 support. All samples were calcined with heating up to 600°C during 5h and at 600°C for 4 h. The (Cr+Zr):Si molar ratio in all samples was 0.8. Nominal chromium content was 4; 7 and 9 wt.% assuming Cr_2O_3 stoichiometry for chromium oxides.

PDH catalytic tests were performed on ULCat-1 catalytic unit (UNISIT, Russia) equipped with fixed-bed continuous-flow quartz reactor at 500, 550, and 600°C, using 100 mg of catalyst, total flow rate was 30 mL/min. Long-term stability tests were carried out at 550°C using 200 mg of catalyst at the same flow rate. Feed gas mixture comprised of 40 vol.% C_3H_8, 60 vol.% N_2. The gas mixture at the output of the reactor was analyzed by GC on a Crystal-5000.2 gas chromatograph (“Chromatec”, Russia) equipped equipped with a Al_2O_3 “S” PLOT capillary column (30 m, id 0.53 mm, “HP”, USA) and a flame ionization detector. Propane conversion and product selectivity was calculated using internal normalization method.

Samples prepared with “one-pot” method exhibit relatively high selectivity and stability during catalytic experiments; the rate of propene formation increases almost proportionally to the Cr loading in the calcined catalysts. The catalytic properties of their counterparts, synthesized by two-step technique, do not directly proportionally depend on the chromium content, which is probably caused by non-uniform chromium distribution and different concentration of active Cr^{6+} species. Detailed study by TPR-H_2, Raman spectroscopy, XRD, SEM-EDX, and XPS provides explanation for the observed features.

This work was supported by the Russian Science Foundation, project number 22-23-00445.
The authors acknowledge support from M.V. Lomonosov Moscow State University
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Generation and analysis of scanning electron microscopy data in the study of dynamic processes in liquid phase

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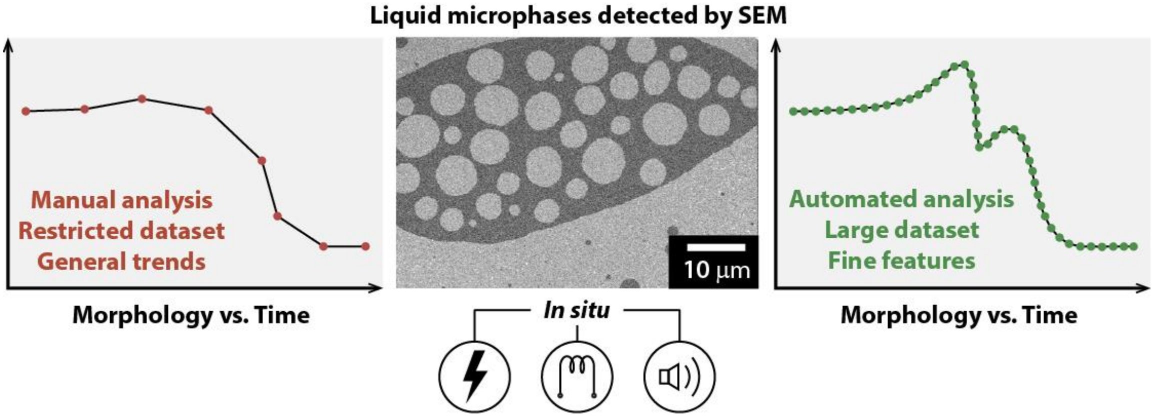
Electron microscopy occupies a special place among the instrumental methods used for analysis of the structure and dynamics of various chemical systems due to the opportunity of direct visualization of the objects under study with a sufficiently high spatial and temporal resolution. The technological progress of the last decades has made it possible to extend the electron microscopy method to liquid-phase systems, which are of key importance for chemistry and materials science. Nevertheless, the hardware design features of most of the used approaches allow dealing with heterogeneous systems with liquid-solid interface rather than with micro- and nanostructured liquids [1].

In our research we paid attention to simple solutions and complex reaction mixtures based on ionic liquids (ILs), because they occupy a huge niche in the field of structured reaction media, and also they can be studied directly under electron microscopy conditions without additional stabilization [1, 2]. The application of ILs as a media and tuning of the scanning electron microscopy (SEM) observation parameters allowed us to carry out the *in situ* monitoring of the liquid-liquid interface dynamics at microscopic level under different stimuli including electron beam irradiation, external heating [3], and action of electric field or ultrasound [4].



Recording of the observed processes on electron microscopy videos in real time made it possible to generate thousands of individual images (frames) within a single experiment. The application of computer algorithms based on neural networks for the fast automated processing of the obtained datasets revealed the fine features of the liquid-phase dynamics [3]. The speed of analysis was increased by nearly 10000 times compared to standard manual processing, which allowed to reduce the sampling interval and, as a result, to improve the temporal resolution.

This work was supported by the Russian Science Foundation (RSF grant № 22-13-00286)

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$NiSO_4{\cdot}6H_2O$ single crystals doped with titanium dioxide TiO_2 nanoparticles: growth, structure, properties, and applications

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Nickel (II) sulphate hexahydrate $NiSO_4{\cdot}6H_2O$ (α–NSH) is an ideal material for creating solar-blind UV filters (200–300 nm), having high transmission efficiency (> 80%) in the narrow range 250–340 nm, moderate transmission at 450–600 nm and strong absorption over all other wavelengths [1]. In addition, α-NSH has been actively studied in recent years as an efficient catalyst due to its non-toxicity, stable synthesis, and easy removal and recovery after achievement of the reaction for an eventual recycling [2].

Nanoparticles of titanium dioxide are the most promising and popular functional components for nanocomposites due to low cost, availability, high reactivity, ease of preparation, low toxicity, and a variety of modifications. Their introduction into a system with α-NSH can affect the actual composition and structural behavior of the material. The system of α-NSH doped with titanium dioxide sols, demonstrating high antimicrobial activity, is of practical interest. It is possible that doped $NiSO_4{\cdot}6H_2O{:}TiO_2$ (α–NSH:Ti) crystals may exhibit improved performance compared to nominally-pure α-NSH crystals or even show new functional properties. The purpose of this work is to establish the role of titanium dioxide introduced into the system with α–NSH in the form of sols on the structural parameters of α–NSH:Ti.

Sols SOL-1 (sample NSH:Ti-1) and SOL-2 (sample NSH:Ti-2) were obtained by mixing $TiOSO_4$ with the addition of H_2O, keeping the mixture at 80°C with vigorous stirring on a laboratory magnetic stirrer, followed by a decrease in temperature in two stages to 50°C and subsequent cooling to room temperature. NSH:Ti-1 and NSH:Ti-2 crystals were grown in crystallizers with a volume of 0.4 and 5 liters, respectively, using seed crystals.

X-ray diffraction analysis resulted in sp. gr. $P4_32_12$ ($Z = 4$) for NSH:Ti-1 and NSH:Ti-2 with the unit cell parameters $a = 6.7746(1)$ Å, $c = 18.2574(6)$ Å and $a = 6.7779(2)$ Å, $c = 18.2272(8)$ Å, respectively. In the NSH:Ti structure, the S atom is tetrahedrally surrounded by oxygen atoms, the Ni atom is coordinated by six O atoms in an octahedral configuration, and each octahedron is hydrogen-bonded to six SO_4-groups.

Refinement of the occupancies of the crystallographic sites in the α-NSH:Ti structures indicates vacancies in the Ni sites and interstitial Ti^{4+} ions near the Ni defect site. As a result, the real compositions of α-NSH:Ti crystals can be written as $[(Ni^{2+}_{0.994}\square_{0.006})(Ti^{4+}_{i})_{0.004(1)}]SO_4$ (NSH:Ti-1) and $[(Ni_{0.990}\square_{0.010})(Ti_{i})_{0.010(4)}]SO_4$ (NSH:Ti-2). Moreover, an increase in the content of Ti^{4+} ions in the crystal is accompanied by an increase in the a cell parameter and a decrease in the c parameter with a corresponding change in the hydrogen bond distances.

The work was supported by Ministry of Science and Higher Education: grant № 075-15-2021-1362

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Volatile organic compounds (voc) and odor removal in trout bioorganic waste management

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The problems and causes of the unpleasant odors appearance while handling bioorganic waste are considered, the composition of emissions generated during the storage and accumulation of waste from trout farms in Karelia is analyzed, the results of the experimental biological product "Liquidator" use are presented.

During the decomposition of bioorganic waste, volatile organic compounds (VOCs) of various nature are released and produce unpleasant odor. Numerous works by scientists from China, Canada, Europe [1-8] quite fully present the results of the volatile products study, these products are formed during the decomposition of bioorganic waste at landfills and MSW dumps, at composting sites, as well as during the decomposition of domestic sewage sludge. Thus, more than sixty different VOCs were identified in the emissions of the MSW transfer station [5], among which five priority pollutants were identified - methanethiol, hydrogen sulfide, ethanol, dimethyl disulfide and dimethyl sulfide, while the highest contribution to the appearance of odor (> 90%) is made by methanethiol . The main emitted VOCs in the waste disposal area at the MSW landfill are styrene, toluene, xylene, acetone, methanol, n-butanone, n-butylaldehyde, acetic acid, dimethyl sulfide, dimethyl disulfide and ammonia, however, acetaldehyde, ethylbenzene, xylene, methylamine and dimethylformamide can be considered as typical odorants, and the most dangerous [6]. At the same time dichloroethane, trichlorethylene, as well as naphthalene and acrolein are weakly smelling substances, and were found in emissions at all stages of technological processing. Their values exceeded the permissible values of carcinogenic risk (>1) [8].

The present study of organic compounds emissions - decomposition products of waste from a trout farm (Tishkozero, Karelia), including fish remains and silt deposits, was carried out according to the author's method for identifying volatile compounds aspirated and concentrated on a sorbent in the form of fine-crystalline glass, by subsequent desorption and separation of vapors using two-dimensional gas chromatography with cryomodulation and mass spectrometric detection. In the work, the quantitative ratio of emissions' components was determined, the presence of more than 60 organic compounds was confirmed, there were not only typical odorants characteristic of landfill and MSW emissions, such as xylene, indolizine, toluene, phenol, cresol, naphthalene, biphenyl, but also there were shown the presence of non-volatile organic compounds - squalene, ascaricide DETA (diethyltoluamide), higher fatty acids - palmitic, dodecanoic and tetradecanoic and their amides - palmitamide, dodecanamide, tetradecanamide, as well as unsaturated compounds - dodecene, tetradecene. The dynamics of changes in the emissions composition with the addition of the experimental biological product "Liquidator" was traced. It was shown that the addition of a biological product does not lead to a significant change in the qualitative composition of emitted odorous substances (VOCs), does not significantly affect the content of fat decomposition products in emissions - palmitic acid and oleamide, but significantly reduces the content of toxic components in emissions - phenol, naphthalene and phthalic acid. acid, styrene and diphenyl, as well as DETA ascaricide. At the same time, a significant increase in the content of biologically active substance - squalene - was noted in emissions. The proposed method for identifying volatile organic compounds, including odorants, can be successfully used for qualitative analysis, and in the case of using a more selective sorbent, for quantitative analysis of emissions generated during the decomposition (rotting) of bioorganic waste.

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Catalytic features of complex molybdenum-containing oxides

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Studies show that the presence of molybdenum particles in the catalytic system has a positive effect on the selectivity (up to 90% increase in ethane [1]) and yield [2] when using such systems in the propane cracking reaction.

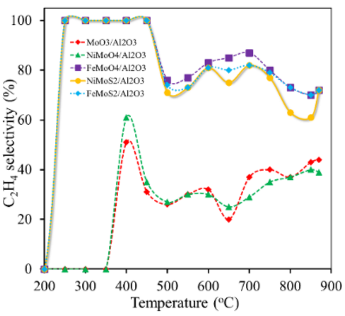
The purpose of this research was to explore the catalytic process of propane cracking in the study of highly active and selective catalysts based on molybdenum deposited on an alumina substrate (MoO_3/γ-Al_2O_3, $FeMoO_4$/γ-Al_2O_3, $NiMoO_4$/γ-Al_2O_3, $NiMoS_2$/γ-Al_2O_3, $FeMoS_2$/γ-Al_2O_3).

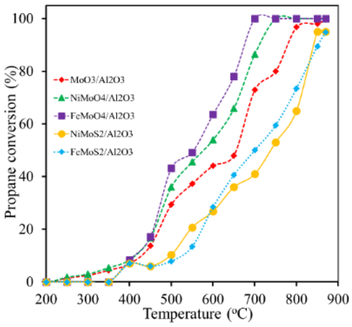
It has been established that molybdenum oxides deposited on γ-Al_2O_3 have a developed specific surface area; the modification of molybdenum-based catalytic systems with nickel and iron atoms does not reduce the specific surface area.

A high catalytic activity was revealed for both oxide and sulfide systems based on molybdenum. In both cases, the conversion reaches a maximum at 1000 K. It was noted that for sulfide systems, an increase in catalytic activity is observed during repeated catalytic experiments due to the formation of carbide compounds.

It has been shown that catalytic systems of composition $BMoO_4$ /γ-Al_2O_3 (B = Fe, Ni) stimulate the mechanism of propane destruction due to a larger number of Bronsted centers, access to which is open due to the mesoporous surface with a polymodal distribution.

It was found that the studied molybdenum-containing catalytic systems have high catalytic activity and selectivity for the formation of target products in the form of light olefins. The maximum selectivity for ethylene is observed in $FeMoO_4$/γ-Al_2O_3, reaching a value of 80%.





Based on the conducted studies, it can be concluded that the introduction of other metals into the composition of molybdenum oxide and molybdenum sulfide systems is an effective solution for propane catalytic cracking, so our further work will continue to develop in this direction.

The publication was made with the support of the RUDN University
Strategic Academic Leadership Program

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Preparation, crystal structure and microstructure of $H_{(4-n)x)}[T^{n+}_{x}Si^{4+}_{12-x}O_{24}]\times wH_2O$ catalytic systems with T=Al, Ti

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Application of HZSM-5 polycrystalline zeolites (sp. gr. Pnma or $P2_1/n$, z=8; MFI structural type) of general composition $(H_{(4-n)x})[T^{n+}_{x}Si^{4+}_{2-x}O_{24}]\times wH_2O$ (T=Al^{3+}, Ti^{4+}) are associated with their operational properties (catalytic and adsorption activity, non-toxicity, biocompatibility), which are determined by the composition (Si/*T*, content of water and OH groups) and characteristics of the crystal structure (symmetry, type and size of voids, Si/*T*, *T* atoms distribution over the structure crystallographic positions), and microstructure (specific surface area, total pore volume and pore size distribution), which, in turn, depend on the method and conditions of zeolites fabrication. The objects of study were commercial HZSM-5 zeolites with Si/Al = 12 and with Si/Ti (TS-1 -batch 1; TS-2 and TS-3 - batch 2) and synthesized in Boreskov Institute of Catalysis by the hydrothermal method HZSM-5 zeolites with the initial silicate modules Si/Al = 25, 40, 40C (different template: TEABr for 40 and TPAOH for 40C) and TS-4. All the samples were characterized by a complex of traditional and modern methods using high-tech MegaScience facilities with the use of synchrotron (TS-(1-4); ID22 beamline of ESRF, France) and neutron radiation (HZSM-5 with Si/Al; IBR-2 pulsed reactor, Russia).

The crystal structures and samples composition (including unknown for commercial HZSM-5(12), TS-(1-3)), were refined by the Rietveld method. Real Si/*T* values and the most probable sites occupied by T^{n+} ions in the HZSM-5 structure were found. It was established that *T* sites occupation in HZSM-5 structure differ depending on Si/Al, while samples with the same silicate module (Si/Al=40 and 40C) obtained under different synthesis conditions differ in the distribution of Al^{3+} ions over *T* sites of the structure. Moreover, TS-2 and TS-3 samples from different batches with the same initial compositions and refined Si/Ti=47 have different distributions over the sites of HZSM-5 structure. With an increase in Si/Al, the sizes of rings from tetrahedra in HZSM-5 structure and their area decrease [1], but the diameter of spherical particle formations on SEM images increases [2].

HZSM-5 catalytic properties study results [3], indicate the relationship between the characteristics of properties and Si/Al, the content of physically adsorbed water, "zeolite water" with OH groups, specific surface area, meso- and micropores volume, surface energy of adsorption centers, and the content of acid sites. However, a relationship between the content of Al atoms in a particular tetrahedral position and the characteristics of catalytic properties was not revealed. Nevertheless, in nitrous oxide (N_2O) catalytic decomposition the conversion value (α, %) differs on HZSM-5 with the initial Si/Al=40, but different synthesis conditions and Al^{3+} atoms distribution over *T* sites ($\alpha_{HZSM-5(40C)} < \alpha_{HZSM-5(40)}$). While the catalytic activity of samples with Si/Ti = 47, but with different titanium distribution over *T*-sites in the process of allyl chloride epoxidation to epichlorohydrin (30°C) [4] and in the reaction of propane conversion (250-900 °C) is almost the same.

This research was funded by Ministry of Science and Higher Education of the Russian Federation, grants No. 0706-2020-0026 and 075-15-2021-1362

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CO-hydrogenation of carbon oxides on catalytic systems of gadolinium ferrites modified with Ca/Ba

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The excessive dependence of the world countries on traditional fuels, such as oil, gas, coal, will lead to an increase in the average temperature over the global land which will lead to global catastrophes: food shortages, an increase in the number of extreme weather events and global warming. In addition, oil reserves are limited, and they are decreasing over time. This decline, along with other economic and political factors, affects world oil prices. The use of alternative fuel sources is inevitable [1].

Fischer-Tropsch synthesis (FTS) has aroused great interest among researchers in recent decades, since it is believed that the production of liquid hydrocarbons using a promising environmentally friendly technology can become an alternative method that can solve the problem of shortage of liquid fuel transport [2].

This work is devoted to the study of the catalytic properties of systems with perovskite structure $Gd_{1-x}(Ca/Ba)_xFeO_3$ (x=0; 0.01; 0.05) in the hydrogenation reactions of carbon oxides. The main purpose was to study the catalytic activity of perovskite-like iron-containing gadolinium oxides doped in A-position with calcium or barium in the hydrogenation reactions of carbon oxides, to establish a relationship between the composition of complex oxides and their catalytic characteristics under reaction conditions, as well as the effect of the composition of the reaction mixture on selectivity for target products.

The main results of the work can be summarized:

1. The physicochemical and catalytic properties complex oxides $Gd_{1-x}(Ca/Ba)_xFeO_3$ (x=0; 0.01; 0.05) have been synthesized and studied in the hydrogenation reactions of carbon oxides.

2. It is shown that during hydrogenation of carbon monoxide alone, for all the samples studied, carbon monoxide conversions reached 90-95%; the introduction of both calcium and barium into the A–position of the perovskite lattice led to a slight decrease in CO conversions, and the introduction into the reaction mixture increased.

3. While hydrogenating only carbon monoxide, the introduction of both calcium and barium leads to a decrease in the apparent activation energies of methane formation; the activation energies of ethylene formation for almost all samples were comparable; the minimum values of Ea* for both methane and ethylene were obtained on a sample with 1%Ca;

4. During the reaction in the presence of CO_2, an increase in the content of the latter led to a decrease in the Ea* of methane for all catalysts except $Gd_{0,99}Ca_{0,01}FeO_3$; a similar trend was observed for the activation energies of ethylene formation;

5. Doping of gadolinium ferrite with calcium or barium leads to a decrease in the number of active centers ($\ln k_o$) responsible for the formation of methane for all catalysts, for ethylene – only for a sample with 1%Ca* during the hydrogenation of carbon monoxide

6. The introduction of carbon dioxide into the reaction mixture only for the sample $Gd_{0,99}Ca_{0,01}FeO_3$ leads to an increase in the number of active centers for both paraffins and olefins.

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Kinetic Modeling for the Cellulose Hydrogenolysis to Glycols over Ru@Fe$_3$O$_4$/Polymer Catalyst

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Glycols are the most important raw materials for many branches of modern industry. [1]. Magnetically recoverable catalysts have received considerable attention in the last decade due to the possibility of magnetic separation, which makes it easy to recovery with minimal catalyst losses. In addition, this leads to energy savings and a catalyst made of rare metals and leads to cheaper target products [2].

In the current study, the magnetically separable Ru-containing catalysts were synthesized for the first time using the polymeric matrix of hypercrosslinked polystyrene (HPS) as support. The synthesis method of catalyst (Ru@Fe$_3$O$_4$/HPS) was developed. The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water at 255 °C, 60 bar hydrogen pressure in 50 min allows PG and EG selectivities of 20.0 and 22.6%, respectively, at 100% of cellulose conversion. The catalyst is stable under hydrothermal conditions of the process; it is easily separated from the liquid phase with the external magnetic field and can be reused. The formal description of the kinetics of glucose hydrogenolysis as one of the stages of cellulose conversion into glycols was obtained (Figure 1). The mathematic model of glucose hydrogenolysis to glycols in the presence of Ru@Fe$_3$O$_4$/HPS was proposed. The kinetic parameter estimation was performed according to the model developed.

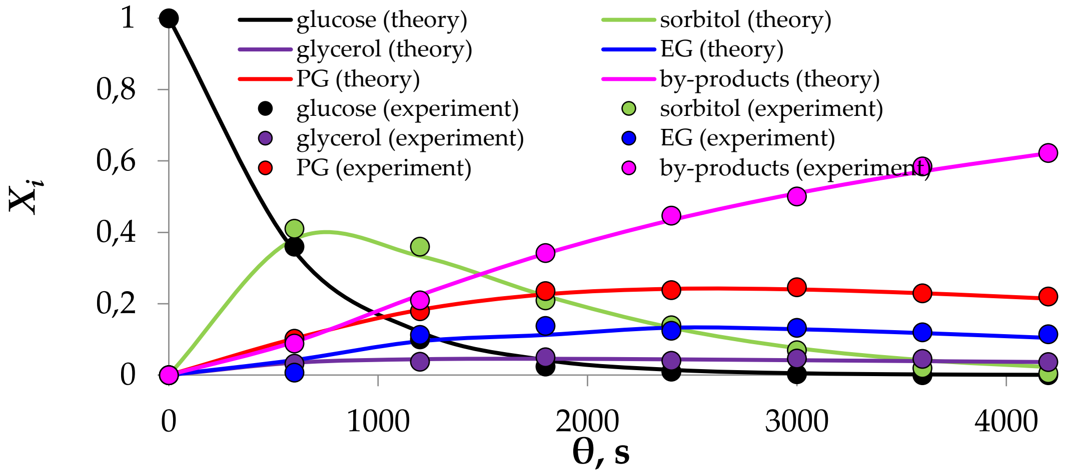

Figure 1. X~θ dependence for glucose hydrogenolysis over Ru@Fe$_3$O$_4$/HPS.

The results obtained can be used for the development of the effective technology of natural polysaccharides conversion into chemicals and fuels.

This work was supported by the Russian Foundation for Basic Research (grant № 20-08-00079)

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Features of the synthesis of stable composite materials

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Porous solid materials have found application in various fields of science and technology, for example, as adsorbents, catalysts, and supports for catalytic systems and in the processes of purification and separation of chemical compounds. The development of new classes of hybrid organic-inorganic highly ordered materials with tailored physicochemical characteristics is of extreme importance for the successful development of new technological areas [1]. Metal-organic frameworks (MOF) or porous coordination polymers (PCP), which represent a new class of porous hybrid materials, are currently considered promising hybrid materials. These materials possessing high porosity and large surface area are intensively used in the development of new technologies for gas storage and separation; active studies on the possible use of MOF as catalysts in various chemical and petrochemical processes are underway.

The aims of this study are to create MOF-199 based materials resistant to a change in the medium pH due to introduction of a coordination compound into the composition of the carbon matrix and to investigate of their physicochemical properties.

The introduction of metal-organic compounds into activated carbons considerably decrease volume of the adsorption space, because bulky organic molecules occupy almost the entire volume and do not allow even small nitrogen molecules to adsorb in the sorbent pores. Moreover, the specific surface area decreases sharply due to the contraction of micropores, while the characteristic energy of adsorption grows.

Thus, the metal-organic compound Cu-BTC (MOF-199) is stable in the pH range from 3.1 to 8.5. Upon fixation of the metal-organic complex in the carbon matrix more stable composite materials are formed which possess stability in a wider pH range of the medium. The highest stability is exhibited by the material obtained using the AR-V activated carbon as a matrix, which is characterized by the highest acidity of the surface among the tested samples. Further increase in the acidity of the surface of carbon matrices through their preliminary oxidation leads to the formation of metal-organic composite materials more resistant to acids or alkalis.

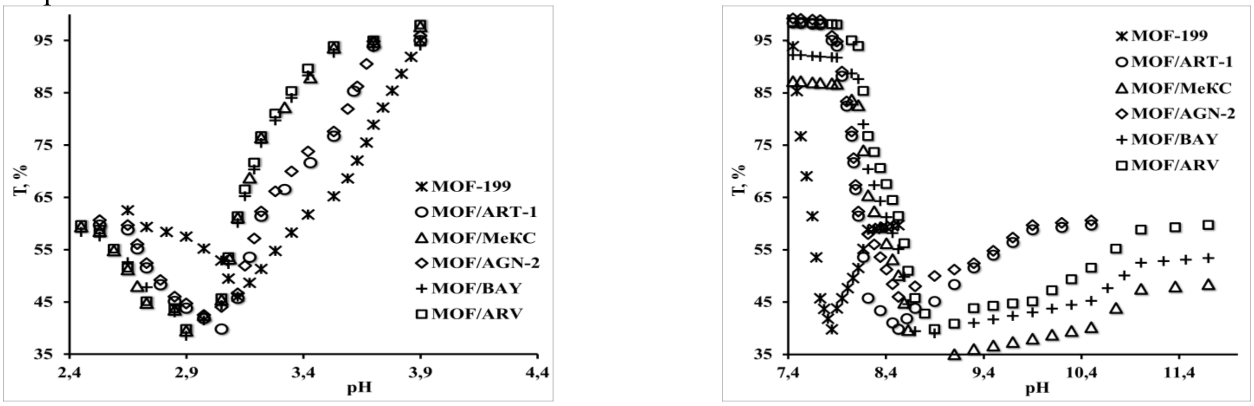

Figure 1. stability of framework compounds depending on pH at a constant wavelength: (a) acidic environment and (b) alkaline environment

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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Anion sorption in deformable xerogels of hydrated alumina – zirconia

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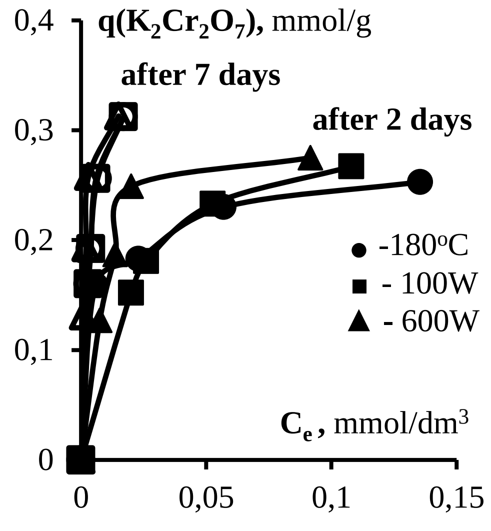
Multi oxide xerogel AZ(Yb)Sr with molar content 35%Al_2O_3–64%[97%ZrO_2-3%Yb_2O_3] – 1%SrO was obtained by sol-gel method and dried by different mode – convective (180°C) and in microwave conditions (100W or 600W of power). These three sorbents were characterized by FTIR, SEM, TG/DSC, XRD, BET/BJH methods. The xerogels adsorption capacity for organic and inorganic anions (methyl orange MO and dichromate DC) was determined by use of spectrophotometer. The adsorption isotherms of dichromate (Fig.), both after 2 and 7 days of duration correspond by the Langmuir model. The values of q_e and k are monolayer capacity and Langmuir adsorption equilibrium constants respectively (table 1).



Adsorption isotherms (25 °C)

Table 1. Langmuir parameters of adsorption isotherms (q_e, µmol DC/g, k - g/dm^3)

Drying	q_e^2	q_e^7	q_e^7/q_e^2	k^2	k^7	k^7/k^2
180°C	265	394	**1,49**	137	234	**1,71**
100W	300	387	**1,29**	68	246	**3,62**
600W	299	343	**1,15**	130	710	**5,46**

Table 2. Adsorption kinetics data (q_e, µmol/g)

	MO			DC		
Drying	q_e	q_e*	q_e*/q_e	q_e	q_e*	q_e*/q_e
180°C	0,78	15,3	**19,6**	6,8	58,8	**8,6**
100W	0,96	15,4	**16,1**	33	58,5	**1,8**
600W	0,59	16,9	**28,7**	4,9	58,5	**11,9**

The sorption results for AZ(Yb)Sr system indicate the phenomenon of xerogels auto-deformation during adsorption, which is similar to the DC sorption by AZ(Yb) xerogels. SAXS data confirmed an increase in total porosity of the xerogels AZ(Yb) in sorption medium [1].

The results of anions removal for short time (up to 10 min) and long time (1-7 days*) contact with sorbents were in a good agreement with *pseudo*-second order kinetic equation. The values of monolayer capacity q_e and q_e* are shown in table 2. There is a sharp increase in the q_e values with a stronger effect for MO in compare with $Cr_2O_7^{2-}$· The degree of sorbent structure deformation, induced by sorption, as ratio q_e*/q_e increases in the series of 100W–180°C–600W drying samples. The rearrangement of xerogels frame easily occurs with a layered material and depends firstly on the hydro gel drying conditions.

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Alumina-zirconia supports for nickel catalyst of the DRM reaction

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Dry reforming of methane $CH_4+CO_2 = 2CO + 2H_2$ (DRM catalytic reaction) is considered as promising way for converting two greenhouse gases into hydrogen, syngas and carbon nano materials like nanofibers, nanotubes, graphene. Nickel is preferable catalyst in DRM and its state and dispersion on thermally stabile metallic oxides as support plays an important role [1].

The focus of this study is to compare the activity of supported on $Al_2O_3$and Al_2O_3-ZrO_2 5% wt. Ni catalysts in DRM tests at atmospheric pressure between 500 and 750 °C.

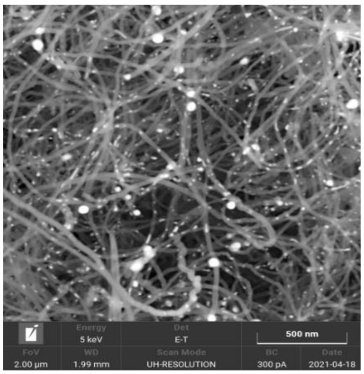
A feature of this catalytic experiment was that the AZ carrier after impregnation in nickel nitrate solution was not reduced as usual in H_2 flow, and the formation of active Ni^{+2}/Ni^0 centers occurred due DRM reaction itself with Ni^{+2}/AZ sample previously treated in CO_2 at 400 °C.

Composite carriers Al_2O_3-ZrO_2(AZ) of 35% and 65% mol% of alumina (65% and 35% ZrO_2 respectively), as well as 65AZYb with 3 mol.% Yb_2O_3 from ZrO_2content were obtained by sol-gel method with drying (180°C) and calcinations (500 °C) procedures as in fabrication of AZ ceramics` materials [2]. The final heat treatment of the catalysts was carried out in a mixture of $CH_4 + CO_2$ at 750°C. The AZ supports, fresh and spent catalysts were characterized by BET/BJH method, XRD, DTG-DSC, SEM, EDS, ESR spectra. Catalytic tests were performed in flow mode with online GC Crystal 2000M (Ar, TCD,30 mL·min^{-1}, Porapak Q).

Due to carbon formation the largest mass gain after catalysis was observed for Ni/ZrO_2 sample which was 26 times greater relative to Ni/Al_2O_3 and 3 times greater relative to Ni/65AZ. The lowest carbon deposition was in the Ni/35AZ sample. The catalyst surface is overgrown with carbon fibers; Ni particles are redispersed onto its surface (see SAM image).

Conversions X, selectivity S, molar ratio *H_2/CO* at 700°C and apparent activation energy of products formation on Ni–catalysts

№	Support	X%		S %		H_2/CO	Ea, kJ/mol	
		CH_4	CO_2	H_2	CO		H_2	CO
1	Al_2O_3	21	19	30	62	0,54	82	72
2	35AZ	43	56	44	50	0,82	35	37
3	65AZ	66	79	48	53	0,89	70	42
4	65AZYb	**72**	**90**	**50**	**47**	**1,03**	**28**	**25**



The most suitable carrier 65AZYb had a specific surface area of 213 m^2/g, a pore volume of 0.27 cm^3/g, a pore radius of 4 nm.

The higher activity of NiO/Ni particles on AZ carriers can be explained by mutual inhibition of m-ZrO_2 and α-Al_2O_3crystallization, which preserves meta stable forms of oxides and/or their solid solutions. Binary oxides found to be more effective supports as mono oxide substrates for Ni catalysts of the DRM reaction. The introduction of Yb^{+3} cations into AZ carrier for stabilization of t-ZrO_2 phase helps not only increase the sorption parameters, but also to promote the activity of Ni centers. The effect of the mixed oxide carrier on carbon deposition and the transition of the active nickel phase to carbon deposits require special study.

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Iron-containing zeolites based on HZSM-5 in catalytic process of propane cracking

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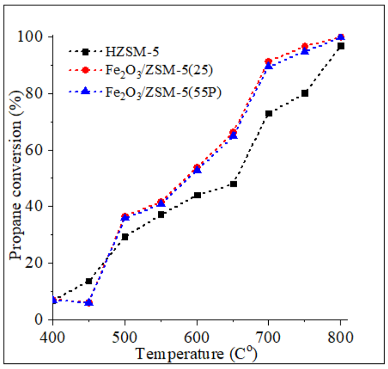
As is known, zeolite ZSM-5 exhibits high catalytic activity in propane cracking [1]. However, the addition of iron (III) oxide contributes to an increase in adsorption and, as expected, catalytic properties. It is worth noting that iron (III) oxide, like zeolites, is not expensive, therefore, iron-containing zeolite composites are not expensive materials, which accentuate the interest in these objects.

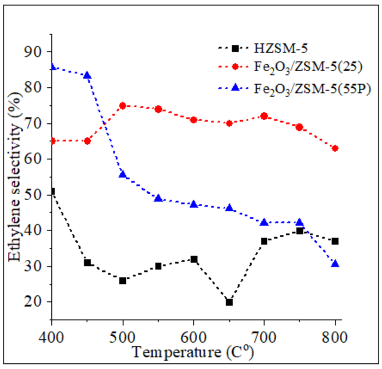
The objective of this work was to study the physicochemical and catalytic properties in propane cracking of iron-containing composites Fe_2O_3/ZSM-5(25) and Fe_2O_3/ZSM-5(55P), in which the zeolite matrix has a different modality.

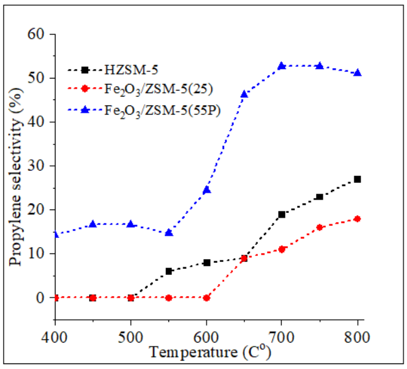
The studied objects were synthesized by chemical deposition. The ratio of iron oxide and zeolite matrix in two samples is 1:1 by weight. To do this, HZSM-5 zeolite was added to the $Fe(NO_3)_3$ solution with the appropriate modality, NaOH solution was added drop by drop while stirring until pH = 10 was reached, after which the resulting solution was mixed for 24 hours. Then the precipitate was separated from the solution by filtration, annealed in air at a temperature of 300 °C for 3 hours.

The obtained composites were characterized by the method of low-temperature nitrogen adsorption, pyridine adsorption from solution. Fe_2O_3/ZSM-5(25) and Fe_2O_3/ZSM-5(55P) have a porous surface of 155.8 and 190.4 m^2/g, respectively, with a predominance of mesopores and a single-modal pore distribution with a size of 4.2 and 3.8 nm, respectively. The adsorption of pyridine from the solution showed that the addition of iron (III) oxide significantly increases the acidity of these materials to 1.57×10^{-4} and 1.08×10^{-4} G/mol, respectively, due to the fact that iron is a Lewis acid.

Testing of the studied composites in the process of catalytic cracking of propane showed that the addition of iron (III) oxide to the zeolite framework contributes to a greater conversion of propane. At the same time, the process of destruction of propane (ethylene formation) is mainly observed regardless of the presence of iron (III) oxide on the zeolite matrix, however, more selective ethylene formation occurs on the Fe_2O_3/ZSM-5(25) composite, when, as on Fe_2O_3/ZSM-5(55P), destruction and dehydrogenation of propane compete.







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Hyper-cross-linked aromatic polymers as a basis for development of Pd-containing catalysts for cross-coupling and hydrogenation processes

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Among different polymers, nanostructured cross-linked aromatics have the greatest potential as catalytic supports due to their exceptional thermal and chemical stability and preservation of the active phase morphology [1]. Hyper-cross-linked aromatic polymers (HAPs) allow using its microporous structure for stabilization of metal nanoparticles (NPs). In this work we explore the efficiency of Pd/HAPs catalysts in cross-coupling reactions (i.e. Suzuki reaction) also in selective hydrogenation of triple carbon-carbon bond. Two types of polymers were used: (i) commercial hyper-cross-linked polystyrenes (HPS) and (ii) amorphous microporous organic polymers (MOPs) synthesized by one-step cross-linking with formaldehyde dimethyl acetal according to the procedure described elsewhere [2, 3] using different aromatic monomers (e.g. benzene, naphthalene, etc.). It is noteworthy that amorphous MOPs can be successfully used in catalysis as supports of both Pd complexes and growing Pd NPs [4-6].

In the case of Suzuki reaction carried out by the example of model compounds (4-bromoanisole and phenylboronic acid) while using HPS-based catalysts, experimental data revealed that Pd NPs can be retained in the HPS environment during the repeated runs at chosen conditions though the changes in NPs morphology and sizes distribution take place depending on the initial oxidation state of Pd. It was interesting that PdAu and PdZn bimetallic systems had advantages in Suzuki reaction as compared to monometallic Pd/HPS samples, which allowed synthesizing highly active catalysts working at Pd concentrations of about 0.14-0.28 mol.%. In hydrogenation of triple bonds, the efficiency of Pd/HPS catalysts strongly depended on the substrate nature: for acetylene alcohols synthesized catalysts were found to be active, selective and stable, while in the case of phenylacethylene as a substrate reaction proceeded homogeneously resulting in the decrease of catalyst stability.

Novel Pd-containing catalysts synthesized while using different amorphous MOPs were studied in Suzuki reaction as well as in hydrogenation of triple bond by the example of 2-methyl-3-butyn-2-ol (MBY). It was shown that Pd/MOP catalysts have high specific surface area (about 1000 m^2/g) and allows high activity and selectivity in chosen model reactions. For example, in hydrogenation of MBY more than 99% selectivity with respect to 2-methyl-3-buten-2-ol (MBE) alcohol was detected at 95% conversion at the activity of 2.9 $mol_{MBE}/(mol_{Pd}*s)$, which is promising result for unmodified Pd catalysts. In Suzuki reaction more than 97% of the aryl halide conversion (at the 94% share of cross-coupling product among the reaction products) was achieved for 60 min of the reaction while using 0.20 mol.% of palladium.

This work was supported by the Russian Science Foundation (20-19-00386)

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Ambivalent hybrid photocatalystsb on porphyrin SURMOFs and graphene oxide

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In this work, we report a new method for the synthesis of ambivalent hybrid photocatalysts comprising graphene oxide (GO) and zinc porphyrin complexes ordered into surface-attached metal organic frameworks (SURMOFs). To obtain the SURMOF/GO hybrids in a powdered form, we developed a one-pot synthesis of these materials in the GO-stabilized oil-in-water Pickering emulsions. The oxidized groups on the GO sheets promote the adsorption of metal clusters followed by anchoring of porphyrins to the surface of 2D carbon.

The results of experimental studies involving X-ray diffraction, UV-vis spectroscopy, BET nitrogen absorption, gas chromatography-mass-spectrometry and MALDI-TOF spectroscopy. The data suggest that these mesoporous SURMOF/GO hybrids can exploit two different mechanisms yielding different products of photocatalytic degradation of model organic compounds such as rhodamine 6G (Rh6G) and 1,5-dihydroxynaphtalene (DHN). The oxidation through photoinduced generation of singlet oxygen on porphyrin centers occurs in the presence of oxygen. In anaerobic conditions, the catalysts can promote reduction by a direct electron transfer to the substrates in the SURMOF pores. Their size controls the efficiency of the anaerobic process. The SURMOF/GO with the pore size of 1.6 nm can transform both Rh6G and DHN (fig. 1), whereas the material with 1.1-nm pores is active only with respect to the small DHN molecules. The results provide a rational basis for the substrate-selective GO-based hybrid photocatalytic materials integrated with SURMOF components with tunable porosity [1].

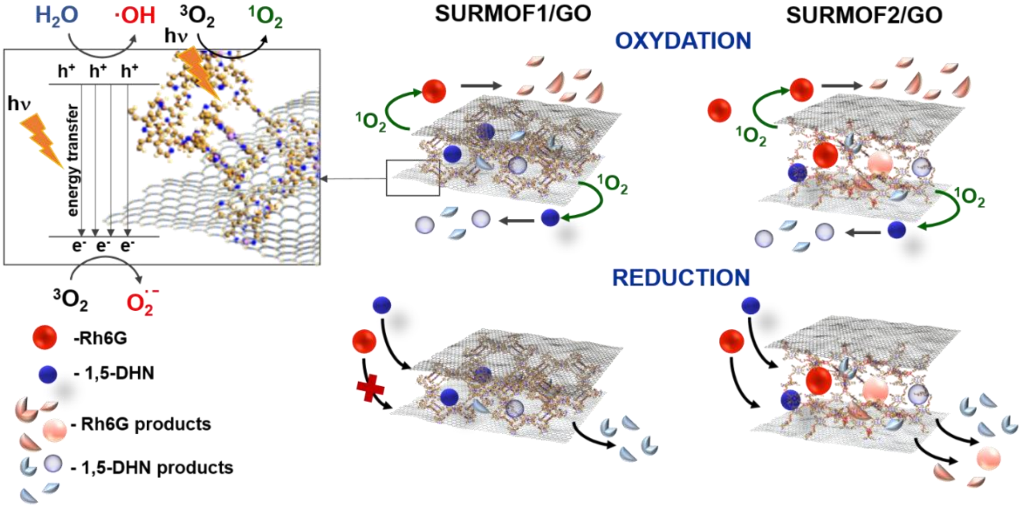

Fig. 1. Schematic illustration of the proposed size-selective mechanism of photodestruction of Rh6G and DHN in the presence of the SURMOF1/GO and SURMOF2/GO under aerobic and anaerobic conditions.

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Pectin coated liposomes as a potential carrier for pulmonary delivery of novel antitubercular drug

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Oral and systemic administration of antitubercular drugs can be complicated due to the toxicity to cells and tissues that are not infected by Mycobacterium tuberculosis. Delivery of antitubercular drugs via polymer coated or surface decorated liposomes directly to the infected cells has the potential to maximize efficiency and minimize toxicity [1]. It is reported that surface decoration of liposome by different biopolymers can improve the stability of liposomes in the storage condition and in the biological systems [2].

The aim of the present work is to develop and characterize pectin coated liposomes as a potential for delivery of new antitubercular drug to the lung. The antitubercular compound under research is 3- (3,5-dimethylpyrazole-1-yl) -6-(isopropylthio) imidazo [1,2-b] [1,2,4,5] tetrazine, which was synthesized in the Institute of Organic Synthesis, Russian Academy of Science. Several formulations of this drug loaded positively charged liposomes were developed and characterized in terms of particle size (PS), polydispersity index (PDI), zeta potential (ZP) and entrapment efficiency (EE%). The results showed that the sample with Tween 80 (0.1% w/v) that hydrated with 1 % sugar solution has mean PS about 205.3 nm ± 3.94, PDI 0.28 and ZP about +36.37 mv.

The optimum liposome formulation was prepared and coated with several concentrations of previously prepared low methoxylated pectin solutions: 0.01, 0.05, 0.1, 0.3 and 0.5% w/v. The mean PS ranged from 292.67 nm to 853.67 nm with PDI from 0.586 to 0.722 by increasing the concentration of LMP solution. ZP was from +42.63 to -42.67. The liposomal preparation coated with 0.1 % w/v LMP solution showed the most physically stable one. In more diluted liposomal preparations and diluted LMP solution (lipid to LMP ratio 0.2: 0.02), the mean PS was 248.3 nm, PDI 0.28 and ZP -27.5. Transmission electron microscopy (TEM) and in vitro release studies of pectin coated liposomes was performed to demonstrate surface characteristics and investigate the effect of LMP in the release of tetrazine derivative in comparison to uncoated liposomal formulations.

We planned to introduce our formulation in an aerosol or nebulizer for pulmonary inhalation. Further studies will carry out to determine the aerodynamic diameter, mucoadhesive properties and the pharmacokinetics of the formulation after inhalation. In conclusion, pectin coated liposome might be a promising drug delivery system for pulmonary delivery of antitubercular drug.

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Study the role of carbon containing materials as support for $KCoMoS_2$ catalysts in HAS from syngas

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Higher alcohols synthesis (HAS) (C1-C5) from syngas remains a cost-effectively appealing technique for production chemicals and fuels [1]. HAS over alkali-doped MoS_2 catalysts, promoted with cobalt has shown great potential for large scale studies [2]. The comparative study of the catalytic behavior of K-modified $CoMoS_2$-catalysts supported on Al_2O_3 and carbon covered alumina (CCA). The supports and catalysts were characterized by N_2 adsorption-desorption isotherms, pyridine adsorption UV procedure, SEM, EDX, and TEM. The effect of different carbon-containing materials, used as supports for transition metal sulfide (TMS) based catalysts; on catalytic properties for synthesis gas conversion to alcohols has been studied. The supports used are γ-Al_2O_3, carbon-coated alumina (CCA), and two types of commercial activated carbons (AC): AG-3 and BAW. Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM), X-ray Fluorescence (XRF), X-ray Photoelectron Spectroscopy (XPS), UV-spectral analysis of Pyridine adsorption, and N_2 physisorption were used to characterize the supports and supported $KCoMoS_2$ catalysts. Coating alumina with carbon increases the selectivity to alcohols, but the AC supported catalysts show even higher alcohol selectivity. The obtained experimental results show that increase of micropore surface area and micropore volume of supported-$KCoMoS_2$ catalysts leads to increased CO conversion, total liquid yield, and selectivity to ethanol, methanol, and propanol-1 (simple linear-chain alcohols). Mesoporous structures were found to be more selective to the hydrocarbons and branched-chain alcohol such as i-butanol and i-pentanol alcohol (Figure 1).

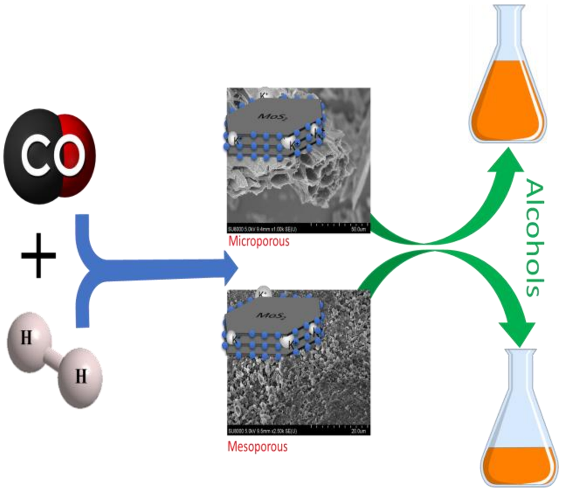

Fig. 1. Effect of textural characteristics on the catalytic performance of supported-KCoMoS2 in HAS from syngas

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HAS from syngas over supported and modified TMS catalysts: Effect of novel fiber and powder commercial activated carbon supports

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The design of molybdenum sulfide based catalysts for alcohol production from syngas attracts interest both of academic and industrial research because of several reasons. Alcohols have extensive applications as precursors of surfactants, fragrance compounds, plasticizers, extragents, etc [1]. In the present study, a series of KCoMoS catalysts with compositions of $K_{10}Co_{3.6}Mo_{12}$ supported over novel commercial activated carbons such as powder materials (DAC and OBC-1) and fiber materials (fabric active sorption (TCA) and nonwoven activated material (AHM)) were prepared and characterized by Brunauer-Emmett-Teller (BET), X-ray fluorescence (XRF), scanning electron microscopy (SEM), SEM−energy dispersive X-ray (EDX), and transmission electron microscopy (TEM). The catalytic activities for higher alcohol synthesis from syngas, conducted at $T = 300{-}360$ °C, $P = 5$ MPa, GHSV = 760 L h^{-1} (kg cat)$^{-1}$, and H2/CO = 1.0, were investigated. Cat-TCA and Cat-AHM have shown a filamentous morphology with a strip axial arrangement and that a few longitudinal grooves and many irregular particles are distributed on the fiber surfaces (Figure 1). The degree of entanglement of the strip axial arrangement in AHM was found to be more than that in TCA, thus leading to form tangled MoS_2 slabs on AHM and long linear slabs on TCA with long rim sites [2]. The obtained results revealed that the CO conversion increases in the order Cat-TCA < Cat-OBC- 1 < Cat-DAC < Cat-AHM. Ethanol, propanol-1, and methanol are the most predominant alcohol products in the collected liquid products, with the byproducts containing mainly butanol-1, isobutanol, amyl alcohol, and isoamyl alcohol. Cat-DAC and Cat-OBC-1 show higher selectivity toward C_{3+}, C_{4+}, propanol-1, butanol-1, isobutanol, and amyl alcohol-1 than Cat-TCA and Cat-AHM. For powdered activated carbons, microporous catalysts inhibited isomerization because the catalyst that contains the highest micropores (Cat-DAC) produced a considerable amount of linear alcohols compared with Cat-OBC-1.

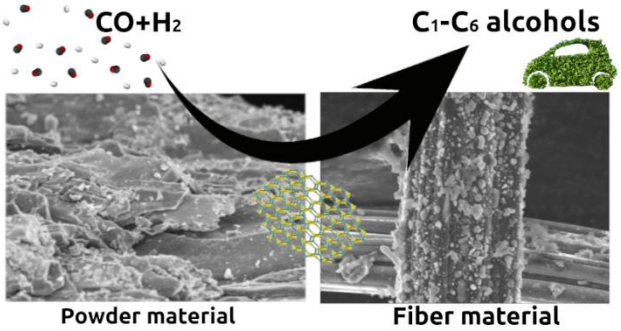

Figure 1. The role surface morphology of powder and fiber activated carbon in production of higher alcohols.

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Production of higher alcohols from syngas and ethanol using K-modified TMS–catalysts supported on graphene nanosheets

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The comparative study of the catalytic behavior of K-modified $CoMoS_2$-catalysts supported on Al_2O_3, carbon covered alumina (CCA) and graphene coated alumina (GCA containing 0.4, 1.2, and 1.7% of graphene) in synthesis gas and ethanol conversion (separately) to higher alcohols (HAS) and other oxygenates has been carried out. The supports and catalysts were characterized by N_2 adsorption-desorption isotherms, pyridine adsorption, SEM, EDX, and TEM. In HAS from syngas, the catalyst supported on GCA materials showed better catalytic performances than the catalysts supported on alumina and carbon coated alumina (Cat-GCA > Cat-CCA > Cat-Al_2O_3). The spectroscopic and acidic results have established that the homogenous uniform coating of alumina by graphene nanosheets follows the order: GCA1 (1.7%) > GCA2 (1.2%) > GCA3 (0.4%). The yield of ethanol has a positive correlation with graphene wt. % in GCA.

Catalytic performance of $KCoMoS_2/Al_2O_3$ improved after coating Al_2O_3 by carbon and graphene nanosheets (Cat-Al2O3 < Cat-CCA (1.7%) < Cat-GCA (1.7)). The carbon materials decreased the interaction between alumina and the KCoMoS active phase (Figure 1), which decreased adsorption of hydride hydrogen and accelerated hydrogenation.

In ethanol conversion, graphene attenuate the interaction of the support/active site $KCoMoS_2$ and with it its selectivity towards dehydrogenation/ condensation reactions. The GCA1 supported catalyst exhibits low activity for the water–gas shift (WGS) reaction compared to its counterpart. Explanations of the observed phenomena have been suggested [1].

These findings give deeper insight into the mechanism of HAS synthesis over supported transition metal sulfide-based catalysts. The obtained results have been used to design the mechanism of the synthesis gas conversion over the K-modified CoMoS catalyst [2]. The KCoMoS-based catalysts are expected to be suitable for large scale production of alcohols from syngas.

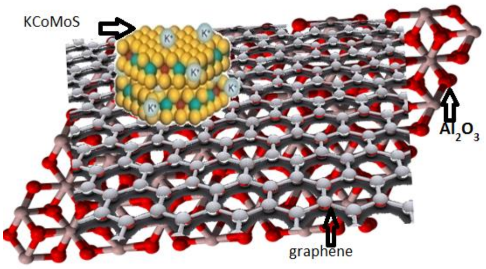

Figure 1. Role of graphene in the GCA carrier for conversion of syngas via the $KCoMoS_2$ catalyst.

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Visible light driven photocatalytic activity of 3d-doped tin dioxide nanoparticles for wastewater remediation: main affecting factor and way for improvement

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Significance of the wastewater treatment has been gradually increasing lately and it becomes a main improvement tool of sanitarian and epidemiological state of the environment. The need for novel ecological water remediation approaches has caused an active development of semiconductor photocatalysis, an advanced technology for the environment cleaning from cyclic organic compounds under visible light irradiation. However, the improvement of Vis-light photocatalytic activity as well as the main affecting factor is still under discussion.

We synthesized sub-5 nm spherical SnO_2-based nanoparticles (NPs) (considered as the simplest material with photocatalytic activity under visible light) with rutile crystal structure, tolerant to substitution even at high concentration of dopant. The NPs parameters were varied by introducing 11 and 33 mol% of dopants with different radius (Ni^{2+}, Cu^{2+}, Co^{2+}), and by regulation of NPs formation rate that were altered by acidic and neutral pH values. As-prepared samples were fully characterized using different techniques (XRD, FTIR, TEM, SSA measurement, XPS, Raman spectroscopy, DLS, UV-adsorption spectroscopy, quantum-chemical calculations). The lattice parameters, crystallite size, zeta-potential, hydrodynamic size were determined. The presence of low-intensity energy level in band gap, which could provide the photocatalytic activity under vis-light irradiation were demonstrated. The amount of oxygen vacancies and defects and the dopant position in SnO_2 crystal structure were found using our original approaches.

Based on the detailed study of photocatalysis according to our proposed protocol, including the calculation of the interaction energies between NPs surface and pollutant molecule followed by the deep investigation of NPs and solutions after treatment, it can be concluded that, among all the factors affecting the photocatalytic activity in the case of doped tin dioxide, the ratio of oxygen vacancies to defects is the main one. For Cu and Ni-doped samples the photodegradation percent vs ratio dependencies are linear, and for Co-doped samples it has convex shape. For all the samples together the tendency towards an increase of photocatalytic activity with a simultaneous increase in the number of oxygen vacancies and a decrease in the number of defects can be clearly seen.

For the optimal sample Co-doped SnO_2, almost complete degradation of the dye (84%) is achieved after 60 minutes under irradiation of commercially available cheap bulb, for the Ni-doped samples, which produce mainly superoxide radicals during the irradiation, the antibacterial effect against E.Coli was demonstrated.

The work is financially supported by the Russian Foundation for Basic Research (project no. 20-03-00762 A). Scientific research were performed at the research park of St. Petersburg State University: Centre for X-ray Diffraction Studies, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre, Centre for Physical Methods of Surface Investigation, Computing Centre, Centre for Optical and Laser Materials Research, Interdisciplinary Resource Centre for Nanotechnology

Computational and experimental methodologies for studies of Pd and Pt (pre)catalysts

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Catalytic cross-coupling and functionalization reactions are often successfully approximated with a classic one-active-center model, and the corresponding mechanisms are successfully deciphered with NMR and mass spectroscopy, as well as with quantum chemical modeling. However, as others and our groups showed, these reactions exhibit many non-classic off-cycle intermediates and non-classic active centers [1-3]. Deciphering the underlying molecular mechanisms of organic reactions is a complex task for which we developed a number of tools and methodologies [3-6].

Our new findings in the field of quantum chemical modeling of Pd and Pt (pre)catalysts of cross-coupling and functionalization reactions will be presented. We will discuss how quantum chemical modeling can be combined with machine learning and NMR and mass spectroscopy to gain insight into (pre)catalytic species' chemical structure.

This work was supported within the project MK-2955.2022.1.3. M.V.P. thanks Anton Bondarenko, Yulia Vlasova, Eugenia Ondar, Valentina Ilyushenkova, and Valentine Ananikov for help, collaboration, and fruitful discussions

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Co-based porous alloys: synthesis, physicochemical properties and catalytic testing

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Bimetallic nanoalloys have properties different from monometallic counterparts and can be used in medicine (magnetic hyperthermia, targeted drug delivery) and as magnetic materials. Among the variety of nanoalloy structures, porous nanoalloys stand out, which are promising materials due to a larger active surface, a larger number of active sites, high conductivity, and an extensive network of channels that promote ion diffusion. The special properties of platinum metal alloys with a porous structure are stability, corrosion resistance, and the ability to catalyze various chemical processes. By varying the composition and synthesis conditions of the alloyed porous catalyst, one can change its morphology and control its activity.

One of the processes in which porous nanoalloys of platinum metals can exhibit high catalytic activity is the synthesis of carbon nanofibers (CNF) by the decomposition of hydrocarbons on metal catalysts, known in the literature as CCVD – Catalytic Chemical Vapor Deposition [1]. It is known that metals of the iron family can be active catalysts of this process, and the alloying of these metals with others makes it possible to improve their catalytic properties. The structure of CNF and their textural characteristics are determined by the reaction conditions, composition, and morphology of the catalyst used. Thus, the development of efficient catalysts for the synthesis of CNF with desired physicochemical properties and structural characteristics seems to be an urgent scientific problem.

The report presents a method for the synthesis of porous alloys by reductive thermolysis under controlled conditions of specially prepared precursors ("single-source precursors") containing all components of the synthesized alloy in the required proportions. The ratio of components, phase composition and microstructure of the resulting alloys were studied by a number of physicochemical methods: ICP-AES, AAS, XRD, TEM, SEM, low-temperature nitrogen adsorption by the BET method.

The activity of cobalt porous alloys containing other transition metals (Cu, Ni, Fe, Pt, Pd, Mo, W) was screened for the decomposition of hydrocarbons (ethylene, propane-butane mixture). The dependence of the activity of catalysts on the content of the additional metal, the type and temperature of their thermolysis of the initial precursors has been studied using the example of the most catalytically active Co-Cu and Co-Pd alloys.

This work was supported by the Russian Science Foundation (grant № 21-13-00414)

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Novel heterogeneous catalytic systems for the basic processes of organic chemistry

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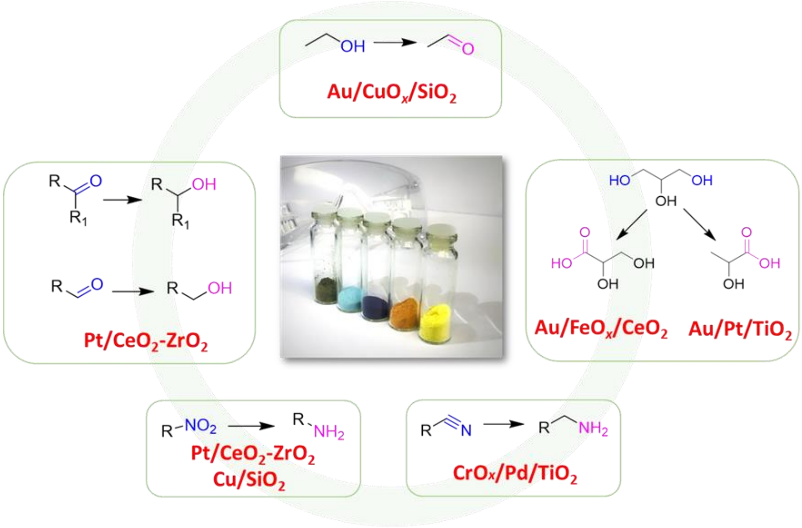
Modern organic chemistry has been turning to be more environmentally friendly and energy efficient. One of the key points of such a transformation is implementation of heterogeneous catalysis in basic organic processes, i.e., oxidation and reduction reactions. At the same time, the common industrially available catalysts are not effective for fine organic synthesis because of the low selectivity and the need in harsh conditions to provide the target reaction. Here we want to present some new mono and -bimetallic catalytic systems, which were developed and prepared in our group by original methods, for the reactions of selective oxidation and hydrodeoxygenation of bioavailable alcohols [1-3], low-temperature hydrogenation of carbonyl, nitro compounds, as well as nitriles [4-6], realized with the requirements of “green” chemistry and energy efficiency.



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Feasibility of in-situ combustion technique for recovering heavy oil with high sulfur content

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The use of catalysts is considered an effective method to improve the efficiency of the in-situ combustion process (ISC) for heavy oil recovery. Various oil-soluble metal-based catalysts were evaluated using this small-scale combustion tube for the ISC process for heavy oil recovery. In-situ combustion (ISC) is a promising heat recovery oil (EOR) recovery method for heavy oils. However, its field application is still limited due to low combustion efficiency, difficulty in ignition, unstable combustion front. To improve the success of the ISC process, we evaluated the effectiveness of copper-based oil-soluble catalysts for combustion catalysis [1].

It was found that the ISC process can effectively improve heavy oil recycling by about 49%, which is evident by a significant decrease in viscosity and an increase in API. The presence of copper-based oil-soluble catalysts can further improve the quality by significantly reducing the resin and asphaltene content [2-3].

A medium porous thermal effect cell (PMTEC) is designed to study the catalytic combustion of heavy oil in a porous medium under air flow. An intuitive combustion tube (VCT) was developed to study the catalytic effect of the catalyst on the ISC process, including improved combustion front diffusion, on-site updating of heavy oils and oil recovery. However, in situ oil upgrades in the ISC process are achieved by copper-based catalysts at the expense of an unstable combustion front and less oil recovery (about 9% less than without catalysts).

All these results showed that the copper-based oil-soluble catalyst has great potential to improve the efficiency of the ISC process and to update the oil in situ. Applying it can help improve success. The presence of copper-based catalysts not only further updates the oil, but also improves the stability of the combustion front and results in more oil recovery (about 8% higher without catalysts). PEMTC experiments also showed that the combustion temperature of heavy oil combustion in a porous medium in an air stream by a copper-based catalyst was reduced by about 55°C. VCT experiments showed that in the presence of a copper-based oil-soluble catalyst, the combustion rate spreads faster, the oil recovery was 9% faster than without the catalyst, and a deep oil was obtained in situ with a significant viscosity reduction.

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Polystyrene composites reinforced with fungi mycelium

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Polymer composite materials have a number of excellent properties, in particular, they have high strength and wear resistance, good tunable physical, mechanical, thermal properties, etc. However, their main drawback is non-biodegradable performance [1].

Natural fibers can be used as a reinforcing filler to synthetic polymers to improve their biodegradability, mechanical and physical properties, to ensure their compatibility with other polymers. The most common biodegradable additive to polymers is cellulose. Cellulose obtaining is associated with non-ecological and energy-consuming operations, which limits the widespread application of materials based on it. Materials based on the self-growing mycelium of basidiomycetes fungi are promising materials with ecofriendly profile [2].

Mycelium has a porous structure consisting of fibrous filaments called hyphae, which vary in diameter from 1 to 10 microns depending on fungi strain and cultivation conditions [3]. So, mycelium fibers can be used as matrix filler for polymer materials.

In this work, mycelium-based polystyrene composites were synthesized. Initially mycelium cultivation was carried out and then styrene polymerization on the fungi fibers was performed. The influence of the component ratio in the composite on the properties of the final material was estimated. The morphological, physical, mechanical properties and biodegradation ability of mycelium-based polystyrene composites were studied.

The authors acknowledge the support from the Ministry of Science and Higher Education of the Russian Federation (subject number FSZE-2022-0003)

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Self-assembly of porphyrin-based metal-organic framework on planar inorganic matrices

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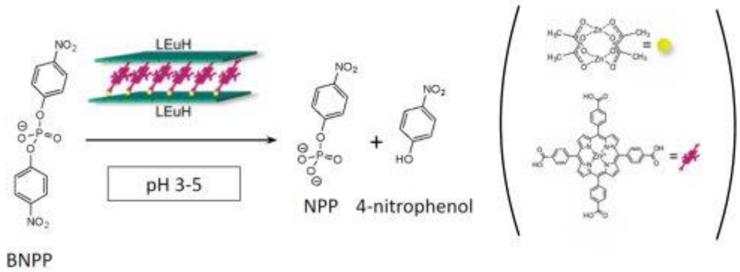
Porphyrin-based metal-organic frameworks (MOF) are the class of coordination polymers highly useful for applications in gas separation, sensors and heterogeneous and photocatalysis due to combination of coordination chemistry and optical properties of porphyrin complex and porosity of metal-organic ordered structure. Nevertheless, weak coordination bonds in these materials can undergo decomposition in the chemically active or aggressive environment and do not provide sufficient stability of materials. A possible strategy for solving this problem is the assembly of MOFs on the solid surface of planar inorganic particles. This approach makes it possible to integrate the functional properties of porphyrin MOFs with those of supporting inorganic solids in a single hybrid structure. In this work we realized this idea through the intercalation of 5,10,15,20-tetrakis(4-carboxyphenyl) zinc porphyrinate (ZnTCPP) and a binuclear complex of zinc acetate as the MOF components into the layered europium (III) hydroxychloride (LEuH) as planar inorganic matrix with anion-exchange, coordination and luminescent properties. [1]

We studied the catalytic activity of the material in a course of the hydrolysis of bis(4-nitrophenyl) phosphate, which is widely used as a model reaction for DNA phosphodiesterase. By studying the kinetics of the catalyzed hydrolysis with the UV-vis absorption spectroscopy, we showed that the intercalated hybrid exhibits synergetic catalytic effect on the process when compared to the activity of the non-intercalated LEuH matrix and ZnTCPP-based MOF. To investigate the origin of this synergy, we studied the changes in the structure and chemistry of the catalyst by using Raman, FTIR and UV–vis spectroscopies, MALDI-TOF spectrometry and the X-ray diffraction.



The obtained results suggest that the hybrid material showed symbimetic properties, that is, mimicking the behavior of biological symbionts, due to the mutual stabilization of the components in the reaction media. The mutual stabilization of the components provides the catalytic synergy of the hybrid material since only mutually integrated porphyrin MOF and LEuH can efficiently catalyze the hydrolysis of organic phosphates. We believe that this strategy can advance rational design of the wide range of efficient catalytic hybrid materials based on various inorganic planar matrices and organic functional compounds.

This work was supported by the Russian Foundation for Basic Research (grant 18-29-04026 MK)

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Highly efficient dual-metal CoCu catalyst for ethanol formation from syngas via targeted chemical and electronic structure modification

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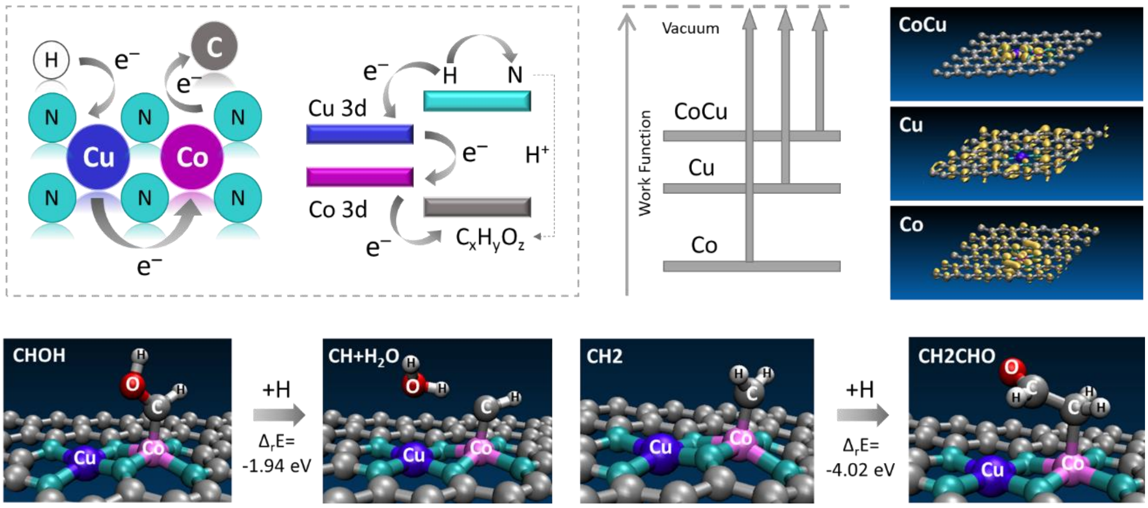
The formation of long-chain hydrocarbons and alcohols from syngas, obtained by processing natural gas, coal and other raw materials, is an important technological task. To accomplish it, a catalyst enabling this reaction to occur selectively and efficiently at a moderate gas pressure and temperature is required. Its rational design via targeted modulation of the chemical and electronic structure allows for decreasing the energy barriers and facilitating the electron exchange process in the redox reactions, such as CO hydrogenation. A powerful approach for this purpose is the mixed-metal strategy [1,2] allowing to adjust the material's reducibility characteristics [3,4]. In this work, it is illustrated using molecular modeling on an example of a dual-metal CuCo nitrogen-doped graphene catalyst (CuCo/C-N) for ethanol synthesis [5]. It is shown that the Co site is responsible for stabilizing CH_x moieties, Cu favors O-end adsorption of intermediate species, while surrounding N atoms act as a hydrogen tank. The synergistic effect of Cu and Co induces a peculiar electronic structure, facilitating the electron accumulation on the metal sites and their injection towards the adsorbates. A barrierless C–C coupling and an alleviated proton-assisted C–O dissociation are thus enabled. The resulting catalyst demonstrates excellent performance with the 81.7% CO conversion and the space-time yield 851.8 mg/g·h, placing it among the best in this class. The unraveled working principles can serve to design other catalysts of similar chemical reactions.



The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University. The Siberian Branch of the Russian Academy of Sciences (SB RAS) Siberian Supercomputer Center is gratefully acknowledged for providing supercomputer facilities.

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Features of the kinetics of impregnation of a polymer carrier trialkylamine

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The immediacy of the problem under study is due to the lack of data on the kinetics of polymer carrier impregnation with extraction agents. The aim of this investigation is obtaining of the kinetic characteristics of the impregnation of a polymeric macroporous carrier – a weakly acidic cation resin with carboxyl groups – with trialkylamine and its solutions in acetone. The integral kinetic curves of the extraction agent adsorption on the carrier were obtained. This allowed estimating the time of equilibrium by the limited solution volume method. This time was 25-30 hours, decreasing with the application of a dilution agent and with the increase in temperature.

The kinetic impregnation characteristics were calculated by means of the pseudo-second-order, Elovich, and internal diffusion models. The pseudo-second-order model describes the experimental kinetic data with a high correlation degree (R^2 0.995-0.997) and points out that interaction with two sorption centres possibly takes place with the adsorption of a single trialkylamine molecule. The impregnation rate constants via an extraction agent were calculated using all kinetic models (Table).

Table. Rate constant values of the TAA carrier impregnation

Pseudo-first-order model		Pseudo-second order model		Internal diffusion model		Elovich model	
k_1, min^{-1}	R^2	k_2, $g \cdot mg^{-1} \cdot min^{-1}$	R^2	k_p, $mg \cdot g^{-1} \cdot min^{-0.5}$	R^2	β, $g \cdot mg^{-1}$	R^2
Trialkylamine (295K)							
0.0011	0.862	0.00025	0.994	2.79	0.829	0.085	0.967
Solution of trialkylamine in acetone (295K)							
0.0019	0.592	0.00017	0.986	2.12	0.796	0.059	0.937
Trialkylamine (323K)							
0.0037	0.573	0.00091	0.998	1.37	0.745	0.133	0.902

Based on the apparent activation energy magnitude (37±14 kJ/mol), it can be assumed that diffusion is the rate-limiting step of the impregnation process.

It was investigated the impregnation of tributylphosphate of polymeric carrier.

This material can be useful for creating impregnates containing extraction agents of various classe.

Structured micro-fibrous catalysts: flexibility as a source of mass transfer intensification

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The use of the geometrical structuring approach opens the way for creation of new highly efficient types of catalysts with improved apparent activity, high mass transfer efficiency and low pressure drop. Such structuring is efficient when it involves all scale levels of the catalyst: from active component structure at the nanometer level and up to macro levels corresponding to the structured catalyst beds and catalytic reactors. The important challenge in this area is integration of all structures at different scale levels into multi-scale system with the best possible inter-level interaction (fig. 1).

Micro-fibrous supports may be used for creation of new catalysts with efficient integration of multi-scale structuring. The most widely known and studied systems of this class are the glass-fiber catalysts (GFCs), using the glass micro-fibers with a typical thickness of few micrometers as basic support, demonstrating advantageous performance in various catalytic reactions like deep oxidation of volatile organic compounds, selective oxidation of H_2S, oxidation of SO_2 and others [1].

The experimental study included the measurement of the apparent reaction rates in the GFC packing of different structure. Test reaction of deep oxidation of toluene in air at Pt-containing GFC was used.

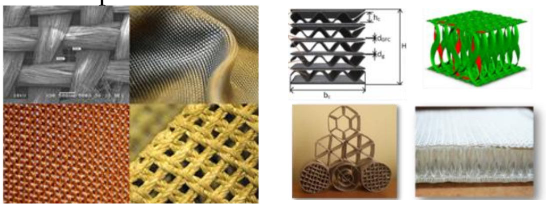

Fig. 1. Different GFCs (left) and GFC packing structures (right).

The toluene oxidation reaction appeared to be fast and, to the significant extent, limited by diffusion limitations – the apparent reaction rate visibly depended upon the gas fluid velocity and catalytic cartridge geometry. In general, in the combination of the practically important characteristics (mass transfer intensity, use of the potential of the active components, specific pressure drop) the structured GFC cartridges seem to be one of the most efficient catalyst shapes (or even the most efficient) among all known types of catalytic structures. The highest mass transfer efficiency was observed at lemniscate type GFCs.

Interesting that mass transfer in GFC cartridges is higher than that for wire mesh cartridges with similar geometry. It was shown that beneficial performance of GFCs is directly connected with their mechanical flexibility: under the in influence of moving reaction fluid the catalyst cloth may undergo mechanical fluctuations, resulting in the higher turbulization of the flow and, consequently, the better mass exchange. In case of lemniscate GFCs, such fluid/catalyst interaction may even lead to changing of catalyst shape, with increase of external mass transfer interface surface at higher gas velocities. Such phenomena are impossible for packed beds of any conventional solid catalysts.

In the overall performance, the catalysts on the base of micro-fibrous supports with purposeful multi-scale structuring at the different scale levels and efficient inter-level interaction seem to be of the most promising among all existing and prospective multi-scale catalyst structures. The additional gain in mass transfer efficiency is caused by their mechanical flexibility and improved interaction with reaction fluid, this being quite a novel effect in respect to structured catalyst beds.

The most promising application areas for such catalysts are the fast reaction in the gas and liquid phase, as well as reactions, where selectivity is sensible to diffusion limitations.

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Effect of zinc oxide-based shell on the magnetic properties and MRI signal of stabilized magnetite nanoparticles

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Magnetic Resonance Imaging (MRI) is a non-invasive imaging technique that produces multiplane detailed anatomical images. The image in MRI can be obtained due to such important property of tissues as proton relaxation times (T1 and T2) therefore there are two main MRI imaging modes – T1 and T2-weighted images. Fe_3O_4 ferrimagnetic nanoparticles are one of the most promising materials to T2 contrast agent production due to their superparamagnetic properties, ability to shorten the transverse proton relaxation (T2) and approved biocompatibility. However, Fe_3O_4 magnetic nanoparticles are not widely used in clinical practice probably due to the surface oxidation, which lead to aggregation and reduced sensitivity in MRI.

To solve this problem it was proposed to protect magnetite core with zinc oxide shell and thereby increase nanoparticles chemical and thermal stability. Magnetic core-shell nanoparticles (MNPs) Fe_3O_4@ZnO are most suitable for biomedical applications material due to their improved stability, less cytotoxicity, biocompatibility and expected excellent stability. In our previous work [1] it is shown that the parameters of hydroxyapatite shell could affects the NPs MRI contrast, and in recent study we focused on the examination of such dependencies in the case of zinc oxide shell. To obtain MNPs with different shell parameters we engaged two different synthesis procedures (sequential and simultaneous reagent adding) and used three different temperatures to impact on shell formation process.

Morphological parameters of were characterized using XRD, FTIR, HR-TEM, BET, XPS and Mössbauer spectroscopy, VSM and TGA-DSC measurement are also be done. It was shown that magnetite core had the average size of 12 nm and shell thickness varied from 2.1 to 2.9 nm depending on synthesis procedure. The saturation magnetization slightly variates from 57 to 63 emu/g and blocking temperatures diapason was found to be from 337 to 393 K. All samples have not been oxidized according to the TGA-DSC curves, thus, ZnO shell protects well the magnetite surface. Joint consideration of all received data and computer simulated ZFC-FC curves made it possible to determine that not only the shell thickness but also its structure influences on the MNPs behavior through the affecting the core surface and formation of the intermediate layer. All correlations between studying parameters were revealed and described.

MRI *in vitro* experiments have shown that relaxation time T2 varies from 5.7 to 13.3 ms, determined by shell density and falls with the shell density increase which opens up opportunities to its variation.

Scientific research was performed using the St. Petersburg State University Research Park equipment (Chemical Analysis and Materials Research Centre, Centers for X-ray Diffraction Studies, Innovative Technologies of Composite Nanomaterials, Optical and Laser Materials Research and Magnetic Resonance). The authors would like to acknowledge Vladimir Potanin Foundation Scholarship Programme for providing financial assistance

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Chemical technological processes intensification by vibroacoustic fields

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At present, the problem of chemical-technological processes intensification that form chemical-technological systems in the Russian Federation requires a comprehensive solution. A significant number of foreign companies have left the Russian market, which imposes significant restrictions on the use of foreign patents, licenses and technologies. Nevertheless, the existing reality is formed by the need not only to import substitution of the chemical industry individual products, but also to develop fundamentally new technologies based on the results of fundamental research in the field of physical and chemical processes.

One of the approaches for the intensification of various chemical-technological processes is the use of low-energy impacts, which are environmentally friendly, energy- and resource-saving. One of such influences is the vibroacoustic physical fields of the infrasonic and the beginning of the sound range, which are characterized by a small amplitude of the hardware device that generates such influences. Based on many years of research, such effects can affect various chemical processes, such as emulsification, dispersion, homogenization, degassing, etc. [1-3]. Recent works in the field of research of low-frequency sonochemical processes suggest that infrasonic vibroacoustic effects can intensify surface treatment processes [4] and change the rate of redox reactions [5].

However, despite the existing results on the possibility of degassing with the help of low-frequency vibroacoustic fields [1], the team obtained results on the fundamental possibility of liquid gasification and absorption of gas located at the liquid-gas interface under external low-frequency exposure. Using the example of indigo carmine + reducing agent model system, it has been established that low-frequency fields can lead to aeration of reaction media similarly to the bubbling process. For the technological application of the water-soluble gas absorption process under vibration action at the liquid-gas interface, the result of this work is a fundamental basis that contributes to the formation of the scientific knowledge basis in the field of low-frequency and low-energy sonochemistry.

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Self-assembly of semiconductor nanowires from lutetium bis-phthalocyanine for recyclable organic electronics

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Herein we suggest a supramolecular strategy to obtain long conductive nanowires from phthalocyanines without doping. We use cooperative self-assembly of lutetium crown-substituted double-decker phthalocyaninate (LuL_2) via crown-assisted coordination with K^+ for fabricating supramolecular nanowires with an average length up to 50 μm, thickness down to 5 nm. The conductivity of the film obtained with deposition of nanowires from the dispersion in chloroform under slow evaporation of the solvent is 11.4 $S\cdot cm^{-1}$. This value is the highest measured in non-doped phthalocyanine assemblies. The ability of crown-groups of the LuL_2 complex to interact with K^+ ions dictate the full conjugation of macrocyclic rings of phthalocyanine complexes in 1D aggregate and the efficiency of charge transfer along the nanowires.

The high sensitivity of K^+-LuL_2 assemblies to the electric field makes it possible to use field-assisted method for the arrangement of the already prepared nanowires on solid supports. The voltage applied between the electrodes guides the oriented deposition of the already formed nanowires from their solution onto the surface. The nanowires are oriented along the field lines from anode to cathode immediately after field switch on. The deposition proceeds within 20 minutes yielding the continuously ordered layer of nanowires on the support. The packing density of the nanowires within the layer can be tuned by varying the concentration of K^+-LuL_2 dispersion.

The recyclability of the self-assembled nanowires is a significant advantage over conventional covalently linked polymers for fabricating organic-based devices for a next-generation "green" electronics. The K^+-LuL_2 nanowires, otherwise stable in water and most organic solvents, can be easily disintegrated into starting components in acetonitrile and then separated for further re-application without adding any other chemicals.

We believe that self-assembled conductive nanostructures obtained through coordination bonding may therefore offer an alternative to covalently linked polymers for future progress toward green electronics.

The work is supported by Russian Science Foundation (N◦ 20-13-00279)

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Physical and Colloidal Chemistry
Poster Session

Study of the effect of amino acids on the conditions of hydroxyapatite synthesis

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Dental tissues are a biocomposite material, where the mineral component is formed by hydroxyapatite crystals located in an organic matrix [1]. At the same time, dental tissues are exposed daily to destructive influences that can lead to damage to teeth. This process can lead to the development of concomitant diseases of internal organs. Unfortunately, the human body does not have the ability to regenerate tooth enamel [2]. The most promising is to carry out the process of restoring tooth tissue directly in the oral cavity. Despite the complexity of implementing such an approach, possible solutions to this problem are already being proposed today [3].

The mineral matrix of tooth enamel consists mainly of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], as well as carbonate-apatite [$Ca_{10}(PO_4)_6(CaCO_3)_2$], chlorapatite [$Ca_{10}(PO_4)_6(Cl)_2$], fluorapatite [$Ca_{10}(PO_4)_6(F)_2$], calcium carbonate, magnesium carbonate. The organic matrix is represented by enamel proteins: enamelins, amelogenins, ameloblastins and taftelins [4]. They are characterized by a high content of glycine. The function of the organic matrix is the adsorption of minerals, which leads to the formation of apatite crystals of a certain morphology around enamel proteins [5].

During the analysis of the results of the synthesis of hydroxyapatite by the reaction of $Na_2HPO_4 \times 12H_2O + Ca(HCO_3)_2$ with the addition of glycine, the complex nature of the effect of the amino acid on the course of the process was revealed.

The use of certain amounts of glycine in the synthesis of hydroxyapatite allows not only to increase the yield of the target product while reducing the yield of calcium carbonate, but also to create conditions for obtaining a bioidentical material containing the building blocks for creating a protein matrix. Without the participation of an amino acid, the highest yield of hydroxyapatite is observed in a reaction where calcium bicarbonate $Ca(HCO_3)_2$ was used as a calcium donor, and acid sodium phosphate $Na_2HPO_4 \times 12H_2O$ was the donor of the phosphate group in a stoichiometric ratio of 1:1. In syntheses involving glycine, the yield of hydroxyapatite increases sharply (from 48.4% to 67.8%) and the maximum value of this indicator is observed at an amino acid concentration of 0.45% by weight. The decrease in the yield of hydroxyapatite with a further increase in the glycine content in the reaction mass is obviously due to the influence of the micelle formation process on the course of the reaction under study.

The experiments have shown that the process of hydroxyapatite synthesis in the conditions of oral homeostasis in the presence of amino acids is of great practical importance.

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Synthesis of $GdCoO_3$ for dry reforming of methane

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With the actual growth of the GTL (Gas To Liquid) technologies as well as the potential and availability of natural gas, reforming of methane gas is getting increasing attention. The methane reforming with carbon dioxide, also called dry reforming of methane (DRM), is an endothermic reaction occurred under the influence of a catalyst to generate synthesis gas involved in the Fischer-Tropsch reaction, which can produce liquid products.

However, one of the key areas of reaction research is to increase the activity and stability of the catalyst to prevent carbon deposition and sintering of the metal precursor. Physical and chemical properties of a catalyst depend not only on the nature of the chemical elements in its composition, but also on the method of obtaining a catalyst [1].

According to the experimental data, perovskite-type complex oxides $GdCoO_3$ obtained by two methods have different activity in the DRM reaction. In the first method, $GdCoO_3$ was synthesized by the sol-gel method using citric acid and ethylene glycol. In another method, a complex oxide was obtained by precipitation of a solution containing salts of gadolinium and cobalt with solutions of sodium hydroxide and ammonium carbonate. The composition and structure of the synthesized oxides were studied using IR, XRD and BET analysis.

As a result of the DRM reaction, it was found that the sol-gel method makes it possible to obtain samples with higher catalytic characteristics compared to the co-precipitation method. The use of sol-gel samples leads to a shift of the reaction to lower temperatures (**Figure 1a**). On the other hand, for the sol–gel samples at the final temperature of catalysis (T = 1223 K), the CO and H_2 selectivity turned out to be ≈ 80%, in contrast to other catalytic systems, for which the hydrogen selectivity takes higher values than the carbon monoxide selectivity. For this reason, the H_2:CO ratio for samples obtained by co-precipitation method was almost two (**Figure 1b**). However, despite the fact that the "co-precipitated" oxides have a high H_2:CO ratio, their use leads to inhibition of a side process - the reverse steam reforming of carbon monoxide.

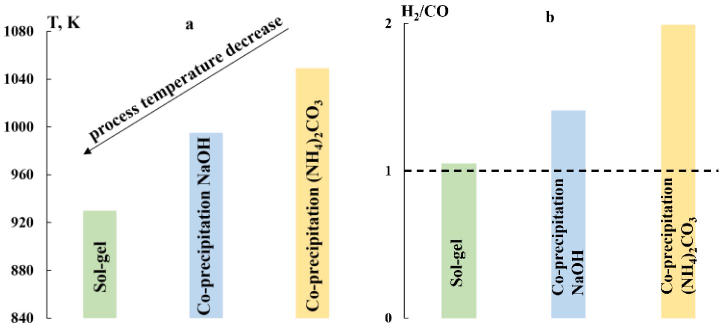

Figure 1. Optimal temperatures of DRM – reaction at 50% methane conversion (a) and H_2:CO ratio (b) for $GdCoO_3$ catalyst

This publication has been supported by the RUDN University Scientific Projects Grant System, project № 021521-2-174 and the scholarship of the President of the Russian Federation (№ СП-686.2021.1)

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Zirconium framework-structured phosphates with alkali metals as catalysts for the ethanol conversion

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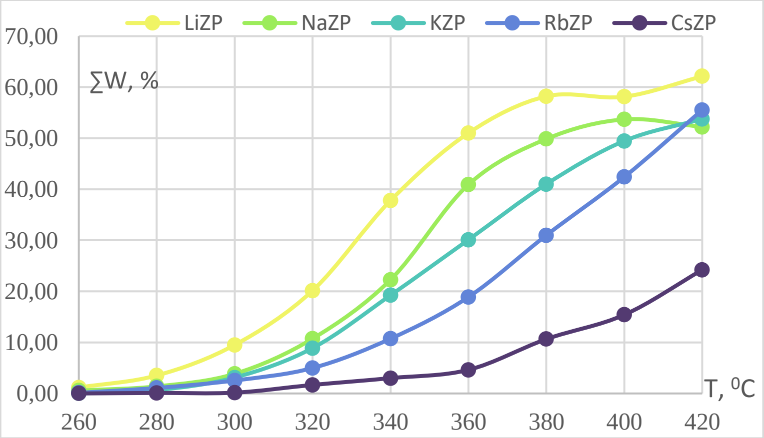
Recently, the interest in ethanol production from renewable natural sources has been receiving much attention as an alternative form of energy. The low-cost accessibility of ethanol has been seen as an interesting topic, leading to the extensive study of the distinct chemicals formation, such as ethylene, diethyl ether, acetaldehyde, ethyl acetate, starting from ethanol as a raw material [1].

According to the literature, range of catalysts have been investigated in ethanol conversion, such as zeolites, mixed metal oxides, metal catalysts on different supports [2]. In addition, there is a growing focus on complex phosphates with framework structure [3].

In this work, we investigated the physico-chemical properties of double NASICON-type phosphates with general formula $AZr_2(PO_4)_3$, where A = Li, Na, K, Rb, Cs, and the influence of the alkaline ion nature introduced into the conduction channels of compounds on catalytic properties in the ethanol conversion reaction. The catalysts were characterized by X-ray diffraction analysis and IR spectroscopy. The catalytic transformations were studied in a flow-through catalytic unit with gas chromatographic analysis of products in the temperature range 260-420^{0}C.

The samples were found to belong to orthophosphates with the NZP structure. The ethanol conversion on the studied catalysts is shown in figure.



For all the phosphate samples the converted products mainly consisted of ethylene, diethyl ether and acetaldehyde. Based on the results obtained, the highest conversion of ethanol (S = 78% and $\Sigma W = 62\%$ at 420^{0}C) was obtained on the $LiZr_2(PO_4)_3$ catalyst. The increase in the radius of the alkaline ion-compensator led to a decrease in the total conversion of ethanol and significantly change of the process selectivity.

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The use of new effective preparative forms of fungicides to increase the productivity of winter rapeseed

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The program for the development of agriculture and regulation of markets for agricultural products, raw materials and food provides for the creation of zonal environmentally friendly technologies for rapeseed cultivation. Rapeseed is a valuable oilseed crop, a source of high-quality vegetable oil and feed protein [1]. Winter rapeseed, like no other crop, successfully combines a high potential yield of seeds with a high content of oil (45-48%) and protein in seeds (22-25%) and in green mass (3-4%). Rapeseed oil is a high–calorie product widely used in food, in the production of margarine and mayonnaise, as well as in soap, textile and other industries. From the point of view of the physiology of human nutrition, rapeseed oil belongs to the best vegetable oils, since it contains all physiologically important acids in an optimal ratio, and the content of oleic acid is close to olive oil [1]. Rapeseed oil is attracting more and more attention as a source of renewable raw materials for the chemical industry and energy [2]. The range of its use for technical purposes is extremely wide - from the starting material for chemical synthesis to application in the form of lubricants and fuel.

In the conditions of the central zone of Russia, optimal technological methods for obtaining high yields of seeds of winter rapeseed varieties were identified, consisting in the use of modified preparative forms of complex-acting pesticides. During field tests, the expediency of using pesticides of various mechanisms of action was proved and practically confirmed. Based on field, laboratory and production experiments, optimal norms, and an assortment of modern plant protection products for suppressing the growth of weeds, phytopathogens and phytophagous in the acrocyanosis of winter rapeseed have been identified, increasing the yield of winter rapeseed seeds and the production of environmentally safe products.

In studies on the biological effectiveness of fungicides against alternariosis and fomosis, different consumption rates of the new fungicide Tebumet (100 g/l) and the standard Folicur (250 g/l) were studied. The treatments were carried out at the appearance of the first signs of diseases and in the phase of pulling the stems (the beginning of the formation of pods in the lower tier). The effectiveness of the studied drug increased as the consumption rate increased: against Alternaria's 93.9% (1.0 l/ha) with the development of the disease in the control 55.4%; and, against Fomosis 93.3% (1.0 l/ha) with the development of the disease in the control 32.1-53.8%. The yield increase obtained in the variant with the tested preparation was 42.5% (1.0 l/ha).

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Magnetic resonance approaches to study structure of biomolecules complexes

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The report provides a review of our work on the study of the structure of biomolecules and their complexes using magnetic resonance methods - pulsed dipole EPR spectroscopy [1], Dynamic polarization of nuclei [2, 3], NMR with paramagnetic amplification [4], 19F ENDOR [5].

A review of the functional properties of spin labels based on nitroxyl [6] and triarylmethyl radicals [7], as well as methods for their preparation and introduction into biomolecules [7, 8], was carried out.

The results of the study of complex complexes of ribosomal proteins and RNA [9], albumin dimerization [10], penetration of unstructured proteins into cells [11] are presented.

This work was supported by the Russian Foundation for Basic Research (grant № 15-33-20187)

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A plasma-activated Cu/(Al_2O_3-ZrO_2-CeO_2) catalyst for the ethanol dehydrogenation

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Non-equilibrium plasma, with features of low temperature and a large concentration of high-energy electrons, is one of the most efficient ways of activating molecules. The previous studies showed that plasma techniques can be successfully applied to the preparation and treatment of metal particle supported on various oxides [1], zeolites [2] and phosphate [3] catalysts.

Cu-supported catalysts have been found to be one of the most active catalysts for the non-oxidation dehydrogenation of ethanol. Cu^{+1} has also been identified to be the active species over complex Al-Zr-Ce-oxides supports [4]. However, the low-temperature activity and stability of Cu-active species need to be further improved. In this work, we attempt to improve 5%Cu/5%Al_2O_3-(CeO_2-ZrO_2) catalyst using Ar- or H_2/Ar- glow discharge plasma treatment (PT).

Preparation of catalysts and catalytic performance were described in [4]. The glow discharge plasma treatment was performed in the quartz setup at 10^{-4} mm Hg pressure. The current-voltage characteristics of glow discharge was 150-200 mA, 1-1.4 kV. Treatment was performed for 20 min. A violet-rosy glow was observed inside the discharge (Fig.1). In determining the most favorable treatment's condition, the catalytic activity value of Cu catalyst pretreated under H_2 atmosphere at 400^0C was used as the reference [4].

Fig.1. Cu-supported Al-Zr catalyst before and after glow discharge Ar-plasma.

To elucidate the plasma treatment effect, XRD, XPS, TEM and BET techniques were used for catalyst characterization. Comparison of the efficiency in the ethanol's dehydrogenation on the Cu-based catalysts prepared by PT with those catalyst prepared by high temperature reduction treatment showed that the former ones exhibited a higher activity and selectivity toward acetaldehyde formation. The ethanol conversion of 83 % and selectivity of 100 % to acetaldehyde were obtained on Ar-plasma pretreated catalyst at 360°C.

The research was supported by RSF (project No. 22-29-01135)

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The process of modifying industrial activated carbons by ultrasound

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The development of global industrial production leads to a deterioration of the environmental situation due to the release of toxic waste into the environment [1]. Volatile organic compounds (VOCs) are among the most common pollutants that enter the environment with gas emissions or with untreated wastewater from industrial enterprises [2]. Among VOCs, a prominent place is occupied by organic solvents, which are used in the synthesis, purification operations and preparation of commercial forms of chemical products. Currently, there are several technological solutions that allow not only to achieve a significant reduction in the VOC content in the atmosphere and wastewater, but also to solve the problem of creating closed production cycles. At the same time, deep purification of gas emissions and water effluents is achieved, and organic solvents are recycled into the technological process [2]. To achieve the necessary efficiency in solving environmental problems, a combination of several cleaning methods is often used, designed for pre-and final treatment of contaminated water or air.

In modern cleaning technologies, activated carbons are of considerable practical interest. They have a high sorption capacity in relation to chemical compounds of various nature and composition, are capable of regeneration, have a low cost and are successfully used at the stage of final purification of water and gas emissions [1]. High technical characteristics make these carbon sorbents important components of modern world technologies. Therefore, conducting scientific research aimed at developing new types of activated carbons is an urgent task. A significant role in the development of a new sorption material is played by methods of modifying existing carbon sorbents, which may consist in their chemical or physico-chemical treatment [2].

Ultrasonic modification of activated carbon was performed on the US-device in an ethyl alcohol medium for 60 minutes at a power of 440 W/ cm^2. After the modification process was completed, the absorbed ethyl alcohol was removed from the sorbent by step heating at atmospheric pressure: 72 hours at 150 °C and 8 hours at 300 °C. During the conducted studies, the quantitative regularities of the process of adsorption of ethanol vapors by industrial activated carbon BAU-A and ultrasound-modified activated carbon BAU-A-US were studied. It is shown that after ultrasound treatment, the specific sorption capacity of the carbon adsorbent increases by 3.5 %. In this case, there is a change in the formal order of the process from the pseudo-first to the pseudo-second and a change in the diffusion model used to describe the process.

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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Optimization of MOF composites shaping for most efficient diffusion of guest molecules

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Metal-organic frameworks are perspective materials due to high porosity and exceptional tunability of the pore structures. The materials can be applied in many fields of industry such as catalysis, selective sorption, separation and many others. However, MOFs are synthesized as thin powders, which often are not suitable for industrial applications. The key is shaping of MOFs from powders to convenient form without losing strong points of MOFs.

Shaping of MOFs is one of the crucial steps toward their industrial applications. A number of methods for preparation of pellets containing MOF-micro/nanoparticles have been developed up to date; however, the uptake rates of guest molecules by such shaped MOFs and their dependence on preparation procedure were not analyzed in detail.

Since optimization of the uptake rates is vital for practical use, in this work we employ spin-probe Electron Paramagnetic Resonance (EPR) to study solvent diffusion into MOF based pellets. Spin-probe, added into solution during MOF synthesis, is trapped by MOF cavity and can not leave it. The method of synthesis allows us to place sensible to environment and visible to EPR spectroscopy spin-probe into MOF cavity without changed structure of MOF. This dedicated approach allows one to selectively monitor the impregnation of MOF particles embedded in the pellet, and corresponding diffusion coefficients can be obtained for the molecules of interest.

We established that diffusion properties of obtained pellet, besides depending of binders and plasticizers, strongly depends on preparation procedure even in case of the same binder and the same plasticizer. We explained the phenomenon via decreasing on-surface MOF blockage by binder. Particle size of MOF takes place in uptake of guest molecules as well. MOF nanoparticles usage instead of macroparticles for pellets preparations leads to faster uptake rate.

Studied ways of shaping procedure optimization upon EPR control yields robust pellets with pore filling rates comparable to those for powdered MOF. The proposed methodology yield highly permeable MOF-based pellets and is promising for future application in shaping of various MOFs.

This work was supported by the Russian Science Foundation (grant № 22-73-10239)

Photoprocesses of covalently linked dimers of 3,3'-dimethilcarbocyanin and its complexes with cucurbit[7,8]urils

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The spectral-luminescent and spectral-kinetic properties of polymethine dyes have been studied widely [1,2]. An important property of polymethine dyes is their ability to aggregate in aqueous solutions with the formation of the dimers as the simplest aggregates. At the same time, the tendency of polymethines to dimerize increases significantly with the addition of cavitands such us cucurbiturils in aqueous solution. The presence of a cavity in cucurbiturils makes it possible to form the inclusion complexes with cationic dye, which results in a significant change of the photophysical and photochemical properties of the complexes [3]. The complexation of 3,3'-dimethylthiacarbocyanine with cucurbit[7,8]urils results in the appearance of regular and delayed fluorescence of the dimeric complexes, as well as in an increasing of both the yield and the lifetime of molecules in the triplet state, which makes it possible to use the complexes in the triplet energy and electron transfer.

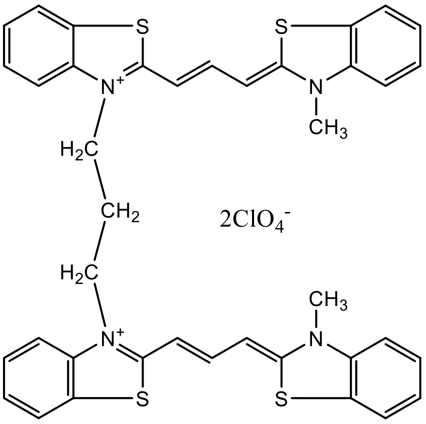

Fig.1. The structure of covalently linked dimers based on 3,3'-dimethylthiacarbocyanine

The next step of the study of the dimers and dimeric complexes of polymethines is the investigation of covalently linked dimers. In this work, we studied the photoprocesses of covalently linked dimers based on 3,3'-dimethylthiacarbocyanine (Fig. 1) and their complexes with cucurbit[7,8]urils.

The work was supported by the Russian Science Foundation (grant № 22-13-00064) and the Ministry of Science and Higher Education as a part of the State Order of the FSRC “Crystallography and Photonics” RAS

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Ethanol conversion over micro/mesoporous MFI zeolite nanocomposites

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The main efforts of researchers in the last two decades have been aimed at improving heterogeneous catalysts to achieve high process performance under mild conditions consistent with the principles of green chemistry. These requirements are met by zeolites - an extensive class of compounds with a structure consisting of vertex-connected tetrahedra (primary structure), in which voids (cavities) of various configurations and sizes connect to form channels (secondary structure) with different characters of geometry (topology) and dimensions which contains atoms, atom groups, water etc. [1].

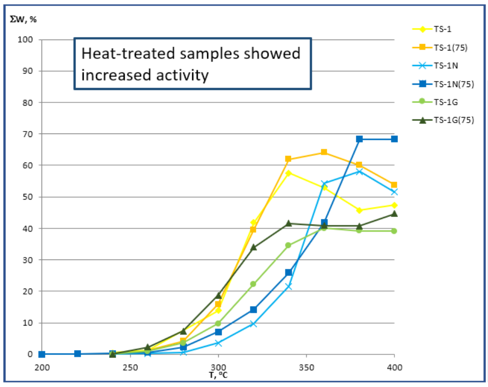
The objective of this work was to study the physicochemical and catalytic properties in bio-ethanol conversion reaction and to find influence of composition, surface acidity and defects of structure on catalytic properties.

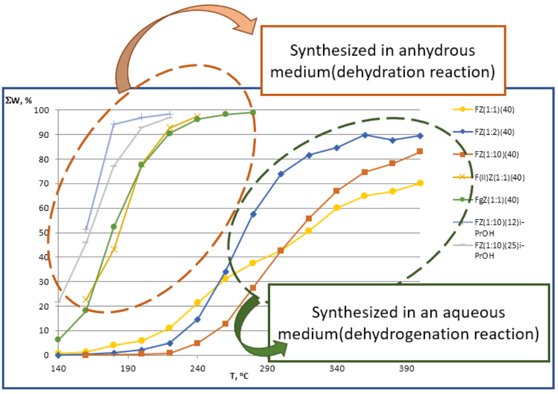
Titanosilicates and Fe_2O_3-containing zeolites were studied. Titanosilicates were purchased from "Zeolyst international". Fe_2O_3-containing zeolites were synthesized by chemical precipitation as well as from gas phase. As a result, Fe_2O_3-containing zeolites with various Fe_2O_3 content, silicate modules and structures were obtained.

The obtained samples were studied by low-temperature nitrogen adsorption method (BET), XRD, XAS, FT-IR, DSC, pyridine adsorption, detected by UV-VIS spectroscopy. Ethanol conversion reaction was used to characterize catalytic properties.

Physicochemical and catalytic properties of commercial titanosilicates TS have been studied. It was found that the amount of chemisorbed water on the surface of titanosilicates TS-1, TS-1N, TS-1G and their thermally treated versions TS-1(75), TS-1N(75), TS-1G(75) affects the activity in the ethanol conversion reaction: with an increase in the content of chemisorbed water in the sample, the catalytic activity of the sample and selectivity for the formation of ethylene is reduced.

The properties of iron-containing nanocomposites based on HZSM aluminosilicates have been investigated. It was found that the method of obtaining Fe_2O_3/HCl nanocomposites significantly affects the catalytic activity. Composites obtained in an anhydrous medium (isopropanol medium and gas phase deposition) demonstrated 100% ethanol conversion at temperatures of 180-200°C. It was shown that the amount of iron in the nanocomposite affects the catalytic activity in the ethanol conversion reaction and the carburization of the catalyst. The higher the iron content, the higher are the activity and carburizability of the catalyst. It was established that the silicate module of the zeolite used (under the constant content of iron (III) oxide) affects its catalytic activity: with an increase in the silicate module, the conversion of ethanol increases.


Heat-treated samples showed increased activity


Synthesized in anhydrous medium(dehydration reaction)

Synthesized in an aqueous medium(dehydrogenation reaction)

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Influence of processing conditions of complex salts on the activity of the synthesis gas conversion catalysts

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It was previously shown that double complex salts (DCSs) are active in the CO hydrogenation reaction [1, 2]. It was found [2] that, during the DCS thermolysis, it is possible to form a catalytic system of the required composition for the conversion of CO without a preliminary activation stage, which, of course, has a positive economic effect.

This work is aimed at studying the properties of DCS-based catalysts formed in various gaseous media and determining the effect of the pre-activation stage on the main parameters of the Fischer-Tropsch synthesis. In this work, DCS $[Co(NH_3)_6][Fe(CN)_6]$ was used as a catalyst precursor. Thermal decomposition was carried out in argon (650 ºC) (**I**) and hydrogen (380 ºC) (**II**) media. When calcined in hydrogen, DCS was additionally applied to the aluminum gel. The catalytic compositions consisted of the $Co_{0.5}Fe_{0.5}$ intermetallic compound. A large amount of X-ray amorphous carbon (24 wt %) is also observed in the case of the thermolysis in argon.

The CO hydrogenation was carried out in a fixed-bed reactor at 2 MPa, 1000 h-1, 210-330°C, both without the pre-activation stage and with it. Activation was carried out in CO for 12 hours at 2 MPa, 1000 h-1, 300°C. The catalyst **I** was active in the CO hydrogenation reaction over the entire temperature range (activity was 1–31 molCO·gMe^{-1} s^{-1}). The conversion reaches 50-90% regardless of the presence of activation. However, the CO treatment leads to an increase in the liquid hydrocarbon selectivity with increasing temperature. In the range of 250–290°C, the C_{5+} hydrocarbon selectivity on a catalyst without activation was 36–46%, and CO activation makes it possible to increase it to 57–82%. Pre-activation by CO also affects the distribution of liquid product composition: longer chain hydrocarbons (C_{19+}) increases from 1-5% to 5-13% and the ASF parameter increases from 0.69-0.74 to 0.73-0.8. The catalyst **II** was active in the CO hydrogenation reaction over the entire temperature range (activity is 1–27 molCO·gMe^{-1} s^{-1}). The conversion reaches 50-60% regardless of the activation. However, the carbon monoxide treatment leads to some decrease in the C5+ hydrocarbon selectivity in the range of 250–290°C from 49–57% (without activation) to 43–44% (with activation). The catalyst reduction by CO makes it possible to slightly increase the proportion of C_{19+} hydrocarbons and reduce the content of olefins in the composition of liquid synthesis products.

This work was supported by Grant of President of Russian Federation (MK-5323.2021.1.3), has been carried out in the framework of Scientific Research Contracts № FMEZ-2022-0017

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Regularities of electrochemical decomposition of organochlorine pesticides in aqueous solutions using modified electrodes

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The use of chemical plant protection products is essential to address the problem of increasing global food production. However, the use of pesticides can have a negative impact on human health and the environment. The accumulation of the pesticide in the soil is associated with its resistance to the action of destructive environmental factors. When these chemical compounds harmful to human health enter natural reservoirs, water resources are polluted. Currently, there are many methods of water purification from organic pollutants. Electrochemical water treatment technologies have advantages over other methods that use special materials and reagents [1].

In the reactions of electrooxidation of chloroorganic substances (2,4-dichlorophenoxyacetic acid (2,4-D) and its sodium salt), lead-modified platinized electrodes were investigated [2]. The activity of the prepared Pt (Pb) / Pt and Pt (Pb) / Ti materials in the reaction of anodic oxidation of 2,4-D and sodium salt 2,4-D in the sour water solution is confirmed by changes in the form of potentiometric dynamic curves. The formation of unstable intermediate substances absorbing in UV spectra at 260 nm was detected during electrooxidation for all studied electrodes (Pt, Pt / Ti, Pt (Pb) / Ti). The nature of the possible intermediate decomposition of herbicides proposed. The developed method of electrochemical decomposition of pesticides can be used for wastewater treatment of industrial plants.

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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Molecular photonics of supramolecular complexes of bis-aza-18-crown-6-containing dienones with alkanediammonium salts

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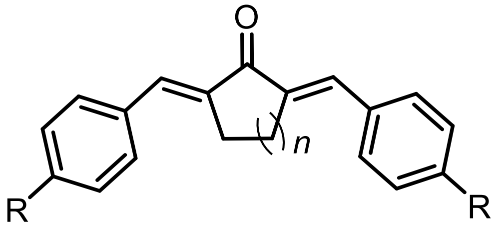
Cross-conjugated dienones – derivatives of cyclic ketones – attract much attention due to their rich synthetic chemistry, primarily to produce heterocycles, as well as due to wide application, especially in biology, agriculture and the creation of a new materials [1]. The solvatochromic properties of dienones are the reason to use them as fluorescent probes. The tendency of this class of compounds to intersystem crossing to the triplet state makes it promising to produce the dienones as singlet oxygen sensitizers in photodynamic therapy. Double bonds of dienones allow these compounds to be involved in the trans-cis-photoisomerization and [2 + 2]-photocycloaddition reactions (PCA) [2]. Stereoselectivity of PCA reactions can be controlled by supramolecular preorganization of double bonds in order to create the most suitable geometry as the starting dimer that makes these compounds suitable for the formation of supramolecular systems.



1-2a-b

R = NEt_2 (**a**), aza-18-crown-6-ether (**b**)

n = 1 (**1**), 2 (**2**)

In the recent work, we studied spectral, luminescent, and kinetic properties of deoxygenated solution of cycloalkanone-based dienones containing two diethylamino and two aza-18-crown-6 ether in the presence of the $EtNH_3^+$ and $^+H_3N(CH_2)_{12}NH_3^+$ ions in MeCN. It was found that homoditopic bis-azacrown dienones and ethylammonium ions form 1:1 and 1:2 complexes, whereas alkanediammonium ions form only pseudo-cyclic 1:1 complexes. The ns-laser excitation of complexes results in the intersystem crossing to the triplet state and the formation of a product at 720 nm with the lifetime 5×10^{-5} s.

This work was supported by the Russian Science Foundation (grant № 22-13-00064)

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Investigation of the aminomethylation reaction of 6-aminopyridine-2(1H)-chalcogenones

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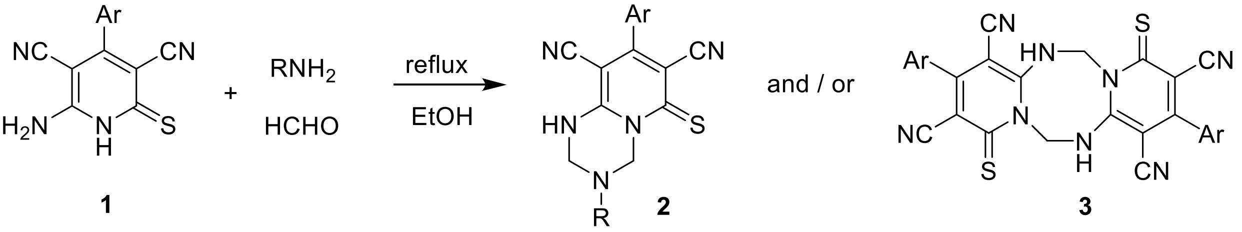
The Mannich reaction occupies an important place in synthetic organic chemistry, as it opens up broad prospects for the synthesis of heterocyclic compounds and is widely used to produce many drugs and natural substances. We have studied the behavior of some available pyridine derivatives under the conditions of the aminomethylation reaction.

Thus, it was found that the Mannich reaction involving 6-amino-4-aril-2-thioxopyridine-3,5-dicarbonitriles **1** proceeds as N,N-diaminomethylation. The structure of the products of the aminomethylation reaction depends on the structure of the primary amine used. Thus, thioxopyridines **1**, when interacting with a twofold excess of primary aliphatic amine (or benzylamine) and a multiple excess of formalin in boiling ethanol, are smoothly aminomethylated by nitrogen atoms to form pyrido[1,2-*a*][1,3,5]triazines **2** with yields close to quantitative.



However, in the case of less nucleophilic aromatic amines, either a mixture of pyridotriazine **2** and the dipyrido[1,2-*a*:1′,2′-*e*][1,3,5,7]tetrazocyne-2,4,9,11-tetracarbonitrile **3** in various ratios is formed, or exclusively dipyridotetrazocines **3**. The latter compounds apparently arise from the competitive Mannich reaction, in which 6-aminopyridine-2(1*H*)-thiones **1** play the roles of the substrates and the amine components simultaneously.

More detailed studies have shown that the reaction proceeds more easily in the presence of Et_3N. Catalytic effect of the base addition is associated with the enhanced nucleophilicity of the substrates caused by their conversion to pyridine-2-thiolates and better solubility of the last species in EtOH than the starting thiones.

It should be noted that the direction of the aminomethylation reaction of 6-aminopyridine-2(1*H*)-ones of a similar structure does not depend on the nature of the amine component, and only pyrido[1,2-*a*][1,3,5]triazine derivatives were isolated as the reaction product.

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Cycloaddition reaction of benzyl vinyl ether to nitrile oxides: a comparative quantum-chemical study of reaction pathways

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One of the most successful synthetic approaches in organic chemistry, directed at producing new carbo- and heterocyclic systems, are dipolar cycloaddition reactions. Here we studied the formation of isoxazoles from nitrile oxides by addition of benzyl vinyl ether (Figure 1, *left*). The products of these transformations, substituted isoxazoles, are can be used in pharmacology and in the synthesis of some commercially available drugs. [1-3]

In this work we performed quantum-chemical modeling of the cycloaddition reaction of benzyl vinyl ether to substituted nitrile oxides (R = H, Br, Me, OMe, NO_2). We modeled the structures of reactants, pre-reaction and transition states, final products of cycloaddition reaction, calculated total electronic energies and thermodynamic functions (enthalpy, Gibbs free energy) of compounds. For both pathways (Figure 1, *left*), thermodynamic and kinetic parameters were compared. The substituent effect was evaluated by performing a Hammet study *in silico* (Figure 1, *right*).

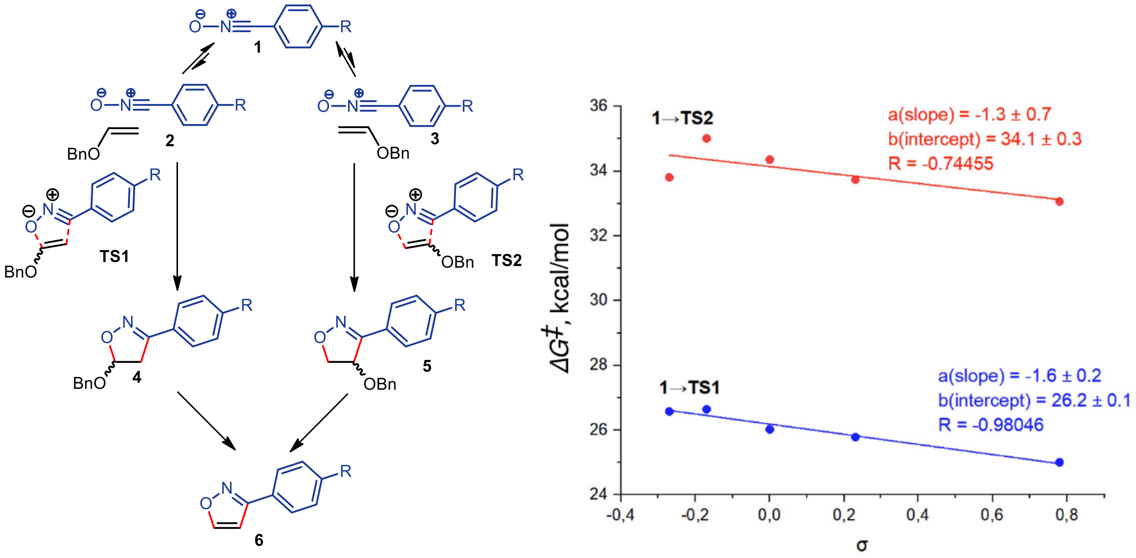

Fig. 1. *Left:* model reaction mechanism; *right:* the Hammet plot in which $\Delta G^{\ddagger}$ along both reaction pathways are compared.

DFT calculations were performed with ORCA 4.2.1. Geometry optimizations and vibrational frequencies calculations were performed at two levels of the theory: B97-3c and PBE0-D4/def2-TZVP. The range-separated hybrid functional wB97X-V and def2-TZVP was also used for single point energy evaluations at optimized geometries. The SMD approach was used to simulate the reaction medium (benzene solution).

The work was supported by the Russian Science Foundation (Project № 19-7310032)

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Thermodynamic characteristics synthesis of N-methyl-D-glucosamine

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Most often, amines can be synthesized by direct amination of alkyl halides or by direct amination of alcohols [1].

Sample Ni-25 wt. % - HPS showed the highest activity, so all further experiments were carried out using this sample.

During the experiments, N-methyl-D-glucosamine, N-methyl-D-glucosamine were detected in the reaction medium and will be considered as the main products. The study of the effect of temperature on the yield of N-methyl-D-glucosamine and N-methyl-D-glucosimine is shown in Figure 1. Increasing the reaction temperature leads to an increase in the yields of N-methyl-D-glucosamine and N-methyl-D-glucosimine [2].

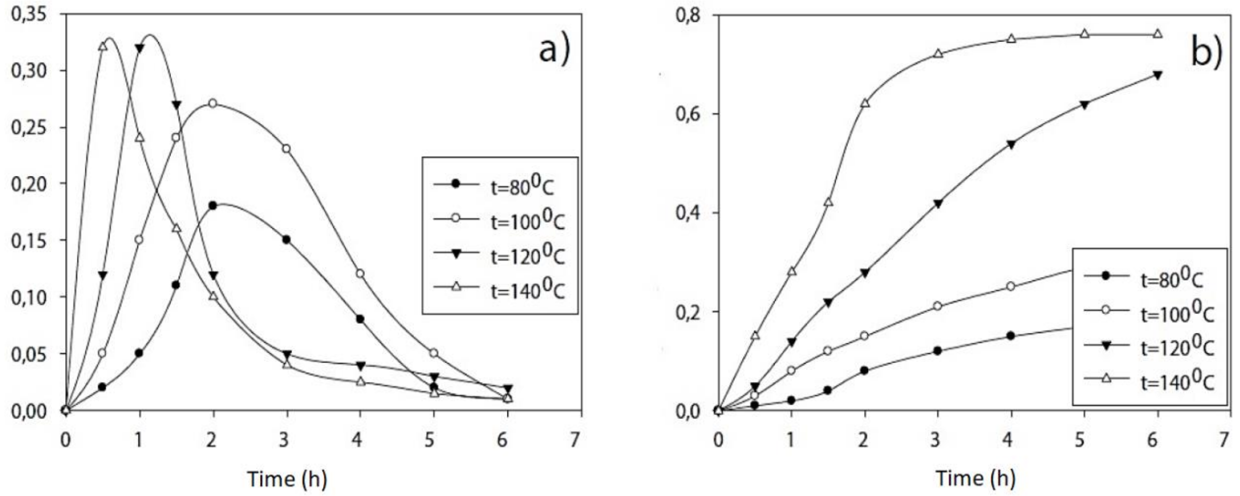

Figure 1: Effect of temperature on N-methyl-D-glucosamine synthesis. a) methylglutimine concentration (mol/l); b) concentration of methylglutamine (mol/l)

It was determined that the initial activity of the catalyst is 1.3 kg (glu)/(kg (cat)*h) at 99.3–99.6% conversion of D-glucose. The selectivity of the process to N-methyl-D-glucosamine was 97.6–97.8%.

The work was supported by FOND-M (Agreement 16436GU/2021)

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Ru-containing heterogeneous catalysts based on aromatic polymer for the selective hydrogenation of levulinic acid

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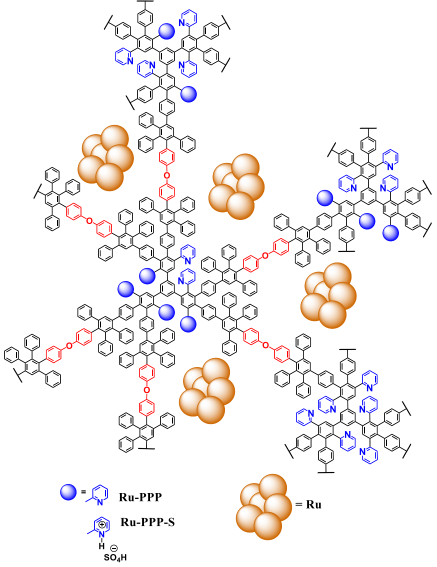
Gamma-valerolactone (GVL) is a promising compound with a great potential for use, obtained by selective hydrogenation of levulinic acid. In particular, GVL is a component of liquid fuel and an industrially important chemical compound [1].

The aim of this work is to synthesize and study the catalytic activity of Ru-containing heterogeneous catalysts based on an aromatic polymer in the reaction of selective hydrogenation of levulinic acid.

For the goal, two new Ru-containing catalysts were obtained, in which metal nanoparticles are stabilized by a hyperbranched pyridylphenylene polymer. The resulting composites were thoroughly characterized by transmission electron microscopy, FTIR spectroscopy, energy dispersive X-ray spectroscopy, and thermogravimetric analysis. Functionalization of the nanocomposite with sulfuric acid led to a significant increase in catalytic activity and allowed one to obtain a quantitative yield of GVL under mild reaction conditions (100°C, 2 MPa), low catalyst loading (0.016 mol%), and aqueous media. The catalysts preserve its activity in four consecutive catalytic cycles.



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Plasmon resonance-enhanced absorption of visible light in ultrathin films of organic chromophores and gold nanoparticles

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The ability of gold nanoparticles (AuNP) to generate a strong electromagnetic field near the surface under light radiation due to the excitation of surface plasmon makes it possible to boost optical properties of organic molecules trapped within this field. Unlike SERS, surface-enhanced IR absorption and fluorescence, direct observations of plasmon resonance enhanced absorption (PREA) are difficult because the enhancement occurs only in ultrathin organic layer bordering the particle due to a fast decay of the plasmon in a condensed phase.

Herein, we report a novel strategy for direct observations of the enhancement of visible light absorption in ultrathin hybrid films based on perylene and diacetylene derivatives by using the 2D gold plasmonic antennas with tunable optical properties. Two types of organic layers were used. First system represents a layer of nanowires assembled from disubstituted pentacosadiynoic perylene diimide. Perylene and diacetylene parts are covalently bonded in it. The length of the nanowires reaches 30 μm and the width is up to 40 nm. Second one contains chromophores separated in space. Glutamic diimide perylene and 10,12-pentacosadiynoic acid are combined into an ultrathin film due to the adsorption on graphene oxide (GO) sheets. Diacetylene was polymerized to PDA under UV irradiation in both systems.

Colloid-induced condensation of the cation-anion surfactant mixture onto the surface of gold hydrosol was used to assemble plasmonic antennas with spectral characteristics tuned in a range of 520-660 nm. This method permits to realize the general principle of resonance effects: overlapping of absorption maxima of the nanoparticle ensemble and the organic film. Hybrid systems were obtained by transferring plasmonic antennas with appropriate spectrum onto a support coated with organic films.

Comparison of experimental absorption spectrum with the model one calculated as a sum of spectra of the organic film and the plasmonic antenna showed that PREA-effect was realized only in the GO/perylene/PDA system at the absorption band of the perylene. Systems containing both types of organic films and plasmonic antennas with optical properties matched to PDA absorption exhibited additive optical behavior. We believe that the geometry of contact between the gold nanoparticles and the chromophore film controls the propagation of the plasmon field into the organic phase and, thereby, the occurrence of PREA-effect at the organic-coated interface. When AuNPs lay on top of nanowires and PDA crystallites the plasmon field doesn’t trap into organic layers. In GO/perylene/PDA system contact area between AuNPs and loose GO sheets with adsorbed perylene molecules is increased. Hence, the plasmon field spreads within the layer and the plasmon enhanced absorption occurs.

Our results enlightened the mechanism of plasmon enhanced absorption in the hybrid ultrathin surface coatings that might be important for the improvement of the efficiency of organic solar cells, heterogeneous photocatalysts and other organic electronics devices.

The authors acknowledge the financial support from the Russian Science Foundation (№ 20-13-00279)

Synthesis and investigation of the properties of hexamolybdochromate (III) and hexamolybdocobaltate (III) pyridine-3-carboxylic acid

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During the experiments, new organo–inorganic complex compounds of hexamolybdochromate (III) and hexamolybdocobaltate (III) pyridine–3-carboxylic acid of the general composition $(H_3O)_3[ЭMo_6(OH)_6O_{18}]{\cdot}(C_6H_5NO_2)_2{\cdot}5H_2O$ where (E–Cr(III), Co(III)) were synthesized. Their properties were studied using X-ray, TGA, IR and NMR spectroscopy. The compounds belong to the Perloff type structure and consist of three oxonium H_3O^+ cations, two nicotinic acid molecules and five crystallization water molecules (Fig. 1 and Fig. 2). The central atom in the heteropolyanion has a coordination number equal to 6, is in the center of an almost regular octahedron, at the vertices of which OH groups are located.

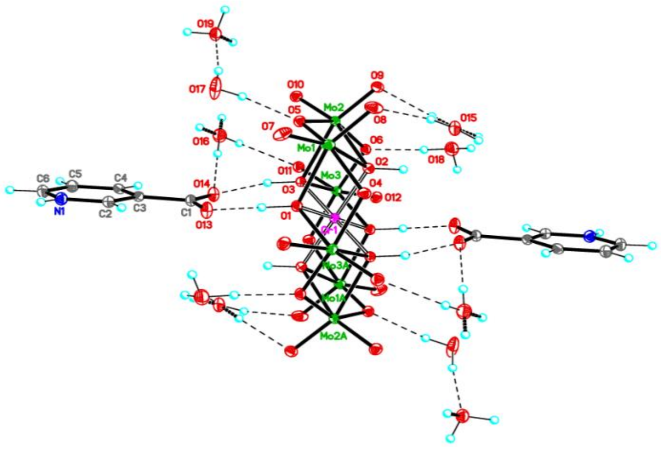

Fig. 1. The structure of hexamolybdenochromate of pyridine-3-carboxylic acid.

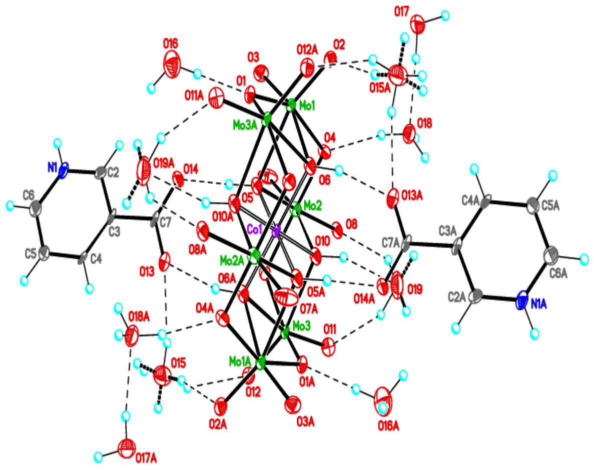

Fig. 2. The structure of pyridine-3-carboxylic acid hexamolybdocobaltate.

The complexes crystallize in the triclinic syngony in the space group P-1. Parameters of the unit cell of the compound (fig.1): $a = 9.1640(8)$ Å, $b = 10.6441(11)$ Å, $c = 10.8241(12)$ Å, $\alpha = 95.968(10)°$, $\beta = 109.864(12)°$, $\gamma = 105.059(11)°$, $V = 937.2(2)$ Å^3, $\rho_{cal} = 2.500$ mg/m^3, Z = 1; of the compound (fig. 2): $a = 9.2303(19)$ Å, $b = 10.700(2)$ Å, $c = 10.850(2)$ Å, $\alpha = 95.95(3)°$, $\beta = 110.01(3)°$, $\gamma = 105.11(3)°$, $V = 949.9(4)$ Å^3, $\rho_{cal} = 2.479$ mg/m^3, Z = 1.

An increase in the value of the polarizing effect from 3.95 for Cr3+ to 4.00 for Co3+ leads to an increase in the force constant (f), a decrease in the interatomic distance of Co-O. This fact explains the increased thermal stability and solubility of the Co3+ compound compared to the Cr3+ compound. Similar patterns are characteristic of isostructural GPS, which confirms the principle of trans-influence described by M.A. Poray-Koshits and L.O. Atovmyan for oxo compounds of molybdenum and tungsten.

The obtained coordination compounds simultaneously contain a metal ion of variable valence and a pyridine fragment. This fact suggests that these chemical compounds can be used as promising catalysts for organic synthesis processes.

Improving biodiesel fuel properties using eco-friendly materials

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Biodiesel, which refers to fatty acid alkyl esters, has attracted considerable attention as an environmentally friendly alternative fuel for diesel engines, and biodiesel has several advantages as a renewable, biodegradable, and nontoxic fuel. In the present study, several biodiesel optimization scenarios have proposed [1]. Sodium hydroxide and mixed natural zeolite (96.6 % Thomsonite and 3.4% Analacime) catalysts were used to produce jatropha biodiesel to meet the demand for green and clean production. The XRD and XRF techniques were used to identify the natural zeolite catalyst. The synthesized biodiesel were characterized by GC/MS, ICP, and Physico-chemical characteristics of biodiesel were determined according to American Society for Testing and Materials (ASTM) standard methods, characteristics are: density, kinematic, viscosity, flash point, cloud point, colour, ash content, water content, carbon residue, sulfur content, copper strip corrosion, and cetane number.

A 15 biodiesel samples (MJ1-15) were produced from optimization of the trans-esterification of Jatropha oil using NaOH, the reaction has carried successfully because all free fatty acids have trans-esterified to biodiesel except some compounds such as 9-Octadecenoic acid(Z) , Octadecanoic acid and -2,2-dimethyl -1,3-,4-[{(2-methoxy-4-hexadecenyl)oxy}methyl] Dioxolane, that may attributed to the high concentration of compounds in oil or stereo-congestion. The highest cetane number has detected for MJ6 sample with the highest MEFA compounds [2]. Moreover, the biodiesel has synthesized successfully via natural zeolite (96.6%Thomsonite and dicalcium 3.4%) because more of FFA trans-esterified to FAME.

Previously, the physico-chemical properties of petro-diesel fuel have improved after treatment by furfural. The furfural shows high ability in extraction of aromatic, cyclic, and branched hydrocarbons, a total of 81 organic compounds have removed by furfural. The synthesized biodiesel has also treated by different ratio of furfural. Improvement accomplished by the eco-friendly blend furfural has removed alcohols, carbonyl, cyclic, and other compounds, such compounds exhibit a negative effect on the cetane number of diesel fuel.

Furfural has proved to be an eco-friendly efficient non-expensive, comparing with sulfur compound adsorbent and thermal unstable cetane number improver, hence furfural can act as a bio-based alternative to the thermally unstable 2-ethylhexyl nitrate. Although these results are very promising, some more studies and improvements are needed.

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Catalytic activity of supported-$KCoMoS_2$ catalysts in HAS from Syngas: Impact of sulfidation method

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Higher alcohols are a potential gasoline blending stock to improve the octane number of the motor gasoline and reduce the emissions of NOx, ozone, CO, and aromatic vapours [1]. $KCoMoO_4$ catalysts supported on activated carbon (AG-3) were prepared from organic (Co $(AC)_2$; KOH) and inorganic precursors ($Co(NO_3)_2$; K_2CO_3; K_2CO_3) using witness impregnation method. In order to study the impact of sulfidation methods, the prepared oxide catalysts were sulfided by hydrogen sulfide and Chemical Vapor Deposition (CVD) method. Sulfided catalysts were characterized using high-resolution transmission electron (HRTEM) microscopy, scanning electron microscopy (SEM), Energy Dispersive X Ray, X-ray photoelectron spectroscopy (XPS) to study their structural properties and morphology. The prepared catalysts were tested for syngas conversion in a fixed-bed flow reactor [2]. The results of the study indicate that the method of sulfidation of oxide precursors using CVD technology allows the formation of an active KCoMoS phase of catalysts deposited on activated carbon from oxide precursors.

Comparison of catalysts synthesized from inorganic and organic precursors showed higher pore filling in the second case, counting organic precursor residues. In sulfidation by hydrogen sulfide, these residues are removed contrary to the sulfidation by CVD method. In the case of synthesis of an oxide precursor from inorganic precursors, such a problem does not arise, and the catalyst sulfidated by the CVD method shows greater activity and selectivity for target products than its analogue sulfidated with hydrogen sulfide.

Such conclusions make promising further research on the topic of designing the morphology of the active phase of the KCoMoS catalyst using the CVD method.

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Synthesis and catalytic properties of bimetallic nanoparticles containing iron and nickel

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Today, catalytic technologies are often used in industrial production. The use of catalysts is of great importance in the processing of natural gas and oil. It is known that catalyst nanoparticles often exhibit higher activity than the starting material. Therefore, the synthesis and study of the properties of nanoscale catalytic systems is of great interest.

In this work, the synthesis and investigation of the properties of bimetallic Fe/Ni nanoparticles obtained by radiolysis under anaerobic conditions and based on the chemical reduction of cations in the presence of oxygen and quercetin in reverse micellar solutions was carried out. The main advantage of this synthesis method is that with proper control of the synthesis parameters, these nanoreactors can be used to produce individual particles up to the nanoscale level with new and special properties. During the conducted research, the possibility of obtaining various nanocomposites with abnormal catalytic, magnetic functional activity was considered.

Chemical synthesis of bimetallic Fe/Ni nanoparticles was carried out under aerobic conditions by mixing aqueous solutions of two salts in a 150 mm solution of quercetin in AOT/isooctan. During the synthesis, the volumes necessary to obtain solutions with a ratio of [Fe]/[Ni] equal to 1:1, 1:2 and 2:1 were determined [1]. Optical absorption spectra of the initial solutions and samples after the synthesis of LF were recorded using a Hitachi U-3310 spectrophotometer relative to AOT/isooctan solution at room temperature in the presence of air.

Analysis of the obtained results showed that the absorption bands λmax= 290 nm and λmax= 220 nm have the highest intensity on the obtained spectra, confirming the presence of Fe and Ni nanoparticles, respectively [2]. At the same time, in the spectra of bimetallic nanoparticles with a ratio of Fe and Ni = 2:1, the intensity of the main bands was higher than in the spectrum of Fe/Ni nanoparticles with a lower iron content (1:2). However, information about the differences in the functional activity of metallic and bimetallic nanocomposites and nanocomposites based on them can be obtained only by studying the electrocatalytic characteristics of these nanostructures [3].

The conducted studies have shown that the obtained nanoscale catalysts containing iron and nickel nanoparticles have high efficiency and can be used in the electrochemical synthesis of some organic compounds.

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Polymorphism induced by the conformation of a solvent molecule

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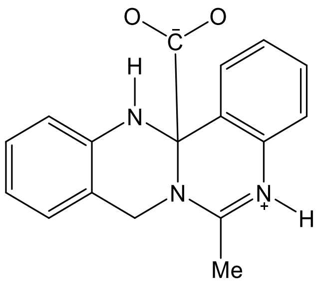
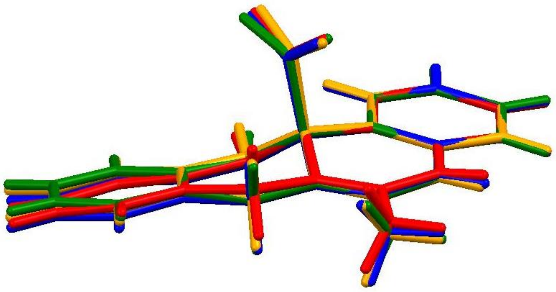
Polymorphism is an important phenomenon for molecular crystals. Many organic compounds exist in two or more crystalline forms, which differ in conformation of the molecule and/or crystal packing. The crystallization of a certain form is usually defined by crystallization conditions, including the interactions with solvent molecules during crystallization. Polymorphism is known not only for pure compounds, but also for multi-component structures such as co-crystals of solvates. It is important that in case of crystal solvates, the crystal packing is mainly defined by interaction of the parent compound, as solvent molecules are usually much smaller. For a flexible solvent, it is possible that differences in its conformation cause polymorphism; however, such cases are unusual and require detailed consideration.

Compound (**1**) 8*H*-6-methyl-13a-carboxy-quinazolino[3,4-*b*]quinazolin-5-ium crystallizes in two polymorphic forms of acid crystal solvate with a stoichiometric ratio of 1:1, **1a** (sp. gr. $P2_1/c$, Z'=1) and **1b** (sp. gr. $P2_1/c$, Z'=3). Despite certain similarity of the unit cell parameters, molecular geometry and supramolecular organization of the main compound, the structures are very different in conformation and crystal packing of the solvent molecules. Thus, in **1a** the acetic acid molecule in *trans*-conformation (which is itself not very typical), while in **1b** two symmetry independent molecules are in *trans*- and one is in *cis*-conformation. As a result, instead of infinite H-bonded chains in **1a**, in **1b** the solvent molecules form only a trimeric associate that is additionally bonded to the main compound.

The features of the supramolecular organization, the results of the quantum-chemical calculations of the associates and crystal structures are reported; and possible reasons leading to the observed polymorphism are discussed.





This work was supported by the Russian scientific foundation (grant № 22-23-00570)

Study of the catalytic properties of $Pr_2Zr_2O_7$

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One of the ways to convert propane to propylene is the non-oxidative dehydrogenation of propane [1]. This process is carried out on catalysts with CrO_x or Pt–Sn particles, usually supported on Al_2O_3. However, compounds containing Cr are toxic and pose health and environmental problems. On the other hand, Pt-based catalysts are environmentally friendly, but very expensive.

The aim of our study was to find a supported base metal oxide catalyst that would be inexpensive while still exhibiting high catalytic activity. It is known that coordinatively unsaturated Zr cations are active sites for propane dehydrogenation [2].

The range of the studied temperature range of propane cracking was from 298 °C to 1143 °C, with a step of 50 °C, since an increase in the process temperature above 1143 °C leads to instantaneous carbonization of the catalyst due to the formation of resins and heavy.

The degree of propane conversion was determined when the steady state was reached by the amount of propane that reacted.

It has been determined that $Pr_2Zr_2O_7$ is a non-porous material with S(sp)=5 m^2/g, with a wide distribution. Catalytic activity in the reaction of propane cracking has been revealed. It has been shown that carrying out the process in the presence of $Pr_2Zr_2O_7$ promotes an increase in the degree of conversion to 50% at 700 K. By determining the pore size from 7.4 to 41.2 nm. (Fig.1)

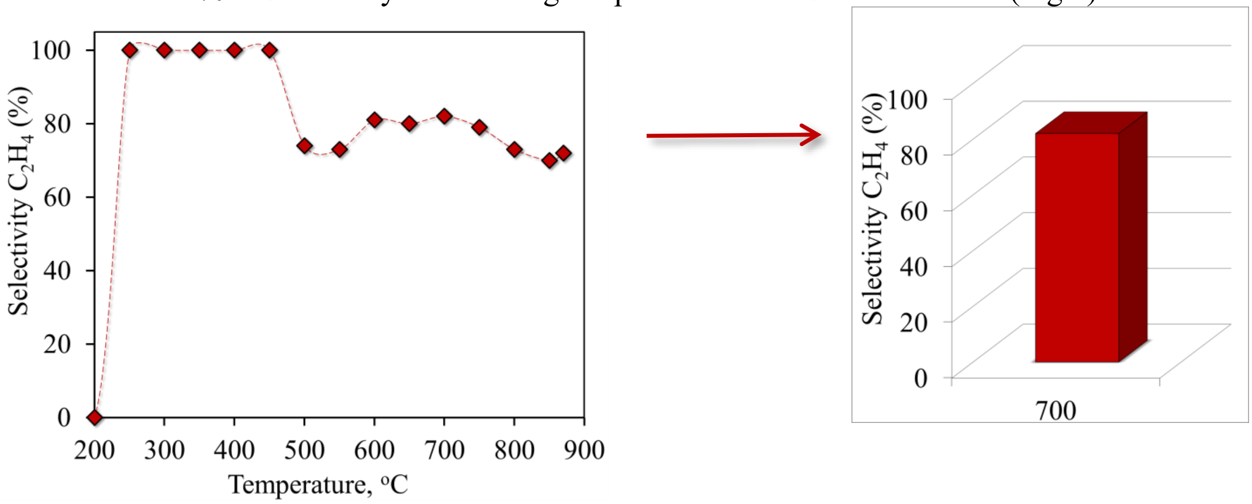

Figure 1. Ethylene selectivity of the propane cracking reaction

It has been established that the $Pr_2Zr_2O_7$ catalyst dominates the degradation process with a maximum ethylene yield of 82% at 700 °C.

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Electrochemical decomposition of (4-methylphenyl)-N-methylcarbamate in aqueous solution

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The development of the world economy is impossible to imagine without modern agricultural technologies for food production. Without the use of chemical plant protection products, a significant part of the grown crop is irretrievably lost [1]. Therefore, the prospects for further development of agriculture are associated with the use of highly effective chemical reagents. These chemical compounds are used to control weeds, harmful insects, and pathogens.

The practical use of any pesticides should be strictly controlled. Getting pesticides into food, drinking water and other objects can harm human health and the environment. To prevent the negative impact of pesticides on the environment, they must have a predictable persistence. Water solutions with a high content of pesticides formed during their production and practical use pose a significant danger to human health and the environment. New wastewater treatment technologies are being developed to address these issues. The use of electrochemical methods for cleaning pesticide-contaminated water is an important problem [2].

Various urea derivatives and carbamates are widely used in agriculture as pesticides of various action spectrum. Urea compounds are used as herbicides, and carbamic acid esters are used as insecticides. As an object of research, we used aqueous solutions of (4-methylphenyl)-N-methylcarbamate, which is a well-known insecticide. The correct choice of process conditions and electrode materials has an important impact on the efficiency of oxidative decomposition of organic pollutants. In this work, we intended to study the electrocatalytic decomposition of carbamate pesticides using electrodes made of electrodeposited nanostructured graphite. This electrode has a wide range of electrochemical potential, high efficiency of decomposition of organic compounds and the ability to work under environmental conditions. Preliminary results showed that the method used to remove carbamate pesticides from aqueous solutions has several advantages over other methods. The removal efficiency of these drugs is about 90%. A similar result was previously obtained with the degradation of 1-naphthyl-N-methylcarbamate in an aqueous solution. This fact proves the effectiveness of the proposed method of decomposition of carbamates pesticides.

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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Stability of silver(I) complexes with N- and N,N'-thiourea derivatives in aqueous solution

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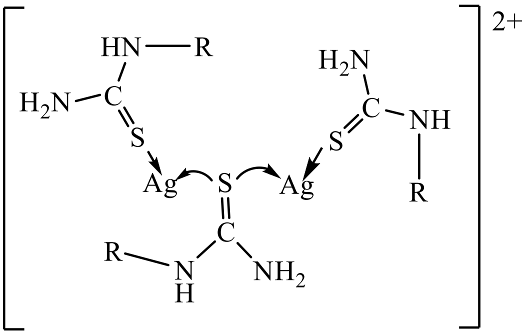
The study of equilibria in aqueous solutions of silver(I) compounds with thiourea and its derivatives is extremely interesting both from a scientific and practical point of view. These results can be used in hydrometallurgy for the extraction of precious metals from secondary raw materials, and in pharmacology for the creation of pharmaceuticals. At the same time, data for equilibria in a wide range of concentrations of these systems are very limited.

The processes of complex formation of silver (I) with thiourea (Tu), N-phenylthiourea (Phtu), N,N'-diphenylthiourea (Bphtu), N-acetylthiourea (Actu), and thiosemicarbazide (Tsc) in aqueous solution at I = 0.11 mol·l^{-1} (0.1 $NaNO_3$ + 0.01 HNO_3) were studied by the potentiometric method. The complexation proceeds according to the following equations: $Ag^+ + i\ L = AgL_i^+$, β_{1i}, $2Ag^+ + i\ L = Ag_2L_i^{2+}$, β_{2i} (i =1–5). The main form of binuclear complexes is $Ag_2L_3^{2+}$. The hypothetical structure of these form is shown in Scheme 1.

Scheme 1.



Where R –H, NH_2, C_6H_5

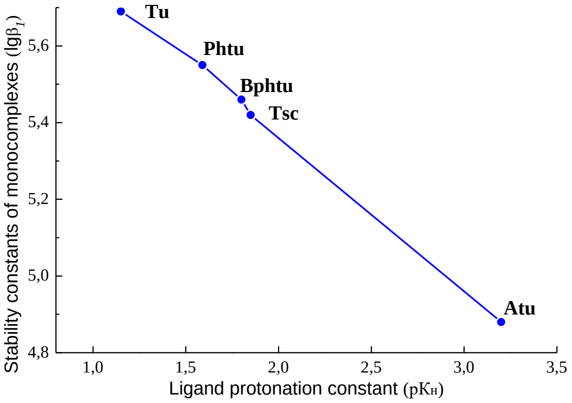


Fig. 1. Dependences of lgβ_1 on ligand protonation constants at T=298.2 K.

The obtained values of the constants of monocoordinated complexes (AgL^+) are lgβ_1 = 4.88 (Actu); 5.41 (Tsc); 5.56 (Bphtu); 5.58 (Phtu); 5.59 (Tu). In the series Actu < Tsc < Bphtu < Phtu < Tu, the stability of the complexes increases. This regularity correlates well with the equilibrium constants (K_H of ligands) of the ligand protonation reaction $L + H^+ = HL^+$, ($pK_{Actu} = 3.20$; $pK_{Tsc} = 1.85$; $pK_{Bphtu} = 1.80$; $pK_{Phtu} = 1.59$; $pK_{Tu} = 1.15$ [1]) (Fig. 1.) .

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Exfoliation-assisted fabrication and functionalization of single-sheet MoS_2 nanoparticles with porphyrin-based quasi-MOFs

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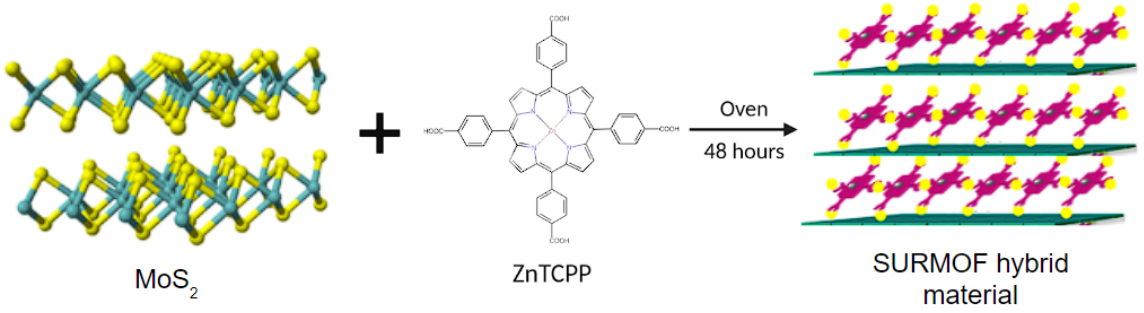
Functionalization of two-dimensional materials with organic molecules is among the most extensively developing areas of materials chemistry. Fabrication of hybrid materials from 2D semiconductors such as dichalcogenides of transition metals is particularly important for the applications exploiting donor-acceptor interactions between components to initiate charge/energy transfer. These materials might be broadly useful for catalysis, photocatalysis, selective chemical sensing and organic electronics.

Nanodispersed dichalcogenides exhibit a number of useful properties such as optical transparency and strong luminescence. By combining these inorganic semiconducting matrices with potent organic chromophores, it is therefore potentially possible to imitate a synergy of components properties by light-induced energy transfer between them. Porphyrins are especially interesting organic components for this purpose because of their photochemical and receptor properties providing them both sensing and photocatalytic activity. However, the integration of 2D dichalcogenides with such bulky discotics into organized architectures orchestrating their functioning remains a challenging issue.

In this work, we use a novel method of liquid phase exfoliation in the saturated solution of 2-methylimidazole to obtain chemically pure ultra-thin MoS_2 nanoflakes [1]. These nanoflakes were functionalized by porphyrin molecules through coordination bonding with zinc acetate metal clusters using self-assembly method. The integration of components was confirmed using XRD and fluorescent spectroscopy methods. This self-assembly strategy can be extended to a wide variety of porphyrin complexes for obtaining such hybrid materials without covalent pre-functionalization of the particle surface.



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Monoclinic structure of REM molybdates as a potential catalyst for the dehydrogenation of light alkanes

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Processing of natural and associated petroleum gas is one of the main sources of olefins in industry. Previously, it was shown in [1–2] that REM vanadates and vanadites exhibit catalytic activity in propane cracking. The replacement of vanadium ions with a more active metal in the processes of dehydrogenation of light alkanes can potentially shift this process to the region of lower cracking temperatures.

Of interest is lanthanum molybdate, which crystallizes into a monoclinic structure of the α-$La_2(MoO_4)_3$ type (Fig. 1).

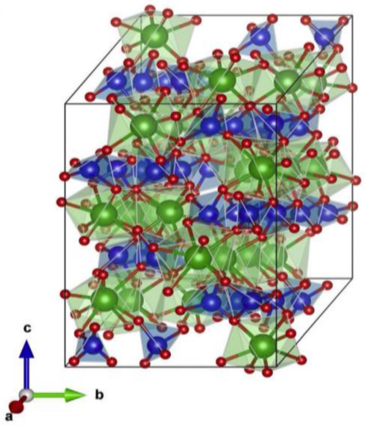

Fig. 1. Polyhedral representation of the crystal structure of $La_2(MoO_4)_3$

It has been shown that $La_2(MoO_4)_3$ catalytic systems have an undeveloped specific surface area of 1.9 m²/g, with a narrow pore size distribution from 10 nm to 42 nm.

This catalyst provokes propane cracking by the dehydrogenation mechanism with the formation of propylene as the main product. The maximum thermodynamic parameters are achieved at a temperature of 700ºC with a degree of conversion of 90%, a selectivity for ethylene of 13%, and a selectivity for propylene of 70% (Fig. 2).

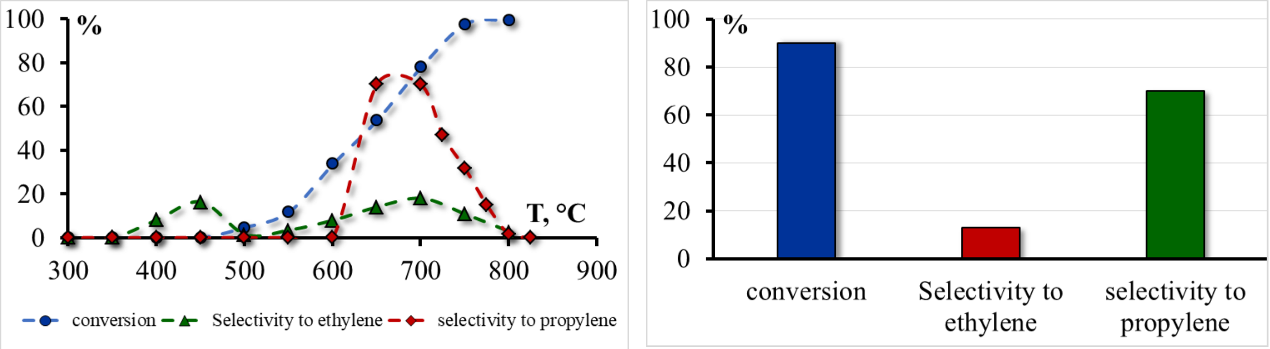

Fig. 2. Technological characteristics of the propane cracking reaction

The use of a catalyst reduces the activation energy compared to thermal cracking by 13 kJ/mol. For thermal cracking, the activation energy is 104 kJ/mol, while for $La_2(MoO_4)_3$ this value is 91 kJ/mol. The activation energy data suggest that the use of $La_2(MoO_4)_3$ catalytic systems facilitates propane cracking while suppressing side processes.

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Greenhouse gases and modern catalytic technologies for their processing

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Currently, it is established that the climate of our planet is constantly changing due to the release of greenhouse gases into the atmosphere. Scientists are actively studying this climate change, discovering its consequences in many areas. Human activity, namely the burning of fossil fuels to generate heat, electricity and industrial development, has been repeatedly associated with an increase in temperature. Understanding how these conclusions were drawn is of paramount importance, as evidence-based arguments provide the best basis for making the right decisions to preserve the balance of natural.

Greenhouse gases are trapped in the troposphere, thereby heating the surface. Without the presence of greenhouse gases, the average temperature in the world would be 0 degrees Fahrenheit, which proves that the greenhouse effect is necessary to support life on Earth [1-2]. However, with the addition of greenhouse gases to the atmosphere due to human activity, more heat is trapped between the surface and the troposphere than is necessary. This additional amount of heat causes the temperature of the earth's climate to rise much faster than it can withstand. As a result, climate change is taking place, the devastating consequences of which we observe every day. There is currently no single way to mitigate the effects of climate change. To solve this global problem, we will have to combine many different solutions [3]. Renewable energy sources include solar energy, geothermal energy, wind turbines, ocean wave and tidal energy, waste and biomass energy, and hydropower. Since they do not burn fossil fuels, these renewable energy sources do not emit greenhouse gases into the atmosphere when generating electricity. Nuclear power also does not create greenhouse gas emissions, so it can be considered as a solution to the problem change of climate.

For example, dry methane reforming (DRM) is an environmentally friendly process, since it processes two main greenhouse gases (CH_4 and CO_2) to produce valuable synthesis gas [4]. The main goal of research in this area is to develop a suitable catalyst to produce synthesis gas, which would have high activity, stability, and minimum coking rate. The catalytic activity of the proposed catalysts is estimated in the temperature range of 500-800 °C. Studies have shown that the catalytic efficiency depends on the nature of the carrier and the properties of the catalytic centers. Among all the tested catalysts, materials with the use of precious metals (Rh> Pt >Pd~Ir >Ru) showed the greatest activity and stability. But these catalytic systems have a high cost. Nickel catalysts exhibit high catalytic activity in dry reforming of methane. However, they have a significant drawback, which is associated with the loss of activity during the deposition of carbon on the surface of the catalyst. Catalysts in which nickel is deposited on the main carriers are least affected by this effect. So, if the Ni/Al_2O_3 catalyst has the greatest activity in the initial period of operation, then the catalysts Ni/Mg, Ni/Cu, Ni/Mn, Ni/ZrO_2 surpass it in operational qualities, showing resistance to deactivation. The development of new catalysts for dry reforming of methane (DRM) is a global urgent task. The synthesis gas obtained during the reforming can be used for the industrial production of synthetic motor fuels, alcohols, and other important organic compounds.

Thus, one of the promising areas of greenhouse gas processing is dry methane reforming, which allows reducing the content of two main greenhouse gases (carbon dioxide and methane) in the atmosphere and obtaining valuable chemical products from them.

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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Synthesis of components of plastic scintillators

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Currently, there are several organic compounds, without which it is impossible to produce plastic scintillators. The most important of these are para-terphenyl and its derivatives. The history of the development of scintillation technology is inextricably linked with research in the field of chemistry and practical application of polyphenylenes [1]. Among these chemical compounds, it is p-terphenyl that occupies the most prominent place. Without the use of this material, it is currently impossible to manufacture most plastic scintillators. As a result of the research, three methods for the synthesis of scintillation-quality p-terphenyl were developed and implemented, which can be used to create a low-tonnage production. To identify the synthesized product and confirm its quality indicators, analytical research methods were developed, which were based on well-known methods of modern instrumental analysis [2].

A progressive method for the synthesis of scintillation-quality p-terphenyl is the use of a cross-coupling reaction, which is currently considered the best laboratory method for obtaining high-quality p-terphenyl with a high technological yield. For its implementation, palladium or nickel complexes are used as catalysts. As a halogen-containing reagent, 1,4-dibromobenzene or 4-brombiphenyl is most often used, and as a component combined with them – phenylboronic acid (Suzuki cross-coupling reaction) or phenyl magnesium bromide (Kumada cross-coupling reaction).

The comparative analysis showed that, in contrast to the Ullman reaction, the proposed method for producing p-terphenyl is characterized by a higher technological yield (70.0 %), process conditions and the use of ready-made commercial reagents. To implement this method for the synthesis of p-terphenyl requires a significant amount of palladium-containing catalyst.

The use of the Kumada cross-coupling reaction instead of the Suzuki reaction in the synthesis of p-terphenyl makes it possible to abandon the palladium catalyst. However, this leads to a decrease in the technological yield and the need to synthesize phenyl magnesium bromide instead of phenylboronic acid as a combined component.

This paper has been supported by the RUDN University Strategic Academic Leadership Program

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