

# ADVANCES IN SYNTHESIS AND COMPLEXING

**Book of abstracts**

**The Fifth International Scientific Conference**

*In Two Parts*

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**Organic Chemistry Section**

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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.

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Dear Colleagues,

I'd like to personally welcome each of you to the 5-th International conference "Advances in Synthesis and Complexing" (RUDN University, Moscow, Russia).

RUDN University is confronting a time of many changes and we're meeting these changes during a time of larger nation-wide and global change. This series of conferences has attracted many leading scientists.

The 5-th International conference "Advances in Synthesis and Complexing" addresses the following research topics

*- Modern problems of organic chemistry. New methods in organic synthesis, synthesis and properties of heterocyclic compounds, multi-component and domino reactions, stereochemistry of organic compounds, chemistry of macrocyclic compounds, biologically active compounds, chemistry of natural products.*

*- Heterogenic and homogenic catalysis. Physico-chemical methods of investigation, quantum-chemical calculations.*

*- Modern problems of inorganic chemistry. Complexing of metals with polyfunctional N,O,S-containing ligands, physico-chemical investigations of inorganic and coordination compounds and new materials, solidphase synthesis. X-RAY analysis.*

This conference is a platform for promoting cooperation between scientists sharing scientific interests in organic, inorganic and physical chemistry as well as interdisciplinary research in this field.

We are most grateful to all the scientists who have travelled from all corners of the world to Moscow. Throughout this conference, I ask you to stay engaged, keep us proactive and help us shape the future of RUDN University.

My personal respect and thanks goes out to all of you.

We hope that you will find your participation in the 5-th International conference "Advances in Synthesis and Complexing" intellectually stimulating and socially enjoyable.

Chair of the organizing committee

Prof. Dr. Leonid G. Voskressensky



# Plenary Lectures



## From Interlocked and Knotted Rings to Molecular Machines

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The area referred to as "Chemical Topology" is mostly concerned with molecules whose molecular graph is non-planar, i.e. which cannot be represented in a plane without crossing points. The most important family of such compounds is that of **catenanes**. The simplest catenane, a [2]catenane, consists of two interlocking rings. **Rotaxanes** consist of rings threaded by acyclic fragments (axes). These compounds have always been associated to catenanes although, strictly speaking, their molecular graphs are planar. Knotted rings are more challenging to prepare. One of the most spectacular topologies in this respect is the **trefoil knot**. Our group has been much interested in knots and, in particular, in their properties in relation to coordination chemistry or chirality.

Since the mid-90s, the field of **artificial molecular machines** has experienced a spectacular development, in relation to molecular devices at the nanometric level or as mimics of biological motors. In biology, motor proteins are of utmost importance in a large variety of processes essential to life (ATP synthase, a rotary motor, or the myosin-actin complex of striated muscles behaving as a linear motor responsible for contraction or elongation). Many examples published by a large number of highly creative research groups are based on complex rotaxanes or catenanes acting as switchable systems or molecular machines. Particularly significant examples include a "pirouetting catenane", "molecular shuttles" (Stoddart and others) as well as multi-rotaxanes reminiscent of muscles. More recent examples are those of multi-rotaxanes able to behave as compressors and switchable receptors. The molecules are set in motion using electrochemical, photonic or chemical signals. Particularly impressive light-driven rotary motors have been created by the team of Feringa.

Finally, potential applications will be mentioned as well as possible future developments of this active area of research.

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## Very strong and confined acids enable a general approach to asymmetric Lewis acid catalysis

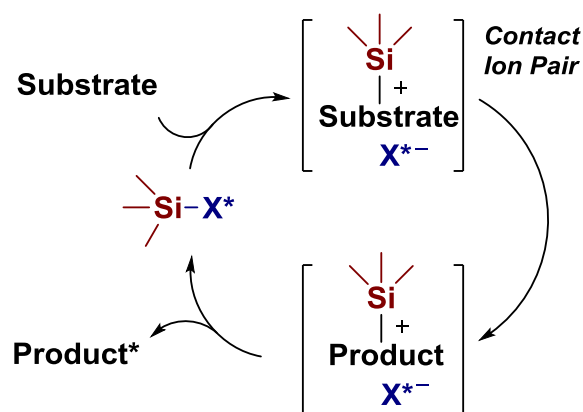
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As a fundamental activation mode, Lewis acid catalysis enables key reactions in chemical synthesis, such as the Diels–Alder and Friedel–Crafts reactions, and various aldol, Mannich, and Michael reactions. Consequently, substantial efforts have been directed towards the development of enantiopure Lewis acids, which have enabled important asymmetric variations of such reactions. Despite the plethora of elegant catalysts and methodologies developed in this context, a key limitation of enantioselective Lewis acid catalysis is the frequent need for relatively high catalyst loadings, which result from issues such as insufficient Lewis acidity, product inhibition, hydrolytic instability, and background catalysis.

We have recently proposed a new design for asymmetric Lewis acid catalysis. We developed in situ silylated disulfonimide-based organocatalysts, which address some of the above problems in various highly enantioselective Mukaiyama-type reactions involving silicon-containing nucleophiles with unprecedentedly low catalyst loadings. As an example of asymmetric counteranion-directed catalysis (ACDC), these reactions proceed via silylation of an electrophile, generating a cationic reactive species that ion-pairs with an enantiopure counteranion and reacts with a silylated nucleophile. We became interested in expanding this “silylium-ACDC” concept to, in principle, all types of Lewis acid catalyzed reactions, including those that do not involve silylated reagents. In my presentation, I will discuss how the concept evolved from our studies on ACDC. I will furthermore describe its first realization with the development of extremely active organic Lewis acid catalysts that enable asymmetric versions of highly challenging Diels–Alder reactions. The confined acids that form the basis of our latest catalyst design not only enable the utilization of small and unbiased substrates but, because of their high acidity, also the activation of previously inaccessible substrates for organocatalysis.

Katalysatordatenbank



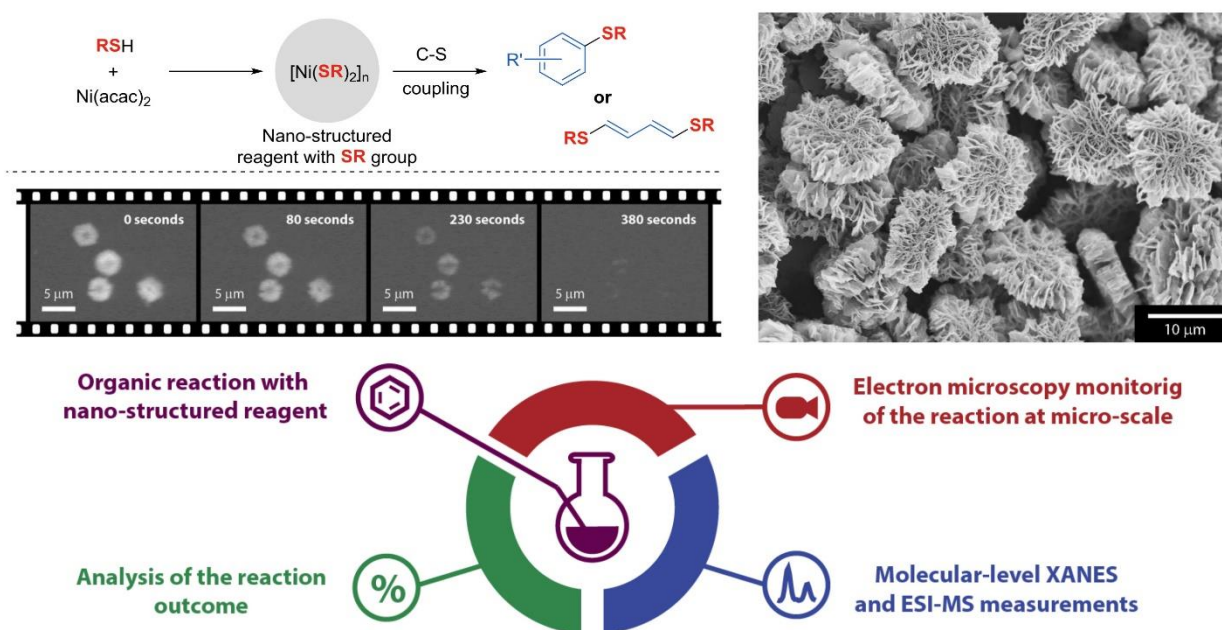
**Silylium-ACDC**

# Dynamic catalytic systems for organic synthesis and sustainable development

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Transition metal catalysis is the most powerful technique for carrying selective organic synthesis in a diverse range of reactions developed in academic research and transformed as core methodologies for industrial processes. Exploring dynamic phenomena in catalysis brings a new wave in sustainable development [1], usage of novel type of reagents [2], resolving reproducibility issues [3] and mechanistic understanding [4].



**Figure 1.** Dynamic catalytic system with nanostructured reagents [2].

New opportunities and challenges of dynamic phenomena in catalytic systems will be presented and discussed in view of organic synthesis and sustainable development.

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## Development of novel C–H functionalization methodologies

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We have developed a set of new transition metal-catalyzed C–H functionalization methodologies employing a silicon-tether motif. These methods feature: (a) use of silyl group as a tether between a substrate and a reagent, thus transforming intermolecular reaction into intramolecular reaction; (b) employment of a silicon-tethered directing group, which is traceless or easily convertible into valuable functionalities; (c) use of silyl-tethered hydrosilane reagent; and (d) introduction of new N/Si-chelation concept that allows for a remote activation of aliphatic C–H bonds.

We have also uncovered new reactivity of hybrid Pd-radical species, generated at room temperature under visible light without exogenous photosensitizers, which lead to development of novel transformations, including new types of Heck reaction, aliphatic C–H functionalization methods, as well as new cascade transformations. These methods employ removable silicon-based, and amide linkers.

The scope of these transformations will be demonstrated and the mechanisms will be discussed.

## **Nickel catalysis for C-C and C-heteroatom bond forming reactions**

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Catalytic C-C and C-heteroatom bond forming reactions represent key transformations for the synthesis of valuable products or advanced intermediates. In this presentation our introduction to the field of C-O bond activation as well as our the recent efforts for the development of new and valuable nickel catalyzed functional group interconversions will be highlighted. These include direct dealkoxylative, decarbonylative, deformylative and decarboxylative reactions [1-2] Furthermore, light mediated combined metal and photoredox catalyzed transformations, including C(sp<sup>3</sup>)-H functionalizations and olefin functionalizations will be presented.

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## **2D materials: Inorganic nanotubes and fullerene-like nanoparticles at the crossroad between materials science and nanotechnology and their applications**

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After almost 100 years of research inorganic layered (2D) materials, like MoS<sub>2</sub>, are currently used as catalysts, lubricants, and perhaps most importantly in rechargeable Li-ion batteries. Much research is currently focused on monolayers (beyond graphene) of 2D materials and hybrids thereof in relation to their electronic and optoelectronics properties. After a short briefing on the history of 2D materials research,<sup>1</sup> the concepts which led to the first synthesis of hollow-cage nanostructures, including nanotubes (INT) and fullerene-like (IF) nanoparticles from 2D compounds, will be presented. The progress with the high-temperature synthesis and characterization of new inorganic nanotubes (INT) and fullerene-like (IF) nanoparticles (NP) will be presented. In particular, the synthesis and structure of nanotubes from the ternary and more recently quaternary “misfit” layered compounds (MLC), like LnS-TaS<sub>2</sub> (Ln= La, Ce, Gd, etc), CaCoO-CoO<sub>2</sub> and numerous other MLC will be discussed.

Major progress has been achieved in elucidating the structure of INT and IF using advanced microscopy techniques, like aberration corrected TEM and related techniques. Mechanical, electrical and optical measurements of individual WS<sub>2</sub> nanotubes reveal their unique quasi-1D characteristics. This analyses demonstrate their altered behavior compared with the bulk phase, including quasi-1D superconductivity. Applications of the IF/INT as superior solid lubricants and reinforcing variety of polymers and light metal alloys was demonstrated. Some of this research resulted in commercial products (a few spin-off companies) which are exploited world-wide with rapidly expanding marketshare. Few recent studies indicate that this brand of nanoparticles is less toxic than most nanoparticles. With expanding product lines, manufacturing and sales, some of these nanomaterials are gradually becoming an industrial commodity.

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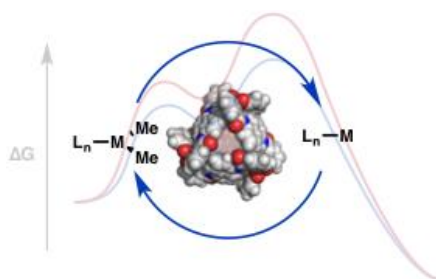
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## Catalysis in confined spaces

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We have been exploring organic and organometallic reactions that occur in the confined space of self-assembled water-soluble tetrahedral  $M_4L_6$  clusters. For example, cationic phosphinegold(I) complexes encapsulated by an anionic  $Ga_4L_6$  tetrahedral demonstrated higher turnover numbers, rate acceleration and/or produced different products compared to the unencapsulated catalysts [1]. In addition to serving as hosts for transition metal catalysts, these supramolecular assemblies can serve as catalysts themselves, both for organic and organometallic reactions (Figure 1) [2]. This lecture will focus on our most recent studies of reactions promoted by encapsulation in these supramolecular hosts, induced thermally and/or photochemically, and the mechanisms of these reactions [3].



**Figure 1.**

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## **The use of Kramers ions for the design of new single magnets and molecule-based magnetic materials**

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The structure and magnetic properties of single ion magnets (SIM) related to Co(II) complexes have been considered. Specific features of the structure and magnetic anisotropy of Co complexes with coordination number being, 4, 5, 6, 7, and 8, and the influence of the ligand surrounding on the distortion of Co coordination and slow magnetic molecule relaxation are under consideration.

Particular attention has been paid to the results of experiments and theoretical modeling of hexacoordinated complexes of Co(II) with negative and positive magnetic anisotropy. To analyze magnetic anisotropy of these complexes, additional experimental techniques, such as SQUID magnetometry, Multi High Frequency EPR Spectroscopy, and Far-infrared Magnetic Spectroscopy have been used, as well as theoretical modeling using parametrized Griffith's Hamiltonian with parameters obtained from ab initio calculations. As follows from the analysis, magnetic anisotropy of these complexes is mainly triaxial, with different signs of axial components. Independently on the sign of the axial anisotropy, Co(II) complexes exhibit a slow paramagnetic relaxation in the constant magnetic (DC) field, i.e., belong to the class of field induced non-monoaxial single ion magnets (FI-SIMs). Such type of SIM behavior is due to Kramer's character of Co(II) ion.

*This work was performed in accordance with the state task, state registration No 0089-2019-0011. The work was financially supported by the Ministry of Education and Science of Russian Federation (Agreement No. 14.W03.31.0001-Institute of Problems of Chemical Physics of RAS, Chernogolovka)*

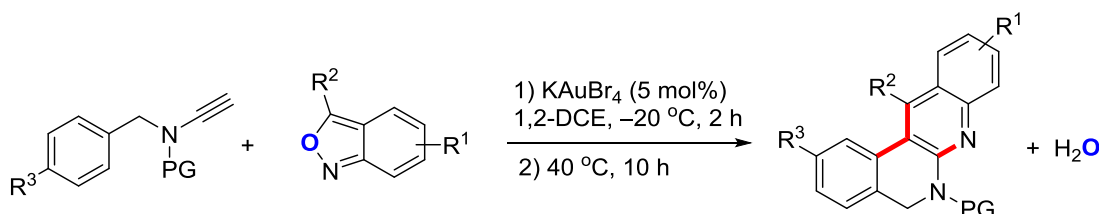
## Gold catalysis: functionalized carbenes, dual activation, light

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Only after two papers from 2000 had demonstrated the full potential of gold catalysis for organic transformations by a high increase of molecular complexity, [1, 2] homogeneous gold catalysis was developed to a versatile tool for organic synthesis [3, 4]. For a long time, the field was exclusively focused on electrophilic and nucleophilic species, radical intermediates were not involved, but this changed in 2013 [5].

Apart from the synthesis of different heterocycles, the use of these principles also allows a number of C-C coupling reactions, which in a formal sense can also address C-H bonds [6]. Principles like dual activation, and the use of di- and even mononuclear gold(I) complexes for photochemical reactions will be discussed.



**Scheme 1.** Intermolecular reaction of an anthranil derivative with an ynamide to provide a multi-annulated heterocyclic system in only one step.

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# Key-note Speakers



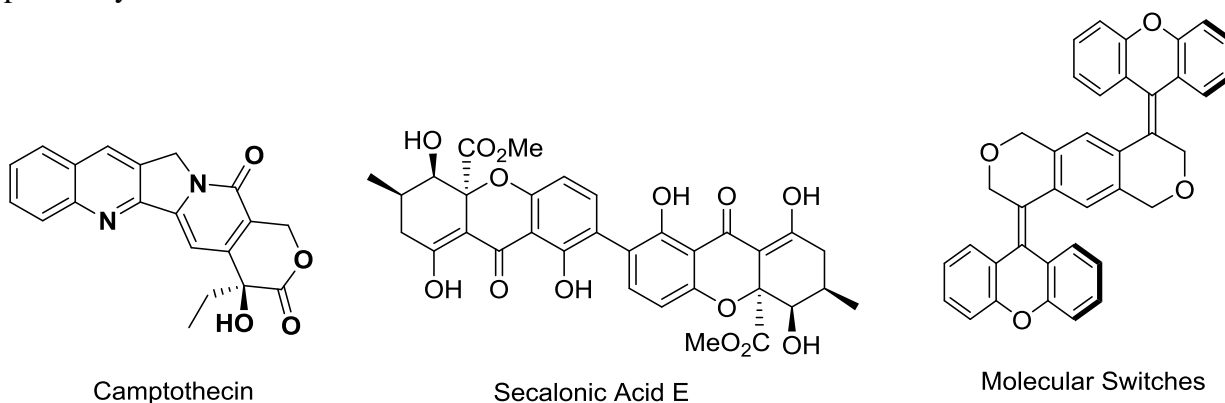
## Catalytic Domino reactions for the ecologically and economically favorable synthesis of natural products and materials

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Catalytic processes either using organo- or transition metal-catalytic processes are very important for an ecologically and economically favourable synthesis. A further improvement would be the incorporation of these methods in the domino concept [1], which has been introduced by us. In the lecture the synthesis of alkaloids as the pyrroloquinoline alkaloid camptothecin and the ipecacuanha alkaloid emetine will be presented [2]. Here, a domino Knoevenagel/Hetero-Diels Alder reaction as a three and four-component transformation has been used.

Moreover, the preparation of vitamin E and the complex acetogenins secalonic acid E and dicerandrol will be described using enantioselective Pd-catalysed processes [3, 4]. The final group of compounds which will be presented are molecular switches with two switching units using a CH-activation reaction as the last part of the sequence [5]. Here, also the importance of proximity effects will be discussed.



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**Discovery, target identification and validation of a novel class of potent highly selective anti-colon cancer small molecules**

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Our laboratory focuses on the synthesis of complex molecular architectures, including both designed and naturally occurring substances with novel structural features and interesting biological function. To facilitate the execution of efficient and practical syntheses, we also develop novel methodology relevant to medicinal chemistry and complex natural products synthesis. We take advantage of the collaborative, multi-disciplinary research environment at UTSW, and have significantly fortified our chemistry program with molecular pharmacology, biochemistry, and discovery biology.

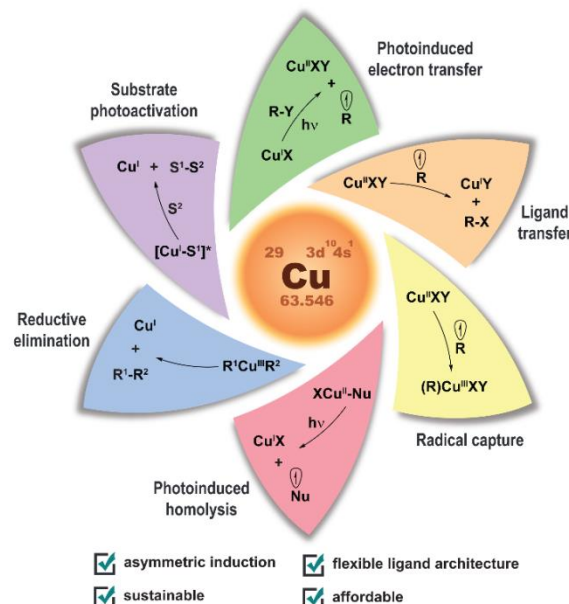
I will present our work related to the discovery of small molecules with potent selective activity against colon cancer cell lines containing a mutation in the Adenomatous Polyposis Coli tumor suppressor gene, termed TASINs (Truncated APC-Selective Inhibitors). We undertook a large medicinal chemistry campaign (~200 analogs) to understand the structure activity relationships within this compound series. These studies led to potent picomolar analogs with no toxicity to normal cells or other cell lines that do not carry the truncating APC-mutation. Several analogs were found with suitable pharmacological properties that displayed significant efficacy in genetic animal models of colorectal cancer. Finally, we also prepared a collection of probe reagents that were used to identify the molecular target of TASINs.

## Cornucopian copper rocks the house of visible-light photoredox catalysis

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Synthetic organic chemistry undertakes great efforts to develop new catalytic transformations that utilize greener reagents and avoid stoichiometric additives. In this regard, visible-light photoredox catalysis offers a unique activation mode of molecules, which is serving as an alternative to many thermal transition-metals catalyzed reactions. The vast majority of photoredox catalyzed processes capitalizes on heavy metals namely, Ru(II) or Ir(III)-complexes which can serve as single electron oxidant or reductant in their photoexcited states. As a low cost-alternative, organic dyes are also frequently used photocatalysts but suffer in general from lower photostability. Copper based photocatalysts are rapidly emerging, offering not only economic and ecologic advantages, but in addition are able to interact with substrates beyond electron transfer via inner sphere mechanisms, which has been successfully utilized to achieve challenging transformations. Moreover, the combination of conventional photocatalysts with copper(I) or copper(II) salts allows a most efficient merger of photoredox and transition metal based catalysis.



Selected synthetic applications from our laboratory, highlighting the complementary opportunities of copper and iridium based photocatalysts, will be discussed.

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## **New avenues in synthesis via organic photoredox catalysis**

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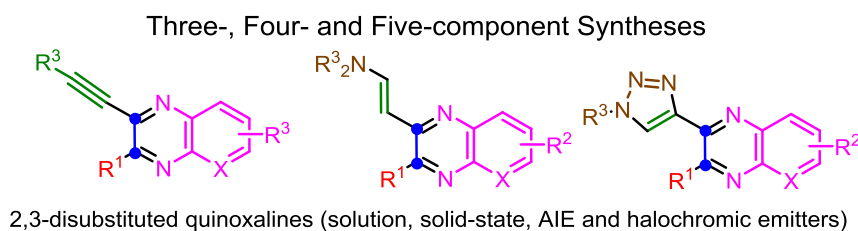
Single electron pathways are prevalent in numerous biosynthetic pathways that are crucial to life on our planet. As synthetic chemists, we seek to harness the power of these open-shell processes to achieve uncommon but valuable chemical reactivity. To this end, my laboratory is interested in accessing single electron pathways via the use of organic photoredox catalysis. This seminar will highlight the recent synthetic methods developed by my laboratory, C-H functionalization reactions of aromatic and aliphatic compounds as well as catalysis of the nucleophilic aromatic substitution of methoxyarenes. Where, applicable, data in support of mechanistic hypotheses will be presented.

## Multicomponent syntheses of quinoxalines – aggregation induced and solvatochromic emission

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Multi-component reactions are efficient and effective methods for sustainable and diversity-oriented synthesis of functional chromophores [1], and transition metal catalyzed multicomponent sequences elegantly allow for the one-pot syntheses of heterocycles [2] and fluorophores [3], in particular for AIE (aggregation induced emission) chromophores [4]. Various AIE and emission solvatochromic quinoxalines are readily accessible via Cu-catalyzed four- or five-component processes [5, 6]. New sequences furnish angular donor-quinoxaline-triazole conjugates [7] and Au-catalyzed anellations of 3-ethynyl-2-indolylquinoxalines lead to 8*H*-indolo[3,2-*a*]phenazines, angularly rigidified pentacycles with interesting luminescence properties [8]. The conceptual synthetic one-pot approach, photophysical studies on selected fluorophores, and aggregation induced emission will be presented and discussed.



*This work was supported by the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft (DFG)*

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## The development of cross-dehydrogenative-coupling (CDC)

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The efficient making of new molecules is central to any new product in the pharmaceutical, materials science, microelectronics, and biotech industries. Exploration of new chemical reactivities towards a sustainable future has been a long-term objective of our laboratory [1]. We have explored various unconventional chemical reactivities that can potentially simplify synthesis, decrease overall waste and maximize resource utilization. Within the last decade, we have studied the development of various unconventional methodologies directed at increasing efficiency for multi-step chemical synthesis [2-4]. These include the development of a wide range of Grignard-type reactions in water, transition-metal catalysis in air and water, alkyne-aldehyde-amine coupling ( $A^3$ -coupling), and the Cross-Dehydrogenative-Coupling (CDC) reactions, biomass conversions and catalytic conversion of methane. Many of these new reactions can also be used to functionalize biomass directly. This talk will discuss the development of the concept of the Cross-Dehydrogenative-Coupling (CDC) reaction and synthetic examples.

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## Alkanes as potential feedstocks in metal catalyzed organic synthesis

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Alkanes, the major components of natural gas and oil and a highly rich natural carbon source, have been applied mainly as non-renewable fossil fuels where they are burnt and carbon (upon full oxidation to CO<sub>2</sub>) is lost to the atmosphere with environmental concerns.

In fact, the inertness of alkanes has hampered their potential application as a feedstock for organic synthesis of functionalized products with an added value, and such an overall synthetic approach based on alkanes concerns one of the greatest challenges in modern chemistry.

The development of sustainable and direct processes to achieve functionalized products from alkanes would be highly advantageous even in terms of simplicity, in comparison with the current multi-stage and often energy demanding processes used in industry for such organic products. Approaches followed by the author's research Group will be discussed, namely concerning the following types of reactions: Oxidation of alkanes to alcohols and ketones; Oxidation of cyclohexane to adipic acid; Carboxylations of alkanes to carboxylic acids.

The application of various types of media (water, ionic liquid or organic solvent) and of catalysts (based on either transition metals or non-transition ones, with a diversity of ligands; homogeneous or supported ones) and mechanistic proposals will be addressed. Some systems display the highest reported catalytic activities in this field.

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*The co-authors cited in the references are gratefully acknowledged*

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- [2] Preface (A.J.L. Pombeiro, M.F.C. Guedes da Silva);
- [3] Ch.1 (A.J.L. Pombeiro): Overview;
- [4] Ch.7 (D.S. Nesterov, O.V. Nesterova, A.J.L. Pombeiro): Oxidation with multinuclear heterometallic catalysts;
- [5] Ch.16 (M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, A.J.L. Pombeiro): Oxidation with V and Cu catalysts;
- [6] Ch.19 (A.M.F. Phillips, A.J.L. Pombeiro): Carbonylation and hydroxycarboxylation;
- [7] Ch.24 (A.P.C. Ribeiro, E.C.B.A. Alegria, A. Palavra, A.J.L. Pombeiro): Functionalization under unconventional conditions;
- [8] Ch.25 (K.T. Mahmudov, M.F.C. Guedes da Silva, F.I. Zubkov, A.J.L. Pombeiro): Non-covalent interactions in alkane chemistry.



# Invited Lectures



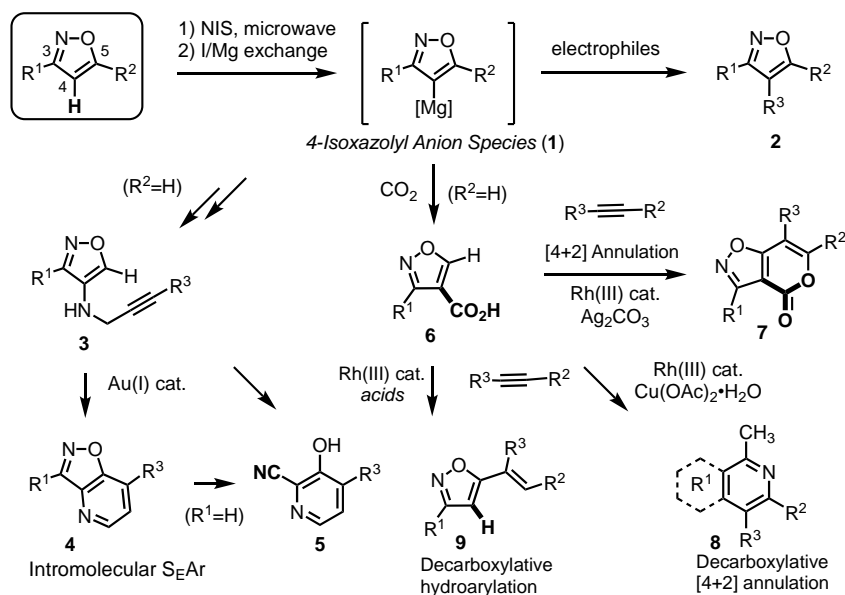
## Isoxazole-based transformations via direct C-H activations

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Isoxazole is one of the most important frameworks in pharmaceuticals and agrochemicals. Although various approaches based on ring construction have been reported for the synthesis of functionalized isoxazoles, direct functionalization of isoxazole ring has not been established [1]. We have developed isoxazole-based transformation via direct C-H activations. The use of isoxazolyl anion is recognized as an extremely difficult task due to its lability. We succeeded in the generation of 4-isoxazolyl anion via iodine/magnesium exchange using turbo Grignard reagent which enabled facile access to structurally diverse isoxazoles **2-4** without inducing decomposition of isoxazole ring [2]. Furthermore, due to its low nucleophilicity, there were no reports of electrophilic aromatic substitution reaction at the C3 or C5-positions. We succeeded in the gold(I)-catalyzed cyclization of 4-(propargylamino)isoxazoles **3** that is the first example of  $S_EAr$  type reaction of isoxazole at the C5-position [3]. The resulting isoxazolopyridines **4** were readily converted into 3-hydroxypicolonitriles **5**, which are important intermediate for 2,3,4-trisubstituted pyridines [4].

A directing group (DG) is able to facilitate C-H activation by enhancing the effective coordination with catalysts, resulting in both high reactivity and selectivity. Especially, the carboxylate has been focused as a simple DG. We demonstrated the first carboxylate-directed C-H functionalizations of isoxazoles. We achieved the development of Rh(III)-catalyzed direct C-H activation of isoxazolyl-4-carboxylic acids **6** with internal alkynes for systematic synthesis of pyranoisoxazolones **7** ([4+2] annulation), isoquinolines **8** (N-O cleaved decarboxylative [4+2] annulation), and 5-alkenylisoxazoles **9** (decarboxylative hydroarylation) [5].



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## Photoredox catalysis for the synthesis of *gem*-difluorinated compounds

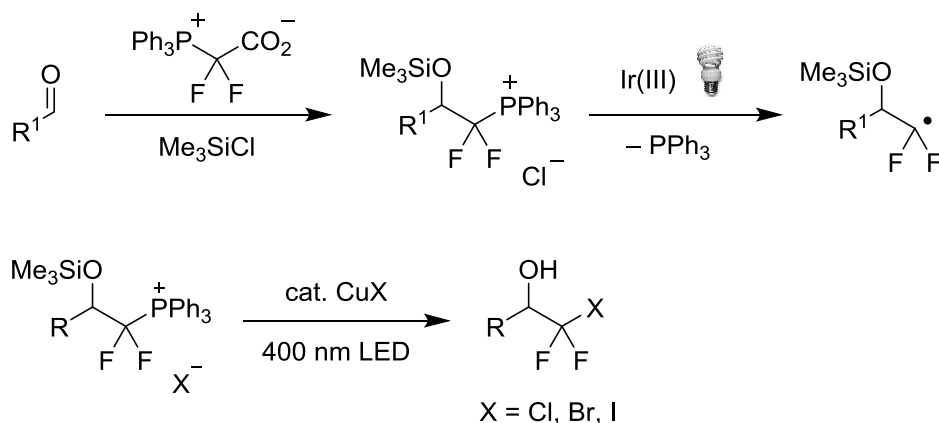
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Photoredox catalysis has emerged as a powerful methodology for performing radical reactions. Fluorinated halides serve as good substrates for photoredox reactions, since they readily accept one electron with the generation of radical species via dissociation of carbon-halogen bond.

We showed that *gem*-difluorinated phosphonium salts, which are readily generated via difluorocarbene approach [1], can serve as sources of difluorinated radicals under photoredox conditions [2]. These radicals can be trapped with alkenes leading to various fluorinated products.

In the difluorinated phosphonium salts, the phosphonium fragment can be substituted by a halide (chloride, bromide or iodide) in the presence of copper(I) salts [3]. This reaction constitutes a convenient method to access alcohols bearing the halodifluoromethyl group. The iododifluoromethyl group can be further functionalized by activation of the C-I bond [4].



*This work was supported by the Russian Science Foundation  
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## New chemical reactivities in continuous-flow synthesis

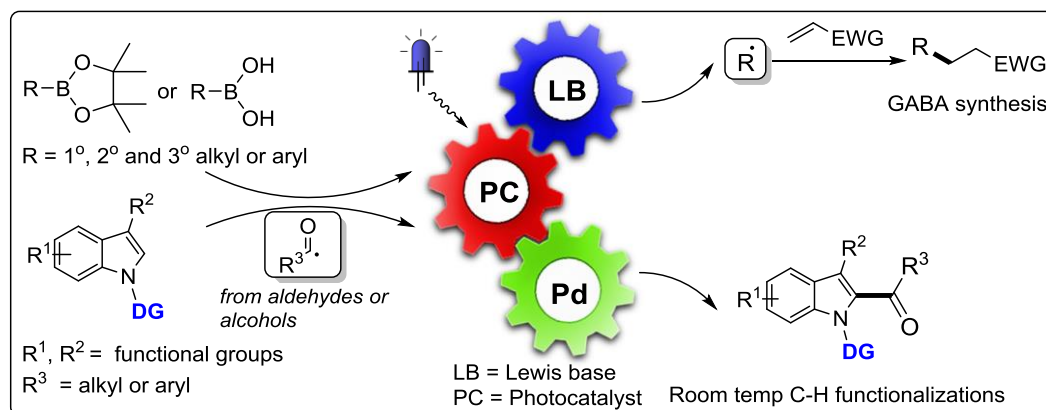
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The development of new and benign strategies facilitating the atom-economical construction of biologically and industrially important molecules is a key pursuit from the viewpoint of *Sustainable Chemistry*. Construction of carbon-carbon and carbon-nitrogen bonds *via* the generation of carbon or nitrogen-centered radicals is a rapidly growing field in the realms of synthetic organic chemistry [1]. In this direction, visible-light photocatalysis has been playing a tremendous role for the translation of odd-electron transfer processes into mild catalytic cycles that have previously been elusive in comparison to their two-electron analogues [2]. However, to make a long-standing impact and wide applicability in pharmaceutical industry, medicinal chemistry as well as material sciences, visible-light photocatalysis has to deal with scale-up as well as severe solubility issues associated with the stoichiometric use of inorganics or the use of charged substrates. This presentation will highlight and discuss our efforts in this direction [3] how flow chemistry [4] in combination with C-H functionalization and/or photochemistry can solve these issues when combined with right substrates and catalyst under mild reaction conditions, besides its application in pharmaceutical synthesis (Scheme 1).



**Scheme 1:** Photocatalytic C-C bond formations in batch and continuous flow.

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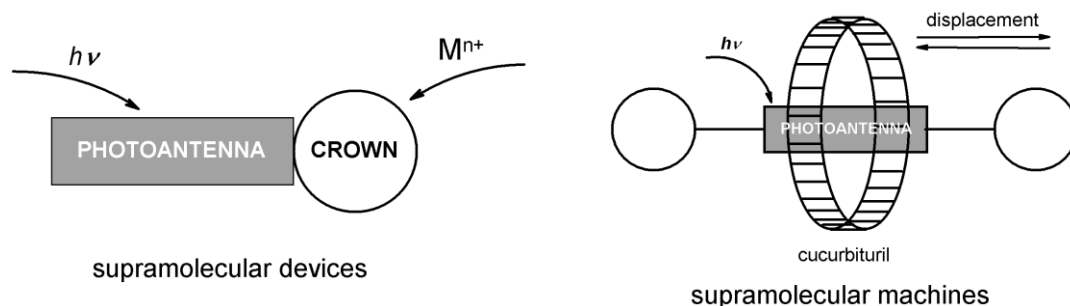
## Molecular meccano of photoactive supramolecular devices and machines based on unsaturated and macrocyclic compounds

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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.



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, 5].

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## Stereoelectronic chameleons: radical addition to isonitriles

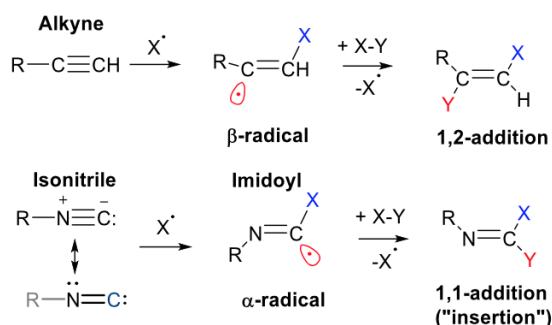
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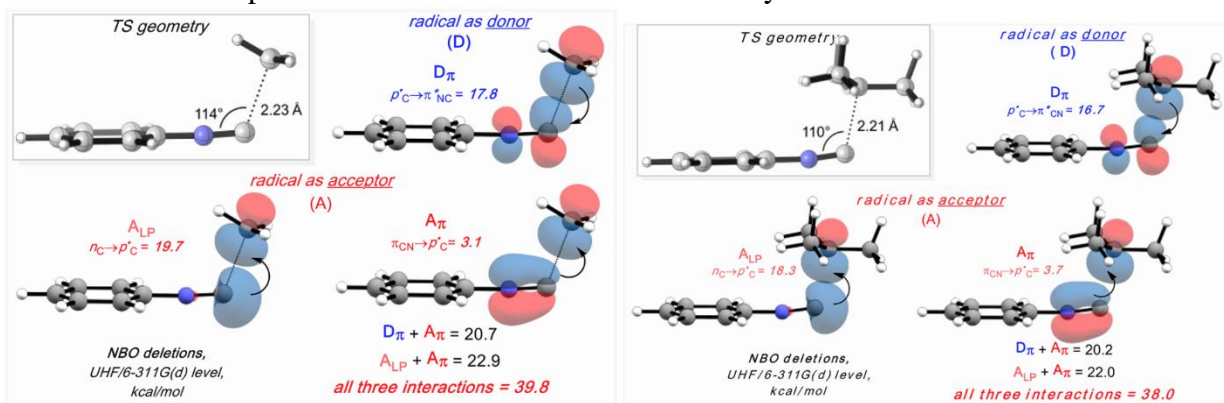
Stereoelectronic factors account for the apparent reversal of donor/acceptor properties of a variety of functional groups by a simple change of their orientation in space. The new reactivity patterns that arise from spatial anisotropy are associated with *chameleonic* behavior of common organic functionalities [1]. Because donor and acceptor properties are often engraved into our thinking about functional groups by the current educational paradigms, such a stereoelectronic “umpolung” can unlock useful ways of thinking about chemical reactivity and open new doors for reaction design.

Isonitriles (isocyanides) combine rich and diverse reactivity with an intriguing dichotomy of electronic properties. In particular, in radical addition to triple nitrogen-carbon bond the substrates demonstrate that they behave as *stereoelectronic chameleons* [2].

Unlike reactions with alkenes and alkynes, radical addition to isonitriles proceeds in 1,1-addition-manner, which means we deal here with unique non-Markovnikov case. Addition of alkyl, aryl, heteroatom-substituted and heteroatom-centered radicals reveals a number of electronic, supramolecular, and conformational effects potentially useful for the practical control of isonitrile-mediated radical cascade transformations.



In addition to polarity and low steric hindrance, radical attack at the relatively strong  $\pi$ -bond of isonitriles is assisted by *chameleonic* supramolecular interactions of the radical center with both the isonitrile  $\pi^*$ -system and carbon's lone pair. These interactions are yet another manifestation of supramolecular control of radical chemistry.



We are looking forward to new examples of *stereoelectronic chameleons* in control of structure and reactivity.

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## Unusual result of Michael addition of indoles to nitrostyrenes

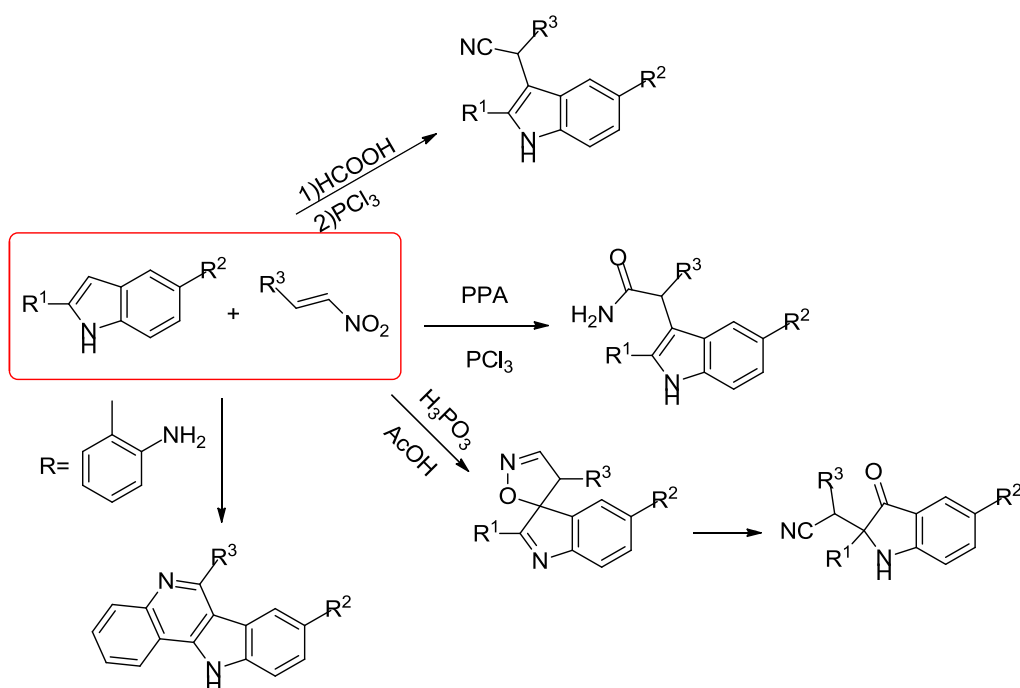
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Nitroalkenes are versatile reagents for fine organic synthesis, medicinal and pharmaceutical chemistry and drug design, that are primarily used as electrophilic components in Michael additions, as electron-deficient dienophiles in the Diels-Alder and hetero-Diels-Alder reactions, or as powerful dipolarophiles or heterodienes for various formal [3+2] and [4+2] cycloadditions. Several novel modes of reactivity have been recently investigated in our laboratories, involving interaction of nitroalkenes with indoles in the presence of phosphorus(III) compounds. In particular, unusual and highly diastereoselective (4+1) spirocyclization was discovered, in which nitroalkene serves as formal 1,4-dipole of CCNO-type, while C-3 site of indole works as C1-component. In addition, formation of structural analogs of natural alkaloid isocryptolepine was observed in reactions of nitroalkenes with indole substrates possessing 2-aminophenyl substituents at C-2.



*This work was supported by the Russian Science Foundation  
(Grant #18-13-00238)*

## Enamides - Versatile tools for the construction of complex molecules containing multiple continuous stereocenters

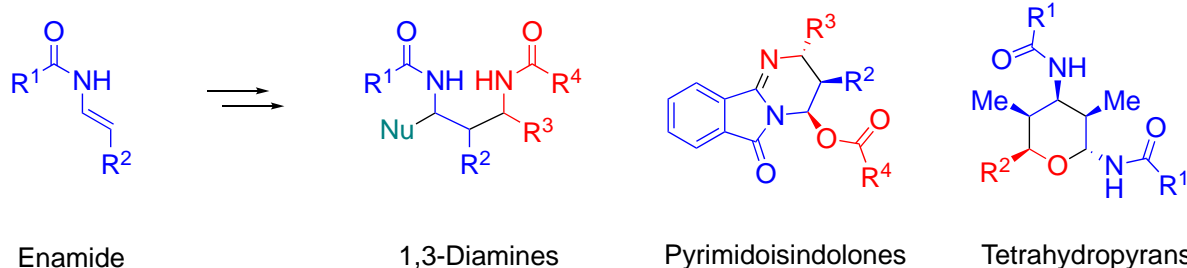
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In recent years, enamides have emerged as valuable building blocks for the introduction of nitrogen functionalities into organic molecules [1]. The electron-withdrawing substituent at the nitrogen renders enamides less nucleophilic than their parent enamines. This tempered reactivity leads in term to an increased stability. The balance between reactivity and stability can be modulated by the nature of the electron-withdrawing substituent. Therefore, enamides can be considered as stable and tunable enamine surrogates.

Enamides can react as a nucleophile with a variety of different electrophiles, thereby generating a highly electrophilic N-acylimine species, which in turn can be trapped with a terminal nucleophile. We have utilized this reactivity to develop several highly stereoselective processes for the construction of nitrogen-containing molecules:

- i) a highly modular platform for the stereodivergent synthesis of 1,3-diamines, which provides access to all possible diastereomers of the 1,3-diamine scaffold [2];
- ii) a stereoselective one-pot-synthesis of dihydropyrimido[2,1-a]isindolone-6(2H)-ones, giving access to an uncommon heterocyclic motif [3];
- iii) a highly diastereoselective synthesis of highly substituted tetrahydropyrans containing five continuous stereogenic centers [4].



simple access to complex molecules with up to five continuous stereocenters

These novel procedures enable a rapid, modular and controlled construction of complex molecules bearing up to five continuous stereocenters from simple buildings blocks.

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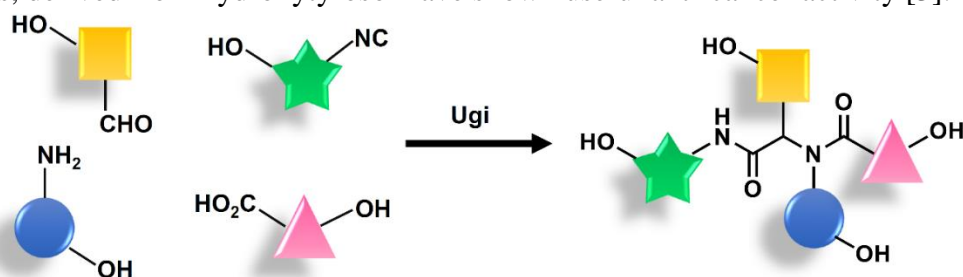
## From natural, renewable sources to complex biologically active compounds exploiting multicomponent reactions

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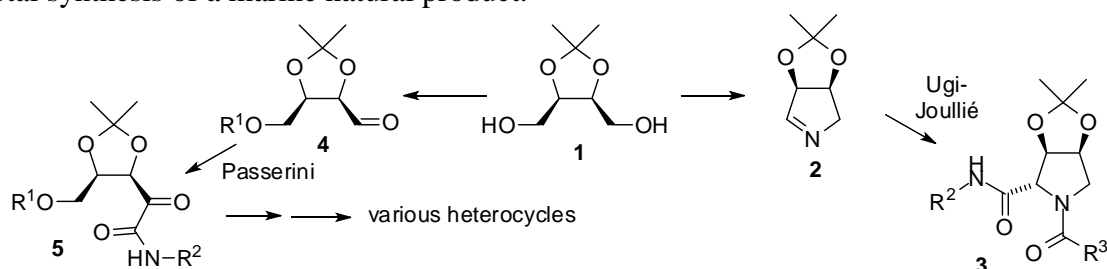
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Recently, we have been deeply involved in applying multicomponent reactions to the combinatorial assembly of relatively complex products starting from small natural molecules, derived from renewable sources. Two cases will be discussed, regarding the synthesis of artificial, yet "natural-like", polyphenols, and the stereoselective derivatization of erythritol, a polyfunctionalized renewable building block.

Natural polyphenols of plant origin are endowed with a variety of biological properties [1]. Their synthetic modification is often difficult, hampering a thorough modulation of their pharmacodynamic and pharmacokinetic properties. We used the Ugi MCR to build up, starting from simple phenolic natural compounds (e.g. ferulic acid), a library of polyphenols, which have been later investigated as inhibitors of  $\beta$ -amyloid aggregation [2]. The preliminary results allowed to select a lead that demonstrated promising *in vitro* and *in vivo* activity. Other polyphenols, derived from hydroxytyrosol have shown useful anti-cancer activity [3].



Protected erythritol **1** has been first enzymatically desymmetrized to give both enantiomers of the corresponding monoester, and then converted into either pyrrolines **3** or aldehydes **4**. The former were employed in highly diastereoselective Ugi-Joullié reactions [4]. On the latter, an unprecedented diastereoselective Passerini reaction was realized [5]. Passerini adducts **5** were then converted into a variety of heterocycles. This strategy was also exploited in the total synthesis of a marine natural product.



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## Post-Ugi transformation of *N*-substituted-2-alkyneamides for the construction of diverse heterocyclic scaffolds

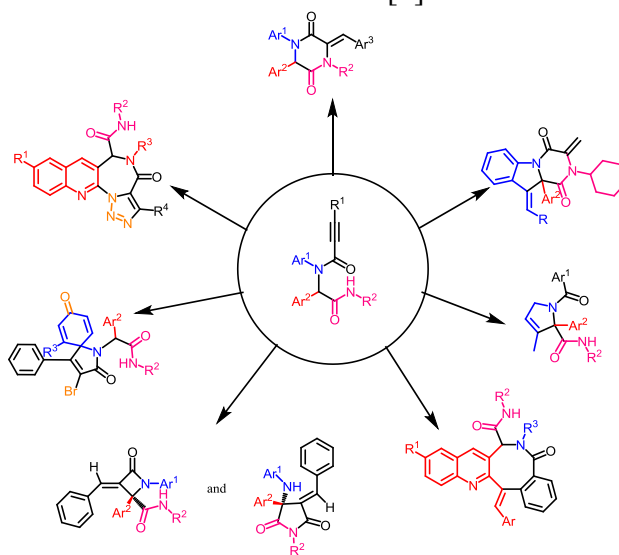
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The selection of a functionalized alkyne is an efficient approach for the synthesis of heterocycles and also multifunctional compounds. Cyclization of alkynes could be done through  $\pi$ -activation with metal salts or formation of the desired metal acetylide [1].

The combination of established Ugi-4CR with post-transformational reactions has become a useful tool for generating complex and diverse molecular libraries with novel properties [2]. Thus a logical extension is to use post-transformational reactions through the deployment of secondary functional groups in the initial starting materials. Post-Ugi transformations showed high potential in the synthesis of complex molecules such as functionalized  $\beta$ -lactams and benzoindolizidine alkaloids [3]. In this personal account, our endeavors in the area of post-Ugi transformation reactions of *N*-substituted-2-alkyneamides to access diverse heterocyclic skeletons are summarized [4].



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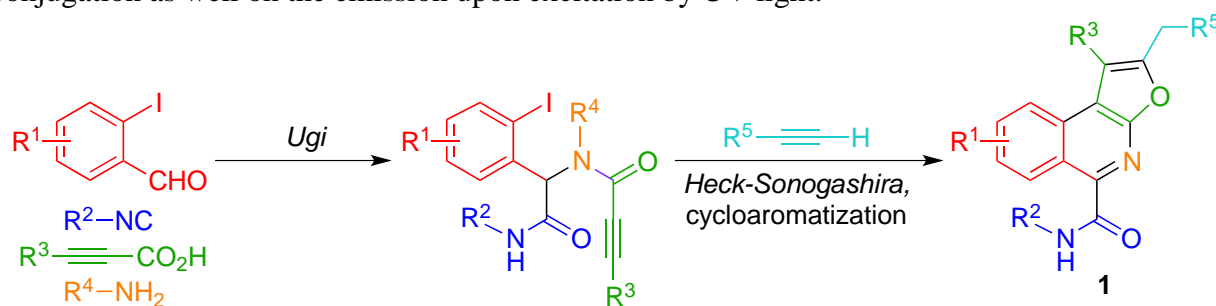
## Diversity oriented synthesis of furans and tetrahydrofurans using multicomponent reactions

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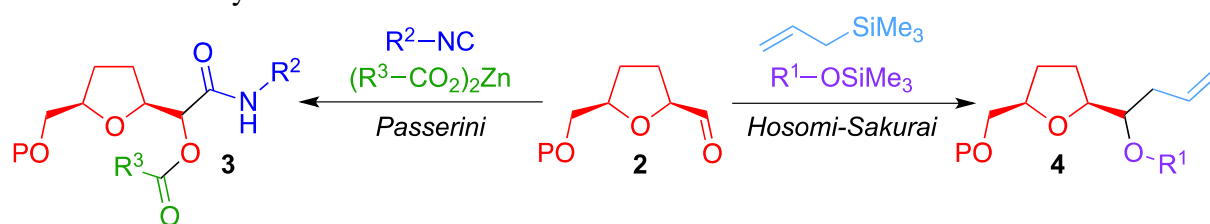
Furans and tetrahydrofurans are very important heterocyclic scaffolds, which are often included in fluorescent molecules or in bio-based polymers and are present in many natural products [1]. Both scaffolds have been object of study within different projects involving multicomponent reactions.

The synthesis of furo[2,3-*c*]isoquinolines **1** by coupling the Ugi reaction with a complex palladium catalyzed cascade sequence, involving a Heck-Sonogashira reaction, followed by a cycloaromatization will be discussed [2]. These molecules are all intensively blue emissive and some of them display aggregation induced emission (AIE). The photophysical properties have been deeply investigated for understanding the influence of the substituents and of an extended conjugation as well on the emission upon excitation by UV light.



We recently developed a diastereoselective Passerini reaction on a bio-based chiral aldehyde, demonstrating that the stereoselectivity is largely influenced by the addition of  $\text{ZnBr}_2$  [3]. As a continuation of this project we extended the scope to protected aldehyde **2**, obtained from bio-based 5-hydroxymethylfurfural after a chemoenzymatic procedure developed by us. This time we used an unprecedented methodology for controlling the stereoselectivity, that is the use of an appropriate zinc carboxylate, as carboxylic component and activating Lewis acid as well, to afford **3**.

The same aldehyde has also been involved in a diastereoselective Hosomi-Sakurai multicomponent reaction for the synthesis of protected homoallylic ethers **4**, involving either achiral or chiral silyl ethers.



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## New methods for benzyne generation and some synthetic applications

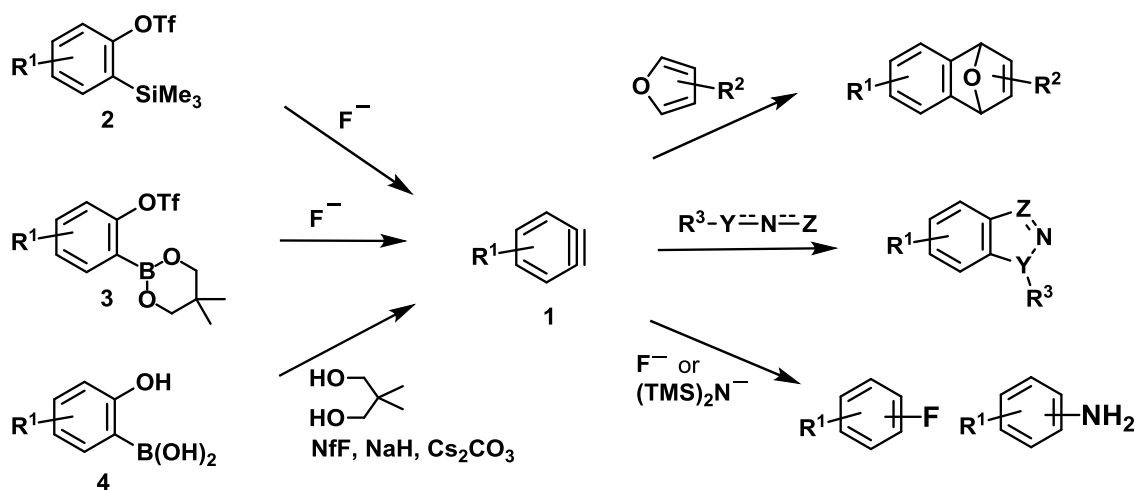
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Reactions of benzyne **1** are among the oldest and most potent multi-bond-forming processes for the synthesis of polysubstituted and/or ring-fused benzenes. A variety of benzyne precursors have been developed so far, in which 2-(trimethylsilyl)phenyl triflates **2** have gained a high reputation because of fluoride-ion-mediated mild conditions for the benzyne generation that have led to the development of a variety of new benzyne reactions in the past few decades. However, the synthesis of **2** having a range of functional groups  $R^1$  is difficult since it requires strongly basic conditions to install the silyl group on the benzene ring. In this symposium, we present new methods for the generation of functionalized benzyne **1**.

At first, we have discovered that 2-[(neopentyl glycolate)boryl]phenyl triflates **3** generate **1** at 120 °C in the presence of a fluoride ion. The precursors **3** have two major advantages; (i) the ready availability of **3** through the palladium-catalyzed Miyaura borylation of 2-iodophenols and (ii) the efficient generation of **1** bearing various reactive functional groups, such as carbonyl, cyano, bromo, and primary amino groups. The generated **1** immediately underwent the (4+2) and (3+2) cycloadditions to give the benzo-fused cyclic compounds while maintaining the functional groups [1]. Next, we have further improved the above-mentioned method to achieve direction generation of **1** from 2-hydroxyphenylboronic acids **4** [2]. Currently, more than 120 kinds of 2-hydroxyphenylboronic acids **4** are commercially available, which will be potentially applicable to the direct generation of functionalized benzyne **1**.

We will also report the deoxyfluorination [3] and deoxyamination [4] of phenol derivatives through benzyne generation.



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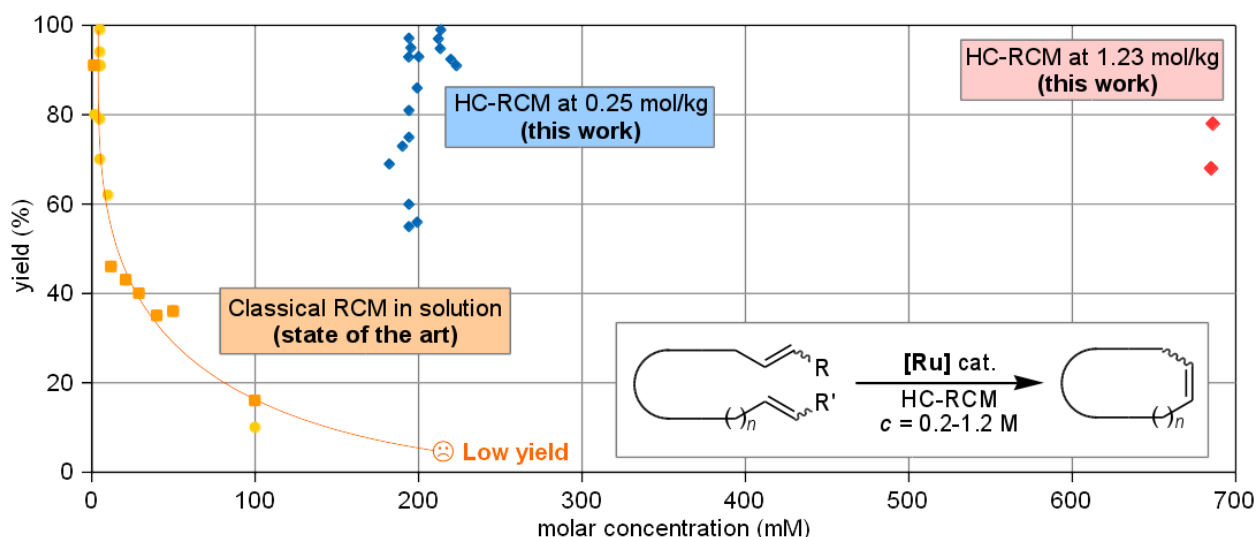
# Olefin metathesis macrocyclization at high concentration and other "Missions Impossible"

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Macrocyclic lactones, ketones, and ethers can be obtained in the High-Concentration Ring-Closing Metathesis (HC-RCM) reaction in high yield and selectivity at concentrations 40 to 380 times higher than those typically used by organic chemists for similar macrocyclizations.

The new method consists of using tailored ruthenium catalysts together with applying vacuum to distill off the macrocyclic product as it is formed by the metathetical backbiting of oligomers. Unlike classical RCM, no large quantities of organic solvents are used, but rather inexpensive nonvolatile diluents, such as natural or synthetic paraffin oils. Moreover, use of a protecting atmosphere or a glovebox is not needed, as the new catalysts are perfectly moisture and air stable. In addition, some other cyclic compounds previously reported as unobtainable by RCM in neat conditions, or in high dilutions even, can be formed with the help of the HC-RCM method [1].



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## Synthesis and biological evaluation of new water-soluble photoactive chlorin conjugates for targeted delivery

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A range of new water-soluble conjugates consisting of a PDT-active chlorin-based photosensitizer and an EGFR/VEGFR 4-arylaminoquinazoline ligands were synthesized in 7 - 33 steps. An increased accumulation of these compounds in cells with overexpression of EGFR was observed, in comparison with cell uptake into cells with low-level EGFR-expression. The prepared conjugates exhibited dark and photoinduced cytotoxicity at nano- and micromolar concentrations with pronounced difference in  $IC_{50\text{dark}}/IC_{50\text{light}}$  ratio up to 300. After intravenous administration into tumor-bearing mice, the conjugates preferentially accumulated in the tumor tissues.

*We thank the Russian Foundation for Basic Research  
(project number 18-33-20041)*

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## New axially chiral bipyridines and their application in asymmetric catalysis

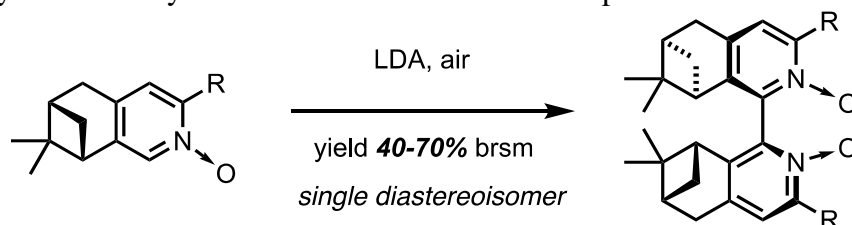
Fukazawa Y.<sup>[A]</sup>, Vaganov V.Yu.<sup>[B]</sup>, Shipilovskikh S.A.<sup>[B]</sup>, Rubtsov A.E.<sup>[B]</sup>, Malkov A.V.\*

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Complexes of chiral bipyridines with transition metals have a very rich chemistry including catalytic asymmetric transformations [1]. On the other hand, the related bipyridine *N*-oxides have become important players in enantioselective nucleophilic organocatalysis [2]. Despite these successes, synthesis and application of axially chiral bipyridine derivatives has not reached the level of maturity, which in part is due to the lack of good coupling methods for joining the pyridine units together in a highly stereoselective fashion.

Herein, we present an expedient mild procedure for coupling of two chiral pyridine-*N*-oxide units, where the central chirality of the terpene fragment efficiently controls formation of the chiral axis [3]. The synthesised bipyridine-*N*-oxides can be reduced to the respective chiral bipyridines with a complete retention of the axial chirality. Several applications of both bis-*N*-oxides and bipyridines in asymmetric transformations will be presented.



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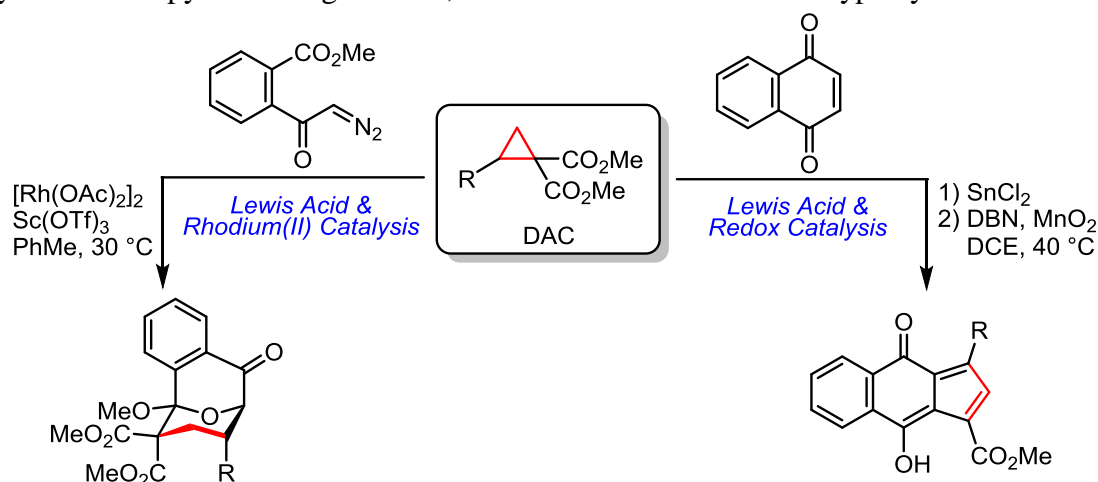
## Donor-acceptor cyclopropanes as unique building blocks for the synthesis of carbo- and heterocyclic compounds

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Donor-acceptor cyclopropanes (DACs) are highly strained entities which are unique building blocks for hetero- and carbocyclic systems [1,2]. For the last decade, we have been developing novel methodologies starting from these type of three-membered rings leading to oligopyrroles, chalcogen-containing heterocycles, and 1,3-bisfunctionalized products [3], just to name a few. To get deeper insights into their intrinsic reactivity in-depth physical organic studies were performed recently [4].

Besides the common activation of DACs by Lewis acids even a synergistic catalytic approach can be applied to generate fleeting intermediates to react with the strained systems. Two examples, one using Lewis acid and Rh catalysis (affording intermediate carbonyl ylides) [5] and another using Lewis acid and redox catalysis are presented [6]. In the former example highly substituted pyranes are generated, in the latter unusual fulvene-type dyes.



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**Benign-by-design methodologies for a more sustainable future:  
from nanomaterials design to advanced catalytic applications**

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The design of benign and environmentally sound methodologies has been the driving force of scientists in recent years. Attractive and innovative protocols that nowadays are even part of industrial ventures including biomass-derived porous carbonaceous materials, designer nanomaterials for (photo)catalytic applications and catalytic strategies for biomass/waste conversion into useful materials, chemicals and fuels have been recently developed in our group in recent years.

In this lecture, we aim to provide an overview of recent efforts from our group in leading the future of global scientists from chemical engineers to (bio)chemists, environmentalists and materials scientists in benign-by-design methodologies and processes for a more sustainable future chemical industry. These will include case studies from past/ongoing projects for the group based on nanoscale chemistry, heterogeneous (photo)(bio)catalysis and organic chemistry.

# Oral Reports



## Recent developments in hydrated imidazoline ring expansion (HIRE)

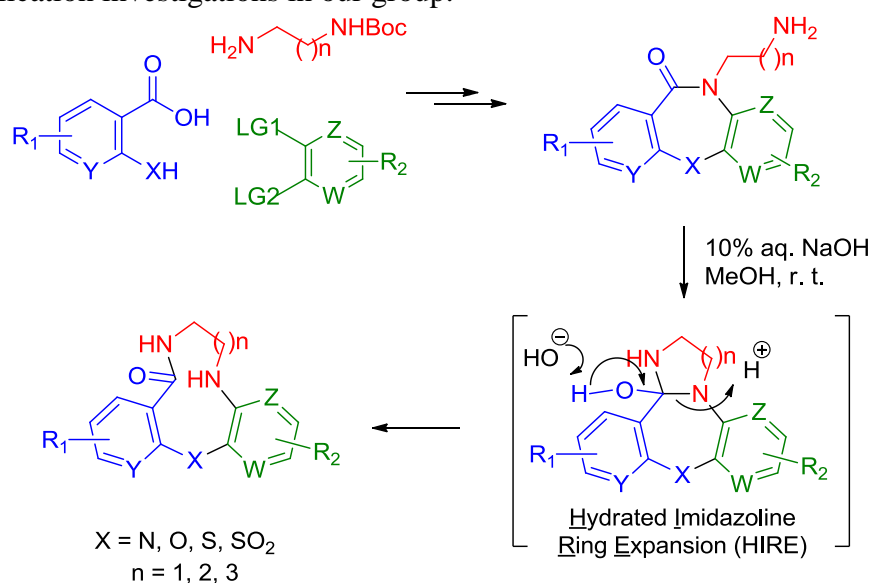
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Recently, we have developed a novel method to access difficult-to-synthesize medium-sized rings from a lot more available seven-membered precursors. The method entails elaboration of an imidazoline ring in its hydrated form which then leads to a three-atom ring expansion. Application of homologous cyclic amidines can, in principle, lead to larger ring formation (up to 12-membered). However, three-atom expansions which we termed Hydrated Imidazoline Ring Expansion (HIRE) are the most facile and are currently subject of extensive scope and application investigations in our group.



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## Sustainable pathways to amines via coupling and hydrogen borrowing reactions

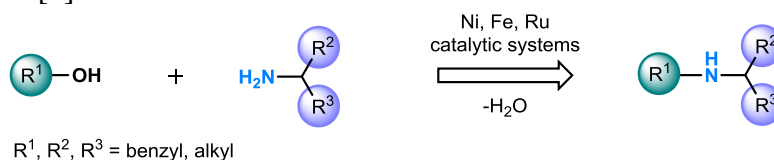
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The development of efficient and selective methodologies is of prime importance to achieve the goals of green chemistry. Hydrogen borrowing (hydrogen auto transfer) reactions are considered to be eco-friendly, atom economic alternatives to conventional synthesis methods since they result in only water as a side product. Moreover, they allow for the utilization of widely available alcohols as substrates that can also be derived from renewable resources. These catalytic methods received a huge attention in the last decades, mainly focusing on the use of noble metals [1]. In recent years, iron [2], cobalt [3], and manganese [4] complexes have been well studied in hydrogen borrowing reactions.

Herein, we show our recent developments in the *N*-alkylation of amines with alcohols using Ni, Fe and Ru based catalytic systems via the hydrogen borrowing approach. More specifically, we have developed a highly active and easy-to-prepare Ni based catalyst system [5], that is *in situ* generated from Ni(COD)<sub>2</sub> and KOH under ligand-free conditions. The observed catalytic system is very efficient for the functionalization of aniline and derivatives with a wide range of aromatic and aliphatic alcohols as well as diols and exhibits excellent functional group tolerance. Moreover, novel methodologies using Ru and Fe complexes for the synthesis of  $\beta$ -aminoacid esters and *N*-substituted heterocycles will be presented.

Additionally, we demonstrate our recent achievements regarding the use doped porous metal oxides as catalysts in catalytic conversion of lignocellulose and lignocellulose derived chemicals to higher-value building blocks including amines via cross-coupling and hydrogen borrowing reactions [6].



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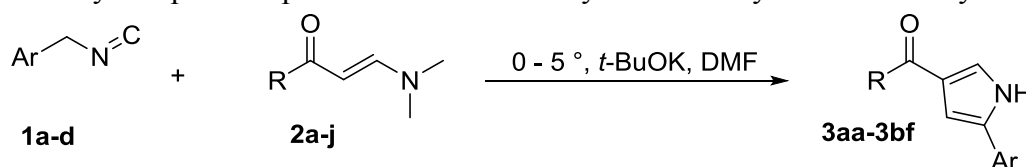
## Novel and convenient route toward 2,4-disubstituted pyrroles based on the reaction of enaminones and isocyanides

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Pyrrole core is the basis of many pharmacologically active compounds [1, 2]. For example, 3-substituted pyrroles are found in a variety of medicinal and agrochemical applications, such as efficient inhibitors of histone deacetylase [3], HIV-1 transcriptase [4], and COX-1/COX-2 cyclooxygenases [5]. Furthermore, the 4-acetyl pyrroles (JWH series) has moderate affinity for the CB1 receptor [6]. Besides a wide range of applications in medicinal chemistry pyrroles are also found to be electronically polarizable and oxidizable building blocks for polymeric and supramolecular structures for applications in nonlinear optics [7].

Herein, we suggest novel and convenient route toward 2,4-disubstituted pyrroles based on the reaction aromatic enaminones and isocyanides, having active methylene group. Our experiments has show that the best reaction conditions include using potassium tert-butoxide as base and DMF as solvent at 0-5 °C. It was found, that reaction was finished immediately after addition all amount of isocyanide. Finally, 30 new 4-acetylpyrrole were synthesized and fully characterized by complex of spectral methods of analysis and X-ray structural analysis.



This work was supported by the Russian Foundation for Basic Research  
(grant № 19-33-70021\18)

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## C-H and C-C bond activation. Looking under the Street Lamps

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Selective activation of strong C-H and C-C bonds is one of the fundamental challenges in rational catalyst design. The generally accepted mechanism of C-H bond activation [1] is common for bulk transition metal and their complexes. Predissociated  $\sigma$ -complexes, formed by donation of  $\sigma(\text{C-H})$  electron density to empty metal d-orbitals, are the key intermediates in this mechanism, and  $\pi$  backdonation from occupied d-orbitals into a  $\sigma^*$  C-H orbital is the critical driving force in the transition state. Activation of C-H bonds by metal oxides follows a different mechanism with different intermediates, energetics and usually even end products [2]. It was shown that, in selective oxygenation and oxidative dehydrogenation of hydrocarbons, lattice oxygen atoms serve as the direct oxidant, with subsequent catalyst regeneration by  $\text{O}_2$  or another oxygen donor (Mars-van-Krevelen mechanism) [3]. There is no general theory of C-C bond cleavage, although the importance of metal-carbon bond formation has been stressed [4]. Thus, the fundamental mechanistic aspects of the C-H and C-C activation reactions still remain incompletely understood.

Quantum chemical calculations have become an essential tool in mechanistic studies. However, the complexity of catalytic systems usually requires simplified models so that some important effects may be ignored. A more realistic model generally dictates the use of lower level computational methods and this in turn leads to less accurate results. In this work, we combine the advantages of the modern computational methods with the application of *real* models of metal and metal oxide catalysts. We gain fundamental insight into transition metal-promoted C-H and C-C bond activation from a diverse experimental database and extensive high-level DFT calculations of Rh pincer complexes in which these reactions occur intramolecularly. We show that these reactions proceed through a single complex featuring an unprecedented  $\eta^3\text{-C-C-H}$  agostic interaction [5].

Polyoxometalates (POMs) are a class of molecular inorganic compounds with a metal oxide surface structure that are widely used by experimentalists to study reactions on oxide surfaces. Recent advances in computer power and computational methods make it possible to perform accurate calculations of catalytic reactions with POMs. In this work, activation of  $\text{sp}^2$  and  $\text{sp}^3$  C-H bonds by a bimetallic POM is used to understand the mechanistic details of the catalytic action of metal oxides in activating hydrocarbons [6]. We will discuss the structure and properties of predissociated complexes on the metal and metal oxide catalysts, thermodynamic and kinetic factors in oxidative addition of C-C and C-H bond, hydrogen transfer vs. proton coupled electron transfer as a key stage in C-H bond activation, and key factors in C-C bond activation.

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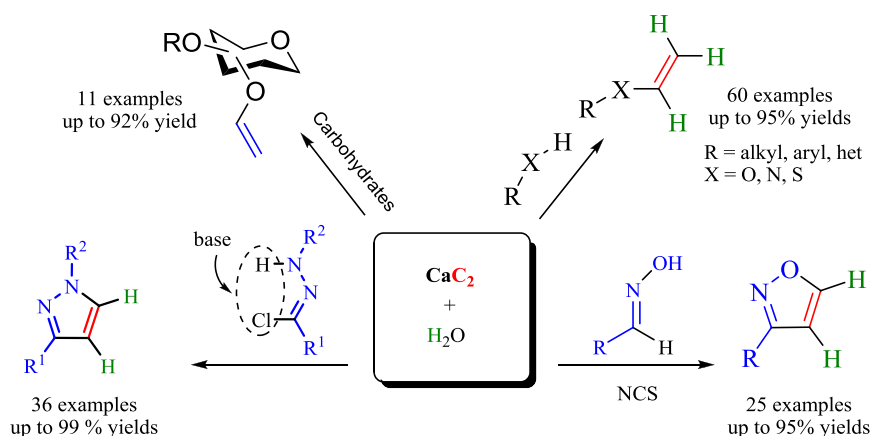
## Calcium carbide – multipurpose reagent in organic syntheses

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Outstanding potential of calcium carbide in organic transformations was revealed in various synthetic procedure [1]. Calcium carbide has a number of advantages over gaseous acetylene: there is no need to use complicated high-pressure equipment; working with calcium carbide is safer and more convenient; usage of carbide-based technologies opens a number of sustainable opportunities. Potentially, calcium carbide can be utilized instead of acetylene in a plenty of water-tolerant reactions.

Practical  $\text{CaC}_2$ -based transformations were successfully developed in our group in recent years, and access to a wide range of valuable compounds was demonstrated. Valuable vinyl ethers [2] of different alcohols [3] and carbohydrates [4], thiols [5] and amines [6] can be easily obtained from commercial available starting materials. Incorporation of acetylene core from calcium carbide is also possible for building heterocyclic moieties. Such procedures lead to isoxazoles [7] and pyrazoles [8] with excellent yields.



Demanding synthetic challenges and the requirements of “green” and sustainable development will further stimulate emerging development of carbide-based reactions, which will be presented and discussed in this study.

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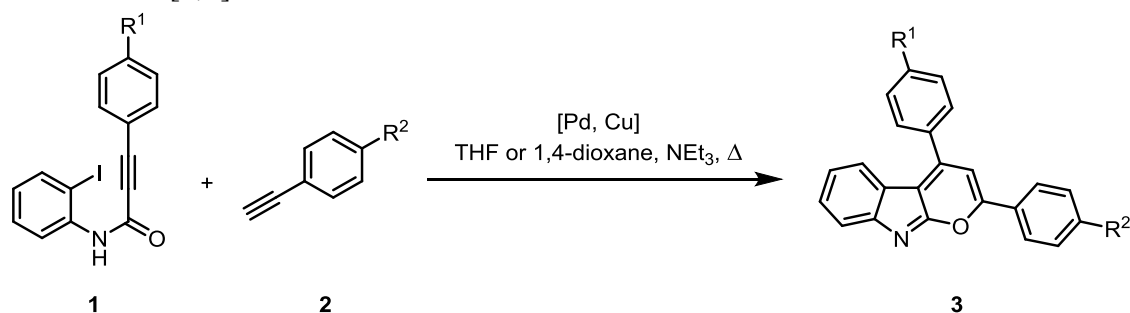
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## 2,4-Diarylpyrano[2,3-*b*]indoles – Acidochromic turn-on luminophores for a broad range of polarity

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Functional chromophores are widely applied and used for instance in dye-sensitized organic solar cells [1], light-emitting diodes [2], or as chemosensors [3]. For the latter, an embedded switching element like a basic nitrogen atom or an acidic phenolic hydroxyl group is needed. Upon binding to an analyte, the chemosensor significantly changes its absorption or emission properties [4]. As shown by our group, 2,4-diarylpyrano[2,3-*b*]indoles **3** can be synthesized *via* a Pd-Cu-catalyzed insertion-coupling-cycloisomerization domino reaction. Starting from alkynoyl *o*-iodo anilides **1** and terminal arylacetylenes **2** the tricyclic systems are obtained in moderate yields. 2,4-Diarylpyrano[2,3-*b*]indoles **3** are essentially nonfluorescent in the solid-state and in solution. However, upon complexation with metal ions, protonation or quaternation bright green fluorescence is detected. Therefore, they can be potentially interesting as chemosensors [5,6].



A prerequisite for cation- and proton-sensitive chemosensors is their solubility in a broad spectrum of solvent polarity. Therefore, various 2,4-diarylpyrano[2,3-*b*]indoles **3** have been synthesized. Additionally, branched oligo(ethylene glycol) side chains or long alkyl chains, for increasing the solubility in either organic or aqueous media were introduced. Solubility studies in various solvents and solvent mixtures were performed, ultimately employing the photophysical changes as a readout. Additionally, the particle size of a selected, insoluble 2,4-diarylpyrano[2,3-*b*]indole in aqueous solution has been determined by dynamic light scattering, indicating the formation of larger clusters with a diameter of around 125 nm.

*This work was supported by the Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft (Mu 1088/9-1)*

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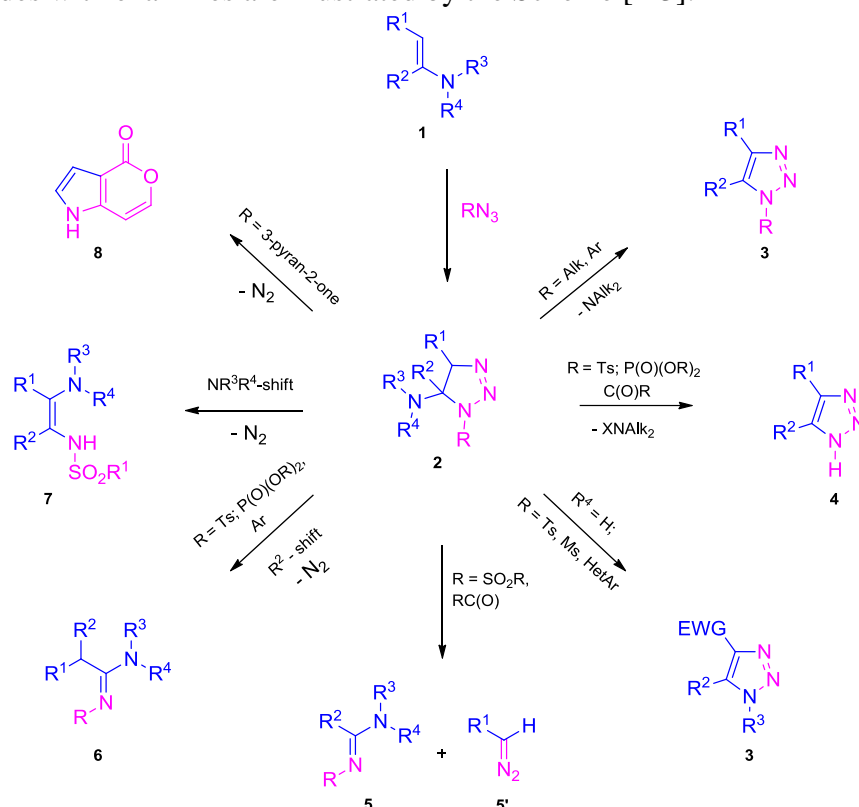
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## Synthesis and transformations of 5-amino-1,2,3-triazolines

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Enamines show high reactivity in 1,3-dipolar cycloaddition reactions towards azides in comparison with other ethene derivatives. This report includes the reactions of heterocyclic enamines with various types of azides. The primary reaction products, *i.e.* 1,2,3-triazolines are unstable and are capable to various rearrangements and transformations. This is the background to new synthetic methods and new reactions. A variety of the compounds prepared from the reaction of azides with enamines are illustrated by the Scheme [1-3].



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## A unified access to diverse (hetero)aromatic scaffolds for various applications using the (element)arynes

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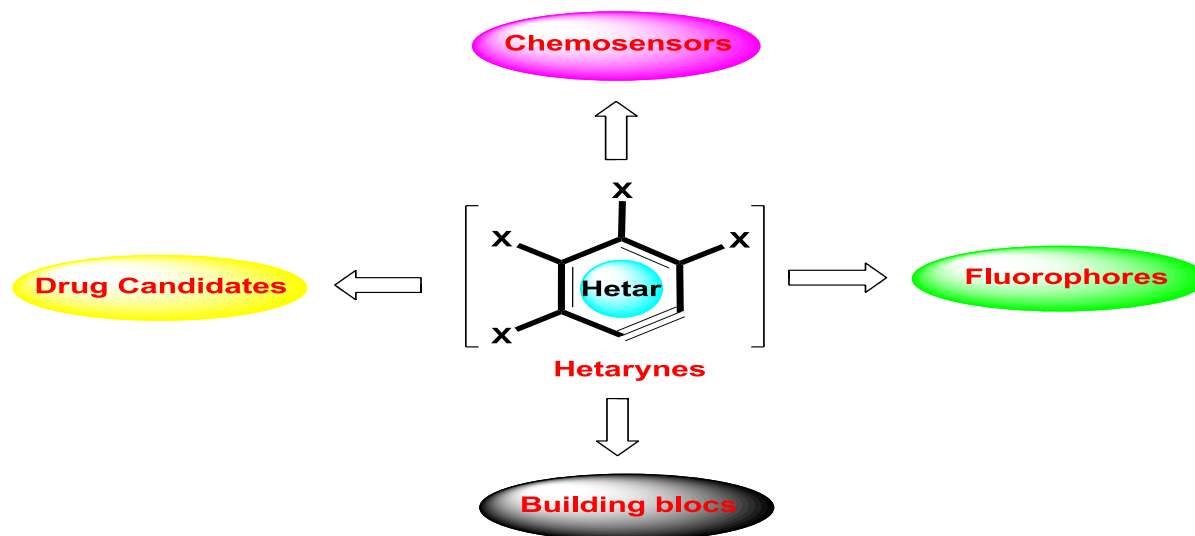
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The current state of synthetic organic, materials, pharmaceutical chemistry and related fields requires the development of new efficient methods for the synthesis of diverse (hetero)aromatic compounds for various applications.

Aryne intermediates [1, 2] (arynes) are among the most intriguing intermediates in synthetic organic chemistry due to their very interesting reactivity in interactions with various simple and complex (in)organic molecules.

In our researches [3, 4] we are intensively studying the aryne chemistry as a convenient synthetic tool for the one-pot (one-step) preparation of various (hetero)aromatic scaffolds for their following use as drug candidates, components of functional materials, fluorophores and chemosensors. The most updated results will be reported.



This work was supported by the Russian Scientific Foundation  
(Grant № 18-13-00365)

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## Donor-acceptor cyclopropanes in the synthesis of carbo- and heterocycles: isomerization, dimerization and ring expansion

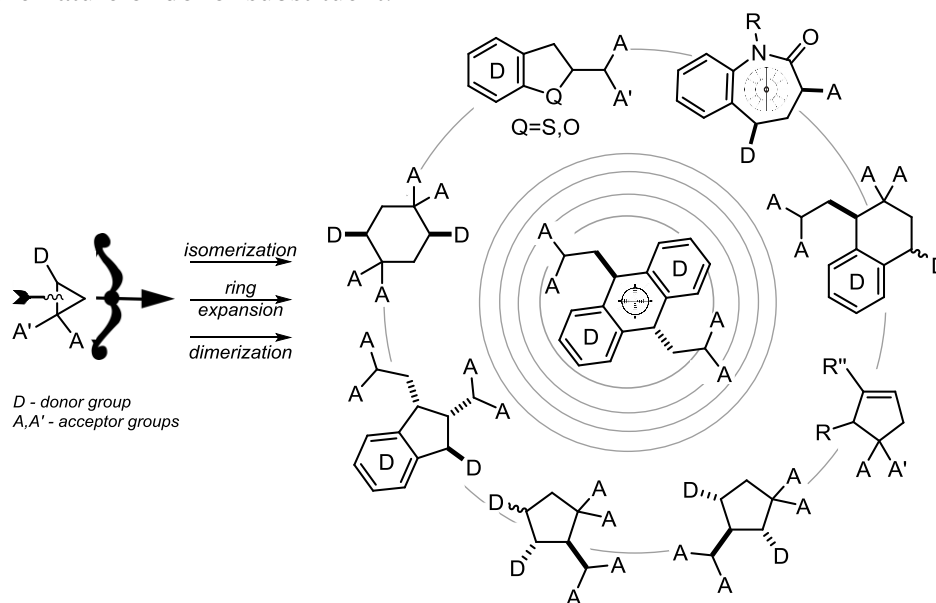
Ivanova O.A.,<sup>1,2</sup> Chagarovskiy A.O.<sup>2,3</sup>, Trushkov I.V.<sup>2,3</sup>

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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 Brønsted 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 transformations of D–A cyclopropanes *without any reaction partner*. These are: a) isomerizations including ring enlargement processes and b) various cyclodimerizations producing a large diversity of carbocycles, from simple ones to complex polycyclic systems. These transformations are promising routes to the synthesis of various bioactive compounds. The process chemo- and stereoselectivity are controlled by the reaction conditions, primarily by the Lewis acid applied, as well as by the nature of donor substituent.



This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00954)

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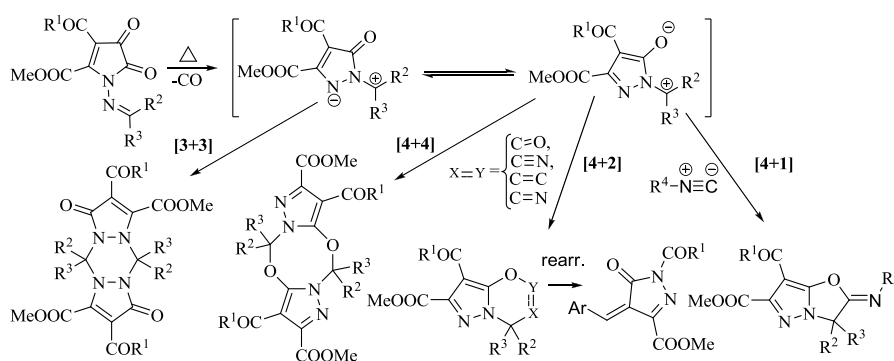
## Chemical transformations of heterocumulenes and azomethynimines generated by thermolytic decarbonilation of 1*H*-pyrrol-2,3-diones

Maslivets A.N., Zhulanov V.E., Dmitriev M.V., Rubin M.

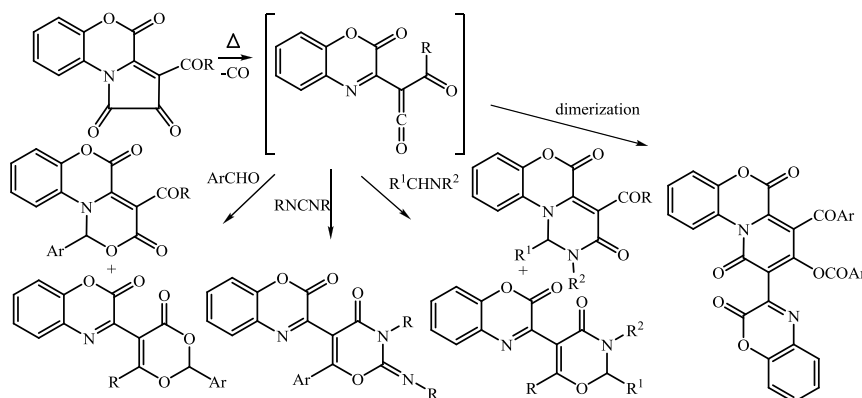
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It was previously demonstrated, that thermal decarbonylation of *N*-substituted 2,3-dihydro-2,3-pyrroldiones afforded imidoylketenes, whose chemical behavior largely depends on the nature of substituents at *N*-1. In the frame of our continuous studies of related transformations of imidoylketenes we pondered about possibility of generating hydrazoylketenes in a similar way, and investigating their subsequent transformations.

It was discovered that *N*-(diphenylenamino)pyrrolediones experienced facile CO-extrusion at elevated temperatures and the resulting hydrazonoketenes underwent further 5-*exo-trig* ring closures to provide a zwitterionic dihydropyrazolone species, which can be represented by enolate-iminium 1,4-dipole resonance form. In the absence of dipolarophiles, the products of [4+4]-cyclodimerization – bis(pyrazolo)dioxadiazocines – were formed in high yields. We further elaborated on the development of various synthetic schemes involving cycloaddition of these unusual 1,4-dipoles. To this end, we generated the ketenes in the presence of alkyl vinyl ethers, aldehydes, ketenes, nitriles and isocyanides targeting products of dipolar cycloadditions.



Acyl(hetaryl)ketenes of different classes, generated by thermolysis of 4-acyl-1*H*-pyrrole-2,3-diones, annelated by azaheterocycles by the [*e*] side, in the absence of partners, stabilized intra- or intermolecularly and participate in the reactions [4 + 2]-cycloaddition with dienophiles.



The study was performed under the financial support of the Russian Ministry of Education and Science (project 4.6774.2017/8.9) and the Government of Perm Krai (scientific schools, MIG)

# Synthesis of pharmacophore-containing push-pull systems based on styryl quinazolines and pyrazolo[1,5-a]pyrimidines

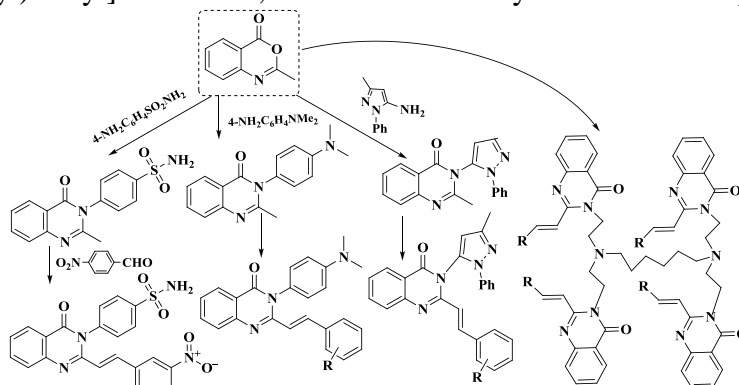
Danagulyan G.G.<sup>1,2</sup>, Harutyunyan A.A.<sup>1,2</sup>, Arakelyan M.R.<sup>2</sup>, Ghukasyan G.T.<sup>1,2</sup>

<sup>1</sup>Russian-Armenian University

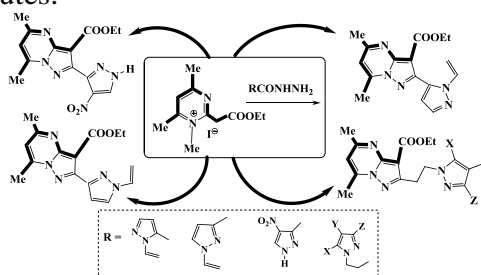
<sup>2</sup>The Scientific Technological Centre of Organic and Pharmaceutical Chemistry  
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Derivatives of quinazolines and other condensed pyrimidine systems have been intensively explored as biologically active substances, in particular, of anti-inflammatory, sedative, antimicrobial, antiviral, antitumor action. As is the case with the majority of pyrimidine systems, such an interest is provoked by high activity exhibited by them, specifically, by the ability to inhibit threonine kinases involved in the regulation of cell division and tubulin polymerization [1]. In continuation of the previously research conducted by us, the present communication describes the synthesis of new 2-methyl-4(3H)-quinazolin-4-ones and their 2-[(*E*)-2-aryl(hetaryl)-vinyl]derivatives, as well as cluster systems based on quinazoline.



By the previously observed in our laboratory [2,3] recyclization of pyrimidine salts under the action of pyrazolyl carboxylic acid hydrazides, other condensed pyrimidine systems have been synthesized: polysubstituted pyrazolyl derivatives of pyrazolo[1,5-a]pyrimidine, which are difficult to access by other routes.



The work was carried out within the framework of the grant of the Ministry of Education and Science of the Russian Federation for research activities of the Russian-Armenian University

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## Design and antiproliferative activity of aminothioglycolurils

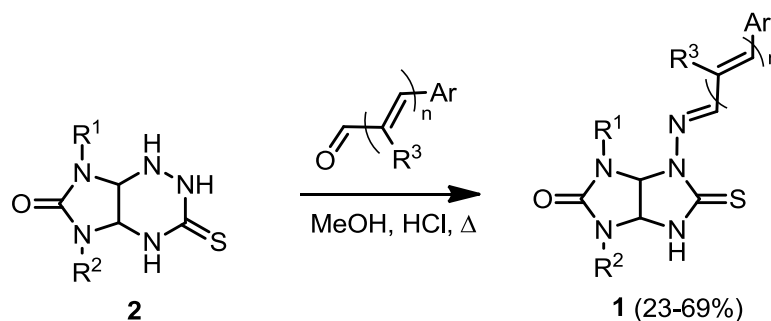
Gazieva G.A.,<sup>a</sup> Anikina L.V.,<sup>b</sup> Pukhov S.A.<sup>b</sup>

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e-mail: gaz@ioc.ac.ru

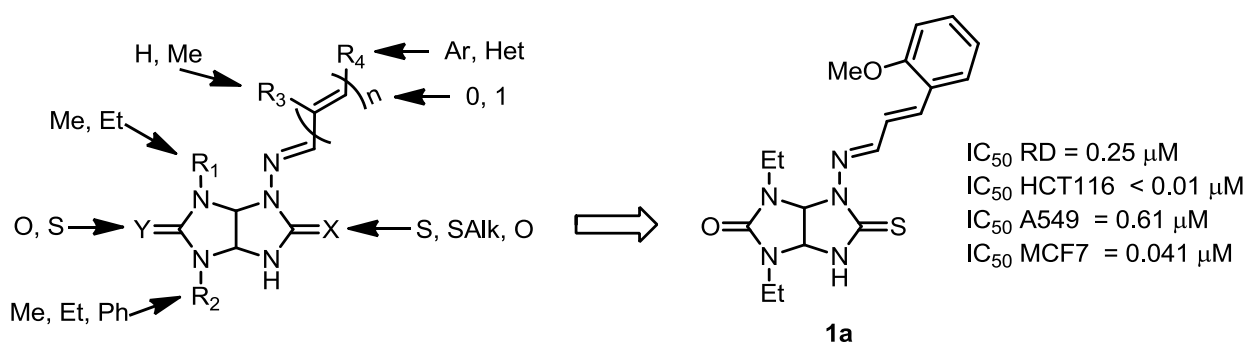
The discovery of new classes of N-heterocyclic bioactive compounds and effective methods for their synthesis are actual tasks of organic and medicinal chemistry.

Recently, we have developed original method for the synthesis of aminothioglycolurils **1** based on tandem hydrazone formation and triazine ring contraction reaction of perhydroimidazotriazines **2** with aromatic aldehydes and (*E*)-3-phenyl(furan-2-yl)acrylaldehyde derivatives [1,2].



R<sup>1</sup> = Alk, R<sup>2</sup> = H, Ph, R<sup>3</sup> = H, Me, n = 0, 1

The antiproliferative activity of representative thioglycolurils **1** against cancer cell lines has been investigated. Structure–activity relationship studies revealed that the substituents at the nitrogen atoms significantly affected on the antiproliferative activity. The lead compound **1a** has been discovered.



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## Substituted 1,10-phenanthroline ligands and their Ru(II)-complexes: synthesis and application

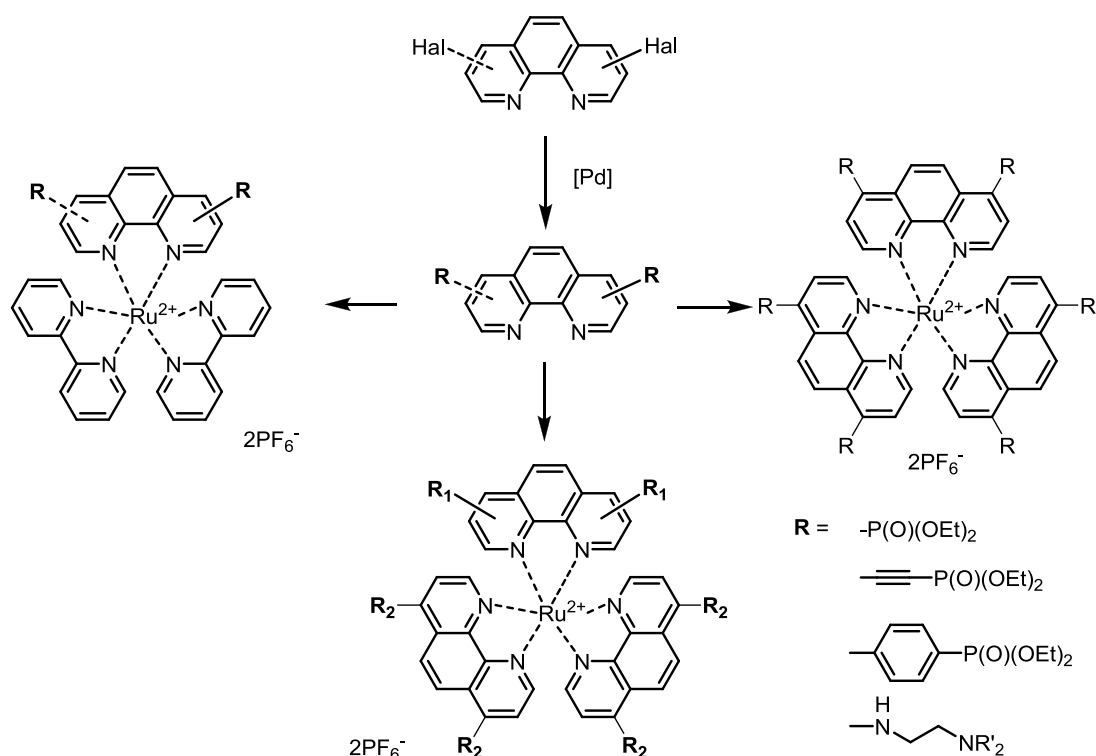
Abel A.S.,<sup>1</sup> Morozkov G.V.,<sup>1</sup> Zenkov I.S.,<sup>1</sup> Mitrofanov A.Yu.,<sup>1</sup> Averin A.D.,<sup>1</sup> Lemeune A.G.,<sup>2</sup> Beletskaya I.P.<sup>1</sup>

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Fluorescent polypyridine complexes of ruthenium have found wide application in different areas of chemistry as catalysts, signaling groups, dyes, etc. though their use is still limited due to many difficulties in the synthesis of such compounds. 1,10-Phenanthroline is a promising platform for creation of the ligands to be used in the synthesis of the complexes with target properties.

In this work we report a synthetic approach to previously unknown substituted 1,10-phenanthrolines and corresponding fluorescent Ru complexes incorporating various nitrogen- or phosphonate-containing units. Corresponding substituted 1,10-phenanthrolines were obtained using Pd catalysis: halogeno- and dihalogenosubstituted 1,10-phenanthrolines were introduced in the Buchwald-Hartwig, Suzuki-Miyaura and Sonogashira reactions providing new functionalized ligands. Non-catalytic approaches were also employed. On the basis of these compounds various fluorescent complexes with Ru(II) were synthesized and characterized.



The spectral properties of these complexes, their application for metal ions detection, photocatalysis and hybrid materials synthesis will be discussed.

*This work was supported by the Russian Foundation for Basic Research (grants № 18-33-00279 and 18-29-04030)*

# New 1,2,3-triazolylsubstituted furocoumarins as a potential antibacterial and antitumor agents

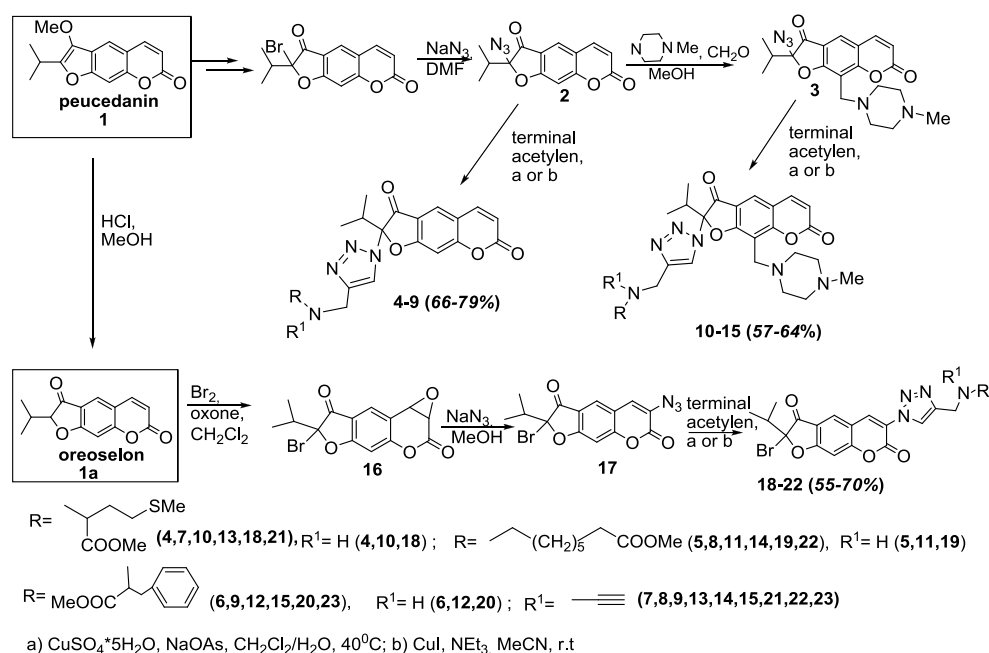
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Linear furocoumarins have attracted intensive interest in recent years because of their biological and pharmacological properties [1]. Anticoagulant and antithrombotic actions of coumarin derivatives were clinically proved. Besides various coumarins have anticancer and antimicrobial activities [2,3].

We have synthesized new derivatives of plant furocoumarins with substituents in C(2), C(6) and C(9)-positions of the furocoumarin skeleton, starting from oreoselone and peucedanin **1**. By CuAAC-reaction of 2-azidooreoselons **2**, **3** with various terminal alkynes were synthesized 2-(arylamidomethyltriazol-4-yl)substituted oreoselons **4-9** (yields 66-79%) and 2-aryltriazolyloreoselons **10-15** (yields 57-64%) (scheme 1).

2-Bromo-6-(1,2,3-triazolyl)substituted derivatives **18-22** were obtained from available furocoumarin oreoselon **1a** over the stages of compounds **16** and **17** with high yields (55-70%).



Structures of compounds were confirmed with spectral methods and elemental analysis data. For some synthesized compound were found significant antibacterial and antitumor activities.

*This work was supported by Russian Foundation for Basic Research (grant No 17-73-10099)*

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## How to improve activity of metal-based anticancer compounds

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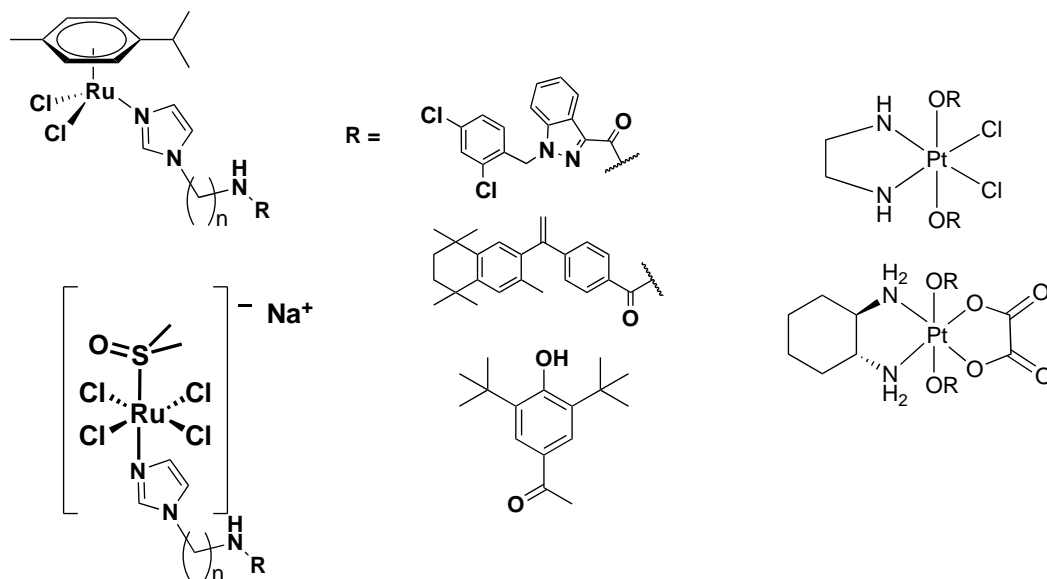
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The majority of new metal-based anticancer compounds contain cytotoxic platinum centre [1]; however, in recent years there has been shift of interest in the development of non-classical platinum or non-platinum anticancer drugs and the Pt(IV) and ruthenium-based compounds are the most promising candidates.

The activity and specificity of metal-based anticancer compounds can be finely tuned by ligand around a metal atom. Attachment of Pt or Ru moiety to the targeting biologically active organic molecules can drastically increase anticancer properties. In our group, we applied lonidamine, bexarotene or antioxidant as bioligands. Lonidamine is known to inhibit the aerobic glycolysis in cancer cells while simultaneously enhancing glycolysis in the normal cells. Bexarotene is known as an agonist of the retinoid X receptor and specific against T-cell lymphoma.

In our presentation will focus on the hybrid complexes based on lonidamine, bexarotene or 3,5-di-*tert*-butyl-4-hydroxyphenyl moiety tethered to the ruthenium or platinum unit. Pt(IV), Ru(II) and Ru(III) compounds found to be highly cytotoxic against the number of the human cancer cell lines.

Investigations of *in vivo* cytotoxicity of Pt(IV), Ru (II/III) complexes show low toxicity.



This work was supported by RFBR (17-03-00892, 17-03-01070)

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## Synthesis and biological activity of some indoloquinoline derivatives

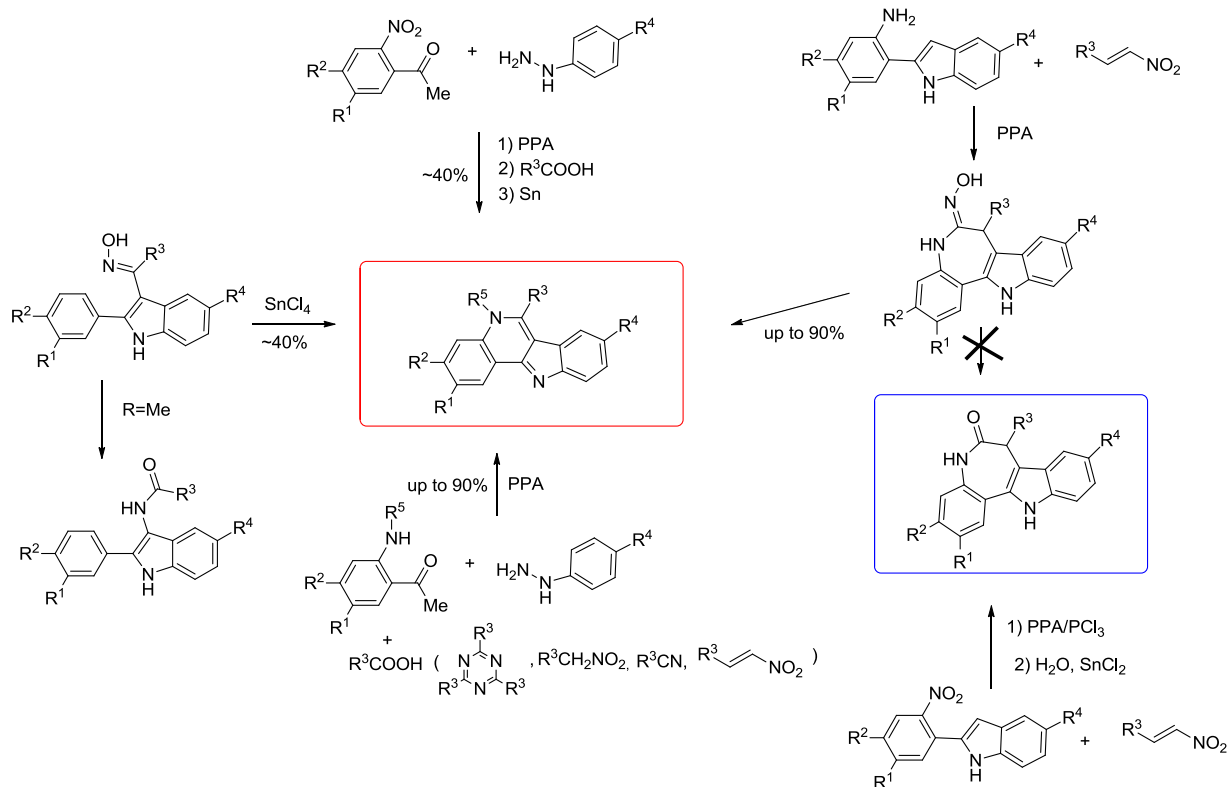
Aksenov N.A., Gasanova A.Z., Aksenova I.V., Aksenov A.V.

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The development of new drugs is one of the most important driving forces of chemical science. Now more than ever, the problem of cancer treatment is acute, since the development of technology puts the problems with cardiovascular diseases into the background. The problems of previously successfully treated, but having developed resistant forms of diseases, such as malaria, are also relevant.

Aqueous extract of the root and leaves of *Cryptolepis sanguinolenta* is traditionally used in West and Central Africa for the treatment of malaria and malignant neoplasms. Among the alkaloids of this plant represented a wide range of different indoloquinolines responsible for its activity.

In our laboratory, a number of methods for the synthesis of indolo[3,2-c]quinolines were developed, each of which has its own limits of application, which allows you to accumulate a large library of derivatives of this heterocyclic system and identify substances with high activity against cancer cell lines.



This work was supported by the Russian Science Foundation  
(Grant #17-73-10301)

## Protic ionic liquids: new generation solvents, catalysts and reagents in the nucleophilic ring opening reactions of donor–acceptor cyclopropanes

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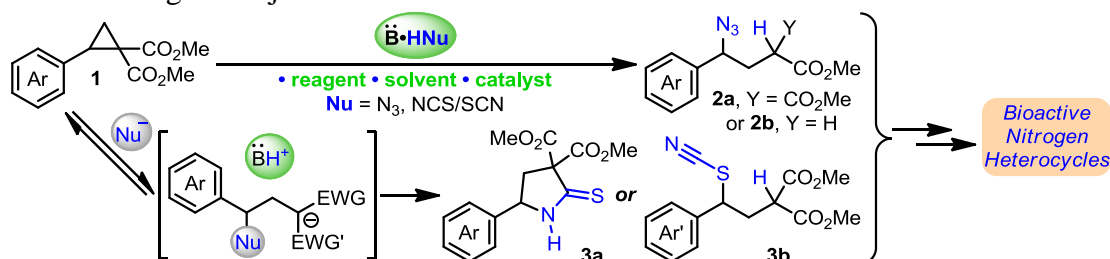
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The ring-opening reactions of donor-acceptor (D–A) cyclopropanes **1** with *N*-containing nucleophiles serve as crucial steps in the preparation of a variety of medicinally important *aza*-heterocycles [1-3]. Moreover, most of such transformations comprising conventional inorganic metal salts, for example, cyanides, cyanates, thiocyanates, selenocyanates, and several other anions, are briefly studied or not described at all in the literature primarily due to the ambident behavior of these nucleophiles, as well as multiple side processes observed during the course of these reactions and their reversible nature.

To overcome the issue of reversibility, we have applied **protic ionic liquids (PILs)**, and other salts formed by organic **bases (B̄)** and **Brønsted acids (HNu)** acting as multipurpose regenerable reagents, catalysts, and solvents. The exhaustive optimization efforts finalized in conditions for the ring-opening of D–A cyclopropanes **1** with organic-soluble azide-based reagent: (2-azido-2-arylethyl)malonates **2a** or the corresponding 4-azido-4-arylbutyrates **2b** were obtained according to the judicious choice of the PIL media.



Employing PILs containing ambident thiocyanate ion D–A cyclopropanes **1** were transformed into pyrrolidine-2-thiones **3a** (*N*-attack) or (2-aryl-2-thiocyanatoethyl)malonates **3b** (*S*-attack) depending on both the aryl-moiety and the PIL reagent nature. The presence of several functional groups allowed further modifications of the obtained compounds **2** and **3** providing valuable bioactive nitrogen-containing heterocycles.

*This work was supported by the President of the Russian Federation scholarship for young scientists, working on R&D in top-priority areas vital to the modernization of the Russian economy (medical technologies area, № CII-4317.2018.4)*

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## Styryl bases and dyes: dimerization and photoreactions with and without cavitands

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Kuz'mina L.G.<sup>4</sup>, Gromov S.P.<sup>1,2</sup>

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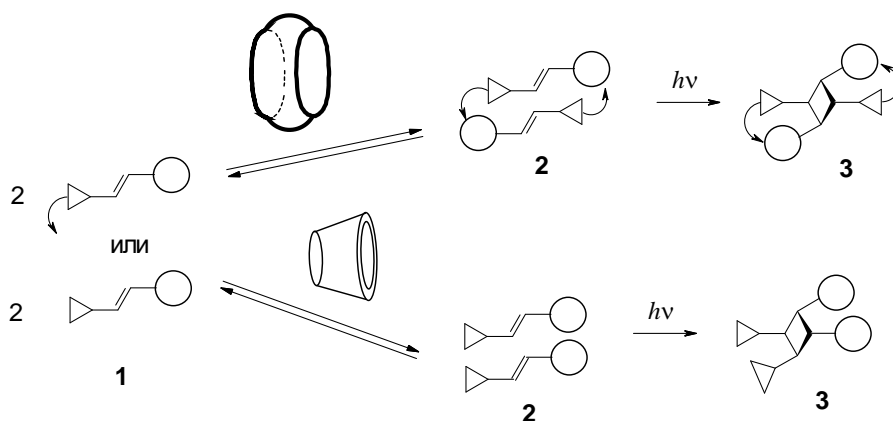
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A number of styryl dyes **1** and their corresponding bases were synthesized. It was found that dyes **1** can spontaneously form dimers **2** in both the solid state and in solution (MeCN, CH<sub>2</sub>Cl<sub>2</sub>). The dimers have a head-to-tail pseudocyclic structure. The dimerization stability constants for dyes **1** were estimated by <sup>1</sup>H NMR titration in MeCN-*d*<sub>3</sub> (log*K*<sub>d</sub> up to 8.0) [1, 2]. The complexation of styryl dyes and bases **1** with cucurbit[*n*]urils (CB[*n*], *n* = 7, 8) and β-, γ-cyclodextrins (CD) was studied by electron spectroscopy, NMR and X-ray [3, 4]. It was found that in aqueous solutions the addition of complementary cavitands (CB [7], β-CD) to compounds **1** lead to inclusion complexes of 1: 1 with a pseudorotaxane structure. For cavitands with a large cavity size (CB [8], γ-CD), the formation of complexes **2** of higher stoichiometry is also possible.



[2+2] photocycloaddition reaction generate cyclobutane derivatives **3**. For dyes the photocycloaddition quantum yield was varied between 0 and 0.38. The possibility of reaction passing depends on the nature of the compound **1** and the steric volume of its fragments. The structures of **1-3** were studied by X-ray diffraction and NMR spectroscopy. Dyes and bases **1** can be utilized in systems of optical registration and storage of information.

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### 3-(Ethylthio)phenyl-substituted phthalocyanines and 2,3-naphthalocyanines: synthesis and investigation of physicochemical properties

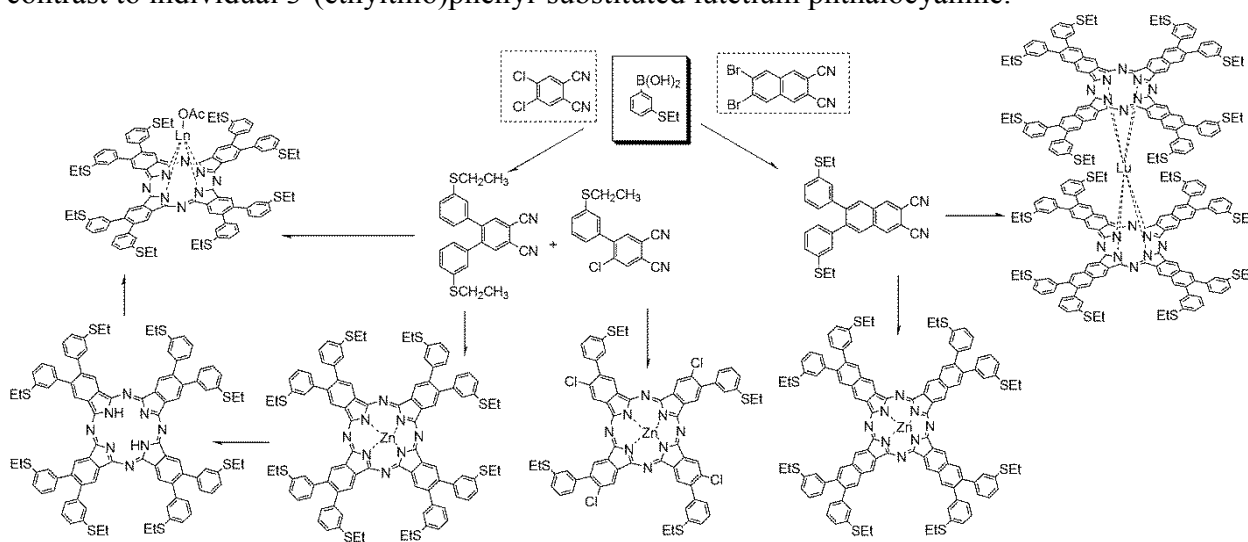
Dubinina T.V., Tychinsky P.I., Borisova N.E., Krasovskii V.I., Kulikovskiy A.V., Tomilova L.G.

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Selective approaches for the synthesis of novel mono- and di-(3-ethylthio)phenyl-substituted phthalonitriles were developed using the Suzuki cross-coupling reaction. This approach was also successfully realized for the synthesis of 6,7-di(3-(ethylthio)phenyl)-2,3-dicyanonaphthalene. The assignments of signals in  $^{13}\text{C}$  NMR spectra were made by a combination of  $^1\text{H}$ - $^{13}\text{C}$  HMBC and  $^1\text{H}$ - $^{13}\text{C}$  HSQC experiments. Zinc complexes of 3-(ethylthio)phenyl-substituted phthalocyanines and naphthalocyanine were obtained based on the corresponding nitriles with high yields. Novel lanthanide (III) complexes of 3-(ethylthio)phenyl-substituted phthalocyanine were obtained using template synthesis ( $\text{Ln}=\text{Er}$ ,  $\text{Lu}$ ) and metallation of phthalocyanine ligand (two-stage method,  $\text{Ln}=\text{Tb}$ ). In comparison with complexes of diamagnetic metals, presence of paramagnetic erbium leads to strong downfield shift of phthalocyanine proton signals to 22.35 ppm in  $^1\text{H}$  NMR spectrum. Opposite shift-effect is characteristic for terbium complex: the phthalocyanine proton signals are shifted to  $-59.06$  ppm.

Hybrid of gold nanoparticles (30nm in diameter) coated with 3-(ethylthio)phenyl-substituted lutetium phthalocyanine were prepared. The formation of hybrid nanoparticles was proven by TEM. Elemental composition found from the TEM experiment correlates well with proposed structure of the hybrid. In thin films the presence of gold nanoparticles resulted in aggregation of phthalocyanine molecules around the gold core was shown (from AFM experiment). Thus the higher ordered “island-type” texture was observed for hybrid material in contrast to individual 3-(ethylthio)phenyl-substituted lutetium phthalocyanine.



We are grateful to the Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grants MK-3115.2018.3.), Russian Foundation for Basic Research (Grant 16-02-00694 A) and Daniil A. Tyurin for ESR measurements

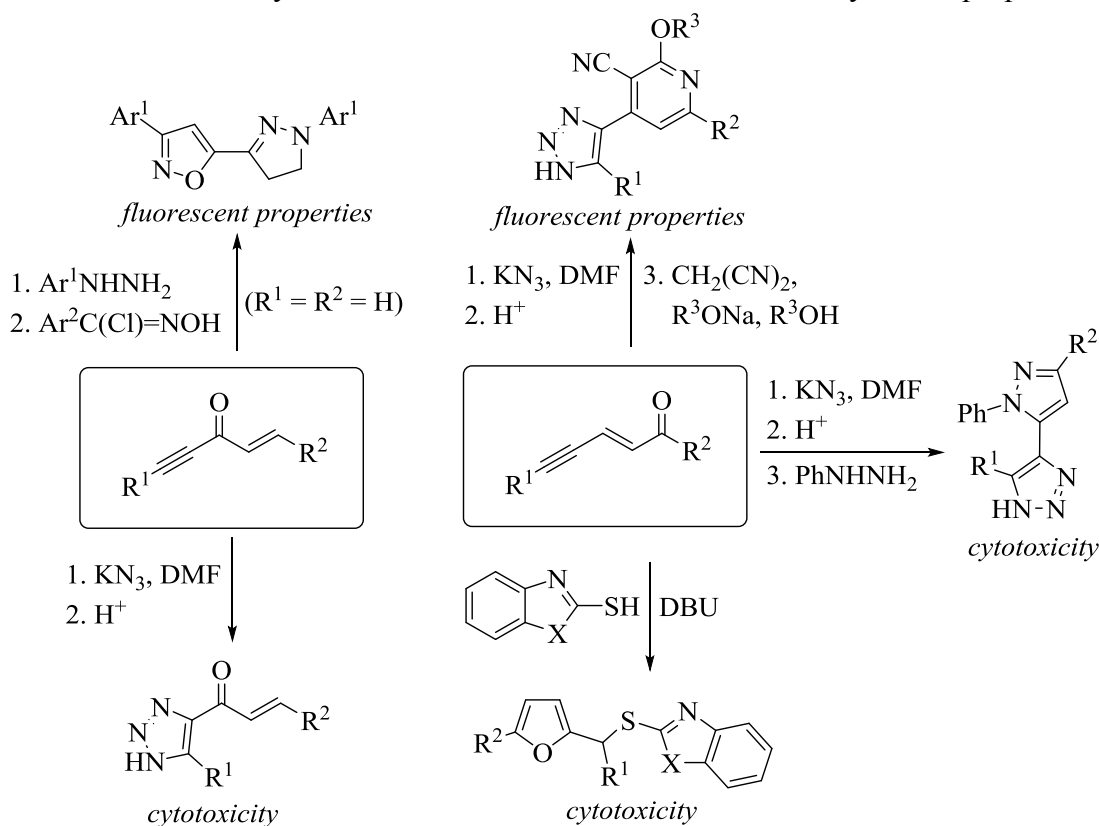
## Vinyl ethynyl ketones: preparation, properties, use in organic synthesis

Golovanov A.A.,<sup>1</sup> Zlotsky S.S.,<sup>2</sup> Anoshina O.S.,<sup>1</sup> Odin I.S.,<sup>1</sup> Gusev D.M.<sup>1</sup>

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The conjugated vinyl ethynyl ketones (enynones) can be used as efficient building blocks in the synthesis of various heterocyclic compounds, including natural compounds and their analogues. In this report discussed the methods of synthesizing these polyfunctional compounds, as well as their use in the synthesis of substances with fluorescent and cytotoxic properties [1–3].



Based on conjugated vinyl ethynyl ketones we obtained furan, 1,2,3-triazole, pyridine and isoxazole derivatives.

This work was supported by the grant of the Russian Science Foundation  
No. 18-13-00008

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## Regiodirected alkylation of diheterophosphanes conjugated with resorcinarenes or dinaphthylmethanes

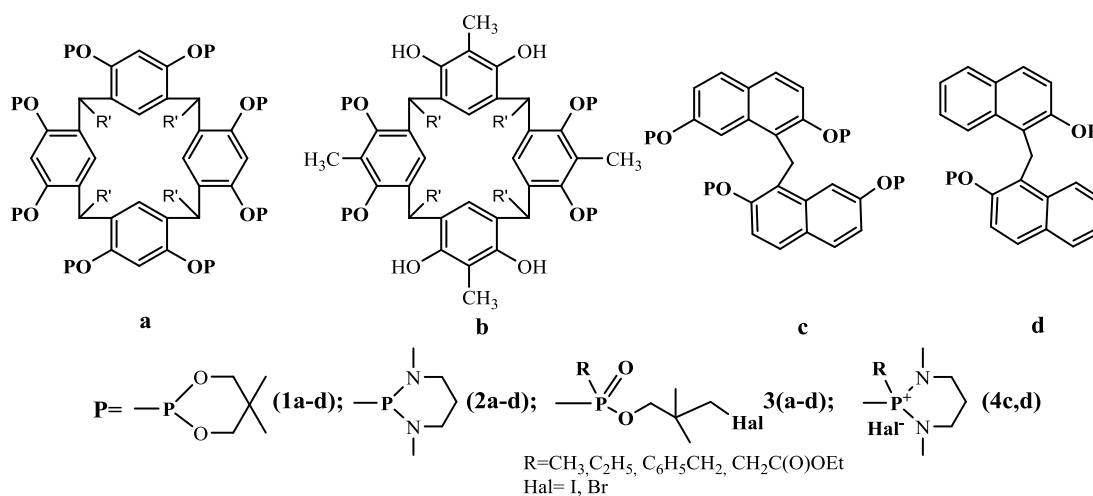
Serkova O.S., Kamkina A.V., Begicheva A.P., Maslennikova V.I.

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The interaction of octa- and tetra-(diheterophosphinanyl)-resorcinarenes **1,2a,b**, tetra- and di- (diheterophosphinanyl)-dinaphthylmethanes **1,2c,d** with various alkylation reagents (simplest haloalkanes, bromobenzyl, bromoethyl acetate) was considered. The factors affecting on the process's regiodirection such as: the pre-organization of the oligocyclic platform, the diheterophosphinane cycles were immobilized on, the nature of heteroatom, the reaction conditions were studied.

The alkylation of dioxaphosphanes **1a-d** fixed on the resorcinarene or dinaphthylmethane base proceeded with opening of the cyclic structure. As a result, compounds **3a-d** containing 2, 4, and 8 non-symmetric linear phosphonate fragments with terminal haloalkyl groups in the molecule were obtained. Number and orientation in space of phosphonate groups was determined by the structure and conformational mobility of the aromatic matrix. More efficiently reactions proceeded in a microwave reactor in dichlorobenzene solution at 100-110° C. Products **3a-d** were isolated in 58-90% yields [1].



In case of diazaphosphinane derivatives **2**, the reaction was carried out even at the room temperature, and the regiodirection of the process depended on the nature of the solvent used. In non-polar solvents, alkylation of nitrogen atoms occurred, accompanied by the opening of the heterocycle and the formation of P-Hal derivatives. In polar solvents, due to the alkylation of P atoms, the reaction ended with the formation of quasiphosphonium salts **4**.

*This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00347a)*

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## CaC<sub>2</sub>-D<sub>2</sub>O mixture in deuteration reactions

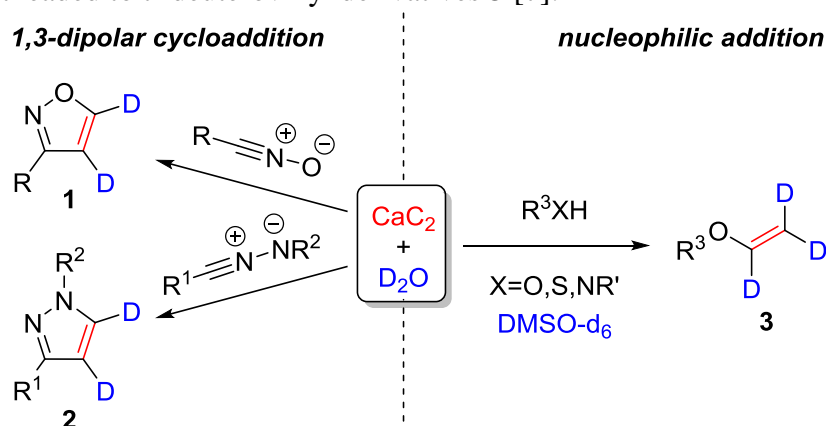
Ledovskaya M.S.,<sup>a</sup> Voronin V.V.,<sup>a</sup> Rodygin K.S.<sup>a</sup>, Ananikov V.P.<sup>a,b</sup>

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The high difference in C-D and C-H bond strength is actively used in various chemical and biomedical researches. The comparison of the C-H bond and C-D bond reactivity extensively used in the study of reaction mechanisms [1]; the substitution of hydrogen by deuterium was also applied to alter the reactions selectivity [2] and for the management of pharmacokinetic profile of drugs [3]. The latter advances in this field (like the actual improvement of the first deuterated drug, deutetrabenazine [4]) made the synthesis of new deuterated substances a demanded goal for organic and pharmaceutical chemistry.

Three novel synthetic methodologies were proposed. The common feature of them is the use of calcium carbide-deuterium oxide mixture for the generation of acetylene-d<sub>2</sub> directly in the reaction mixture. The first two methods are based on the 1,3-dipolar cycloaddition reactions of *in situ* generated nitrile oxides or nitrile imines to dideuteroacetylene. By this way novel dideuteroisoxazoles **1** [5] and dideuteropyrazoles **2** [6] of excellent isotopic purity were synthesized. The last method is a nucleophilic addition of alcohols, thiols and aromatic nitrogen compounds to acetylene-d<sub>2</sub>, accompanied by the exchange reactions with deuterated solvent (DMSO-*d*<sub>6</sub>), that led to trideuterovinyl derivatives **3** [7].



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## Quaternary cyanomethyl salts of azines, *O*-hydroxybenzaldehydes and nucleophiles in the one-pot three-component reaction with oxidative step

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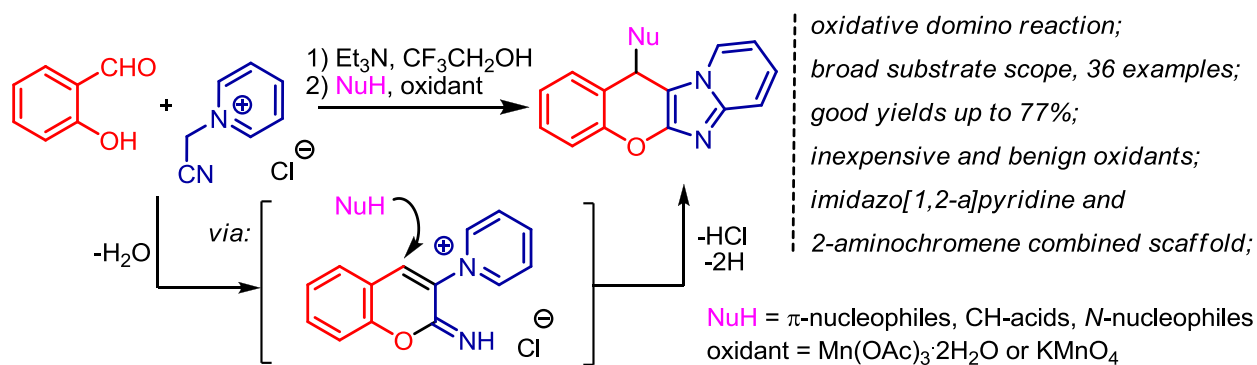
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Domino reactions are well recognized for their ability to effectively synthesize organic compounds, as far as creating two and more chemical bonds in one-step decreases waste, resources and time, and makes the development of methodology of synthesis in a domino fashion a substantial task [1]. Recently, much attention in research was given to domino reactions with an oxidation step, revealing possibilities for shifting the equilibrium by making products more stable or in situ generating reactive intermediates [2]. In its turn, multicomponent reactions (MCRs), usually occurring as domino processes with three or more reactants mixed together, became a valuable tool for the synthetic chemistry to produce diverse and complex compounds in an efficient and sustainable way. The use of oxidative conditions in MCRs was found to be useful, but challenging due to difficulty to match the redox potentials of three or more reactants at a time and employment of a sequential one-pot strategy may become one of the reasonable solutions.

Following our interest in domino and MCR chemistry and taking an advantage of 2-iminochromene reactivity, herein we report a sequential three-component domino reaction of salicylaldehydes and *N*-(cyanomethyl)pyridinium salts with a broad scope of nucleophiles to produce diversely substituted valuable chromenoimidazopyridines under oxidative conditions (Scheme 1).

Scheme 1



The reported study was funded by RFBR according to the research project № 18-33-00536

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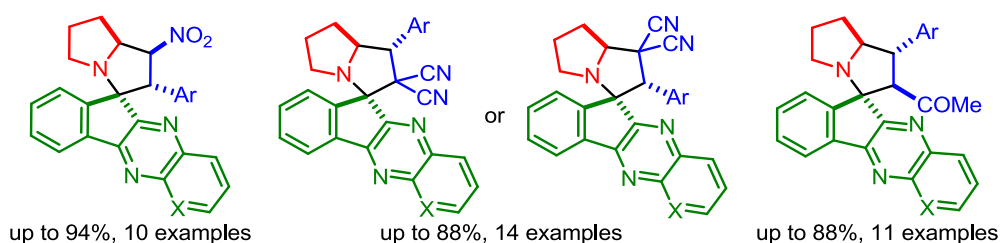
# 11*H*-Indeno[1,2-*b*]quinoxalin-11-one and 6*H*-indeno[1,2-*b*]pyrido[3,2-*e*]pyrazin-6-one-based azomethine ylides in synthesis of spiroyrrolizidines

Zimnitskiy N.S., Korotaev V.Yu., Kutyashev I.B., Barkov A.Yu., Sosnovskikh V.Ya.

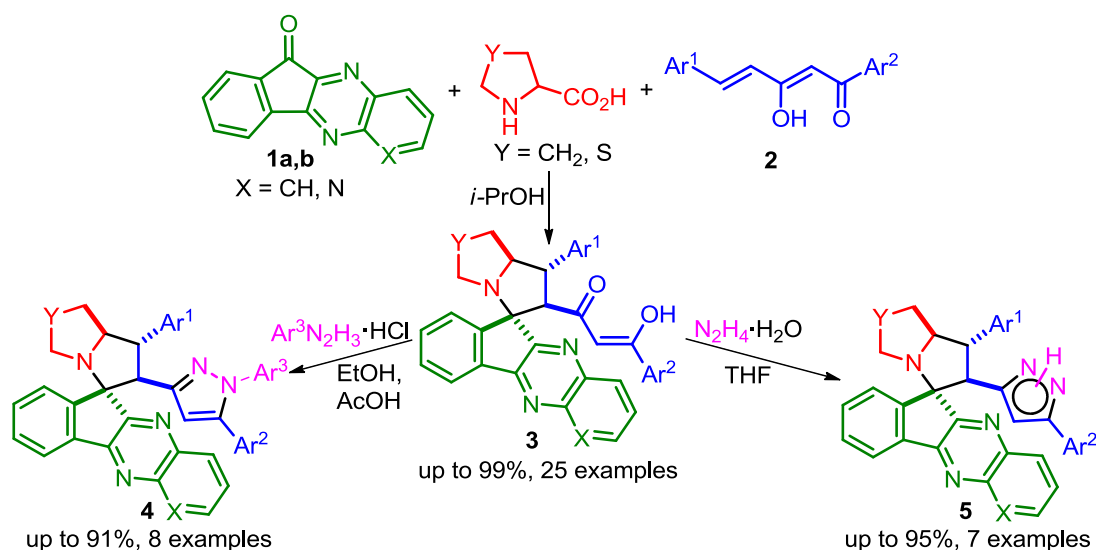
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The 1,3-dipolar cycloaddition reaction of azomethine ylides at the activated double bond of various alkenes is an effective one-step method for regio- and stereoselective synthesis of spiroyrrolizidines and spiroyrrolizidines with several chiral centers.

In the present work we have studied [3+2] cycloaddition between stabilized azomethine ylides derived *in situ* from 11*H*-indeno[1,2-*b*]quinoxalin-11-one **1a** or 6*H*-indeno[1,2-*b*]pyrido[3,2-*e*]pyrazin-6-one **1b** and  $\alpha$ -amino acid (proline and thiaproline) with  $\beta$ -nitrostyrenes, arylidenemalononitriles and arylideneacetones. Reactions proceeded smoothly to give corresponding spiroadducts with regiochemistry and stereoconfiguration depending on the type of the conjugated alkene used.



The reaction of (2*Z*,4*E*)-3-hydroxy-1,5-diarylpenta-2,4-dien-1-ones **2** with the abovementioned ylides proceeded regio- and stereoselectively as well, giving corresponding spiroyrrolizidines **3** in yields from good to quantitative. 1,3-Dicarbonyl moiety of these adducts **3** have performed well in reactions with *N*-nucleophiles, namely hydrazine hydrate and arylhydrazine hydrochloride. Obtained spiroyrrolizidine-pyrazol conjugates **4** and **5** are of undeniable interest for medicinal chemistry.



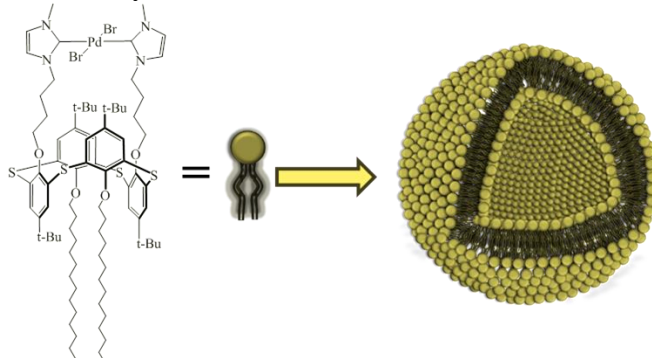
This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-00635)

## New NHC palladium complexes based on *p*-*tert*-butylthiacalix[4]arene derivatives: synthesis and catalytic activity research

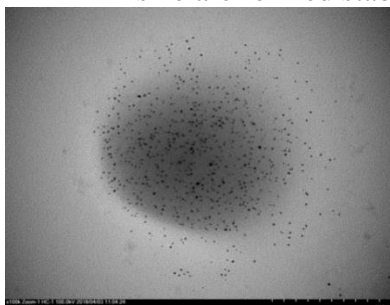
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The idea of creating micellar catalysts that can solubilize water-insoluble substrates and conduct traditional organic transformations in water have attracts much attention of scientist. Catalytic systems based on NHC complexes of transition metals have got high activity and stability to moisture and air. To create micellar catalysts based on NHC palladium complexes, we used a macrocyclic platform. Macrocyclic compounds acting as ligands are able to arrange their functional groups in area in such a way that a finished chelate compound is formed in which a complexing ion is built in. So the combination of thiacalix[4]arene platform with NHC ligands will make it possible to creating palladium macrocyclic complexes used as catalysts. In addition, due to the structural features of the macrocyclic platform, it is possible to synthesize molecules with amphiphilic properties, which makes it possible to obtain various functional nanosystems used in micellar catalysis.



This work is devoted to the development of effective and universal approaches to the synthesis of palladium complexes based on amphiphilic thiacalix[4]arene derivatives for the creation of self-organizing catalytic nanosystems. As a result of this work, an approach was proposed to the synthesis of new palladium complexes based on imidazolium derivatives of *p*-*tert*-butylthiacalix[4]arene in the stereoisomeric form of *1,3*-*alternate*, which makes it possible to obtain the target compounds with high yields. Palladium complexes showed high catalytic activity and selectivity in cross-coupling reactions, as well as in the reduction reaction in water-organic systems. With transmission electron microscopy was shown that during the reduction reaction palladium nanoparticles of ~2 nm in size are formed stabilized by an organic scaffold.



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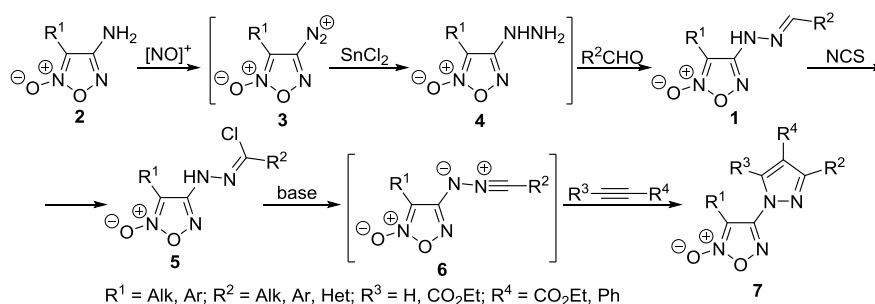
## Novel approach to the synthesis of (*N*-furoxanyl)hydrazones and their utilization in the synthesis of hetarylfuroxans

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A global trend in modern organic and medicinal chemistry is directed towards the construction of molecular architectures with various degrees of complexity in view of creation of practical technologies and sustainable development [1]. In recent years, enhanced efforts were directed to the synthesis of pharmacologically oriented structures comprising a framework capable of nitric oxide (NO) release, including 1,2,5-oxadiazole 2-oxides (furoxans), which are prone to the exogenous NO release in the presence of thiol cofactors [2]. Furoxan scaffold has attracted considerable attention due to high stability of the furoxan cycle under ambient conditions and absence of nitrate tolerance under continuous therapy [3]. The incorporation of the furoxan motif as potential NO donor into drug candidates with known pharmacological activity became now an efficient tool in the design of novel drug candidates and, as a result, new hybrid structures with various pharmacological activities were revealed [4].

In present work, a novel one-pot approach for the construction of previously unknown (*N*-furoxanyl)hydrazones **1** was developed. This method is based on a cascade of one-pot reactions including diazotization of initial aminofuroxans **2**, *in situ* reduction of generated diazonium salts **3** and condensation of formed furoxanylhydrazines **4** with corresponding aldehydes. It is important to note that initial aminofuroxans are readily available compounds which can be easily synthesized on gram-scale according to our recently developed procedure [5]. Hydrazones **1** were easily converted to the chloro derivatives **5** which were used as nitrilimines **6** precursors to construct pyrazolylfuroxan core **7**.



*This work was supported by the Russian Foundation for Basic Research (grant № 18-33-20030)*

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## Dichotomy in Lewis acid-induced transformations of donor-acceptor cyclopropanes bearing *N*-arylcarbamoyl group: pyrrolidones vs benzo[*b*]azepinones

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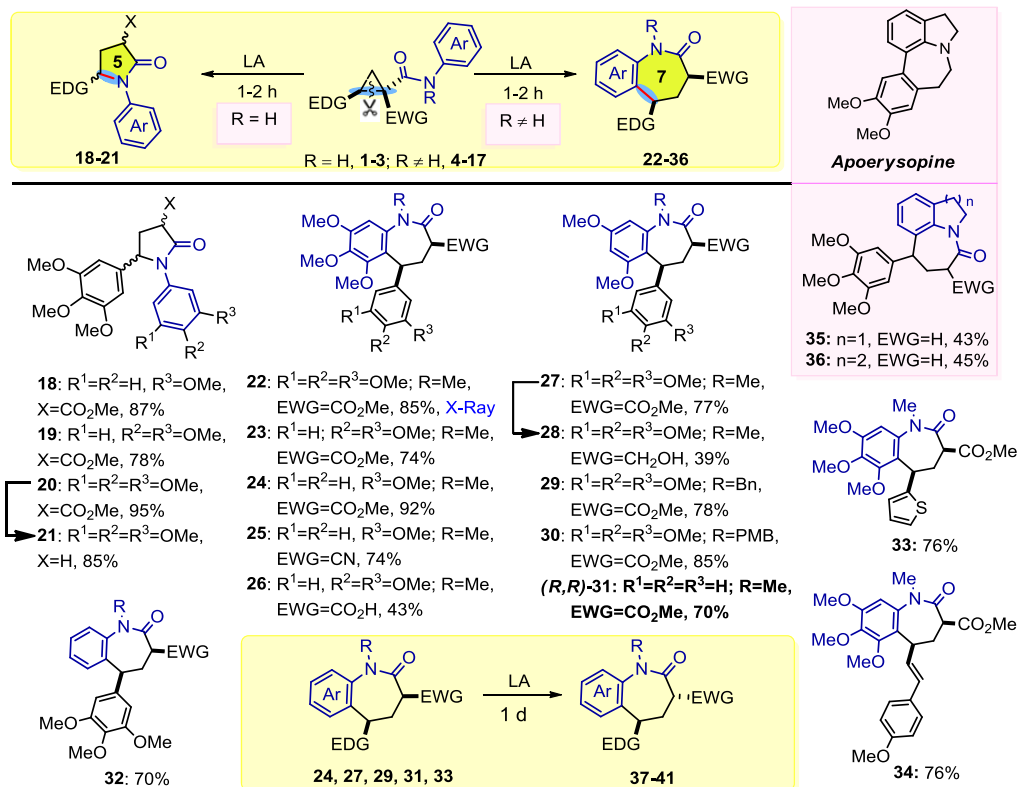
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Three-membered ring expansion of the activated cyclopropanes is among the most efficient tools for the synthesis of diverse carbo- and heterocycles [1]. Herein, we report the Lewis acid-induced ring expansion of donor-acceptor cyclopropanes containing *N*-phenylcarbamoyl moiety as one of the acceptor groups. The reaction chemoselectivity was found to be regulated by a second substituent at the nitrogen atom: *NH*-anilides **1–3** rearranged into 1,5-diarylpyrrolidones while *N*-alkylanilides **4–17** produced 5-arylbenz[*b*]azepin-2-ones. The ring expansion of the optically pure substrate was found to proceed with a full inversion at the electrophilic center supporting S<sub>N</sub>2-like mechanism. The process diastereoselectivity can be efficiently controlled by the reaction time. Under short duration (1–2 h), *cis*-products were formed; the increase of the reaction time to 1 d led to the exclusive formation of *trans*-isomers.



This work was supported by Russian Science Foundation (grant № 18-13-00449)

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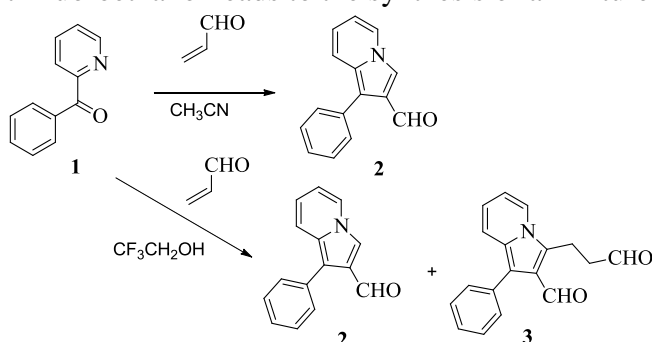
# 1-Aroylisoquinoline and 2-benzoylpyridine in reactions with acrolein

Nevskaya A.A., Miftyahova A.R., Borisova T.N., Voskressensky L.G., Varlamov A.V.

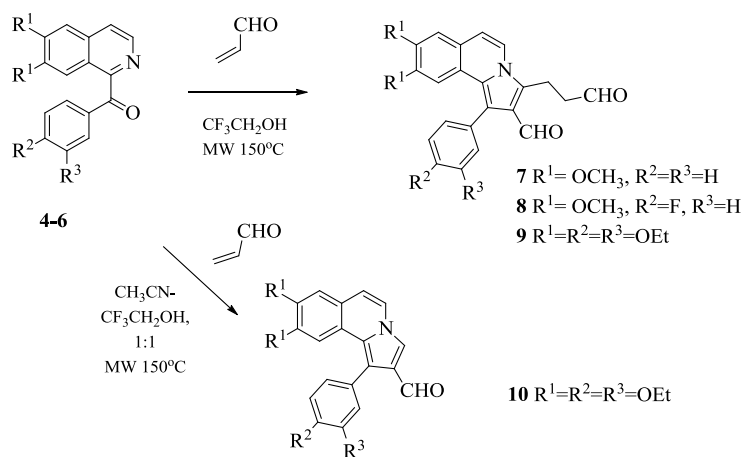
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Recently, the conversion of 1-aryl-3,4-dihydroisoquinolinolines in domino reactions with activated alkenes was studied in the Department of Organic Chemistry at RUDN University. [1]. The aim of the work was to study similar transformations based on aromatic analogues. Aromatic pyrroloisoquinoline has a more pronounced biological activity, as evidenced by the literature data.

We have found that when the reaction of 2-benzoylpyridine **1** is carried out in boiling acetonitrile, in the presence of TMSOTf, a product of interaction with one mole of acrolein, indolizine **2**, is obtained in 77% yield in 30 minutes. The replacement of the solvent with trifluoroethanol leads to the synthesis of a mixture of two indolizines **2** and **3** in a 1: 1 ratio.



The reaction of 1-aryloisoquinolines **4-6** was carried out in acetonitrile and trifluoroethanol under microwave conditions at 150 °C. When we carried out the reaction in trifluoroethanol, two moles of acrolein were added to form pyrroloisoquinolines **7-9**. Using the example of the drotaveraldine analogue - isoquinoline **4**, it was shown that changing the solvent to a mixture of acetonitrile and trifluoroethanol, 1: 1, one mole of acrolein was added to form aldehyde **10**.



It should be noted that in the reactions of 1-aryl-3,4-dihydroisoquinolines the products of addition of two moles of acrolein were not observed [1].

The structure of the compounds obtained is confirmed by a complex of spectral data.

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The reported study was funded by RFBR and Moscow city Government according  
to the research project № 18-31-00001*

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## Transformations of 1-*R*-1-phenylethynylisoquinolines triggered by terminal alkynes in fluorine-containing alcohols

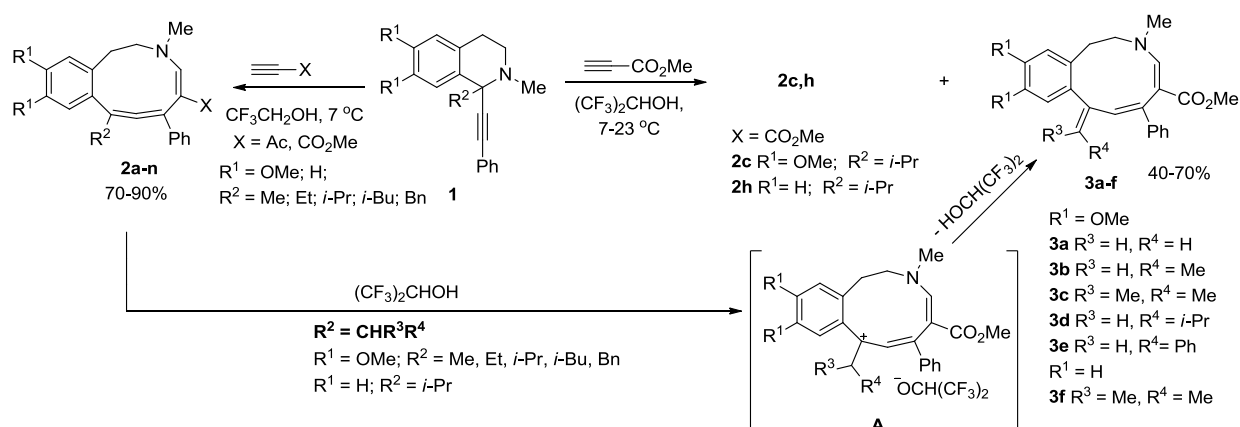
Kobzev M.S., Titov A.A., Voskressensky L.G., Listratova A.V., Varlamov A.V.

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Nitrogen-containing macrocycles are widespread in nature being a part of the structural fragment of some alkaloids [1,2]. The ten-membered benzazecines containing the allene fragment have been still remaining unexplored, as there is a lack of methods for their preparation. We have developed a new method for the synthesis of these compounds starting from 1-*R*-1-phenylethynylisoquinolines **1** [3]. The reactions with methyl propiolate and acetylacetylene occur in trifluoroethanol at 7 °C and the yields of the target products **2** are 70-90%.

In hexafluoroisopropanol 1-alkyl-1-phenylethynylisoquinolines **1** under the action of methyl propiolate undergo transformations leading to 8-ylidene substituted benzazecindienes-4,5 **3**, as a *E*-isomer regarding the double bond at C-8.

We presume that allene **2** is formed in hexafluoroisopropanol, but due to the greater acid-phobicity of the solvent, the allene system is protonated to form cation **A**, the deprotonation of which leads to **3**. Isopropyl substituted isoquinoline **1** ( $R^2 = i\text{-Pr}$ ) in hexafluoroisopropanol forms a mixture of **2** ( $R^2 = i\text{-Pr}$ ) and 8-isopropyl substituted **3** ( $=\text{CMe}_2$ ), which is associated with steric hindrance of the formation of ion **A** and its deprotonation.



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(project № 18-73-10057)

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## $\alpha$ -Fluoronitroalkenes: useful building blocks for the construction of novel fluorinated heterocycles

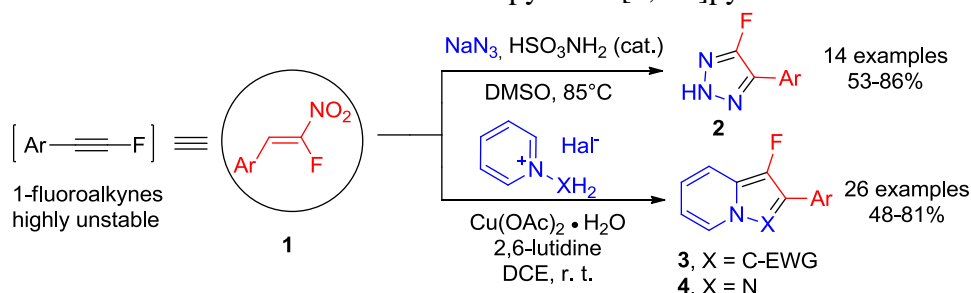
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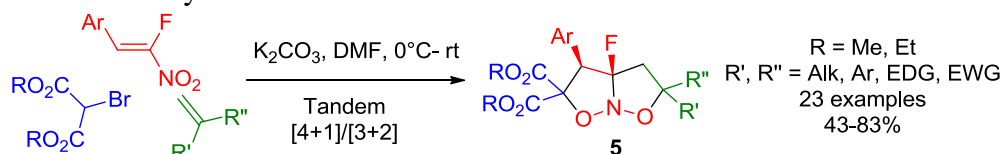
Fluorine-containing molecules are widely used as important pharmaceuticals and agrochemicals. Among them fluorinated heterocycles are the compounds of special interest [1].

We have previously reported the efficient method for the two-step synthesis of  $\alpha$ -fluoronitroalkenes from aromatic aldehydes [2]. In the present work the reactivity of fluoronitroalkenes in cycloaddition reactions, both as  $2\pi$ - and  $4\pi$ -components, was explored; this enables new routes to a number of previously inaccessible fluorinated heterocycles.

First, the reactivity of  $\alpha$ -fluoronitroalkenes in [3+2]-cycloadditions as  $2\pi$ -components was studied. While synthesis of different fluorinated heterocycles via [3+2]-cycloaddition was limited due to extreme instability of 1-fluoroalkynes [3],  $\alpha$ -fluoronitroalkenes **1** were found to act as their suitable synthetic equivalents. Thus, a route to previously inaccessible 4-fluoro-1,2,3-NH-triazoles **2** by cycloaddition with sodium azide was developed. Sulfamic acid was found to be the optimal catalyst for this transformation. Oxidative [3+2]-annulation of  $\alpha$ -fluoronitroalkenes with pyridinium ylides and imines mediated by copper (II) acetate provides a direct route to novel fluorinated indolizines **3** and pyrazolo[1,5-*a*]pyridines **4**.



Next, the reactivity of nitroalkenes as  $4\pi$ -components was explored. The one-pot reaction of  $\alpha$ -fluoronitroalkenes, bromomalonate and different dipolarophiles in basic conditions resulted in formation of bicyclic 5,5-annulated nitroso acetals **5**. The mechanism of the tandem [4+1]/[3+2]-cycloaddition was discussed. Nitroso acetals formed with complete regioselectivity and high diastereoselectivity, and both electron-rich and electron-deficient dipolarophiles were suitable substrates for cycloaddition.



This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00810)

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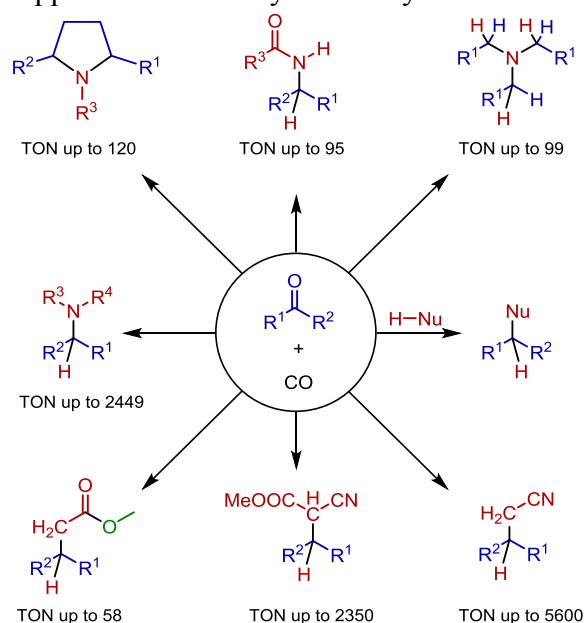
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## Strategy for selective C-N, C-C, C-O bond formation with tolerance to functional groups

Chusov D., Afanasyev O.I., Runikhina S.A., Tsygankov A.A., Kuchuk E., Podyacheva E.

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Herein we present the concept of using carbon monoxide for atom economical reductive addition without external hydrogen source [1-8]. Following this concept, we have shown that N-H, O-H and C-H bonds of the reagents could be used as hydrogen source. The process proceeds with high selectivity. Such approach can widely use for synthesis of heterocycles.



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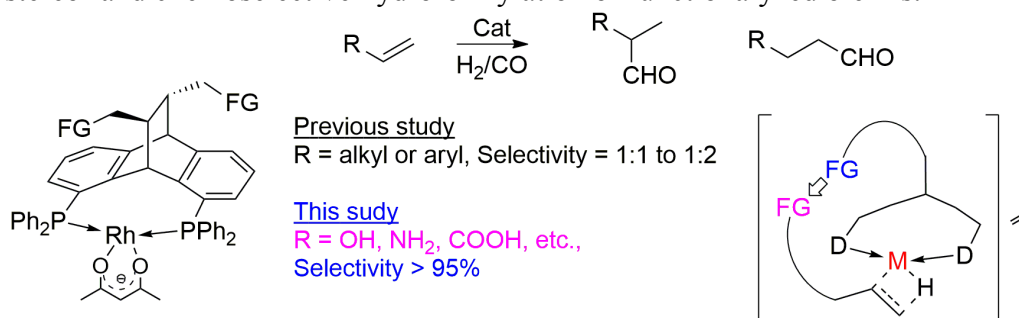
## Stereo- and chemoselective hydroformylation of functional olefins using catalysts with secondary coordination sphere

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Small-molecule catalysts, equipped with a supplementary coordination sphere, have already proved themselves highly efficient in many important chemical transformations. It was previously demonstrated that attractive interactions between the secondary coordination environment and the substrate largely govern stereoselectivity and the reactivity of the primary catalytic site. This approach may become truly practical if divergent synthesis of libraries of such multifunctional catalysts is available, thus allowing facile shuffling of functional groups in the primary and secondary coordination spheres.

We now wish to demonstrate that the modular 3-D ligands developed by our group<sup>1-3</sup> may serve as a universal platform to examine catalytic reactions guided by secondary coordination sphere-substrate attractive interactions. We now report the results of our investigation on a series of bifunctional PC(*sp*<sup>3</sup>)P complexes equipped with different outer-sphere auxiliaries, that allowed stereo- and chemoselective hydroformylation of functionalized olefins.



**Figure 1.**

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## Catalytic interaction of diazoesters with substituted 1,3-oxathiolanes

Raskil'dina G.Z.<sup>1</sup>, Sakhabutdinova G.N.<sup>1</sup>, Zlotsky S.S.<sup>1</sup>, Sultanova R.M.<sup>1,2</sup>

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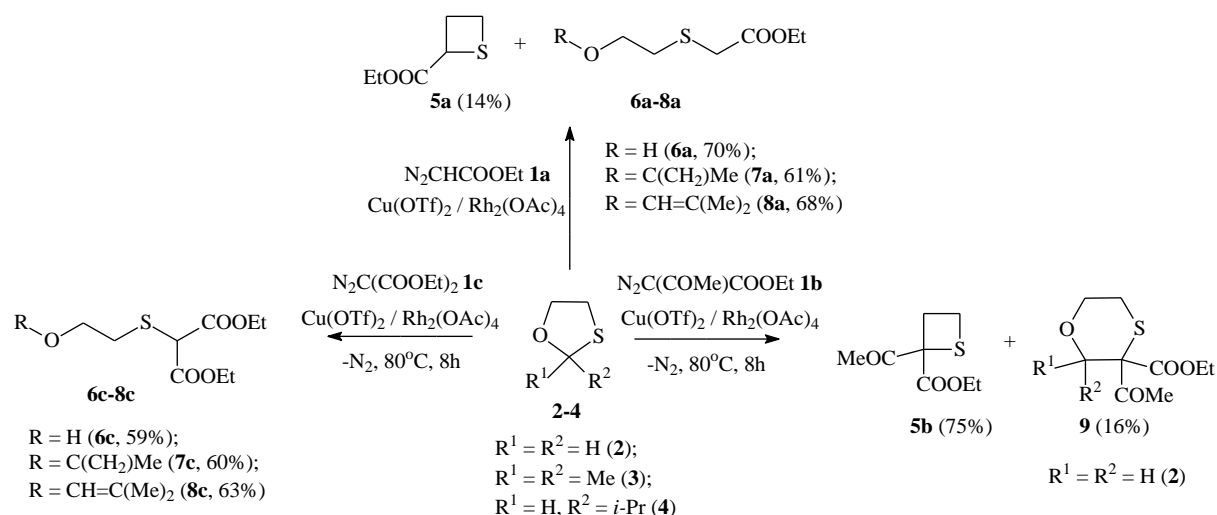
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Diazocarbonyl compounds are widely used in the synthesis of polyfunctional heterocycles [1,2].

This paper is devoted to the study of catalytic interaction of diazo-carbonyl compounds with substituted 1,3-oxathiolanes in the presence of Cu-Rh-containing catalysts. It was shown that the reaction is accompanied by the introduction of an alkoxy-carbonylmethylene fragment into a 5-membered cycle and leads to the formation of both cyclic and linear products.

So, ethyldiazoacetate **1a** reacts with 1,3-oxathiolanes **2-4** (benzene, 80°C, 8 hours) in the presence of both Cu(OTf)<sub>2</sub> and Rh<sub>2</sub>(OAc)<sub>4</sub> with the formation of a mixture of products – thietane **5a** and linear compounds **6a-8a** with yields 10-14% and 68-70%, respectively.



For ethyl 2-diazo-3-oxobutanoate **1b** with 1,3-oxathiolane **2**, under similar conditions, it was found that the presence of alkoxy-carbonylcarbene by the C(2)-Sc bond in the presence of Cu(OTf)<sub>2</sub> is observed to form 1,4-oxathian **9**, and substituted with 1,3-oxathiolanes **3,4**, the reaction proceeds with the formation of a single product - ethyl 2-acetylthietane-2-carboxylate **5b** with a yield of 72-75%, respectively.

The reaction of 1,3-oxathiolanes **2-4** with diethyldiazomalonate **1c** in the presence of both Rh<sub>2</sub>(OAc)<sub>4</sub> and Cu(OTf)<sub>2</sub>, under selected conditions, also proceeds with the formation of linear products **6c-8c**. The possible mechanism of this reaction is discussed in the report.

*This work was supported by the grant of the Republic of Bashkortostan for young scientists (from 08.02.2019)*

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# Synthesis of stable, industrially scalable, efficient metathesis Hoveyda-Grubbs catalysts with a N→Ru or N→S coordinate bond in a six-membered ring

Polyanskii K.B., Raspertov P.V., Kumandin P.A., Alekseeva K.A., Zubkov F.I.

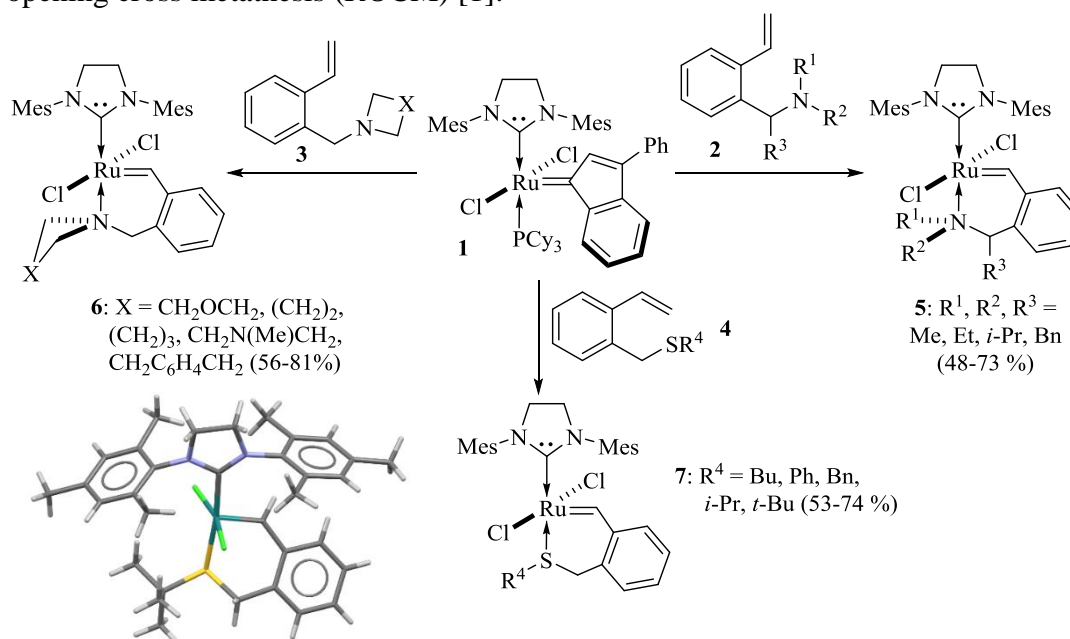
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The widespread application of various catalysts is required to achieve the best results in each of the many directions of metathesis reactions. This fact motivates the search of new, efficient, stable, and highly selective catalytic system.

In this work the multigram synthesis of ruthenium catalysts was carried out using methods based on the interaction of the well known *complex 1* with styrenes **2-4** that gave target Hoveyda-Grubbs type catalysts **5-7** in good yields [1-3].

The synthesized catalysts demonstrated prominent stability in air at room temperature for at least 5 years. The catalysts have good solubility in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and hence, can be used in any types of metathesis reactions.

Catalytic properties of metallo-complexes **5-7** were demonstrated in different "standard" metathesis reactions such as cross metathesis (CM), ring-closing metathesis (RCM) and ring-opening cross metathesis (ROCM) [1].



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# Poster Session



## Spectrophotometric sorption of palladium (II) ions with maleic anhydride styrene copolymer-norsulfazolum system

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One of the important ecological problem is control of Pd(II) in natural and industrial objects on level their limit permissible concentration and below. Therefore, arise a necessity in elaboration new methods of collection palladium with following determination different methods. For the extraction of palladium metal is used complexing sorbents containing functional analytical groups of atoms for example group nitrogen. In this paper, was obtained by a new polymeric sorbent containing fragment of norsulfazolum.

This invention censer to derives of copolymer of malein anhydride-styrene and can be used in analytical chemistry and hydrometallurgy for sorption of palladium metal and its concentration. Radical copolymerization of maleic anhydride with styrene was carried out by the known technique. Counted quantity of formalin and of norsulfazolum is added to the received copolymer. Reaction was performed on sand bath with continuously mixing. The reaction was performed in water medium; therefore, copolymer's anhydride groups were hydrolyzed. In system from interaction formaldehyde and amine is formed unstable carbonyl amine, which interacts with carboxyl group consist in macromolecule with the result that amino fragment falls into macromolecule. The sorbent possesses high sorption characteristic to palladium ions. As follows, sorption capacity to palladium ion in water solution 451 mg/g and degree of sorption - 97%.

In static condition has been researched influence pH an ionic strength liquid phase to sorption ions by the synthesized sorbent. The install time, sorption equilibrium does not exceed 180 minutes. The palladium metal content in solution was determined by photometric method. Adsorption and desorption processes has been revealed in static condition.

Results are illustrated on the table below.

Table 1. The metrological characteristics of sorption-photometric determination of palladium

metal	pHopt	Ionic strenght $\mu$ mol/l	Sorption capacity mq/q	Degree of sorbtion, %	Suitable eluent 0,5M
Pd(II)	5	0,8	451	97,7	HClO <sub>4</sub>

*This work was supported by the grant "50-50", BSU, Azerbaijan*

## Catalytic synthesis of 2-ethoxynaphthalene and 1-ethyl-2-naphthol combination

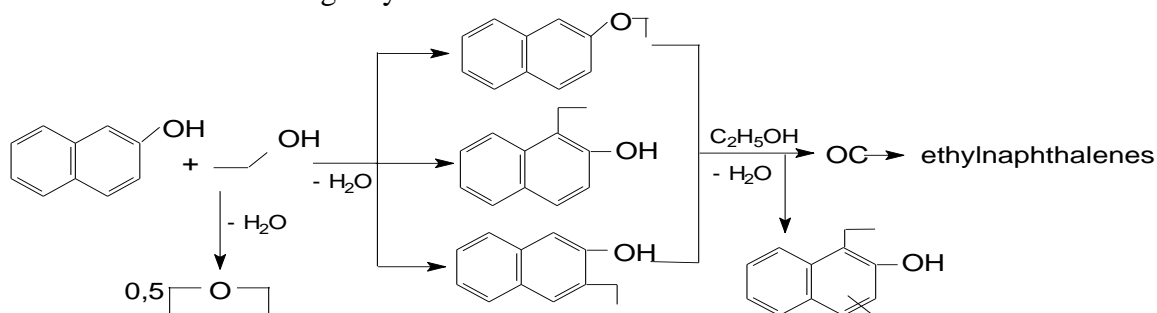
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Methyl and ethyl derivatives of naphthols are used in the production of resins, vitamins, dyes, fragrant substances and additives. The main source for getting them is anthracite and brown coal, peat processing and light oil fractions from pyrolysis resin, and naphthalene and its alkyl homologs in the composition of liquid products. One of the synthetic methods of alkyl naphthols is based on the interaction of naphthols with alcohols.

The thesis provides the results of alkylation reaction of 2-naphthol with ethanol in the presence of complex zirconium catalyst.

The experiments were carried out using chromatographic and spectral methods for the analysis of the products taken at the reactor which it has a stationary layered catalyst. In the catalysts obtained are 2-ethoxy naphthalene, 1-ethyl-2-naphthol, 3-ethyl-2-naphthol, naphthalene and its ethyl derivatives, 2-naphthol which is not converted to ethyl ether and ethanol. The products that are not accurately identified are those oxy-compound and their quantity is low and disappears with an increase in temperature. The main and side effects of the catalytic process can be illustrated in the following way.



Chemical and isomeric content, yield and selectivity of the obtained ethyl naphthols depend on the reaction conditions, including the temperature, volume velocity and mole ratio of the initial components.

The total yield of the 2-ethoxynaphthalene and 1-ethyl-2-naphthol formed in the determined conditions (T-280°C,  $\nu$ -1.0 h<sup>-1</sup>,  $\nu = 1: 4$  mol / mol) calculated by converted 2-naphtholate was 96.5%, single-conversion of 2-naphthol is 25.0%, and the mole ratio of 2-ethoxynaphthalene and 1-ethyl-2-naphthol is 1:0,6.

The thesis also shows the description of the alkylation reaction of 2-naphthol with ethanol.

## Mesoionic 1,2,3-triazol-5-ylidene – tunable platform for photoluminescent Ir(III) complexes

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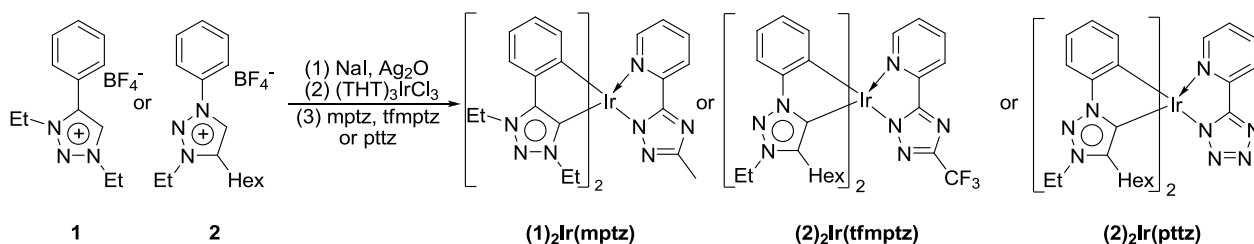
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Phosphorescent Ir(III) complexes are widely used as photosensitizers in photodynamic therapy, photocatalysts for water splitting, phosphorescent labels in biomolecules, and oxygen sensors. The most important field of application of Ir(III) complexes is their use as phosphorescent pigments in electroluminescent devices, such as organic light-emitting diodes and light emitting electrochemical cells.

Most of Ir(III) complexes used in OLEDs are homoleptic tris-cyclometallated Ir(III) complexes  $[\text{Ir}(\text{C}^{\wedge}\text{N})_3]$  or neutral heteroleptic bis-cyclometallated complexes  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})]$  ( $\text{C}^{\wedge}\text{N} = \text{C}^-$ , N-donor cyclometallated ligand,  $\text{L}^{\wedge}\text{X} =$  auxiliary ligand).

N-heterocyclic carbenes are widely investigated as ligands, allowing to elevate the energy of the lowest unoccupied molecular orbital (LUMO). They are strong-field ligands due to weak  $\pi$ -acceptor and strong  $\sigma$ -donor properties, which leads to higher LUMO level and, consequently, higher energy of emitted photons (that is, blue shift of the spectrum), together with high-energy d–d level of the excited state, which reduces the probability of thermally activated non-radiative MC decay. In addition to classic NHC ligands, intense attention is directed towards a new class of NHCs, mesoionic carbenes (MIC) based on the 1,2,3-triazol-5-ylidene core. However, triazolylidene cyclometallated Ir(III) complexes have never been synthesized and studied for their luminescence previously.

The triazolium salts **1** and **2** were obtained via CuAAC click reaction, followed by alkylation with  $\text{Et}_3\text{OBF}_4$ . Three-step one-pot reaction sequence involving: (1) generation of silver carbene complex; (2) carbene transfer to iridium and subsequent cyclometallation via C-H activation in phenyl ring; and (3) addition of the pyridyl triazolate chelate ligand. Structures of complexes **(1)<sub>2</sub>Ir(mptz)** and **(2)<sub>2</sub>Ir(tpmptz)** were determined in solid state using XRD.



All complexes exhibit photoluminescence in 496-550 nm region. Thus, it was shown that cyclometallated 1,2,3-triazol-5-ylidene ligands can serve as tunable platform for preparation of iridium(III) complexes that can be utilized in OLEDs and other photophysical applications.

*This work was supported by the Russian Science Foundation (RSF)  
(project number 17-73-20023)*

## Efficient electrophilic iodination of 2-aminopyridines

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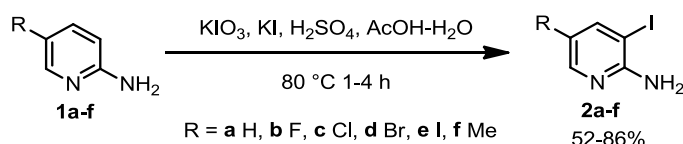
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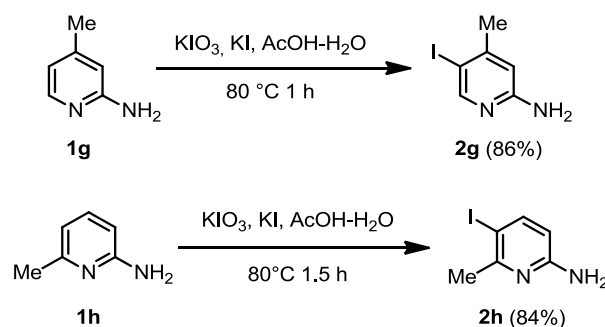
Aromatic iodides have found increasing applications in organic synthesis due to their functionalization through metal catalyzed cross-coupling reactions. They also can be used as substrates for the synthesis of bioactive molecules.

The iodination reactions with using NaIO<sub>4</sub> and NaIO<sub>3</sub> as the oxidants, proved to be very effective in the case of a number of deactivated arenes, including nitrobenzene and benzoic acid [1], [2]. Pyridine and its derivatives **1a-1h** were not considered.

Pyridine reluctantly enters into an electrophilic substitution reaction, but the presence of an electron-donating NH<sub>2</sub>-group facilitates the task. Iodination process involves the use of KIO<sub>3</sub>/KI/AcOH/H<sub>2</sub>SO<sub>4</sub> system. From these reactions we isolated 8 iodinated products in good yields (52-86%).



In the case of 4- and 6-methylpyridines **1g** and **1h** CH<sub>3</sub>- and NH<sub>2</sub>-groups have a consistent orienting effect. Iodination process in this case proceeds smoothly in the absence of H<sub>2</sub>SO<sub>4</sub>.



The using of inexpensive and environmentally-friendly inorganic reagents, makes the iodination process more attractive. In the near future we are planning to use 2-amino-3-iodopyridines **2a-h** in Pd-catalyzed intramolecular cross-coupling Heck reaction.

### References

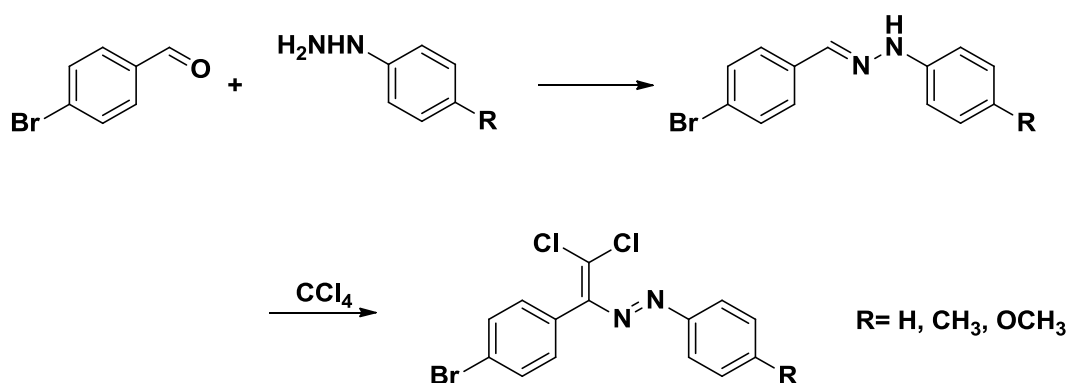
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## The synthesis of (*E*)-1-(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(4-substituted phenyl)diazenes and X-ray analysis

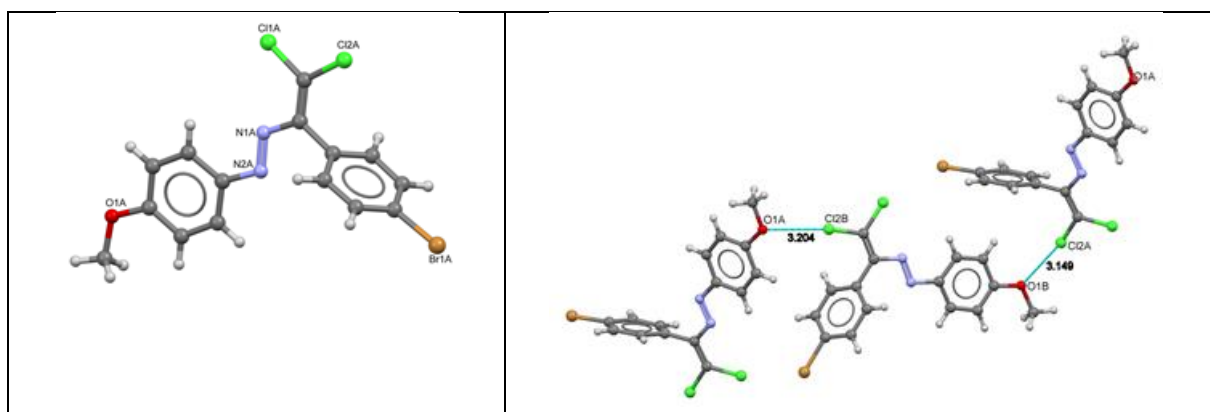
Ahmadova N.E., Suleymanova G.T., Babayeva G.V., Garazadeh Kh.A., Gurbanova N.V.,  
Mamedova G.Z., Shikhaliyev N.G.

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In our previous studies, the synthesis of dichlorodiazadienes was carried out in the conditions of catalytic olefinization reaction of phenyl hydrazones synthesized on the basis of benzoic aldehyde and its derivatives. The monocrystals of the obtained compounds were grown and the presence of halogen-halogen, pnikogen,  $\pi \cdots \pi$ , tetral bonds were studied by us through the X-ray analysis [1-2]. Given all this, synthesis of dichlorodiazadienes was carried out on the basis of phenylhydrazones of 4-bromobenzaldehyde based on hydrazines that contain donor groups.



The presence of non-covalent bonds in the crystal structures of the compounds obtained was investigated by X-ray analysis



*This work was carried out with the financial support of the Foundation for the Development of Science under the President of the Republic of Azerbaijan-Grant No EIF-BGM-4-RFTF-1 / 2017-21/13/4 and Intra University Grant Program 50 + 50, Baku State University*

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## Licorice root extract is a source of triterpene saponins

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In experimental biochemistry and Bioorganic chemistry, methods of distribution, absorption and thin-layer chromatography using various sorbents and carriers (aluminum oxide, silica gel, etc.) are widely used to separate extractive biologically active substances from plant materials. It is known that depending on the place of growth of licorice and its variety, the content of extractive substances in the composition of the raw material changes. In this regard, it is of scientific and practical interest to extract and study the composition of different types (genera) of licorice. We have chosen the object of study the composition of licorice root extract growing on the territory of the Torgai steppe of Kostanay region (Republic of Kazakhstan). The raw materials were collected in October 2018. Type of raw material-licorice (*Glycyrrhizae radices*). The licorice root contains more than 20% of triterpene saponin glycyrrhizin. Triterpene saponin glycyram in the rhizome of licorice is not fully investigated, so given their high biological activity is of interest to their in-depth study. To this end, we have carried out the isolation and separation of organomineral complex of licorice (*Glycyrrhizae radices*). Using extraction and chromatography methods, extractive substances were extracted from licorice root. The composition of extractive substances of raw materials includes proteins, carbohydrate components, unsaturated carboxylic acids, micro - and macronutrients. In licorice is valuable root and rhizome, which is used for medicinal purposes. Licorice root is rich in triterpene compounds, it has starch, sucrose, essential oils, glucose, ascorbic acid, pectin, as well as a number of minerals. Licorice substances have a wide range of medicinal properties including antiviral, anti-inflammatory, hemostatic, cytotoxic, etc. It should be noted that it is often used in cancer, as it has a pronounced anti-tumor property, and to some extent inhibits the growth of malignant tumors. It is known that the authors studied the qualitative and quantitative analysis of raw materials and licorice preparations. In this paper, we describe that the dominant component of licorice is glycyrrhizin (triterpene saponin) and likurazid (flavanone). In the field of chemistry of natural compounds development of rational extraction technology is an extremely urgent task. And due to this, we have begun to search for the extraction of biologically active substances from the licorice root, using methods of extraction and chromatography. We had a task in pure form to highlight the triterpene saponin and likurazid and their further chemical modification.

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## Easy protocol to solve the selectivity problem in Cu(II) catalyzed Chan-Evans-Lam (CEL) reactions

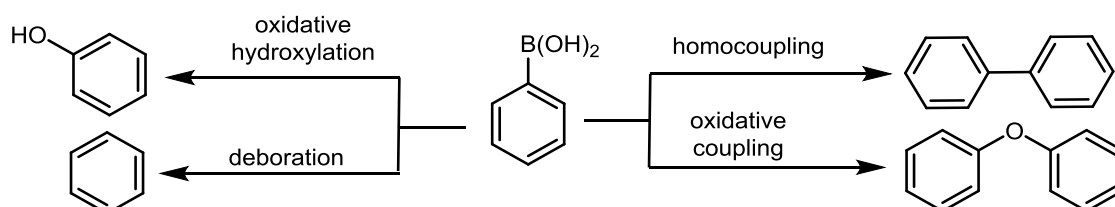
Akatyev N.V., Ilyin M.M., Ilyin M.M. (Jr.), Lependina O.L., Kudryavtsev K.R., Belokon Y.N.

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In 1998 Chan, Evans, and Lam in three back-to-back publications reported the oxidative coupling of amines with arylboronic acids promoted with copper salts in air. The reaction was later called CEL reaction [1]. The couplings proceed under mild conditions, often at a room temperature. In the following years, different research groups made considerable progress in expanding the scope of the copper-mediated coupling methodology [2].

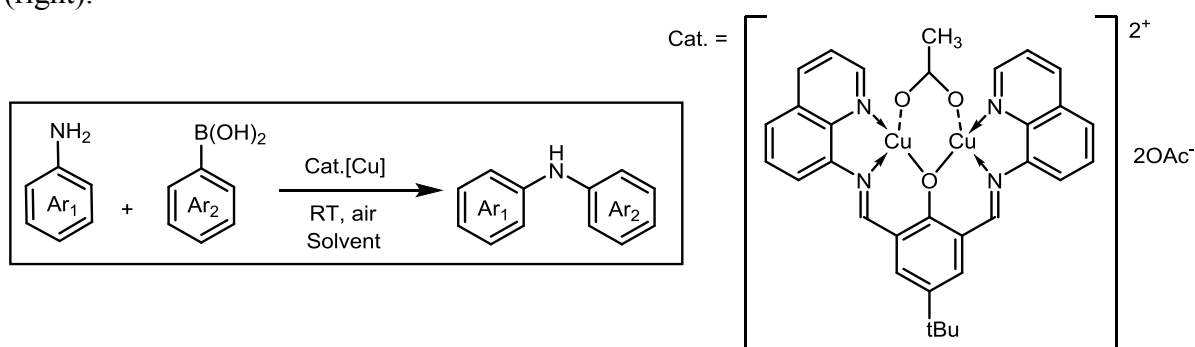
Unfortunately, there are some undesirable couplings, accompanying the main reaction (Fig.1) [3].



**Figure 1.** Side reactions in CEL-couplings

Evidently, there is a need to elaborate a new family of catalysts, selectively providing the desired CEL-coupling and avoiding the undesired side reactions. Herein we synthesized and investigated more than 30 mono- and dinuclear copper(II) complexes and tested them in a CEL-reaction (Fig. 2, left). The nature of the copper counter anions and the number of copper(II) ions in the catalyst had the paramount importance for both the efficiency and the selectivity of the CEL-reaction.

The most efficient catalyst was found to be the dinuclear complex depicted on Fig. 2 (right).



**Figure 2.** The Chan-Evans-Lam reaction

*This work was supported by Russian Science Foundation (grant № 15-13-00039)*

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## New synthesis of [1,2,4]triazolo[1,5-*a*]heterocycle via electrophilic activation of nitroalkanes

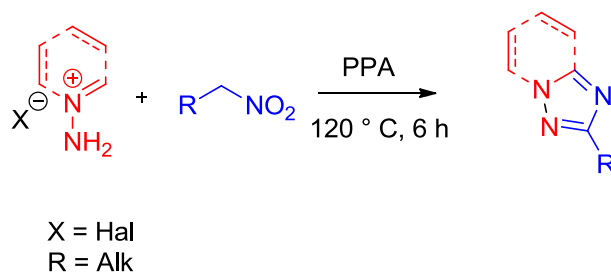
Aksenov A.V., Khamraev V.F., Aksenov N.A., Kirilov N.K.

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New efficient synthesis of [1,2,4]triazolo[1,5-*a*]heterocycle, from different *N*-imino heterocycle such as *N*-iminopyridine, *N*-iminoquinoline via electrophilic activation of nitroalkanes in polyphosphoric acid and further cyclocondensation is reported.

Quinoline containing fused *N*-heterocyclic compounds have also shown significant bioactivities and important representatives, such as lutonin A, dactolisib, pyronaridine.

We wondered the way of employing 1-aminopyridin-1-ium salt and other heterocyclic imides en route to 2-ethyl[1,2,4]triazolo[1,5-*a*]pyridine scaffolds (Scheme 1). The reaction proceeds at 140°C with high yields (60-80%).



Scheme 1

The novel one-pot reaction sequence of heterocyclic imides involving cyclocondensation with activated nitroalkanes under mild condition is reported.

*This work was financed by the Russian Foundation for Basic Research  
(grant № 19-03-00308 a)*

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## Unsaturated nitro compounds in reactions with indoles in the presence of trivalent phosphorus compounds

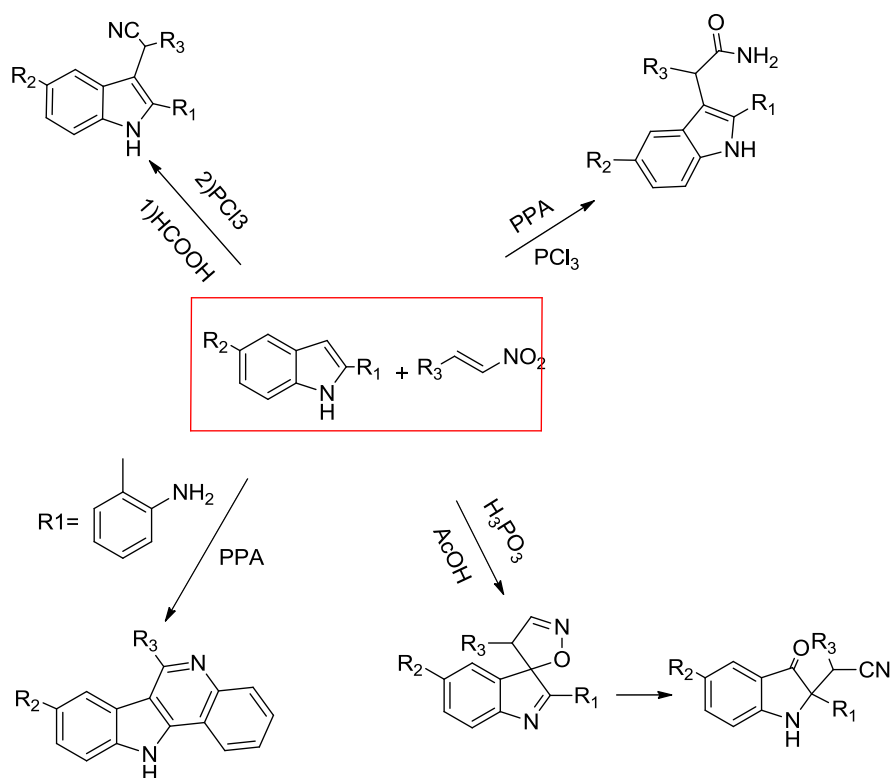
Aksenov D.A.,<sup>a</sup> Aksenov N.A.<sup>a</sup>, Rubin M.<sup>a,b</sup>, Rubacheva A.A.<sup>a</sup>, Gorobec K.A.<sup>c</sup>, Aksenov A.V.<sup>a</sup>

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As it was known, nitroalkanes are multipurpose reagents in organic synthesis, which are more often used as electrophilic components in Michael addition reactions, as dipolarophiles in some [3+2] cycloadditions and as electron poor dienophiles in Diels-Alder or hetero Diels-Alder reactions.



In our laboratory was researched some new directions in reactions unsaturated nitro compounds with indoles in the presence of trivalent phosphorus compounds and the formation of the precursors of the alkaloid isocryptolepine in the presence of the 2-aminophenyl substituent in the 2 position of the indole.

Also, diastereoselectivity of the reaction in the presence of phosphorous acid should be noted.

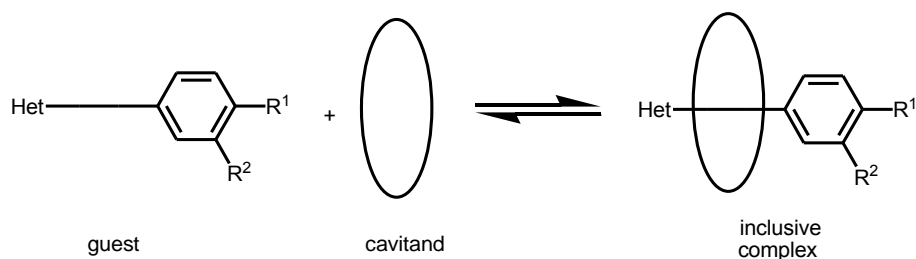
*This work was supported by the Russian Science Foundation  
(Grant № 18-13-00238)*

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

Aleksandrova N.A., Lobova N.A., Vedernikov A.I., Gromov S.P.

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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<sub>2</sub>O 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) –  $\beta$ -cyclodextrins and cucurbit[7]uril – was studied by electronic and <sup>1</sup>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 Russian Science Foundation (project № 14-13-00076)*

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## Unexpected diastereoselective formal [4+1] cycloaddition of indoles in reaction with nitrostyrenes in the presence of trivalent phosphorus compounds

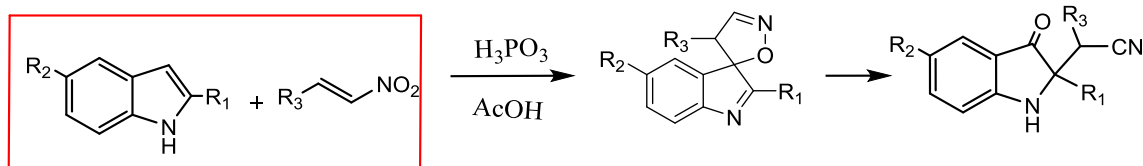
Alexandrova E.V., Aksenov N.A.<sup>a</sup>, Rubin M.<sup>a,b</sup>, Aksenov D.A.<sup>a</sup>, Aksenov A.V.<sup>a</sup>

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Although heterocyclic compounds with 4'H-spiro[indoline-3,5'-isoxazole] and 4'H-spiro[indole-3,5'-isoxazole]cores do not occur in nature, these synthetic drugs can potentially demonstrate promising biological activity. Our group has interest in the development of Bronsted acid-assisted cascade heterocyclizations of nitro-compounds. Nitroalkenes were successfully employed as synthetic equivalents of 1,4-dipoles of CNNO-type in a highly diastereoselective formal [4+1]-cycloaddition reaction of indoles in phosphorous acid to afford 4'H-spiro[indole-3,5'-isoxazole]derivatives



In our laboratory was researched some new directions in reactions unsaturated nitro compounds with indoles in the presence of trivalent phosphorus compounds

Also, should be noted diastereoselectivity of the reaction in the presence of phosphorous acid.

*This work was supported by the Russian Science Foundation  
(Grant № 18-13-00238)*

## Cinnamyl-amine based approach to different isoindole-containing heterocycles

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Peoples' Friendship University of Russia (RUDN University)

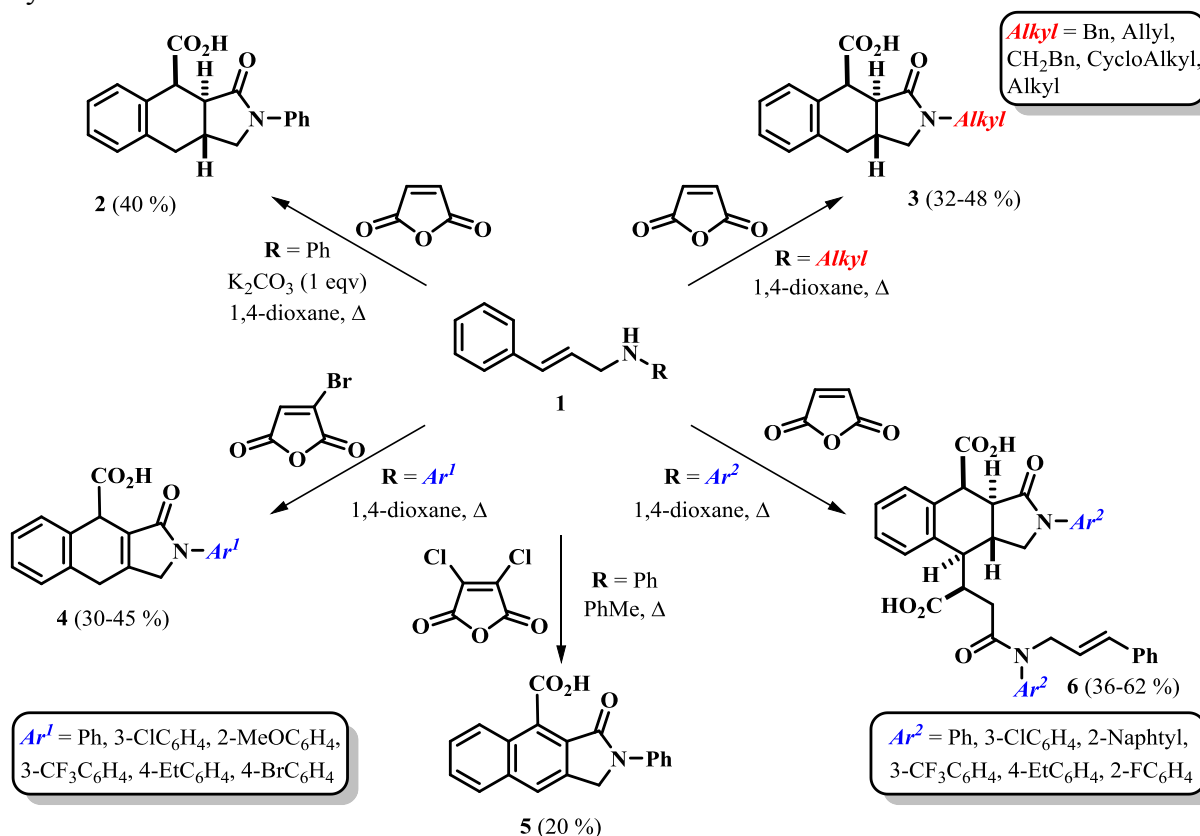
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Recently we have proposed several easy IMDAV (the IntraMolecular Diels-Alder Vinylarenes reaction) approaches to the synthesis of heterocyclic compounds based on the interaction of 3-(aryl)allyl amines (**1**) with maleic anhydride [1,2].

The present study is an extension of this methodology to the synthesis of other derivatives of isoindole.

Various adducts of the tandem reaction of acylation / [4+2] cycloaddition: hexahydro-1*H*-benzo[*f*]isoindoles **2** и **3** (R = *Alkyl* and R = Ph), tetrahydro-1*H*-benzo[*f*]isoindoles **4** (R = *Ar*<sup>1</sup>), 2,3-dihydro-1*H*-benzo[*f*]isoindoles (R = Ph) **5** or dimers **6** (R = *Ar*<sup>2</sup>) can be obtained from the initial cinnamyl-amines (**1**) depending on reaction conditions and substituents in maleic anhydride.



This work was supported by the Russian Foundation for Basic Research (grant № 17-53-45016)

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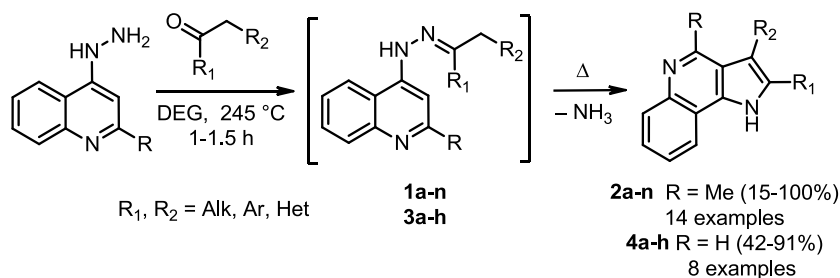
## New synthetic approach to isocryptolepine alkaloids via Fischer cyclization

Alekseyev R.S.<sup>a</sup>, Hasanov T.N.<sup>b</sup>, Terenin V.I.<sup>a</sup>

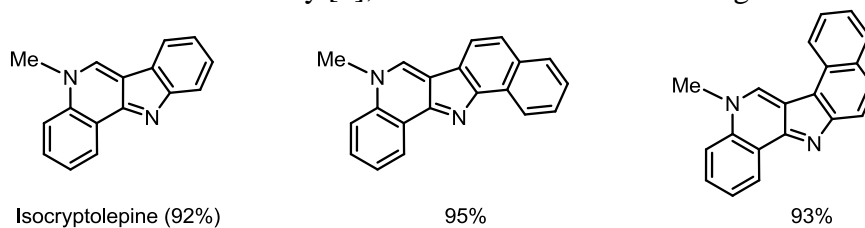
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Pyrrolo[3,2-*c*]quinoline and its derivatives have interesting physicochemical properties and a wide spectrum of biological effects. In particular, it is the pharmacophoric fragment of the isocryptolepine alkaloid [1], which is currently obtained by various methods. We have proposed a simple and effective procedure for the synthesis of pyrrolo[3,2-*c*]quinoline structures based on the Fischer reaction. We have shown in numerous examples that the Fischer reaction can be successfully used for the synthesis of 2,3-disubstituted pyrrolo[3,2-*c*]quinolines. The Fischer cyclization of 2-methyl-4-quinolyl hydrazones of various carbonyl compounds **1a-n** (including the heterocyclic furan and thiophene series) under the conditions proposed by us (DEG, 245 °C, 1-1.5 h) results in a corresponding 2,3-disubstituted 4-methyl-1*H*-pyrrolo[3,2-*c*]quinolines **2a-n**. The cyclization of 4-quinolyl hydrazones of ketones **3a-h**, previously not used in other studies, leads to the corresponding 2,3-disubstituted 1*H*-pyrrolo[3,2-*c*]quinolines **4a-h** with a wide range of yields.



Based on the indolo[3,2-*c*]quinolines obtained by the Fischer reaction, we have proposed and implemented an original approach to the synthesis of isocryptolepine – the alkaloid, which has anticancer and antimalarial activity [2], and its benzannelated analogs.



### References

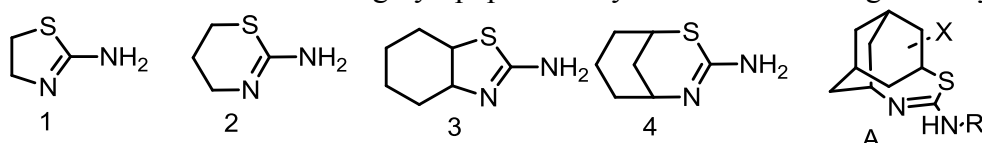
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## Novel structural type of bridged urea derivatives

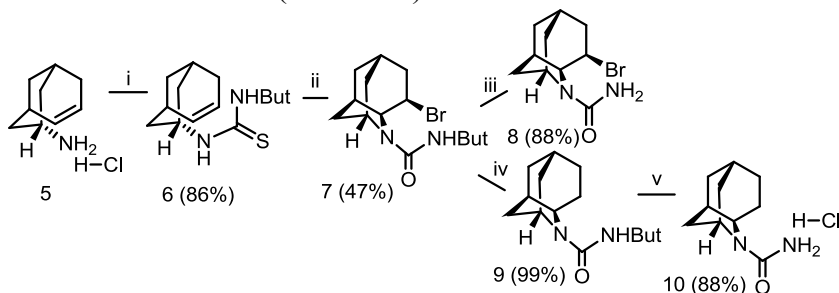
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Cyclic isothioureas, such as 2-amino-2-thiazoline (**1**) and 2-amino-5,6-dihydro-4*H*-1,3-thiazine (**2**), possess pronounced and short-term effect against septic shock and radioactive irradiation due to their ability to inhibit enzyme nitric oxide synthase (NOS). Recently we synthesized more lipophilic bicyclic isothioureas **3** and **4**, which maintained the activity of parent molecules **1** and **2**, but compound **3** displayed prolonged antihypotensive action *in vivo* [1, 2]. These results stimulated us to obtain highly lipophilic tricyclic isothiourea of general type **A**.



In an attempt to synthesize 4-thia-6-azatricyclo[5.3.1.1<sup>3,9</sup>]dodecan-5-imine (**A**, R=H, X=H), a reaction of 1-[(1*RS*,3*SR*,5*SR*)-bicyclo[3.3.1]non-6-en-3-yl]-3-*tert*-butylthiourea **6** in the presence of bromine was undertaken (Scheme 1).



**Scheme 1** i) DIPEA, Bu<sup>t</sup>NCS, CH<sub>2</sub>Cl<sub>2</sub>, rt, 12 h; ii) 1. Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h; 2. NaHCO<sub>3</sub>, H<sub>2</sub>O; iii) HCl<sub>aq</sub>, reflux, 3 h; iv) *n*-Bu<sub>3</sub>SnH, AIBN, toluene, 100°C, 6 h; v) HCl<sub>aq</sub>, reflux, 3 h; The marked configuration of compounds is relative (they represent racemic mixtures)

The intramolecular cyclization under atmospheric *moisture* conditions however did not lead to a product of intramolecular cyclization by sulphur atom (as was observed earlier for bicyclic compounds **3** and **4**) but was accompanied by precursive oxidation of thiourea to urea fragment and proceeded via nitrogen atom yielding the bridged tricyclic urea derivative **7** (as determined by X-ray analysis and liquid chromatography–mass spectrometry technique for compound **8**). As though the structural template of compounds **7** and **8** is unique and have never been studied earlier, we carried out a reductive debromination of bromine derivative **7** and (via compound **9**, Scheme 1) obtained unsubstituted urea bearing azatricyclo[4.3.1.0<sup>3,8</sup>]decane moiety **10**. It belongs to a novel and unusual structural type of bridged tricyclic ureas.

*This work was supported by Russian Fund of Fundamental Research  
(grant №18-03-00524)*

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## Synthesis of 3-aminoanthra[2,3-*b*]thiophene-2-carboxylic acid

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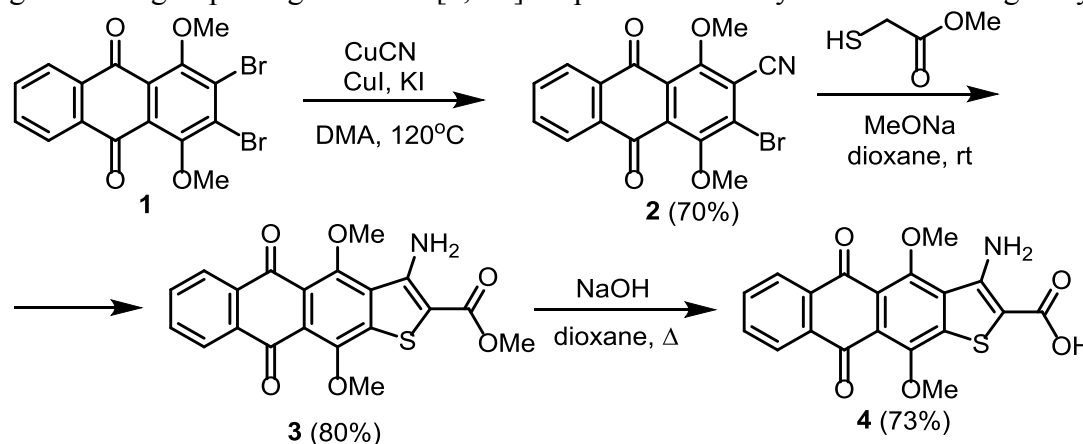
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Heteroarene-fused anthracenediones are promising compounds for the search of new chemotherapeutic agents with improved antitumor characteristics. Amides of anthra[2,3-*b*]furan-3-carboxylic acid demonstrated a high biological activity, inhibiting tumor cell proliferation *in vitro* and *in vivo* [1]. Bioisosteric modification of the heterocyclic core of anthra[2,3-*b*]furans to anthra[2,3-*b*]thiophene derivatives has provided a prospective direction for further studies of anthracenediones fused with heteroarene rings.

2,3-Dibromo-1,4-dimethoxyanthracene-9,10-dione (**1**) was chosen as a starting compound for the synthesis [2]. It is known that halogen substituents in arenes can be replaced with a cyano group in the presence of transition metal catalysts. In particular, the Rosenmund–von Braun reaction was used to transform bromo derivative **1** by treatment with CuCN in DMA under inert atmosphere into nitrile **2**. The methyl ester of 3-amino-4,11-dimethoxyanthra[2,3-*b*]thiophene-2-carboxylic acid was obtained by the condensation of nitrile **2** with methyl ester of thioglycolic acid in the presence of base. The alkaline hydrolysis of compound **3** led to the cleavage of ester group and gave anthra[2,3-*b*]thiophene-2-carboxylic acid **4** with a good yield.



The structure of the obtained compounds **2-4** was proved by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and high-resolution mass spectra. Currently, the synthesis of target anthra[2,3-*b*]thiophene-2-carboxamides is carrying out.

*The study was performed with partial financial support from the Grants Council of the President of the Russian Federation for state support of young scientists in Russia (grant MK-2474.2018.3)*

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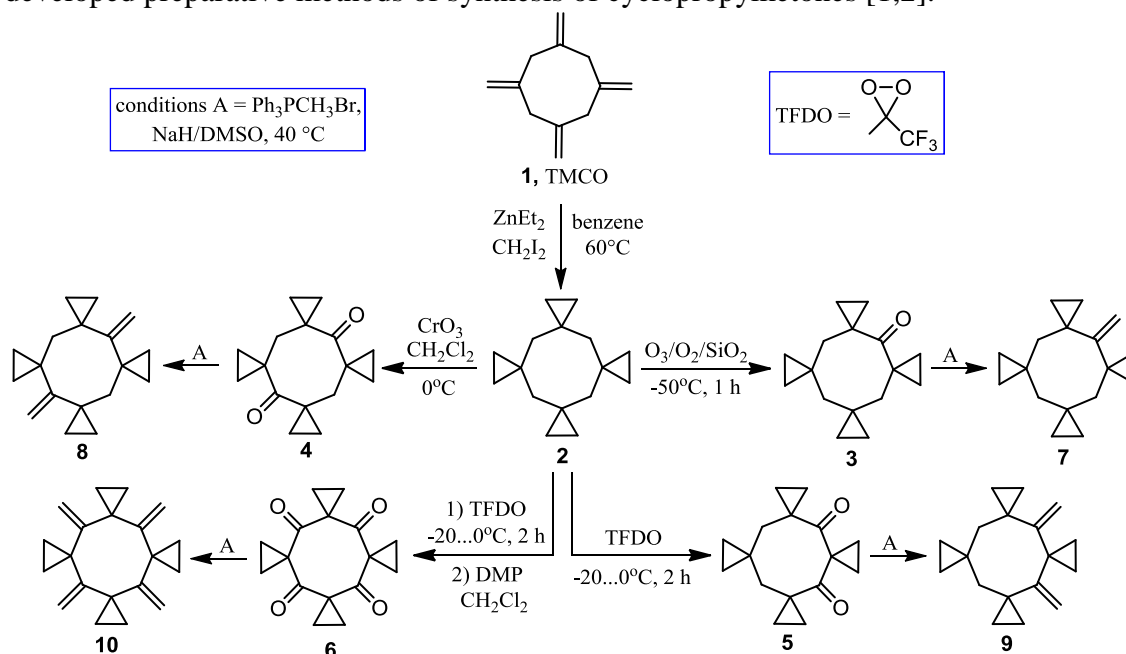
# 1,3,5,7-Tetramethylenecyclooctane as a synthetic precursor of unique polyspirocyclopropane structures and [8]-rotane

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Polyspirocyclic structures containing three-membered rings have unusual chemical properties, high enthalpies of formation, and occupy an important place in the investigation of the nature of C–C-bonds. Due to the high internal strain, such compounds are both promising high-energy compounds and valuable reagents in organic synthesis.

An effective strategy allowing increasing the number of spirocyclopropane fragments in a molecule is the oxidation of activated methylene groups at the  $\alpha$ -position of a cyclopropane fragment to a carbonyl function followed by methylation and cyclopropanation. In this connection, we have systematically studied a number of oxidants (ozone, dioxiranes, chromium (VI) and ruthenium (VIII) oxides) in the reactions with cyclopropane-containing hydrocarbons and developed preparative methods of synthesis of cyclopropylketones [1,2].



Polyspirocyclopropane hydrocarbon 2 obtained from TMCO (1) has been studied under the treatment with above-mentioned oxidizing agents. The conditions for the oxidation of hydrocarbon 2 affording mono- and polyketones 3–6 were found. The reactivity of the obtained carbonyl groups was demonstrated by the reaction of ketones 3–6 with the phosphorus ylide leading to the alkenes 7–10, that opens the possibility for further transformations of the obtained carbonyl compounds and makes them promising synthetic precursors of [8]-rotane.

*This work was supported by the Russian Foundation for Basic Research (grant 16-03-00467-a)*

## References

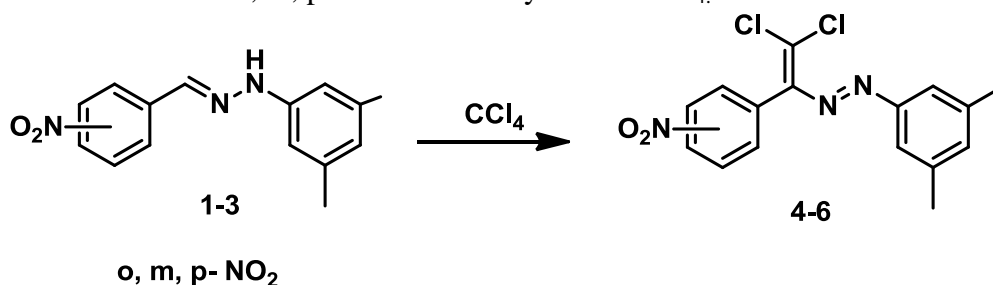
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## The synthesis of dichlorodiazadienes on the basis of *o*, *m*, *p*-benzaldehyde

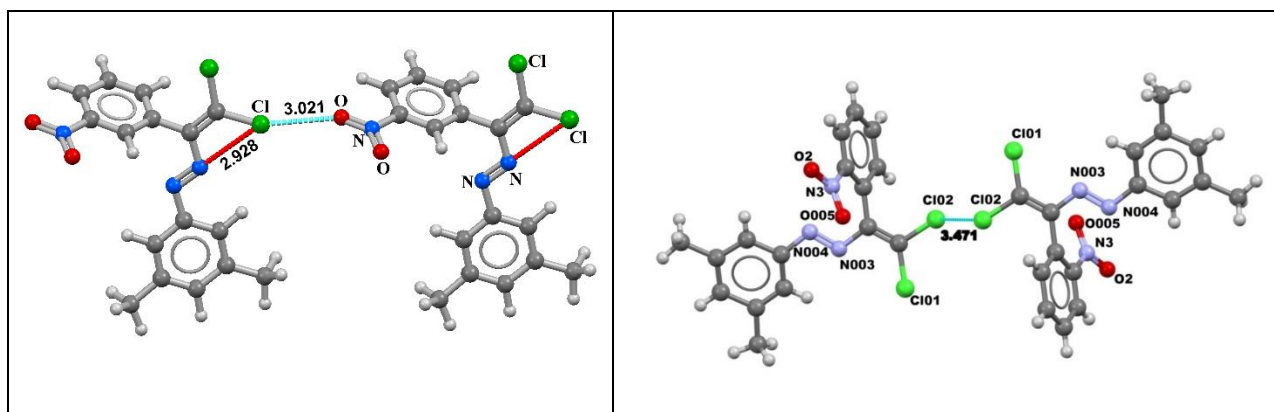
Askerova U.F., Suleymanova G.T., Muxatova S.H., Mamedova N.A., Mikayilova N.F.  
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In previous studies carried out by us, the synthesis of phenylhydrazones and on their basis dihalorodiazadiens in the condition of catalytic olefinization reaction caused great interest in both organic synthesis and microbiology. As we know, some drugs have chemical origin in nitroaromatic compounds. Such compounds are bioactive metabolites found in plants and mushrooms. Thus, insecticides obtained from synthesis of several nitroaromatic compounds have a wide range of applications. Taking into account the application in medicine and agrochemistry, it is important that these functional groups exist in the synthesized compounds. Thus, the corresponding dichlorodiazadienes were obtained from the reaction of phenylhydrazones synthesized on the basis of *o*, *m*, *p*-nitrobenzaldehyde with  $\text{CCl}_4$ .



The structure of the compounds obtained was determined by NMR and X-ray methods. At the same time, the presence of non-covalent bonds in the compounds has been confirmed.



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## Synthesis of new analogues of azasugars on the basis of optically active diethyl (S)-3-(hydroxymethyl)-3,6-dihydropyridazine-1,2-dicarboxylate

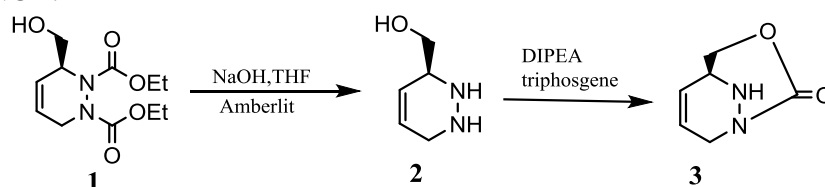
Axundova F.N.<sup>1</sup>, Kurbanova M.M.<sup>1</sup>, Huseynzada A.E.<sup>1</sup>, Alves M.J.<sup>2</sup>

<sup>1</sup>Baku State University, Organic Chemistry Department, Z. Khalilov 23, Baku, AZ 1148

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Aza sugars or imino sugars are subject to intense current interest [1–3]. A while ago it was found that subtle change, by moving the nitrogen to the pseudo-anomeric position (the position that corresponds to the anomeric position in a monosaccharide) in the classical imino sugar inhibitor of nojirimycin type, gave a very potent class of glycosidase inhibitors, the so-called 1-aza sugars [4,5]. It was found that a member of this class of compounds, 1-azafagomine inhibits both  $\alpha$ - and  $\beta$ -glucosidase strongly [6,7]. The reason of biological activity of 1-azafagomine is caused by the fact that it mimics the transition states of  $\alpha$ -glucoside and  $\beta$ -glucoside cleavage in the protonated form [8]. This fact stimulate scientists to synthesize new various analogues of iminosugars which further investigations revealed the presence of a wide spectrum of biological activity among this class of compounds. On the basis of them were prepared different drugs which are used during diabetes, cancer, AIDS, hepatit, Gaucher diseases [8,9]. Obviously, the field of iminosugars have become very exciting area for research on both chemical and biological fronts.

Considering the importance of iminosugars, new derivatives of iminosugars **2** and **3** were synthesized on the basis of optically pure (S)-Diethyl-3-(hydroxymethyl) pyridazine-1,2(3H,6H)-dicarboxylate (**1**), which was obtained according to Bols's protocol by using chiral catalyst (S)-BINOL.



Target compounds **2** and **3** were synthesized in high yields. Obtained compounds were investigated against *S. aureus* and *E. coli* bacteria and promising results were obtained

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## A new approach to the chiral resolution of the dispiroindolinones for increasing of biological activity

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Dispiroindolinones, that had been previously proposed in our laboratory as potential anticancer drugs [1], were synthesized by the reaction of [1,3]-dipolar cycloaddition of 5-arylidene derivatives of 2-thiohydantoin and hydantoin to azomethylilides, which were generated from sarcosine and isatins. The biological effect of these compounds is based on the interaction with MDM2 protein - a natural inhibitor of the tumor suppressor p53. A series of 40 compounds were obtained.

These compounds contain 3 chiral centers in their structure, and the existence of 8 stereoisomers is theoretically possible. However, [1,3]-dipolar cycloaddition reaction is diastereoselective, it has been proven that as a result of the reaction only 2 enantiomers are formed. It was also shown that only one of the enantiomers exhibits cytotoxic activity. Thus, the purpose of this work is the separation of dispiroindolinones into individual stereoisomers.

The use of HPLC with chiral stationary phase is inefficient for these substances. Therefore, a method that employs introduction of an additional chiral center with a fixed configuration into different positions of the synthesized dispiroindolinones is discussed (Figure 1).

A separation procedure of dispiroindolinones into individual stereoisomers is proposed. A method of removing the chiral group to isolate enantiomerically pure dispiroindolinone using hydrogenolysis reactions and splitting with strong acids is discussed[2].

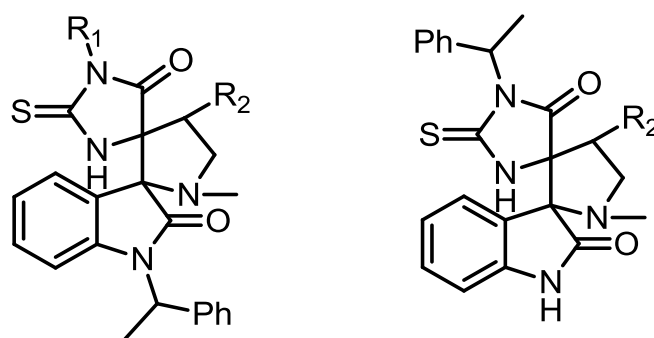


Figure 1. Types of synthesized dispiroindolinones

*This work was supported by Russian Foundation for Basic Research, project № 18-33-01159*

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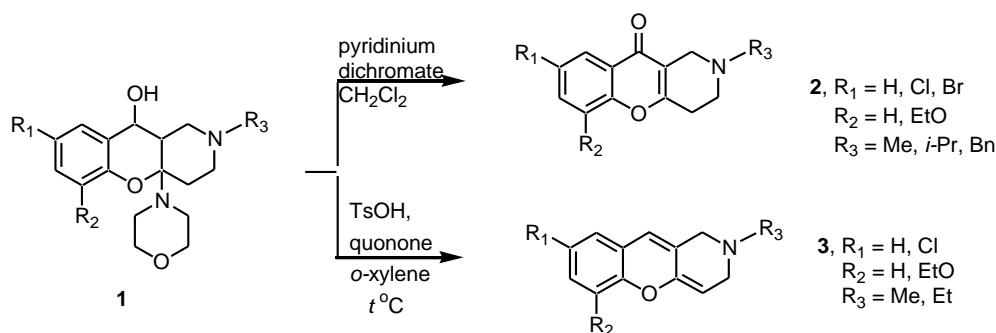
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## Synthesis of substituted 2,3-dihydro-1*H*-chromeno[3,2-*c*]pyridines

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Lately, we synthesized a series of chromeno[3,2-*c*]pyridines with different substituents in benzene ring and at nitrogen atom and investigated their reactions of with activated alkynes under different conditions [1]. It turned out that the parent chromenopyridines and their reaction products are promising inhibitors of acetylcholinesterase (AChE inhibitors) and monoamine oxidase (MAO inhibitors) [1,2]. We supposed that varying the substituent in chromenopyridine and replacing the central cycle from chromene to pyran would lead to compounds with improved biological characteristics. The starting chromenopyridines **1** were prepared according to a known two-step procedure starting from *N*-substituted pyrrolidones and aromatic aldehydes [3]. The target compounds **2** and **3** were obtained from chromenopyridines **1** through oxidation with pyridinium dichromate or acid-catalyzed oxidative dehydration in *o*-xylene under reflux.



The structures of all synthesized compounds were proved using NMR  $^1\text{H}$ ,  $^{13}\text{C}$  and IR spectroscopy and mass-spectrometry.

Mass and IR spectra were registered using instruments of of the Shared Research and Educational Center of Physic-Chemical Studies of New Materials, Substances and Catalytic of RUDN

The publication has been prepared with the support of the "RUDN University Program 5-100"

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## Synthesis of fluorescent dyes based on siloxane linear matrixes and DBMBF<sub>2</sub> derivatives

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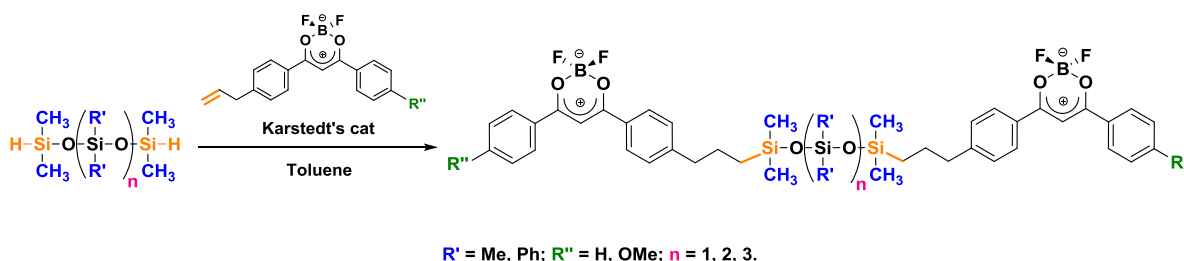
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Difluoroboron  $\beta$ -diketonate complexes (DBMBF<sub>2</sub>) are highly luminescent organoboron complexes with several valuable attributes such as strong fluorescence in both solution and solid state, large extinction coefficients and tunable fluorescent emission. These organic luminescent compounds can be used in such various fields as chemosensing, biolabeling, bioimaging and organic light emitting diodes (OLEDs) [1].

It is known that DBMBF<sub>2</sub> derivatives aggregate in solutions and form excimers in the excited state. Such excimers are of special interest for materials science, in particular for organic electronics, where they can be used as sensors and organic light-emitting diodes (OLED).

There are several methods to obtain excimers. One of them is the fixation of fluorophores in one molecule at a close distance with the possibility of intramolecular interfluorophore  $\pi$ - $\pi$  interaction. Linear and stereoregular cyclic siloxanes are convenient matrices for fixation of fluorophores, such structures allow several fluorophores to be located in one plane, promoting interfluorophore  $\pi$ - $\pi$  interaction and the formation of excimers in the excited state.

In this work we describe the synthesis of series multichromophore siloxane dyes of linear structure based on DBMBF<sub>2</sub> derivatives (Scheme 1).



**Scheme 1.** Synthesis of linear siloxane derivatives DBMBF<sub>2</sub>

The structure of obtained compounds were confirmed by the <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>29</sup>Si NMR spectroscopy, IR spectroscopy, mass spectrometry (ESI), and their photophysical properties were studied.

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

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## Convenient approach to polyoxygenated dibenzo[*c,e*]pyrrolo[1,2-*a*]azepines from donor–acceptor cyclopropanes

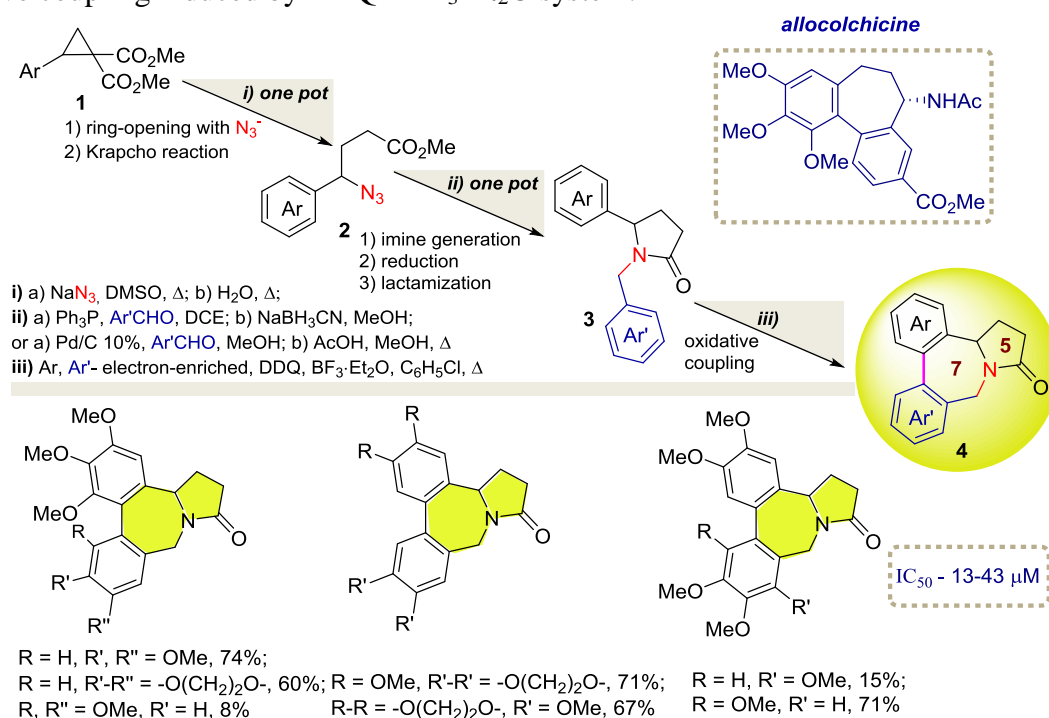
Boichenko M.A.,<sup>1</sup> Chagarovskiy A.O.,<sup>2,3</sup> Trushkov I.V.,<sup>2,3</sup> Ivanova O.A.<sup>1,3</sup>

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The development of rapid and efficient synthetic approaches to the bioactive polycyclic azaheterocycles is one of the most important challenges in organic synthesis. In this work we report an original method for the synthesis of polyoxygenated dibenzo[*c,e*]pyrrolo[1,2-*a*]azepines from donor–acceptor cyclopropanes. This approach includes three synthetic steps: 1) nucleophilic ring-opening of donor–acceptor cyclopropanes **1** with azide ion and *one-pot* Krapcho decarboxylation; 2) stepwise imine generation from azide **2** and aldehyde followed by reductive cyclization leading to pyrrolidone; 3) C(Ar)-C(Ar') bond formation by means of oxidative coupling induced by DDQ – BF<sub>3</sub>·Et<sub>2</sub>O system.



The particular focus was on the synthesis of structural analogs of colchicine which is used for treating gout, pericarditis and some other diseases due to its ability to inhibit polymerization/ depolymerization of tubulin and was considered as a lead compound in the search of anti-cancer agents. The synthesized compounds demonstrated moderate cytotoxicity towards HEK-293, MCF-7, A549, PC3, VA13 cell lines with IC<sub>50</sub> up to 13 μM [1].

This work was supported by the Russian Science Foundation  
(grant № 17-73-10404)

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## Manganese catalyzed multicomponent synthesis of pyrroles *via* acceptorless dehydrogenation hydrogen autotransfer catalysis- experiment and computation

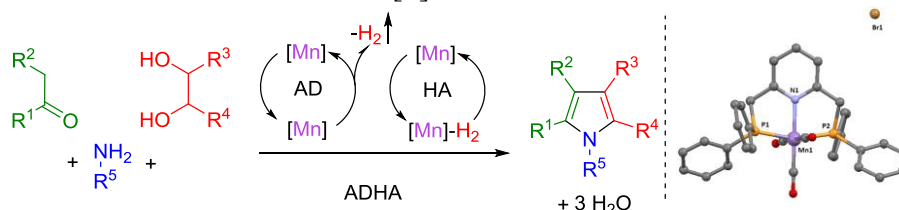
Borghs J.C.,<sup>a</sup> Azofra L.M.,<sup>b</sup> Biberger T.,<sup>a</sup> Linnenberg O.,<sup>c</sup> Cavallo L.,<sup>b</sup> Rueping M.,<sup>a,b</sup> El-Sepelgy O.<sup>a</sup>

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Classical routes for the synthesis of heterocycles suffer from major drawbacks due to generation of substantial amounts of toxic waste produced during the multi-step pre-functionalization of the starting materials [1]. Hence, it is highly desirable to find alternative environmentally friendly routes to heterocycles from renewable resources, such as lignocellulosic materials which are indigestible, but can be converted to various alcohols. Thus, finding new routes for generating valuable compounds from alcohols will contribute not only to reduced toxic chemical waste but also to decrease CO<sub>2</sub> emissions by avoiding the use carbon fossil sources [2].

Next to conserving fossil resources it is highly desirable to avoid the use of noble metals by finding suitable catalysts made from earth abundant metals. Recently, substantial work was dedicated to the metal catalyzed activation of alcohols, opening a more benign alkylating route by formation of reactive carbonyl intermediates simultaneously generating metal hydrides (“hydrogen borrowing”, BH or “hydrogen autotransfer”, HA) [3a] or releasing H<sub>2</sub> (“acceptorless dehydrogenation”, AD) [3b]. These carbonyl intermediates can undergo coupling reactions *via* condensation cascades to give more complex target molecules. Interestingly, to date no catalytic system based on a metal-ligand complex has been reported which combines both concepts, the AD and HA for the synthesis of heterocycles. Thus, a unified ADHA base metal catalyzed process could potentially be a valuable addition to the field of sustainable catalysis and reaction development in general.

Here, we report a manganese catalyzed sustainable multicomponent synthesis of pyrroles from abundant 1,2-diols leaving water and hydrogen gas as the sole by-products of this transformation. Detailed experimental and computational mechanistic studies support the merging of both AD- and HA-mechanisms [4].



*J.C.B. is thankful for financial support of the German Federal Environmental Foundation (DBU). This work was supported by the supercomputer Shaheen II (KAUST) by providing the computational resources*

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## New semiconductors for organic electronic

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Organic electronics is a fast developing field of science and technic. Usage of organic materials enables the opportunity of low cost, light, flexible and transparent innovative optoelectronic device creation. Organic field-effect transistors (OFETs) are one of the basic device in the field of organic electronics, which working principle is based on the opportunity of utilizing  $\pi$ -conjugated oligomers and polymers as semiconductor molecules. Nowadays development of efficient self-assembled monolayer field-effect transistors (SAMFETs) is a great challenge of organic electronics [1-2]. Recently we reported organosilicon derivatives of oligothiophenes allowing monolayer formation at the water-air interface, which were used for fast and efficient SAMFETs fabrication by Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques [3-6]. In this work we synthesized several novel derivatives of dialkyl substituted [1]benzothieno[3,2-b][1]benzothiophene (BTBT) containing flexible aliphatic spacers of various length linked to disiloxane anchor groups via bromine protection-deprotection of the terminal alkenyl double bonds in combination with Friedel-Crafts acylation, Wolff-Kishner reduction and hydrosilylation reactions [7]. Also we designed and synthesized several novel derivatives of [3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (TTA). New materials were successfully used in monolayer OFETs with the charge carrier mobilities up to 0.02 cm<sup>2</sup>/Vs, threshold voltage close to 0 V and On/Off ratio up to 10,000. Influence of the chemical structure of the molecules synthesized on the morphology, molecular 2D ordering in the monolayers and their semiconducting properties is considered [8]. We report on a new design of highly sensitive gas sensors based on Langmuir-Blodgett, Langmuir-Schaefer and spin-coating monolayer organic field-effect transistors (OFETs) [9,10]. The devices fabricated are able to operate in air and allow an ultrafast detection of different analytes at low concentrations down to tens of parts per billion. The results reported open new perspectives for the OFET-based gas-sensing technology and pave the way for easy detection of the many types of gases, enabling the development of complex air analysis systems based on a single sensor.

*This work was supported by Russian Science Foundation (grant 18-73-10182) and performed in the framework of leading science school NSh-5698.2018.3*

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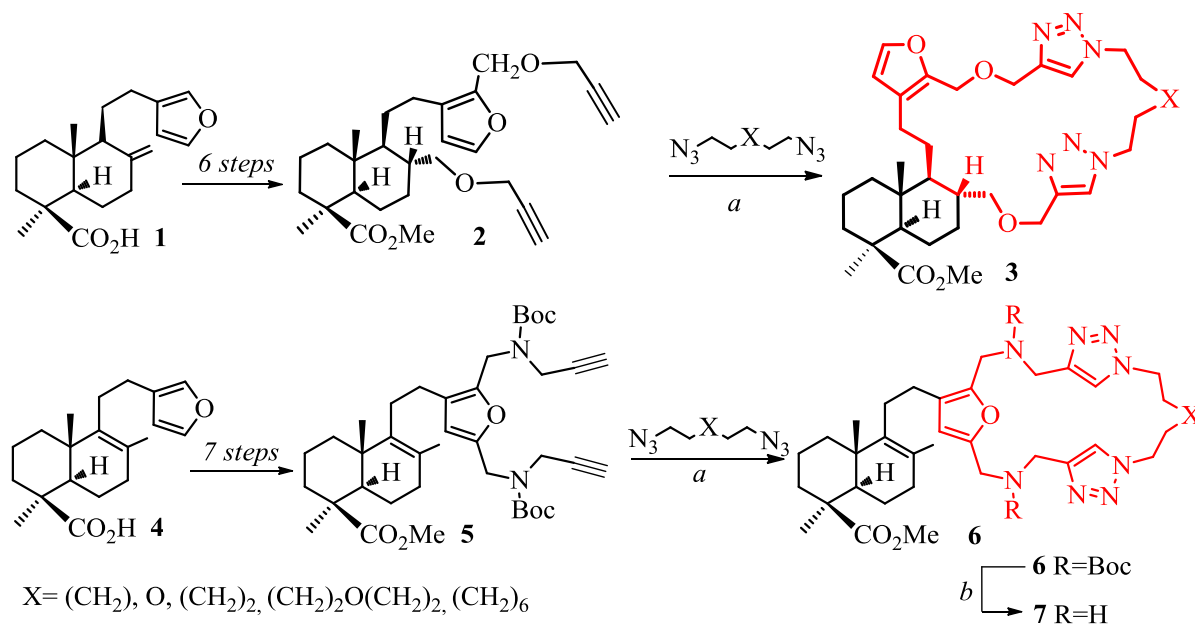
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## Synthesis and spectroscopic studies of chiral *bis*-triazolium macrocycles with a furan bridge possessing structural fragment natural diterpenoids

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The 1,2,3-triazoles are substances of considerable interest as biologically active compounds and effective complexants capable of forming complexes with various substrates. In this work, we describe the synthesis of 1,2,3-triazolyl containing macrocyclic molecules based on lambertianic **1** and phlomysoic **4** acids - natural diterpenoids of labdane type. The obtained macrocyclic structures we were used the copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction of terpenoid dialkyne **2** and **5** with diazides. Metal ion complexing properties of the macrocycles **3** and **7** were investigated by <sup>1</sup>H NMR and UV titration experiments. The macrocyclic furanolabdanoid derivatives **3** linked by 1,2,3-triazole rings in the 16,17-positions of furanolabdanoid showed high selectivity and affinity for Hg<sup>2+</sup> ion by 1,2,3-triazole and furan rings. The macroheterocyclic compounds **7** linked by 1,2,3-triazole rings in the 15,16-positions are binding of Zn<sup>2+</sup> ion by furan and the 1,2,3-triazole rings or nitrogen atoms with 2:1 and 1:1 stoichiometries in DMSO.



Conditions and reagents: a. CuSO<sub>4</sub>, AcsNa, CH<sub>2</sub>Cl<sub>2</sub>-H<sub>2</sub>O, 40°C; b: CF<sub>3</sub>CO<sub>2</sub>H, CH<sub>2</sub>Cl<sub>2</sub>, rt.

*This work was supported in part by the Russian Science Foundation and the Government of the Novosibirsk Region (research project № 17-43-543235)*

## Nonstabilized azomethine ylides in the synthesis of aryl cucurbitine derivatives

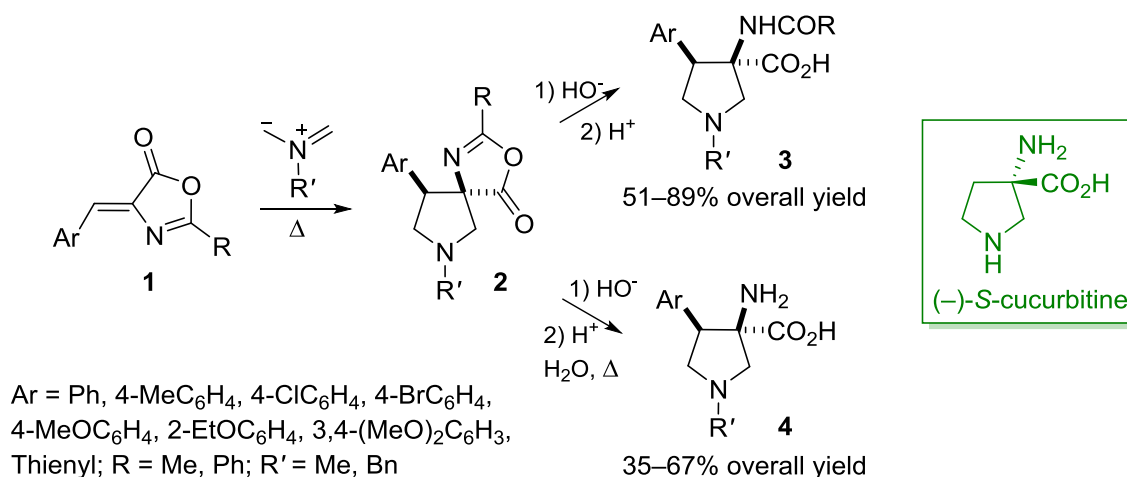
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The pyrrolidine core is an important structural moiety which is present in a wide range of natural products and synthetic biologically active compounds. One of the most straightforward approaches to the synthesis of pyrrolidines is the [3+2]-cycloaddition of azomethine ylides with electron-deficient alkenes.

During the course of our studies in this field, we became interested in the synthesis of various derivatives of natural (*S*)-3-aminopyrrolidine-3-carboxylic acid, cucurbitine, which was first isolated from *Cucurbita moschata* and has valuable anthelmintic activity. A simple and direct approach for the synthesis of aryl cucurbitine derivatives could involve the reaction of an azomethine ylide with the Erlenmeyers arylidene azlactones **1**, which could be readily obtained as a single *Z*-isomer.



It was found that arylidene azlactones **1** smoothly react with nonstabilized azomethine ylides generated *in situ* to give spiro[pyrrolidine–azlactones] **2** in almost quantitative yields. The latter were utilised in the one-pot synthesis of amidopyrrolidines **3** in 51–89% overall yield by hydrolysis in 0.4M NaOH at 40 °C and subsequent neutralization with an equimolar amount of HCl. Moreover, aryl cucurbitines **4** were obtained in 35–67% overall yield as hydrochlorides by similar one-pot approach, consisted of the cycloaddition step and subsequent complete hydrolysis of azlactone ring.

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(Grant 17-73-20070)*

## Synthesis of 7-aminoderivatives of quinoxaline-2-carbonitrile 1,4-dioxide

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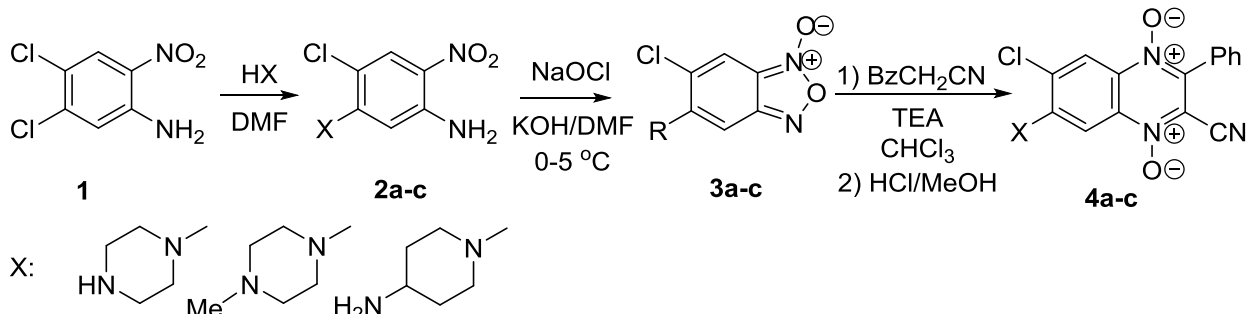
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Quinoxaline 1,4-dioxide derivatives are known as effective hypoxia-selective agents [1]. Previously described quinoxaline-2-carbonitrile 1,4-dioxide derivatives are water insoluble that complicated their biological evaluation. To overcome this disadvantage, a series of amino derivatives of 3-phenyl-quinoxaline-2-carbonitrile 1,4-dioxides have been obtained and evaluated.

To synthesize the quinoxaline-2-carbonitrile 1,4-dioxides with amino groups at the position 7, a three steps transformation of nitroaniline **1** including nucleophilic substitution of chlorine atom with mono-Boc protected cyclic diamines, oxidation of the resulting derivatives **2a-c** by treatment with NaOCl in the presence of the base and subsequent condensation of benzofuroxanes **3a-c** with benzoylacetonitrile was developed [2]. Methanesulphonic acid and solution of HCl in methanol were used for deprotection of the resulting Boc-intermediates yielded methanesulphonates and hydrochlorides of 3-phenylquinoxaline-2-carbonitrile 1,4-dioxides **4a-c** that showed good solubility in aqueous medium.

All final compounds **4a-c** were characterized by NMR spectra (<sup>1</sup>H, <sup>13</sup>C), UV, HRMS ESI and HPLC analysis. The antiproliferative activity of **4a-c** was evaluated in normoxia (21%O<sub>2</sub>) and hypoxia (1%O<sub>2</sub>) by MTT test (72 h growth with compounds).



All 7-amino-6-chloroquinoxaline 1,4-dioxides demonstrated high antiproliferative potency and hypoxia selectivity against tested breast adenocarcinoma cell lines (MCF-7, MDA-MB-231). Importantly, the MCF-7 cell line was more susceptible to these agents under hypoxia (IC<sub>50</sub> = 0.2-2.3 μM) and normoxia (IC<sub>50</sub> = 0.6-7.9 μM), than triple negative breast cancer cells (MDA-MB-231). Obtained derivatives were 10-20-fold more potent than the reference drug Tirapazamine. Thus, these results suggest that quinoxaline 1,4-dioxides seem to be promising bioreductive agents for selective death of hypoxic cells and can be useful for improving cancer treatment efficacy.

*The experiments were supported by RFBR grants 18-53-34005 (chemistry) and 18-015-00422 (biology)*

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## Quantum-chemical study of the complexes of the functional derivatives of the amphotericin B with ergosterol and cholesterol

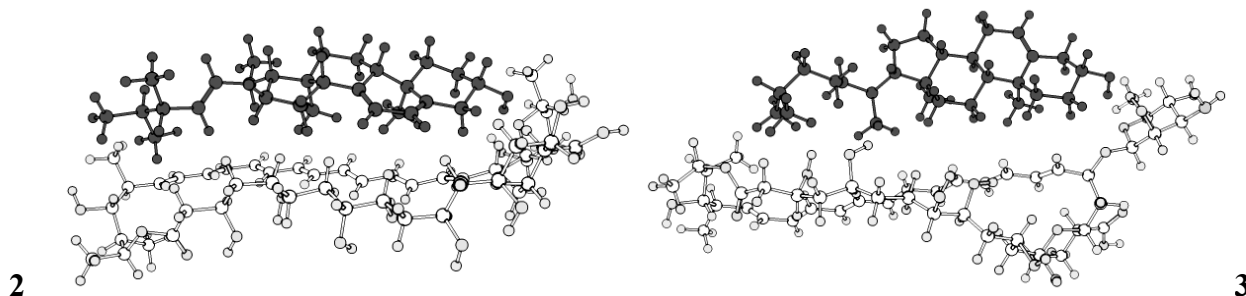
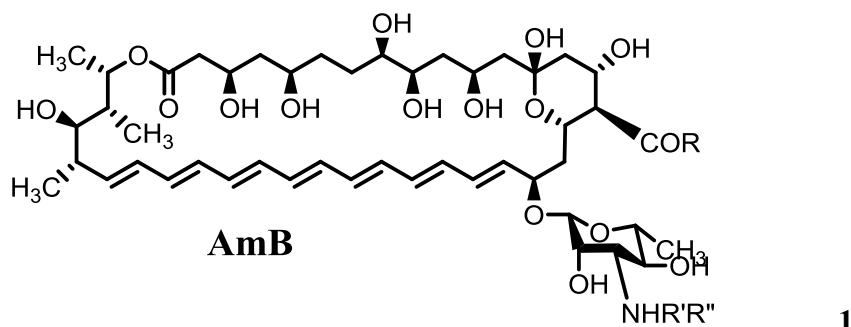
Bykov E.E.<sup>1</sup>, Olsufyeva E.N.<sup>1</sup>, Tevyashova A.N.<sup>1,2</sup>

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The PM6 quantum chemical semi-empirical method calculated [1] the structures of possible complexes resulting from the interaction of the functional derivatives [2] of the antibiotic amphotericin B (1) [3] with ergosterol (2), which is part of the cell membranes of pathogenic fungi, and with cholesterol (3), which is part of the human cell membranes.



A correlation of the geometric and energy parameters of the calculated structures of the complexes with the experimentally determined data of antifungal effect and pore formation in the membranes composed of DPhPC:Chol or DPhPC:Erg [4] was found. Our results confirm a possible working hypothesis about the "sterol-binding" mechanism [5] of action of the antibiotic derivatives amphotericin B.

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## Ring opening reactions of donor–acceptor cyclopropanes with hydrazines: synthesis of *aza*-heterocycles

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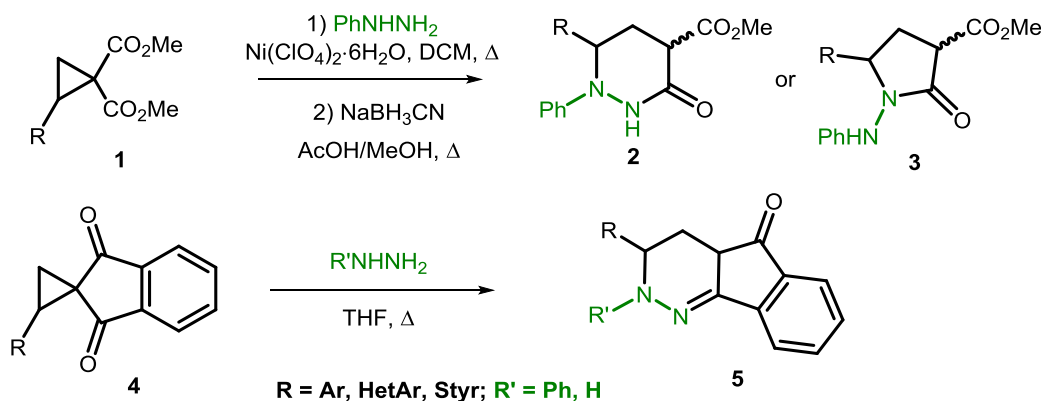
<sup>2</sup> Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow, 119991, Russia

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The construction of *aza*-heterocycles is one of the most challenging and solicited tasks for contemporary organic synthesis. In this perspective, the utilization of donor-acceptor cyclopropanes (DAC) as powerful building blocks in synthesis has received significant attention in the past decade<sup>1</sup>. Interactions of DAC with different *N*-containing nucleophiles (amines, amides, nitromethane, azide ion) provide simple and straightforward routes to a variety of heterocyclic scaffolds.

The present study is devoted to investigation of reactivity of DAC towards hydrazine derivatives. We discovered that 2-arylsubstituted DAC in reactions with phenylhydrazine in the presence of Lewis acids yield derivatives of hexahydropyridazin-3-one **2** or 5-alkenyl-1-(phenylamino)pyrrolidin-2-one **3**, depending on the nature of substituents in the parent cyclopropane<sup>2</sup>.

On the other hand cyclopropanes **4** obtained from indandione in reaction with hydrazines do not call for the presence of Lewis acids and were found to afford tetrahydro-5H-indeno[1,2-*c*]pyridazin-5-ones **5** under thermal activation.



*This work was supported by the Russian Science Foundation  
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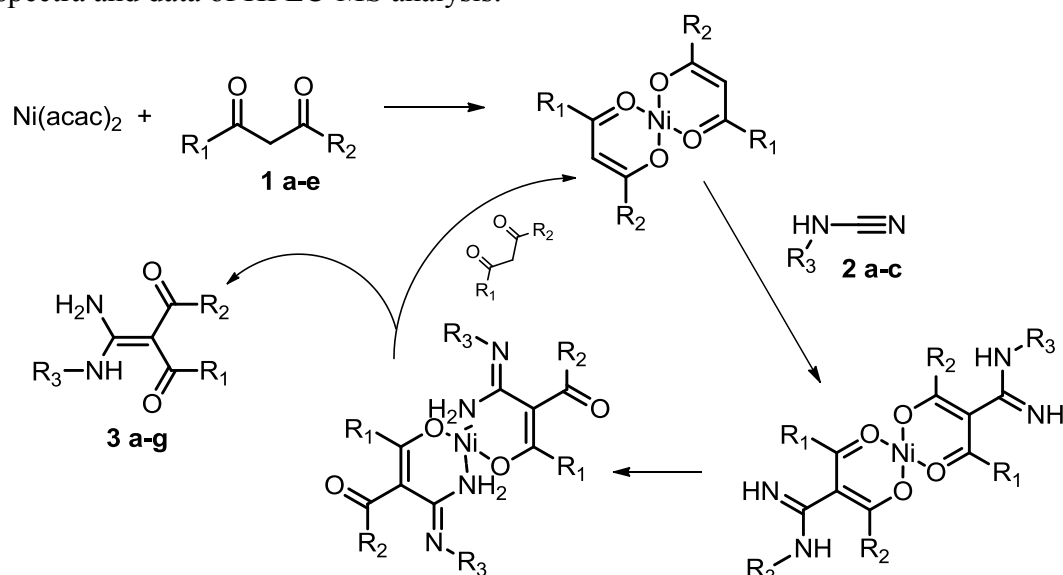
## The addition of 1,3-diketones to monosubstituted cyanamides catalysed by nickel acetylacetonate

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It is known that the coupling of  $\beta$ -dicarbonyls with nitriles in the presence of transition metal complexes leads to the formation of a carbon-carbon bond [1]. We endeavored to synthesize new diacylketenes and etoxyacetylketenes N,N-acetals by the reaction of 1,3-diketones **1a,c-e** and ethylacetoacetate **1b** with monosubstituted cyanamides **2a-c**.

The addition of  $\beta$ -dicarbonyl compounds to phenylcyanamide and benzoylcyanamide proceeded smoothly in boiling THF or toluene in the presence of 5 mole % Ni(acac)<sub>2</sub> (reaction of acetylacetone with 4,6-dimethylpyrimidin-2-yl cyanamide was carried out using an excess of acetylacetone). The yield of diacylketenes **3a,c,e-g** and etoxyacetylketenes N,N-acetals **3b,d** was 30-70%. The structures of all synthesized compounds were confirmed by means of IR and <sup>1</sup>H NMR spectra and data of HPLC-MS analysis.



**1:** R<sub>1</sub>=R<sub>2</sub>=Me (**a**); R<sub>1</sub>=Me, R<sub>2</sub>=OEt (**b**); R<sub>1</sub>=Me, R<sub>2</sub>=4-MeOPh (**c**); R<sub>1</sub>=Me, R<sub>2</sub>=tienyl (**d**); R<sub>1</sub>=R<sub>2</sub>=4-tolyl (**e**);

**2:** R<sub>3</sub>=Ph (**a**); R<sub>3</sub>=Bz (**b**); R<sub>3</sub>=4,6-dimethylpyrimidin-2-yl (**c**);

**3:** R<sub>1</sub>=R<sub>2</sub>= Me, R<sub>3</sub>=4,6-dimethylpyrimidin-2-yl (**a**); R<sub>1</sub>=Me, R<sub>2</sub>=OEt, R<sub>3</sub>=Ph (**b**); R<sub>1</sub>=R<sub>2</sub>=4-tolyl, R<sub>3</sub>=Ph (**c**); R<sub>1</sub>=Me, R<sub>2</sub>=OEt, R<sub>3</sub>=Bz (**d**); R<sub>1</sub>=R<sub>2</sub>=4-Tol, R<sub>3</sub>=Bz (**e**); R<sub>1</sub>=Me, R<sub>2</sub>=4-MeOPh, R<sub>3</sub>=Bz (**f**); R<sub>1</sub>=Me, R<sub>2</sub>=tienyl, R<sub>3</sub>= Bz (**g**).

The mechanism of catalysis is, apparently, in the displacement of the ligand in nickel acetylacetonate by  $\beta$ -dicarbonyl compound and activation of its bridging carbon atom in the resulting complex compound. Further restructuring of the complex leads to the formation of a coordination bond between the nickel atom and the nitrogen atom of the C $\equiv$ N group. This leads to the formation of a stable carbon-carbon bond.

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## The use of 1-cyanoacetyl-3,5-dimethylpyrazole in heterocyclic synthesis

Chigorina E.A.<sup>1</sup>, Dotsenko V.V.<sup>2</sup>

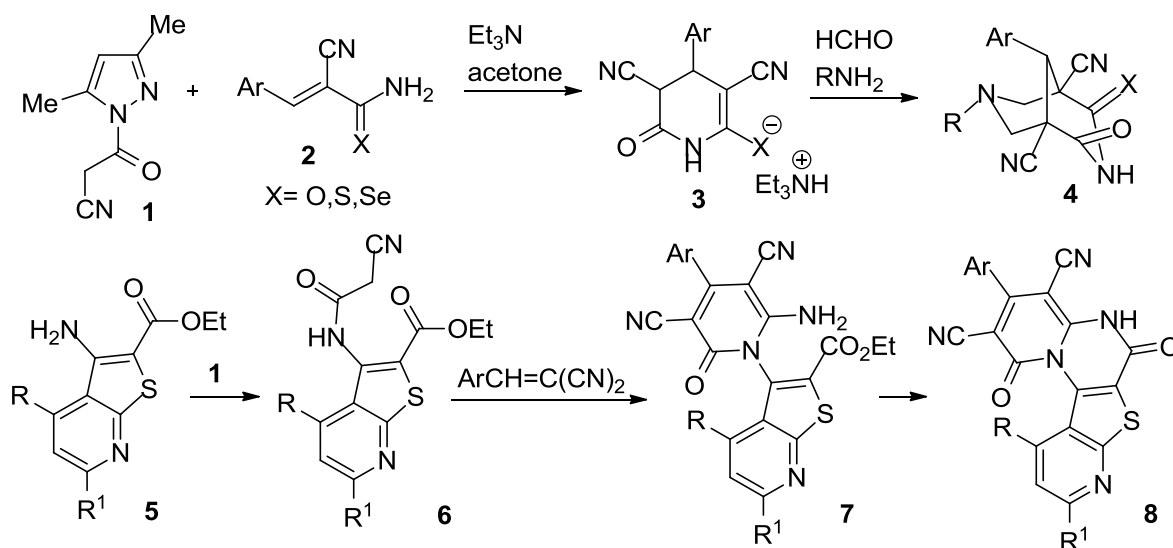
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1-Cyanoacetyl-3,5-dimethylpyrazole **1** has had a long history since it was first described in 1957 [1]. Cyanoacetylpyrazole **1** was shown to be a mild and effective cyanoacetylating agent, primarily in respect to various N-nucleophiles: amines, hydrazine derivatives, hydrazides, semicarbazides [2].

We successfully used cyanoacetylpyrazole **1** in the synthesis of O,S,Se-containing analogs of Guareschi imides – tetrahydropyridines **3** [3-5]. Thus, the reaction of pyrazolide **1** with (thio-, seleno-)amides **2** in the presence of a base leads to tetrahydropyridines **3** in the form of a mixture of *cis* and *trans* diastereomers. Upon treatment with primary amines and an excess of HCHO under Mannich conditions, tetrahydropyridines **3** undergo double aminomethylation to afford 3,7-diazabicyclo[3.3.1]nonanes **4**.

3-Aminothiено[2,3-*b*]pyridines **5** react 1-cyanoacetyl-3,5-dimethylpyrazole **1** to give cyanoacetylation products **6**. The latter under action of arylmethylene malononitriles formed either pyridines **7** or polycyclic structures **8**, depending on the reaction conditions.



This study was financially supported by the Ministry of Education and Science of the Russian Federation (project 4.5547.2017/8.9)

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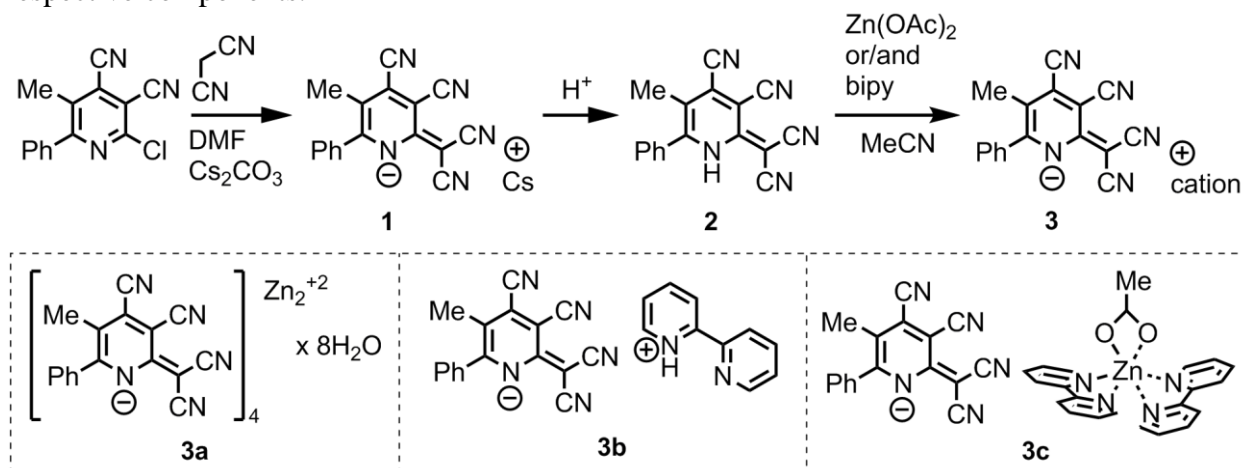
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## Novel cyanopyridine-based metal–organic frameworks

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Earlier, we presented a method for synthesizing new chromophores based on 4-cyano substituted by TriCyanoPyridine (4-CN-TCPy) **2** [1], which have fluorescence in the powder in the near-IR region. It was observed that the synthesis of 4-CN-TCPy proceeds through the stage of formation of cesium salt **1**. This fact was the impetus for the study of new 4-CN TCPy-based metal – organic frameworks (MOF). MOF **3a-3c** was prepared in acetonitrile by mixing the respective components.



The structure of compounds **3a** and **3c** has been proven using X-ray crystallography. It was found that the elementary unit of crystal packing of compound **3a** is a complex consisting of two 6 coordination atoms of zinc, surrounded by four 4-CN-TCPy molecules and eight water molecules, six of which act as ligands and another 2 in the outer coordination sphere. The NMR spectrum of compound **3b** showed that the ratio of 4-CN-TCPy anion and bipyridine cation in this salt is 1:1. However, experimental studies show that salt formation is possible on the basis of these ions, but already in a 2:1 ratio of components. The 4-CN-TCPy molecules in the crystal package of compound **3c** form an anionic wall and are held together by face-to-face  $\pi$ -stacking. The cation wall is formed by complexes consisting of zinc, with a coordination number of six, as a coordination centre, two molecules of bipyridine and acetate, acting as ligands.

The study of the fluorescent properties of these compounds in the form of powders showed the presence of a bathochromic shift of the maxima of the solid-phase fluorescence of the complexes in order **3a** > **3b** > **3c**, which are at 538, 600 and 622 nm, respectively.

*The work was supported by a grant from the Russian Science Foundation  
(Project № 17-13-01237)*

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## The synthesis of pyrimidines and condensed systems based on 2-acetylcyclopentanone

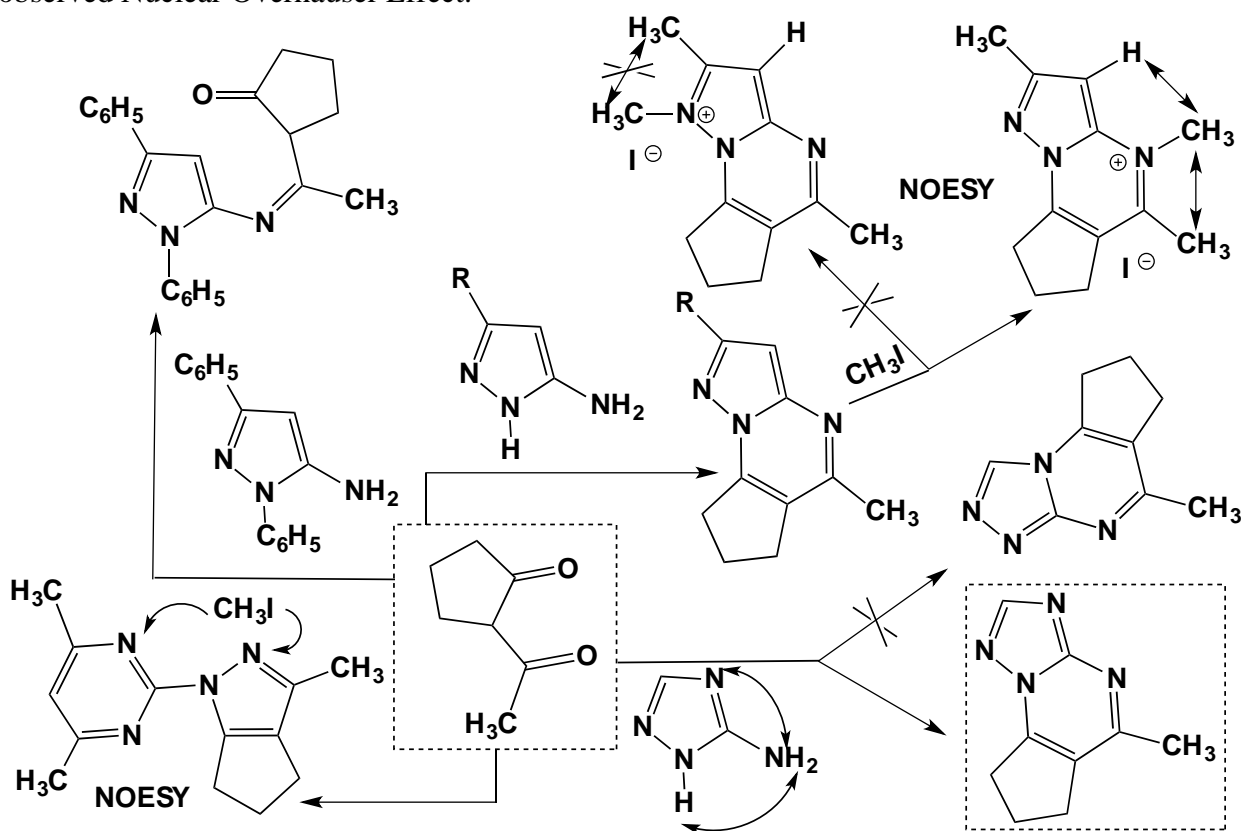
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The synthesis of various heterocycles based on 2-acetylcyclopentanone, in particular, new derivatives of pyrazole, pyrimidine and condensed systems of pyrazolo[1,5-a]pyrimidine and 1,2,4-triazolo[1,5-a]pyrimidine has been studied. The structure of the synthesized compounds in some cases was proved by the NOESY NMR spectroscopy technique, due to the observed Nuclear Overhauser Effect.



The research was carried by the funds allocated under the subsidy of the Ministry of Education and Science of the Russian Federation to finance research activities at Russian-Armenian University

## Cu(II) catalyzed N-vinylation of nitroazoles and 5-aryltetrazoles by *t*-styrylboronic acid

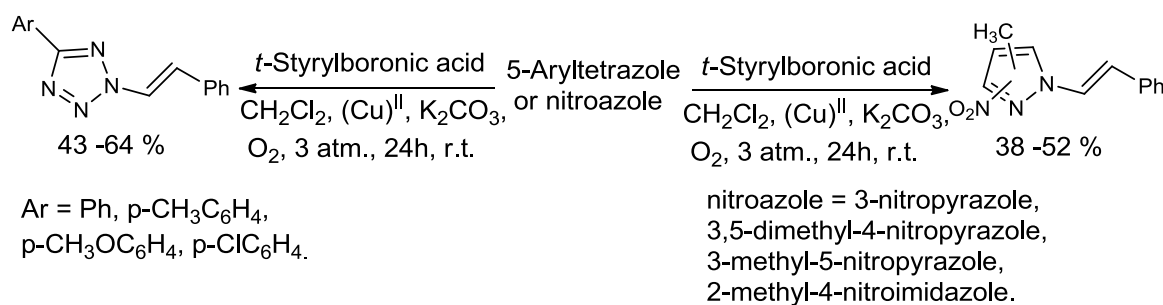
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N-Modified nitroazoles [1] and tetrazoles [2] are famous classes of pharmacologically active molecules broadly used in medicine. So for example N-vinylnitroimidazoles possess antiparasitic activity [3] and are precursors for the synthesis of nucleoside analogues [4], while N-vinyltetrazoles are used as monomers for preparation of polymers with various medical and industrial properties [5,6]. According to chemical literature interesting N-styrylazoles were synthesized only by multistep classical processes. In our opinion, the optimal method of N-styrylazoles synthesis is direct selective styrylation of these azoles by appropriate reagents.

Earlier, we have proposed methods for the selective N-arylation of some tetrazoles [7] and nitroazoles [8]. by diaryliodonium salts in the presence of copper salts. However we were failed to synthesize target N-styrylnitroazoles by this method. We could not obtain desirable products using Pd-catalyst also [9]. The synthetic success was reached only with *t*-styrylboronic acid as reagent in the presence of Cu(II) salts according to Chen-Evans-Ley protocol [10]. For all substrates the main product was N-styryl-isomer with the participation of the less sterically hindered nitrogen atom eliminating 3-methyl-5-nitropyrazole, where the ratio of isomers was 2:1 in favor of 1-*t*-styryl-3-methyl-5-nitro-pyrazole. The best regioselectivity of process was obtained using  $[\text{Cu}_2(\text{TMEA})_2(\text{OH})_2]\text{Cl}_2$  as catalyst:



The structures of products obtained were correctly established by spectroscopic methods (NMR <sup>1</sup>H, NMR <sup>13</sup>C, NOE-experiments and HRMS).

### References

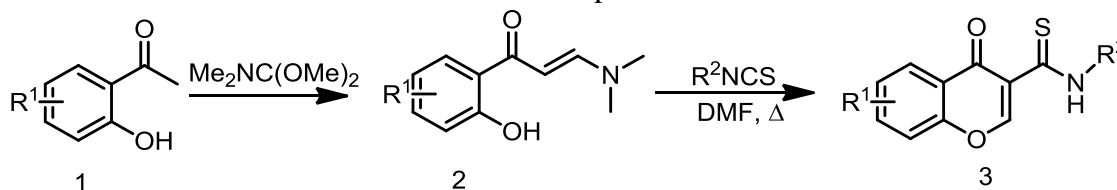
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## Synthesis of 2-amino-chromone-3-carbaldehyde hydrazones from 3-thiocarbamoyl chromones and hydrazines

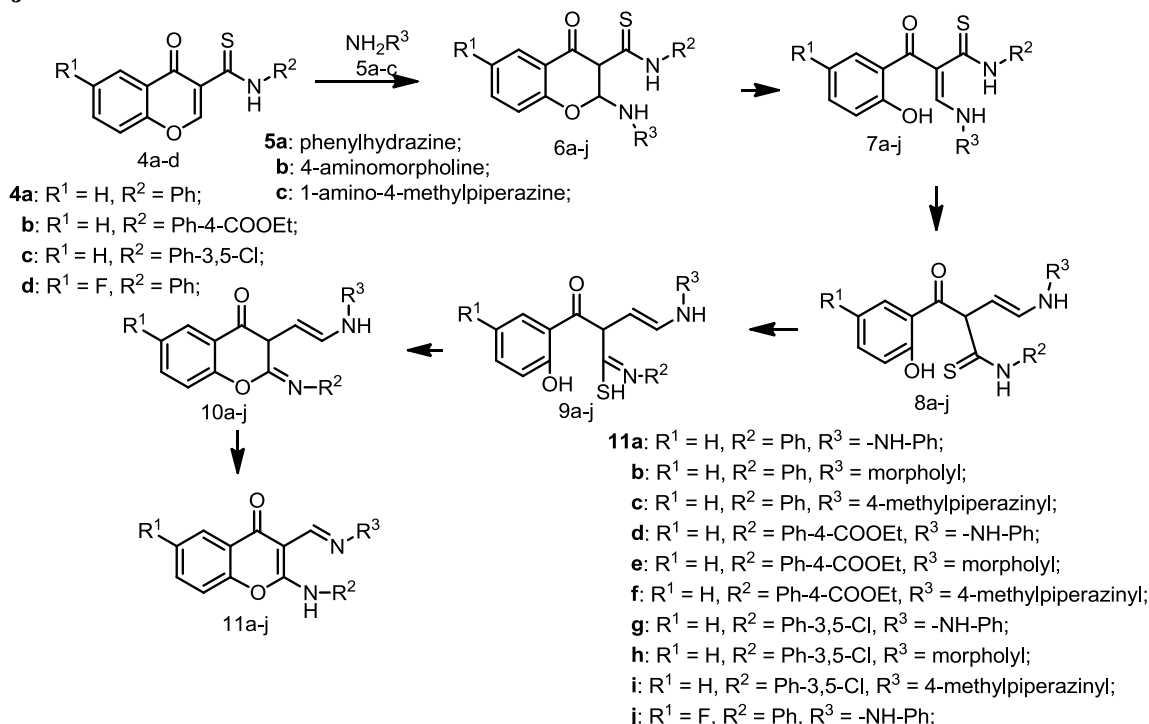
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A promising direction in the creation of new chromone derivatives is the use of substrates containing in position 3 electron-withdrawing substituents, which increase the propensity for ring transformation reactions under the influence of nucleophiles. Previously, we developed a new method for obtaining practically unexplored 3-thiocarbamoylchromones **3**, which consists in the interaction of *o*-hydroxyarylenaminones **1** with isothiocyanates **2**, which allowed the study of their transformations under the influence of nucleophiles.<sup>1</sup>



We have shown that the interaction of 3-thiocarbamoylchromones **4a-c** with hydrazines **5a-c** in alcohol is accompanied by sequential processes leading to the formation of hydrazones **11a-j**.



The structure of the compound was confirmed using two-dimensional homo- and heteronuclear correlation techniques  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HSQC и  $^1\text{H}$ - $^{13}\text{C}$  HMBC.

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## Adamantyl-substituted PEPPSI-type palladium(II) N-heterocyclic carbene complexes: synthesis and catalytic application for C-H activation of substituted thiophenes and imidazoles

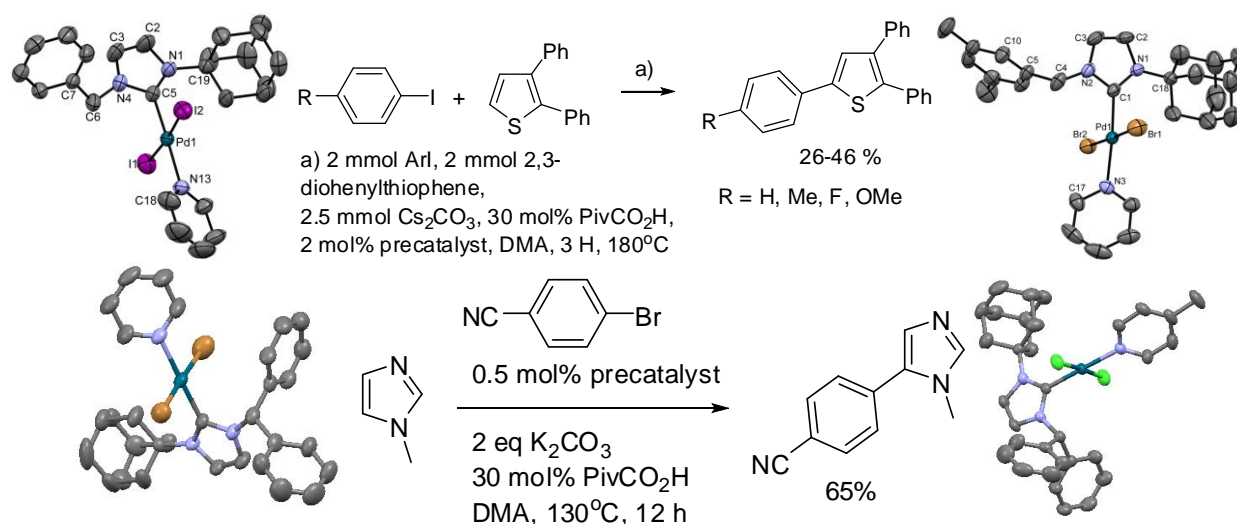
Denisov M.<sup>1</sup>, Dmitriev M.V.<sup>2</sup>, Gorbunov A.<sup>1</sup>, Glushkov V.<sup>1,2</sup>

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The first isolable stable NHC (N-heterocyclic carbene) related to 1,3-bis-adamantyl substituted imidazole salt. Surprisingly, we find that 1-adamantyl-3-arylmethyl-substituted imidazole salts, corresponding carbenes and PEPPSI-type complexes were not known before our investigations. So, here we present PEPPSI (Pyridine Enhanced Precatalysts: Preparation, Stabilisation and Initiation) complexes from adamantyl-imidazole salts [1-5]. Their structure was proved by X-ray single crystal analysis, conductivity test, IR, NMR <sup>1</sup>H and <sup>13</sup>C spectra. PEPPSI complexes were tested as precatalyst for thiophene and imidazole arylation by C-H activation.

The scheme of C-H activation/arylation is presented below:



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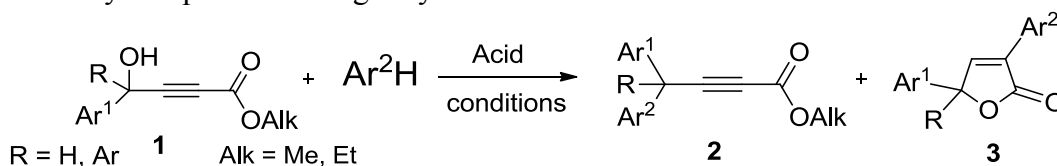
## Reactions of alkyl esters of propargyl type acetylene carboxylic acids

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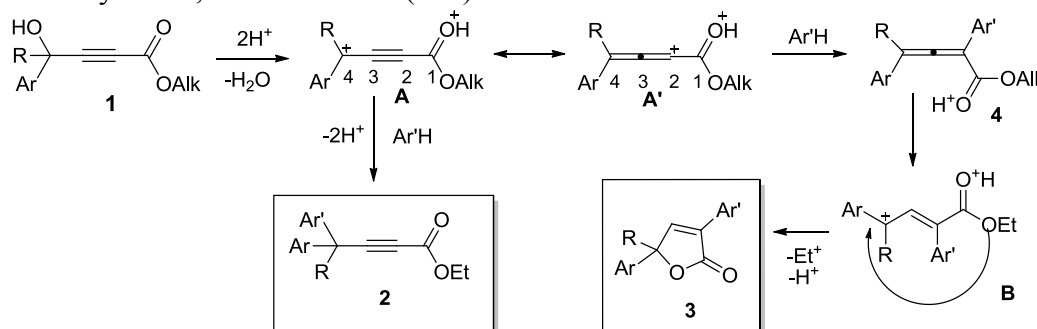
Electrophilic reactions have a long history. In particular, reactions of aromatic electrophilic substitution are widespread. They play an important role in organic synthesis not only in the laboratory, but also in industry.

We studied reactions of compounds of **1** with various arenes under acidic conditions. Depending on the structure of **1**, reaction temperature and acid, products **2** and **3** are formed in different yields. Substrates **1** (R = H, Alk = Me) give compounds **2** and **3** in TfOH at room temperature in low yields. Substances **1** (R = H, Alk = Et) can react with zeolites CBV-720 at high temperature (120 °C), producing the target compounds **2** and **3**. Diarylated substances **1** form selectively compound **2** in higher yields with TfOH.



In the first stage of this reaction, the hydroxyl group in compound **1** is protonated, followed by dehydration, that gives the cation **A**. The latter has two electrophilic centers, it can be represented as mesomeric forms **A** and **A'**. Further, compound **2** is formed, as a result of interaction of species  $\text{A} \leftrightarrow \text{A}'$  with arene  $\text{Ar}'\text{H}$  at the propargyl position **C4**. In the case of reaction with the arene at the electrophilic center **C2**, cation **A** gives allene **4**. The latter is protonated forming cation **B**, which is cyclized to furanone **3**.

Intermediates of this reaction were studied by DFT calculation. In the course of the reactions, intermediate compounds, allens **4**, and target products **2** and **3** were isolated and characterized by NMR, IR and HRMS (ESI).



Furanones are biologically active compounds. Up to the moment, it is known that they have moderate activity against filamentous fungi. Also they are metabolites from *Streptomyces griseus* and angelicalactone, a flavoring agent [1].

*This work was supported by the Russian Science Foundation  
(grant № 18-13-00008)*

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## Synthesis of *m*-substituted anilines by three-component reaction

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There is a class of drugs containing *m*-trifluoromethyl- or *m*-carbamoylaniline moiety (Fig.1).

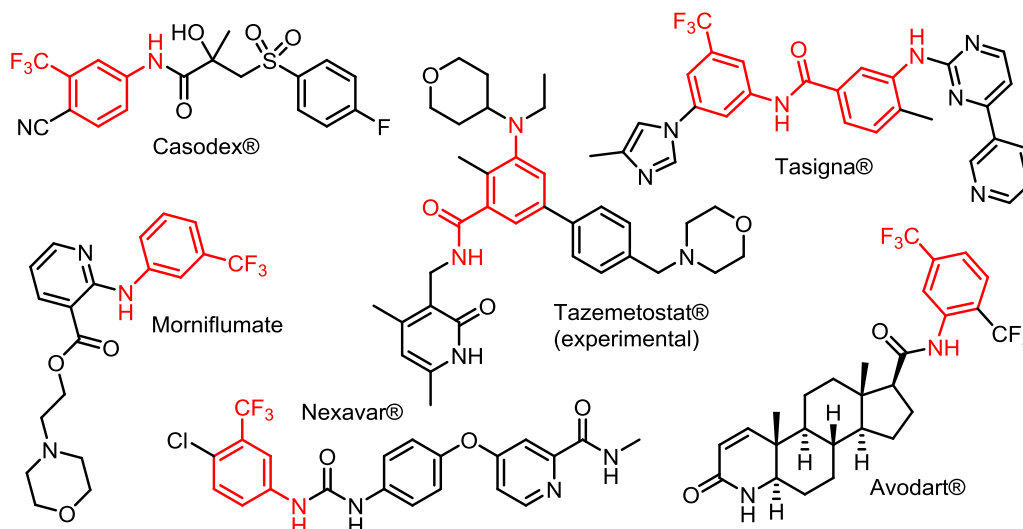


Fig.1

Modification of the aromatic cycle catalyzed by transition metals are usually used for the synthesis of substituted anilines [1, 2]. The construction of aniline core is an alternative approach. There are a few examples with significant disadvantages.

Herein, we report novel methodology for the synthesis of anilines, based on the sequence of condensation-aromatization with the construction of an aromatic core (Fig.2).

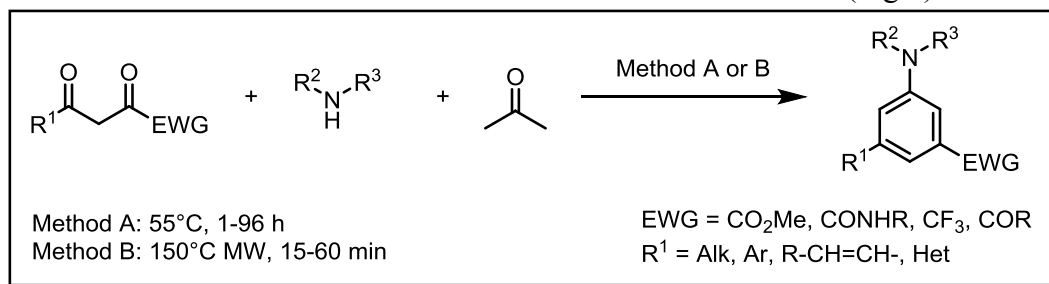


Fig.2

The multicomponent reaction of diketones bearing an EWG, primary or secondary aliphatic or aromatic amines and acetone, which also acts as a solvent, leads to the formation of *m*-substituted anilines with good yields.

*This study was performed under the financial support of the Russian Foundation for Basic Research (grant № 18-33-01084)*

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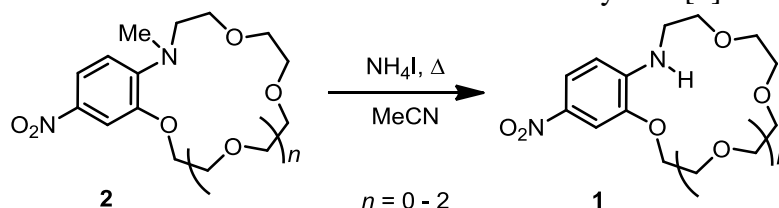
## Nitro-derivatives of benzoazacrown ethers: synthesis, structure, and complexation with metal and ammonium cations and fluoride anion

Dmitrieva S.N., Kurchavov N.A., Kuz'mina L.G., Vedernikov A.I., Churakova M.V., Sazonov S.K., Howard J.A.K., Gromov S.P.

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Previously, we developed a new strategy for the synthesis of formyl and nitro *N*-alkylbenzoazacrown ether derivatives with different macrocycle size and macrocycle nitrogen atom being linked to the benzene ring. It is based on the stepwise transformation of the macrocycle of accessible benzocrown ethers used as synthons [1, 2]. We also synthesized dinitrodibenzodiazacrown ethers by one-step transformation of the *cis*-dinitrodibenzo-18-crown-6 ether macrocycle on treatment with aliphatic diamines [2]. And we prepared formyl derivatives of benzoazacrown ethers with N–H group in the macrocycle using two methods [3]. Nitrobenzoazacrown ethers **1** containing NH group in the macrocycle have been unknown until now.

We elaborated a method for the synthesis of nitrobenzoazacrown ethers **1** by *N*-demethylation of *N*-methyl-nitrobenzoazacrown ethers **2** on treatment with ammonium iodide, resulting in the formation of benzoazacrown ethers in 95–100% yields [4].



The spatial structure of nitrobenzoazacrown ethers and their complexation behavior towards alkali and alkaline-earth metal cations, ammonium ions, and fluoride anions were investigated using X-ray diffraction and <sup>1</sup>H NMR spectroscopy. It was shown that the stability of host–guest type complexes of nitrobenzoazacrown ethers with metal and ammonium cations in MeCN-*d*<sub>3</sub> is lower than the stability of complexes formed by *N*-alkyl-substituted analogues with the same macrocycle size. It was shown that fluoride anions in DMSO-*d*<sub>6</sub> or MeCN-*d*<sub>3</sub> can bind to nitrobenzoazacrown ethers via hydrogen bonding with the NH group of the macrocycle [4].

The resulting nitro benzoazacrown ethers are of interest as synthons for the synthesis of functional derivatives at the macrocycle nitrogen atom.

*This work was supported by the RFBR, the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS*

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## Three component [2+2+1] gold(I)-catalyzed oxidative generation of fully substituted 1,3-oxazoles involving internal alkynes

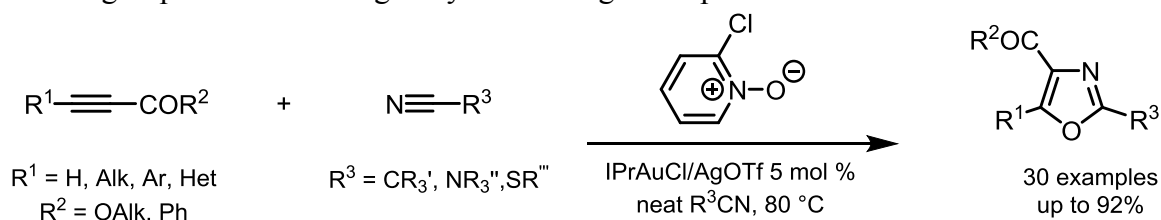
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Today, homogeneous catalysis involving gold(I) species comprises one of the most effective methods for the activation of alkynes leading to a substantial diversity of follow-up chemical transformations [1]. In particular, Au-catalyzed reactions of acetylenes are successfully utilized in the synthesis of various carbo- and heterocyclic structures, including natural compounds [2]. Intermolecular transformations of alkynes that utilize gold  $\alpha$ -oxo carbenes generated *in situ* are of special interest due to the possibility of a facile growth of the molecular complexity using relatively small building blocks [3]. Although the reactions of  $\alpha$ -oxo carbenes derived from *terminal* alkynes are studied rather actively, only single examples of relevant transformations of *internal* alkynes are known and, moreover, these examples are limited to the usage of such highly reactive acetylenes as internal ynamides [4].

1,3-Oxazole derivatives have attracted an increasing attention as these species are widespread in natural objects and, furthermore, numerous synthetic oxazoles exhibit some useful biological activity modes [5]. Hence, the development of new effective synthetic strategies for assembly of highly substituted 1,3-oxazole framework is highly desirable.

Efficient heterocyclization of alkynyl esters and ketones *via* gold-catalyzed alkyne oxidation by 2-chloropyridine *N*-oxide has been developed using nitriles, cyanamides and thiocyanates as both the reacting partner and the reaction solvent, offering a wide range of fully substituted oxazoles. The advantages of this method include mild reaction conditions and high functional-group tolerance with good yields of target compounds at the same time.



*This work was supported by the Russian Science Foundation  
(grant № 18-73-00026)*

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## Transformation of arylthienylethenes to the nafto[1,2-*b*]thiophenes: substituents influence on *cis-trans* isomerization and photocyclization

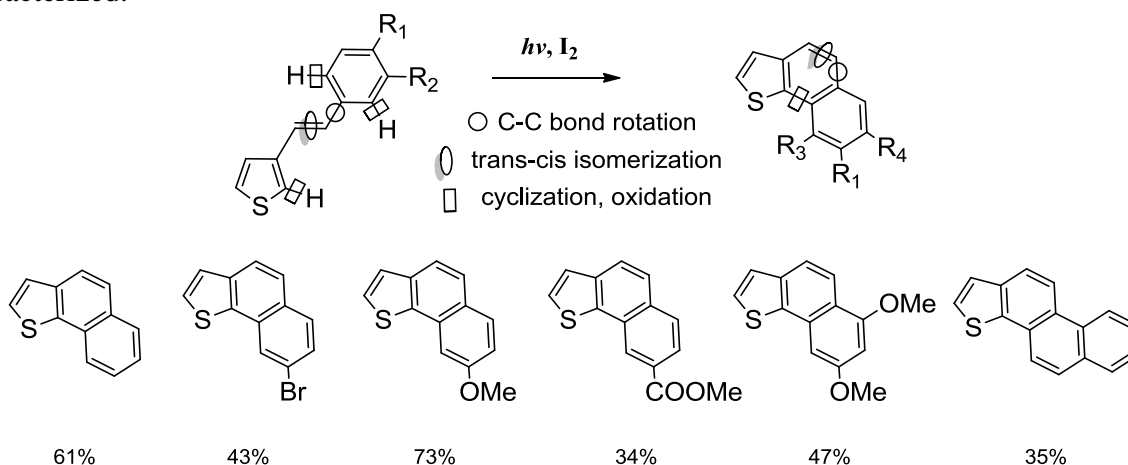
Dyachenko N.V.<sup>a,b</sup>, Tokarev S.D.<sup>a,b</sup>, Khoroshutin A.V.<sup>a</sup>, Boblyyova A.A.<sup>a</sup>,  
Fedorov Yu.V.<sup>b</sup>, Anisimov A.V.<sup>a</sup>, Sotnikova Yu.A.<sup>a</sup>, Fedorova O.A.<sup>a,b</sup>

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Phototransformation of stilbenes to phenanthrenes via a photo-induced 6-electron conrotatory electrocyclic ring closure followed by oxidation of a dihydrophenanthrene intermediate is extensively studied [1] as an alternative to multi-step sequences [2] for annelated polycyclic aromatics. Heteroatom analogs of this reaction would result in products potentially applicable as perspective materials for electroluminescent devices, organic conductors and photovoltaic systems [3].

This work is aimed at the synthesis of substituted phenylethynylthiophenes, study of their light-induced transformations, i.e. *cis-trans* isomerization and photocyclization, and the influence of the structure of the initial compounds and the reaction conditions on the outcome of the reaction. In addition, optical properties of the formed naphtho[1,2-]thiophenes were characterized.



The quantum yields of direct and inverse photoinduced *cis-trans* isomerization were measured for some compounds. For the products of photocyclization, the presence of two competing radiative relaxation paths of the excited state were shown, their lifetimes were measured.

*This study was supported by the Russian Science Foundation  
(Grant № 18-73-00047)*

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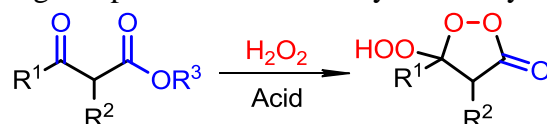
## Acid-catalyzed peroxidation of $\beta$ -ketoesters

Ekimova M.V.<sup>1,2</sup>, Vil' V.A.<sup>1</sup>, Terent'ev A.O.<sup>1</sup>

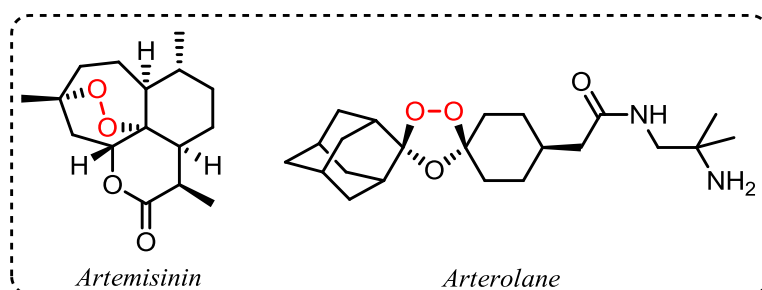
<sup>1</sup>N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation

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The biological activity of organic peroxides is usually associated with the antimalarial properties of artemisinin (a natural peroxide isolated from *Artemisia Annuua* leaves). Analysis of published data shows that organic peroxides exhibit various types of biological activity, in particular, antiparasitic, antiviral, fungicidal and antitumor. However, the selective synthesis of organic peroxides is a difficult issue, since it is often lead to difficult separate mixture of oxidation and transformation products. A search for convenient, effective methods for the synthesis of new classes of organic peroxides is currently underway.



New class of organic peroxides  
with promising antimalarial activity



A method has been developed for producing a neglected class of cyclic peroxides,  $\beta$ -hydroperoxy- $\beta$ -peroxylactones, from  $\beta$ -ketoesters and  $\text{H}_2\text{O}_2$  [1].  $\text{BF}_3\cdot\text{Et}_2\text{O}$  is an effective catalyst for the process. There is a rare transformation in this reaction - peroxidation of the ester group. The formation of the Baeyer-Villiger reaction products is not observed.

*This study was supported by Russian Science Foundation  
(grant № 18-73-00315)*

### References

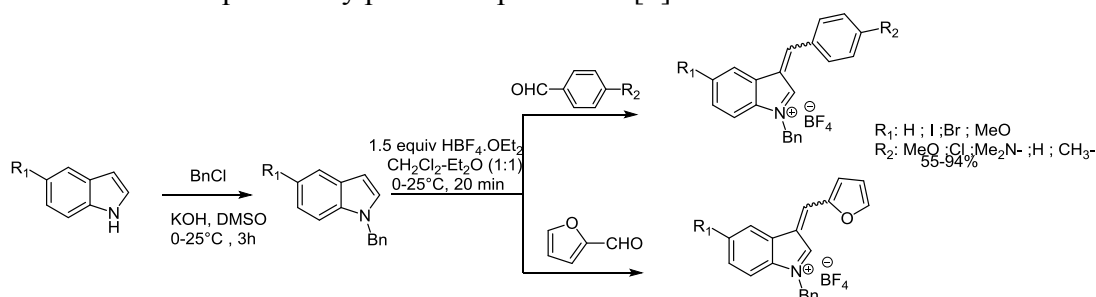
[1] V. A. Vil', G. P. Gomes, O. V. Bitukov, K. A. Lyssenko, G. I. Nikishin, I. V. Alabugin, A. O. Terent'ev. *Angew. Chem. Int. Ed.*, **2018**, 57, 3372.

## Isocyanide-based Multicomponent Reactions of 3-Arylidene-3*H*-indolium Salts

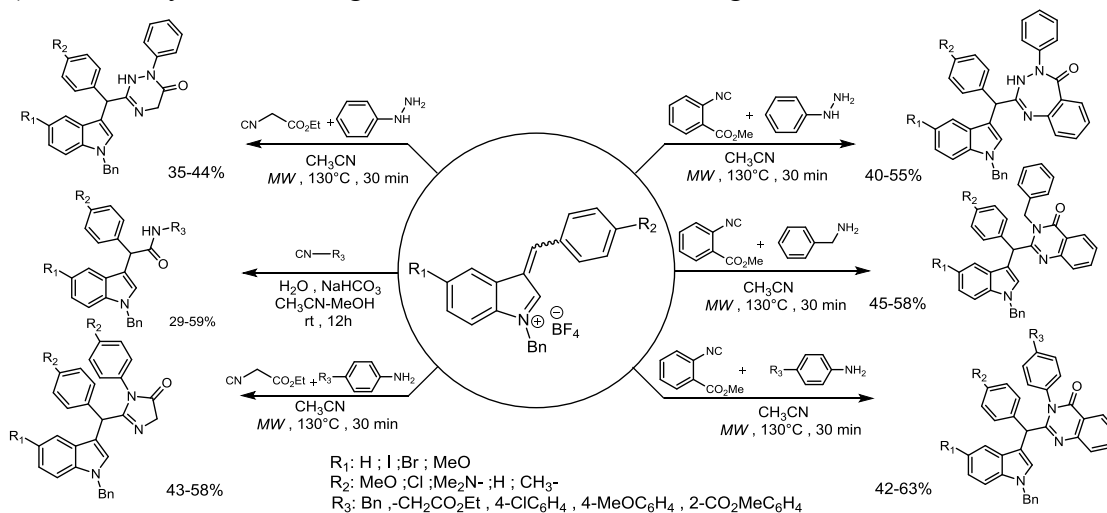
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The distinctive feature of electrophilic addition to isocyano group is the formation of highly reactive species that can react further with various nucleophilic reagents. Thereby opening a great multitude of synthesis pathways, which are capable of providing access to hundreds of heterocyclic scaffolds [2], recently we have been investigating the use of 3-arylideneindolium salts as a vinylogue of iminium ions for our synthetic strategy, these salts were obtained with conditions similar to a previously published procedure [1].



As a part of our work, we developed a new synthetic methodology based upon consecutive multicomponent reaction based upon the reaction of 3-arylideneindolium salts with isocyanides and amines to synthesis a large amount of a new heterocyclic compounds (see figure below). Which may have a biologic activities for further testing.



The structure of synthesized compounds was confirmed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and Mass spectra

This work was supported by RFBR (research project No. № 17-53-10012 KO\_a)

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## Synthesis, biological activity, molecular docking and DFT studies of a new series of condensed 1,2,4-triazoles

El Bakri Y. <sup>a,b</sup>, Anouar E.A. <sup>c</sup>, Essassi E.M. <sup>a</sup>, Mague T.J.T. <sup>d</sup>

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A ring transformation of 6-methyl-7*H*[1,2,4]triazolo[4,3-*b*][1,2,4]triazepine-8(9*H*)-ones (thiones) in the presence of acetic anhydride give rise to a new series of 17 condensed 1,2,4-triazole derivatives. Plausible mechanisms are proposed and show the formation of a beta fused  $\beta$ -lactam moiety. The compounds were tested for their (i) inhibitory potential on digestive enzymes ( $\alpha$ -amylase and  $\alpha$ -glucosidase), and (ii) antioxidant activity using radical scavenging (DPPH and ABTS radicals) and ferric reducing power assays. The compounds show interesting and promising antidiabetic activities. Molecular docking study have been carried out to determine the binding mode interactions between these derivatives and the targeted enzymes. The results showed the strength of hydrogen bonding to be important in rationalizing the observed inhibition results. DFT calculations were performed at the B3LYP/6-31++G(d,p) level using the polarizable continuum model. The obtained results show that the mechanism of action depends on the basic skeleton and the presence of substituted functional groups in these derivatives.

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## Domino-reactions of 1-aryl-3,4-dihydrobenzo[*h*]isoquinolines with activated alkynes and alkenes

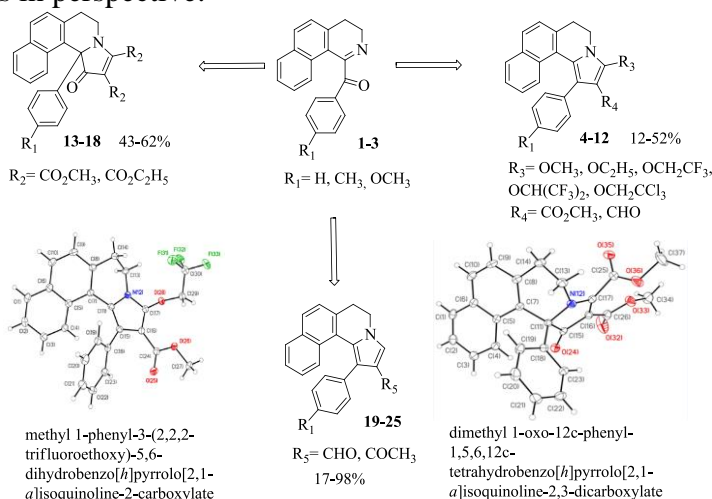
Ershova A.A., Borisova T.N., Voskressensky L.G., Nguyen V.T., Le T.A.

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Pyrrolo[2,1-*a*]isoquinolines have attracted continuing interest for the synthesis and reactivity because of their biological activity. Benzo[*h*]pyrrolo[2,1-*a*]isoquinolines have a unique nitrogen-containing tetracyclic structure, the synthesis of which has been poorly represented in scientific literature. Completely unsubstituted benzo[*h*]pyrrolo[2,1-*a*]isoquinoline was obtained by electrophilic cyclization of the *N*-acylpyrrolidine ion [2]. The research and development of new methods for the synthesis of benzo[*h*]pyrrolo[2,1-*a*]isoquinolines derivatives have become an interesting, important and attractive goal in organic synthesis. In order to achieve our scientific goal, we developed a new synthetic route to the 1-aryl-3,4-dihydrobenzo[*h*]isoquinolines and used them as precursors in the domino reactions with activated alkynes and alkenes.

Three-component reactions of 1-aryl-3,4-dihydrobenzo[*h*]isoquinolines **1-3** with methyl propiolate were performed in various alcohols. The products **4-12** were obtained with low and moderate yields. The reactions were conducted either under reflux or under microwave activation in a sealed reaction vessel. Another direction of the transformations of 1-aryl-3,4-dihydrobenzo[*h*]isoquinolines **1-3** is the reaction with symmetric alkynes such as dimethylacetylenedicarboxylate and diethylacetylenedicarboxylate. Reactions were carried out in dry toluene at 150°C under microwave activation. The products **13-18** were obtained with moderate yields. The reactions of 1-aryl-3,4-dihydrobenzo[*h*]isoquinolines with acrolein and methyl vinyl ketone proceed smoothly in trifluoroethanol under microwave activation. We suppose, that the bio screening of benzo[*h*]pyrrolo[2,1-*a*]isoquinoline derivatives can reveal some useful activities in perspective.



The publication has been prepared with the support of the «RUDN University Program 5-100».

This work was supported by the Russian Foundation for Basic Research (grant № 19-53-54001)

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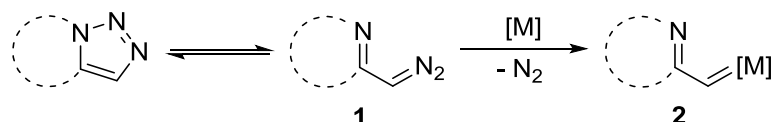
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## Cascade transformations of *o*-(iodotriazolyl)benzoic acids

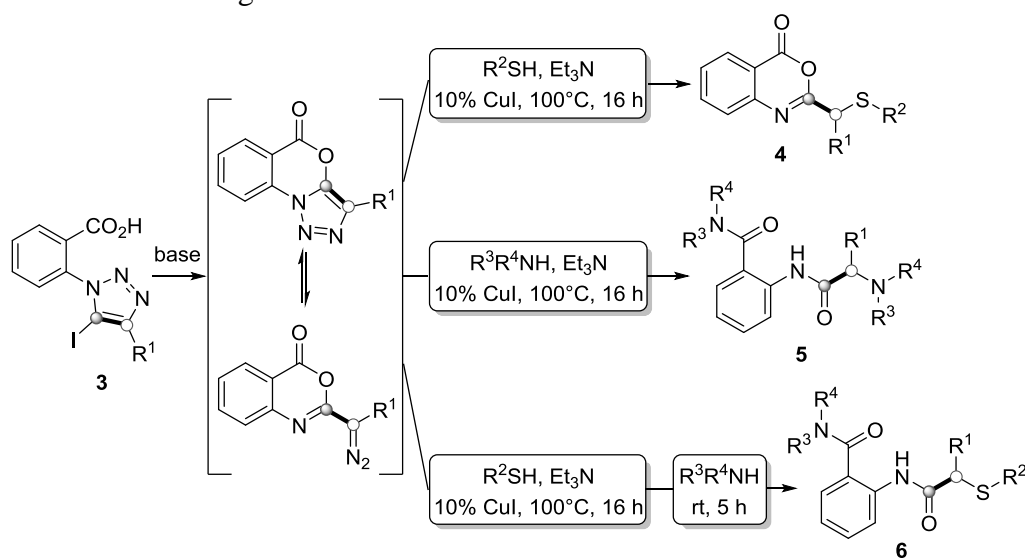
Erzunov D.A., Voloshkin V.A., Kotovshchikov Y.N., Latyshev G.V., Lukashev N.V.,  
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Tautomerization of fused 1,2,3-triazoles into diazoimine **1** is utilized in organic synthesis, in particular, due to the possibility of intercepting the latter by transition metals generating metalcarbenoid **2**. However, research studies in this area is mainly limited to triazolopyridines [1].



Recently we have proposed a new approach to benzoxazoles based on cyclization of *o*-(iodotriazolyl)phenols. Intermediately formed annulated triazole tautomerizes into diazoimine, which can be trapped *in situ* [2]. In the present study we have extended this approach to *o*-(iodotriazolyl)benzoic acids **3**. Copper-catalyzed interception of diazo group by thiols affords the corresponding benzoxazinones **4** without any further transformations. In the case of amines, insertion of copper carbenoid to NH bond is accompanied by nucleophilic opening of heterocyclic lactone leading to diamides **5**.



The difference in reactivity of thiols and amines in this reaction can be utilized for the interception of diazo group by thiol and subsequent amine opening of benzoxazinone. This approach allows implementing double functionalization *in one pot* and obtaining compounds **6**.

*This work was supported by RFBR (grant № 18-33-01024 mol\_a)*

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## 1-(2-Imino-2*H*-chromen-3-yl)pyridin-1-ium perchlorates as precursors for the synthesis of (*E*)-4-(nitromethylene)-4*H*-chromen-2-amines

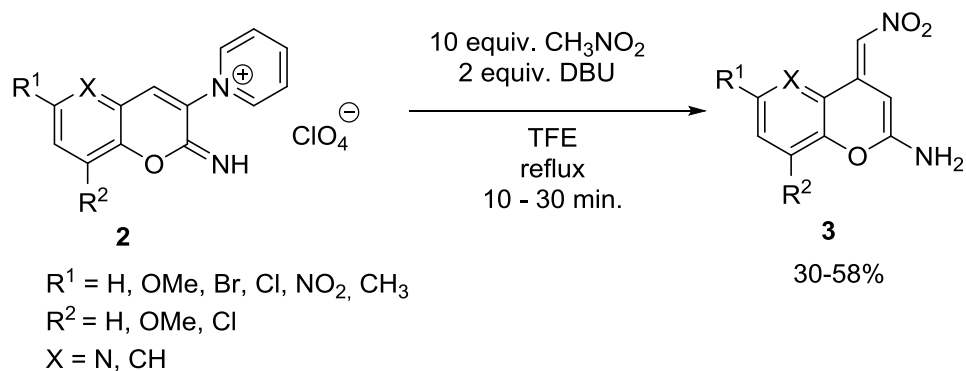
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Vast bioactivity (antiproliferative, anti-inflammatory etc.) of 2-aminochromes makes this scaffold of great interest for researchers and synthesis of such compounds still an actual task.

Here we describe a new approach towards 2-aminochromes via reaction of 1-(2-imino-2*H*-chromen-3-yl)pyridin-1-ium perchlorates with nitromethane (Scheme 1), that presumably proceeds through the initial Michael addition to the 2-iminochromene followed by the formation of cyclopropane intermediate (with elimination of pyridine), which in its turn cleaves and tautomerization finally gives the 2-aminochromene.

Scheme 1



The reported study was funded by RFBR according to the research project № 18-33-00536

## Cyclopropene 1,3-dipolar cycloadditions to the stable *N*-protonated azomethine ylide derived from Ruhemann's purple

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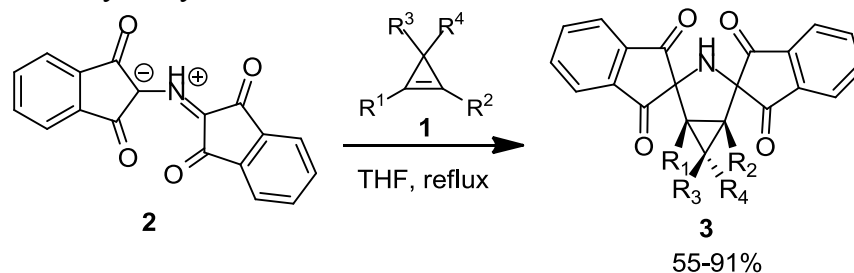
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The 1,3-dipolar cycloaddition reaction is considered one of the most reliable methods for the construction of five-membered heterocycles. The main benefit of 1,3-dipolar cycloaddition is its concert nature, resulting in stereoselective formation of a wide range of heterocyclic frameworks. In recent years, a great deal has been done to develop the enantio- and diastereoselective methods for the synthesis of biologically relevant scaffolds by utilizing various 1,3-dipoles and dipolarophiles.

Cyclopropenes demonstrate unique reactivity due to high strain and low distortion energy and may act as dipolarophiles by providing access to heterocycles containing a cyclopropane ring. During the last two years, we investigated the 1,3-dipolar cycloadditions of cyclopropenes with azomethine ylides generated *in situ* by decarboxylative condensation of isatins [1], 11*H*-indeno[1,2-*b*]quinoxaline-11-ones [2] and tryptanthrines [3] with  $\alpha$ -amino acids. These reactions were found to be valuable methods for the diastereoselective synthesis of cyclopropa[*a*]pyrrolizine and 3-azabicyclo[3.1.0]hexane frameworks.

Herein, we report the 1,3-dipolar cycloaddition reaction of different substituted cyclopropenes **1** to the stable azomethine ylide protonated Ruhemann's purple **2**. The reactions proceed smoothly under mild conditions to give dispiro[indene-2,2'-[3]azabicyclo[3.1.0]hexane-4',2''-indene] derivatives **3** in moderate to high yields (55-91%). In the case of prochiral 3-methyl-3-phenylcyclopropene, the reaction has been characterized by high diastereofacial selectivity. The structures of the resulting 1,3-dipolar cycloadducts were verified by NMR spectroscopy and X-ray analysis.



The results of this work contribute to chemistry of cyclopropenes, as well as enrich methods for the construction of polycyclic compounds with a cyclopropane fragment.

*This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-00464)*

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## Oxindoles spiroconjugated with $\beta$ -lactam ring: novel approach to synthesis and further evaluation as tumor proliferation inhibitors

Filatov V.E., Kukushkin M.E., Kusnetsova J.V., Beloglazkina E.K., Zyk N.V., Majouga A.G.

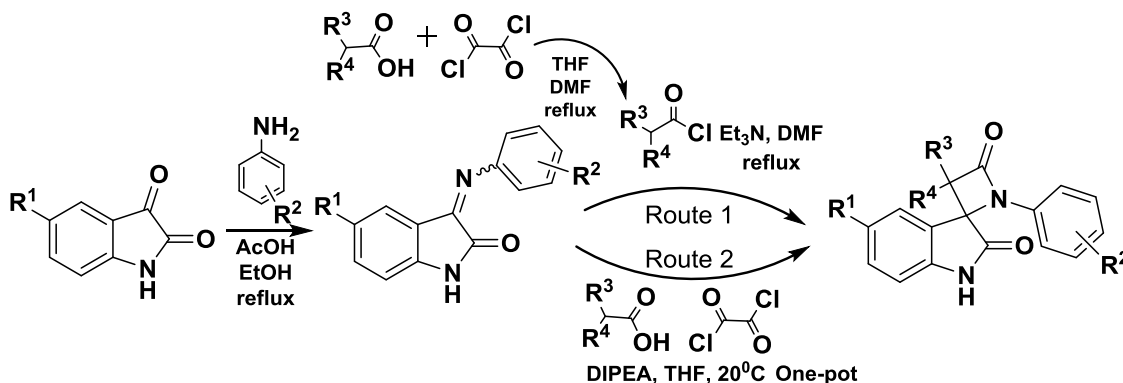
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Approximately 50% of cancers are known to proliferate due to genetic mutations leading to hyperexpression of MDM2 protein. Excessive concentration of such protein leads to complete inhibition and then biodegradation of significant protein p53, which controls cell cycles by keeping DNA integrity in check and activates apoptosis in case irreparable damage occurs. Thus mutations accumulate leading to tumor proliferation [1]. So among potential strategies of cancer treatment an inhibition of interactions between proteins p53 and MDM2 is taking great interest, making MDM2 a mark for targeted therapy. Aside from cis-imidazolines based on first successful example of desired inhibitor – Nutlin-3a – spiro-oxindole SAR405838 which is currently under clinical Phase I investigation is of great interest. Spiro-oxindoles are class of inhibitors designed after Trp23 of p53 chain which is responsible for strong binding between two proteins [2]. Thus inhibitors based on spiro-oxindoles are supposed to have the greatest affinity to target molecule.

Previously our research team also reported new structural type of dispirooxindoles which had shown good results at *in vitro* test [3].

Inspired by obtained results we decided to further improve performance of desired inhibitors using  $\beta$ -lactam ring spiroconjugated with oxindol thus potentially reducing biodegradation in addition to maintaining conformational stability.

Implementation of previously reported method (route 1 on Scheme) [4] led us to obtaining of two diastereomers with ratio of 1:2. Looking for a way to turn diastereoselectivity around our team has successfully created novel one-pot technique of  $\beta$ -lactam synthesis (route 2 on Scheme).



Several of obtained substances have shown promising results at *in vitro* tests giving the basis for further development of subject. In the near future we are planning to expand the library of small-molecule inhibitors to specify relation between structure of substance and its biological activity.

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## Unexpected transformations of CF<sub>3</sub>-containing enaminoketones into 2,6-di(het)aryl-4-trifluoromethylpyridines

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Earlier we found unusual reactions of fluorine-containing enaminoketones ( $\beta$ -aminovinyl ketones or AVK) **1** into AVK **2** [1, 2], and also the exchange of functional groups between AVK **1** and  $\beta$ -diketones or  $\beta$ -aminovinylthiones [3, 4]. In the present communication, we wish to report unexpected transformations of AVK **1** into 2,6-di(het)aryl-4-trifluoromethylpyridines **3**, which take place on reflux of AVK **1** in glacial acetic acid (or in ethanol in the presence of manganese acetate (II)), thus demonstrating a novel approach to pyridines **3**. We revealed the role of isomerization of AVK **1** into AVK **2** in the pyridines **3** formations. It is worth noting that no transformations of AVK **2a-e** have been observed under similar reaction conditions.

The features of the crystal structure of pyridine **3a** have been established by X-ray analysis.

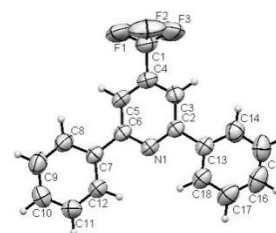
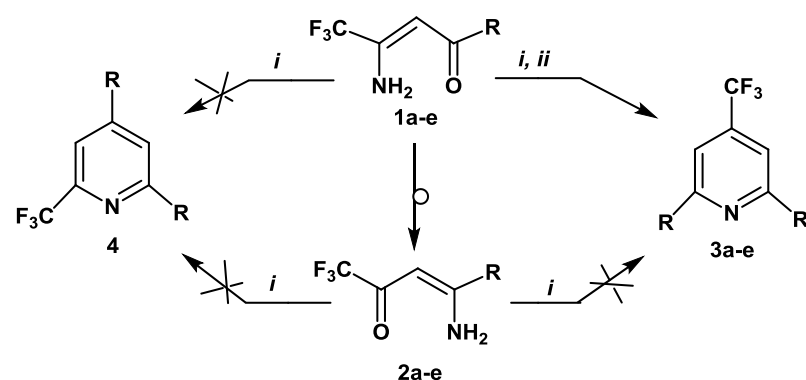


Fig. 1. General view of compound **3a** shown with the thermal ellipsoids with 50% probability

**R** = Ph (**a**), *p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub> (**b**), 2-pyridyl (**c**), 3-pyridyl (**d**), 4-pyridyl (**e**)

**i**: AcOH, reflux (yields of pyridines **3** from 40 to 70%)

**ii**: EtOH, Mn(OAc)<sub>2</sub>, reflux (yields of pyridines **3** from 60 to 96%)

The work was carried out within the framework of the theme of the state task

№ AAAA-A19-119011790134-1. Analytical studies were carried out by using equipment of the Center for Joint Use "Spectroscopy and Analysis of Organic Compounds"

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## Structure and spectral properties of supramolecular complexes of cyanine dyes containing terminal ammonium groups with *bis*(18-crown-6)stilbene

Fomina M.V., Nikiforov A.S., Vedernikov A.I., Kurchavov N.A., Kuz'mina L.G., Gromov S.P.

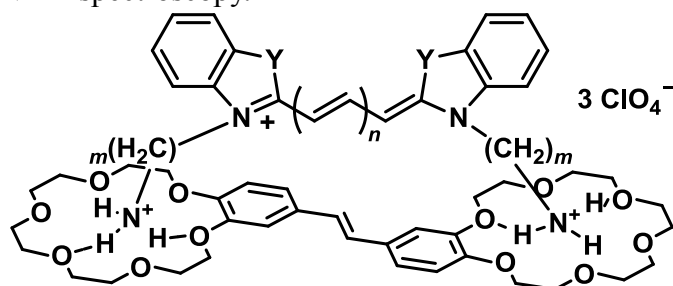
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Self-assembled photoactive supramolecular systems formed by non-covalent interactions attract considerable attention. Cyanine dyes can be employed as light-sensitive components for the design of such supramolecular systems.

In order to elucidate the possibility to construct photoactive "host-guest" complexes based on cyanine dyes as a guest and the influence of their structure on the properties of supramolecular complexes, we synthesized cyanine dyes with ammonioalkyl substituents at the heterocyclic nitrogen atoms with yield up to 51%. Structure obtained dyes was determined by NMR-, IR-, UV spectroscopy, X-ray diffraction data, and elemental analysis [1].

The presence of primary ammonium groups capable of hydrogen bonding enables self-assembly of dyes with macroheterocyclic molecules containing electron-donating oxygen heteroatoms to form supramolecular complexes. Complexation was studied using absorption, luminescence and  $^1\text{H}$  NMR spectroscopy.



Y = S, CMe<sub>2</sub>; m = 3 - 6; n = 0 - 2

We demonstrated the possibility to construct the supramolecular systems based on cyanine dyes with two ammonioalkyl *N*-substituents using their complexes with *bis*(18-crown-6)stilbene as an example. It was shown that the components form highly stable bimolecular and relatively unstable trimolecular complexes in which the dye ammonium groups are hydrogen-bonded to the crown ether moieties of stilbene and their  $\pi$ -conjugated moieties are located one above the other. The stability constants for some of these complexes were determined, and the stability of the complexes was shown to depend on the dye structure, in particular, on the geometric matching of components, which is manifested as the distance between the ammonium groups of the dye and the stilbene binding sites.

The synthesized cyanine dyes and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

*This work was supported by the Russian Science Foundation  
(project № 19-13-00020)*

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## Synthesis of new bis-pyridinium salts with diphenyl and diphenyl ether spacer

Frolov N.A., Vereshchagin A.N.

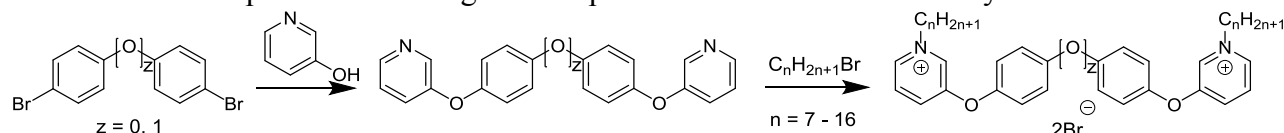
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Antiseptics and disinfectants are widely used in the social sphere for the prevention and control of infectious agents. Recent days, microorganisms develop resistance to antiseptics and disinfectants, which raises the problem of the synthesis of new substances with antibacterial activity.

An example of such compounds is quaternary ammonium salts (QAC). It is one of the most commonly used classes of disinfectants, which are used in hospitals, textile, paint and food industries due to their relatively low toxicity to humans and animals, as well as due to their wide specificity of antimicrobial actions.

An important subgroup of QAC is quaternary salts of pyridinium and bis-pyridinium. These compounds are widely used as biocides, due to their strong antimicrobial action even at very low concentrations on a wide range of gram-positive and gram-negative bacteria, fungi, and some viruses. These salts can be used for medical purposes in contact with human skin (treatment of skin, wounds, bandages, surgical and dental instruments, etc.) [1, 2].

Bipyridine salts based on diphenyl and diphenyl ether were synthesized, and showed themselves as compounds exhibiting a wide spectrum of antibacterial activity.



*This work was supported by the Russian Science Foundation  
(grant № 17-73-20260)*

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## First total synthesis of furanocembranoid-1

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In 2007, Khanitha Pudhom et al. isolated a new class of furanocembranoids [1] **1-3** (Figure 1) from the hexane extract of croton oblongifolius roxb sp. Furanocembranoids **1** showed cytotoxicity against BT474 (human breast ductal carcinoma), CHAGO (human undifferentiated lung carcinoma), Hep-G2 (human liver hepatoblastoma), KATO-3 (human gastric carcinoma) and SW-6 (human colon adenocarcinoma). The presence of two stereogenic centers and a network of diverse and distributed functionalities on its novel framework, together with its potential bioactivity, make furanocembranoid-1 a challenging and attractive target molecule for synthetic chemists. Strategically, the most challenging problem is the construction of the furan ring system as well as the structural moiety possessing the asymmetric centers bearing an isopropyl group and Tran's double bonds. The total synthesis of *Furanocembranoid 1* involves stereoselective Evan's aldol reaction, Sharpless epoxidation, HWE olefination and Ring-closing metathesis are currently under way.

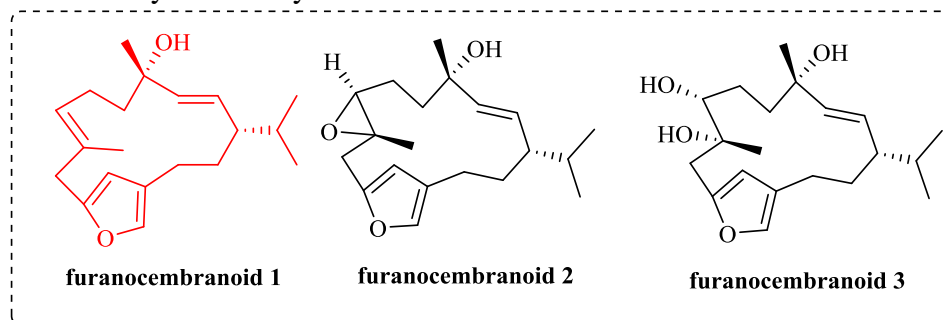


Figure 1: A class of furanocembranoid molecules

The publication was prepared with the support of the "RUDN University Program 5-100" and the Russian Science Foundation (RSF), project № 18-13-00456

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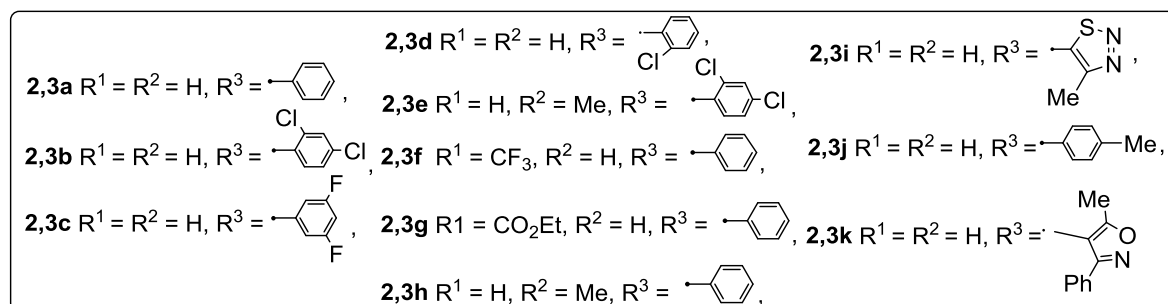
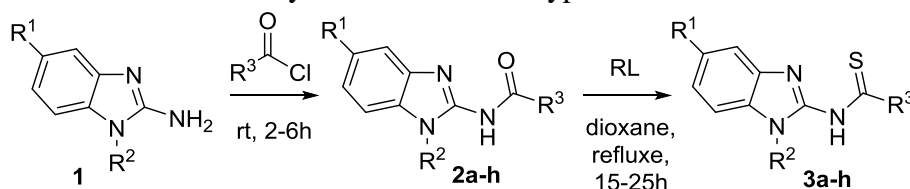
## Synthesis of biological active derivatives of benzimidazole

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Benzimidazole nucleus is a part of numerous therapeutic agents while its derivatives exhibit various types of bioactivity including antioxidant, anticancer, analgesic, antimicrobial, antiviral, anti-inflammatory, antiparasite etc. Modification of amino group, nitrogen atoms of imidazole ring, and C–H bonds of benzene ring also results in formation of biologically active compounds.

The starting amides **2a-h** were prepared in high yields in the reaction of commercially available 2-aminobenzimidazoles with different acetyl reagents. The novel thioamides **3a-h** were prepared by treatment of amides **2a-h** in boiling 1,4-dioxane with Lawesson's reagent, which was found earlier efficient for the synthesis of various types of thioamides.



Some target compounds were evaluated for their *in vitro* fungicidal activities. They exhibited the similar or better activity than other against *P. infestans*, *C. coccodes* and *R. solani*. The fungicidal activity of compounds **3b**, **c**, **e** illustrated that introduction of F and Cl into the molecule could increase antifungal activity.

In the near future we are planning to measure inhibitory effects of selected compounds on the kinase activity of CK1 isoforms, because our previously work was shown that thioamides were tested for their ability to inhibit CK1 isoforms *in vitro* and to inhibit the growth of tumor cell lines [1].

The structures of all new compounds were reliably confirmed by the combination of  $^1H$  and  $^{13}C$  NMR spectroscopy including 2D HMBC and HSQC experiments, as well as mass spectrometry.

This work was supported by the Russian Science Foundation  
(grant № 18-13-00161)

### References

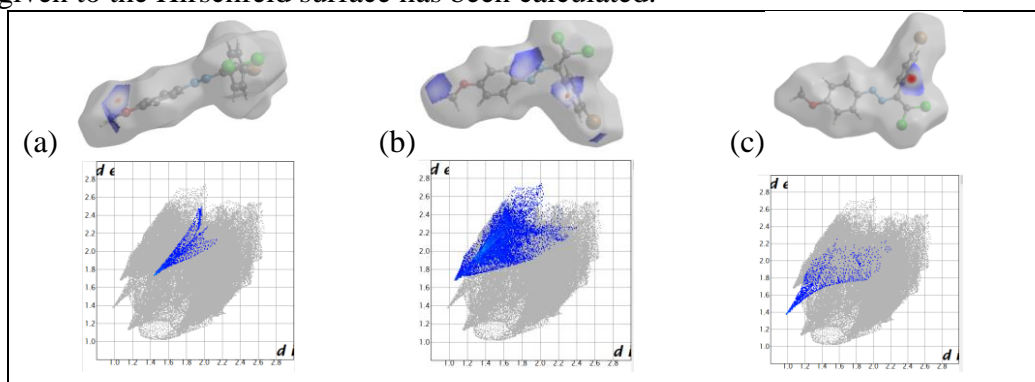
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## Hirschfeld surface analysis and energy of non-covalent interactions between molecules in (*E*)-1(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(4-methoxyphenyl)diazene

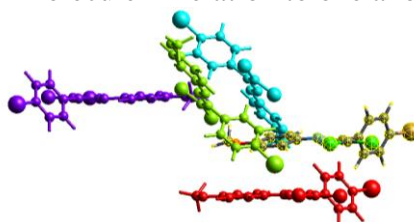
Garazadeh Kh.A., Bagirova Kh.N., Suleymanova G.T., Amrahov N.İ., Gajar A.M., Ahmadova I.C., Shikhaliyev N.G.

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In the crystal, formed by the (*E*)-1(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(4-methoxyphenyl) diazene molecule relatively strong C-H ... N hydrogen bonds and weak C-Cl...O, C-H...Cl halogen bonds and O ...  $\pi$  stacking interactions were detected via the most common and widely used method of Hirschfeld surface analysis for determining interactions between molecules (Figure 1). Also, the share of the interactions between molecules in the crystal given to the Hirschfeld surface has been calculated.



**Figure 1.** Hirshfeld surface for (a) O ... Cl, (b) H ... Cl (c) H ... N and corresponding fingerprints. Also energies of intermolecular interactions were calculated in the Crystal Explorer program on the HF / 3-21G model, and it became clear that the main share to the intermolecular force of attraction is of the dispersion forces, and the electrostatic and polarization interactions are very weak and the exchange forces are repulsive (Figure 3). The energy of intermolecular interactions is dependent not only on the distance between molecules, but also on the spatial location of molecule to one another.



**Figure 2.** The molecules around the selected (yellow) molecule are shown in different colors

	N	Sim. ə.	R	Elektron sıxlığı	E_ele	E_pol	E_dis	E_müb	E_tam
Red	1	-	4.75	HF/3-21G	-9.2	-3.8	-77.0	39.2	-49.5
Green	1	-	9.81	HF/3-21G	-5.6	-1.0	-22.4	10.2	-18.3
Cyan	1	-	10.83	HF/3-21G	-1.7	-0.6	-9.7	6.8	-5.4
Purple	1	-	18.00	HF/3-21G	-2.0	-0.6	-5.6	3.3	-4.9

**Figure 3.** Mutually affecting energies (kJ/mole) between selected molecules and other colored molecules.

*This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan- Grant No EIF-BGM-4-RFTF-1/2017- 21/13/4*

## Synthesis of 4(5)-isomers of tetraethylaminorhodamine

Glushko V.N., Zhila M.Yu., Blokhina L.I.

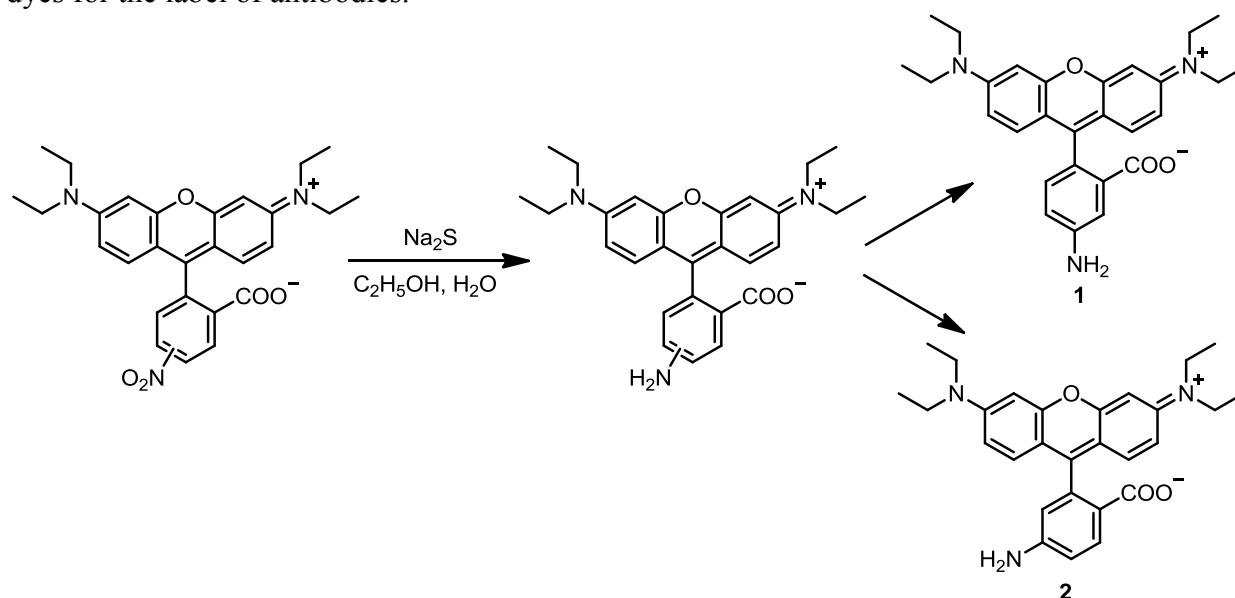
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The immunofluorescence method is a specific and sufficiently accurate morphological analysis, which success largely depends on the purity and activity of the fluorescent dyes forming part of the luminescent antibodies [1].

Tetramethylrhodamine isothiocyanate (TRITC), tetraethylrhodamine isothiocyanate (RITC) and dichlorotriazinylaminorhodamine (DTAR) are widely used in practice fluorochromes with red luminescence [2].

We have developed a method for producing individual 4- and 5-isomers (**1**, **2**) of tetraethylaminorhodamine with high purity, which are the key substances used in the synthesis of dyes for the label of antibodies.



Isomer separation was carried out on a 40/100 silica gel column. The optical characteristics of the resulting compounds are presented in the table below.

	Wavelength, nm			Molar extinction coefficient, $\epsilon_{\lambda_{\max}}$ , $\text{m}^2/\text{mol}$
	excitation, $\lambda_{\text{ex}}$	luminescent, $\lambda_{\text{lum}}$	absorption peak, $\lambda_{\text{max}}$	
4-tetraethylaminorhodamine	552	578	$552 \pm 2$	$(8,85 \pm 0,1) \cdot 10^4$
5-tetraethylaminorhodamine	552	575	$552 \pm 2$	$(9,48 \pm 0,08) \cdot 10^4$

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## Microwave assisted synthesis and transformation of oligoalkylated C-naphthyl-calix[4]resorcinarenes

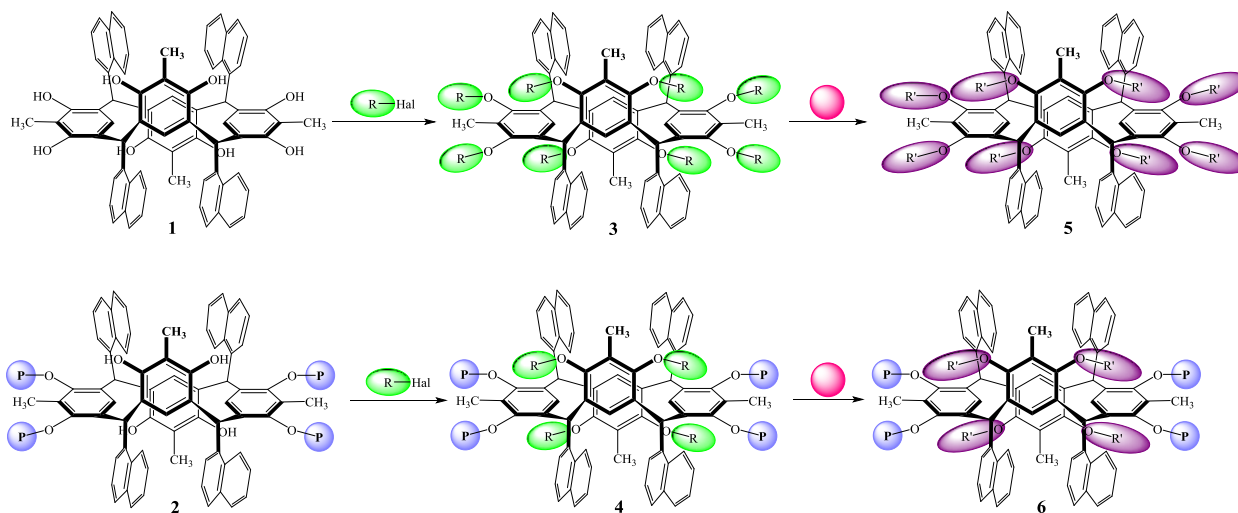
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O-Alkylation of C-tetranaphthyl-calix[4]resorcinarenes **1,2** by further transformable reagents, such as 2-bromoethyl acetate, propargyl bromide and bromoacetonitrile, has been studied. As substrates, we chose *rc*tt resorcinarenes **1,2** characterized by rigid structure and conformational stability. They differ in number and spatial location of hydroxyl groups. Thus, they are suitable basis for synthesis of homo- and heterofunctional derivatives [1].

Variation of the alkylation conditions for **1,2** showed that it was most efficient in a microwave reactor. The temperature and the solvent used depended on the initial compounds: tetraalkylation of resorcinarene **2** required harder conditions (140°C, 1,2-dichlorobenzene) than octafunctionalization of resorcinarene **1** (80°C, acetonitrile). In all cases, the conversion of **1,2** was total and the yields of products **3,4** were 56-85% [2].



Compounds **3,4** were further modified depending on the nature of introduced groups. As the result, obtained compounds **5,6** are convenient precursors for the subsequent transformation and the design of dendrimers, polymers and ligands for cations, anions and neutral organic molecules.

*This work was financially supported by the Russian Foundation for  
Basic Research (grant no. 18-03-00347a)*

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## Vinyl ethynyl ketones: preparation, properties, use in organic synthesis

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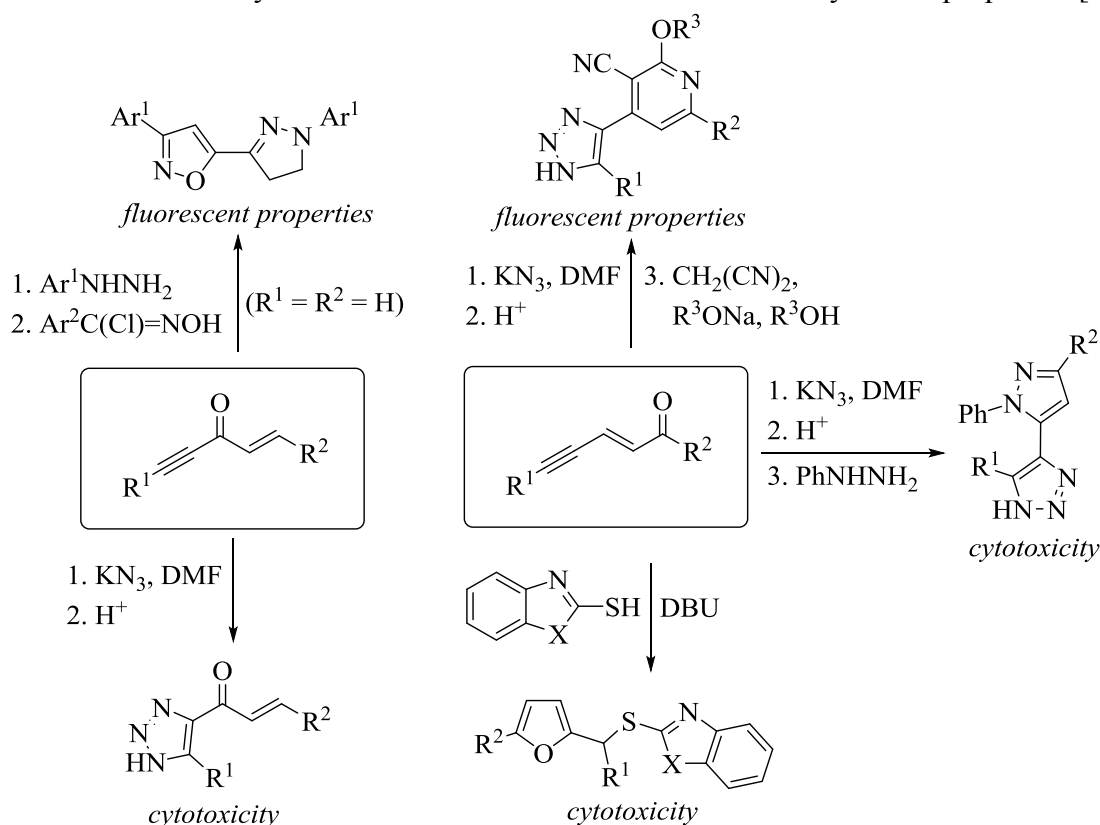
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The conjugated vinyl ethynyl ketones (enynones) can be used as efficient building blocks in the synthesis of various heterocyclic compounds, including natural compounds and their analogues. In this report discussed the methods of synthesizing these polyfunctional compounds, as well as their use in the synthesis of substances with fluorescent and cytotoxic properties [1–3].



Based on conjugated vinyl ethynyl ketones we obtained furan, 1,2,3-triazole, pyridine and isoxazole derivatives.

*This work was supported by the grant of the Russian Science Foundation*

*No. 18-13-00008*

### References

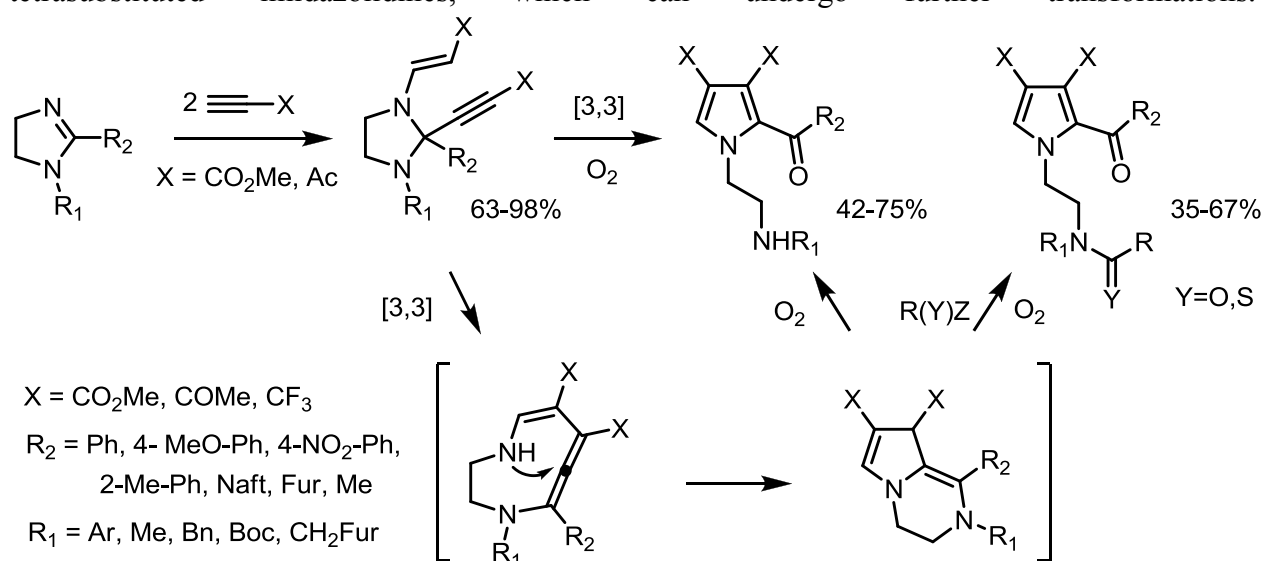
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## A domino route from imidazolines and electron-deficient alkynes to polysubstituted pyrroles

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Nitrogen-containing heterocyclic compounds, which are the most important material for drug discovery, functional materials research and catalysis, continue to attract the interest of scientists. In particular, pyrrolo [1,2-a] pyrazine derivatives have neuropsychotropic properties. It should be noted that in recent times several new preparative methods for the preparation of 2-imidazolines have been discovered, which allows us to consider them as convenient starting materials. The present work work discloses our latest results, concerning pseudo three-component reaction of 2-imidazolines and electron-deficient terminal alkynes to form tetrasubstituted imidazolidines, which can undergo further transformations.



Obtained tetrasubstituted imidazolidines have a concentrated set of reaction centers - an amino-ester fragment, an electron-deficient triple bond, what allows us to expect a high synthetic potential of these compounds. It can be interesting as for investigation a mechanism of the proceeding reaction as for synthesis aimed at expanding molecular diversity. It turned out that under microwave conditions in the presence of a base imidazolidines can undergo 3,3-sigmatropic rearrangement with the formation of a 9-membered allene, followed intramolecular nucleophilic addition along the allene fragment with the formation of a bicyclic system and consequent oxidation of electron-enriched double bond by atmospheric oxygen furnishes pyrroles with aminoethyl moiety.

*This work was supported by the Russian Science Foundation  
(grant № 18-73-00017)*

## ***N*-Cyanomethyl quaternary salts, *O*-hydroxybenzaldehydes and CH-acids in synthesis of imidazo[1,2-*a*]pyridines annulated with chromene moiety**

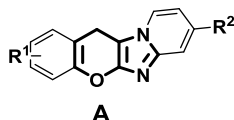
Golubenkova A.S., Festa A.A., Storozhenko O.A.

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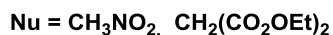
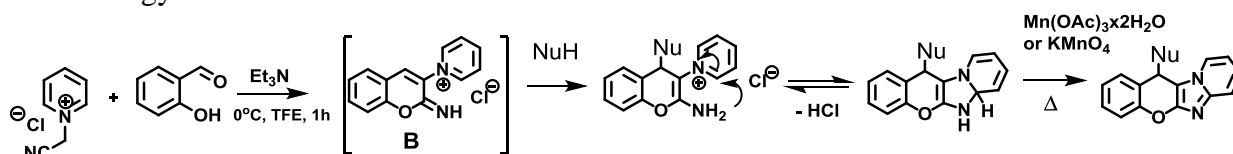
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Imidazoles annulated with chromenes **A** have recently been characterized as cytotoxic agents against HCT116 cancer cells due to their ability to induce cell cycle arrest and apoptosis without significant effects on normal cells [1].



Due to the useful biological activity of chromenoimidazopyridines **A** we decided to broaden the scope of such compounds through the introduction of different substituents at the methylene group. This concept has been successfully realized. At first step we generated iminochromenes **B**[2] and then added nitromethane and diethylmalonate followed by an oxidant and series of different chromenoimidazopyridines has been obtained through developed methodology.



*The reported study was funded by RFBR according to the research project № 18-33-00536*

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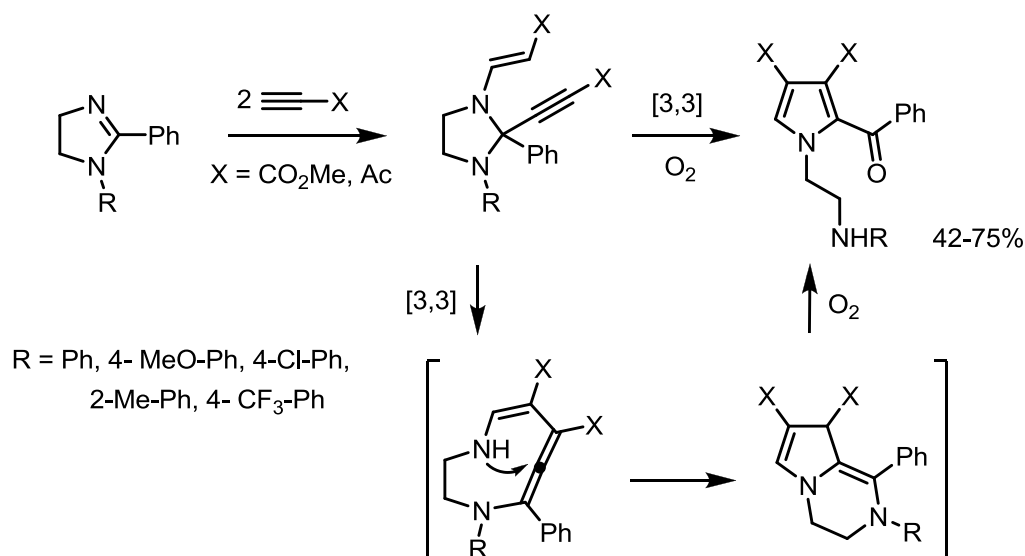
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## A domino route from imidazolines to polysubstituted pyrroles

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Pyrroles are an important class of heterocycles. They are found in an enormous number of various natural compounds. Polysubstituted pyrroles exhibit a wide range of biological activities, such as antibiotic, anti-inflammatory, and antitumor activities. Moreover, they are an exceptionally universal class of intermediates in organic synthesis. Consequently, the development of transition-metal-free, step-economic and atom-economic methodologies for pyrroles synthesis from easily available substrates continues to be of great interest. Cascade reactions have attracted much attention due to their high synthetic efficiency in the construction of complex molecules. Thus, such reactions are economically and environmentally attractive and have become an important area of research in heterocyclic chemistry.



This work discloses our latest results, concerning pseudo three-component reaction of 2-imidazolines and electron-deficient terminal alkynes to form tetrasubstituted imidazolidines, which can undergo further transformations to appropriate pyrroles. The cascade reaction proceeds through a thermal [3,3]-sigmatropic rearrangement, followed by an intramolecular nucleophilic addition of nitrogen atom to allene fragment. Consequent oxidation of electron-enriched double bond by atmospheric oxygen furnishes pyrroles with aminoethyl moiety.

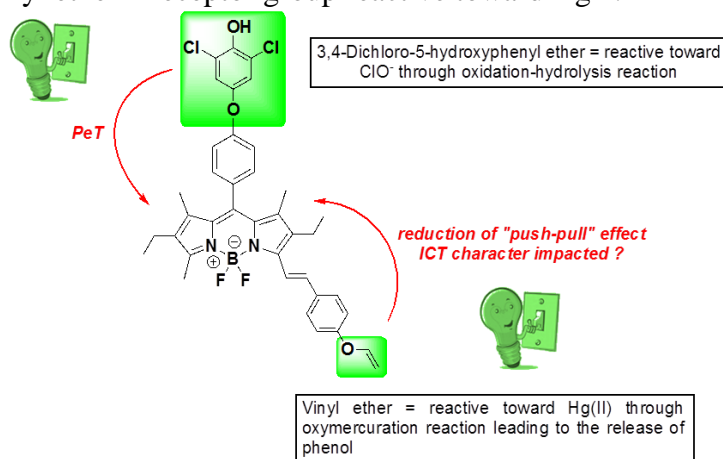
*This work was supported by the Russian Foundation for Basic Research (grant № 19-03-00502 a)*

## Dual Hg(II)/ClO<sup>-</sup> - fluorogenic "turn-on" probe based on a fluorogenic bis-phenolic Bodipy dye

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Hypochlorous acid (HOCl) is responsible for functions in important biological processes such as development and innate immunity and it is one of the most poorly understandable form of ROS. Mercury in any form is poisonous, with mercury toxicity most commonly affecting the neurologic, gastrointestinal and renal organ systems [1,2]. The fundamental interest was the combination of the receptor groups for the mercury cation and hypochlorite anion in one molecule due to the difficulty of detecting mercury in the presence of various bioanalysis [3]. Therefore in the present work dual-reactable probe was designed using the bis-phenolic Bodipy fluorescent platform, along with 3,4-dichloro-5-hydroxyphenyl ether - receptor group reactive toward ClO<sup>-</sup>, and vinyl ether – receptor group reactive toward Hg<sup>2+</sup>.



The synthesis of probe was achieved in 4 steps and required the preparation of derivative of *p*-hydroxybenzaldehyde. The Bodipy chromophore was obtained by condensation between latter benzaldehyde and kryptopyrrole (3-ethyl-2,4-dimethylpyrrole). The probe is promising for the simultaneous detection of both mercuric cations and hypochlorite anions by off-on fluorescence response.

The reported study was supported by RFBR, research project № 17-53-16012 НЦНИЛ\_a

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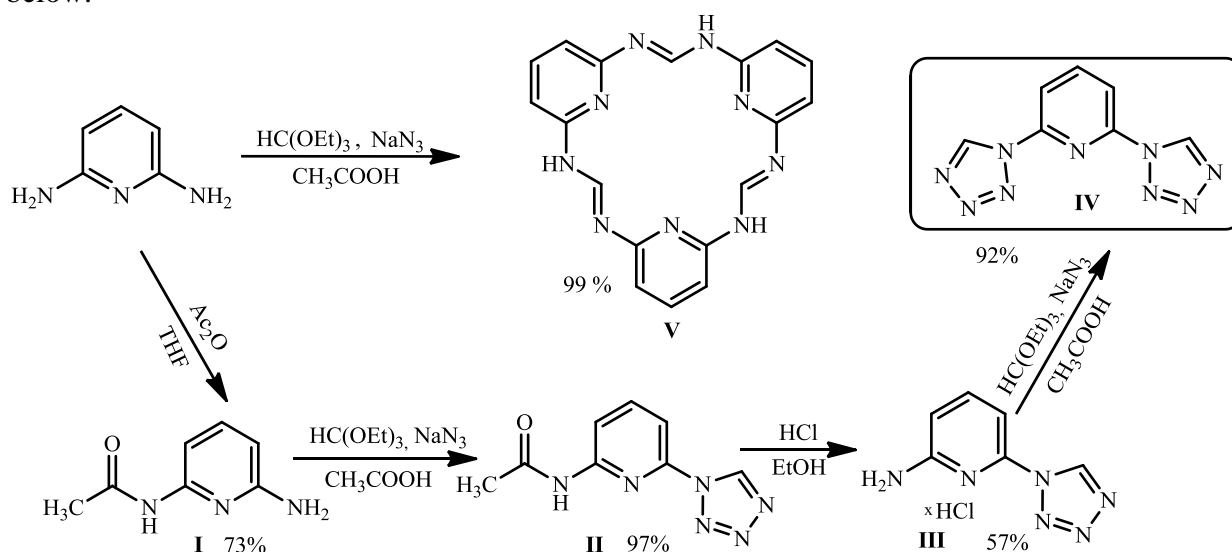
## Synthesis of 2,6-di(1H-tetrazol-1-yl)pyridine

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Modern achievements in coordination chemistry are mainly connected with the creation of new ligand systems, which can realize certain types of coordination modes. This opens up abilities for the rational design of various supramolecular structures in order to obtain functional materials with desired properties. From this point of view, 1-monosubstituted tetrazoles are of great interest. Heterocyclization of primary amines with triethylorthoformate and sodium azide is a convenient method for synthesis of these substances [1].

In present work we investigated behavior of 2,6-diaminopyridine in above heterocyclization reaction in order to prepare novel bistetrazole ligand, namely 2,6-di(1H-tetrazol-1-yl)pyridine (**IV**). It was found, that the direct reaction between 2,6-diaminopyridine, triethyl orthoformate and sodium azide doesn't allow to obtain target ligand **IV**, but leads to product **V** formed by trimerization of initial amine with triethyl orthoformate. Tetrazole **IV** was isolated only as by-product (~ 1% yield) after reflux of reaction mixture at 100°C for 100 h. In this connection four-stage synthesis of **IV** has been developed. Scheme of synthesis is given below.



The implementation of this scheme allows to obtain tetrazole **IV** with overall yield 37%. Moreover, hitherto unknown N-(6-(1H-tetrazol-1-yl)pyridin-2-yl)acetamide (**II**) and 2-amino-6-(1H-tetrazol-1-yl)pyridine hydrochloride (**III**) attractive as multi-topic ligands were prepared. Compounds prepared were characterized by elemental analysis, NMR spectroscopy and X-ray crystallography.

*This study is supported by Belarusian Republican Foundation for Fundamental Research, project X18P-043*

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## Interaction of 1,2-phenylenediamine with carbonyl compounds in the presence of a hierarchical zeolite Y

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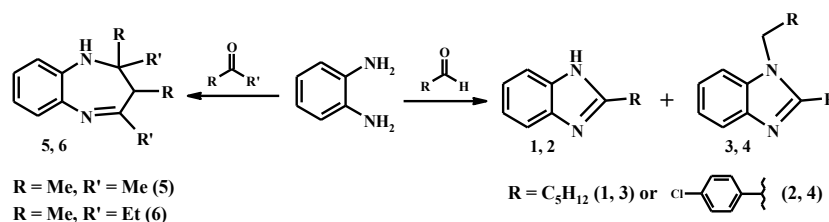
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Benzimidazole derivatives are widely used in medicinal preparations [1], organic light-emitting diodes and membranes [2]. Benzodiazepines have a sedative, hypnotic, anticonvulsant effects [3].

Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences has developed a method for the synthesis of granulated Ymmm zeolite [4], the porous structure of which is formed not only from micropores but also meso- and macropores. According to the XRF data and the parameters of adsorption capacities for H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub> vapours, the degree of crystallinity of H-Ymmm zeolite it is 92%. The specific surface area of the secondary porous structure of the H-Ymmm zeolite, measured by mercury porosimetry, makes 12.1 m<sup>2</sup>\*g<sup>-1</sup>. The volumes of micro-, meso-, and macropores are 0.28, 0.15 and 0.15 cm<sup>3</sup>\*g<sup>-1</sup>, respectively. According to the NH<sub>3</sub> TPD data two peaks are present in the zeolite acidity spectra: low-temperature having a maximum in the range of 250-300 °C 370 μmol\*g<sup>-1</sup> and a high-temperature peak with a maximum in the range of 350-450 °C 460 μmol\*g<sup>-1</sup>, characterizing “weak” and “strong” acid sites, respectively.

This abstract presents the results of studies of the catalytic properties of H-Ymmm zeolite in the synthesis of benzimidazoles and benzodiazepines by the reaction of 1,2-phenylenediamine with aldehydes (hexanal, p-chloro-benzaldehyde) and ketones (acetone, butan-2-one) (scheme).

Scheme



Interaction of 1,2-phenylenediamine with aldehydes in the presence of air proceeds with the formation of a monosubstituted product – benzimidazoles **1** and **2**, respectively, selectivity 92-97% it has been found. In an inert atmosphere, the formation of a mixture of mono- and bis-substituted products – benzimidazoles **1**, **2** and **3**, **4** in a ratio of 1: 4, respectively, is observed. The main product of the reaction of 1,2-phenylenediamine with ketones under the action of a hierarchical zeolite H-Ymmm is 1,5-benzodiazepines **5** and **6**, respectively, selectivity 86-99%.

### References

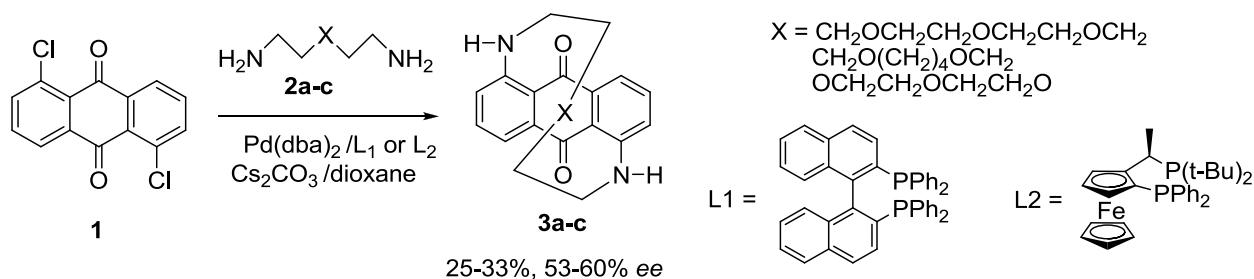
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## Anthraquinone-based enantioselective fluorescent chemosensors

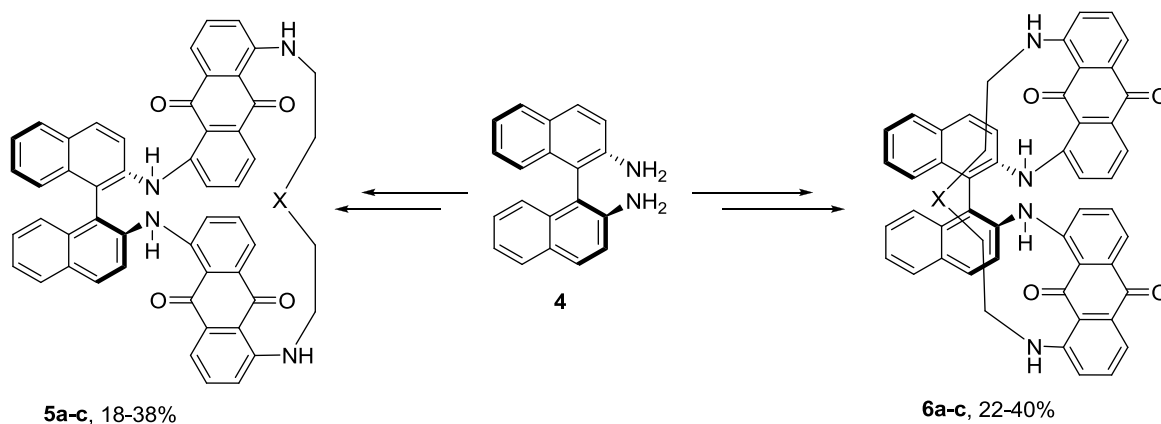
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The synthesis of the macrocyclic compounds with planar chirality has been always been a challenge. Our approach to macrocycles of this type employing the Pd(0)-catalyzed amination of 1,5-dichloroanthraquinone (**1**) with a series of oxadiazines **2a-d** in the presence of chiral diphosphine ligand Josiphos opened the way to enantiomerically enriched planar chiral macrocycles **3a-c** [1]. Due to the fact that 1,5-diaminoanthraquinone moiety possesses acceptable fluorescent properties, chiral macrocycles were investigated as potential fluorescent enantioselective chemosensors for a series of amino alcohols. The addition of some amino alcohols caused intensive increase in the emission intensity of the macrocyclic ligands.



Another type of chiral macrocycles incorporates 2,2'-dimaino-1,1'-binaphthalene moiety (BINAP) characterized by C<sub>2</sub>-chirality and two 1,5- or 1,8-diaminoanthraquinone structural fragments **5a-c**, **6a-c**. These compounds were obtained by two consecutive Pd(0)-catalyzed amination processes from (*S*)-BINAM **4** [2]. They possess a stronger fluorescent moiety, i.e. diaminobinaphthalene, and also were successfully tested as enantioselective fluorescent detectors of amino alcohols.



This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00709)

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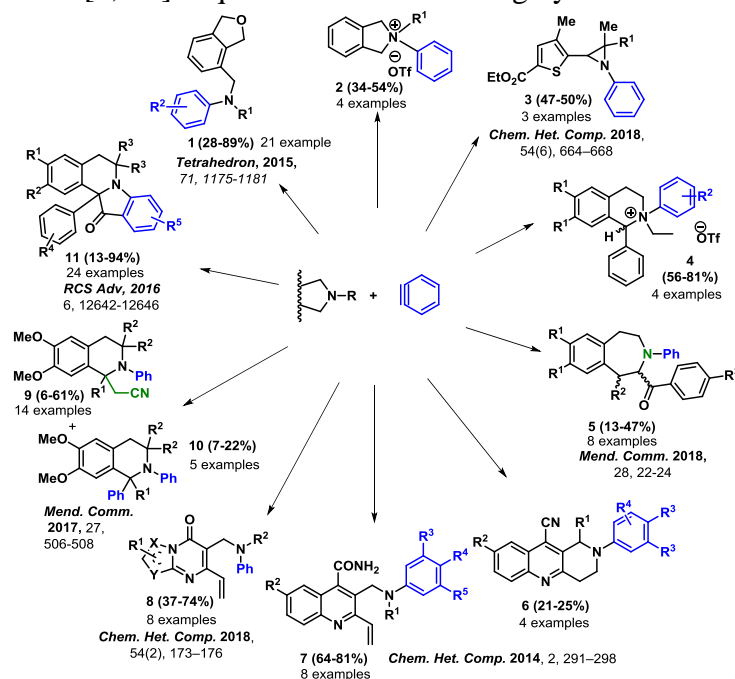
## Arynes in the synthesis of nitrogen containing heterocycles

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Dedicated to the 80<sup>th</sup> anniversary of my ex PhD supervisor – Alexey V. Varlamov

Arynes represent a versatile tool for the synthesis of a wide range of heterocyclic compounds, including architecturally complex ones. The presence of the triple bond in six membered aryne ring provides an extremely high reactivity resulting in a broad range of reactions that arynes undergo. In our laboratory we investigated transformations of nitrogen-containing heterocycles, having pyrroline or tetrahydropyridine motif in their core with dehydrobenzene and derivatives thereof. It was found that isoindolines bearing hydroxymethyl group at C-4 position react with arynes with the formation of phthalans **1** in good yields. Unsubstituted dihydroisoindoles in the same conditions gave only salts **2** in moderate yields. The similar behavior was observed for tetrahydroisoquinolines (salts **4**). Surprisingly, thienopyrrolines underwent an unusual cascade of ring-opening/1,6-H shift/4 $\pi$ -electrocyclization furnishing thienylaziridines **3**. Tetrahydroisoquinolines bearing CH<sub>2</sub>COAr group at nitrogen atom reacted with dehydrobenzene with the formation of benzoazepines **5** as a result of Stevens' rearrangement. 10-Cyanosubstituted naphthiridines underwent 1,2-rearrangement giving products **6** in low yields. 10-Carbamoylsubstituted naphthiridines as well as fused pyridopyrimidines under the reaction conditions let to products of Hoffman cleavage **7** and **8**, correspondently. The products of formal acetonitrile insertion **9** were isolated from reactions of 3,4-dihydroisoquinolines with aryne, in some cases products of double aryne addition **10** were observed. The interaction of 1-arylsubstituted tetrahydroisoquinolines with arynes furnished fluorescent dihydroindolo[2,1-*a*]isoquinolinones **11** with high yields.



This work was financially supported in different times by President grant for young scientists MK-2367.2013.03, RFBR grants №14-03-00311, 16-33-00640 mol\_a, contract 02.a3.21.0008

## Pnycogenic, halogen and hydrogen bonds in (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(*para*-substituted phenyl)diazenes

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Mamedov I.G.<sup>1</sup>, Babaeva G.V.<sup>1</sup>, Nenajdenko V.G.<sup>2</sup>

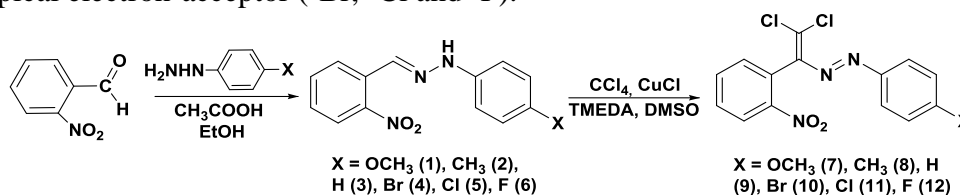
<sup>1</sup>*Faculty of Chemistry, BSU, Zahid Khalilov str, 23, Baku, AZ-1073/1, the Republic of Azerbaijan*

<sup>2</sup>*Faculty of Chemistry, Moscow State University named M.V. Lomonosov, Moscow, Russia,*

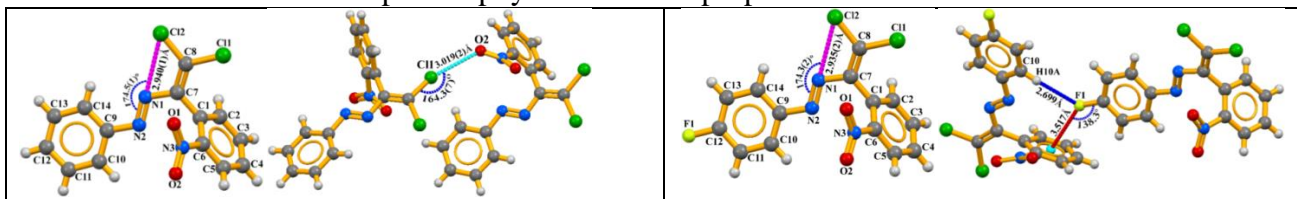
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In recent years, copper-catalyzed conversion of hydrazones to halogenated diazenes (catalytic olefination) has received an increased interest of researchers due to the mutual action of N = N and C = C conjugated bonds leading to chromophore properties. The intramolecular pnycogenic bond N ••• Cl can also contribute to N = N and C = C conjugation in diazene dyes and absorb a certain photon emission energy of visible light. Therefore, we decided to investigate systematically the structure-property dependence of the (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(*para*-substituted phenyl)diazenes series in the perspective of their intramolecular pnycogenic bond, also the strength of the intermolecular halogen bond. The *para*-substituents in the aromatic fragment range from typical electron-donor groups (-OCH<sub>3</sub> and -CH<sub>3</sub>) to typical electron-acceptor (-Br, -Cl and -F).



Single-crystal X-ray analysis of compounds **9** and **12** indicates intramolecular pnycogenic bonds N ••• Cl. Intermolecular halogen and hydrogen bonds also contribute to the stabilization of crystalline structures **9** and **12**. In a DMSO solution, compounds **1–12** exist in an *E*-isomeric form, which is stabilized by intra- and intermolecular non-covalent interactions. The solvatochromic behavior of the ultraviolet absorption spectra of azo dyes **7–12** was studied in CH<sub>2</sub>Cl<sub>2</sub>, DMF, and MeOH, which λ<sub>max</sub> depends on the *para* position of the attached substituent of the aromatic fragment. The results obtained may be useful for decorating new dyes and functional materials with improved physicochemical properties.



Molecular structures of (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-*p*-tolylidiazene and (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(4-fluorophenyl)diazene

*This work was carried out with the financial support of the Foundation for the Development of  
Science under the President of the Republic of Azerbaijan-Grant  
№EIF-BGM-4-RFTF-1/2017-21/13/4*

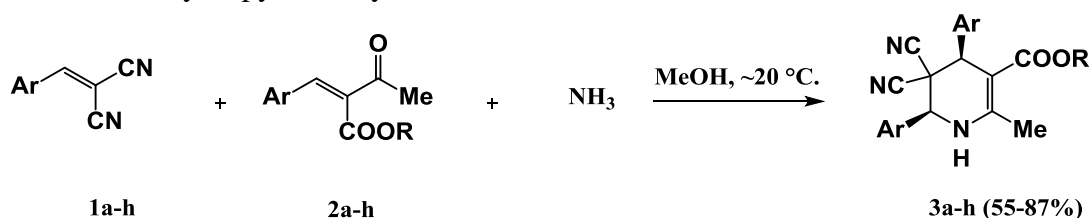
**Diastereoselective multicomponent synthesis of esters  
(4*RS*,6*SR*)-4,6-diaryl-2-methyl-5,5-dicyano-1,4,5,6-tetrahydropyridine-  
3-carboxylic acids**

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Tetrahydropyridine and its analogues, such as 1,4-dihydropyridine, piperidine and pyridine, have a wide range of biological and pharmaceutical properties. For example, it is well known that tetrahydropyridines are therapeutic agents for hypertension and angina pectoris [1,2], which also exhibit various types of pharmacological activity, including neuroprotection, non-competitive inhibition of topoisomerase I, anti-cancer activity and inhibition of HIV protease [3-5].

Three-component synthesis of substituted tetrahydropyridines from alkylidenemalonitriles, esters, 2-acetyl-3-aryl acrylic acids and aqueous ammonia as a nitrogen source for the tetrahydropyridine cycle has been carried out.



№	Ar	R	t/h	product	output %
1	Ph	Me	4	3a	79
2	4-MeC <sub>6</sub> H <sub>4</sub>	Et	8	3b	70
3	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	12	3c	66
4	4-FC <sub>6</sub> H <sub>4</sub>	Me	4	3d	78
5	2-ClC <sub>6</sub> H <sub>4</sub>	Me	4	3e	73
6	4-ClC <sub>6</sub> H <sub>4</sub>	Me	4	3f	72
7	4-BrC <sub>6</sub> H <sub>4</sub>	Me	4	3g	87
8	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me	2	3h	55

Conditions: Compound 1 (3 mmol), Compound 2 (3 mmol), ammonia (6 mmol, 25% aqueous solution), methanol (5 ml), stirring, room temperature. The course of the reaction was monitored by TLC (eluent — hexane — ethyl acetate, 5: 1).

*This work was supported by the Russian Science Foundation,  
project №. 17-73-20260*

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## New approaches to synthesis of C-substituted thiadiazines

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In a number of recent publications it was shown that six-membered heterocyclic compounds like thiadiazines, have the ability to block the process of blood aggregation [1-2].

In order to developing new approaches to such kind of compounds preparation, we have investigated the interaction of some urea derivatives with hydroxyl ketones.

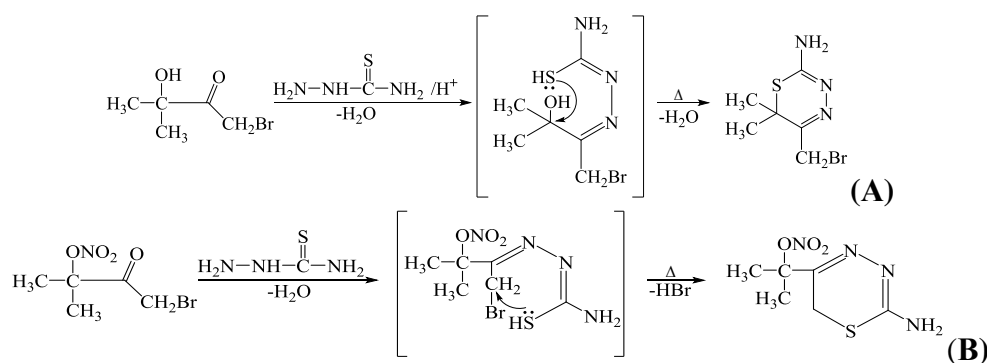
In our previous publication [3] was indicated that interaction of hydroxyketones with urea bi-nucleosides, in the intermediate stage, leads to formation of hydrazones. The cyclization of hydrazones to thiadiazines took place spontaneously under the action of catalytic amounts of trifluoroxyacetic acid.

The data presented in this paper addressed to involving other reagents to this reaction. In this way we have examined interaction of bromine derivatives of hydroxyl ketones and their nitro esters with urea bi-nucleosides.

During usage of oxyketone nitroesters the reaction starts with attack by atom the sulfur of the thiol group into the bromine methylene group to form product (1b) and (1c). In case of implementation the oxyketone containing a bromomethylene group, reaction proceeds by two stages. At the initial stage, the formation of hydrazone is noted. Further, direction depends on whether hydroxyl group free or blocked by nitro group.

In first case the reaction proceeds under the action of catalytic amounts of trifluoroacetic acid to formation of cyclic product (A) with involving of the hydroxyl group. In second case isomeric cyclic thiadiazine (B) occurs by means of interaction thiol group with methylene bromide.

The received thiadiazines differ in chemical shifts of methylene protons 7.36 ppm for the cycle and 6.28 ppm for the exocyclic one.



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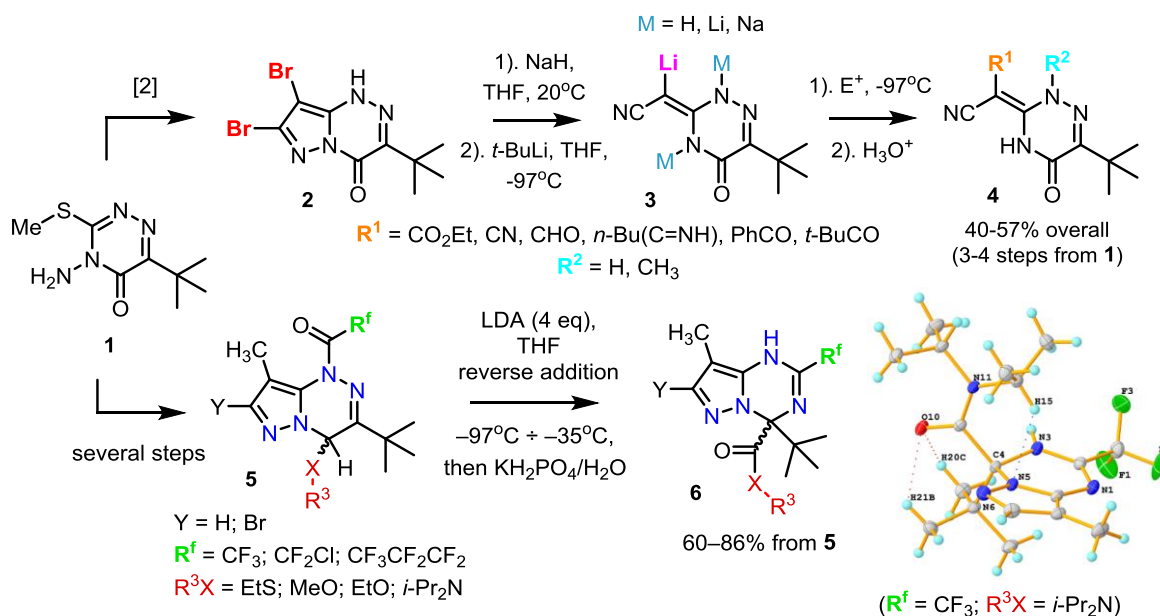
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## Low-temperature rearrangements of polymetalated species *en route* to highly functionalized 1,2,4- and 1,3,5-triazines

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The reactivity and transformations of metalated heterocycles represent an interesting yet still largely unexplored area of modern heterocyclic chemistry. In the present work, 1,7,8-polymetalated 3-*tert*-butyl-8-*R*-4-oxo-4*H*-pyrazolo[5,1-*c*][1,2,4]triazines have been generated for the first time using NH deprotonation and Li/Br exchange method at  $-112 \div -97^\circ\text{C}$ . The rapid ring opening degradation of the unstable 7-lithio-4-oxopyrazolo[5,1-*c*][1,2,4]triazines at  $-97^\circ\text{C}$  led to formation of 2-(6-*tert*-butyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2*H*)-ylidene)acetonitriles. Furthermore, lithium, sodium ((6-*tert*-butyl-5-oxo-5*H*-1,2,4-triazin-2,4-diid-3-ylidene)(cyano)methyl)lithium (**3**) was successfully generated from 7,8-dibromosubstituted derivative **2**, and an electrophile trapping using various electrophiles allowed the selective side-chain functionalization.



Hitherto unknown (3-*tert*-Butyl-4- $\text{R}^f$ -1- $\text{R}^3$ -1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazin-4-yl)lithiums were also generated from the corresponding 1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazines **5** and LDA at  $-97^\circ\text{C}$ . It was found that in the case of perfluorinated  $\text{R}^f$  substituents, the intermediate 4-lithio species underwent an unexpected complex rearrangement with formation of 4-*tert*-butyl-2- $\text{R}^f$ -1,4-dihydropyrazolo[1,5-*a*][1,3,5]triazine-4-carboxylic acid derivatives (**6**). The structures of the starting materials and the isolated products were established on the basis of IR, NMR, HRMS data and X-ray single crystal diffraction analysis.

*This work was supported by the Russian Foundation for Basic Research (grant № 18-33-00019)*

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## A new approach to selective synthesis of di- and triarylisoxazole scaffolds

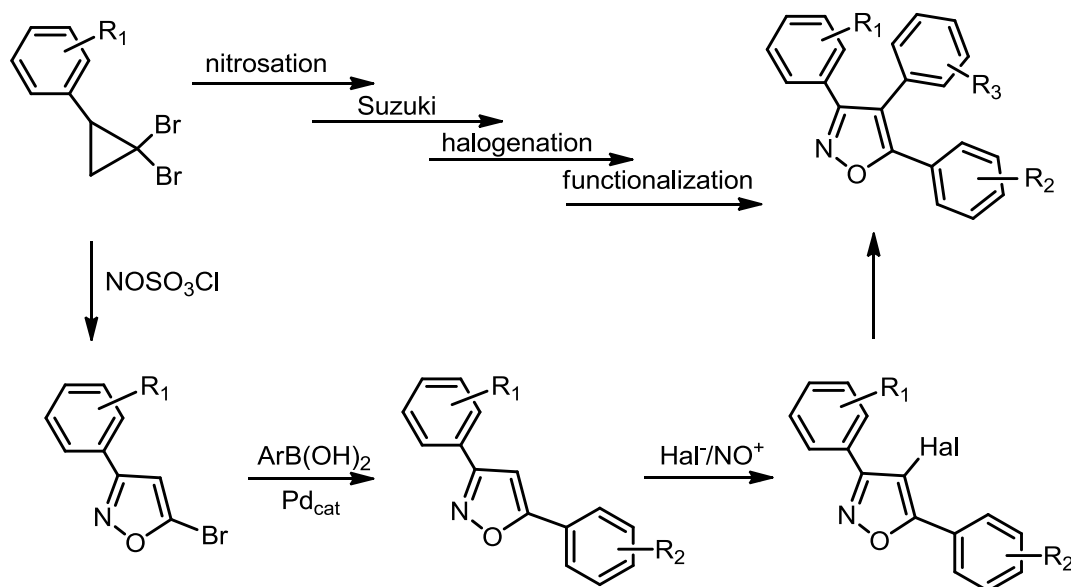
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Di- and triarylisoxazoles are applied as materials and pharmaceuticals. 3,5-Diarylisoxazoles are used as liquid crystals and light-harvesting systems due to their rigid structure [1,2]. They are also useful in a search for new therapeutic agents. Thanks to their usually low cytotoxicity, arylated isoxazole derivatives are popular scaffolds for the development of new agents with variable biological activities, such as antimicrobial, antiviral, anticancer, anti-inflammatory, immunomodulatory, anticonvulsant or anti-diabetic properties [3].

We have developed a new route for construction of non-symmetric di- and triarylisoxazole scaffolds based on the sequence of reactions including nitrosation of 2-aryl-1,1-dibromocyclopropanes followed by arylation of the formed 5-bromoisoxazoles using Suzuki cross-coupling reaction, halogenation of the resulting 3,5-diarylisoxazoles under nitrosation conditions and arylation/functionalization of the isoxazole ring at the final stage.



Advantages of the route:

- Available initials
- High regioselectivity at every stage
- Good to excellent yields of the products
- Opportunity of combinatorial synthesis

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-01109)

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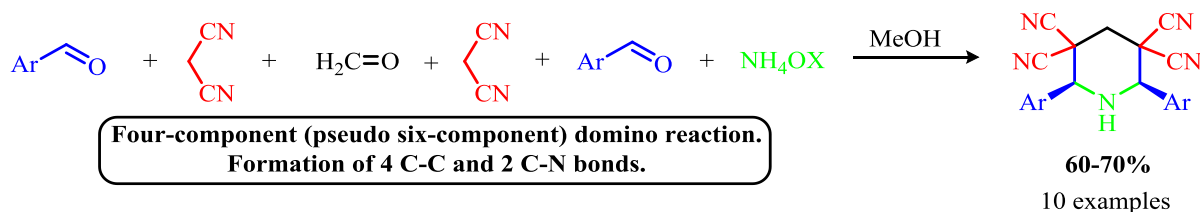
## Four-component stereoselective domino malononitrile, formaldehyde and substituted aromatic aldehydes: 'one-pot' efficient synthesis of 2,6-diaryl-3,3,5,5-tetracyanopiperidines

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Piperidine containing compounds have been used as synthetic drugs. There are derivatives of piperidine exhibiting antiviral activity (*N*-methyl-2,4,6-triphenylpiperidine is effective against smallpox virus) [1]. Also, there are derivatives of piperidine, having herbicidal effect [2]. Presently a few examples of synthesis of substituted piperidines is known in the literature [3, 4]. The development of cost-effective methods for the synthesis of piperidines is an actual problem of modern organic chemistry.

We have established that four-component (pseudo six-component) domino reaction of malononitrile, formaldehyde and aromatic aldehydes in the presence of ammonium acetate or ammonia hydrate in methanol results in to the formation of 2,6-diaryl-3,3,5,5-tetracyanopiperidines, with 60-70% yields:



The procedure found by us utilizes simple equipment; it is easily carried out and is valuable from the viewpoint of environmentally benign diversity-oriented large-scale processes. Final compounds do not require further purification and isolated by simple filtration followed by washing with a small amount of methanol.

*This work was supported by the Russian Science Foundation  
(RSF Grant 17-73-20260)*

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## Understanding the binding information of 1-imino-1,2-dihydropyrazino[1,2-*a*]indol-3(4*H*)-one with bovine serum albumin and 5-hydroxytryptamine receptor 1B using computational approach

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The present study was focused to understand the binding interaction mechanism of, a newly synthesized 1-imino-1,2-dihydropyrazino[1,2-*a*]indol-3(4*H*)-one compound in bovine serum albumin and 5-hydroxytryptamine receptor 1B using molecular docking and molecular dynamics simulation studies. The docking result shows that 1-imino-1,2-dihydropyrazino[1,2-*a*]indol-3(4*H*)-one compound have good binding affinity with both bovine serum albumin and 5-hydroxytryptamine receptor 1B microenvironment. Further, the best binding poses were taken for molecular dynamics studies and the dynamic result shows that the 1-imino-1,2-dihydropyrazino[1,2-*a*]indol-3(4*H*)-one compound was stable in both bovine serum albumin and 5-hydroxytryptamine receptor 1B complex system during the 50 ns simulation.

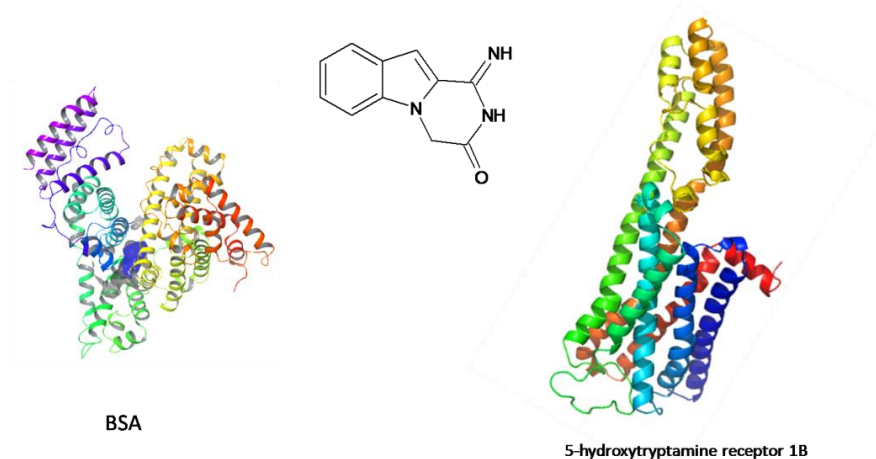


Figure shows 2D chemical structure of 1-imino-1,2-dihydropyrazino[1,2-*a*]indol-3(4*H*)-one compound with bovine serum albumin (BSA) and 5-hydroxytryptamine receptor 1B

## Methods for the synthesis of heterocycles bearing thietane ring

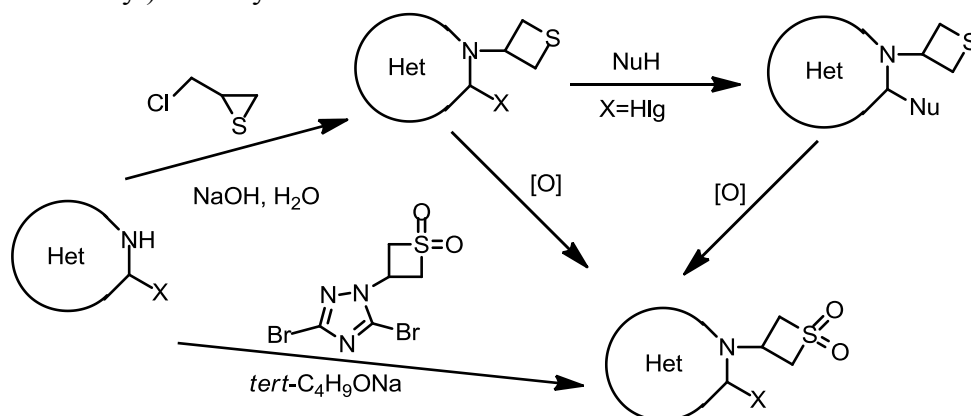
Khaliullin F.A., Klen E.E., Shabalina Yu.V., Makarova N.N., Valieva A.R., Sharipov I.M.

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Heterocycles are common fragments of the vast majority of marketed drugs and play the central role in modern drug design. However, derivatives of thietane have so far remained little-investigated compounds both in the sense of methods of preparation and with respect to biological activity. Introduction into heterocycles of thietane ring could considerably extend the potential of the resulting compounds as biologically active substances. Consequently, the development of efficient methods for the synthesis of heterocycles bearing thietane ring is one of the tasks of pharmaceutical chemistry.

In general, there are some major routes to synthesize the compounds bearing thietane ring: through cycloaddition of sulfenes to alkenes or enamines; through intramolecular cyclization of acyclic compounds; and through transformation of three-, four-, and five-membered rings. The last one is efficient and of general use.

We propose two methods to obtain heterocycles bearing thietane ring: first, via introduction of a thietane ring by alkylation of heterocycles with 2-chloromethylthiirane in aqueous medium in the presence of alkali [1]. The reaction is accompanied by thiirane–thietane rearrangement with formation of the corresponding N-(thietan-3-yl)-substituted heterocycles. Further modification of N-(thietan-3-yl)heterocycles by the action of nucleophiles allowed the synthesis of various derivatives, which also can be oxidized to thietane 1,1-dioxides. Another method for the introduction of a thietane 1,1-dioxide ring into heterocycles is based on the use of 3,5-dibromo-1-(1,1-dioxothietanyl-3)-1,2,4-triazole as the dioxothietanylation reagent [2]. It was found that reaction of the azoles with 3,5-dibromo-1-(1,1-dioxothietanyl-3)-1,2,4-triazole in *tert*-butanol in the presence of sodium *tert*-butoxide gave the N-dioxothietanylation products N-(1,1-dioxothietan-3-yl)heterocycles.



Het = xanthinyl, 1,2,4-triazolyl, imidazolyl, benzimidazolyl, pyrazolyl

It was shown that heterocycles bearing thietane ring exhibit antiaggregant, antidepressant, immunotropic and hypoglycemic activity and affect liver monooxygenase system and may be of interest as potential drugs.

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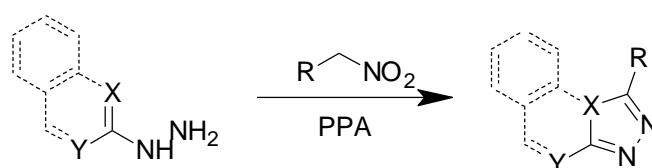
## Efficient synthesis of *N*-heterocycles via electrophilic activation of nitroalkanes

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Recently our research group has reported efficient synthesis of 1,3,4-oxadiazoles, containing different substituents in **2** and **5** positions via electrophilic activation of nitroalkanes in polyphosphoric acid and further cyclocondensation with acylhydrazides [1].

We wondered about the possibility of employing 2-hydrazinoquinoline and other heterocyclic hydrazines en route to [1,2,4]triazolo[4,3-*a*]quinolone scaffolds (Scheme 1). The reaction proceeds at 130 °C with high yields (60-99%).



X = O, S, N  
Y = Alk, (het)Ar, NH<sub>2</sub>, CH  
R = H, Alk, Ar,

Scheme 1.

The novel one-pot multistep reaction sequence involving cyclocondensation with nitroalkanes has been investigated.

*This work was financed by the Russian Foundation for Basic Research (grant # 18-33-20021 mol\_a\_ved) and President Grant for State Support of Young Scientists (grant # MK-3089.2018.3)*

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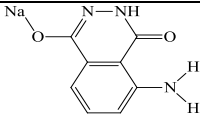
## Synthesis of the pharmaceutical substances 5-amino-1,2,3,4-tetrahydrophthalazin-1,4-dione sodium salt

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It is known that the sodium salt of 5-Amino-1,2,3,4-tetrahydrophthalazine-1,4-dione is an immunomodulator, it has an anti-inflammatory effect, due to the effect on the regulation of the function of cells of the monocytic-macrophage series, it also has antitumor effect. The properties of the substance are given in Table 1.

Table 1. Properties FS sodium salt 5-Amino-1,2,3,4-tetrahydrophthalazine-1,4-dione.

№	Name of indicator	Value
1	Structural formula	
2	Appearance	white powder
3	Name by IUPAC	5-Amino-1,2,3,4-tetrahydrophthalazine-1,4-dione sodium salt
4	Empirical formula	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub> N <sub>3</sub> Na
5	Molecular weight, g/mol	199,14
6	Content of the basic substance, not less than, %	99,0
7	Melting point	above 300 <sup>0</sup> C

It can be obtained as, a result of a number of transformations of 3-nitrophthalic acid.

The most interesting stage is the last one - preparation of sodium salt 5-amino-1,2,3,4-tetrahydrophthalazine-1,4-dione (II) from 3-aminophthalic acid (I) hydrazide. Under the action of alkali, isomerization occurs, and the proton from nitrogen migrates to the oxygen atom of the carbonyl group, forming hydroxyl with very pronounced acidic properties, which forms the sodium salt, Fig 1.

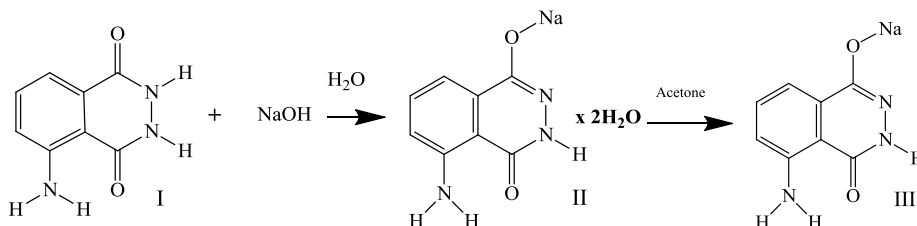


Fig 1. Preparation of anhydrous sodium salt of 5-amino-1,2,3,4-tetrahydrophthalazine-1,4-dione

Technical sodium salt of 5-amino-1,2,3,4-tetrahydropyrazin-1,4-dione crystallization of water in the form of the dihydrate gross formula C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>N<sub>3</sub>Na×2H<sub>2</sub>O (II) with a basic substance content of about 82 %, while the content of water of crystallization may be different in different batches, for example, due to its losses during the drying process.

Therefore, our task was to develop a method for producing a sodium salt substance 5-amino-1,2,3,4-tetrahydrophthalazine-1,4-dione (III) without crystallization water. This problem was successfully solved by crystallization of the substance in the presence of water-soluble organic solvent – acetone. It turned out that in this case another crystal form's, formed that does not contain crystallization water. Validation of the process of obtaining the substance was carried out, experimental and industrial designs were developed and the technical documentation necessary for the start of industrial production of this pharmaceutical substance was developed.

## Synthesis of organometallic compounds based on organosilicon bis- $\beta$ -diketones

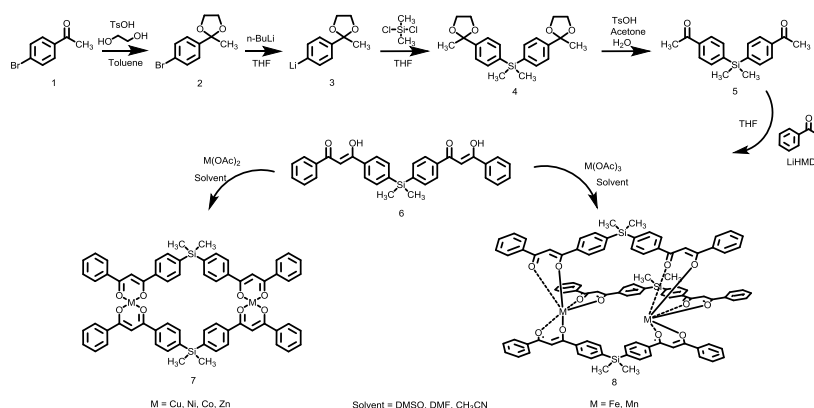
Kim E.E.<sup>a,b</sup>, Kononevich Yu.N.<sup>b</sup>, Korlyukov A.A.<sup>b</sup>, Volodin A.D.<sup>b</sup>, Muzafarov A.M.<sup>b</sup>

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The design and synthesis of complicated multidentate ligands for the creation of polynuclear complexes with predetermined functions or structures occupy an increasingly prominent place in coordination chemistry [1]. This approach has become common practice in such wide contexts as bioinorganic modelling, photochemistry, or molecular devices. Various ligands with distinct geometries and coordination modes have been designed and the  $\beta$ -diketones have been proven to be qualified to construct the new supramolecular architectures. Among  $\beta$ -diketones there are multi-chelating species made of molecules that feature more than one  $\beta$ -diketone moiety within their structure. The progressive use of such ligands in coordination chemistry is leading to a growing family of supramolecular architectures that could have not been observed otherwise [2]. One of the interesting ligands of this type are bis- $\beta$ -diketones. The opportunity to control the shape, flexibility and functionality allows bis- $\beta$ -diketones to be excellent building units for the creation of cyclic structures as well as multiple-stranded helicates, MOF's, linear molecular platforms, coordination polymers and metallamacrocycles. Metallo-supramolecules have generated a great deal of interest due to their various interesting properties, among which the catalytic, magnetic and optical activity must be mentioned.

In this work, new bis- $\beta$ -diketone ligands based on organosilicon derivatives of dibenzoylmethane were synthesized and their interaction with transition metal ions was studied (Scheme 1).



**Scheme 1.** Synthesis of bis- $\beta$ -diketone ligand and complex compounds.

The structure of the obtained compounds was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopy, IR spectroscopy, mass spectrometry (ESI), elemental analysis and X-ray diffraction analysis.

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

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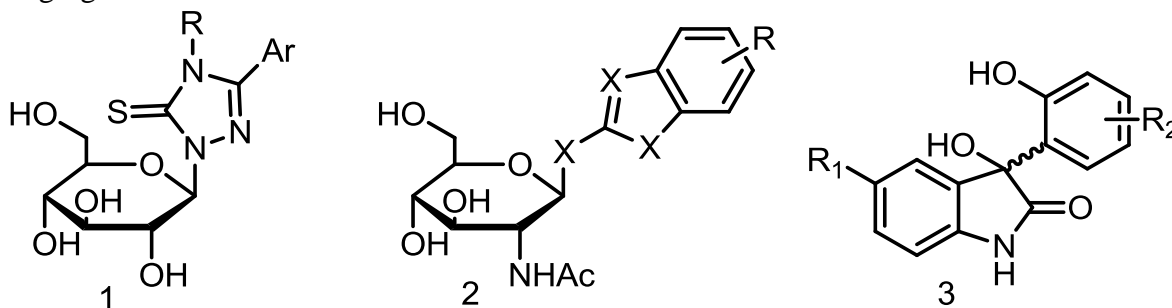
## New non-galactose ligands of the asialoglycoprotein receptor

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Asialoglycoprotein (ASGP) receptor is a promising target for delivery to hepatocytes of therapeutic and diagnostic agents. However, most of the literature to date works on targeted delivery using ASGPR, describes the ligands of carbohydrate nature based on galactose and galactosamine derivatives. The search for new selective ligands to the ASGP receptor is an important stage in the design of new promising targeted delivery systems [1]. In this paper, we consider potential synthetic approaches to ASGP receptor ligands that do not contain galactose fragments.

Based on the results of molecular docking and the study of binding to ASGPR by surface plasmon resonance [2], the following structural types of organic compounds were selected as promising ligands:



R = All, Bz, Ph

X = O, NH, S

In the presented work the search for synthetic approaches to compounds of these structural types for subsequent biological testing is carried out.

### References

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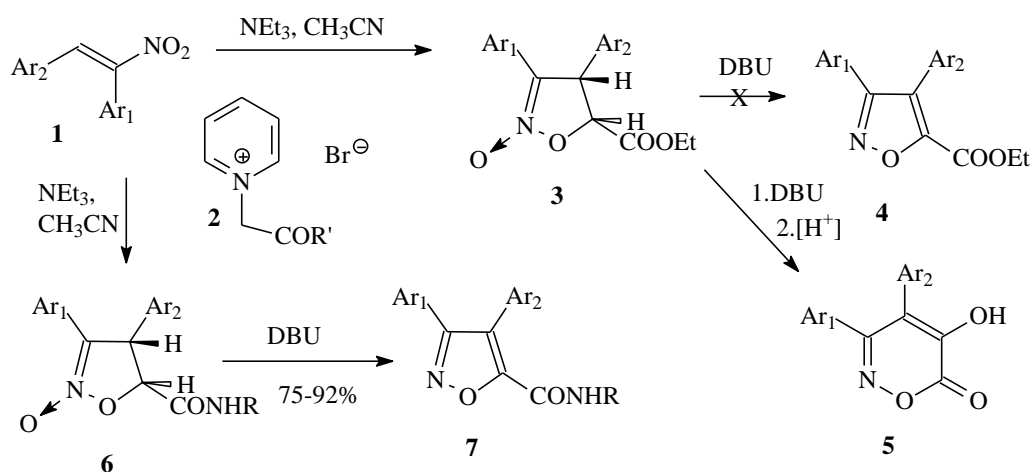
## Recyclization of isoxazoline-*N*-oxides into 3,4-diaryl-isoxazol-5-carboxamides and 5-hydroxy-3,4-diaryl-6*H*-1,2-oxazin-6-ones

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Some of *ortho*-diaryl-substituted isoxazole-3-carboxamides are showing considerable promise as inhibitors of chaperone heat shock protein 90 (HSP90) which is involved in the activation of different oncogenic ‘client proteins’ [1,2].

In this work, isoxazoline-*N*-oxides **3** and **6** were prepared by condensation of nitrostilbenes **1** and corresponding pyridinium salts **2** with yields 30-60%. Unexpectedly, recyclization of isoxazoline-*N*-oxides **3** leads to 5-hydroxy-3,4-diaryl-6*H*-1,2-oxazin-6-ones **5**; ethyl isoxazole-5-carboxylates **4** were not isolated from reaction mixtures. A 1,2-oxazin-6-one core structure was established by single-crystal XRPD. Amides of 3,4-diaryl-isoxazole-5-carboxylic acids **7** were obtained by recyclization of isoxazoline-*N*-oxides **6** under basic conditions in high yields.

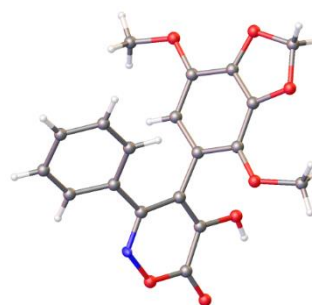
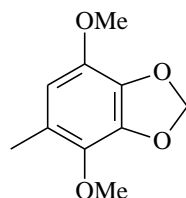


R'=OEt, NHR.

R=H; Et; CF<sub>2</sub>ClO-Ph; BrPh; (MeO)<sub>2</sub>PhCH<sub>2</sub>CH<sub>2</sub>

Ar<sub>1</sub>, Ar<sub>2</sub>= Ph; 4-MeOPh; 3,4-(MeO)<sub>2</sub>Ph;

3,4,5-(MeO)<sub>3</sub>Ph; 2,4-(MeO)Ph;



### References

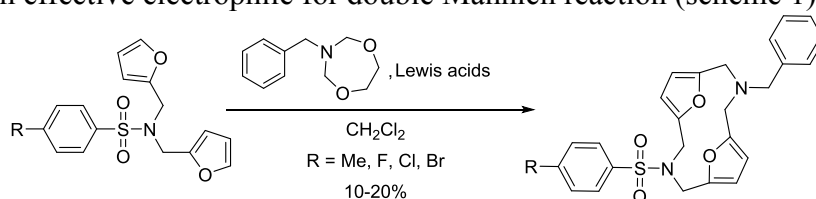
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## Novel small macrocycles on the basis of *bis-furfurylsulfamides*

Kletskov A.V., Zubkov F.I., Grudova M.V., Mertsalov D.F., Chervyakova L.V., Zaytsev V.P.

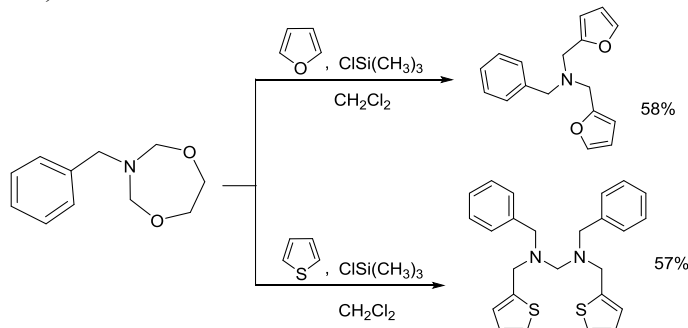
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The constant growth of interest in different macrocycles can be mainly explained by their broad scope of possible applications. Macrocycles were proven to be valuable bioactive substances [1] and complexing agents [2]. Among those, furan-containing macrocycles stand out as both valuable intermediates for the synthesis of other macrocyclic substances through convenient transformations, such as Diels-Alder reaction [3], as well as promising bioactive compounds [4]. Herein we report a novel approach to the synthesis of small furan macrocycles, containing pharmacophore arylsulfamides group based on the reaction of *N*-benzyl-1,5,3-dioxazepane – an effective electrophile for double Mannich reaction (scheme 1) [5].



Corresponding macrocycles are both promising as bioactive substances as well as intermediates in organic synthesis.

It's worth mentioning that on the initial stage of our research we found out that the reaction of *N*-benzyl-1,5,3-dioxazepane proceeds differently in the case of unsubstituted furan and thiophene (scheme 2).



We believe this peculiarity in case of reaction with thiophene will be further used as a basis for the synthesis of new thiophene ligands.

*This work was supported by the Russian Foundation for Basic Research (grant 19-03-00807 A)*

*The publication was prepared with the support of the "RUDN University Program 5–100"*

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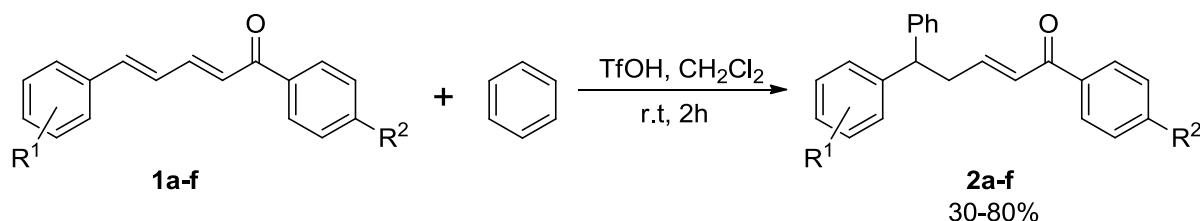
## Selective addition of arenes to C=C bond of 1,5-diarylpenta-2,4-dien-1-ones in TfOH

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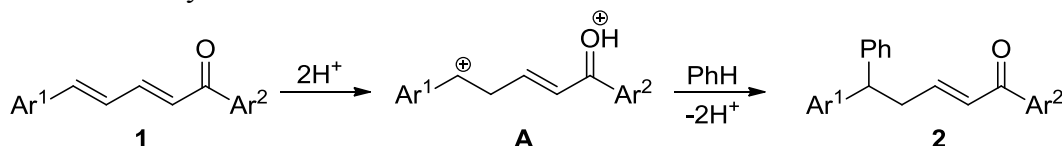
There are many addition reactions to compounds with unsaturated bonds nowadays. Actual problem in this chemistry is how to add selectively a reagent to only one double bond in conjugated dienes. 1,5-Diarylpentadienones **1** are important class of compounds. They are used in medicine as inhibitors of *M. tuberculosis*, tuberculosis pathogen, and as antibacterial agents against gram-positive types of bacteria [1].

In this work, reactions of dienones **1a-f** with arenes in superacid  $\text{CF}_3\text{SO}_3\text{H}$  (TfOH) were studied. It was found that dienones **1a-f** with benzene in TfOH at room temperature for 2h afforded products of hydroarylation of only one double bond **2a-f**.

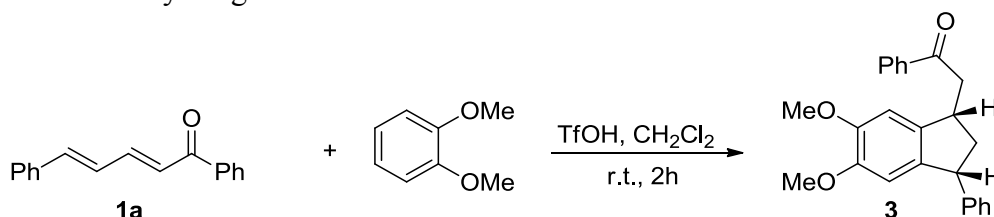


**1,2:**  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{H}$  (**a**),  $\text{Me}$  (**b**),  $\text{MeO}$  (**c**),  $\text{Br}$  (**d**);  $\text{R}^1 = 4\text{-Me}$ ,  $\text{R}^2 = \text{H}$  (**e**);  $\text{R}^1 = 2\text{-MeO}$ ,  $\text{R}^2 = \text{H}$  (**f**).

Plausible the reaction mechanism includes an intermediate formation of dication **A**, which were studied by DFT calculations.



Reaction of dienone **1a** with veratrole resulted in stereoselective formation of indane **3**, which was obtained as a result of hydroarylation of C=C bond followed by intermolecular cyclization into veratryl ring.



*This work was supported by the Russian Science Foundation  
(grant № 18-13-00008)*

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## Synthesis of hydroxamic acids with quinazoline moiety

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Khachatryan D.S.<sup>1</sup>

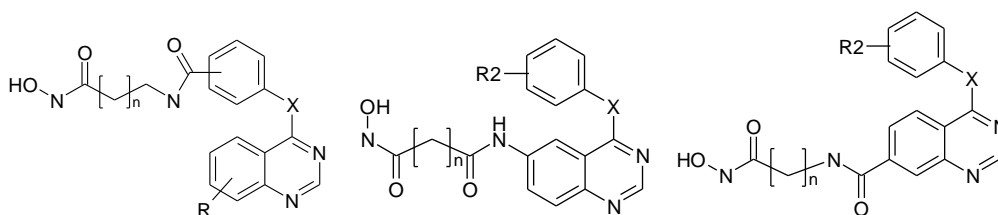
<sup>1</sup>NRC «Kurchatov Institute» – IREA, Bogorodsky val, 3, Moscow, 107076, Russia,  
<sup>2</sup>“NMRC of oncology N. N. Blokhin” of the Health Ministry of Russia, 115478, Moscow,  
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Chemistry of hydroxamic acids is an intensively developing area of synthetic organic chemistry. In medical chemistry, derivatives of hydroxamic acids are considered mostly as inhibitors of histone deacetylases, which are an important target in the treatment of cancer. [1].

The chemical flexibility of the hydroxamate group allows it to be introduced into various natural and synthetic compounds, as well as into known drugs [2, 3], which leads to a more pronounced therapeutic effect. Multi-purpose hybrids based on histone deacetylase inhibitors are becoming a new tool for anticancer therapy. [4].

The report discusses the strategy for creating bifunctional compounds by conjugating hydroxamic acids with a quinazoline moiety.

The results of work on the synthesis of new compounds containing hydroxamic acid and a heterocyclic fragment are presented.



The synthesized compounds are potential bifunctional antitumor agents acting on histone deacetylase and various tyrosine kinases.

*This work was supported by the Ministry of Education and Science of the Russian Federation, grant agreement № 075-11-2018-172 (RFMEFI62418X0051)*

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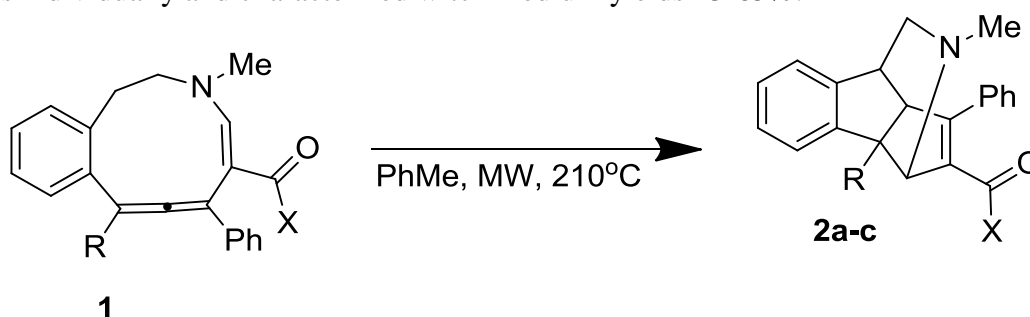
## The thermolysis of azacyclic allenes under microwave conditions

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Cyclic allenes with azaheteroatom in the cycle are the rare compounds. In the literature there are only a few examples [1, 2]. The ten-membered allene systems are stable at room temperature. However, when heated, the allenes show the ability to dimerize. Having a sufficient amount of the initial benzo-[d]-3-aza-cyclodec-4,6,7-trienes **1**, we studied their thermal transformation into complex framework structures - compounds **2**.

Epiminomethane cyclopentaindenes **2** are formed from azacyclic allenes **1** by the microwave activation in boiling toluene at 180 °C. The products were isolated from the reaction mixtures individually and characterized with medium yields 43-65%.



**R = Ph**  
**2a** : X = OMe (59%)  
**2b** : X = Me (65%)  
**R = i-Pr**  
**2c** : X = OMe (43%)

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## Synthesis and studies of photophysical properties of phenyl-substituted palladium pyrazinoporphyrazine

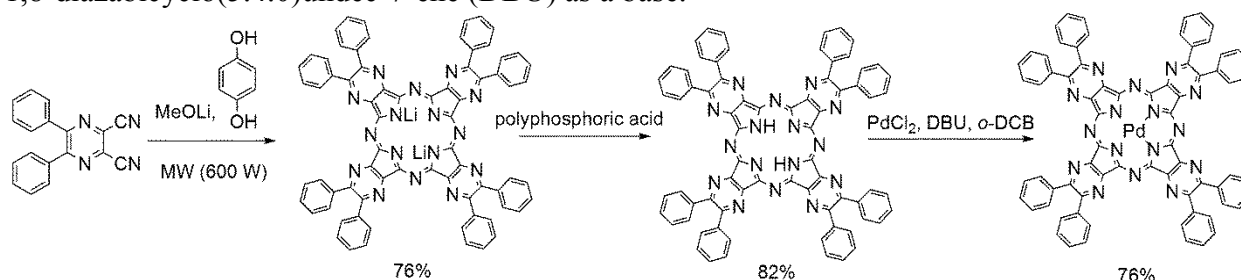
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Tetrapyrazinoporphyrazines and their metal derivatives are the most widely studied class of azaanalogues of phthalocyanines. However, the photophysical properties of their complexes with platinum group metals were not studied in such detail as, for example, the properties of their phthalocyanine and porphyrin analogs.

Effective approach to phenyl-substituted palladium tetrapyrazinoporphyrazine was developed. Firstly, dilithium complex was obtained from 5,6-diphenylpyrazine-2,3-dicarbonitrile using template method under microwave (MW) irradiation. *p*-Hydroquinone was employed as a reaction medium and as a reducing agent in the process of porphyrazine macrocycle formation. Then dilithium complex was demetallated by freshly obtained polyphosphoric acid. Target palladium complex was obtained from porphyrazine ligand in a boiling *o*-DCB in a presence of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as a base.



The yield of target complex was 76%. All compounds were identified by <sup>1</sup>H NMR, IR spectroscopy, MALDI TOF/TOF mass spectrometry and UV/Vis spectroscopy.

It was observed, that palladium complex possesses phosphorescence at 298K with maximum at 681 nm. The lifetime of phosphorescence is 180–50 μs.

The quantum yield of singlet oxygen generation was determined using a chemical trap. Meso-tetraphenylporphine was used as a standard compound. 1,3-Diphenylisobenzofuran was used as a chemical trap. The calculated quantum yield is 0.35±0.05.

*We are grateful for financial support from the Russian Foundation for Basic Research (Grant No. 18-33-00519) and Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grants MK-3115.2018.3.)*

## Detailed FT-IR characterisations of charge transfer complexes: comparable IR studies of 1-methoxy-pyridine and 1-ethoxy-pyridine with 7,7,8,8-TCNQ

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Recently the research on the conducting materials has been quickly increasing. The design of the new chemical structures of semiconducting, conducting and superconducting materials that possess the requested properties is growing to be crucial for the important applications of these materials, such as electronic devices having super- and semi-conducting properties, solar energy storage etc. Furthermore, Charge Transfer Complexes play a significant role in the synthesis/analysis of different pure forms of drugs and in pharmaceutical studies of drug's syntheses as well as a lot of biological applications [1-3]. The discovery of Charge Transfer Complex (CTC) tetratiofulvalene / tetracyanoquinodimethane (TTF/TCNQ), showing a conductivity value of 100 S/cm at T= 50K, was highly significant for the research intensification and the technological applications of given complexes: a class of conducting materials including the complexes was formed to study them carefully and the topic of research on the heterocyclic N-Oxides with TCNQ has been given a great deal of attention. Much more this research has been progressing for the devices applications, as an important result, for example, in the Patent JP6296701B2 in 2018.

The new charge transfers complexes containing different heteroaromatic N-oxides: N-methoxypyridine, N-ethoxypyridine with 7,7,8,8-tetracyanoquinodimethane (TCNQ) were synthesized. The complexes were characterized by using UV-Vis and FT-IR spectroscopy, The strong sharp band ( $\lambda_{\max} = 395$  nm) [bathochromic shift] due to  $\pi$ - $\pi^*$  transition of the conjugated benzenoid rings was observed. The UV-visible spectrum of samples didn't show peaks at 743 nm and at 843 nm attributable to the ion-radical structure of 7,7,8,8-TCNQ. Thus, the samples resulted to be formed of one N-oxide molecule and two neutral molecules of 7,7,8,8-TCNQ. The FT-IR comparison studies of complexes of N-methoxy-pyridine and N-ethoxy-pyridine with 7,7,8,8-TCNQ were presented and discussed in detail.

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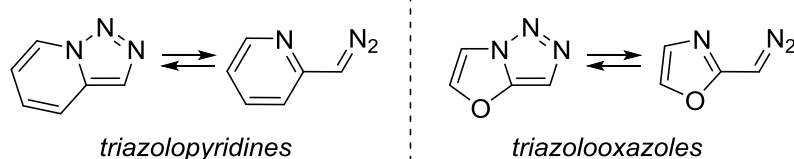
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## New synthetic approach to thio-substituted benzoxazoles based on domino-reactions involving fused triazoles

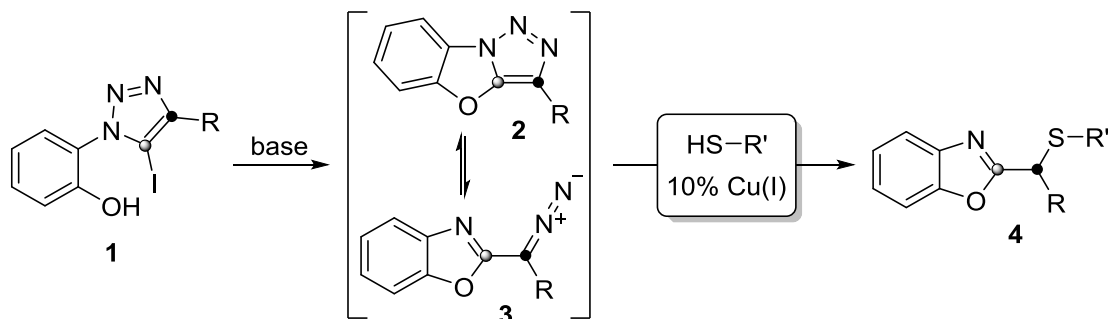
Kotovshchikov Yu.N., Kirillova E.A., Latyshev G.V., Lukashev N.V., Beletskaya I.P.

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Fused 1,2,3-triazoles represent an interesting class of heterocyclic scaffolds due to the known ring-chain equilibrium between the triazole and the corresponding tautomeric diazo imine. This equilibrium is inherent for those fused triazoles, which produce stable aromatic heterocycles with relatively non-nucleophilic nitrogen upon electrocyclic ring opening. In particular, triazolopyridines were successfully employed as convenient diazo surrogates in several useful transformations [1]. Nevertheless, the synthetic utility of a similar equilibrium in the case of other fused triazoles was so far illustrated only by rare and not general examples.



Recently we have utilized readily available 5-iodo-1,2,3-triazoles as convenient and stable diazo precursors [2]. We have shown that annulation of a new aromatic ring to 1,2,3-triazole shifts tautomeric equilibrium from fused triazole (**2**) to highly reactive diazobenzoxazole (**3**). In the present study we optimized conditions for the Cu-catalyzed thiolative trapping of the *in situ* generated diazo intermediates. As a result an efficient protocol for the preparation of thio-substituted benzoxazoles (**4**) has been proposed.



This work was supported by RFBR (grant № 18-33-01024 mol\_a)

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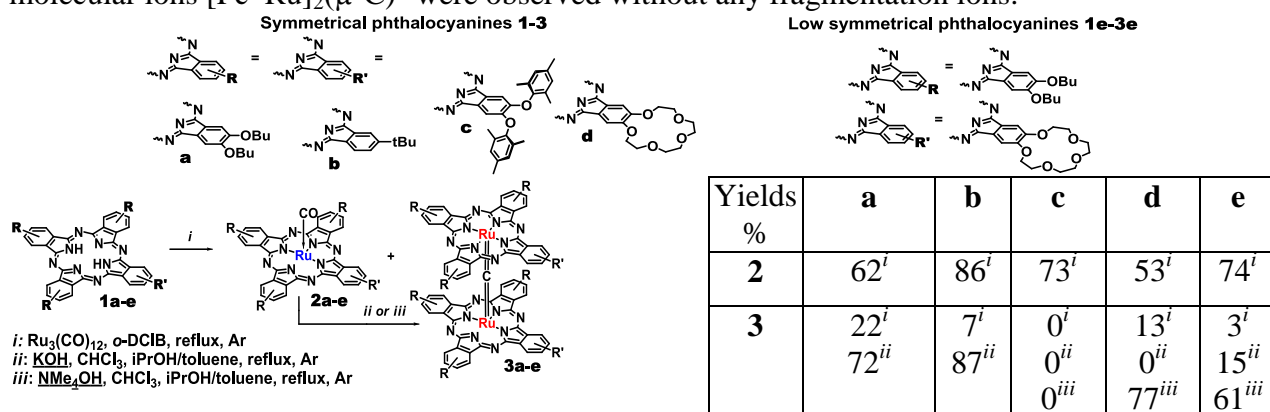
## Synthesis and characterization of novel mono- and binuclear ruthenium phthalocyaninates

Kroitor A.P.,<sup>a</sup> Pytskii I.S.,<sup>b</sup> Martynov A.G.,<sup>b</sup> Gorbunova Yu.G.,<sup>b,c</sup> Tsivadze A.Yu.<sup>b,c</sup>

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<sup>b</sup> A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninskii pr., 31, bldg. 4, Moscow, 119071, Russia; <sup>c</sup> N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Leninskii pr., 31, Moscow, 119991, Russia;  
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Ruthenium phthalocyaninates reveal numerous unique properties valuable for practical applications, such as catalytic activity and nonlinear optics. Recently on the example of octa-*n*-butoxyphthalocyanine **1a** we have shown that its metalation with Ru<sub>3</sub>(CO)<sub>12</sub> in refluxing *o*-dichlorobenzene (*o*-DCIB) yielded monomeric Ru(II) complex [(BuO<sub>8</sub>PcRu)(CO) – **2a** accompanied with the unexpectedly formed binuclear Ru(IV) complex with μ-carbido-bridge - [(BuO<sub>8</sub>PcRu)<sub>2</sub>(μ-C) – **3a** which revealed catalytic activity in carbene transfer reactions.<sup>[1]</sup> Extension of this approach to other phthalocyanines **1b-e** afforded new monomeric and dimeric complexes, except the case of mesityloxy-substituted phthalocyanine **1c** which yielded solely monomeric complex **2c** because of sterical hindrance which precluded formation of carbido-dimer **3c**. Interaction of complexes **2a,b** with CHCl<sub>3</sub> in the presence of excess of KOH in refluxing isopropanol/toluene gave complexes **3a,b** in 87% and 72% yields respectively. However, under these conditions mono-crown-substituted complex **2e** yielded dimer **3e** only in 15% yield and tetra-crown-substituted complex **2d** did not form dimer **3d** at all, probably because of concurrent binding of K<sup>+</sup> ions with crown-ether rings. Therefore, we tried to use the base with noncoordinating cations – NMe<sub>4</sub>OH, which afforded complexes **3d** and **3e** in high yields – 61% and 77% respectively. Complexes were studied by MALDI-TOF mass-spectrometry. Complexes **2a-e** underwent decarbonylation upon laser desorption/ionization with the formation of [Pc\*Ru]<sub>2</sub><sup>+</sup> ions. Increase of laser power resulted in decrease of intensity of [Pc\*Ru]<sub>2</sub><sup>+</sup> ions and appearance of both monomeric ions [Pc\*Ru]<sup>+</sup> and [Pc\*Ru]<sub>3</sub><sup>+</sup> in the case of **2a,b,e** and tetramer [Pc\*Ru]<sub>4</sub><sup>+</sup> in case of **2b**. In mass-spectra of binuclear carbido-dimers only molecular ions [Pc\*Ru]<sub>2</sub>(μ-C)<sup>+</sup> were observed without any fragmentation ions.



This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-20187 mol\_a\_ved)

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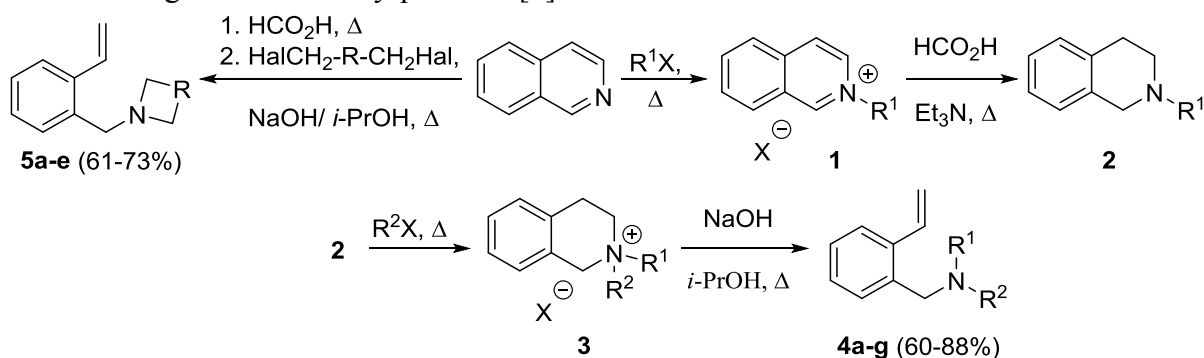
## An efficient approach to *N*-substituted 2-vinylbenzylamines for synthesis of the new generation of the Grubbs catalysts

Kumandin P.A., Raspersov P.V., Alekseeva K.A., Polyanskii K.B., Zubkov F.I.

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The assembly of the new catalysts of Hoveyda-Grubbs type possessing a six-membered ruthenium-containing ring with the N→Ru coordination bond, requires preliminary synthesis of *ortho*-vinylbenzylamines (**4**, **5**). However, for today, in the literature there are not suitable approaches for the synthesis of these styrenes. Therefore, this work describes a preparative scalable method for the preparation of vinyl benzenes from readily accessible reagents in good yields avoiding formation of by-products [1].



**Scheme:**  $\text{R}^1\text{X} = \text{Me}_2\text{SO}_4, \text{Et}_2\text{SO}_4$  or  $\text{BnCl}$ ;  $\text{HalCH}_2\text{-R-CH}_2\text{Hal} = \text{Br}(\text{CH}_2)_4\text{Br}, \text{Br}(\text{CH}_2)_5\text{Br}, (\text{ClCH}_2\text{CH}_2)_2\text{O},$

The synthesis of 2-vinylbenzylamines involves the following steps: alkylation of isoquinolines to afford isoquinolinium salts (**1**), its reduction to tetrahydroisoquinolines (**2**), which upon alkylation gave quaternary salts (**3**), finally these salts underwent the Hofmann elimination to form *N,N*-dialkylaminomethyl styrenes (**4**). The application of terminal dihalogen derivatives afforded styrenes **5** with a cyclic tertiary amino group.

Funding for this research was provided by the Russian Science Foundation (RSF) (project № 18-13-00456)

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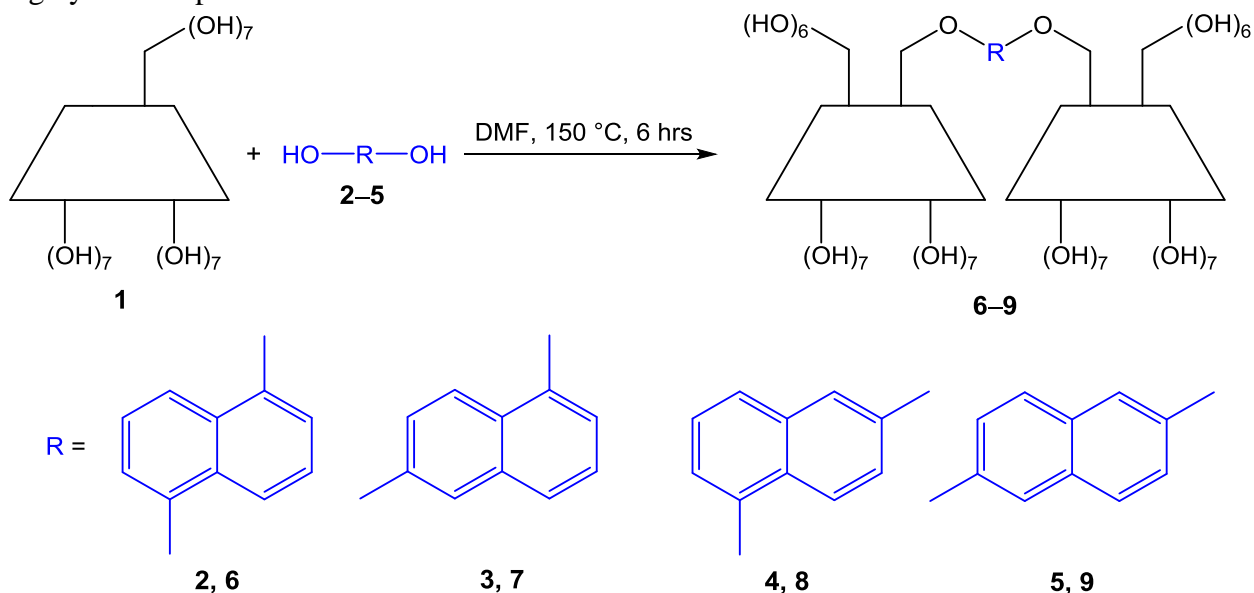
## Dimeric $\beta$ -cyclodextrin derivatives as molecular containers for drugs

Kutyasheva N.V., Emelianova E.Y., Bulkin S.A.,  
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Cyclodextrins (CDs) and some their derivatives have found wide practical application. In comparison with native CDs and monomodified CDs, dimeric CDs exhibit the significantly high binding abilities and molecular selectivity through the cooperative binding of two adjacent CD units [1]. Thus, dimeric CDs could be successfully utilized in carriers [2], solubilizers [3], catalysis [4], templated synthesis [5], photochemical materials [6, 7], etc.

In the present work we investigated a possibility of the direct reaction of  $\beta$ -cyclodextrin **1** with different dihydroxynaphthalenes **2–5** as linkers to obtain dimeric  $\beta$ -cyclodextrin derivatives. The syntheses were carried out in DMF using molecular sieves  $3\text{\AA}$  at  $150^\circ\text{C}$  for 6 h to receive in high yield compounds **6–9**.



The structure of compounds **6–9** were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR data. The correctness of the signals assignment of all obtained compounds **6–9** was additionally confirmed by the analysis of 2D NMR spectra of homo- (HOMOCOR  $\{^1\text{H}-^1\text{H}\}$ ) and heteronuclear (HETCOR  $\{^1\text{H}-^{13}\text{C}\}$ ) correlations and registering in the DEPT mode.

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## Synthesis of pyridines using reaction of linear conjugated enynones with malononitrile

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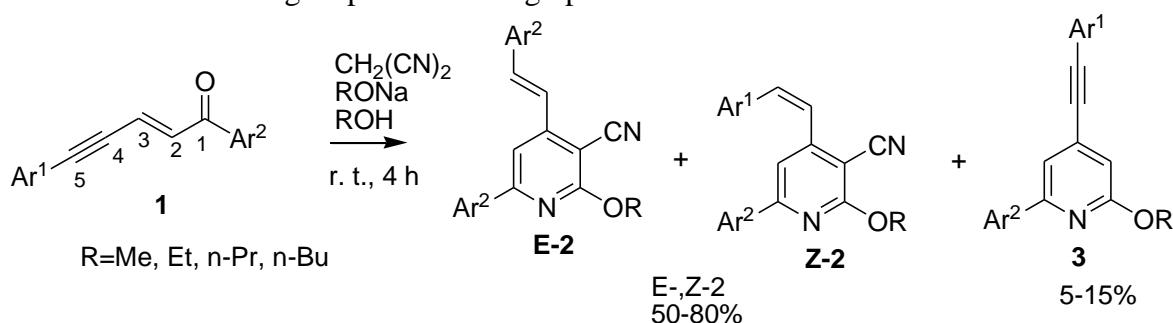
<sup>1</sup>Saint-Petersburg State University, Saint-Petersburg, Russia

<sup>2</sup>Togliatti State University, Togliatti, Russia

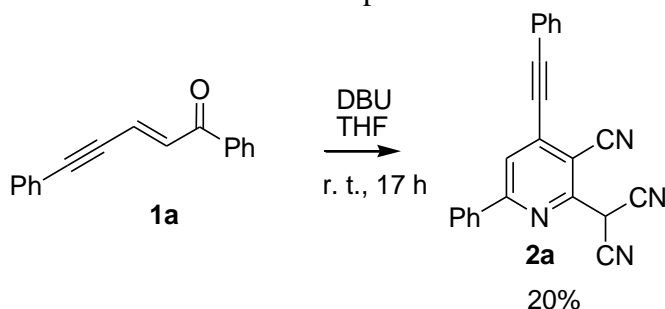
e-mail: kuznetsova.happy@yandex.ru

Linear conjugated 1,5-diarylpent-2-en-4-yn-1-ones **1** have three electrophilic centers on the carbon atoms C<sup>1</sup>, C<sup>3</sup>, C<sup>5</sup>. Nucleophilic attack may occur at any of these positions.

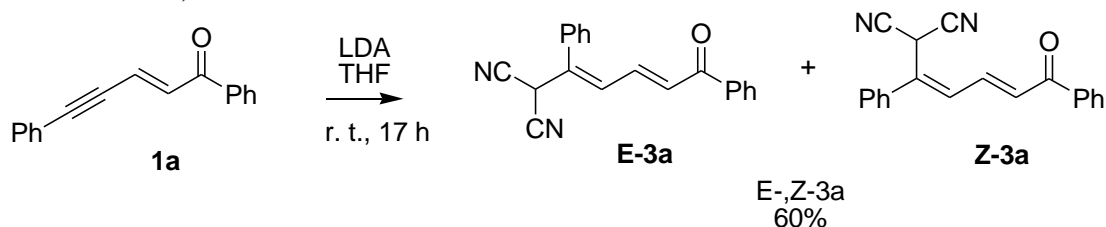
We found, that enynones **1** in reaction with malononitrile and sodium alcoholates, as a base, gave mixtures of (E)- and (Z)-2-alkoxy-6-aryl-4-(2-arylethenyl)pyridine-3-carbonitriles **E-2**, **Z-2** and 2-alkoxy-6-aryl-4-arylethynylpyridines **3**. Donor substituents in aryl ring attached to the carbonyl group increase the yield of reaction products. Compounds **2**, **3** are found to be unstable under the action of silicagel upon chromatographic isolation.



Enynone **1a** reacts with malononitrile in the presence of DBU leading to pyridine **2a**.



In the case of LDA, as a base, malononitrile addition occurs to the triple bond of **1a** with the formation of E-,Z-dienones **3a**.



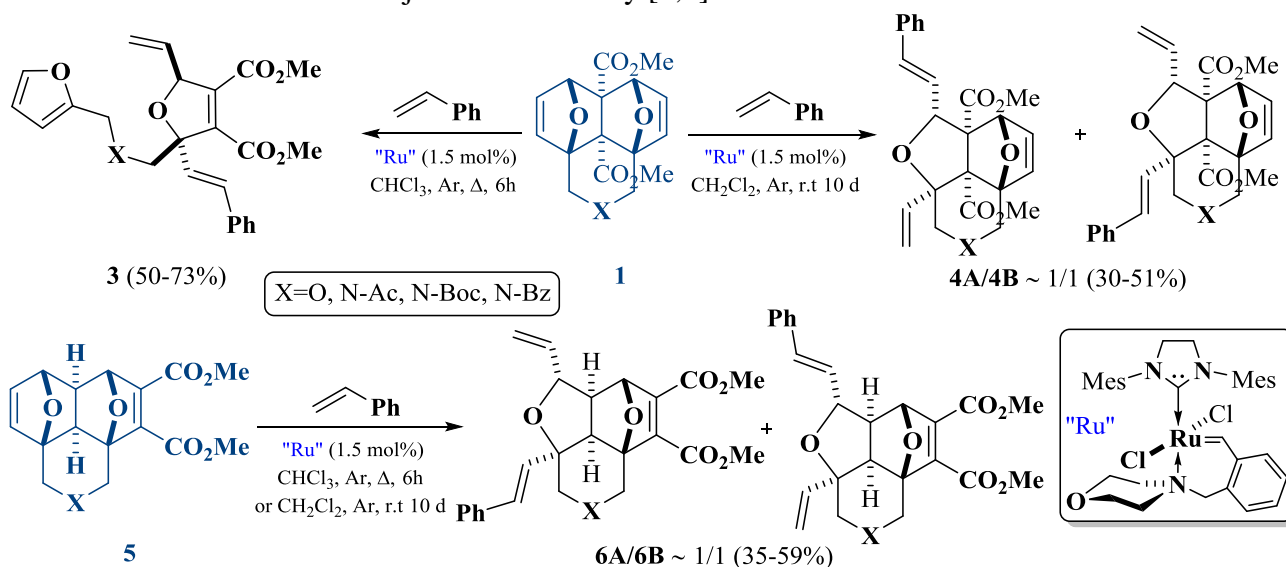
The work was supported by Russian Science Foundation  
(grant no. 18-13-00008)

## New type of Hoveyda-Grubbs catalysts for ROCM reactions of oxabicycloheptenes with styrene

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This work is devoted to the study of the catalytic activity of the new Hoveyda-Grubbs catalysts in ROCM (ring-opening cross metathesis) reactions [1]. Oxabicycloheptene systems **1** and **2** were chosen as model objects for this study [2,3].



It has been shown that the ROCM reaction of «pincer» adducts (**1**) with styrene is carried out at room temperature and leads to ring opening products **4** as a pair of distereoisomers in the ratio of 1: 1. Under heating, the same reaction is accompanied by the retro-Diels-Alder reaction leading to dihydrofurans **3**. In the case of «domino» adducts (**5**) we obtained ring opening products **6** both under heating and at room temperature.

Funding for this research was provided by the Russian Science Foundation (RSF),  
project № 18-13-00456

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## The influence of microenvironment on photochemical behaviour of betaine & amphiphilic styryl dyes

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In this work the styryl dyes behavior in environments of different polarity upon visible light irradiation is studied.

The research objects are styryl dyes derivatives **1-6** (fig. 1) differing in steric volume of aromatic fragment and length and charge of *N*-substituent. Sulfonatoalkyl compounds **1-4** show high solubility in water due to betaine structure, that allows to explore them in aqueous solutions. Dyes **5, 6** with a hydrophobic *N*-substituent can undergo intramolecular photocyclization as shown for analogues in [1].

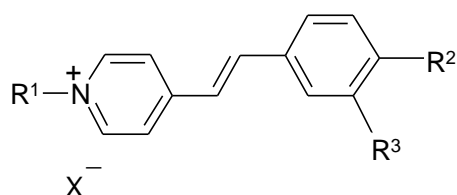


Fig. 1. Structures of dyes **1-6**

	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X
1:	(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	OMe	OMe	нет
2:	(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> <sup>-</sup>	OMe	OMe	нет
3:	(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>5</sub> O		нет
4:	(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> <sup>-</sup>	(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>5</sub> O		нет
5:	C <sub>18</sub> H <sub>37</sub>	OMe	OMe	ClO <sub>4</sub>
6:	C <sub>18</sub> H <sub>37</sub>	(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>5</sub> O		ClO <sub>4</sub>

Styryl dyes form stable inclusion complexes with cucurbit[7,8]urils of 1:1 and 2:1 ratio in aqueous solutions (fig. 2). We examined their stability and spectral properties.

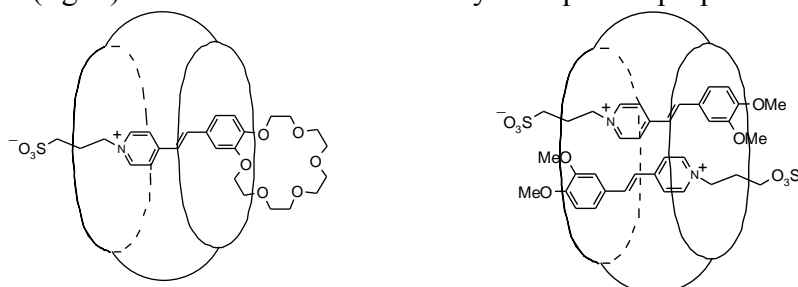


Fig. 2. **3**@CB[7] и **1**<sub>2</sub>@CB[8] complexes

Upon visible light irradiation inside cucurbit[8]uril cavity two dye molecules are able to undergo [2+2]-photocycloaddition [2]. The factors impacting this reaction's possibility to proceed were studied. Also it was determined that their hydrophobic analogues **5** and **6** undergo various phototransformations depending on environment.

*This work was supported by the Russian Foundation for Basic Research (grant 18-03-00214)*

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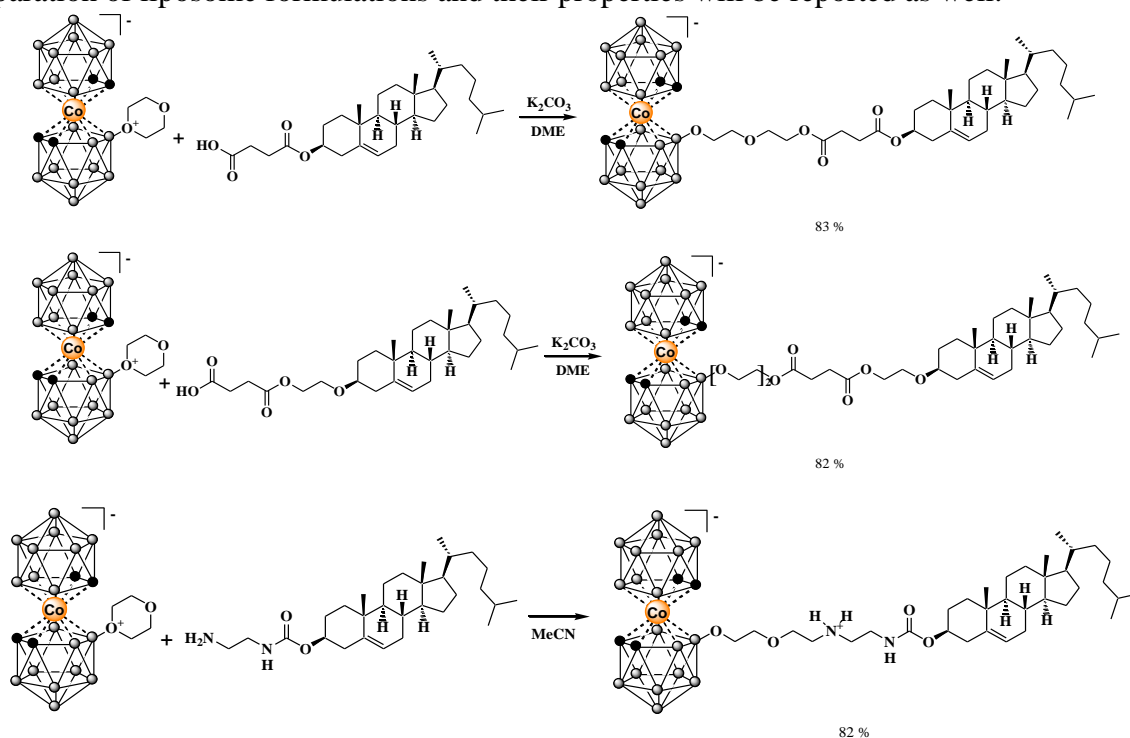
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## New macromolecular bioconjugates for boron-containing liposomes

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Boron neutron capture therapy (BNCT) is a binary method for the treatment of cancer which is based on the nuclear reaction of two essentially nontoxic species, nonradioactive  $^{10}\text{B}$  and low-energy thermal neutrons. Selective delivery and high accumulation of boron into the tumor tissue are the most important requirements for efficient BNCT [1]. Liposomes are the most efficient drug delivery vehicles as they can transport their contents to various tumors in a manner that is essentially independent of their contents and protect their contents from the action of external media, particularly enzymes and inhibitors. One way of introducing boron atoms into liposomes is to obtain boron-containing derivatives of cholesterol, which can be incorporated into the structure of lipid membranes. It is known that the 1,4-dioxane derivative of cobalt bis(dicarbollide) can react with different nucleophiles with the ring opening and formation of the corresponding derivatives [2]. We synthesized a series of new boron-containing cholesterols by the reactions of the 1,4-dioxane derivative of cobalt bis(dicarbollide) with modified cholesterols containing carboxylic and amine functional groups (Scheme 1). Preliminary results on preparation of liposome formulations and their properties will be reported as well.



Scheme 1

This work was supported by the Russian Foundation for Basic Research  
(grant № 17-53-80099)

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## Synthesis of 5,12-dihydroxynaphtho[2,3-g]quinoline-3-carboxylic acid

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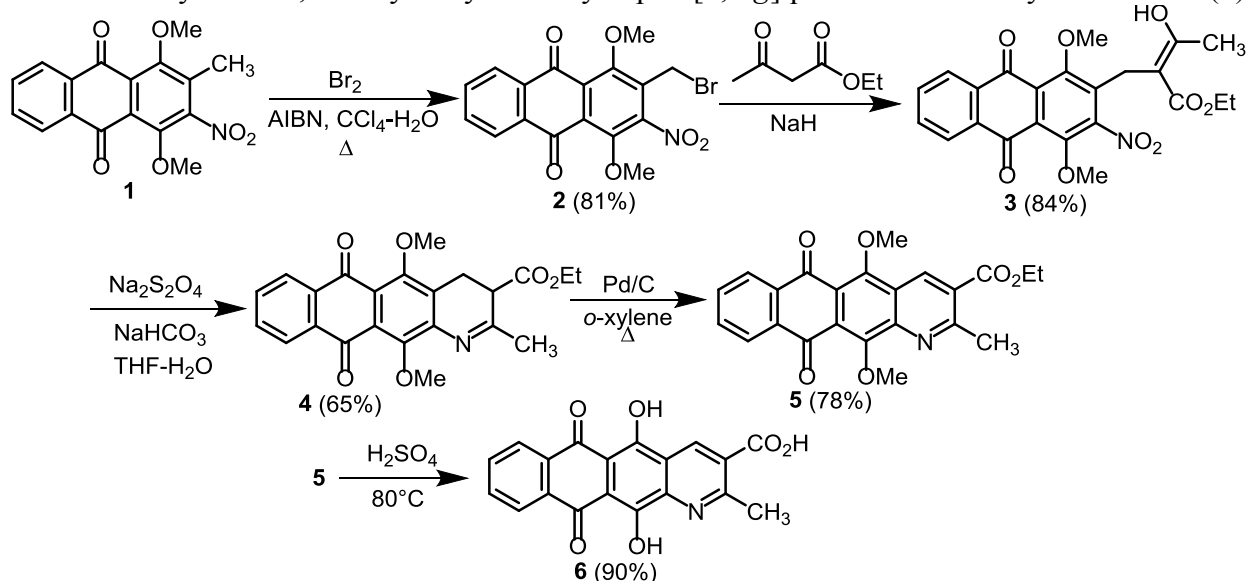
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Azole-fused derivatives of anthracene-9,10-dione represent a potent class for the development of new antitumor drugs [1,2]. In particular, 3-aminomethylnaphto[2,3-f]indoles and naphto[2,3-f]indole-3-carboxamides inhibit topoisomerase 1 and 2, demonstrating a high cytotoxic activity and effectiveness on animal models.

In continuation of the research, we expanded a heterocyclic core of indole to quinoline analogues to evaluate the effect of the heterocyclic nucleus on biological activity.

Previously obtained 2-methyl-3-nitroanthracene-9,10-dione **1** [2] was underwent radical bromination in the presence of AIBN to form product **2**. Then the acetoacetate ester was alkylated with a bromomethyl derivative of anthraquinone **2**. Reduction of the nitro group of compound **3** by sodium dithionite is accompanied by intramolecular heterocyclization to ethyl 3,4-dihydroquinoline-3-carboxylic acid **4**. Its further oxidation with Pd/C in xylene gives ester **5**. The ester group along with 4,11-methoxy groups were cleaved with concentrated sulfuric acid at 80°C to yield 4,11-dihydroxy-2-methylnaphto[2,3-g]quinoline-3-carboxylic acid (**6**).



The structure of the obtained compounds **2-6** was proved by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and high-resolution mass spectra. Currently, the synthesis of target naphtho[2,3-g]quinoline-3-carboxamides is carrying out.

*The study was performed with partial financial support from the Grants Council of the President of the Russian Federation for state support of young scientists in Russia (grant MK-2474.2018.3)*

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## Characterisation of metals in amine-thiol solution, for use in solution processed kesterite solar cells

Lowe J.C., Wright L.D., Togay M., Eremin D.B., Burykina Y.V., Ananikov V.P., Bowers J.W., Malkov A.V.

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Kesterite ( $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ ) solar cells are becoming increasingly popular due to their tuneable band gap, relative affordability of the constituent elements, and the ability to produce high efficiency devices from solution processes, however often expensive and toxic materials are used in production [0,0]. This has prompted further research into producing efficient kesterite solar cells from cheap and non-toxic materials.

Current kesterite solar cells with the highest efficiency used hydrazine as a solvent, which is highly toxic [0]. In an attempt to reduce the toxicity of the process, a variety of groups have shown that an amine-thiol solvent system can dissolve Cu, Sn, and Zn [3]. However, amine-thiol systems can still be highly toxic and malodorous. Therefore, kesterite solar cells from less hazardous amine-thiol solvents were sought after in order to improve commercial viability.

For our amine-thiol solvent system, cysteamine and ethanolamine were selected due to their relatively low toxicity and cost. The interactions between these solvents and the metal precursors were investigated by various techniques such as mass spectrometry, thermogravimetric analysis, and RAMAN spectroscopy. This furthered our understanding of the solvent system, enabling the optimisation of our current solvent system and also to discover new solvent systems that bond in a similar matter.

Through mass spectrometry the metal complexes formed in solution were discovered, it was shown that in the majority of cases two cysteamine molecules bound to the metals as bidentate ligands. The ethanolamine/cysteamine system was used to produce devices of up to 7.36% via spin coating.

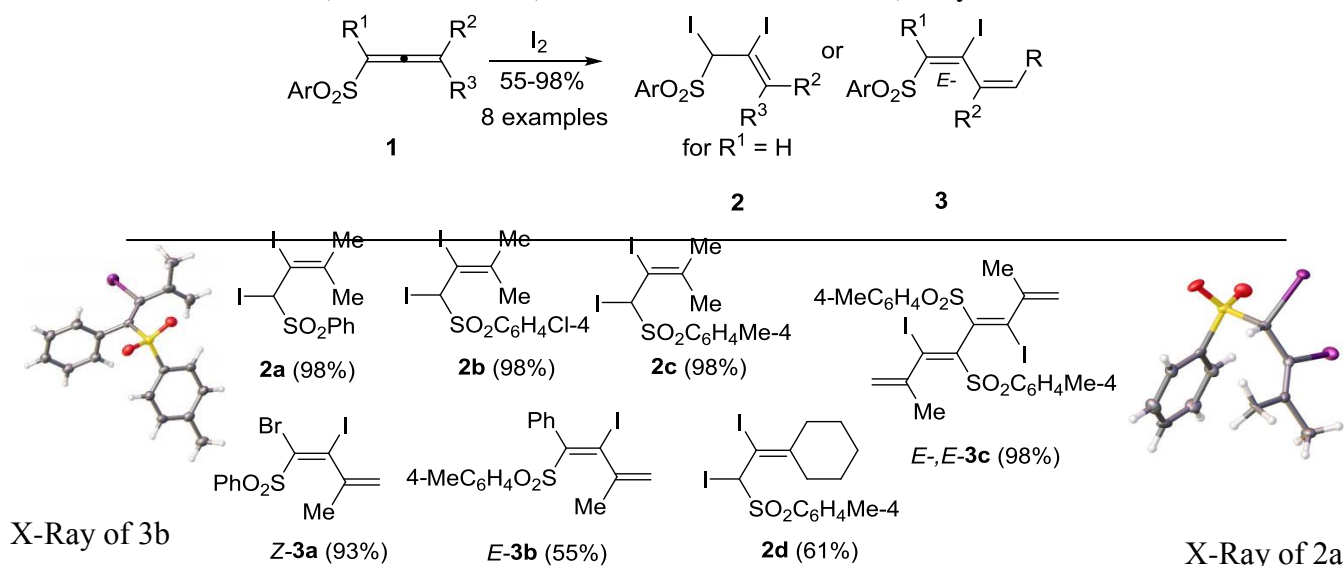
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## Unusual iodination of arylsulfonyl allenes

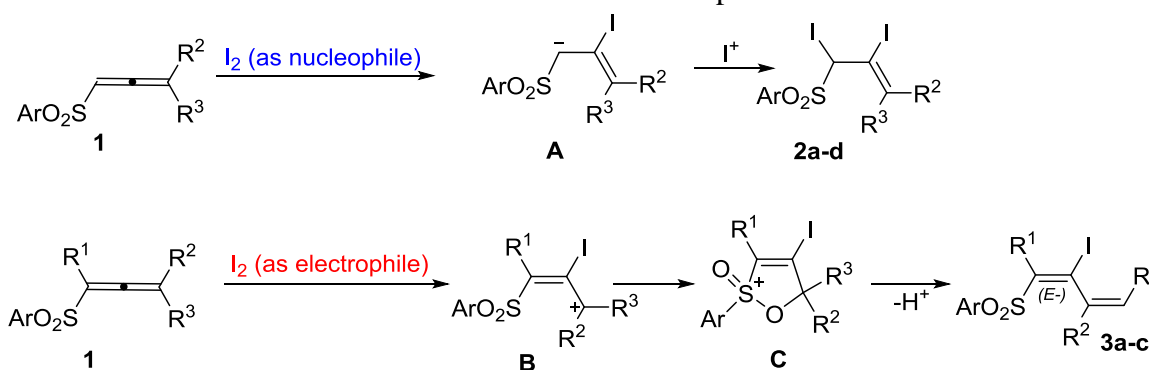
Lozovskiy S.V.<sup>a</sup>, Vasilyev A.V.<sup>a,b</sup><sup>a</sup>Department of Organic Chemistry, Institute of Chemistry, Saint Petersburg State University, Universitetskaya nab., 7/9, Saint Petersburg, 199034, Russia<sup>b</sup>Department of Chemistry, Saint Petersburg State Forest Technical University, Institutsky per., 5, Saint Petersburg, 194021, Russia

Arylsulfonyl allenes ( $\text{ArSO}_2\text{-CR}^1\text{=C=CR}^2\text{R}^3$ ), depending on their structure, react with iodine with the formation of two kinds of reaction products, diiodoalkenes ( $\text{ArSO}_2\text{-CHI-CI-CR}^2\text{R}^3$ , for  $\text{R}^1 = \text{H}$ ) or iododienes ( $\text{ArSO}_2\text{-CR}^1\text{=CI-CR}^2\text{=CHR}$ ), in yields of 55-98%.



We found, that the iodination of allenes **1** in solutions of  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  required heating in high pressure glass tube (Table 1). Diiodination took place into positions 1 and 2 of allenes **1**, having no substituents in position 1 of the allene triad, that led to the formation of diiodoalkenes **2**. On the other hand, 1-substituted allenes **1** reacted with  $\text{I}_2$  under milder conditions (entries 4-6,8) forming monoiododienes **3**.

Plausible mechanisms of iodination of allenes **1** are presented in Scheme 1



**Scheme 1.** Plausible mechanisms of reactions allenes **1** with iodine.

## The synthesis of spiro[thiazole-5,2'-pyrrol] spiro-heterocyclization of pyrrolbenzoxazinones under the influence of thiosemicarbazones of aromatic and heteroaromatic aldehydes

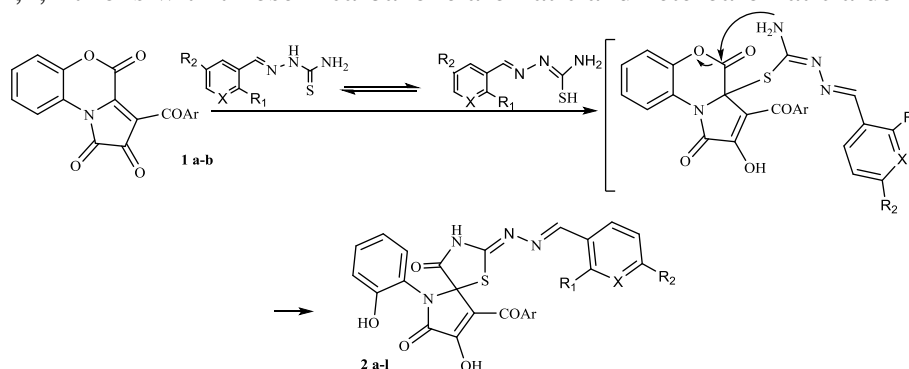
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An interest in such polyfunctional reagents as thiosemicarbazides and its derivatives is based on the fact that a great number of biologically active compounds can be found in its series.

On the interaction of thiosemicarbazides and its derivatives with polyelectrophilic substrates, currently it is possible to obtain derivatives of thiazoles, pyrazoles, thiadiazoles, triazoles, and other nitrogen-containing heterocycles, on the interaction of thiosemicarbazides and its derivatives with polyelectrophilic substrates.

We obtained spiro compounds **2 a-l** in the interaction of 3-arylpyrrole [1,2-c] [4,1] benzoxazin-1,2,4-trions with thiosemicarbazone aromatic and heteroaromatic aldehydes.

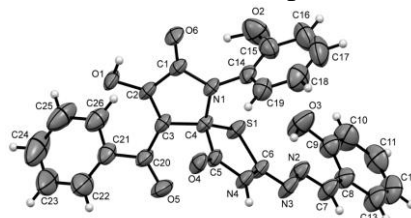


X = H, N;

**1:** Ar = Ph (**a**), C<sub>6</sub>H<sub>4</sub>Br-4 (**b**);

**2:** X=H, Ar = Ph, R<sup>1</sup> = R<sup>2</sup> = H (**a**); Ar= C<sub>6</sub>H<sub>4</sub>Br-4, R<sup>1</sup> = R<sup>2</sup> = H (**b**); Ar = Ph, R<sup>1</sup> = F, R<sup>2</sup> = H (**c**); Ar= C<sub>6</sub>H<sub>4</sub>Br-4, R<sup>1</sup> = F, R<sup>2</sup> = H (**d**); Ar = Ph, R<sup>1</sup> = OH, R<sup>2</sup> = H (**e**); Ar= C<sub>6</sub>H<sub>4</sub>Br-4, R<sup>1</sup> = OH, R<sup>2</sup> = H (**f**); Ar = Ph, R<sup>1</sup> = NO<sub>2</sub>, R<sup>2</sup> = H (**g**); Ar= C<sub>6</sub>H<sub>4</sub>Br-4, R<sup>1</sup> = NO<sub>2</sub>, R<sup>2</sup> = H (**h**); Ar = Ph, R<sup>1</sup> = H, R<sup>2</sup> = OH (**i**); Ar= C<sub>6</sub>H<sub>4</sub>Br-4, R<sup>1</sup> = H, R<sup>2</sup> = OH (**j**); X=N, Ar = Ph, R<sup>1</sup> = R<sup>2</sup> = H (**k**); Ar = C<sub>6</sub>H<sub>4</sub>Br-4, R<sup>1</sup> = R<sup>2</sup> = H (**l**).

The structure of the obtained compounds was confirmed by the data of IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and X-ray diffraction data for compound **2e**.



**Fig.1.** Compound **2e** structure

Nowadays, we are optimizing the conditions of the reactions of pyrrolbenzoxazine triones with thiosemicarbazones of aliphatic aldehydes.

*This study was performed under the financial support of the Government of Perm Krai, and the Russian Ministry of Education and Science (projects nos. 4.6774.2017/8.9, 4.5894.2017/7.8)*

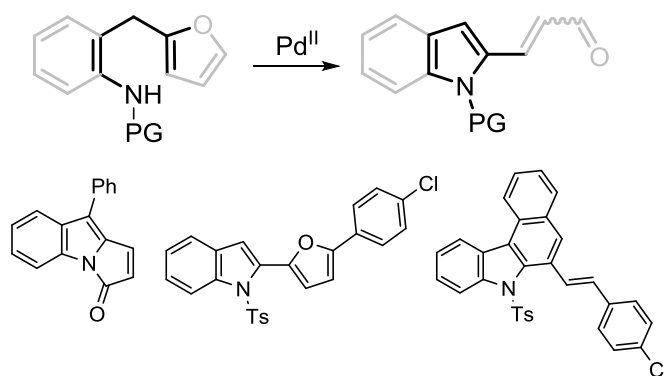
## Intramolecular oxidative amination of furans as convenient method toward substituted indoles

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Oxidative amination is known to be robust methodological solution for the straightforward synthesis of nitrogen-containing heterocycles. Originally, the first reported application of oxidative amination appeared to be the synthesis of indole derivatives [1].

Low aromatization energy of the furan ring is responsible for unordinary chemical reactivity. In particular, the furan ring may serve as a carbon-carbon double bond equivalent, thereby exhibiting typical chemical behavior of an olefin. We rationalized that benzylfurans could imitate the reactivity of *ortho*-allylaniline in oxidative amination conditions providing indole derivatives possessing highly reactive enone fragment.



Scope and limitations of the developed method, as well as synthetic potential of obtained products will be discussed.

*This work was supported by Ministry of education and science of the Russian Federation (project № 4.5371.2017/8.9) and the Russian Foundation for Basic Research (grant number 16-03-00513)*

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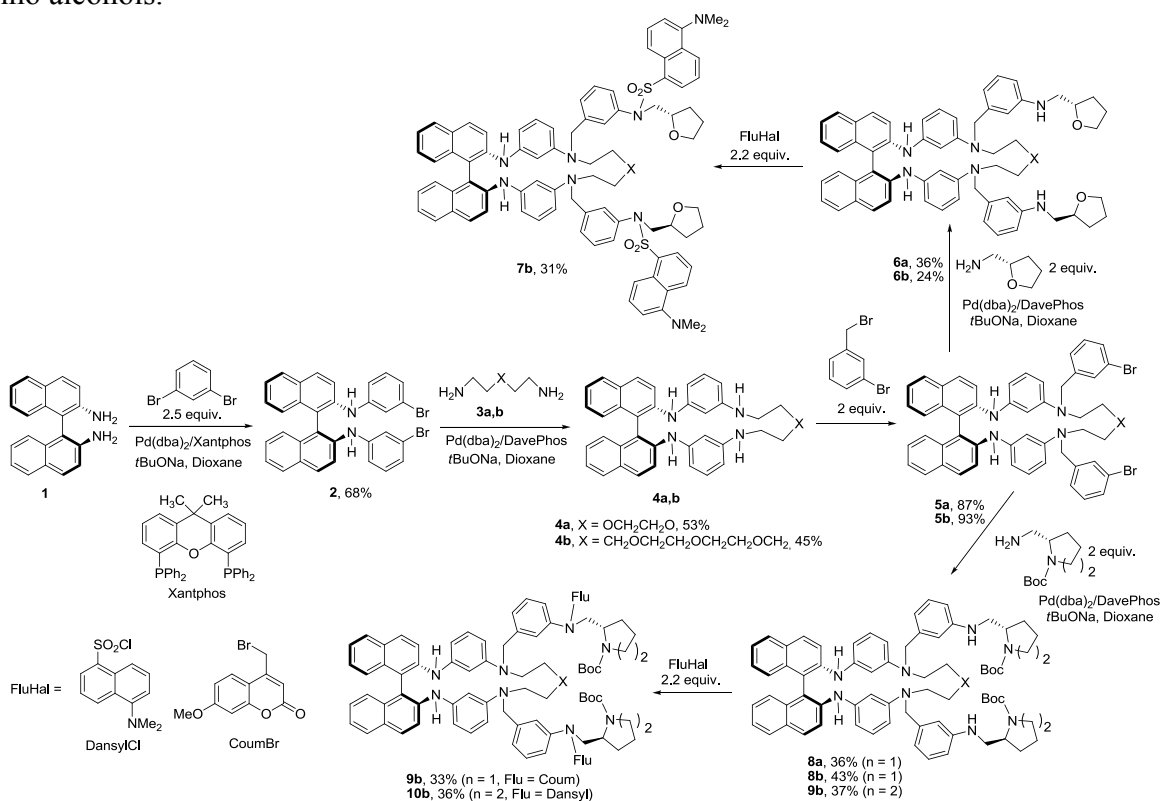
# BINAM-based macrocycles and macrobicycles and fluorescent detection of chiral amino alcohols

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The development of fluorescent enantioselective detectors is highly demanded by a need to elaborate simple, efficient and veritable methods of identification of enantiomers as their role in modern chemistry and industry has been steadily increasing. We developed a general method for the synthesis of macrocycles **4** comprising an endocyclic C2-chiral structural fragment of 2,2'-diamino-1,1'-binaphthalene (BINAM) which also possesses useful fluorescent properties [1]. These macrocycles can be easily synthesized in two steps using Pd(0)-catalyzed amination reactions from (*S*)-BINAM **1** via *N,N'*-di(3-bromophenyl)derivatives **2**. Further these compounds were modified with 3-bromobenzyl substituents and macrocycles **5** were introduced in the Pd(0)-catalyzed amination with chiral amines to give macrocycles **6** and **9** possessing chiral podand groups. These molecules were decorated with exocyclic strong fluorophore groups like dansyl and 7-methoxycoumarin which contain additional coordination site. The resulting compounds **6-10** were investigated as fluorescent enantioselective detectors for a series of optically pure amino alcohols.



This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00709)

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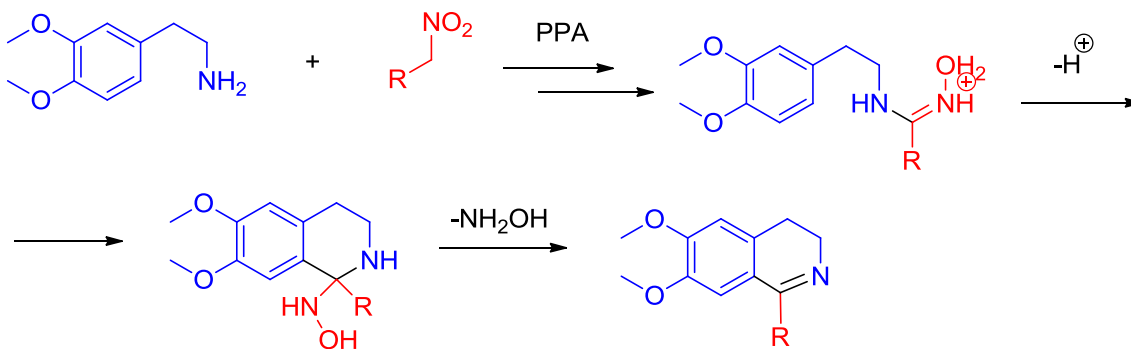
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## Synthesis of 3,4-dihydroisoquinolines using nitroalkanes in polyphosphoric acid

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A new method for the synthesis of 6,7-dimethoxy-3,4-dihydroisoquinoline based on the reaction of 2-(3,4-dimethoxyphenyl)ethan-1-amine (homoveratrylamine) with aliphatic nitro compounds in polyphosphoric acid (PPA) was developed (Scheme 1).



R = H, Me, Et, Ph, C<sub>7</sub>H<sub>15</sub>, PhCH<sub>2</sub>

Scheme 1.

6,7-dimethoxy-3,4-dihydroisoquinoline, containing different substituents in 1 positions was synthesized via electrophilic activation of nitroalkanes in polyphosphoric acid and further cyclocondensation with 2-(3,4-dimethoxyphenyl)ethan-1-amine.

*This work was financed by the Russian Foundation for  
Basic Research (grant № 19-03-00308 a)*

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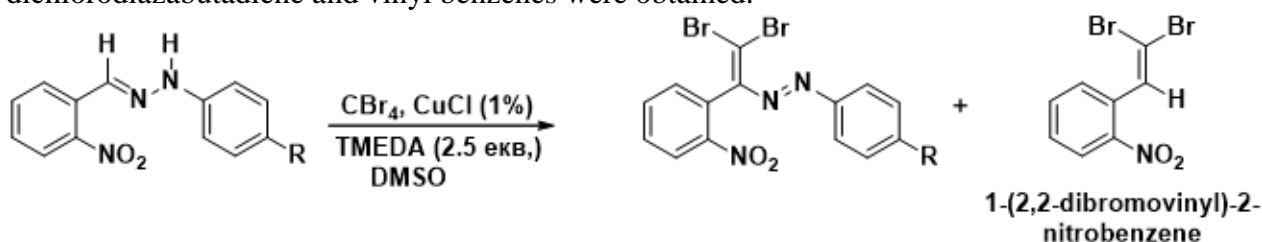
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## Synthesis based on hydrazones of *o*-nitrobenzaldehyde

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As well known, hydrazones are very popular compounds as synthons in organic synthesis. As a rule, compounds containing a nitro group, bromine are bioactive metabolites and are part of a number of drugs. We initially synthesized hydrazones of *o*-nitrobenzaldehyde and then based on them reactions with CBr<sub>4</sub>. As a result, nitro and bromo derivatives of dichlorodiazabutadiene and vinyl benzenes were obtained.



The structure of compounds obtained was confirmed by NMR spectroscopy. Such compounds as 1-(2,2-dibromovinyl)-2-nitrobenzene have biological activity, and are used as gem-enedyines, which have anticancer properties, and insect sex pheromones 1 in literature.

*This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan- Grant No EIF-BGM-4-RFTF-1/2017- 21/13/4*

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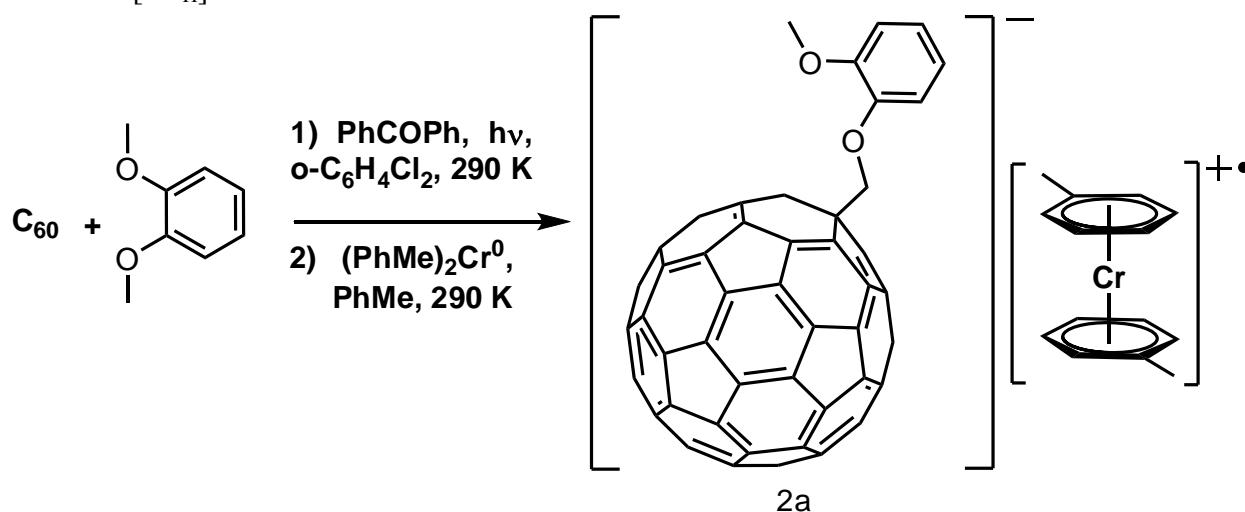
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## Bis(arene)chromium 1-((2-methoxyphenoxy)methyl)-1-hydro[60]fulleride

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Bis(toluene)chromium reacts with 1-((2-methoxyphenoxy)methyl)-1,2-dihydro[60]fullerene (**1a**) in toluene at 293 K to form salt bis(toluene)chromium 1-((2-methoxyphenoxy)methyl)-1-hydro[60]fulleride (**2a**) as a brown precipitate. Fulleride **2a** is stable at 293K. Fulleride **2a** is insoluble in hexane, sparingly soluble in PhMe, soluble in THF. NIR spectrum of fulleride **2a** in THF at 293 K indicates absorption bands at 994 and 648 nm typical for anion [**1a<sub>H</sub>**]<sup>-</sup>.



Fullerene **1a** was obtained by irradiation of fullerene  $C_{60}$ , veratrole and benzophenone in *o*-dichlorobenzene solution with 1:50:120 molar ratio and 3.2 mg/ml  $C_{60}$  concentration at 313 – 323 K using luminescent UV lamp 370 nm 10x10w in an evacuated and sealed pyrex ampoule. After solvent evaporation in vacuo, the residue was washed by hexane, acetone, dried in vacuo. Column chromatography over silica gel with decaline : benzene (6:1) as eluent gave first unreacted [60]fullerene and then fullerene **1a** in 20% isolated yield as amorphous brown solid. Fullerene **1a** is insoluble in hexane, soluble in  $\text{CHCl}_3$  and THF. The UV/vis spectra of **1a** in decaline at 292 K show absorption bands at 707, 695, 672, 640, 433, 326, 308, 255, 211 nm typical for 1,2 [60]fullerene derivatives. All reactions were carried out under an inert atmosphere.

*The work was performed using the instrumental base of the Analytical Center of the G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences and in the framework of the Russian state assignment*

## Stereospecific [2+2]-cross-photocycloaddition in a supramolecular donor–acceptor complex

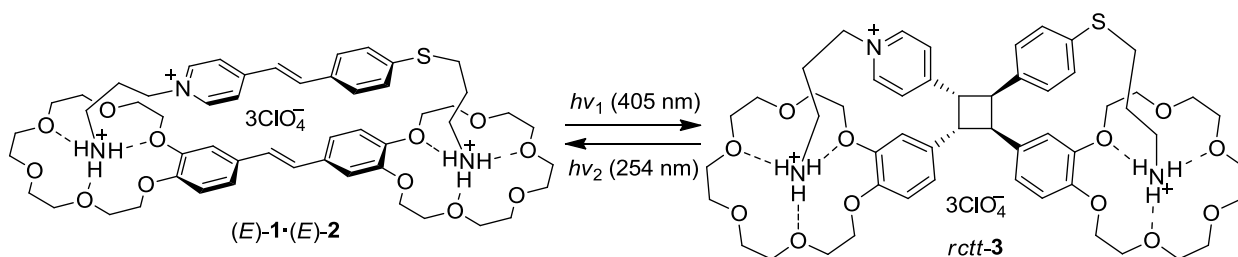
Martyanov T.P.<sup>a,b</sup>, Ushakov E.N.<sup>a,b</sup>, Sazonov S.K.<sup>b</sup>, Vedernikov A.I.<sup>b</sup>, Gromov S.P.<sup>b</sup>

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To date, a variety of supramolecular approaches have been developed to control the efficiency and selectivity of the [2+2] photocycloaddition (PCA) reaction both in solution and in the solid state [1,2]. Most attention has been paid to auto-PCA, i.e. [2+2]-photodimerization, whereas supramolecular cross-PCA reactions remain less studied [3]. This especially concerns the reactions between electron-donor and electron-acceptor olefins, when photoinduced intermolecular electron transfer can be a competing process. In this case, it is rather difficult to predict the PCA efficiency, because both competing photoreactions are significantly dependent on the geometric properties of the supramolecular assemblies.

In this work, we have shown that styrylpyridinium dye (*E*)-**1**, which was synthesized for the first time, forms a highly stable bimolecular complex with bis(18-crown-6) stilbene (*E*)-**2** in solution owing to ditopic coordination via hydrogen bonds. The complex formation results in much faster deactivation of the excited states of both compounds, which is explained by photoinduced electron transfer from the stilbene derivative to the styrylpyridinium dye. Despite this, the complexed olefins undergo [2+2]-cross-photocycloaddition upon selective excitation of the dye to afford solely the *syn*-cycloadduct (*rc*tt-**3**). The retro-photocycloaddition occurs readily upon UV irradiation of cyclobutane *rc*tt-**3** and leads to the initial bimolecular complex.



To the best of our knowledge, compound *rc*tt-**3** is the first representative of a 1-pyridyl-2,3,4-triphenyl cyclobutane derivative.

*This work was supported by the Russian Science Foundation (grant No. 19-13-00020)*

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## Chemical transformations of pyrrolo[1,2-*c*][4,1]benzoxazepinetriones under the action of binucleophiles

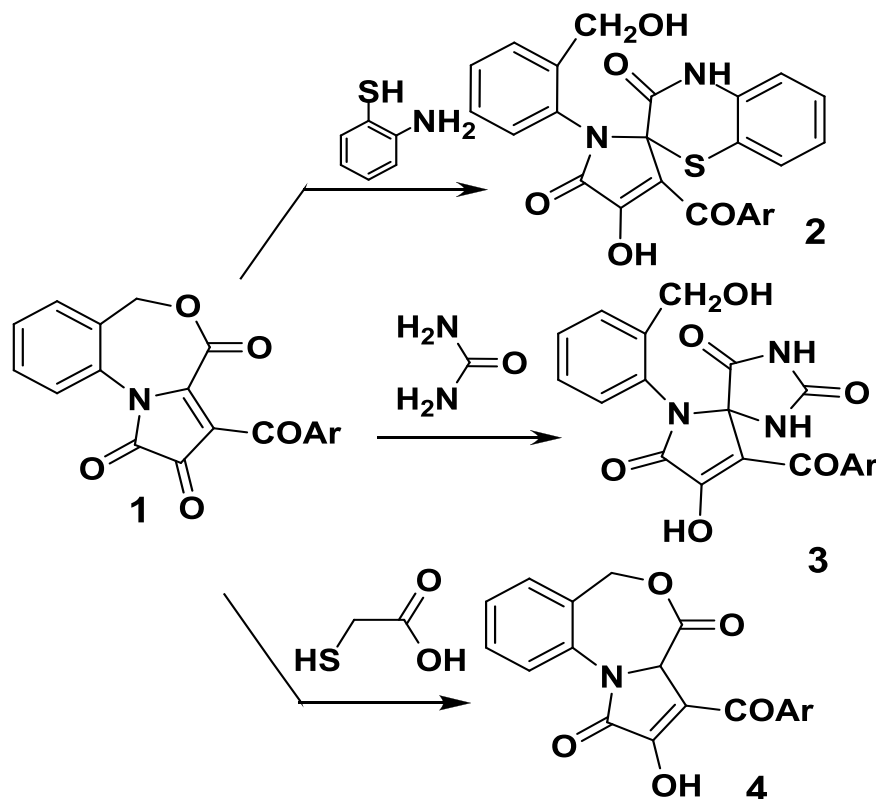
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Spiro-heterocyclizations and recyclizations of different classes of hetareno[*e*]pyrrole-2,3-diones under the action of binucleophiles proceed through various ways. We have synthesized new class of hetareno[*e*]pyrrole-2,3-diones, 3-arylpyrrolo[1,2-*c*][4,1]benzoxazepine-1,2,4-triones **1**, and studied their reactions with *o*-aminothiophenol, urea and thioglycolic acid.

The reactions were carried out by heating the reactants in boiling chloroform for 5-60 min. As a result, we isolated 1'-substituted 3'-aryloxy-4'-hydroxy-1'-(2-(hydroxylmethyl)phenyl)spiro[benzo[*b*][1,4]thiazine-2,2'-pyrrole]-3,5'(1*H*,4*H*)-diones **2**, 9-aryloxy-8-hydroxy-6-(2-(hydroxymethyl)phenyl)-1,3,6-triazaspiro[4.4]non-8-ene-2,4,7-triones **3** and 3-aryloxy-2-hydroxy-3a-hydro-1*H*,6*H*-benzo[*e*]pyrrolo[2,1-*c*][1,4]oxazepine-1,4-diones **4** respectively.

The formation of compounds **2** and **3** occurs apparently due to the addition of the SH and NH<sub>2</sub> group of *o*-aminothiophenol and two NH<sub>2</sub> groups of urea to the carbon atoms in the positions 3*a* and 4 of compounds **1** with the cleavage of the oxazinone ring at the C<sup>4</sup>-O<sup>5</sup> bond. As a result of the interaction of pyrrolo[1,2-*c*][4,1]benzoxazepinetriones **1** with thioglycolic acid reduced compounds **4** were received.



The study was performed under the financial support of the Russian Ministry of Education and Science (project no.4.6774.2017/8.9) and the Government of Perm Krai

## Synthesis of ethynyl substituted 3-hydroxyquinoline-4-carboxylic acids

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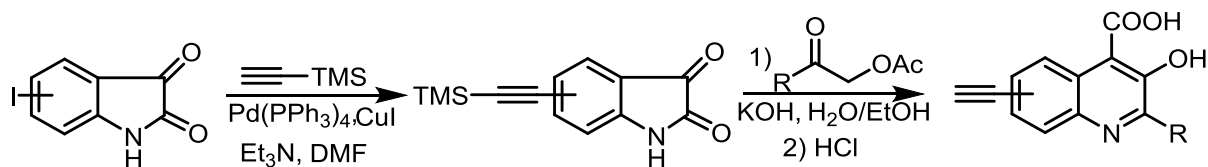
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Asialoglycoprotein receptor (ASGP-R) is a transmembrane protein that predominantly found on the surface of parenchymal liver cells [1]. ASGPR is a promising target for targeted drug delivery in hepatocytes and liver tumor cells [2]. It is known that most of the ASGPR ligands contain galactose- n-acetylgalactosamine residues, while non-carbohydrate structures are poorly studied. Recently, we have observed that quinolines containing a carboxyl group in the fourth position are able to effectively bind to ASGPR [3].

Azide-alkyne copper-catalyzed cycloaddition reaction is a convenient method of modification functional groups of biological active compounds. In order to use this method, it is necessary to add azido group or terminal triple bond into a molecule. Here we report a synthetic approach to novel ethynyl substituted 3-hydroxyquinoline-4-carboxylic acids.



Physicochemical and biological properties of newly obtained compounds are also going to be discussed.

*This work was supported by the Russian Foundation for Basic Research (grant №18-33-01237\18.)*

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## Unexpected rearrangement of derivatives of 4-hydroxy-6-methyl-2H-pyran-2-one to 1,5-dihydro-2H-pyrrol-2-ones. Synthesis of pyrrolo[3,4-*b*]pyridine-4,5-dione

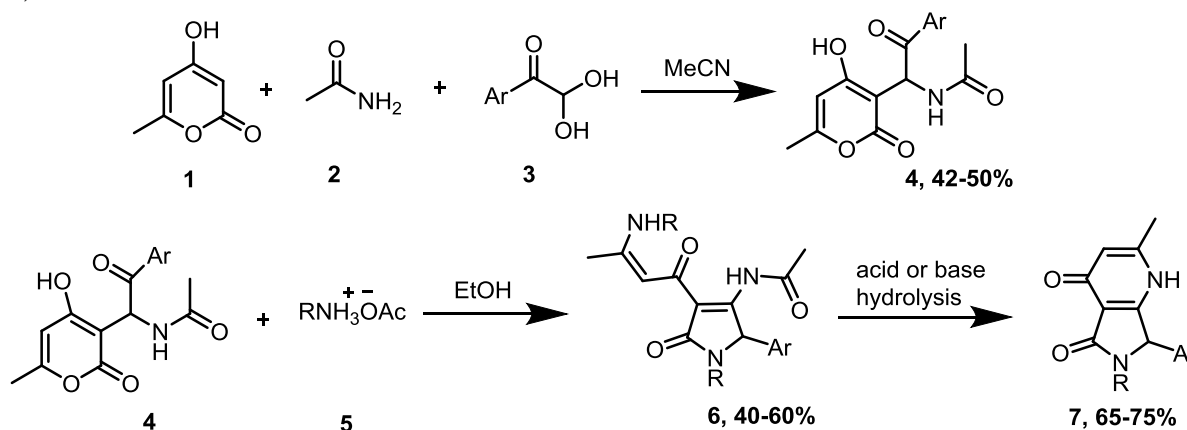
Melekhina V.G.,<sup>1</sup> Mityanov V.S.,<sup>1,2</sup> Komogortsev A.N.,<sup>1</sup> Lichitsky B.V.,<sup>1</sup> Krayushkin M.M.<sup>1</sup>

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Natural products containing the tetramic acid core scaffold often display wide ranging and potent biological activities including antibacterial, antiviral and antitumoral activities [1]. In consequence of this, an actual task is to develop new approaches to the synthesis of heterocyclic systems containing a fragment of dihydropyrrol-2-one.

We have discovered a previously unknown rearrangement of N-(1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-2-oxo-2-arylethyl)acetamides **4** to N-(4-(3-aminobut-2-enoyl)-5-oxo-2-aryl-2,5-dihydro-1H-pyrrol-3-yl)acetamides **6**. The reaction was carried out in ethanol in the presence of aliphatic amines acetates **5**. Starting compounds **4** were obtained by three-component condensation of 4-hydroxy-6-methyl-2H-pyran-2-one **1** with acetamide **2** and arylglyoxal **3** in acetonitrile. Further alkaline or acid hydrolysis of products **6** resulted in pyrrolo[3,4-*b*]pyridine-4,5-dione **7**.



Ar = 4-ClC<sub>6</sub>H<sub>4</sub>; 4-BrC<sub>6</sub>H<sub>4</sub>; 4-FC<sub>6</sub>H<sub>4</sub>; 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; 4-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>.  
R = H; Alk; (CH<sub>2</sub>)<sub>n</sub>-Ar.

The studied reaction may be carried out in one step, intermediates **6** were subjected to hydrolysis without additional isolation. The advantage of this approach is a higher total yield of final products **7**, in this case losses at the stage of isolation and purification of compounds **6** are excluded.

The structure of compounds **6** and **7** definitely proved by 2D NMR (HMBC) and HRMS.

*The study was supported by the Russian Science Foundation  
(Project No. 18-13-00308)*

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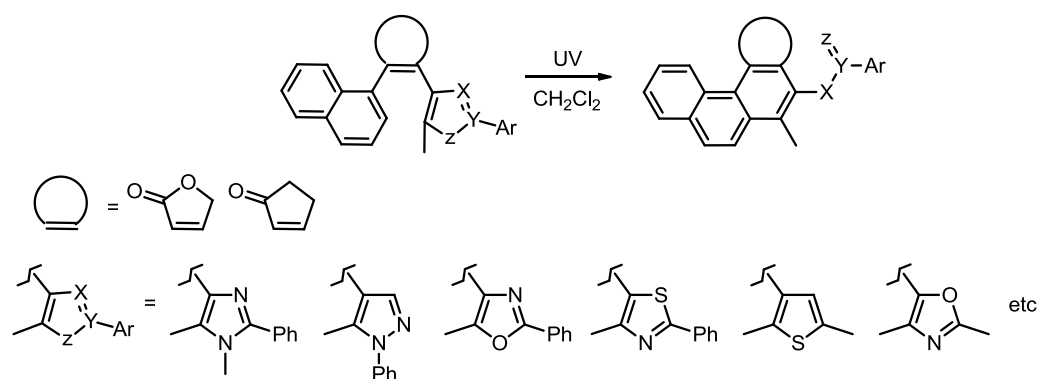
## Photoinduced skeletal rearrangement of naphthalene diarylethenes

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Photochemical reactions are widely used in organic synthesis to obtain polyaromatic compounds. Recently, we have demonstrated that diarylethenes bearing oxazole and phenyl residues readily undergo a photorearrangement with high yields. [1-3] The purpose of this work is to study the light-induced reaction of  $6\pi$ -electrocyclization of naphthalene diarylethenes. Diarylethenes with naphthalene and different five-membered heterocycles (imidazole, pyrazole, oxazole, thiazole, etc.) as aryl moieties have been tested.



It was found that all the investigated diarylethenes under UV light undergo a rearrangement to form phenanthrene derivatives comprising different functional groups. The method provides previously unknown phenanthrene derivatives with good yields. The structures of target compounds have been proved by different spectral methods. The obtained target phenanthrene derivatives are of interest as biologically active compounds and synthons for the development of photosensitive smart materials.

*This work was supported by the Russian Foundation for Basic Research  
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## Synthesis and antibacterial activity of new eremomycin carboxamides containing alkylpyridinium substituent

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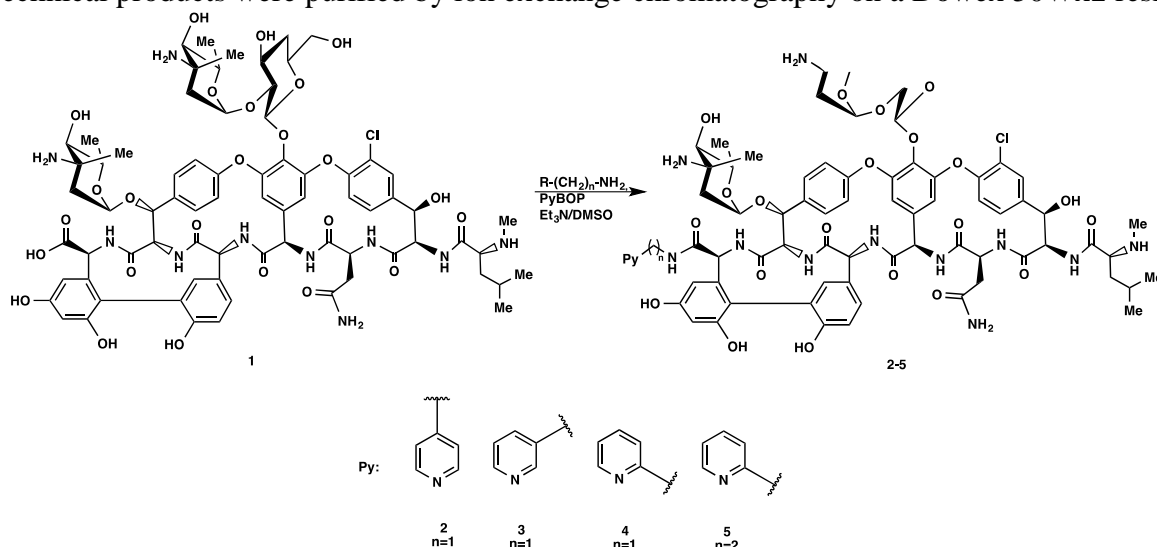
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The list of bacteria resistant to antibiotics that pose the greatest threat to human health, published by WHO in 2017, has a high priority for the search for new treatments, among others, *S.aureus* strains (neutral as well as methicillin and vancomycin-resistant) and *E.faecium* strains (vancomycin-resistant) [1]. This circumstance requires constant updating of the armory of the drugs for treating infections by obtaining semisynthetic antibiotics with improved chemotherapeutic properties.

It is well-known that activity of glycopeptide antibiotics can be increased by the introduction of hydrophobic substituent [2]. Moreover, the introduction of aromatic groups into the carboxamide fragment of the glycopeptide antibiotic generally improves the activity of the natural compound, especially against VRE strains [3].

Taking into account these data, the new eremomycin carboxamides with variable position of pyridine and alkyl length 2-5 from eremomycin acylamide were obtained. The condensation was carried out by PyBOP as a condensing agent in the presence of the base (Et<sub>3</sub>N) in DMSO. Technical products were purified by ion exchange chromatography on a Dowex 50Wx2 resin.



Eremomycin isomeric picolylamides 2-4 were 10–20 times more active than «gold-standard» vancomycin. An increase in antibacterial activity was observed both with respect to glycopeptide-sensitive reference strains and with clinical isolates with intermediate sensitivity to glycopeptides. The activity of picolylamides 2-4 in respect of glycopeptide resistant strains of *E. gallinarum* 1308 and *E. faecium* 3567 was 2 times lower than in sensitive but significantly higher than vancomycin. N-2-(2-pyridyl)ethylamide 5 shown similar activity, as derivative with methyl linker 4.

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## 1*H*-Pyrrole-2,3-diones as dipolarophiles in 1,3- and 1,4- dipolar cycloaddition reactions

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1,3-Dipolar cycloaddition (1,3-DC), also known as classic Huisgen reaction, is one of the most convenient methods for obtaining pharmacologically important five-membered nitrogen-containing heterocyclic compounds [1]. 1,4-Dipolar cycloaddition reactions are not so widely studied as 1,3-DC and can be used for synthesis of various six-membered heterocycles [2].

Carbonyl compounds are often used as privileged dipolarophiles in dipolar cycloaddition reactions. Along with that, polycarbonyl compounds containing several reactions centers are of special interest. Highly substituted 1*H*-pyrrole-2,3-diones, being such available dipolarophiles, react with various 1,3- and 1,4-dipoles at the polarized C(4)=C(5), C(3)=O and C(2)=O bonds forming unique heterocyclic scaffolds.

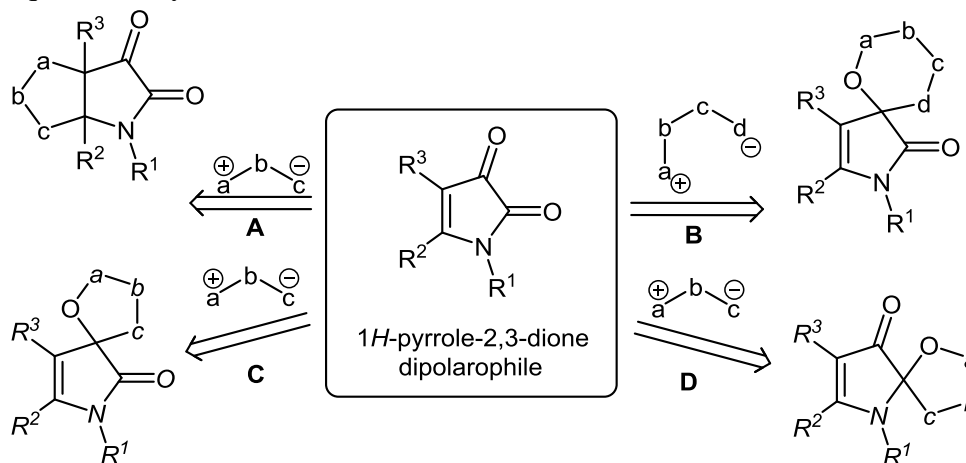


Fig. 1

Herein, we report reactions between highly substituted 1*H*-pyrrole-2,3-diones with various 1,3- and 1,4-dipoles. This paper presents new reaction pathways. (fig.1).

*This study was performed under the financial support of the Government of Perm Krai, and the Russian Ministry of Education and Science (projects nos. 4.6774.2017/8.9, 4.5894.2017/7.8)*

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## New 2-thienylbenzadiazine derivatives as perspective components for optical materials

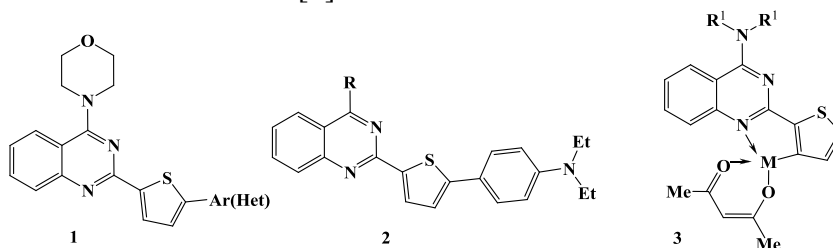
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Benzazine derivatives have attracted attention because of their potential applications as components for optical materials. Thienyl-substituted diazine molecular structures with extended  $\pi$ -conjugated systems are under investigation due to their promising electrochemical and electronic structural properties [1, 2]. Also 2-(thiophen-2-yl)quinazolines can be used as ligands for cyclometalated complexes formation [3].

The synthesis of the series of push-pull quinazoline derivatives **1** has been achieved through bromination and subsequent palladium-catalyzed cross-coupling reactions, and the ability of some of these molecules to function as colorimetric and luminescent pH sensors has been demonstrated with significant color change and luminescence switching upon the introduction of acid [4]. Modification of compound **1** at position 4 is of interest to tuning the photophysical properties. Optical studies of 2-[5-(4-diethylaminophenyl)thiophen-2-yl]quinazoline derivatives **2** have shown that 4-cyanoquinazoline **2** (R = CN) possesses low photoluminescence whereas its 3H-quinazolin-4-one counterpart **2** (R = OH) represents promising photoluminescent molecule [5].



The Pd(II) and Pt(II) complexes **3** based on 2-(thiophen-2-yl)-4-cycloalkyliminoquinazolines have been obtained from dimeric complexes  $[\text{PtL}(\mu\text{-Cl})_2]$  or  $[\text{PdL}(\mu\text{-OAc})_2]$  on reflux in acetone with an excess of sodium acetylacetonate. Upon photoexcitation, complexes **3** (M = Pt) were found to show large Stokes shift values but low-intensity orange luminescence at room temperature [6]. The photophysical properties of complex **3** (M = Pd) are under investigation.

*This work was supported by the Russian Foundation for Basic Research  
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## (Ni)CoMoW/Al<sub>2</sub>O<sub>3</sub> catalysts prepared on the basis of mixed Mo-W heteropolyacid: Difference in synergetic effect

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Trimetallic CoMoWS hydrotreating catalysts are attracting all the more growing attention from researchers [1, 2], although the data on their activity are ambiguous. For example, in accordance with [2], massive NiMoWS catalysts are much more active than CoMoWS analogs. However, as was reported recently by Pawelec et al.[1], due to increased acidity (connected to the partial replacement of Mo atoms with W ones), the CoMoW/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst shows a considerably high activity in the hydrodesulfurization (HDS) of dibenzothiophene (DBT), even higher than the activity of commercial CoMo/Al<sub>2</sub>O<sub>3</sub> sample.

The aim of this work was to explore the effect of Co promotion for the CoMoW/Al<sub>2</sub>O<sub>3</sub> trimetallic catalysts.

CoMo<sub>3</sub>W<sub>9</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared using the Keggin structure mixed heteropolyacid H<sub>4</sub>SiMo<sub>3</sub>W<sub>9</sub>O<sub>40</sub> and cobalt citrate. CoMo<sub>12</sub>/Al<sub>2</sub>O<sub>3</sub> and CoW<sub>12</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts based on H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, respectively, were synthesized as reference samples. Sulfided catalysts were analyzed by high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Catalytic properties were investigated in model reactions of DBT HDS and naphthalene hydrogenation (HYD).

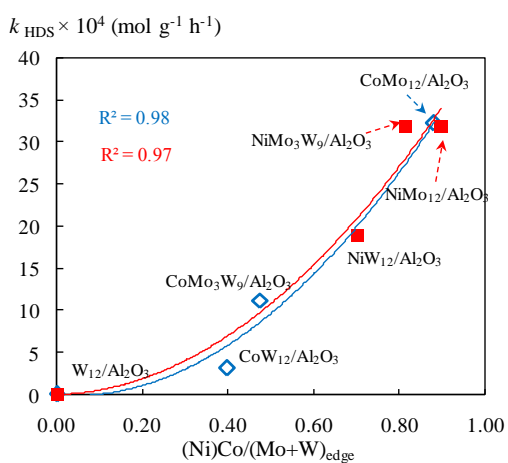


Fig. 1. Dependence of the rate constant of DBT HDS on the edge promotion degree of active phase particles in Co- and Ni-promoted catalysts.

As a result, the NiMo<sub>3</sub>W<sub>9</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is much more active than the CoMo<sub>3</sub>W<sub>9</sub>/Al<sub>2</sub>O<sub>3</sub> analogue.

*This work was supported by the Russian Science Foundation Grant No. 17-73-20386*

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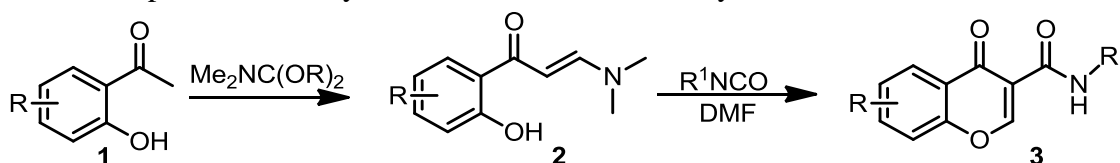
## Synthesis of 5-oxo-2-arylamino-5*H*-chromeno[4,3-*b*]pyridine-3-carbonitriles from 3-carbamoylchromones and malononitrile

Myannik K.A., Yarovenko V.N., Krayushkin M.M.

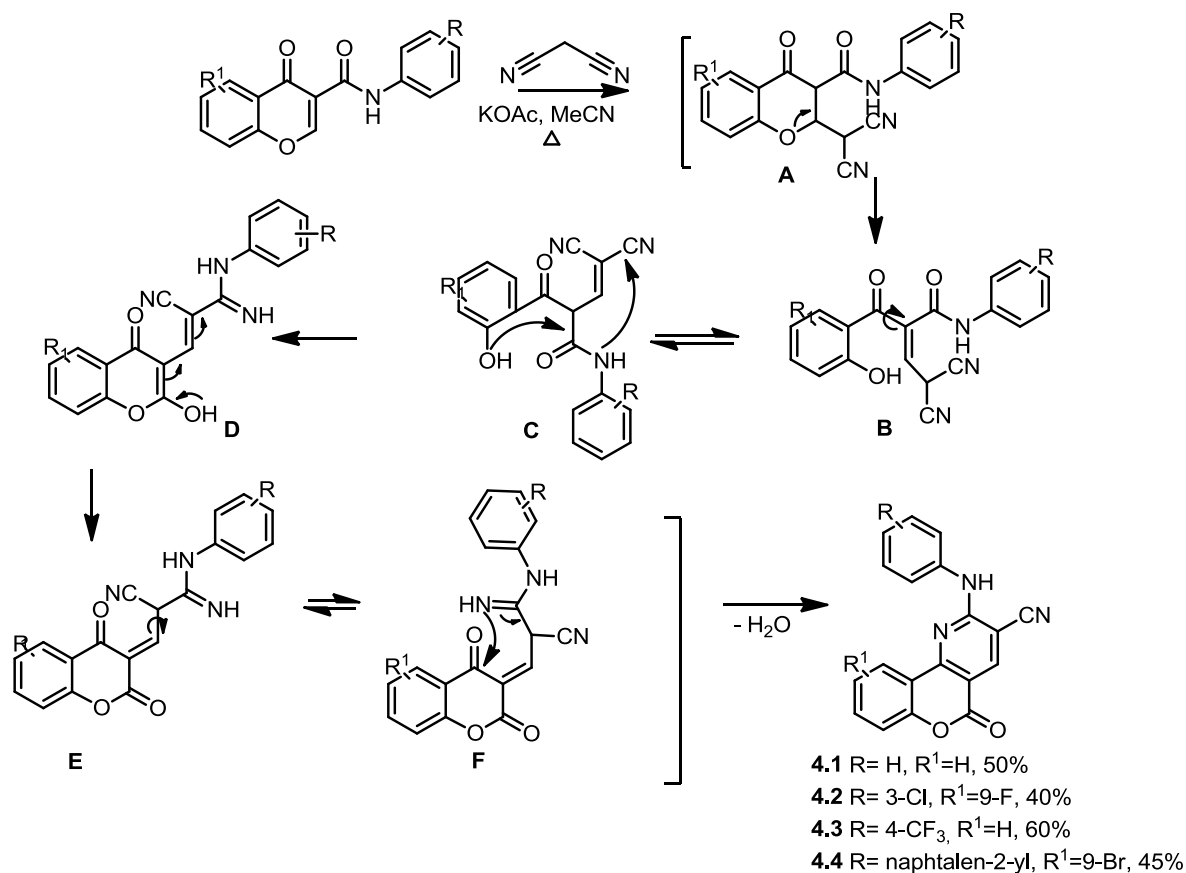
*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation.*

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Previously, we developed a new method for obtaining 3-carbamoylchromones **3**, which composes of *o*-hydroxyarylenaminone **2** and isocyanates interaction. That made possible to study almost the unexplored reactivity of *N*-substituted 3-carbamoylchromones.



It is known that the interaction of activated electron-withdrawing substituents of chromones with nitriles is often accompanied by recyclization reactions (RORC). We have demonstrated the formation of previously undescribed 5-oxo-2-arylamino-5*H*-chromeno[4,3-*b*]pyridine-3-carbonitriles **4a-d**, which, apparently, is the result of the domino processes shown in the scheme.



### References

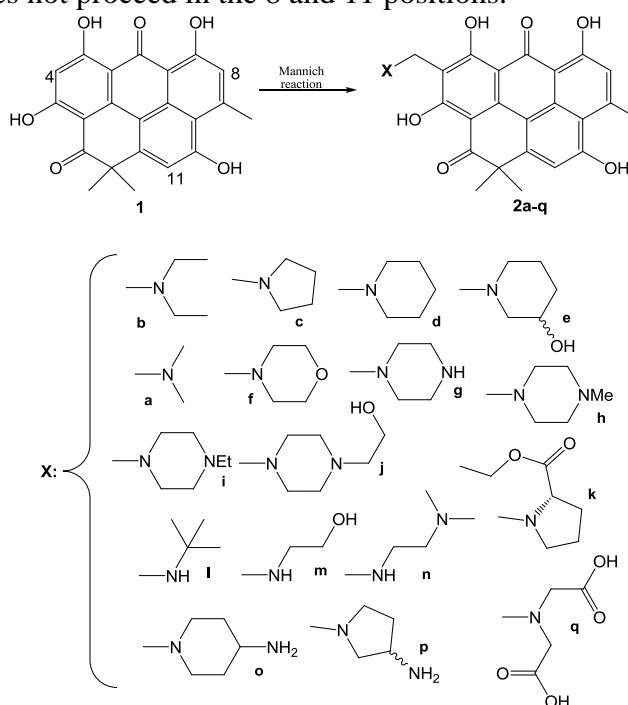
[1] K. A. Myannik, I. S. Semenova, V. N. Yarovenko, M. M. Krayushkin. *WPI. An Ser. Chem.* **2019**, *1*, 104.

## Aminomethylation of the heliomycin antibiotic

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Heliomycin (**1**) is a secondary metabolite produced by some bacteria of the *Streptomyces* family. The presence of heliomycin properties such as antiviral, antibacterial and antiproliferative activity make it extremely promising to modify its structure in order to obtain new derivatives. However, it is worth noting that the poor solubility of the antibiotic severely limits its wide researching [1]. Thus, conditions were found for the selective aminomethylation of the benzopyrene nucleus in the 4-position by the Mannich reaction. Completely new, undescribed 4-aminomethyl derivatives with various aminomethyl moiety, possessing cytotoxicity, were obtained. It is important to note that the reaction proceeds just in 4 position of the structure due to the presence of two electron-withdrawing substituents in the adjacent puffs directing the attack by an electrophile in 4 positions. At the same time, even under more hard conditions, the reaction does not proceed in the 8 and 11 positions.



A series of new derivatives was obtained by two different methods - for **2a**: by reaction of heliomycin (**1**) with N,N-dimethyl(methylene)ammonium chloride in DMF at 75 °C and for **2b-q** by reaction of heliomycin with an aqueous solution of formaldehyde with the corresponding amine in acetic acid at 40 °C. Synthesized structures were confirmed by NMR.

Obtained derivatives **2a-q** were evaluated on a panel of mammalian tumor cells including colon adenocarcinoma HCT116, its subline HCT116p53KO, K562 and its MDR subline K562/4, murine leukemia L1210, human T-cell leukemia CEM and cervical carcinoma HeLa. The majority of new derivatives **2a-q** effectively killed tumor cells (IC<sub>50</sub> values in the low micromolar to submicromolar range) [1].

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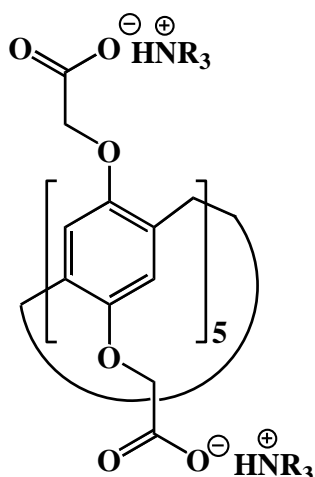
## Synthesis of some water-soluble ammonium salts based on pillar[5]arene

Nazarova A.A., Yakimova L.S., Stoikov I.I.

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In recent years, molecular recognition has become increasingly important in such areas of science as chemistry, biology, materials science, environmental science. In this regard, the main efforts are aimed to the creation of new synthetic receptors that can selectively and effectively bind guest molecules. Among the variety of synthetic receptors, special attention is focused to the creation of water-soluble receptors, as most biological processes take place in aqueous media.

After previously synthesized and well-studied crown ethers, cyclodextrins, calixarenes, cucurbiturils and others, the promising class of supramolecular hosts attracting the attention of researchers are pillar[n]arenes, especially pillar[5]arenes. The pillar[5]arene molecule is a hydrophobic core formed by benzyl fragments that are located between two rims containing different substituents. The repeating hydroquinone units of the macrocycle are connected by methylene bridges in *para*-positions, forming a unique pillar-like architecture. Pillar[5]arenes can be easily functionalized, which makes them promising compounds to use in molecular recognition, nanomaterials, and creation of supramolecular polymers. In addition, these macrocyclic compounds are capable to bind both neutral and charged guests due to the hydrophobic cavity.



Thus, under this research work, a number of novel water-soluble ammonium salts based on pillar[5]arene were synthesized. The structure of the new synthesized derivatives was fully proved by NMR <sup>1</sup>H, <sup>13</sup>C, IR spectroscopy, mass spectrometry (ESI) and elemental analysis.

*This work was supported by the Russian Science Foundation  
(grant № 18-73-10094)*

## Novel tetrahydroquinazoline derivatives with promising biological activity

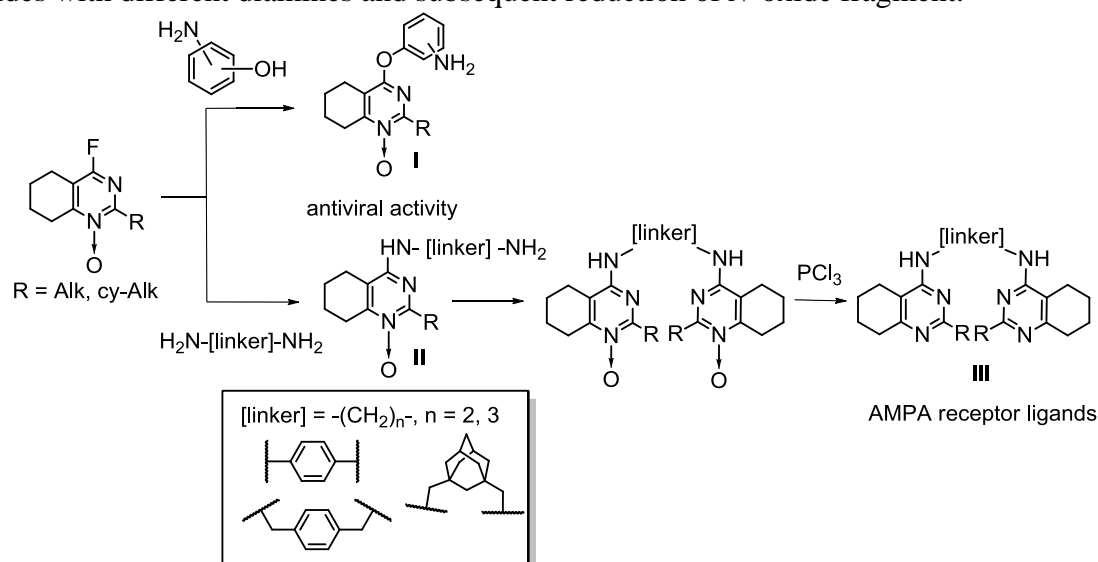
Nazarova A.A.<sup>a</sup>, Sedenkova K.N.<sup>a,b</sup>, Palyulin V.A.<sup>a,b</sup>, Averina E.B.<sup>a,b</sup>

<sup>a</sup> Lomonosov Moscow State University, Chemistry Department, 119991, Moscow, Leninskie gory 1-3, Russian Federation

<sup>b</sup> Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation

Pyrimidine derivatives are of high importance in living organisms and reveal a wide spectrum of biological activity [1]. Recently novel reaction of three-component heterocyclization of *gem*-dihalocyclopropanes, nitrating or nitrosating agents and nitriles resulting in previously unknown 4-halogenopyrimidine *N*-oxides was discovered in our laboratory [2].

In this work the synthetic approach to novel tetrahydroquinazoline derivatives based on this reaction was developed and a large series of heterocycles was obtained for studying their antiviral activity (structures **I,II**) and activity towards AMPA receptor (structures **III**). Pyrimidine *N*-oxides **I** were obtained *via* the reaction of aromatic nucleophilic substitution. The synthetic approach to bis(pyrimidines) **III** included double  $S_NAr$  reaction of 4-fluoropyrimidine *N*-oxides with different diamines and subsequent reduction of *N*-oxide fragment.



Biological activity of pyrimidine *N*-oxides containing *o*-, *m*- or *p*-aminophenol and diamine moieties in C4 position and substituents of different size in C2 position (**I,II**) was investigated and the majority of compounds were found to possess antiviral activity in micromolar concentration. Also, bis(pyrimidines) with different diamine linkers (**III**) were found to act as AMPA-receptor negative modulators.

*This work was supported by the Russian Foundation for Basic Research, grant no. 18-03-00651 and the Russian Science Foundation, grant no. 17-15-01455*

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## New tautomeric receptors for metal cations based on Crown-containing imines of 1-hydroxyanthraquinone

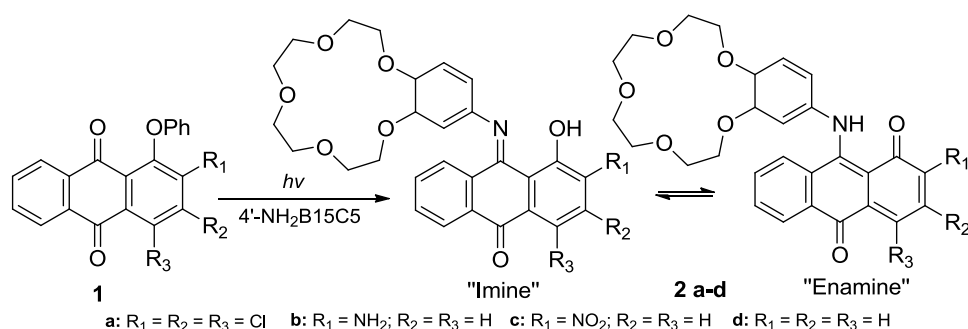
Neznaeva D.A.<sup>1</sup>, Kudrevatykh A.A.<sup>1</sup>, Martyanov T.P.<sup>2</sup>, Klimenko L.S.<sup>1</sup>

<sup>1</sup> Yugra State University, 628012, Khanty-Mansiysk, Russian Federation.

<sup>2</sup> Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow Region, Russian Federation.  
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Design of simple and selective receptors for determination of the elements and their compounds contained in the environment is an important part of contemporary chemistry. Detection of metal cations that influence on the biological processes in living organisms arouses particular interest. Crown ethers and their derivatives are widely used as receptors in optical molecular sensors. Intensely colored anthraquinone derivatives were used as a signal part in the synthesis of new chemosensors due to the variety of properties and possibilities for changing their molecular structure [1].

We have shown earlier [2] that crown-containing 1-hydroxy-9,10-anthraquinone-9-imines are representatives of a rare class of the tautomeric chromoionophores. New macrocyclic imines of anthraquinone were prepared photochemically from the corresponding photoactive 1-phenoxyanthraquinones and 4'-aminobenzo-15-crown-5 ether.



The study of the complex formation of the synthesized compounds **2a-d** with Group Ia and IIa metal perchlorates in MeCN and DMSO was investigated by spectrophotometric titration method. Hypsochromic shifts of the long-wavelength absorption band were observed for all compounds. It was discovered that introduction of electron-withdrawing groups in the anthraquinone moiety increases the range of spectral changes: the greatest shift was observed for the chlorine derivative **2a** (56 nm). Such significant differences in the ionochromic properties can be explained by a change in the ratio of the tautomeric forms of «imine-enamine» to NH-form.

The complexation properties of new crown-containing imines of 1-hydroxyanthraquinone bearing electron-donating and electron-withdrawing groups in the anthraquinone moiety were studied. The regularities established in this paper will allow carrying out a targeted synthetic search for optical chemosensors for the visual test selective determination of metal cations.

*This work was supported by the RFBR (grant № 18-43-860005)*

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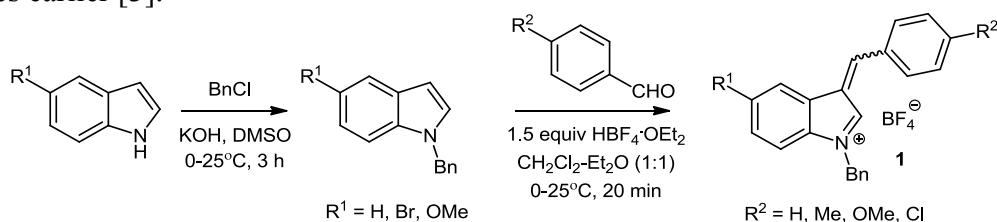
## Three-component reactions of 3-arylidene-3*H*-indolium salts, isocyanides and aromatic amines

Nguyen H.M., Golantsov N.E., Voskressensky L.G.

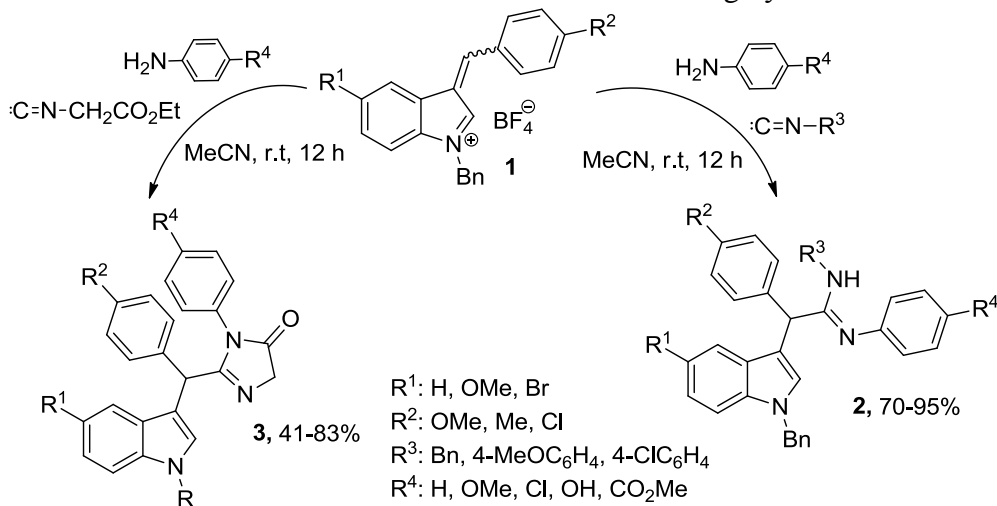
Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: hungtheadhv2008@gmail.com

Multicomponent reactions (MCR) serve as a powerful and widely used instrument in organic synthesis [1]. A special place among them is occupied by transformations with the participation of isocyanides, unique reagents where nucleophiles and electrophiles attack the same atom [2].

Starting salts **1** were obtained by alkylation of corresponding indoles followed by reaction with aromatic aldehydes in conditions similar to a previously published procedure.<sup>3</sup> In solution salts **1** exist as a mixture of *E*- and *Z*-isomers, what was also noted for 2-unsubstituted derivatives earlier [3].



To the best of our knowledge, reactions of arylideneindolenines or the corresponding salts with isocyanides have not been published yet. Herein, we report the three-component reaction of 3-arylideneindolium salts with isocyanides and aromatic amines. As a result imidamides **2** and imidazolones **3** were obtained in moderate to high yields.



The structure of synthesized compounds was confirmed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and Mass spectra.

This work was supported by the Russian Foundation for Basic Research (grant № 17-53-10012 KO\_a)

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## Synthesis of new imines, amides, ureas and thioureas containing sterically hindered benzylphosphonate fragment

Nguyen T.T.<sup>1,2</sup>, Gibadullina E.M.<sup>1</sup>, Burilov A.R.<sup>1</sup>

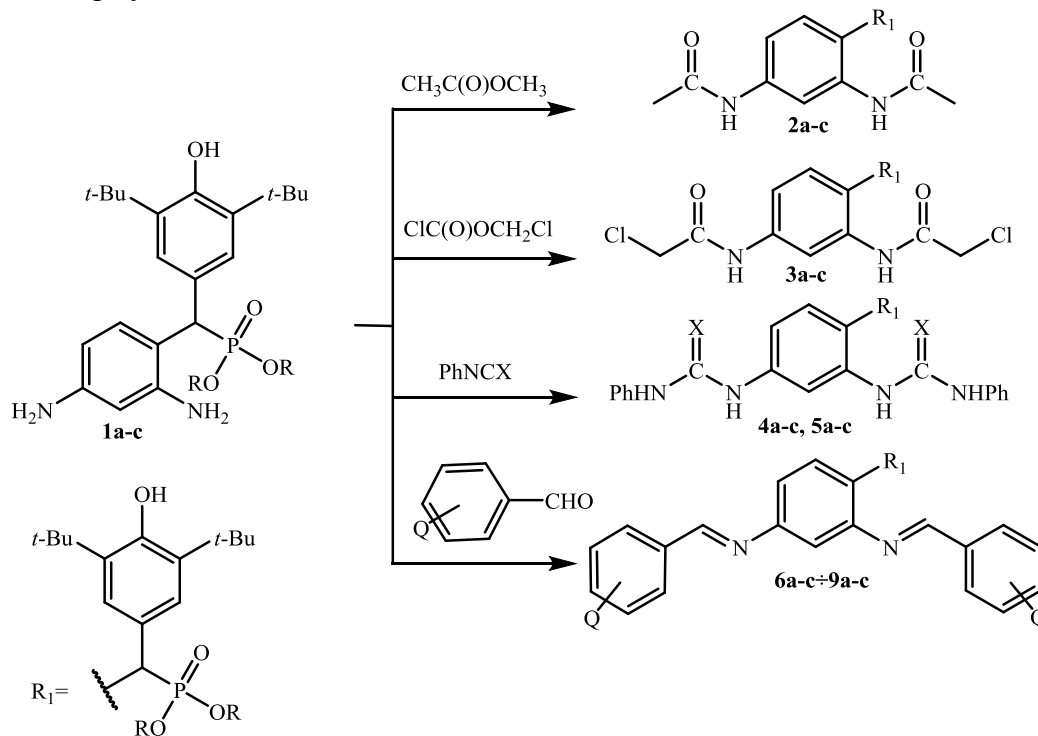
<sup>1</sup>Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Russian Federation, 420088, Kazan, Arbuzov str. 8

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A perspective field the construction of polyfunctional drug compounds is the synthesis of compounds with broad-spectrum activity. Presence of the sterically hindered phenolic fragments can lead to increase of the activity and decrease of the toxicity of the target compounds. Derivatives of sterically hindered phenols containing phosphoryl groups can slow down the process of lipid peroxidation and reduce the oxidative stress. Derivatives of *m*-phenylenediamine, containing sterically hindered benzylphosphonate fragment, are convenient platform for the synthesis of new imines (Schiff bases), amides, ureas and thioureas due to the presence of free amino groups.

In this work, the dialkyl(diphenyl)((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2,4-diaminophenyl)methyl)phosphonates **1a-c** were used as a starting compounds for the synthesis of antioxidant and biologically active compounds. As the result of the reaction of phosphonates **1a-c** with acetic anhydride, chloroacetyl chloride, phenyl isocyanate, phenyl isothiocyanate and aromatic aldehydes (benzaldehyde, *o*-, *m*- and *p*-hydroxybenzaldehydes), new imines, amides, ureas and thioureas containing sterically hindered benzylphosphonate fragment **2a-c**÷**9a-c** were produced in high yields.



$\text{R}_1 = \text{Me}(\mathbf{a}), \text{Et}(\mathbf{b}), \text{Ph}(\mathbf{c}); \text{X} = \text{O}(\mathbf{4a-c}), \text{S}(\mathbf{5a-c}); \text{Q} = \text{H}(\mathbf{6a-c}), \text{o-OH}(\mathbf{7a-c}), \text{m-OH}(\mathbf{8a-c}), \text{p-OH}(\mathbf{9a-c})$

The structure of all synthesized compounds **2a-c**÷**9a-c** was proved by <sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P-NMR, IR spectroscopy, mass spectrometry (MALDI), the composition was confirmed by elemental analysis.

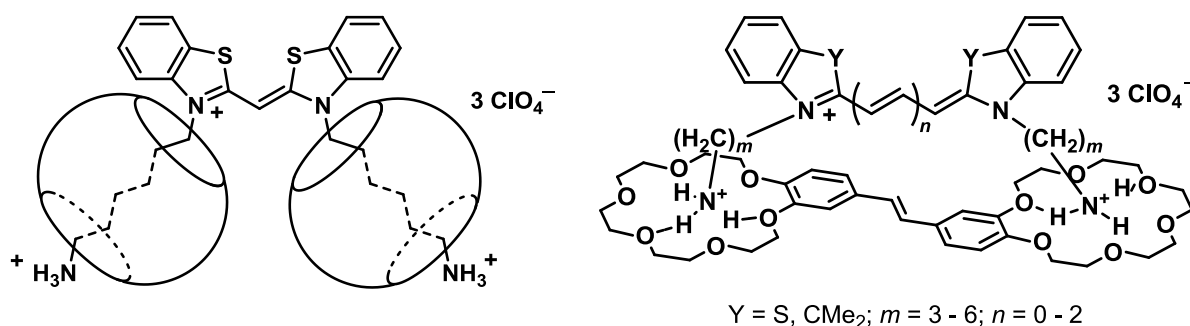
## Self-assembly through hydrogen bonding supramolecular complexes of cyanine dyes containing terminal ammonium groups

Nikiforov A.S., Fomina M.V., Vedernikov A.I., Kurchavov N.A., Avakyan V.G., Kuz'mina L.G., Gromov S.P.

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The "host-guest" complexes of macrocycles with organic molecules, in which the guest molecule has a chromophoric moiety, are of particular interest for supramolecular photochemistry.

In order to elucidate the possibility to construct photoactive "host-guest" complexes based on cyanine dyes as a guest and the influence of their structure on the properties of supramolecular complexes, we synthesized cyanine dyes with terminal ammonium groups in the *N*-substituents of heterocyclic residues [1]. The presence of primary ammonium groups capable of hydrogen bonding enables self-assembly of the dye with macroheterocyclic molecules containing electron-donating oxygen heteroatoms to form supramolecular complexes.



We demonstrated the possibility to construct the supramolecular systems based on cyanine dyes with two ammonioalkyl *N*-substituents using their complexes with cucurbit[7]uril and bis(18-crown-6)stilbene as an example.

Supramolecular complexes with cucurbit[7]uril were investigated. It was shown that inclusion of the dye molecule into cucurbituril cavity highly influence dye fluorescence spectra.

It was also shown that stilbene form highly stable bimolecular and relatively unstable trimolecular complexes in which the dye ammonium groups are hydrogen-bonded to the crown ether moieties of stilbene and their  $\pi$ -conjugated moieties are located one above the other. The stability constants for some of these complexes were determined, and the stability of the complexes was shown to depend on the dye structure.

The synthesized cyanine dyes and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

*This work was supported by RFBR (project № 18 03 00214)*

### References

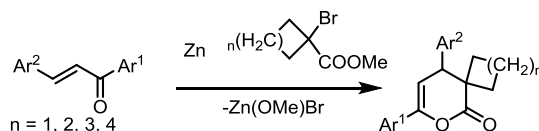
- [1] Gromov, S.P.; Fomina, M.V.; Nikiforov, A.S.; Vedernikov, A.I.; Kuz'mina, L.G.; Howard J.A.K. *Tetrahedron*, **2013**, *69*, 5898.

## Interaction of 1-bromocyclohexancarboxylate and zinc with 1-(2-hydroxyphenyl)-3-arylprop-2-en-1-ones

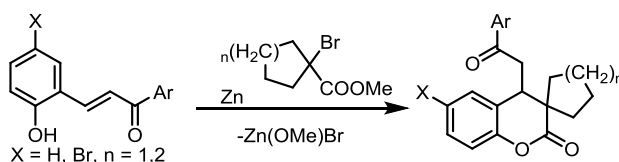
Nikiforova E.A., Baibarodskikh D.V., Kirillov N.F., Shurov S.N., Subbotina D.Yu.

Perm State University, Russia, 614990, Perm, Bukireva str. 15,  
e-mail: vikro@ya.ru

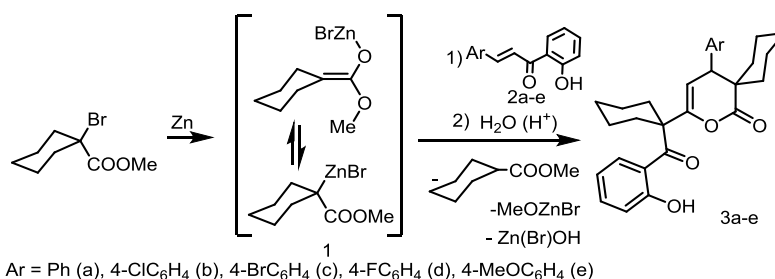
Previous studies found that carbocyclic Reformatsky reagents interact with chalcones to form substituted spirodihydropyran-2-ones, possessed analgesic activity [1-3]:



and with 1-aryl-3-(2-hydroxy(or 5-bromo-2-hydroxy)phenyl)prop-2-en-1-ones to form substituted spirochroman-2-ones, possessed analgesic activity too [4]:



We studied the interaction of Reformatsky reagent **1**, derived from 1-bromocyclohexancarboxylate and zinc, with 1-(2-hydroxyphenyl)-3-arylprop-2-en-1-ones **2a,e**. As a result unexpected spirodihydropyran-2-ones **3a-e**, containing the 1-(2-hydroxybenzoyl)cyclohexyl substituent at 6 position of heterocycle, was isolated. The compositions and structures **3a-e** were confirmed by their elemental analyses, IR, NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra, and X-ray analysis of compound **3a**.



The mechanism of formation of compounds **3** proposed by the authors and confirmed by quantum-chemical calculations.

*This work was supported by the Russian Foundation for Basic Research (grant № 18-33-00509)*

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## Fused nitropyridines – a new type of HIV-1 integrase inhibitors

Nikol'skiy V.V.<sup>1,2</sup>, Fedorenko A.K.<sup>1,2</sup>, Bastrakov M.A.<sup>1</sup>, Starosotnikov A.M.<sup>1</sup>, Korolev S.P.<sup>3</sup>, Gottikh M.B.<sup>3</sup>

<sup>1</sup>N.D. Zelinsky Institute of Organic Chemistry RAS, 119991, Moscow, Leninsky prosp., 47

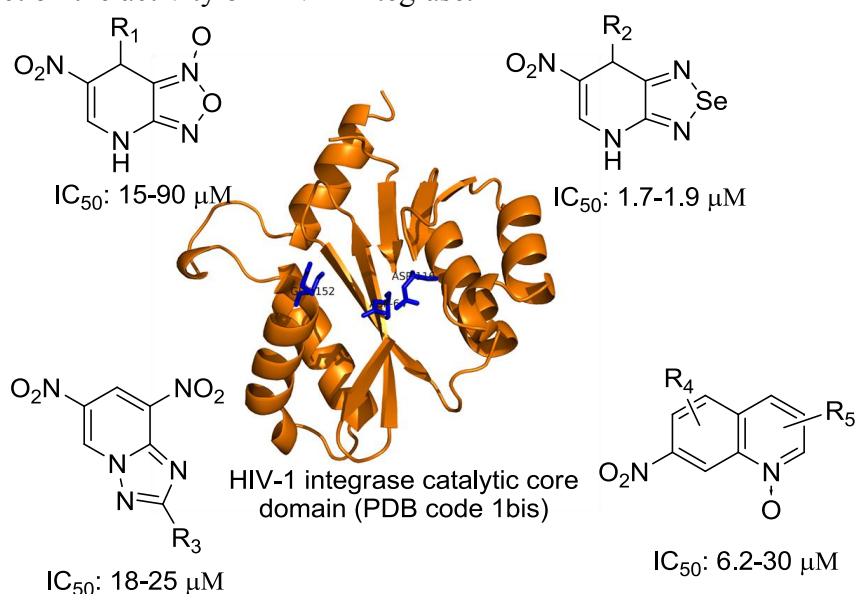
<sup>2</sup>Chemistry Department Lomonosov Moscow State University, 119991, Moscow, Leninskie gory, 1/3

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Human immunodeficiency virus (HIV-1) causes one of the most dangerous diseases of our time, the syndrome of acquired human immunodeficiency (AIDS). Therefore, an extremely important and promising task of modern medical chemistry is the creation of compounds that possess inhibitory activity against HIV-1 [1,2]. Recently, we have found that aromatic nitro compounds such as nitro substituted benzofuroxans and benzofurazans, are able to inhibit catalytic activity of one of three HIV-1 enzymes, known as integrase [3,4].

In this study we have synthesized new fused nitropyridine derivatives and studied their inhibitory effect on the activity of HIV-1 integrase.



This work was supported by the Russian Foundation for Basic Research (grant № 17-03-00809\_a)

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## Bimetallic Pd-catalysts based on modified oxide and carbon supports

Novoselov A.M.<sup>a</sup>, Bumagin N.A.<sup>a</sup>, Kletskov A.V.<sup>b</sup>, Belov D.C.<sup>a</sup>

<sup>a</sup>*M.V. Lomonosov Moscow State University, Leninskii Gory, 1/3, Moscow 119991, Russia;*

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The Pd-catalyzed cross-coupling processes of C-C bond formation are widely used in modern organic synthesis as effective methods for producing polyfunctional biaryls, arylated olefins and acetylenes, as well as their heterocyclic analogs. Compounds of this type are the structural elements of pharmaceuticals, natural products, and functional organic materials. For the development of environmentally friendly catalytic technologies of organic synthesis, convenient methods for non-covalent modification of mesoporous oxide and carbon supports by low molecular weight chitosan, ionic liquids and nitrogen-containing compounds (L) have been proposed. Using the obtained materials, the bimetallic palladium composites Pd-M-L/Al<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub>), Pd-M-L/C (M = Ni, Co, Fe; Pd:M = 1:100) were synthesized. Among the many supports used in heterogeneous catalysis, magnetic are of particular practical interest, since they are easily separated from the reaction medium by an external magnet. We have created new heterogeneous bimetallic Pd catalysts based on magnetic iron oxide Fe<sub>3</sub>O<sub>4</sub> nanoparticles coated with a layer of chitosan. The choice of chitosan is due to the presence in its composition of amino groups capable of complexing with salts of transition metals, as well as its availability, low cost and safety for the environment. Usually the coating with chitosan is carried out from its dilute solution (1-2 wt.%) in acetic acid, which is not very technological, but also requires a long period of time [1]. We have developed a "one pot" method for coating magnetite nanoparticles with chitosan. The formation of a bimetallic coating on the obtained magnetic support Fe<sub>3</sub>O<sub>4</sub>@Ch was carried out by successive deposition of the metal salt, reduction and electroless deposition of palladium. The magnetic bimetallic composites Pd-M-Fe<sub>3</sub>O<sub>4</sub>@Ch and Pd-ML/Al<sub>2</sub>O<sub>3</sub>(SiO<sub>2</sub>), Pd-M-L/C (M = Co, Cu; Pd : M = 1 : 100) not only show high catalytic activity in cross-coupling and reduction reactions in aqueous media but are also stable and retain their catalytic activities for several catalytic runs (94-98% yields even at the 10th catalytic run). Quantum-chemical calculations of structural and electronic parameters of small bimetallic clusters Pd-M<sub>n</sub> at the PBE0/LANL2TZ(f) level of the theory [2, 3] suggested a substantial M to Pd charge transfer which resulted in a highly negatively charged Pd centre, a favourable site for facile oxidative addition of aryl halides, and hence enhanced catalytic activity for supported Pd-nanoparticle catalysts (synergistic effect).

All studied reactions proceed with practically quantitative yields; therefore, it is not necessary to use expensive and laborious chromatographic methods for the isolation and purification of reaction products. After completion of the reaction, the reaction mixture is diluted with water (water-soluble products) or diethyl ether (water-insoluble products), the catalyst is separated using an external magnet or filtered, washed with water, alcohol, and then reused (5-10 times without loss of activity).

*This work was supported by the Russian Foundation for Basic Research  
(grant № 17-08-00633)*

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## Mixed 1,2-azole heterocycles in homogeneous and heterogeneous catalysis in aqueous media

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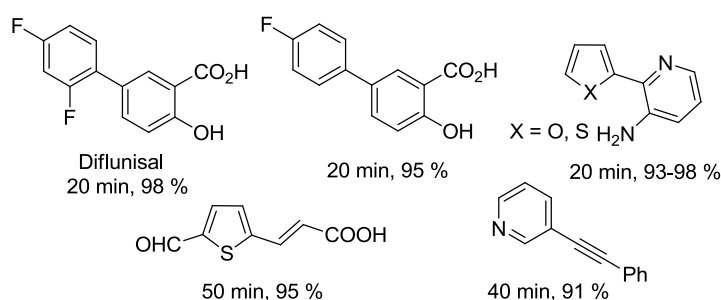
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As a result of joint researches, methods of the synthesis of mixed heterocyclic ligands and their complexes with palladium and nickel were obtained. Corresponding ligands provide coordination cores with different electronic properties (for example, 1,2-azole-1,2,3-triazole, 1,2-azole-pyridine, 1,2-azole-pyrimidine). Palladium isoxazole-1,2,3-triazole complexes are so active as catalysts for cross-coupling and reduction reactions in aqueous media that they can be used in trace amounts (1–10 ppm) [1]. For the first time, a promising and very active in catalysis of cross-coupling and reduction reactions hybrid bimetallic materials Pd-Ni-B-L [L - isoxazole-1,2,3-triazole(pyrimidine) ligands] were synthesized.

The ability of Pd-Ni-B-L, as well as Co and Fe analogues, to form stable colloidal solutions in methanol made it possible to develop a method of their simple deposition on mesoporous supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, styrene-divinylbenzene copolymer - DIAION HP20) and to create on their basis active heterogeneous catalysts. The following bimetallic composites were obtained: Pd-M-B-L/Al<sub>2</sub>O<sub>3</sub>(SiO<sub>2</sub>), Pd-M-B-L/HP20 (M = Ni, Co, Fe; Pd: M = 1: 100). In the presence of new catalysts, reactions proceed in practically quantitative yields, which make it possible to simplify the isolation procedure of target compounds as much as possible. Developed catalytic materials are readily recovered from the reaction mixture and can be reused up to 5-10 times without loss of activity. The synthetic potential of new catalysts has been studied in several types of cross-coupling reactions on a wide range of aryl halides, arylboronic acids, olefins and terminal acetylenes, as well as their heterocyclic analogs. Examples of practically significant compounds synthesized by the Suzuki, Heck and Sonogashira reactions in the presence of reusable bimetallic catalysts (0.01 mol% Pd) are presented at the scheme.



This work was supported by the Russian Foundation for Basic Research (grants № 16-58-00059-Bel\_a, 18-58-00013-Bel\_a), and Belarus' Republic Foundation for Fundamental Research (grants № X16P-006, X18P-010)

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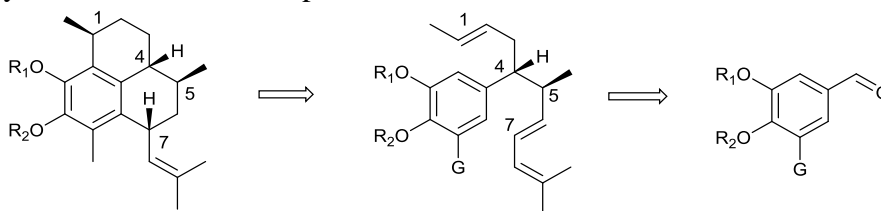
## Towards a bi-directional double cyclization route to pseudopterosin aglycones: challenges in diastereo/regioselectivity

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Pseudopterosins are a group of marine diterpene glycosides which have been shown to possess anti-inflammatory, anti-tuberculosis, anti-cancer, protective and neuromodulatory effects<sup>1-5</sup>. Experimental studies towards the synthesis of pseudopterosin aglycones are on-going. Enantioselective crotylation followed by anionic oxy-Cope rearrangement<sup>6</sup> are the key steps for introduction of chirality at C-4 and C-5, while a bi-directional double cyclization installs the remaining chiral centers at C-1<sup>6</sup> and C-7.

In this poster, we discuss synthetic challenges in the construction of the amphilectane core of pseudopterosins, especially with respect to diastereoselectivity and regioselectivity and show how they are addressed, where possible.



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## Domino reactions of 1-aryl-3,4-dihydroisoquinolines with cross-conjugated ketones — search for selectivity

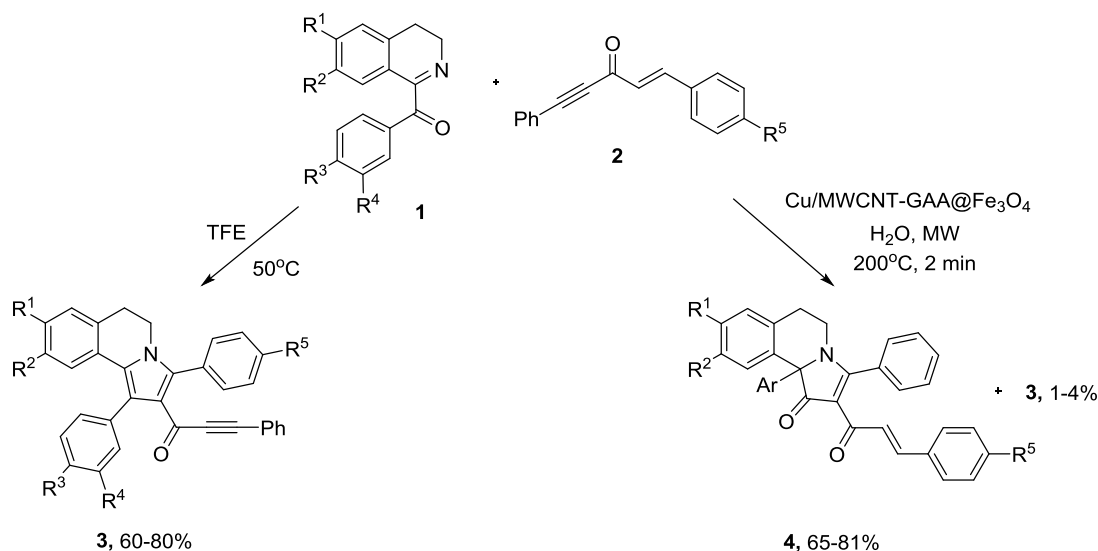
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Pyrrolo[2,1-*a*]isoquinoline derivatives exhibit a wide range of biological activity, which causes interest in the development of new approaches to the synthesis of this heterocycle.

The addition of 1-aryl-substituted 3,4-dihydroisoquinolines containing imino-ketone fragment to vinyl ethynyl ketones has not been studied. We carried out a search for conditions for alternative addition, taking into account the ambidensity of vinyl ethynyl ketones.

As a result, it was established that the reaction of isoquinolines **1** with vinyl ethynyl ketones **2** proceeds mainly with the participation of the double bond of the reagent in 2,2,2-trifluoroethanol at 50°C. Pyrrolo[2,1-*a*]isoquinolines **3** with ethynyl ketone group was obtained with yields of 60-80%. Regioselective addition was carried out with activation of the triple bond using copper-containing catalysts in water under microwave radiation. A series of pyrrolo[2,1-*a*]isoquinolines **4** with vinyl ketone group was obtained in yields of 65–81% (Scheme 1) [1].



This work was supported by the Competitiveness Enhancement Program RUDN “5-100” and RFBR grants №17-53-560020

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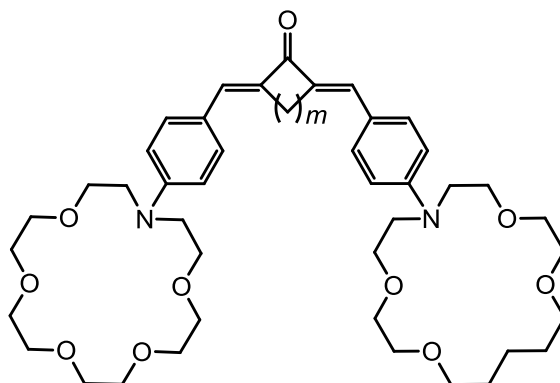
## Self-assembled supramolecular complexes of bis(azacrown)dienones with alkanediammonium cations

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During the last two decades, considerable research interest has been devoted to the design of crown ether substituted chromophores. These compounds were mainly studied for their photochromic and fluorescence properties. In order to elucidate the possibility to construct photoactive supramolecular systems based on dienones we synthesized symmetrical dienones **1** substituted with two azacrown ethers moieties. The behavior of dienones in acetonitrile in the presence of alkanediammonium ions  $^+\text{NH}_3(\text{CH}_2)_n\text{NH}_3^+$  ( $n = 1-12$ ) was studied by UV/vis absorption spectroscopy, fluorescence and NMR  $^1\text{H}$  spectroscopy.

The formation of complexes **1a–c** and alkanediammonium ions **2** is caused by interaction of the ammonium groups of **2** with the crown ether moieties. Spectra of the dienones undergo significant changes in the presence of alkanediammonium ions. The stability constants of the formed complexes were determined.



**1**:  $m = 1(\mathbf{a}), 2(\mathbf{b}), 3(\mathbf{c})$

**2**:  $^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+ 2\text{ClO}_4^-; n=1-12$

It was shown that in a dilute solution bis(azacrown)dienones **1a–c** forms stable 1:1 and 1:2 complexes with alkanediammonium ions. The stoichiometry and the stability constants of the complexes the dienone with alkanediammonium ions depends on the geometric matching of components, which is manifested as the distance between the terminal ammonium groups of alkanediammonium ions and the dienones binding sites. The dienones form 1:2 complexes with short alkanediammonium ions ( $n = 1-5$ ) and high stable 1:1 complexes with long ions. Protonation of azacrown moieties which competes with complexation takes place in some cases. Influence of rigidity of central cycle on complexation was also demonstrated.

The results of this study can be used for directional design of photoactive supramolecular assemblies and optical molecular sensors.

*This work was supported by the Russian Science Foundation  
(project № 19-13-00020)*

## Synthesis of novel betulinic acid's glycoconjugate with superior pharmacological properties to HepG2 cell line

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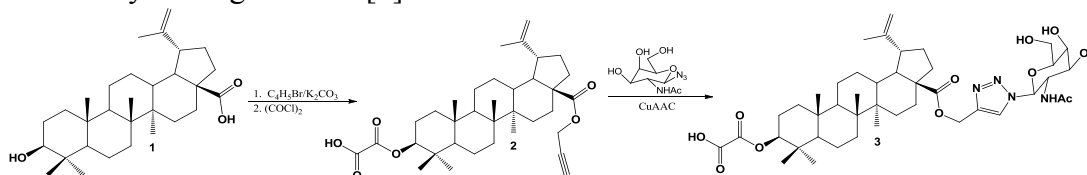
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Pentacyclic triterpenoids are a class of natural compounds widely represented in plant sources. It is known, that triterpenoids are characterized by diverse biological activity, especially antitumor. For example, betulinic acid is in stage II clinical trials as an antitumor agent against melanoma [1]. Most terpenoid structures are characterized by common drawbacks – low solubility and bioavailability, instability to metabolism [2]. In addition, they have a weak pharmacological effect at low concentrations [3]. As a result, research on the chemical modification of the initial carbocyclic backbone in order to search for new biologically active compounds with an improved pharmacological profile and advanced mechanism of action with respect to tumor cell lines has been greatly developed. Various methods for delivery of triterpenes to biological targets are being actively studied [4].

At present work, new derivatives of betulinic acid **2** and **3** were synthesized and characterized. Initially, interaction of betulinic acid **1** with propargyl bromide followed by introduction of oxalic acid fragment were carried out. Subsequent conjugation of acetylenic moieties in **2** with 1-azido-*N*-acetylgalactosamine led to selective formation of new triterpenoid based glycoconjugate **3**. Residues of specific «GalNAc» monosaccharides is known to provide selective binding of conjugates with ASGP-receptor in hepatocytes and thus is known to conduct targeted delivery of drugs to liver [5].



Compound **3** exhibited a high level of cytotoxicity against the target HepG2 cell line. Affinity study of **3** by SPR-spectroscopy showed the  $K_d$  values, comparable to the conventional branched ASGPr-ligands. Therefore, the synthesized glycoconjugate is promising for a detailed study on the subject of targeted antitumor properties against hepatocarcinoma *in vitro*. Also, the proposed approach is planned to be used for other pentacyclic triterpenoids.

*This work was supported by the Russian Foundation for Basic Research (grant № 18-33-20106)*

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## Synthesis of the epi-oligomycin A

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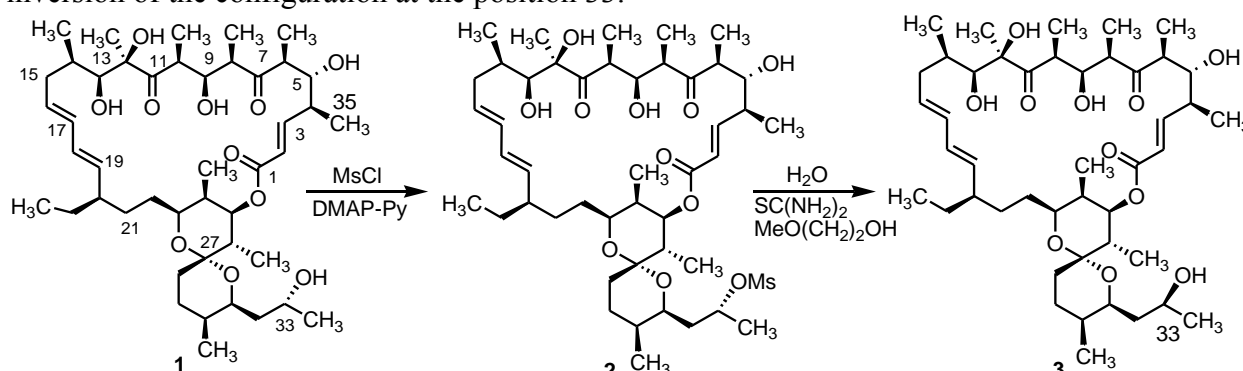
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Oligomycin A has been recognized as a potent ATP-ase inhibitor since 1958 by Lardy et al [1]. The inhibitory effect of oligomycin A is connected with blocking protons transfer through c subunit of F<sub>0</sub> part [2]. Also, it was mentioned that hydroxypropyl side-chain might play an important role in binding of oligomycin A to c-subunit [2].

Since absolute configuration of biologically active compounds in most cases determines their mode of action and potency, preparation and biological evaluation of oligomycin A stereomers might be valuable for SAR studies. We performed two-step synthesis of (33S)-oligomycin A and investigation of its biological activity in comparison with parent antibiotic.

We have previously reported preparation of the 33-O-mesyl oligomycin A and showed its application for further functionalization of C-33 position [3]. Mesyl protection group can be removed by heating with sodium acetate in the mixture of 2-methoxyethanol and water to give parent oligomycin A, whereas the presence of thiourea in the same conditions led to the (33S)-oligomycin A (**3**) as the major product of this reaction. The substitution of mesylate with hydroxyl in 33-O-mesyloligomycin A (**2**) proceeded via S<sub>N</sub>2 mechanism that led to Walden inversion of the configuration at the position 33.



The structure of derivative **3** was confirmed by extension NMR studies, high-resolution mass spectrometry and elemental analysis. Investigation of biological activity of (33S)-oligomycin A in comparison with parent antibiotic revealed that inversion of C-33 hydroxyl group led to decreasing of toxicity toward mammalian cells while therapeutic valuable activity against myelogenous leukemia cell line K562 and corresponding doxorubicin-resistant subline K562/4 retained at the same level or surpasses those for oligomycin A.

*This work was supported in part by the Russian Science Foundation (grant № 15-15-00141)*

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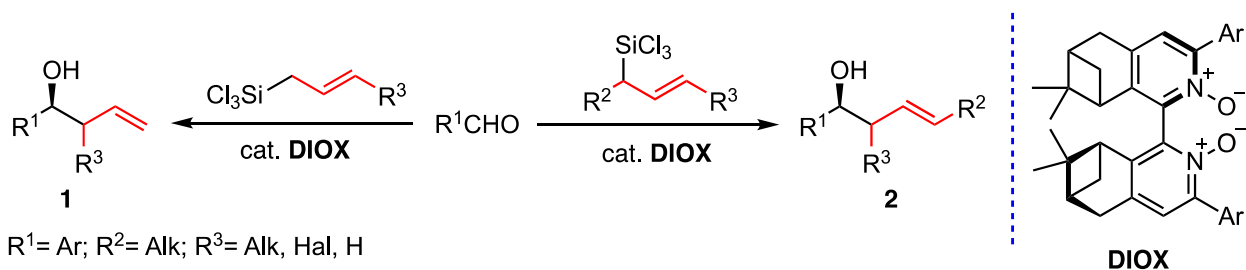
## Synthesis of chiral homoallylic alcohols via bipyridine *N,N'*-dioxides catalyzed allylation of aldehydes

Orlov N.V., Kondratyev N.S., Malkov A.V.

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Homoallylic alcohols are valuable building blocks in organic synthesis. A number of approaches towards these compounds has been developed however they need either expensive reagents or catalysts to perform transformations with high enantioselectivity [1]. Previously bipyridine *N,N'*-dioxides were shown to be highly efficient catalysts in the enantioselective allylation of aldehydes with allyltrichlorosilanes [2]. While utilization of linear allylsilanes resulting in homoallylic alcohols with terminal double bond **1** has been studied quite extensively [3] there are still no examples of organocatalyzed allylations with branched substrates which can lead to homoallylic alcohols with internal double bond **2**.

The aim of the current study was to develop an efficient bipyridine *N,N'*-dioxide catalysts for the synthesis of homoallylic alcohols **2** starting from racemic chiral allylsilanes.



The results of catalysts screening and substrates scope as well as an approach towards natural products synthesis will be presented.

*This work was supported by the Leverhulme Trust Research grant RGP-2015-351*

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## Design of macrobicyclic anthracene probes for anion detection in water solutions

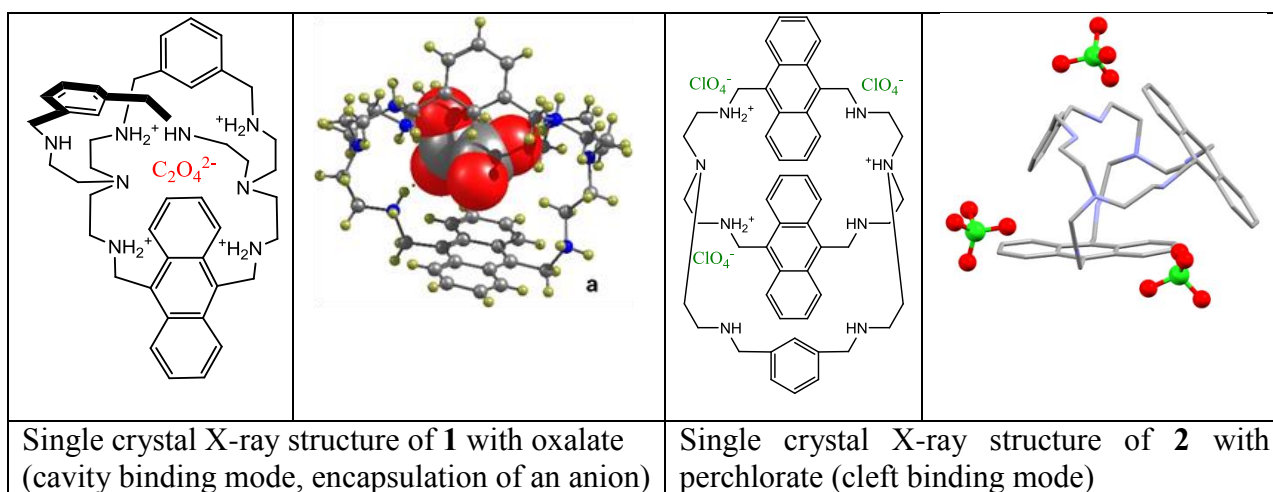
Oshchepkov A.S.,<sup>a,b\*</sup> Namashivaya S.S.R.,<sup>b</sup> Khrustalev V.N.,<sup>a</sup> Kataev E.A.<sup>b</sup>

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Anions are ubiquitous and their importance in biology and the environment resulting from anthropogenic activities is well established [1]. Unfortunately, current strategies for anion detection require expensive instruments and long processing times. Moreover, in many cases the techniques have poor selectivity and high detection limits [2]. In an effort to meet this challenge we have embarked on the anion templated construction of positively charged interlocked host molecules and demonstrated their ability to bind anions in aqueous solvent media.

Here we proposed to develop a novel anthracene azacryptands - macrocyclic molecules composed of trenamine units, connected via anthracene bridges [3]. These compounds were prepared in moderate yields by a stepwise construction of cycles. The receptor **1** binds  $C_2O_4^{2-}$  anion, while receptor **2** nitrate anion with a strong fluorescence enhancement, while other anions show either little response or quenching. The reported crystal structures of anion-cryptand complexes show that receptors tend to bind strong coordinative anions in a cavity mode (encapsulation of an anion), while weak coordinative favor cleft binding mode



We thank ESF-Project «NitraMon» and RUDN University Program “5-100” for A.S.O. and V. N. Kh. for financial support

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## Design of self-assembling capsules based on thiacalixarene derivatives for the delivery of doxorubicin

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The development of self-assembling supramolecular systems based on macrocyclic compounds capable of molecular recognition of drugs and biomacromolecules is one of the promising trends in organic, supramolecular, medical, and biological chemistry.

It is known that doxorubicin (Fig. 1) is an extremely effective anticancer agent, but its use is limited by low water solubility. Doxorubicin's bioavailability can be improved by enclosing it in biodegradable and non-toxic macromolecular nanocontainers.

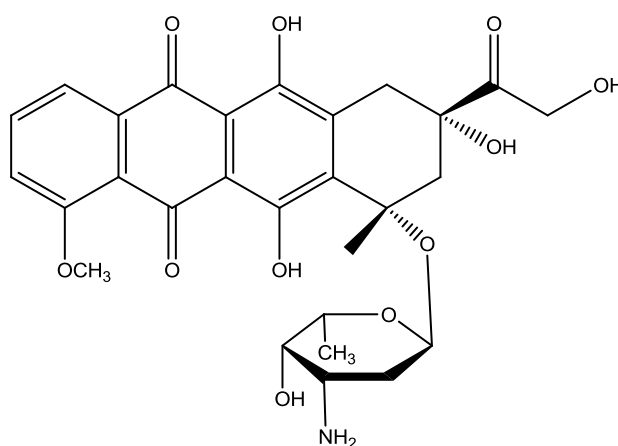


Fig. 1. Doxorubicin structure.

Selective and effective binding of doxorubicin by nanoscale supramolecular structures based on water-soluble derivatives of *p-tert*-butylthiacalix[4]arene can increase its solubility, biopermeability in combination with targeted delivery to target cells.

In this work, polyamino acids, new water-soluble tetrasubstituted thiacalix[4]arene derivatives containing amide and quaternary ammonium groups as well as amino acid fragments (glycine, phenylalanine, tryptophan) were obtained. The interaction of the obtained compounds with doxorubicin was studied by the UV, NMR and fluorescence spectroscopy.

*This work was supported by the Russian Foundation for  
Basic Research (grant № 18-33-20148)*

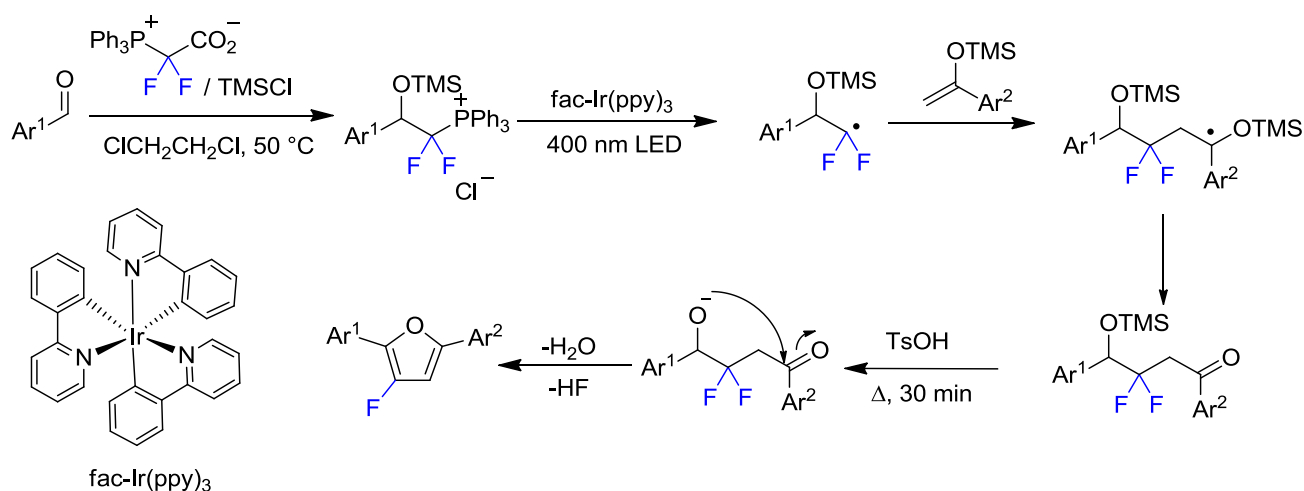
## Generation of radicals from *gem*-difluorophosphonium salts and their use in organic synthesis

Panferova L.I.,<sup>1</sup> Vevin V.V.,<sup>1</sup> Trifonov A.L.,<sup>1,2</sup> Dilman A.D.<sup>1</sup>

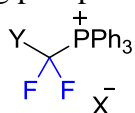
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In the interaction of aldehyde and difluoromethylenephosphobetaine in the presence of trimethylchlorosilane, difluorophosphonium salts are well obtained. These salts enter into photocatalytic reactions of radical addition to various substrates, such as silicate and acrylonitrile. In the case of attachment to silylenolates, the product undergoes intramolecular cyclization to produce new substituted fluorofurans.



A series of new fluorine-containing phosphonium salts was obtained.



Y = heteroatom

This work was supported by the Russian Foundation for Basic Research (project No. 18-33-00331\_mol\_a)

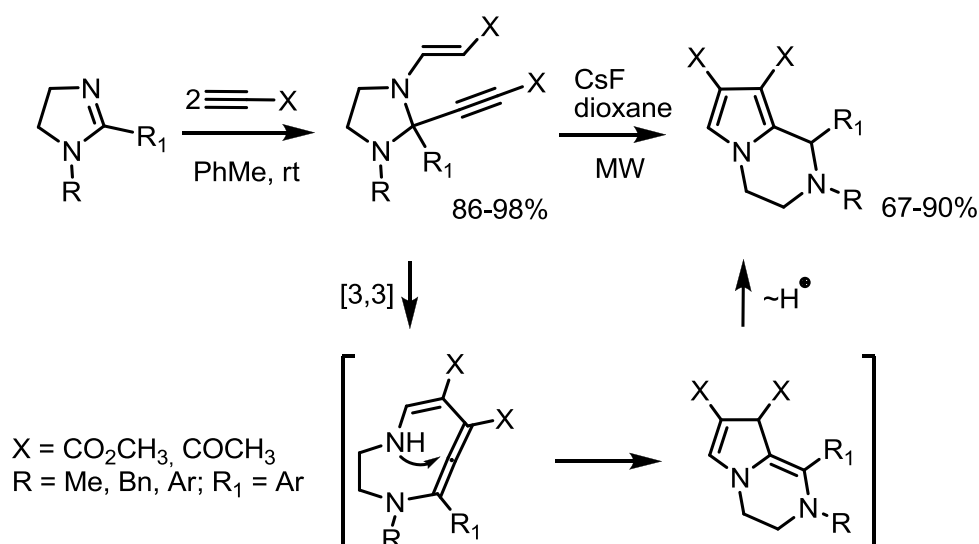
## A Domino route from imidazolines to polysubstituted tetrahydropyrrolo[1,2-*a*]pyrazines

Parshina D.V., Golubenkova A.S., Golantsov N.E., Voskressensky L.G.

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Nitrogen-containing heterocycles are an important class of organic compounds with numerous applications in drug discovery, functional materials research and catalysis. In particular, pyrrolo[1,2-*a*]pyrazine derivatives have neuropsychotropic properties.

Due to high synthetic efficiency in the design of complex molecules, domino-reactions have become an important area of research in heterocyclic chemistry. Consequently, the development of transition-metal-free, step-economic and atom-economic methodologies for tetrahydropyrrolo[1,2-*a*]pyrazines synthesis from easily available substrates continues to be of great interest. In recent times several new preparative methods for 2-imidazolines have been discovered, which allows us to consider them as convenient starting materials.



This work discloses our latest results, concerning pseudo three-component reaction of 2-imidazolines and electron-deficient terminal alkynes to form tetrasubstituted imidazolidines, which can undergo further transformations. The cascade reaction proceeds through a thermal [3,3]-sigmatropic rearrangement, followed by intramolecular nucleophilic addition of nitrogen atom to allene fragment, and terminates by tautomerization to the corresponding 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazine.

*This work was supported by the Russian Foundation for Basic Research (grant № 19-03-00502 a)*

## Synthesis of novel 5-arylisoxazole derivatives of malonic acid

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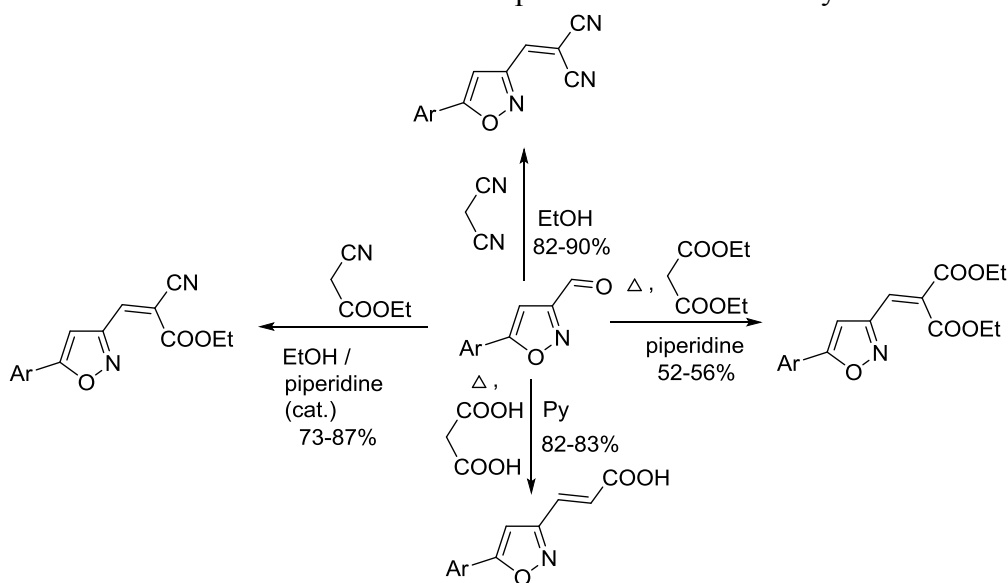
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5-Arylisoxazoles were proven to be valuable pharmacophores in the synthesis of many bioactive substances [1], as well as useful intermediates in the development of new materials, such as palladium-based catalysts for cross-coupling reactions [2]. Corresponding 5-aryl(heteryl)isoxazoles are easily available through successive transformation of affordable aryl(heteryl)-3,4,4-trichlorallylketones [3,4].

Herein we report synthesis of 5-arylisoxazole derivatives of malonic acid - reagents that allow introducing both isoxazole core and alkene fragment into a molecule, thus providing a possibility of IMDA reaction in resulting molecule and insertion of the pharmacophore isoxazole heterocycle.

Corresponding reagents were synthesized through condensation of 5-arylisoxazole-3-carbaldehydes with various derivatives of malonic acid under condition of basic catalysis. In case of condensation with malononitrile reaction proceeded without catalysts.



Similar transformation were performed on the basis of 4,5-dichlorisothiasol-3-carbaldehyde.

*This work was supported by the Russian Foundation for Basic Research (grant 19-53-04002) and the Belarusian Republican Foundation for Fundamental Research (grant X19PM-003)*

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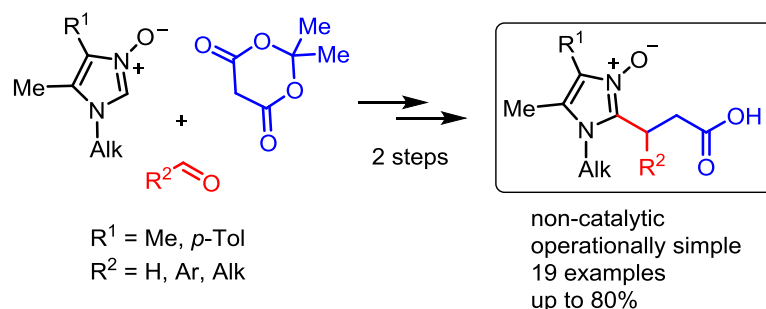
## A new facile method for the synthesis of 3-imidazolylpropionic acids *N*-oxides

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Productions of imidazole are biologically active compounds and play an important role in various biochemical processes. The imidazole core is a part of the regulators of the most important physiological processes, nucleic acids and proteins, and also the imidazole fragment is often used as pharmacological or toxicological agents, for example, chemotherapeutic agents, psychotropic drugs, antibiotics [1]. The creation of new approaches to the modification of imidazoles is an important problem in organic chemistry. The described methodology allow to obtain new compounds with functional groups and fragments that are difficult or impossible to introduce with usage of known reactions.

In this way, we developed synthetic protocol suitable for the preparation of 3-imidazolylpropionic acids *N*-oxides by acid hydrolysis (refluxing in 10% aqueous hydrochloric acid and treatment with solution of sodium hydroxide, sodium acetate, or even boiling in the water in the open flask) of the products of condensation of imidazole *N*-oxide with Meldrum's acid and aldehyde [2, 3].



By this method, 3-imidazolyl propionic acids were obtained. The possibility of introducing a wide spectrum of aldehydes and *N*-oxides of imidazole in this reaction in combination with the ease and simplicity of the procedure makes this synthesis method useful for the functionalization of imidazole *N*-oxides. The developed synthesis protocol opens up easy and fast access to imidazole derivatives, which are difficult to synthesize in another way.

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## The effect of new phenol derivatives on SOD-protector activity of the Russian sturgeon liver

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<sup>1</sup>Astrakhan State Technical University, 414025, Russia, Astrakhan, st. Tatishcheva 16

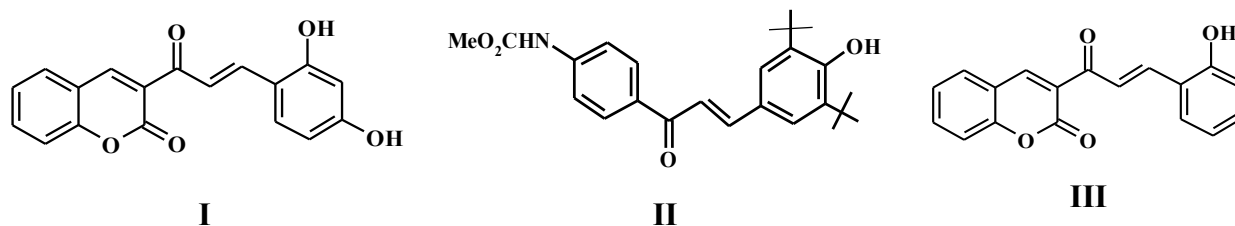
<sup>2</sup>Federal Research Centre the SSC of the RAS, 344006, Russia, Rostov-on-Don, st. Chehova, 41

<sup>3</sup>Astrakhan State Technical University, 414056, Russia, Astrakhan, st. Tatishcheva, 20a

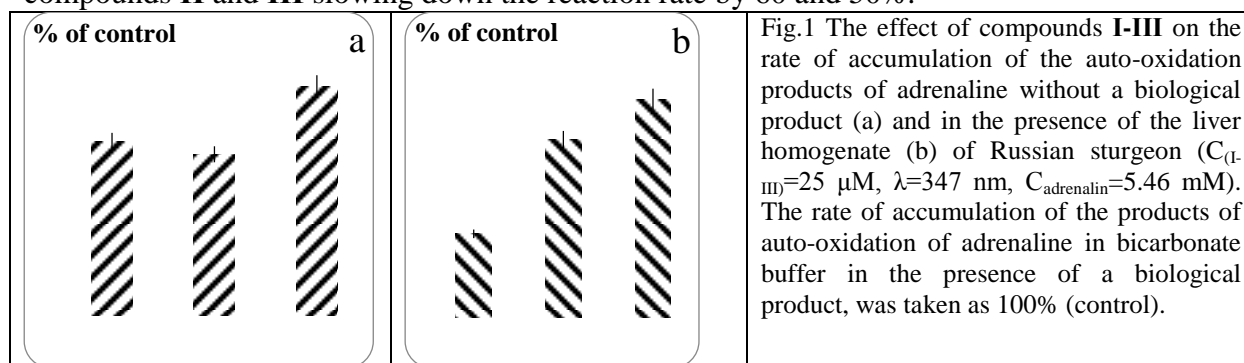
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Superoxide dismutase (SOD) is the metalloenzyme of the antioxidant protection of cell membranes against the damaging effects of highly toxic reactive oxygen species (ROS), which are generated in large quantities when activated by lipid peroxidation. SOD is present in all cells that consume oxygen and is an essential element of antioxidant protection as it catalyzes the dismutation of singlet oxygen produced by the passage of electrons through the respiratory chain. The activity of this antioxidant enzyme in the body decreases with various pathologies, therefore, for successful treatment, drugs with SOD-protector activity in biological media are necessary.

In this work the effect of new derivatives of hindered phenol (**I-III**) on the rate of superoxide anion-radical ( $O_2^{\cdot-}$ ) generation in the auto-oxidation reaction of adrenaline in an alkaline medium was investigated. The effect of the compounds on the SOD-protector activity of a biological product, the liver of the Russian sturgeon, was also studied.



It was found that all compounds exhibit both antiradical and SOD-tread activity (Fig. 1). Compounds **I** and **II** reduce the rate of adrenaline oxidation in alkaline bicarbonate buffer by 50%, and compound **III** by 25%. Compound **I** shows the highest SOD-tread activity in the presence of the Russian sturgeon liver homogenate, reducing the  $O_2^{\cdot-}$  generation rate by 80%, compounds **II** and **III** slowing down the reaction rate by 60 and 50%.



Thus, in this work, the antiradical activity of new derivatives of spatially obstructed phenol and their ability to increase the SOD-protector activity of the Russian sturgeon liver homogenate was discovered, which allows considering these compounds as potential antioxidants.

*This work was supported by the Russian Foundation for Basic Research (grant № 19-03-00006 A)*

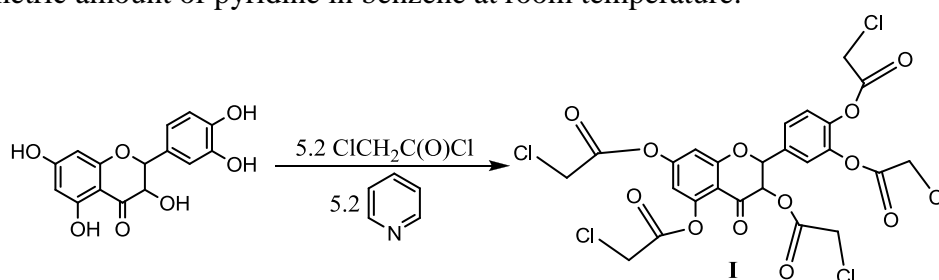
## Synthesis of morpholinium salts based on chloroacetylated dihydroquercetin derivatives

Pozdeev A.O., Koroteev A.M., Pimankina S.N., Koroteev M.P.

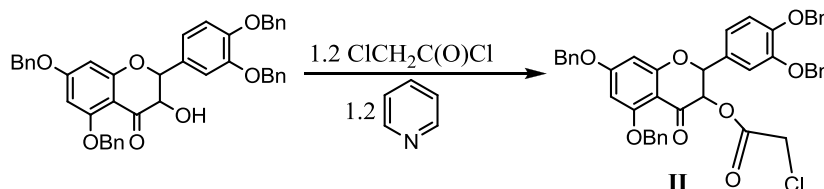
Moscow Pedagogical State University, 129164, Moscow, Kibalchich str. 6, b.2  
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One of the methods for modifying flavonoids and increasing their drug activity is the acylation reaction. As known, such compounds have low solubility in water. To solve this problem, the synthesis of acyl derivatives with water solubility was carried out. In this work, at the first stage, new acylated derivatives based on dihydroquercetin and its modifications - tetrabenzyl-3-hydroxydihydroquercetin were obtained. Based on these compounds, morpholine-containing salts were synthesized.

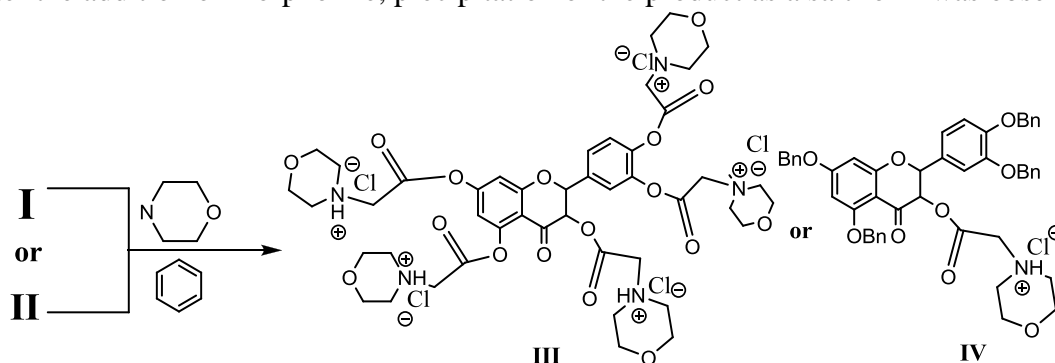
The total acylation of dihydroquercetin was carried out with chloroacetic acid chloride with a stoichiometric amount of pyridine in benzene at room temperature:



The acylation of tetrabenzyl-3-hydroxydihydroquercetin was also carried out at room temperature in benzene:



After the addition of morpholine, precipitation of the product as a salt form was observed:



Thus, a series of water-soluble acyl derivatives of dihydroquercetin was synthesized.

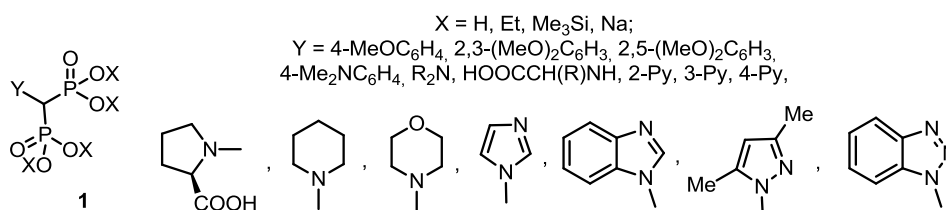
*This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00466)*

## New functionalized methylenediphosphonic acids with azaheterocycles and amino acids moieties as perspective bioactive compounds

Prishchenko A.A., Alekseyev R.S., Livantsov M.V., Novikova O.P., Livantsova L.I.,  
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Functionalized methylenediphosphonic acids and their derivatives with aromatic and heterocyclic moieties are well-known biomimetics of hydroxy- or aminocarboxylic acids and natural pyrophosphates, and some of them such as zoledronic, risedronic, and minodronic acids are widely used in medicine [1]. Organosilicon-mediated synthesis of functionalized organophosphorus acids and their derivatives was used recently by us as convenient method of creating of P-C bonds. We have synthesized the new functionalized methylenediphosphonic acids and their derivatives **1** including aromatic, azaheterocyclic, and amino acids moieties *via* addition of tris(trimethylsilyl) phosphite to corresponding formamides in the presence of effective catalyst – trimethylsilyl triflate under mild conditions [2,3]. Also trimethylsilyl-containing organophosphorus compounds easily react with methanol excess or with sodium methylate in methanol giving water soluble acids or their sodium salts in high yields.



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 the Russian Foundation for  
Basic Research (grant № 17-03-00169)*

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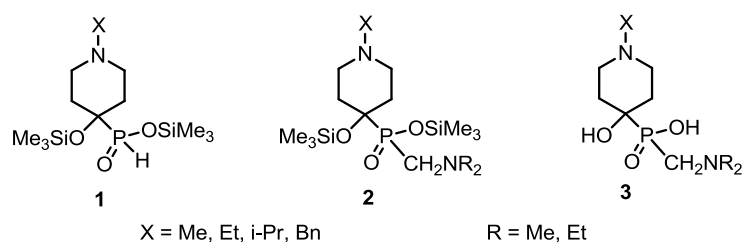
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## Synthesis of new functionalized aminomethylphosphonic acids with *N*-alkyl 4-hydroxypiperidines moieties

Prishchenko A.A., Alekseyev R.S., Livantsov M.V., Novikova O.P., Livantsova L.I., Petrosyan V.S.

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The synthesis of new compounds containing several bioactive groups around the organoelement moieties currently is a modern trend of bioorganoelement chemistry. Functionalized phosphonic acids and their derivatives with two bioactive groups are of special interest because these groups are connected by phosphoryl scaffold *via* two stable non-hydrolysable P-C bonds. Functionalized phosphonic and phosphinic acids as well as their derivatives are the important organophosphorus biomimetics of natural amino (hydroxyl) substituted carboxylic acids, and some of them are found in living systems. Many of these substances exhibit properties as antibacterial, antiviral and antitumor agents, antibiotics, enzyme inhibitors, plant growth regulators and pesticides. Functionalized hydroxymethylphosphonic acids and corresponding phosphonopeptides compete with the carboxyl containing analogues for the active sites of the enzymes and cell receptors, and also they inhibit the enzymes involved in the metabolism of hydroxy carboxylic acids, thus affecting various biological processes in the cell. In addition, hydroxymethylphosphonates and their derivatives are useful synthetic receptors and chiral ligands in metal complexes and selective highly efficient complexones, extractants and analytical reagents [1]. We have proposed the convenient synthesis of new aminomethylphosphonic acids and their derivatives containing *N*-alkyl 4-hydroxypiperidines moieties. So the addition of bis(trimethylsiloxy)phosphine to *N*-alkyl 4-piperidones proceeds under mild conditions to give PH-phosphinates **1** as key compounds for preparation of trimethylsilyl esters **2** of above acids *via* interaction with various amins. The further treatment of phosphonic acids trimethylsilyl esters **2** with the methanol resulted in the water-soluble corresponding acids **3** in high yields [2].



*This work was supported by the Russian Foundation for Basic Research (grant № 17-03-00169)*

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## Synthesis of 1-phenyl-5-(indol-3-yl- and -2-yl)imidozolidin-2-ones

Protopopova P.S.<sup>a</sup>, Sviridova L.A.<sup>b</sup>, Kochetkov K.A.<sup>a</sup>

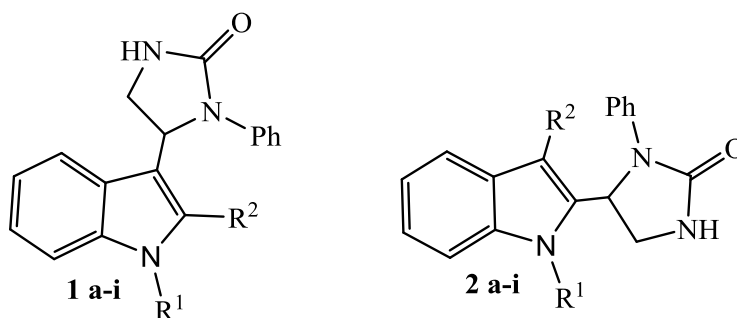
<sup>a</sup> A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), 119991, Moscow, Vavilova St. 28

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It is known that the combination of pharmacophoric fragments in a single molecule often leads to a strengthening and/or to a change in the pharmacological properties of the molecule. In this connection there is significant interest in studying compounds which contain indole and imidazolidone fragments in the molecule.

Previously, had been reported a simple synthesis 2-alkyl-3-(indol-3-yl- and -2-yl)-isoindol-2-ones [1] and 1-alkyl-5-(indol-3-yl)-pyrrolidin-2-ones [2] by means of amidoalkylation reaction. We use this method for the synthesis of -phenyl-5-(indol-3-yl- and -2-yl)-imidozolidin-2-ones **1 a-i** and **2 a-i** from corresponding derivatives imidazole and indoles.



**a** R<sup>1</sup>=H; R<sup>2</sup>=H

**b** R<sup>1</sup>=H R<sup>2</sup>=Me

**c** R<sup>1</sup>=H R<sup>2</sup>=*p*-TOL

**d** R<sup>1</sup>=H R<sup>2</sup>= Ph

**e** R<sup>1</sup>=H R<sup>2</sup>= Bn

**f** R<sup>1</sup>=Me R<sup>2</sup>=Me

**g** R<sup>1</sup>=Me R<sup>2</sup>=*p*-TOL

**h** R<sup>1</sup>=Me R<sup>2</sup>= Ph

**i** R<sup>1</sup>=Me R<sup>2</sup>= Bn

It was shown that related structures such as 5-indolyl-imidazolones possess high protein kinase C inhibitory activities [3] and may be of interest as potential drugs for the treatment of r CNS-degenerative disorders. In the near future we are planning to set about biological tests for the all of -phenyl-5-(indol-3-yl- and -2-yl)-imidozolidin-2-ones **1** and **2** synthesized in the framework of this study.

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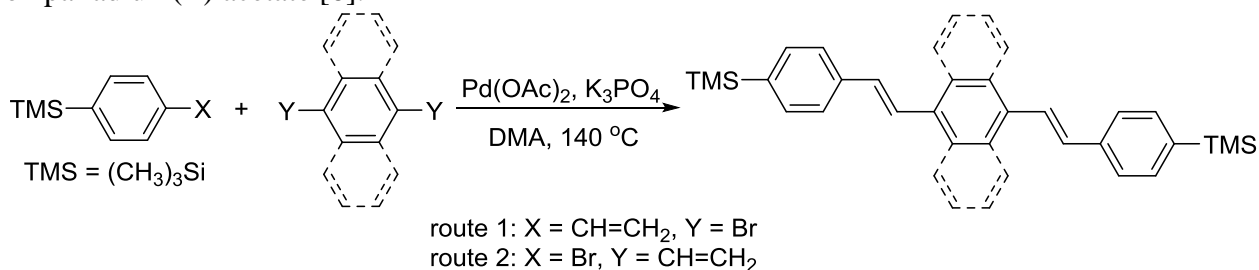
## Novel organosilicon arylenevinylenes prepared via Heck reaction

Pyatakov D.A., Borshchev O.V., Skorotetcky M.S., Ponomarenko S.A.

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Oligo- and poly(arylenevinylenes) are of great interest as materials for production of organic light-emitting diodes (OLEDs) [1], organic field-emitting transistors (OFETs) [2] and other organic electronics devices [3] since the moment of discovery of electroluminescence in poly(phenylenevinylene). It was recently shown that optic and electric properties of oligoarylenes could be successfully improved by silicon atoms in their structures [4, 5].

In present work, we studied two alternative strategies for synthesis of symmetric silicon-containing oligoarylenevinylenes via Heck reaction from TMS-substituted styrene and commercially available dibromoarenes (route 1, scheme 1), and TMS-substituted bromobenzene from corresponding divinylarenes (route 2, scheme 1), using ligand-free catalytic system based on palladium(II) acetate [6].



It was found that the nature of substrates crucially influences on synthetic schemes. Oligoarylenevinylenes with central benzene ring could be successfully obtained through the both routes in good yields, while oligoarylenevinylenes with anthracene fragment could be synthesized from dibromoanthracene and silicon-containing styrenes since divinylanthracene reacts very poorly with TMS-substituted bromobenzene, and the synthesis is accompanied with desilylation of target oligoarylenevinylene. These data will be applied for synthesis of branched organosilicon oligo- and poly(arylenevinylenes).

The structures of the synthesized compounds were confirmed by means <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopic data, and elemental analysis. Thermostability of new oligoarylenevinylenes was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Optic properties (absorption and emission spectra) were examined in diluted solutions, thin films and crystals.

*The work was supported by the Russian Foundation for Basic Research  
(project no. 18-03-00699) and performed in the framework of leading  
science school NSh-5698.2018.3*

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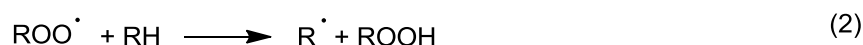
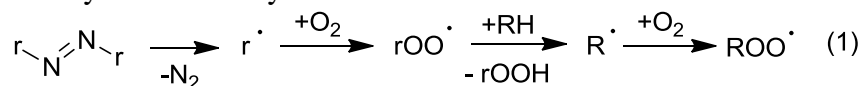
## The kinetics of free radical oxidation of (2,2-dichlorocyclopropyl)-benzene

Raskil'dina G.Z., Borisova Yu.G., Grabovskii S.A., Zlotsky S.S.

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Products based on gem-dichlorocyclopropylketone are promising syntons for the production of biologically active and medicinal compounds [1]. A possible approach to its synthesis can be the liquid-phase oxidation of a styrene derivative – phenyl-gem-dichlorocyclopropane with decomposition of the intermediate hydroperoxide according to a known scheme [2].

Using kinetic methods on an automated manometric unit with constant regulation of oxygen pressure with computer registration, the kinetics of phenyl-gem-dichlorocyclopropane 1 oxidation initiated by azobisisobutyronitrile has been studied.



The initiation rate was determined using a known inhibitor of radical chain oxidation of  $\alpha$ -tocopherol. Using the modern DFT method M06-2X / MG3S, calculations of the bond dissociation energy are carried out. This method allows determining the bond strength with high accuracy ( $\sim 1.5 \text{ kcal}\cdot\text{mol}^{-1}$ ).

It was established that under the conditions studied ( $60^\circ\text{C}$ , the initiator is AIBN,  $W_i = 5.3 \times 10^{-8} \text{ mol} (\text{l}\cdot\text{s})^{-1}$ ), the initiated oxidation of compound **1** proceeds via a radical-chain mechanism with a quadratic chain break. This is confirmed by the fact that the oxidation rate ( $W_0$ ) does not depend on pressure in the range of 90–100 kPa and is directly proportional to concentration **1** and the square root of the initiation rate. The obtained value of the oxidizability parameter for **1** is  $k_2 \cdot k_6^{-0.5} = 5 \cdot 10^{-5} (60^\circ\text{C})$  [3]. The rate constant for the continuation of the chain  $k_2$  is estimated. The bond strengths calculated by the M06-2X / MG3S method are consistent with the values obtained.

Thus, the obtained values of  $k_2 \cdot k_6^{-0.5}$  and  $k_2$ , as well as the calculated strength values of the tertiary C-H bonds in compound **1** indicate that the corresponding hydroperoxide from **1** cannot be formed in sufficient concentration (in 24 hours at  $60^\circ\text{C}$  its yield does not exceed 0.1%).

*This work was supported by the Russian Foundation for  
Basic Research (grant № 19-33-80002\19)*

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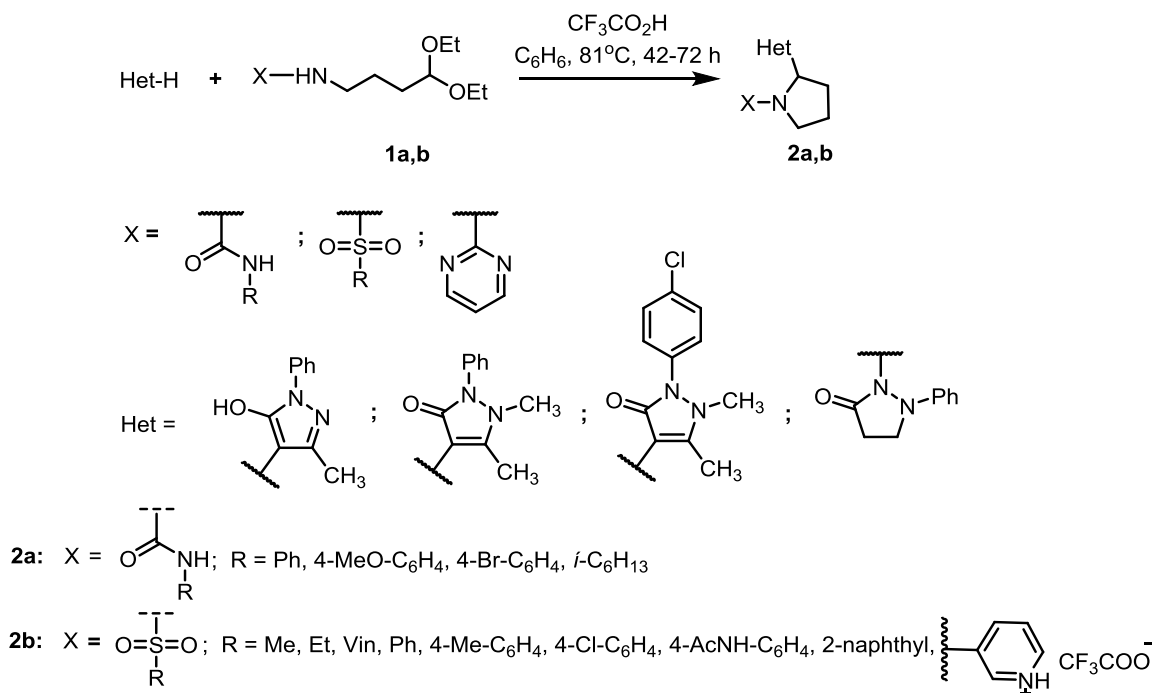
## Synthesis of new 2-pyrazolylpyrrolidines based on acid-catalyzed reaction of 4,4-diethoxybutan-1-amine derivatives with pyrazolones

Rizbayeva T.S., Smolobochkin A.V., Gazizov A.S., Burilov A.R., Pudovik M.A.

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Russia, 420088, Kazan, Academician Arbuzov str. 8  
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Heterocyclic compounds over the past decades continue to be the object of close attention of both synthetic chemists and researchers engaged in the search for new biologically active substances.

Earlier in our group, a convenient and simple method of synthesis of 2-arylpiperidines based on acid-catalyzed reaction of 1-(4,4-diethoxybutyl)ureas with phenols was developed [1,2]. Taking in account that the enol form of pyrazol-5-on can be considered as an aromatic hydroxypyrazole, we have suggested that these compounds can be used as a heterocyclic analogs of phenols in reactions with acetals. Indeed, it turned out that the interaction of 1-(4,4-diethoxybutyl)ureas **1a** and 1-(4,4-diethoxybutyl)sulfonamides **1b** with pyrazole-5-ones leads to the formation of previously unknown 2-pyrazolylpyrrolidines **2a,b**. In addition, it was found that a saturated heterocycle — 1-phenyl-3-pyrazolidone — also reacts with acetals **1a** to form an *N*-alkylation product.



This work was supported by the Russian Foundation for Basic Research (grant № 18-33-20023)

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## Coordination properties of *S*-(2-(1-imidazolyl)ethyl)-3-mercaptopropionic acid

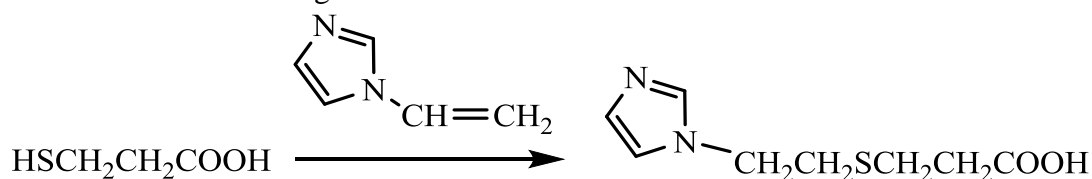
Rodionova A.P., Slepukhin P.A., Pestov A.V.

*Postovsky Institute of Organic Synthesis Ural Branch of the Russian Academy of  
Sciences, 620137, Yekaterinburg, Sofia Kovalevskoy str., 22*

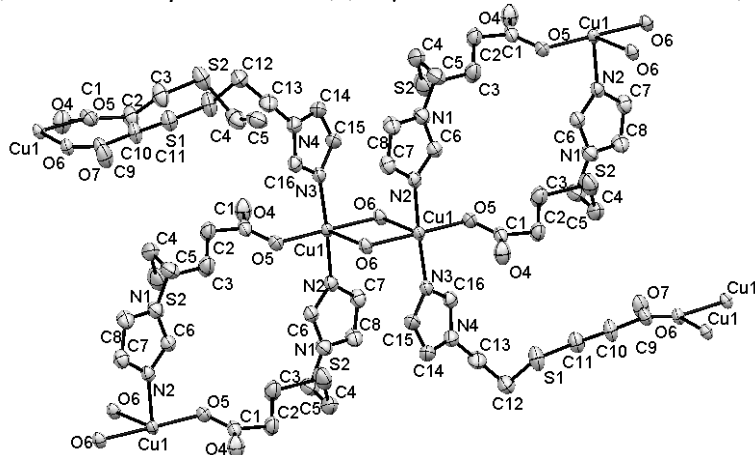
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Imidazole is one of the main aromatic systems of the class of five-membered heterocycles. This plays an important role at the present time, not only in biochemical processes, but also in technical ones, due to the combination of the small size of the molecule and unique chemical properties. Scientists are developing on the basis of imidazole surfactants, complexing agents and polynuclear complexes, ionic liquids, elements of molecular electronics, adhesive and anticorrosive materials, medicines, etc. Many fairly simple imidazole derivatives remain unexplored to date, despite the large number of publications on this topic. Ligands with a dentate of three based on  $\beta$ -alanine showed promise in the field of producing cluster complex compounds earlier. Expansion of a number of potential complexing agents based on imidazole derivatives, obtaining *S*-(2-(1-imidazolyl)ethyl)-3-mercaptopropionic acid and a complex compound based on this is the purpose of this work.

The addition of 3-mercaptopropionic acid to *N*-vinylimidazole in the presence of a radical initiator to obtain the target substance was used.



The copper complex *S*-(2-(1-imidazolyl)ethyl)-3-mercaptopropionic acid is stable. Structure of complex investigated by using X-ray structural analysis. Crystal system – monoclinic, space group  $P1\ 21/n1$ , crystallographic parameters:  $a=11.8008(3)\ \text{\AA}$ ,  $b=12.8681(2)\ \text{\AA}$ ,  $c=14.5956(4)\ \text{\AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 102.463(2)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V\ \text{\AA}^3 = 2164.17(8)$ ,  $Z=4$ .



Copper metal centers are combined into dimers with distance  $\text{Cu}\dots\text{Cu}\ 3,405\ \text{\AA}$ . The coordination environment of each metal center is a square pyramid. Two nitrogen atoms of the imidazole rings and two oxygen atoms of the carboxyl groups of different ligands form its base. The bridging oxygen atom of the carboxyl group is at the apex.

Thus, the *S*-(2-(1-imidazolyl)ethyl)-3-mercaptopropionic acid in copper complex is monodentate ligand. Chelate cycles are not formed.

## Synthesis of functionalized azo dyes and their siloxane derivatives to obtain colored polymer microspheres

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Nowaday, there are various methods of polymer microspheres dyeing. Such spherical particles consist of crosslinked vinyl type polymer. The colored microspheres are used for the most important areas of research, such as: studies of fluid flow, tracking of processes inside the cells, or studies of phagocytosis. Therefore, the development of new approaches for dyeing of the polymer microspheres are of great importance [1]. One of the methods for dyeing of polymer microspheres is covalent binding of dye molecules to polymer molecules in the bulk of the particles. This method has many advantages, the main of which is the absence of dye migration from the surface of a particle due to covalent binding. To implement this method of dyeing, it is necessary to develop a molecular design of a dye molecule capable of copolymerizing with the vinyl type monomers.

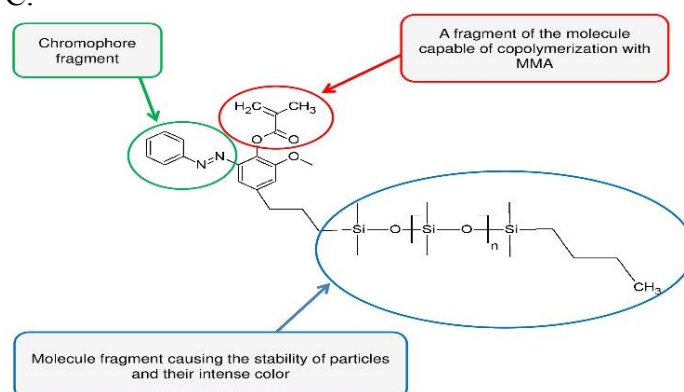
In this work, the synthesis of various methacryloxy-functionalized azo dyes and their copolymerization with MMA were shown.

At the first stage of this work, various phenol-type azo dyes as model compounds were obtained and characterized. It was shown, that methacrylic group, being introduced into the structure of the obtained azo dyes, can be involved in polymerization of vinyl type monomers to form colored microspheres.

Next, it was assumed, that introduction of siloxane fragments will allow to obtain stable and intensely colored polymeric microspheres. For these purposes siloxane fragments with various lengths were introduced into the structure of eugenol (see the scheme below). For the synthesis of siloxane derivatives of azo dyes, eugenol, which is a natural, multifunctional derivative, was taken as the initial, basic substance [2]. After that, the chromophore phenylazo group was introduced into the structure of the products obtained by azo coupling reaction with aniline.

At the third stage, the obtained methacryloxy-derived azo dyes with MMA were copolymerized to form colored microspheres with siloxane fragments.

All of the intermediate compounds and resulting copolymers are characterized by NMR, UV-spectroscopy, GPC.



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## NHC Platinum(0) complexes: highly active *ortho*-selective catalysts in undirected C–H borylation of arenes

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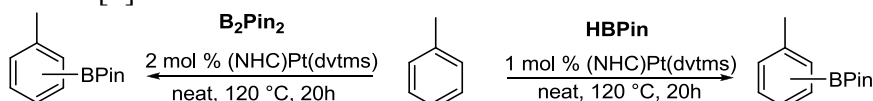
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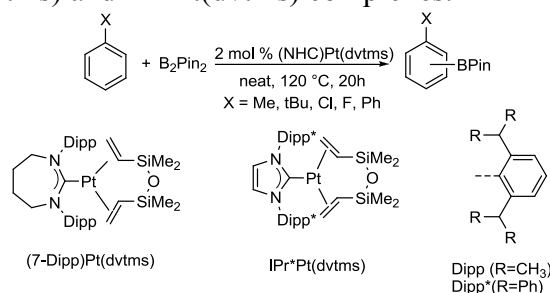
Platinum complexes bearing sterically encumbered NHCs (N-heterocyclic carbenes) are highly active in C-H borylation of arenes. Borylation with B<sub>2</sub>Pin<sub>2</sub> proceeds predominantly in *ortho*-position even in absence of a directing group (*o*:*m*:*p* ratio up to 10:3:1). We also report on efficient platinum mediated C-H borylation of arenes with HBPIn for the first time.

Catalytic properties of (NHC)Pt(dvtms) complexes were compared in the reaction of dehydroboration with bis(pinacolato)diboron and with pinacolborane under the same conditions. Series of experiments was aimed to reproduce the procedure reported by Furukawa et al. using toluene as a substrate [1].



It was found that the nature of a carbene ligand significantly influence the catalytic activity and selectivity of the reactions. Most surprising specific feature of the platinum NHC complexes is the unusual *ortho*-selectivity of C–H activation in monosubstituted benzenes: *o* : *m* : *p* ratio up to ~ 10 : 3 : 1 in dehydroboration of toluene using (7-Dipp)Pt(dvtms). The nature of such *ortho*-selectivity is unclear. We have also observed that in some cases, when sterically bulky NHC ligands were used, the excessive yields (> 100%) of borylation products were obtained. This have led us to the assumption that dehydroboration of arenes can proceed not only with B<sub>2</sub>Pin<sub>2</sub>, but also with HBPIn, which is released in the course of the reaction. Indeed, in the experiments with HBPIn, we were the first to show that pinacolborane can serve as suitable reagent in platinum mediated dehydroboration of toluene.

We also conducted a series of experiments on dehydroboration of various arenes mediated by (7-Dipp)Pt(dvtms) and IPr<sup>\*</sup>Pt(dvtms) complexes.



*This work was supported by the Russian Foundation for Basic Research, research project number 16-29-10706 ofi\_m*

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## Diboration of alkenes catalyzed by expanded-ring *N*-heterocyclic carbene platinum(0) complexes

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Nechaev M.S.<sup>1,2</sup>, Asachenko A.F.<sup>1,2</sup>

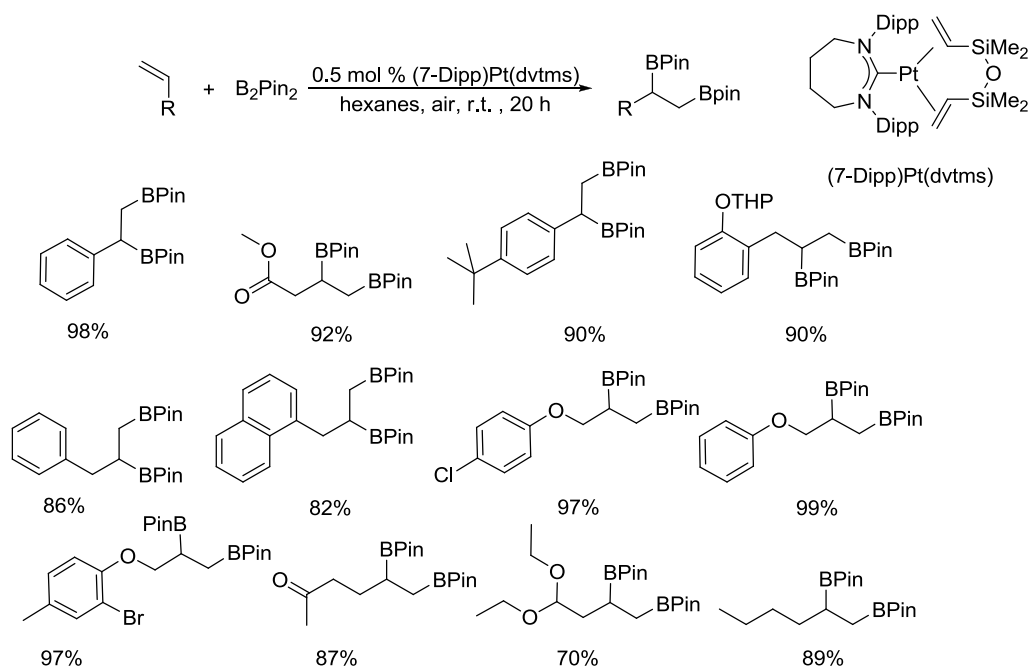
<sup>1</sup> *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospect 29, Moscow, 119991, Russia*

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1,2-Diborated alkanes are useful building blocks in C-C, and C-X (X=N, O, S) bond forming reactions. A number of articles on the transition metal catalyzed alkenes diboration were published. Herein, a study on alkene diboration by a series of novel NHC platinum(0) complexes is reported.

We synthesized a series of (NHC)Pt(dvtms) complexes by direct reaction of Karstedt's catalyst Pt<sub>2</sub>(dvtms)<sub>3</sub> with free carbenes in THF. Structure of (7-Dipp)Pt(dvtms) complex was determined by XRD. Catalytic activity of synthesized platinum(0) complexes was studied in the model reaction of styrene and B<sub>2</sub>Pin<sub>2</sub> in different solvents. (7-Dipp)Pt(dvtms) in hexanes solution showed highest performance (TON = 4250).

We performed a series of experiments on diboration of various terminal alkenes mediated by (7-Dipp)Pt(dvtms) complex.



*This work was supported by the Russian Foundation for Basic Research, research project number 16-29-10706 ofi\_m*

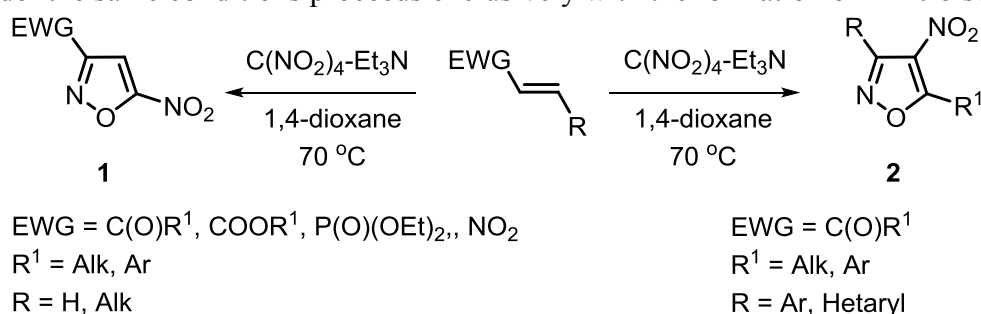
## Novel $\pi$ -conjugated systems based on 4-nitroisoxazoles: synthesis and fluorescent properties

Sadovnikov K.S.<sup>a</sup>, Tukhbatullina A.R.<sup>a</sup>, Vasilenko D.A.<sup>a</sup>, Averina E.B.<sup>a,b</sup>

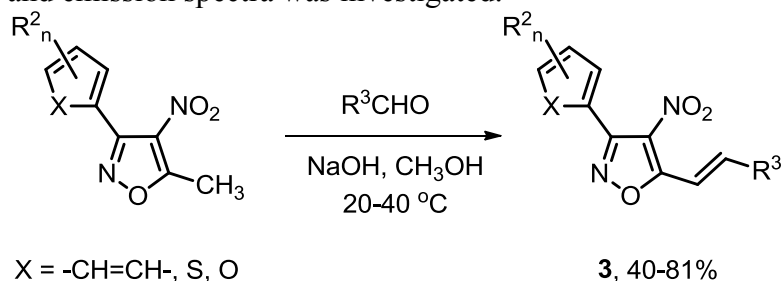
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Recently, a chemo- and regioselective approach to 5-nitroisoxazoles **1** based on heterocyclization of electrophilic alkenes under the treatment of activated tetranitromethane (TNM) has been elaborated [1, 2]. However, heterocyclization of aryl substituted  $\alpha,\beta$ -unsaturated ketone under the same conditions proceeds exclusively with the formation of 4-nitroisoxazole **2**.



Heterocycles **2** bearing the methyl group in position 5 was studied in the reaction of condensation with various types of aromatic aldehydes and the large series of novel  $\pi$ -conjugated structures **3** was synthesized in a good yields. Photophysical properties of the obtained compounds were studied and the influence of the aryl/hetaryl substituents in isoxazole cycle on the absorption and emission spectra was investigated.



R<sup>2</sup><sub>n</sub> = H, 4-MeO, 4-Br, 3,4,5-(MeO)<sub>3</sub>, 4-Ph, naphthyl  
R<sup>3</sup> = Ar, naphthyl, furyl, thiophenyl

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## New ditopic organic ligands with terpyridine and 5-(2-pyridyl)-2-thio-imidazole-4-one fragments

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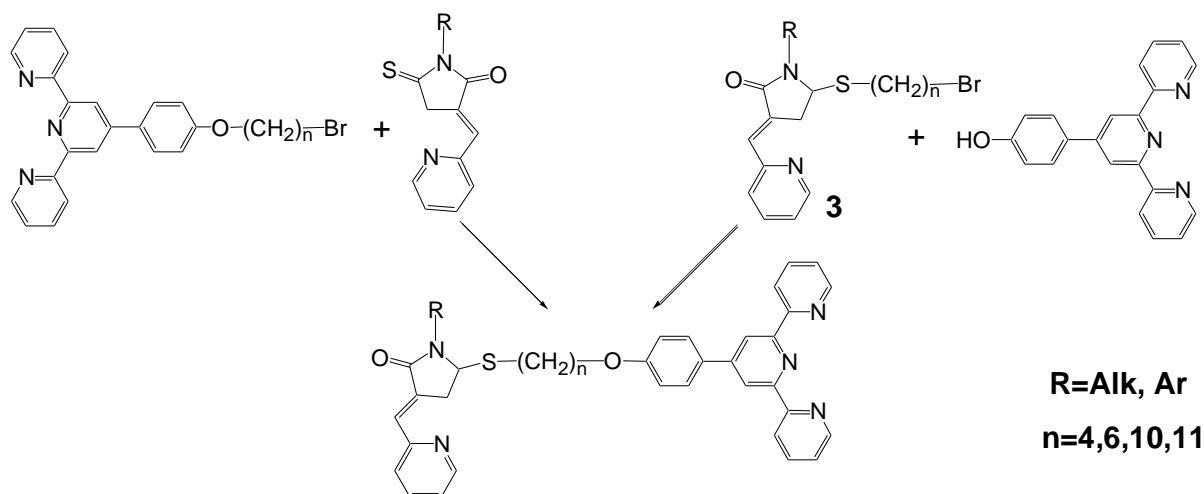
One of the perspective trends in organic chemistry is the synthesis and investigation of coordination compounds of transition metals (Cu, Ru, Rh, Pt) with nitrogen-containing heterocyclic ligands. Such coordination compounds are attractive for several reasons, such as ease of preparation and a wide range of applicability in various fields of science and technology, for example, as antitumor agents, catalysts, in photochemistry and optoelectronics [1-3].

Previously the coordination compounds transition metals based on 4'-substituted terpyridines and 2-thiohydantoin were obtained in our scientific group. It was shown that ligands of such types bind to various metals, forming complexes that can be used as antitumor agents and catalysts [4-6].

Currently, we have developed a synthetic approach to the synthesis of mixed-ligand complex compounds, which contain two different fragments – terpyridine and 5-(pyridyl)-2-thio-imidazole-4-one. The synthesis of such ligands was offered to be obtained in two ways. (Scheme 1).

Synthesized compounds have two different coordinating fragments which can be coordinated with different metals.

### Scheme 1. Synthetic strategy for the obtaining of ditopic ligands



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## Pseudo-three-component reactions of 1*H*-pyrrole-2,3-diones with enols

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The syntheses of spiro[furo[3,2-*c*]chromen-3,2'-pyrroles] and spiro[furo[3,2-*c*]quinoline-3,2'-pyrroles] through two-component spiro-heterocyclization of 1*H*-pyrrole-2,3-diones with 4-hydroxycoumarin and substituted 4-hydroxyquinolin-2-ones, respectively, were described earlier [1]. Pseudo-three-component reactions of 1*H*-pyrrole-2,3-diones and two molecules of dimedone or 4-hydroxycoumarin leading to the formation of spiro[pyrrol-3,9'-xanthenes] [2] or spiro[pyrano[3,2-*c*:5,6-*c'*]dichromen-7,3'-pyrroles] [3] were investigated (Fig.1).

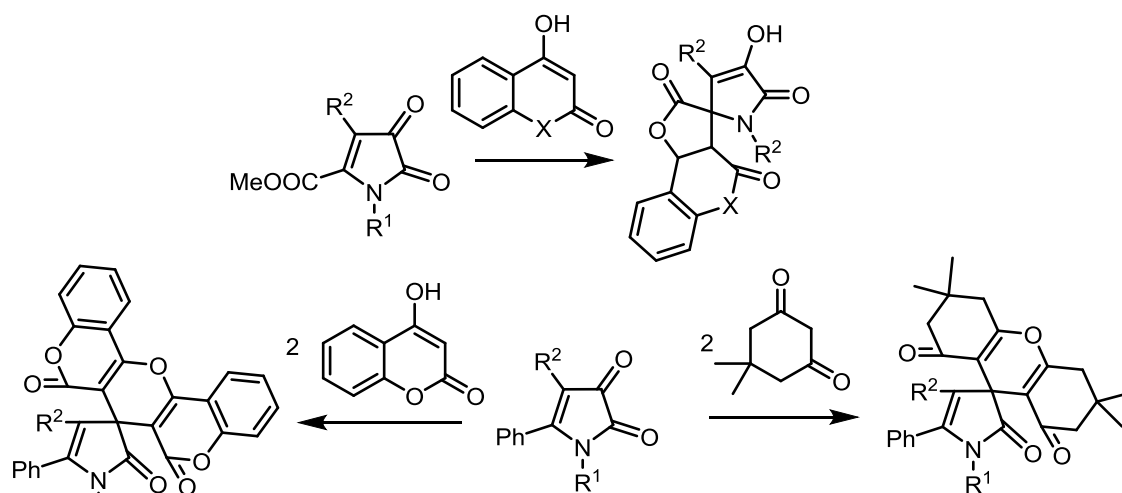


Fig.1

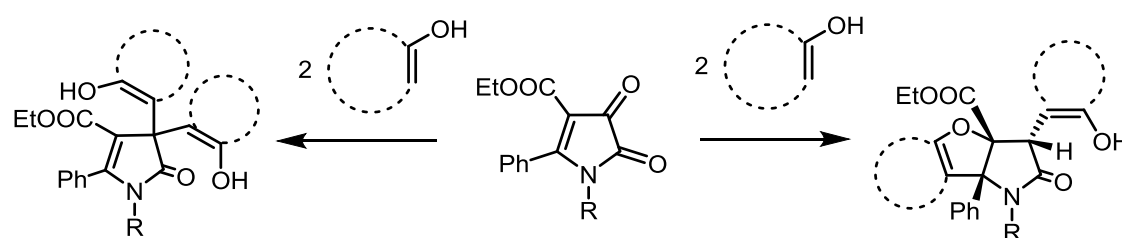


Fig.2

Herein, we report novel reaction pathways for pseudo-three-component reactions of 1*H*-pyrrole-2,3-diones with enols (fig.2).

*This study was performed under the financial support of the Government of Perm Krai, and the Russian Ministry of Education and Science (projects nos. 4.6774.2017/8.9, 4.5894.2017/7.8)*

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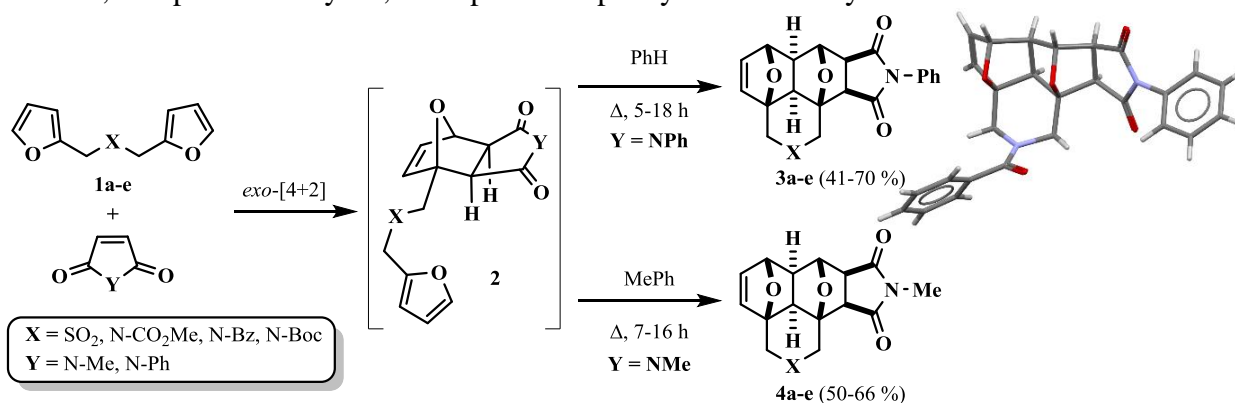
## Tandem Diels-Alder reaction of *bis*-furyl derivatives with electron-deficient alkenes

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This report is a development of our previous researches in the area of the intramolecular [4+2] cycloaddition in furan derivatives (the IMDAF reaction) [1,2]. In our precedent works the IMDAF reaction between *bis*-furans and DMAD or hexafluorobutyne was studied [3,4]. It has been shown, that depending on temperature the reaction can lead to the kinetically controlled adducts or to the thermodynamically controlled adducts.

In this work, we planned to establish the scope and limitations of applicability of this approach for a construction of polycyclic compounds. Here, we used in the same reaction less reactive, compared to alkynes, dienophiles: N-phenyl and N-methyl maleimides.



Compound	X	Yield 3, %	Yield 4, %
<b>a</b>	N-Boc	41	52
<b>b</b>	N-CO <sub>2</sub> Me	70	50
<b>c</b>	N-Bz	68 (X-ray)	58
<b>d</b>	O	49	66
<b>e</b>	SO <sub>2</sub>	45	52

Interaction of *bis*-furans (**1**) with maleic amides includes the initial intermolecular Diels-Alder reaction leading to formation of intermediate adduct **2** and the subsequent IMDAF reaction of the unsaturated fragment to the furan ring into the intermediate **2**. The sequence results in adducts **3** and **4** with a high degree of diastereoselectivity and in a total yields of 40-70%.

The publication has been prepared with the support of the "RUND University Program 5-100".  
The reported study was funded by RFBR projects № 19-03-00807 A  
and № 19-53-04002 Бел\_мол\_a

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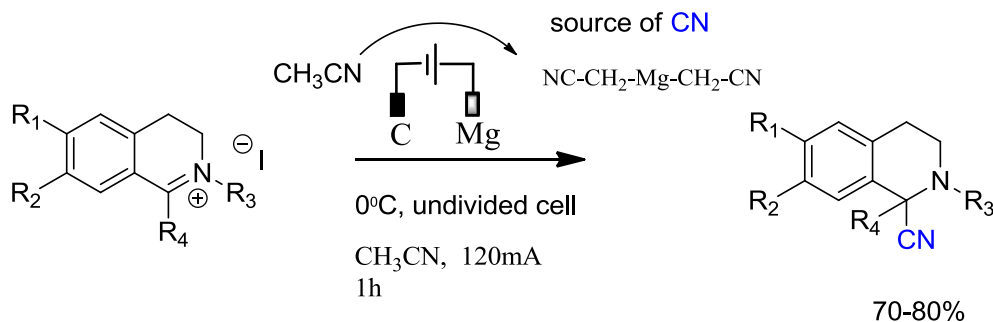
## A facile one pot synthesis of 1,2,3,4-tetrahydroisoquinoline-1-carbonitrile via the electrogenerated acetonitrile

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The nitrogen heterocycle presents a very important use in the pharmaceutical and agrochemicals synthesis [1]. In this case the substituted tetrahydroisoquinoline has a broad range of biological activities [2, 3].

The synthetic study of 1,2,3,4-tetrahydroisoquinoline-1-carbonitrile was reported in different condition by using the cyanopotassium (KCN) with 2-methyl-3,4-dihydroisoquinolin-2-ium iodide in acetonitrile [4, 5]. In this work our approach is focused mainly on developing new and safe strategy for the conversion of 3,4-dihydroisoquinolin-2-ium iodide substrates into these highly valuable 1,2,3,4-tetrahydroisoquinoline-1-carbonitrile derivatives that proceeds through a process with good yield and is promoted by a high current efficiency EGB (as shown in the scheme).



This method has the advantages i) very easy and simple procedure, ii) the formation of the final product is very fast on one pot synthesis iii) no need to add oxidative reagents.

*This work was supported by the Russian Foundation for Basic Research (grant № 5-100)*

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## Determination of carbon tetrachloride in aerosols with GC

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Today, its are known more than forty freons, most of which are produced by industry. Among them there are several types that differ in chemical formulas and physical properties [1]. Due to its thermodynamic properties, freons have found wide practical application as coolants in refrigerating machines, in air conditioners, in perfumery and medicine for making aerosols.

A number of aerosol preparations are produced by freon 12 currently. Freon 12 have been restricted for production and use in the Russian Federation, but present on the market of our country [2]. Aerosol preparations include perfume and foam sprays. For example, it is the antiburn liniment of the composition [3].

There is evidence to suggest that so-called of Freon 12, which still exists, so-called "intermediate mixtures" are sold in which main components are HCFC-based refrigerants - R124, R22 and / or R142b. Also manufacturers add the hydrofluorocarbon R152a or R600a as the third component. This replacement substitutive mixture has a significantly lower cost. It has been operated for more than 30 years successfully and it is not inferior to Freon 12 [4].

But in any case, freon 12 or freon 22 [2] (it is allowed for production and use in the Russian Federation as part of a propellant mixture), the criteria and set of quality indicators for these freons are focused on the use in refrigeration technology mainly.

Freons 12 and 22 are synthesized by reaction with anhydrous hydrogen fluoride in a gaseous medium, in the presence of a catalyst based on antimony fluoride, from carbon tetrachloride or chloroform. Therefore, in addition to the main product of synthesis, both the starting materials and intermediate products can be present in the final product, as well as compounds obtained as a result of the side reactions. The main impurities that may be present in freon 12 and in freon 22 are shown chromatograms of samples given in the corresponding State Standards.

The most toxic compound from the list of substances is carbon tetrachloride, its content in the medicines according to the requirements of the European Pharmacopoeia 8 ed. should not exceed 4 ppm. Since the same freon is used in medicinal preparations that is used in other industries and its quality is normalized by GOST 19212-87, that in the freon used in medicinal preparations the content of carbon tetrachloride is allowed at the level of 0.1% (1000 ppm), which 250 times exceed the EP limit (4ppm). Even taking into account dilution by other components of the drug up to 10 times, the concentration of CCl<sub>4</sub> is obtained unacceptable.

For this reason, development of the analytical tools that allow testing carbon tetrachloride in medical aerosols is paramount task.

For the identification and quantitative determination of carbon tetrachloride in propellants using in the composition of finished drugs was used the method of gas-liquid chromatography with detection of electronic capture.

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## Modification of polyvinyl alcohol and polyvinylphenol by dialkylcarbonates

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Currently, the polymers are widely have been used for the production of structural materials, medical materials (implants), medicines, optical materials, films for various purposes, etc. [1]. There are some poly-alcohols, such as cellulose, polyvinyl alcohol, polyvinyl phenol, are capable of chemical modification due to their high chemical activity [2]. Chemical modification of polymers is a promising direction, because it allows to synthesize polymers with a given set of properties. New polymers can have be used in the special areas. Moreover, they can replace the known polymers for new polymers with improved performance [3].

To obtain new polymers containing the carbonate functional group in the side chain, polyvinyl alcohol and poly-(4-vinylphenol) were subjected to carbmetoxylation with dimethyl carbonate in the presence of imidazole.

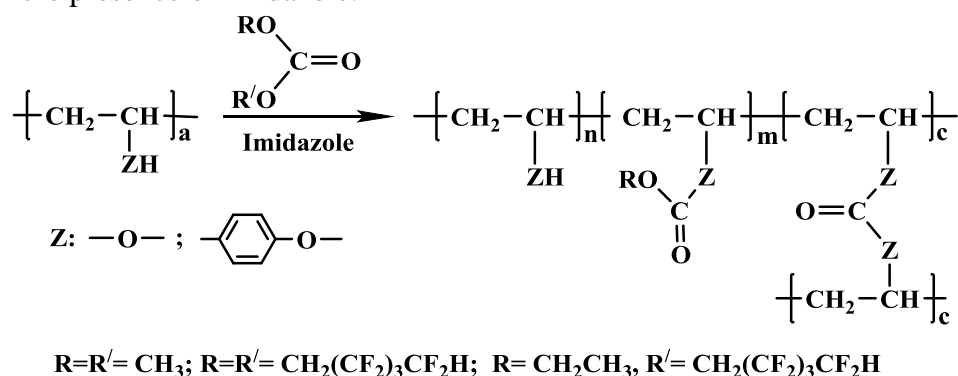
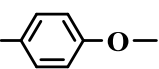


Table. The results of the transesterification of dialkylcarbonates

Z	R	R'	n	m	c
-O-	CH <sub>3</sub>	CH <sub>3</sub>	0,74	0,16	0,10
	CH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H	CH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H	0,82	0,02	0,16
	CH <sub>3</sub>	CH <sub>3</sub>	0,44	0,56	0
	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H	0	0,89	0,11
	CH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H	CH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H	0,99	0	0,01

The composition and structure of the obtained compounds were characterized by elemental analysis, IR and NMR <sup>1</sup>H spectroscopy. Information about carbalkoxylation polymers in the literature are practically absent. In this regard, the studies of the reactions of carbalkoxylation of polyvinyl alcohol and polyvinylphenol with dialkylcarbonates (including fluorine-containing) are relevant and allow to develop a method for producing film-forming polymers of a new type.

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## Chemistry at the speed of sound

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A blockbuster drug generates > \$ 1 billion revenues per year. Each day not on the market corresponds to a loss of > \$ 2.7 million. Multiple benchmark reports suggest development costs of drugs are skyrocketing while the introduction of novel drugs is decreasing or at best stagnating. Part of the problems can be attributed to the preclinical drug discovery and development involving expensive high throughput screening (HTS) and hit-to-lead campaigns using mostly traditional technologies. Here we introduce a fundamentally novel approach towards preclinical drug discovery and development by blending Instant Chemistry, nL dispensing, acoustic-MS, uHTS and artificial intelligence.

Acoustic droplet ejection (ADE) technology allows for the fast, contact-less and accurate transfer of very small droplets (nL) from plate to plate of different high density formats. ADE has had a dramatic impact in different technology areas, including drug discovery, cancer research and genomic research and is used in many laboratories world-wide. However, ADE has never been used in miniaturization and acceleration of library synthesis for uHT to dramatically accelerate the preclinical drug discovery cycle. One-pot multicomponent reactions (Instant Chemistry, MCRs) are suitable to create very large libraries of small molecules and macrocycles. A prototype instrumentation platform is developed which allows for the parallel synthesis of hundreds of libraries of scaffolds on an unprecedented dense format.

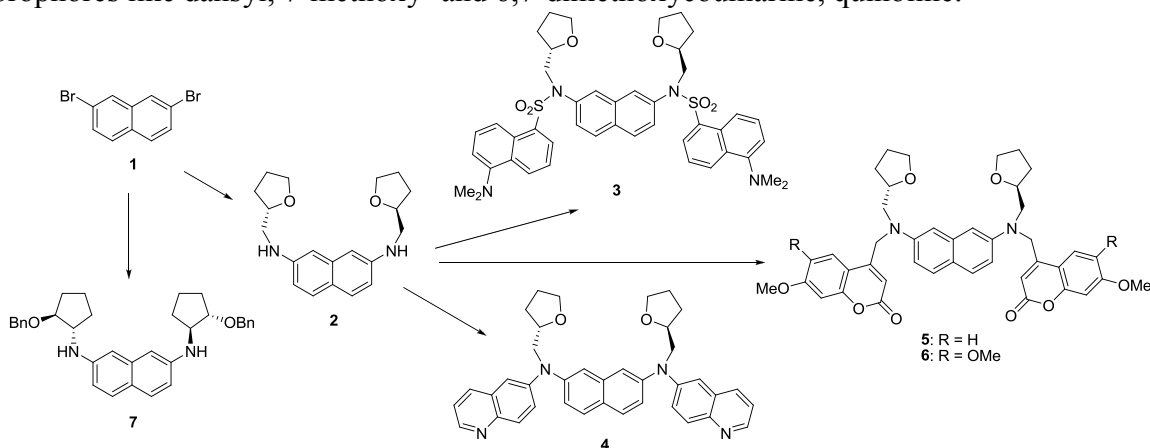
## Chiral derivatives of biphenyl and naphthalene for enantioselective fluorescent recognition

Shaferov A.V., Malysheva A.S., Grigorova O.K., Averin A.D., Beletskaya I.P.

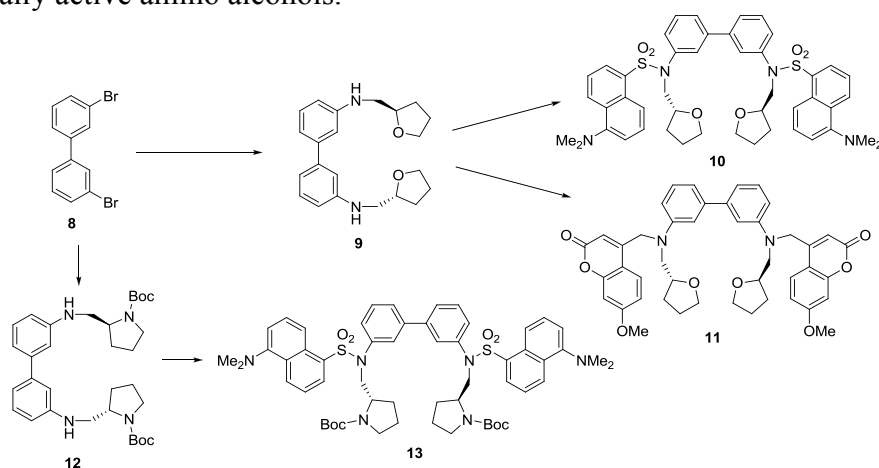
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The search for novel efficient chemosensors of chiral compounds is an important task. Fluorescent spectroscopy is being widely used in modern analytical methods, thus the goal of this work is to develop new ligands able to enantioselective fluorescent recognition of optically active small organic molecules. Naphthalene possesses fluorescent properties and can be exploited as the scaffold for attaching two chiral podands bearing coordination atoms (N or O). Using Pd(0)-catalyzed amination 2,7-dibromonaphthalene (**1**) was converted into corresponding optically active molecules **2** and **7**. Compound **2** was further modified with several additional fluorophores like dansyl, 7-methoxy- and 6,7-dimethoxycoumarin, quinoline.



Similar approach was used in the synthesis of chiral receptors on the basis of 3,3'-disubstituted biphenyl. All compounds should be modified with additional fluorophores in this case. The investigation of the detecting possibilities of these ligands is being carried out using a panel of optically active amino alcohols.



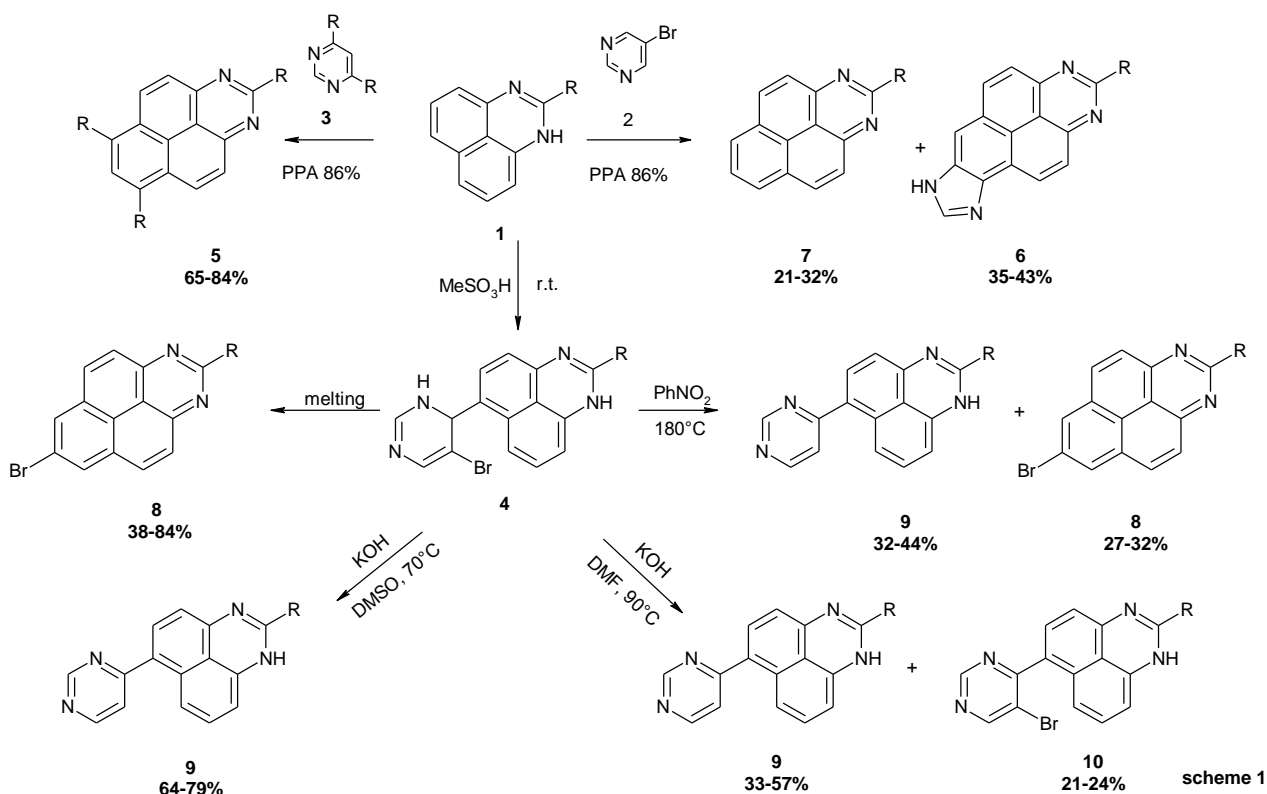
This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00709)

## Study of the 6-(5-bromo-3,4-dihydropyrimidin-4-yl)-1*H*-perimidine oxidation reaction

Shcherbakov S.V., Aksenov A.V., Khristaforov O.V., Magometov A.Yu., Pogrebnoy P.V.

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Earlier we developed a method for the synthesis of 6-(5-bromo-3,4-dihydropyrimidin-4-yl)-1*H*-perimidine **4**, based on the reaction of perimidine with **1** 5-bromopyrimidine **2** in methanesulfonic acid. It is noteworthy that, in contrast to 4,6-substituted -pyrimidine **3**, the reaction with 5-bromopyrimidine **2** in polyphosphoric acid led to the formation of 7*H*-imidazo[4',5':4,5]benzo[1,2,3-*gh*]perimidines **6** and 1,3-diazopyrenam **7** (**Scheme 1**):



We noticed that compounds **4** decomposed without melting. Mass spectral analysis of melts showed that in these compounds a loss of the “CH<sub>4</sub>N<sub>2</sub>” fragment occurred with preservation of the bromine atom. As a result, previously unknown 7-bromo-1,3-diazapirenes **8** were isolated from melts of compounds **4**. With boiling **4** in nitrobenzene, 6-(pyrimidinyl-4)-1*H*-perimidines **9**. Compound **9**, as a single product, can be obtained by heating 6-(5-bromo-3,4-dihydropyrimidin-4-yl)-1*H*-perimidines in DMSO at 60°C. Changing the solvent to DMF, in addition to compound **9**, allows to obtain previously unknown 6-(6-bromopyrimidinyl-4)-1*H*-perimidines **10**.

This investigation was supported by Russian Foundation for Basic Research (grant #18-33-00849 mol\_a)

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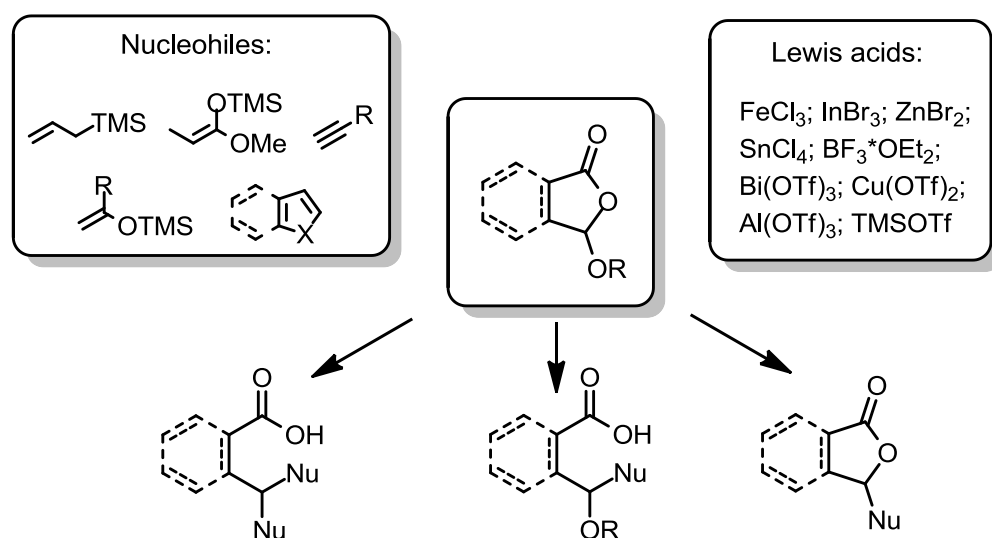
## Some aspects of C-nucleophiles addition to $\gamma$ -oxocarboxylic acids

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$\gamma$ -Oxocarboxylic acids are promising substrate for fine organic synthesis, the diverse reactivity of which is caused not only by the presence of carbonyl and carboxyl groups in the molecule, but also by their mutual influence, manifested, for example, by the presence of ring-chain tautomerism [1]. Among all representatives of  $\gamma$ -oxocarboxylic acids, levulinic and 2-formylbenzoic acids are most in demand in organic synthesis. So, the first one is readily available from biomass [2] and is considered as a platform compound [3,4], and 2-formyl benzoic acid is used in the synthesis of natural and biologically active compounds [5,6].

Depending on the reaction conditions used, nucleophilic reagents and structural features of  $\gamma$ -oxocarboxylic acids and their derivatives, the formation of three different products is observed: mono addition with or without lactone ring closure, and double nucleophile addition.



The presented report discusses the results of studies of the reactivity of levulinic acid, pseudo-levulinic acid esters, 2-formylbenzoic acids and their pseudoesters with such nucleophiles as 1-alkynes, allylsilanes, silyl ketene acetals, silyl esters of enols and some electron-excess heterocycles in the presence of Lewis acids.

*This work was supported by the Russian Science Foundation  
(project No. 17-73-10251)*

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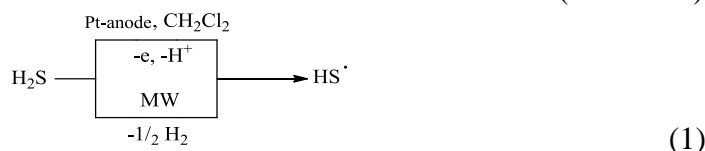
## Electro- and microwave synthesis of organic di-, trisulfides with the participation of hydrogen sulfide

Shinkar E.V.<sup>1</sup>, Shvetsova A.V., Zakharov A.D., Berberova N.T.

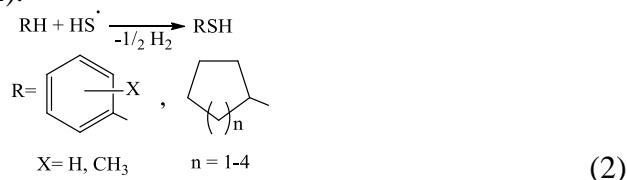
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The organic di- and trisulfides, widely distributed in the nature and contained in plant raw materials, have recently been actively used in medicine. These compounds possess biological activity and are promising as precursors in the synthesis of important drugs. There is a wide variety of methods (chemical and electrochemical) for their preparation, with thiols and sulfur being a basis. As a rule, hydrogen sulfide is almost never used to produce organic di- and trisulfides with various substituents. This is due to its low reactivity in reactions with organic compounds under mild conditions.

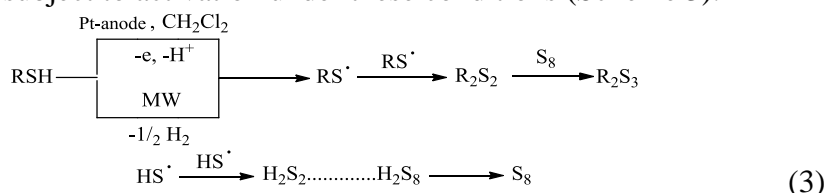
In this paper we discuss two basic ways of hydrogen sulfide activation (electrochemical and microwave) in the reactions with cycloalkanes C<sub>5</sub>-C<sub>8</sub> and aromatic hydrocarbons. Both approaches contribute to the generation of the thiyl radical from a hydrogen sulfide molecule when applying electrode potential or under the action of microwave irradiation (Scheme 1).



In the case of electrochemical initiation of the reaction at oxidation potential of H<sub>2</sub>S, a cation radical is formed and its fragmentation leads to to eliminate the proton. Under the conditions of microwave activation of H<sub>2</sub>S the homolytic decomposition of hydrogen sulfide molecule occurs. Then the thiyl radical interacts with aromatic and alicyclic compounds to form the corresponding thiols (Scheme 2).



Thiols are also subject to activation under these conditions (Scheme 3).



As a result of the dimerization of thiyl radicals, disulfides are formed. Trisulfides are able to be formed due to the accumulation of S<sub>8</sub> in the course of electrical and microwave synthesis. The sulfur is formed by single-electron oxidation of inorganic polysulfanes or by their homolysis under the action of microwave irradiation. The similar yield of R<sub>2</sub>S<sub>2</sub> (34-42%) and R<sub>2</sub>S<sub>3</sub> (20-28%) was achieved when carrying out the reactions 30 (MW) and 90 (Pt-anode) min. The yield of the target reaction products depends on the nature of the substrate, the duration of the synthesis and the power of microwave irradiation. The advantages of MW synthesis are the absence of organic solvent and the high rate of interaction.

*This work was supported by the Russian Science Foundation under grant 17-13-01168*

## Synthesis of tetrathienoacene conjugation block for organic field-effect transistors

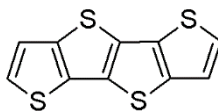
Skorotetcky M.S.<sup>1</sup>, Borshchev O.V.<sup>1</sup>, Ponomarenko S.A.<sup>1,2</sup>

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To date, there are many classes of conjugated molecules that are used in organic electronics devices. Materials based on tetrathienoacene (TTA) derivatives shows their high practical potential due to strong intermolecular interactions, extensive intramolecular  $\pi$ -conjugation, and close intermolecular  $\pi$ - $\pi$  stacking [1,2]. However, they are still poorly studied, and synthetic methods for their preparation have a several significant drawbacks: the high cost of the initial reagents, the multi-stage and complexity of purification, low yields.

This work describes a method for preparation of 2,6-dibromo-thieno[3,2-b]thieno[2',3":4,5]thieno[2,3-d]thiophene (TTA), an important building block of conjugated organic materials. The synthesis route involves the preparation of 3-bromothieno[3,2-b]thiophene from 3,4-dibromothiophene, followed by the preparation of the corresponding disulfide and oxidative ring closure to produce TTA. The combination and adaptation of various literature methods [3,4] allowed to increase the total reaction yields in the case of 3-bromothieno[3,2-b]thiophene from 54% to 72% and TTA from 27% to 45%.



TTA

Another advantage is that most of the stages do not require additional purification, and the procedures themselves are quite simple. Although some changes introduced are small, they turn out to be significant in terms of their impact, and also help to summarize the scattered literature materials.

*This work was supported by Russian Science Foundation (grant 18-73-10182) and performed in the framework of leading science school NSh-5698.2018.3*

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## Combined fractionation of protopectin decomposition products

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Today, the Russian Federation is in first place in the production of sugar from beet, which means the presence of a large amount of secondary phytomass. A rational way of recycling the secondary phytomass including beet pulp is to obtain pectic polysaccharides. Pectic polysaccharides are the decomposition products of protopectin, a high-molecular complex that is localized in the cell wall of higher flowering plants. The physico-chemical parameters of pectic polysaccharides depend on the process of decomposition of protopectin, therefore its study is actual. For the first time, a comparative study was conducted of the decomposition of the protopectin (PP) of beet pulp in the static and dynamic modes of acid hydrolysis-extraction in a wide range of temperature and pH of the hydrolyzing agent. The advantage of the dynamic method, which ensures the unchanged pH value and leads to an increase in the yield of the target products: microgel (MG), pectin substances (PT) and oligosaccharides (OS), and their enrichment with galacturonic acid units (HA) has been established.

The developed method of hydrolysis-extraction in a dynamic mode allowed to combine the stage of purification and fractionation. In this way, for the first time, by the method of chromatographic purification and combined fractionation in a dynamic mode, the process of decomposition of the protopectin decomposition products into fractions differing in the content of galacturonic acid units and molecular weight parameters was studied. Identified the identity of the process, regardless of the physico-chemical parameters of hydrolysis-extraction. Using the idea of the decomposition of protopectin, as a sequential reaction of the transformation of protopectin - microgel - pectin substances and taking the total content of galacturonic acid in the microgel and pectin substances equal to the content of HA in the feedstock, the experimental data were processed based on the hydrodynamic equation, which allowed us to estimate the main parameters and calculate the constants decomposition reaction rate in the hydrolyzate solution stream. Considering the fact that a microgel was formed as an intermediate, the experimental data of the process of decomposition of the protopectin and the combined fractionation of reaction products were dynamically processed based on the sequential reaction equation in the flow, which made it possible to estimate the apparent rate constants of these reactions for each isolated fraction.

The high correlation of the logarithm of the rate constants of the total decay of the protopectin ( $\ln k$ ) and the sequential reaction of the transformation PP-MG-PS ( $\ln k_1$  and  $\ln k_2$ ) from the inverse temperature was established. The apparent activation energies ( $E(k)$ ,  $E(k_1)$  and  $E(k_2)$ ) of the corresponding reactions in the hydrolyzate solution stream are estimated. The revealed constancy of the value of  $E(k_1)$  at the volume of the output of fractions up to 200 ml, followed by a sharp decrease and stabilization indicates the completion of the decomposition reaction of the protopectin in the initial region and the subsequent fractionation of the PP decomposition products by gel-chromatography.

The obtained data and the identified patterns of the process of decomposition of the protopectin in a dynamic mode in combination with purification and fractionation make a fundamental contribution to the study of the structure of one of the most complex high-molecular complexes of the cell wall from secondary phytomass, which allows to obtain target products from one type of raw material in one production cycle, enriched with galacturonic acid units for medicine and pharmaceuticals, and the associated fractions used for the food industry.

## Russian Chemical Bulletin (Izvestiya Akademii Nauk. Seriya Khimicheskaya)

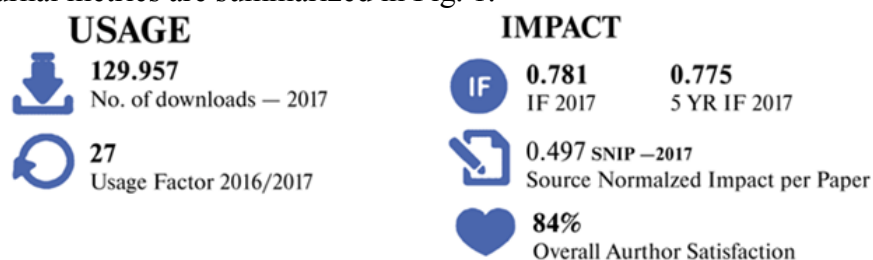
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The Journal metrics are summarized in Fig. 1.



**Fig. 1.** The *Russian Chemical Bulletin* metrics (IF is impact factor; 5 YR IF is 5 Year Impact Factor).

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## Synthesis of novel 2-selenoxo-tetrahydro-4H-imidazole-4-one ligands: precursors for biologically active transition metal complexes

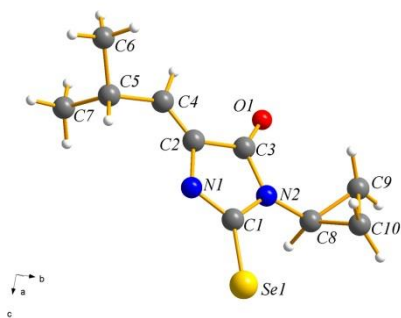
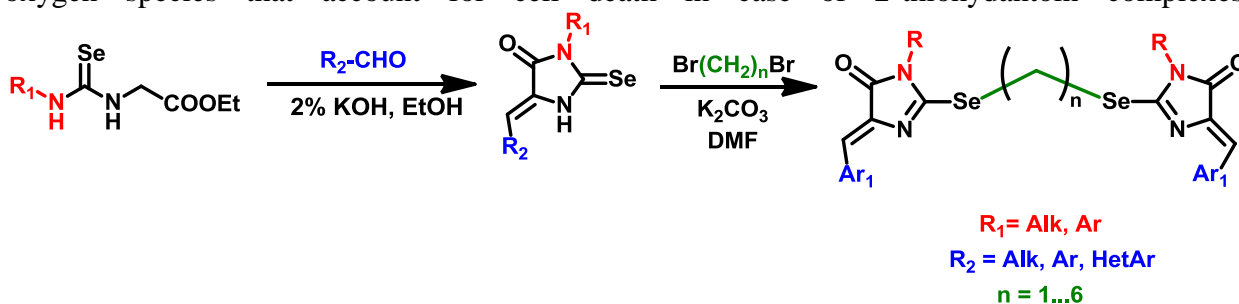
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Development of novel anticancer metal-based drugs is a rapidly growing field of medicinal chemistry. In recent years, there has been a rapid expansion in elaboration and search for such compounds to improve effectiveness and decrease its general toxicity.

Previous studies revealed high biological activity of substances containing hydantoin core. They proved to be cytotoxic against different malignant cell lines [1]. Being 2-thiohydantoin derivatives, Enzalutamide and Apalutamide are successfully employed in the treatment of prostate cancer.

In vitro tests showed binuclear copper(I, II) complexes comprising substituted 2-alkylthio-5-arylmethylene-4H-imidazolin-4-ones to inhibit some key polymerases (human telomerase, HIV reverse transcriptase, T7 RNA polymerase) with its simultaneous accumulation in the cellular nucleus causing DNA degradation and cell death being a downside to further therapeutic application [2]. Introduction of selenium instead of the sulfur atom to these complexes may become a solution since it is capable of suppressing the formation of reactive oxygen species that account for cell death in case of 2-thiohydantoin complexes.



In the current work, initial scope of 3,5-substituted-2-selenohydantoin was obtained by treating corresponding selenourea with aromatic, heteroaromatic or aliphatic aldehyde in the presence of 2 mol.% KOH in ethanol. The key step in the formation of the selenohydantoin backbone was achieved by a Se-alkylation reactions with various dibromoalkanes in the basic conditions. All reactions afforded target molecules in acceptable yields.

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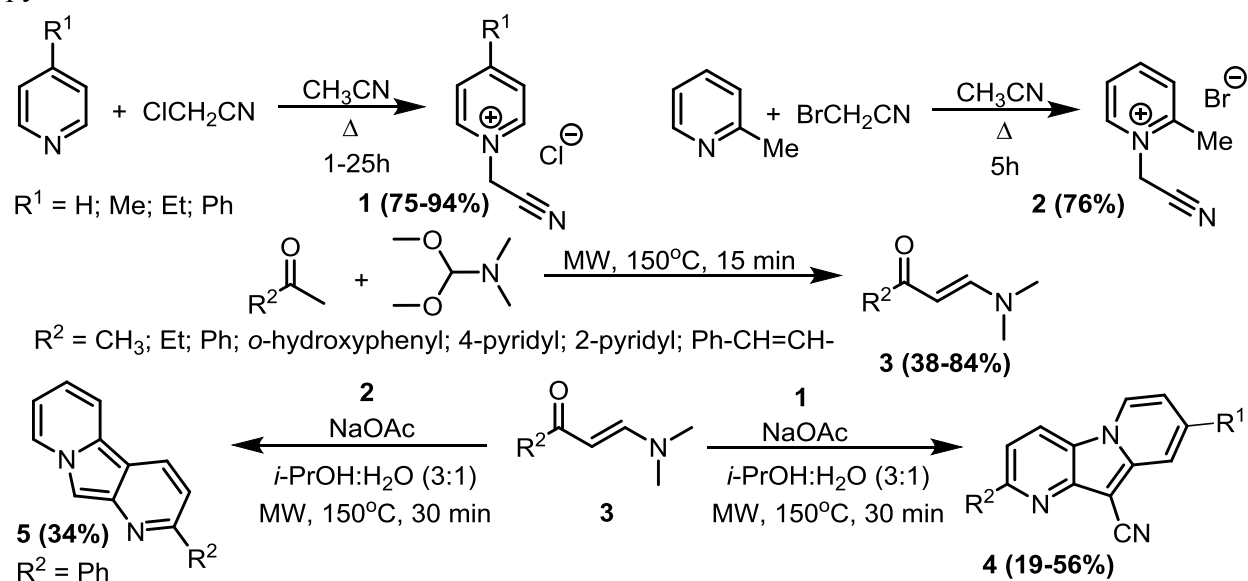
## Synthesis of 2-substituted pyrido[2,3-*b*]indolizine-10-carbonitriles - promising compounds with fluorescent properties

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The optical properties of organic compounds are important for medicinal purposes [1], as well as for creating electronic devices (e.g. OLED) [2]. Derivatives of pyrido[2,3-*b*]indolizine-10-carbonitriles have pronounced fluorescent properties and may be of practical importance in the development of OLED technology or biology.

As starting compounds for the synthesis of pyridoindolizine derivatives, we obtained pyridinium salts **1-2** and enaminones **3**.



The interaction of **1** and **3** proceeds as a pseudo-three-component reaction and gives the corresponding target compounds **4** with moderate yields. The reaction of 2-methylpyridinium bromide **2** with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one, the process proceeds with the formation of compound **5**.

We investigated the optical properties of some of the compounds obtained and calculated their quantum yield. *Coumarin 153* was used as standard.

Compound <b>4</b>	$D (\lambda = 415 \text{ nm})$	QY
$R^1 = H; R^2 = Me$	0.0273	0.89
$R^1 = Ph; R^2 = Me$	0.0374	0.82
$R^1 = Me; R^2 = Ph$	0.0355	0.89
$R^1 = Et; R^2 = Ph$	0.0362	0.92
<i>Coumarin 153</i>	0.0509	0.53

This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-20101)

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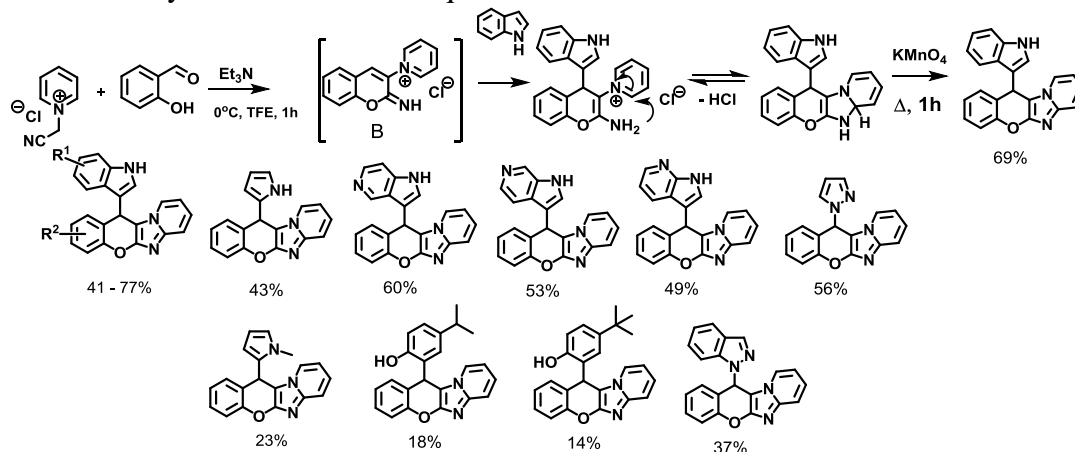
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## Mn-Mediated sequential three-component domino Knoevenagel/cyclization/Michael addition/oxidative cyclization reaction towards annulated imidazo[1,2-*a*]pyridines

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The sequential three-component reaction between *o*-hydroxybenzaldehydes, N-(cyanomethyl)pyridinium salts and a nucleophile towards substituted chromenoimidazopyridines under oxidative conditions has been developed. The employment of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O or KMnO<sub>4</sub> as stoichiometric oxidants allowed the use of a wide range of nucleophiles, such as nitromethane, (aza)indoles, pyrroles, phenols, pyrazole, indazole and diethyl malonate. The formation of the target compounds presumably proceeds through a domino Knoevenagel/cyclization/Michael addition/oxidative cyclization reaction sequence.



The reported study was funded by RFBR according to the research project № 18-33-00536

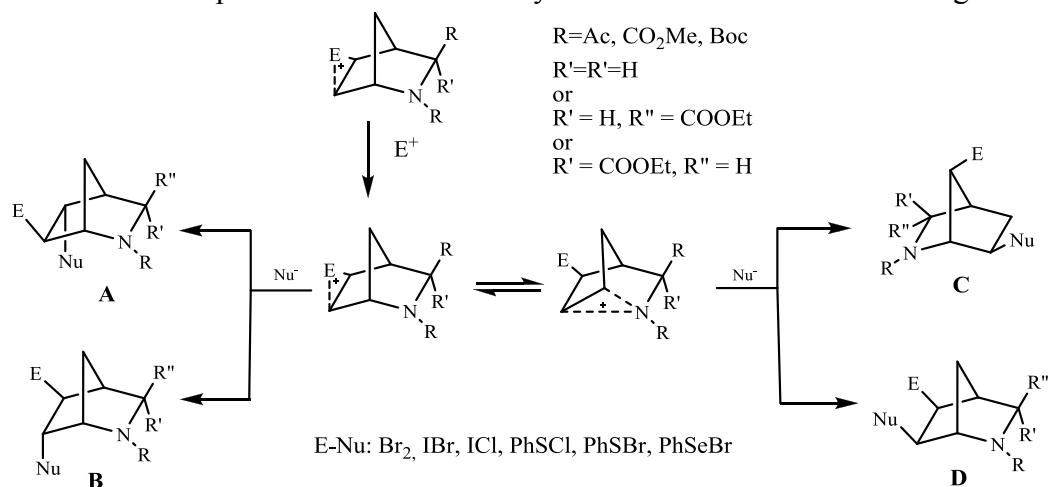
## Halogenation and chalcogenation of 2-azanorbornene derivatives

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Azanorbornene derivatives are of interest as biologically active compounds and intermediates in the synthesis of biologically active compounds [1]. However, in electrophilic addition reactions, they have been studied undeservedly little, despite the fact that the high regio- and stereoselectivity of the AdE reactions allows introducing functional groups with the creation of optically active centers with a known configuration, which can become an indispensable tool in modifying both azabicyclic structures and their derivatives.

We have studied the influence of substituents in the second and third positions of 2-azabicyclo[2.2.1]heptenes on the direction of halogenation with potassium dihalogenoiodates and bromine and chalcogenation with phenylsulfenyl chloride, phenylsulfenbromide and systems PhSOEt-Me<sub>3</sub>SiHal (Hal = Cl, Br). The structure of the products of electrophilic addition to 2-azanorbornene derivatives depends on the degree of nitrogen participation in the stabilization of the carbocation. In the case when the NHR group is involved in stabilizing the carbocation, rearrangement products are formed (path "C") or 1,2-cis-attachment products are formed (path "D", when the attack of the external nucleophile can be carried out only from the *exo*-side). If the participation of nitrogen in the stabilization of the carbocation is small, 1,2-trans-addition products are formed (paths "A", "B"). Moreover, the predominant is the path "A", because the carbocation in the sixth position is destabilized by the inductive influence of nitrogen.



In the case of the *endo*-isomer, stabilization of the "aziridinium type" carbocation prevails both for halogenation and for chalcogenation. It leads to the formation of rearrangement products ("C"). For the *exo*-isomer, stabilization of the carbocation with the participation of nitrogen also prevails over the formation of halogenonium ions. However, the situation is changing for the sulfenylation and selenation of *exo*-isomers, when the contribution of episulfonium and selenonium ions is significant. Nevertheless, even in this case, we observed a competition of processes. An increase in the participation of nitrogen in the stabilization of the carbocation in the series Ac - COOMe - COOBut was noted, which can be explained by the decrease of the participation of the nitrogen pair in conjugation with the carbonyl group.

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## Synthesis of new antitumor platinum prodrugs with axial ligands based on 2-thioimidazolin-4-ones

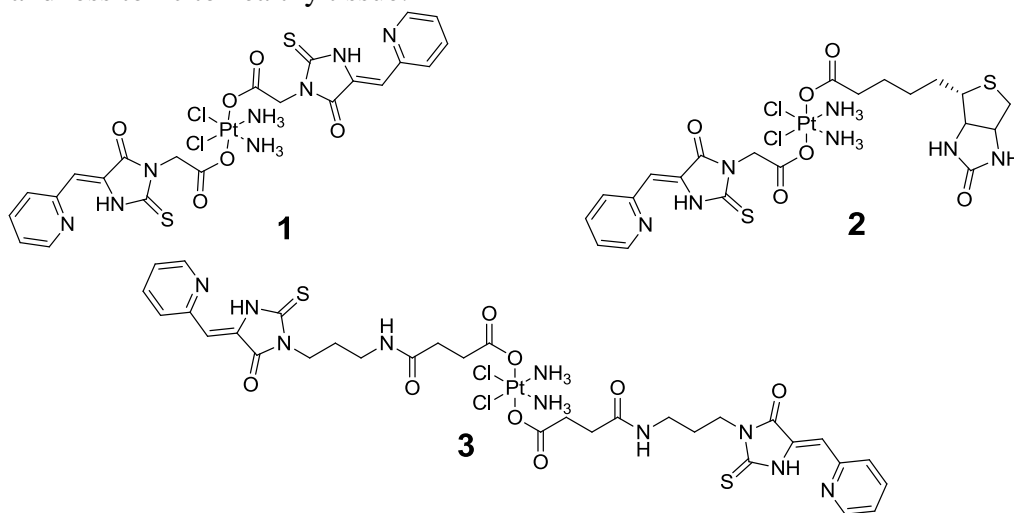
Spektor D.V., Krasnovskaya O.O., Vlasova K.Y., Semkina A.S., Kovalev S.V., Skvortsov D.A., Zyk N.V., Beloglazkina E.K., Majouga A.G.

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Platinum (II) drugs, such as cisplatin are in wide clinical use in antitumor therapy. However, platinum compounds possess a number of crucial drawbacks, such as high overall toxicity and acquired resistance [1]. One of the approaches to overcome those drawbacks is development of platinum (IV) prodrugs. Upon oxidation, platinum (II) square-planar complex becomes a six-coordinate octahedral, with the addition of two ligands in axial position.

Platinum (IV) complexes are kinetically more inert than their platinum (II) precursors, consequently, the unwanted reactions are minimized which leads to reduced side-effects and overall toxicity. The prodrugs are able to reduce after the tumor cell penetration, releasing the cytotoxic platinum (II) complex and axial ligands. Also, the addition of bioactive molecules as axial ligands allows to create a multiple action prodrug [2].

We have developed new platinum (IV) prodrugs with axial ligands based on 2-thioimidazolin-4-one, which chelates Cu ions in cells. Cu plays vital role in cancer progression and it is reported that tissue and serum from cancer patients have increased Cu level [3]. A combination of platinum therapeutic agents with copper chelators leads to increase in anti-cancer therapy efficiency [4]. As a result, the developed platinum (IV) prodrugs are potentially more effective and less toxic to healthy tissue.



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## Cluster approach in liquid structure modeling

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Common knowledge considers a condensed phase formation as the superposition of weak coulomb interaction, arising between dipoles. In some cases for organic liquids the reason of phase stability is the hydrogen bonding (or other type of strong non-covalent interaction). But in terms of such interpretation seem to be not clear the nature of phase stability for many non-polar and hydrogen bondless compounds, for example, alkanes or alkenes, benzene, especially taking into account their high boiling temperature, i.e. the destruction energy of liquid phase. It is known the cases, when this temperature can be higher than for polar organic compounds or systems with hydrogen bond. Moreover, the more polar molecules can be the gases and less polar ones are liquids as it is observed for carbon tetrahalides.

In this work the IR spectroscopic findings, obtained for such organic liquids as tetrachlorides of carbon, silicon and germanium, benzene, as well as for methyl iodide and acetonitrile at ambient condition also for their vapours and solid films at low temperature are presented in order to discuss the mechanism of molecular interaction in condensed state. The selected compounds have either negligible total and bond dipole moments, strong bond dipole moment only, or considerable bond and total dipole moments.

Benzene is a planar molecule assigning to  $D_{6h}$  symmetry point group. It means that only one CH stretching IR band (E-specie) for similar molecule should be active in accordance with the selection rules. However three bands are observed in real spectra of liquid benzene. The picture in CH stretching region can be caused by the existence of clusters. In this case the cluster formation can be assigned to the carbon-carbon binding between parallel rings. This assignment is confirmed by the spectra of benzene vapour at ambient conditions. The complicated view of absorption with the manifestation of rotational structure is the display of low-symmetrical shape with several bonded molecules. At heating up to 473K the vapour spectra are simplified and manifest the superposition of cluster and non-bonded shape.

The molecules of tetrachlorides ( $ECl_4$ , where  $E=C, Si, Ge$ ) attribute to high symmetry  $T_d$  point group. The selection rules require the occurring of only one stretching  $ECl$  band in IR spectra. However carbon tetrachloride in liquid state and in solid film at 25K has two bands at 786 and 761  $cm^{-1}$  with approximately equal intensities. The second component disappears at heating the sample up to 423K. At the same time for silicon and germanium tetrachlorides only one E-Cl stretching band was found. Therefore the appearance of two bands in  $CCl_4$  spectrum cannot be assigned to the CCl stretching of chlorine isotopes and is the manifestation of cluster formation, for example of  $(\cdot\cdot C-Cl\cdot\cdot C-Cl)$  bonded chains. Unlike  $CCl_4$  in tetrachlorides of silicon and germanium the clusters exist due to the  $d-d$  orbitals interaction of central atoms. It does not lead to the sufficient distortion of initial molecular symmetry. During the transition from liquid to solid state (film at 25 K), the  $CH_3I$  spectrum changes, namely, only one band remains in the region of stretching vibrations of CH bonds. It indicates on a change of the molecular symmetry type (transformation from  $C_{3v}$  to  $D_{3h}$ ). It can be caused due to the shift of iodine atom to neighboring molecule and formation of almost planar  $CH_3$  fragment. The IR stretching of CN bond in acetonitrile has two components instead of an expected one. This effect justifies the interaction between molecules under CN group. The second component disappears at heating the sample up to 423K.

The presented data can be taken as reliable evidence of existence in condensed phase of the interaction between molecules, different from coulomb and H-bonding mechanism, leading to formation of cluster shapes.

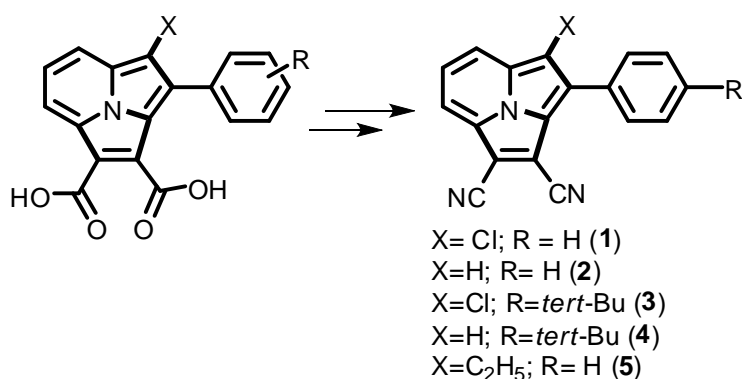
## New dicarbonitriles based on 3-phenyl[3.2.2]cyclazine-1,2-dicarboxylic acids

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[3.2.2]Cyclazines and their derivatives are characterized by an extended 10- $\pi$ -electron conjugation system, which makes them interesting objects for the possible production of corresponding annelated porphyrazines with absorption in the near-IR range [1]. Thus, studies conducted earlier in our group showed the possibility of the formation of a macroheterocycle based on 1,2-dicarbonitrile **1**. In this work, macrocyclization of 1,2-dicarbonitrile **2** was first carried out. However, during the isolation and characterization of macrocycles based on **1** and **2**, difficulties arose due to their limited solubility.

The main emphasis in the current work is on the synthesis of [3.2.2]cyclazine-1,2-dicarbonitriles, which have sufficient solubility for reliable identification using a wide range of physicochemical methods, primarily NMR. Compounds **1–5** were identified using one- and two-dimensional  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR spectroscopy, ESI and MALDI-TOF mass-spectrometry.



On the example of structures **1–5**, at present, search and optimization of methods for obtaining macrocycles, which in the case of **3–5** should have increased solubility, are also ongoing.

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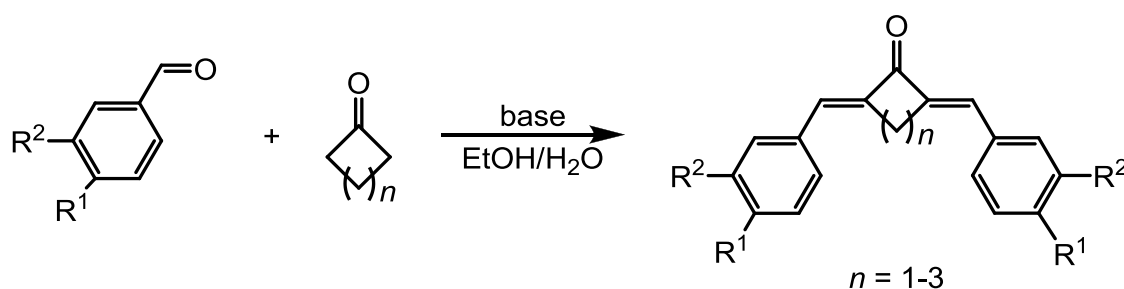
## Synthesis of bis(azacrown)dienones and supramolecular complexes based on them

Starostin R.O., Fomina M.V., Dmitrieva S.N., Kurchavov N.A., Nuriev V.N., Gromov S.P.

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Cross-conjugated dienones of cyclic ketones are widely known for their photochromic and fluorescence properties, which determine their applicability, first of all, as fluorescent probes in biology and agriculture [1-2]. The purpose of this study was to synthesize a series of dienones with various donor substituents, including azacrown-containing dienones, to study the photophysical properties of the obtained compounds and the possibility to construct photoactive supramolecular systems based on them.



$R^1, R^2 = H, OMe, SMe, NEt_2, \text{azacrown-ether}$

Dienones with various donor substituents and azacrown-containing dienones were obtained by the alkaline aldol-crotonic condensation of aromatic aldehydes with cyclic ketones in the presence of a base (Claisen-Schmidt reaction). The structure of the obtained dienones was determined by NMR-, IR-, UV spectroscopy and elemental analysis.

The formation of supramolecular complexes of azacrown-containing dienones with alkaline and alkaline earth metal cations was studied by electronic spectroscopy methods. The complexation is accompanied by changes in the absorption and fluorescence spectra of dienones. It was found that azacrown-containing dienones forms complexes of different stoichiometry with metal cations. The stability constants of the complexes were determined.

The synthesized dienones and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

*This work was supported by the Russian Science Foundation (project № 19-13-00020) and the RAS (Program №38 of the Presidium of RAS)*

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## Synthesis and biological activity of S-arylated dispiro derivatives of imidazole-4-one

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Dispirooxindole ring systems possess interesting structural properties and have been reported to exhibit strong bioactivity profiles including potent non-peptide inhibition of the p53–MDM2 interaction [1]. Earlier in our laboratory, a new method was developed for the synthesis of inhibitors of the protein-protein interaction of the p53-MDM2 dispiroindolinone series, the structure of which has a rigid framework of three spiro-articulated heterocycles, assembled in one stage from the corresponding isatins, N-substituted glycines and derivatives 2-thioxotetrahydro-4H-imidazol-4-ones (Figure 1 (a)) [2].

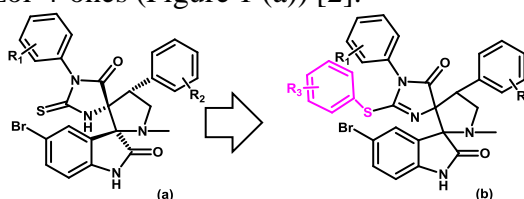


Figure 1. Dispiro derivatives of 2-thiohydantoin (a) and S-arylated 2-thiohydantoin (b).

On the other hand, being 2-thiohydantoin derivatives, Enzalutamide and Apalutamide are successfully employed in the treatment of prostate cancer. Previous studies of S-arylation of 2-thiohydantoin revealed high biological activity of substances containing hydantoin core [3].

Therefore, elegant coupling of two privileged scaffolds (spiro-oxindole and S-arylated 2-thiohydantoin moieties) in the same molecule presumably provides compounds with a wide spectrum of physiological activity, including the most paramount anticancer indication.

Conventional one-pot, multicomponent reactions (MCRs) are considered to be one of the most efficient strategies in organic and medical chemistry for synthesizing structurally diverse compounds and biologically active natural products, usually in a stereoselective-manner [4].

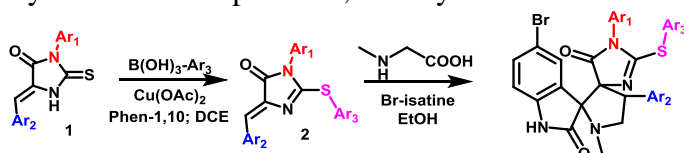


Figure 2. Key steps of synthesis.

In the current work, initial S-arylation of 2-thiohydantoin (Figure 2 (1)) was obtained by treating corresponding 3,5-substituted-2-thiohydantoin (Figure 2 (2)) with boronic acids in the presence of copper salts and phenantroline-1,10. The key step in the formation of spiro derivatives of S-arylated 2-thiohydantoin (Figure 2 (3)) was achieved by 1,3-dipolar cycloaddition reaction with sarcosine and isatin in ethanol. All reactions afforded target molecules in acceptable yields.

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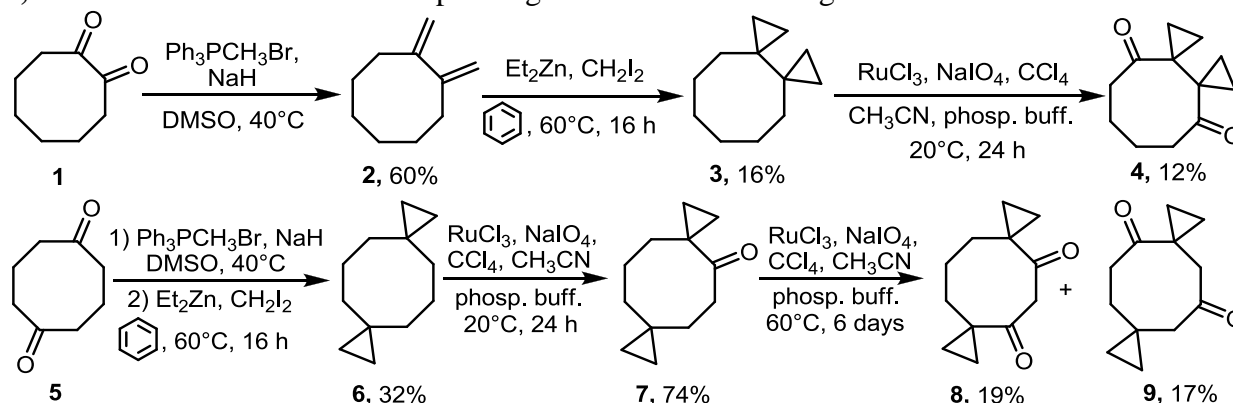
## The approaches to novel polycyclopropane structure based on 1,2-, 1,3- and 1,5-diketones of cyclooctane series

Stepanova S.A., Sedenkova K.N., Andriasov K.S., Averina E.B.

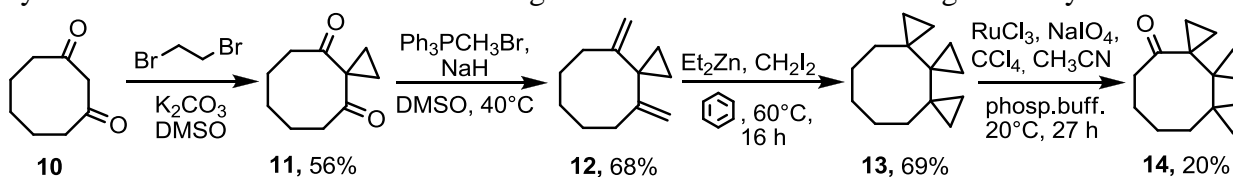
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$\alpha$ -Ketocyclopropanes are abundant in both natural compounds and pharmaceuticals and represent versatile precursors with wide applicability in organic synthesis. Polycyclopropane-containing compounds are of special interest in terms of their structure, physical and chemical properties. In this connection, the aim of the work was to investigate new synthetic approaches to unknown polycyclic cyclopropylketones.

The proposed approach to  $\alpha$ -ketocyclopropanes starting from ketones includes sequential methylenation, cyclopropanation and direct oxidation of methylene group activated by adjacent cyclopropane moiety [1]. In the course of this approach, cyclopropane-containing hydrocarbons **3,6** were obtained from the corresponding diketones and investigated in oxidative conditions.



Readily enolizable 1,3-diketone **10** was inert in Wittig reaction, while the product of its cyclic dialkylation **11** could be involved in the methylenation process. Thus, through a sequence of Wittig methylenation and Simmons–Smith cyclopropanation previously unknown hydrocarbon **13** was obtained and investigated in oxidative conditions to give solely ketone **14**.



As a result, the series of previously unknown polycyclic cyclopropylketones with cyclooctane core were obtained. Ketone **14** and 1,4-diketone **4**, in particular, represent promising precursors of [8]-rotane.

*This work was supported by the Russian Foundation for Basic Research (grant 16-03-00467-a)*

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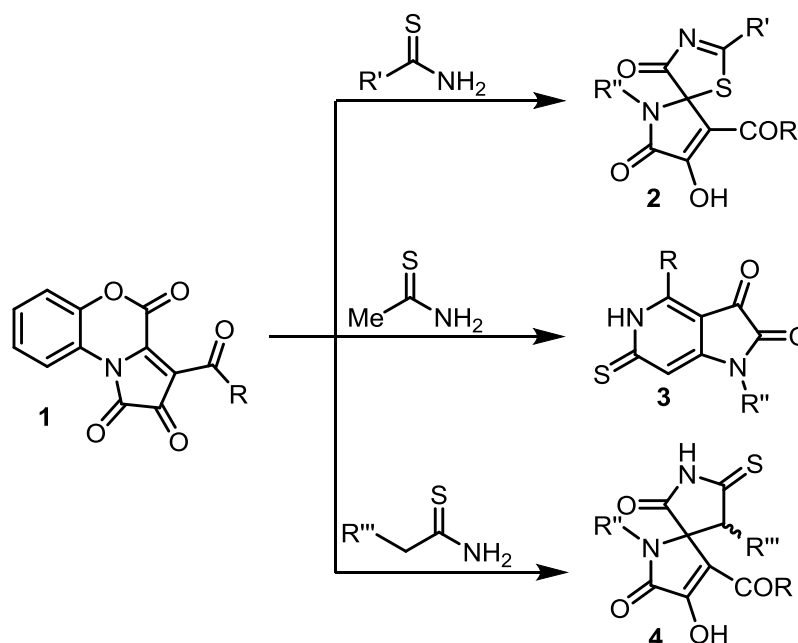
## Diversity-oriented synthesis of three distinct heterocycles *via* interaction of 1*H*-pyrrole-2,3-diones with thioamides

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In the last two decades, diversity-oriented synthesis (DOS) has become an intensifying trend in small molecule drug discovery. This approach allows to investigate wider chemical space creating diverse compounds collections from a limited set of reagents. Implementation of this methodology requires search for available polyfunctional reagents and investigation of their scope in DOS.

1*H*-Pyrrole-2,3-diones are polyelectrophilic reagents bearing a pharmacophoric pyrrole-2-one motif. We succeeded to develop a DOS of three distinct pharmaceutically interesting heterocycles *via* interaction of 1*H*-pyrrole-2,3-diones fused to a 1,4-benzoxazine-2-one moiety (pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones) **1** with various thioamides [1, 2].



The resulting 1-thia-3,6-diazaspiro[4.4]nonanes **2**, 5-azaisatins **3** and 1,7-diazaspiro[4.4]nonanes **4** were tested for antimicrobial activity. Compounds **2** and **4** have shown good inhibitory activities against *E. Coli*, *St. Aureus* and *M. Avium*. Azaisatins **3** have shown moderate inhibitory activity against *St. Aureus*.

*The study was performed under the financial support of the Russian Ministry of Education and Science (project no. 4.6774.2017/8.9) and the Government of Perm Krai*

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## Determination of the dielectric properties of the cucurbituril cavity based on the solvatochromism effect of the styryl dye

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Determination of the dielectric properties of the cucurbit [7] uril (CB[7]) cavity based on the Onsager-Liptay model [1] was carried out by analyzing the solvatochromic shift of the absorption spectrum of 1- (3ammoniumpropyl) -4 - [(E) -2- (3,4-dimethoxyphenyl) ethynyl]pyridinium (D1) upon the formation of the inclusion complex with CB[7] in a water solution. The CB[7] cavity was considered as a polar environment into which the dye chromophore is placed. [2] Positions of the maxima of the dye absorption spectra were measured experimentally in the following solvents: methanol, ethanol, i-propanol, n-butanol and water with known dielectric and optical properties. These values were used for parameterization of the Onsager-Liptay equation. Quantum-chemical method of the combined cluster available in the Gamess-US software package was used to calculate molecular structures, dipole moments of the ground and excited states, and polarizability [2].

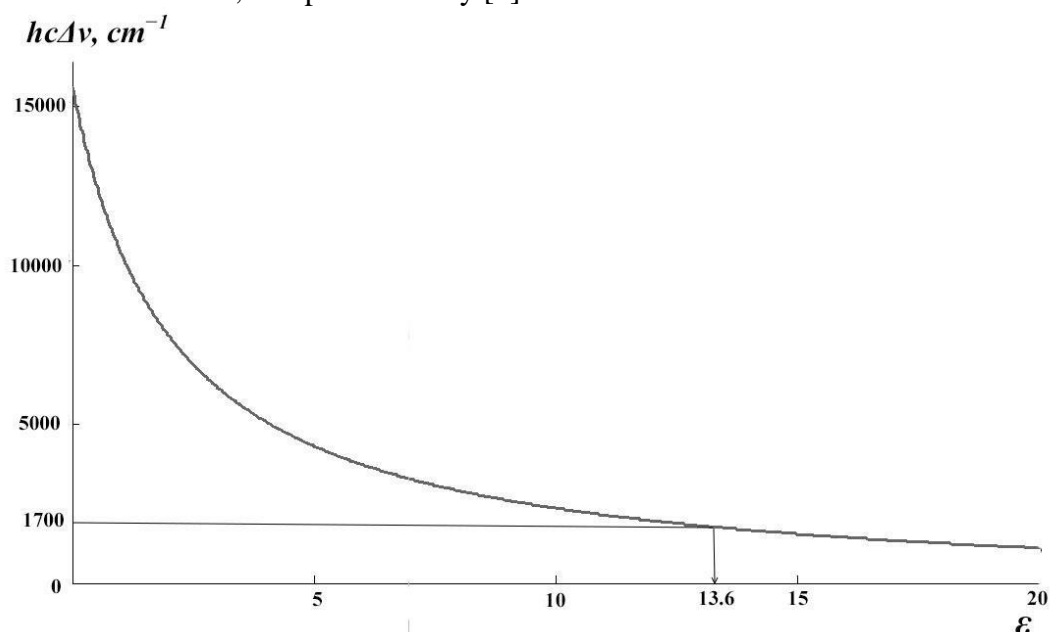


Fig. 1. Determination of the effective permittivity of the cavity of CB [7] based on the theoretical dependence of the solvatochromic shift on  $\epsilon$

The theoretical value of the effective dielectric permittivity of the cavity ( $\approx 13.6$ ) is in good agreement with the literature data derived by another method. [3] Thus, we propose a new method for estimating the dielectric properties of a host molecule in a supramolecular inclusion complex, according to the experimental shift of the dye molecule optical absorption spectrum due to the formation of the inclusion complex with CB[7].

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## Mixed *er*-NHC/Phosphine Pd(II) complexes and their catalytic activity in Buchwald-Hartwig reaction under solvent-free conditions

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<sup>1</sup> *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospekt 29, Moscow, 119991, Russia*

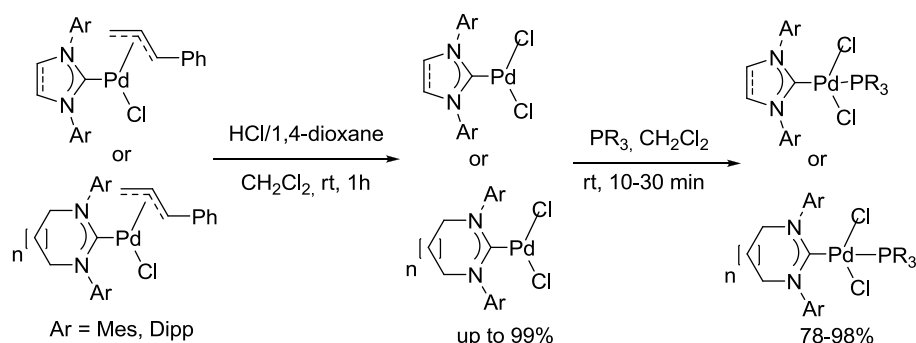
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Palladium-catalyzed cross-coupling reactions leading to formation of C–N bonds have become widely used in laboratory practice due to its simplicity and accessibility. The Buchwald-Hartwig amination is one of the most popular cross-coupling reactions, allowing the efficient synthesis of N- and N,N-substituted arylamines. Typically, cross-coupling reactions are carried out in solutions, but the absence of solvents can have its advantages, for example considerably higher reactant and catalyst concentrations drastically facilitate the reaction.

Previously it was shown that the introduction of auxiliary ligands to NHC-Pd complexes can be beneficial. Introduction of phosphine ligand inevitably causes alteration in both reactivity and selectivity of the resulting mixed NHC-phosphine palladium complex. That's why we decided to study a series of NHC-Pd-phosphine complexes with different combinations of NHC/phosphine ligands and find the most efficient catalyst for the solvent-free Buchwald-Hartwig reaction.

There are three main ways for mixed NHC-phosphine palladium complex synthesis: introduction of NHC into phosphine-Pd complex ( $\text{Pd}(\text{PR}_3)_2\text{Cl}_2$ ), introduction of phosphine ligand into NHC-Pd complex ( $[(\text{NHC})\text{PdCl}_2]_2$ ) and one-pot synthesis from NHC·HCl, palladium(II) chloride and phosphine in presence of weak base. The second one is more common, and it was used.



Introduction of phosphine into bridged palladium dichloride complex proceeds quickly and smoothly, affording corresponding mixed NHC-phosphine complex in less than half an hour. In order to find the most efficient catalyst in arylation reaction of both  $\text{RNH}_2$  and  $\text{R}_2\text{NH}$  under solvent-free conditions, synthesized complexes were tested in the Buchwald-Hartwig reaction of 1-bromonaphthalene with aniline and 1-bromo-4-methoxybenzene with diphenylamine. The most efficient complex for both types of solvent-free Buchwald-Hartwig amination was (6-Dipp) $\text{PdCl}_2$ -SPhos.

*This work was supported by the Russian Science Foundation (RSF)*  
*(project number 17-19-01595)*

## Synthesis of dichlorodiazadienes on the basis of phenyl hydrazones of 3-nitrobenzoic aldehyde

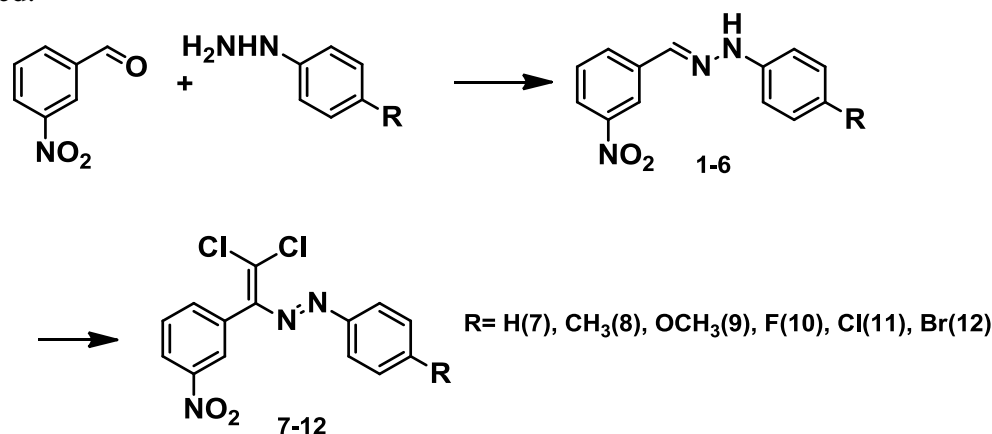
Suleymanova G.T.<sup>1</sup>, Shikhaliyev N.G.<sup>1</sup>, Maharramov A.M.<sup>1</sup>, Ganbarova C.G.<sup>1</sup>, Garazadeh Kh.A.<sup>1</sup>, Niyazova A.A.<sup>1</sup>, Gurbanov A.V.<sup>1</sup>, Nenajdenko V.G.<sup>2</sup>

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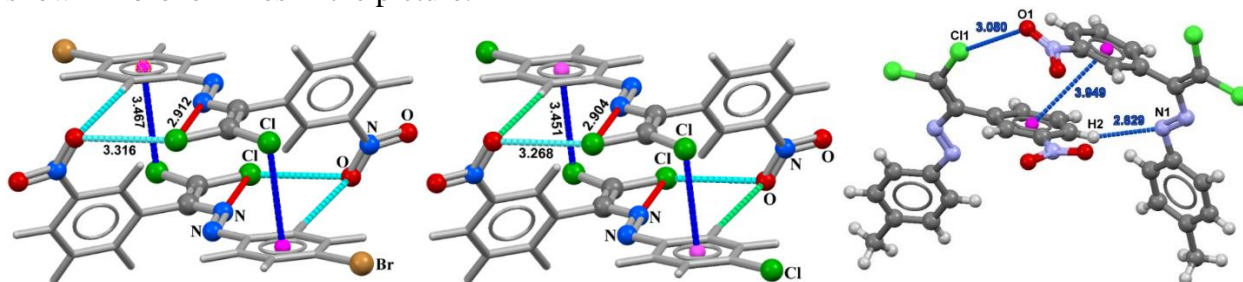
<sup>2</sup>Moscow State University, Moscow, Russia 119991

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In previous studies, results have been obtained about the application of dichlorodiazadienes as azodyes, synthesized on the basis of o-NO<sub>2</sub>. It was noted that, the single crystal X-ray analysis of substances evidence the intramolecular N···Cl pnicoen bonds which is significantly strengthened in view of the planarity of the four atoms involved in the 1,4-membered synthon. In DMSO solution substances exist in the *E*-isomeric form, which stabilized by inter- and intramolecular noncovalent interactions. [1]. Given all this, (*E*)-1-(2,2-dichloro-1-(3-nitrophenyl)vinyl)-2-(4-substituted phenyl)diazines on the basis of 3-nitro benzaldehyde were synthesized.



The structures of the compounds obtained have been confirmed by the NMR and X-ray methods. The presence of intermolecular and intramolecular non-covalent interactions in the formation of the crystal structures of compounds 8, 11 and 12 was identified. These bonds are shown in broken lines in the picture.



This work was supported by the Foundation for the Development of Science under the President of the Republic of Azerbaijan - Grant № EIF-BGM-4-RFTF-1 / 2017-21 / 13/4

This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan - Grant No EIF-BGM-4-RFTF-1/2017- 21/13/4

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## The [2 + 2] photocycloaddition of styryl dyes in 1:2 host-guest complexes with cucurbit[8]urils

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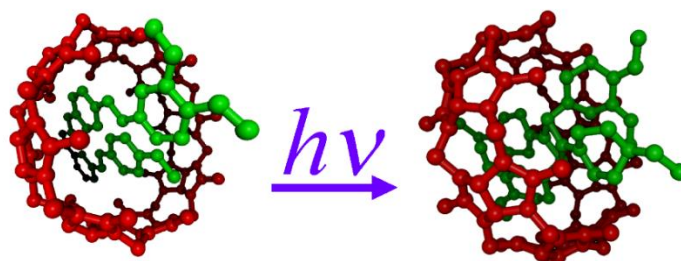
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The [2+2] photocycloaddition (PCA) is one of the most frequently used photoreaction for producing carbocyclic products. However, photochemical reactions usually do not proceed as a regio- and/or stereo-specific process that prevents photochemistry from being a common tool in chemical synthesis. Preorganization of reactants either in the solid state or in supramolecular host-guest assemblies can be used to control and manipulate photoreactions [1].

The photocycloaddition of styryl dyes 4-[(E)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethyl pyridinium perchlorate (dye **1**), mediated by 1:2 host-guest complexes with cucurbit[8]urils (CB[8]) - the binding constant  $\lg K = 11.9$  ( $L^2 \text{ mol}^{-2}$ ) - was studied by fluorescence upconversion techniques [2, 3]. The lifetime of 14.5 ps for photoexcited dye **1** in aqueous solution and 3.8 ps for the 1:2 complex were gained from the fluorescence decay. The rate constant of quenching being obtained within the diffusion control limit. Theoretical calculations confirmed that unexcited pairs of dye **1** inside CB[8] does not fit the topochemical principles. According to time-resolved fluorescence anisotropy measurement in the range of 5 ps, a translational movement of a dye molecule inside CB[8] cavity under photoexcitation is required to form a reaction-ready structure.



*The work was supported by the Russian Foundation for Basic Research  
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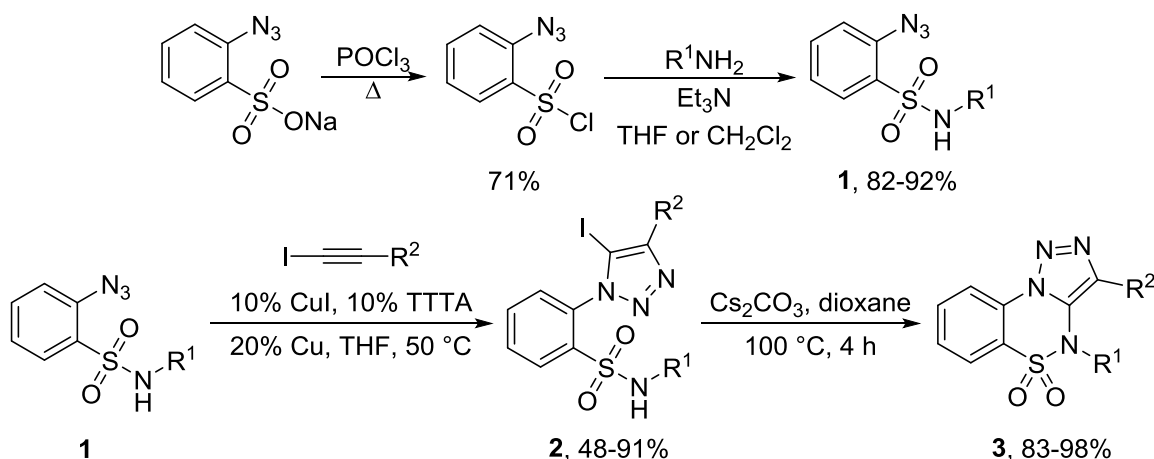
## New approach to 1,2,3-triazole-fused cyclic sulfonamides based on intramolecular nucleophilic substitution in iodotriazoles

Tatevosyan S.S., Kotovshchikov Yu.N., Latyshev G.V., Lukashev N.V., Beletskaya I.P.

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Fused 1,2,3-triazoles represent an important class of heterocyclic compounds exhibiting diverse biological activity [1]. However, the preparation of some types of fused triazoles is complicated and remains a challenging task. Recently we have shown that intramolecular nucleophilic substitution in readily available 5-iodo-1,2,3-triazoles can be used as a straightforward approach to annulated triazoles [2]. In the present study, we applied this synthetic strategy to the preparation of triazole-fused cyclic sulfonamides.

Sulfonamide-containing iodotriazoles **2** were prepared from *o*-azidobenzenesulfonamides **1** by the Cu-catalyzed azide-iodoalkyne cycloaddition in the presence of Cu powder. Optimization of conditions for the base-mediated cyclization of iodotriazoles **2** revealed that the reaction can be performed efficiently in the presence of Cs<sub>2</sub>CO<sub>3</sub> in dioxane at 100 °C. Thus, various triazole-fused sultams **3** were obtained in excellent yields (up to 98 %).



The mechanism of intramolecular nucleophilic substitution in iodotriazoles **3** was studied by DFT calculations.

*This work was supported by RFBR (grant № 18-33-01024 mol\_a)*

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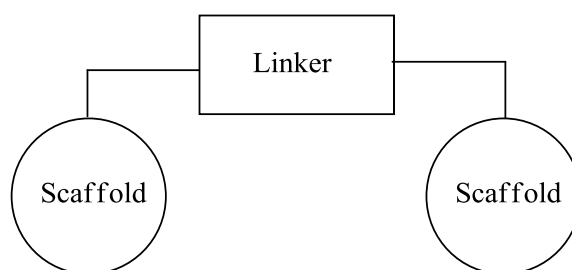
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## Synthesis of Novel Modulators of AMPA Receptors

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The development of medicinal compounds, which could be used for the cure or correction of neurodegenerative diseases and other brain disorders is an important problem. Positive allosteric modulators (PAM) of AMPA receptors have a significant influence of learning and memory, while negative modulators could be useful for the cure of epilepsy [1, 2]. The structure of PAM binding site in the interface of AMPA receptor ligand-binding domains was analyzed. Based on the results of molecular design, a number of compounds of structure **1** were proposed as promising ligands of AMPA receptors potentially having the necessary properties for the correction of central nervous system disorders.



A series of compounds **1** with aliphatic and aromatic scaffolds and linkers, as well as variety of functional groups was synthesized using commercially available amines and various acids or acyl halides.

*We thank the Russian Science Foundation, grant no. 17-15-01455  
for financial support of this work*

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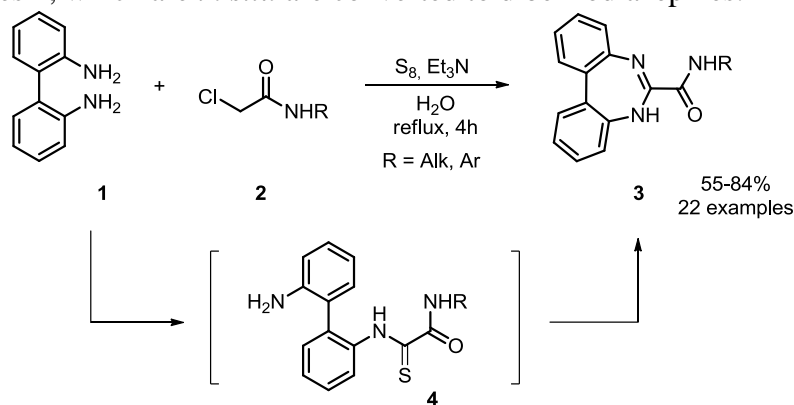
## A distinct novel approach for an efficient synthesis of dibenzo[1,3]diazepines

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One of the beneficial area of modern organic chemistry is a synthesis of aromatic heterocyclic systems, containing benzodiazepine scaffold.[1] Apart from their use as catalysts in a number of useful transformations such as enantioselective Michael addition, Mannich, Strecker, and Diels-Alder reactions, benzodiazepines are of particular interest for supramolecular assembly, and imperative to the biological activity of many pharmaceuticals.[2]

Herein, we developed a simple and efficient one-pot strategy for the synthesis of a new family of imidazodiazepines. We have shown that the reaction of chloroacetamides **1** with a diphenyl-2,2'-diamine **2**, and elementary sulfur leads to carbamoyl-containing 5H-dibenzo[*d,f*][1,3]diazepines **3**. The process apparently proceeds through the formation of monothiooxamides **4**, which are *in situ* are converted to dibenzodiazepines.



The proposed method meets the concept of “green chemistry” since reaction smoothly occurs in water. Starting materials are readily available, and functional group tolerance is quite good. A number of aryl- and alkylcarboxamide-substituted dibenzo[1,3]diazepines were obtained with the high yields. The ease of construction of 5H-dibenzo[*d,f*][1,3]diazepine core and the broad availability of reagents implies that an extensive range of substituents can be selectively incorporated in the side carboxamide chain.

*This work was supported by the Russian Foundation for Basic Research (project № 18-33-20087)*

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## Photodegradation of Combretastatin A-4 derivatives

Trofimova V.V.<sup>a,b</sup>, Yadykov A.V.<sup>b</sup>, Lvov A.G.<sup>b</sup>, Shirinian V.Z.<sup>b</sup>

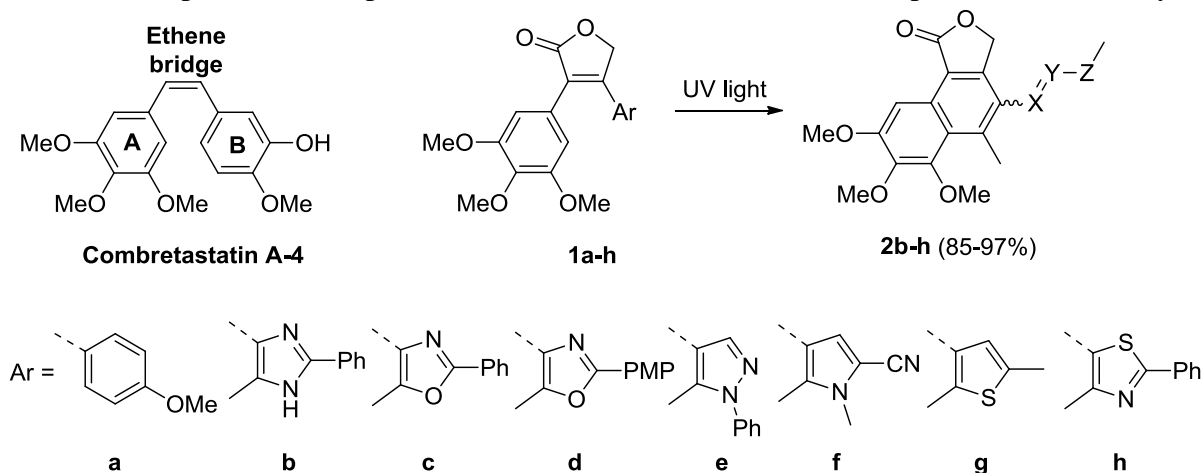
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Combretastatins are a class of natural stilbenes. A variety of different natural combretastatin molecules are present in the bark of *Combretum caffrum*, commonly known as South African Bush Willow. Members of the combretastatin family possess varying ability to cause vascular disruption in tumors by binding to the  $\beta$ -subunit of tubulin, so they attract a lot of interests in modern chemistry.

Molecules that fall into the combretastatin family generally share 3 common structural features: a trimethoxyphenyl "A"-ring, a "B"-ring containing substituents often at C3' and C4', and an **ethene bridge** between the two rings which provides necessary structural rigidity. Most combretastatin A-4 analogs are extremely potent inhibitors of tubulin polymerization and have strong cytotoxicity against several cancer cell lines, including multi-drug resistant cancer cell lines. The aim of this work is the synthesis of CA-4 analogues with a furanone ring as an ethene linker and the study of their photodegradation under UV irradiation. We have synthesized lactones **1a-h** with a heterocyclic fragment as cycle B. In the work both synthesized analogues of CA-4 and their photoreaction products have been studied on in vitro antiproliferative activity.



We propose to develop new analogues of CA-4 with high antiproliferative activity and resistant to light (UV irradiation).

*Financial support by Russian Foundation for Basic Research (RFBR Grant 18-53-05019) is gratefully acknowledged*

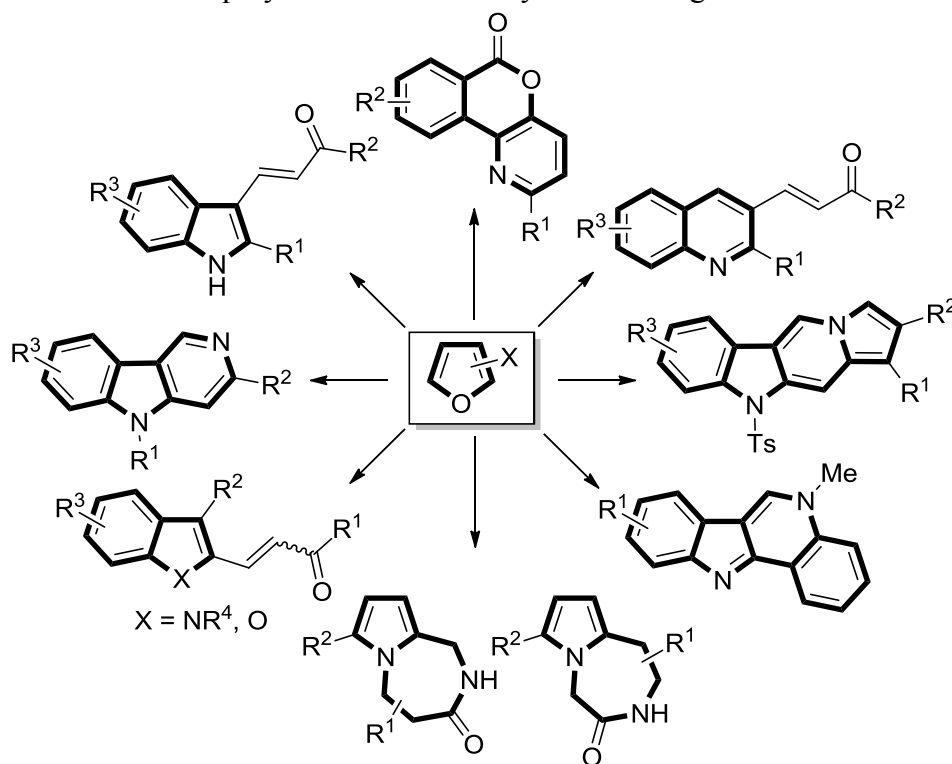
## Transformations of furans in heterocycles synthesis

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Due to low energy of aromaticity furan substrates may undergo chemical transformations which are unusual to those of arenes or other heterocycles. In such transformations furan nucleus may serve as masked 1,3 diene, enol ether or 1,4-dicarbonyl compound. This unique reactivity allows furans to be utilized in synthesis of a large variety of useful products, from alkanes to prostaglandines. Nitrogen-containing heterocycles are considered as ones of the most important among organic molecules, thus this is highly attractive to develop new synthetic routes toward such heterocyclic systems based on the utilization of so-called "furan platform". That would provide an inexpensive way toward valuable objects exploiting products of biomass processing.

During the last decade we have developed general synthetic approaches toward functionalized heterocycles based on the furan rearrangement strategy. Recent results, discussion on mechanisms of specific transformations along with the scope and limitations of furan rearrangements into diverse polysubstituted heterocycles will be given.



*This work was supported by Ministry of education and science of the Russian Federation (project № 4.5371.2017/8.9) and the Russian Foundation for Basic Research (grant number 16-03-00513)*

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## Tandem Diels-Alder reaction in 2,6-difurylpiperidin-4-ones

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The first stage of the present work was the synthesis of a piperidin-4-one (**1**) by the Petrenko-Kritchenco reaction. The reaction was carried out according to the classical method, in an alcohol solution containing equimolar amounts of ketone, NH<sub>4</sub>OAc and a two-fold molar excess of furfural at room temperature [1].

At the second stage, piperidin-4-ones **2** with different substituents at the nitrogen atom were synthesized under various conditions indicated in Table 1. Thus, the corresponding piperidin-4-ones **2a-c** were obtained in moderate yields.

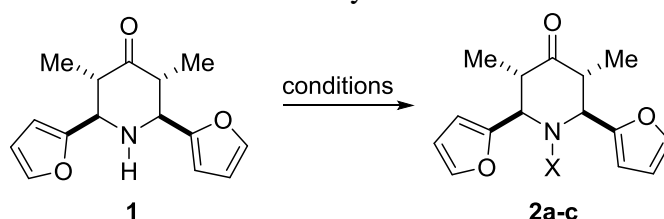


Table 1. Conditions for the synthesis of compounds **2a-c** and their yields.

Compound	X	Conditions	Yield, %
<b>2a</b>	Me	MeI, Na <sub>2</sub> CO <sub>3</sub> , acetone, stirring, 0 °C → r.t.	66
<b>2b</b>	Bn	BnBr, K <sub>2</sub> CO <sub>3</sub> , DMF, r.t., stirring	61
<b>2c</b>	Ac	(CH <sub>3</sub> CO) <sub>2</sub> O, toluene, Δ, 2h	76

The key stage of the work was the tandem reaction of [4+2]/[4+2] cycloaddition of DMAD with *N*-X-2,6-difurylpiperidin-4-ones (**2a-c**). We have shown that the successful formation of the target domino-type adducts **3a-c** was possible only in relatively higher-boiling solvents (Table 2).

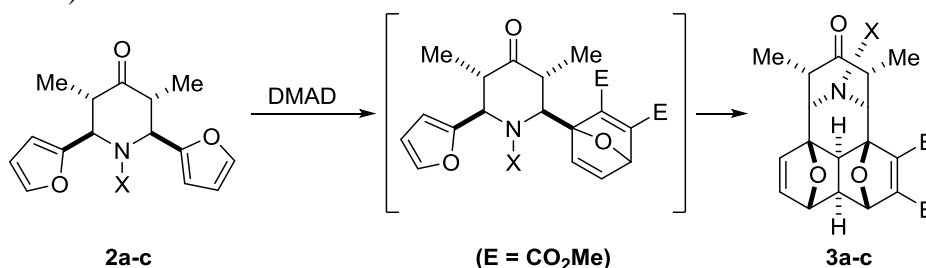


Table 2. Conditions for the synthesis of compounds **3a-c** and their yields.

Initial comp.	X	Conditions	Adduct	Yield, %
<b>2a</b>	Me	<i>o</i> -xylene, Δ, 7 h	<b>3a</b>	33
<b>2b</b>	Bn	<i>o</i> -xylene, Δ, 8 h	<b>3b</b>	27
<b>2c</b>	Ac	<i>o</i> -xylene, Δ, 10 h	<b>3c</b>	48

Funding for this research was provided by the Russian Science Foundation (RSF),  
project № 18-13-00456

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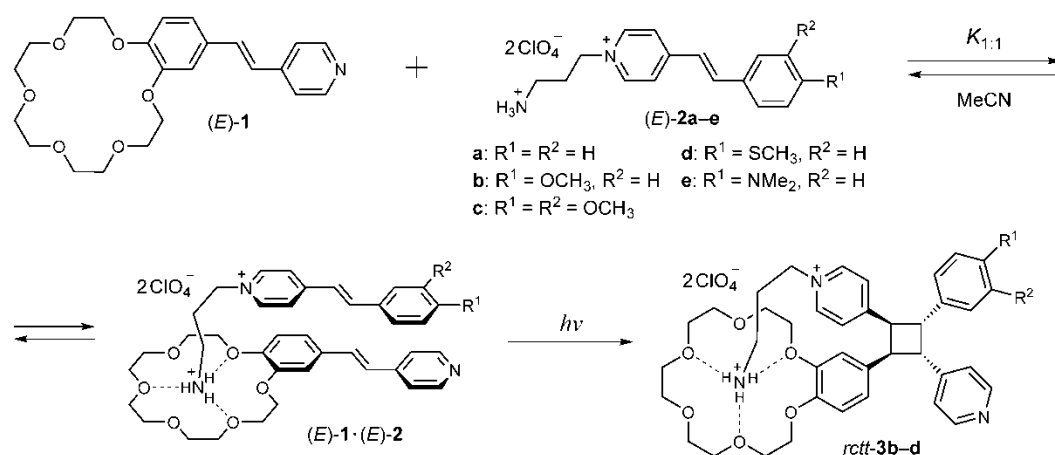
## Substituent effect on the supramolecular [2 + 2]-cross-photocycloaddition between functionalized styrylpyridine derivatives

Ushakov E.N.<sup>a,b</sup>, Martyanov T.P.<sup>a,b</sup>, Sazonov S.K.<sup>b</sup>, Vedernikov A.I.<sup>b</sup>, Gromov S.P.<sup>b</sup>

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Crown-containing styrylpyridine (*E*)-**1** is able to bind styrylpyridinium dyes (*E*)-**2a–e** [1,2] *via* hydrogen bonding to form pseudodimeric complexes (*E*)-**1**·(*E*)-**2** in which the styrylpyridine and styrylpyridinium moieties are arranged one over the other owing to stacking interactions. The stability constants ( $K_{1:1}$ ) of complexes (*E*)-**1**·(*E*)-**2** in MeCN were measured using spectrophotometric titration. It was found that the substituents on the benzene ring of (*E*)-**2** have insignificant effect on the complex stability constant.



The photochemical and photophysical properties of styrylpyridinium dyes (*E*)-**2** in free forms and in complexes with styrylpyridine (*E*)-**1** were studied by electronic spectroscopy methods. It was found that the complexation of dyes (*E*)-**2b–d** with (*E*)-**1** induces a stereospecific [2 + 2]-cross-photocycloaddition reaction yielding cyclobutanes *rctt*-**3b–d**. The quantum yields of this supramolecular photoreaction were measured upon selective excitation of the styrylpyridinium dye. An unexpected result is that with an increase in the  $S_1$  excited state lifetime of the dye ( $2b < 2c < 2d$ , more than 20 times), the photocycloaddition quantum yield decreases ( $2b > 2c > 2d$ , twofold). In order to interpret this effect, the structures of complexes (*E*)-**1**·(*E*)-**2b,d** in MeCN were studied using density functional theory calculations.

*This work was supported by the Russian Science Foundation (grant No. 19-13-00020) and the Ministry of Science and Higher Education of the Russian Federation (State Assignment No. 0089-2019-0003)*

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## Synthesis of Bicyclic Piperazine Mimetics of the Peptide $\beta$ -turns via the Castagnoli–Cushman Reaction

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Scaffold-oriented synthetic strategy based on post-condensation modification of the Castagnoli–Cushman reaction has been developed in our laboratory. And novel condensed bicyclic scaffolds with three points of diversity in three-dimensional space and containing two stereogenic centers have been obtained in pure diastereomeric form [1] (structures *i-iv*, Fig. 1).

While “6/6” bicyclic piperazinones *i-ii* (tetrahydro-1*H*-pyrazino-[1,2-*a*]pyrazine-1,4,7-trione) are relatively well-represented in the synthetic organic and medicinal chemistry literature [2-3], tetrahydropyrazino[1,2-*a*][1,4]diazepine-3,6,10-trione core (*iii*) is completely novel. Likewise, its “6/8” version (*iv*) has not been described in the literature.

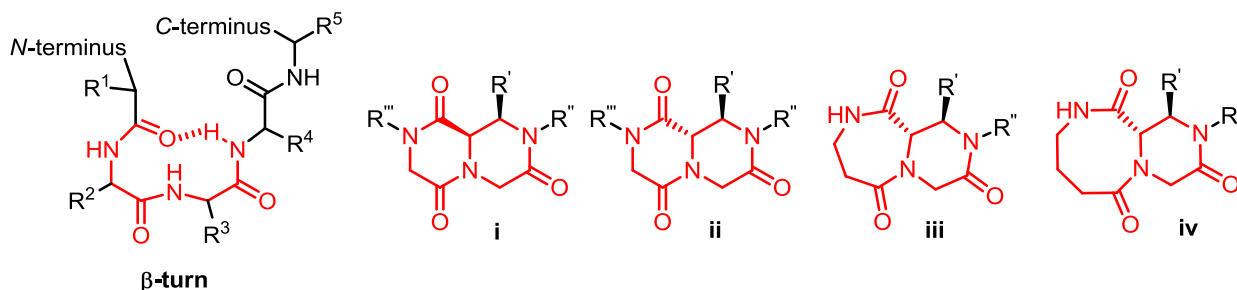


Fig. 1. Structure of peptide  $\beta$ -turn and its bicyclic piperazine mimetics *i-iv*.

All these scaffolds are conformationally constrained, hold a privileged structural motif (diketopiperazine core) and also have a highly saturated (so-called high- $F_{sp^3}$ ) template containing two stereogenic centers. These features give the considering cores attractiveness for drug design in general. In particular, they can be exploited as a novel chemotype for peptidomimetic drug design and hydrolytically stable replacement for the ten-membered cyclic motif featured in the  $\beta$ -turn [4] (Fig. 1). The latter have been shown in our work by spatial overlay of structures *i-iv* with peptide  $\beta$ -turn.

*This research was supported by the Russian Scientific Foundation  
(Project Grant 14-50-00069)*

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## Synthesis of antimitotic drug conjugates based on PSMA ligands

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Recently, methods of selective delivery of drugs and other agents directly to the tumor, including prostate, have been actively developing. A promising protein marker for the diagnosis and treatment of prostate cancer is the prostate-specific membrane antigen, PSMA. The high expression of PSMA in prostate cancer cells compared with normal cells and vascular tumors has made it very promising for study. Urea-based low molecular weight ligands are described, providing selective binding to PSMA, and used to create therapeutic and diagnostic conjugates [1].

To obtain a new series of PSMA ligands, a computer simulation was performed. The results of docking show that ligands containing dipeptide linkers, based on amino acid residues of phenylalanine and tyrosine, has good affinity to PSMA and show high selectivity. The dipeptide linkers for urea-based ligands PSMA were optimized in present work. *In vitro* tests of 21 PSMA ligands with linker were observed. Ligands demonstrating the highest selectivity ( $IC_{50} = 22,5$  nM and 9,7 nM for LNCaP) were selected, while urea-based ligand without modification has low selectivity ( $IC_{50} = 2149$  nM for LNCaP). High selective ligands were used for further synthesis with antimitotic drug Docetaxel.

Docetaxel drug conjugates were characterized and *in vitro* tests were performed on prostate cancer cell lines 22Rv1 (PSMA +) and PC-3 (PSMA -). The results show that cytotoxicity of new conjugates comparable to Docetaxel without modification.

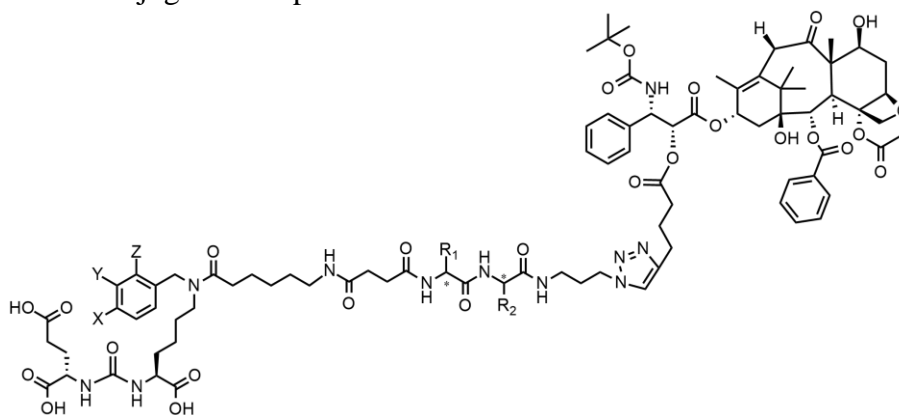


Fig. 1. General scheme of the structure of the conjugate

The approaches to the synthesis of these conjugates and the results of biological studies will consider in this report.

*This work was kindly supported by the Ministry of Education and Science of the Russian Federation (№ IP-MSU/10-14 (NKR 185/17))*

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## Dicarboxylated pseudo-crown ethers as a novel scaffold for the development of heavy metal cations - selective fluorescent probes

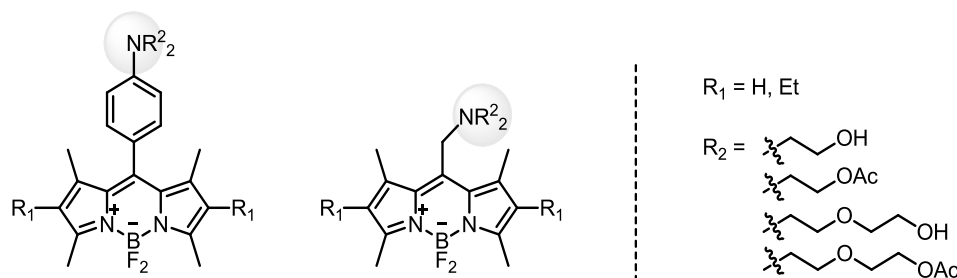
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Design of fluorescent chemosensor for selective detection of heavy metal cations is an active field of organic chemistry [1]. Recently, open-chain analogues of crown ethers, so-called pseudo-crowns, have gained much attention as highly promising, readily available metals cations ligating agents [2, 3].

Herein, we performed the systematic evaluation of the boron-dipyrromethene dyes (Bodipy) series functionalized with pseudo-crown ethers at *meso*-position against metal cations and revealed their potential as off-on fluorescent probes for heavy metal cations. We incorporated 2-((2-(2-acetoxyethoxy)ethyl)amino)ethyl and structurally similar pendants at the C-8 positions of the Bodipy core using a phenyl and methylene linker. Six novel pseudo-crown-based sensor molecules were synthesized and comprehensively characterized by UV-Vis and fluorescence methods.



Investigations of their photophysical properties in the presence of a number metal cations showed that probes bearing the 2,6-H-Bodipy core and probes deprived of acetyl groups at the chelator exhibit off-on fluorescence responses in the presence of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$  ions. In contrast, probes derived from kryptopyrrole using the 2-((2-(2-acetoxyethoxy)ethyl)amino)ethyl acetate group were selective to  $\text{Al}^{3+}$ ; they showed ratiometric UV and strong fluorescence turn-on responses. Thus, pseudo-crown modified Bodipy molecules can be considered as promising probes for detection of heavy metal cations in solutions.

*This research was financially supported by the Russian Foundation for Basic Research (Projects 17-53-16012)*

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## Changes in molecular weight parameters of collagen during enzymatic hydrolysis with pancreatic

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The development of new tissue-substituting materials to restore the function of damaged tissues is one of the most urgent tasks of modern medicine. When solving such problems, natural and synthetic polymers are used as cell matrices (scaffolds) - as the basis of tissue engineering design [1-3].

The purpose of this work is to analyze the molecular mass characteristics of high-molecular collagen isolated from cod, pig and chicken skin, and the dynamics of their change during enzymatic hydrolysis with pancreatin under standard conditions, which are most often used in the formation of scaffolds based on biopolymers.

The main task here is the control of the molecular mass characteristics of collagen and their comparison for collagen of different nature. Thus, using gel permeation chromatography, it was shown that the values of molecular weight, polymer polydispersity coefficient, as well as particle size, according to the light scattering method, differ markedly depending on the nature of collagen. During enzymatic hydrolysis with pancreatin (mass ratio collagen : pancreatin = 1.0 : 0.1) under standard conditions, the main part of the high molecular weight fraction is hydrolyzed within the first minute, while the hydrolyzate has a polydispersity coefficient of ~ 1.0 and different molecular weights. Collagen from cod skin during the time of control - three days - is fully hydrolyzed, for the remaining samples the molecular weight parameters after the first minute during this period of control remain almost unchanged. The conducted studies are of interest for the field of tissue engineering, associated with the development and research of the properties of scaffolds based on natural biopolymers, to establish the relationship of chemical and biological processes.

*The work was performed in the framework of the project "Biomimetic composite universal materials based on biodegradable biopolymers and mineral fillers for tissue engineering", (Competition Russian Science Foundation, application N 19-73-20156) using the equipment of the Collective Use Center "New materials and resource-saving technologies"*

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## Effect of deuterium on polymerization of vinyl derivatives

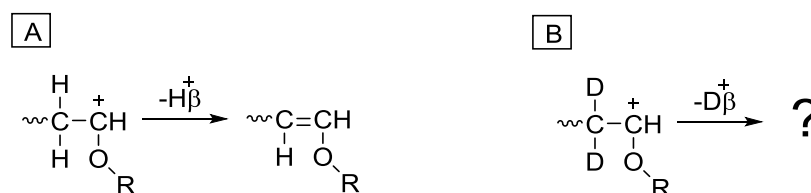
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New demands in the area of smart polymeric materials impose new requirements on the main properties of final products. Controlling molecular weights and molecular weight distributions is the key task in polymer synthesis. Special initiators, temperature parameters and dry solvents are principal tools for controlling these values. However, in the case of challenging substrates, requirements on molecular weight and molecular weight distributions are much more specific.

Transfer is an important chain-breaking factor in cationic polymerizations of alkenes. Transfer reactions decrease molecular weight of the resulting polymers and increase the variations of molecular weight distributions. One of the most common transfer reactions in carbocationic polymerization is  $\beta$ -H elimination. The reaction leads to unsaturated end groups (scheme, part A).

In our laboratory, a wide range of vinyl monomers is synthesized [1] and polymerized according to procedures described elsewhere [2]. We have previously developed an efficient route to vinyl derivatives based on calcium carbide as an acetylene source and currently investigate the effects of substitution of hydrogen atoms with deuterium. We show that deuteration at double bonds of the monomers enhances the rate of cationic polymerization and increases the molecular weight of the polymer. The influence may be caused by decreasing of the transfer reaction rate constant for deuterated monomers as compared with non-deuterated.



Kinetics of cationic polymerization of deuterated vs non-deuterated vinyl monomers is presented. Potentially, incorporation of deuterium instead of protium into a vinyl group delays its elimination due to the higher strength of carbon-deuterium bonds compared to carbon-protium bonds. Accordingly, the side chain-breaking reactions will proceed slower and contribute less to locking of the main process. The observed isotope effect has great potential as an additional tool for controlling specificity of polymerization. It allows isolation of polymers with higher molecular weight and better distribution.

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## Preparation and structure investigations metal complexes based on 2-(3-iodopyridin-2-yl)-1H-benzo[d]imidazole

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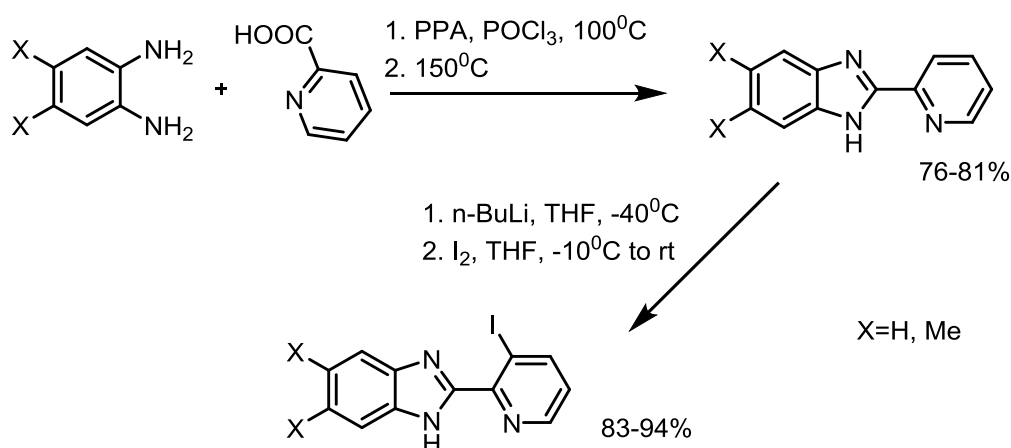
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Hypervalent iodine compounds are now routinely used in organic synthesis as reagents for various selective transformations of complex organic molecules due to environmental sustainability and commercial availability.[1]

Presently, among the great variety of hypervalent iodine compounds, polyvalent iodine (III) derivatives with I-N bonds have been much less investigated than those containing I-O bonds.[1-2] In several, the coordination of oxygen donor atoms to hypervalent iodine centers has been a common strategy, while related nitrogen donor coordination appears significantly less encountered.[3-5]

At the same time, the organic compounds containing a nitrogen atom in their structure are excellent ligands for transition metals, which is able to influence on the reactivity of iodonium species [6]. In our contribution, we proposed the synthetic pathways for the preparation of ligands, containing iodine atom for the further complexation of metals and oxidation of iodine.



This work was supported by Grant of Russian Science Foundation № 17-73-20066

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## Synthesis and antiproliferative activity evaluation of steroidal imidazo[1,2-a]pyridines

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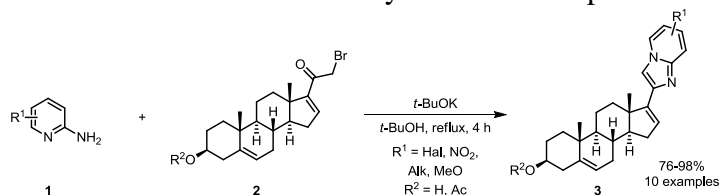
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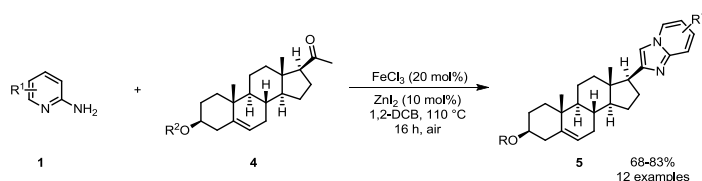
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Hormone-dependent cancers (HDC), including those of the breast and prostate, are of the most commonly diagnosed cancers in women/men [1]. Typical medicines used to treat breast/prostate cancers are derived from sex steroid hormones, playing role of the primary modulators in steroidogenesis of malignant growths. Thus, heterosteroids of the estrane and androstane series containing the aza-substituent on ring D are privileged scaffolds for the anti-HDC drug discovery. Recently, we found that steroidal imidazo[1,2-a]pyridines of estrane series have remarkable cytotoxic activity against breast cancer cells at  $\mu\text{M}$  level [2].

Inspired by a potential of many cytotoxic agents for treatment of prostate cancer containing a steroidal moiety along with the aza-heterocycle, herein, we report an original approaches for the direct installation of an imidazo[1,2-a]pyridine group at the C-17 position of androstane core. Condensation of readily available 2-aminopyridines **1** with 21-bromo-16-dehydropregnenolone **2** under basic conditions was found efficient in the synthesis of compounds **3**.



A series of imidazo[1,2-a]pyridines **5** were synthesized from 2-aminopyridines **1** and pregnanolones **4** via generation of 21-iodo-pregnenolone *in situ* by treatment with  $\text{ZnI}_2$  under  $\text{FeCl}_3$  catalysis.



Antiproliferative activity of steroidal imidazopyridines was evaluated against 22Rv1 (AR+) and DU145 (AR-) human cell lines by the MTT assay. Almost all compounds were found to be active at  $\mu\text{M}$  level, and thus can be considered for the development of new drug candidates against prostate cancers.

*The chemistry part was supported by RFBR Indo-Russian joint project 17-53-45127*

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## Study on Willgerodt-Kindler reaction of chloromethylphosphonates with aliphatic diamines

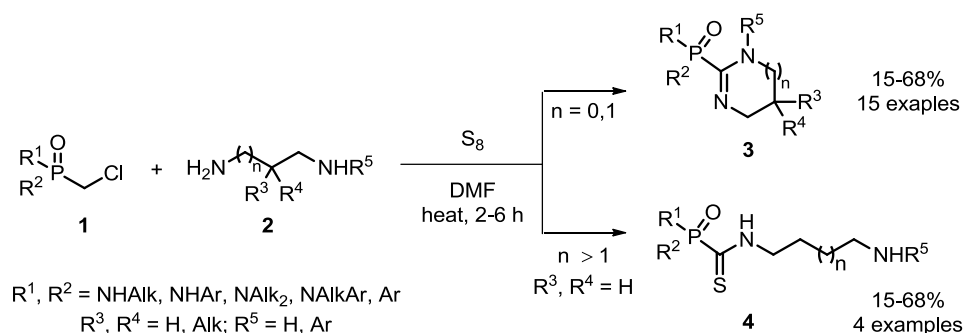
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Phosphoryl-substituted heterocycles are one of the most prominent classes of elementoorganic compounds [1]. They are widely used in various fields - medicine, materials science and industry [2]. Therefore, development of novel synthetic approaches to phosphoryl-substituted heterocycles is of particular interest for chemists.

Here, we have elaborated general and efficient method for the synthesis of  $PO(R^1R^2)_2$ -substituted 4,5-dihydro-1*H*-imidazoles and 1,4,5,6-tetrahydropyrimidines. It was shown that aliphatic diamines **2** with  $n = 0,1$  smoothly undergo in cyclization with chloromethylphosphonic acid derivatives **1** under the conditions of Willgerodt-Kindler reaction providing products **3**.



The reaction proceeds through the formation of thioformamides, which are *in situ* converted to cyclic products with elimination of  $H_2S$ . 4,5-Dihydro-1*H*-imidazoles and 1,4,5,6-tetrahydropyrimidines yields were ranging from moderate to high. Starting materials are readily available, and functional group tolerance is quite good.

Additionally, a representative series of diamidothiocarbamoylphosphonates **4** were obtained by reactions of **1** with aliphatic diamines **2** with  $n > 1$ . All synthesized compounds are of interest as chelating agents for heavy metal cations.

*This research was financially supported by the Russian Science Foundation  
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## Ullmann and Chan-Evans-Lam reactions in the synthesis of 5-arylidene-3-substituted-2-(arylselanyl)-imidazoline-4-ones

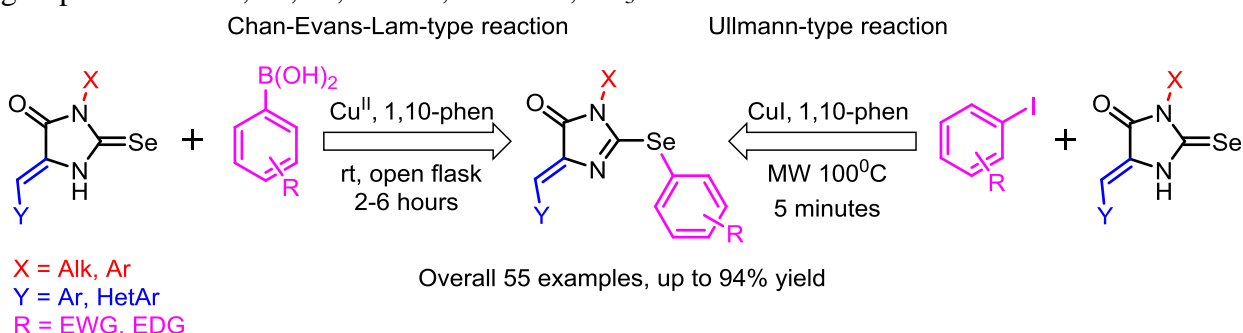
Vyhivskiy O., Finko A.V., Skvortsov D.A., Zyk N.V., Majouga A.G., Beloglazkina E.K.

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The elaboration of novel and efficient approaches to synthesis of new compounds with cytotoxic activity is a complicated challenge for medicinal chemistry nowadays.

During the last decade compounds containing hydantoin core such as Enzalutamide and Apalutamide have shown the anticancer activity against different cancer cell lines. Therefore, nowadays they are widely applied in the treatment of prostate cancer. Moreover, we showed the inactivation of MDM2 protein - one of the most important elements in prostate cancer evolution - by S-arylated thiohydantoin in our recent investigation [1]. Thus the replacement of sulfur atom by Se atom in such compounds is expected to lead to the better performance and new properties to these molecules and provide the creation of efficient analogues of Enzalutamide and Apalutamide [2].

In the current work we used two classic C-heteroatom cross-coupling reactions for the synthesis of Se-arylated products. The first one implies the reaction between 2-selenohydantoin and aryl boronic acid in the presence of  $\text{Cu}^{\text{II}}$  salts whereas the second one involves aryl iodide (second co-substrate),  $\text{CuI}$  as the catalyst and 1,10-phenanthroline as ligand in the presence of sodium tert-butoxide. We obtained wide range of final compounds with average yield 74% and 82% for the first and second methods respectively. The high tolerance towards various functional groups such as CN, Br, Cl, COOR, CONHR,  $\text{CF}_3$  was observed in both methods.



The biological activity of final products was tested *in vitro* against A549, HepG2, SiHa, and MCF-7 cells. It was shown that cytotoxicity of the resulted Se-arylated hydantoin is close to the nonspecific adverse cytotoxicity of Enzalutamide and Doxorubicin. In addition, the minor selectivity of three final compounds against lung adenocarcinoma A549 cell line was found.

*This work was supported by the Russian Science Foundation (grant № 17-74-10065)*

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## Catalytic transfer hydrodebenzylation with low palladium loading

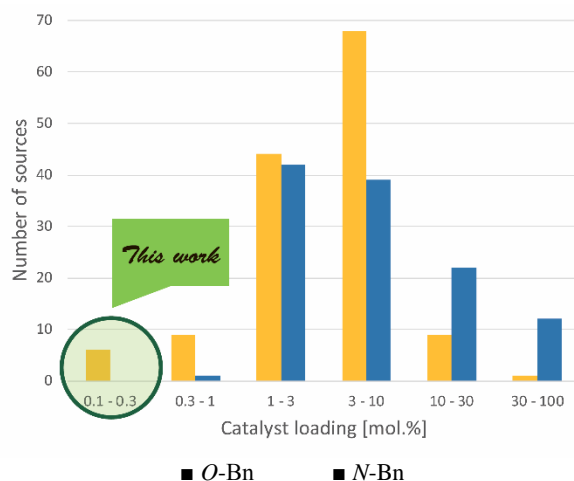
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Palladium catalysis is one of the most intensively developing area in organic chemistry. Due to its unique applicability it has become an indispensable tool for chemical synthesis both in academia and in industry. Novel catalytic systems with improved activity and selectivity appear permanently; consequently, this allows to decrease the amount of a catalyst, which is required for full conversion of a substrate.

Recently, an attractive approach for preparation of palladium on carbon catalysts was reported [1]. It consisted of one-step deposition of Pd nanoparticles simply by stirring a solution of tris(dibenzylideneacetone) dipalladium(0) complex with a suitable carbon material. The applied metal complex was smoothly prepared and its purity could be easily controlled by  $^1\text{H}$  NMR [2]. An extraordinarily rapid catalyst preparation procedure ( $< 5$  min) under mild conditions and its excellent performance in cross-coupling and hydrogenation reactions were demonstrated [1].

Further, a detailed examination of the activity of these catalysts in catalytic transfer hydrodebenzylation reaction was accomplished [3].



Analysis of reported data clearly shows that the hydrodebenzylation reaction is usually carried out using 1-10 mol.% of a catalyst. It should be noted that *N*-benzyl bond cleavage is considered to be more demanding; such examples with sufficient catalyst loading less than 1 mol.% can hardly be found. Also, only few reports of deprotection of ordinary *O*-benzylated substrates with applied catalyst loading of  $\approx 0.1$  mol.% have been reported to date.

In this work we revealed the ability of the derived catalyst, namely 1% Pd/Vulcan, which was prepared in accordance with the “mix-and-stir” approach, to successively cleave both *O*-Bn and *N*-Bn bonds in 25 various substrates in short reaction time applying unusually low catalyst loading ( $\leq 0.3$  mol.%) [3]. Also, the catalyst possessed notable activity toward hydrodehalogenation of arylbromides and arylchlorides.

### References

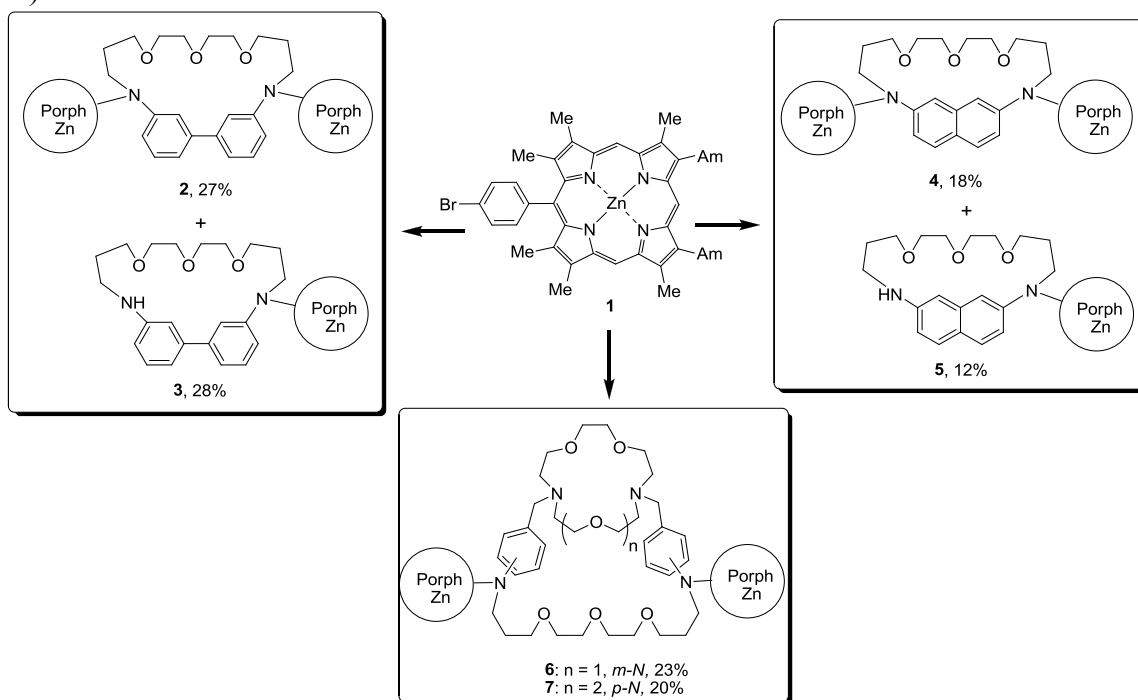
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## Porphyrin-macrocyclic conjugates in the fluorescent detection of metal cations

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The importance of the creation of novel chemosensors for detecting metal cations, especially those that are toxic and harmful to environment, cannot be overestimated. In this connection new synthetic approaches to compounds able to selectively detect certain metals are always in the focus of the synthetic chemistry. Our contribution to this field of research is the application of Pd(0)-catalyzed amination in creating macrocyclic and polymacrocyclic compounds of new architecture which possess binding sites to coordinate metal cations and fluorophore moieties as fluorescent methods in detection are being widely developed for the sake of their high sensibility and selectivity. This work is dedicated to the synthesis and investigation of the porphyrin conjugates with nitrogen- and oxygen-containing macrocycles and macrobicycels. The Pd(0)-catalyzed amination was carried out between Zn(II) porphyrinate **1** and various macrocyclic compounds described by us earlier. As a result, bi-, tri- and tetramacrocyclic compounds **2-7** were obtained [1, 2]. Fluorescent investigations revealed that they can act as chemosensors or molecular probes for Cu(II) and in several cases for Al(III) and Cr(III) cations.



This work was supported by the Russian Foundation for Basic Research (grant № 16-29-10685)

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## The synthesis of previously inaccessible 1,3-unsubstituted imino- and thioiminoglycolurils based on monoithio- and dithioglycolurils

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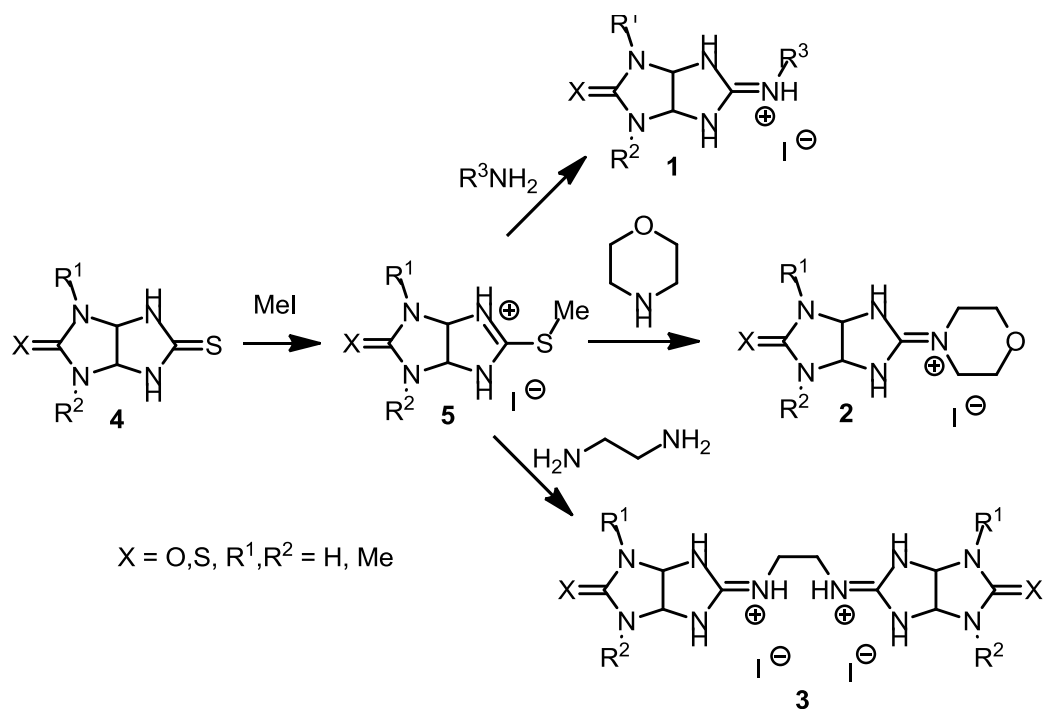
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The glycolurils with guanidine moieties or iminoglycolurils are little-known in the literature; however, there have been found antibacterial agents, antioxidants, mimetics neutrophils growth factor G-CSF and high-energy density materials among them. Therefore, the development of approaches for the synthesis of new derivatives of this class of compounds and their thioanalogues is relevant.

In this work we have developed a facile two step synthesis of 1,3-unsubstituted imino- and thioiminoglycolurils **1-3** using easily accessible reagents (thioglycolurils **4**, MeI and different amines). On the first stage we prepared thiouronium salts **5** from thioglycolurils **4** and MeI. At the second step the different amines and thiouronium salts **5** were condensed to form imino- or thioiminoglycolurils **1-3**.



The structure of compounds **1-3,5** was confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, HRMS (ESI) and X-Ray for some compounds. A number of the obtained 1,3-unsubstituted imino- and thioiminoglycolurils were sent for biological tests for anticancer and antimicrobial activities.

*This work was supported by the Russian Science Foundation  
(Project 17-73-10415)*

## Reductive Domino Synthesis of 12,12-dihydrochromeno[2,3-*c*]isoquinolin-5-amine

Yue X., Festa A.A., Voskressensky L.G.

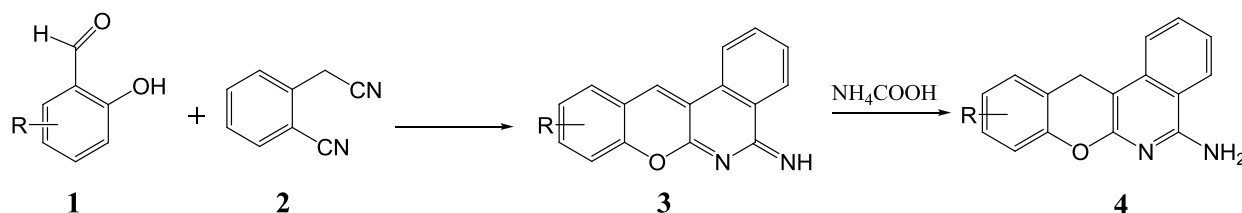
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Multicomponent domino reactions used in syntheses of natural products and complex structure are highly desirable. Designing new selective cascade reactions is a continuing challenge at the forefront of organic synthetic chemistry.

The anionic domino reaction is the most often encountered domino reaction in literature especially by combining Michael additions and condensation. A number of multicomponent reactions via continuous nucleophilic addition could be successfully used to develop new domino-processes.

An effective preparative three-component synthesis of 12-substituted chromeno[2,3-*c*]isoquinolin-5-amine was previously developed with high yields. It comprised sequential reactions of salicylaldehydes with homophthalonitrile and with nitromethane under MW irradiation [1].

Initial condensation between **1** and **2** after two cyclizations forms intermediate imine **3**, which can undergo a reductive tautomerization in the presence of H-atom donor. A series of amines **4** were obtained with good yields.



*The work was prepared with the support of the "RUDN University Program 5-100"  
and RFBR grant 18-33-20040*

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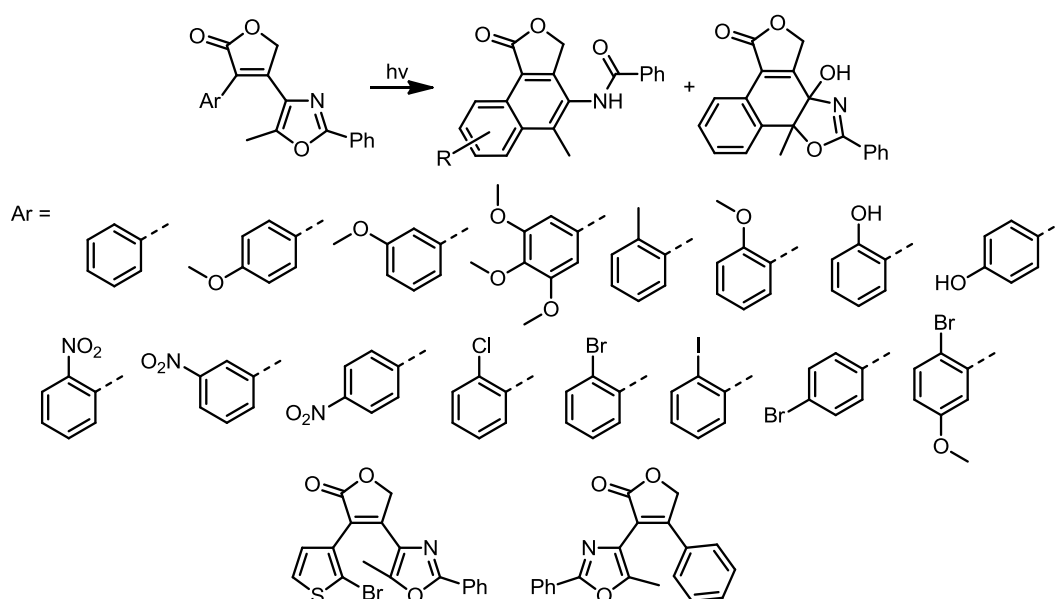
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## Photoinduced rearrangement of diarylethenes: substituents effects

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Photochemical reactions are being actively studied to develop practically important materials and devices for various purposes, such as optical memory, molecular switches, solar cells, etc. One of the important sections of this field of chemistry is  $6\pi$ -electrocyclization of diarylethenes.



The work is a continuation of our study on the photoreaction of diarylethenes. [1-3] This report is devoted to the study of the effect of various substituents in the benzene ring (methyl, methoxy, hydroxy, chlorine, bromine, nitro, etc.) on the photorearrangement process. It was found that the position of the substituent in the benzene ring has a strong influence on the photoreaction. In the work the mechanism of the reaction and spectral-kinetic characteristics of the starting compounds and obtained products is also discussed.

*This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-00394)*

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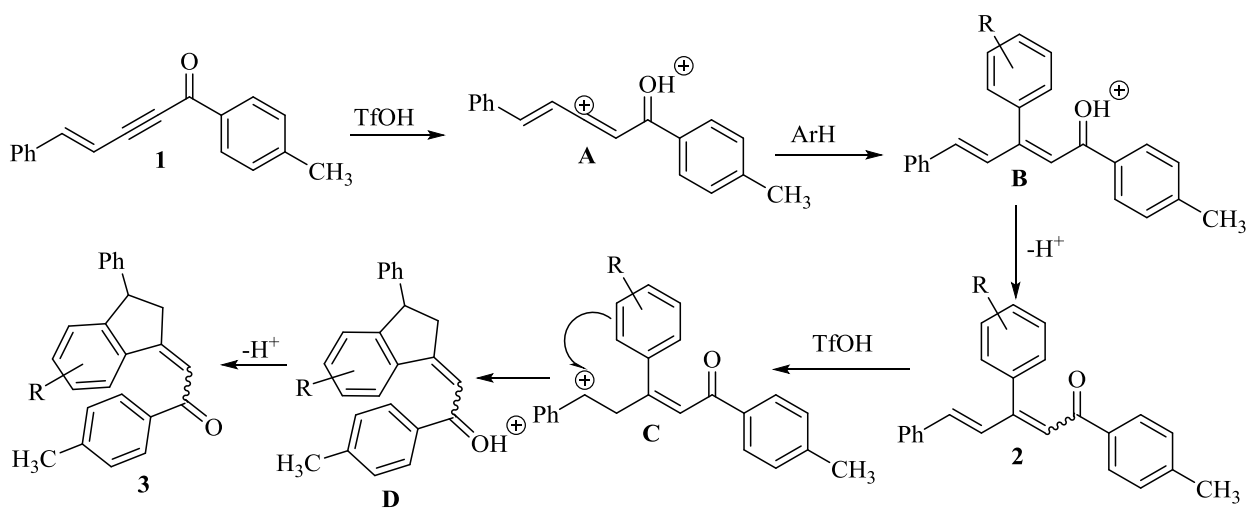
## Superelectrophilic activation of conjugated (*E*)-5-phenyl-1-(*p*-tolyl)pent-4-en-2-yn-1-one in CF<sub>3</sub>SO<sub>3</sub>H

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Conjugated 1,5-diarylpent-4-en-2-in-1-ones **1** under the action of superacid can be protonated to form species, which may have several electrophilic centers. In this study, we investigated transformation of the compound **1** in CF<sub>3</sub>SO<sub>3</sub>H. It was found, that 1,5-diarylpent-4-en-2-in-1-ones gave of the corresponding products **2** and **3** in the reactions with arenes.

Starting compounds were protonated in the presence of 1.5 equivalents of CF<sub>3</sub>SO<sub>3</sub>H to form intermediate **A**. The following interaction with arenes led to products **2**. Under the action of 20 equivalents of CF<sub>3</sub>SO<sub>3</sub>H specie **C** was generated. Intramolecular cyclization of dication **C** occurred, forming of the corresponding products **3**.



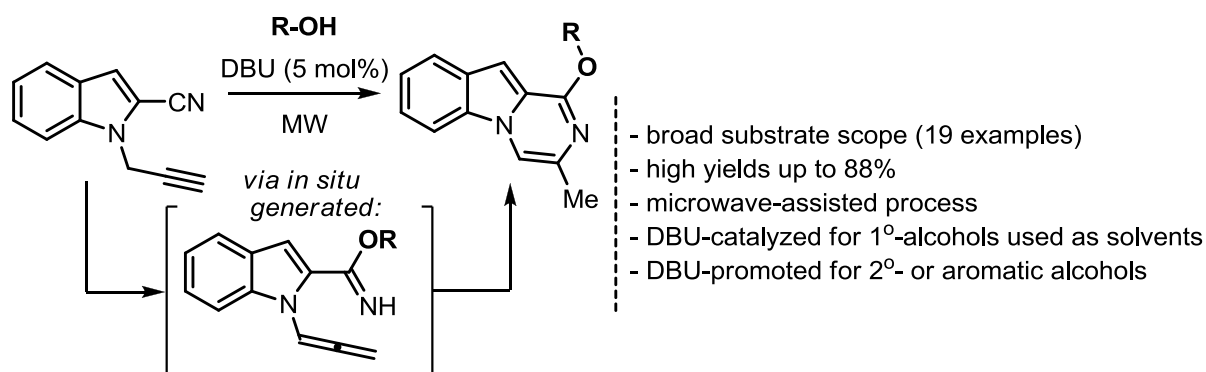
Scheme 1

## DBU-Catalyzed alkyne–imidate cyclization toward 1-alkoxy-pyrazino[1,2-*a*]indole synthesis

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1-(Propargyl)indol-2-carbonitriles react with alcohols to afford 1-alkoxy-pyrazino[1,2-*a*]indoles under DBU-catalyzed microwave-assisted conditions. The reaction scope includes a wide range of indoles, primary and secondary alcohols, and a thiol. The initial mechanistic study shows that the domino process presumably proceeds through an alkyne–allene rearrangement, imidate formation, and nucleophilic cyclization reaction sequence.



We have developed an effective microwave-assisted route toward the 1-alkoxy-pyrazino[1,2-*a*]indole scaffold through a DBU-catalyzed isomerization/double nucleophilic addition reaction sequence in an alcohol medium [1]. The reaction tolerated a wide range of indoles and primary alcohols. We also elaborated on analogous transformations for secondary alcohols and alcohols which were difficult to use as solvents, including thiol. We envision that the reaction will be interesting in the field of medicinal chemistry for the synthesis of drug like structures. A more extensive study using a wider range of nucleophile initiators will follow in due course.

*The work was prepared with the support of the “RUDN University Program 5-100” and RFBR grant 18-33-20040*

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## A general synthetic route to isomeric pyrrolo[1,2-*x*][1,4]diazepinones

Zelina E.Y.,<sup>a</sup> Nevolina T.A.,<sup>a</sup> Sorotskaja L.N.,<sup>b</sup> Uchuskin M.G.<sup>a</sup>

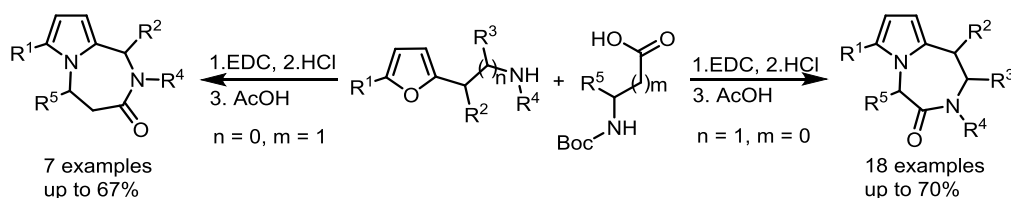
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In recent decades, the combination of two medicinally privileged scaffolds in one polyheterocyclic frame has received particular attention in drug discovery and development. This is due to the ability of heterocyclic moieties for efficient binding to diverse molecular targets. This stimulated us to develop a general approach to subclasses of heterocyclic molecules containing a privileged 1,4-diazepinone moiety annulated to the pyrrole ring. The choice of the pyrrole and 1,4-diazepinone fragment was based on the fact that this ring is present in a large number of natural and synthetic compounds with beneficial properties.

A simple *one-pot* method for the synthesis of isomeric pyrrolo[1,2-*x*][1,4]diazepinones in reasonable yields was developed. The method is based on the condensation of readily available *N*-Boc amino acids with biomass-derived furans containing aminoalkyl groups followed by deprotection, furan ring opening, and the Paal-Knorr cyclization. Using this approach, we synthesized pyrrolo[1,2-*a*][1,4]diazepin-3(2*H*)-ones from furfurylamines and  $\alpha$ -amino acids and pyrrolo[1,2-*d*][1,4]diazepin-4(5*H*)-ones from 2-(2-furyl)ethylamines and  $\beta$ -amino acids.

We investigated the cytotoxicity of the synthesized pyrrolo[1,2-*a*][1,4]diazepin-3(2*H*)-ones as well as pyrrolo[1,2-*d*][1,4]diazepin-4(5*H*)-ones against HEK293T, VA13, MCF7, and A549 cell lines. It was found that some pyrrolo[1,2-*d*][1,4]diazepin-4(5*H*)-ones demonstrated low-to-moderate cytotoxicity while isomeric pyrrolo[1,2-*a*][1,4]diazepin-3(2*H*)-ones were found to be inactive. This opens the possibility to further study the bioactivity of the synthesized pyrrolo[1,2-*x*][1,4]diazepines [1].



Scope and limitations of this type of the amine-tethered furans rearrangements to azaheterocycles will be discussed.

*This work was supported by the Russian Science Foundation  
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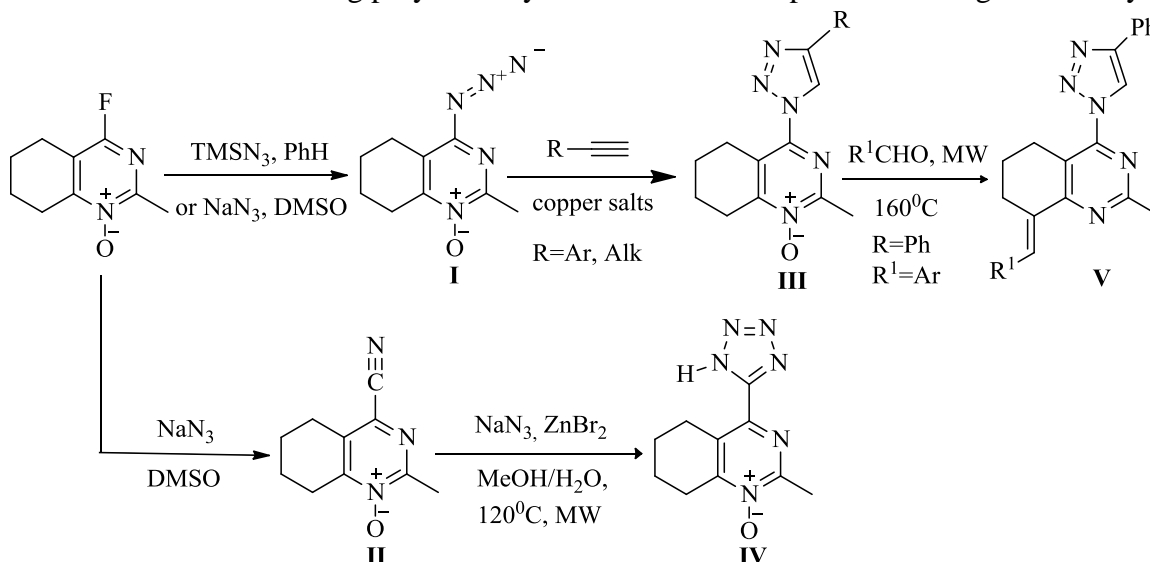
## The synthetic approach to the derivatives of 4-triazolyl- and 4-tetrazolylpyrimidine oxides via 1,3-dipolar cycloaddition

Zharmukhambetova Z.T., Nazarova A.A., Sedenkova K.N., Averina E.B.

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Pyrimidine is a unique heterocyclic scaffold, particularly important in living organisms as a core of pyrimidine bases in nucleic acids, and also present in a number of drugs, including those with anticancer, antiviral, antibacterial and antihypertensive activities. Previously a three-component heterocyclization of *gem*-bromofluorocyclopropanes under the action of nitrating or nitrosating agents in the presence of organic nitriles leading to 4-fluoropyrimidine *N*-oxides was discovered in our laboratory [1].

Synthetic accessibility and high reactivity of 4-fluoro substituted heterocycles in  $S_NAr$  processes allowed obtaining new types of heterocyclic structures, namely, 4-azido- and 4-cyanopyrimidine *N*-oxides (**I** and **II**), representing excellent precursors for the functionalization via CuAAC reactions affording polyheterocyclic structures with potential biological activity.



The optimal conditions for the 1,3-dipolar cycloaddition of 4-azido pyrimidine *N*-oxide **I** with aromatic and aliphatic acetylenes and of 4-cyanopyrimidine *N*-oxide **II** with sodium azide were found. A series of previously unknown 4-triazolyl and 4-tetrazolylpyrimidine *N*-oxides (**III** and **IV**) was synthesized in the optimized conditions. The possibility of further functionalization of heterocycles **III** via condensation with aromatic aldehydes was demonstrated as well.

In summary, previously unknown types of heterocyclic compounds, containing both pyrimidine oxide and triazole or tetrazole moieties, were obtained to study their biological (antiviral and anticancer) activity.

*This work was supported by the Russian Foundation for Basic Research, grant no. 18-03-00651*

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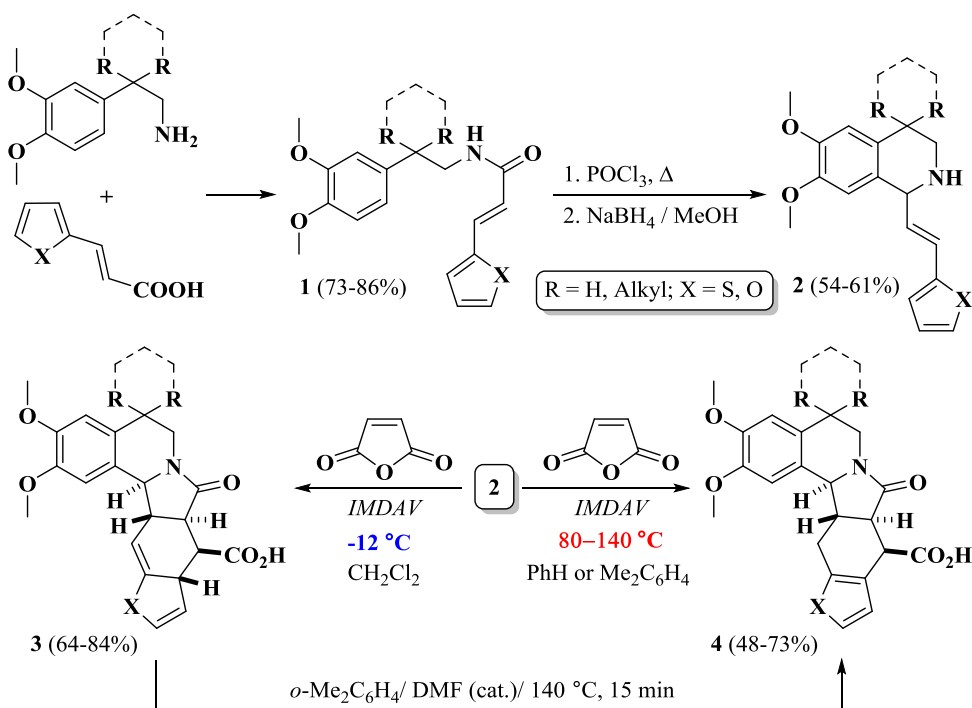
# 1-(Vinylhetaryl)isoquinolines in the tandem reaction of the acylation / [4 + 2] cycloaddition with maleic anhydride

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The following example describes a rare case of the diastereospecific [4 + 2] cycloaddition of maleic anhydride to 1-(vinylhetaryl)tetrahydroisoquinoline **2** [1-3].

1,2,3,4-Tetrahydroisoquinolines **2** were obtained from amides **1** by the Bischler-Napiralski reaction, followed by reduction of the C=N bond. The interaction of compounds **2** with maleic anhydride proceeds through the stage of nitrogen atom acylation and the subsequent intramolecular Diels-Alder reaction, which allows to obtain polycycles **3** or **4** as individual diastereomers in one step. Moreover, at temperatures below zero degrees, it is possible to isolate the "non-aromatic" adducts **3**. At high temperatures, the adducts **3** undergo prototropic tautomerism, turning into compounds **4** with an aromatic furan (thiophene) cycle. The reaction of transformation **2** to **4** can be carried out without isolation of intermediate product **3**.



This work was supported by the Russian Foundation for Basic Research, grants. № 17-53-45016 and 16-03-00125

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## Domino reactions of 4-aryl-6,7-dihydrothienopyridines with electron deficient alkynes and alkenes

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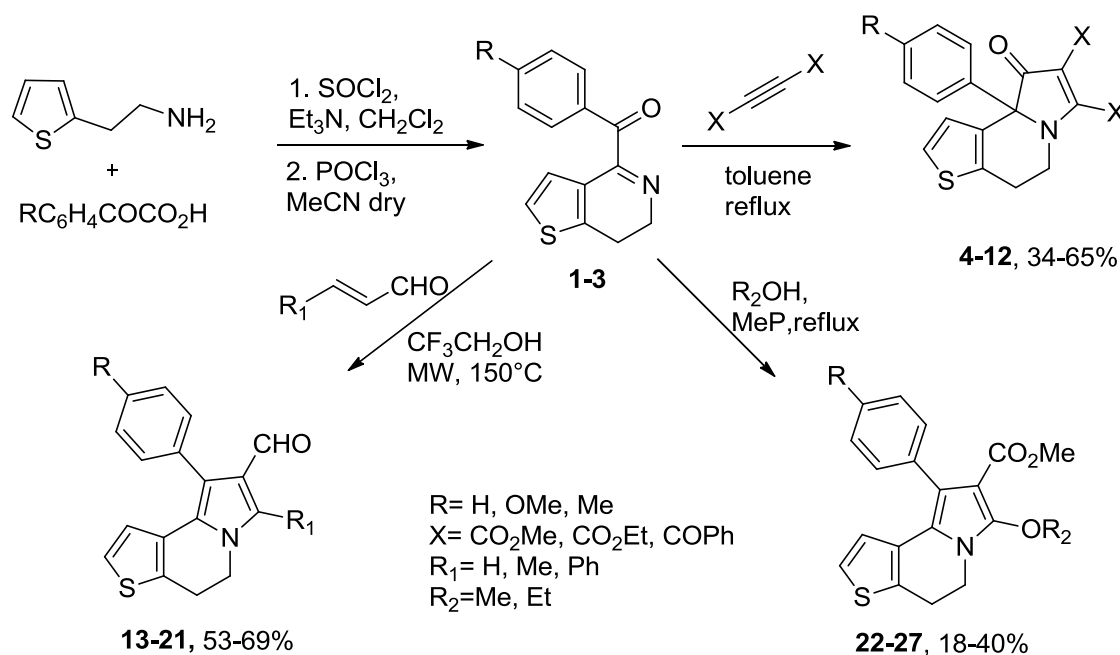
It is well known that thienoindolizines exhibit a high biological activity [1]. For example, thieno[2,3-g]indolizines, containing an aryl substituent in the pyrrole ring, are able to inhibit the aggregation of blood platelets [1]. The various pharmacological properties of thienoindolizines are of interest to the development of new methods for the synthesis of such heterocyclic systems.

A novel method of synthesis of substituted thienopyridines containing an aryl group in the fourth position has been developed. It is supposed to study the thieno[3,2-c]pyridines **1-3** in the reactions with electron-deficient alkynes and alkenes.

The reactions with symmetric alkynes were carried out in a boiling dry toluene. As a result, it was established that after rearrangement thieno[2,3-g]indolizines **4-12** were formed with the vicinal arrangement of functional groups. The products were isolated by column chromatography with medium yields.

Thieno[2,3-g]indolizines **13-21** were obtained with good yields by interaction of 4-aryltienopyridines with  $\alpha,\beta$ -unsaturated aldehydes. Reactions were carried out in trifluoroethanol in an argon atmosphere under microwave radiation.

Moreover, thieno[2,3-g]indolizines **22-27** were synthesized via the reaction of 4-aryl-6,7-dihydrothienopyridines **1-3** with methyl propiolate in ethanol and methanol in yields of 18–40%.



Further study of biological activity for the obtained thieno[2,3-g]indolizines is expected.

This work was supported by the Competitiveness Enhancement Program RUDN "5-100" and RFBR grants №19-53-54001

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## Novel chiral nano-sized supports for asymmetric heterogeneous catalysis

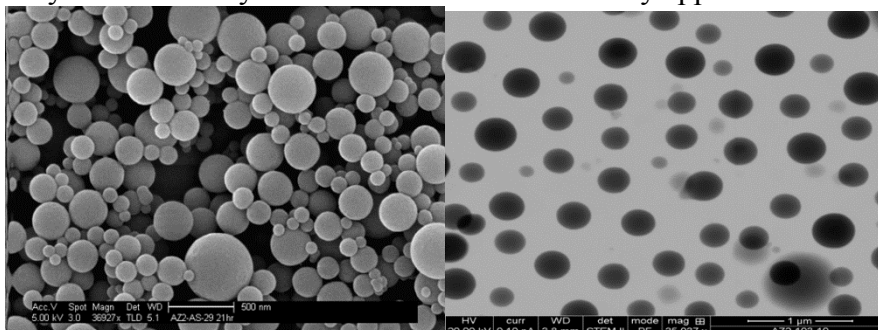
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Over the past few decades, asymmetric transition metal catalysis has become the domain of very intense research activity and greatly expanded the scope of catalytic asymmetric transformations that can be performed with high efficiency. Consequently, large libraries consisting of hundreds of (expensive) chiral ligands and thousands of the corresponding transition metal complexes have been developed for various homogeneously catalyzed organic transformations. However, despite this spectacular progress, only a limited number of asymmetric catalysts found industrial large-scale applications due to the high cost of the metal and of the chiral ligands (both are unrecoverable).

Over the past few decades, a number of strategies have been developed for heterogenizing homogenous (molecular) transition metal catalysts. Roughly, stationary supports may be organic macromolecules (e.g. linear/cross-linked polymers or dendrimers), inorganic or hybrid materials (e.g. graphite, activated carbon, amorphous silica/alumina, zeolites, mesoporous silica/alumina, periodic mesoporous organosilica, metal organic frameworks, etc.). Noteworthy, in all these cases, enantioselection originates from the chiral pocket provided by the chiral ligand, while supports are generally inert and play no active role over the course of the catalytic cycle.

Our group is interested to design efficient heterogeneous asymmetric catalytic systems based on robust achiral transition metal particles incorporated into novel chiral non-racemic porous network and, thus, to establish a new approach to the development of practical heterogeneous asymmetric catalysts for industrial and laboratory applications.



**Figure 1.** SEM image of chiral organosilane nanoparticles (Left), STEM image of chiral organosilane nanoparticles (Right).

## Development of pH-sensitive conjugates of 2-thio-imidazol-4-ones with redox-active ferrocene-containing boronic acids

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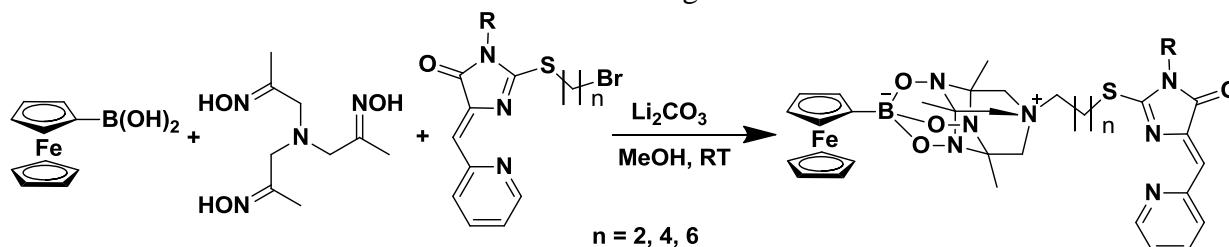
Currently known anticancer drugs, including cytotoxic coordination compounds of transition metals, show high activity against various cell lines of malignant neoplasms, but do not have noticeable selectivity for tumor cells in the body [1].

Previously, our scientific group synthesized redox-active Cu (I,II) coordination compounds containing ferrocene-substituted 2-alkylthio-5-arylmethylene-4-imidazol-4-ones, which showed high cytotoxicity to a number of cancer cell lines and unusual physical chemical properties [2].

Thereby not the design of new cytotoxic drugs, but the development of methods for selectivity improvement of already known therapeutic agents is becoming increasingly important.

In particular, a promising approach is the modification of a cytotoxic drug with a pH-sensitive linker capable of releasing the active substance under acidified intercellular area of tumor tissues (pH = 6.2-7.0 against 7.2-7.4 for healthy tissues) [3].

In the course of this work, were developed synthetic approaches to obtain pH-sensitive conjugates of 2-thioimidazol-4-ones with redox-active ferrocene-containing boronic acids based on a new click-reaction - coupling of boronic acids with triols [4]. Model compounds were synthesized, fully characterized by <sup>1</sup>H, <sup>13</sup>C NMR and HRMS, and the hydrolysis of the pH-sensitive linker in an acidic medium was studied using LC-MS method.



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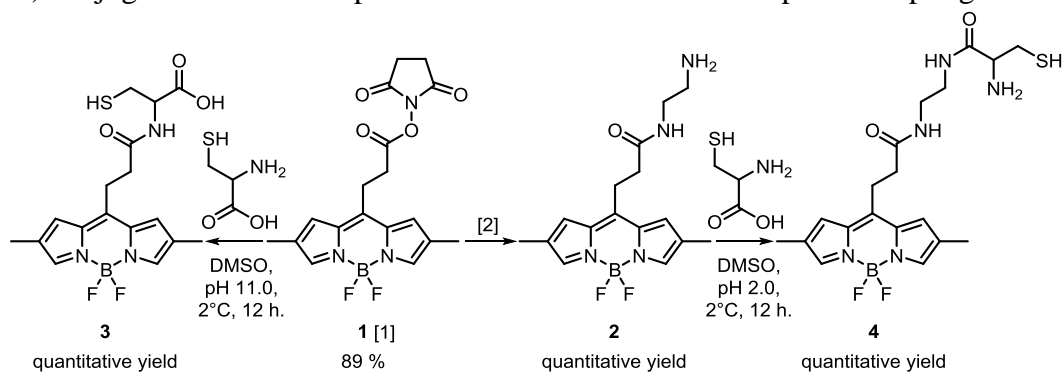
## Cysteine-BODIPY conjugates: synthesis and spectral properties study

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Developing water-soluble biocompatible fluorescent markers is a promising field of modern science. That is why conjugates of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and amino acids are of interest of researchers.

Here, we report the results of synthesis and investigation of two cysteine-BODIPY (Cys-BODIPY) conjugates differ in the position of amino acid and fluorophore coupling.



The first step of the work was obtaining the BODIPY precursors **1** and **2** for further conjugation with cysteine. At the first stage, the succinimidyl ester of 3-(4,4-difluoro-2,6-dimethyl-4-bora-3a,4a-diaza-s-indacene-8-yl)propionic acid **1** was synthesized on the basis of [1] with a minor modifications. At the second stage, the N-(2-aminoethyl)-3-(4,4-difluoro-2,6-dimethyl-4-bora-3a,4a-diaza-s-indacene-8-yl)propanamide **2** was synthesized from **1** on the basis of [2]. The second step of the work was obtaining Cys-BODIPY conjugates **3** and **4** by direct coupling of BODIPY precursors dissolved in DMSO and L-Cys dissolved in buffer solutions with fixed pH values. Due to structural features of amino acids, at  $\text{pH} \geq 11.0$  binding of the fluorophore and the amino acid occurs through the amino group of Cys, while at  $\text{pH} \leq 2.0$  the binding occurs through the carboxyl group of Cys. The compounds synthesized **1** – **4** were characterized by means of the  $^1\text{H}$  and  $^{11}\text{B}$  NMR-spectroscopy, IR-spectroscopy, MALDI-TOF-spectrometry. All the data are in accordance with the proposed structures.

A number of spectral characteristics were obtained for **1** – **4**. Due to structural features of the conjugates, it is observed a small  $\sim 2$  nm bathochromic shift in absorption and emission spectra of **3** and **4** in comparison with **1** and **2** but at the same time there is a considerable  $\sim 50$  % decrease in fluorescence quantum yields. Although spectral changes after conjugation are not significant, the conjugates have high solubility in polar solvents. This property is conditioned by the presence of a hydrophilic amino acid fragment in the hydrophobic fluorophore molecule. Thus, the unique properties of the conjugates synthesized enable us to use them for visualization of bioactive macromolecules as well as biochemical processes in living cells.

*The research was carried out using scientific equipment of ISUCT and ISC RAS.*

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