M.V. Lomonosov Moscow State University Faculty of Chemistry

ORGANIC CHEMISTRY DEPARTMENT



Postal address: Chemistry Department Moscow State University 119991 Moscow Russia

BRIEF HISTORY

1929-1938. Head of Department – academician *N.D. Zelinskiy*

Professor Zelinsky was one of the founders of theory on<u>organic</u> catalysis. He is the inventor of the first effective filtering activated charcoal gas mask in the world (1915). His main research area was the chemistry of cyclic hydrocarbons and catalytic transformations (paraffin dehydrogenation, hydrogenolysis cyclopentanes, gidropolimerizatsiya olefin alkylation and catalytic cracking, the catalytic conversion of sulfur and heterocyclic compounds.



N.D. Zelinskiy (1861-1953)

1938-1950. Head of Department – academician *S.S. Nametkin*

Russian chemist, a prominent researcher in terpene chemistry and rearrangement of camphenes. The Nametkin rearrangement is the shift of a methyl group in this scheme and called the 'Nametkin' step. The shift of the ring bond is actually a standard Wagner-Meerwein shift. The reaction can in fact be used to make the terpene, using chlorocamphene. He took an active interest in the history of chemistry.

1950-1978. Head of Department – academician *A.N. Nesmeyanov*

Professor Nesmeyanov was the President of the Academy of Sciences of the USSR in 1951–1961. As the rector of the Moscow State University in 1948–1951, he oversaw the construction of its new campus at Sparrow Hills. Prof. Nesmeyanov had popularized the term "organometallic chemistry" and became the leader of this science in USSR. He had also organized the investigations of artificial and synthetic food chemistry. Prof. Nesmeyanov had discovered the reaction of diazo-compounds with metal halides which was later named after him. He had also developed a number of industrial chemistry processes.



A.N. Nersmeyanov (1899-1980)

S.S. Nametkin (1876-1950)

1978-1994. Head of Department – academician *O.A. Reutov*

Laboratory of theoretical problems of organic chemistry which was established in Moscow University by Professor Reutov has long been one of the few places in Russia, where graduates received the most modern education, mastering both synthetic methods of organic chemistry, and the problems of the theory. Wwide study of reaction mechanisms of organometallic compounds was initiated in the laboratory with the assistance of the most modern methods and concepts of physical chemistry. He was the founder of a large scientific school and also wrote the books "Theoretical Problems of Organic Chemistry" (1956) and "Theoretical Foundations of Organic Chemistry" (1964.).



O.A. Reutov (1920-1998)

1994-2014. Head of Department – academician *N.S. Zefirov*

He had developed methods of synthesis of polycyclic and heterocyclic compounds, as well as discovered new conformational effectsThe head of the scientific school. Under his guidance St. 50 master's theses, St. 20 students became doctors of sciences. Professor Zefirov initiated the creation of a new specialization - medical chemistry at the Chemistry Faculty of Moscow State University opening.

President of the Russian Society of Medical Chemistry

From 2014. Head of Department – professor V.G. Nenajdenko

Research interests - organic synthesis, chemistry of heterocyclic, sulfur- and fluorine-containing compounds, catalysis, asymmetric synthesis, medicinal chemistry. Professor Nenajdenko is the head of methodological commission of the International Mendeleev school students Olympiad in chemistry.



N.S. Zefirov (born 1935)



V.G. Nenajdenko (born 1967)

Research priorities

- Molecular design of organic structures and organic reactions; research, synthesizing, and testing new organic compounds developed for practical purposes
- 2. Element-organic compounds as reagents and catalysts in the synthesis of organic and organo- metallic compounds
- 3. Catalysis, physical chemistry of surface, supramolecular chemistry, photochemistry
- 4. Modern methods of analysis of organic substances, ecology and environmental chemistry



Teaching

In the quest of academic excellence, the Department is dedicated to providing the best quality and up-to-due education for uor students. At present, the Department has _____ academic staff members, ____ professor and ____ associated professors. The Department currently supervise around 130 graduate students and around 40 postgraduate student.

The basis of the educational process at the department is the **general course of lection** and the **laboratory classes** on organic chemistry. The course **«Organic Chemistry»** is offered for Chemical Faculty, Physical Faculty, Biological Faculty, Faculty of Fundamental Phisyco-Chemical Engineering, Faculty of Bioengineering and Bioinformatics, Geological Faculty, and Faculty of Fundamental Medicine of Moscow University.

For students of all faculties of the Moscow University the courses **«Chemistry and the environment»** and **«Mass spectrometry»**.are also offered.

Traditional laboratory classes give students the basic skills of experimental work on modern organic synthesis.

Our Department members also offer various effective courses in many different specialties. These courses are arranged to bridge our junior students to modern scientific research in various topics in modern chemistry. Students are encouraged to participate in undergraduate research to gain research experience. Topics of special courses, offering at present, are, for example, «Organic Synthesis Strategy», «Chemistry of organoelement compounds», «Catalysis in Organic Synthesis», «Chemistry of Heterocyclic Compounds», «Coordination compounds of transition metals in organic chemistry - theory and practice», «The reactivity of organic compounds: the orbital approach», «Synthetic methods of organic chemistry and stereoselective synthesis», «Advanced NMR Course», «Electrochemistry», «Supramolecular chemistry and nanotechnology of organic materials», «Chemistry of fluoroorganics», «Silicon chemistry and organophosphorus compounds», «Environmental ecology».



Laboratories

Organic Synthesis

Head – **Professor Valentin G. Nenajdenko** Phone: +7-(495) -939-22-76 e-mail: nenajdenko@org.chem.msu.ru

• Phisical Organic Chemistry Head - Professor Valery S. Petrosyan Phone: +7-(495) -939-56-43 e-mail: petros@org.chem.msu.ru

Organoelement Compounds
 Head - Full member of Russian Academy of Sciencies Irina P. Beletskaya
 Phone: +7-(495) -939-36-18
 e-mail: beletska@org.chem.ru

• Coordination Organometallic Compounds Head - Professor Dmitry A. Lemenovskiy Phone: +7-(495) -939-12-34; e-mail: dali@org.chem.msu.ru

• Biologically Active Organic Compounds Head - Professor Nikolai V. Zyk телефон: +7-(495)-939-46-52 e-mail: zyk@org.chem.msu.ru

• Organic Reragents Head - Professor Vladimir I. Terenin Phone: +7-(495)-939-52-47 e-mail: vter@org.chem.msu.ru

• Supramolecular Chemistry and Nanotechnology of Organic Materials Head – Corresponding member of Russian Academy of Sciencies Sergey P. Gromov Phone: +7-(495)-939-30-65 e-mail: spgromov@mail.ru

Physico-Chemical Methods of Analysis
Head - Professor Albert T. Lebedev
Phone: +7-(495)-939-19-76
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Laboratory of Organic Synthesis



Head of the laboratory: Professor Valentine G. Nenajdenko Room 316, phone: +7-(495)-939-22-76, e-mail: <u>nenajdenko@gmail.com</u>

Laboratory staff: professor Nenajdenko V.G., professor Evgeny V. Babaev, leading scientist Bumagin N.A., associate professor Demyanovich V.M.leading scientist Dunina V.V., senior researcher Muzalevskiy V.M., associate professor Shishkina I.N., senior researcher Shmatova O.I.



Professor Valentine G. Nenajdenko

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Research Interests

- Organic synthesis, asymmetric catalysis, the chemistry of sulfur and fluorine containing compounds, heterocyclic chemistry, multicomponent reactions
- Synthesis of natural products
- Heterocyclic Chemistry
- Organometallic chemistry, transition metal catalysis

rearrangement. Org. Lett., **2013**, 15, 2726–2729.

3. V. G. Nenajdenko, V. M. Muzalevskiy, A. V. Shastin, E. S. Balenkova, E. V. Kondrashov, I. A. Ushakov, A. Y. Rulev Fragmentation of Trifluoromethylated Alkenes and Acetylenes by N,N-Binucleophiles. Synthesis of Imidazolines or imidazolidines (Oxazolidines) Controlled by Substituent // J. Org. Chem., **2010**, 75, 5679-5688.

4. Nenajdenko, V.G. Ed., *Fluorine in Heterocyclic Chemistry*, Springer, **2014**.

Selected Publications

 Nenajdenko V. G., Goldberg A. A., Muzalevskiy V. M., Balenkova E. S., Shastin A. V. Design and synthesis of novel family of fluorinated liquid crystals *Chem. Eur. J.*, **2013**, 2370–2383.
 Rulev A.Y., Muzalevsky V.M., Kondrashov E.V., Ushakov I. A., Romanov A. R., Nenajdenko V.G. Reaction of αbromoenones with 1,2-diamines. Cascade assembly of 3-cf3-piperazine-2-ones via



Senior researcher Vasily M. Muzalevskiy

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Research Interests

• organic synthesis, focusing on fluorinated alkenes and heterocycles



Selected Publications

1. V. G. Nenajdenko, V. M. Muzalevskiy, and A. V. Shastin, Polyfluorinated ethanes as versatile fluorinated c2-building blocks for organic synthesis, *// Chem. Rev.*, **2015**, 115, 973–1050.

2. V. M. Muzalevskiy, Yu. A. Ustynyuk, I. P. Gloriosov, V. A. Chertkov, A. Yu. Rulev, E. V. Kondrashov, I. A. Ushakov, A. R. Romanov, V. G. Nenajdenko. Experimental and Theoretical Study of an Intramolecular CF3-Group Shift in the Reactions of α -Bromoenones with 1,2-Diamines, *Chem. Eur. J.* **2015**, 21, 16982–16989.

3. V.M. Muzalevskiy, A. V. Shastin, , A. D. Demidovich, N.G. Shikhaliev, A.M. Magerramov, V. N. Khrustalev, R. D. Rakhimov, S. Z. Vatsadze, V.G. Nenajdenko A new approach to ferrocene derived alkenes via copper-catalyzed olefination *Beilstein J. Org. Chem.*, **2015**, *11*, 2072–2078.

4. V. Muzalevskiy, A. Iskandarov, and V. Nenajdenko, Synthesis of dibromo substituted

cf3-enones and their reactions with n-nucleophiles, // Mendeleev Commun, **2014**, 24, 342–344.

5. 2. Rulev A.Y., Muzalevsky V.M., Kondrashov E.V., Ushakov I. A., Romanov A. R., Nenajdenko V.G. Reaction of α -bromoenones with 1,2-diamines. Cascade assembly of 3-cf3-piperazine-2-ones via rearrangement. *Org. Lett.*, **2013**, 15, 2726–2729.

6. O. V. Serdyuk, V. M. Muzalevskiy, V. G. Nenajdenko Synthesis and Properties of Fluoropyrroles and Their Analogues // *Synthesis*, **2012**, *44*, 2115-2137.

7. Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Haufe, G.; Nenajdenko, V. G. Synthesis of α -trifluoromethyl-phenethylamines from α -trifluoromethyl β -aryl enamines and β -chloro- β -(trifluoromethyl)styrenes *J. Fluorine Chem.*, **2011**, 132, 1247-1253.

8. V. M. Muzalevskiy, A. V. Shastin, E. S. Balenkova, G. Haufe, V. G. Nenajdenko, Synthesis of Trifluoromethyl Pyrroles and Their Benzo Analogues // *Synthesis* **2009**, 3905-3929.

9. V. M. Muzalevskiy, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, G. Haufe alpha-Trifluoromethyl-beta-aryl enamines in the synthesis of trifluoromethylated heterocycles by the Fischer and the Pictet-Spengler reactions *// Tetrahedron* **2009**, *65*, 7553-7561.

10. V. M. Muzalevskiy, V. G. Nenajdenko, A.Y. Rulev, I.A. Ushakov, G. V. Romanenko, A. V. Shastin, E. S. Balenkova, G. Haufe Selective synthesis of alpha-trifluoromethyl-beta-aryl enamines or vinylogous guanidinium salts by treatment of beta-halo-beta-trifluoromethylstyrenes with secondary amines under different conditions *// Tetrahedron* **2009**, *65*, 6991-7000.



General chemistry of indolizine and its heteroanalogs. Simultaneous electro- and nucleophilic substitution, cross-coupling and cycloaddition.



Mutual rearrangements of heterocyclic compounds: pyri(mi)dines to imida(oxa)-zoles, oxazoles to pyrroles.



Novel reactions of alpha-halogen pyridinium salts. Synthesis of novel mesoionic compounds.



Professor Evgeny V. Babaev

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- Babaev E.V. Pyrroles from oxazoles (Review) // Chem.Heterocycl.Comp. 2012, 48 (1), 59.
- Khoroshilov G.E., Tverdokhleb N.M., Brovarets V.S., Babaev E.V. Simple stepwise route to 1-substituted 2-amino-3ethoxycarbonylindolizines // Tetrahedron 2013, 69, 4353.
- Rybakov V.B., Babaev E.V. Transformations of Substituted Oxazolo[3,2-a]Pyridines to 5,6-Disubstituted Indolizines: Synthesis And X-ray Structural Mapping // Chem.Heterocycl.Comp. 2014, 50(2), 225.
- Babaev E.V. Fluorinated Indolizines. In: Fluorine in Heterocyclic Chemistry, *Ed. V.Nenajdenko.* Springer Wien, **2014**, 1, 157.
- Babaev E.V., Nevskaya A.A., Dlynnikh I.V. Rearrangement of oxazolo[3,2-a]pyridines as an approach of synthesizing aza[3.3.2]cyclazines. // Chem. Heterocycl. Comp. 2015, 51(3), 269.
- Shadrin I.A., Rzhevskii S.A., Rybakov V.B., Babaev E.V. Sonogashira Reaction of the Indolizine Ring // Synthesis 2015, 47(19), 2961.



Senior researcher Olga I. Shmatova

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Research Interests

• Cyclic imines like a building block for simultaneously incorporating an alkaloid-like cyclic amine fragment



• Various reactions of imines, especially multicompoment reactions Ugi and Passerini



Chiral organocatalisys

Selected Publications

1. «Fischer Reaction with 2-Perfluoroalkylated Cyclic Imines — An Efficient Route to 2-Perfluoroalkyl-Substituted Tryptamines and Their Derivatives and Homologues» Olga I. Shmatova, Nikolay E. Shevchenko, Valentine G. Nenajdenko //

European Journal of Organic Chemistry, **2015**, 6479-6488.

2. «Aza-Henry reaction with CF₃-ketimines. Efficient approach to trifluoromethylated β -nitroamines, 1,2-diamines, α -aminooximes and imidazolidinones» I. V. Kutovaya, O. I. Shmatova, V. M. Tkachuk, N. V. Melnichenko, M. V. Vovk, V. G. Nenajdenko // *European Journal of Organic Chemistry*, **2015**, 6749-6761.

3. «Synthesis of Tetrazole-Derived Organocatalysts via Azido-Ugi Reaction with Cyclic Ketimines» Shmatova Olga I., Nenajdenko Valentine G. // *Journal of Organic Chemistry*, **2013**, том 78, № 17, 9214-9222.

4. «Highly β-Regioselective Friedel-Crafts aminoalkylation of pyrroles with cyclic perfluoroalkylated imines» Shmatova Olga I., Shevchenko Nikolay E., Balenkova Elisabeth S., Gerd-Volker Röschenthaler, Nenajdenko Valentine G. // European Journal of Organic Chemistry, **2013**, № 15, 3049-3058.

5. «Tetrazole substituted 5, 6 and 7-membered cyclic amines bearing perfluoroalkyl groups. Efficient synthesis via azido-Ugi reaction» Shmatova Olga I., Nenajdenko Valentine // European Journal of Organic Chemistry, **2013**, 6397-6404.

6. «Aminoalkylation of indoles with αpolyfluoroalkylated cyclic imines» Shevchenko Nikolay E., Shmatova Olga I., Balenkova Elisabeth S., Gerd-Volker Röschenthaler, Nenajdenko Valentine G. // European Journal of Organic Chemistry, **2013**, № 11, 2237-2245.



• Development and studies of efficient heterogeneous catalysts based on nanosized carbon-oxide materials and mono- or bimetallic nanoparticles of transition metals. New catalysts exhibit the highest catalytic activity in cross-couplig reactions in aqueous media.



• Elaboration of novel and technically simple method of deposition of finely dispersed palladium on carbon supports.



• Synthesis and catalysis of aminopyridine (1,2-azole) homogeneous and heterogeneous Pd-catalysts.



Selected Publications

Professor Nikolay A. Bumagin

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- <u>Bumagin N.A., Zelenkovskii V.M., Kletskov A.V.,</u> <u>Petkevich S.K., Dikusar E.A., Potkin V.I.</u> <u>Functionally substituted isoxazoles and isothiazoles:</u> <u>Synthesis, palladium(II) complexes and their catalytic</u> <u>activity</u>. <u>Russian Journal of General Chemistry</u>, 2016, <u>86</u>, 68-81.
- Bumagin N.A. High-turnover aminopyridine-based Pd-catalysts for Suzuki–Miyaura reaction in aqueous media *Catalysis Communications*, 2016, 79, 17-20.
- Bumagin N.A, Potkin V.I. Isoxazole and isothiazole functionalized ligands: design, synthesis, palladium complexes, homogeneous and heterogeneous catalysis in aqueous media. *Izvestiya AN. Chemical Series*, 2016, 321-332.
- Potkin V.I., Bumagin N.A., Petkevich S.K., Dikusar E.A., Semenova E.V., Kurman P.V., Zolotar' R.M., Pashkevich S.G., Gurinovich T.A., Kul'Chitskii V.A. Synthesis of functional isoxazole derivatives proceeding from (5-arylisoxazol-3-yl)chloro-methanes. *Russian Journal of Organic Chemistry*, 2015, *51*, 1119-1130.
- Potkin V.I., Bumagin N.A., Zelenkovskii V.M., Petkevich S.K., Livantsov M.V., Golantsov N.E. 5-(Naphth-1-yl)- and 5-[(1,1'-biphenyl)-4-yl]isoxazole-3-carbaldehyde oximes: Synthesis, complexes with palladium, and application in catalysis. *Russian Journal of General Chemistry*, 2014, 84, 1782-1792.
- Bumagin N.A., Veselov I.S., Belov D.S. An Effective Activation of Palladium Phosphine Complexes in Aqueous Phase Reactions of Hetero-Aromatic Boronic Acids with Aryl Halides. *Chemistry of Heterocyclic Compounds*, 2014, 50, 19-25.
- Potkin V.I., Bumagin N.A., Petkevich S.K., Lyakhov A.S., Rudakov D.A., Livantsov M.V., Golantsov N.E. 5-(p-Tolyl)isoxazol-3-amine Palladium(II) Complex: Preparation, Structure, and Catalytic Application in the Suzuki-Miyaura Reaction in Water. SYNTHESIS-STUTTGART 2012, 44, 151-157.
- Korolev D.N., Bumagin N.A. An improved protocol for ligandless Suzuki-Miyaura coupling in water. *Tetrahedron Letters*, 2006, 47, 4225-4229.
- Pd-EDTA as an efficient catalyst for Suzuki-Miyaura reactions in water. Korolev D.N., Bumagin N.A. Tetrahedron Letters, 2005, 46, 5751-5754.
- Bumagin N.A., Bykov V.V. Ligandless palladium catalyzed reactions of arylboronic acids and sodium tetraphenylborate with aryl halides in aqueous media. *Tetrahedron*, **1997**, *53*, 14437-14450.



Stereochemical studies in the field of synthesis of enantiopure chiral bi- and polyfunctional compounds (aminoalcohols,aminoketones, oxygen- and nitrogen-containig heterocycles) with useful properties.



The functionalization of 1-phenylethanamine via



ortho-lithiation followed by condensation with different electrofils



Associated Professor Valeriya M.Demyanovich

Associated Professor Irina N.Shishkina

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Selected Publications

I.N.Shishkina,V.M.Demyanovich, K.A. Potekhin, A.V.Gurbanov, N S.Zefirov. Potential antidepressants. Synthesis and configuration of (1S,3R)- and (1R,3R)-1-(3,4dimethoxyphenyl)-1,3-dimethyl-1,3dihydroisobenzofurans. *Mendeleev Communications*, **2015**, 25, 11.

I.N.Shishkina, E.Y.Sokolovskaya, V.M.Demyanovich, K.A.Potekhin. Synthesis and configuration of (1*S*,3*R*,4*S*)-1methyl-3,4-diphenyl-3,4-dihydro-1*H*-isochromen-3,4-diol. *Mendeleev Communications*, **2013**,23, 350

I.A Dotsenko, I.N.Shishkina, V.M.Demyanovich, N.A. Bumagin, N.S.Zefirov. Palladiumcatalyzed reaction of halogen derivatives of N,Ndimethyl-1-phenylamine with arylboronic acids as a novel approach to ther synthesis of biaryls with central and axial chirality. *Doklady Chemistry*, **2012**, 445, 166

I.N.Shishkina, E.Yu.Sokolovskaya, K.A.Potekhin, Yu V.Nelyubina, V.M. Demyanovich. New Chiral ligands: 1,4-diols prepared from (S)-1-phenylethanol. *Russian Journal* of Organic Chemistry, **2010**, 46, 1332.

V.M.Demyanovich, I.N.Shishkina N.S.Zefirov The Effect of Intramolecular Interactions on Circular Dichroism of *ortho*-Substituted 1-Phenethylamines. *Chirality*, **2004**, 16, 486



• Chiral cyclopalladated compounds: novel structural and stereochemical types (*V. Dunina, O. Gorunova*):



• New routes to chiral palladacycles: diastereoselective "decomposition" and asymmetric transmetallation (*V. Dunina, O. Gorunova, E. Razmyslova*):



• Planar chiral palladacycles in asymmetric catalysis (*V. Dunina*, *O. Gorunova*);



Selected Publications

- O.N. Gorunova, I.M. Novitskiy, Y.K. Grishin, I.P. Gloriozov, V.A. Roznyatovsky, V.N. Khrustalev, K.A. Kochetkov, V.V. Dunina. Determination of the Absolute Configuration of *CN*-Palladacycles by ³¹P{¹H} NMR Spectroscopy using (1*R*,2*S*,5*R*)-Menthyloxydiphenylphosphine as the Chiral Derivatizing Agent: Efficient Chirality Transfer in Phosphinite Adducts. *Organometallics* **2016**, *35*, 75-90.
- O.N. Gorunova, I.M. Novitskiy, M.V. Livantsov, Y.K. Grishin, K.A. Kochetkov, V.V. Dunina. En-

Leading scientist Valery V. Dunina

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antiopurity determination of *CN*-palladacycles using ³¹P NMR spectroscopy with (1*R*,2*S*,5*R*)-menthyloxydiphenylphosphine as chiral derivatizing agent. *J. Organomet. Chem.* **2015**, 783, 96-104.

- O.N. Gorunova, M.V. Livantsov, Y.K. Grishin, M.M. Ilyin Jr., K.A. Kochetkov, A.V. Churakov, L.G. Kuz'mina, V.N. Khrustalev, V.V. Dunina. Evidence on palladacycle-retaining pathway for Suzuki coupling. Inapplicability of Hg-drop test for palladacycle catalysed reactions. *J. Organomet. Chem.* 2013, 737, 59-63.
- V.V. Dunina, O.N. Gorunova, M.V. Livantsov, Y.K. Grishin, K.A. Kochetkov, A.V. Churakov, L.G. Kuz'mina. First enantiopure phosphapalladacycle with a palladium bonded stereogenic carbon as the sole chirality source. *Polyhedron* 2011, 30, 27-32.
- V.V. Dunina, O.N. Gorunova, P.A. Zykov, K.A. Kochetkov. Cyclopalladated complexes in enan-tioselective catalysis. *Russ. Chem. Rev.* 2011, 80, 51-74.
- V.V. Dunina. Chiral cyclopalladated compounds: new structures, methodologies and applications. A personal account. *Curr. Org. Chem.* 2011, *15*, 3415-3440.
- V.A. Stepanova, V.V. Dunina. I.P. Smoliakova. Reactions of Cyclopalladated Complexes with Lithium Diphenylphosphide. *Organometallics* 2009, 28, 6546-6558.
- V.V. Dunina, P.A. Zykov, M.V. Livantsov, I.V. Glukhov, K.A. Kochetkov, I.P. Gloriozov, Y.K. Grishin. First Optically Active Phosphapallada-cycle Bearing a Phosphorus Atom in an Axially Chiral Environment. *Organometallics* 2009, *28*, 425-432.
- V.V. Dunina, E.D. Razmyslova, O.N. Gorunova, M.V. Livantsov, Yu.K.Grishin. New principle of palladacycle resolution: diastereoselective monomer to dimer conversion. *Tetrahedron: Asymmetry* 2005, *16*, 817-826.
- V.V. Dunina, E.D. Razmyslova, O.N. Gorunova, M.V. Livantsov, Yu.K. Grishin. Asymmetric exchange of cyclopalladated ligands with a high level of asymmetric induction: a new route to optically active phosphapalladacycles. *Tetrahedron: Asymmetry* 2003, 14, 2331-2333.

Laboratory of Physical Organic Chemistry

Head of the Laboratory: Dr. Valery S. Petrosyan, Distinguished Professor of Russian Federation and of Moscow State University, Vice-President and Chairman of Division of Chemistry at Russian Academy of Natural Sciences. 7 (495) 939-56-43; <u>valpetros@mail.ru</u>.

On the photo below: 1st row - Dr. N.N. Meleshonkova, Dr. E.A. Shuvalova, Dr. E.D. Gopius, Prof. V.S. Petrosyan, Dr. E.K. Kochetova, Eng. I.A. Averochkina, 2nd row – Dr. S.V. Gruner, Dr, A.A. Prishchenko, Dr. L.I. Livantsova, Eng. T.O. Reutova, Dr. O.P. Novikova, Dr. M.V. Livantsov, Dr. P.I. Demyanov.



Principal fields of research:

- Physical Organic Chemistry
- Chemistry of Organoelement Compounds
- Chemistry and Toxicology of the Environment

Drs. A.A. Prishchenko, M.V. Livantsov, L.I. Livantsova, O.P. Novikova and N.N. Meleshonkova perform their research in the field of new types of organophosphorous compounds, find the new synthetic ways for various classes of organic derivatives of phosphorus, investigate their structures and reactivities, as well as their complexing abilities and biological properties.

Dr. S.V. Gruner, working many years with organic derivatives of silicon, germanium and tin, has been obtaining recently the big series of hypercoordinated compounds of tin, which have extremely interesting structural peculiarities and show very unusual reactivities.

Dr. P.I. Demyanov performs his research in all three principal fields of the Laboratory, investigating structures and reactivities of organoelement compounds, studying the behavior of natural and anthropogenic organic compounds in the Environment and during the last ten years developing the new ideas and approaches in the modern quantum chemistry, which allows to explain in the new ways the nature of chemical bonds in organic and organoelement compounds.

Dr. E.D. Gopius, working many years in the field of chemistry of carbocations, is also the Deputy Head of the Laboratory and the coordinating person for the teaching of organic chemistry at the Department of Biology.

Dr. E.A. Shuvalova performs her research in the field of organic chemistry of aquatic ecosystems, developing the new methods and approaches for accomplishing the chemical safety for the sustainable water use in megapolises.

Dr. E.K. Kochetova is the widely known specialist in the field of chemical informatics and actively working today at the Department of Chemistry with students.

Engs. I.A. Averochkina and T.O. Reutova are taking part in the research on the problems of the Environment and take care of organization of the educational projects within the Open Ecological University program, which has been organized in 1987 by Prof. Valery S. Petrosyan, who is till now the Head of this educational program.

History



Acad. O.A. Reutov (on the left) has found the Laboratory of theoretical problems of organic chemistry in 1957, which has attracted the attention of the researchers all over the world due to the results, obtained in the fields of kinetical, stereochemical and isotopic research of mechanisms of nucleophilic and electrophilic substitution reactions at the carbon atoms. These results were obtained by Acad. O.A. Reutov and his first pupils



Какадемик Реутов О.А (Profs. I.P. Beletskaya, Yu.G. Bundel and V.I. Sokolov)

Development in the Laboratory of new methods (NMR spectroscopy, electrochemical) has allowed to receive the unique data on electronic and spatial structures of various organic and organoelement compounds, to investigate their behavior in solutions and in the solid state. The new generation of leading researchers (Profs. K.P. Butin, A,L. Kurts and V.S. Petrosyan) has increased the world interest to the school of Acad. O.A. Reutov. He asked in 1988 Prof. V.S. Petrosyan (on the right) to become the Head of the Laboratory and since then it is called Laboratory of Physical organic Chemistry. The research, which has been performed afterwards, has attracted attention in many countries. The graduates of the Laboratory became famous around the world (Acads. I.P. Beletskaya, Yu.N. Bubnov, M.P. Yegorov, Profs. V.I. Bakhmutov, V.I. Sokolov, N.Yu. Tretyakova) and heading the research Institutes and Laboratories in Russian Federation and in the United States

Laboratory of Organoelement Compounds

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Laboratory staff: professor Lukashev N.V., professor Kashi A.N., associate professor Cheprakov A.V., associate professor Gulyukina N.S., associate professor Veits Yu.A., leading scientist Averin A.D, senior scientist Tarasenko E.A., senior scientist Latyshev G.V., senior scientist Titanyuk I.D., scientist Trostyanskaya I.G., scientist Davydov D.V., scientist Sazonov P.K., scientist Anokhin M.V., scientist Savinova T.S. junior scientist Ganina O.G., junior scientist Kazantsev A.V., junior scientist Bondarenko G.N., junior scientist Mitrofanov S.M., junior scientist Desyatkin V.G.



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Research Interests

Synthesis of porphyrin triads using "click"reactions. Modifications of porphyrins with heteroaromatics and phosphoryl groups using a direct $C(sp^2)$ -H activation.



Synthesis of the pincer systems without phosphine ligands. They were found not to be real catalysts of the cross-coupling reactions but rather serve as a "reservoir" for Pd nanoparticles which on reacting with aryl halides were dissolved and participated in the catalytic cycle.



We obtained direct evidence of the homogeneous character of the Suzuki reactions catalyzed by Pd nanoparticles. Analogous phenomenon was noted for Pd nanoparticles synthesized in the carbon multiwall nanotubes. The first step is heterogeneous oxidative addition of ArX to PdNPs followed by homogeneous steps which is the explanation for the "leaching" phenomenon.



Selected Publications

- Sigeev, A.S., A.S. Peregudov, A.V. Cheprakov, and I.P. Beletskaya, *The Palladium Slow-Release Pre-Catalysts and Nanoparticles in the "Phosphine-Free" Mizoroki-Heck and Suzuki-Miyaura Reactions.* Advanced Synthesis & Catalysis, 2015. **357**(2-3): p. 417-429.
- Khemchyan, L.L., J.V. Ivanova, S.S. Zalesskiy, V.P. Ananikov, I.P. Beletskaya, and Z.A. Starikova, Unprecedented Control of Selectivity in Nickel-Catalyzed Hydrophosphorylation of Alkynes: Efficient Route to Monoand Bisphosphonates. Advanced Synthesis & Catalysis, 2014. 356(4): p. 771-780.
- Mikhailov, K.M., I.V. Shelaev, F.E. Gostev, Y.P. Yashchuk, V.S. Tyurin, I.P. Beletskaya, and V.A. Nadtochenko, *Femto-Picosecond Relaxation of Triazole-Bridged Bis(Zinc Porphyrin)*. High Energy Chemistry, 2014. **48**(4): p. 276-281.
- Orlov, N.V., I.V. Chistyakov, L.L. Khemchyan, V.P. Ananikov, I.P. Beletskaya, and Z.A. Starikova, Exclusive Selectivity in the One-Pot Formation of C-C and C-Se Bonds Involving Ni-Catalyzed Alkyne Hydroselenation: Optimization

of the Synthetic Procedure and a Mechanistic Study. Journal of Organic Chemistry, 2014. **79**(24): p. 12111-12121.

- Kashin, A.N., O.G. Ganina, A.V. Cheprakov, and I.P. Beletskaya, *The Direct Non-Perturbing Leaching Test in the Phosphine-Free Suzuki-Miyaura Reaction Catalyzed by Palladium Nanoparticles.* Chemcatchem, 2015. **7**(14): p. 2113-2121.
- Mikhalitsyna, E.A., V.S. Tyurin, and I.P. Beletskaya, Synthesis of new porphyrin dimers linked by diamines and their supramolecular assemblies. Journal of Porphyrins and Phthalocyanines, 2015. 19(7): p. 874-886.
- Klimova, E.I., M. Martinez Garcia, J.J. Sanchez Garcia, T. Ramirez Apan, A.V. Churakov, and I.P. Beletskaya, *Reactions of 2-cyano-3-ferrocenylacrylonitrile with malononitrile: formation of 4-ferrocenylpyridine-3,5-dicarbonitrile derivatives and sodium polymeric complexes containing carbanionic ligands.* Pure and Applied Chemistry, 2014. **86**(11): p. 1839-1852
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- Nyuchev, A.V., K.V. Schegravin, M.A. Lopatin, V.V. Fokin, I.P. Beletskaya, and A.Y. Fedorov, Synthesis of Fluorescent Boron Difluoride Complexes of 3-Acyl-4-hydroxycoumarins. Synthesis-Stuttgart, 2014. 46(23): p. 3239-3248.
- Polevaya, Y.P., V.S. Tyurin, and I.P. Beletskaya, *Linear conjuncted porphyrin trimer synthesis via* "click" reaction. Journal of Porphyrins and Phthalocyanines, 2014. 18(1-2): p. 20-34.
- Selivanova, A.V., V.S. Tyurin, and I.P. Beletskaya, Palladium Nanoparticles Supported on Poly(N-vinylimidazole-co-N-vinylcaprolactam) as an Effective Recyclable Catalyst for the Suzuki Reaction. Chempluschem, 2014. 79(9): p. 1278-1283.
- Trostyanskaya, I.G. and I.P. Beletskaya, Copper (II)-catalyzed regio- and stereoselective addition of H/P(O)R-2 to alkynes. Tetrahedron, 2014. **70**(15): p. 2556-2562.



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Leading scientist Alexei D. Averin Scientist Maksim V. Anokhin

Research Interests



Use of Pd(0)- and Cu(I)-catalyzed amination of aryl halides for the synthesis of macrocycels and macropolycycles containing fluorophore moieties which serve as potential fluorescent sensors for metal cations. Asymmetric catalysis using polymersupported Lewis acids and organocatalysts. Synthesis of polytopic polymacrocycles containing porphyrins. Enantioselective catalytic synthesis of chiral macrocycles and macrobicycles. Cu(I)-catalyzed (hetero)arylation of polyamines.

- A. S. Abel, A. Yu. Mitrofanov, Y. Rousselin, F. Denat, A. Bessmertnykh-Lemeune, A. D. Averin, I. P. Beletskaya. Ditopic Macrocyclic Receptors with 4,7-diamino-1,10-phenanthro-line fragment for multimodal detection of toxic metal ions. *ChemPlusChem*, **2016**, *81*, 35-39
- Panchenko S. P., Averin A. D., Anokhin M. V., Maloshitskaya O. A., Beletskaya I. P. Cu(I)-catalyzed N,N'-diarylation of natural diamines and polyamines with aryl iodides. <u>Beilstein J.</u> Org. Chem., 2015, 11, 2297-3305.
- A. A. Yakushev, A. D. Averin, M. V. Anokhin, O. A. Maloshitskaya, F. Lamaty, I. P. Beletskaya. Copper-catalyzed amination in the synthesis of polyoxadiamine derivatives of aza- and diazacrown ethers. *Macroheterocycles*, **2014**, 7, (4), 358-364.
- A. A. Yakushev, N. M. Chernichenko, M. V. Anokhin, A. D. Averin, A. K. Buryak, F. Denat, I. P. Beletskaya. Pd-Catalyzed Amination in the Synthesis of a New Family of Macropolycyclic Compounds Comprising Diazacrown Ether Moieties. *Molecules*, **2014**, *19* (1), 940-965.
- Yu. A. Volkova, B. Brizet, P. D. Harvey, A. D. Averin, C. Goze, F. Denat. BODIPY Dyes Functionalized with Pendant Cyclic and Acyclic Polyamines. *Eur. J. Org. Chem.*, **2013**, (20), 4270-4279.
- A.S. Abel, A.D. Averin, O.A. Maloshitskaya, E.N. Savelyev, B.S. Orlinson, I.A. Novakov, I.P. Beletskaya. Palladium-catalyzed amination of dichloroquinolines with adamantane-containing amines. *Molecules*, **2013**, *18*, 2096-2109.
- A. A. Guryev, M. V. Anokhin, A. D. Averin, I. P. Beletskaya. <u>Polymer-immobilized α,α-bis[bis-3,5-(trifluoromethyl)phenyl]prolinol silyl ether: synthesis and application in the asymmetric α-amination of aldehydes</u>. *Mendeleev Commun.*, **2015**, *25*, 410-411.





Synthesis of pincer and tripodal bile acid-based receptors for anions and neutral molecules. Application of modern Cu- and Pd-catalyzed reactions for modification of steroids.

Development of large scale synthesis of steroidal drugs.



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- Kotovshchikov Y.N., Latyshev G.V., Lukashev N.V., Beletskaya I.P. Alkynylation of steroids via Pd-free Sonogashira coupling. *Org. Biomol. Chem.*, 2015, 13, 5542–5555.
- Erzunov D.A., Latyshev G.V., Averin A.D., Beletskaya I.P., Lukashev N.V. CuAAC Synthesis and Anion Binding Properties of Bile Acid Derived Tripodal Ligands. *Eur. J. Org. Chem.*, **2015**, 6289–6297
- Bunik V.I., Artiukhov A.V., Kazantsev A.V., Goncalves R.L., Daloso D.M., Oppermann H., Kulakovskaya E.A., Lukashev N.V., Fernie A.R., Brand M.D., Gaunitz F. Specific inhibition by synthetic analogs of pyruvate reveals that the pyruvate dehydrogenase reaction is essential for metabolism and viability of glioblastoma cells. *Oncotarget.* 2015, *6*, 40036-40052
- Kotovshchikov Y.N., Latyshev G.V., Lukashev N.V., Beletskaya I.P. Synthesis of novel 1,2,3-triazolyl derivatives of pregnane, androstane and D-homoandrostane. Tandem "click" reaction/Cucatalyzed D-homo rearrangement. Org. Biomol. Chem., 2014, 12, 3707–3720.
- Kotovshchikov Y.N., Latyshev G.V., Lukashev N.V., Beletskaya I.P. An Efficient Approach to Azolyl-Substituted Steroids through Copper-Catalyzed Ullmann C–N Coupling. *Eur. J. Org. Chem.*, **2013**, 7823–7832.
- Savinova T.S., Lukashev N.V., Huy L.D., Beletskaya I.P. Autooxidation of Delta(17(20))-20-Hydroxy Derivatives of Steroids. Synthesis of 3β-Acetoxy-17α-hydroperoxy-16α-methylpregn-5-en-20-one and Its Reduction to 17α-Hydroxy Derivative. *Russ. J. Org. Chem.*, **2011**, *47*, 54-61.
- Sokolova N.V., Latyshev G.V., Lukashev N.V., Nenajdenko V.G. Design and synthesis of bile acid-peptide conjugates linked via triazole moiety. *Org. Biomol. Chem.*, **2011**, 9, 4921-4926.





• We are working on the synthesis of potentially bioactive organophosphorus compounds. The methods for the preparation of optically active α -functionalized phosphates via the homogeneous catalytic asymmetric hydrogenation of prochiral precursors bearing carbon-carbon or carbon-heteroatom double bond have been elaborated.



 $Z = CO_2Et, CH_2OH, NH_2$ R = H, Me, Ph, 4-BrC₆H₄, 4-(EtO)₂P(O)C₆H₄, 4-I4-MeC₂H₄-CCIC₂H₄, 4-I4-(EtO)₂P(O)C₂H₄, CCIC₂H₄,

A new strategy for the synthesis of substituted 1-amino cyclopropylphosphonic acids as well as cyclopropyl phosphonates with functional group at C(2)-atom was developed based on the 1,3-dipolarcycloaddition reaction of vinyl phosphonates to diazo compounds. Thus a novel

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synthetic approach to pyrazolyl phosphonates has been proposed. Selected Publications

- Makukhin N.N., Goulioukina N.S., Bessmertnykh-Lemeune A.G., Brandes S., Guilard R., Beletskaya I.P. Exploiting Palladium-Catalyzed Cross-Coupling for the Synthesis of 2-Aryl-Substituted 1-Aminocyclopropylphosphonates. Synthesis, 47(2), 279-288 (2015).
- Goulioukina N.S., Shergold I.A., Bondarenko G.N., Ilyin M.M., Davankov V.A., Beletskaya I.P. Palladium-Catalyzed Asymmetric Hydrogenation of N-Hydroxy-α-imino Phosphonates Using Bronsted Acid as Activator: The First Catalytic Enantioselective Approach to Chiral N-Hydroxyα-amino Phosphonates. *Adv. Synth. Cat.*, **354**(14-15), 2727-2733 (2012).
- Goulioukina N.S., Makukhin N.N., Beletskaya I.P. 1,3-Dipolar cycloaddition of diazoalkanes onto dimethyl 1-(formylamino) ethylenephosphonate: a new route to 1aminocyclopropanephosphonic acids and 3phosphorylated pyrazoles. *Tetrahedron*, 67(49), 9535-9540 (2011).
- Goulioukina N.S., Bondarenko G.N., Bogdanov A.V., Gavrilov K.N., Beletskaya I.P. Asymmetric Hydrogenation of α-Keto Phosphonates with Chiral Palladium Catalysts. *Eur. J. Org. Chem.*, 2009(4), 510-515 (2009).
- Goulioukina N.S., Bondarenko G.N., Lyubimov S.E., Davankov V.A., Gavrilov K.N., Beletskaya I.P. Catalytic hydrogenation of α-iminophosphonates as a method for the synthesis of racemic and optically active α-aminophosphonates. *Adv. Synth. Cat.*, **350**(3), 482-492 (2008).
- Goulioukina N.S., Dolgina T.M., Bondarenko G.N., Beletskaya I.P., Ilyin M.M., Davankov V.A., Pfaltz A. Highly enantioselective hydrogenation of α,β-unsaturated phosphonates with iridium-phosphinooxazoline complex: synthesis of a phosphorus analogue of naproxen. *Tetrahedron: Asymmetry*, **14**(10), 1397-1401 (2003).

 $^{4-[4-}MeC_6H_4CC]C_6H_4$, $4-[4-(EtO)_2P(O)C_6H_4]C_6H_4$, $4-[mpa_{H_c}(EtO)_2P(O)CH=CH]C_6H_4$,





• Preparation of polymer-based recyclable catalytic systems for the reactions proceeding under organometallic and organic catalysis conditions.

• Lewis acid catalyzed benzylic C-H bond functionalization of methyl azaarenes: asymmetric addition to imines.









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- Tarasenko E.A., Tyurin V.S., Lamaty F., Beletskaya I.P. Poly(N-vinylimidazole) as efficient recyclable catalyst for the Michael addition of CHacids to electron deficient alkenes in water. *Russian Chemical Bulletin*, **2011**, *60* (12), 2613-2616.
- Beletskaya I.P., Tarasenko E.A., Khokhlov A.R., Tyurin V.S. Poly(N-vinylimidazole) as an efficient and recyclable catalyst of the aza-Michael reaction in water. *Russian Journal of Organic Chemistry.* **2010**, 46 (4), 461-467.
- Beletskaya I.P., Khokhlov A.R., Tarasenko E.A., Tyurin V.S. Palladium supported on poly(Nvinylimidazole) or poly(N-vinylimidazole-co-Nvinylcaprolactam) as a new recyclable catalyst for the Mizoroki–Heck reaction. *J. Organomet. Chem.* 2007, 692, 4402–4406.



The major fields of research are heterogeneous catalysis by gold, silver, copper, palladium and platinum nanoparticles, design and testing of new catalytic systems based on NPs, investigation of the mechanism, recyclability, morphology of the surface of the catalyst, influence of the size of particles in hydrogenation, carboxylation, carbonylation, Hirao's phosphorylation, addition to alkynes and homo- and cross-coupling reactions, and its application in the synthesis of biologically active compounds.



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- Bondarenko G.N., Beletskaya I.P., Activated carbon as an efficient support for gold nanoparticles that catalyze the hydrogenation of nitro compounds with molecular hydrogen, *Mendeleev Commun.*, **2015**, 25, 443-445.
- A.N.Kashin, O.G. Ganina, A.V. Cheprakov, I.P. Beletskaya, The Direct Non-Perturbing Leaching Test in the Phosphine-Free Suzuki-Miyaura Reaction Catalyzed by Palladium Nanoparticles. *ChemCatChem*, **2015**. 7(14): p. 2113-2121.
- Pigaleva M.A., Bulat M.V., Bondarenko G.N., Abramchuk S.S., Laptinskaya T.V., Gallyamov M.O., Beletskaya I.P., Moller M.. Formation of easy-to-recover polystyrene-block-poly(4-vinylpyridine) micelles decorated with Pd nanoparticles in solutions of self-neutralizing carbonic acid. ACS macro lett., 2015, 4(7), 661-664.
- G.N. Bondarenko, O.G. Ganina, R.K. Sharma, I.P. Beletskaya. Catalytic activity of Pd catalysts on different supports in hydrogenation of 1phenylethenylphosphonic acid. *Rus. Chem. Bull*, **2014**, *63* (8), 1856-1859.
- Goulioukina N.S., Shergold I.A., Bondarenko G.N., Ilyin M.M., Davankov V.A., Beletskaya I.P. Palladium-Catalyzed Asymmetric Hydrogenation of N-Hydroxy-α-imino Phosphonates Using Brønsted Acid as Activator: The First Catalytic Enantioselective Approach to Chiral N-Hydroxy-α-amino Phosphonates. *Adv. Synth. Catal.*, 2012, 354(14-15), 2727-2733.
- I. P. Beletskaya, O.G. Ganina. Hydroxy- and alkoxycarbonylation of aryl iodides catalyzed by polymer-supported palladium. *React. Kinet., Mech. Cat.*, **2010**, 99 (1), 1-4.
- Goulioukina N.S., Bondarenko G.N., Bogdanov A.V., Gavrilov K.N., Beletskaya I.P. Asymmetric hydrogenation of α-keto phosphonates with chiral palladium catalysts. *Eur. J. Org. Chem.*, **2009**, *4*, 510-515.
- Ganina O.G., Daras E., Bourgarel-Rey V., Peyrot V., Andresyuk A.N., Finet J.-P., Fedorov A.Y, Beletskaya I.P., Combes S. Synthesis and biological evaluation of polymethoxylated 4-heteroarylcoumarins as tubulin assembly inhibitor. *Bioorg. Med. Chem.*, **2008**, *16* (19), 8806-8812.



• Synthesis and applications of new optical materials in the long-wavelength visual and near infrared regions for in vitro oxygen sensing, metal ion detection, triplet-triplet annihilation up-conversion, solar light harvesting, photovoltaics, etc., based on new π -extended dipyrromethene and tetrapyrrolic dyes.



Selected Publications

- Andrianov, D.S., Rybakov, V.B., Cheprakov, A.V. Between porphyrins and phthalocyanines: 10,20-diaryl-5,15tetrabenzodiazaporphyrins. Chemical Communications, 2014, 7953.
- Filatov, M.A., Baluschev, S., Ilieva, I.Z., Enkelmann, V., Miteva, T., Landfester, K., Aeshchenkov, S.E., Cheprakov, A.V. Tetraaryltetraanthra 2,3 porphyrins: Synthesis, Structure, and Optical Properties.

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Journal of Organic Chemistry, **2012**, 77, 11119.

- Filatov, M.A., Cheprakov, A.V. The synthesis of new tetrabenzo- and tetranaphthoporphyrins via the addition reactions of 4,7-dihydroisoindole. *Tetrahedron*, **2011**, *67*, 3559.
- Cheprakov, A.V., The Synthesis of pi-Extended Porphyrins, in Handbook of Porphyrin Science with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine, Vol 13: Synthesis and Structural Studies, K.M. Kadish, K.M. Smith, and R. Guilard, Editors. 2011, 1-149.
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- Filatov, M.A., Lebedev, A.Y., Mukhin, S.N., Vinogradov, S.A., Cheprakov, A.V. pi-Extended Dipyrrins Capable of Highly Fluorogenic Complexation with Metal Ions. *Journal of American Chemical Society*, 2010, 132, 9552.
- Lebedev, A.Y., Cheprakov, A.V., Sakadzic, S., Boas, D.A., Wilson, D.F., Vinogradov, S.A. Dendritic Phosphorescent Probes for Oxygen Imaging in Biological Systems. ACS Applied Materials Interfaces, 2010, 1, 1292.
- Baluschev, S., Yakutkin, V., Miteva, T., Avlasevich, Y., Chernov, S., Aleshchenkov, S., Nelles, G., Cheprakov, A., Yasuda, A., Muellen, K., Wegner, G. Blue-green upconversion: Noncoherent excitation by NIR light. Angewandte Chemie-International Edition, 2007, 46, 7693.



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Selected Publications

- Sazonov P.K., Ptushkin D.S., Khrustalev V.N., Kolotyrkina N.y.G., Beletskaya I.P., *Radicalchain oxidative addition mechanism for the reaction of an Re(CO)*₍₅₎⁽⁻⁾ *anion with* α*bromostilbene*. Dalton. Trans., 2013. **42**(12): p. 4223-4232.
- Sazonov P.K., Oprunenko Y.F., Beletskaya I.P., Predicting the direction of nucleophilic attack in vinyl halides: Halogenophilic versus carbophilic reactivity of metal carbonyl anions. J. Phys. Org. Chem., 2013. 26(2): p. 151-161.
- Sazonov P.K., Beletskaya I.P., Dualism of ionpairing effects in nucleophilic vinylic substitution with transition-metal carbonyl anions. ChemPlusChem, 2013. 78(9): p. 1190-1194.
- Sazonov P.K., Artamkina G.A., Beletskaya I.P., Nucleophilic substitution at the halogen atom (halogenophilic reactions). Russian Chemical Reviews, 2012. 81(4): p. 317-335.
- Sazonov P.K., Oprunenko Y.F., Khrustalev V.N., Beletskaya I.P., C-F ...M⁺ interaction in anionic alpha-fluorovinyl rhenium oxycarbene complexes and their beta-fluoroenolate analogs. J. Fluorine Chem., 2011. 132(9): p. 587-595.
- Sazonov P.K., Artamkina G.A., Beletskaya I.P., Nucleophilicity of metal carbonyl anions in vinylic substitution reactions. J. Phys. Org. Chem., 2008. 21(3): p. 198-206.
- Ivushkin V.A., Sazonov P.K., Artamkina G.A., Beletskaya I.P., *Halophilic reactions of pentafluorohalobenzenes with transition-metal carbonyl anions*. J. Organomet. Chem., 2000. 597(1-2): p. 77-86.

Research Interests

Nucleophilic reactivity of metal- and elementcentered anions, especially anionic transition metal carbonyl complexes $(M(CO)_nL]^-)$.

Studying the reactivity of carbonylmetallates allows us to understand the differences in the behavior of the metal-centered from heteroatombased nucleophiles. The main focus is on the mechanisms of reactions with π -electrophiles, such as aryl- and alkenyl halides, which show a great diversity of reaction pathways. Carbonylmetallates have a marked preference for halogenophilic attack and nucleophilic substitution with carbonylmetallates is often not a direct process, but proceeds through the initial attack at halogen with the subsequent coupling of carbanion and HalM(CO)_nL intermediates. And it is not the only peculiarity of these fascinating organometallic nucleophiles.



Laboratory of Coordination Organometallic Compounds



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"Supercritical fluids in synthetic chemistry" group (the head of group - senior scientist Dmitrii P. Krut'ko)



Research Interests

On the base of *Supercritical Fluid Technology Center* researches on various directions are carried out: polymerizations, chemical synthetic reactions, obtaining supramolecular structures and composite aerogels (including various metals as well).

The processes in supercritical fluids characterized by high efficiency and environmental friendliness (it is well known that liquid and supercritical carbon dioxide have provided a powerful tool for the development of "Green chemistry"), and also have a number of advantages in the isolation and purification procedures.



In particular, polylactides and acrylonitrile copolymers were synthesized in SC CO_2 and CHF₃ medium. The first synthesis of oligolactide dendrimer with unsaturated terminal groups in the SC CHF₃ medium was implemented.

It was found that in the reactions of electrophiles with organic diamines with different aminogroups carried out in the SC or liquid CO_2 medium, the latter can serve as the soft selective protective reagent for more basic aminogroup. It opens new methodical opportunities to manage the selectivity of the reactions with participation of these groups.





Associated professor Galina P. Brusova (Secretary of State Examination Board)

"Organometallic synthesis and catalysis" group



Leading scientist Sergey S. Karlov (the head of group) e-mail: sergey@org.chem.msu.ru

Research Interests

Synthesis and study of useful properties of transition and non-transition metals derivatives based on ligands capable of forming additional intramolecular coordination.

• Synthesis and catalytic study of complexes of aluminum, titanium and zinc in the preparation of biodegradable polymers based on cyclic esters







Associated professor Galina S. Zaitseva



L-LA polymerization: conversion 92-95 % (BnOH, 80° C, 20 h), M_n 2600-4300, PDI 1.10-1.25 "immortal" polymerization

• Synthesis of stable heavy analogues of carbenes (silylenes, germylenes, stannylenes, plumbylenes) based on the cyclic coordinating type ligands.



• Low molecular weight compounds of Group 14 elements (E = Si, Ge, Sn), containing the bond element - element (heavy analogues of saturated hydrocarbons) are of considerable



interest as "molecular wires". Useful properties of "molecular wires": photo-luminescence, thermochromism, nonlinear optical properties, UV absorption.



Group members fruitfully cooperated with various research groups in Russia and abroad: in Moscow - Institute of Organic Chemistry, Institute of Inorganic Chemistry, Tomsk State Pedagogical University), Minsk (Belorussian State University), Graz (University of Technology), Marburg (Philipps-Universität).

"Organometallic precursors for modern materials and biomarkers" group (the head of group - associate professor Victor P. Dyadchenko)



Research Interests

Directed synthesis of ferrocene derivatives with rod-like side chain.

These compounds are important in preparation of new functional materials (liquid crystals or markers for biological objects such as proteins, for example). The investigations are performed in collaboration with Zhejiang University, China. On this basis new methods of immunoassay are developed now in this scientific group in collaboration with Research Institute of Influenza (St. Petersburg). Recently it was discovered that ferrocene derivatives with rod-like side chain synthesized in scientific group of V. Dyadchenko reveal a significant anti-cancer activity. Further investigations in this regard are in progress.



The novel direct alkynylation reaction of ferrocene.



Smectic phase of one of the liquid crystals obtained.



Ferrocenyl containing boroxine dimer.

Selected Publications

• Aluminum complexes based on pyridine substituted alcohols: synthesis, structure, and catalytic application in ROP / M. M. Kireenko, E. A. Kuchuk, K. V. Zaitsev, V. A. <u>Tafeenko</u>, Y. F. <u>Oprunenko</u>, A. V. <u>Churakov</u>, E. Kh. <u>Lermontova</u>, G. S. <u>Zaitseva</u>, S. S. <u>Karlov</u> // *Dalton Transactions*. — 2015. — Vol. 44, no. 26. — P. 11963–11976.

• Compounds of group 14 elements with an element-element (e = Si, Ge, Sn) bond: Effect of the nature of the element atom / K. V. Zaitsev, E. Kh. Lermontova, A. V. Churakov, V. A. <u>Tafeenko, B. N. Tarasevich</u>, O. Kh. Poleshchuk, a. V. Kharcheva, T. V. Magdesieva, O. M. Nikitin, G. S. Zaitseva, S. S. Karlov // Organometallics. — 2015. — Vol. 34. — P. 2765–2774.
Titanium(IV) complexes based on tridentate

N,N,O ligands – synthesis, structure, and thermal decomposition / V. S. Cherepakhin, K. V. Zaitsev, Y. F. Oprunenko, A. V. Churakov, E. Kh. Lermontova, G. S. <u>Zaitseva</u>, S. S. <u>Karlov</u> // European Journal of Inorganic Chemistry. — 2015. — P. 5903–5912.

• New oligogermane with a five coordinate germanium atom: the preparation of 1-germylgermatrane / K. V. Zaitsev, A. V. Churakov, O. K. Poleshchuk, Y. F. Oprunenko, G. S. <u>Zaitseva</u>, S. S. <u>Karlov</u> // Dalton Transactions. — 2014. — Vol. 43, no. 18. — P. 6605– 6609.

• Palladium complexes with stabilized germylene and stannylene ligands / M. M. Kireenko, K. V. Zaitsev, Y. F. Oprunenko, A. V. Churakov, V. A. Tafeenko, S. S. <u>Karlov</u>, G. S. <u>Zaitseva</u> // *Dalton Transactions*. — 2013. — Vol. 42, no. 22. — P. 7901–7912.

germylenes Stabilized based on diethylenetriamines and related diamines: Synthesis, structures, and chemical properties / M. Huang, M. M. Kireenko, K. V. Zaitsev, Y. F. Oprunenko, A. V. Churakov, J.A.K.Howard, E. Kh. Lermontova, D. Sorokin, T. Linder, J. Sundermeyer, S. S. Karlov, G. S. Zaitseva // European Journal of Inorganic Chemistry. — 2012. — no. 23. — P. 3712–3724.

• Alkynylation of ferrocene by terminal alkynes. Part I. A simple one-step synthesis of ferrocenylacetylenes / <u>Dyadchenko V.P.</u>, Dyadchenko M.A., Okulov V.N., <u>Lemenovskii D.A.</u>// Journal of Organometallic Chemistry. – 2011. – Vol. 696, no. 2, P. 468-472.

• Rod-like derivatives of ferrocenylacetylene: syntheses and structure / Yu, Wang Li, Dyadchenko V.P.// *Mendeleev Communications*. - 2015. - Vol. 25, P. 171-173.

• Synthesis of new ferrocene derivatives with rodlike structure / Okulov V.N., Popov D.A., Panfilova A.V., Dyadchenko M.A., Lemenovskii D.A., Dyadchenko V.P.// *Mendeleev Communications.* - 2015. -Vol. 25, P. 111-113.

• Synthesis of polyacrylonitrile copolymers as potential carbon fibre precursors in CO₂. / Shlyahtin Andrei V., <u>Nifant'ev I.E.</u>, Bagrov V.V., <u>Lemenovskii D.A.</u>, Tavtorkin A.N., Timashev Peter S.// *Green Chemistry*. -2014. – Vol. 16, no. 3, P. 1344-1350.

• Carboxylation of aromatic compounds in a supercritical carbon dioxide medium / A.V. Shlyakhtin, S.Z. Vatsadze, D.P. Krut'ko, D.A. Lemenovskii, M.V. Zabalov // *Russian Journal of Physical Chemistry B*. – 2012 – Vol. 6, no. 7, P. 818-826.

• A study of the morphology of acrylonitrilemethylacrylateitaconic acid/itaconic acid derivative copolymers synthesized in a supercritical carbon dioxide medium / Shlyakhtin A.V., Nifant'ev I.E., Lemenovsky D.A., Krut'ko D.P., Bagrov V.V., Timashev P.S., Popov V.K., Bagratashvili V.N. // *Russian Journal of Physical Chemistry B.* – 2014 – Vol. 8, no. 8, P. 1049-1053.

Laboratory of Biologically Active Organic Compounds



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Laboratory staff: professor Beloglazkina E.K., professor Terenin V.I., associate. professor Antipin R.L., associate professor Mazhuga A.G., leading scientist Grishina G.V., leading scientist Sviridova L.A., leading scientist Yurovskaya M.A., senior scientist Karchava A.V., senior scientist Alekseev R.S., senior scientist Bondarenko O.B., senior scientist Gavrilova A.Yu., scientist Vorozhtsov N.I., scientist Yudina A.V., scientist Zotova M.A., junior scientist Veselov I.S., junior scientist Kabanova E.V., junior scientist Fin'ko A.V., junior scientist Yudin I.V. junior scientist Krasnovskaya O.O., junior scientist Rudakovskaya P.G., engineer Ovcharenko A.A., engineer Panova E.I.



• Electrophilic addition to unsaturated compounds under the action of activated electrophiles weak (*N. Zyk, A. Gavrilova*)

$$X-Y + SO_3 \longrightarrow \begin{bmatrix} \bullet & 0 \\ \bullet & -Y - SO_0 \\ 0 \end{bmatrix} \longrightarrow \begin{bmatrix} d^+ & 0 \\ X-O - S - Y \\ 0 \end{bmatrix} \longrightarrow \begin{bmatrix} d^+ & 0 \\ X-O - S - Y \\ 0 \end{bmatrix} \xrightarrow{\bullet} Y \xrightarrow{\bullet} X^{\oplus} \begin{bmatrix} 0 \\ 0 \\ -S - Y \\ 0 \end{bmatrix}$$



$$X = O, Hal = Cl, Br$$

• Electrophilic nitrosation of cyclopropane ring, accompanied by subsequent heterocyclization (*N. Zyk, O. Bondarenko*);



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- O.B. Bondarenko, A.Yu. Gavrilova, D.S. Murodov, S.S. Zlotskii, N.V. Zyk, N.S. Zefirov. Regiospecificity of the nitrosation of di(*gem*-dichlorocyclopropanes) obtained from butadiene and isoprene *Tetrahedron Letters*, **2013**, *54*, 1845.
- Zyk N.V., Gavrilova A.Y., Nechaev M.A., Bondarenko O.B., Zefirov N.S. Reaction of unsaturated compounds with the thiobisamine-SOHal₂ system. *Moscow University Chemistry Bulletin*, **2015**, 69, 254.
- Bondarenko O.B., Vinogradov A.A., Danilov P.A., Nikolaeva S.N., Gavrilova A.Yu, Zyk N.V. Nitrosation of 2-aryl-1,1-dibromocyclopropanes: synthesis of 3-aryl-5-bromoisoxazoles. *Tetrahedron Letters*, **2015**, *56*, 6577.
- Bondarenko O.B., Gavrilova A.Yu, Polunina V.V., Starikova Z.A., Zyk N.V., Zefirov N.S Unexpected mode of reactivity in nitrosation of cis-1, 1-dichloro-2, 3-iphenylcyclopropane with NOCI-2SO₃. *Mendeleev Communications*, 2009, 19, 12.
- Zyk N.V.,Bondarenko O.B., Gavrilova A.Yu, Chizhov A.O. Zefirov N.S. gem-Dichloro(alkyl)cyclopropanes in reactions with NOCI•2SO3: synthesis of alkyl-5chloroisoxazoles. *Russian Chemical Bulletin*, 2011, 60, 328.
- Antipin R.L.,Beloglazkina E.K.,Zyk N.V.,Zefirov N.S. Arylselenenation of conjugated dienes by arylselenenamides in the presence of phosphorus(V) oxyhalides. *Tetrahedron Letters*, 2007, 48, 729.
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• Modeling of the active sites of metalloenzymes and the synthesis of their synthetic analogs.



• Transition metal complexes with organic ligands as the catalysts of biomimetic reactions.



• Reactivity of organic ligands in reactions with transition metal ions.



• Coordination compounds of copper as promising anti-tumor agents.



Selected Publications

- Beloglazkina E.K., Manzheliy E.A., Moiseeva A.A., Maloshitskaya O.A., Zyk N.V., Skvortsov D.A., Osterman I.A., Sergiev P.V., Dontsova O.A., Ivanenkov Y.A., Veselov M.S., Majouga A.G. Synthesis, characterization, cytotoxicity and antibacterial activity of ruthenium(II) and rhodium(III) complexes with sulphur-containing terpyridines. *Polyhedron*, **2016**, *107*, 27
- Beloglazkina E.K., Majouga A.G., Mironov A.V., Yudina A.V., Kuznetsova O.Yu, Zyk N.V. Conversion of 2-thiohydantoins and their derivatives

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> to the corresponding hydantoins in the processes of complexation reactions with copper(II) chloride dihydrate. *Polyhedron*, **2014**, *76*, 45

- Beloglazkina E.K., Majouga A.G., Antipin R.L., Myannik K.A., Moiseeva A.A., Zyk N.V. Novel copper(II) and cobalt(II) complexes with selenium substituted imidazolyl imines. The molecular and crystal structure of [N-(2-(phenylseleno)ethyl)-N-(imidazol-2ylmethylene)amine]copper(II) dichloride. *Polyhedron*, 2013, 50, 4.
- A.G. Majouga, E.K. Beloglazkina, et al., Cleavage of the C-S bond with the formation of a binuclear copper complex with 2-thiolato-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4H-imidazole-4-on. A new mimic of the active site of N₂O reductase, *Dalton Transactions*, **2013**, *42*, 6290.
- Chernysheva A.N., Beloglazkina E.K., Moiseeva A.A., Antipin R.L., Zyk N.V., Zefirov N.S. Co-II complex of N-[2-(phenylseleno)cyclohexyl]-N-(pyridin-2-ylmethylene)amine: synthesis, electro-chemistry and catalysis of triphenylphosphine and norbornene oxidation by nitrous oxide. *Mendeleev Communications*, 2012, 22, 70.
- Beloglazkina, Majouga, Zyk, Zefirov Nikolai S.Oxidation of triphenylphosphine and norbornene by nitrous oxide in the presence of (CoLCl₂)-L [L=3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin]: the first example of Co¹catalyzed alkene oxidation by N₂O. *Mendeleev Communications*, **2009**, *19*, 69.
- Beloglazkina E.K., Majouga A.G, Romashkina R.B., Moiseeva A.A., Zyk N.V. The preparation, crystal structure and electrochemistry of (5Z,5 ' Z)-2,2 '-(alkane-alpha,omega-diylsulfanyldiyl)bis(5-(3-pyridylmethylene)-3,5-di hydro-4H-imidazol-4-ones) and their complexes with cobalt(II) chloride. *Polyhedron*, **2007**, *26*, 797
- Beloglazkina E.K., Majouga A.G., Romashkina R.B., Zyk N.V. A novel catalyst for alkene epoxidation: a polymer-supported (CoLCl₂)L {L=2-(alkylthio)-3-phenyl-5-(pyridine-2ylmethylene)-3,5-dihydro-4H-imidazole-4-one} complex. *Tetrahedron Letters*, **2006**, *47*, 2957.



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Research Interests

• Theoretical and experimental approach to new coordination compounds of copper as promising anti-tumor agents



• Synthesis and biological evaluation of promising anticancer therapeutics.



• The development of effective and adaptable laboratory methods for the synthesis of materials based on magnetic nanoparticles for MRT diagnostics



Selected Publications

 A.G. Majouga, M.I. Zvereva, M.P. Rubtsova, et al., Mixed Valence Copper(I,II) Binuclear Complexes with Unexpected Structure: Synthesis, Biological Properties and Anticancer Activity. J. Med. Chem., 2014, 67, 6252.

- Ivanenkov Y.A., Veselov M.S., Rezekin I.G., Skvortsov D.A., Sandulenko Y.B., Polyakova M.V., Bezrukov D.S., Vasilevsky S.V., Kukushkin M.E., Moiseeva A.A., Finko A.V., Koteliansky V.E., Klyachko N.L., Filatova L.A., Beloglazkina E.K., Zyk N.V., Majouga A.G, Synthesis, isomerization and biological activity of novel 2selenohydantoin derivatives. *Bioorganic & Medicinal Chemistry*, 2016, 24, 802.
- Majouga A.G., Beloglazkina E.K., Yudina A.V., Mironov A.V., Zyk N.V. Oxidative dehydrogenation of 5-(pyridine-2-yl-methyl)-2-thioxo-4imidazolidinones in complexation reaction with copper(II) chloride. *Inorganic Chemistry Communication*, **2015**, *51*, 114.
- Ivanenkov Y.A., .Majouga A.G. Design, synthesis and biological evaluation of novel potent MDM2/p53 small-molecule inhibitors *Bioorganic and Medicinal Chemistry Letters*, 2015, 25, 404
- Majouga A., Sokolsky-Papkov M., Kuznetsov A., Lebedev D., Efremova M., Beloglazkina E., Rudakovskaya P., Veselov M., Zyk N., Golovin Yu, Klyachko N., Kabanov A.Enzyme-functionalized gold-coated magnetite nanoparticles as novel hybrid nanomaterials: synthesis purification and control of enzyme function by low-frequency magnetic field. *Colloids and Surfaces B: Biointerfaces*, 2015, *125*, 10.
- Vagin M.Yu, Trashin S.A., Beloglazkina E.K., Majouga A.G. Direct reagentless detection of the affinity binding of recombinantHis-tagged firefly luciferase with a nickel-modified gold electrode. *Mendeleev Communications*, **2015**, 25, 290.
- Majouga A.G., Udina A.V., Beloglazkina E.K., Skvortsov D.A., Zvereva M.I., Dontsova O.A., Zyk N.V., Zefirov N.S. Novel DNA fluorescence probes based on 2-thioxo-tetrahydro-4Himidazol-4-ones: synthetic and biological studies. *Tetrahedron Letters*, **2012**, *53*, 51.



Senior scientist Lyudmila A. Sviridova

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Research Interests

• The group has extensive experience in the synthesis of 2-pyrazolones, including derivatives containing functional substituents in different positions of the pyrazoline ring. This allows a previously unknown synthesis of substituted pyrazolines from 2substituted benzaldehydes as well as the hydrazine and substituted arylhydrazines.



• Synthesis of hydroxydiamines and triamines via reductive cleavage of N-N bond in substituted pyrazolidines.



- L. A. Sviridova, G. A. Golubeva, A. N. Tavtorkin, K. A. Kochetkov, Synthesis of Hydroxydiamines and Triamines via Reductive Cleavage of N-N-Bond in Substituted Pyrazolidines. *Amino acids*, 2012, 43, 1225
- Mysova N.E., Kovrov A.E., Sadovoy A.V., Sviridova L.A., Golubeva G.A., Vorozhtsov N.I. Synthesis and spectral features of new 1-alkyl-5-(indol-2(3)-yl)pyrrolidin-2-ones. Chemistry of Heterocyclic Compounds, 2013, 48, 1634.
- Sviridova L.A., Tavtorkin A.N., Shalynina N.A., Vorozhtsov N.I., Protopopova P.S., Urmambetova ZhS., Kochetkov K.A. Synthesis of 4,5-dihydro-1H-pyrazoles with chiral substituents at position 3 or 5. *Russian Chemical Bulletin, International Edition*, 2015, 64, 1078.
- Vorob'Ev M.M., Sviridova L.A., Vorozhtsov N.I., Ambartsumyan A.A., Kochetkov K.A. 1-Amino-3-(4-methoxybenzylamino)-1phenylpropane as a new water-soluble fluorescent reagent to zinc ion. *Russian Chemical Bulletin*, **2013**, *62*, 575.
- Ambartsumyan A.A., Sviridova L.A., Vorozhtsov I., Goryunov E.I., Bodrin G.V., Goryunova I.B., Uryupin A.B., Vasil'eva T.T., Chakhovskaya O.V., Kochetkov K.A.,Nifant'Ev E.E. Diarylphosphoryl-containing β-diketones: Methods of synthesis and transformation into pyrazoles. *Doklady Chemistry*, **2013**, *448*, 35.



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Research Interests

 Development of methodological bases receiving and synthesis of new nitrogencontaining heterocyclic compounds (versatile efficient methods and of synthesis of substituted indoles, isomeric azaindoles, and azabenzofuranes, as well other nitrogen containing as heterocycles)



Selected Publications

- Yurovskaya M.A., Alekseyev R.S. New perspectives of classical heterocyclic reactions involving pyrrole derivatives (Review). *Chemistry of Heterocyclic Compounds*, **2014**, *49*, 1400.
- F.S. Melkonyan, D.E. Kuznetsov, M.A. Yurovskaya, A.V. Karchava, One-pot synthesis of substituted indoles via titanium(iv) alkoxide mediated imine formation-copper-catalyzed Narylation. RSC Adv., 2013, 3, 8388.
- Yurovskaya M.A., Fluoirinated Oxazoles, Thiazoles and Selenazoles, In book: Fluorine in

Heterocyclic Chemistry", Springer, **2014**, vol. 1, p. 419-458

- R.S. Alekseyev, A.S. Ivanov, A.V. Kurkin, M.A. Yurovskaya, Stereoselective Reduction of Active Substance of Medicinal Preparation Dimebon to the Corresponding trans-1,2,3,4a,9a-Hexahydro Derivatives, *Chemistry of Heterocyclic Compounds*, 2011, 46, 1239.
- F. Melkonyan, A. Topolyan, A. Karchava, M. Yurovskaya, A general synthesis of Nsubstituted 1,4-benzoxazine- and 1,4benzothiazine-2-carboxylates via copper- catalyzed intramolecular amination of arylbromides, *Tetrahedron*, 2011, 67, 6826-6832
- A.A. Utkina, A.V. Kurkin, M.A. Yurovskaya, Use α-Amination Reaction for Synthesis of Pyrazole Derivatives Containing Carbo- and Heterocyclic Substituents on the Nitrogen atom,). *Chemistry* of Heterocyclic Compounds, **2012**, 48, 327.
- N. S. Ovchinnikova, A. A. Goryunkov, P. A. Khavrel, N. M. Belov, M. G. Apenova, I. N. loffe, M. A. Yurovskaya, S. I. Troyanov, L. N. Sidorov, E. Kemnitz, Unexpected fullerene dimerization *via* [5,6]-bond upon functionalization of C_s-C₇₀(CF₃)₈ by the Bingel reaction, *Dalton Trans.*, 2011, 40, 959–965
- V. Kurkin, A. A. Bernovskaya, M. A. Yurovskaya, Synthesis of N-alkylanthranilamides with a chiral substituent at the nitrogen atom, *Tetrahedron: Asymmetry*, **2010**, 21, №17, 2100-2107.
- A.V. Kurkin, A. A. Bernovskaya, M. A. Yurovskaya, Synthesis of isatins with a chiral substituent at the nitrogen atom, *Tetrahedron: Asymmetry*, **2009**, 20, №17, 1500-1505.
- F.Melkonyan, A.Topolyan, M.Yurovskaya, A.Karchava, Synthesis of 1-Amino-1H-indole-3carboxylates by Copper(I)-Catalyzed Intramolecular Amination of Aryl Bromides, *Eur.J.Org.Chem*, **2008**, 5952-5956.



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Research Interests

• Chemistry of condensed heterocycles with bridging nitrogen atoms.



• Synthesis of hard-to-reach N-terocycles.





- Alekseyev R.S., Amirova S.R., Terenin V.I. Preparation of 2,3-Disubstituted 5-Bromo-1Hpyrrolo[2,3-b]pyridine Framework by Fischer Cyclization. *Synthesis*, **2015**, *47*, 3169.
- Alekseyev R.S., Amirova S.R., Kabanova E.V., Terenin V.I. The Fischer Reaction in the Synthesis of 2,3-Disubstituted 7-Azaindoles. Chemistry of Heterocyclic Compounds, 2014, 50, 1305.
- Romashkina R.B., Beloglazkina E.K., Khlobystov A.N., Majouga A.G, Pichugina D.A., Terenin V.I., Zyk N.V., Zefirov N.S. Copper(II) coordination compounds as building blocks for the formation of gold nanoparticle dimmers. Mendeleev Communications, 2011, 21, 129.
- Terenin V.I., Butkevich M.A., Ivanov A.S., Kabanova E.V. Acylation of pyrrolo[1,2a]pyrazines. Chemistry of Heterocyclic Compounds, 2008, 44, 200.
- Voskresensky L.G., Borisova T.N., Kamalitdinova T.M., Terenin V.I., Titov A.A., Varlamov A.V. First example of the synthesis of pyrrolo[1,2-d][1,4]diazocine by the reaction of tetrahydropyrrolo[1,2a]pyrazines with activated alkynes *Chemistry* of Heterocyclic Compounds, **2008**, 44, 634.
- Terenin V.I., Butkevich M.A., Ivanov A.S., Tselischeva N.A., Kabanova E.V. Formylation of pyrrolo-[1,2-a]pyrazines. *Chemistry of Heterocyclic Compounds*, **2008**, *44*, 73.



Senior scientist Galina V. Grishina

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Research Interests

• Design and investigation of new molecular switch based on the cis- and trans-3(4)-amino-4(3)–hydroxypiperidines and trans-3,4-diacyloxypiperidines.



3, n = 1 4, n = 5

• Stereoselective synthesis and stereochemistry of trans-3-amino-4hydroxypiperidines.

Lipid phase separation, lipid bilayer permeation



- Samoshin A.V., Hyun J., Korneichuk A.Ya, Veselov I.S., Grishina G.V., Samoshin V.V., Samoshina N.M.trans-3-Hydroxy-4-morpholinopiperidine the pH-triggered conformational switch with a double flip *Tetrahedron Letters*, 2013, 54, 1020.
- Grishina G.V., Luk'yanenko E.R., Borisenko A.A., Antipin M.Yu. Asymmetric synthesis and stereochemistry of chiral cis- and trans-3-alkyl-4aminopiperidines. *Chemistry of Heterocyclic Compounds*, 2012, 48, 733.
- Samoshin A.V., Veselov I.S., Chertkov V.A., Yaroslavov A.A., Grishina G.V., Samoshina N.M., Samoshin V.V. Fliposomes: new amphiphiles based on trans-3,4-bis(acyloxy)piperidine able to perform a pH-triggered conformational flip and cause an instant cargo release from liposomes. *Tetrahedron Letters*, 2013, 54, 5600.
- Grishina G.V., Veselov I.S., Nelyubina Y. V., Surovaya A.N., Zefirov N.S. Optically pure trans-1-benzyl-4-aminopiperidin-3-ols. Synthesis and absolute configuration. *ARKIVOC*, **2011**, 107.
- Samoshin A.V., Veselov I.S., Huynh L., Shestakova A.K., Chertkov V.A., Grishina G.V. Trans-3,4-diacetoxypiperidine as a model for novel pH-triggered conformational switches. *Tetrahedron Letters*, **2011**), *52*, 5375.
- Terent'ev P.B., Parshikov I.A., Grishina G.V., Piskunkova N.F., Chumakov T.I., Bulakhov G.A. Hydroxylation of the Multiple Bond in 1Benzyl-3-methyl-Δ3-piperideine by Micellar Fungi. ChemInform, 2010, 29, № 1.
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Research Interests

• New synthetic approaches to the small molecule inhibitors of beta-lactamase.



• Selenium-containing organic ligands and metallocomplexes.



- Kuznetsova O.Yu, Antipin R.L., Udina A.V., Krasnovskaya O.O., Beloglazkina E.K., Terenin V.I., Koteliansky V.E., Zyk N.V., Majouga A.G. An Improved Protocol for Synthesis of 3-Substituted 5-Arylidene-2-thiohydantoins: Twostep Procedure Alternative to Classical Methods. *Journal of Heterocyclic Chemistry*, 2015
- Chernysheva A.N., Beloglazkina E.K., Antipin R.L., Moiseeva A.A., Zyk N.V.New Sulfanyl- and Selanyl-Substituted Schiff BasesDerived from 2-Chalcogenoalkylamines and Aromatic Aldehydes.Synthesis and Complex Formation Reactions. *Russian Journal of General Chemistry*, 2013, 83, 311.
- Beloglazkina E.K., Majouga A.G., Antipin R.L., Myannik K.A., Moiseeva A.A., Zyk N.V. Novel copper(II) and cobalt(II) complexes with selenium substituted imidazolyl imines. The molecular and crystal structure of [N-(2-(phenylseleno)ethyl)-N-(imidazol-2ylmethylene)amine]copper(II) dichloride. *Polyhedron*, **2013**, *50*, 4.
- Chernysheva A.N., Beloglazkina E.K., Moiseeva A.A., Antipin R.L., Zyk N.V., Zefirov N.S. Co-II complex of N-[2-(phenylseleno)cyclohexyl]-N-(pyridin-2-ylmethylene)amine: synthesis, electro-chemistry and catalysis of triphenylphosphine and norbornene oxidation by nitrous oxide. *Men-deleev Communications*, **2012**, *22*, 70.
- Chernysheva A.N., Antipin R.L., Borisenko A.A., Beloglazkina E.K., Zyk N.V.beta-Aminoselenenation of alkenes with arylselenenamides in the presence of sulfamic acid. *Russian Chemical Bulletin*, 2011, 60, 198.
- Antipin R.L., Beloglazkina E.K., Zyk N.V., Zefirov N.S. Arylselenenation of conjugated dienes by arylselenenamides in the presence of phosphorus(V) oxyhalides. *Tetrahedron Letters*, **2007**, *48*, 729.
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Laboratory of Supramolecular Chemistry and Nanotechnology of Organic Materials



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Laboratory staff: professor Vatsadze S.Z., associate professor Nuriev V.N., senior scientist Gavrilova G.V., senior scientist Rakhimov R.D., scientist Moiseeva A.A.; junior scientist Medved'ko A.V.



• Synthesis of macrocyclic compounds for the construction of organic supramolecular assemblies.



• Study of self-assembly and selforganization processes in solutions and crystals.

"Single crystal-to-single crystal" topophotochemical trans-



• Creation of photoswitchable supramolecular devices and photocontrolled supramolecular machines.



• Investigation of photophysical properties and photochemical transformations of supramolecular nanosized systems and organic materials on their base.

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- Gromov S.P., Vedernikov A.I., Lobova N.A. et al. Synthesis, Structure, and Properties of Supramolecular Photoswitches Based on Ammonioalkyl Derivatives of Crown-Ether Styryl Dyes. *J. Org. Chem.* 2014, 79, 11416.
- Ushakov E.N., Vedernikov A.I., Lobova N.A., Dmitrieva S.N., Kuz'mina L.G., Moiseeva A.A., Howard J.A.K., Alfimov M.V., Gromov S.P. Supramolecular Dimerization and [2+2] Photocycloaddition Reactions of the Crown Ether Styryl Dyes Containing a Tethered Ammonium Group: Structure – Property Relationships. *J. Phys. Chem.* A. **2015**, 119, 13025.



• Synthesis of new supramolecular tectons and study on novel supramolecular synthons.



• Study on self-organization and selfassembly phenomena in crystals and gels; application of supecritical fluids for modification of new materials.



• New radiofarmachemicals based on copper chelates (⁶⁴Cu) for the study of congnitive processes and of the effect of radiation on neuro-psycological human behavior.



• Biologically active heterocycles and bioluminescent agents on their base: atom precision synthetic methodology.

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• Ferrocene-containing polymers and biologically active molecules.



- Nenajdenko V.G., Vatsadze S.Z., Rakhimiv R.D. et al. A new approach to ferrocene derived alkenes via copper-catalyzed olefination. *Beilstein J. Org. Chem.* 2015, *11*, 2072.
- Balakhonov S.V., Vatsadze S.Z., Churagulov B.R. Effect of supercritical drying parameters on the phase composition and morphology of aerogels based on vanadium oxide. *Russ. J. Inorg. Chem.* 2015, 60, 9.
- Vatsadze S.Z., Kudryavtsev K.V. et al. Synthesis of novel bridged dinitrogen heterocycles and their evaluation as potential fragments for the design of biologically active compounds. *Tetrahedron* 2014, 70, 7854.
- Vatsadze S.Z., Medved'ko A.V., Nuriev V.N. Supramolecular gels as a new class of smart materials, *in* Development of new methods in modern selective organic synthesis: preparation of functionalized molecules with atomic precision. *Russ. Chem. Rev.* 2014, *83*, 885.
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Laboratory of Physico-Chemical Methods of Analysis



Research Interests

Proteomics

The elucidation of the sequence of amino acids in proteins and peptides by means of mass spectrometry is called MS sequencing. The group studies possible versions of chemical modifications of the authentic peptides in order to increase reliability of the analysis and the sequence coverage. Amphibian skin peptides became an object of the studies. The selection of frogs as a source of peptides is not occasional. These animals are famous for their powerful immune system due to the presence of an array of bioactive peptides secreted onto the skin under the stress. These peptides although considering prospective pharmaceuticals of the next generation are not studied in details. Besides developing mass spectrometric approaches for the sequencing the group tests newly discovered peptides for various types of biological activity. More than 200 new peptides were discovered. Besides that several problems of sequencing including intramolecular S-S bonds, cyclization of short peptides, differentiation between isomeric leucin and isoleucine residues were successfully resolved.



Mass-spectrometry group

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Ecology

Mass spectrometry is a unique method allowing for the successful environmental studies. The environmental analysis by mass spectrometry provides a complete list of contaminants of all types giving a chance to find the correct source of pollution. Environmental samples from all over the world are studied. Another issue deals with identification of disinfection byproducts.



Selected Publications

• Lebedev A.T., Damoc E., Makarov A.A., Samgina T.Yu. Discrimination of Leucine and Isoleucine in Peptides Sequencing with Orbitrap Fusion Mass Spectrometer. *Analytical Chemistry*, 2014, 86, 7017.

• Lebedev A.T. Ambient ionization mass spectrometry. Russ. Chem. Rev., 2015, 84, 665

• Samgina T.Yu, Tolpina M.D., Trebse P., Torkar G., Artemenko K.A., Bergquist J., Lebedev A.T. LTQ Orbitrap Velos in routine de novo sequencing of non-tryptic skin peptides from the frog Rana latastei with traditional and reliable manual spectra interpretation. *Rapid Communications in Mass Spectrometry*, **2016**, 30, 265.

Molecular electrochemistry group



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Organic electrochemistry constitutes a modern research area which solves the problems of organic and organometallic chemistry using wide possibilities of electrochemical techniques. Much of the behavior of molecules can be viewed in terms of the movement of electrons. This view is obvious in the case of oxidation and reduction reactions, but so too catalysis can be viewed as the movement of electons from one set of bonds to another, pho-ephysical behaviors involve the movement of electrons between different energy levels and spatial distributions, and photovoltaics and molecular electronics depend on the transfer of electrons.



The scope of tasks which can be solved using electrochemical approaches is rather broad. It involves electrochemical activation of reactants, electrocatalysis, electrosynthesis, investigation of reaction mechanism (insight into electron structure of complex multifunctional and polynuclear compounds, kinetic measurements for the fast reactions, detection of short-lived intermediates, etc.), electrochemical modeling of active sites of redox-enzymes and some other items.



It should be emphasized that organic electrochemistry (which is also named as "molecular electrochemistry") is much more associated to organic chemistry than to physical chemistry or classical electrochemistry; and this arrangement can't be explained by formal evidence (organic objects and non-aqueous solvents) only but is mainly owing to the essence of its goals.



Synthetic organic and organometallic chemistry is making major strides in all areas mentioned above. Electrochemistry represents a complementary approach to electron-transfer-initiated reactivity of organic compounds: instead of individual "classic" chemical oxidation/reduction agents, the electrode serves as a "clean" electron donor/acceptor. Moreover, its oxidation/reduction ability can be easily and continuously changed by the applied potential. Electrochemical experiments are thus rich in information concerning thermodynamics, kinetics, equilibria, reversibility, and mechanism. This issue brings together organic chemists and electrochemists to illustrate the breadth and power of electrochemical studies of organic molecules and organic reactions.



Selected publications

• Magdesieva, T.V., Shvets, P.V., Nikitin, O.M., Obraztsova, E.A., Tuyakova, F.T., Sergeyev, V.G., Khokhlov, A.R., Obraztsov, A.N., Electrochemical characterization of mesoporous nanographite films. *Carbon*, **2016**, *105*, 96.

• Rybalchenko, A.V., Apenova, M.G., Semivrazhskaya, O.O., Belov, N.M., Markov, V.Y., Troyanov, S.I., loffe, I.N., Lukonina, N.S., Sidorov, L.N., Magdesieva, T.V., Goryunkov, A.A., Electron affinities of [5,6]-open and [5,6]closed adducts of trifluoromethylfullerene Cs-C70(CF3)8: Even one bond matters! *Electrochimica Acta*, **2016**, *191*, 980.

• Magdesieva, T.V., Levitskiy, O.A., Grishin, Y.K., Ambartsumyan, A.A., Kochetkov, K.A., New binuclear Ni(II)-glycinate homologues: Electrochemically distinguishable diastereomers. Electrochimica Acta (2015) 179, pp. 263-275.

• Magdesieva, T.V., Levitskiy, O.A., Grishin, Y.K., Ambartsumyan, A.A., Kiskin, M.A., Churakov, A.V., Babievsky, K.K., Kochetkov, K.A. Electrochemically deprotonated chiral nickel(II) glycinate in stereoselective nucleophilic addition to Michael acceptors: Advantages and limitations, *Organometallics*, **2014**, 33, 4629.

• Magdesieva, T.V., Levitskiy, O.A., Grishin, Y.K., Ambartsumyan, A.A., Paseshnichenko, K.A., Kolotyrkina, N.G., Kochetkov, K.A., Chiral Nickel(II) binuclear complexes: Targeted diastereoselective electrosynthesis. *Organometallics*, **2014**, *33*, 4639.

• Magdesieva, T.V., Nikitin, O.M., Zolotukhina, E.V., Vorotyntsev, M.A. Palladium nanoparticles-polypyrrole composite as an efficient catalyst for cyanation of aryl halides. *Electrochimica Acta*, **2014**, *122*, 289.

• Samoylova, N.A., Belov, N.M., Brotsman, V.A., Ioffe, I.N., Lukonina, N.S., Markov, V.Y., Ruff, A., Rybalchenko, A.V., Schuler, P., Semivrazhskaya, O.O., Speiser, B., Troyanov, S.I., Magdesieva, T.V., Goryunkov, A.A. [6,6]-Open and [6,6]-closed isomers of C70(CF2): Synthesis, electrochemical and quantum chemical investigation. *Chemistry - A European Journal*, **2013**, *19*, 17969.



 Molecular modeling donor ability, softness, M-C bond strength



stability



 $PhGeCl_3 + 2 Et_3GeOCH_2CH_2NMe_2 \xrightarrow{THF} PhGe(OCH_2CH_2NMe_2)_2Cl + 2 Et_3GeCl$



• Stable carbene chemistry



n=1, 2; Ar=Mes, Dipp

• Transition metal homogeneous catalysis



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- Khrustalev, V. N.; Portnyagin, I. A.; Borisova, I. V.; Zemlyansky, N. N.; Ustynyuk, Y. A.; Antipin, M. Y.; Nechaev, M. S. Donor-stabilized germyl cations. Stable pentacoordinate germanium chloride PhGe(OCH2CH2NMe2)(2) Cl. Organometallics 2006, 25, 2501-2504.

Winter School of Organic Chemistry (WSOC)



Since January 2015, annually School-Conferences for Young Scientists in organic chemistry are held by the Organic Chemistry Department. The main objective of the School is to introduce the postgraduate and young scientists into the latest world achievements and trends in the development of organic chemistry.



Participants of the School-Conference in front of entrance in the 2nd Corps centers, January 2015

The school is held on the basis of a recreation center Krasnovidovo (Moscow region). Several educational mini-courses that read leading world scientists are organized in the Conference. In addition, leading Russian scientists speak with plenary reports during the four days of school working. All young scientists taking part in school-conference with oral presentations of their work. A contest of young scientists presentations carried at the conference, and the winners receive valuable prizes.

The school program includes round tables on actual problems of modern chemistry.

Cultural program of school-conference includes a fascinating chemical quiz among the teams combining both students and professors.



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