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Fields of research

- Bioremediation of organic pollutants in soil and sewage
- Immobilization of biocatalysts, living cells or enzymes, into organic or organic-inorganic matrices by sol-gel process
- Whole cell optical sensors
- Application of immobilized biocatalysts in optical sensors
- Dehydrocoupling reactions catalyzed by titanium complexes
- Structure of silyl moieties through $J(^{29}\text{Si}-^{13}\text{C})$ couplings as determined by triple $\{^1\text{H}, ^{13}\text{C}\}^{29}\text{Si}$ NMR experiment
- Synthesis of helicene derivatives and $[n]$ phenacene derivatives
- Carbosilane metallodendrimers
- Heavy fluorinated cyclopentadienes and cyclopentadienyl ligands
- Synthesis of ionic liquids for separation techniques and electrochemical sensing

Applied research

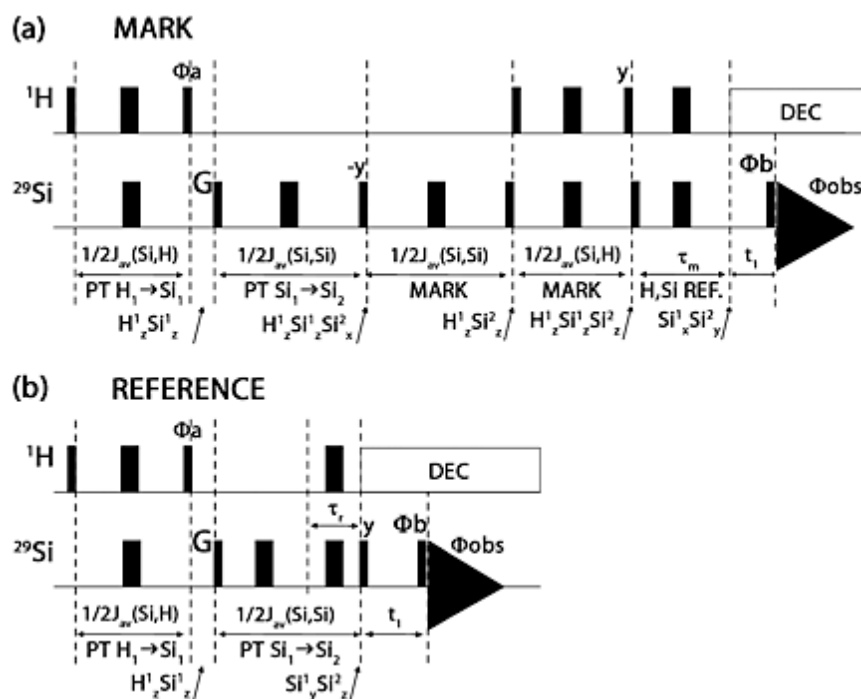
- Enzymatically catalyzed synthesis of alkyd resins
- Development of new analytical methods
- Analytical services to the research departments of ICPF
- Multigram scale production of helicenes and $[n]$ phenacenes

Research projects

Spectra edited by relative signs of homonuclear couplings of low abundance nuclei

(V. Blechta, blechta@icpf.cas.cz; supported by GA AVCR, project No. IAA400720706, and GACR, project No. 203/08/P412)

The proposed homonuclear coupling sign edited (HCSE) experiment can detect signed homonuclear couplings between low abundant nuclei like ^{13}C , ^{29}Si and ^{15}N in linear spin systems, that is, in systems where two nuclei are coupled by the measured coupling, and one of them is coupled by a second coupling to a nucleus of different kind. The third nucleus is usually high abundant hydrogen. Two spectra are measured during the HCSE experiment. Their weighed sum and difference yield two other spectra, one containing peaks coupled only by positive measured couplings and the other having peaks coupled by negative measured couplings. The usual E-COSY-type experiment requires all three couplings in the three spin system (triangular spin system) and not only two couplings as the HCSE experiment. The experiment was successfully tested on known carbon–carbon and silicon–silicon two bond couplings. A set of six simple siloxanes with $^2J(\text{Si-O-Si})$ couplings ranging from 0.5 to 9.0 Hz was measured for the first time, and all the couplings were found to be positive. [Ref. 1]



Scheme of HCSE experiment with silicon–silicon coupling detection

BIO-OPT-XUV Research team advancement at the FBME CTU

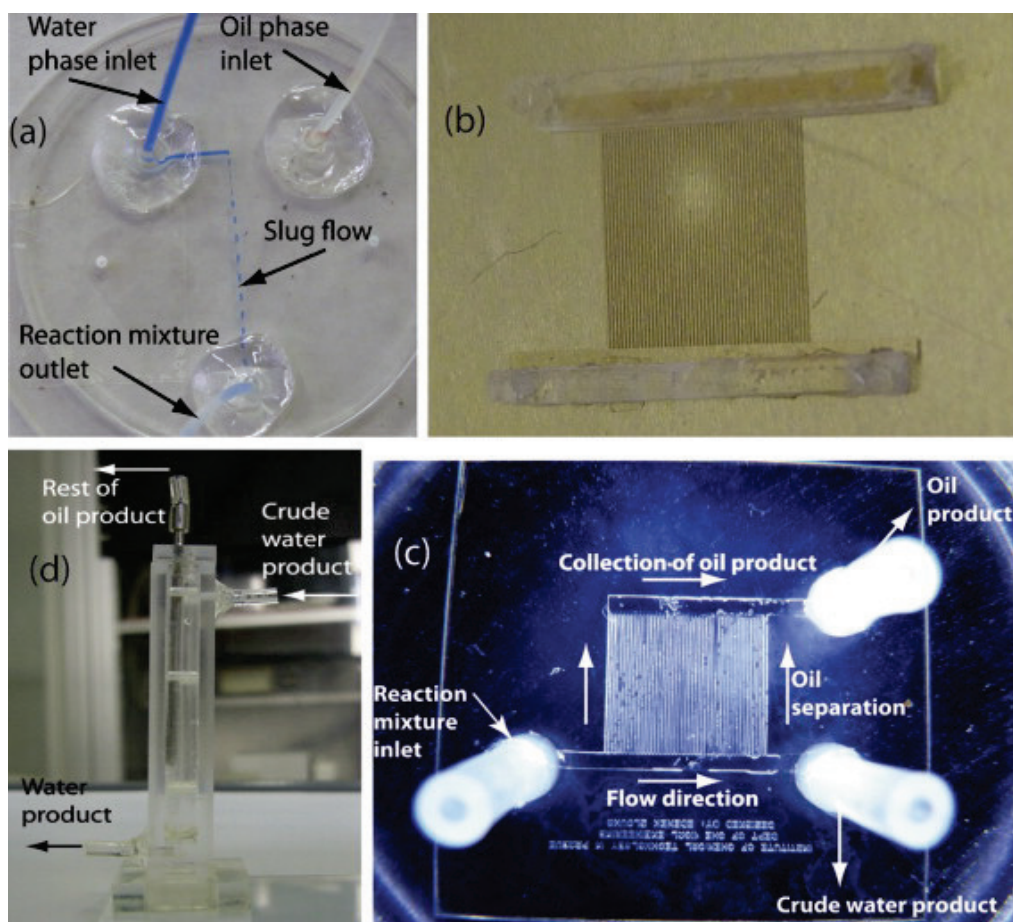
(G. Kuncová, kuncova@icpf.cas.cz; supported by MEYS, ESF, project No. CZ.1.07/2.3.00/20.0092)

Aim of this project is to strengthen education and build up a research team at the FBME (Faculty of Biomedical Engineering) CTU. In the academic year 2012/2013, experiments of three Bc. projects of the students of FBME CTU were realized in the laboratory of Immobilized Biocatalyst and Optical Sensors. The topic of these projects comprised developing XUV radiation sources and their applications in biology and medicine, enzymatic optical sensor, optical fiber biosensor and optical fiber whole-cell sensor of benzene, toluene, xylene and ethyl benzene (BTEX).

Enzyme hydrolysis of soybean oil in a slug flow microsystem

(G. Kuncová, kuncova@icpf.cas.cz; joint project with ICT and University of Notre Dame, USA; supported by MEYS, KONTAKT ME892, project No. MSM6046137306)

We report on the development of a continuous microfluidic reaction system for hydrolysis of soybean oil catalyzed with *Thermomyces lanuginosus* lipase (Lipolase 100 L). The microfluidic reaction system generates water–oil emulsions in the form of a hydrodynamically well controlled slug flow and automatically separates the oil phase after the hydrolysis by employing two microfluidic separators. All elements of this reaction system were tested at different hydrodynamic conditions and showed the ability to operate in a wide range of reactant flow rates. 25–30% conversion of triglyceride was reached in setting the residence time of the emulsion mixture to 10 min. This conversion increased to almost 50% for the residence time of 1 h. These results are comparable with those published for the same enzyme reaction system. This feature along with the benefits stemming from the use of microfluidics make our developed system a useful, easy to control and easy to scale-up technology for fast production of fine chemicals. Moreover, our calculations indicate that our slug flow system allows for significant savings of the mechanical energy. [Ref. 3]



(a) Microfluidic generator of the slug flow. Blue water solution is introduced in one microchannel for the interface contrast enhancement, (b) primary microseparator – SU8 master on phosphorbronze substrate, (c) primary microseparator – PDMS microchip, and (d) secondary microseparator

Preparation of helicene based chiral stationary phase for HPLC

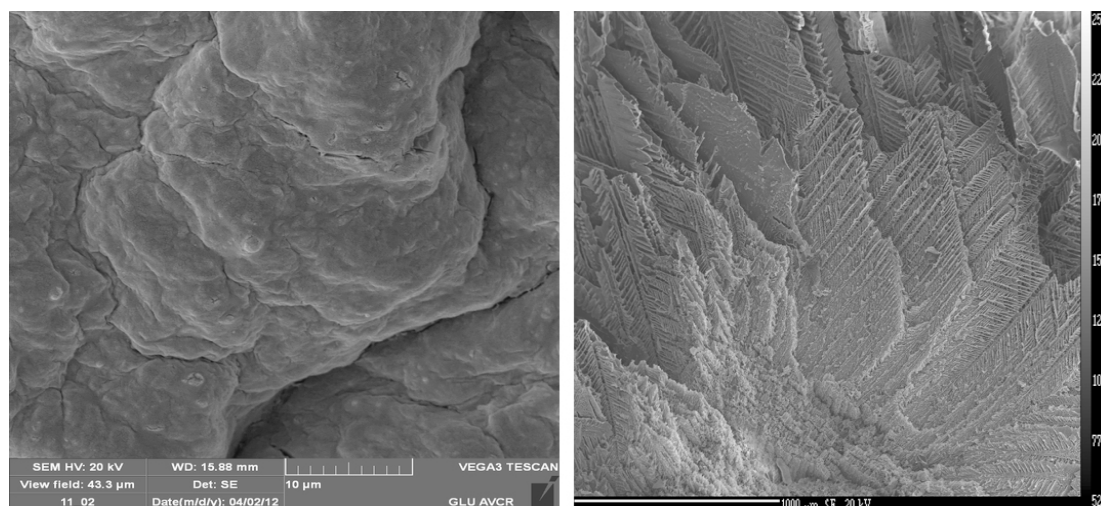
(J. Sýkora, sykora@icpf.cas.cz; joint project with Watrex Praha, s.r.o.; supported by TACR, project No. TA01010646)

The main aim of the project is to develop a new stationary phase for HPLC which would serve for column manufacturing. Further testing of its properties and evaluation of the relevancy for possible production and sale is also part of the objectives. [Ref. 15]

Novel inorganic-organic hybrid nanomaterials

(S. Šabata, sabata@icpf.cas.cz; joint project with ICT Prague, IMC, University of West Bohemia Plzeň, supported by ASCR, project No. IAAX08240901)

Na⁺ montmorillonite was silanized with methoxy- and ethoxy- organosilanes having various functional groups. The modified montmorillonites were characterized with X-Ray diffraction and used as catalyst carriers. Three types of microbial lipases were adsorbed on the modified montmorillonites. These biocatalysts with adsorbed enzymes were uniaxially frozen in liquid nitrogen (ISISA), dried and characterized with X-Ray diffraction. Activities of newly synthesized nanostructured biocatalysts were compared with commercial one. Esterification of stearic acid with propanol in hexane was chosen as a model reaction. Conversions of stearic acid were 25% in case of lipase – montmorillonite biocatalyst (A) and 92% for biocatalyst frozen in liquid nitrogen (B).

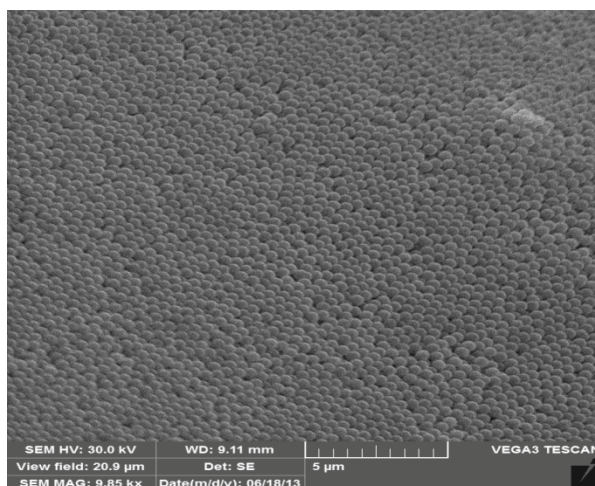


**Structure of lipase – montmorillonite biocatalyst (A)- dried at ambient temperature
(B) – frozen in liquid nitrogen (ISISA)**

Calixarene-porphyrin conjugates for selective complexation and separation of fullerenes

(S. Šabata, sabata@icpf.cas.cz; joint project with ICT and IIC; supported by GACR, project No. 203/09/0691)

The silanized tetraammoniumporphyrine, which we had synthesized in 2010, was chemically bounded on surfaces of inorganic materials; montmorillonite and various silica nanoparticles. Commercially available LUDOX and monodisperse spherical silica particles prepared by modified Ströber method were used. These composite materials comprising silanized tetraammoniumporphyrine were mixed with tetraethoxysilane and filled into empty chromatography columns (Ø 4 mm, length 150 mm). After gelation, interconnected hierarchical micro-/meso-/macroporous networks were created by ice segregation induced self-assembly method. Such monolithical chromatography columns performed low separation abilities due to presence of large pores.

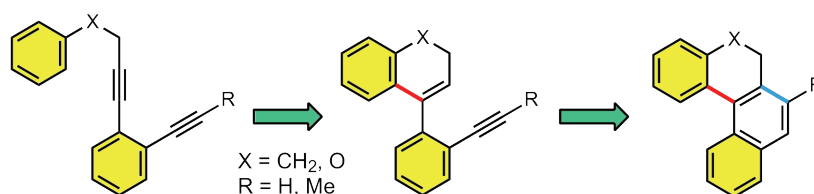


Monodisperse spherical silica particles with chemically bounded silanized tetraammoniumporphyrine

Synthesis of helicenes *via* cycloisomerization of biphenylnaphthalene and 1,8-diaryl-naphthalene derivatives

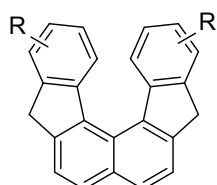
(J. Čermák, J. Storch, cermak@icpf.cas.cz, storchj@icpf.cas.cz; supported by GACR, project No. 207/10/1124)

The new PtCl₂/PtCl₄ catalyzed hydroarylation / cycloisomerization cascade reaction leading to formation of two aromatic or heteroaromatic rings in one step is reported. The strategy developed is exemplified by the synthesis of 5,6-dihydrobenzo[*c*]phenanthrene and 6*H*-naphtho[2,1-*c*]chromene skeletons. Attempts to [8]helicene-like molecules were also investigated. The results were published in *Eur. J. Org. Chem.* **2013**, 2, 260-263.



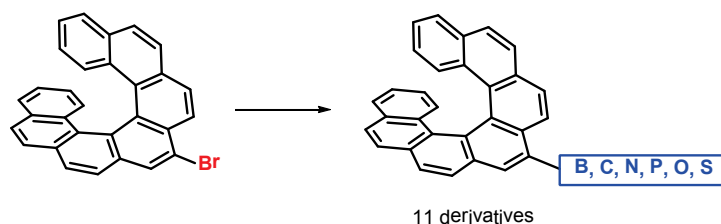
Hydroarylation / cycloisomerization cascade reaction

The synthesis of [6]helicene-like molecules - *pseudo*-helicenes was also developed. Incorporated pyridine rings or diamino derivatives, phosphines and/or diphosphines could find use in coordination chemistry, e.g. as ligands in metal catalysis and organocatalysis. Deprotonated form with cyclopentadienyl ring stabilized with metals (ferrocene-like structures) could exhibit increased racemization barrier and thus be applicable in asymmetric reactions. Results on synthesis of model compounds will be published soon.



Exploration of 9-bromo[7]helicene reactivity mainly in Pd-catalyzed reactions is reported. Palladium catalyzed carbon – carbon and carbon – heteroatom coupling reactions provide a large portfolio of racemic helicenes bearing different functional groups in good to excellent yields. Many of the reactions were performed in the microwave reactor saving reaction time to

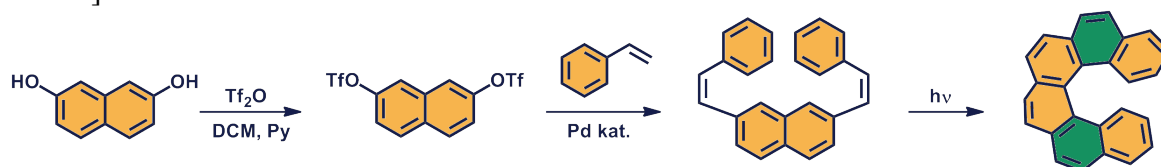
a minimum comparing with conventional and known synthetic methods. These results were submitted in December to *Tetrahedron* **2013**, *69*, 6213-6218.



9-bromo[7]helicene reactivity

Technology of the oxidative photocyclization leading to helicenes (J. Storch, storchj@icpf.cas.cz; supported by MIT, project No. FR-TI3/628)

The project is aimed at development of photocyclization apparatus enabling multigram-scale production of various helicenes for distribution in the Czech Republic and abroad. The technology makes exploitation of helicenes in various areas such as separation techniques, supramolecular chemistry, catalysis etc. possible. Intellectual property produced within this project concerning to method and apparatus for production of [6]helicenes was also patented. [Ref. 15]

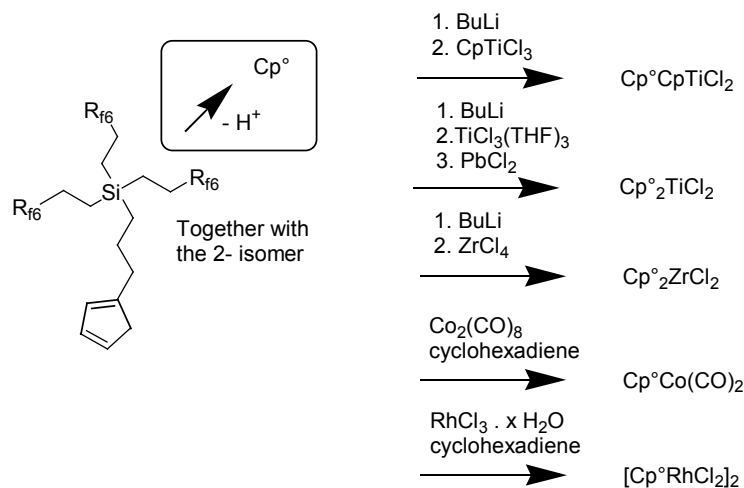


Synthesis of [6]Helicene from 2,7-dihydroxynaphthalene

Highly fluoruous cyclopentadienes for applications in catalysis

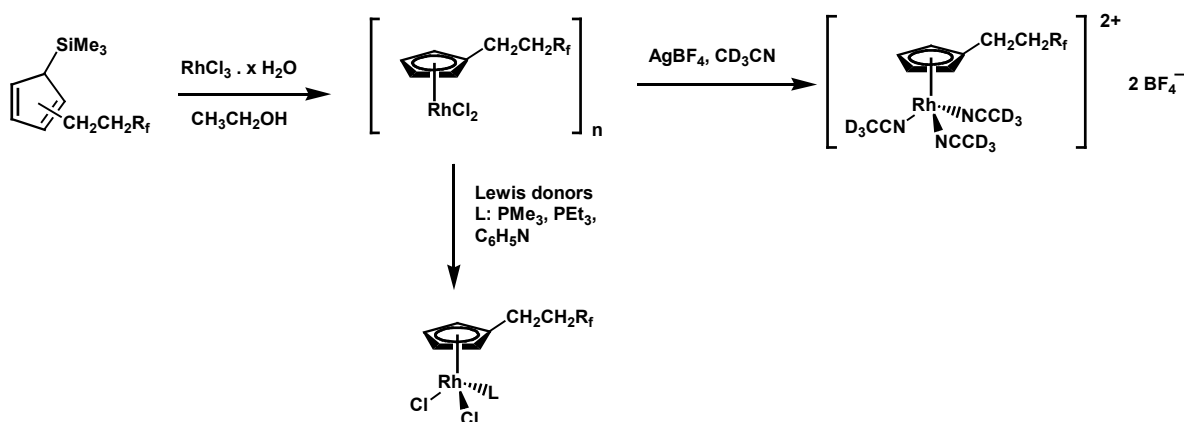
(J Čermák, cermak@icpf.cas.cz; supported by GACR, project No. P106/12/1372)

Two new approaches to synthesis of heavy fluoruous (i.e. showing high fluorophilicity) cyclopentadienes and cyclopentadienyl ligands were studied. In the first approach silicon is used as a branching atom and three (perfluoroalkyl)ethyl substituents are attached to it. The whole fluoruous tag could be used for fluorophilization of cyclopentadienes. Other nucleophilic substitution reactions provided various functional groups in the core of the tag.



Tagged cyclopentadiene and its reactions

The other approach uses stepwise alkylation of trimethylsilylcyclopentadiene to provide cyclopentadienes polyalkylated with (perfluoroalkyl)ethyl groups. Rhodium complexes of the monosubstituted cyclopentadienyl ligand were prepared and characterized by NMR.



Rhodium complexes with (perfluoroalkyl)ethyl substituent

International co-operations

Centre for Environmental Biotechnology, University of Tennessee, Knoxville, TN, USA:

Improved biomaterials for the encapsulation of living cells

Environmental Sciences Division Oak Ridge National Laboratories, Oak Ridge, TN, USA:

Application of nanomaterials and novel organic-inorganic materials in optical sensors

Graz University of Technology, Graz, Austria: ^{29}Si and ^{119}Sn NMR

Institut de Chimie Moléculaire de Reims, CNRS 7312, France: ESI-MS of titanocene-containing dendrimers

Lehrstuhl für Organische Chemie I, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany: Chemistry of hetero[n]phenacenes

Teaching

J. Čermák: UJEP, Faculty of Science, courses “Organic chemistry I and II”, “Chemistry of heterocyclic and organometallic compounds”, “Introduction to the spectral methods in organic chemistry”

G. Kuncová: ICT, Faculty of Chemical Engineering, postgraduate course “Optical sensors for measurement in chemical and biological reactors”

Publications

Original papers

- [1] Blechta V., Kurfürst M., Schraml J.: Spectra Edited by Relative Signs of Homonuclear Couplings of Low Abundant Nuclei. *Magn. Reson. Chem.* 50(2), 135-141 (2012).
- [2] Blechta V., Šabata S., Sýkora J., Hetflejš J., Soukupová L., Schraml J.: The Effect of Solvent Accessible Surface on Hammett-Type Dependencies of Infinite Dilution ^{29}Si and ^{13}C NMR Shifts in Ring Substituted Silylated Phenols Dissolved in Chloroform and Acetone. *Magn. Reson. Chem.* 50(2), 128-134 (2012).

- [3] Čech J., Schrott W., Slouka Z., Příbyl M., Brož M., Kuncová G., Šnita D.: Enzyme Hydrolysis of Soybean Oil in a Slug Flow Microsystem. *Biochem. Eng. J.* 67, 194-202 (2012).
- [4] Karban J., Císařová I., Strašák T., Červenková Šťastná L., Sýkora J.: Skeletal Rearrangements Resulting from Reactions of 1,6:2,3- and 1,6:3,4-Dianhydro-beta-D-hexopyranoses with Diethylaminosulphur Trifluoride. *Org. Biomol. Chem.* 10(2), 394-403 (2012).
- [5] Krupková A., Čermák Jan: Carbosilane Metallo dendrimers with Cyclopentadienyldichlorotitanium(IV) End Groups. *J. Inorg. Organomet. Polym. Mater.* 22(2), 470-477 (2012).
- [6] Pinkas J., Císařová I., Karban J., Schraml J., Sýkora J.: Identification of Branched Oligosilanes in the Phenylsilane Dehydrocoupling Reaction. *J. Organomet. Chem.* 710, 20-25 (2012).
- [7] Rychtáriková R., Seisenbaeva G. A., Kuncová G., Kessler V. G.: Biocompatible Titania Hydrogels with Chemically Triggered Release of a Photosensitive Dye. *J. Sol-Gel Sci. Technol.* 62(3), 370-377 (2012).
- [8] Rychtáriková R., Šabata S., Hetflejš J., Kuncová G.: Photodynamic Efficiency of Porphyrins Encapsulated into Polysilsesquioxanes. *Chem. Pap.* 66(4), 269-277 (2012).
- [9] Rychtáriková R., Šabata S., Hetflejš J., Kuncová G.: Composites with Photosensitive 5,10,15,20-tetrakis(N-methylpyridinium-4-yl)porphyrin Entrapped into Silica Gels. *J. Sol-Gel Sci. Technol.* 61(1), 119-125 (2012).
- [10] Slavík P., Dudič M., Flídrová K., Sýkora J., Císařová I., Böhm S., Lhoták P.: Unprecedented Meta-Substitution of Calixarenes: Direct Way to Inherently Chiral Derivatives. *Org. Lett.* 14(14), 3628-3631 (2012).
- [11] Strašák T., Čermák Jan, Sýkora J., Horský J., Walterová Z., Jaroschik F., Harakat D.: Carbosilane Metallo dendrimers with Titanocene Dichloride end Groups. *Organometallics* 31(19), 6779-6786 (2012).
- [12] Varga V., Horáček M., Bastl Z., Merna J., Císařová I., Sýkora J., Pinkas J.: Zirconocene Silanolate Complexes and Their Heterogeneous Siliceous Analogues as Catalysts for Phenylsilane Dehydropolymerization. *Catal. Today* 179(1), 130-139 (2012).

Review papers

- [13] Trögl J., Chauhan A., Ripp S., Layton A.C., Kuncová G., Sayler G.S.: *Pseudomonas fluorescens* HK44: Lessons Learned from a Model Whole-Cell Bioreporter with a Broad Application History. *Sensors* 12(2), 1544-1571 (2012).

Patents

- [14] Petříčkovič R., Uchytíl P., Řezníčková J., Setničková K., Storch J.: Způsob separace plynu ze směsi plynů. Pat. No. PV 2012-725. Applied: 12.10.25.
- [15] Storch J., Církva V., Bernard M., Vokál J.: Způsob výroby [6]helicenů fotocyklizací a zařízení k jeho provádění. (Czech) Method and Apparatus for Production of [6]Helicenes. Pat. No. PV 2012-245. Applied: 12.04.11.