

## Department of Organic Synthesis and Analytical Chemistry

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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
- Spin-spin coupling constants  $J(^{13}\text{C} - ^{13}\text{C})$
- 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
- Preparation of helicene based chiral stationary phases for HPLC

## Research projects

### Measurement of signed carbon-carbon couplings: methods improvements and their application

(V. Blechta, [blechta@icpf.cas.cz](mailto:blechta@icpf.cas.cz); supported by ICPF)

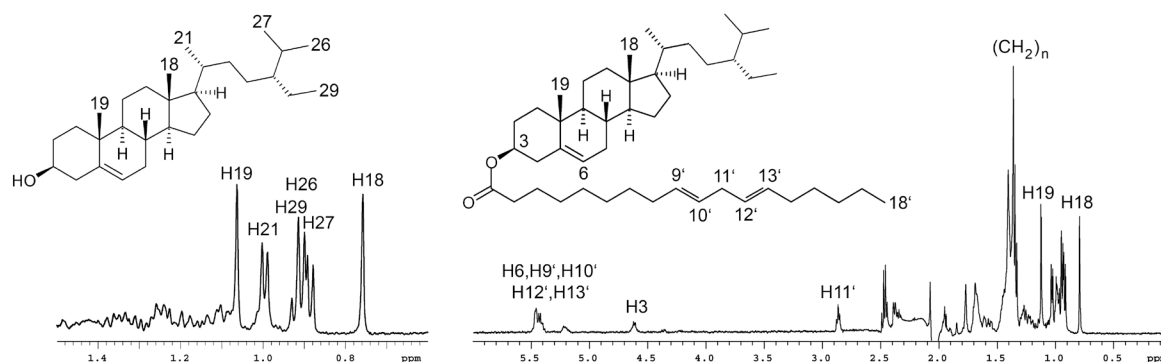
Signed values of all intra-ring  $^{2,3,4}J(C,C)$  couplings in 9 monosubstituted benzenes ( $C_6H_5-X$  where  $X = F, Cl, Br, CH_3, OCH_3, Si(CH_3)_3, C\equiv N, NO, NO_2$ ) were experimentally determined mainly by new HCSE method as well as 9 couplings to substituent carbons. It was confirmed that while all the vicinal intra-ring  $^3J(C,C)$  are positive and all geminal  $^2J(C_2,C_4)$  are negative, both signs are found for geminal  $^2J(C_1,C_3)$  couplings. All the determined signs agree with those already predicted by theoretical calculations.

Performance of HCSE experiment applied to detection of signed carbon-carbon couplings was discussed using a set of already measured samples of 9 monosubstituted benzenes. It was shown that coupling sign detection is insensitive to the settings of carbon-carbon polarization transfer delays. The HCSE spectra of 10 from the total of 43 measured carbon-carbon couplings were considerably influenced by relaxations and proton-proton strong couplings. These effects were quantitatively discussed. The results of HCSE and SLAP experiments were compared. It was shown that the two methods may complement each other in detection of signed carbon-carbon couplings. [Refs. 1, 2]

### LC-NMR technique in the analysis of phytosterols in natural extracts

(J. Sýkora, [sykora@icpf.cas.cz](mailto:sykora@icpf.cas.cz); supported by ICPF and TACR, project No. TA01010578)

The method shows ability of LC-NMR to detect simultaneously free and conjugated phytosterols in natural extracts. The advantages and disadvantages of a gradient HPLC-NMR method were compared to the fast composition screening using SEC-NMR method. Fractions of free and conjugated phytosterols were isolated and analyzed by isocratic HPLC-NMR methods. The results of qualitative and quantitative analyses were in a good agreement with previously published literature data. [Ref. 3]



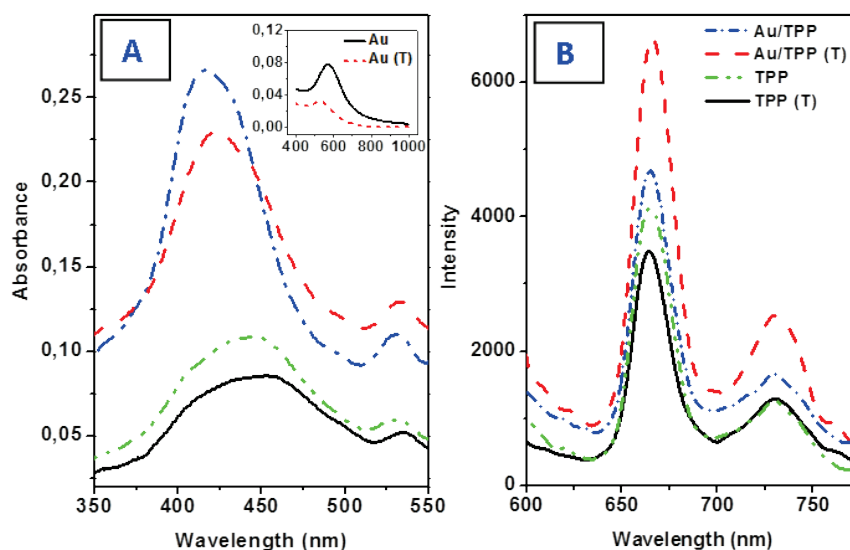
$^1H$  NMR spectra of free (left) and conjugated (right)  $\beta$ -sitosterol.  
Spectra were collected in a stop-flow LC-NMR experiment

### Surface morphology and optical properties of porphyrin/Au and Au/porphyrin/Au systems

(A. Solovyev, [solovyev@icpf.cas.cz](mailto:solovyev@icpf.cas.cz); supported by GACR, project No. 108/11/P840 and 108/12/1168)

Porphyrin/Au and Au/porphyrin/Au systems were prepared by vacuum evaporation and vacuum sputtering onto glass substrate. The surface morphology of as-prepared systems and

those subjected to annealing at 160 °C was studied by optical microscopy, atomic force microscopy, and scanning electron microscopy techniques. Absorption and luminescence spectra of as-prepared and annealed samples were measured. Annealing leads to disintegration of the initially continuous gold layer and formation of gold nanoclusters. An amplification of Soret band magnitude was observed on the Au/meso-tetraphenyl porphyrin (TPP) system in comparison with mere TPP. Additional enhancement of luminescence was observed after the sample annealing. In the case of sandwich Au/porphyrin/Au structure, suppression of one of the two porphyrins' luminescence maxima and sufficient enhancement of the second one were observed. [Ref. 5]



**Absorption(A) and luminescence(B) spectra of Au/TPP and TPP films annealed (T) at 1600 °C for 24 h**

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

(G. Kuncová, [kuncova@icpf.cas.cz](mailto: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).

### Printed Optical Chemical Sensors (POS)

(G. Kuncová, [kuncova@icpf.cas.cz](mailto:kuncova@icpf.cas.cz); joint project with Invos, s.r.o.; supported by TACR, project No. TA03010544)

We developed a fibre optical sensor of biogenic amines with the enzyme diamine oxidase from *Pisum sativum* immobilized on magnetic carriers (chitosan and acrylate micro beads) with optical oxygen transducer. Application of magnetic carriers enabled substantial simplification of enzyme immobilization. Attenuation of excitation and emission light due to absorption on the dark magnetic microparticles was fully compensated by the electrooptical system. The limits of detection for the biogenic amines putrescine and cadaverine are 25 – 30  $\mu\text{mol L}^{-1}$ , and responses are linear up to a concentration of 1  $\text{mmol L}^{-1}$ . [Ref. 8]

### Enzymatically catalyzed synthesis of alkyd resins

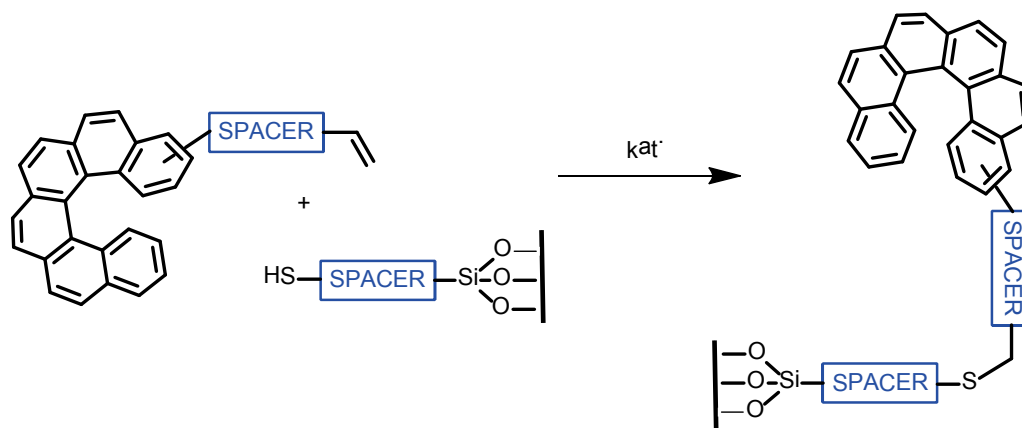
(G. Kuncová, [kuncova@icpf.cas.cz](mailto:kuncova@icpf.cas.cz); joint project with Synpo, a.s.; supported by MIT, project No. 2A-3TP1/108)

Processes for preparing alkyd resins and/or urethane alkyds and/or urethane oils based on plant and/or animal oils, conducting in two or more steps, lies in enzymatic alcoholysis, at temperature 40 - 70 °C. In the first step plant and/or animal oils and/or fatty acids and/or alkylesters of fatty acids of plant and or animal oils are subjected to transesterification. In the second step alcoholyzates are polycondensated with monocarboxylic and/or polycarboxylic acids and /or monoalcohols and/or polyalcohols. The third step is an addition reaction of alcoholyzate and polycondensate products, in which at first soever isocyanate sequentially monoalcohol are added. In case of preparation of urethane oils the first and third steps of this process are conducted only. [Ref. 15]

### Preparation of helicene based chiral stationary phase for HPLC

(J. Sýkora, [sykora@icpf.cas.cz](mailto: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 chiral stationary phase for HPLC which would serve for column manufacturing. The stationary phase is helicene based. The procedure for large scale production of helicene derivatives has been developed and patented. During the third year of project we has explored the 9-bromo[7]helicene reactivity and developed strategy for [7]helicene anchoring. Next step is the enantiomer separation and synthesis of the final chiral stationary phase. Further testing of its properties and evaluation of the relevancy for possible HPLC column production and sale is also part of the project objectives. [Refs. 13, 14]

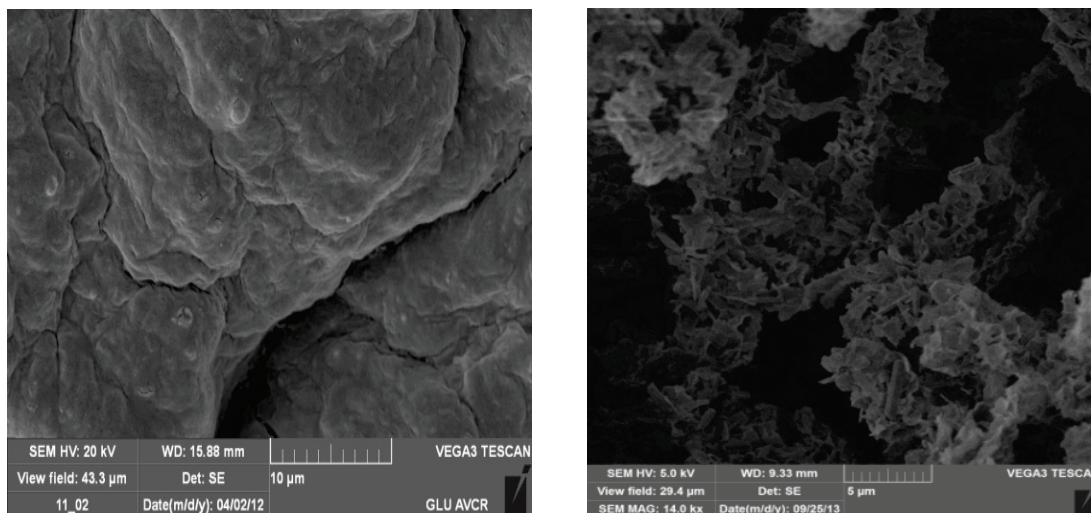


Schematical depiction of the helicene anchoring in order to form stationary phase

### Novel inorganic-organic hybrid nanomaterials

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

Na<sup>+</sup> 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 and 92% for biocatalyst frozen in liquid nitrogen.

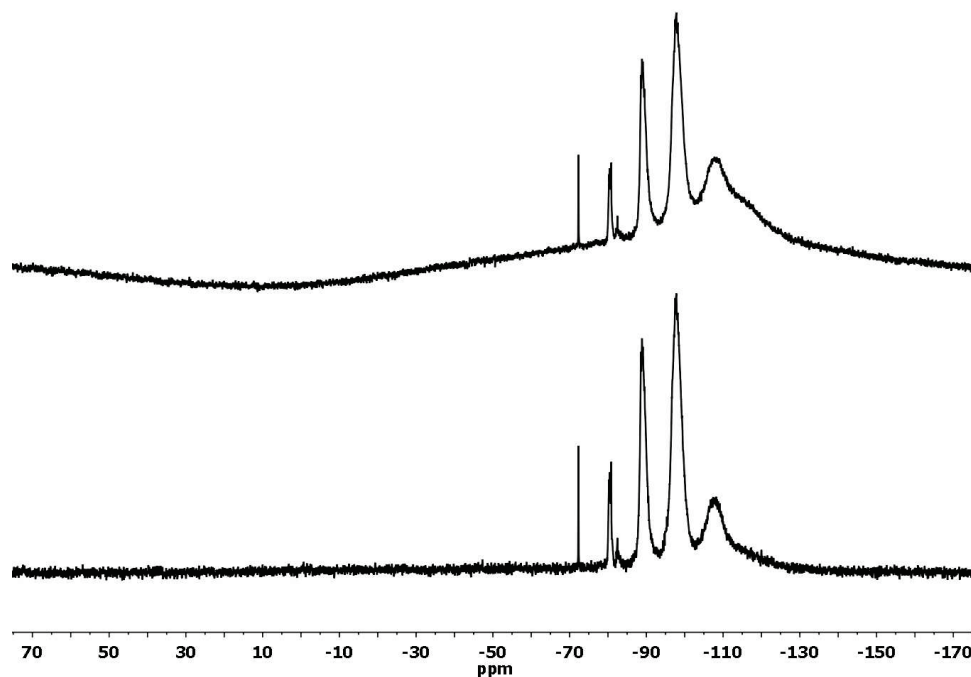


**Structure of lipase – montmorillonite biocatalyst (A) - dried at ambient temperature  
(B) – frozen in liquid nitrogen (ISISA)**

### Improved Baseline in $^{29}\text{Si}$ NMR Spectra of Water Glasses

(J. Schraml, [schraml@icpf.cas.cz](mailto:schraml@icpf.cas.cz); supported by ICPF)

In comparison with traditional NMR measuring methods (top trace) pulse sequence RIDE (bottom trace) eliminates background signal and dramatically improves baseline in  $^{29}\text{Si}$  NMR spectra of water glasses. [Ref. 10]



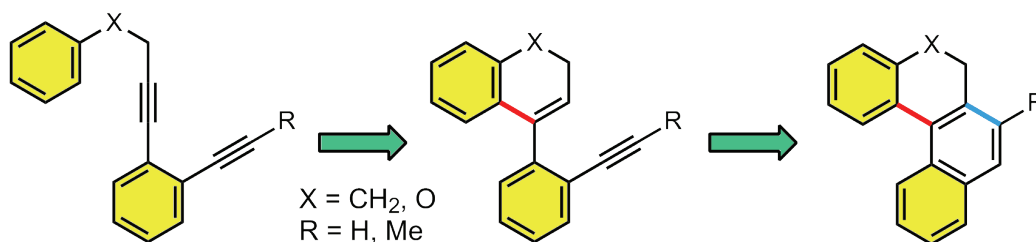
**$^{29}\text{Si}$  NMR spectra of a sodium water glass measured by one-pulse (top)  
and RIDE (bottom) pulse sequence**

### Intramolecular Cascade Hydroarylation/Cycloisomerization Strategy for the Synthesis of Polycyclic Aromatic and Heteroaromatic Systems

(J. Storch, [storchj@icpf.cas.cz](mailto:storchj@icpf.cas.cz); supported by TACR, project No. TA01010646)

In the quest of our previous investigations in the field of heterohelicenes for utilization in separation techniques and asymmetric catalysis, we have developed new  $\text{PtCl}_2/\text{PtCl}_4$  catalyzed

hydroarylation/cycloisomerization cascade reaction leading to formation of two aromatic or heteroaromatic rings in one step was reported. The strategy developed is exemplified by the synthesis of 5,6-dihydrobenzo[*c*]phenanthrene and 6H-naphtho[2,1-*c*]chromene skeletons. Attempts to [8]helicene-like molecules were also investigated. [Ref. 11]

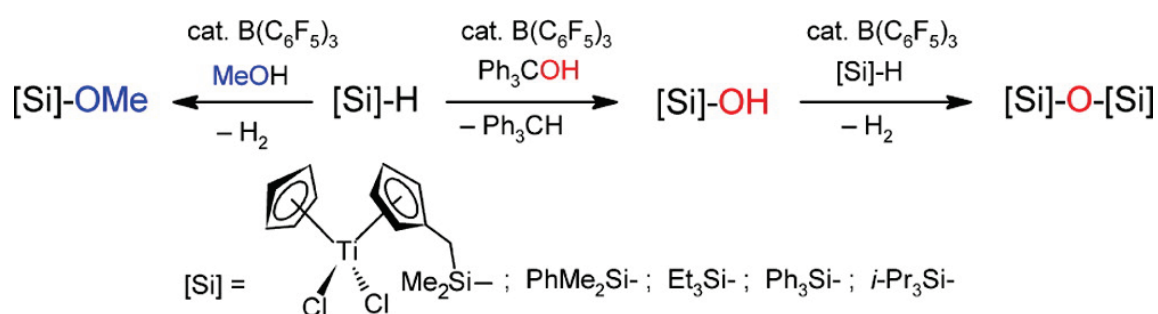


#### Hydroarylation / cycloisomerization cascade reaction

#### Reactivity of a Titanocene Pendant Si-H Group toward Alcohols

(T. Strašák, [strasak@icpf.cas.cz](mailto:strasak@icpf.cas.cz); joint project with JH IPC; supported by GACR, project No. 203/09/1574 and P207/12/2368).

This work has demonstrated the ability of a novel titanocene dichloride bearing a pendant methylenedimethylsilane group, to achieve methanol silylation in the presence of a catalytic amount of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in a way similar to that known for commercially available hydrosilanes. A possible extension of the reaction scope to a variety of alcohols could lead to a direct modification of the titanocene periphery with various alkoxy groups in one reaction step. However, Ph<sub>3</sub>COH reacted with prepared complex in a different way, and the dimeric titanocene complex with a bis(methylene)tetramethylsiloxane bridge between cyclopentadienyl rings was formed. A detailed study of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-mediated reaction of Ph<sub>3</sub>COH with the model hydrosilane PhMe<sub>2</sub>SiH showed that the siloxane formation proceeds in two consecutive steps. The fast initial step consists of hydroxyl group transfer from the trityl moiety to the silicon atom with concomitant formation of the silanol PhMe<sub>2</sub>SiOH and Ph<sub>3</sub>CH. In the next step, the in situ formed silanol undergoes a B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed silylation with a second equivalent of hydrosilane to form a siloxane and H<sub>2</sub>. The scope of the reaction could be extended to a variety of hydrosilanes. [Ref. 12]



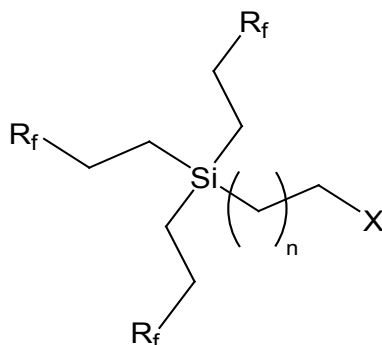
#### Reactivity of a Si-H group toward alcohols catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

#### Highly fluoruous cyclopentadienes for applications in catalysis

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

New approach to the synthesis of heavy fluoruous (i.e. showing high fluorophilicity) cyclopentadienes and cyclopentadienyl ligands was studied. The silicon atom is used as a branching atom and three (perfluoroalkyl)ethyl substituents are attached to it. The polyfluorinated synthons of the general formula shown below can be prepared by the reaction of the in situ formed organolithium reagent with silanes Cl(CH<sub>2</sub>)<sub>n</sub>SiCl<sub>3</sub> (n = 2, 3). The X group could

be either halogen ( $X = \text{Cl}, \text{Br}, \text{I}$ ) or halogen substituent could be replaced by other functional group leading thus to various useful products ( $X = \text{N}_3, \text{C}\equiv\text{CH}, \text{C}_5\text{H}_5$ ). [Ref. 16]



**Polyfluorinated synthons and their products;  $n = 2, 3$ ;  $R_f = \text{C}_6\text{F}_{13}$**

## 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:  $^{29}\text{Si}$  and  $^{119}\text{Sn}$  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

## Visitors

S. Ripp, University of Tennessee, USA

## 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., Schraml J.: Small Carbon-Carbon Couplings in Monosubstituted Benzenes - Their Signs and Magnitudes Determined by HCSE Method. *Magn. Reson. Chem.* 51(6), 378-381 (2013).
- [2] Blechta V., Schraml J.: HCSE Method for Detection of Small Carbo-Carbon Couplings and Their Signs, Comparison with SLAP Pulse Sequence. *Magn. Reson. Chem.* 51(11), 743-749 (2013).

- [3] Horník Š., Sajfrtová M., Karban J., Sýkora J., Březinová A., Wimmer Z.: LC-NMR Technique in the Analysis of Phytosterols in Natural Extracts. *J. Anal. Meth. Chem.* 2013, 526818 (2013).
- [4] Hudeček O., Budka J., Dvořáková H., Cuřínová P., Císařová I., Lhoták P.: Anion Receptors based on Ureidocalix[4]arenes Immobilised in the Partial cone Conformation. *New J. Chem.* 37(1), 220-227 (2013).
- [5] Kalachyova Y., Lyutakov O., Solovyev A., Slepíčka P., Švorčík V.: Surface Morphology and Optical Properties of 3 Porphyrin/Au and Au/Porphyrin/Au Systems. *Nanoscale Research Lett.* 8, 547 (2013).
- [6] Mačková M., Himl M., Budka J., Pojarová M., Císařová I., Eigner V., Cuřínová P., Dvořáková H., Lhoták P.: Self-assembly of 5,11,17,23-Tetranitro-25,26,27,28-tetramethoxythiacalix[4]arene with Neutral Molecules and its Use for Anion Recognition. *Tetrahedron* 69(4), 1397-1402 (2013).
- [7] Padělková Z., Švec P., Kampová H., Sýkora J., Semler M., Štěpnička P., Bakardjieva S., Willem R.: Unusual Reactivity of a C,N-Chelated Stannylene with Siloxanes and Silanols. *Organometallics* 32(8), 2398-2405 (2013).
- [8] Pospíšková K., Šafařík I., Šebela M., Kuncová G.: Magnetic Particles-based Biosensor for Biogenic Amines Using Optical Oxygen Sensor as a Transducer. *Microchim. Acta* 180(3-4), 311-318 (2013).
- [9] Sajfrtová M., Sovová H., Karban J., Rochová K., Pavela R., Barnet M.: Effect of Separation Method on Chemical Composition and Insecticidal Activity of Lamiaceae Isolates. *Ind. Crop. Prod.* 47, 69-77 (2013).
- [10] Schraml J., Sandor P., Korec S., Krump M., Foller B.: Improved Baseline in <sup>29</sup>Si NMR Spectra of Water Glasses. *Magn. Reson. Chem.* 51(7), 403-406 (2013).
- [11] Storch J., Bernard M., Sýkora J., Karban J., Čermák J.: Intramolecular Cascade Hydroarylation/Cycloisomerization Strategy for the Synthesis of Polycyclic Aromatic and Heteroaromatic Systems. *Eur. J. Org. Chem.* 2013(2), 260-263 (2013).
- [12] Strašák T., Sýkora J., Lamač M., Kubišta J., Horáček M., Gyepes R., Pinkas J.: Reactivity of Titanocene Pendant Si-H Group towards Alcohols. Unexpected Formation of Siloxanes from the Reaction of Hydrosilanes and Ph<sub>3</sub>COH Catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. *Organometallics* 32(15), 4122-4129 (2013).
- [13] Žádný J., Velíšek P., Jakubec M., Sýkora J., Církva V., Storch J.: Exploration of 9-bromo[7]Helicene Reactivity. *Tetrahedron* 69(30), 6213-6218 (2013).

#### Patents

- [14] Storch J., Církva V., Bernard M., Vokál J.: Způsob výroby [6]helicenů fotocyklizací. (Czech) Method and Apparatus for Production of [6]Helicenes. *Pat. No. 303997/PV 2012 - 245*. Applied: 12.04.11, Patented: 13.06.26.
- [15] Vlček T., Kuncová G., Šabata S., Hetflejš J.: Způsob přípravy alkydových pryskyřic, urethanizovaných alkydů a urethanových olejů. (Czech) Process for Producing Alkyd Resins, Urethane Alkyds and Urethane Oils. *Pat. No. 303842/PV 2012-147*. Applied: 12.03.01, Patented: 13.04.11.
- [16] Strašák T., Čermák J.: Polyfluorované činidlo a způsob jeho přípravy. (Czech) Polyfluorinated Reagent and Its Synthesis. *Pat. No. PV 2013-325*. Applied: 13.05.02.