



AHeRoC

Aromatic HeteRoCycles: A Wonderful Pool of Organic Materials

Virtual Meeting
March 16–17, 2022
Pardubice, Czech Republic

Organized by the
Department of Organic Materials
(BURES Group)
Institute of Organic Chemistry and Technology
Faculty of Chemical Technology
University of Pardubice
Czech Republic

Book of Abstracts

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Welcome from the Chairman

Dear colleagues and friends,

it is our immense pleasure to welcome you at the first meeting on Aromatic HeteRoCycles (AHeRoC). At the BURES group, we always look on organic molecules as perspective materials and are mostly interested in their functionality and added value. We perceive this viewpoint far more general, as an element gluing the community of chemists, physicists, engineers, and materials scientists. In this respect, aromatic compounds represent a very burgeoning and long-lasting area of research, which has significantly infiltrated modern organic devices across organic electronics, batteries, switches, sensors, catalysts, drugs and many others. In addition, the presence of a heteroatom within the aromatic structure brings new and even pronounced fundamental physico-chemical properties that may be further utilized in various fields.

Upon several years of consideration, we present herein the AHeRoC as a wonderful pool of organic materials. We strongly hope the AHeRoC would become a platform for sharing and exchanging ideas, knowledge, methodologies, organic molecules, and mostly to learn novel and fascinating applications of organic pi-systems. The latter is the main focus of the conference. In view of the current pandemic situation, we decided to organize the meeting online. Unfortunately, this decision has detrimental effect on meeting in person, but we also believe that it would significantly facilitate your attendance as no traveling is needed. The AHeRoC will comprise of several invited talks as well as contributed lectures that are mostly devoted to younger researchers. In order to make your attendance easier, the meeting is free-of-charge. Only a registration is required, you can attend even without a contribution. A link to online meeting will be send to all registered participants during March 2022. In addition, a special issue devoted to the AHeRoC is organized jointly with the Organics journal.

A HeRo of our meeting is Carbon!

We look forward to see your favorite aromatic (hetero)cycles and their function on 16-17th March 2022.

Filip Bureš

List of Speakers

AHeRoC Invited Speakers

Achelle Sylvain (University of Rennes, France)
Albrecht Łukasz (Lodz University of Technology, Poland)
Bhattacharya Santanu (Indian Institute of Science, India)
Castet Frédéric (University of Bordeaux, France)
Cibulka Radek (University of Chemistry and Technology, Prague, Czech Republic)
Fakis Mihalīs (University of Patras, Greece)
Hill Jonathan (National Institute for Materials Science, Japan)
Kivala Milan (Institute of Organic Chemistry, Heidelberg University Germany)
Młostoń Grzegorz (University of Łódź, Poland)

AHeRoC Contributed Lecturers

Bartáček Jan (University of Pardubice, Czech Republic)
Bouit Pierre-Antoine (University of Rennes, France)
Burešová Zuzana (University of Pardubice, Czech Republic)
Dey Nilanjan (Birla Institute of Technology and Science Pilani, Hyderabad Campus, India)
Hruzd Mariia (University of Rennes, France)
Jasiński Marcin (University of Lodz, Poland)
Kamlar Martin (Charles University, Czech Republic)
Klikar Milan (University of Pardubice, Czech Republic)
Kocúrik Martin (University of Pardubice, Czech Republic)
Marek Lukáš (University of Pardubice, Czech Republic)
Mongin Florence (University of Rennes, France)
Pavlovská Tetiana (University of Chemistry and Technology, Czech Republic)
Podlesný Jan (Institute of Technology and Business in České Budějovice, Czech Republic)
Pochobradský Jaroslav (University of Pardubice, Czech Republic)
Postils Ribó Verònica (University of Bordeaux, France)
Tydlitát Jiří (University of Pardubice, Czech Republic)
Ulč Jan (Charles University, Czech Republic)
Váňa Jiří (University of Pardubice, Czech Republic)

Organizing Committee

BUReS Group <https://bures.upce.cz>:

Filip Bureš - chairman

Zuzana Burešová

Milan Klikar

Jiří Kulhánek

Miroslav Ludwig

Patrik Pařík

Jiří Tydlitát

Jarmila Vlčková

Technical Support

Jiří Šarfa (University of Pardubice)

General Information

Topics Covered but Not Limited To:

(Hetero)aromatic compounds and general pi-systems.

Synthesis, purification, and characterization.

Fundamental and physico-chemical properties, studied both experimentally and theoretically.

Perspective applications of aromatic (hetero)cycles (unlimited).

Dates and Deadlines:

Abstract submission and registration: 18. 2. 2022

Date of the meeting: 16.-17. 3. 2022

Contributions:

Invited lecture: 40 min lecture + 10 min discussion

Contributed lecture: 15 min lecture + 5 min discussion

Presentation:

Teams software has been selected as online platform. ***The appropriate link will be sent to all speakers on Monday 14th March 2022 afternoon.*** You will share your slides directly from your computer, feel free to use any favorite software when preparing your presentation.

The technical session is scheduled on Monday 14th March 2022 at 8:00-10:00 AM (GMT+1); all speakers are requested to test their connection and ability to properly share your slides. ***A separate link*** will be sent to all speakers and attendees to this session. Brief instructions how to get connected will be provided at the conference webpage.

All attendees are requested to connect into Teams via your name or email address you have used during registration, otherwise we may not grant access to the online meeting.

Language:

The official language of the meeting is English.

A Virtual Visit:

The Faculty of Chemical Technology, University of Pardubice can be 3D-visited here (only in Czech):

<https://fcht.upce.cz/fcht/virtualni-3d-modely-fakulty>

Special Issue - Organics

Organics became the AHeRoC publishing partner. All speakers and listeners are encouraged to submit their manuscript to a special issue devoted to AHeRoC:

https://www.mdpi.com/journal/organics/special_issues/AH_WPOM

Sponsor

The AHeRoC meeting is supported by the European Regional Development Fund-Project “Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)”, No. CZ.02.1.01/0.0/0.0/16_025/0007445.



EUROPEAN UNION
European Structural and Investment Funds
Operational Programme Research,
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Scientific Program

All times are listed in GMT+01:00 (Prague)! (IND GMT+05:30, CHN GMT+8:00, JPN GMT+09:00)

Wednesday March 16th, 2022

8:50-9:00		Bureš F.	Opening and Invitation
9:00-9:50	PL1	Hill J. P.	The Pyrazinacenes
9:50-10:10	CL1	Hruzd M.	Tuning the Luminescence Properties of Cyclometallated Platinum(II) Complexes based on Phenylidiazine N [^] C Ligands
10:10-10:30	CL2	Dey N.	Y-shaped Push-Pull Heterocyclic Dyes for 'Naked-eye' Detection of Environmental Toxins via Mild Chemical Reactions
10:30-11:20	PL2	Castet F.	Dynamics of the Second-Order Nonlinear Optical Responses of Organic Materials
11:20-11:40	CL3	Postils Ribó V.	Second-order NonLinear Optical Properties of Λ -Shaped Pyrazine Derivatives Enlarged with 2,5-Thiophene Groups
11:40-12:00	CL4	Podlesný J.	Isomeric Thienothiophene Push-Pull Molecules with Tunable (Non)Linear Properties and Photoinduced <i>E/Z</i> Switching
12:00-13:00	<i>Lunch</i>		
13:00-13:50	PL3	Achelle S.	Development of π -Conjugated Pyrimidine Derivatives as Applied Luminescent Materials
13:50-14:10	CL5	Tydlitát J.	Controlled Emission with Pyridin
14:10-14:30	CL6	Klikar M.	Tripodal Fluorophores with Diazine Acceptors at the Periphery
14:30-15:20	PL4	Fakis M.	Photodynamics and 2-Photon Absorption Properties of Push-Pull Molecules with Heterocycle Substituents by Means of fs Laser Spectroscopy
15:20-16:10	PL5	Cibulka R.	Flavins – Not Only Cofactors but Also Versatile Photocatalysts
16:10-16:30	CL7	Burešová Z.	Electrochemical Study on Viologen Based Azinium Heteroaromatics
16:30-16:50	CL8	Pavlovská T.	An Efficient One-Pot Three-Component Synthesis of Functionalized 5-Aryldeazaflavins for the Photoredox Catalysis

Thursday March 17th, 2022

9:00-9:50	PL6	Bhattacharya S.	Covalent Organic Square Lattice Building Blocks toward the Supercapacitive Energy Storage
9:50-10:10	CL9	Bouit P.-A.	Twisting and Bending π -System with 7-Membered P-Rings
10:10-10:30	CL10	Pochobradský J.	Use of Isochinoline-Oxazoline Ligand in Heterogenous Catalysis
10:30-10:50	CL11	Kamlar M.	Enantioselective PCCP Brønsted Acid-Catalyzed Synthesis of 2,3-Dihydroquinazolinone
10:50-11:40	PL7	Kivala M.	Alkynes and Bridged Triarylamines as Versatile Construction Elements for Functional Molecular Materials
11:40-12:00	CL12	Ulč J.	Iridium and Rhodium Catalysed C–C Bond Cleavage in 1-Aza-[3]triphenylene
<i>12:00-13:00 Lunch</i>			
13:00-13:50	PL8	Mlostoń G.	Imidazole <i>N</i> -Oxides as Promising Substrates for Generation of Nucleophilic Carbenes (NOHCs) and for Synthesis of Naturally Occurring Imidazole Alkaloids (Lepidilines A-D)
13:50-14:10	CL13	Kocúrik M.	Palladium (II) Complex of Pyridine-Oxazoline-Type Ligand as a Homogeneous/Heterogeneous Catalyst for Enantioselective Addition of Arylboronic Acids to Cyclic Ketimines
14:10-14:30	CL14	Jasiński M.	Synthesis of 3-Trifluoromethylpyrazoles via 1,3-Dipolar Cycloaddition Reactions and Subsequent Oxidative Aromatization of Cycloadducts Derived from Trifluoroacetonitrile Imines
14:30-15:20	PL9	Albrecht Ł.	New Dearomative Strategies in Stereocontrolled Organic Synthesis
15:20-15:40	CL15	Mongin F.	From Aromatic Iodides to Heterocycles of Interest
15:40-16:00	CL16	Bartáček J.	Polymer-supported Palladium (II) Complex of Pyridine-Oxazoline as a Recyclable Catalyst for an Asymmetric Addition of Arylboronic Acids to Conjugated Cyclic Enones
16:00-16:20	CL17	Váňa J.	Reactivity and Site-selectivity of C–H Functionalization Reactions: The Acid Effect
16:20-16:40	CL18	Marek L.	Transformations of Thioiminium Salts Derived α -Bromoamides
16:40-16:45		Bureš F.	Closing

Plenary Lectures

The Pyrazinacenes

Jonathan P. Hill,^a Gary J. Richards,^b David Miklík^c

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^b Department of Applied Chemistry, Graduate School of Engineering and Science, Shibaura Institute of Technology, Fukasaku 307, Minuma-ku, Saitama-shi, Saitama 337-8570, Japan.

^c Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic

Acenes and azaacenes lie at the core of molecular materials' applications due to their important optical and electronic features. A critical aspect is provided by their heteroatom multiplicity, which can strongly affect their properties. Here we discuss pyrazinacenes [1] containing fused oligopyrazine chromophores, including decaazapentacene [2] and higher chromophores [3], and compare their properties/functions at metal substrates or in solution. We find a distinguished, oxidation-state-dependent conformational adaptation and self-assembly behaviour and discuss the analogies and differences of planar benzo-substituted decaazapentacene and octaazatetracene forms. Decaazapentacenes and the higher tetradecaazaheptacene analogues studied here combine a planar molecular backbone with conformationally flexible substituents. They provide a rich model case to understand the properties of a redox-switchable π -electronic system in solution and at interfaces. Pyrazinacenes represent an unusual class of redox-active chromophores whose properties depart from usual acenes and lower heteroacenes.

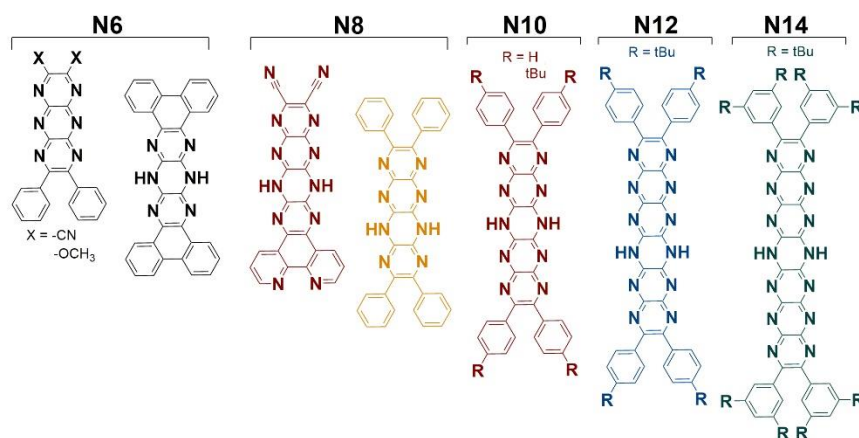


Figure 1. Pyrazinacenes discussed in this work.

Acknowledgement: This work was partly supported by World Premier International Research Center Initiative (WPI Initiative), MEXT, Japan.

References:

- [1] Richards, G. J.; Hill, J. P. The Pyrazinacenes. *Acc. Chem. Res.* **2021**, *54*, 3228.
- [2] Miklík, D.; Mousavi, S. F.; Jung, T. A.; Hill, J. P.; *et al.*; *Commun. Chem.* **2021**, *4*, 29.
- [3] Richards, G. J.; Hill, J. P.; *et al.* *J. Am. Chem. Soc.* **2019**, *141*, 19570.

Dynamics of the Second-Order Nonlinear Optical Responses of Organic Materials

Frédéric Castet

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Quantum chemical calculations have been widely used during the last thirty years for rationalizing the second-order nonlinear optical (NLO) responses of small molecules or π -conjugated organic chromophores. However, most of theoretical reports assume a rigid picture of the investigated systems, the NLO responses being computed on the basis of the most stable geometry of the chromophores. Yet, recent theoretical reports combining classical molecular dynamics simulations and DFT calculations have evidenced the significant role of structural fluctuations, which may induce broad statistical distributions of the NLO responses. In this talk, we will present some case studies in which theoretical simulations have highlighted the crucial role of dynamical disorder onto the NLO responses of the investigated systems. Selected examples will include photochromic systems in solution, [1] as well as large and flexible supramolecular assemblies such as nanoparticles [2] and self-assembled monolayers [3] (Figure 1).

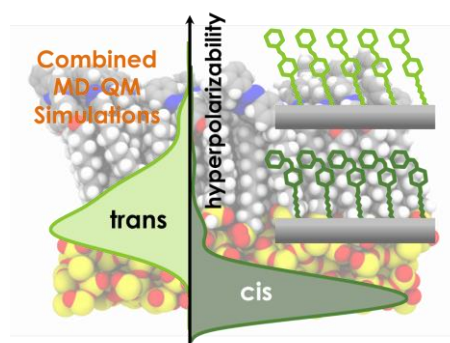


Figure 2. Illustration of the hyperpolarizability contrast upon commutation in azobenzene-based monolayers.

References:

- [1] Pielak, K.; Tonnelé, C.; Sanguinet, L.; Cariati, E.; Righetto, S.; Muccioli, L.; Castet, F.; Champagne B. Dynamical behavior and second harmonic generation responses in acido-triggered molecular switches *J. Phys. Chem. C*. **2018**, *122*, 26160-26168.
- [2] Lescos, L.; Beaujean, P.; Tonnelé, C.; Aurel, P.; Blanchard-Desce, M.; Rodriguez, V.; de Wergifosse, M.; Champagne, B.; Muccioli, L.; Castet F. Self-assembling, structure and nonlinear optical properties of fluorescent organic nanoparticles in water *Phys. Chem. Chem. Phys.* **2021**, *23*, 23643-23654.
- [3] Tonnelé, C.; Champagne, B.; Muccioli, L.; Castet F. Nonlinear Optical Contrast in Azobenzene-Based Self-assembled Monolayers *Chem. Mater.* **2019**, *31*, 6759-6769.

Development of π -Conjugated Pyrimidine Derivatives as Applied Luminescent Materials

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During the past two decades, there has been great interest in the synthesis of pyrimidine fluorophores. Pyrimidine is a six-membered heterocycle with two nitrogen atoms (1,3-diazine) that exhibits strong electron-withdrawing character. When the pyrimidine ring is combined with electron-donating fragments via π -conjugated linkers, intramolecular charge transfer (ICT) occurs, generally leading to strong emission. During the last ten years we have described more than 250 pyrimidine fluorophores [1]. In this contribution we will focus on selected examples of pyrimidine chromophores used as advanced luminescent materials. Our presentation will focus particularly on fluorescent sensors for the detection of nitroaromatic explosives (Figure 1) [2], white-light emitting materials obtained by controlled protonation (Figure 2) [3] or combination of locally excited and long-lived, intramolecular charge-transfer states [4], and two-photon excitation fluorescence [5].

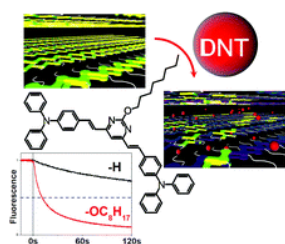


Figure 1.

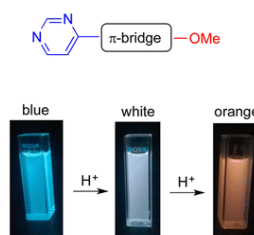


Figure 2.

References:

- [1] Achelle, S.; Rodríguez-López, J.; Robin le-Guen F. Photoluminescence properties of aryl-, arylvinyl-, and aryethynylpyrimidine derivatives. *ChemistrySelect* **2018**, *3*, 1853-1886.
- [2] Malval J.-P.; Cranney M.; Achelle, S.; Akdas-Kiliç, H.; Fillaut, J.-L.; Cabon, N.; Robin-le Guen, F.; Soppera, O.; Molard, Y. Porosity-driven large amplitude dynamics for nitroaromatic sensing with fluorescent films of alternating D- π -A molecules. *Chem. Commun.* **2019**, *55*, 14331-14334.
- [3] Achelle, S.; Rodríguez-López, J.; Bureš, F.; Robin-le Guen, F. Tuning the photophysical properties of push-pull azaheterocyclic chromophores by protonation: A brief overview of a French-Spanish-Czech Project. *Chem. Rec.* **2020**, *20*, 440-451.
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- [5] Kournoutas, F.; Fihey, A.; Malval, J.-P.; Spangenberg, A.; Fecková, M.; le Poul, P.; Katan, C.; Robin-le Guen, F.; Bureš, F.; Achelle, S.; Fakis M. Branching effect on the linear and nonlinear optical properties of styrylpyrimidines. *Phys. Chem. Chem. Phys.*, **2020**, *22*, 4165-4176.

Photodynamics and 2-Photon Absorption Properties of Push-Pull Molecules with Heterocycle Substituents by Means of fs Laser Spectroscopy

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Over the past decades there has been tremendous progress in the field of fs laser technology. Nowadays, state of the art fs spectroscopic techniques, based on fs lasers, allow us to disentangle complex dynamics and to investigate non-linear optical properties by providing great temporal resolution, high accuracy, broadband spectral coverage, extreme light intensities while on the same time by avoiding thermal effects.

Push-pull heterocycle molecules are considered model molecules for studying fundamental processes such as Intramolecular Charge Transfer (ICT), white light emission through protonation and selective energy transfer, as well as for applications in non-linear optics, sensors etc. Within, the last years we have studied a great amount of push-pull heterocycle molecules exhibiting rich photodynamics and enhanced non-linear optical properties [1-4]. Here, we will review some laser spectroscopy techniques based on fs lasers and we will focus on describing the most important results regarding ultrafast dynamics and 2-photon absorption for pyridine, pyrimidine, tria-zine and quinazoline chromophores.

References:

- [1] Plaza-Pedroche, R.; Georgiou, D.; Fakis, M.; Fihey, A.; Katan, C.; Robin-le Guen, F.; Achelle, S.; Rodríguez-López, J. Effect of protonation on the photophysical properties of 4-substituted and 4,7-disubstituted quinazoline push-pull chromophores. *Dyes Pigm.* **2021**, *185*, 108948.
- [2] Fecková, M.; Kalis, I. K.; Roisnel, T.; le Poul, P.; Pytela, O.; Klikar, M.; Robin-le Guen, F.; Bureš, F.; Fakis, M.; Achelle, S. Photophysics of 9,9-dimethylacridan substituted phenylstyrylpyrimidines exhibiting long lived intramolecular charge transfer fluorescence and aggregation induced emission characteristics. *Chem. A Europ. J.* **2021**, *13*, 1145-1159.
- [3] Kournoutas, F.; Fihey, A.; Malval, J.-P.; Spangenberg, A.; Fecková, M.; le Poul, P.; Katan, C.; Robin-le Guen, F.; Bureš, F.; Achelle, S.; Fakis, M. Branching effect on the linear and nonlinear optical properties of styrylpyrimidines. *PhysChemChemPhys* **2020**, *22*, 4165-4176.
- [4] Kournoutas, F.; Kalis, I. K.; Fecková, M.; Achelle, S.; Fakis, M. The effect of protonation on the excited state dynamics of pyrimidine chromophores. *J. Photochem. Photobiol. A: Chem.* **2020**, *391*, 112398.

Flavins – not only cofactors but also versatile photocatalysts

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Photoexcitation allows chemical transformations that are not accessible by conventional methods. Use of visible light combined with a photocatalyst even improves classical photochemical methodologies avoiding side reactions of functionalities sensitive to UV light and making photochemistry available for most laboratories. Nowadays, photo-redox catalysis with organic photocatalysts is of a growing interest because of low costs of organic dyes and new reactions that they are able to mediate thus expanding the boundaries of organic synthesis [1].

Several organic dyes including simple aromatic heterocyclic compounds have been found to provide a certain type of transformations involving either photoreductive or photooxidative catalytic cycle. However, there is only limited number of photocatalysts, which are characterized by versatile reactivity [2]. Flavins (Figure 1), prominent natural chromophores, are characterized by several stable redox and excited states [3]. Additionally, three-ring flavin (isoalloxazine) structure offers great option to tune redox and photophysical properties. Thus, flavin-based photocatalysts are destined to drive a diverse range of chemical reactions. Among flavin derivatives, one can find ethylene-bridged flavinium salts **1**, behaving as strong oxidizing species [4]. On the other hand, an excited radical anion of 5-phenyldeazaflavin **2** is one of the strongest reducing species comparable with alkaline metals [5]. In the presentation, rational design of flavin-based photocatalytic systems and their application in aerial oxidations, C-H activations, and in photoreductions will be discussed.

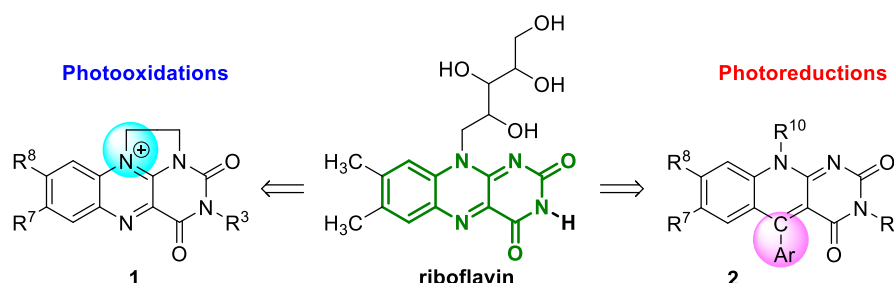


Figure 3. Riboflavin with highlighted isoalloxazine ring and flavin derivatives used in photoredox catalysis.

Acknowledgement: Author thanks the Czech Science Foundation (grant No 21-14200K) for financial support.

References:

- [1] Sideri, I. K.; Voutyritsa, E.; Kokotos, C. G. *Org. Biomol. Chem.* **2018**, *16*, 4596-4614.
- [2] Targos, K.; Williams, O. P.; Wickens, Z. K. *J Am Chem Soc* **2021**, *143*, 4125-4132.
- [3] Cibulka, R.; Fraaije, M. W. In *Flavin-Based Catalysis* 2021, p 97-124.
- [4] Pokluda, A.; Anwar, Z.; Boguschová, V.; Anusiewicz, I.; Skurski, P.; Sikorski, M.; Cibulka, R. *Adv. Synth. Catal.* **2021**, *363*, 4371-4379.
- [5] Graml, A.; Neveselý, T.; Jan Kutta, R.; Cibulka, R.; König, B. *Nature Comm.* **2020**, *11*, 3174.

Covalent Organic Square Lattice Building Blocks toward the Supercapacitive Energy Storage

Santanu Bhattacharya

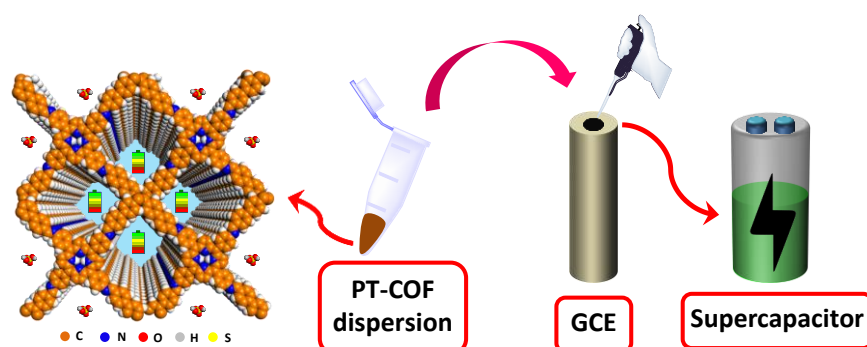
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Covalent organic frameworks (COFs) are of growing interest in the field of materials science. Polymerizations of the topologically fitted monomers into two-dimensional (2D) structures with periodic order often make them crystalline. The existence of this structural periodicity and regular pores makes them effective for facile ion transport and storage applications. We have synthesized a Porphyrin-Tetraphenyl ethylene COF (**PT-COF**) which possesses high crystallinity along with a large surface area of nearly $2000 \text{ m}^2 \text{ g}^{-1}$. The presence of porphyrin unit inside the framework helps for good redox activity in the acidic media.



Alkynes and Bridged Triarylaminines as Versatile Construction Elements for Functional Molecular Materials

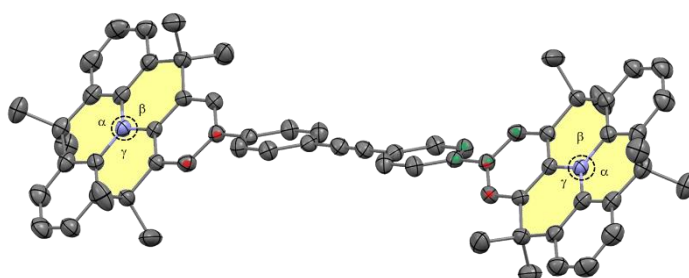
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<https://www.uni-heidelberg.de/fakultaeten/chemgeo/oci/akkivala/index.html>

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Triarylaminines and their bridged counterparts have in the meanwhile become ubiquitous in the area of organic electronics owing to their appreciable electron donor and hole transport properties [1]. We have recently realized that various structurally relatively simple triarylaminines in combination with the highly reactive acetylenic moieties may serve as versatile building blocks for the construction of novel nitrogen-containing polycyclic aromatic hydrocarbons (PAHs). In these compounds nitrogen readily adopts a planar sp^2 -hybridized geometry to provide for efficient electronic communication with the surrounding π system [2,3]. The resulting PAHs are highly attractive objects for fundamental studies as defined molecular fragments of heteroatom-doped carbon allotropes on one hand and as functional materials for diverse applications on the other.



In this talk, our recent synthetic efforts will be presented and the fundamental characteristics of the resulting compounds discussed.

Acknowledgement: This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) – Project number 182849149 – SFB 953 and Project number 281029004 – SFB 1249.

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Imidazole *N*-Oxides as Promising Substrates for Generation of Nucleophilic Carbenes (NOHCs) and for Synthesis of Naturally Occurring Imidazole Alkaloids (Lepidilines A-D)

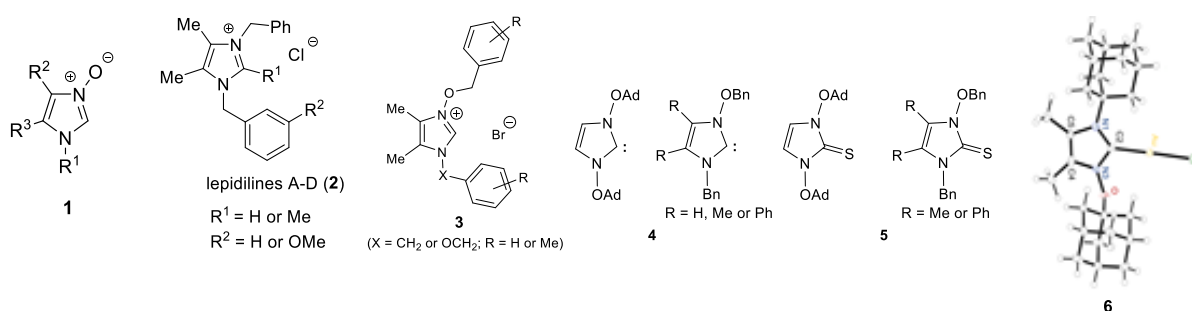
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Heterocyclization of α -hydroxyiminoketones with methyldieneamines, leading to 2-unsubstituted imidazole *N*-oxides **1** can be performed either in boiling EtOH or in AcOH at room temperature [1]. In addition, mechanochemical approach, based on a ball-milling procedure, have recently been elaborated in our group [2]. The *N*-oxides **1** are known to act as versatile substrates for preparation of more complex and practically useful imidazole derivatives and their 1,3-dipolar cycloadditions offer a superior method for these multi-step conversions. In this paper, synthesis of lepidilines A-D (**2**) [3a] as well as their benzyloxy analogues **3** [3b], starting with imidazole *N*-oxides **1**, will be discussed.



In recent three decades, nucleophilic carbenes (NHCs) attract great attention. In a series of recent publications, efficient methods for generation of mono- and dialkoxyimidazol-2-ylidenes, e.g. **4** (NOHCs) as well as their further sulfurization leading to non-enolizable imiazole-2-thiones **5** have been published [3]. Optically active NOHCs have also been in situ generated and converted into corresponding imidazole-2-thiones **5** [4]. In contrast to the Arduengo carbene, free NOHCs could not be isolated but they were efficiently trapped with Au(I), Ag(I), and Cu(I) salts forming respective metal complexes e.g. **6** ([1-adamantyloxy-3-adamantyl-4,5-dimethylimidazol-2-ylidene]·AuCl) [5].

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New Dearomative Strategies in Stereocontrolled Organic Synthesis

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Identification of new reactivity pathways constitutes one of the most significant tasks in the contemporary organic chemistry. In particular, the development of enantioselective reactions where prochiral substrates are converted into enantiomerically enriched products in the presence of chiral catalyst are of great importance [1]. Recently, asymmetric organocatalysis, where simple organic molecules are used as catalysts of various enantiodifferentiating reactions, has become a highly useful synthetic tool enabling for the efficient asymmetric induction based on diverse activation modes [2]. Within this research area, the application of dearomative strategies created new synthetic opportunities for the functionalization of (hetero)aromatic compounds [3]. Herein, we report our studies on organocatalytic, enantioselective dearomative strategies for the synthesis and functionalization of biologically relevant heteroaromatic compounds [4].

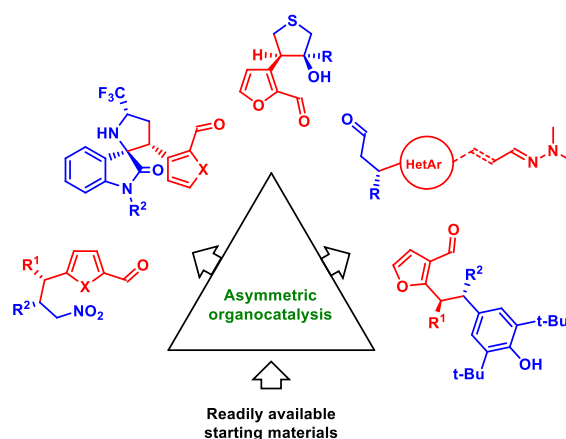


Figure 4. Organocatalytic dearomative strategies for the functionalization of heteroaromatic frameworks.

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Contributed Lectures

Tunning the Luminescence Properties of Cyclometallated Platinum(II) Complexes based on Phenylidiazine N[^]C Ligands

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Organic light-emitting diodes (OLEDs) have attracted much attention in the past few decades and are considered as remarkably attractive candidates for flat panel display technologies and solid-state lighting [1]. Phosphorescent heavy-metal complexes, such as platinum(II) complexes, with long-lived excited state lifetime are able to efficiently harvest both singlet and triplet electro-generated excitons, thus opening the possibility to achieve theoretically 100% internal quantum efficiency in such devices [2].

Cyclometallated platinum(II) complexes based on diazines ligands display strong phosphorescence and electroluminescence (EL) and they could be utilized as light emitting materials in OLEDs [3]. It is easy to alter electronic structures and photophysical properties of platinum complexes by modification of the coordinated ligands [4,5].

In a preliminary communication we have demonstrated that some Pt(II) complexes with phenylpyrimidine N[^]C ligands can exhibit interesting emission properties in solution and solid state when judiciously substituted [6]. In this presentation, we will describe the synthesis and photophysical properties of a new series of Pt(II) complexes with phenyl(benzo)diazine ligand. The influence of various structural modification on photophysical properties had been thoroughly studied and structure properties relationships were highlighted.

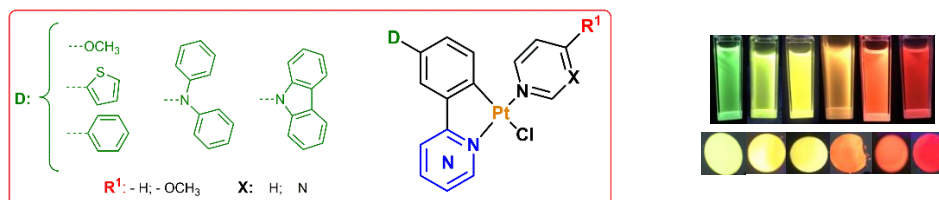


Figure 5. Chemical structures and picture (taken under UV) of the investigated cyclometallated platinum(II) complexes.

Acknowledgements: M. H. thanks Region Bretagne and the Département des Côtes d'Armor for funding.

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Y-shaped Push-Pull Heterocyclic Dyes for 'Naked-eye' Detection of Environmental Toxins via Mild Chemical Reactions

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Organic dipolar molecules have recently captivated enormous attention due to their wide structural diversity and tunable optoelectronic properties. In a typical organic D- π -A molecule, the electron donor (D = NR₂ or OR groups) and acceptor (A = NO₂ or CN groups) moieties are connected via a π -conjugated spacer unit. The polarizability of such compounds depends on the overall chemical structure, such as the electronic characteristics of the donor and acceptor units, geometry, length, as well as nature of the π -conjugated linker. Thus, these photoresponsive materials are often utilized in two-photon-absorbing devices, optoelectronics and data storage systems, organic light-emitting diodes, organic photovoltaic cells, etc. Sometimes, five-membered heteroaromatic rings, such as thiophene or imidazole, are incorporated in the spacer unit to construct a robust π conjugated backbone with a larger hyperpolarizability. On the other hand, the fluorescence response of such dye molecules also depends on the nature of the π -linker (electronic characteristics, rigidity etc). Despite these, application of such systems in biomolecular analysis remained underexplored. Considering these, herein we have employed heterocycles-Functionalized Y-Shaped Push-Pull Dyes for reaction-based recognition of toxic ions (such as Cu²⁺, Hg²⁺ etc) and gaseous analytes (nerve gas mimics). Analyte-coordination at the heterocycle (thiophene or imidazole) residue of the π -linker diminishes the extent of the intramolecular charge-transfer (ICT) interaction, leading to hypsochromic shift in absorption maxima.

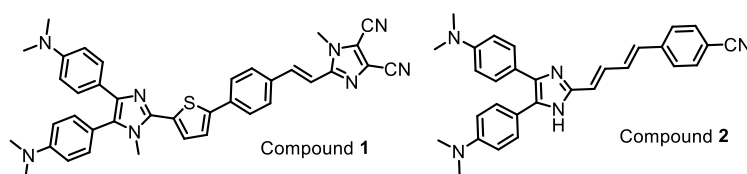


Figure 6. Push-Pull Heterocyclic Dyes involved in the optical sensing of environmental toxins.

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Second-order NonLinear Optical Properties of Λ -Shaped Pyrazine Derivatives Enlarged with 2,5-Thiophene Groups

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The linear and nonlinear optical (NLO) properties of two new series of pyrazine derivatives have been investigated by means of density functional theory [1]. The derivatives comprise cyano groups as acceptor units, methoxy groups as donor units, and 2,5-thiophene groups as π -conjugated linkers that systematically enlarge the Λ shape of the chromophores. The two series of compounds differ in the relative position of the donor and acceptor groups in the pyrazine, forming 2,3- or 2,6-isomers. Both series of isomers present potential C_{2v} symmetry with a different orientation of the C_2 axis and the σ_v plane of the symmetry point group: in the pyrazine plane but perpendicular to the N-N pyrazine's axis for the 2,3-isomers, and in the pyrazine plane and containing the N-N pyrazine's axis for the 2,6-isomers (Figure 1). Focusing on the different orientation of the C_{2v} symmetry elements and how these structural changes affect the electronic structure and the characterization of the electronic excited states of the chromophores, a rationalization of the second-order nonlinear responses (mainly Hyper-Rayleigh Scattering (HRS) hyperpolarizabilities) will be done from a fundamental point of view [2].

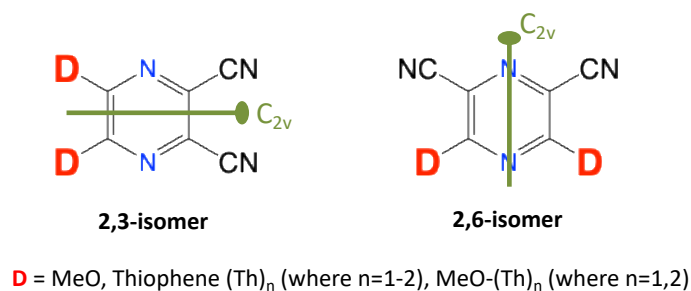


Figure 7. Pyrazine derivatives investigated in this work.

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Isomeric Thienothiophene Push-Pull Molecules with Tunable (Non)Linear Properties and Photoinduced *E/Z* Switching

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Twenty new push-pull chromophores derived from electron-donor thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene heterocycles (Figure 1.) were prepared through facile synthetic routes [1,2]. Tailoring of optical, electrochemical and thermal properties was achieved by alternation of acceptor units or extension of the π -linker between electron-donating and electron-withdrawing moieties. Detailed study focused on structure-property relationships elucidation was performed using UV-VIS absorption spectroscopy, cyclic voltammetry, differential scanning calorimetry, thermogravimetric analysis and investigation of second- and third harmonic generation. Gathered experimental data were also supplemented by DFT calculations to study spatial and electronic properties of all synthesized target heterocyclic compounds. Based on the structural arrangement, extended thieno[3,2-*b*]thiophene chromophores with an inserted double bond proved to be photoinducible molecular *E/Z* switches. The *Z* isomer can be partly obtained by Royal Blue LED irradiation, while *E* isomeric form is subsequently fully regenerated in the dark.

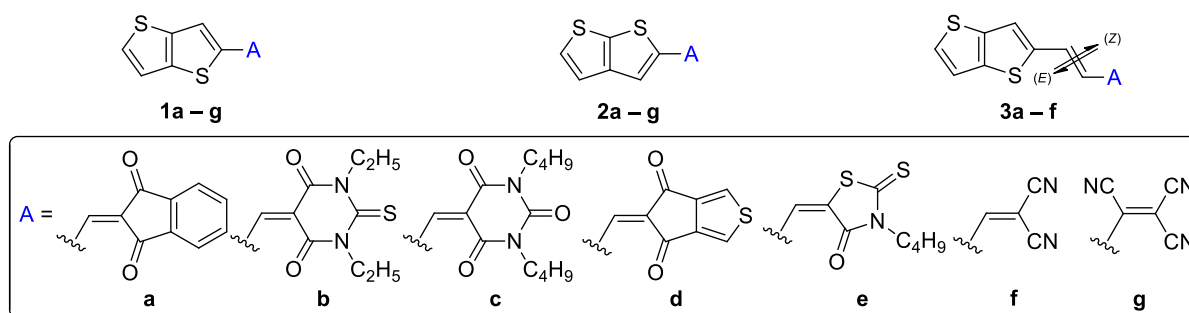


Figure 8. Synthesized thienothiophene push-pull chromophores.

Acknowledgement: This work has been supported by the European Regional Development Fund-Project “ORGBAT” No. CZ.02.1.01/0.0/0.0/16_025/0007445.

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Controlled Emission with Pyridin

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During early '50s, electroluminescence of organic compounds, namely acridine and carbazole derivatives, was observed for the first time. Despite this fact, a new branch of organic chemistry, organic electronics, began to develop in late '80s. The interest in organic materials is mainly due to several advantages over inorganic materials. These include lower price and toxicity, facile property tuning by simple structural modifications as well as easier fabrication. Organic emissive and color-changing materials found wide applications. D- π -A chromophores with various shapes [1] belong to such materials with variable donors, acceptors and π bridges and manifold applications in OLEDs, OPVs, NLO, and emissive materials for sensors. Triphenylamine (TPA) is widely used as central unit of D- π -A molecules. Upon its decoration with various number of peripheral pyridine acceptors as well as various peripheral donors, we have prepared push-pull compounds, with various emissions [2,3] (Figure 1).

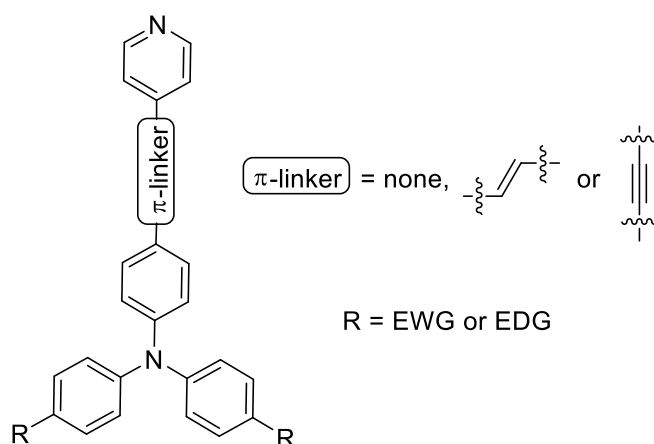


Figure 9. Pyridine-TPA fluorophores.

Acknowledgement: This work has been supported from European Regional development Fund-Project "Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)" No.CZ.02.1.01/0.0/0.0/16_025/0007445.

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Tripodal Fluorophores with Diazine Acceptors at the Periphery

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To date, a wide variety of push-pull chromophores have been designed and synthesized employing a diverse portfolio of D, π , and A moieties. A number and mutual arrangement of D, π , and A parts can be further evolved to form π -systems with unique shapes and octupolar character [1]. Among them, the tripodal D-(π -A)₃ chromophores based on the central triphenylamine (TPA) donor have a privileged position. Moreover, star-shaped TPA chromophores are well-known to bring expanded conjugation leading to enhancement of two-photon absorption (2PA) properties [2].

Among others, heteroaromatics possessing sp²-hybridized nitrogen atom(s) such as (di)azines represent very popular acceptor units in this field. It is well known that (di)azine-based chromophores exhibit a remarkable emissive and nonlinear optical response, which is reflected in the enhanced fluorescent and 2PA behavior [3]. Hence, we designed and synthesized a series of TPA-based tripodal fluorophores with peripheral diazine acceptors featuring exceptional optical properties (Fig. 1). This study can serve as a reliable systematic photophysical guide comparing the (non)linear optical response of particular diazine regioisomers.

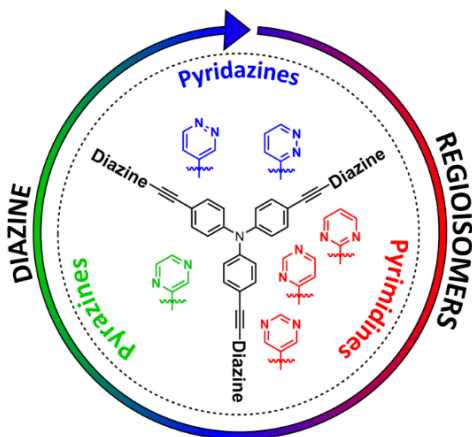


Figure 10. Tripodal triphenylamine-based fluorophores with attached electron-withdrawing diazine regioisomers.

Acknowledgement: This work has been supported from European Regional development Fund-Project "Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)" No.CZ.02.1.01/0.0/0.0/16_025/0007445.

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Electrochemical Study on Viologen Based Azinium Heteroaromatics

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Heteroaromatics containing nitrogen atom(s) can be found across dozens of research fields and one of such are redox flow batteries (RFBs) utilizing various heteroaromatics. For instance, viologen (*N,N'*-dialkyl-4,4'-bipyridinium), a famous herbicide, was intensively studied as an anolyte in aqueous RFBs during last decade [1].

In this contribution, we report structural modifications on parent 4,4'-bipyridinium moiety and subsequent study of fundamental electrochemical properties. The structural modifications of viologen scaffold comprises shortening, isomerization, elongation and fusion of the π -system, while mono and twofold *N*-alkylation(s) were performed. All derivatives were subjected to cyclic voltammetry in aqueous electrolytes. Perspective compounds featuring reversible redox processes were subsequently characterized by a rotating disc glassy carbon electrode. Electrochemical stability was studied in flow battery half-cell with *post mortem* NMR analysis of the electrolytes [2,3].

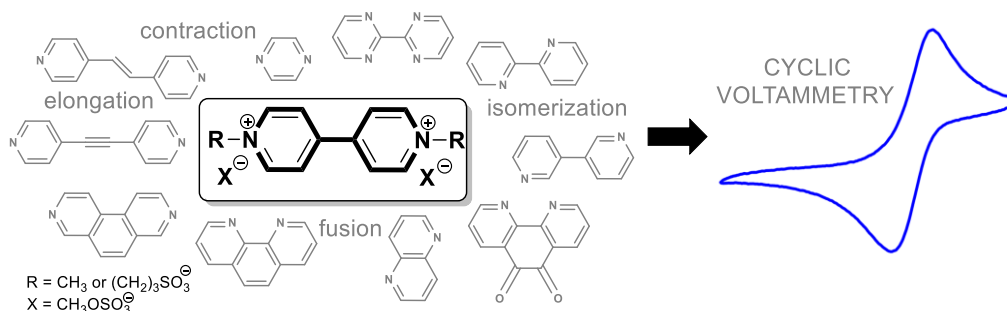


Figure 11. Structural variation of viologen moiety followed by electrochemical measurements.

Acknowledgement: This work has been supported by the European Regional Development Fund-Project “Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)”, No. CZ.02.1.01./0.0/16_025/0007445.

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An Efficient One-Pot Three-Component Synthesis of Functionalized 5-Aryldeazaflavins for the Photoredox Catalysis

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A simple, efficient, and high yielding one-pot protocol for the synthesis of 5-arylpyrimido[4,5-*b*]quinoline-2,4(3*H*,10*H*)-diones (5-aryldeazaflavins) has been developed by three-component domino reaction of *N*-substituted anilines, aromatic aldehydes, and *N*-methylbarbituric acid in AcOH media promoted by PPA. 5-Deazaflavins are usually involved in two-electron enzymatic redox reactions in a variety of biological systems and are structurally similar to flavins with position N-5 of isoalloxazine ring substituted by methine group [1,2]. Synthesized 5-aryldeazaflavins appeared to be powerful catalysts for the redox photocatalysis and showed excellent results in the reductive photodehalogenation of electron-rich aromatic halides.

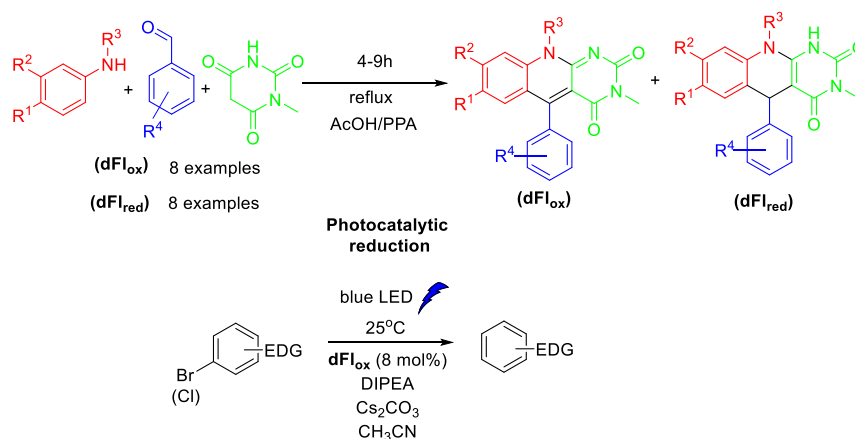


Figure 12. Synthesis and application of the 5-deazaflavins

Acknowledgement: This work has been supported by Czech Science Foundation (project No 19-09064S).

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Twisting and Bending π -System with 7-Membered P-Rings

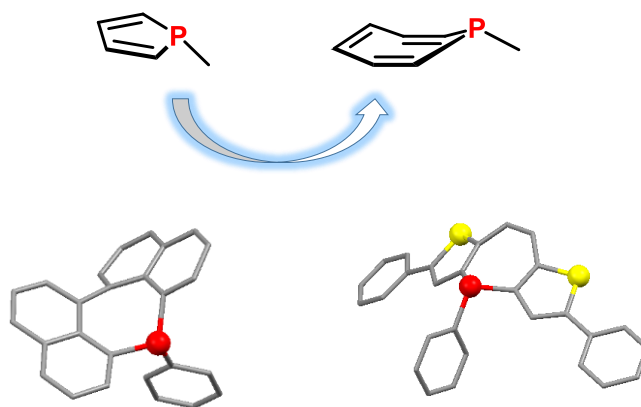
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During the last two decades, the research on P-containing π -conjugated systems based on small molecules, oligomers and polymers has increased substantially thanks to the development of “plastic electronic” devices. Compared to purely organic π -systems, the presence of a heteroatom such as phosphorus affords multiple molecular engineering strategies in order to tune the chemical structure and the physico-chemical properties. Our research team showed that phospholes (Fig.) were excellent candidate to prepare Organic Light Emitting Diodes (OLEDs) [1]. In this communication, we will study the modification coming from the substitution of the 5-membered P-ring by a 7-membered P-ring (phosphepine, Fig.). In particular, this cycle induces molecular distortion (bending, twisting ...). And eventually chirality. These modifications will be studied through an experimental and theoretical approach. Finally, preparation of opto-electronic devices will highlight the potential of these derivatives for organic electronics [2].



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Use of Isochinoline-Oxazoline Ligand in Heterogenous Catalysis

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Ligands bearing an oxazoline moiety in combination with palladium metal are an efficient catalytical system for Hayashi-Miyaura reaction, the addition of boronic acids to an electron-deficient double bond [1]. Hayashi-Miyaura addition gives access to useful nitro compounds with a tertiary stereocenter, which can be taken advantage of in a further synthesis [2].

One of the most successful works describing Hayashi-Miyaura addition of arylboronic acids to β -nitrostyrenes has been published by *He et al* [3]. They described the use of oxazoline-isoquinoline ligand in combination with palladium(II) trifluoroacetate as an efficient catalyst [3].

This work focuses on the above-mentioned catalytic system. Copolymerization strategy was chosen and a ligand bearing a styryl moiety was designed and prepared. Thusly prepared ligand was copolymerised, and several copolymers were prepared. Effect of the copolymer composition and the way of preparation on catalytical activity and enantioselectivity for the addition of arylboronic acids to β -nitrostyrenes are discussed in this work.

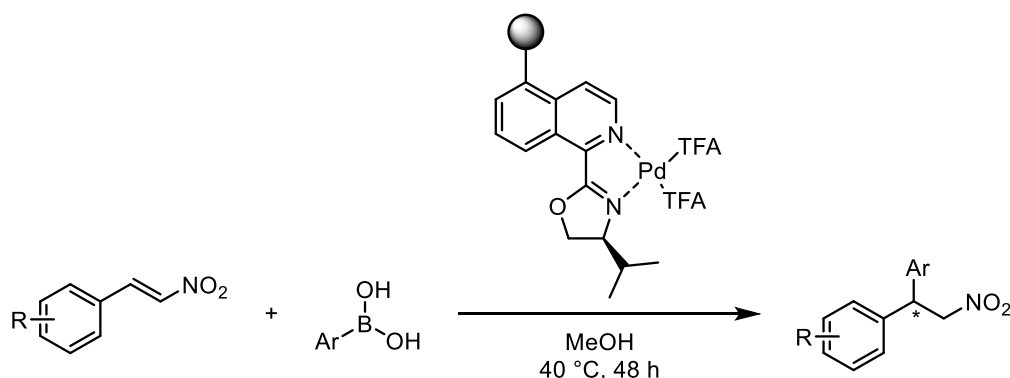


Figure 13. Addition of arylboronic acids to β -nitrostyrenes

Acknowledgement: The authors thank the Czech Ministry of Education, Youth and Sports (project number SGS_2022_003) for financial support.

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Enantioselective PCCP Brønsted Acid-Catalyzed Synthesis of 2,3-Dihydroquinazolinone

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Synthesis of enantiomerically pure compounds is an important objective in synthetic organic chemistry and thus considerable effort has been devoted to develop synthetic methodologies allowing full control over enantioselective outcome of such reactions. In the scope of organocatalysis chiral Brønsted acids are important group of catalysts to address this issue. Chiral phosphoric acids are commonly used representatives in Brønsted acid organocatalysis, though the access to such catalysts is synthetically laborious and financially demanding. To evade this issue pentacarboxycyclopentadienes (PCCPs) offer a synthetically useful platform for Brønsted acid-catalyzed transformations due to less laborious synthetic protocol and low pK_a values. This makes them an interesting alternative for chiral Brønsted acid-catalyzed transformations firstly reported by Lambert and co-workers [1].

In this contribution we would like to demonstrate that chiral pentacarboxycyclopentadiene (PCCP) derivatives could be used in the enantioselective aminalization of aldehydes with anthranilamide derivatives [2]. Corresponding 2,3-dihydroquinazolinone derivatives are obtained with high yield and with good enantiomeric purity.

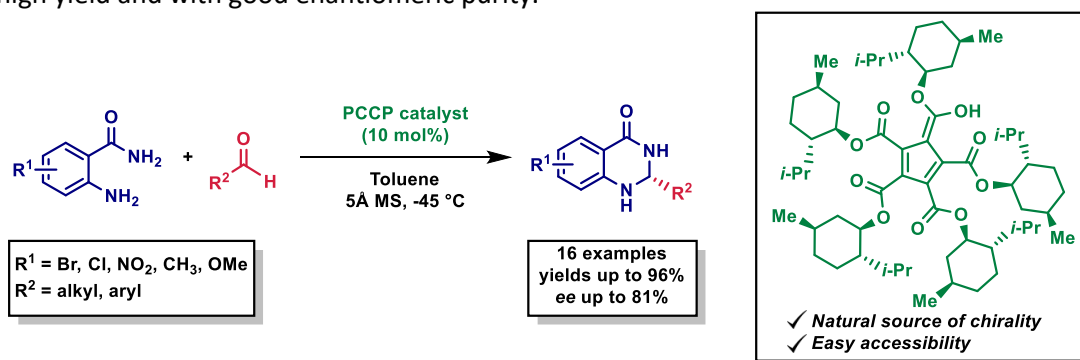


Figure 14. PCCP catalyzed aminalization of aldehydes.

Acknowledgement: This work has been supported by the Czech Science Foundation (20-29336S) and by Charles University Research Centre program No. UNCE/SCI/014. The authors acknowledge the support of the Charles University program START No. CZ.02.2.69/0.0/0.0/19_073/0016935 (START/SCI/084).

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Iridium and Rhodium Catalysed C–C Bond Cleavage in 1-Aza-[3]triphenylene

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The selective C–C bond cleavage of unreactive C–C bond and formation of the new one is most important and challenging goal in organic chemistry. Activation of unreactive C–C bond could lead to new unique products. One possible strategy is activation of C–C bonds in strained rings. Recently, we developed and presented regioselective catalytic cleavage of the proximal or distal C–C bonds in 1-azabiphenylene, which provided benzo[*f*]- and benzo[*h*]-quinolines [1].

Herein, we present a combined computational and experimental study in an effort to understand regioselective C–C bond activation in linear 1-aza-[3]triphenylene. Linear 1-aza-[3]triphenylene contains four nonequivalent C–C bond in two different cyclobutadienes, and there arise a question which one will be preferentially cleaved. DFT calculations gave us some initial insight which one should be preferential activated. The relevant experiments confirmed the prediction, and it enabled to design Ir-catalyzed C–C bond activation/alkyne annulation process and gain access to polyaromatic hydrocarbons with extended π -conjugated system (Figure 1).

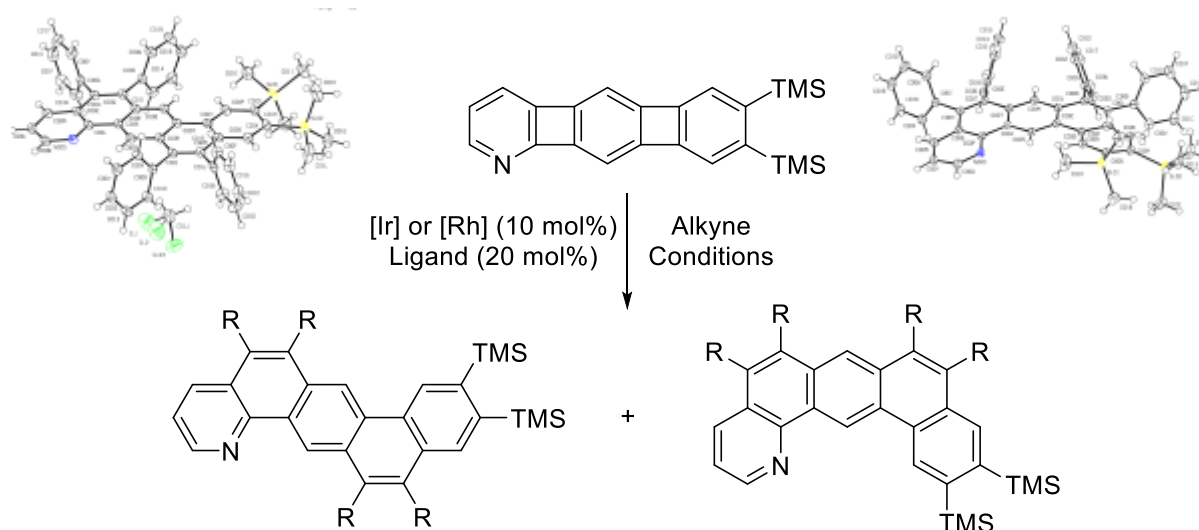


Figure 15. C–C bond cleavage in linear 1-aza-[3]triphenylene and X-ray structure of products

Acknowledgement: This work was supported by the Czech Science Foundation (21-29124S).

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Palladium (II) Complex of Pyridine-Oxazoline-Type Ligand as a Homogeneous/Heterogeneous Catalyst for Enantioselective Addition of Arylboronic Acids to Cyclic Ketimines

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The use of palladium catalyst for an asymmetric addition of arylboronic acids to cyclic ketimines was for the first time reported by Zhang [1]. In this work we present the Pd(TFA)₂ complex with (*S*)-4-(*tert*-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole as a new one catalyst for an enantioselective addition of arylboronic acids to cyclic ketimines, which provides excellent results in homogeneous reaction conditions. Such ligand was designed and prepared with various spacers, which allow immobilization on solid carriers. The advantage of our immobilization strategy is a cheap and commercially available starting compound, which can be elegantly immobilized in three reaction steps.

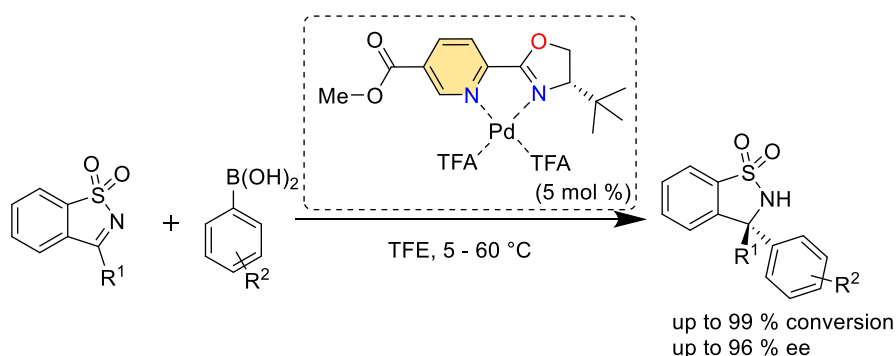


Figure 16. Addition of arylboronic acids to cyclic ketimines catalysed by Pd(TFA)₂ complex of pyridine-oxazoline [1].

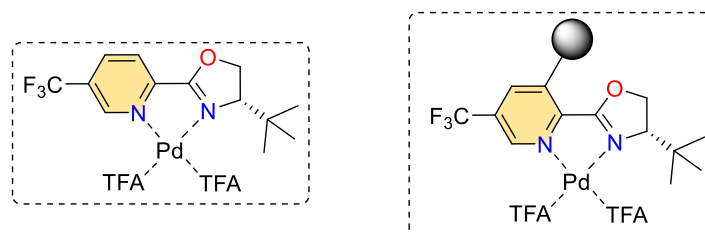


Figure 2. The Novel homogeneous and heterogeneous catalyst for enantioselective addition of arylboronic acids to cyclic ketimines.

Acknowledgement: This work has been supported by the Czech Ministry of Education Youth and Sports (project number SGS_2022_003)

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Synthesis of 3-Trifluoromethylpyrazoles via 1,3-Dipolar Cycloaddition Reactions and Subsequent Oxidative Aromatization of Cycloadducts Derived from Trifluoroacetonitrile Imines

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Trifluoromethylated pyrazoles are considered as privileged structural motifs for drug discovery and for this reason, they received great attention in the last two decades [1]. In search for CF₃-synthons useful for preparation of the title heterocycles we turned to trifluoroacetonitrile imines **A**, which can be *in situ* generated through base-mediated dehydrohalogenation of the respective hydrazoneyl precursors [2]. Subsequently, these reactive 1,3-dipoles can easily be trapped with such dipolarophiles as thiocarbonyl compounds and alkenes as well as with some bifunctional agents to give five- or six-membered N-heterocyclic products [3]. More importantly, in certain cases subsequent aromatization of the initially formed (3+2)-cycloadducts, e.g. pyrazolines, can be fully controlled, e.g. by the type of solvent used, leading to products possessing different substitution patterns. Our recent results related to exploration of nitrile imines **A** for preparation of 3-trifluoromethylated pyrazoles and mechanisms of the studied reactions, will be summarized and discussed.

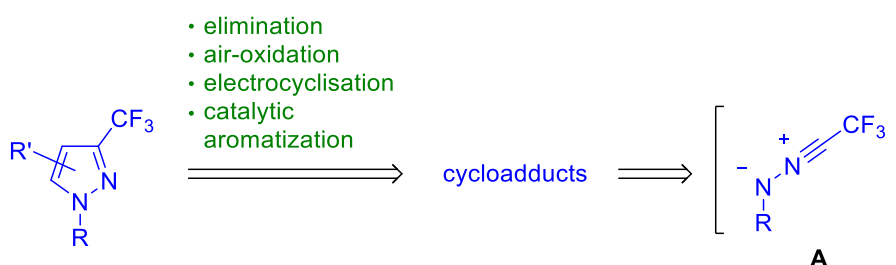


Figure 17. Selected strategies leading to 3-trifluoromethylpyrazoles discussed in the paper.

Acknowledgement: This work has been supported by the University of Lodz in the framework of the IDUB program (M.J.; grant no. 3/IDUB/DOS/2021)

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From Aromatic Iodides to Heterocycles of Interest

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Aromatic heterocycles are present in a myriad of molecules used for numerous applications. In the group, synthetic methodologies are developed to selectively introduce iodine onto heteroaromatic compounds. Besides direct iodination [1], deprotometalation reactions followed by iodolysis have been applied to substrates sensitive to nucleophilic attacks [2]. To overcome the low tolerance of some functional groups toward organolithiums, hindered lithium amide-metal trap tandems have been designed. The generated aromatic iodides have been converted by transition metal-catalyzed cross-couplings, for instance combined with cyclizations, to access original heterocycles. Their properties have been evaluated in the frame of collaborations, and a few showed valuable bioactivities [1-3].

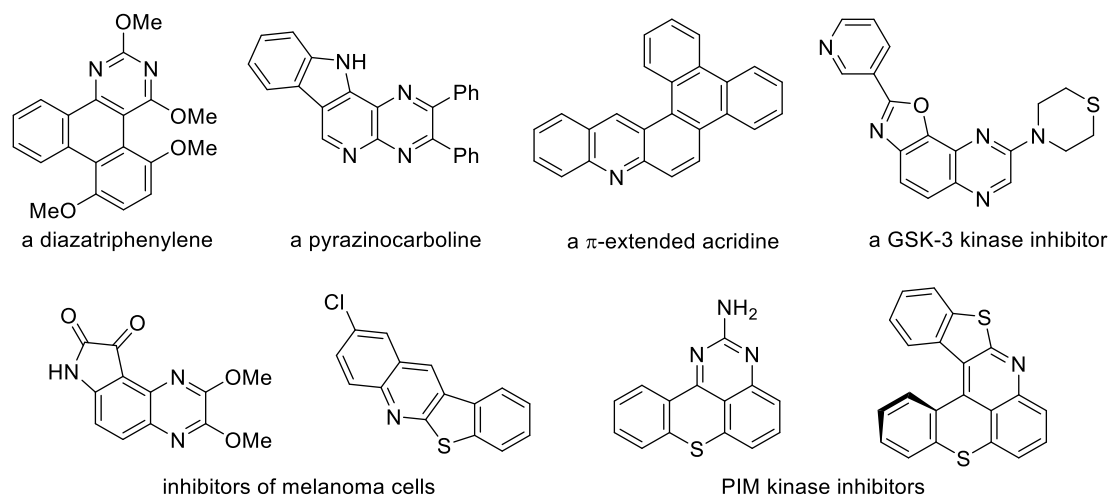


Figure 18. Heterocycles synthesized from aromatic iodides.

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Polymer-Supported Palladium (II) Complex of Pyridine-Oxazoline as a Recyclable Catalyst for an Asymmetric Addition of Arylboronic Acids to Conjugated Cyclic Enones

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Swellable pearl-like copolymers of (*S*)-4-(*tert*-butyl)-2-(4-(4-vinylphenyl)pyridin-2-yl)-4,5-dihydrooxazole with styrene and various cross-linkers were designed and prepared. Catalytic activity of palladium (II) complexes of the prepared copolymers was tested on addition of various arylboronic acid to 3-methyl-2-cyclohexenone. It was possible to use the catalyst at least 6 times and their catalytic activity was comparable with homogenous conditions. Such system was the very first recyclable catalytic system for palladium-catalysed asymmetric addition of arylboronic acids to conjugated cyclic enones.

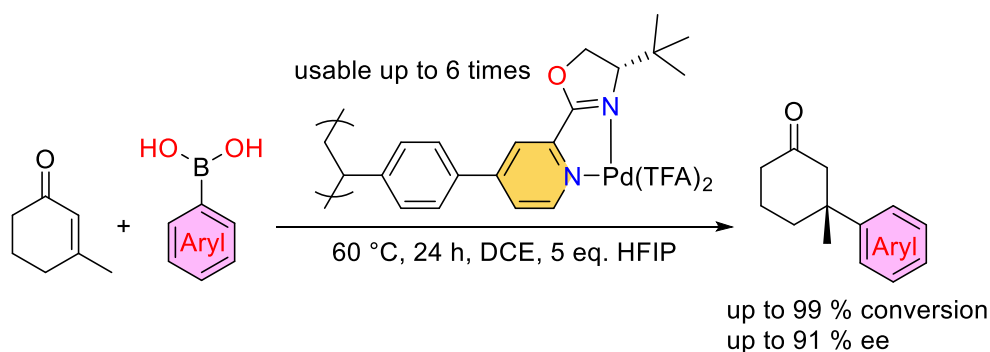


Figure 19. 1,4-addition of arylboronic acids to cyclic enones catalysed by polymer-supported palladium (II) complex of pyridine-oxazoline.

Acknowledgement: This work has been supported by Czech Ministry of Education Youth and Sports (project number SGS_2022_003).

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Reactivity and Site-selectivity of C–H Functionalization Reactions: The Acid Effect

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Late-stage functionalization (LSF) of C–H bonds is a powerful tool for the efficient synthesis of functionalized complex molecules. It enables synthesis of compound libraries by decoration of basic skeleton at the end of synthetic pathway. LSF is challenging because the C–H bond is functionalized in the presence of various other functional groups. However, these groups can be in some cases (DGs) advantageously used to control site-selectivity. This contribution will introduce a simple way for switching the DGs assisted site-selectivity of C–H functionalization of aromatic bonds by acid additives [1].

This concept is based on the fact that the stronger DG tends to be more basic. Therefore, addition of acid to the reaction mixture causes its protonation and thus loss of DG ability. Then, the weaker DG directs the reaction [2].

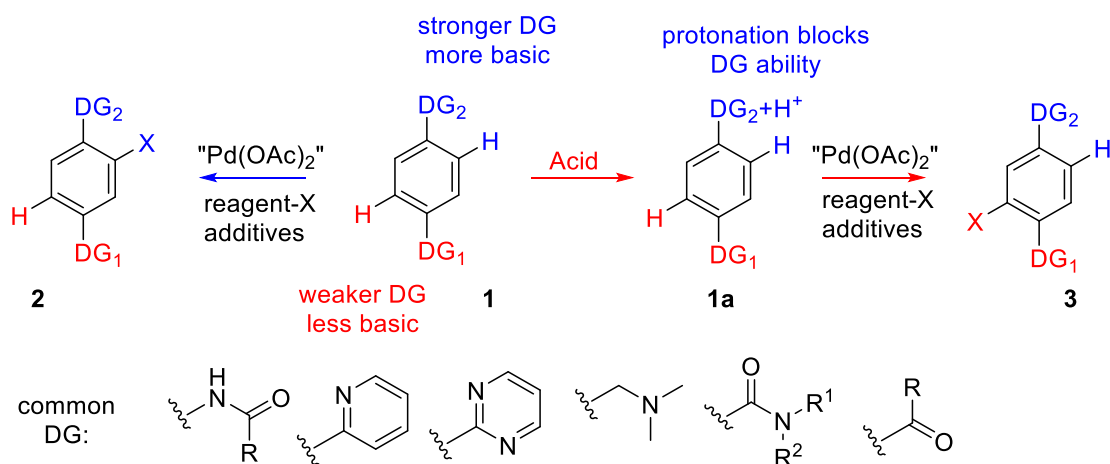


Figure 20. Basic principle of site-selectivity switch.

Acknowledgement: This work has been supported by project number SGS_2022_003.

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Transformations of Thioiminium Salts Derived α -Bromoamides

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Our research group is constantly involved in the exploration of substitution and condition-dependent transformations of thioiminium salts derived from α -bromoamides to heterocycles containing nitrogen and sulfur. Originally, we intended to use abovementioned building blocks for synthesis of highly fluorescent 4-hydroxythiazoles. However, recently, we have found that the salts formed by reaction of 3-bromoindol-2-one with thioamides can also undergo thiophile-free *Eschenmoser* reaction under specific conditions, to give pharmaceutically valuable vinylogous amides [1]. Essentially, these two chemical transformations are competing each other and final reaction course depends both on reaction conditions (polarity of the solvent, temperature, base addition) and electronic effects.

In order to better understand to the reactivity, we further investigated possible transformation pathways of structurally related thioiminium salts derived from acyclic subst. 2-bromophenylacetamides (**1**) and their cyclic counterparts, i.e. 4-bromo-1,1-dimethyl-1,2-dihydroisoquinolin-3(4*H*)-ones (**2**) (Figure 1). Reaction of α -thioiminium salts derived from 2-bromophenylacetamide and prim./sec. thiobenzamides afforded 2,5-diaryl-4-hydroxythiazoles (**3**) or zwitterionic 3-methyl-2,5-diphenylthiazol-3-ium-4-olates (**4**) in moderate yields. When cyclic α -bromolactam **2** was reacted with prim. thioamides, 5,5-dimethyl-2-phenyl-4,5-dihydrothiazolo[4,5-*c*]isoquinoline (**5**) was isolated. Heating the same salts in the excess of thiophile (trimethyl phosphite) did not result in formation of conjugated vinylamines, but only *N*-methylation leading to thiazole **6** has occurred. On the other hand, reaction of cyclic bromoamide **2** with sec. thioamides led to an *Eschenmoser* reaction products **7** in moderate to good yields even without thiophile.

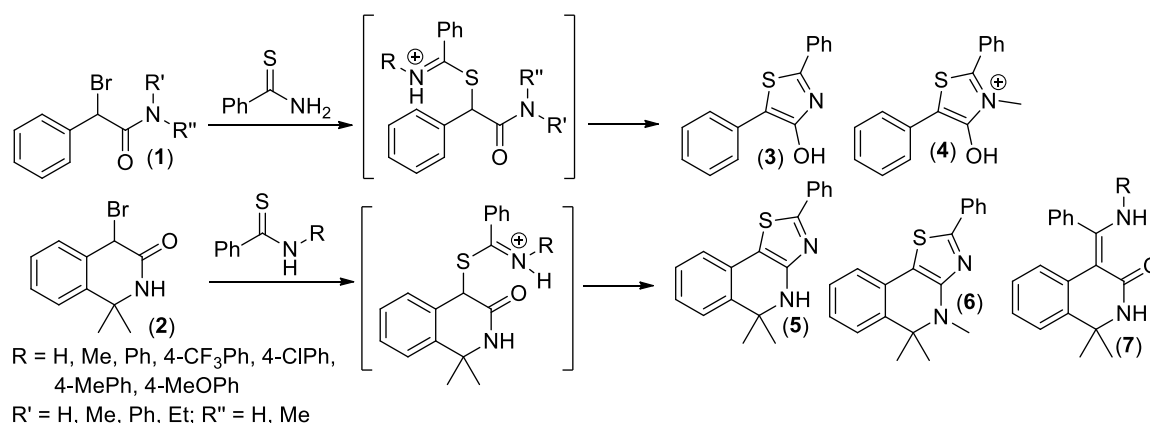


Figure 21. Structure scaffolds formed by reaction of (a)cyclic α -bromoamides and prim./sec. thioamides.

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