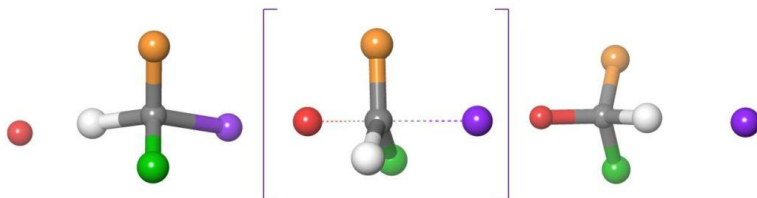


September 25-26, 2025
Riga, Latvia



Paul Walden 14th Symposium on Organic Chemistry



Latvian
Institute of
Organic
Synthesis



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Paul Walden 14th Symposium on Organic Chemistry

PROGRAM AND ABSTRACT BOOK

Riga, Latvia
September 25-26, 2025
<https://walden.osi.lv>

Dear participants, colleagues and symposium guests

On behalf of the Organizing Committee, it is my great pleasure to welcome you to the 14th Paul Walden Symposium in Organic Chemistry.

The Walden Symposium has a proud history spanning more than 25 years, beginning in 1998 under the initiative of *Dr. Pēteris Trapencieris*. Since then, it has grown into a significant scientific event in the Baltic region. As Prof. Edwin Vedejs once remarked, “*Science has to contact people, and scientists have to contribute to education.*” These words capture the very essence of the Walden Symposium that aims to

- Inspire and educate the young generation of Latvian and Baltic chemists
- Promote interactions between chemists of different countries to foster collaborations and joint research projects

The Walden **symposium** program reflects these goals, and it features:

1. Lectures delivered by distinguished international speakers
2. Poster sessions in a stimulating and collegial atmosphere
3. Short talks by selected PhD students, as well as 3-minute poster pitch session.

The scientific scope of this year’s symposium covers a wide range of contemporary organic chemistry, including enantioselective catalysis by transition metal complexes, asymmetric organocatalysis, synthetic organic electrochemistry and photocatalysis, site-selective atom replacements and machine learning for chemistry. We hope the symposium will serve as an ideal venue to explore current advances in these areas, exchange ideas and create new scientific connections.

We are deeply grateful to the Latvian Institute of Organic Synthesis (LIOS), Riga Technical University and all our supporters, without whom the symposium would not be possible. Our sincere thanks also go to the invited speakers for contributing to an outstanding program and to the poster contributors providing a record number of high-quality presentations. A special thanks goes to the members of the Organizing Committee for their commitment and dedication.

We wish you an inspiring and fruitful symposium experience. May your time here not only enhance your professional knowledge but also foster new collaborations and friendships.

Prof. Edgars Sūna

Chair of the Organizing Committee

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Paul Walden 14th Symposium on Organic Chemistry
September 25-26, 2025; Riga, Street Elizabetes 24
Tallink Hotel Riga

Program

Thursday, September 25

- 8:15** *Registration*
- 8:45** Welcoming remarks
Prof. **Edgars Sūna** (Chairman of the Scientific Board, Latvian Institute of Organic Synthesis)
- 8:50** Presentation of the Paul Walden medal to Prof. **Eriks Rozners** (University of Binghamton, USA) by Prof. **Māris Turks**, Dean of the Faculty of Natural Sciences and Technology (Riga Technical University)
- 9:00** Prof. **Eriks Rozners** (University of Binghamton, USA)
Amide-Modified RNA: Using Protein Backbone to Modulate Function of RNA
- 9:50** Prof. **Mariola Tortosa** (Universidad Autónoma de Madrid, Spain)
Catalysis to Increase Complexity: Stereoselective Synthesis of sp³-rich Building Blocks
- 10:40** Symposium group photo and Coffee break
- 11:10** Prof. **Kevin Lam** (University of Greenwich, UK)
Your Chemistry has “Potential” Highly Reactive Intermediates Without the “Bang”
- 12:00** Poster Pitches (PhD students)
- 12:20** Lunch
- 14:10** Prof. Dr. **Frank Glorius** (University of Münster, Germany)
On Data, Discovery & Sensitivity in (Photo)Catalysis
- 15:00** Poster Pitches (PhD students)
- 15:20** Coffee break
- 15:50** Poster Pitches (PhD students)
- 16:10** Prof. **Darren Dixon** (University of Oxford, UK)
Catalyst Control in Complex Molecule Synthesis
- 17:00** Poster Session
- 18:00** Guided tour of the Paul Walden and Wilhelm Ostwald monuments

Friday, September 26

- 9:00** Prof. **Alois Fürstner** (Max-Planck-Institut für Kohlenforschung, Germany)
An Inadvertent Excursion into Rhodium Carbene Chemistry
- 9:50** Prof. Dr. **Franziska Schoenebeck** (RWTH Aachen, Germany)
Mechanism-Driven and Machine Learning-Enhanced Strategies for Accelerated Molecular Synthesis
- 10:40** Coffee break
- 11:00** **Aleksandrs Čižikovs** (Latvian Institute of Organic Synthesis, Latvia)
Development of novel methods for the synthesis of heterocycles using cobalt catalysis
- 11:30** Prof. **Cristina Nevado** (University of Zurich, Switzerland)
Nickel-Catalyzed Asymmetric Difunctionalization of Alkenes
- 12:20** Lunch
- 13:30** Poster Session
- 15:30** **Artūrs Sperga** (Latvian Institute of Organic Synthesis, Latvia)
Fluorinated Synthons Transfer from Sulfonium Salts
- 16:00** Prof. **Mark D. Levin** (University of Chicago, USA)
Replacing Atoms
- 16:50** Poster awards and Closing remarks

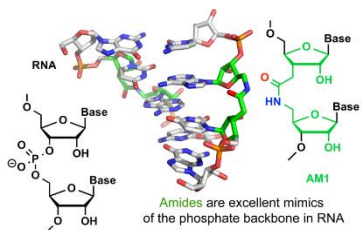
PLENARY LECTURES

Amide-modified RNA: using protein backbone to modulate function of RNA

Eriks Rozners

Department of Chemistry, Binghamton University, USA

RNA-based technologies to control gene expression, such as, RNA interference (RNAi) and CRISPR-Cas9 have become powerful tools in molecular biology and genomics. The development of RNAi and CRISPR-Cas9 as new therapeutic approaches has further reinvigorated interest in chemically modifying RNA to improve its properties for in vivo applications. Our current work is focused on the development of novel nonionic analogues of RNA that have the phosphates replaced by amide linkages (AM1 in Figure). This presentation will discuss synthesis, structure and biological activity of amide-modified siRNAs and CRISPR RNAs (crRNAs).¹ Structural studies show that amides are excellent mimics of the phosphate linkages in RNA. The local conformational changes caused by the amides were accommodated easily by small adjustments in the RNA structure. A crystal structure of a short amide-modified DNA-RNA hybrid in complex with RNase H shows that amide can remodel RNA-protein interactions by acting as H-bond donor, which is not possible for phosphate. RNAi activity assays show that amides are well tolerated at internal positions in both strands of siRNAs and, when placed at certain hot spots, significantly improve the specificity of siRNAs. Replacement of a single phosphate linkage with an amide abolished the undesired off-target activity of the passenger strand. Amide modifications in the seed region significantly reduced the microRNA-like off-target activity of the guide strand.² In a related project, we showed that amide modifications did not interfere with CRISPR-Cas9 activity when placed in the protospacer adjacent motif distal region of crRNAs.³ In contrast, modification of the seed region of crRNAs led to loss of DNA cleavage activity at most but not all positions. Preliminary GUIDE-Seq results show that amide modifications of crRNAs significantly improve Cas9 specificity compared to unmodified crRNA.



Collectively, our results suggest that amides are excellent mimics of phosphate backbone in RNA and have potential to optimize biological and pharmacological properties of therapeutic siRNAs and crRNAs. These findings are unexpected and raise the possibility that RNA may tolerate even more substantial modifications than tried so far.

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Catalysis to increase complexity: stereoselective synthesis of sp³-rich building blocks

Mariola Tortosa

Universidad Autónoma de Madrid, Organic Chemistry Department, Spain

Transition-metal catalysis is at the core of modern chemistry and has become increasingly important for the pharmaceutical industry. As the pharmaceutical industry is shifting from compounds with a strong sp² character to libraries of compounds with enlarged three-dimensionality, the need to develop catalytic methods to provide compounds with an increased sp³ character becomes apparent. In our group, we have recently focused on the development of catalytic enantioselective and stereospecific transformations for the preparation of sp³-rich building blocks, providing tools for stereodefined carbon-boron bond formation, synthesis of benzene bioisosteres and selective carbon-nitrogen bond cleavage. These methods have allowed us to prepare a broad variety of useful synthetic intermediates, with special emphasis on the synthesis of functionalized strained-rings.¹ Some of these transformations will be presented in this talk.

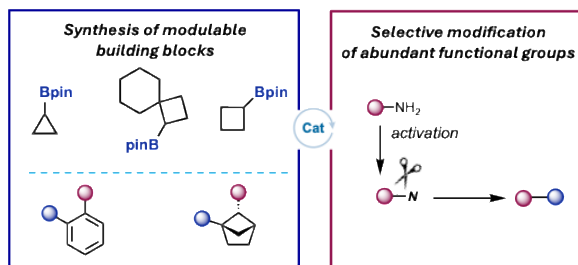


Figure 1. Synthesis of sp³-rich building blocks

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Your chemistry has “potential” Highly reactive intermediates without the “bang”

Kevin Lam

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Chemistry thrives on highly reactive intermediates - remarkable tools for building complex molecules. But one might ask: shouldn't their synthesis involve fewer risks than a special life insurance policy?

Synthetic organic electrochemistry, which has its roots in the pioneering work of Faraday and Kolbe on the electrolysis of aliphatic carboxylic acids, has become a powerful tool for sustainable chemical synthesis. Despite numerous successful industrial applications, its wider potential remains under-exploited. However, the increasing demand for greener, safer and more cost-effective synthetic methods has spurred the development of innovative electrosynthetic techniques.

In this talk, we will review novel, safe, green and economically viable electrosynthetic methods for the preparation of highly reactive organic intermediates, including iso(thio)cyanates, isocyanides, carbocations and diazo compounds. These methods significantly reduce the inherent risks associated with traditional synthetic approaches, while improving efficiency and sustainability. We will also highlight the scalability of these processes through flow electrosynthesis and their impactful real-world applications within the pharmaceutical industry, with case studies in collaboration with GSK, AstraZeneca and Johnson & Johnson.



On data, discovery & sensitivity in (photo)catalysis

Frank Glorius

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Catalysis is a key technology, since it allows for increased levels of selectivity and efficacy of chemical transformations. While significant progress can be made by rational design or engineered step-by-step improvements, many pressing challenges in the field require the discovery of new and formerly unexpected results. Arguably, the question “How to discover?” is at the heart of the scientific process. In this talk, (smart) screening strategies for accelerated discovery and improved reproducibility will be presented,¹ machine learning for chemistry will be discussed,² together with new photocatalytic transformations.^{3,4} In addition, two other exciting areas will be addressed briefly:

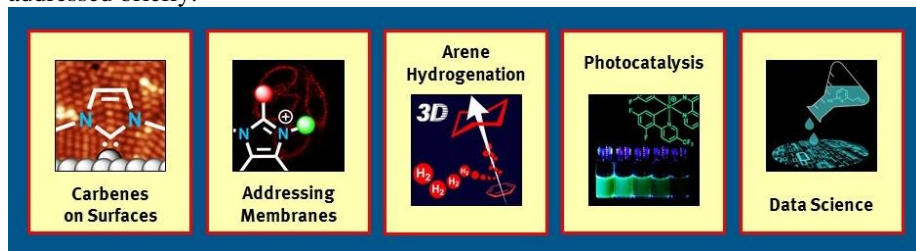


Figure 1. Graphical teaser for the work presented.

N-Heterocyclic Carbenes (NHCs)⁵ are powerful ligands in catalysis due to their strong electron-donating properties and their ability to form very stable bonds to transition metals. In addition, they can stabilize and modify nanoparticles or flat metals surfaces, outperforming established phosphine or thiol ligands regarding structural flexibility, electron-donating properties and stability. Current research is highly interdisciplinary and focusses on the basic understanding of the binding mode, mobility and the elucidation of the impact on the surface properties. Exciting applications in materials science, heterogeneous catalysts and beyond are within reach.⁶

Biological membranes and their constituents are some of the most important and fundamental building blocks of life. However, their exact role in many essential cellular processes as well as in the development of diseases such as cancer or Alzheimer's is still not very well understood. Thus, we design, synthesize and evaluate imidazolium-based lipid analogs that can integrate into biological membranes and can be used as probes for live cell imaging or to manipulate membranes.⁷

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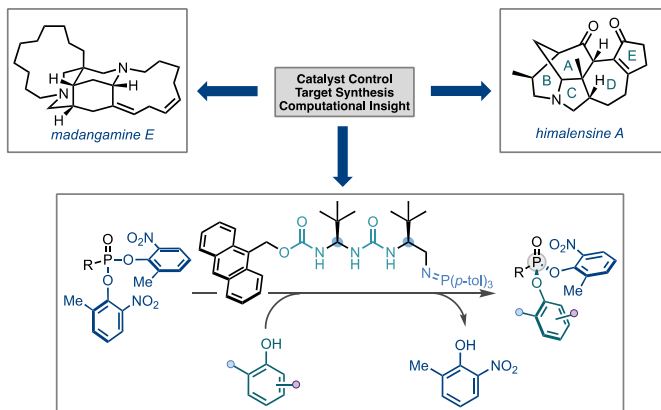
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Catalyst control in complex molecule synthesis

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New catalysts are key for unlocking previously unknown molecular reactivity and unexplored chemical space, as well as governing the 3-dimensional structure of product molecules of interest to chemistry, biology and medicine. In this lecture, new synthetically relevant chemistry linked to two distinct types of catalyst systems will be presented. In the first part, recent developments from our group for the direct synthesis of alpha and beta-functionalised amines from amides and lactams via highly chemoselective reductive activation using known and new iridium catalysts will be described. In the second part, recent findings employing bifunctional chiral organosuperbases for accessing chiral phosphorous (V) compounds, as well as other medicinally relevant motifs and building blocks, with high enantioselectivity will be presented. Across both topics, details of the newly arising methodologies as well as their provenance and applications in natural product or drug molecule total synthesis, will be discussed.¹⁻⁵



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An inadvertent excursion into rhodium carbene chemistry

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Rhodium carbenes formed by reaction of diazo derivatives with (chiral) dirhodium tetracarboxylates gained tremendous importance in organic synthesis but defied direct inspection for decades. Our group managed to isolate a set of representative complexes of this type. XRD analyses unveiled important aspects concerning structure, bonding and the conformation of the (chiral) binding site.^{1,2} Complementary information on the electronic nature of the catalysts was obtained with the aid of ¹⁰³Rh NMR spectroscopy in combination with DFT calculations.³

The newly gained insights inspired new catalyst design, which resulted in the development of exceptionally active and selective heterobimetallic [BiRh] paddlewheel complexes stabilized by interligand London dispersion; these catalysts excel in asymmetric [2+1] cycloadditions and C–H functionalization reactions.^{4,5,6} In parallel, heteroleptic dirhodium complexes were developed, which proved uniquely effective at engaging α -stannylated (silylated) diazoacetate into asymmetric cyclopropanation.^{7,8} Finally, an entirely new class of paddlewheel complexes was designed, in which an array of only three different achiral ligands renders the two rhodium centers inequivalent and chiral-at-the-metal each.⁹

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Mechanism-driven and machine learning-enhanced strategies for accelerated molecular synthesis

Franziska Schoenebeck

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This presentation will give an overview of our group's recent research activities at the interface of synthetic organic, mechanistic chemistry and homogeneous catalysis. The emphasis will be on novel strategies that were recently identified in our laboratory to simplify and accelerate the synthesis of structurally diverse molecules. These include, for example, the (i) use of organogermanes as orthogonal coupling partners in C_{sp2} and C_{sp3} space, (ii) metalloradical-catalyzed stereomutations, (iii) late-stage alkylations & (iv) routes to synthesize previously inaccessible fluorinated motifs. The development, scope and mechanistic underpinnings (based on experimental & computational/data science studies) of these novel processes will be discussed.

Nickel-catalyzed asymmetric difunctionalization of alkenes

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Our group has recently explored the reactivity of C and N centered radicals, in combination with transition metals, to streamline the functionalization of π -systems. Here, we will present our efforts to generate and harvest these valuable intermediates in synthetically relevant contexts, including recent results towards their application in asymmetric transformations.¹ Examples of Nickel catalyzed dicarbofunctionalizations of alkenes and alkynes in a chemo-, regio- and stereoselective manner utilizing radicals as well as studies on the mechanistic features underlying these transformations will be presented in this lecture.²

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Replacing atoms

Mark D. Levin

University of Chicago, USA

Transformations that allow for the replacement of one atom for another in aromatic ring systems will be presented, with a specific emphasis on C-to-N replacements. Key takeaways include the strategies and concepts that enable site-selective replacements without perturbation of the remaining molecular skeleton. Though the chemical modalities employed to accomplish such transformations are diverse, photochemistry and reagent design are a significant focus.

STUDENT PRESENTATIONS

Development of novel methods for the synthesis of heterocycles using cobalt catalysis

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The development of novel methods for the synthesis of heterocyclic compounds, both new and known, could not only contribute to the development of new synthetic approaches but also reduce the cost of production of existing pharmaceuticals. Today, it is possible to use cheaper, less toxic and more environmentally friendly 3rd row transition metal catalysts (Ni, Co, Fe etc.) for the C-H bond activation and functionalization as an alternative to the typically employed noble metal catalysts.¹ Therefore, our research is focused on the development of novel cobalt-catalyzed C-H bond activation and functionalization methods for the synthesis of various heterocyclic compounds (Figure 1). The methods developed are based on high-valent cobalt catalysis, using simple Co(II) salts in combination with bidentate directing group as precursors of Co(III) species.

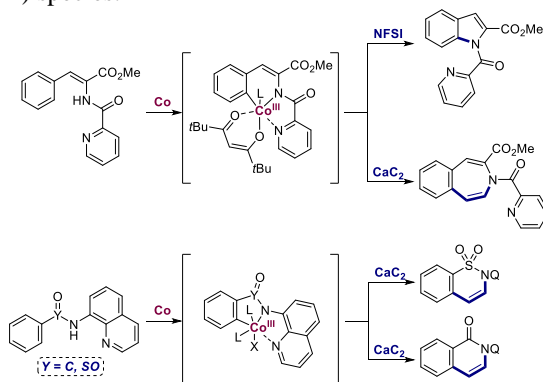


Figure 1. Possible synthetic approaches for various heterocycles *via* cobalt catalysis.

Acknowledgements. This research was funded by the Latvian Institute of Organic Synthesis internal grants IG-2023-05 and IG-2024-03 as well as by Recovery and Resilience Facility (5.2.1.1.i.) doctoral career grants (No. 01/OSI/DG; No. 22/OSI/DG) and academic career grant No. 04/OSI/ZG.

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Fluorinated synthon transfer from sulfonium salts

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Organofluorine compounds play a pivotal role in the development of novel pharmaceuticals, agrochemicals, and materials.¹ An alternative to direct fluorination of molecules is the use of fluorinated synthon transfer reactions,² particularly those in which fluorine is directly attached to a reactive carbon center. While strategies for the introduction of trifluoromethyl and difluoromethyl groups are fairly well developed, the transfer of monofluorinated synthons remains less explored.

We envisioned that substituted fluoromethyl sulfonium salts could serve as efficient reagents for the transfer of unique monofluorinated synthons. Herein, we report novel sulfonium salts capable of transferring carbene and electrophilic monofluorinated synthons, thereby providing access to highly valuable monofluorinated compounds (Figure 1).³⁻⁵

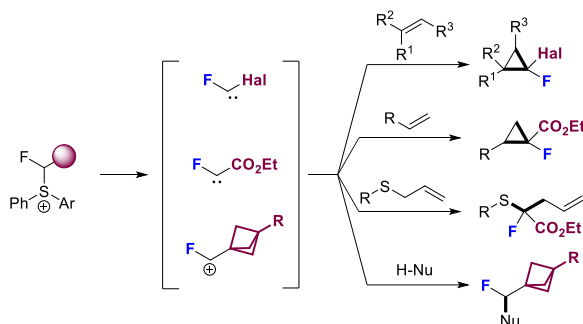


Figure 1. Synthetic application of sulfonium salts.

Acknowledgements. This research was funded by the Latvian Council of Science project lzp-2022/1-0335, Strengthening of PhD students and academic personnel of Riga Technical University and BA School of Business and Finance in the strategic fields of specialization No. 8.2.2.0/20/I/008, Latvian Organic Synthesis institute grant IG-2023-06, Recovery and Resilience Facility (RRF) (5.2.1.1.i.) Grant Nr.14/OSI/ZG.

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POSTERS

List of posters

- B-1** **Entry to 2-aminoprolines via electrochemical decarboxylative amidation of *N*-acetylamino malonic acid monoesters**
*Olesja Koleda, * Janis Sadauskis, Darja Antonenko, Edvards Janis Treijs, Raivis Davis Steberis, Edgars Suna**
- B-2** **Electrochemical alcohol oxidation using TEMPO-modified polymethacrylate film**
*Luīza Lote Irbe, Anna Lielpētere**
- B-3** **Synthesis and investigation of 2-(4-chlorophenyl)-*N*-(heteroaryl)acetamides**
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- D-5 Sulfur-specific alkylation of sulfinamides by Zn carbenoids**
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- D-7 Development of reversible covalent SUB1 protease inhibitors**
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- D-8 Progress toward 1-fluoropropellane: synthesis of advanced [1.1.1]propellane intermediates**
Māris Koniševs, Valerija Krušinska, Andrei Baran, Janis Veliks**
- D-9 Asymmetric electro-organocatalytic functionalization of aldehydes enabled by iodine**
*Anastasiya Krech, Marharyta Laktsevich-Iskryk, Davide Pusceddu, Maksim Ošeka**
- D-10 Copper-catalyzed arylation of propargyl silanes with iodanes featuring the 1,2-silyl shift**
*Rasma Kronkalne, Māris Turks**
- D-11 New synthetic applications of electrochemical SOMO-organocatalysis**
Marharyta Laktsevich-Iskryk Maksim Ošeka, Daniele Mazzarella**
- D-12 The synthesis of naturally occurring fragrances via one-pot ester hydrosilylation/acatalization sequence**
*Rebeka Ločmele, Anastasija Ture, Zigmaris Leitis, Gábor Szilvágyi, József Répási, Gints Šmits**

- D-13 Electrooxidative iodination of carbonyl compounds**
*Biswadeep Manna, Nora Deil, Monika Merje Meinberg, Maksim Ošeka**
- D-14 Overcoming metallo- β -lactamase driven antibiotic resistance with a codrug approach**
*Nauris Narvaišs, Edgars Suna**
- D-15 Synthesis of novel 3-[(2,4-difluorophenyl)amino] propanoic acid derivatives and evaluation of their biological properties for potential pharmacological applications**
*Guoda Pranaitytė, Povilas Kavaliauskas, Birutė Grybaitė**
- D-16 Design and synthesis of novel styrylpyridinium compounds with aggregation-induced emission for photodynamic therapy**
Reinis Putrālis, Kristaps Krims Dāvis, Meldra Ķemere, Aiva Plotniece, Kārlis Pajuste,* Anatolijs Šarakovskis**
- D-17 Synthesis of Modular and Functionalizable Supramolecular Cavitands**
*Nojus Radzevičiu, Eivydas Trioška, Edvinas Orentas**
- D-18 Butyllithium-free access to lithium amide bases via mechanochemistry**
Suman Sahoo, Martin Trebunski, Dzmitry Kananovich, Riina Aav**
- D-19 Synthesis of acyclic diaryl λ^3 -bromanes**
*Andrejs Savkins, Igors Sokolovs**
- D-20 Emerald emission: benzothiazoline Cu(I) complexes for high-efficiency green OLEDs**
*Zanis Sisojevs, Armands Ruduss, Kaspars Traskovskis**
- D-21 Electrochemical Ferrier rearrangement in flow**
*Pallav Suman, Mihhail Fokin, Maksim Ošeka**
- D-22 Electrochemical decarboxylative fluorination of malonic acid derivatives**
Jānis Šadauskis, Olesja Koleda Edgars Suna**
- D-23 Sulfur heterocycle synthesis by methylenecyclopropane ring-expansion with SO₂**
*Emanuels Šūpulnieks, Miķelis Zelmenis, Māris Turks**

- D-24 Anion assisted glycosylation of galactose: a computational study**
*Kerli Tali, Tõnis Kanger, * Irina Osadchuk**
- D-25 New approach to fused heterocycles via tandem 1,2-silyl shift – Friedel–Crafts cyclization**
*Artjoms Ubaidullajevs, Rasma Kronkalne, Māris Turks**
- D-26 Enantiopure piperidines via stereoselective Ireland–Claisen rearrangement: modular access to secologanin-based alkaloids**
*Niklāvs Ūdris, Gints Šmits**
- D-27 design and synthesis of structurally simple supramolecular capsule**
*Domantas Valčekas, Gabija Sergejevaitė, Edvinas Orentas**
- D-28 New synthetic approach to synthesis of 3,4-dihydro-1H-[1,4]oxazino[4,3-*a*]indole derivatives using activated glycerol carbonate**
*Inesa Zagorskytė, Eglė Arbačiauskienė, * Algirdas Šačkus**
- D-29 Harnessing protons as the only oxidants for photoredox dehydrogenative coupling**
*Jonas Žurauskas, Paulius Vaickūnas, Gustautas Snarskis, Barbara Chatinovska, Nojus Radzevičius, Gediminas Kreiza, Steponas Raišys, Mantas Šimėnas, Vidmantas Kalendra, Kęstutis Zakarauskas, Karolis Kazlauskas, Edvinas Orentas**

Entry to 2-aminoprolines *via* electrochemical decarboxylative amidation of *N*-acetylamino malonic acid monoesters

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Non-proteinogenic cyclic amino acids are widely recognized as valuable building blocks in the design of small-molecule therapeutics and peptidomimetics.¹ For instance, clinically used anesthetics such as remifentanyl, as well as the FDA-approved antipruritic agent difelikefalin, contain cyclic α,α -disubstituted piperidine-derived amino acid subunits. Their frequent appearance in successful drug scaffolds highlights both the demand for new structural analogs and the importance of efficient synthetic methods to access these pharmacologically significant motifs.

We recently reported an electrochemical strategy for constructing tetrahydrofuran- and tetrahydropyran-containing amino acid derivatives through anodic decarboxylation of *N*-acetylamino malonic acid monoesters by generating stabilized carbocations under Hofer–Moest conditions.² Herein we extend the approach by showing that *N*-protected amines also serve as effective nucleophiles, enabling cyclization to 2-aminoproline and 2-aminopiperic acid derivatives (Figure 1).

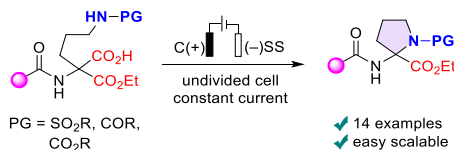


Figure 1. Developed electrochemical decarboxylative amidation.

Under constant current conditions in aqueous acetonitrile, anodic decarboxylation generates stabilized cations that cyclize with tethered nitrogen nucleophiles, including sulfonamides, carbamates, and benzamides. The resulting *N*-protected 2-aminoproline derivatives are readily adapted into dipeptides, offering versatile motifs for peptidomimetic design.

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Electrochemical alcohol oxidation using TEMPO-modified polymethacrylate film

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TEMPO derivatives have been proven as efficient and reusable mediators in electrosynthesis and can be employed both as a soluble redox-active polymer¹ and as a surface-confined polymer (a.k.a. film).^{1,2} However, using the soluble kind means a more complex separation method (e.g. membrane filtration, precipitation, dialysis), therefore, using a modified electrode for alcohol oxidization is understandably a more attractive strategy, and has already been used by some researchers.^{3,4}

In this study, our goal is to find a combination of polymer, crosslinker and application method/electrode modification method for best film stability and catalytic activity to perform electrochemical alcohol oxidation. We have used a simple, two-step method for TEMPO-modified polymethacrylate synthesis, and explored how the polymer structure and method of application on electrode (Fig.1, 2) impacts the films stability and catalytic activity.

We have managed to find several TEMPO-modified polymethacrylates with promising stability and catalytic activity, and alcohol oxidation tests with these polymers are underway.

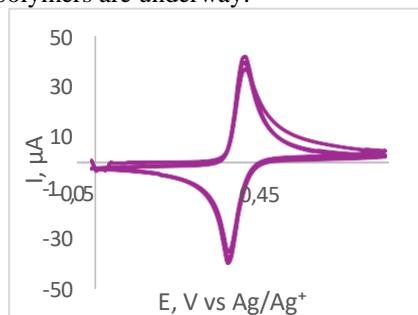


Figure 1. CV of electrode modified drop-casting.

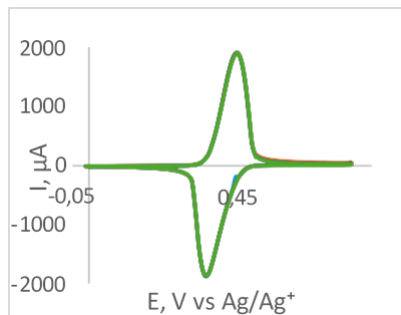


Figure 2. CV of electrode modified by polymer electrodeposition.

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Synthesis and Investigation of 2-(4-chlorophenyl)-N-(heteroaryl)acetamides

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Amide functional group can be found in various biologically active molecules, including proteins and naturally existing or synthetic pharmaceutically active ingredients. It can form hydrogen bonding, which further improves solubility and bioavailability. 2-(4-Chlorophenyl)-N-(benzimidazol-2-yl)acetamides constructed following similar procedures can be successfully applied against pathogenic protozoa *Trypanosoma cruzi* and *Trypanosoma brucei*.^{1,2} These protozoa are causative agents of infectious diseases that often progress to chronic ones because there is no reliable treatment.

After reviewing the published results, it was decided that it would be interesting to investigate whether the activity of the compounds would improve if the benzimidazole moiety was replaced with a smaller heterocycle – pyridine or thiophene. In collaboration with scientists from Vytautas Magnus University, it was decided to conduct initial studies with non-pathogenic protozoa for safety reasons.

The aim of this project was to prepare 2-(4-chlorophenyl)-N-(benzimidazol-2-yl)acetamide analogues with potential activity for *in vitro* studies against infusoria.

For the synthesis of the target compounds, it was chosen to carry out the reactions of 2-(4-chlorophenyl)acetic acid with amino-heterocycles. For carboxylic acid activation a combination of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and 1-hydroxybenzotriazole was used. To reliably prove the structure of the obtained compounds, spectral analysis IR and NMR (standard and two-dimensional) along with mass spectrometric analysis (MS) methods were used. All compounds prepared for biological studies were purified to at least 97% purity (LC-MS).

Key results of primary biotesting data will be presented along with synthesis data.

Acknowledgements. This project has received funding from the Research Council of Lithuania (LMT), agreement No S-SV-25-277.

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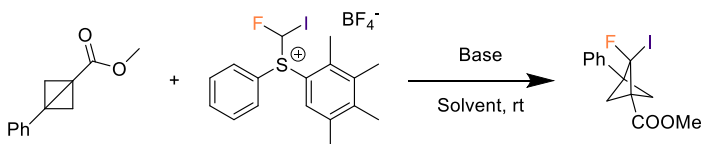
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Access to 2,2-fluoriodobicyclo[1.1.1]pentanes

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Bicyclo[1.1.1]pentanes (BCPs) have become well established as useful bioisosteres for the replacement of substituted benzene rings.¹ The three-dimensional conformation of BCPs provides a variety of beneficial properties compared to their aromatic counterparts. The introduction of fluorine atoms has also been extensively studied and shown to improve various pharmacokinetic properties.² However, the synthesis of highly substituted BCP compounds—especially those incorporating a fluorine atom—has remained rather challenging and not well explored.



Scheme 1. Synthesis of fluoriodo-BCPs.

Herein, we report a simple method for the synthesis of previously inaccessible fluoriodo-BCPs, utilizing our previously developed fluoriodomethylsulfonium salt.³

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From classroom to industry: learning organic chemistry through Ibuprofen synthesis

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Ibuprofen is one of the most widely used nonsteroidal anti-inflammatory drugs. Along with sporadic users, more than 30 billion doses are taken each year.¹ It serves as an excellent educational model for illustrating key concepts in organic synthesis. This work focuses on the Hoechst-Celanese process for large-scale production of ibuprofen. The synthesis begins with a Friedel–Crafts acylation of *p*-isobutylbenzene, followed by reduction to a secondary alcohol, conversion to the corresponding alkyl chloride, and subsequent Grignard formation. Each step highlights fundamental reaction types—including electrophilic aromatic substitution, carbonyl chemistry, nucleophilic substitution, organometallic transformations, and acid–base processes. This pathway not only exemplifies important synthetic strategies but also underscores the industrial significance of ibuprofen production in modern pharmaceutical chemistry.

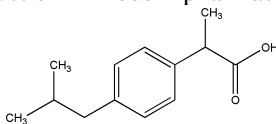
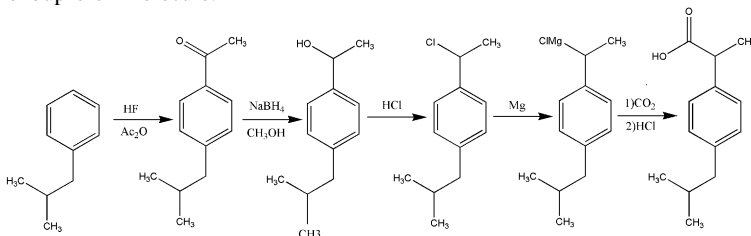


Figure 1. Ibuprofen molecule.



Scheme 1. Synthesis of ibuprofen.²

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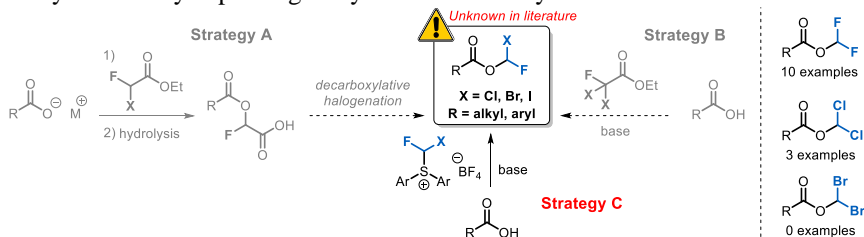
Synthetic Access to Fluorohalomethyl Esters

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Fluorinated moieties significantly influence the physical, chemical, and biological properties of target molecules.¹ The rapid growth of fluorine-containing pharmaceuticals and agrochemicals has driven extensive efforts to develop efficient methods for incorporating fluorine-containing groups.²

The synthesis of fluorohalomethyl esters has been mainly limited to the preparation of difluoromethyl esters using various difluorocarbene sources – TMSCF₂Br,³ difluoromethylene phosphobetaine,⁴ deuteriodifluoromethyl sulfonium ylides⁵ and fluorosulfonyldifluoroacetic acid.⁶ However, further application of these esters in the synthesis of fluorine-containing compounds remains scarcely explored. Moreover, the preparation of mixed esters, such as fluorochloro-, fluorobromo-, or fluoroiodomethyl esters, has not been reported at all. The access of fluorohalomethyl esters may open opportunities for the development of novel reagents for introduction of fluorinated moieties. Herein, we demonstrate a simple and practical method for the synthesis of various mixed fluorohalomethyl esters via electrophilic fluorohalomethylation of carboxylic acids by exploiting diarylfluorohalomethyl sulfonium salts.⁷



Scheme 1. Synthesis of unknown fluorohalomethyl esters.

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Unprecedented 1,2-germanium shift in propargyl germanes upon reaction with electrophiles

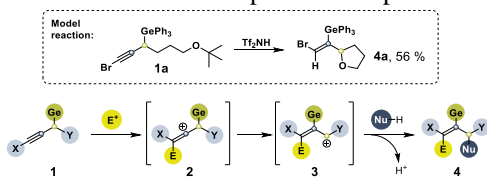
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In the last few decades, the volume of organogermanium-focused research has been constantly increasing. Many reports highlight germanium(IV) compounds as the “golden middle” between relatively unreactive organosilicon and too reactive organotin analogues. While organogermanes demonstrate anomalous resistance towards nucleophilic attack including fluoride, electrophilic activation converts them into highly reactive and labile functionalities.¹ In this context, germanium compounds demonstrate unique reactivity in some cases, most of which remain unexplored yet.

Herein we report a 1,2-germanium shift that takes place in propargyl germanes reacting with electrophiles. The concept is based upon the early observations of carbocation β -stabilization effect by group IVA elements.² As a general trend, cation stabilization increases within the metallic properties of the element: C < Si < Ge < Sn < Pb. At the same time, a β -stabilizing group can also undergo elimination or 1,2-shift following the same reactivity pattern.

Some evidence of cationic 1,2-migrations employing germanium has already been reported.³ Hence, we decided to use our previously developed 1,2-silyl shift methodology⁴ to highlight propargyl germanes as precursors to functionalized vinyl germanes of type **4** (Scheme 1). A putative mechanism of this transformation likely includes the following steps: 1) electrophilic addition to alkyne **1** with formation of vinyl cation **2**; 2) a germyl group 1,2-shift leads to the formation of allyl cation **3**; 3) the latter reacts with a nucleophile to afford a substituted vinyl germane **4**. Scope and limitations of substrate-electrophile-nucleophile combinations will be discussed.



Scheme 1. Synthetic methodology involving 1,2-germyl shift in propargyl germanes and its mechanistic proposal.

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[#]both authors contributed equally.

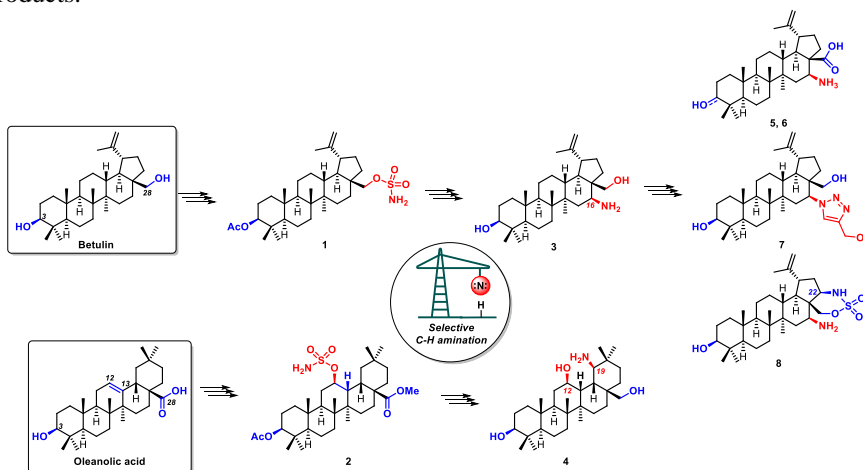
Synthesis and application of amino- derivatives of pentacyclic triterpenoids

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Naturally abundant pentacyclic triterpenoids are important secondary metabolites, which have aroused huge interest by possessing wide range of remarkable biological activities such as antitumor, antidiabetic, anti-inflammatory and antiviral activities¹. Oleanolic acid and betulin are one of the most recognizable compounds of this branch, which are isolated from various plants.

The aim of this work² is to obtain novel triterpenoid amino derivatives *via* C-H amination, forming new C-N bonds. For this purpose, precursors **1** and **2** bearing sulfamate directing groups were synthesized and treated according to *Du Bois* conditions³ - amino derivatives **3** and **4** were obtained². Amine **3** proved to be useful in further modifications yielding amino acids, triazoles and secondary C-H amination products.



Scheme 1. Selective C-H amination of betulin and oleanolic acid.

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Design and synthesis of novel cytotoxic C-ring substituted PBDS

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Antibody-drug conjugates (ADCs) represent a rapidly expanding class of cancer therapeutics, offering targeted delivery of cytotoxic agents to tumor cells.¹ Pyrrolobenzodiazepines (PBDs) are among the most effective ADC payloads due to their ability to covalently bind to the minor groove of DNA, resulting in potent cytotoxic effects.² However, the structural diversity of available ADC payloads remains limited, highlighting the need for novel chemotypes to enhance therapeutic options. In this work, we describe the design and synthesis of novel C-ring-substituted PBD analogs, intending to broaden the chemical space of PBD-based payloads. The cytotoxicity of these new compounds was evaluated across multiple cancer cell lines to assess their potential for future application in ADC development.

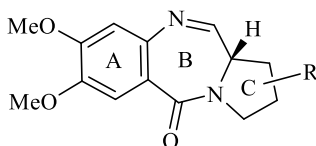


Figure 1. PBDs scaffold.

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Development of MOF-luminophore for solid-state gas sensor applications

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In recent years, solid-state organic luminophores have garnered attention for their potential applications in light-emitting diodes due to their low production costs. One of the breakthroughs in solid-state organic luminophores was the discovery made by K. Leduskrasts in 2019,¹ where solid-state luminescence was achieved by utilizing $\pi^+ - \pi$ interactions in a pyridinium – carbazole system. Further research by K. Leduskrasts and his team led to the discovery of the structure of luminophore **1** and its derivatives, achieving quantum yields up to 85 %.²

In collaboration with the Institute of Atomic Physics and Spectroscopy, we observed that luminophore **1** exhibits changes in its optical properties upon exposure to ammonia and acetic acid vapors, highlighting its potential as a solid-state gas sensor.³ Our recent studies suggest that the interaction mechanism occurs at the surface layer of the luminophore. To exploit this effect, we developed composite material **3**, in which the surface area is enhanced by coupling organic luminophore **1** with metal-organic framework (MOF) **2** (Figure 1).

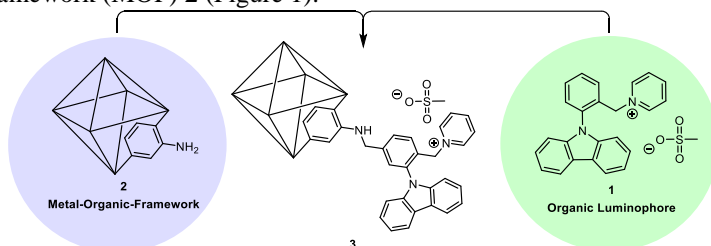


Figure 1. Development of MOF-luminophore **3**.

Acknowledgements. The research is financed by the Recovery and Resilience Facility project “Internal and External Consolidation of the University of Latvia” (No.5.2.1.I.i.0/2/24/I/CFLA/007) grant no. LU-BA-PA-2024/1-0040 “Design of pyridinium luminophore structural and optical properties for tailored sensor response”.

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Nonlinear optical activity of through space charge transfer organic salts

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In nonlinear optics (NLO), intense light fields produce unusual material responses including frequency conversion and intensity-dependent refractive indices, that are used in telecommunications, imaging, data processing, and laser technologies.¹ NLO responses are classified by order (e.g., second, third, fifth), reflecting the degree of a material's NLO susceptibility. While organic materials with strong second- and third-order responses have been extensively studied, the fifth-order NLO behavior of small organic molecules remains virtually unexplored.

Herein, we demonstrate a novel approach to organic NLO material design based on a through space charge transfer (TSCT) architecture. By synthesizing molecules featuring a heteroaromatic π^+ -system placed in close spatial proximity to an electron-donating π system, efficient intramolecular TSCT is achieved together with a strong NLO response. Compounds with a general structure **1** (Figure 1) exhibited a pronounced fifth order NLO response without measurable third-order contribution as measured using the z-scan method in solution. These findings highlight π^+ -system containing TSCT architecture as a powerful design motif for engineering tailored, high-order optical nonlinearities in small-molecule systems and open new avenues for organic material development in advanced photonic devices.

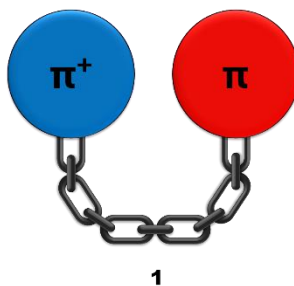


Figure 1. TSCT π^+ – π interactions.

Acknowledgements. This work was funded by RRF grant No.30/OSI/PG (RRF project No.5.2.1.1.i.0/2/24/I/ CFLA/001).

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Stabilization of amorphous empagliflozin using core-shell electrospun nanofibers

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Coaxial electrospinning technology was used to form microfibers with a core-shell structure to obtain a stabilized amorphous solid dispersion empagliflozin, a selective sodium-glucose cotransporter 2 inhibitor. The fibers with optimal properties were obtained by dissolving empagliflozin in a mixture of ethanol and DMSO, adding *Soluplus* as the core polymer and using *Kollicoat* as the shell polymer.

The amorphous state of the obtained solid dispersions was verified by X-ray powder diffraction (XRPD) and differential scanning calorimetry (DSC). The morphology of the obtained microfibers was characterised by scanning electron microscopy (SEM), see Figure 1b. The obtained dispersions were also characterized by Fourier transform infrared spectroscopy (FTIR) and photoluminescence spectroscopy.

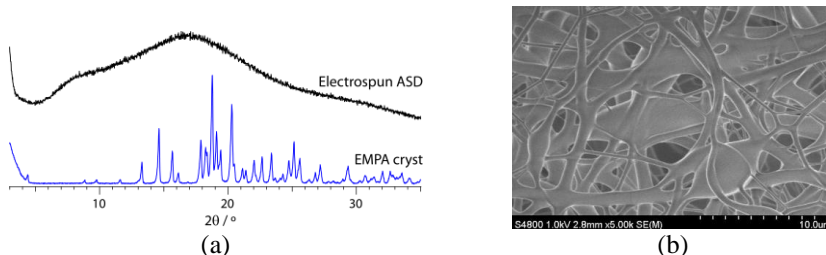


Figure 1. (a) XRPD of electrospun ASD and crystalline EMPA, (b) SEM micrograph of the obtained electrospun ASD.

The obtained structures were demonstrated to prevent long-term recrystallisation of the empagliflozin and protects it from degradation by UV radiation and temperature.

Acknowledgement. The research is financed by the Recovery and Resilience Facility project "Internal and External Consolidation of the University of Latvia" (No.5.2.1.1.i.0/2/24/I/CFLA/007), grant number LU-BA-PA-2024/1-0062.

2-(Aryl)-N-(heteroaryl)acetamides: synthesis and antibacterial activity

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Artificial intelligence systems are increasingly being used to predict the structure of potential pharmaceutically active compounds, although their effectiveness remains uncertain. The traditional method of creating new potentially biologically active substances by combining various fragments that have previously shown similar activity still holds importance. Once initial assessments of these compounds are conducted, further structural modifications can be made based on the results of biological testing.

It is well known that ability to form hydrogen bonding is important for biological activity and therefore amide functional group might be valuable element in the structure of potentially antibacterial active compounds. The aim of this work was to prepare several low molecular weight novel 2-aryl-N-(heteroaryl)acetamides and evaluate their biological activity. The priority was given to simple one step amides synthesis by reacting aryl acetic acids with amino heterocycles. Several combinations of carboxylic acid functional group activators were tested.

Additionally results of the prepared 2-(aryl)-N-(heteroaryl)acetamides antibacterial properties against the *E.Coli dh5a* bacterial line evaluation will be presented.

5-Substituted-1,3,4-oxadiazol-2-thiols: synthesis, modification and biotesting

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In drug development, creating new, effective, and safe medications is a constant challenge. Scientists are always trying to improve the efficiency of drugs, focusing on heterocyclic compounds to create pharmaceutically active ingredients that can selectively target diseases while minimizing side effects and toxicity. The synthesis and study of novel heterocyclic compounds is of ongoing relevance as scientists continuously strive to improve the efficiency and accuracy of drugs. While computational programs are increasingly used to predict how a drug might work, they cannot fully replace real-world laboratory testing. Comparing the results from these theoretical calculations with actual lab results is crucial. This helps scientists refine and improve the algorithms used in computational programs, building a stronger foundation of knowledge. Combining two or more heterocycles along with added specific functional groups can also increase a drug's specificity for its target.

The aim of this project was to obtain 1,3,4-oxadiazole analogues capable of acting on the enzyme succinate dehydrogenase (SDH). Mutations in succinate dehydrogenase are believed to be responsible for the progression of some cancers, as excessive amounts of succinate accumulate in the cytosol and intracellular fluid of cells leading to tumor formation. In collaboration with researchers at Palacký University, an initial theoretical library of 5-substituted-1,3,4-oxadiazol-2-thiols and thioethers have been developed and a theoretical in-silico study of their interaction with SDH has been performed.

The most selective compounds were selected, synthesis of them was performed. Preliminary results of the bioassays show that a correlation between the theoretical calculations and the experimental results will be presented. To reliably prove the structure of the obtained compounds, spectral analysis IR and NMR (standard and two-dimensional) along with mass spectrometric analysis (MS) methods were used. All compounds prepared for biological studies were purified to at least 97% purity (LC-MS).

Synthesis of Bio-inspired Insensitive Energetic Materials

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Energetic materials play a crucial role in modern technology, with applications spanning the military, mining, construction, and aviation industries. Recent advances in this field have focused on developing safer, more environmentally sustainable, and highly efficient compounds. A notable subgroup within secondary explosives is insensitive high-energy density materials (IHEDMs), which combine strong performance with remarkable resistance to external stimuli.¹ A growing strategy in IHEDM design involves exploiting hydrogen bonding, as the introduction of donor and acceptor groups fosters both intra- and intermolecular interactions, thereby enhancing stability and density.² Although nucleobases possess excellent hydrogen-bonding capabilities, their use in IHEDM development has been only minimally explored.

In this work, we present the design and synthesis of adenine- and uracil-based energetic materials, along with an evaluation of their energetic properties (Figure 1). Various explosophoric groups—including azido, nitro, amino, hydroxylamino, and tetrazolyl amino—are incorporated to generate new IHEDMs, with efforts directed toward determining optimal conditions for constructing the proposed molecular frameworks.

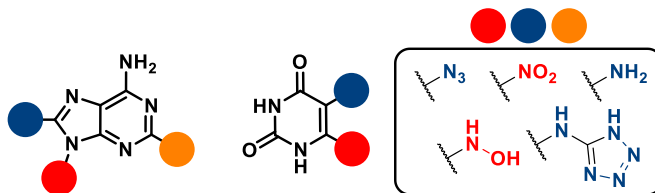


Figure 1. Adenine and uracil derivatives modified with explosophoric groups.

Acknowledgements. Supported by research and development grant No RTU-PA-2024/1-0033 under the EU RRF project No 5.2.1.1.i.0/2/24/1/CFLA/003.

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Synthesis and investigation of phenothiazine and phenoxazine SAMs in perovskite solar cells

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In the search of alternative energy sources, solar cells have emerged as one of the best contenders. Even though the technology is working well, its production remains complicated, expensive and energy-intensive process. To address this issue, new types of solar cells are being developed. Currently perovskite solar cells are aiming to replace or supplement silicon solar cells. Perovskite has significantly simpler fabrication, since most of the layers can be formed using solution-based methods. Moreover, this technology tends to surpass silicon based solar cells' efficiency in laboratory conditions.¹ The best-performing perovskite solar cells are currently employing lead salts in the absorber layer, which poses a serious environmental concern if these solar cells are widely adopted. A rather simple solution to this problem was proposed: using tin instead of lead. This approach fully eliminates the dangers of lead salts but also opens another can of worms.² Tin-based perovskite is a rather new concept, which is only now getting more attention from the scientific community. Current main concerns with tin perovskite are its long-term stability and low efficiency. These problems are partially created by the lack of charge transporting materials specifically made for this perovskite type. In this work new phenothiazine- and phenoxazine-based self-assembling monolayers forming p-type semiconductors, which are specifically tailored for tin-based perovskite were synthesized to address this issue. These semiconductors provide better interaction with the perovskite layer which as a result gave us record efficiency of 7.7% for DMSO free tin perovskite solar cells. In summary, this research demonstrates that by modifying phenothiazine and phenoxazine central fragments, we can adapt them to achieve more efficient tin perovskite solar cells.

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Synthesis of structurally simplified Diazonamide A analogs

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Diazonamide A is a structurally unique secondary metabolite first isolated by Fenical and coworkers from the colonial marine ascidian *Diazona angulata*.¹ The structurally complex diazonamide A (**1**) was found to be highly cytotoxic anticancer agent against several types of cancer cell lines.² Studies conducted by Suna³ revealed that compound **2a**, a structurally simplified analog of **1**, can be synthesized more easily while retaining high antiproliferative properties. However, **2a** lacks some ADME properties which renders it from entering preclinical studies. To optimize the structure of analog **2a** for further development as anticancer agent, we designed a series of compounds, **2b** and **2c**, by replacing the indane cycle in **2a** with more polar isoindoline and benzofuran moieties.

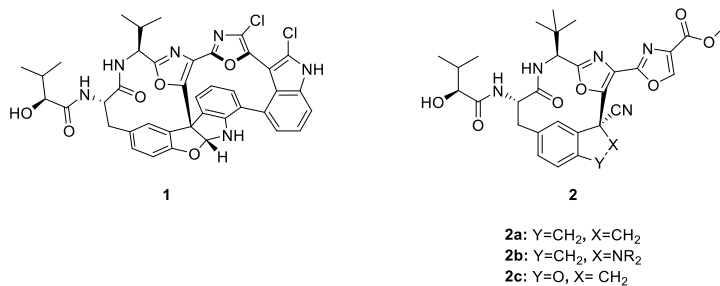


Figure 1. Structures of diazonamide A (**1**), simplified analog **2a** and compounds **2b** and **2c**.

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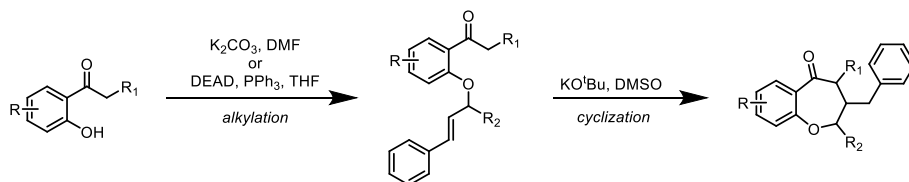
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Synthesis of oxepane derivatives based on enolate addition to alkene

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Oxepane heterocycles are valuable structural motifs in pharmaceutical agents and natural products. Despite their significance, the synthesis of these seven-membered heterocycles remains challenging as currently known methods suffer from significant drawbacks,¹ including harsh reaction conditions, use of expensive transition metals or multi-step procedures. To address these challenges, we present a novel one-step strategy for the efficient formation of oxygen containing seven-membered rings using enolate addition to non-activated double bonds. The procedure utilizes affordable 2-hydroxyacetophenone derivatives appended with styrene functionalities as starting materials. The reactions proceed under very mild conditions using potassium tert-butoxide as a base, yielding the desired oxepane derivatives in moderate to good yields.



Scheme 1. Synthesis of oxepane derivatives.

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Synthesis and properties of lipophilic Meldrum's acids

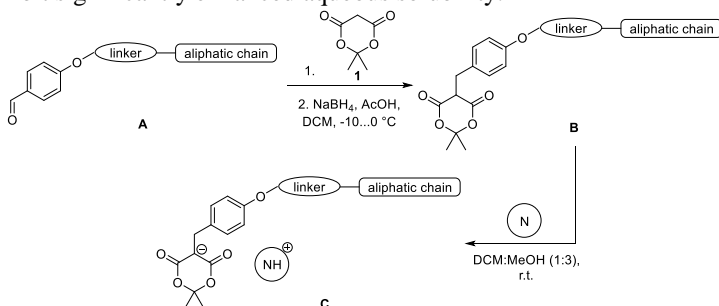
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Meldrum's acid and its monosubstituted derivatives are potential antioxidants capable of inhibiting the autooxidation of polyunsaturated fatty acid derivatives.¹ Some structural similarities between lipophilic Meldrum's acid's ammonium salts and anionic surfactants can be observed. Therefore, this study focuses on the possibility of constructing dual-nature compounds that would simultaneously exhibit properties of surfactants and antioxidants.² The addition of long saturated lipophilic chain improves their solubility in fats, therefore extending their applicability in various oil-based products.

The target compounds were synthesised by the Knoevenagel condensation reactions of Meldrum's acid (**1**) and aldehydes with different linkers **A**, followed by reduction reaction and the subsequent synthesis of ammonium salts **C** (Scheme 1). The antiradical activity of lipophilic Meldrum's acids and their ammonium salts was determined by DPPH test.³ Monosubstituted derivatives showed twice the antiradical activity as Meldrum's acid (**1**).

Whereas the lipophilic Meldrum's acid is practically insoluble in water, the corresponding ammonium salts bearing hydrophilic, polar substituents on the amine moiety exhibit significantly enhanced aqueous solubility.



Scheme 1. Synthesis of Meldrum's acids and their ammonium salts.

Acknowledgements. The author thanks *Dr. chem.* K. Lazdovica for IR analysis and *Dr. sc. ing.* I. Juhneva for XRD analysis.

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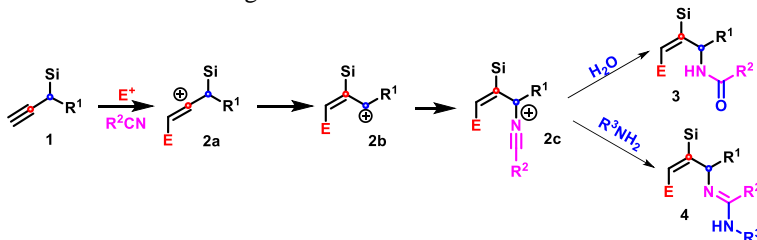
Sequential 1,2-silyl shift – Ritter – type reaction for synthesis of functionalized amides and amidines

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In the classical Ritter reaction, the presence of an acid enables the generation of a carbenium ion from alkenes or alcohols, which subsequently reacts with a nitrile and water to afford amides.¹ Carbenium ions, however, can also be derived from alternative substrates. In our previous work, we demonstrated the synthesis of amide **3** from propargyl silanes **1**, wherein carbenium ion **2a** is formed via a 1,2-silyl shift (Scheme 1).² Our group also found that, in this transformation, water can be replaced by other nucleophiles, most notably *p*-toluenesulfonamide, resulting in the formation of amidine derivatives **4**.

The present study is focused on the development of a novel four-component reaction (Scheme 1).^{3,4} Various electrophilic reagents, such as *N*-halogenated succinimides, were employed to initiate the 1,2-silyl shift and subsequent generation of a carbenium ion **2b**. Secondary nucleophiles such as *p*-toluenesulfonamide, imidazole, or 1,2,4-triazole were used in the reaction to react with the nitrilium ion **2c**. The reaction conditions for amidine synthesis were optimized by varying the temperature, solvents, and the concentration of starting materials.



Scheme 1. General representation of amide **3** and amidine **4** synthesis.

Acknowledgements. This work was supported by the Latvian Council of Science Grant LZP-2023/1-0576. R. K. thanks EU RRF within project No 5.2.1.1.i.0/2/24/I/CFLA/003 academic career doctoral grant, ID 1134.

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The development and study of quinoxaline and phenanthroimidazole derivatives as luminophores for organic light-emitting diode applications

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In recent decades, organic light-emitting diodes (OLEDs) have garnered significant attention from researchers and have advanced greatly, offering numerous advantages, including high contrast ratios, wide viewing angles, flexibility, and energy efficiency.¹ Hybridized local and charge transfer (HLCT) emitters offer a promising strategy for the advancement of high-performance, cost-effective, and environmentally sustainable OLEDs. Due to their elevated photoluminescence quantum yields (PLQY) and robust thermal stability, phenanthroimidazole derivatives that integrate phenanthrene and imidazole moieties are promising prospects for the advancement of HLCT-based fluorophores. Recent research examined quinoxaline-based compounds for use in OLEDs, demonstrating that OLEDs employing these materials show significant potential, attaining high photoluminescence quantum yields and enhanced external quantum efficiencies.^{4,5} This study investigates the synthesis and analysis of several derivatives of quinoxaline and phenanthroimidazoles as potential materials for organic light-emitting diodes (OLEDs). The evaluation of these materials revealed that the produced compounds demonstrated ionization potential of 5.64 eV and 5.98 eV. The compounds, when molecularly dispersed in the stiff inert polymer Zeonex, demonstrated high-intensity emission with PLQY values of 45 and 56, making them viable candidates for OLEDs.

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Synthesis of oxadiazole derivatives and evaluation of their biological properties

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A great need for new biologically active compounds remains, regarding the pathogen resistance, the possible shortage of agents, the lack of efficiency or the accuracy of the impact. Heterocyclic compounds may be significant. This class includes oxadiazole, distinguished by a five-membered unsaturated ring and two main atomic positions.¹ They are characterized by exceptional chemical, physical, pharmacokinetic properties, excellent opportunities for interaction with macromolecules, sufficient reactivity and stability. Growing interest is given to 1,3,4-oxadiazole analogues with substitutions in second and fifth positions, which also becomes an important topic of medicinal chemistry research.^{2,3} The aim of the work is to synthesize a group of new oxadiazole compounds with different aromatic structural bases by applying the principles of alkylation reactions in the hope of obtaining compounds with biological properties. In this work, it was decided to start the synthesis of the target compounds from the preparation of oxadiazole thiol according to the known methodology.⁴ The resulting product is further cyclized under basic conditions. The starting oxadiazole thiol is then treated with substituted halides. The starting thiols were obtained in very good yields, and three series of different target compounds were synthesized in good to very good yields. Detailed spectroscopic studies confirmed the structures and high purity of the target compounds. Parasitic nematodes and worms, which can infect plants, animals or humans, have a negative impact on the quality of life and cause significant economic losses. Helminths acquire increasing resistance to known medicines and treatment methods, making it difficult to effectively control parasitic infections.⁵ It is known from literature that oxadiazole derivatives can also have anthelmintic properties.⁶ It was decided to evaluate the properties of synthesized compounds for research using model nematodes *C. elegans*. Utilizing a chitinase test it was found that the development of model nematode *C. elegans* was most influenced by two synthesized compounds.

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Meldrum's acid functionalized dendrimers as radical scavengers

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Arylmethyl Meldrum's acids are 1,3-dicarbonyl type antioxidants¹ with excellent radical scavenging abilities.² Our recent research has aimed to modify the activity of arylmethyl Meldrum's acids through covalent binding to dendrimers.³ In this work we have synthesized dendrimers **1**, which contain various cores (derived from small polyols or polycarboxylic acids) linked to arylmethyl Meldrum's acid moieties through a 1,2,3-triazole based linker (Figure 1). The synthesis is achieved by, firstly, propargylating the core moiety **2**. Then the 1,2,3-triazole linker is established through a “click” reaction between the polyalkyne core **3** and the azide **4**. Next, Meldrum's acid (**5**) moieties are introduced in the structure through the Knoevenagel condensation with the aldehyde **6**. Finally, the arylidene **7** is reduced to the desired product **1**.

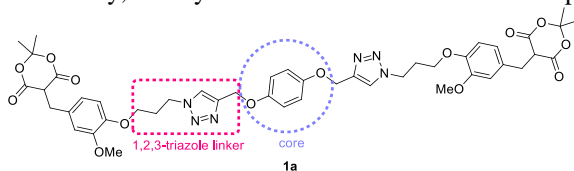
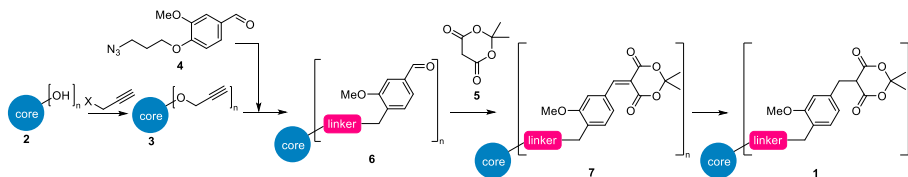


Figure 1. Example structure of dendrimers **1**.



Scheme 1. Synthesis of dendrimers.

The assessment of the radical scavenging ability of dendrimers **1** showed activity on par with other arylmethyl acids, and, under specific conditions, exceeding that of commercial antioxidants BHT and ascorbic acid.

Acknowledgements. This work was supported by the EU RRF within project No. 5.2.1.1.i.0/2/24/I/CFLA/003 academic career doctoral grant, ID 1028.

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Synthesis reevaluation of BAH chromophore family

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Introduction of **BAH** family chromophores by Huajun Xu et al.¹ established an evolutionary step towards organic second-order nonlinear optically (NLO) active materials. As a representative of this compound series, **BAH13** achieved a state-of-the-art r_{33} value of 1100 (pmV⁻¹). Therefore, this molecular design has attracted significant attention in the field. However, during our research we found that the originally reported synthetic pathway gives an unsatisfactory yield of the target compound.

Herein, we report an optimized synthesis of **BAH**-family compounds. The most problematic stage is the final synthetic step – Claisen–Schmidt condensation with tricyanofuran (TCF) derivatives, which is widely used for the acquisition of similar chromophores. Under the reported reaction conditions, the products decomposed into unidentified side products, leading to low yield (typically reported 40%, in our case around 5%). We have developed modified reaction protocol that overcomes this limitation and allows yields exceeding 90%.

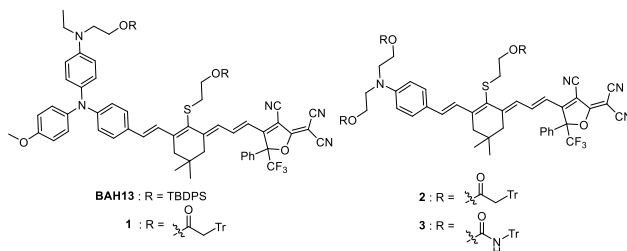


Figure 1. Obtained materials.

For the improvement of material design, we proposed alternative amorphous phase-promoting groups, namely, a trityl group attached either via an ester (**1** and **2**) or a carbamoyl (**3**) functionality. The obtained materials show promising properties as second-order NLO candidates and are currently under investigation by our colleagues from the Institute of Solid State Physics, University of Latvia.

Acknowledgements. This work was supported by the Horizon 2020 programme through grant 101070332 (PHORMIC).

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Sulfur-specific alkylation of sulfinamides by Zn carbenoids

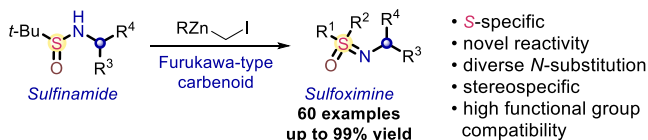
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Relatively scarcely represented in chemical research before 2000, sulfoximines have recently experienced an exponential growth in popularity. While remarkable progress has been achieved in asymmetric synthesis¹ of this versatile moiety, the overwhelming majority of current approaches ultimately target only *NH*-sulfoximines. On the other hand, a chiral substituent at the *N*-atom could be obtained via *S*-selective alkylation of readily accessible Ellman's sulfinamide derivatives. Although the latter generally undergo *N*-specific alkylation, we serendipitously discovered² that Zn carbenoids react exclusively at the *S*-atom. This novel transformation significantly expands the diversity of currently available sulfoximines and offers promising opportunities in drug design. Based on these findings, efforts to extend the developed methodology from *S*-alkylation of sulfinamides to the corresponding alkylation of sulfinamidines are currently underway in our laboratory.



Scheme 1. Sulfur-specific alkylation of sulfinamides.

Supervisor: Dr. Chem. Prof. E. Suna

Acknowledgements

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Molecular engineering and synthesis of asymmetric thiazolothiazole-derived luminogens for modern optoelectronic devices

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Asymmetric thiazolothiazole (TT)-based luminogens have recently emerged as promising candidates for optoelectronic applications.^{1,2} We report the single-step synthesis of three asymmetric TT derivatives containing tetraphenylethylene moiety to induce aggregation-induced emission enhancement and suppress aggregation-caused quenching. To enhance intramolecular charge transfer, solvatofluorochromism, and photoluminescence quantum yield (PLQY), electron-donating moieties such as triphenylamine, carbazole, and fluorene were introduced.^{3,4,5} The toluene solution of one derivative showed PLQY of 53% with a sub-nanosecond emission lifetime. The ionization potentials of 5.38–5.70 eV suggest balanced charge injection in OLEDs. The compounds show robust thermal stability, favorable charge-transporting properties, and high PLQYs in both solutions and solid state, positioning them as promising candidates for next-generation sustainable optoelectronic devices.

Donor-TT-TPE

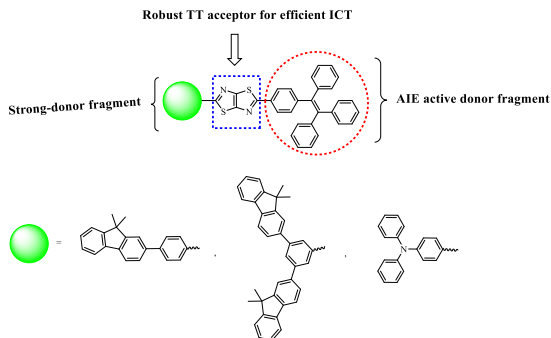


Figure 1. Emitters based on donor-acceptor-donor architectures.

Acknowledgement: This project received funding from the Research Council of Lithuania (LMTLT), agreement No. S-LU-24-6.

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Development of reversible covalent SUB1 protease inhibitors

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Malaria is mosquito-borne disease caused by the *Plasmodium* genus parasites which are responsible for over 600 000 deaths annually.¹ When the disease progresses to the blood-stage an essential subtilisin-like serine protease called SUB1 is responsible for the release (egress) of merozoites from the infected blood cells² which makes it an attractive target for new antimalarials.

Peptidomimetic boronic acid **1** is a known inhibitor of SUB1 protease.² In our follow-up study we decided to modify the **P**₅ and **P**₃ positions as well as depeptidise the **P**₁ – **P**₂ position by replacing it with an aryl ring in order to modify the physiological properties of the active compound as well as increase its derivatization potential (Figure 1).

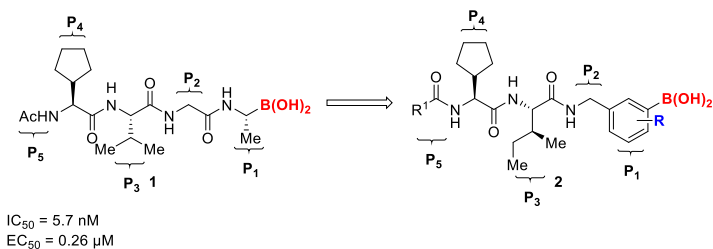


Figure 1. P₁ – P₂ depeptidization.

Acknowledgements. This project is funded by Recovery and Resilience Facility (RRF grant No. 21/OSI/DG) and by student grant from Latvian Institute of Organic Synthesis (IG-2025-09).

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Progress toward 1-fluoropropellane: synthesis of advanced [1.1.1]propellane intermediates

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Fluorinated propellanes represent a tantalizing yet scarcely explored class of strained molecules whose unusual reactivity and electronic properties could enable breakthroughs in molecular design. Simple [1.1.1]propellanes have already found use as scaffolds for new drugs, as frameworks for molecular materials, and as tools to probe bioisosterism where bicyclopentane derivatives mimic para substituted benzene rings or alkynes in biological systems— but their fluorinated counterparts remain virtually unknown. Building on the dichloroacetone–Wittig route to substituted propellanes reported by Bothe & Schlüter,¹ the polymerizable derivatives obtained via MOM protection by Freudenberger et al.,² and the robustness of TBDMS-protected pathways described by Klopsch et al.,³ we sought to overcome long-standing barriers to fluorinated analogues. The method of Werner et al.,⁴ while elegant, proved unsuitable for dichloroacetone-derived systems due to premature alkene polymerization.

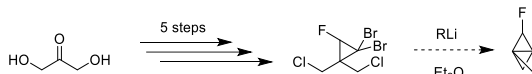


Figure 1. Developed pathway to [1.1.1] propellanes.

To address this, we developed a route beginning from the inexpensive starting material dihydroxyacetone, employing TBDMS protection, Wittig extension, and cyclopropanation to generate stable precursors of 1-fluoropropellane. This approach offers a versatile entry point into fluorinated propellane derivatives and supports further synthetic exploration toward bicyclopentanes and related frameworks as suitable bioisosteres.

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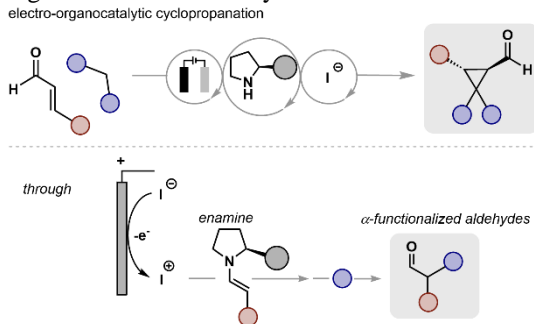
Asymmetric electro-organocatalytic functionalization of aldehydes enabled by iodine

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The combination of asymmetric organocatalysis and electrochemistry provides a powerful strategy for developing novel enantioselective transformations in a sustainable and efficient manner.¹ By using electricity as a clean reagent, the use of hazardous reagents is minimized while enabling unconventional reactivity patterns.² In particular, aminocatalyzed asymmetric transformations driven by anodic oxidation have attracted growing interest, especially those proceeding via iminium ion activation.

Our group's efforts are aligned to address this gap. In our initial work, we developed an iminium ion-promoted asymmetric synthesis of cyclopropanes via an electrocatalytic, iodine-mediated ring closure.³ The reaction is driven by the mild and controlled electrochemical generation of electrophilic iodine species in catalytic amounts, which allows to protect the organocatalyst from decomposition. Our current focus is on developing new asymmetric organocatalytic functionalization reactions of aldehydes using halogen-mediated electrosynthesis.



Scheme 1. Electrochemical iodine-mediated organocatalysis for enantioselective functionalization of aldehydes.

Acknowledgements. We thank Nora Deil, Mihhail Fokin, Mariliis Kimm and Marine Pinaud for their contribution to these projects.

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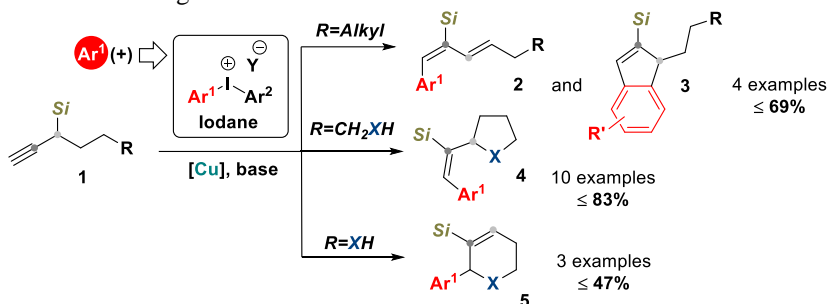
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Copper-catalyzed arylation of propargyl silanes with iodanes featuring the 1,2-silyl shift

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Following our previous studies on propargyl silane functionalization,¹ we now explore the arylation of propargyl silanes **1**, using iodanes as formal carbon electrophiles. In the absence of a propargylic silyl group, transition metal-catalyzed (Cu, Pd) approaches typically result in terminal alkyne C(sp)–H arylation.² In contrast, propargyl silanes, depending on C-skeleton length, undergo either 1,3- or 1,1-carbodifunctionalization (Scheme 1). In substrates containing an internal nucleophile, this leads to the formation of 5-membered heterocycles **4**, containing a styryl side chain, or 6-membered heterocycles **5**. In the case of aliphatic propargyl silanes, an arylation - β -H elimination event occurs, leading to aryl dienes **2** and indenes **3**. The introduction of a variety of (hetero)aromatic groups with electron-donating and electron-withdrawing substituents was studied for this reaction.



Scheme 1. Cu-catalyzed arylation of propargyl silanes featuring iodanes.

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New synthetic applications of electrochemical SOMO-organocatalysis

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Organo-SOMO catalysis presents intriguing new opportunities in organic synthesis by altering the reactivity of enamine intermediates—from engaging with electrophilic partners to reacting with nucleophilic ones. Since MacMillan's seminal contributions,¹ this strategy has remained largely unexplored for over a decade, primarily due to the demanding reaction conditions typically required, including superstoichiometric amounts of oxidants, low temperatures, inert atmosphere, and prolonged reaction times.² Furthermore, commonly used aminocatalysts are prone to degradation under oxidative conditions. In this context, electrochemistry can offer a promising solution. Following the pioneering work of MacMillan and recent advances in asymmetric electrochemical α -functionalization of aldehydes promoted by a redox shuttle,³ we report the extension of this approach to novel transformations (Figure 1).⁴

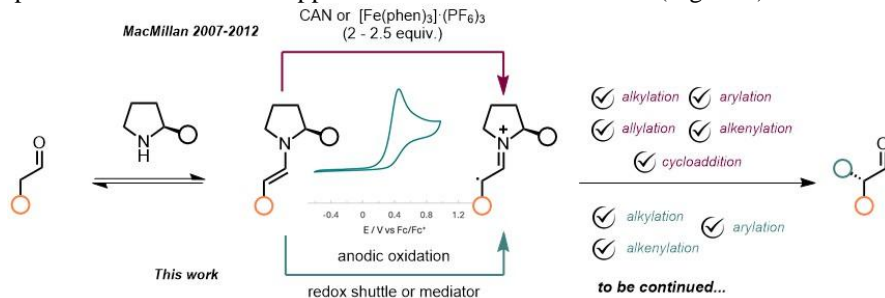


Figure 1. Reactions enabled by the single-electron oxidation of chiral enamines.

Acknowledgements. We thank for financial support from the European Union through the EU4Belarus SALT II (Support to Advanced Learning and Training).

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The synthesis of naturally occurring fragrances *via* one-pot ester hydrosilylation/acatalization sequence

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Acetals are among the most widely used protecting groups for aldehydes in organic synthesis.¹ Beyond their role as protective groups, acetals also participate directly in a variety of important chemical transformations. Additionally, acetals are valued as stable, storable precursors to aldehydes and find practical use as pre-fragrances in the perfume industry.

The most common precursors for acetals are their parent aldehydes, typically synthesized through redox reactions—either by reducing carboxylic acid derivatives or oxidizing alcohols. While numerous reliable methods exist for oxidizing alcohols to aldehydes, reducing esters and other carboxylic acid derivatives can be considerably more challenging. In recent years, catalytic ester hydrosilylation has emerged as a powerful method to overcome many of the limitations associated with ester reduction. In this work,² we present an extension of the ester hydrosilylation methodology³⁻⁴ that enables the direct conversion of esters into their corresponding acetals. Our one-pot process involves ester hydrosilylation catalyzed by heteroleptic triaryl boranes, followed by quenching with a suitable alcohol or thiol. The transformation proceeds under low catalyst loading (0.1 mol%), utilizes readily available silanes and demonstrates broad functional group tolerance.

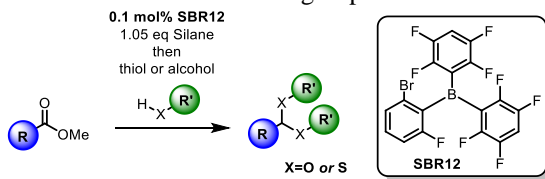


Figure 1. Ester Hydrosilylation/Acatalization Sequence.

Acknowledgements. This research is partially funded by the Latvian Council of Science, project “Application of catalytic hydrosilylation in the valorization of renewables,” project No. lzp-2023/1-0413 and Recovery and Resilience Facility (RRF) project Nr. 5.2.1.1.i.0/2/24/1/CFLA/001, Doctoral Grant Nr.20/OSI/DG.

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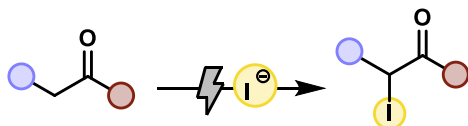
Electrooxidative iodination of carbonyl compounds

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Iodine-containing organic molecules hold significant value in both industrial processes and medicinal chemistry. Moreover, they are useful intermediates and synthons in organic synthesis, particularly in numerous carbon-carbon bond forming¹ and iodine-metal exchange reactions.²

Herein, we describe a direct anodic iodination of carbonyl compounds, protocol enables selective formation of α -iodocarbonyls under mild condition. This work comprises quaternary ammonium salt as halogen source, which is commercially available, stable, cheap, and commonly used for organic reactions.³ Our work eliminates the use of external oxidant, usually used to oxidize iodide and we utilizes electrons as a potent, controllable, and traceless alternative oxidant. The protocol shows electrochemical oxidation of iodide (I^-) to electrophilic I^+ , which reacts with carbonyls to form our desired product.



Scheme 1. Electrooxidative Iodination of Carbonyls.

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Overcoming metallo- β -lactamase driven antibiotic resistance with a codrug approach

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The global spread of metallo- β -lactamases (MBL) is becoming a major challenge for the treatment of severe infections by most of the clinically used β -lactam antibiotics (BLA). Despite efforts, in contrast to serine- β -lactamase (SBL) inhibitors (SBLi), no MBL inhibitors (MBLi) have been approved to date for clinical use.¹ In addition to difficulties leading to a pan-MBL inhibitor capable to inhibit all classes of clinically relevant MBLs (VIM, NDM, IMP), the development of fixed dose combinations (FDC) is especially demanding.² A mutual prodrug or codrug approach provides an alternative pathway to developing an effective antibiotic.³

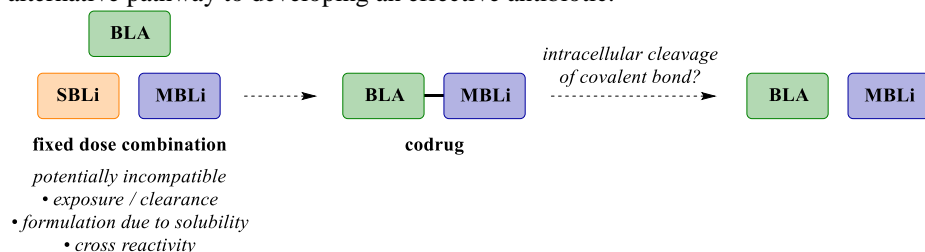


Figure 1. Strategy of antibacterial codrugs.

Herein, we report the development of BLA-MBLi codrugs based on carbapenem and cephalosporin scaffolds. Synthesized conjugates display potent enzyme inhibition and optimization for microbiological activity is ongoing.

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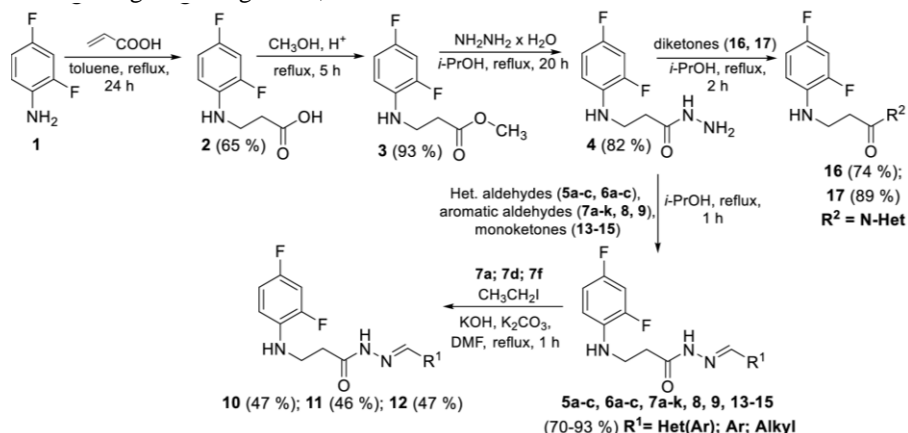
Synthesis of novel 3-[(2,4-difluorophenyl)amino] propanoic acid derivatives and evaluation of their biological properties for potential pharmacological applications

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With the increasing number of oncological diseases, the demand for chemotherapeutic drugs is constantly growing.¹ By including fluorine atoms in drug molecules, it is possible to change their properties such as drug-target interaction, metabolic stability, lipophilicity.² The starting compound 3-((2,4-difluorophenyl)amino)propanoic acid (**2**) was prepared by the reaction of 2,4-difluoroaniline (**1**) with acrylic acid in toluene. Later it was transformed into methyl propanoate **3** by an esterification reaction. Propanehydrazide **4** was synthesized by the reaction of hydrazine monohydrate in refluxing 2-propanol. In the further step of the synthesis, reactions with heterocyclic, aromatic aldehydes, mono- and diketones were investigated. The alkylation reaction of compounds **7a**, **7d** and **7f** was carried by dissolving the starting material in DMF, using iodoethane (Scheme 1). The biological activity of the synthesized compounds was investigated using A549, Caco-2 and THP-1 cell lines.



Scheme 1. Synthesis of 3-((2,4-difluorophenyl)amino)propanoic acid derivatives.

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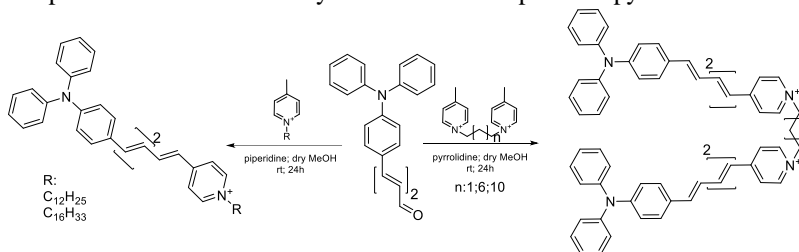
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Design and synthesis of novel styrylpyridinium compounds with aggregation-induced emission for photodynamic therapy

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Photodynamic therapy offers a promising strategy for cancer treatment. However, most near-infrared (NIR) photosensitizers suffer from aggregation-caused quenching, which limits reactive oxygen species (ROS) generation. To overcome this challenges, new molecular designs are needed that combine fluorescence in the NIR region, aggregation-induced emission (AIE) and self-assembling properties. Styrylpyridinium (SP) derivatives are promising candidates, as their structures can be modified to obtain desired properties.¹ SP derivatives were synthesized *via* Knoevenagel condensation (Scheme 1).² In total, five new SP compounds were synthesized with high yields ranging from 73% to 86%. The structures of the final products were confirmed by ¹H and ¹³C NMR spectroscopy.



Scheme 1. Synthesis of styrylpyridinium derivatives *via* Knoevenagel condensation.

Liposomes prepared by the injection method were characterized by dynamic light scattering method, confirming stable nanoparticles with a polydispersity index of 0.19–0.32, an average size of 156–225 nm, and remain stable for at least one month. Fluorescence spectra confirmed AIE, with the compounds showing up to 7-fold fluorescence enhancement in liposomal form compared to ethanol solution, and an emission maximum at 810 nm, successfully reaching the NIR region. MTT assays on HeLa and NIH3T3 cells demonstrated that light irradiation increased the compounds cytotoxicity, reducing the IC₅₀ to 5.5 μM compared to >10 μM without light. ROS production was confirmed, and confocal microscopy revealed that the compounds entered cells, localizing near mitochondria. Upon light irradiation, ROS-induced mitochondrial damage was observed, indicating cancer cell apoptosis.

Acknowledgements. This work was funded by LIOS internal student grant IG-2025-03 and FLPP project No. lzp-2024/1-0364.

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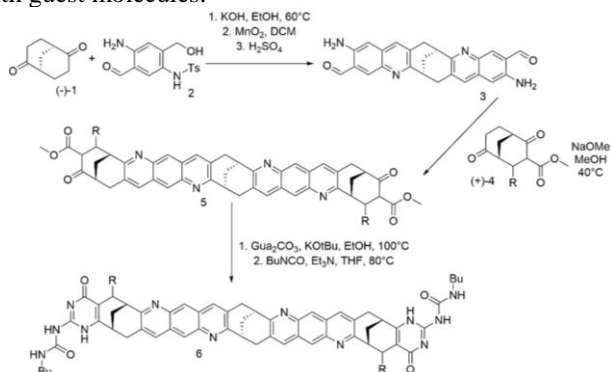
Synthesis of Modular and Functionalizable Supramolecular Cavitands

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Cavitands are a class of macrocyclic molecules characterised by an intrinsic internal cavity capable of reversibly binding guest molecules through non-covalent interactions. Such host guest recognition, often highly selective, allows for a wide range of potential applications, such as molecular sensing,¹ drug delivery,² and catalysis.³ However, conventional cavitands such as calixarenes or cyclodextrins are constrained by their limited structural diversity, restricted variation of cavity size and geometry, and poor functionalization potential.

In this work, we report the preparation of a novel supramolecular tetrameric cavitand featuring a large cross-shaped cavity. The system is assembled from monomer **6**, which forms cyclic tetramers stabilised by quadruple self-complementary hydrogen bonds between the terminal ureidopyrimidinone motifs, as well as the semi-rigid structure arising from the use of enantiomerically pure bicyclononane[3.3.1] derivatives fused with aromatic linkers. The spatial structure of the monomer is oriented to allow for formation of tetrameric aggregates, the presence of which in CDCl₃ solution was confirmed by diffusion-ordered NMR spectroscopy. The synthetic route is highly modular, allowing for easy modification of the cavity size and geometry. Moreover, multiple sites for functionalization are available, which allows for incorporation of functional groups that can be used to modulate solubility or for interaction with guest molecules.



Scheme 1. Synthesis of cavitand monomer **6**.

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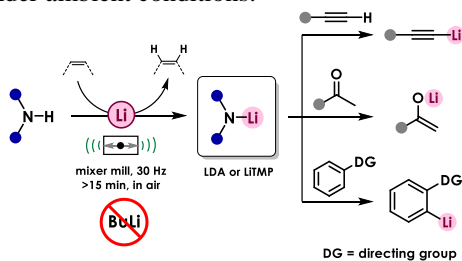
Butyllithium-free access to lithium amide bases *via* mechanochemistry

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In recent years, mechanochemistry has emerged as a valuable tool for activating zero-valent metals in organic synthesis,¹ enabling the preparation and use of organometallic reagents under ambient conditions and without the need for bulk organic solvents or inert atmospheres. Organolithium compounds are powerful carbon nucleophiles used in the formation of carbon–carbon and carbon–heteroatom bonds. The fundamental method for generating organolithium species involves the reaction of organic halides with lithium metal, a process that has recently been adapted to mechanochemistry.² Once organolithium reagents such as butyllithium (BuLi) are prepared, a variety of other organolithium compounds can be accessed via metalation using BuLi itself or strong lithium amide bases derived from it.³

Herein, we report the mechanochemical generation of strong lithium amide bases, such as lithium diisopropylamide (LDA) directly from lithium metal and the corresponding amine using a mixer mill. This Birch-type transformation employs unsaturated hydrocarbons as sacrificial oxidants, thereby avoiding the use of BuLi. The reaction proceeds efficiently without solvent additives, although the use of THF or hexane as liquid-assisted grinding (LAG) agents accelerates the reaction, achieving full conversion within 15 minutes. The solid-state generated LDA was successfully applied to a range of transformations, including the enolization of ketones, conversion of terminal alkynes into lithium acetylides, and directed ortho-metalation (DoM)³ of aromatic substrates under ambient conditions.



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Synthesis of acyclic diaryl λ^3 -bromanes

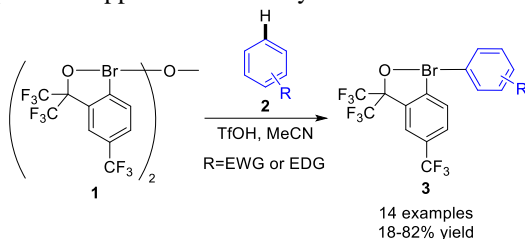
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Nowadays the chemistry of hypervalent bromine(III) compounds is undergoing rapid development. Bromine(III) species show higher reactivity compared to corresponding iodine(III) analogues, due to the higher electronegativity and ionization potential of the bromine atom.¹ Cyclic biaryl λ^3 -bromanes exhibit unique reactivity: they can be used as halogen-bonding catalysts in Michael reaction or as precursors for aryne generation under mild conditions.^{2,3} Compared to cyclic biaryl λ^3 -bromanes, which can be synthesized by the chemical or electrochemical oxidation of bromobiphenyls, all reported methods for preparing acyclic diaryl λ^3 -bromanes from non-prefunctionalized arene rely on the use of highly toxic and extremely reactive BrF_3 .³⁻⁵

Herein, we report the synthesis of the acyclic diarylbromanes **3** via Friedel-Crafts reaction between the stable electrochemically generated Br(III) compound **1** and arenes **2**, which contain different electron-donating or electron-withdrawing groups (Scheme 1). The potential applications of diarylbromanes **3** will also be demonstrated.



Scheme 1. Synthesis of diarylbromanes **3**.

Acknowledgements. This research is funded by the Latvian Institute of Organic Synthesis internal student grant IG-2025-07.

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Emerald emission: benzothiazoline Cu(I) complexes for high-efficiency green OLEDs

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Carbene-metal amides (CMAs) are a promising class of luminescent materials with efficient thermally activated delayed fluorescence (TADF), enabling high-performance organic light emitting diodes (OLEDs).¹ Our group showed that thiazoline-based copper(I) CMAs are suitable for white OLEDs due to dual emission from monomeric and dimeric species.^{2,3} However, their high carbene-centered LUMO levels widen the bandgap and favor unwanted local triplet emission. Expanding the carbene ring's π -system can lower LUMO energy and prevent this.⁴

This study examines the photophysical and structural properties of new CMA complexes featuring a benzo[d]thiazolidine carbene. Complexes **1** and **2** show bright green luminescence with lifetimes below one microsecond as well as high photoluminescent quantum yields (Φ_{PL}) of 0.96 and 0.99 respectively. Complex **3** shows bluish-green emission with sub-microsecond lifetimes and Φ_{PL} of 0.75.

OLED device containing complex **1** at 2 – 4 wt% deliver green emission with exceptionally high brightness which is rare amongst Cu(I) based CMA complexes.

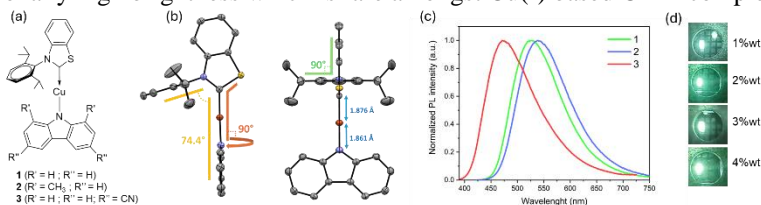


Figure 1. (a) Chemical structures of synthesized compounds. (b) X-ray structure of complex **1**. (c) PL spectra of doped PMMA 5 wt% films in N₂. (d) Fabricated OLED's containing complex **1** at 1 – 4 wt%.

Acknowledgements. This work has been supported by research and development grant No RTU-PA-2024/1-0092 under the EU RRF project No 5.2.1.1.i.0/2/24/I/CFLA/003.

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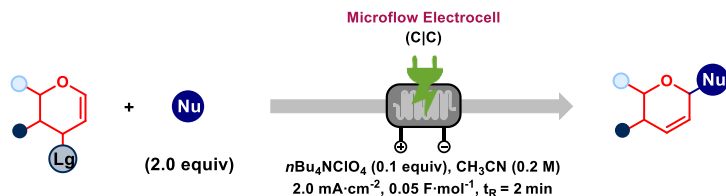
Electrochemical Ferrier rearrangement in flow

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The use of electricity in synthetic organic chemistry is undergoing a renaissance, with laboratories exploring both innovative and traditional approaches to expand its applications. This paradigm shift enables access to unique reaction pathways, thereby simplifying conventional multi-step reaction sequences. A key enabler of this shift is the integration of microfluidic technologies, particularly flow chemistry, which addresses limitations of traditional batch electrochemistry, such as poor mass transfer and high ohmic resistance. Flow reactors, with their high surface-to-volume ratio and short interelectrode distance, allow reactions to proceed with very small amounts of supporting electrolyte and minimal applied charge, enhancing both sustainability and operational simplicity.¹

In this work, we report a flow-enabled electrochemical variant of the Ferrier rearrangement (Scheme 1), a transformation that typically relies on strong acids or stoichiometric oxidants to convert glycols into unsaturated glycosyl derivatives.² This work demonstrates broad substrate compatibility, allowing various glycols and nucleophiles to furnish 2,3-unsaturated glycosyl derivatives efficiently. Notably, the reaction performs reliably at faster flow rates, making it readily scalable for continuous synthesis. This approach outperforms the earlier batch version and represents a significant advancement in the application of flow electrochemistry for carbohydrate synthesis.³



Scheme 1. Flow-enabled electrochemical Ferrier rearrangement.

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Electrochemical decarboxylative fluorination of malonic acid derivatives

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Aliphatic compounds containing fluorinated fragments are highly important in medicinal chemistry because the selective introduction of fluoroalkyl groups into bioactive molecules can significantly influence binding affinity, metabolic stability, lipophilicity, membrane permeability, and overall biological activity. In addition, the greater stability of the C–F bond relative to the C–H bond has fuelled growing interest in the development of fluorinated pharmaceuticals in recent years, and many commercially available drugs, bioactive molecules, and agrochemicals now incorporate aliphatic monofluoro, gem-difluoro, or trifluoromethyl substituents.^{1,2} Prior studies have established electrochemical decarboxylative fluorination³, however, none employ readily available malonic acid derivatives as starting materials in this transformation. In the present study, galvanostatic electrolysis was carried out, affording α,α' -difluoroester **2** from α -fluorinated malonic acid monoester **1**. Upon hydrolysis, compound **2** can be further oxidized to yield a trifluoromethyl-containing derivative **5**.

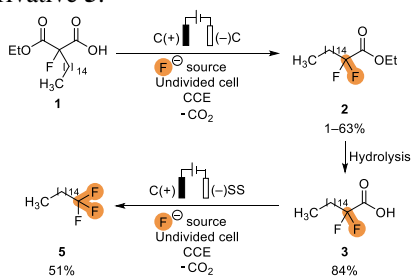


Figure 1. Electrochemical synthesis of α,α' -difluoroester **2** and trifluoromethyl- group containing compound **5**.

Preliminary results indicate that fluorine-containing salts such as Bu_4NPF_6 and Bu_4NBF_4 , inexpensive inorganic fluorides (KF , NaF), and the ionic liquid $\text{Et}_3\text{N}\cdot 3\text{HF}$ can serve as fluoride sources in the electrochemical decarboxylation/oxidation reaction. Moreover, both carboxyl groups of starting malonic acid derivative can be electrochemically decarboxylated and substituted with fluorine.

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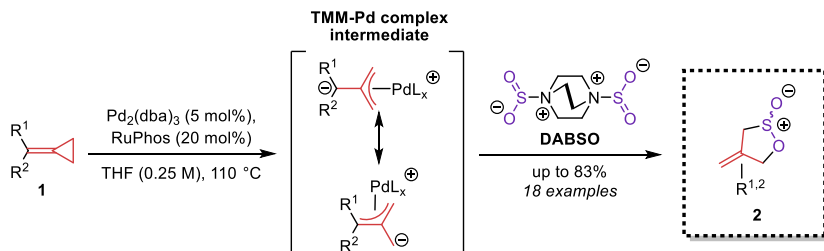
Sulfur heterocycle synthesis by methylenecyclopropane ring-expansion with SO₂

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Antibiotics, cardiovascular drugs and vitamin B₇ are just a few examples of biologically active molecules that contain sulfur heterocycles, nevertheless, methods for such heterocycle synthesis are less developed than for nitrogen- or oxygen-containing heterocycles.¹ Reactivity, cost-effectiveness, and recently increased accessibility through various surrogates, such as DABSO (Scheme 1),² make sulfur dioxide an attractive source of sulfur for sulfur heterocycle synthesis.

We have developed a new method for 4-methylene- γ -sultine **2** synthesis through palladium-catalyzed cycloaddition of methylenecyclopropanes **1** (MCPs) to sulfur dioxide (Scheme 1). This rare scaffold holds promise for novel reactivity and offers diverse options for derivatization into other sulfur-containing compounds.³ Its utility has been demonstrated by derivatization to sulfoxides, indenes and allylamine. Interestingly, the regioselectivity toward various sultine **2** isomers is influenced by the substituents at the MCP's double bond and the reaction conditions.



Scheme 1. MCP ring-expansion with SO₂ for sultine **2** synthesis.

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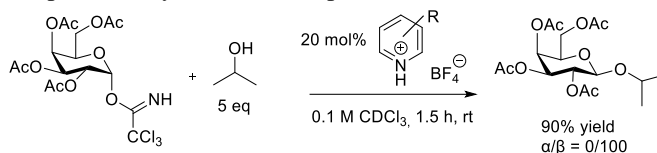
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Anion assisted glycosylation of galactose: a computational study

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Carbohydrate chemistry is an emerging field of significant contemporary importance. Mechanistically, glycosylation reactions involving a triflate activating agent have received widespread attention so far.¹⁻³ However, other organocatalysts have also shown promising results in achieving high stereoselectivity, for example, the reaction shown in Scheme 1 is 100% β -selective. The mechanism of this reaction was investigated computationally (with semiempirical, force field and DFT methods).



Scheme 1. Glycosylation reaction investigated.

Systematic investigation of the reaction system showed that substitution is rate-determining step and proceeds through an S_N2 mechanism. H-bond donors present in solution, such as *i*PrOH and TCA, can significantly decrease the energy of substitution, in addition to BF_4^- catalyst. The most effective stabilization was achieved when transition state was stabilized by cocatalysts at both A and B positions (Figure 1). After substitution step, proton transfer takes place, which does not require the presence of catalyst to proceed.

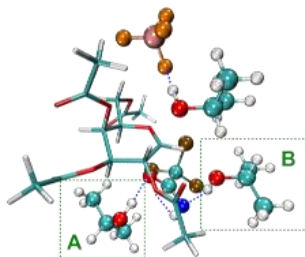


Figure 1. Geometry of transition state cocatalysed by acceptor molecules.

Acknowledgements. Authors acknowledge Dr. Kadri Kriis for the performed experiments.

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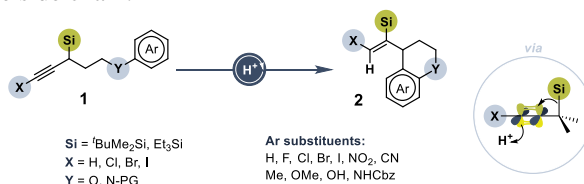
New approach to fused heterocycles via tandem 1,2-silyl shift – Friedel–Crafts cyclization

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Fused heterocycles such as chromanes and 1,2,3,4-tetrahydroquinolines are common structural fragments in natural products and pharmaceuticals. Here we report a novel synthetic pathway to fused heterocycles with highly functionalized alkene side chain from propargyl silanes (Scheme 1). The key stage proceeds via a domino process involving electrophile addition – 1,2-silyl shift – Friedel–Crafts cyclization. Under highly acidic conditions alkyne **1** undergoes protonation, which induces silyl group migration. This provides a relatively stable allylic cation intermediate prone to react with intramolecular π -system to afford Friedel–Crafts product **2**. Previously, our scientific group successfully applied tandem 1,2-silyl shift – cyclization concept in the synthesis of 5-membered carbocycles¹ or heterocycles.² In this work, we expand our method to the obtain larger cycles (up to 7-membered rings).

Propargyl silanes **1** can be obtained from commercially available alkynols in three steps: *O*-silylation, retro-Brook rearrangement³ under Schlosser conditions and modified Mitsunobu reaction⁴ with phenols and anilines as nucleophiles. Additionally, halogen atom moiety can be introduced in the terminal alkyne position via silver(I) catalysis. Corresponding haloalkynes demonstrate enhanced reactivity (for Cl and Br) and under the same catalytic conditions provide various fused heterocycles with *Z*-selective alkene side chain.



Scheme 1. Brønsted acid catalyzed Friedel–Crafts cyclization of propargyl silanes via 1,2-silyl shift.

Acknowledgements. The authors thank the Latvian Council of Science Grant No. LZP-2023/1-0576 for financial support. This work was also supported by the EU Recovery and Resilience Facility within project No. 5.2.1.1.i.0/2/24/I/CFLA/003 academic career doctoral grant, ID 1091.

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Enantiopure piperidines *via* stereoselective Ireland–Claisen rearrangement: modular access to secologanin-based alkaloids

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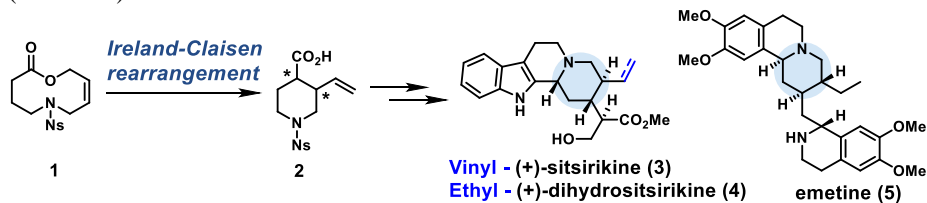
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The piperidine fragment is the second most prevalent nitrogen-containing heterocycle in FDA-approved drugs from the past decade¹ and a widely found structural motif in numerous pharmacologically significant natural products.

The key structural motif of sitsirikine (**3**), dihydrositsirikine (**4**) and emetine (**5**) is a tetrasubstituted piperidine ring. Although numerous elegant total syntheses of these and related alkaloids have been reported stereo convergent assembly of core structure still poses a considerable challenge. Herein, we report a convenient method for the construction of the piperidine (**2**) core and its further incorporation into a secologanin-based alkaloid scaffold.

Emetine, found in roots of *ipecacuanha* (*ipecac*) plant, is an alkaloid with promising antiviral activities, especially against SARS and MERS coronaviruses.² It has been recently shown that monoterpene indole alkaloid sitsirikine exhibit vasorelaxant activity against phenylephrine-induced contraction of rat mesenteric arteries at a micromolar level.³

The key piperidine building block is obtained via a stereoselective Ireland-Claisen rearrangement of an achiral 10-membered lactone (**1**) setting the stage for the total synthesis of (+)-sitsirikine and (+)-dihydrositsirikine⁴ and formal synthesis of emetine (scheme 1).



Scheme 1. Ireland-Claisen rearrangement approach to secologanin-based alkaloids.

Acknowledgements. RRF grant No. 30/OSI/DG (RRF project No.5.2.1.1.i.0/24/I/CFLA/001)
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Design and synthesis of structurally simple supramolecular capsule

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Molecular recognition is one of the main aims of supramolecular chemistry that is achieved by utilizing well-defined molecular assemblies. These are often constructed by employing methods such as dynamic covalent chemistry (DCC), coordination or hydrogen bonding (H-bonding), of which the latter two are extremely well suited to gain insight into the nature of non-covalent interactions.¹ Unambiguous formation of capsular aggregates is ensured by preorganization of the recognition elements which is most commonly achieved by rigid, geometrically fixed scaffolds at the cost of more difficult chemical synthesis. On the other hand, flexible building blocks offer easier synthesis but have difficulty forming desired aggregates as they do not possess preorganization required to lower entropic penalty of formation. In our report, we present a new approach to forming supramolecular capsules from monomers made utilizing multiple 4 H-bond forming ureidopyrimidinone (UPy) moieties connected with flexible amide linkers (Fig.1). We have shown these monomers quantitatively forming dimeric capsules via H-bonding. Moreover, we observed secondary H-bonds between amide and UPy carbonyl that ensure stabilization of capsule. The prepared monomers are capable of supramolecular phenomena such as forming varied-geometry capsules, self-sorting and encapsulating guests, for example, cyclophane and adamantane.

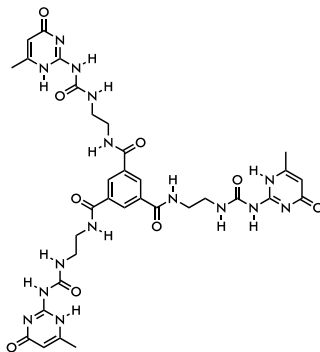


Figure 1. Structure of the supramolecular monomer.

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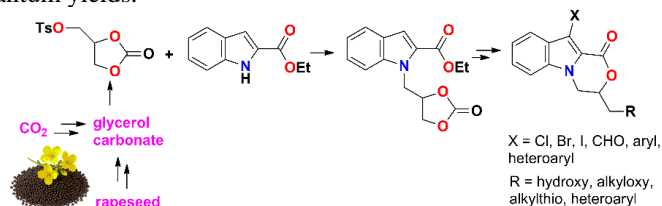
New synthetic approach to synthesis of 3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indole derivatives using activated glycerol carbonate

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Glycerol-1,2-carbonate is a green reagent, derived from glycerol waste, commonly used as a biodegradable solvent, with a growing interest in application as a synthetic intermediate.¹ Recently, we have reported an efficient synthesis of pyrazole-containing heterocyclic systems employing glycerol-1,2-carbonate as a convenient reagent.² To continue investigating the tosylated glycerol-1,2-carbonate mediated approach application for more sustainable synthesis of potentially bioactive aza-heterocyclic oxazines, alkylation reactions with ethyl 1*H*-indole-2-carboxylates were first explored and investigated. The following 3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indole system was obtained from *N*-glycerylated indole-2-carboxylates by a functionalization through halogenation, formylation, and condensation at the reactive C-10 position of the ring. Reactivity of the 3-hydroxymethyl appendage was also investigated by performing various *O*-, *S*-, and *N*-alkylation methods. Some of the synthesized 3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indole derivatives exhibited significant Stokes shifts and good quantum yields.³



Scheme 1. Synthesis and functionalization of 3,4-dihydro-1*H*-[1,4]oxazino[4,3-*a*]indole derivatives from tosylated glycerol carbonate.

The structures of the obtained compounds were confirmed by using ¹H-, ¹³C-, and ¹⁵N-NMR, IR spectroscopy, high-resolution mass spectrometry, and X-ray crystallography analyses. The optical properties of the selected compounds were measured by using UV-vis and fluorescence spectroscopy techniques.³

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Harnessing protons as the only oxidants for photoredox dehydrogenative coupling

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Here we present a metal-free light-driven protocol for extremely electron poor arene C–H aminations that relies on an acridinium-derived photocatalyst¹ and evolves molecular H₂ as the only side product. Within one catalytic cycle, the photocatalyst successively performs as an oxidant, a hydrogen-atom shuttle, and a hydride source, making external oxidants unnecessary for closing the catalytic cycle. Operating under violet visible light, the method exploits the high excited state redox potential of the catalyst, enabling transformations of even electron-deficient arenes. The mechanistic concept introduced here provides a general foundation for constructing cross-dehydrogenative processes with applications in medicinal organic chemistry.

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