ESOC
2019

ESOC
2019
Vienna
July 14th – 18th, 2019

Institute of Applied Synthetic Chemistry
TU Wien
and
Institute of Organic Chemistry
University of Vienna
Austria

http://esoc2019.conf.tuwien.ac.at/
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Dear Colleagues,

It is our great pleasure to cordially welcome you to the 21st edition of the European Symposium on Organic Chemistry (ESOC), which will be held on July 14 – 18, 2019, at the Vienna Exhibition Center (Messe Wien). This latest edition of what has become the premier event in organic chemistry in Europe is organized jointly by the Institute of Applied Synthetic Chemistry of TU Wien (Vienna University of Technology) and the Institute of Organic Chemistry of the University of Vienna and in cooperation with the COST Action CHAOS (C-H activation in organic synthesis), which is organizing a special session on Tuesday the 16th.

ESOC looks back at a long tradition, starting exactly 40 years ago in 1979 in Cologne (Germany) and over the years has been held in many different cities in the continent and we are proud that the 21st ESOC is the first edition to be hosted in Austria. This current edition covers all aspects related to Organic Synthesis highlighting modern trends in Total Synthesis and Methodology, Catalysis, Medicinal Chemistry and Chemical Biology, Supramolecular Chemistry, Organic Materials and Physical and Computational Organic Chemistry.

The program was designed with the aim to provide a unique forum for exchange - besides 11 plenary and 13 invited lectures, there are 28 slots for short oral presentations (15 min) and more than 550 posters. It is also our great honour that the first “Dr. Margaret Faul Award for Women in Chemistry” will be presented at ESOC 2019.

Additionally, for the first time at ESOC 2019 we shall host a job fair for PhD students and Postdoctoral researchers, with company interviews on site. Participation is a free of charge add-on for our participants.

Ideally located in the center of Europe, Vienna has a long-standing tradition as a major conference site since the “Congress of Vienna” in 1815. Its unique atmosphere will provide inspiration for a fruitful scientific meeting, and the participants will have ample time to enjoy a wealth of culture and historical places in and around Austria’s capital city, not to forget the exquisite Viennese cuisine and Austrian wines. Join us in enjoying excellent science in a terrific environment together with true Viennese hospitality!

Sincerely,
Michael Schnürch and Nuno Maulide
(Conference Chairs)
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**INVITED SPEAKERS**

**PLENARY LECTURERS**

Thorsten **BACH** *TU München, Germany*
Phil **BARAN** *The Scripps Research Institute, USA*
Alois **FÜRSTNER** *Max-Planck-Institut für Kohleforschung, Germany*
Lukas **GOOSSEN** *Ruhr-Universität Bochum, Germany*
Veronique **GOVERNEUR** *University of Oxford, UK*
Syuzanna **HARUTYUNYAN** *University of Groningen, The Netherlands*
Kenichiro **ITAMI** *Nagoya University, Japan*
Paolo **MELCHIORRE** *ICIQ Institut Catala d’Investigació Quimica, Spain*
Sir James Fraser **STODDART** *Northwestern University, USA*
Roderich **SÜßMUTH** *TU Berlin, Germany*
John **SUTHERLAND** *MRC Laboratory of Molecular Biology, UK*

**INVITED LECTURERS**

Roey **AMIR** *Tel Aviv University, Israel*
Tatiana **BESSET** *Université de Rouen, France*
Jesús **CAMPOS** *CSIC-University of Sevilla, Spain*
Denis **CHUSOV** *Russian Academy of Sciences, Russia*
Anna **HIRSCH** *Helmholtz Institute for Pharmaceutical research Saarland, Germany*
Thomas **MAGAUCER** *Universität Innsbruck, Austria*
Sarah **REISMAN** *California Institute of Technology, USA*
Jana **ROITHOVÁ** *Charles University in Prague, Czech Republic*
Sara **SATTIN** *Università degli Studi di Milano, Italy*
Troels R. **SKRYDSTRUP** *Aarhus University, Denmark*
Martin D. **SMITH** *University of Oxford, UK*
Marcin **STEPIEN** *University of Wroclaw, Poland*
Martin **OESTREICH** *Technische Universität Berlin, Germany*
Alexandros **ZOGRAFOS** *Aristotle University of Thessaloniki, Greece*
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COMMITTEES

ORGANIZING COMMITTEE

The conference is organized by the Institute of Applied Synthetic Chemistry at the TU Wien, the Institute of Organic Chemistry at the University of Vienna and co-organized by the COST Action CHAOS (C-H Activation in Organic Synthesis).

Conference Chairs: Michael SCHNÜRCH and Nuno MAULIDE

- Heinz A. KREBS
- Marko D. MIHOVILOVIC
- Florian RUDROFF
- Christian STANETTY
- Florian UNTERSTEINER

NATIONAL SCIENTIFIC COMMITTEE

- Rolf BREINBAUER, TU Graz
- Oliver KAPPE, University of Graz
- Wolfgang KROUTIL, TU Graz
- Mario WASER, JKU Linz
- Marko D. MIHOVILOVIC, TU Wien
- Darryl MCCONNELL, Boehringer Ingelheim

PAST MEETINGS

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- Chemical Science
- European Journal of Organic Chemistry
- Organic Chemistry Frontiers
- Molecules – Open Access Journal
- Synthetic Reaction Updates
- Organic & Biomolecular Chemistry
- Georg Thieme Verlag KG

ACKNOWLEDGEMENTS

The organizers acknowledge the support given by the TU Wien, in particular by Sabine Seidler (rector) and the University of Vienna, in particular by Heinz Engl (rector).
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EXHIBITORS
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GENERAL INFORMATION

CONGRESS SITE
All lectures will take place in the main lecture hall at the Congress Center (cf. Venue Map, p31).

Reed Messe Wien GmbH
Congress Center

Messeplatz 1
A-1021 Wien

INTERNET-FACILITIES
Access to the internet will be provided by Wireless Lan. Please connect to the SSID “ESOC2019”.

REGISTRATION CENTER AND INFORMATION DESK
The registration and information desk will be located near the entrance on the ground floor of the Congress Center (cf. Venue Map, p 31), with the following business hours:

- Sunday, July 14th, 14:00 to 19:00
- Monday, July 15th, 8:00 to 17:00
- Tuesday, July 16th, 8:00 to 17:00
- Wednesday, July 17th, 8:00 to 13:00
- Thursday, July 18th, 8:00 to 13:00

INSTRUCTIONS FOR SPEAKERS
Speakers are requested to hand in their final version of their lecture on electronic media the day before their session. The slide center will be located on the ground floor of the conference center (cf. Venue Map, p 31) adjacent to the registration center.

Opening hours:
- Sunday, July 14th, 14:00 to 19:00
- Monday, July 15th, 8:00 to 17:00
- Tuesday, July 16th, 8:00 to 17:00
- Wednesday, July 17th, 8:00 to 13:00
- Thursday, July 18th, 8:00 to 13:00
Dispenser, Evaporators, Hoods, Reactors, Deep Well and Filter Plates and Glass for Chemistry
INSTRUCTIONS FOR POSTER PRESENTATION

The poster boards will be positioned in the area in front of the lecture hall. They will be numbered consecutively. Authors are requested to be in front of their poster during the official poster session hours.

The official sessions for poster presentations are:
- Monday, July 15\textsuperscript{th}: Poster with odd numbers (PO-1, PO-3, PO-5, ..) Posters should be mounted by Sunday evening and must be removed at the beginning of the lunch break on Tuesday at the latest
- Tuesday, July 16\textsuperscript{th}: Poster with even numbers (PO-2, PO-4, PO-6, ..) Posters should be mounted during the lunch break on Tuesday and must be removed on Thursday, 3pm, at the latest.

Posters that are not removed on time will be dismounted by staff members and can be re-claimed in the Slide Center until Thursday, 4pm (however, we do not take responsibility for any damage to the posters).

POSTER PRIZES

Poster prizes will be selected by public vote (no poster committee!). You can find your personal QR voting code on your registration card. Please note that you can vote for any poster besides posters from your own institution.

The voting will be closed on Thursday, July 18\textsuperscript{th}, 2pm.

If you have not installed a QR-code reader on your mobile device please visit http://esoc2019.conf.tuwien.ac.at/vote/ and enter the code by hand. Contact the slide center in any case you need help.

REGISTRATION OFFICE AND TRAVEL AGENCY

Austropa Interconvention
Verkehrsbüro Business Travel GmbH
Lasallestrasse 3
A-1020 Vienna (Austria)
Tel.: +43 1 58800 516
Fax: +43 1 58800 520
Email: esoc2019@vb-mice.at
WWW: http://www.austropa-interconvention.at/

TRANSPORTATION

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Would you like to know more about Elsevier products? Then please contact us and we gladly consult with you on following topics (amongst others):

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About Elsevier

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SOCIAL PROGRAM

WELCOME MIXER
All congress participants and their accompanying persons are cordially invited to the reception on Sunday evening, July 15th, 2019, 18:45. This informal get-together will take place within the Exhibition and Lunch Area of the Conference Center (cf Venue Map, p31).

CONFERENCE DINNER
Participants will experience a memorable evening in the Viennese "Heurigen" village "Neustift am Walde". Enjoy a few hours in a warm atmosphere with music, wine and home cooked local speciality food (non-alcoholic beverages and diet food can be served as an alternative).

Busses will leave after the closing ceremony, July 18th, in front of the main entrance of the Congress Center (cf Campus Area Map, p 29).

For the return trip busses are available starting at 22:00, the last bus will depart at 23:30.

Weingut Fuhrigassl-Huber
Neustift am Walde 68
1190 Vienna

LUNCH
Lunch on Monday, Tuesday and Thursday will be offered in the Exhibition & Lunch Area. Different meals and drinks are offered as self-service buffet.

LUNCH AT “PRATER ALM”
On Wednesday, July 17th, we will invite you to a Viennese restaurant, rich in tradition and inseparably linked with the Prater. The “Prater Alm” provides a large beer garden for outdoor seating and also beautiful and rustically indoor seating options in case of bad weather. A buffet of Austrian specialties will be served on each table.

You may choose any meal and drink from the menu card. For payment please use the voucher of your registration card.

The restaurant is in walking distance (8 min) from the Conference Venue, please follow the dotted line on the Campus Area Map (p 29).

EXCURSIONS
The busses for the excursions (“Historical Vienna”, “Kahlenberg - Klosterneuburg”, or “Viennese Impressions”) will depart at 14:00 in front of the Conference Venue.

Please leave the restaurant in time (not later than 13:45) and please bring your excursion voucher with you.
EuChemS, the European Chemical Society, aims to nurture a platform for scientific discussion and to provide a single, unbiased European voice on key policy issues in chemistry and related fields.

Representing more than 160,000 chemists from more than 40 Member Societies and other chemistry related organisations, EuChemS relies on a unique network of active researchers involved in all the fields of chemistry. Through this network, EuChemS organises several specialised academic conferences as well as the biannual EuChemS Chemistry Congress, the European congress of chemical sciences. EuChemS also promotes the role and image of the chemical sciences among the general public and policy-makers through social media, newsletters and through the organisation of conferences and workshops open to the society.

Through the promotion of chemistry and by providing expert and scientific advice, EuChemS aims to take part of the solution to today’s major societal challenges.

For more information about the European Chemical Society (EuChemS), please visit www.euchems.eu or contact us at:

EuChemS aisbl
Rue du Trône 62
1050 - Brussels
Belgium

Phone: +32 2289 25 67 | +32 2289 26 90

Email: secretariat@euchems.eu

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WORKSHOPS

Benchtop NMR spectroscopy: Applications in academia and industry

Wednesday, July 17, 10-12
1st Floor, room: Schubert 1-2

Benchtop NMR system has become popular analytical lab instruments in the last years. With the recent launch of the Spinsolve Ultra the magnetic field homogeneity has been improved to match a line's shape that is comparable to superconducting magnets, while the Spinsolve 80 MHz system pushes the limits in chemical shift spreading and sensitivity for a benchtop system. During the workshop an overview of applications that can be addressed with benchtop NMR systems in academic and industrial environments will be given. There is as well a live system available for practical demonstrations.

Opening the editor's black box: Insider tips for successful submissions

Wednesday, July 17, 14-16
1st Floor, room: Schubert 1-2

This workshop with Editors of Angewandte Chemie and the European Journal of Organic Chemistry is specifically tailored to the needs of master and PhD students and postdocs.

Publishing papers in reputed journals is an integral part of the research cycle. In this workshop, we will open the Editor's black box by explaining how manuscripts are processed from submission to publication. In addition, we will discuss ethical aspects of publishing and give tips on how to prepare your manuscript for submission and improve your chances for successful publication. Topics to be covered include:

How do I simplify my writing and improve the presentation of my results?
How do I choose the right journal for submission?
What do Editors and referees look for?
How do I improve the visibility of my research?
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JOB FAIR

An additional benefit introduced for the first time at ESOC 2019 is a job fair for PhD and postdoc students, where Merck Sharp & Dohme, Patheon – Part of Thermo Fisher, and Johnson & Johnson (Janssen Pharmaceutica) will conduct interviews on side. Below you find a short description of the respective companies.

The interviews will take place in the 1st floor of the conference venue in Business Lounge 1.

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With $76.5 billion in 2017 sales, Johnson & Johnson is the world's most comprehensive and broadly-based manufacturer of health care products, pharmaceuticals and medical devices. The Janssen Pharmaceutical Companies of Johnson & Johnson conduct research and development in a variety of therapeutic areas to discover novel therapeutic approaches to address unmet medical conditions. From heart disease to HIV, Alzheimer’s disease to cancer, we are committed to issues that touch everyone’s lives.

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legacy for over a century. MSD’s success is backed by ethical integrity, forward momentum, and an inspiring mission to achieve new milestones in global healthcare. MSD is on a quest for cures and is committed to being the world’s premier, most research-intensive biopharmaceutical company. By capitalizing on MSD’s leading discovery capabilities and world-class small molecule and biologics R&D expertise, we aim to create breakthrough science that radically changes the way we approach serious diseases.

Our organization is currently seeking exceptional chemists for positions within our discovery and process chemistry departments. The successful candidate will join multidisciplinary, highly collaborative teams to invent and manufacture novel medicines by applying innovative synthetic chemistry, analytical techniques, and data analysis. A proven track record of solving complex problems is required. Candidates must also possess strong written and oral communication skills, and the ability to work effectively in a team environment. Your role at MSD is integral to helping the world meet new breakthroughs that affect generations to come, and we’re counting on your skills and inventiveness to help make meaningful contributions to global medical advancement. At MSD, we’re inventing for life.

The MSD London Discovery Centre aims to “speed up research to slow down diseases of aging” and will be a fully integrated Drug Discovery site, translating basic science through collaboration into medicines. We are looking to identify synergies and areas of complementary disease biology with MRL US, with an initial focus on mechanisms of cell homeostasis and resilience during aging that are associated with neurodegenerative disorders. To harness new thinking in disease biology, we are establishing collaborations with UK and European researchers, and building capabilities in cell biology, target discovery and drug discovery. The MSD Chemistry team will be initially based within the Francis Crick Institute in London, an institute founded by the Medical Research Council (MRC), Cancer Research UK, Wellcome, UCL, Imperial College London and King’s College London, and dedicated to understanding the fundamental biology underlying health and disease. We are currently recruiting for Medicinal Chemistry roles at the MSD site in London, and aim to have additional recruitment opportunities as we grow the group over the coming months. The MSD team will work closely with the wider Merck network to prosecute the best science and deliver on the portfolio, harnessing the capabilities, infrastructure, technologies and experience available across the network. If you are passionate about science and want to use that to help patients, we would love to hear from you.
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A  Congress Venue (Messeplatz 1)
   Lecture Hall
B  Departure for Conference Dinner on Thursday
C  "Prater Alm" – Lunch on Wednesday
D  Wiener Riesenrad – Giant Ferris Wheel
E  “Praterstern”
   Railway and Underground Station
F  Hotel Courtyard Marriott
G  Underground Station purple line
   U2 – Messe
H  Underground Station purple line
   U2 – Krieau

dotted line:
   way from from the the Conference Center to “Prater Alm” for lunch
Molecules (ISSN 1420-3049, CODEN: MOLEFW) provides an advanced forum for science of chemistry and all interfacing disciplines. The aim is to provide rigorous peer review and enable rapid publication of cutting-edge research to educate and inspire the scientific community worldwide. The Impact Factor for Molecules is 3.098 (2017 Journal Citation Reports® Science Edition, Clarivate Analytics, 2018).

34.6 days
average publication time in 2018

31 days
median publication time in 2018

13.6 days
submission to first decision provided to authors

4.7 days
acceptance to publication

The scope of Molecules includes (but are not limited to):

Organic Chemistry
Natural Products Chemistry
Medicinal Chemistry
Computational and Theoretical Chemistry
Green Chemistry
Photochemistry
Bioorganic Chemistry
Organometallic Chemistry
Inorganic Chemistry
Physical Chemistry
Analytical Chemistry
Nanochemistry
Chemical Biology
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Intuitive

- Streamlined user interface
- Defined user’s roles
  - Group Manager
  - Project Manager
  - Bench Chemist
  - Administrator
  - Guest
- Simple chemistry workflow
  - Projects
  - Reactions
  - Experiments
- Automated or customized reports (pdf)

Chemistry centered

- Designed by chemists for chemists
- Analytical data integration
  - Process
  - Analyze
  - Store
  - Review and interact
- Integrated chemical compound database
- Embedded molecular sketcher
- Stoichiometric calculations done for you

Seamless collaboration

- Powerful searching tool (by structure and text)
- Cloud hosted solution with in-house option
- In-app messaging system
- No installation is required
- Automatic updates and maintenance
- Flexible architecture to customize yours needs
- Experiment supervision (witnessing and approval)
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<td>11:00</td>
<td>IL-2 Th. Magauer</td>
<td>IL-6 M.D. Smith</td>
<td>IL-10 M. Oestreich</td>
<td>IL-12 T. Besset</td>
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<td>OC-1 E. Wellin</td>
<td>OC-7 T. Akiyama</td>
<td>OC-13 Y. Takemoto</td>
<td>OC-18 A. Spilman</td>
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<td>OC-2 S. Coote</td>
<td>OC-8 Chr.J. Whiteoak</td>
<td>OC-14 D. Katsyev</td>
<td>OC-19 D.B. Wier</td>
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<td>OC-3 R. Pollice</td>
<td>OC-9 J. Deska</td>
<td>OC-15 M.J. Fink</td>
<td>OC-20 C. Townley</td>
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<tr>
<td>12:00</td>
<td>OC-4 A. Gollner</td>
<td>OC-10 D. Kananovich</td>
<td>OC-16 V. Pace</td>
<td>OC-21 A. Giosello</td>
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<td>OC-5 D. Kolarzki</td>
<td>OC-11 G. Guru Rucheter</td>
<td>OC-17 M. Zanini</td>
<td>OC-22 A. Abell</td>
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<tr>
<td>13:00</td>
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<td>Lunch @ Prateralm</td>
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<tr>
<td>14:00</td>
<td>IL-3 J. Campos</td>
<td>IL-7 S. Sattin</td>
<td>IL-13 T.R. Skydstrup</td>
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<tr>
<td>15:00</td>
<td>Registration</td>
<td>Coffee Break</td>
<td>Coffee Break</td>
<td>OC-25 R. Greensaw</td>
<td>Coffee Break</td>
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<tr>
<td></td>
<td>OC-6 L. Capdevila</td>
<td>OC-12 P. Poeschauer</td>
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<td>OC-26 H. Valkenier</td>
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<tr>
<td>16:00</td>
<td>PL-5 Th. Bach</td>
<td>PL-8 J. Sutherland</td>
<td>Excursion &amp; Job Fair</td>
<td>OC-27 M. Lazzarotto</td>
<td>OC-28 A. Quinzavalla</td>
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<tr>
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<td>PL-4 D. Chusov</td>
<td>IL-8 S. Reisman (M. Feul Awardee)</td>
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<td>IL-14 A. Zografos</td>
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<tr>
<td>17:00</td>
<td>Opening</td>
<td>PL-1 Sir J.F. Stoddart</td>
<td>PL-11 P. Melchiorre</td>
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<td></td>
<td>PL-2 A. Fürstner (Patai Lecture)</td>
<td>Poster Session odd numbers</td>
<td>Poster Session even numbers</td>
<td>ESOC2021 OC/Poster Prizes Final Remarks</td>
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<tr>
<td>18:00</td>
<td>Welcome Reception</td>
<td>Speakers Dinner</td>
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<td>Conference Dinner „Heuriger“</td>
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<td>19:00</td>
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Michael Stanek, Ph.D.
VP Business Management,
API Global Pharma Services
Linz, Austria

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Session Overview

ESOC 2019

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Located in the garden of Schloss Schönbrunn (built in 1881)
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Session overview

Sunday, July 14

17:00 Opening Ceremony

Chair: Nuno Maulide

17:15 Sir J.F. Stoddart  
Northwestern University, Illinois, United States  
PL-1 sponsored by FCIO

RADICAL CHEMISTRY IN THE DESIGN AND SYNTHESIS OF ARTIFICIAL MOLECULAR MACHINES

Chair: Ilan Marek

Patai-Rappoport Lecture

18:00 Alois Fürstner  
Max-Planck-Institut für Kohleforschung, Mülheim/Ruhr, Germany  
PL-2

SURPRISES WITH ALKYNES: A NEW REACTIVITY PARADIGM AND ITS APPLICATIONS

18:45 Welcome Reception

Monday, July 15

08:30 Opening

Chair: Nuno Maulide

09:00 Kenichiro Itami  
Nagoya University, Nagoya, Japan  
PL-3 sponsored by TCI

MAKING NEW FORMS OF NANOCARBONS

Chair: Wolfgang Kroutil

09:45 Marcin Stępień  
University of Wroclaw, Wroclaw, Poland  
IL-1

DONOR–ACCEPTOR OLIGOPYRROLES

10:15 Coffee Break sponsored by TCI

10:45 Thomas Magauer  
University of Innsbruck, Innsbruck, Austria  
IL-2

TOTAL SYNTHESIS OF POLYCYCLIC NATURAL PRODUCTS

11:15 Eric Welin  
California Institute of Technology, Pasadena, USA  
OC-1

CONCISE TOTAL SYNTHESES OF (−)-JORUNNAMYCIN A AND (−)-JORUMYCIN ENABLED BY ASYMMETRIC CATALYSIS
<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
<th>Institution</th>
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<tbody>
<tr>
<td>11:30</td>
<td>Susannah Coote</td>
<td>4-π-PHOTOCYCLISATION OF DIHYDROPYRIDAZINES: ACCESS TO VERSATILE BICYCLIC DIAZETIDINES</td>
<td>Lancaster University, Bailrigg, UK</td>
</tr>
<tr>
<td>11:45</td>
<td>Robert Pollice</td>
<td>REACTION PROGRESS KINETIC ANALYSIS BY DIRECT ANALYSIS OF CONCENTRATION-TIME PROFILES</td>
<td>ETH Zürich, Zürich, Switzerland</td>
</tr>
<tr>
<td>12:00</td>
<td>Andreas Gollner</td>
<td>SEQUENTIAL MULTI-BOND FORMING REACTIONS APPLIED TO THE SYNTHESIS OF CONFORMATIONALLY RESTRICTED MDM2-p53 INHIBITORS SUITABLE FOR INTERMITTENT DOSING</td>
<td>Boehringer Ingelheim RCV GmbH and Co KG, Vienna, Austria</td>
</tr>
<tr>
<td>12:15</td>
<td>Dušan Kolarski</td>
<td>CONTROLLING THE CIRCADIAN CLOCK WITH HIGH TEMPORAL RESOLUTION THROUGH PHOTODOSIMETRY</td>
<td>University of Groningen, Groningen, The Netherlands</td>
</tr>
<tr>
<td>12:30</td>
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<td>Lunch</td>
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<tr>
<td>14:00</td>
<td>Jesús Campos</td>
<td>INTERACTION VS. FRUSTRATION IN BIMETALLIC COOPERATIVE SYSTEMS</td>
<td>Universidad de Sevilla, Sevilla, Spain</td>
</tr>
<tr>
<td>14:30</td>
<td>Syuzanna R. Harutyunyan</td>
<td>LEWIS ACID ENABLED NOVEL REACTIVITIES IN ASYMMETRIC COPPER CATALYSIS</td>
<td>University of Groningen, Groningen, The Netherlands</td>
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<tr>
<td>15:15</td>
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<td>Coffee Break</td>
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<tr>
<td>15:45</td>
<td>Lorena Capdevila</td>
<td>CHEMO-DIVERGENT NICKEL(0)-CATALYZED ARENE C-F ACTIVATION WITH ALKynes: UNPRECEDENTED DOUBLE-INSERTION</td>
<td>Universitat de Girona, Girona, Spain</td>
</tr>
<tr>
<td>16:00</td>
<td>Thorsten Bach</td>
<td>ENANTIOSELECTIVE CATALYSIS OF PHOTOCHEMICAL REACTIONS</td>
<td>Technical University Munich, Garching, Germany</td>
</tr>
<tr>
<td>16:45</td>
<td>Denis Chusov</td>
<td>STRATEGY FOR SELECTIVE REDUCTIVE ADDITION</td>
<td>Russian Academy of Sciences, Moscow, Russia</td>
</tr>
<tr>
<td>17:15</td>
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<td>Poster Session 1 odd numbers</td>
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**Synthetic Reaction Updates**
This literature updating service keeps you aware of recent developments and the latest transformations in chemical synthesis.

[rsc.li/synthetic-reaction-updates]
Tuesday, July 16

COST – Sessions Day

Chair: Michael Schnürch

09:00 Lukas Gooßen
PL-6
Ruhr-Universität Bochum, Bochum, Germany
CARBOXYLATES AS DIRECTING AND LEAVING GROUPS IN CATALYTIC BOND FORMATION

09:45 Jana Roithova
IL-5
Radboud University, Nijmegen, The Netherlands
TRAPPING OF REACTIVE INTERMEDIATES

10:15 Coffee Break sponsored by TCI

Chair: John Sutherland

10:45 Martin D. Smith
IL-6
University of Oxford, Oxford, UK
COUNTER-ION MEDIATED APPROACHES TO CONTROLLING AXIAL CHIRALITY

11:15 Takahiko Akiyama
OC-7
Gakushuin University, Tokyo, Japan
ENANTIOSELECTIVE FRIEDEL-CRAFTS ALKYLATION REACTION OF TRIFLUOROMETHYLATED N-H KETIMINE WITH HETEROARENES BY MEANS OF CHIRAL PHOSPHORIC ACID

11:30 Christopher J. Whiteoak
OC-8
Sheffield Hallam University, Sheffield, UK
ACCESS TO UNUSUAL HETEROCYCLIC COMPOUNDS UTILIZING A KEY COBALT-CATALYZED C-H FUNCTIONALIZATION APPROACH

11:45 Jan Deska
OC-9
Aalto University, Espoo, Finland
THE HUNT FOR ARTIFICIAL REACTIVITIES IN BIOCATALYSIS: FUNGAL COPPER-DEPENDENT METALLOPROTEINS AS MEDIATORS FOR PERICYCLIC REACTIONS

12:00 Dzmitry Kananovich
OC-10
Tallinn University of Technology, Tallinn, Estonia
QUEST FOR ASYMMETRIC KULINKOVICH REACTION: FROM MECHANISM TOWARDS ENHANCED ENANTIOSELECTIVITY

12:15 Olga García Mancheño
OC-11
University of Münster, Münster, Germany
RATIONAL DESIGN OF NEW, MORE POTENT ACRIDINIUM VISIBLE LIGHT ORGANO-PHOTOCATALYSTS BY C-H FUNCTIONALIZATION

12:30 Lunch
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Tuesday, July 16

COST – Sessions Day

Chair: Adrian Minaard

14:00 Sara Sattin
Università degli Studi di Milano, Milan, Italy
TARGETING BACTERIAL PERSISTERS IN THE POST-ANTIBIOTIC ERA

14:30 Phil S. Baran
Scripps Research, La Jolla, USA
TRANSLATIONAL CHEMISTRY

15:15 Coffee Break

Chair: Rolf Breinbauer and Florian Rudroff

15:45 Peter Poechlauer
Thermo Fisher Scientific, Linz, Austria
DEVELOPMENT AND SCALE-UP OF CONTINUOUS FLOW PROCESSES FOR THE MANUFACTURE OF ACTIVE PHARMACEUTICAL INGREDIENTS

16:00 John D. Sutherland
MRC Laboratory of Molecular Biology, Cambridge, UK
ORIGINS OF LIFE SYSTEMS CHEMISTRY

Dr. Margaret Faul Award for Women in Chemistry

16:45 Sarah E. Reisman
California Institute of Technology, Pasadena, USA
NECESSITY IS THE MOTHER OF INVENTION: NATURAL PRODUCTS AND THE CHEMISTRY THEY INSPIRE

17:15 Poster Session 2 even numbers
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Wednesday, July 17

Chair: Marko Mihovilovic

09:00 Véronique Gouverneur  
*University of Oxford, Oxford, UK*

**FLUORINE CHEMISTRY FOR APPLICATIONS IN MEDICINE**

09:45 Anna K.H. Hirsch  
*Saarland University, Saarbrücken, Germany*

**DISCOVERY OF THE FIRST ANTIBACTERIAL AGENT INHIBITING THE ENERGY-COUPLING FACTOR (ECF) TRANSPORTERS BY STRUCTURE-BASED VIRTUAL SCREENING**

10:15 **Coffee Break** sponsored by Boehringer Ingelheim

Chair: Véronique Gouverneur

10:45 Martin Oestreich  
*Technische Universität Berlin, Berlin, Germany*

**TRANSFER OF REACTIVE GASES FROM ONE MOLECULE TO ANOTHER**

11:15 Yoshiji Takemoto  
*Kyoto University, Kyoto, Japan*

**TOTAL SYNTHESIS OF AVENAOL VIA ASYMMETRIC O-ALKYLATION USING CHIRAL AMMONIUM SALT**

11:30 Dmitry Katayev  
*Swiss Federal Institute of Technology, Zürich, Switzerland*

**N-NITROHETEROCYCLES: EASILY ACCESSIBLE, BENCH-STABLE AND BROADLY APPLICABLE NITRATING REAGENTS**

11:45 Michael J. Fink  
*Harvard University, Cambridge, USA*

**STORAGE OF INFORMATION USING SMALL ORGANIC MOLECULES**

12:00 Vittorio Pace  
*University of Vienna, Vienna, Austria*

**DESIGNING NEW SYNTHETIC CONCEPTS FOR IMPARTING MOLECULAR COMPLEXITY WITH C-1 SOURCES**

12:15 Margherita Zanini  
*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*

**GOLD-CATALYZED CROSS-COUPLING-TYPE REACTION OF Bromoalkynes WITH ALLYLISILANES THROUGH A CONCEALED REARRANGEMENT**

12:30 **Lunch @Prater Alm**

14:00 **Excursion and Job Fair**
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### Thursday, July 18

**Chair: Mario Waser**

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<th>Speaker</th>
<th>Institution</th>
<th>Title</th>
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<tr>
<td>09:00</td>
<td>Roderich D. Süßmuth</td>
<td>Technical University of Berlin, Berlin, Germany</td>
<td>PEPTIDE DRUGS FROM NATURE – STRUCTURAL AND (BIO)SYNTHETIC ASPECTS OF NEW ANTIBIOTICS</td>
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<tr>
<td>09:45</td>
<td>Roey Amir</td>
<td>Tel-Aviv University, Tel-Aviv, Israel</td>
<td>THE FINE BALANCE BETWEEN STABILITY AND ENZYMATIC DEGRADABILITY OF POLYMERIC CARRIERS - THE IMPORTANCE OF MOLECULAR PRECISION</td>
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<td>10:15</td>
<td><strong>Coffee Break</strong></td>
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<td>sponsored by TU Wien</td>
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<tr>
<td>10:45</td>
<td>Tatiana Besset</td>
<td>Normandie Université, Rouen, France</td>
<td>RECENT ADVANCES TO ACCESS FLUORINATED SCAFFOLDS</td>
</tr>
<tr>
<td>11:15</td>
<td>Alex Szpilman</td>
<td>Ariel University, Ariel, Israel</td>
<td>NOVEL REACTIONS VIA ELECTROPHILIC ENOLONIUM SPECIES</td>
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<tr>
<td>11:30</td>
<td>Daniel B. Werz</td>
<td>TU Braunschweig, Braunschweig, Germany</td>
<td>SYNERGISTIC CATALYSIS IN DONOR-ACCEPTOR CYCLOPROPANE CHEMISTRY</td>
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<tr>
<td>11:45</td>
<td>Chloe Townley</td>
<td>University of Leeds, Leeds, United Kingdom</td>
<td>A TOP-DOWN APPROACH TO DIVERSE LEAD-LIKE SCAFFOLDS</td>
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<tr>
<td>12:00</td>
<td>Antimo Gioiello</td>
<td>Universita di Perugia, Perugia, Italy</td>
<td>EXPANDING THE BILE ACID CHEMICAL SPACE: SYNTHETIC STRATEGIES FOR LEAD DISCOVERY AND DEVELOPMENT</td>
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<tr>
<td>12:15</td>
<td>Andrew Abell</td>
<td>University of Adelaide, Adelaide, Australia</td>
<td>THE SYNTHESIS AND OPTIMISATION OF NEW ANTIBIOTICS</td>
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<tr>
<td>12:30</td>
<td><strong>Lunch</strong></td>
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Unsere Chemikalien-Marken: Qualität aus eigener Produktion
### Thursday, July 18

**Chair: Roderich Süßmuth**

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<tbody>
<tr>
<td>14:00</td>
<td>Troels Skrydstrup</td>
<td>RECENT DEVELOPMENTS IN LOW PRESSURE CARBONYLATIONS</td>
<td>Aarhus University, Aarhus, Denmark</td>
</tr>
<tr>
<td>14:30</td>
<td>Davide Audisio</td>
<td>DYNAMIC CARBON ISOTOPE EXCHANGE OF PHARMACEUTICALS WITH LABELED CO₂</td>
<td>Université Paris-Saclay, Gif-sur-Yvette, France</td>
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<tr>
<td>14:45</td>
<td>Josep Cornella</td>
<td>LOW-VALENT Bi(I)→Bi(III) REDOX CATALYSIS</td>
<td>Max-Planck-Institut für Kohleforschung, Mülheim/Ruhr, Germany</td>
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<tr>
<td>15:00</td>
<td>Rebecca Greenaway</td>
<td>HYBRID DISCOVERY WORKFLOW FOR ORGANIC MATERIALS AND SUPRAMOLECULAR SELF-ASSEMBLIES</td>
<td>University of Liverpool, Liverpool, United Kingdom</td>
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<tr>
<td>15:15</td>
<td>Coffee Break</td>
<td>sponsored by University of Vienna</td>
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<tr>
<td>15:45</td>
<td>Hennie Valkenier</td>
<td>MACROCYCLIC ANION CARRIERS</td>
<td>Université libre de Bruxelles, Bruxelles, Belgium</td>
</tr>
<tr>
<td>16:00</td>
<td>Mattia Lazzarotto</td>
<td>ORGANO- AND BIOCATALYSIS FOR LIGNAN NATURAL PRODUCT SYNTHESIS</td>
<td>University of Graz, Graz, Austria</td>
</tr>
<tr>
<td>16:15</td>
<td>Arianna Quintavalla</td>
<td>1,2-DIOXANES AS POTENTIAL ANTI-LEISHMANIAL DRUGS</td>
<td>University of Bologna, Bologna, Italy</td>
</tr>
<tr>
<td>16:30</td>
<td>Alexandros Zografos</td>
<td>DIVERGENT SYNTHESIS OF NATURAL SESQUITERPENE LACTONES: ONE PLAN, MANY PITFALLS TO AVOID</td>
<td>Aristotle University of Thessaloniki, Thessaloniki, Greece</td>
</tr>
<tr>
<td>17:00</td>
<td>Paolo Melchiorre</td>
<td>ORGANIC SYNTHESIS IN THE EXCITED STATE</td>
<td>Institut Català d’Investigació Química (ICIQ), Tarragona, Spain</td>
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<tr>
<td>17:15</td>
<td>Closing Ceremony</td>
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<tr>
<td>18:30</td>
<td>Conference Dinner</td>
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Johann Strauss (Son, 1825-1899), Austrian composer
RADICAL CHEMISTRY IN THE DESIGN AND SYNTHESIS OF ARTIFICIAL MOLECULAR MACHINES

Sir James Fraser Stoddart

Northwestern University, Department of Chemistry, Evanston, IL 60208, USA

Sir James Fraser Stoddart works in the area of supramolecular chemistry and nanotechnology. Stoddart has developed highly efficient syntheses of mechanically-interlocked molecular architectures such as molecular Borromean rings, catenanes and rotaxanes utilizing molecular recognition and molecular self-assembly processes. He has demonstrated that these topologies can be employed as molecular switches. His group has even applied these structures in the fabrication of nanoelectronic devices and nanoelectromechanical systems (NEMS).

Stoddart shared the Nobel Prize in Chemistry together with Ben Feringa and Jean-Pierre Sauvage in 2016 for the design and synthesis of molecular machines. [1]

SURPRISES WITH ALKYNES:
A NEW REACTIVITY PARADIGM AND ITS APPLICATIONS

Alois Fürstner

Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Germany
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Metal catalyzed hydrogenation reactions invariably result in cis-delivery of the two H-atoms of H₂ to the π-bond of a given substrate. This canonical course, however, is violated in reactions of internal alkynes catalyzed with [Cp*Ru]-based complexes, which afford E-alkenes by direct trans-hydrogenation. Connected to this unorthodox transformation is an even more surprising reactivity mode, in which both H-atoms of H₂ are delivered to one and the same C-atom of the triple bond with concomitant formation of discrete metal carbene complexes; such geminal hydrogenation of stable carbogenic compounds is without precedent.

In this lecture I intend to describe the current state of the art and summarize our growing mechanistic understanding [1]. At the same time, it will be shown that trans-hydrogenation is by no means a singularity: rather, the underlying principle is also manifest in trans-hydroboration, trans-hydrosilylation and trans-hydrostannination reactions. These transformations are particularly robust and functional group tolerant and have already stood the test of natural product synthesis. A few selected examples will be presented to showcase scope and limitations of this novel catalytic reactivity paradigm.

MAKING NEW FORMS OF NANOCARBONS

Kenichiro Itami

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Our group is trying to create a range of structurally uniform nanocarbons of fundamental and practical importance by bottom-up chemical synthesis (Nature Rev. Mater. 2016). Representative achievements include: (1) the development of single-step aromatic π-extension (APEX) methods for the rapid and programmable synthesis of nanocarbon molecules (Science 2018, Nature Commun. 2015, Nature Chem. 2015); (2) the synthesis of carbon nanorings, nanobelts and pure nanotubes (ACIE 2009, Science 2017, Nature Chem. 2013, Nature Commun. 2018); (3) the first precision synthesis of graphene nanoribbons controlling width, edge structure, and even length (Nature, in press); and (4) the synthesis of topologically unique nanocarbons such as warped nanographenes, carbon nanocages, all-benzene catenanes, and trefoil knots (Nature Chem. 2013, etc).

In this talk, most recent beautiful molecular nanocarbons as well as our recently initiated nanocarbon biology project will be presented.
Our research program [1-7] is aimed at the development of novel catalysis concepts for the asymmetric synthesis of chiral functional molecules. In 2011 we introduced an entirely new role for Cu(I)-based catalysts, facilitating highly enantioselective carbon-carbon bond forming reactions between organometallics and enolisable carbonyl as well as imine compounds. Following this initial discovery, we established Cu(I)-catalysis, in combination with Lewis acids/Grignard reagent, as a powerful tool to tackle the reactivity of inherently unreactive substrates for carbon-carbon bond forming reactions. In this lecture I will focus on how we can use these concepts to access valuable chiral heteroarenes and amides, as well as tertiary alcohols and amines, in catalytic and enantioselective fashion. Recent results involving Lewis acid strategy that enabled dearomatisations as well as tackling the reactivity of unprotected carboxylic acids will also be presented.
The creation of chirality is one of the most fundamental challenges in synthetic organic chemistry. Our group has worked for some time on enantioselective catalytic photochemical reactions [1] mediated by triplet energy transfer and by chromophore activation. The first approach is based on a triplet energy transfer by chiral hydrogen-bonding catalysts [2] which in turn are derived from a previously described template. The second approach relies on the use of Brønsted or Lewis acids which change the photophysical properties of the chromophore [3] and ideally allow for a selective excitation in the chiral environment they provide. Beyond [2+2] photocycloaddition chemistry, our studies are directed towards photochemical rearrangement and deracemization reactions with a potential for synthetic applications. The background of the above-mentioned experiments will be discussed and the latest results of our research efforts in this area will be presented.

CARBOXYLATES AS DIRECTING AND LEAVING GROUPS IN CATALYTIC BOND FORMATION

Lukas J. Gooßen, G. Zhang, A. Biafora, L. Huang, Y. Gao

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Carboxylic acids are versatile substrates for catalytic C-C and C-X bond formations.[1] A new concept is the use of carboxylates as deciduous directing groups, which stay in place just long enough to direct a C–H functionalization reaction into a specific position and are shed tracelessly as soon as the new C–C or C–heteroatom bond has formed.

In the carboxylate-directed, Ag/Cu-catalyzed C–H alkoxylation,[2] an alkoxide group is introduced selectively in the ortho position of aromatic carboxylates. The new substituent destabilizes the C–COOH bond to an extent that swift protodecarboxylation occurs, precluding further substitution of the second ortho-C–H bond. A similar reaction concept is utilized in a Ru-catalyzed decarboxylative hydroarylation of alkynes with formation of vinyl arenes[3] and a regiospecific synthesis of 1,1-disubstituted alkenes from α,β-unsaturated carboxylic acids.[4] In the presence of a Rh/In catalyst, benzoic acids react with α,β-unsaturated ketones with formation of two new C–C bonds along with the selective cleavage of non-activated C–H, CO–OH and C–COR bonds to give indanones.[5]

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There can be no more noble undertaking than the invention of medicines. Chemists that make up the engine of drug discovery are facing incredible pressure to do more with less in a highly restrictive and regulated process that is destined for failure more than 95% of the time. How can academic chemists working on natural products help these heroes of drug discovery – those in the pharmaceutical industry? With selected examples from our lab and others, this talk will focus on that question highlighting interesting findings in fundamental chemistry and new approaches to scalable chemical synthesis.


How can chemistry morph into biology? This is the key question about the origin of life, be it on our planet several billion years ago, or elsewhere and so we need to think about chemistry in the context of planetary science if we want to know where we came from and whether or not we are likely to be alone in the Universe.

The chemistry used by biology to fabricate its various components is by and large hopelessly inefficient in the absence of enzyme catalysts, so we need to look for different chemistry that can make the same componentry efficiently without enzymes. But where do we look?

One approach is to guess at the environment and then use laboratory simulation to investigate its chemistry. The problem with this is the guesswork – there were presumably many different environments on early Earth and it is not obvious what chemistry they might be associated with. An alternative approach is to explore chemistry in a pretty much unconstrained way to try and find out if all the molecules needed to kick-start biology can be made under similar conditions from plausible feedstocks. If they can and the conditions required correspond to a particular environment on early Earth then that environment is strongly implicated and can further guide chemical investigations. In this lecture, I will present the results of this latter approach and demonstrate how hellish conditions on Hadean-Archean Earth could have set the stage for the transition from chemistry to biology.
The invention of chemical reactions to create fluorine-containing molecules is an important aspect of modern medicine. Positron Emission Tomography (PET) with short-lived \(^{18}\text{F}\)-radiotracers is an imaging modality that can diagnose diseases, and monitor how patients respond to therapy. Moreover, the stable isotope \(^{19}\text{F}\) is commonly used in drug discovery to identify lead molecules and improve their properties. In this lecture, we will provide an overview of the key reactions we have developed to advance fluorine-based medicine, a rewarding process that has enhanced our fundamental understanding of fluorine chemistry, more specifically fluoride reactivity.
PEPTIDE DRUGS FROM NATURE – STRUCTURAL AND (BIO)SYNTHETIC ASPECTS OF NEW ANTIBIOTICS

Roderich D. Süssmuth

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Recently, peptides have gained increased interest as drugs, since they display properties which are unmet by small molecules or biologics. In nature, ribosomal (RiPPs) [1] and non-ribosomal peptides (NRPs) [2] from bacteria and fungi provide an enormous structural diversity which is linked to remarkable bioactivities, e.g. antibacterial, antifungal, anticancer and others. Next to classical screening approaches, the discovery of new bioactive peptides from nature meantime has embraced genome mining.

The lecture presents recent findings on the discovery, structure elucidation and biosynthesis of new peptide natural products with the potential to be developed as antibacterial drugs. These are the lipolanthines [3] and albicidin [4, 5], unusual RiPP and NRP structures with a remarkable activity against multi-resistant Gram-positive and Gram-negative bacteria of the ESKAPE-group. Furthermore, we will report on the biosynthetic and synthetic assembly of these compounds, as well as bioactivity and resistance mechanisms. In addition, the past years have seen an enormous progress in the understanding of biosynthetic assembly, e.g. unexpected biosynthetic findings for peptide backbone N-methylation [6], which also could impact the engineering and (re)design of structural diversity e.g. by combinatorial biosynthesis approaches.

ORGANIC SYNTHESIS IN THE EXCITED STATE

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The chemical reactivity of electronically excited molecules differs fundamentally from that in the ground state. This is the underlying reactivity concept of photochemistry,[1] which has traditionally allowed the development of unique chemical transformations not achievable via conventional ground-state pathways.[2] For example, an excited-state molecule is both a better electron-donor (i.e. a better reductant) and electron-acceptor (i.e. a better oxidant) than in the ground state. This explains why the light excitation of organic molecules can unlock unconventional reactivity manifolds. In this context, our laboratory has been exploring the potential of some organocatalytic intermediates to directly reach an electronically excited state upon visible-light absorption to then switch on novel catalytic functions unavailable to ground-state organocatalysis.[3] Here, the new synthetic possibilities, opened up by the excited-state reactivity of organocatalytic intermediates,[4] will be discussed.[5]

[5] Acknowledgement: Research supported by MINECO (project CTQ2013-45938-P), and the European Research Council (ERC 681840 - CATA-LUX).
Invited Lectures

ESOC 2019

St. Stephen’s Cathedral
Vienna’s landmark
Systematic tuning of optical bandgaps in organic molecules can be achieved by homologation (oligomerization) of linear π-conjugated motifs, by ring expansion of π-conjugated macrocycles, and by extension of fused ring systems in two dimensions. A complementary approach relies on combining donor and acceptor (D–A) moieties, with diverse recent applications in small-molecule and polymer chemistry. The D–A paradigm is particularly suitable for the development of tunable building blocks, which can be constructed by judicious merging of existing electron-deficient and electron-rich motifs. A simple and potentially productive design of such a hybrid structure is achieved by combining naphthalenemonoimide (NMI, red) and pyrrole (blue), as shown below [1,2]. We will discuss the application of such pyrroles as building blocks for the synthesis of diverse polycyclic aromatics, including macrocycles [2], nanographenoids [3,4], and bipyrroles [5,6], some of which are characterized by persistent helicene-like chirality. These systems reveal rich redox chemistry, spanning multiple oxidation levels, as well as tunable optical signatures extending into the near infrared.

TOTAL SYNTHESIS OF POLYCYCLIC NATURAL PRODUCTS

Thomas Magauer, Matthias Schmid, Franz L. Haut, Christoph Habiger, Lukas Wein, Gabriele Prina Cerai, Christian Steinborn, Julian Feilner, Lukáš Maier, Kevin Sokol, Sofia Torres Venegas and Ivica Zamarija

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Natural products constitute a vast and largely unexplored library of complex molecular architectures, and are a fundamental source for novel bioactive agents. However, the complex architecture of these molecules often prevent their application in medicinal chemistry. For us, this is an inspiration to think about innovative retrosynthetic bond disconnections which enable rapid access to the target compounds. We want to discover, design and develop powerful transformations such as cationic cyclizations and ring-expansions and apply them to the synthesis of biologically relevant complex natural products and simplified analogs thereof. The goal of these projects is to shed light on proposed biosynthetic processes, to identify new molecular targets and ultimately provide new lead compounds for the treatment of human diseases.
INTERACTION VS. FRUSTRATION IN BIMETALLIC COOPERATIVE SYSTEMS

Jesús Campos

In the early 80s Chisholm proposed that “all the types of reactions which have been studied for mononuclear transition metal complexes will also occur for dinuclear transition metal complexes”.\[1\] Almost 40 years later, continued research on the area of bimetallic systems has proven that claimed and gone beyond. Regarding catalytic applications, there are many important transformations that require the concerted action of pairs of active metal sites, paralleling what is often found in metalloenzymes. We recently started to investigate late-transition bimetallic systems characterized by the use of novel sterically hindered phosphine ligands, which has allowed us to kinetically stabilize many uncommon low-coordinated structures.\[2\] In the last two years, we have focused on the competition between the formation of M-M bonds versus M···M frustration and investigated the reactivity derived from a variety of bimetallic systems, an example of which is depicted in the Figure below.\[3\] Our results pertaining their reactivity and potential in catalysis will be discussed.

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STRATEGY FOR SELECTIVE REDUCTIVE ADDITION

Denis Chusov\textsuperscript{a}, Oleg I. Afanasyev\textsuperscript{a}, Sofiya Runikhina\textsuperscript{a}, Olga Chusova\textsuperscript{b},
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Herein we present the concept of using carbon monoxide for atom economical reductive addition without external hydrogen source [1-9]. Following this concept, we have shown that N-H, O-H and C-H bonds of the reagents could be used as hydrogen source. The process proceeds with high selectivity. Such approach can widely use for synthesis of heterocycles.

This work was supported by Russian Foundation for Basic Research (18-33-20065) and the RUDN “5-100” program.
TRAPPING OF REACTIVE INTERMEDIATES

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Identification of reactive intermediates is the key step towards understanding chemical reactions. Often, controversies exist about reaction mechanisms, about the nature of rate-determining transition states or about the role of intermediates. We are developing methods to identify the intermediates and to investigate their structure. We are using mass spectrometry which is a unique method among other analytical techniques in its sensitivity and thus in detection of low abundant species in an ionic form. We trap these ions and study their properties by infrared and visible photodissociation spectroscopy. This techniques allows us to investigate, for example, highly reactive metal complexes or elusive intermediates in organic reactions or short lived intermediates in photocatalytic reactions. I will show and discuss examples of trapping elusive intermediates in phosphate chemistry and in flavinium-catalyzed photooxidation reactions.
Counter-ions affect both the reactivity and selectivity of anionic reactions. In this lecture I will describe my group’s work on counter-ion-directed cyclization and mechanism and demonstrate how lessons learned in this area can be applied in the development of new enantioselective methods, with a particular focus on controlling axial chirality.\textsuperscript{[2-5]}

Extension of this chemistry to complexity-generating reactions will also be outlined.


TARGETING BACTERIAL PERSISTERS IN THE POST-ANTIBIOTIC ERA

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Persister cells[1] are a dormant bacterial phenotype temporary tolerant to antibiotic treatment; this distinctive trait distinguishes them from well-known genetically resistant variants, and hints their role in chronic and recurrent infections. Inhibition of the intracellular accumulation of guanosine tetra- or pentaphosphate ((p)ppGpp), the triggering event of the signalling cascade that allows bacteria to activate this phenotypic switch (i.e. the stringent response), may prevent the insurgence of persisters and therefore the incomplete sterilization that is often responsible of relapsing infections[2].

In particular, we aim to interfere with (p)ppGpp production by gaining control of the key upstream regulatory proteins RSH (RelA/SpoT-Homologue superfamily, a.k.a. Rel). To this end, we are adopting a multidisciplinary approach, comprising computational studies,[3] synthesis[4] and ligand-protein interaction assays. Our recent insights into the many facets of this problem will be presented.

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NECESSITY IS THE MOTHER OF INVENTION: NATURAL PRODUCTS AND THE CHEMISTRY THEY INSPIRE

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The chemical synthesis of natural products provides an exciting platform from which to conduct fundamental research in chemistry and biology. Our group is currently pursuing the synthesis of a number of structurally complex natural products, including the diterpenoids perseanol and talatisamine. The densely-packed arrays of heteroatoms and stereogenic centers that constitute these polycyclic targets challenge the limits of current technology and inspire the development of new synthetic strategies and tactics. This seminar will describe the latest progress in our methodological and target-directed synthesis endeavors.
DISCOVERY OF THE FIRST ANTIBACTERIAL AGENT INHIBITING THE ENERGY-COUPLING FACTOR (ECF) TRANSPORTERS BY STRUCTURE-BASED VIRTUAL SCREENING

Anna K. H. Hirsch

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The emergence of drug resistance against important pathogens poses an ever-growing health threat. The pipeline of novel drug candidates should be filled with molecules featuring an unprecedented mode of action and a novel chemical structure. We tackle both challenges by adopting several established and unprecedented hit-identification strategies such as structure-based design, virtual screening and dynamic combinatorial chemistry\(^1\) on an unexplored anti-infective target.\(^2\) ECF transporters are a class of ATP-binding cassette (ABC) transporters that mediate the uptake of vitamins in prokaryotes. They consist of an energizing module and a substrate-binding protein (S-component). Different S-components can interact with the same energizing module.\(^3\)

We embarked on a structure based drug design (SBDD) of thiamine analogue as binders of the integral membrane protein ThiT, the S-component for thiamine. We designed and synthesized thiamine analogues in order to elucidate the mechanism of substrate binding and transport. The new compounds bind with high affinity to ThiT (\(K_d = 4–660\) nM) and the predicted binding mode was confirmed by co-crystallization studies.\(^4,5\)

A structure-based virtual screening campaign afforded the first allosteric inhibitors of the transporter for folate.\(^6\) We synthesized a series of derivatives that display good \textit{in vitro} activity, excellent ADMET properties and antibacterial activity (MIC = 4 M) against a range of pathogenic Gram positive bacteria (\textit{Staphylococcus aureus, Enterococcus faecium} and \textit{Streptococcus pneumoniae}).\(^7\) A pharmacokinetic study showed them to be present in plasma at high concentration. Thus, the inhibitors constitute an excellent starting point for the development of novel antibiotics and are currently being investigated in an \textit{in vivo} infection model.\(^7\)

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TRANSFER OF REACTIVE GASES FROM ONE MOLECULE TO ANOTHER

Martin Oestreich

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This talk tells the story of how our work on tamed silicon cations [1–3] led us to introduce the new concept of ionic transfer hydrosilylation [4], even with monosilane [5]! The electron-deficient boron Lewis acid tris(pentafluorophenyl)borane catalyzes the release of hydrosilanes from cyclohexa-2,5-dien-1-yl-substituted silanes. The same boron catalyst will then activate the Si–H bond for the reaction with representative π- and σ-donating substrates. The net transformation is a transfer hydrosilylation. That strategy also enables the related hydrogenation [6] and even transfer hydrocyanation [7], and has been extended to Brønsted acid-catalyzed transfer hydrohalogenation processes [8].

![Concept of cyclohexadiene-based ionic transfer reactions](image)

(El = electrofuge and Nu = nucleofuge)

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THE FINE BALANCE BETWEEN STABILITY AND ENZYMATIC DEGRADABILITY OF POLYMERIC CARRIERS – THE IMPORTANCE OF MOLECULAR PRECISION

Roey J. Amir\textsuperscript{a,b,c}

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\textsuperscript{b}The Tel Aviv University Center for Nanoscience and Nanotechnology
\textsuperscript{c}The Blavatnik Center for Drug Discovery, Tel-Aviv University, Tel-Aviv 6997801, Israel

Deep understanding of the factors that define the stability and degradability of polymeric assemblies is crucial for the development of biodegradable materials for biomedical applications ranging from drug delivery systems to tissue engineering. The poor accessibility of lipophilic substrates that may be hidden inside hydrophobic domains to the degrading enzymes seems to be one of the key parameters that determine enzymatic degradability. In the past several years, we designed and synthesized well-defined amphiphilic PEG-dendron hybrids with enzymatically cleavable hydrophobic end-groups. The high molecular precision of the hydrophobic dendritic block, enabled us to observe how precise minor changes of the hydrophobic blocks significantly affect the stability and degradation rates of polymeric assemblies [1]. Furthermore, we demonstrated that the micellar stability in serum may result in different internalization mechanism of the polymeric assemblies into living cells [2].

Our results strongly imply that the enzymatic degradation of polymeric amphiphiles occurs at their monomeric state outside of the micelle through the micelle-monomer exchange. This equilibrium-based mechanism may explain the poor degradability that is often reported for many polymeric assemblies. Based on our molecular understanding, we recently started to design novel multi-responsive polymeric assemblies that can overcome the challenge of designing stable and yet enzymatically degradable polymeric assemblies [3].

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RECENT ADVANCES TO ACCESS FLUORINATED SCAFFOLDS

Tatiana Besset

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Over the last years, the organofluorine research field has known a fast expansion, [1] as shown by the plethora of pharmaceuticals and agrochemicals containing at least one fluorine atom [2]. Consequently, a special attention was paid to the development of modern strategies in organofluorine chemistry. Besides, transition metal catalyzed direct C-H bond functionalization has known tremendous progress over the last decade allowing new retrosynthetic disconnections and innovative approaches [3]. In that context, we focused on the development of new methodologies to introduce fluorinated groups onto molecules based on the combination of organofluorine chemistry and transition metal catalyzed C-H bond functionalization. Besides, a special attention was paid to the design of original electrophilic reagents [4].


RECENT DEVELOPMENTS IN LOW PRESSURE CARBONYLATIONS

Troels Skrydstrup

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Carbon monoxide (CO) represents an important C1 building block for the construction of some of the most fundamental chemical functionalities carrying a carbon-oxygen single or double bond. Transition metal catalysis plays a key role in promoting such transformations with CO. We have earlier shown that the combination of palladium catalysis with CO releasing molecules and the two-chamber reactor, COware, provides both a convenient and safe means for performing traditional but low pressure Pd-catalyzed carbonylative couplings, and a platform for discovering new carbonylation reactions and carbon isotope labeling techniques [1–3]. In this talk, I provide a short overview of our latest findings in this area, but also discuss our efforts to develop viable Ni-mediated carbonylations with alkyl substrates [4].

\[ \text{CO} (1.5 \text{ equiv.}) \]

\[ R' \text{M} \]

\[ R'' \text{X} \]

\[ \text{Ni}^{II} \text{Cl} \]

\[ \text{NR}_2 \text{(cat.)} \]

\[ \text{DBU} \]

\[ \text{Ni}^{II} \text{Cl} \]

\[ \text{NR}_2 \text{(cat.)} \]

\[ \text{CO} (1.5 \text{ equiv.}) \]

\[ R'' \text{X} \]

\[ \text{Ni(COD)}_2 \]

\[ \text{Ts} \]

\[ \text{NH} \]

\[ \text{O} \]

\[ 13\text{CO} \text{(1.5 equiv.)} \]

from Si$^{13}$COgen

\[ R'' \text{X} \]

\[ \text{Ts} \]

\[ \text{NH} \]

\[ \text{O} \]

\[ 13\text{CO} \text{(1.5 equiv.)} \]

from $^{13}$COgen

\[ R'' \text{X} \]

\[ \text{DBU} \]

\[ \text{Ni(COD)}_2 \]

\[ \text{Ts} \]

\[ \text{NH} \]

\[ \text{O} \]

\[ 13\text{CO} \text{(1.5 equiv.)} \]

from $^{13}$COgen


DIVERGENT SYNTHESIS OF NATURAL SESQUITERPENE LACTONES: ONE PLAN, MANY PITFALLS TO AVOID

Alexandros L. Zografos

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The emergence of preparing diverse natural product scaffolds is firmly associated with the need of our society for more potent and selective biomodulators. In response, nowadays, divergent synthesis utilizing common synthetic scaffolds that can be readily transformed to an array of diverse natural compounds is progressively gaining ground in drug discovery.\(^1\) The lecture will focus on drawbacks and solutions towards the development of a unified synthetic plan for accessing highly cytotoxic sesquiterpene lactones.\(^2\)\(^-\)\(^4\)

![Diagram]

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Oral Contributions

ESOC 2019

Vienna State Opera
First major building on the Vienna Ringstrasse, completed in 1869
The bis-tetrahydroisoquinoline (bis-THIQ) natural products have been studied intensively over the past four decades for their exceptionally potent anticancer activity, in addition to strong Gram-positive and Gram-negative antibiotic character. Synthetic strategies toward these complex polycyclic compounds have relied heavily on electrophilic aromatic chemistry, such as the Pictet–Spengler reaction, that mimics their biosynthetic pathways. Herein, we report an approach to two bis-THIQ natural products, jorunnamycin A and jorumycin, that instead harnesses the power of modern transition-metal catalysis for the three major bond-forming events and proceeds with high efficiency (15 and 16 steps, respectively). By breaking from biomimicry, this strategy allows for the preparation of a more diverse set of nonnatural analogs.
4-π-PHOTOCYCLISATION OF DIHYDROPYRIDAZINES: ACCESS TO VERSATILE BICYCLIC DIAZETIDINES

Thomas K. Britten\textsuperscript{a}, Susannah C. Coote\textsuperscript{a}, Paul D. Kemmitt\textsuperscript{b} and Nathan R. Halcovitch\textsuperscript{a}

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Despite their utility in a wide variety of applications, the synthesis of four-membered carbo/heterocycles is often difficult, especially if specific substituent patterns are required. Recently, we have shown that bicyclic diazetidines 2 can be easily accessed on multigram scale through the 4-π-photocyclisation of 1,2-dihydropyridazines 1 \cite{1,2}, an intriguing reaction that has been studied only sporadically since its first introduction in 1968 \cite{3}. Bicyclic diazetidines 2 are highly strained but bench-stable, and are not only interesting target molecules in themselves but also valuable synthetic intermediates – the straightforward conversion of 2 to a variety of novel building blocks (examples given in the scheme below) will be presented.

\begin{center}
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\begin{thebibliography}{9}
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REACTION PROGRESS KINETIC ANALYSIS BY DIRECT ANALYSIS OF CONCENTRATION-TIME PROFILES

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The rapid development of analytical methods have rendered reaction-monitoring to obtain kinetic data a routine step in the development of new chemical reactions and the study of reaction mechanisms. However, analysis and interpretation of kinetic profiles have not enjoyed a parallel development. Only in recent years, with the advent of the Reaction Progress Kinetic Analysis (RPKA) model, introduced by Blackmond, the systematic use of the wealth of information available from kinetic profiles has become commonplace [1]. Recently, Burés furthered the approach by introducing Time Normalization Analysis (TNA) [2,3], which utilizes concentration-time data directly, instead of rate-time data, to determine partial reaction orders of reactions. However, still not all the information contained in kinetic profiles is utilized. Additionally, most of the current analysis methods are not suitable for automatic analysis required for high-throughput experimentation in machine-driven laboratories as they require significant human intervention. Herein, we report on a new general method, which we term Order Fitting Analysis (OFA), to analyze full concentration-time profiles of chemical reactions and extract information regarding the reaction order with respect to substrates, the presence of multiple kinetic regimes, and the presence of kinetic complexities, such as catalyst deactivation, product inhibition, and substrate decomposition. Being in its essence a simple nonlinear fitting approach, it has the potential to be straightforwardly implemented in automated high-throughput kinetic analysis procedures.

MDM2 is a main and direct inhibitor of the crucial tumor suppressor p53. Reports from initial clinical trials showed that blocking this interaction with an inhibitor can be of great value in the treatment of p53 wild-type tumors. Dose-limiting hematological toxicities and drug-induced resistance have been identified as main issues in the clinic. We aimed for an inhibitor with superior potency and pharmacokinetic properties to ultimately achieve full efficacy with less-frequent dosing schedules.

The discovery and optimization of novel, chemically stable spiro-oxindole compounds that are not prone to epimerization as observed for other MDM2-p53 inhibitors will be presented. Structure based optimization accompanied by conformational restriction served as guiding optimization principal and led to complex fused ring systems. The complex structures were prepared efficiently by the application of various multi-bond forming reactions (e.g.: cycloadditions, reductive cyclisation cascades, Davis-Beirut reactions) to enable accelerated optimization. In vivo efficacy in disease relevant xenograft models even when given as low single doses will be presented exemplified by the development candidate BI-0282.

CONTROLLING THE CIRCADIAN CLOCK WITH HIGH TEMPORAL RESOLUTION THROUGH PHOTODOSIMETRY

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Inspired by the crucial role of circadian clock disruption in disease development,[1] during the last decade chemical biology studied how to adjust cellular clocks using small molecule modifiers.[2] Unfortunately, these modifiers are still facing a big drawback when in vivo application is needed: due to the similarity in cellular regulation of clocks, besides curing the disrupted biological rhythm they would affect all the others, healthy rhythms in other cells. To overcome this problem, a potential strategy would be photocaging - based on the regulation of a compound’s bioactivity with light, which can be delivered precisely in space and time.[3]

Here, we show for the first time the possibility to control the circadian rhythm with high temporal resolution. Lengthening of the circadian period was achieved in mammalian cells, tissue, and zebrafish just by choosing an interval of visible light irradiation (400 nm) in order to release longdaysin – a known CKI inhibitor and compound that exhibits a drastic effect on the circadian period.[4]

![Scheme 1](image.png)

**Scheme 1.** a) Photo-deprotection of the protected longdaysin; b) correlation diagram of period lengthening, concentration, and light exposure time in cells and tissue explant.

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Fluorinated compounds are key structural moieties in numerous areas of chemistry, with applications to catalysis, medicine and material sciences.[1] The introduction of fluorinated motifs changes properties of a given molecule, and in the pharmaceutical industry context, improves the stability and lifetime of F-containing pharmaceuticals. However, the stability is often too pronounced and the lead compound is frequently poorly biodegradable. Therefore, it is furthermore desirable to develop new sustainable methods for the functionalization of aromatic C-F bonds, as a useful strategy to establish novel chemical transformation of aryl fluorides. Transition metal-catalyzed Ar–F functionalization is considerably more challenging than classical Ar–H or Ar–Hal (Hal = I, Br, Cl) activation, generally showing low selectivities and requiring electronically biased polyfluorinated substrates.[2] In particular, C–C formation reaction via C–F cleavage of fluoroarenes using nickel catalyst has been reported using activated aryl nucleophiles, such as highly reactive Grignard reagents, zincates and boronic acids as the coupling partner for C–C formation via transmetallation [3]. Herein we show Nickel-catalyzed C–F activations enabled chemo-divergent C–C formation with alkynes by chelation assistance. The judicious choice of the alkynes electronic properties thus allowed the selective synthesis of alkyne mono-annulation or double-insertion aromatic homologation products. A key unprecedented 9-membered nickelocyclic intermediate species was isolated and crystalized, unravelling the mechanistic pathway to the aromatic homologation product by challenging double C-F/C-H activation.

Construction of α-trifluoromethylated amines in optically pure form is one of the important topics of research interest because of its interesting biological activity. Nucleophilic addition to N-protected trifluoromethylated ketimine, and subsequent deprotection of the N-protecting group will furnish α-trifluoromethylated N-free amines.\(^\text{[1]}\) Trifluoromethylated N-H ketimine is known to be relatively stable among N-H ketimines. Nucleophilic addition toward trifluoromethyl N-H ketimine will provide a straightforward method for the preparation of α-trifluoromethylated N-free amines because deprotection of the N-protecting group is obviated. As part of our continued interest in the chiral phosphoric acid catalysis, we investigated Friedel-Crafts alkylation reaction of heteroarenes, such as indole and pyrrole, with trifluoromethylated N-H ketimines by means of chiral phosphoric acid. Corresponding α-trifluoromethylated amines were obtained in good yields and with good to excellent enantioselectivity (Schemes 1 and 2)\(^\text{[1]}\). Interestingly, N-PMP (\(p\)-methoxyphenyl) substituted ketimine did not participate in the reaction and the corresponding N-PMP amine was not obtained (Scheme 3). It was found that N-H ketimines are more reactive than N-PMP ketimine.


ACCESS TO UNUSUAL HETEROCYCLIC COMPOUNDS UTILIZING A KEY COBALT-CATALYZED C-H FUNCTIONALIZATION APPROACH

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Since the publication of Matsunaga and Kanai in 2013 demonstrating the potential of Cp*Co[III]-type catalysts in C-H functionalization protocols[1], the field has rapidly expanded and engaged the interest of a large number of researchers[2]. In general, these reports can be divided into two key areas; (a) linear couplings and (b) new/efficient routes to heterocycle formation. The latter of these areas is of significant interest as most of the small molecule drugs approved by the FDA in 2017 contained complex heterocyclic motifs[3] and as a result novel, improved methods for their synthesis is likely to be an important innovation. In this context, we have engaged in the use of Cp*Co[III] catalysts, with readily available benzamide substrates, for the preparation of some more unusual heterocyclic compounds through either a cascade reaction[4] or a two-step sequential one-pot protocol[5] using C-H functionalization as the key step in both cases. In addition to these synthetic results, studies of their mechanisms using DFT have revealed key aspects of the catalytic cycles, allowing for a fuller understanding of the observed selectivities and reactivities. In summary, this contribution showcases the potential for rapidly building up molecular complexity exploiting efficient and sustainable first-row transition metal catalysis as the key tool.

Biocatalysis is increasingly gaining ground as a powerful module in the organic chemist's toolbox for the synthesis of well-defined building blocks, thanks to unrivalled selectivities and good availability of stable and optimized enzyme preparations. The lack of biosynthetic precedence for numerous synthetically relevant reactions and the consequent lack of biocatalysts to promote those reactions need to be considered a major drawback, since this prevents an even broader application of enzyme catalysts in classical synthetic chemistry. For many years, catalytic promiscuity, the enzymes' capability to catalyze fundamentally different chemical interconversions, has been in the scientific focus,[1] however, just recently entirely abiotic transformations came within reach by means of specialized, evolved proteins.[2-4]

In our search of biological catalysts with abilities to address synthetically important reactions beyond the biosynthetic repertoire, various wild-type metalloenzymes were identified as effective promoters in a range of unnatural transformations for the synthesis of O-heterocyclic compounds.[5-7] In this presentation, our most recent discoveries exploiting copper-proteins will be disclosed that emerged as versatile biocatalysts in pericyclic reactions. On one side, copper-dependent oligosaccharide-degrading oxidoreductases are introduced as powerful mediators in sigmatropic rearrangements enabling the preparation of complex tetrahydrofurans in high stereoselectivities.[8] Moreover, the synthesis of stereodefined N-heterocycles by means of blue multicopper enzymes through ene-type rearrangements will be discussed.

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QUEST FOR ASYMMETRIC KULINKOVICH REACTION: FROM MECHANISM TOWARDS ENHANCED ENANTIOSELECTIVITY

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Discovery of titanium-catalyzed cyclopropanation of carboxylic esters in the late 1980s by the group of Kulinkovich commenced the era of titanacyclopropanes in organic synthesis. Despite the high synthetic value of the Kulinkovich reaction and its congeners, asymmetric version remains an unsolved challenge. The latest advances were possible due to ingenious insight that pentacoordinated titanium ate complexes, rather than tetracoordinated titanium species, mediate the process \cite{1}. Mechanistic and solution NMR studies strongly support the idea of ate complex intermediates as a prerequisite of high enantiocontrol, while degradation of ate species result in dramatic erosion of enantioselectivity. Based on these findings, an improved protocol has been development for asymmetric Kulinkovich reaction, allowing preparation of (1S,2S)-cyclopropanols with up to 90\% ee by using titanium (4R,5R)-TADDOLates. Expansion of the same methodology to hydroxycyclopropanation of prochiral olefins via a more convenient olefin ligand exchange method will be also presented \cite{2}.

\begin{equation}
R^2\text{C}═\text{C}-(\text{CH}_2)\text{CCl}_2\text{Br}, \quad \{\text{TADDOL} \}_\text{Ti}(\text{Oi-Pr})_2
\end{equation}

\begin{equation}
R^1\text{C}═\text{C}-(\text{CH}_2)\text{CCl}_2\text{Br}, \quad \{\text{TADDOL} \}_\text{Ti}(\text{Oi-Pr})_2
\end{equation}

\begin{equation}
\text{up to 84\% ee}
\end{equation}

\begin{equation}
\text{up to 90\% ee}
\end{equation}

\begin{equation}
\text{titanacyclopropane ate complex}
\end{equation}

\begin{equation}
\text{titanacyclopropane ate complex}
\end{equation}

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RATIONAL DESIGN OF NEW, MORE POTENT ACRIDINIUM VISIBLE LIGHT ORGANO-PHOTOCATALYSTS BY C-H FUNCTIONALIZATION

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In recent years, visible-light organo-photoredox catalysis was found as a valid and potent alternative for the commonly used photoredox catalysts based on ruthenium and iridinium complexes.[1] In this regard, the acridinium-based photoredox catalysts have attracted a vast interest, especially in the form of the corresponding 9-mesityl derivatives.[2] Indeed, from the pioneering work of Fukuzumi and co-workers,[2a] the 9-mesityl N-methyl acridinium salt was found as one of the most powerful photoredox catalysts. However, it still presents substantial reactivity and stability limitations, for which more stable and active structures are needed. Aiming at solving some of the current limitations, and based on our expertise in acridane oxidative Csp3-H functionalization,[3] we have developed an innovative one-pot strategy towards C9-substituted acridinium salts, in which an oxidative Ugi-type process is involved as key step.[4]

We present herein a new class of easily tunable acridine-based structures with enhanced photoredox catalytic activity respect to the well-established C9-mesityl acridinium salt.[4] Various applications in photoredox-catalysis will be presented.[4][5] Moreover, based on DFT-calculations, fluorescence and quenching studies, the reasons of their superior performance are unveiled and discussed.

DEVELOPMENT AND SCALE-UP OF CONTINUOUS FLOW PROCESSES FOR THE MANUFACTURE OF ACTIVE PHARMACEUTICAL INGREDIENTS.

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An increasing fraction of new „small molecule“ active pharmaceutical ingredients (APIs) is discovered by small companies that focus on library synthesis and screening. The actual synthesis development, manufacturing and formulation is done by “custom development and manufacturing organizations” (CDMOs). Patheon, part of Thermo Fisher Scientific is among the biggest CDMOs worldwide.

Synthetic routes used in library synthesis are designed to allow for maximum substrate variability, but not for scalability and efficiency. Our first task as a CDMO is to scout for a synthetic route that can be developed into an efficient and reliable large-scale process: We investigate and compare details of the chemistry, the kinetics and thermodynamics of candidate routes and develop options to scale up the selected reaction sequence.

The lecture focuses on

• Criteria to select routes for scale-up, based on safety, materials efficiency and product quality.
• Ways to develop such routes into reliable processes using state-of-the-art process technology and analytics.

We pay specific attention to the development and application of continuous flow processes and their role in pharmaceutical manufacturing. Several large-scale examples have demonstrated the virtues of continuous processing in this field. Here we give examples to illustrate our way of identifying, developing and implementing continuous flow processes to render processes scalable and safe even if they require extreme process conditions such as low temperatures.

We give details on the chemistry, our considerations on analytics, on suitable reactors, and on options and methods for continuous improvement of such processes, with a focus on the multidisciplinary nature of such development tasks.
TOTAL SYNTHESIS OF AVENAOL VIA ASYMMETRIC O-ALKYULATION USING CHIRAL AMMONIUM SALT

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Strigolactones (SLs) constitute a new class of plant hormones of increasing importance in plant science. Avenaol, isolated from the allelopathic plant black oat, is the first C20 germination stimulant related to SLs, and consists of a bicyclo[4.1.0]heptanone skeleton containing a cyclopropane ring bearing three main chains projecting in the same direction. We have completed the first total synthesis of (±)-avenaol using a robust strategy involving the formation of an all-cis-substituted cyclopropane via an alkylidenecyclopropane [1]. The key factors in the success of the synthesis include the Rh-catalysed intramolecular cyclopropanation of allene (1→2), an Ir-catalysed diastereoselective double-bond isomerization (3→4), and the differentiation of two prochiral hydroxymethyl groups (5→6). Furthermore, we have explored the enantioselective O-alkylation of enols with racemic chloro butenolide 8 using chiral PTC-1. The application of this method to racemic synthetic intermediate 7 successfully provides optically active avenaol via 2’-acetal 9 [2]. This study confirms the proposed structure of avenaol, including its unique all-cis-substituted cyclopropane moiety.


**N-NITROHETEROCYCLES: EASILY ACCESSIBLE, BENCH-STABLE AND BROADLY APPLICABLE NITRATING REAGENTS**

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Nitro compounds are essential constituents of drugs and intermediates in the synthesis of biorelevant molecules, agrochemicals and materials. The most frequently exploited synthetic method for the nitration of various C–H bonds involves the use of a mixture of concentrated nitric and sulphuric acid. The methodology is limited in its application in the synthesis of complex molecules, since such harsh conditions do not tolerate acid-sensitive functionalities, and results in numerous by-products. Herein, we report the design, synthesis and applications of one of the first, bench-stable non-metal based, organic nitrating reagents, which can be prepared from cheap, commercially available chemicals in one-step on a large scale [1]. These reagents act as a controllable source of both the nitronium ion using Lewis acid catalysis and the nitryl radical species using photoredox catalysis. In the first case, broad range of Lewis acids were found to be efficient catalysts to promote an electrophilic nitration through the direct or ipso-substitution reaction of aromatic and heteroaromatic compounds. Due to the reagent’s excellent reactivity and the very mild and neutral conditions of methods, reactions exhibit an unprecedentedly broad substrate scope, and were successfully used for the nitration of various pharmaceuticals and biorelevant molecules. Furthermore, a single-electron reduction enables the formation of NO₂ radicals in a controlled and selective fashion under visible-light photocatalytic conditions, allowing access to nitrated molecules such as nitroolefins, β-nitrohydrines and 3-acylisoxazoles [2].

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Digital information grows exponentially, while societal requirements and individual desires to store it for long times do not subside. Current technology creates an increasingly large burden in power consumption and other efforts required to keep information intact over long periods of time at low cost (e.g., spinning hard disks in idle, refrigerating and copying magnetic tapes every few years). We have developed a fundamentally new concept to store digital information, using mixtures of small molecules. The presence or absence of a readily available, stable, low-molecular-weight organic compound (MolBit) in a mixture indicates a “1” or “0” in a string of binary digits, and a molecular property (e.g., mass) determines the sequence of information. The mixtures are stored as arrayed spots on metallic or polymeric surfaces. Using a library of 32 oligopeptides for a demonstration, we have encoded, written, stored, and read a total of approximately 400 kilobits (with greater than 99% recovery of information, written at 8 bits/s, read at 20 bits/s). We project that MolBits are as stable as, but 10⁶-fold more efficient in cost and writing speed than DNA-based storage and can plausibly be scaled to write terabytes per day.
DESIGNING NEW SYNTHETIC CONCEPTS FOR IMPARTING MOLECULAR COMPLEXITY WITH C-1 SOURCES

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The direct transfer of a reactive nucleophilic CH₂X unit into an existing linkage enables the formal introduction of the moiety with the precisely defined degree of functionalization. Upon the fine tuning of the reaction conditions governing the transformation, the initial homologation event can serve as the manifold for triggering unusual rearrangement sequences leading to complex architectures through a unique synthetic operation. The direct – full chemoselective - conversion of a ketone into the homologated all-carbon quaternary aldehyde (via a)² and, the telescoped homologation of imine-surrogates to quaternary aziridines (via b)³ will illustrate these unprecedented concepts. Additionally, the one-step mono-fluoromethylation of carbon electrophiles with extremely labile fluoromethylolithium reagents will provide a novel entry to valuable fluorinated building-blocks without the needing of using protecting elements for fluoro-containing carbanions (via c).⁴

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GOLD-CATALYZED CROSS-COUPLING-TYPE REACTION OF BROMOALKYNES WITH ALLYLSILANES THROUGH A CONCEALED REARRANGEMENT

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Recent advances in homogeneous gold(I) catalysis show the versatility of vinylidenes intermediates. These species are usually formed starting from a gold(I) acetylide precursors or via alkyne-vinylidene isomerization.[1]

Our group reported the gold(I)-catalyzed [2+2] intermolecular cycloaddition of terminal alkynes with alkenes to form cyclobutenes.[2] In contrast, the gold(I)-catalyzed reaction of bromoalkynes with alkenes leads to a novel way of access to gold(I) vinylidenes. The reaction occurs via transformation of the cyclopropyl gold(I) carbene into an unprecedented cyclic bromonium intermediate and a subsequent bromine migration. Mechanistic studies revealed that linear gold(I) vinylidenes can be involved in hydroarylation reaction, while aryl substituted gold(I) vinylidene are distorted towards a vinylidenephononium-gold(I) cation allowing a concealed 1,2-aryl-migration to form 1,4-enynes in a cross-coupling-type reaction.

\[ \text{Br}^+ \text{AuL} \rightarrow \text{Br}^+ \text{R} \]

NOVEL REACTIONS VIA ELECTROPHILIC ENOLONIUM SPECIES

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Nucleophilic Enolates and enol ethers of carbonyl compounds is mainstay of classical organic synthesis. Recently, we have reported on the umpolung of ketone enolates to discrete electrophilic Enolonium Species using hypervalent iodine. The ability to prepare these enolonium species in a discrete manner has made their reaction with a large number of previously incompatible nucleophiles possible. We will give an overview of the development, scope and mechanistic studies of enolonium species in alkylation, allylation, arylation, N-heteroarylation, azidation as well in coupling with enolates. Furthermore, we will report on the first Umpolung Morita-Baylis-Hillman reaction (unpublished results). The resulting α-products should find great utility in the synthesis of functional molecules.

\[
\begin{align*}
\text{Enolonium Species} & \text{ Zn(Alk)₂} \\
\text{OTMS} & \text{Ph} \\
\text{R¹} & \text{R²} \\
\text{O} & \text{R³} \\
\text{Alk} & \\
\end{align*}
\]

*Angew. Chem. Int. Ed.* 2017, 56, 2599

*Org. Lett.* 2017, 19, 6312


*Org. Lett.* 2015, 17, 282

*Org. Biomol. Chem.* 2015, 13, 2546

*Beilstein J. Org. Chem.* 2018, 14, 992
SYNERGISTIC CATALYSIS IN DONOR-ACCEPTOR CYCLOPROPANE CHEMISTRY

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Donor-acceptor cyclopropanes (DACs) are highly strained entities which are unique building blocks for hetero- and carbocyclic systems [1,2]. For the last decade, we have been developing novel methodologies starting from these type of three-membered rings leading to oligopyrroles, chalcogen-containing heterocycles, and 1,3-bisfunctionalized products [3], just to name a few. To get deeper insights into their intrinsic reactivity in-depth physical organic studies were performed recently [4].

In this contribution, we will present our newest contributions using cyclopropanes in synergistic catalytic reactions. Commonly, DACs require the activation by Lewis acids. However, the other component to react with might be generated as a fleeting intermediate in situ by a second catalytic system. Two examples, one using Lewis acid and Rh catalysis (affording intermediate carbonyl ylides) [5] and another using Lewis acid and redox catalysis are presented [6]. In the former example highly substituted pyranes are generated, in the latter unusual fulvene-type dyes.

\[ \text{DAC} \xrightarrow{\text{Lewis Acid & Rhodium(II) Catalysis}} \text{Pyranes} \]

\[ \text{DAC} \xrightarrow{\text{Lewis Acid & Redox Catalysis}} \text{Fulvene-Type Dyes} \]

Control of molecular properties is essential in the design of new bioactive compounds, due to the inherent link between molecular properties of lead compounds and their successful progression through the stages of clinical development. Through the optimization process compounds tend to gain in molecular weight, lipophilicity and complexity, therefore a set of guidelines have been established to aid the design of lead-like molecules. In order to realise efficient lead-oriented synthesis a “top-down” approach has been employed whereby complexity is encoded to give a key polycyclic intermediate. It is vital that this intermediate contains functionality that can facilitate annulations, ring contractions and ring cleavage reactions. The use of this approach will be demonstrated using [5+2] cycloaddition chemistry as the complexity generating reaction in the synthesis of a library of highly 3-dimensional compounds, which have the correct properties to target lead-like chemical space. A toolkit of reactions has been applied to the parent compound creating a diverse range of lead-like scaffolds. Each scaffold contains a number of functional handles which can be decorated to create a large number of lead-like screening compounds.
EXPANDING THE BILE ACID CHEMICAL SPACE: SYNTHETIC STRATEGIES FOR LEAD DISCOVERY AND DEVELOPMENT

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Bile acid-responsive receptors are widely recognized as relevant targets for drug discovery. The key members of this family, namely FXR and TGR5, are exploited for the treatment of several liver and metabolic diseases including non-alcoholic steatohepatitis (NASH) and diabesity.[1] Following the success of obeticholic acid (Ocaliva™),[2] in the last years our efforts have been devoted to exploring the structure–activity relationships of bile acids as FXR/TGR5 ligands, to identifying functional hot spots responsible for selectivity and efficacy, and to disclosing powerful chemical probes for phenotypic studies in biochemical, cell-based and animal models. The development of these compounds has also revealed how apparently minor chemical modifications of the steroidal cholanoic scaffold greatly influence the physicochemical, pharmacokinetic, and biodistribution profile of the resulting molecules thereby determining their fate in clinical settings of metabolic disorders.[3]

Unquestionably, an important challenge for the discovery and development of new bile acids with improved properties is to solve synthesis designs that enable to expand the bile acid chemical space and simultaneously ensure the synthetic accessibility of unexplored ‘hidden’ positions of the biliary scaffold. In this communication, case studies related with the synthesis and optimization of novel, nature-inspired bile acid lead candidates are reported and discussed.

The rise of antibiotic-resistant micro-organisms is a major threat for healthcare providers across the world and new classes of antibiotic are desperately required. One emerging target for the development of such antibiotics is the essential metabolic enzyme, biotin protein ligase (BPL). BPL catalyses protein biotinylation through the formation of the adenylated reaction intermediate, biotinyl-5’AMP, from its substrates biotin and ATP. Here we report the rational design, synthesis and evaluation of chemical analogues of biotinyl-5’AMP that function as inhibitors of the BPLs from pathogenic bacteria such as *Escherichia coli*, *Staphylococcus aureus* and *Mycobacterium tuberculosis*.

Detailed studies are presented on *in situ* synthesis optimization of inhibitors using the target enzyme as a template; the importance of halogenation in optimising antimicrobial activity; protein crystallography, computation and simulation to optimize inhibitor design, synthesis, and biological profile; and the synthesis and development of fluorescent probes for super-imaging fluorescence microscopy. The fluorescent probes provide new insights into the mechanism of uptake, efflux and metabolism of BPL inhibitors in *S. aureus*. Studies on developing a photoswitchable antibiotic to minimise toxicity and resistance will also be presented.
DYNAMIC CARBON ISOTOPE EXCHANGE OF PHARMACEUTICALS WITH LABELED CO₂

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Carbon-14 radiolabeling is a unique tool that, in association with β-counting and β-imaging technologies, provides vital knowledge on the fate of synthetic organic molecules such as pharmaceuticals and agrochemicals [1]. Traditional multistep synthesis and the associated costs have limited its utilization. Hydrogen isotope exchange reactions are routinely utilized for deuterium and tritium labeling; however, in the field of carbon isotope labeling, this concept has remained unexplored until recently [2]. We report a dynamic carbon isotope exchange with ¹⁴CO₂, the most fundamental and readily available source of radiocarbon [3]. This new process expands the concept of late-stage carbon radiolabeling with substrates bearing Csp² carboxylic acids and provides a direct access to end-use labeled pharmaceuticals.

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LOW-VALENT Bi\textsuperscript{I} ⇄ Bi\textsuperscript{II} REDOX CATALYSIS

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A catalytic transfer-hydrogenation utilizing a well-defined Bi(I) complex as catalyst and ammonia-borane as transfer agent has been developed. This transformation represents a unique example of low-valent pnictogen catalysis cycling between oxidation states I and III, and proved useful for the hydrogenation of azoarenes and the partial reduction of nitroarenes. Interestingly, the bismuthinidene catalyst performs well in presence of low-valent transition-metal sensitive functional groups and presents orthogonal reactivity compared to analogous phosphorous-based catalysis. Mechanistic investigations suggest the intermediacy of an elusive bismuthine species, which is proposed to be responsible for the hydrogenation and the formation of hydrogen
HYBRID DISCOVERY WORKFLOW FOR ORGANIC MATERIALS AND SUPRAMOLECULAR SELF-ASSEMBLIES

Rebecca L. Greenaway\textsuperscript{a}, Valentina Santolini\textsuperscript{b}, Enrico Berardo\textsuperscript{b}, Michael J. Bennison\textsuperscript{a}, Ben Alston\textsuperscript{a}, Chloe Pugh\textsuperscript{a}, Marc A. Little\textsuperscript{a}, Rachel Kearsey\textsuperscript{a}, Marcin Miklitz\textsuperscript{b}, Michael E. Briggs\textsuperscript{a}, Kim E. Jelfs\textsuperscript{b}, and Andrew I. Cooper\textsuperscript{a}

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Supramolecular synthesis is a powerful tool for assembling complex organic molecules, such as macrocycles, cages, and catenanes. However, targeted design of such molecules can be challenging, especially as the systems become more elaborate. High-throughput automation can be used to screen a broad synthetic space, but when applied blindly, this approach is inefficient. We have developed a hybrid discovery workflow that fuses computational screening with robotic synthesis for discovering new organic cages – a class of self-assembled molecule that contain permanent intrinsic cavities accessible through windows, and by extension, other supramolecular assemblies [1]. By fusing our computational toolkit to predict the most likely topology and shape-persistence based on the precursors used, with a robust synthetic route which made translation onto an automated synthesis platform possible, the hybrid workflow led to the synthesis of 49 new cages, rapidly accelerating the discovery process. Furthermore, it led to the serendipitous discovery of a unique cage topology – covalently bridged cage catenanes, and has been applied in the discovery of a number of other organic materials and supramolecular assemblies, such as completely unsymmetrical cages [2], socially self-sorted pots and dumbbells, and porous liquids.

Absence or malfunction of membrane proteins forming anion channels is the cause of several channelopathies, such as cystic fibrosis. Synthetic anion carriers have the potential to take over part of the function of these proteins [1]. Such carriers extract the anion from the aqueous phase, move it across the apolar interior of the lipid bilayer while shielding its charge, to then release it on the other side of the membrane.

Macrocyclic receptors are preorganised in a particular way, often leading to remarkable selectivities in binding and hence unique behaviour in anion transport. A first example are bambus[6]uril macrocycles, which are highly efficient in exchanging Cl\(^-\) and HCO\(_3^-\) [2], while related biotin[6]urils do not show any transport of HCO\(_3^-\) [3]. This can be rationalised based on the different affinities and binding modes that these macrocycles have for the different anions [2,3]. Another example are calix[6]arene tris(thio)ureas, of which the cavity can be exploited to transport organic ion pairs [4].

Figure 1. Liposomes with the dye lucigenin encapsulated (a) were used to study anion exchange by bambus[6]urils (b), biotin[6]urils (not shown), and calix[6]arenes (c).

Lignan natural products are a large class of polyphenols produced by plants that exhibit important antiviral, anti-cancer and antimicrobial bioactivities.

Chiral phosphoric acids like 3,3′-Bis(2,4,6-trisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate (TRIP) can provide catalytic stereoinduction on the allylation of benzaldehydes. This methodology was applied for the synthesis of (-)-hydroxymatairesinol [1]. We have extended the short total synthetic procedure to other four lignans, namely (+)-yatein, (-)-α-conidendrin, (+)-iso- and (+)-neoisostegane with high overall yields and enantiomeric purity via only four steps.

In addition, a chemoenzymatic approach has been used to target podophyllotoxin. The asymmetric information has been given by a 2-oxoglutarate dependent dioxygenase from *Podophyllum hexandrum* that performs a biocatalytic kinetic resolution of the rac-4-hydroxyyatein substrate thus achieving the aryltetralin scaffold. Enantiopure deoxy-, isodeoxy-, epi- and podophyllotoxin have been obtained. With the same approach new potential APIs, namely dihydroxy-dibenzylbutyrolactones have been produced.

1,2-DIOXANES AS POTENTIAL ANTI-LEISHMANIAL DRUGS

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Leishmaniasis is one of the most important neglected tropical diseases, endemic in around 100 countries, with more than 350 million people living at risk of infection and over 20000 deaths estimated annually. Leishmaniasis, caused by protozoa of the genus \textit{Leishmania}, can manifest as tegumentary or visceral leishmaniasis, the latter being fatal if untreated. The currently available drugs are not only expensive and toxic, but are beginning to lose efficacy due to the increasing of parasitic resistance. Thus, the design of novel, efficient and safer drugs is of uttermost importance. The natural peroxide artemisinin (1) and its derivatives have shown good efficacy against parasites such as \textit{Plasmodium}, and are widely used for the malaria treatment. Some synthetic peroxides, \textit{i.e.} tetraoxanes (2) or trioxolanes (3), are now considered valid anti-malarials. Much less is known about the anti-leishmanial properties of peroxides. We recently proposed a novel family of synthetic simple 1,2-dioxanes (4) as potential anti-malarials [1]. Here we report our studies on the synthesis and the anti-leishmanial bioactivity of a selected group of 1,2-dioxanes [2]. 13 compounds showed a good \textit{in vitro} inhibitory activity on \textit{L. donovani} promastigotes (IC\textsubscript{50} range = 1.6 - 16.4 μM). Moreover, the 6 compounds exhibiting the best selectivity index proved to be active also against \textit{L. tropica}, \textit{L. major} and \textit{L. infantum} promastigotes and against \textit{L. donovani} amastigotes, highlighting their potential as hits for lead optimization.

\[ \text{Promastigotes:} \]
- \( C_{50} (\text{L. donovani}) = 4.4 \text{ μM} \)
- \( S = 35.0 \)
- \( C_{50} (\text{L. major}) = 3.2 \text{ μM} \)
- \( C_{50} (\text{L. tropica}) = 2.0 \text{ μM} \)
- \( C_{50} (\text{L. infantum}) = 2.6 \text{ μM} \)

\[ \text{Amastigotes:} \]
- \( IC_{50} (\text{L. donovani}) = 10.5 \text{ μM} \)


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<td>Žolnowska, B.</td>
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XELSIUS
Highspeed Solubility & Synthesis Reactor

-20°C | +150°C

Introduction

inspired by the possibilities of lab automation!

XELSIUS solubility & synthesis reactor, is capable of taking charge of precise and individual temperature controlling, stirring and turbidity measurements. The right fit in a wide range of applications in fully automated chemical processing.

A high grade of modularity makes this product accessible for small research facilities, as well as large scale industry-level development labs. XELSIUS offers up to 10 individual reactor cells, but can easily be customized. Controlled by an easy-to-use software interface.

XELSIUS can be easily combined with our SAMPLIFY product family.

Key Features

- Up to 10 reaction cells per unit
- Independent control of each individual reactor cell
- from -20°C to +150°C
- Individual stirring
- Turbidity measurement
- Individual and easy-to-use programming

Application

- Temperature studies
- Chemical processing
- Crystallization analysis
- Solubility profiles
- Process Optimization
- DoE reactor
- Screening studies

A smart combination

- Combinable with a flexible and easy to use robotic system:
- Time scheduled sample taking
- Flexible dosage of reagents
- Customized app programming
- Integrated sample preparation
- Direct data-export to Excel ®

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### Advantages

- Rich variety of cycloparaphenylenes (CPP) (From the possible smallest [5]CPP up to [12]CPP)
- Diverse light absorption and emission depending on the ring size
- Unit structure of carbon nanotube (CNT)
- Ring-shaped carbon materials with unique and unexplored properties

### Related product

- (6,6)Carbon Nanobelt Bis(tetrahydrofuran) Adduct ([12]CNB-2THF) 10mg [I1078]
Carbon Nanoring Material Cycloparaphenylene (CPP)

Properties and applications of CPP

Relation between no. of phenylene (n) and HOMO, LUMO in [n]CPP

![Graph showing the relation between no. of phenylene (n) and HOMO, LUMO in [n]CPP]

HOMO-LUMO gap decreases with decreasing ring size.

CPP-iodine complex

Encapsulation of fullerene by CPP

Electrically activated conductivity and white light emission

Functionalization of CPP

CPP growth to CNT

One phenylene ring can be readily functionalized.

Bottom up synthesis of CNT with uniform diameter

References


For further information please refer to our website at www.TCIchemicals.com.

Or access to https://www.tcichemicals.com/eshop/en/de/category_index/12955/