



ESOC 2019

21st European Symposium on Organic Chemistry

Vienna / Austria

July 14-18, 2019



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**ESOC
2019**



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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CONTENTS:

Welcome from the Conference Chairs	<i>p 5</i>
Plenary & Invited speakers	<i>p 7</i>
General information	<i>p 15</i>
Social program	<i>p 19</i>
Area maps	<i>p 29</i>
Time schedule	<i>p 33</i>
Session overview	
Sunday, 14 th	<i>p 37</i>
Monday, 15 th	<i>p 37</i>
Tuesday, 16 th	<i>p 41</i>
Wednesday, 17 th	<i>p 45</i>
Thursday, 18 th	<i>p 47</i>
Abstracts	
Plenary lectures (PL-1 to PL-11)	<i>p 53</i>
Invited lectures (IL -1 to IL-14)	<i>p 67</i>
Oral presentations (OP-1 to OP-28)	<i>p 93</i>
Poster index	
Catalysis	
PO-1 to PO-172	<i>p 113</i>
Medicinal Chemistry and Chemical Biology	
PO-173 to PO-253	<i>p 126</i>
Organic Materials	
PO-254 to PO-298	<i>p 133</i>
Physical and Computational Organic Chemistry	
PO-299 to PO-322	<i>p 137</i>
Supramolecular Chemistry	
PO-323 to PO-333	<i>p 139</i>
Total Synthesis and Methodology	
PO-334 to PO-556	<i>p 140</i>
Late Poster	
PO-557 to PO-561	<i>p 156</i>
Author index	<i>p 159</i>

WELCOME FROM THE CHAIRS OF THE XXIst ESOC 2019

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!

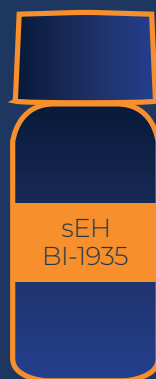
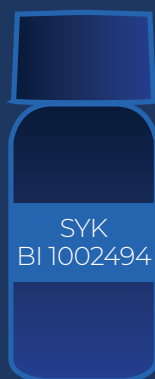
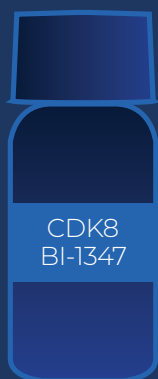


Sincerely,
Michael Schnürch and Nuno Maulide
(Conference Chairs)

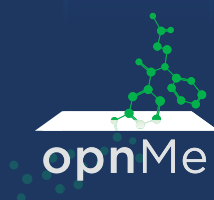


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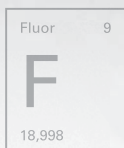
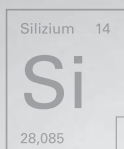
INVITED SPEAKERS

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 Català d'Investigació Química, 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 **MAGAUER** *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 Wrocław, Poland*
Martin **OESTREICH** *Technische Universität Berlin, Germany*
Alexandros **ZOGRAFOS** *Aristotle University of Thessaloniki, Greece*



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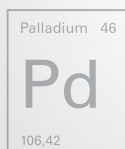
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COMMITTEES

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

ESOC 20	Cologne, Germany	July 2-6, 2017
ESOC 19	Lisbon, Portugal	July 12-16, 2015
ESOC 18	Marseille, France	July, 07-12, 2013
ESOC 17	Crete Greece	July, 10-15, 2011
ESOC 16	Prague, Czech Republic	July 12 – 16, 2009
ESOC 15	Dublin, Ireland	July 8 – 13, 2007
ESOC 14	Helsinki, Finland	July 4 – 8, 2005
ESOC 13	Dubrovnik, Croatia	September 10-15, 2003
ESOC 12	Groningen, Netherland	July 13 – 18, 2001
ESOC 11	Goteborg, Sweden	July 23-28, 1999
ESOC 10	Basel, Switzerland	June 22-27, 1997
ESOC 9	Warszawa, Poland	June 18-23, 1995
ESOC 8	Barcelona, Spain	August 29 - September 3, 1993
ESOC 7	Namur, Belgium	July 15-19, 1991
ESOC 6	Beograd, Yugoslavia	September 10-15, 1989
ESOC 5	Jerusalem, Israel	August 30 - September 3, 1987
ESOC 4	Aix-en-Provence, France	September 2-6, 1985
ESOC 3	Canterbury, England	September 5-9, 1983
ESOC 2	Stresa, Italy	June 1-5, 1981
ESOC 1	Cologne, Germany	August 20-23, 1979



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Grünenthal GmbH
Idorsia Pharmaceuticals Ltd
Novartis AG
Patai online
TU Wien alumni club

Chemical Science
European Journal of Organic Chemistry
Organic Chemistry Frontiers
Molecules – Open Access Journal
Synthetic Reaction Updates
Organic & Biomolecular Chemistry
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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).

News Flash

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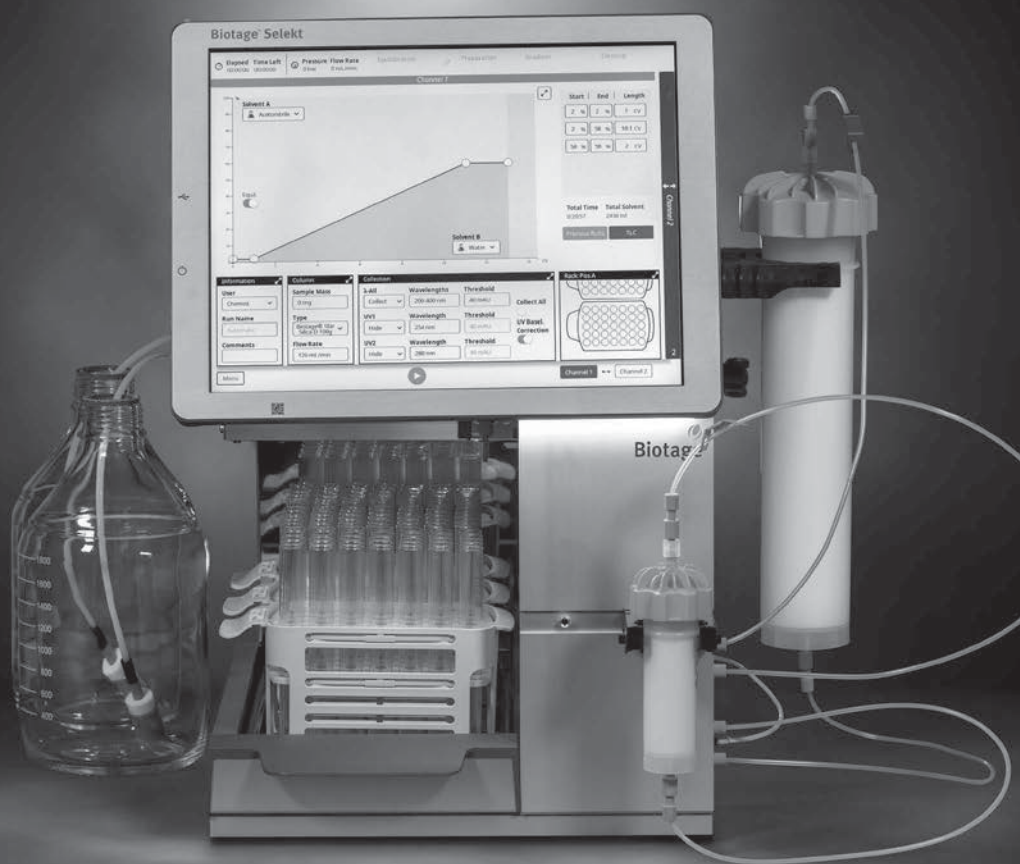
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GENERAL INFORMATION

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

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

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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 15th: 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 16th: 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 dismantled 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 18th, 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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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 Fuhrgassl-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.



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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:

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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 site. 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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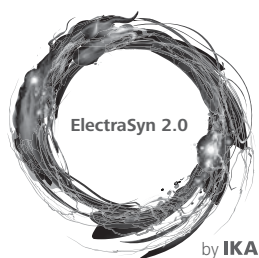
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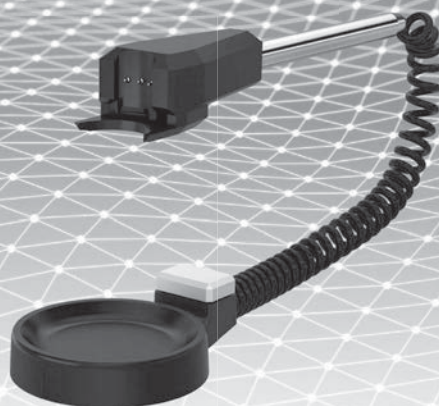
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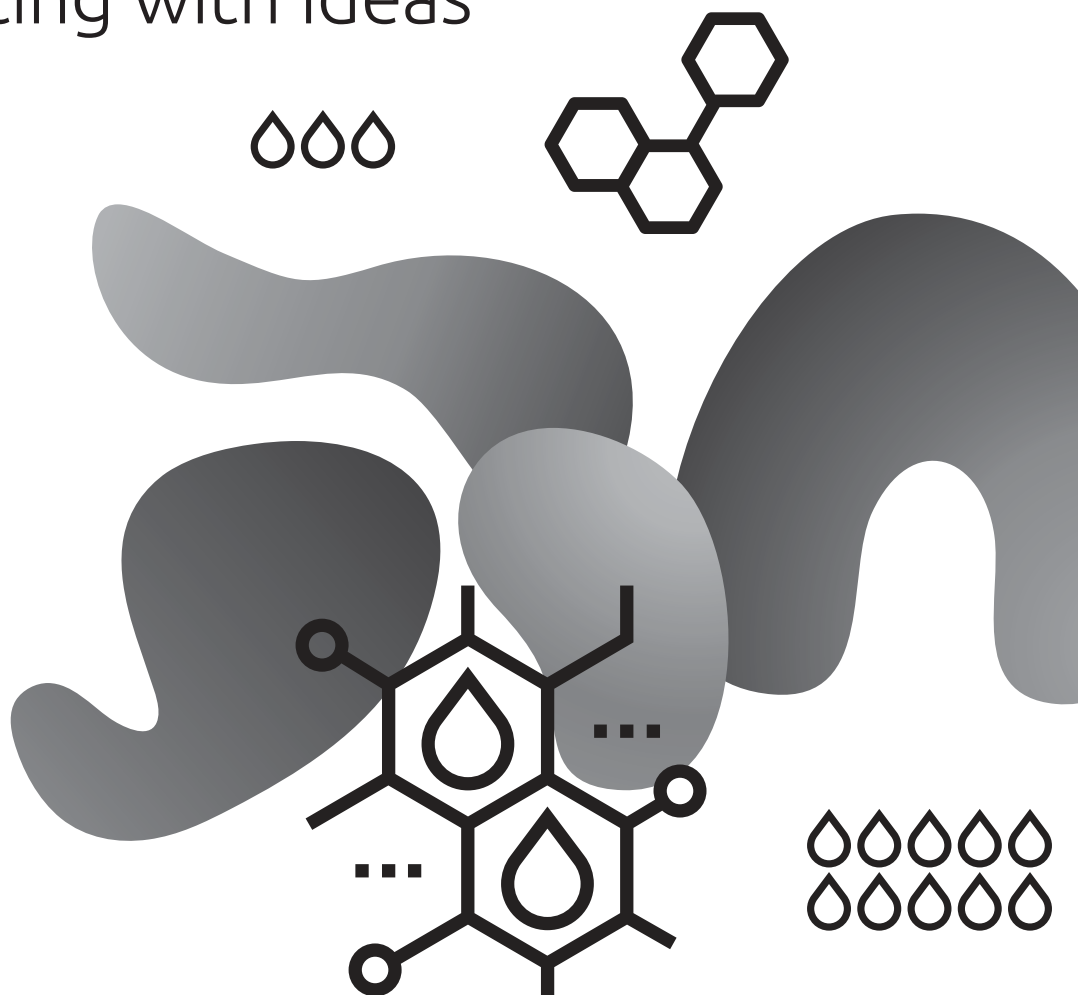
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CAMPUS AREA MAP – MESSE/PRATER WIEN

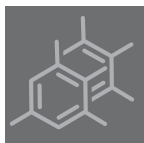


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- A Congress Venue (Messeplatz 1)
Lecture Hall
- B Departure for Conference Dinner on Thursday
- C "Prater Alm" – Lunch on Wednesday
- D Wiener Riesenrad – Giant Ferris Wheel
- E "Praterstern"
Railway and Underground Station
- F Hotel Courtyard Marriott
- 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



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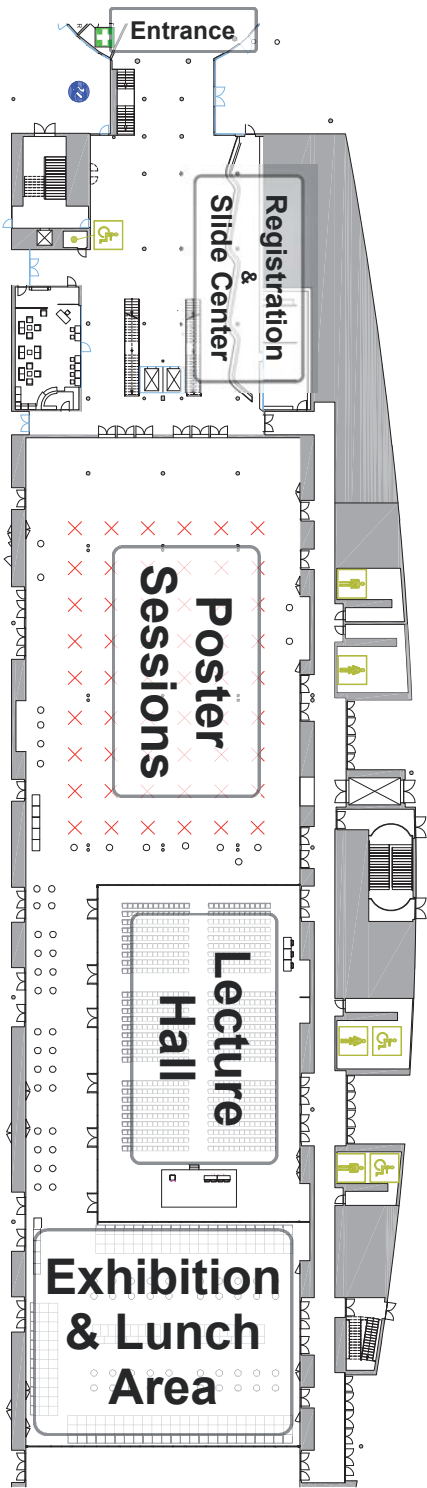
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TIME SCHEDULE

Sunday July 14		Monday July 15	Tuesday July 16	Wednesday July 17	Thursday July 18	
		Opening				
09:00		PL-3 K. Itami	PL-6 L. Gooßen	PL-9 V. Gouverneur	PL-10 R. Süßmuth	09:00
10:00		IL-1 M. Stepien	IL-5 J. Roithova	IL-9 A. Hirsch	IL-11 R. Amir	10:00
		Coffee Break	Coffee Break	Coffee Break	Coffee Break	
11:00		IL-2 Th. Magauer	IL-6 M.D. Smith	IL-10 M. Oestreich	IL-12 T. Besset	11:00
		OC-1 E. Welin	OC-7 T. Akiyama	OC-13 Y. Takemoto	OC-18 A. Szpilman	
		OC-2 S. Coote	OC-8 Chr.J. Whiteoak	OC-14 D. Katayev	OC-19 D.B. Werz	
		OC-3 R. Pollice	OC-9 J. Deska	OC-15 M.J. Fink	OC-20 C. Townley	
12:00		OC-4 A. Gollner	OC-10 D. Kananovich	OC-16 V. Pace	OC-21 A. Gioiello	12:00
		OC-5 D. Kolarski	OC-11 O. García Mancheño	OC-17 M. Zanini	OC-22 A. Abell	
13:00		Lunch	Lunch	Lunch @Prateralm	Lunch	13:00
14:00		IL-3 J. Campos	IL-7 S. Sattin		IL-13 T.R. Skrydstrup	14:00
		PL-4 S. Harutyunyan	PL-7 Ph. Baran		OC-23 D. Audisio	
					OC-24 J. Cornella	
15:00	Registration	Coffee Break	Coffee Break		OC-25 R. Greenaway	15:00
		OC-6 L. Capdevila	OC-12 P. Poechlauer		Coffee Break	
					OC-26 H. Valkenier	
16:00		PL-5 Th. Bach	PL-8 J. Sutherland	Excursion & Job Fair	OC-27 M. Lazzarotto	16:00
					OC-28 A. Quintavalla	
		IL-4 D. Chusov	IL-8 S. Reisman (M. Faul Awardee)		IL-14 A. Zografos	
17:00	Opening				PL-11 P. Melchiorre	17:00
	PL-1 Sir J.F. Stoddart				ESOC2021 OC/Poster Prizes Final Remarks	
18:00	PL-2 A. Fürstner (Patai Lecture)	Poster Session odd numbers	Poster Session even numbers			18:00
19:00						19:00
	Welcome Reception				Conference Dinner „Heuriger“	
20:00		Speakers Dinner				20:00
21:00						21:00



Michael Stanek, Ph.D.
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Sunday, July 14

17:00 Opening Ceremony

Chair: Nuno Maulide

17:15	Sir J.F. Stoddart <i>Northwestern University, Illinois, United States</i>	PL-1 <i>sponsored by FCIO</i>
RADICAL CHEMISTRY IN THE DESIGN AND SYNTHESIS OF ARTIFICIAL MOLECULAR MACHINES		

Chair: Ilan Marek

Patai-Rappoport Lecture

18:00	Alois Fürstner <i>Max-Planck-Institut für Kohleforschung, Mülheim/Ruhr, Germany</i>	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 <i>Nagoya University, Nagoya, Japan</i>	PL-3 <i>sponsored by TCI</i>
MAKING NEW FORMS OF NANOCARBONS		

09:45	Marcin Stępień <i>University of Wrocław, Wrocław, Poland</i>	IL-1
DONOR-ACCEPTOR OLIGOPYRROLES		

10:15 Coffee Break *sponsored by TCI*

Chair: Wolfgang Kroutil

10:45	Thomas Magauer <i>University of Innsbruck, Innsbruck, Austria</i>	IL-2
TOTAL SYNTHESIS OF POLYCYCLIC NATURAL PRODUCTS		

11:15	Eric Welin <i>California Institute of Technology, Pasadena, USA</i>	OC-1
CONCISE TOTAL SYNTHESIS OF (–)-JORUNNAMYCIN A AND (–)-JORUMYCIN ENABLED BY ASYMMETRIC CATALYSIS		

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Monday, July 15		
11:30	Susannah Coote <i>Lancaster University, Bailrigg, UK</i>	OC-2
	4- π -PHOTOCYCLISATION OF DIHYDROPYRIDAZINES: ACCESS TO VERSATILE BICYCLIC DIAZETIDINES	
11:45	Robert Pollice <i>ETH Zürich, Zürich, Switzerland</i>	OC-3
	REACTION PROGRESS KINETIC ANALYSIS BY DIRECT ANALYSIS OF CONCENTRATION-TIME PROFILES	
12:00	Andreas Gollner <i>Boehringer Ingelheim RCV GmbH and Co KG, Vienna, Austria</i>	OC-4
	SEQUENTIAL MULTI-BOND FORMING REACTIONS APPLIED TO THE SYNTHESIS OF CONFORMATIONALLY RESTRICTED MDM2-p53 INHIBITORS SUITABLE FOR INTERMITTENT DOSING	
12:15	Dušan Kolarski <i>University of Groningen, Groningen, The Netherlands</i>	OC-5
	CONTROLLING THE CIRCADIAN CLOCK WITH HIGH TEMPORAL RESOLUTION THROUGH PHOTODOSIMETRY	
12:30	Lunch	
	Chair: Thorsten Bach	
14:00	Jesús Campos <i>Universidad de Sevilla, Sevilla, Spain</i>	IL-3
	INTERACTION VS. FRUSTRATION IN BIMETALLIC COOPERATIVE SYSTEMS	
14:30	Syuzanna R. Harutyunyan <i>University of Groningen, Groningen, The Netherlands</i>	PL-4
	LEWIS ACID ENABLED NOVEL REACTIVITIES IN ASYMMETRIC COPPER CATALYSIS	
15:15	Coffee Break	
	Chair: Syuzanna Harutyunyan	
15:45	Lorena Capdevila <i>Universitat de Girona, Girona, Spain</i>	OC-6
	CHEMO-DIVERGENT NICKEL(0)-CATALYZED ARENE C-F ACTIVATION WITH ALKYNES: UNPRECEDENTED DOUBLE-INSERTION	
16:00	Thorsten Bach <i>Technical University Munich, Garching, Germany</i>	PL-5
	ENANTIOSELECTIVE CATALYSIS OF PHOTOCHEMICAL REACTIONS	
16:45	Denis Chusov <i>Russian Academy of Sciences, Moscow, Russia</i>	IL-4
	STRATEGY FOR SELECTIVE REDUCTIVE ADDITION	
17:15	Poster Session 1 odd numbers	

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Tuesday, July 16
COST – Sessions Day

Chair: Michael Schnürch

09:00	Lukas Gooßen <i>Ruhr-Universität Bochum, Bochum, Germany</i>	PL-6
	CARBOXYLATES AS DIRECTING AND LEAVING GROUPS IN CATALYTIC BOND FORMATION	
09:45	Jana Roithova <i>Radboud University, Nijmegen, The Netherlands</i>	IL-5
	TRAPPING OF REACTIVE INTERMEDIATES	
10:15	Coffee Break <i>sponsored by TCI</i>	

Chair: John Sutherland

10:45	Martin D. Smith <i>University of Oxford, Oxford, UK</i>	IL-6
	COUNTER-ION MEDIATED APPROACHES TO CONTROLLING AXIAL CHIRALITY	
11:15	Takahiko Akiyama <i>Gakushuin University, Tokyo, Japan</i>	OC-7
	ENANTIOSELECTIVE FRIEDEL-CRAFTS ALKYLATION RECTION OF TRIFLUOROMETHYLATED N-H KETIMINE WITH HETEROARENES BY MEANS OF CHIRAL PHOSPHORIC ACID	
11:30	Christopher J. Whiteoak <i>Sheffield Hallam University, Sheffield, UK</i>	OC-8
	ACCESS TO UNUSUAL HETEROCYCLIC COMPOUNDS UTILIZING A KEY COBALT-CATALYZED C-H FUNCTIONALIZATION APPROACH	
11:45	Jan Deska <i>Aalto University, Espoo, Finland</i>	OC-9
	THE HUNT FOR ARTIFICIAL REACTIVITIES IN BIOCATALYSIS: FUNGAL COPPER-DEPENDENT METALLOPROTEINS AS MEDIATORS FOR PERICYCLIC REACTIONS	
12:00	Dzmitry Kananovich <i>Tallinn University of Technology, Tallinn, Estonia</i>	OC-10
	QUEST FOR ASYMMETRIC KULINKOVICH REACTION: FROM MECHANISM TOWARDS ENHANCED ENANTIOSELECTIVITY	
12:15	Olga García Mancheño <i>University of Münster, Münster, Germany</i>	OC-11
	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** **IL-7**
Università degli Studi di Milano, Milan, Italy

TARGETING BACTERIAL PERSISTERS IN THE POST-ANTIBIOTIC ERA

14:30 Phil S. **Baran** **PL-7**
Scripps Research, La Jolla, USA

TRANSLATIONAL CHEMISTRY

15:15 Coffee Break

Chair: Rolf Breinbauer and Florian Rudroff

15:45 Peter **Poechlauer** **OC-12**
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** **PL-8**
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** **IL-8**
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 <i>University of Oxford, Oxford, UK</i>	PL-9
FLUORINE CHEMISTRY FOR APPLICATIONS IN MEDICINE		
09:45	Anna K.H. Hirsch <i>Saarland University, Saarbrücken, Germany</i>	IL-9
DISCOVERY OF THE FIRST ANTIBACTERIAL AGENT INHIBITING THE ENERGY-COUPPLING FACTOR (ECF) TRANSPORTERS BY STRUCTURE-BASED VIRTUAL SCREENING		
10:15	Coffee Break <i>sponsored by Boehringer Ingelheim</i>	

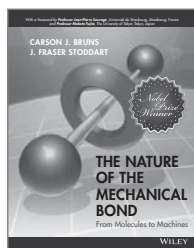
Chair: Veronique Gouverneur

10:45	Martin Oestreich <i>Technische Universität Berlin, Berlin, Germany</i>	IL-10
TRANSFER OF REACTIVE GASES FROM ONE MOLECULE TO ANOTHER		
11:15	Yoshiji Takemoto <i>Kyoto University, Kyoto, Japan</i>	OC-13
TOTAL SYNTHESIS OF AVENAOL VIA ASYMMETRIC O-ALKYLATION USING CHIRAL AMMONIUM SALT		
11:30	Dmitry Katayev <i>Swiss Federal Institute of Technology, Zürich, Switzerland</i>	OC-14
N-NITROHETEROCYCLES: EASILY ACCESSIBLE, BENCH-STABLE AND BROADLY APPLICABLE NITRATING REAGENTS		
11:45	Michael J. Fink <i>Harvard University, Cambridge, USA</i>	OC-15
STORAGE OF INFORMATION USING SMALL ORGANIC MOLECULES		
12:00	Vittorio Pace <i>University of Vienna, Vienna, Austria</i>	OC-16
DESIGNING NEW SYNTHETIC CONCEPTS FOR IMPARTING MOLECULAR COMPLEXITY WITH C-1 SOURCES		
12:15	Margherita Zanini <i>Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain</i>	OC-17
GOLD-CATALYZED CROSS-COUPPLING-TYPE REACTION OF BROMOALKYNES WITH ALLYLSILANES THROUGH A CONCEALED REARRANGEMENT		
12:30	Lunch @Prater Alm	
14:00	Excursion and Job Fair	

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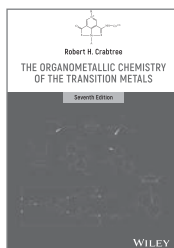


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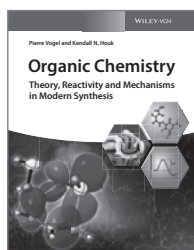


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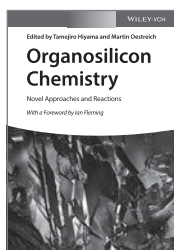


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Thursday, July 18

Chair: Mario Waser

09:00	Roderich D. Süssmuth <i>Technical University of Berlin, Berlin, Germany</i> PEPTIDE DRUGS FROM NATURE – STRUCTURAL AND (BIO)SYNTHETIC ASPECTS OF NEW ANTIBIOTICS	PL-10
09:45	Roey Amir <i>Tel-Aviv University, Tel-Aviv, Israel</i> THE FINE BALANCE BETWEEN STABILITY AND ENZYMATIC DEGRADABILITY OF POLYMERIC CARRIERS - THE IMPORTANCE OF MOLECULAR PRECISION	IL-11
10:15	Coffee Break <i>sponsored by TU Wien</i>	

Chair: Christian Stanetty

10:45	Tatiana Besset <i>Normandie Université, Rouen, France</i> RECENT ADVANCES TO ACCESS FLUORINATED SCAFFOLDS	IL-12
11:15	Alex Szpilman <i>Ariel University, Ariel, Israel</i> NOVEL REACTIONS VIA ELECTROPHILIC ENOLONIUM SPECIES	OC-18
11:30	Daniel B. Werz <i>TU Braunschweig, Braunschweig, Germany</i> SYNERGISTIC CATALYSIS IN DONOR-ACCEPTOR CYCLOPROPANE CHEMISTRY	OC-19
11:45	Chloe Townley <i>University of Leeds, Leeds, United Kingdom</i> A TOP-DOWN APPROACH TO DIVERSE LEAD-LIKE SCAFFOLDS	OC-20
12:00	Antimo Gioiello <i>Università di Perugia, Perugia, Italy</i> EXPANDING THE BILE ACID CHEMICAL SPACE: SYNTHETIC STRATEGIES FOR LEAD DISCOVERY AND DEVELOPMENT	OC-21
12:15	Andrew Abell <i>University of Adelaide, Adelaide, Australia</i> THE SYNTHESIS AND OPTIMISATION OF NEW ANTIBIOTICS	OC-22
12:30	Lunch	

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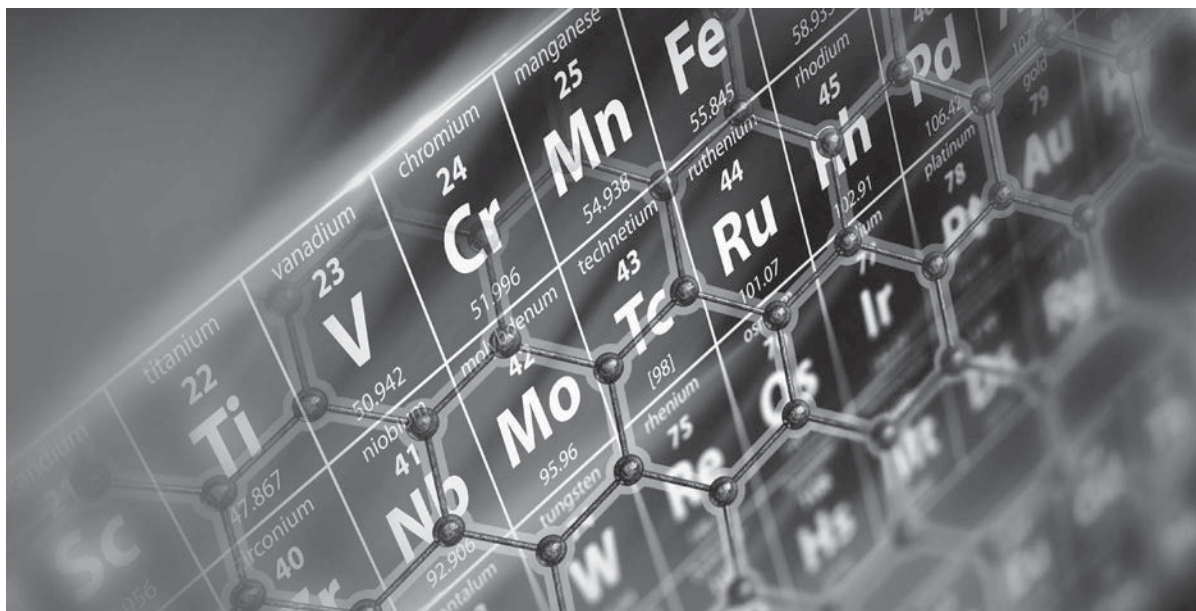
Thursday, July 18

Chair: Roderich Süßmuth

14:00	Troels Skrydstrup <i>Aarhus University, Aarhus, Denmark</i>	IL-13
RECENT DEVELOPMENTS IN LOW PRESSURE CARBONYLATIONS		
14:30	Davide Audisio <i>Université Paris-Saclay, Gif-sur-Yvette, France</i>	OC-23
DYNAMIC CARBON ISOTOPE EXCHANGE OF PHARMACEUTICALS WITH LABELED CO₂		
14:45	Josep Cornella <i>Max-Planck-Institut für Kohleforschung, Mülheim/Ruhr, Germany</i>	OC-24
LOW-VALENT Bi(I)⇌Bi(III) REDOX CATALYSIS		
15:00	Rebecca Greenaway <i>University of Liverpool, Liverpool, United Kingdom</i>	OC-25
HYBRID DISCOVERY WORKFLOW FOR ORGANIC MATERIALS AND SUPRAMOLECULAR SELF-ASSEMBLIES		
15:15	Coffee Break <i>sponsored by University of Vienna</i>	

Chair: Ivo Stary

15:45	Hennie Valkenier <i>Université libre de Bruxelles, Bruxelles, Belgium</i>	OC-26
MACROCYCLIC ANION CARRIERS		
16:00	Mattia Lazzarotto <i>University of Graz, Graz, Austria</i>	OC-27
ORGANO- AND BIOCATALYSIS FOR LIGNAN NATURAL PRODUCT SYNTHESIS		
16:15	Arianna Quintavalla <i>University of Bologna, Bologna, Italy</i>	OC-28
1,2-DIOXANES AS POTENTIAL ANTI-LEISHMANIAL DRUGS		
16:30	Alexandros Zografos <i>Aristotle University of Thessaloniki, Thessaloniki, Greece</i>	IL-14
DIVERGENT SYNTHESIS OF NATURAL SESQUITERPENE LACTONES: ONE PLAN, MANY PITFALLS TO AVOID		
17:00	Paolo Melchiorre <i>Institut Català d'Investigació Química (ICIQ), Tarragona, Spain</i>	PL-11
ORGANIC SYNTHESIS IN THE EXCITED STATE		
17:15	Closing Ceremony	
18:30	Conference Dinner	



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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]

[1] Wikipedia, https://en.wikipedia.org/wiki/Fraser_Stoddart (as of June 17, 2019)

**SURPRISES WITH ALKYNES:
A NEW REACTIVITY PARADIGM AND ITS APPLICATIONS**

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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*-hydrostannation 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.

[1] A. Fürstner, *J. Am. Chem. Soc.* **2019**, *141*, 11.

MAKING NEW FORMS OF NANOCARBONS

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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.



Carbon nanobelts



Graphene nanoribbons and nanographenes



Warped nanographenes



Carbon nanocages



All-benzene catenane



All-benzene trefoil knot



Mobius nanobelts

LEWIS ACID ENABLED NOVEL REACTIVITIES IN ASYMMETRIC COPPER CATALYSIS

Syuzanna R. Harutyunyan

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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 us dearomatisations as well as tackling the reactivity of unprotected carboxylic acids will also be presented.

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- [1] . Y. Guo, J. Kootstra, S. R. Harutyunyan *Angew. Chem. Int. Ed.*, 57, 13547, 2018
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- [4] J. Rong, J. F. Collados, P. Ortiz, R. P. Jumde, E. Otten, S. R. Harutyunyan, *Nature Communications*, 7, 13780, 2016
- [5] R. P. Jumde, F. Lanza, M. Veenstra, S. R. Harutyunyan, *Science*, 352, 433, 2016
- [6] J. Rong, T. Pellegrini, S. R. Harutyunyan, *Chem. Eur. J.*, 11, 3558, 2016
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ENANTIOSELECTIVE CATALYSIS OF PHOTOCHEMICAL REACTIONSThorsten Bach

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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.

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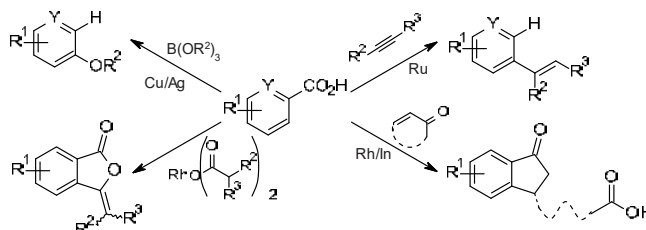
[3] Short review: C. Brenninger, J. D. Jolliffe, T. Bach, *Angew. Chem. Int. Ed.* **2018**, *57*, 14338.

CARBOXYLATES AS DIRECTING AND LEAVING GROUPS IN CATALYTIC BOND FORMATION

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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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[3] a) L. Huang, A. Biafora, G. Zhang, V. Bragani, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2016**, 55, 6933-6937.

[4] a) J. Tang, D. Hackenberger, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2016**, 55, 11296-11299; b) Y. Gao, Y. Ou, L. J. Gooßen, *Chem. Eur. J.*, **2019**, doi: 10.1002/chem.201902022.

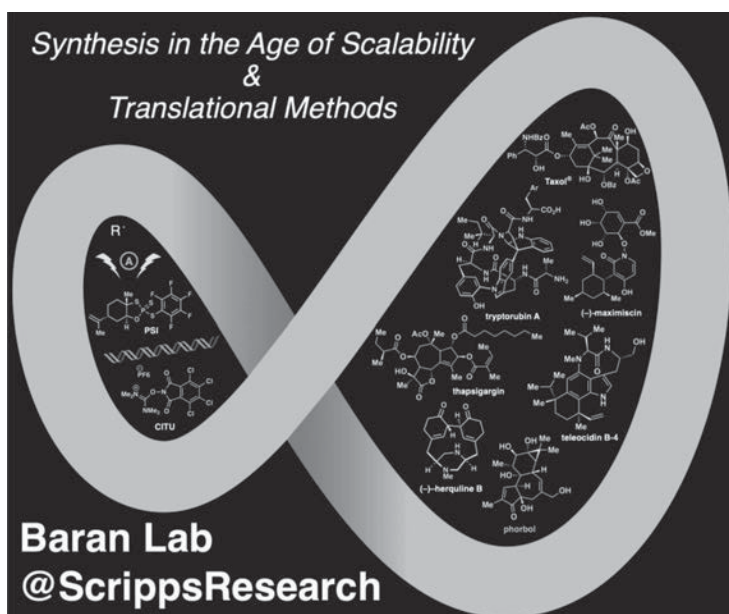
[5] G. Zhang, Z. Hu, F. Belitz, Y. Ou, N. Pirkel, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2019**, 58, 6435-6439.

TRANSLATIONAL CHEMISTRY

Phil S. Baran

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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.



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ORIGINS OF LIFE SYSTEMS CHEMISTRY

John D. Sutherland

MRC Laboratory of Molecular Biology, Cambridge UK

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.

FLUORINE CHEMISTRY FOR APPLICATIONS IN MEDICINE

Véronique Gouverneur

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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}F -radiotracers is an imaging modality that can diagnose diseases, and monitor how patients respond to therapy. Moreover, the stable isotope ^{19}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

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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.

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ORGANIC SYNTHESIS IN THE EXCITED STATE

Paolo Melchiorre

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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]

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[2] A. Albini, M. Fagnoni, in *Handbook of Synthetic Photochemistry*, Wiley-VCH, 2010.

[3] (a) E. Arceo, I. D. Jurberg, A. Álvarez-Fernández, P. Melchiorre, *Nature Chem.* **2013**, 5, 750–756. (b) J. J. Murphy, D. Bastida, S. Paria, M. Fagnoni, P. Melchiorre, *Nature* **2016**, 532, 218–222.

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[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

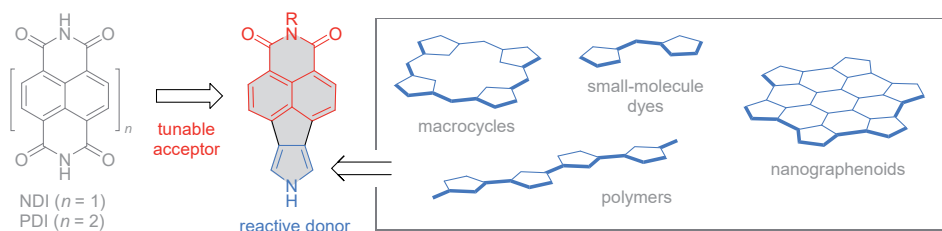
Vienna's landmark

DONOR–ACCEPTOR OLIGOPYRROLES

Marcin Stepień

Faculty of Chemistry, University of Wrocław, Wrocław, Poland

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.



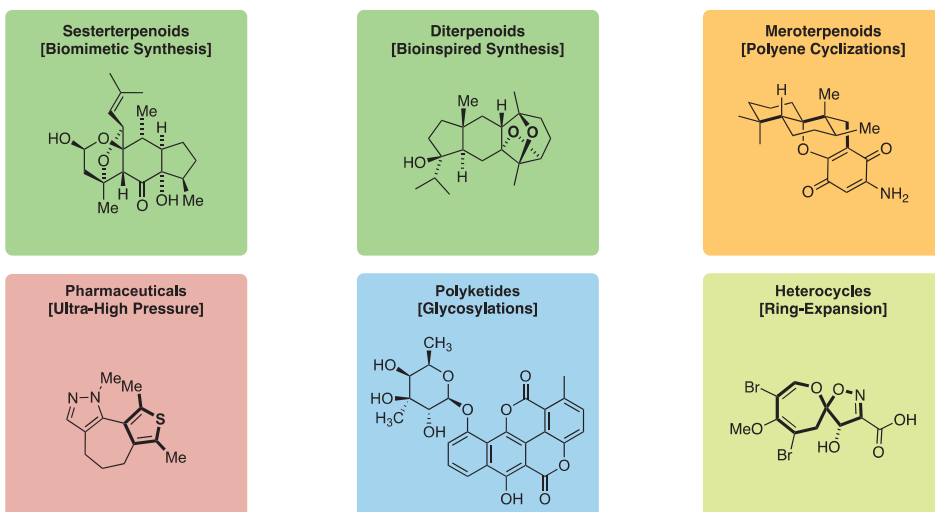
- [1] H. Zhylitskaya, M. Stepień, *Org. Chem. Front.* **2018**, 5, 2395–2414.
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TOTAL SYNTHESIS OF POLYCYCLIC NATURAL PRODUCTS

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.

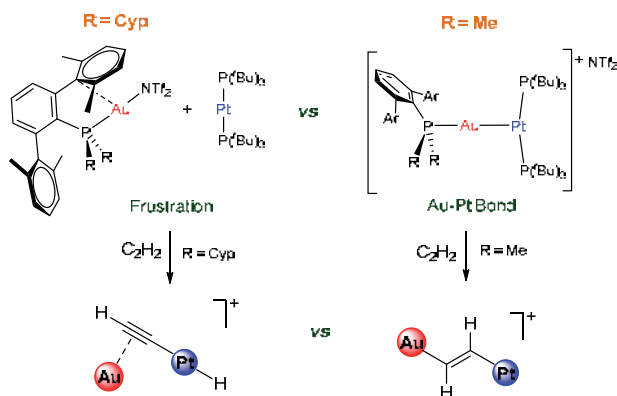


INTERACTION VS. FRUSTRATION IN BIMETALLIC COOPERATIVE SYSTEMS

Jesús Campos

Instituto de Investigaciones Químicas (IIQ), Centro de Innovación en Química Avanzada (ORFEO-CINQA). Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla. Av. Américo Vespucio 49, 41092 Sevilla (Spain)

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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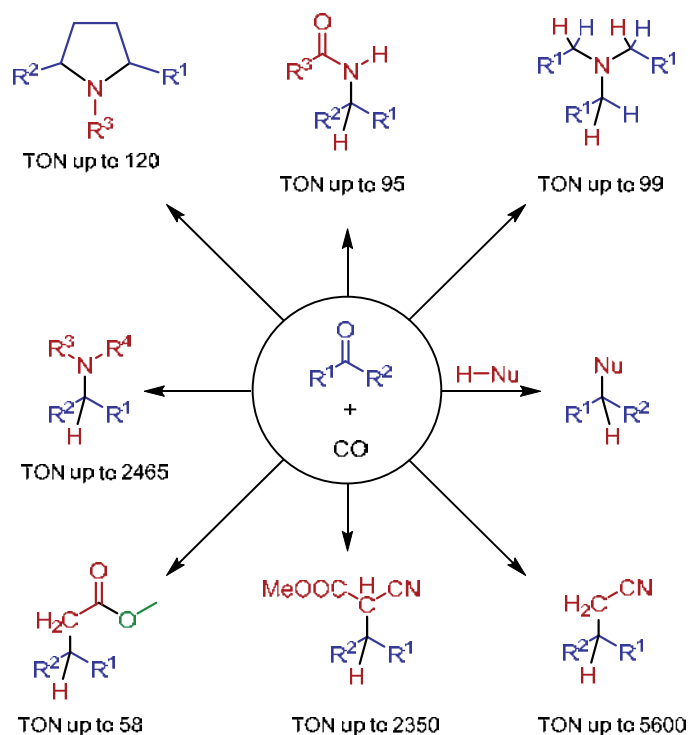
STRATEGY FOR SELECTIVE REDUCTIVE ADDITION

Denis Chusov^a, Oleg I. Afanasyev^a, Sofiya Runikhina^a, Olga Chusova^b,
Alexei Tsygankov^a, Ekaterina Kuchuk^a, Evgeniya Podyacheva^a

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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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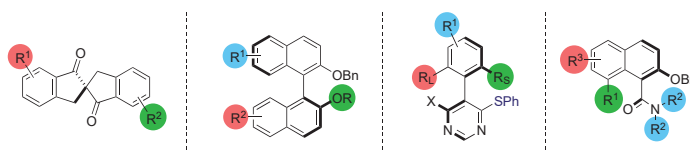
Identification of reactive intermediates is the key step towards understanding chemical reactions. Often, controversies exist about reaction mechanisms, about the nature of rate-determining transition states or about the role of intermediates. We are developing methods to identify the intermediates and 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 technique 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-ION MEDIATED APPROACHES TO CONTROLLING AXIAL CHIRALITY

Martin D. Smith

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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^[1] 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.^[2-5]



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

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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 chemistry¹ 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 ($K_d = 4\text{--}660\text{ nM}$) 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 *in vitro* activity, excellent ADMET properties and antibacterial activity ($\text{MIC} = 4\text{--}16\text{ }\mu\text{M}$) against a range of pathogenic Gram positive bacteria (*Staphylococcus aureus*, *Enterococcus faecium* and *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 *in vivo* infection model.⁷

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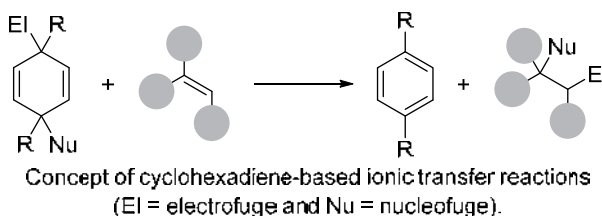
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TRANSFER OF REACTIVE GASES FROM ONE MOLECULE TO ANOTHER

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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].



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

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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

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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].

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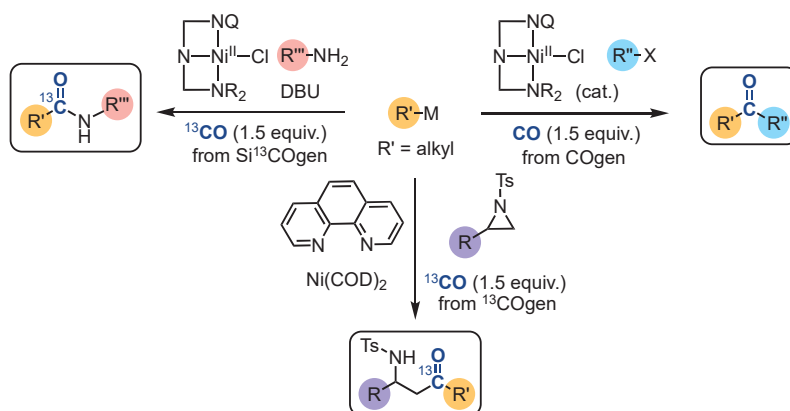
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RECENT DEVELOPMENTS IN LOW PRESSURE CARBONYLATIONS

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].



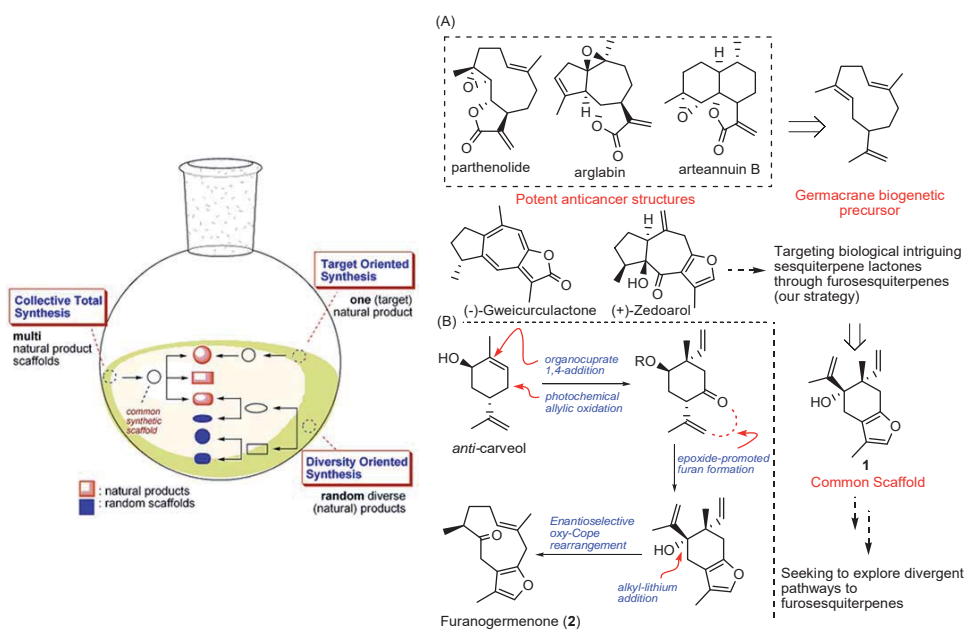
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DIVERGENT SYNTHESIS OF NATURAL SESQUITERPENE LACTONES: ONE PLAN, MANY PITFALLS TO AVOID

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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



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Oral Contributions

ESOC 2019



Vienna State Opera

First major building on the Vienna Ringstrasse, completed in 1869

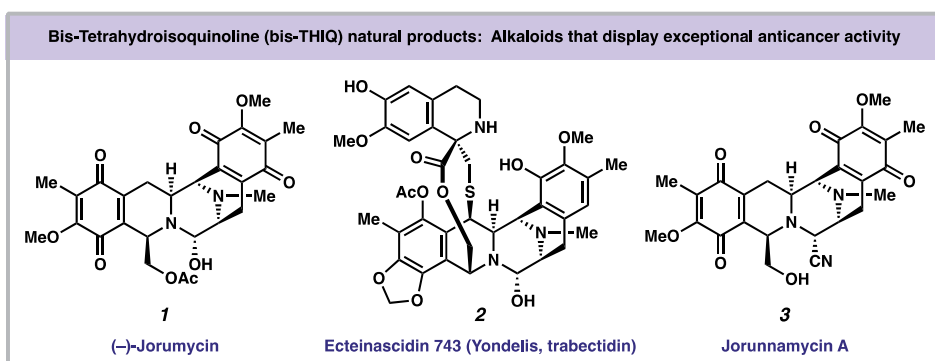
CONCISE TOTAL SYNTHESIS OF (–)-JORUNNAMYCIN A AND (–)-JORUMYCIN ENABLED BY ASYMMETRIC CATALYSIS

Eric Welin^a, Aurapat Ngamnithiporn^a, Max Klatte^a, Guillaume Lapointe^a, Gerit Pototschnig^a, Martina McDermott^b, Dylan Conklin^b, Christopher Gilmore^a, Pamela Tadross^a, Emil Glibstrup^a, Kenji Negoro^a, Christian Grünanger^a, Scott Virgil^a, Dennis Slamon^b, Brian Stoltz^a

^a California Institute of Technology, Pasadena, CA

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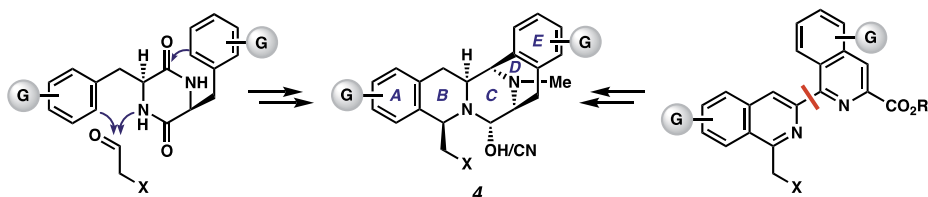
The bis-tetrahydroisoquinoline (bis-THIQ) natural products have been studied intensively over the past four decades for their exceptionally potent anticancer activity, in addition to strong Gram-positive and Gram-negative antibiotic character. Synthetic strategies toward these complex polycyclic compounds 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.



Conventional, Biomimetic Approach:
Pictet–Spengler, Bischler–Napieralski

Pentacyclic bis-THIQ Core

Our Approach (this research):
Cross Coupling/Reductive Cyclization



A non-biomimetic approach will produce complementary analogs for bioactivity and medicinal chemistry studies

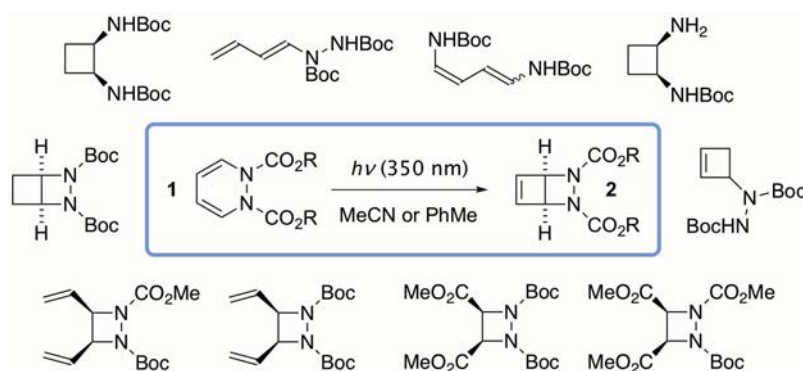
4- π -PHOTOCYCLISATION OF DIHYDROPYRIDAZINES: ACCESS TO VERSATILE BICYCLIC DIAZETIDINES

Thomas K. Britten^a, Susannah C. Coote^a, Paul D. Kemmitt^b and Nathan R. Halcovitch^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** [1,2], an intriguing reaction that has been studied only sporadically since its first introduction in 1968 [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.



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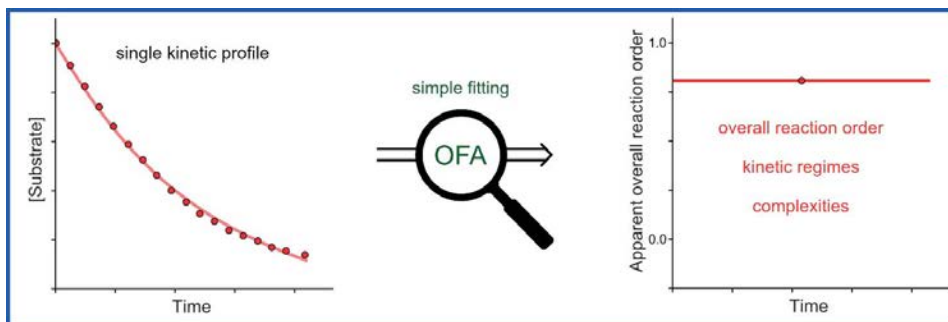
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REACTION PROGRESS KINETIC ANALYSIS BY DIRECT ANALYSIS OF CONCENTRATION-TIME PROFILES

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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.



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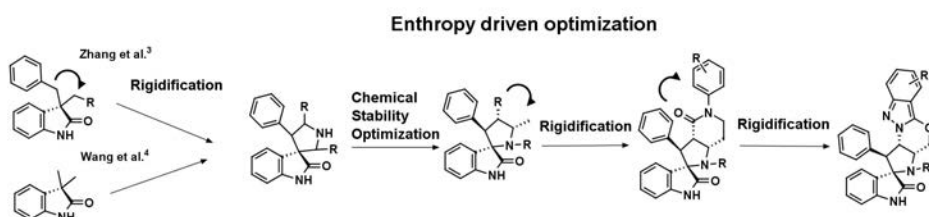
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SEQUENTIAL MULTI-BOND FORMING REACTIONS APPLIED TO THE SYNTHESIS OF CONFORMATIONALLY RESTRICTED MDM2-p53 INHIBITORS SUITABLE FOR INTERMITTENT DOSING

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MDM2 is a main and direct inhibitor of the crucial tumor suppressor p53.¹ 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.² 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.

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CONTROLLING THE CIRCADIAN CLOCK WITH HIGH TEMPORAL RESOLUTION THROUGH PHOTODOSIMETRY

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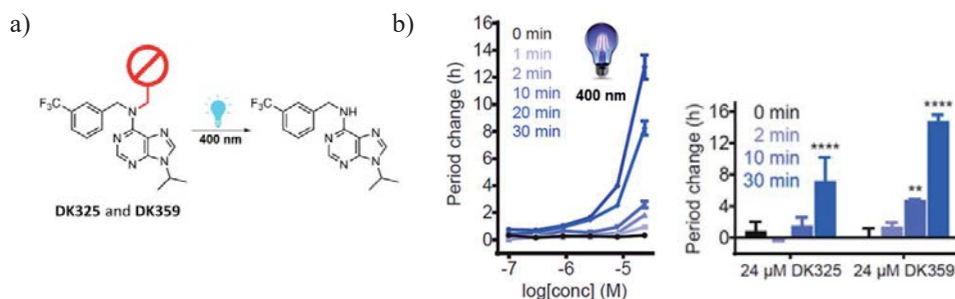
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Inspired by the crucial role of circadian clock disruption in disease development,[1] during the last decade chemical biology studied how to adjust cellular clocks using small molecule modifiers.[2] Unfortunately, these modifiers are still facing a 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. 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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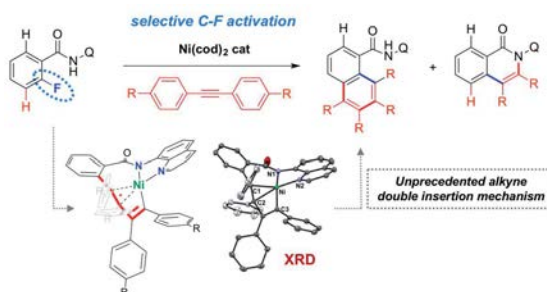
CHEMO-DIVERGENT NICKEL(0)-CATALYZED ARENE C-F ACTIVATION WITH ALKYNES: UNPRECEDENTED DOUBLE-INSERTION

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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 transmetalation [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.



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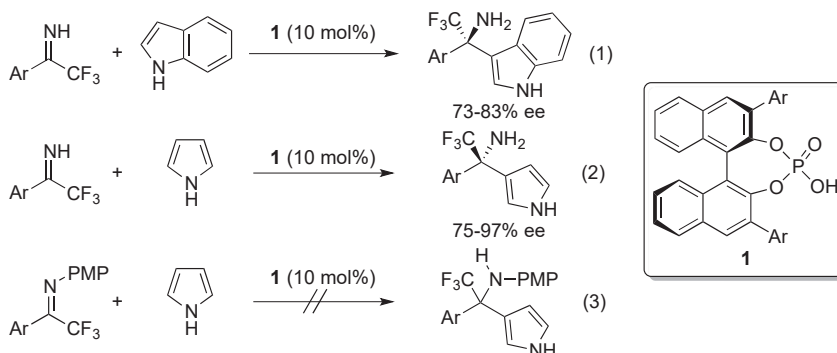
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ENANTIOSELECTIVE FRIEDEL-CRAFTS ALKYLATION REACTION OF TRIFLUOROMETHYLATED N-H KETIMINE WITH HETEROARENES BY MEANS OF CHIRAL PHOSPHORIC ACID

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Construction of α -trifluoromethylated amines in optically pure form is one of the important topic 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.^[1] Trifluoromethylated *N*-H ketimine is known to be relatively stable among *N*-H ketimines. Nucleophilic addition toward trifluoromethyl *N*-H ketimine will provide 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).^[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.



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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.

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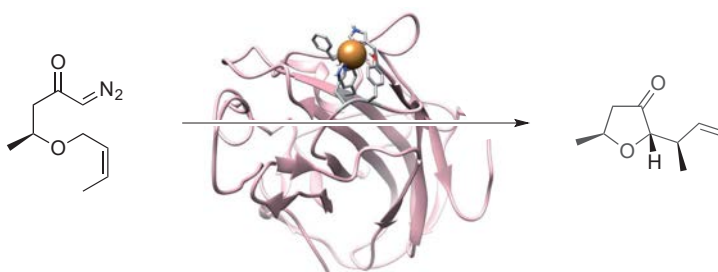
**THE HUNT FOR ARTIFICIAL REACTIVITIES IN BIOCATALYSIS:
FUNGAL COPPER-DEPENDENT METALLOPROTEINS
AS MEDIATORS FOR PERICYCLIC REACTIONS**

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Biocatalysis is increasingly gaining ground as 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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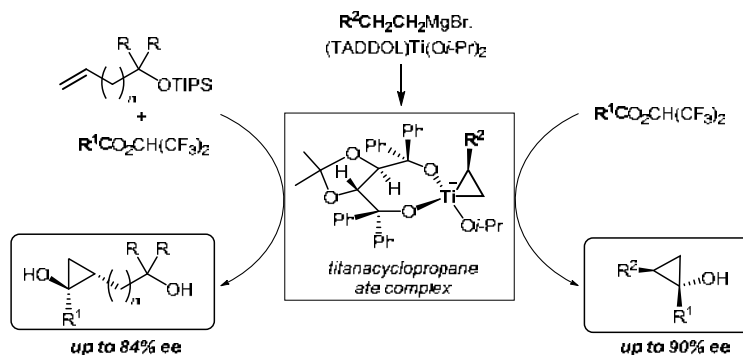
QUEST FOR ASYMMETRIC KULINKOVICH REACTION: FROM MECHANISM TOWARDS ENHANCED ENANTIOSELECTIVITY

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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 [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 developed for asymmetric Kulinkovich reaction, allowing preparation of (1*S*,2*S*)-cyclopropanols with up to 90% ee by using titanium (4*R*,5*R*)-TADDOLates. Expansion of the same methodology to hydroxycyclopropanation of prochiral olefins via a more convenient olefin ligand exchange method will be also presented [2].



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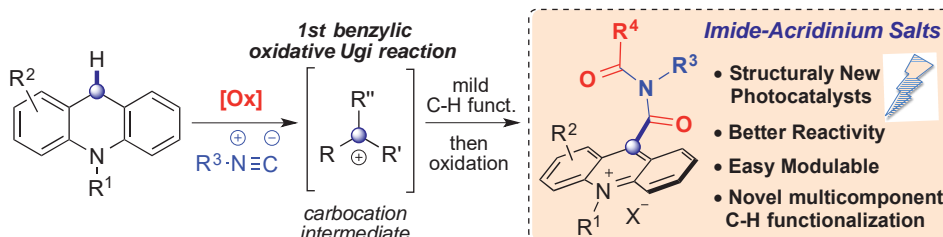
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RATIONAL DESIGN OF NEW, MORE POTENT ACRIDINIUM VISIBLE LIGHT ORGANO-PHOTOCATALYSTS BY C-H FUNCTIONALIZATION

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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 iridium 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.

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

Paul Kohls, Peter Poechlauer, Christian Schuster, Maria Vasiloiu

Thermo Fisher Scientific, Linz, Austria

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.

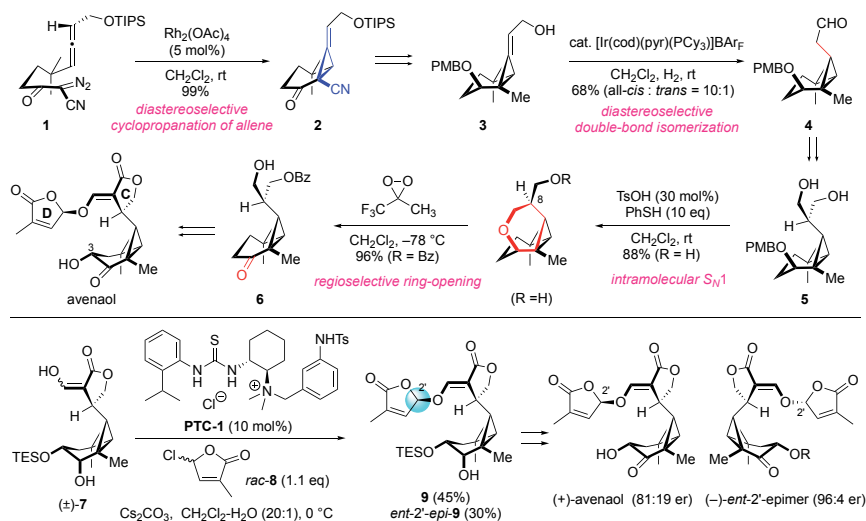
We give details on the chemistry, our considerations on analytics, on suitable reactors, and on options and methods for continuous improvement of such processes, with a focus on the multidisciplinary nature of such development tasks.

TOTAL SYNTHESIS OF AVENAOL VIA ASYMMETRIC *O*-ALKYLATION 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 (\pm)-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 stereoselective 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.



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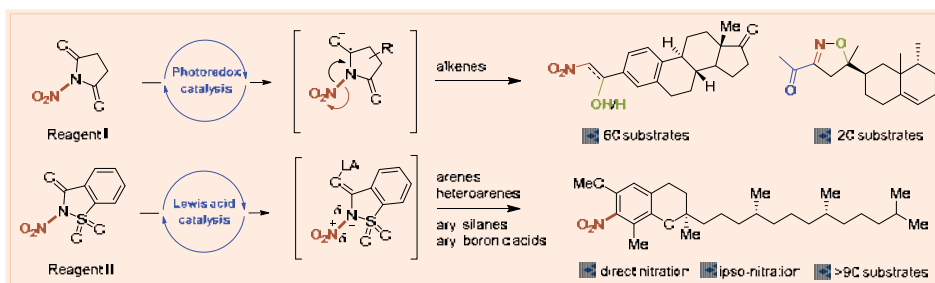
[2] Manuscript under preparation.

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 nitril 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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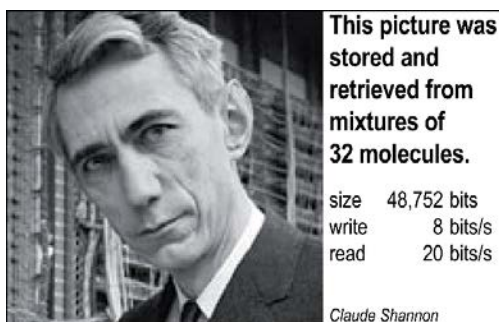
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STORAGE OF INFORMATION USING SMALL ORGANIC MOLECULES

Michael J. Fink, Brian Cafferty, Alexei Ten, Dan Preston, Amit Nagarkar,
Milan Mrksich, George M. Whitesides

Department of Chemistry and Chemical Biology, Harvard University

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 10^6 -fold more efficient in cost and writing speed than DNA-based storage and can plausibly be scaled to write terabytes per day.



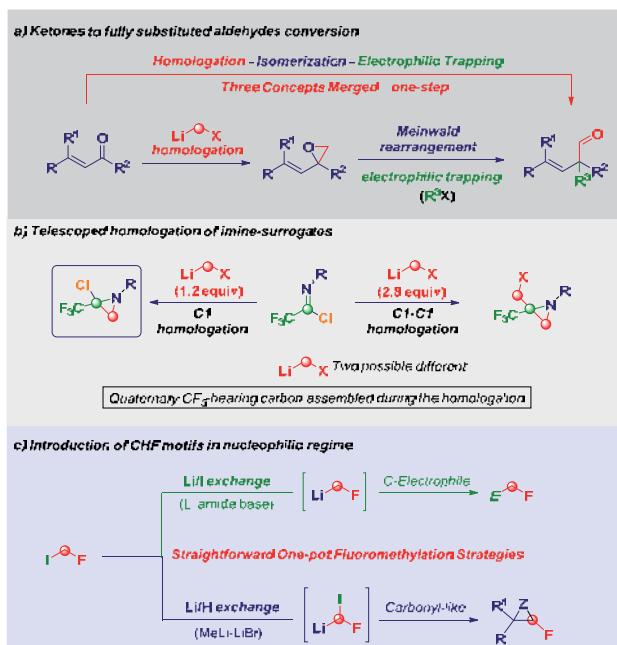
DESIGNING NEW SYNTHETIC CONCEPTS FOR IMPARTING MOLECULAR COMPLEXITY WITH C-1 SOURCES

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The direct transfer of a reactive nucleophilic CH_2X unit into an existing linkage enables the formal introduction of the moiety with the precisely defined degree of functionalization.¹ 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 fluoromethyl lithium 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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(3) Ielo, L.; Touqeer, S.; Roller, A.; Langer, T.; Holzer, W.; Pace, V. *Angew. Chem. Int. Ed.* 2019, 58, 2479-2484.

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

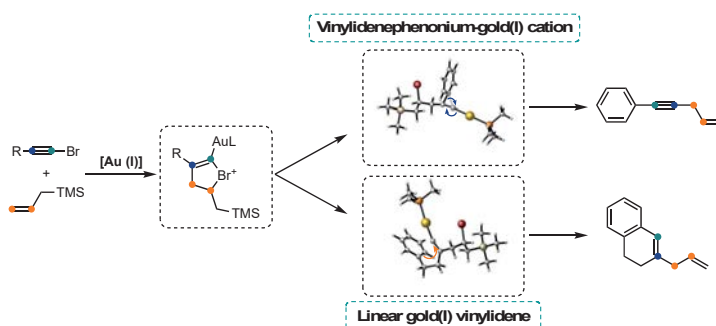
Margherita Zanini,^{a,b} M. Elena de Orbe,^{a,b} Ophélie Quinonero,^a
and Antonio M. Echavarren^{a,b}

^a Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

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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 vinylidenephonium-gold(I) cation allowing a concealed 1,2-aryl-migration to form 1,4-enynes in a cross-coupling-type reaction.



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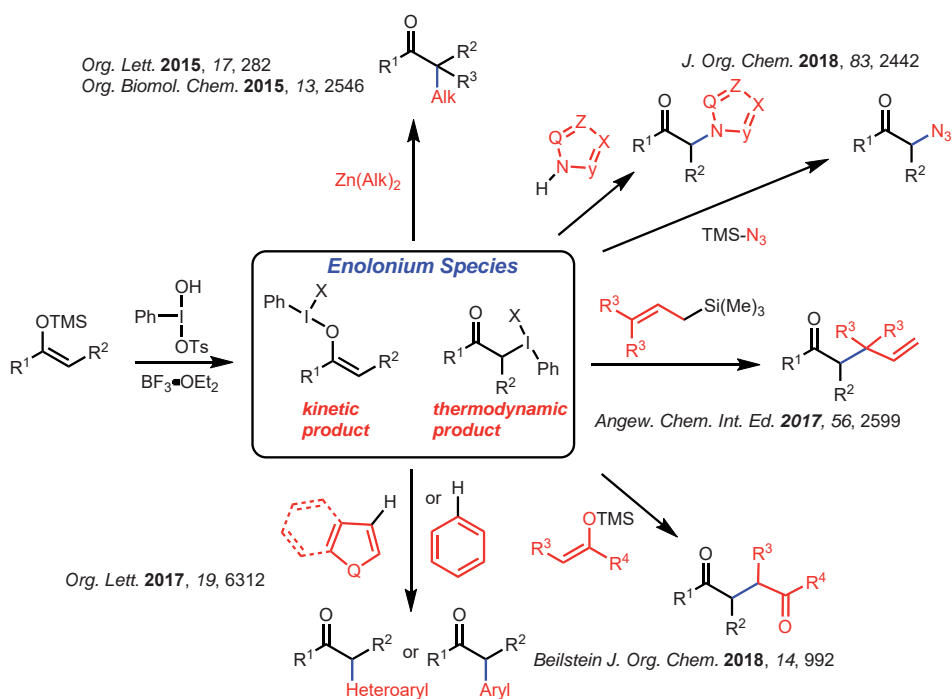
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NOVEL REACTIONS VIA ELECTROPHILIC ENOLONIUM SPECIES

Alex M. Szpilman

Department of Chemical Sciences, Ariel University, Israel

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.



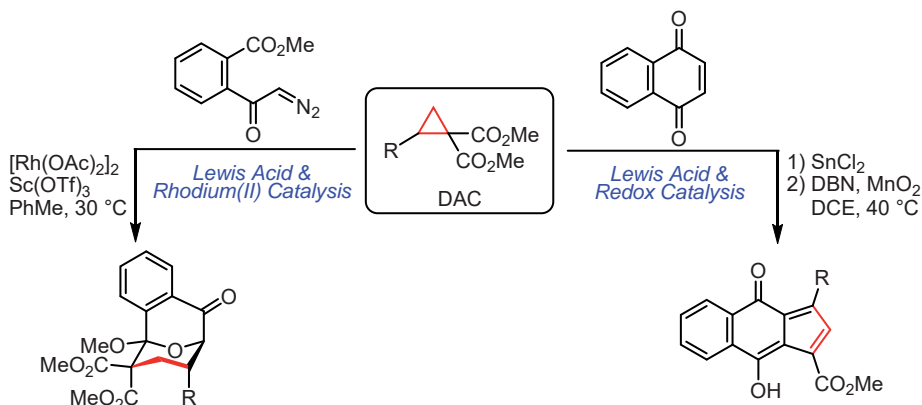
SYNERGISTIC CATALYSIS IN DONOR-ACCEPTOR CYCLOPROPANE CHEMISTRY

Daniel B. Werz

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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.



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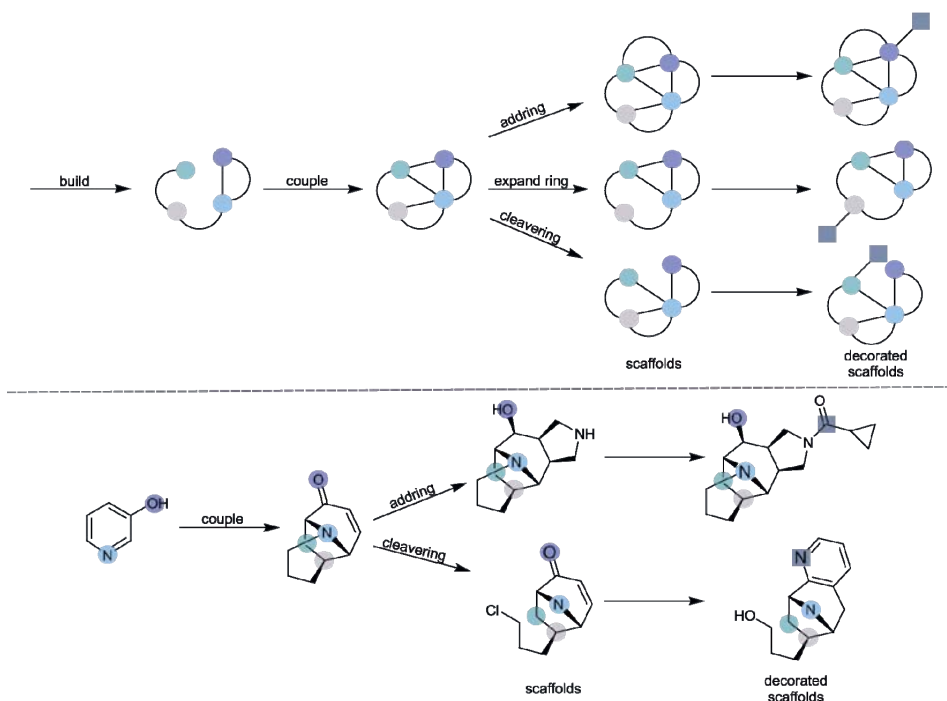
A TOP-DOWN APPROACH TO DIVERSE LEAD-LIKE MOLECULAR SCAFFOLDS

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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 diabetes.[1] Following the success of obeticholic acid (OcalivaTM),[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.

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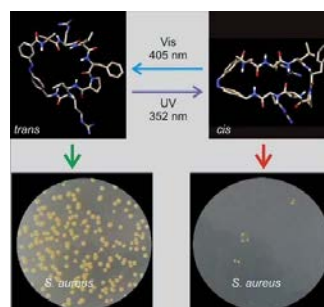
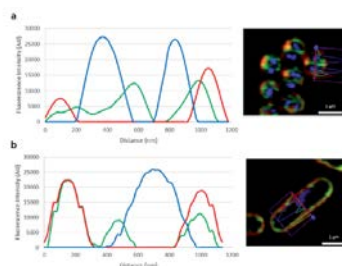
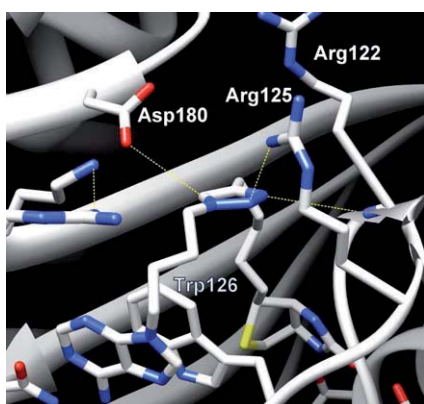
THE SYNTHESIS AND OPTIMISATION OF NEW ANTIBIOTICS

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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.



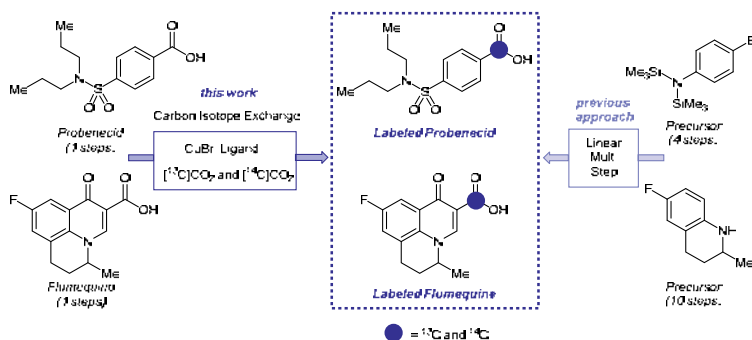
DYNAMIC CARBON ISOTOPE EXCHANGE OF PHARMACEUTICALS WITH LABELED CO₂

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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.



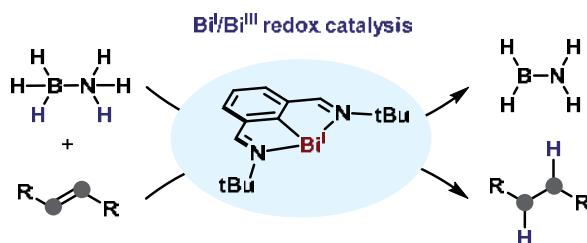
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LOW-VALENT Bi^I⇌Bi^{III} REDOX CATALYSISFeng Wang, Oriol Planas, and Josep CornellaMax-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,
45470, Mülheim an der Ruhr, Germany

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



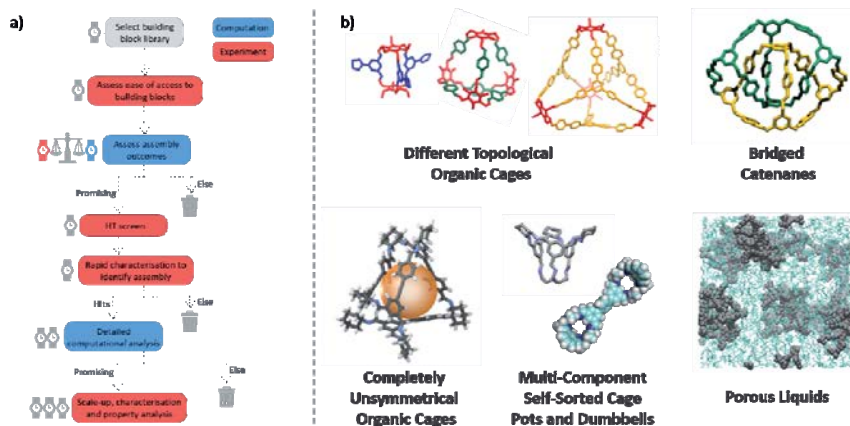
HYBRID DISCOVERY WORKFLOW FOR ORGANIC MATERIALS AND SUPRAMOLECULAR SELF-ASSEMBLIES

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



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MACROCYCLIC ANION CARRIERS

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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].

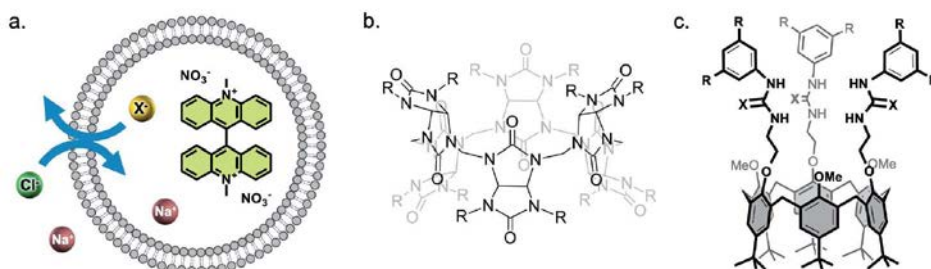


Figure 1. Liposomes with the dye lucigenin encapsulated (a) were used to study anion exchange by bambus[6]urils (b), biotin[6]urils (not shown), and calix[6]arenes (c).

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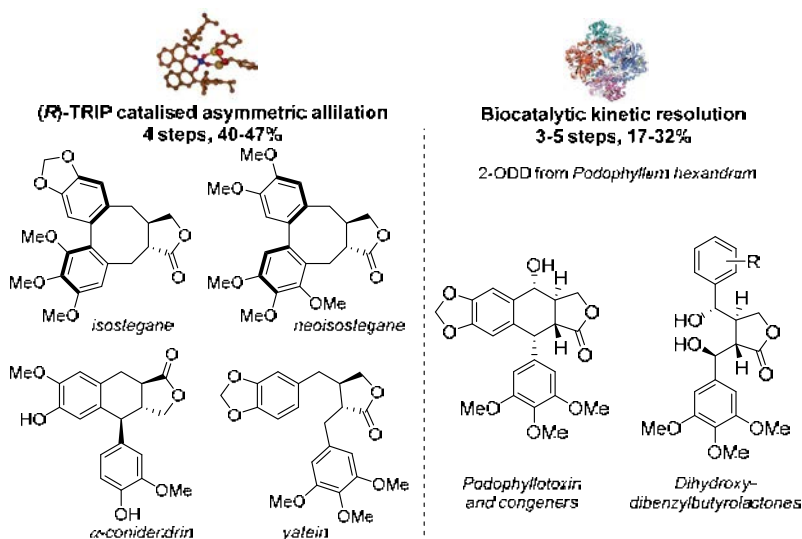
ORGANO- AND BIOCATALYSIS FOR LIGNAN NATURAL PRODUCT SYNTHESIS

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 Peter Sagmeister,^a Lorenz Steiner,^a Peter Hartmann,^a Ferdinand Belaj,^c
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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-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (TRIP) can provide catalytic stereinduction 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-hydroxy-yatein 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.

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1,2-DIOXANES AS POTENTIAL ANTI-LEISHMANIAL DRUGS

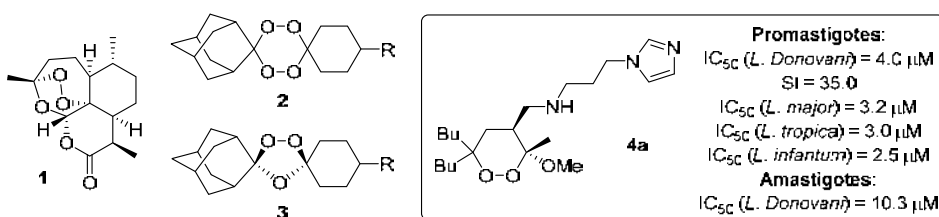
Marco Lombardo^a, Margherita Ortalli^b, Arianna Quintavalla^a, Claudio Trombini^a,
and Stefania Varani^b

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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 *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 *Plasmodium*, and are widely used for the malaria treatment. Some synthetic peroxides, *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 *in vitro* inhibitory activity on *L. donovani* promastigotes (IC_{50} range = 1.6 - 16.4 μ M). Moreover, the 6 compounds exhibiting the best selectivity index proved to be active also against *L. tropica*, *L. major* and *L. infantum* promastigotes and against *L. donovani* amastigotes, highlighting their potential as hits for lead optimization.



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Poster Index

ESOC 2019



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Catalysis

- Eman Abdelraheem** *PO-1*
Delft University of Technology, Delft, The Netherlands
ENANTIOSELECTIVE SEQUENTIAL ALDOL CONDENSATION
- Nurtalya Alandini** *PO-2*
Institut Català d'Investigació Química (ICIQ), Tarragona, Spain
PHOTOREDOX / NICKEL-CATALYZED CARBAMOYLATION OF (HETERO)ARYL BROMIDES
- Łukasz Albrecht** *PO-3*
Lodz University of Technology, Lodz, Poland
VINYLOGY CONCEPT IN THE SYNTHESIS OF SELECTED CARBO- AND HETEROCYCLES
- Anna Albrecht** *PO-4*
Lodz University of Technology, Lodz, Poland
DECARBOXYLATIVE, AMINOCATALYTIC CASCADES IN THE SYNTHESIS OF 3,4-DIHYDROCOUMARINS
- Teresina Ambrosio** *PO-5*
GSK Carbon Neutral Laboratories for Sustainable Chemistry, Nottingham, UK
BIOMIMETIC HALOGENATIONS AT UNACTIVATED C-H BONDS
- Mariarosa Anania** *PO-6*
Charles University, Prague, Czech Republic
REACTION INTERMEDIATES IN PALLADIUM-CATALYZED CARBONYLATION OF OLEFINS
- Julien Annibaleto** *PO-7*
Normandie Université, Rouen, France
MULTICOMPONENT ORGANOCATALYTIC SYNTHESIS OF ISOXAZOLIDIN-5-ONES
- Soumitra Athavale** *PO-8*
University of Illinois, Urbana, United States
DEMYSTIFYING THE SOAI REACTION
- Tomasz Bauer** *PO-9*
University of Warsaw, Warsaw, Poland
ZIRCONIUM IN THE CROWN. ENANTIOSELECTIVE ALKENYLATION OF ALDEHYDES WITH PROTECTED PROPARGYLIC ALCOHOLS IN THE PRESENCE OF CROWN ETHER: A NOVEL APPROACH TO THE INHIBITION OF ACHIRAL BACKGROUND REACTIONS
- Yann Baumgartner** *PO-10*
University of Basel, Basel, Switzerland
ONE-POT ALKENE HYDROBORATION/MIGRATORY SUZUKI-MIYaura CROSS-COUPING
- Srikrishna Bera** *PO-11*
Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland
BORON DIRECTED, Ni-CATALYZED REDUCTIVE COUPLING OF UNACTIVATED ALKYL AND ARYL HALIDES WITH INTERNAL ALKENES
- Brigitte Bibal** *PO-12*
Université de Bordeaux, Talence cedex, France
PHOTOREDUCTIBLE Au(III) COMPLEXES FOR CATALYSIS
- Jacqueline Bitai** *PO-13*
University of St. Andrews, St. Andrews, Scotland
TANDEM CATALYTIC FORMATION AND ENANTIOSELECTIVE [2,3]-REARRANGEMENT OF FUNCTIONALISED ALLYLIC AMMONIUM YLIDES

- Clemens Blasius** *PO-14*
Ruprecht-Karl-University Heidelberg, Heidelberg, Germany
HIGHLY ENANTIOSELECTIVE IRON-CATALYZED REDUCTION OF FUNCTIONALIZED KETONES AND NON-PRIVILEGED IMINES
- Lea T. Brechmann** *PO-15*
Technische Universität Berlin, Berlin, Germany
USING H₂ AS A HYDRIDE SOURCE - A CHEMO- AND REGIOSELECTIVE REDUCTIVE COUPLING REACTION/ALLYLIC REDUCTION
- Jean-François Brière** *PO-16*
Normandie Université, Rouen, France
C5-DISUBSTITUTED MELDRUM'S ACID DERIVATIVES AS PLATFORM FOR THE ORGANOCATALYTIC SYNTHESIS OF C3-ALKYLATED DIHYDROCOUMARINS
- Aleksandra Brzozowska** *PO-17*
RWTH Aachen University, Aachen, Germany
METAL-LIGAND CATALYZED HETEROCYCLIZATION OF ALLENIC ALCOHOLS
- Aleksandra Błocka** *PO-18*
Polish Academy of Science, Warsaw, Poland
TANDEM PALLADIUM-CATALYZED INTRAMOLECULAR ADDITION OF ACTIVE METHYLENE COMPOUNDS TO ALKYNES FOLLOWED BY COUPLING WITH (HETERO)ARYL BROMIDES
- Ilaria Caivano** *PO-19*
Charles University of Prague, Prague, Czech Republic
SYNTHESIS OF 2,4-DISUBSTITUTED 9,9'-SPIROBIFLUORENES AND FLUORO DISPIROINDENO[2,1-C]FLUORENES THROUGH CATALYTIC [2+2+2] CYCLOTRIMERIZATION
- Wojciech Chaładaj** *PO-20*
Polish Academy of Science, Warsaw, Poland
Pd-CATALYZED REDUCTIVE CARBOPERFLUOROALKYLATION OF ALKYNES WITH PERFLUOROALKYL AND ARYL IODIDES VIA BOROPERFLUOROALKYLATION
- Mu-Yi Chen** *PO-21*
Normandie Université, Rouen, France
Pd-CATALYZED TRIFLUOROMETHYLTHIOLATION OF ACRYLAMIDES AND AROMATIC AMIDES BY C-H BOND ACTIVATION
- Paula Chirila** *PO-22*
Sheffield Hallam University, Sheffield, UK
ONE-POT PREPARATION OF 1,2,3-BENZOTRIAZIN-4(3H)-ONES AND ACETYLBENZOTRIAZOLES USING A KEY Cp*Co(III)-CATALYZED C-H AMIDATION STEP
- Hong Sub Choi** *PO-23*
Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea
NICKEL CATALYZED HYDROXYCARBONYLATION OF ACETYLENE TO ACRYLIC ACID
- Patrícia Čmelová** *PO-24*
Comenius University Bratislava, Bratislava, Slovakia
STEREOSELECTIVE MICHAEL ADDITION OF ALDEHYDES TO HETEROCYCLIC NITROALKENES CATALYZED BY HYBRID PEPTIDE-THIOUREA CATALYSTS
- Hugo Collin** *PO-25*
Aarhus University, Aarhus, Denmark
COTab: A SIMPLE AND PRACTICAL SETUP FOR Pd-CATALYZED CARBONYLATION CHEMISTRY
- Nicola Della Ca'** *PO-26*
Università di Parma, Parma, Italy
SITE-SELECTIVE CARBONYLATIVE ROUTES TO FUSED POLYHETEROCYCLIC STRUCTURES

- Antonin Desmecht** **PO-27**
 Université Catholique de Louvain (UCL), Louvain-la-Neuve, Belgium
SYNTHESIS AND CATALYTIC APPLICATIONS OF DENDRIMER-CARBON NANOTUBES HYBRIDS
- Vasudevan Dhayalan** **PO-28**
 University of the Negev, Beer-Sheva, Israel
ENANTIOSELECTIVE BENZOIN REACTION CATALYZED BY *N*-HETEROCYCLIC CARBENE BORONIC ESTERS (NHC-BE)
- Davide Di Francesco** **PO-29**
 Stockholm University, Stockholm, Sweden
LIGNIN VALORIZATION BY COBALT-CATALYZED FRACTIONATION OF LIGNOCELLULOSE TO YIELD MONOPHENOLIC COMPOUNDS
- Aske Skyum Donslund** **PO-30**
 University of Aarhus, Aarhus, Denmark
DIRECT ACCESS TO β -KETONITRILES VIA NICKEL-CATALYZED CARBONYLATIVE COUPLING OF α -BROMONITRILES WITH ALKYLZINC REAGENTS
- Qingwei Du** **PO-31**
 Southern University of Science and Technology, Shenzhen, China
ENANTIOSELECTIVE SYNTHESIS OF HETEROCYCLIC NUCLEOSIDES THROUGH ASYMMETRIC [3+2] ANNULATION OF α -PURINE-SUBSTITUTED ACRYLATES WITH NITRONES
- Krzysztof Dzieszkowski** **PO-32**
 Nicolaus Copernicus University, Toruń, Poland
ENANTIOSELECTIVE SYNTHESIS OF CHROMANONES WITH QUATERNARY STEREOGENIC CENTER VIA NHC ORGANOCATALYSIS
- Andreas Eitzinger** **PO-33**
 Johannes Kepler University Linz, Linz, Austria
HIGHLY ENANTIOSELECTIVE PHASE-TRANSFER CATALYZED ADDITION OF ISOXAZOLIDIN-5-ONES TO MBH CARBONATES AND PARA QUINONE METHIDES: ACCESS TO FUNCTIONALIZED $\beta^{2,2}$ -AMINO ACIDS
- Hasnaa El Said El Sayed** **PO-34**
 University of Twente, Enschede, The Netherlands
LIGHT-RESPONSIVE LIGANDS CONTROLLING BIMETALLIC CATALYSTS FORMATION
- Firas El-Hage** **PO-35**
 Leibniz Institute for Catalysis, Rostock, Germany
PHOTO-MEDIATED INTERMOLECULAR HYDROAMINATION OF ACTIVATED OLEFINS USING UNPROTECTED PRIMARY AMINES
- Daniele Fiorito** **PO-36**
 University of Geneva, Geneva, Switzerland
COPPER-CATALYZED BORYLATION OF OLEFINS: A QUEST FOR REACTIVITY AND SELECTIVITY
- Ivana Fleischer** **PO-37**
 University of Tübingen, Tübingen, Germany
CATALYTIC FORMATION OF C-S BONDS
- Steven Frippiat** **PO-38**
 Normandie Université, Rouen, France
Pd(0)-CATALYZED DIRECT INTER- AND INTRAMOLECULAR C₂ OR C₅-H FUNCTIONALIZATION OF 4-CARBOXYIMIDAZOLES
- Mateusz Garbacz** **PO-39**
 Polish Academy of Science, Warsaw, Poland
AN ENTRY TO ENANTIOENRICHED ALLYLAMINES VIA PHOTOCHEMICAL CROSS-COUPLING AND ICHIKAWA REARRANGEMENT

- Irma García-Monzón** *PO-40*
 Instituto de Productos Naturales y Agrobiología, San Cristóbal de La Laguna, Spain
REUSABLE POLYSTYRENE-SUPPORTED ORGANOCATALYSTS
- Víctor García-Vázquez** *PO-41*
 Stockholm University, Stockholm, Sweden
BASE-CATALYZED STEREOSPECIFIC ISOMERIZATION OF ALLYLIC HALIDES
- Mariana Gavendova** *PO-42*
 Waterford Institute of Technology, Waterford, Ireland
NOVEL β -AMINO ACID DERIVED ASYMMETRIC ORGANOCATALYSTS TOWARDS 3,3-DISUBSTITUTED-2-OXINDOLES
- Martin Gazvoda** *PO-43*
 University of Ljubljana, Ljubljana, Slovenia
THE REVISED MECHANISM OF COPPER-FREE SONOGASHIRA CROSS-COUPPLING REACTION
- Paul Gehrtz** *PO-44*
 Weizmann Institute, Rehovot, Israel
CROSS-COUPPLING OF CHLORO(HTERO)ARENES WITH THIOLATES EMPLOYING A Ni-PRECATALYST
- Kron Kumar Ghosh** *PO-45*
 Westfälische Wilhelms-Universität Münster, Münster, Germany
C(sp³)-H ACETOXYLATION OF FREE CARBOXYLIC ACIDS
- Tim Glaesel** *PO-46*
 Johannes Kepler University Linz, Linz, Austria
NOVEL APPROACH TO HETEROCYCLES BY TRANSITION METAL CATALYZED [2+2+2] CYCLOADDITIONS
- Melania Gómez-Martínez** *PO-47*
 University of Münster, Münster, Germany
HIGHLY ENANTIOSELECTIVE DEAROMATIZATION OF PYRYLIUM DERIVATIVES WITH A HELICAL MULTIDENTATE ANION-BINDING CATALYST
- Matija Gredicak** *PO-48*
 Rudjer Boskovic Insitute, Zagreb, Croatia
AN ANION-DIRECTED APPROACH TO ENANTIOENRICHED α -TRIARYL AMINES
- Yiting Gu** *PO-49*
 The Barcelona Institute of Science and Technology, Tarragona, Spain
A MILD AND DIRECT SITE-SELECTIVE sp² C-H Silylation OF (POLY)AZINES
- Mahmoud Hachem** *PO-50*
 Normandie Université, Rouen, France
NEW METHODS OF DIRECT CATALYTIC ALKYLATION OF HETEROCYCLES
- Victoria Haider** *PO-51*
 Johannes Kepler University Linz, Linz, Austria
SYNTHESIS AND APPLICATIONS OF CHIRAL QUATERNARY AMMONIUM SALT HYDROGEN BOND DONOR CATALYSTS
- Ulf Hanefeld** *PO-52*
 Technische Universiteit Delft, Delft, The Netherlands
REPLACING Cr(VI) WITH AN ENZYME: CLEAN OXIDATIONS
- Natalie Hofmann** *PO-53*
 University of Vienna, Vienna, Austria
SWITCHABLE BASE METAL CATALYZED HYDROGEN BORROWING PROCESSES

- Fung-E Hong** *PO-54*
National Chung Hsing University, Taichung, Taiwan
AMIDO-GROUPS AS REMOVABLE DIRECTING GROUPS IN PALLADIUM CATALYZED CARBON-HYDROGEN BOND FUNCTIONALIZATION OF BENZOQUINONE DERIVATIVES
- Longcheng Hong** *PO-55*
Justus Liebig University Giessen, Giessen, Germany
BORYL RADICAL MEDIATED LIGNIN DEGRADATION: DEPOLYMERIZATION AND RECONNECTION
- Fabian M. Hörmann** *PO-56*
Technical University Munich, Garching, Germany
EVIDENCE FOR TRIPLET SENSITIZATION IN THE VISIBLE-LIGHT-INDUCED [2+2]-PHOTOCYCLOADDITION OF ENIMINIUM IONS
- Huan-Ming Huang** *PO-57*
Westfälische Wilhelms-Universität Münster, Münster, Germany
DIALKYLATION OF 1,3-DIENES BY DUAL PHOTOREDOX AND CHROMIUM CATALYSIS
- Long Huang** *PO-58*
RWTH Aachen University, Aachen, Germany
DIRECT CROSS-COUPPLING OF ALLYLIC C(sp³)-H BONDS WITH ARYL- AND VINYL BROMIDES BY COMBINED NICKEL AND VISIBLE-LIGHT CATALYSIS
- Viktor Iaroshenko** *PO-59*
Polish Academy of Sciences, Łódź, Poland
REGIOSELECTIVE C-H ARYLATION OF NITRO HETEROCYCLES AND FURTHER TRANSFORMATION OF MANIPULABLE NITRO GROUP
- Ester Iniesta** *PO-60*
The Barcelona Institute of Science and Technology, Tarragona, Spain
SUPRAMOLECULARLY REGULATED COPPER-BISOXAZOLINE CATALYSTS FOR THE EFFICIENT INSERTION OF CARBENOID SPECIES INTO HYDROXYL BONDS
- Axel Jacobi von Wangelin** *PO-61*
University of Hamburg, Hamburg, Germany
STEREOSELECTIVE ADDITIONS TO ALKYNES BY IRON AND COBALT CATALYSTS
- Yoon-kyung Jang** *PO-62*
RWTH Aachen University, Aachen, Germany
MANGANESE CATALYZED ALKYLATION OF AMIDES AND ESTERS
- Liyin Jiang** *PO-63*
CATALYTIC CLEAVAGE OF C(sp²)-C(sp²) BONDS WITH METAL-CARBYNOIDS
- Martin Johansen** *PO-64*
Aarhus University, Aarhus, Denmark
COPPER CATALYZED AND ADDITIVE FREE DECARBOXYLATIVE TRIFLUOROMETHYLATION OF (HETERO)AROMATIC IODIDES
- Benyapa Kaewmee** *PO-65*
Technische Universität Berlin, Berlin, Germany
NI-CATALYZED E-SELECTIVE ALKYNE SEMIHYDROGENATIONS
- Anna Kajetanowicz** *PO-66*
University of Warsaw, Warsaw, Poland
ISOMERIZATION IN METATHESIS REACTIONS: UNDESIRED SIDE PROCESS OR USEFUL TRANSFORMATION
- Nikolaos Kaplaneris** *PO-67*
Georg-August-Universität, Göttingen, Germany
LATE-STAGE DIVERSIFICATION THROUGH MANGANESE-CATALYZED C-H ACTIVATION: ACCESS TO ACYCLIC, HYBRID, AND STAPLED PEPTIDES

- Prasad Mahesh Kathe** *PO-68*
University of Tübingen, Tübingen, Germany
PALLADIUM-CATALYZED TANDEM ISOMERIZATION/HYDROTHIOLATION OF ALLYL ARENES
- Salman Khan** *PO-69*
Indian Institute of Technology Bombay, Mumbai, India
BRØNSTED ACID CATALYZED C-H FUNCTIONALIZATION OF ARYL SULFOXIDES VIA A CHARGE ACCELERATED [3,3]-SIGMATROPIC REARRANGEMENT OF BUTADIENYL SULFONIUM CATION INTERMEDIATES
- Sung-Gon Kim** *PO-70*
Kyonggi University, Suwon, Republic of Korea
ASYMMETRIC BRØNSTED ACID-CATALYZED FRIEDEL-CRAFTS REACTION OF CYCLIC N-SULFIMINES AND SULFAMIDATES WITH INDOLES
- Christoforos Kokotos** *PO-71*
National and Kapodistrian University of Athens, Athens, Greece
PHENYLGLYOXYLIC ACID AS THE CATALYST FOR PHOTOCHEMICAL TRANSFORMATIONS
- Martin Kotora** *PO-72*
Charles University of Prague, Prague, Czech Republic
CATALYTIC C-C/C-H ACTIVATION RELAY: SYNTHESIS OF NAPHTHOQUINOLIZINIUM SALTS FROM 1-AZABIPHENYLENE
- Dominik Krisch** *PO-73*
Johannes Kepler University Linz, Linz, Austria
FLUOROFUNCTIONALIZATION OF METAL CORROLES
- Steffan K. Kristensen** *PO-74*
Aarhus University, Aarhus, Denmark
GOLD-PROMOTED ANTI-MARKOVNIKOV HYDROTHIOLATION OF OLEFINS USING EX SITU GENERATED METHANETHIOL
- Wolfgang Kroutil** *PO-75*
University of Graz, Graz, Austria
ASYMMETRIC BIOCATALYTIC PICTET-SPENGLER REACTION TO SHORTCUT ORGANIC SYNTHESIS
- Marios Kydonakis** *PO-76*
University of Crete, Heraklion, Greece
REGIOSELECTIVE DISILYLATION OF ALLENES BY DIHYDROSILANE CATALYZED BY GOLD NANOPARTICLES
- Marco Lessi** *PO-77*
Universita di Pisa, Pisa, Italy
A PRELIMINARY STUDY ON THE REGIOSELECTIVE C-H ARYLATION OF IMIDAZO[2,1-b]THIAZOLE
- Guillaume Levitre** *PO-78*
Université Paris-Saclay, Gif-sur-Yvette, France
ASYMMETRIC ORGANOCATALYSIS - SYNTHESIS OF CYCLOHEPTA[B]INDOLES BY (4+3) CYCLOADDITION
- Zhong-Liang Li** *PO-79*
Southern University of Science and Technology, Shenzhen, China
RADICAL MIGRATION FOR SYNTHESIS OF MEDIUM-SIZED RINGS
- Dawid Lichosyt** *PO-80*
University of Strasbourg, Strasbourg, France
DUAL-CATALYTIC TRANSITION METAL SYSTEMS FOR FUNCTIONALIZATION OF UNREACTIVE SITES OF MOLECULES

- Terry Shing-Bong **Lou** *PO-81*
University of Oxford, Oxford, UK
PALLADIUM-CATALYSED SYNTHESIS OF MULTIFUNCTIONAL ALKENYL SULFONYL FLUORIDES
- Ildikó **Madarász** *PO-82*
AVICOR Ltd., Szeged, Hungary
STEREOSELECTIVE ACID-CATALYZED C(sp³)-C(sp³) BOND FORMATION IN THE INTRAMOLECULAR SYNTHESIS OF cis-1,2-DIARYL CYCLOPROPANES
- Giovanni **Maestri** *PO-83*
Università di Parma, Parma, Italy
A BIO-INSPIRED POLYCYCLIZATION OF DIEN-N-YNES DRIVEN BY VISIBLE LIGHT
- Giandomenico **Magagnano** *PO-84*
Institut Català d'Investigació Química (ICIQ), Tarragona, Spain
ENANTIOSELECTIVE PHOTOCHEMICAL ORGANOCASCADE CATALYSIS
- Christopher **Mairhofer** *PO-85*
Johannes Kepler University Linz, Linz, Austria
DACH-BASED BIFUNCTIONAL UREA/AMMONIUM SALT CATALYZED ASYMMETRIC α -HYDROXYLATION OF β -KETOESTERS
- Jere **Mannisto** *PO-86*
University of Helsinki, Helsinki, Finland
ONE-STEP SYNTHESIS OF SUBSTITUTED 2-OXAZOLIDINONES VIA BASE-CATALYZED CO₂-FIXATION AND AZA-MICHAEL ADDITION
- Beata **Marcol-Szumilas** *PO-87*
University of Silesia, Katowice, Poland
PROCESS FOR OBTAINING LOW AND HIGH BOILING 1-PROPENYL AND BIS(1-PROPENYL) ETHERS AND SULPHIDES TOWARDS RENEWABLE CATALYTIC SYSTEMS
- Tatenda **Mareya** *PO-88*
Waterford Institute of Technology, Waterford, Ireland
BIOTRANSFORMATIONS EMPLOYING NITRILE HYDROLYZING ENZYMES TOWARDS THE ENANTIOSELECTIVE SYNTHESIS OF β -AMINO ACIDS
- Gilles **Marghem** *PO-89*
Université Catholique de Louvain (UCL), Louvain-la-Neuve, Belgium
COPPER CATALYZED 1,4-BROOK REARRANGEMENT OF α,β -UNSATURATED ACYLSILANE
- Raul **Martin-Montero** *PO-90*
Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain
NICKEL CATALYZED REDUCTIVE DEAMINATIVE ARYLATION AT sp^3 CARBON CENTERS
- Daniele **Mazzarella** *PO-91*
Institut Català d'Investigació Química (ICIQ), Tarragona, Spain
ASYMMETRIC PHOTOCATALYTIC C-H FUNCTIONALIZATION OF TOLUENE AND DERIVATIVES
- Roisin **McCarthy** *PO-92*
University College Dublin, Dublin, Ireland
APPLICATIONS OF (THIO)OXALAMIDES IN ORGANOCATALYSIS: SYNTHESIS AND ACTIVITY OF OXALIC DERIVATIVES
- Calum **McLaughlin** *PO-93*
University of St. Andrews, St. Andrews, Scotland
INTERMOLECULAR CATALYST TURNOVER IN ENANTIOSELECTIVE AMMONIUM ENOLATE CATALYSIS: A SYNTHETIC AND MECHANISTIC STUDY

- Andrea Menichetti** *PO-94*
University of Pisa, Pisa, Italy
DEVELOPING NEW WAYS TO INTRODUCE THE BORON ATOM IN ORGANIC MOLECULES BY RING-OPENING REACTIONS
- Luuk Mestrom** *PO-95*
Delft University of Technology, Delft, The Netherlands
ANOMERIC CONTROL FOR TREHALOSE TRANSFERASE
- Tjark H. Meyer** *PO-96*
Georg-August-Universität, Göttingen, Germany
RESOURCE ECONOMY BY COBALTAELECTROCATALYSIS: MERGING ELECTROCHEMISTRY AND C–H ACTIVATION
- Mateja Mihelač** *PO-97*
University of Ljubljana, Ljubljana, Slovenia
PALLADIUM CATALYZED INTERMOLECULAR IMINE FORMATION
- Jun Miyatake Onozabal** *PO-98*
University of London, London, United Kingdom
PHOTOCATALYTIC TRANSFORMATIONS OF ALKENES: STUDIES ON PHOTOREDUCTION AND E→Z ISOMERIZATION
- Jasper Möhler** *PO-99*
ETH Zürich, Zürich, Switzerland
CONTROL OVER ENAMINE PYRAMIDALIZATION GIVES ACCESS TO N-HETEROCYCLIC SUBSTITUTED γ -NITROALDEHYDES
- Arup Mondal** *PO-100*
Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany
DUAL LIGAND-ENABLED NONDIRECTED C-H CYANATION OF ARENES
- Daniel Moock** *PO-101*
Westfälische Wilhelms-Universität Münster, Münster, Germany
HYDROGENATION OF BORYLATED ARENES
- Brigita Mudráková** *PO-102*
Comenius University Bratislava, Bratislava, Slovakia
DIASTEREOSELECTIVE PALLADIUM-CATALYZED C–H ARYLATION OF FERROCENYLMETANEAMINES WITH ARYLBORONIC ACIDS AND PINACOL ESTERS
- Francesco Mutti** *PO-103*
University of Amsterdam, Amsterdam, The Netherlands
RECENT DEVELOPMENTS IN BIOCATALYTIC REDOX REACTIONS
- Agnieszka Nawara-Hultsch** *PO-104*
University of Vienna, Vienna, Austria
UNSYMMETRICAL Mn(I) PNNOP Pincer Catalysts for Hydrogen Borrowing Reactions
- Andrea Nikolic** *PO-105*
University of Belgrade, Belgrade, Serbia
PALLADIUM CATALYZED N-ARYLATION OF 1H-TETRAZOLE-5-AMINES
- Hidetoshi Noda** *PO-106*
Institute of Microbial Chemistry (BIKAKEN), Tokyo, Japan
SYNTHESIS OF UNPROTECTED, BICYCLIC AND SPIROCYCLIC β -AMINO ACIDS
- Ryan O'Gara** *PO-107*
University College Dublin, Dublin, Ireland
LIGAND DESIGN IN THE ASYMMETRIC SYNTHESIS OF TERTIARY ALCOHOLS

- Gerardo M. Ojeda** *PO-108*
University of Leuven, Leuven, Belgium
DEALING WITH CYCLIZATION IN THE SYNTHESIS OF SPIROINDOL(EN)INES AND TETRAZOLE-ISOQUINOLONES/PYRIDONES HYBRID
- Patrizio Orecchia** *PO-109*
Technische Universität Berlin, Berlin, Germany
TRANSFER HYDROCYANATION OF α - AND α,β -SUBSTITUTED STYRENES CATALYZED BY BORON LEWIS ACIDS
- Marlyn Ortiz** *PO-110*
Universidad Industrial de Santander, Piedecuesta, Colombia
SYNTHESIS OF C-1 ALKYNYL TETRAHYDROISOQUINOLINE DERIVATIVES THROUGH THE A³ REDOX-NEUTRAL COUPLING USING COPPER-CATALYSIS AND PHOTOCATALYSIS
- Bünyamin Özkaya** *PO-111*
RWTH Aachen University, Aachen, Germany
ELECTRON-HOLE CATALYZED ORTHO-HYDROARYLATION
- Benedetta Palucci** *PO-112*
Universitat Rovira i Virgili, Tarragona, Spain
Pd-CATALYZED HYDROFORMYLATION USING FORMALDEHYDE AS SYNGAS SURROGATES
- Ádám Márk Pálvölgyi** *PO-113*
TU Wien, Vienna, Austria
NOVEL CARBAMATE-BASED P,O-LIGANDS IN ASYMMETRIC ALLYLIC ALKYLATIONS
- Naziya Parveen** *PO-114*
Indian Institute of Technology Madras, Chennai, India
STABLE AND REUSABLE Pd-BNPs CATALYSED STEREOSELECTIVE SYNTHESIS OF (E)-3-ALKYLIDENE OXINDOLES
- Martin Pauze** *PO-115*
University of the Basque Country, Donostia/San Sebastian, Spain
UNPRECEDENTED MULTICOMPONENT ORGANOCATALYTIC SYNTHESIS OF PROPARGYLIC ESTERS VIA CO₂ ACTIVATION
- Marie-Idrissa Picher** *PO-116*
University of Stuttgart, Stuttgart, Germany
IRON-CATALYZED CYCLOPROPANATION OF 1,3-ENYNES UNDER THERMAL OR PHOTOCHEMICAL CONDITIONS
- Giovanni Poli** *PO-117*
Sorbonne Universités, Paris, France
STUDIES ON THE Ru-CATALYZED CARBONYLATIVE MURAI REACTION
- Simona Pompei** *PO-118*
University of Graz, Graz, Austria
REGIOSELECTIVITY IN BIOCATALYTIC O-METHYLATION OF CATECHOLS
- Martin H. G. Precht** *PO-119*
Roskilde Universitet, Roskilde, Denmark
PARADIGMS OF COOPERATIVE VS. NON-COOPERATIVE LIGANDS IN METAL Pincer COMPLEXES IN (DE)HYDROGENATION REACTIONS
- Mahesh Puthanveedu** *PO-120*
Max-Planck-Institute for Molecular Physiology, Dortmund, Germany
CATALYTIC METAL-FREE CROSS-COUPLING OF HETEROAROMATIC N-OXIDES WITH ORGANOSILANES

- Deyun Qian** *PO-121*
Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland
ENANTIOSELECTIVE SYNTHESIS OF CHIRAL SULFONES BY BASE METAL-CATALYZED ASYMMETRIC CROSS-COUPPLING REACTION
- Shen Qu** *PO-122*
University of St. Andrews, St. Andrews, Scotland
ISOTHIUREA-CATALYSED REGIOSELECTIVE ACYLATIVE KINETIC RESOLUTION OF AXIALLY CHIRAL BIARYL DIOLS
- Maria-João R.P. Queiroz** *PO-123*
Universidade do Minho, Braga, Portugal
PEG₄₀₀ AS SOLVENT IN THE SYNTHESIS OF NEW 7-[4-ALKYL OR (HET)ARYL-1*H*-1,2,3-TRIAZOL-1-YL]THIENO[3,2-*b*]PYRIDINES BY Cu(I)-CATALYZED AZIDE-ALKYNE CYCLOADDITION
- Mirae Ra** *PO-124*
Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea
A POTENTIAL N-HETEROCYCLIC BASED LIQUID ORGANIC HYDROGEN CARRIERS
- Adam Rajkiewicz** *PO-125*
University of Warsaw, Warsaw, Poland
IODONIUM SALTS AS GROUP TRASFER REAGENTS - N-HETEROCYCLIC CARBENE-CATALYZED SYNTHESIS OF VINYL AND PROPARGYL KETONES
- Fabian Rami** *PO-126*
University of Stuttgart, Stuttgart, Germany
IRON-CATALYSED HYDROBORATION OF UNSATURATED C-C BONDS: BORON-SOURCE CONTROLLED SELECTIVITY
- Xavi Ribas** *PO-127*
Universitat Autònoma de Barcelona, Bellaterra, Spain
OXIDANT-FREE Au(I)/Au(III) C-HETEROATOM CROSS-COUPPLING CATALYSIS
- Saara Riuttamäki** *PO-128*
University of Jyväskylä, Jyväskylä, Finland
CARBOXYLATE CATALYSED ISOMERISATION OF UNSATURATED NAC-THIOESTERS
- Sylvain Roland** *PO-129*
Sorbonne Universités, Paris, France
BORYLATION OF ALKYNES WITH CYCLODEXTRIN-ENCAPSULATED N-HETEROCYCLIC CARBENE COPPER COMPLEXES
- Tamal Roy** *PO-130*
University of Copenhagen, Copenhagen, Denmark
CARBON DIOXIDE-CATALYZED STEREORELECTIVE CYANATION OF COUMARINS
- Daniel Sack** *PO-131*
Karlsruhe Institute of Technology, Karlsruhe, Germany
SHORT PEPTIDES WITH PHOTOCATALYTIC ACTIVITY FOR THE NUCLEOPHILIC ADDITION OF METHANOL TO STYRENE DERIVATIVES
- Aleksi Sahari** *PO-132*
University of Helsinki, Helsinki, Finland
ASYMMETRIC LACTONE SYNTHESIS BY REDUCTIVE OLEFIN ACTIVATION AND CO₂-FIXATION
- Aitor Sainz Martinez** *PO-133*
TU Wien, Vienna, Austria
CONTINUOUS TRANSFORMATION OF CARBON DIOXIDE USING SUPPORTED IONIC LIQUIDS

- David Savary** *PO-134*
University of Basel, Basel, Switzerland
ENANTIOSELECTIVE SYNTHESIS OF FLUORADENES BY C(sp²)-H ARYLATION AND APPLICATION TO THE SYNTHESIS OF BUCKYBOWLS
- Fabian Scharinger** *PO-135*
TU Wien, Vienna, Austria
ASYMMETRIC TRANSFER HYDROGENATION OF ENONES VIA COUNTERANION ENHANCED CATALYSIS
- Florian Schiel** *PO-136*
Boehringer Ingelheim RCV GmbH & Co KG, Vienna, Austria
DUAL PHOTOREDOX CATALYSED sp²-sp³ CROSS-ELECTROPHILE COUPLING IN A SELF-DESIGNED AND 3D PRINTED PHOTOREACTOR
- Christian Schiwiek** *PO-137*
Technical University of Munich, Munich, Germany
HIGHLY ENANTIOSELECTIVE CHROMIUM(II) PINCER CATALYZED HYDROSILYLATION OF KETONES
- Martin Schnurr** *PO-138*
ETH Zürich, Zürich, Switzerland
Cy-SUBSTITUENTS AS TOOLS TO INFLUENCE THE REACTIVITY AND STEREOSELECTIVITY OF PROLINE BASED CATALYSTS
- David Schönbauer** *PO-139*
TU Wien, Vienna, Austria
TETRAALKYLAMMONIUM SALTS AS SURROGATES FOR OLEFINS IN C-H ACTIVATION
- Ayato Sekine** *PO-140*
Waseda University, Tokyo, Japan
CONSECUTIVE INTRAMOLECULAR DEHYDRO-DIELS-ALDER REACTIONS OF HETEROATOM-TETHERED TETRAYNES FOR THE SYNTHESIS OF HETEROLE-CONTAINING POLYCYCLIC COMPOUNDS
- Eloisa Serrano** *PO-141*
Westfälische Wilhelms-Universität Münster, Münster, Germany
DIASTEREODIVERGENT SYNTHESIS OF ENANTIOENRICHED α,β -DISUBSTITUTED γ -BUTYROLACTONES VIA COOPERATIVE CATALYSIS
- Saad Shaaban** *PO-142*
Max-Planck-Institute for Molecular Physiology, Dortmund, Germany
ENANTIOSELECTIVE C-H ACTIVATION WITH Rh(I)JasCp COMPLEXES
- Ji-cheng Shi** *PO-143*
Guangdong University of Petrochemical Technology, Maoming, China
TERPHENYL PHOSPHANES: A NEW GENERATION OF LIGAND FOR PALLADIUM-CATALYZED AMINATION OF ARYL HALIDES WITH PRIMARY AND SECONDARY ARYL AMINES
- Jack Slater** *PO-144*
Sheffield Hallam University, Sheffield, UK
PHOTOREDOX MEDIATED SYNTHESIS OF SULFINATE ESTERS FROM TOSYLHYDRAZONE SUBSTRATES
- Rosie J. Somerville** *PO-145*
Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain
DINICKEL OXIDATIVE ADDITION COMPLEXES IN C-O CLEAVAGE: RELEVANCE IN CATALYTIC C-Si BOND-FORMATION
- Filip Stanek** *PO-146*
Polish Academy of Science, Warsaw, Poland
VISIBLE-LIGHT-MEDIATED α -OXYGENATION OF 3-(N,N-DIMETHYLAMINOMETHYL)-INDOLES TO ALDEHYDES

- N. Sundaravelu** *PO-147*
Indian Institute of Technology Madras, Chennai, India
THIOL-COORDINATED IODONIUM ION CATALYSIS: A DOMINO SYNTHESIS OF Z-SELECTIVE α,β -DIPHENYLTHIO ENONES FROM EASILY ACCESSIBLE SECONDARY ALCOHOLS
- Redouane Tabti** *PO-148*
University of Strasbourg, Strasbourg, France
AMINO-IMIDAZOLONES AS NOVEL CHELATORS FOR METAL IONS: SYNTHESIS, SOLUTION POTENTIOMETRIC STUDY
- Hideaki Takano** *PO-149*
Waseda University, Tokyo, Japan
RHODIUM-CATALYZED REGIOSELECTIVE ACTIVATION OF STERICALLY HINDERED C-C BOND OF BIPHENYLENE
- Tobias Täufer** *PO-150*
Leibniz Institute for Catalysis, Rostock, Germany
SYNTHESIS OF ACYCLIC DIALKYL AMINES VIA BUCHWALD-HARTWIG AMINATION
- Gaël Tran** *PO-151*
University of Geneva, Geneva, Switzerland
ENANTIOSELECTIVE NICKEL-CATALYZED AMINATION OF 2-SUBSTITUTED 1,3-DIENES
- Ilerasia Triandafillidi** *PO-152*
National and Kapodistrian University of Athens, Athens, Greece
PHOTOCATALYTIC SYNTHESIS OF γ -LACTONES FROM ALKENES: HIGH RESOLUTION MASS SPECTROMETRY AS A TOOL TO STUDY PROTOREDOX REACTIONS
- Paz Trillo** *PO-153*
Umeå University, Umeå, Sweden
STRAIGHTFORWARD SYNTHESIS OF α -AMINO NITRILES THROUGH $\text{Mo}(\text{CO})_6$ -CATALYZED REDUCTIVE FUNCTIONALIZATION OF CARBOXAMIDES
- Matic Urlep** *PO-154*
University of Ljubljana, Ljubljana, Slovenia
SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF $\text{Pt}(\text{II})$ PCP PINCER COMPLEXES
- Erik Van der Eycken** *PO-155*
Katholieke Universiteit Leuven, Leuven, Belgium
GOLD-TRIGGERED DEAROMATIZATION CASCADES
- Greta Vastakaite** *PO-156*
ETH Zürich, Zürich, Switzerland
CATALYTICALLY ACTIVE PEPTIDES FOR CONJUGATE ADDITION REACTIONS
- Tomas Vojkovsky** *PO-157*
Okinawa Institute of Science and Technology Graduate University, Onna, Japan
CYCLOPROPANATION OF ALIPHATIC ESTERS AND ALCOHOLS EXTENDED TO ONE-STEP CATALYTIC LINEAR SULFONE
- Michael Winter** *PO-158*
Johannes Kepler University Linz, Linz, Austria
UMPOLUNG REACTIONS OF IMINES FOR THE SYNTHESIS OF α -TRIFLUOROMETHYLATED AMINO ACIDS
- Sina Witzel** *PO-159*
Heidelberg University, Heidelberg, Germany
RECENT ADVANCES IN "ONLY" GOLD-CATALYZED PHOTOCHEMISTRY
- Jiufeng Wu** *PO-160*
University of St. Andrews, St. Andrews, UK
PROBING THE REACTIVITY OF α,β -UNSATURATED ACYL AMMONIUM INTERMEDIATES

- Shaohua Xiang** *PO-161*
Southern University of Science and Technology, Shenzhen, China
ORGANOCATALYTIC ASYMMETRIC SYNTHESIS OF ATROPISMERIC BIARYLS
- Shoko Yamazaki** *PO-162*
Nara University of Education, Nara, Japan
INTRA- AND INTERMOLECULAR STEREOSELECTIVE [2+2] CYCLOADDITION REACTIONS OF ETHENETRICARBOXYLATES AND STYRENES
- Kosuke Yasui** *PO-163*
Osaka University, Osaka, Japan
N-HETEROCYCLIC CARBENE-CATALYZED CONCERTED NUCLEOPHILIC AROMATIC SUBSTITUTION OF ARYL FLUORIDES BEARING α,β -UNSATURATED CARBONYL MOIETY
- Jian-Heng Ye** *PO-164*
Westfälische Wilhelms-Universität Münster, Münster, Germany
Cp*Ir(III) CATALYZED BRANCH SELECTIVE ALLYLIC AMIDATION OF UNACTIATED OLEFINS
- Congjun Yu** *PO-165*
RWTH Aachen University, Aachen, Germany
Cu(II)-CATALYZED CROSS-DEHYDROGENATIVE ORTHO-AMINOMETHYLATION OF PHENOLS
- Yu-Chao Yuan** *PO-166*
Université de Rennes 1, Rennes, France
SELECTIVE FUNCTIONALIZATION OF CYCLIC IMIDES AND AMIDES WITH RUTHENIUM CATALYSTS
- Lei Zhang** *PO-167*
Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
PHOTOELECTROCATALYTIC ARENE C-H AMINATION
- Zhikun Zhang** *PO-168*
Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
ALKENE HYDROSILYLATION CATALYZED BY EASILY ASSEMBLED Ni(II)-CARBOXYLATE MOFs
- Birte M. Zimmermann** *PO-169*
Technische Universität Berlin, Berlin, Germany
CHEMOSELECTIVE COPPER(I)-CATALYZED CONJUGATE REDUCTIONS OF ENOATES USING H₂
- Christoph Zippel** *PO-170*
Karlsruhe Institute of Technology, Karlsruhe, Germany
RHODIUM CATALYZED CYCLOPROPANATION WITH α -ALKYL- α -DIAZO ESTERS
- Viktoriia Zubar** *PO-171*
RWTH Aachen University, Aachen, Germany
CO₂-DERIVED CARBONATES AND POLYCARBONATES TO METHANOL AND DIOLS VIA METAL LIGAND COOPERATIVE CATALYSIS
- Erna Zukic** *PO-172*
TU Wien, Vienna, Austria
FROM RENEWABLE TO USABLE - BIOTRANSFORMATION FROM CARVONE TO CARVOLACTONE AND ITS COPOLYMERISATION WITH LACTIDE

Medicinal Chemistry and Chemical Biology

- Dan Adolfsson** *PO-173*
 Umeå University, Umeå, Sweden
SYNTHESIS OF MULTI RING-FUSED PEPTIDOMIMETICS INTERACTING WITH α -SYNUCLEIN FIBRILS
- Eirin Alme** *PO-174*
 University of Bergen, Bergen, Norway
SYNTHESIS AND OPTIMIZATION OF 10H-PHENOTHIAZINE ANALOGUES FOR THE INHIBITION OF AUTOPHAGY
- Usama Ammar** *PO-175*
 Korea Institute of Science and Technology, Seoul, Republic of Korea
ANTICANCER PROFILE OF NEWLY SYNTHESIZED B-RAF INHIBITORS POSSESS 5(PYRIMIDIN-4-YL)IMIDAZO[2,1-b]OXAZOLE SCAFFOLD
- Francesco Angelucci** *PO-176*
 University of Bergen, Bergen, Norway
DEVELOPING NOVEL PET TRACERS FOR HYPOXIA
- Ove Alexander Høgmoen Åstrand** *PO-177*
 University of Oslo, Oslo, Norway
OVERCOMING METALLO- β -LACTAMASE MEDIATED RESISTANCE IN BACTERIA
- Fadi M. Awadallah** *PO-178*
 Cairo University, Cairo, Egypt
INHIBITION STUDIES ON A PANEL OF HUMAN CARBONIC ANHYDRASES WITH N1-SUBSTITUTED SECONDARY SULFONAMIDES INCORPORATING THIAZOLINONE OR IMIDAZOLONE-INDOLE TAILS
- Aleksandra Balliu** *PO-179*
 Stockholm University, Stockholm, Sweden
SYNTHESIS AND CHEMICAL MODIFICATIONS OF PEPTIDE CONJUGATES: INVESTIGATING PEPTIDE-PROTEIN INTERACTIONS
- Christine Beemelmans** *PO-180*
 Hans-Knöll Institute (HKI), Jena, Germany
UNLOCKING NATURES CHEMICAL TREASURE TROVE - NOVEL NATURAL PRODUCTS FROM MICROBIAL SYMBIONTS
- Dattatry Bhosale** *PO-181*
 Veterinary Research Institute, Brno, Czech Republic
SYNTHESIS, CHARACTERIZATION AND EVALUATION OF AMINOXY AND IONIZABLE LIPIDS FOR THE MODULAR ASSEMBLY OF LIPID-BASED NANOPARTICLES FOR EFFICIENT DELIVERY OF THERAPEUTIC NUCLEIC ACIDS
- Karol Biernacki** *PO-182*
 Gdansk University of Technology, Gdansk, Poland
NEW POTENT STEROID SULFATASE (STS) INHIBITORS BASED ON FLUORINATED 4-(1-PHENYL-1H-[1,2,3]TRIAZOL-4-YL)-PHENYL SULFAMATES. SYNTHESIS AND BIOLOGICAL EVALUATION
- Spyridon Bousis** *PO-183*
 Saarland University, Saarbrücken, Germany
ENERGY-COUPPLING FACTOR TRANSPORTER, A NOVEL TARGET FOR ANTIBIOTIC DEVELOPMENT
- Glen Brodie** *PO-184*
 University of Glasgow, Glasgow, United Kingdom
BACTACS: A POTENTIAL STRATEGY FOR THE SELECTIVE DEGRADATION OF PROTEINS WITHIN PROKARYOTES

- Ana T. **Carmona** **PO-185**
Universidad de Sevilla, Sevilla, Spain
INHIBITION OF LYSOSOMAL GLYCOSIDASES BY MULTIMERIC PRESENTATIONS OF PYRROLIDINE-BASED IMINOSUGARS
- Tomás **Chávez** **PO-186**
University of Chile, Santiago, Chile
ERINE 242^{5,46} AND ALANINE 222^{5,46} AS DETERMINANTS OF 5-HT_{2A/2C} SELECTIVITY
- Slim **Chiha** **PO-187**
University of Cologne, Cologne, Germany
MAKING THE UNDRUGGABLE *DRUGGABLE*: SYNTHETIC PROLIN-DERIVED MODULES (ProMs) AS BUILDING BLOCKS FOR RATIONAL AND LIBRARY-BASED DRUG DEVELOPMENT
- Daniela **Cintulova** **PO-188**
TU Wien, Vienna, Austria
SYNTHESIS AND BIOLOGICAL PROFILING OF MEPHEDRONE METABOLITES
- Davide **Cirillo** **PO-189**
University of Bergen, Bergen, Norway
DRUG REPURPOSING: SULFASALAZINE AS A NEW ANTICANCER TREATMENT. STUDY OF TUMOUR DRUG DISTRIBUTION THROUGH PET AND MRI IMAGING
- Rafaela **Conceicao** **PO-190**
TU Wien, Vienna, Austria
SYNTHESIS OF DOUBLE-CLICK AZOBENZENES FOR AN EASY FUNCTIONALIZATION OF BIOMOLECULES
- Toan **Dao-Huy** **PO-191**
Hanoi University of Science and Technology, Hanoi, Vietnam
SYNTHESIS OF BENZO-FUSED NEOLIGNANS AS POTENTIAL ANTI-INFLAMMATORY AGENTS
- Alice **Di Pasquale** **PO-192**
University of Birmingham, Birmingham, United Kingdom
SYNTHESIS OF BENZOBOROXOLE DERIVATIVES AS RECEPTORS FOR SIALIC ACID
- Clemens **Dialer** **PO-193**
Ludwig-Maximilians University, Munich, Germany
A CLICK-CHEMISTRY LINKED 2'3'-cGAMP ANALOGUE
- Tamas **Farkas** **PO-194**
PROGRESSIO Engineering Bureau Ltd., Budapest, Hungary
SYNTHESIS AND BIOLOGICAL EVALUATION OF THE PRECURSOR OF RADIOACTIVE IODINELABELED BIOACTIVE COMPOUND
- Minghao **Feng** **PO-195**
Université Paris-Saclay, Gif-sur-Yvette, France
REGIOSELECTIVE CHLORINATION OF IMINOSYDNONE FOR ULTRAFast CLICK AND RELEASE
- Riham **George** **PO-196**
Cairo University, Cairo, Egypt
SYNTHESIS, ANTI-PROLIFERATIVE ACTIVITY AND 2D-QSAR STUDY OF SOME 8-ALKYL-2,4-BISBENZYLIDENE-3-NORTROPINONES
- Sascha **Heinrich** **PO-197**
Ruhr-Universität Bochum, Bochum, Germany
SEMISYNTHESIS OF NOVEL MACROLIDE-BASED ANTIBIOTICS
- Fabian **Hogenkamp** **PO-198**
Heinrich-Heine-University Düsseldorf, Jülich, Germany
SYNTHESIS OF PHOTOCAGED CARBOHYDRATES

- MariaTeresa Iorio** *PO-199*
 TU Wien, Vienna, Austria
NEW MODIFICATIONS OF AN OLD SCAFFOLD: PYRAZOLOQUINOLINONE DERIVATIVES AND ANALOGUES AS ACTIVE COMPOUNDS ON GABA_A RECEPTORS
- Ivanka Jeric** *PO-200*
 Ruđer Bošković Institute, Zagreb, Croatia
SYNTHESIS OF 1,2-DIAZETIDIN-3-ONES VIA THE UGI REACTION COMPRISING α -HYDRAZINO ACIDS
- M. Consuelo Jiménez** *PO-201*
 Universitat Politècnica de València, València, Spain
PHOTOBINDING OF TRIFLUSAL TO HUMAN SERUM ALBUMIN INVESTIGATED BY FLUORESCENCE, PROTEOMIC ANALYSIS AND COMPUTATIONAL STUDIES
- Kwan-Young Jung** *PO-202*
 Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea
NICLOSAMIDE DERIVATIVES INHIBIT CIP2A AND REACTIVATE TUMOR SUPPRESSOR PROTEIN PHOSPHATASE 2A IN NON-SMALL CELL LUNG CANCER CELLS
- Zoltan Kaleta** *PO-203*
 PROGRESSIO Engineering Bureau Ltd., Budapest, Hungary
SI-SUBSTITUTED XANTHENE FLUORESCENT DYES WITH NEAR-INFRARED EMISSION
- Prashant Khirsariya** *PO-204*
 Masaryk University, Brno, Czech Republic
NOVEL CHK1 INHIBITOR MU380 EXHIBITS SIGNIFICANT SINGLE-AGENT ACTIVITY IN TP53-MUTATED CHRONIC LYMPHOCYTIC LEUKEMIA CELLS
- Susanne Kirchner** *PO-205*
 Karlsruhe Institute of Technology, Karlsruhe, Germany
PHOTOCHROMIC PEPTIDES FOR LIGHT-TRIGGERED DRUG DELIVERY AND BEYOND
- Philipp Klahn** *PO-206*
 Technical University of Braunschweig, Braunschweig, Germany
SYNTHESIS AND BIOCHEMICAL EVALUATION OF AN ARTIFICIAL, FLUORESCENT GLUCOSINOLATE (GSL)
- Eva Korytiaková** *PO-207*
 Ludwig-Maximilians University, Munich, Germany
INVESTIGATION OF ACTIVE DEMETHYLATION OF 5-METHYL-2'-DEOXYCYTIDINE
- George Koutoulougenis** *PO-208*
 National and Kapodistrian University of Athens, Athens, Greece
SYNTHESIS OF NITRO DERIVATIVES AND FATTY ACID ESTERS OF RICINOLEIC ACID STARTING FROM CASTOR OIL
- Frank Kraus** *PO-209*
 University of Stuttgart, Stuttgart, Germany
A SHORT SYNTHETIC APPROACH TO A LIBRARY OF NON NATURAL PPAP DERIVATIVES WITH ANTIMICROBIAL PROPERTIES AND INSIGHTS INTO THEIR ANTIBIOTIC MECHANISM
- Bernhard Markus Krause** *PO-210*
 University of Cologne, Cologne, Germany
ENZYME-TRIGGERED CO-RELEASING MOLECULES (ET-CORMs) AS VERSATILE AND POWERFUL MEDICINAL AGENTS
- Mounsef Lahboubi** *PO-211*
 Université libre de Bruxelles, Bruxelles, Belgium
A BROADLY APPLICABLE AND STRAIGHTFORWARD ENTRY TO SELECTIVELY DEUTERATED AMINES

- Tlabo Leboho** **PO-212**
University of the Witwatersrand, Johannesburg, South Africa
THE ACID-CATALYSED SYNTHESIS OF 7-AZAINDOLES FROM 3-ALKYNYL-2-AMINOPYRIDINES AND THEIR ANTIMICROBIAL ACTIVITY
- Daniel Lechnitz** **PO-213**
Hans-Knöll Institute (HKI), Jena, Germany
EFFICIENT SYNTHESIS OF SPHINGOLIPID AND SPHINGOSINE-TYPE CHEMICAL MEDIATORS OF MICROBIAL ORIGIN
- Dimas Lima** **PO-214**
Federal University of Alagoas
SYNTHESIS AND EVALUATION OF THE LARVICIDAL ACTIVITY OF THE DERIVATIVES OF THE CINNAMIC ACID IN THE COMBAT TO *Aedes Aegypti*
- Priscila López Rojas** **PO-215**
Universidad de La Laguna, La Laguna, Spain
SYNTHESIS OF ANTHRAQUINONES AS HUMAN PROTEIN KINASE CK2 INHIBITORS
- Frida Lundevall** **PO-216**
University of Bergen, Bergen, Norway
SYNTHESIS AND INVESTIGATION OF Ag-NHC COMPLEXES WITH CYTOTOXIC PROPERTIES TOWARDS CELL LINES MODELLING ACUTE MYELOID LEUKEMIA
- Antonin Lycka** **PO-217**
Research Institute for Organic Syntheses (VUOS), Pardubice, Czech Republic
IMIDAZO[1,2-c]PYRIMIDIN-5(6H)-ONE AS A NOVEL CORE OF CYCLINDEPENDENT KINASE 2 INHIBITORS
- Pratibha Magar** **PO-218**
University of Pardubice, Pardubice, Czech Republic
SYNTHESIS AND ANTICANCER ACTIVITY OF NOVEL SALICYLAMIDE DERIVATIVES
- Bruno Aleksander Martek** **PO-219**
University of Ljubljana, Ljubljana, Slovenia
¹H-¹⁵N HMBC NMR AS A TOOL FOR RAPID IDENTIFICATION OF AZAINDOLE CANNABINOID DRUGS
- Michal Maryška** **PO-220**
University of Chemistry and Technology, Prague, Czech Republic
DESIGN, SYNTHESIS AND EVALUATION OF NOVEL INHIBITORS OF KYNURENINE AMINOTRANSFERASE II
- Viktoras Masevicius** **PO-221**
Vilnius University, Vilnius, Lithuania
NOVEL FUNCTIONALITYS OF ADOMET ANALOGS FOR NUCLEIC ACIDS LABELING
- Ján Matyašovský** **PO-222**
Academy of Science of the Czech Republic, Prague, Czech Republic
2-SUBSTITUTED dATP DERIVATIVES AS BUILDING BLOCKS FOR ENZYMATIC SYNTHESIS OF DNA MODIFIED IN THE MINOR GROOVE
- Lukas Mikulu** **PO-223**
University of Chemistry and Technology, Prague, Czech Republic
SYNTHETIC DERIVATIVES OF PHYTOCANNABINOIDS
- Takashi Misawa** **PO-224**
National Institute of Health Sciences, Kanagawa, Japan
DEVELOPMENT OF AMPHIPATHIC CELL-PENETRATING FOLDAMERS FOR DELIVERY OF BIOMACROMOLECULES
- Antonio J. Moreno-Vargas** **PO-225**
Universidad de Sevilla, Sevilla, Spain
CYSTEINE-SPECIFIC DUAL LABELLING OF PROTEINS USING STRAINED [2.2.1]AZABICYCLIC VINYL SULFONES

- Viktoria Mrden Debono** **PO-226**
Georg-August-Universität, Göttingen, Germany
SYNTHESIS OF FLUOROGENIC PROBES FOR STABILIZATION OF SUPEROXIDE DISMUTASE (SOD1)
- Zeeshan Muhammad** **PO-227**
University of Bergen, Bergen, Norway
SYNTHESIS AND STRUCTURE-BASED STUDIES OF FMN RIBOSWITCH LIGANDS: EXPLORING FMN RIBOSWITCH TARGET TO FIND NEW ANTIBIOTICS
- Hayate Nagabuchi** **PO-228**
Fukuoka University, Fukuoka, Japan
SYNTHETIC STUDIES OF NOVEL SPIRO PYRAZOL-3-ONES CONTAINING QUINAZOLINE AND/OR OXIRANE MOIETY
- Sebastian Neidig** **PO-229**
Ludwig-Maximilians University, Munich, Germany
EN ROUTE TO NEISSERIA MENINGITIDIS SEROGROUP Y FULLY SYNTHETIC VACCINE CANDIDATES
- Michał Nowak** **PO-230**
Gdansk University of Technology, Gdansk, Poland
SYNTHESIS AND ANTIFUNGAL ACTIVITY STUDY OF TRIMETHYL LOCK-MODIFIED GLUCOSAMINE-6-PHOSPHATE SYNTHASE INHIBITOR
- Ephraim Okolo** **PO-231**
University of Leeds, Leeds, United Kingdom
A "TOP DOWN" APPROACH TO THE SYNTHESIS OF COMPLEX, DIVERSE LEAD-LIKE SCAFFOLDS
- Stuart Pearson** **PO-232**
AstraZeneca, Macclesfield, United Kingdom
RECENT ADVANCES IN HETEROCYCLIC SYNTHESIS IN AstraZeneca ONCOLOGY
- Karine Porte** **PO-233**
Université Paris-Saclay, Gif-sur-Yvette, France
CONTROLLED RELEASE OF MICELLE PAYLOAD VIA SEQUENTIAL ENZYMATIC AND BIOORTHOGONAL REACTIONS IN LIVING SYSTEMS
- Monireh Pourghasemi Lati** **PO-234**
Stockholm University, Stockholm, Sweden
SYNTHESIS OF A NOVEL CYCLIC PEPTIDE LIBRARY ENABLED BY C-H FUNCTIONALIZATIONS AND THE DNA-ENCODED LIBRARY TECHNOLOGY
- Maja Przybyłowska** **PO-235**
Gdańsk University of Technology, Gdańsk, Poland
SYNTHESIS OF PHOSPHORUS TACRINE ANALOGUES AS A NEW POTENTIAL ANTI-ALZHEIMER'S DISEASE AGENTS
- Luka Raguz** **PO-236**
Hans-Knöll Institute (HKI), Jena, Germany
TOTAL SYNTHESIS OF SPHINGOLIPIDS AND SPHINGOSINE-TYPE SIGNALING MOLECULES OF MICROBIAL ORIGIN
- Kheironnesae Rahimidashaghoui** **PO-237**
Academy of Science of the Czech Republic, Prague, Czech Republic
RADICAL FLUOROALKYLATION OF NITROGEN HETEROCYCLES AND AROMATIC AMINO ACID RESIDUES IN PEPTIDES AND PROTEINS
- Gemma Maria Rodriguez-Muñiz** **PO-238**
Universitat Politècnica de València, València, Spain
SYNTHESIS OF A POTENTIAL COMPOUND BASED ON A DIAMINODIPHENYLBUTADIENE TO REPAIR DNA-LESIONS

- Laura G Sarbu** *PO-239*
Alexandru Ioan Cuza University of Iasi, Iasi, Romania
TRICYCLIC FLAVONOIDS WITH 1,3-DITHIOLIUM SUBSTRUCTURE: SYNTHESIS AND ANTIBACTERIAL ACTIVITY
- Souvik Sarkar** *PO-240*
Umeå University, Umeå, Sweden
DESIGN, SYNTHESIS AND EVALUATION OF NOVEL Δ^2 -THIAZOLINO 2-PYRIDONE DERIVATIVES AS MYCOBACTERIUM TUBERCULOSIS TOLERANCE INHIBITORS
- Robert Schirmacher** *PO-241*
CBIN Göttingen, Göttingen, Germany
THE SYNTHESIS OF 2,5-DISUBSTITUTED PYRROLES FOR THE INHIBITION OF SOD1 AGGREGATION IN ALS
- Inga Shchelik** *PO-242*
University of Zurich, Zurich, Switzerland
CAGING AND CONTROLLED RELEASE OF AN ANTIBACTERIAL DRUG BY CELL SURFACE FUNCTIONALIZATION
- Benjamin Smith** *PO-243*
Stanford University, Stanford, USA
IDENTIFICATION OF ONCOGENE CONTROLLED SIALOSIDES
- Rufus Smits** *PO-244*
Latvian Institute of Organic Synthesis, Riga, Latvia
SYNTHESIS OF CURCUMIN HETEROCYCLIC DERIVATIVES
- Łukasz Tomorowicz** *PO-245*
Medical University of Gdańsk, Gdańsk, Poland
SYNTHESIS AND ANTICANCER ACTIVITY OF 2-(1,3,5-TRIAZIN-2-YLMETHYLTHIO)-N-(IMIDAZOLIDIN-2-YLIDENE)-5-METHYLBENZENESULFONAMIDE DERIVATIVES
- Eric S.E. van Beelen** *PO-246*
Waters Corporation, Milford, USA
THE EFFECTS OF SFC PREPARATIVE SCALE-UP ON THROUGHPUT, PURITY AND RECOVERY OF AN IMPURITY IN AN API MIXTURE
- Eric S.E. van Beelen** *PO-247*
Waters Corporation, Milford, USA
SMALL SCALE COMPOUND ISOLATION USING MASS DIRECTED PURIFICATION
- Tomáš Vašíček** *PO-248*
Academy of Science of the Czech Republic, Prague, Czech Republic
3,3'- DISUBSTITUTED THIOGALACTOSIDES AS INHIBITORS OF GALECTINS
- Blanca Angelica Vega Alanis** *PO-249*
TU Wien, Vienna, Austria
SELECTIVITY OF PYRAZOLOQUINOLINONE DERIVATIVES TOWARDS THE ALPHA1+/-BETA1- INTERFACE OF THE GABA_A RECEPTOR
- Lucia Veselovska** *PO-250*
Academy of Science of the Czech Republic, Prague, Czech Republic
SYNTHESIS OF NOVEL HETERO-FUSED 7-DEAZAPURINE RIBONUCLEOSIDES
- Maximillian Viera** *PO-251*
National University of Singapore, Singapore, Singapore
SYNTHESIS OF A CHONDROITIN SULFATE PROBE AND ITS APPLICATION IN PROSTATE CANCER CELLS
- Tristan Wegner** *PO-252*
Westfälische Wilhelms-Universität Münster, Münster, Germany
NOVEL ADDRESSABLE CHOLESTEROL ANALOGUES FOR LIVE IMAGING OF CELLULAR MEMBRANES

Martin Wilkovitsch

TU Wien, Vienna, Austria

PO-253

HIGHLY REACTIVE DIENOPHILES FOR BIOORTHOGONAL TETRAZINE LIGATIONS

Organic Materials

- Mandeep K. Bal** **PO-254**
 Manchester Metropolitan University, Manchester, United Kingdom
METABOLISM MIMICRY: AN ELECTROSYNTHETIC METHOD FOR THE SELECTIVE DEETHYLATION OF TERTIARY BENZAMIDES
- Nico Balzer** **PO-255**
 Karlsruhe Institute of Technology, Karlsruhe, Germany
SYNTHESIS OF FUNCTIONALIZED MOLECULAR TRIPODS FOR SURFACE APPLICATIONS
- Paulina Bartos** **PO-256**
 University of Lodz, Lodz, Poland
NEW ACCESS TO PLANAR BLATTER RADICALS: π EXTENDED HETEROCYCLES WITH HIGH SPIN DELOCALIZATION
- Denis Borisov** **PO-257**
 Russian Academy of Sciences, Moscow, Russia
1,2-ZWITTERIONIC Ga COMPLEXES OF METHYLIDENEMALONATES AND THEIR REACTIONS WITH ACETYLENES
- Nikos Chronakis** **PO-258**
 University of Cyprus, Nicosia, Cyprus
TETHER-DIRECTED REGIOSELECTIVE SYNTHESIS OF AN *EQUATORIAL*_{FACE} BISADDUCT OF AZAFULLERENE USING CYCLO-[2]-OCTYLMALONATE
- Mowpriya Das** **PO-259**
 Westfälische Wilhelms-Universität Münster, Münster, Germany
MOLECULAR ADSORBATES SWITCH ON HETEROGENEOUS CATALYSIS: INDUCTION OF REACTIVITY BY N-HETEROCYCLIC CARBENES
- Isabella Eder** **PO-260**
 Johannes Kepler University Linz, Linz, Austria
A NEW APPROACH TO PREPARE α -FLUORINATED β -AMINO ACIDS, BEARING A TETRASUBSTITUTED STEREOGENIC CENTER
- Jomana Elaridi** **PO-261**
 Lebanese American University, Beirut, Lebanon
CYCLOTRIMERIZATION OF NUCLEOBASE-LINKED NITRILES FOR THE PRODUCTION OF NOVEL S-TRIAZINES
- Leonid Fershtat** **PO-262**
 N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia
NEW DIRECTIONS IN THE HETARENE N-OXIDES CHEMISTRY
- Sarah R. Geenen** **PO-263**
 Heinrich-Heine-University Düsseldorf, Düsseldorf, Germany
MONO- AND DISUBSTITUTED PSORALENS FOR INTERCALATION AND PHOTOADDITION INTO DNA
- Benjamin Günther** **PO-264**
 Heidelberg University, Heidelberg, Germany
SYNTHESIS AND CHARACTERIZATION OF NON-PLANAR TETRAAZAPEROPYRENES (TAPPS) VIA BAY-SUBSTITUTION
- Brigitte Holzer** **PO-265**
 TU Wien, Vienna, Austria
SYNTHESIS AND CHARACTERIZATION OF SELENOPHENE-BASED ORGANIC SEMICONDUCTORS
- Sebastian Intorp** **PO-266**
 Ruprecht-Karl-University Heidelberg, Heidelberg, Germany
COLOR TUNING OF ELECTROCHROMIC HETEROPHENOQUINONES

- Mingyeong Jeong** *PO-267*
Kwangwoon University, Seoul, Korea
Ru(II) COMPLEXES CONTAINING EXTENDED π -CONJUGATION BIPYRIDYL ANCILLARY LIGAND: SYNTHESIS AND APPLICATION FOR DSSCs
- Soon Kwan Jeong** *PO-268*
Korea Institute of Energy Research, Daejeon, Korea
CHEMICAL REGENERATION OF AMINE SOLVENTS USING CALCIUM HYDROXIDE FOR CO₂ CAPTURE PROCESS
- In Hwan Jung** *PO-269*
Kookmin University, Seoul, Republic of Korea
DEVELOPMENT OF ORGANIC POLYMER DONOR FOR EFFICIENT TERNARY ORGANIC SOLAR CELLS
- Thomas Kader** *PO-270*
TU Wien, Vienna, Austria
PLANARIZED PYRIDINE-BASED TRIARYLAMINES FOR FUNCTIONAL ORGANIC MATERIALS
- Zigfrids Kapilinskis** *PO-271*
Riga Technical University, Riga, Latvia
SYNTHESIS OF AMORPHOUS FLUORESCENT PURINE HYBRIDS CONTAINING FIVE-MEMBERED HETEROCYCLES
- Gabriella Kervefors** *PO-272*
Stockholm University, Stockholm, Sweden
REGIOSPECIFIC N-ARYLATION OF ALIPHATIC AMINES UNDER MILD AND METAL-FREE REACTION CONDITIONS
- Aisha Khalifa** *PO-273*
University College Dublin, Dublin, Ireland
THE DOUBLE REDUCTION OF CYCLIC BENZO-FUSED SULFONAMIDES
- Attila Kunfi** *PO-274*
Hungarian Academy of Sciences, Budapest, Hungary
CONSTRUCTION OF HETEROGENEOUS CATALYSTS AND DYNAMIC INTERFACES ON A POLYDOPAMINE PLATFORM
- Aneta Kurpanik** *PO-275*
University of Silesia, Katowice, Poland
NEW POSSIBILITIES OF 3,9-DIAMINOSUBSTITUTED PERYLENES CORE EXTENSION VIA DIELS-ALDER CYCLOADDITION TO BAY REGION
- Hyejeong Lee** *PO-276*
Dong-A University, Busan, Republic of Korea
TANDEM INDIUM-MEDIATED REDUCTIVE REACTION/N-ANNULATION REACTION: SYNTHESIS OF BIS-PYRROLEARENE DERIVATIVES FROM ELECTRON DEFICIENT NITROANILINES
- Zsófia Makra** *PO-277*
AVIDIN Ltd., Szeged, Hungary
IBX/NIS INDUCED OXIDATIVE INTRAMOLECULAR ANNULATION
- Laura Mayer** *PO-278*
Heinrich-Heine-University Düsseldorf, Düsseldorf, Germany
DIVERSITY-ORIENTED SYNTHESIS OF DIARYL SUBSTITUTED HETEROCYCLES VIA SEQUENTIAL PALLADIUM CATALYSIS
- Kasjan Misztal** *PO-279*
Saule Research Institute Foundation, Wrocław, Poland
SYNTHESIS, CHARACTERIZATION AND APPLICATION OF NOVEL FULLERENE DERIVATIVES IN PEROVSKITE SOLAR CELLS

- Monica-Irina Nan** *PO-280*
"Babes Bolyai" University, Cluj-Napoca, Romania
SYNTHESIS AND CHARACTERIZATION OF NOVEL PYRENE AND PHENOTHIAZINE BASED BUILDING BLOCKS FOR ORGANIC SOLAR CELLS AND MOLECULAR ELECTRONICS
- Jonas S. Niedballa** *PO-281*
Heinrich-Heine-University Düsseldorf, Düsseldorf, Germany
ONE-POT MULTI-COMPONENT COUPLING-ADDITION SYNTHESIS OF HYDROXYPYRAZOLES, ALKOXYPYRAZOLES, AND β -AMINO ENOATES
- Jela Nociarová** *PO-282*
Comenius University Bratislava, Bratislava, Slovakia
DONOR-SUBSTITUTED PYRIDOBENZO(BIS)THIAZOLES AS TWO PHOTON ABSORBING FLUOROPHORES FOR BIOIMAGING
- Eric Pasquinet** *PO-283*
CEA, Monts, France
NITRENE-BASED N-N BOND FORMATION: AN EFFICIENT METHOD TOWARDS NITROGEN-RICH TRICYCLIC TRIAZAPENTALENES
- Raúl Pérez-Ruiz** *PO-284*
Universitat Politècnica de València, València, Spain
BORYLATION OF THIOPHENES DRIVEN BY PHOTOCATALYST-FREE VISIBLE LIGHT
- Apurba Ranjan Sahoo** *PO-285*
TU Wien, Vienna, Austria
SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS OF SUPPORTED POLYMERIC IONIC LIQUIDS (SILPS)
- Finn Schulz** *PO-286*
University of Stuttgart, Stuttgart, Germany
FLUOROPHOBIC EFFECT LEADS TO NOVEL LIQUID CRYSTALLINE DONOR ACCEPTOR DYES
- Manuel Schupp** *PO-287*
Karlsruhe Institute of Technology, Karlsruhe, Germany
CONDUCTIVITY STUDIES OF DIALLYETHYLENE-MODIFIED DNA VIA SCANNING TUNNELING MICROSCOPY
- Armands Sebris** *PO-288*
Riga Technical University, Riga, Latvia
AMORPHOUS PURINE-AZOLE CONJUGATES AND THEIR PHOTOPHYSICAL PROPERTIES
- Philipp Seubert** *PO-289*
University of Stuttgart, Stuttgart, Germany
CROWN ETHER-BASED MESOGENS WITH BRANCHED ALKYL CHAINS
- Yushin Shibuya** *PO-290*
Kobe University, Kobe, Japan
SYNTHESIS AND STRUCTURE OF REGIOREGULAR POLY(1,4-POLY-ARYLENE)
- Pavel Šimon** *PO-291*
University of Pardubice, Pardubice, Czech Republic
SYNTHESIS AND CHARACTERIZATION OF NEW HIGHLY FLUORINATED DIAMINES SUITED FOR POLYMERIZATION
- Maroš Smolíček** *PO-292*
Comenius University Bratislava, Bratislava, Slovakia
BENZOTHAZOLE ANALOGUES OF BODIPY DYES WITH A QUADRUPOLEAR (D- π -A- π -D) ARCHITECTURE FOR BIOIMAGING

- Irena G. **Stará** **PO-293**
 Czech Academy of Sciences, Prague, Czech Republic
DIASTereo- AND ENANTioPURE HELICENE 2,2'-BIPYRIDINES: A NEW TYPE OF CHIROPTICAL SWITCHES
- Jiří **Tůma** **PO-294**
 University of Chemistry and Technology, Prague, Czech Republic
MECHANOCHEMICALLY INDUCED SWITCHING OF SPIROPYRANS
- Carlijn L. F. **van Beek** **PO-295**
 University of Groningen, Groningen, The Netherlands
CONTROL OVER SURFACE WETTABILITY BY SURFACE-IMMOBILISED MOLECULAR MOTORS
- Miha **Virant** **PO-296**
 University of Ljubljana, Ljubljana, Slovenia
TOWARDS THE TRIARYLATED TRIAZOLIUM SALTS
- Ming-Ming **Wang** **PO-297**
 Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland
DIVERGENT 1,3-DIFUNCTIONALIZATION OF AMINOCYCLOPROPANES
- Expédite **Yen-Pon** **PO-298**
 Université Paris-Saclay, Gif-sur-Yvette, France
SYDNONE-BASED APPROACH TO HETEROHELICENES THROUGH 1,3-DIPOLAR-CYCLOADDITIONS

Physical and Computational Organic Chemistry

- Shar Saad Al-Shihry** *PO-299*
King Faisal University, Hufuf, Saudi Arabia
DESIGN AND ASSESSMENT OF NOVEL POLYMERS BASED ON 5-DIHYDRAZINYL-1, 3,4-THIADIAZOLE AS INHIBITORS FOR STEEL PIPELINES CORROSION IN CO₂-SATURATED OILFIELD
- Ivana Antol** *PO-300*
The Ruđer Bošković Institute, Zagreb, Croatia
A DFT STUDY OF REGIOSELECTIVITY IN DIELS-ALDER CYCLOADDITION OF E-BENZILIDENEGUANIDINE WITH 4,5-, 5,6- AND 6,7- INDOLYNES
- Nicholas Beattie** *PO-301*
University of Manchester, Manchester, United Kingdom
COMPUTATIONAL INVESTIGATIONS INTO ENANTIOSELECTIVE SAMARIUM DIODIDE-MEDIATED RADICAL CYCLISATION REACTIONS
- Christoph Bickmann** *PO-302*
Karlsruhe Institute of Technology, Karlsruhe, Germany
DNA FROM AN ELECTRICAL POINT OF VIEW - POTENTIAL BUILDING BLOCKS FOR MOLECULAR ELECTRONICS
- Alba Carretero-Cerdán** *PO-303*
Stockholm University, Stockholm, Sweden
BASE-CATALYZED ISOMERIZATION OF DIENYL ALKYL ETHERS AND DIENOLS: DFT STUDIES
- Monica Civera** *PO-304*
Università degli Studi di Milano, Milan, Italy
A CHIMERA MODEL OF Rel_{Seq} PRE-CATALYTIC STATE
- Harvey Dale** *PO-305*
The University of Edinburgh, Edinburgh, UK
TAMING AMBIDENT TRIAZOLE NUCLEOPHILES: REGIOSELECTIVE ION-PAIRING AND PHASE-TRANSFER ORGANOCATALYSIS
- Louis Evans** *PO-306*
University of Greenwich, Chatham Maritime, U.K.
MECHANISTIC INSIGHTS INTO THE SILYL-PRINS REACTION
- Nico Fleck** *PO-307*
Universität Bonn, Bonn, Germany
C-C CROSS COUPLING OF TRITYL RADICALS: REACTIVITY AND SPIN DENSITY DELOCALIZATION
- Francesca Fontana** *PO-308*
University of Bergamo, Bergamo, Italy
SYNTHESIS AND CHARACTERIZATION OF SERS-ACTIVE HETEROAROMATIC MOLECULES
- Zoran Glasovac** *PO-309*
Ruđer Bošković Institute, Zagreb, Croatia
COMPUTATIONAL DESIGN OF NOVEL BICYCLO[2.2.2]OCTANE BASED PROTON SPONGES
- Imre Gyűjtő** *PO-310*
Budapest University of Technology and Economics, Budapest, Hungary
REARRANGEMENT OF 1,2,3-BENZOTHIADIAZINES
- Karol Kraszewski** *PO-311*
University of Warsaw, Warsaw, Poland
MECHANISTIC STUDIES ON OXIDATIVE DEAROMATIZATION OF PHENOLS PROMOTED BY HYPERVALENT IODINE SPECIES

- Marole Maluleka** *PO-312*
University of South Africa, Florida, South Africa
POTENTIALLY TAUTOMERIC 3-ARYLQUINOLIN-4(1H)-ONES VERSUS 3-ARYLQUINOLIN-4-OLS: sPECTROSCOPIC, DFT AND X-RAY ANALYSES
- Boris Maryasin** *PO-313*
University of Vienna, Vienna, Austria
COMPUTATIONAL CHEMISTRY AND ORGANIC SYNTHESIS: LET US BUILD A BRIDGE
- Toni Metsänen** *PO-314*
University of Jyväskylä, Jyväskylä, Finland
SYNTHETIC KETOREDUCTASE MIMICS
- Jihye Na** *PO-315*
Kwangwoon University, Seoul, Korea
MORPHOLOGICAL CHANGES OF ORGANIC PHOTOVOLTAICS: MOLECULAR DYNAMICS SIMULATION STUDIES
- Sebastián Richter-Morales** *PO-316*
Universidad de Chile, Santiago, Chile
A BONDING EVOLUTION THEORY PERSPECTIVE OF THE aza-SNAr MECHANISM
- Steven Roldan-Gomez** *PO-317*
Universitat de Girona, Girona, Spain
COMPUTATIONAL "DIVE" INTO A NICKEL(0)-CATALYZED ARENE C-F ACTIVATION WITH ALKYNES
- Alexey Salin** *PO-318*
Kazan Federal University, Kazan, Russia
UNUSUAL SECONDARY KINETIC ISOTOPE EFFECTS IN REACTION OF TERTIARY PHOSPHINES WITH ELECTRON-DEFICIENT ALKENES
- Lia Sotorrios** *PO-319*
University of the Basque Country, Donostia/San Sebastian, Spain
MECHANISTIC INVESTIGATION OF AN OXIME ETHER ELECTROCYCLIZATION
- Nicola Tonge** *PO-320*
Mestrelab Research S.L., Santiago de Compostela, Spain
SPECTROSCOPIC DATA TO ASSIST CHEMICAL SYNTHESIS
- Simon Turega** *PO-321*
Sheffield Hallam University, Sheffield, UK
INVESTIGATING MONOAMINE OXIDASE ISOFORM SELECTIVITY FOR NEUROTRANSMITTER SUBSTRATES THROUGH THE PRODUCTION OF THERMODYNAMIC CYCLES
- Giovanna Zanella** *PO-322*
Universidad del País Vasco, San Sebastián, Spain
DFT STUDY OF THE REACTIVITY OF TRANSIENTLY GENERATED CYCLIC DIENOLATES VERSUS THE ACYCLIC COUNTERPARTS IN ADDITION REACTIONS

Supramolecular Chemistry

- Jan Alfuth** *PO-323*
Gdansk University of Technology, Gdansk, Poland
SUPRAMOLECULAR SELF-ASSEMBLY OF HALOGEN-BOND-FORMING QUINOLINE DERIVATIVES
- Lucian M Birsa** *PO-324*
Alexandru Ioan Cuza University of Iasi, Iasi, Romania
INTRAMOLECULAR INTERACTIONS IN [2.2]PARACYCLOPHANES
- Patrick Boaler** *PO-325*
The University of Edinburgh, Edinburgh, UK
MECHANISTIC INVESTIGATIONS INTO CATALYTIC, CAPSULE-MEDIATED ARENE ALLYLATIONS
- Leo Frkanec** *PO-326*
Ruđer Bošković Institute, Zagreb, Croatia
TRANSCRIPTION OF SELF-ASSEMBLED GEL NETWORKS EMBEDDED WITH REACTIVE VINYL GROUPS TO NANOSTRUCTURED POLYMERS
- Sabrina Gonglach** *PO-327*
Johannes Kepler University Linz, Linz, Austria
MOLECULAR Co-CORROLE COMPLEX FOR THE HETEROGENEOUS ELECTROCATALYTIC REDUCTION OF CARBON DIOXIDE ON CARBON FIBER ELECTRODES
- Michael Haas** *PO-328*
Johannes Kepler University Linz, Linz, Austria
INCREASING THE π -ELECTRON CONJUGATION OF CORROLES VIA SONOGASHIRA-CROSS-COUPLING
- Dong Hwan Kim** *PO-329*
University of Ulsan, Ulsan, Republic of Korea
ACCEPTOR METAL-DIRECTED SUPRAMOLECULAR TOPOLOGIES
- Saša Opačak** *PO-330*
The Ruđer Bošković Institute, Zagreb, Croatia
SECONDARY STRUCTURAL MOTIFS IN DISUBSTITUTED FERROCENE AMIDES
- Marcelle D. Perretti** *PO-331*
Universidad de La Laguna (ULL), Tenerife, Spain
BUILDING COVALENT MOLECULAR CAPSULES BY THIOL- MICHAEL ADDITION CLICK REACTION
- Lidia Pop** *PO-332*
"Babes Bolyai" University, Cluj-Napoca, Romania
SUPRAMOLECULAR ARCHITECTURES SUPPORTED BY CATEMERS OF 2,7-DIPYRIDYLFLUORENE WITH ORTHO-, META- OR PARA- DIODOTETRAFLUOROBENZENE ISOMERS
- Manuel Rondelli** *PO-333*
Instituto de Productos Naturales y Agrobiología, San Cristóbal de La Laguna, Spain
RATIONAL DESIGN OF COOPERATIVITY IN A SYNTHETIC RECEPTOR

Total Synthesis and Methodology

- Suresh Alati** **PO-334**
 Indian Institute of Technology Bombay, Mumbai, India
**SYNTHESIS OF BENZOFURANYLINDOLINONES AND SPIRONAPHTHOQUINONES BY
 REACTION OF 3-SUBSTITUTED PHTHALIDES AND OXINDOLE DERIVED NITRO-OLEFINS**
- Mostafa Amer** **PO-335**
 University of Bristol, Bristol, UK
**STEREOSELECTIVE SYNTHESIS OF MEDICINALLY-RELEVANT
 DIHYDROISOQUINOLINONES**
- Emy Andre-Joyaux** **PO-336**
 University of Bern, Bern, Switzerland
RADICAL CYCLIZATIONS OF α -OXY CARBON CENTERED RADICALS
- André U. Augustin** **PO-337**
 TU Braunschweig, Braunschweig, Germany
**EXPLOITING ORGANOSULFUR COMPOUNDS IN DONOR-ACCEPTOR CYCLOPROPANE
 CHEMISTRY**
- Andreas Baumann** **PO-338**
 Ludwig-Maximilians University, Munich, Germany
**ELECTROCHEMICAL TRANSFORMATION OF TETRAORGANO BORATES TOWARDS
 HIGHLY FUNCTIONALIZED ALKENES**
- Sarah Bauspieß** **PO-339**
 Saarland University, Saarbrücken, Germany
**SULFOXIDE CONTROLLED SUZUKI C-C COUPLING FOR THE SYNTHESIS OF
 CYCLOPHANE TYPE AXIALLY CHIRAL BIARYLS**
- Marius Bayer** **PO-340**
 University of Tübingen, Tübingen, Germany
THE SYNTHESIS OF DODECO-6,7-DIULOSES
- Steven Bennett** **PO-341**
 University of Bristol, Bristol, UK
**DEVELOPMENT OF BICYCLO[1.1.0]BUTYL BORONATE COMPLEXES FOR THE
 DIASTEREOSELECTIVE SYNTHESIS OF CYCLOBUTANES**
- Martin Berger** **PO-342**
 University of Vienna, Vienna, Austria
**C-H ACTIVATION ENABLES A CONCISE AND STEREOSELECTIVE TOTAL SYNTHESIS
 OF QUININE AND ANALOGUES**
- Helge Berneaud-Kötz** **PO-343**
 Leibniz University Hannover, Hannover, Germany
DEVELOPMENT OF A TOTAL SYNTHESIS OF CEBULACTAMS A1 AND A2
- Frédéric Bihel** **PO-344**
 Université de Strasbourg, Illkirch, France
**A VERSATILE KETONE FORMATION VIA HIGHLY ACTIVE PRECATALYST "POXAP":
 APPLICATION TO THE SYNTHESIS OF ISOPREKINAMYCIN**
- Matteo Borgini** **PO-345**
 University of Siena, Siena, Italy
LARGAZOLE, A PROMISING SCAFFOLD FOR HDAC INHIBITORS
- Christina Bub** **PO-346**
 RWTH Aachen University, Aachen, Germany
PHENOTHAZINIMIDES: ATOM-EFFICIENT ELECTROPHILIC AMINATION REAGENTS

- Robert Bujok** *PO-347*
Polish Academy of Science, Warsaw, Poland
SYNTHESIS OF THE DIARYLACETYLENES BEARING ELECTRON WITHDRAWING GROUP VIA THE SMILES REARRANGEMENT
- Finn Burg** *PO-348*
Technical University Munich, Garching, Germany
BIOMIMETIC SITE- AND ENANTIOSELECTIVE C–H OXYGENATION OF QUINOLONE ANALOGUES MEDIATED BY HYDROGEN BONDING
- Marcel Bürger** *PO-349*
Technical University of Braunschweig, Braunschweig, Germany
ACTIVATED THIOCYANATES - THE CYANOSULFENYLATION OF INTERNAL ALKYNES
- Dmitry Bystrov** *PO-350*
Russian Academy of Sciences, Moscow, Russia
NEW METHOD FOR THE SYNTHESIS OF (N-FUROXANYL)HYDRAZONES
- Brenda Callebaut** *PO-351*
Ghent University, Ghent, Belgium
AN INTRAMOLECULAR CYCLOADDITION APPROACH TO THE KAURANOID FAMILY OF DITERPENE METABOLITES
- Roxan Calvo** *PO-352*
Swiss Federal Institute of Technology, Zürich, Switzerland
FACILE ACCESS TO NITROARENES AND NITROHETEROARENES USING N-NITROSACCHARIN: AN ELECTROPHILIC NITRATING REAGENT
- Tomáš Čarný** *PO-353*
Slovak University of Technology, Bratislava, Slovakia
ONE-STEP SYNTHESIS OF ISOINDOLO[2,1-a]INDOL-6-ONES VIA TANDEM Pd-CATALYZED AMINOCARBONYLATION AND C-H ACTIVATION REACTION
- Anna Chamberlain** *PO-354*
University of Oxford, Oxford, UK
STEREOSELECTIVE SYNTHESIS OF SATURATED NITROGEN HETEROCYCLES VIA HYDROGEN BORROWING CATALYSIS
- Wei Wen Chen** *PO-355*
Catalonia Institute for Advanced Chemistry, Barcelona, Spain
IODANE-DIRECTED ORTHO C-H ALLYLATION AS GATEWAY TOWARDS ADDED VALUE CORES
- Yong Sheng Chng** *PO-356*
National University of Singapore, Singapore, Singapore
PROTECTING-GROUP-FREE SYNTHESIS OF CHONDROITIN 6-SULFATE DISACCHARIDE AND TETRASACCHARIDE
- Mien Christiaens** *PO-357*
Ghent University, Ghent, Belgium
STEREOSELECTIVE AND MODULAR ASSEMBLY METHOD FOR DAUCANE, CYATHANE AND TIGLIANE TERPENOID SCAFFOLDS
- Cecilia Ciccolini** *PO-358*
University of Urbino "Carlo Bo", Urbino, Italy
Zn(II)-CATALYZED [3+2] AND [4+2] ANNULATION OF INDOLES WITH AZOALKENES: DIVERGENT SYNTHESIS OF POLYCYCLIC INDOLINES
- Yair Cohen** *PO-359*
Israel Institute of Technology, Haifa, Israel
CARBOMETALLATION OF CYCLOPROPENYLSILANES
- Anthony Cohen** *PO-360*
Israel Institute of Technology, Haifa, Israel
REMOTE FUNCTIONALIZATION OF STEREODEFINED SUBSTITUTED CYCLOPROPANES

- Laurent Commeiras** *PO-361*
Aix-Marseille Université, Marseille, France
DIVERGENT COBALT-MEDIATED FORMAL (2+2+3)-CYCLOADDITION OF ENEDIYNES: EXPERIMENTAL AND THEORETICAL INSIGHTS
- Ben Cons** *PO-362*
Astex Pharmaceuticals, Cambridge, UK
ENABLING FRAGMENT GROWTH WITH PHOTOREDOX CATALYSIS THROUGH HIGH-THROUGHPUT EXPERIMENTATION
- Massimiliano Cordaro** *PO-363*
Università di Messina, Messina, Italy
SYNTHESIS OF BODIPY HETERODIMER FORMED BY HYDROGEN BONDING FOR ELECTRONIC TRANSFER INVESTIGATIONS
- Massimiliano Cordaro** *PO-364*
Università di Messina, Messina, Italy
SYNTHESIS OF BODIPY HETERODIMER FORMED BY HYDROGEN BONDING FOR ELECTRONIC TRANSFER INVESTIGATIONS
- Axel Daikeler** *PO-365*
University of Tübingen, Tübingen, Germany
SYNTHETIC PATHWAYS TOWARDS CARBOHYDRATE-SUBSTITUTED ALPHA-DIKETONES
- Andrew Dalling** *PO-366*
University of Bristol, Bristol, UK
RHODIUM-CATALYSED (3+1+2) CYCLOADDITIONS OF ELECTRON-POOR CYCLOPROPANES
- Arif Dastan** *PO-367*
Atatürk University, Erzurum, Turkey
ONE-POT SYNTHESIS OF DIAZANAPHTHALENE DIMERS AND TRIMERS VIA C-H SUBSTITUTION
- Thomas Davies** *PO-368*
University of Oxford, Oxford, UK
GENERATING AND EXPLOITING SULFINYL NITRENES
- Samuel Delgado-Hernandez** *PO-369*
Instituto de Productos Naturales y Agrobiología, Tenerife, Spain
INTEGRATIVE PERICYCLIC CASCADE: AN ATOM ECONOMIC, MULTI C-C BOND-FORMING STRATEGY FOR THE CONSTRUCTION OF MOLECULAR COMPLEXITY
- Damien Dewez** *PO-370*
Université libre de Bruxelles, Bruxelles, Belgium
TOTAL SYNTHESIS OF PALIURINE E: A HIGHLY CONVERGENT "BLOCK" APPROACH
- Giovanni Di Mauro** *PO-371*
University of Vienna, Vienna, Austria
HYDRATIVE AMINOXYLATION OF THIOALKYNES
- Raquel Diana** *PO-372*
Instituto de Productos Naturales y Agrobiología, Tenerife, Spain
SYNTHESIS AND REACTIVITY OF ALKYNYL VYNIL HYDRAZINES
- Abián Díaz** *PO-373*
Instituto de Productos Naturales y Agrobiología, Tenerife, Spain
2,2-DIMETHYL-2H-PYRANS: DIENES FOR DOMINO DIELS-ALDER / RETRO DIELS-ALDER REACTIONS IN THE SYNTHESIS OF POLYSUBSTITUTED 2-NAPHTHOATES
- Marta Diaz** *PO-374*
Universitat Ramon Llull, Barcelona, Spain
GEMINAL SILICON/BORON BIMETALLOIDS: VERSATILE BUILDING BLOCKS FOR MOLECULAR DIVERSITY

- Markus Draskovits** *PO-375*
 TU Wien, Vienna, Austria
M-HETEROCYCLIC CARBENE CONTROLLED DIVERGENT DEHOMOLOGATION OF ALDOSES
- Julia Dürner** *PO-376*
 Technical University Munich, Garching, Germany
SYNTHESIS OF NEW STERICAL DEMANDING CHIRAL AMINES
- Louise Eagling** *PO-377*
 University of Bristol, Bristol, UK
DEVELOPING A 'REVERSE-BIOMIMETIC' SYNTHESIS OF AROGENATE AND ITS ANALOGUES
- Sabria Ederwish** *PO-378*
 University of Strasbourg, Strasbourg, France
SYNTHESIS OF SPIRO- γ -HYDROXYLACTAM OXINDOLES AS HYBRID PROHIBITIN-2 LIGANDS
- Tereza Edlová** *PO-379*
 University of Chemistry and Technology, Prague, Czech Republic
BROMINATION OF 1,2-DISUBSTITUTED CYCLOBUTENES
- Abdelaziz Ejjommany** *PO-380*
 Université Hassan II de Casablanca, Mohammedia, Maroc
DESIGN AND REGIOSELECTIVE FUNCTIONALIZATION OF NEW 2,4-SUBSTITUED PYRIDO[1',2':1,5]PYRAZOLO[3,4-*d*]PYRIMIDINES AND 2,4-SUBSTITUED PYRIDO[1',2':1,5]PYRAZOLO[4,3-*d*]PYRIMIDINES VIA Pd-CATALYZED SEQUENTIAL ARYLATION
- Gábor Zoltán Elek** *PO-381*
 Tallinn University of Technology, Tallinn, Estonia
DIVERGENT ACCESS TO HISTONE DEACETYLASE INHIBITORY CYCLOPEPTIDES VIA LATE-STAGE CYCLOPROPANE RING CLEAVAGE STRATEGY. SHORT TOTAL SYNTHESIS OF CHLAMYDOCIN
- Jessica Elwood** *PO-382*
 University of Glasgow, Glasgow, United Kingdom
CENTROSYMMETRIC APPROACH TOWARDS THE SYNTHESIS OF FUSED POLYCYCLIC ETHER NATURAL PRODUCTS
- Julian Erver** *PO-383*
 University of Cologne, Cologne, Germany
STUDIES TOWARDS THE TOTAL SYNTHESIS OF DYSIHERBOL A
- Joshua Farndon** *PO-384*
 University of Bristol, Bristol, UK
BIFUNCTIONAL AMINO-REAGENTS FOR C-N BOND FORMATION
- Jerome Fischer** *PO-385*
 Université de Nantes, Nantes, France
CINCHONA AND BODIPY: AN APPEALING CATALYTIC STRATEGY FOR CHIMIOSELECTIVE PHOTOOXYGENATION
- James Fordham** *PO-386*
 University of Bristol, Bristol, UK
PREPARATION OF VINYL BORONIC ESTERS VIA A HOMOLOGATION REACTION: BIDIRECTIONAL SYNTHESIS OF MACHILLENE
- Sebastian Frey** *PO-387*
 Saarland University, Saarbrücken, Germany
ENANTIOSELECTIVE SYNTHESIS OF HYPERFORIN

- Silvia **Gazzola** *PO-388*
University of Insubria, Como, Italy
NOVEL Mg-BASED APPROACH FOR THE REGIOSELECTIVE FUNCTIONALIZATION OF PURINE DERIVATIVES
- Manoj **Ghosh** *PO-389*
University of Warsaw, Warsaw, Poland
METAL-FREE REGIOSELECTIVE C-H ARYL-ARYL CROSS-COUPLING - ARYLATION OF 2-NAPHTHOLS WITH DIARYLIODONIUM SALTS
- Thomas **Glachet** *PO-390*
Normandie Université, Caen, France
DIRECT TRANSFORMATION OF AMINO ACIDS INTO DIAZIRINES AND $^{15}\text{N}_2$ -DIAZIRINES AND THEIR APPLICATION AS HYPERPOLARIZED MARKERS
- Mladena **Glavaš** *PO-391*
Ruđer Bošković Institute, Zagreb, Croatia
SYNTHESIS OF MACROCYCLIC COMPOUNDS VIA CONSECUTIVE SONOGASHIRA-UGI-SONOGASHIRA REACTIONS
- Carlos **Gonçalves** *PO-392*
University of Vienna, Vienna, Austria
A UNIFIED APPROACH TO THE CHEMOSELECTIVE α -FUNCTIONALIZATION OF AMIDES
- Hanusch **Grab** *PO-393*
Technical University Munich, Garching, Germany
TOWARDS THE TOTAL SYNTHESIS OF VIOPROLIDES A-D
- Julian **Greb** *PO-394*
Heinrich-Heine-University Düsseldorf, Jülich, Germany
OXIDATIVE PHENOL COUPLING IN NATURAL PRODUCT SYNTHESIS
- Nándor **Győrfi** *PO-395*
Servier Research Institute of Medicinal Chemistry, Budapest, Hungary
PHOTOREDOX-CATALYZED ALKYLATION OF HETEROAROMATIC BASES USING ETHYL ACETATE AS ALKYLATING AGENT
- Lamouri **Hammal** *PO-396*
University of Science and Technology Houari Boumediene (USTHB), Algiers, Algeria
SYNTHESIS OF PYRRAZOLE AND PYRIMIDINE STRUCTURE
- Maxwell **Haughey** *PO-397*
University of Oxford, Oxford, UK
STUDIES TOWARDS THE TOTAL SYNTHESIS OF HETEROCLITIN F AND TAIWANSCHIRIN A, B, C AND D
- Taiki **Hayashi** *PO-398*
Westfälische Wilhelms-Universität Münster, Münster, Germany
STEREOSPECIFIC α -SIALYLATION BY SITE-SELECTIVE FLUORINATION
- Xin **He** *PO-399*
Xi'an Jiaotong University, Xi'an, China
PHOSPHINE-CATALYZED ACTIVATION OF ALKYLIDENECYCLOPROPANES: REARRANGEMENT TO FORM POLYSUBSTITUTED FURANS AND DIENONES
- Tamás **Hergert** *PO-400*
Budapest University of Technology and Economics, Budapest, Hungary
A STEREOFLEXIBLE ACCESS TO 2-ALKENYLATED INDOLES
- Yuto **Hioki** *PO-401*
Kobe University, Kobe, Japan
DEPROTONATIVE GENERATION OF CYCLOALKYNES USING METAL AMIDES

- Oskar Hoff** *PO-402*
University of Oxford, Oxford, UK
TOWARDS THE SYNTHESIS OF (+)-LOPHOTOXIN
- Suvi Holmstedt** *PO-403*
Tampere University, Tampere, Finland
A SHORT TOTAL SYNTHESIS OF NATURAL CARBASUGAR
- Mira Holzheimer** *PO-404*
Rijksuniversiteit Groningen, Groningen, The Netherlands
TOWARDS THE TOTAL SYNTHESIS OF CRENARCHAEOL
- Marcel Holzwarth** *PO-405*
University of Stuttgart, Stuttgart, Germany
COMPARISON OF TWO SYNTHETIC STRATEGIES TOWARDS 1-ACYL-2-VINYLCYCLOPROPANES
- Alexander Horn** *PO-406*
Saarland University, Saarbrücken, Germany
STEREOSELECTIVE MODIFICATION OF "α-HYDROXY ACID PEPTIDES" BY PALLADIUM CATALYZED ALLYLIC ALKYLATION
- Day-Shin Hsu** *PO-407*
National Chung Cheng University, Chiayi, Taiwan
FORMAL SYNTHESIS OF PLATENCIN FROM O-VANILLIN BY INTERMOLECULAR AND INTRAMOLECULAR DIELS-ALDER STRATEGIES, RESPECTIVELY
- Manish Kumar Jaiswal** *PO-408*
Indian Institute of Technology Dehli, New Dehli, India
ORGANOCATALYTIC HIGHLY ENANTIOSELECTIVE VINYLOGOUS ALDOL REACTION: RAPID ACCESS TO δ-QUARTERNARY α-HYDROXYPHOSPHONATO-3-ALKYLIDENE-2-OXINDOLES
- Jiwon Jang** *PO-409*
Hanyang University, Seoul, Republic of Korea
ASYMMETRIC [3,3]-SIGMATROPIC REARRANGEMENT IN GOLD(I)-CATALYZED INTERMOLECULAR CARBOALKOXYLATION
- Antoine Joosten** *PO-410*
Normandie Université, Rouen, France
REGIO- AND CHEMOSELECTIVE DEPROTECTION OF PRIMARY ACETATES BY ZIRCONIUM HYDRIDES
- Wolfgang Jud** *PO-411*
University of Graz, Graz, Austria
AN ELECTROCHEMICAL APPROACH TO RADICAL TRIFLUOROMETHYLATIONS AND OXYTRIFLUOROMETHYLATIONS
- Martin Juhl** *PO-412*
University of Copenhagen, Copenhagen, Denmark
UMPOLUNG MEDIATED CARBOXYLATION OF ALDEHYDES
- Tobias Jung** *PO-413*
Saarland University, Saarbrücken, Germany
STEREOSELECTIVE SYNTHESIS OF NATURAL MYRTUCOMMULONES
- Lukas Junk** *PO-414*
Saarland University, Saarbrücken, Germany
LATE-STAGE INDOLE SYNTHESIS ENABLES THE TOTAL SYNTHESIS OF TRYPTOPHAN CONTAINING PEPTIDES
- Maximilian Kaiser** *PO-415*
TU Wien, Vienna, Austria
TOWARDS THE TOTAL SYNTHESIS OF ELISABETHIN A

- Hubert Kalaus** *PO-416*
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KINETIC QUANTIFICATION OF ALDOSE OPEN-CHAIN CONTENT
- Claire Kammerer** *PO-417*
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SYNTHESIS OF A FAMILY OF STAR-SHAPED MOLECULAR GEARS
- Jurij Kessler** *PO-418*
University of Tübingen, Tübingen, Germany
THE SYNTHESIS OF CARBON BRIDGED C-DISACCHARIDES VIA LITHIATED GLYCALS
- Pankaj Khairnar** *PO-419*
National Taiwan Normal University, Taipei, Taiwan
HIGHLY EFFICIENT SYNTHESIS OF TRISUBSTITUTED PYRAZOLES AND DISUBSTITUTED ISOXAZOLES VIA INTRAMOLECULAR WITTIG REACTIONS: A DIVERSITY-ORIENTED SYNTHESIS OF HETEROARENE SCAFFOLDS
- Viktor Khutorianskyi** *PO-420*
Academy of Science of the Czech Republic, Prague, Czech Republic
VICARIOUS NUCLEOPHILIC CHLOROMETHYLATION OF NITROAROMATICS
- Thorsten Kinsinger** *PO-421*
Saarland University, Saarbrücken, Germany
C-H FUNCTIONALIZATION OF N-METHYLATED AMINO ACIDS AND PEPTIDES AS TOOL IN NATURAL PRODUCT SYNTHESIS
- Alexander Klaiber** *PO-422*
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NOVEL PATHWAY TOWARDS STANNYLATED GLUCALS
- Thomas Klein** *PO-423*
University of Tübingen, Tübingen, Germany
GLYCOCONJUGATED AB₃-SECO-PORPHYRAZINES AS POTENTIAL PHOTSENSITIZERS IN PHOTODYNAMIC THERAPY
- Immo Klose** *PO-424*
University of Vienna, Vienna, Austria
STEREODIVERGENT SYNTHESIS OF 1,4-DICARBONYLS VIA A TRACELESS SULFOXIDE REARRANGEMENT
- Christian Knittl-Frank** *PO-425*
University of Vienna, Vienna, Austria
A SHORT SEMISYNTHESIS OF HEDERAGONIC ACID BY C-H ACTIVATION
- Mikhail Kornev** *PO-426*
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USE OF CHROMONE-3-CARBOXYLIC ACID AND ITS DERIVATIVES IN THE SYNTHESIS OF HETEROCYCLES
- Teresa Kösel** *PO-427*
Leibniz University Hannover, Hannover, Germany
RADICAL CHEMISTRY OF POLYMER-SUPPORTED DIAZIDOIODATE(I)
- Ondřej Kováč** *PO-428*
Palacky University, Olomouc, Czech Republic
 α,β -UNSATURATED α -BENZOTHIAZOLYLSUFONYL DERIVATIVES - PREPARATION AND APPLICATIONS
- Nicolas Kratena** *PO-429*
TU Wien, Vienna, Austria
TOTAL SYNTHESIS OF HUMAN PHASE I STEROID METABOLITES

- Alexander Kreft** *PO-430*
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DONOR-ACCEPTOR CYCLOPROPANES: A REACTIVITY STUDY
- Timothy Kwok** *PO-431*
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TOWARDS THE TOTAL SYNTHESIS OF PECTENOTOXIN-4
- Dániel Lasányi** *PO-432*
 Eotvos Lorand University, Budapest, Hungary
COPPER CATALYZED RING OPENING REACTIONS OF [1.1.1]PROPELLANE
- Guillaume Le Calvez** *PO-433*
 University of Groningen, Groningen, The Netherlands
TOTAL SYNTHESIS OF MYCOSEROSIC ACID FROM MYCOBACTERIUM TUBERCULOSIS AND THE PHEROMONE FROM MARGARODES PRIESKAENSIS
- Stian Legøy Årvik** *PO-434*
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RESPONSE SURFACE MODELLING OF MICROWAVE ASSISTED BISCHLER-NAPIERALSKI REACTION: SYNTHESIS OF EUDOSTOMIN H
- Miran Lemmerer** *PO-435*
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A UNIFIED APPROACH TO THE CHEMOSELECTIVE ALPHA-FUNCTIONALIZATION OF AMIDES
- Marcel Leroux** *PO-436*
 Ludwig-Maximilians University, Munich, Germany
LATE-STAGE FUNCTIONALIZATION OF PEPTIDES AND CYCLOPEPTIDES USING ORGANOZINC REAGENTS
- Vladimir Levchenko** *PO-437*
 University of Oslo, Oslo, Norway
AQUA REGIA IN GOLD(III) CHEMISTRY
- Malte Leverenz** *PO-438*
 Technical University Munich, Garching, Germany
LEWIS-ACID CATALYZED PHOTOREARRANGEMENT OF 2,4-CYCLOHEXADIENONES
- Yan-Cheng Liou** *PO-439*
 National Taiwan Normal University, Taipei, Taiwan
SYNTHESIS OF FUNCTIONALIZED BENZOFURANS FROM PARA-QUINONE METHIDES VIA PHOSPHA-1,6-ADDITION/O-ACYLATION/WITTIG REACTION
- Dylan Lynch** *PO-440*
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DEVELOPMENT OF A NOVEL LIGATION STRATEGY FOR SYNTHESIS OF THERAPEUTIC GLYCOPEPTIDES
- Anton S. Makarov** *PO-441*
 Perm State University, Perm, Russia
RHODIUM-CATALYZED REARRANGEMENT OF 2-FURYL TETHERED 1-TOSYL-1,2,3-TRIAZOLES
- Nina Makhova** *PO-442*
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SYNTHESIS OF NEW PHARMACOLOGICALLY ORIENTED NO-DONOR FUROXAN-BASED HETEROCYCLIC ENSEMBLES
- Marvin Mantel** *PO-443*
 Heinrich-Heine-University Düsseldorf, Jülich, Germany
NEW BENCH-STABLE ALLYLATION REAGENTS - HOW TUNING THE REACTIVITY ENABLES HIGHLY ENANTIOSELECTIVE ACCESS TO ALL STEREOISOMERS OF TERTIARY HOMOALLYLIC ALCOHOLS

- Athanasios Markos** *PO-444*
Academy of Science of the Czech Republic, Prague, Czech Republic
N-FLUOROALKYL-1,2,3-TRIAZOLES: EASILY AVAILABLE COMPOUNDS WITH HIGH SYNTHETIC POTENTIAL
- Lisa Marx** *PO-445*
Saarland University, Saarbrücken, Germany
SYNTHESIS OF AXIALLY CHIRAL BIS(BIBENZYL)S DERIVED FROM PERROTTETIN E VIA C-H ACTIVATED HECK TYPE CYCLIZATION
- Itai Massad** *PO-446*
Israel Institute of Technology, Haifa, Israel
SURPRISINGLY SIMPLE CATALYTIC ACCESS TO STEREODEFINED FULLY-SUBSTITUTED ALDEHYDE ENOLATES
- Jeferson B. Mateus-Ruiz** *PO-447*
Universidad Nacional Autónoma de México, Ciudad de México, México
STEREOSELECTIVE TOTAL SYNTHESIS OF ASPERGILLIDE A
- Tsubasa Matsuzawa** *PO-448*
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SYNTHESIS OF DIVERSE BENZOTHIOPHENES VIA REACTION OF ARYNES WITH ALKYNYL SULFIDES
- Joshua McLean** *PO-449*
Trinity College Dublin, Dublin, Ireland
DEVELOPMENT OF NOVEL THIOL-ENE MEDIATED PEPTIDE LIGATION STRATEGIES
- Claudio Flavio Meyer** *PO-450*
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HYDRODIFLUOROMETHYLATION OF ALKENES WITH DIFLUOROACETIC ACID
- Jean Michalland** *PO-451*
Ecole Polytechnique, Palaiseau, France
ALTERNATING RADICAL STABILITIES. A CONVERGENT ROUTE TO TERMINAL AND INTERNAL BORONATES
- Pierre Milbeo** *PO-452*
Trinity College Dublin, Dublin, Ireland
THIOL-ENE CLICK LIGATION AS AN EFFICIENT APPROACH FOR PEPTIDE MACROCYCLIZATION
- Marco Minneci** *PO-453*
Università degli Studi di Milano, Milan, Italy
OPTIMIZED SYNTHESIS OF THE BACTERIAL MAGIC SPOT (p)ppGpp CHEMOSENSOR PyDPA
- Malte Moeller** *PO-454*
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IMPROVED SYNTHESIS OF CYSTOBACTAMID 861-2 AND ANALOGS
- Kazuki Morii** *PO-455*
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SYNTHETIC STUDIES ON LAMELLARINS
- Vladimir Motornov** *PO-456*
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ALPHA-FLUORONITROALKENES: USEFUL BUILDING BLOCKS FOR THE CONSTRUCTION OF NOVEL FLUORINATED HETEROCYCLES
- Bastian Muriel** *PO-457*
Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland
PHOTOREDOX-MEDIATED RADICAL DIFUNCTIONALIZATION OF CYCLOPROPENES

- Arif Music** *PO-458*
Ludwig-Maximilians University, Munich, Germany
BIARYL COUPLING OF TETRA(HETERO)ARYL BORATES VIA ELECTROCHEMICAL OXIDATIONS
- Yu Nakamura** *PO-459*
Tokyo Medical and Dental University (TMDU), Tokyo, Japan
FACILE SYNTHESIS OF DIVERSE BENZOPYRAN DERIVATIVES VIA GOLD-CATALYZED CYCLIZATION AND GENERATION OF ARYNES
- Aleksandra Narczyk** *PO-460*
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THE SYNTHESIS OF β,β -DISUBSTITUTED ALLYL ALCOHOLS AND THEIR TRANSFORMATION INTO UNNATURAL AMINO ACIDS
- Stéphanie Norsikian** *PO-461*
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TOWARDS THE TOTAL SYNTHESIS OF TIACUMICIN B: PREPARATION OF GLYCOSIDIC FRAGMENTS AND GLYCOSYLATION
- Dmitry Obydenov** *PO-462*
The Ural Federal University, Ekaterinburg, Russia
CARBAMOYLATED ENAMINONES AS VERSATILE BUILDING BLOCKS FOR THE SYNTHESIS OF AZAHETEROCYCLES
- Lukas Ochmann** *PO-463*
Justus Liebig University Giessen, Giessen, Germany
ALKOXYDIPHENYLPHOSPHINITES AS CARBOCATION SYNTHONS
- Derek Yiren Ong** *PO-464*
Nanyang Technological University, Singapore, Singapore
CONTROLLED REDUCTION OF CARBOXAMIDES TO ALDEHYDES, ALCOHOLS OR AMINES
- Jekaterina Ongouta** *PO-465*
Symrise AG, Holzminden, Germany
STUDIES TOWARDS THE TOTAL SYNTHESIS OF ASADANIN
- Dmitry Osipov** *PO-466*
Samara State Technical University, Samara, Russia
Zn- AND Sm-INDUCED REDUCTIVE REARRANGEMENT OF 2-ACYL-2,3-DIHYDROBENZOFURANS INTO 4H-CHROMENES
- Vitaly Osyanin** *PO-467*
Samara State Technical University, Samara, Russia
NEW APPROACHES TO SYNTHESIS OF 4H-CHROMENES
- Sándor B. Ötvös** *PO-468*
University of Graz, Graz, Austria
MULTISTEP CONTINUOUS FLOW SYNTHESIS OF THE CHIRAL KEY INTERMEDIATE OF PAROXETINE
- Padmaja** *PO-469*
Indian Institute of Technology Bombay, Mumbai, India
CASCADE RADICAL CYCLISATION ON ALKYNYL VINYLOGOUS CARBONATES FOR THE DIVERGENT SYNTHESIS OF TETRASUBSTITUTED FURANS AND DIHYDROFURANS
- Soumyaranjan Pati** *PO-470*
Indian Institute of Technology Bombay, Mumbai, India
SYNTHESIS OF FUNCTIONALIZED OLEFINS VIA BASE MEDIATED 1,6-ADDITION OF DIAZO COMPOUNDS AND THEIR ACTIVE METHYLENE PRECURSORS TO *p*-QUINONE METHIDES

- Andreas Paul** *PO-471*
University of Tübingen, Tübingen, Germany
NEW STUDIES TOWARDS THE TOTAL SYNTHESIS OF GULMIRECIN B
- Agnese Petrini** *PO-472*
Università degli Studi di Siena, Siena, Italy
TRIFUNCTIONAL SELF-IMMOLATIVE SPACERS LINKED TO AMIDES: A NEW OPPORTUNITY FOR BIOCONJUGATION
- Cristofer Pezzetta** *PO-473*
Dr. Reddy's Laboratories Ltd., Cambridge, UK
ENANTIOSELECTIVE SYNTHESIS OF N-BENZYLIC HETEROCYCLES: A NICKEL- AND PHOTOREDOX-DUAL CATALYSIS APPROACH
- Igor Philippov** *PO-474*
Novosibirsk Institute of Organic Chemistry, Novosibirsk, Russia
SYNTHESIS OF PYRAZOLO[1,5-a]PYRIDINES CONTAINING PHOSPHONATE MOIETY
- Jean-Marie Pohl** *PO-475*
Justus Liebig University Giessen, Giessen, Germany
MICROWAVE ASSISTED SYNTHESIS OF H-PHOSPHONATES
- Achim Porzelle** *PO-476*
Apollo Scientific Ltd., Cheshire, UK
100 G TO 1 KG - THE FORGOTTEN SCALE?
- Achim Porzelle** *PO-477*
Apollo Scientific Ltd., Cheshire, UK
CHIRAL AND NON CHIRAL N-BOC PROTECTED 7-AZAINDOLES IN BATCH AND FLOW
- Pauline Poutrel** *PO-478*
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COPPER CATALYZED ASYMMETRIC FORMATION OF ENANTIOENRICHED β -CF₃ ESTER & NITRILE DERIVATIVES
- Alexander Preinfalk** *PO-479*
University of Vienna, Vienna, Austria
DIRECTED ENANTIOSELECTIVE COUPLING OF ALDEHYDES AND ALKENES
- Felix Preusch** *PO-480*
University of Tübingen, Tübingen, Germany
CARBOHYDRATE DERIVED LIGANDS FOR CATALYTIC STEREOSELECTIVE CARBENOID CYCLOPROPANATION REACTIONS
- Salvatore Princiotta** *PO-481*
Università degli Studi di Siena, Siena, Italy
CONTINUOUS FLOW APPROACH FOR THE SYNTHESIS OF MAYTANSINOL, AS ADC-BASED THERAPY CYTOTOXIC AGENT
- Stefano Protti** *PO-482*
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ARYLAZO SULFONES: PHOTOACTIVATABLE SUBSTRATES FOR METAL-FREE ARYLATIONS
- Mikus Puriņš** *PO-483*
Riga Technical University, Riga, Latvia
CATIONIC 1,2-SILYL SHIFT IN PROPARGYL SILANES
- Adrien Quintard** *PO-484*
Aix-Marseille Université, Marseille, France
MULTI-CATALYTIC ENANTIOSELECTIVE METHODOLOGY AS ENTRY TO NEW SUPRAMOLECULAR TOOLS

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TOTAL SYNTHESIS OF α -TOCOPHEROL THROUGH ENANTIOSELECTIVE IRIIDIUM-CATALYZED FRAGMENTATION OF A SPIRO-CYCLOBUTANOL INTERMEDIATE
- Felix Reiners** *PO-486*
Ludwig-Maximilians University, Munich, Germany
THIETES: A NEW PLATFORM FOR MOLECULAR DIVERSIFICATION
- Luka Rejc** *PO-487*
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RADIOISOTOPE-ENABLED TRACKING OF SUBSTRATES IN SUZUKI CROSS-COUPPLING REACTION
- Evelien Renders** *PO-488*
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RUTHENIUM-CATALYZED REDUCTIVE ARYLATION OF *N*-(2-PYRIDINYL)AMIDES WITH ISOPROPANOL AND ARYLBORONATE ESTERS
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BICYCLIC β -LACTAM INTERMEDIATES FOR THE DIVERGENT SYNTHESIS OF MARINE POLYCYCLIC GUANIDINIUM ALKALOIDS
- Batoul Rkein** *PO-490*
Normandie Université, Rouen, France
DEAROMATIZATION OF ELECTRON POOR ARENES BY (4+2) CYCLOADDITION REACTION
- Joel Roesslein** *PO-491*
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PREPARATION OF INDOLENINES VIA NUCLEOPHILIC AROMATIC SUBSTITUTION
- Nicolai Rosenbaum** *PO-492*
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FORMAL SEMISYNTHESIS OF DEMETHYLGORGOSTEROL USING AN ENANTIOSELECTIVE CYCLOPROPANATION AS KEY STEP
- James Rossi-Ashton** *PO-493*
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TUNEABLE ACCESS TO MEDICINALLY RELEVANT SCAFFOLDS VIA AN ENANTIOSELECTIVE DEAROMATIVE CYCLISATION CASCADE
- Amanda L. Rousseau** *PO-494*
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SYNTHESIS OF 2,4-DIAMINOPYRIMIDINES AS POTENTIAL ANTIFOLATES
- Lukas Rycek** *PO-495*
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APPLICATION OF [2+2+2] CYCLOADDITION IN THE TOTAL SYNTHESIS OF SELAGINPULVILINES
- Bram Ryckaert** *PO-496*
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NOVEL BUILDING BLOCK TOWARDS HIGHLY FUNCTIONALIZED CYCLOPENTANOID SCAFFOLDS
- Dmytro Ryzhakov** *PO-497*
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RADICAL-MEDIATED DEAROMATIZATION OF INDOLES WITH SULFINATE REAGENTS AND PHOSPITHES FOR THE SYNTHESIS OF FLUORINATED AND PHOSPHONATED SPIROCYCLIC INDOLINES

- Malvika Sardana** *PO-498*
AstraZeneca, Gothenburg, Sweden
VISIBLE-LIGHT ENABLED LATE-STAGE AMINOCARBONYLATION OF ALKYL IODIDES WITH CARBON MONOXIDE
- Göran Schulz** *PO-499*
Leibniz University Hannover, Hannover, Germany
TRANSITION-METAL-MEDIATED RADICAL DEFORMYLATION OF ALDEHYDES USING VARIOUS AMINOXYL RADICALS
- Lydia Scott** *PO-500*
Monash University, Melbourne, Australia
SIMPLIFYING THE SYNTHESIS OF VIRGINIAMYCIN MII ANALOGUES FOR CRYO-EM GUIDED DRUG DEVELOPMENT
- Yang Feng Anders See** *PO-501*
Nanyang Technological University, Singapore
TOWARDS THE SYNTHESIS OF SAMROIYOTMYCINS A & B
- Alessio Sferrazza** *PO-502*
IRBM SpA, Rome, Italy
IMPROVED SYNTHESIS OF DEUTERIUM LABELED ATYPICAL BILE ACID METABOLITES AS ANALYTICAL STANDARDS FOR BILE ACID DISORDER DIAGNOSIS
- Alexandr Shafir** *PO-503*
The Barcelona Institute of Science and Technology, Tarragona, Spain
TOWARDS IODANE-DIRECTED ITERATIVE C-H ALKYLATION
- Seunghoon Shin** *PO-504*
Hanyang University, Seoul, Republic of Korea
UMPOLUING ALKYLATION BASED ON THE OXIDATION OF YNAMIDES
- Rajeev Shrestha** *PO-505*
Yeungnam University, Gyeongsan, Republic of Korea
METAL- FREE BASE MEDIATED TANDEM BENZANNULATION OF N-TOSYLHYDRAZONES WITH 3 FORMYLCHROMONES: A GENERAL ROUTE TO DIVERSE AND POLYFUNCTIONALIZED XANTHONES
- Moritz Sinast** *PO-506*
University of Stuttgart, Stuttgart, Germany
SYNTHESIS OF THE AB RING SYSTEM OF CLIFEDNAMIDE
- Veronika Šlachtová** *PO-507*
Palacky University, Olomouc, Czech Republic
NOVEL APPROACHES TO 2-AMINO BENZOXAZOLES
- Manolis Sofiadis** *PO-508*
University of Crete, Heraklion, Greece
ORGANOCATALYTIC [3+2]-ANNULATIONS OF β,γ -UNSATURATED- γ -LACTAMS WITH α,β -UNSATURATED ALDEHYDES
- Olga Sokolova** *PO-509*
University of Bristol, Bristol, UK
C-C BOND ACTIVATION INITIATED CASCADE PROCESSES
- Patrycja Sokołowska** *PO-510*
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FIRST SYNTHESIS OF CRYPTANDS WITH SUCROSE SCAFFOLD
- Magdalena Sommer** *PO-511*
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ELECTROCATALYTIC IODOPERFLUOROALKYLATION OF UNSATURATED HYDROCARBONS

- Stefanie Spindler** *PO-512*
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STUDIES TOWARDS THE TOTAL SYNTHESIS OF TUSCORON C
- Laura Srsan** *PO-513*
University of Tübingen, Tübingen, Germany
SYNTHESIS OF NEW GLYCOPEPTIDES
- Simone Stegbauer** *PO-514*
Technical University Munich, Garching, Germany
CHROMOPHORE ACTIVATION AT ITS BEST - INFLUENCING THE SELECTIVITY OF PHOTOREACTIONS BY ADDITION OF LEWIS ACIDS
- Michael Steinacher** *PO-515*
TU Wien, Vienna, Austria
TOWARDS THE TOTAL SYNTHESIS OF PROVIDENCIN
- Maria Stiblarikova** *PO-516*
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FIRST TOTAL SYNTHESIS OF VARIOXIRANOL A
- Barbara Stoessel** *PO-517*
ETH Zürich, Zürich, Switzerland
STUDIES TOWARD THE TOTAL SYNTHESIS OF NAHUOIC ACID A
- Manolis Stratakis** *PO-518*
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GOLD NANOPARTICLE-CATALYZED SILABORATION OF CYCLOPROPYL ALDEHYDES FORMING REARRANGED SILYLOXY BORONATES
- Abdusalom Suleymanov** *PO-519*
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SYNTHESIS AND APPLICATIONS OF VINYL TRIAZENES
- Tímea Szabó** *PO-520*
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TOTAL SYNTHESIS OF INDOLE ALKALOIDS
- Milena Szewczyk** *PO-521*
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CYCLIZATION OF 5-(1*H*-INDOL-3-YL)-3-OXOPENTANOIC ACID ESTERS AND AMIDES PROMOTED WITH TRANSITION METAL TRIFLATES
- Nicholas Tappin** *PO-522*
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REACTIVITY AND SYNTHETIC UTILITY OF α -BORYL CARBON CENTERED RADICALS: TWO OPPOSING REACTION MANIFOLDS
- Ömer Taspınar** *PO-523*
University of Cologne, Cologne, Germany
STUDIES TOWARDS THE SYNTHESIS OF EURYSTEROL A
- David Tejedor** *PO-524*
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A GENERAL HYDROCYANATION OF ACTIVATED TERMINAL ALKYNES
- Johanna Templ** *PO-525*
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TOWARDS THE TOTAL SYNTHESIS OF EUPHOSALICIN AND PEPLUANIN A - ROUTE TO A HIGHLY OXYGENATED CYCLOPENTANE KEY FRAGMENT
- Pierre Thesmar** *PO-526*
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DIVERGENT TOTAL SYNTHESIS OF (+)-EPICOCCIN G AND (-)-ROSTRATIN A ENABLED BY DOUBLE C(sp³)-H ACTIVATION

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DOUBLE ELECTROPHILIC ACTIVATION OF YNAMIDES: A STRAIGHTFORWARD ENTRY TO α -HALO-CARBOXYL DERIVATIVES
- Raju S Thombal** *PO-528*
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In/Ag-CATALYZED CONSTRUCTION OF *N*-ARYLPYRAZOLES VIA REGIOSELECTIVE [2+2+1]-OXIDATIVE *N*-ANNULATION: TWO IS BETTER THAN ONE
- Karolina Tiara** *PO-529*
 Polish Academy of Science, Warsaw, Poland
STEREOCONTROLLED DEBENZYLATING CYCLOETHERIFICATION DEPENDED ON SUBSTRATE REACTIVITY
- Gergely L. Tolnai** *PO-530*
 Eotvos Lorand University, Budapest, Hungary
SYNTHESIS OF VERSATILE BICYCLOPENTANE BUILDING BLOCKS FROM [1.1.1]PROPELLANE
- Danjan Trenz** *PO-531*
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ENANTIOSELECTIVE SYNTHESIS OF PROPARGYL ALCOHOLS WITH DIYNES UNDER CARREIRA CONDITIONS
- Krishna Nand Tripathi** *PO-532*
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ORGANO PHOTOINDUCED DECARBOXYLATIVE ALKYLATION OF COUMARINS WITH *N*-(ACYLOXY)PHthalimide
- Johan Van der Eycken** *PO-533*
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TOTAL SYNTHESIS AND BIOLOGICAL EVALUATION OF PELOFEN, A NEW MICROTUBULE-STABILIZING AGENT
- Szilárd Varga** *PO-534*
 Hungarian Academy of Sciences, Budapest, Hungary
CHIRAL BUILDING BLOCKS IN THE TOTAL SYNTHESIS OF MONOTERPENE INDOLE ALKALOIDS
- Georgios Vassilikogiannakis** *PO-535*
 University of Crete, Heraklion, Greece
DOUBLE VINYLOGOUS REACTIVITY OF THE γ AND γ' POSITIONS OF CYCLIC 2-ENONES: ORGANOCATALYSED ASYMMETRIC SYNTHESIS OF FUSED CARBOCYCLES
- Timo von Keutz** *PO-536*
 University of Graz, Graz, Austria
GENERATION AND UTILIZATION OF UNSTABLE CARBENOID INTERMEDIATES USING CONTINUOUS FLOW TECHNOLOGY
- Aleksey Vorob'ev** *PO-537*
 Novosibirsk Institute of Organic Chemistry, Novosibirsk, Russia
SYNTHESIS OF FLUORINATED PYRAZOLO[1,5-*a*]PYRIDINES
- Sebastian Wienhold** *PO-538*
 Technical University Munich, Garching, Germany
TOWARDS THE TOTAL SYNTHESIS OF (-)-PULVOMYCIN
- Jason D. Williams** *PO-539*
 University of Graz, Graz, Austria
FLOW PHOTOCHEMISTRY FOR EFFICIENT AND SCALABLE SYNTHESIS

- Lukas Martin Wingen** *PO-540*
University of Bonn, Bonn, Germany
SYNTHESIS OF NOVEL LIPID I AND LIPID II ANALOGS
- Bernhard Wölfl** *PO-541*
Max-Planck-Institut für Kohleforschung, Mülheim/Ruhr, Germany
TOTAL SYNTHESIS OF CALLYSPONGIOLIDE
- Yikang Wu** *PO-542*
Chinese Academy of Sciences, Shanghai, China
CHEMOSELECTIVITY IN PERHYDROLYSIS OF KETONES, KETALS, AND EPOXIDES
- Silong Xu** *PO-543*
Xi'an Jiaotong University, Xi'an, China
LEWIS BASE-CATALYZED REARRANGEMENTS OF ELECTRON-POOR CYCLOPROPANES
- Yi-Chi Yang** *PO-544*
National Chiao Tung University, Hsinchu, Taiwan
PALLADIUM-CATALYZED SEQUENTIAL ARYLATION OF CYCLIC VINYLOGOUS ESTERS
- Zhu-Jun Yao** *PO-545*
Nanjing University, Jiangsu, China
CONCISE SYNTHESIS OF ALL-CIS-3,4,5-SUBSTITUTED PIPERIDINES THROUGH CASCADE RADICAL CYCLISATION INITIATED BY VISIBLE LIGHT-PROMOTED HYDROSILYLATION OF ALKENES
- Liu Ye** *PO-546*
Southern University of Science and Technology, Shenzhen, China
C-H BOND-INVOLVED INTRAMOLECULAR ASYMMETRIC RADICAL CYCLIZATION
- Suguru Yoshida** *PO-547*
Tokyo Medical and Dental University (TMDU), Tokyo, Japan
SINGLE C-F BOND CLEAVAGE OF TRIFLUOROMETHYLARENES WITH A LATENTLY TRANSFORMABLE ORTHO-SILYL GROUP
- František Zálešák** *PO-548*
Palacky University, Olomouc, Czech Republic
BENZO[d]THIAZOLE-2-SULFONYL GROUP AS A NITROGEN ACTIVATING AND PROTECTING GROUP
- Wojciech Zawodny** *PO-549*
University of Vienna, Vienna, Austria
KETONE ACTIVATION ENABLES METAL-FREE ALPHA-ARYLATION AND ALPHA-OXYAMINATION OF ACETOPHENONES
- Andreas Zech** *PO-550*
Technical University Munich, Garching, Germany
PHOTOCHEMICAL REACTION CASCADE FROM O-PENT-4-ENYL-SUBSTITUTED SALICYLATES TO COMPLEX MULTIFUNCTIONAL SCAFFOLDS
- Yufen Zheng** *PO-551*
The University of Hong Kong, Hong Kong, P.R. China
INTRAMOLECULAR (4+3) CYCLOADDITIONS OF THIOPHENES
- Egor Zhilin** *PO-552*
N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia
SYNTHESIS OF DOUBLE NO-DONORS INCORPORATING FUOXAN AND AZASYDNONE RINGS
- Yuxiang Zhu** *PO-553*
University of Oxford, Oxford, UK
HFIP SOLVENT ENABLES ALCOHOLS TO ACT AS ALKYLATING AGENTS IN STEREOSELECTIVE HETEROCYCLIZATION

- Benjamin Zonker** *PO-554*
Justus Liebig University Giessen, Giessen, Germany
SIGMATROPIC REARRANGEMENT OF IMINIUM SALTS EXEMPLIFIED ON NORADAMANTANE DERIVATIVES
- Robert Zscherp** *PO-555*
Technical University of Braunschweig, Braunschweig, Germany
THE SYNTHESIS OF AN ARTIFICIAL, BACKBONE MODIFIED ENTEROBACTIN ANALOGUE
- Tobias Zweiböhmer** *PO-556*
University of Tübingen, Tübingen, Germany
SYNTHESIS OF NOVEL AZA-BODIPY DERIVATES FOR PHOTODYNAMIC THERAPY

Late Poster

- Denis Nihuel Prada Gori** *PO-557*
Universidad Nacional de Rosario, Rosario, Argentina
DESIGN OF A SELECTIVE AND TUNABLE RCEYM-HYDROGENATION ONE-POT PROCESS
- Yang Yang** *PO-558*
University of Copenhagen, Copenhagen, Denmark
EXPLORING THE ROLE OF BASES IN CARBOXYLATION OF GRIGNARD REAGENTS WITH CO₂
- Birgit Meindl** *PO-559*
TU Wien
SYNTHESIS OF N SUBSTITUTED INDOLO[3,2,1-jk]CARBAZOLE BASED SYSTEMS FOR ORGANIC ELECTRONICS
- Nikolaus Poremba** *PO-560*
TU Wien
RECENT PROGRESS OF AZAINDOLO[3,2,1-jk]CARBAZOLE BASED DONOR-ACCEPTOR MATERIALS AS POTENTIAL TADF EMITTERS
- Clare Muhanji** *PO-561*
The Technical University of Kenya, Nairobi, Kenya
SYNTHESIS OF BENZISOTHIAZOLE DERIVATIVES AS POSSIBLE HIV-1 NUCLEOCAPSID PROTEIN-7 (NCp7) INHIBITORS

Author Index

ESOC 2019



Giant Ferris Wheel

Famous landmark for the Prater amusement park

Presenting authors in bold italics.

A

Abdelraheem, E. **PO-1**
 Abdulla, H.O. PO-482
 Abell, A. **OC-22**
 Abid, S. PO-417
 Ackermann, L. OC-6
 PO-67, PO-96, PO-317
 Adamsen, T.Ch.H. PO-189
 Ådén, J. PO-173
 Adler, P. PO-392, PO-435
 Adolfsson, D. **PO-173**
 Adolfsson, H. PO-153
 Afanasyev, O. IL-4
 Aggarwal, V. PO-341, PO-386
 Aillard, P. PO-342
 Ajdacic, V. PO-105
 Akiyama, T. **OC-7**
 Akssia, M. PO-380
 Al-Shihry, S. **PO-299**
 Alandini, N. **PO-2**
 Alassad, Z. PO-28
 Alati, S. **PO-334**
 Albrecht, A. **PO-4**, PO-465
 Albrecht, L. **PO-3**
 Alfuth, J. **PO-323**
 Allegrini, P. PO-481
 Allwood, D. PO-144
 Alme, E. **PO-174**
 Almqvist, F. PO-173, PO-240
 Alston, B. OC-25
 Altmann, K.-H. PO-517
 Alvarenga, N. PO-52
 Amable, L. PO-108
 Amatore, M. PO-361
 Ambrosio, T. **PO-5**
 Amer, M. **PO-335**
 Amesty, Á. PO-215
 Amin, H.I.M. PO-482
 Amir, R. **IL-11**
 Ammar, U. **PO-175**
 An, X. PO-542
 Anand, B. PO-256
 Anania, M. **PO-6**
 Andre-Joyaux, E. **PO-336**
 Angelucci, F. **PO-176**, PO-434
 Angibaud, P. PO-38
 Angyal, P. PO-534
 Annibaletto, J. **PO-7**, PO-16
 Antol, I. **PO-300**

Antonchick, A.P. PO-120, PO-142
 Arends, I. PO-52
 Arlinghaus, H.F. PO-252
 Armstrong, R. PO-354
 Asad, K. PO-258
 Åstrand, O.A.H. **PO-177**
 Athavale, S. **PO-8**
 Aubert, C. PO-361
 Aubin, A.J. PO-246, PO-247
 Audisio, D. **OC-23**, PO-195
 PO-233, PO-298, PO-498
 Augustin, A.U. **PO-337**
 Awadellah, F.M. **PO-178**
 Aynetdinova, D. PO-402
 Ayoub, I. PO-196
 Azofra, L.M. PO-17, PO-171

B

Baaziz, S. PO-396
 Babić, D. PO-330
 Bacchi, A. PO-26
 Bach, Th. **PL-5**, PO-56. PO-348
 PO-376, PO-393, PO-438
 PO-514, PO-538, PO-550
 Backenköhler, A. PO-206
 Backes, M. PO-465
 Bai, L. PO-168
 Baik, M.-H. PO-130
 Bal, M.K. **PO-254**
 Balázs, Á. PO-82
 Ball, L. PO-5
 Ball-Jones, M.P. PO-319
 Balliu, A. **PO-179**
 Balzer, N. **PO-255**
 Bamberger, J. PO-47
 Bampali, K. PO-249
 Bandow, J. PO-197
 Banks, C.E. PO-254
 Baran, Ph.S. **PL-7**
 Barilone, J.L. PO-294
 Barman, S. PO-327
 Barros, M.E. PO-214
 Bartens, Ch. PO-173
 Bartos, P. **PO-256**
 Barysevich, M. OC-10
 Bates, R. PO-501
 Baudequin, Ch. PO-38
 Baudoin, O. PO-10, PO-134, PO-526
 Bauer, T. **PO-9**

Baumann, A. **PO-338**, PO-486
 Baumann, A.N. PO-458
 Baumgartner, Y. **PO-10**
 Bauspieß, S. **PO-339**
 Bayer, M. **PO-340**
 Baykal, A. PO-209
 Beattie, N. **PO-301**
 Beau, J.-M. PO-461
 Bednárová, L. PO-293
 Bedringaas, S. PO-216
 Beemelmans, Ch. **PO-180**, PO-213, PO-236
 Beier, P. PO-237, PO-420, PO-444
 Belaj, F. OC-27
 Belal, M. PO-532
 Bellec, N. PO-396
 Bellina, F. PO-77
 Belousoff, M. PO-500
 Benckendorff, C. PO-227
 Bende, A. PO-332
 Bendl, Ch. PO-104
 Bennett, S. **PO-341**
 Bennison, M. OC-25
 Bentouhami, E. PO-148
 Bentzinger, G. PO-506
 Bera, S. **PO-11**
 Berardo, E. OC-25
 Bergander, K. PO-398
 Berger, M. **PO-342**, PO-425
 Bergman, J. PO-498
 Berini, Ch. PO-7
 Bernardes, G.J.L. PO-225
 Berneaud-Kötz, H. **PO-343**
 Bernstein, M. PO-320
 Bertozzi, C. PO-243
 Besset, T. **IL-12**, PO-21
 Beytlerova, N. PO-495
 Bhasin, A. PO-506
 Bhosale, D. **PO-181**
 Biafora, A. PL-6
 Biagetti, M. PO-77
 Bialy, L. PO-319
 Bibal, B. **PO-12**
 Biber, N. PO-209
 Bickmann, Ch. PO-287, **PO-302**
 Bier, C. PO-198
 Biernacki, K. **PO-182**
 Bihel, F. **PO-344**
 Binder, D. PO-198
 Birsa, L.M. PO-239, **PO-324**

- Bitai, J. **PO-13**
 Bjørsvik, H.-R. PO-174, PO-176
 PO-189, PO-216, PO-434
 Blasius, C. **PO-14**
 Boaler, P. **PO-325**
 Bogdan, E. PO-280
 Böhmer, W. PO-103
 Bojanowski, J. PO-4
 Bojarová, P. PO-248
 Boldrini, C. PO-94
 Bonifazi, D. PO-473
 Börgel, J. PO-252
 Borges-González, J. PO-40, PO-333
 Borgini, M. **PO-345**
 Borisov, D. **PO-257**
 Böse, D. PO-136
 Botta, M. PO-345
 Boudný, M. PO-204
 Bouhadir, K. PO-261
 Bousis, S. **PO-183**
 Bouvet, S. PO-503
 Bower, J. PO-366, PO-384, PO-509
 Bracke, M. PO-533
 Braganca, C.R.S. PO-88
 Bräse, St. PO-170, PO-492
 Brauns, M. PO-443
 Brea, J. PO-186
 Brechmann, L.T. **PO-15**
 Brenk, R. PO-227
 Breton, G. OC-5
 Breugst, M. PO-443
 Breukelaar, W. PO-75
 Bricard, J. PO-344
 Brière, J.-F. PO-7, **PO-16**
 Briggs, M. OC-25
 Britten, Th. OC-2
 Brode, J. PO-307
 Brodie, G. **PO-184**
 Broggin, G. PO-117
 Brown, S. PO-89
 Brulíková, L. PO-507
 Bruneau, Ch. PO-166
 Brzozowska, A. **PO-17**
 Bua, S. PO-178
 Bub, Ch. **PO-346**
 Bujok, R. **PO-347**
 Bunz, U. PO-266
 Bures, J. PO-145
 Burg, F. **PO-348**
 Bürger, M. **PO-349**
 Burke, H. PO-440
 Buron, F. PO-380
 Butsi, K. PO-494
 Buzzetti, L. PO-2
- Bystrov, D. PO-262, **PO-350**, PO-552
 Blocka, A. **PO-18**
- ## C
- Cafferty, B. OC-15
 Cairns, A. PO-173
 Caivano, I. **PO-19**
 Callebaut, B. **PO-351**
 Calvo, R. **PO-352**
 Cambeiro, X.C. PO-98
 Cammarella, C. PO-94
 Campos, J. **IL-3**
 Candeias, N. PO-403
 Cantat, T. OC-23
 Cantillo, D. PO-411, PO-536
 Capaccio, V. PO-33
 Capdevila, L. **OC-6**, PO-317
 Cardona, F. PO-185
 Carell, Th. PO-193, PO-207
 Cariati, L. PO-103
 Carissan, Y. PO-361
 Carmona, A.T. **PO-185**
 Čarný, T. **PO-353**
 Carretero-Cerdán, A. **PO-303**
 Carrillo, R. PO-331
 Cassels, B. PO-186
 Castellón, S. PO-112
 Castriciano, M.A. PO-363, PO-364
 Cavalli, D. PO-10
 Cavallo, L. PO-17, PO-171
 Cerai, G.P. IL-2
 Cerkovnik, J. PO-154
 Cerra, B. OC-21
 Chamberlain, A. **PO-354**
 Champagne, P.A. PO-298
 Chang, R. PO-315
 Chang, T. PO-23, PO-124
 Chataigner, I. PO-490
 Chávez, T. **PO-186**
 Chaladaj, W. PO-18, **PO-20**
 Chen, H. PO-100
 Chen, M.-Y. **PO-21**
 Chen, W.W. **PO-355**
 Cheng, C.-W. PO-54
 Chi, K.-W. PO-329
 Chiba, S. PO-464
 Chiha, S. **PO-187**
 Chirila, P. OC-8, **PO-22**
- Chiu, P. PO-551
 Chng, Y.S. **PO-356**
 Cho, S.J. PO-202
 Choi, H.S. **PO-23**
 Choi, J.-H. PO-119
 Choppin, S. PO-339, PO-445
 Christiaens, M. **PO-357**
 Chronakis, N. **PO-258**
 Chung, T.S. PO-56
 Churakov, A. PO-442
 Chusov, D. **IL-4**
 Chusova, O. IL-4
 Ciccolini, C. **PO-358**
 Cieślak, M. PO-245
 Cigan, E. OC-27
 Cintulova, D. **PO-188**
 Cirillo, D. **PO-189**
 Čisářová, I. PO-19, PO-72
 Civera, M. **PO-304**
 Claasen, B. PO-405
 Clarhaut, J. PO-233
 Clark, J.S. PO-382
 Claver, C. PO-112
 Clayden, J. PO-335, PO-377
 Čmelová, P. **PO-24**
 Cobas, C. PO-320
 Coeffard, V. PO-385
 Coffey, L.V. PO-42, PO-88
 Cohen, A. **PO-360**
 Cohen, Y. **PO-359**
 Colell, J. PO-390
 Collin, H. **PO-25**
 Collini, E. PO-363, PO-364
 Colomer, I. PO-553
 Commeiras, L. **PO-361**
 Conceicao, R. **PO-190**
 Conklin, D. OC-1
 Cons, B. **PO-362**
 Conti, G. PO-453
 Cooper, A. OC-25
 Coote, S. **OC-2**
 Coppola, G. PO-108
 Cordaro, M. **PO-363**, **PO-364**
 Cordero-Vargas, A. PO-447
 Cornella, J. **OC-24**
 Cornelius, J. PO-533
 Corrado, M. PO-103
 Correa, K. PO-243
 Costa, M. PO-103
 Cox, L. PO-366
 Crisenza, G. PO-91
 Croci, F. PO-103

Cuenca, A.B. PO-355, PO-374
Cui, W.-C. PO-545
Cuzzola, A. PO-77
Czechitzky, W. PO-319
Czekelius, C. PO-511

D

Dąbrowski, M. PO-66
Daikeler, A. **PO-365**
Dale, H. **PO-305**
Dalling, A. **PO-366**
Daniel, M. PO-283
Daniliuc, C.G. PO-141
Danowski, W. PO-295
Dao-Huy, T. **PO-191**
Das, M. PO-164, **PO-259**
Daskalakis, K. PO-508
Daško, M. PO-182
Dastan, A. **PO-367**
Daum, M. PO-229
Davidson, R. PO-473
Davies, J. PO-90
Davies, Th. **PO-368**
De, R. PO-327
de Koning, C. PO-212, PO-494
de la Torre, A. PO-342
De Orbe, M.E. OC-17
De Wever, O. PO-533
Dehaen, W. PO-220
Delgado-Hernández, S. **PO-369**, PO-524
Della Ca', N. **PO-26**
Delorme, M. PO-361
Delpiccolo, C.M.D.L. PO-557
Demidov, M. PO-466
Demirel, P. PO-240
Demitri, N. PO-196
Demizu, Y. PO-224
Demkowicz, S. PO-182
Denisov, D. PO-257
Denmark, S. PO-8
Denton, E. PO-341
Derat, E. PO-129
Désaubry, L. PO-148, PO-378
Deska, J. **OC-9**
Desmecht, A. **PO-27**
Destro, G. OC-23
Deuchmann, A. PO-173
Deutzmann, A. PO-243
Dewez, D. **PO-370**
Dhayalan, V. **PO-28**
Di Francesco, D. **PO-29**
Di Mauro, G. PO-313, **PO-371**

Di Pasquale, A. **PO-192**
Dialer, C. **PO-193**
Diamanti, E. PO-183
Diana, R. **PO-372**
Díaz, A. **PO-373**
Díaz, M. **PO-374**
Didier, D. PO-338, PO-458, PO-486
Diederichsen, U. PO-226, PO-241
Dobbs, A. PO-306
Dohanosova, J. PO-516
Doltsinis, N. PO-259
Domański, S. PO-20
Donohoe, T. PO-354, PO-397
PO-402, PO-431, PO-553
Donslund, A.S. **PO-30**
Dooley Cullinane, T.-M. PO-88
Doris, E. PO-233
Dorn, F. PO-103
Dove, Ch. PO-243
Draskovits, M. **PO-375**
Drennhaus, T. PO-394
Drepper, Th. PO-198
Drescher, M. PO-313, PO-371
Drexler, D. PO-193
Du, Q. **PO-31**
Duarte, F. PO-368
Dugave, Ch. PO-498
Duman, E. PO-554
Durandetti, M. PO-490
Dürner, J. **PO-376**
Dydio, P. PO-80
Dzierzbicka, K. PO-235
Dzieszkowski, K. **PO-32**

E

Eagling, L. **PO-377**
Echavarren, A.M. OC-17
Eddhif, B. PO-233
Eder, I. **PO-260**
Ederwish, S. **PO-378**
Edlová, T. **PO-379**
Eger, E. PO-75
Egyed, O. PO-534
Eitzinger, A. **PO-33**, PO-260
Ejjoumany, A. **PO-380**
El Hakmaoui, A. PO-380
El Said El Sayed, H. **PO-34**
El Sepelgy, O. PO-17
El-Hage, F. **PO-35**
El-lateef, H.M.A. PO-299

El-Sepelgy, O. PO-62, PO-171
Elaridi, J. **PO-261**
Elbaum, D. PO-502
Elek, G.Z. **PO-381**
Elmore, C. PO-498
Eltantawy, A.I.A. PO-462
Elwood, J. **PO-382**
Enev, V. PO-415
PO-429, PO-515, PO-525
Epishina, M. PO-442
Erbland, G. PO-417
Ericsson, C. PO-498
Eriksen, M.E. PO-434
Ernst, J. PO-259
Ernst, M. PO-199, PO-249
Erver, J. **PO-383**
Espinosa, M. PO-106
Estévez-Braun, A. PO-215
Evano, G. PO-211, PO-370, PO-527
Evans, L. **PO-306**
Evans, P. PO-273

F

Fabbrini, D. PO-502
Fagnoni, M. PO-482
Faigl, F. PO-400
Farkas, T. **PO-194**, PO-203
Farndon, J. **PO-384**
Favi, G. PO-2, PO-358
Fawcett, A. PO-341
Fedoseev, P. PO-108
Feilner, J. IL-2
Felsher, D. PO-243
Feng, M. **PO-195**
Feringa, B.L. OC-5, PO-295
Fernandez Bieber, M. PO-512
Fershtat, L. **PO-262**
PO-350, PO-442, PO-552
Fey, N. PO-384
Fink, M.J. **OC-15**
Fiorito, D. **PO-36**
Fischer, J. **PO-385**
Fischer, T. PO-47
Fleck, N. **PO-307**
Fleischer, I. **PO-37**, PO-44, PO-68
Flentie, K. PO-240
Font, P. PO-127
Fontana, F. **PO-308**
Fontana, G. PO-481
Fordham, J. **PO-386**
Forschner, R. PO-405

- Fraga-Timiraos, A.B. PO-238
 França, S. PO-214
 France, D. PO-184
 Franck, X. PO-390
 François-Heude, M. PO-461
 Fredriksen, T.-A. PO-434
 Freitas, R. PO-25
 Freudenberg, J. PO-266
 Frey, S. **PO-387**
 Fripiat, S. **PO-38**
 Frkanec, L. **PO-326**
 Fröhlich, J. PO-265
 PO-270, PO-559, PO-560
 Fröh, M.L. PO-422
 Fu, L. PO-181
 Fuchs, M. OC-27
 Fuentes Pineda, R. PO-279
 Fulco, F. PO-183
 Funk, L.-M. PO-226, PO-241
 Fürstner, A. **PL-2**, PO-541
- G**
- Gabillet, S. PO-298
 Gabriele, B. PO-26
 Gade, L.H. PO-14, PO-137, PO-264
 Gadekar, S.C. PO-28
 Gademann, K. PO-242, PO-491
 Gagnebin, A. PO-457
 Galla, H.-J. PO-252
 Gallardo-Fuentes, S. PO-316
 Gallo, M. PO-502
 Garbacz, M. **PO-39**
 García, F. PO-373
 García Mancheño, O. **OC-11**, PO-47
 García-Monzón, I. **PO-40**
 García-Tellado, F. PO-369, PO-372, PO-524
 García-Vázquez, V. **PO-41**
 Gärtner, P. PO-415
 PO-429, PO-515, PO-525
 Gatlik, B. PO-20
 Gao, Y. PL-6
 Gavel, M. PO-410
 Gavendova, M. **PO-42**
 Gazvoda, M. **PO-43**, PO-97
 Gazzola, S. **PO-388**
 Geenen, S.R. **PO-263**
- Geerdink, D. PO-342
 Gehrtz, P. PO-37, **PO-44**
 Geier, M. PO-172
 Geiger, V. PO-44
 Gelis, C. PO-78
 George, R. **PO-196**
 Gerke, V. PO-252
 Gharpure, S.J. PO-469
 Ghosh, K.K. **PO-45**
 Ghosh, M. **PO-389**
 Gil de Montes, E. PO-225
 Gilheany, D. PO-107
 Gilmore, Ch. OC-1
 Gilmour, R. PO-398
 Gioiello, A. **OC-21**
 Gisbert, Y. PO-417
 Gjertsen, B.T. PO-216
 Glachet, Th. **PO-390**
 Glaesel, T. **PO-46**
 Glasovac, Z. **PO-309**, PO-326
 Glavac, D. PO-48
 Glavaš, M. **PO-391**
 Glessi, C. PO-437
 Glibstrup, E. OC-1
 Glieder, T. PO-172
 Glindemann, C.P. PO-206
 Glorius, F. PO-57, PO-101, PO-141
 PO-164, PO-252, PO-259
 Gmeiner, G. PO-188, PO-429
 Gnaegi-Lux, M. PO-522
 Godard, C. PO-112
 Gollner, A. **OC-4**
 Gómez-Bengoa, E. PO-145
 PO-303, PO-319, PO-322
 Gómez-Martínez, M. **PO-47**
 Gómez-Vallejo, V. PO-487
 Gómez-Bengoa, E. PO-115
 Gonçalves, C.R. **PO-392**, PO-435
 Gonglach, S. PO-73, **PO-327**, PO-328
 González, L. PO-313, PO-392, PO-435
 González-Bello, C. PO-201
 Goößen, L. **PL-6**
 Gordon, M.R. PO-388
 Goto, C. PO-224
 Göttlich, R. PO-475
 Götz, F. PO-209
- Gouverneur, V. **PL-9**, PO-450
 Grab, H. **PO-393**
 Gracza, T. PO-353, PO-516
 Grainger, R. PO-362
 Gramage-Doria, R. PO-166
 Grätzel, M. PO-167
 Gravel, E. PO-233
 Greb, J. **PO-394**
 Gredičak, M. **PO-48**, PO-391
 Greenaway, R. **OC-25**
 Greenhalgh, M. PO-122
 Gregorić, T. PO-326
 Grela, K. PO-66
 Grill, D. PO-252
 Grimm, Ch. PO-118
 Grogan, G. PO-75
 Grosu, I. PO-280, PO-332
 Grosu, I.G. PO-332
 Gruber, K. OC-27
 Grünanger, Ch. OC-1
 Grunenberg, J. PO-430
 Gu, Y. **PO-49**
 Guariento, S. PO-77
 Guder, M. PO-443
 Guillaumet, G. PO-283, PO-380
 Günther, B. **PO-264**
 Guttroff, C. PO-209
 Györfi, N. **PO-395**
 Gyűjtő, I. **PO-310**
 Gyuris, M. PO-395
- H**
- Haas, M. PO-73, PO-327, **PO-328**
 Habiger, Ch. IL-2
 Hachem, M. **PO-50**
 Hädade, N.D. PO-280
 Haenle, J.C. PO-286
 Hagedoorn, P.-L. PO-1, PO-95
 Haidar, S. PO-215
 Haider, V. **PO-51**
 Halcovitch, N. OC-2
 Hale, L.V.A. PO-145
 Hall, A. PO-368
 Hamilton, A. OC-8, PO-22, PO-144
 Hammal, L. **PO-396**
 Hammerer, L. OC-27
 Hanefeld, U. PO-1, **PO-52**, PO-95
 Hapke, M. PO-46

- Harper, S. PO-502
Harrison, G. PO-240
Harrity, J.P.A. PO-319
Hartmann, P. OC-27
Harutyunyan, S.R. **PL-4**
Hashmi, A.St.K. PO-159, PO-441
Haug, B.E. PO-227
Haughey, M. **PO-397**
Haupenthal, J. PO-183
Hauptmann, R. PO-35
Haut, F.L. IL-2
Havránek, M. PO-181
Hayashi, T. **PO-398**
He, X. **PO-399**, PO-543
Hegedus, N. PO-194, PO-203
Heideman, G.H. PO-295
Heinrich, S. **PO-197**
Hell, S.M. PO-450
Helmuellet, S. PO-246
Hempel, K. PO-465
Hendrychová, D. PO-218
Hergert, T. **PO-400**
Hermann, S. PO-131
Hermans, S. PO-27
Herrera-Luna, J. PO-284
Hetmann, M. OC-27
Hett, T. PO-307
Hiebel, M.-A. PO-283
Hilgers, F. PO-198
Hioki, Y. **PO-401**
Hirota, T. OC-5
Hirsch, A.K.H. **IL-9**, PO-183
Hoarau, Ch. PO-38, PO-50
Hocek, M. PO-222, PO-250
Hodges, G. PO-305
Höfener, S. PO-264
Hoff, O. **PO-402**
Hoffmann-Röder, A. PO-229
Hofmann, N. **PO-53**
Hogenkamp, F. **PO-198**
Holmstedt, S. **PO-403**
Holz, J. PO-506
Holzer, B. **PO-265**
Holzheimer, M. **PO-404**
Holzwarth, M. **PO-405**
Hong, F.-E. **PO-54**
Hong, L. **PO-55**
Hopfner, K.-P. PO-193
Horkel, E. PO-265
Hörmann, F.M. **PO-56**
Horn, A. **PO-406**
Hosoya, T. PO-448, PO-459, PO-547
Houk, K. PO-8, PO-75, PO-298
Houwman, J. PO-103
Hrdina, R. PO-554
Hrobárik, P. PO-282, PO-292
Hsu, D.-S. **PO-407**
Hu, X. PO-11
Huang, H.-M. **PO-57**
Huang, L. PL-6
Huang, L. **PO-58**
Huang, Q. PO-451
Hubálek, M. PO-237
Huber, F. PO-491
Hudspith, L. PO-321
Huerta Uribe, A. PO-184
Hullaert, J. PO-351, PO-496
Hultzsck, K. PO-53, PO-104
Hwang, T.-Y. PO-407
Hyun, O. PO-175
Häddade, N.D. PO-332
Iaroshenko, V. **PO-59**
Iglesias, I. PO-320
Imhof, D. PO-540
Imramovský, A. PO-218
Iniesta, E. **PO-60**
Inkiewicz-Stepniak, I. PO-235
Intorp, S. **PO-266**
Ioffe, S. PO-456
Iorio, M. **PO-199**
Ireland, E. PO-213, PO-236
Iskryk, M. OC-10
Itami, K. OC-5, **PL-3**
Ito, M. PO-401
Ito, T. PO-149
Iwan, K. PO-207
Izquierdo, S. PO-503
Jablonski, J.-A.M. PO-247
Jacko, J. PO-72
Jacobi von Wangelin, A. **PO-61**
Jacobs, N. PO-533
Jaeger, K.-E. PO-198
Jaiswal, M.K. **PO-408**
Jakob, M. PO-56
Jang, J. **PO-409**
Jang, Y.-K. PO-17, **PO-62**
Jansa, J. PO-217
Jarosz, S. PO-510, PO-529
Jarret, M. PO-497
Jauch, J. PO-387, PO-413, PO-531
Jautzus, T. PO-236
Jelfs, K. OC-25
Jelinek, L. PO-181
Jeong, K. PO-124
Jeong, M. **PO-267**
Jeong, S.K. **PO-268**
Jeric, I. **PO-200**
Jerić, I. PO-391
Jhou, J.-N. PO-54
Jia, Z.-J. PO-142
Jiang, L. **PO-63**
Jiménez, M.c. **PO-201**, PO-284
Jiménez-Moreno, E. PO-225
Jin, R. PO-346
Johansen, M. **PO-64**
Johnson, M. PO-298
Jones, A.M. PO-254
Jones, P.G. PO-337, PO-349, PO-430
Joosten, A. **PO-410**
Jorda, R. PO-218
Jose, J. PO-215
Jubault, P. PO-21, PO-478
Jud, W. **PO-411**
Juhl, M. **PO-412**
Jung, I.H. **PO-269**
Jung, K.-Y. **PO-202**
Jung, T. **PO-413**
Junk, L. **PO-414**
Jurberg, I. PO-313
Kader, Th. **PO-270**, PO-559, PO-560
Kadziola, A. PO-130
Kaewmee, B. **PO-65**
Kählig, H. PO-313
Kaiser, D. PO-313, PO-392, PO-435
Kaiser, M. PO-342, **PO-415**
Kaiser, R.P. PO-19
Kajetanowicz, A. **PO-66**
Kalaitzakis, D. PO-508, PO-535
Kalaus, H. PO-375, **PO-416**
Kaldre, D. PO-313, PO-424

- Kalek, M.
PO-125, PO-311, PO-389
- Kaleta, Z.
PO-194, **PO-203**
- Kamitani, M. PO-163
- Kammerer, C. **PO-417**
- Kampová, H. PO-291
- Kananovich, D.
OC-10, PO-381
- Kanemoto, K. PO-547
- Kang, G. PO-130
- Kang, J.M. PO-268
- Kanizsai, I. PO-277
- Kantchev, E. PO-72
- Kanyiva, K.S.
PO-140, PO-149
- Kapilinskis, Z. **PO-271**
- Kaplaneris, N. **PO-67**
- Kappe, C.O. PO-411
- PO-468, PO-536, PO-539
- Karaghiosoff, K. PO-436
- Karchner, J. PO-205
- Kaszyński, P. PO-256
- Katayama, K. PO-162
- Katayev, D.
OC-14, PO-352
- Katea, S.N. PO-29
- Kathe, P.M.
PO-37, **PO-68**
- Kato, A. PO-185
- Kato, D. PO-10
- Katsonis, N. PO-34
- Kautny, P.
PO-270, PO-559, PO-560
- Kawiak, A. PO-245
- Kazmaier, U.
PO-406, PO-414, PO-421
- Kearsey, R. OC-25
- Kehr, G. PO-398
- Kemmitt, P. OC-2
- Kervefors, G. **PO-272**
- Kessler, J. **PO-418**
- Khairnar, P. **PO-419**
- Khalifa, A. **PO-273**
- Khan, S. **PO-69**
- Khaskin, E. PO-157
- Khirsariya, P.
PO-204
- Khutorianskyi, V.
PO-420
- Kidonakis, M. PO-518
- Kildahl-Andersen, G.
PO-177
- Kim, B. PO-267
- Kim, B.H. PO-276
- Kim, D.H. **PO-329**
- Kim, E. PO-276
- Kim, H. PO-409
- Kim, J.-S. PO-202
- Kim, M.J. PO-130
- Kim, S.
PO-124, PO-130
- Kim, S.-G. **PO-70**
- Kim, Y. PO-547
- King, N.
PO-213, PO-236
- Kinsella, M.
PO-42, PO-88
- Kinsinger, T. **PO-421**
- Kirchner, A. PO-207
- Kirchner, S. **PO-205**
- Kirin, S. PO-330
- Kirres, J. PO-289
- Kirschning, A.
PO-343, PO-427
- PO-454, PO-465, PO-499
- Klahn, P. **PO-206**, PO-555
- Klaiber, A. **PO-422**
- Klatte, M. OC-1
- Klauk, H. PO-264
- Klein, S. PO-281
- Klein, Th. **PO-423**
- Klemenc, S. PO-219
- Klepetářová, B. PO-420
- Klimánková, I. PO-237
- Klimochkin, Y.
PO-466, PO-467
- Klívar, J. PO-293
- Klose, I.
PO-313, **PO-424**
- Knaus, T. PO-103
- Knecht, F. PO-289
- Knecht, T. PO-164
- Knittl-Frank, Ch.
PO-342, **PO-425**
- Knochel, P. PO-436
- Kobosil, S.C.K. PO-169
- Koch, G. PO-436
- Kočovský, P. PO-6
- Kohlbecher, R. PO-278
- Kohls, P. OC-12
- Köhn, A. PO-506
- Kokotos, C.
PO-71, PO-152
- Kokotos, G. PO-208
- Kokotou, M. PO-152
- Kolarski, D. **OC-5**
- Kolb, B. PO-405
- Koóš, P. PO-353
- Koppel, K. PO-381
- Kornev, M. **PO-426**
- Kornigg, S. PO-136
- Körsgen, M. PO-252
- Korytiaková, E.
PO-207
PO-427
- Kösel, T.
PO-43, PO-97
- Košmrlj, J.
PO-219, PO-296, PO-487
- Kotora, M.
PO-19, **PO-72**, PO-495
- Kotschy, A. PO-395
- Kotzabasaki, V.
PO-76, PO-518
- Kouklovsky, C. PO-497
- Kourtellaris, A. PO-258
- Koutoulogenis, G. **PO-208**
- Kouznetsov, V. PO-110
- Kováč, O. **PO-428**
- Krammer, G. PO-465
- Kraszewski, K. **PO-311**
- Kratena, N. **PO-429**
- Kraus, F. **PO-209**
- Krause, B.M. **PO-210**
- Krauss, S. PO-209
- Kreft, A. **PO-430**
- Křen, V. PO-248
- Krisch, D. **PO-73**
- Kristensen, S.K. **PO-74**
- Krompiec, St.
PO-87, PO-275
- Kroutil, W.
OC-27, **PO-75**, PO-118
- Krückel, T. PO-62
- Krupička, M. PO-294
- Kryštof, V.
PO-217, PO-218
- Kubiński, K. PO-182
- Kuchař, M.
PO-220, PO-223
- Kuchuk, E. IL-4
- Kühne, R. PO-187
- Kulhánek, J. PO-291
- Kulikov, A. PO-442
- Kunfi, A. **PO-274**
- Kunz, D. PO-405
- Kurpanik, A. **PO-275**
- Kushida, S. PO-266
- Kwok, T. **PO-431**
- Kydonakis, M. **PO-76**
-
- L**
- Lagerblom, K. PO-86
- Lahboubi, M. **PO-211**
- Lakhdar, S. PO-490
- Lam, Y.
PO-251, PO-356
- Lanaridi, O. PO-285
- Lang, M. PO-302
- Lapointe, G. OC-1
- Larionova, N. PO-98
- Larsson, C. PO-240
- Lasányi, D.
PO-432, PO-530
- Laschat, S. PO-286
- PO-289, PO-405, PO-506
- Lasikova, A. PO-516
- Latkoliik, S. PO-191

- Layton, C. PO-246
Lazarotto, M. **OC-27**
Le Calvez, G. **PO-433**
Lebedev, Y. PO-171
Leboho, T. **PO-212**
Lecomte, M. PO-211
Lee, H. **PO-276**
Lee, H.-Y. PO-130
Lee, J. PO-124
Lee, J. PO-558
Lee, J.-W. PO-130, PO-412
Lee, J.H. PO-23
Lee, Y.R. PO-528
Legros, J. PO-490
Legøy Årvik, S. **PO-434**
Leichnitz, D. **PO-213**, PO-236
Lemmerer, M. PO-392, **PO-435**
Lence, E. PO-201
Lennon, C.M. PO-42, PO-88
Leonard, D. PO-335, PO-377
Lepsik, M. PO-217
Leroux, M. **PO-436**
Lesieur, C. PO-461
Lessi, M. **PO-77**
Lethu, S. PO-355
Levacher, V. PO-7, PO-16
Levchenko, V. **PO-437**
Leverenz, M. **PO-438**
Levitre, G. **PO-78**
Lewis, I. PO-436
Leyssens, T. PO-89
Lhiaubet-Vallet, V. PO-238
Li, H. PO-142
Li, J. PO-392, PO-435, PO-479
Li, W.Ch. PO-512
Li, Z.-L. **PO-79**
Liardet, L. PO-167
Lichosyt, D. **PO-80**
Lima, D. **PO-214**
Lima, L. PO-214
Lin, W. PO-419, PO-439
Lin, Y.-C. PO-489, PO-544
Linde, E. PO-272
Lindell, S.D. PO-388
Lindhardt, A. PO-25, PO-64
Liou, Y.-C. **PO-439**
Lipparini, F. PO-77
Little, M. OC-25
Liu, X.-Y. PO-79, PO-546
Liu, Y. PO-36
Llewellyn, B. PO-477
Llop, J. PO-487
Lloyd-Jones, G. PO-305, PO-325
Loch, M. PO-349
Loke, I. PO-506
Lombardo, M. OC-28
London, G. PO-274
Lopez de Moraga, A. PO-355
López Rojas, P. **PO-215**
Lopp, M. PO-381
Loreau, O. OC-23
Lou, T.S.-B. **PO-81**
Loza, M. PO-186
Lozinšek, M. PO-154
Lu, Z. PO-143
Lücht, A. PO-430
Luis, J.M. OC-6, PO-317
Lukášek, J. PO-255
Lukashenko, A. PO-467
Lumpi, D. PO-265
Lundevall, F. **PO-216**
Luo, J. PO-167
Lupton, D. PO-500
Lusby, P. PO-325
Lycka, A. **PO-217**
Lynch, D. **PO-440**
Mantel, M. **PO-443**
Mantellini, F. PO-358
Mantzourani, C. PO-208
Marcol-Szumilas, B. **PO-87**
Marcon, E. OC-23
Marek, I. PO-359, PO-360, PO-446
Mareya, T. **PO-88**
Margetić, D. PO-300, PO-309
Marghem, G. **PO-89**
Mari, G. PO-358
Markos, A. **PO-444**
Markovič, M. PO-353
Marsden, S. OC-20, PO-231
Marsden, St.R. PO-95
Martek, B.A. **PO-219**
Martin, G. PO-534
Martin, R. PO-49, PO-90, PO-145
Martín, T. PO-40, PO-333
Martín-Matute, B. PO-41, PO-303
Martin-Montero, R. **PO-90**
Martínez-Bailén, M. PO-185
Martinez-Erro, S. PO-41, PO-303
Martynow, D. PO-230
Martzel, Th. PO-16
Maruoka, H. PO-228
Marx, L. **PO-445**
Maryasin, B. **PO-313**
Maryška, M. PO-392, PO-435, PO-549
Maryska, M. **PO-220**
Masevicius, V. PO-223
Masman, M. **PO-221**
Massad, I. PO-103
Masson, G. **PO-446**
Masumoto, E. PO-78
Maslyk, M. PO-228
Mata, G. PO-182
Matassini, C. PO-541
Mateus-Ruiz, J.B. PO-185
Máth, D. **PO-447**
Mathe, D. PO-530
Matos, A.L.L. PO-203
Matoušek, V. PO-252
Mátravölgyi, B. PO-237
Matsuzawa, T. PO-400
Matthies, D. **PO-448**
Matussek, M. PO-186
Matyašovský, J. PO-275
Maulide, N. **PO-222**
PO-313, PO-342, PO-371
Ma, X. PO-384
Madarász, I. **PO-82**
Maes, B. PO-488
Maestri, G. **PO-83**
Magagnano, G. **PO-84**
Magar, P. **PO-218**
Magauer, Th. **IL-2**
Mahmoud, W. PO-178
Maier, L. IL-2
Maier, M.E. PO-471
Mairhofer, Ch. **PO-85**
Majeti, R. PO-243
Makarov, A.S. **PO-441**
Makhova, N. PO-262
PO-350, **PO-442**, PO-552
Małosza, M. PO-347
Makowiec, S. PO-521
Makra, Z. **PO-277**
Makrević, J. PO-326
Malikénas, M. PO-221
Maliszewski, B. PO-9
Maluleka, M. **PO-312**
Mancuso, R. PO-26
Mannchen, F. PO-405
Mannisto, J. **PO-86**, PO-132
Mannucci, E. PO-472

PO-392, PO-424, PO-425
 PO-435, PO-479, PO-549
 Mayer, A. PO-240
 Mayer, F. PO-188
 Mayer, L. **PO-278**
 Mayor, M. PO-255
 Mazet, C.
 PO-36, PO-151
 Mazzarella, D. **PO-91**
 Mazzeo, P.P. PO-26
 McCarthy, R. **PO-92**
 McCreanor, N.
 PO-366, PO-509
 McDermott, M. OC-1
 McDouall, J. PO-301
 McGarrigle, E. PO-92
 McLaughlin, C. **PO-93**
 McLean, J. **PO-449**
 McMurray, L. OC-20
 McSweeney, L. PO-449
 Meerpoel, L. PO-488
 Meindl, B. **PO-559**
 Melchiorre, P. **PL-11**
 PO-2, PO-84, PO-91
 Menche, D.
 PO-512, PO-540
 Mendes, P. PO-192
 Méndez, M. PO-319
 Menichetti, A. **PO-94**
 Merad, J. PO-78
 Mestrom, L. **PO-95**
 Metsänen, T. **PO-314**
 Meyer, A. PO-307
 Meyer, C.F. **PO-450**
 Meyer, T.H.
 OC-6, **PO-96**, PO-317
 Michael, J. PO-212
 Michalland, J. **PO-451**
 Michalska, W. PO-522
 Miclăuș, M. PO-332
 Miguel, A.B. PO-487
 Mihelač, M.
PO-97, PO-219
 Mihovilovic, M.D.
 PO-172, PO-188
 PO-190, PO-191, PO-199
 PO-249, PO-375, PO-416
 Miklitz, M. OC-25
 Mikula, H. PO-253
 Mikulů, L.
 PO-220, **PO-223**
 Milbeo, P.
 PO-449, **PO-452**
 Milen, M. PO-520
 Milewska, M. PO-230
 Milewski, M. PO-66
 Miller, A.D. PO-181
 Miller, K. PO-144
 Milo, A. PO-28

Minnaard, A.
 PO-404 PO-433
 Minneci, M. **PO-453**
 Miranda, M.A.
 PO-201, PO-238
 Misale, A. PO-450
 Misawa, T. **PO-224**
 Mishevskia, M. PO-549
 Misztal, K. **PO-279**
 Mitake, A. PO-140
 Miyagawa, N. PO-290
 Miyatake Ondozaabal, J. **PO-98**
 Miyazawa, M. OC-7
 Moazami, Y. PO-489
 Moeller, M. **PO-454**
 Möhler, J. **PO-99**
 Molins-Molina, Ó.
 PO-201
 Möller, D. PO-197
 Molleti, N. PO-303
 Moncol, J. PO-516
 Mondal, A. **PO-100**
 Mondal, S.
 PO-141, PO-164
 Monsù Scolaro, L.
 PO-363, PO-364
 Montagnon, T. PO-535
 Moock, D. **PO-101**
 Mora-Radó, H. PO-319
 Moreno-Vargas, A.J.
 PO-185, **PO-225**
 Mori, A.
 PO-290, PO-401, PO-455
 Morii, K. **PO-455**
 Morimoto, T. PO-162
 Moser, S. PO-492
 Mosinger, J. PO-19
 Motornov, V.
 PO-444, **PO-456**
 Mphahlele, M.J. PO-312
 Mrđen Debono, V.
 PO-241, **PO-226**
 Mrksich, M. OC-15
 Mudráková, B. **PO-102**
 Mugica, O. PO-322
 Muhammad, **PO-227**
 Müller, F. PO-193
 Muller, G. PO-298
 Müller, T.J.J.
 PO-263, PO-278, PO-281
 Muratsugu, S. PO-259
 Muriel, B. **PO-457**
 Music, A.
 PO-338, **PO-458**
 Mutti, F. **PO-103**

N
 Na, J. **PO-315**
 Nada, H. PO-178
 Nagabuchi, H. **PO-228**
 Nagai, R. PO-140
 Nagarkar, A. OC-15
 Nagy, A. PO-89
 Nainytė, M. PO-221
 Naito, M. PO-224
 Nakagawa, N. PO-290
 Nakamura, Y. **PO-459**
 Namboothiri, I.N.N.
 PO-334, PO-470
 Nan, M.-I. **PO-280**
 Narczyk, A. **PO-460**
 Nardi, V. PO-502
 Nava, P. PO-361
 Nawara-Hultsch, A. **PO-104**
 Nečas, D. PO-19, PO-72
 Negoro, K. OC-1
 Neidig, S. **PO-229**
 Nelson, A.
 OC-20, PO-231
 Neumann, K.T. PO-30
 Neuville, L. PO-78
 Ngamnthiporn, A. OC-1
 Nguyen, N.H. PO-504
 Nguyen, Q.H. PO-504
 Niedballa, J.S. **PO-281**
 Nieger, M. PO-86
 Nielsen, D. PO-25
 Niemi, T. PO-86
 Nikitin, K. PO-92
 Nikolic, A. **PO-105**
 Nizi, E. PO-502
 Nocentini, A. PO-178
 Nociarová, J. **PO-282**
 Noda, H. **PO-106**
 Norris, M.D. PO-454
 Norsikian, S. **PO-461**
 Novacek, J. PO-51
 Novikov, R. PO-257
 Novosjolova, I.
 PO-271, PO-288
 Nowak, M. **PO-230**
 Nun, P. PO-385
 Nyffenegger, C. PO-283
 Nyulászi, L. PO-310

O
 O'Gara, R. **PO-107**
 Oba, M. PO-224
 Obie, J. PO-117
 Obydenov, D.
 PO-426, **PO-462**
 Ochmann, L. **PO-463**
 O'Donovan, D. PO-342

- Oestreich, M. **IL-10**, PO-109
 Ohoka, N. PO-224
 Oiarbide, M. PO-322
 Øien-Ødegaard, S. PO-437
 Ojeda, G.M. **PO-108**
 Okabe-Nakahara, F. PO-228
 Okamura, H. PO-193
 Okano, K. PO-290, PO-401, PO-455
 Okolo, E. **PO-231**
 Oliveira, B. PO-225
 Olofsson, B. PO-272
 Olszewska, T. PO-323
 Ong, D.Y. **PO-464**
 Ongouta, J. **PO-465**
 Opačak, S. **PO-330**
 Oppedisano, A. PO-425
 Opsenica, I. PO-105
 Orden, A. PO-103
 Orecchia, P. **PO-109**
 Ormazabal-Toledo, R. PO-316
 Ortalli, M. OC-28
 Ortiz, M. **PO-110**
 Osipov, D. **PO-466**, PO-467
 Ossi, P. PO-308
 Osuský, P. PO-282
 Osyenin, V. PO-466, **PO-467**
 Ötvös, S.B. **PO-468**
 Oudeyer, S. PO-7, PO-16
 Özkaya, B. **PO-111**
- P**
 Pace, V. **OC-16**
 Padmaja **PO-469**
 Palomo, C. PO-322
 Palucci, B. **PO-112**
 Pálvölgyi, Á.M. **PO-113**, PO-135
 Pancrazzi, F. PO-26
 Pang, J. PO-306
 Pannecoucke, X. PO-478
 Papastavrou, A.T. PO-115
 Pape, F. PO-15
 Papot, S. PO-233
 Parak, M. PO-516
 Parella, T. PO-127
 Park, J. PO-124
 Park, J.H. PO-23
 Parrain, J.-L. PO-361
 Paruch, K. PO-204
 Parveen, N. **PO-114**
 Pasquinet, E. **PO-283**
 Passera, A. PO-352
 Pasturaud, K. PO-490
 Paterson, K. PO-354
 Pati, S. **PO-470**
 Patureau, F. PO-111, PO-165, PO-346
 Paul, A. **PO-471**
 Paul, S. PO-327
 Paulisch, T. PO-57
 Pauze, M. **PO-115**
 Pawłowski, R. PO-146
 Pearson, S. **PO-232**
 Peinsipp, Ch. PO-136
 Pellicciari, R. OC-21
 Peng, C.-C. PO-213, PO-236
 Péraudeau, E. PO-233
 Pérez Márquez, L.A. PO-331
 Pérez-Ruiz, R. PO-201, **PO-284**
 Perić, B. PO-330
 Pericàs, M.A. PO-468
 Perisic, M. PO-172
 Permingeat, C. PO-557
 Perretti, M.D. **PO-331**
 Petersen, L. PO-174
 Petkova, D. PO-342
 Petracca, R. PO-449, PO-452
 Petrini, A. **PO-472**
 Pezzetta, C. **PO-473**
 Philippov, I. **PO-474**
 Pianowski, Z. PO-205
 Picher, M.-I. **PO-116**
 Pichler, A. PO-193
 Piekarski, D.G. PO-47
 Pierce, J. PO-489
 Pieters, G. PO-298
 Pietruszka, J. PO-198, PO-394, PO-443
 Pihko, P. PO-128, PO-314
 Pillwein, F. PO-327
 Pineschi, M. PO-94
 Pinggen, D. PO-119
 Pinter, B. PO-43, PO-97
 Pinto, A. PO-313
 Pipaon, N. PO-374
 Plamont, R. PO-34
 Planas, O. OC-24
 Planke, T. PO-454
 Plevová, K. PO-102
 Plietker, B. PO-116, PO-126, PO-209
 Plougastel, L. PO-298
 Pluvinaige, J. PO-243
 Podyacheva, E. IL-4
 Poechlauer, P. **OC-12**
 Pohl, J.-M. **PO-475**
 Poinot, P. PO-233
 Poisson, Th. PO-478
 Poli, G. **PO-117**, PO-345
 Pollice, R. **OC-3**
 Polychronidou, V. PO-120
 Pompei, S. **PO-118**
 Ponte, S. PO-320
 Poole, D. PO-397
 Pop, L. **PO-332**
 Popella, P. PO-209
 Porcs-Makkay, M. PO-310
 Poremba, N. PO-270, **PO-560**
 Porte, K. **PO-233**
 Porzelle, A. **PO-476**, **PO-477**
 Pospech, J. PO-35, PO-150
 Pospíšil, J. PO-428, PO-548
 Potopnyk, M. PO-529
 Pototschnig, G. OC-1
 Poullain, D. PO-283
 Pourghasemi Latif, M. **PO-234**
 Poutrel, P. **PO-478**
 Połoński, T. PO-323
 Prada Gori, D.N. **PO-557**
 Prasath, V. PO-469
 Prechtel, M.H.G. **PO-119**
 Preinfalk, A. **PO-479**
 Preston, D. OC-15
 Preusch, F. **PO-480**
 Princiotta, S. **PO-481**
 Princivalle, A. PO-321
 Procter, D. PO-301
 Prokopcová, H. PO-488
 Protti, S. **PO-482**
 Pryk, N. PO-197
 Przybyłowska, M. **PO-235**
 Puerto, C. PO-110
 Pugh, C. OC-25
 Pungor, D. PO-530
 Punter, A. PO-361
 Puriņš, M. **PO-483**
 Purkait, N. PO-272
 Puskás, L.G. PO-82, PO-277
 Pusztai, G. PO-310
 Puthanveedu, M. **PO-120**

Q

Qian, D. **PO-121**
 Qu, S. **PO-122**
 Queiroz, M.-J.R.P. **PO-123**
 Querolle, O. **PO-38**
 Quinonero, O. **OC-17**
 Quintard, A. **PO-484**
 Quintavalla, A. **OC-28**

R

Ra, M. **PO-124**
 Rachoń, J. **PO-182**
 Rafiński, Z. **PO-32**
 Raguz, L. **PO-236**
 Rahimidashaghoul, K. **PO-237**
 Raja, A. **PO-506**
 Rajkiewicz, A. **PO-66, PO-125**
 Rakers, C. **OC-5**
 Rami, F. **PO-126**
 Ramondenc, Y. **PO-38**
 Ranjan, P. **PO-108**
 Rank, Ch. **PO-111**
 Rapenne, G. **PO-417**
 Ratsch, F. **PO-485**
 Rautiainen, S. **PO-29**
 Ravinder, R. **PO-461**
 Raviola, C. **PO-482**
 Rayi, S. **PO-470**
 Reboul, V. **PO-390**
 Rehman, S. **PO-199**
 Rehorova, K. **PO-223**
 Reichetseder, A. **PO-416**
 Reindl, M. **PO-229**
 Reiners, F. **PO-486**
 Reis, W. **PO-25**
 Reisman, S.E. **IL-8**
 Rejc, L. **PO-487**
 Ren, D. **PO-167**
 Ren, X. **PO-130**
 Renaud, P. **PO-336, PO-522**
 Renders, E. **PO-488**
 Renoux, B. **PO-233**
 Repo, T. **PO-86, PO-132**
 Riant, O. **PO-27, PO-89**
 Ribas, X. **OC-6, PO-127, PO-317**
 Ribaucourt, A. **PO-489**
 Richardson, M. **PO-431**
 Richert, S. **PO-307**
 Richter-Morales, S. **PO-316**
 Riszter, G. **PO-203**
 Riuttamäki, S. **PO-128**
 Rivera, D.G. **PO-108**

Rizzo, S. **PO-77, PO-308**
 Rkein, B. **PO-490**
 Robina, I. **PO-185, PO-225**
 Rodrigues, J.M. **PO-123**
 Rodriguez, E. **PO-56**
 Rodriguez-Muñiz, G.M. **PO-238**
 Roe, A. **PO-184**
 Roesslein, J. **PO-491**
 Rogge, T. **PO-67**
 Rohrbach, S. **PO-522**
 Roithova, J. **IL-5**
 Roithová, J. **PO-6**
 Rok Lee, Y. **PO-505**
 Roland, S. **PO-129**
 Roldán-Gómez, S. **OC-6, PO-317**
 Roling, L. **PO-252**
 Roller, A. **PO-104**
 Roncali, J. **PO-280**
 Ronchi, P. **PO-77**
 Rondelli, M. **PO-333**
 Rongved, P. **PO-177**
 Ronson, Th. **PO-488**
 Rosenbaum, N. **PO-492**
 Rossi-Ashton, J. **PO-493**
 Rouchet, J.B. **PO-50**
 Roudesly, F. **PO-117**
 Roulland, E. **PO-461**
 Rousseau, A.L. **PO-494**
 Routier, S. **PO-380**
 Roy, S. **PO-327**
 Roy, T. **PO-130**
 Rudroff, F. **PO-172**
 Rueping, M. **PO-17**
 Ruider, S. **PO-58, PO-62, PO-171**
 Rumlová, M. **PO-313**
 Runco, J. **PO-220**
 Runikhina, S. **PO-246**
 Rycek, L. **IL-4**
 Ryckaert, B. **PO-495**
 Ryzkowska, M. **PO-496**
 Ryzhakov, D. **PO-521**
 Ryzhakov, D. **PO-497**

S

Sack, D. **PO-131**
 Sagmeister, P. **OC-27**
 Sahari, A. **PO-86, PO-132**
 Sahoo, A. **PO-133, PO-285**
 Sainz Martinez, A. **PO-133**
 Sala, R. **PO-117**
 Salin, A. **PO-318**
 Sámál, M. **PO-293**
 Samec, J.S.M. **PO-29**

Samir, M. **PO-175**
 Samir, N. **PO-196**
 Sánchez Quesada, J. **PO-112**
 Santolini, V. **OC-25**
 Sanz-Marco, A. **PO-41, PO-303**
 Saraiva-Rosa, N. **PO-390**
 Sarbu, L.G. **PO-239, PO-324**
 Sardana, M. **PO-498**
 Sarkar, S. **PO-240**
 Sarris, J. **PO-535**
 Sarró, P. **PO-63**
 Sass, P. **PO-209**
 Sasse, F. **PO-506**
 Sattin, S. **IL-7, PO-304, PO-453**
 Sauermann, N. **PO-96**
 Savary, D. **PO-134**
 Sayed, A.R. **PO-299**
 Scanlan, E. **PO-440, PO-449, PO-452**
 Schaefer, M. **PO-436**
 Scharinger, F. **PO-135**
 Schiel, F. **PO-136**
 Schiemann, O. **PO-307**
 Schiffers, S. **PO-207**
 Schilder, D. **PO-103**
 Schirmacher, R. **PO-226, PO-241**
 Schiwek, Ch. **PO-137**
 Schlundt, W. **PO-485**
 Schmalz, H.-G. **PO-187, PO-210**
 Schmauck, J. **PO-383, PO-485, PO-523**
 Schmid, M. **PO-443**
 Schmidt, L. **IL-2**
 Schmidt, T. **PO-492**
 Schmitt, M. **PO-44**
 Schmitt, M. **PO-344**
 Schnaars, Ch. **PO-177**
 Schneider, C. **PO-38, PO-50**
 Schneider, T. **PO-540**
 Schnitzer, T. **PO-99**
 Schnürch, M. **PO-139, PO-191, PO-199**
 Schnurr, M. **PO-138**
 Schnurrer, F. **PO-19**
 Schobert, R. **PO-506**
 Schöffberger, W. **PO-73, PO-327, PO-328**
 Schönbauer, D. **PO-139**
 Schörgenhumer, J. **PO-33**
 Schou, M. **PO-498**
 Schoup, J. **PO-104**
 Schreiner, P. **PO-463**

- Schrittwieser, J. PO-75
 Schröder, K. PO-113
 PO-133, PO-135, PO-285
 Schulte, A. OC-5
 Schulz, F. PO-197, **PO-286**
 Schulz, G. **PO-499**
 Schupp, M. **PO-287**
 Schuster, Ch. OC-12
 Schuster, R. PO-302
 Schwarz, J.L. PO-57
 Schwermann, Ch. PO-259
 Scott, L. **PO-500**
 Šebesta, R. PO-24, PO-102
 Sebris, A. **PO-288**
 See, Y.F.A. **PO-501**
 Sekar, G. PO-114, PO-147
 Sekine, A. **PO-140**
 Seoane, F. PO-320
 Serier-Brault, H. PO-385
 Serra, J. PO-127
 Serrano, E. **PO-141**
 Servajean, V. PO-461
 Setyawati, I. PO-183
 Seubert, P. **PO-289**, PO-405
 Severin, K. PO-519
 Sferrazza, A. **PO-502**
 Shaaban, S. **PO-142**, PO-313
 Shafir, A. PO-355, **PO-503**
 Shalaby, E. PO-196
 Shao, W. PO-151
 Sharma, U.K. PO-108
 Shchelik, I. **PO-242**
 Shelke, Y.G. PO-469
 Shen, Y. PO-49
 Shi, J.-C. **PO-143**
 Shibasaki, M. PO-106
 Shibata, T. PO-140, PO-149
 Shibuya, Y. **PO-290**
 Shimomori, K. PO-547
 Shin, S. PO-409, **PO-504**
 Shine, C. PO-452
 Shiozawa, N. PO-149
 Shmam, F. PO-321
 Shrestha, R. **PO-505**
 Shukla, R.K. PO-69
 Siebert, D.C.B. PO-249
 Sigmundová, I. PO-282
 Sikorski, A. PO-323
 Simeone, X. PO-199, PO-249
 Simig, G. PO-310
 Simon, A. PO-8, PO-75
 Šimon, P. **PO-291**
 Simon, T. PO-103
 Sinast, M. **PO-506**
 Singh, J. PO-329
 Singh, P. PO-173
 Singh, R.P. PO-408, PO-532
 Singha, S. PO-141
 Sirvinskaite, G. PO-67
 Sitte, H.H. PO-188
 Sklyaruk, J. PO-17
 Skrydstrup, T. **IL-13**
 PO-25, PO-30, PO-74
 Skwarecki, A. PO-230
 Šlachťová, V. **PO-507**
 Slamon, D. OC-1
 Slater, J. **PO-144**
 Slotboom, D. PO-183
 Smith, A. PO-13, PO-93, PO-122
 Smith, A.D. PO-160
 Smith, B. **PO-243**
 Smith, M.D. **IL-6**
 Smits, R. **PO-244**
 Smolíček, M. **PO-292**
 Sofiadis, M. **PO-508**, PO-535
 Sokol, K. IL-2
 Sokolova, O. **PO-509**
 Sokołowska, P. **PO-510**
 Sollogoub, M. PO-129
 Somerville, R.J. **PO-145**
 Sommer, H. PO-446
 Sommer, M. **PO-511**
 Soós, T. PO-534
 Sosnovskikh, V. PO-426, PO-462
 Sotorrios, L. **PO-319**
 Speicher, A. PO-339, PO-445
 Spicer, R. PO-325
 Spindler, S. **PO-512**
 Spiwok, V. PO-248
 Spoehrle, S. PO-13
 Sreekumar, S. PO-327
 Sršan, L. PO-44
 Srsan, L. **PO-513**
 Stallings, Ch. PO-240
 Stanek, F. **PO-146**
 Stanetty, Ch. PO-375, PO-416
 Stará, I.G. **PO-293**
 Starý, I. PO-293
 Stazzoni, S. PO-193
 Stecko, S. PO-39, PO-460
 Stegbauer, S. **PO-514**
 Steinacher, M. **PO-515**
 Steinborn, Ch. IL-2
 Steiner, L. OC-27
 Stępień, M. **IL-1**
 Stergiou, A. PO-258
 Stiblarikova, M. **PO-516**
 Stirling, A. PO-26
 Stöckl, Y. PO-286
 Stoddart, J.F. **PL-1**
 Stodulski, M. PO-146
 Stoessel, B. **PO-517**
 Stöger, B. PO-265, PO-270, PO-559
 Stoltz, B. OC-1
 Stratakis, M. PO-76, **PO-518**
 Strieker, M. PO-206
 Suc Sajko, J. PO-200
 Sugiyama, A. OC-5
 Suleymanov, A. **PO-519**
 Sundaravelu, N. **PO-147**
 Supuran, C. PO-178
 Süßmuth, R.D. **PL-10**
 Sutherland, J.D. **PL-8**
 Suzenet, F. PO-283
 Suzuki, T. PO-290
 Svatunek, D. PO-253
 Sytniczuk, A. PO-66
 Szabó, G. PO-310
 Szabó, T. **PO-520**
 Szafranski, K. PO-245
 Szewczyk, M. **PO-521**
 Szollosi, D. PO-194, PO-203
 Szpilman, A. **OC-18**
 Sztanó, G. PO-86
 Szymanski, W. OC-5
 Ślawiński, J. PO-245
T
 Tabolin, A. PO-456
 Tabti, R. **PO-148**
 Taddei, M. PO-472, PO-481
 Tadross, P. OC-1
 Tagmatarchis, N. PO-258
 Takano, H. **PO-149**
 Takemoto, Y. **OC-13**
 Tali Shandiz, S. OC-21
 Tama, F. OC-5
 Tan, B. PO-161
 Tanaka, M. PO-224
 Tang, S.-Q. PO-344
 Tang, Y. PO-399, PO-543
 Tappin, N. **PO-522**
 Taran, F. OC-23
 PO-195, PO-233, PO-298
 Taspınar, Ö. **PO-523**
 Täufer, T. **PO-150**

- Taylor, R. PO-493
Teichert, J.F. PO-15, PO-65, PO-169
Tejedor, D. PO-369
PO-372, PO-373, **PO-524**
Templ, J. **PO-525**
Ten, A. OC-15
ten Dijke, P. PO-187
Terec, A. PO-280, PO-332
Teskey, C.J. PO-435
Teskey, Ch. PO-392, PO-549
Theis, Th. PO-390
Thesmar, P. **PO-526**
Thibaut, C. PO-410
Thiel, N.O. PO-65
Thilmany, P. **PO-527**
Thomas, F. PO-226, PO-241
Thomas, L. PO-410
Thombal, R.S. **PO-528**
Thuéry, P. PO-298
Tian, C. PO-96
Tiara, K. **PO-529**
Tiffner, M. PO-51
Tilby, M. PO-368
Tilset, M. PO-437
Tischberger, S. PO-188
Tishin, D. PO-426
Tittmann, K. PO-226, PO-241
Tkaczyk, S. PO-371
Tobisu, M. PO-163
Tobrman, T. PO-379
Tolnai, G.L. PO-432, **PO-530**
Tomilov, Y. PO-257
Tommasini, M. PO-308
Tommasone, S. PO-192
Tomorowicz, Ł. **PO-245**
Tonge, N. **PO-320**
Tonin, F. PO-1, PO-52
Törnroos, K.W. PO-216
Townley, C. **OC-20**
Trabanco, A.A. PO-450
Tran, G. **PO-151**
Trapani, M. PO-363, PO-364
Traskovskis, K. PO-271, PO-288
Trbušek, M. PO-204
Trenz, D. **PO-531**
Tresse, C. PO-461
Triandafillidi, I. **PO-152**
Triantafyllakis, M. PO-508
Trillo, P. **PO-153**
Tripathi, K.N. **PO-532**
Trombini, C. OC-28
Trusso, S. PO-308
Tseliou, V. PO-103
Tsukano, C. OC-13
Tsygankov, A. IL-4
Tüma, J. **PO-294**
Tungasmita, D.N. PO-29
Turega, S. **PO-321**
Turks, M. PO-271, PO-288, PO-483
Tükenmez, H. PO-240
Twin, H. PO-354
Tyagi, M. PO-173
- ## U
- Ucar, S. PO-367
Uchida, K. PO-448
Uchuskin, M.G. PO-441
Ulč, J. PO-72
Ullrich, P. PO-443
Um, T.-W. PO-504
Unsworth, W. PO-493
Urankar, D. PO-487
Urlep, M. **PO-154**
Urruzuno, I. PO-322, PO-377
Uttry, A. PO-45
- ## V
- Vaccaro, L. PO-481
Väisänen, T. PO-314
Valášek, M. PO-255
Valkenier, H. **OC-26**
Valle, M. PO-25
van Beek, C.L.F. **PO-295**
van Beelen, E.S.E. **PO-246, PO-247**
Van den Bossche, D. PO-533
van der Eijk, H. PO-95
Van der Eycken, E. **PO-155**, PO-108
Van der Eycken, J. **PO-533**
van Gemmeren, M. PO-45, PO-100
van Leeuwen, P.W.N.M. PO-119
Van Steijvoort, B. PO-488
van Vuuren, S. PO-212
Varani, S. OC-28
Varga, S. **PO-534**
Vašíček, T. **PO-248**
Vasilenko, V. PO-14, PO-137
Vasilikogiannaki, E. PO-76, PO-518
Vasiloiu, M. OC-12
Vassilikogiannakis, G. PO-508, **PO-535**
Vastakaite, G. **PO-156**
Vázquez-Hernández, M. PO-197
Vega Alanis, B.A. **PO-249**
Venegas, S.T. IL-2
Verner, J. PO-204
Veselovska, L. **PO-250**
Veth, S. PO-193
Vidal-Ferran, A. PO-60
Viera, M. **PO-251**
Vilím, J. PO-103
Vincent, G. PO-497
Virant, M. PO-43, PO-97, **PO-296**
Virgil, S. OC-1
Vogt, D. PO-119
Vojkovsky, T. **PO-157**
Volk, B. PO-310, PO-520
Völkl, M. PO-549
Volla, C.M.R. PO-69
Volvrová, S. PO-444
von Keutz, T. **PO-536**
Vorherr, T. PO-436
Vorob'ev, A. **PO-537**
Vorohev, A. PO-474
Vougioukalakis, G.C. PO-115
- ## W
- Wadepohl, H. PO-264
Wagenknecht, H.-A. PO-131, PO-287, PO-302
Waldmann, H. PO-142
Wang, D. PO-252
Wang, F. OC-24
Wang, G.-W. PO-509
Wang, H. PO-67, PO-209
Wang, J. PO-31, PO-370
Wang, M.-M. **PO-297**
Wang, S. PO-545
Wang, X. PO-488
Wang, Z. PO-63
Ward, J. PO-335, PO-377
Waser, J. PO-297, PO-457
Waser, M. PO-33, PO-51
PO-85, PO-158, PO-260
Wedi, P. PO-100

Wegner, H.A. PO-55
Wegner, T. **PO-252**
Wein, L. IL-2
Welin, E. **OC-1**
Wen, Z. PO-129
Wennemers, H.
PO-99, PO-138, PO-156
Werz, D.B. **OC-19**
PO-337, PO-349, PO-430
Westin, G. PO-29
Wezenberg, S.J. PO-295
Whiteoak, Ch. **OC-8**, PO-22
Whitesides, G.M. OC-15
Wienhold, S. **PO-538**
Wijkhuizen, A. PO-233
Wilkovitsch, M. **PO-253**
Williams, J.D. **PO-539**
Willis, M.
PO-81, PO-368
Wimmer, L.
PO-188, PO-249
Wingen, L.M. **PO-540**
Wink, M. PO-196
Winkler, S. PO-183
Winne, J.
PO-357, PO-496
Winne, J.M. PO-351
Winter, M. **PO-158**
Winterhalter, P. PO-465
Witte, G. PO-193
Witte, M.D. PO-433
Wittstock, U. PO-206
Witzel, S. **PO-159**
Wojciechowska, N.
PO-125
Wojciechowski, K.
PO-279
Wölfl, B. **PO-541**
Wollenburg, M. PO-101
Woźniak, PO-84
Wu, J. **PO-160**
Wu, Y. PO-503, **PO-542**
Wu, Y.-K. PO-544
Wulff, S. PO-252
Wurster, M. PO-405
Wybon, C. PO-488

X

Xiang, S. **PO-161**
Xie, D. PO-181
Xie, J. PO-159
Xu, J. PO-143
Xu, S. PO-399, **PO-543**

Y

Yamada, A. OC-13
Yamane, Y. PO-455
Yamauchi, T. PO-366
Yamazaki, S. **PO-162**
Yang, Y. PO-130
Yang, Y. PO-558
Yang, Y.-C. **PO-544**
Yao, Z.-J. **PO-545**
Yasui, K. **PO-163**
Yasui, M. OC-13
Yatham, R. PO-90
Ye, J.-H. **PO-164**
Ye, J.Z. PO-52
Ye, L. **PO-546**
Yempala, T. PO-186
Yen-Pon, E. **PO-298**
Yin, H. PO-90
Yin, R. PO-67
Yip, G. PO-251
Yip, G.W.C. PO-356
Yoshida, M. OC-7
Yoshida, S.
PO-448, PO-459, **PO-547**
Youn, M. PO-268
Young, T. PO-384
Young Jr, V.G. PO-256
Youssef, A. PO-261
Yu, C. **PO-165**
Yu, J. PO-181
Yu, J.-S. PO-106
Yuan, W. PO-109
Yuan, Y.-C. **PO-166**
Yukioka, T. PO-401

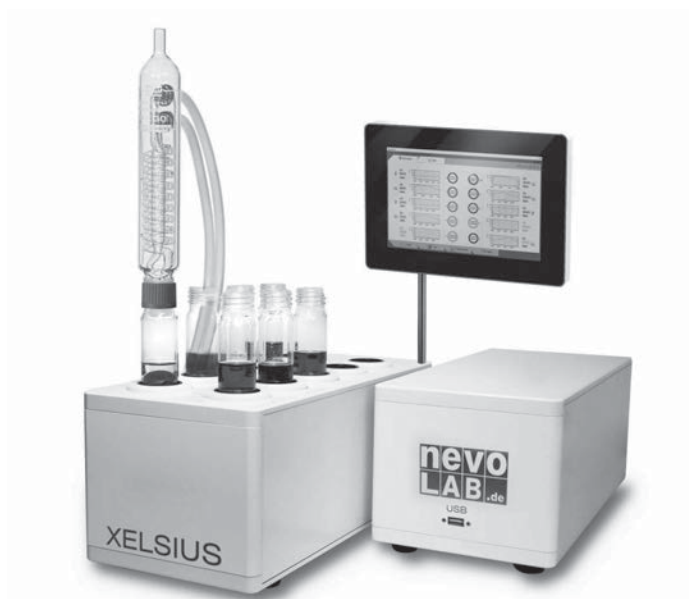
Z

Zálesák, F. **PO-548**
Zamarija, I. IL-2
Zanchi, C. PO-308
Zanella, G. **PO-322**
Zanini, M. **OC-17**
Zapata-Torres, G.
PO-186
Zarate, C. PO-49
Zard, S. PO-451
Zawodny, W. **PO-549**
Zech, A. **PO-550**
Zelenka, J. PO-291
Zemanová, J. PO-204
Zens, A. PO-405
Zha, Q. PO-542
Zhang, G. PL-6
Zhang, G. PO-390
Zhang, K. PO-352
Zhang, L.
PO-143, **PO-167**
Zhang, P. PO-129
Zhang, Q. PO-181
Zhang, Z. **PO-168**
Zhao, Q. PO-21
Zheng, Y. **PO-551**
Zhilin, E.
PO-262, **PO-552**
Zhou, F. PO-143
Zhu, J. PO-545
Zhu, Y. **PO-553**
Ziegler, Th.
PO-340, PO-365
PO-418, PO-422, PO-423
PO-480, PO-513, PO-556
Zimmermann, B.M. **PO-169**
Zippel, Ch. **PO-170**
Zografos, A. IL-14
Zonker, B. **PO-554**
Żołnowska, B. PO-245
Zscherp, R. **PO-555**
Zschieschang, U.
PO-264
Zubar, V.
PO-17, **PO-171**
Zukic, E. **PO-172**
Zweiböhmer, T. **PO-556**

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Highspeed Solubility & Synthesis Reactor

-20°C | +150°C



Introduction

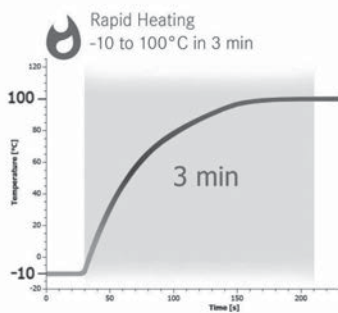
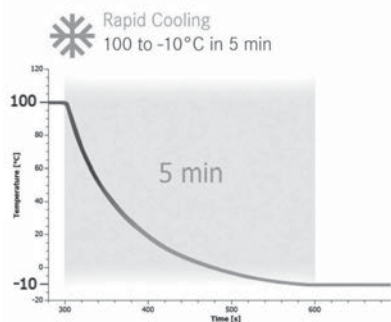
inspired by the possibilities of lab automation!

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 ®

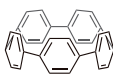

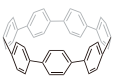
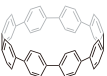
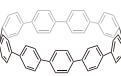
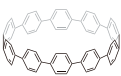
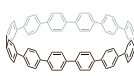



















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Carbon Nanoring Material Cycloparaphenylene (CPP)

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

							
	[5]CPP [C2931]	[6]CPP [C3386]	[7]CPP [C3571]	[8]CPP [C3544]	[9]CPP [C3465]	[10]CPP [C3493]	[12]CPP [C2449]
Solid							
Solution							
Fluorescence							

※[5]CPP is the smallest synthesizable cycloparaphenylene.

[5]Cycloparaphenylene ([5]CPP)	20mg / 100mg [C2931]
[6]Cycloparaphenylene ([6]CPP)	20mg [C3386]
[7]Cycloparaphenylene ([7]CPP)	10mg [C3571]
[8]Cycloparaphenylene ([8]CPP)	20mg [C3544]
[9]Cycloparaphenylene ([9]CPP) (This product is unavailable in the U.S.)	20mg [C3465]
[10]Cycloparaphenylene ([10]CPP)	20mg [C3493]
[12]Cycloparaphenylene ([12]CPP)	10mg [C2449]

Related product

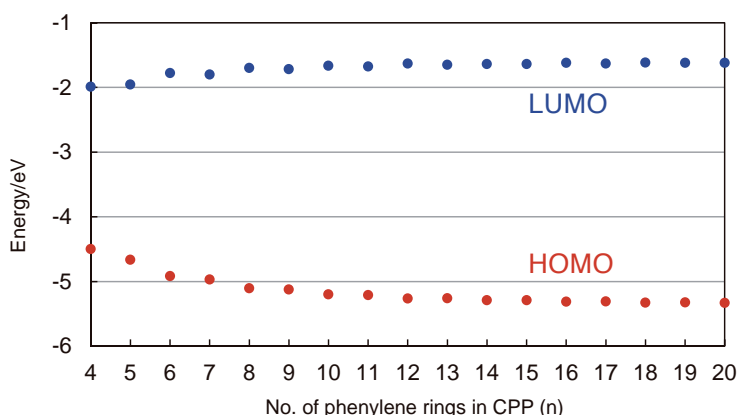
(6,6)Carbon Nanobelt Bis(tetrahydrofuran) Adduct ([12]CNB-2THF)

10mg [I1078]

Carbon Nanoring Material Cycloparaphenylene (CPP)

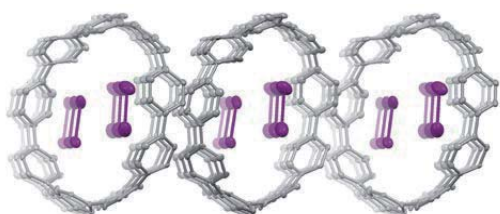
Properties and applications of CPP

Relation between no. of phenylene (n) and HOMO, LUMO in [n]CPP¹⁾



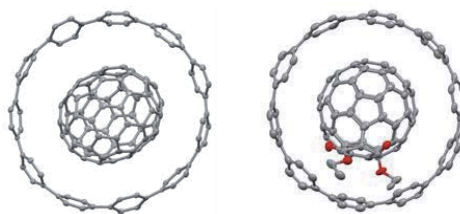
HOMO-LUMO gap decreases with decreasing ring size.

CPP-iodine complex²⁾



Electrically activated conductivity and white light emission

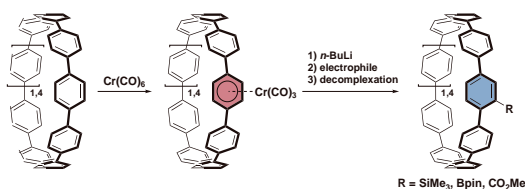
Encapsulation of fullerene by CPP³⁾



[11]CPP \supset C₇₀

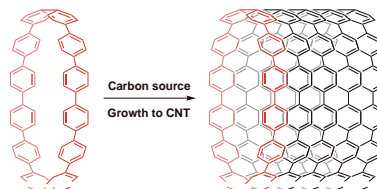
[10]CPP \supset C₇₀C(CO₂Et)₂

Functionalization of CPP⁴⁾



One phenylene ring can be readily functionalized.

CPP growth to CNT⁵⁾



Bottom up synthesis of CNT with uniform diameter

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

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