MODERN ASPECTS OF

GREEN AND SUSTAINABLE ORGANIC SYNTHESIS

26-29 NOVEMBER 2024

SHIV NADAR
INSTITUTION OF EMINENCE DEEMED TO BE
UNIVERSITY
DELHI NCR

SCHOOL OF NATURAL SCIENCES

Content:

About Shiv Nadar Institution of Eminence & Department of Chemistry

Shiv Nadar Institution of Eminence (SNIOE), Deemed to be University is a comprehensive, multidisciplinary, research-focused and student-centric institution that is bringing a paradigm shift in higher education in India through its innovative curriculum, interdisciplinary focus, and cross-disciplinary thinking across a wide range of disciplines. The University is building an eco-system of knowledge to promote recognition of the inter-connectedness of ideas, systems, and environments nation- and world-wide. The University has 5 Schools, 18 Departments and 6 Research Centers engaged in teaching, practice, and research in disciplines as diverse as Engineering, Humanities & Social Sciences, Management, Natural Sciences, Art, Design, Performing Arts, Communication, and Extended Education & Professional Development. The Schools offer Bachelor, Master, and Doctoral degrees along with multidisciplinary curriculum to enable students in exploring subjects and disciplines that may be widely different from their chosen Majors – Learning is choice-driven.

- The University received Institution of Eminence Deemed to be University status by the Government of India in August 2022.
- In the **NIRF** (Government's National Institutional Ranking Framework), SNIoE has been the youngest institution in the 'top 100' *Overall* list, and the score has been rising steadily. SNIoE ranked 61 in the *University* category, and 94 '*Overall*' in NIRF 2022.
- The University has been accredited with **'A' Grade** by the National Assessment and Accreditation Council **(NAAC)**, valid for a period of 5 years from 26 November 2019.
- SNIoE is also among a select group of green-field institutions in the country, which were awarded the prestigious **Atal Incubation Center** grant by the Niti Aayog, Government of India, in the very first round in 2017.

About the Chemistry Department:

The Department is committed to pursuing research on fundamental and applied problems through scientific inquiry, and stimulating the development of innovative interdisciplinary research programs around key areas of excellence. The immediate mission of Chemistry Department is to:

- Contribute to advancing and disseminating chemical knowledge through educational programs, internationally reputed publications and translating research as innovative patents.
- Devise robust and novel solutions to address the needs of society by promoting research in chemical and interdisciplinary projects.
- Train undergraduate, graduate students and research fellows to transform them future independent scientists to serve the needs of society, academia and industries.

Our vision is to make the world a better place through societal-impact cutting-edge research and innovation at Shiv Nadar Institution of Eminence, Deemed to be University.

Research Infrastructure

Our chemistry labs are equipped with fume-hoods, Schlenk lines, eyewash stations and safety showers. Lab facilities include advanced analytical instruments such as EPR, AFM, Flash Chromatography, Gas Chromatography with MS, Gel Permeation Chromatography, HPLC (Prep & Analytical), FPLC, NMR, LCMS-qToF, MALDI-ToF, DSC, TGA, Single-crystal X-ray Diffractometer, Electrochemical Analyzer, Fluorimeter, TCSPC, Polarimeter, UV-visible, High-resolution FTIR, Raman Spectrometers, Microwave Reactor, Inverted Microscope, Fluorescent Microscope, Hot-stage Polarized Microscope, Ferroelectric-Piezoelectric-Pyroelectric test system, Bio-safety Cabinets, CO2 Incubators, Shaker Incubators, Glove box, Multimode Plate Reader, Electroporator, Deep freezer, Cell Counter etc.

Computational facilities that include a high-performance IBM cluster (“Magus”) having 8064-cores along with two nodes with GPGPU processors, delivering a theoretical peak performance of ~320TF. Additionally, several Linux workstations are used for teaching as well as research purposes. Software for bioinformatics and cheminformatics, molecular modeling, molecular dynamics, quantum chemistry, data analysis, and statistical learning are also available.

Our library, housed in a modern 5-storey building, provides online access from anywhere in the campus to a large number of electronic journals and databases, including APS, AIP, ACS, RSC, AMS, SIAM, Springer, Elsevier, Wiley and Nature journals, in addition to various books, e-books and other learning resources.

Please visit following links to know more about our research laboratories and facilities.
https://chemistry.snu.edu.in/research/laboratories
https://snu.edu.in/research/facilities

Our Motto: To Provide the Opportunity of Learning Through Research Experience

Experiential and Effective Learning: Teacher & Student Ratio (1:9) and a Research Ecosystem

We offer: Core and Elective courses that are highly relevant to current scenario

B.Sc. (Research) | M.Sc. (Research) | Integrated M.Sc.-Ph.D. | Ph.D.

ABOUT THE CONFERENCE

The growing concern over our depleting environment has prompted a global awareness about its preservation and sustainability. Numerous facets of our daily life such as households, transportations, hospitality, consumer industries, food and beverages, life care etc., are presently being scrutinized and the corresponding processes are being improved to make them ecologically compatible.

To protect the environment the scientific communities from the academia and industry have discovered, and are still developing, strategies for performing sustainable organic synthesis. Based on this assessment, we have organized this scientific congregation consisting of 1.5 days of workshop and 2.5 days of conference aiming to discuss and highlight numerous Green and Sustainable organic processes, as well as technologies, from students, academicians, and industry personnel involved in this research area.

Conference theme:

- Sustainable organic chemistry
- Photolytic and photocatalytic organic reaction
- Mechanochemistry in organic synthesis
- Electrochemical Organic Reactions
- Photo-electrochemical organic reactions
- Sustainable radical reactions in organic chemistry

FOREWORD FROM THE CONVENOR

Dear Speakers, Poster Presenters, Attendees, and Sponsors of MAGSOS

Good morning!

We are pleased to welcome you all to the Shiv Nadar Institute of Eminence, Deemed to be University, located on our beautiful and scenic campus in Delhi NCR. Over the next four days, we invite you to step away from your busy schedules and immerse yourselves in meaningful discussions on advancing synthetic organic chemistry while safeguarding our environment.

For over a century, our field has been deeply focused on discovery and innovation, often without considering its ecological impact. However, the advent of green organic synthesis a few decades ago has gradually instilled a growing awareness of sustainable practices in organic synthesis—or SOS. MAGSOS provides a unique platform to bring together like-minded scientists from across India and around the globe. Here, we will explore diverse strategies and innovative approaches to implementing sustainable organic synthesis, both in academic laboratories and industrial settings.

We hope you enjoy this opportunity to interact, network, and exchange ideas on the modern aspects of green and sustainable synthesis—what we proudly call MAGSOS!

Wishing you all an inspiring and productive time ahead.

Best

regards,

Bimlesh

Ludo

Subho

PROGRAMME SCHEDULE OF THE CONFERENCE

SHIV NADAR
INSTITUTION OF EMINENCE DEEMED TO BE
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DELHI NCR

SCHOOL OF NATURAL SCIENCES

Day 1: November 26, 2024 (Tuesday)	
REGISTRATION & BREAKFAST (8:30-9:30)	
INAUGURATION	
9:30-10:30	Welcome by Vice-chancellor/ Head of the Department/ Convenor of OrganizingInstitution, MAGSOS – 2024
Workshop	
WORKSHOP SESSION-I (10:30-12:15)	
Micro and Milli Reactors for Scalable Chemical Synthesis and 3D Printing Innovations Dr. V. M. Rajesh (SNIoE)	
LUNCH BREAK (12:15-14:00)	
WORKSHOP SESSION-II (14:00-15:30)	
Green Chemistry in the Synthetic Process Development for Pharmaceuticals Prof. Joydev K. Laha-NIPER Mohali	
TEA/COFFEE BREAK (15:30-16:00)	
WORKSHOP SESSION-III (16:00-17:30)	
How to perform scale up for filtration and/or distillation from laboratory scale to production scale with simulation and prediction tools- this title is not matching with abstract title Prof. Ludovic Gremaud (HEFR)	
End of the Day 1	

PROGRAMME SCHEDULE OF THE CONFERENCE

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SCHOOL OF NATURAL SCIENCES

Day 2: November 27, 2024 (Wednesday)	
BREAKFAST (8:00-9:00)	
WORKSHOP SESSION-IV (9:00-10:30)	
En-Light-ening C-H functionalization Prof. Debabrata Maiti-IIT Bombay	
TEA/COFFEE BREAK (10:30-11:00)	
WORKSHOP SESSION-V (11:00-12:30)	
Mechanochemistry Prof. Carsten Bolm (RWTH Aachen)	
WRAP-UP WORKSHOP (12:30-13:00)	
LUNCH (13:00-14:30)	
WELCOME & CONFERENCE REGISTRATION	
14.30-15.00	Welcome by Dean of School of Natural Science/ Convenor of Organizing Institution, MAGSOS – 2024
	SESSION-I Chairperson: Prof. Vijay Kumar
15:00-16:00	Plenary Lecture (PL-01): Prof. Debabrata Maiti-IIT Bombay
	TEA/COFFEE BREAK (16:00 - 16:30)
	SESSION-II Chairperson: Dr. Bappaditya Gole
16:30-17:30	Plenary Lecture (PL-02): Prof. Rutjes Flores, Radboud University
End of the Day 2 (Gala Dinner)	

PROGRAMME SCHEDULE OF THE CONFERENCE

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Day 3: November 28, 2024 (Thursday)	
BREAKFAST (8.00-9.00)	
SESSION-III Chairperson: Prof. Bimlesh Lochab	
9:00-10:00	Plenary Lecture (PL-03): Prof. Carsten Bolm, RWTH Aachen
10:00-10:40	Keynote lecture (KNL-01): Prof. Akkattu T. Biju, IISC Bangalore
TEA/COFFEE BREAK (10:40-11:00)	
SESSION-IV Chairperson: Dr. Debdas Ray	
11:00-11:40	Keynote lecture (KNL-02): Prof. Tan Choon Hong, NTU Singapore
11:40-12:20	Keynote lecture (KNL-03): Prof. Akhilesh K. Verma, Delhi University
LUNCH & POSTER SESSION (12:20 to 14:00)	
SESSION-V (14.00-15.45) Chairperson: Dr. Basab Bijayi Dhar	
14.00-14.35	Invited Lecture (IL-01): Prof. Joydev K. Laha, NIPER Mohali
14:35-15:10	Invited Lecture (IL-02): Prof. Indresh Kumar, BITS Pilani
15.10-15.45	Invited Lecture (IL-03): Prof. Pritam Mukhopadhyay, JNU Delhi
TEA/COFFEE BREAK (15:45 - 16:00)	
SESSION-VI (16.00-18.00) Chairperson: Dr. Animesh Samanta	
16:00-16:35	Invited Lecture (IL-04): Dr. Sukalyan Bhadra, CSIR Bhavnagar
16:35-17:10	Invited Lecture (IL-05): Dr. Modhu Sudan Maji, IIT Kharagpur
17:10-17:45	Invited Lecture (IL-06): Dr. Koena Ghosh, Presidency University, Kolkata
17:45-18:05	Flash Talk (FL-01): Dr. Deepak Asthana, Ashoka University, Sonipat
18:05-18:20	Flash Talk (FL-02): Dr. Munmun Ghosh, Ashoka University, Sonipat
End of the Day 3	

LIST OF ABSTRACTS OF THE CONFERENCE

SHIV NADAR INSTITUTION OF EMINENCE DEEMED TO BE UNIVERSITY DELHI NCR | SCHOOL OF NATURAL SCIENCES

Day 4: November 29, 2024 (Friday)	
BREAKFAST (8.00-8.45 am)	
SESSION-VII (8:45 – 10:30) Chairperson: Dr. Biswajit Guchhait	
8:45-9:20	Invited Lecture (IL-07): Dr. Sudipta Raha Roy, IIT Delhi
9:20-9:55	Invited Lecture (IL-08): Dr. Pankaj Chauhan, IIT Jammu
9:55-10:30	Invited Lecture (IL-09): Dr. Tanmay Chatterjee, BITS Pilani
TEA/COFFEE BREAK (10:30 - 11:00)	
SESSION-VIII (11:00-11:45) Chairperson: Dr. Kshatresh Dutta Dubey	
11:00-11:20	Flash Talk (FL-03): Dr. Debajit Maiti, SNIoE Delhi NCR
11:20-11:40	Flash Talk (FL-04): Dr. Jawahar L. Jat, Baba Saheb Bhimrao Ambedkar University (A Central University), Lucknow
SESSION-X (11:45-13:00) Chairperson: Prof. Parthapratim Munshi	
11.45-12.20	Invited Lecture (IL-10): Dr. Ramakrishna G. Bhat, IISER Pune
12:20-12:55	Invited Lecture (IL-11): Prof. S. S. V. Ramasastry, IISER Mohali
LUNCH & POSTER SESSION (13:00 to 14:15)	
SESSION-XI (14:15-17:00) Chairperson: Dr. Tatini Rakshit	
14:15-14:50	Invited Lecture (IL-12): Prof. Manmohan Kapur, IISER Bhopal
14:50-15:25	Invited Lecture (IL-13): Dr. Basab Bijayi Dhar, SNIoE, Delhi-NCR
15:25-16:00	Invited Lecture (IL-14): Dr. Pushkar S. Shejwalkar, ZDHC Foundation
Valedictory Session and End of Conference	

LIST OF PARTICIPANTS FOR THE POSTER PRESENTATION

Serial No	Name of the Participant	Name of the Institute	Poster Number
1	**Subhankar Bera**	SNIoE	**P01**
2	**Jaipriya Khatri**	SNIoE	**P02**
3	**Monika**	SNIoE	**P03**
4	**Ainala Naresh**	BITS, Pilani	**P04**
5	**Ajay B. Shelke**	SNIoE	**P05**
6	**Asrar Ahmad**	SNIoE	**P06**
7	**Bhavika Bhatia**	SNIoE	**P07**
8	**Haya Khan**	SNIoE	**P08**
9	**Imtiyaz Ahmad Shah**	BITS, Pilani	**P09**
10	**Amit Kumar**	SNIoE	**P10**
11	**Rashmi Yadav**	SNIoE	**P11**
12	**Ashirwad Divedi**	Babasaheb Bhimrao Ambedkar University, Lucknow	**P12**
13	**Jinti Moni Kumar**	SNIoE	**P13**
14	**Shivam Bhargav**	Babasaheb Bhimrao Ambedkar University, Lucknow	**P14**
15	**Swagata Choudhury**	IIT-Delhi	**P15**
16	**Prashansa Gupta**	SNIoE	**P16**
17	**Gopal Chakrabortty**	IIT-Delhi	**P17**
18	**Ajay Kumar Dhiya**	IIT-Roorkee	**P18**
19	**H. Sai Keerthana**	BITS Pilani-Hyderabad	**P19**
20	**Shweta Singh**	SNIoE	**P20**
21	**Himani Rani**	IIT-Jammu	**P21**
22	**Solaim**	IIT-Jammu	**P22**
23	**Vaishaly Duhan**	SNIoE	**P23**
24	**Rafique Sanukhan**	SNIoE	**P24**
25	**Tejas Prabakar**	SNIoE	**P25**
26	**Saroj**	SNIoE	**P26**

Workshop-I

Micro and Milli Reactors for Scalable Chemical Synthesis and 3D Printing Innovations

Dr. V. M. Rajesh*

Department of Chemical Engineering, Shiv Nadar Institution of Eminence

Abstract:

Micro and milli reactors are revolutionizing chemical synthesis, offering unparalleled precision, efficiency, and scalability in applications such as biofuel production and specialty chemical synthesis. These reactors enable enhanced heat and mass transfer, facilitating more efficient and sustainable reactions compared to traditional batch systems. Focusing on scalable solutions, this presentation will explore how milli-reactor configurations bridge the gap between the high-control environment of microreactors and the production capacity needed for industrial applications. The session will also highlight recent advances in 3D printing technology, which enable the rapid prototyping of complex reactor geometries, tailored to optimize specific reactions. These innovations not only improve reactor performance but also support sustainable practices in chemical manufacturing, marking a significant leap forward in reactor design and application.

Workshop-II

Green Chemistry in the Synthetic Process Development for Pharmaceuticals

Prof. Joydev K. Laha*

Department of Pharmaceutical Technology (Process Chemistry, Biotechnology and Formulations)
National Institute of Pharmaceutical Education and Research
S. A. S. Nagar, Punjab 160062, India

E-mail: jlaha@niper.ac.in

Abstract:

With increasing concern of environmental hazards and pollution, the implementation of green chemistry in the pharmaceutical industries for the synthesis of pharmaceuticals becomes paramount important. With more emphasize on green chemistry, featuring reduced number of steps, avoiding substrates like acid chloride, avoiding stoichiometric amount of corrosive Lewis acids, use of cheap reagents, "reagentless" synthesis, chromatography-free synthesis, etc. Selected references: orthodox and old-age synthetic routes of traditional drugs are changing towards new generation processes incorporated with green chemistry elements. The execution of green chemistry can be performed by designing a holistic synthetic route of the active pharmaceutical ingredient (API), minimizing hazards and pollution, and capitalizing the resource efficiency in the synthesis. The green chemistry may be comprehensively implemented in the synthesis of

pharmaceuticals by choosing no or a green solvent (preferably water), one-pot synthesis, multicomponent reactions (MCRs), continuous processing, and process intensification approaches for atom economy and waste minimization. After giving an overview of green parameters, the talk will cover examples of green pharmaceutical synthesis.

References:

1. Kar, S.; Sanderson, H.; Roy, K.; Benfenati, E.; Leszczynski, J. Green Chemistry in the Synthesis of Pharmaceuticals. *Chem. Rev.* **2022**, *122*, 3637-3710.
2. Gupta, A.; Laha, J. K. Growing Utilization of Radical Chemistry in the Synthesis of Pharmaceuticals, Chem. Rec. **2023**, *23*, e202300207.
3. Laha, J. K.; Gulati, U.; Gupta, A.; Indurthy, H. K. Improved, gram-scale synthesis of sildenafil in water using arylacetic acid as the acyl source in the pyrazolo[4,3-d]pyrimidin-7-one ring formation, *New J. Chem.* **2021**, *25*, 2643-2648.
4. Keshri, A.; Gupta, A.; Gulati, U.; Bhatt, T. D.; Kashyap, M.; Laha, J. K. A Telescopic, Scalable and Industrially Feasible Method for the Synthesis of Antidepressant Drug, Moclobemide, *Helv. Chim. Acta*, **2024**, *107*, e202400075.

Workshop-III

Assessing industrial filtration strategy by combination of Dynochem and practical laboratory: It’s not that easy

Prof. Ludovic Gremaud*

School of Engineering and Architecture of Fribourg, Department of Chemistry - Institute of Chemical Technology, HES-SO University of Applied Sciences and Arts Western Switzerland Boulevard de Pérolles, 80 - 1700 Fribourg (Switzerland)

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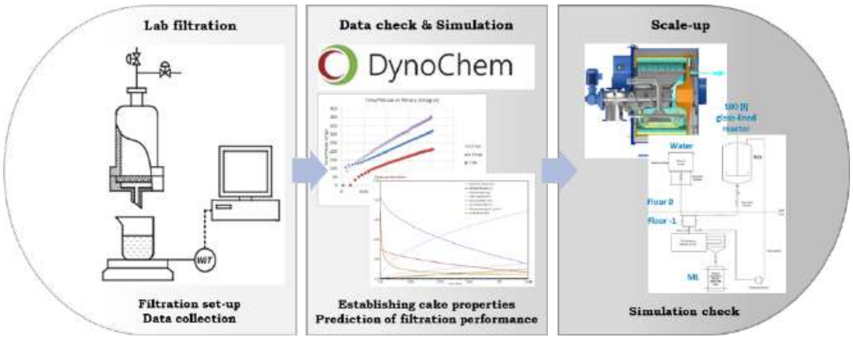
Abstract:

Moving high or low adding-value products to an industrial production scale is capital intensive. It also requires a multi-year investment period in order to get approvals from the authorities. Increasing competitive pressures and the need to accelerate the development process and reduce the time-to-market has made the need for reliable scale-up ever more important. At present, industries often decide to cut “KiloLab” and “Pilot” development campaigns to shorten development times. These decisions have proven costly since development campaigns offer a valuable set of information especially on scale-up. Scaling-up is a complex activity requiring risk management with care based on highly disciplined data collecting in a cross-functional and even multidisciplinary environment. In this context, fast-moving process development requires a deep understanding of the way in which chemical process and operational parameters determine the overall performance of a specific operation without adverse effects on yield and quality because out-of-specification products can’t be sold!!! Because of the complex nature of filter cake formation, filtration has long been developed through practical and empirical knowledge rather than through cake formation understanding and properties and this even if filtration is a key operation at many stages of manufacturing processes to isolate chemicals. Multiple approaches of varying degrees of complexity are used to characterize cake properties. In this workshop, an accurate calculation of the cake properties from a detailed filtration study will be presented and discussed as well as the results obtained for the filtration at larger scale.



Workshop-IV

En-Light-ening C-H functionalization

Prof. Debabrata Maiti*

IIT Bombay, dmaiti@iitb.ac.in

Abstract:

Over years' transition metal-catalyzed C-H activation has propelled the field of organic synthesis for the construction of structurally complex and diverse molecules in resource-economical fashion. In this context, non-directed C-H activation has gained unprecedented attention for attaining region-specific C-H functionalizations in a step-economic mode. Unlike traditional Fujiwara-Moritani reaction, this approach relies on ligand assistance and thus uses arene as the limiting reagent. However, all existing non-directed C-H functionalizations utilize high thermal energy to induce the functional group which eventually put the regioselectivity at stake. In addition, use of super stoichiometric costly silver salts to regenerate the catalyst produces unwanted metal waste. In aid of developing a more sustainable and environmentally benign approach, we have established a photoredox catalytic system by a merger of palladium/organo-photocatalyst(PC) which forges highly regeiospecific C-H olefination of diverse arenes and heteroarenes. Visible light nullifies the requirement of silver salts and thermal energy in executing "region-resolved" Fujiwara-Moritani reaction.

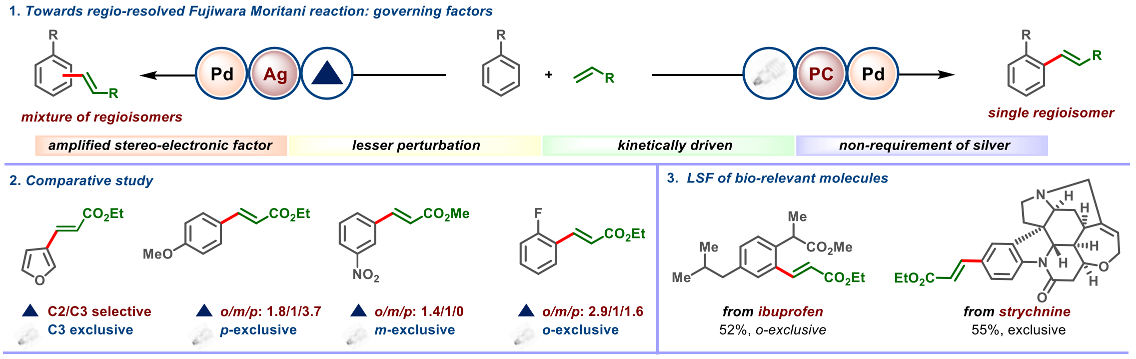


Figure 1. Overview of photoinduced regio-resolved Fujiwara-Moritani reaction

References:

1. Saha, A.; Guin, S.; Ali, W.; Bhattacharya, T.; Sasmal, S.; Goswami, N.; Prakash, G.; Sinha, S. K.; Chandrashekar, H. B.; Panda, S.; Anjana, S. S.; Maiti, D. *J. Am. Chem. Soc*. **2022**, *144*, 1929-1940.
2. Saha, A.; Ghosh, A.; Guin, S.; Panda, S.; Mal, D. K.; Majumdar, A.; Akita, M.; Maiti, D. *Angew. Chem. Int. Ed.* **2022**, e202210492.
3. Sinha, S. K.; Panja, S.; Grover, J.; Hazra, P. S.; Pandit, S.; Bairagi, Y.; Zhang, X.; Maiti, D. *J. Am. Chem. Soc.,* **2022,** *144*, 12032-12042.
4. Dutta, U.; Maiti, S.; Bhattacharya, T.; Maiti, D. *Science.* **2021***, 372,* 701.
5. Sinha, S. K.; Guin, S.; Maiti, S.; Biswas, J. P.; Porey, S.; Maiti, D. *Chem. Rev.* **2022**, *122*, 5682.

Workshop-V

Mechanochemistry

Prof. Carsten Bolm*

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Email: Carsten.Bolm@oc.RWTH-Aachen.de

Abstract:

Synthesis and catalysis rely on selective bond activations. In many cases, heating has been used for initiating a desired reaction. More recently, photo- and electrochemical activations became prominent. *Mechanochemistry* offers additional options because there, chemical reactions are "induced by the direct absorption of mechanical energy".[1]

The current presentation will
1. provide a historical background of *mechanochemistry*,
2. illustrate its value by discussing recent applications,
3. present the required devices,
4. describe up-scaling options, and
5. discuss future perspectives, also in industrial settings.[2]

References:

1. For the IUPAC definition of a "mechano-chemical reaction", see: *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), Blackwell Scientific Publications, Oxford, 1997 and cited in *PAC* **2004**, *76*, 889.
2. For selected reviews on mechanochemistry, see: (a) James, S. L.; Collier, P.; Parkin, I.; Hyett, G.; Braga, D.; Maini, L.; Jones, B.; Friscic, T.; Bolm, C.; Krebs, A.: Mack, J.; Waddell, D. C.; Shearouse, W. C.; Orpen, G.; Adams, C.; Steed, J. W.; Harris, K. D. M. *Chem. Soc. Rev.* **2012**, *41*, 413; (b) Hernández, J. G.; M Bolm, C. *J. Org. Chem.* **2017**, *82*, 4007; (c) Do, J. L.; Friščić, T. *ACS Cent. Sci.* **2017**, *3*, 13; (d) Howard, J. L; Cao, Q.; Browne, D. L. *Chem. Sci.* **2018**, *9*, 3080; (e) Colacino, E.; Porcheddu, A.; Charnay, C.; Delogu, F. *React. Chem. Eng.* **2019**, *4*, 1179; (f) Bolm, C.; Hernández, J. G. *Angew. Chem. Int. Ed.* **2019**, *58*, 3285; (g) Friščić, T.; Mottillo, C.; Titi, H. M. *Angew. Chem. Int. Ed.* **2020**, *59*, 1018; h) Egorov, I. N.; Santra, S.; Kopchuk, D. S.; Kovalev, I. S.; Zyryanov, G. V.; Majee, A.; Ranu, B. C.; Rusinov, V. L.; Chupakhin, O. N. *Green Chem.* **2020**, *22*, 302; (i) Ardila-Fierro, K. J.; Hernández, J. G. *ChemSusChem* **2021**, *14*, 2145; (j) Mateti, S.; Mathesh, M.; Liu, Z.; Tao, T.; Ramireddy, T.; Glushenkov, A. M.; Yang, W.; Chen, Y. I. *Chem. Commun.* **2021**, *57*, 1080; (k) Williams, M. T. J.; Morrill, L. C.; Browne, D. L. *ChemSusChem* **2022**, *15*, e202102157; (l) Cuccu, F.; De Luca, L.; Delogu, F.; Colacino, E.; Solin, N.; Mocci, R.; Porcheddu, A. *ChemSusChem* **2022**, *15*, e202200362; (m) Juaristi, E.; Avila-Ortiz, C. G. *Synthesis* **2023**, *55*, 2439; (n) I. Silva, D. A.; Bartalucci, E. Bolm, C.; Wiegand, T. *Adv. Mater.* **2023**, *35*, e2304092; (o) Wenger, L. E.; Hanusa, T. P. *Chem. Commun.* **2023**, *59*, 14210; (p) Ardila-Fierro, K. Hernández, J. G. *Angew. Chem. Int. Ed.* **2024**, *63*, e202317638.

Plenary Lecture (PL-01)

Unlocking new chemical space via selective catalysis

Prof. Debabrata Maiti*

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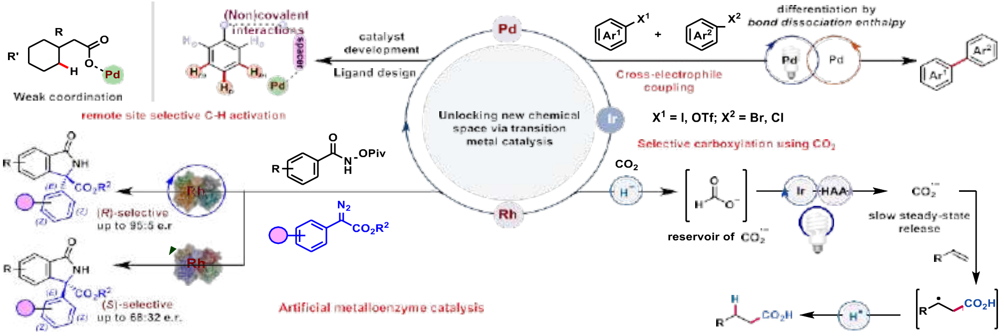
Email : dmaiti@iitb.ac.in

Abstract:

The limitations of cross-coupling such as the availability of prefunctionalized coupling partners, instability, and synthesis expense remain, posing significant barriers to unlocking new chemical space for molecular complexity. To solve these underlying problems of cross-coupling we are mainly focused on the development of techniques for direct C–H functionalization and cross- electrophile coupling. Selectively targeting a remote C–H bond in a molecule remains more challenging due to the inaccessibility of these sites in formation of energetically favorable organometallic pre-transition states. We believe that the direct release of the reactive metal catalyst in close proximity to the targeted remote C–H bond could solve this problem. We devised covalently attached template-directed methods that require precise spatial positioning of the directing group in order to selectively activate remote C–H bonds. We recently demonstrated that various non-covalent interactions are also successful in recognizing the perfect orientation of catalyst and the substrate to achieve selective C–H bond activation. In this vein, we have developed a method for the activation of methylene C–H bond in presence of methyl C–H bondsto form unsaturated bicyclic lactones utilizing the weak coordinating nature carboxylic acid towards palladium. Cross-electrophile coupling (XEC) approach would be a powerful tool for theconstruction of (hetero)biaryl moiety because of the widespread availability and stability of (hetero)aryl electrophiles. We have demonstrated a ligand controlled visible light driven monometallic cross-electrophile coupling platform for the synthesis of unsymmetrical (hetero)biaryls directly from (hetero)aryl halides and pseudohalides. In addition, our lab is pursuing the development of a paradigm in which small molecules such CO_2, SO_2 *etc.* can be converted into a wide range of chemicals and materials using renewable visible light photocatalysis.



References:

1. Dutta, U.; Maiti, S.; Bhattacharya, T.; Maiti, D. *Science.* **2021***, 372,* 701.
2. Goswami, N.; Sinha, S. K.; Mondal, P.; Adhya, S.; Datta, A.; Maiti, D. *Chem.* **2023**, *9*, 989.
3. Saha, A.; Guin, S.; Ali, W.; Bhattacharya, T.; Sasmal, S.; Goswami, N.; Prakash, G.; Sinha, S. K.; Chandrashekar, H. B.; Panda, S.; Anjana, S. S.; Maiti, D. *J. Am. Chem. Soc.* **2022**, *144*, 1929.
4. Das, J.; Ali, W.; Ghosh, A.; Pal, T.; Mandal, A.; Teja, C.; Dutta, S.; Pothikumar, R.; Ge, H.; Zhang, X.; Maiti, D. *Nat. Chem.* **2023**, *15*, 1626.
5. Maiti, S.; Ghosh, P.; Raja, D. K.; Ghosh, S.; Chatterjee, S.; Sankar, V.; Roy, S.; Lahiri, G. K.; Maiti, D. *Nat. Catal.* **2024.**
6. Mukherjee, P.; Sairaman, A.; Deka, H. J.; Jain, S.; Mishra, S. K.; Roy, S.; Bhaumik, P.; Maiti, D. *Nat. Synth.* **2024**

Plenary Lecture (PL-02)

Enantiopure Compounds through Mechanical Grinding

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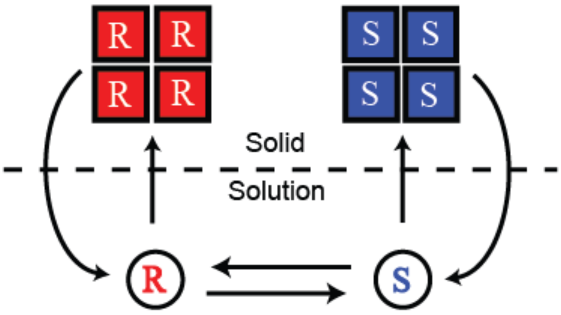
Abstract:

An emerging solid-state method capable of causing deracemization of racemic mixtures is Viedma ripening.[1] This method involves vigorous glass bead enhanced grinding of a slurry of crystalline chiral compounds, resulting eventually in solid-phase deracemization and hence formation of only one of the two enantiomers (Figure 1).

Figure 1: Schematic representation of the deracemization process.



In order to successfully apply Viedma ripening, two conditions need to be fulfilled.[2] Firstly, it must be possible to racemize the molecule in solution under the crystallization conditions. Secondly, the molecule must crystallize as a racemic conglomerate, meaning that the two enantiomers crystallize into different crystals.

This ins and outs of this approach will be discussed and various examples showing its scope and limitations will be highlighted.

References and Notes:

1. Noorduin, W. L.; Izumi, T.; Millemaggi, A.; Leeman, M.; Meekes, H.; Van Enckevort, W. J. P.; Kellogg, R. M.; Kaptein, B.; Vlieg, E.; Blackmond, D. G.; *J. Am. Chem. Soc.* **2008,** *130*, 1158-1159.
2. Sogutoglu, L. C.; Steendam, R. R. E.; Meekes, H.; Vlieg, E.; Rutjes, F. P. J. T.; *Chem. Soc. Rev.* **2015,** *44*, 6723-6732.
3. (a) Engwerda, A. H. J.; Maassen, R.; Tinnemans, P.; Meekes, H.; Rutjes, F. P. J. T.; Vlieg, E.; *Angew. Chem. Int. Ed.* **2019**, *58*, 1670-1673. (b) Engwerda, A. H. J.; Meekes, H.; Bickelhaupt, F. M.; Rutjes, F. P. J. T.; Vlieg, E.; *Chem. Eur. J.* **2019**, *25*, 9639-9642. (c) Belletti, G.; Schuurman, J.; Stinesen, H.; Meekes, H.; Rutjes, F. P. J. T.; Vlieg, E.; *Cryst. Growth. Des.* **2022**, *22*, 1874, 1881.

Plenary Lecture (PL-03)

The Use of Mills in Synthetic Organic Chemistry

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Abstract:

IUPAC defines a "mechano-chemical reaction" as a "chemical reaction that is induced by the direct absorption of mechanical energy".[1] We are using such activation in synthesis and catalysis, where it has proven beneficial.[2] Here, selected recent examples from our group will be presented.[3]

References:

1. IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), Blackwell Scientific Publications, Oxford, 1997 and cited in *PAC* **2004**, *76*, 889.
2. James, S. L.; Collier, P.; Parkin, I.; Hyett, G.; Braga, D.; Maini, L.; Jones, B.; Friscic, T.; Bolm, C.; Krebs, A.: Mack, J.; Waddell, D. C.; Shearouse, W. C.; Orpen, G.; Adams, C.; Steed, J. W.; Harris, K. D. M. *Chem. Soc. Rev.* **2012**, *41*, 413.
3. (a) Amer, M. M.; Hommelsheim, R.; Schumacher, C.; Kong, D.; Bolm, C. *Faraday Discus.* **2023,** *241*, 79. (b) Schumacher, C.; Fritz, L.; Hanek, L. M.; Sidorin, V.; Brüx, D.; Bolm, C. *Molecules* **2023**, *28*, 807. (c) Hu, C.; van Bonn, P.; Demco, D. E.; Bolm, C.; Pich, A. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305783. (d) Krake, E.; Backer, L.; Andres, B.; Baumann, W.; Handler, N.; Buschmann, H.; Holzgrabe, U.; Bolm, C.; Beweries, T. *ACS Cent. Sci.* **2023**, *9*, 1150. (e) van Bonn, P.; Ke, J.; Weike, C.; Ward, J. S.; Rissanen, K.; Bolm, C. *CCS Chem.* **2023***, 5*, 1737. (f) Passia, M.; Amer, M. M.; Demaerel, J.; Bolm, C. *ACS Sustainable Chem. Eng.* **2023**, *11*, 6838. (g) Bartalucci, E.; Schumacher, C.; Hendrickx, L.; Puccetti, F.; d'Anciães Almeida Silva, I.; Dervişoğlu, R.; Puttreddy, R.; Bolm, C.; Wiegand, T. *Chem. Eur. J.* **2023**, *23*, e202203466. (h) Puccetti, F.; Rinesch, T.; Suljić, S.; Rahimi, K.; Herrmann, A.; Bolm, C. *Chem* **2023**, *9*, 1318. (i) d'Anciães Almeida Silva, I.; Bartalucci, E.; Bolm, C.; Wiegand, T. *Adv. Mater.* **2023**, *35*, e202304092. (j) Schumacher, C.; Truong, K.-N.; Ward, J.; Rajala, A.; Lassila, E.; Bolm, C.; Rissanen, K. *Org. Chem. Front.* **2024**, *11*, 781. (k) Biswas, S.; Bolm, C. *Org. Lett.* **2024**, *26*, 1511; (l) Sahu, C. C.; Biswas, S.; Hommelsheim, R.; Bolm, C. *RSC Mechanochemistry* **2024**, *1*, 38. (m) Pan, S.; Mulks, F.; Wu, P.; Rissanen, K.; Bolm, C. *Angew. Chem. Int. Ed.* **2024**, *63*, e202316702. (n) Amer, M.; Backer, L.; Buschmann, H.; Handler, N.; Scherf-Clavel, O.; Holzgrabe, U.; Bolm, C. *Anal. Chem.* **2024**, *96*, 13166. (o) Biswas, S.; Bolm, C. *Org. Lett.* **2024**, *26*, 1511; (p) Quaranta, C.; d'Anciães Almeida Silva, I.; Moos, S.; Bartalucci, E.; Hendrickx, L.; Fahl, B M. D.; PasqualinI, C.; Puccetti, F.; Zobel, M.; Bolm, C.; Wiegand, T. *Angew. Chem. Int. Ed.* **2024**, *63*, e200410801. (q) Pan, S.; Wu, P. Bampi, S.; Ward, J. S.; Rissanen, K.; Bolm, C. *Angew. Chem. Int. Ed.* **2024**, *63*, e202413181.

Keynote Lecture (KNL-01)

Sustainable N-Heterocyclic Carbene (NHC) Organocatalysis

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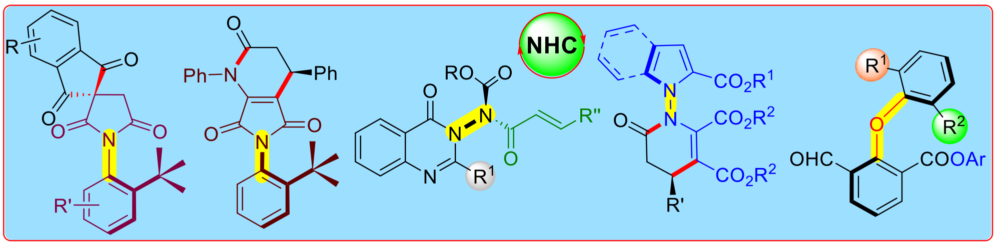
Abstract:

N-Heterocyclic carbene (NHC)-catalyzed umpolung of aldehydes is widely used for the unconventional access to target molecules.[1] Although NHC catalysis for the assembly of axially chiral C-C bonds leading to the atroposelective synthesis of biaryls and related compounds are well-known, the analogous synthesis of compounds bearing axially chiral C-Heteroatom bonds are relatively rare using NHC catalysis. We have recently reported the NHC-catalyzed atroposelective synthesis of N-aryl succinimides having an axially chiral C-N bond via the desymmetrization of N-aryl maleimides.[2] Moreover, we have demonstrated the NHC-catalyzed kinetic resolution of N-aryl aminomaleimides allowing the synthesis of C-N axially chiral N-aryl aminomaleimides via remote chirality control.[3,4] In addition, NHC-catalyzed selective amidation reaction leading to the atroposelective synthesis of N-N axially chiral 3-amino quinazolinones has been realized recently.[5,6] Further, we have uncovered the NHC-catalyzed synthesis of C-O axially chiral diaryl ethers via atroposelective esterification of dialdehyde-containing diaryl ethers via a desymmetrization strategy.[7] The details of these works will be presented.



References:

1. For reviews, see: (a) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A. Rovis, T. *Chem. Rev.* **2015**, *115*, 9307. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (c) Biju, A. T. *N-Heterocyclic Carbenes in Organocatalysis*; Wiley-VCH Verlag GmbH & Co. KGa A: Boschstr. 12, 69469.
2. Barik, S.; Shee, S.; Das, S.; Gonnade, R. G.; Jindal, G.; Mukherjee, S.; Biju, A. T. *Angew. Chem. Int. Ed.* **2021**, *60*, 12264.
3. Barik, S.; Das, R. C.; Balanna, K.; Biju, A. T. *Org. Lett.* **2022**, *24,* 5456.
4. Barik, S.; Ranganathappa, S. S.; Biju, A. T. *Nat. Commun*. **2024,** *15*, 5755.
5. Balanna, K.; Barik, S.; Barik, S.; Shee, S.; Manoj, N.; Gonnade, R. G.; Biju, A. T. *ACS Catal.* **2023**, *13*, 8752.
6. Ranganathappa, S. S.; Dehury, B, S.; Singh, G. K.; Shee, S.; Biju, A. T. *ACS Catal.* **2024**, *14*, 6965.
7. Shee, S.; Ranganathappa, S. S.; Gadhave, M. S.; Gogoi, R.; Biju, A. T. *Angew. Chem. Int. Ed.* **2023**, *62*, e202311709.

Keynote Lecture (KNL-02)

Chiral Cationic Ion Pair Catalysis using Guanidiniums

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School of Chemistry, Chemical Engineering and Biotechnology
Nanyang Technological University

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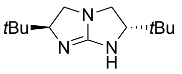
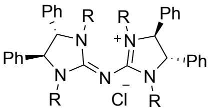
Abstract:

Chiral cations have proven to be highly effective as phase transfer catalysts, particularly when paired with inorganic basic salts such as hydroxides and carbonates for basic reactions. Over the past decade, we have developed several chiral cation catalysts, including pentanidium and bis-guanidinium. In this report, we present three key areas of research related to these catalysts. First, we examine their role in ion pair catalysis, specifically in reactions where they partner with polyoxometalates such as tungstate and molybdate. Next, we explore their involvement in reactions involving hypervalent silicate intermediates. Finally, we discuss how these catalysts have been instrumental in investigating the role of halogen bonding in catalysis, as well as in the desymmetrization of sulfinates, which provides a pathway to a variety of enantioenriched sulfur stereogenic centers.



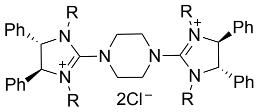
Bicyclic Guanidine

Brönsted Base Catalysis



Pentanidium

Halogen Bonding in Catalysis



Bisguanidinium

Chiral Cationic Ion Pair Catalysis

Selected Publications:

1. Leow, D.; Tan, C. H. Chiral guanidines catalyzed enantioselective reactions, *Chemistry - An Asian Journal*. **2009**, *4*, 488-507.
2. Ma, T.; Fu, X.; Kee, C. W.; Zong, L.; Pan, Y.; Huang, K. W.; Tan, C. H. Pentanidium catalyzed enantioselective phase transfer conjugate addition reactions, *Journal of the American Chemical Society*. **2011**, *133*, 2828-2831.
3. Zong, L.; Tan, C. H. Phase transfer and ion pairing catalysis of pentanidiums and bisguanidiniums, *Accounts of Chemical Research*. **2017**, *50*, 842-856.
4. Zhang, X.; Ren, J.; Tan, S. M.; Tan, D.; Lee, R.; Tan, C. H. Enantioconvergent Halogenophilic Nucleophilic Substitution (SN2X) Reaction, *Science*. **2019**, *363*, 400-404.
5. Zhang, X.; Esther.; Ang, C. X.; Yang, Z.; Kee, C. W.; Tan, C. H. Synthesis of chiral sulfinate esters by asymmetric condensation, *Nature*. **2022**, *604*, 298-303.

Keynote Lecture (KNL-03)

o-Alkynyl/alkenyl Arylnitrile: A New Building Block for Construction of Small Organic Molecules of Pharmaceutical Interest

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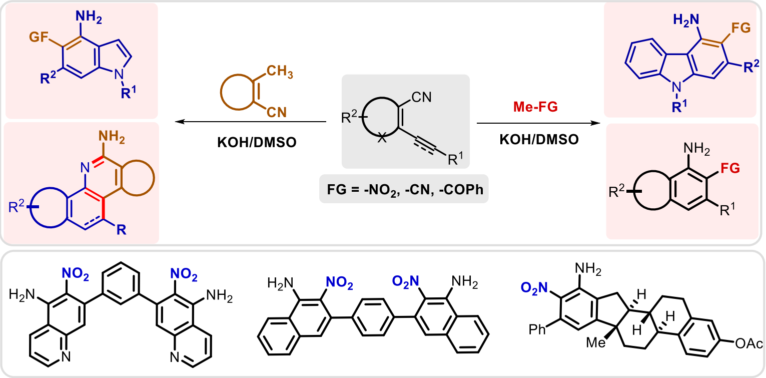
Abstract:

The simplicity, efficiency, and generality of reactions using alkynes have led to its applications in the synthesis of a wide variety of small organic molecules and natural products. Developing synthetic strategies for the direct synthesis of amino-substituted small molecules in terms of selectivity, operational simplicity, functional group tolerance, and environmental sustainability is in constant demand as the majority of drugs; drug-like compounds contain hetero atoms at their core. In continuation of our interest in the synthesis of small organic molecules using alkynes and super-base chemistry, we have successfully engineered the synthesis of a variety of biologically important scaffolds using *ortho*-alkynyl/alkenyl aryl nitriles. In this presentation, I would like to discuss some recent results in this chemistry.



References:

1. Patel. M.; Saunthwal. R. K.; Verma. A. K. *Acc. Chem. Res.* **2017**, *50*, 240.
2. Verma. A. K.; Saunthwal. R. K.; Patel. M. *Org. Lett*. **2016,** *18,220.*
3. Verma**.** A. K.**;** Danodia. A. K.; Saunthwal. R. K.; Patel. M.; Choudhary. D. *Org. Lett.* **2015,** *17*, 3658.
4. Verma. S.; Kumar. M.; Verma. A. K. *Org. Lett.* **2020**, *22*, 130.
5. Verma. S.; Kumar. M.; Verma .A. K. *Chem. Commun.* **2023**, *59*, 3723.

Invited Lecture (IL-01)

Scalable Synthetic Process Development of Pharmaceuticals

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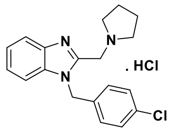
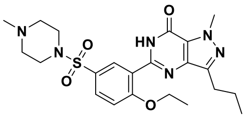
Abstract:

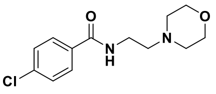
India's overwhelming dependence on China for generic active pharmaceutical ingredients (APIs) to the extent over 65 percent of the requirement is a serious concern in the production of affordable medicines used in current health care in India. While many Indian pharmaceutical companies produce generic APIs, the similar research activities in academia are rarely postulated. Evolution of innovative, cost-effective green processes for generic API synthesis in academia could help promote the production of generic APIs in industry. Our group is involved in the development of new or improved green processes for APIs and Key Starting Materials (KSMs) (some selected APIs and KSM are shown below). Our on-going efforts on the synthesis of various APIs [including APIs under Production Linked Incentive (PLI) scheme] and KSMs involving reduced number of steps, avoiding stoichiometric amount of corrosive Lewis acids, utilizing cheap reagents, using green and sustainable approaches, etc will be discussed. The underlying challenges during translation of a gram scale to scale up (>100 g) synthesis will also be covered.



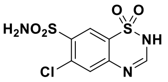
Clemizole Hydrochloride



Sildenafil



Moclobemide



Chlorothiazide

Selected references:

1. Laha, J. K.; Patel, K. V.; Tummalapalli, K. S. S.; Dayal, N. Formation of Amides, their Intramolecular Reactions to the Synthesis of *N*-Heterocycles, and Preparation of a Marketed Drug, Sildenafil: A Comprehensive Coverage, *Chem. Comm.* **2016**, *52*, 10245-10248.
2. Laha, J. K.; Gulati, U.; Gupta, A.; Indurthy, H. K. Improved, gram-scale synthesis of sildenafil in water using arylacetic acid as the acyl source in the pyrazolo[4,3-*d*]pyrimidin7-one ring formation, *New J. Chem.* **2021***, 25*, 2643-2648.
3. Laha, J. K.; Gulati, U.; Gupta, A. Decarboxylative Amidation of Aryl/Heteroarylacetic Acids via Activated Esters through Traceless *α*-Functionalized Benzylic Radicals, *Org. Lett.* 2023, *25*, 3402-3406.
4. Gupta, A.; Laha, J. K. Growing Utilization of Radical Chemistry in the Synthesis of Pharmaceuticals, *Chem. Rec.* **2023**, 23, e202300207.
5. Keshri, A.; Gupta, A.; Gulati, U.; Bhatt, T. D.; Kashyap, M.; Laha, J. K. A Telescopic, Scalable and Industrially Feasible Method for the Synthesis of Antidepressant Drug, Moclobemide, *Helv. Chim. Acta***,** 2024**,** *Advance Article* (**DOI**: 10.1002/hlca.202400075).
6. Laha, J. K.; Gulati, U. A process for preparing a pyrazolo-pyrimidinone compound and using the said compound for the preparation of Sildenafil, Indian patent application no. 202011000343 filed on December 31, 2020.
7. Laha, J. K.; Gulati, U. Process for preparing dioxopyrrolidine benzoate compounds and use thereof, Indian patent application no. 202211011928 filed on March 04, 2022.
8. Laha, J. K.; Gupta, P. A low cost, improved telescopic process for preparing Clemizole Hydrochloride for industrial production, Indian Patent application no. 202311000179 filed on January 02, 2023.
9. Laha, J. K.; Gupta, A.A process for the preparation of Chlorothiazide, Indian patent application no. 202411029501 filed on April 11, 2024.
10. Laha, J. K.; Gupta, A.; Keshri, A.; Kashyap, M. A process for the preparation of Moclobemide Intermediate, Indian patent application no. 202411048138 filed on June 23, 2024.

Invited Lecture (IL-02)

Direct Access to C3-Functionalized Pyrrole

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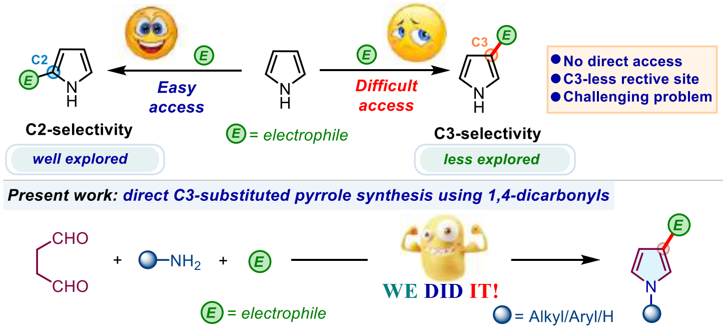
Abstract:

Due to mitigated nucleophilicity, the C3-position of pyrrole is usually considered a non-reactive site in conventional chemistry; thus, the majority of SEAr/Friedel-Craft reactions occur at the C2-(α)-position of pyrrole. Therefore, achieving functionalization at the pyrrole's β-(C3) position is challenging in synthetic chemistry and requires multistep/indirect strategies.[1] These methods can be strictly distributed in two ways: (i) directed functionalization using bulky or electron-withdrawing on pyrrole, and (ii) C3-functionalization-aromatization of N-substituted pyrrolidine. Using amine-catalyzed annulation reactions, we have explored the chemistry of 1,4-dicarbonyls as donor-acceptor (D-A) precursors for synthesizing five-membered N-heterocycles in asymmetric and non-asymmetric fashion.[2] Recently, we have developed a stimulating and straightforward method to access β-(C3)-functionalized pyrrole using mild Lewis acid and catalyst-free conditions.[3] Details of the concept, design, and synthetic strategy for accessing C3-substituted pyrrole in a non-asymmetric/symmetric fashion will be presented here.



References:

1. Tsuchimoto, T. *Chem. Eur. J.* **2011**, *17*, 4064.
2. (*a*) Kumar, I.; Mir, N. A.; Gupta, V. K.; Rajnikant. *Chem. Comm.* **2012**, *48*, 6975. (*b*) Kumar, I.; Mir, N. A.; Ramaraju, P.; Wakhloo, B. P. *RSC Adv.* **2012**, *2*, 8922. (*c*) Mir, N. A.; Choudhary, S.; Ramaraju, P.; Singh, D.; Kumar, I. *RSC Adv*. **2016**, *6*, 39741. (*j*) Ramaraju, P.; Mir, N. A.; Singh, D.; Kumar, I. *RSC Adv*. **2016**, *6*, 60422. (*d*) Choudhary, S.; Singh, A.; Yadav, J.; Mir, N. A.; Anthal, S.; Kant, R.; Kumar, I. *New J. Chem.* **2019**, *43*, 953. (*n*) Singh, A.; Vanaparthi, S.; Choudhary, S.; Krishnan, R.; Kumar, I. *RSC Adv*. **2019**, *9*, 24050.
3. (a) Pawar, A. P.; Yadav, J.; Mir, N. A.; Iype, E.; Rangan, K.; Anthal, S.; Kant, R.; Kumar, I. *Chem. Commun*. **2021**, *57*, 251. (b) Pawar, A. P.; Yadav, J.; Dolas, A. J.; Iype, E.; Rangan, K.; Kumar, I. *Org. Biomol. Chem*. **2022**, *20*, 5747. (c) Pawar, A. P.; Yadav, J.; Dolas, A. J.; Nagare, Y. K.; Iype, E.; Rangan, K.; Kumar, I. *Org. Lett*., **2022**, *24*, 7549.

Invited Lecture (IL-03)

Sustainable Synthesis towards Organic Radicals and Multi-Redox states

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Abstract:

Synthesis of ambient-stable radicals continues to intrigue researchers for their multifaceted properties.[1,2] From our initial findings of transformation of electron-deficient molecules into colorful organic radical ions (S=1/2 systems) in solution (which existed only up to few hours), I will present our journey involving the various molecular design aspects leading to stabilization of the radical ions under ambient conditions.[3]

We will discuss our group's progress in the sustainable, green synthesis and isolation of air-stable, colorful organic radical ions.[4] We will also show how the frontier molecular orbitals of these radicals can be engineered to accomplish electron transfer (eT) reactions that were possible only with inorganic reagents.[5] On similar lines, we extended our design aspects to synthesize new multi-electron acceptors[6a-c] and other redox-systems with new functional and catalytic[6d] properties.

Finally, I will demonstrate how electrolytic processes can be controlled to synthesize and crystallize pure redox-sates separated by few hundreds of millivolts.[7]

References:

1. a) Stable Radicals: Fundamental and Applied Aspects of Odd-electron Compounds; R. Hicks, Ed.; Wiley-Blackwell, New York, 2010. b) Morita, Y.; Suzuki, S.; Sato, K.; Takui, T. *Nature Chem*. **2011**, *3*, 197.
2. *Radical Ion Probes*: a) Ajayakumar, M. R.; Mukhopadhyay, P. *Chem. Commun*. **2009**, *25*, 3702. b) Ajayakumar, M. R.; Yadav, S.; Ghosh, S.; Mukhopadhyay, P. *Org. Lett.* **2010**, *12*, 2646. c) Ajayakumar, M. R.; Hundal, G.; Mukhopadhyay, P. *Chem. Commun*. **2013**, *49*, 7684.
3. *Stabiliztion and Isolation of Radicals*: a) Kumar, Y.; Kumar, S.; Bansal, D.; Mukhopadhyay, P. *Org. Lett.* **2019**, *21*, 2185. b) Kumar, Y.; Kumar, S.; Mandal, K.; Mukhopadhyay, P. *Angew. Chem. Int. Ed*. **2018**, *57*, 16318. c) Kumar, S.; Ajayakumar, M. R.; Hundal, G.; Mukhopadhyay, P. *J. Am. Chem. Soc*. **2014**, *136*, 12004.
4. Kumar, S.; Mukhopadhyay, P. *Green Chem*. **2018**, *20*, 4620.
5. Shukla, J.; Kumar, S.; Rustam.; Mukhopadhyay, P. *Org. Lett.* **2020**, *22*, 6229.
6. *Electron-Poor Systems*: a) Kumar, S.; Shukla, J.; Kumar, Y.; Mukhopadhyay, P. *Org. Chem. Front.*, **2018**, *5*, 2254. b) Shukla, J.; Ajayakumar, M. R.; Kumar, Y.; Mukhopadhyay, P. *Chem. Commun*. **2018**, *54*, 900. c) Shukla, J.; Bera, S. P.; Ajayakumar. M. R.; Konar, S.; Mukhopadhyay, P. *Chem. Eur. J.* **2024**, e202401334. d) Datta, A.; Ritu.; Kumar, S.; Chorol, S.; Mukhopadhyay, P.; Jain, N. *Org. Lett*. **2024**, *26*, 7357.
7. Krishna Kumar M.S.; Mukhopadhyay (to be submitted)

Invited Lecture (IL-04)

New Strategies for 3d-Metal-Catalyzed Single Electron Transfer-Induced Reactions

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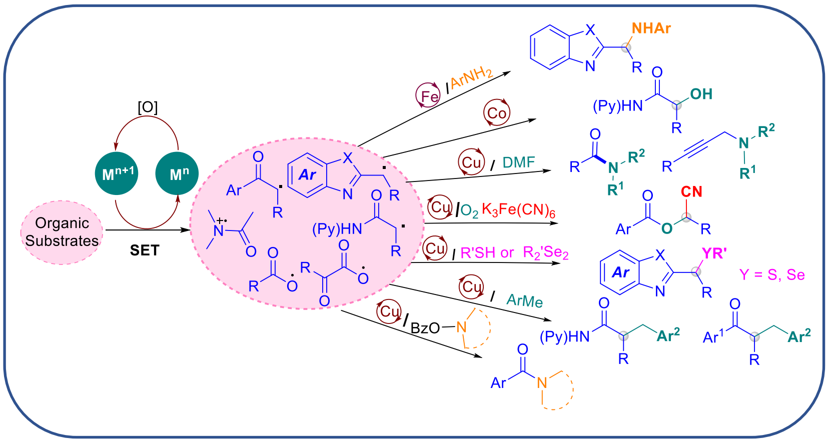
Abstract:

The 3d-metal catalyzed single electron transfer (SET) processes are very much common in biological systems and have received wide-ranging applications in synthetic chemistry lately. Higher-valent 3d metals can act as a single electron acceptor for a variety of carbon- and heteroatom-based nucleophiles, thereby facilitating a SET process in organic substrates.[1] We have studied the 3d-metal catalyzed highly chemo- and regioselective activation of O–H, N–H and even C–H bonds of a variety of organic substrates via SET mechanism.[2] In these reactions, the organic substrate served as a single electron donor to the metal catalyst. The heteroatom- and/or carbon-centered radicals, thus generated from the substrate, have been subsequently trapped by either a radical species via radical-radical coupling process or a nucleophile under oxidative condition to give coupled products. The merits of these strategies combine the low-cost of earth abundant 3d-metal catalysts with the broad scope, scalability and selectivity of those transformations giving expedient access to structurally diversified compound range in step- and atom-economic manner.



References:

1. Gupta, A.; Kumar, J.; Rahaman, A.; Singh, A. K.; Bhadra, S. *Tetrahedron* **2021**, *98*, 132415.

2. (a) Gupta, A.; Rahaman, A.; Bhadra, S. *Org. Lett.* **2019**, *21*, 6164-6168. (b) Kumar, J.; Suresh, E.; Bhadra, S. *J. Org. Chem.* **2020**, *85*, 13363-13374. (c) Singh, A. K.; Chauhan, S. S.; Bhadra, S. *Chem. Commun.* **2023**, *59*, 11544-11547. (d) Rahaman, A.; Bhadra, S. *Synlett* **2023**, *34*, 2481-2485. (e) Rahaman, A.; Shinde, R. D.; Bhadra, S. *J. Org. Chem.* **2023**, *88*, 1884-1889. (f) Shinde, R. D.; Paraskar, A. R.; Kumar, J.; Ghosh, E.; Paine, T.K.; Bhadra, S. *J. Org. Chem.* **2024**, *89*, 9666-9671.

Invited Lecture (IL-05)

APEX Reaction at Masked-Bay Region Involving Ketone as Traceless Directing Group

Dr. Modhu Sudan Maji*
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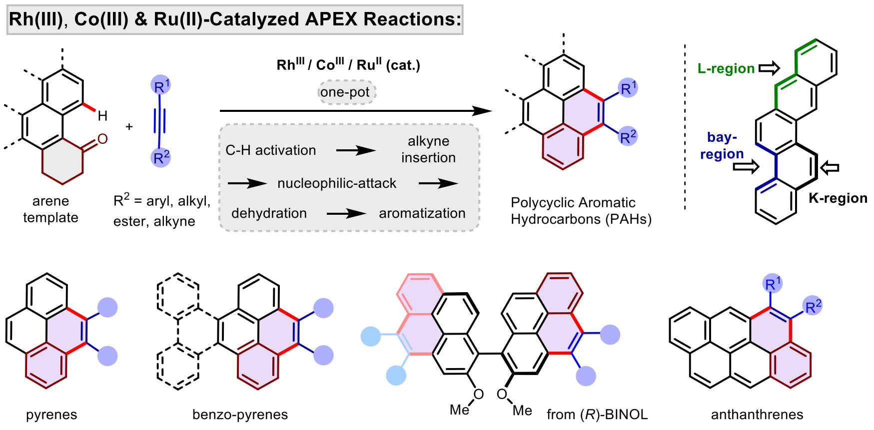
Abstract:

Synthesis of polyaromatic hydrocarbons (PAH), nano-graphenes, and graphene nano-ribbons through bottom-up strategy is the central theme of nano carbon chemistry and related material sciences to access these challenging molecules possessing precise structure.[1] The synthesis of PAH possessing unique shape, edge structure and substitution can enhance their solubility as well as desired photophysical properties. Moreover, the residual functional group after APEX can assist for a second APEX or their ready derivatization. To this end, total synthesis approach is a key synthetic strategy which rely only on handful of available synthetic strategy, and thus development of novel synthetic strategy is highly desirable for their ready access with atom-by-atom precision. Among different regions present at the edge of arene templates, APEX at the bay region is highly challenging owing to availability of the respective functionalized precursors and Diels-Alder cycloaddition reaction is only method known prior to our work. We addressed this problem by developing ketone directed APEX reaction at the masked-bay region by involving C–H bond functionalization employing various arene derived ketones as templets and internal alkynes.[2] The reactions were executed by employing Rh, Co and Ru-based catalysts providing direct access to a range of exotic PAHs.[3] Mechanistically this reaction proceeds through four distinct steps, showed excellent regioselectivities, and oxygen acted as terminal oxidant.



• bottom-up approach • excellent scope • ketone as traceless directing group • access to highly-conjugated PAHs

Figure 1. APEX-Reactions by Ketone Directed C–H bond functionalization.

References:

1. Itami *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 11144.

2. Maji *et al.* (a) *Org. Lett.* **2018**, *20,* 134. (b) *Adv. Synth. Catal.* **2021**, *363*, 4605. (c) *Adv. Synth. Catal.* **2018**, *360*, 2204. (d) *J. Org. Chem.* **2017**, *82*, 420. (e) *Adv. Synth. Catal.* **2019**, 585. (f) *Org. Chem. Front.* **2020**, *7*, 19. (g) *Chem. Eur. J.* **2019**, *25*, 1806. (h) *Org. Lett.* **2019**, *21*, 835. (i) *Org. Lett.* **2020**, 22, 2615. (j) *Chem. Commun.* **2022**, *58*, 10865.

3. Maji *et al.* (a) *Angew. Chem. Int. Ed.* **2023**, *62*, e202305258. (b) *Org. Lett.*, **2023**, *25,* 8622.

Invited Lecture (IL-06)

Synthesis and application of biologically relevant azoles and indoles through greener approach

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Abstract:

The demand for the rapid generation of diverse molecular scaffolds with pharmaceutical relevance is an area of priority research in organic chemistry. In this domain, development of new methodology towards sustainable chemistry is the prime focus. Remarkable progress in this area has been accomplished over past few decades in homogeneous catalysis.[1,2] Typically, *N*-heretocyclic core is advantageous from application point of view. Often, they play crucial role in regulating various biological processes that are relevant for the maintenance of life. Among *N*-heterocycles, azoles and indoles are privileged substructures owing to their wide occurrence in a large number of natural products, bioactive compounds and materials of industrial relevance.[3-5] Consequently, design of new molecules incorporating appropriate functionalities to various *N*-heterocycles e.g. pyrazolines, pyrazoles, indoles, indolines etc. is advantageous from medicinal chemistry point of view[6].

Donor-acceptor cyclopropane (DAC) due to its higher ring strain and polarised structure, offers wide reaction opportunities under Lewis acid, transition metal or organocatalytic activation.[7,8] In recent years, stereoselective transformations of DAC have received the major attention. [9]

Recently, we explore the reactivity of various azoles to DAC's under organocatalytic or Lewis acid activation to achieve highly functionalized annulated products in regio- or stereoselective fashion.

References:

1. Walsh, P. J.; Kozlowski, M. C. Fundamentals of Asymmetric Catalysis (University Science Books, 2009).
2. Dyson, P. J.; Jessop, P. G. *Catal. Sci. Technol.* **2016**, *6*, 3302-3316.
3. Kochanowska-Karamyan, A. J.; Hamann, M. T. *Chem. Rev.* **2010**, *110*, 4489.
4. Olgen, S. *Mini-Rev. Med. Chem.* **2013**, *13*, 1700.
5. Sidhu, J. S.; Singla, R.; Mayank, E. Y.; Jaitak, V. *Med. Chem.* **2015**, *16*, 160.
6. Larik, F. A.; Saeed, A.; Fattah, T. A.; Muqadar, U.; Channar, P. A. *Appl. Organometal. Chem.* **2017**, *3*, 31:e3664.
7. Cavitt, M. A.; Phun, L. H.; France, S. *Chem. Soc. Rev*. **2014**, *43*, 804.
8. Ghosh, K.; Das, S. *Org. Biomol. Chem.* **2021**, *19*, 965.
9. Reyes, E.; Uria, U.; Prieto, L.; Carrillo, L.; Vicario, J. L. *Tetrahedron Chem*. **2023**, 100041.

Invited Lecture (IL-07)

Integrating Noncovalent Interactions with Renewable Energy Sources for Sustainable Organic Synthesis

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Abstract:

Functionalization of C-H bonds owing to the large kinetic barrier associated with its bond cleavage has always been most dynamic topics to synthetic chemists.[1] Tremendous advancements have been done in the field of metal catalyzed C-H bond functionalization to achieve diverse functionalities.[2] These viable strategies offer great opportunities for the synthesis of pharmaceutically relevant molecules, agrochemicals, natural products and complex molecular scaffolds.[3] The classical methods mainly rely on utilization of pre-activated precursors for both reactivity as well as selectivity. However, the requirement for installation of an activating group prior to transformation adds cost to the synthetic route and lead to production of unwanted byproducts. Therefore, development of more atom and step-economical methodologies for direct C-H functionalization without any pre-activation of starting material is highly desirable. As a part of our ongoing interest on the functionalization of C-H bonds[4], how the readily available and cost-effective building-blocks can be utilized to functionalize C(sp^2)-H bond in the presence of light and electricity will be discussed in this lecture.

References:

1. Morton, D.; Davies, H. M. L. *J. Org. Chem.* **2016**, *81*, 343-350.
2. Revathi, L.; Ravindar, L.; Fang, W. Y.; Rakesh, K. P.; Qin, H. L. *Adv. Synth. Catal.* **2018**, *360*, 4652-4698.
3. Abrams, D. J.; Provencher, P. A.; Sorensen, E. *J. Chem. Soc. Rev.* **2018**, *47*, 8925-8967.
4. a) Roy, V. J.; Roy, S. R. *Org. Lett.*, **2023**, 25, 923-927. b) Sen, P. P.; Roy, S. R. *Org. Lett.* **2023**, *25*, 1895-1900. c) Sen, P. P.; Saha, N.; Roy, S. R. *ACS Catal.* **2024**, *14*, 907-920.

Invited Lecture (IL-08)

Enabling Light-Induced Carbene Generation & Relay Photoredox-Organocatalysis for Stereo-/Chemoselective Reactions

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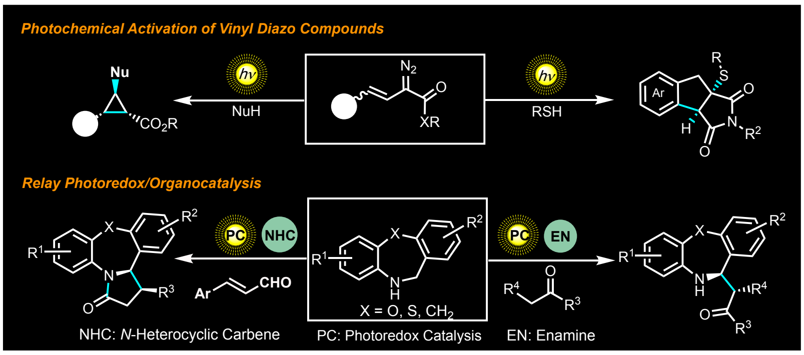
Applications of light energy to carry out organic reactions lead to orthogonal reactivities to that of ground-state thermal reactions. Previously, strong UV-radiations have been exploited to activate molecules, enabling them to react in the excited state. However, certain limitations are associated with these high-energy UV-light-driven organic processes, *viz.,* the requirement of specialized reaction vessels, undesired side reactions, and decomposition of reactants, thereby restricting its broad applications. Recently, the development of reactions under low-energy UV light and visible light, directly or facilitated with photocatalysis has opened new gates for efficient organic synthesis. The renaissance of photocatalysts led to tremendous progress in organic photochemical reactions by activating non-absorbing organic molecules with photo-redox catalysts. These developments provided new avenues for unusual reactivities and assessing complex molecular architectures with high selectivity, which have not been achievable through conventional organic synthesis. We have explored the applications of photoredox catalysis and direct activation of organic molecules with low-energy light to generate valuable reactive intermediates that have been probed further to discover new reactivities in highly chemo- and stereo-selective fashions. In this context, we have developed photochemical chemo- and stereo-selective transformations of vinyl diazo carbonyl compounds.[1,2] Alternatively, we have investigated the relay photoredox/organocatalysis for diastereo-/enantioselective synthesis of valuable seven-membered scaffolds.[3,5] The detailed results of our investigations will be presented.



References and Notes:

1. Hussain, Y.; Prasanna R.; Empel, C.; Sharma, D.; Kloene, L.; Zhu, W. F.; Kaiser, A.; Weizel, L.; Proschak, E.; Koenigs, R. M.; **Chauhan**, **P.** *Angew. Chem. Int. Ed*. **2024,** *63*, e202416956.
2. Hussain, Y.: Empel, C.; Koenigs, R. M.; **Chauhan**, **P.** *Angew. Chem. Int. Ed.* **2023**, *62*, e202309184.
3. Hussain, Y.; Sharma, D.; Tamanna, **Chauhan**, **P.** *Org. Lett.* **2023**, *25*, 3772-3777.
4. Hussian, Y.; Sharma, D.; Kotwal, N.; Kumar, I. **Chauhan**, **P.** *ChemSusChem* **2022**, *12*, e202200415.

Invited Lecture (IL-09)

Green Synthesis of Stereodefined Tri-/Tretrasubstituted Alkenes by 100% Atom-Economical, Regio- and Stereoselective Halo-Chalcogenations of Alkynes

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Abstract:

Stereodefined tetrasubstituted alkenes are ubiquitous in numerous pharmacologically or biologically active molecules, natural products, and marketed drugs. However, the synthesis of stereodefined all-carbon substituted olefins is really challenging, and among various strategies, the difunctionalization of alkynes is the most used one. The main challenge associated with the difunctionalization strategy of alkynes is to control the regio- and stereoselectivity of the reaction. We developed a 100% atom-economic, and green synthetic method for the high regio- and stereoselective radical iodo-sulfenylation of alkynes (anti-addition) using only iodine (0.5 equiv.) and disulfides (0.5 equiv.) to access important classes of stereodefined tri-/tretrasubstituted alkenes, *i.e.*, (*E*)-*β*-iodoalkenyl sulfides in moderate to excellent yields up to 96% (Fig. 1).[1] Significantly, one product, (*E*)-(2-iodo-1,2-diphenylvinyl)(phenyl)sulfane was synthetically diversified to various other potential classes of stereodefined tetrasubstituted alkenes, including a marketed anti-breast cancer drug, tamoxifen. Recently, we disclosed a solvent-controlled strategy for the 100% atom-economic and high regio- and stereoselective *syn*-halo-chalcogenations of a special kind of alkynes, *i.e.*, ynamides in toluene at room temperature for the synthesis of a wide variety of stereodefined tetrasubstituted alkenes bearing four different functional groups in excellent yields (Fig. 1).[2] The green chemistry metrics for the reactions are excellent.

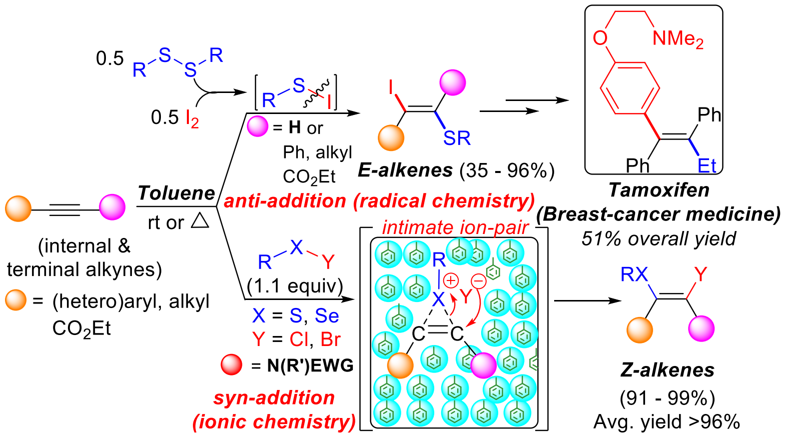

Figure 1: 100% Atom-economical halo-chalcogenations of alkynes.

References and Notes:

1. Satyanarayana, A. N. V.; Mukherjee, N.; Chatterjee, T.; *Green Chem.* **2023**, *25*, 779-788.
2. Satyanarayana, A. N. V.; Pattanayak, P.; Chatterjee, T.; *J. Org. Chem.* **2024**, *89*, 11455-11466.

Invited Lecture (IL-10)

Versatile Reactivity of Diazo Carbonyl Compounds Towards Metal Catalysts and Visible Light

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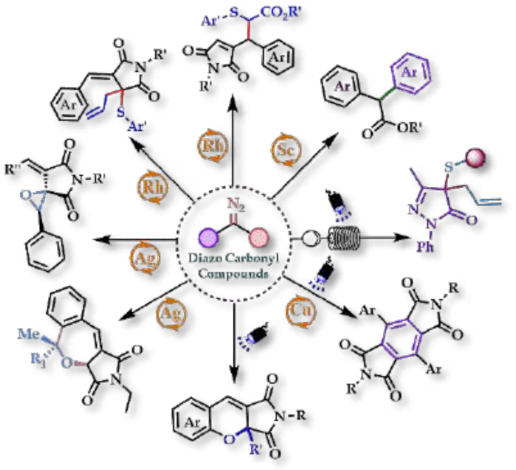
Abstract: Diazo carbonyl compounds have broad and tuneable reactivity.[1] Developing catalytic methods for the chemo- and regio-selective C-H bond functionalization is highly desirable as well as challenging. Over the years, we have been exploring the reactivity of diazo carbonyl compounds both under metal and visible light catalysis. We have developed a robust propargyl α-aryl-α-diazoacetate as a new class of reagent for the effective C-H bond functionalization of unactivated arenes, 1,3 diketones & β-keto acids via scandium catalysis to access useful functionalized compounds.[2] Likewise, we have been exploring the diverse reactivity of diazo arylidene succinimides (DASs) under metal as well visible light catalysis to access useful compounds like 2*H*-chormenes, PMDI etc.[3] This presentation will provide an overview of some of the recent advancements from our research group.



References and Notes:

1. a) Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.*, **2011**, *40*, 1857-1869 b) Ribas, X.; Ma, D.; Spivey, J. J.; Casitas, A.; Fairlamb, I. J. S.; Vedernikov, A. N.; Mirica, L. *C-H and C-X Bond Functionalization: Transition Metal Mediation*; Royal Society of Chemistry: Cambridge, U.K. b) Lednicer, D. *Strategies for Organic Drug Synthesis and Design*; Wiley: Hoboken, **2008**; pp 43-88.
2. a) Navale, B. S.; Laha, D. and Bhat, R.G. *Tetrahedron Lett.* **2019**, *60*, 1899–1903 b) Navale, B. S.; Laha, D.; Banerjee, S.; Vanka, K.; Bhat, R. G. *J. Org. Chem.* **2022**, *87*, 13583–13597
3. a) *Laha, D.;* Bhat, R. G. *Asian J. Org. Chem.* **2020**, *9*, 918-921 b) Bankar, O. S.; Laha, D.; Meher, K. B.; Bhat, R. G. *Chem Asian J.* **2023**, *e202300774. c) Laha, D.; Meher, K. B.; Bankar, O. S.;* Bhat, R. G. *Asian J. Org. Chem.* **2022**, e202200062 d) Bankar, O. S.; Pal, C.; Laha, D.; Abhijeet S. Sabale, Bhat, R. G. *Organic Lett.,* **2024**, *26, 9191–9197 e) Laha, D.;* Bankar, O. S.; Navale, B. S.; Santra, S.; Gosh, D.; Bhat, R. G. *Organic Lett.* **2024**, *26,* 8674–8679 *f) Meher, K. B. Laha, D. Dharpure, P. D.; Bhat, R.G. Organic Lett.* **2024**, *26, xxxx -xxxx (Just Accepted).*

Invited Lecture (IL-11)

The Discovery and the Development of an Interrupted Corey-Chaykovsky Reaction

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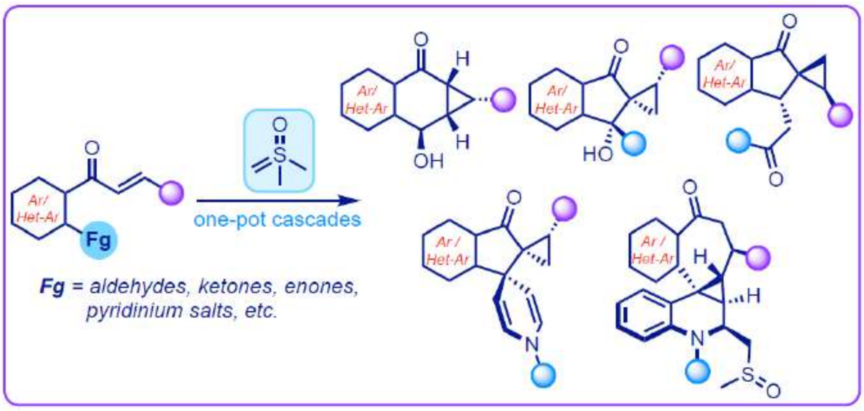
Abstract:

Cyclopropanes are crucial structural units in several bioactive natural products and pharmaceutically relevant compounds, including a few marketed drugs.1 The enhanced metabolic stability and conformational rigidity of cyclopropanes are critical during drug design and development. The Corey-Chaykovsky reagent [dimethyloxosulfonium methylide (DOSM)] is typically employed to prepare cyclopropanes from electron-deficient olefins. However, we utilized DOSM as a nucleophilic trigger to induce cascade transformations and accessed new classes of fused- and spirocyclopropanes with multiple stereocenters (Figure 1). 2-6 Further, the cyclopropanoids were elaborated to various privileged structures with distinctive substitution patterns. In my talk, I will describe how we accidentally entered this exciting research area and showcase the progress made so far.



Summary of our work on the interrupted Corey-Chaykovsky reaction

References and Notes:

1) Selected reviews: (a) Chen, D. Y. K.; Pouwer, R. H.; Richard, J. A. *Chem. Soc. Rev.* **2012**, *41*, 4631. (b) Chawner, S. J.; Cases-Thomas, M. J.; Bull, J. A. *Eur. J. Org. Chem.* **2017**, 5015.
2) Mishra, U. K.; Patel, K.; Ramasastry, S. S. V. *Org. Lett.* **2019**, *21*, 175.
3) Patel, K.; Mishra, U. K.; Mukhopadhyay, D.; Ramasastry, S. S. V. *Chem. Asian J.* **2019**, *14*, 4568 [*Invited for a special issue on the 20th anniversary of the CRSI*]
4) Mishra, U. K.; Patel, K.; Ramasastry, S. S. V. *Org. Lett.* **2020**, *22*, 3815.
5) Singh, B.; Ansari, A. J.; Malik, N.; Ramasastry, S. S. V. *Chem. Sci.* **2023**, *14*, 6963.
6) Maurya, J. P.; Ramasastry, S. S. V. *Org. Lett.* **2024**, *26*, 2282 [*Invited for a special issue on the 25th anniversary of the CRSI*].

Invited Lecture (IL-12)

Palladium-Catalyzed Highly Regio-, Stereo-, and Enantiospecific *Anti*-carboxylation of Unactivated Internal Allenes

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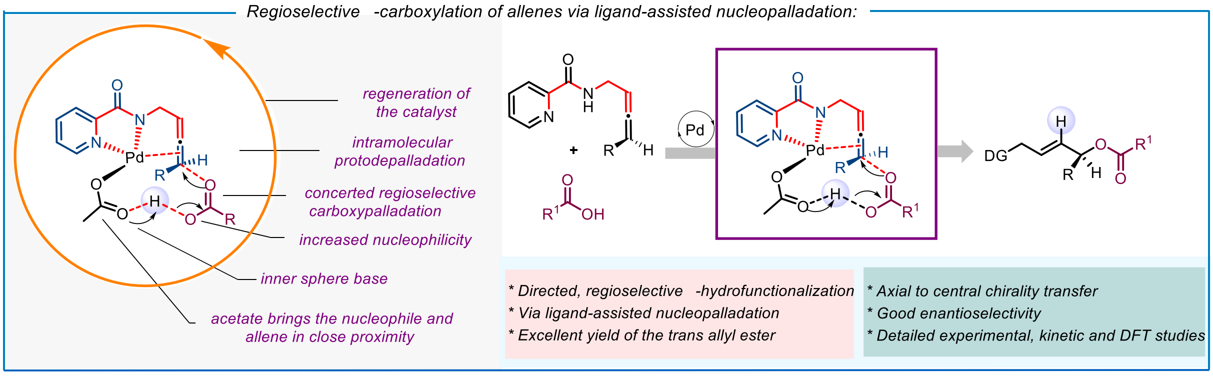
Abstract:

Allenes often suffer from regioselectivity issues in TM-catalyzed functionalizations and it becomes more complex when these are disubstituted.[1-3] In order to address these challenges, we have developed a directing group assisted Pd-catalyzed, regioselective -hydrofunctionalization of unactivated allenes.[4] The potential of this concept has been demonstrated by the development of the first example of the chiral version of this transformation by using axial to central chirality transfer (Scheme 1). The underlying studies of this methodology development shall be discussed in this seminar.



Regioselective -carboxylation of allenes via ligand-assisted nucleopalladation:

* Directed, regioselective -hydrofunctionalization
* Via ligand-assisted nucleopalladation
* Excellent yield of the trans allyl ester

* Axial to central chirality transfer
* Good enantioselectivity
* Detailed experimental, kinetic and DFT studies

Scheme 1

References:

1) Ma, S. *Chem. Rev.* **2005**, *105*, 2829.
2) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067.
3) (a) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679. (b) Ghosh, C.; Nagtilak, P. J.; Kapur, M. *Org. Lett.* **2019**, *21*, 3237.
4) Nagtilak, P. J.; Mane, M. V.; Hirapara, D. R.; Jain, A.; Kapur, M. (*manuscript submitted*).

Invited Lecture (IL-13)

Sustainable Catalyst Development for C-H Halogenation

Dr. Basab Bijayi Dhar*,[a] Monika,[a] Jaipriya Khatri,[a] Rachana Chaudhary,[a] Sarban Yadav,[a] Kritika Dogra[a]

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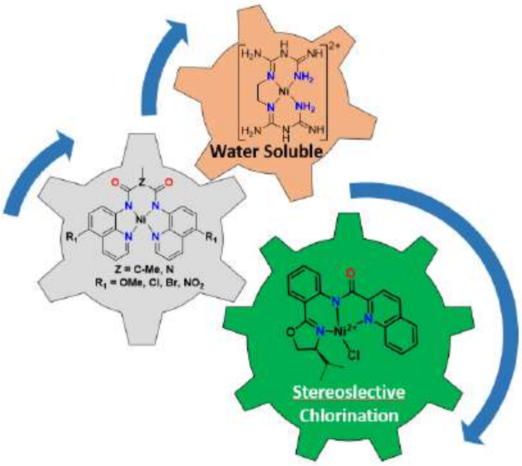
Abstract:

In organic chemistry, C–H bonds are often viewed as unreactive and referred to as "unfunctional groups," making direct functionalization challenging. Taking this into account, Ni(II) complexes consisting of tetradentate-amido quinoline and guanidine based ligands were synthesized and characterized by various analytical methods.[1, 2] These Ni-complexes successfully carried the C-H chlorination and bromination of a series of hydrocarbons using sodium hypochlorite (NaOCl) and acetic acid (AcOH) at room temperature for 30 minutes. Exclusively chlorinated products (TON: 680 ± 60 for cyclohexane, C(sp^3)-H bond energy: 99.3 kcal mol^{-1}) were obtained without any hydroxylated products, thus mimicking the activity of the halogenase enzyme. Ni(III) species was identified by electron paramagnetic resonance (EPR) spectroscopy and the plausible mechanism for chlorination is confirmed by DFT calculation.

Now, a chiral catalyst of Ni(II) complexes using chiral tridentate amido-oxazoline ligands were developed to synthesize enantiomerically pure chiral organic molecules. Chlorination of benzylic C-H bonds using NaOCl as an oxidant in the presence of acetic acid catalysed by these chiral Ni(II) complexes showed excellent enantiomeric excess within 2 hour at -1 °C. In case of ethylbenzene substituted with the electron donating group, the chiral complexes showed an enantiomeric excess (ee) of 96%.



References:

1. a) Adhikari, S.; Sarkar, A.; Dhar, B. B. *Chem. Commun.* **2022**, *58*, 4075-4078. b) Monika.; Sarkar, A.; Dhar, B. B.; Adhikari, S. *Dalton Trans.* **2023**, *52*, 540-545.

2. Khatri, J.; Mari, V.; Sarkar, A.; Karmodak, N.; B. B. Dhar, B. B.; Communicated, **2024.**

Invited Lecture (IL-14)

Input Management For Sustainable Chemistry

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ZDHC Foundation, India
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Abstract:

Sustainable chemistry, is a fundamental approach to chemical management that aims to minimise adverse effects of chemicals on the environment and human health whilst maximising resource efficiency. It involves the design, manufacture, and use of efficient, effective, safe, and more environmentally benign chemical products and processes. This integration can be accomplished by implementing sustainable processes and technologies at an industrial scale by adopting green and sustainable chemical practices in the manufacturing of chemicals, materials, and products. With the United Nations Environment Programme (UNEP) and the Organisation for Economic Co-operation and Development (OECD) highlighting the significance of sustainable chemistry in risk management and the life-cycle assessment of chemicals, materials, and products, the concepts of green and sustainable chemistry have gathered a great deal of attention globally. In the context of chemical management, the application of sustainable chemistry principles can lead to the development of safe and sustainable alternatives for chemicals of concern, the sustainable sourcing of resources and feedstocks, and the advancement of sustainability in production processes and products.

In the implementation of sustainable programs, the end-of-pipe scrutiny, and treatment thereof is invariably considered as the significant step. However, we believe that sustainable chemistry starts with “INPUT MANAGEMENT” and it is therefore a crucial stage for chemical industries. We believe that clean input delivers clean output.

For the Input management, we have created MRSL (Manufacturing Restricted Substances List), which is a list of chemicals, known to be hazardous for various reasons (including but not limited to be classified as CMR/PBT/vPvB). By restricting the chemicals in the input stream, the contamination in the output (whether be it a product, wastewater, air emission, or the sludge developed) can be controlled. These outputs are directly related to the consumers or to the environment, thereby reducing the adverse impact.

Our Vision is to create a world where better chemistry leads to the protection of life, land, air, and water.

Flash Talk (FL-01)

SOLID-STATE EMITTERS FOR CIRCULALRLY POLARISED LUMINESCENCE

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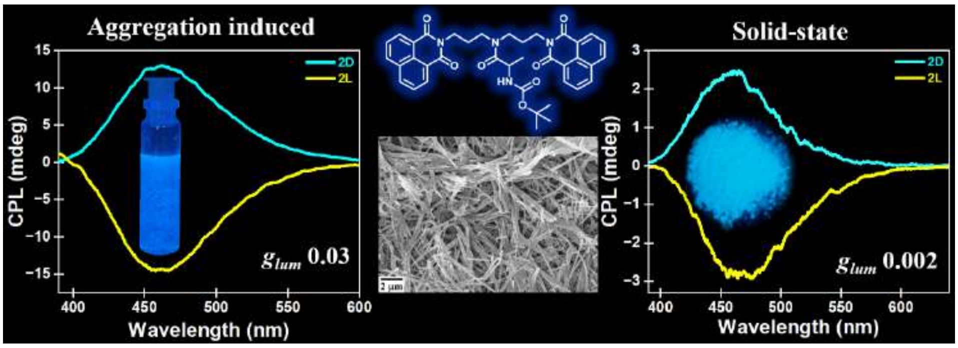
Abstract:

In the recent past, Circularly Polarized Luminescence (CPL) has attracted tremendous amount of research interest due to its potential applications in optical devices and imaging technology.[1] Various strategies have been tried to prepare CPL active materials showing high dissymmetry factors (g_{lum}), which can have a maximum value of 2.0. However, organic fluorophore, owing to their unfavourable electric dipole transitions, usually exhibit much lower values that range between 10^{-5} to 10^{-3}.[2] Additionally, achieving solid-state fluorescence is quite challenging, consequently chances of obtaining solid-state CPL activity becomes an arduous task.

In the present talk, I will discuss about the solid-state CPL properties of a chiral naphthalene-imide (NI) derivative.[3] This NI system shows aggregation induced enhancement of emission (AIEE) and bright fluorescence in the powder form. CPL measurements performed in aggregated (MeCN/Water) and in solid-states revealed impressively high dissymmetry factors in both states (Scheme-1). CPL in solid-state is undeniably a much-desired property, as it widens the possibility of integrating CPL materials in devices.



Scheme: Schematic diagram showing chemical structure of the prepared NI derivative and emission of circularly polarised light in aggregated & solid-state.

References and Notes:

1. a) Stachelek, P.; MacKenzie, L.; Parker, D.; Pal, R. *Nat. Commun.* **2022**, *13*, 553. b) Brandt, J. R.; Salerno, F.; Fuchter, M. J.; *Nat. Rev. Chem.* **2017**, *1*, 0045.
2. Mori, T.; *Circularly polarized luminescence of isolated small organic molecules*, Springer, 2020.
3. Likhar, A. R.; Cheran, A.; Sengupta, A.; Dutta, C.; Kumar, J.; Asthana, D.; *Chem. Commun.* **2024**, *60*, 9022.

Flash Talk (FL-02)

Modifying the Ligands for Better Electrocatalytic Hydrogen Evolution Activity

Dr. M.Ghosh*,[a] M Bharath,[a] M. Rana,[a] P. Kumar,[a] S. Pattanayk,[a] R. Gupta,b A. Ghosh [a]

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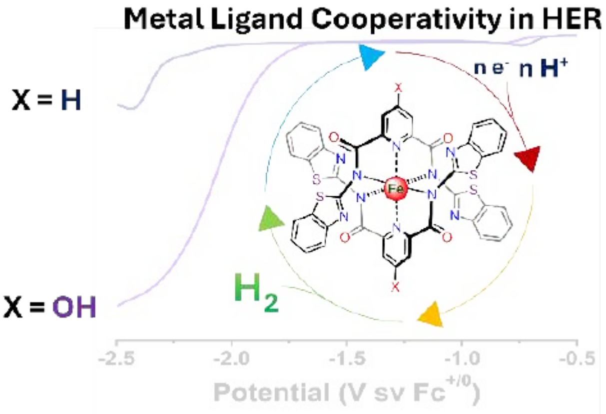
Abstract:

Growing energy demands and concerns on carbon emission have pushed the need for carbon neutral energy sources like green hydrogen as fuel. Molecular catalysts mimicking natural metalloenzymes which catalyze hydrogen production has been a trend for a long time and A great deal of literatures are available for the same.[1,2] In Chemistry, a small change in the molecular structure impact a lot on the catalytic activity. Herein we studied and compared the electrocatalytic Hydrogen evolution reaction (HER) of two novel non-heme Fe(III) complexes $(Fe^{III}[L^1]_2)^{2-}$ with N3 pincer type 4-hydroxy pyridine-2,6-dicarboxamide ligand and $(Fe^{III}[L^1]_2)^{1-}$ without hydroxy group. The first complex showed better electrocatalytic activity for HER with an overpotential of ~900 mV and almost three-fold increase in catalytic rates compared to second complex. It highlights the significant effect of hydroxy functional group in catalyst activation for HER. A thorough theoretical and experimental investigation lead us to conclude that both the catalysts follow a ligand centered HER mechanism. The details will be presented during the conference.



References and Notes:

1. Wittkam, F.; Senger, M.; Stripp, S. T.; Apfel, U. P. *Chem. Commun*. **2018**, *54*, 5934-5942.
2. Ahmed, M. E.; Dey, A.; *Curr. Opin. Electrochem*. **2019**, *15*, 155-164.

Flash Talk (FL-03)

Alternate Electrode Electrolysis: A New Tool for Electrosynthesis

Subhankar Bera,[a] Prof. Subhabrata Sen[a]*, and Dr. Debajit Maiti [a,*]
[a]Shiv Nadar IoE Deemed to be University, Dadri, GB Nagar, UP, India, 201314
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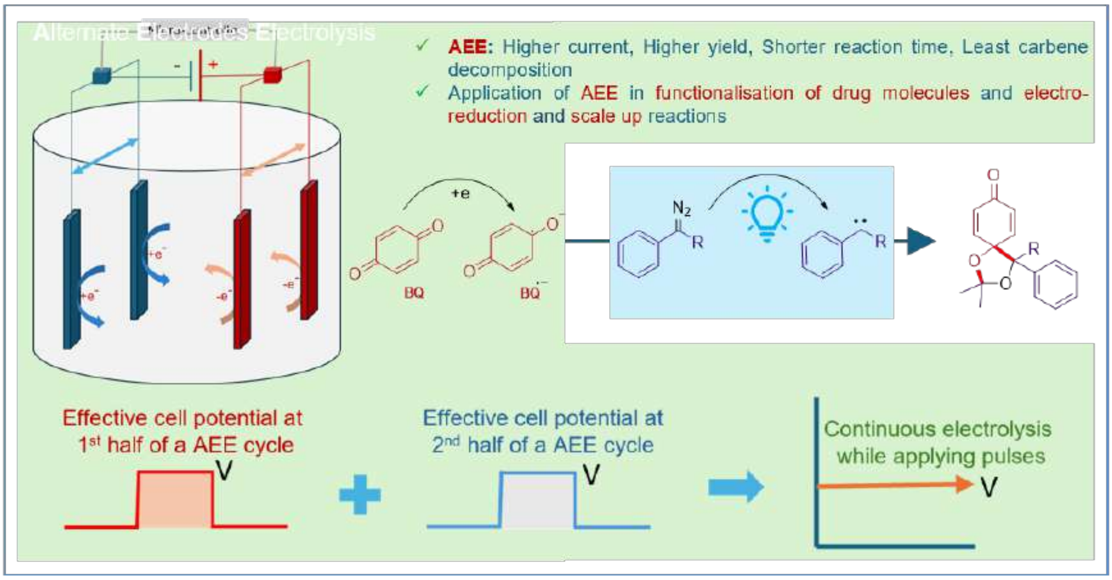
Abstract:

A new electrosynthesis technique called Alternate Electrode Electrolysis (AEE) will be discussed in this talk. This is an innovation in electrode assembly used in electrochemical reaction. The AEE setup consists of two pairs of cathode−anode compared to the conventional setup of one pair. Each pair would be polarized or in a resting stage with a preset interval of choice. This would maintain a continuous potential resulting in maximum current and would facilitate the mass transport, thereby increasing the overall efficiency of the reaction. Through AEE one can perform Pulsed Electrolysis without resting phase. As application we demonstrated that AEE offers the efficient utilization of photochemically generated carbenes. We extended AEE applications in paired photo-electrolysis reactions for the late-stage functionalization of bioactive molecules and pharmaceutical agents, hydroxylation of fluorinated benzene and the reduction of benzonitrile to benzyl amine. We believe that it holds great promise in the field of electrochemical organic synthesis.

Figure/Scheme:



- ✓ **AEE:** Higher current, Higher yield, Shorter reaction time, Least carbene decomposition
- ✓ Application of AEE in functionalisation of drug molecules and electro-reduction and scale up reactions

References and Notes:

Journal of the American Chemical Society, *146*, 36, 25166-25175.

Flash Talk (FL-04)

Amidation of Enones via Beckmann Rearrangement

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[b]Department of Biological and Synthetic Chemistry, Centre of Biomedical Research, SGPGIMS-Campus, Raebareli Road, Lucknow-226014, India
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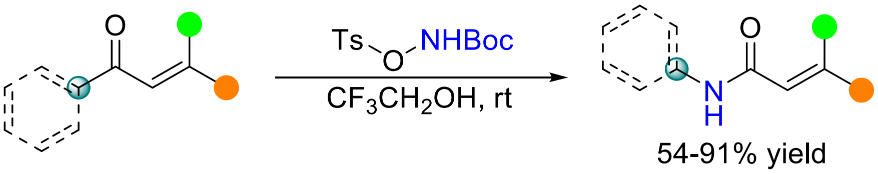
Abstract:

In this article we have reported the first chemoselective direct Beckmann rearrangement on enones using *O*-substituted hydroxylamines under metal-free reaction condition for a facile access to acrylamides. The details will be presented during the conference. The Beckmann reaction is efficient for making amides from ketones, but using it with enones is challenging due to their complex reactivity. We have developed a new method that efficiently converts enones into α,β-unsaturated amides with high yields.[1]



- First direct Beckmann rearrangement of enones
- Chemoselective amidation
- Metal and additive-free process
- *N*-aryl/alkyl acrylamides, 41 examples

Scheme: First direct Beckmann rearrangement for enones

Reference:

1. Saumya, V.; Vikram, S.; Jawahar, L. J.; Bhoopendra, T. *J. Org. Chem.* **2024**, *89, 11*, 8201-8207.

Poster Presentation (P-01)

Substituted Diaziridines *Via* [2+1] And [3+2] Cycloaddition Of Dialkyl Azodicarboxylates And There *In Situ* Conversion To Arene/ Drug-Hydrazine Conjugates

Subhankar Bera,[a] Haya Khan,[a] Dhiraj Barman,[a] Ritwik Bhattacharya,[a] Khushi Verma,[a] Prateek Rai,[b] Souvik Banerjee,[b] and Subhabrata Sen [a,*]

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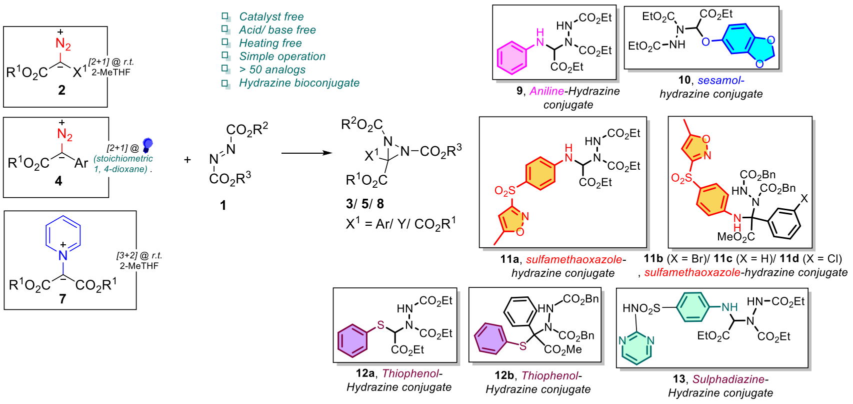
Abstract:

In this article We have reported the [2+1] and [3+2] cycloaddition reactions of dialkyl azodicarboxylate with various nitrogen sources from diazoesters and pyridinium ylides, leading to the formation of substituted diaziridines in high yields. Remarkably, these reactions are performed without the use of acids, bases, metal catalysts, or photosensitizers, highlighting a robust method for synthesizing structurally diverse diaziridines. Additionally, the resulting diaziridines can be treated in situ with a variety of arenes, natural products, and pharmaceutical compounds, producing a range of hydrazine bioconjugates.

Scheme:



References and Notes:

1. Ravindra, S.; IrafanaJesin, C. P.; Shabashini, A.; Nandi, G. C. *Adv. Synth. Catal*. **2021**, *363*, 1756-1781.
2. Abendroth, H. J.; Henrich, G. *Angew. Chem. Int. Ed*. **1959**, *71*, 283-283.

Poster Presentation (P-02)

C-H Bond Chlorination and Bromination Using Water Soluble Nickel (II) Guanidine Complexes

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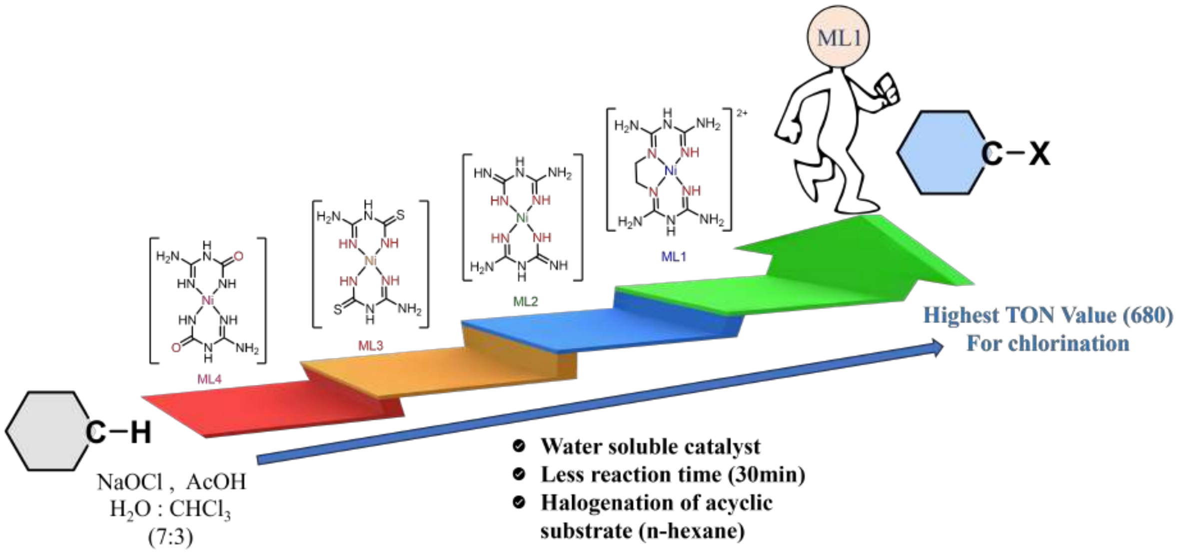
Abstract:

Water soluble Nickel(II)- guanidine based complexes (ML1, ML2, ML3 and ML4) were synthesised and characterised by various analytical techniques such as single crystal XRD (S-XRD), Nuclear Magnetic Resonance (NMR), cyclic voltammetry (CV), ultraviolet-visible (UV-Vis) and high-resolution mass spectroscopy (HR-MS) etc.[1] These Ni-complexes successfully carried the C-H chlorination of a series of hydrocarbons using sodium hypochlorite (NaOCl) and acetic acid (AcOH) in water-chloroform mixture (7:3) at room temperature for 30 minutes. Here, NaOCl is acting as an oxidant and a source of chlorine. The bond dissociation energy of the C(sp^3)-H bond of the substrates varies from 99.3 kcal mol^{-1} (cyclohexane) to 87 $kcal^{-1}$ (ethylbenzene).[2] Exclusively chlorinated products (TON: 680 ± 60 for cyclohexane) were obtained without any hydroxylated products, thus mimicking the activity of the halogenase enzyme. We successfully achieved C-H bond chlorination of *n*-hexane with high selectivity towards 2° products. Ni(III) species was identified by electron paramagnetic resonance (EPR) spectroscopy and the plausible mechanism for chlorination is confirmed by DFT calculation. Furthermore, C-H bond bromination of cyclohexane, *n*-hexane and toluene was also carried out using NaOCl in presence of NaBr and AcOH.



References:

1. Ray, P.; *Chem. Rev.* **1961**, *61*, 313.
2. Adhikari, S.; Sarkar, A.; Dhar, B. B. *Chem. Comm.* **2022**, *58*, 4075-4078.

Poster Presentation (P-03)

First-Row Transition Metal Complexes Utilising Amido-Based Ligand Frameworks: Application in Aromatic C-H Activation, and Asymmetric C-H Chlorination

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[a]Department of Chemistry, Shiv Nadar Institution of Eminence, U.P.-201314

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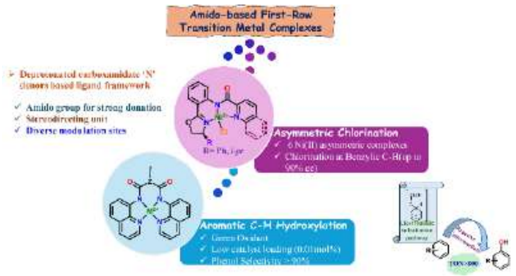
Abstract:

The incorporation of deprotonated carboxamidate ‘N’ donors into the ligand framework imparts distinctive properties that can significantly influence the reactivity, stability, and selectivity of metal complexes.[1] Cu (II) complexes consisting of tetradentate-amido quinoline ligands (L1 and L2) were synthesized and characterized by various analytical methods. Cu(II) complexes effectively catalysed the single-step hydroxylation of aromatic C-H bonds using H_2O_2 as an oxidant without using an external base and afforded greater than 90% selectivity for phenol with a TON of 810 for benzene. Based on our experimental findings (KIE value, Hammett plot, EPR, etc.) DFT calculations, a plausible mechanism for aromatic C-H hydroxylation was proposed where Cu(II)-OOH was the reactive intermediate.[2]

A chiral catalyst featuring Ni(II) complexes with chiral tridentate amido-oxazoline ligands was developed for the synthesis of enantiomerically pure organic molecules. The chlorination of benzylic C-H bonds, using NaOCl as an oxidant and acetic acid as a solvent, was catalyzed by these chiral Ni(II) complexes, resulting in excellent enantiomeric excess within 2 hours at -1 °C. In the case of ethylbenzene substituted with an electron-donating group, the chiral complexes achieved an enantiomeric excess (ee) of 96%.



References:

1. Panda, C.; Sarkar, A.; Gupta, S. S. *Coordination Chemistry Reviews.* **2020**, *417*, 213314.
2. Monika.; Sarkar, A.; Dhar, B. B.; Adhikari, S. *Dalton Trans.* **2023**, *52*, 540.

Poster Presentation (P-04)

Metal- and Oxidant-free, Electricity-driven, Oxidative C–H Selenylative and Tellurylative annulation of N-(2-alkynyl)anilines

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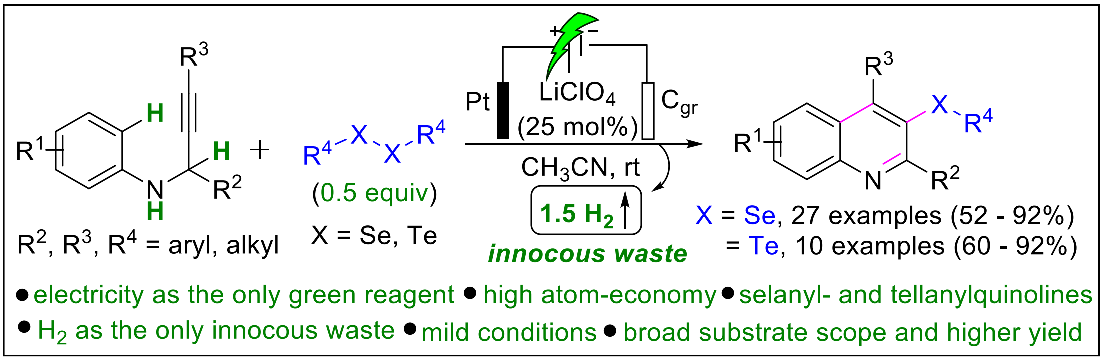
tanmay@hyderabad.bits-pilani.ac.in

Abstract:

In this article we reported a metal- and oxidant-free, radical C–H selenylative and tellurylative annulation of N-(2-alkynyl)anilines with diorganyl dichalcogenides, in particular, diorganyl diselenides and ditellurides is developed under electrochemical conditions for the sustainable synthesis of valuable 3-selanyl/tellanylquinolines up to 92% yield at room temperature (Scheme 1).[1] The developed protocol required only electricity as the green reagent and offers high atom economy, broad substrate scope, and efficient scalability. This method also offers several advantages as compared to the previously published ones.[2] The details will be presented during the conference.



Scheme 1. Electricity-driven, oxidative C–H selenylative and tellurylative annulation of N-(2-alkynyl)anilines for the sustainable synthesis of 3-selanyl/tellanylquinolines

References and Notes:

1. Naresh, A.; Keerthana, H. S.; Mukherjee, N.; Chatterjee, T.; *Chem. Commun.* **2024**, *60*, 7057-7060.
2. a) Zhu, C.; Nurko, M. C.; Day, S.; Lukesh, J. C. *J. Org. Chem.* **2022**, *87*, 8390-8395.
   b) Zhang, X.; Campo, M. A.; Yao, X. T.; Larock, R. C. *Org. Lett.* **2005**, *7*, 763-766.

Poster Presentation (P-05)

Design and Synthesis of Efficient Initiator for Photoinduced Radical Polymerisation Utilizing the Anomeric Effect of Five-Membered Ring Molecules

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Abstract:

Photochemical reactions are becoming essential tools both in academia and industry due to it's operational simplicity, environmentally friendly and economically sustainable nature in comparison to thermochemistry.[1] Particularly scientific community are attracted towards photoinduced radical polymerization (PRP) reaction due to it's various applications in the areas of dental restoration process, tissue engineering, artificial bone generation and 3D-Printing.[2] Herein we report the design of new initiator for PRP reaction via intramolecular hydrogen atom transfer reaction utilizing the inherent anomeric effect of five membered ring containing molecules. We have synthesized new efficient photoinitiator via barrier less sequential conjugate addition reaction.

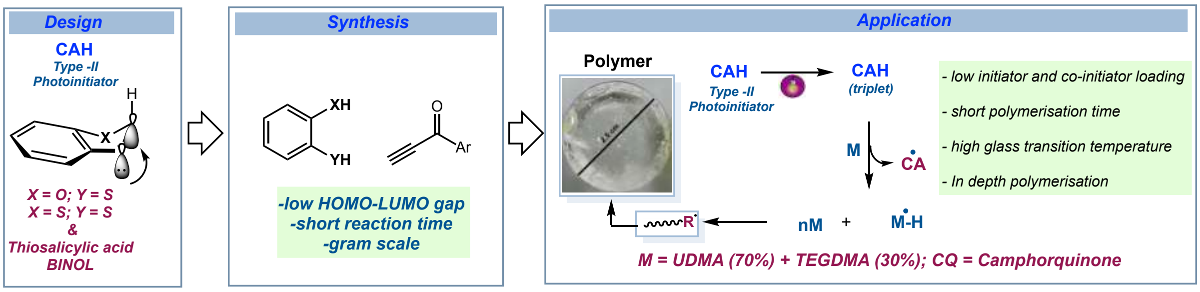

Figure: Retrosynthetic plan to access bicyclic framework: Application in PRP

Polymerization of diurethane dimethacrylate (UDMA, 70%) and triethylene glycol dimethacrylate (TEGDMA, 30%) in presence of 450 nm LED (15 W) under the aerobic conditions turned out to be very efficient (71 seconds) using our newly synthesized 1,2-benzenedithiol (DTH) based initiator and the resultant polymeric material has excellent physical properties.[3, 4] Higher efficiency of this initiator is due to the low bond dissociation energy of C-H bond adjacent to the two heteroatoms and puckered ring structure of the five membered rings. This hypothesis was further supported by X-Crystal structure of the initiator, NMR and computational data.

References:

1. Dadashi-Silab, S.; Doran, S.; Yagci, Y. *Chem. Rev.* **2016**, *116*, 10212.
2. Bagheri, A.; Jin, J. *ACS Appl. Polym. Mater.* **2019**, *1*, 593.
3. Ahmad, A.; Siddiqui, S. A.; Mittal, G.; Sukumar, N.; Dubey, K. D.; Kapat, A. *Chem. Eur. J.* **2023**, *29*, e2023018.
4. Ahmad, A.; Shelke, A. B.; Kapat, A. *Manuscript under preparation.*

Poster Presentation (P-06)

Synthesis of 6,5-bicyclic Benzofuran Framework: Application in Dual PI$_3$K/VEGFR$_2$ Inhibitors Targeting Cancer

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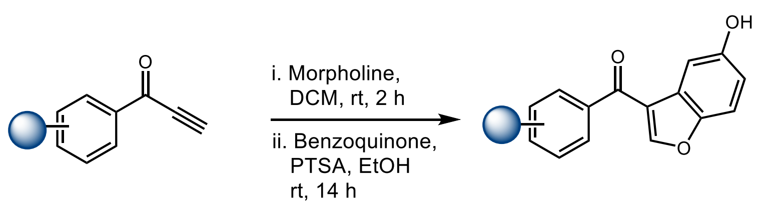
Abstract:

Benzofuran moieties are widely distributed in the central core of various active pharmaceuticals (dronedarone, amiodarone etc.), agrochemical agents and natural products. These molecular architectures are used for the treatment of various diseases such as diabetes, HIV, tuberculosis, epilepsy, and Alzheimer's. Particularly, these scaffolds are becoming very effective against various types of Cancers. Recently El-Messery and its group first reported benzofuran-based new drugs that inhibit both PI$_3$K and VEGFR$_2$.[1] Reported synthetic protocol suffers from drawbacks, such as multi-step synthesis with low overall yield and limited opportunities for post-modification. In the past few years, we have harnessed the reactivity of ynone utilizing 1,4-conjugate addition of various nucleophiles to ynones to access bicyclic scaffolds.[2] Recently, we have developed a new synthetic protocol to access benzofuran core with by altering the reactivity of ynone utilizing corresponding enamine via amine conjugate addition reaction of morpholine.[3] Subsequently, this enamine was treated with benzoquinone to afford various benzofurans with good to excellent yield.



-Metal-free bicyclic ring formation

- High yielding

- 33 substrates

- PI$_3$K/VEGFR$_2$ inhibitor

Figure: Retrosynthetic plan to access benzofuran framework.

Computational-guided late-stage modification has been carried out to modify benzofuran scaffolds that can be utilized to inhibit both PI$_3$K and VEGFR$_2$. The docking score of the synthesized molecules is comparable to the marketed drugs such as *Alpelisib* (PI3K inhibitor) as well *Sorafenib* (VEGFR2 Inhibitors), which may indicate the dual inhibitory mechanism.

References:

1. El-Khouly, O. M.; Henen, M. A.; El-Sayed, M. A.; El-Messery, S. M. *Sci. Rep.* **2022**, *12*, 17104.
2. Ahmad, A.; Siddiqui, S.; Mittal, G.; Sukumar, N.; Dubey, K. D.; Kapat, A. *Chem. Eur. J.* **2023**, *29*, e202308.
3. Ahmad, A.; Dixit, A.; Singh, P. B.; Kapat, A. *Manuscript under preparation*.

Poster Presentation (P-07)

Programming Photodegradability into Biobased Polybenzoxazine Networks

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Abstract:

Development of a practical, affordable, and non-toxic biodegradable polymers is one of the many global issues existing today to tackle the depletion of resources, waste accumulation and the harmful effects of microplastics. The notion of reuse, recycle and refuse provides right social guidance, yet polymers fulfil a vital role in many aspects ae are deemed irreplaceable. Today, developing strategies towards controlled polymer degradation remains a key challenge.[1] To overcome this issue, introduction of dynamic covalent bonds to the polymeric backbone which are responsive to stimuli have been explored widely. Specifically, light regulation of bond cleavage and formation process are excessively discovered to address the limitations of the conventional thermoset systems which lack repairability and removability.[2] Photo-dimerization reactions that can be reversed upon application of appropriate wavelength of light have gained interest as it allows the fabrication of thermosets with an additional merit of reversibility. In this work, coumarin derivative is used in synthesis of various benzoxazine monomers due to their stimuli-responsive properties and its ability to show reversibility.[3] Benzoxazine monomers have been synthesized and characterized using various spectroscopic methods i.e., ^{1}H and ^{13}C NMR, mass spectroscopy and is subjected to undergo [2+2] cycloaddition upon exposure to UV wavelength greater than 300 nm to form a cyclobutane linked dimer which can be cleaved upon irradiation at different wavelength. Furthermore, thermal stability of the Co based poly-benzoxazines are studied using TGA, DSC and DMA analyses. Photodegradation of the polymer has also been studied with the aid of GPC, and FTIR spectroscopy.

References:

1. Ji, Z.; Liu, J.; Sakkiah, S.; Guo. W.; Hong, H. *ACS Sustainable Chem. Eng.* **2021**, *9*, 2433-2446.
2. Zheng, J.; Png, Z. M.; Quek, X. C. N.; Loh, X. J.; Li, Z. *Green Chem.* **2023**, DOI: 10.1039/D3GC03086E.
3. Do, P. T.; Poad, B. L.; Frisch, H. *Angew. Chem. Int. Ed.* **2023**, *62*, e202213511.

Poster Presentation (P-08)

Optimization of Blue LED Photo-Flow Synthesis in Continuous Flow Reactors Using Design of Experiments (DoE): Efficient Synthesis of Diverse Di-aryl Ketones

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[2]Department of Chemical Engineering, School of Engineering, Shiv Nadar Institution of Eminence Deemed to be University, Dadri, Chithera, Gautam Buddha Nagar, UP 201314, India
[3]Department of Chemistry, SRM University-AP, Amaravati, AP 522240, India

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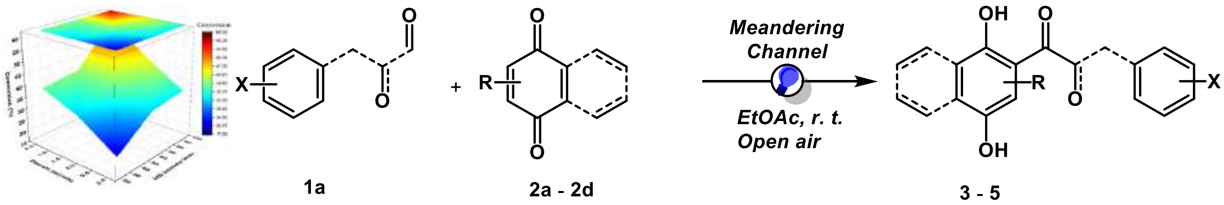
Abstract:

Herein, we demonstrated the optimization of a blue LED (450 nm) induced C-C bond formation between various aryl and heteroaryl aldehydes with 1,4-quinones at room temperature in ethyl acetate using Design of Experiments (DoE). This reaction was conducted within a flow (micro and milli-fluidic) device using a millifluidic meandering channel reactor (MC2), resulting in a library of diversely substituted diaryl ketones with moderate to good yields. Control experiments and density functional theory (DFT) based computational investigations were performed to elucidate the reaction mechanism.



● *DoE based reaction optimisation* ● *Millifluidic reaction set-up* ● *Blue LED @ r. t.* ● *metal/ acid/ base free* ● *35 examples*

Figure 1: Blue LED induced millifluidic reactions of aryl diazo esters and 1, 4-quinones

References and Notes:

1. Hommelsheim, R.; Guo, Y.; Yang, Z.; Empel, C.; Koenigs, R. M. Blue-Light-Induced Carbene-Transfer Reactions of Diazoalkanes. *Angew. Chem. Int. Ed.* **2019**, *58*, 1203-1207.
2. Reis, N. M.; Puma, G. L.; *Chem. Commun*. **2015**, *51*, 8414-8417.

Poster Presentation (P-09)

Organocatalytic [4+2] Benzannulation Between 1,4-Dithiane-Based Enal and Nitroolefins to Access 2-Nitrobiaryls

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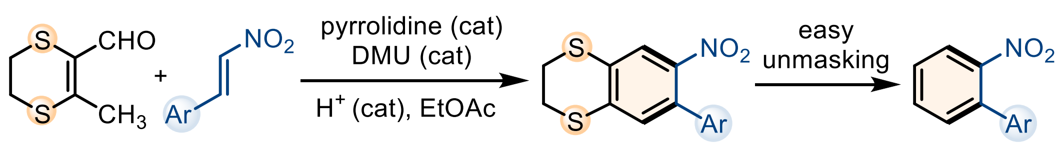
Abstract:

[4+2] Benzannulation reactions are an interesting and alternative way to access various benzene derivatives.[1,2] Herein, we have developed a simple and organocatalytic [4+2] benzannulation between substituted 1,4-dithiine-2-carbaldehyde and nitroolefins for constructing unsymmetrical 2-nitro biaryls. The focal theme of the present work is based on taking advantage of the HOMO-raising effect of temporary substitutions as 1,4-dithiane-tethered enals on in situ generated dienamine intermediate with amine-catalyst for a [4+2] benzannulation, which could be removed easily after the reaction. Easy unmasking of 1,4-dithiine units results in a benzannulation product like that of unsubstituted biaryls, which are difficult to access. Several 2-nitrobiaryls have been accessed with moderate to good yields and with promising synthetic applications. In this direction, 1,4-dithiane-type functionalized building blocks have been explored for assembling important structural frameworks (Scheme 1c).[3] However, utilizing 1,4-dithiine-enals for [4+2] annulation remains elusive. Herein, we resent our initial study in this direction.

[4+2] bezannulation of nitro-styrene and enals with temporary handle



- *matal-free approach*
- *removable substitution on enals*
- *extended applications*

References:

1. Magar, K. B. S.; Xia, K. L.; Lee, Y. R. *Chem. Commun*. **2015**, *51*, 8592.
2. Ghosh, B.; Harariya, M. S.; Mukherjee, S. *Angew. Chem. Int. Ed*. **2022**, *61*, e202204523.
3. a) Ryckaert, B.; Demeyere, E.; Degroote, F.; Janssens, H.; Winne, J. M. *J. Org. Chem*. **2023**, *19*, 115. b) Hullaert, J.; Winne, J. M. *Angew. Chem., Int. Ed.* **2016**, *55*, 13254. c) Guaragna, A.; Napolitano, C.; D'Alonzo, D.; Pedatella, S.; Palumbo, G. *Org. Lett.* **2006**, *8*, 4863.

Poster Presentation (P-10)

Copper Catalyzed Synthesis of β-Amino Carbonyl Compounds

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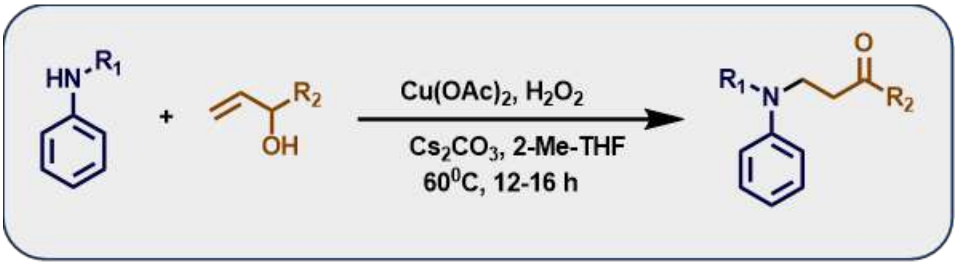
Abstract:

The β-aminoketones are pivotal in heterocyclic synthesis, serving as essential scaffolds for diverse synthetic molecules.[1] They are widely available in natural products, drugs, and bioactive molecules.[2-4] This study presents a Cu-catalyzed synthesis of β-amino ketones by reacting allyl alcohols with anilines in 2-Me-THF at 60°C, using hydrogen peroxide and cesium carbonate. Use of allyl alcohols eliminate the requirement of unstable and expensive enones[5] and employs affordable copper acetate, making it more environmentally friendly than third-row transition metals like Pd. We also aim to explore β-amino ketones through an intramolecular α-arylation method for rapid access to indolines and quinolines, as well as the synthesis of 1-Phenylpiperidine.



Scheme 1. Copper catalysed addition of the aryl amines to allyl alcohols.

Keywords:

Amination , β-aminoketones, heterocyclic synthesis, indolines and quinolines.

References:

1. Hammoudaab, M. M.; Elattar,K. M. *RSC Adv*. **2022**, *12*, 24681-24712.
2. Pham, N. N.; Janke, S.; Salman, G. A.; Dang, T. T.; Le, T. S.; Spannenberg, A.; Ehlers, P.; Langer, P. *Eur. J. Org. Chem*. **2017**, 5554-5565.
3. Ravn, A.; Vilstrup, M.; Noerby, P.; Daasbjerg, K.; Daasbjerg, T. *J. Am. Chem. Soc.* **2019**, *141*, 11821-11826.
4. Du, Y.; Li, Q.; Xiong, B.; Zhang, D.; Wang, M. *Bioorg. Med. Chem.* **2010**, *18*, 4255-4268.
5. Kumar, G. S.; Singh, D.; Kumar, M.; Kapur, M. *J. Org. Chem.* **2018**, *83*, 3941-395.

Poster Presentation (P-11)

Multicolor Fluorescent Probes for Nitric Oxide Detection in Cellular Organelles and In Vivo Zebrafish Models

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Abstract:

Nitric oxide (NO) is a vital signalling molecule involved in neurotransmission, vasodilation, osteofunction, reproduction, and oxidative stress regulation.[1] However, conventional NO-sensing fluorophores, primarily based on orthophenylene diamine (OPD), often require controlled methylation steps, resulting in complex mixtures of mono-, di-, and tri-substituted products that complicate their application.[2,3] To address these limitations, we developed a novel fluorophore using a streamlined synthesis approach. We designed a ligand with an inherent secondary amine to improve sensitivity and conjugated it to a pentacyclic pyrylium scaffold, yielding a probe with high selectivity and sensitivity for NO.[4] Comprehensive photophysical studies confirmed its efficacy under physiological conditions. We then applied our fluorophore in various biological systems. First, we demonstrated its ability to detect NO in human microglial (HMC3) cells, which are essential for exploring neuroinflammation and brain function. Extending our research, we utilized the probe to monitor NO within exosomes derived from HMC3 cells, marking a pioneering step in studying intercellular signalling pathways mediated by these vesicles. Finally, we validated the probe's functionality in an in vivo zebrafish model, taking advantage of its well-developed vascular system to investigate NO's role in vascular system. This work highlights the fluorophore's potential as a robust, real-time sensor for nitric oxide in complex biological environments, offering new insights into NO-related signalling mechanisms and facilitating advanced research in chemical biology.

References:

1. Andrabi, S. M.; Sharma, N. S.; Karan, A.; Shahriar, S. M. S.; Cordon, B.; Ma, B.; Xie, J. Nitric Oxide: Physiological Functions, Delivery, and Biomedical Applications. *Adv. Sci.* **2023**, *10* (30). https://doi.org/10.1002/advs.202303259.
2. Kojima, H.; Nakatsubo, N.; Kikuchi, K.; Kawahara, S.; Kirino, Y.; Nagoshi, H.; Hirata, Y.; Nagano, T. Detection and Imaging of Nitric Oxide with Novel Fluorescent Indicators: Diaminofluoresceins. *Anal. Chem.* **1998**, *70* (13), 2446-2453. https://doi.org/10.1021/ac9801723.
3. Terai, T.; Nagano, T. Fluorescent Probes for Bioimaging Applications. *Curr. Opin. Chem. Biol.* **2008**, *12* (5), 515–521. https://doi.org/https://doi.org/10.1016/j.cbpa.2008.08.007.
4. Chen, X. X.; Niu, L. Y.; Shao, N.; Yang, Q. Z. BODIPY-Based Fluorescent Probe for Dual-Channel Detection of Nitric Oxide and Glutathione: Visualization of Cross-Talk in Living Cells. *Anal. Chem.* **2019**, *91* (7), 4301-4306. https://doi.org/10.1021/acs.analchem.9b00169.

Poster Presentation (P-12)

O-(2-Pyrimidinyl)-*N*-Boc Hydroxylamine (PymONHBoc): A novel aminating agent for metal-free direct synthesis of sec.amides and nitriles

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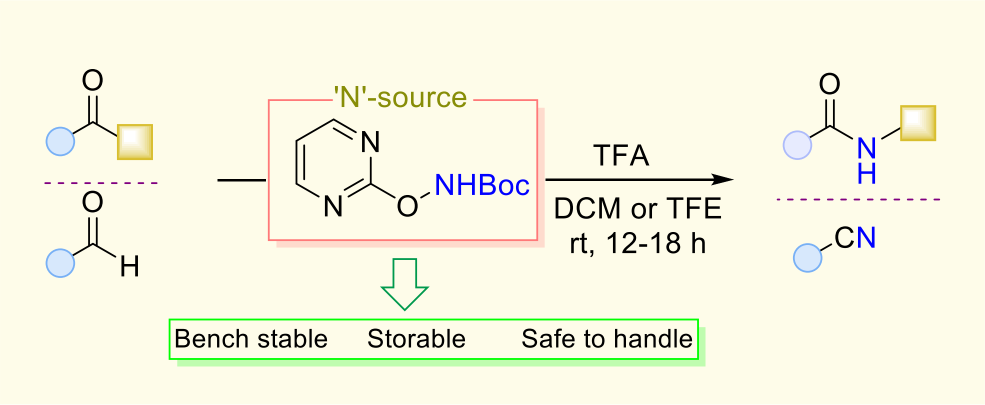
Abstract:

In this article we have reported a metal-free methodology for the direct conversion of ketones and aldehydes into sec-amides and nitriles using PymONHBoc as hydroxylamine-derived novel aminating agent. This reagent demonstrates superior shelf stability and ease of handling compared to other hydroxylamine-derived reagents. This method efficiently converts a wide range of aliphatic, aromatic, and α,β-unsaturated carbonyl compounds into the corresponding amides and nitriles with good to excellent yields under ambient conditions. The use of PymONHBoc is advantageous as it facilitates the insitu generation of the activated oxime intermediate, concomitantly producing a non-interfering, neutral byproduct. This property enhances the overall efficiency of the process, minimizing potential side reactions and byproduct.The details will be presented during the conference.

Scheme: Synthesis of sec-amides and nitriles using novel "N"-source



References and Notes:

1. Divedi, A.; Verma, S.; Chandra, D.; Bhargav, S.; Jat, J. L. Indian Patent [IN202211052690 A 2022-09-23]. (Manuscript submitted to *EJOC*).

Poster Presentation (P-13)

Living Photo-Oligomerization Behaviour Of Diazaanthracene-Derived Macrocycle

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Abstract:

Macrocycles occupy a very prominent space in supramolecular chemistry due to their well-defined cavity suitable for molecular recognition, sensing, catalysis, etc.[1] Recently, stimuli-responsive macrocycles have gained significant attention because of their reversible dynamic function.[2] Light serves as an ideal stimuli because of its tunability over a wide range of wavelengths, noninvasive nature, and avoids the generation of waste compared to other responsive systems. In this regard, the integration of photo-responsive components into macrocycles and subsequent light-induced oligomerization of those has been an attractive and efficient approach for the preparation of carbon-rich covalently linked macromolecules.[3] However, capturing intermediate oligomers in photopolymerization reactions to study their properties often proves challenging. We intended to use the classic [4+4] cycloaddition reaction of anthracene and extend it to the 1,8-diazaanthracene system which also shows similar behavior. However, interestingly, it gives an *anti-parallel* photodimer, minimizing the dipolar repulsion from the endocyclic nitrogens.[4] Taking advantage of this phenomenon, we prepared a planar aromatic oligoamide macrocycle comprising 1,8-diaza-anthracene unit which undergo efficient photo-oligomerization in a stepwise manner through intermolecular *anti-parallel* photodimerization of 1,8-diaza-anthracene. We strategically tuned the side chains to control their regioselectivity, favoring the *exo*-product over the *endo*-isomers. We were able to isolate and completely characterize the oligomers up to octamer having molecular weight >10 kDa, which is close to the molar mass of some low molecular weight polymers.[5] Additionally, the oligomers retained sufficient photoreactivity to undergo further oligomerization, either by themselves or by adding fresh monomers, exhibiting living polymerization-like behavior. These oligomers are thermally reversible, allowing the recovery of monomers. Our findings demonstrate an efficient approach to generating higher molecular weight oligomers in a single-step process, which can be valuable for optoelectronic materials.

References:

1. Escobar, L.; Ballester, P. *Chem. Rev.* **2021**, *121*, 2445.
2. Frasconi, M.; Fernando, I. R.; Liu, Y. W. Z.; Liu, W. G.; Dyar, S. M.; Barin, G.; Wasielewski, M. R.; Goddard, W. A.; Stoddart, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 11057.
3. Kory, M. J.; Wörle, M.; Weber, T.; Payamyar, P.; vandePoll, S. W.; Dshemuchadse, J.; Trapp, N.; Schluter, A. D. *Nature Chem.* **2014**, *6*, 779.
4. Berni, E.; Dolain, C.; Kauffmann, B.; Leger, J. M.; Zhan, C.; Huc, I. *J. Org. Chem.* **2008**, *73*, 2687.
5. Kumar, J. M.; Ferrand, Y.; Gole, B. *Manuscript submitted.*

Poster Presentation (P-14)

Metal-free direct approach for the Synthesis of *N-tert*-Butyl Amides from Aldehydes

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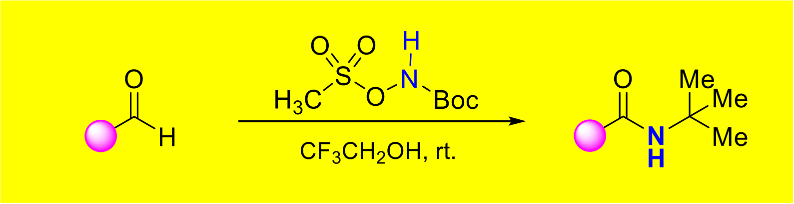
Abstract:

In this article we have reported the economical and practical approach for the synthesis of *N-tert*-Butyl Amides from readily available aldehydes using *N*-Boc-*O*-mesylhydroxylamine (MsONHBoc) as nitrogen source. This direct and metal-free method provided good to excellent yields of products and tolerates a wide range of functional groups. Self-stability, low-cost, and ease of handling of MsONHBoc introduce an additional advantage. This method works in weakly acidic solvent and generated water-soluble byproduct (MsOH), that can be easily removed by basic aq. work-up. The details will be presented during the conference.[1]

Scheme: Metal-free direct conversion of aldehydes to N-tert-Butyl Amides using MsONHBoc.



- ✓ *Metal free, one step, tandem process*
- ✓ *Mild, open air, operationally simple*
- ✓ *Effective aminating agent*
- ✓ *Water-soluble byproduct*
- ✓ *Broad substrate scope*
- ✓ *Good to excellent yield*

Reference:

1. Bhargav, S.; Kumar, P.; Divedi, A.; Jat, J. L. **2024**. *Manuscript under preparation (Unpublished work)*

Poster Presentation (P-15)

Photoinduced Decarbonylative Synthesis of Vinyl Sulfones

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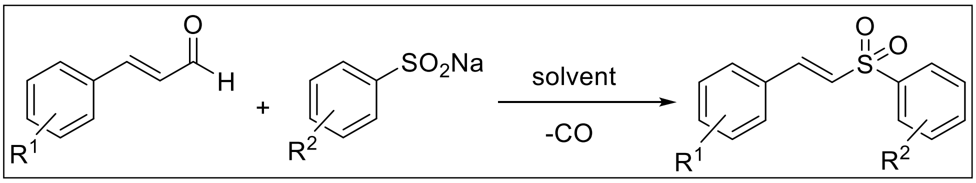
Abstract:

Decarbonylation of aldehydes and ketones is a fascinating topic because it provides a reliable and effective framework for the synthesis of bioactive products. Decarbonylative functionalization is typically achieved at high temperatures with transition metal catalysts for the C-C bond formation. We have developed a photoinduced transition metal-free decarbonylative strategy utilizing non-covalent interactions for $C_{sp}{}^{2}$-S bond formation. In line with the rising desire for more environmentally friendly chemical processes, the ongoing investigation of metal-free decarbonylation holds promise for improving the sustainability and efficiency of chemical synthesis. This photoinduced decarbonylative pathway operates via a radical mechanism initiated by a photoinduced intrasystem SET process and providing a sustainable substitute for conventional metal-catalyzed procedures. With this method, a variety of vinyl sulfones may be produced with good to outstanding yields (up to 93%) and good tolerance for functional groups.



References and Notes:

1. Eschinazi, H.; Pines, H. *J. Org. Chem*. **1959**, *24*, 1369.
2. Cao, D.; Ataya, M.; Chen, Z.; Zeng, H.; Peng, Y.; Khaliullin, R. Z.; Li, C.J. *Nat Commun.* **2022**, *13*, 1805.

Poster Presentation (P-16)

Degradable Spiroacetal-Bridged Bio-derived Polybenzoxazine Thermosets

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Abstract:

Thermoset resins including phenolic, epoxy, and benzoxazine showed a high heat resistance due to high cross linkages network in their structures. Particularly, benzoxazines are privileged structures with promising and attractive chemical and mechanical properties. However, degradation and recyclability are the key challenges due to high cross-linkages in PBzs. Recently, various dynamic covalent bonds like diacetal, Diels-alder, disulfides linkages etc. have been incorporated in the polymers to address the recyclability problem. In addition, hydrolysis of acetal linkages has attracted its incorporation into polymers to resolve the degradation problem. The salient features of diacetal linkages such as high heat resistant, dynamic bond exchange, hydrolysis etc. encourages us to incorporate the acetal linkage in the benzoxazine scaffolds in order to generate new derivatives. Herein, we design, green synthesize bio-based new benzoxazine derivatives (abbreviated as PH_{ace}-fa, V_{ace}-fa, and V_{ace}-ha) which are fully characterized by NMR, HRMS, FT-IR, TGA and DSC analysis. Furthermore, DMA, LSS, and degradation studies of poly-benzoxazines are studied and on the basis of structure and properties, a structure-properties relationship was stabilized.

References:

1. Wang, P.; Zhang, S.; Xu, W.; Xiao, T.; Ran, Q. High heat-resistant and degradable polybenzoxazines with a diacetal structure. *ACS Sustainable Chem. & Eng.* **2021**, *9*, 7913-7921.
2. Zhang, W.; Gao, F.; Chen, X.; Shen, L.; Chen, Y.; Lin, Y. Recyclable, degradable, and fully bio-based covalent adaptable polymer networks enabled by a dynamic diacetal motif. *ACS Sustainable Chem. & Eng.* **2023**, *11*, 3065-3073.

Poster Presentation (P-17)

Photoinduced LMCT Process to Access Cross-Dedydrogenative Coupling of Indoles

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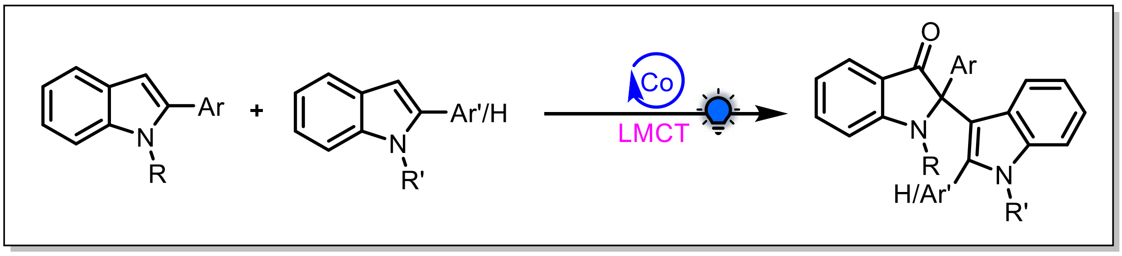
Abstract:

In recent years, the replacement of precious metal complex having excellent photoredox catalytic activities can be done by using an earth abundant metal catalyst via visible light-induced LMCT process. A metal-ligand complex can undergo excitation on visible light irradiation resulting a ligand based radical through homolysis of metal ligand bond. Herein, we have demonstrated the involvement of commercially available cobalt catalyst in visible light-induced LMCT process for the homo and hetero cross- dehydrogenative coupling indoles under mild condition. This method provides diverse substrate scope with good yields along with synthesis of metagenediindole A. The visible light-induced LMCT process of cobalt was validated with a series of mechanistic studies such as UV-vis spectroscopy, EPR analysis and XPS studies.



References and Notes:

1. Cremer, C.; Patureau. F. W. *JACS Au*. **2022**, *2*, 1318-1323.

2. Nagare, Y. K.; Shah, I. A.; Yadav, J.; Pawar, A. P.; Rangan, K.; Choudhary, R.; Iype, E.; Kumar, I. *J Org Chem.* **2022**, *87*, 15771-15782.

Poster Presentation (P-18)

Radical-Mediated Deoxygenative Alkynylation of Heterocyclic *N*-oxides under Ball Milling

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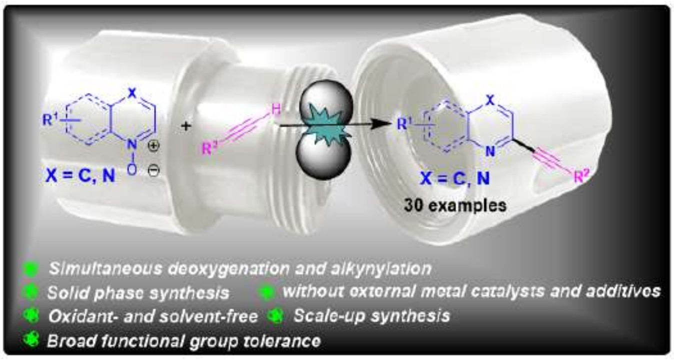
Abstract:

In this article we have reported the first example of a sustainable, and unprecedented stainless steel-induced deoxygenative C-2 alkynylaion of heterocyclic *N*-oxides under ball milling via a radical-mediated pathway. The current approach afforded the corresponding alkynylated quinolines/pyridines through alkynylation and deoxygenation in one step. Significant tolerance of structural variations with electron-rich and electron-deficient substituents both in the quinoline/pyridine N-oxides and in phenyacetylenes has been observed, affording a library of targeted products in moderate to excellent yields. Detailed mechanistic investigations based on extensive control experiments and XPS analysis corroborated the significant role of Fe(III) species present in the milling equipment (stainless steel) as well as the mechanical impact of the milling equipment (Fe/Zr-jar/balls), in initiating the reaction via a radical pathway. In addition, excellent green chemistry metrics highlight the economic sustainability and efficiency of our protocol. The method has been successfully applied to the synthesis of two mGluR5 antagonists.



Scheme: Graphical abstract

Poster Presentation (P-19)

Visible-Light-Induced, Organophotoredox Catalyzed Trifluoromethylative Annulation of 3-(2-(ethynyl)phenyl)quinazolinones: Sustainable Synthesis of 5-(trifluoromethyl)-12*H*-quinolino[2,1-*b*]quinazolin-12-ones

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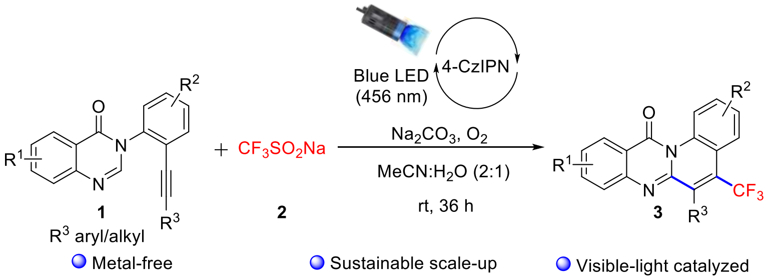
Abstract:

We have developed a metal-free, visible-light-induced oxidative trifluoromethylative annulation strategy with 3-(2-(ethynyl)phenyl)quinazolinones for the sustainable synthesis of a biologically-active highly-fused *N*-heteroaromatic, i.e., 12*H*-quinolino[2,1-*b*]quinazolin-12-one[1-3], in particular, a new class of molecules, *i.e.*, 5-(trifluoromethyl)-12*H*-quinolino[2,1-*b*]quinazolin-12-ones using 4CzIPN as a organophotoredox catalyst and Langlois reagent, *i.e.*, sodium trifluoromethanesulfinate (CF_3SO_2Na) as the trifluoromethylating agent (Scheme 1). This organophotocatalytic method possesses several notable advantages such as metal-free protocol, broad substrate scope, straight-forward scalability, mild reaction conditions such as reaction at room temperature under blue LEDs irradiation. The details will be presented during the conference.



Scheme 1. Visible-light-induced trifluoromethylative annulation of 3-(2-(ethynyl)phenyl)quinazolinones for the sustainable synthesis of 6-alkyl-5-(trifluoromethyl)-12*H*-quinolino[2,1-*b*]quinazolin-12-ones.

References and Notes:

1. Zeng, F. L.; Zhang, Z. Y.; Yin, P. C.; Cheng, F. K.; Chen, X. L.; Qu, L. B.; Cao, Z. Y.; Yu, B. *Org. Lett.* **2022**, *24*, 7912-7917.
2. Fan, J.; Yan, Q.; Liu, H.; Li, L.; Liu, Z. Q.; Li, Z. *New J. Chem.* **2023**, *47*, 20713-20717.
3. Zeng, F.L.; Wang, L.; Luo, Y.; Chen, J.; Li, J.; Yuan, J. *Chem. Commun.* **2024**, *60*, 7228-7231.

Poster Presentation (P-20)

Catalyst-Free Electro-Photochemical Insertion Reactions Of Carbene Anion Radicals By Convergent Paired Electrolysis

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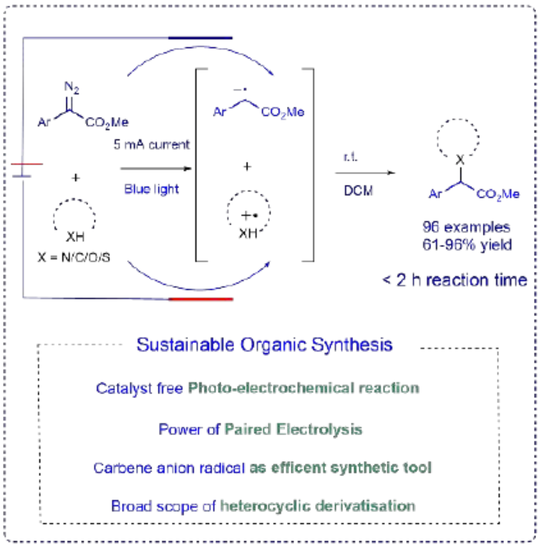
Abstract:

Electrochemical and photochemical reactions have garnered tremendous attraction in recent times [1]. Paired electrolysis is an energy-efficient electrochemical reaction where both anodic and cathodic electron flow directly induces product formation with maximum faradaic efficiency. Herein we report a metal-free convergent pair electro-photochemical strategy to generate radical cation and anion that resulted in the N-alkylation of various N-heterocycles, amines, and sulfonamides. The strategy also facilitated site-selective CH-alkylation of benzo fused morpholine, indolines, and OH- and SH- alkylation of phenols and thiophenols with aryl diazo esters. Mild reaction condition such as 5mA constant current and 5 W blue LED were sufficient to complete the reaction within 2 h. Late-stage and site-selective alkylation of APIs such as sulfadiazines and privileged scaffolds like sulfonamides and diazepanes have been achieved successfully. This paired photo-electrolysis strategy establishes a new energy-efficient way to achieve important reactions with better productivity and shorter reaction time over the existing strategies.



References:

1. Yan, M.; Kawamata, Y.; Baran, P.S. *Chem. Rev.* **2017**, *117*, 13230-13319.

Poster Presentation (P-21)

Photoredox Catalyzed [3+2] Annulation Reaction Of Diazo Compounds: An Efficent Entry To The Heteroaryl Fused Furans

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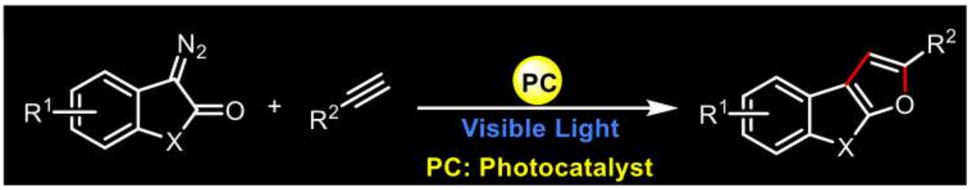
Abstract:

The development of sustainable synthetic strategies is one of the major goals in modern organic synthesis. In this context, light serves as a green and renewable energy source that has been utilized to activate organic molecules to carry out chemical transformations. Among the light sources, visible light has emerged as an efficient energy source to activate molecules by the direct irradiation or indirect activation *via* a photocatalyst. For the light mediated reactions, the diazo compounds have emerged as versatile reagents to carry out [2+1] cycloaddition, X-H and C-H insertion reactions, ylide formation and Wolff rearrangements by generating free carbenes as intermediates.[1] However, the light-assisted [3+2] cycloaddition reactions of diazo compounds for accessing valuable five-membered scaffolds are not well explored. Therefore, we have devised a general and practical protocol for the synthesis of fused heterocyclic rings, through the photolysis of heterocyclic diazo compounds assisted by photo-redox catalyst leading to the formation of 1,3-diradical intermediate which undergo [3+2] cycloaddition reaction with alkynes.[2] With this process, a new class of fused heteroaryls have readily been accessed. The detailed results of our investigation will be presented.



References:

1. a) Su, Y. L.; Dong, K.; Zheng H.; Doyle, M. P. *Angew. Chem. Int. Ed.* **2021**, *60*, 18484-18488. b) Yang, Z.; Stivanin, M. L.; Jurberg, I. D.; Koenigs, R. M. *Chem. Soc. Rev.* **2020**, *49*, 6833-6847.
2. Rani, H.; Hussain, Y.; Chauhan. P. Manuscript under preparation.

Poster Presentation (P-22)

Grinding-Assisted Organocatalytic Asymmetric Synthesis Of Eight-Membered Carbocyclic Bridged Biaryls

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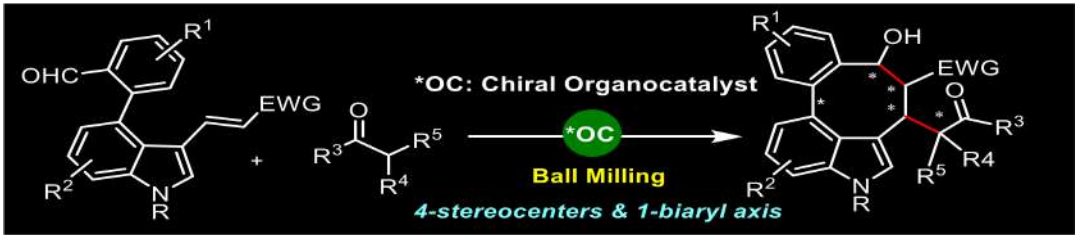
Abstract:

Despite the ubiquitous occurrence of medium-sized bridged-biaryl scaffolds in valuable natural products, bioactive compounds, chiral catalysts, and molecular motors, their asymmetric synthesis remained undeveloped.[1] Among medium-sized bridged biaryls, there are still some reports on enantioselective synthesis of sevenmembered ring systems[1,2] but the synthesis of related eight membered scaffolds did not receive much attention. However, the latter class of molecules are configurationally more stable due to the possible cage-like structure.[3] The higher configurational stability of eight membered ring systems enables them to be readily resolved as atropisomers. Acquainted with the importance of developing asymmetric methods for acquiring eight-membered biaryl-bridged skeletons, we developed a protocol to enantioselectively access these molecules *via* domino 1,4-/1,2-addition reaction by utilizing a much greener alternative *i.e.* grinding with ball-milling.[4] We have devised a new class of substrates having indole tethered biaryl moiety having acceptor sites on the aryl ring and C-3 position of indole. It was envisioned that despite offering higher mechanical energy, the selected nucleophile and substrate both get activated with a bifunctional hydrogen-bonding organocatalyst, to furnish the indole based eightmembered carbo-cyclic biaryl-bridged compounds bearing multiple chiral centers and a chiral axis in highly stereoselective manner. The findings of our research in this endeavour will be presented in detail.



References:

1. Kotwal, N.; Tamanna, Chauhan, P. *Chem. Commun.* **2022**, *58*, 11031-11044.
2. Kotwal, N.; Tamanna, Chauhan, P. *Org. Lett.* **2023**, *25*, 7523-7528.
3. Tabata, H.; Suzuki, H.; Akiba, K.; Takahashi, H.; Natsugari, H. *J. Org. Chem.* **2010**, *75*, 5984-5993.
4. Solaim, Kotwal, N.; Sinhmar. J.; Chauhan, P. *Manuscript under preparation.*

Poster Presentation (P-23)

The mechanochemical synthesis of environmentally benign fully biobased 4th generation benzoxazines and their polymers: mechanistic insights into the catalytic activity of latent catalysts

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Abstract:

Innovative sustainable techniques, like mechanochemical mixers, have transformed compound synthesis by significantly reducing time and improving yields. In this study, we synthesized a new series of 4^{th} generation benzoxazine (BZ) monomers using a straightforward, highly scalable, and efficient mechanochemical ball-milling process, proving superior to traditional methods. These advanced BZ monomers were composed entirely of bio-based synthons (vanillin, ortho-vanillin, and furfuryl amine) and were purified without complex separation processes. Our findings indicate that variations in aryl substitution (with and without phenolic–OH) at the oxazine C_2 center strongly influence the polymerization temperature, monomer volatility, polymerization kinetics, and thermal and mechanical properties. As anticipated, the control monomer lacking inherent phenolic–OH exhibited a high polymerization temperature, while the regioisomeric effects of vanillin facilitated polymerization with minimal volatile release. Both temperature-dependent NMR and SCXRD studies confirmed a latent catalytic effect within the monomer. Notably, a distal phenolic–OH was more labile, enabling polymerization at a lower temperature compared to its ortho-positioned counterpart. This configuration resulted in a welldefined polymer network with a notable glass transition temperature (T_g) of 116 °C, thermal stability (T_{max} of 348 °C), and a char yield of 36%. Additionally, it demonstrated excellent storage modulus and adhesive properties, surpassing many traditional petroleum-based polybenzoxazines. This work highlights the advantages of copolymerizing two generations of benzoxazines at lower temperatures, establishing these innovative BZ monomers as sustainable adhesives with enhanced stability, thereby broadening their potential for practical and innovative applications.

References:

1. Duhan, V.; Yadav, S.; Len, C.; Lochab, B. Green Chem. 2024.
2. Lochab, B.; Duhan, V.; Yadav, S.; Mukherjee, S. Adhesive Properties of Sustainable 4th Generation Benzoxazine, Indian Patent Application No.: 202311050482, dt. 7/26/2023.
3. Lochab, B.; Duhan, V.; Mukherjee, S. A Green Process for Synthesis of 4 th Generation Benzoxazine Monomers, Indian Patent Application No.: 202311028812, dt. April 20, 2023. **GRANTED**

Poster Presentation (P-24)

Early Detection of Type 2 Diabetes Using a Glyoxylate-Specific Fluorescent Probe

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Abstract:

Glyoxylic acid (GA) is a reactive carbonyl species (RCS) widely used in the cosmetic industry and generated through various glycolate enzymatic pathways. It has been identified as a metabolic biomarker for Type 2 diabetes (T2D), as its overproduction can upregulate oxalate levels, contributing to the onset of T2D and renal disorders.[1] Therefore, regular monitoring of GA is crucial for early diagnosis and disease management. Traditional diagnosis of Diabetes based on cost effective HPLC method that requires expert skills.[4]

In this study, we introduce a novel fluorescent probe based on N1-methylbenzene-1,2-diamine conjugated with a pentacyclic pyridinium fluorophore, specifically designed for the selective detection of GA. This is the first report of such a probe, offering a cost-effective and straightforward fluorescence-based detection method. The probe exhibits high selectivity for GA over other dicarbonyl species like methylglyoxal (MGO)[2,3] and glyoxal (GO) within a specific pH range and shows a sustained response to formaldehyde (FA).[5] This dual functionality enables the quantification of both GA and formaldehyde in biological samples, such as urine, thus demonstrating its potential for clinical diagnostics. Moreover, the probe's exceptional selectivity and ability to discriminate between structurally similar RCSs highlight its applicability in clinical and environmental monitoring.

References:

1. Nikiforova, V. J., Giesbertz, P., Wiemer, J., Bethan, B., Looser, R., Liebenberg, V.,Rein, D. *Journal of diabetes research*, **2014**, *1*, 685204.
2. Yang, M., Fan, J., Zhang, J., Du, J., & Peng, X. *Chemical science*, **2018**, *9*, 6758-6764..
3. Xie, Q., Zhan, Y., Guo, L., Hao, H., Shi, X., Yang, J.,Lin, Z. (2022).*ChemistryOpen*, **2022**, *11*, e202200055.
4. Abdulwahed, M., Mamoly, L., & Bosnali, W. *International Journal of Analytical Chemistry*, **2020**, 1, 5417549.
5. Jana, A., Joseph, M. M., Munan, S., Shamna, K., Maiti, K. K., & Samanta, A. *Journal of Photochemistry and Photobiology B: Biology*, **2021**, *214*, 112091.

Poster Presentation (P-25)

Blue LED Mediated Site Selective Amino-Oxidation Of Indoles *via* C(sp^2)-H Functionalization: C3-Oxo-C2-Amino Indoles As Fluorophores To Detect Lipid Droplets

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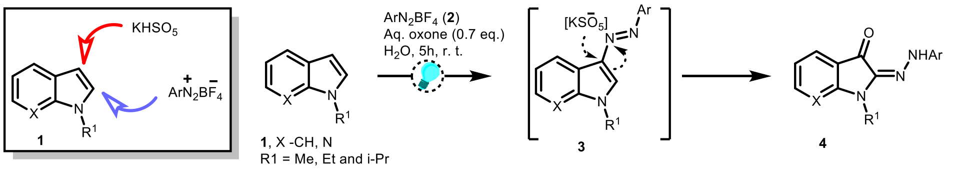
Abstract:

By virtue of their ubiquitous presence in natural products and pharmaceutical drug candidates, indoles are extremely crucial building blocks among the pharmaceutical scientists and medicinal chemists.[1] Hence, functionalization of indoles has garnered considerable attention. Among such indole derivatives, C-2 amino C-3 oxo indoles are niche compounds with myriad applications in the material, pharma and cosmetic industries.[2-4]

Here-in, we have reported a blue LED induced, oxone promoted (0.7 equiv.) cascade reaction sequence in water for a one pot oxidation and amination at C3 and C2 positions of indoles and azaindoles respectively with aryl diazonium salts at ambient temperature excellent yield. This novel reaction sequence demonstrated functional group tolerance and excellent regioselectivity. Control experiments, crystal structures, and computational studies based on density functional theory provided mechanistic insight which indicates formation of C3-diazenyl indoles as intermediates and subsequently oxone induced oxidation and migration of the diazinyl moieties from C3 to the C2 position of the indoles to provide the desired products. Experimental and theoretical photophysical studies and subsequent cellular uptake and colocalization experiments revealed that these compounds bind to lipid droplets and they could be used as fluoroprobes to detect lipid droplets.

Figure/Scheme:



- One pot oxidation-amination
- Aqueous reaction
- Metal free
- 38 examples
- Potential fluoroprobe to detect lipid droplets

References:

1. Wan, Y.; Li, Y.; Yan, C.; Yan, M.; Tang, Z. Indole: A privileged scaffold for the design of anti-cancer agents. *Eur. J. Med. Chem*., **2019**, *183,* 111691-111708.
2. Ishikura, M.; Abe, T.; Choshi, T.; Hibino, S. Simple indole alkaloids and those with a nonrearranged monoterpenoid unit. *Nat. Prod. Rep*. **2010**, *27,* 1630-1680.
3. Wibowo, J. T.; Ahmadi, P.; Rahmawati, S. I.; Bayu, A.; Putra, M. Y.; Kijjoa, A. Marine-Derived Indole Alkaloids and Their Biological and Pharmacological Activities. *Mar. Drugs,* **2022**, *20*, 3.
4. Chauhan, M.; Saxena, A.; Saha, B. An insight in anti-malarial potential of indole scaffold: A review. *Eur. J. Med. Chem*. **2021**, *218*, 113400-113412.

Poster Presentation (P-26)

Extracellular Vesicles: An Emerging Multifunctional Platform For Biomedical Applications

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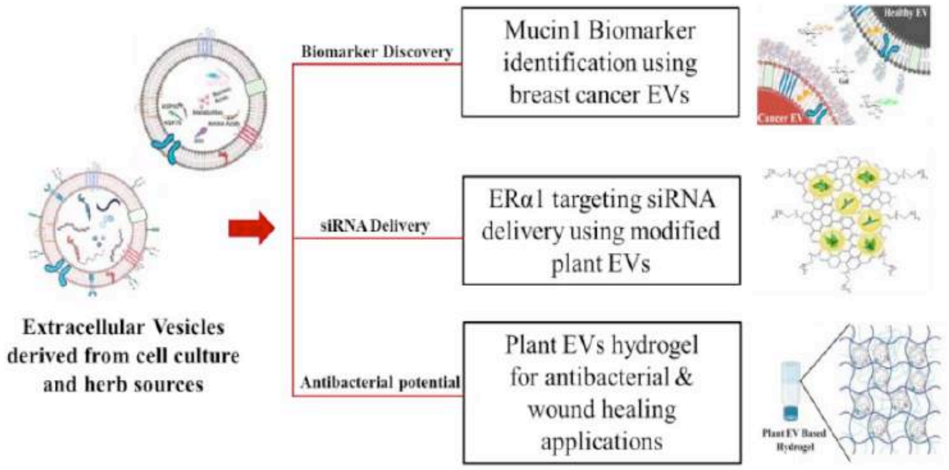
Abstract:
Extracellular vesicles (EVs) are lipid bilayer-enclosed structures produced by all types of cells. These nanoparticles hold great potential in different biomedical applications including biomarker elucidation, drug delivery, antibacterial assays etc. [1]. We studied breast cancer EVs to explore the aberrant glycosylation of Mucin1 protein, a critical breast cancer biomarker utilizing various biochemical and biophysical techniques [2]. Next, we engineered plant EVs with chitosan and PEGylated graphene oxide. We utilized them to deliver the ERalpha1 specific siRNA to breast cancer cells [3]. Recently, we formulated a mint-EV-hydrogel. We performed antibacterial assays against gram-positive and gram-negative bacteria. We utilized this EV-hydrogel formulation for antibacterial wound dressing in a rat model. [4].



References and Notes:

1. Kalluri, R.; LeBleu, V. S. *Science*, **2020**, *7*, 6478-6977.
2. Saroj, S.; Paul, D.; Ali, A.; Andreou, C.; Pal, S.; Rakshit, T. *ACS Applied Bio Materials*, **2023**, *6*, 4944-4951.
3. Saroj, S.; US, P.; Patil, S.; Paul. D.; Saha, S.; Ali, A.; Pal, S.; Lochab, B.; Rakshit, T. *ACS Applied Bio Materials*, **2024**, *7*, 2741-51.
4. Saroj, S.; Saha, S.; Ali, A.; Gupta, S. K.; Bharadwaj. A.; Agrawal, T.; Pal, S.; Rakshit , T. *ACS Applied Bio Materials*, **2024,** ASAP article (2024), DOI: 10.1021/acsabm.4c00992.

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