ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ISOFR 14 2026

The 14th International Symposium on Organic Free Radicals

Book of Abstracts

7–10 June 2026

BOLOGNA

Welcome

Benvenuti a Bologna,

*The 14th **I**nternational **S**ymposium on **O**rganic **F**ree **R**adicals* (**ISOFR-14**) will serve as a global forum for scientific exchange, bringing together experienced researchers, early-career scientists, and industrial chemists with a shared interest in radical reactivity. The program will feature two distinguished talks, five plenary lectures, 25 invited presentations, 14 contributed oral communications, and two poster sessions – all designed to foster discussion, inspire collaboration, and highlight cutting-edge research.

ISOFR was first launched in Italy in 1974; by hosting the 14th edition in Bologna, this international symposium returns to its roots, and will showcase the latest advances in the field of organic free radical chemistry.

We look forward to welcoming you to Bologna for four days of engaging science and meaningful connections across the radical chemistry community.

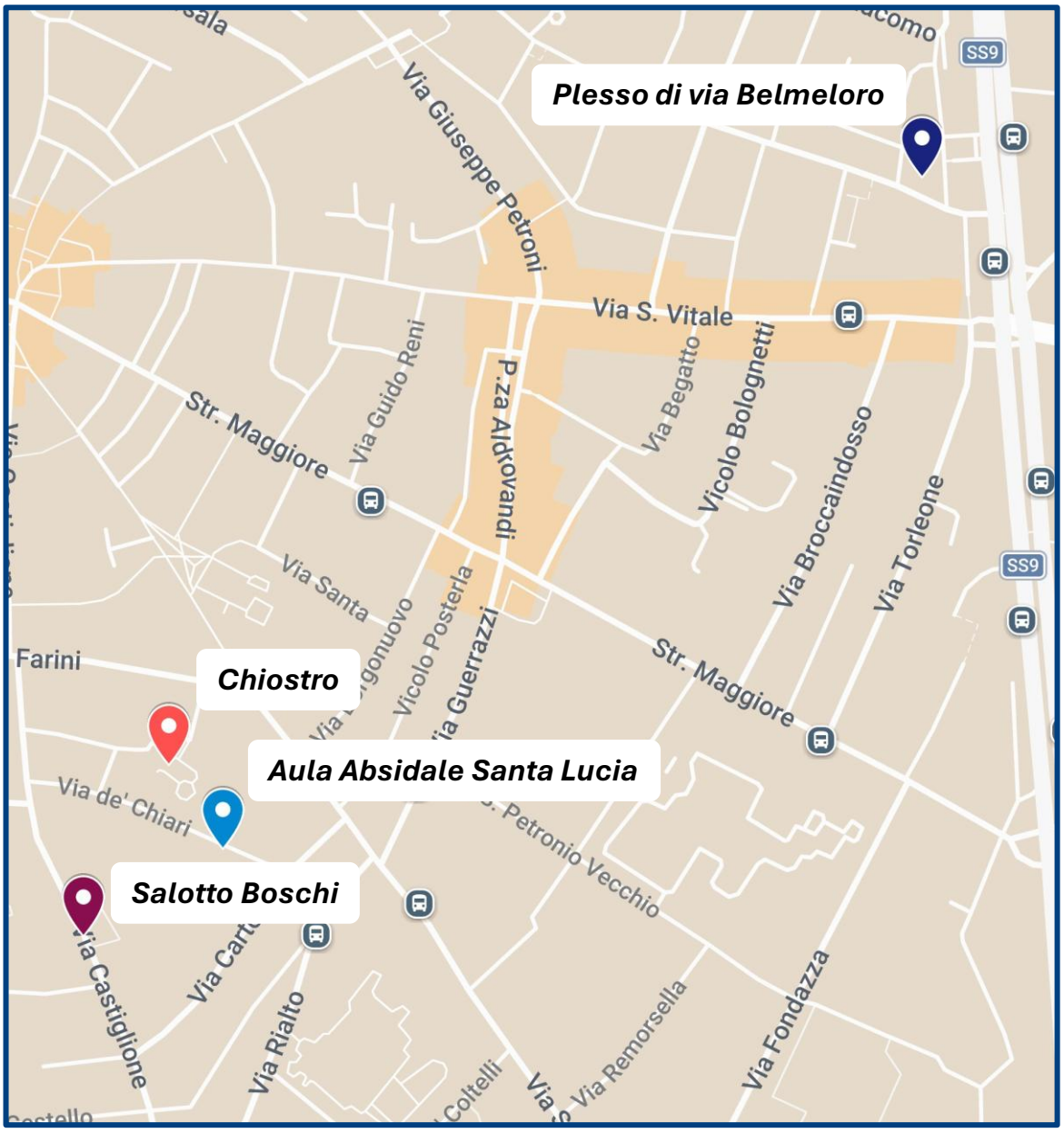
Prof. Paolo Melchiorre
Chair

Giorgio Bencivenni
Associate Professor at the University of Bologna
Industrial Chemistry Department '*Toso Montanari*'

Isabella Cioccolini
Research Manager
University of Bologna – Alma Mater Studiorum
Industrial Chemistry Department '*Toso Montanari*'

Paolo Melchiorre
Professor at the University of Bologna
Industrial Chemistry Department 'Toso Montanari'

Ciro Romano
Junior Assistant Professor
University of Bologna
Industrial Chemistry Department 'Toso Montanari'



We have created a Google Map of the venues, alongside some local landmarks, to help guide you. Please either click the QR code or visit the link below:

https://tinyurl.com/ISOFR14MAP

ISOFR 14 2026

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With 90 years of experience, Chiesi is headquartered in Parma (Italy), with 31 affiliates worldwide, and counts more than 7,900 employees. The Group's research and development centre in Parma works alongside 6 other important R&D hubs in France, the US, Canada, China, the UK, and Sweden.

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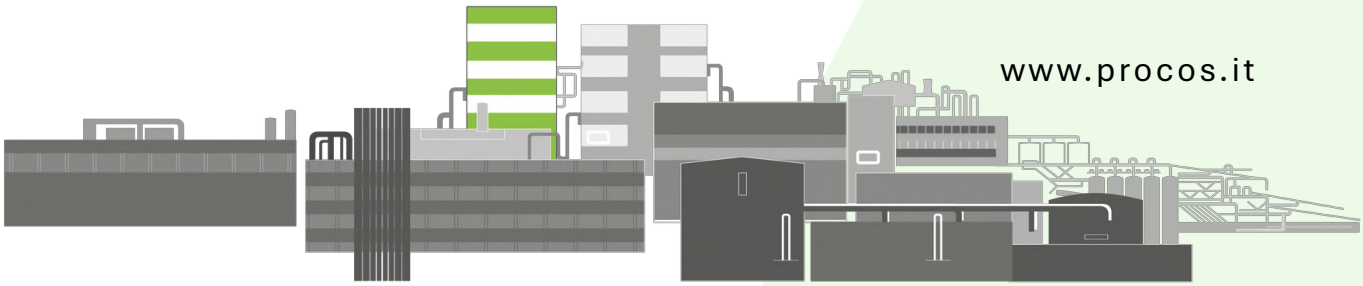

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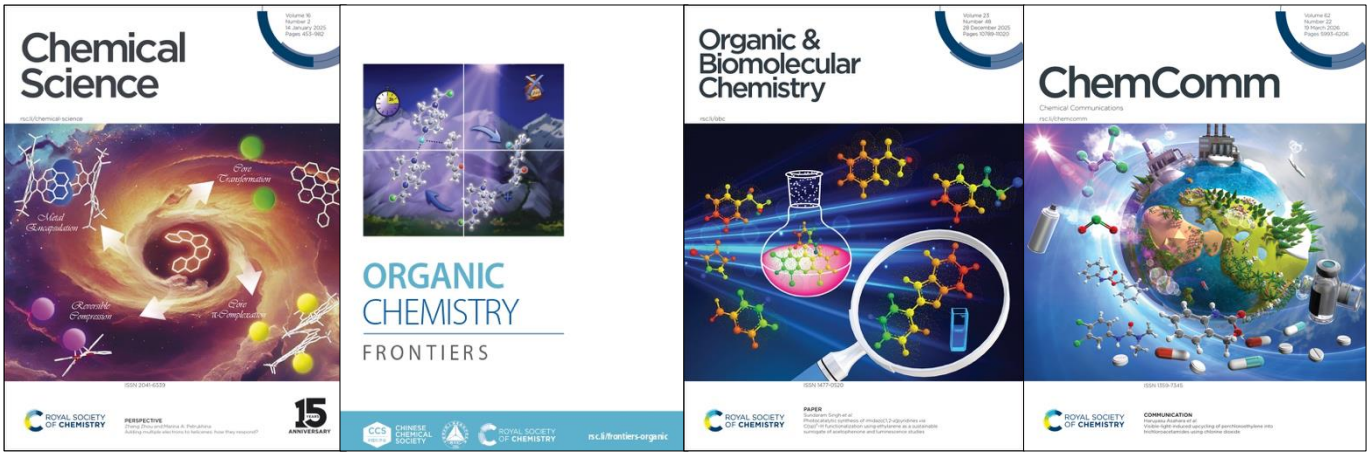

Chemical Science is our flagship general chemistry journal, publishing free-to-read research including the latest developments in organic and synthetic chemistry. *Organic Chemistry Frontiers* and *Organic & Biomolecular Chemistry* offer a venue for sharing your latest findings with researchers in the area of organic chemistry while *ChemComm* welcomes high impact, urgent Communication-format manuscripts.

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UNIVERSITÀ DI BOLOGNA
DEPARTMENT OF INDUSTRIAL CHEMISTRY
"TOSO MONTANARI"

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UNIVERSITÀ DI BOLOGNA
DEPARTMENT OF CHEMISTRY
"GIACOMO CIAMICIAN"

ISOFR 14 2026

Programme

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ISOFR 14 2026

June 7-10 2026
Bologna

XIV International Symposium of Free Radicals

SUNDAY, June 7th 2026 - Aula Absidale Santa Lucia

14.00 - 15.00 Registration

15.00 - 15.10 Opening

15.10 - 15.20 **Ned Porter** - ISOFR: Origins, Evolution, and Scientific Legacy

From Radical Foundations to Modern Reactivity Design

Session supported by Chiesi

Chairperson: Mukund Sibi

15.20 - 15.50 **Bernd Giese**
University of Fribourg, Switzerland
50 years of the Giese reaction (Distinguished speaker)

15.50 - 16.20 **Chrys Chatgilialoglu**
ISOF-CNR Bologna, Italy
Adam Mickiewicz University, Poznan, Poland
Fifty Years of Free Radicals: it's been an incredible journey (Distinguished speaker)

16.20 - 17.05 **PL 1**
Armido Studer
University of Münster, Germany
Regioselective Pyridine C-H Functionalization and Skeletal Editing

17.15 - 20.30 Welcome Cocktail & Dinner

MONDAY, June 8th 2026

Designing Radical Reactivity: Catalysis and Reaction Control

Session supported by Procos

Chairperson: Bartholomäus Pieber

09.00 - 09.45 **PL 2**
Abigail Doyle
University of California, Los Angeles
Phosphine and Photoredox Catalysis

09.45 - 10.10 **IL 1**
Luca Dell'Amico
University of Padova, Italy
Mechanistic investigations in light-driven synthetic chemistry: from direct photochemistry to organophotoredox catalysis

10.10 - 10.25 **OC 1 - Fabio Juliá**
Universidad de Murcia, Spain
Ferrioxalate Photocatalysis

10.25 - 10.40 **OC 2 - Giacomo E. M. Crisenza**
University of Manchester, UK
Electroreductive Strategies for the Ring-Opening of Heterocycles

10.40 - 11.05 **IL 2**
David Nicewicz
University of North Carolina Chapel Hill, USA
Excited State Acridyl Radical Chemistry

11.05 - 11.30 Coffee break

11.30 - 11.55 **IL 3**
Garret Miyake
Colorado State University, USA
ChemSocRev Pioneering Investigator Lectureship
Super-Reducing Organic Photoredox Catalysts

From Radical Reactivity to Complex Functional Systems and Materials

Session supported by Angewandte Chemie

Chairperson: Kirsten Zeitler

11.55 - 12.20 **IL 4**
Yang Yang
University of California Santa Barbara, USA
New Strategies for Stereoselective Radical Biocatalysis

12.20 - 12.35 **OC 3 - Christoph K. Winkler**
University of Graz, Austria
Radicals Under Enzymatic Control: The Photoenzyme CvFAP as a Platform for New-to-Nature Biocatalysis

12.35 - 13.00 **IL 5**
Athina Anastasakis
ETH Zurich, Switzerland
Monomers from Polymers: Reversing Radical Polymerization

13.00 - 14.00 Lunch and Posters 1

Modern Radical Methods in Synthesis and Industry

Session supported by Johnson & Johnson

Chairperson: Ciro Romano

14.00 - 14.25 **IL 6**
Giulia Bergonzini
AstraZeneca, Mölndal, Sweden
Chemistry at the Forefront: Technology-Enabled Drug Discovery

14.25 - 14.50 **IL 7**
Shunsuke Chiba
Nanyang Technological University, Singapore
Skeletal and peripheral remodeling of azaheteroarenes via SET-driven dearomatization

14.50 - 15.15 **IL 8**
Pier Giorgio Cozzi
Department of Chemistry 'Giacomo Ciamician', University of Bologna, Italy
Supramolecular Photoactive Titanium Complexes for HAT Reactions

15.15 - 15.30 **OC 4 - Dmytro M. Volochnyuk**
Enamine LTD, Kiev, Ukraine
Shono-type electrochemical synthesis of cyclic Encarbamates

15.30 - 15.55 Coffee break

15.55 - 16.20 **IL 9 - lecture supported by Thieme**
Xin-Yuan Liu
Department of Chemistry, Southern University of Science and Technology (SUSTech), Shenzhen, China
Cu/Chiral Anionic Ligand-Catalyzed Enantioselective Radical Reactions

16.20 - 17.05 **PL 3**
Christina White
University of Illinois, Urbana-Champaign, USA
Site-Selective C—H Oxidations

17.05 - 18.50 **Posters 1 and wine tasting/beers**

20.00 Speakers' dinner

TUESDAY, June 9th 2026

Decoding Radical Reactivity: Physical Organic, Theory and Excited-State Control

Session supported by RSC

Chairperson: Joshua Barham

09.00 - 09.45 **PL 4**
Daniele Leonori
RWTH Aachen University, Germany
Novel Synthetic Methods in Photochemistry and Photocatalysis

09.45 - 10.10 **IL 10**
Rob Paton
Colorado State University, USA
Computational Strategies for Predicting Triplet-State Reactivities and Selectivities

10.10 - 10.35 **IL 11**
Massimo Bietti
Università di Roma "Tor Vergata", Roma, Italy
Role of Structural and Medium Effects in Chemoselective HAT-based C(sp3)-H Bond Functionalizations

10.35 - 11.00 **IL 12**
Oliver Wenger
University of Basel, Switzerland
Organic Radical Reactivity in Photoredox Catalysis

11.00 - 11.30 Coffee break

11.30 - 11.45 **OC 5 - Paola Ceroni**
University of Bologna, Italy
Thermally Activated Delayed Fluorescence and photocatalysis: generation of radical anion from S1 and T1 excited states

Designing Radical Reactivity: From Methodology to Catalytic Strategy

Session supported by Linev System

Chairperson: Patricia Z. Musacchio

11.45 - 12.10 **IL 13**
Sungwoo Hong
Department of Chemistry, KAIST, Daejeon, Korea
A Photocatalytic Platform for Atom Transfer and Diversification via Reversible Triplet Activation of Pyridinium Ylides

12.10 - 12.25 **OC 6 - Daniele Mazzarella**
University of Rome Tor Vergata, Roma, Italy
Wired for Stereoselectivity: The Merger of Electrochemistry and Aminocatalysis for SOMO Applications

12.25 - 12.40 **OC 7 - Huan-Ming Huang**
ShanghaiTech University, China
Radical Based Divergent Synthesis

12.40 - 13.05 **IL 14**
Franziska Schoenebeck
RWTH Aachen University, Germany
Radically New Pathways in Metal Catalysis & Beyond

13.05 - 14.10 **Lunch and Posters 2**

Advanced Radical Methodology: Catalysis, Selectivity and Reaction Design

Session supported by Alfatech

Chairperson: Sara Cuadros

14.10 - 14.35 **IL 15**
David Nagib
The Ohio State University
Radical Polarity (2.0)

14.35 - 14.50 **OC 8 - Yoonsu Park**
KAIST, Daejeon, South Korea
Photocatalytic Furan-to-Pyrrole Conversion

14.50 - 15.05 **OC 9 - Dmitry Katayev**
University of Bern, Switzerland
Radical Ligand Transfer Catalysis for Molecular Design

15.05 - 15.30 **IL 16**
Kirsten Zeitler
Leipzig University, Germany
PCET beyond Simple pKa-Related Base Effects

16.00 Guided tours of Bologna

20.00 Gala Dinner (Salotto Boschi)

WEDNESDAY, June 10th 2026

Fundamental Radical Chemistry: Mechanism, Structure and Reactivity in Complex Environments

Session supported by BASF

Chairperson: Luca Valgimigli

09.00 - 09.45 **PL 5**
Takashi Ooi
Institute of Transformative Bio-Molecules (ITbM), Nagoya University, Japan
Development of Organic Radical Catalysts

09.45 - 10.10 **IL 17**
Olivier Ouari
Aix Marseille University / CNRS, Marseille, France
The Many Lives of Radicals: Powering Energy Storage and Transforming NMR Spectroscopy

10.10 - 10.35 **IL 18**
Derek Pratt
University of Ottawa, Canada
Suppressing Chain Reactions in Subcellular Spaces to Treat Disease

10.35 - 11.00 **IL 19**
Rebecca Melen
School of Chemistry, Cardiff University, UK
Single or Double? A Radical Approach to Frustrated Lewis Pairs

11.00 - 11.30 Coffee break

Translational Radical Chemistry: From Discovery to Application

Chairperson: Fabrice Dénès

11.30 - 11.45 **OC 10 - Patricia Z. Musacchio**
University of Buffalo, USA
A Redesigned Approach to Accessing Cationic Intermediates

11.45 - 12.00 **OC 11 - Joshua P. Barham**
University of Strathclyde, Glasgow, UK
Auto-Photoredox Catalysis

12.00 - 12.15 **OC 12 - Anastasios Polyzos**
University of Melbourne, Australia
The Photocatalytic Generation of Carbanion Equivalents

12.15 - 12.40 **IL 20**
Jesus Alcazar
Johnson & Johnson, Toledo, Spain
Applications of photochemistry to enable chemical space in Drug Discovery

12.40 - 13.05 **IL 21**
Cristina Nevado
University of Zurich, Switzerland
Asymmetric Remote Functionalization of Alkenes

13.05 - 14.00 **Lunch and Posters 2**

Radical Reactivity: Mechanism, Design and Molecular Complexity

Session supported by the Italian Chemical Society SCI

Chairperson: Giorgio Bencivenni

14.00 - 14.25 **IL 22**
David J. Procter
University of Manchester, UK
Sulfonium salts and light

14.25 - 14.50 **IL 23**
Sami Lakhdar
CNRS / Université de Toulouse, France
Mechanistically Guided Strategies for the Design and Synthesis of Organophosphorus Compounds

14.50 - 15.05 **OC 13 - John A. Murphy**
University of Strathclyde, Glasgow, Scotland
How KOtBu and Other Alkoxides Initiate Radical Reactions

15.05- 15.20 **OC 14 - Javier Mateos**
University of Vienna, Austria
Bench-stable Selenium Salts – From Stable Radicals to Red-Light Absorbing Photocatalysts

15.20 - 15.35 **OC 15 - Bartholomäus Pieber**
Institute of Science and Technology Austria, Vienna, Austria
Photoredox control of SN2 reactivity via synchronized nucleophile and electrophile generation

15.35 - 16.00 **IL 24**
Corey Stephenson
University of British Columbia, Vancouver, Canada
Radical Ideas: The Origins and Evolution of Visible-Light Photocatalysis

16.00 - 16.30 Closing remarks & poster prizes

ISOFR 14 2026

Distinguished Speakers

Bernd Giese

Professor of Chemistry
Guest Professor of Chemistry at the University of Fribourg, Switzerland
E-mail: bernd.giese@unifr.ch

Academic Positions & Education

Since 2011	Guest Professor, University of Fribourg (Switzerland)
1989-2010	Professor, University of Basel (Switzerland)
1978-1988	Professor, Technical University of Darmstadt (Germany)
1972-1978	Habilitation, Universities of Münster and Freiburg (Germany)
1969-1971	Research Chemist at the BASF, Ludwigshafen (Germany)
1965-1969	MSc and PhD at the University of Munich (Germany)
1959-1964	Studies at the Universities of Heidelberg and Hamburg (Germany)

Research Interests.
How chemistry fulfills the needs of biology; redox reactions in microorganisms; electron transfer through DNA, peptides and living cells; physical, synthetic and biochemical radical chemistry; stereochemistry; photochemistry; carbene chemistry; nanoparticles; total synthesis, enthalpy-entropy compensation.

Honors & Awards
Karl-Winnacker Award (1976), Carl-Duisberg Award (1977), Gottfried Wilhelm Leibniz Prize (1987), Merck-Schuchardt Award (1988), Member of the German Academy of Sciences, Leopoldina (1999), Foreign Honorary Member of the American Academy of Arts and Sciences (2003) Tetrahedron Prize for Creativity in Organic Chemistry & Bio-Medicinal Chemistry (2005), Emil Fischer Medal of the Gesellschaft Deutscher Chemiker (2006), Norris Award in Physical Organic Chemistry of the American Chemical Society (2009), Paracelsus Prize of the Swiss Chemical Society (2012)

Selected Publications

1. Spichty, M.; Zipse, H.; Majouri, M.; Fromm, K. M.; Giese, B, 50 Years of Giese Reaction – a Personal View, *Angew. Chem. Int. Ed*. **2026,** e24825.
2. Kharamash, M.; Stumpe, M.; Dengjel, J.; Salgueiro, C. A.; Giese, B.; Fromm, K. M., Fe^{2+}/Hemes Regulate Electron Flux in *Geobacter sulfurreducens*, *Front. Microbiol*. **2022**,13:90919.
3. Kracht, S.; Messerer, M.; Lang, M.; Eckhardt, S.; Lauz, M.; Groberty, M.; Fromm, K. M.; Giese, B. On the Formation of Silver Nanoparticles: Electron Transfer in Peptides, Angew. Chem. Int. Ed. **2015**, 54, 2912.
4. Giese, B.; Amaudrut, Köhler, A. K.; Spormann, M.; Wessely, S., Direct observation of hole transfer through DNA by hopping between adenine bases and tunneling, *Nature* **2001**, 412, 318
5. Giese, B.; Wettstein, P.; Stähelin, C.; Barbosa, F.; Neuburger, M.; Zehnder, M.; Wessig, P., Memory of Chirality in Photochemistry, *Angew. Chem. Int. Ed*. **1999**, 38, 2586.
6. Meggers, E.; Michel-Beyerle, M. E.; Giese, B., Hole Transport in DNA, *J. Am. Chem. Soc*. **1998**, 120, 12950.
7. Lenz, R.; Giese, B., Mechanism of Ribonucleotide Reductase, *J. Am. Chem. Soc*. **1997**, 119, 2784.
8. Curran, D. P.; Porter, N. A.; Giese, B., Stereochemistry of Radical Reactions, VCH, Weinheim **1996**.
9. Abel, S.; Faber, D.; Hüter, O.; Giese, B., Total Synthesis of Soraphen, *Angew. Chem. Int. Ed*. **1994**, 33, 2466.
10. Giese, B., Radicals in Organic Synthesis, Pergamon Press, Oxford, **1986.**
11. Giese, B., The Isoselective Relationship, *Acc. Chem. Res*. **1984**, 17, 438.
12. Giese, B., Formation of CC-Bonds by Addition of Radicals to Alkenes, *Angew. Chem. Int. Ed*. **1983**, 22, 753.
13. Giese, B.; Meister, J., Addition of Alkanes to Olefins, *Chem. Ber.* **1977**, 110, 2588.
14. Giese, B., Temperature Dependence of the Selectivity of Radicals, *Angew. Chem.int. Ed*. **1976**, 15, 173.

14th International Symposium on Organic Free Radicals (ISOFR-14)
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50 Years of the Giese-Reaction

Bernd Giese

Department of Chemistry, University of Fribourg (Switzerland)
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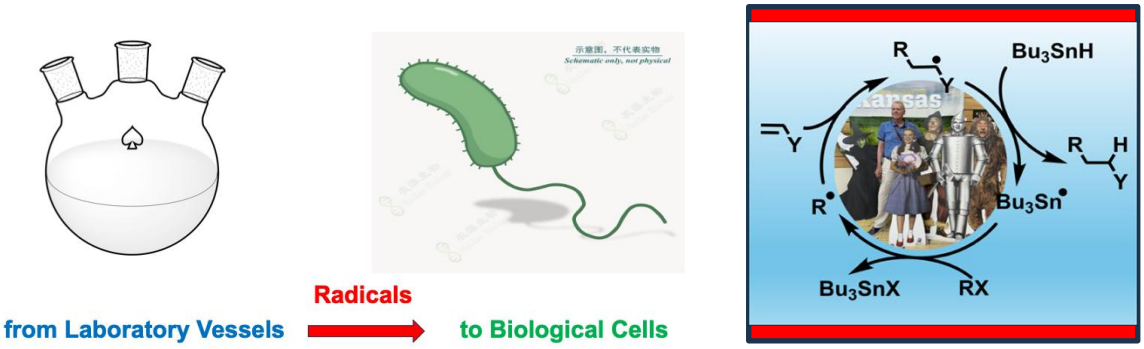
Keywords: Three component syntheses ● long-distance ET ● chemical lab versus biological cell reactions



50 years ago, we discovered a synthetic method in which alkyl radical precursors, alkenes and hydrogen atom donors selectively yield 1:1:1-addition products in a cyclic radical chain reaction. This paved the way for many superb three-component syntheses with C,C-bond formation as the central step. For successful syntheses the different chain carrying radicals have to follow reactivity and selectivity rules. This requires knowledge of the substituent influence on rates as well as on substrate-, regio- and stereoselectivity. Their rules were experimentally elucidated, and the synthetic method was coined “Giese- Reaction”. 20 years after its discovery in the chemical laboratory, biologists observed that microorganisms use a similar synthetic strategy, which triggered our studies of living cells. Although inherent chemical rules in laboratory vessels and biological cells are the same, the different set-ups lead to very different features. Syntheses between mobile educts in homogeneous solution of a laboratory vessel is driven by kinetic effects: a successful synthesis solves a kinetic problem. In contrast, most reactions in biological cells, which occur at protein/water interfaces, are driven by thermodynamic effects: interactions between enzymatic amino acids and educts immobilize the reactants and place them in close contact to each other. This paves the way for product formation, and both reactivity as well as selectivity conditions are switched off. In addition, biochemical radical and redox processes often start with metallo-cofactors that are far away from the interface where the synthetic reactions occur, and electron transfer through the enzyme (protein) generates the reactive intermediates at the interface. Such long-distance ET occurs in a hopping mechanism, which uses aromatic and sulfur-containing amino acids as well as metal complexes as stepping stones.[1]

Reference

[1] Spichty, M.; Zipse, H.; Majouri, S., Fromm, K. M.; Giese, B. *Angew. Chem. Int. Ed*. **2026,** e24825.

Chryssostomos Chatgilialoglu

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Homepage: https://chatgilialoglu-group.com
Wikipedia: https://en.wikipedia.org/wiki/Chryssostomos_Chatgilialoglu

Career

Since 2019	Visiting Professor, Adam Mickiewicz University, Poznań (Poland)
2020-2024	Senior Research Associate at ISOF-CNR, Bologna (Italy)
2016-2019	Research Director at ISOF-CNR, Bologna (Italy)
2014-2016	Director of INN at NCSR “Demokritos”, Athens (Greece)
1991-2014	Research Director at ISOF-CNR, Bologna (Italy)
1983-1991	Researcher at ICoCEA-CNR, Bologna (Italy)
1980-1982	Research Associate at NRCC, Ottawa (Canada)
1977-1979	Postdoctoral Fellow at York University (United Kingdom)

Research Interests
Radical chemistry and biology, reaction mechanism, kinetics, silicon-centered radicals, sulfur-centered radicals, oxidative stress, reactive oxygen species, biomimetic models, ionizing radiation, hydroxyl radical, DNA damage and repair, and trans-lipids

Selected Honors & Awards
Director, NATO Advanced Study Institute on *Sulfur-Centered Reactive Intermediates in Chemistry and Biology* (1989); Fluka Prize: Reagent of the Year (1990); NATO Senior Fellowship (1991); Director, NATO Advanced Study Institute on *Chemical Synthesis: Gnosis to Prognosis* (May 1994); Chair, COST Action CM0603: *Free Radical in Chemical Biology* (2007–2011); The Cheves Walling Lecture (2009); Chairman, EUCHEM Conference on *Organic Free Radicals* (2010); Chair, COST Action CM01201: *Biomimetic Radical Chemistry* (2012–2016). IOCF Yoshida Lectureship, Kyoto/Osaka (2017). Maria Skłodowska-Curie Medal, Kraków (2025).
Visiting Scientist/Professor at NRCC Ottawa (1986), University of Basel (1990), University of Melbourne (1999), Université Pierre et Marie Curie (2000), Ludwig-Maximilians-Universität München (2008), Université Pierre et Marie Curie (2009), Adam Mickiewicz University (2019). Co-Founder and President of the spin-off company Lipinutragen (2005-2023).

Publications in Chemical Reviews

1. Chatgilialoglu, C. Structural and chemical properties of silyl radicals. *Chem. Rev.* **1995** *95*, 1229.
2. Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. Chemistry of acyl radicals. *Chem. Rev.* **1999***, 99*, 1991.
3. Chatgilialoglu, C.; Ferreri, C.; Melchiorre, M.; Sansone, A.; Torreggiani, A. Lipid geometrical isomerism: from chemistry to biology and diagnostics. *Chem. Rev.* **2014**, *114*, 255.
4. Chatgilialoglu, C.; Ferreri, C.; Landais, Y.; Timokhin, V.I. Thirty years of $(TMS)_3SiH$: a milestone in radical-ba sed synthetic chemistry. *Chem. Rev.* **2018**, *118*, 6516.

Fifty Years of Free Radicals: *It's been an incredible journey*

Chryssostomos Chatgilialoglu[a,b]

[a] *Center for Advanced Technologies, Adam Mickiewicz University, 61-614 Poznań, Poland*
[b] *Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, 40129 Bologna, Italy*
chachr@amu.edu.pl or chrys@isof.cnr.it

Keywords: free radical ● silane ● thiol ● DNA damage ● trans lipid

This retrospective provides a comprehensive overview of a five-decade research journey at the forefront of free radical chemistry.

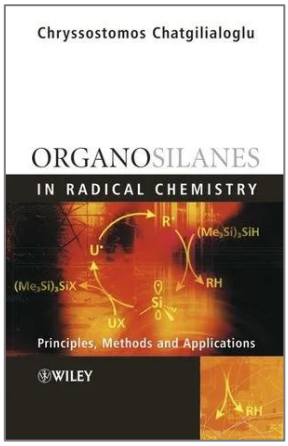
Our early work redefined the role of Group 14 elements—specifically silyl radicals—leading to the discovery of transformative reagents for synthetic organic chemistry and the development of innovative materials.

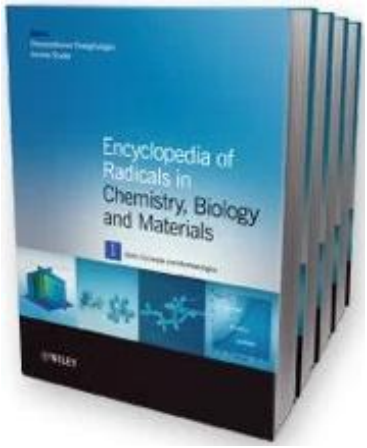
Transitioning from pure synthesis to the biological frontier, we pioneered biomimetic radical chemistry to decode radical behavior within the complex aqueous and lipid environments of living cells. A cornerstone of this research is the discovery of radical-based *cis-trans* isomerization in phospholipids, a mechanism that effectively bridges fundamental chemical kinetics with clinical diagnostics.

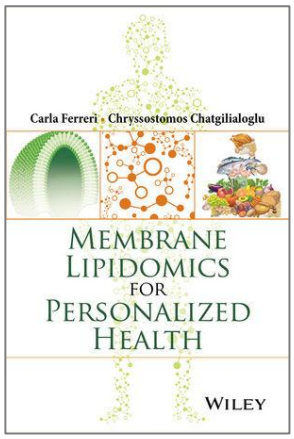
By leveraging ionizing radiation as a tool for fundamental discovery, we identified specific chemical signatures of oxidative stress and established robust analytical protocols for damage assessment. Notable breakthroughs include the characterization of unique DNA lesions, such as 5',8-cyclopurines, and the elucidation of sulfur-centered radical chemistry in peptide and protein modifications.

Collectively, these contributions underscore the indispensable role of free radicals as a multidisciplinary bridge linking Chemistry, Biology, and Medicine.

Selected Books







Plenary Speakers

Armido Studer

Professor of Chemistry
University of Münster, Germany
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Academic Positions & Education

Since 2009	Full professor (W3) of Organic Chemistry at the University of Münster.
2004-2009	Full professor (C4) of Organic Chemistry at the University of Münster.
2000-2004	Associate Professor (C3) at the Philipps-University Marburg, Germany.
2000	Habilitation at ETH Zurich, Switzerland.
1996-2000	Independent researcher at the ETH Zurich.
1995-1996	Postdoctoral fellow, University of Pittsburgh (Dennis P. Curran), USA.
1991-1995	PhD work at ETH in Zurich (Dieter Seebach), Switzerland,
1987-1991	Study of chemistry at the ETH in Zurich, Switzerland.

Research Interests

Methods development, asymmetric catalysis, photochemistry, radical chemistry, polymer chemistry, and on-surface chemistry.

Honors & Awards

Steinhofer Lecturer, University of Freiburg (2005), *Novartis Young Investigator Award* (2006), *Solvias Ligand Contest Award* (2007), *RSC/GE Healthcare Lecture*, Cardiff (2008), *Guest Professorship,* Pierre et Marie Curie University (2008), *Guest Professorship,* University of Bordeaux (2009), *Scientific Guest, CNR Bologna* (2010), *Spokesman SFB 858* (2010-2022), *IOCF Yoshida Lectureship*, Kyoto (2014), *Research Award,* University of Münster (2014), *ERC Advanced Grant* (2016), *Highly Cited Researcher* (Clarivate 2017-2022), *Jiaxi Lu Overseas Guest Professor*, CAS, Fuzhou (2018), *Elected member,* North Rhine-Westphalian Academy of Sciences, Humanities and the Arts (2018), *Fellow,* Royal Society of Chemistry (2019), *Pedler Award,* Royal Society of Chemistry (2019), *Elected member,* German National Academy of Sciences “Leopoldina” (2020), *Guest Professorship,* University of Sassari (2021), *Elected member,* Academia Europaea (2021), *Spokesman IRTG 2678* (since 2021), *Elected member,* European Academy of Sciences (2024), *Arthur C. Cope Late Career Scholars Award*, ACS (2024), *Paracelsus Prize*, Swiss Chemical Society (2024), *Tarrant Distinguished Visiting Professorship*, University of Florida (2024), *ERC Advanced Grant* (2024), *Adolf-von-Baeyer-Denkmünze*, GDCh (2025), *Gottfried Wilhelm Leibniz-Prize*, DFG (2026).

Selected Publications

1. Studer, A.; Curran, D.P. Catalysis of Radical Reactions: A Radical Chemistry Perspective, *Angew. Chem. Int. Ed*. **2016**, *55*, 58-102.
2. Cao, H.; Cheng, Q.; Studer, A. Radical and ionic meta-C–H functionalization of pyridines, quinolines, and isoquinolines, *Science* **2022**, *378*, 779-785.
3. Zhang, J.; Mück-Lichtenfeld, C.; Studer, A. Photocatalytic phosphine-mediated water activation for radical hydrogenation, *Nature* **2023**, *619*, 506-513.
4. Wang, Z.; Xu, P.; Guo, S.-M.; Daniliuc, C.G.; Studer, A. C-to-N atom swapping and skeletal editing in indoles and benzofurans, *Nature* **2025**, *642*, 92-98.

Regioselective Pyridine C-H Functionalization and Skeletal Editing

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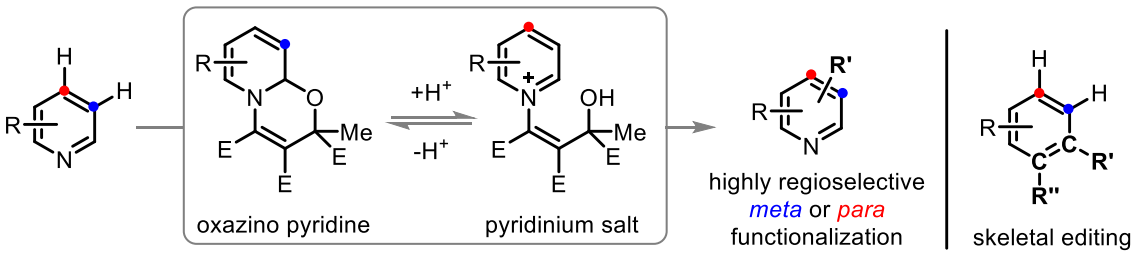
Keywords: radicals ● pyridines ● late stage functionalization ● skeletal editing ● azaarenes

Pyridines belong to the most abundant heteroarenes in medicinal chemistry and in agrochemical industry. In the lecture, highly regioselective pyridine C-H functionalization through a dearomatization/rearomatization sequence will be discussed. The dearomatized oxazino pyridines can be easily prepared on a large scale, and meta-functionalization becomes achievable through light-initiated radical alkylation and ionic transformations.[1] As example, using such an approach meta-fluorinated pyridines are readily accessible.[2] The same intermediates upon protonation to give the corresponding pyridinium salts also allow the highly regioselective radical *Minisci* para-alkylation.[3,4] In addition, Cu-catalyzed meta-arylation[5] and switchable radical para/meta-difluoromethylation[6] through such intermediates will be presented. Radical *meta*-nitration[7] and ionic *meta*-hydroxylation[8] work equally well through such intermediates. Finally, it will be shown that this dearomatization concept is also applicable to pyridine skeletal editing.[9] Further, it will be discussed that an alternative radical dearomatization process can be used for C to N mutation in indoles and benzofurans.[10]



Acknowledgements
This work was financially supported by the Deutsche Forschungsgemeinschaft and the Alexander von Humboldt Foundation.

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[2] Haring, M.; Balanna, K.; Cheng, Q.; Lammert, J.; Studer, A. *J. Am. Chem. Soc.* **2024**, *146*, 30758.
[3] Cao, H.; Bhattacharya, D.; Cheng, Q., Studer, A. *J. Am. Chem. Soc.* **2023**, *145*, 15581.
[4] Wang, Z.; Xu, P.; Studer, A. *Org. Chem. Front.* **2024**, *11*, 3849.
[5] Guo, S.-M.; Xu, P.; Studer, A. *Angew. Chem. Int. Ed*. **2024**, *63*, e202405385.
[6] Xu, P.; Wang, Z.; Guo, S.-M.; Studer, A. *Nat. Commun.* **2024**, *15*, 4121.
[7] Balanna, K.; Studer, A. *J. Am. Chem. Soc.* **2025**, *147*, 7485.
[8] Bhattacharya, D.; Studer, A. *Angew. Chem. Int. Ed.* **2025**, *64*, e202423512.
[9] Cheng, Q.; Bhattacharya, D.; Haring, M.; Cao, H.; Mück-Lichtenfeld, C.; Studer, A. *Nat. Chem.* **2024**, *16*, 741.
[10] Wang, Z.; Xu, P.; Guo, S.-M.; Daniliuc, C. G.; Studer, A. *Nature* **2025**, *642*, 92.

Abigail Doyle

Saul Winstein Chair in Organic Chemistry
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Academic Positions & Education

Since 2021	Saul Winstein Chair in Organic Chemistry, UCLA
2017-2021	A. Barton Hepburn Professor, Princeton University
2008-2017	Assistant, Associate, & Professor, Princeton University
2003-2008	NSF Graduate Fellow, Harvard University, Ph.D.
2002-2003	Graduate Student, Stanford University
1998-2002	Chemistry and Chemical Biology, Harvard University, A.B. & A.M.

Research Interests

The Doyle lab conducts research at the interface of organic, organometallic, and physical organic chemistry, enhanced by the use of modern data science and machine learning tools. Our goal is to address unsolved problems in organic synthesis through the development of novel catalysts, catalytic reactions, and synthetic methods. We implement mechanistic and computer-assisted techniques to uncover general chemical principles, predict unseen reactivity, and discover new reactions.

Honors & Awards

Cell Press 50 Scientists that Inspire (2024); OMCOS award (2023); Finalist of the 2022 Blavatnik National Awards for Young Scientists; Friedrich Wilhelm Bessel Research Award (2022); EJ Corey Award for Outstanding Original Contribution in Organic Synthesis by a Young Investigator (2022); The Camille and Henry Dreyfus Foundation Machine Learning in the Chemical Sciences and Engineering Award (2021); American Chemical Society Fellow (2020); RSC Fluorine Award (2019); 15th Hirata Prize (2019); BMS Unrestricted Grant in Synthetic Organic Chemistry (2016)

Selected Publications

1. Fan, F.; Sedillo, K. F.; Maertens, A. J.; Doyle, A. G. **"Markovnikov hydroamination of terminal alkenes via phosphine redox catalysis"** *Nature*, **2026**, *652*, 96–104.

2. Gallarati, S.; Bucci, E. M.; Doyle, A. G.; Sigman, M. S. **"Transferable enantioselectivity models from sparse data"** *Nature*, **2026**, *651*, 637-646.

3. Raab, T. Judah.; Doyle, A. G. **"Reactivity Studies of Bipyridine-Ligated Nickel(I) and Nickel(0) Complexes Inform the Mechanism in Modern Cross-Coupling Reactions"** *J. Am. Chem. Soc.*, **2025**, *147*, 33991.

4. Ruos, M.; Romer, N.; Deichert, J.; Alabanza, L. M.; Gandhi, S.; Brown, G.; Walroth, R.; Cruz, K.; Gosselink F.; Hong, A.; Sigman, M. S.; Doyle, A. G., **"Data Science-Guided Development of Deoxyfluorination Reagents with Enhanced Reactivity, Practicality, and Safety."** *J. Am. Chem. Soc.* **2025**, *147*, 25815.

Phosphine and Photoredox Catalysis

Abigail G. Doyle[a]

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Keywords: photoredox catalysis ● phosphines ● physical organic chemistry ● synthetic methodology development

Phosphines serve foundational and diverse roles in organic synthesis, ranging from stoichiometric reagents and versatile ligands to powerful main group catalysts. Our group has focused on expanding the utility of phosphorus beyond its traditional closed-shell reactivity by investigating the chemistry of odd-electron phosphorus species known as phosphoranyl radicals. We envisioned that these high-energy intermediates could be accessed under mild conditions by merging phosphines with visible-light photoredox catalysis in the presence of a nucleophile. This talk will describe our exploration of the synthetic opportunities afforded by these intermediates to promote a variety of transformations, including catalytic deoxygenation and hydroamination reactions. By leveraging phosphorus as a redox mediator, we have developed methods that facilitate challenging bond-forming events from simple and abundant precursors. Furthermore, we will discuss our detailed mechanistic studies directed at understanding the structure-reactivity relationships that govern these systems. Through a combination of experimental and computational analysis, we have elucidated how the phosphine structure and reaction parameters dictate reactivity and selectivity. Ultimately, these findings provide a predictive framework for the continued development of phosphorus-mediated radical catalysis in modern synthetic chemistry.

Acknowledgements
This work was financially supported by National Institute of Health, NIGMS R35 GM126986

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[1] (a) Fan, F.; Sedillo, K. F.; Maertens, A. J.; Doyle, A. G. **"Markovnikov hydroamination of terminal alkenes via phosphine redox catalysis"** *Nature*, **2026**, *652*, 96–104. (b) Sedillo, K.; Fan, F.; Knowles, R. R.; Doyle, A. G. **Cooperative Phosphine-Photoredox Catalysis Enables N–H Activation of Azoles for Intermolecular Olefin Hydroamination**. *J. Am. Chem. Soc.* **2024**, *146*, 20349. (c) Chinn, A. J.; Sedillo, K.; Doyle, A. G. **Phosphine/Photoredox Catalyzed anti-Markovnikov Hydroamination of Olefins with Primary Sulfonamides via a-Scission from Phosphoranyl Radicals.** *J. Am. Chem. Soc.* **2021**, *143*, 18331–18338. (d) Stache, E. E.; Ertel, A. B.; Rovis, T.; Doyle, A. G. **C–O Generation of Phosphoranyl Radicals via Photoredox Catalysis Enables Voltage-Independent Activation of Strong C–O Bonds**. *ACS Catalysis* **2018**, *8*, 11134–11139.

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Academic Positions & Education

Since 2011	Professor of Chemistry, University of Illinois
2009-2011	Associate Professor of Chemistry, University of Illinois
2005-2008	Assistant Professor of Chemistry, University of Illinois
2002-2005	Assistant Professor, Harvard University
1999-2002	NIH Postdoctoral Fellow, Harvard University
1993-1998	PhD, Johns Hopkins University (Prof. Gary H. Posner)

Research Interests

C-H oxidation and amination, catalyst design, late-stage functionalisation

Honors & Awards

Herbert C. Brown Award (2026), ACS Award (2019), Mitsui Catalysis Award (2019), Mukaiyama Award (2016), Fellow of the Royal Society of Chemistry (2014), RSC Merck Award (2013), Fellow of AAAS (2012), Cope Scholar Award (2009), Camille Dreyfus Teacher-Scholar Award (2008), Alfred P. Sloan Research Fellow (2008).

Selected Publications

1. Chen, M.S.; White, M.C., A Predictably Selective Aliphatic C—H Oxidation Reaction for Complex Molecule Synthesis., *Science*, **2007**, *318*, 783-787.
2. Chen, M.S.; White, M.C., Combined Effects on Selectivity in Fe-Catalyzed Methylene Oxidation., *Science* **2010**, *327*, 566
3. Clark, J.R.; Feng, K.; Sookezian, A.; White, M.C., Manganese-Catalyzed Benzylic C(sp3)—H Amination for Late-Stage Functionalization., *Nature Chemistry* **2018**, *10*, 583.
4. Feng, K.; Quevedo, R.E.; Kohrt, J.T.; Oderinde, M. S.; Reilly, U.; White, M.C., Late-Stage Oxidative C(sp3)-H Methylation, *Nature* **2020**, *580*, 621-627.
5. Ali, S.Z.; Budaitis, B.G.; Fontaine, D.F.A.; Pace, A.L.; Garwin, J.A.; White, M.C., Allylic C—H Amination Cross-Coupling Furnishes Tertiary Amines by Electrophilic Metal Catalysis., *Science* **2022**, *376*, 276.
6. Kaster, S.H.M.; Zhu, L.; Lyon, W. L.; Ma, R. Amman, S.E.; White, M.C., Cross-coupling of alcohols with olefins via positional tuning of a counteranion in transition metal catalysis, *Science*, **2024**, *385*, 1067.
7. Ahn, C.; Gomez, A.; Hartmann, M. A.; White, M.C., Selective methylene oxidation in a,b-unsaturated carbonyl natural products, *Nature*, **2025**, *648,* 607.

14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Site-Selective C—H Oxidations

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Academic Positions & Education

Since 2022	W3 Chair in Organic Chemistry, RWTH Aachen University (Germany)
2020-2022	Professor of Organic Chemistry, University of Manchester (UK)
2018-2020	Reader in Organic Chemistry, University of Manchester (UK)
2017-2018	EPSRC Early Career Fellow, University of Manchester (UK)
2014-2017	Lecturer of Organic Chemistry, University of Manchester (UK)
2012-2014	Research Officer, University of Bristol (UK) under the supervision of Prof. Varinder K. Aggarwal FRS
2011-2012	Postdoctoral Research Associate, Max Planck Institute under the supervision of Prof Peter H. Seeberger
2010-2011	Postdoctoral Research Associate, RWTH-Aachen University (Germany)under the supervision of Prof. Magnus Rueping
2007-2010	PhD, University of Sheffield (UK) under the supervision of Prof. Iain Coldham

Research Interests

Synthetic organic chemistry, catalysis, photochemistry, radical chemistry.

Honors & Awards

ERC Consolidator Grant (2024); ERC Proof-of-Concept (2024); Organic Letter Oustanding Publication Award (2023); EuChemS Division of Organic Chemistry Young Investigator Award (2021); Philip Leverhulme Prize (2019); AstraZeneca Award for Outstanding Achievements in Organic Synthesis (2019); RSC Harrison-Meldola Memorial Prize (2018); ERC Starting Grant (2018); Thieme Chemistry Journal Award (2017); EPSRC Early Career Fellowship (2017).

Selected Publications

1. J. Mancini, C. Stavagna, F. Pileri, G. Lonardi, E. M. Arpa, M. Galeotti, S. Sisti, F. Julia, M. Salamone,* D. Leonori,* and M. Bietti* “Importance of Polar Effects in Halogen Atom Transfer from Alkyl Iodides to α-Aminoalkyl Radicals. A Kinetic and Computational Evaluation of the Role of Structural and Medium Effects” *JACS Au* **2026**, *6*, 103.
2. Z. Zhang, G. Lonardi, T. Sephton, Y. C. Guersoy, C. Stavagna, G. V. A. Lenardon, M. Bietti, and D. Leonori* “Deaminative Cross-Coupling of Amines by Boryl Radical β-Scission” *Nature* **2025**, *647*, 913.
3. W. J. Olivier, P. T. Blyszczyk, E. M. Arpa, K. Hitoshio, M. Gomez-Mendoza, V. De la Peña O'Shea, I. Marchand, T. Poisson, A. Ruffoni,* and D. Leonori* “Excited-State Configuration of Nitroarenes Enables Oxidative Cleavage of Aromatics over Alkenes” *Science* **2025**, *387*, 1167.
4. B. Roure, M. Alonso, G. Lonardi, D. Berna Yildiz, C. S. Buettner, T. dos Santos, Y. Xu, M. Bossart, V. Derdau, M. Méndez, J. Llaveria, A. Ruffoni* and D. Leonori* “Photochemical Permutation of Thiazoles, Isothiazoles and Other Azoles” *Nature* **2025**, *637*, 860.

Novel Synthetic Methods Using Photochemistry and Photocatalysis

Daniele Leonori[a]

[a] *Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, Aachen, Germany*
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Keywords: photochemistry ● photocatalysis ● boryl radicals ● radical functionalization

Aromatic compounds are among the most important structural motifs in high-value materials, including pharmaceuticals, agrochemicals, and functional materials. Their synthesis traditionally relies on the stepwise installation of substituents onto an aromatic core, following well-established reactivity rules that dictate regioselectivity and functional group compatibility. While powerful, this approach inherently constrains access to diverse substitution patterns and often requires lengthy synthetic sequences.

In this presentation, I will discuss our recent work demonstrating how amine-ligated boryl radicals can be harnessed to directly target and borylate a broad range of aromatic compounds, including azines, azoles, and benzenes.[1] This reactivity provides a fundamentally different, metal-free approach to aromatic C–H borylation that bypasses the need for traditional transition-metal-mediated C–H activation strategies. Particular emphasis will be placed on the factors governing reactivity and site selectivity, including the electronic and structural features that control borylation at specific positions within aromatic frameworks. Mechanistic studies revealing how radical polarity, aromatic substitution patterns, and intermediate stability influence the outcome of these transformations will also be discussed.

Acknowledgements
This work was financially supported by the ERC.

References

[1] (a) N. Yasukawa,* W. Okada, M. Fimm, R. Kawamura, R. Nomura, T. Takehara, T. Suzuki, D. Leonori,* and S. Nakamura* “Amine-Ligated Boryl Radical Enables Direct C─F Borylation and Cross-Couplings of Polyfluoroarenes” *Angew. Chem. Int. Ed.* **2025**, *64*, e202514741. (b) J. Corpas, M. Alonso and D. Leonori* “Boryl Radical-Mediated Halogen-Atom Transfer (XAT) Enables the Sonogashira-Like Alkynylation of Alkyl Halides” *Chem. Sci.* **2024**, *15*, 19913. (c) C. S. Buettner, C. Stavagna, M. J. Tilby, B. Górski, J. J. Douglas, N. Yasukawa* and D. Leonori* “Synthesis and Suzuki–Miyaura Cross-Coupling of Alkyl Amine-Boranes. A Boryl Radical-Enabled Strategy” *J. Am. Chem. Soc.* **2024**, *146*, 24042. (d) J. H. Kim, T. Constantin, M. Simonetti, J. Llaveria, N. S. Sheikh and D. Leonori* “A Radical Approach for the Selective C–H Borylation of Azines” *Nature* **2021**, *596*, 677.

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Academic Positions & Education

Since 2013	Principal Investigator, Institute of Transformative Bio-Molecules (ITbM)
Since 2006	Professor, Department of Molecular and Macromolecular Chemistry Graduate School of Engineering, Nagoya University
2001-2006	Associate Professor, Kyoto University
1995-2000	Assistant Professor and Lecturer, Hokkaido University
1994-1995	Postdoctoral Fellow, Department of Chemistry, MIT (Prof. J. Rebek, Jr.)
1991-1994	PhD, Department of Applied Chemistry, Nagoya University (Prof. H. Yamamoto)
1989-1991	MSc, Department of Applied Chemistry, Nagoya University
1989	BSc, Department of Applied and Synthetic Chemistry Nagoya University

Research Interests
Design and precise structural control of organic molecular catalysts, particularly ion-pair and radical-pair catalysts, for selective organic synthesis.

Honors & Awards
Chugai Award in Synthetic Organic Chemistry, Japan (1997), Chemical Society of Japan Award for Young Chemist (1999), Thieme Journal Award (2006), JSPS Prize (2010), IBM Japan Science Prize (2011), Inoue Prize for Science (2013), Daiichi-Sankyo Award for Medicinal Organic Chemistry (2017), Swiss Chemical Society Lectureship Award (2019), Chemical Society of Japan Award (2020), and he was named a Fellow of the Royal Society of Chemistry (2014).

Selected Publications

1. Suzuki, R.; Ando, T.; Deufel, F.; Ohmatsu, K.; Ooi, T. Photocatalytic carbyne reactivity of phosphorus ylides for three-component formal cycloaddition reactions. *Nat. Synth.* **2024**, *3*, 1385–1391.
2. Kikura, T.; Taura, Y.; Aramaki, Y.; Ooi, T. *p*-Diarylboryl Halothiophenols as Multifunctional Catalysts via Photoactive Intramolecular Frustrated Lewis Pairs. *J. Am. Chem. Soc.* **2024**, *146*, 20425–20431.
3. Schirmer, T. E.; Kürschner, J. C. G.; Uchida, Y.; Taura, Y.; Gabriel, P.; Næsborg, L.; Yokogawa, D.; Aramaki, Y.; Ooi, T. Regiodivergent Photocatalytic Annulation for the Synthesis of *gem*-Difluorinated Cyclic Hydrocarbons. *Angew. Chem., Int. Ed.* **2025**, *64*, e202502450.
4. Ando, T.; Yokogawa, D.; Ohmatsu, K.; Ooi, T. Deoxygenative [3 + 2] Annulation of α,β-Unsaturated Carbonyl Compounds and Electron-Rich Olefins via Photocatalytic Umpolung of Triarylphosphine. *J. Am. Chem. Soc.* **2025**, *147*, 23220–24224.

14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Development of Organic Radical Catalysts

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Keywords: excited state ● ion pairs ● photocatalysts ● radical pairs ● triplet biradicals

Radical reactions constitute one of the most basic tools for molecular transformations with characteristics distinctly different from ionic reactions due to the intrinsic property of a radical as an open-shell species with an unpaired electron. The unique reactivity of organic radical intermediates allows for otherwise inaccessible forms of bond construction, yet selectivity issues that determine the product bond connectivity and stereochemistry must be addressed for taking full advantage of the radical reactions in assembling organic molecules. We have tackled this challenge by simply merging the organic ion-pair catalysis with single-electron oxidation and reduction processes with visible-light photosensitizers and have demonstrated the effectiveness of this approach.[1] At the same time, we have been pursuing the development and application of organic radical catalysts capable of facilitating radical generation and subsequent bond formations. One direction is the design of photocatalysts, specifically zwitterionic acridinium amidates (**1**)[2] and diarylboryl halothiophenols (**2**)[3], considering the lack of diversity in the structure and function of catalysts that act harnessing the energy of visible light. These catalysts exert multiple functions via the generation of excited-state radical pairs. Another direction is to devise modular thiazole-2-thiones (**3**)[4] that form excited-state triplet biradicals effective for radical covalent catalysis. In this presentation, I would like to share recent advancements in these research streams, with a focus on the latter attempt.

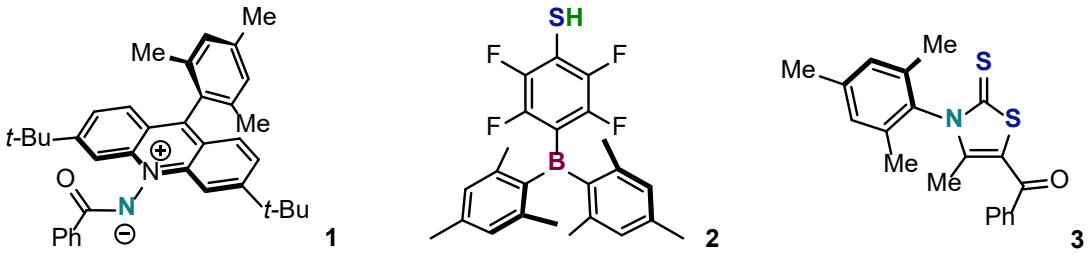

Figure 1. Representative structures of organic radical catalysts

Acknowledgements
This work was financially supported by JSPS KAKENHI Grant Numbers JP23H04901 and JP23H04907 (Green Catalysis Science).

References
[1] Uraguchi, D.; Kimura, Y.; Ueoka, F.; Ooi, T. *J. Am. Chem. Soc.* **2020**, *142*, 19462–19467.
[2] Entgelmeier, L.-M.; Mori, S.; Sendo, S.; Yamaguchi, R.; Suzuki, R.; Yanai, T.; García Mancheño, O.; Ohmatsu, K.; Ooi, T. *Angew. Chem., Int. Ed.* **2024**, *63*, e202404890.
[3] Kikura, T.; Taura, Y.; Aramaki, Y.; Ooi, T. *J. Am. Chem. Soc.* **2024**, *146*, 20425–20431.
[4] Kawaguchi, T.; Shioda, Y.; Hanai, Y.; Nakashima, T.; Ooi, T. *J. Am. Chem. Soc.* **2026**, *148*, 5585–5593.

Invited Speakers

Luca Dell'Amico

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Academic Positions & Education
11/2021 – present. Associate Professor in Organic Chemistry, University of Padova, Italy.
11/2019 – 11/2021. Assistant Professor (tenured – RTDb), University of Padova, Italy.
10/2016 – 11/2019. Researcher (fixed term – RTDa), University of Padova, Italy.
04/2014 – 09/2016. Marie-Curie Postdoctoral Fellow (Prof. Paolo Melchiorre), ICIQ, Spain.
01/2011 – 03/2014. PhD in Synthetic Chemistry (Prof. Franca Zanardi), University of Parma.
08/2012 – 04/2013. Visiting PhD (Prof. Karl Anker Jørgensen), Aarhus University, Denmark.
10/2004 – 07/2010. MSc. in Medicinal Chemistry (Prof. Giovanni Casiraghi), University of Parma, Italy.

Research Interests
Organic synthesis, photochemistry, radical chemistry, mechanistic investigation: identification and characterization of transient intermediates, development of new organic photocatalysts and related reactivity

Honors & Awards
2026 Liebig Lectureship2026, form GDCh (German Chemical Society). 2024 Representative for the Department of Chemical Sciences in the Equal Opportunities Commission of the University of Padova. 2022 ERC-Starting Grant 2021. 2020 JSP (Junior Scientists Participations) fellow – by the Swiss Chemical Society. 2020 YourJOC Talents collection in Eur. JOC (Eur. J. Org. Chem. 2020, 43, 6718–6722). 2020 Thieme Chemistry Journals Award. 2019 Giacomo Ciamician Medal 2019, from the Italian Chemical Society. 2018 Chem. Comm. Emerging Investigators Issue (Chem. Comm. 2018, 54, 6820-6823)

Selected Publications
1 Corti, V., Simionato, G., Rizzo, L., Serapian, S. A., Pelosi, G., Natali, M., **Dell'Amico, L.*** "Triplet state reactivity of iminium ions in organocatalytic asymmetric [2 + 2] photocycloadditions" *Nat. Chem.* **2026**, *18*, 189–197.
2 Rodríguez, R. I., Corti, V., Rizzo, L., Visentini, S., Bortolus, M., Amati, A. Natali, M., Pelosi, G., Costa, P., and **Dell'Amico, L.*** "Radical strain-release photocatalysis for the synthesis of azetidines" *Nat. Catal.* **2024**, *7*, 1223–1231.
3 Bortolato, T., Simionato, G., Vayer, M., Rosso, C., Paoloni, L., Benetti, E. M., Sartorel, A., Lebœuf,* D., **Dell'Amico, L.*** "The Rational Design of Reducing Organophotoredox Catalysts Unlocks Proton-Coupled Electron-Transfer and Atom Transfer Radical Polymerization Mechanisms" *J. Am. Chem. Soc.* **2023**, 145, 1835–1846.
4 Mateos, J., Rigodanza, F., Costa, P., Natali, M., Vega-Peñaloza, A., Fresch, E., Collini, E., Bonchio, M., Sartorel, A., **Dell'Amico, L.*** "Unveiling the impact of the light-source and steric factors on [2+2] heterocycloaddition reactions" *Nat. Synth.* **2022**. *2*, 26–36.

Mechanistic investigations in light-driven synthetic chemistry

From direct photochemistry to organophotoredox catalysis

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Keywords: Photochemistry ● Synthetic methods ● Mechanistic investigation ● Strain molecules ● Small rings

In this presentation, I will focus on two different topics from my research group, moving from the design of new photosensitizers to the development of powerful redox catalysts

1. Based on experimental evidence and mechanistic information, we have identified and structurally optimized a new family of photosensitiser.[1] This class of molecules is characterized by a short S1-T1 gap. We observed and increased selectivity in the strain-release functionalization of azabyclic scaffolds. This new reaction manifold grants access to highly functionalized azetidine scaffolds.

2. We have designed and developed two new classes of photoredox catalysts (PCs) capable of activating diverse types of redox inert substrates. To do so, we have used i) a catalytic proton-coupled electron-transfer (PCET) manifold;[2] and ii) an unconventional regenerative photocatalytic mechanism.[3]

Acknowledgements
The authors are grateful to the European Research Council for the ERC-St. Grant SYNPHOCAT.

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[2] Bortolato, T.; Simionato, G.; Vayer, M.; Rosso, C.; Paoloni, L.; Benetti, E. M.; Sartorel, A.; Lebœuf, D.; Dell'Amico, L. *J. Am. Chem. Soc.* **2023**, *145*, 1835–1846.
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Academic Positions & Education

2024-present	W.R. Kenan, Jr., Distinguished Professor, UNC Chapel Hill
2020-2024	Royce Murray Professor, University of North Carolina at Chapel Hill
2018-2020	Professor, University of North Carolina at Chapel Hill
2015-2018	Associate Professor, University of North Carolina at Chapel Hill
2009-2015	Assistant Professor, University of North Carolina at Chapel Hill
2007-2009	Ruth L. Kirschstein Postdoctoral Fellow, Princeton University
2006	Ph.D. in Chemistry, University of North Carolina at Chapel Hill
2002	M.S. in Chemistry, University of North Carolina at Charlotte
2000	B.S. in Chemistry, University of North Carolina at Charlotte

Research Interests

Catalysis, reaction development, photochemistry, radical chemistry, radiolabeling and targeted radiotherapy development. Co-founder of two companies: LED Radiofluidics and dGenThera.

Honors & Awards

Eli Lilly New Faculty Award (2009), James Moeser Award for Distinguished Research (2011), Packard Fellowship in Science and Engineering (2012), Boehringer Ingelheim New Investigator Award (2013), Amgen Young Investigator Award (2014), Eli Lilly Grantee Award (2015), Ruth Hettleman Prize for Artistic and Scholarly Achievement (2015), Camille Dreyfus Teacher-Scholar Award (2015), Padwa Lecture, Columbia U. (2016), Allergan Lecture, U. California, Irvine (2016), Abbvie Lecture, California Institute of Technology (2016) The Hirata Award (2017), E. Abrose White Lecture, U. Kansas (2018), Blavatnik National Awards, Finalist (2019), Andrew S. Kende Distinguished Lecturer, U. of Rochester (2019), Alphora/Eurofins Lectureship, U. of Toronto (2019), ACS Cope Scholar Award (2022), Abbvie Lecture in Organic Chemistry, Northwestern U. (2023), Negishi Lecturer in Organic and Organometallic Chemistry, Purdue U. (2024), Novartis Chemistry Lectureship (2025), Pharmaron Symposium on Synthetic & Medicinal Chemistry (2025), Warren Lectureship, Vanderbilt U. (2026)

Selected Publications

1. Akkawi, N. R.; Nicewicz, D. A. “Photochemically Enabled Total Syntheses of Stemoamide Alkaloids.” *J. Am. Chem. Soc.* **2025**, *147*, 15482-15489.
2. Chen, W.; Wang, H.; Tay, N. E. S.; Pistritto, V. A.; Li, K.-P.; Wu, Z.; Nicewicz, D. A.; Li, Z. “Arene Radiofluorination Enabled by Photoredox-Mediated Halide Interconversion” *Nature Chem.* **2022**, *14*, 216-223.
3. Chen, W.; Huang, Z.; Tay, N. E. S.; Giglio, B.; Wang, M.; Wu, Z.; Nicewicz, D. A.; Li, Z. “Arene C-H Fluorination with $^{18}F^-$ via Organic Photoredox Catalysis.” *Science* **2019**, *364*, 1170-1174.
4. Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. “Site-Selective Arene C–H Amination via Photored ox Catalysis.” *Science*, **2015**, *349*, 1326-1330.

Excited State Acridyl Radical Chemistry

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Keywords: photoredox ● reduction ● radical ● electron ● photochemistry

Acridinium salts have been employed as excited state oxidation catalysts for numerous synthetic transformations as they readily access excited state reduction potentials in excess of +2.0 V vs. SCE.[1] Recently, our laboratory has discovered that the one-electron reduced species, the neutral acridyl radical, can also undergo photoexcitation to access a twisted intramolecular charge transfer (TICT) excited state (Figure 1), which is a potent single electron reductant ($E_{1/2}$ = –3.36 V vs. SCE).[2] While the TICT was characterized by transient absorption spectroscopy, the mechanism of reduction it is capable of was unknown. This lecture will present transient absorption, electrochemical and EPR spectroscopic data that has elucidated the mechanism of the reductive chemistry of this TICT state along with the organic transformations that are possible utilizing this potent excited state reductant.

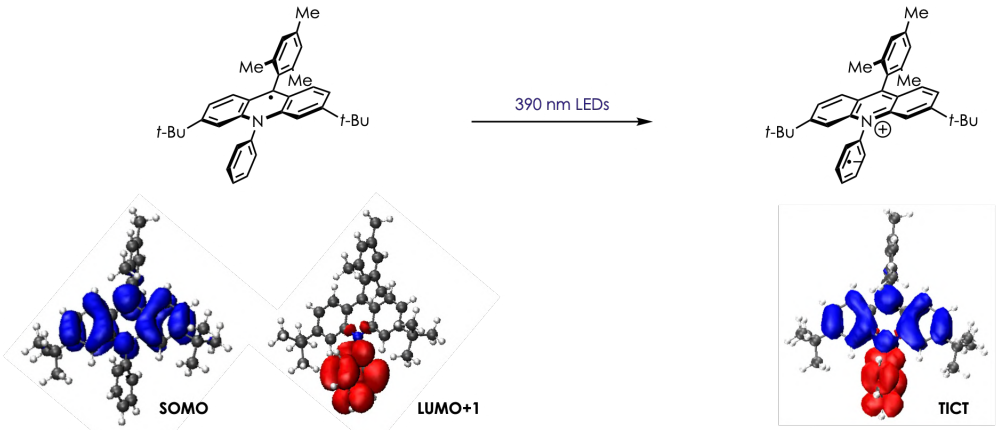

Figure 1. Acridyl Radical Excited State Electronic Transition

Acknowledgements
This work was financially supported by the National Institute of General Medical Sciences (R35 GM136330)

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Academic Positions & Education

Since 2022	Professor, Colorado State University
Since 2023	Director of the NSF CCI Center for Sustainable Photoredox Catalysis
2019-2022	Associate Professor, Colorado State University
2017-2019	Assistant Professor, Colorado State University
2011-2014	Postdoctoral Research Fellow, Caltech
2005-2011	PhD in Chemistry, Colorado State University
2001-2005	BS in Chemistry, Pacific University

Research Interests

Photoredox catalysis, sustainable plastics.

Honors & Awards

ChemSocRev Pioneering Investigator Lectureship (2025), Colorado State University Vice President for Research Scholarship Impact Award (2025), Finalist Blavatnik National Awards for Young Scientists (2024 and 2025), ACS Division of Polymeric Materials: Science and Engineering Journal of Polymer Science Innovation Award (2021), *Camille Dreyfus Teacher-Scholar Award* (2019), *Cottrell Scholar Award* (2018), ACS Division of Polymer Chemistry Herman F. Mark Young Scholar Award (2017), Sloan Research Fellow (2017).

Selected Publications

1. A. K. Bains, A. Sau, B. S. Portela, K. Kajal, A. R. Green, A. M. Wolff, L. F. Patin, R. S. Paton, N. H. Damrauer, G. M. Miyake. Efficient Super-Reducing Organic Photoredox Catalysis with Proton-Coupled Electron Transfer Mitigated Back Electron Transfer. *Science* **2025**, *388*, 1294.
2. X. Liu, A. Sau, A. R. Green, M. V. Popescu, N. F. Pompetti, Y. Li, Y. Zhao, R. S. Paton, N. H. Damrauer, G. M. Miyake. Photocatalytic C-F Bond Activation in Small Molecules and Polyfluoroalkyl Substances. *Nature* **2025**, *637*, 601-607.
3. J. C. Theriot, C.-H. Lim, H. Yang, M. D. Ryan, C. B. Musgrave, G. M. Miyake. *Science* **2016**, *352*, 1082-1086.
4. Y. Zhao, E. M. Rettner, K. L. Harry, Z. Hu, J. Miscall, N. A. Rorrer, G. M. Miyake. Chemically Recyclable Polyolefin-Like Multiblock Polymers. *Science* **2023**, *382*, 310-314.

Super-Reducing Organic Photoredox Catalysts

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Keywords: photoredox ● catalysis ● super-reducing ● organocatalysis

This presentation will discuss the design of organic photoredox catalysts and their employment in polymer and small molecule synthesis.[1]

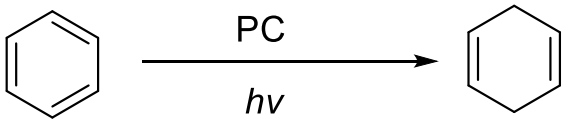

Figure 1. Reduction of arenes to cyclohexadienes using an organic photoredox catalyst.

Acknowledgements
This work was financially supported by the National Science Foundation.

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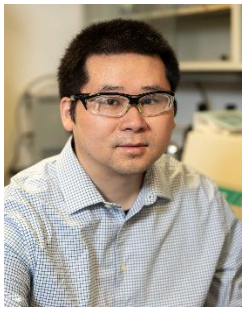
Yang Yang



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Academic Positions & Education

Since 2025	Associate Professor, University of California Santa Barbara
2020-2025	Assistant Professor, University of California Santa Barbara
2018-2020	NIH Postdoctoral Fellow, California Institute of Technology
2016-2018	Miller Postdoctoral Fellow, University of California Berkeley
2011-2016	Graduate Research, Massachusetts Institute of Technology

Research Interests

Biocatalysis, de novo protein design, asymmetric catalysis, photochemistry, radical chemistry

Honors & Awards

2026 Frontiers of Science Fellow, NAS 2025 Padwa Lectureship, Emory University 2025 Howard Hughes Institute Freeman Hrabowski Scholar 2025 Camille Dreyfus Teacher-Scholar Award 2025 Novartis Early Career Award 2024 Department of Energy Early Career Award 2024 Amgen Young Investigator Award 2024 American Chemical Society Division of Organic Chemistry Young Investigator 2024 Stanley and Leslie Parsons Award in Biochemistry 2024 Sloan Research Fellowship 2024 Bürgenstock JSP Fellowship 2024 CAPA Distinguished Junior Faculty Award 2023 David & Lucile Packard Fellowship in Science and Engineering 2023 Army Research Office (ARO) Young Investigator Award 2023 Thieme Chemistry Journals Award 2022 National Institutes of Health (NIH) Maximizing Investigators' Research Award 2022 National Science Foundation (NSF) CAREER Award 2022 ACS Herman Frasch Foundation Agricultural Chemistry Grantee 2022 ACS Petroleum Research Fund New Doctoral Investigator Award 2022 UCSB Faculty Career Development Award 2021 UCSB Regent's Junior Faculty Fellowship Award 2018-2020 NIH Ruth L. Kirschstein Postdoctoral Fellowship 2016-2018 Miller Postdoctoral Fellowship

Selected Publications

1. "Diversity-Oriented Photobiocatalytic Synthesis via Stereoselective Three-Component Radical Coupling." Chen Zhang†, Jun Zhou†, Pei-Pei Xie, Silvia M. Rivera, Turki M. Alturaifi, James Finnigan, Simon Charnock, Peng Liu, and Yang Yang* *Science* **2025**, *389*, eadx2935.
2. "De Novo Design of Porphyrin-Containing Proteins as Efficient and Stereoselective Catalysts." Kaipeng Hou†, Wei Huang†, Miao Qi, Thomas H. Tugwell, Turki M. Alturaifi, Yuda Chen, Xingjie Zhang, Lei Lu, Samuel I. Mann, Peng Liu, Yang Yang* and William F. DeGrado* *Science* **2025**, *388*, 665-670.
3. "Stereoselective Amino Acid Synthesis by Photobiocatalytic Oxidative Coupling." Tian-Ci Wang, Binh Khanh Mai, Zheng Zhang, Zhiyu Bo, Jiedong Li, Peng Liu* and Yang Yang*, *Nature* **2024**, *629*, 98–104.
4. "Stereoselective Amino Acid Synthesis by Synergistic Photoredox-Pyridoxal Radical Biocatalysis" Lei Cheng, Dian Li, Binh Khanh Mai, Zhiyu Bo, Lida Cheng, Peng Liu* and Yang Yang*, *Science* **2023**, *381*, 444–451.
5. "Stereodivergent atom-transfer radical cyclization by engineered cytochromes P450." Qi Zhou, Michael Chin, Yue Fu, Peng Liu, and Yang Yang*, *Science* **2021**, 374, 1612–1616.

New Strategies for Stereoselective Radical Biocatalysis

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Keywords: biocatalysis ● radical chemistry ● asymmetric catalysis ● photochemistry ● cooperative catalysis

Radical reactions have enjoyed widespread applications in both small molecule and macromolecule synthesis. However, it remains challenging to control the stereochemistry of radical transformations and to discover novel modes of radical catalysis which are not known in either organic chemistry or biochemistry. Combining synthetic chemistry, enzymology and protein engineering, our group advanced two new biocatalytic strategies for stereoselective free radical processes. First, by capitalizing on the innate redox properties of first-row transition-metal cofactors, we repurposed and evolved natural metalloproteins to catalyze unnatural radical reactions in a stereocontrolled fashion. Through a metalloenzyme-catalyzed (pseudo)halogen transfer mechanism (XAT, X = F, Cl, Br, I, N_3, SCN and OCN), a range of radical C–C, C–F and other C–X bond forming reactions proceeded with excellent total turnover numbers (up to 20,000) and outstanding stereocontrol. Second, by merging visible light photoredox catalysis and biocatalysis, we advanced a novel mode of pyridoxal radical biocatalysis which is new to both chemistry and biology. Cooperative photobiocatalysis allowed us to repurpose structurally and functionally diverse pyridoxal phosphate (PLP)-dependent enzymes as radical enzymes, leading to novel radical PLP enzymology. Pyridoxal radical biocatalysis provides stereoselective and protecting-group-free access to numerous useful non-canonical amino acids, including those bearing a stereochemical triad and/or tetrasubstituted stereocenters which remained difficult to prepare by other chemical and biocatalytic means. The ability to perform diversity-oriented synthesis combinatorially through previously elusive biocatalytic C–C bond formation marks a synthetically valuable advance, paving the way for broader adaptation and application of biocatalysis in medicinal chemistry. Furthermore, we demonstrate that the exploitation of biocatalyst-photocatalyst synergy affords a new paradigm to design and develop a range of stereoselective intermolecular radical reactions using new mechanisms.

Acknowledgements
This work was financially supported by the Howard Hughes Medical Institute, National Institutes of Health, National Science Foundation, Department of Energy, Defense Advanced Research Projects Agency (DARPA), Army Research Office and Office of Naval Research.

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Academic Positions & Education

Since 2025	Associate Professor, ETH Zurich
2019-2024	Assistant Professor, ETH Zurich
2016-2018	MSCA Global Fellow, University of California Santa Barbara (USA)
2015-2016	Monash/Warwick Research Fellow, Monash University (Australia)
2011-2014	PhD in Polymer Chemistry, University of Warwick (UK)
2007-2011	B.Sc. in Chemistry, University of Athens (Greece)

Research Interests
Chemical recycling, depolymerization, controlled radical polymerization, sustainable polymer chemistry, polymer self-assembly

Honors & Awards
ACS Sustainable Chemistry & Engineering Lectureship Award (2025), ACS Global Outstanding Mentor & Graduate Student Award (2025), Kavli Foundation Emerging Leader in Chemistry Award (2024), 9th Polymer International IUPAC Award (2024), Werner Prize, Swiss Chemical Society (2024), Journal of Polymer Science Innovation Award (2024), EuChemS Lecture Award (2023), C&EN Talented 12 (2023), ACS Macro Letters/Biomacromolecules/Macromolecules Young Investigator Award (2023), Ruzicka Prize, ETH Zurich (2022), PMSE Young Investigator Award, American Chemical Society (2022), ERC Starting Grant (2020),and Hanwha-Total IUPAC Young Scientist Award (2020)

Selected Publications

1. Wang, Agrachev, Kim, Truong, Choi, Jeschke, Anastasaki *Science* **2025**, *387*, 874-880
2. Lohmann, Poon, Whitfield, Matyjaszewski, Mougel, Anastasaki, *J. Am. Chem. Soc.* **2026**, *148*, 8067-8072
3. De Alwis, Lohmann, Lutz-Bueno, Truong, Armes, Anastasaki, *J. Am. Chem. Soc.* **2026**, *148*, 5400-5408
4. Wang, Parkatzidis, Junkers, Truong, Anastasaki, *Chem* **2024**, *10*, 388-401
5. Jones, Antonopoulou, Truong, Anastasaki, *J. Am. Chem. Soc.* **2024**, *146*, 35023-35028

Monomers from Polymers: Reversing Radical Polymerization

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Keywords: Depolymerization ● Chemical Recycling ● Controlled Radical Polymerization

The accumulation of plastic waste presents one of the most significant environmental challenges of the 21st century, necessitating a transition from a linear to a circular polymer economy. While traditional recycling methods often result in "downcycling" and loss of material properties, chemical depolymerization offers a pathway to recover high-purity monomers which can then be used to make new virgin grade materials.[1] For some vinyl polymers, depolymerization is thermodynamically favorable at relatively low temperatures (e.g. below 200°C). However, the primary kinetic barrier lies in the "reactivation" of an inert polymer chain into a reactive macroradical capable of unzipping. Our group has demonstrated that polymers synthesized via reversible deactivation radical polymerization (RDRP) can be effectively exploited for low-temperature depolymerization. In these systems, well-defined chain-end functionality provides a chemically accessible initiation point, enabling high monomer conversion driven thermally, photolytically, or electrochemically. The "control" inherent to RDRP can also afford a precisely managed depropagation process, serving as a powerful analytical tool for sequencing multiblock copolymers, and enabling the morphological tuning of polymeric micelles.[2, 3] Despite these successes in "recyclability-by-design," commercial materials like Plexiglass (PMMA) lack specialized end groups. To address this, we developed a mid-chain activation approach.[4] By strategically abstracting hydrogen atoms from the polymer backbone, we generate unstable mid-chain radicals that undergo beta-scission and subsequent unzipping. This method facilitates the low-temperature chemical recycling of commercial-grade PMMA, bridging the gap between sophisticated synthetic polymers and the bulk materials currently found in the waste stream.

Acknowledgements

This work was financially supported by ETH Zurich and the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (DEPO: Grant No. 949219).

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[1] Jones, G. R.; Wang, H. S.; Parkatzidis, K.; Whitfield, R.; Truong, N. P.; Anastasaki, A. Reversed Controlled Polymerization (RCP): Depolymerization from Well-Defined Polymers to Monomers. *J. Am. Chem. Soc.* **2023**, *145* (18), 9898–9915.

[2] Wang, H. S.; Parkatzidis, K.; Junkers, T.; Truong, N. P.; Anastasaki, A. Controlled radical depolymerization: Structural differentiation and molecular weight control. *Chem* **2024**, *10* (1), 388–401.

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[4] Wang, H. S.; Agrachev, M.; Kim, H.; Truong, N. P.; Choi, T. L.; Jeschke, G.; Anastasaki, A. Visible light-triggered depolymerization of commercial polymethacrylates. *Science* **2025**, *387* (6736), 874–880.

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Positions & Education

Since 2023	Director of Chemistry, Parallel Synthesis, AZ, Sweden
2023	Director of Chemistry – DEL & CCE, AZ, Sweden
2020-2023	Associate Principal Scientist, Medicinal Chemistry, AZ, Sweden
2017-2020	Senior Research Scientist, Medicinal Chemistry, AZ, Sweden
2016	Process Development Chemist, GSK, UK
2014-2016	PostDoc University of Gothenburg, Sweden
2012	Internship, Boston University, USA
2009-2013	PhD, ICIQ (Institute of Chemical Research of Catalonia), Spain
2004-2009	BSc and MSc, Industrial Chemistry, University of Bologna, Italy

Research Interests

Chemistry automation, Chemistry Miniaturization, High-throughput synthesis, Photochemistry, Radical Chemistry, Sustainable Chemistry, Flow Chemistry, Chemistry AI

Honors & Awards

Doctoral Extraordinary Award, Universitat Rovira I Virgili (2015), FPU "traslado temporal" internship grant, Ministry of Science and Innovation (MICCIN) of Spain (2012), FPU predoctoral fellowship (AP2009-0950) Ministry of Science and Innovation (MICCIN) of Spain (2009), "*Le Migliori laureate" Award for the best female academic qualification in the University of Bologna (Italy) in "Products, Materials and Processes for Industrial Chemistry" (2010), Toso Montanari foundation fellowship for outstanding students, Alma Mater Studiorum-University of Bologna (2004).*

Selected Publications

1. George V., Pattanaik A., Maddox D., Sigmund L. M., Mejia G., Pahlén S., Angerer S. O., Schmoll M., Schneider L. M., Selmi N., Kabeshov M., Bergonzini G., Rehbein J., König B. Geminal Difunctionalization of Ketones via C–S Bond Insertion of Photogenerated Donor–Donor Diazo Compounds. *Angew. Chem. Int. Ed.* **2026**, e6162809.
2. Assante M., Pahlén S., Pijper B., Cao L., Specht O., Simeth N., Lapkin A., Green C., Engkvist O., Bergonzini G., Kabeshov M., *ACS Catalysis* **2026**, *16*, 3547–3560.
3. Sigmund,L. M. Seifert T., Halder R., Bergonzini G., Johansson M. J., Norrby P. O., Jorner K., Kabeshov M., Predicting Reaction Feasibility and Selectivity of Aromatic C–H Thianthrenation with a QM–ML Hybrid Approach *Angew. Chem., Int. Ed.* **2025**, e202510533.
4. Schmalzbauer M., Svejstrup T.D., Fricke F., Brandt P., Johansson M. J., Bergonzini G., König B., Redox-Neutral Photocatalytic C−H Carboxylation of Arenes and Styrenes with CO_2. *Chem* **2020**, 2658-2672.

Chemistry at the Forefront: Technology-Enabled Drug Discovery

Giulia Bergonzini

Compound Synthesis and Management, Discovery Sciences, BioPharmaceuticals R&D, AstraZeneca, Gothenburg, Sweden

Drug discovery is constantly evolving to be able to generate differentiated candidate drugs towards unmet medical needs. Synthetic chemistry plays a key role towards this goal, and by applying emerging technologies, the pharmaceutical industry is undergoing a dramatic transformation journey. Advances in chemistry automation, robotics, AI and novel synthetic methods have the potential to accelerate the Design-Make-Test-Analysis (DMTA) cycle while saving resources. Novel synthetic methods that use abundant starting materials for the synthesis of chemically diverse building blocks and/or high-quality library molecules with desired properties and improved sustainability are highly desirable. Visible-light photocatalysis, allowing chemistry under mild conditions, broad functional group compatibility and site-selectivity, has emerged as one of these technologies and found broad application in drug discovery. At the same time, automation and miniaturisation have dramatically accelerated SAR exploration. The vast amount of data generated can be used to build AI models for predicting chemistry feasibility and optimal reaction conditions to enhance the success rate of chemical synthesis and advance synthesis planning. Finally, the convergence of these technologies and robotics into end-to-end synthesis platforms has the potential to dramatically increase scale, efficiency and pace of chemical space exploration.

Shunsuke Chiba

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Academic Positions & Education

Since 2016	Professor, NTU Singapore
2012-2016	Associate Professor, NTU Singapore
2007-2012	Assistant Professor, NTU Singapore
2005-2007	Research Associate, The University of Tokyo
2003-2006	PhD in Chemistry, The University of Tokyo
2001-2003	MSc in Chemistry, The University of Tokyo

Research Interests
Synthetic chemistry, catalysis, organic free radicals, and complex molecule synthesis

Honors & Awards
GSK-SNIC Award in Organic Chemistry (2014), Mitsui Chemicals Catalysis Science Award of Encouragement (2014), The Zasshi-Kai Lectureship, The University of Tokyo (2017), Mukaiyama Award (2019), IOCF Zen-ichi Yoshida Lectureship (2025).

Selected Publications

1. Li, H.; Tang, X.; Pang, J. H.; Wu, X.; Yeow, E. K. L.; Wu, J.; Chiba, S. Polysulfide anions as visible light phot oredox catalysts for aryl cross-couplings. *J. Am. Chem. Soc.* **2021**, *143*, 481.
2. Tan, E. Y. K.; Mat Lani, A. S.; Sow, W.; Liu, Y.; Li, H.; Chiba, S. Dearomatization of (Hetero)arenes through P hotodriven Interplay between Polysulfide Anions and Formate. *Angew. Chem. Int. Ed.* **2023**, *62*, e20230976 4.
3. Tan, E. Y. K.; Dehdari, A.; Mat Lani, A. S.; Pratt, D. A.; Chiba, S. Dearomative dimerization of quinolines and their skeletal rearrangement to indoles triggered by single-electron transfer. *Chem* **2024**, *10*, 3722.
4. Tan, E. Y. K.; Peng, T.; Wakabayashi, T.; Chiba, S. Peripheral aryl group transposition on pydirines using ph otoredox catalysis. *Nat. Synth*. **2026**, DOI: 10.1038/s44160-026-01023-6.

Skeletal and peripheral remodeling of azaheteroarenes via SET-driven dearomatization

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Keywords: azaheteroarenes ● radicals ● dearomatization ● aryl migration ● single electron transfer

This talk will present our recent efforts on molecular transformations and functionalization of azaheteroarenes such as quinolines and pyridines via SET-driven dearomatization under photoredox catalysis. The resulting 1,4-dihydroquinoline/pyridine radicals, having an electron-rich enamine character, could be manipulated through subsequent redox events, resulting in unique skeletal rearrangement[1] and peripheral functional group transposition.[2]

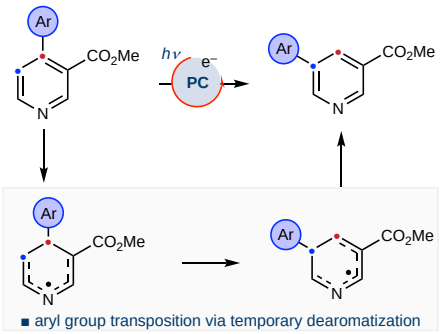

Figure 1. Peripheral aryl group transposition on pyridines

Acknowledgements

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Academic Positions & Education

Since 2014	Full professor, University of Bologna
2001-2013	Associate Professor, University of Bologna
1994-2000	Assistant Professor, University of Bologna
1989-1994	Research Associate, University of Lausanne, with C. Floriani
1984-1989	MSc in Chemistry, University of Milan

Research Interests

Asymmetric catalysis, photochemistry, radical chemistry, organometallic chemistry: development of dual photoredox catalysis with metals (Ni, Co, Ti, V, and others) using visible light. Development of strong photoreductants.

Honors & Awards

"Chemistry Europe Fellow" (2019), European Chemical Society
*"*Gònzales-Ciamician" Award, (2018) Royal Spanish Society
*"*Piero Pino*"* Gold Medal, (2015) Italian Chemical Society
"JSPS Scholarship" (2013), Chemistry Society of Japan,
"C.I.N.M.P.I.S" (2007), Italian Chemical Society,

Selected Publications

1. Calogero F., Pinosa E., Gualandi A., Sensoli L., Dutta S., Maity B., Cavallo L., Fermi A., Ceroni P., Cozzi P. G., *ACS Catal.* **2025**, *15*, 8303–8316.
2. Villa, M.; Fermi, A.; Calogero, F.; Gualandi, A.; Franchi, P.; Lucarini, M.; Ventura, B.; Cozzi, P. G.; Ceroni, P.; *Angew. Chem. Int. Ed.* **2025**, *64*, e202420009.
3. T. Calogero, F.; Wilczek, L.; Pinosa, E.; Gualandi, A.; Dorta, R.; Herrera, E.; Dai, Y.; Rossignol, A.; Negri, F.; Ziani, Z.; Fermi, A.; Ceroni, P.; Cozzi, P. G. *Angew. Chem. Int. Ed.* **2024**, *63,* e202411074.
4. Villa, M.; Fermi, A.; Calogero, F.; Wu, X.; Gualandi, A.; Cozzi, P. G.; Troisi, A.; Ventura, B.; Ceroni, P. *Chem. Sci.*, **2024**,*15*, 14739-14745.

Supramolecular Photoactive Titanium Complexes for HAT Reactions

Luca Sensoli,[a] Andrea Gualandi,[a] Federica Fina, [a] Andrea Fermi,[a] Paola Franchi,[a] Marco Lucarini,[a] Paola Ceroni,[a,] and Pier Giorgio Cozzi[a,b]

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Keywords: Photoredox Dual Catalysis ● Titanium ● HAT reactions ● Aldehydes ● Supramolecular Chemistry

Photoactive Cp titanium complexes operate via LMCT states, producing active Ti(III) complexes by fragmentation.[1] Unfortunately, this pathway also decomposes the titanium complex via Cp radical formation.[1] In order to bypass this detrimental pathway and utilize a HAT mediator in Ti(III)-promoted radical addition, we discovered a new active supramolecular adduct formed by an inexpensive and readily available Cp titanium complex and a HAT mediator.[2] This new complex can promote the addition of C-formed radicals to aromatic aldehydes without the need for a sacrificial agent.

The titanium complex and the HAT mediator are both employed in catalytic amounts under green light irradiation, opening the door to new studies and applications in photoredox titanium chemistry.

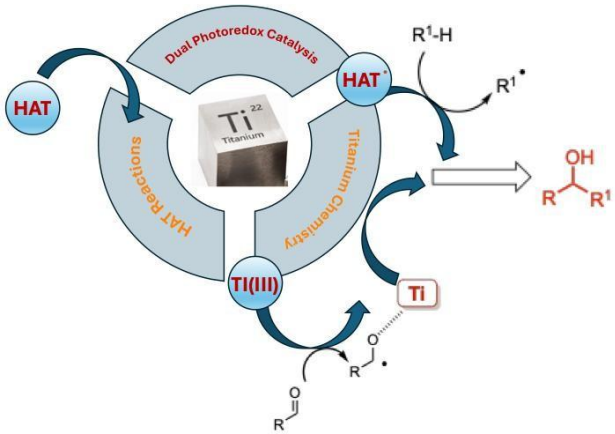

Figure 1. Supramolecolar Titanium-HAT photoredox catalysis

Acknowledgements

A.G. and P.C. acknowledge the University of Bologna for financial support. PC acknowledge the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3—Call for tender No. 1561 of 11. 10. 2022 of Ministero dell'Università e della Ricerca (MUR), funded by the European Union—

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[2] Zhang, J; Rueping, M. Metallaphotoredox catalysis for sp^3 C–H functionalizations through hydrogen atom transfer (HAT). *Chem. Soc. Rev.* **2023**, *52*, 4099-4120.

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Academic Positions & Education

Since 2022 Chair Professor, Southern University of Science and Technology, China.
Since 2018 Tenured Full Professor, Southern University of Science and Technology,China.
2012-2017 Associate Professor, Southern University of Science and Technology, China.
2010-2012 Postdoctoral, the University of Hong Kong and The Scripps Research Institute.
2006-2010 Ph.D. The University of Hong Kong.
2001-2004 M.S. Shanghai Institute of Organic Chemistry (SIOC), CAS in cooperation with Anhui Normal University AHNU.
1997-2001 B.S. Anhui Normal University (AHNU).

Research Interests

Asymmetric Radical Chemistry.

Honors & Awards

Fellow of the Chinese Chemical Society (2026), New Cornerstone Investigator Program (2025), First-Class Guangdong Natural Science Award (2024), CCS-BASF Innovation Prize (2024), XPLORER PRIZE (2023), Boehringer Ingelheim Lectureship (Boston College) (2023), Young Chiral Chemistry Investigator Award (2021), National Science Fund for Distinguished Young Scholars (2020), CAPA Distinguished Faculty Award (2019), ACP Lectureship Awards (2019), The Scholar Program-Youth Project (2018), National Science Fund for Excellent Young Scholar (2017).

Selected Publications

1. Zhang, Y.-F.; Wang, B.; Chen, Z.; Liu, J.-R.; Yang, N.-Y.; Xiang, J.-M.; Liu, J.; Gu, Q.-S.; Hong, X.; Liu, X.-Y. *Science* **2025**, *388*, 283.
2. Chen, J.-J.; Fang, J.-H.; Du, X.-Y.; Zhang, J.-Y.; Bian, J.-Q.; Wang, F.-L.; Luan, C.; Liu, W.-L.; Liu, J.-R.; Dong, X.-Y.; Li, Z.-L.; Gu, Q.-S.; Dong, Z.; Liu, X.-Y. *Nature* **2023**, *618*, 294-300.
3. Tian, Y.; Li, X.-T.; Liu, J.-R.; Cheng, J.; Gao, A.; Yang, N.-Y.; Li, Z.; Guo, K.-X.; Zhang, W.; Wen, H.-T.; Li, Z.-L.; Gu, Q.-S.; Hong, X.; Liu, X.-Y. *Nat. Chem.* **2024**, *16*, 466-475.
4. Cheng, Y.-F.; Yu, Z.-L.; Tian, Y.; Liu, J.-R.; Wen, H.-T.; Jiang, N.-C.; Bian, J.-Q.; Xu, G.-X.; Xu, D.-T.; Li, Z.-L.; Gu, Q.-S.; Hong, X.; Liu, X.-Y. *Nat. Chem.* **2023**, *15*, 395-404.
5. Wang, F.-L.; Yang, C.-J.; Liu, J.-R.; Yang, N.-Y.; Dong, X.-Y.; Chang, X.-Y.; Li, Z.-L.; Xu, G.-X.; Yuan, D.-L.; Zhang, Y.-S.; Gu, Q.-S.; Hong, X.; and Liu, X.-Y. *Nat. Chem.* **2022**, *14*, 949-957.
6. Dong, X.-Y.; Zhang, Y.-F.; Ma, C.-L.; Gu, Q.-S.; Wang, F.-L.; Li, Z.-L.; Jiang, S.-P.; Liu, X.-Y. *Nat. Chem.* **2019**, *11*, 1158-1166.

Cu/Chiral Anionic Ligand-Catalyzed Enantioselective Radical Reactions

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Keywords: Asymmetric Radical Reaction ● Chiral Anionic Ligand

Radical reactions have emerged as one of the most powerful and efficient tools for the construction of carbon–carbon and carbon–heteroatom bonds in organic synthesis. However, the development of catalytic asymmetric radical reactions to realize the stereochemical control of open-shell intermediates still remains a formidable challenge owing to the high reactivity of such free radical species. To solve this problem, our group has developed copper(I)/chiral anionic ligand catalyst to achieve a number of enantioselective radical transformations: such as the C–H functionalization, alkene difunctionalization and cross-coupling of alkyl halides, etc. The role of chiral anionic ligand is dual: it not only tunes the reducing capability of copper for the reaction initiation but also provides excellent stereocontrol induction of the reactive radical species through multiple models.

Acknowledgements
This work was financially supported by Southern University of Science and Technology (SUSTech), the National Natural Science Foundation of China (NSFC), and the Ministry of Science and Technology of China.

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6. Dong, X.-Y.; Zhang, Y.-F.; Ma, C.-L.; Gu, Q.-S.; Wang, F.-L.; Li, Z.-L.; Jiang, S.-P.; Liu, X.-Y. *Nat. Chem.* **2019**, *11*, 1158-1166.

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Academic Positions & Education

Since 2021	Professor, Colorado State University, USA
2018-2021	Associate Professor, Colorado State University, USA
2014-2018	Associate Professor, University of Oxford, UK
2010-2014	University Lecturer, University of Oxford, UK
2009-2010	Fulbright Postdoctoral Fellow, UCLA, USA
2005-2008	PhD in Chemistry, University of Cambridge, UK
2000-2004	MSc in Natural Sciences, University of Cambridge, UK

Research Interests

Computational chemistry, physical organic chemistry, machine learning and development of open-source tools, transition state modeling, and quantum chemical workflows, with applications in asymmetric catalysis, energy transfer and photoredox catalysis.

Honors & Awards

Harrison-Meldola Memorial Prize, Royal Society of Chemistry (2015), ACS COMP Division OpenEye Outstanding Junior Faculty Award (2015), Co-Chair of the Gordon Conference on Computational Chemistry (2024), Lu Jiaxi Lecturer, Xiamen University (2025), CNS Professor Laureate Award, Colorado State University (2026), Chair of IUPAC Conference on Physical Organic chemistry (2028).

Selected Publications

1. St John, P.; Guan, Y.; Kim, Y.; Kim, S.; Paton, R. S. Prediction of homolytic bond dissociation enthalpies for organic molecules at near chemical accuracy with sub-second computational cost. *Nat. Commun.* **2020**, *11*, 2328.
2. Sowndarya, S. S. V.; St. John, P. C.; Paton, R. S. A Quantitative Metric for Organic Radical Persistence Using Thermodynamic and Kinetic Features. *Chem. Sci.* **2021**, *12*, 13158–13166.
3. Sowndarya, S. S. V.; Law, J.; Tripp, C.; Duplyakin, D.; Skordilis, E.; Biagioni, D.; Paton, R. S.; St. John, P. C. Multi-objective goal-directed optimization of de novo stable organic radicals for aqueous redox flow batteries. *Nat. Mach. Intell.* **2022**, *7*, 720–730.
4. Popescu, M. V.; Paton, R. S. Dynamic Vertical Triplet Energies: A metric for predicting triplet energy transfer. *Chem* **2024**, *10*, 3428–3443.
5. Hughes, W. B.; Popescu, M. V.; Paton, R. S. Fundamental Study of Density Functional Theory Applied to Triplet State Reactivity: Introduction of the TRIP50 Dataset. *J. Chem. Theory Comput.* **2026**, *22*, 3530–3542.

Computational Strategies for Predicting Triplet-State Reactivities and Selectivities

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[a] *Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523-1872, United States*
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Keywords: Photocatalytic mechanisms ● triplet excited states ● machine learning ● computation

Photochemical and radical reactions have transformed modern synthesis, enabling bond disconnections and selectivities that are difficult to achieve through closed-shell, two-electron pathways. Yet the open-shell intermediates and excited states that drive these reactions remain notoriously hard to characterize, and harder still to predict. This talk will describe how computational chemistry, combined with machine learning, can illuminate the mechanisms of triplet-state and radical reactions and provide synthetic chemists with predictive tools for reaction design.

I will first describe machine learning approaches that predict homolytic bond dissociation enthalpies with near-DFT accuracy in milliseconds.[1] ALFABET has found applications in radical site-selectivity prediction, hydrogen-atom-transfer catalysis, and reagent design. We have also developed models for radical reactivity,[2] and for oxidation and reduction potentials, that have enabled us to think about the computer-aided design of persistent organic radicals.[3]

I will then turn to triplet excited states, where standard computational protocols often fail in subtle but consequential ways. Dynamic vertical triplet energies, obtained from quasi-classical dynamics rather than single equilibrium structures, provide a predictive metric for triplet energy transfer that enables quantitative prediction of catalyst–substrate compatibility.[4] We have also characterized the pitfalls of incorrect SCF convergence to higher triplet states in DFT calculations, that can result in incorrect predictions of triplet energies and reactivities.[5]

These tools enable mechanistic dissection of photocatalytic reactions, including enantioselective cycloadditions and a recently uncovered concerted photoeliminative cyclization.[6] Together, these examples illustrate how predictive computation can guide the rational design of photochemical and radical reactions in synthesis.

Acknowledgements
This work was financially supported by the NIH (1R01GM151533) and the NSF Center for Sustainable Photoredox Catalysis (CHE-2318141)

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Massimo Bietti

Professor of Chemistry
Professor of Organic Chemistry at the Dipartimento di Scienze e Tecnologie Chimiche, University of Rome “Tor Vergata”, Italy
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Academic Positions & Education

2019-	Full Professor, University of Rome “Tor Vergata”
2010-2011	Visiting Professor, Columbia University, USA
2002-2019	Associate Professor, University of Rome “Tor Vergata”,
1996-2002	Senior Research Associate, University of Rome “Tor Vergata”,
1995-1996	Postdoc, Max-Planck Institut für Strahlenchemie, Germany
1992-1995	PhD in Chemical Sciences, University of Rome “la Sapienza”

Research Interests

Organic reactive intermediates, mechanistic radical and radical-ion chemistry, hydrogen atom and halogen atom transfer reactions, C(*sp3*)–H bond oxygenations promoted by metal-oxo species and dioxiranes, medium effects.

Honors & Awards

“A. Mangini” Gold Medal, Organic Chemistry Division of the Italian Chemical Society (2023). Research Prize "*Organic Chemistry in its Methodological Aspects*", Organic Chemistry Division of the Italian Chemical Society (2017). Fulbright Research Scholar Grant (2010).

Selected Publications

1. Mancini, J.; Stavagna, C.; Pileri, F.; Lonardi, G.; Arpa, E.; Galeotti, M.; Sisti, S.;. Juliá, F.; Salamone, M.; Leonori, D.; Bietti M. "The Importance of Polar Effects in Halogen-Atom Transfer (XAT) from Alkyl Iodides to α-Aminoalkyl Radicals. A Kinetic and Computational Evaluation of the Role of Structural and Medium Effects." *JACS Au* **2026**, *6*, 103-112.
2. Palone, A.; Call, A.; Garcia-Roca, A,; Luis, J. M.; Sigman, M. S.; Bietti, M.; Nevado, C.; Costas, M. "Shaping of a Reactive Manganese Catalyst Enables Access to Polyfunctionalized Cyclohexanes via Enantioselective C(sp^3)−H Bond Oxidation of 1,3-meso Diethers." *Angew. Chem. Int. Ed.n* **2025**, *64*, e202507755.
3. Sisti, S.; Galeotti, M.; Scarchilli, F.; Salamone, M.; Costas, M.; Bietti, M. "Highly Selective C(sp^3)–H Bond Oxygenation at Remote Methylenic Sites Enabled by Polarity Enhancement." *J. Am. Chem. Soc.* **2023**, *145*, 22086-22096.
4. Galeotti, M.; Salamone, M.; Bietti, M. "Electronic control over site-selectivity in hydrogen atom transfer based C(sp^3)–H functionalization promoted by electrophilic reagents." *Chem. Soc. Rev.* **2022**, *51*, 2171-2223.
5. Salamone, M.; Galeotti, M.; Romero-Montalvo, E.; Van Santen, J.; Groff, B. D.; Mayer, J. M.; DiLabio, G. A.; Bietti, M. "Bimodal Evans-Polanyi Relationships in Hydrogen Atom Transfer from C(sp^3)–H Bonds to the Cumyloxyl Radical. A Combined Time-Resolved Kinetic and Computational Study." *J. Am. Chem. Soc.* **2021**, *143*, 11759-11776.

Role of Structural and Medium Effects in Chemoselective HAT-based C(sp^3)–H Bond Functionalizations

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Keywords: hydrogen atom transfer ● solvent effects ● C–H bond oxygenation ● Mn-oxo species ● dioxiranes

Site-selective C(sp^3)−H bond functionalization represents an important goal of modern synthetic chemistry. Among the available methodologies, those based on hydrogen atom transfer (HAT) to radical and radical-like species have attracted considerable interest and accordingly, the factors that govern reactivity and site-selectivity in these processes have been discussed in detail.[1] These include bond strengths, electronic, steric and stereoelectronic effects, conjugation and hyperconjugation, and, with cyclohexane derivatives, torsional effects. Medium effects have also emerged as a powerful tool that has been successfully employed to alter reactivity and site-selectivity in HAT based C(sp^3)−H functionalization procedures.[2]

Within this framework, we have been interested in the study of HAT reactions from C(sp^3)−H bonds, with the main objective of obtaining quantitative information on the role of structural and medium effects on reactivity, chemoselectivity and stereoselectivity. This goal has been achieved through time-resolved kinetic studies on the reactions of a prototypical alkoxyl radical such as cumyloxyl ($PhC(CH_3)_2O$, CumO•) with a wide variety of substrates, accompanied by studies on C(sp^3)−H oxygenation of selected substrates with dioxiranes and with hydrogen peroxide catalyzed by manganese complexes. Some results of these studies will be discussed, accompanied by recent examples on the application of these concepts to synthetically useful C(sp^3)−H functionalization procedures, with particular attention being devoted to the role of solvent effects on the reaction chemoselectivity.

References

[1] (a) Newhouse, T.; Baran, P. S. *Angew. Chem. Int. Ed.* **2011**, *50*, 3362-3374. (b) White, M. C.; Zhao, J. *J. Am. Chem. Soc.* **2018**, *140*, 13988-14009. (c) Capaldo, L.; Ravelli, D.; Fagnoni, M. *Chem. Soc. Rev.* **2022**, *122*, 1875-1924. (d) Galeotti, M.; Salamone, M.; Bietti, M. *Chem. Soc. Rev.* **2022**, *51*, 2171-2223.
[2] Bietti, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 16618-16637.

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Academic Positions & Education

Since 2012	Professor, University of Basel (Switzerland)
2009-2012	Associate Professor, University of Göttingen (Germany)
2006-2009	Assistant Professor, University of Geneva (Switzerland)
2004-2006	Postdoctoral Fellow, University of Strasbourg (France)
2002-2004	Postdoctoral Fellow, California Institute of Technology (USA)
1998-2002	PhD in Chemistry, University of Bern (Switzerland)
1994-1998	Diploma degree in Chemistry, University of Bern (Switzerland)

Research Interests

Photophysics and photochemistry of organic molecules and coordination compounds, mechanistic photocatalysis, development of transition metal based luminophores and photocatalysis, light-driven charge accumulation.

Honors & Awards

Japan Gateway Program, Kyoto (2017), Ambassadeur de CNRS Chimie, Centre national de la recherche scientifique, France (2019), *ERC Advanced Grant* – BREAKING KASHA (2024), Presidential Award of the Inter-American Photochemical Society (2025).

Selected Publications

1. Sinha, N.; Wegeberg, C. Häussinger, D.; Prescimone, A.; Wenger, O. S. Photoredox-active chromium(0) luminophores featuring photophysical properties competitive with Ru(II) and Os(II) complexes. *Nat. Chem.* **2023**, *15*, 1730.
2. Wang, C.; Li, H.; Bürgin, T. H.; Wenger, O. S. Cage escape governs photoredox reaction rates and quantum yields. *Nat. Chem.* **2024**, *16*, 1151.
3. Brändlin, M.; Pfund, B.; Wenger, O. S. Photoinduced double charge accumulation in a molecular compound. *Nat. Chem.* **2025**, *17*, 1777.

Organic Radical Reactivity in Photoredox Catalysis

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Keywords: cage escape ● ConPET ● anti-Kasha reactivity ● transient absorption spectroscopy

The first part of this presentation focuses on the role of cage escape of geminate radical pairs formed in photoredox catalysis and on how this elementary step influences the overall quantum yields of photochemical reactions.[1]

The second part addresses excited organic radicals and their function in photoredox catalysis. Using time resolved laser spectroscopy, we directly observe photoinduced electron transfer from excited organic radicals to substrate molecules and identify preaggregation of the organic radicals with the substrates as a prerequisite for this reactivity, owing to the picosecond excited state lifetimes of the radicals.[2]

Furthermore, we provide direct evidence for photoreactions originating from higher electronically excited states of organic radicals (Figure 1),[3] thereby bypassing a long-standing principle rooted in photophysics, which implies that only the lowest electronically excited state of a given spin multiplicity exhibits appreciable photoreactivity.

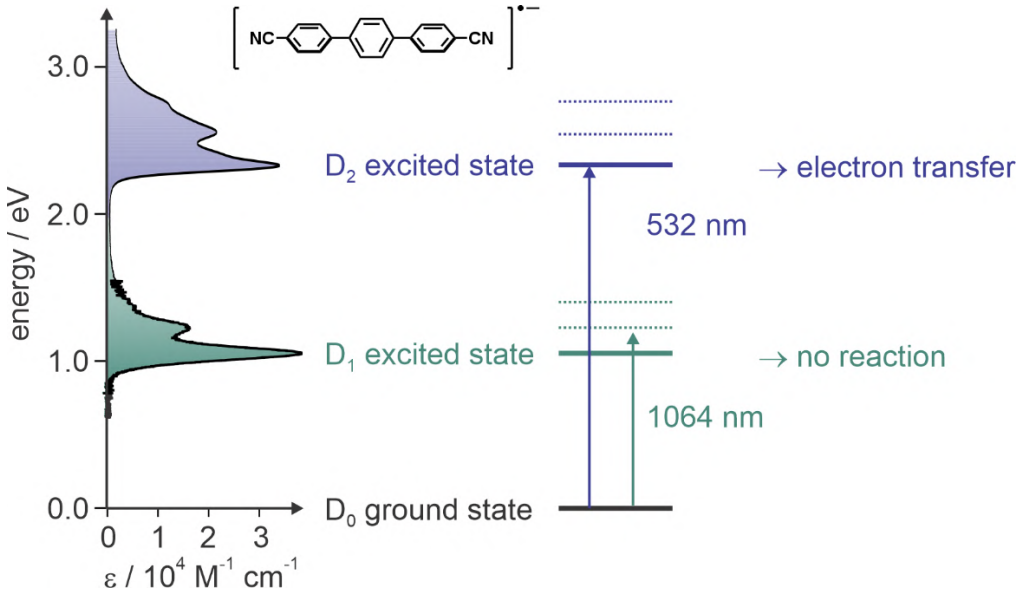

Figure 1. Bypassing Kasha's rule with electronically excited organic radicals.

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[2] Pfund, B.; Gejsnaes-Schaad, D.; Lazarevski, B.; Wenger, O. S. *Nat. Commun.* **2024**, *15*, 4738.
[3] Pfund, B.; Wenger, O. S. *J. Am. Chem. Soc.* **2025**, *147*, 26477−26485.

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Professor of Chemistry at Korea Advanced Institute of Science and Technology (KAIST) & IBS, Korea
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Academic Positions & Education

Since 2009	Professor, Korea Advanced Institute of Science and Technology (KAIST)
Since 2018	Associate Director at CCHF (IBS)
2006-2009	Principal Scientist, GlaxoSmithKline
2004-2006	Postdoctoral Fellow, Harvard University (Prof. Corey)
2000-2004	PhD in Chemistry, Pennsylvania State University (Prof. Weinreb)

Research Interests

Development of new reactions, synthesis, catalysis, sustainable synthesis using visible light, medicinal chemistry, chemical biology.

Honors & Awards

Fellow of KAST (2023), Academic Excellence Award (2022), Shim Sang Cheol Academic Award (2018) Young Organic Chemist Award (2012). Co-Chair, Asian Journal of Organic Chemistry (2020 – present)

Selected Publications

1. Lee, W.; Koo, Y.; Jung, H.; Chang, S.; Hong, S. Energy-Transfer-Induced [3+2] Cycloadditions of N−N Pyridinium Ylides. *Nature Chem.* **2023**, *15,* 1091.
2. Lee, C.; Kim, M.; Han, S.; Kim, D.; Hong, S. Nickel-Catalyzed Hydrofluorination in Unactivated Alkenes: Regio- and Enantioselective C–F Bond Formation. *J. Am. Chem. Soc.* **2024**, *146,* 9375.
3. Jeong, J.; Cao, S.: Kang, H.-J; Yoon, H. ; Lee, J. ; Shin, S.; Kim, D.; Hong, S. Divergent Enantioselective Access to Diverse Chiral Compounds from Bicyclo[1.1.0]butanes and α,β-Unsaturated Ketones under Catalyst Control. *J. Am. Chem. Soc.* **2024**, *146,* 27830.
4. Tao, X.; Han, H.; Jeong, J.; Kim, D.: Hong, S. Transformation of Pyridines into 2D and 3D Fused Bicyclic Heterocycles. *J. Am. Chem. Soc.* **2025***, 147,* 21143.
5. Choi, W.; Jang, A.; Hong, S. Pyridine-to-Pyridazine Skeletal Editing. *J. Am. Chem. Soc.* **2025***, 147,* 42042
6. Kim, C.; Jeong, J.; Lee, W.; Hong, S. Photocatalytic Reconstruction of Bicyclo[1.1.0]butanes to Oxygenated Bicycles. *J. Am. Chem. Soc.* **2026***, in press*.

A Photocatalytic Platform for Atom Transfer and Diversification via Reversible Triplet Activation of Pyridinium Ylides

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Keywords: pyridinium ylides ● BCB ● triplet energy transfer ● atom-transfer reagent

Here I will present pyridinium ylides as a new class of photocatalytic atom-transfer reagents that enable oxygen- and nitrogen-group transfer with high chemoselectivity and broad functional-group tolerance. The fundamental principle of this platform originates from our discovery that N–N pyridinium ylides undergo reversible triplet–triplet energy transfer under visible-light irradiation to generate highly reactive triplet diradicals. This controllable open-shell intermediate enabled stepwise radical [3+2] cycloadditions with activated and unactivated alkenes, delivering diastereoselective pyridyl lactams. Upon photocatalytic excitation, pyridinium ylides function as programmable oxene and imino surrogates, enabling aziridination, epoxidation, and oxo- and imino-transfer reactions. Furthermore, this atom-transfer logic extends to strain-release reactivity. In bicyclo[1.1.0]butanes, selective C–C bond cleavage followed by photoinduced ring reclosure provides oxygenated bicyclic architectures with new exit vectors, expanding access to saturated benzene bioisosteres. By positioning pyridinium ylides as photocatalytic atom-transfer reagents grounded in reversible triplet diradical activation, this work establishes a unified and programmable platform for single-atom incorporation, diversification, and heterocycle construction under mild photochemical conditions.

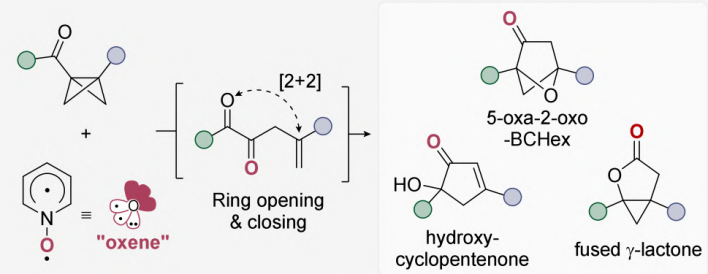

Figure 1. Programmed ring opening and reclosing of BCBs under visible-light photocatalysis

Acknowledgements
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[1] Kim, C.; Jeong, J.; Lee, W.; Hong, S. Photocatalytic Reconstruction of Bicyclo[1.1.0]butanes to Oxygenated Bicycles. *J. Am. Chem. Soc.* **2026**, *in press.*
[2] Lee, W.; Kim, C.; Jang, A.; Hong, S. Pyridinium Ylides as Photocatalytic Atom Transfer Reagents. *J. Am. Chem. Soc.* **2026**, *Nature Commun.* ***2025****, 16,* 10716*.*
[3] Lee, W.; Koo, Y.; Jung, H.; Chang, S.; Hong, S. Energy-Transfer- induced [3+2] Cycloadditions of N−N Pyridinium Ylides. *Nature Chem.* **2023**, *15*, 1091.

Franziska Schoenebeck

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Academic Positions & Education

Since 2016	Full Professor & Chair (W3), RWTH Aachen University (Germany)
2013-2016	Professor (W2), RWTH Aachen University (Germany)
2010-2013	Junior Group Leader/Assistant Professor, ETH Zürich
2008-2010	AvH Feodor Lynen Postdoctoral Fellow, UCLA (USA)
2004-2008	PhD in Organic Chemistry, University of Strathclyde, Glasgow (UK)
2001-2004	BSc Hons in Chemistry, TU Berlin & University of Strathclyde (UK)

Research Interests

Our research brings together synthetic organic chemistry, homogeneous catalysis, mechanistic insight, computational studies and machine learning to uncover new principles of chemical reactivity, design innovative catalysts and tackle key challenges in modern synthesis.

Honors & Awards

2025 EJ Corey Award for Outstanding Original Contribution in Organic Synthesis by a Young Investigator; 2025 Dr. Margaret Faul Women in Chemistry Award; 2025 RSC/GDCh Alexander Todd-Hans Krebs Lectureship in Chemical Sciences; 2024 Thieme-IUPAC Prize; 2023 IPMI Carol Tyler Award; 2022 Tetrahedron Young Investigator Award; 2020 Klung-Wilhelmy-Wissenschafts-Preis ; EROS Best Reagent Award 2020; ERC Consolidator Grant (2020-2025); ERC Starting Grant (2015-2020); 2014 ORCHEM Prize ; 2014 Dozentenpreis, Fonds der Chemischen Industrie; 2014 JPOC Award for Early Excellence in Physical Organic Chemistry ; 2012 ADUC Prize (in 2013).

14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Radically New Pathways in Metal Catalysis

Franziska Schoenebeck[a]

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Keywords: Metal ● Mechanism ● Experiment ● Computation ● One-electron step

This lecture will highlight case studies that reveal alternative elementary steps involving one-electron processes in widely employed metal-catalyzed reactions, rationalize their occurrence and demonstrate how such pathways can be predicted.

David A. Nagib

Harold and Betty Miller Professor of Organic Chemistry
Department of Chemistry, The Ohio State University
Columbus, USA
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Homepage: https://research.cbc.osu.edu/nagib.1/

Academic Positions & Education

Since 2022	Professor of Organic Chemistry, The Ohio State University
2020-2022	Associate Professor of Chemistry, The Ohio State University
2014-2020	Assistant Professor, The Ohio State University
2011-2014	NIH Postdoctoral Fellow, University of California, Berkley
2006-2011	PhD, Princeton University (Prof. D. W. C. MacMillan
2002-2006	BS, Boston College

Research Interests

Radical chemistry, carbene chemistry, synthetic methodology, C-H activation, C-O activation.

Honors & Awards

JACS ‘Most Read’ Article (2024), Blatvanik Finalist (2024), Brown Investigator Award (2023)m Arthur C. Cope Scholar (2021), Merck Outstanding Chemists of Colour (2021), Lilly Young Investigator (2020), Sloan Research Fellowship (2019), JACS Young Investigator (2018)

Selected Publications

1. Nguyen, K.N.M.; † Mo, X.; † DeMuynck, B. M.; Elsayed, M.; Garwood, J.J.A.; Ngo, D. T.; Rana, I. K.; Nagib, D. A.*, Harnessing carbene polarity: Unified catalytic access to donor, neutral, acceptor carbenes, *Science*, **2025**, 389, 183–189
2. Garwood, J. J. A.; Chen, A. D.; Nagib, D. A.*, Radical Polarity, *J. Am. Chem. Soc.*, **2024**, 146, 28034–28059
3. Zhang, L.; DeMuynck, B. M.; Paneque, A. N.; Rutherford, J. E.; Nagib, D. A.*, Carbene Reactivity from Alkyl and Aryl Aldehydes, *Science*, **2022**, 377, 649–654
4. Wang, L.; Lear, J. M.; Rafferty, S.; Fosu, S.C.; Nagib, D. A.*, Ketyl radical reactivity via atom transfer catalysis, *Science*, **2018**, 362, 225−229

14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Radical Polarity (2.0)

David Nagib[a]

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Keywords: radicals ● polarity ● machine learning ● big data analysis ● kinetics vs thermodynamics

Radical chemistry is often considered primarily in terms of thermodynamic factors (e.g. BDE). However, kinetic aspects (e.g. radical polarity) are similarly important in predicting and troubleshooting radical reactivity. We have recently reported a database with experimentally validated DFT calculations of >500 radicals that are commonly invoked in organic synthesis.[1] Enabled by machine learning (ML) tools, we have now expanded this database to >10 million radicals whose polarity can be instantly predicted, including through a new web application. With this larger dataset, we then conducted a meta-analysis on hundreds of rates for each radical reaction class – quantifying the relative impacts of various thermodynamic and kinetic factors (BDE, polarity, sterics). We are excited to share these preliminary findings with our fellow radical enthusiasts.

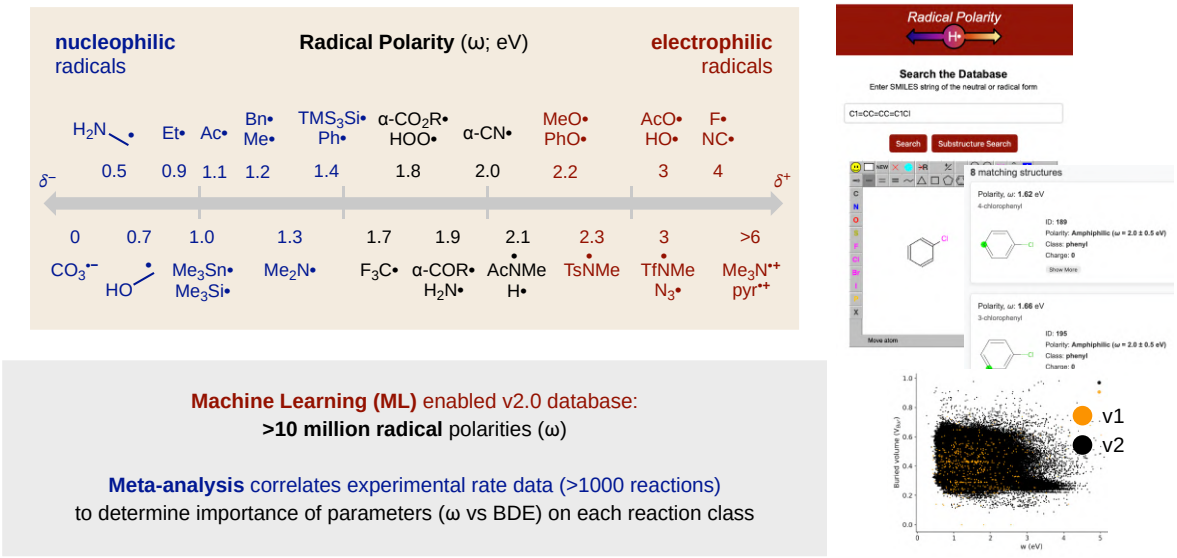

Figure 1. Radical Polarity (v2.0): A significantly larger database and meta-analysis enabled by machine learning

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Garwood, J. J. A.; Chen, A. D.; Nagib, D. A. Radical Polarity. *J. Am. Chem. Soc.,* 2024, *146*, 28034–28059.

Unpublished.

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Academic Positions & Education

Since 2012	Professor of Organic Chemistry and Catalysis, Leipzig University
2011-2012	University Docent, Universität Regensburg, Germany
2008-2011	Habilitand, Universität Regensburg, Germany
2007-2008	Deputy Professor, LMU München, Germany
2004-2007	Postdoctoral Fellow, University of Pennsylvania, USA
1996-2001	PhD, LMU München, Germany (Prof. Wolfgang Steglich)

Research Interests

Photocatalysis, organocatalysis, biomimetic transformations, NHC catalysis

Honors & Awards

Best habilitation, Universität Regensburg (2011), Award of the Otto-Röhm-Memorial Foundation (2008), Thieme Journal Award (2005), Liebig Fellowship of the Fonds der Chemischen Industrie (2004), Postdoctoral Fellowship of the German Academic Exchange Service (DAAD) (2001)

Selected Publications

1. Chen, M.S.; White, M.C., A Predictably Selective Aliphatic C—H Oxidation Reaction for Complex Molecule Synthesis., *Science*, **2007**, *318*, 783-787.
2. Chen, M.S.; White, M.C., Combined Effects on Selectivity in Fe-Catalyzed Methylene Oxidation., *Science* **2010**, *327*, 566
3. Clark, J.R.; Feng, K.; Sookezian, A.; White, M.C., Manganese-Catalyzed Benzylic C(sp3)—H Amination for Late-Stage Functionalization., *Nature Chemistry* **2018**, *10***,** 583.
4. Feng, K.; Quevedo, R.E.; Kohrt, J.T.; Oderinde, M. S.; Reilly, U.; White, M.C., Late-Stage Oxidative C(sp3)-H Methylation, *Nature* **2020**, *580*, 621-627.
5. Ali, S.Z.; Budaitis, B.G.; Fontaine, D.F.A.; Pace, A.L.; Garwin, J.A.; White, M.C., Allylic C—H Amination Cross-Coupling Furnishes Tertiary Amines by Electrophilic Metal Catalysis., *Science* **2022**, *376*, 276.
6. Kaster, S.H.M.; Zhu, L.; Lyon, W. L.; Ma, R. Amman, S.E.; White, M.C., Cross-coupling of alcohols with olefins via positional tuning of a counteranion in transition metal catalysis, *Science*, **2024**, *385*, 1067.
7. Ahn, C.; Gomez, A.; Hartmann, M. A.; White, M.C., Selective methylene oxidation in a,b-unsaturated carbonyl natural products, *Nature*, **2025**, *648,* 607.

14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Unlocking Inaccessible Substrates for Direct Intermolecular Photocatalytic Ring-Opening Remote Alkylative C-C-Functionalization of Cycloalkanols – PCET beyond Simple pK_a-Related Base Effects

Michael Klimkait,[a] Nele Berg,[b] Silvan Allerbeck, [a] Ruth M. Gschwind[b] and Kirsten Zeitler[a]

[a] *Institute of Organic Chemistry, Leipzig University, D-04103 Leipzig, Germany*
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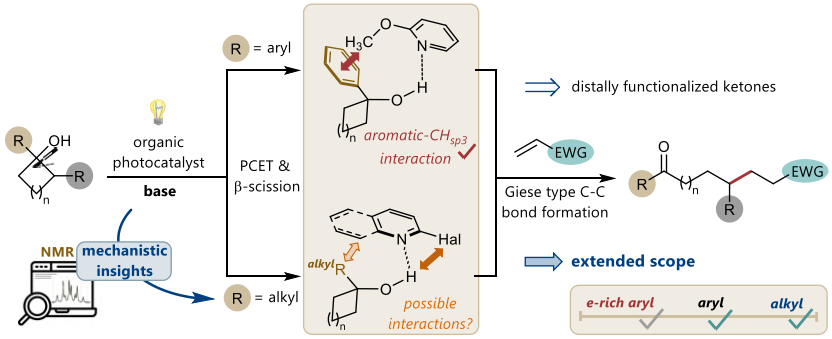
Keywords: photoredox catalysis ● PCET ● hydrogen-bridge bonds ● alkoxy radicals ● remote functionalization

Oxidative multisite proton-coupled electron transfer (MS-PCET) reactions, particularly those occurring under metal-free pho¬to¬catalytic conditions using visible light, have emerged as a promising tool for the activation of strong O-H bonds in (cyclo)alkanols. However, these methods often require the use of e-rich arene-containing derivatives (*para*-methoxyphenyl (PMP), etc.) – a factor that greatly restricts their broader applicability.

Herein, we report the successful implementation of targeted modulation of the base partner in photocatalytic cascade reactions of cyclic alcohols, unlocking previously rather inaccessible, non-activated substrates. This approach successfully circumvents the prevalent limitations of ring-opening transformations of cycloalkanols by deliberately promoting base-alcohol interactions. As a result, we here demonstrate a general, operationally simple and widely applicable protocol for the redox-neutral transformations of cycloalkanols into terminally C(sp^3)-C(sp^3)-coupled, functionalized open-chain products.[1]



In-depth NMR-based H-bond analysis have elucidated the key importance of additional weak interactions in promoting a pivotal productive alcohol-base pre-organization were directly put into practice to successfully pioneer remote alkylative Giese-type C-C-bond formations of previously challenging *alkyl*-substituted cycloalkanols.

Acknowledgements
Financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through grant TRR 325 “Assembly Controlled Chemical Photocatalysis” (grant no. 444632635, projects B3, B6 and C2) is gratefully acknowledged.

References
[1] Klimkait, M.; Berg, N.; Gschwind, R. M.; Zeitler, K., *ChemRxiv* **2025**, DOI: 10.26434/chemrxiv-2025-j62j0.

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https://scholar.google.com/citations?user=ZKSWKxYAAAAJ&hl=en

Academic Positions & Education

Since 2020	Professor, Aix Marseille University
2005-2020	Associate Professor, Aix Marseille University
2003-2005	Postdoctoral Fellow in Chemistry, University of Texas in Dallas (USA)
2003	Postdoctoral Fellow in Chemistry, UNED, Madrid (Spain)
2000-2002	Research assistant, Aix Marseille University
1999-2000	Postdoctoral Fellow in Chemistry, UCL (Belgium)
1995-1999	PhD in Chemical Sciences, Aix Marseille University

Research Interests

Free radicals, nitroxide chemistry; nuclear spin hyperpolarization and DNP/ssNMR, water-soluble redox active organic electrolytes for energy storage, photochemical spin polarization, and EPR spectroscopy.

Selected Publications

1. De Biasi, F.; Karthikeyan, G.; Visegrádi, M.; Levien, M.; Hope, M.A.; Brown, P.J.; Wasielewski, M. R.; Ouari, O.; Emsley, L. Light-Induced ^{1}H NMR Hyperpolarization in Solids at 9.4 and 21.1 T.n*J. Am. Chem. Soc.* **2024**, 146, 19667-19672.
2. Boutamine, K.; Casano, G.; Bassil, P.; Gauden, S.; Poderi, C.; Pepe, E.; Favier, F.; Le Vot, S.; Ouari, O. High Power Isoindoline-based Nitroxides as Posolytes for Aqueous Organic Redox Flow Batteries. *ChemSusChem*, **2026**, 19, e202502461.
3. Venkatesh, A.; Casano, G; Wei, R; Rao, Y; Lingua, H; Karoui, H; Yulikov, M; Ouari, O.; Emsley, L. Rational design of dinitroxide polarizing agents for dynamic nuclear polarization to enhance overall NMR sensitivity. *Angew. Chem. Int. Ed.* **2024**, 63, e202317337.

The Many Lives of Radicals: Powering Energy Storage and Transforming NMR Spectroscopy

Sebastien Gauden,[a] Soléyah Houguet,[a] Gilles Casano,[a] Karthikeyan Ganesan,[a] Hakim Karoui,[a] Steven LeVot,[b] Moreno Lelli,[c] Anne Lesage,[d] Lyndon Emsley,[e] and Olivier Ouari[a]

[a] *ICR, Aix Marseille University, CNRS, Marseille*
[b] *ICGM, University of Montpellier CNRS, Montpellier*
[c] *CERM, University of Florence, Firenze*
[d] *CRMN, University of Lyon, Villeurbanne*
[e] *LMR,* EPFL, Lausanne

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Keywords: stable and transient radicals ● DNP ● CIDNP ● organic aqueous redox flow battery

Stable and transient free radicals constitute versatile molecular platforms owing to their distinctive redox, magnetic, and (photo)chemical properties. Through rational design, radical-based systems can be tailored *de novo* to meet the specific requirements of advanced applications, including enhanced nuclear magnetic resonance (NMR) spectroscopy and energy storage in aqueous organic redox flow batteries (OARFBs).

In this work, we demonstrate that expanding the chemistry of nitroxide (bi)radicals opens new avenues in both spin dynamics and energy storage. Also, we show that transient spin-correlated radical pairs generated from donor–chromophore–acceptor architectures can enhance ^{1}H NMR signals by up to two orders of magnitude.

The intrinsically low sensitivity of NMR spectroscopy remains a major limitation for probing structure and dynamics in solids. Dynamic nuclear polarization (DNP), based on microwave-driven polarization transfer, has emerged as a powerful strategy to enhance NMR sensitivity across a wide range of sample types. Complementarily, optical approaches can generate ^{1}H and ^{13}C hyperpolarization in solids at high magnetic fields. Here, we report a photochemically induced DNP (photo-CIDNP) mechanism enabled by a donor–chromophore–acceptor system, in which the excited-state electron–electron interaction matches the nuclear Larmor frequency. This design allows efficient hyperpolarization under high-field conditions. Via polarization relay, bulk signal enhancements ($\varepsilon \approx 100$) were achieved for ^{1}H nuclei at 9.4 and 21.1 T under magic-angle spinning at 100 K.[1] These results establish a general framework for light-driven hyperpolarization strategies in high-field solid-state NMR.

Beyond spectroscopy, the transition toward renewable energy sources necessitates efficient and sustainable energy storage technologies. Aqueous organic redox flow batteries represent a promising alternative to current vanadium-based systems, benefiting from the use of earth-abundant and tunable organic materials. However, further improvements in solubility, redox properties, kinetics, and long-term stability are required. We show that finely tuned radical organic molecules (ROMs) provide a powerful platform to address these challenges,[2] towards the development of high-performance, cost-effective, and environmentally benign OARFB systems.

References

[1] De Biasi, F. et al. *J. Am. Chem. Soc*. **2024**, *146*, 19667−19672.
[2] Boutamine, K. et al. *Energy Storage Materials*, **2025**, *80*, 104379-104388.

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Academic Positions & Education

Since 2016	Professor, University of Ottawa
2010-2016	Associate Professor, University of Ottawa
2005-2010	Assistant Professor, University of Ottawa
2003-2005	Postdoctoral Fellow in Chemistry, University of Illinois
1999-2003	PhD in Chemistry, Vanderbilt University
1993-1999	BSc in Chemistry, Carleton University

Research Interests

radical chemistry, mechanisms, hydrogen atom transfer, lipid peroxidation, antioxidants, ferroptosis

Honors & Awards

Clarivate Highly Cited Researcher (2025), Bernard Belleau Award, Canadian Society for Chemistry (2024), Howard Alper Award for Excellence in Research, uOttawa (2023), University Research Chair in Free Radical Chemistry (2021-2026), Excellence in Research Award, Faculty of Science, uOttawa (2020), Friedrich Wilhelm Bessel Award, Alexander von Humboldt Foundation (2019), Discovery Accelerator Award, NSERC (2016), Keith Fagnou Award, Canadian Society for Chemistry (2015), Canada Research Chair in Free Radical Chemistry (2011-2016), Polanyi Prize in Chemistry (2007), Early Researcher Award, Ontario Ministry of Research and Innovation (2006), Journal Award, Thieme (2006), Canada Research Chair in Free Radical Chemistry (2005-2010)

Selected Publications

1. Farmer, L. A.; Wu, Z.; Poon, J.-F.; Zilka, O.; Lorenz, S. M.; Huehn, S.; Proneth, B.; Conrad, M.; Pratt, D. A. Intrinsic & Extrinsic Limitations to the Design and Optimization of Inhibitors of Lipid Peroxidation and Associated Cell Death. *J. Am. Chem. Soc.* **2022**, *144*, 14706-14721.
2. Donohoe, M. N.; Upadhyay, A.; Pratt, D. A. Ligand-Based Radical Reactivity of Metal Thiosemicarbazones Prompts the Identification of Platinum(II)-Based Cytoprotectants. *J. Am. Chem. Soc.* **2024**, *146*, 31307-31320.
3. Wu, Z.; Vlaming, R.; Donohoe, M. N.; Pratt, D. A. Interrupted Homolytic Substitution Enables Organoboron Compounds to Inhibit Radical Chain Reactions Rather than Initiate Them. *J. Am. Chem. Soc.* **2024**, *146*, 1153–1166.
4. Dehdari, A.; Poon, J.-F.; Pratt, D. A. Intramolecular Hydrogen Atom Transfer Enables Hydroperoxyl Radical Formation During the Peroxidation of Unsaturated Lipids. *J. Am. Chem. Soc.* **2025**, *147*, 41897–41912.

Suppressing Chain Reactions in Subcellular Spaces to Treat Disease

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Keywords: hydrogen atom transfer ● lipid peroxidation ● radical-trapping antioxidants ● ferroptosis ● neurodgeneration

Hydrogen atom transfer between the unsaturated sidechains of membrane phospholipids and peroxyl radicals derived therefrom propagates lipid peroxidation, a chain reaction that leads to cell death.[1] This form of cell death, termed ferroptosis, contributes to neurodegeneration and ischemia-reperfusion injury following organ transplant or stroke. Despite decades of research on the inhibition of lipid peroxidation by small molecules, no clinically validated therapies that selectively target ferroptosis are available. Phenoxazines are among the most reactive compounds to peroxyl radicals identified so far ($k > 10^7$ $M^{-1}s^{-1}$), easily out-competing surrounding lipids for propagating radicals, and unlike other similarly reactive scaffolds, are remarkably robust in air.[2] These unique attributes translate to biological contexts, where they are among the most potent inhibitors of lipid peroxidation and ferroptotic cell death, and – with appropriate substitution – resistant to oxidative metabolism.[3] We recently discovered[4] that directing phenoxazines to the membranes of lysosomes markedly enhances their activity. A similar increase in the potency of phenolic and non-canonical inhibitors of lipid peroxidation suggests that lysosome-targeting represents a general strategy for augmenting ferroptosis suppression. Molecular dynamics simulations indicate that lysosome-targeted phenoxazines accumulate near the membrane–water interface, in proximity to the unique reactive sites of the polyunsaturated lipids implicated in ferroptosis. A representative lysosome-targeted phenoxazine afforded unprecedented protection from acute kidney failure and death resulting from inactivation of ferroptosis suppressor GPX4. These findings identify subcellular localization and proximity to the membrane interface as determinants of ferroptosis suppression and support a functional role for lysosomes in ferroptotic cell death, while providing a widely bioavailable, brain-penetrant scaffold to advance toward the clinic.

Acknowledgements
This work was financially supported by the Natural Sciences and Engineering Research Council of Canada.

References
[1] Conrad, M.; Pratt, D. A. *Nat. Chem. Biol.* **2019**, *15*, 1137-1147.
[2] Farmer, L. A.; Haidasz, E. A; Griesser, M.; Pratt, D. A. *J. Org. Chem.* **2017**, *82*, 10523-10536.
[3] Farmer, L. A.; Wu, Z.; Poon, J.-F.; Zilka, O.; Lorenz, S. M.; Huehn, S.; Proneth, B.; Conrad, M.; Pratt, D. A. *J. Am. Chem. Soc.* **2022**, *144*, 14706-14721.
[4] Upadhyay, A.; Farmer, L. A.; Lorenz, S. M.; Dehdari, A.; Kiesewetter, D.; Novikova, M.; Kiliç, E.; Mallais, M.; Donohoe, M. N.; Barayeu, U.; Gräter, F.; Dixon, S. J.; Proneth, B.; Conrad, M.; Pratt, D. A. submitted.

Rebecca Melen

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Academic Positions & Education

Since 2021	Professor, Cardiff University (UK)
2019–2021	Reader, Cardiff University (UK)
2017–2019	Senior Lecturer, Cardiff University (UK)
2015–2016	Visiting Professorship with Prof. Dr. Martin Oestreich, Technische Universität Berlin (Germany)
2014–2017	Lecturer, Cardiff University (UK)
2013–2014	Alexander von Humboldt Fellowship with Prof. Dr. Lutz H. Gade, Ruprecht-Karls-Universität Heidelberg, (Germany)
2012–2013	Postdoctoral Fellowship with Prof. Douglas W. Stephan, University of Toronto (Canada)
2008–2012	PhD with Prof. Dominic S. Wright, University of Cambridge (UK)
2007–2008	MSc, University of Cambridge (UK)
2004–2007	BA, University of Cambridge (UK)

Research Interests
Catalyst Design: ligand design and developing catalysts based upon the main group elements. Metal-Free Catalysis: main group catalysis and frustrated Lewis pair chemistry. Reaction Mechanisms: using DFT, EPR and kinetic studies to elucidate reaction mechanisms. Industrial Applications: working with pharmaceutical, petrochemical and semiconductor industries.

Honors & Awards
RSC Dalton Young Researcher Award (2013), Clara Immerwahr award (2016), Fellow Higher Education Academy (2016), Thieme Journal Award Winner (2018), EPSRC Fellowship (2018), Learned Society of Wales, Dillwyn Medal (2019), RSC Harrison Meldola Memorial Prize (2019), Bürgenstock Conference Fellowship (2019), Philip Leverhulme Prize (2022), Elected Fellow of the Learned Society of Wales (2022), RSC Sir Geoffrey Wilkinson Prize (2025), ERC consolidator Grant “RadicalCAT” (2025).

Selected Publications

1. Van der Zee, L.; Pahar, S.; Richards, E.; Melen, R.L.; Slootweg, J.C. *Chem Rev.*, **2023**, *123*, 9653.
2. Ayan, D.; Richards, E.; Melen, R. L. *Angew. Chem. Int. Ed.* **2021**, *60*, 53.
3. Dasgupta, A.; Stefkova, K.; Babaahmadi, R.; Buurma, N. J.; Yates, B. F.; Ariafard, A.; Richards, E.; Melen, R. L. *J. Am. Chem. Soc*. **2021**, *143*, 11, 4451.
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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Single or Double? A Radical Approach to Frustrated Lewis Pairs

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Keywords: Frustrated Lewis Pair ● Boron ● Phosphorus ● Radical ● Catalysis

The donor-acceptor ability of frustrated Lewis pairs (FLPs) has led to widespread applications in recent years.[1] Recently, it was shown that single electron transfer (SET) from a Lewis base donor to a Lewis acid acceptor can produce a frustrated radical pair (FRP) species. This depends on both the substrate and energy required (photochemical or thermal) to promote an FLP into an FRP.[2] In this talk, I will discuss C–C[3,4] (see Figure 1), C–N, and C–S[5,6] bond forming reactions using FLPs. The nature of these reaction pathways as well as their selectivity has been investigated by extensive electron paramagnetic resonance (EPR) studies, kinetic studies, and density functional theory (DFT) calculations to elucidate the mechanism of these coupling reactions.

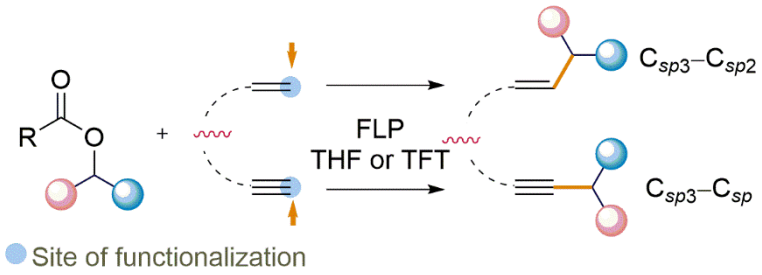

Figure 1. Cross-coupling reactions using FLPs.

Acknowledgements
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[6] Pramanik, M; Alotaibi, N.; Boruah, T.; Buurma, N. J.; Babaahmadi, R.; Wirth, T.; Melen, R. L. *J. Am. Chem. Soc*. **2026**, *148,* 5325.

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Academic Positions & Education

Since 2022	Assoc Director
2013-2022	Senior Principal Scientist
2002-2013	Principal Scientist
1995-2002	Senior Scientist
1993 and 1994	Research Period, Royal Danish School Pharmacy, Copenhagen (DK)
1991-1996	PhD in Chemical Sciences, University of Castilla-La Mancha
1985-1990	MSc in Chemistry, University of Castilla-La Mancha

Research Interests
Medicinal chemistry, Flow Chemistry, Photochemistry, Radical chemistry and Organic Synthesis. How to enable novel chemistry for the discovery of new drugs.

Honors & Awards
Implementation of 3 different technologies: microwave, H-CUBE and Flow chemistry, technologies that are currently used at J&J worldwide. Several J&J awards, among others Lead Discovery outstanding scientist (2015), Innovation Leadership award (2020). Impact on programs from different therapeutic areas, such as Oncology, Infectious Diseases, Neurosciences and Immunology.

Selected Publications

1. Ruizhe Chen, Nicholas E. Intermaggio, Jiaxin Xie, James A. Rossi-Ashton, Colin A. Gould, Robert T. Martin, Jesús Alcázar, David W. C. MacMillan, P. Alcohol-alcohol cross-coupling enabled by SH2 radical sorting. *Science.* **2024**, *383*, 1350.
2. Wei Liu, Marissa N. Lavagnino, Colin A. Gould, Jesús Alcázar, David W. C. MacMillan. A biomimetic SH2 cross-coupling mechanism for quaternary sp3-carbon formation. *Science.* **2021**, *374*, 1258.
3. Brenda Pijper, Irini Abdiaj, Javier Mazuela, Maria Lourdes Linares, José Enrique Gómez, Raquel Rodriguez, Belén Chaves Arquero, Eduardo Palao, Santiago Cañellas, Jesús Alcázar. Multistep and multivectorial assembly line library synthesis in flow. *Chem Catalysis.* **2024**, 101118.
4. Brenda Pijper, Lucía M. Saavedra, Matteo Lanzi, Maialen Alonso, Alberto Fontana, Marta Serrano, José Enrique Gómez, Arjan W. Kleij, Jesús Alcázar, Santiago Cañellas. Addressing Reproducibility Challenges in High-Throughput Photochemistry. *JACS Au* **2024**, *4*, 2585.

Applications of photochemistry to enable chemical space in Drug Discovery

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Keywords: Photochemistry ● Flow Chemistry ● Drug Discovery ● Radical Chemistry

Since 2015 we have been implementing Photochemistry in flow at Johnson & Johnson as a new tool to access challenging chemical compounds to accelerate our Discovery programs. We have achieved important impacts on several programs from different therapeutic areas: neuroscience, oncology, infectious diseases and immunology to name a few. We have also made photochemistry a common tool for increasing F(sp3) and improving pharmacokinetic properties on our molecules by enabling key transformations, such as C(sp3)-C(sp2) bond formation.

In order to maximize these methodologies, we combined flow photochemistry with automation to enable the preparation of challenging molecules in library format, optimize novel transformations using High Throughput Experimentation (HTE) and combine different chemistries to enable multistep synthesis of drug like compounds in an assembly line mode.

In this presentation we will show how we can harness different photochemical approaches to be used in medicinal chemistry and expand the chemical space available for drug discovery.

Cristina Nevado

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Professor of Organic Chemistry at the Chemistry University of Zurich, Switzerland
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Homepage: Nevado Research Group |

Academic Positions & Education

2004 – 2007 Post–Doctoral Associate "*Total Synthesis of Iejimalide B",* Prof. Alois Fürstner, Max Planck Institut für Kohlenforschung (MPI) – Mülheim a. d. Ruhr, Germany
2000 – 2004 Doctoral Thesis (*Summa Cum Laude*) "*Reaction of enol ethers & arenes with alkynes catal. by transition metals*", Prof. A. M. Echavarren, Autonoma University (UAM) – Madrid, Spain
2000 – 2001 Master Thesis "*Alcoxy- and Hydroxycyclization of 1,6- Enynes catalyzed by $PtCl_2$*", Prof. A. M. Echavarren, Autonoma University (UAM) – Madrid, Spain
2002 Complementary Research, Prof. Eiichi Nakamura, Tokyo University (TU) – Tokyo, Japan
1996 – 2000 BSc. (*with Honours 3.4 / 4*), Autonoma University (UAM) – Madrid, Spain

Research Interests

Homogeneous catalysis, radical chemistry, organometallic chemistry of gold, medicinal chemistry and natural product synthesis.

Honors & Awards

Médaille SCF Sud-PACA (2025); UCB-ICIQ Lectureship Award (2024), Novartis Lectureship (2023), Margaret Faul Women in Chemistry Award (SOS-Thieme 2021), Royal Spanish Chemical Society (RSEQ)-Exellence Research Trajectory Award (2020); Pharmaron Lectureship (University of Toronto 2020), RSC Award in Organometallic Chemistry (2019), Werner Prize Swiss Chemical Society (2011); Chemical Society Reviews Emerging Investigator Award (2011), Chemical Society Reviews Emerging Investigator Award (2011), Thieme Chemistry Journal Award (2011), NJC Young Pleanary Speaker Price at the EuCOMC XIX (2011), Young Investigator Award (Royal Spanish Chemical Society, RSEQ) (2008), Eli&Lilly –Best Graduate Student Award (2003)

Selected Publications

1. "Advancing Sulfinyl Radical Chemistry: An Asymmetric Smiles Rearrangement with Chiral Sulfoxides" Y. Hu, T. Schreyer, C. Nevado* Angew. Chem. Int. Ed. 2025 (https://doi.org/10.1002/anie.202509470).
2. "Redox-neutral photocatalytic cleavage and gem-difluoroalkenylation of lignin linkages" X. Hu, L. Ribadeau-Dumas, C. Nevado* Science Adv. 2025, (https:// doi: 10.1126/sciadv.ady2227).
3. "Chiral arylsulfinylamides as reagents for visible light-mediated asymmetric alkene aminoarylations" C. Hervieu, M. S. Kirillova, Y. Hu, S. Cuesta-Galisteo, E. Merino*, C. Nevado* *Nat. Chem*. **2024**, 607.
4. "Asymmetric,visible light-mediated radical sulfinyl-Smiles rearrangement to access all-carbon quaternary stereocenters" C. Hervieu, M. S. Kirillova, T. Suárez, M. Müller, E. Merino*, C. Nevado* *Nat. Chem.* **2021**, *13*, 327-334.

Asymmetric Remote Functionalization of Alkenes

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Keywords: Radical ● Remote functionalization ● Alkenes ● Smiles ● Asymmetric

The sulfinyl-Smiles rearrangement has emerged as a powerful platform for stereocontrolled aryl migration, enabling the synthesis of enantioenriched architectures under mild photoredox conditions. In this talk we will discuss how chiral sulfinylamides and sulfoxides bearing olefinic moieties were designed to achieve asymmetric alkene functionalization through radical-mediated difunctionalization and remote arylation.

A visible-light-driven remote arylation of alkenes was developed, proceeding via radical addition, site-selective 1,n-hydrogen atom transfer (1,n-HAT), and stereocontrolled sulfinyl-Smiles rearrangement. This cascade furnishes chiral α-arylated amides with excellent enantioselectivity (up to >99:1 er). Mechanistic studies indicate that the sulfinamido auxiliary dictates stereocontrol, with aryl migration as the rate-determining step.

In addition, a stereocontrolled 1,5-carbosulfonylation and dicarbofunctionalization of vinylcyclopropanes was realized through a radical sequence involving addition, C–C bond cleavage, aryl migration, and desulfinylation, affording diverse chiral α-allylic amides with broad functional group tolerance.

Finally, an atom-economical variant employing chiral sulfoxides as radical acceptors enables simultaneous formation of one C–S and two C–C bonds while retaining the sulfoxide moiety, delivering valuable sulfoxides and sulfones with high enantiocontrol (up to 96:4 er).

This body of work establishes the sulfinyl-Smiles rearrangement combined with alkene difunctionalization as a versatile strategy for accessing complex enantioenriched molecules through asymmetric radical chemistry.

David J. Procter

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Academic Positions & Education

Since 2020	Head of Department, Professor, University of Manchester
2008-2020	Professor, University of Manchester
2004-2008	Reader, University of Manchester (UK)
1997-2004	Lecturer & Senior Lecturer, University of Glasgow (UK)
1995-1997	Postdoctoral Fellow, R. A. Holton, Florida State University (USA)
1992-1995	PhD, Prof. C. M. Rayner, University of Leeds
1989-1992	BSc in Chemistry, University of Leeds

Research Interests
Radicals, organosulfur chemistry, photocatalysis/chemistry, natural product synthesis.

Honors & Awards
Invited Chair, Royal Society of Chemistry (RSC), Heterocyclic and Synthesis Group (since 2025); Charles Rees Prize, RSC (2020); Batsheva de Rothschild Fellowship, Israel Academy of Sciences & Humanities (2020); Erdtman Lecture, KTH, Stockholm (2019); PKU-WuXi AppTec Lectureship, Peking University, China (2019); EPSRC Established Career Fellowship (2015-2020); Young Heterocyclic Chemist Award, RSC (2015); Liebig Lectureship, German Chemical Society (2014); Bader Award, RSC (2014); Leverhulme Research Fellowship (2013).

Selected Publications

1. Zhao, H; Fillippini, D; Chen, Y; Gallego-Gamo, A; Natrajan, L. S; Romano, C.; Procter, D. J. Activation of alcohols as sulfonium salts in the photocatalytic hetero-difunctionalization of alkenes. *Nat. Chem.* **2026**, *18*, 398.
2. Conboy, Ó; Rushworth, E. Q.; Taylor, C. J.; Levy, C. W.; Ortmayer, M.; Whitehead, G. F. S.; Yen, A.; Romano, C.; Green, A. P.; Procter, D. J. Biocatalytic activation of sulfur heteroaromatics facilitates dearomatizing cross-couplings to set stereogenic centres or axes. *J. Am. Chem. Soc.* **2025**, *147*, 43057.
3. Roy, D.; Mansell, J. I.; Barison, G.; Yu, S.; Katavic, R.; Romano, C.; Kaltsoyannis, N.; Procter, D. J. SmI_2-Catalyzed Coupling of Alkyl Housane Ketones and Alkenes in an Approach to Norbornanes. *Angew. Chem. Int. Ed.* **2025**, e202512018.
4. Zhao, H.; Cuomo, V. D.; Rossi-Ashton, J. A.; Procter, D. J. Aryl Sulfonium Salt Electron Donor-Acceptor Complexes for Halogen Atom Transfer: Isocyanides as tuneable coupling partners. *Chem.* **2024**, *10*, 1240.
5. Mansell, J. I.; Yu, S.; Li, M.; Pye, E.; Yin, C.; Beltran, F.; Rossi-Ashton, J. A.; Romano, C.; Kaltsoyannis, N.; Procter, D. J. Alkyl cyclopropyl ketones in catalytic formal [3+2] cycloadditions: the role of SmI_2 catalyst stabilization. *J. Am. Chem. Soc.* **2024**, *146*, 12799.
6. Agasti, S.; Beltran, F.; Pye, E.; Kaltsoyannis, N.; Crisenza, G.E.M.; Procter, D. J. A catalytic alkene insertion approach to bicyclo[2.1.1]hexane bioisosteres. *Nat. Chem.* **2023**, *15*, 535.
7. Dewanji, A.; van Dalsen, L.; Rossi-Ashton, J.; Gasson, E.; Crisenza, G. E. M.; Procter, D. J. A general arene C–H functionalization strategy *via* electron donor-acceptor complex photoactivation. *Nat. Chem.* **2023**, *15*, 43
8. Peter, Á.; Crisenza, G. E. M.; Procter, D. J. Asymmetric Total Synthesis of (–)-Phaeocaulisin A. *J. Am. Chem. Soc.* **2022**, *144*, 7457.

Sulfonium salts and light

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Keywords: sulfonium salts ● alkoxy radicals ● photocatalysis ● photochemistry

Sulfonium salts are now established as indispensable partners in cross-coupling.[1] For example, in photocatalytic and photochemical couplings,[2,3] their use can offer advantages over processes involving organohalides or other pseudohalides in delivering carbon-centered radical intermediates for precision bond formation.

We have shown that oxygen-centered radicals can also be formed from sulfonium salts.[4] Convenient activation of simple and complex alcohols as alkoxysulfonium salts,[5] formed by straightforward coupling of alcohols with sulfoxides, allows alkoxy radical generation under mild photochemical conditions.[4] Exploitation of the alkoxy radicals in efficient intermolecular[4] and intramolecular[6] couplings to alkenes delivers complex ethers, while fragmentation and rearrangement processes allow alcohols to be repurposed and valorized.[7]

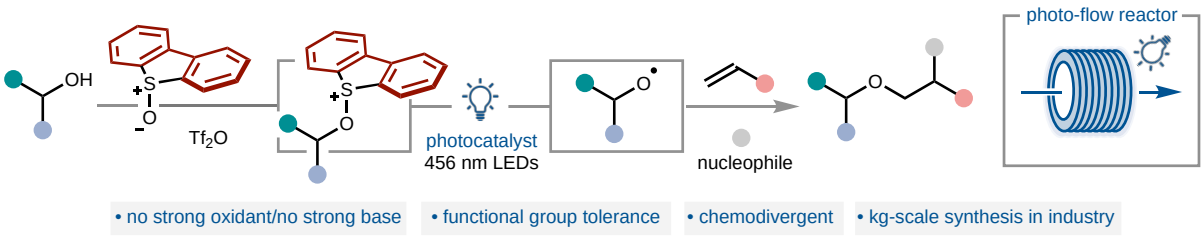

Figure 1. Activation of alcohols as sulfonium salts in photocatalytic intermolecular additions to alkenes

Acknowledgements
The Engineering and Physical Sciences Research Council (EPSRC) (EP/T013419/1), University of Manchester, and Pharmaron UK.

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[7] Zhao, H.; Duran, J.; Berreur, J.; Procter, D. J. *Unpublished results.*

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Academic Positions & Education
Since 2024 : Professeur Chargé de Cours (PCC) - Ecole Polytechnique (Palaiseau)
Since 10/2023: Research director at CNRS (LHFA)
Since 03/2020: Group leader at LHFA–Toulouse.
01/2013–02/2020: CNRS researcher at ENSI–Caen (Normandie Université).
01/2007-12/2012: Postdoctoral researcher at LMU (group of Prof. Dr. Herbert Mayr).
11/2006 : Dissertation in Organic Chemistry, Institut Lavoisier Versailles (ILV), France, (Prof. François Terrier)
09/1996 – 03/2001: Studies of chemistry at the University of Monastir, Tunisia.

Research Interests
Physical Organic Chemistry, Phosphorus Chemistry; Photoredox Catalysis

Honors & Awards
Alexander von Humboldt Fellowship (2007-2009); Klaus Römer award for postdoctoral researchers (2013); Thieme Journal Award (2013); Jean-Pierre Sauvage Award from the French Chemical Society (SCF) (2019); Jean-Marie Lehn Award from the French Chemical Society (SCF) (2024), and Minafin Prize from the French Academy of Sciences (2024).

Selected Publications
1. Rammal, F.; Gao, D.; Boujnah, S.; Hussein, A. A.; Lalevée, J.; Gaumont, A.–C.; Morlet-Savary, F.; Lakhdar, S. Photochemical C–H Silylation and Hydroxymethylation of Pyridines and Related Structures: Synthetic Scope and Mechanisms. *ACS Catal*. **2020**, *10*, 13710.
2. Chérif, S. E.; Ghosh, A.; Chelli, S.; Dixon, I. M.; Kraiem, J.; Lakhdar, S. Merging Grubbs second-generation catalyst with photocatalysis enables Z-selective metathesis of olefins: scope, limitations, and mechanism. *Chem. Sci*. **2022**, *13*, 12065.
3. Ghosh, A.; Nguyen, T. H. V.; Bellanger, C.; Chelli, S.; Ahmad, M.; Saffon-Merceron, N.; Taillier, C.; Dalla, V.; Mayer, R. J.; Dixon, I. M.; Lakhdar, S. Unraveling C–Selective Ring-Opening of Phosphiranes with Carboxylic Acids and Other Nucleophiles: A Mechanistically-Driven Approach. *Angew. Chem. Int. Ed*. **2024**, *64*, e202414172.
4. Ghosh, A.; Hussein, A. A.; Liu, J.; Wu, H.; Chelli, S.; Saffon-Merceron, N.; Guo, X.; Lakhdar, S. Visible-Light Unlocked Carbene Insertion and Radical Release in a Structurally Constrained Pincer Phosphorus Compound. *Angew. Chem. Int. Ed.* **2026**, e9531020.

Mechanistically Guided Strategies for the Design and Synthesis of Organophosphorus Compounds

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Keywords: Main Group chemistry ● Physical Organic Chemistry ● Photochemistry

In recent years, the field of visible light-mediated organic transformations has undergone a significant revival, profoundly influencing the methodologies for synthesizing organic molecules.[1]

This talk will explore the crucial role of physical organic chemistry in both understanding and innovating photoinduced chemical reactions.

The first part of the talk will focus on the formation of carbon-carbon and carbon-heteroatom bonds facilitated by visible light, while the second part will examine how well-designed phosphorus molecules can activate inert chemical bonds when exposed to light.[2]

Acknowledgements
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[1] For a comprehensive review, see: Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev*. **2013**, *113*, 5322–5363.
[2] For key contributions from the author's lab, refer to: a) *Chem. Sci*. **2022**, *13*, 12065; b) *Angew.Chem. Int. Ed* .**2024**, DOI: 10.1002/anie.202414172.; c) *Angew. Chem. Int. Ed*, **2021**, *60,* 19526; d) *ACS Catal*. **2020**, *10*, 13710; e) *Org. Lett*. **2020**, *22*, 4404; f) *J. Am. Chem. Soc*. **2016,** *138*, 7436.

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Academic Positions & Education

Since 2024	Professor of Chemistry, University of British Columbia
2015-2024	Professor of Chemistry, University of Michigan
2013-2015	Associate Professor, University of Michigan
2007-2013	Assistant Professor, Boston University
2005-2007	Postdoctoral Fellow, ETH Zurich
1998-2005	PhD, University of Pittsburgh (Prof. P. Wipf)

Research Interests

Photoredox methodology, complex molecule synthesis, biomass degradation, flow synthesis.

Honors & Awards

Canada Excellence Research Chair (2024); ACS Arthur C. Cope Scholar (2020); Pfizer Green Chemistry Award (2015), Camille Dreyfus Teacher-Scholar Award (2013); Eli Lily Grantee Award (2013); Novartis Early Career Award (2012); Alfred P. Sloan Research Fellow (2011); NSF Career Award (2011).

Selected Publications

1. Noten, E. A., Ng, C. H., Wolesensky, R. M., Stephenson, C. R. J.*, A general alkene aminoarylation enabled by N-centered radical reactivity of sulfinamides, *Nat. Chem.,* **2024**, 16, 599.
2. Monos, T. M., McAtee, R. C., Stephenson, C. R. J.*, Arylsulfonylacetimides as Bifunctional Reagents for Alkene Aminoarylation, *Science*, **2018**, 361, 1369.
3. Keylor, M. H., Matsuura, B. S., Griesser, M., Chauvin, J.-P. Harding, R. A, Kirillova, M. S., Zhu, X., Fischer, O. J., Pratt, D. A., Stephenson, C. R. J.*, Synthesis of Resveratrol Tetramers via a Stereoconverent Radical Equilibrium, *Science*, **2016**, 354, 1260.
4. Nguyen, J. D., D'Amato, E. M., Narayanam, J. M. R., Stephenson, C. R. J.*, Engaging Unactivated Alkyl, Alkenyl and Aryl iodides in Visible-Light Mediated Free Radical Reactions, *Nat. Chem*., **2012**, 4, 854.

14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Radical Ideas: The Origins and Evolution of Visible-Light Photocatalysis

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ISOFR 14 2026

Oral Contributions

Ferrioxalate Photocatalysis

Fabio Juliá[a]

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Keywords: photocatalysis ● ferrioxalate ● ligand-to-metal charge-transfer (LMCT) ● organic synthesis

The use of transition-metal catalysis has become an indispensable asset for organic synthesis, particularly for the assembly of C–C bonds.[1] Among all possible metals, the use of Earth-abundant iron for this task would represent a promising and sustainable new tool for synthesis.[2] However, the challenging reduction of benchmark iron salts to active species represents an important obstacle that hinders the broad development of reductive iron catalysis.

Inspired by the classic photochemistry of ferrioxalate, which is known for 130 years[3] and is routinely used as standard for quantum yield determination, we have developed the use of oxalate salts as photo-activable, traceless 2-electron reductants for iron catalysis. This new activation mode, unprecedented within the arena of transition-metal catalysis, enable access to versatile reduced Fe species exploiting the innate reactivity of ligand-to-metal charge-transfer (LMCT) excited states of iron complexes. In this communication it is presented the discovery and development of ferrioxalate photocatalysis,[4] a general catalytic platform with multiple synthetic applications featuring mild conditions and broad functional group compatibility. The multitasking ability of iron complexes to act as photocatalysts, reductants and organometallic intermediates enable transformations hitherto inaccessible to previous strategies based on iron catalysis or LMCT reactivity, representing a privileged new system to discover unprecedented transformations for organic synthesis.

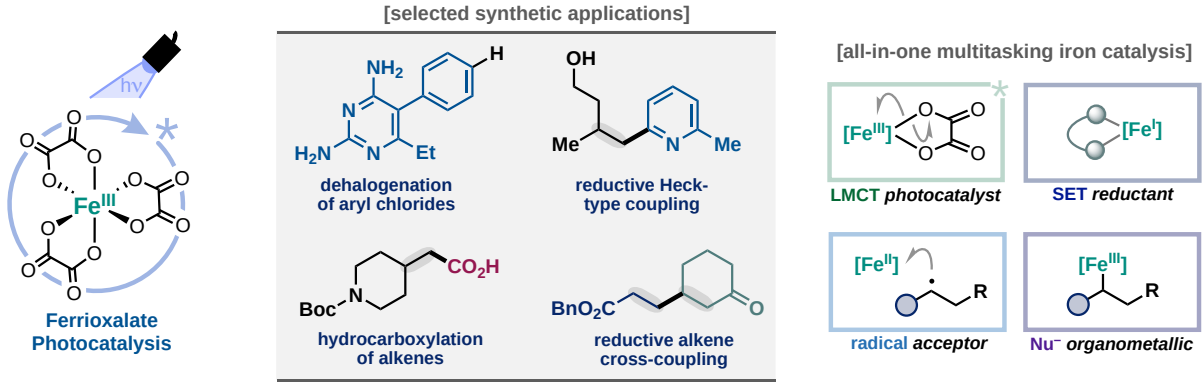

Figure 1. Ferrioxalate Photocatalysis

Acknowledgements
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References
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Electroreductive Strategies for the Ring-Opening of Heterocycles

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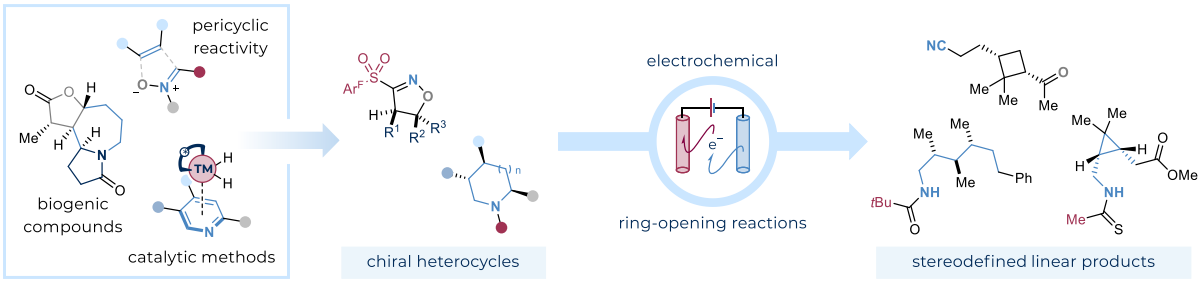
Keywords: electrosynthesis ● heterocycles ● C=C functionalization ● C–N activation ● radical reactivity

Ring-opening reactions provide an effective platform for converting readily accessible, widely available chiral hetero- and carbocycles into hard-to-attain stereodefined linear carbon chains. While Nature relies on enzymes to build complex enantiopure heterocyclic natural products, synthetic chemists can count on an ever-growing, wide-ranging suite of transformations to access chiral cyclic scaffolds (including cyclisations, ring-closing cross-couplings, hydrogenations, pericyclic cycloadditions and cascade reactions; among many others), often with excellent control over multiple stereocentres formed in a single step. Conversely, the synthesis of linear frameworks featuring multiple stereogenic centres is considerably more challenging, especially when the stereochemical information is located away from reactive functionalities (*e.g.* amines or carbonyls). Yet such linear motifs are prevalent in lead compounds and blockbuster drugs, embedded in aliphatic chains and macrocycles. Our target is to leverage the enhanced complexity-generating ability and stereocontrol provided by the formation and functionalisation of cyclic systems to access highly decorated, stereodefined linear architectures via electrochemically driven ring-opening fragmentation reactions.

To realise this, we developed a practical, general and selective strategy for the regio- and stereoselective functionalisation of C=C bonds, named "*sew & cut*".[1] This hinges on the design of novel reagents − consisting of a 1,3-dipole precursor equipped with a sulfonyl redox handle. These can selectively di-functionalise alkenes via "click" 1,3-dipolar cycloadditions, and then facilitate the telescoped SET reduction and radical fragmentation of the resulting heterocyclic intermediate, furnishing stereodefined building blocks. More recently, we extended this concept to more challenging C(sp³)–N bond cleavage reactions in saturated *N*-heterocycles.[2] Here, we leveraged electrochemical conditions to facilitate the two-electron cathodic reduction of *N*-carbonyl protecting groups, generating umpoled α-amino–α-oxy-carbanion species that promote the heterolytic ring-opening of a broad array of unstrained cyclic amines (including pyrrolidines, piperidines, azepines, azocanes, and *N*-macrocycles), protected as *N*-amides, thioamides, carbamates or ureas. Our electroreductive protocol is readily scalable and amenable to miniaturisation for high-throughput experimentation, and it efficiently converts stereochemically rich *N*-heterocycles into highly decorated, stereodefined linear amides.



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This work was financially supported by the Royal Society of Chemistry, the Engineering and Physical Science Research Council from UKRI and the University of Manchester.

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Radicals Under Enzymatic Control: The Photoenzyme *Cv*FAP as a Platform for New-to-Nature Biocatalysis

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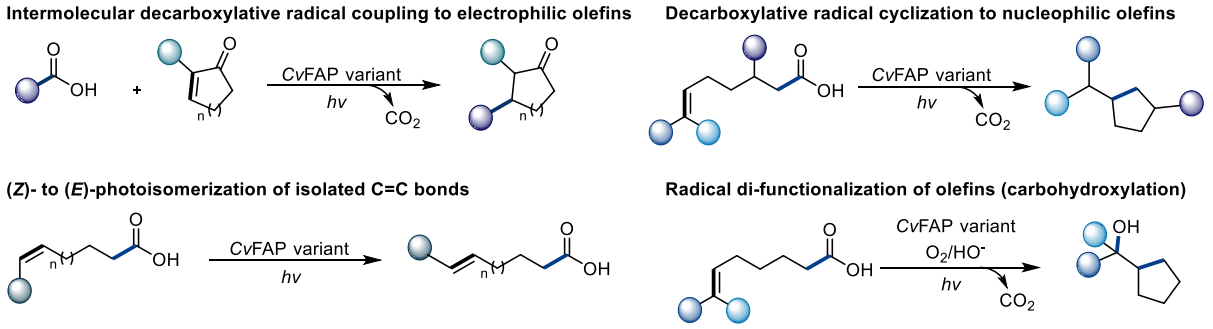
Keywords: photobiocatalysis ● radical coupling ● fatty acid photodecarboxylase ● isomerization

Fatty acid photodecarboxylases (FAPs) are unique light-driven enzymes that catalyze the redox-neutral decarboxylation of fatty acids through carbon-centered radical intermediates.[1] By systematically redirecting this radical pathway, we have repurposed the photodecarboxylase from *Chlorella variabilis* (*Cv*FAP) to greatly expand its emerging photo-promiscuous reaction landscape.[2] Specifically, herein we report four new-to-nature radical transformations catalyzed by *Cv*FAP variants (**Scheme 1**): (*i*) inter-molecular Giese-type coupling of fatty acids with cyclic enones, enabling selective radical addition within the enzyme active site; (*ii*) intra-molecular decarboxylative radical cyclization in which nucleophilic radicals engage isolated C=C bonds of matching philicity; (*iii*) cysteine-mediated (*Z*)→(*E*) photoisomerization of unsaturated fatty acids, revealing an unexpected thiyl-radical-assisted mechanism; and (*iv*) radical carbohydroxylation, demonstrating the enzyme's capability of olefin bis-functionalization. Guided by computational modelling, directed evolution delivered variants with enhanced cyclization efficiency, highlighting the evolvability of *Cv*FAP toward novel radical reactivities.



Scheme 1. New reactions catalyzed by variants of the fatty acid photodecarboxylase *Cv*FAP.

Together, these studies illustrate that photoenzymes can harness and channel radicals to enable selective bond formations from abundant carboxylic acid feedstocks and present *Cv*FAP as a versatile, evolvable platform for developing novel selective radical biotransformations.

Acknowledgements
This research was funded in whole or in part by the Austrian Science Fund (FWF) [Grant-DOI: 10.55776/PAT1643724].

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Shono-type electrochemical synthesis of cyclic encarbamates

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Keywords: electrochemistry ● green chemistry ● cyclic enecarbamates ● Shono oxidation

The well-known electrochemical Shono oxidation of Boc-protected cyclic amines was revised. Boc-protected morpholine **1**, which in described conditions gives the mixture of products, was used as a model compound. The process was optimized for the synthesis of carbamate **3** in 500g from 1 synthetic run. The optimized procedure was applied to the multigram synthesis of carbamates **6-11**. Further electrophilic functionalization of the carbamates leads to latent 1,3-bielectrophilic compounds type **12**, which was subjected to classical heterocyclization with binucleophilic reagents. In a case of hydrazine, the corresponding pyrazoles **13**, decorated in an unusual manner, were prepared. The proposed methodology appears to be a straightforward tool for the design and synthesis of MedChem-relevant building blocks. For example, using commercially available cyclic α-aminoacids type **14**, the 5-step synthesis leads to the formation of α-aminoacids **15** with different linkers between the aminoacids fragment and the pyrazole nuclei. In the report, the scope and limitations of the above-mentioned methodology will be discussed.

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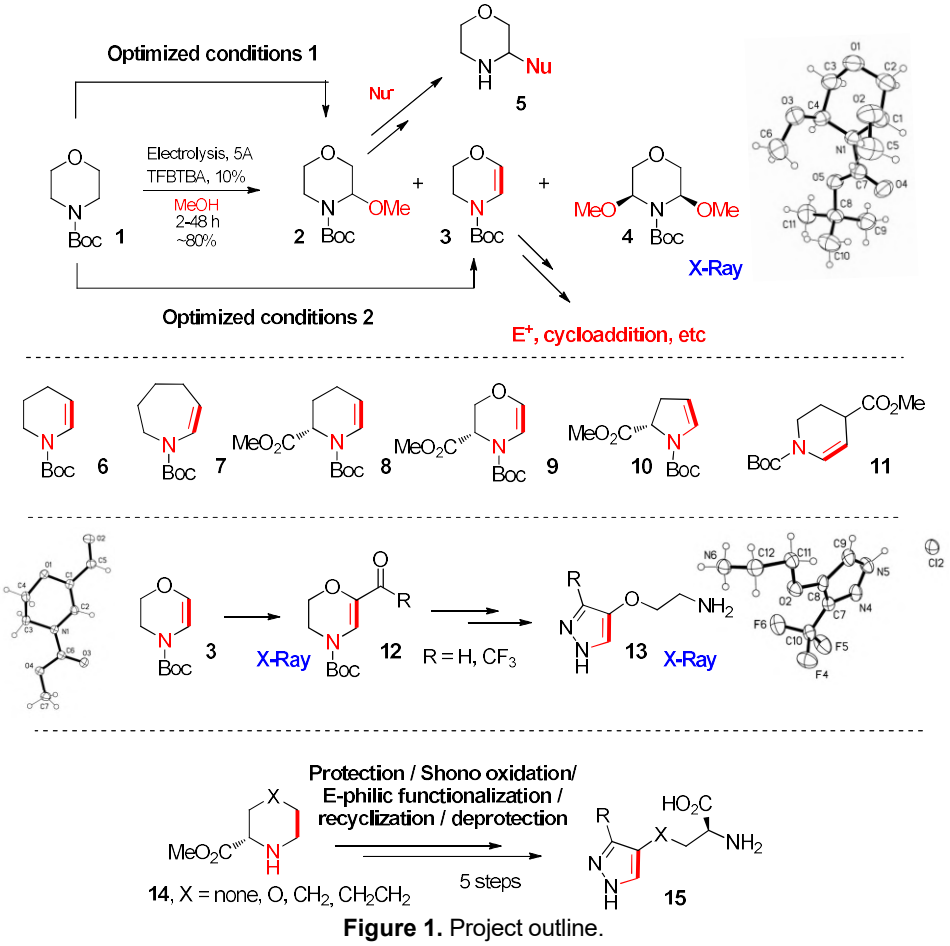

Figure 1. Project outline.

Thermally Activated Delayed Fluorescence and photocatalysis: generation of radical anion from S_1 and T_1 excited states

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Keywords: TADF ● quenching ● cage escape ● electron transfer ● radical anion

Photocatalysts exhibiting thermally activated delayed fluorescence (TADF) are widely employed as photocatalysts. It has been demonstrated that both the lowest singlet (S_1) and triplet (T_1) excited states are photocatalytically active and, in presence of a sacrificial electron donor, can form the corresponding radical anion, which has been demonstrated to be able to photogenerate solvated electrons.[1]

These photocatalysts display complex excited-state kinetics that challenge conventional kinetic analyses. While several approaches have been proposed to extract radiative and non-radiative rate constants from experimentally accessible observables, many neglect the intrinsic singlet–triplet coupling that defines TADF systems. Here, we present a combined modeling and experimental investigation of quenching kinetics in TADF chromophores, focusing on the roles of singlet (S_1) and triplet (T_1) excited states in photocatalytic processes.[2]

Experimental studies on representative cyanoarene TADF chromophores reveal that reductive quenching proceeds significantly faster from S_1 than T_1 states, while oxidative quenching shows comparable rates.[2] Electronic structure calculations suggest that these differences arise from distinct spatial distributions of hole–electron density in the excited states. On the other hand, T_1 quenching is generally more productive than S_1 quenching because of different cage escape yields. Due to spin-selection rules, cage escape from the triplet-derived radical pair is typically more efficient than from its singlet counterpart. As a consequence, we observed a counterintuitive result: the product quantum yield reaches a maximum at a specific quencher concentration and then decreases upon further increasing the quencher concentration.[3]

Overall, this work highlights the importance of rigorous kinetic modeling for understanding and optimizing the production of organic radicals via TADF-based photocatalytic systems.

Acknowledgements
This work was financially supported by the University of Bologna.

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Wired for Stereoselectivity: The Merger of Electrochemistry and Aminocatalysis for SOMO Applications

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Keywords: Electrosynthesis ● Aminocatalysis ● SOMO ● Redox Mediator ● Asymmetric Synthesis

In the realm of asymmetric organic synthesis, aminocatalysis stands out as a well-established strategy for the preparation of enantioenriched compounds under mild conditions.[1] Beyond its classic utilization, aminocatalysis has emerged as a highly versatile mode of molecular activation, as demonstrated by its successful integration with various synthetic approaches.[2] While combinations with metal catalysis[3] and photochemistry[4] have been extensively explored, the synergy between aminocatalysis and electrochemical activation remains largely unexplored. Herein, we present the successful merger of electrochemistry and aminocatalysis to perform SOMO-type transformations (Figure 1), expanding the toolkit for asymmetric electrochemical synthesis.[5] The methodology harnesses electricity to promote the oxidation of catalytically generated enamines, which engage in a variety of enantioselective radical processes, to afford α-functionalized aldehydes. Mechanistic investigations reveal the crucial role of redox additives in preventing catalyst degradation, furnishing the coveted compounds in good yield and high enantioselectivity.

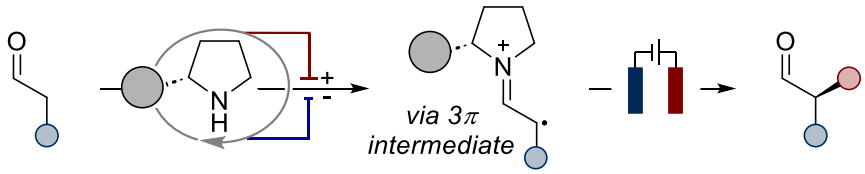

Figure 1. Electrochemistry and Aminocatalysis for SOMO Applications

Acknowledgements
This work was financially supported by RSC Research Fund (R25-5016356185) and FIS3 Starting Grant (FIS-2024-00206).

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Photochemical Diradical Rearrangements

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Keywords: Radical ● Energy-transfer ● Photochemical rearrangement ● Divergent synthesis ● Bioisosteres

Radical chemistry has emerged as an indispensable tool across synthetic, medicinal, and materials chemistry.[1] A central challenge, however, remains the precise control over the reactivity and selectivity of these highly reactive open-shell intermediates.[2] This presentation will highlight our group's recent efforts in radical-based divergent synthesis, a strategy that leverages common radical intermediates to access structurally diverse molecular architectures.

We will discuss two key approaches: (1) functional group translocation via energy transfer catalysis, where we have discovered a series of photochemically generated diradical intermediates. Their rearrangement pathways can be divergently controlled simply by tuning the substrate design or the reaction time, leading to distinct molecular scaffolds from a common precursor.[3] (2) Divergent assembly via photoexcited palladium catalysis, where the choice of ligand dictates the reaction pathway, enabling the selective and programmable synthesis of distinct 1-azabicyclo[n.1.1]alkane bioisosteres.[4] These examples demonstrate how tailored catalytic platforms can predictably harness radical reactivity to build molecular complexity from simple precursors.

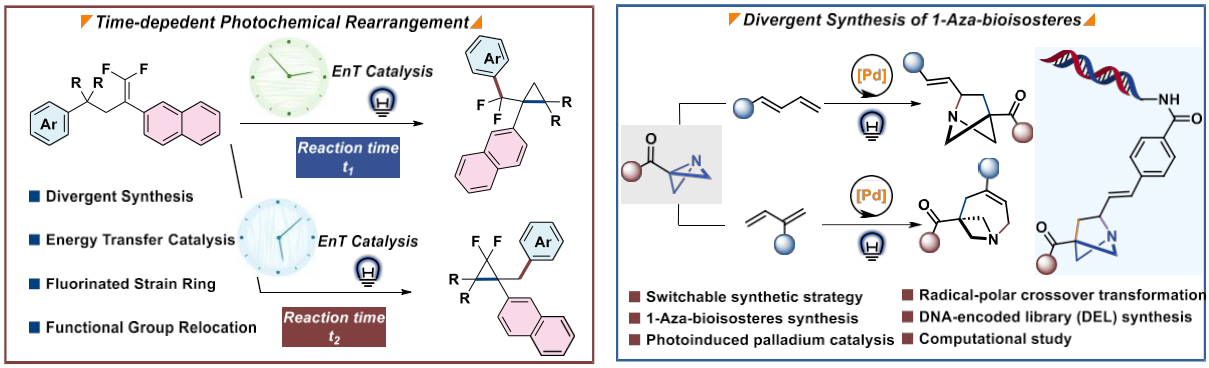

Figure 1. Radical based divergent synthesis

Acknowledgements

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Photocatalytic Furan-to-Pyrrole Conversion

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Keywords: Skeletal editing ● Photocatalysis ● Mechanism

A single atom in aromatic heterocycles determines the unique properties and activity of functional molecules, such as natural products and pharmaceutical drugs. However, systematic evaluation of the single-atom effect has posed a synthetic challenge, and multi-step procedures have been inevitable based on classical approaches. In this talk, I will present single-step, catalytic protocols that directly exchange a single atom in an aromatic heterocycle with the isoelectronic congeners under redox-neutral conditions. Broad compatibility was observed with various substrates and nucleophiles that contain common functional groups encountered in the drug discovery process. The applicability in late-stage functionalization was studied, where synthetic short-cuts en route to the heterocyclic analogs were demonstrated. Mechanistic analyses suggested that radical-based ring-opening was initiated by polarity inversion, and further spin delocalization kinetically unlocks the underdeveloped pathway of direct atom exchange.

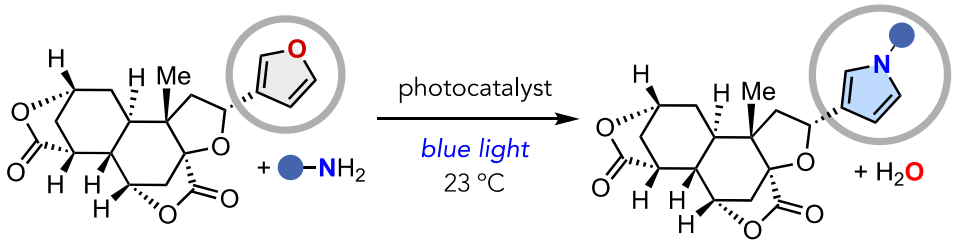

Figure 1. Photocatalytic Furan-to-pyrrole Conversion

Acknowledgements
This work was funded by the National Research Foundation of Korea (NRF) grant RS-2023-00213491, funded by the Korea government (MSIT); the Creative Research Program and the KAIST Cross-Generation Collaborative Lab Project at KAIST; and the POSCO Science Fellowship of POSCO TJ Park Foundation.

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Radical Ligand Transfer Catalysis for Molecular Design

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Keywords: RLT catalysis ● earth-abundant metals ● photochemistry ● electrochemistry ● alkene functionalization

Inspired by biological rebound processes, radical ligand transfer (RLT), also referred to as oxidative ligand transfer (OLT), has emerged as a powerful and versatile strategy for the selective functionalization of alkyl radicals [1]. RLT enables direct carbon-halogen or carbon-heteroatom bond formation *via* homolytic substitution at a metal-bound ligand/functional group (M-FG) and demonstrates broad functional-group tolerance and high catalytic potential. A key advantage of this outer-sphere mechanistic event is its versatility in radical-based transformations and tunable kinetics, enabling catalytic and selective bond formation. Despite growing interest and mechanistic understanding, the broader application of RLT strategies remains underdeveloped.

In this lecture, I will discuss some of the latest works from my group on how RLT catalysis can be boosted to open new frontiers in radical-mediated functional group transfer. By combining this mode of reactivity with energy sources such as visible light, electricity, or mechanical energy, we have introduced pathways for programmable functionalization of both activated and non-activated alkenes [2-5]. In addition, careful selection of organic and inorganic reagents enables the execution of modulative transformations that simultaneously introduce two distinct functionalities across small, medium, and complex alkene-based molecules. Exciting mechanistic studies of radical ligand transfer powered by various energy sources will also be highlighted.

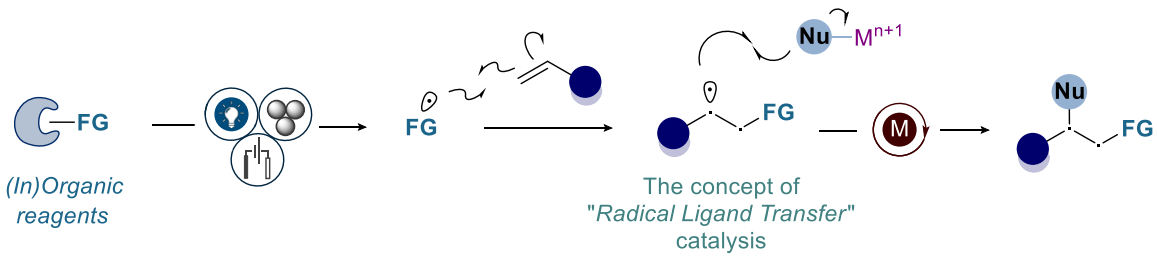

Figure 1. Synergistic catalysis enabling controllable and modulative alkene difunctionalization.

Acknowledgements
This work was financially supported by the University of Bern and the Swiss National Science Foundation (SNSF).

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A Redesigned Approach to Accessing Cationic Intermediates

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Keywords: photoredox catalysis ● radical cations ● difunctionalization ● electrophilic shuttling

Efforts in the Musacchio research group are on the development of enabling chemical transformations to accessing valuable cationic intermediates using mild catalysis from unconventional starting synthons via radical intermediates. In the past few years, we have successfully established a visible-light photoredox catalysis platform to orchestrate the generation of carbocations directly from C(sp^3)–H bonds to avoid the harsh requirements of classical S_N1 conditions from organohalides, protected alcohols, etc.[1] In this talk, we will detail a recent discovery in our lab that this platform can also be used to generate alkene radical cations from homobenzylic C–X motifs (i.e. alkyl halides, protected and unprotected alcohols, and alkyl azides).[2] Computational studies reveal a concerted HAT and spin-center shift (SCS) process to access the radical cation intermediate. We leverage this mechanism to establish a 1,2-difunctionalization of C(sp^3)–X motifs. This photocatalytic platform allows us to develop a suite of transformations that depart from current conventional synthetic logic for which alkyl C–X scaffolds are confined to single-site substitutions, now transforming them into nonintuitive precursors for building vicinal complexity. Incorporation of the spin-center shift process in the platform ultimately allows for transfer of electrophilic reactivity from one carbon to another, allowing for the establishment of a new synthetic concept – 'electrophilic shuttling.'

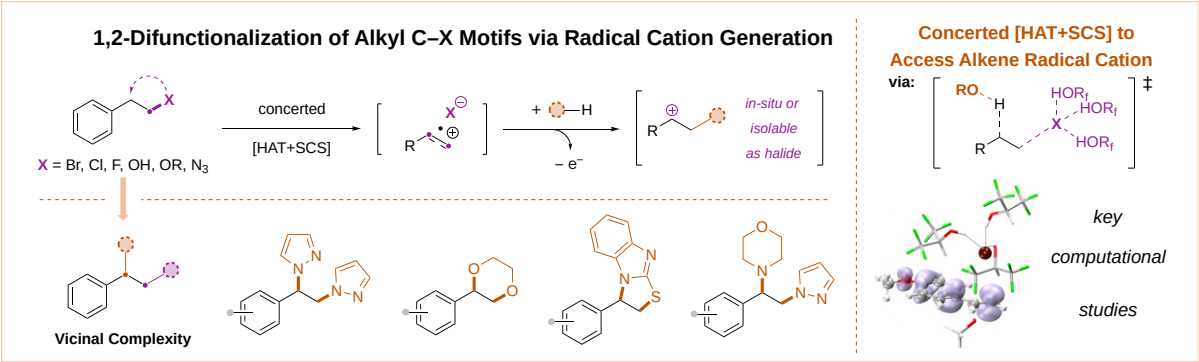

Figure 1. Development of a 1,2-difunctionalization of alkyl C–X motifs via a radical cation intermediate.

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Auto-Photoredox Catalysis

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Keywords: photoredox ● autocatalysis ● sulfonamide ● combinatorial library ● flow chemistry

Dichotomous thinking Dichotomous thinking dominated synthetic photochemistry; a reaction needs a photocatalyst, or not. On one hand, exogeneous photocatalysts harvest light energy to induce single electron transfer (SET) events with target substrates.[1] On the other hand, light-absorbing target substrates or electron donor-acceptor (EDA) complexes (generally between stoichiometric reactants) are required.[2] Unbeknownst to many, 'auto-photoredox catalysis' (auto-PRC) is a phenomenon possessing intermediary characteristics of the two. A reaction intermediate, or product, acts as a photocatalyst for its own formation. Although autocatalysis is an important process in biochemistry, supramolecular chemistry and in prebiotic chemistry / origins of chirality,[3] it has enjoyed limited attention and practical applications in synthetic photochemistry. Elsewhere, sulfonamide and biaryl motifs are relevant in medicinal chemistry and ubiquitous in pharmaceuticals. Cyclic biaryl sulfonamides (BASNs) are emerging bioactive motifs with anticancer potential.[4] This work discloses a novel reductive auto-PRC pathway – applied to BASNs.[5] The power of auto-PRC is demonstrated via in situ photocatalyst library construction and screening. This is exemplified by identifying potent reductive photocatalysts applied to diverse organoradical precursors (60 synthetic transformations). Sulfonamides are showcased as a novel class of organophotocatalyst[5,6] with 'multi-tasking' potential that are cheap, rapidly diversifiable via auto-PRC, and scalable in flow. 'Hidden' autocatalysis was unveiled in numerous reports on photocatalysis in recent years and another example from our laboratory will be highlighted.[7,8]

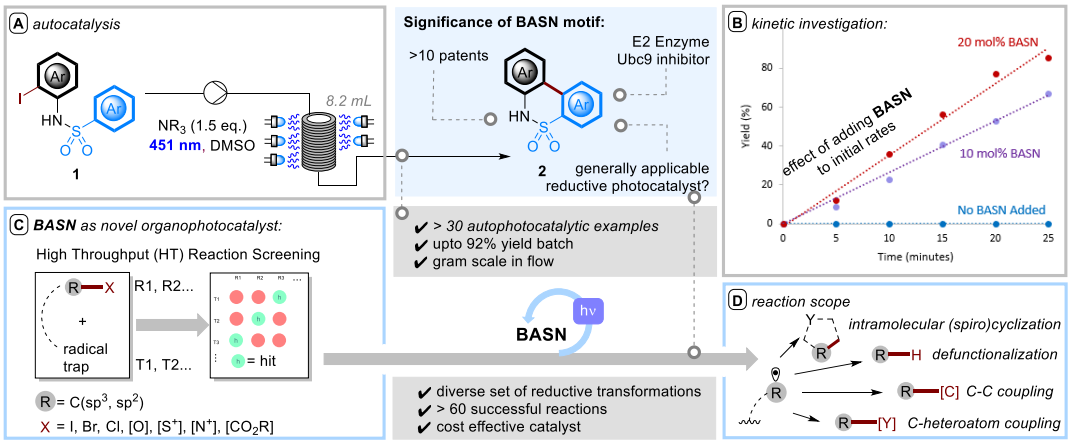

Figure 1. A: Autophotocatalytic synthesis of BASNs. **B:** Kinetic investigations. **C:** High throughput screening concept. **D:** Diverse scope of reactivity.

Acknowledgements
This work was financially supported by the Alexander von Humboldt Foundation, the Bayerische Staatsministerium für Wissenshaft und Kunst and the German Academic Exchange Service (DAAD).

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The Photocatalytic Generation of Carbanion Equivalents

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Keywords: multiphoton ● alkene ● radical anion ●

Organometallic reagents are routinely used as fundamental building blocks in organic chemistry to rapidly diversify molecular fragments via carbanion intermediates. However, the catalytic generation of carbanion equivalents, particularly from sp^3-hybridized alkyl scaffolds, remains an underdeveloped goal in chemical synthesis. Here we disclose an approach for the generation of alkyl carbanions via single electron reduction of aryl alkenes, enabled by multiphoton photoredox catalysis.[1] We demonstrate that photocatalytically induced alkyl carbanions engage in intermolecular C-C bond-forming reactions with carbonyl electrophiles. Central to this method is controlled formation of an alkene distonic radical anion intermediate[2,3] that undergoes nucleophilic addition, followed by a kinetically favoured reductive polar crossover to produce a second carbanion available for further diversification. This versatility of this protocol was illustrated by the development of four distinct intermolecular C-C bond forming reactions with aromatic alkenes: hydroalkoxylation, hydroamidation, aminoalkylation and carboxyaminoalkylation to generate a range of valuable, and complex scaffolds.[4]

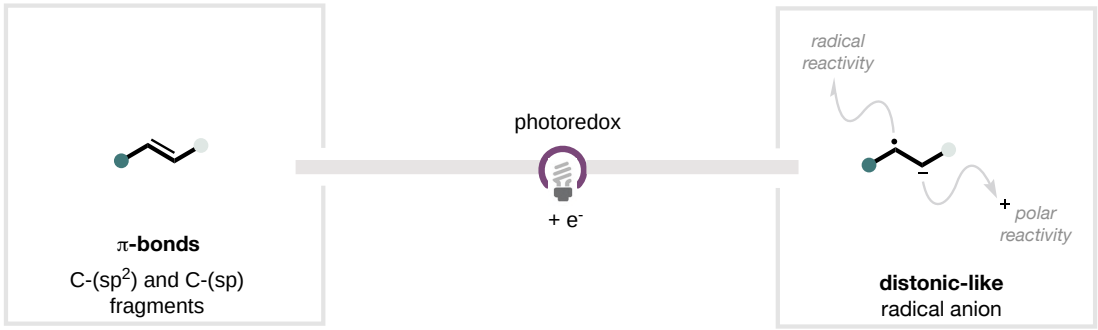

Figure 1. caption

Acknowledgements
This work was financially supported by the Australian Research Council

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How KO*t*Bu and Other Alkoxides Initiate Radical Reactions.

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Keywords: alkoxide ● radical ● benzyne ● BHAS ● electron transfer

Since the 19th century, alkali metal alkoxides have been reported to cause hydrodehalogenation of aryl halides, *i.e.* conversion of aryl halides to arenes. This happens when the reactions are conducted in solvents with weak C-H bonds.[1] The topic has been reviewed.[2] More recently, when aryl halides are heated with alkoxides in arene solvents, then coupling to arenes occurs to form biaryls.[3,4] Both these reaction types are known to involve aryl radical intermediates, but the unanswered question relates to the origin of the radicals. The consensus has been that alkali metal alkoxides undergo electron transfer to aryl halides to form the radicals, but crucial evidence has been missing.

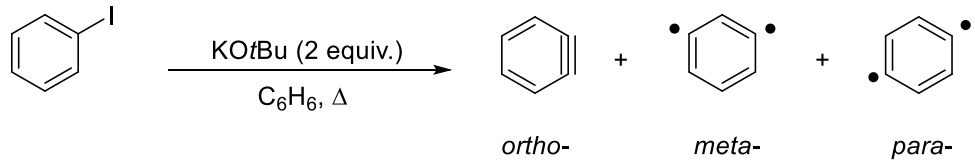

Figure 1. Simultaneous formation of benzyne regioisomers.

We now show through deuterium isotope studies that deprotonation of the substrates leads to benzynes that initiate radical chemistry. Surprisingly, *o*-, *m*-, *p*- and, in appropriate cases, *r*- (remote) benzynes are simultaneously formed.
During reactions with KO*t*Bu, we observed low-level methylation of arenes for the first time, resulting from methyl radicals derived from *tert*-butoxide. Until now, forming methyl radicals from KO*t*Bu has been attributed to electron transfer from *tert*-butoxide ions, followed by radical fragmentation. However, here we show that a different and novel mechanism applies. We will show the generality of the findings and suggest other cases where deprotonation of arenes by alkoxide bases may be important.

Acknowledgements
This work was financially supported by EPSRC (EP/W522260/1), GlaxoSmithKline, AstraZeneca and the University of Strathclyde.

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Bench-stable Selenium Salts – From Stable Radicals to Red-Light Absorbing Photocatalysts

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Keywords: main-group ● selenium ● red-light ● photocatalysis

This talk will provide an overview of the research carried out in our laboratory at the University of Vienna, focused on the design of novel reagents and catalysts that use selenium as an enabling element. The presentation will progress from an initial interest in bench-stable Se(III) radicals[1] to the development of red-light-absorbing organic photocatalysts that merge concepts from transition-metal and organic catalyst design.[2]

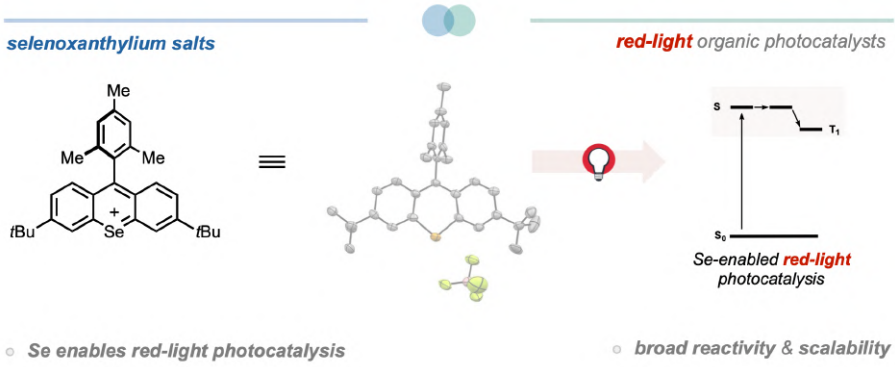

Figure 1. Selenoxanthylium salts as red-light absorbing photocatalysts

Special emphasis will be on our group's first work on red-light photocatalysis. We have recently proven that selenoxanthylium salts operate as red-light-absorbing organic photocatalysts under excitation at 650 nm. Incorporation of selenium into a xanthylium core shifts absorption toward the red region relative to lighter chalcogens (O and S). Photophysical studies define the excited-state topology, distinguishing locally excited and charge-transfer states. Under red-light irradiation, the photocatalysts engage in reductive quenching and operate on up to 5.0 mmol scale. Catalytic activity is demonstrated across multiple transformations, including [4+2] and [2+2] cycloadditions, C–H aminations, boronic acid oxidations, aza-Henry reactions, and trifluoromethylations.

Acknowledgements
This work was financially supported by the University of Vienna.

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Photoredox control of S_N2 reactivity via synchronized nucleophile and electrophile generation

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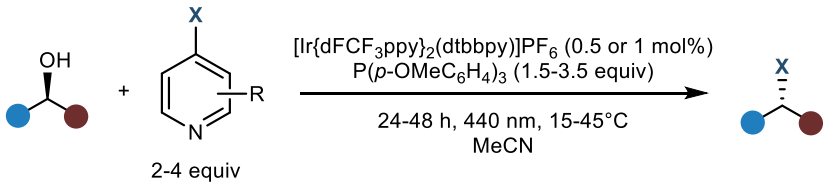
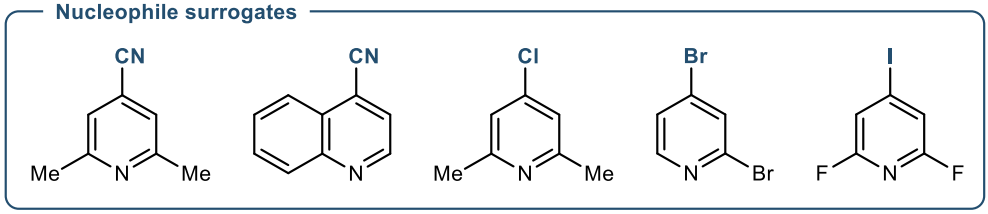
Keywords: photoredox ● S_N2 ● cyanation ● halogenation

Alcohols are among the most abundant and accessible functional groups in organic synthesis, yet their direct use as electrophiles in nucleophilic substitution reactions remains fundamentally challenging due to the poor leaving-group ability of hydroxide. Classical solutions to this problem—most notably Mitsunobu and Appel reactions—circumvent this limitation by converting alcohols into activated oxyphosphonium intermediates that undergo SN2 displacement. Despite their enduring utility, these methods rely on explosive azo reagents in Mitsunobu chemistry and ozone-depleting polyhalogenated reagents (CX_4) in Appel halogenations, leading to safety and environmental concerns.

In this talk, I will describe a photoredox-enabled strategy that recreates the core reactivity logic of Mitsunobu and Appel reactions without relying on their traditional two-electron activation modes. Photoredox catalytic single electron transfer processes are used to transiently access a radical manifold that synchronizes the generation of oxyphosphonium intermediates with on-demand nucleophile generation from benign precursors. This radical–polar crossover enables classical S_N2 substitution to proceed under mild conditions, with radical chemistry serving as an enabling platform rather than the bond-forming pathway itself.

Using cyanation as a lead example, we demonstrate on-demand generation of cyanide from a stable heteroarene surrogate that is immediately consumed in substitution, eliminating the need for cyanide salts. The same mechanistic framework extends to halogenation reactions, providing Appel-type reactivity without the use of ozone-depleting reagents. Together, these results illustrate how photoredox catalysis can be used to orchestrate polar substitution chemistry, modernizing foundational activation strategies while preserving the predictability and stereochemical fidelity of S_N2 reactions.





Posters

Poster Session I, June 8th, 17:05-18:50

001	Wayne Sow	**023**	Fabio Ioele	**045**	Sejin Park
002	Alexios Stamoulis	**024**	Marco Lucarini	**046**	Donghyeon Kim
003	Marco Villa	**025**	Estíbaliz Merino	**047**	Expedite Yen-Pon
004	Stefano Visentini	**026**	Áron Péter	**048**	Chiara Antenucci
005	Margaux Walter	**027**	Daniel Reta	**049**	Yassine Benhamidat
006	Xavier Abel-Snape	**028**	Ricardo Rodriguez	**050**	Christos Christou
007	Debora Belmonte	**029**	Cristian Rosso	**051**	Luigi Dolcini
008	Tynchtyk Amatov	**030**	Marco Rusconi	**052**	Lucas Gonçalves
009	Simone Baldon	**031**	Natalia Sanchez Rodriguez	**053**	Claudio Gotti
010	Maryia Barysevich	**032**	Tristan Von Münchow	**054**	Hojin Hong
011	Joshua Barham	**033**	Maurizio Fagnoni	**055**	Amirah Mat Lani
012	Thomas Boddaert	**034**	Marco Colella	**056**	Filippo Preti
013	Monica Fiorenza Boselli	**035**	Ha Eun Kim	**057**	Luna Raineri
014	Luca Capaldo	**036**	Jing Liu	**058**	Francesco Riina
015	Stefan Chakarov	**037**	Shengqi Zhou	**059**	Jacopo Saglietto
016	Prakash Chandra Tiwari	**038**	Changhee Park	**060**	Fabian Scharinger
017	Preslav Smits	**039**	Ronny Hardegger	**061**	Luca Sensoli
018	Kirti Khanna	**040**	Hayoung Shin	**062**	Laura Spirio
019	Vasco Corti	**041**	Minsoo Kim	**063**	Marcelo Straesser Franco
020	Sara Cuadros	**042**	Ying Zhang	**064**	Giorgia Urriani
021	Paulina Hartmann	**043**	Hui Ran	**065**	Airi Yamaguchi
022	Niklas Hölter	**044**	Kai-Dian Li	**066**	Kirill Zhiliaev

Poster Session II, June 9th 13:05-14:00, and June 10th 13:05-14:00

067	Nieves Ramirez Hernandez	**089**	Quentin Ordan	**111**	Simone Scaringi
068	Abhilash Pedada	**090**	Sunaina Sardana	**112**	Jonathan Trimble
069	Manuele Vitali	**091**	Colin Stein	**113**	David Montoto
070	Morgan Regnier	**092**	Arezoo Tanbakoochian	**114**	Luca Aimi
071	Youngsuk Kim	**093**	Kenta Tanaka	**115**	Mahdi Berro
072	Souvik Majumder	**094**	Lokesh Gupta	**116**	David Martin
073	Xavier Companyó	**095**	Carlos Bernabeu Rodriguez	**117**	Akshay Nair
074	Anne-Doriane Manick	**096**	Dalila Arnaldi	**118**	Serhiy Ryabukhin
075	Roberta Marino	**097**	Leander Spierling	**119**	Petros Gkizis
076	Vittoria Martini	**098**	Michael Bergami	**120**	Bi Jia-Xuan
077	Younes Massad	**099**	Swagata Choudhury	**121**	Mihaela-Lavinia Ciutu
078	Luca Massaro	**100**	Shalu Deshwal	**122**	Alexandru-Gabriel Bucur
079	Ang Chen	**101**	Julie Kong	**123**	Fabrice Dénès
080	Pratik Avinash	**102**	Anastasia Maria Antonaki	**124**	Gabriela-Elena Ioniță
081	Bitasik Khatua	**103**	Wansen Xie	**125**	Shixue Zhang
082	Christoforos Kokotos	**104**	Stéphane Gastaldi	**126**	Dilara Berna Yildiz
083	Weiqun Suo	**105**	Tatsuhiro Kawaguchi	**127**	Ajay Dhyia
084	Filip Meger	**106**	Anupam Roy	**128**	Alexandros Zografos
085	Karunamayee Mondal	**107**	Patrick Dahlhoff	**129**	Kevin Stefanoni
086	Simon Schmid	**108**	Parashuram Sharma	**130**	Bartosz Bieszczad
087	Indrisish Dey	**109**	Qi-Xin Dong	**131**	Maksim Nikitin
088	Aurore Dietsch	**110**	Stephan Vrabl	**132**	Santosh Pagire

Equimolar cross-coupling of arenes and azoles by alternating current electrolysis

Wayne Sow,[a] Siriphong Somprasong,[a] Dnyaneshwar Aand,[b] Stella Sze Yue Ng,[b] Fangyuan Zhang,[b,c] Taku Wakabayashi,[a,c] Eugene Yew Kun Tan,[a] Saif A. Khan,[b,c] and Shunsuke Chiba[a,c]

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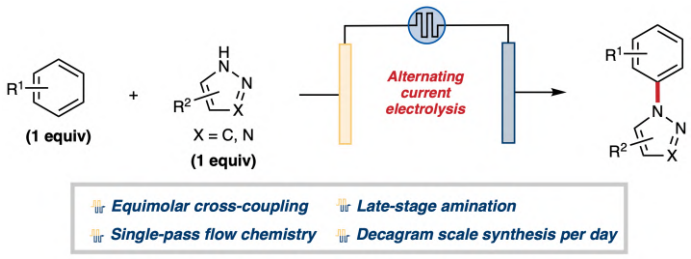
Keywords: Electrochemistry ● Alternating current ● C-H amination

Herein, we report an electrochemical method for the equimolar cross-coupling of functionalized arenes and azoles, enabled by a galvanostatic alternating current (AC) waveform (square wave, 0.2 Hz).[1] In contrast to conventional direct current electrolysis, this AC regime mitigates electrode passivation and overoxidation by promoting periodic reorganization of the electric double layer, resulting in improved mass transport and enhanced selectivity under mild conditions.[2] The method exhibits broad functional group tolerance and enables late-stage amination of complex drug molecules, including gliquidone and fenofibrate, while accommodating diverse functionalities such as carbohydrate and steroid moieties to access macromolecules with molecular weights up to 910. Notably, benzene displays unusual reactivity under these conditions, undergoing sequential fourfold C–N bond formation via six single-electron oxidation events to afford 3,3,6,6-tetrapyrazolyl-1,4-cyclohexadiene. Furthermore, the process is readily scalable through implementation in a tubular electro-flow reactor, achieving continuous single-pass operation with productivities of up to 300 mmol/day.



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Financial support was provided by Nanyang Technological University (NTU Singapore) for S.C., National University of Singapore (NUS) for S.A.K., the Singapore National Research Foundation Prime Minister's Office, Singapore under its Competitive Research Programme (NRF-CRP27-2021-0001) for S.C. and S.A.K. and under its Campus for Research Excellence and Technological Enterprise (CREATE) programme through CREATE Thematic Programme in Decarbonisation (SM3: Sustainable Manufacture of Molecules and Materials) for S.C. and S.A.K.

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Exploring the Redox-Dependent Photochemistry of *N,C,N*-Bi Pincer Complexes: Fundamental Studies and Catalytic Applications

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Keywords: bismuth ● photochemistry ● catalysis ● free radicals ● mechanistic studies

The last decade has witnessed significant advances in the field of metallaphotoredox catalysis, enabling a wealth of novel retrosynthetic disconnections. However, the field has largely been dominated by Ru and Ir-based photocatalysts and transition metal complexes. Herein, we detail the rich photochemistry of an *N,C,N*-bismuth pincer complex, which is responsible for both light-harvesting and bond breaking/forming steps with substrates, thus merging aspects of photoredox and transition-metal catalysis in a single main-group species.

Initial studies revealed that the parent *N,C,N*-Bi(I) complex, owing to its low HOMO-LUMO gap, can undergo oxidative addition into various aryl electrophiles upon irradiation with low-energy red light.[1,2] This occurs via a dissociative electron transfer / recombination mechanism, resulting in well-defined LBi^{III}(aryl)(I) complexes. When irradiated with blue light, the latter species can release aryl radicals, forming the basis for several light-promoted C–C coupling reactions proceeding via a $Bi^{I/II/III}$ catalytic manifold.[3,4] While such couplings can be extended to alkyl iodides, these reactions follow a distinct mechanistic pathway, wherein catalytic XAT between the alkyl iodide and a photogenerated LBi^{II} intermediate can form C-centered radicals in situ. Notably, this represents a rare example of a *bona fide* catalytic XAT catalyst. These insights are leveraged to develop several light-promoted coupling reactions of alkyl iodides that employ an air-stable $LBiI_2$ precatalyst. These mechanistically-guided developments expand the utility of bismuth in synthetic photocatalysis.

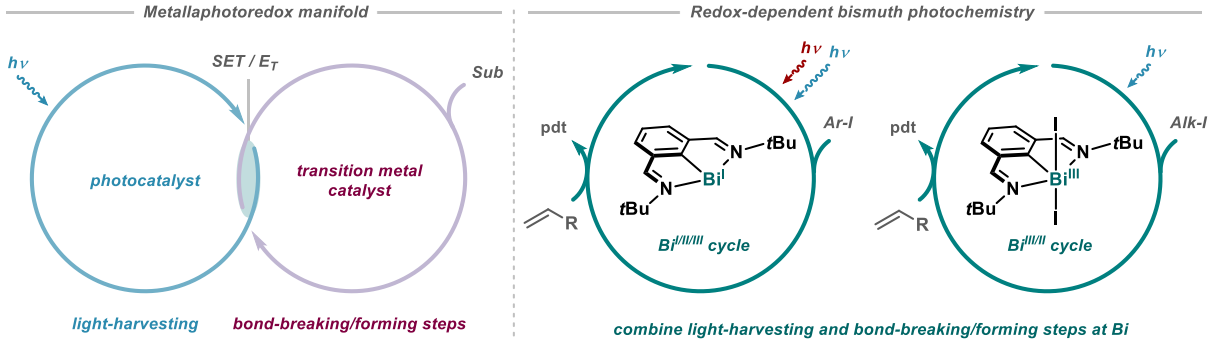

Figure 1. Conceptual relevance between metallaphotoredox manifolds and bismuth photocatalysis – bismuth complexes are able to harvest photons and also mediate downstream reactivity

Acknowledgements
This work was financially supported by the Max-Planck-Gesellschaft, the Max-Planck-Institut für Kohlenforschung, the European Research Council (ERC Starting Grant No. 850496), and the European Union's Horizon Europe research and innovation programme for a Marie Skłodowska-Curie postdoctoral fellowship to A.S. (MSCA-IF Grant No. 101151827).

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Organic photocatalysts generate solvated electrons via two consecutive photoinduced processes

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Keywords: Photocatalysis ● TADF chromophores ● solvated electron

Organic photocatalysts offer a solution to drive chemical transformations that are endergonic in the dark. The consecutive photoinduced electron transfer mechanism (ConPET), based on isophthalonitrile chromophores (4CzIPN or 4DPAIPN)[1], proposes a mechanism in which the photocatalyst (PC) is reduced to a radical anion, $PC^{\bullet-}$, followed by the absorption of a second photon that generates a highly reducing species, $*PC^{\bullet-}$.
We report the investigation of the radical anions $4CzIPN^{\bullet-}$ and $4DPAIPN^{\bullet-}$, which do not behave as super-reducing agents: they are short-lived (ca. 20 ps), non-emissive, and are not quenched by common organic substrates. Instead, the photogeneration of solvated electrons is observed through a consecutive two-photon induced mechanism (ConPies). These photogenerated solvated electrons are responsible for the exceptional reducing power of these photocatalytic systems.[2]

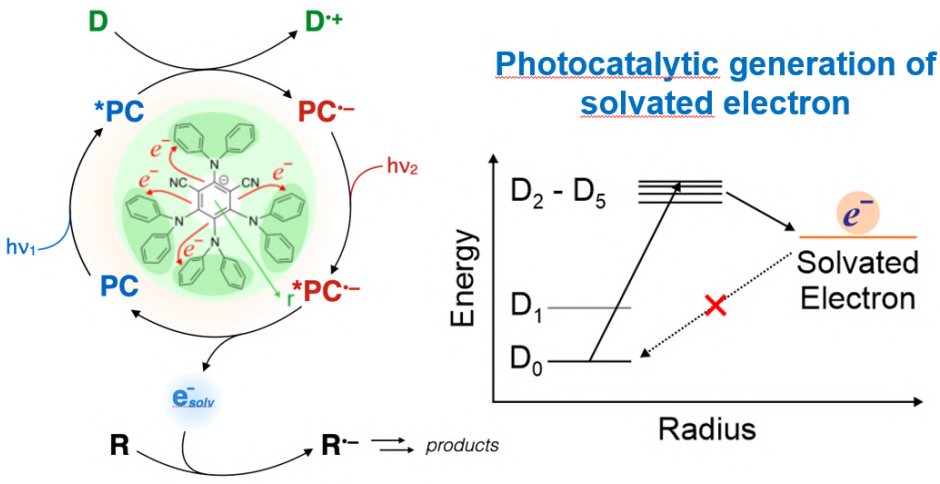

Figure 1. Two consecutive photon-driven generation of solvated electrons

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An *in-situ* Generated Hydrogen-Bonded Complex drives Electrophotocatalytic Processes

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Keywords: electrophotocatalysis ● spectroelectrochemistry ● organic radical anions

In recent years electrophotocatalysis (ePC) has gained more attention as a new and accessible tool for organic synthesis, involving the combination of light and electricity to close the catalytic cycle for the synthesis of diverse products [1]. Among the different species used in the literature as electrophotocatalysts in this approach, the 9,10-dicyanoanthracene (DCA) is widely used due to its neutral and reduced species' adequate electrochemical and photochemical properties [2]. However, one important point to be considered in any catalytic reaction is the stability of the catalyst during the whole reaction. Here, we reveal that under electrophotochemical conditions, the DCA radical anion ($DCA^{\bullet-}$) undergoes a cascade of transformations leading to an unconventional dimeric intermediate that acts as the effective photocatalyst in the reaction. Using operando UV-Vis spectroelectrochemistry, we tracked the real-time evolution of DCA through its radical anion to the formation of 9,10-anthraquinone, which then evolves towards the catalytically active hydrogen-bonded dimeric complex in presence of trace of water and oxygen. Density functional theory (DFT) and time-dependent DFT calculations not only corroborate the dimeric structure but also predict its facile photoexcited reactivity within the synthetic framework.

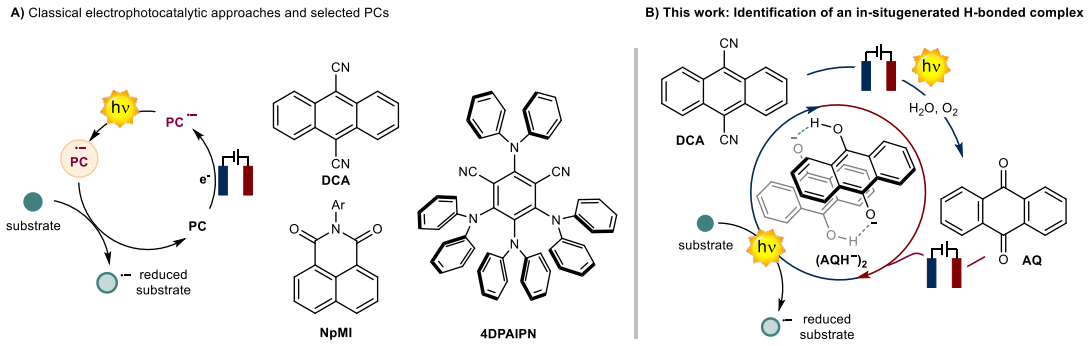

Figure 1. A) Classical approaches in electrophotocatalysis and corresponding PCs. B) This work: the identification and study of an in-situ electrophotogenerated H-bonding complex derived from DCA.

Acknowledgements

This work was financially supported by University of Padova, and the (European Research Council) ERC-Starting Grant 2021 SYNPHOCAT 101040025

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Oxidation of Dihydrotetrazine Triggered by Near Infrared Photocatalysis for Photoclick Chemistry: A Radical Pathway?

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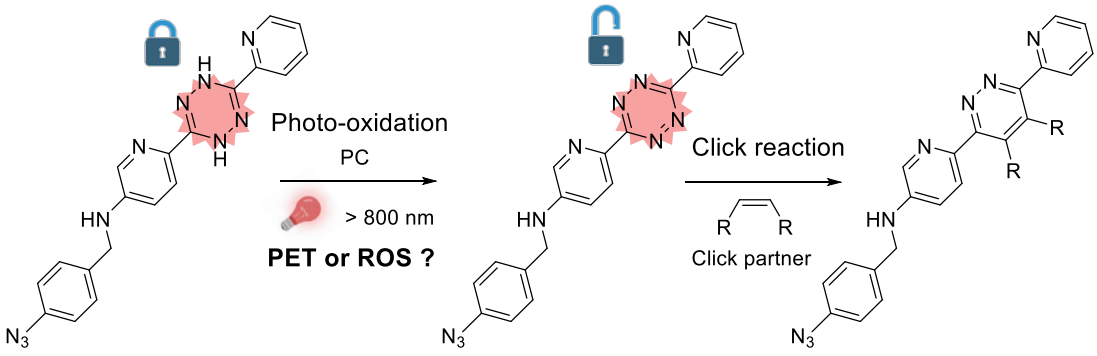
Keywords: Photoclick ● Photocatalysis ● Cyanine ● Dihydrotetrazine ● Bioconjugation chemistry

Synthetic chemists aspire to control each parameter involved in organic transformations, such as efficiency, selectivity (chemo-, regio-, enantio-selectivity), and kinetics. The next level of control needed for applications is the reaction's temporal and spatial trigger. This is particularly required for biological/pharmaceutical applications such as drug delivery or medical diagnostics. [1] Governing the reaction through a simple switcher is appealing, and the photo-click concept is a wonderful tool for achieving this goal. Thus the click reaction, which has many advantages (kinetic, selectivity…), and is triggered by light. Until now, the photoclick concept has been developed from UV to visible light. [2] However, near-infrared light presents many advantages, such as light penetration, biocompatibility and low energy. [3]

Based on our previous works on NIR-photocatalysis driven by cyanines and squaraines[4, 5], we tackle the challenge of NIR-Photoclick. Herein, the NIR-photooxidation of dihydrotetrazine to deliver the clickable tetrazine is presented. This study includes photocatalyst design, optimization, and mechanistic discussion. The last point is crucial to reach the best photocontrol. Does the reaction proceed through a photoinduced electron transfer, reactive species of O_2 or both?[6]



Scheme 1: Near-Infrared Light triggered click reaction

Acknowledgements
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Macrocyclic Core Diversification Enabled By Light-Induced Processes

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Keywords: macrocycle ● bicyclobutane ● ring expansion ● photocatalysis ● DeMayo reaction

The synthesis of macrocyclic scaffolds poses a provocative challenge in modern drug discovery.[1] Conceptuality and practicality aside, the ability to selectively modify structural patterns on already existing macrocyclic bioactive compounds as well as drug candidates by means of late-stage editing would provide a new gateway to access compounds with utmost relevance in drug discovery while significantly reducing the costs for accessing new macrocycles with preclinical data (**Figure 1**, top).

We thereby report two new methods for the highly efficient construction of C(sp³)–C(sp³)-linked macrocycles using visible light, the first via a Pd-catalyzed decarboxylation strategy[2] and the second, a DeMayo-type reaction.[3,4] These approaches leverage readily available macrolactones and mild reaction conditions to enable direct, modular 2-atom ring expansions of macrocycles (**Figure 1**, bottom).

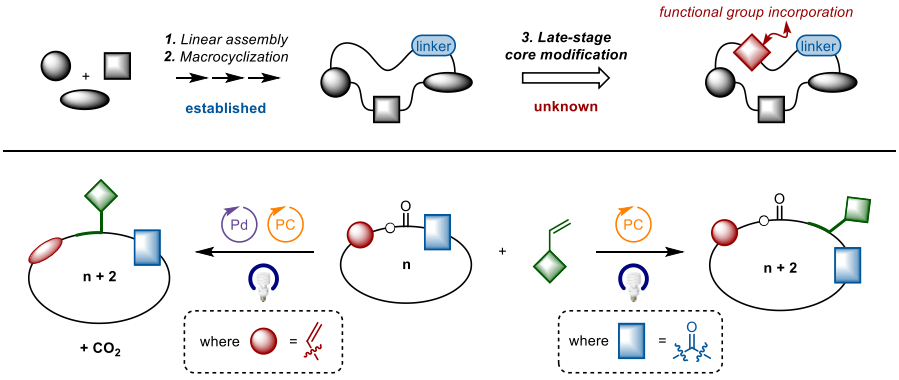

Figure 1. Comparative Approaches to Macrocycle Syntheses (top) and Summary of our Current Work on Macrocyclic Ring Expansion (bottom)

Acknowledgements

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Enantioselective Alkene Difunctionalization with Group 14 Hydrides via Ni/Photoredox Catalysis

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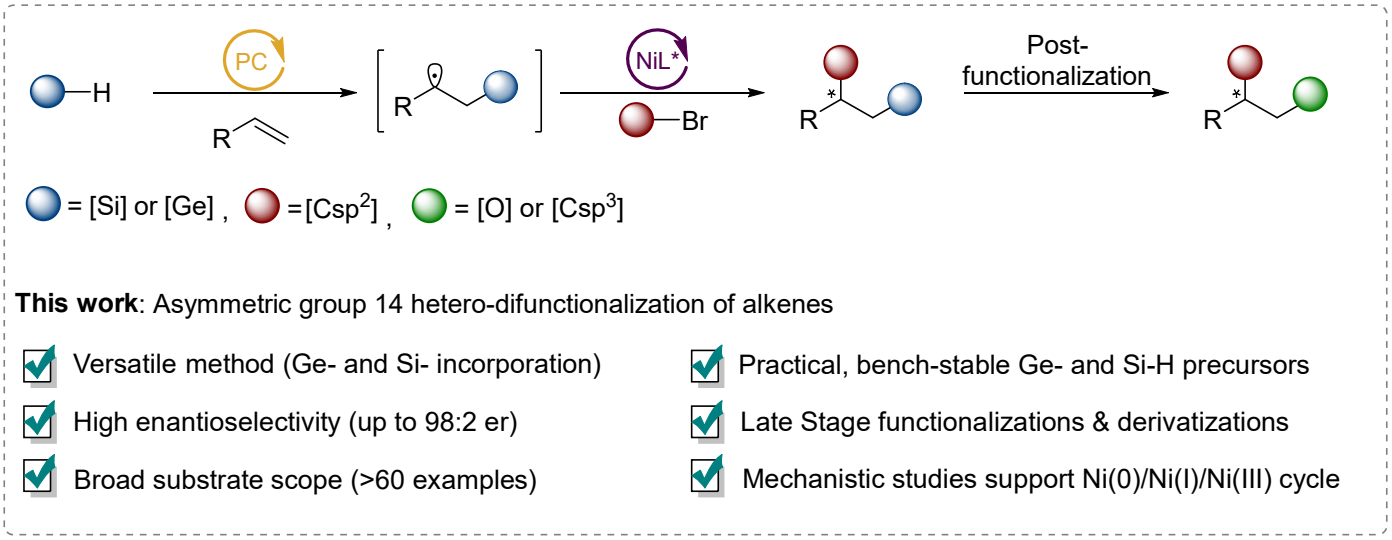
Organic group-14 compounds (Si, Ge, Sn) are important building blocks in materials science, drug discovery, and organic synthesis.[1] While organotin reagents are widely used in cross-coupling reactions, their toxicity has driven the development of safer alternatives. Organosilanes and organogermanes offer high stability, low toxicity, orthogonal reactivity, and serve as effective radical precursors for C–C bond formation under complementary, operationally simple conditions.[2] However, enantioenriched organosilanes and organogermanes remain challenging to access, and asymmetric methods for incorporating heavier group-14 elements lag behind those for carbon analogues.[3]

Here we report a unified Ni/photoredox dual-catalytic platform for the asymmetric hetero-difunctionalization of alkenes using readily accessible, bench-stable silanes and germanes. The method affords highly enantioenriched β-aryl germanes, β-aryl silanes, and β-vinyl silanes with broad substrate scope, excellent functional-group tolerance, and compatibility with late-stage modification of complex bioactive scaffolds. The synthetic utility of these products is demonstrated through diverse downstream transformations, including the first C–C bond-forming reaction employing a chiral germane as a radical precursor. Mechanistic studies support a Ni(0)/Ni(I)/Ni(III) catalytic cycle, establishing a general approach to stereodefined organosilicon and organogermanium architectures.



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Beyond Nitroxyls: Sustainable Synthesis and Catalysis Enabled by Nitrogen-Centered Persistent Radicals

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Keywords: persistent radicals ● Kuhn verdazyls ● C-H functionalization ● borylation ● organocatalysis

The persistent (2,2,6,6-tetramethylpiperidin-1-yl)oxyl radical (TEMPO) is the quintessential example of oxygen-centered persistent radicals (nitroxides or nitroxyl radicals) and has inspired the development of numerous analogues for applications spanning synthesis, catalysis, chemical biology, and beyond.[1] In contrast, nitrogen-centered persistent radicals remain largely underexplored as redox mediators in organic synthesis, despite their stability comparable to that of nitroxides, straightforward preparation, and highly tunable redox properties.

Recently, we have demonstrated that electron-rich organic nitrogen-centered persistent radicals, specifically Kuhn verdazyls, first discovered over 60 years ago,[2] are efficient and tunable ground-state redox catalysts.[3] Their distinct redox properties enable organocatalytic redox-neutral bond-forming transformations that are inaccessible with TEMPO, thereby overcoming key limitations of nitroxide-based persistent radicals. In this presentation, we will describe how this redox tunability and catalytic versatility enable important synthetic transformations, including organocatalytic C–H arylation/trifluoromethylation and C–B bond formation reactions. Additionally, we present noncatalytic applications through unprecedented, conceptually novel metal-free synthetic processes.

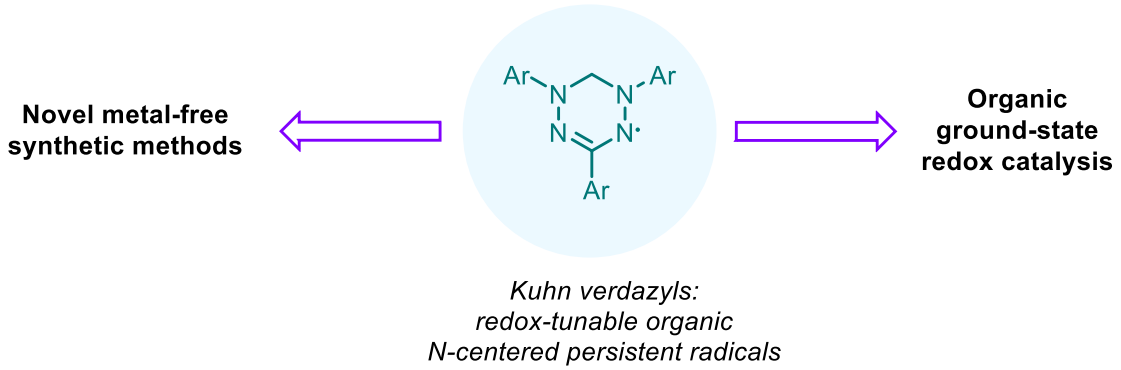

Figure 1. Unique applications of Kuhn verdazyls as redox catalysts and mediators.

Acknowledgements
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Photocatalitic radical cyclization of fluorinated sulfoximines for the synthesis of seven-membered heterocycles

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Keywords: sulfoximine ● fluorine ● photoredox ● cyclization

Sulfoximines have recently gained increasing popularity in pharmaceutical and agrochemical research as versatile bioisosteric replacement of different functional groups, such as sulfones and ketones.[1]

On the other hand, fluorine-containing molecules are of great interest because of their significant pharmacological properties.

Despite their value, the synthesis and use of cyclic sulfoximines remains largely unexplored, as well as their fluorinated variants. [2]

Building on our previous studies on the photocatalytic difluorosulfoximination of olefins and propellanes,[3] we have now investigated a peculiar radical ring-closing process that grants selective access to complex seven-membered heterocyclic systems.

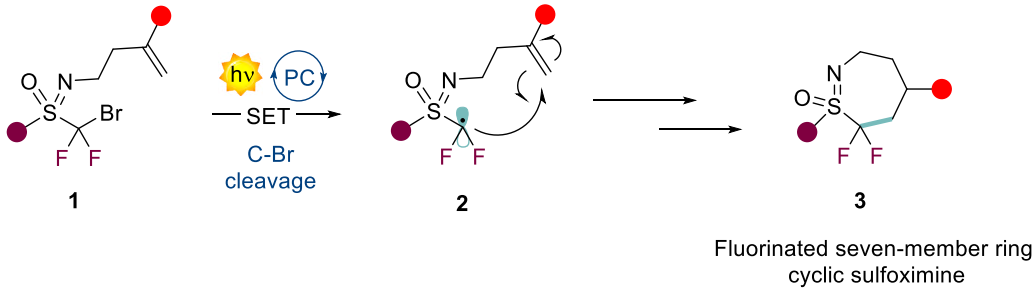

Figure 1. Photoredox synthesis of fluorinated seven-membered cyclic sulfoximines.

Here, a wide variety of seven-member cyclic sulfoximines are obtained under mild organophotoredox conditions. Using this synthetic strategy, we accessed structurally diverse cyclic derivatives **3** (20 examples, up to 80% yield), with high tolerance toward different functionalities, including halogens, ester, nitrile, etc.

Acknowledgements
This work was supported by MUR (Ministero dell'Università) PRIN2022PNRR23_01 and (European Research Council) ERC-Starting Grant 2021 SYNPHOCAT 101040025.

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Halogen-bond promoted *α*-C–H difluoroalkylation of amines

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Keywords: amine ● halogen-bonding complex ● radical-polar crossover ● difluoroalkylation ●

β,β-Difluoroamino motif is frequently encountered in bioactive molecules.[1] The difluoromethylene group located adjacent to the nitrogen atom can significantly lower its basicity, thereby influencing the physicochemical properties and pharmacokinetic profiles of a potential drug molecule. Additionally, as an oxygen atom bioisostere, the difluoromethylene group may offer enhanced potency and metabolic stability.[2]
Current approaches to the synthesis of difluoroalkylated amines usually require the use of prefunctionalised amides, imines, or benzotriazole derivatives as starting materials.[3] Herein, we present a novel method for the direct *α*-C–H difluoroalkylation of tertiary amines with structurally diverse and readily accessible difluoroalkyl halides (Figure 1). The reaction is proposed to operate via thermally and photochemically mediated homolysis of a halogen-bonding (HB) complex between the amine and difluoroalkyl halide. Halogen-atom transfer (XAT) then provides an iminium ion, while the addition of Zn facilitates a reductive radical-polar crossover of the polarity-mismatched difluoroalkyl radicals to render a reactive difluoro-organozinc reagent. Subsequent coupling of the iminium and organozinc reagent leads to the formation of diverse difluoroester, -amide and -ketone derivatives of amines.

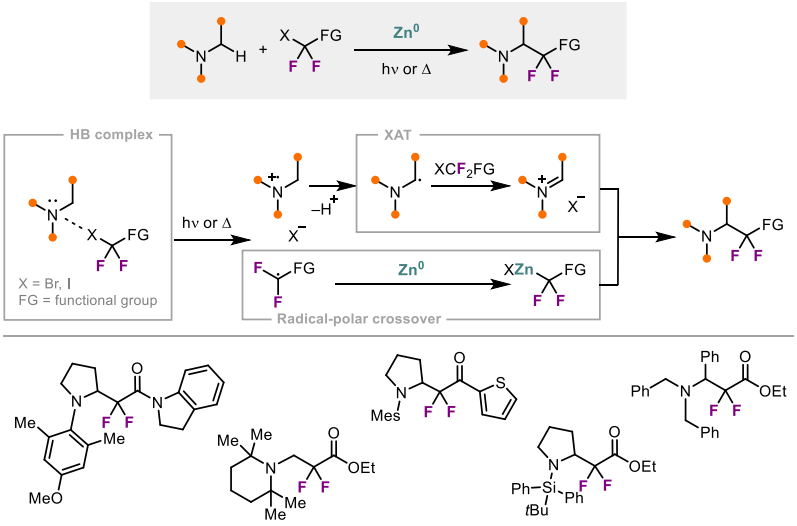

Figure 1. Halogen-bond promoted *α*-C–H difluoroalkylation of amines via *in situ* generation of iminium ion and difluoro-organozinc reagent

Acknowledgements
This work was financially supported by EPSRC.

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Light-driven metal-free thiocarbonyl – olefin metathesis

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Keywords: photochemistry ● metathesis reactions ● thietanes ● hindered olefins ● domino sequences

Because of their ubiquitous nature, alkenes have been the subject of extensive research and the olefin metathesis reaction rapidly supplanted the Wittig olefination to become the method of choice for preparing them.[1] More recently, metal-catalyzed and photochemical carbonyl-olefin metathesis reactions, including the formation of the oxetane ring followed by the cycloreversion of the strained ring, emerged as reliable alternative strategies.[2-3]

In contrast to oxetanes, fragmentation of thietanes,[4] which are their sulfur analogs, has been way less explored to date due to their synthetic access, which remained challenging until recently. Indeed, our group newly reported a domino photochemical synthesis of a wide variety of thietanes, where unstable thiocarbonyls are generated in situ via a Norrish-type II fragmentation of phenacyl[5] or pyrenacyl[6] sulfide precursors, which then participate in a thia-Paternò–Büchi reaction with diverse alkene partners.

Leveraging the straightforward synthesis to functionalized thietanes, we thoroughly investigated the light-induced cycloreversion of these four-membered ring sulfur-containing heterocycles and established a metal-free photochemical thiocarbonyl – olefin metathesis.[7] In this domino sequence, which provided access to a broad range of tri- and tetra-substituted alkenes, light irradiation promotes both the regioselective formation and subsequent fragmentation of the thietane intermediate.

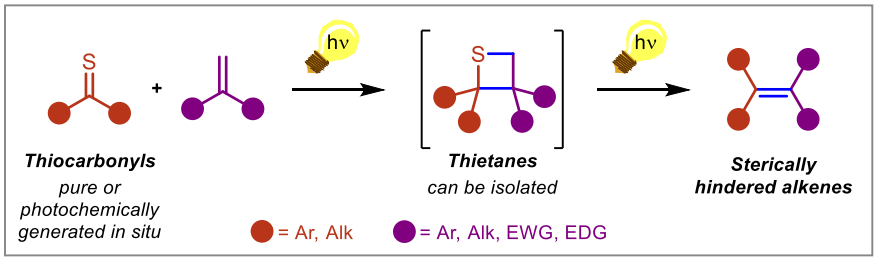

Figure 1. Metal-free thiocarbonyl - olefin metathesis

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Photogenerated *N*-oxazolidinone radicals and their addition to π-systems

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Keywords: Photocatalysis ● Nitrogen radicals ● Flow chemistry ● EDA complex ● Dual catalysis

Oxazolidinone rings are essential structural motifs in organic chemistry, widely present in natural products and clinically important drugs, such as antibiotics and antiepileptics. Existing methods for synthesizing *N*-functionalized oxazolidinones often require harsh conditions, toxic reagents, or complex catalytic systems. [1] In this context, we recently reported the photoredox-catalyzed generation of unprecedented *N*-oxazolidinone radicals and their addition to variously functionalized arenes and hetarenes, starting from a novel class of *N*-radical precursors. [2] During the control experiments, we observed that pyridinium ion precursors **1a-b** are able to form an Electron Donor–Acceptor (EDA) complex both with inorganic bases such as $NaHCO_3$ (*EDA-1*) or with the arenes (*EDA-2*) (Figure 1A). Precursors **1a-b** and 1-methylindole were selected as model substrates. After a fine tuning of the reaction conditions, we were able to obtain regioselectively the desired 3-(1-methyl-1*H*-indol-2-yl)oxazolidin-2-one in 81% of isolated yield under mild metal-free conditions.

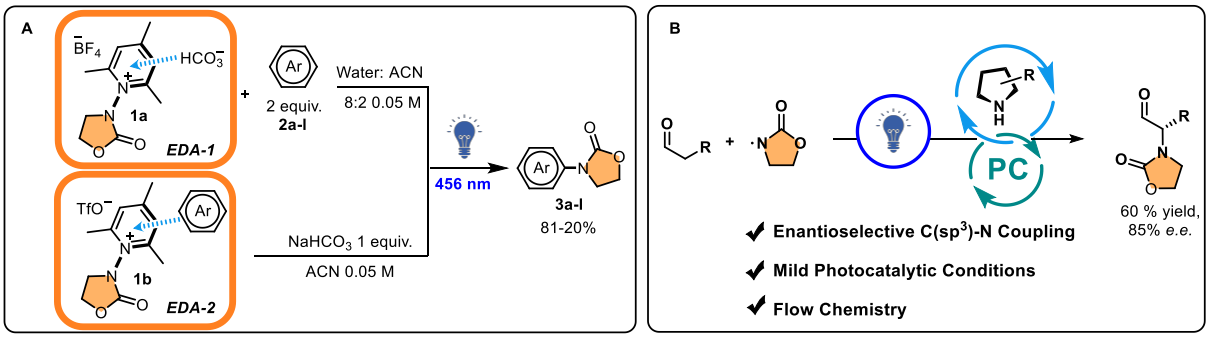

Figure 1. *N*-oxazolidinone radical addition to A) (het)arenes via EDA complex and B) aldehydes (enantioselective).

The reaction scope was expanded to 13 different *N*-arylated oxazolidin-2-ones (20-81% yield) including unprotected indoles, thus offering the opportunity for the direct functionalization of tryptophan dipeptides and tripeptides. The photochemical reaction can be easily transferred to continuous flow conditions, thus greatly improving the reaction productivity. UV-vis absorption spectroscopy confirmed the presence of an EDA complex in the reaction solution. [3] After exploring the reactivity of these new class of electrophilic amidyl radicals with aromatic nucleophiles, we employed *in situ* formed chiral π-enriched enamines as compatible substrates. In a dual catalytic approach, we selected, as model reaction, precursor **1b** and hydrocinnamaldehyde in the presence of a chiral imidazolidinone as the organocatalyst and 4-CzIPN as the photocatalyst. After preliminary experiments resulting in moderate *e.e.*, the effect of the temperature and of the organocatalyst structure were carefully evaluated and the reaction mechanism was investigated. We were then able to isolate (*S*)-3-(1-hydroxy-3-phenylpropan-2-yl)oxazolidin-2-one in 60% yield and 85% *e.e.* under mild metal-free conditions. Lastly, flow chemistry was used to enhance the reaction performance, resulting in higher productivity and improved enantioselectivity (Figure 1B). [4]

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[4] *Unpublished results.*

Photochemical and Electrochemical Halogen Atom Transfer (XAT) with NHC-Boryl Radicals

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Keywords: ligated boryl radicals ● XAT ● photochemistry ● electrochemistry ● C−C bond formation

In the realm of radical chemistry, halogen-atom transfer (XAT) is re-emerging as a powerful activation strategy in synthetic endeavors to engage otherwise recalcitrant organic halides (R_3C−X, X: halogen).[1] Here, a halogen-abstracting entity is responsible for the formation of a C-centered radical by homolytically cleaving the C−X bond. Tin radicals have been in the spotlight as halogen abstractors for decades,[2] but more recently photocatalysis has brought to light more sustainable options, such as silyl[3a] and α-aminoalkyl radicals.[3b]
N-heterocyclic carbene (NHC)-ligated boryl radicals, i.e. boron-centered radicals where the boron atom is coordinated with a NHC, have been proposed as XAT agents as well. Their use, however, has been mainly applied to reductive dehalogenation.[4]

In this contribution, we present an overview of our research on NHC-ligated boryl radicals for C(sp^3)–C(sp^3) bond formation via XAT through photochemical and electrochemical pathways (Figure 1).[5] The mildness of the present approach is demonstrated by the fact that derivatives of medicinally-relevant compounds and biologically-active molecules were smoothly functionalized. The key role of the NHC-ligated boryl radicals in the operative reaction mechanism has been uncovered through a combination of experimental, spectroscopic and computational studies.

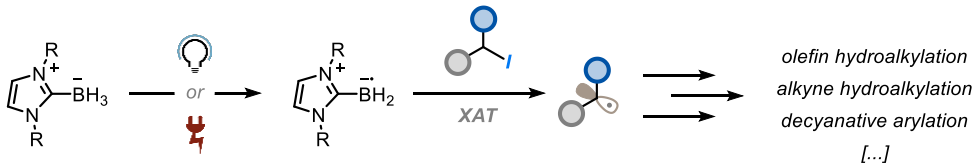

Figure 1. NHC-ligated boryl radicals can be generated from the corresponding boranes via photochemical and electrochemical manifolds. These intermediates can be leveraged for XAT and disclose efficient synthetic methodologies.

Acknowledgements
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Radical Hydrogenation of Olefins

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Keywords: ● radical hydrogenation ● hydrogen radical ● photoredox catalysis ● formic acid ● hydrogen atom transfer

Hydrogenation of alkenes is a cornerstone transformation in organic synthesis, yet its implementation remains dominated by transition-metal catalysis and polar hydride transfer pathways. In contrast, the direct use of hydrogen radicals for alkene reduction has remained elusive, largely due to the harsh conditions typically required for the generation of a hydrogen atom.
Herein, we report the first example of a radical hydrogenation of olefins using formic acid as the hydrogen atom source. This organophotoredox catalytic strategy enables the controlled generation of hydrogen radicals under mild, metal-free conditions, allowing efficient reduction of a broad range of terminal alkenes. The reaction proceeds *via* an open-shell hydrogen radical transfer mechanism that is fundamentally distinct from classical hydrogenation approaches.
Beyond showcasing a new paradigm for olefin hydrogenation, this work establishes single hydrogen atoms as practical reagents in organic synthesis, enabling access to previously underexplored reactivity of the smallest radical.

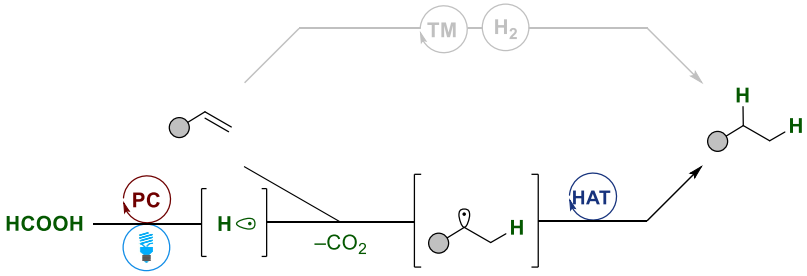

Figure 1. Organophotoredox-catalysed radical hydrogenation of terminal alkenes using formic acid as the hydrogen atom source, in contrast to conventional transition metal (TM)-catalysed methods.

Acknowledgements
This work was financially supported by Department of Chemistry, University College London.

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Late-Stage C1-C4 alkylation of (Hetero)arene with Light Alkanes enabled by Hydrogen Atom Transfer in Flow

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***Keywords**: Light Alkanes • Photocatalysis • Cross-Coupling • Flow Chemistry • Late Stage functionalization*

The use of gaseous reagents in the production of active pharmaceutical ingredients (APIs) presents a scientific challenge due to safety concerns and efficiency limitations. However, the implementation of continuous-flow reactors has rapidly advanced gas-handling technology, offering several advantages such as increased interfacial area, improved mass and heat transfer, and seamless scale-up. These studies introduce a photocatalytic platform that facilitates the alkylation of (hetero)arenes using abundant gaseous C1-C4 alkanes under continuous-flow conditions, overcoming the typical challenges of C−H bond cleavage that generally require high temperatures and pressures. By employing hydrogen atom transfer (HAT) catalysis, or a combination of HAT and nickel-catalyzed cross-coupling at room temperature, we achieve efficient alkylation of pharmaceutically relevant compounds without the need for prefunctionalized reagents2-3. This scalable and sustainable method is applicable to the functionalization of marketed drugs and natural products. Taken together, the results highlight the utility of gaseous feedstocks for late-stage functionalization, offering a promising strategy for lead diversification and optimization in drug discovery.

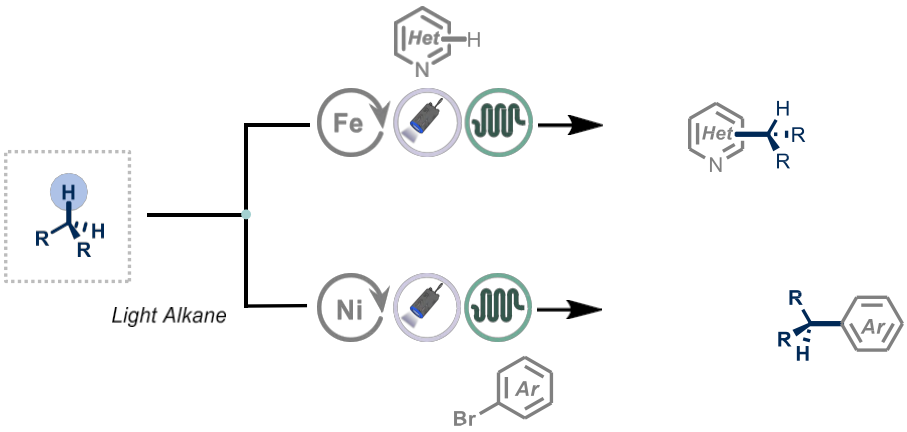

Figure 1. Gaseous Alkanes Functionalization: Design of an Efficient Arylation of Light Hydrocarbon

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Reduced *N*-Heterocyclic carbene radical anion species: isolation and characterisation

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Keywords: *N*-Heterocyclic carbenes ● DFT ● electrochemistry ● isolation

N-Heterocyclic carbenes (NHCs), popular species with applications as ligands or organocatalysts,[1] have been given relatively little attention to their explicit redox properties. Although electrogeneration of carbenes by reduction of their parent imidazolium salts is well known,[2] only 1 example of direct observation of a reduced carbene radical anion species has been reported previously.[3] Other efforts have been largely limited to transient methods or analysis of decomposition products, due to the instability of the reduced products.[4]

We present an exploration of the intrinsic electronic properties hindering the stabilisation of the reduced form of NHCs within progressively more delocalised frameworks and identify several potentially isolable radical anion species. These efforts are then crowned with our recent success in the isolation and crystallization of the first stable singly reduced carbene radical anion. Finally, through reactivity studies, the potential applications of this species are investigated.

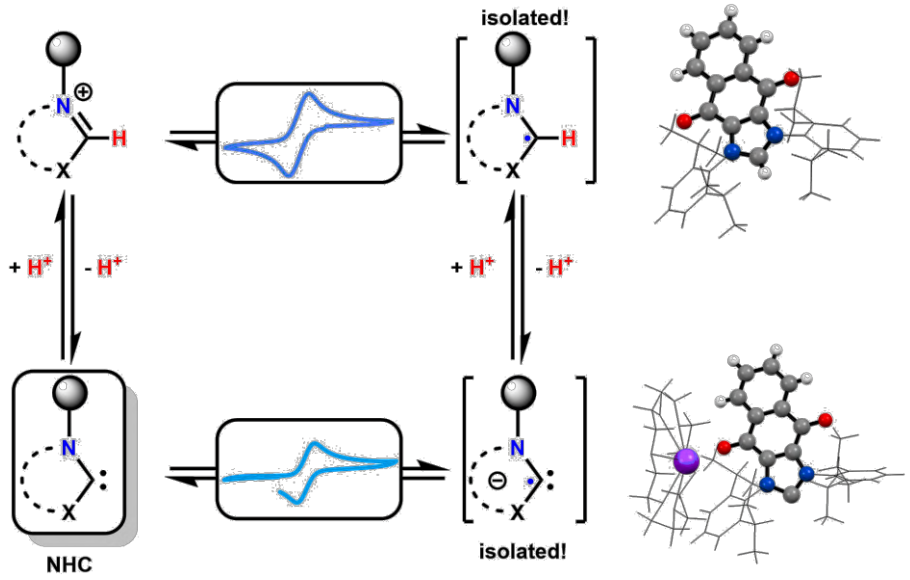

Figure 1. Square scheme highlighting the electrochemical accessibility of a carbene radical anion species, along with the crystal structures of the isolated species

Acknowledgements
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Photochemical, Pd-Catalyzed Activation of Alkyl Bromides and Chlorides for Alkylative Cascade Cyclization of *o*-Cyano Acrylamides and 1,7-enynes

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Keywords: Photocatalysis ● C-H Activation ● Alkyl-Palladium hybrid Species ● Phenanthridines

The development of excited-state palladium-catalyzed alkylative cyclization reactions has emerged as a powerful strategy for the construction of complex heterocyclic frameworks, including O-cyanoacrylamides and spirocyclic architectures derived from 1,7-enynes. In this context, direct alkyl C–H functionalization represents an atom- and step-economical approach, circumventing the need for pre-functionalized substrates while enabling the use of readily available alkyl radical precursors. Despite significant progress in photoredox-mediated radical chemistry, cascade cyclizations of O-cyanoacrylamides and 1,7-enynes involving alkyl radicals generated from both activated and unactivated alkyl halides remain largely unexplored. the development of a general, broadly applicable protocol for such alkylative cyclizations is highly desirable. In the present strategy, a diverse array of primary, secondary, and tertiary alkyl halides is employed as radical progenitors under photoredox conditions, enabling the efficient generation of alkyl radicals. These radicals undergo addition to the carbon-carbon double bond of N-arylacrylamide[2], involves cyano insertion and cyclization, ultimately leading to the formation of alkylated phenanthridines derivatives under photoredox conditions[3-4]. simple catalytic system and mild reaction conditions, eliminating the need for harsh oxidants or elevated temperatures are the key highlights of this method. Hence this methodology significantly expands the synthetic utility of alkyl radical-mediated cascade cyclizations and provides a practical and efficient route to structurally complex heterocycles.

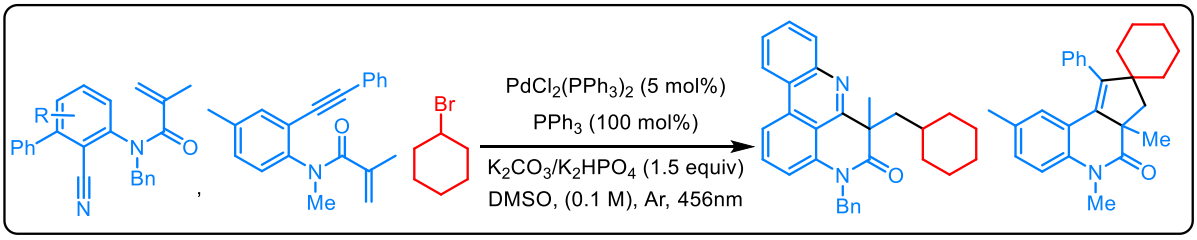

Figure 1. Cascade cyclization of o-cyano Acrylamide and 1, 7-enynes.

Acknowledgements
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Catalytic enantioselective [2 + 2] photocycloadditions for the dearomatization of heterocycles

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Keywords: Asymmetric synthesis ● Photochemistry ● Organocatalysis ● Photocycloadditions ● Dearomatizations

The direct transformation of readily available aromatic feedstocks into structurally diverse three-dimensional heterocycles makes catalytic asymmetric dearomatization (CADA) reactions[1] of broad interest, providing a sustainable and straightforward synthetic route to medicinally relevant archetypes. However, the inherent difficulty of the disruption of aromaticity demands a large energy input during the dearomatization process, which could be incompatible with the typical conditions required by asymmetric catalysis. One promising approach to overcome this issue is the investigation of the excited-state reactivity of (hetero)arenes that may display different reactivity patterns compared to the original ground-state ones.
In this contribution, the successful combination of asymmetric organocatalysis with the direct activation of visible light[2] to develop an array of interesting organocatalytic asymmetric [2 + 2] dearomative photocycloadditions of the indole core[3] is presented. This methodology[4] relies on the excited state reactivity of transiently generated catalytic intermediates, thus enabling the construction of optically active polycyclic products in high levels of yield and stereoselectivity. The scope of the reaction was explored using a broad range of alkene partners, including strained substrates such as bicyclobutanes (BCBs). In addition, the catalytic system was successfully translated to flow conditions, demonstrating promising improvements in reaction efficiency and scalability.

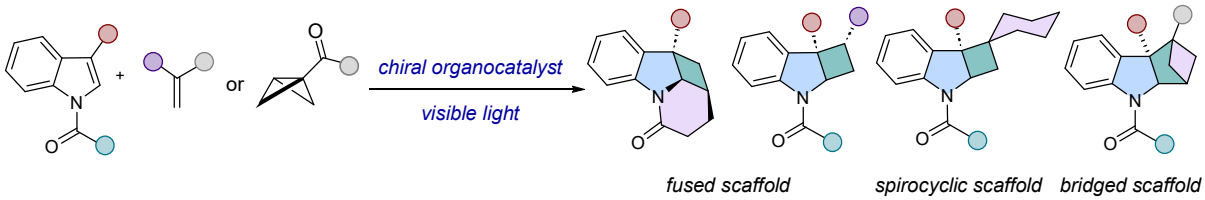

Figure 1. Organocatalytic enantioselective [2+2] photocycloadditions of indole derivatives

Acknowledgements
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Dual-role Iron Species in Photoelectrocatalytic Radical Trifluoromethylation with Trifluoroacetates

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Keywords: synthetic methods ● photoelectrocatalysis ● iron catalysis ● radical trifluoromethylation ●

Trifluoromethylation is a fundamental transformation in pharmaceutical research, contributing to the success of numerous marketed drugs. Recent advances in iron ligand-to-metal charge transfer (LMCT) catalysis have enabled the use of trifluoroacetates as CF_3 radical sources in (hetero)arene trifluoromethylation.[1] However, current approaches often rely on inorganic stoichiometric oxidants to regenerate photoactive iron species, thereby restricting functional group compatibility and broader applicability.
In this work, we report a photoelectrocatalytic strategy that uses *in situ*-formed multifunctional iron catalysts to achieve C(sp²)–H trifluoromethylation without external oxidants, producing traceless byproducts. [2] Mechanistic investigations reveal catalytically active iron species that simultaneously drive trifluoroacetate photodecarboxylation and facilitate redox turnover. The method operates under mild, tunable and scalable conditions using visible light and electrical current, and demonstrates broad substrate compatibility, including challenging electron-rich and easily oxidizable substrates. Overall, this strategy offers a practical and sustainable approach for late-stage trifluoromethylation in drug discovery workflows.

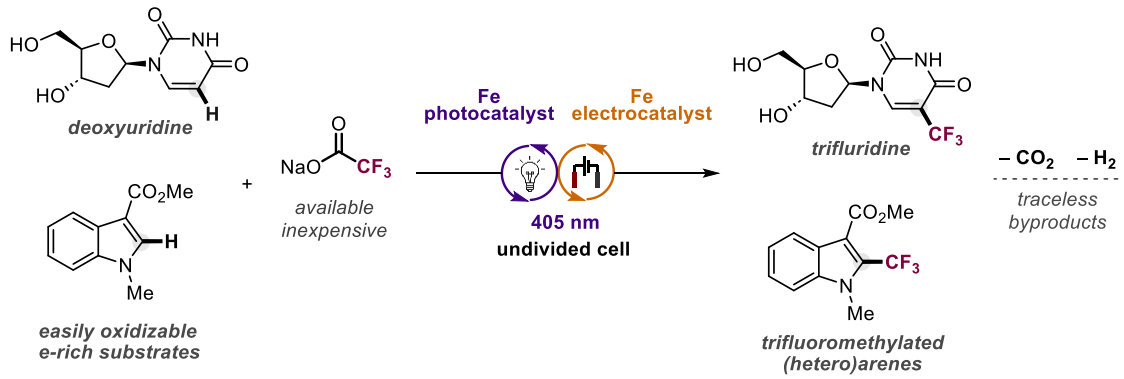

Figure 1. Radical C-H trifluoromethylation of (hetero)arenes with trifluoroacetates by synergistic iron electro- and photocatalysis.

Acknowledgements
This work was financially supported by grants CNS2022-135161 (to I.B.); CNS2023-145163, PID2023-15452NB-I00 and RYC2018-024643-I (to F.J.H.); RYC2024-048858-I (to S.C) and PRE2021-099616 (to S.F.G.), funded by MICIU/AEI/10.13039/501100011033 and by the "European Union NextGenerationEU/PRTR". GVA (grants CIAICO/2022/017 to J.C.G.G and SEJIGENT/2021/005 to I.B) are also acknowledged.

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Photocatalytic Birch-type reduction of 2-Pyridones

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Keywords: Birch-type reduction ● Energy-transfer catalysis ● Monocyclic heteroarenes ● Partial saturation ● 2-Pyridones

The Birch reduction enables the partial hydrogenation of otherwise inert aromatic rings and remains a cornerstone for arene dearomatization.[1] However, the requirement for pyrophoric metals and cryogenic conditions limits its scalability and operational safety, motivating the development of milder alternatives. We therefore aimed to develop a mild and practical energy transfer catalyzed Birch-type reduction on heteroarenes, such as 2-Pyridones. These substrates combine monocyclic aromatic systems amenable to energy-transfer catalysis[2] with broad relevance as structural motifs in biologically active and pharmaceutical compounds.[3] In this study, we report the partial saturation of 2-pyridones by triplet excitation and subsequent hydrogen-atom transfer (HAT) events.

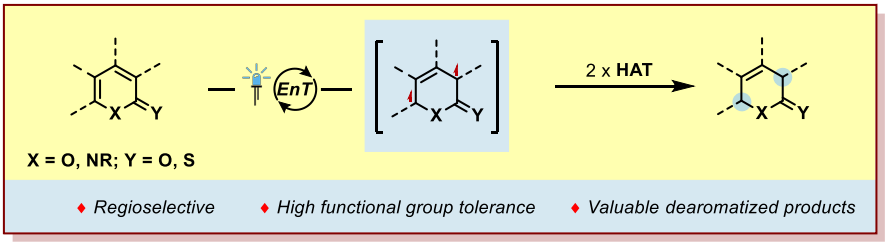

Figure 1: Energy-transfer catalyzed Birch-type reduction on 2-Pyridones.

Our methodology shows exceptional regioselectivity, forming the thermodynamically disfavored regioisomer. In addition, the developed protocol was discovered to tolerate a vast number of functional groups, including reductively sensitive moieties such as nitriles, alkynes, alkenes, ketones, and halogens. A mechanistic investigation was performed to gain a greater understanding of the propsed *EnT*-HAT reaction pathway and, in combination with DFT computation, the nature of the formation of the thermodynamic unfavored product was elucidated. Overall, we believe that this study can provide a platform from which further investigations into the partial saturation of monocyclic arenes can be built upon.

Acknowledgements

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Data-Driven Discovery and Mechanistic Interrogation of Triplet Energy Transfer Catalysis by Predictive Machine Learning and Automated High-Throughput Spectroscopy

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Keywords: Energy Transfer Catalysis ● Accelerated Reaction Discovery ● High-Throughput Spectroscopy ● Molecular Machine Learning● Laboratory Automation

Triplet energy transfer (EnT) photocatalysis has emerged as a powerful mode of catalysis, providing an efficient way for the rapid and facile construction of complex molecules starting from simple reactants.[1] However, discovering new, suitable substrates and reactivity modes is hindered by the high cost of experimental and computational screening methods and the vastness of chemical space. To accelerate the discovery of novel EnT-mediated synthetic transformations, we developed an integrated digital platform that guides substrate identification, reaction development, and facilitates mechanistic interrogation. By training machine learning (ML) models on a large dataset of organic molecules annotated with computed triplet-state properties, we enable rapid and accurate prediction of the thermodynamic feasibility of EnT processes between a photocatalyst and a quencher.[2] Notably, these predictions are generated within milliseconds and require only the molecular structure as input. This capability allows for the high-throughput, *in silico* identification of unexplored substrates, which are subsequently evaluated experimentally using parallelized and automated screening techniques.

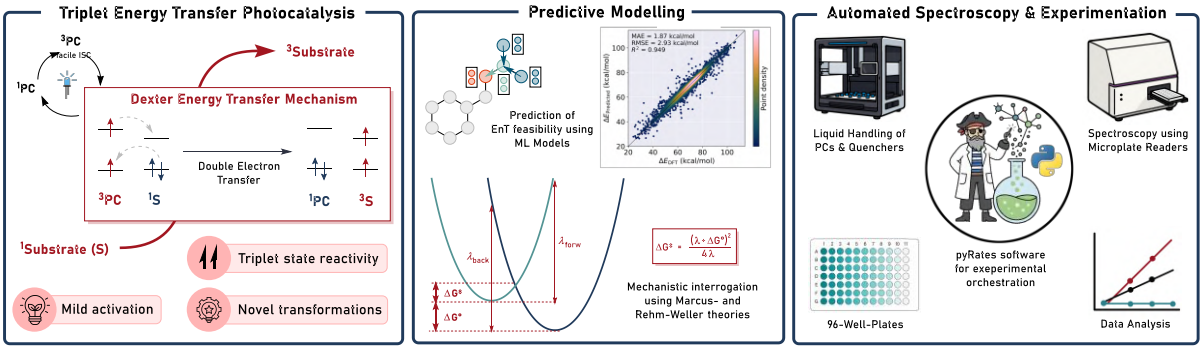

Figure 1. Prediction and investigation of EnT catalysis by machine learning and high-throughput experiments

Beyond substrate and reaction discovery, we generate mechanistic insights by coupling ML-based predictions with established physical-organic frameworks, such as Marcus and Rehm–Weller theory, to account for kinetic barriers associated with Dexter-type energy transfer.[3] To validate and translate computational predictions into experimental reality, we further develop an automated robotic platform and an associated open-source software suite. This system autonomously plans, executes, and analyzes high-throughput spectroscopic experiments—such as Stern–Volmer quenching studies,[4] electron donor–acceptor (EDA) complex screenings, and spectral scans—thereby enabling rapid feedback between prediction, experiment, and mechanistic understanding.

Acknowledgements
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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Desymmetrization of Cyclopropane Derivatives via Non-directed Enantioselective C(*sp*^{3})-H Bond Oxidation

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Keywords: enantioselective C−H bond oxygenation ● hydrogen atom transfer ● Mn-catalysis ● solvent effects ● hyperconjugative activation

The functionalization of nonactivated C(*sp*^{3})–H bonds represent a very powerful reaction, since such processes open to the possibility of converting these relatively inert bonds into functional groups suitable for further chemical transformations[1]. In this context, among the available strategies for selective C(*sp*^{3})–H bond functionalization, methodologies based on hydrogen atom transfer (HAT) have proven to be successful. Factors governing HAT reactivity and site-selectivity have been discussed in detail.[2,3] Control over enantioselectivity remains however a challenging goal. Here, we describe a catalytic enantioselective oxidation with H_2O_2 and a chiral manganese catalyst of methylenic C(*sp*^{3})–H bonds in spiro[2.5]octane derivatives bearing different functional groups (FGs) at position 6. The reaction proceeds through a mechanism that involves the formation of a high-valent Mn-oxo species that engages in HAT from a substrate C−H bond, followed by a fast and stereoretentive hydroxyl transfer (O−H *rebound*) to the intermediate carbon radical[4].

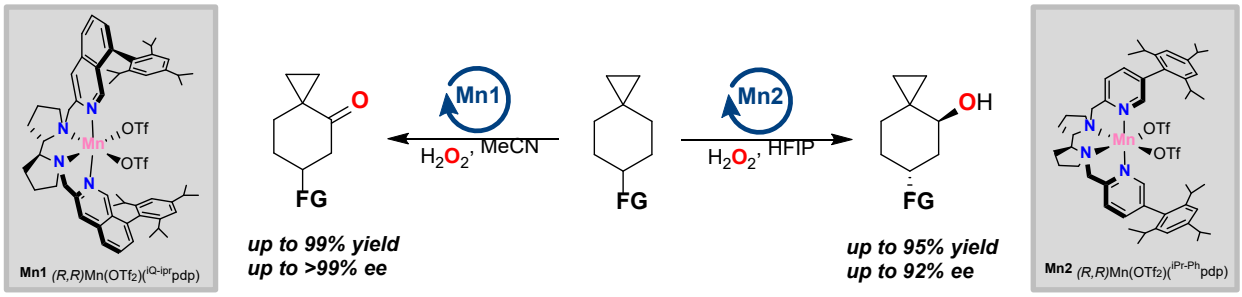

Figure 1. Manganese catalyzed methylenic C-H bond oxidation with hydrogen peroxide

Reaction optimization, carried out in MeCN and in the strong hydrogen bond donor solvent HFIP, identified Mn1 and Mn2 (Figure 1) as the best performing catalysts. In keeping with the hyperconjugative activation of the C−H bonds α- to the cyclopropane ring, highly site-selective oxygenation products (alcohols and ketones) at this site are achieved in excellent yield and enantioselectivity under mild conditions. Product chemo and diastereoselective hydroxylation is obtained when changing the solvent from MeCN to HFIP. The synthetic versatility of these newly installed groups, together with the possibility to promote cyclopropane ring-opening, enable straightforward elaboration of the obtained chiral products. These follow-up transformations provide access to new structural motifs while simultaneously preserving the chiral information acquired in the oxidation step.

Acknowledgements
Financial support from the European Research Council (AdvG 883922 to M.C.) is gratefully acknowledged.

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Mechanically Interlocked Catalysts for Aerobic Oxidation of Primary Alcohols

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Keywords: Rotaxanes ● Nitroxides ● Catalysis ● EPR ● Supramolecular Chemistry

Nitroxide radicals are widely utilized as catalysts for the oxidation of primary alcohols. In this work the aerobic catalytic oxidation cycle of nitroxide radicals has been implemented within a mechanically interlocked rotaxane architecture. Two examples will be described: in the first one the rotaxane consists of a paramagnetic crown ether, which is confined by a molecular axle containing a dialkylammonium station and a 1,2,3-triazole unit. In the other example the nitroxide paramagnetic unit is incorporated in the axle and the wheel is represented by a standard crown ether.
These rotaxane are engineered to exploit the oxidation of a primary alcohol: the primary catalyst is the nitroxide radical capable of altering its oxidation state during the catalytic cycle, while the co-oxidant is the Cerium(IV)/O_2 couple. The synthesis of the proposed rotaxanes, along with their characterization using EPR, HRMS, voltammetry and NMR data, will be described. EPR and NMR were further employed to investigate the aerobic catalytic oxidation cycle. This study can aid in the design of autonomously driven molecular machines that exploit the aerobic catalytic oxidation of nitroxide radicals.[1]

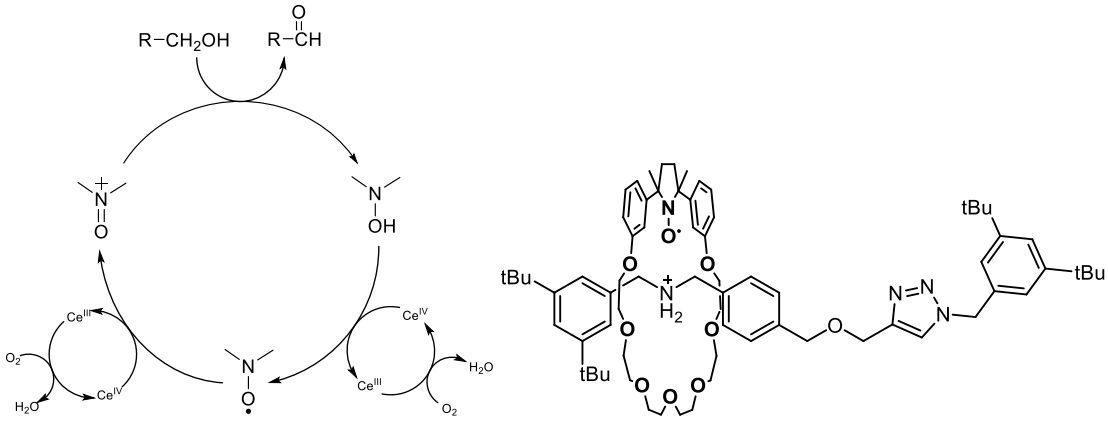

Figure 1. Catalytic cycle of the oxidation of primary alcohols promoted by nitroxide radicals and structure of one of the rotaxane synthetized and investigated in the present study.

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Switchable Regioselective Transformations of Azobenzenes

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Keywords: alkynylazobenzenes ● photocatalysis ● indazoles ● quinolines ● gold

The photoisomerization of azobenzenes is well established, yet the photoreactivity of alkynylazobenzenes has remained largely unexplored. We show that these substrates undergo intermolecular alkynyl difunctionalization under visible light, enabling oxoamination, sulfenoamination and deamination processes without the need for photocatalysts or transition metals.[1] We have also developed a regiodivergent cyclization of 2-alkynylazobenzenes that provides distinct azapolyaromatic products depending on the catalytic system. Under visible-light irradiation with an iridium photocatalyst, a 1,5-carboamination occurs to give 11*H*-indolo[1,2-*b*]indazoles, whereas the addition of $AuCl_3$ redirects the reaction toward a 1,6-cyclization, affording indazolo[2,3-*a*]quinolines. Control experiments and DFT studies reveal mechanistic divergence: a radical pathway leads to indoloindazoles, while a predominantly polar mechanism forms indazoloquinolines.[2]
Additionally, fine-tuning of reaction conditions enables the regioselective hydroamination ofalkyes to access 3-alkenyl-2*H*-indazoles, either via dual gold/photoredox catalysis[3] or copper catalysis.[4] In the gold/ruthenium system, radical and polar pathways operate in parallel, whereas the copper-catalyzed reaction proceeds through C-N bond formation, followed by a rate-determining 1,2-hydride shift as supported by DFT.

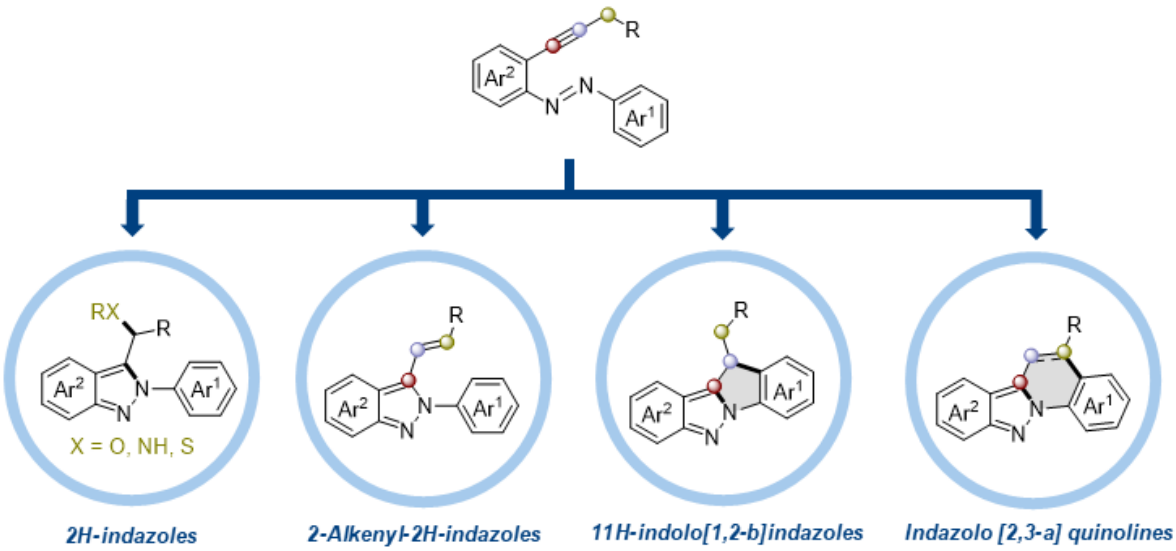

Figure 1. Visible-light and metal-controlled divergent transformations of 2-alkynylazobenzenes

Acknowledgements
Financial support was provided by Comunidad de Madrid Research Talent Attraction Program (Grants 2018-T1/IND-296 10054 and 2022-5A/IND-24227), the Spanish Ministry of Science and Innovation (MICINN) (Grants CNS2022-135304 and TED2021-129634B-I00), and Universidad de Alcalá (Grant IUAH21/CC-003 and CCG20/CC-009).

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Sulfonyl Hydrazides as a General Redox-Neutral Platform for Radical Cross-Coupling

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Keywords: Redox-Neutral ● Cross-Coupling ● Nickel-Catalysis ● Alkyl Radical ● Sulfonyl Hydrazides

Radical cross-couplings experienced a renaissance over the past decade in retrosynthetic analysis due to the simple, convergent disconnections of challenging C-C bonds. In practice, all the widely employed radical precursors require some sort of exogenous redox activation mode. Thus, a simpler means to achieve radical cross-coupling without the use of exogenous redox methods would be highly attractive. Building on a provocative report cyclising in situ derived diazenes from sulfonyl hydrazides by Taber in 1993, we disclosed a remarkably general platform for metal-catalysed redox-neutral radical cross-couplings to forge a variety of C-C bonds.[1] Sulfonyl hydrazides are stable and crystalline substances that can be accessed in a variety of ways, including transiently from hydrazones, to achieve a net reductive arylation of carbonyl compounds. We show their utility as versatile radical precursors, as exemplified with seven C-C bond-forming, redox-neutral cross-couplings with activated olefins, alkyl halides, redox-active esters, (hetero)aryl halides, alkenyl halides, alkynyl halides, and a trifluoromethylating reagent, to forge C(sp^3)-C(sp^3), C(sp^2)-C(sp^3), and C(sp)-C(sp^3) bonds. Exogenous redox (chemical, photo/electrochemical) additives are not necessary because these functional groups serve the dual role of radical precursor and electron donor. The homogeneous, water-compatible reaction conditions are operationally simple and contribute to streamlining synthesis and mild late-stage functionalization.

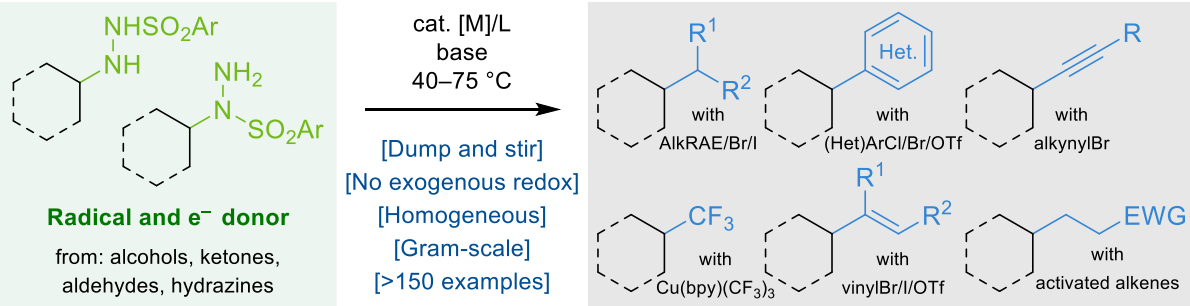

Figure 1. Versatility of sulfonyl hydrazides as simultaneous radical and e⁻ donors.

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Unlocking Nitroaromatic Radicals: Formation & Reactivity

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Keywords: Nitroaromatics ● SET ● regioselective ● cross-coupling ● EPR

Organic radicals—metal-free molecules with unpaired electrons—exhibit unique magnetic and reactivity properties, enabling applications ranging from qubit implementations[1] to valuable chemical transformations.[2] However, their reactive nature and the synthetic challenges associated with their preparation impose strict structural and electronic constraints, limiting broader exploitation. Developing general strategies for radical formation under mild conditions, using readily available and inexpensive reagents, and applicable to a broad range of molecules, remains a key challenge.

Here, we present our efforts to establish nitroaromatic compounds as a versatile platform for radical formation, enabled by a single-electron transfer (SET) process from a wide range of anionic organo bases. Building on proof-of-concept studies of nitrobenzene,[3] and combining continuous wave (cw) X-band EPR spectroscopy, quantum chemical calculations, and synthesys, we demonstrate that this SET-induced mechanism operates across a broad set of commonly used nitroaromatic compounds, including FDA-approved drugs – these findings suggest a previously overlooked prevalence of nitroaromatic radical species. We further show how this framework resolves contested reaction mechanisms[4] and enables the rational exploitation of SET-derived radical pairs to access C-X (X=N, C, S) functionalization of nitroaromatic compounds regioselectively and in mild conditions.

Overall, our work highlights the untapped potential of SET-driven radical formation in nitroaromatic compounds and opens the door to extending radical properties to other Lewis acids.

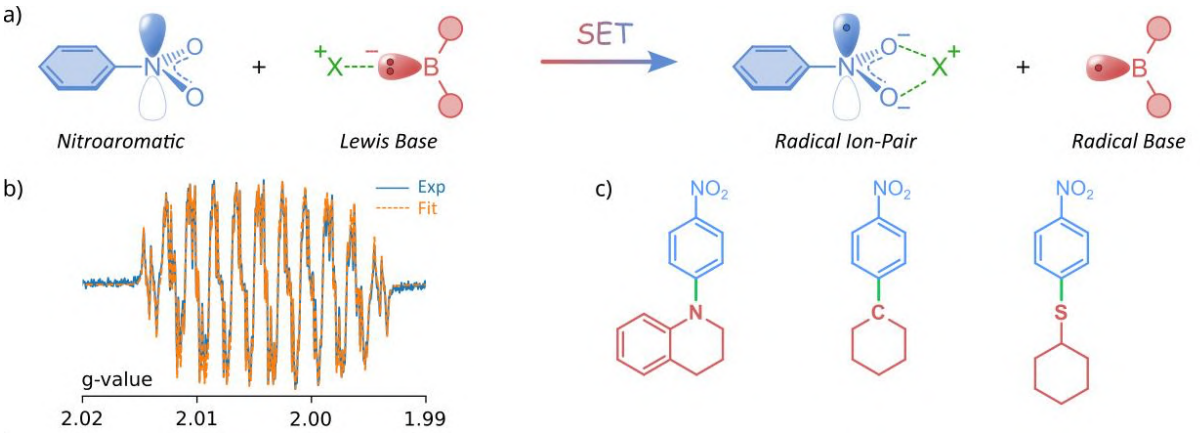

Figure 1. a) Schematic representation of SET between nitroaromatics and Lewis bases. b) cw X-band EPR spectrum of SET generated nitro radical. c) Examples of para-functionalized isolated compounds via SET-driven radical cross-coupling reactions.

Acknowledgements

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Divergent Photocatalysis for the Synthesis of Fluorinated Azetidines

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Keywords: strain release ● photocatalysis ● fluorine ● azetidine

The growing interest in four-membered rings as privileged motifs in drug discovery has driven the synthetic chemistry community to adapt and reinvent classical approaches for constructing these motifs. Strain-release strategies have drawn notable attention for building complex architectures. Yet, while many routes exist for accessing small carbocyclic derivatives, azetidine synthesis remains comparatively underdeveloped. Recently, we reported a photocatalytic radical approach to densely functionalized azetidines derived from azabicyclo[1.1.0]butanes (ABBs)[1] This three-component method employs TBCzTrz as a photocatalyst and proceeds via triplet sensitization of an imine to furnish C3-SCF_3 sulfonylazetidines **A**, with Phth-SCF_3 acting as a SOMOphile to incorporate the SCF_3 group. In an unexpected twist, performing the same reaction under non-anhydrous conditions yielded compounds **B** through, switching from an energy transfer- to a photoredox-pathway.

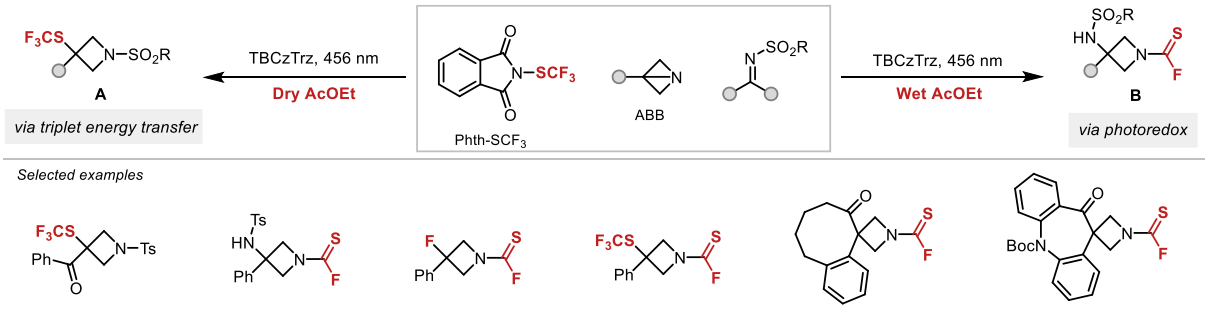

Figure 1. Dual photochemical performance for the synthesis of fluorinated azetidines

Our study reveals an unforeseen photochemical reactivity of Phth–SCF_3 that is governed by light-absorbing organic molecules, enabling fluorine incorporation at distinct positions under mild, user-friendly conditions.[2] The successful implementation of this discovery enables the direct transformation of strained ABBs and other readily available amines into structurally complex thiocarbamoyl fluorides, rejuvenating the chemistry of Phth-SCF_3.

Acknowledgements
This work was financially supported by European Union's Horizon Europe research and innovation programme. Marie Sklodowska-Curie grant agreement ChirAzaL 101105828. L. D. acknowledges Minister of the University (MUR) grant PRIN 2022PNRR23_01 and European Research Council (ERC) Starting Grant 2021 SYNPHOCAT 101040025.

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Bimodal Multiphoton Catalysis via Structural Regeneration

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Keywords: photoredox catalysis ● radical coupling ● mechanistic studies ● synthetic methods ● electrons

Visible-light photocatalysis enables radical transformations under mild conditions, but the limited energy of one-photon excitation and the narrow redox windows of most photocatalysts (PCs) restrict accessible reactivity. Although sequential two-photon excitation can expand photoredox chemistry, reported systems generally rely on reductive quenching with sacrificial reductants that do not contribute to product formation. Moreover, combining opposite redox manifolds with a single reaction remains difficult because of catalyst instability, self-quenching, and uncontrolled radical reactivity.[1] Here we introduce bimodal multiphoton catalysis, in which a structurally dynamic PC undergoes controlled bond cleavage after initial photoactivation to generate intermediates that, upon a second photochemical stimulus, mediate complementary reductive and oxidative processes. Radical recombination then regenerates the original PC, closing the catalytic cycle.

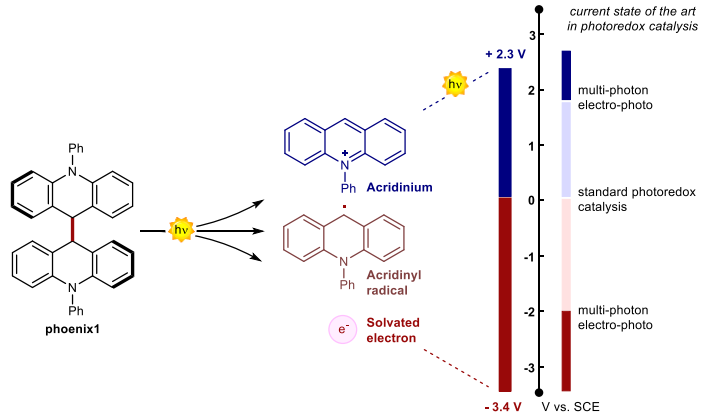

Figure 1. Bimodal Multiphoton Catalysis via Structural Regeneration.

The resulting solvated electrons (E_{red} < −3.3 V vs. SCE) activate inert C–Cl, C–Br, C–B, and C–O bonds, while the photoexcited acridinium fragment acts as a strong oxidant (E^*_{red} = +2.3 V vs. SCE) toward silanes, BF_3 salts, and boronic esters. The resulting radical partners combine to form the products (52 examples, up to 78% yield). Selectivity is governed by reversible in-situ radical coupling and by a transient acridine catalytic species, avoiding radical sorting agents. This platform merges two thermodynamically opposed redox cycles, spans a 5.7 V redox window, and operates under mild conditions, low catalyst loading, and without external oxidants or reductants.

Acknowledgements
This work was financially supported by the European Union, ERC-StG 2021 (101040025).

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

B-H Functionalization *via* Site-Selective HAT towards Xanthyl-*closo*-Carboranes as Bench-Stable Entry Point to Organosulfur Boron Clusters

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Keywords: B-H activation ● Boryl radicals ● Carboranes ● HAT ● Xanthates

Carboranes are icosahedral clusters,[1] distinguished by unique electronic and structural properties employed as analogues of aromatic moieties in known drugs, or as promising Boron Neutron Capture Therapy (BNCT) agents.[2] Currently, the heterolytic activations of B-H sites generally require costly transition metal-based catalysts and pre-installed moieties acting as directing groups.[3] The closely related chemical environment allow only subtle differences in both B-H bond dissociation energies (BDEs),[4] therefore the regioselective discrimination of a single B-H vertex among the ten boron sites within a carborane cage remains highly challenging. Lately, the photoinduced formation of B-centered *closo*-carboranyl radicals from B-I or B-N_2 sites has emerged as a valuable alternative route, although so far only one example focuses on the direct B-H activation.[5] In this work, we describe a light mediated site-selective B-H functionalization to afford previously unreported xanthyl-*closo*-carboranes *via* a nitrogen-centered radical (NCR)-mediated hydrogen atom transfer (HAT) process. The obtained boryl xanthates act as novel bench-stable and versatile synthetic platforms for the functionalization of the carborane cage to sulfur-containing functionalities, such as alkyl- and aryl sulfides, thiols, thioesters and sulfonyl chlorides. A deep experimental and computational study contributes to the mechanism, confirming a radical pathway involving the B(9) site as the most electron-rich boron vertex with the lowest B−H BDE.

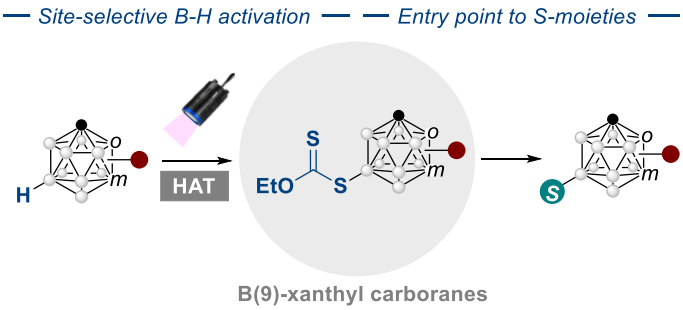

Figure 1. Site-selective B(9)-H xanthylation of *closo*-carboranes as novel synthetic platforms

Acknowledgements

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Bioinspired Radical 1,2-Amino Migrations for Synthesis of Amines and Chiral Amino Acids

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Keywords: radical rearrangement ● 1,2-amino migration ● photochemistry ● amino-alcohols ● C-O activation

Nature employs highly selective chemical reactions to construct nitrogen-containing molecules through enzymatic processes, such as amino-group transposition catalysed by 2,3-aminomutase.[1] Inspired by these transformations, our group investigates radical 1,2-amino migrations that proceed in the absence of enzymes.

This approach enables skeletal reorganization as an alternative to *de novo* synthesis, offering new routes to amines and amino acids, including access to β-amino acids from readily available α-amino acid precursors.[2] In this project, we explore C–O bond activation strategies to access β-amino radical intermediates essential for the rearrangement (Figure 1). 1,2 Amino-alcohols serve as simple and accessible model systems for studying nitrogen rearrangements, with current work focused on identifying general trends in reactivity and structure toward the development of new radical approaches for complex amine synthesis.

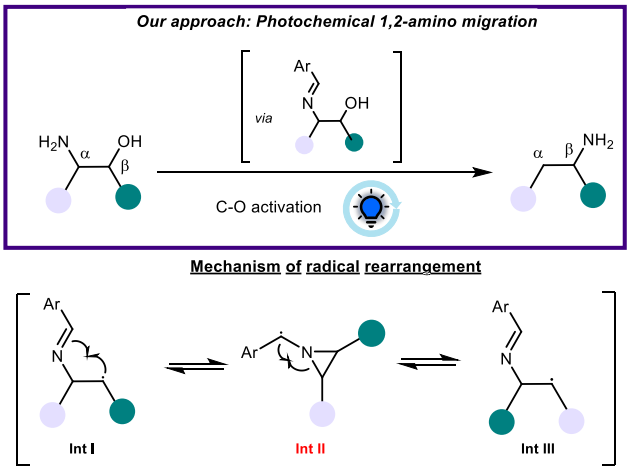

Figure 1. Our approach: Photochemical 1,2-amino migration

Acknowledgements

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Stereoretentive Norrish–Yang Photocyclization through Conformational Gating

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Keywords: Photochemistry ● Stereoselectivity ● Radical Chemistry ● Chirality ● Photocyclization

The Norrish–Yang photocyclization[1] of aryl alkyl ketones is a classical photochemical transformation that proceeds through triplet 1,4-diradical intermediates[2] whose conformations govern the fate of the reaction[3]. Despite decades of mechanistic understanding[4], directing the reactivity of this diradical remains difficult because it can evolve through competing pathways, including cyclization and Norrish type II fragmentation[5]. Achieving stereocontrol is even more challenging because radicals generated from enantiopure substrates are expected to undergo rapid configurational scrambling[6].
Here we show that hydrogen-bond interactions encoded within chiral substrates impose conformational gating on the photogenerated 1,4-diradical, thereby controlling its reactivity. This strategy enables stereoretentive Norrish–Yang cyclizations while suppressing competing fragmentation pathways, providing access to highly enantioenriched cyclobutanols bearing two stereocentres. These results show that conformational gating can preserve stereochemical information in photogenerated chiral radicals, enabling a rare memory-of-chirality scenario[7] in solution.

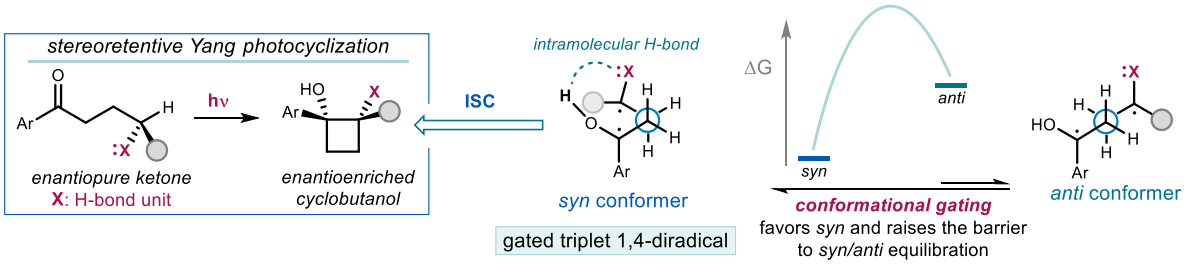

Figure 1. Design principle of this study: intramolecular hydrogen bonding enabled by an H bonding unit (X) within an enantiopure ketone substrate imposes conformational gating on the triplet 1,4-diradical, favoring *syn* conformers and slowing *syn/anti* equilibration, thus enabling stereoretentive Yang photocyclization.

Acknowledgements
Financial support was provided by the European Research Council ERC AdG PHOTOZYME (101141690). A.P. thanks the EU for a Horizon 2024 Marie Skłodowska–Curie Fellowship (HORIZON-MSCA2024-PF-01, 101204530). T.v.M. thanks the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for a Walter Benjamin fellowship (572739603).

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Aldehydes as CO Releasing Molecules: *in-situ* and *ex-situ* Giese Reactions and Palladium Catalyzed Aminocarbonylations

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Keywords: Decatungstate anion ● Hydrogen Atom transfer ● Pd catalysis 3 ● Photocatalysis ● Giese reaction

Carbon monoxide is an important C1 synthon that can be used in valuable carbonylation reactions. Due to the hazard in handling CO, scientists adopted its *in situ* (photo)release starting from safer and stable compounds dubbed as CORMs (CO Releasing Molecules).[1] A drawback of this approach is that the remaining part of the CORM (after CO loss) is wasted thus impacting the atom economy of the reaction. Recently, we successfully tested some aldehydes where the formyl group was dubbed as "HAcTive group" having the role to direct the photocatalyzed hydrogen atom abstraction in the substrate.[2] In such a way, an acyl radical resulted that upon CO loss easily gave access to various substituted carbon-based radicals (e.g. *tert*butyl, benzyl, α-oxy etc).[2] We then envisaged a two-chambers apparatus (Figure 1, left) where in Chamber A an aldehyde underwent a HAT process upon light irradiation in the presence of the tetrabutylammonium salt of the decatungstate anion (TBADT). The carbon radical released in Chamber A then engaged a Giese reaction to forge a C-C bond via conjugate addition onto Michael acceptors. Meanwhile, the CO photogenerated is free to reach Chamber B and used in Palladium catalyzed aminocarbonylations (Figure 1, right). As a result, both *in situ* and *ex-situ* reactions were performed in two distinct chambers assuring a 100% product incorporation of the CORM structure.[3]

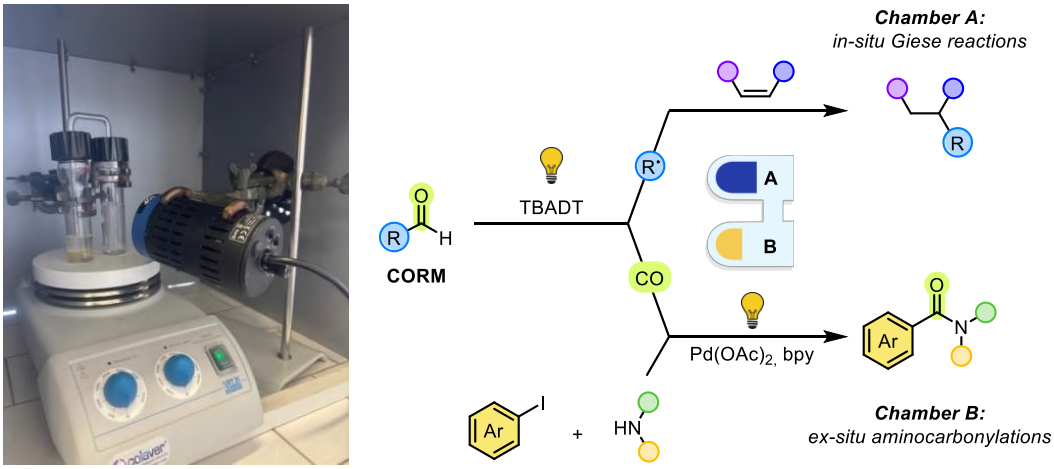

Figure 1. Two chambers reactor for the *in-situ* Giese reaction and ex situ Palladium catalyzed aminocarbonylations

Acknowledgements
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Chemoselective Visible-Light Radical Decarboxylation for Modular Molecular Diversification

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Keywords: Radical Decarboxylation ● Giese Reaction ● Continuous Flow ● Chemoselective Functionalization ● Modular Diversification

Ubiquitous and bench-stable carboxylic acids stand out as adaptive functional groups for accessing open-shell intermediates via light-mediated radical decarboxylation.[1,2] Indeed, while decarboxylative functionalization strategies often rely on preactivated derivatives-in the form of redox-active esters or as ligands for hypervalent iodine reagents-the direct use of native carboxylic acids is highly desirable. In this scenario, we recently described the use of naturally occurring and readily available α-hydroxy carboxylic acids (AHAs) as platforms for visible light-mediated oxidative CO_2 extrusion, generating α-hydroxy radicals that serve as versatile C_1 to C_n hydroxyalkylating agents.[3] Similarly, we have developed a mild strategy for the monofluoroalkylation of a broad range of Giese acceptors using α-monofluorocarboxylic acids.[4] These approaches are operationally simple and enable molecular connectivity typically inaccessible through conventional polar chemistry. In this communication, we report our efforts to take a step forward in this field by describing visible-light-mediated CO_2 extrusion from organic molecules bearing other photoredox-sensitive functional handles. The judicious choice of reaction parameters allows the controlled excision of carbon dioxide, generating carbon-centered radicals that can be intercepted by Giese acceptors while preserving these valuable functional groups for subsequent synthetic elaboration. The use of flow technology further enhances scalability and improves the green credentials of this methodology.

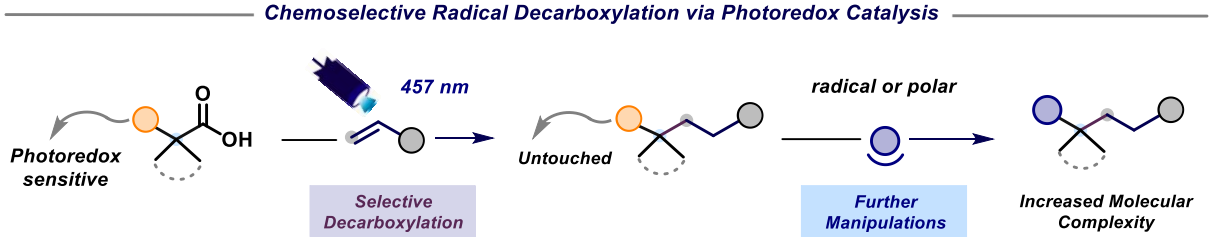

Figure. Chemoselective visible-light-mediated CO_2 extrusion toward increased molecular complexity.

Acknowledgements

This work was financially supported by the European Commission – Horizon Europe Framework, project SusPharma, grant agreement No. 101057430, and by the University of Bari for the project ERCSEEDSUNIBA "FlashPhotoFlow", code: 2023-UNBACLE-0243177.

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Organic Reaction Forecasting and Retrosynthetic Analysis: Enhancing Predictive Performance via Data Augmentation

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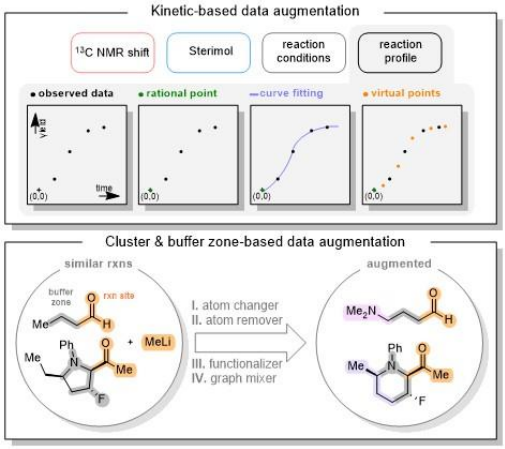
Keywords: Reaction Forecasting ● Augmentation ● Data Generation ● Retrosynthetic Analysis

Machine learning (ML) has emerged as a powerful approach for reaction design, but its reliance on large datasets continues to limit its practical use for many experimental chemists. In this work, we redirect attention from model architecture to the often underappreciated step of data preprocessing. Specifically, we introduce two strategies—kinetics-driven data augmentation and virtual reaction generation—to improve model performance under data-scarce conditions.

First, we established an ML framework capable of predicting reaction profiles for geminal bromofluoroolefination using a minimal dataset.[1] Sparse experimental data were fitted to sigmoidal kinetic models, enabling the generation of augmented datasets based on easily obtainable descriptors, such as ^{13}C NMR chemical shifts at reactive sites and Verloop's Sterimol parameters. Importantly, integrating this augmentation approach with a conditional tabular generative adversarial network (CTGAN) led to a synergistic improvement in predictive performance.

Second, to address the constraints of conventional SMILES-based enumeration in retrosynthetic analysis, we developed a cluster-based method combined with a reaction site-centered buffer zone strategy.[2] These concepts were implemented in modules for atom substitution, deletion, and molecular graph recombination, allowing the generation of diverse and chemically meaningful artificial reactions beyond conservative transformations.

Because both strategies operate at the preprocessing stage, they can be readily incorporated into a wide range of existing and future ML models. Overall, this study highlights the importance of thoughtful data preprocessing in enabling more effective integration of ML into synthetic chemistry, particularly in settings where data availability is limited.



Acknowledgements

This research was supported by the National Research Foundation of Korea funded by the Ministry of Science and ICT (RS-2024-00411137 and RS-2024-00409659), the AI-based GIST Research Scientist Project grant in 2025, and the InnoCORE program of the Ministry of Science and ICT of Korea (N10250153 and 1.250022.01).

Investigation on Phosphorus-Mediated Photocatalytic Hydrogenation of Alkenes

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Keywords: phosphorus-centered radicals ● photocatalytic cycle ● mechanistic investigation ● U-PSD TREPR

Phosphorus-centered radicals are pivotal in diverse fields, yet their transient nature has hindered direct observation and mechanistic understanding in photocatalysis. Here, we employ advanced ultrawide single-sideband phase-sensitive detection time-resolved electron paramagnetic resonance (U-PSD TREPR) spectroscopy [1] to directly interrogate phosphorus radical intermediates within a photocatalytic alkene hydrogenation system. Our findings unveil an unprecedented pathway that revises the traditional Ar_3P–OH• radical model.[2] Rate constant comparisons reveal that $Ar_3P^{\bullet+}$ adds preferentially to alkenes rather than to water, as evidenced by the direct observation of the resulting carbon-centered radical adducts. Subsequent HAT yields quaternary phosphonium salts, which, upon complexation with sulfur-centered anions, undergo intramolecular electron transfer to generate phosphorane radicals. α-Scission of the phosphorane radicals subsequently furnishes carbon radicals, which undergo HAT to produce the final hydrogenated products, thereby completing and elucidating the photocatalytic cycle. Anchored by direct spectroscopic evidence, this mechanistic pathway not only rationalizes the observed reactivity but also provides a predictive foundation for the rational design of next-generation photocatalytic systems.

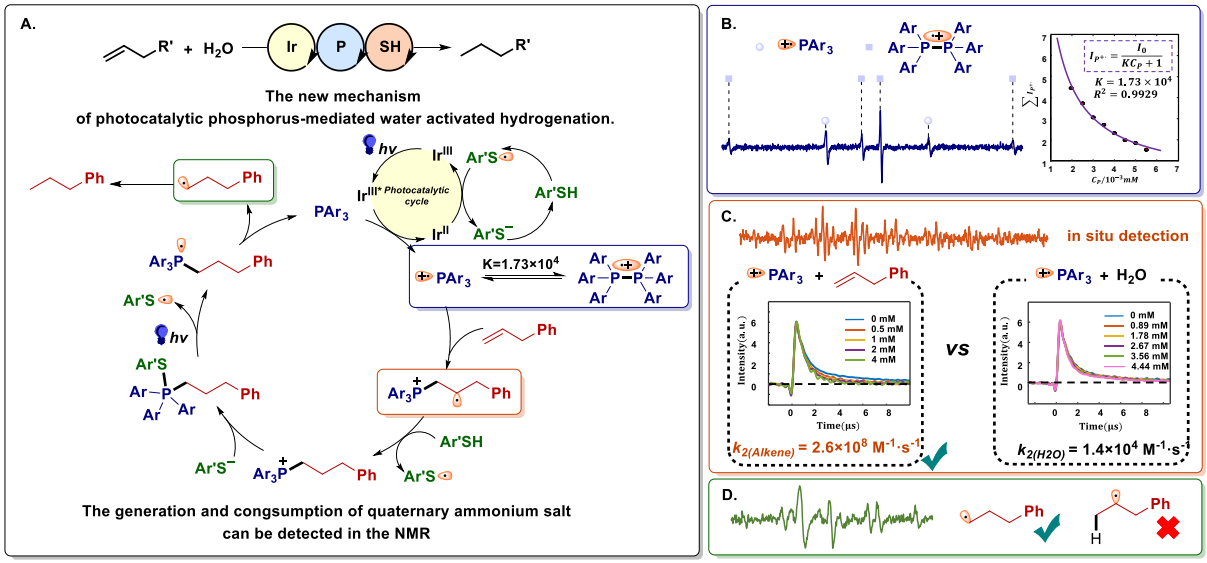

Figure 1. The Mechanism of Phosphine-Mediated Photocatalytic Hydrogenation of Alkenes: (A). The reaction and the proposed mechanism; (B). The transient EPR signals and equilibrium constants for the mono- and di-phosphorus radicals. (C). The transient EPR signal corresponding to the carbon-centered radical formed via addition of $Ar_3P^{\bullet+}$ to the Alkene, and rate comparison: alkene vs water. (D) α-Cleavage generates the carbon radical signal.

Acknowledgements
This work was financially supported by Tsinghua University Dushi Program.

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Direct Observation of Radical Chain Transformations in Boryl-Radical-Mediated Defluorination by TREPR

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Keywords: time-resolved EPR ● radical chain reaction● transient radical ● mechanism visualization

Radical-mediated defluorination of polyfluoroarenes has emerged as a powerful strategy for C–F functionalization, yet the radical chain mechanisms governing these reactions remain poorly understood due to the transient nature of key intermediates.

Here we investigate a boryl-radical-mediated defluorination reaction using ultrawide single-sideband phase-sensitive detection time-resolved electron paramagnetic resonance (U-PSD TREPR).[1] Three key radical intermediates involved in the reaction were directly detected and spectroscopically characterized, including the initiating pyridine-boryl radical and two downstream carbon-centered radicals formed during C–F activation and subsequent transformations. Well-resolved hyperfine structures enable clear identification of these transient species.

Quantitative calibration using TEMPO further enables determination of transient radical concentrations on the micromolar scale, allowing the evolution of the radical pool to be monitored across different time regimes. Comparison of the transient kinetic profiles reveals that these intermediates participate in a dynamic radical chain equilibrium rather than a simple sequential process. Furthermore, systematic variation of water content, trapping alkenes and polyfluoroarene substrates demonstrates that these components regulate the radical pool and modulate the chain equilibrium.

These results provide direct spectroscopic insight into radical transformations and regulation in a boryl-radical-mediated defluorination process.

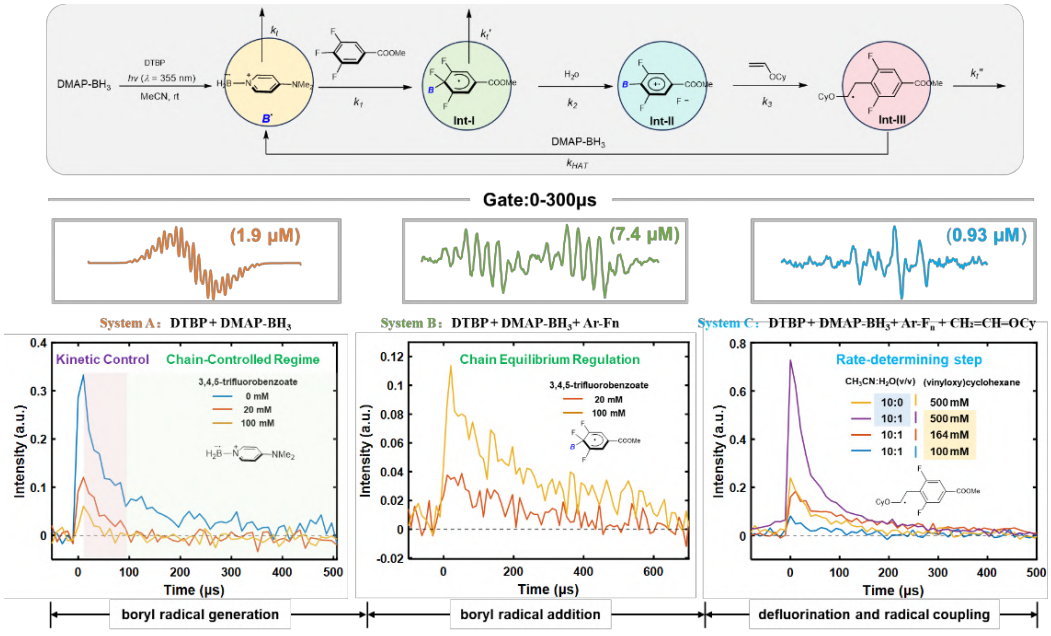

Figure 1. Direct Visualization of Radical Transformations and Regulation in a Complex Radical Chain Reaction.

Acknowledgements

This work was financially supported by Tsinghua University Dushi Program.

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Transition-Metal-Free Cyclopropanation of Alkenes with Dichloromethane and Chloroform via Halogen Atom Transfer Using Amine Carboxyborane

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Keywords: cyclopropanation ● amine carboxyborane ● halogen atom transfer ● radical-polar crossover

Cyclopropanes are privileged structural motifs in medicinal chemistry, frequently serving as bioisosteric replacements for arenes, alkenes, and small alkyl groups.[1] Despite their significance, traditional synthesis methods often rely on toxic and hard-to-handle reagents, such as iodomethylzinc or diazo compounds, and frequently require transition-metal catalysts.[2] Herein, we report a novel, transition-metal-free, photoredox-catalyzed cyclopropanation of diverse alkenes. This method exploits a halogen atom transfer (XAT) process between dichloromethane, which serves as an abundant and cost-effective C_1 synthon, and amine-ligated boryl radicals generated from amine carboxyborane. The reaction proceeds under exceptionally mild conditions, exhibits a broad substrate scope, and demonstrates excellent scalability.
Furthermore, the synthetic utility of this protocol is highlighted by its modularity. The use of deuterated dichloromethane enables the synthesis of deuterated cyclopropanes, whereas substitution with chloroform or deuterated chloroform affords valuable chlorocyclopropanes and their isotopically labeled derivatives. This advancement is expected to offer a valuable strategy for the late-stage incorporation of cyclopropyl groups into pharmaceutically relevant molecules, while potentially expanding the synthetic utility of amine carboxyboranes and ligated boryl radicals.

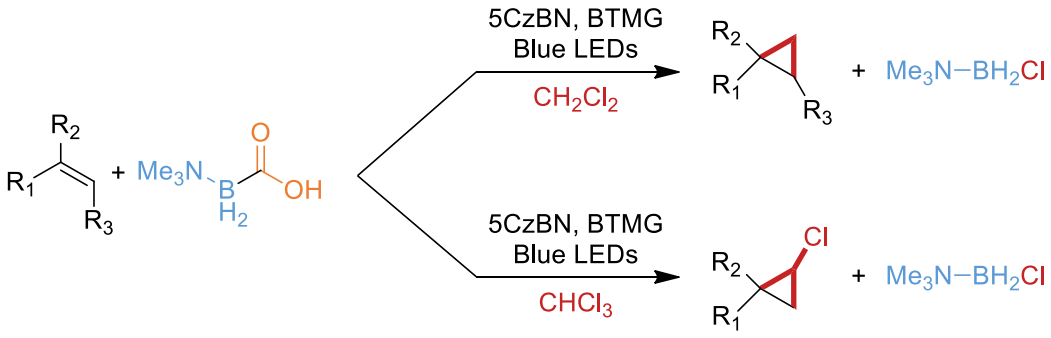

Figure 1. Strategy for cyclopropanation

Acknowledgements
This work was financially supported by the National Research Foundation (NRF) of Korea and funded by the Ministry of Science and ICT(RS-2024-00454580). The supercomputing resources of this work were supported by the Grand Challenging Project of Supercomputing AI Education and Research Center, DGIST.

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Insights into Photoredox Catalysis Beyond Diffusion with Excited Trisaminocyclopropenium Radical Dication

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Keywords: Radical Ions ● Preassociation ● Ultrafast PET ● Oxidative ConPET ● Photocatalysis

Excited radical ions have frequently been proposed as key species in photoredox catalysis, yet their role as active photocatalysts remains debated due to their picosecond lifetimes, which are typically considered too short for diffusion-controlled photoinduced electron transfer (PET).[1] Here, we present direct spectroscopic evidence identifying the excited trisaminocyclopropenium radical dication ($^{*}TAC^{\bullet 2+}$) as the catalytically active species. Mechanistic studies revealed preassociation between photocatalyst and substrate, enabling productive electron transfer on timescales beyond the diffusion limit.[2]

Based on these insights, we employed a consecutive photoinduced electron transfer (ConPET) strategy to generate $^{*}TAC^{\bullet 2+}$. This approach complements photoelectrochemical methods for radical ion generation and enables oxidative functionalization of arenes such as mesitylene and benzene under aerobic conditions.[3]

These results help resolving the ongoing controversy surrounding radical ion photocatalysis and expand the conceptual scope of multiphoton photoredox strategies.

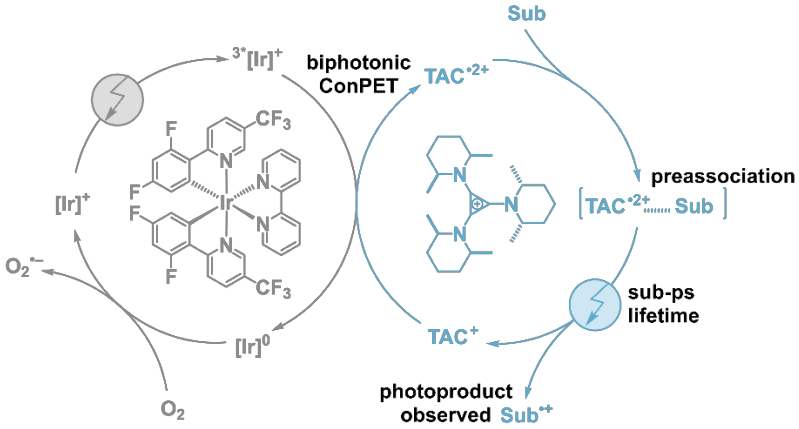

Figure 1. Oxidative ConPET using TAC^{+} and $[Ir]^{+}$ as photocatalysts for arene functionalization along with mechanistic insights.

Acknowledgements
Funding from the Swiss National Science Foundation through grant number 10001855 is gratefully acknowledged.

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7–10 June 2026, Bologna, Italy

Mechanochemical nitrogen activation and synthesis of N-heterocycles

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Keywords: Nitrogen activation ● Mechanochemistry ● Molecular editing ● Nitrogen insertion ● Transmutation

The activation of dinitrogen (N_2) and direct incorporation into organic molecules is considered an attractive strategy in modern synthetic chemistry, yet it remains challenging when particularly aiming for mild and sustainable conditions. Previous studies have primarily focused on transition metal complexes for N_2-splitting and functionalization.[1] However, the development of an operationally simple, fast, and mild protocol with general applicability remains underdeveloped. Here, we report a novel mechanochemical strategy that enables metal-mediated N_2 reduction under ambient conditions in a remarkably short time (within 2 min). The reaction proceeds regardless of the grinding material, pressure, and temperature. Through this reaction, the reduced form of N_2 is generated as a single product, which can be used as an efficient N-atom transfer reagent for the synthesis of various N-heterocycles. We have developed two series of O-to-N transmutation reactions, including photoredox catalysis, with this specific nucleophile to produce various pyrroles and pyridines. The reactions display broad compatibility and easy access to ^{15}N-labeling.

Acknowledgements
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Isolable organoboron-based radical ions enable potent single electron transfer with wide photoredox window

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Keywords: singular molecular architecture ● organoboron-based compound ● isolated radical ● excited-state reactivity ● potent photoredox properties

Redox processes underpin energy transfer in charge transport in electronic materials, biological systems, and the synthesis of complex chemical compounds.[1] The redox potential of the reactants fundamentally determine the thermodynamic spontaneity of electron flow. Inspired by natural photosystems, single-molecule sensitizers capable of harnessing the reactivity of electron- or hole-primed radical states have been studied for driving challenging chemical reactions, and the strategy is especially recognized in the field of photoredox catalysis.[2,3] Enabling access to extremely negative and positive redox potentials within a singular molecular architecture is a longstanding goal yet to be fully realized. Herein, we report a organoboryl compound capable of being preparatively isolated as electron-primed radical anions and hole-primed counterparts, displaying exceptionally wide photoredox window under irradiation. Comprehensive structural and spectroscopic analyses provided detailed insights into the excited-state dynamics of isolated radical species. Broad and tunable redox potentials were measured, enabling previously inaccessible catalytic transformations under mild conditions. This work provides a principle for designing stable radical species with controlled excited-state reactivity, expanding the potential and versatility of photoredox catalysis.

Acknowledgements
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Radical-Mediated Divergent Synthesis of Nitrogen-Containing Scaffolds

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Keywords: Radical-mediated synthesis ● Nitrogen-containing scaffolds ● Divergent Synthesis ● word 4 ● word 5

Cyclic amine scaffolds are of considerable importance in drug design and lead discovery because of their conformational restriction and pronounced three-dimensional structural features[1,2]. From a synthetic perspective, however, the efficient preparation of cyclic amine frameworks remains challenging. On the one hand, cyclization must proceed under mild conditions; on the other hand, skeletal diversification should ideally be achieved within a unified strategic framework. More importantly, selective control in cyclic amine synthesis is often difficult to achieve under traditional thermochemical conditions. To address these limitations, this work employs photo-driven radical methods as a central platform and develops reaction systems directed toward cyclic amine scaffolds of different structural dimensions, thereby enabling both efficient formation and diversity-oriented synthesis of cyclic amines.

By integrating proton-coupled electron transfer with radical–polar crossover cycloaddition strategy into the synthesis of unstrained saturated cyclic amines, the longstanding problems of low ring-closing efficiency and poor regioselective control in previous methods were addressed, enabling the divergent construction of unstrained saturated cyclic amines[3].

Increasing three-dimensional structural complexity represents another important dimension in the diversity-oriented synthesis of nitrogen-containing heterocycles. As bioisosteric motifs that have attracted substantial attention in recent years, 1-azabicyclo[n.1.1] frameworks are typically accessed through lengthy synthetic sequences and are often limited by narrow substrate scope. In this context, single-electron-transfer-induced radical generation and transition-metal-mediated cross-coupling act cooperatively, enabling a precise one-step transformation of simple ABB precursors into three-dimensionally complex azabicyclic scaffolds[4]. This dual-catalytic system exhibits remarkable chemoselectivity, and the structurally diverse bicyclic products show high compatibility with the construction and subsequent derivatization of DNA-encoded libraries.

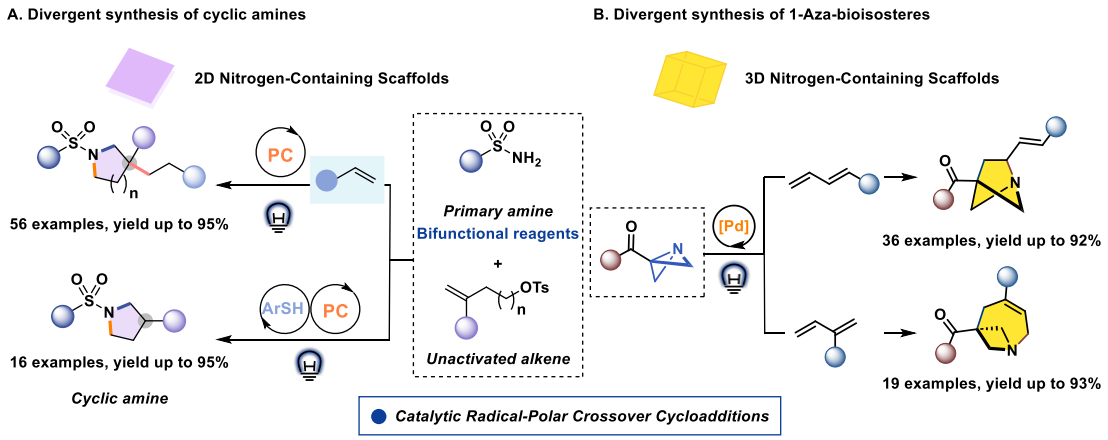

Figure 1 Divergent Synthesis of Nitrogen-Containing Scaffolds

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (22201179 & 22471168 to H.- M.H.) and the startup funding from ShanghaiTech University (H.-M.H.).

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Photocatalytic Radical-Polar Crossover Enables Modular Access to Bicyclo[2.m.njalkane Alcohol Bioisosteres

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Keywords: Radical ● Bioisosteres ●Bicyclic Alcohol

The strategic replacement of aromatic rings with saturated bioisosteres has become a pivotal strategy in medicinal chemistry, offering a proven path to improve the metabolic stability and safety profiles of drug candidates.[1] Conventional access to these valuable saturated scaffolds, however, heavily relies on strain-release strategies that mandate the use of highly strained, synthetically challenging precursors.[2] Herein, we report a general platform based on a visible-light-induced radical–polar crossover manifold. [3]This method employs readily available, bench-stable γ- and δ-keto acids as radical precursors, which, upon activation, engage in cross-coupling with a diverse array of π-systems. This straightforward approach provides direct and efficient access to a wide range of synthetically elusive saturated bicyclic alcohol bioisosteres. By circumventing the need for pre-strained intermediates, our strategy delivers the target architectures in high yields with excellent functional group tolerance.

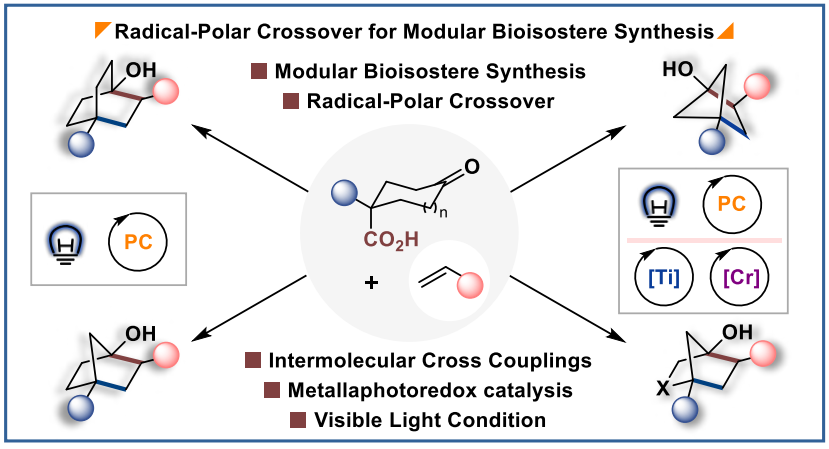

Figure 1. Radical-Polar Crossover for Modular Bioisostere Synthesis

Furthermore, successful product derivatizations underscore the synthetic utility of this method, while mechanistic investigations corroborate the proposed radical-polar crossover pathway. Together, these findings establish our platform as a practical and robust alternative to current paradigms.

Acknowledgements

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Redirecting Radical Phosphonylation via Energy-Transfer Enabled Diradical Rearrangement

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Keywords: Phosphonylation ● Energy-Transfer ● rearrangement ● three-membered rings

The widespread application of novel organophosphorus compounds in synthetic chemistry, agrochemicals, pharmaceutical development, and materials science has established their construction as a central focus in chemical research. The resurgence of radical chemistry has introduced diverse radical pathways in this field, primarily through phosphorus radical cation intermediates[1] and phosphoranyl radical intermediates[2]. In recent years, radical rearrangement has emerged as a powerful and selective strategy for efficiently constructing complex molecular architectures. A notable example was demonstrated by Han and his team, who achieved fluoroalkylphosphorylation of unactivated alkenes via visible-light-induced electron transfer through the radical rearrangement of alkoxyphosphines[3].

Despite these advances, energy transfer-mediated photochemical rearrangements involving organophosphorus compounds remain largely unexplored. Here we show an unprecedented photochemical diradical rearrangement driven by energy transfer catalysis, which enables the direct and efficient synthesis of phosphorylated cyclopropanes from readily accessible homoallylic alcohols and P(III) reagents. This method operates under mild conditions, exhibits broad functional group tolerance, and provides access to a valuable class of strained organophosphorus frameworks. We anticipate that this strategy will inspire further exploration into leveraging excited-state reactivity for constructing challenging molecular targets through novel photochemical mechanisms.

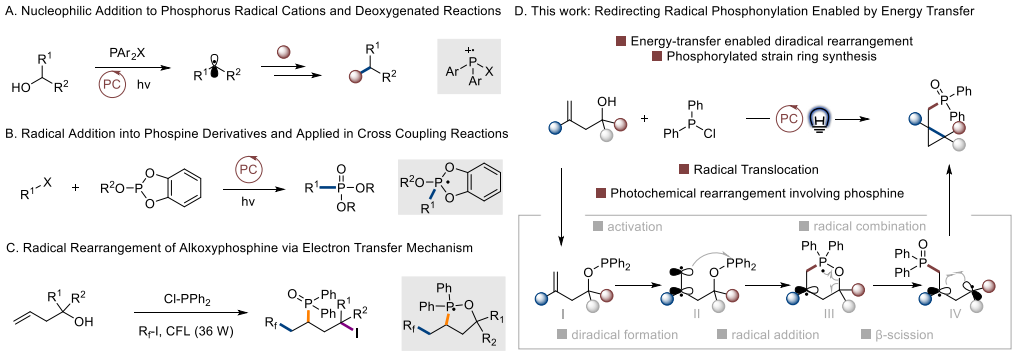

Figure 1. Background and rational design

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Photoactive and Photoluminescent First-Row Transition Metal Complexes

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Keywords: Photoluminescence ● first-row transition metal complexes ● Earth-abundant metals ● excited state dynamics ● coordination chemistry

Luminescent molecular complexes have been extensively explored in applications such as dye-sensitized solar cells and photoinduced electron or energy transfer catalysis, due to their distinctive photochemical and photophysical properties. To date, molecular luminophores based on precious metals such as platinum (Pt), iridium (Ir), and ruthenium (Ru) have dominated this field. Their strong spin–orbit coupling (SOC) enables efficient intersystem crossing (ISC), leading to long-lived excited states at room temperature and excellent performance in light-driven processes. Despite their robust performance, the use of noble metal-based luminophores poses sustainability concerns due to their high cost and limited natural abundance. In light of these concerns, first-row transition metals have emerged as promising alternatives, given their substantially higher abundance in the Earth's crust.[1-4] Herein, we present a novel tridentate ligand design that induces strong room temperature photoluminescence upon coordination with 3d transition metals. This study highlights a new class of first-row transition metal-based luminophores and provides insight into their photophysical behavior and excited-state dynamics.

Acknowledgements
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Photocatalytic furan-to-pyrrole conversion

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Keywords: Skeletal editing ● Photochemistry ● Heterocycles

The identity of a heteroatom within an aromatic ring influences the chemical properties of that heterocyclic compound. Systematically evaluating the effect of a single atom, however, poses synthetic challenges, primarily as a result of thermodynamic mismatches in atomic exchange processes. We present a photocatalytic strategy that swaps an oxygen atom of furan with a nitrogen group, directly converting the furan into a pyrrole analog in a single intermolecular reaction.

High compatibility was observed with various furan derivatives with various furan derivatives and nitrogen nucleophiles commonly used in drug discovery, and the late-stage functionalization furnished otherwise difficult-to-access pyrroles from naturally occurring furans of high molecular complexity. Mechanistic analysis suggested that polarity inversion through single-electron transfer initiates the redox-neutral atom exchange processes at room temperature.

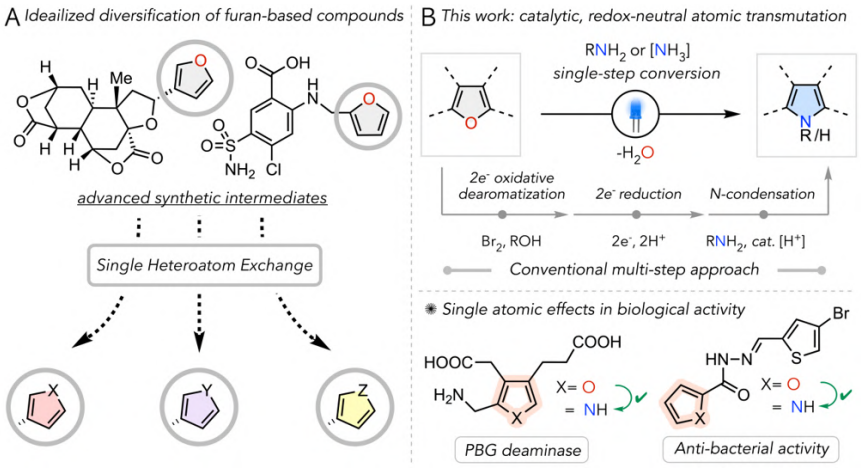

Figure 1. Direct conversion of furan into pyrrole analog

Acknowledgements

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Light-induced annulative π extension enabled by thianthrenium salts

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Keywords: sulfonium salt ● polycyclic aromatic compound ● photocatalysis

Polycyclic aromatic compounds (PAC) are of key importance in the field of materials science and bioimaging.[1] However, their lengthy and demanding synthesis impede the full extent of their abilities. In order to modify and tune their properties on demand, a straightforward access to complex scaffolds is required. Sulfonium salt chemistry is mainly employed in aromatic C(sp^2)–H functionalization reactions,[2] and has recently been extended to alkenyl derivatives.[3] This provides a powerful approach for the late-stage modification of complex arenes, by exploiting robust and well-known organometallic cross coupling reactions. In comparison, its use under photocatalytic conditions remains largely underexplored.[4]
In this context, we investigated the use of sulfonium salts in the formation of new C(sp^2)–C(sp^2) bonds through a photochemical process to construct extended *π*-conjugated systems. Our strategy involves using the less-explored styryl feedstock [5] to access PAC *via* the formation of the corresponding thianthrenium salts (figure 1). This two-step one-pot process offers access to a variety of planar and non-planar PAC in a short reaction time.

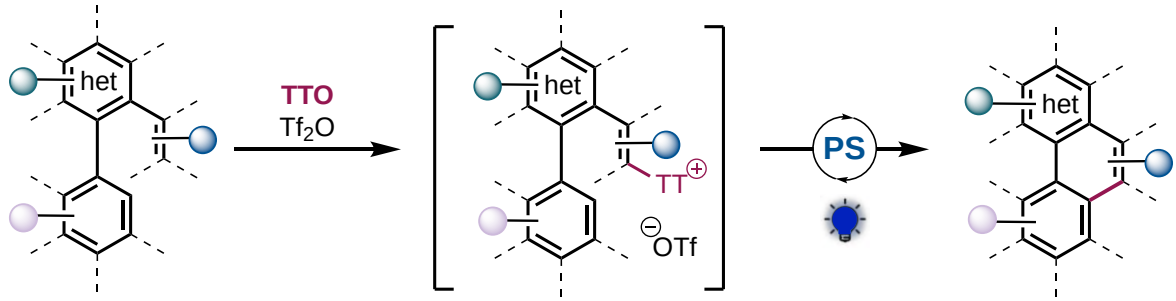

Figure 1. photoinduced annulative π extension of PAC

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Synthesis of Amino-2,3-Dihydrofurans by Radical–Polar Crossover Visible-Light Photoredox Ring Expansion of α-Ketoaziridines

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Keywords: photoredox catalysis ● ring expansion ● radical polar crossover ● α-ketoaziridines ● dihydrofurans

Photoredox catalysis driven by visible light has become a powerful and established strategy in organic synthesis to allow the precise formation of radical intermediates under very mild conditions.[1] One of the most noteworthy reaction models enabled by this methodology is the radical-polar crossover (RPC) pathway, in which these radical species undergo single-electron transfer (SET) to yield ionic intermediates, employing the complementary properties of both radical and polar chemistry.[2]
In this context, an interesting class of versatile building blocks for the synthesis of functionalized heterocycles through photocatalysis are the ring-strained α-ketoaziridines. These substrates have been studied for the possibility of photocatalytic ring opening and ketyl radical-anion formation, followed by radical trapping. [3] Along this line, our group has recently reported the first intramolecular photocatalytic ring-expansion of N-arylsulfonyl α-ketoaziridines into δ-sultams.[4]
In this work, we present our latest studies on the preparation of amino-2,3-dihydrofurans by a photoredox-catalyzed radical–polar crossover intermolecular approach, implying a visible light photo-induced ring opening of α-ketoaziridines, followed by radical trapping with alkenes and final polar cyclization.

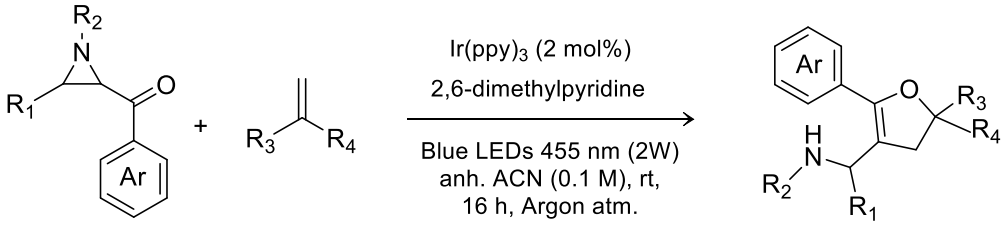

Figure 1. RPC ring expansion to amino- 2,3 dihydrofurans.

The generality of the reaction was explored across a broad range of substrates, showing a good functional group tolerance as well as a ten-fold upscaling robustness, opening new possibilities for the construction of functionalized heterocycles by photoredox-mediated RPC ring expansion reactions.

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Light-driven perfluoroalkylation of heterocyclic amino acid derivatives

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Keywords: perfluoroalkylation ● visible light ● amino acids ● photoredox catalysis ● heteroarenes

Amino acids are essential to life, and their modification can significantly impact on the physicochemical and biological properties of peptides and proteins. In the last decades, the introduction of fluorine atoms into the structure of organic compounds has gained attention for its ability to enhance metabolic stability, alter structure, and increase lipophilicity. [1] This has stimulated the use of fluorinated amino acids in fields such as medicine, enzymology, and agricultural chemistry, where they are valuable for modulating biological activity.[2] In the past years photocatalysis is being imposed as one of the most efficient and convenient synthetic approaches for fluoroalkylations of organic compounds. Many photocatalytic methods have been developed for inserting perfluoroalkyl groups on aromatic and heteroaromatic rings.[3] 5-Carboxy-1,3-azoles are heterocyclic amino acid derivatives that found applications in medicinal chemistry.[4] Few examples of fluoroalkylations of such scaffolds have been reported in literature. All of them involve introduction of trifluoromethyl or sulfonyldifluoromethyl groups, substrates devoid of aromatic substituents (that poses problems of regioselectivity), and use synthetically demanding fluoroalkyl radical's sources.[5]
Herein we present a light-driven method, using silver salts as additives, with a wide scope of substrates and perfluoroalkyl groups. Aromatic groups at C-2 are tolerated. Furthermore, mechanistic studies are described in this communication.

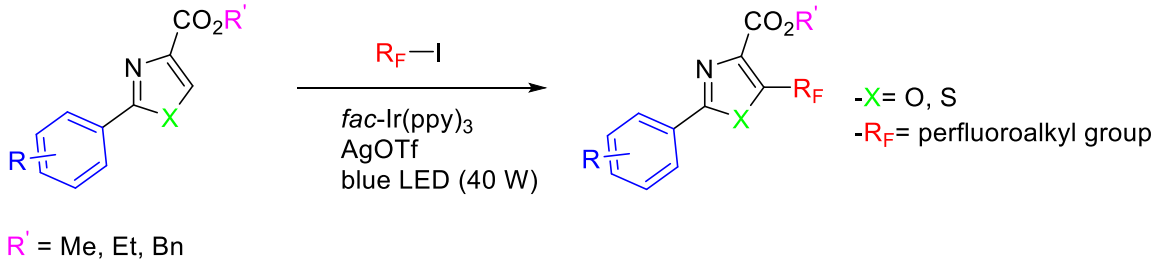

Figure 1. Current approach for photoredox-catalyzed perfluoroalkylation reaction

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SUPRAMOLECULARLY DIRECTED ENANTIOSELECTIVE γ-LACTONIZATION OF CARBOXYLIC ACIDS USING BIOISNPIRED MANGANESE CATALYSTS

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Keywords: catalysis ● C-H oxidation ● HAT ● γ-lactonization ● enantioselective ● supramolecular chemistry

Lactones are a particularly important class of compounds due to their broad range of biological activities, making their selective synthesis a key goal in organic chemistry. Among the available strategies, the direct lactonization of carboxylic acids via C(sp³)–H oxidation is especially appealing, although still challenging. Iron- and manganese-based biomimetic complexes bearing tetraazadentate nitrogen ligands have shown promise in promoting the enantioselective oxidation of secondary C(sp³)–H bonds using hydrogen peroxide under mild conditions. [1]
However, important limitations remain, including the low intrinsic reactivity of C(sp³)–H bonds, difficulties in achieving high chemo- and stereoselectivity in substrates with multiple nonequivalent sites, and the risk of overoxidation leading to loss of enantiopurity. [2]

In this work, we introduce conceptual a supramolecular approach that incorporates substrate recognition into the catalyst design. Specifically, our system takes advantage of the interaction between the protonated amine of α,ω-amino acids and a crown ether receptor located remotely on the ligand, while the carboxylic acid group activates hydrogen peroxide at the metal center. This combination helps organize the substrate in space, enabling improved control over both site- and enantioselectivity during lactonization. [3]
In addition, the use of simple linear α,ω-amino acids allows us to probe how the distance between the recognition site and the catalytic center influences selectivity, providing insight into distance-dependent effects in these transformations. (Figure 1c.)

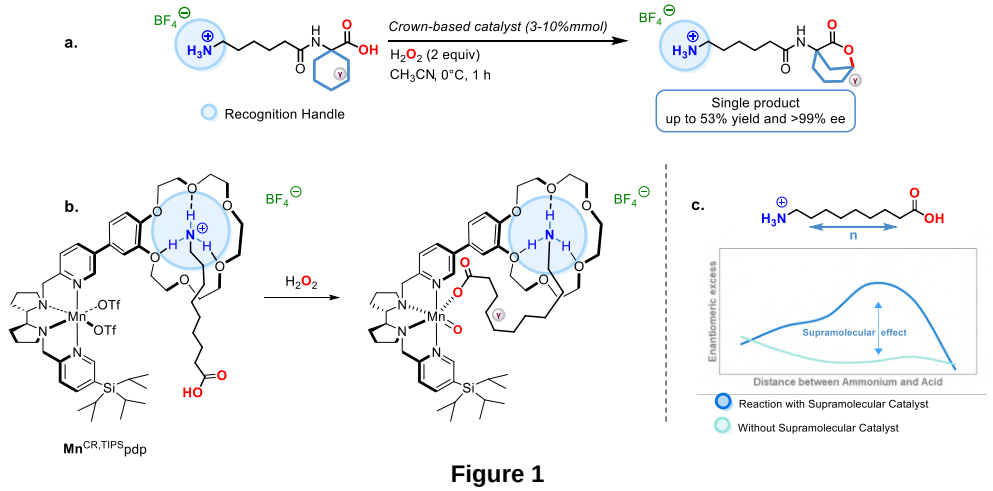

Figure 1

Acknowledgements
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Electron poor acridones for HAT-type engagement of carboxylic acids in a photoelectrochemical approach

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Keywords: photoelectrochemistry ● HAT ● carboxylic acids

Carboxylic acids are naturally abundant feedstocks, predominantly present as esters in lipids. They have been extensively employed as starting materials in radical chemistry, where the driving force is the release of gaseous CO_2 following the formation of a carboxyl radical. The generation of this radical directly from the unfunctionalized acid, however, remains the main challenge. It can be achieved using stoichiometric reagents (e.g., external oxidants or activation as redox-active esters) or through catalytic approaches, such as photocatalysis and electrocatalysis. In particular, photocatalysis has enabled the single-electron oxidation of carboxylates, leading to a rapid expansion in the use of these compounds as radical precursors.[1] In the past year, several reports have demonstrated that unfunctionalized carboxylic acids can be activated directly through a simpler hydrogen atom transfer (HAT) strategy, employing catalysts such as xanthone or azaanthraquinones.[2] The formation of a hydrogen bond between the photocatalyst and the carboxylic acid enables a HAT process that would otherwise be thermodynamically unfavorable, given the high bond dissociation energy of the C(O)–O–H bond (BDE for AcO-H = 112 kcal/mol). Building on our group's expertise in synthetic photoelectrochemistry (PEC)[3] and the use of electron-poor acridone catalysts,[4] we sought to extend this concept to transformations involving the synergistic use of light and electricity. Herein, we report a photoelectrochemical strategy in which a photochemically generated alkyl radical adds to the heteroaromatic, and anodic oxidation of the intermediate delivers the alkylated product. This complements previous PEC methods using trifluoroborate radical precursors[5] or strongly acidic conditions.[6]

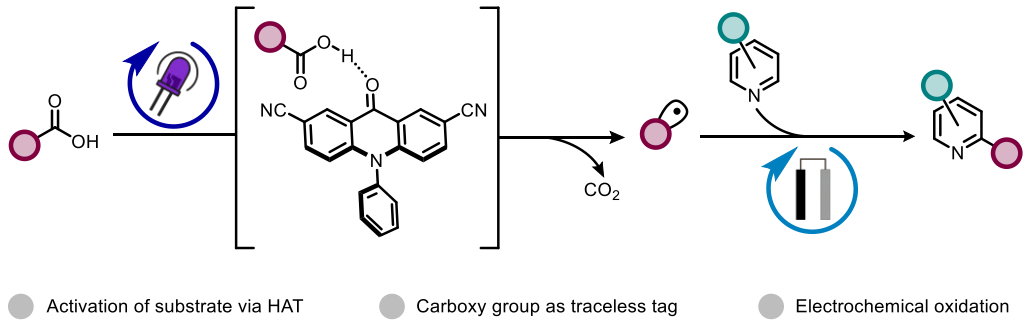

Figure 1. Photoelectrochemical HAT activation of carboxylic acids followed by coupling with heteroarenes

Acknowledgements
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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Fluorinated Solvents for Chemoselective Oxidations: A Strategy toward Synthetic Ideality in Natural Product Synthesis

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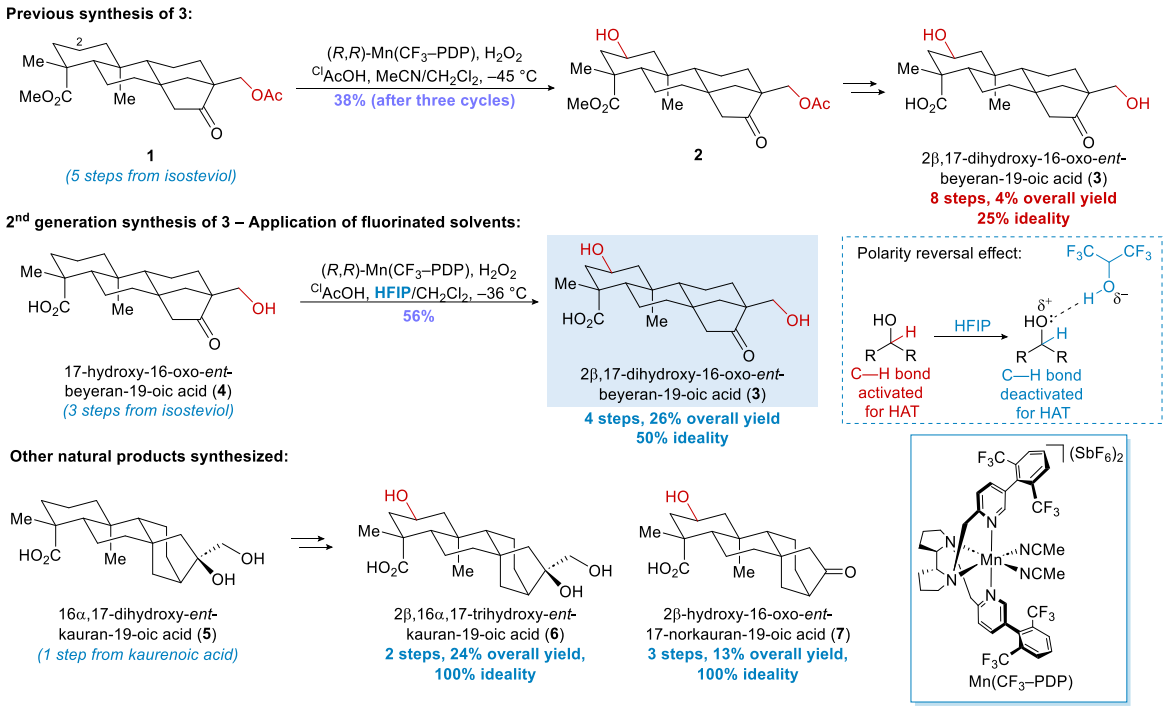
Keywords: chemoselectivity ● oxidation ● fluorinated solvents ● diterpenes ● natural products

The choice of solvents in organic chemistry plays an essential role in the development of new reactions, as they are not only responsible for dissolving the species in the reaction medium but also exert a significant influence on reactivity,[1] chemoselectivity[2] and synthetic ideality[3]. However, their use as key agents in achieving more ideal reactions remains underappreciated. Due to noteworthy properties such as high polarity, low nucleophilicity and strong hydrogen bond donating ability,[4] fluorinated solvents such as 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) became widespread. In the oxidation of C—H bonds in hydroxyl-containing substrates, HFIP and TFE have shown to mitigate overoxidation products by reversing the polarity of the substrate.
These effects enabled us to achieve a second-generation synthesis of metabolite **3**, as well as the first synthesis of natural products **6** and **7**.



Scheme 1. Synthesis of natural products **3**, **6** and **7** employing fluorinated solvents.

Acknowledgements
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Accessing metal-free alkylation of aza-arenes through electrochemical deoxygenation of alcohol derivatives

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The C-O bond cleavage for activation of alcohols is synthetically useful and practically challenging.[1] In this context carbazates have recently emerged as alcohol-derived alkylating agents, activated through electrochemical oxidation.[2, 3] Carbazates are easily prepared, bench stable derivatives, oxidized under mild electrochemical conditions, releasing CO_2 and N_2 as sole byproducts.

In this work, we studied the applicability of carbazates in the Minisci-type alkylation of unactivated aza-arenes. Electrochemical reactions have been performed in a simple homemade cell reported in Figure 1B. The setup allowed control of electrode immersed area, as well as inert atmosphere. First, reaction conditions were optimized. We discovered that coordination of heteroaromatics with Lewis acids was beneficial for the formation of the desired product in good yields. Best conditions were then employed in the alkylation of functionalized quinoline and isoquinoline substrates (Figure 1A), achieving yields up to 49% with alkyl- and aryl-substituted quinoline derivatives. Quinolines bearing heteroatoms were also tolerated under cell conditions, although lower yields were achieved.

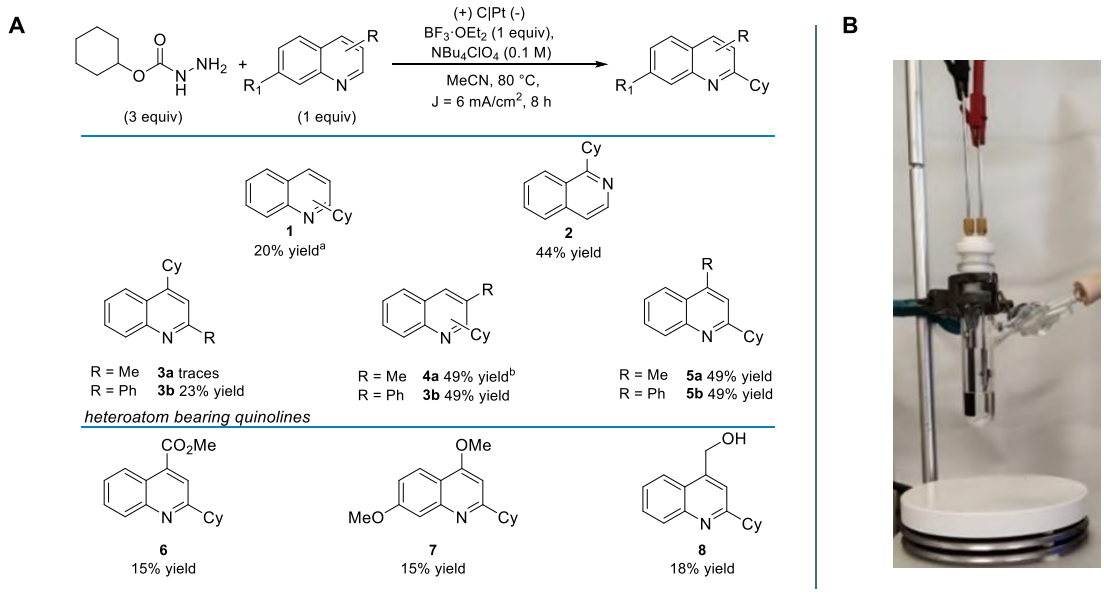

Figure 1. (A) Substrate scope of Minisci type reaction. [a] 3.1:1 mixture of 2- and 4-alkylated products separated via FCC. [b] 3:1 mixture of 2 and 4 alkylation products separated via FCC. **(B)** Homemade setup for the electrochemical transformations

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14th International Symposium on Organic Free Radicals (ISOFR-14)
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Direct Conversion of Furan to *N*-(hetero)arylpyrrole

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Keywords: Skeletal editing ● Photochemistry ● *N*-arylpyrrole

Skeletal-editing protocols have emerged as powerful tools for the rapid and modular construction of molecular libraries while maintaining precise control over atomic composition[1]. In particular, methods that enable formal single-atom exchange have attracted paramount interest, as they allow practitioners to promptly assess single-atom effects on the pharmacokinetic properties of medicinal compounds. Among the various privileged heterocycles explored for such editing strategies, pyrroles stand out, as they constitute a plethora of medicinal libraries[2]. To address the growing demand for diverse pyrrole scaffolds in pharmacology[3], we previously developed a photocatalytic furan-to-pyrrole transmutation that employs alkylamines or ammonia surrogates as nitrogen sources[4]. Herein, we report a visible-light-driven single-atom skeletal editing platform that converts readily available furans into *N*-(hetero)aryl pyrroles via a dearomative ring-opening/closure sequence. Building on our earlier oxidative furan ring-opening, we now identify and characterize key intermediates, including the long-sought ring-opened Zincke-type resting states and ring-closed intermediates, thereby providing direct experimental support for an ANRORC-type pathway adapted to five-membered heterocycles. Guided by these mechanistic insights, we overcome the intrinsically low nucleophilicity and challenging oxidation profiles of (hetero)arylamines through judicious photocatalyst and additive selection, enabling mild, modular access to *N*-(hetero)aryl pyrroles that previously required harsh Lewis-acid conditions and suffered from poor functional group tolerance[5]. This strategy expands the scope of skeletal editing from six-membered to five-membered heteroaromatics and offers a general blueprint for late-stage, single-atom editing of pharmaceutically relevant heterocycles.

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Dearomative Dimerization of Quinolines For The Rapid Assembly of Potent Antiferroptotic Agents

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Keywords: polysulfide anions ● photoredox catalysis ● redox reactions ● ferroptosis ● radical trapping agent

Photochemical activation enables new strategies for transforming aromatic heterocycles into structurally complex and biologically relevant scaffolds. Herein, we developed a visible-light-driven dearomative dimerization of quinolines mediated by polysulfide anions photocatalysis to generate sp^3-rich polyheterocyclic scaffold through radical anion intermediates. Reductive single electron transfer (SET) induces umpolung reactivity of quinolines, promoting intermolecular C–C bond formation followed by divergent reaction pathways controlled by the reaction conditions. Under reductive conditions, this process culminates in quinoline dimer formation *via* radical coupling.[1] Importantly, the dearomatized quinoline dimers exhibit potent radical-trapping antioxidant activity and effectively suppress lipid peroxidation, inhibiting ferroptotic cell death.[2] This work demonstrates how SET-driven dearomatization can simultaneously expand synthetic chemical space and deliver functional small molecules, establishing quinoline dimerization as a platform for the rapid discovery of antiferroptotic agents.

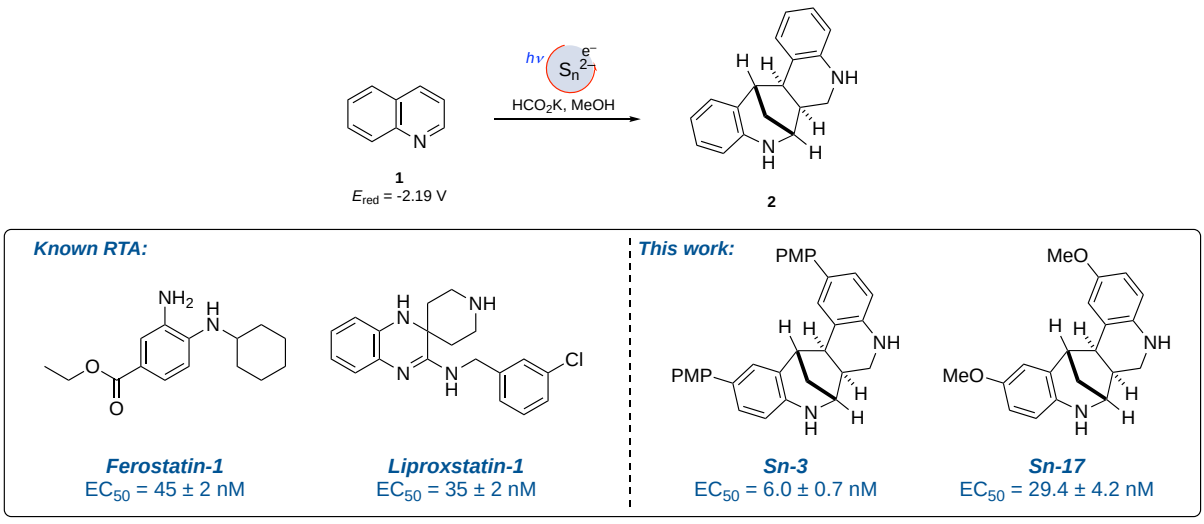

Figure 1. Dearomative dimerization of quinoline mediated by polysulfide anions and formate to yield unique scaffold identified as potent antiferroptotic agent.

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Continuous Flow Technology for the Synthesis of 2-azabicyclo[2.2.0]hex-5-ene derivatives

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Keywords: 1,2-dihydropyridines ● electrocyclization ● flow chemistry ● photochemistry ● scale up

The strained geometry of 2-azabicyclo[2.2.0]hex-5-enes makes them an attractive scaffold in medicinal chemistry (Figure 1A).[1] Their synthesis is achieved via the light-induced electrocyclization of N-carboxy-1,2-dihydropyridine derivatives, which are in turn obtained by hydride reduction of pyridines in the presence of a chloroformate.[2] Reported batch procedures are characterized by long reaction times (up to 7 days) and generally low yields, likely as a result of inefficient light penetration and poor irradiation homogeneity.
Continuous-flow technology overcomes these limitations by improving light penetration, ensuring more uniform irradiation, and enabling the straightforward scale-up of photochemical transformations.[3] In this context, we developed a continuous flow methodology for the synthesis of 2-azabicyclo[2.2.0]-hex-5-enes that significantly reduced reaction times and increased productivity. Reaction conditions were optimized on model substrate **1a** by tuning residence time, concentration, and solvent. Under the optimized conditions (30 min residence time, 0.1 M in MTBE upon 304 nm light irradiation), the desired product **2a** was obtained in 93% yield, with a productivity exceeding 31 mmol/day. Compared with the corresponding batch protocol, the flow procedure delivered a 93-fold increase in productivity and a 64-fold increase in space-time yield.

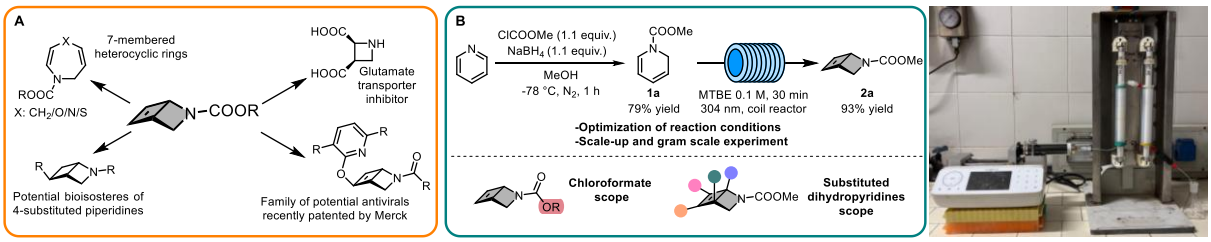

Figure 1. A): 2-azabicyclo[2.2.0]-hex-5-enes relevance; B): Optimized process for the synthesis of compound **2a** and reaction scope

The scope of the reaction was subsequently expanded to a variety of chloroformates and substituted pyridines (Figure 1B). While the nature of the chloroformate has a minimal influence on the cyclization efficiency, substitution on the pyridine ring had a pronounced impact on the reaction outcome. Electron-rich substrates afforded the desired products in good yields, whereas electron-poor substrates proved to be more challenging. In particular, 3-halo-substituted derivatives were obtained in low yields. Further investigations are currently ongoing in our laboratories.

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Aliphatic Aldehydes as CO Surrogates via Photocatalyzed Hydrogen Atom Transfer

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Keywords: photocatalysis ● Hydrogen Atom Transfer ● TBADT ● carbon monoxide ● carbonylation reaction

The introduction of a carbonyl group enables smooth access to a wide plethora of bulk chemicals such as ketones, amides and esters[1]. The use of carbon monoxide (CO) is ideal for large-scale carbonylation in industry, where infrastructure allows its safe and efficient handling[2]. However, most academic laboratories lack the expertise and equipment required to safely manage even small amounts of this lethal gas, thus inhibiting methodological development.
A controlled release of carbon monoxide on a lab scale is possible thanks to CO surrogates[3], which however often implies harsh conditions (strong acids or bases, expensive transition-metal catalysts, prohibitively high temperatures).
Herein, we propose aliphatic aldehydes as a new class of CO photosurrogates. Photocatalyzed decarbonylative Hydrogen Atom Transfer (HAT) [4] is leveraged to cleave the formyl C(sp2)−H bond of these chemicals to generate an acyl radical [5]. The latter species rapidly undergoes decarbonylation to provide carbon monoxide. We demonstrate how this simple but effective concept can be exploited to smoothly carry out benchmark aminocarbonylation, carbonylative Suzuki, cyclocarbonylation, and photochemical alkoxycarbonylation reactions. Our approach shows several advantages over the state of the art: i) it is atom-economical, ii) it does not involve the use of expensive or toxic reagents and iii) it can be controlled literally with the flip of a switch.

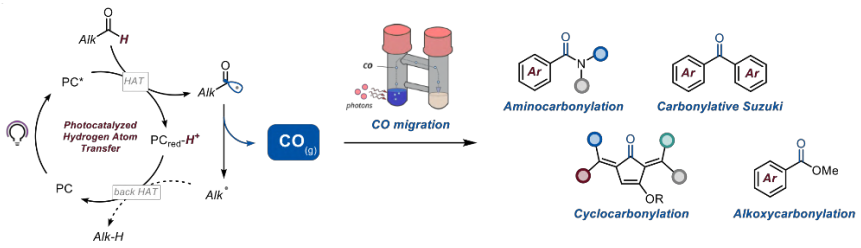

Figure 1. Aliphatic aldehydes as CO photosurrogates via photocatalyzed Hydrogen Atom Transfer (HAT) and some applications

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Synthesis of α-*C*-glycoside conjugates *via* a Giese-like reaction triggered by photoactivated electron donor–acceptor (EDA) complexes and *in situ* photocatalytic species

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Keywords: Coupling ● Giese ● EDA ● Radical ● α-C-glycoside

Two visible-light-mediated, catalyst-free strategies for the synthesis of α-*C*-glycoside conjugates are reported. The methods exploit electron donor–acceptor (EDA) complex activation and *in situ* generated photocatalytically active species to trigger Giese-like radical additions from glycosyl iodides to electron-poor olefins under mild conditions. Iodide-derived glycosyl donors participate, enabling the formation of *C*-glycosidic linkages across a broad range of mono- and disaccharide substrates, dehydroalanine derivatives, and bisphosphonate acceptors. Mechanistic studies indicate that distinct activation pathways operate depending on the reaction conditions: deprotonated Hantzsch ester–halogen EDA complexes in the presence of a base, and autocatalytic photoredox processes involving transient streptocyanine-type dyes generated from tertiary amines under irradiation. These findings demonstrate that selective C–C bond formation at the anomeric position can be achieved without exogenous photocatalysts, while highlighting the non-innocent role of amines in visible light-driven radical transformations.

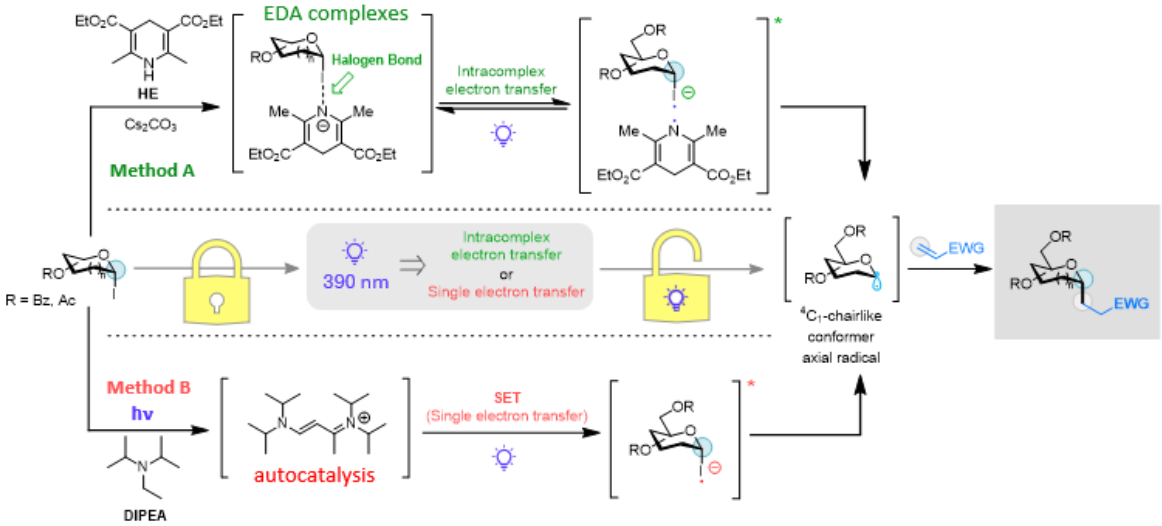

Figure 1. Graphical Abstract

Acknowledgements
This work was financially supported by University of Ferrara.

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Photochemical [2+2]-cycloadditions of Alkoxyallenes with *N*-Methylmaleimide

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Keywords: allenes ● cycloaddition ● photochemistry ● maleimide ● cyclobutanes

Cyclobutanes are prominent motifs in medicinal chemistry due to their conformational rigidity and ability to access three-dimensional chemical space. Photochemical [2+2]-cycloadditions represent a powerful strategy for their construction under mild conditions.[1]
Despite the synthetic potential of alkoxyallenes in photochemical transformations, intermolecular [2+2]-photocycloadditions remain largely underexplored, with only few examples reported to date. Most studies instead rely on intramolecular systems, in which the allene and the alkene are tethered within the same molecular framework.[2]
Herein, we report our studies on the [2+2]-photocycloaddition between a series of alkoxyallenes and *N*-methylmaleimide, performed under irradiation at 370 nm. The reaction provides efficient access to functionalized cyclobutane derivatives bearing both imide and alkoxy functionalities.
A range of alkoxyallenes was successfully employed, demonstrating the generality of the transformation. Notably, the reaction proceeds with moderate to good regioselectivity, affording two regioisomeric cyclobutanes, favoring the product featuring an exocyclic double bond. This selectivity suggests a preferential orientation during the cycloaddition step, potentially governed by electronic factors of the allene substituents.[3]
Ongoing work is focused on expanding the substrate scope, improving regioselectivity, and gaining deeper mechanistic insight into the reaction pathway.

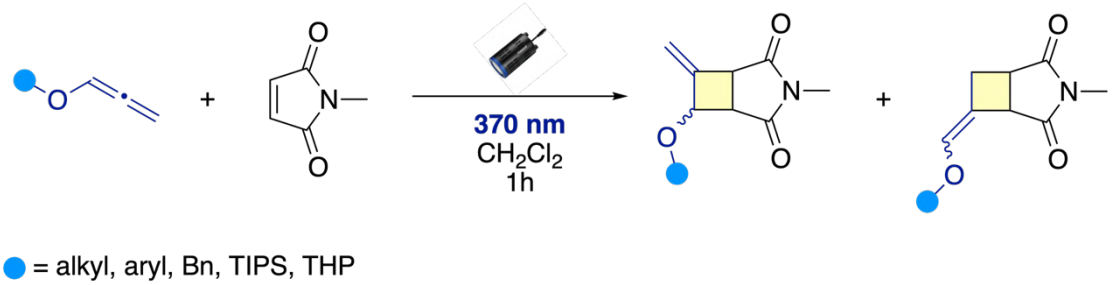

Figure 1. [2+2]-cycloaddition of alkoxyallenes with *N*-methylmaleimide.

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

A Unified Visible-Light Photoredox Strategy for the Intramolecular Assembly of Oxindoles and Indolines

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Keywords: oxindoles ● indolines ● photoredox catalysis ● photoreactor design ● organic radicals

Nitrogen-containing heterocycles constitute the core of the majority of small-molecule pharmaceuticals, with oxindoles and indolines representing particularly important privileged scaffolds found in numerous drugs, natural products, and bioactive molecules. Their structural diversity and broad biological activity have made them key targets in medicinal chemistry and synthetic methodology development. [1-3]

Herein, we report a unified visible-light-driven photoredox strategy that enables the divergent intramolecular assembly of both scaffolds from closely related precursors. By tuning the oxidative cleavable group, the reaction pathway can be selectively directed toward carbamoyl radical formation, affording oxindoles, or alkyl radical generation, yielding indolines. The transformation proceeds via a Giese-type addition to activated alkenes followed by intramolecular cyclization under mild visible-light irradiation. The protocol employs inexpensive organic photocatalysts and operates under operationally simple conditions, demonstrating broad functional group tolerance and good efficiency across a diverse substrate scope. Notably, the embedded electron-withdrawing group not only facilitates the initial transformation but also enables access to other pharmaceutically relevant bicyclic heterocyclic compounds. Mechanistic studies, including radical trapping, deuterium labeling, and light on/off experiments, support a photocatalytic radical pathway requiring continuous light activation. In addition, a target-made 3D-printed photoreactor ensures reproducible irradiation and enables efficient parallel reaction screening. This unified and switchable approach provides a versatile platform for accessing structurally related heterocycles and highlights the potential of combining modular substrate design with visible-light photoredox catalysis for divergent synthesis.

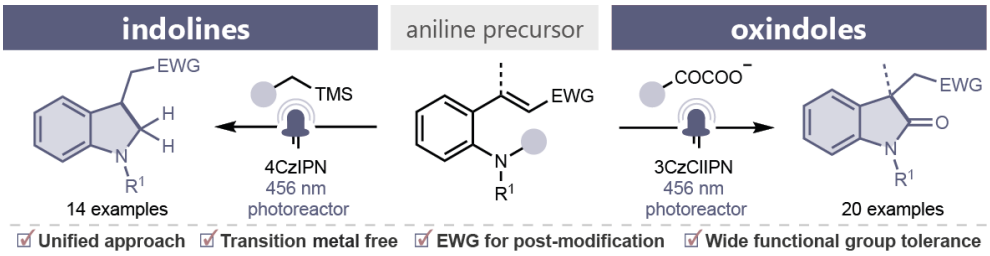

Figure 1. Synthesis approach.

Acknowledgements

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Cp_2TiCl_2-photoredox catalyzed HAT activation of unfunctionalized substrates toward radical coupling reactions

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Keywords: metallaphotoredox catalysis ● HAT ● Ti catalysis ● radical coupling

The combination of photoredox and metal catalysis has demonstrated to have huge potential for the development of more sustainable and wider scope synthetic methodologies.[1] Titanium catalysis is particularly appealing because of the high abundance and low toxicity of this metal.[2] Combining photoredox catalysis enabling substrate activation by HAT and Ti(III/IV) catalysis, we can generate matched radical couples toward aromatic aldehyde alkylation, without the need of any stoichiometric reductant and pre-functionalized substrates (Figure 1), unlike previously methodologies developed by our group.[3]

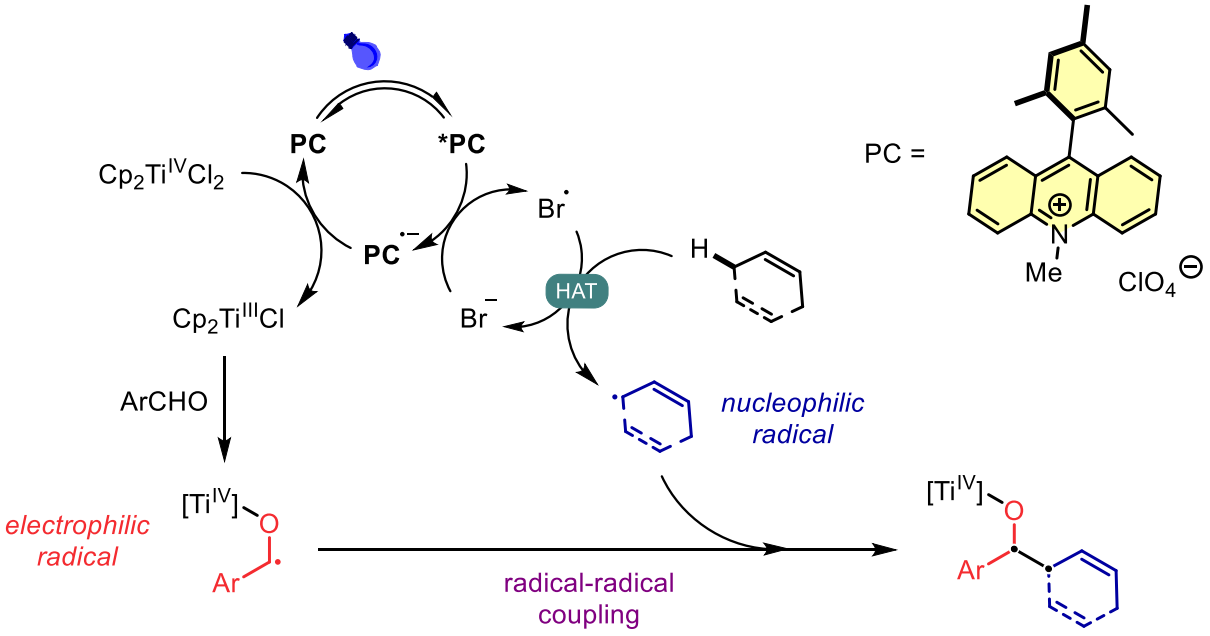

Figure 1. Conceptual mechanism of titanium-photoredox catalyzed HAT activation of unfunctionalized substrates in radical-radical coupling reactions.

The method proved to have wide functional group tolerance affording products in moderate to good yields. Careful photophysical studies were also conducted. This demonstrates the potential of combining HAT chemistry with titanium catalysis.

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Kinetic studies on the autoxidation of human skin lipids to develop heterogeneous biomimetic models

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Keywords: Lipid ● peroxidation ● Kinetic ● Biomimetic systems

Lipids are the main constituents of the *Stratum Corneum,* mainly including cholesterol, free fatty acids and ceramides. Each of these undergoes lipidic autoxidation (peroxidation) [1], an autocatalytic free-radical chain reaction responsible for the oxidative destruction of organic molecules and related to oxidative stress, aging, cancer. To counteract this process, antioxidants are necessary. Their development and study are, therefore, key to the design of skin protecting products, along with understanding the skin lipids peroxidation kinetics. Surprisingly, little is known in this regard and current knowledge is only limited to some prototypical models. This work is focused on filling this gap and unrevealing the kinetic aspects governing the autoxidation of such complex system determining the pertinent kinetic parameters (k_p, k_t and oxidizability) [2]. Selected ceramides like Ceramide NP (or Ceramide 3) and Ceramide EOP (Ceramide 1) alone and combined with other lipid components have been studied using reference heterogeneous biomimetic systems such as micelles and liposomes, monitoring the oxygen uptake during controlled autoxidation in the presence of well know antioxidants used as references, to determine the kinetic constants. Additional DLS measures have been carried out to characterize the particle's geometry. Autoxidation kinetics data are then used to build multicomponent skin-lipid models so to set up a reference mimic to be used in rational antioxidants research.

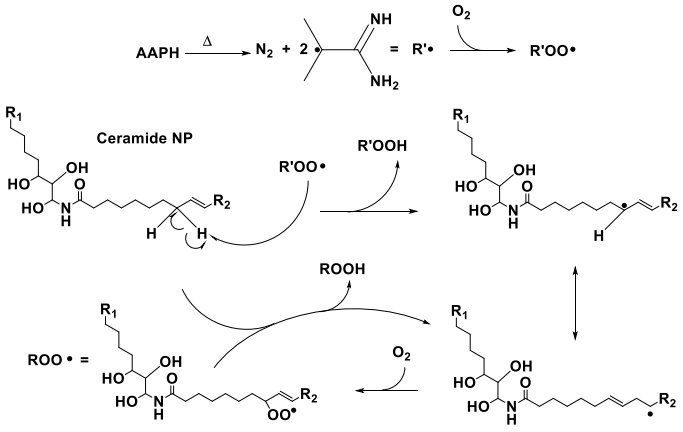

Figure 1. simplified scheme of Ceramide NP autoxidation reaction steps in micelle model

Acknowledgements
This work was financially supported by University of Bologna, "Giacomo Ciamician" Che,istry Department

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Asymmetric Photocatalysis under Continuous-Flow Conditions for the Synthesis of Enantioenriched α-Amino Acid Derivatives

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Keywords: *asymmetric photocatalysis ● continuous-flow ● α-amino acid derivatives ● radical addition ● enantioselective synthesis*

Enantiomerically enriched α-amino acids (α-AAs) and their derivatives are essential building blocks, widely used in the pharmaceutical industry, drug discovery, catalysis, and materials science.[1] Consequently, the development of straightforward and versatile synthetic methods remains highly desirable.[2] Herein, we report a photochemical enantioselective addition of alkyl radicals, generated from dihydropyridines, to prochiral α-imino esters, mediated by bifunctional rhodium(III) catalysts, under continuous-flow conditions.[3] This approach enables rapid and direct access to enantioenriched derivatives of both natural and unnatural α-amino acids, delivering yields of up to 75% and enantiomeric ratios of up to 1:99. Notably, this strategy expands the scope of asymmetric photocatalysis in flow and provides a streamlined platform for the synthesis of biologically active molecules and pharmaceutical intermediates.

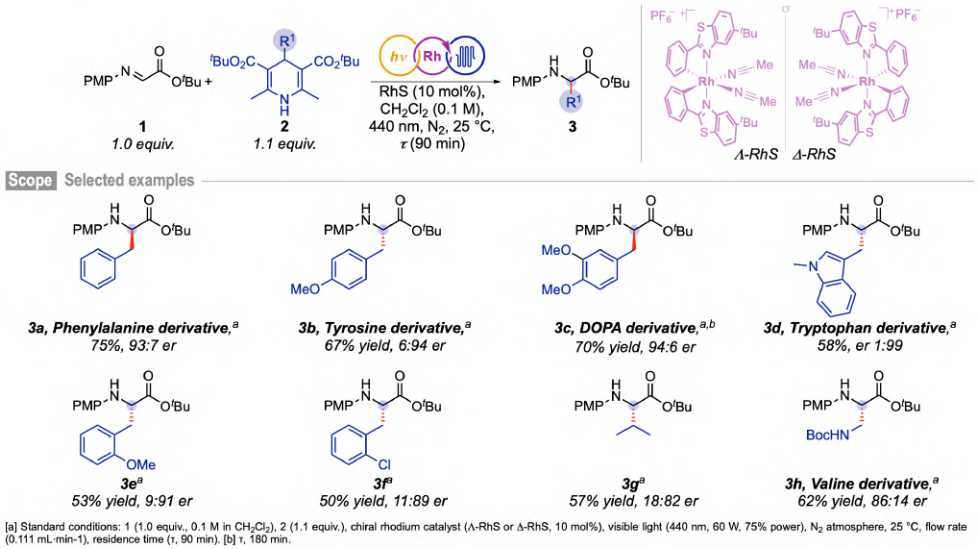

Figure 1. Enantioselective RhS-catalyzed photochemical Giese-type alkylation of α-imino esters in continuous flow.

Acknowledgements

This work was financially supported by São Paulo Research Foundation – FAPESP (Grant N.: MSF, 2022/15574-1; RCS, 2023/07466-7, 2025/02336-3; EYL, 2024/17686-7; JMBJ, 2023/12475-5; JCP, 2021/06661-5); Brazilian National Council for Scientific and Technological Development – CNPq (JCP, 308540/2021-2); Coordination for the Improvement of Higher Education Personnel – CAPES; Centre for Scientific Computing (NCC/GridUNESP).

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Selective C-H Functionalization directed by Dynamic Covalent Chemistry

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Keywords: recognition ● boron ● directed ● selectivity ● C-H functionalization

The functionalization of non-activated C-H bonds represents a significant challenge due to their low intrinsic reactivity that makes control of selectivity particularly difficult. Classical methodologies rely on intermolecular reactions that occur on the most reactive substrate site or intramolecular radical processes that are typically limited to δ position of the chain.[1] However, in both cases, C-H bonds remote from functional groups remain largely indistinguishable and cannot be selectively functionalized. Moreover, the reaction site is often difficult to predict, especially when there are minimal differences in the electronic and steric properties of the substrate C-H bonds.

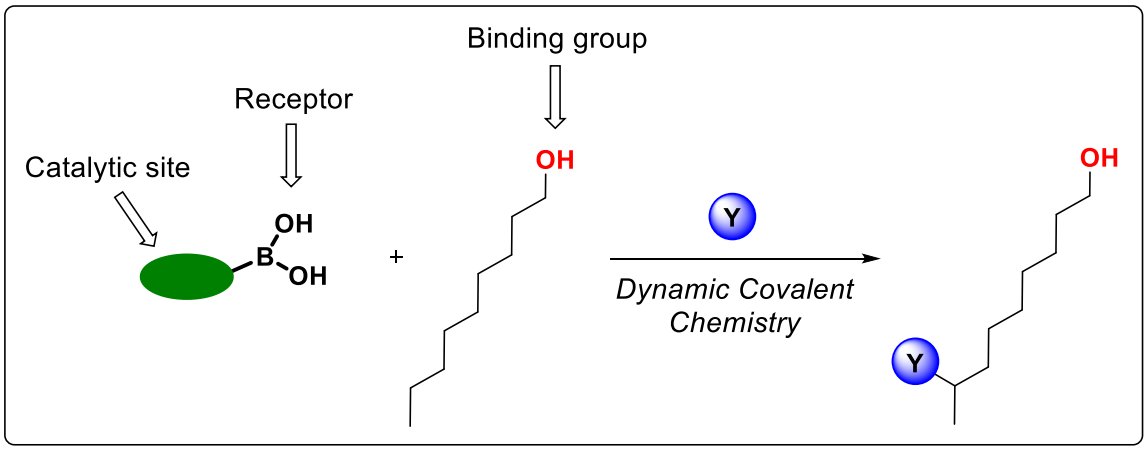

Figure 1. Functionalization of remote C-H bonds using dynamic covalent chemistry.

Seeking to overcome these limitations, we designed a C-H functionalization catalyst equipped with a boronic acid receptor capable of reversibly interacting with alcohols and diols through dynamic covalent chemistry (Figure 1).[2] Such binding places remote, non-intrinsically activated positions of the substrate in the range of the catalytic site, thus enabling a geometrical control of the reaction selectivity.[3] By exploiting proximity, we aim to use radical processes such as HAT or others to introduce different functional groups at well-defined positions on the substrate, predictable based on their distance from the binding group. Herein, we will report the application of this strategy to the selective functionalization of alcohols using radical and/or radical-like reactants.

Acknowledgements
This work was financially supported by University of Rome “La Sapienza”.

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Keywords: Photocatalysis ● Perfluoroalkylation ● Radical fluorine chemistry ● Metal-Free ● Visible-light

Fluorinated organic compounds show unique properties, including high metabolic stability, enhanced lipophilicity, and strong carbon-fluorine bonds, making them indispensable in pharmaceuticals, agrochemicals, and functional materials. Esprciallu, perfluoroalkylated amides represent an especially valuable structural motif because of their hydrogen-bonding ability and chemical robustness. Accordingly, the development of efficient and sustainable synthetic methods for accessing such compounds remains an important challenge.

Conventional synthetic approaches for fluorinated amides typically depends on unstable acid derivatives, such as acyl halides and acid anhydrides, as well as in situ-generated activated acid derivatives, and metal-mediated cross-coupling strategies, which may involve toxic reagents or multi-step protocols. In addition, direct oxidative conversion of amines into perfluoroalkylated amides remains underdeveloped in comparison to other perfluoroalkylation strategies.

Herein, we report a complete metal-free, visible-light-induced perfluoroalkylation of amines that directly affords perfluoroalkylated amides using perfluoroalkyl iodides as fluorine sources and an organic photocatalyst. Under irradiation with a 2.4 W white LED in the presence of fluorescein and DBU under air, pyrrolidine reacted smoothly with perfluoroalkyl iodide to give the corresponding perfluoroalkylated amide in up to 96% yield. The reaction proceeds under ambient atmosphere without the need for transition-metal catalysts.

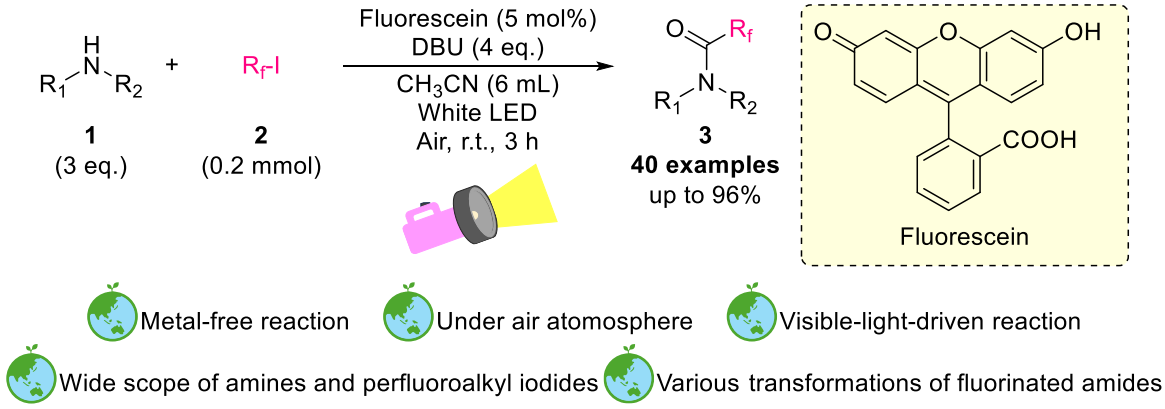

Figure 1. This work.

Acknowledgements
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Cationic Selenuranes – Bench-Stable Sources of Se(III) Radicals

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Keywords: chalcogen● main-group● radical ● selenium

Chemical processes involving the formation of free-radical species have found numerous applications in organic synthesis. The high reactivity of radicals is an attractive feature from a synthetic standpoint, but it also represents a limitation, as in most cases it requires the *in situ* generation of these open-shell species. In contrast, bench-stable salts are compounds that can be safely stored and handled without decomposition or unwanted reactivity. Their ease of use, affordability, and versatility make them central to chemical practice.

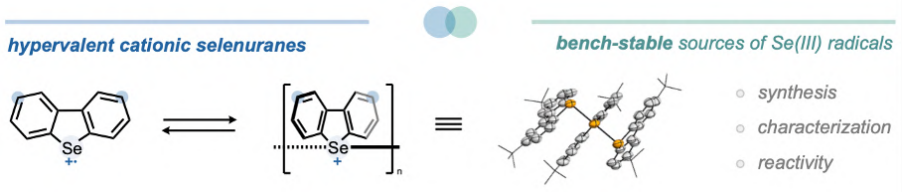

Figure 1. New class of organoselenium compounds: cationic selenuranes

We have recently developed cationic selenuranes as bench-stable reservoirs of selenium radical cations,[1] a class of species that remains scarcely explored in organic chemistry.[2,3] These compounds can be prepared, isolated, and characterized on multigram scale and exhibit remarkable stability under ambient conditions for more than one month, without requiring an inert atmosphere. A distinctive feature is their reversible head-to-head dimerization, which allows controlled Se(III) radical release in solution due to the unusually weak Se–Se σ bond. Their reactivity spans oxidation and substitution chemistry with hydrazines, alcohols, sulfinates, borates, silanes, and stannanes, including applications to structurally complex substrates and further transformations of selenonium salt products.

Acknowledgements
This work was financially supported by the Doctoral School of Chemistry (DoSChem) of the University of Vienna.

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Eosin Y Disproportionation Promoted Alkene Hydrofunctionalizations in Fluorinated Assemblies

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Keywords: Alkenes ● Nucleophiles ● Radicals ● Photocatalysis ● Fluorinated Assemblies

Alkenes are one of the most versatile functional groups in organic synthesis due to the π-character of the double bond. Over the years, synthetic chemists have developed numerous strategies to transform alkenes into a variety of products, such as nucleophile addition, epoxidation, and reduction. However, the use of strong acids and harsh conditions is often necessary, resulting in lower selectivity and yields, as well as the formation of by-products.
Radical chemistry is an interesting alternative for obtaining compounds with higher structural complexity using alkenes as precursors (e.g., the Mukaiyama-Aldol reaction). Over the past decade, photoredox catalysis has emerged as a powerful tool for functionalizing alkenes via radical intermediates using milder conditions. However, it often necessitates the use of photocatalysts with strong oxidizing potential or the addition of additives in stoichiometric amounts. Remarkably, the developed methods are limited to alkenes with an oxidation potential of less than 2 V, which excludes most unconjugated alkenes.[1]
In this context, fluorinated alcohols (R_fOH) are used as 'magic solvents' in synthesis thanks to fluorine's exceptional physicochemical properties.[2] Additionally, they can modulate the physical properties of photocatalysts due to their strong hydrogen-bonding affinity. Recently, our group observed the disproportionation of Eosin Y (EY) to $EH^{\cdot}$ and $EH_3^{\cdot}$ in the presence of fluorinated solvents during photocatalytic polyene cyclizations. This clearly demonstrates the indispensable nature of the interaction between EY and R_fOH, since direct oxidation of the alkene ($E_{ox} \approx 2$ V *vs* SCE) by excited EY (E_{Red} ($^3EH_2^*/EH_2^{\cdot-}$ = 0.83 V *vs* SCE)) is chemically impossible.[3] Herein, we present our work on developing mild and selective hydrofunctionalization beyond the limits of alkenes' photooxidation.

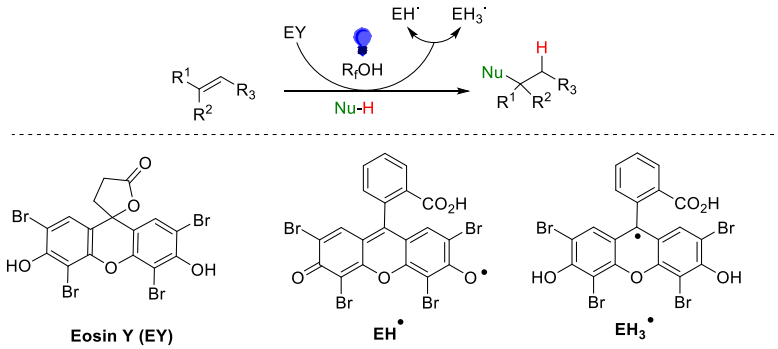

Figure 1. Eosin Y Disproportionation Promoted Alkene Hydrofunctionalization in Fluorinated Assemblies.

Acknowledgements
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Aryl Carbonyl Photochemistry: Access to Carbonyl Ylides via Skeletal Rearrangement

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The photochemistry of Aryl carbonyl compounds underpins a wide range of modern synthetic transformations [1]. However, photoinduced rearrangements, despite their unique potential for skeletal reorganization, remain conspicuously underexplored. In this study, we demonstrate that vinyl acetophenones undergo photoinduced isomerization to generate carbonyl ylides. Mechanistic studies confirm initial cyclization via oxygen-centered radical addition to the alkene [2], followed by skeletal rearrangement through a spirocyclic cyclopropane intermediate. The corresponding carbonyl ylides are prone to undergo isomerization and cycloaddition [3] reactions depending on the specific conditions.

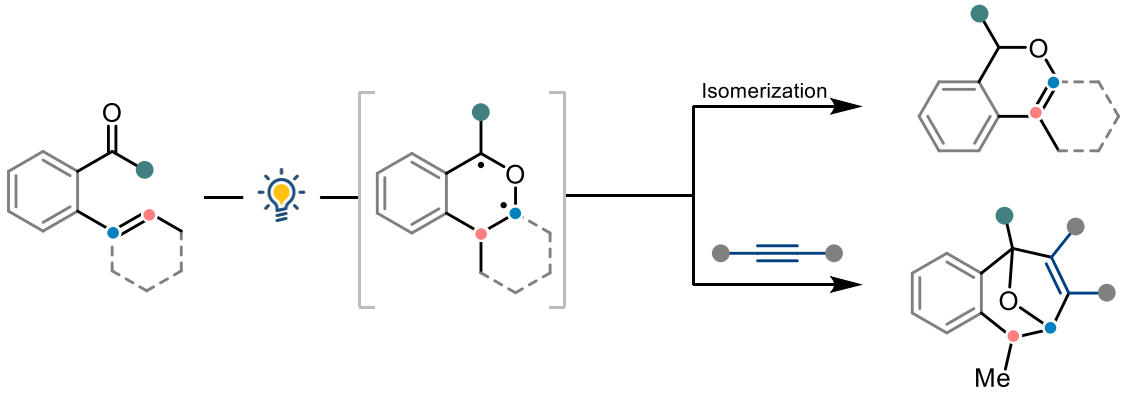

Figure 1. Photochemical rearrangement of Styrenyl Ketones

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Monitoring the Fate of Low- and High-Molecular-Weight Nitroxides in Polyolefins by ESR Spectroscopy

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Keywords: HALS ● Nitroxides ● Polymer ● ESR ● Light stabilizers

Hindered Amine Light Stabilizers (HALS) are the most effective thermal and photo-oxidative stabilizers for polymers, particularly polyolefins. Their stabilization mechanism involves the formation of persistent nitroxyl radicals derived from the tetramethylpiperidine ring. These nitroxide species can be directly detected and quantitatively analyzed by Electron Spin Resonance (ESR) spectroscopy, making ESR a powerful tool for monitoring HALS activity.[1]
In many applications, such as polymer tapes, the final article is stabilized using a combination of high-molecular-weight (HMW) and low-molecular-weight (LMW) HALS.[2] This dual-stabilizer strategy balances two functional requirements: *a)* surface protection, achieved by LMW HALS, which can migrate toward the polymer surface to protect the most exposed regions from light- and heat-induced degradation; *b)* long-term stability, ensured by HMW HALS, which exhibit lower volatility and reduced migration, thereby maintaining stabilizing performance over extended service lifetimes.
Monitoring the fate and relative contribution of each stabilizer type throughout the lifecycle of the polymer article is essential for optimizing formulation design and tailoring performance to specific application requirements. However, when different HALS are used in combination, their ESR signals largely overlap because both generate nitroxide radicals with the same paramagnetic moiety.
Here, we demonstrate that deconvolution of the ESR spectra enables discrimination between low- and high-molecular-weight nitroxides. Specifically, overlapping nitroxide signals can be resolved based on differences in their effective rotational correlation times, allowing differentiation between freely mobile LMW and HMW nitroxides. This level of spectral resolution is essential for elucidating stabilizer migration behavior, long-term persistence, and overall stabilization performance. Moreover, it enables independent tracking of the temporal evolution and relative contribution of each stabilizer component throughout the service life of the polymer article.

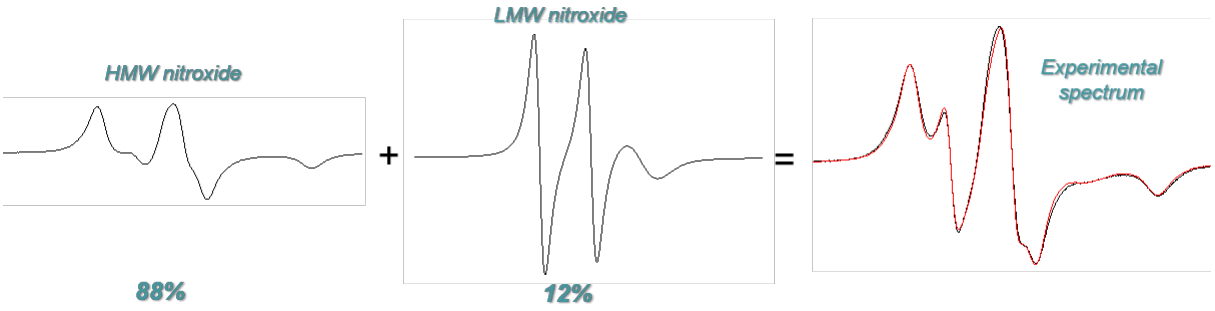

Figure 1. ESR spectra of polyolefin films containing a HMW HALS, a LMW HALS, and their mixture. The theoretical simulation of the spectra related to the mixture is shown in red.

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Autonomous Exploration of Flow Electrochemistry with eRobochem: A Data-Guided Optimization Platform

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Keywords: Self driving laboratory ● Electrochemistry ● Machine learning ● Reaction optimization ● Radical chemistry

Synthetic electrochemistry holds the promise to enable milder and novel chemical approaches, thereby expanding the toolbox of synthetic chemists.[1] As it is inherently heterogeneous, electrochemistry benefits from a translation to continuous flow to improve selectivity and scalability.[2] Thus, optimizing a flow electrochemical reaction not only depends on "traditional" chemical variables (e.g reagents, equivalents) but also electrochemical (e.g electrode materials, current density, coulombs) and flow parameters (e.g residence time, reactor geometry). Here, eRoboChem (Figure 1) is presented as an autonomous platform for optimizing electrochemical reactions in flow and batch.

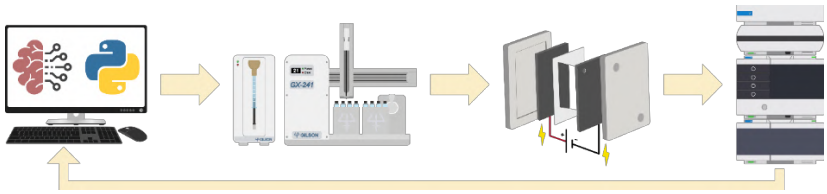

Figure 1. eRoboChem's workflow for closed-loop optimization of electrochemical reactions in batch and flow.

To highlight the capabilities and versatility of the platform, optimization of paired, reductive and oxidative flow electrochemistries were conducted.[3-5] A comparison between one variable at a time and Bayesian optimization strategies was conducted to benchmark the performance of the machine learning against traditional approaches. Finally, eRobochem autonomously optimized a novel electrosynthetic cyclopropanation. As screening electrode materials and handling slow reactions is a particularly challenging in flow, batch high-throughput experimentation was used in a closed-loop system. Through these campaigns, eRoboChem demonstrates its ability to navigate complex (electro)chemical spaces, identify scalable reaction conditions, work with multiple analytic readouts, handle challenging reaction parameters such as gas evolution and perform make use of the strengths of both batch and flow systems.

Acknowledgements

M.R. and G.H. acknowledge funding from Horizon Europe (MSCA MiEL, No. 101073003, MSCA Postdoctoral Fellowship program INSPIRE, No. 101203461). O.B. acknowledges funding from the Molecular and Material Design Technology Hub of the Faculty of Science of the University of Amsterdam. A.B. acknowledges funding from the Italian government (PNRR-PE11–3A-ITALY). E.S. acknowledges funding from the European Innovation Council (reaCtor, No. 101099405).

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Carbene-Derived Sulfur-Based Radicals

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Keywords: Sulfide radical ● Carbene ● Radical cation ● Stable radical ● Main-group radical

Radicals are widely recognized as key intermediates in diverse chemical transformations, exhibiting distinctive and versatile reactivity. Although traditionally regarded as transient species, the recent development of stable organic radicals has enabled their utilization as functional materials.[1] In particular, sulfide radical cations play crucial roles in organic chemistry, biochemistry, and polymer and materials science. However, the development of air- and water-stable sulfide radical cations has remained a significant challenge. In this study, highly stable sulfide radical cations supported by two cyclic (alkyl)(amino)carbene (CAAC) moieties have been synthesized.[2] In addition to demonstrating high air- and water stability, these radical cations can withstand harsh conditions, including exposure to reactive chemicals such as sulfuric acid and hydrogen peroxide, as well as elevated temperatures. Combined experimental and computational studies reveal that the sulfur-centered unpaired electron is stabilized through electronic delocalization and steric protection provided by the CAAC substituents. These findings establish a new class of exceptionally stable sulfur-based radicals and pave the way for their potential applications as functional materials.

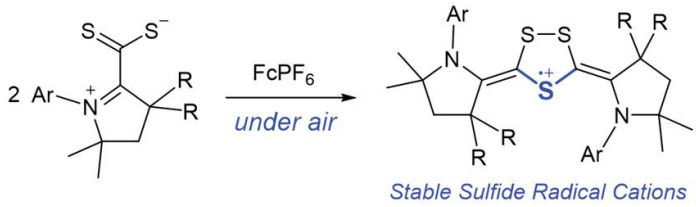

Figure 1. CAAC-derived stable sulfide radical cations.

Acknowledgements
This work was supported by the National Research Foundation of Korea (NRF) (RS-2023-00210804, RS-2025-02215028, RS-2023-00301938).

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Dual Reactivity of Formate: From Carboxylation to Reductive Catalysis

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Keywords: Regioselective carboxylation ● Formate as reductant for ConPET ● Kinetics driven exocyclic carboxylation

Formate salts, a sustainable non-gaseous and cost-effective C-1 building blocks. Recently, they use under photoredox catalysis attracted attentions due its distinct character to produce carbon dioxide radical anion ($CO_2^{\bullet-}$), a reactive incipient and short-lived transient radical intermediate with very high (negative) reduction potential (ECO_2 = −2.22 *V vs SCE*).[1] The nucleophilic character of $CO_2^{\bullet-}$ show an intrinsic property to undergo a Giese-type addition to alkenes. Followed by Wickens,[2] $CO_2^{\bullet-}$ has been installed at the terminal position to produce mainly a linear product. Our successful combination of the MHAT strategy by Co/Brønsted acid/photocatalysis switched the regioselectivity to the Markovnikov type carboxylation yielding branched products. The key to creating the kinetic match between formate activation and MHAT was to introduce a diprotonated DABCO salt as a novel bench and air-stable dual precatalyst (BAT) for both the cycles (Figure 1). [3]

Upon successful carboxylation, we targeted to employ the extremely low reduction potential of $CO_2^{\bullet-}$ in presence of CO_2 gas, where the latter would act as C-1 source and the methodology was further expanded to difunctionalisation of aryl oxyallenes. Therefore, we developed a tunable photocatalytic platform that strategically bridges carbon dioxide radical anion $CO_2^{\bullet-}$-mediated reduction and consecutive photoinduced electron transfer (ConPET) to access super reducing regimes. The kinetic study revealed that relative rate of the reaction *o*-chloro phenoxyallenes are *120 times* slower than *o*-bromo substrates. Thus, to drive the reduction of chloro substrates, we have introduced ConPET where formate act as essential electron donor to the photocatalyst, contrasting to the trivial ConPET where amines are generally required. While $CO_2^{\bullet-}$ or ConPET generate aryl radical from the haloarenes and successive ring annulation, the final carboxylation takes place *via* reductive radical-polar crossover (RRPCO) and successive CO_2 capture. [4]

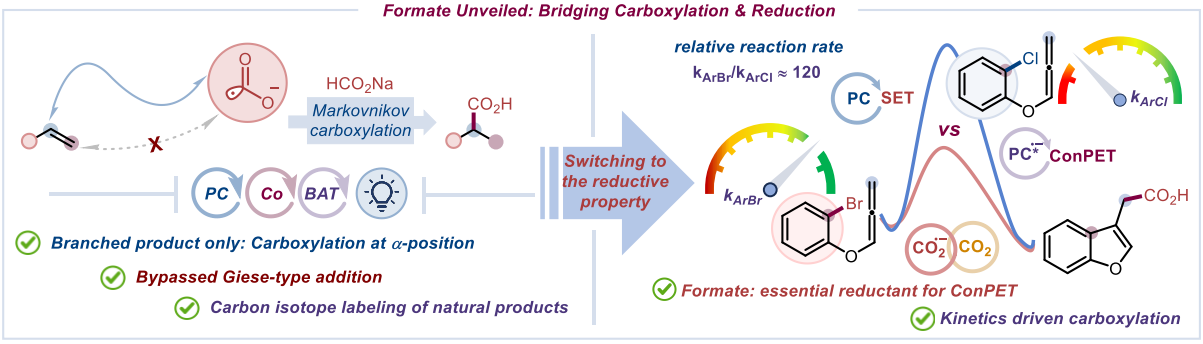

Figure 1. Dual nature of formates: As carboxylation source (left) & exploiting its reducing nature (right).

Acknowledgements
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Electrochemical Polarity Inversion of Azlactones to Access α–Quaternary Amino Acids

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Keywords: Electrochemistry ● Polarity inversion ● Quaternary amino acids ● Azlactones ● Oxazolones

Unnatural amino acids are key building blocks in modern organic chemistry, with broad applications in drug discovery, chemical biology, protein engineering, and materials science.[1] In particular, α-quaternary amino acids represent highly valuable structural motifs, as they can enhance chemical stability and enforce defined peptide conformations.[1] Despite significant advances in the synthesis of unnatural α-amino acids,[2] methods enabling access to their α,α-disubstituted counterparts remain comparatively limited as the steric congestion around the α-carbon poses a considerable synthetic challenge.[3]

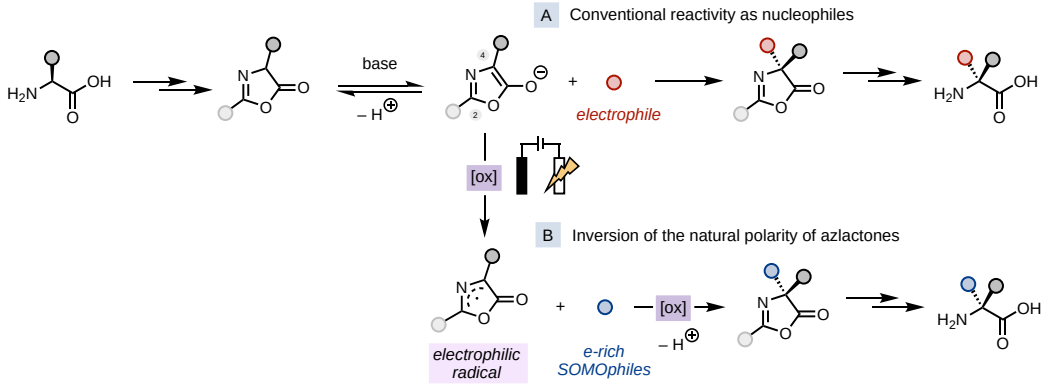

Figure 1. (A) Conventional polar reactivity of azlactones as nucleophiles. (B) This work – Electrochemical polarity inversion of azlactones enables radical functionalisation with electron-rich species.

In this context, a well-established strategy to access α-quaternary amino acids relies on the use of azlactones as nucleophiles. Upon enolization, the nucleophilic nature of the C4 enables a wide range of functionalisations with electrophilic coupling partners (Figure 1A).[4]

Herein we show that the electrochemical oxidation of the azlactone enolate allows to form a radical species with electrophilic character that can engage with various electron-rich SOMOphiles, thereby reversing its natural polarity (Figure 1B).[5] This electrochemical methodology allows to forge both Csp^3–Csp^2 and Csp^3–Csp^3 bonds, providing access to a new array of α-quaternary amino acid derivatives with electron-rich coupling partners. The method can be successfully scaled up and enables the incorporation of biologically relevant natural products into the amino acid core.

Acknowledgements

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A new family of paracyclophane-derived photocatalysts for sunlight-driven thiol–ene reactions

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Keywords: Photocatalysis ● Green chemistry ● Organic chemistry

Photosensitizers are light-sensitive molecules that can generate reactive species such as radicals, cations, or anions, upon excitation by a light stimulus. Light-induced processes continue to evolve rapidly and are increasingly integrated into industrial applications. Nowadays, the development of high-performance photosensitizers that are efficient, environmentally friendly, non-toxic, and responsive to visible light is a major research focus. Most conventional photosensitizers are highly sensitive to UV light.[1] Consequently, the limited number of visible-light photosensitizers highlights the need for the development of new structures specifically designed to exhibit controlled reactivity.

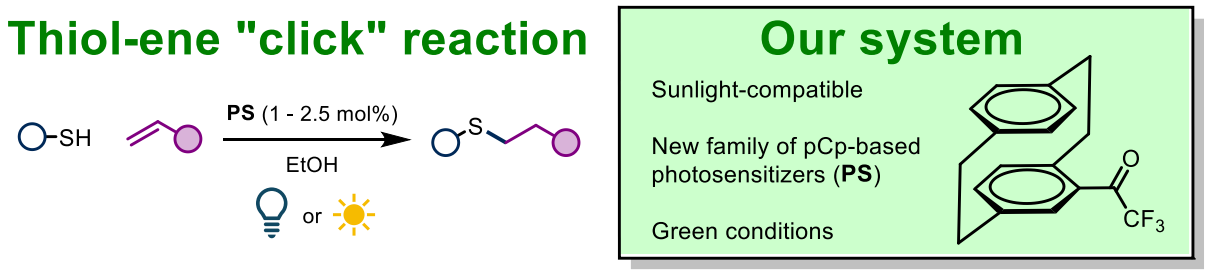

Figure 1 Thiol-ene “click” reaction using [2.2]paracyclophane derivative as photosensitizer

In our research, we focused on the design of novel photosensitizers by using the unique properties of [2.2]paracyclophane frameworks. Recent advances in radical chemistry have demonstrated that through-space electron delocalization within such scaffolds can significantly enhance the stability of carbon-centered radicals.[2] Building on this concept, we synthesized a trifluoromethylketone-substituted [2.2]paracyclophane derivative. This molecule exhibits absorption in the visible region, specifically at 405 nm. This new compound acts as an efficient photocatalyst for thiol-ene “click” reaction under green conditions, including the use of green solvent, low catalyst loading, ambient temperature and sun-light compatible.[3]

Acknowledgements
This work was financially supported by “la Fondation de la Maison de la Chimie », the CNRS, AMU and the Ministère de l’Enseignement Supérieur, de la Recherche et de l’Innovation.

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Fe-promoted Amination with Hydroxylamine-Derived reactants: from free radical to metal-based reactivity

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Keywords: amination ● iron ● aminyl radicals ● nitrenoid ● arene functionalization

The relevance of amine functions in biologically active compounds calls for the design of amination reactions with improved efficiency, selectivity, and sustainability. Fe-mediated amination with hydroxylamine-derived reactants has gained significant attention in recent years[1], as it relies on non-toxic, cheap, and abundant iron salts or complexes and bench-stable reactants. This reaction enables NH_2 insertion on arenes in a single step, making this chemistry remarkably attractive. Over the years, different types of hydroxylammonium-derived reactants featuring electron-withdrawing O-substituents have been designed.

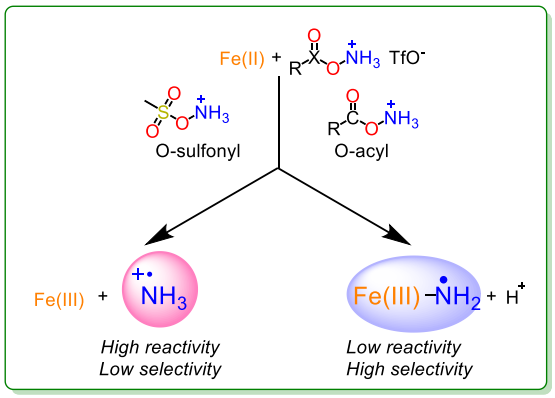

Figure 1: Radical vs metal-based pathways in Fe-promoted amination with hydroxylammonium reactants

Two distinct aminating species, either radical cation $NH_3^{+\bullet}$ or an iron-coordinated aminyl radical can be involved. We investigated how the structure of the hydroxylammonium reactant controls the operating mechanism, i.e. which aminating species is formed.[2] O-sulfonyl hydroxylammonium ($MsONH_3^+$) are associated with a free radical pathway, competent for effective yet poorly selective amination of arenes as well as organic materials like graphene[3]. In contrast, O-acyl hydroxylammonium salts are connected to a metal-based mechanism, that produces an iron-aminyl radical[4] competent for selective and controllable amination of arenes.

Acknowledgements
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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Photoredox-Mediated Radical-Polar Crossover Ring Expansion of α-Ketoaziridines: Easy Access to Heterocycles

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Keywords: photoredox catalysis ● α-ketoaziridines ● radical polar crossover ● ring expansions ● heterocycles

Visible-light photoredox catalysis has expanded synthetic methodologies enabling access to reactive radical intermediates under mild conditions.[1] Among these, radical-polar crossover (RPC) strategies have emerged as powerful tools for constructing cyclic frameworks through the merger of radical and ionic reactivity.[2] Within this context, ring-strained α-ketoaziridines have garnered increasing attention due to their ability to undergo photocatalytic ring opening, generating ketyl radical anions that can participate in downstream functionalization processes.[3] In this work, we report two novel photocatalytic ring-expansion methodologies of α-ketoaziridines, providing efficient access to valuable heterocyclic scaffolds.

First, we discovered an intramolecular reactivity of N-sulfonyl-protected α-ketoaziridines that proceeds via an iridium-photoredox-catalyzed RPC ring-expansion, affording δ-sultams with an unprecedented 2,3-disubstitution pattern.[4] The method exhibits a broad substrate scope and scalability. Mechanistic investigations support a pathway involving single-electron transfer (SET) reduction to a ketyl radical anion, followed by aziridine ring opening, intramolecular radical cyclization, SET oxidation and final rearomatization.

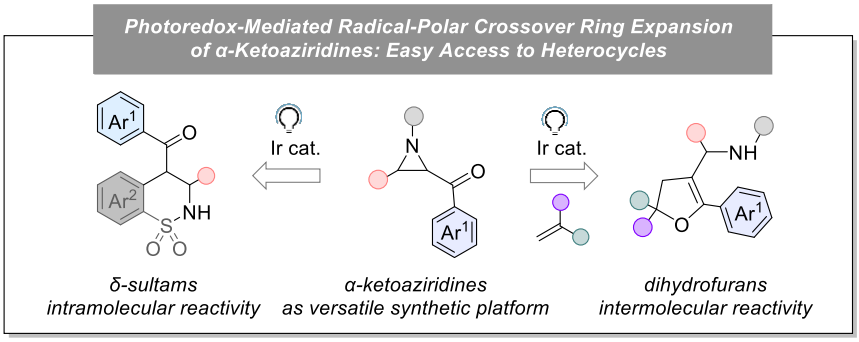

Figure 1. Versatility of α-ketoaziridines as synthetic platforms for heterocycle synthesis through photocatalysis.

Second, a complementary intermolecular strategy was developed in presence of olefins, an iridium photocatalyst and an organic base under visible-light irradiation. This robust approach enables the chemoselective synthesis of amino-2,3-dihydrofurans in good yields, with broad substrate generality and scalability. Overall, these findings establish α-ketoaziridines as versatile platforms for photoredox RPC reactions, offering efficient and sustainable access to structurally diverse heterocyclic frameworks.

Acknowledgements

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H-Bond Mediated Photocatalyzed Oxidation of Oximes under visible light and Air. A General Route toward Dioxazoles, Oxadiazoles and Isoxazoles.

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Keywords: Photocatalysis ● Free Radicals ● Oximes ● Green Chemistry ● Oxazole

The [3+2] cycloaddition of nitrile oxides onto unsaturated bond systems is widely recognized as an efficient and versatile approach for constructing nitrogen-containing heterocycles, including dioxazoles, isoxazoles, and oxadiazoles.[1] Nitrile oxide itself can be generated from various precursors, involving the use of oxidizing agents.[2] However, conventional oxidizing processes come with some challenges, including the significant use of stoichiometric reagents, potential safety considerations, and the formation of by-products that may require additional purification steps, affecting overall efficiency.[3] We describe here a metal-free photocatalyzed oxidation of oximes using 4-DPAIPN as a photocatalyst under blue light irradiation and atmospheric air as the oxidant, leading to heterocycles mentioned above in generally high and reproducible yields. Mechanistic investigations using EPR, fluorescence quenching and transient absorption spectroscopy suggest the formation of an iminoxyl radical as a key intermediate, generated through the oxidation of the oxime bound to the photocatalyst through hydrogen bonding. Subsequent oxidation of the iminoxyl radical into a nitrile oxide, followed by [3+2] cycloaddition with ketones, nitriles, or alkynes, affords streamlined access to the corresponding heterocycles. This strategy provides a green alternative to conventional methods, minimizing wastes, while delivering valuable nitrogen–oxygen atoms containing heterocycles with potential applications in pharmaceutical and materials chemistry.

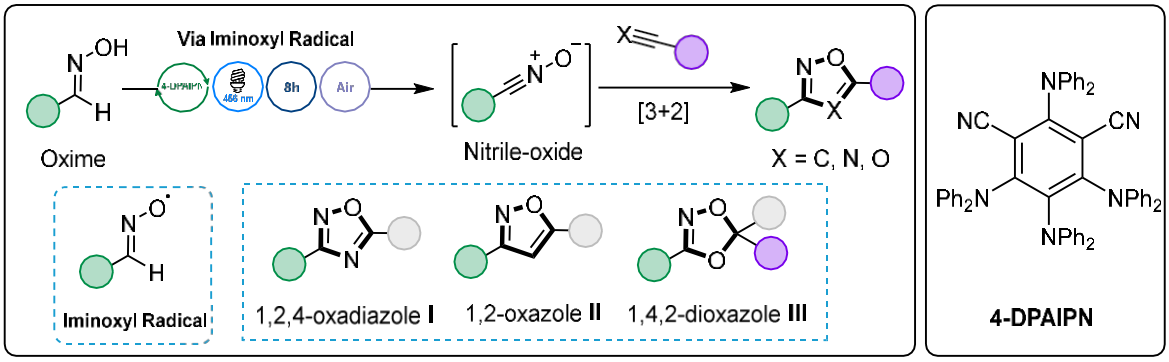

Figure 1. Photocatalyzed oxidation of oximes using 4-DPAIPN under blue light irradiation.

Acknowledgements

YM thanks the “Consulat général de France à Jérusalem” for a PhD grant. We are grateful to the French government in the framework of the University of Bordeaux’s IdEx “Investments for the Future” program/Grand Programme de Recherche entitled Post-Petroleum Materials (PPM) for a postdoctoral grant to AZ, as well as the ANR (GreeNCO, N°24-CE07-4305-01) and the CNRS for financial support.

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Memory of Chirality in Radical Cross-Couplings

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Keywords: Stereoretention ● Nickel-catalysis ● Radicals ● Cross-couplings ● Sulfonyl-hydrazides

The oral presentation will highlight stereoretentive radical cross-coupling as a new paradigm for constructing chiral C(sp³)–C(sp³) and C(sp³)–C(sp²) bonds from readily available building blocks. Central to this strategy is a nickel-mediated, diazene-enabled radical generation process in which rapid, in-cage radical rebound to the metal outcompetes picosecond racemization of free radicals,[1] enabling direct chirality transfer from enantioenriched precursors. Two interconnected projects from my postdoctoral research at Scripps Research will be presented. First, a stereoretentive radical–polar cross-coupling that enables enantiospecific alkyl–aryl bond formation using an achiral nickel catalyst.[2] This mechanistic framework is then translated to stereoretentive radical–radical cross-coupling, where careful kinetic control permits selective C(sp³)–C(sp³) bond formation between two unstabilized alkyl fragments.[3] Together, these studies show how managing radical capture at nickel can unlock new retrosynthetic disconnections for the efficient synthesis of complex, medicinally relevant chiral scaffolds.

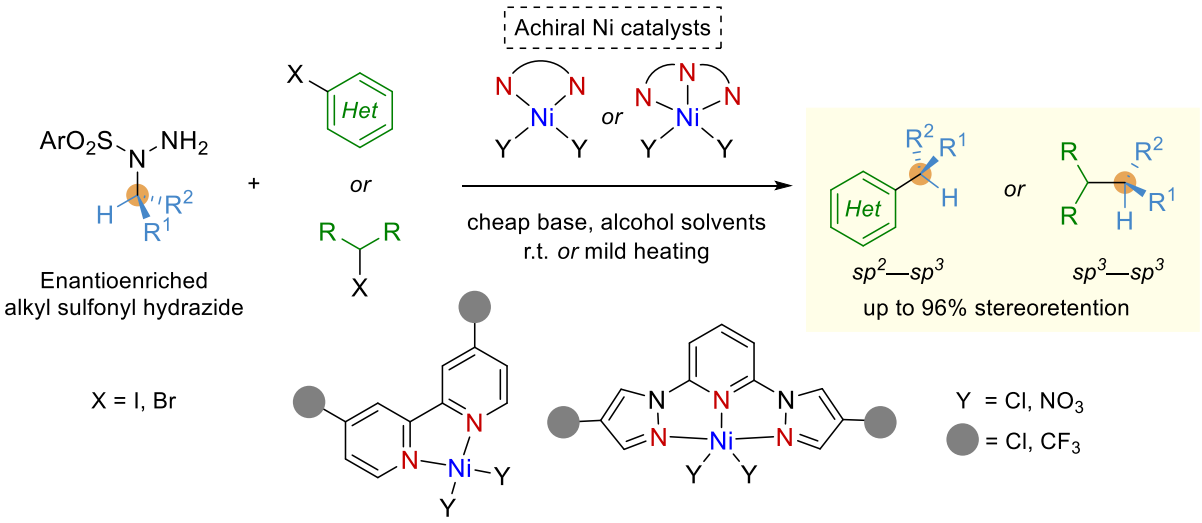

Figure 1. Stereoretentive Ni-catalyzed radical cross-coupling of enantioenriched alkyl sulfonyl hydrazides with (hetero)aryl or alkyl halides, enabling C(sp²)–C(sp³) and C(sp³)–C(sp³) bond formation with up to 96% stereoretention under mild, redox-neutral conditions.

Acknowledgements
This work was financially supported by the Swedish Research Council (Vetenskapsrådet, VR-2023-00499) through a postdoctoral fellowship and by Scripps Research.

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Catalytic Selective Functionalization of Poly(organoborons)

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Keywords: radical coupling reaction ● organoboron chemistry ● photocatalysis ● C-X bond formation

1,n-Bis(boronic) esters are valuable building blocks for modular synthesis, yet controlling their reactivity and selectivity remains a significant challenge, limiting their application in late-stage functionalization. (1) Regiodivergent Alkynylation: We achieved the first controllable regiodivergent alkynylation of 1,3-bis(boronic) esters. The selectivity is governed by the unique chelation patterns of different organometallic reagents. This method overcomes the inherent low reactivity of these substrates and provides access to non-classical products beyond the scope of traditional radical chemistry. (2) Selective Radical B–X Exchange: We developed an operationally simple protocol for selective functional group exchange in diverse 1,n-diborons. This reaction proceeds through unprecedented primary radical intermediates, overcoming unfavorable electronic effects. Mechanistic studies reveal a radical chain process where a key sulfonyl radical selectively activates one boronic ester over the other, ensuring high fidelity.

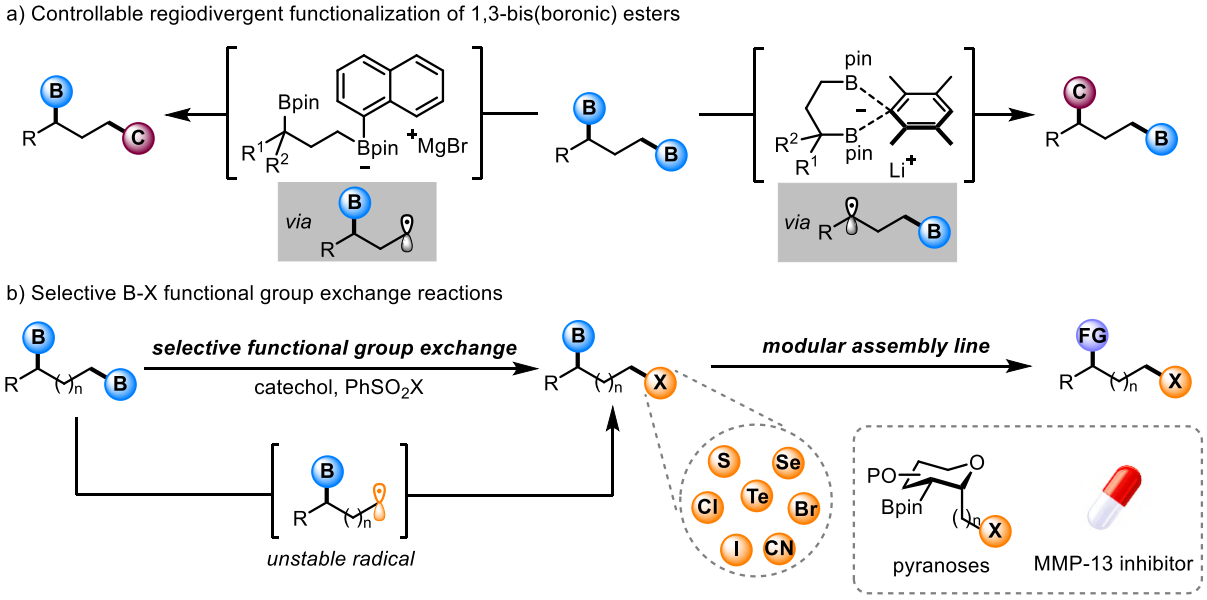

Figure 1. 1,n-Bis(boronic) Esters: alkynylation and B–X exchange reaction

Both strategies effectively tackle the longstanding issues of reactivity and selectivity in poly-boronic ester chemistry. The alkynylation method enables regiodivergent C–C bond formation, while the B–X exchange offers a versatile handle for downstream diversification. Together, they provide powerful and complementary toolkits for the programmable synthesis of complex, bioactive molecules from readily accessible boronic ester precursors.

Acknowledgements
These works were supported by NSFC (22471166, 22101177 and 22078192), the Science and Technology Commission of Shanghai Municipality (23YF1426700), and start-up funding of ShanghaiTech University.

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Asymmetric Hydrogen Atom Transfer using Chiral P-H Donor

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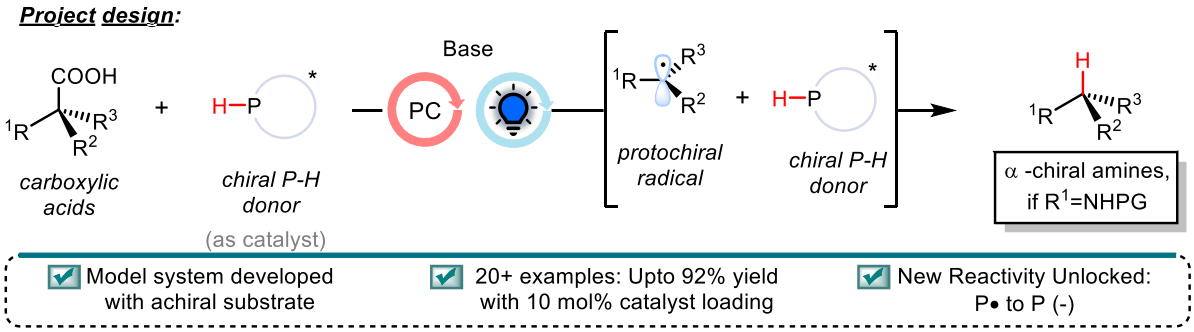
Keywords: Catalysis ● Enantioselective HAT ● Chiral Amines

Chiral amines are omnipresent among natural products and APIs.[1] Despite the continued interest, methods for their asymmetric synthesis are still lacking.[2] Herein, we report a dual catalytic system, which allows the synthesis of chiral amines *via* hydrogen atom transfer (HAT). A photocatalyst works in tandem with catalytic P-H* donors, opening the possibility of enantioselective HAT between a pro-chiral radical and chiral H-atom source (Scheme 1). To date, only reagents derived from Sn, S, and Si have been used for the asymmetric HAT reaction, but they are far from providing a general solution. [3]



Scheme 1: Project Design

Phosphorus is an excellent and yet unexplored alternative. Organophosphorus compounds have weak P-H bonds, P-centered radicals are well studied[4], and asymmetric chemistry of P-compounds is well-established, with many chiral scaffolds available.

We have successfully developed a model system, and we discovered an unprecedented catalysis with a P-H donor, facilitated by previously elusive reduction of P-centered radical to P-centered anion. The preliminary screening has been performed across > 20 substrates, with yields > 92%. Currently, we are optimizing the enantioselective variant of the reaction.

Acknowledgements
This work was financially supported by Research Ireland (22/PATH-S/10609).

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Photocatalytic Synthesis of *β*-Keto Primary Chlorides by Selective Chlorocarbonylation of Olefins

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Keywords: Ni/phototoredox ● Olefins ● Acid chlorides ● Chlorocarbonylation ● Primary chlorides

Dual Ni/photoredox catalysis has emerged as a powerful platform for chlorine radical (Cl•)-mediated transformations.[1] We report an efficient protocol for the regioselective chlorocarbonylation of unactivated alkenes to access *β*-keto primary chlorides.[2a, 2b] The key mechanistic step involves photoinduced Ni(III)–Cl bond homolysis,[3a, 3b] generating chlorine radical (Cl•) that undergoes selective addition to olefins followed by Ni-catalysed cross-coupling reaction. A wide range of acid chlorides act as both chlorine source and coupling partner, enabling broad substrate scope, excellent functional group tolerance, and scalability. Detailed mechanistic experiments and DFT studies support the proposed catalytic pathway. This work demonstrates the potential of Ni/photoredox catalysed chlorine radical chemistry for olefin functionalisation under mild condition.

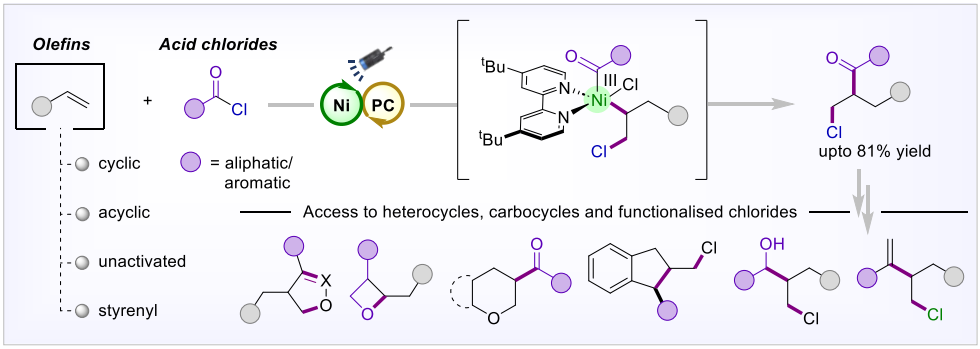

Figure 1. Ni/photoredox catalysed synthesis of *β*-keto primary alkyl chlorides

Acknowledgements

This work was financially supported by Science and Engineering Research Board, India (CRG/2020/000800) and CSIR for the fellowship to Bitasik Khatua.

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Light-Induced Allylation of Aldehydes or Alkanes Using Vinyl Cyclopropanes

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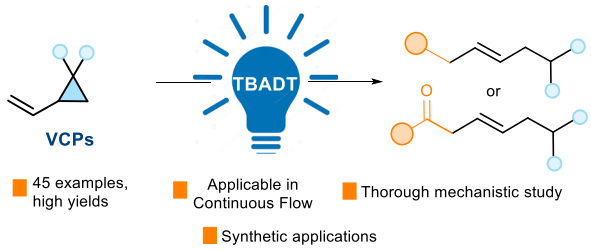
Keywords: Vinyl Cyclopropanes ● Photochemistry ● TBADT ● Allylation ● Site-selective functionalization

Vinyl Cyclopropanes (VCPs) are versatile and highly reactive building blocks, owing to the significant strain of the three-membered ring, combined with the presence of a vinyl group. These features allow VCPs to participate in a wide range of chemical transformations. Traditionally, transition-metal catalysis, such as palladium, rhodium or iron, have been used to promote cycloaddition and rearrangement reactions, while more recent radical and photocatalytic strategies have further broadened their synthetic utility. In contrast, reactions between VCPs and aldehydes remain comparatively underdeveloped. Herein, we report a new light-driven protocol, employing TBADT that enables site-selective coupling of VCPs with aldehydes or alkanes, affording allyl ketones and alkenes in high efficiency and with excellent selectivity. The transformation proceeds under mild photochemical conditions and is readily adaptable to continuous-flow operation, enhancing its practicality and scalability.[1]



Scheme 1. Photochemical allylation of alkanes or aldehydes using VCPs.

Acknowledgements

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Unveiling the Invisible: U-PSD TREPR Enables Direct Observation and Kinetic Interrogation of Transient Radicals

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Keywords: U-PSD TREPR ● Transient Radicals ● Reaction Kinetics ● Photocatalysis ● Halogen Atom Transfer

Understanding radical mechanisms requires direct observation of transient open-shell intermediates which is a long-standing challenge in photocatalysis and radical chemistry. Using our newly developed ultrawide single-sideband phase-sensitive detection time-resolved electron paramagnetic resonance (U-PSD TREPR) technique, we achieved simultaneous in situ monitoring and kinetic interrogation of all transient radical species in the photocatalytic addition of pempidine to tert-butyl acrylate.[1] For the first time, the complete photocatalytic cycle was visualized through the fine structures, kinetic profiles, and spin dynamics of all open-shell intermediates, including amine radical cations, α -aminoalkyl radicals, and radical adducts.[2] Furthermore, we extended this methodology to quantify elementary step kinetics, enabling direct measurement of halogen atom transfer (XAT) rate constants for α-aminoalkyl radicals.[3] This quantitative approach led to a significant revision of their previously reported reactivity, establishing an authentic XAT reactivity scale that is 3–5 orders of magnitude lower than tin radicals. Our work establishes a new paradigm for radical chemistry, where transient species are not merely detected but precisely characterized and quantified.

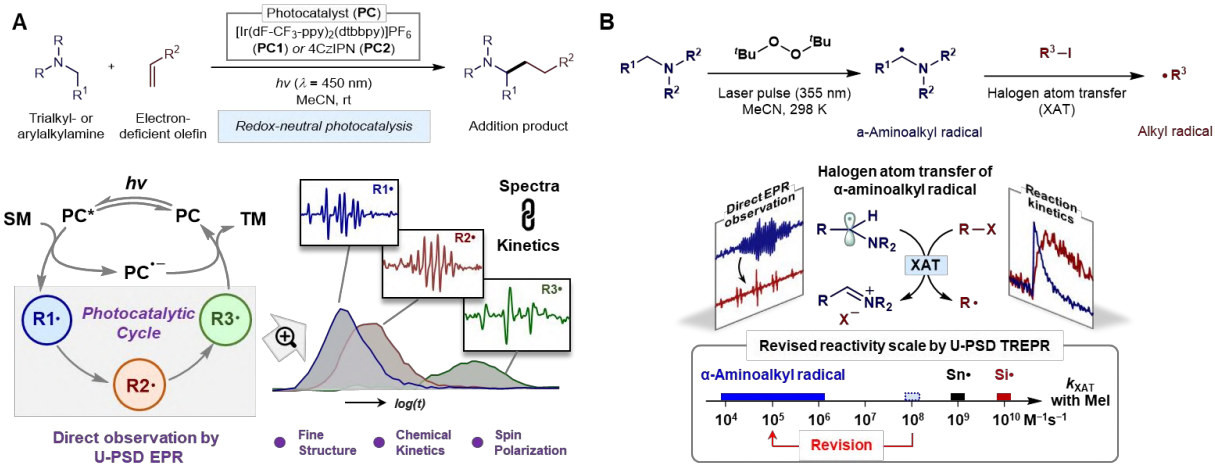

Figure 1. (A) Direct observation of a photocatalytic cycle with the U-PSD TREPR. (B) Direct observation of the XAT process of α-aminoalkyl radicals by U-PSD TREPR.

Acknowledgements

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Pd-Catalyzed Photoinduced Interceptive Decarboxylative Allylation

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Keywords: Palladium ● Photoredox ● Decarboxylation ● Allylation ● Radical

We describe a photoinduced Pd-catalyzed interceptive decarboxylative allylation of allyl esters.[1] The combination of Pd and photoredox catalysis overcomes the inherent pK_a-limitations of existing metal catalysed interceptive decarboxylative allylation methods whilst also broadening the scope of olefins.[2,3] Our protocol provides a new gateway to enable atom pair swaps or a series of contractions and elongations, thus offering unconventional disconnections and a modular, yet broadly applicable, tool for rapidly and reliably accessing C(sp^3) rich architectures.

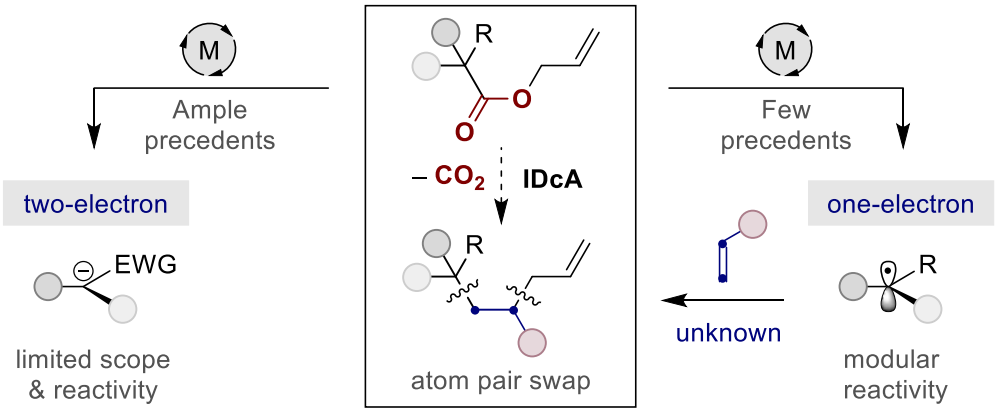

Figure 1. Pd-Catalyzed Photoinduced Interceptive Decarboxylative Allylation.

Acknowledgements
We thank the ICIQ, the project PID2024-160739NB-I00, financed by MICIU/AEI/10.13039/501100011033 /FEDER,UE and the European Research Council (ERC) under European Union's Horizon 2020 research and innovation program (grant agreement No 883756) for financial support. Filip S. Meger also thanks the grant PRE2022-101700, financed by MCIN/AEI/10.13039/501100011033 and by the FSE+.

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Visible-Light Driven Carbon-Centered Radical Cascades: Unveiling XAT and SET Pathways

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Keywords: XAT strategy ● α-aminoalkyl radical ● phenanthridinone core ● EDA-complex ● radical Truce-Smiles arrangement ● olefin-olefin coupling ● biologically relevant alkaloids

Visible light-induced photocatalysis is fundamental in organic chemistry, garnering significant attention from the synthetic community. In this context, we have developed a XAT strategy utilizing α-aminoalkyl radicals[1] for the generation of aryl radicals at room temperature, which is applied for intramolecular cyclization reactions *en route* to biologically relevant alkaloids. Starting from simple halogen-substituted benzamides under visible light irradiation in the presence of an organophotocatalyst (4CzIPN) and nBu$_3$N allows the modular construction of the phenanthridinone core, offering facile access to drug analogs and alkaloids from the Amaryllidaceae family. The reaction pathway most likely involves a quantum mechanical tunneling-enabled transfer event to achieve aromatization-halogen atom transfer.[2] Meanwhile a photocatalyst-free visible-light-induced EDA-based[3] radical cascade reaction of *N*-allylbromodifluoroacetamides and *N*-alkylacrylsulfonamide, featuring a radical Truce-Smiles arrangement, is identified for the modular construction of the difluoroamid pyrolidone core.[4] The details of these findings will be presented as a poster during the conference.

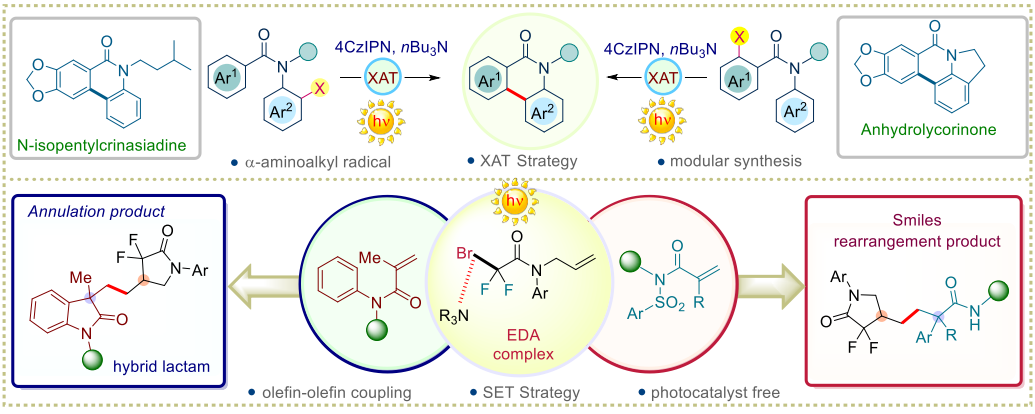

Figure 1: Carbon-centered radical-mediated cascade process via *XAT* and *SET* events

Acknowledgements

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Photoelectrochemical Heterodifunctionalization of Olefins: Carboamidation Using Unactivated Hydrocarbons

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Keywords: Photoelectrochemistry ● Hydrogen Atom Transfer ● Ritter Reaction ● Difunctionalization

Efficiently activating inert C(sp^3)−H bonds for organic synthesis is a topic of great interest, however, the elusive oxidative potential associated with unactivated alkanes renders their activation by single electron transfer (SET) highly challenging. Instead, direct hydrogen atom transfer (HAT) by photoexcited species can surmount the high bond dissociation energies (BDEs) of inert C(sp^3)−H bonds and has become a widely employed strategy to transform them into alkyl radicals.[1]

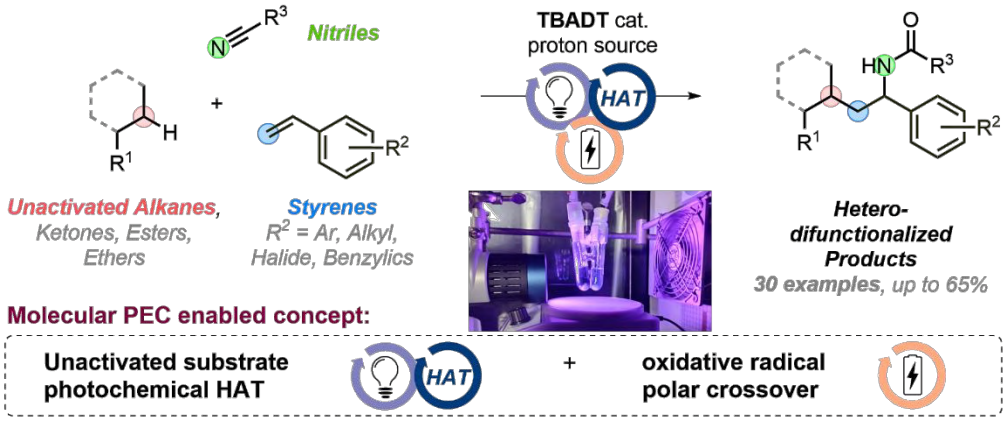

Figure 1. Overview of photoelectrochemical carboamidation of styrenes via HAT, radical addition, oxidative radical polar crossover and Ritter-type amidation.

Herein, we present a mild carboamidative difunctionalization of electronically different styrenes with diverse hydrocarbons developed by merging photocatalysis and electrochemistry without using external oxidants.[2] The reaction proceeds through a tandem photocatalytic hydrogen atom transfer (HAT), radical addition to styrenes, radical polar crossover, and subsequent Ritter-type amidation. Key to engaging unactivated alkanes was the use of tetrabutylammonium decatungstate (TBADT) as a HAT photocatalyst, which was regenerated from its reduced form by anodic oxidation. A diverse set of C(sp^3)−H precursors, including unactivated alkanes was successfully utilized. Styrenes bearing different functionalities in their arene rings were selectively difunctionalized and several nitriles were employed as nucleophiles. Overall, we demonstrated how photoelectrochemistry forges unconventional reactivity by merging photocatalyzed HAT with an oxidative radical polar crossover.

Acknowledgements
This work was financially supported by the Alexander von Humboldt Foundation, the Elite Network of Bavaria and the University of Regensburg.

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Cyclic Bifunctional Reagents Enabling a Strain Release-Driven Formal [3 + 2] Cycloaddition of 2H-Azirines by Cascade Energy Transfer

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Keywords: Photocatalysis ● Energy Transfer Catalysis ● Cyclic Bifuntional Reagents ● Heterocycles

Over the past years, isoxazolones received increasing attention by synthetic chemists because of their versatile sides of reactivity and appearance in natural products.[1] In this context, it was shown, by using iridium catalysis under thermal conditions, that 2H-azirines as well as their fully substituted counterparts could be generated by CO_2 release in a ring contraction reaction.[2]

Herein, we report for the first time the formation of highly substituted N-heterocycles via cascade energy transfer, starting from isoxazolones. Mechanistic investigations suggest the formation of highly substituted azirines as key intermediates, undergoing selective carbon–carbon bond cleavage and further formal [3+2] cycloaddition with olefins, whereas a combination of CO_2- and strain-release appear to be the crucial driving forces. The reaction proceeds with high regio- and diastereoselectivities to form complex nitrogen-containing heterocycles. Besides olefins, also unsaturated molecules like alkynes could be employed in this protocol, giving access to valuable pyrrole-type moieties.

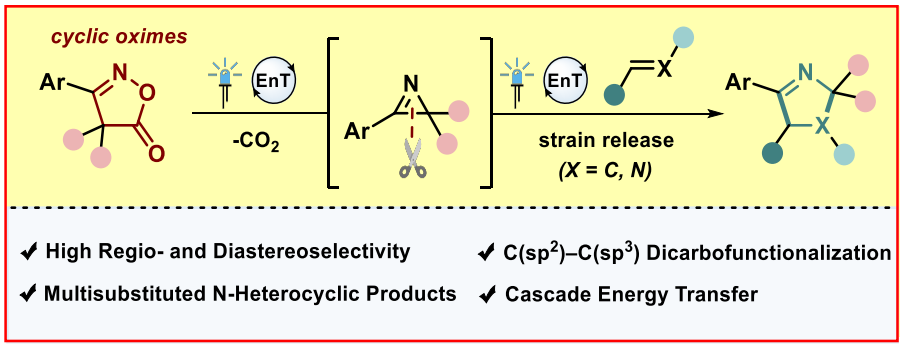

Figure 1. General reaction overview. Isoxazolones as photolabile precursors of 2H-azirines. Photoexcited 2H-azirines as a novel class of C,C-bifunctional linkers.

Acknowledgements
Generous financial support from the Alexander von Humboldt Foundation (A.P.), the ERC Advanced Grant (Agreement No. 101098156, HighEnT), and the Deutscher Akademischer Austauschdienst (P.C.) is gratefully acknowledged.

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Visible-Light Palladium Photocatalyzed Carbofunctionalization

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Keywords: photocatalysis ● palladium ● radical ● carbofunctionalization

Visible-light photocatalysis has transformed organic synthesis by enabling radical processes under mild and more sustainable conditions. Recently, new reactivities were observed through light-excited metal entities such palladium complexes giving access to high-energy species leading to unique radical and metal-based redox sequences.[1] For instance, Gevorgyan pioneered Pd(0) photocatalyzed single-electron transfer (SET) to vinyl iodide precursors.[2] This type of formal homolytic Csp²–X bond cleavage was applied to aryl iodide derivatives by Lautens allowing a domino intramolecular carbo-iodation reaction to an alkene pendant.[3] In parallel, Glorius and Chen investigated domino intramolecular carbo-Heck sequences under mild conditions.[4]

Based on these backgrounds, we report herein a strategy for the intramolecular domino carbofunctionalization of alkenes based on mild photocatalytic palladium conditions, relying on the generation of putative vinylic hybrid Pd(I)–radical intermediates for the construction of cyclic frameworks (Figure 1).

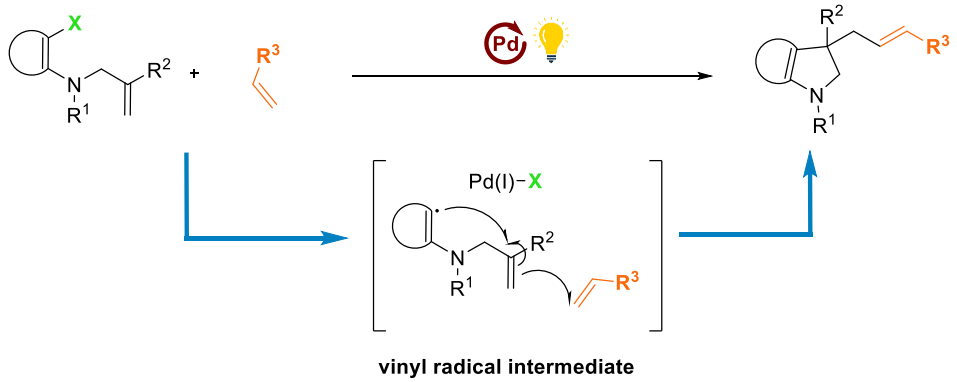

Figure 1. carbofunctionalization of Csp^2 bonds using photocatalytic palladium conditions

Acknowledgements
This work is part of the Industrial Chair COLIBRI (ANR-22-CHIN-0008). This work has been partially supported by University of Rouen Normandy, INSA Rouen Normandy, the Centre National de la Recherche Scientifique (CNRS), European Regional Development Fund (ERDF), Région Normandie, Labex SynOrg (ANR-11-LABX-0029), Carnot Institute I2C, the graduate school for research XL-Chem (ANR-18-EURE-0020 XL CHEM).

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Copper mediated trifluoromethyl radical generation *via* photoinduced LMCT

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Keywords: trifluoromethylation ● visible light ● decarboxylation ● radical-polar crossover

The trifluoromethyl groups (CF3) are key components in pharmaceuticals and agrochemicals.[1]
Many strategies and reagents design have been developed to introduce these fluoroalkyl groups into organic molecules. Yet, most of them rely on reagents with poor atom economy and limited scalability.[1] In another hand, trifluoroacetates are the most abundant and accessible sources of CF3 groups through decarboxylation, which makes them very attractive candidates as trifluoromethylating reagents. However, their very high oxidation potential constitutes a major obstacle.
In the recent years, alongside other groups with various metals [2][3], we developed a methodology to enable the direct decarboxylation of trifluoroacetates with iron photocatalysts for the trifluoromethylation of (hetero)arenes.[4] Under visible light irradiation, the decarboxylation is triggered through an inner-sphere electron transfer (LMCT), which operates independently of redox potentials.
In this communication, we show the decarboxylation step thanks to copper salts to broaden the scope of this reactivity to the versatile difunctionalisation of alkenes, introducing both a CF3 group and a range of nucleophiles across the double bond. The reaction conditions are very simple and practical, requiring only a readily available copper salt [5] that serves a dual role: triggering photoinduced decarboxylation and acting as an oxidant to facilitate the radical-polar crossover (RPC). Taken together, our protocol enables rapid access to a diverse array of densely functionalized products bearing industrially relevant fluoroalkyl groups, starting from available and inexpensive chemical feedstocks.

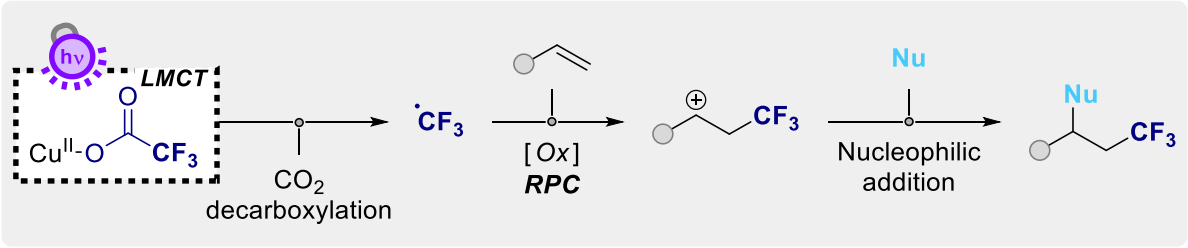

Figure 1. Copper LMCT trifluoromethylation

Acknowledgements
We thank MCIN/AEI/10.13039/501100011033 and “ESF Investing in your future” (PID2023-151452NB-I00, CNS2023-145163 and PREP2023-001569) for financial support.

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Strain Release Difunctionalization by Cu-photocatalysis: A General route to functionally rich cyclobutanes

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Keywords: difunctionalization ● radical ● strain-release● Copper-photocatalysis ● cyclobutanes

Cyclobutanes are valuable molecular scaffolds due to their high density of sp^3-hybridized carbon atoms and rigidity.[1] Despite their promise, the selective functionalization of these strained, saturated frameworks remains challenging and continues to attract significant interest, particularly in light of their increasing importance in medicinal chemistry.[2] Bicyclobutanes (BCB's), in particular, are highly susceptible to radical-induced ring opening, offering opportunities for the construction of complex architectures.[3] We employed Cu-based photocatalytic atom transfer radical addition (ATRA)[4] to construct functionally rich cyclobutanes from diverse class of BCBs. This mild conditioned methodology encompasses four different class of ATRA reagents. The compatibility of multiple BCBs, with multiple ATRA reagents is what makes this work stand-out as a general di-functional strategy in the highly competitive field of photo-induced strain-release functionalization.

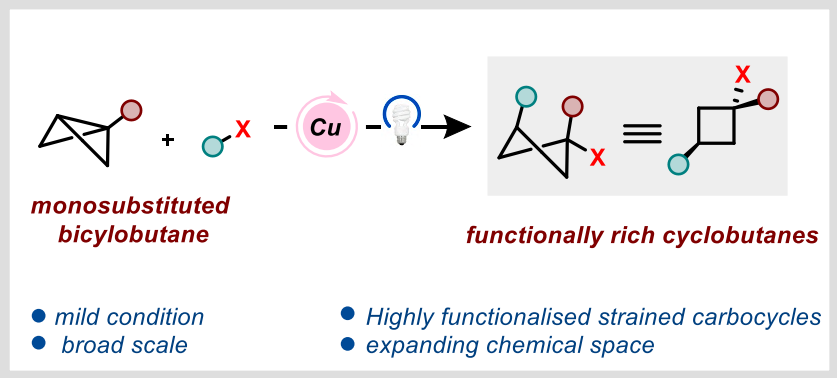

Figure 1. Fuctionalisation of bicyclobutanes using Copper photocatalysis.

Acknowledgements
This work was financially supported by German Academic Exchange (DAAD), IDK-PEC and the University of Regensburg.

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Three Component Cyclisation enabled by Triplet Sensitized Biradical Interception

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Keywords: Photocatalysis ● Energy-Transfer ● Multicomponent ● Cycloaddition ● Biradical interception

Photocyclization reactions remain as some of the most powerful transformations in the synthetic toolbox for the construction of complex and highly strained molecular scaffolds poorly accessible through closed shell reactivity. In addition to more established direct excitation, which often relies on harsh conditions and highly energetic photons in the ultraviolet region, photocatalytic energy transfer (EnT) has seen a surge in popularity in recent years.[1] By transferring the triplet state of a suitable photocatalyst in Dexter EnT mechanistic fashion, comparatively long-lived triplet states of common organic molecules may be accessed through the usage of the milder visible light region, which often circumvents expected reactivity.[2]

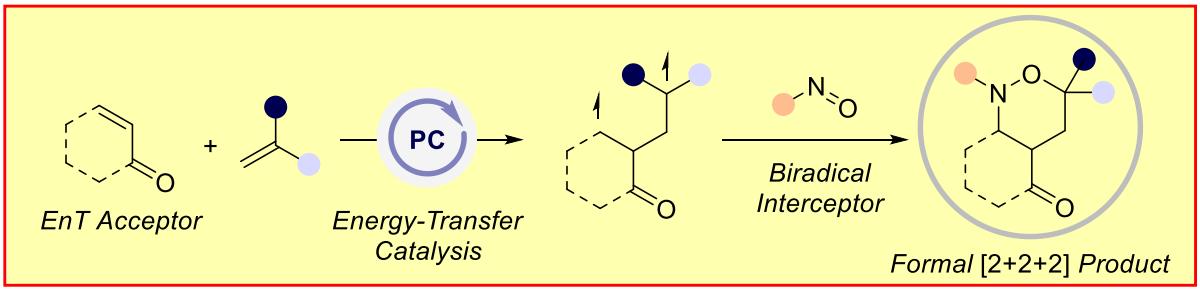

Figure 1. General reaction overview. Upon triplet excitation, a suitable energy transfer acceptor reacts with an activated alkene in intermolecular fashion. Extended lifetimes of the biradical T^1 state, compared to its S^1 state, are presumed to be integral to allow for interception by a third reaction partner, in this case nitrosoarenes, prior to ISC and [2+2] ring closure.

Whereas recent efforts have focused on two-component reactivity, we reasoned that through careful reaction design, in accordance with established guidelines regarding radical-stability and -philicity,[3] the usual limitations of biradical intermediates towards non-canonical reactivity beyond intramolecular recombination and fragmentation, which originate from their relatively short lifetimes, may be overcome. We identified nitrosoarenes, known to be superior spin traps,[4] as ideal reaction partners to enable biradical interception prior to intersystem crossing (ISC) and [2+2] ring closure of EnT acceptors and activated alkenes. We were accordingly able to mimic a hypothetical three-component collision complex which enables the formal [2+2+2] construction of saturated, sp^3-rich systems in intermolecular fashion. The products thus formed contain rare N–O heteroatomic bonds in multifused ring systems and are otherwise difficult to access.

Acknowledgements
This work was financially supported by Deutsche Forschungsgemeinschaft (GRK 2678–437785492, C.S.; Leibniz Award).

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Regio-and Stereoselective-β-Sulfonylamination of Alkynes vie Dearomative Migratory Rearrangement of 2-Oxypyridines

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Keywords: Copper, Photocatalyst, Energy transfer photocatalyst, 2-oxypridines

Nitrogen-centered radicals (NCRs) have emerged as versatile synthetic intermediates for the construction of functional nitrogen-containing molecules[1]. Owing to their unique electronic properties and high reactivity, NCRs enable diverse bond-forming transformations under mild conditions, often providing complementary reactivity to ionic pathways. Recent advances in radical generation strategies, including photoredox[2] and electrochemical methods, have significantly expanded their synthetic utility. As a result, NCR-based approaches have become powerful tools for assembling complex amines, amides, and heterocycles with broad relevance to pharmaceuticals and materials science.

Herein, we report a highly efficient visible-light-induced, regio- and stereoselective β-Sulfonylamination of terminal alkynes. In this protocol, 2-oxypyridines are employed to generate nitrogen-centered radicals via S–O bond cleavage, followed by a dearomative migratory rearrangement[3] to form NCRs, enabling a straightforward route to N-substituted 2-pyridones. Mechanistic investigations indicate a base-accelerated energy-transfer (EnT) photocatalytic pathway involving NCR formation, radical addition to alkynes, and subsequent sulfonylation processes.

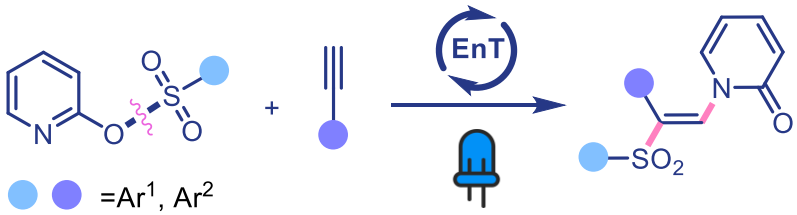

Figure 1. β-Sulfonylamination of Alkynes vie Dearomative Migratory Rearrangement of 2-Oxypyridines

Acknowledgements
This work was financially supported by University of Regensburg an Eliten NetzwerkBayern (IDK)

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Mono- and Bis-Phosphonylation of Aryl Chlorides via Phenothiazine Organophotoredox Catalysis

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Keywords: Photoredox catalysis ● Phenothiazine ● Phosphonylation ● Visible light ● Aryl chloride

Aryl phosphonates are important structural motifs in a variety of fields, including pharmaceuticals and functional materials. While methods for the phosphonylation of aryl iodides and bromides have been widely developed, the corresponding transformation of aryl chlorides remains relatively unexplored due to the high energy barrier associated with the activation of C(sp^2)−Cl bonds. In particular, bis-phosphonylation of aryl chlorides remains largely unexplored.[1] Recently, we have designed and synthesized organophotoredox catalysts and developed visible-light-induced various photochemical transformations.[2] Here, we report the mono- and bis-phosphonylation of aryl chlorides using a strongly reducing helical phenothiazine organophotoredox catalyst (PTHS).[3] The reaction is applicable to various mono- and bis-chlorinated benzenes to obtain the corresponding aryl phosphonates. This method offers versatile access to functionalized aryl phosphonates, thus rendering it a promising tool for the synthesis of pharmaceuticals and functional materials.

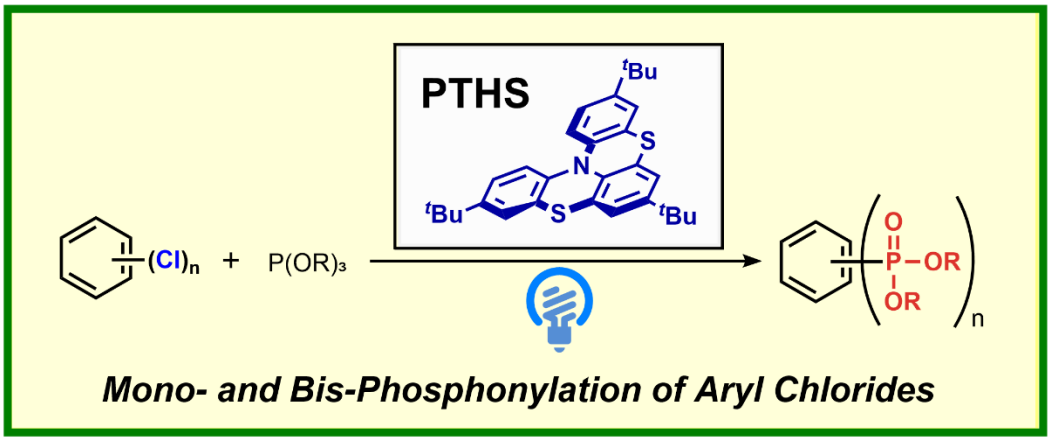

Figure 1. Phenothiazine Organophotoredox Catalyzed Mono- and Bis-Phosphonylation of Aryl Chlorides

Acknowledgements
This work was financially supported by Mazda Foundation, Fujikura Foundation, Okayama Foundation for Science and Technology, Wesco Scientific Promotion Foundation, and JSPS KAKENHI Grants JP 25K18038.

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Metalloradical Catalysed Olefin Hydrogenation: A New Approach To Radical Hydrogenation

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Keywords: Radical hydrogenation ● Metalloradical catalyst ● Transfer hydrogenation ● Small molecule activation ● External hydrogen free hydrogenation

Abstract: Radical hydrogenation via Hydrogen Atom Transfer (HAT)/ Transfer Hydrogenation to alkenes is an increasingly important transformation for the formation of thermodynamically more stable alkane isomers. Current single-catalyst-based hydrogenation methods require a stoichiometric oxidant in addition to a hydride (H^-) source[1]. Hydrogenation based on radical, metal-catalysed hydrogen atom transfer (mHAT), *transfer hydrogenation* mechanisms offer an outstanding opportunity to overcome these difficulties, enabling the mild reduction of these challenging olefins with selectivity that is complementary to traditional hydrogenations with H_2.

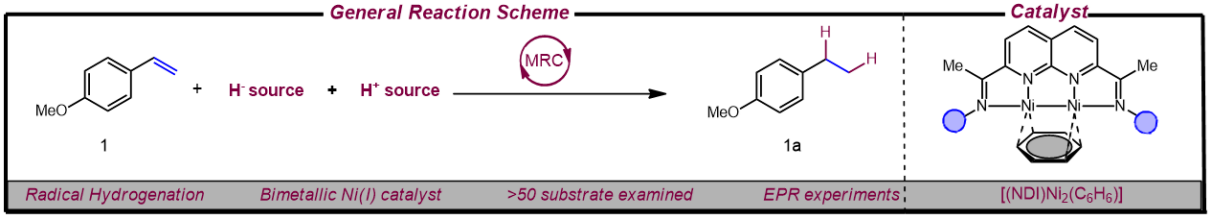

Figure: Metalloradical(MRC) catalysed radical hydrogenation of olefines

Furthermore, it provides an opportunity for asymmetric induction through transfer hydrogenation using two different hydrogen sources.[2] [3] Herein, we disclose the first report on metalloradical (MRC) catalysed radical hydrogenation of olefins using two distinct hydrogen sources ($NaBH_4$ & $Et_3N.3HF$). Control reaction confirms the generation of the H_2 molecule, which is further activated and subsequently donated to olefins via MRC-catalysed HAT. The bimetallic nature of MRC makes it even oxidant free. The mechanistic insights suggest the radical hydrogenation pathway. Together, this catalytic system allows us to hydrogenate different classes of molecules and introduces a new approach to radical hydrogenation.

Acknowledgements
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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Suzuki-type reaction via Ferrioxalate Photocatalysis

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Keywords: Suzuki ● Iron ● Photocatalysis

The development of new pharmaceuticals, agrochemicals and materials hinges on the use of palladium-catalysed cross-coupling reactions and, in particular, the coupling between aryl halides and organoborons (known as Suzuki-type coupling) has historically held a prominent position as the main tool to assemble new Csp^2-Csp^2 bonds in academic and industrial settings.[1] However, in view of the high cost and the volatile availability of palladium, chemists are facing the challenge of replacing reactions catalysed by this and other precious metals with more abundant and sustainable ones.[2] Among the various existing alternatives, iron has emerged as one of the most attractive and promising ones in view of its low toxicity and large abundance, among other desirable properties.[3] Although some advances in recent years have led to the development of iron-catalysed Suzuki-type couplings, existing methodologies are limited by the general use of strong bases such as LDA and Grignard or the requirement of directing groups, limiting their general applicability.[4]

In this work, we present the use of light as an unprecedented approach to overcome these limitations. To achieve this, we have made use of ferrioxalate photocatalysis[5] to access highly-reducing low-valent iron species that enable the reduction of aryl halides to aryl radicals. Using this catalytic system we have carried out Suzuki-type couplings, following a non-canonical radical pathway that offers an orthogonal approach to traditional strategies based on transmetalation. Thus, this new method constitutes a sustainable and fast method in the absence of strong bases, with reaction conditions that show exceptional tolerance to functional groups and a wide structural diversity in the coupling between aryl halides and alkenyl organoboron compounds inaccessible under iron-catalysed methodologies (Figure 1).

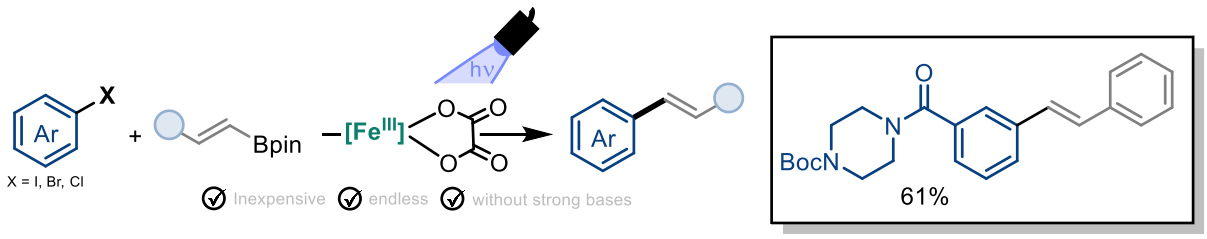

Figure 1. Suzuki-type reaction via Ferrioxalate Photocatalysis.

Acknowledgements
We are grateful for financial support from European Union (ERC, ExCEL, 101116163). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council Executive Agency. Neither the European Union nor the granting authority can be held responsible for them. C.B. also acknowledges University of Murcia for a predoctoral contract.

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Radical Cross-Coupling between Ketones and Alkenes under Ferrioxalate Photocatalysis

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Keywords: ketone-olefin cross coupling ● iron photocatalysis ● radical chemistry

Ketones and alkenes are ubiquitous in feedstock chemicals or bioactive compounds. These two functional groups are archetypal textbook examples of reactivity handles for organic synthesis,[1] however, the direct coupling between them to obtain tertiary alcohols remains limited. Some of the most successful strategies rely on radical chemistry to assembly new C–C bonds, are mediated by SmI_2, metal hydrides or photoredox catalysis.[2] Nevertheless, reported strategies are mainly focused on intramolecular couplings or require the use of activated substrates. In this context, the intermolecular coupling between unactivated alkenes and ketones with broad scope remains a longstanding ambition.[3]

Recently, our group introduced the use of ferrioxalate photocatalysis in diverse reductive transformations based on the effective generation of catalytic species with unexplored synthetic potential.[4] In this work we present how ferrioxalate catalysis can enable ketone-olefin coupling reactions. Photoactivation of iron catalysts allows to perform this challenging transformation under exceptionally mild reaction conditions (visible light, room temperature), without the use of strong bases or stoichiometric metal reductants, and present a broad scope in both coupling partners. The implementation of this blueprint has unlocked the use of ketones and alkenes as building blocks for intermolecular C–C bond formation in presence of multiple functionalities, opening new opportunities for fragment coupling strategies.

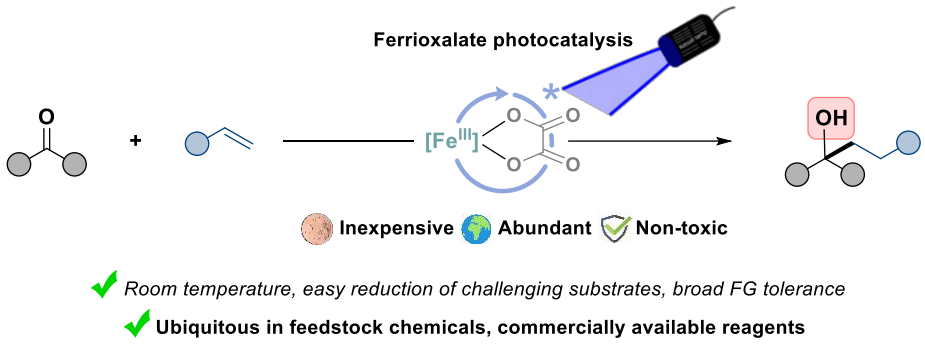

Figure 1. Ferrioxalate photocatalysis mediated ketone-olefin cross coupling

Acknowledgements
This work is funded by the European Union (ERC, ExCEL, 101116163). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council Executive Agency. Neither the European Union nor the granting authority can be held responsible for them.

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Phenothiazine Sulfoxides as Active Photocatalysts for the Synthesis of γ-Lactones

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Keywords: Transient spectroscopy ● mechanistic elucidation ● radical trapping ● photocatalysis ● malonyl peroxides

N-substituted phenothiazines are widely recognized as highly effective organic photoredox catalysts due to their strong reducing properties.[2,3] Recently, their radical cations have also been examined as photocatalysts for oxidations.[4,5] In contrast, phenothiazine sulfoxides—easily formed via oxidation—have remained largely unexplored in photocatalysis. Here, we report the discovery and application of *N*-phenylphenothiazine sulfoxide as a novel photocatalyst for the reductive activation of cyclic malonyl peroxides, enabling the direct synthesis of complex γ-lactones from simple olefins. Comprehensive mechanistic studies were conducted to elucidate the in situ formation of the active catalyst from *N*-phenothiazine via its radical cation as well as the overall photocatalytic mechanism via a radical cascade. Our approach employed a combination of time-resolved spectroscopy, transient UV–vis absorption spectroscopy, spectroelectrochemistry, cyclic voltammetry, isotopic labeling, radical trapping, NMR spectroscopy, and DFT calculations. The synthetic utility of this protocol was demonstrated through a broad substrate scope, providing efficient access to biologically relevant spirocyclic γ-lactones.

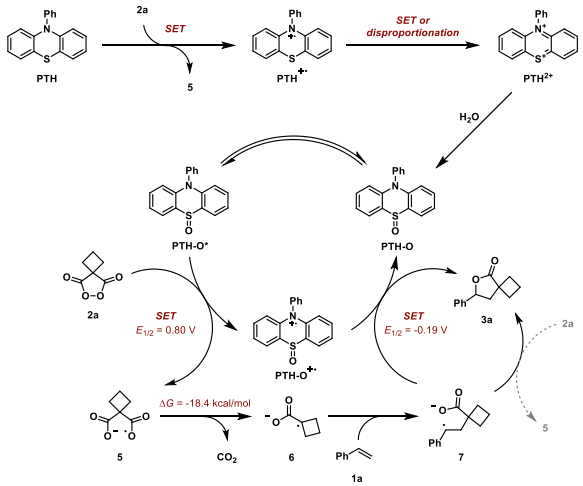

Figure 1. Elucidated mechanism of the interconversion of photocatalytic species and the formation of γ-Lactones.

Funding

ERC Advanced Grant (F.G., N.H., and R.K., Agreement No. 101098156), German National Academic Foundation (N.H.R.), Swiss National Science Foundation (O.S.W. and L.S., grant number 10001855)

Acknowledgements

The authors warmly thank Dr. Jasper L. Tyler, Dr. Subhabrata Dutta, Dr. Yan-Bo Li, Colin Stein, Debanjan Rana, and Johannes Erchinger (University of Münster) for helpful scientific discussions. We also thankfully acknowledge analytical support from Timon Reckmann, Klaus Bergander, Jens Paweletz, and Jessika Lammert (University of Münster). O.S.W. acknowledges funding by the Swiss National Science Foundation (grant number 10001855).

C(sp^3)-H functionalization of N-Boc-4-piperidone by Decatungstate Anion Photocatalysis

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Keywords: C-H activation● Decatungstate● Azacycle ● Giese's reaction

Catalytic C(sp^3)-H functionalization at the α position to nitrogen in saturated azacycles is a broad and extremely challenging field in organic chemistry. In recent years, numerous successful examples based on transition metals catalysis combined with directing group strategies[1]. In parallel, photocatalytic protocols have emerged over the past few decades as powerful alternatives for promoting this kind of reactions and others. Within the field of sp^3 C-H activation, the transformation of C-H bonds at the α-position to the nitrogen atom in saturated cyclic amines is of particular importance, since such heterocyclic motifs can be found in an impressive number of natural products and marketed drugs.
Photocatalytic C(sp^3)-H alkylation and arylation of azacycles are well described, and numerous examples of halogenation, sulfonylation, oxidation, and amination have also been reported, employing metal-based or metal-free photoredox catalysts.
In this field, Tetrabutylammonium decatungstate (TBADT) has demonstrated an outstanding photochemical activity, that motivates its use as a competent photocatalyst in organic chemistry[2].
Here we proposed the first application of decatungstate anion in a Giese-type reaction on N-Boc-4-piperidone, a foundamental substrate in the total synthesis of drug molecules, such as fentanyl derivatives or spiropiperidines.
Using various acrylates (linear, branched and cyclic), it was possible to site-selective mono-functionalized the α position to nitrogen, leading to a new wide range of compounds, which can be applied as building blocks for the synthesis, for example, of bicyclic 6+5 member rings.

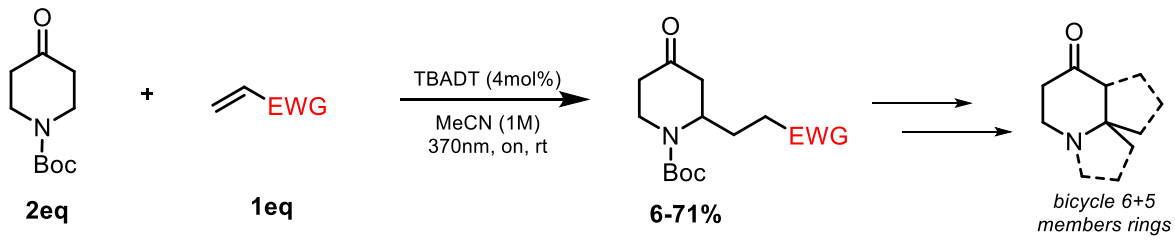

Figure 1. Synthetic pathway for C(sp^3)-h functionalization of N-Boc-4-Piperidone catalyzed by TABDT.

Acknowledgements
This work was financially supported by University of Ferrara (IT).

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Aggregation-induced Emission: A Synthetic Tool for Enhanced Photoinduced Reactivity in Anti-Markovnikov Hydroarylation

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Keywords: AIE ● Real time reaction monitoring ● Sustainable synthesis ● Photochemical transformation ● Anti- Markovnikov selectivity.

A photoinduced radical-polar pathway was established, in which Aggregation Induced Emission (AIE) triggers the anti-Markovnikov hydroarylation reaction and it also serves as an eco-friendly, real-time indicator for monitoring the progress of the reaction. The need of auxiliary fluorescent probe or waste-generating analytical tool can be removed by this methodology, making this a sustainable photochemical process. This method not only offers a greener and more economical alternative, but also utilizes AIE as an in-situ indicator for determining reaction efficiency. This methodology also follows several principles of green chemistry by avoiding non-toxic reagent, transition metal catalyst, using acetonitrile and water as green solvent. This process has impressive eco-scale and E-factor value. This method exhibits broad substrate scope and it can be easily scaled up, showing its practical applicability. Mechanistic insights from deuterium labelling, spectroscopic studies, and DFT calculations confirm the involvement of both radical and anionic intermediate and highlight a radical-polar crossover pathway as the primary mechanistic route. The study highlights that AIE could be effectively utilized to monitor organic transformations and providing direct insight into reaction progress. By correlating emission intensity with product formation, this approach offers a practical framework for rapidly identifying optimal conditions and systematically improving reaction yields.

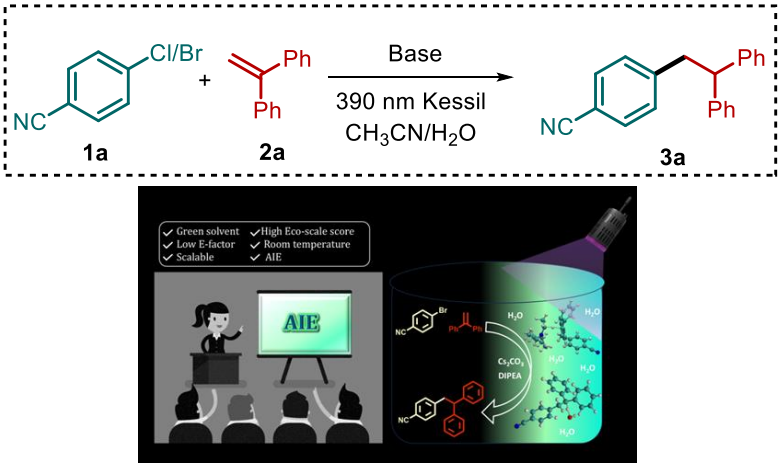

Figure 1. Photochemical anti-Markovnikov hydroarylation reaction

Acknowledgements
This work was financially supported by SERB (CRG/2022/002306).

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Visible-Light-Induced [5 + 1] Annulation of Vinyl Cyclopropane with Nitrene

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Keywords: Nitrene ● Annulation ● Visible light ● Tetrahydropyridines ● Pyridines

A metal- and reagent-free, visible-light-mediated [5 + 1] annulation of vinyl cyclopropanes with iminoiodinanes has been successfully developed, providing a sustainable and operationally simple strategy for the construction of valuable nitrogen-containing heterocycles. This transformation enables efficient access to a wide range of 1,2,3,6-tetrahydropyridines under mild conditions without the need for transition-metal catalysts or additional chemical reagents. Notably, the protocol exhibits broad substrate generality, accommodating aryl-, alkyl-, and heteroaryl-substituted vinyl cyclopropanes, thereby demonstrating excellent functional group tolerance and synthetic versatility.
The resulting tetrahydropyridine scaffolds serve as highly useful intermediates, as they can undergo base-promoted aromatization to furnish 2,5-diarylpyridines, which are important structural motifs frequently encountered in medicinal chemistry, agrochemicals, and functional materials. Furthermore, these products can be subjected to diverse downstream derivatizations, highlighting the potential of this methodology for late-stage functionalization and the rapid generation of structurally diverse pyridine-based frameworks.

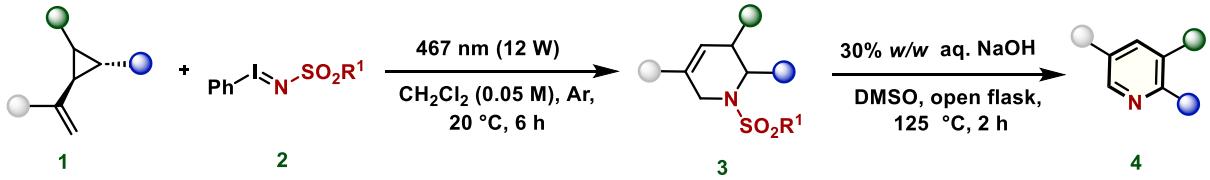

Figure 1. [5 + 1] Annulation of Vinyl Cyclopropane with Nitrene

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Photocatalyzed Decarboxylative Truce-Smiles Rearrangement

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Keywords: Photocatalysis ● Truce-Smiles ● Decarboxylation ● *β*-amino acids

Photocatalytic transformation has drawn significant attention due to its ability to generate high-energy key intermediates under mild conditions while affording wide functional group tolerance and new opportunities for organic synthesis. Regarding the Truce-Smiles rearrangement, radical pathways facilitated the transfer of various aryl groups, which was often limited to electron-deficient aryl groups in ionic pathways.[1] Several methods of radical Truce-Smiles rearrangement has been developed to synthesize *β*-arylethylamine derivatives,[2] a valuable scaffold for pharmaceuticals and bioactive compounds.[3] Among them, the decarboxylative sequence of activated *β*-amino esters by Greaney and co-workers is noteworthy.[4]

In this context, we propose the synthetic approach of *β*-arylethylamine derivatives by an intramolecular radical Truce-Smiles rearrangement induced by a decarboxylative photocatalyzed approach, starting from *N*-protected *β*-amino acid compounds (Figure 1).

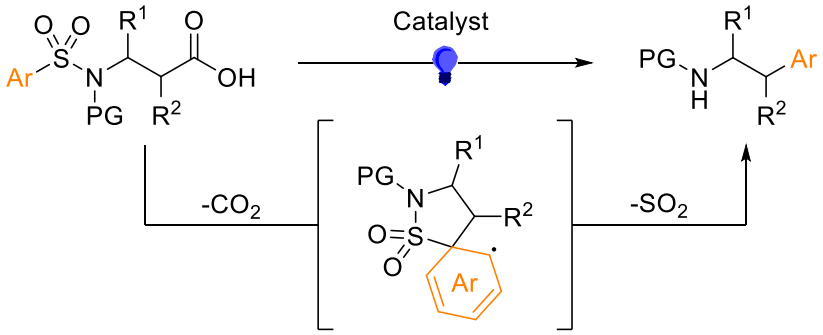

Figure 1. Photocatalyzed intramolecular Truce-Smiles rearrangement of *β*-amino acid

Acknowledgements
This work is part of the Industrial Chair COLIBRI (ANR-22-CHIN-0008). This work has been partially supported by University of Rouen Normandy, INSA Rouen Normandy, the Centre National de la Recherche Scientifique (CNRS), European Regional Development Fund (ERDF), Région Normandie, Labex SynOrg (ANR-11-LABX-0029), Carnot Institute I2C, the graduate school for research XL-Chem (ANR-18-EURE-0020 XL CHEM).

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Graphitic Carbon Nitride Photocatalysis for Visible-Light Aerobic Oxidations

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Keywords: Graphitic Carbon Nitride ● Aerobic Oxidation ● Sulfides ● Boronic acids ● Photochemistry

While traditional oxidation methods often rely on stoichiometric oxidants such as CrO_4^{2-} and MnO_4^-, molecular oxygen represents an ideal alternative; however, its application remains relatively limited. In recent years, the rapid advancement of photochemistry has enabled the development of photocatalytic aerobic oxidation protocols as powerful tools for activating atmospheric oxygen.[1] Among the various photocatalytic semiconductors, graphitic carbon nitride (g-C_3N_4) stands out due to its metal-free nature, low cost, and strong redox potential under visible-light irradiation, offering an environmentally benign approach to selective photocatalytic oxidations using O_2 under mild conditions.[2] Herein, we report a systematic study of chemoselective transformations under blue and green light irradiation, focusing on the oxidation of sulfides to sulfoxides and boronic acids to the corresponding hydroxy derivatives.[3],[4]

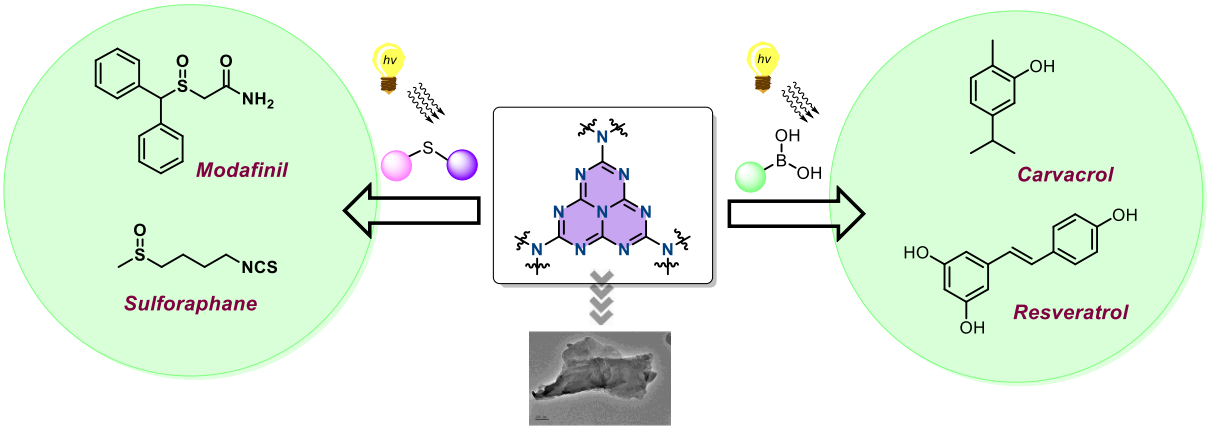

Figure 1. g-C_3N_4-mediated aerobic oxidation of sulfides and boronic acids under visible-light irradiation.

Acknowledgements
This work was financially supported by ProGnosis Biotech S.A.

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Divergent asymmetric synthesis of heterohelicenes via sequential organocatalyzed Povarov reaction and aromatization

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Keywords: Heterohelicenes ● Asymmetric synthesis ● Povarov reaction ● Chiral phosphoric acid ● Divergent synthesis

Incorporating main-group elements into the backbone of helicenes can significantly modulate their electronic and optical properties, making the asymmetric synthesis of heterohelicenes an attractive research direction. Based on this, the present study employs a key Povarov reaction catalyzed by chiral phosphoric acids to achieve the divergent asymmetric synthesis of two distinct types of heterohelicenes from the same starting material. Specifically, via a one-pot asymmetric Povarov reaction/oxidative aromatization, C1 ortho-phenol-substituted [5]/[6] pyridohelicenes were synthesized; further Pd(II)/base-mediated furan ring formation yielded longer [7]/[8] heterohelicenes containing both furan and pyridine units. The successful derivatization of the resulting chiral helicenes, coupled with their excellent photophysical and chiroptical properties, further demonstrates the significant value of this synthetic method

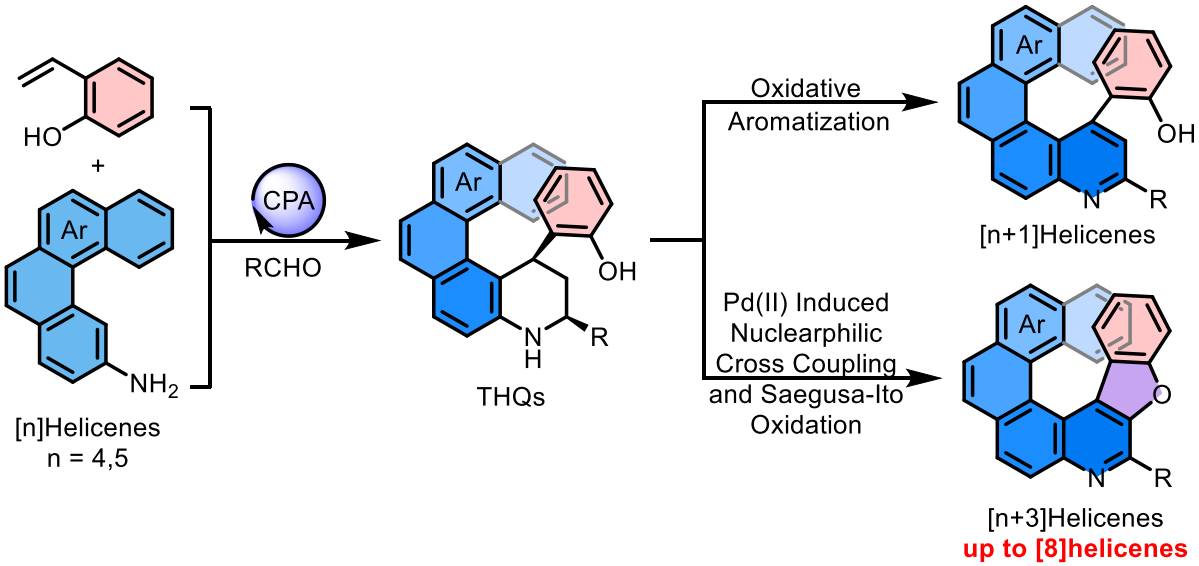

Figure 1. Divergent asymmetric synthesis of heterohelicenes via a CPA-catalyzed Povarov reaction, followed by either oxidative aromatization or Pd(II)-induced intramolecular cyclization.

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Direct di-functionalization of ynamides mediated by visible light

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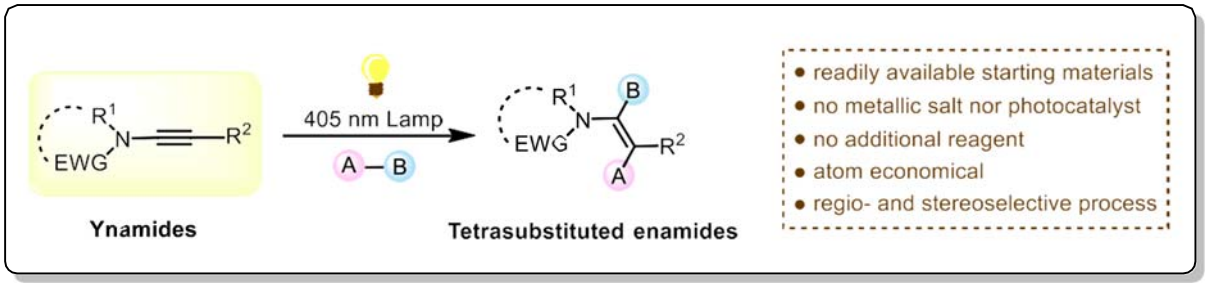
Keywords: Alkoxyamine ● Photocatalysis ● nitroxide

Enamides are stable electron rich double bonds that are commonly used in organic synthesis for incorporation of nitrogen functionality.[1] The stability of these units, related to their diminished enaminic reactivity, as the result of the presence of electron-withdrawing group on the nitrogen atom, is well demonstrated by their occurrence in various bioactive natural products.[2] During the course of our investigation on the reactivity of ynamides in radical chemistry,[3] we found out a strategy for accessing these powerful and versatile building blocks from ynamides in a simple, clean, and atom economical manner. The process occurs with high yield and high regio- and stereoselectivity leading to complex alkenes bearing no less than three heteroatoms.



Acknowledgements

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Designer Dithiocarbamates as Radical Covalent Catalysts via Excited-State Triplet Biradicals: Application to Skeletal Reorganization of Vinylaziridines

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Keywords: Radical Covalent Catalyst ● Biradical ● Dithiocarbamate ● Photocatalyst

Dithiocarbamates have been exploited for facilitating radical-mediated bond formations by leveraging their general reactivity arising from the weak carbon-sulfur bonds.[1] In particular, the C–S bond homolysis induced by irradiating with UV light or the generation of dithiocarbamate radical cations by using photoredox catalysts have expanded the reactivity modes of dithiocarbamates and their utility in radical addition-fragmentation chain transfer (RAFT)/cationic polymerization[2] as well as C–C bond formations.[3] Despite the significant advances in the utilization of these modes of reactivity relying on C–S bond cleavage for selective chemical synthesis, the potential of dithiocarbamates as molecular catalysts that exert reactivity and selectivity originating from their distinct structural and electronic attributes remains unexplored.

In this research, we uncovered the novel reactivity of dithiocarbamates as radical covalent catalysts through the development of modular thiazole-2-thiones for achieving the skeletal reorganization of *N*-sulfonyl vinylaziridines to the corresponding aminocyclopentanes with adjacent vinyl appendages under photocatalytic conditions (Figure 1).[4] A series of mechanistic investigations underpinned that the predominant pathway involved the triplet biradical of an appropriately modified thiazole-2-thiones, formed via energy transfer from an iridium-based photocatalyst, as a catalytically active species viable to engage in the covalent activation of vinylaziridines for the ensuing radical cascades.

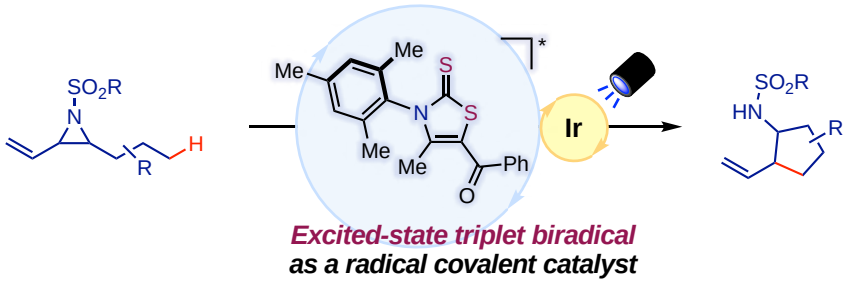

Figure 1. Skeletal reorganization of vinylaziridines by radical covalent catalysts via excited-state triple biradicals.

Acknowledgements
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Halogen Radical Generation via Protonated Nitro Triplets Enables Direct C-H Bromination

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Keywords: photochemistry ● nitro triplet state ● halogen radicals ● radical C-H functionalization ● metal-free

The development of mild methods for generating halogen radicals from simple halide salts remains an important objective in radical chemistry.[1] We report a metal-free, visible-light-promoted approach that enables direct benzylic C-H bromination using readily available simple halide salts. Photoexcitation of nitroarene generates a reactive triplet, enabling controlled formation of bromine radicals from bromide anion. The transformation proceeds without conventional radical initiators or preactivated halogenating reagents and provides efficient access to benzylic bromides in good to excellent yields.

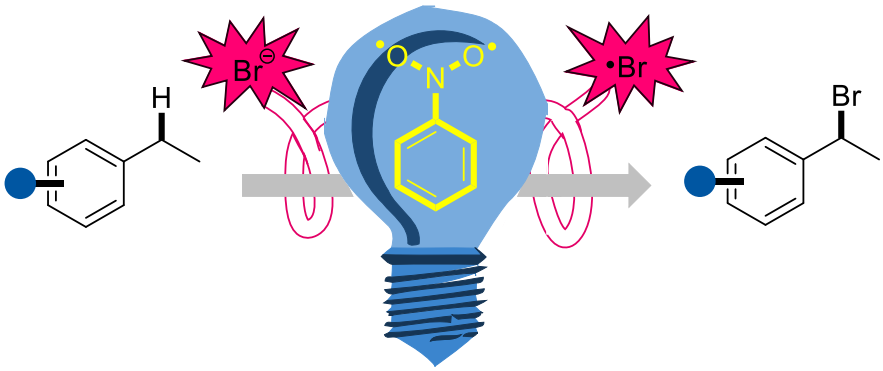

Figure 1. Benzylic C-H Bromination

This work highlights a practical strategy for halide utilization in photochemical C-H functionalization and thus expands the scope of sustainable radical generation methods and the synthetic utility of excited-state nitro chemistry.

Acknowledgements
This work was financially supported by RWTH Aachen University, Germany.

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Organic single electron donor-initiated amidation of esters *via N,N*-diboranes

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Keywords: *N,N*-diboranes● amidation ● nitroarenes ● single electron donor

An organic single-electron donor system based on B_2pin_2, LiO*t*Bu and 1,10-phenanthroline enables a single electron reduction of nitroarenes at room temperature. Trapping of intermediary nitrosoarenes with B_2pin_2 allows full reduction of the nitro group, resulting in the bis-borylation of nitrobenzene derivatives. The use of these underexplored aromatic *N,N*-diboranes[1] revealed a highly nucleophilic nitrogen center, as evidenced by their ability to promote direct amidation of esters at room temperature.

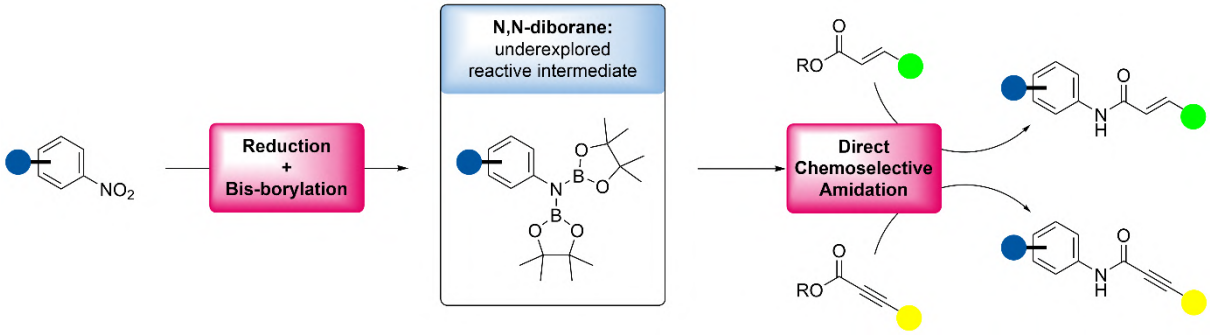

Figure 1: Organic single electron donor-initiated amidation of esters *via N,N*-diboranes.

Moreover, *N,N*-diboranes react with excellent chemoselectivity as demonstrated by the amidation of α,β-unsaturated and propargylic esters. In summary, alkyne esters were amidated directly with nitroarenes as nitrogen source in a one pot reaction. Generality and high functional group tolerance of this method is demonstrated in a broad reaction scope.

Acknowledgements
This work was financially supported by RWTH Aachen University, Germany.

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Polarity-Reversed Trifluoroacetyl Radical Three-Component Assembly of Alkene-Heteroarene Frameworks via Consecutive Photoinduced Electron Transfer

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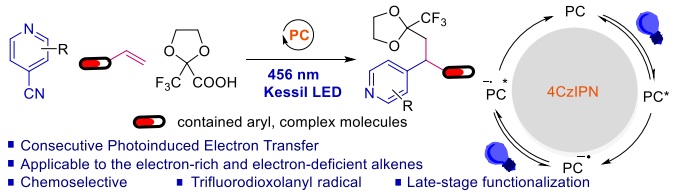
Keywords: **CONPET ● Multicomponent reaction ●Fluorination ● Reverse polarity●**

The incorporation of fluorinated motifs, particularly CF_3CO- groups, into electron-deficient molecular frameworks remains a persistent challenge due to the intrinsic electrophilic character. Herein, we report a three-component, mild and efficient protocol that achieves both trifluoroacetylation and heteroarylation of broad class of alkenes. Our strategy employs a masked trifluoroacetyl precursor to invert the native electrophilicity of the CF_3CO unit. Mechanistically, the reaction operates via a consecutive photoinduced electron transfer (ConPET) pathway involving two-photon excitation process. This protocol is compatible with late-stage functionalization of structurally complex unsaturated coupling partner and proposed mechanism is corroborated by a detailed mechanistic study.



Acknowledgements
Indian Institute of Technology, Kanpur

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Photochemical rearrangement of isonitriles via energy transfer catalysis

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Keywords: photochemistry ● radical ● rearrangement ● EnT ● isonitrile

Functional group interconversion, a pivotal synthetic technique for precise editing of molecular building blocks, is particularly rare when facilitated by energy transfer catalysis. Herein, we showcase two instances of photochemical rearrangement of isonitriles, facilitated by energy transfer catalysis under visible light. The di-π-ethane rearrangement and di-π-propane rearrangement proceed through a six-membered transition state, offering a fresh synthetic paradigm for constructing three- and five-membered molecular architectures. Notably, these open-shell rearrangements demonstrate a vast substrate scope, compatibility with diverse functional groups, and applicability to complex drug and natural product derivatives, thereby presenting a complementary strategy for advancing energy transfer-enabled functional group inter conversion. Furthermore, the photochemical rearrangements of isonitriles have been supported by computational studies.

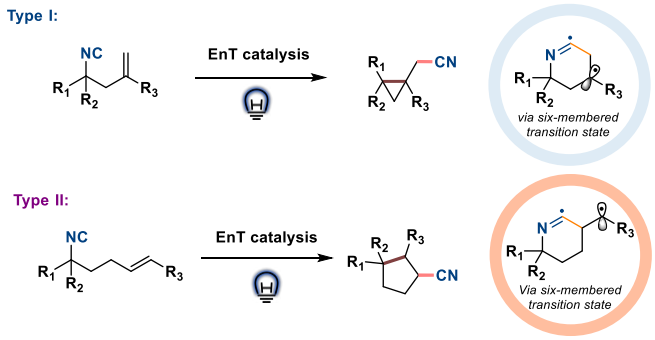

Figure 1. Two types of isonitriles photochemical rearrangement.

We successfully demonstrated two types of photochemical rearrangements: di-π-ethane and di-π-propane rearrangements of isonitrile functional groups, facilitated by energy transfer catalysis under visible light conditions. These rearrangements exhibit a broad substrate scope and functional group tolerance, producing three- or five-membered cyclic architectures in high to excellent yields [1].

Acknowledgements
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Enzymatic α-Hydroxylation of Fatty Acids through a Radical Intermediate with Excellent Regio- and Stereoselectivity

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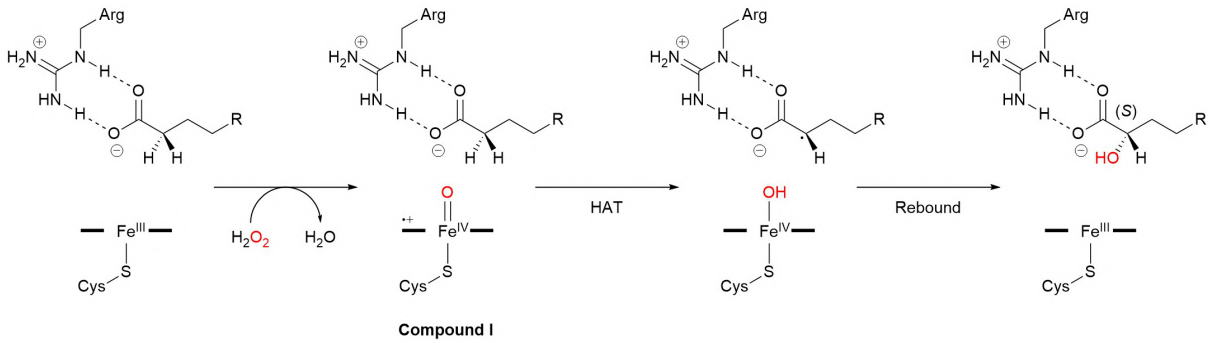
Keywords: Biocatalysis ● C–H Oxidation ● α-Hydroxylation ● Cascade

Cytochromes P450 (CYPs) can catalyze the monooxygenation of non-activated aliphatic (sp^3) and aryl (sp^2) C–H bonds utilizing a high-valent Fe(IV)-oxo porphyrin π-cation radical – referred to as Compound I (Scheme 1) – as the active intermediate.[1] Upon formation of Compound I, which is facilitated by reductive activation of molecular oxygen or by a ferric hydrogen peroxide (H_2O_2) species, homolytic C–H cleavage occurs and the resulting radical is terminated through OH rebound, generating the monooxygenated product (Scheme 1).[2] The highly ordered environment provided by the protein scaffold ensures that the monooxygenation reaction occurs with excellent regio- and stereoselectivity.[3]

In this work, the H_2O_2-utilizing cytochrome P450 $PO_{SPα}$ (CYP152 family, isolated from *Sphingomonas paucimobilis*[4]) was engineered for the improved synthesis of α-hydroxylated medium-chain fatty acids. The best variant (V3-P04) exceeded the parent in terms of hydrogen peroxide tolerance, expression yields, and specific activity for the functionalization of octanoic acid. V3-P04's improved performance was underlined in preparative-scale experiments, where it reached turnover numbers of up to 48,333. Additionally, the stereoselectivity for the $PO_{SPα}$-mediated overoxidation of 2-hydroxyoctanoic acid was investigated and found to be stereocomplementary to the first oxidation, with a preference for the conversion of the minor formed (*R*)-enantiomer, leading to an improvement of the optical purity of (*S*)-2-hydroxyoctanoic acid with increasing overoxidation in a cooperative cascade.



Scheme 1: CYP152-Mediated α-hydroxylation of a fatty acid substrate. The substrate's carboxylate group is bound in proximity to the reaction center by a conserved arginine residue. Hydrogen peroxide acts as electron and oxygen donor facilitating the formation of the active intermediate (Compound I). Homolytic C–H cleavage and hydrogen atom transfer (HAT) lead to the formation of a $C_α$-radical which is terminated by OH rebound to the α-hydroxy acid.

Acknowledgements

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Chemometrically-Guided Electrochemical HAT-driven α-C(sp3)–H Alkylation of Alcohols

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Keywords: Organic electrochemistry ● C-H activation ● α-oxy radicals ● Giese reaction ● Chemometrics

Alcohols are a ubiquitous functional group among organic molecules and frequently serve as a reactive handle to generate molecular complexity.[1] Although their reactivity as oxygen-centered nucleophiles has been extensively exploited, their potential as carbon-centered nucleophiles has only recently gained significant momentum.[2] In this context, whereas thermal and photochemical strategies exploiting HAT mediators to generate nucleophilic α-oxy radicals are well established, analogous electrochemical approaches remain comparatively underdeveloped.[3] With the aim of expanding the synthetic toolbox towards sustainable C(sp3)-H functionalization of alcohols, we developed a complementary electrochemical platform for the HAT-driven generation of nucleophilic α-oxy radicals, enabling their subsequent engagement in Giese-type additions with electron-poor olefins to forge C(sp³)–C(sp³) bonds (**Figure 1**).

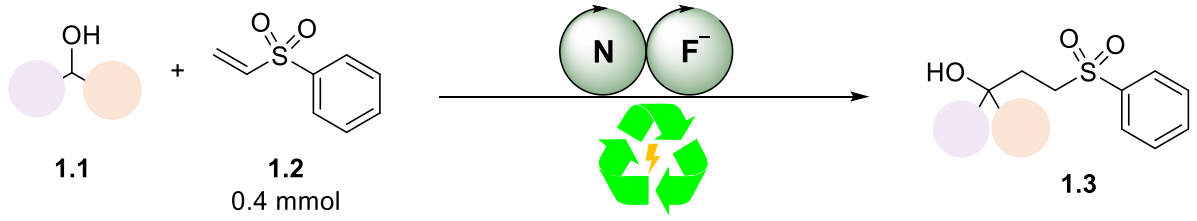

Figure 1. Electrochemical HAT-driven α-C(sp3)–H alkylation of alcohols.

To identify suitable reaction conditions, we adopted a chemometrics-guided strategy.[4] Initially, a D-optimal design was used to circumscribe the relevant chemical space and identify influential reaction parameters, followed by a factorial design to evaluate interaction effects and determine optimal conditions. Key features of this mild and operationally simple method include the use of a tertiary amine as HAT mediator; a hydrogen-bond-acceptor fluorinated additive, and porous electrodes under galvanostatic conditions. Scope evaluation is underway using structurally diverse alcohols **1.1** in slight excess and phenyl vinyl sulfone **1.2** as limiting radical acceptor. Preliminary results demonstrate formation of desired alkylated alcohols **1.3** in good yields with a broad functional group tolerance and excellent selectivity.

Acknowledgements

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Engineered Iminium Photodecarboxylases for Stereoselective Radical Catalysis

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Keywords: Photochemistry ● Biocatalysis ● Directed Evolution ● Radical Chemistry ● Asymmetric Catalysis

Photocatalysis has demonstrated its potential as a powerful platform for generating radical intermediates, enabling a wide range of synthetic transformations that are inaccessible *via* conventional two-electron pathways. Despite the prevalence of radical mediated processes in complex biological systems, enzymatic photochemical transformations remain scarce in nature[1-3]. Merging highly preorganized and tunable enzyme active sites with excited state chemistry offers a particularly innovative, sustainable, and highly efficient strategy for the synthesis of valuable chiral molecules[4]. Our group has recently disclosed a cofactor-free photoenzymatic platform utilizing direct photoexcitation of enzyme-bound intermediates[5]. Specifically, a class I aldolase (DERA-MA) forms iminium ions with enals via a catalytic lysine residue[8]. Upon irradiation, these intermediates undergo single-electron transfer, enabling activation of carboxylic acids to generate radicals. Stereocontrolled radical–radical coupling within the enzymatic pocket then affords alkylated products with enantiomeric excesses of up to 99% (Figure 1). Building on this pioneering approach, we have implemented high-throughput directed evolution workflows to rapidly expand the capabilities of our photoenzymatic platform. Engineered enzymes have been developed to process a diverse range of radical precursors, including challenging primary aliphatic radicals from abundant fatty acid feedstocks, with excellent enantiocontrol (up to 99% *ee*). Our photoenzymes can also address unmet selectivity challenges, demonstrating a memory of chirality effect to enable divergent diastereocontrol using enantiopure starting materials (d.r. up to 15:1). Additionally, select enzyme variants can begin move beyond traditional point chirality and achieve excellent control (99% *ee*) when forging a novel chiral axis.

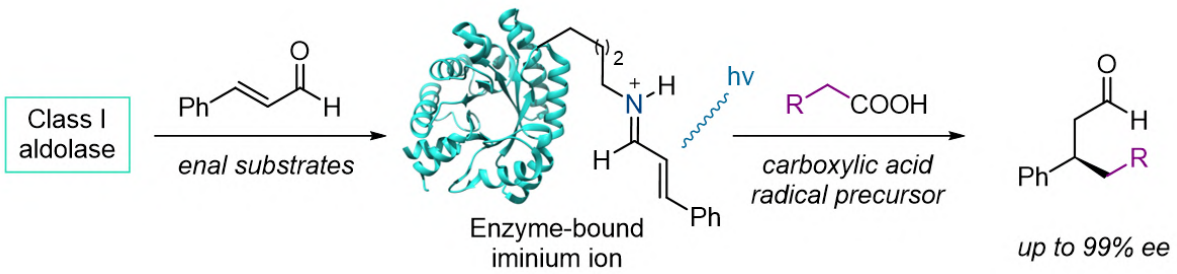

Figure 1. Concept of a novel iminium photodecarboxylase enzyme for stereocontrolled radical-radical couplings.

Acknowledgements
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Carbon–carbon bond-forming radical reactions driven by the redox metabolism of bacteria

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Keywords: Chemical biology ● microbiology ● biochemistry ● bacteria ● radical arylation

Living cells can be regarded as microscopic factories that perform thousands of chemical reactions in a highly regulated manner. However, the synthetic scope of biological systems is limited to a range of biochemical transformations required by Nature. This constrain can be relieved by interfacing the metabolism with non-enzymatic, new-to-nature synthetic processes.[1] Inspired by the significant advances in synthetic reactions involving single-electron transfer (SET) processes, we envisioned harnessing the cellular metabolism to drive non-natural, bond-forming radical reactions. Several precedents have already demonstrated that the redox metabolism of bacteria can be used to initiate radical polymerization reactions.[2] Here, we demonstrate the use of the natural redox metabolism of bacteria to promote radical arylations and radical-based annulations. These reactions may have biomedical applications, such as the localized *in situ* synthesis of drugs promoted by bacteria.

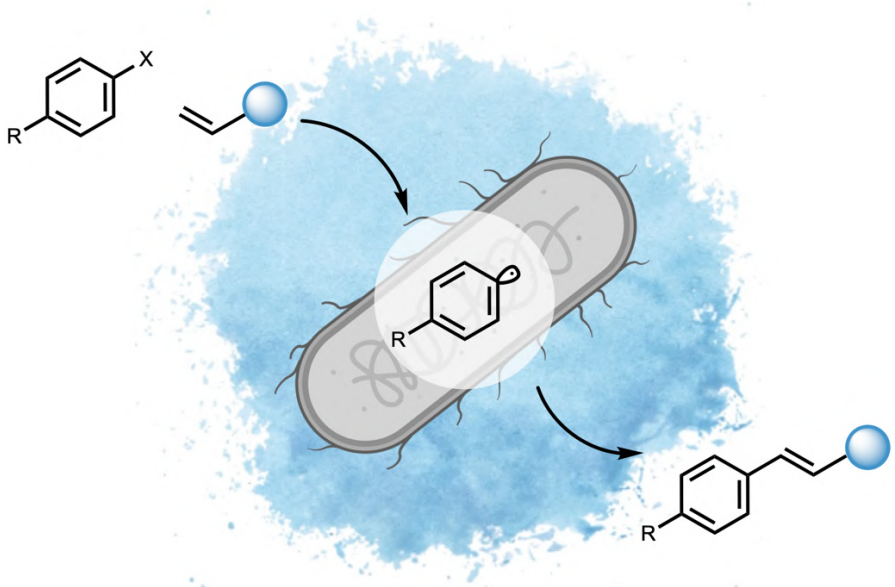

Figure 1. Carbon–carbon bond-forming radical reactions driven by the redox metabolism of bacteria.

Acknowledgements
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2-Silyloxyfurans Go Radical: Photochemical Access to γ-Functionalized Butenolides

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Keywords: 2-Silyloxyfurans ● Photoredox catalysis ● Radical–polar crossover ● γ-Functionalization

2-Silyloxyfurans **1**, one of the most exploited heterocyclic nucleophiles in vinylogous polar processes, are herein unlocked as versatile platforms in radical-mediated, vinylogous transformations.[1] We have developed a set of photopromoted strategies which unveiled a dual, complementary reactivity of **1**: *i*. as electron-rich dienes capable to intercept electrophilic α-ketoradicals **2**•[2] or suitable benzyl carbocations **3**$^+$ selectively at the γ-position; and *ii*. as precursors of easily accessible silyl radical cation intermediates **1**$^{•+}$ capable of engaging a radical-radical coupling with nucleophilic, open shell intermediates **3**•.[3]
These pathways provide direct γ-functionalization of the butenolide core, delivering structurally diverse chiral products in one step, namely ε-ketobutenolides **4** and γ-benzylbutenolides **5**. The resulting scaffolds proved their versatility as starting platforms to build fused heterobicyclic lactones and bioactive phenyl-γ-valerolactone derivatives **6**.[4]
In this poster presentation the results of our endeavor will be presented, elevating 2-silyloxyfurans as strategic hubs for expanding the scope of vinylogous transformations.

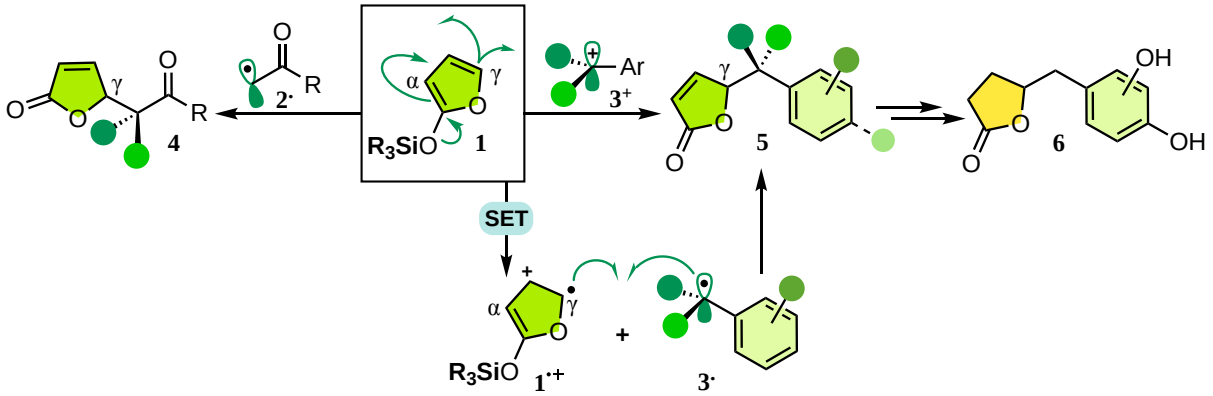

Figure 1. Photochemical γ-functionalization of 2-silyloxyfurans **1** via novel radical reactivity.

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Uranyl based photo-decarboxylation: from mechanistic insights to catalytic fuel production

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Keywords: Biofuel ● Decarboxylation ● Fatty acids ● Uranyl ● Photocatalysis

Depleted uranium is produced in large quantities as uranyl nitrate, an abundant and largely underexploited by-product of the nuclear fuel industry. While uranium chemistry is well documented in geochemical and environmental contexts, its catalytic reactivity remains far less explored despite renewed interest in recent years. Identifying new valorisation routes for depleted uranium is therefore highly desirable, particularly in the energy sector, where its stakeholders already operate.

Fossil fuel use remains a major contributor to global warming through CO_2 emissions, driving the search for sustainable alternatives. In this context, green hydrocarbons are attractive drop-in biofuels, offering both high compatibility with existing infrastructure and access from renewable feedstocks. [1] However, conventional production routes often rely on harsh thermocatalytic conditions, while current photocatalytic approaches still require expensive catalysts, stoichiometric base, or multiple additives.

Building on pioneering studies by Heckler and co-workers [2] showing that photoexcited uranyl species promote the decarboxylation of organic acids in water, we investigate uranyl-based photocatalysis for renewable-fuel production from abundant biosourced feedstocks, including acetic acid and waste lipids.

We elucidate the mechanistic features of the acetic acid system through luminescence studies, kinetic isotope effects, isotopic labelling experiments, and correlations between uranyl speciation and catalytic activity. Building on this understanding, this reactivity is extended to long-chain fatty acids provides access to gasoline-, kerosene-, and diesel-range hydrocarbons. Overall, the system operates under mild conditions, with water as the only additive and low photocatalyst loadings, thus offering a potential route for the valorization of depleted uranium through visible-light-driven conversion of abundant bio-sourced feedstocks in aqueous medium.

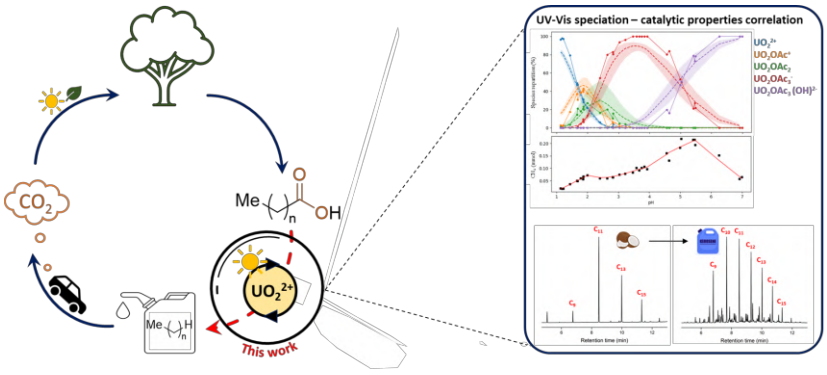

Figure 1. Graphical abstract

Acknowledgements
This work was supported by UraMeth (reg. No. ANR-23-CE07-0052)

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Electron transfers to (and from) N-Heterocyclic Carbenes: a new playground for radical organocatalysis?

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Keywords: N-Heterocyclic Carbenes ● radicals ● organocatalysis ● reductive activation● electrochemistry

N-heterocyclic carbenes (NHC) have been engaged for decades as organocatalysts. While these processes usually follow ionic mechanisms, an increasing number of NHC-organocatalyzed radical transformations have been reported recently, either in presence of aldehyde derivatives (Breslow-type catalysis) or in absence (free-NHC promoted radical reactions).[1]

Our team has undergone electrochemical and mechanistic studies of the underlying redox processes[2] and took advantage of the resulting insights for designing catalytic systems for the reductive activation of challenging substrates.[3] We will present the latest development of this research project. In addition, to the redox chemistry of Breslow intermediates (see Figure 1),' we will also discuss the possible observation and relevance of radical ions of free NHC, which have been hypothesized, but have remained elusive to date.

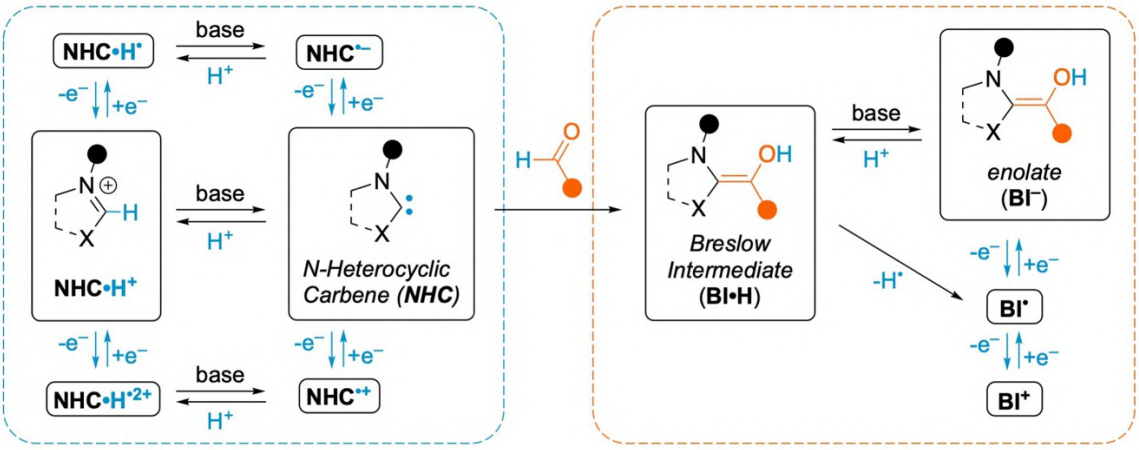

Figure 1. Square schemes for proton/electron transfers of key intermediates in NHC-promoted radical reactions.

Acknowledgements

This work was financially supported by the Arcane Labex and the french National Agency for research (ANR).

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Accessing Molecular Complexity from Methane and Other Gaseous Alkanes via Photocatalytic Cascade Cyclization

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Keywords: Methane ● Cyclization ● Molecular complexiety ● Photocatalysis ● Iron

The direct transformation of simple and abundant feedstocks into structurally complex molecules remains a central challenge in modern organic synthesis. Methane, the simplest alkane and a potent greenhouse gas, is one of the most abundant carbon-based feedstocks on the planet. Thus, its efficient conversion into complex organic molecules would represent one of the most transformative avenues in organic synthesis. However, the inertness of C─H bonds (BDE~105 kcal/mol, pKa~50) in methane makes its functionalization highly challenging. Consequently, strategies for efficient methane functionalization remain scarce. Methods to directly achieve molecular complexity from methane and other gaseous (C2-C4) alkanes remain elusive.

We have recently developed a method for the oxidative cascade cyclization of *N*-aryl and *N*-benzoyl acrylamide derivatives, promoted by methane and other gaseous alkanes.[1] This transformation is enabled by a readily available iron catalyst in combination with *N*-fluorobenzenesulfonimide (NFSI) as the oxidant, proceeding under mild conditions to afford a diverse array of N-heterocyclic frameworks in high yields. Late-stage functionalization studies highlight the utility of methane in the synthesis of biologically relevant scaffolds. Moreover, the Fe/NFSI system facilitates a radical sampling regime that enables the selective functionalization of less reactive primary C─H bonds. Overall, this work establishes a sustainable and versatile platform for constructing molecular complexity directly from gaseous alkane.

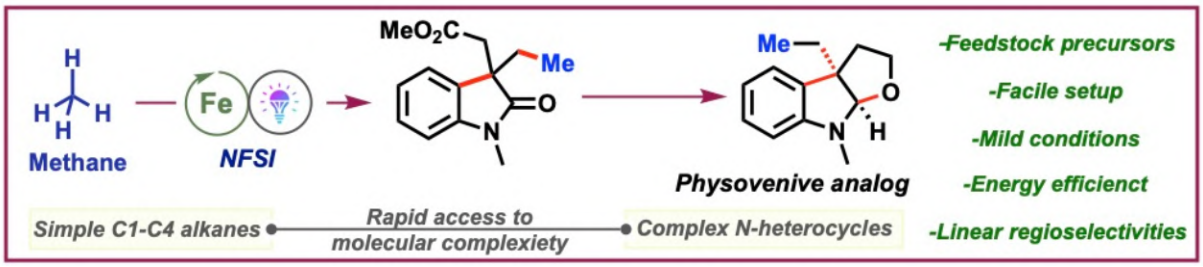

Figure 1. Overview of the work

Acknowledgements

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7–10 June 2026, Bologna, Italy

Site-selective C–H-Alkylation of Pyrimidin-2(1*H*)-ones Enabled by Visible Light-Induced Organophotocatalysis

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Keywords: organophotocatalysis ● visible-light ● Pyrimidin-2(1*H*)-ones ● C–H-alkylation ● selectivity

A visible-light-driven photocatalytic method for regioselective C–H alkylation of N1-substituted pyrimidin-2(1H)-ones at the C4 and C6 positions is presented. Using alkyl trifluoroborates, an acridinium-based photocatalyst, and potassium persulfate as the oxidant, the protocol enables stepwise introduction of secondary and tertiary alkyl groups *via* a radical pathway. This approach expands the accessible chemical space of substituted pyrimidines in a straightforward and efficient manner. The effects of substituents at the N1 and C5 positions, as well as acid additives, were examined to establish scope and optimize conditions. The methodology is operationally simple and demonstrates strong potential for parallel synthesis and multigram-scale preparation of densely decorated pyrimidines.

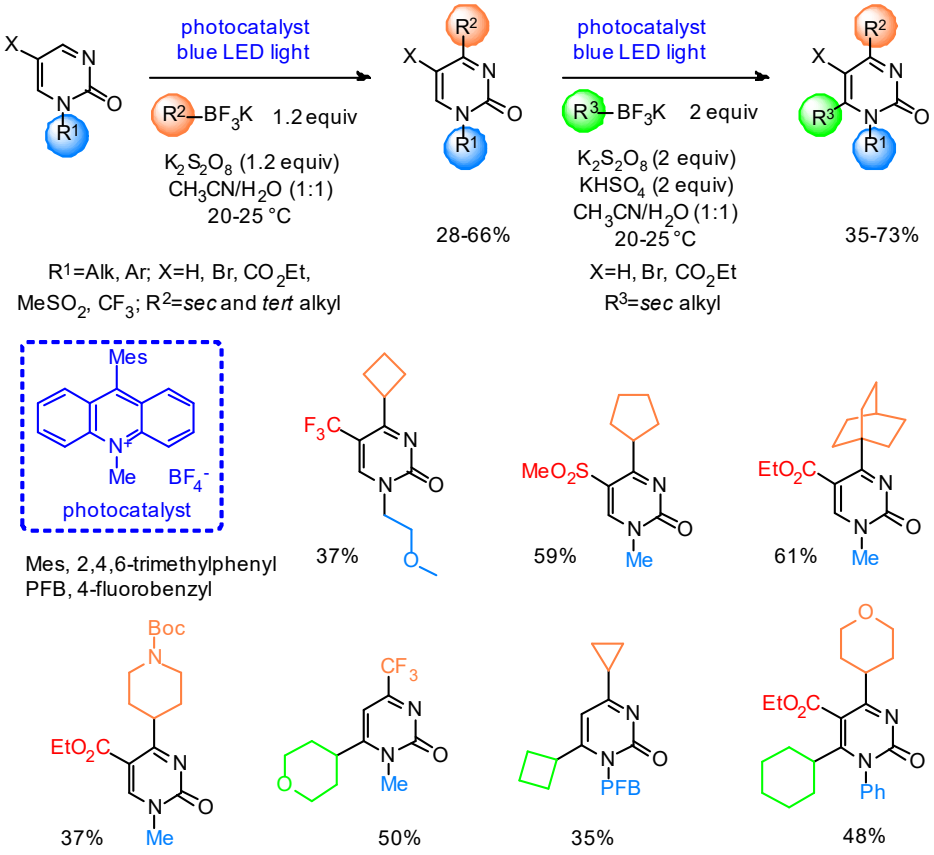

Figure 1. Project outline.

EDA-complexes enabling Photoacid Generation

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Keywords: Photochemistry ● EDA complex ● Photoacid generator ● Iminosulfonates ● Indole derivatives

Photochemistry is a field of chemistry that investigates chemical reactions triggered by the absorption of light, which enables transformations that are otherwise inaccessible under traditional thermal conditions.[1] Electron donor–acceptor (EDA) complexes play a prominent role in light-induced methodologies.[2] Among the catalysts involved in photochemical reactions, photoacid generators (PAGs) are particularly important.[3] The study of PAGs is of significant interest because, upon irradiation, they release acids through a controlled and relatively slow liberation of their acidic component. In this context, the formation of an EDA complex between indole derivatives and iminosulfonates results in the gradual release of *p*-toluenesulfonic acid (p-TSA), thereby promoting a series of acid-catalyzed reactions. In the present work, we report the development of mild and environmentally friendly methods for the functionalization of the indole moiety, avoiding the use of metal catalysts and toxic solvents.[4]

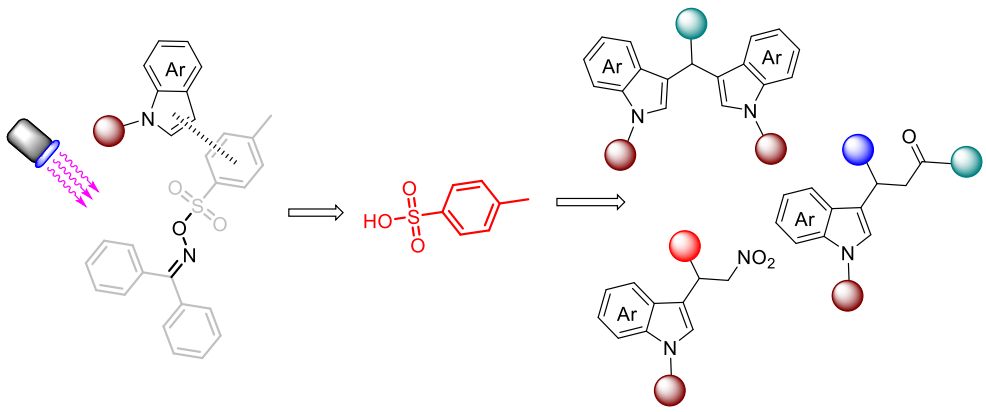

Figure 1. Generation of *p*-TSA through EDA-complex formation.

Acknowledgements
The authors gratefully acknowledge the support by ProGnosis Biotech S.A. in this work.

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Radical Chain Diversification of Alkylborons Enabled by Catechol as the Sole Activator

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Keywords: radical coupling reaction ● organoboron chemistry ● catechol ● C-X bond formation

Boronic pinacol esters (Bpin) are widely recognized as versatile reagents and privileged synthetic intermediates owing to their facile and modular late-stage transfor-mations. Despite long-standing awareness of their potential for alkyl radical generation, the full synthetic utility of Bpin moieties, especially alkylboronic esters, has been limited by two inherent challenges: the high oxidation potential of alkylboronic pinacol esters (APEs) and their relatively weak Lewis acidity. We have developed a simple and air-tolerant method for functionalizing alkylboronic esters to form diverse carbon–heteroatom and carbon–carbon bonds. Using catechol as the sole activator, this protocol facilitates boronic ester exchange and initiates radical formation under thermal conditions or through catechol-mediated pathways. The resulting alkyl radicals readily couple with a wide range of $PhSO_2X$ reagents under ambient air, enabling efficient C–X bond construction without the need for sensitive organometallics, expensive photocatalysts, or transition-metal catalysts. This approach overcomes key limitations of traditional methods by offering a straightforward and practical platform for converting C–B bonds into various functional groups. Mechanistic studies indicate that boron transesterification is the key initiating step, generating an alkyl radical that reacts with $PhSO_2X$ to form the product along with a benzenesulfonyl radical. This radical further interacts with alkylboronic esters (Bpin or Bcat), sustaining a radical chain process. Given its operational simplicity and broad applicability, this methodology holds significant promise for the modification of small-molecule pharmaceuticals and bioactive compounds in drug development.

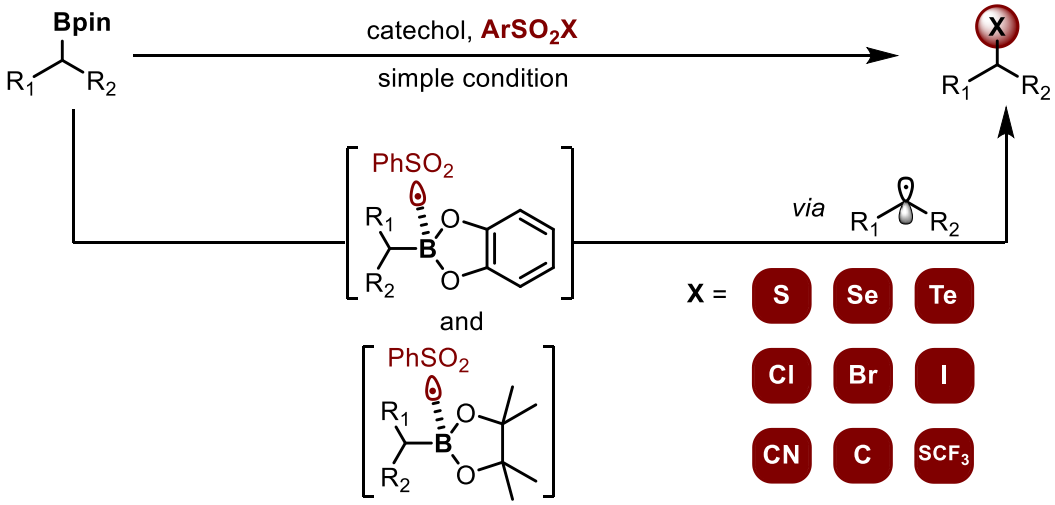

Figure 1. Radical chain diversification of alkylborons enabled by catechol

Acknowledgements

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The interaction between nitronyl-nitroxide halogenated derivatives and complexation with cucubituril (CB[7])

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Keywords: EPR spectroscopy ● nitronyln nitroxide ● halogen functionalization ● cucurbit[7]uril ● host-guest

The effect of halogen substitution on the inclusion behavior of aromatic nitronyl nitroxide radicals in cucurbit[7]uril (CB[7]) was investigated by EPR spectroscopy, a method widely used to probe host–guest interactions.[1] In this study there were used fluorinated, chlorinated, and brominated aromatic derivatives. The EPR response strongly depended on the halogen atom. While the F- and Cl-substituted radicals showed only small spectral changes upon CB[7] addition, the Br-substituted derivative displayed pronounced modifications and a distinct signal corresponding to the inclusion complex. These findings suggest that bromine substitution promotes a more evident host–guest interaction with CB[7], leading to a clearer spectroscopic signature of complex formation. The results show that halogen-dependent structural effects are important in controlling supramolecular recognition and EPR detectability.

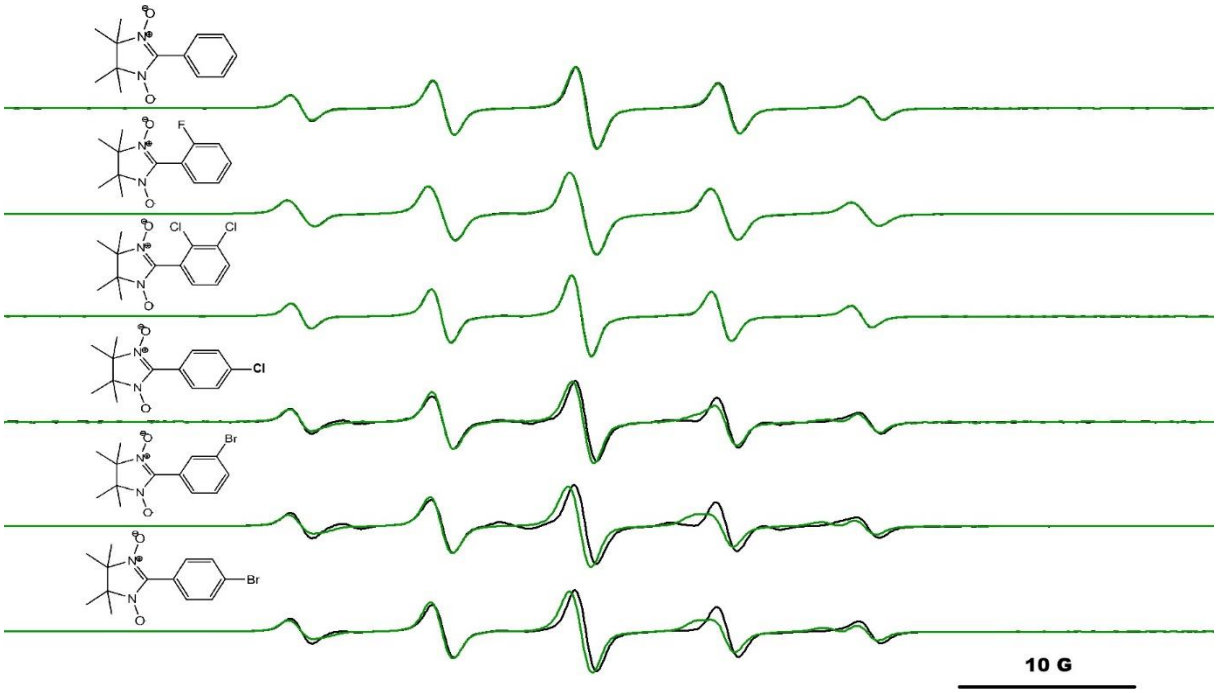

Figure 1. Structures and EPR spectra (black – water, green – CB[7]) of analyzed spin probes.

Acknowledgements

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Influence of stereochemistry on the inclusion of β-phosphorylated nitroxide radicals in cyclodextrins

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Keywords: EPR spectroscopy ● diastereomers ● intramolecular H-bonding ● inclusion geometry

The inclusion complexation of β-phosphorylated cyclic nitroxide radicals with β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD) was investigated by EPR spectroscopy[1], with emphasis on the effect of radical functionalization. Alongside the previously studied hydroxyl-substituted radicals, the corresponding acetate- and adamantane-functionalized derivatives were also examined. The results show that both functionalization and stereochemistry influence the host–guest interactions. For the hydroxyl-substituted radicals, differences in the ability to form an intramolecular hydrogen bond lead to distinct inclusion behavior, with stronger association observed for one stereoisomer in γ-CD. In the presence of β-CD, no significant differences were found between the hydroxyl- and acetate-substituted radicals. In contrast, the adamantane-functionalized derivatives exhibited a different complexation pattern, suggesting that inclusion occurs from another side of the molecule compared with the other radicals. These findings demonstrate that subtle structural modifications can strongly affect cyclodextrin binding and provide useful insight for the design of tunable supramolecular spin systems.

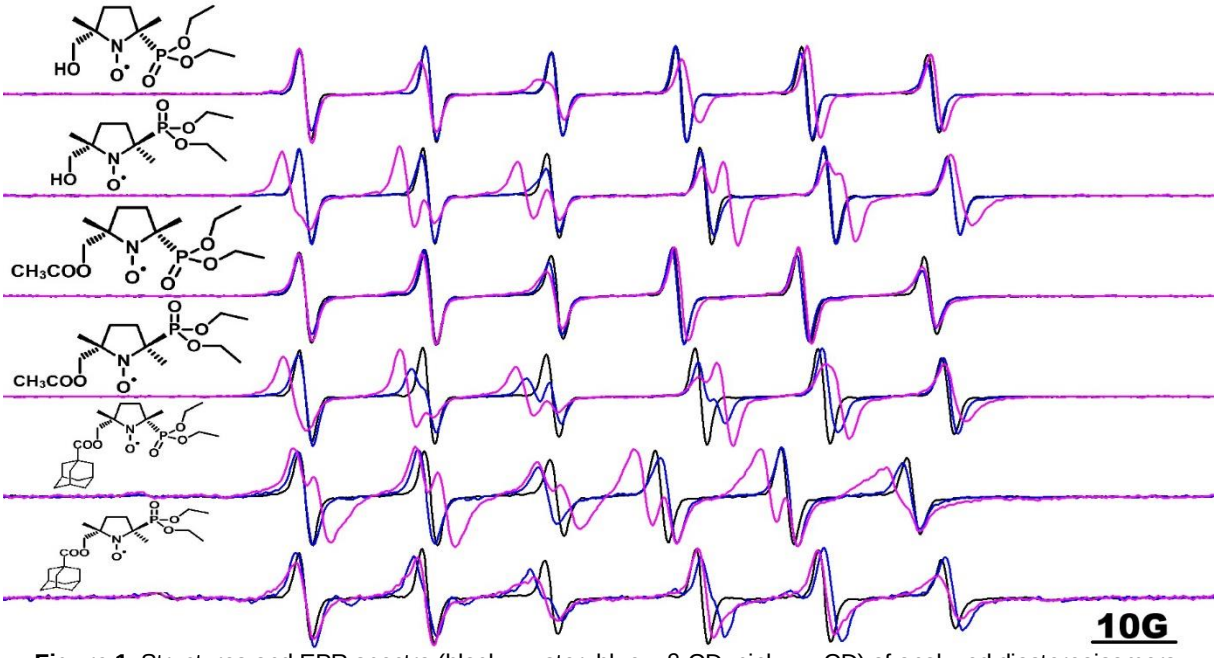

Figure 1. Structures and EPR spectra (black – water, blue – β-CD, pink – γ-CD) of analyzed diastereoisomers.

Acknowledgements
This work was financially supported by PNRR-III-C9-2023-I8 “Chemical host-guest molecular systems for health applications (OMRI for identification of inflammatory pathologies)”, contract no. 760283/27.03.2024, Ministry of research, innovation and digitalisation, Romania, funded by European Union – NextGenerationEU

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A Radical Cascade with Double Intramolecular Hydrogen Atom Transfer

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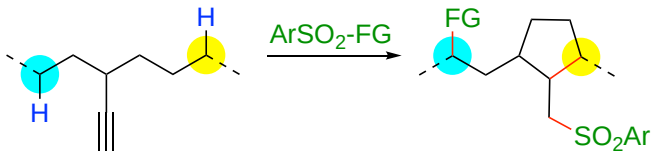
Keywords: Radical Cascade ● C–H Bond Activation ● Double HAT ● Sulfonyl Radical ● Diquinane

Radical cascade reactions are very powerful to achieve the preparation of complex molecules from easily assembled starting materials. The incorporation of an intramolecular hydrogen atom transfer step (*i*-HAT) in the cascade enhances the level of complexity that can be achieved. Despite the synthetic potential of radical *i*-HAT for selective activation of aliphatic C–H bonds, the development of radical cascades involving multiple intramolecular C–H bond functionalization on a single substrate has remained largely underexplored.

Since the pioneering work of Heiba and Dessau in the 1960s,[1] the usefulness of radical addition translocation cyclisation (RATC) processes using sources of heteroatom-centered radicals including thiols,[2] dialkylphosphites and thiophosphites[3] to access functionalized 5-membered ring carbo- and heterocycles has been demonstrated. A few years ago, we reported a (RATC) process mediated by sulfonyl radicals, in which the last step involved an intermolecular HAT from the non-innocent solvent THF to the α-sulfonylated radical resulting from the RATC process.[4]
We report here an efficient radical cascade promoted by sulfonyl-based reagents and that involves the activation of two aliphatic C–H bonds in a regioselective, sequential manner.[5] This original radical cascade composed of a series of five elementary steps converts efficiently terminal alkynes into polyfunctionalized cyclopentylmethyl arylsulfones and involves reactive α-sulfonylalkyl radicals.[6]



5-step cascade with:

- two C–H activations
- three new C–C and C-heteroatom bonds
- one 5-membered ring
- two new functional groups

Scheme 1. Selective double C–H activation

The methodology has been applied to the preparation of di- and triquinanes possessing a rare *trans* ring junction.[5] The scope and limitation of the methodology will be discussed.

Acknowledgements
This work was financially supported by the Swiss National Science Foundation (Project 200020_201092). FD thanks Nantes Université and CNRS for funding (“Projet international de coopération scientifique” N° PICS07936).

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Monitoring Human Neutrophil Elastase Activity by EPR Using Peptide-Functionalized Nitroxide Radicals

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Keywords: EPR spectroscopy ● Human neutrophil elastase ● Peptide-functionalized nitroxide radicals

Protease activity involved in numerous diseases can be exploited for the development of responsive MRI probes.[1] In this study, we investigated the hydrolysis of MeO-Suc-$(Ala)_2$-Pro-Val linked to TEMPO and two β-phosphorylated nitroxide radical diastereoisomers by human neutrophil elastase (HNE). The reaction was monitored by EPR spectroscopy in the absence and presence of γ-cyclodextrin.

The TEMPO derivative showed no significant EPR changes upon enzymatic treatment. By contrast, the β-phosphorylated nitroxide radicals displayed clear variations in spectral parameters under both conditions. Enzymatic hydrolysis led to a change in the hyperfine splitting constant of 1.22 G without cyclodextrin and 1.9 G in the presence of γ-cyclodextrin. In cyclodextrin-containing samples, the spectra consisted of two components, consistent with the coexistence of free and complexed radical species. These findings indicate that γ-cyclodextrin improves detection of the enzymatic process. ESI-MS analysis further confirmed the hydrolysis products.

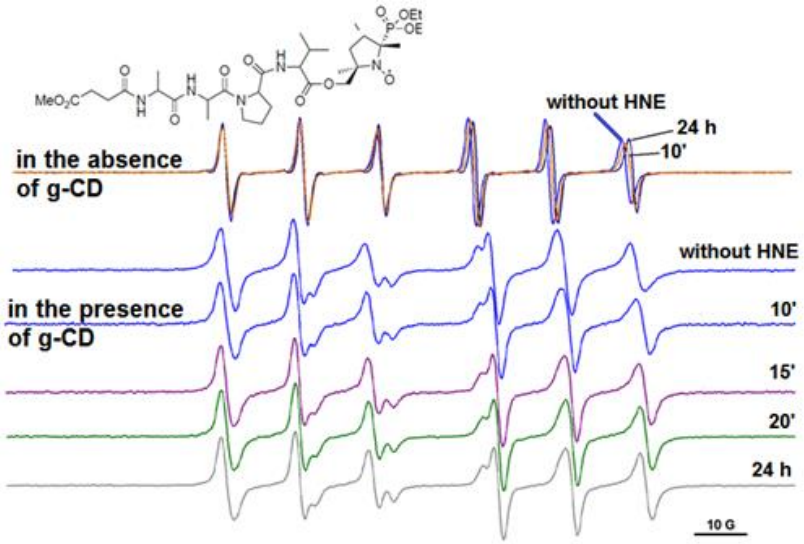

Figure 1. EPR spectra of the β-phosphorylated nitroxide in the absence of γ-CD and in the presence of γ-CD; effect of HNE.

Acknowledgements

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Characterization of Transient Enamine Radical Intermediates in Photoredox Catalysis Cycle

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Keywords: ● aminocatalysis ● radical chemistry ● electron paramagnetic resonance ● direct observation ● time-resolved technique

Enamine-derived radicals are key intermediates in singly occupied molecular orbital (SOMO) catalysis. The SOMO catalytic reaction has successfully established a series of transformations, using primary amine catalysts.[1] Despite remarkable synthetic value of these transformations, direct observation of the key SOMO radical intermediate is still quite limited. Recently, we developed an advanced time-resolved electron paramagnetic resonance technique, named the ultrawide single sideband phase-sensitive detection (U-PSD EPR).[2] This technique is particularly suitable for detecting weak signals of transient radicals under near-synthetic conditions.

By applying the U-PSD EPR, we were able to directly observe the α-imino radical cation and deprotonated radical intermediates involved in the chiral primary amine-catalyzed allylation of β-ketoesters for the first time.[3] The acquired EPR spectra and kinetic profiles allowed us to confirm the authentic identity of the chiral radicals and quantify their reactivities. Furthermore, the U-PSD EPR method enabled the determination of the pK_a value of radical cation through a titration-type experiment. This direct observation of transient radical species in the photoredox catalysis involving enamines grants us deeper mechanistic insights that hold immense promise for the rational design of radical-mediated catalysis.

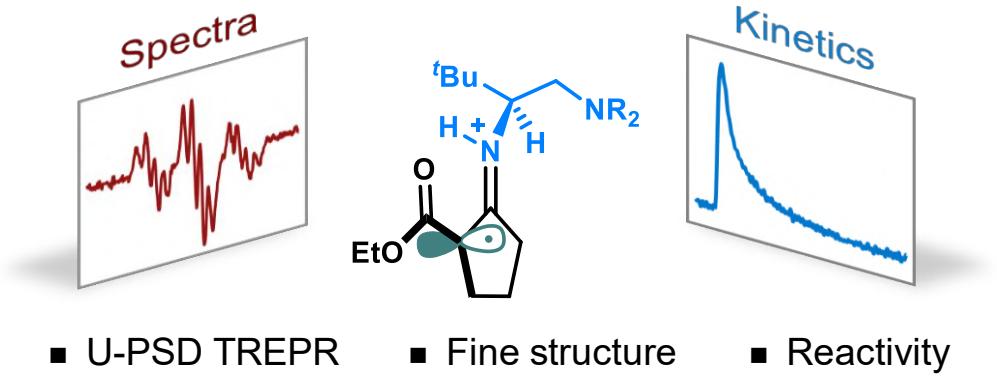

Figure 1. spectra and kinetics of α-imino radical intermediates

Acknowledgements

We acknowledge the financial support of this work provided by the Tsinghua University Dushi Program, China, the National Natural Science Foundation of China (grant nos. 22031006, 22193011, 22373056, and 22393891), the Haihe Laboratory of Sustainable Chemical Transformations, China, and the National Science & Technology Fundamental Resource Investigation Program of China (grant no. 2023YFA1500008).

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Designing B–N Platforms to Enable Quantum Tunneling in HAT

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Keywords: boryl radicals ● HAT ● quantum mechanical tunneling ● B-N compounds ● DFT

Photocatalytic alkene hydrogenation using ammonia-borane as a hydrogen source has been reported as an efficient, metal- and H_2-free platform for radical-mediated reduction chemistry.[1] In that study, the mechanism was interrogated by computational chemistry, with multiple competing pathways systematically examined. Although one candidate channel featured a strong quantum-mechanical tunneling contribution, this signature was not experimentally observable because alternative pathways were both kinetically and thermodynamically preferred under the reported conditions, thereby dominating the overall reactivity.

Here, we aim to identify a new B–N compound platform that steers the reaction toward the tunneling-sensitive pathway and away from competing routes that mask the effect. High-level calculations are used first to compare the key pathways and to select the most promising candidates before experiments. We specifically target systems where the tunneling step is not only present but also becomes the preferred route under practical conditions. This should allow tunneling to be detected experimentally through clear kinetic signatures, such as temperature dependence and isotope effects.

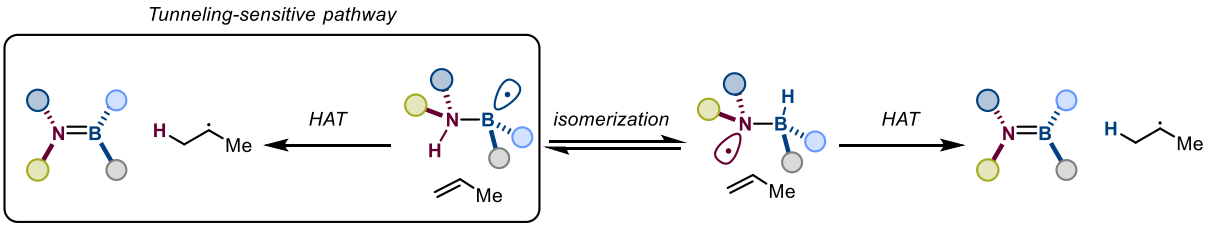

Figure 1. Tunneling-sensitive HAT pathway and competing isomerization in a B–N radical system

Acknowledgements
D.B.Y acknowledges the financial support of the Study Abroad Postgraduate Education Scholarship (YLSY) awarded by the Ministry of National Education of Türkiye. Computations were performed with computing resources granted by RWTH Aachen University under projects RWTH1268 and P0021519, and with the High Performance and Grid Computing Center (TRUBA resources) at TUBITAK ULAKBIM.

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Deoxygenative Route to Alkynylation of Heterocyclic *N*-oxides under Ball Milling

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Keywords: ● Deoxygenative alkynylation ● Heterocyclic *N*-oxides ● Radical pathway ● Stainless steel ● Ball-milling

We disclose the first example of stainless steel-induced deoxygenative C-2 alkynylation 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 various electron-donating (-Me, -OMe, -Et, -^{n}Bu, -OEt) and electron-withdrawing substituents (-I, -Br, -Cl, -F, -CF_3, -NO_2), both in the quinoline/pyridine *N*-oxides and in phenylacetylene derivatives, has been observed, affording thirty-four products in 61-94% yields. The method has been successfully applied to the synthesis of two mGluR5 antagonists[1]. 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 facilitating the reaction via a radical pathway.

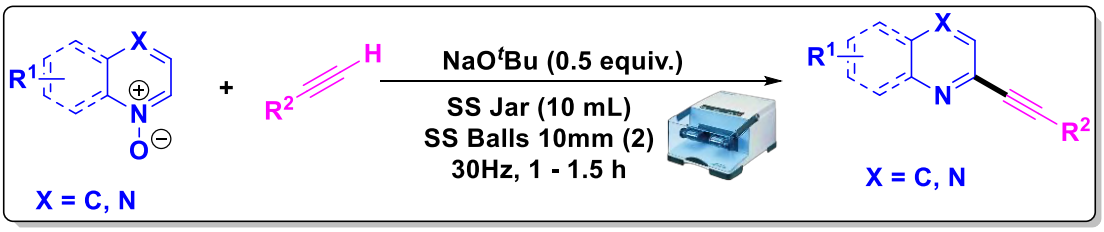

Figure 1. Stainless steel-induced deoxygenative C-2 alkynylation of heterocyclic *N*-oxides under ball milling.

Acknowledgements
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Simplifying biosynthesis: how to access the natural complexity of sesquiterpenoids following easy steps

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Keywords: radical retrosynthesis ● radical oxidation ● divergent total synthesis ● biomimetic ● cascades

The growing need for potent and selective biomodulators to address contemporary health challenges underscores the importance of innovative synthetic strategies. Divergent synthesis, which harnesses common synthetic scaffolds to generate a diverse array of natural product-like compounds, is emerging as a powerful tool in modern drug discovery.

By identifying and emulating these common synthetic scaffolds,[1-2] modern total synthesis can integrate selective, biosynthetic-like radical reactions,[3] offering a sustainable and efficient approach to drug discovery. This presentation will explore cutting-edge approaches to developing a unified synthetic strategy, focusing on the radical retrosynthesis and biomimetic radical oxidation steps,[4] inspired by nature's two-phase biosynthesis.

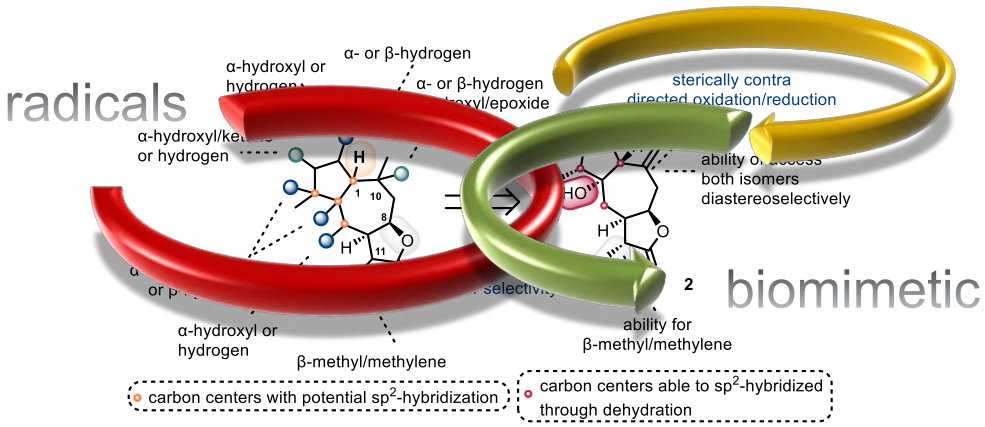

Figure 1: Building diversity in sesquiterpenoids

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14th International Symposium on Organic Free Radicals (ISOFR-14)
7–10 June 2026, Bologna, Italy

Bichromophoric Ruthenium Complexes for Photocatalyzed Late-Stage Functionalization of Indolizines

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Keywords: Photoredox ● Indolizines ● Catalyst Design ● Late-Stage Functionalization ● Radicals

Indolizine derivatives are a class of important single-nitrogen-containing heterocycles that can be found both in drugs and functional organic materials.[1] Over the past two decades chemists developed and implemented new and greener processes to prepare and functionalize this scaffold. Recently, visible-light photoredox catalysis and electrochemical synthesis proved to be suitable tools for the direct access of this scaffold and for its late-stage functionalization.[2-4] Herein, optimized conditions for the photoredox radical late-stage functionalization of indolizines have been developed. By tuning the redox properties of Ru-based bichromophoric photocatalysts it is possible to achieve excellent yields and further apply the optimized conditions to a broad variety of substrates. This approach enables the efficient generation of a broad spectrum of radicals, including trifluoromethyl-, trifluoromethylthio-, and carbon-centered radicals. Combined theoretical and spectroscopic findings also have revealed the superiority of the designed complex over commonly used photocatalysts. To further highlight the significance of indolizines in medicinal chemistry, the functionalized products have been used as scaffold for drugs design and analogues of biologically active compounds have been synthesized with excellent yields.[5-7]

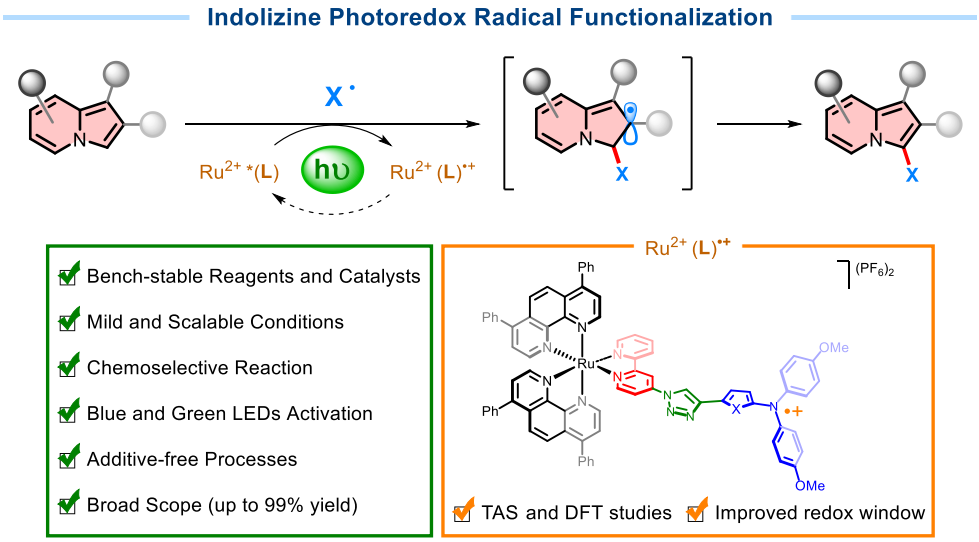

Figure 1. Bichromophoric Ru(II) Complex Photocatalyzed Radical Functionalization of Indolizines.

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Hydrogen Atom Transfer using Catalytic P-H Donors

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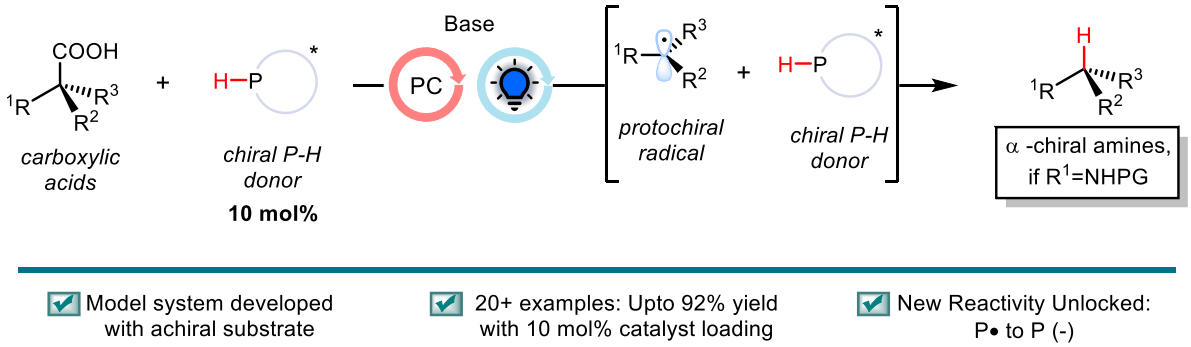
Keywords: Catalysis ● Radical Phosphorus chemistry ● Chiral Amines

We report a dual catalytic system for decarboxylative reduction of carboxylic acids. A photocatalyst works in tandem with organophosphorus catalyst (P-H* donors) to deliver a hydrogen atom to a pro-chiral radical. This method opens the possibility of enantioselective hydrogen atom transfer (HAT) reaction from a chiral P-H species.



Scheme 1: HAT using catalytic P-H donors

At the moment, only reagents derived from Sn, S, and Si have been used for the asymmetric HAT reaction, but they are far from providing a general solution.[1]

Phosphorus is an excellent and yet unexplored alternative.[2] Organophosphorus compounds have weak P-H bonds, P-centered radicals are well studied and asymmetric chemistry of P-compounds is well-established, with many chiral scaffolds available.[3] Organophosphorus species have been used before as H-atom donors (e.g. Barton's hypohopshorus acids), but only in stoichiometric and over-stoichiometric amounts.[4]

Here we have successfully developed a model system and we discovered unprecedented catalysis with a P-H donor, facilitated by the previously elusive reduction of P-centered radical to P-centered anion. The preliminary screening has been performed across > 20 substrates, with yields > 92%. Currently, we developing the enantioselective variant of the reaction.

Acknowledgements
This work was financially supported by Research Ireland (22/PATH-S/10609).

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Directing-Group-Assisted Chemo- and Site-Selective Thioetherification Cross-Coupling Reactions under Base-Free Conditions

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Keywords: nickel ● photoredox ● site-selective ● cross-coupling ● catalysis

Transition metal-catalyzed cross-coupling reactions are indispensable tools in modern organic synthesis, enabling the rapid construction of molecular complexity. Although palladium has long been the metal of choice for these transformations, the advent of metallaphotoredox catalysis has significantly expanded the synthetic toolbox available to chemists. Recently, we introduced Adaptive Dynamic Homogeneous Catalysis (AD-HoC), a concept based on the *in situ* formation of catalytically competent species assemblies. Among the reactions enabled by this approach, AD-HoC-mediated C(sp^2)-S cross-coupling is particularly notable because it operates under conditions that differ markedly from those of conventional cross-couplings: the protocol requires no external base, ligand, or additive.[1-5]

Herein, we report a nickel-catalyzed chemo- and site-selective thioetherification protocol that operates through a directing-group strategy under base-free conditions. In contrast to conventional methods, this approach enables the efficient synthesis of thioethers from polyhalogenated anilines under mild and operationally simple conditions. NMR coordination studies indicate that the amino group coordinates to the nickel center even in the presence of thiols, while kinetic analysis reveals a several-fold increase in reaction rate relative to substrates lacking the directing group. This effect enables the efficient conversion of challenging electron-rich and sterically demanding substrates to the corresponding thioethers. Furthermore, the high level of regioselective control allows sequential one-pot C(sp^2)-S/C(sp^2)-S cross-couplings, while the chemoselectivity of the protocol enables the rapid one-pot synthesis of pharmaceutically relevant targets.

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Emergence of Radical Phosphonylation: From Ambiphilic Phosphite Traps to Iron-Catalyzed C(sp³)–H Functionalisation

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Keywords: radical phosphonylation ● phosphoranyl radicals ● ambiphilic phosphite ● photocatalysis ● alkyl phosphonates

Carbon-centered C(sp³) radicals are inherently poorly reactive toward traditional trialkyl phosphites used in Arbuzov-type chemistry, even under forcing thermal conditions (≈100 °C), which has historically limited radical phosphonylation strategies. We report the emergence of radical phosphonylation as a general and mild platform for C–P bond formation enabled by reagent design and iron photocatalysis.[1]

An ambiphilic phosphite radical trap, BecaP, enables efficient trapping of alkyl radicals under visible-light photoredox conditions, allowing redox-neutral decarboxylative and deboronative phosphonylation with broad scope and late-stage applicability.[2] Building on this foundation, atom-economy limitations associated with prefunctionalised substrates were addressed through an iron-catalyzed C(sp³)–H phosphonylation of unactivated alkanes.[3]

Together, these studies establish radical phosphonylation as a distinct and general strategy for accessing phosphonates from both feedstock radical precursors and native hydrocarbons.

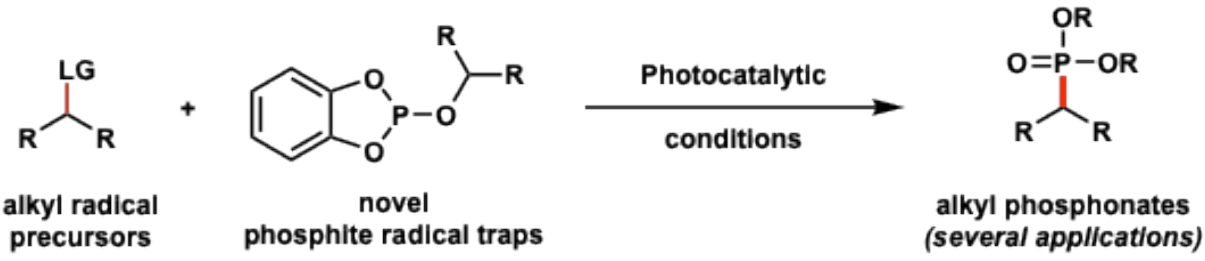

Figure 1. Light-driven alkyl radical phosphonylation using novel phosphite radical traps

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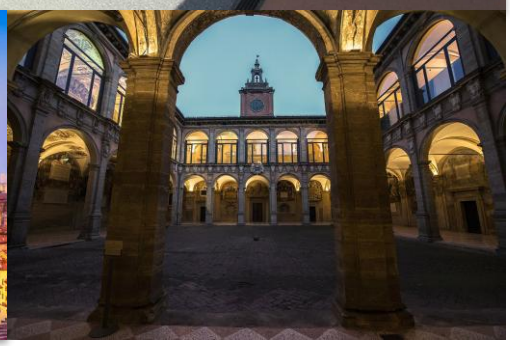

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