TAIPEI, TAIWAN

ICCEOCA

2024

The 17th International Conference on Cutting-Edge Organic Chemistry in Asia

NOV. 29 - DEC. 2

Abstract Book

Program at a Glance

Time	Nov-29	Nov-30	Dec-01	Dec-02
09:00–09:20		**Opening Remarks**	**IL-10** Masaru Enomoto (JP)	**IL-21** Yu Zhao (SG)
09:20–09:40		**IL-01** Yong Huang (HK)	**IL-11** Young Ho Rhee (KR)	**IL-22** Takahiko Akiyama (JP)
09:40–10:00		**IL-02** Rei Kinjo (SG)	**IL-12** Hayato Ishikawa (JP)	**IL-23** Qian Miao (HK)
10:00–10:20		**IL-03** Yoonsu Park (KR)	**One-minute Poster Presentations (PC)**	**IL-24 (TH)** Charnsak Thongsornkleeb
10:20–10:40		**One-minute Poster Presentations (PA)**		**Coffee Break**
10:40–11:00			**Poster Session C & Coffee Break**	
11:00–11:20		**Poster Session A & Coffee Break**		**IL-25** Min Hee Lee (KR)
11:20–11:40				**IL-26** Ken Kamikawa (JP)
11:40–12:00			**IL-13** Ru-Yi Zhu (SG)	**IL-27** Yen-Ju Cheng (TW)
12:00–12:20		**Group Photo**	**IL-14** Jean-Ho Chu (TW)	**IL-28** Takayuki Iwata (JP)
12:20–12:40		**Lunch**	**Lunch**	**Lunch**
12:40–13:40		**Vendor Workshop**		**Excursion**
13:40–14:00		**IL-04** Jiun-Jie Shie (TW)	**IL-15** Takuya Hashimoto (JP)	
14:00–14:20		**IL-05** Seiji Suga (JP)	**IL-16** Rungnapha Saeeng (TH)	
14:20–15:00		**One-minute Poster Presentations (PB)**	**One-minute Poster Presentations (PD)**	
15:00-16:00		**Poster Session B & Coffee Break**	**Poster Session D & Coffee Break**	
16:00–16:20	**Registration**	**IL-06** Hyunwoo Kim (KR)	**IL-17** Chien-Fu Liang (TW)	
16:20–16:40		**IL-07** Wei-Yu Lin (TW)	**IL-18 (TH)** Jumreang Tummatorn	
16:40–17:00		**IL-08** Jian He (HK)	**IL-19** Keisuke Asano (JP)	
17:00–17:20		**IL-09** Hiroshi Shinokubo (JP)	**IL-20** Anna Lee (KR)	
17:20–18:00		Transportation	Transportation	
18:00-18:30	**18:00-20:30 Welcome Reception**			
18:30 onwards		**Friendship Dinner 1**	**Friendship Dinner 2**	**Banquet & Award Ceremony**

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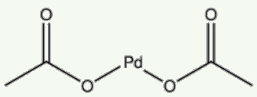
SILICYCLE

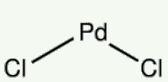
A

鈀催化劑 5G/25G

UR-IPAL002 $Pd(OAc)_2$



UR-IPAL001 $PdCl_2$



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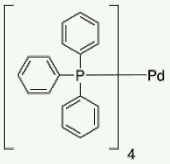

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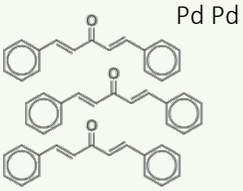
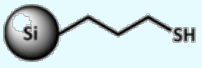


B

鈀移除劑

SY-R51030B Si-Thiol



10G/25G/100G

A

鉑/銥/釕催化劑 5G/25G

UR-H2PTCL6	UR-IPOT002	UR-IPOT001	UR-IIR001	UR-IRUT001
H_2PtCl_6	K_2PtCl_6	K_2PtCl_4	$IrCl_3$	$RuCl_3$

B

鉑/銥/釕移除劑

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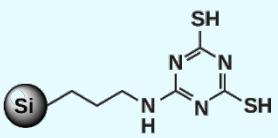

10G/25G/100G

Contents

FOREWORD

On behalf of the organizing committee of the 17th International Conference on Cutting-Edge Organic Chemistry in Asia (ICCEOCA-17), it is our great pleasure to extend a warm welcome to all participants. This conference will be held at Academia Sinica (Taipei, Taiwan) from November 29 to December 2, 2024.

ICCEOCA-17 continues the tradition of annual conferences organized by member countries and regions of the Asian Cutting-Edge Organic Chemistry Promotion Network (ACP) on a rotating basis. Since the inaugural event in 2006 in Okinawa, Japan, this program has been thriving, and the annual conferences have become one of the most significant events in organic chemistry and related fields in the Asian region. Due to the pandemic, this tradition was temporarily paused after 2019 but successfully resumed with a virtual conference hosted by Hong Kong in July 2022, followed by an in-person event in Singapore in 2023. This November, we are excited once again to host the 17th conference in person here in Taiwan.

At ICCEOCA-17, we anticipate the participation of around 150 researchers from Hong Kong, Japan, Korea, Taiwan, Thailand, and Singapore, who will exchange their up-to-date research findings in organic chemistry. The conference is also open to researchers from other regions, whether or not they are presenting a poster. We are honored to have you with us as we gather to explore the most recent developments in organic chemistry and foster future research collaborations with leading chemists in Asia. The four-day program features invited lectures, poster sessions with one-minute oral presentations, and social activities showcasing popular attractions in Taiwan.

This year's ICCEOCA-17 brings together leading experts in various fields, including organic reaction methodology development, asymmetric catalysis, natural product synthesis, organic materials, and bio-organic chemistry. These renowned scholars will share their pioneering work and contribute to advancing cutting-edge organic chemistry.

We extend our sincere gratitude to the local organizing committee and international coordinators, whose dedication has made this conference possible. We thank our supporting institutions, National Tsing Hua University, National Taiwan Normal University, Academia Sinica, the National Science and Technology Council, and the Ministry of Education for their generous support. We look forward to welcoming you to Taiwan and appreciate your participation and contributions in making ICCEOCA-17 a success.

Chun-Cheng LIN
Conference Chair, ICCEOCA-17
Professor, Department of Chemistry
National Tsing Hua University

Hsyueh-Liang WU
Taiwan Coordinator, ACP
Professor, Department Chemistry
National Taiwan Normal University

CONFERENCE COMMITTEE

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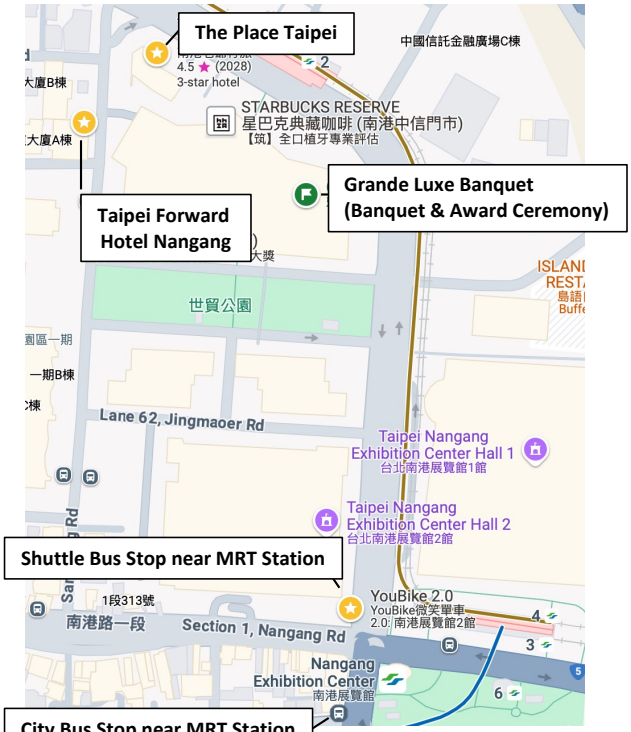
GENERAL INFORMATION

Conference Website: https://www.icceoca17.org

Transportation Information



Shuttle Bus

11/29 Welcome reception

Departure	Location
17:05	Taipei Forward Hotel Nangang
17:10	The Place Taipei
17:15	Stop near MRT Station

11/30, 12/01, 12/02 Morning

Departure	Location
8:20	Taipei Forward Hotel Nangang
8:25	The Place Taipei
8:30	Stop near MRT Station

***Coffee Session before the conference: 8:30 AM to 9:00 AM**

Conference Venues

Reception & Scientific Session:

Humanities and Social Science Building

Academia Sinica, No. 128, Section 2, Academia Rd, Nangang District, Taipei City

Friendship Dinner (Nov 30th):

豐 FOOD 海陸百匯

No. 8, ZhiFu Rd, Zhongshan District, Taipei City

Banquet & Award Ceremony

Grande Luxe Banquet

3F, CTBC Financial Park, No. 166

Jingmao 2nd Rd, Nangang District, Taipei City

DAIIY PROGRAM

Friday, Nov 29, 2024

16:00-18:00 **Registration**

18:00-20:30 **Welcome Reception**

Saturday, Nov 30, 2024

International Conference Hall, 3F

9:00-9:20 **Opening Remarks**

9:20-10:20 **Session 1 –** *Organometallic and Photo-catalysis*

Chair: Yoshiaki NAKAO

9:20 **Invited Lecture-01: Yong HUANG**

The Hong Kong University of Science and Technology, Hong Kong

Development of Iodonium Sulfoxonium Ylides for Carbene Relay Catalysis

9:40 **Invited Lecture-02: Rei KINJO**

Nanyang Technological University, Singapore

The Chemistry of Cyclic (Alkyl)(Amino)Aluminium(I) Species

10:00 **Invited Lecture-03: Yoonsu PARK**

Korea Advanced Institute of Science and Technology, Korea

Photocatalytic Single-atom Transmutation

10:20-12:00 **Poster Session A**

10:20 **One-minute Poster Presentations (PA)**

11:00 **Poster Session A & Coffee Break**

PA-01	Takahiro MORI	"Molecular basis for the diversification of lincosamide biosynthesis by pyridoxal phosphate-dependent enzymes"
PA-02	Kuo-Ting CHEN	"Development of Novel Heterocyclic Nitrile/1,2-Aminothiol Click Reactions: Applications in Molecular Imaging"
PA-03	Jeung Gon KIM	"Understanding a bit more about mechanochemistry – Mixing"
PA-04	Kosuke ONO	"Ammonia Adsorption Using a CO_2H-Functionalized Cyclic Oligophenylene"

PA-05	Kwok-Kong MONG	"Asymmetric 1,1'-Disaccharides for Total Synthesis of Glycosylated Natural Products"
PA-06	Franco King-chi LEUNG	"Supramolecular Assemblies of Photoresponsive Molecular Amphiphiles"
PA-07	Yu-Wen HUANG	"Total Synthesis of (±)-Arnicenone via a Stereodivergent Angular Triquinane Synthesis"
PA-08	Jieun JUNG	"Photoinduced Hydrogenation of Carbonyl Compounds at Mild Conditions Using a PNNP-type Ir Complex"
PA-09	Sunisa AKKARASAMIYO	"Synthesis of (*Z*)-Cinnamic Acid Derivatives via Stereoinvertive Deoxygenation of trans-Epoxides"
PA-10	Hayato TSURUGI	"Decarboxylative Functionalization of Carboxylic Acids by Metal Clusters Under Visible Light"
PA-11	Sang Kook WOO	"Development of Alkyl Radical Precursors from Benzyl Alcohols for Visible Light Photocatalyzed C-C Bond Formation"
PA-12	Jeng-Liang HAN	"Switchable Synthesis of Tritylone Alcohols and 2-Benzoylbenzoate Esters from Spiroindane-1,3-diones"
PA-13	Aspen X.-Y. CHEN	"Helical Cyclodextrin Nanochannels"
PA-14	Yasushi NISHIHARA	"Palladium-Catalyzed Decarbonylative Halogenation of Acyl Fluorides via Reductive Elimination of the C–X Bond"
PA-15	Sarah Yunmi LEE	"Harnessing Chiral Cyclopropenimine-Based Organocatalysts in Stereoselective Chemical Synthesis"
PA-16	Chih-Chien CHU	"One-Pot Synthesis of Cyclopentane-Fused Coumarin Photocages via Heck-Aldol Annulation"
PA-17	Manabu ABE	"Is π-Single Bonding (C–π–C) Possible? A Challenge in Organic Chemistry"
PA-18	Pei-Jhen LI	"Solvent-Free Approach in the Development of *O*-Sialylation Chemistry"
PA-19	Takeshi YASUI	"Cobalt/Photoredox Dual Catalysis-Enabled Cycloisomerization of 1,6-Diynes via Chemo- and Enantio-Selective C(sp^3)–H Activation"
PA-20	Cheng-Kun LIN	"Rapidly Diverse Synthesis of *N*-Aryl-5-Substituted-2-Oxazolidinones via Nucleophilic Epoxide Ring Opening and Intramolecular Acyl Substitution"
PA-21	Worawat NIWETMARIN	"Photoinduced acylation of quinoxalin-2(1*H*)-ones via electron donor-acceptor complexes"
PA-22	Jun TAKAYA	"Pyrrolidine Synthesis via Ring Contraction of Pyridines"
PA-23	Hsyueh-Liang WU	"Asymmetric Desymmetrization of Alkynyl-Tethered 2,5-Cyclohexadienones"
PA-24	Go HIRAI	"Linkage-Editing Strategy for Creation of pseudo-Glycans"
PA-25	Ya-Chu HSIEH	"Synthetic Approaches to C−Si Bond Formation via Hydrosilanes"
PA-26	Yusuke MASUDA	"1,2-*P*-Migrative [3+2] Cycloaddition of tri(*t*-butyl)phosphine with Alkynes"
PA-27	Sungwoo HONG	"Energy-Transfer-Induced [3+2] Cycloadditions of N−N Pyridinium Ylides"

PA-28	Takashi OHSHIMA	"Catalytic α-deuteration of amides and esters"
PA-29	Wen-Hua CHIOU	"Stereodivergent Syntheses of Two Families of *Ascidian* Alkaloids Lepadiformine and Fasicularin through Double Consecutive Epimerizations"
PA-30	Tiow-Gan Ong	"The Chemistry of Carbone"

12:00-12:20 Group Photo

12:20-13:40 Lunch

12:40-13:00 Vendor Workshop
永續發展－綠色化學工作流程探索(Sustainability-Green Chemistry Worflow)

13:40-14:20 Session 2 – *Heterocycles and Electrochemical Catalysis*
Chair: Nopporn THASANA

13:40 Invited Lecture-04: Jiun-Jie SHIE
Academia Sinica, Taiwan
Molecular Editing of 5-Alkynyl 1,2,3-Triazines Through a Skeletal Recasting Approach: Flexible Synthesis of Functionalized Pyrroles, Furans and Thiophenes

14:00 Invited Lecture-05: Seiji SUGA
Okayama University, Japan
Cyanomethylation of Aldehydes on Electrochemical Microflow: Utility of Machine Learning-Assisted Reaction Condition Exploration

14:20-16:00 Poster Session B

14:20 One-minute Poster Presentations (PB)

15:00 Poster Session B & Coffee Break

PB-01	Eun Joo KANG	"Iron Redox Catalysis in Radical Cation Cycloaddition Reactions"
PB-02	John CHU	"Lasso peptide MccJ25 as a supramolecular scaffold"
PB-03	Atsushi MINAMI	"Total Biosynthesis of Melleolides; Mechanistic Analysis of the Multi-Functional GMC oxidase Mld7"
PB-04	Pauline CHIU	"(4+3) Cycloadditions of Oxetanyl and Azetidinyl Enolsilanes"
PB-05	Ryo TANAKA	"Borataanthracenide: a novel type of counteranion for addition polymerizations"
PB-06	Guo-Ming HO	"Stereoconvergent Synthesis of Allylsilanes from an *E*/*Z* Mixture of Alkenyl Ethers *via* Ni/Ru Catalysis"

PB-07	Takanori SHIMA	"Hydroamination of Alkenes with Dinitrogen and Titanium Polyhydrides"
PB-08	Chun-Cheng LIN	"Controllable Enzymatic Synthesis of Natural Asymmetric Human Milk Oligosaccharides"
PB-09	Yosuke ASHIKARI	"In-Line Analysis of Reactive Intermediates in Flow Microreactors: A Flash Monitoring Strategy"
PB-10	Panuwat PADUNGROS	"Base-free Acylation of Phenols and Alcohols Catalyzed by Dialkyldithiocarbamate Organocatalyst"
PB-11	Tohru OISHI	"Convergent Synthesis of the WXYZA'B'C'D'E'F' Ring Segment of Maitotoxin"
PB-12	Day-Shin HSU	"Synthetic Studies Towards Phellinusfurans A and B"
PB-13	Songyi LEE	"Two Strategies to Enhance the Therapeutic Potential of Coumarin-based fluorophore: Integration of a Protonatable Moiety and BSA-Mediated Nanoparticle Formation"
PB-14	Shintaro ISHIDA	"Dearomative Cycloaddition of *N*-Heteroaromatic Compounds with a Divalent Silicon Species"
PB-15	Chau Ming SO	"Rational Design of Alkyl-Pyrazole-Based Phosphine Ligands for Palladium-Catalyzed Chemoselective Cross-Coupling Reactions"
PB-16	Yoshiaki NAKAO	"Reductive Cross-Coupling of Phenolic or Benzylic Ethers with Chlorosilanes by Cooperative Rhodium/Lanthanum Catalysis"
PB-17	Chien-Wei CHIANG	"Photoredox and Electrochemical Catalysis for the Selective Bioconjugation"
PB-18	Bandar ALYAMI	"Development of ratiometric fluorescent probe for determination of melamine in milk and infants' formulas based on dual-emissive nature of carbon dots and sulfhydryl-modified copper nanoclusters"
PB-19	Fumika YAKUSHIJI	"Development of novel chemical probes targeting a histone methyltransferase"
PB-20	Cheon-Gyu CHO	"Asymmetric Intramolecular Diels-Alder Reactions of Dienophile-tethered 2-Pyrones for the Total Synthesis of Lycopladine A, Cyanthiwigin B, and Platensimycin"
PB-21	Ching Tat TO	"Mechanochemical Aromatic Halogenation Enabled by Ball-Milling"
PB-22	Yoshihiro NISHIMOTO	"The Transformation of C–F Bond Mediated by Photocatalyst and Lewis Acid"
PB-23	Wen-Tai LI	"Divergent Synthesis of Oxa- and Azatricyclic Compounds from g-Alkynyl-1,3-diketones"
PB-24	Kazuya KANEMOTO	"N-Terminal-Specific Dual Modification of Peptides via [3+2] Cycloaddition"
PB-25	Ken Cham-Fai LEUNG	"Self-assemblies of Janus Nanosheets"
PB-26	Yasushi YOSHIDA	"Chiral Halonium Salt Catalysis Driven by Halogen Bonding"
PB-27	Yen-Chun LEE	"A kinetic-controlled chemoselective peptide macrocyclization approach to access the cyclization mode and topological diversity"

PB-28	Punlop KUNTIYONG	"Enantiodivergent Synthesis of Lycorine and Cephalotaxine from L-Aspartic acid"
PB-29	Yen-Ku WU	"Palladium-Catalyzed Direct γ'-Arylation of Cyclic Vinylogous Esters for Strategic Synthesis of α-Arylcycloalkenones"
PB-30	Ye ZHU	"Inherently chiral cavitands through ionic catalyst-controlled cross-coupling"

16:00-16:40 **Session 3 –** *Electrochemical and Flow Chemistry*

Chair: Go HIRAI

16:00 **Invited Lecture-06: Hyunwoo KIM**

Pohang University of Science and Technology, Korea

Electrochemistry Unlocks New Possibilities in Difluoromethylation of Alkenes

16:20 **Invited Lecture-07: Wei-Yu LIN**

Kaohsiung Medical University, Taiwan

Selective C-N Bond Cleavage to Unlock Amides Bond in Batch and Continuous Flow Processes

16:40-17:20 **Session 4 –** *Metal-Organic Framework and Functional π-Conjugated Systems*

Chair: Yen-Ku WU

16:40 **Invited Lecture-08: Jian HE**

The University of Hong Kong, Hong Kong

Developing Framework-Supported Transition-Metal Catalysts for Organic Synthesis

17:00 **Invited Lecture-09: Hiroshi SHINOKUBO**

Nagoya University, Japan

Extremely Close π-Stacking of Antiaromatic Porphyrins Through Double Bonding

17:20-18:30 **Transportation**

18:30 **Friendship Dinner 1**

豐 FOOD 海陸百匯

Sunday, Dec 01, 2024

International Conference Hall, 3F

9:00-10:00 **Session 5 –** *Total Synthesis of Natural Product*

Chair: Eun Joo KANG

9:00 **Invited Lecture-10: Masaru ENOMOTO**

Tohoku University, Japan

Biomimetic Total Synthesis of (–)-Rossinone B

9:20 **Invited Lecture-11: Young Ho RHEE**

Pohang University of Science and Technology, Korea

De novo Synthesis of 2-Deoxyoligosaccharide Natural Products

9:40 **Invited Lecture-12: Hayato ISHIKAWA**

Chiba University, Japan

Bioinspired Total Syntheses of Monoterpenoid Indole Alkaloids

10:00-11:40 **Poster Session C**

10:00 **One-minute Poster Presentations (PC)**

10:40 **Poster Session C & Coffee Break**

PC-01	Pawaret LEOWANAWAT	"Color-Tunable Fluorescent Heptagon-Embedded Polycyclic Aromatic Dicarboximides"
PC-02	Toi KOBAYASHI	"Oxygen-Embedded Quinoline Oligomers for A New Entry to Polydentate Ligands"
PC-03	Chin-Fa LEE	"Cesium Carbonate-Catalyzed Thiolation of Phosphonothioates"
PC-04	Chung Whan LEE	"Tailoring the Degradation of Cyano-arene based Photocatalysts for Enhanced Visible-Light-Driven Halogen Atom Transfer"
PC-05	Kazuaki ISHIHARA	"Oxidative Dearomative Coupling of Electron-deficient Arenols Catalyzed by Quaternary Ammonium Hypohalites"
PC-06	Woo-Jin YOO	"Synthesis of *ortho*-Substituted Phenol Bioisosteres via SmI_2-Mediated Reductive Cyclization Reactions"
PC-07	Gavin Chit TSUI	"Synthesis and Application of Well-Defined $[Ph_4P]^+[Cu(CF_2CF_3)_2]^-$ Complex as a Versatile Pentafluoroethylating Reagent"
PC-08	Yi-Tsu CHAN	"Building Complexity: Advanced Self-Assembly Strategies for Supramolecular Architectures"
PC-09	Ken OHMORI	"Stereoselective Transformation of Prochiral Sulfenate Anions to Chiral Sulfoxides: Mechanism and Applications"
PC-10	Chunyan CHI	"Fully Conjugated Carbon Nanobelts"

PC-11	Cheng-Che TSAI	"Stereodivergent Synthesis of Chiral 1,3-Disubstituted Isoindolines via Palladium/Brønsted Acid-Catalyzed Intramolecular Allylation"
PC-12	Yosuke TANI	"Fast and Efficient Organic Room-Temperature Phosphorescence in Solution"
PC-13	Yongseok KWON	"Catalytic Dynamic Kinetic Resolutions for the Synthesis of Axially Chiral Biaryls"
PC-14	Tsuyoshi MITA	"Photocatalytic Ring-Opening Diphosphination of Strained Cyclic Molecules: Experimental and Computational Insights"
PC-15	Che-Sheng HSU	"Iodide-umpolung catalytic system for nontraditional amide coupling from nitroalkanes and amines"
PC-16	Poramate SONGTHAMMAWAT	"Intramolecular Diels–Alder Approach toward Tricyclic 9–Methyl–7–aryl–tetrahydro–6*H*–benzo]c [chromen–6–ones of Morusalisin A"
PC-17	Jun SHIMOKAWA	"Development of -Si(pan), a Seven-Membered Dialkoxysilyl Unit"
PC-18	Duen-Ren HOU	"Nitrosonium ion Initiated Halogenation and C-N Bond Formation of Arenes"
PC-19	Zhenpin LU	"Boosting the reactivity of borate anions"
PC-20	Ching-Ching YU	"Substrate-controlled Glycosylation for the Enzymatic Synthesis of Asymmetrically Branched Human Milk Oligosaccharides"
PC-21	Hironori OKAMURA	"Synthetic study of stagonosporyne G and structurally related natural products"
PC-22	Hsuan-Hung LIAO	"contra-Thermodynamic Positional Isomerization: From Enoates to Alkenyl α-Stereogenic Esters."
PC-23	Sunwoo LEE	"Selective Isomer Synthesis of N-Acyl-Sulfonyl Hydrazides: The Impact of Base Counter Cations in Palladium-Catalyzed Aminocarbonylations."
PC-24	Kosuke NAMBA	"Total Synthesis of Palau'amine"
PC-25	Wai Chung FU	"Stereoselective Synthesis of Polysubstituted Pyrrolidines by a Photoredox-catalyzed Cascade"
PC-26	Yoichi M. A. YAMADA	"Sustainable Chemistry Unleashed: Continuous-Flow Ritter Reaction with a Recyclable Polymeric Acid Catalyst"
PC-27	Gary Jing CHUANG	"Oxidative Scission of Bicyclo[2.2.2]octenones: Untying the α,α-dimethoxycarbonyl"
PC-28	Kosuke DODO	"Simple purification of small-molecule-labelled peptides via palladium enolate formation from β-ketoamide tags"
PC-29	Cheoljae KIM	"Chiral Degradable Polymers *via* Metathesis Polymerizations"
PC-30	Po-Chiao LIN	"Dihydroquinolin-4-imine (DQI) mediated fluorogenic strategy for to the study of cell migration"

11:40-12:20 **Session 6 –** *Organometallic and Asymmetric DNA Catalysis*

Chair: Gavin Chit TSUI

11:40 **Invited Lecture-13: Ru-Yi ZHU**

National University of Singapore, Singapore

New Advances in Asymmetric DNA Catalysis

12:00 **Invited Lecture-14: Jean-Ho CHU**

National Taitung University, Taiwan

Recent Advances in Palladium-Mediated C-H Bond Activation and Functionalization

12:20-13:40 **Lunch**

13:40-14:20 **Session 7 –** *Carbon-Heteroatom Bond Formations*

Chair: Chin-Fa LEE

13:40 **Invited Lecture-15: Takuya HASHIMOTO**

RIKEN, Japan

C-N Bond Formations Enabled by an N-Fluorosulfonyl Group

14:00 **Invited Lecture-16: Rungnapha SAEENG**

Burapha University, Thailand

The new methods of C-S, C-Se and C-C bond formation for functionalization of indole

14:20-16:00 **Poster Session D**

14:20 **One-minute Poster Presentations (PD)**

15:00 **Poster Session D & Coffee Break**

PD-01	Kenward VONG	"Bioorthogonal release and synthesis of anticancer drugs via propargylbenzoxime (PBO) precursors"
PD-02	Che-Jen LIN	"Stimuli-Responsive Luminescent Materials: Harnessing Fluorous Interactions and Strained Azacyclic Substituents for Tunable Emission"
PD-03	Hiroaki ITOH	"Functional Enhancement of Menaquinone-Targeting Antibiotics by a Solid-Phase Total Synthesis-Based Approach"
PD-04	Nopporn THASANA	"Metabolomics Analysis of Selaginella Plants: Discovery of Bioactive Biflavonoids and Chemotaxonomic Markers"
PD-05	Po-Ting CHOU	"The dye-based sensor detected silver ions using either a liquid or solid system"
PD-06	Junichiro YAMAGUCHI	"Heteroaromatic Swapping in Aromatic Ketones"
PD-07	Sunkyu HAN	"Natural Product-Inspired Molecular Photoswitch"
PD-08	Haruhiko FUWA	"Iriomoteolide-1a and -1b: Structure Elucidation by Integrating NMR Spectroscopic Analysis, Theoretical Calculation, and Total Synthesis"

PD-09	Sheng-Kai WANG	"Synthetic Polyproline Nanoscaffolds for Manipulation of Multivalent Carbohydrate Interactions"
PD-10	Hugh NAKAMURA	"Atroposelective Total Synthesis of Cihunamide B"
PD-11	Jin Kyoon PARK	"Electrochemical transformation of oximes and hydrazones into 5- and 7-membered heterocycles and their further modifications"
PD-12	Yan-Duo LIN	"Judicious Molecular Design of 5H-Dithieno[3,2-b:2' ,3' -d]pyran-based Hole-Transporting Materials for Highly Efficient and Stable Perovskite Solar Cells"
PD-13	Takaaki SATO	"Toward Concise Total Synthesis of Complex Alkaloids"
PD-14	Jen-Chieh HSIEH	"Nickel-Catalyzed Denitrogenative Cyclization of Nitrile-Containing 1,2,3-Benzotriazin-4(3*H*)-ones for the Synthesis of Polycyclic Quinazolinone Alkaloids"
PD-15	Yusuke KURODA	"Mono-Acylation of Diols Enabled by Resin Catalysis"
PD-16	Cheuk Lam HO	"Molecular Engineering of Functional Materials for Photocatalytic Hydrogen Generation"
PD-17	Tsz Fai LEUNG	"Advancing First-row Transition Metal Catalysis with Phosphine-Stabilized Dicarbon Ligands"
PD-18	Aya OHNO	"Development of Convoluted Polymeric Palladium Catalysts and Polymeric Auxiliary Materials for Continuous-Flow Suzuki-Miyaura Coupling"
PD-19	Aurapat NGAMNITHIPORN	"Sultines as *o*-Quinodimethane Precursors in hetero-Diels–Alder Reactions"
PD-20	Hidetoshi TOKUYAMA	"Divergent Total Synthesis of Discorhabdin Alkaloids"
PD-21	Chien-Tien CHEN	"Vanadyl Species-Catalyzed, Asymmetric Radical Type 1,2-Oxyphosphinonylation and Sulfenylation to Styrenes"
PD-22	Hyunwoo KIM	"Multi-Substrate Chiral Screening by ^{19}F NMR"
PD-23	Tadachika MIYASAKA	"Synthetic studies on a proposed biosynthetic intermediate of tetrodotoxin"
PD-24	Hong Geun LEE	"Halogen Atom Transfer-Induced Homolysis of C–F Bonds"
PD-25	Tetsuhiro NEMOTO	"Total Synthesis of Dragmacidins G and H"
PD-26	Hsiang-Yu CHUANG	"Total Synthesis of 13-Deoxyserratine"
PD-27	Michinori SUGINOME	"Helical-polymer-based Chirality-switchable Phosphoramidite Ligand for Asymmetric Catalysis"
PD-28	Chih-Ming CHOU	"Carboxylate-Directed Oxidative Annulation via C(Alkenyl)—H Activation/Double Alkyne Insertion/1,4-Pd Migration: Synthesis of Highly Functionalized Naphthalenes"
PD-29	Jiann-Jyh HUANG	"Copper(I)-Catalyzed Tandem Reactions of 2'-Substituted 2-(2-Bromophenyl)-N-phenylacetamides for the Synthesis of New Tetracyclic Anticancer Heterocycles"
PD-30	Chong TIAN	"Synthesis of Mechanically Planar Chiral (MPC) Polyrotaxanes via Artificial Molecular Pump"

16:00-16:40 **Session 8 -** *Carbon-Heteroatom Bond Formations and Photocatalytic Reaction*

Chair: Mamoru TOBISU

16:00 **Invited Lecture-17: Chien-Fu LIANG**

National Chung Hsing University, Taiwan

Sodium Thiosulfate Mediated the C-S/C-O/C-N Bond Formation

16:20 **Invited Lecture-18: Jumreang TUMMATORN**

Chulabhorn Research Institute, Thailand

Leveraging Ortho-Alkynylarylcarbonyl Derivatives for the Synthesis of Structurally Diverse Chemical Compounds

16:40-17:20 **Session 9 –** *Photocatalysis*

Chair: Chau Ming SO

16:40 **Invited Lecture-19: Keisuke ASANO**

Hokkaido University, Japan

Photocatalytic Bromination toward Biomolecular Labeling

17:00 **Invited Lecture-20: Anna LEE**

Jeonbuk National University, Korea

Hydrosulfonylation of Alkynes for Stereodivergent Synthesis of Vinyl Sulfones

17:20-18:30 **Transportation**

18:30 **Friendship Dinner 2**

A: 龍都酒樓 中山店 (Dragon Restaurant)

B: 享鮮餐廳 南港分店

C: 公館薪僑園水源婚宴會館 (La Marée)

D: 微風崔妮傑恩餐廳 中研院店 (Trine & Zen Breeze)

Monday, Dec 02, 2024

International Conference Hall, 3F

9:00-9:40 **Session 10 –***Asymmetric Catalysis*

Chair: Jeung Gon KIM

9:00 **Invited Lecture-21: Yu ZHAO**

National University of Singapore, Singapore

Enantioconvergent Redox-Neutral Functionalization of Alcohols via Borrowing Hydrogen Catalysis

9:20 **Invited Lecture-22: Takahiko AKIYAMA**

Gakushuin University, Japan

Chiral Phosphoric Acid−Palladium(II) Complex Catalyzed Asymmetric Desymmetrization of Biaryl Compounds by C(sp3)−H Activation

9:40-10:20 **Session 11 –** *Conjugated Nanobelts and Photocatalysis*

Chair: Tetsuhiro NEMOTO

9:40 **Invited Lecture-23: Qian MIAO**

The Chinese University of Hong Kong, Hong Kong

Recent Progress in the Chemistry of Conjugated Nanobelts

10:00 **Invited Lecture-24: Charnsak THONGSORNKLEEB**

Chulabhorn Research Institute, Thailand

Electron Donor-Acceptor Photocatalyst in the First Photochemical Machetti–De Sarlo Reaction

10:20-11:00 **Coffee Break**

11:00-11:40 **Session 12 –** *Bioorganic Chemistry and Macromolecules*

Chair: Rong-Jie CHEIN

11:00 **Invited Lecture-25: Min Hee LEE**

Chung-Ang University, Korea

Design and Synthesis of Organic Compounds Exhibiting Fluorescence Response to Biomolecules and Their Applications in Living Systems

11:20 **Invited Lecture-26: Ken KAMIKAWA**

Osaka Metropolitan University, Japan

Stereoselective Synthesis of Noncentral Chiral Molecules Using Arynes or Substrates Derived from Arynes

11:40-12:20 **Session 13 –** *Functional Organic Materials*

Chair: Chunyan CHI

11:40 **Invited Lecture-27: Yen-Ju CHENG**

National Yang Ming Chiao Tung University, Taiwan

Development of C-Shaped ortho-Benzodipyrrole-based A-D-A type Acceptors for High-Performance Organic Photovoltaics

12:00 **Invited Lecture-28: Takayuki IWATA**

Kyushu University, Japan

Synthesis of Higher Order Iptycenes Using Ambident Anthracene

12:20-12:40 **Lunch**

12:40-18:30 **Excursion**

Kavalan Distillery

18:30 **Banquet & Award Ceremony**

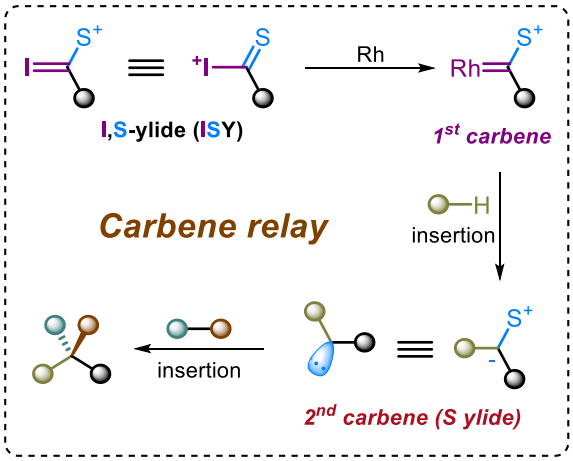
雅悅會館 (Grande Luxe Banquet)

IL-01

Development of Iodonium Sulfoxonium Ylides for Carbene Relay Catalysis

Li Li, Zhaofeng Wang, Fengjin Wu, Yichi Zhang, Yajie Xing, Ji-Wei Zhang and Yong Huang*
Department of Chemistry, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong SAR, China
E-mail: yonghuang@ust.hk

Our research group is focused on advancing highly selective catalytic transformations, particularly those involving well-defined transient intermediates. Carbenes, in particular, represent a unique class of reactive species, offering significant potential for innovation in synthetic organic chemistry. To better understand and exploit the versatile reactivities of these divalent species, we have developed novel approaches to carbene catalysis that enhance the structural diversity of carbene-mediated transformations. In this symposium, I will present our recent work on the development of a novel reagent, iodonium sulfoxonium ylides (ISYs), for carbene relay catalysis. ISYs function as bis-carbene precursors, sequentially generating two transient carbene species and enabling highly chemo- and stereoselective multi-insertion reactions.



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[2] Li, L.; Mi, C.; Huang, G.; Huang, M.; Zhu, Y.; Ni, S.-F.; Wang, Z.; Huang, Z. *Angew. Chem. Int. Ed.* **2023**, *62*, e202312793.
[3] Wu, F.; Zhang, Y.; Zhu, R.; Huang, Y. *Nat. Chem.* **2024**, *16*, 132–139.
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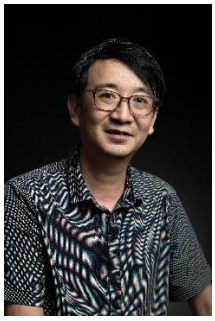

Yong Huang (黄湧). Yong Huang received his bachelor's degree from Peking University in 1997 and his Ph.D. in Organic Chemistry from the University of Chicago in 2004 under Prof. Viresh H. Rawal. He then joined Prof. David MacMillan's group at Caltech as a postdoctoral researcher. Moving to industry, he worked as a senior medicinal chemist at Merck Research Laboratories in Rahway, NJ, from 2004 to 2009. In 2009, he became an independent PI at Peking University Shenzhen Graduate School and recently moved to the Hong Kong University of Science and Technology (HKUST). He is currently a Professor in the Department of Chemistry of HKUST. His research group explores various topics in organic and medicinal chemistry.

IL-02

The Chemistry of Cyclic (Alkyl)(Amino)Aluminium(I) Species

Rei KINJO*

School of Chemistry, Chemical Engineering and Biotechnology,
Nanyang Technological University, Singapore
21 Nanyang Link, Singapore 637371
Email: rkinjo@ntu.edu.sg

Since the groundbreaking report by Aldrich and Goichoechea in 2018 that the isolation of a nucleophilic aluminium(I) anion is attainable,[1] a handful of anionic Al(I) species have been prepared and structurally authenticated,[2] most of which are diamino- and dialkyl-substituted derivatives. In this presentation, we report the synthesis, structure, and computational studies of cyclic (alkyl)(amino)aluminium(I) anions based on the five-membered ring scaffold.[3] The dicoordinate aluminum center features both a lone pair of electrons and an unoccupied p orbital (**Figure 1**), rendering them isoelectronic with carbenes. The reactivity including bond activation, small molecule activation, cyclization, as well as the formation of an unsaturated bond will be introduced. Furthermore, other relevant results will also be presented.[4]

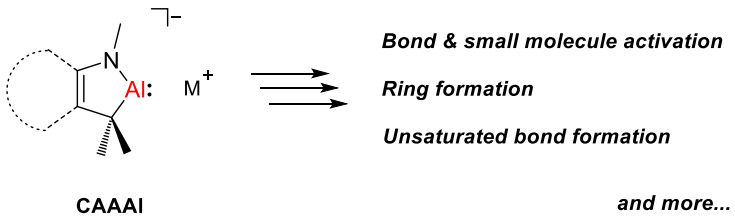

Figure 1. Schematic drawing of a cyclic (alkyl)(amino)aluminium(I) anion and the examples of its reactivity.

Reference

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[2] (a) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2021**, *60,* 1702. (b) M. P. Coles, M. J. Evans, *Chem. Commun.* **2023**, *59,* 503.
[3] K. Koshino, C. Yan, R. Kinjo, (a) *J. Am. Chem. Soc.* **2020**, *142,* 9057. (b) *Organometallics* **2021**, *39,* 4183. (c) *J. Am. Chem. Soc.* **2021**, *143,* 18172. (d) *Angew. Chem. Int. Ed.* **2022**, *61,* e202211800.
[4] C. Yan, K. Koshino, L. Zhu, R. Kinjo, *Nat. Synth.* **2024**, *3,* 858.

Rei KINJO (金城 玲).

University of Tsukuba: (PhD 2007).
University of California, Riverside: (2007-2011)
Nanyang Technological University: (2007 Nanyang Assistant Professor) (2017 Associate Professor) (2020 Full Professor)

Main group chemistry and catalysis.

IL-03

Photocatalytic Single-atom Transmutation

Yoonsu Park*
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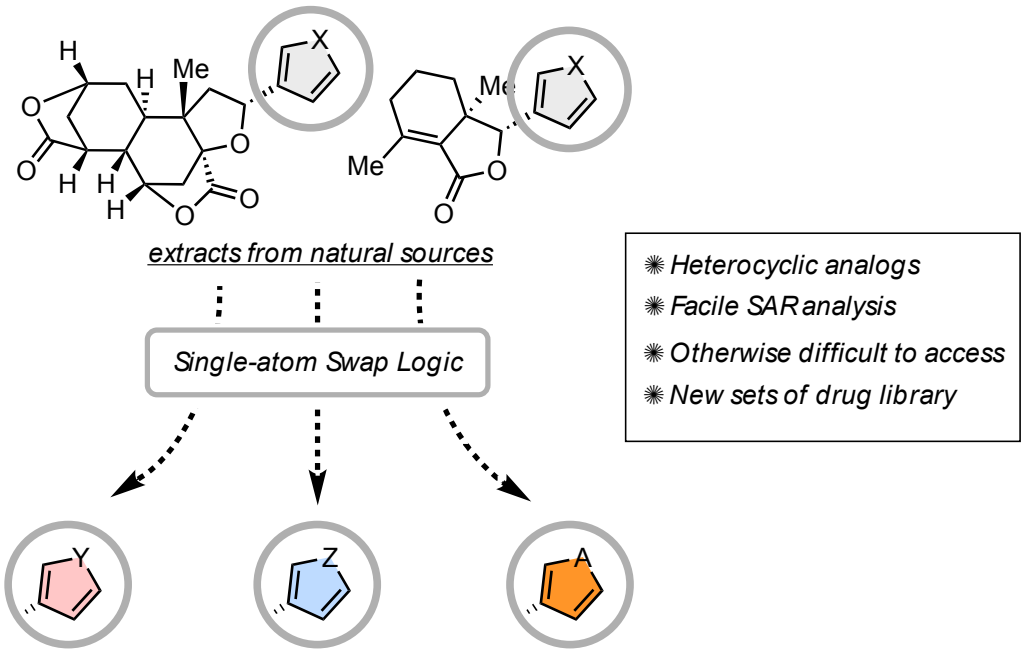
A single atom in aromatic heterocycles confers unique properties and activity of functional molecules, such as natural products and pharmaceutical drugs. However, systematic evaluation of the single-atom effect has posed a synthetic challenge, and multi-step procedures have been inevitable based on classical 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.



Reference
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Yoonsu Park (박윤수). KAIST (Ph.D., 2019, advisor: Sukbok Chang). Princeton University (2019-2021, advisor: Paul J. Chirik). KAIST (2022-to date). Organic, organometallic, and photochemistry.

IL-04

Molecular Editing of 5-Alkynyl 1,2,3-Triazines Through a Skeletal Recasting Approach: Flexible Synthesis of Functionalized Pyrroles, Furans and Thiophenes

Jiun-Jie Shie,* Hsiang-Wen Chen, Chia-Hao Chang and Wan-Hsuan Liu
Institute of Chemistry, Academia Sinica, Taipei, Taiwan, 11529
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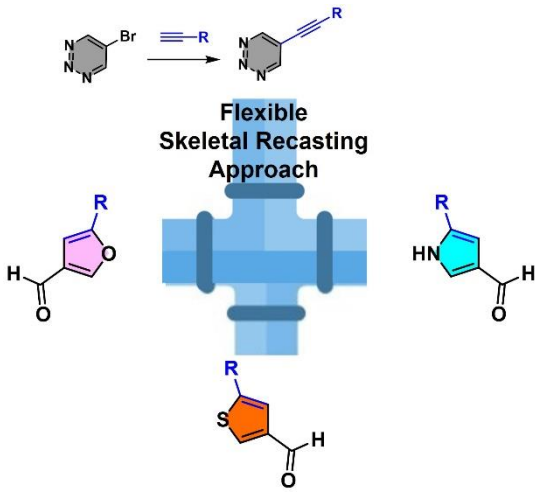
Triazines represent a significant class of heterocycles characterized by the presence of three nitrogen atoms. In contrast to 1,3,5- and 1,2,4-triazines, 1,2,3-triazines have not been as extensively studied due to their electron-deficient ring system, which is considered the least stable. Recently, we demonstrated that 5-bromo-1,2,3-triazine can be efficiently functionalized under mild reaction conditions to access various nitrogen-containing building blocks for organic synthesis.[1,2] In this report, we present a skeletal recasting approach using 5-alkynyl-1,2,3-triazines for the switchable construction of functionalized pyrroles, furans, and thiophenes. This flexible and adaptable method for heterocycle editing involves the nucleophilic ring-opening of triazines, followed by subsequent annulation. The process can be finely tuned by adjusting the sustainable reaction conditions. This protocol offers several advantages, including substrate availability, ease of handling, and atom economy, providing a new perspective on the efficient synthesis of five-membered aromatic heterocycles.[3,4]



Reference
[1] Wu, C.-C.; Ambre, R.; Lee, M.-H.; Shie, J.-J. *Org. Lett.* **2022**, *24*, 2889–2893.
[2] Ou Yang, C.-H.; Liu, W.-H.; Yang, S.; Chiang, Y.-Y.; Shie, J.-J. *Eur. J. Org. Chem.* **2022**, e202200209.
[3] Wang, Y.-C.; Yu, Y.-C.; Wu, C.-C.; Liu, W.-H.; Shie, J.-J. *Green Chem.* **2024**, under revision.
[4] Chen, H.-W.; Liu, W.-H.; Chang, C.-H.; Shie, J.-J. *Org. Lett.* **2024**, submitted.

Jiun-Jie Shie (謝俊結). National Taiwan University (Ph.D., 2005). Assistant Research Fellow (2015–2022). Associate Research Fellow (2023–present). [Field of research] Organic Chemistry and Chemical Biology.

IL-05

Cyanomethylation of Aldehydes on Electrochemical Microflow: Utility of Machine Learning-Assisted Reaction Condition Exploration

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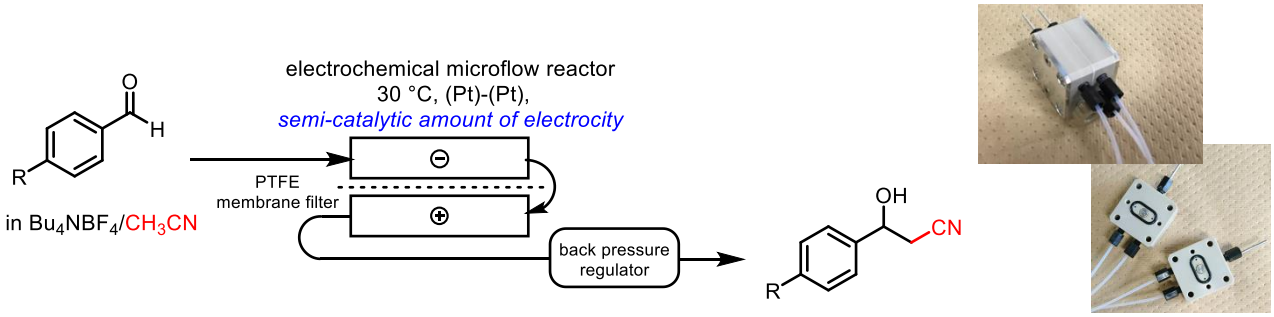
Cyanomethylation of carbonyl compounds affords a β-hydroxy nitrile, which is very useful motif in synthetic organic chemistry. Deprotonation of acetonitrile by a strong base affords a cyanomethyl anion, and the anion can often be used to various transformations including nucleophilic addition. On the other hand, organic electrosynthesis has attracted attention in recent years as an energy-efficient and environmentally friendly method that does not use chemical reactants. Although several electrochemical methods have also been reported to achieve cyanomethylation of carbonyl compounds, dehydration from an adduct as a major side reaction is a significant issue that needs to be prevented. We herein report the cathodic reduction-promoted cyanomethylation of carbonyl compounds in acetonitrile on the electrochemical microflow reactor [1]. The use of flow reactor enables a significant increase of the reaction efficiency with a suppression of side reactions such as dehydration. We also demonstrated the machine learning-assisted reaction condition exploration to find the "best" reaction conditions for each starting material with various functional groups [2]. The constructed model well suggested the reasonable reaction conditions with various aromatic aldehydes. Our cyanomethylation reaction was completed within a semi-catalytic amount of electricity, which conflicted with the conventional basic conditions and the electro-generated base mechanism.



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[2] (a) (a) Sato, E.; Fujii, M.; Tanaka, H.; Mitsudo, K.; Kondo, M.; Takizawa, S.; Sasai, H.; Washio, T.; Ishikawa, K.; Suga, S. *J. Org. Chem.* **2021**, *86*, 16035–16044; (b) Sato, E.; Tachiwaki, G.; Fujii, M.; Mitsudo, K.; Washio, T.; Takizawa, S.; Suga, S. *Org. Process Res. Dev.* **2024**, *28*, 1422–1429.

Seiji SUGA (菅　誠治). Nagoya University (Doctor of Science, 1995). JSPS Postdoc, University of Oxford (1995). Assistant Professor, Kyoto University (1996). Lecturer, Kyoto University (1999). Associate Professor, Kyoto University (2003). Professor, Okayama University (2008). Senior Vice President, Okayama University (2023) [Field of research] Organic Electrochemistry, Flow Chemistry, Asymmetric Catalysis

IL-06

Electrochemistry Unlocks New Possibilities in Difluoromethylation of Alkenes

Seonyoung Kim and Hyunwoo Kim*
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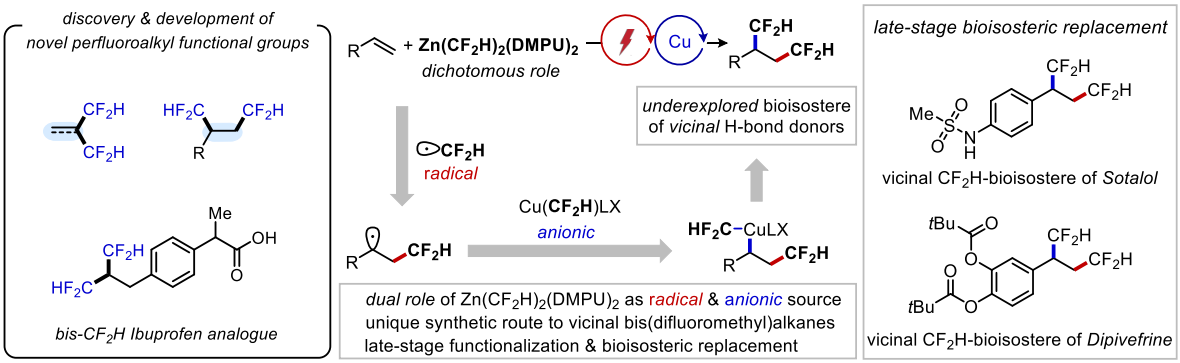
The difluoromethyl group (CF_2H) serves as an essential bioisostere in drug discovery campaigns according to Lipinski's Rule of 5 due to its advantageous combination of lipophilicity and hydrogen bonding ability, thereby improving the ADME properties. However, despite the high prevalence and importance of vicinal hydrogen bond donors in pharmaceutical agents, a general synthetic method for doubly difluoromethylated compounds in the vicinal position is absent. Here we describe a copper-electrocatalyzed strategy that enables the vicinal bis(difluoromethylation) of alkenes. By leveraging electrochemistry to oxidize $Zn(CF_2H)_2(DMPU)_2$–a conventionally utilized anionic transmetalating source–we paved a way to utilize it as a CF_2H radical source to deliver the CF_2H group in the terminal position of alkenes. Mechanistic studies revealed that the interception of the resultant secondary radical by a copper catalyst and followed reductive elimination is facilitated by invoking Cu(III) intermediate, enabling the second installation of CF_2H group in the internal position. The utility of this electrocatalytic 1,2-bis(difluoromethylation) strategy has been highlighted through the late-stage bioisosteric replacement of pharmaceutical agents such as Sotalol and Dipivefrine.



Electrocatalytic Bis(difluoromethylation)

Reference

[1] Kim, S.; Kim, H. *J. Am. Chem. Soc.* **2024**, *146,* 22498–22508.
[2] Kim, S.; Hwang, K. H.; Park, H. K.; Kwak, J.; Lee, H.; Kim, H. *Commun. Chem.* **2022**, *5*, 96.
[3] (a) Sap, J. B. I.; Meyer, C. F.; Straathof, N. J. W.; Iwumene, N.; Am Ende, C. W.; Trabanco, A. A.; Gouverneur, V. *Chem. Soc. Rev.* **2021**, *50*, 8214-8247. (b) Meanwell, N. A. *J. Med. Chem.* **2011**, *54*, 2529-2591. (c) Sessler, C. D.; Rahm, M.; Becker, S.; Goldberg, J. M.; Wang, F.; Lippard, S. J. *J. Am. Chem. Soc.* **2017**, *139*, 9325-9332.

Hyunwoo Kim (김현우). KAIST (B.S., 2013). KAIST (Ph.D., 2018) Cornell Univ. (Postdoc, 2019-2020). Ewha Womans University (Assistant Professor, 2020-2022). Pohang University of Science and Technology (POSTECH) (Assistant Professor, 2022-present). Research field: [Synthetic Organic Methodology, Organic Electrosynthesis].

IL-07

Selective C-N Bond Cleavage to Unlock Amides Bond in Batch and Continuous Flow Processes

Wei-Yu Lin Group
Department of Medicinal and Applied Chemistry, Kaohsiung Medical University

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The development of twisted amides has been an essential tool that served as the most beneficial application, significantly strengthening the utility of amide bond functional group interconversions. Recently, a novel methodology that employs selective ring opening followed by C-N cleavage, which is a critical intermediate in the efficient construction of nitrogen-containing functional groups, was developed in my laboratory. The reaction features a common method, provides a range of valuable functional groups, is easy to perform, and tolerates a broad substrate's scope. Notably, the power of this new method was also demonstrated, and the continuous-flow method successfully affording the desired products.

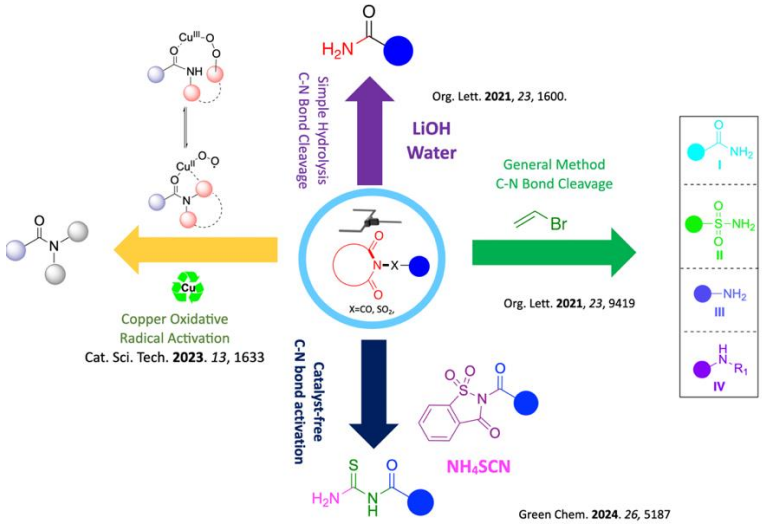

Figure 1. *Summary of C-N bond activation.*

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IL-08

Developing Framework-Supported Transition-Metal Catalysts for Organic Synthesis

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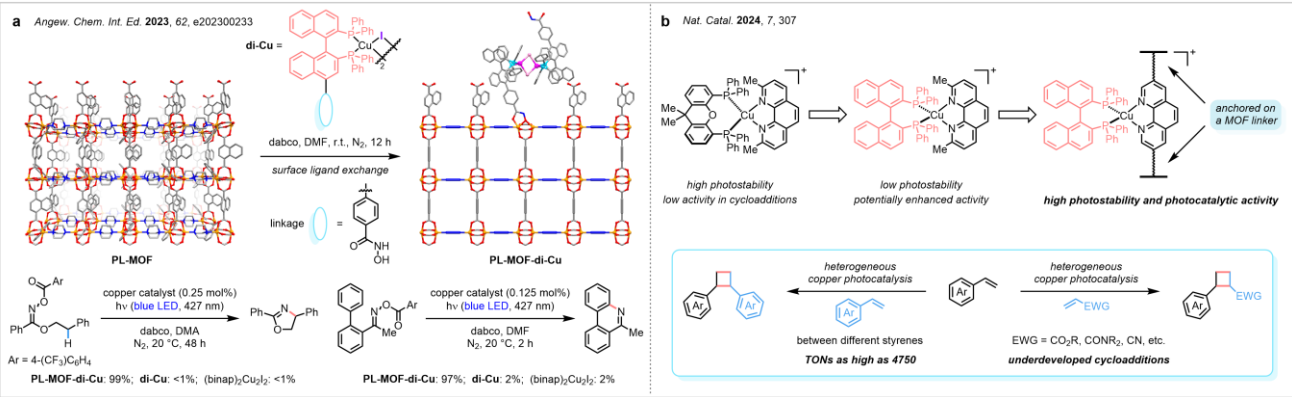
The development of heterogeneous catalysts with high activity, selectivity, and stability is essential for making catalytic organic reactions practically useful. While many organic transformations have been achieved in homogeneous catalytic systems, the need to address their synthetic limitations, such as high catalyst loadings, poor selectivity, and the use of toxic and expensive reagents, presents both challenges and opportunities for the next generation of chemists. Designing novel catalysts that marry the benefits of heterogeneous catalysis with those of homogeneous catalysis to solve long-standing challenges in organic synthesis is appealing and highly desirable. Here we develop a variety of metal–organic framework supported copper catalysts that can efficiently promote electron/energy transfer-mediated reactions under visible light irradiation. The newly developed catalysts exhibit outstanding stability and recyclability due to catalyst-site isolation. Upon heterogenization, the photoexcited copper(I) species show increased transition energy and lifetime, which is critical for boosting their catalytic performance. Notably, the substrate scope can be expanded beyond what was previously attainable in homogeneous catalysis. Furthermore, we employ post-synthetic metalation on covalent organic frameworks to produce a series of robust heterogeneous palladacycle catalysts for C–H activation reactions.



Metal-Organic Framework-Based Copper Photocatalytic Systems

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IL-09

Extremely Close π-Stacking of Antiaromatic Porphyrins Through Double Bonding

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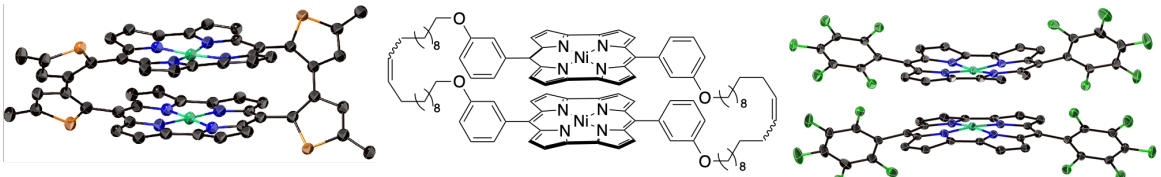
Norcorrole is a ring-contracted antiaromatic porphyrin, which lacks two *meso*-carbons from porphyrin. We have synthesized stable norcorrole Ni(II) complexes and investigated their reactivities, optical properties, and electrochemical properties, which are markedly different from aromatic porphyrins.[1] We previously reported that norcorrole dimer **1** exhibited a closely stacked orientation.[2] The remarkable proximity of the two norcorrole units is rationalized by the emergence of the stacked-ring aromaticity between two antiaromatic systems.[3]

Recently, we have prepared norcorrole cyclophane **2**.[4] Interestingly, cyclophane **2** exhibited crystal polymorphism leading to three different solid-state structures, in which the orientation of the two norcorrole units is different. Importantly, the stacked-ring aromaticity of **2** is dependent on the twist angle between two norcorrole units. Furthermore, the introduction of electron-withdrawing C_6F_5 substituents to norcorrole resulted in even a shorter stacking distance of less than 3.0 Å in **3**.[5] We have elucidated that the extremely close stacking originates from intermolecular double bonding interactions between two antiaromatic molecules.



	1	2	3
stacking distance =	3.09 Å	3.08 Å	2.97 Å

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IL-10

Biomimetic Total Synthesis of (–)-Rossinone B

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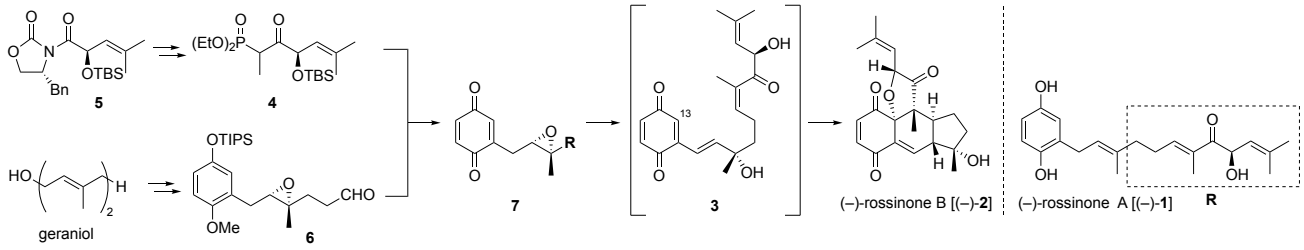
Rossinones A (**1**) and B (**2**) are meroterpenoids with several pharmacologically important biological properties such as antiproliferative and antiviral activities [1]. The biosynthetic pathway for **2** proposed by Trauner and co-workers involves the intramolecular Diels–Alder reaction of vinyl quinone derivative **3**, a potential oxidation product of **1**, followed by several further transformations [2]. Tang and co-workers also disclosed a similar biosynthetic pathway for **2** and achieved the first total synthesis of (±)-**2** utilizing the intramolecular Diels–Alder reaction of the C13-methoxy derivative of (±)-**3** [3]. However, although 12 years have passed since its first isolation, no asymmetric synthesis of **2** has been reported to date. In this conference, I will talk about a biomimetic synthesis of (–)-**2** that features a reaction cascade of **7** into (–)-**2**.

Initially, phosphonate segment **4** was prepared from a known oxazolidinone derivative **5** via the removal of an oxazolidinone moiety under moderate conditions using $Yb(OTf)_3$. Next, aldehyde segment **6** was prepared from geraniol in a five-step sequence, including the Sharpless asymmetric epoxidation. After the Horner–Wadsworth–Emmons reaction of the aldehyde segment **6** with phosphonate **4** under Toste's conditions [4], the resulting enone was converted to quinone **7**. Treatment of **7** with a base in the presence of an oxidant resulted in a reaction cascade, starting with the epoxide ring-opening of **7** and followed by the intramolecular Diels–Alder reaction of the resulting intermediate **3**, furnishing (–)-**2** in a biomimetic manner with a satisfactory yield.



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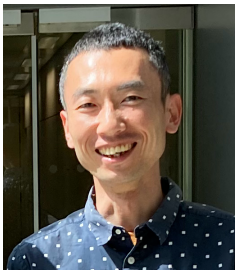

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IL-11

De novo Synthesis of 2-Deoxyoligosaccharide Natural Products

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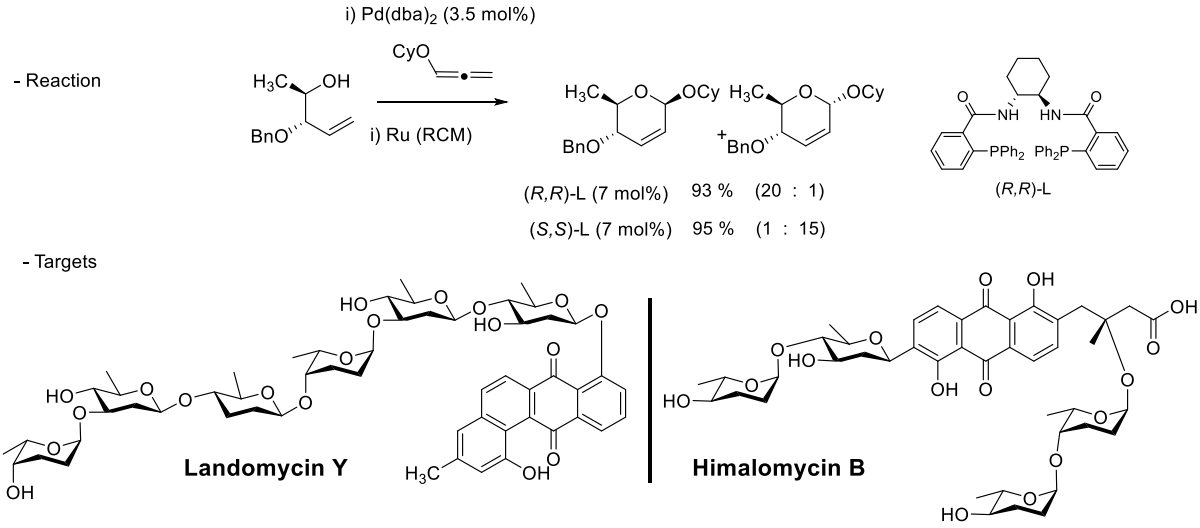
2-Deoxyoligosaccharides are found in numerous bioactive natural products as a conjugate form to structurally diverse aglycons. Both the length and the stereochemistry of the oligosaccharide moieties are known to have a profound effect on the bioactivities. Despite this significance, synthetic methods that gives an access to 2-deoxyoligosaccharide natural products are still very limited. This is mainly because the lack of hydroxyl group at the 2-position makes the anomeric stereocontrol a very difficult task. Moreover, efficient conjugation of the 2-deoxyoligosaccharide moiety to aglycon moiety raises another challenge. In this presentation, we wish to report our recent progress on the development of *de novo* deoxyoligosaccharide synthesis based upon asymmetric metal catalysis. A signature event is highlighted by the Pd-catalyzed asymmetric addition of alcohol nucleophiles to ene-alkoxyallenes, in which the anomeric selectivity is controlled by the chiral ligands (Figure 1).

Figure 1. Reaction and Targets



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IL-12

Bioinspired Total Syntheses of Monoterpenoid Indole Alkaloids

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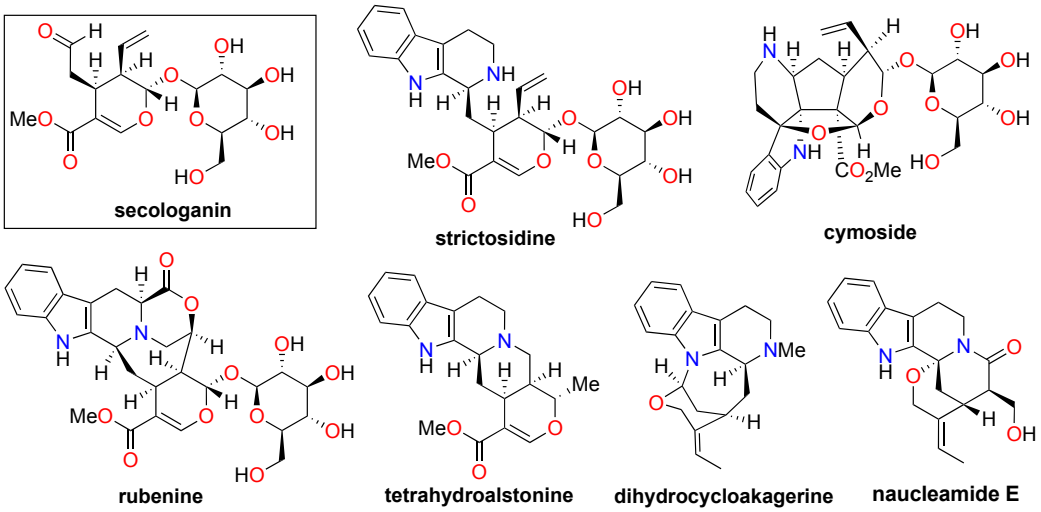
We successfully achieved a collective total synthesis of 40 secologanin-related natural products, including monoterpenoid indole alkaloids (MITAs) via bioinspired transformations, initiated by the first total synthesis of secologanin.[1] The key strategy of our secologanin synthesis was a rapid and stereoselective construction of the secologanin scaffold through an *anti*-selective organocatalytic Michael addition/Fukuyama reduction/spontaneous cyclization/Schmidt glycosylation sequence, and we obtained a key intermediate, secologanin tetraacetate, on a decagram scale in seven steps.[2] Then, Pictet-Spengler cyclization with L-tryptophan methyl ester or (*R*)-α-cyanotryptamine using secologanin tetraacetate proceeded to construct 3*S* center stereoselectivity to give 5-carboxystrictosidine and strictosidine, respectively.[2] These biosynthetic intermediates of naturally occurring alkaloids were converted into complex alkaloids, including rubenine, cymoside, tetrahydroalstonine, dihydroakagerine and naucleamide E via bioinspired transformation on the highly reactive secologanin reaction sites.[2,3]



Secologanin-related natural products

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IL-13

New Advances in Asymmetric DNA Catalysis

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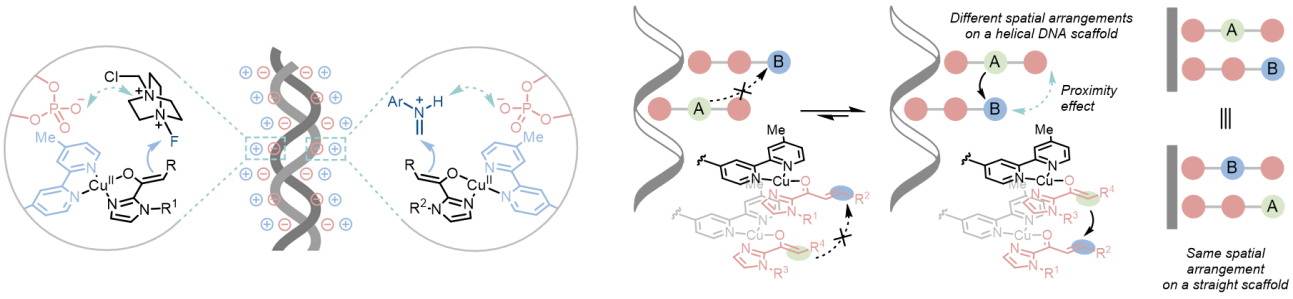
DNA is an underexplored scaffold for asymmetric catalysis, offering untapped potential due to its programmable structure, which can be engineered to adopt enzyme-like three-dimensional conformations or architectures akin to metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). A significant challenge in this area is the site-specific incorporation of co-factor-like small-molecule catalysts onto DNA without relying on highly specialized and limited solid-phase DNA synthesis techniques. In this presentation, I will first introduce a recently developed chemoenzymatic conjugation strategy that enables the incorporation of virtually any unprotected functional group into DNA at specific sites. This approach has led to the first reported example of atroposelective catalysis mediated by DNA. Building upon this method, I will explore the novel utilization of the ubiquitous phosphate backbone of DNA for ion-pairing catalysis. This represents the first instance of such catalysis using DNA phosphates, and I will elaborate on the design of a "phosphate scanning" (PS) experiment that identifies the critical phosphates directly involved in the enantio-determining steps of the reaction. Combined with computational studies, this work uncovers an intriguing mechanism in which stereoselectivity is modulated by counter cations, leading to a switch in the enantiomeric outcome. Finally, I will describe how the helical structure of DNA, when paired with a bimetallic catalytic center, introduces a new mode of stereocontrol that is distinct from traditional steric-based mechanisms. This bimetallic DNA catalyst facilitates the construction of molecules with two or three consecutive stereogenic carbon centers, offering switchable enantioselectivity, a feat currently unattainable by other catalytic systems.



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IL-14

Recent Advances in Palladium-Mediated C-H Bond Activation and Functionalization

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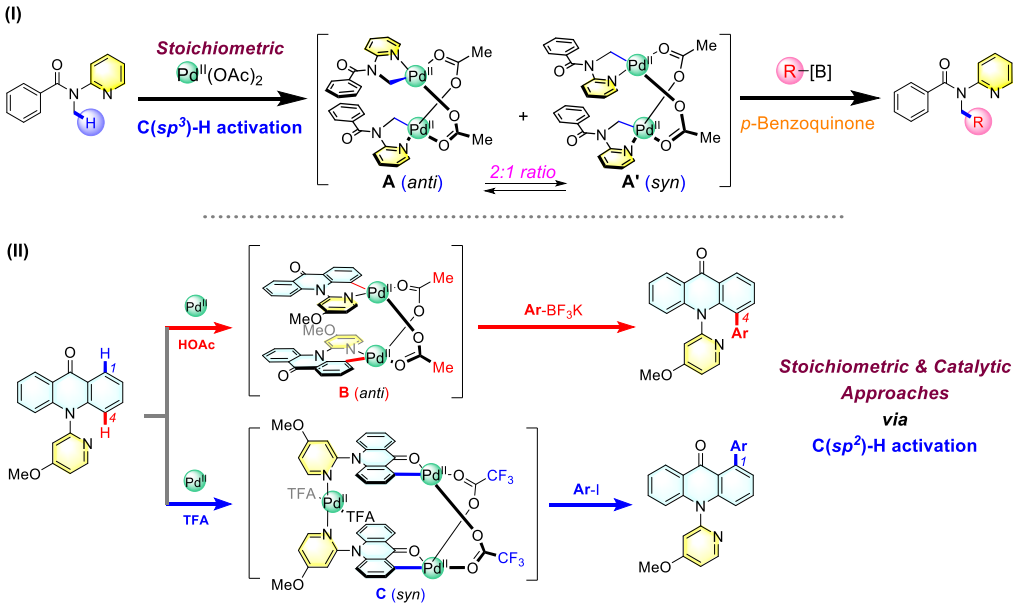
Our group has developed facile methodologies for synthesizing *N*-aryl/alkyl-CH_2-substituted *N*-(pyridin-2-yl)benzamides and 4- and 1-aryl/alkyl-substituted 9(10*H*)-acridinones using a palladium-mediated C-H bond activation strategy. The reaction mechanisms were thoroughly investigated through the isolation of palladacycles, their X-ray crystal analysis and NMR spectroscopic characterization, along with controlled experiments, kinetic isotope effect studies, and theoretical calculations. Additionally, the synthetic utility of these compounds was demonstrated through the removal of directing groups and structural transformations.



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IL-15

C-N Bond Formations Enabled by an N-Fluorosulfonyl Group

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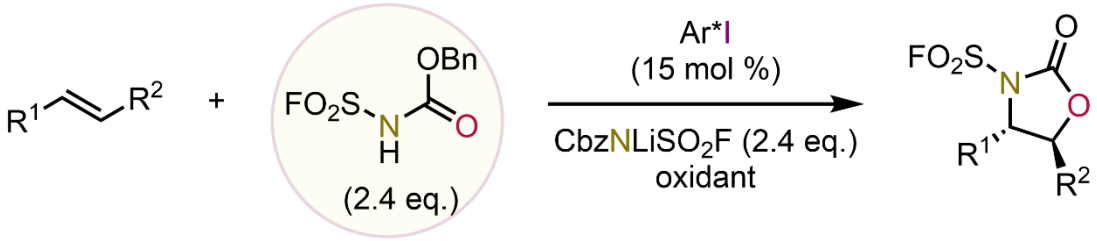
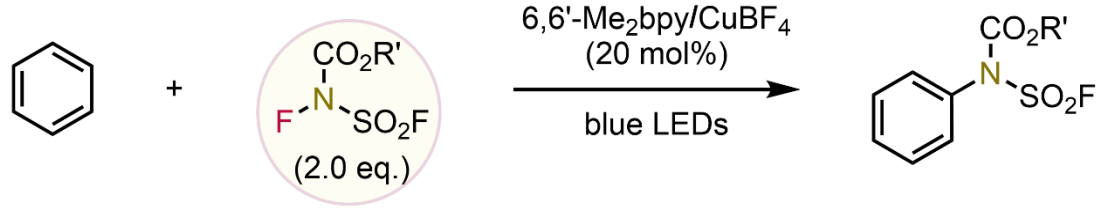
Nitrogen functionalization of molecules has been a major research topic, since the dawn of synthetic organic chemistry. Among hundreds of procedures established to this day, reagent-based protocols have been playing a key role in these developments. Recently, we discovered a new oxyaminating reagent, benzyl N-(fluorosulfonyl)carbamate, which acts as a nitrogen and oxygen nucleophile for the organoiodine(I/III)-catalyzed enantioselective intermolecular functionalization of alkenes. The established procedure was applicable to a broad range of styrenes and also aliphatic terminal alkenes with high enantioselectivities.1a,b The products could be deprotected easily to give enantioenriched amino alcohols.



Prompted by this discovery, we shifted our focus on the development of another reagent, N-fluorinated N-(fluorosulfonyl)carbamate. The reagent, named NFC, was synthesized by using fluorine gas, and applied in the copper-catalyzed C-H imidation of arenes and imido-cyanation of alkenes.1c,d The synthetic appeal of NFC compared with NFSI was its higher reactivity, easier deprotection and more importantly, its role as a SuFEx functionality for further derivatization.



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IL-16

The new methods of C-S, C-Se and C-C bond formation for functionalization of indole

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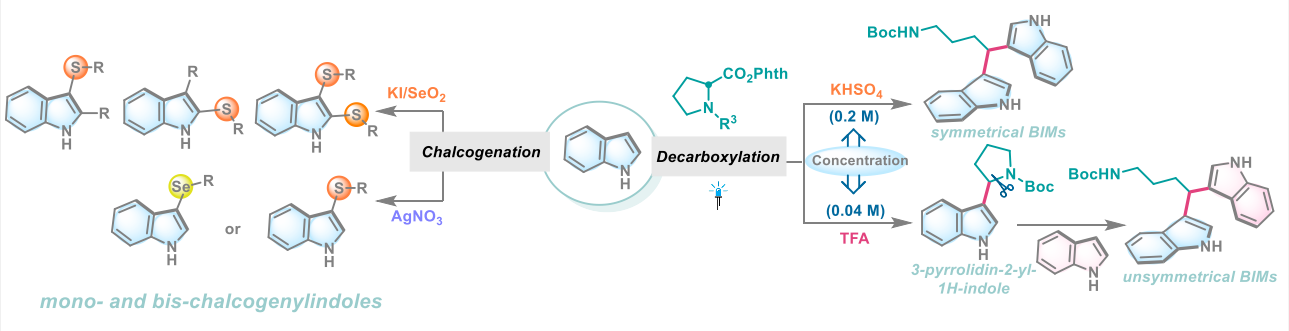
Indoles are important heterocyclic scaffolds, widely distributed in naturally occurring and synthetic bioactive molecules. Although various versatile methods have been developed to construct the indole backbone, there is still a strong demand for more concise and straightforward routes to access indole derivatives. Our group focuses on the functionalization reactions of indoles, categorized into two main types: (i) chalcogenation reactions for the construction of C−S and C−Se bonds, and (ii) decarboxylation reactions for the formation of C−C bonds. In the first approach, we designed the efficient methods of C–Se and C–S bond formation of indole which consists of two methods containing selective synthesis of chalcogenylindoles *via* silver-catalyzed direct chalcogenation with dichalcogenides and controllable synthesis of mono- and bis-sulfenylindoles from indoles and various sulfenylation agents using KI/SeO_2 system. In the second approach, we reported the first controlled decarboxylative Friedel−Crafts alkylation reaction of indoles and α-amino acid (*L*-proline)-derived redox-active esters using visible light to successfully and selectively yield single addition product 3-pyrrolidin-2-yl-1*H*-indole or double-addition product, symmetrical BIMs through simply changing the reaction conditions. The concentration of the reactants and acidic additives played a critical role in controlling product distribution. Furthermore, the reaction has been exploited to develop a facile synthesis of unsymmetrical BIMs. These approaches are highly effective for the construction of indole derivatives under mild conditions.



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IL-17

Sodium Thiosulfate Mediated the C-S/C-O/C-N Bond Formation

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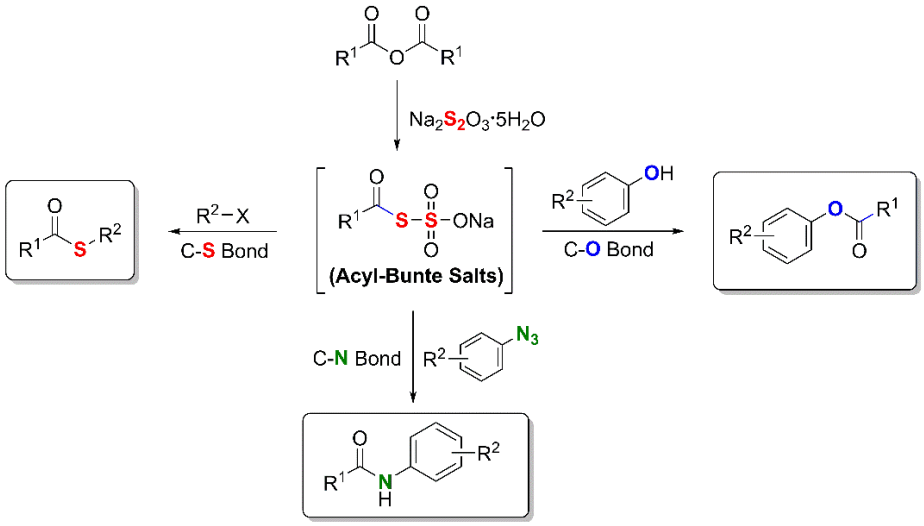
Thioacids are a versatile class of chemical compounds that have found in diverse synthetic applications. Moreover, thioacids can function as acylating agents that react with azides, isocyanates, isonitriles, nitroarenes, thiocarbamates, and amines for the synthesis of amides, imides and sulfonamides under the effects of base agents or metal catalysts or photocatalysis. Although thioacids have been successfully verified in many synthetic methods, these methods have limited use because of the difficulty in accessing thioacid reagents and issues with their stability. Therefore, new synthetic methods that are more feasible and environmentally friendly than the conventional methods are still in strong demand. Relatedly, our group used sodium thiosulfate as a sulfur surrogate for thioester formation, through the *in situ* generation of acyl-Bunte salts. Based on this concept of an acyl-Bunte salt structure, we continually developed new synthetic methods that involve the used of sodium thiosulfate for diverse organic group transformations. Hence, we report the successfully synthesis of phenolic esters and aryl amides under transition metal- and oxidant-free conditions, in which anhydrides were coupled with sodium thiosulfate to generate acyl-Bunte salts, which were then used as an acylating source.



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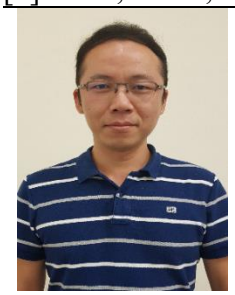

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IL-18

Leveraging Ortho-Alkynylarylcarbonyl Derivatives for the Synthesis of Structurally Diverse Chemical Compounds

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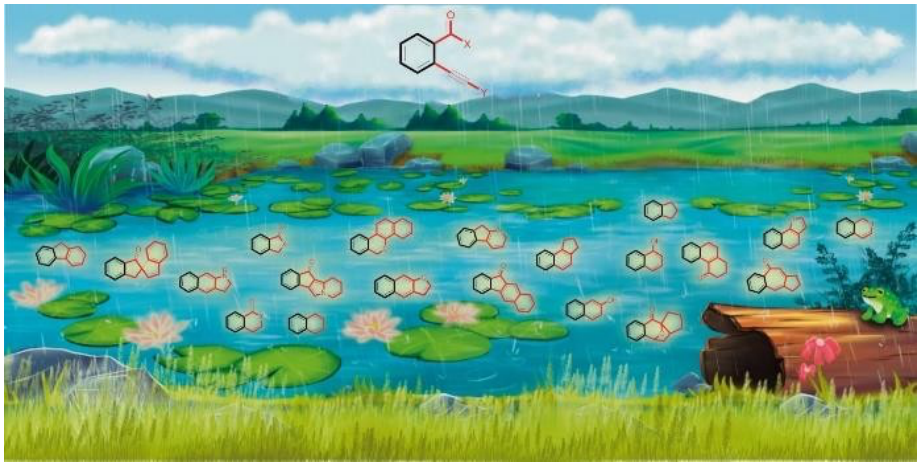
The creation of structurally diverse chemical compounds is a fundamental goal in organic synthesis, with far-reaching implications for fields such as drug discovery, materials science, and chemical biology. Ortho-alkynylarylcarbonyl derivatives have proven to be powerful intermediates, facilitating the synthesis of complex molecular structures through a range of innovative reaction mechanisms. These derivatives exhibit unique reactivity profiles, particularly in cyclization, rearrangement, and annulation processes, enabling the construction of highly functionalized and stereochemically rich molecules. This presentation will explore the versatility of ortho-alkynylarylcarbonyl compounds in promoting chemo-, regio-, and stereoselective transformations, highlighting their potential to access molecular scaffolds that are otherwise difficult to obtain. Key reaction strategies and examples from recent research will be discussed to illustrate the growing importance of these derivatives in advancing organic synthesis and contributing to the development of novel chemical compounds.



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IL-19

Photocatalytic Bromination toward Biomolecular Labeling

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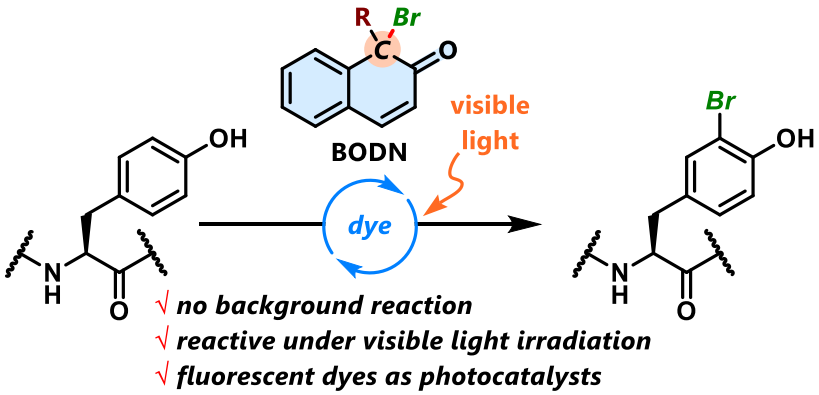
Photocatalytic labeling of amino acid side chains in proteins is crucial for understanding significant biomolecular communications. However, amino acid residues with limited surface exposure, such as tyrosine, exhibit lower reactivity, resulting in decreased sensitivity in mass analyses of labeled molecules despite their biological importance. The bromo group serves as a sensitive mass tag that is valuable for analyzing complex macromolecules due to the relative abundance of bromine isotopes. However, biocompatible methodologies for photocatalytic bromination remain underdeveloped. In this study, we investigated the photochemical reactivity of 1-bromo-2-oxo-1,2-dihydronaphthalene-1-carboxylates (BODNs).[1] These compounds remain stable in the dark under physiological conditions but become activated as brominating reagents under visible light irradiation in the presence of a catalyst during tyrosine modification. Photocatalytic reactions offer advantages such as the use of less invasive light with a longer wavelength as compared to non-catalytic reactions and the spatiotemporal control of bromination. In our reaction system, the fluorescent dyes commonly utilized in bioimaging probes serve as photocatalysts. This characteristic facilitates the applications of BODNs as chemical biology tools enabling the installation of attractive labeling tags on tyrosine-containing peptides and proteins.



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IL-20

Hydrosulfonylation of Alkynes for Stereodivergent Synthesis of Vinyl Sulfones

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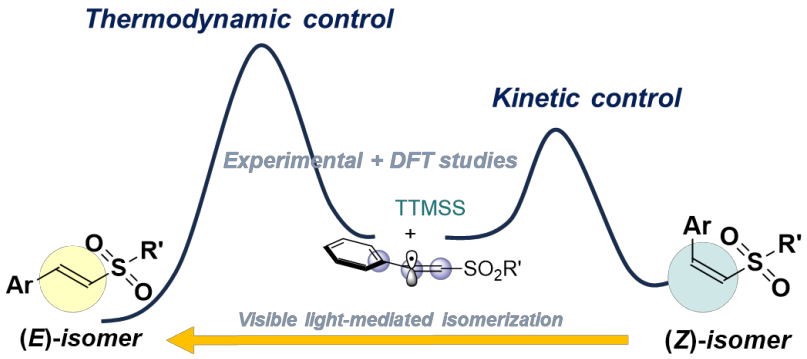
Recently, visible-light-mediated photoredox catalysis has become a powerful tool in organic synthesis.[1] Transition metal-based photocatalysts, such as ruthenium and iridium polypyridyl complexes, have been widely employed with great success. However, due to the limitations associated with utilizing transition metals, it is crucial to develop green activation modes in photoredox systems. The direct synthesis of thermodynamically less favorable (*Z*)-vinyl sulfones presents a notable challenge in organic synthesis. In addition, the development of a stereodivergent synthesis for (*E*)- and (*Z*)-vinyl sulfones is crucial but remains elusive. In this presentation, I will discuss our recent work on the hydrosulfonylation of alkynes for the stereoselective synthesis of (*E*)- and (*Z*)-vinyl sulfones under mild reaction conditions.[2]



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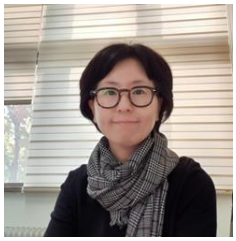

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IL-21

Enantioconvergent Redox-Neutral Functionalization of Alcohols via Borrowing Hydrogen Catalysis

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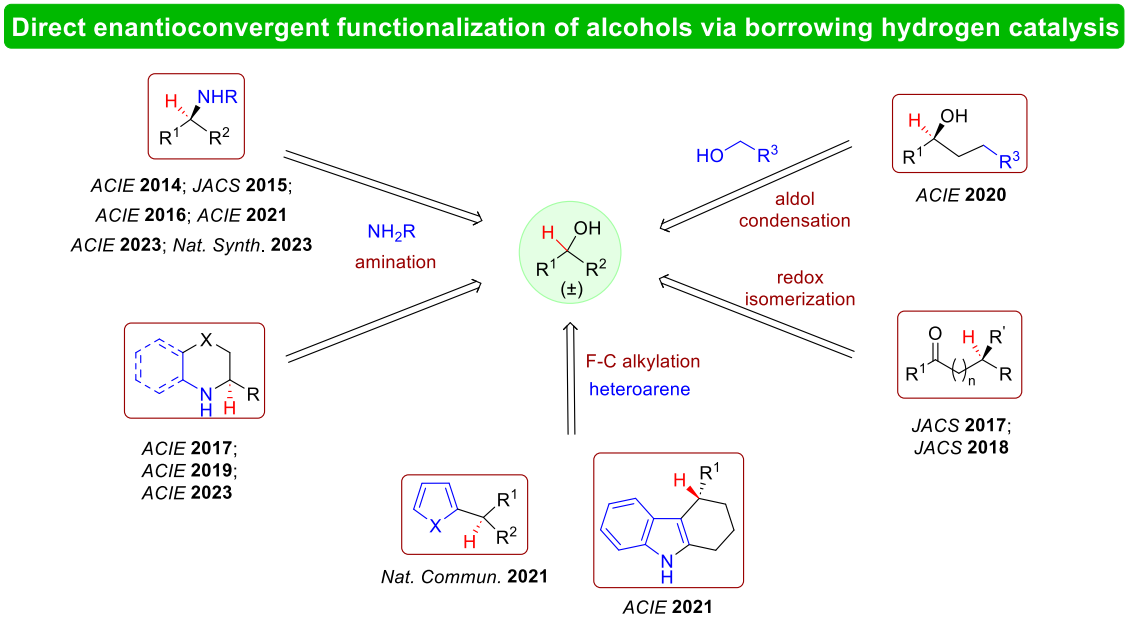
The development of economical and selective catalytic methods is of significant importance for the promotion of sustainable chemical synthesis. My group at National University of Singapore has focused on the identification of catalytic enantioselective redox-neutral transformations that directly convert feedstock materials to valuable chiral entities with wide application in organic synthesis. In particular, we have achieved a series of direct stereoconvergent "substitution" of readily available racemic alcohols via borrowing hydrogen catalysis for economical access to chiral amines, N-heterocycles, alcohols and ketones, etc. Recent progress in identifying new catalytic processes along these lines will be discussed in details in this presentation.



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Professor (NUS, 2024-)
[Field of research] Organic Chemistry

IL-22

Chiral Phosphoric Acid−Palladium(II) Complex Catalyzed Asymmetric Desymmetrization of Biaryl Compounds by C(sp3)−H Activation

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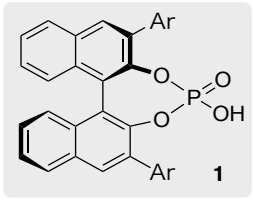
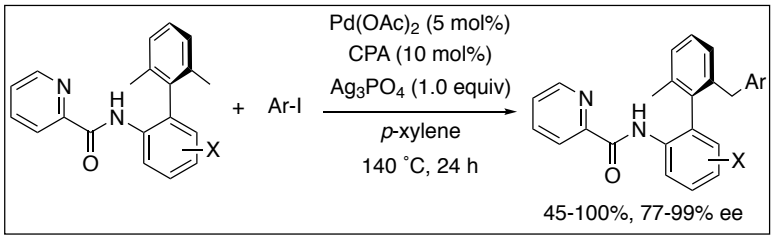


Construction of axially chiral compounds have attracted much attention of organic chemists as well as medicinal chemists because of their utility as ligands, catalysts, and biologically activity. A number of efficient method for the construction of axially chiral compounds have been reported lately. We already reported that chiral phosphoric acid (CPA) **1**, derived from (*R*)-BINOL, functioned as a chiral Brønsted acid catalyst for a number of transformations.[1] As part of our continued interest in the chiral phosphoric acid catalysis, we already reported construction of chiral biaryls by desymmetrization of biaryls by bromination,[2] and dynamic kinetic resolution using the transfer hydrogenation of imine.[3]

C-H activation is a useful strategy for the atom-economical functionalization method, and a range of C-H activation reaction has been developed. Its application to catalyzed, enantioselective reaction has been actively studied. Although construction of axially chiral biaryls by C(sp^2)-H functionalization has been already reported, formation of axially chiral compounds by the desymmetrization of biaryls based on C(sp^3)−H activation had not been reported.

We have found that desymmetrization of biaryl compounds was achieved by C(sp^3)−H activation catalyzed by a chiral phosphoric acid−Pd complex in the presence of Ag_3PO_4 in xylene under heating conditions. The chiral Pd(II)-phosphate enabled asymmetric CMD type C−H functionalization with picolinamide as the directing group, affording biaryl compounds with high to excellent enantioselectivity (Scheme 1).[4]



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IL-23

Recent Progress in the Chemistry of Conjugated Nanobelts

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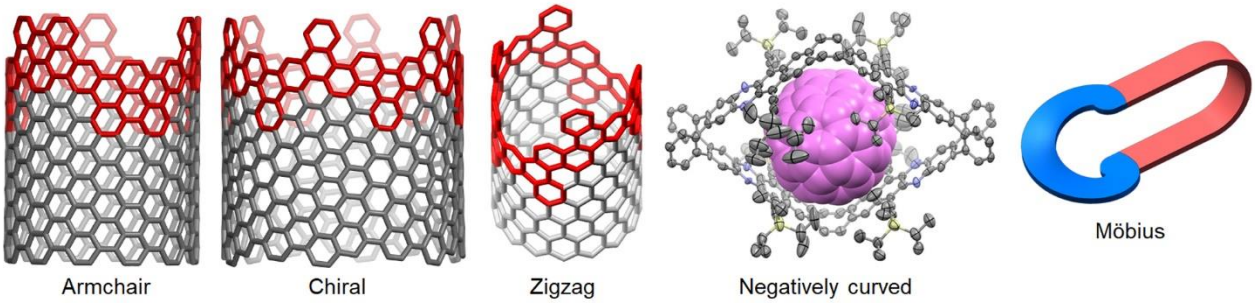
Conjugated nanobelts are attractive molecules of aesthetic appeal, synthetic challenges, unique properties and interesting applications. Specifically, carbon nanobelts, which exclusively consist of sp^2 carbon atoms, represent a fragment of carbon nanotubes. They have long been sought after by organic chemists for synthesis and hold promise as templates for bottom-up, chirality-specific synthesis of single-walled carbon nanotubes. The first part of this presentation will introduce our work on synthesis of all the three kinds of carbon nanobelts (armchair, chiral and zigzag) using Scholl reactions.[1, 2] The geometries of conjugated nanobelts can be further diversified by introducing nonbenzenoid rings or Möbius topology. The second part of this presentation will showcase our most recent research, focusing on negatively curved nanobelts containing eight-membered rings,[3] and a Möbius nanobelt derived from helicene.[4]



Acknowledgement: The research presented herein was supported by the Research Grants Council of Hong Kong (CRF C4001-23GF).

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Qian Miao (繆謙). University of Science and Technology of China (B.Sc. 2000), Columbia University (PhD, 2005). University of California, Los Angeles (Postdoctoral researcher, 2005-2006), the Chinese University of Hong Kong (Assistant Professor 2006–2012, Associate Professor 2012–2016, Professor 2016 to present). Research interests: design and synthesis of novel polycyclic aromatic molecules with interesting structures and useful applications; exploring precise synthesis of carbon nanomaterials; and developing high-performance organic semiconductor materials and devices, using tools from organic synthesis, as well as supramolecular chemistry and surface chemistry.

IL-24

Electron Donor-Acceptor Photocatalyst in the First Photochemical Machetti–De Sarlo Reaction

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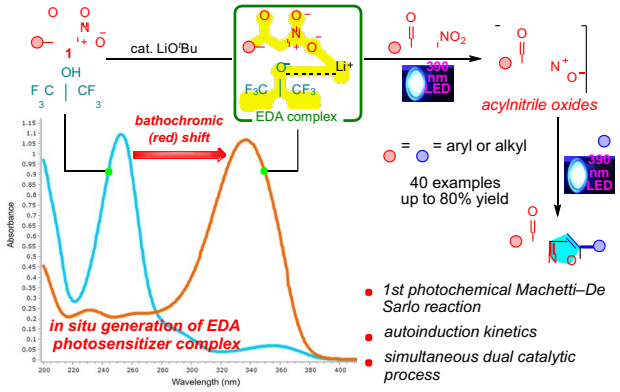
We report a new photochemical protocol for the Machetti–De Sarlo reaction using an electron donor- acceptor (EDA) photocatalyst formed from an acylnitromethane substrate and catalytic LiO^{t}Bu in HFIP. The EDA photocatalyst was confirmed by the red shift in the UV-Vis absorption spectrum of the reaction mixture compared to individual reactants. The kinetic profile showed autoinduction kinetic, similar to the thermal conditions. Under optimal conditions, acylnitromethanes are converted to acylnitrile oxides, which undergo 1,3-dipolar cycloaddition with terminal alkynes to produce 3- acylisoxazoles in various capacities.



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Chulabhorn Graduate Institute (2009-present)
Field of research: Organic Synthetic Methodology.

IL-25

Design and Synthesis of Organic Compounds Exhibiting Fluorescence Response to Biomolecules and Their Applications in Living Systems

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Quantitative determination of specific analytes is essential for a variety of applications ranging from life sciences to environmental monitoring. Optical sensing allows for non-invasive measurements within biological milieus, parallel monitoring of multiple samples, and less invasive imaging. Among the optical sensing methods currently being explored, small molecule-based fluorescence sensing has received particular attention as a technique with the potential to provide precise and quantitative analyses and real-time fluorescence monitoring. So far, our laboratory has developed a variety of sensing probes using activatable fluorescent molecules for sensing, imaging, and biomedical applications. Today, I will talk about development of activatable fluorescent molecules capable of sensing several bioactive components such as hydrogen sulfide (H_2S), human NAD(P)H:quinone oxidoreductase 1 (hNQO1), nitroreductase (NTR), reduced nicotinamide adenine dinucleotide (NADH), and exploring dual sensing of nitric oxide (NO) and cellular viscosity, recently reported in our laboratory. The basic design concepts involving small fluorescent molecules composed of a fluorescent reporter and recognition moiety that undergo a fluorogenic reaction in response to analytes will be described. In addition, some biological results demonstrating the validation of fluorescent molecules' operation will be presented in a variety of biological models such as live cancer cells, cancer cell spheroids and tissues.

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IL-26

Stereoselective Synthesis of Noncentral Chiral Molecules Using Arynes or Substrates Derived from Arynes

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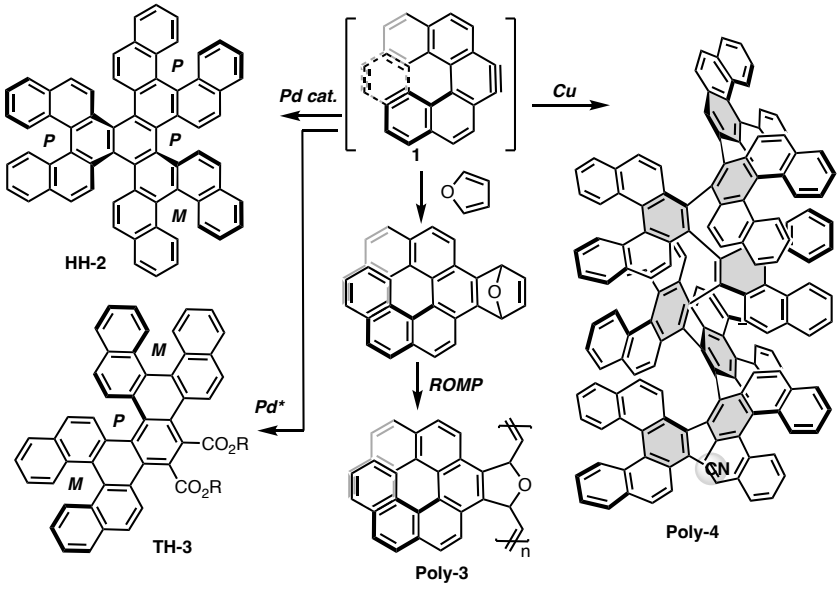
Recent studies have increasingly focused on reactions involving arynes, which are known for their elusive nature. However, the development of stereoselective synthetic reactions utilizing arynes remains underdeveloped, necessitating further research.[1] We have developed a generation of helicenyl aryne **1** and successfully applied it to the synthesis of various polycyclic aromatic compounds. Notably, we achieved the stereoselective synthesis of hexahelicene (**HH-2**), a compound comprising six [5]helicenes, via a [2+2+2] cycloaddition reaction in the presence of a Pd catalyst. Remarkably, we were able to selectively obtain a single stereoisomer, (*P,M,P,P,P,M,P*)-**2** (**HH-2**), out of ten possible diastereomers.[2] Furthermore, employing a Pd-catalyzed asymmetric cross [2+2+2] cyclotrimerization of **1** with dimethyl acetylenedicarboxylate, we synthesized the optically active triple helicene (**TH-3**) with a 49% yield and 96% ee using (*S*)-QUINAP as the chiral ligand.[3] Helicenylarynes can apply for the polymerization reactions for the synthesis of multiple helicenes, such as ring-opening metathesis polymerization (ROMP) [4] to form **poly-3** and direct aryne polymerization for **poly-4**.



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Field of research: Synthetic Organic Chemistry, Structure Chemistry, Organometallic Chemistry

IL-27

Development of C-Shaped *ortho*-Benzodipyrrole-based A-D-A type Acceptors for High-Performance Organic Photovoltaics

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The high-performance Y6-based nonfullerene acceptors (NFAs) feature a C-shaped A-DA'D-A-type molecular architecture with a central electron-deficient thiadiazole (Tz) A' unit. In this work, we designed and synthesized a new A-D-A-type NFA, termed as CB16, having a C-shaped ortho-benzodipyrrole-based skeleton of Y6 but with the Tz unit eliminated.[1] When processed with non-halogenated xylene without using any additives, the binary PM6:CB16 devices display a remarkable power conversion efficiency (PCE) of 18.32% with a high Voc of 0.92 V, surpassing the performance of the corresponding Y6-based devices. In contrast, the similarly synthesized SB16, featuring a S-shaped *para*-benzodipyrrole-based skeleton, yields a low PCE of 0.15% due to the strong side-chain aggregation of SB16. The C-shaped A-D_NB_ND-A skeleton in CB16 and the Y6-series NFAs constitutes the essential structural foundation for achieving exceptional device performance. The central Tz moiety or other A' units can be employed to finely adjust intermolecular interactions. The X-ray single crystal structure reveals that *ortho*-benzodipyrrole-embedded A-D_NB_ND-A plays an important role in the formation of a 3D elliptical network packing for efficient charge transport. Solution structures of the PM6:NFAs detected by SWAXS indicate that removing the Tz unit in the C-shaped skeleton could reduce the self-packing of CB16, thereby enhancing the complexing and networking with PM6 in the spin-coating solution and the subsequent device film. Elucidating the structure-property-performance relationships of A-DA'D-A-type NFAs in this work paves the way for the future development of structurally simplified A-D-A-type NFAs. [2]

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Research field: Methodologies for Synthesizing Conjugated Molecules and Polymers; Functional Organic and Polymeric Materials for Organic Photovoltaics, Organic Field-Effect Transistors, Thermoelectric Devices, Stretchable Optoelectronics and Photocatalytic Hydrogen Evolution.

IL-28

Synthesis of Higher Order Iptycenes Using Ambident Anthracene

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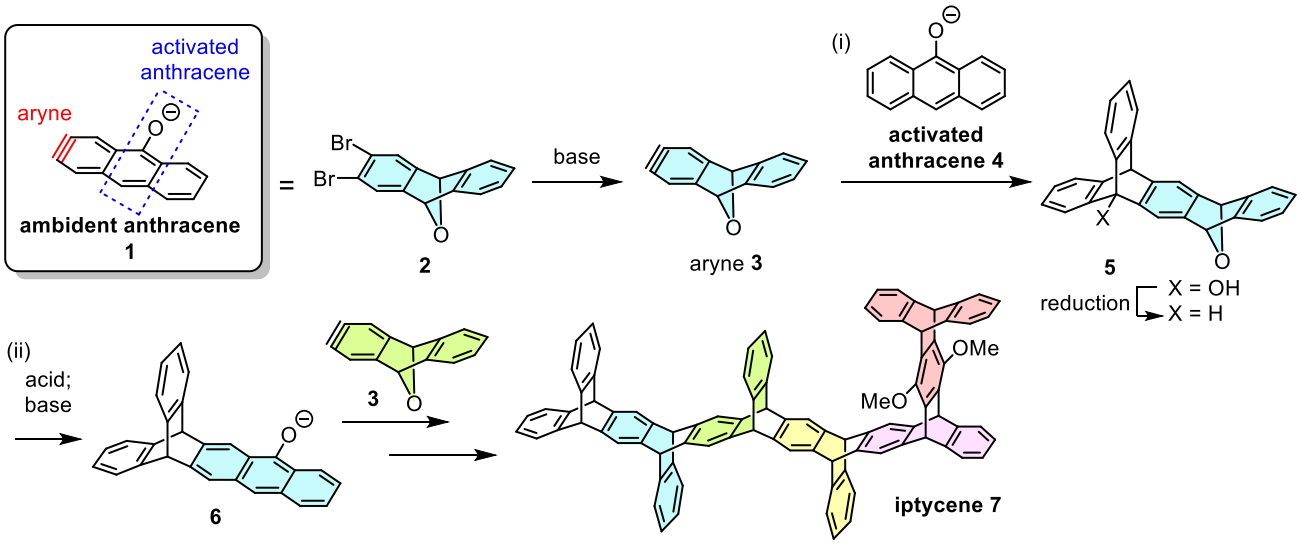
Iptycene, which is aromatic molecule composed of triptycene units, have rigid framework and have been applied in various functional molecules such as porous polymers and host molecules. However, their synthetic methods are limited, and it is highly desired to develop a versatile method to synthesize varying size of iptycenes. Recently, we have reported an efficient synthesis of triptycene using an activated anthracene, which is highly electron-rich and thus significantly reactive toward arynes.[1] In this study, we developed an efficient method to synthesize iptycenes using the "ambident anthracene **1**", which incorporates both the aryne moiety and the activated anthracene (arynophile) moiety.

We prepared 6,7-dibromo-1,4-dihydro-1,4-epoxyanthracene (**2**) as a precursor of ambident anthracene **1**. (i) Benzyne **3**, generated by the treatment of **2** with base, reacted with activated anthracene **4** to construct the triptycene scaffold. Afterward, (ii) the product **5** was converted into activated anthracene **6** through the sequential treatment of acid and base, and it was reacted with aryne **3** again. By repeating these two steps, we synthesized various iptycenes with different sizes and branching patterns, including linear iptycene **7** with 13 benzene rings, the longest ever synthesizsed.[2]



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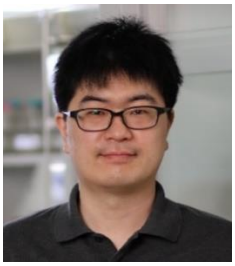

Takayuki Iwata (岩田 隆幸). Osaka University (Ph.D., 2015). Boston University (2015-2016). Kyushu University (2016-). [Field of research] Synthetic Organic Chemistry.

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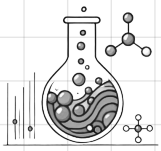

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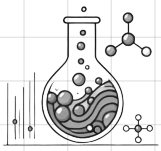

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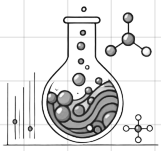

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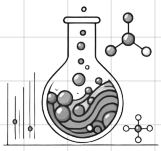

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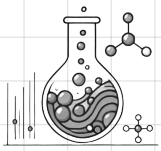

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PA-01

Molecular basis for the diversification of lincosamide biosynthesis by pyridoxal phosphate-dependent enzymes

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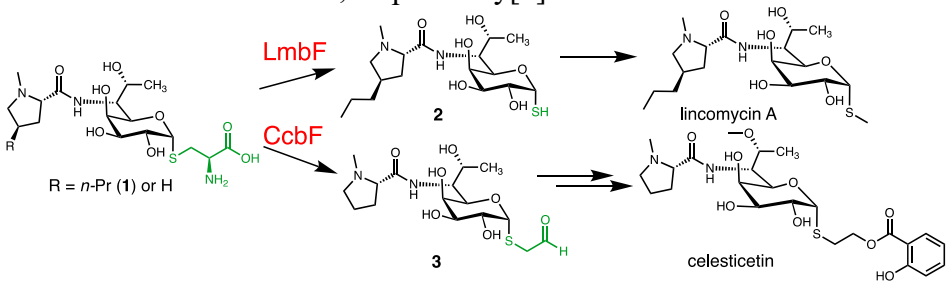
Lincosamides, isolated from Streptomyces species, are thiooctose-containing natural products that are a class of clinically used antibiotics[1]. In the biosynthesis of lincosamide antibiotics lincomycin A and celesticetin, the pyridoxal 5'-phosphate (PLP)-dependent enzymes LmbF and CcbF are responsible for the bifurcation of the pathway[2,3]. While these enzymes recognize the same S-glycosyl-L-cysteine structure of the substrate, LmbF and CcbF convert the cysteine moiety into thiol and S-acetaldehyde, respectively, through β-elimination and decarboxylation-coupled oxidative deamination reactions. We present here the structural and functional analyses of these enzymes to understand the molecular basis for the diversification of the structures of lincosamides.

The PLP-binding structures of LmbF and CcbF were solved at 1.7 and 1.8 Å resolution, respectively. The crystal structures, docking simulations, and molecular dynamics simulations revealed the intimate structural details for the S-functionalization of the thiooctose core in lincosamide biosynthesis. The active site tryptophan and tyrosine residues play key roles in controlling the binding mode of the cysteine moiety of the substrate to determine the reaction selectivity. Furthermore, structure- and calculation-based mutagenesis study successfully altered the reaction selectivity in CcbF from oxidative-deamination to b-elimination and decarboxylative-oxidation to produce LmbF product and an unnatural lincosamide derivative, respectively[4].



Reactions of LmbF and CcbF

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[Field of research] Natural Product Chemistry.

PA-02

Development of Novel Heterocyclic Nitrile/1,2-Aminothiol Click Reactions: Applications in Molecular Imaging

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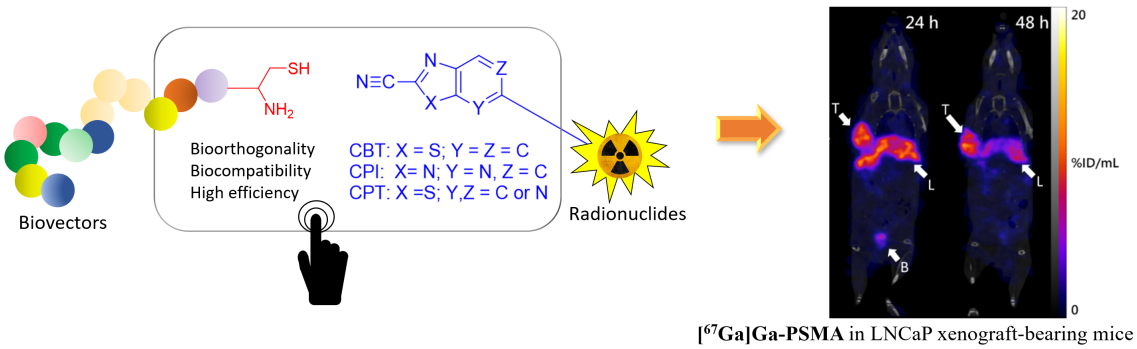
Radiopharmaceuticals play a crucial role in cancer diagnosis and treatment, offering a targeted approach to address malignant cells. Nuclear imaging technologies, such as positron emission tomography (PET) and single-photon emission computed tomography (SPECT), enable the non-invasive visualization of cancer lesions in the human body, paving the way for personalized and targeted therapies. Bioorthogonal click reactions, such as strain-promoted [3+2] azide-alkyne cycloaddition (SPAAC) and inverse-electron demand Diels-Alder (IEDDA) reactions, feature their fast kinetics, high selectivity, and biocompatibility, which are widely applied in nuclear imaging probe preparations. Recently, a novel bioorthogonal chemistry employing the cyclization between 2-cyanobenzothiazole (CBT) and 1,2-aminothiol group has gained great attention, however, its reaction rate is suboptimal for radiolabeling applications. Therefore, we herein describe the designs and syntheses of a series of modified heterocyclic nitriles, *cyanopyridothiazole* (CPTs) and cyanopyridoimidazoles (CPIs), which exhibit better stability and faster kinetic than CBT moiety. Extensive investigations of the applications of these novel click reactions in molecular imaging were conducted by an animal SPECT imaging study. Via the attachment of a PSMA biovector, our ^{67}Ga-labeled probe were successfully detected in the LNCaP xenograft-bearing mice. We envisioned that our chemistry can advance the development of new nuclear imaging probes.



[^{67}Ga]Ga-PSMA in LNCaP xenograft-bearing mice

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PA-03

Understanding a bit more about mechanochemistry - Mixing

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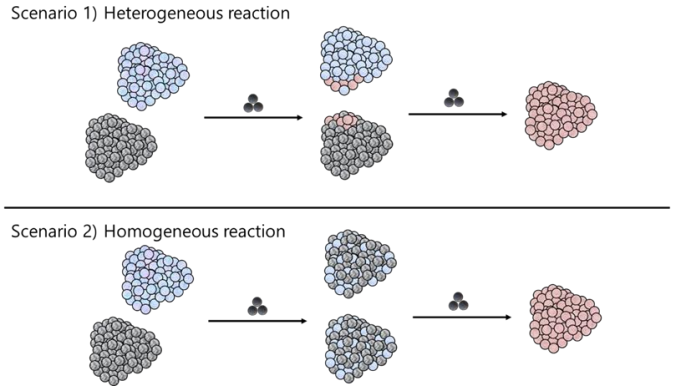
Mechanochemistry has demonstrated its ability to achieve outcomes that other processes cannot.[1] Unique reaction conditions, such as placing reactants in moving parts like ball mills and twin-screw extruders, have facilitated numerous chemical reactions. The collision or shearing forces generated by ball milling or twin-screw extruders provide sufficient mixing of chemical reagents and the necessary activation energy. As mechanochemistry rapidly advances, researchers have sought to understand the events occurring within these processes. This presentation focuses on mixing and phase behavior. In solution-based reactions, reagents are dissolved, ensuring that all molecules are evenly dispersed and ready to react. However, solid-state ball milling operates differently. Heterogeneous starting mixtures undergo chemical transformations driven by mechanical force, sometimes at a faster rate than in solution. Traditionally, many mechanochemical studies have assumed that reactions occur at the surfaces of reactants A and B, classifying them as heterogeneous. However, accumulating evidence suggests that some of these transformations might be homogeneous. Through our experience and new investigations, we have sought to determine whether mechanochemical transformations are homogeneous or heterogeneous. Three case studies will provide insights into this question: (1) the copolymerization of immiscible monomers,[2] (2) the phase transition of chiral L-lactide and D-lactide,[3] and (3) the cross-metathesis of similar vinyl compounds.[3] These studies aim to shed light on the processes occurring within the "black box" of mechanochemistry.



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PA-04

Ammonia Adsorption Using a CO_2H-Functionalized Cyclic Oligophenylene

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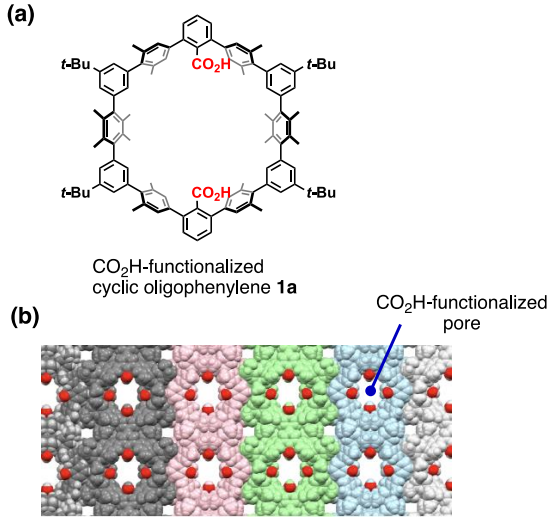
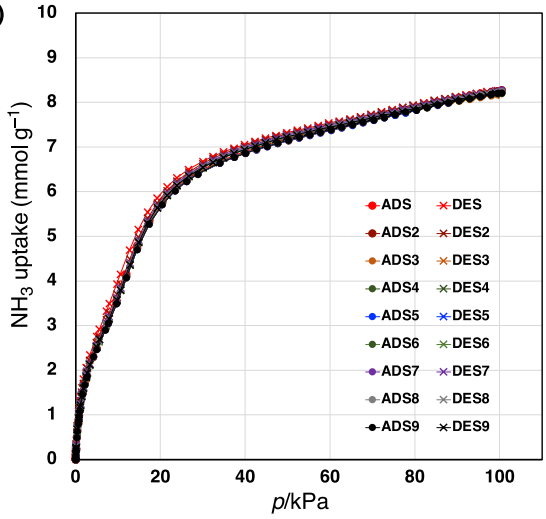
Ammonia is viable candidate for the storage and distribution of hydrogen due to its exceptional volumetric and gravimetric hydrogen energy density. Therefore, it is desirable to develop NH_3 storage materials that exhibit robust stability across numerous adsorption-desorption cycles. While porous materials with polymeric frameworks are often used for NH_3 capture, achieving reversible NH_3 uptake remains a formidable challenge, primarily due to the high reactivity of NH_3. We have recently reported the synthesis of *endo*-functionalized cyclic oligophenylene **1** that show high chemical stability.[1] Here, we advocate the use of CO_2H-functionalized cyclic oligophenylene **1a** with high chemical stability as a novel single-molecule-based adsorbent for NH_3.[2] Simple reprecipitation of **1a** selectively yielded microporous crystalline solid **1a** (**N**). Crystalline **1a** (**N**) adsorbs up to 8.27 mmol/g of NH_3 at 100 kPa and 293 K. Adsorbed NH_3in the pore of **1a** (**N**) has a packing density of 0.533 g/cm^3 at 293 K, which is close to the density of liquid NH_3(0.681 g/cm^3 at 240 K). Crystalline **1a** (**N**) also exhibits reversible NH_3 adsorption over at least nine cycles, sustaining its storage capacity and crystallinity. During each desorption cycle, NH_3 was removed from **1a** (**N**) under reduced pressure (~65 Pa), leaving <3% of the total uptake, and **1a** (**N**) was fully purged under dynamic vacuum conditions before the subsequent adsorption cycles. Thus, microporous crystalline **1a** (**N**) can reliably adsorb and desorb NH_3 repeatedly, which avoids the need for heat-based activation between cycles.



Packing structure of crystalline **1a**(**N**)



Isotherms for nine cycles of NH_3 adsorption–desorption in crystalline **1a**(**N**)

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Kosuke Ono (小野　公輔). The University of Tokyo (Ph. D., 2009). University of California, Santa Barbara (Postdoc, 2009); Tokyo Institute of Technology (Project Assistant Prof., 2010); Tokyo University of Science, (Assistant Prof., 2015); Tokyo Institute of Technology (Associate Prof., 2019); Institute of Science Tokyo (Associate Prof., 2024). Research field: Supramolecular Chemistry.

PA-05

Asymmetric 1,1'-Disaccharides for Total Synthesis of Glycosylated Natural Products

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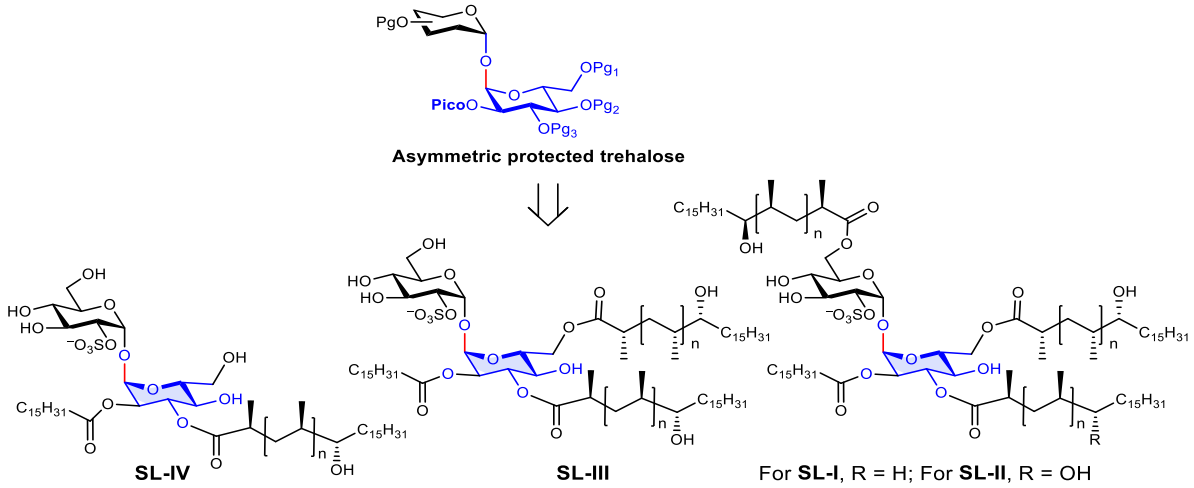
Asymmetric 1,1'-Disaccharide are common structural units found in a variety bacterial glycolipids particularly in the cell walls of at least ten Mycobacterium species including the pathogenic *M. tuberculosis* (*Mtb*).[1,2] Given the unique features and immunological relevance of bacterial glycolipids, this poster describes a practical protocol to prepare asymmetric 1,1'-disaccharide from orthogonally protected trimethylsilyl (TMS) α-glucoside acceptor.[3] In this poster, we report a practical yet highly stereoselective method for preparation of TMS α-glucosides and subsequent application of this method to total synthesis of diverse *Mtb* sulfoglycolipids (SGL) including newly isolated monoacyl SGL, sulfolipids I (SL-I), SL-II, SL-III, and SL-IV.[4,5]



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Kwok-Kong Tony Mong (蒙國光). The Chinese University of Hong Kong (PhD, 2000). The Scripps Research Institute (Postdoctoral research associate, 2002). National Chiao Tung University (Assistant Professor , 2005; Associate Professor, 2010; Professor, 2014). National Yang Ming Chiao Tung University (Professor, 2021) [Field of research] Carbohydrate Chemistry.

PA-06

Supramolecular Assemblies of Photoresponsive Molecular Amphiphiles

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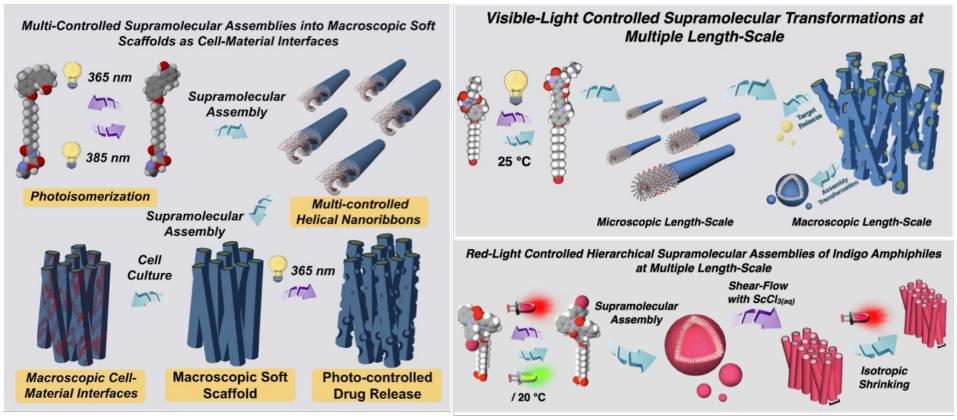
Recent advancements in supramolecular chemistry and soft functional materials design have enabled various supramolecular assembling systems responsive to external stimuli, *e.g.*, light, heat, pH, small organic molecules, and ions. Among the various external stimulations, light provides as a non-invasive method with high-spatial and high-temporal precision in controls of supramolecular assembling structures in both organic and aqueous media. Implementations of photoresponsive molecular functionalities into molecular amphiphilic motifs, *i.e.*, photoresponsive molecular amphiphile, have constructed a series of synthetic photoresponsive supramolecular systems at air-water interface and in aqueous media, enabling controlled interfacial properties, reversible nanoscale assembly, and artificial muscle functions. Some of these photoresponsive molecular amphiphiles are capable to assemble across multiple length-scale, fabricating photoresponsive soft materials at macroscopic length-scale. However, the biocompatibility remains unsolved in the reported bio-damaging UV-light activated systems. We discuss our recent works on the biocompatible supramolecular actuator of photoresponsive DASA amphiphiles[1] and other visible-light controlled supramolecular soft materials.[2]



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Dr. Franco King-Chi Leung (梁敬池) studied his BSc in Chemistry at The Hong Kong Polytechnic University where he carried out his Masters research. He expanded his research scopes in his PhD to supramolecular chemistry and material science under guidance of Prof. Takanori Fukushima in Tokyo Institute of Technology. In 2017, he joined Prof. Ben L. Feringa's group in University of Groningen, the Netherlands, as a postdoc fellow and later he was awarded the Croucher Postdoctoral Fellow, where he is developing photo-responsive soft materials of molecular motors and switches. Since June 2019, he is serving as an Assistant Professor in Department of Applied Biology and Chemical Technology, PolyU. He was awarded the prestige Croucher Innovation Award (2021), PolyU Young Innovative Researcher Award (2022), and Rising Star in Polymer Science (Nov 2023). His main research interests are dynamic supramolecular polymers, functional molecular assembly, and biocompatible functional materials.

PA-07

Total Synthesis of (±)-Arnicenone via a Stereodivergent Angular Triquinane Synthesis

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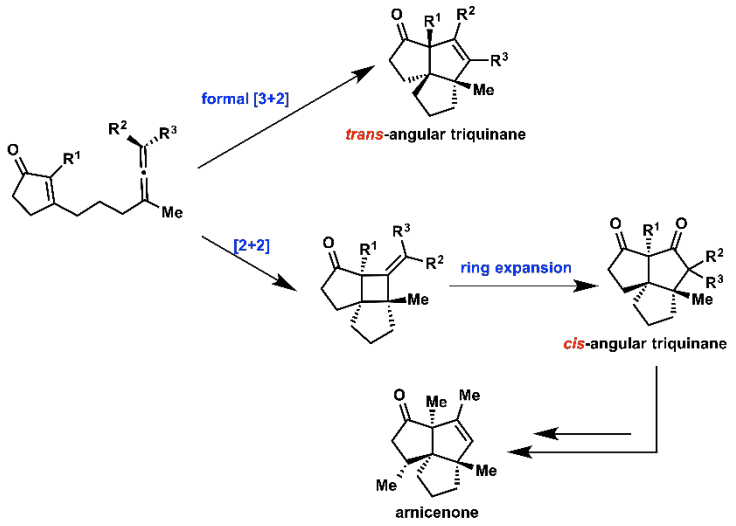
Angular triquinane consists of cyclopentanes fused in *cis*-fashions with multiple all-carbon quaternary stereocenters embedded in the ring junctions. Its unique structural complexity possesses a synthetic challenge. Therefore, natural products, such as isocomene, siphenene, arnicenone,[1, 2] waihoensene, and crinipellin A, containing angular triquinane have drawn a great deal of attention in synthetic community. Here, we will discuss our strategy in the total synthesis of arnicenone. During our study, we've developed stereodivergent pathways access to both *cis*- and *trans*-angular triquinane skeletons. These pathways include an acid-promoted formal [3+2] cycloaddition for the synthesis of *trans*-angular triquinane. In addition, a [2+2] cycloaddition followed by a ring expansion route enabled the formation of *cis*-angular triquinane, ultimately leading to the synthesis of arnicenone.



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[Field of research] Natural Product Synthesis.

PA-08

Photoinduced Hydrogenation of Carbonyl Compounds at Mild Conditions Using a PNNP-type Ir Complex

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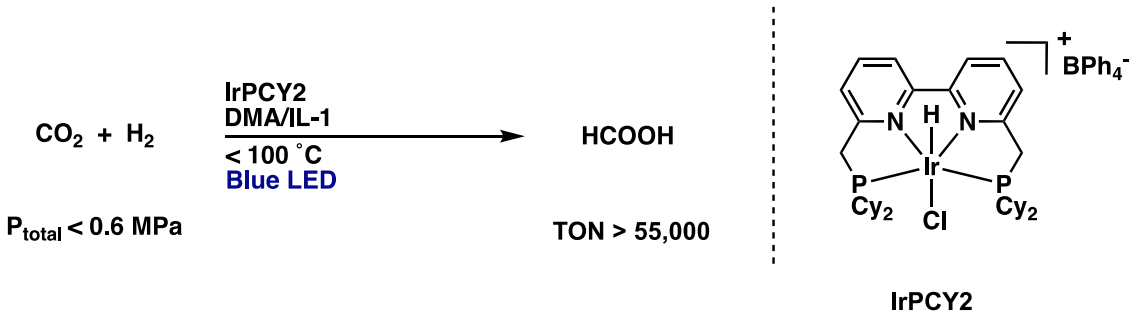
Methanol, formic acid (HCOOH), and carbon monoxide are synthetically valuable carbon sources that can be utilized for pharmaceutical synthesis. Carbon dioxide (CO_2) has gained attention as a C_1-feedstock for obtaining these one-carbon compounds and conversion of CO_2 utilizing hydrogen (H_2) could potentially allow for the clean generation of energy. In our laboratory, catalytic hydrogenation of CO_2 under a high temperature and pressure has been achieved using an iridium complex with a tetradentate PNNP ligand.[1] However, the high temperature and pressure conditions (~200 °C, ~10 MPa) have posed challenges for practical applications. We report here very mild hydrogenation of CO_2 under light irradiation with the same complex (**IrPCY2** in Scheme 1), expanding its scope beyond carbonyl compounds. Efficient CO_2 hydrogenation was achieved at mild conditions (~0.6 MPa, ~100 °C) when an ionic liquid (**IL-1**) was employed in the reaction solution, furnishing HCOOH as a main product with a turnover number (TON) of >55,000. UV-vis measurements and various experiments suggest that that the role of light in the system was catalyst induction, and that induction of catalytically active species most likely is achieved by light-induced hydrogenation of the ligand backbone of the Ir catalyst.



Scheme 1. CO_2 hydrogenation using **IrPCY2** under light irradiation

Reference

[1] Grømer, B.; Saito, S. *Inorg Chem*. **2023**, *62*, 14116.

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Research field: Photocatalysis, Photochemistry, Artificial photosynthesis, Electron-transfer chemistry

PA-09

Synthesis of *(Z)*-Cinnamic Acid Derivatives via Stereoinvertive Deoxygenation of *trans*-Epoxides

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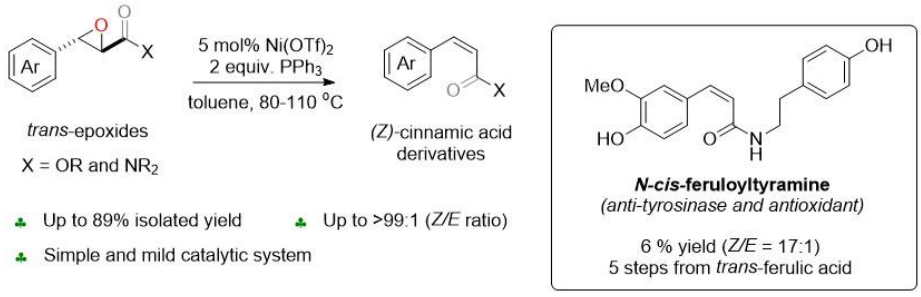
Cinnamic acid and its derivatives are versatile compounds that show diverse biological activities and have been used as precursors in numerous chemical transformation. However, most of the reported methods for synthesizing this class of compounds provide *(E)*-products. Therefore, developing a synthetic method to access *(Z)*-isomer is essential and challenging due to the *(E)*- and *(Z)*-isomers interact differently with reagents and biomolecular targets. We have developed a stereoinvertive deoxygenation of *trans*-epoxides to access thermodynamically less stable *(Z)*-cinnamic acid derivatives such as ester, amides, alcohols and amines by using a catalytic system of nickel triflate and triphenylphosphine. The desired products were obtained with good to excellent yield and excellent *Z/E* ratio. Based on the experimental results, a reaction mechanism involving epoxide activation via coordination of the epoxide oxygen atom and the neighboring O- or N-atoms to the nickel catalyst, ring-opening of the epoxide by PPh_3 then the formation of the Ph_3P-carbon bond is proposed. Biologically active natural product, *N-cis*-feruloyl tyramine was synthesized in 5 steps from *trans*-ferulic acid to give the desired product in 6 % isolated yield (*Z/E* = 17:1).



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PA-10

Decarboxylative Functionalization of Carboxylic Acids by Metal Clusters Under Visible Light

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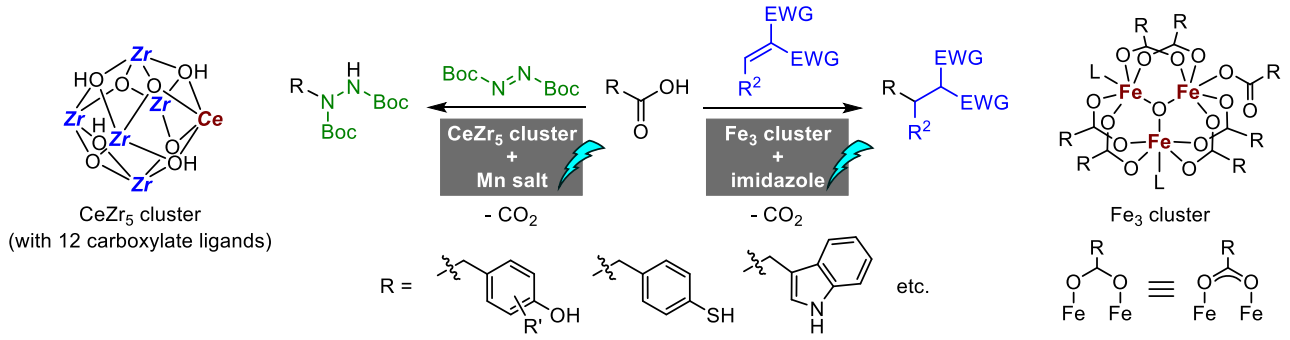
Decarboxylative functionalization of carboxylic acids through the generation of carboxyl radicals has attracted attention due to the widespread availability and versatility of the carboxylic acids as the starting materials in organic synthesis.[1] Carboxyl radicals can be produced from carboxylic acids *via* single-electron oxidation of their anions or through the thermal decomposition of their metal salts; however, these methods often lead to the degradation of sensitive oxidizable functional groups associated with the carboxylic acids. In this context, the photo-induced homolysis of metal–oxygen bonds in metal carboxylates, facilitated by ligand-to-metal charge transfer, presents a appropriate strategy for generating carboxyl radicals.[2] Our previous research has demonstrated that hexanuclear Ce(IV) clusters with oxo/hydroxo bridges and carboxylate ligands, $Ce_6O_4(OH)_4(OCOR)_{12}$, serve as effective photo-catalysts for the generation of carboxyl radicals from carboxylic acids under blue LED irradiation, giving the decarboxylative oxygenated products, including alcohols and carbonyl compounds, in the presence of dioxygen.[3] To address the challenges associated with the transformation of redox-labile carboxylic acids, we have developed single Ce(IV)-incorporated heterometallic clusters, $CeZr_5O_4(OH)_4(OCOR)_{12}$, which facilitate the decarboxylative hydrazination of carboxylic acids containing phenolic functionalities.[4] Furthermore, the decarboxylative alkylation of carboxylic acids has been successfully accomplished using imidazole-coordinated oxo-bridged Fe(III) clusters, $Fe_3O(OCOR)_7(Im)_2$, as the catalysts.[5]



Decarboxylative functionalization under visible light using metal clusters as photo-catalysts

Reference

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PA-11

Development of Alkyl Radical Precursors from Benzyl Alcohols for Visible Light Photocatalyzed C-C Bond Formation

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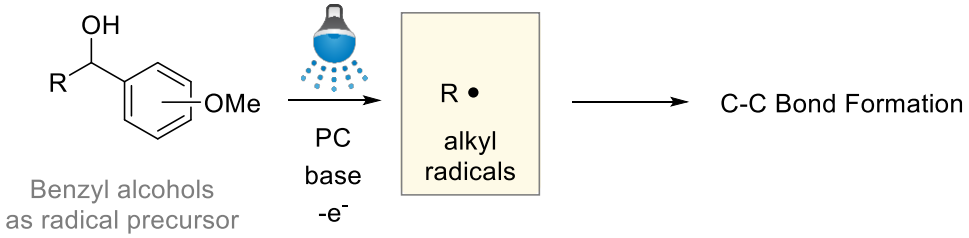
The formation of C-C bond is fundamental to constructing versatile organic compounds. The development of photochemistry and photocatalyst has encouraged chemists to explore various radical precursors for generating reactive intermediates in C-C bond formation. Numerous radical precursors have been developed; however, they are often constrained by challenges such as complex synthesis, low atom economy, or limited ability to generate diverse alkyl radicals. In this study, we have developed a novel radical precursor derived from easily synthesized benzyl alcohols. These precursors facilitate the generation of primary, secondary, and tertiary alkyl radicals via visible-light photoredox catalysis, presenting a versatile and efficient method for C-C bond formation in organic synthesis. This method involves intermolecular PCET, where the generated O-centered radicals induce β-scission of adjacent C-C bonds, leading to the formation of alkyl radical species that facilitate C-C bond formation. In this study, we developed benzyl alcohol precursors with various electronic properties and investigated the suitable photoredox catalysts for these precursors. Additionally, we utilized these precursors to develop various C-C bond-forming reactions.



Benzyl alcohols as alkyl radical precursors for C-C bond formation

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PA-12

Switchable Synthesis of Tritylone Alcohols and 2-Benzoylbenzoate Esters from Spiroindane-1,3-diones

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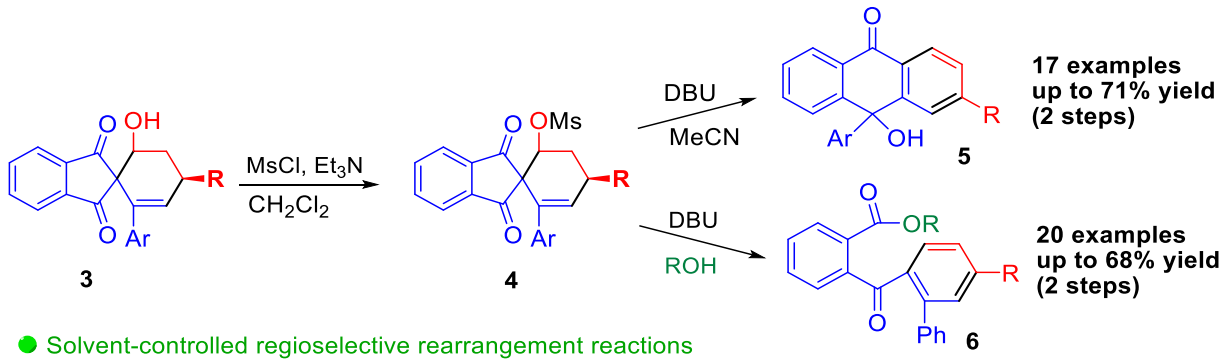
Tritylone derivatives[1] constitute an important class of organic polycyclic system that embedded in a plethora of synthetic compounds, which were used as precursors for the synthesis of fluorophores for bioimaging applications[1b] and organic light-emitting diodes.[1c] The 2-benzoylbenzoate derivatives have been applied to photochemically trigger the activity of serine proteases[2a], control release of fragrances[2b], or act as radical photoinitiators.[2c] In this study, we report a divergent synthesis of tritylone alcohols and 2-benzoylbenzoate esters through unprecedented solvent-controlled rearrangement reactions with spiroindane-1,3-diones[3], which were generated from 2-alkylidene 1,3-indandiones and enals according to our previous work with pyrrolidine as the catalyst.[4]



- Solvent-controlled regioselective rearrangement reactions
- Divergent synthesis of tritylone alcohols and 2-benzoylbenzoate esters
- Good to high yields of reaction products

Reference

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[2] (a) Jones, P. B.; Porter, N. A. *J. Am. Chem. Soc.* **1999**, *121*, 2753. (b) Pika, J.; Konosonoks, A.; Sing, P.; Gudmundsdóttir, A. D. *Spectrum* **2003**, *16*, 8. (c) Baltaa, D. K.; Karahanb, Ö.; Avcib, D.; Arsu, N. *Prog. Org. Coat.* **2015**, *78*, 200.
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PA-13

Helical Cyclodextrin Nanochannels

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Helicates are a defining element of DNAs and proteins with functions that are critical to a variety of biological processes. Cyclodextrins are promising candidates for forging multiple-stranded helicates with well-defined helicity, but a lack of available tools has precluded the construction of artificial helical nanochannels with controllable geometry and helicity from these widely available chiral building blocks. This presentation will introduce our group's foray into the construction of a rare class of metal-coordinated helical cyclodextrin nanochannels. These new nanochannels were interconnected by metal cations in the solid-state, resulting in the formation of extended 2D networks. By tuning the steric environment of the coordinating ligand on cyclodextrins, the helicity and geometry of the nanochannels can be precisely controlled.

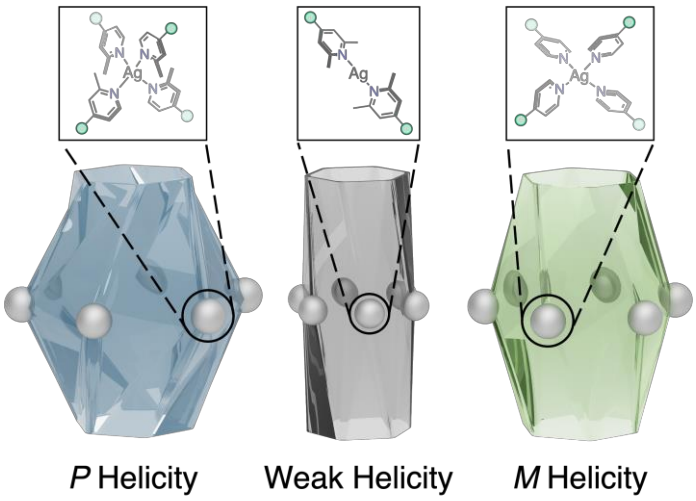

Figure 1. Cyclodextrin Nanotubes with Divergent Geometry and Helicity

Reference

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Synthetic and Supramolecular Chemistry

PA-14

Palladium-Catalyzed Decarbonylative Halogenation of Acyl Fluorides via Reductive Elimination of the C–X Bond

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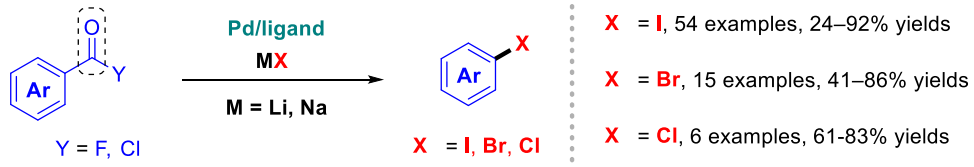
The long-held belief that the oxidative addition of aryl halides to Pd(0) is an irreversible process has been a focal point of significant debate and research over the past 30 years. Today, much of the attention in transition-metal-catalyzed halogenation reactions is directed towards the reductive elimination of C–X bonds from oxidatively induced high-valent metal centers.[1] In 2001, Hartwig conducted a mechanistic study on the Pd(II)-mediated reductive elimination of C–I, C–Br, and C–Cl bonds, discovering that this process was significantly accelerated by the bulky ligand P^{t}Bu$_3$.[2] Subsequently, Buchwald extensively investigated catalytic C–X bond reductive elimination, demonstrating the formation of C–Br,[3] C–Cl,[3] and even C–F[4] bonds from aryl triflates using sterically bulky BrettPhos or ^{t}BuBrettPhos ligands. However, efficient iodination has remained a challenging issue.

In a different approach, acyl fluorides—readily available derivatives of carboxylic acids—have garnered considerable interest as versatile intermediates for constructing various C–C and C–heteroatom bonds through decarbonylative coupling under transition metal catalysis.[5] Our research has led to the development of a Pd-catalyzed decarbonylative halogenation of acyl fluorides, enabling highly efficient and practical iodination, bromination, and chlorination using inexpensive lithium halides as halogen sources. Mechanistically, acyl fluorides act as mediators in the in-situ formation of acyl iodides, facilitating unimolecular fragment coupling (UFC) under mild conditions.[6]



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[Field of research] Organometallic Chemistry, Synthetic Organic Chemistry, Organic Functional Materials

PA-15

Harnessing Chiral Cyclopropenimine-Based Organocatalysts in Stereoselective Chemical Synthesis

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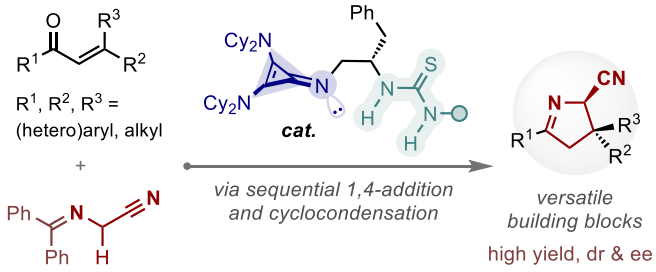
Chiral 1-pyrrolines containing a nitrile motif serve as crucial structural scaffolds in biologically active molecules and exhibit diversity as building blocks, owing to their valuable functional groups; however, the asymmetric synthesis of such compounds remains largely unexplored. Herein, we present an enantio- and diastereoselective method for the synthesis of α-chiral nitrile-containing 1-pyrroline derivatives bearing vicinal stereocenters through the design and introduction of chiral cyclopropenimine-based bifunctional catalysts featuring a thiourea moiety. This synthesis entails a highly stereoselective conjugate addition of α-iminonitriles to a wide array of enones, followed by cyclocondensation, thereby affording a series of cyanopyrroline derivatives, some of which contain all-carbon quaternary centers. Moreover, we demonstrate the synthetic utility of this strategy by performing a gram-scale reaction with 1% catalyst loading, along with a variety of chemoselective transformations of the product, including the synthesis of a vildagliptin analogue. Finally, we showcase the selective synthesis of all four stereoisomers of the cyanopyrroline products through *trans*-to-*cis* isomerization, highlighting the versatility of our approach.



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PA-16

One-Pot Synthesis of Cyclopentane-Fused Coumarin Photocages via Heck-Aldol Annulation

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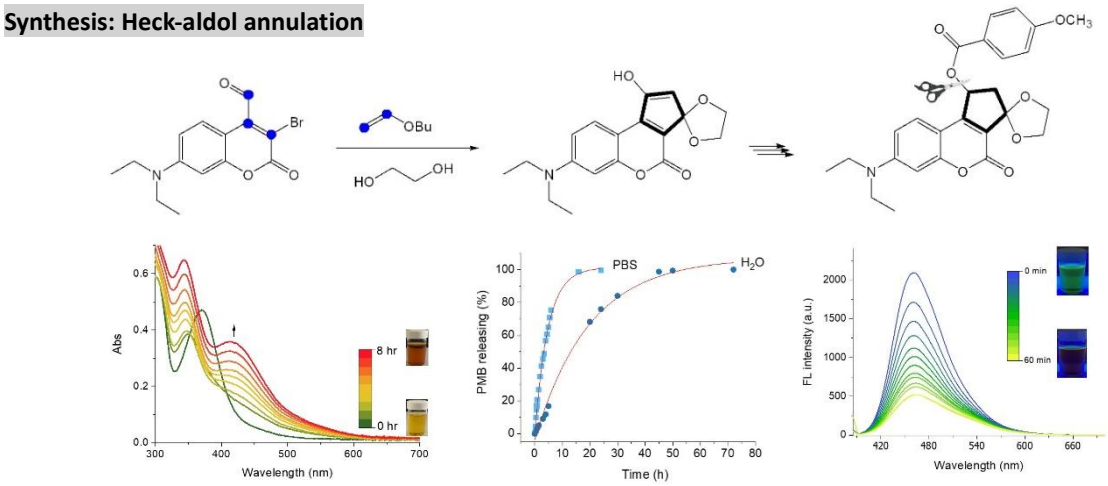
Coumarin derivatives with photocleavage properties are commonly employed in photo-induced drug release applications. In this study, we proposed a synthetic protocol for preparing cyclopentane-fused coumarin compounds with the photolysis property. A one-pot Heck-aldol-type annulation was introduced to synthesize the fused coumarin derivatives using ethylene glycol as the promotor and activator. The change in UV-Vis absorption profiles under 405-nm LED exposure clearly suggests the photoactive feature of the fused coumarins. Furthermore, red-shifted wavelengths and changes in color appearance implied a photo-elimination mechanism, which is consistent with the Specht's work[1]. The rate constants base on the payload releasing in HPLC analysis were well-fitted by the first-order kinetics. By further analyzing photo-induced uncaging quantum yields (Φ_u) in MeOH/H_2O and MeOH/PBS environments, a significant 4-fold enhancement in uncaging efficiency in PBS buffer was confirmed ($\Phi_u = 3.8 \times 10^{-3}$). We assumed that the phosphate ions favor the β-deprotonation to produce corresponding alkene motif during the elimination process. Additionally, the fused coumarin compounds exhibit remarkable fluorescent property with a quantum yield of Φ_f = 0.58. This feature also allows for monitoring the photolytic reaction through decreasing in the fluorescence intensity under light irradiation. In conclusion, these findings hold promise for the applications in light-regulated delivery systems.



Visible-triggered photoresponsive behaviors and kinetic study

Reference
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Professor
[Field of research] Organic materials for biomedicinal applications.

PA-17

Is π-Single Bonding (C–π–C) Possible? A Challenge in Organic Chemistry

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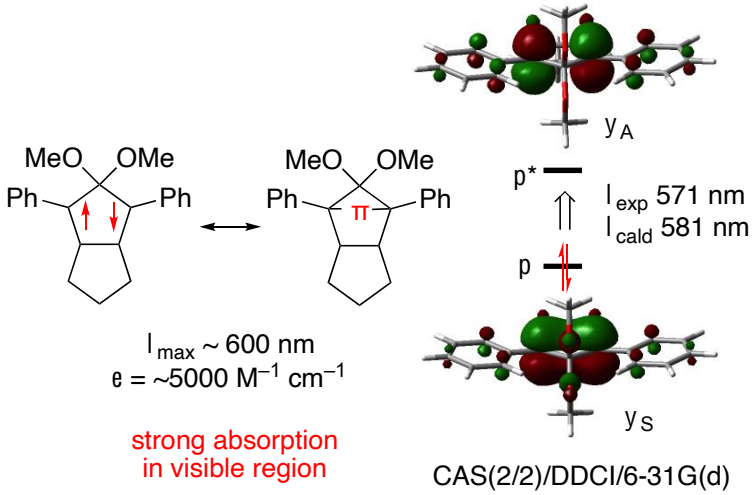
Chemical bonding systems determine the nature of molecules. In organic chemistry, there are two bonding types for carbon–carbon connections: σ-bonding and π-bonding. In this presentation, several aspects of studies in the last two decades addressing a naive question "Is π-single bonding (C–π–C) possible?" will be presented: (1) features of π-single bonded species; (2) molecular design for π-single bonding; (3) generation and detection of singlet diradicaloids with a π-single bonding character; (4) future prospects of π-single bonded species.



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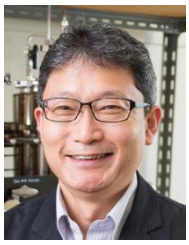

Kyoto Institute of Technology (Ph.D. 1995, Professor Akira Oku). Assistant Professor, Associate Professor, Department of Applied Chemistry, Osaka University (1995-2007). Since 2007, Professor, Department of Chemistry, Hiroshima University (HU). Chair of IUPAC Subcommittee on Structural and Mechanistic Chemistry. Research Interests: Reactive Intermediates Photochemistry, and Computational Chemistry

PA-18

Solvent-Free Approach in the Development of *O*-Sialylation Chemistry

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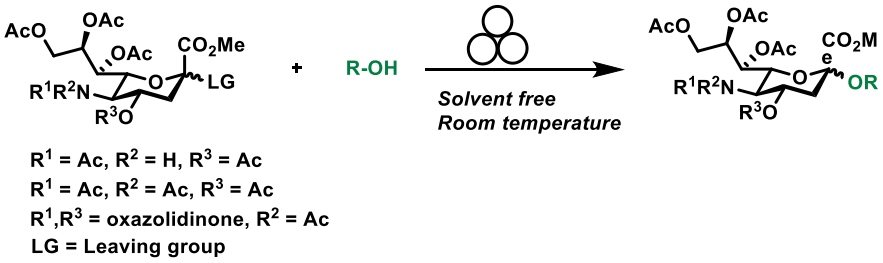
α-Sialylation represents highly significant synthetic targets because of their prevalence in natural oligosaccharides, which play key roles in various biological processes. Achieving high α-stereoselectivity remains a significant challenge in the synthesis of sialyl oligosaccharides, as sialylation reactions generally demand strictly anhydrous conditions and low temperature. In the previous study, we developed a robust strategy using $Yb(OTf)_3$ to indirectly activate the 2-α-fluorosialyl donors. The 2-α-fluorosialyl donor with a 5-*N*,4-*O*-oxazolidinone ring consistently yields exclusive α-linkages to the C3 hydroxyl group of galactosides. This approach reliably delivers good to excellent yields with minimal hydrolysis and elimination side-products, highlighting its broad applicability. However, this approach requires improvement in terms of the stereoselective α-linkages to the primary hydroxyl group of galactosides and glucosides. To achieve high α-stereoselectivity in linking to primary hydroxyl groups, this study presents a mechanochemical approach that facilitates solvent-free sialylations using a ball mill, enabling the highly stereoselective synthesis of α-sialosides. We obtained exclusive α-linkages by using $Yb(OTf)_3$ to react with 2-β-fluorosialyl donor and various acceptors.



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Pei-Jhen Li (李珮甄). National Chung Cheng University

Assistant professor (3 years). Carbohydrate Chemistry.

PA-19

Cobalt/Photoredox Dual Catalysis-Enabled Cycloisomerization of 1,6-Diynes via Chemo- and Enantio-Selective C(sp^3)–H Activation

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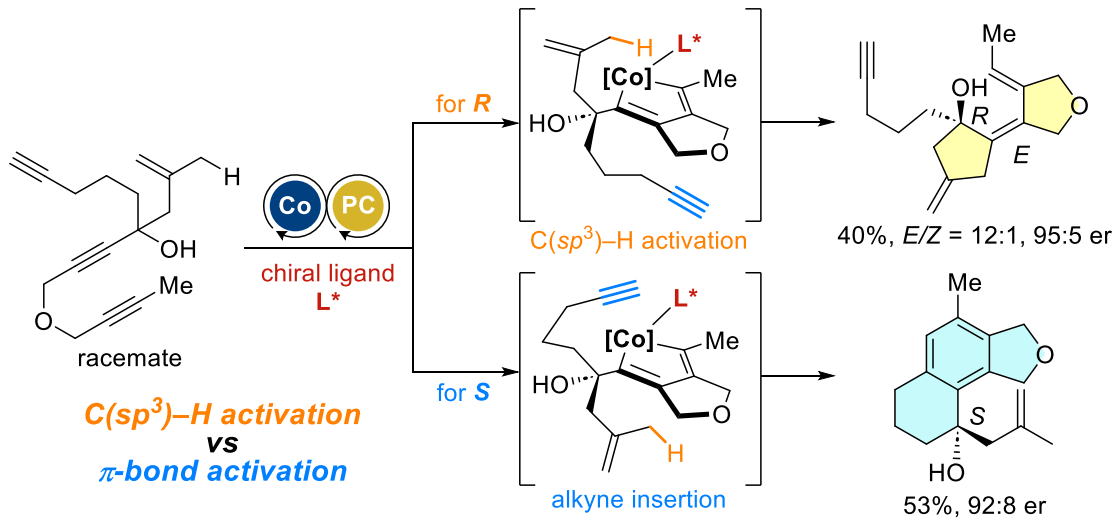
Metalloles are generally recognized as key intermediates for cycloaddition reactions to access benzene and pyridine derivatives via π-bond activation such as alkyne and nitrile insertion. In contrast, metalloles can also facilitate the C–H bond activation via σ-complex-assisted metathesis to access multi-substituted 1,3-dienes, which can be further transformed into complex 3D polycyclic molecules via double bond functionalizations. However, cycloaddition reactions via the metallole-mediated C(sp^3)–H bond activation are still very challenging, especially in the presence of more reactive π-component such as alkynes or alkenes. In this presentation, we disclose the cycloisomerization of 1,6-diyne derivatives via the metallole-mediated chemo-selective C(sp^3)–H bond activation. We demonstrated the enantioselective desymmetrization of symmetrical dienediynes using a chiral ligand to afford the corresponding 1,3-diene products with high enantioselectivity. Furthermore, we also demonstrated the chemo-divergent parallel kinetic resolution of unsymmetrical substrates such as enetriynes, dienediynes, and diynenitriles.



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Takeshi Yasui (安井 猛). Nagoya University (Ph. D., 2013). Takeda Pharmaceutical Company Limited (Scientist, 2013; Principal Scientist, 2016). Tri-Institutional Therapeutics Discovery Institute (Scientist, 2014–2015). Nagoya University (Assistant Prof., 2017). Field of research: Synthetic Organic Chemistry, Development of Transition-Metal-Catalyzed Transformations.

PA-20

Rapidly Diverse Synthesis of *N*-Aryl-5-Substituted-2-Oxazolidinones via Nucleophilic Epoxide Ring Opening and Intramolecular Acyl Substitution

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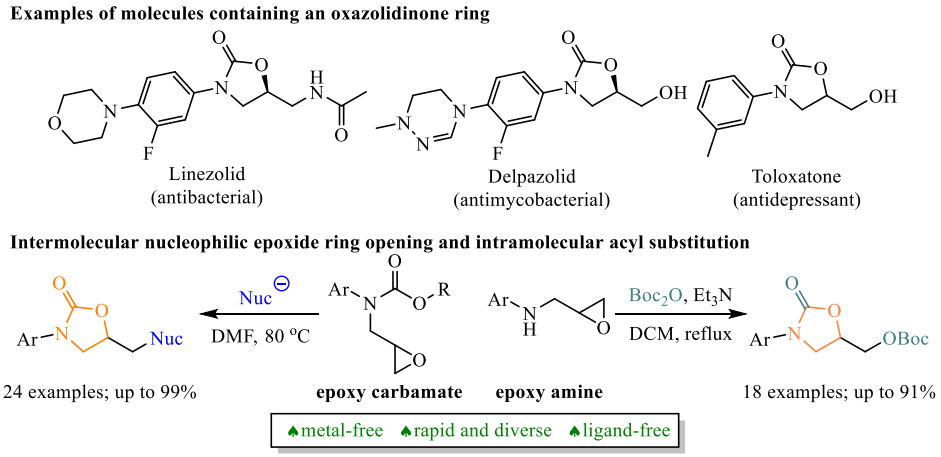
Oxazolidinones (1,3-oxazolidin-2-ones) rank 15th among the top 100 most commonly used heterocyclic ring systems in small-molecule drugs, underscoring their significant pharmaceutical importance due to diverse pharmacological properties like antibacterial and antidepressant activities. This study presents efficient and scalable methods for synthesizing oxazolidinone derivatives. Firstly, we outline an innovative one-step method for converting epoxy carbamates to oxazolidinones by combining intermolecular nucleophilic epoxide ring opening with intramolecular acyl substitution. This approach addresses challenges associated with expensive reagents, harsh reaction conditions, and prolonged reaction times. It demonstrates favorable reactivity across a diverse range of aryl groups and with benzyl or *tert*-butyl carbamates, consistently yielding satisfactory results with oxazolidinone formation ranging from 55% to 99% over 24 examples. Notably, the synthesized oxazolidinones hold substantial promise as intermediates for the synthesis of crucial synthetic molecules. Secondly, we introduce a simple and practical synthesis of 5-(hydroxymethyl)oxazolidin-2-one derivatives using Boc_2O, which serves a dual role by providing both the carbonyl and hydroxymethyl groups. This method yields good to excellent results, exceeding 90% for stable substrates. A substrate scope study revealed the influence of epoxide stability and aryl substituent electronic effects on reaction efficiency.



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Cheng-Kun Lin (正坤 林). National Chung Hsing University (Ph. D., 2011). Genomics Research Center, Academia Sinica (Postdoctoral Fellow, 2011); Department of Chemistry, National Chung Hsing University (Assistant Prof., 2018; Associate Prof., 2024). Research field: Heterocycle Chemistry, Asymmetric Synthesis, Total Synthesis.

PA-21

Photoinduced acylation of quinoxalin-2(1*H*)-ones *via* electron donor-acceptor complexes

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Electron donor-acceptor (EDA) complex formation has opened new avenues for synthetic chemists in photochemical strategy by diminishing the reliance on exogenous photocatalysts. This strategy is enabled by the direct photoexcitation of a new absorption band, generated from the association of an electron-rich donor and an electron-deficient acceptor, to produce a reactive radical species. The applicability of this approach has been demonstrated through the implementation with a diverse range of radical precursors, including alkyl halides, redox-active esters, arylphosphine oxides, arylsulfinate anions, and Katritzky salts. Herein, we aim to develop a photoinduced acylation protocol under metal- and photocatalyst-free conditions that employs EDA complex formation. The attachment of an electron-accepting group on acyl oxime esters can form a key EDA complex with DBU, leading to the generation of acyl radicals under blue light irradiation. This facile methodology enabled the efficient synthesis of acylated quinoxalin-2(1*H*)-one derivatives in moderate to good yields. Furthermore, subsequent MTT assays revealed a potent antiproliferative activity of benzo[*g*]quinoxalinone derivatives against A549 cell lines.

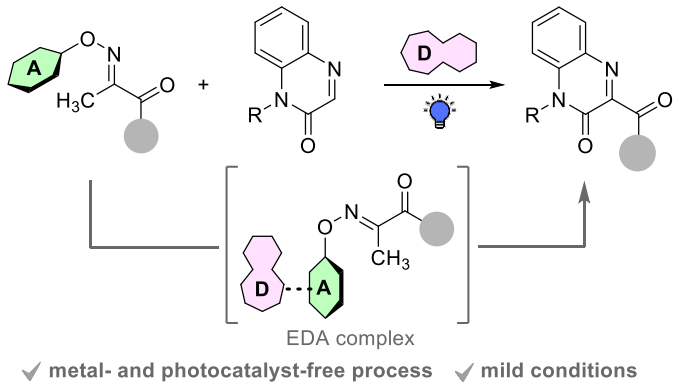

Figure 1. Photoinduced acylation and the key EDA complex

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Worawat Niwetmarin (วรวัช นิเวศน์มรินทร์). University of Bristol (Ph.D., 2017, Advisors: Prof. Timothy C. Gallagher and Prof. Varinder K. Aggarwal). Lecturer (Chulabhorn Graduate Institute, 2017 - 2023). Assistant Professor (Chulabhorn Graduate Institute, 2023 - present). [Synthetic methodology] Organic Chemistry.

PA-22

Pyrrolidine Synthesis via Ring Contraction of Pyridines

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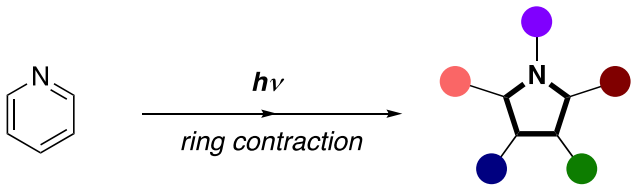
Creation of innovative catalysts and reactive species that enable efficient transformation of unreactive bonds and molecules has been a formidable challenge in synthetic chemistry and catalysis science. We have been working on design, synthesis, and utilization of heterobimetallic transition metal catalysts having metal-metal bonds supported by precisely designed organic scaffolds, which enable efficient transformation of carbon dioxide and other organic molecules.[1] We also achieved an unprecedented C–C σ-bond cleavage reaction of ambiphilic phosphine-borane compounds under photoirradiation conditions enabled by transiently generated excited Frustrated Lewis Pairs.[2] Furthermore, we have demonstrated that the new cooperative catalysis merging photochemistry and transition metal catalysis enables unprecedented C–C σ-bond cleavage and functionalization of arylketones.[3]

In this presentation, we discuss our new findings on a photochemical reaction of pyridines that enables efficient synthesis of pyrrolidine derivatives via ring contraction.[4] A ring contraction of easily available cyclic compounds to smaller cycles that are valuable but difficult to synthetically access is one of important skeletal editing strategies. We found that pyridine reacted with some reagent under photochemical reaction conditions to afford pyrrolidine derivatives with broad substrate scope and high functional group compatibility. The details and reaction mechanism will be discussed in the poster presentation.



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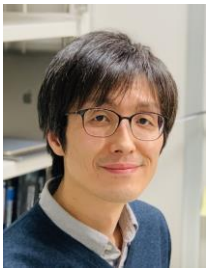

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PA-23

Asymmetric Desymmetrization of Alkynyl-Tethered 2,5-Cyclohexadienones

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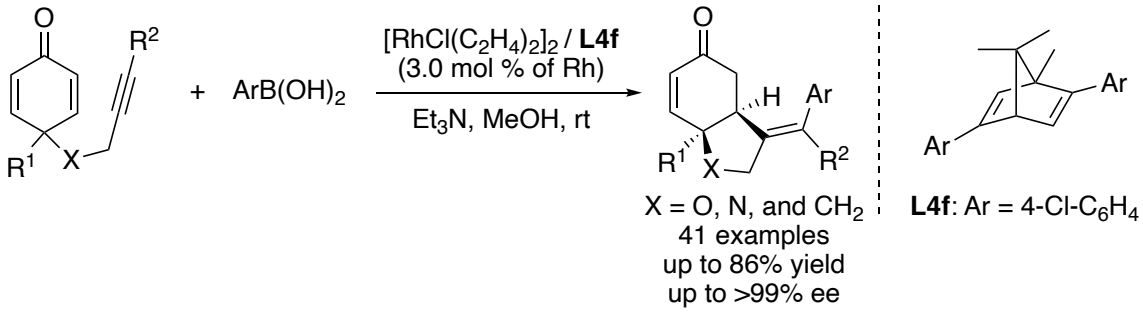
Cis-hydrobenzofurans, *cis*-hydroindoles, and *cis*-hydrindanes, privileged structural motifs found in numerous biologically active natural and synthetic compounds, are efficiently prepared by a Rh(I)-catalyzed cascade *syn*-arylation/1,4-addition protocol. This approach starts with the regioselective syn-arylation of the alkyne tethered to 2,5-hexadienone moieties, using a chiral Rh(I) catalyst generated *in situ* from a chiral bicyclo[2.2.1]hepatadiene ligand **L4f**. By forging two new carbon−carbon bonds and introducing two chiral centers, the resulting alkenylrhodium species undergoes desymmetrization via an intramolecular 1,4-addition reaction, delivering annulated products with high yields and enantioselectivities.



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Hsyueh-Liang Wu (吳學亮). National Tsing-Hua University (PhD, 2004). Professor (2017). [Field of research] Synthetic Organic Chemistry; Asymmetric Catalysis

PA-24

Linkage-Editing Strategy for Creation of pseudo-Glycans

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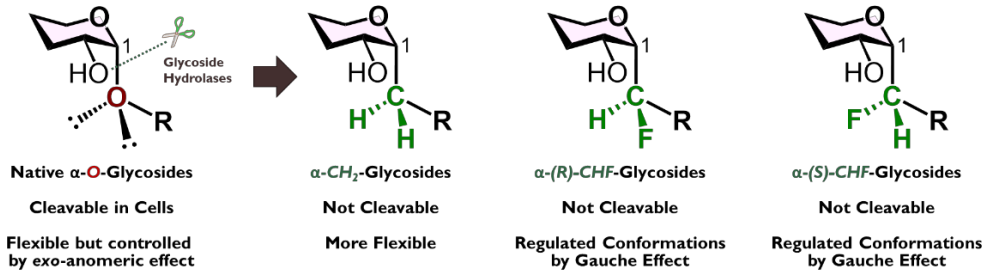
Our research interest is to develop glycan or glycoconjugate analogs (pseudo-glycans or glycoconjugates) with enhanced or different biological functions while preserving their structures as much as possible in order to contribute to the glycobiology and drug discovery research. In this talk, we will present the development of pseudo-glycans with a C-glycosidic linkage that is not degraded by glycoside hydrolases in cells.1 We have recently established an efficient method to stereoselectively obtain C-glycoside analogs by controlling anomeric radical species generated by a photoredox catalytic system.2 Based on this methodology, we aimed to synthesize pseudo-glycans with CH2- and CHF-linkages, similar to O-glycoside in bond lengths, angles, and bulkiness, but with different conformational distribution patterns (Linkage-Editing Strategy). Their efficient preparation was realized through fluorovinyl C-glycosylation and selective hydrogenation reactions. Application of this strategy for biologically active glycans such as isomaltose, a promoter of amylase expression, resulted in the discovery of pseudo-glycans with enhanced or altered biological functions.3 These results indicated the usefulness of the Linkage-Editing Strategy, which can create unique biologically-active molecules that are resistant to glycoside hydrolases.



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Go Hirai (平井 剛). Tohoku University (Ph.D, 2002). Assistant professor, IMRAM, Tohoku University (2002-2004). Research Scientist, RIKEN (2004-2010). Senior Research Scientist, RIKEN (2010-2016). Professor, Kyushu University (2016-). [Field of research] Synthetic Organic Chemistry, Bioorganic Chemistry, Chemical Biology

PA-25

Synthetic Approaches to C–Si Bond Formation via Hydrosilanes

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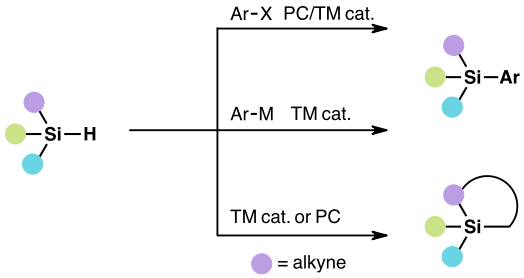
Organosilanes, featured with carbon-silicon bonds, constitute a fundamental compound class in organosilicon chemistry. They exhibit broad applications in material science and medicinal chemistry. The construction of organosilicon molecular structure has predominantly relied on the nucleophilic substitution of the chlorosilane with Grignard or organolithium reagents, the Kipping method. However, the use of strong basic reagents in these synthetic methods leads to poor functional group tolerance and limited reaction scope. Therefore, development of novel synthetic methods for the C–Si bond construction is essential to enhance molecular diversity, structural complexity, and functional group compatibility.

Hydrosilanes serve as versatile synthetic precursors for preparation of organosilanes. Si–H bonds can be activated via transition metal catalyzed oxidative addition or thermal- or photo-induced hydrogen atom transfer (HAT). Herein, several synthetic methods for constructing C–Si bond via Si–H bond activation are designed and currently being studied in progress. The first approach involves the dual photoredox and transition metal catalyzed cross coupling of hydrosilanes with aryl halides to yield aryl silanes.[1] Additionally, the second synthetic strategy explores the aryl silylation using aryl boronic acid/ester as coupling partners.[2] Finally, the transition metal-catalyzed intramolecular silylation is also being investigated as a promising approach for the synthesis of novel silicon-incorporated organic materials.[3]



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National Cheng Kung university (PhD, 2017). National Chi Nan University (Assistant Professor, 2022-present).

Research field: Organic Synthesis, Organosilane Chemistry.

PA-26

1,2-*P*-Migrative [3+2] Cycloaddition of tri(*t*-butyl)phosphine with Alkynes

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Alkyl radical species can undergo 1,2-migration of various β-substituents, generating thermodynamically more stable alkyl radicals at the β-position.[1] Most studies dealt with carbon atom migrations, and 1,2-migrations of heteroatoms have rarely been reported so far. Specifically, 1,2-phosphorus migration of alkyl radicals has not been reported.

Herein reported is a photocatalytic [3+2] cycloaddition of tri(*t*-butyl)phosphine with terminal alkynes involving 1,2-phosphorus migration of β-phosphonioalkyl radicals.[2] When a mixture of tri(*t*-butyl)phosphonium tetrafluoroborate, tri(*t*-butyl)phosphine (10 mol%), and methyl propargyl ether (2.0 equiv) in acetonitrile was irradiated with blue light at ambient temperature for 15 h in the presence of a photoredox catalyst (4-CzIPN, 5 mol%), cyclic phosphonium salt was obtained in 84% yield (Figure 1). The product had a Me,Me-disubstituted quaternary carbon atom β to the phosphorus atom of the phospholane ring, indicating the occurrence of 1,2-*P*-migration. The reaction exhibits broad functional group tolerance and could be combined with the Wittig reaction to synthesize structurally diverse phosphine oxides. Experimental and theoretical studies suggest that the 1,2-*P*-migration of a β-phosphonioalkyl radical proceeds through a phosphine radical cation–alkene van der Waals complex as a pseudointermediate, and the two fragments in the intermediate are bound to each other through multiple noncovalent interactions.

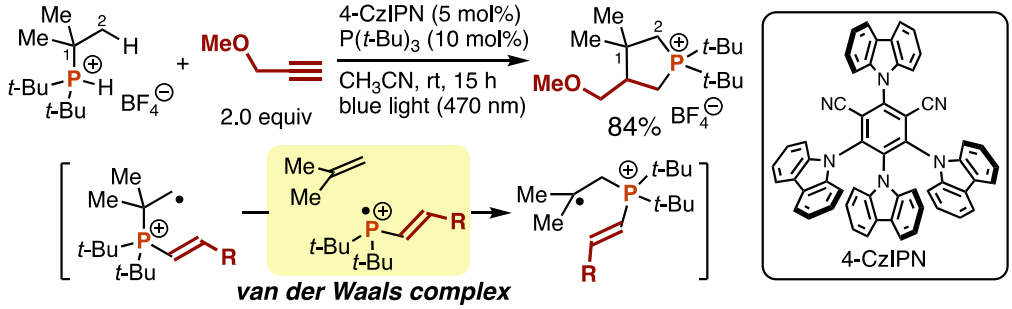

Figure 1. Photocatalytic 1,2-*P*-migrative [3+2] cycloaddition

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Kyoto University (PhD, 2017). Post-doctoral fellow at California Institute of Technology (2017-2018). Specially appointed assistant professor at Kyoto University (2018-2021). Assistant professor at Hokkaido University (2021-). [Field of research] Synthetic Chemistry, Organometallic Chemistry.

PA-27

Energy-Transfer-Induced [3+2] Cycloadditions of N−N Pyridinium Ylides

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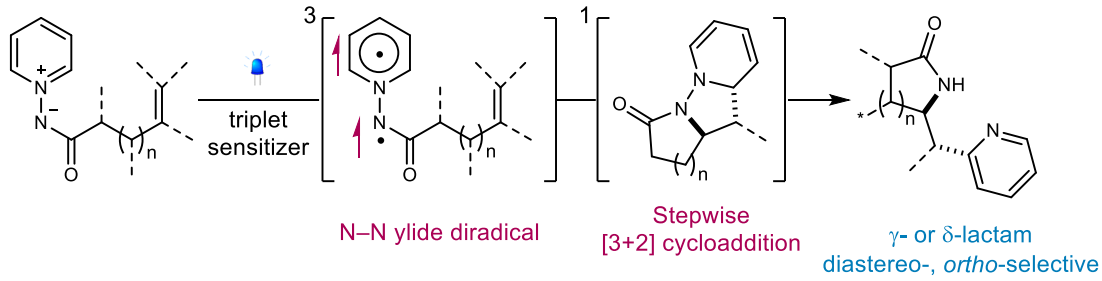
Photocycloaddition is a powerful reaction to enable the conversion of alkenes into high-value synthetic materials that are normally difficult to obtain under thermal conditions. Herein, we describe an efficient approach to diastereoselective pyridyl lactamization via a photoinduced [3+2] cycloaddition, based on the unique triplet-state reactivity of N−N pyridinium ylides in the presence of a photosensitizer. The corresponding triplet diradical intermediates allow the stepwise radical [3+2] cycloaddition with a broad range of activated and unactivated alkenes under mild conditions. This method exhibits excellent efficiency, diastereoselectivity, and functional group tolerance, providing a useful synthon for *ortho*-pyridyl *γ*- and *δ*-lactam scaffolds with *syn*-configuration in a single step. Combined experimental and computational studies reveal that the energy transfer process leads to a triplet-state diradical of N−N pyridinium ylides, which promotes the stepwise cycloaddition.

We will provide our recent contributions to the development of *N*-functionalized pyridinium salts and ylides and summarize the cornerstones of organic reactions that successfully employ these pyridinium reagents under visible light conditions.



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PA-28

Catalytic α-deuteration of amides and esters

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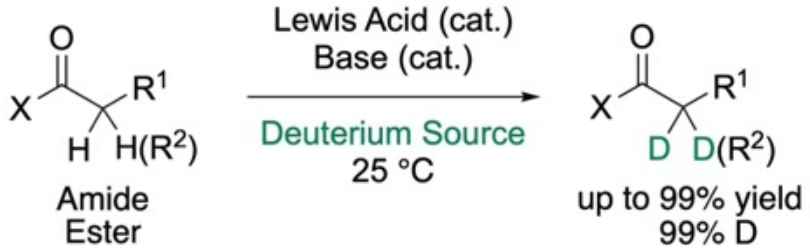
Deuterium atoms, which are stable isotopes of hydrogen, are easy to handle and compounds substituted with deuterium can be made more durable with minimal change in the overall properties of the molecule. Deuterium compounds are therefore attracting attention as products with a long product life and high environmental compatibility. While deuterium atoms naturally exist, the commercial product range is limited to simple low-molecular compounds such as solvents. The current high cost of deuterium compounds is therefore a barrier to their expanded use and practical application.

In recent years, significant efforts have been directed towards the development of catalytic deuteration through hydrogen-deuterium (H-D) exchange reactions.[1] However, practical catalytic deuteration reactions encounter challenges such as the requirement for harsh reaction conditions and precious metal catalysts, as well as difficulties in controlling the position of deuterium introduction.

In this study, we have successfully developed an efficient and practical synthetic method for the catalytic deuteration of amide and esters under mild conditions.[2] The broad substrate scope, which includes natural products and pharmaceuticals, demonstrates its high applicability to the late-stage deuteration of complex molecules. This operationally simple catalytic protocol allows for rapid access to various deuterated molecules.



- ✔ Enolizatiton without stoichiometric amount of Brønsted base
- ✔ Direct α-deuteration of amides and esters inclooding pharmaceuticals
- ✔ Transformations into various structures with retention of deuterium

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PA-29

Stereodivergent Syntheses of Two Families of *Ascidian* Alkaloids Lepadiformine and Fasicularin through Double Consecutive Epimerizations

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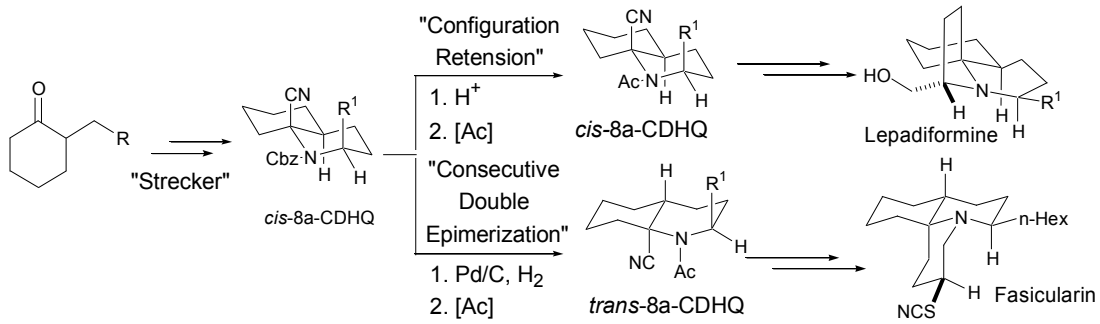
We describe here stereodivergent syntheses of two families of *Ascidian* alkaloids lepadiformine and fasicularin, include-ing their epimers and derivatives. The syntheses feature stereocontrolled syntheses of the N-acetyl-8a-cyano- decahydroquinoline frameworks from sterically well-defined α-aminonitrile, the base-mediated intramolecular cyclization to establish the spiral quaternary center of the tricyclic framework, and reductive function-alization of a tertiary γ-lactam.
The approach allows us to accomplish two tricyclic core structures efficiently from readily available starting materials through simple operations. Thanks to the unexpected consecutive epimerizations at two contiguous stereocenters, observed on the basis of single-crystal X-ray analyses of the intermediates and derivatives, the epimerization mechanism has been elucidated through a series of deuterium-labelling controlled experi-ments.



Reference
1. Yu-Tang Wang (王昱棠), Jui-Lin Wu (吳瑞麟) and **Wen-Hua Chiou** (邱文華)* "Total Synthesis of (±)-Fasicularin through Double Consecutive Epimerizations" *Org. Lett.* **2022**, *24,* 5957-5961.
2. Jui-Lin Wu (吳瑞麟) and **Wen-Hua Chiou** (邱文華)* "Diastereocontrolled Formal Syntheses of (±)-Lepadiformines A, B and C and the Divergent Synthesis of 2-*epi*-Lepadiformine C through Unexpected Double Consecutive Epimerizations" *J. Org. Chem.* **2020**, *85,* 9051-9063.

Wen-Hua Chiou (邱文華), National Tsing Hua University (BS, 1993; MS, 1995), State University of New York at Stony Brook (Ph.D. 2005), OSI Pharmaceutical Inc., (Post Doc., 2006), Professor of National Chung-Hsing University since 2015. Research Interest: (1). Development of the domino reactions such as Rh-catalyzed Domino Hydroformylation Double Cyclization. (2) Syntheses towards natural products with medicinal bioactivity or structure interests, especially through a *domino design* or a *stereodivergent* pathway of the new methodologies.

PA-30

The Chemistry of Carbone

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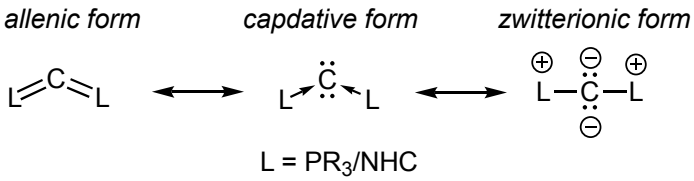
Carbones (L→C←L) have emerged recently as a new class of organic molecules featuring carbon(0) directly stabilized by two electron-rich groups (L) through Lewis donor-acceptor interaction.[1] Other mesomeric features can also be understood in terms of allenic or zwitterionic form. Owing to the peculiar bonding situation and the zero-valent nature of the central atoms, carbones have attracted much attention in the chemical community as NHC alternatives because their strong σ-donating ability broadly impacts transition-metal coordination, small molecule activation, main-group chemistry, redox non-innocent coordination, and catalysis.[2] This presentation will describe the synthetic preparation and chemical properties of the carbone as well as its application toward supporting metallic complexes for catalysis in tandem photoredox, cross-coupling reaction via tandem C–H and C–O bond activation and a new spin in diversifying FLP reactivity with co-modulator benzyl alcohol.



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[Field of research] Organometallic Chemistry

PB-01

Iron Redox Catalysis in Radical Cation Cycloaddition Reactions

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Since the advent of photochemistry, there has been a significant push to replace the photoredox catalysts containing Ru and Ir with those of earth-abundant and sustainable metals; metals such as Cr, Mn, Fe, Co, Ni, and Cu are particularly attractive in the first-row transition metals.[1] Green-light-driven $Fe^{III}(btz)_3$ photocatalysis[2] for the radical cationic [4+2] cyclo-addition of terminal styrenes and nucleophilic dienes has been investigated. The Fe-MIC (mesoionic carbene) complex forms a ligand-to-metal charge-transfer transition state with relatively high oxidation potentials which can selectively oxidize terminal styrene derivatives, which are difficult to form by traditional metal photocatalysis. Unique multi-substituted cyclohexenes and structurally complex bio-relevant cyclohexenes were constructed highlighting the usefulness of this mild and practical first-row transition metal complex system.[3]

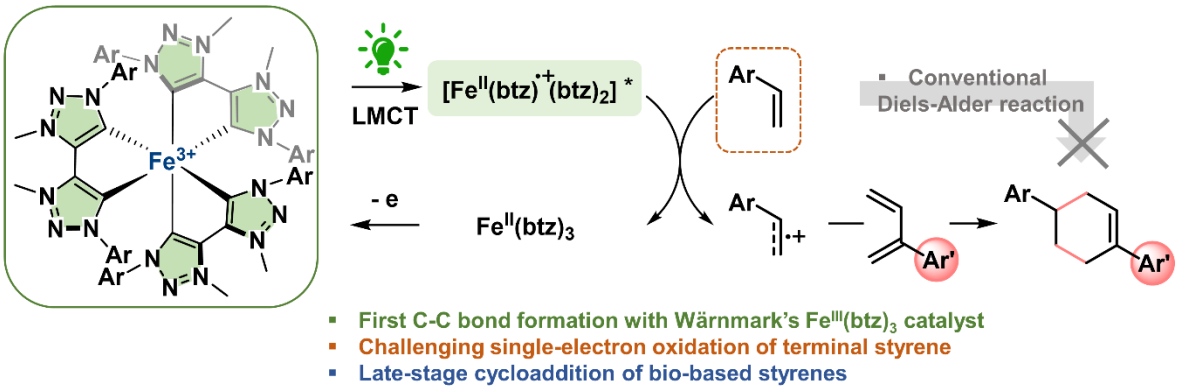

Figure 1. Fe-MIC complex for radical cationic [4+2] cycloaddition

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[Field of research] Iron Catalysis, Photoredox Chemistry, Organophoto Catalysis, CO_2 Utilization.

PB-02

Lasso peptide MccJ25 as a supramolecular scaffold

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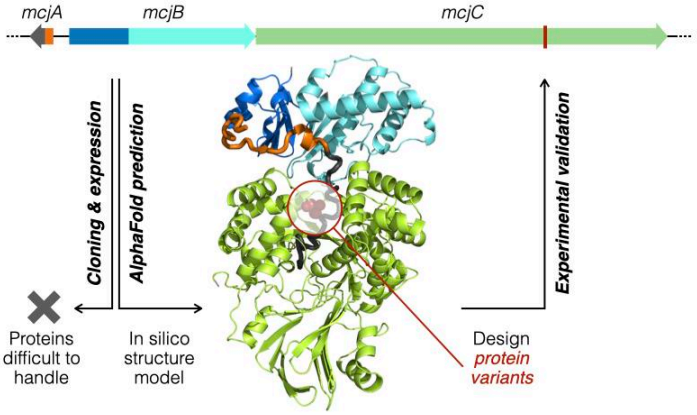
Microcin J25 (MccJ25), a lasso peptide antibiotic with a unique structure that resembles the lariat knot,[1] has been a topic of intense interest since its discovery in 1992.[2] The precursor (McjA) contains a leader and a core segment. McjB is a protease activated upon binding to the leader, and McjC converts the core segment into the mature MccJ25. Modification of MccJ25 has thus far been limited to those that are tolerated by its biosynthetic enzymes, whereas our knowledge of the structural and molecular intricacies of MccJ25 biosynthesis remains very limited.[3] To close this knowledge gap, we used AlphaFold2 to predict the structure of the precursor (McjA) in complex with its biosynthetic enzymes (McjB and McjC) and queried critical predicted features by protein engineering.[4] Based on the predicted structure, we designed protein variants to verify that McjB can still be functional and form a proficient biosynthetic complex with McjC when its recognition and protease domains were circularly permutated, or split into separate proteins. Specific residues important for precursor recognition were also identified. Furthermore, we have developed a chemoenzymatic method to manipulate MccJ25 and enabled the incorporation of practically any molecular building block.[5] While MccJ25 research (and that of lasso peptides in general) has long been mired by challenges to experimentally handle it and its associated enzymes,[6] our combined use of artificial intelligence tools (AlphaFold2), protein engineering, and chemical synthesis opened a new avenue for the study of this class of supramolecular natural products.



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Natural Product Chemistry / Bioactive Small Molecules

PB-03

Total Biosynthesis of Melleolides; Mechanistic Analysis of the Multi-Functional GMC oxidase Mld7

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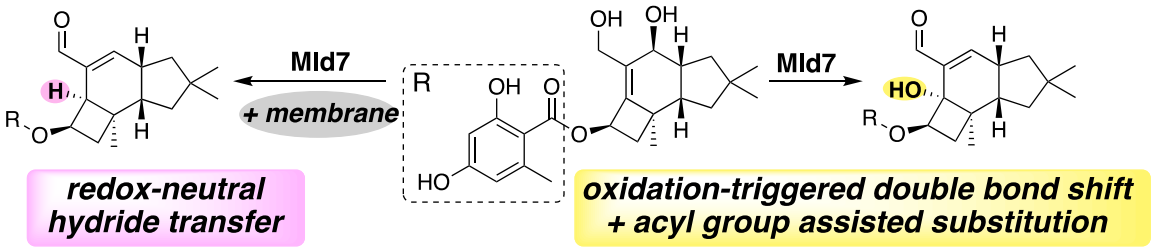
Melleolides isolated from mushroom are representative sesquiterpenoids with a characteristic protoilludane skeleton. The successful identification of a terpene synthase provided opportunities to elucidate the biosynthetic pathway. In this study, we applied a recently established hot spot knock-in method to elucidate the biosynthetic pathway leading to 1α-hydroxymelleolide [1]. The biosynthesis of the sesquiterpene core involves the cytochrome P450 catalyzing stepwise hydroxylation on the Δ^6-protoilludene framework and a stereochemical inversion process at the C5 position catalyzed by short-chain dehydrogenase/reductase family proteins. The highlight on the biosynthesis is that the flavoprotein Mld7 catalyzes an oxidation triggered double bond shift accompanying dehydration and acyl group assisted substitution with two different nucleophiles at the C6 position to afford the Δ^7-protoilludene derivatives such as melleolide and armillarivin. The complex reaction mechanism was proposed by density functional theory (DFT) calculations. Of particularly importance is that product distribution is regulated by the interaction with cell membrane. This proposed biosynthetic pathway provides an opportunity to understand the structural diversification mechanisms of melleolides and protoilludane sesquiterpenes.



Proposed function of GMC oxidase Mld7

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[Field of research] Bioorganic Chemistry, Natural Product Chemistry.

PB-04

(4+3) Cycloadditions of Oxetanyl and Azetidinyl Enolsilanes

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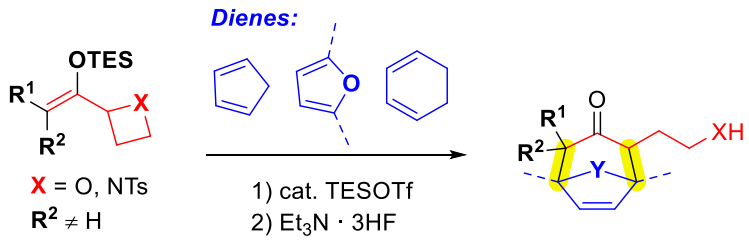
(4+3) Cycloadditions construct functionalized seven-membered carbocyclic rings—frameworks which are featured in many natural products. The design of precursors that serve as three-carbon dienophiles for (4+3) cycloadditions with dienes result in differently functionalized cycloadducts.

Oxetanes can react as electrophiles in a variety of ring opening reactions.[1] However, to the best of our knowledge, all the reactions of oxetanes or azetidines that form more than one new bond have only produced heterocycles: no cycloadditions involving the formation of two C–C bonds to produce carbocycles has been reported. This is not unexpected because ring openings of oxetanes or azetidines reveal highly nucleophilic oxygen or nitrogen residues that would compete and react effectively with the electrophilic species present.

We have been studying the applications of epoxy and aziridinyl enolsilanes to generate active dienophiles, that undergo (4+3) cycloadditions with dienes successfully.[2] Extending this work, we were interested in the feasibility of oxetanyl and azetidinyl enolsilanes to undergo (4+3) cycloadditions to generate cycloheptane frameworks.[3] Compared with epoxides and aziridines, the attenuated strain of oxetanes and azetidines, as well as their different geometrical alignment and steric hindrance are factors that could impact the success of the desired cycloaddition. In this poster, we will report on the outcomes of the studies on these inter- and intramolecular (4+3) cycloadditions.



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PB-05

Borataanthracenide: a novel type of counteranion for addition polymerizations

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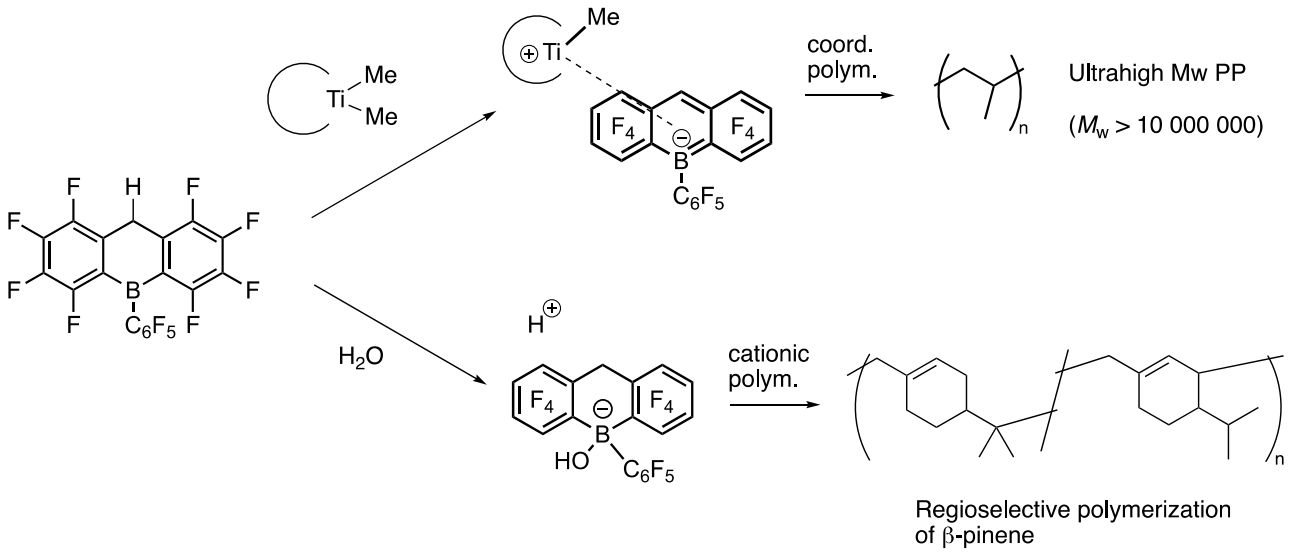
The development of new metal complexes has long been studied in the coordination olefin polymerization chemistry because electronic and steric effects of the ligands greatly influence the polymerization behavior such as activity and stereospecificity. However, the design of ligand has becoming more and more and complicated and the state-of-art catalyst often requires over 10 steps of synthesis. Most of coordination polymerization applies cationic metal alkyls as active species, and thus the design of anionic counterpart also pays attention to orthogonally controlling the polymerization behavior in the recent studies [1].
We have recently succeeded in synthesizing ultrahigh-molecular weight polypropylene using newly developed borataanthracenide as a counteranion [2]. This counteranion is generated *in situ* by contacting neutral metal alkyl and 9,10-dihydroboraanthracene precursors via alkane elimination. Moreover, this borataanthacenide anion also helps control rearrangement reactions during the cationic polymerization of β-pinene [3]. In this presentation, the recent progress in these chemistries will be summarized.



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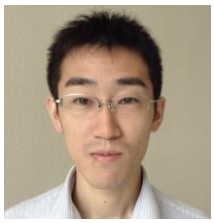

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[Field of research] Polymer Chemistry, Organometallic Chemistry.

PB-06

Stereoconvergent Synthesis of Allylsilanes from an *E*/*Z* Mixture of Alkenyl Ethers *via* Ni/Ru Catalysis

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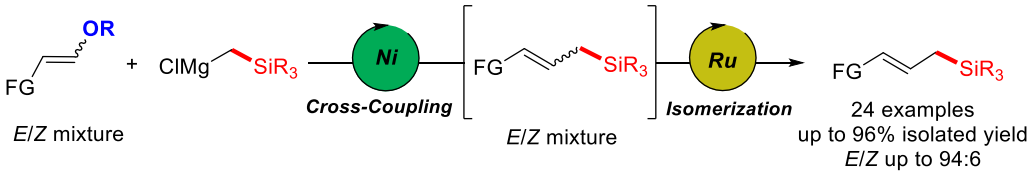
In recent years, C–O electrophiles have been proven to be a viable and powerful alternative to organohalides in cross-coupling reactions. In particular, C–OMe electrophiles have attracted much attention due to their easy accessibility, excellent stability, low toxicity, atom-efficiency, and potential reactivity to orthogonal cross-couplings in the presence of organohalides. Despite these diverse advantages, phenol derivatives are the most commonly used C–OMe electrophiles. Less attention has been paid to carbonyl enolate derivatives, probably because the most common access to alkenyl ethers through the carbonyl olefination often leads to a mixture of *E*/*Z*-alkenyl ether isomers. As a result, there is a need to develop a stereoconvergent approach to their transformation into stereodefined products. Once achieved, the stereoselective preparation of pure *E* or *Z* alkenyl ethers and the laborious purification of an *E*/*Z* mixture of alkenyl ether isomers can be circumvented. To meet this challenge, we have developed an efficient protocol based on [Ni/Ru] catalytic sequential cross-coupling/isomerization reactions. The bimetallic sequence is triggered by a nickel-catalyzed C−O cross-coupling of the *E*/*Z* mixture of alkenyl ethers with Grignard reagents, followed by a ruthenium-catalyzed stereoconvergent isomerization of the *in situ* generated *E*/*Z* mixture of allylsilane intermediates, delivering the final products in good to high yields with good functional group tolerance and excellent *E*-selectivity.



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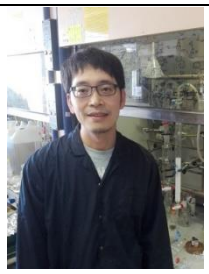

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PB-07

Hydroamination of Alkenes with Dinitrogen and Titanium Polyhydrides

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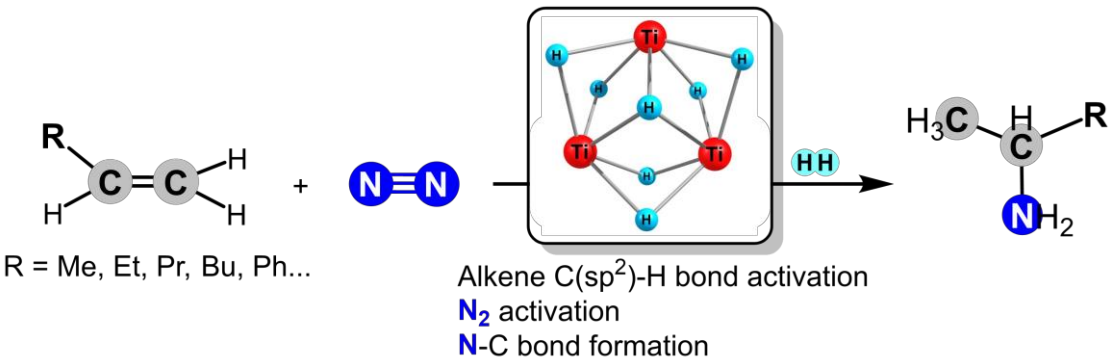
The direct use of abundant and easily accessible molecules such as dinitrogen (N_2) and alkenes as feedstocks for the synthesis of alkyl amines[1] is of great interest and importance. Typically, N_2 functionalization requires electrophilic carbon sources to facilitate the C–N bond formation.[2,3,4] In contrast, N_2 functionalization with simple hydrocarbons remains a challenge. Here we report hydroamination of nonactivated alkenes with N_2 at a trititanium hydride framework,[5,6] which can serve as an excellent platform for the activation of both alkenes and N_2 and lead to selective C–N bond formation between these two substrates, efficiently affording the corresponding alkyl amines upon further hydrogenation and protonation.[7] Computational studies reveal the mechanistic details of N_2 activation and selective C–N bond formation. This work demonstrates a new strategy for transformation of N_2 and simple hydrocarbons into nitrogen-containing organic compounds mediated by multinuclear hydride frameworks.



Titanium polyhydride (center) directly converts simple alkenes and dinitrogen (left) into alkyl amines (right).

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PB-08

Controllable Enzymatic Synthesis of Natural Asymmetric Human Milk Oligosaccharides

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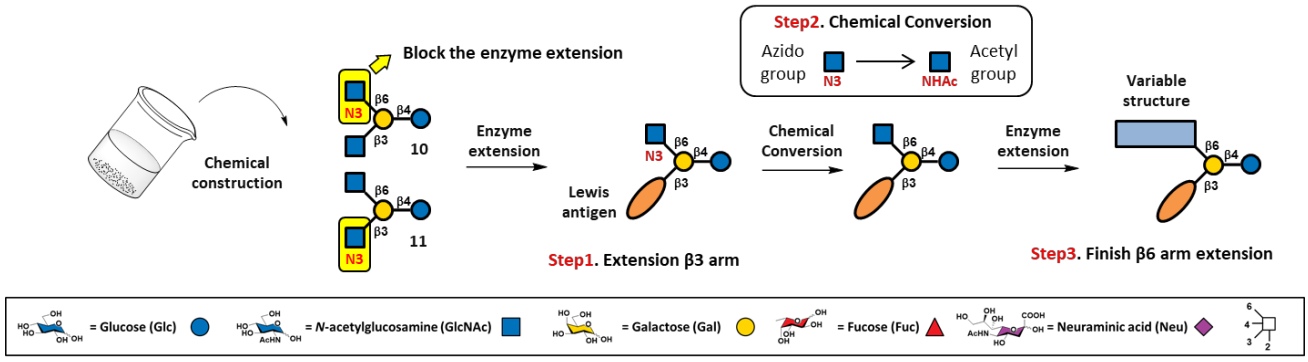
Among HMOs, linear HMOs are synthesized through mature but varied routes. Although branched HMOs can be synthesized by chemical, enzymatic, or chemoenzymatic methods, these methods cannot be easily applied to the synthesis of asymmetric multiantennary oligosaccharides. Herein, we developed a controllable method to synthesize asymmetric biantennary HMOs. In our synthetic route, GlcNAcβ1,3(GlcN3β1,6)Glaβ1,4Glc was first chemically synthesized as the core tetrasaccharide, which contains β1,6GlcN3 as the "stop" sugar in transferase-catalyzed glycosylation. The desired sugars at the GlcNAcβ1-3Gal arm can be assembled using galactosyltransferase, N-acetylglucosaminyltransferase, and fucosyltransferase. Then, the Staudinger reaction and acetylation were used to transform GlcN3 to GlcNAc and assemble sugars by initiating the "go" process. By manipulating transferase-catalyzed glycosylations, 22 natural asymmetric biantennary oligosaccharides were synthesized.



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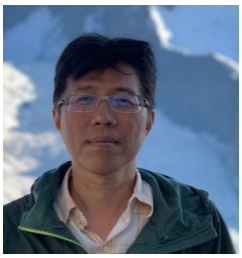

Chun-Cheng Lin (俊成 林). The Scripps Research Institute (Ph. D., 1997). Institute of Chemistry, Academia Sinica (Assistant Research Fellow, 1998; Associate Research Fellow 2003); Department of Chemistry, National Tsing Hua University (Associate Prof., 2006; Prof., 2007; Distinguished Prof., 2016), Chairman (2018). Research field: Carbohydrate Chemistry, Bioorganic Chemistry, Protein Immobilization and Modification.

PB-09

In-Line Analysis of Reactive Intermediates in Flow Microreactors: A Flash Monitoring Strategy

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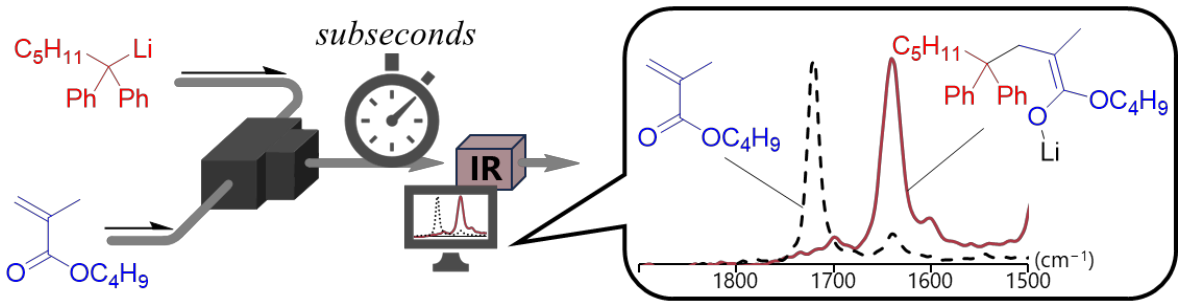
Flow microreactors are beneficial for the reactions mediated by reactive intermediates, especially those who have lifetimes less than seconds.[1] With their precise time-controllability, we have developed anionic polymerizations where anionic intermediates play crucial roles.[2] In this study, we introduce an innovative in-line monitoring approach within flow microreactors to directly observe unstable reactive intermediates in real-time.[3] Our methodology allows the precise analysis of intermediates, such as those involved in anionic polymerization reactions, within milliseconds, providing unprecedented insights into their behavior and stability. Utilizing flow microreactors, we achieved the rapid and controlled generation of reactive species like carbanions, and monitored their real-time transformation into polymer chains. Specifically, the anionic polymerization of alkyl methacrylates was studied, revealing critical information about the reactive intermediates and the progression of the polymerization process. The capability to directly observe both living and deactivated species in these reactions has significant implications for improving the efficiency and selectivity of polymer synthesis. This approach not only enhances our understanding of these critical intermediates but also opens new avenues for the design and optimization of advanced synthetic methodologies in organic chemistry.



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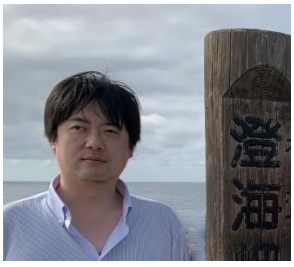

Yosuke ASHIKARI (芦刈洋祐). Kyoto University (Ph. D., 2013). University of Washington (Postdoc, 2014), Keio University (Postdoc, 2017), Kyoto University (Postdoc, 2019). Hokkaido University (Specially Appointed Assistant Professor, 2022). Research field: Flowmicro Chemistry Electro-organic Chemistry.

PB-10

Base-free Acylation of Phenols and Alcohols Catalyzed by Dialkyldithiocarbamate Organocatalyst

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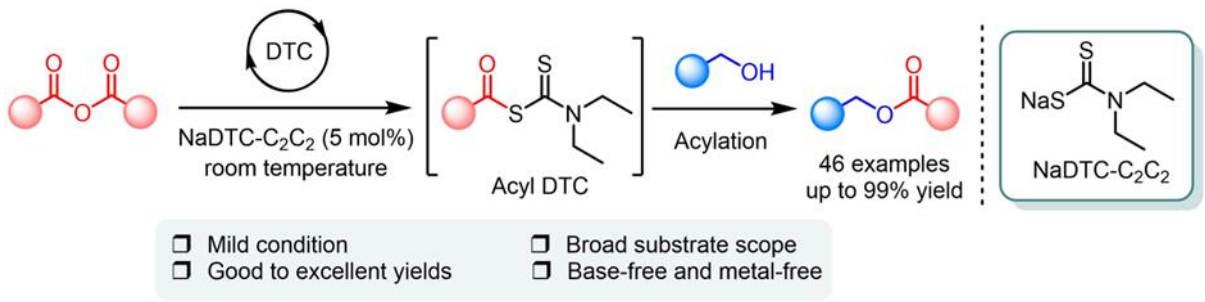
Dialkyldithiocarbamates (DTCs) are recognized as versatile ligands in coordination chemistry, with significant applications in agriculture (as fungicides, e.g., Mancozeb and Ziram) and medical science due to the strong nucleophilicity of the dithiocabamoyl group. Herein, we present an efficient acylation method using sodium *N*, *N*-diethyldithiocarbamate (NaDTC-C_2C_2) as an organocatalyst in 5 mol% under base- and metal-free conditions, achieving high to excellent yields of esters. The scope of acylation was demonstrated on the phenols (25 substrates) and alcohols (22 substrates), with yields ranging from 67–98%. Gram-scale synthesis was demonstrated to underscore its effectiveness and scalability. The proposed mechanism involves the activation of acid anhydride *via* the formation of acyl DTC intermediate followed by the substitution of phenolic or alcoholic nucleophiles to afford the ester and releasing the carboxylic acid as a byproduct. The simplicity and mild conditions highlight its potential applications in synthetic chemistry and the pharmaceutical industry. Moreover, the utilization of long-chain dialkyldithiocarbamate, namely *N*,*N*-didodecylamonium *N*,*N*-didodecyldithiocarbamate (AmDTC-$C_{12}C_{12}$) as CatAnionic vesicular nanoreactors for the cascade synthesis on *trans*-β-nitrostyrene derivatives in aqueous medium will be discussed.[1,2]



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Assistant Professor (2016–present). [Field of research] Green Chemistry, Carbohydrate Chemistry.

PB-11

Convergent Synthesis of the WXYZA'B'C'D'E'F' Ring Segment of Maitotoxin

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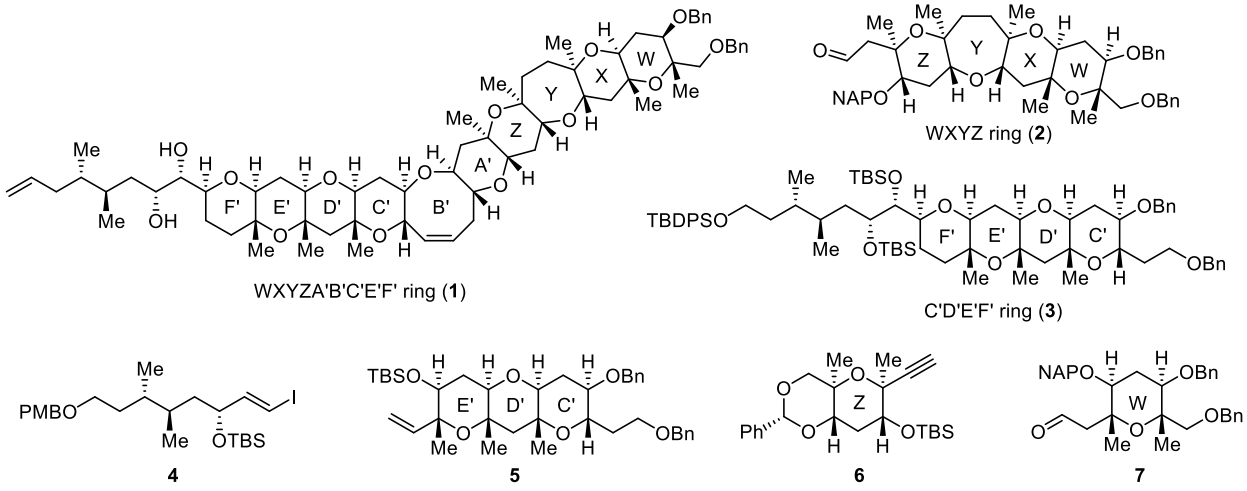
Maitotoxin (MTX) is a ladder-shaped polyether produced by the dinoflagellate *Gambierdiscus toxicus*.[1] Because of the potent biological activity and striking molecular structure, MTX attracts much attention among synthetic community. During the course of our program on structure-activity relationship study based on chemical synthesis of partial structure of MTX, convergent synthesis of the WXYZA'B'C'D'E'F' ring segment (**1**) of MTX was examined. The WXYZ ring (**2**) was synthesized based on the convergent strategy via two-ring construction from **6** and **7**,[2] and the C'D'E'F' ring (**3**) was synthesized via Suzuki–Miyaura coupling and Pd(II) catalyzed cyclization from **4** and **5**.[3] Coupling of the WXYZ (**2**) and C'D'E'F' (**3**) rings by the convergent strategy developed in our laboratory via ring-closing metathesis and radical reduction of *O*,*S*-acetal culminated in the convergent synthesis of the WXYZA'B'C'D'E'F' ring of MTX.[4] The longest linear sequence is 53 steps with 104 total steps, and the molecular weight of the synthesized compound (**1**) is 1140.



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PB-12

Synthetic Studies Towards Phellinusfurans A and B

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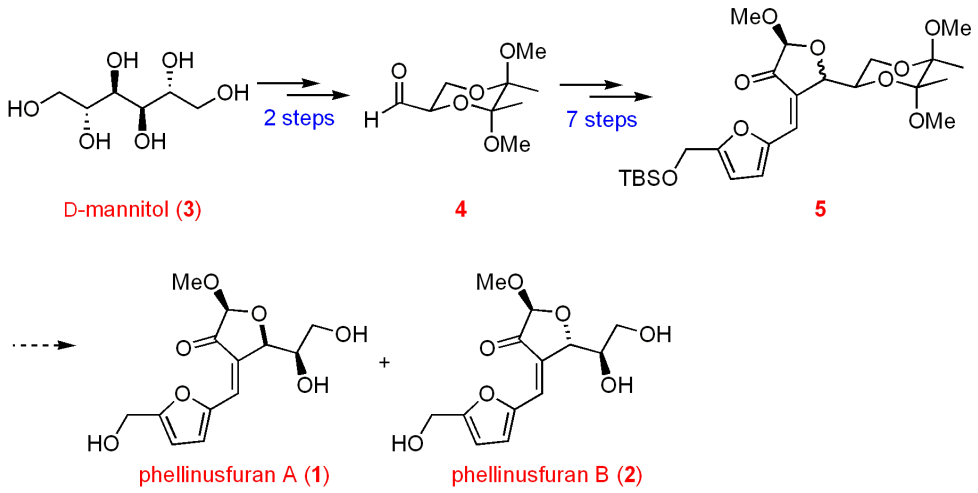
Phellinusfurans A (**1**) and B (**2**) were isolated from the fruiting body of *Phellinus linteus* which exhibited significant anti-complement activity with IC_{50} values of 33.6 and 33.7 μM, respectively, in inhibiting the hemolytic activity of human serum against erythrocytes.[1] The synthesis was started from known aldehyde **4**, which was prepared from D-mannitol (**3**) in 2 steps.[2] Morita-Baylis-Hillman reaction and the intermolecular Heck reaction were the key steps in this synthesis. The desired *Z*-enone **5** was obtained from aldehyde **4** in 7 steps. The detail will be discussed.



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2021-2024 Chairman, National Chung Cheng University
Research interests: Asymmetric chemistry, methodology development, and total synthesis.

PB-13

Two Strategies to Enhance the Therapeutic Potential of Coumarin-based fluorophore: Integration of a Protonatable Moiety and BSA-Mediated Nanoparticle Formation

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Photodynamic therapy (PDT) is a non-invasive cancer treatment that uses photosensitizers (PSs) activated by light to generate reactive oxygen species (ROS) for cell death. The effectiveness of PDT is improved by integrating fluorescence imaging, which allows real-time monitoring and precise targeting of cancer cells. Coumarin-based PSs are promising due to their biocompatibility, structural flexibility, and photophysical properties, making them suitable for both therapeutic and diagnostic applications. Recent advancements focus on targeting specific cellular organelles, such as lysosomes, to enhance therapeutic outcomes. Additionally, using biocompatible carriers like bovine serum albumin (BSA) nanoparticles (NPs) can further enhance photodynamic efficiency by promoting favorable photophysical interactions. These strategies aim to maximize PDT's therapeutic potential while minimizing adverse effects.

In this study, we synthesize **COM**, a coumarin-based fluorescent probe, to improve cancer cell death through two strategies. First, **COM** is designed with a lysosome-targeting morpholine moiety that becomes protonated in lysosomes. This protonation enhances ROS generation, leading to lysosomal dysfunction and increased cancer cell apoptosis. Second, **COM** forms hydrophobic interactions and hydrogen bonds with BSA amino acid residues, causing aggregation. This aggregation reduces the energy gap (ΔE_{ST}) between the singlet and triplet states, leading to higher intersystem crossing rates (k_{ISC}) and longer triplet state lifetimes, thereby enhancing PDT efficacy. We show that incorporating a lysosome-targetable protonatable moiety into the probe and using BSA NPs for aggregation improves fluorescence imaging and PDT effectiveness.

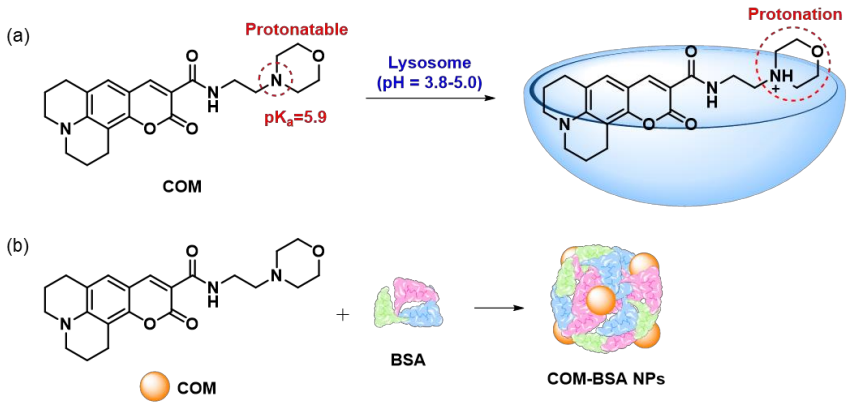

Figure 1. Two strategies to enhance ROS generation and promote cancer cell death: (a) Introduction of a protonatable lysosome-targeting moiety. (b) Formation of aggregates through BSA.

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PB-14

Dearomative Cycloaddition of *N*-Heteroaromatic Compounds with a Divalent Silicon Species

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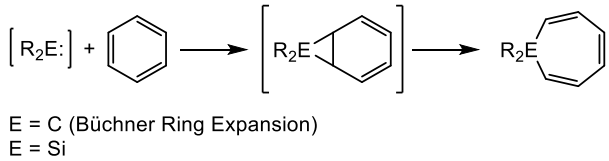
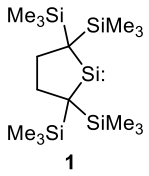
Büchner ring expansion is a fascinating dearomative cycloaddition of various aromatic compounds with carbenes to afford seven-membered ring compounds via norcaradienes (Scheme 1).[1,2] Herein, we report dearomative cycloaddition reactions of *N*-heteroaromatic compounds such as pyridines and bipyridines with an isolable dialkylsilylene (**1**)[3].

Scheme 1.

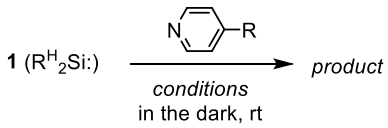


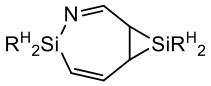
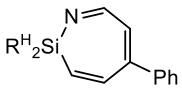
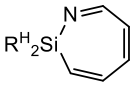
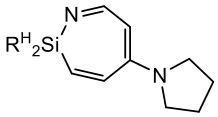
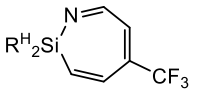


1

The reaction of pyridine with **1** afforded a 1:2 adduct (**2**) in 33% yield, and a 1:1 adduct (**3a**) was not observed despite the stoichiometric reaction (Table 1). Reactions of **1** with 4-trifluoromethylpyridine, 4-phenylpyridine, and 4-pyrrolidinopyridine furnished **3b-3d**. An electron-deficient pyridine reacted faster with **1**.

Table 1. Dearomative Cycloaddition of Pyridines with **1**



R	*conditions*	*product*	R	*conditions*	*product*
H	1 equiv. hexane, rt, 5 d	 **2** (33%)	Ph	5 equiv. C_6D_6, 22 h	 **3c** (74%)
		 **3a** (0%)		10 equiv. toluene, 27 h	 **3d** (43%)
CF_3	1 equiv. hexane, 10 h	 **3b** (62%)			

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PB-15

Rational Design of Alkyl-Pyrazole-Based Phosphine Ligands for Palladium-Catalyzed Chemoselective Cross-Coupling Reactions

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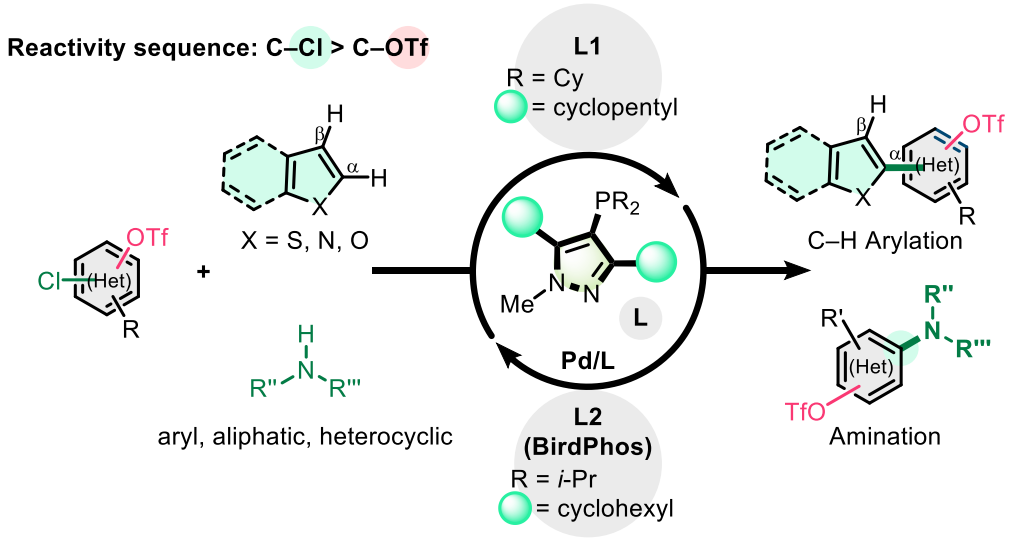
A novel series of pyrazole-alkyl phosphine ligands with varying cycloalkyl ring sizes at the C3 and C5 positions has been synthesized and effectively applied in chemoselective transformations. These ligands demonstrate exceptional performance in both C–H arylation and amination reactions. In C–H arylation, Pd/**L1** achieves outstanding α/β selectivity across a range of heterocycles, including benzo[*b*]thiophene, thiophene, furan, benzofuran, and thiazole, with high regio- and chemoselectivity under additive-free conditions.[1] Concurrently, in amination processes, Pd/**L2** (BirdPhos) facilitates the efficient coupling of aromatic, aliphatic, and heterocyclic amines with polyhalogenated aryl triflates, exhibiting remarkable chemoselectivity for C–Cl bonds over C–OTf bonds.[2] Mechanistic investigations, complemented by experimental data and density functional theory calculations, suggest that the optimized ring sizes of the pyrazole phosphine ligands play a key role in lowering energy barriers in both reaction pathways. The successful late-stage functionalization via chemoselective C–H arylation and the synthesis of drug analogs through chemoselective intermolecular amination underscore the potential applicability of this ligand system in pharmaceutical and industrial fields.



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- The Hong Kong Polytechnic University (Ph.D., 2010)
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PB-16

Reductive Cross-Coupling of Phenolic or Benzylic Ethers with Chlorosilanes by Cooperative Rhodium/Lanthanum Catalysis

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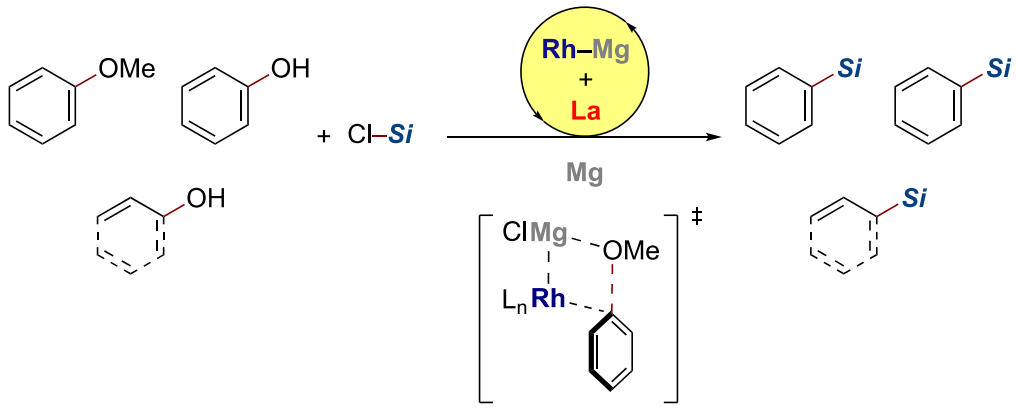
Here we describe the cross-electrophile-coupling (XEC) reaction of ethers with chlorosilanes with magnesium reductant by cooperative rhodium and lanthanum catalysis.[1] This reaction allows a range of anisole derivatives as well as benzylic ethers, phenols, benzylic alcohols, allylic ethers, and allylic alcohols to be transformed into various organosilicon compounds in a single step. Mechanistic studies including kinetics, stoichiometric organometallic reactions, XAS, and theoretical calculations suggest a heterobimetallic complex bearing a Rh–Mg[2] and/or Rh–La bond as a key catalytically active species. This method can be applied to the development of novel silicon-containing organic materials and drugs containing silicon as a carbon isostere. On the other hand, the XEC of phenol derivatives enables the use of biomass-derived resources as an alternative to petroleum to produce useful compounds in a sustainable manner.[3]



cooperative C–O activation by heterobimetallic bonds

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[Field of research] Organic Synthesis, Organometallic Chemistry

PB-17

Photoredox and Electrochemical Catalysis for the Selective Bioconjugation

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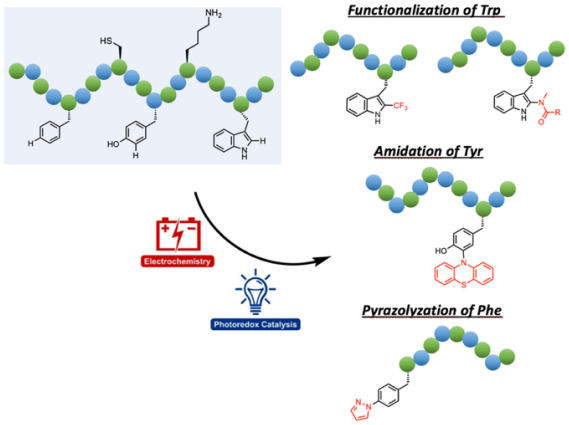
In the ever-evolving fields of chemical biology and pharmaceutical science, innovative strategies continually redefine the boundaries of molecular modification. Herein, we introduce an integrated framework that harmonizes these domains, seamlessly orchestrating late-stage functionalization, photoredox catalysis, and electrochemical synthesis to establish a versatile pathway for modifying amino acids, peptides, and proteins. At its core, this approach encompasses an array of techniques, including late-stage photoredox C-H amidation for the direct fusion of N-unprotected indoles and aryloxyamides. Complementing this, we have devised electrochemical protocols that introduce indirect trifluoromethylation and sulfenylation tailored specifically for tryptophan-containing peptides. Concurrently, a strategy emerges that marries electrochemical synthesis with photoredox catalysis, demonstrated through the successful photoelectrochemical bioconjugation of N-terminal phenylalanine and β-position amination of tryptophan residues. Furthermore, in the realm of protein modification, a groundbreaking photoredox approach unveils the site-selective bioconjugation of phenylalanine, effective across both peptides and insulin proteins. This transformative technique introduces pyrazole labeling and facilitates the dissociation of insulin hexamers. The culmination of these interdisciplinary endeavors births an innovative toolkit with expansive applications spanning pharmaceuticals and chemical biology, highlighting its potential to fundamentally reshape these disciplines.



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Field of research: Photoredox Catalysis, Electrochemical Synthesis, Bioconjugation Chemistry.

PB-18

Development of ratiometric fluorescent probe for determination of melamine in milk and infants' formulas based on dual-emissive nature of carbon dots and sulfhydryl-modified copper nanoclusters

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Melamine, often used as an adulterant in infant formula due to its high nitrogen content, which artificially elevates protein levels, poses significant health risks when ingested in large quantities. Excessive consumption can lead to the formation of melamine-cyanurate co-crystals in infants, potentially causing kidney damage. In this study, we developed a radiometric fluorometric probe for the sensitive and selective detection of melamine, utilizing carbon dots (CDs) and 4-mercapto benzoic acid-protected copper nanoclusters (CDs/4-AMBA@CuNCs). Upon excitation at 320 nm, the constructed probe exhibited two distinct emission peaks: one at 455 nm corresponding to the CDs and another at 650 nm corresponding to the 4-AMBA@CuNCs. The addition of Hg^{2+} ions resulted in a decrease in the fluorescence emission at 650 nm from the 4-AMBA@CuNCs, while the fluorescence emission at 455 nm from the CDs remained stable. When melamine was introduced, the fluorescence emission at 650 nm was restored due to the strong chelation between melamine and Hg^{2+} ions. Under optimal conditions, the fluorescence intensity ratio (F_{650}/F_{455}) increased proportionally with melamine concentration in the range of 0.05 to 85 µM, with a detection limit of 0.0025 µM (S/N = 3). The 4-AMBA@CuNCs probe was successfully applied to detect melamine in liquid milk and infant formula, yielding acceptable recovery rates and low standard deviation values. Additionally, the results were compared with those obtained using the HPLC/UV method, demonstrating the reliability of the proposed fluorometric technique for detecting melamine in real samples.

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PB-19

Development of novel chemical probes targeting a histone methyltransferase

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Post-translational modifications of histone proteins are important epigenetic mechanisms that regulate chromatin structures and gene expression. Many kinds of histone-modifying enzymes are reported, and regulation strategies for such protein complexes have been actively studied. In the field of chemical epigenetics, it is required to develop novel chemical probes that can modulate activity of target histone-modifying enzymes. However, it is still difficult to identify specific chemical probes because of the structural complexity of these proteins.

We aimed to develop novel compounds that modulate the levels of histone H3 lysine 27 (H3K27) methyl marks by targeting the polycomb repressive complex 2 (PRC2). PRC2 contains four subunits (EZH2, EED, SUZ12, and RbAp46/48), and catalyzes sequential methylation reactions at H3K27. Both the gain-of-function and loss-of-function mutations of PRC2 have been reported in several types of cancers.[1] Therefore, the development of PRC2 inhibitors, and also activators can be effective for some types of cancers.[2]

In this presentation, our recent results will be shown to discuss strategies for modulating H3K27 methylation using novel chemical probes.

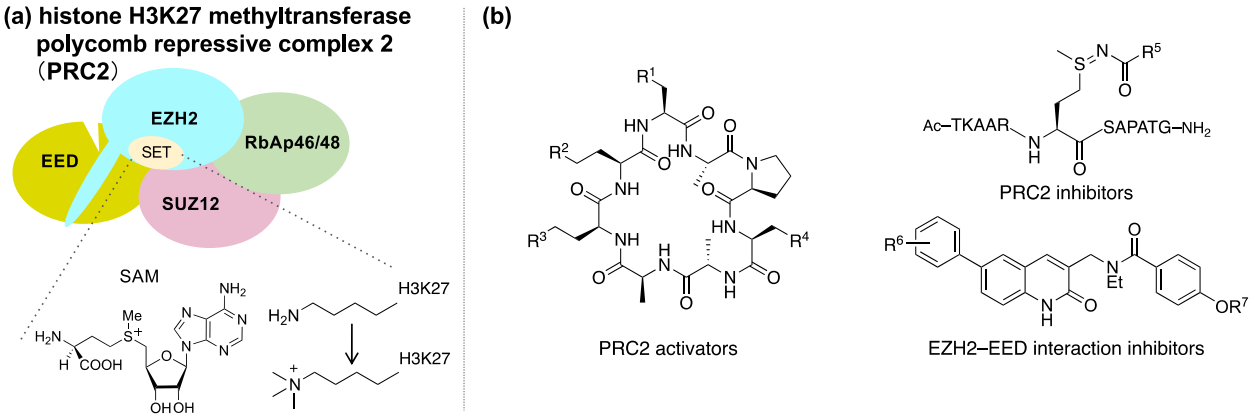

Fig. (a) Structure of polycomb repressive complex 2 (PRC2). (b) Chemical structures of novel PRC2 chemical probes.

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PB-20

Asymmetric Intramolecular Diels-Alder Reactions of Dienophile-tethered 2-Pyrones for the Total Synthesis of Lycopladine A, Cyanthiwigin B, and Platensimycin

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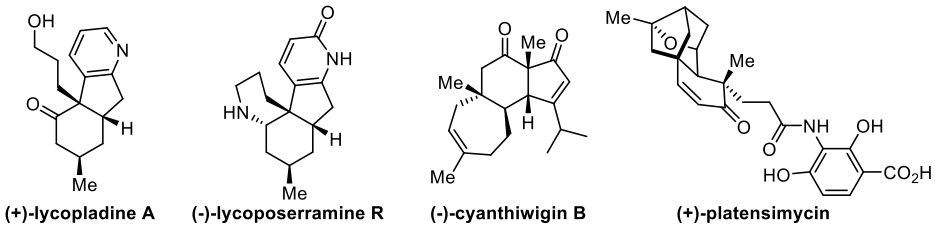
We have been exploring the utility of 3,5-dibromo-2-pyrone as a new enophile synthon in Diels-Alder chemistry. Its synthetic versatility has been further exuberated by the discovery that either of the two C-Br groups can be selectively functionalized through transition metal-catalyzed coupling reactions. The resultant 3- or 5-substituted 2-pyrones were found to be potent neutral dienes and may undergo cycloaddition to afford an array of densely functionalized cyclohexenes. Recently, 2-pyrones with an asymmetrically positioned hydroxyl group in the tether have been found to undergo intramolecular Diels-Alder reactions with remarkably high π-facial- and endo-selectivities. The resulting diastereomerically and enantiomerically pure cycloadducts were transformed into various natural products. Recent findings on our unique diastereoselective IMDA reactions of 2-pyrones and their synthetic applications to (+)-lycopladine A, (-)-lycoposerramine R, (-)-cyanthiwigin B and (+)-platensimycin will be presented.



(+)-lycopladine A (-)-lycoposerramine R (-)-cyanthiwigin B (+)-platensimycin

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PB-21

Mechanochemical Aromatic Halogenation Enabled by Ball-Milling

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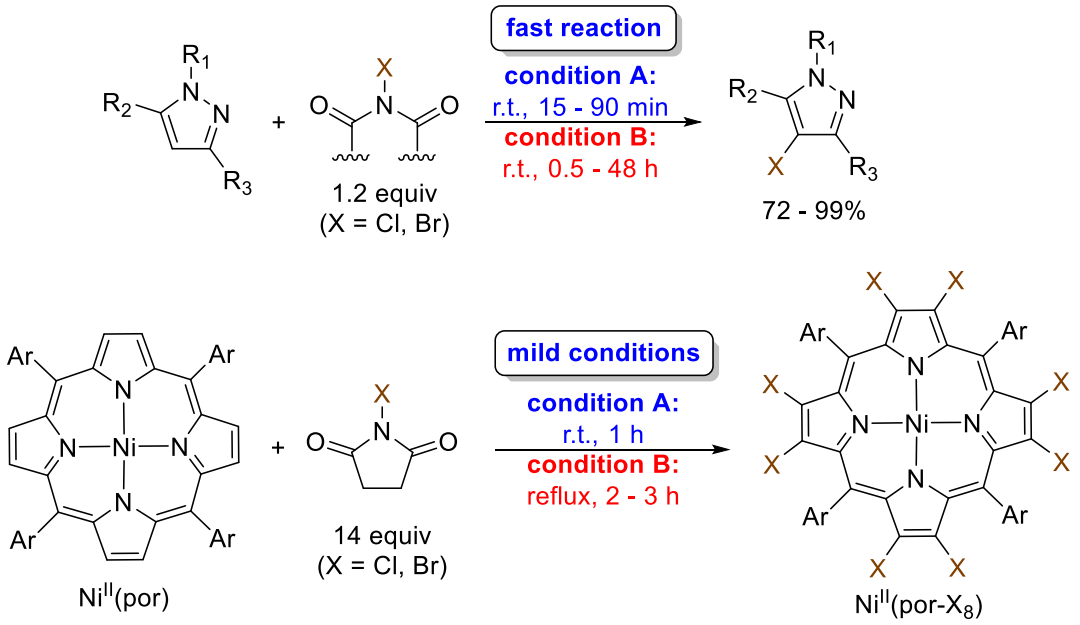
Mechanochemical reactions via automated ball milling become an emergent field of research.[1] The merits of ball-milling over traditional solvent-based reaction include solventless conditions, enhanced reaction rate, increased selectivity, and utilization of poorly soluble reagents.[2] Our group has communicated the green protocol for halogenation of some electron-rich heterocycles with N-haloamines in a mixer-type ball mill with much shorter reaction times and milder conditions.[3]



* condition A = ball-milling; condition B = solvent conditions

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Research Interests: (1) organometallic chemistry; (2) mechanochemistry;

PB-22

The Transformation of C–F Bond Mediated by Photocatalyst and Lewis Acid

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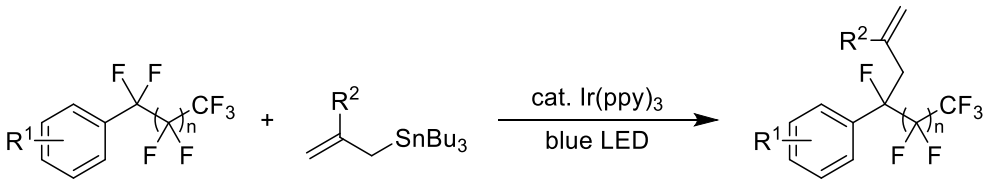
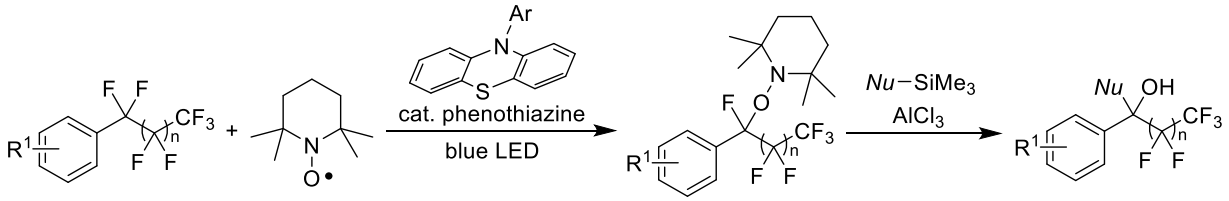
The transformation of C–F bonds in perfluoroalkyl compounds is a significant synthetic method in organic chemistry. Also, this is an important issue to solve PFAS enviromental problems. Herein, we report site-selective and direct C–F bond transformation of perfluoroalkylarenes with allylic stannanes via an iridium photoredox catalyst system.[1]



Also, a sequential C–F bond transformation of perfluoroalkylarenes was achieved by photocatalyzed aminoxylation and Lewis acid-mediated nucleophilic substitution with organosilicon reagents.[2] Mechanistic studies including transient absorption spectroscopy and DFT calculation revealed that the two Me groups on phenothiazine-based catalyst play crucial roles to promote catalyst regeneration.



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[Field of research] Organic Synthesis, Main-group Chemistry, Lewis Acids, Photo Chemical Reaction

PB-23

Divergent Synthesis of Oxa- and Azatricyclic Compounds from γ-Alkynyl-1,3-diketones

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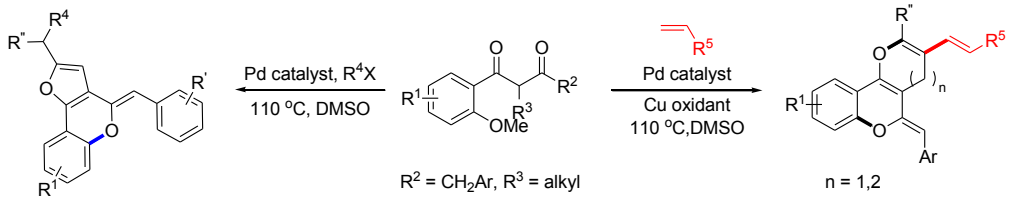
Oxygen-containing heterocycles such as chromone, xanthone, and pterocarpan are the key structural units of many natural products and medicinally important molecules. These molecules are ubiquitous as the backbones of traditional Chinese medicines and organic materials. Oxygen-containing heterocyclic motifs have attracted considerable attention due to their preventative and curative effects in a variety of diseases. Therefore, the preparation of O-containing heterocyclic derivatives exhibiting anti-cancer, anti-inflammatory, and anti-bacterial activities is of interest in organic chemistry.

A novel cascade Pd(II)-catalyzed *endo-dig* cycloisomerization and olefination reaction of 2-benzyl-3-alkynyl chromones with activated/unactivated alkenes has been developed for the synthesis of fused oxatricyclic compounds. This novel Pd-catalyzed cascade transformation is synthetically versatile and proceeds via selective O-attack *endo-dig* cyclization to generate a 4*H*-pyrano[3,2-*c*]chromene-Pd intermediate. Upon further cross-coupling with both activated and unactivated alkenes, the intermediate gives the target molecules in good to excellent yield. Evaluation of the cytotoxic activities of select oxatricyclic analogues revealed that some of the derivatives exhibit cytotoxic activity in human cancer cells.



Synthesis of Oxatricyclic Compounds

Reference

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PB-24

N-Terminal-Specific Dual Modification of Peptides via [3+2] Cycloaddition

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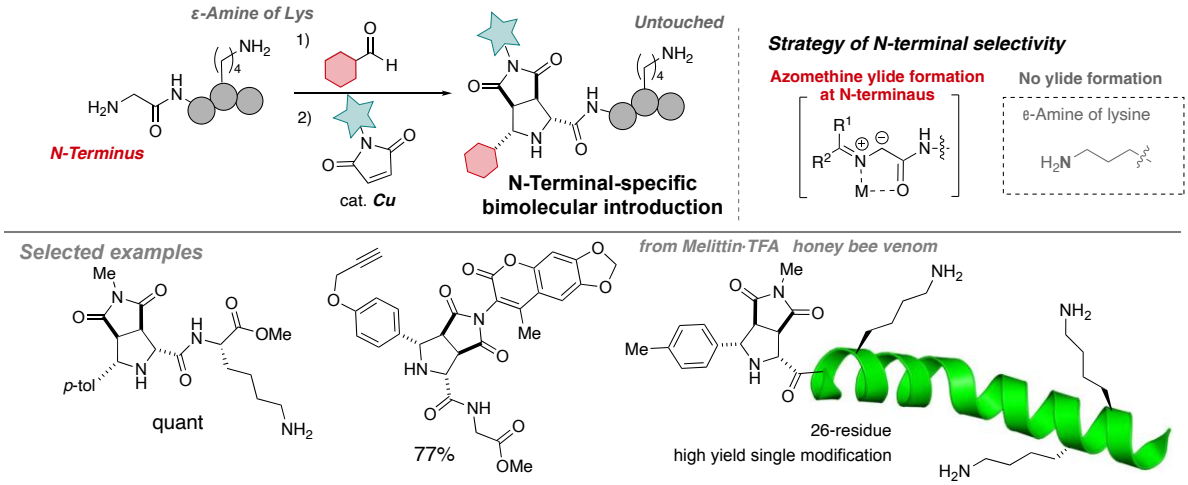
Peptides play essential roles as therapeutic agents, drug candidates, and chemical biology probes. Thus, methods for peptide modification and conjugation have received significant attention for modulating peptide structures. Nevertheless, site-specific modification of peptides remains challenging due to the presence of various nucleophilic sites, such as the lysine ε-amine. In this context, N-terminal selective peptide modification[1] is attractive due to the uniqueness of the N-terminus.



In this work, we have developed a method for the N-terminal-specific dual modification of peptides through a three-component [3+2] cycloaddition with aldehydes and maleimides.[2,3] The present method capitalizes on the site-specific generation of azomethine ylide at the N-terminus of iminopeptides and its highly efficient [3+2] cycloaddition with maleimides under copper catalysis. The reaction affords a variety of pyrrolidine cycloadducts in excellent yields with complete *exo*-diastereoselectivities, with tolerance to various functional groups and functional molecules, including the ε-amine of a lysine residue. Furthermore, the one-pot three-component protocol allows for the straightforward assembly of diverse di-, tri-, and oligopeptides with aldehydes and maleimides, thus offering an opportunity for the expeditious construction of doubly functionalized peptides.

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[Field of research] Organic Chemistry (sulfur/peptide chemistry).

PB-25

Self-assemblies of Janus Nanosheets

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Two-dimensional (2D) materials exhibit unique surface chemistry properties. The development of stable Janus architectures with different entities on both sides of the 2D sheets holds significant importance. A novel approach for interfacial supramolecular self-assembly has been introduced, resulting in 2D Janus nanosheets exhibiting an amphiphilic nature [1]. Novel structural designs of 2D supramolecular materials have led to the development of as well as dual substrate release and catalysts [1,2].

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PB-26

Chiral Halonium Salt Catalysis Driven by Halogen Bonding

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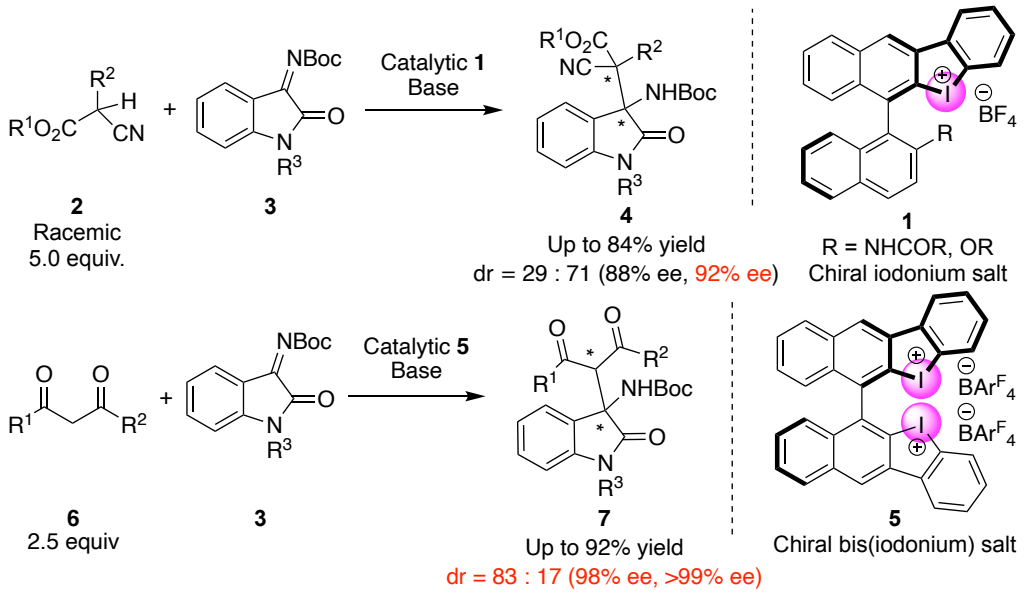
Halogen bonding is a non-covalent interaction between electron-deficient halogen atoms and Lewis bases, which has been focused in wide field of chemistry in these decades. Previously, we have developed the binaphthyl-based chiral halonium salts **1** with hydrogen bond donating functionality, which showed excellent catalytic activities in Mannich reactions[1] and thiol addition reaction to imines.[2] In this presentation, we would like to show developments and catalytic applications of their analogs without hydrogen bonding functionalities.

The chiral iodonium salt with silyl ether moiety **1b** and the chiral bis(iodonium) salt **5** were prepared from commercial optically pure NOBIN (2-amino-2'-hydroxy-1,1'-binaphthyl) or BINAM (1,1'-Binaphthyl-2,2'-diamine) in several steps, which were applied to stereoselective reactions as catalysts. **1b** worked well in Mannich reaction with cyanoesters, and **5** behaved as excellent catalyst in Mannich reaction of 1,3-dicarbonyl compounds to form corresponding products in up to 92% ee and >99% ee, respectively.[3]



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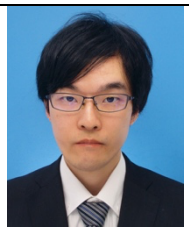

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[Field of research] Organic Synthesis, Asymmetric Catalysis

PB-27

A kinetic-controlled chemoselective peptide macrocyclization approach to access the cyclization mode and topological diversity

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Peptide macrocycles, which leverage the biophysical properties of peptide-based therapeutics, play a significant role in the field of pharmacy, biology, and chemistry.[1] The cyclization mode and topological diversity of peptides, including mono-, di-, and tri-cyclic structures, enables the development of novel peptide drugs targeting "undruggable" proteins. Canonical amino acids such as cysteine and lysine are widely utilized in three-component macrocyclizations, though different nucleophile pairings (*S*/*S*, *N*/*N*, and *S*/*N*) which require different cross-linking reagents. To generalize the macrocyclization reactions of unprotected amino acids and facilitate the exploration of topological diversities, we introduce a kinetic-controlled chemoselective macrocyclization (KCCM) approach. This method employs an electron-deficient arene and fine-tunes kinetic factors to enable symmetrical and asymmetrical cross-linking (*S*/*S*, *N*/*N*, and *S*/*N*) generating diverse peptide macrocycles through S_NAr chemistry. The excellent chemoselectivity of this approach pave the way for the assembly of multicyclic peptides with different topologies. Bi- and tricyclic peptides can be prepared by sequentially adding the electron-deficient arene twice or with other macrocyclization reagents in one-pot manner. The synthesized cyclic peptides are tested for their cell permeability and inhibitory activity toward the GTPase. Overall, the KCCM approach is a simple, robust, and versatile synthetic method for designing cyclic peptides with diverse linkers, cyclization patterns, and topologies.

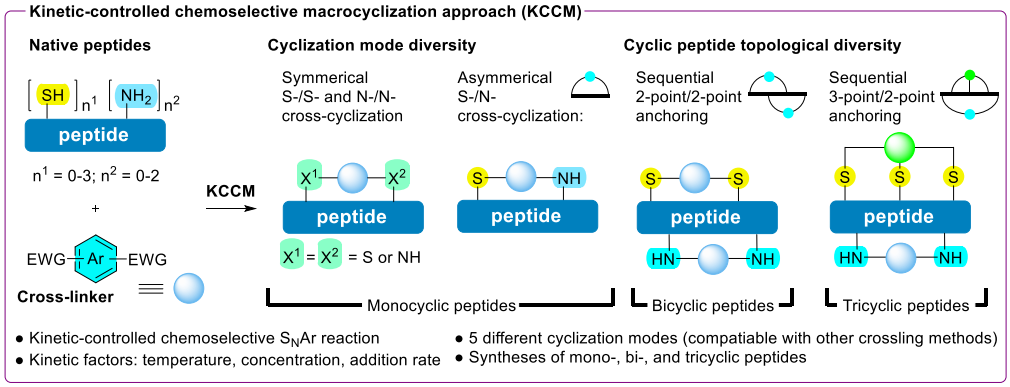

Figure 1. A kinetic-controlled chemoselective macrocyclization approach (KCCM) enables 3 peptide cyclization modes (*S*/*S*, *N*/*N*, and *S*/*N*) and 3 classes of cyclic peptides (mono-, bi-, and tricycle).

Reference

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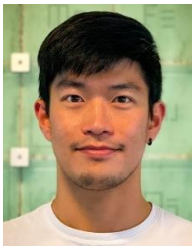

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[Field of research] Peptide chemistry and organic synthesis.

PB-28

Enantiodivergent Synthesis of Lycorine and Cephalotaxine from L-Aspartic acid

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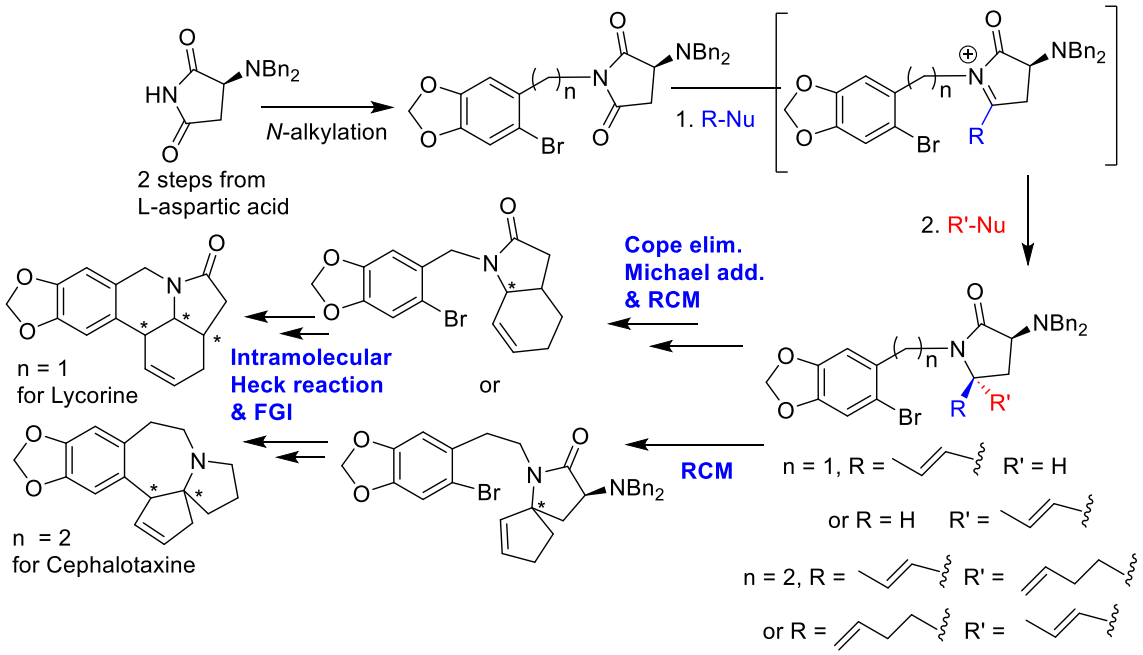
Enantiodivergent synthesis of lycorine and cephalotaxine is described. Chiral *N*-(6-bromopiperonyl)-succinimide and *N*-(6-bromohomopiperonyl)-succinimide prepared in 3 steps from L-aspartic acid were used as the key precursor for lycorine and cephalotaxine synthesis, respectively. Nucleophilic addition to the succinimide carbonyl led to chiral *N*-acyliminium ion intermediate and subsequent diastereoselective addition of the second nucleophile was controlled by steric hindrance of the dibenzylamino group. Alternating the order of addition of the two nucleophiles led to diastereomeric intermediate with opposite configuration at the new stereogenic tertiary carbon. Each diastereomer was used for synthesis of opposite enantiomers of lycorine and cephalotaxine. Other key transformations include ring closing metathesis to form tetrahydrooxindole precursor of lycorine and spiro[pyrrolidone-cyclopentene] precursor for cephalotaxine and their intramolecular Heck reaction to form the full carbon skeletons of the natural products.



Enantiodivergent synthesis outline of lycorine and cephalotaxine

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PB-29

Palladium-Catalyzed Direct γ'-Arylation of Cyclic Vinylogous Esters for Strategic Synthesis of α-Arylcycloalkenones

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We recently developed the catalytic monoarylation and polyarylation of cyclic vinylogous esters (CVEs).[1,2] The deprotonative arylation reactions occur at the relatively acidic α and/or γ' carbons of CVEs (Figure 1). Significantly, the regioselectivity of these processes could be well controlled under customized conditions. This presentation will focus on the γ'-arylation reaction of CVEs and its synthetic applications. Overall, this collection of arylation reactions has offered a unique opportunity to rapidly assemble a variety of functionalized aryl-containing scaffolds.

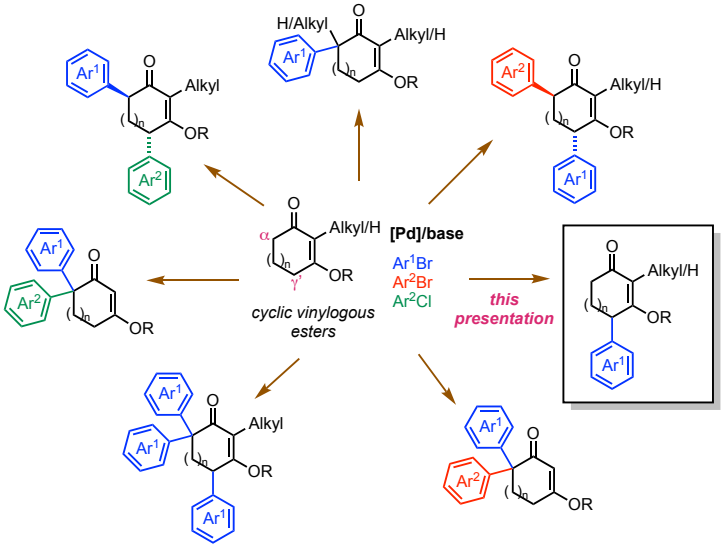

Figure 1. Arylation Reactions of Cyclic Vinylogous Esters.

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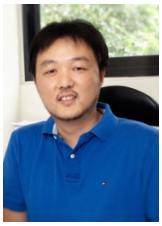

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PB-30

Inherently chiral cavitands through ionic catalyst-controlled cross-coupling

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Cavitands have emerged as privileged architectures in supramolecular chemistry. Nonetheless, achieving structural diversity and tunability through heterofunctionalization along the rims of macrocycles has remained a formidable challenge. As a rudimental example, stepwise conversion of C_{4v}-symmetric scaffolds to inherently chiral ABCD patterns is synthetically impractical owing to the low theoretical yields (0.8%) and the need for chromatographic enantioseparation. We have developed a catalytic desymmetrization strategy to access inherently chiral cavitands. Through engineering ionic chiral palladium catalysts, diverse functionalities, including aryl, alkenyl, alkynyl, and amino groups, can be installed on the large rims with high site- and stereoselectivity. An adaptable stepwise protocol has been established to furnish designer ABCD-type cavitands in accordance with the choreography of coupling partners. Experimental and computational studies reveal synergistic electrostatic steering and electrostatic catalysis by the ionic catalyst–substrate interactions.

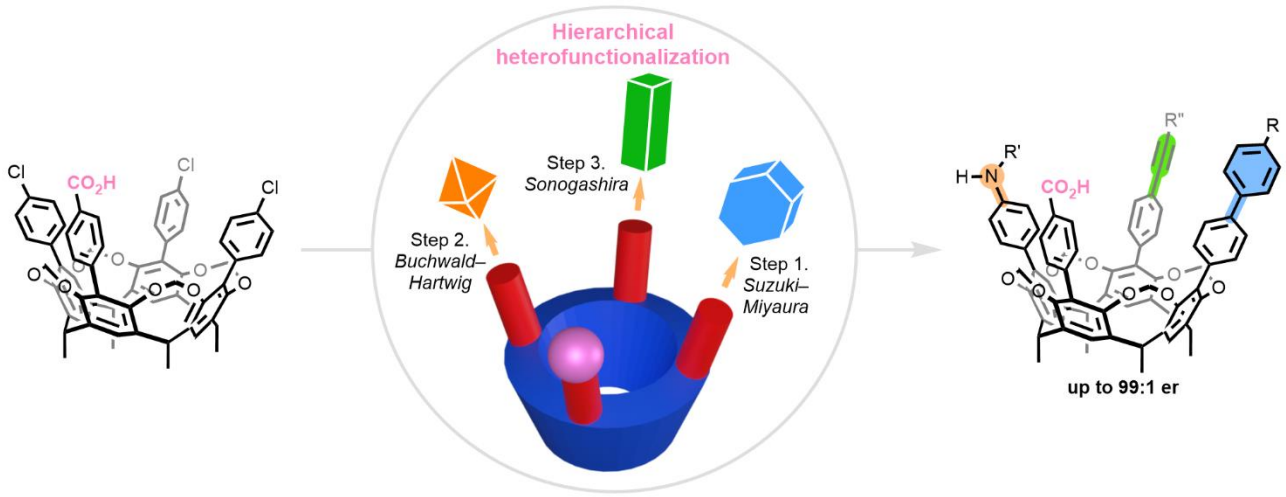

Figure 1. Catalyst-controlled stepwise cross-coupling reactions to access inherently chiral cavitands

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ZHU Ye (朱烨). Peking University (B.S., 2006). The University of Chicago (Ph.D., 2012). Postdoctoral, Massachusetts Institute of Technology (2014). Senior Research Investigator, Bristol-Myers Squibb (2018). Assistant Professor, National University of Singapore (2018 to present). Organic synthesis, stereochemistry, catalysis.

PC-01

Color-Tunable Fluorescent Heptagon-Embedded Polycyclic Aromatic Dicarboximides

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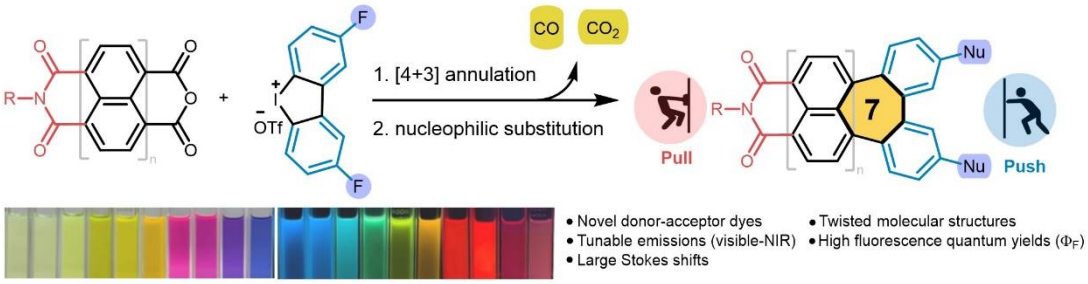
Polycyclic aromatic hydrocarbons (PAHs) containing seven-membered rings have drawn significant attention due to their distinctive dynamic behaviors, aromaticity, electronic characteristics, and self-assembly properties, resulting from their saddle-shaped surfaces with negative curvature. However, despite their intriguing stereochemical dynamics and optoelectronic properties, research on heptagon-embedded PAHs remains limited, largely because of the scarcity of efficient synthetic methods to incorporate heptagons into polyarene frameworks. Typically, heptagon-embedded PAHs exhibit weak to moderate fluorescence quantum yields (Φ_F), likely due to the inherent flexibility of their molecular structures. In this study, we developed a palladium-catalyzed cascade [4+3] decarbonylative/decarboxylative annulation, followed by a nucleophilic substitution as a new strategy for synthesizing fluorescent heptagon-embedded polycyclic aromatic dicarboximides. The incorporation of a push-pull system within the heptagonal skeletons efficiently modulates their optical properties, resulting in enhanced fluorescence quantum yields and tunable emission across the visible to near-infrared (NIR) spectrum.



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PC-02

Oxygen-Embedded Quinoline Oligomers for A New Entry to Polydentate Ligands

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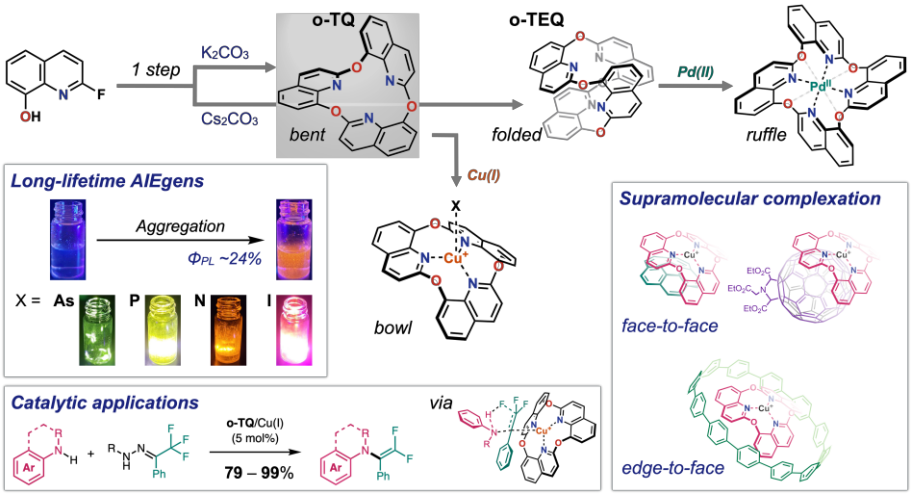
Recently, a head-to-tail type quinoline oligomers comprising of three or four quinolines concatenated at 2,8-positions, TriQuinoline (TQ) and TEtraQuinoline (TEQ), were uncovered as π-materials exhibiting unusual physicochemical properties.[1,2] We newly designed non-flat quinoline trimer oxa-TriQuinoline (o-TQ) and its tetrameric analog, oxa-TEtraQuinoline (o-TEQ), where each quinoline units are linked by oxygen atoms. Both o-TQ and o-TEQ were readily synthesized from 2-fluoroquinolin-8-ol by conventional S_NAr reaction in a single step. The embedded oxygen atoms were pivotal to acquire appropriate rigidity. Complexation with a Cu(I) cation in a tridentate fashion furnished a conformationally fixed bowl-shaped o-TQ/Cu(I) complex, which displayed aggregation-induced emission (AIE) properties, supramolecular complexation properties with non-flat aromatics of specific curvature *via* π-π and CH-π interactions, as well as catalytic proficiency in various reactions *via in situ* generation of carbenes and nitrenes. o-TEQ preferred folded conformation as the most stable conformation, except under Pd(II) accommodation, which provided a ruffle-shaped complex.



Synthetic strategy and versatile physicochemical properties of non-flat quinoline oligomers.

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PC-03

Cesium Carbonate-Catalyzed Thiolation of Phosphonothioates

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Sulfur-containing molecules are important skeletons in organic synthesis and pharmacetical industry.[1] Phosphorodithioates[2-4] are well-known as the antiviral agents, plant growth regulators, enzyme inhibitors, and lubricants. However, the known procedures for preparing phosphorodithioates suffered from some drawbacks, for example, the use of toxic reagents, harsh reaction conditions, narrow substrate scopes, and the involvement of air-sensitive reagents. Therefore, the synthesis of phosphorothioates under milder and environmentally friendly conditions is highly desirable. Cross-dehydrative coupling (CDC) reactions have gained significant attention for their ability to enhance reaction efficiency and improve atom economy. However, the oxidative CDC of thiols and phosphonates to form P-S bond remains challenging because the P-H and S-H bonds are readily oxidized by stoichiometric oxidants. Molecular oxygen (O_2), a green and ideal oxidant, is widely used in organic synthesis. Here, we present a simple Cs_2CO_3-catalyzed aerobic oxidative cross-dehydrative coupling between thiols and phosphonates for the synthesis of dithiophosphates.[4]

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PC-04

Tailoring the Degradation of Cyano-arene based Photocatalysts for Enhanced Visible-Light-Driven Halogen Atom Transfer

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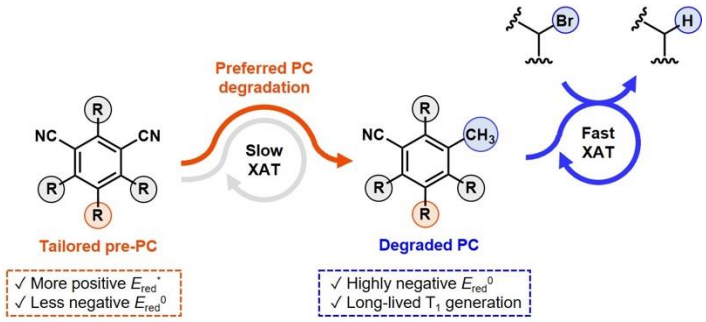
We report the design of donor-acceptor cyanoarene-based photocatalysts (PCs) to enhance beneficial PC degradation for halogen atom transfer (XAT)-induced dehalogenation reactions. Our investigation reveals the competitiion between the catalytic cycle and the degradation, with degradation becoming dominant, for inactivated alkyl halides. The degradation of PCs impacts the efficiency of the XAT, leading to investigation into modification of the degradation behavior in a desirable direction. Dueto the variation in the nature and rate of PC degradation, and its impact on the reaction across the range of PC structures, we designed the PCs to develop a pre-catalyst, named 3DP-DCDP-IPN. The pre-catalyst undergoes rapid degradation into an active form, showed an improved reducing ability in its radical anion form for the better PC regeneration, and the effective XAT reaction.



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PC-05

Oxidative Dearomative Coupling of Electron-deficient Arenols Catalyzed by Quaternary Ammonium Hypohalites

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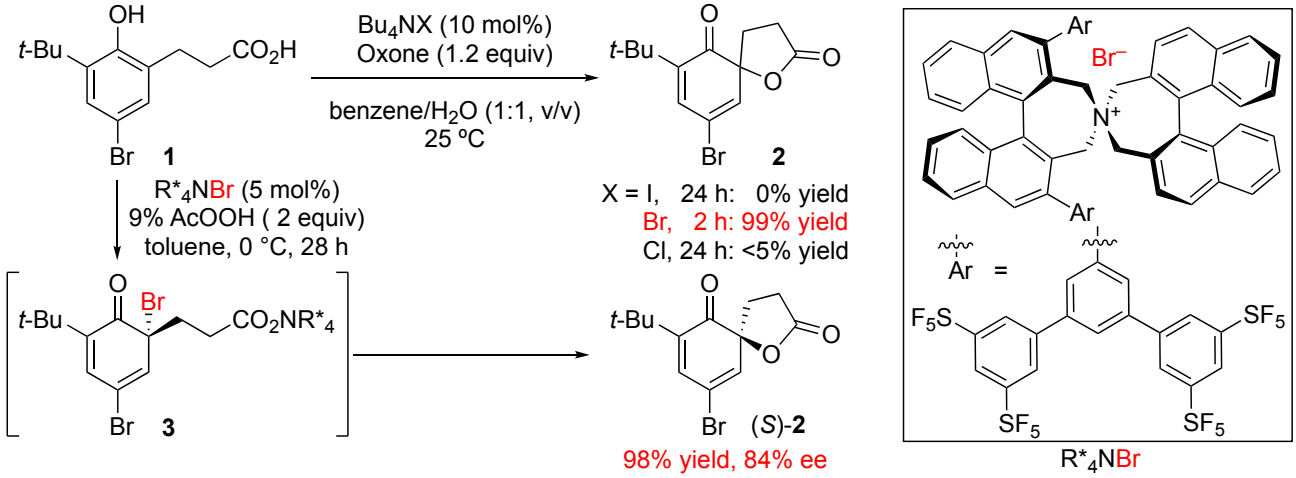
The dearomatization of arenes is a powerful strategy for the construction of complex three-dimensional molecular skeletons from planar feedstocks. We have developed a chiral ammonium-hypoiodite-catalyzed asymmetric dearomatization reactions of arenols using 30% aqueous hydrogen peroxide as an oxidant.[1] However, the substrate scope was limited to 1-naphthols. Recently, we have further described the oxidative dearomatization of arenols using chiral quaternary ammonium iodide and oxone to give the corresponding spirolactones in high yield with high enantioselectivity.[2] Still, the substrate scope of I^+/oxone catalysis has so far been limited to reactive electron-rich arenols, while no reaction was observed for phenols, such as **1**, bearing even mildly electron-withdrawing groups (EWG). We developed a performant in situ hypohalite, especially hypobromite, catalysis for the oxidative dearomatization of low-reactive electron-deficient arenols.[3] The reaction scope encompasses inter- and intramolecular oxidative dearomative C–O, C–N, and C–C coupling reactions. Notably, using a chiral ammonium countercation,[4] we achieved the enantioselective hypobromite catalysis for oxidative dearomative coupling reactions. Mechanistic studies revealed that the reaction mechanisms might differ depending on the halide identity.



Scheme 1. Hypohalite-catalyzed Oxidative Dearomative Coupling of Electron-deficient Phenol **1**

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PC-06

Synthesis of *ortho*-Substituted Phenol Bioisosteres via SmI_2-Mediated Reductive Cyclization Reactions

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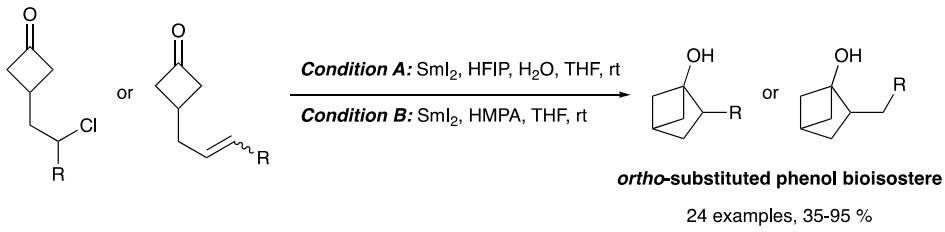
One of the most common structural motifs in chemistry is the aromatic ring and over 45% of FDA-approved small molecule drugs containing one or more benzene rings.[1] On the other hand, the indiscriminate use of aromatic moieties can lead to relatively flat molecules with limited shape diversity and poor physicochemical properties, contributing to late-stage attrition in the drug discovery process.[2] To overcome the physicochemical limitations of aromatic rings, there is significant interest in the replacement of benzene rings with polycyclic saturated hydrocarbons as benzene bioisosteres.[3] In particular, disubstituted bicyclo[2.1.1]hexanes have been recognized as flexible molecular scaffolds that can potentially act as *ortho*- and *meta*-substituted benzene bioisosteres.[4]

In this presentation, the synthesis of a wide range of 2-substituted bicyclo[2.1.1]hexan-1-ols, which have the potential to emulate *ortho*-phenolic derivatives, via SmI_2-mediated reductive cyclization reactions will be disclosed. Furthermore, the bicyclic alcohols generated in this study were transformed into saturated analogs of pharmaceutically relevant compounds, thereby solidifying this approach as a valuable tool in the synthesis of *ortho*-substituted phenol bioisosteres.



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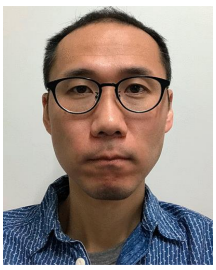

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PC-07

Synthesis and Application of Well-Defined $[Ph_4P]^+[Cu(CF_2CF_3)_2]^-$ Complex as a Versatile Pentafluoroethylating Reagent

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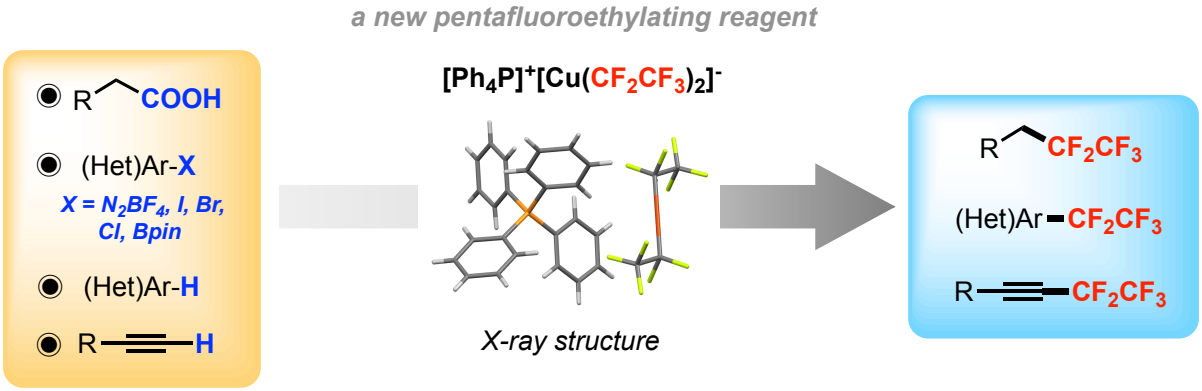
We herein describe the preparation and application of a new bispentafluoroethylated organocuprate $[Ph_4P]^+[Cu(CF_2CF_3)_2]^-$. This complex has demonstrated a remarkable range of reactivities towards carboxylic acids, diazonium salts, organic halides, boronic esters, terminal alkynes and (hetero)arenes as a versatile pentafluoroethylating reagent. The construction of $C(sp^3)$-/$C(sp^2)$-/C(sp)-CF_2CF_3 bonds can therefore be achieved using a single reagent.



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PC-08

Building Complexity: Advanced Self-Assembly Strategies for Supramolecular Architectures

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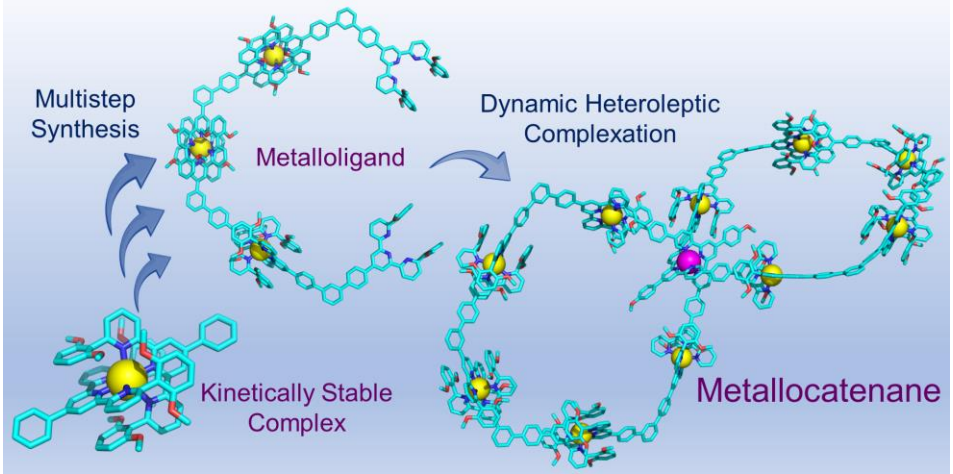
The construction of complex artificial supramolecules with specific functions presents a significant challenge in supramolecular chemistry, primarily due to the absence of efficient and reliable self-assembly strategies. To address this challenge, our research group has systematically investigated the influence of ligand geometry on coordination-driven self-assembled structures. Through these explorations, we have developed a variety of innovative self-assembly strategies for constructing metallo-supramolecular architectures characterized by exceptional structural diversity and complexity. Our strategies encompass dynamic heteroleptic complexation,[1] the integration of orthogonal and selective noncovalent interactions,[2] and the design of metalloligand building blocks.[3] These approaches have facilitated precise control over the formation of intricate metallo-supramolecular structures, thereby opening new avenues for the development of functional materials. In this poster, I will present examples of both one-pot and sequential methods for the rational construction of various metallo-supramolecular architectures.



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PC-09

Stereoselective Transformation of Prochiral Sulfenate Anions to Chiral Sulfoxides: Mechanism and Applications

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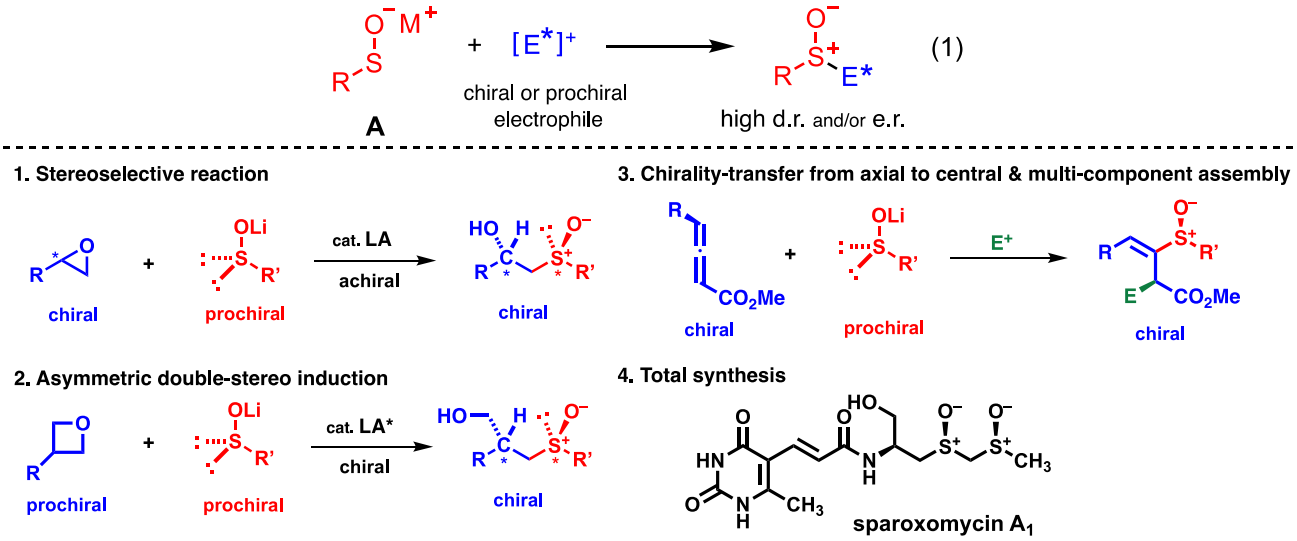
Among functional organosulfur compounds, stereo-defined chiral sulfoxides are widely utilized as ligands, organocatalysts, and chiral building blocks. Furthermore, chiral sulfinyl groups are also present in the structures of natural products and commercial pharmaceuticals, such as sparoxomycins and esomeprazole. As a result, there is a strong demand for efficient synthetic methods to access chiral sulfoxides. Among the various approaches, enantio- or diastereoselective alkylation of prochiral sulfenates has proven to be a promising strategy for constructing chiral sulfinyl groups within complex molecular frameworks.

In this study, prochiral sulfenate anion **A** was employed in reactions with a variety of chiral electrophiles to produce diastereomeric chiral sulfoxides with excellent stereoselectivity (Eq. 1). Specifically, reactions between chiral epoxides and **A** yielded β-hydroxy sulfoxides.1 The reaction of prochiral oxetanes in the presence of a chiral Lewis acid proceeded with high stereoselectivity and specificity, producing the corresponding γ-hydroxy sulfoxides in high yield. Additionally, the nucleophilic attack of **A** to axially chiral allenes, followed by reaction with an electrophile, stereoselectively afforded functionalized vinyl sulfoxides. These results facilitated the total synthesis of sparoxomycin A1. The details will be discussed.



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PC-10

Fully Conjugated Carbon Nanobelts

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Single-walled carbon nanotubes (SWCNTs) are regarded as one of the most promising materials for next generation microelectronics. The length, diameter, and edge structure determine their electronic properties and applications. However, the atomically precise synthesis of SWCNTs seems to be nearly impossible. Fully conjugated, double-stranded carbon nanobelts (CNBs), as sidewall fragments of CNTs, have been regarded as the "laurel" for synthetic chemists because of their unique electronic structures, aesthetic beauty, and synthetic challenges. In recent years, there has been a revival of interest in the bottom-up organic synthesis of CNBs. In this poster, the synthesis and physical properties of zigzag-edged and non-alternant carbon nanobelts (NACNBs) (see Figure 1) will be presented.[1-2] The non-alternant CNBs show a smaller energy gap and intense red emission compared to alternant CNBs. Furthermore, one NACNB can be chemically oxidized into its dication, which exhibits an open-shell singlet ground state and interesting global aromaticity with two weakly coupled annulenes along the edges.

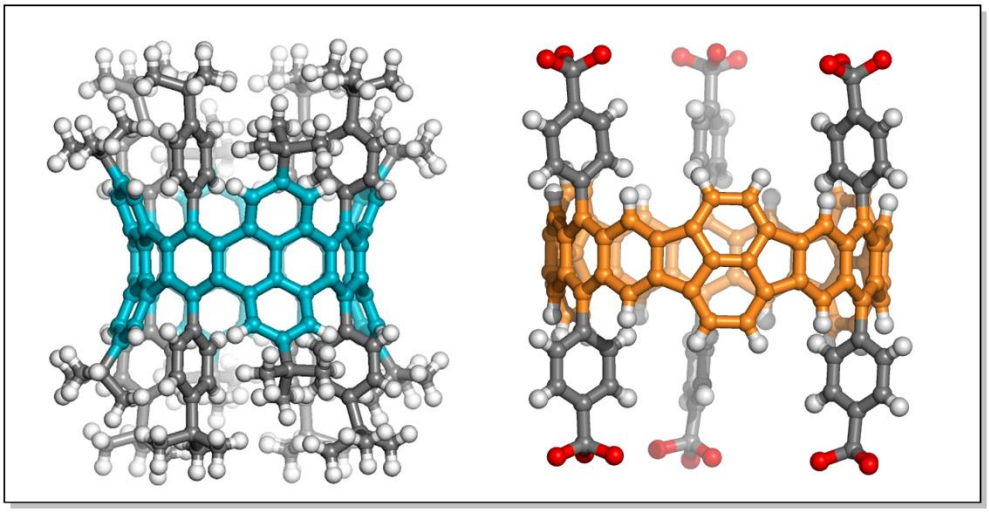

Figure 1. Examples of zigzag-edged (left) and non-alternant (right) carbon nanobelts prepared in the Chi lab.

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PC-11

Stereodivergent Synthesis of Chiral 1,3-Disubstituted Isoindolines via Palladium/Brønsted Acid-Catalyzed Intramolecular Allylation

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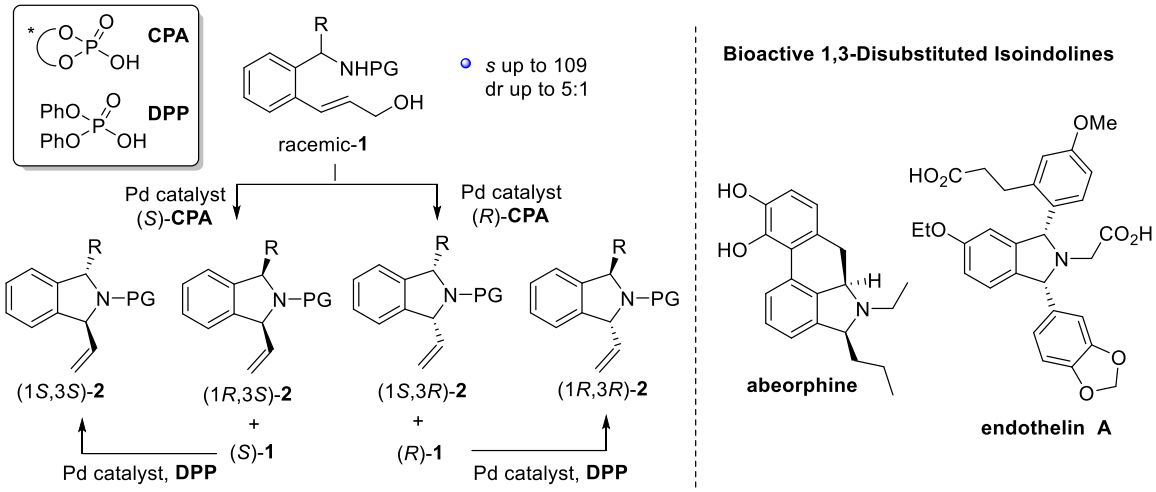
Chiral 1,3-disubstituted isoindolines are core structures in numerous bioactive compounds, such as abeorphine and endotheline A.[1] However, despite their significance, the asymmetric catalytic synthesis of 1,3-disubstituted isoindolines is relatively unexplored and limited to the formation of *cis*-isomers.[2] Herein, we present a stereodivergent approach to access chiral 1,3-disubstituted isoindolines via intramolecular allylation reactions.[3] The kinetic resolution of racemic amines **1** through palladium/chiral phosphoric acid (CPA)-catalyzed allylation yielded chiral *cis*-1,3-disubstituted isoindolines **2** with a selectivity factor of up to 109. Additionally, the *trans*-isomers **2** were readily obtained by conducting the allylation reaction of recovered enantioenriched amine **1** with diphenyl phosphate (DPP) as an achiral Brønsted acid catalyst.



Asymmetric Synthesis of Chiral 1,3-Disubstituted Isoindolines

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PC-12

Fast and Efficient Organic Room-Temperature Phosphorescence in Solution

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Phosphorescence is a fundamental luminescence phenomenon involving spin-flipping, which is quantum mechanically forbidden. While precious-metal complexes can facilitate spin-forbidden processes to emit room-temperature phosphorescence (RTP), more cost-effective and sustainable metal-free organic compounds rarely do so. The most severe limitation in organic RTP would be the inherently slow phosphorescence rate constant k_p (typically 1~10 s^{-1}), causing poor RTP quantum yields (Φ_p).
Herein, we report on metal-free organic 1,2-diketones exhibiting fast and efficient RTP in solution.[1] Their k_p were carefully derived as ~5000 s^{-1}, which is close to those of Pt porphyrin complexes. The significant k_p enabled excellent Φ_p up to 38.2% in solution under Ar. To the best of our knowledge, this value is the highest for organic molecules in common solvents. We will present the mechanism and structure–property relationship of the fast and efficient RTP, including the results of ultrafast spectroscopy and theoretical calculations.

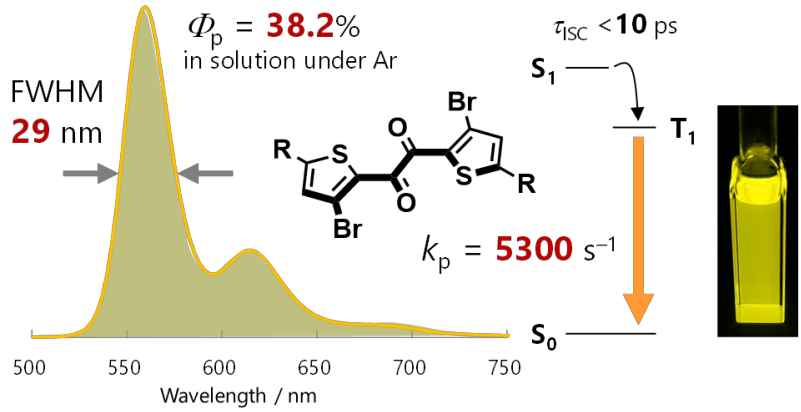

Fig. 1 Chemical structure, steady-state photoluminescence spectrum in cyclohexane (1.0×10^{-5} M, λ_{ex} = 368 nm), and photographic images under UV light.

Reference

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PC-13

Catalytic Dynamic Kinetic Resolutions for the Synthesis of Axially Chiral Biaryls

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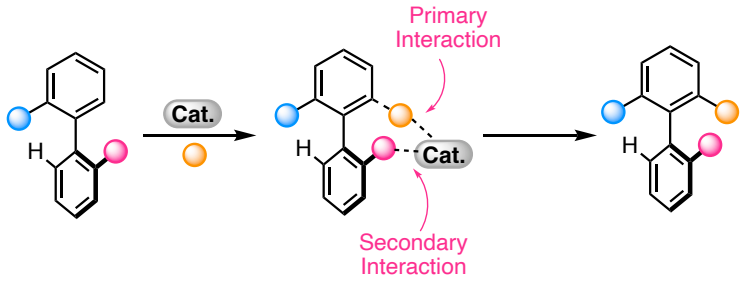
Atropisomerism has garnered significant attention due to its broad applicability in fields such as asymmetric catalysis, medicinal chemistry, and materials science. However, the catalytic enantioselective synthesis of atropisomers remains challenging, as only a limited number of synthetic methodologies have been developed. To broaden the range of accessible axially chiral compounds, it is essential to develop general and versatile atroposelective methods using either chiral organocatalysts or chiral metal complexes. For a reaction to succeed, a primary interaction with a catalyst is required on one side, while a secondary interaction must be established with a catalyst on the opposite side of a pro-stereogenic axis. With this perspective, we have designed reactions and substrates that bear functional groups to facilitate secondary interactions with chiral catalysts. Moreover, computational studies have been conducted to identify secondary interactions in catalytic reactions. This presentation will showcase our recent advancements in atroposelective reactions using dynamic kinetic resolution strategy. This approach will open new opportunities for efficiently accessing various atropisomeric compounds.



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Research field: Asymmetric catalysis, Atropisomerism, Medicinal Chemistry, Organocatalysis.

PC-14

Photocatalytic Ring-Opening Diphosphination of Strained Cyclic Molecules: Experimental and Computational Insights

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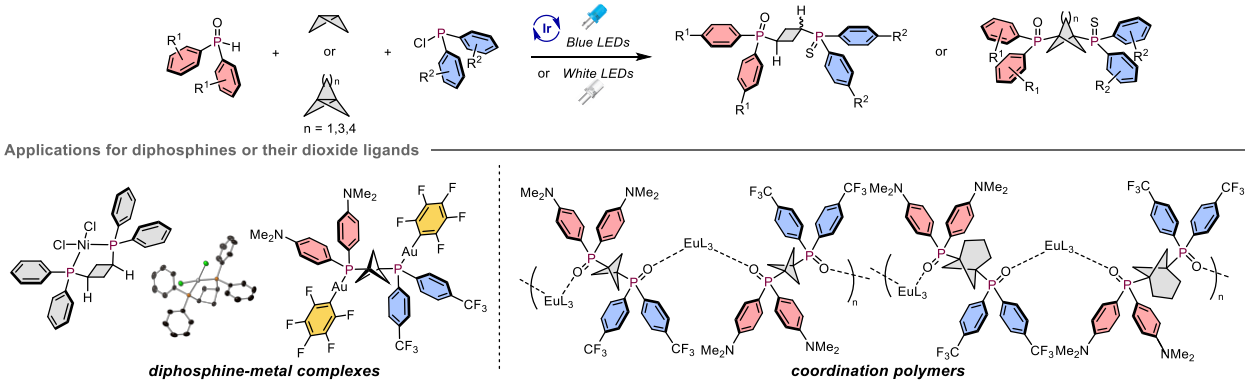
Diphosphine ligands based on cyclobutane, bicyclo[1.1.1]pentane, bicyclo[3.1.1]heptane, and bicyclo[4.1.1]octane were synthesized from the corresponding highly strained, small, cyclic organic molecules, i.e., bicyclo[1.1.0]butane, [1.1.1]propellane, [3.1.1]propellane, and [4.1.1]propellane, employing a ring-opening diphosphination. Under photocatalytic conditions, the three-component reaction of a diarylphosphine oxide, one of the aforementioned strained molecules, and a diarylchlorophosphine results in the smooth formation of the corresponding diphosphines in high yield.[1] The obtained diphosphines can be expected to find applications in functional molecules due to their unique structural characteristics, which likely impart specific properties on their associated metal complexes and coordination polymers. The feasibility of the initial radical addition can be estimated using density-functional-theory (DFT) calculations using the artificial force induced reaction (AFIR) method.[2] This study focuses on the importance of integrating experimental and computational methods for the design and synthesis of new diphosphination reactions that involve strained, small, cyclic organic mole. We also developed novel carboxylation reactions using CO_2 and CO_2 radical anions, based on computational studies.[3]



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HP: https://mitagrouphp.icredd.hokudai.ac.jp/en.html

PC-15

Iodide-umpolung catalytic system for nontraditional amide coupling from nitroalkanes and amines

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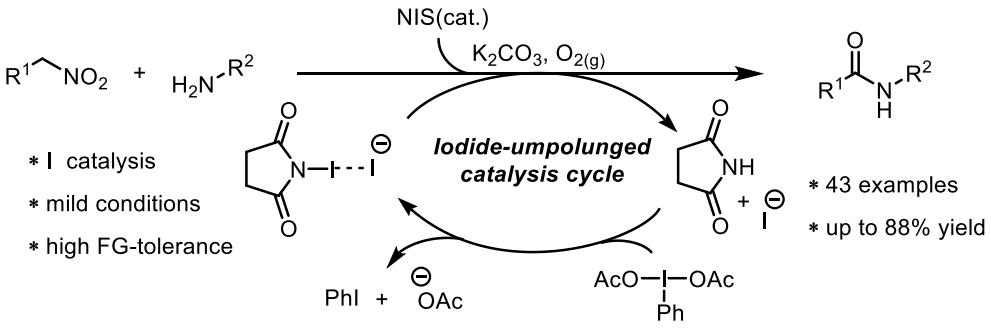
An unusual oxidation using an iodide catalyst was developed for use in the nontraditional synthesis of amide derivatives from nitroalkanes and amines. In contrast to traditional oxidative catalysis this catalysis system involves reversing the polarities of the two catalytic components (Umpolung) by means of a hypervalent iodine reagent. A variety of functional groups were tolerated in the reaction, indicating that it has the potential for use in other types of oxidative catalytic reactions.



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PC-16

Intramolecular Diels–Alder Approach toward Tricyclic 9–Methyl–7–aryl–tetrahydro–6*H*–benzo[*c*]chromen–6–ones of Morusalisin A

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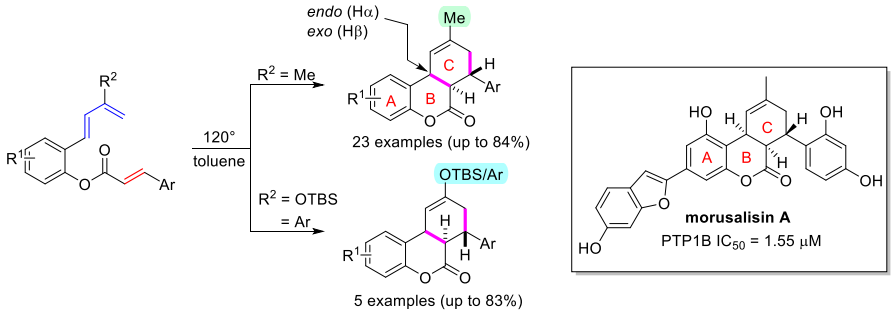
Tricyclic tetrahydro–*6H*–benzo[*c*]chromenes and their analogues are important frameworks of synthetic compounds and natural products with diverse intriguing biological activities. As part of our development of Diels–Alder reaction (DA) for synthesis of natural products[1], we have developed a thermal intramolecular DA reaction of benzo–tethered dienyl cinnamates to furnish the 9–methyl–7–aryl–tetrahydro–6*H*–benzo[*c*]chromen–6–ones of the morusalisin A[2] in up to 84% yield through a simple, three–step procedure starting from simple benzaldehyde derivatives. This developed chemistry could also be applied for synthesis of 9–silyloxy/9–aryl–7–aryl–tetrahydro–6*H*–benzo[*c*]chromen–6–ones. The *endo*/*exo* selectivity was substantially governed by the positioning of substituents on the aryldiene moiety where the substrates with a substituent *ortho* to the diene moiety furnished the *endo* isomer as a major product, while the others predominantly gave the *exo* isomer as a major product. In addition, the resulting cycloadducts could serve as common intermediates for further functionalization such as epoxidation, desilylation and Riley oxidation to furnish the privileged structural motifs in moderate to good yields.[3]



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PC-17

Development of -Si(pan), a Seven-Membered Dialkoxysilyl Unit

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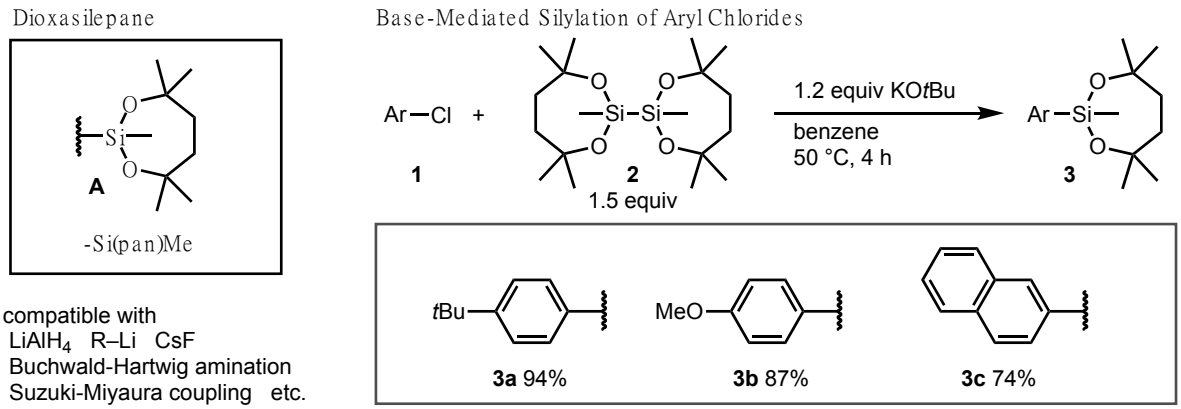
A dialkoxysilane featuring a bulky seven-membered dialkoxy ring structure is designated as dioxasilepane, and is abbreviated as -Si(pan). A methylated version, designated as -Si(pan)Me (**A**), was observed to exhibit remarkable chemical stability across a spectrum of functional group transformations. Remarkably, this group maintains compatibility with reagents such as $LiAlH_4$ or alkyllithiums, which typically exhibit reactivity towards alkoxysilyl groups. Furthermore, **A** can be selectively activated to facilitate coupling reactions with arenes or undergo oxidative conversion to phenols. The unique attributes of this silyl group make it an advantageous candidate for incorporation into complex organic synthesis sequences. Our ongoing research endeavors aim to elucidate the scope and limitation of transformations unique to **A** and its derivatives. The synergy between the substantial steric bulk, ensuring kinetic stability, and the inherent Lewis acidity of the alkoxylated silicon core, endows this functional group with a valuable role in transformations previously deemed challenging. In the current study, we have discovered that dioxasilepanylpotassium (K-Si(pan)Me) species can be synthesized from their corresponding disilane **2** and potassium *tert*-butoxide. The transient silylpotassium intermediate engages in halogen–potassium exchange with **1**, followed by nucleophilic substitution at the silicon center to yield compound **3**, delineating a novel methodology for the introduction of a -Si(pan)Me group. Insights into the reaction mechanism will also be disclosed.



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PC-18

Nitrosonium ion Initiated Halogenation and C-N Bond Formation of Arenes

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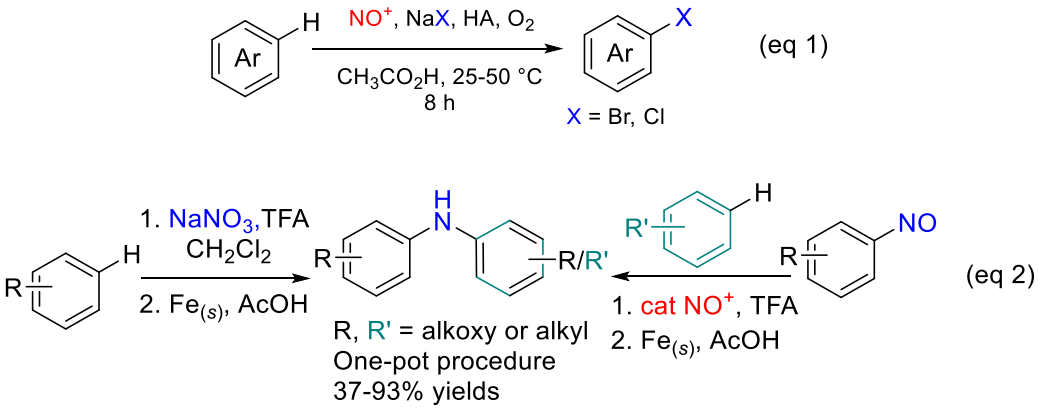
Although nitrosonium ion (NO^+) is a poorer electrophile than nitronium ion (NO_2^+),[1] nitrosonium ion provides versatile reaction pathways in addition to nitrosation of aromatic compounds. Here, we report a nitrosonium-catalyzed halogenation of electron-rich arenes, using bromide/chloride salts as halogen sources, oxygen gas as a terminal oxidant and Brønsted acids (sulfuric acid, TFA or HBr). This arene bromination process is free of transition metals, proceeding in acetic acid and under mild temperatures (25-50 °C) to give brominated or chlorinated arenes with good to excellent yields (eq 1).[2] In addition, nitrosonium ion can be applied to prepare diarylamines *via* the direct C-N bond formations with arenes (eq 2).[3] Our mechanistic study suggested that nitrosoarene is the intermediate and its σ-complex with nitrosonium is responsible to form the second C-N bond. Thus hetereo-diaryl amines could be prepared from pre-formed nitroso-compounds and arenes. These NO^+ initiated reactions provide an inexpensive, alternative method to prepare aryl halides and diarylamines.



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Research field: Organic Chemistry and Synthesis.

PC-19

Boosting the reactivity of borate anions

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In recent years, borate anions have demonstrated valuable applications in various fields, such as organic synthesis, material science, energy storage devices, and biological and pharmaceutical studies.[1] In our research, we have developed two new borate anions, which have shown intriguing reactivities in organic synthesis. We employed bipyridine, a simple yet versatile ligand, to synthesize a reactive borate anion, **1** (Figure 1).[2] The borate anion exhibits remarkable reduction capabilities by reducing Li^+ to produce elemental lithium metal and boron radicals. Moreover, it serves as a highly effective two-electron-reducing reagent, finding versatile applications in reductive homo-coupling reactions and Birch reduction of acridine. Besides, by performing a reductive B-B coupling of 9-borafluorene, we successfully synthesized a hexaaryl-substituted diboron(6) dianion, **2**.[3] Remarkably, it demonstrates the unique capability of undergoing homolytic B-B bond cleavage at room temperature, resulting in the formation of boryl radical anions.

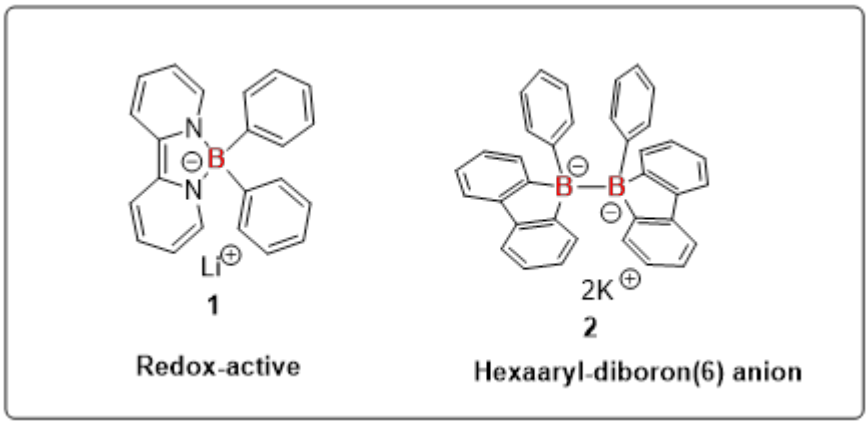

Figure 1. Borate anions.

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Research: [Main-group chemistry] Boron Chemistry.

PC-20

Substrate-controlled Glycosylation for the Enzymatic Synthesis of Asymmetrically Branched Human Milk Oligosaccharides

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To efficiently construct a diverse library of branched human milk oligosaccharides (HMOs), we synthesized three distinct branched tetrasaccharide core structures as foundational substrates for enzymatic glycan extension. Using a "Substrate-controlled Glycosylation on Asymmetrically-branched Reaction sites (SuGAR)" strategy, we achieved precise control over regioselective glycosylation to expand the structural complexity of the HMO library. The SuGAR strategy enabled β1,4-galactosyltransferase to selectively add a galactose (Gal) residue to the C-4 position of the GlcNAc unit, while reactivity at the GlcN unit was minimized. By modifying the C-2 position on glucosamine residues (GlcNAc versus GlcN), we achieved controlled β1,4-galactosylation on the tetrasaccharide core, facilitating the chemoenzymatic synthesis of asymmetrically branched HMOs, including lacto-*N*-hexose (LNH) analogues.[1] To further diversify this HMO library, we synthesized a "reversed" core tetrasaccharide that expanded the substrate scope, allowing for additional glycosylation possibilities. We also applied a "lock-unlock" strategy by incorporating sialic acid (Sia) at specific positions, which regulated glycan chain extension and added a second layer of complexity to the branched structures. Through SuGAR, we generated a variety of asymmetrically branched glycans by incorporating α1,2- and α1,3-linked fucose residues using specialized fucosyltransferases.[2] This process enabled selective fucosylation at predefined positions, resulting in a highly diverse HMO library with various branching and linkage patterns. Overall, we successfully established a broad library of structurally complex HMOs, combining both sialylation and fucosylation modifications. These synthesized glycans possess structural characteristics and branching motifs similar to natural HMOs, making them valuable resources for examining HMO biological activities, such as inhibition of pathogen adhesion, modulation of gut microbiota, and immune response regulation. This comprehensive HMO library marks a significant advancement in synthetic glycobiology, providing a versatile platform for future therapeutic development and functional research.

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[Field of research] Carbohydrate Chemistry, Glycobiochemistry, Enzyme Chemistry, Glycobiology, Protein Enginneering and Directed Evolution.

PC-21

Synthetic study of stagonosporyne G and structurally related natural products

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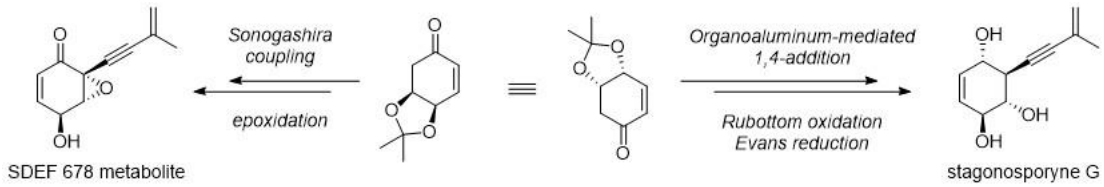
Stagonosporynes are isolated from a major wheat pathogen *Parastagonospora nodorum* SN15 in 2019 [1]. This fungus is known as a causative agent of plant disease Septria nodorum blotch (SNB), leading to a significant crop loss in many regions of world. Structurally, stagonosporynes possess a highly oxygenated cyclohexanoid skeleton with isopropenylacetylene side chain. Among them, stagonosporyne G shows herbicidal activity against *Arabidopsis thaliana* at the highest test concentration (100 μg/mL). Thus, stagonosporynes might be involved in the expression of the pathogenicity of *P. nodorum* on wheat species. Structurally related natural products with isopropenylacetylene side chain also possess attractive biological activities such as herbicidal, antifungal and plant growth promoting. For example, SDEF 678 metabolite, isolated from the ectotrophic Australian fungus, SDEF 678, shows potent inhibitory activity against many soil-borne phytopathogens such as *Gaeumannomyces graminis* var. tritici (Ggt) and *Phytophthora cinnamomi* [2]. With highly oxygenated carbon framework in compact structure and attractive bioactivity, these natural products are attractive synthetic targets. Therefore, we embarked on synthetic study of these natural products from common synthetic intermediate.

Starting from commercially available (−)-quinic acid, the key intermediate was synthesized in 7 steps in good yield on gram scale. From this intermediate, stagonosporyne G was synthesized in 8 steps including alkynylaluminum-mediated 1,4-addition, Rubottom oxidation and Evans reduction. On the other hand, SDEF 678 metabolite was synthesized in 4 steps including Sonogashira coupling and diastereoselective epoxidation. The absolute configuration of these natural products is confirmed by comparison of optical rotation of synthetic materials with those of natural products.



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[page #]

PC-22

contra-Thermodynamic Positional Isomerization: From Enoates to Alkenyl *α*-Stereogenic Esters.

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Carbonyl compounds bearing α-stereogenic centers are ubiquitous motifs found in bioactive natural products and pharmaceutical drugs, which attracts chemists' interest to devote in the synthetic field.[1] Among the most utilized methods to build this valuable motif is through asymmetric alkylation of enolates which often employs chiral auxiliaries or chiral catalysts.[2] Despite its notoriety, this route suffers from common disadvantages like the formation of undesirable side products. Consequently, Norrish Type II Rearrangement has been developed as an alternative route toward constructing quaternary centers. Although Norrish Type II Rearrangement has long been established, the successful case of asymmetric Norrish Type II rearrangement is still limited. Moreover, a step- and atom-economy reaction known as photodeconjugation which involved Norrish Type II rearrangement has been developed. Photodeconjugation reaction mechanistically proceeds through *E*/*Z* isomerization, followed by 1,5-HAT and keto-enol tautomerization to afford the target motif utilizing enones as substrates. In this study, the chiral phosphoric acid-catalyzed asymmetric Norrish type II rearrangement of acyclic *α*, *β*-unsaturated ester under UV light irradiation has been developed. The reaction afforded various acyclic enoates with excellent enantioselectivities and moderate to good yields.

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[Field of research] Organic Synthesis and Catalysis.

PC-23

Selective Isomer Synthesis of N-Acyl-Sulfonyl Hydrazides: The Impact of Base Counter Cations in Palladium-Catalyzed Aminocarbonylations.

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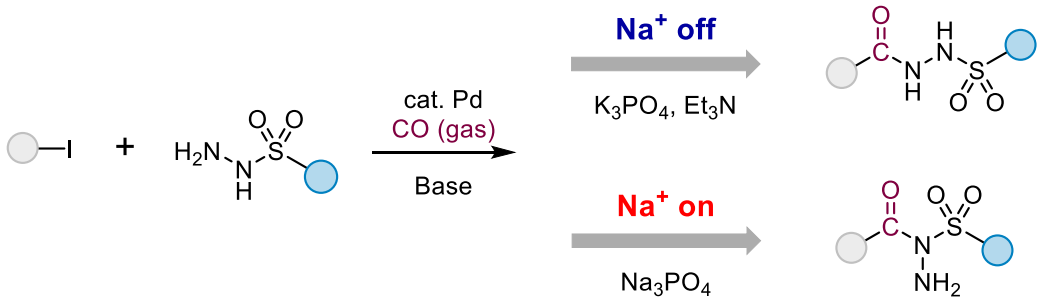
Acyl sulfonyl hydrazides are key intermediates in bioactive compound synthesis, acting as effective inhibitors for targets like KAT6A, BCAT, and MOZ, with potential applications in treating neurodegenerative diseases.[1] Various synthesis methods have been developed, with acylation of tosylhydrazide being common. We previously attempted the synthesis of acyl sulfonyl hydrazides by reacting aryl iodides with sulfonyl hydrazides under carbon monoxide and palladium catalysis, but due to the instability of sulfonyl hydrazides, the reaction resulted in thioester formation.[2] Recently, we developed the selective synthesis of N-acyl-*N*′-sulfonyl and *N*,*N*-acyl-sulfonyl hydrazides from aryl iodides and sulfonyl hydrazides using carbon monoxide and palladium catalysis. Base selection was crucial in determining isomeric selectivity, with general bases favoring *N*-acyl-*N*′-sulfonyl hydrazides and Na_3PO_4 promoting *N*,*N*-acyl-sulfonyl hydrazides. Yields ranged from 62-89% for linear hydrazides and 41-74% for branched hydrazides. Mechanistic studies highlighted the role of sodium ions in promoting branched isomer formation, providing valuable insights into reaction pathways. In this presentation, we will discuss the unusual role of counter cation of base in the selective synthesis of two isomers of *N*-acyl-sulfonyl hydrazide. [3]



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[Field of Research] Cross coupling reaction, Transamidation. .

PC-24

Total Synthesis of Palau'amine

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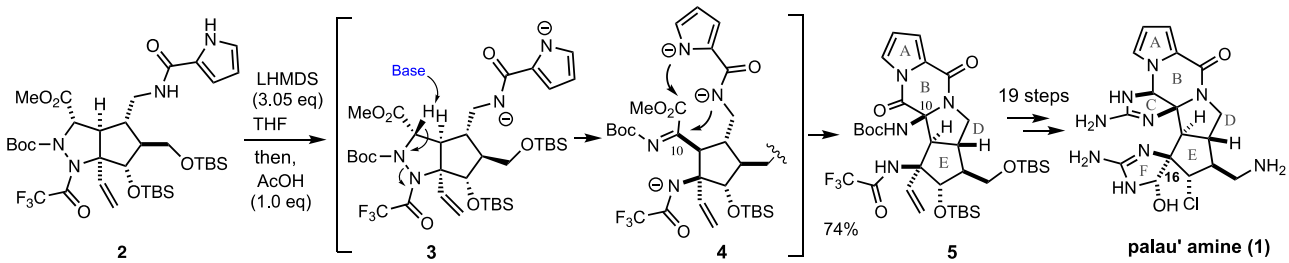
Palau'amine (**1**) was originally isolated from a sponge, *Stylotella agminata*, by Scheuer in 1993 as a novel class of pyrrole-imidazole alkaloids.[1] Palau'amine has received a great deal of attention over the past 30 years as an attractive synthetic target due to its intriguing molecular architecture and significant immunosuppressive activity. However, despite many synthetic studies, only Professor Baran[2] and our group[3] have reported the total synthesis of **1** so far. In this presentation, we discuss our total synthesis of **1**, characterized by the single-step construction of the ABDE tetracyclic ring core including a *trans*-bicylo[3.3.0]octane skeleton.

The key intermediate **2** was prepared from cyclopentene-1-one in 24 steps. The ABDE tetracyclic ring core **5** was constructed by a single-step cascade reaction from **2**. Subsequent construction of C- and F-ring systems and the functional group transformations afforded palau'amine (**1**) in 0.044% overall yield in 44 steps from cyclopentene-1-one.

Next, we have tried to greatly reduce the number of steps as the 2nd generation total synthesis to develop the chemical probes for palau'amine. We succeeded in synthesizing the analog of **1** without chloride and aminomethyl groups in only 20 steps from the same cyclopentene-1-one, elucidating that the analog retained the immunosuppressive activity.[4]



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Kosuke Namba (難波 康祐). Osaka City University (Ph. D., 2001). Colorado State University (Postdoctoral Research Fellow, 2001); Harvard University (Postdoctoral Research Fellow, 2003); Suntory Institute for Bioorganic Research (Associate Researcher, 2005); Tokushima Bunri University (Assistant Prof, 2006); Hokkaido University (Lecturer, 2008; Associate Prof., 2011); Tokushima University (Prof., 2013; Vice Director 2018). Research Field: Total synthesis of biologically active complex natural products, the mechanistic elucidation and practical application of biologically active compounds, and the development of bioimaging probes.

PC-25

Stereoselective Synthesis of Polysubstituted Pyrrolidines by a Photoredox-catalyzed Cascade

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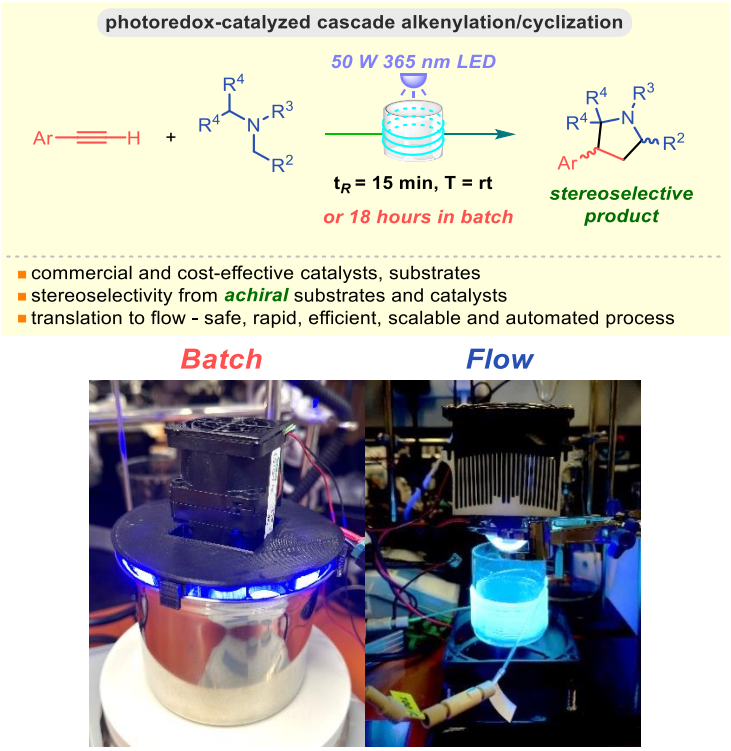
Polysubstituted pyrrolidines constitute important structural motifs in a broad range of bioactive compounds, but the syntheses of these molecules are prone to a multitude of challenges, such as the use of high-cost chiral and transition metal catalysts, inaccessible substrates, multistep syntheses, and poor scalability. Here, a photoredox-catalyzed cascade is developed for the stereoselective and regioselective one-step synthesis of polysubstituted pyrrolidines. The transformation is driven by a sequential alkenylation-cyclization between readily available alkynes and trialkyl amines, in which the amines serve as reductant in the photocatalytic cycle as well as building block of the final pyrrolidine product. Broad substrate scopes are demonstrated with excellent functional group tolerance under both batch and continuous flow conditions. Mechanistic investigations are currently underway.



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[Field of research] Continuous Flow Synthesis, Catalysis, Synthetic Methodology

PC-26

Sustainable Chemistry Unleashed: Continuous-Flow Ritter Reaction with a Recyclable Polymeric Acid Catalyst

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In this study, we present a novel approach to amide synthesis using a continuous-flow Ritter reaction catalyzed by a solid PAFR II polymeric acid catalyst. Operating at 90 °C with just 1 mol% of PAFR II, the reaction in a batch allows for straightforward product workup and demonstrates exceptional efficiency. Remarkably, the catalyst retained its catalytic activity over five cycles without significant loss. The continuous-flow system successfully produced amides from various nitriles and alcohols with yields of up to 87%. The catalyst-packed column maintained its performance for over two weeks. This method stands out for its environmental sustainability, reusability, and scalability. Notably, the continuous-flow amidation of clopropanecarbonitrile and t-BuOH consistently delivered a 90% yield of *N*-(*t*-butyl)cyclopropanecarboxamide over an extended period of more than two weeks (366 h).

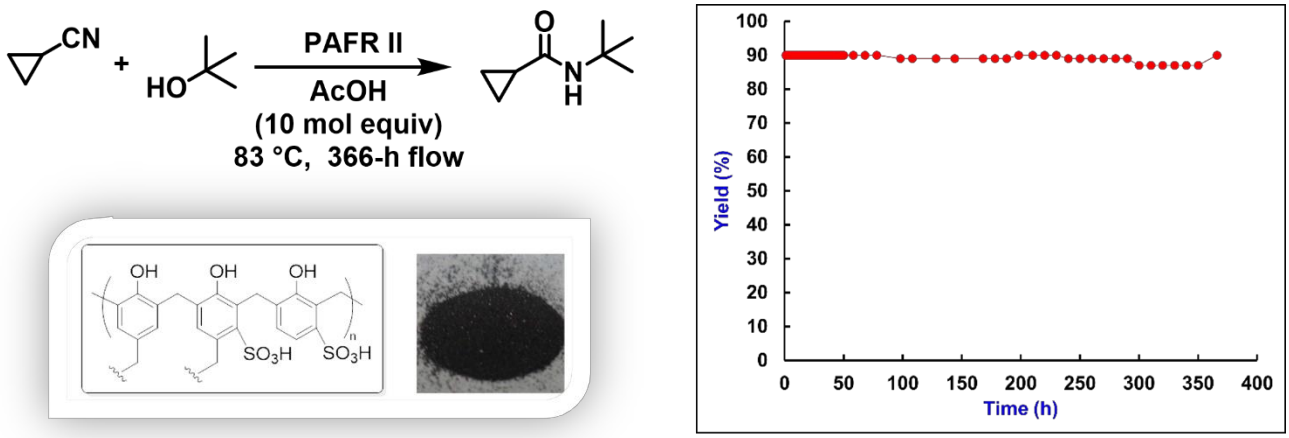

Figure 1. **Flow system for the Ritter reaction**.

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[Field of research] Organic and Catalytic Chemistry, Nano Chemistry

PC-27

Oxidative Scission of Bicyclo[2.2.2]octenones: Untying the α,α-dimethoxycarbonyl

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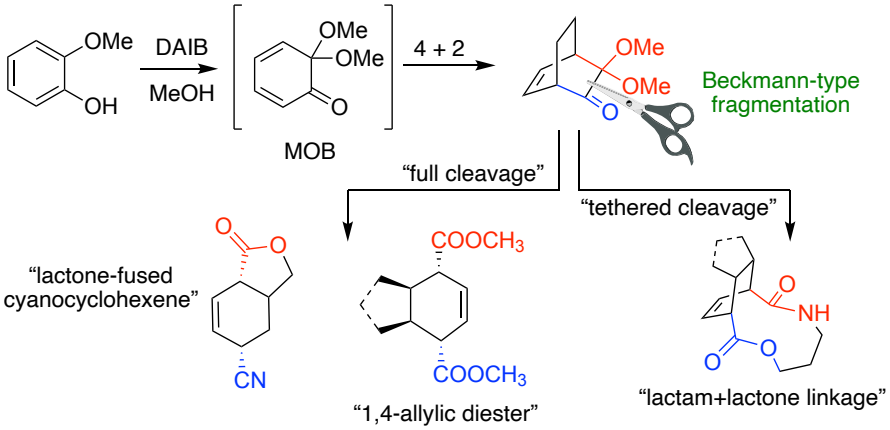
Oxidative rearrangement reactions represent a notable advancement in organic synthesis by merging the transformative capabilities of oxidation with the structural reorganization inherent in rearrangements. These reactions facilitate the contemporary introduction of carbonyl functionalities with the migration of groups within a molecule, enabling the efficient synthesis of complex and functionally diverse products. As an extension of our previous work on the photoinduced rearrangement of bicyclo[2.2.2]octenone systems and their application in natural product synthesis,[1-3] we herein present our latest findings on the oxidative scission of bicyclo[2.2.2]octenones. Through Beckmann-type fragmentation reactions, the α,α -dimethoxycarbonyl functional groups were cleaved, yielding distinct frameworks with a highly functionalized cyclohexene core derived from the original 4+2 adduct of masked *o*-benzoquinone.



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[Field of research] bimetallic catalysis, photo-induced reactions.

PC-28

Simple purification of small-molecule-labelled peptides via palladium enolate formation from β-ketoamide tags

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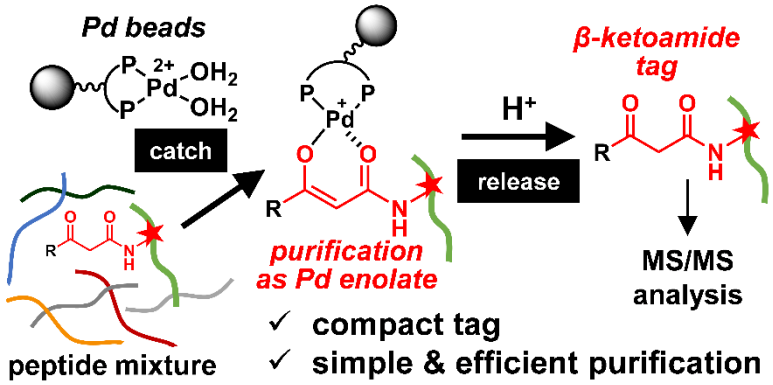
Palladium enolates derived from *β*-ketocarbonyl compounds serve as key intermediates in various catalytic asymmetric reactions. We found that the palladium enolate formed from *β*-ketoamide is stable in air and moisture, and we applied this property to develop a peptide purification system using *β*-ketoamide as a small affinity tag in aqueous media. A solid-supported palladium complex successfully captured *β*-ketoamide-tagged molecules as palladium enolates and released them in high yield upon acid treatment. Optimum conditions for the catch and release of tagged peptides from a mixture of untagged peptides were established. To demonstrate the value of this methodology in identifying the binding site of a ligand to its target protein, we purified and identified a peptide containing the ligand-binding site from the tryptic digest of cathepsin B labelled with a covalent cathepsin B inhibitor containing a *β*-ketoamide tag.



Purification of β-ketoamide-tagged peptide via palladium enolate formation.

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PC-29

Chiral Degradable Polymers *via* Metathesis Polymerizations

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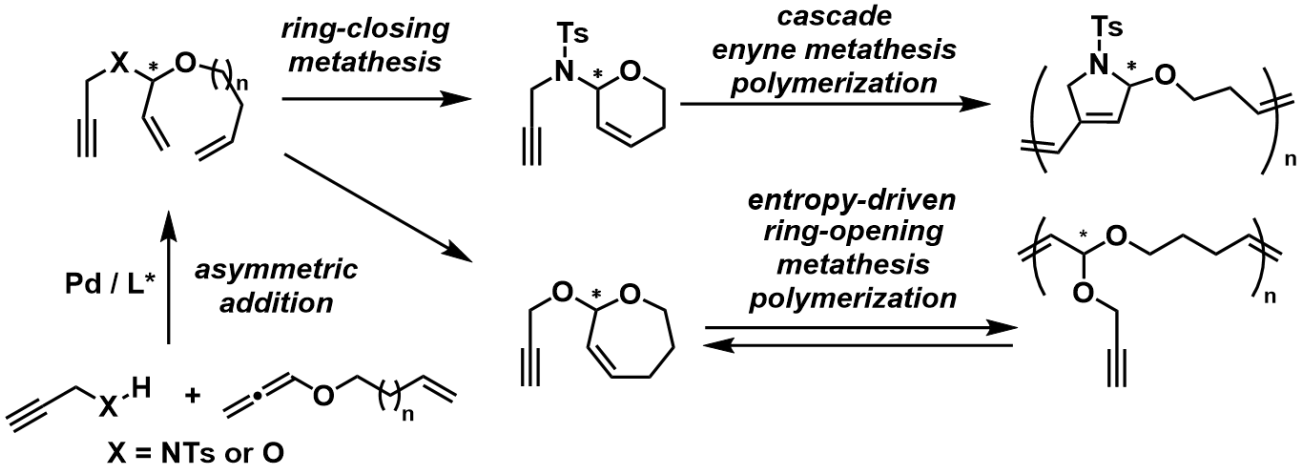
We synthesized chiral acetal-based degradable polymers using metathesis polymerization techniques.[1] Metathesis polymerizations are powerful tools for producing functional polymers with high tolerance for functional groups and selective reaction pathways. Chiral acetals were prepared via Pd-catalyzed asymmetric hydroamination or alkoxylation reactions from alkoxyallenes, followed by ring-closing metathesis to produce the corresponding chiral cyclic monomers. First, we developed a stereocontrolled degradable polymer from chiral enyne monomers through cascade enyne metathesis polymerization.[2] With living characteristics, several block copolymers were precisely synthesized by controlled addition of various monomers. We expanded the application of this technique to produce stereo-block copolymers and demonstrated molecular weight distribution control.[3] Using low-strain cyclic acetals, we demonstrated polymerization via ring-opening metathesis polymerization (ROMP) and depolymerization via ring-closing metathesis depolymerization (RCMD),[4] with both pathways controlled by reaction temperature in entropy-driven ROMP.



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PC-30

Dihydroquinolin-4-imine (DQI) mediated fluorogenic strategy for to the study of cell migration

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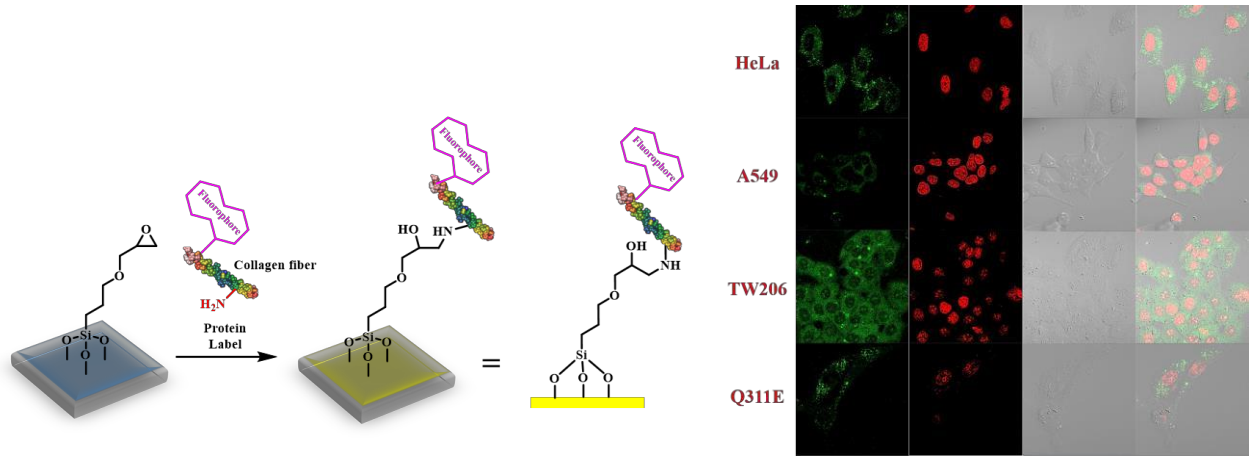
A new series of environment-sensitive fluorophore, 2,3-dihydroquinolin-4-imines (DQIs) with tailored emission color are introduced to the synthetic 2-D biomaterials. The DFT calculation further provides a guideline for preparing DQI analogs with the tailored emission. The solvatochromic property enables the DQI molecule to detect biomolecular interaction with the fluorescence turn-on mechanism on the 2-D material; surface. The fluorescence-enrichment strategy proposed here has been used in the dynamic monitoring of cell behaviors. With the success in tracking cells upon the stimuli. The flexibility of structure complexity makes DQIs ideal pendant molecules for tracking cell responses.



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PD-01

Bioorthogonal release and synthesis of anticancer drugs via propargylbenzoxime (PBO) precursors

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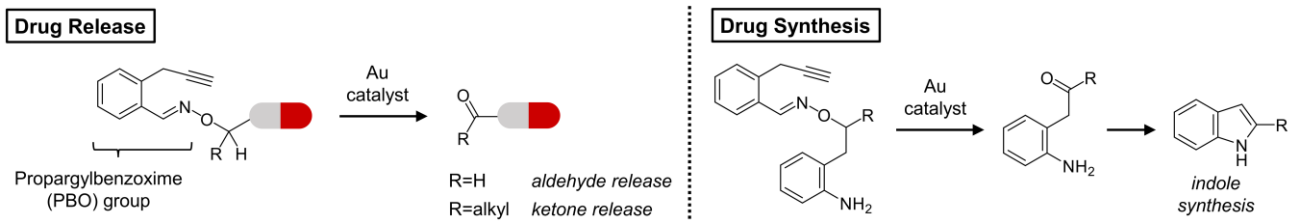
Currently, dissociative biorthogonal metal-catalyzed reactions used for developing prodrugs have largely centered on the release of amines, alcohols, and certain aryl groups. To add to the growing list of these reactions, this study develops what is described as the propargylbenzoxime (PBO) group. When exposed to Au(III) catalysts, the PBO group was found to undergo hydroamination, followed by spontaneous N–O bond cleavage to release aldehydes/ketones under mild and physiological conditions.[1] Further adaptation of the PBO group was then explored so that carbonyl release could elicit the synthesis of an indole core. To highlight their applications for anticancer prodrug therapies, this study then developed PBO-masked prodrugs that can undergo gold-triggered synthesis of indole-based drugs.



Development and adaptation of PBO groups for
drug release (aldehyde/ketone releasing) and drug synthesis (indole forming)

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PD-02

Stimuli-Responsive Luminescent Materials: Harnessing Fluorous Interactions and Strained Azacyclic Substituents for Tunable Emission

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Stimuli-responsive luminescent materials, which change emission colors in response to external stimuli such as heat, vapor, or mechanical forces, are a burgeoning area of research in the field of chemistry and materials science. The critical factor for such materials is the tunability of intermolecular interactions. Common types of these interactions include van der Waals forces, hydrogen bonding, and metal-metal interactions. In this study, we report a significant finding that fluorous interactions play a crucial role in enabling the emission color change of pyrene upon THF vapor fuming and grinding.

Enhancing solid-state emission quantum yields is a crucial challenge in the development of luminescent materials. We have discovered that green fluorescence chromophores (GFPc) with strained azacyclic groups (aziridine and azetidine) exhibit a powder emission quantum yield of approximately 10%. Both aziridine- and azetidine-substituted GFPc demonstrate stimuli-responsive emission upon grinding and DCM fuming. Furthermore, the azetidine-substituted GFPc changes its emission color to green after heating. Our findings offer new strategies for designing chromophores with tunable luminescence properties in response to environmental changes.

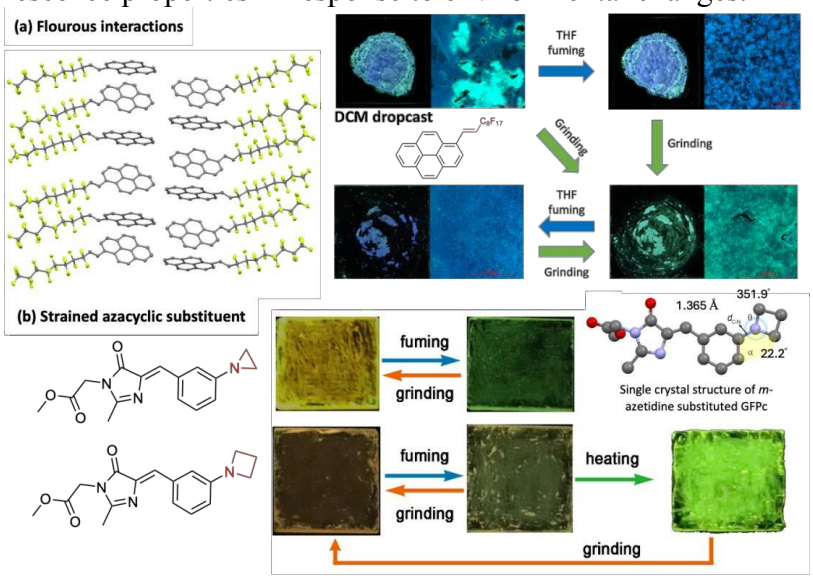

Figure 1. (a) The single crystal molecular packing of pyrene with perfluorooctylethenyl group and the emission color changes with THF-fuming and grinding. (b) The emission color changes with DCM fuming, grinding, and heating of *m*-aziridine and *m*-azetidine substituted GFPc. A single crystal of *m*- azetidine substituted GFPc is shown in the inlet.

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PD-03

Functional Enhancement of Menaquinone-Targeting Antibiotics by a Solid-Phase Total Synthesis-Based Approach

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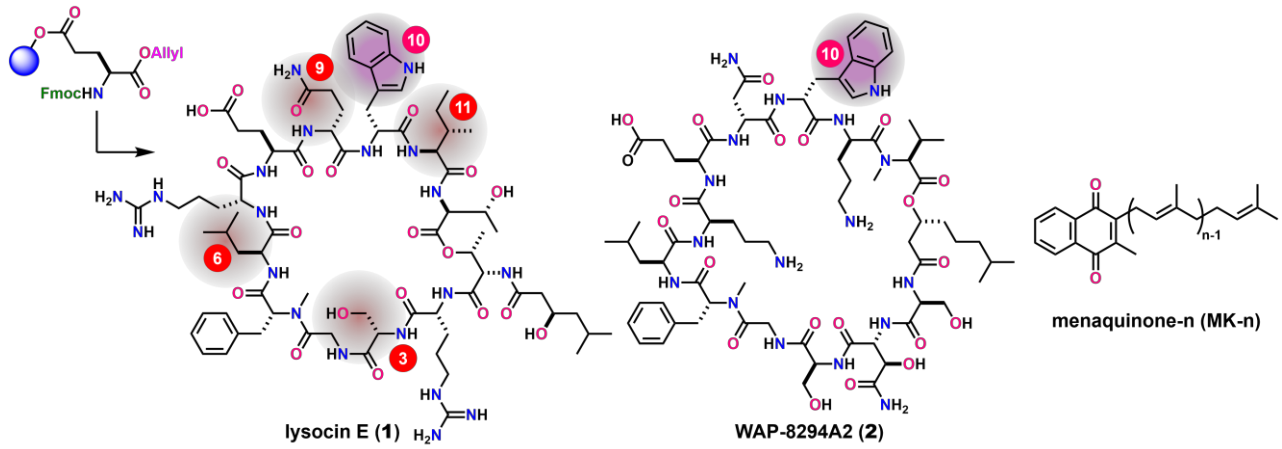
Lysocin E (**1**) and WAP-8294A2 (**2**) are macrocyclic peptidic natural products with highly potent antibacterial activities against Gram-positive bacteria, including methicillin-resistant *Staphylococcus aureus* (MRSA). Both natural products exert their antibacterial activities by forming complexes with menaquinone (MK) in the bacterial membrane.[1,2] The binding of compounds **1** and **2** to MK disrupts membrane integrity, eventually leading to bacteriolysis. Due to this unique mode of action, compounds **1** and **2** are promising lead structures for developing novel antibacterial agents. To fully utilize their molecular properties, we initiated a study on the functional enhancement of compounds **1** and **2** using a solid-phase total synthesis-based approach. Finally, we successfully generated more active analogues by randomizing multiple residues through a one-bead-one-compound (OBOC) strategy.[3] Furthermore, we discovered analogues with high oxidation resistance by substituting the indole ring, which is essential for complexation with MK.[4]



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PD-04

Metabolomics Analysis of *Selaginella* Plants: Discovery of Bioactive Biflavonoids and Chemotaxonomic Markers

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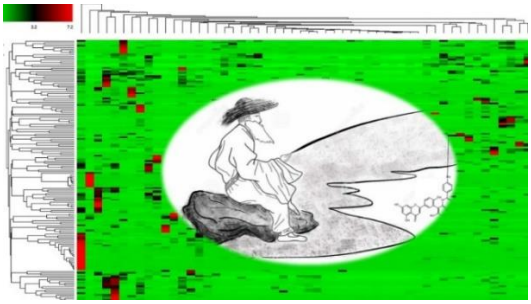
Selaginella plants (Selaginellaceae), early vascular plants known as spike mosses, contain a wide range of biologically active natural products, particularly biflavonoids (BFVs). These BFVs are known for their diverse properties, including anti-cancer, anti-inflammatory, antioxidant, antimicrobial, anti-allergy, anti-diabetes, anti-UV irradiation, anti-hemorrhagic, and antinociceptive activities. Approximately one hundred *Selaginella* samples were collected from Thai natural resources for biodiversity and plant metabolomic studies. Both untargeted and targeted metabolomics of the BFV-rich ethyl acetate extract from *Selaginella* plants were investigated. An in-house database of BFVs was established using HPLC, LC-MS, and NMR techniques. All measurable analytes from the samples, including chemical unknowns, were characterized and biochemically annotated metabolites. This study serves as a valuable tool for expeditious dereplication and identification of known or unknown BFVs and to determine chemotaxonomic markers of *Selaginella* plants using LC-MS analysis and NMR-based metabolomic profiling. It offers potential for amalgamating data from multiple stages of fractionation and bioassays into a cohesive analysis framework.



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Field of research: Methodology Development, Synthesis of Natural Products and Natural Product Chemistry

PD-05

The dye-based sensor detected silver ions using either a liquid or solid system

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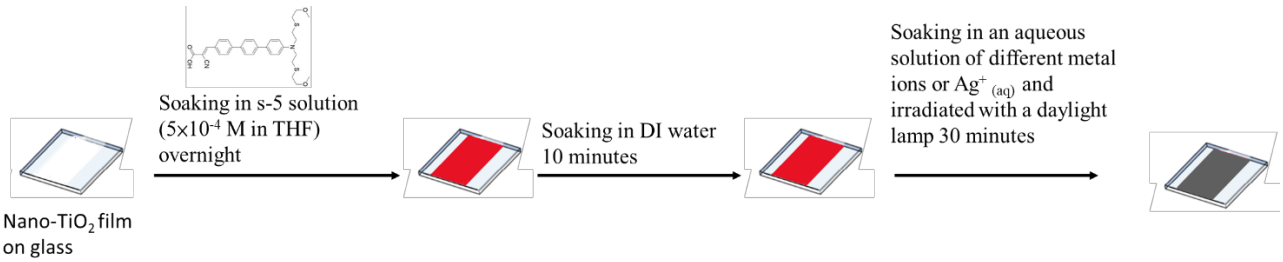
Silver-containing materials are extensively utilized in the electronics industry and antibacterial applications. Although a small amount of silver exposure is generally considered safe for human health, the World Health Organization stipulates that the level of silver ions in drinking water cannot exceed 0.94 μM. Excessive exposure to silver ions can result in silver poisoning, which may adversely affect the mucous membranes of the eyes and the skin. Traditional detection methods, such as atomic absorption spectroscopy and atomic emission spectroscopy, are commonly employed for measuring silver levels; however, these instruments are relatively costly and necessitate skilled personnel for operation. In this study, we have developed a sensor (**s-5)** that can be utilized in a liquid detection environment with THF: H_2O volume ratio of 1:19. In addition, s-5 as dye can be adsorbed on a nano-TiO2 film and irradiated with a daylight lamp for 30 minutes to detect silver ions in the water through the color change caused by the reduction of silver ions to generate silver atoms. In the liquid detection mode, **s-5** demonstrates good selectivity and anti-interference capabilities, with a detection limit of 1.98 μM, and it operates effectively within a pH range of 5 to 10. Additionally, it has successfully passed tests using real water samples. Another system: the solid film also exhibits commendable selectivity. Although measurements obtained through absorption spectroscopy indicate a detection limit of 50.9 μM. Further detailed tests are currently in progress.



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PD-06

Heteroaromatic Swapping in Aromatic Ketones

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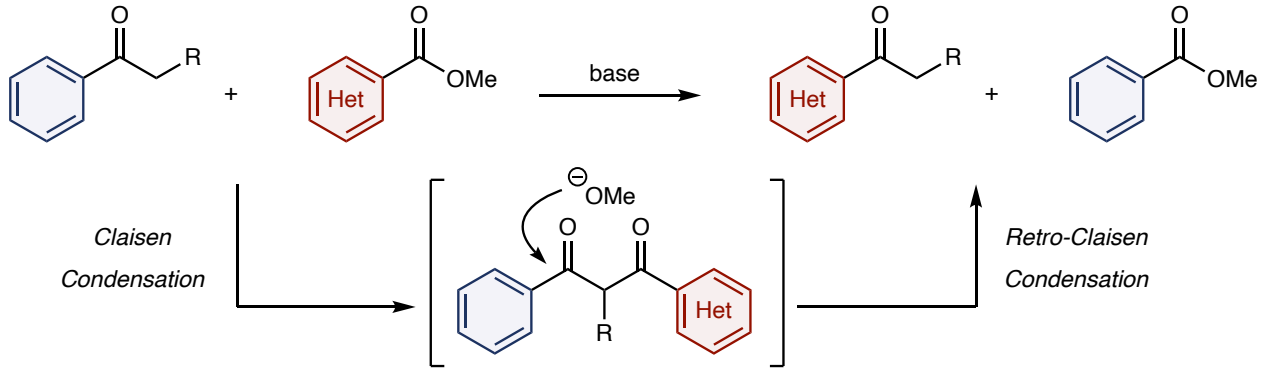
The modification of aromatic rings to heteroaromatic rings is a widely employed strategy in medicinal chemistry for adjusting lipophilicity and enhancing metabolic stability. However, achieving a one-step, comprehensive conversion of aromatic rings to various heteroaromatic rings—termed "Heteroaromatic Swapping"—remains a significant challenge, even with state-of-the-art technologies like Skeletal Editing[1] and transition-metal-catalyzed aromatic ring exchange[2], which often face difficulties with substrate generality. Here, we demonstrate an efficient approach to Heteroaromatic Swapping through a reaction between heteroaryl esters and aromatic ketones under basic conditions. This transformation, proceeding via a Claisen/retro-Claisen mechanism[3], allows for the replacement of aromatic rings with heteroaromatic rings across a broad range of substrates. Importantly, this method overcomes the challenges posed by contemporary techniques, successfully converting many bioactive aromatic ketones into their heteroaromatic analogs. The results extend the possibilities for molecular editing and offer a versatile tool for the synthesis of bioactive compounds with potentially enhanced pharmacokinetic properties.



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PD-07

Natural Product-Inspired Molecular Photoswitch

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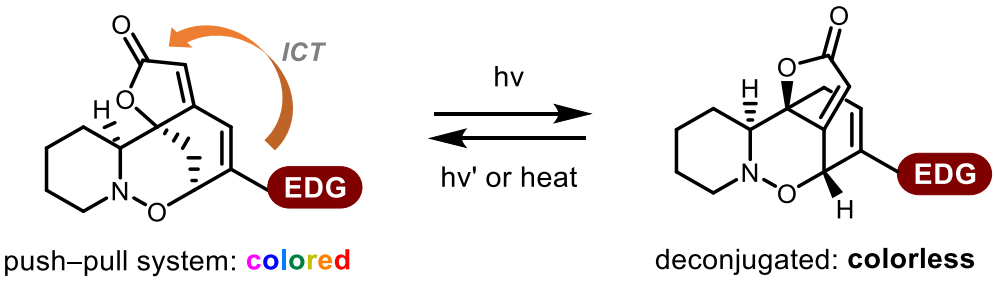
Natural product synthesis has long been pivotal in drug discovery, providing key principles and compounds that have driven the development of new therapeutics. In this presentation, we show that the synthetic exploration of natural products can also extend beyond the realm of pharmaceuticals. We reveal how this approach can lead to the invention of innovative molecular photoswitches.
By leveraging the higher triplet energy of contra-thermodynamic securinine B relative to the more thermodynamically stable secu'amamine D, we achieved a highly efficient photochemical transformation of secu'amamine D to securinine B. Conversely, securinine B was converted back to secu'amamine D under conditions that favor thermodynamic equilibrium. Building on these novel reactivities, we developed a new photoswitching platform by integrating a push-pull system into the securinega framework. This novel photoswitching system was applied into the development of unprecedented photochromic materials and photoresponsive chiral dopants for liquid crystals.



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PD-08

Iriomoteolide-1a and -1b: Structure Elucidation by Integrating NMR Spectroscopic Analysis, Theoretical Calculation, and Total Synthesis

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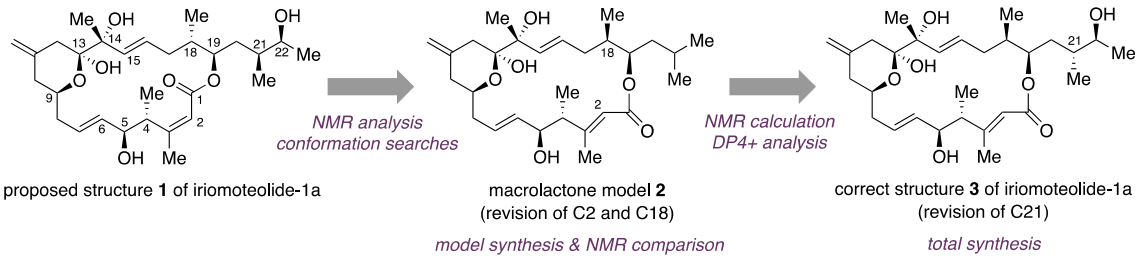
Iriomoteolide-1a (proposed structure **1**) is a cytotoxic macrolide that was isolated by Tsuda from the benthic dinoflagellate *Amphidinium* sp. HYA024 strain, collected off the Iriomote Island, Japan.[1] The gross structure of this natural prouct was established by extensive NMR analysis. The relative configuration was assigned through *J* values and ROESY correlations, and the absolute configuration was determined by modified Mosher method. However, total syntheses of the proposed structure **1**, independently reported by Horne and Ghosh, showed the non-identity of synthetic **1** and natural isolate.[2] While nine additional stereoisomers of **1** were synthesized by Yang, Ghosh, and Dai, all of them did not correspond to natural iriomoteolide-1a.[3]

Aiming at the structure elucidation of irimoteolide-1a, we deployed an integrated strategy that involves NMR spectroscopic analysis, theoretical calculation, and total synthesis. Our study began with re-examination of authentic 2D-NOESY spectrum of the natural product, focusing on the macrocyclic skeleton. With the aid of molecular mechanics conformational searches on possible stereoisomers, we envisaged that macrolactone model **2**, configurationally revised at C2 and C18, should satisfy important NOE correlations observed for natural iriomoteolide-1a. In fact, the NMR spectroscopic data of synthetic **2** were in excellent agreement with those of the macrocyclic skeleton of the natural product. Meanwhile, GIAO NMR calculation/DP4+ analysis focusing on the side chain strongly suggested that the C21 configuration should be revised to be *R*. Finally, the correct structure **3** of iriomoteolide-1a was established in an unambiguous manner through total synthesis. The structure of iriomoteolide-1b, a natural congener, was also established through our integrated strategy.



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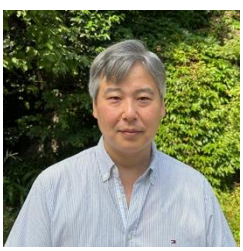

Haruhiko Fuwa (不破春彦). The University of Tokyo (Ph.D., 2002). Tohoku University (Assistant Professor, 2006; Associate Professor, 2009). Chuo University (Professor, 2017; Department Chair, 2021). Research field: Natural Products Chemistry; Total Synthesis; Structure Elucidation; Structure–Activity Relationship.

PD-09

Synthetic Polyproline Nanoscaffolds for Manipulation of Multivalent Carbohydrate Interactions

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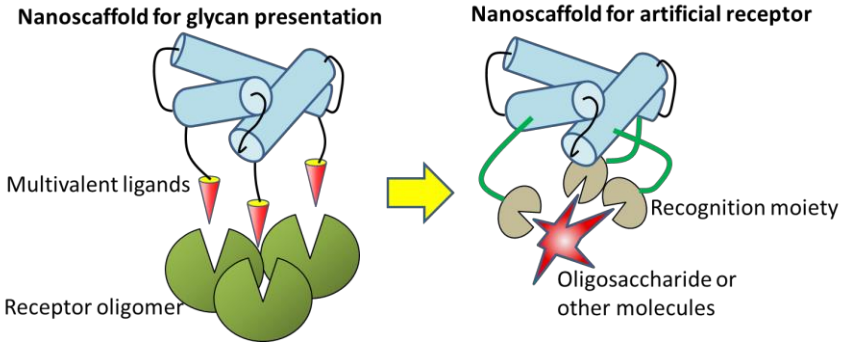
With the versatility of organic synthesis and the defined structure of biomolecules, precisely controlled synthetic nano-objects can be created. We assembled multiple polyproline helices into a nanosized-macrocycle and precisely controlled the sites for carbohydrate ligand conjugation by the sequence of peptides.[1] This tool allowed us to control multiple ligand presentation in a desired pattern at nanoscale for selective multivalent interaction with protein oligomers. We have demonstrated significant selectivity in binding toward DC-SIGN over Langerin by controlling the presentation of multiple oligomannose, which is a ligand for both receptors involved in HIV infection.[2] This strategy can be regarded as a general solution to the cross-reactivity problem in carbohydrate recognition.

In addition to control carbohydrate ligand presentation for selective protein receptor binding, this strategy of carbohydrate recognition can be reversed. The dimension of the synthetic scaffold at few nanometers[3] affords enough space to reach different hexose units within oligosaccharides. The capability to control conjugation sites also allowed us to introduce carbohydrate-binding moieties to the desired sites for individual hexose units. With these features, we turned the polyproline macrocyclic scaffold into a potential artificial receptor for oligosaccharides.



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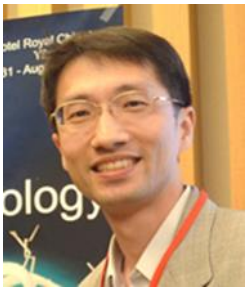

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Field of research: Carbohydrate chemistry, Peptide science, Chemical biology, Nanotechnology

PD-10

Atroposelective Total Synthesis of Cihunamide B

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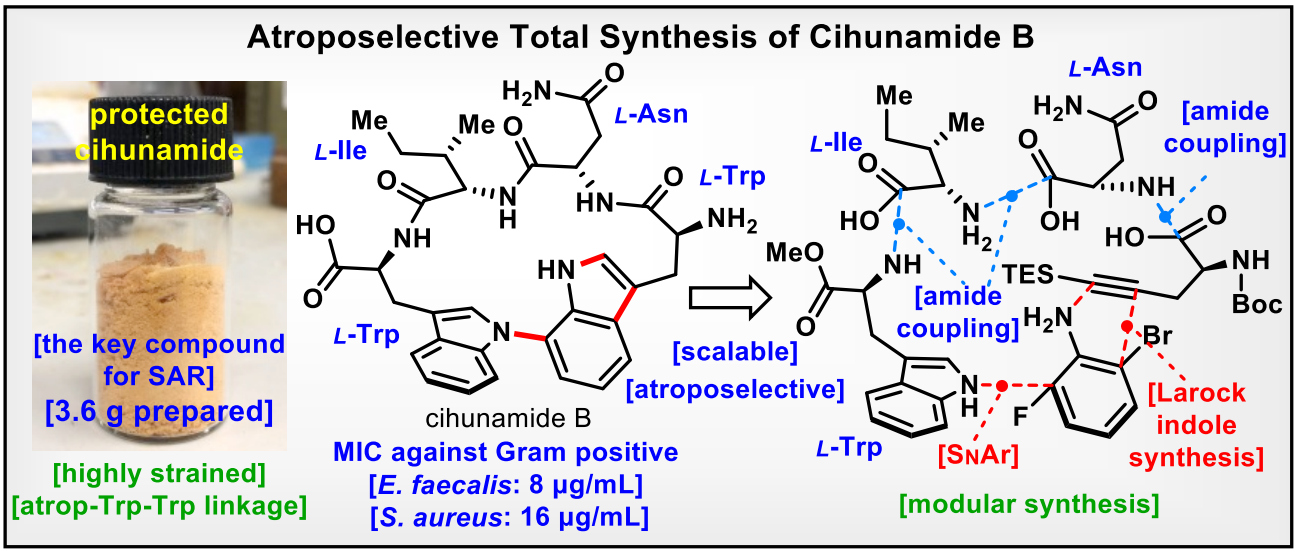
Cihunamide B is a cyclic peptide recently isolated from deep-sea marine sediments near Jeju Island, South Korea. In terms of structure, it possesses a novel architecture featuring an atropisomeric Trp-Trp linkage within a highly strained fused macrocyclic peptide composed of four natural amino acids. The atropisomeric configurations of the cihunamides were characterized using electronic circular dichroism (ECD) spectra and DFT calculations. Regarding its biological effects, it exhibits antibacterial properties (MIC = 8-16 μg/mL) against Gram-positive bacteria such as *Enterococcus faecalis* and *Staphylococcus aureus*, suggesting it is a potential candidate for antibiotic drug. Nevertheless, due to the fact that only 1.2 mg of cihunamide B has been extracted from natural sources, the specifics of its mechanism in bioactivity remain elusive. In this work, the atroposelective and scalable total synthesis of cihunamide B is reported[1].



Reference

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[Field of research] Total Synthesis

PD-11

Electrochemical transformation of oximes and hydrazones into 5- and 7-membered heterocycles and their further modifications

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In recent years, the synthetic community has focused on the employment of sustainable green synthetic procedure and techniques in chemical transformations. In this direction electrochemical synthesis has afforded new opportunities for constructing novel heterocyclic compounds of pharmaceutical interest. Synthetic electrochemistry utilizes readily available electrical current as a sustainable and safe redox reagent, thus avoiding the demand for stoichiometric amounts of chemical oxidants or reducing agents, toxic bases or even catalysts and has attracted increasing attention.

Our study initially focused on the selective electrochemical synthesis of 1H-indazoles and their N-oxide using oxime.[1] Building on this, we successfully synthesized N-aminoindazolium ylides from hydrazone.[2] After achieving the construction of 5-membered rings, we shifted our interest to the formation of larger rings, considering the potential for multifunctionalization of alkenes. While the electrochemical synthesis of 5- and 6-membered rings has been reported in the literature, the electrochemical construction of an oxazepin moiety remains an unachieved and challenging endeavor. Despite significant progress, most methods for synthesizing this scaffold require transition metals, high temperatures, and stoichiometric amounts of sacrificial oxidants. Previous studies primarily focused on using alkenyl oximes or esters to produce 5- and 6-membered oxazacycles through metal-catalyzed or photocatalytic approaches. In line with our commitment to eco-friendly protocols, we present an electricity-driven method for rapid alkene difunctionalization using tosyl hydrazide[3] and alkenyl oximes,[4] yielding tetrahydro-1,2-oxazepines with excellent diastereoselectivity and good yields.[2] This newly developed protocol relies solely on electricity as a green reagent, offering high atom economy, a broad substrate scope, and efficient scalability.

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Jin Kyoon Park (박진균). Seoul National University (BS. 1996; MS. 1998; Ph.D. 2003). LG Chem (OLED R&D, 2004-2009). Florida State University (Visiting Scholar, 2008; Postdoc 2008-2012). Pusan National University (2012-present). [Field of research] Organic Chemistry, Continuous Flow Chemistry, Electro-organic Chemistry.

PD-12

Judicious Molecular Design of 5H-Dithieno[3,2-b:2′,3′-d]pyran-based Hole-Transporting Materials for Highly Efficient and Stable Perovskite Solar Cells

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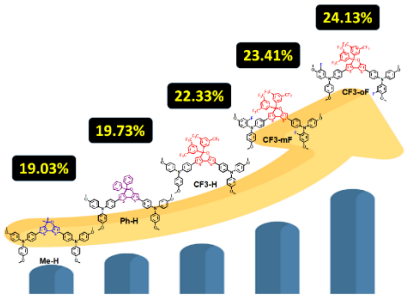
The structural modification of hole-transporting materials (HTMs) is an effective strategy for enhancing the photovoltaic performance in perovskite solar cells (PSCs). Herein, we designed and synthesized a series of dithienopyran (DTP)-based HTMs (**Me-H**, **Ph-H**, **CF3-H**, **CF3-mF**, and **CF3-oF**) by substituting different functional group on the DTP unit and used them in fabricating PSCs. In comparing with **Me-H** having two methyl substituents on the dithienopyrano ring, the **Ph-H** having two phenyl substituents on the ring exhibits higher PCEs. Notably, the incorporation of trifluoromethyl groups in **CF3-H** endows the molecule with larger dipole moment, deeper HOMO energy level, better film morphology, closer molecular stacking, more efficient defect-passivation, enhanced hydrophobicity, and better photovoltaic performance when compared with the **Ph-H** counterpart. Furthermore, the HTMs of **CF3-mF** and **CF3-oF**, which feature fluorine-substituted triphenylamine, demonstrated excellent film-forming properties, more suitable energy levels, enhanced charge mobility, and improved passivation of the buried interface between HTMs and perovskite. As a result, PSCs employing **CF3-mF** and **CF3-oF** gave impressive PCE of 23.41% and 24.13%, respectively. In addition, the large-area (1.00 cm2) PSCs based on **CF3-oF** achieved a PCE of 22.31%. Moreover, the PSCs devices with **CF3** series HTMs exhibited excellent long-term stability under different conditions.



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PD-13

Toward Concise Total Synthesis of Complex Alkaloids

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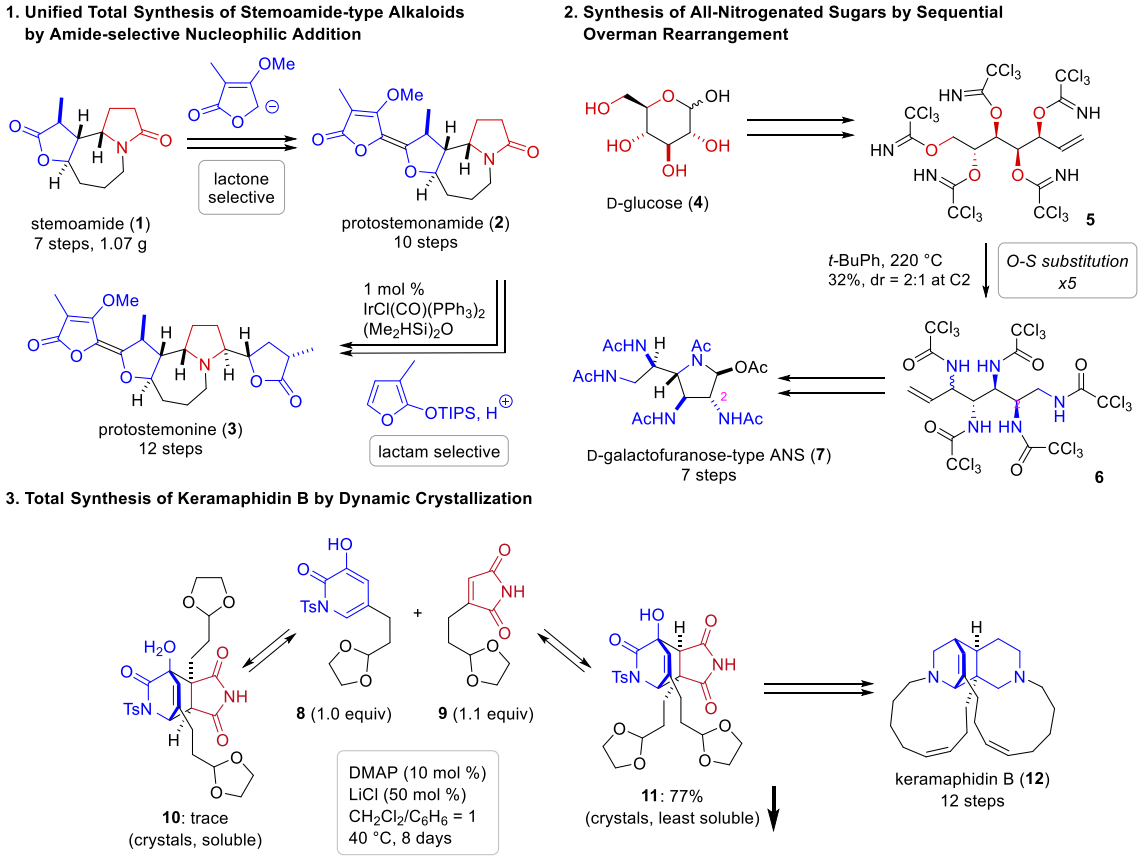
Modern organic synthesis requires compounds of ever-increasing complexity, especially for drug discovery. Our research group has been exploring practical methods for the application to the total synthesis of complex alkaloids. In this presentation, I will show you three topics; 1) total synthesis of stemoamide-type alkaloids,[2] 2) synthesis of all-nitrogenated sugars by sequential Overman rearrangement,[2] and 3) total synthesis of keramaphidin B by dynamic crystallization.[3]



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PD-14

Nickel-Catalyzed Denitrogenative Cyclization of Nitrile-Containing 1,2,3-Benzotriazin-4(3*H*)-ones for the Synthesis of Polycyclic Quinazolinone Alkaloids

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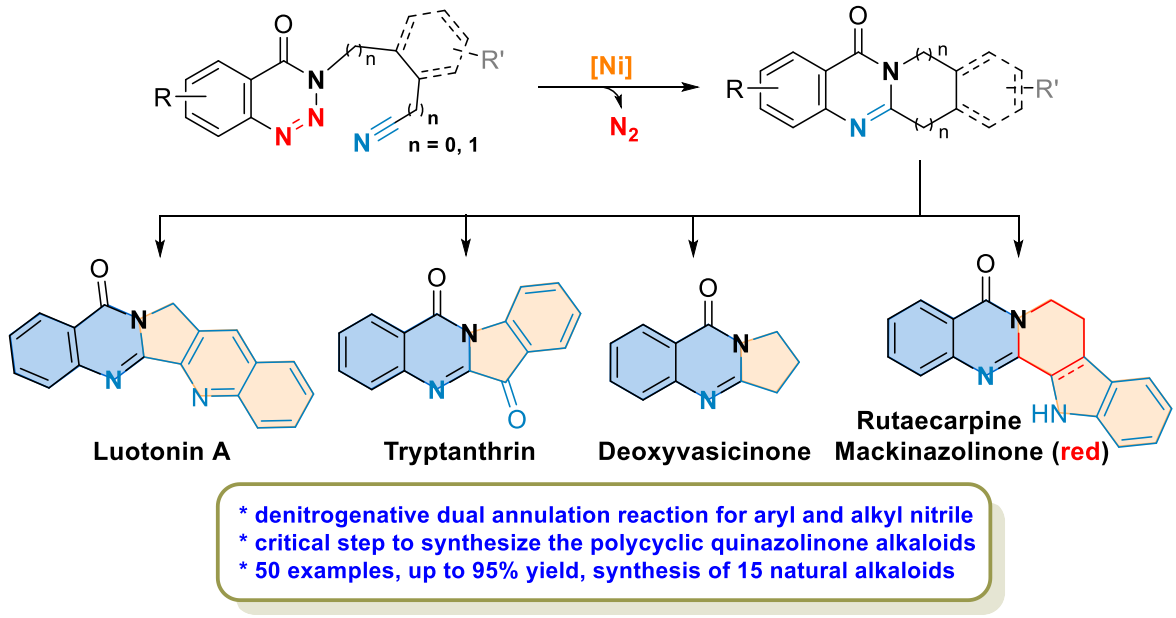
The following Scheme (Scheme 1) indicates the nickel-catalyzed intramolecular denitrogenative annulation reaction of the nitrile-containing 1,2,3-benzotriazine-4(*3H*)-ones to provide various polycyclic quinazolinones. This catalytic reaction demonstrates the tolerance of a wide diversity of substituents and good to excellent yields in most cases. In addition, it can be applied as the critical step to synthesize most of the noted polycyclic quinazolinone alkaloids. We also revealed our synthetic work of fifteen relevant alkaloids to demonstrate the reaction capacity.



Scheme 1. Ni-catalyzed denitrogenative dual annulation

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Jen-Chieh Hsieh (謝仁傑). National Tsing Hua University (Ph.D, 2006). Department of Chemistry, Tamkang University (Assistant Prof., 2010; Associate Prof., 2013; Prf., 2017). Research field: Synthesis of natural alkaloids, transition-metal catalysis, radical reactions.

PD-15

Mono-Acylation of Diols Enabled by Resin Catalysis

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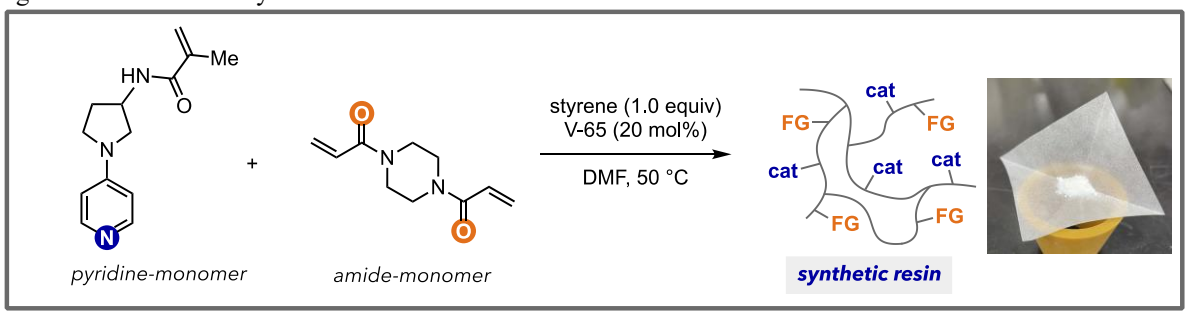
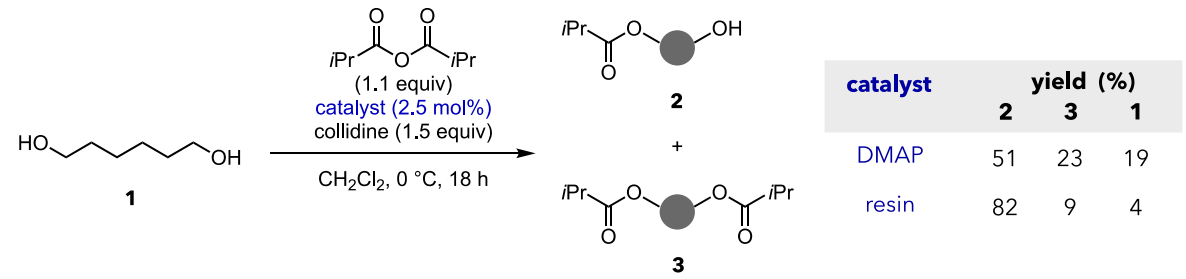
Controlling the selectivity of chemical reactions stands as a cornerstone in synthetic organic chemistry. In contrast to the significant advances in the field of enantioselective catalysis, there remaines a conspicuous lack of catalysts for substrate-selective transformations, where a catalyst distinguishes electronically and sterically similar functional groups to selectively modify a specific substrate within a reaction mixture.[1] Given that enzymes, composed of amino acid monomers, exhibit exquisite selectivity by harnessing the cooperativity of multiple functional groups within a catalytically active site, we questioned whether synthetic resins that are prepared from simple monomers through radical polymerization, could function as catalysts that rival the state-of-the-art small-molecule catalysts for selective transformations. As a testing ground of our hypothesis, we elected to explore the mono-acylation of diols—a seemingly simple yet intricately challenging transformation in organic synthesis due to competing over-acylation of the resultant mono-acylation products.[2] Indeed, treatment of diol **1** with 1.1 equivalents of isobutyric anhydride in the presence of 1.5 equivalents of collidine and 2.5 mol% of 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 yielded mono-acylation product **2** in modest yield (51%), along with a substantial amount of diacylated product **3** (23%) and recovered starting material **1** (19%). Gratifyingly, synthetic resin, prepared from pyridine-monomer, styrene and amide-monomer through conventional radical polymerization employing 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65) as a radical initiator exhibited excellent selectivity, providing mono-acylation product **2** in 82%, along with diacylated product **3** in 9%. In the presentation, detailed studies and further investigations into resin catalysis will be discussed.





catalyst	yield (%) 2	3	1
DMAP	51	23	19
resin	82	9	4

Reference

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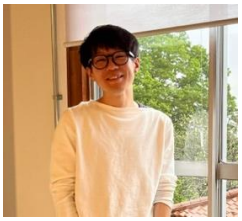

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PD-16

Molecular Engineering of Functional Materials for Photocatalytic Hydrogen Generation

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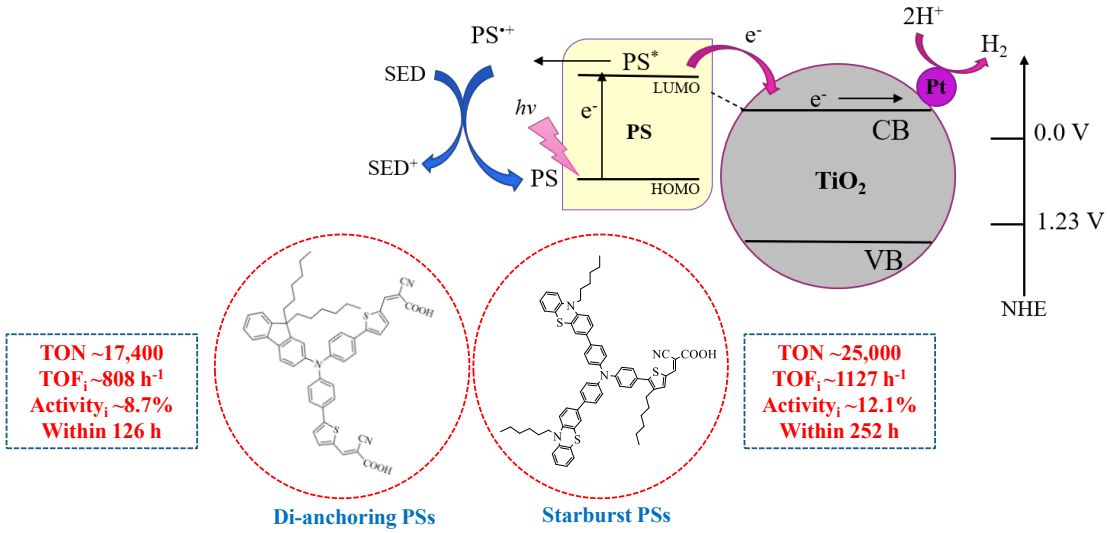
Since the quality of our lives largely depends on the availability of energy, the energy crisis problem will continue to pose a significant threat in the foreseeable future. Energy remains one of the greatest challenges facing the world. Therefore, it is of utmost importance to explore alternative forms of renewable energy sources. One crucial area in this pursuit is the transformation of solar light into chemical fuels, particularly hydrogen, through solar-driven photocatalytic reactions. This field has witnessed tremendous activity, with the development of functional organic molecules as photosensitizers to capture solar light. By fine-tuning the chemical structures of these materials, such as utilizing the starburst and/or di-anchoring structures, their chemical and physical properties can be easily adjusted to create the most optimal materials for solar-to-hydrogen applications. This poster is to provide a perspective on this field, focusing on the fundamental structural design concepts of organic photosensitizers and their current applications.



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PD-17

Advancing First-row Transition Metal Catalysis with Phosphine-Stabilized Dicarbon Ligands

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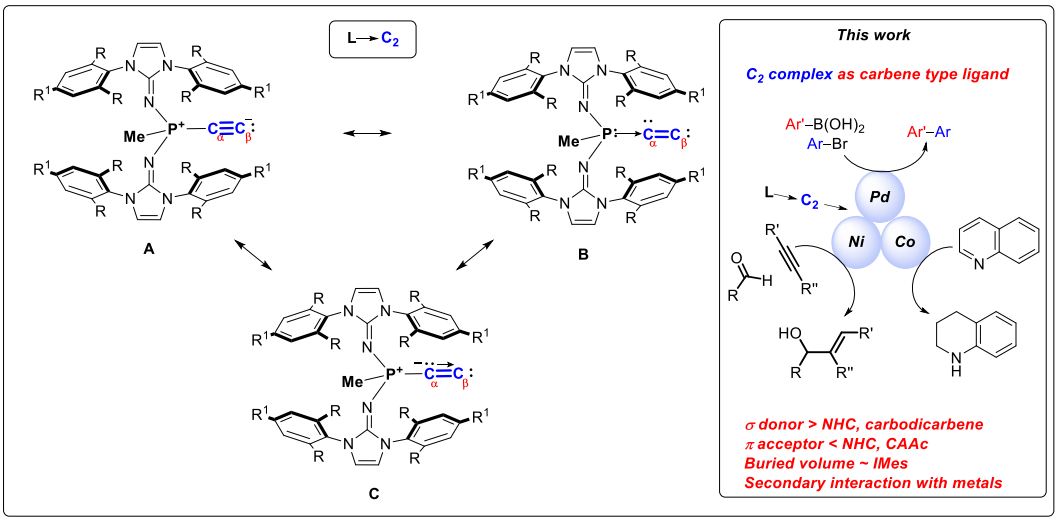
The low abundance of precious metals among second- and third-row transition element series has led to significant consumption throughout the modern era. Considering irreversible resource depletion, synthetic chemists have shifted their focus towards developing well-defined molecular catalysts based on first-row transition metals, which possess 3d-subshells and are far more earth-abundant. Phosphine-stabilized dicarbon (PDC) presents a new carbene-like ligand class that features strong σ-donor properties and weak π-acceptor characteristics. Previous work demonstrated its potential as an innovative and promising ligand in the field of transition metal catalysis. This talk will explore the catalytic applications of these unique ligands in first-row metal catalysis. By controlling the substituents on phosphine, we can exploit active first-row metal catalysts' distinct electronic and steric properties to enhance their catalytic performance significantly. This talk will also focus on their role in facilitating crucial organic transformations, particularly hydroboration and transfer hydrogenation. Additionally, we will highlight the potential of these ligands to improve catalyst efficiency, selectivity, and stability, offering valuable insights into their applicability in sustainable and cost-effective catalytic processes.



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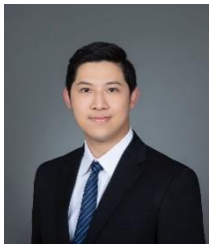

Tsz-Fai Leung (子輝 梁). The Hong Kong University of Science and Technology (Ph. D., 2017); Institute of Chemistry, Academia Sinica (Postdoctoral researcher, 2018); Ruhr-Universität Bochum (Postdoctoral researcher, 2022); National Sun Yat-sen University (Assistant Professor, 2022).

Research field: Ligand design, organometallic chemistry, main group chemistry, Catalysis.

PD-18

Development of Convoluted Polymeric Palladium Catalysts and Polymeric Auxiliary Materials for Continuous-Flow Suzuki-Miyaura Coupling

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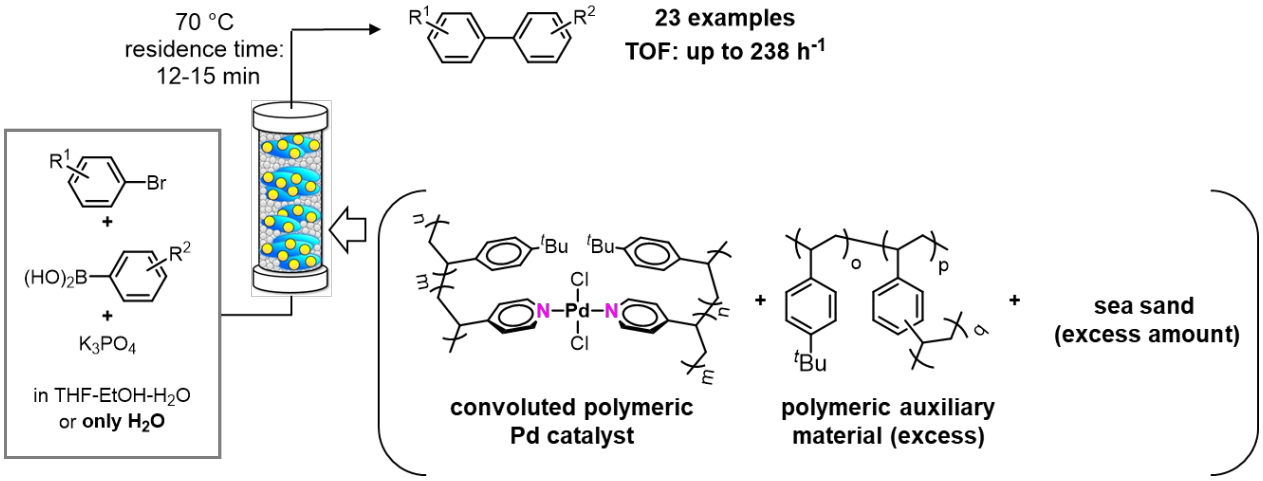
We developed a series of highly active and stable heterogeneous continuous-flow reaction system using polymeric palladium catalysts and crosslinked polymeric auxiliary materials for Suzuki-Miyaura coupling reaction. [1] The catalysts were prepared from linear copolymers of 4-vinylpyridine and 4-*tert*-butylstyrene with palladium (II) species via the previously established molecular convolution methodology. [2] A column packed-bed flow reactor which packed mixture of the convoluted polymeric palladium catalyst, the crosslinked polymeric auxiliary material and sea sand was applied to continuous-flow Suzuki-Miyaura reaction of aryl bromides with aryl boronic acids. The reaction proceeded to give the corresponding biaryl products such as liquid-crystalline materials, organic electroluminescent compounds and pharmaceuticals without significant deactivation of the catalyst. Furthermore, the synthesis of pharmaceuticals (Fenbufen and Felbinac) was carried out using water as the sole solvent with TOF of up to 238 h^{-1}.



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Aya Ohno (大野　綾).

RIKEN Center for Sustainable Resource Science, Green Nanocatalysis Research Team, Technical staff (from 2010)

Research field: Organic Chemistry, Heterogeneous Catalysis

PD-19

Sultines as *o*-Quinodimethane Precursors in hetero-Diels–Alder Reactions

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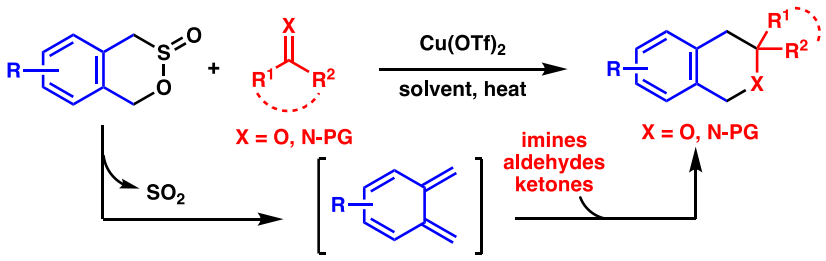
Tetrahydroisoquinolines and isochromans are important building blocks in organic synthesis as they are prevalent scaffolds in natural products and pharmaceuticals. Accordingly, the development of novel and efficient synthetic strategies toward these motifs has continuously garnered interest from the synthetic organic chemistry community, both in academia and industry. Recently, we have been exploring the possibility of employing sultines as *o*-quinodimethane precursors in hetero-Diels–Alder (DA) reactions. Through the extrusion of SO_2 under relatively mild conditions, the transient *o*-quinodimethanes generated in situ were successfully trapped in aza- and oxa-DA reactions with imines and activated carbonyls, respectively. Critical to the success of these reactions is the addition of $Cu(OTf)_2$, which promotes the desired reactivity while also suppressing the competing sulfolene byproduct formation. These developed protocols exhibit broad functional group compatibility, offering complementary access to functionalized tetrahydroisoquinolines and isochromans.



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Chulabhorn Research Institute (Research Scientist, 2021–2024)
Chulabhorn Research Institute (Senior Research Scientist I, 2024-present).
[Field of research] Methodology Development, Total Synthesis, Medicinal Chemistry, and Catalysis.

PD-20

Divergent Total Synthesis of Discorhabdin Alkaloids

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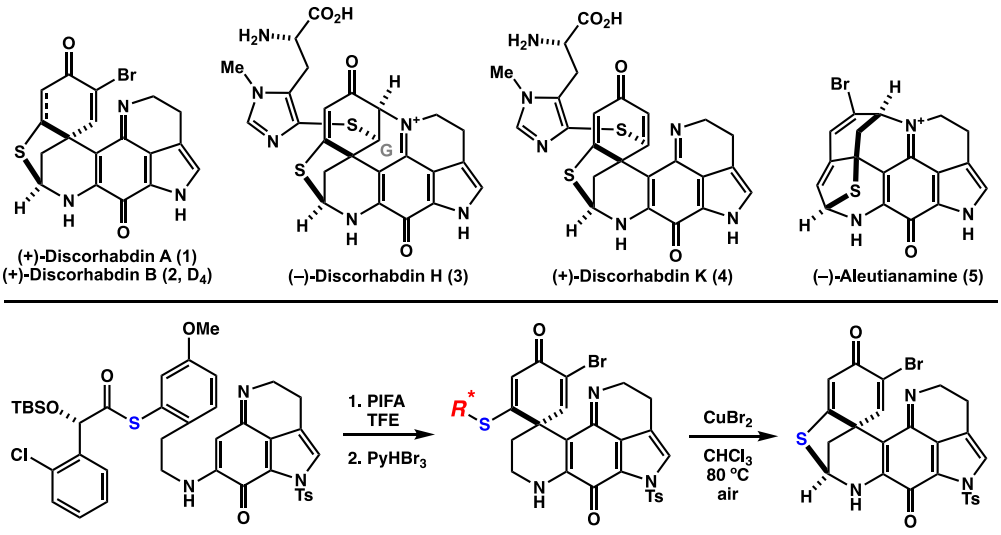
Discorhabdins are marine alkaloids consisting of more than 50 structurally divergent congeners possessing a pentacyclic common skeleton containing of a pyrroloiminoquinone and an aza-spirocyclic dienone moiety. Due to the intriguing structure and rich biological activities, numerous synthetic studies have been reported so far. However, none of the major congeners having a sulfur-bridged F-ring has been reported except for the total synthesis of (+)-discorhabdin A (**1**) by Kita and co-workers. In this research, we accomplished first asymmetric total syntheses of sulfur-bridged discorhabdins, discorhabdin B (**2**), H (**3**), and K (**4**), and aleutianamine (**5**) featuring hypervalent iodine reagent-mediated diastereoselective oxidative spirodienone formation using chiral thiol ester derivative and $CuBr_2$-catalyzed deacylation/oxidative cyclization/*N,S*-acetalization cascade to form the F-ring to provide the *N*-Ts-discorhabdin B. The total syntheses of (–)-discorhabdin H (**3**) and (+)-K (**4**) were achieved via cascade reactions initiated by thia-Michael addition of L-ovothiol A to (+)-*N*-Ts-discorhabdin B. In addition, related congeners were synthesized as well by utilization of the hetero-Michael addition strategy. Finally, the first total synthesis of (–)-aleutianamine (**5**) was also achieved via a skeletal rearrangement triggered by the Luche reduction of (+)-*N*-Ts-discorhabdin B.



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Hidetoshi Tokuyama (徳山 英利). Tokyo Institute of Technology (Ph.D., 1994). University of Pennsylvania (Post-doctoral fellow, 1994-1995), The University of Tokyo (Assist. Prof., Lecturer, Assoc. Prof., 1995-2006). Tohoku University (Professor 2006-present). [Field of research] Synthetic Organic Chemistry, Total Synthesis of Natural Products.

PD-21

Vanadyl Species-Catalyzed, Asymmetric Radical Type 1,2-Oxyphosphinonylation and Sulfenylation to Styrenes

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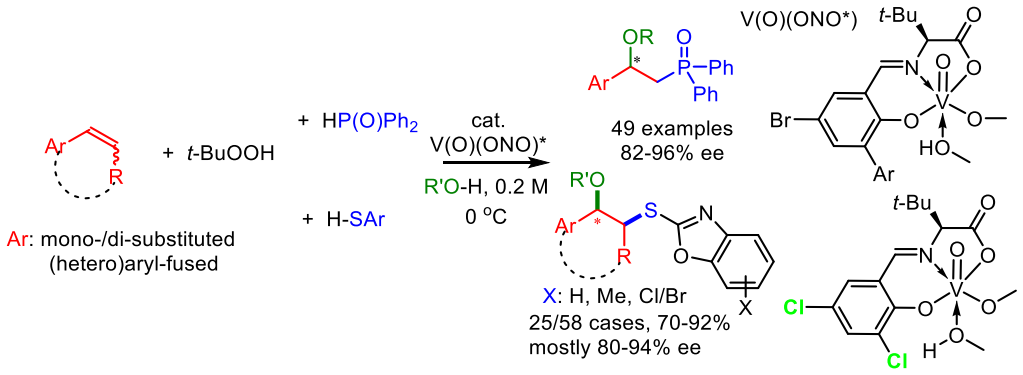
A new strategy of directly introducing both CF_3/P(O)Ph_2/SAr and hydroxyl/aminohydroxyl synthon groups across alkenes with high enantioselectivities by redox-active, chiral VO catalysts in alcohol solvents at room temperature has been developed. Unprecedented, four-component couplings (two molecules of olefin, CF_3 radical, and NOPI (*N*-oxyphthalimide)) can thus be achieved. DFT calculations by Prof. Seiji Mori's group confirmed unusual hydrogen bonding and non-classical weak interactions, including VO and electron-rich fluorine atoms, pi/pi-interactions between phenyl groups. It was found that the C3-substituent on the salicylidene ligand controls the enantioselectivity fashion. The current VO species-mediated catalysis significantly opens a new entry for applying olefins (asymmetric) cross-coupling applications to olefins with unique niches over copper and iron catalysis because of their conceptually different operating mechanisms. Several 2-and 1-substituted, 3-hydroxy-1,3-quinazolin(di)ones were also utilized as radical trapping agents in asymmetric 1,2-oxytrifluoromethylation of styrenes catalyzed by chiral vanadyl methoxide complexes. Further asymmetric 1,2-oxyphosphinoylation and 1,2-oxysulfenylation of styrenes as well as the corresponding intramolecular variants have been successfully established with enantioselectivities of up to 96% ee.



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Chien-Tien Chen (陳建添) PhD Chemistry from University of Illinois at Urbana-Champaign in 1994; Postdoctoral Research at the Scripps Research Institute in 1995; Associate Professor National Taiwan Noraml University 08/1995-01/2000); Full/Research Chair Professor National Taiwan Noraml University 08/2000-01/2010); Full/Distinguished Professor National Tsing Hua University 02/2010-current).
Research Field: Asymmetric Catalysis, Radical Cross coupling, Organic Optoelectronic Materials, Self-Assembly, Organometallic Catalysis

PD-22

Multi-Substrate Chiral Screening by ^{19}F NMR

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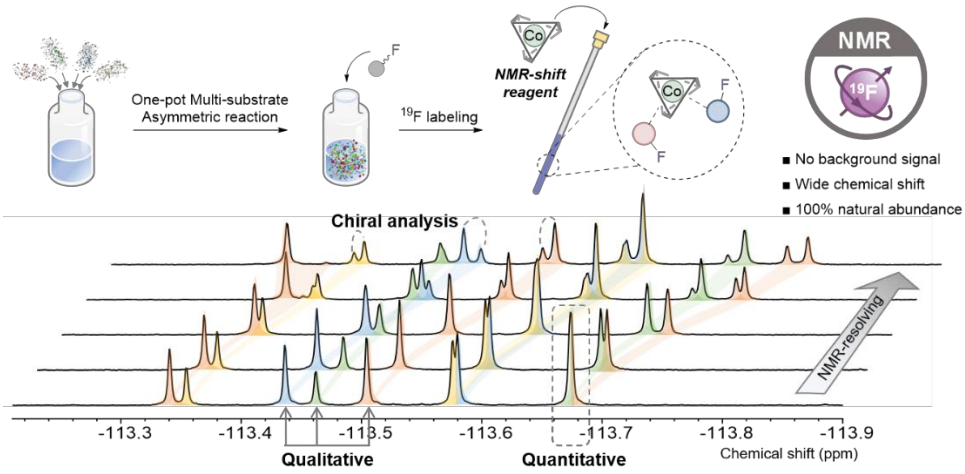
The future of chemistry demands advancements in both synthesis and analysis. Multi-substrate screening, a form of high-throughput screening, represents a promising strategy for achieving multi-dimensional assessment of reaction conditions. However, one of the significant challenges lies in the development of reliable and accurate analytical methods. In this context, Kagan proposed a multi-substrate chiral screening approach, which has primarily been demonstrated using traditional chromatographic techniques. Despite its potential, the method has been limited to the simultaneous analysis of at most 10 compounds.

Recently, Jacobsen reported the use of supercritical fluid chromatography-mass spectrometry (SFC-MS) for the multi-substrate chiral analysis of Pictet-Spengler reactions. In this presentation, we introduce a novel method for multi-substrate chiral analysis of asymmetric reductions using ^{19}F NMR spectroscopy. By employing ^{19}F NMR, we optimized conditions for the chiral screening of 21 starting materials. Through a series of ^{19}F NMR spectra, with the addition of a chiral shift agent, we successfully analyzed the yields and enantiomeric excesses (ees) of all 21 products. To our knowledge, this is the first demonstration of multi-substrate chiral screening using NMR, and we anticipate that this method will find future applications in catalyst development.



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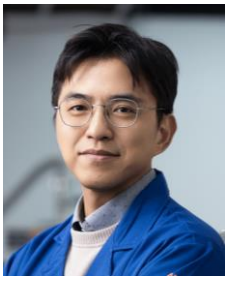

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University of Toronto (Ph.D. 2009). Columbia University (Postdoc 2010)
KAIST (2011-present)
[Field of research] Ligand Design, Catalyst Development, Chiral Aalysis, Bioanalysis.

PD-23

Synthetic studies on a proposed biosynthetic intermediate of tetrodotoxin

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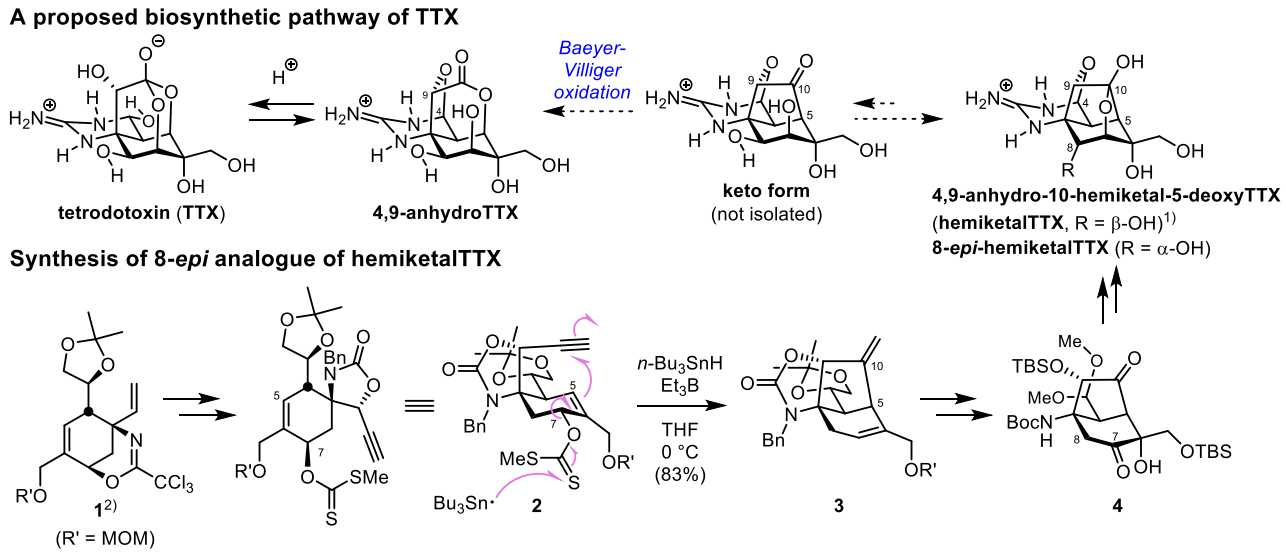
Tetrodotoxin (TTX), a toxic principle of puffer fish intoxication, is one of the most well-kwon natural toxins and found in a wide range of marine and terrestrial animals. Although many TTX-producing microorganisms have been reported, its biosynthetic gene cluster and biosynthetic intermediates have not ever been identified. In 2014, 4,9-anhydro-10-hemiketal-5-deoxytetrodotoxin (hemiketalTTX) was isolated from toxic newt, *Cynops ensicauda popei*, and proposed as a direct biosynthetic precursor of TTX by Baeyer-Villiger type oxidation.[1)] The unique structure of hemiketalTTX and the proposed biosynthetic pathway prompted us to initiate synthetic studies of hemiketalTTX.

Compound **1**,[2)] a common synthetic intermediate of TTX analogues in our laboratory, was converted into methyl xanthate **2** in several steps. Radical cyclization of **2** with Et_3B and *n*-Bu_3SnH smoothly proceeded to give compound **3**, which has the carbon skeleton of hemiketalTTX. Hydrolysis of the cyclic carbamate and oxidation of the cyclohexene ring provided diketone **4**.[3)] Finally, introduction of hydroxy group at C-8 and guanidine moiety afforded 8-*epi* analogue of hemiketalTTX.



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Tadachika Miyasaka (宮坂忠親). Nagoya University (Ph. D., 2021, Assistant professor, 2022).

[Field of research] Organic Chemistry, Total synthesis of natural products.

PD-24

Halogen Atom Transfer-Induced Homolysis of C–F Bonds

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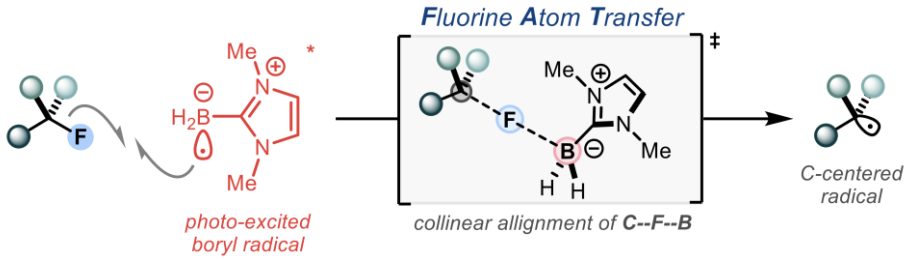
A novel reactivity towards C–F bond functionalization has been developed, which could be designated as fluorine atom transfer (FAT). A photoexcited state of an N-heterocyclic carbene-ligated boryl radical exhibits a transcendent reactivity, capable of activating chemically inert carbon–fluorine bonds through homolysis. Combined experimental and computational studies suggest that the ligated boryl radical species directly abstracts a fluorine atom from the organofluoride substrates to provide valuable carbon-centered radicals.



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Hong Geun Lee (이홍근).

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Assistant and associate professor at Seoul National University (2017-).

[Field of research] Organic synthesis

PD-25

Total Synthesis of Dragmacidins G and H

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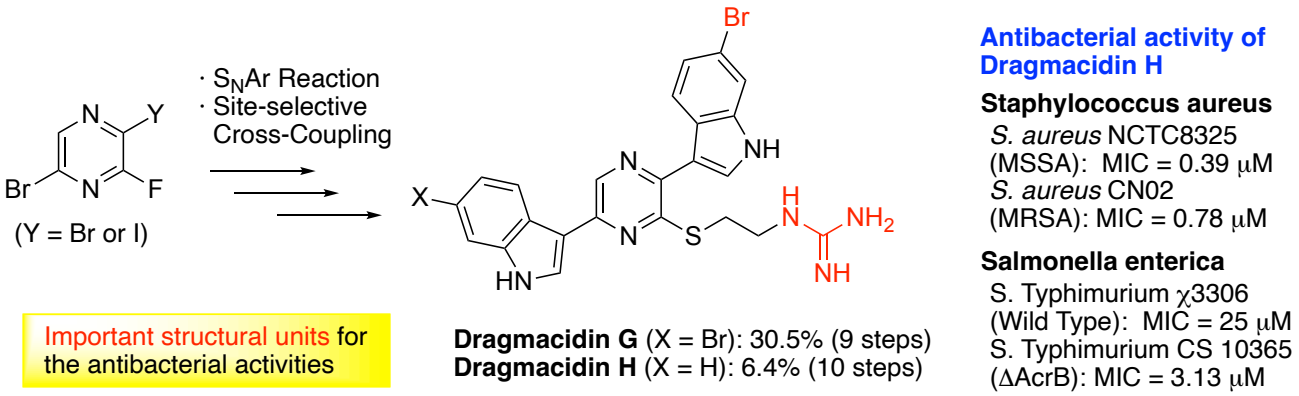
Dragmacidin natural products are marine alkaloids characterized by a bisindole structure in which a 6-bromoindole unit is attached to a nitrogen-containing 6-membered ring such as a piperazine, pyrazinone, or pyrazine ring. To date, 11 derivatives have been isolated from deep-sea sponges, and the biological activities of many of these derivatives have been reported.

Due to the unique structural feature that a sulfide bond exists at the pyrazine 3-position and its antibacterial activity, we were interested in dragmacidins G and H. The total synthesis of dragmacidins G and H was achieved by employing a nucleophilic aromatic substitution and site-selective cross-coupling reactions using appropriately functionalized pyrazines as substrates, with overall yield of 30.5% in 9 steps for dragmacigin G and 6.4% in 10 steps for dragmacigin H. The evaluation of antibacterial activities of dragmacidin G, dragmacidin H, and synthetic analogues against *Staphylococcus aureus* and the efflux pump-deficient *Salmonella* Typhimurium revealed that the presence of a Br group on the indole ring adjacent to the sulfide unit was important for increasing antibacterial activities.



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Tetsuhiro Nemoto was born in Chiba, Japan, in 1976. BS (1999), MS (2001), PhD (2005) from the Graduate School of Pharmaceutical Sciences, the University of Tokyo. Assist. Prof. (2003–), Lecturer (2009–), Assoc. Prof. (2012–) in Prof. Yasumasa Hamada's group at Chiba University. Since 2015, Professor at Chiba University. Research Interest: Asymmetric Synthesis, Catalysis, Organic Synthesis.

PD-26

Total Synthesis of 13-Deoxyserratine

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Serratine-type *Lycopodium* alkaloids have greatly intrigued synthetic chemists since their discovery because of their architectural complexity and potential biological activities. The synthetic challenges of these compact indolizidine molecules feature two contiguous quaternary carbons in the unique 6,5,6,5-tetracyclic structure and a highly oxygenated cyclohexane ring **D**. Over the past two decades, several groups have approached serratine-related molecules through different strategies.[1] Our group has been interested in constructing highly substituted indolizidine and pyrrolizidine structures utilizing 1,3-dipolar cycloaddition reactions. Recently, we have applied the 1,3-dipolar cycloaddition strategy to synthesize the structure of serratine-related alkaloids and accomplished the first asymmetric total synthesis of (–)-13-deoxyserratine.[2,3] Starting from *L*-proline, our group has developed a novel [3,3]-sigmatropic rearrangement and a sequential Cope elimination/1,3-dipolar cycloaddition as key steps to forge the vicinal quaternary stereogenic centers.[2,3] Moreover, ring-closing metathesis of ring **C**, Hosomi-Sakurai reaction in ring **D**, and iridium-catalyzed reductive Strecker reaction in ring **B** as key C-C bond forming reactions completed the total synthesis of (–)-13-deoxyserratine. (Figure 1)

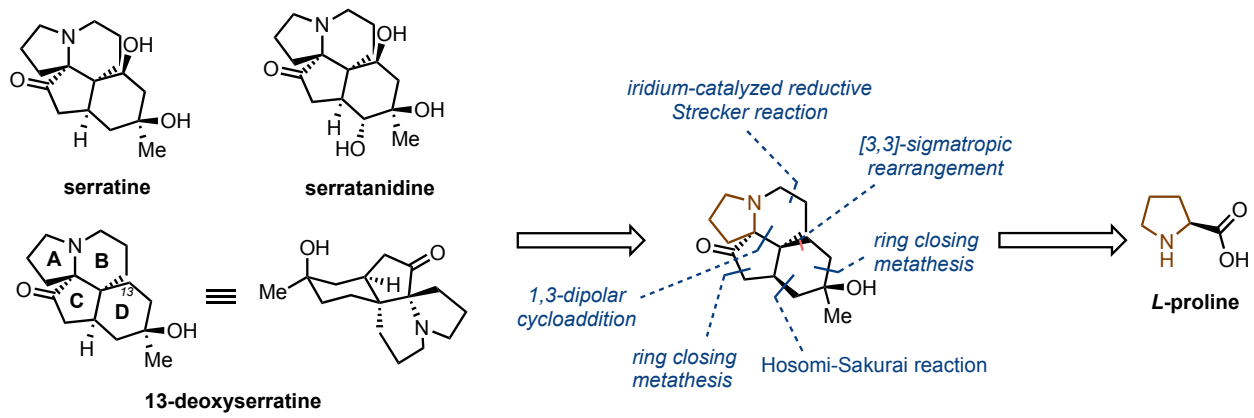

Figure 1.

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Hsiang-Yu Chuang (莊翔宇). National Tsing Hua University (Ph. D., 2017). National Taiwan Normal University (Postdoctoral Fellow, 2018); Vienna University (Postdoctoral Fellow 2019); National Chiayi University (Assistant Professor, 2021-present); Research Field: Organic Chemistry, Natural product Synthesis, Development of New Organic Reactions.

PD-27

Helical-polymer-based Chirality-switchable Phosphoramidite Ligand for Asymmetric Catalysis

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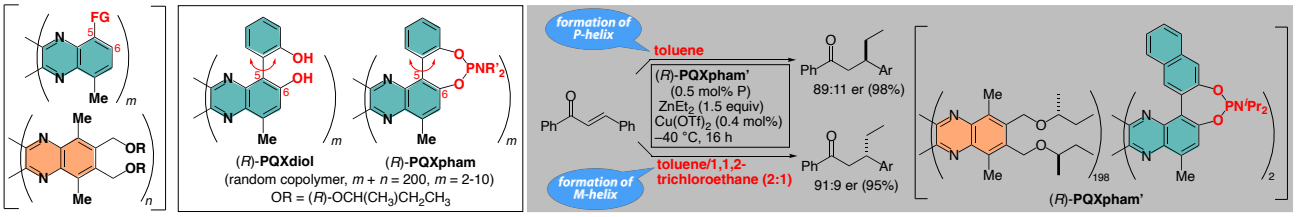
The glorious development of asymmetric catalysis over the past half century has relied on the establishment of various "privileged" chiral structural motifs such as binaphthyl and ferrocenyl which feature their inherent rigid conformations with fixed (non-racemizable) chirality. It seems to be interesting and challenging to bring the concept of "dynamic chirality" into the design of chiral catalysts for enabling fine tuning or even switch of enantioselection in asymmetric catalytic reactions. We have developed a few different classes of chirality-switchable catalysts on the basis of helical macromolecules, poly(quinoxaline-2,3-diyl)s (PQX), whose helical chirality is switchable depending on the solvent effect. A simple design principle has so far been attachment of a planar catalyst group (FG) at the 5-position of the quinoxaline ring with no structural modification at the quinoxaline ring (Fig 1(A)). For further development of the concept of chirality-switchable catalysts, we've pursued the design and synthesis of 2,2'-biphenol-like unit of which chirality is dynamic.

Chiral phosphoramidites ($R_2NP(OR)_2$) have been utilized as versatile chiral ligands in transition-metal-catalyzed asymmetric reactions. In a typical molecular design of the chiral phosphoramidite ligands, C_2-symmetric diol units such as those derived from BINOL are involved as chiral components with further structural tuning provided by the amino group on the phosphorus atom. In our new helical polymer **PQXdiol** (Fig 1(B)), a hydroxy group was introduced at the 6-position of the quinoxaline ring to create 2,2'-biphenol-like structure motif with an *o*-hydroxyphenyl group at the 5-position. PQX-based phosphoramidites, **PQXpham**, was synthesized by post-polymerization functionalization of **PQXdiol** in a single step. Thus synthesized **PQXpham** showed high enantioselectivities in Cu-catalyzed asymmetric conjugate addition of organozinc reagents (Fig 1(C)). Furthermore, by changing the reaction solvent, the enantioselection has been switched with high enantioselectivity. These results show that the solvent-dependent helical macromolecular chirality is transferred to the local chiral conformation at the aryl-quinoxaline axis, leading to the switch of the original chiral reaction environment to its (pseudo)mirror image one. The detail of the structure/selectivity relationship shall be discussed in the presentation.



(A) 1st generation molecular design since 2010 (B) new molecular design of catalyst/ligand units in **PQXdiol** and **PQXpham** (C) Cu-catalyzed asymmetric conjugate addition of Et_2Zn in the presence of (*R*)-**PQXpham'** in different solvents

Figure 1

杉野目道紀. Kyoto University (Ph.D., 1993). Professor in Chemistry (since 2004). Field of research: organometallic chemistry, organic synthesis, and polymer chemistry.

PD-28

Carboxylate-Directed Oxidative Annulation via C(Alkenyl)－H Activation/Double Alkyne Insertion/1,4-Pd Migration: Synthesis of Highly Functionalized Naphthalenes

Cheng-Hao Fu, Manjaly J. Ajitha, Tzu-Yu Hsu, I-Hsuan Sung, Kuo-Wei Huang,* Chih-Ming Chou*
Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung 81148, Taiwan
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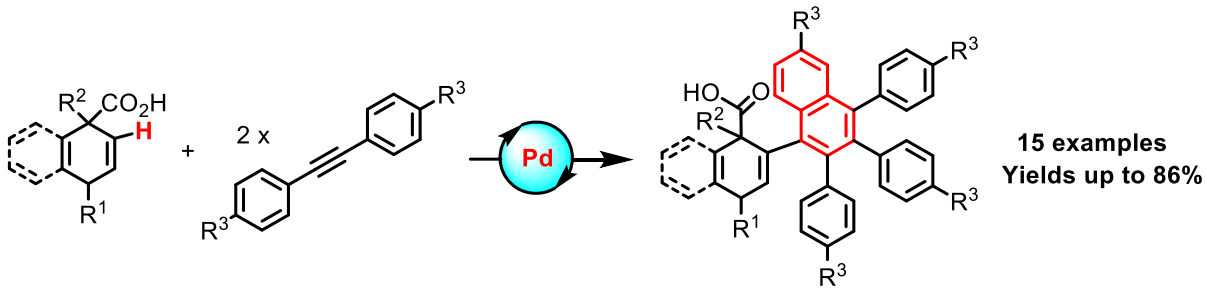
A unique palladium-catalyzed double consecutive C(alkenyl)–H activation/alkyne insertion method utilizing a free carboxylic acid as a directing group in the preparation of highly functionalized naphthalenes is reported. The reaction mechanism involves a sequence of the C (alkenyl)−H activation/alkyne insertion/1,4-palladium migration/reductive elimination steps. The second alkyne insertion occurred at the phenyl ring of the intermediate generated from the first alkyne insertion via 1,4-palladium migration, which is an uncommon case in typical C–H activation/alkyne insertion chemistry, providing highly functionalized naphthalene products. Additionally, the kinetic studies and control experiments as well as theoretical calculations are also investigated to elucidate the reaction mechanism.



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PD-29

Copper(I)-Catalyzed Tandem Reactions of 2'-Substituted 2-(2-Bromophenyl)-*N*-phenylacetamides for the Synthesis of New Tetracyclic Anticancer Heterocycles

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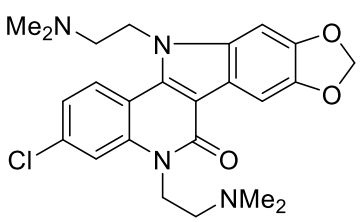
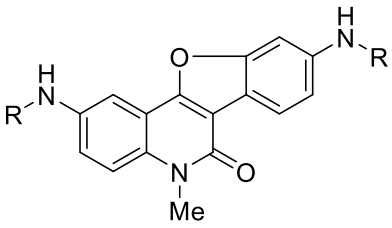
This poster presents two copper(I)-catalyzed tandem reactions of 2'-substituted 2-(2-bromophenyl)-*N*-phenylacetamides for the synthesis of tetracyclic heterocycles as anticancer agents. When the C-2‘ substituent of the substrates was a cyano group, the tandem reaction gave the corresponding 5,11-dihydro-6*H*-indolo[3,2-*c*]quinolin-6-ones in high yields with a good substrate scope. Deriving the indoloquinoliones from the tandem reaction led to 3-chloro-5,12-bis[2-(dimethylamino)ethyl]-5,12-dihydro-6*H*-[1,3]dioxolo[4',5':5,6]indolo[3,2-*c*]quinolin-6-one which exhibited the characteristic DNA topoisomerase-I (Top1) inhibitory mechanism of action with potent in vitro and in vivo anticancer activity. When the C-2‘ substituent of the substrates was a methoxycarbonyl group, the tandem reaction gave a seris of benzofuro[3,2-*c*]quinolinones in high yields. Deriving the formed benzofuroquinolinones gave 2,9-bis{[3-(diethylamino)propyl]amino}-5-methylbenzofuro[3,2-*c*]quinolin-6(5*H*)-one that had good potency to stabilize the G-quadruplex DNA (G4 DNA). At a concentration of 1.0 μM, the melting temperature of G4 DNA was increased by 9.8 °C, which was 4.6-fold than its capability to increase the melting temperature of duplex DNA (2.1 °C).



Top1 inhibitor
GI_{50}: 0.029-0.219 μM
active *in vivo*



G4 DNA stabilizer
ΔT_m 9.8 °C at 1.0 μM for G4
R = $CH_2CH_2NEt_2$

Reference

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PD-30

Synthesis of Mechanically Planar Chiral (MPC) Polyrotaxanes via Artificial Molecular Pump

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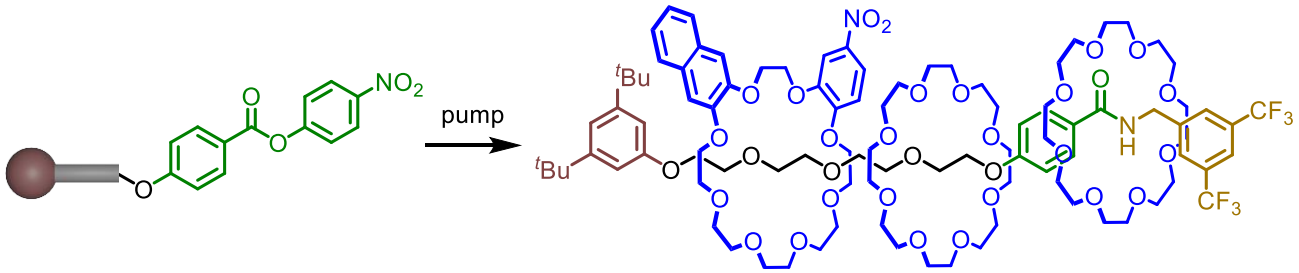
Mechanically planar chiral (MPC) rotaxanes have attracted significant attention due to their unique structures and functions. These mechanically interlocked molecules introduce a new dimension of chirality, distinct from conventional stereochemistry, and pave the way for advanced applications. However, current synthetic methodologies, including kinetic resolution strategies, chiral catalytic methods, and chiral auxiliary synthesis, face substantial challenges in preparing complex MPC rotaxanes, particularly MPC polyrotaxanes.

Here, we report the development of a molecular pump-aided synthesis strategy to efficiently produce MPC polyrotaxanes with multiple asymmetric and/or symmetric macrocycles. The process involves pumping macrocycles onto a collecting axle, introducing a chiral auxiliary to the capping stopper, and separating the resulting stereoisomers. We first obtained enantiopure MPC [2]rotaxanes, which can be prepared and separated on a large scale using standard column chromatography. Additionally, MPC [3]rotaxanes were successfully prepared using an artificial molecular pump.

Given the unique characteristics of MPC rotaxanes, such as enhanced stability, specialized chiral environments, and adjustable intercomponent interactions, this study will not only deepen our understanding of mechanically planar chirality but also facilitate the future access and application of complex MPC architectures.



MPC polyrotaxane synthesis via artificial molecular pump

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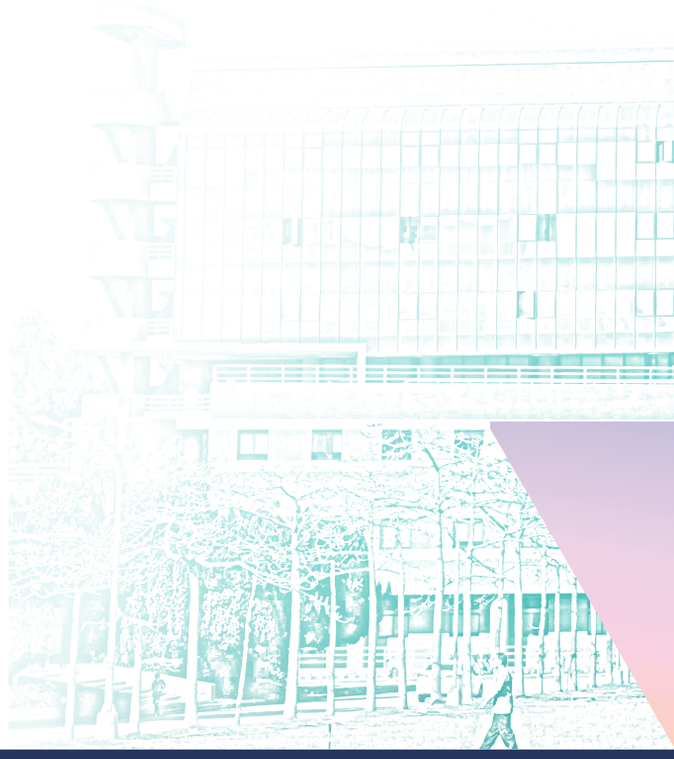

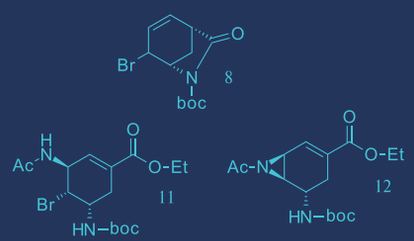
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