The 15th International Conference on Cutting-Edge Organic Chemistry in Asia

Book of Program and Abstracts

Hong Kong

25-26 July 2022

PROGRAME AT A GLANCE

Time	25-Jul	26-Jul
9:00-9:20	Opening Remark	(L16) Cheuk Wai So (SG)
9:20-9:40	(L1) Chuang-Chuang Li (CN)	(L17) Xing-Zhong Shu (CN)
9:40-10:00	(L2) Yusuke Masuda (JP)	(L18) Keisuke Iida (JP)
10:00-10:20	(L3) Zhongxing Huang (HK)	(L19) Sun-Joon Min (KR)
10:20-10:40	Break	Break
10:40-11:00	(L4) Ming Joo Koh (SG)	(L20) Chih-Ming Chou (TW)
11:00-11:20	(L5) Aimi Suhaily Saaidin (ML)	(L21) Yanxing Jia (CN)
11:20-11:40	(L6) Sukwon Hong (KR)	(L22) Makoto Yamashita (JP)
11:40-11:50	Atsuhiko Toyama (Shimadzu, JP)	Fraser White, Hiroyuki Kanda (Rigaku Corporation & JEOL, JP)
11:50-13:00	Poster A	Poster B
13:00-13:20	Lunch	Princess Chulabhorn
13:20-13:40		Closing Remark
13:40-14:00		
14:00-14:20	(L7) Satapanawat Sittihan (TH)	
14:20-14:40	(L8) Yen-Ku Wu (TW)	
14:40-15:00	(L9) Azusa Kondoh (JP)	
15:00-15:20	(L10) Yingchun Chen (CN)	
15:20-15:40	Break	
15:40-16:00	(L11) Yunmi Lee (KR)	
16:00-16:20	(L12) Cheng-Chung Wang (TW)	
16:20-16:40	(L13) Nobutaka Fujieda (JP)	
16:40-17:00	(L14) Guochen Jia (HK)	
17:00-17:20	(L15) Guoyin Yin (CN)	

The 15th International Conference on Cutting-Edge Organic Chemistry in Asia

Book of Program and Abstracts

Hong Kong

July 25-26 2022

Contents

Acknowledgement	A2
Greetings	A3
General Information	A4
Program	A5
Abstracts Oral	P1
Poster	P23
Authors Index	P123
List of participants	P134

Acknowledgement

We would like to express sincere gratitude to the following institutions and organizations：

Sponsored by

Croucher Foundation

Faculty of Science, the Chinese University of Hong Kong

Faculty of Science, University of Hong Kong

State Key Laboratory of Synthetic Chemistry (HKU)

State Key Laboratory of Environmental and Biological Analysis (HKBU)

Hong Kong Baptist University Century Club

Chinese National Engineering Research Center for Tissue Restoration & Reconstruction (HKUST)

Industrial partners

Greetings

Welcome to the 15th International Conference on Cutting-Edge Organic Chemistry in Asia (ICCEOCA-15/ACP 2022)

Dear Colleagues,

It is our great pleasure to invite you to present your outstanding research at the 15th International Conference on Cutting-Edge Organic Chemistry in Asia (ICCEOCA-15/ACP 2022), which will be held online on 25–26 July 2022.

After a two-year hiatus, we are thrilled to be back together for what has been an annual event for organic chemists in Asia! The original ICCEOCA-15 was supposed to be held in year 2020, a year of perfect vision and particularly memorable, as it is the 15th anniversary of the conference started under the Asian Core Program. Unexpectedly in the last two years, the world has experienced great challenges that have changed our lives, our research and our teaching. Even this ICCEOCA conference is operating under a new normal—an online mode for the first time. Different Regional Coordinators will be organizing local get-togethers during ICCEOCA-15 as the situation allows in different cities.

The organizing committee is looking forward to meeting all of you and to invite you to actively participate in this conference. This will take more determination and commitment from all attendees than ever, as instead of being able to socialize we will have to be in front of our monitors. However, the conference will be showcasing the best of organic chemistry from all of our ACP regions, and should be very exciting! The 1.5-day program includes 22 oral presentations, 100 poster presentations with one-minute presentations, two short scientific talks from industry, and virtual socializing. As in previous conferences, ACP Lectureships will be awarded to individuals. Because the conference will be online, more chemists than ever before will be able to join us this year. Finally, on the occasion of the 15th anniversary of the ICCEOCA, Professor Dr. Her Royal Highness, Princess Chulabhorn of Thailand will be giving a special speech to the Asian organic chemistry community.

We look forward to virtually meeting with everyone, to learn about the latest exciting developments in organic chemistry in this part of the world. We hope you will enjoy the conference.

Best wishes,
The Organizing Committee

Pauline Chiu

Ken C F Leung

Jianwei Sun

Ying Yeung Yeung

General Information

- Conference website: https://www.icceoca15.com/. Conference information can be found after you register and login to this website.

- For any technical problem, please send email to us (admin@icceoca15.com). During the conference, we will check this email and try our best to make real-time response.

- Time shown in this abstract book is Hong Kong time. Here is the time difference between different regions:

  Mainland China, Hong Kong, Taiwan, Singapore, Malaysia: 9:00 am
  Japan, Korea: 10:00 am (+1 hour)
  Thailand: 8:00 am (–1 hour)

Program

Monday, July 25

Opening Remark

9:00-9:20	Opening Remark		

Oral Presentations

Chair: Jianwei Sun

9:20-9:40	Chuang-Chuang Li	IL-1	Total Synthesis of Natural Products with Bridged Ring Systems (Southern University of Science and Technology, China)
9:40-10:00	Yusuke Masuda	IL-2	Photocatalytic Synthesis of Organophosphorus Compounds (Hokkaido University, Japan)
10:00-10:20	Zhongxing Huang	IL-3	Access Molecular Complexity by Breaking Symmetry of Dicarbonyl Compounds (University of Hong Kong, Hong Kong)
10:20-10:40			Break
10:40-11:00	Ming Joo Koh	IL-4	N-Heterocyclic Carbene-nickel Complexes as Catalysts for Site- and Stereoselective Olefin Carbofunctionalizations (National University of Singapore, Singapore)
11:00-11:20	Aimi Suhaily Saaidin	IL-5	Design and Synthesis of Ligand-Tag Exchangeable Photoaffinity Probe Utilizing Nosyl Chemistry (Universiti Teknologi MARA)
11:20-11:40	Sukwon Hong	IL-6	Chiral Ligands Providing Attractive Noncovalent Interactions (Gwangju Institute of Science and Technology, Korea)
11:40-11:50	Atsuhiko Toyama		Utility of the compact-sized mass spectrometer and the “Mass-it” data deconvolution for simplifying the routine work in organic chemistry (Shimadzu Corporation)

Poster Presentation Session A

11:50-13:00			
	Chuan He	PA-1	Catalytic Enantioselective Construction of Si-Stereogenic Silanes (Southern University of Science and Technology, China)
	Xinfang Xu	PA-2	Catalytic Diazo-yne Carbocyclization for the Expeditious Assembly of Carbocyclic Frameworks (Sun Yat-Sen University, China)
	Masahiro Kojima	PA-3	Regioselective Deaminative Allylation of Aliphatic Amines via Dual Cobalt and Organophotoredox Catalysis (Hokkaido University, Japan)
	Taiga Yurino	PA-4	Aerobic Allylic Amination Catalyzed by Pd(OAc)2/P(OPh)3 System with Low Catalyst Loading (Hokkaido University, Japan)

Yudai Matsuda	PA-5	Biosynthesis of Complicated Natural Products from Fungi (City University of Hong Kong, Hong Kong)
Hyunwoo Kim	PA-6	Hemilabile P, O-Ligands for Pd-Catalyzed Hydrosilylation of Unactivated Alkenes (Korea Advanced Institute of Science and Technology, Korea)
Min Kim	PA-7	Surface Modification of MOF-based Catalysts for Size-selective Organic Reactions (Chungbuk National University, Korea)
Muhammad Kumayl Abdulwahab	PA-8	Overcoming Resistance to EGFR Inhibitors in NSCLC: Structural Optimization of Quinazoline Scaffold (Universiti Malaya, Malaysia)
Jie Wu	PA-9	Neutral Eosin Y as an Photo Hydrogen Atom Transfer Catalyst for C-H and Si-H Activations (National University of Singapore, Singapore)
Tsung-Shing Andrew Wang	PA-10	A two-step ligand-directed labeling strategy for reporting and reversible activity-regulating intracellular proteins (National Taiwan University, Taiwan)
Aurapat Ngamnithiporn	PA-11	Syntheses of 3-Aryl Tetrahydroisoquinolines via an Intermolecular [4+2] Cycloaddition of Sultines with Imines (Chulabhorn Research Institute, Thailand)
Jianrong Steve Zhou	PA-12	Nickel-Catalyzed Asymmetric Reductive (Hetero)arylation of π -systems using Organohalides (Peking University Shenzhen Graduate School, China)
Shifa Zhu	PA-13	Asymmetric Carbene-Transfer Reactions with Alkynes as Precursors (South China University of Technology, China)
Hidetoshi Tokuyama	PA-14	Recent Advances in Total Synthesis of Alkaloids (–)-Deoxoapodine and (±)-Vinoxine A (Tohoku University, Japan)
Yoshiharu Iwabuchi	PA-15	Chromium-salen/Nitroxyl radical: A Combination for Catalytic Aerobic Intramolecular Dearomative Phenol Coupling (Tohoku University, Japan)
Gavin Chit Tsui	PA-16	Palladium-Catalyzed Stereoselective C-F Bond Functionalization of gem-Difluoroalkenes (The Chinese University of Hong Kong, Hong Kong)
Do Hyun Ryu	PA-17	Catalytic Asymmetric Aldehyde Addition-Rearrangements of Diazo esters (Sungkyunkwan University, Korea)
Jaesook Yun	PA-18	Copper-Catalyzed Asymmetric Coupling of Enynes with Unsaturated Diesters to Construct C(sp3)–C(sp3) Bonds (Sungkyunkwan University, Korea)
Yean Kee Lee	PA-19	Acrylamide-based Magnetic Molecularly Imprinted Polymer (MION-MNP): Synthesis, Characterisation, and Adsorption Studies for The Sulfonamide Drug Recognitions (Universiti Malaya, Malaysia)
Shaozhong Ge	PA-20	Cobalt-Catalyzed Selective Multi-Borylation of Unsaturated Hydrocarbons (National University of Singapore, Singapore)
Ching-Ching Yu	PA-21	Sulfo-Fluorous Tagging Strategy for Site-Selective Enzymatic Glycosylation of para-Human Milk Oligosaccharides (National Chung Cheng University, Taiwan)

Hsuan-Hung Liao	PA-22	Aromatization as an Impetus to Harness Ketones for Metallaphoto-redox-Catalyzed Benzoylation/Benzylation of (Hetero)arenes (National Sun Yat-sen University, Taiwan)
Poramate Songthammawat	PA-23	Total Synthesis of Palodesangrens A and C (Chulabhorn Graduate Institute, Thailand)
Yu-Rong Yang	PA-24	Ir-Catalyzed Asymmetric Total Syntheses of Alkaloids (Kunming Institute of Botony, China)
Jian Liao	PA-25	Stereocontrolled transformations of chiral copper-allenyl species (Chengdu Institute of Biology, China)
Yasushi Yoshida	PA-26	Halogen-bonding Catalysis by Chiral Halonium Salt (Chiba University, Japan)
Shingo Harada	PA-27	Asymmetric Dearomatization of Nonactivated Arenes based on Diazo-free Generation of Chiral Metal-Carbene (Chiba University, Japan)
Ying Wang	PA-28	High Carbon Utilization Efficiency for Electrochemical CO2 Reduction Reaction (The Chinese University of Hong Kong, Hong Kong)
Young Ho Rhee	PA-29	A De Novo Synthetic Approach towards N-Heterocyclic glycosides Natural Products (Pohang University of Science and Technology, Korea)
Hyun-Suk Lim	PA-30	Chemical strategy for targeted protein degradation (Pohang University of Science and Technology, Korea)
Rozana Othman	PA-31	Hit-to-Lead Short Peptides against Dengue Type 2 Envelope Protein (University of Malaya, Malaysia)
Yu Zhao	PA-32	Catalytic Enantioselective Redox-Neutral Processes for Efficient Chemical Synthesis (National University of Singapore, Singapore)
Chien-Wei Chiang	PA-33	Single Electron Transfer-based Aromatic Amino Acid Containing-Peptide/protein Bioconjugations (Soochow University, Taiwan)
Sheng-Kai Wang	PA-34	Polyproline macrocyclic nanoscaffolds: Applications in protein interactions and the structure analysis (National Tsing Hua University, Taiwan)
Jaruwan Chatwichien	PA-35	Identification of active compounds responsible for the bioactivities of Xenostegia tridentata (Chulabhorn Graduate Institute,Thailand)
Qi-Xiang Guo	PA-36	Chiral Aldehyde-Involved Ternary Catalysis (Southwest University, China)
Zhihui Shao	PA-37	Enantiodivergence Enabled by the Development of Acyclic Chiral Secondary Aminocatalysts (Yunnan University, China)
Sobi Asako	PA-38	Spirobipyridine Enables Remote Steric Control and Rate Enhancement in Iridium-Catalyzed C–H Borylation of Arenes (Institute of Physical and Chemical Research, Japan)

	Satoshi Yokoshima	PA-39	Reactions of Ketones Having a 2-Nitrophenyl Group at the α-Position (Nagoya University, Japan)
	Franco King-Chi Leung	PA-40	Controlled Supramolecular Assemblies of Photoresponsive Molecular Amphiphiles at Multiple Length-Scale (The Hong Kong Polytechnic University, Hong Kong)
	Byeong Moon Kim	PA-41	Synergistic bimetallic catalysts for selective organic reactions (Seoul National University, Korea)
	Woo-Dong Jang	PA-42	Self-assemblies formed by of expanded π-aromatic molecules (Yonsei University, Korea)
	Joazaizulfazli Jamalis	PA-43	Novel Thiophene Chalcones-Coumarin as Acetylcholinesterase Inhibitors: Design, Synthesis, Biological Evaluation, Molecular Docking, ADMET Prediction and Molecular Dynamics Simulation (Universiti Teknologi Malaysia, Malaysia)
	Ye Zhu	PA-44	Remote Quaternary Stereocenters Through Distal Ionic Interactions-Directed Desymmetrizing Suzuki–Miyaura Reaction (National University of Singapore, Singapore)
	Cheng-Kun Lin	PA-45	Concise Synthesis of (–)-Negamycin from a Chiral Advanced Epoxide (National Chung Hsing University, Taiwan)
	Chien-Fu Liang	PA-46	An Acyl Bunte salt as a Nucleophilic Catalyst for Selective Phenol Acylation (National Chung Hsing University, Taiwan)
	Zhengren Xu	PA-47	Biomimetic Total Synthesis of Spiroindimicin Family of Natural Products (Peking University, China)
	Shuo Tong	PA-48	Catalytic Enantioselective Synthesis and Switchable Chiroptical Property of Inherently Chiral Macrocycles (Tsinghua University, China)
	Hiroaki Itoh	PA-49	Solid-Phase Total Synthesis and Functional Analysis of Yaku' amide B and Its Analogues (The University of Tokyo, Japan)
	Yusuke Ogura	PA-50	Total Syntheses of Celafolins B-1, B-2, and B-3 Enabled by the Highly Stereocontrolled Synthesis of (–)-Isocelorbicol (The University of Tokyo, Japan)
Lunch			
13:00-14:00			Lunch
Oral Presentations			
			Chair: Ying-Yeung Yeung
14:00-14:20	Satapanawat Sittihan	IL-7	Total Synthesis of Pentaketide Ansamycin Microansamycin H (Chulabhorn Graduate Institute, Thailand)

14:20-14:40	Yen-Ku Wu	IL-8	Capitalizing on Cyclic Vinylogous Esters for Formal g-C−H Arylation of Carbocylic Frameworks:Total Syntheses of O-Methyl Nimbinone, Xiamycins A and H, Simonsol C, Flamvelutpenoid A, epi-Elwesine,and Houpulin B (National Yang Ming Chiao Tung University, Taiwan)
14:40-15:00	Azusa Kondoh	IL-9	Chiral Ureates as Chiral Strong Brønsted Base Catalysts (Tohoku University, Japan)
15:00-15:20	Yingchun Chen	IL-10	The Development of Asymmetric p-Lewis Base Catalysis (Sichuan University, China)
15:20-15:40			Break
			Chair: Vanessa Kar-Yan Lo
15:40-16:00	Sarah Yunmi Lee	IL-11	Catalytic Stereodivergent C–C Bond Formations by Asymmetric Conjugate Additions (Yonsei University, Korea)
16:00-16:20	Cheng-Chung Wang	IL-12	Statistical Analysis: A New Perspective on Stereoselective Glycosylation Reactions (Academia Sinica, Taiwan)
16:20-16:40	Nobutaka Fujieda	IL-13	Stereoselective Synthesis with Protein as Metal Ligands (Osaka Metropolitan University, Japan)
16:40-17:00	Guochen Jia	IL-14	Alkyne Metathesis with Re(V) Alkylidyne Complexes (Hong Kong University of Science and Technology, Hong Kong)
17:00-17:20	Guoyin Yin	IL-15	Migratory Carboboration of Alkenes (Wuhan University, China)

Tuesday, July 26

Oral Presentations

Chair: Ken C. F. Leung

9:00-9:20	Cheuk Wai So	IL-16	Competence of Diborene Compounds in Small Molecules Activation and Catalytic Hydroboration (Nanyang Technological University, Singapore)
9:20-9:40	Xing-Zhong Shu	IL-17	Cross-Electrophile Coupling Involving R3Si-Cl and R3Ge-Cl (Lanzhou University, China)
9:40-10:00	Keisuke Iida	IL-18	Development of a Novel Light-up G-quadruplex Binding Compound (Chiba University, Japan)
10:00-10:20	Sun-Joon Min	IL-19	Development of Chemical Tools for Biomedical Applications Using Synthetic Organic Chemistry (Hanyang University, Korea)
10:20-10:40			Break

10:40-11:00	Chih-Ming Chou	IL-20	Substrate-Directed Regioselective Alkene Functionalizations of (E)-β,γ-Unsaturated Carboxylic Acids (National University of Kaohsiung, Taiwan)
11:00-11:20	Yanxing Jia	IL-21	Total Synthesis of Polycyclic Natural Products (Peking University, China)
11:20-11:40	Makoto Yamashita	IL-22	Chemistry of Reactive Group 13 Element Compounds in Low Oxidation State: Diborane(4) and Al-centered anion (Nagoya University, Japan)
11:40-11:50	Fraser White, Hiroyuki Kanda		XtaLAB Synergy-ED: 3DED/MicroED solutions from the collaboration with Rigaku and JEOL (Rigaku Corporation and JEOL Ltd)

Poster Presentation Session B

11:50-13:00			
	Jin-Dong Yang	PB-1	Reactivity Studies and Synthetic Applications of N-Heterocyclic Phosphines (Tsinghua University, China)
	Rong Zhu	PB-2	Copper-Catalyzed Condensation Polymerization of Propargylic Electrophiles (Peking University, China)
	Masahiro Yamashina	PB-3	Construction of a Self-Complementary Macrocycle by Dual Interaction System (Tokyo Institute of Technology, Japan)
	Ambara R. Pradipta	PB-4	Biofunctional chemistry and reactivity of biogenic acrolein for cancer diagnosis and therapy (Tokyo Institute of Technology, Japan)
	Yangjian Quan	PB-5	Photoinduced Dehydrogenative Borylation via Dihydrogen Bond Bridged Electron Donor and Acceptor Complexes (The Hong Kong University of Science and Technology, Hong Kong)
	Cheol-Hong Cheon	PB-6	Total Syntheses of Iheyamines A and B (Korea University, Korea)
	Iskandar Abdullah	PB-7	CuBr-Catalyzed One-Pot Three-Component Synthesis of Novel 2-(Carbazolyl)benzothiazoles (Universiti Malaya, Malaysia)
	Chunyan Chi	PB-8	Synthesis of a Fully Conjugated Zigzag Carbon Nanobelt (National University of Singapore, Singapore)
	Pei-Jhen Li	PB-9	Syntheses of Glycoprobes as Tools to Interrogate Biological Systems (National Chung Cheng University, Taiwan)
	Sunisa Akkarasamiyo	PB-10	Nickel-Catalyzed Stereoinvertive Deoxygenation of trans-Epoxides to cis-Alkenes (Kasetsart University, Thailand)
	Qingquan Lu	PB-11	Organic Electroreduction: Construction of Alkyl-Based Structures (Wuhan University, China)

Xiao Shen	PB-12	Selective Transformations Enabled by C-Si Bond Activation with Alkoxy Radicals (Wuhan University, China)
Takeharu Haino	PB-13	Synthesis of Sequence-Controlled Supramolecular Terpolymers (Hiroshima University, Japan)
Muhammet Uyanik	PB-14	Enantioselective Ammonium Hypoiodite Catalysis for Oxidative Umpolung of Indoles (Nagoya University, Japan)
Jun (Joelle) Wang	PB-15	Enantio- and Regioselective Construction of 1,4-Diamines via Cascade Hydroamination of Methylene Cyclopropanes (Hong Kong Baptist University, Hong Kong)
Jung Min Joo	PB-16	Systematic Designs of New Redox-Active Heterocyclic Mediators (Pusan National University, Korea)
Won-jin Chung	PB-17	Synthesis of α-Ketoimidoyl Fluorides via Geminal Fluorine-Promoted Azide Rearrangement (Gwangju Institute of Science and Technology, Korea)
Shingo Ito	PB-18	Synthesis and Properties of Fully Conjugated Azacorannulene Dimer (Nanyang Technological University, Singapore)
Hsiang-Yu Chuang	PB-19	Synthetic Studies towards Serratine-Type Alkaloids (National Chiayi University, Taiwan)
Pawaret Leowanawat	PB-20	Synthesis of Dibenzopleiadiene-Embedded Polyaromatics via Palladium-Catalyzed [4+3] Decarbonylative/Decarboxylative Annulation (Mahidol University, Thailand)
Lingkui Meng	PB-21	Sulfonium Ylide in Glycosylation (Huazhong University of Science and Technology, China)
Wanxiang, Zhao	PB-22	Catalytic Borylation of Silyl Enol Ethers (Hunan University, China)
Yoshihiro Ueda	PB-23	Seven-Step Stereodivergent Total Syntheses of Punicafolin and Macaranganin (Kyoto University, Japan)
Kazuhiko Semba	PB-24	Carboallylation of Electron-Deficient Alkenes by Cooperative Metal Catalysis (Kyoto University, Japan)
Ho Yu Au-Yeung	PB-25	Copper Catalyzed C-O and C-C Cross Coupling Reactions: Effects of Mechanical Interlocking in the Ligand Framework (University of Hong Kong, Hong Kong)
Sunwoo Lee	PB-26	Transformation of Amides using C-N Bond Activation (Chonnam National University, Korea)
Jun Hee Lee	PB-27	Highly Chemoselective Deoxygenation of N-Heterocyclic N-Oxides Using Hantzsch Esters as (Dongguk University, Korea)
Han Sen SOO	PB-28	Photoredox Catalysis by Metal Halide Perovskites and Vanadium Complexes (Nanyang Technological University, Singapore)

Cheng-Che Tsai	PB-29	Palladium/Brønsted-Acid-Catalyzed Diastereoselective Cyclization with Chiral Sulfinamides as Nucleophiles (Tunghai University, Taiwan)
Panuwat Padungros	PB-30	Glycosylation of n-Pentenyl Glycosides Activated by Bromodiethylsulfonium Salt (Chulalongkorn University, Thailand)
Xiangfeng Shao	PB-31	Synthesis and Properties of Monoazadichalcogenasumanenes (Lanzhou University, China)
Xiangdong Hu	PB-32	Total Synthesis of (+)-3-Deoxyfortalpinoid F, (+)-Fortalpinoid A, and (+)-Cephinoid H (Northwest University, China)
Yusuke Ano	PB-33	Palladium-Catalyzed 1,1-Alkynylbromination of Alkenes (Osaka University, Japan)
Takuya Kodama	PB-34	Nickel-catalyzed skeletal transformation of tropone derivatives via C–C bond activation: catalyst-controlled access to diverse ring systems (Osaka University, Japan)
Hyunwoo Kim	PB-35	Electrochemically Driven Stereoselective Approach to syn-1,2-Diol Derivatives from Vinylarenes and DMF (Ewha Womans University, Korea)
Yuan Qiao	PB-36	Chemoenzymatic probes reveal peptidoglycan recognition and uptake mechanisms in Candida albicans (Nanyang Technological University, Singapore)
Yen-Chun Lee	PB-37	Combinatorial alanine scanning reveals potent protein-protein interaction inhibitors (National Cheng Kung University, Taiwan)
Pengfei Li	PB-38	A New Chiral Pyridine Unit for Asymmetric Catalysis (Xi'an Jiaotong University, China)
Yu-Ming Zhao	PB-39	Highly Efficient Total Syntheses of Galanthamine and Lycoramine via a Two-Stage Strategy (Shaanxi Normal University, China)
Yoichi M. A. Yamada	PB-40	Second Generation Phenolsulfonic Acid-Formaldehyde Resin Catalyst (PAFR II) for Continuous Flow Esterification (Institute of Physical and Chemical Research, Japan)
Tomoya Miura	PB-41	Synthesis, Structure, and Dynamics of Chiral Macrocycles with Arylene and 1,2-cis-Cyclopropylene Units Alternatively Connected (Okayama University, Japan)
Jung Woon Yang	PB-42	Substrate-Controlled Chemo-/Enantioselective Synthesis of a-Benzylated Enals and Chiral Cyclopropane-Fused 2-Chromanones (Sungkyunkwan University, Korea)
Yongseok Kwon	PB-43	Catalytic Atroposelective Pictet-Spengler Cyclization (Sungkyunkwan University, Korea)
Robin Chi	PB-44	NHC Catalysis: Beyond New Activation Modes (Nanyang Technological University, Singapore)
Guo-Ming Ho	PB-45	Diastereodivergent Synthesis of syn,syn,syn-, syn,anti,syn- and anti,syn,syn-Stereotetrads (National Kaohsiung Normal University, Taiwan)

Yang Li	PB-46	Cleavage of inert chemical bonds related biomass for green H2 and chemicals by photoredox catalysis and transition-metal catalysis (Xi'an Jiaotong University, China)
Seiji Shirakawa	PB-47	Kinetic Resolution of α-Quaternary Carboxylic Acids via Chiral Bifunctional Sulfide-Catalyzed Bromolactonization (Nagasaki University, Japan)
Jean-Ho Chu	PB-48	Synthesis of Novel Bipyrazolo[1,5-a]pyridine as Aggregation-Induced Emission Enhancement Luminogens (National Taitung University, Taiwan)
Hanfeng Ding	PB-49	Tetracyclic Diterpenoid Synthesis Facilitated by an ODI-[5+2] Cascade (Zhejiang University, China)
Takashi Nishikata	PB-50	Cu catalyzed sterically congested C(sp3)-CN bond formations (Yamaguchi University, Japan)

Oral Presentation

Chair: Pauline Chiu

13:00-13:20	Princess Chulabhorn (Thailand)

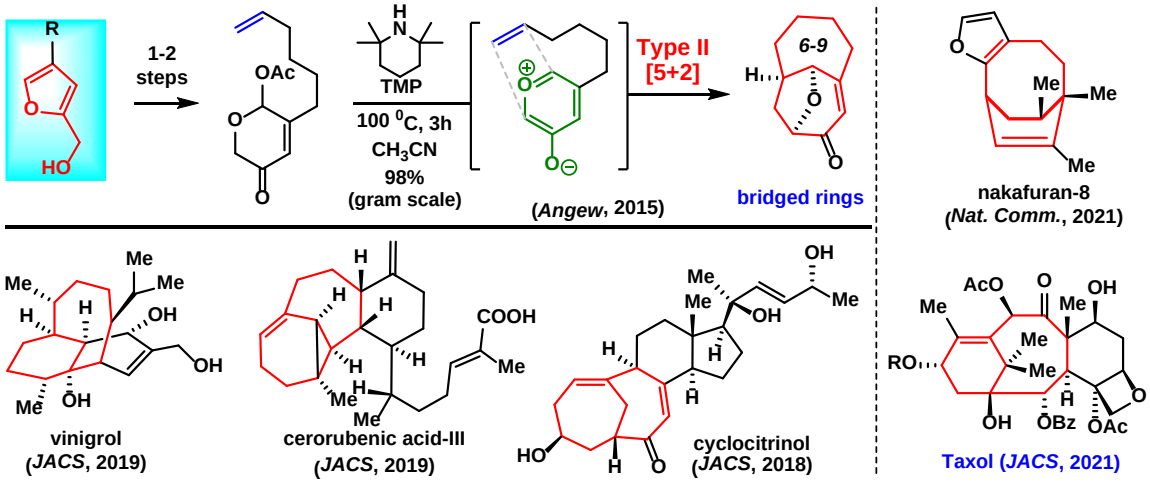
Closing Remark

13:20-13:40	Closing Remark

Total Synthesis of Natural Products with Bridged Ring Systems

Chuang-Chuang Li*
Department of Chemistry, Southern University of Science and Technology (SUSTech)
Shenzhen 518055, China
E-mail: ccli@sustech.edu.cn

Developing efficient reactions for achieving bridged ring systems is a long-standing challenge but very significant in organic chemistry, considering that such motif is widely found in natural products (such as Taxol) with significant biological activities. So far there are few general reactions available for the single-step synthesis of bridged ring systems efficiently. In 2015, we have developed the first **Type II [5+2]** cycloaddition reaction,[1] which allows the efficient and diastereoselective construction of various highly functionalized and synthetically challenging bridged ring systems. The asymmetric total synthesis of cyclocitrinol, cerorubenic acid and vinigrol, have been accomplished via the **Type II [5+2]** cycloaddition. In 2021, we completed the concise asymmetric total synthesis of Taxol in 21 steps.[2]



References

1. (a) Min, L.; Liu, X.; Li, C.-C. *Acc. Chem. Res.* **2020**, *53*, 703. (b) Hu, Y.; Li, L.; Han, J.; Min, L.; Li, C.-C. *Chem. Rev.* **2020**, *120,* 5910. (c) Min, L.; Hu, Y.; Fan, J.; Zhang, W.; Li, C.-C. *Chem. Soc. Rev.* **2020**, *49, 7015.*
2. Hu, Y.; Gu, C.; Wang, X.; Min, L.; Li, C.-C. *J. Am. Chem. Soc.* **2021**, *143*, 17862.

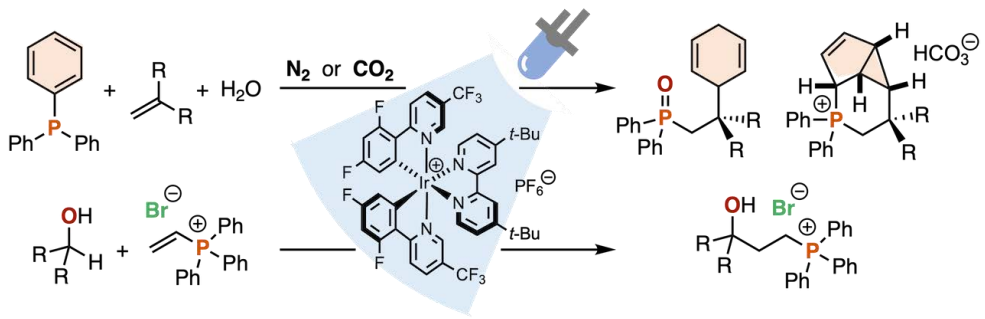
Chuang-Chuang Li (李闯创). Ph.D. student with Prof. Zhen Yang in Peking University (2001-2006); Postdoctoral Fellow with Prof. Phil S. Baran in The Scripps Research Institute (2006-2008); Associate Professor, Peking University Shenzhen Graduate School, China (2008 to 2013). Current position: Professor, Southern University of Science and Technology (2014 to now). Li's research interests are focused on total synthesis of natural products.

Photocatalytic Synthesis of Organophosphorus Compounds

Yusuke Masuda*
Faculty of Science, Hokkaido University, Sapporo, Hokkaido, 060-0810, Japan
E-mail: ymasuda@sci.hokudai.ac.jp

Organophosphorus compounds are not only molecules essential for living organisms such as DNA and ATP, but also have unique functions as synthetic intermediates, ligands for metal catalysts, pharmaceuticals, and many others. This presentation will report that photoinduced radical reactions can provide novel synthetic approaches to organophosphorus compounds through construction of complex molecules from readily available starting materials.

Photoredox catalysis has brought about a revolution in synthetic chemistry, and many unprecedented transformations have been achieved in the last decade.[1] Among them, our efforts led to the discovery of a series of the photocatalytic reactions between tertiary phosphines and unsaturated hydrocarbons. For example, readily available three components, triarylphosphines, alkenes, and water, were put together under photoredox conditions to construct cyclohexadienyl phosphine oxide.[2] When the same reaction was carried out under a carbon dioxide atmosphere, a totally different product, a fused tricyclic phosphonium salt, was formed.[3] These reactions were marked by dearomatization of the phenyl ring. The mechanistic studies were performed, and the gained insights led to further reaction development.[4] The organophosphorus compounds obtained in this study served as synthetic intermediates and ligands for metal catalysts.



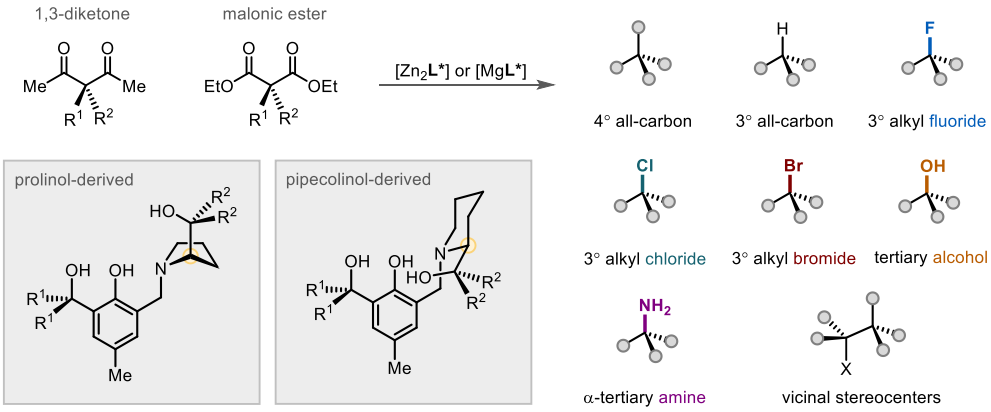
References
1. (a) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898–6926; (b) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075–10166.
2. Masuda, Y.; Tsuda, H.; Murakami, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 3551–3555.
3. Masuda, Y.; Uno, M.; Murakami, M. *Org. Lett.* **2021**, *23*, 8445–8449.
4. Yoshida, M.; Sawamura, M.; Masuda, Y. *Submitted.*

Yusuke Masuda (増田 侑亮). Kyoto University (PhD, 2017). Postdoctoral Fellow, California Institute of Technology (2017-2018). Program-specific Assistant Professor, Kyoto University (2018-2021). Assistant Professor, Hokkaido University (2021-).
Synthetic Chemistry, Organometallic Chemistry, Photochemistry.

Access Molecular Complexity by Breaking Symmetry of Dicarbonyl Compounds

Zhongxing Huang*
State Key Laboratory of Synthetic Chemistry, Department of Chemistry, University of Hong Kong, Hong Kong, China
E-mail: huangzx@hku.hk

1,3-Dicarbonyl compounds represent a prominent family of structures that are easily available and can provide rapid access to complex molecules. When doubly substituted, these compounds can be rapidly converted to valuable tetrasubstituted stereocenters via asymmetric transformations. Here, we report a prolinol- or pipecolinol-derived tetradentate ligand scaffold that can house two zinc centers or a single magnesium atom to desymmetrize a wide range of malonic esters and 1,3-diketones. The reductive desymmetrization of disubstituted malonic ester via hydrosilylation has enabled the stereoselective synthesis of various enantioenriched building blocks, including quaternary stereocenters, tertiary alkyl halides, α-tertiary amines, and tertiary alcohols. Consequently, novel and expeditious approaches to bioactive natural metabolites, such as 2-dechlorohalomon, conagenin, and yezo'otogirins, were devised. Meanwhile, the desymmetric cyanosilylation of acyclic 1,3-diketones afforded two vicinal tetrasubstituted carbons. The polyfunctionalized nature of the chiral cyanohydrin products can be used to access molecules of higher complexity, particularly those with consecutive stereocenters.



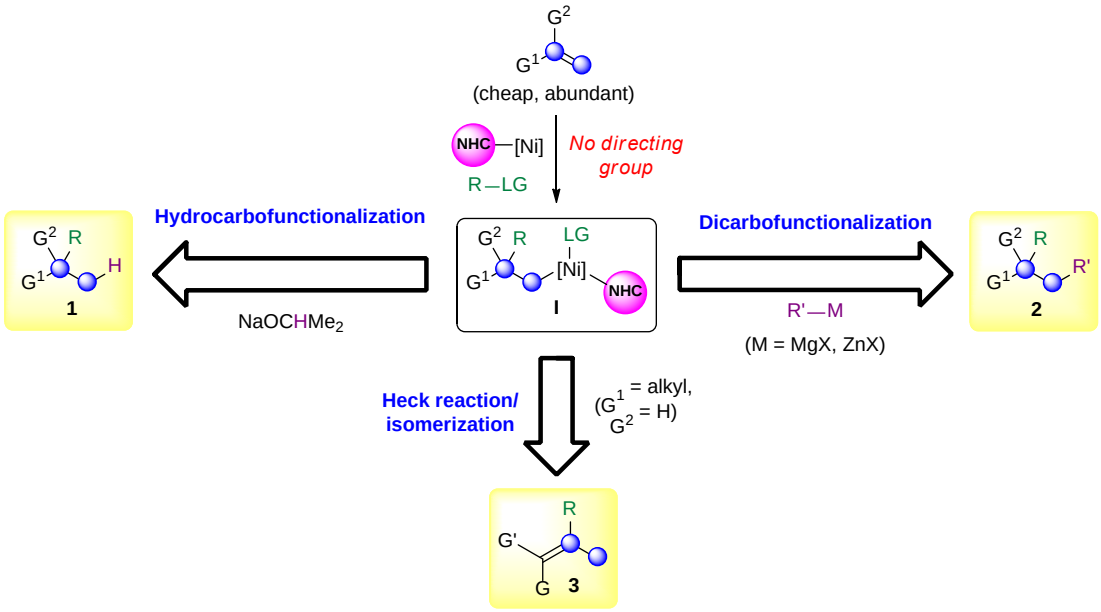
References
1. Xu, P.; Huang, Z. *Nat. Chem.* **2021**, *13*, 634
2. Zheng, Y.; Zhang, S.; Low, K.-H.; Zi, W.; Huang, Z. *J. Am. Chem. Soc.* **2022**, *144*, 1951.
3. Xu, P.; Liu, S.; Huang, Z. *J. Am. Chem. Soc.* **2022**, *144*, 6918.

Zhongxing Huang (黄重行). University of Chicago (Ph.D., 2017). Assistant Professor (2019). [Field of research] Organic Chemistry.

N-Heterocyclic carbene-nickel complexes as catalysts for site- and stereoselective olefin carbofunctionalizations

Ming Joo Koh*
Department of Chemistry, National University of Singapore, 4 Science Drive 2, Republic of Singapore, 117544
E-mail: chmkmj@nus.edu.sg

Catalytic olefin carbofunctionalization represents an attractive class of C–C bond-forming transformations that enable the cross-coupling of readily available olefins with carbon-based reagents for the rapid generation of molecular complexity. However, its widespread adoption in organic synthesis is thwarted by a number of fundamental challenges related to reactivity and selectivity. Recent studies in our group led us to discover that strongly σ-donating and sterically encumbered *N*-heterocyclic carbenes (NHCs) serve as effective ligands to stabilize and tune the reactivity and/or selectivity profiles of nickel-based complexes for olefin cross-coupling. In this talk, we will describe our recent developments in olefin carbofunctionalizations that leverage these NHC-nickel catalysts to promote the efficient assembly of valuable organic building blocks with simultaneous control of regio-, diastereo- and/or enantioselectivities.



Ming Joo Koh (许民瑜). 2008–2012: B.Sc. in Chemistry & Biological Chemistry, First Class Honors, Nanyang Technological University, Singapore. 2012–2018: Ph.D. & Post-Doc in Organic Chemistry, Boston College, MA, USA. 2018–present: President's Assistant Professor, National University of Singapore, Singapore. Research interests: Nonprecious metal catalysis, Radical chemistry.

Design and Synthesis of Ligand-Tag Exchangeable Photoaffinity Probe Utilizing Nosyl Chemistry

Aimi Suhaily Saaidin*[1], Yuta Murai[2], Takuya Ishikawa[3], Kenji Monde[2]
[1]Center of Foundation Studies, Universiti Teknologi MARA, Dengkil, Selangor
[2]Frontier Research Center for Advanced Material and Life Sciences, Hokkaido University
[3]Faculty of Advanced Life Sciences, Hokkaido University
E-mail: aimisuhaily@uitm.edu.my

Comprehending the mechanism of molecular interaction between small bioactive ligands and receptors is an essential step for drug design and discovery. For these purposes, a few approaches such as x-ray crystallography and solution-state NMR have been established. Although these conventional methods provide valuable information, they require having the protein at a reasonable purity. In the early 1960s, photoaffinity labeling (PAL) has been introduced as an efficient technique in pinpointing functional amino acids with protein by Westheimer and co-workers [1]. PAL is an approach that utilizes a chemical probe that can covalently cross-linked to its target protein upon activation with light by using a photoactivatable ligand. Conventional photoaffinity labels are consists of three vital components which are bioactive molecules, photoreactive moiety (e.g., Trifluoromethyl phenyl diazirine) and identification/reporter tag (e.g., Biotin). Despite the simplicity of this cross-linked strategy, low affinity of protein-molecule interactions and purifications of cross-linked peptides are often difficult due to steric interference of bulky functional groups and complexity of the reaction mixtures.

To circumvent these problems, we designed a novel nosyl-type diazirine photoaffinity probe which involves the incorporation of only two functionalities; a photophore (diazirine) and the small molecules of interest. The concept of our approach is 1) to increase the affinity of binding interactions by reducing steric inferences and 2) to install identification/reporter tags into protein complex during later steps via "Meisenheimer complex"[2] (Figure 1).

In this study, we have successfully designed and synthesized a nosyl-type diazirine photoaffinity probe. The mechanism of protein target capture was proved by using a modified thiol containing fluorescence [3].

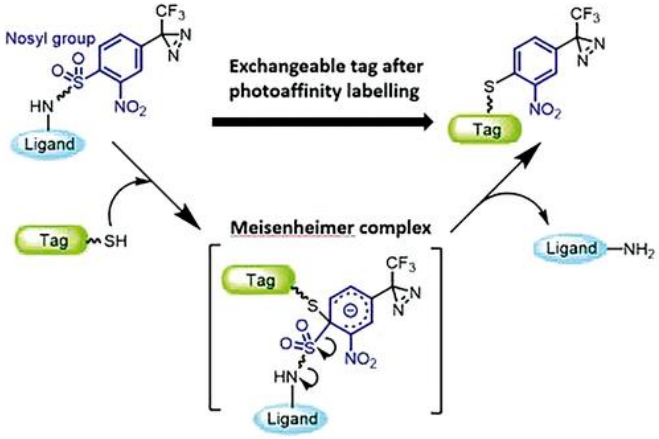


Figure 1. Mechanistic feature of our approach

References

1. Smith, E; Collins, I., *Future Medicinal Chemistry*, **2015**, 7, 159-183.
2. Fukuyama, T., Kan, T., *Chemical Communications*, **2004**, 353-359.
3. Saaidin, Aimi Suhaily; Murai, Y.; Ishikawa, T.; Monde. K., *European Journal of Organic Chemistry*, **2019**, 46, 7563-7567.

Aimi Suhaily Saaidin. Hokkaido University (PhD, 2022). Lecturer (2019). Organic synthesis, Photoaffinity labelling.

Chiral Ligands Providing Attractive Noncovalent Interactions

Sukwon Hong*
Department of Chemistry, Gwangju Institute of Science and Technology (GIST),
Buk-gu, Gwangju 61005, Republic of Korea
E-mail: shong@gist.ac.kr

The application of attractive noncovalent interactions has emerged as an elegant strategy in the asymmetric catalysis. Although conventional asymmetric catalysis utilizes repulsive steric interactions to destabilize transition states of minor enantiomers, attractive noncovalent interactions such as ion-pairing, hydrogen bonding, and aromatic interactions could provide an alternative 'enzyme-like' pathway to stabilize the transition states of major enantiomers. In our laboratory, a series of hydrogen-bond functionalized salen-transition metal catalysts were developed to facilitate bimetallic or bifunctional activation of both reaction partners.[1] Cation-binding salen nickel catalysts were developed for the enantioselective alkynylation of trifluoromethyl ketones in high yield (up to 99%) and high enantioselectivity (up to 97% ee).[2] Palladium complexes with chiral pyridine-dihydroisoquinoline ($Py^{DH}IQ$) ligands enabled highly enantioselective conjugate addition reactions of arylboronic acids to 2-substituted chromones and β-methyl α,β-unsaturated δ-lactams.[3] The effect of π-interactions on the high enantioselectivity was elucidated by DFT calculations and noncovalent interaction analysis.

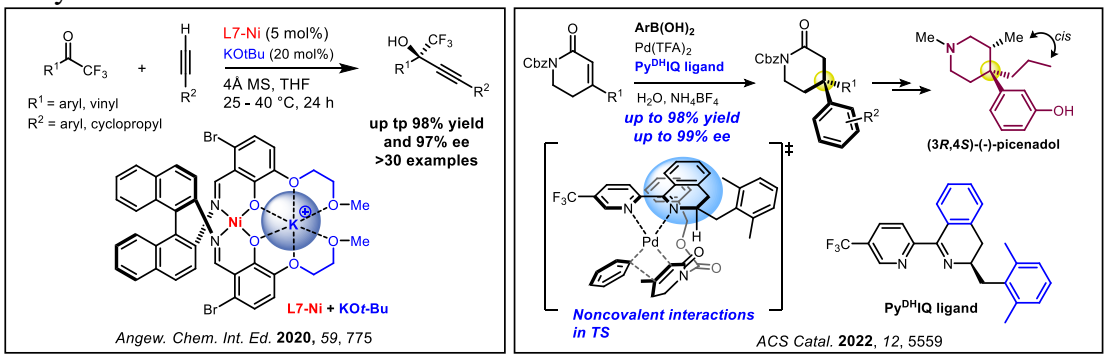


Figure 1. Asymmetric Catalysis Featuring Attractive Noncovalent Interactions

References

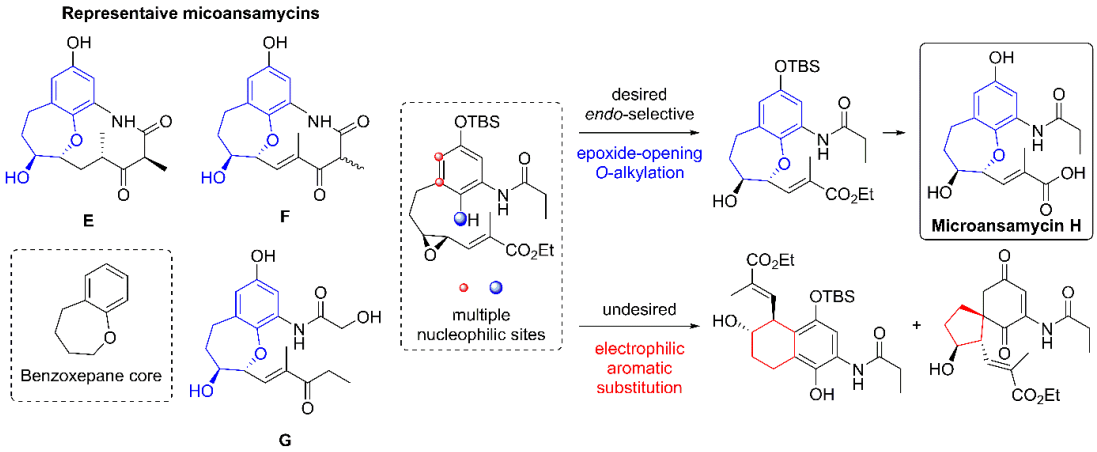
1. (a) Park, J.; Lang, K.; Abboud, K. A.; Hong, S. *J. Am. Chem. Soc*. **2008**, *130*, 16484-16485; (b) Lang, K.; Park, J.; Hong, S. *Angew. Chem. Int. Ed*. **2012**, *51*, 1620-1624.
2. Park, D.; Jette, C. J.; Kim, J.; Jung, W.-O.; Lee, Y.; Park, J.; Kang, S.; Han, M. S.; Stoltz, B. M.; Hong, S. *Angew. Chem. Int. Ed.* **2020**, 59, 775-779.
3. (a) Baek, D.; Ryu, H.; Ryu, J. Y.; Lee, J.; Stoltz, B. M.; Hong, S. *Chem. Sci.,* **2020**, *11*, 4602-4607; (b) Baek, D.; Ryu, H.; Hahm, H.; Lee, J.; Hong, S. *ACS Catal*. **2022**, *12*, 5559-5564.

Sukwon Hong (홍석원, 洪錫湲). Northwestern University (Ph.D, 2003). Postdoctoral Associate, The Scripps Research Institute (2003-2005), Assistant Professor of Chemistry, University of Florida (2005-2012). Associate Professor & Professor of Chemistry, GIST (2012 - present). [Field of research] Organic and Organometallic Chemistry.

Total Synthesis of Pentaketide Ansamycin Microansamycin H

Satapanawat Sittihan,* Somsak Ruchirawat
Program on Chemical Sciences, Chulabhorn Graduate Institute
906 Kamphaeng Phet 6, Laksi, Bangkok 10210, Thailand
E-mail: satapanawat@cgi.ac.th

Ansamycins are a family of macrolactams, in which an aliphatic *ansa* bridge links between two non-adjacent positions of a benzenic or naphthalenic chromophore. In 2018, nine pentaketide ansamycins, namely microansamycins A-I, were isolated from the overexpression of transcriptional regulator gene *mas13* in bacteria *Micromonospora* sp.[1] Regarding the biosynthesis, the backbone of microansamycins represents a novel pentaketide scaffold (3-amino-5-hydroxybenzoic acid–C_2–C_2–C_3–C_3). These nine natural products also highlight the diverse post-polyketide synthase modifications. In terms of the structure, a unique benzoxepane core is common among four congeners, including microansamycins E, F, G and H. Herein, we report the first total synthesis of microansamycin H. Key to our success was the *endo*-selective epoxide-opening *O*-alkylation to construct the seven-membered oxepane. Due to the electron-rich nature of the substituted benzene, our pivotal transformation was hindered by competing electrophilic aromatic substitution that generated kinetically more favored six-membered tetralin and five-membered spiro side products. Judicious choices of Lewis acid activators biased toward the formation of the desired oxepane. After global deprotection, microansamycin H was synthesized in 14 chemical steps with an overall yield of 3.7%.



References

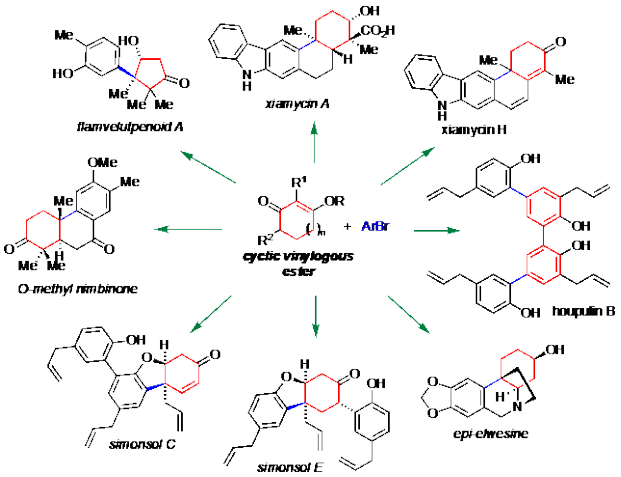
1. Wang, J.; Li, W.; Wang, H.; Lu, C. *Org. Lett*. **2018**, *20*, 1058–1061.

Satapanawat Sittihan (สถาปนวัฒน์ สิทธิหาญ)
Cornell University (BA, 2009), Massachusetts Institute of Technology (PhD, 2017). Chulabhorn Graduate Institute: Lecturer (2017-2021). Assistant Professor (2021-present). [Field of research] Organic chemistry: total synthesis.

Capitalizing on Cyclic Vinylogous Esters for Formal γ-C−H Arylation of Carbocylic Frameworks: Total Syntheses of *O*-Methyl Nimbinone, Xiamycins A and H, Simonsol C, Flamvelutpenoid A, *epi*-Elwesine, and Houpulin B

Yen-Ku Wu*
Department of Applied Chemistry, National Yang Ming Chiao Tung University,
1001 University Road, Hsinchu City, Taiwan 30010
E-mail: yenkuwu@nycu.edu.tw

Cyclic vinylogous esters have served as versatile building blocks for modular syntheses of substituted cycloalkenones. More recently, we[1a, 2] and others[1b-c, 3] have developed mono- and polyarylation reactions of cyclic vinylogous esters, thus enabling new routes to synthetically useful arylated scaffolds. Building on these methodologies, we established a unified strategy for assembling a collection of carbocyclic natural products embedded with a remote aryl substituent.



Scheme 1. Selected Syntheses of Natural Products from Cyclic Vinylogous Esters

References

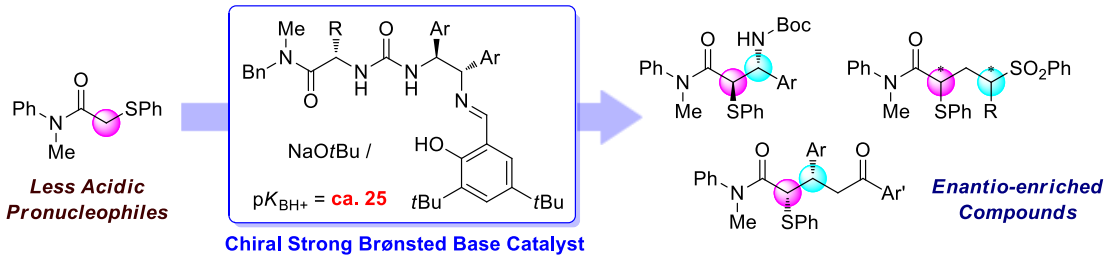
1. (a) Hou, W.-Y.; Wu, Y.-K. *Org. Lett.* **2017**, *19*, 1220; (b) Johnson, T.; Pultar, F.; Menke, F.; Lautens, M. *Org. Lett.* **2016**, *18*, 6488; (c) Zhao, Y.; Zhou, Y.; Liang, L.; Yang, X.; Du, F.; Li, L.; Zhang, H. *Org. Lett.* **2009**, *11*, 555.
2. (a) Yang, Y.-C.; Lin, Y.-C.; Wu, Y.-K. *Org. Lett.* **2019**, *21*, 9286; (b) Lin, Y.-C.; Yen, K.-W.; Lin, H.-J.; Yang, Y.-C.; Wu, Y.-K. *Chem. Commun.* **2021**, *57*, 12119.
3. Shao, L.-D.; Chen, Y.; Wang, M.; Xiao, N.; Zhang, Z.-J.; Li, D.; Li, R.-T. *Org. Chem. Front.* **2022**, *9*, 2308.

Yen-Ku Wu (吳彥谷). National Tsing Hua University (B.Sc., 2004; M.Sc., 2006), The University of Alberta (Ph.D., 2013). The University of Chicago (Postdoc, 2013-2015). National Chiao Tung University (Assistant Professor, 2015-2019; Associate Professor, 2019-2021). National Yang Ming Chiao Tung University (Associate Professor, 2021-present) [Field of research] Organic Chemistry.

Chiral Ureates as Chiral Strong Brønsted Base Catalysts

Azusa Kondoh,* Sho Ishikawa, Rihaku Ojima, Masahiro Terada
Graduate School of Science, Tohoku University, Aoba-ku, Sendai Japan
E-mail: kondoha@tohoku.ac.jp

In recent years, much attention has been paid to the development of enantioselective reactions under Brønsted base catalysis as a useful methodology for organic synthesis. However, the scope of applicable pronucleophiles is highly dependent on the basicity of the catalyst molecules. Therefore, the pronucleophiles have been primarily limited to compounds having a highly acidic proton due to the insufficient basicity of conventional chiral Brønsted base catalysts, such as chiral tertiary amine catalysts. In order to overcome the intrinsic limitation of pronucleophiles and expand the scope of viable enantioselective transformations that are available under Brønsted base catalysis, we have been focusing on the development of chiral Brønsted base catalysts possessing much higher basicity than conventional chiral catalysts. During the course of our study, we envisioned utilizing an ureate, which is the conjugate base of an urea, as a new motif of chiral Brønsted base catalysts due to the distinctive features of ureas. First, pK_a value of a *N,N'*-dialkyl urea in DMSO is estimated to be about 25, and hence its ureate form is potentially basic enough to function as a strong Brønsted base catalyst. Second, ureas can function as a substrate recognition site. Considering that the actual key species in the stereo-determining event of Brønsted base-catalyzed reactions is the conjugate acid of the catalyst molecule, chiral ureates would have great potential to serve as chiral catalysts for controlling the stereochemical outcome. Finally, the synthesis of chiral ureas is well-established, and thus a diverse array of chiral ureates is readily available. Herein, we report the development of a chiral anionic Brønsted base having a *N,N'*-dialkyl ureate moiety as a basic site[1] and its application in enantioselective addition reactions of α-thioacetamides as less acidic pronucleophiles with various electrophiles.



References

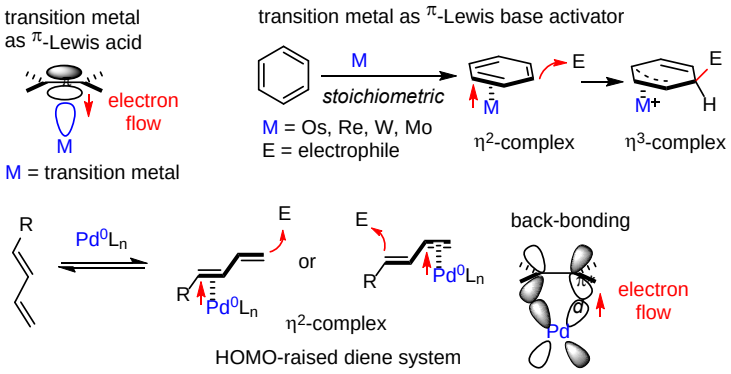
1. (a) Kondoh, A; Ishikawa, S.; Terada, M. *J. Am. Chem. Soc.* **2020**, *142*, 3724; (b) Kondoh, A; Ishikawa, S.; Terada, M. *Org. Biomol. Chem.* **2020**, *18*, 7817.

Azusa Kondoh (近藤 梓). Kyoto University (Ph.D., 2010). Postdoctoral fellow at Max-Planck Institute für Kohlenforschung (2010). Assistant Professor at Tohoku University (2012). Associate Professor at Tohoku University (2020). [Field of research] Synthetic Organic Chemistry; Organocatalysis.

The Development of Asymmetric π-Lewis Base Catalysis

Ying-Chun Chen,* Wei Du, Zhi-Chao Chen
West China School of Pharmacy, Sichuan University, Chengdu 610041, China
E-mail: ycchen@scu.edu.cn

The activation of unsaturated systems by transition metal-based π-Lewis acids has been well established and extensively applied.[1] Transition metals also can donate their *d*-electrons to the empty anti-bonding molecular orbitals of double bonds (π*) via back-bonding after forming the η^2-complexes with olefins, but the relevant catalytic concept has not been disclosed.[2] Here we would like to uncover the development of a palladium(0)-based π-Lewis base activation strategy for diverse electron-neutral or even electron-poor diene systems, which can be HOMO-raised and attack various electrophiles enantioselectively in a vinylogous pattern. Some auto-tandem palladium catalysis can be realized to construct the products with higher molecular complexity.[3]



References

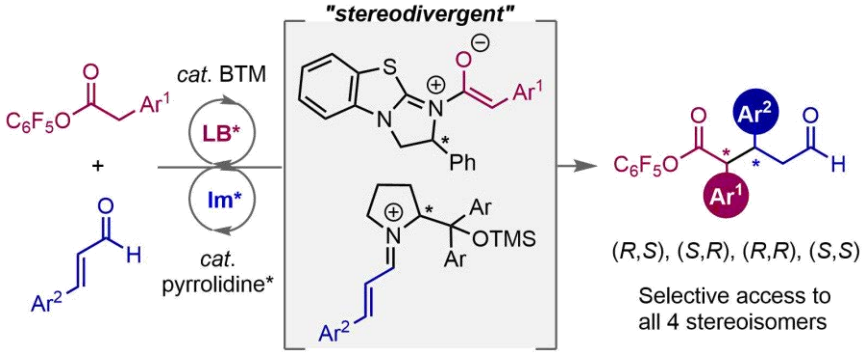
1. Yamamoto, Y. *J. Org, Chem.* **2007**, *72*, 7817.
2. Liebov, B. K.; Harman, W. D. *Chem. Rev.* **2017**, *117*, 13721.
3. (a) Xiao, B.-X.; Jiang, B.; Yan, R.-J.; Zhu, J.-X.; Xie, K.; Gao, X.-Y.; Ouyang, Q.; Du, W.; Chen, Y.-C. *J. Am. Chem. Soc.* **2021**, *143*, 4809; (b) He, Q.; Zhu, L.; Yang, Z.-H.; Zhu, B.; Ouyang, Q.; Du, W.; Chen, Y.-C. *J. Am. Chem. Soc.* **2021**, *143*, 17989; (c) Yang, X.-X.; Yan, R.-J.; Ran, G.-Y.; Chen, C.; Yue, J.-F.; Yan, X.; Ouyang, Q.; Du, W.; Chen, Y.-C. *Angew. Chem., Int. Ed.* **2021**, *60*, 26762; (d) Zhu, J.-X.; Chen, Z.-C.; Du, W.; Chen, Y.-C. *Angew. Chem. Int. Ed.* **2022**, *61*, e202200880.

Ying-Chun Chen (陈应春). Sichuan University (Ph.D, 2001). Professor (2004). [Asymmetric catalysis] Organic Chemistry.

Catalytic Stereodivergent C–C Bond Formations by Asymmetric Conjugate Additions

Sarah Yunmi Lee*
Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea
E-mail: sarahyunmi@yonsei.ac.kr

The control of stereoselectivity has been one of the central goals in synthetic organic chemistry due to the presence of chiral molecules in a wide range of natural products and pharmaceuticals. Despite remarkable advances in asymmetric synthesis, the development of catalyst-controlled processes that precisely control relative and absolute configurations of multiple stereocenters has been a persistent challenge. In this seminar, I describe methods for the stereodivergent carbon-carbon bond formation catalyzed synergistically by two chiral catalysts that furnishes 1,5-difunctionalized compounds containing two adjacent stereocenters. By altering the relative chirality of catalyst combinations, all four stereoisomers of the products are accessible with high enantio- and diastereoselectivity.



References
1. Kim, B.; Kim, Y.; Lee, S. Y. *J. Am. Chem. Soc.* **2021**, *143*, 73–79;

Sarah Yunmi Lee (이윤미). Massachusetts Institute of Technology (Ph.D., 2014). NIH Postdoctoral fellow at UC Berkeley (2015-2017). Assistant professor at Yonsei University (2018-present). [Field of research] catalysis, stereoselective synthesis

Statistical Analysis: A New Perspective on Stereoselective Glycosylation Reactions

Cheng-Chung Wang*
Institute of Chemistry, Academia sinica, Taipei 115, Taiwan
E-mail: wangcc@chem.sinica.edu.tw

Carbohydrates are ubiquitous biomolecules that mediate numerous biological processes and exhibit important pathogenic effects. However, chemical synthesis of glycoconjugates has been hampered by challenges in glycosylation reaction, of which the stereoselectivity and yield are paramount but unpredictable. We develop a database composed of relative reactivity value (RRV)[1-5] and acceptor nucleophilic constant (AKa)[6] to quantify the reactivity of glycosyl donors and nucleophilicity of hydroxyl groups in glycosylation influenced by the steric, electronic and structural effects, providing a connection between experiments and computer algorithm. A diverse range of glycosylation donors and acceptors with well-defined reactivity and promotors were organized and processed by the designed software program "GlycoComputer" for prediction of glycosylation reaction without involving sophisticated computational processing (Figure 1). The applicability of this system was further tested by the synthesis of a Lewis A skeleton to show that the stereoselectivity and yield can be accurately estimated.[6]

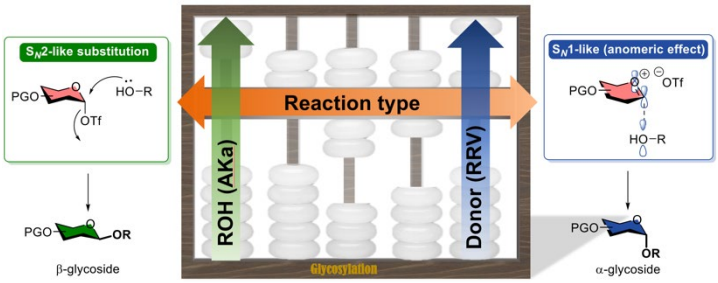
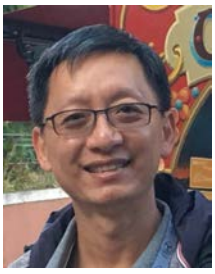


Figure 1. A GlycoComputer Platform

References

1. Chang, C.-W.; Wu, C.-H.; Lin, M.-H.; Liao, P.-H.; Chang, C.-C.; Chuang, H.-H.; Lin, S.-C.; Lam. S.; Verma, V. P.; Hsu, C.-P.;* Wang, C.-C.* *Angew. Chem. Int. Ed.* **2019**, *58*, 16775-16779.
2. Chang, C.-W.; Lin, M.-H.; Wu, C.-H.; Chiang, T.-Y.; Wang, C.-C.* *J. Org. Chem.* **2020**, *85*, 15945-15963.
3. Chang, C.-W.; Lin, M.-H.; Wang, C.-C.* *Chem. Eur. J.* **2021**, *27*, 2556-2568.
4. Asressu, K. H.; Chang, C.-W.; Lam, S.; Wang, C.-C.* *Eur. J. Org. Chem*. **2021**, 4525-4530.
5. Weldu, W. D.; Wang, C.-C.* *J. Org. Chem.* **2021**, *86*, 17906-17917.
6. Chang, C.-W.; Lin, M.-H.; Chan, C.-K.; Su, K.-Y.; Wu, C.-H.; Lo, W.-C.; Lam, S.; Cheng, Y.-T.; Liao, P.-H.; Wong, C-H.;* Wang, C.-C.* *Angew. Chem. Int. Ed.* **2021**, *60*, 12413-12423.



Cheng-Chung Wang (王正中). National Tsing Hua University; TIGP Academia Sinica (Ph.D, 2007). Associate Research Fellow, Academia Sinica (2017). Research Fellow, Academia Sinica (2022). Organic/ Carbohydrate Chemistry.

Stereoselective Synthesis with Protein as Metal Ligands

Nobutaka Fujieda
Osaka Metropolitan University, Nakamozu, Osaka, Japan
E-mail: fujieda@omu.ac.jp

In modern organic synthesis, asymmetric reactions have been achieved by exploiting the additives such as C_2-symmetric chiral ligands and precious metals. However, the resolution of compounds bearing multiple chiral centers is still challenging and a current topic of interest, considering increasing industrial and economic demands. To solve the problems, we have developed the metal-coordinating protein as easy-to-use macromolecular ligands for one of the promising methods to create artificial metalloenzymes.[1] Thermally stable cupin superfamily protein from thermophilic bacteria was repurposed as several enzymes by metal-swapping strategy employing the metal-binding promiscuity. Interestingly, this protein can accommodate a variety of transition metals including precious metals.[2] To fulfill diastereo- and enantio-selective reactions, we have attempted to exploit the library-like mutant-series of a cupin type protein as a screening strategy and created an efficient biocatalyst by harnessing the metal-containing protein.[3] Here, we present some topics about our recent results.

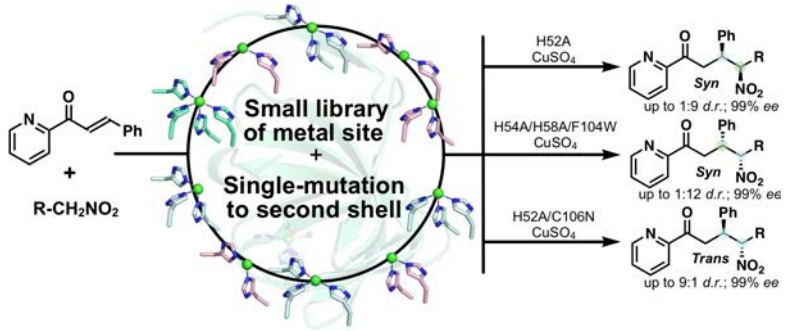


Fig. Schematic representation of stereodivergent synthesis with protein ligand library.

References

1. Fujieda, N., Schätti, J., Stuttfeld, E., Ohkubo, K., Maier, T., Fukuzumi, S., Ward, T.R., *Chem. Sci*., **2015**, 6, 4060.
2. Fujieda, N., Nakano, T., Taniguchi, Y., Ichihashi, H., Sugimoto, H., Morimoto, Y., Nishikawa, Y., Kurisu, G., Itoh, S., *J. Am. Chem. Soc.*, **2017**, 139, 5139.
3. Fujieda, N. Ichihashi, H., Yuasa, M., Nishikawa, Y., Kurisu, G., and Itoh, S., *Angew. Chem. Int. Ed.*, **2020**, 59, 7717.

Nobutaka Fujieda
Kyoto University (PhD, 2006), Designated Assistant Professor at Kyoto University Pioneering Research Unit for Next Generation, Assistant Professor at Osaka University (2009), Associate Professor at Osaka Prefecture University (2017), Full Professor at Osaka Metropolitan University (2021).
[Field of research] Bioinorganic Chemistry, Protein Chemistry, Enzymology, and Biocatalytic Chemistry.

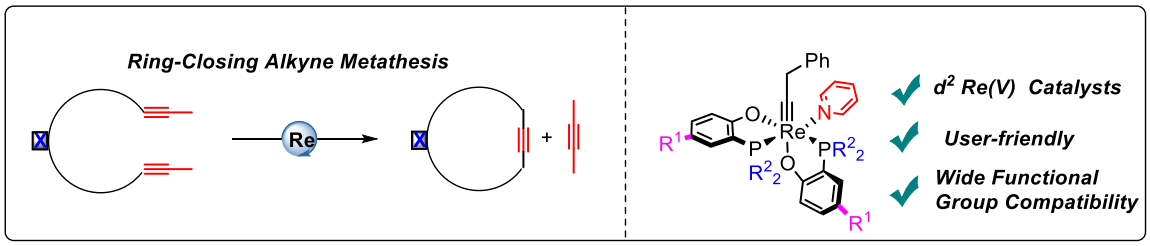
Alkyne Metathesis with Re(V) Alkylidyne Complexes

Guochen Jia

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Email: chjiag@ust.hk

Alkyne metathesis reactions are synthetically very useful reactions for making molecules with an alkynyl functional group. The state-of-the-art catalysts for the transformation are those based on d^0 (high valent) Mo(VI)/W(VI) alkylidyne complexes (an alkylidyne ligand is viewed as a tianionic ligand). In view of the great success of non-d^0 ruthenium carbene complexes (a carbene ligand is viewed as a dianionic ligand) in olefin metathesis, it is highly desirable to search for alkyne metathesis catalysts based on low valent (non-d^0) alkylidyne complexes, which are expected to have the advantages of user-friendiness and broader functional group compatibility. In our efforts to develop alkyne metathesis reactions involving low valent alkylidyne complexes, we have synthesized a series of d^2 Re(V) alkylidyne complexes and studied their alkyne metathesis activity. It was found that the alkyne metathesis activity of these complexes varies significantly with the ligand environments. The most efficient catalysts are d^2 Re(V) alkylidyne complexes bearing two decorated phosphino-phenolates (PO) and a labile pyridine ligand. These Re(V) alkylidyne catalysts can promote homo-metathesis of functionalized internal alkyl- and aryl-alkynes, ring-opening of strained cyclic alkynes, as well as ring-closing alkyne metathesis of methyl-capped diynes forming macrocycles with ring size ≥ 12 efficiently. The Re(V) alkylidyne catalysts tolerate a wide range of functional groups including ethers, esters, ketones, aldehydes, alcohols, phenols, amines, amides and heterocycles, and the catalytic reactions could proceed normally in wet toluene.



References

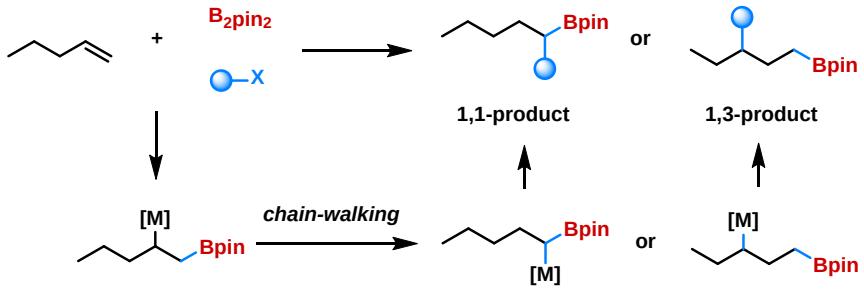
(1) Cui, M.; Sung, H. H. Y.; Williams, I. D.; Jia, G. *J. Am. Chem. Soc.* **2022**, *144*, 6349.

Guochen Jia received his PhD degree in 1989 from The Ohio State University. After carrying out postdoctoral work at University of Toronto and The University of Western Ontario, he joined The Hong Kong University of Science and Technology (HKUST) in 1992. He is now a Chair Professor of Chemistry at HKUST. His research interest is in the areas of organometallic chemistry and homogeneous catalysis.

Migratory Carboboration of Alkenes

Guoyin Yin*
Wuhan University, Wuhan, China
E-mail: yinguoyin@whu.edu.cn

The main research interests of Yin group at Wuhan University is developing transformations involving Chain-walking[1], particularly focusing on boron-related chain-walking reactions and the related mechanistic investigations. Some of the metal migration reactions catalyzed by Ni catalysts discovered by the Yin group have been shown in the scheme below[2-3]. In this talk, recent progresses will be presented.



Migratory carboboration of alkenes

References

1. Li, Y.; Wu, D.; Cheng, H.-G.*, Yin, G.* *Angew. Chem. Int. Ed.*, **2020**, *59*, 7990-8003.
2. (a) Wang, W.; Ding C.; Li, Y.; Li, Z.; Li, Y.; Peng, L.; Yin, G.* *Angew. Chem. Int. Ed.*, **2019**, *58*, 4612-4616. (b) Li, Y.; Pang, H.; Wu, D.; Li, Z.; Wei, H.; Fu, Y.; Yin. G.* *Angew. Chem. Int. Ed.*, **2019**. 58, 8872-8876. (c) Li, Y.; Wei, H.; Wu, D.; Yin. G.* *ACS Catal.* **2020**, *10*, 4888-4894. (d) Wang, W.; Ding, C.; Yin, G.* *Nat. Catal.* **2020**, 3,981. (e) Ding, C.; Ren, Y.; Long, J.; Yin, G.* *J. Am. Chem. Soc.*, **2021**, *143*, 20027-20034.
3. Li, Y.; Shi, H.; Wei, H.; Li, H.; Funes-Ardoiz, I.*; Yin, G.* *Science*, **2022**, *376*, 749-753.

Guoyin Yin (阴国印).
Northeast Agricultural University (Bachelor, 2002-2006).
Shanghai Institute for Organic Chemistry, CAS (PhD, 2006-2011)
Technical University of Munich (Postdoc, 2011-2013).
RWTH Aachen University (Postdoc, 2013-2014)
University of Delaware (Postdoc, 2014-2016)
Wuhan University (PI, 2016.08-2021.10).
Wuhan University (Professor, 2021.11-now)

Transition-Metal Catalysis

Competence of Diborene Compounds in Small Molecules Activation and Catalytic Hydroboration

Cheuk-Wai So*
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore
E-mail: CWSo@ntu.edu.sg

The use of an *N*-phosphinoamidinato NHC-diborene catalyst **1** for hydroboration is described. The *N*-phosphinoamidinato NHC-diborene compound **1** can stoichiometrically activate ammonia-borane and carbon dioxide. It also showed catalytic capability. 2 mol% of **1** catalyzed hydroboration of carbon dioxide (CO_2) with pinacolborane (HBpin) in deuterated benzene (C_6D_6) at 110 °C (Conversion: >99%), which afforded methoxyborane [pinBOMe] (Yield: 97.8%, TOF: 33.3 h^{-1}) and bis(boryl)oxide [$(pinB)_2O$]. In addition, 5 mol% of **1** catalyzed N-formylation of secondary and primary amines by carbon dioxide and pinacolborane to yield the N-formamides (Average yield: 91.6%, TOF: 25.9 h^{-1}). Moreover, **1** showed chemoselectivity toward catalytic hydroboration of carbonyl compounds. In mechanistic studies, the B=B double-bond in compound **1** activated the substrates, the intermediates of which then underwent hydroboration with pinacolborane to yield the products and regenerate catalyst **1**.

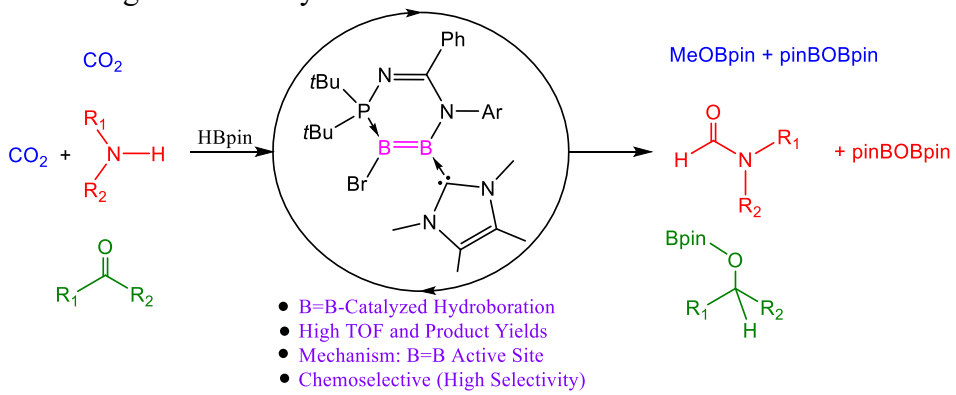


Figure 1. Catalytic hydroboration mediated by an *N*-phosphinoamidinato NHC-diborene catalyst **1**

References

1. Fan, J.; Mah, J.-Q.; Yang, M.-C.; Su, M.-D.; So, C.-W. A N-Phosphinoamidinato NHC-Diborene Catalyst for Hydroboration. *J. Am. Chem. Soc.* **2021,** *143*, 4993.

Cheuk-Wai So. The Chinese University of Hong Kong (PhD, 2003). Associate Professor, Nanyang Technological University (2016 - current). Field of research: Main-Group Chemistry.

Cross-Electrophile Coupling Involving R_3Si-Cl and R_3Ge-Cl

Xing-Zhong Shu*
State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, 222 South Tianshui Road, Lanzhou, 730000, China.
E-mail: shuxingzh@lzu.edu.cn

Chlorosilanes and chlorogermanes are raw materials, but their coupling reactions remain a long-standing challenge for the synthetic community. In 2020, we reported a cross-electrophile C–Si coupling of chlorosilanes by nickel catalysis.[1] This work has established a new platform for the synthesis of organosilanes from carbon electrophiles and chlorosilanes. Various alkenyl and aryl electrophiles coupled well with vinyl chlorosilanes under nickel catalysis. The use of alkyl halides as coupling partners led to the formation of functionalized alkylsilanes.[2] In general, these reactions are dependent on vinyl chlorosilanes. To overcome this limitation, we recently reported a nickel-catalyzed cross-electrophile silylation of chlorohydrosilanes.[3] The reaction proceeded through unconventional cleavage of Si–Cl over Si–H, offering new access to aryl- and alkenylhydrosilanes. Encouraged by these findings, we have recently extended this chemistry to chlorogermanes.[4] Various chlorogermanes coupled well with aryl and alkenyl electrophiles, and the coupling of alkyl bromides with R_3Ge–Cl afforded alkylgermanes.

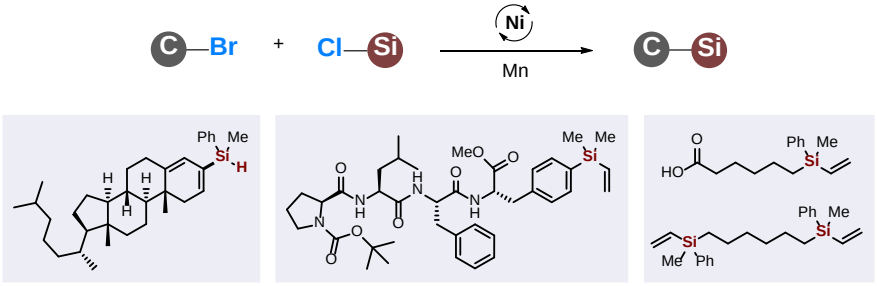
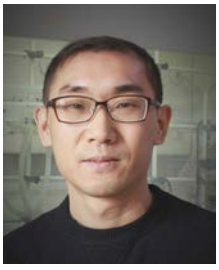


Figure 1. Cross-electrophile coupling of chlorosilanes

References

1. Duan, J.; Wang, K.; Shu, X.-Z.* *et. al*. *Angew. Chem. Int. Ed.* **2020**. *59,* 23083.
2. Duan, J.; Wang, Y.; Shu, X.-Z.* *et. al*. *Org. Lett.* **2021**, *23*, 7855.
3. Zhao, Z.-Z.; Pang, X.; Shu, X.-Z.* *et. al*. *Angew. Chem. Int. Ed.* **2022**, 61, 202200215.
4. Su, P.-F.; Wang, K.; Shu, X.-Z.* *et. al*. *Angew. Chem. Int. Ed*. **2021**, *60*, 26571.



Xing-Zhong Shu (舒兴中). Lanzhou University (Ph. D., 2010).

Postdoc, University of Wisconsin-Madison, 2010─2012
Postdoc, University of California, Berkeley, 2012–2015
Professor and Principal Investigator, Lanzhou University, 2015─Present

Research interests include the cross-electrophile coupling, base metal catalysis, and asymmetric catalysis.

Development of a Novel Light-up G-quadruplex Binding Compound

Keisuke Iida,* Ayano Sasaki, Shunsuke Ishida, and Takayoshi Arai
Department of Chemistry, Graduate School of Science, Chiba University
E-mail: kiida@chiba-u.jp

G-quadruplexes (G4s) are higher-order structures of nucleic acids formed from Hoogsteen base pairs in guanine-rich sequences. G4s regulate a wide variety of biological processes, including transcription, translation, replication, epigenetic reprogramming, and stress granule formation.[1] G4-binding small molecules (G4 ligands) have been played a key role in the progress of this field. Notably, light-up G4 ligands whose fluorescence is selectively enhanced when interacting with G4s are useful for high-sensitivity detection. Therefore, selective and sensitive light-up G4 ligands are required. Moreover, cellular imaging of dynamically forming G4s in biomolecular condensates such as stress granules using small molecules has been poorly investigated. Herein, we present a fluorescent light-up probe with the ability to selectively stabilize G4s and enhance fluorescence upon G4 binding.

The foci of the probe were mainly observed in the nucleoli. These were co-localized with anti-fibrillarin antibodies and anti-G4 antibodies (BG4). Moreover, we tested detection of G4 in stress granules using the developed probe. Stress granules were induced through treatment with not only thapsigargin, but also known G4 ligands (pyridostatin, RHPS4, and BRACO-19). In the stress granules, co-localization between the probe, BG4, and stress granule markers (TIA1 and G3BP1) was detected. We present a practical light-up probe for G4s in stress granules, providing potential targets for G4 ligands.

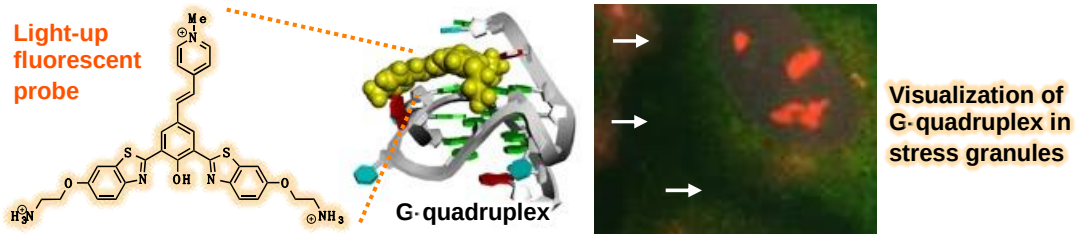


Figure 1. Structure of developed fluorescent probe and schematic image in this study.

References

1. Varshney, D., Spiegel, J., Zyner, K., Tannahill, D. & Balasubramanian, S. *Nat. Rev. Mol. Cell Biol.* **2020**, *21*, 459–474.

Keisuke Iida (飯田 圭介). Soft Molecular Activation Research Center (SMARC), Chiba Iodine Resource Innovation Center (CIRIC), Molecular Chirality Research Center (MCRC), Department of Chemistry, Graduate School of Science, Chiba University 1-33 Yayoi, Inage, Chiba 263-8522, Japan (Assistant Professor). [Field of research] Synthetic Organic Chemistry, Chemical Biology, Nucleic Acids, Fluorophore, G-quadruplex.

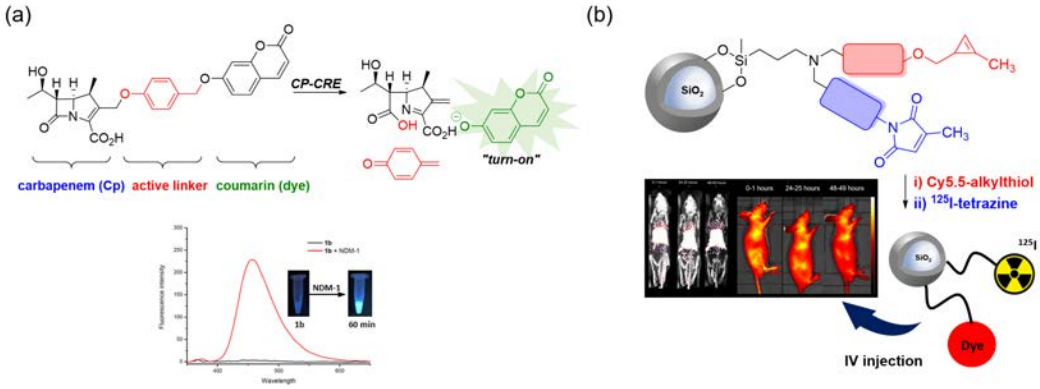
Development of Chemical Tools for Biomedical Applications Using Synthetic Organic Chemistry

Sun-Joon Min*
Department of Chemical & Molecular Engineering/Applied Chemistry, Hanyang University (ERICA), Ansan, 15588, South Korea
E-mail: sjmin@hanyang.ac.kr

My research group is expanding the knowledge of synthetic organic chemistry into various biological applications such as therapeutics, diagnostics, chemical sensors, and drug delivery. Accordingly, two chemical probes, most recently developed in my laboratory will be described in this presentation.

First, the development of novel fluorogenic β-lactamase substrates for the specific detection of the β-lactamase-producing antibiotic resistant bacteria will be presented.[1] This chemical probes consist of β-lactam core scaffolds, appropriate linkers and fluorescence dyes, which can turn on fluorescence signal upon hydrolysis by β-lactamases. The result from clinical assessment of our probes indicated that they would provide practical screening tools for detection of the antibiotic resistant bacteria.

Second, I will focus on the development of new bifunctional silica nanoparticles (SNPs) for in vivo multimodal imaging.[2] The dual linker-grafted SNP, prepared by traceless Staudinger ligation and $Sc(OTf)_3$-catalyzed siloxane formation, successfully loaded both fluorescence dye and isotope on the surface via *one-pot* consecutive bioorthogonal reactions. Positron emission tomography/computed tomography (PET/CT) and fluorescent imaging study of this SNP showed a prolonged circulation in mice, which is conducive to the systemic delivery of therapeutics.



Scheme 1. Fluorogenic β-lactamase substrates (a) and bifunctional SNPs (b)

References

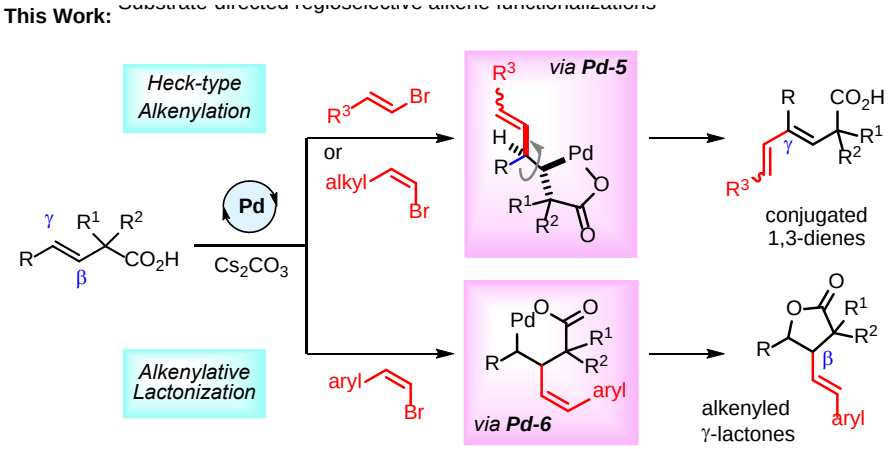
1. Kim, J.; Kim, Y.; Abdelazem, A. Z.; Kim, H. S.; Kim, J. O.; Park, Y.-J.; Min, S.-J. *Bioorg. Chem.* **2020**, *94,* 10405.
2. Lee, K.; Kim, J.; Heo, I.; Kim, S. J.; Jang, S.; Lee, H.-Y.; Jang, K.-S.; Yang, C.-S.; Lee, Y.; Yoo, W. C.; Min, S.-J. *Biomater. Sci.* **2022**, *in press* (10.1039/d2bm00258b)

Sun-Joon Min (민선준). University of California, Los Angeles (PhD, 2005). Columbia University (Postdoc, 2005-2008). Korea Institute of Science and Technology (Principle Research Scientist, 2008-2015). Hanyang University (Professor. 2015-present). [Field of research] Synthetic Organic Chemistry, Medicinal Chemistry, Bioorganic Chemistry.

Substrate-Directed Regioselective Alkene Functionalizations of (*E*)-β,γ-Unsaturated Carboxylic Acids

Chih-Ming Chou,*
Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung 81148, Taiwan
E-mail: cmchou@nuk.edu.tw

Internal alkenes functionalization with high control of the regio- and stereoselectivity has remained challenging owing to the low inherent reactivity of electronically unbiased double bond. Herein, we report a carboxylate-directed regioselective Heck-type alkenylation and alkenylative lactonization of (*E*)-β,γ-unsaturated carboxylic acids by simply substrate control. (*E*) and (*Z*) vinyl bromides avail to five- and six-membered carboxylate palladacyles, access to fully stereocontrolled conjugated 1,3-dienes and alkenyled γ-lactones which are often found in natural products and bioactive molecules. Experimental studies and density functional theory calculations disclosed the excellent regioselectivity is strongly influenced by the steric factors of reactants involved in the palladacycle intermedi-ates. In addition, no exogenous bidentate directing group and ligand are required for this transformation.



References
1. Tsai, H.-C.; Huang, Y.-H.; Chou, C.-M. *Org. Lett.* **2018**, *20*, 1328.
2. Wang, Y.-C.; Huang, Y.-H.; Tsai, H.-C.; Basha, R. S.; Chou, C.-M. *Org. Lett.* **2020**, *22*, 6765.
3. Tsai, J.-J.; Huang, Y.-H.; Chou, C.-M.* *Org. Lett.* **2021**, *23*, 9468.

Chih-Ming Chou (周志明). National Taiwan University (PhD, 2007). [Field of research] Organic Chemistry.

Academic Careers

2015-2018 Assistant Professor, Department of Applied Chemistry, National University of Kaohsiung

2018-2022 Associate Professor, Department of Applied Chemistry, National University of Kaohsiung

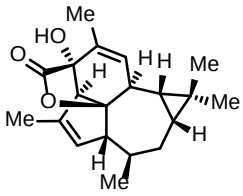
2022-present Professor, Department of Applied Chemistry, National University of Kaohsiung

Total Synthesis of Polycyclic Natural Products

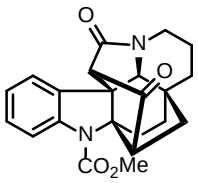
Yanxing Jia
State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, and Chemical Biology Center, Peking University, Beijing 100191, China
E-mail: yxjia@bjmu.edu.cn

Euphorikanin A is an unprecedented diterpenoid lactone which possesses a highly strained 5/6/7/3-fused tetracyclic skeleton bearing a bridged [3.2.1]-*γ*-lactone moiety. We have achieved a bioinspired total synthesis of (+)-euphorikanin A.[1] Key transformations include stereoselective alkylation and aldol condensation to install the main stereocenters, an intramolecular nucleophile-catalyzed aldol lactonization of carboxylic acid-ketone to assemble the five-membered ring, a McMurry coupling to construct the seven-membered ring, and a biomimetic benzilic acid type rearrangement to form the bridged [3.2.1]-*γ*-lactone moiety.

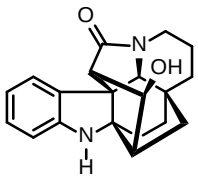
N-Carbomethoxy-10,22-dioxokopsane, epikopsanol-10-lactam, 10,22-dioxokopsane and *N*-methylkopsanone are four kopsane indole alkaloids which share a complex heptacyclic caged ring system. We have achieved their total synthesis.[2] Key transformations include an asymmetric Diels-Alder reaction to assemble the central bicyclo[2.2.2]octane moiety, a SmI_2-mediated cascade reduction/aldol reaction to construct the five-membered ring, and a late-stage cascade reductive amination/cyclization to establish the highly strained caged ring system.



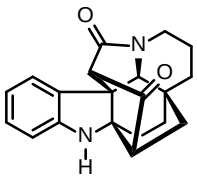
euphorikanin A



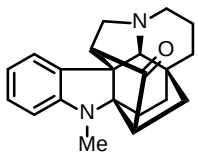
N-carbomethoxy-10,22-dioxokopsane



epikosanol-10-lactam



10,22-dioxokopsane



N-methylkopsanone

References
1. Chen, Z.; Zhao, K.; Jia, Y. *Angew. Chem. Int. Ed.* **2022**, *61*, e202200576.
2. Qin, B.; Lu, Z.; Jia, Y. *Angew. Chem. Int. Ed.* **2022**, *61*, e202201712.

Yanxing Jia (贾彦兴). Lanzhou University (B.Sc, 1997), Lanzhou University (Ph.D. 2002), ICSN, CNRS, France (Postdoc. 2002-2007). Associate professor of Peking University (2007-2011). Professor of Peking University (2011-). [Field of research] (1) Natural product total synthesis, (2) Medicinal chemistry and chemical biology of bioactive natural products, and (3) Synthetic method.

Chemistry of Reactive Group 13 Element Compounds in Low Oxidation State: Diborane(4) and Al-centered anion

Makoto Yamashita
Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan
E-mail: makoto@oec.chembio.nagoya-u.ac.jp

Recently, we reported tetraaryldiborane(4), (*o*-tol)$_2$B-B(*o*-tol)$_2$ (**1**). This compound showed unique reactivity towards H–H bond in H_2, C≡O triple bond in carbon monoxide, and N=N double bond. The strong Lewis acidity of (*o*-tol)$_2$B-B(*o*-tol)$_2$ was originated from lowering LUMO level due to overlapping two vacant p-orbitals as supported by DFT calculations. On the other hand, we recently report synthesis of dialkylalumanylpotassium species **2** by means of a bulky cyclic dialkyl ligand. This compound has a polarized Al–K bond with Al^- and K^+ character. In this talk, characteristic reactivities of these compounds in low oxidation state and their reaction mechanisms will also be presented.

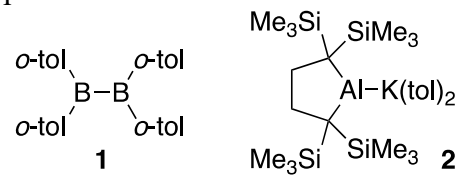


Figure 1. Structure of tetraaryldiborane **1** and alkyl-substituted Al anion **2**.

References

1. (a) Tsukahara, N.; Asakawa, H.; Lee, K.-H.; Lin, Z.; Yamashita, M., *J. Am. Chem. Soc.* **2017,** *139*, 2593. (b) Katsuma, Y.; Tsukahara, N.; Wu, L.; Lin, Z.; Yamashita, M., *Angew. Chem. Int. Ed.* **2018,** *57*, 6109. (c) Akiyama, S.; Yamada, K.; Yamashita, M., *Angew. Chem. Int. Ed.* **2019,** *58*, 11806. (d) Katsuma, Y.; Wu, L.; Lin, Z.; Akiyama, S.; Yamashita, M., *Angew. Chem. Int. Ed.* **2019,** *58*, 317. (e) Akiyama, S.; Ikemoto, S.; Muratsugu, S.; Tada, M.; Yamashita, M., *Organometallics* **2020,** *39*, 500. (f) Akiyama, S.; Yamashita, M., *Chem. Lett.* **2020,** *49*, 721. (g) Suzuki, A.; Guo, X.; Lin, Z.; Yamashita, M., *Chem. Sci.* **2021,** *12*, 917. (h) Suzuki, A.; Wu, L.; Lin, Z.; Yamashita, M., *Angew. Chem. Int. Ed.* **2021,** *60*, 21007.
2. (a) Kurumada, S.; Takamori, S.; Yamashita, M., *Nat. Chem.* **2020,** *12*, 36. (b) Sugita, K.; Nakano, R.; Yamashita, M., *Chem. Eur. J.* **2020,** *26*, 2174. (c) Sugita, K.; Yamashita, M., *Chem. Eur. J.* **2020,** *26*, 4520. (d) Sugita, K.; Yamashita, M., *Organometallics* **2020,** *39*, 2125. (e) Kurumada, S.; Sugita, K.; Nakano, R.; Yamashita, M., *Angew. Chem. Int. Ed.* **2020,** *59*, 20381. (f) Kurumada, S.; Yamashita, M., *J. Am. Chem. Soc.* **2022,** *144*, 4327.

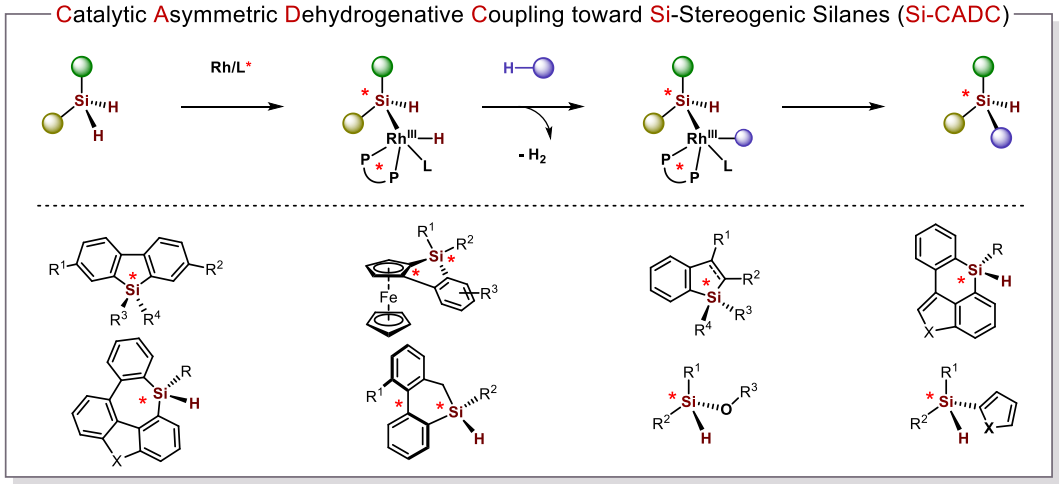
YAMASHITA, Makoto (山下　誠). Hiroshima University (Ph.D., 2002). JSPS research fellow (2001-2004), Research Associate, Assistant Professor, and Lecturer (2004-2011, The University of Tokyo, w. Prof. NOZAKI Kyoko), Associate Professor and Professor (2011-2016, Chuo University), Professor (2016-current, Nagoya University). Main Group Chemistry, Organometallic Chemistry, Catalysis.

Catalytic Enantioselective Construction of Si-Stereogenic Silanes

Chuan He,*
Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China
E-mail: hec@sustech.edu.cn

Chiral molecules play significant roles in areas ranging from life, biology, medicine to materials science. Compared to the extensive studies of chiral compounds bearing carbon-stereogenic centers, synthesis and application of silicon-stereogenic silanes have been much less explored. Due to the inherent properties of the silicon atom, construction of enantioenriched chiral organosilanes bearing a stereocenter at silicon has always been challenging.[1]

During the last three years, our group has developed a series of catalytic asymmetric dehydrogenative coupling reactions for the synthesis of silicon-stereogenic silanes (Si-CADC) with high efficiency.[2] Key to the success is the use of Rh(I) catalyst equipped with bulky and rigid chiral diphosphine ligand for the discrimination of the enantiotopic Si-H bonds of dihydrosilanes. This general Si-CADC protocol unlocks a facile platform toward diverse Si-stereogenic silanes, that could find various applications in many areas.



References

1. Igawa, K.; Tomooka, K. Chiral Silicon Molecules, In *Organosilicon Chemistry: Novel Approaches and Reactions*; Wiley, Germany, **2019**, 495.
2. He, C. et al. *Angew. Chem., Int. Ed.* **2022**, *61*, e202204912; *Angew. Chem., Int. Ed.* **2022**, *61*, e202117820; *J. Am. Chem. Soc.* **2021**, *143*, 5301; *Angew. Chem., Int. Ed.* **2021**, *60*, 13887; *Nat. Commun.* **2021**, *12*, 1249; *J. Am. Chem. Soc.* **2020**, *142*, 13459; *Angew. Chem., Int. Ed.* **2020**, *59*, 22217.

Chuan He (何川). Wuhan University (Ph.D., 2008-2013). University of Cambridge (Postdoc, 2013-2017). Southern University of Science and Technology (Associate Professor, 2018-). [Field of Research] Chiral Organosilicon Chemistry, Chiral Organoboron Chemistry, Asymmetric Catalysis, Transition-Metal Catalysis, Chiral Organic Materials

Catalytic Diazo-yne Carbocyclization for the Expeditious Assembly of Carbocyclic Frameworks

Xinfang Xu*
Guangdong Key Laboratory of Chiral Molecule and Drug Discovery, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China
E-mail: xuxinfang@mail.sysu.edu.cn

Carbocyclic frameworks are pervasive motifs in various areas of synthetic chemistry, medicinal chemistry, and material sciences. Therefore, efforts have been devoted to the development of a variety of catalytic methods for the direct construction of cyclic architectures in past decades. The gold-catalyzed alkyne carbocyclization is one of the practical methods in this area.[1] As the continuation of our interest in catalytic alkyne multi-functionalization,[2] two distinct catalytic protocols have been formulated with alkyne-tethered diazo compounds: the carbene/alkyne metathesis (CAM) process (Path A)[3] and the catalytic diazo-yne carbocyclization (Path B),[4] both delivering the unique vinyl metal carbene intermediate **II**. Herein, we would like to present our discovery in the latter approach, the catalytic diazo-yne carbocyclization pathway (Path B), which directly formed the key vinyl metal carbene **II** without going through the carbene species **I**, leading to a practical method for the expeditious assembly of carbocyclic frameworks with structural diversity through intermolecular cascade reactions (Fig. 1).

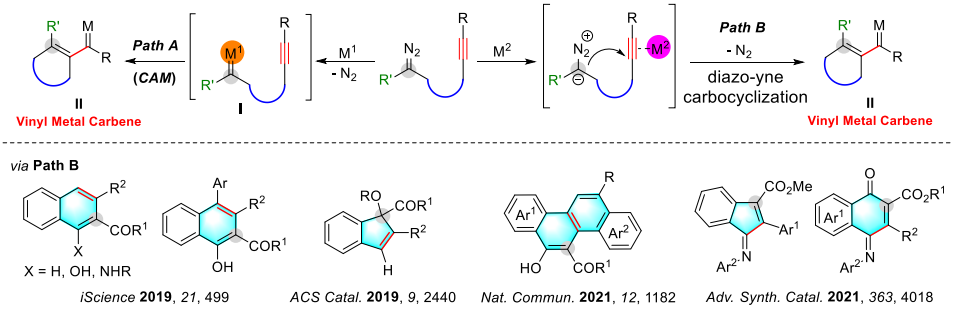


Fig. 1 Catalytic Diazo-yne Carbocyclization and Synthetic Applications

References

1. (a) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180; (b) Zhang, L. *Acc. Chem. Res.* **2014**, *47*, 877; (c) Dorel. R. Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028; (d) Ye, L. Zhu, X. Sahani, R. Xu, Y. Qian, P. Liu, R. *Chem. Rev.* **2021**, *121*, 9039; (e) Gorin, D. J. Toste F. D. *Nature* **2007**, *446*, 395.
2. (a) Zhou, S. Li, Y. Liu, X. Hu, W. Ke, Z. Xu, X. *J. Am. Chem. Soc.* **2021**, *143*, 14703; (b) Bao, M. Chen, J. Pei, C. Zhang, S. Lei, J. Hu, W. Xn, X. *Sci. China Chem.* **2021**, *64*, 778; (c) Dong, G. Bao, M. Xie, X. Jia, S. Hu, W. Xu, X. *Angew. Chem. Int. Ed.* **2021**, *60,* 1992.
3. Pei, C. Zhang, C. Qian, Y. Xu, X. *Org. Biomol. Chem.* **2018**, *16*, 8677.
4. (a) Zhang, C. Li, H. Pei, C. Qiu, L. Hu, W. Bao, X. Xu, X. *ACS Catal.* **2019**, *9*, 2440; (b) Zhang, C. Hong, K. Dong, S. Pei, C. Zhang, X. He, C. Hu, W. Xu, X. *iScience* **2019**, *21*, 499; (c) Zhang, C. Hong, K. Pei, C. Zhou, S. Hu, W. Hashmi, A. S. K. Xu, X. *Nat. Commun.* **2021**, *12*, 1182.

Xinfang Xu (徐新芳). East China Normal University (bachelor, 2005, and PhD, 2010). Postdoctoral at University of Maryland with Prof. Michael P. Doyle (2010-2014). In 2014, full professor in Soochow University. Now he is working as a full professor in school of pharmaceutical sciences at Sun Yat-sen University. His research interests include carbene chemistry, asymmetric catalysis, and catalytic alkyne functionalization.

Regioselective Deaminative Allylation of Aliphatic Amines via Dual Cobalt and Organophotoredox Catalysis

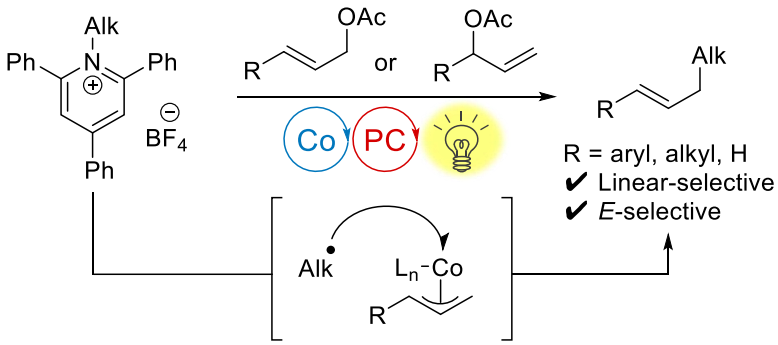
Masahiro Kojima 1,* Tomoyuki Sekino 1, Shunta Sato 1, Tatsuhiko Yoshino 12, Shigeki Matsunaga 12

1 Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, Japan

2 Global Station for Biosurfaces and Drug Discovery, Hokkaido University, Sapporo, Japan

E-mail: m-kojima@pharm.hokudai.ac.jp

Since the epoch-making study by Watson in 2017,[1] Katritzky salts, which are readily available from primary amines, have gained widespread attention as a useful precursor for C–C bond forming reactions. However, catalytic deaminative allylation of Katritzky salts has remained a challenge as carefully designed radicalophilic reagents were required to facilitate the transformation. Inspired by the metallaphotoredox-catalyzed allylation reactions,[2,3] we developed a cobalt-organophotoredox dual catalysis which enables regioselective allylation of Katritzky salts using simple allyl esters.[4] Mechanistic studies indicate the involvement of a π-allylcobalt complex as a radicalophile which mediates C–C bond formation.



References

1. Basch, C. H.; Liao, J.; Xu, J.; Piane, J. J.; Watson, M. P. *J. Am. Chem. Soc.* **2017**, *139*, 5313-5316.
2. Zhang, M.-M.; Wang, Y.-N.; Lu, L.-Q.; Xiao, W.-J. *Trends Chem.* **2020**, *2*, 764-775.
3. Contributions from our group: (a) Takizawa, K.; Sekino, T.; Sato, S.; Yoshino, T.; Kojima, M.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2019**, *58*, 9199-9203; (b) Sekino, T.: Sato, S.; Kuwabara, K.; Takizawa, K.; Yoshino, T.; Kojima, M.; Matsunaga, S. *Synthesis* **2020**, *52*, 1934-1946.
4. Sekino, T.; Sato, S.; Yoshino, T.; Kojima, M.; Matsunaga. S. *Org. Lett.* **2022**, *24*, 2120-2124. <Highlighted in *Synfacts* **2022**, *18*, 0644.>

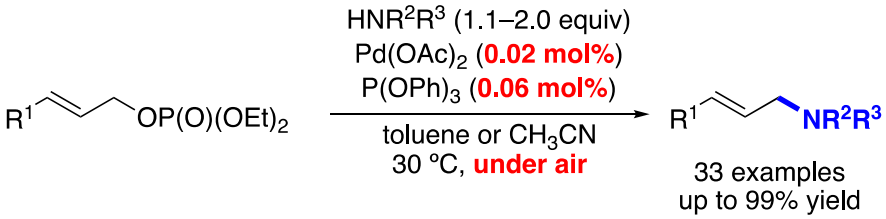
Masahiro Kojima (小島正寛). The University of Tokyo, Kanai Group (PhD, 2017). Postdoctoral researcher (UC Berkeley, Hartwig group. 2017-2018). Assistant Professor (Hokkaido University, Matsunaga group. 2018-present). [Field of research] Transition metal catalysis, Photochemistry.

Aerobic Allylic Amination Catalyzed by $Pd(OAc)_2/P(OPh)_3$ System with Low Catalyst Loading

Taiga Yurino,* Sunaho Saito, Mizuki Ichihashi, Takeshi Ohkuma*
Department of Applied Chemistry, Faculty of Engineering, Hokkaido University
Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido, Japan
E-mail: tyurino@eng.hokudai.ac.jp

Pd-catalyzed allylic substitution (Tsuji–Trost reaction) is one of the most fundamental strategies for constructing highly functionalized organic molecules. Allylic amination is a main family member of them.[1] It is well-known that the allylation reagents are activated by Pd(0) species to form π-allyl-Pd(II) intermediates, and those are the key electrophiles of the reaction. In the allylic amination, Pd(0) complexes or their ligands are often oxygen-sensitive, and thus the reaction conditions are kept avoiding from the aerobic oxidation in most cases.

We successfully demonstrated Pd-catalyzed Tsuji–Trost-type allylic amination under completely aerobic conditions with low catalyst loading.[2] The combination of $Pd(OAc)_2/P(OPh)_3$, and use of allylic phosphate as electrophile are crucial for the formation of the target allylic amines. The catalyst loading can be decreased into 0.02 mol%, and the TOF (turnover frequency) of the catalytic cycle was up to 30,000 h^{-1}. The Pd(0) complex, $Pd[P(OPh)_3]_3$, was quickly formed under atmospheric air. The complex oxidatively activates allylic phosphates to give the corresponding cationic π-allyl-Pd(II) intermediate. The ligand $P(OPh)_3$ has an electron withdrawing property, and thus the titled amination undergoes rapidly. Since the counter anion of phosphate has low coordination ability, the reverse reaction of π-allyl-Pd(II) intermediate to the starting compound was retarded. That is why the aerobic allylic amination undergoes well. On this opportunity, we will present the details of the reaction.



References
1. Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689–1708.
2. Yurino, T.; Saito, S.; Ichihashi, M.; Ohkuma, T. *J. Org. Chem.* **2022**, *87*, 2864–2872.

Taiga Yurino (百合野大雅). Kyoto University (Ph D., 2013). Research Associate, Osaka University (2013). Assistant Professor, Hokkaido University (2015). [Field of research] Organic Chemistry, Organometallic Chemistry, Synthetic Organic Chemistry.

Biosynthesis of Complicated Natural Products from Fungi

Yudai Matsuda*
Department of Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
E-mail: ymatsuda@cityu.edu.hk

Natural products are organic compounds produced by living organisms and have been a rich source for drug discovery and development. Our group has been intensively working on a class of natural products termed meroterpenoids, which are hybrid natural products that are partially derived from terpenoid origin. Notably, meroterpenoids derived from fungi exhibit an extremely wide range of structural diversity and biological activities.[1] Recent advance in genome sequencing technologies and the development of tools for biosynthetic studies have allowed the discovery of many biosynthetic gene clusters for fungal meroterpenoids and intensive research at the genetic/enzymatic level. Our continuous efforts toward understanding fungal meroterpenoid biosynthesis have discovered several fascinating enzymes that catalyze drastic structural rearrangement (Figure 1). For example, we recently identified the cytochrome P450 SetF responsible for the spirofuranone synthesis in setosusin biosynthesis and investigated its reaction mechanism by isotope-incorporation experiments and theoretical calculations.[2] Furthermore, the α-ketoglutarate-dependent dioxygenase BrvJ involved in the biosynthesis of brevione E was found to catalyze the ring-expansion reaction to install the dihydrotropone moiety (unpublished data).

In this poster, I will summarize our general strategy to study fungal natural product biosynthesis using *Aspergillus oryzae* heterologous expression system and how we identified the intriguing enzymes mentioned above. The plausible reaction mechanisms of these reactions will also be discussed.

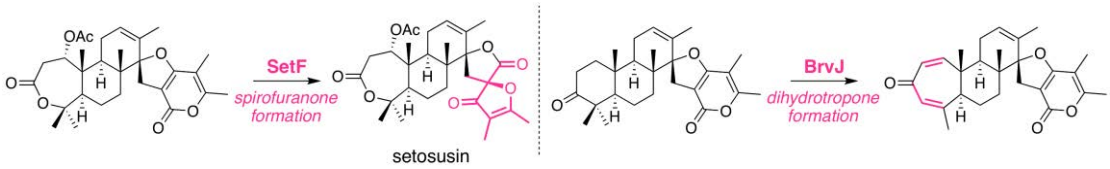


Figure 1. Reactions catalyzed by SetF and BrvJ

References
1. Matsuda, Y., Abe, I. *Nat. Prod. Rep.* **2016**, *33*, 26-53.
2. Wei, X. *et. al*., *J. Am. Chem. Soc.* **2021**, *143*, 17708–17715.

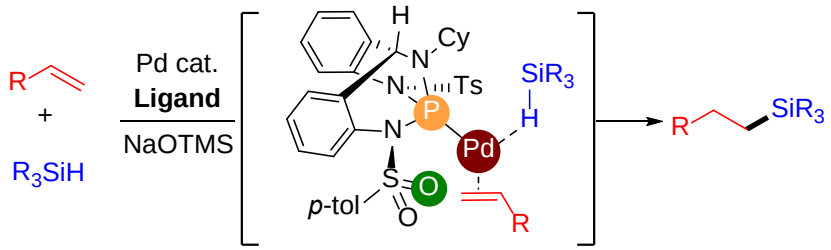
Yudai Matsuda (松田侑大). The University of Tokyo (Ph.D. in Pharmaceutical Sciences, 2015). Assistant Professor, The University of Tokyo (2013-2015). Postdoc, Technical University of Denmark (2015-2017). Project Researcher, The University of Tokyo (2017-2018). Assistant Professor, City University of Hong Kong (2018-present). [Field of research] Natural Product Chemistry.

Hemilabile P, O-Ligands for Pd-Catalyzed Hydrosilylation of Unactivated Alkenes

Hyunwoo Kim,* Sanghyup Seo
Department of Chemistry, KAIST, Daejeon 31313, Korea
E-mail: hwkim@kaist.edu

Phosphorus ligands are important because the catalytic activity and selectivity of metal catalysts can be controlled by the ligands. In this respect, hybrid phosphorus-hetero atom mixed ligands, such as phosphine-oxazoline ligands, have been creatively developed. Among various mixed ligand types, P,O-type hybrid ligands combine a soft phosphorus atom and a hard oxygen atom, providing complementary donor and acceptor properties to the metal center. For the oxygen donor, acetal, sulfonyl, amido, and ether moieties are commonly utilized.

In this presentation, we have developed a new P,O-type hemilabile ligand based on *N*-ditosyl bicyclic bridgehead phosphorus triamide. In addition to the π-acceptor ability of the P atom, the donor O atom can be readily dissociated to provide a vacant site for substrate coordination. With the new P,O-ligands, we investigated Pd-catalyzed hydrosilylation of unactivated alkenes with tertiary alkylsilanes. The mixed P,O ligands are found to be highly efficient and the origin of selectivity has been demonstrated by DFT calculation.



• *Unactivated alkenes* • *Intermediate stabilization effect of ligand* • *upto 96% yield*
• *Tertiary silanes* • *20 examples*

References
1. Seo, S.; Kim, H.* *Chem. Commun.* **2021**, 57, 11240
2. (a) Shin, T.; Kim, H.; Kim, S.; Lee, A.; Seo, M.-S.; Choi, J.; Kim, H.; Kim, H.* *Org. Lett.* **2019**, *21*, 5789. (b) Yu, S.; Shin, T.; Zhang, M.; Xia, Y.; Kim, H*; Lee, S.* *Org. Lett.* **2018**, *20*, 7563. (c) Lee, A.; Kim, H.* *J. Am. Chem. Soc.* **2015**, *137*, 11250.

Hyunwoo Kim (김현우)
University of Toronto (Ph.D 2009), Columbia University (Postdoc, 2010), KAIST (Assiatnat & Associate Professor, 2011-present)
[Field of research] Asymmetric Chemistry, Chiral Analysis, Ligand Development

Surface Modification of MOF-based Catalysts for Size-selective Organic Reactions

Min Kim*
Department of Chemistry, Chungbuk National University, Korea
E-mail: minkim@chungbuk.ac.kr

MOFs (metal-organic frameworks) are emerging porous catalytic platform, which are constructed from coordination bonds between metal and ligands. In addition to sieving effect of MOF's pore, the tunability of structure is also considered as a great advantage of MOFs. In specific, the organic ligand parts of MOFs (i.e., strut of framework) could be modified and decorated with functional groups in relatively ease manners toward target applications such as catalytic reactions.[1] The specific functionalizations with organometallic species and the dispersion of metal catalyst to porous MOF structures allowed a highly active, heterogeneous catalysts for organic transformations.[2]
In addition, the positional functionalizations (e.g., surface vs. core) are possible in this hybrid-heterogeneous material. The catalytic efficiency and substrate selectivity are directly related with the position of catalytic species.
In this presentation, our recent developments for selective MOF-based catalysts for oxidation of primary alcohols and carbonyl-ene reactions will be covered. In case of the surface-deactivated MOF catalyst for oxidation, the enhanced size-selectivity of substrate was achieved from the alcohol mixture,[3] and the poisoning strategy will be discussed for selective carbonyl-ene reactions.

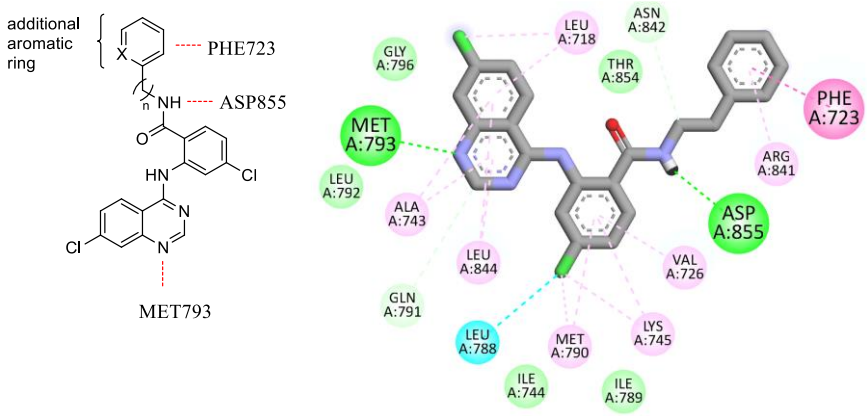
References
1. Kalaj, M.; Cohen, S. *ACS Cent. Sci*. **2020**, *6*, 1046.
2. Jeoung, S.; Kim, S.; Kim, M.; Moon, H. R. *Coord. Chem. Rev*. **2020**, *420*, 213377.
3. Kim, S.; Lee, J.; Jeoung, S.; Moon, H. R.; Kim, M. *Chem. Eur. J*. **2020**, *26*, 7568.

Min Kim (김 민). KAIST (2004 B.Sc., 2006 M. Sc., 2010 Ph.D.). Assistant (2012-2016), Associate (2016-2020), Full (2020-present) professor in Chungbuk National University. [Field of research] Organic Methodology and Metal-Organic Frameworks.

Overcoming Resistance to EGFR Inhibitors in NSCLC: Structural Optimization of Quinazoline Scaffold

Muhammad Kumayl Abdulwahab,* Rashidi Dzulkeflee, Ke Han Tan, Kok Hoong Leong, Choon Han Heh, Azhar Ariffin
Department of Chemistry, Universiti Malaya
E-mail: kumaylabdul@um.edu.my

One of the strategies in molecular targeted therapy to treat non-small cell lung cancer (NSCLC) is the inhibition of epidermal growth factor receptor (EGFR). Unfortunately, current reversible EGFR inhibitors have been resisted by acquired T790M mutation. Although irreversible EGFR inhibitors have been introduced to overcome the initial resistance, they have also been resisted by yet another acquired mutation, C797S. It is understood that the acquired T790M mutation resisted the current reversible inhibitors by increases the affinity of ATP to the mutated kinase to outcompete the inhibitors. In order to overcome the resistance by T790M mutation, a series of quinazoline-based compounds were designed by utilizing the available crystal structures of EGFR kinase. In addition to interactions of the current EGFR inhibitors to several amino acid residues of the kinase including MET793 and a hydrophobic pocket, the compounds were designed to target ASP855 and PHE723 residues. As the targeted interactions were confirmed by the means of molecular docking, the compounds were synthesized, and studied for MTT assays, and EGFR inhibition assay. The results revealed a promising candidate to be further studied as EGFR inhibitor.



The structure quinazoline-based compounds as potential candidate of new EGFR inhibitors

References

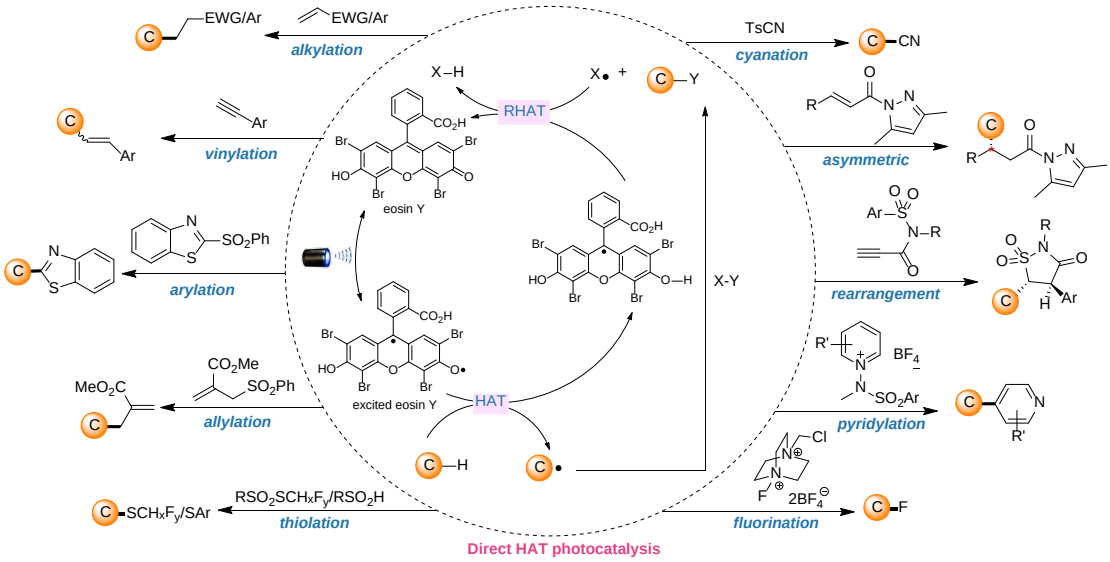
1. Couto, M., García, M.F., Alamón, C., Cabrera, M., Cabral, P., Merlino, A., Teixidor, F., Cerecetto, H., and Viñas, C., *Chem Eur,* **2018**, *24*.
2. Thress, K.S., Paweletz, C.P., Felip, E., Cho, B.C., Stetson, D., Dougherty, B., Lai, Z., Markovets, A., Vivancos, A., Kuang, Y., Ercan, D., Matthews, S.E., Cantarini, M., Barrett, J.C., Jänne, P.A., and Oxnard, G.R., **2015**, *21*.

Muhammad Kumayl Abdulwahab. Universiti Malaya (PhD, 2021). Pharmaceutical Chemist (2015-2017). Lecturer (2021-current). Organic Chemistry.

Neutral Eosin Y as an Photo Hydrogen Atom Transfer Catalyst for C-H and Si-H Activations

Jie Wu,* Xuanzi Fan, Hui Cao, Muliang Zhang
Department of Chemistry, National University of Singapore, Singapore
E-mail: chmjie@nus.edu.sg

Our research group has recently, for the first time, unraveled the unique property of neutral eosin Y, which can function effectively as a direct HAT photocatalyst for C-H functionalizations. Its metal-free, readily available, and low-costing nature, in addition to light absorption in the visible region and unlikely side reactions, makes eosin Y an ideal direct HAT photocatalyst. The neutral eosin Y-based direct photo HAT process provides an extremely convenient and green pathway for C-H functionalities, such as alkylation, vinylation, allylation, arylation, and cyanation.[1] Furthermore, we have proved that the neutral eosin Y-based HAT strategy can be extended to Si-H activation.[2,3]



References

1. Fan, X.; Rong, J.; Wu, H.; Zhou, Q.; Deng, H.; Tan, J. D.; Xue, C.; Wu, L,; Tao, H.; Wu, J. *Angew. Chem. Int. Ed*. **2018**, *57*, 8514-8518.
2. Fan, X.; Xiao, P.; Jiao, Z.; Yang, T.; Dai, X.; Xu, W.; Tan, J. D.; Cui, G.*, Su, H.; Fang, W.; Wu, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 12580.
3. Unpublished results.

Jie WU (吴杰). Boston University (PhD, 2012). National University of Singapore, Assistant Professor (2015-2021); Associate Professor (2021-now). Interested in flow chemistry, automated synthesis, photocatalysis.

A two-step ligand-directed labeling strategy for reporting and reversible activity-regulating intracellular proteins

Wai-Seng Io, Tsung-Shing Andrew Wang*
Department of Chemistry, National Taiwan University, Daan, Taipei, Taiwan 10617
r09223131@ntu.edu.tw

Protein labeling has been a popular topic in biological research fields. With recent developments of small molecular inhibitors and ligands, specific targeting and reversible activity regulation of proteins can be achieved.[1] On the other hand, ligand-directed modifications (LD) developed by Hamachi's group provide possibilities to covalently modify proteins under physiological conditions with high selectivity and site specificity. Although caged-enzymes whose activities can be inactivated are synthesized,[2] reversible activity-regulation by LD modification has not been reported yet. In this work, a two-step modification protocol, which combines the advantages of the above labeling methods is developed. The ligand-directed chemistry modifies a clickable tag on the intact protein in the first step, where the functional moiety consists of the reporting unit and the active-regulating unit is conjugated in the following step, thus constructing a fluorescent-labelled protein whose activity can be reversibly regulated by photo-isomerization of the azobenzene group. (illustrated in Fig. 1)

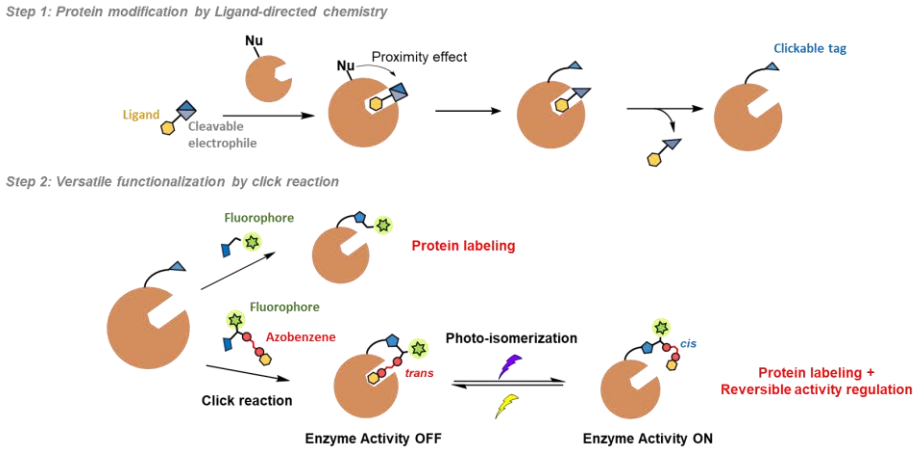


Figure 1: Schematic illustration of the 2-step labeling strategy

References

1. Donthamsetti, P.; Konrad, D. B.; Hetzler, B.; Fu, Z.; Trauner, D.; Isacoff, E. Y. *J. Am. Chem. Soc.* **2021**, *143*, 8951-8956.
2. Ueda, T.; Tamura, T.; Kawano, M.; Shiono, K.; Hobor, F.; Wilson, A. J.; Hamachi, *J. Am. Chem.* **2021**, *143*, 4766-4774.

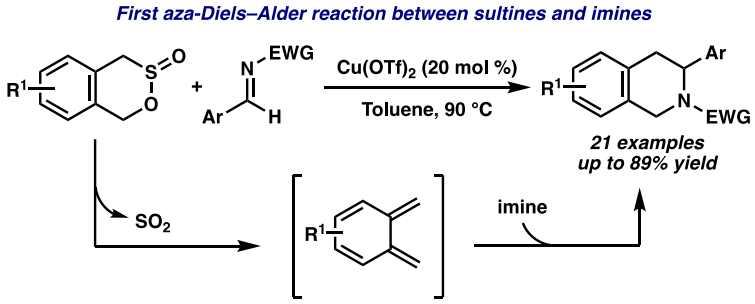
Wai-Seng Io (姚偉成). National Taiwan University (M.S. in Chemistry, 2022). B.S. in Chemistry (2020). M.S. in Chemistry (2022). [Chemical Biology] Organic Chemistry.

Syntheses of 3-Aryl Tetrahydroisoquinolines via an Intermolecular [4+2] Cycloaddition of Sultines with Imines

Aurapat Ngamnithiporn,*[,1] Padon Chuentragool,[1]
Poonsakdi Ploypradith,[1,2,3] Somsak Ruchirawat[1,2,3]

[a] *Laboratory of Medicinal Chemistry, Chulabhorn Research Institute, 54 Kamphaeng Phet 6 Road, Bangkok, 10210, Thailand*
[b] *Program in Chemical Sciences, Chulabhorn Graduate Institute, Chulabhorn Royal Academy, Bangkok 10210, Thailand*
[c] *Center of Excellence on Environmental Health and Toxicology, Office of the Permanent Secretary (OPS), Ministry of Higher Education, Science, Research and Innovation (MHESI), Bangkok 10400, Thailand*
E-mail: aurapat@cri.or.th

A 1,2,3,4-tetrahydroisoquinoline (THIQ) is an important structural motif prevalently found in natural products and biologically active molecules. As a result, the development of efficient synthetic methodologies to prepare this scaffold is a vibrant field of research area, attracting interest from organic chemists both in academia and industry. Recently, we discovered a novel approach to access a wide range of THIQ molecules, featuring an intermolecular aza-Diels–Alder reaction of sultines with imines. Key to the success of this operationally simple method is the utilization of sultines as *o*-quinodimethane precursors and $Cu(OTf)_2$ as a Lewis acid to promote the desired reactivity. We further demonstrated the synthetic utility of these products through the preparation of tetracyclic *N*-heterocycles, including a tetrahydroprotoberberine skeleton.



References
1. Ngamnithiporn, A.; Chuentragool, P.; Ploypradith, P.; Ruchirawat, S. *Org. Lett.* **2022**, *Accepted.*

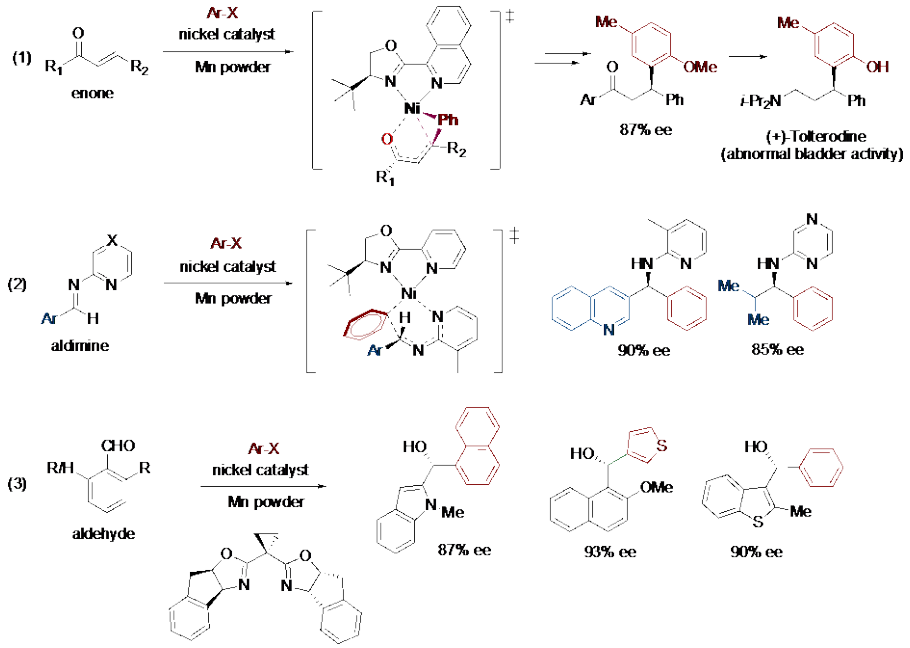
Aurapat Ngamnithiporn (อรภัทร์ งามนิธิพร)
Carleton College (BA in Chemistry, 2015)
California Institute of Technology (Ph.D., 2021)
Chulabhorn Research Institute: Research Scientist (2021–present)
Field of research: Methodology Development, Total Synthesis, Medicinal Chemistry, and Catalysis

Nickel-Catalyzed Asymmetric Reductive (Hetero)arylation of π-systems using Organohalides

Jianrong Steve Zhou*
School of Chemical Biology and Biotechnology
Peking University Shenzhen Graduate School
Room F312, 2199 Lishui Road, Nanshan District, Shenzhen, 518055, China
E-mail: jrzhou@pku.edu.cn

Metal-catalyzed asymmetric additions of aryl nucleophiles to Michael acceptors, imines and aldehydes are an important family of C-C bond forming reactions in organic synthesis. Today, salient examples of these reactions include Cu-catalyzed addition of aryl metals (M = Mg, Li, Al, Zn, etc) and Rh- and Pd-catalyzed additions of soft nucleophiles, especially arylboron reagents. Direct use of aryl halides, not only expands the scope of reagents to aryl electrophiles, but also allows reductive arylations to proceed under mild conditions, which render compatibility of polar functionalities, acidic hydrogens and fragile structures in substrates.

Recently, we realized enantioselective reductive (hetero)arylation of enones, aldimines and aldehydes, by using nickel-diamine catalysts. Importantly, we found that arylnickel species underwent insertion of enones and aldimines via an unconventional elementary 1,4-addition (in collaboration with Prof. Yun-dong Wu).



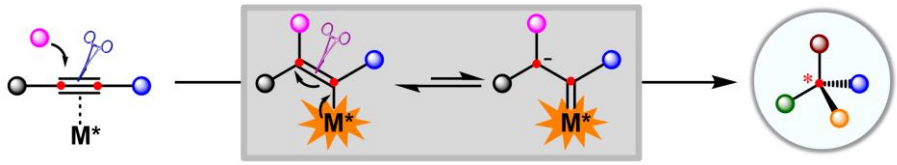
Jianrong Steve Zhou 周建荣. MIT (PhD, 2005).
Assoc Prof, Peking University Shenzhen Graduate School (2019).
[Field of research] Organic Chemistry and Transition Metal Catalysis.

Asymmetric Carbene-Transfer Reactions with Alkynes as Precursors

Shifa Zhu,* Dong Zhu, Rui Wu, Yang Chen
South China University of Technology, Guangzhou, 510640, China
E-mail: zhusf@ scut.edu.cn

In the past decades, few intermediates have attracted as much interest as carbenes. Traditionally, diazo compounds are used as carbene precursors, especially for acceptor-type carbenes. However, rather few examples have been reported for donor-type carbene through diazo approach due to the instability and potential explosiveness of the diazo compounds. These disadvantages severely limit the further applications of donor-type carbenes through the traditional diazo approaches, especially in the asymmetric carbene transfer reaction.

In recent years, alkynes were found to be safe and practical carbene source, which provides a new strategy to generate carbene intermediate in an efficient way, especially for the formation of donor-type carbene.[1] Our group have been making continuous efforts to develop safe and practical carbene chemistry based on alkynes.[2] Such a strategy would be particularly useful for donor- and donor/donor-carbenes because it is safe (no gas emission), practical (no slow addition required), and highly atom-efficient (up to 100% atom efficiency). In addition, the high reactivity, good selectivity, excellent functional-group tolerance, and mild reaction conditions also renders this strategy a feasible route for carbene transfer reactions.



Asymmetric Carbene-Transfer Reactions with Alkynes as Precursors

References

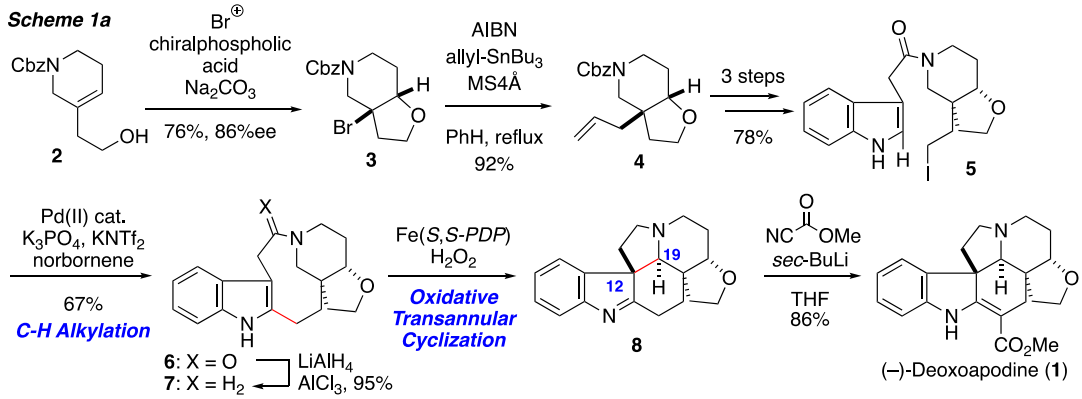
1. (a) Zhu, D.; Chen, L.; Fan, H.; Yao, Q.; Zhu, S. *Chem. Soc. Rev.* **2020**, *49*, 908. (b) Chen, L.; Chen, K.; Zhu, S. *Chem* **2018**, *4*, 1208.
2. (a) Wu, R.; Lu, J.; Cao, T.; Ma, J.; Chen, K.; Zhu, S. *J. Am. Chem. Soc.* **2021**, *143*, 14916; (b) Chen, Y.; Shen, P.; Cao, T.; Chen, H.; Zhao, J.; Zhu, S. *Nat. Commun.* **2021**, *12*, 6165; (c) Wu, R.; Chen, K.; Ma, J.; Yu, Z.-X.; Zhu, S. *Sci. China Chem.* **2020**, *63*, 1230; (d) Zhu, D.; Chen, L.; Zhang, H.; Ma, Z.; Jiang, H.; S. Zhu, *Angew.Chem., Int. Ed.* **2018**, *57*, 12405; (e) Zhu, D.; Ma, J.; Luo, K.; Fu, H.; Zhang, L.; Zhu, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 8452; (f) Zhu, D.; Cao, T.; Chen, K.; Zhu, S. *Chem. Sci.* **2022**, *13*, 1992; (g) Qiu, S.; Gao, X.; Zhu, X.; *Chem. Sci.* **2021**, *12*, 13730; (h) Ma, J.; Chen, K.; Fu, H.; Zhang, L.; Wu, W.; Jiang, H.; Zhu, S. *Org. Lett.* **2016**, *18*, 1322; (i) Luo, H.; Chen, K.; Jiang, H.; Zhu, S. *Org. Lett.* **2016**, *18*, 5208; (j) Ma, J.; Jiang, H.; Zhu, S. *Org. Lett.* **2014**, *16*, 4472.

Shifa Zhu (祝诗发). Shanghai Institute of Organic Chemistry (PhD degree, 2006). Associate Professor (2009). Professor (2013). [Field of research] Alkyne Chemistry.

Recent Advances in Total Synthesis of Alkaloids (–)-Deoxoapodine and (±)-Vinoxine A

Hidetoshi Tokuyama,* Kei Yoshida, Kosuke Okada, Hirofumi Ueda
Graduate School of Pharmaceutical Sciences, Tohoku University, Sendai, Japan
E-mail: tokuyama@mail.pharm.tohoku.ac.jp

(–)-Deoxoapodine (**1**) is one of hexacyclic aspidosperma alkaloids, bearing a fused tetrahydrofuran ring. For this compound, we established a concise 10-steps total synthesis featuring C-H functionalization at the late-stage of synthesis (Scheme 1a).[1] A catalytic asymmetric 5-*endo*-bromocyclization of Cbz-protected commercially available amino alcohol **2** afforded bromide **3**,[2] which was subjected Keck allylation to provide **4**. After condensation with indole unit, intramolecular C-H alkylation based on Bach's condition provided the highly strained 9-membered lactam **6**. The total synthesis of (–)-**1** was completed in over 10 steps via reduction of the lactam, iron catalyzed oxidative transannular reaction, and introduction of the methoxy carbonyl group. In this poster presentation, we will also discuss the recently completed total synthesis of vinoxine (**9**) via stereocontrolled intramolecular radical cyclization (Scheme 1b).



References

1. Yoshida, K.; Okada, K.; Ueda, H.; Tokuyama, H. *Angew. Chem. Int. Ed.* **2020**, *59*, 23089-23093.
2. Xiong, H.; Okada, K.; Yoshida, K.; Ueda, H.; Tokuyama, H. *Tetrahedron Lett*. **2022**, Articles in press (DOI: 10.1016/j.tetlet.2022.153906).
3. Okada, K.; Ueda, H.; Tokuyama H. *Org. Biomol. Chem.* **2022**, Advanced Article (DOI:10.1039/D2OB00274D).

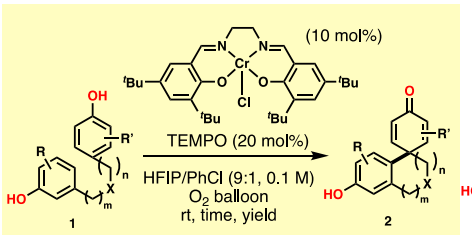
Hidetoshi Tokuyama (徳山　英利). Tokyo Institute of Technology (Ph.D., 1994). University of Pennsylvania (Post-doctoral fellow, 1994-1995), The University of Tokyo (Assist. Prof., Lecturer, Assoc. Prof., 1995-2006). Tohoku University (Professor 2006-present). [Field of research] Synthetic Organic Chemistry,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

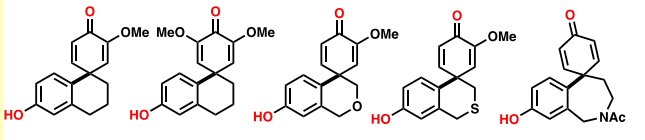
Chromium-salen/Nitroxyl radical: A Combination for Catalytic Aerobic Intramolecular Dearomative Phenol Coupling

Yoshiharu Iwabuchi,* Shota Nagasawa, Shogo Fujiki, Yusuke Sasano
Graduate School of Pharmaceutical Sciences, Tohoku University
E-mail: y-iwabuchi@tohoku.ac.jp

Intramolecular dearomative phenol coupling is a crucial process in the biosynthesis of natural products for expanding molecular complexity and diversity. Especially, this process is a key transformation for biosynthesis of some tyrosine alkaloids such as morphine and galantamine, which possesses significant bioactivities. The fascinating features of these compounds have motivated chemists to reproduce this reaction in a flask. However, most of these precedents require stoichiometric amount of oxidant and the most ideal conditions (i.e., catalytic methodologies which employs O_2 as an oxidant) are very limited.[1]

Based on our experiences in developing an aerobic alcohol oxidation system using copper(I)–nitroxyl radical catalysis[2], we envisioned that the desired coupling reaction would be promoted by combining a transition metal that is known to have a one-electron redox property and a radical mediator. After extensive screening of transition-metal catalyst and radical mediator with tethered phenol **1a**, we found that a Cr–salen complex promoted the desired transformation to give dienone compound **2a**. Note that both of employing HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) as a solvent and addition of nitroxyl radical are crucial for desired transformation.[3]





[a] 20 mol% of Cr-salen and 40 mol% of TEMPO were used. [b] Reaction was conducted at 50 °C.

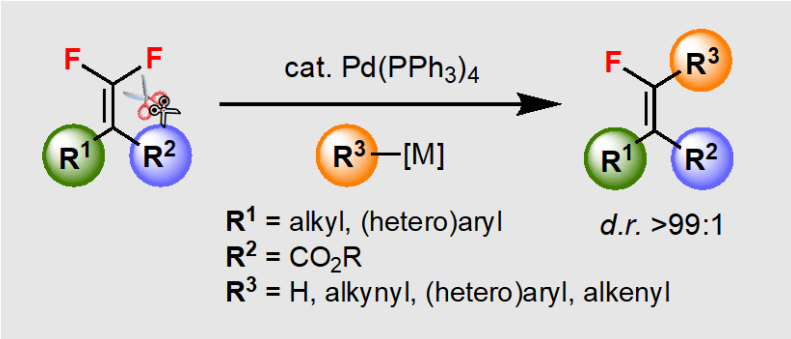
References
1. Gilmartin, H. P.; Kozlowski, M. C. *Org. Lett.* **2020**, *22*, 2914.
2. Sasano, Y.; Nagasawa, S.; Yamazaki, M.; Shibuya, M.; Park, J.; Iwabuchi, Y. *Angew. Chem. Int. Ed.* **2014**, 53, 3236.
3. Nagasawa, S.; Fujiki, S.; Sasano, Y.; Iwabuchi, Y. *J. Org. Chem.* **2021**, *86*, 6952.

Yoshiharu Iwabuchi (岩渕好治) Tohoku Univ. (Ph.D. 1991)
The Scripps Research Institute (Postdoc, Prof. K. C. Nicolaou, 1992)
Protein Engineering Research Institute (Researcher, 1992-1997)
Associ. Prof. Nagasaki Univ. (1997-2002), Prof. Tohoku Univ. (2002-present) [Field of research] natural product synthesis, synthetic methodology

Palladium-Catalyzed Stereoselective C-F Bond Functionalization of *gem*-Difluoroalkenes

Gavin Chit Tsui*
Department of Chemistry, the Chinese University of Hong Kong, Shatin, Hong Kong SAR, China
E-mail: gctsui@cuhk.edu.hk

We herein describe the recent development of a series of highly diastereoselective Pd-catalyzed C-F bond activation of tetrasubstituted *gem*-difluoroalkenes in our laboratory. In the presence of catalytic tetrakis(triphenylphosphine)palladium(0), Sonogashira-type defluorinative coupling, hydrodefluorination (HDF) and base-free Suzuki-Miyaura cross-coupling of *gem*-difluoroalkenes can occur generating densely functionalized (*E*)-monofluoroalkenes with excellent diastereoselectivities (d.r. >99:1). DFT calculations have elucidated an intriguing formal [4+1] cycloaddition/1,5-sigmatropic fluoride migration mechanism for the C-F bond activation process.



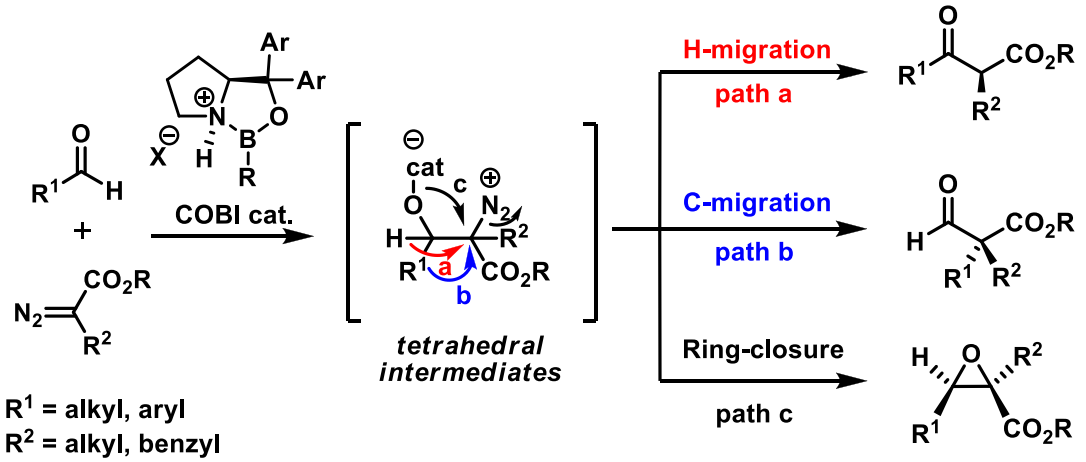
References
(1) Ma, Q.; Wang, Y.; Tsui, G. C.* *Angew. Chem. Int. Ed.* **2020**, *59*, 11293-11297.
(2) Ma, Q.; Liu, C.; Tsui, G. C.* *Org. Lett.* **2020**, *22*, 5193-5197.
(3) Wang, Y.; Qi, X.; Ma, Q.; Liu, P.;* Tsui, G. C.* *ACS Catal.* **2021**, *11*, 4799-4809.

Gavin Chit Tsui 徐哲. University of Toronto (Ph.D, 2013, with Prof. Mark Lautens). Max-Planck-Institut für Kohlenforschung (Postdoc, 2015, with Prof. Benjamin List). The Chinese University of Hong Kong (Associate Professor, 2022-present). [Field of research] Organofluorine chemistry/Homogeneous catalysis

Catalytic Asymmetric Aldehyde Addition-Rearrangements of Diazo esters

Do Hyun Ryu,* Dong Guk Nam, Su Yong Shim, Hye-Min Jeong
Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea
E-mail: dhryu@skku.edu

Diazo esters are versatile reagents that have been applied to various synthetic transformations such as cyclopropanation, C-H insertion and ylide reactions.
We developed highly enantioselective, catalytic tandem reactions of diazo compounds with chiral oxazaborolidinium ion (COBI) as a Lewis acid catalyst. After forming tetrahedral intermediate through nucleophilic addition of diazo esters to aldehyde, H-migration (Roskamp reaction, path a) and C-migration (path b) led to the construction of optically active β-keto ester and the all-carbon quaternary aldehyde, respectively. In this talk, I will present a highly asymmetric catalytic method for the synthesis of trisubstituted α,β-epoxy carbonyl compounds in Darzens-type reaction (path c).



References

1. Nam, D. G., Shim, S. Y., Jeong, H. -M., Ryu, D. H. *Angew. Chem. Int. Ed.* **2021**, *60*, 22236.
2. (a) Gao, L., Kang, B. C., Hwang, G.-S., Ryu, D. H. *Angew. Chem. Int. Ed.* **2012**, *51*, 8322; (b) Gao, L., Kang, B. C., Ryu, D. H. *J. Am. Chem. Soc.* **2013**, *135*, 7126; (c) Shim, S. Y., Choi, Y., Ryu, D. H. *J. Am. Chem. Soc.* **2018**, *140*, 11184; (d) Shim, S. Y., Ryu, D. H. *Acc. Chem. Res.* **2019**, *52*, 2349; (e) Kim, J. Y., Lee, Y. S., Ryu, D. H. *ACS Catal.* **2021**, *11*, 14811.

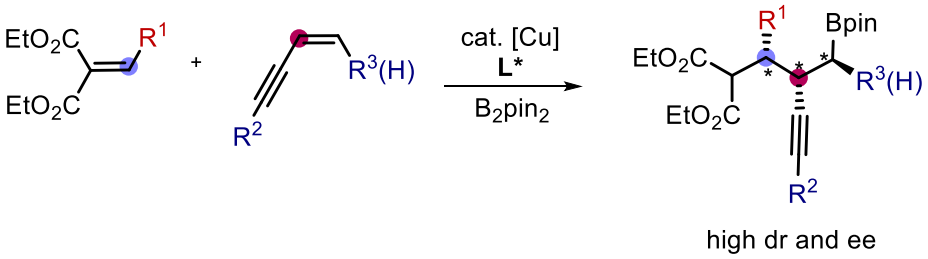
Do Hyun Ryu (류 도현). KAIST (BS, 1991), KAIST (MS, 1993), KAIST (PhD, 1997, Prof. S. H. Kang), Associate researcher (SK Chemicals 1997-2001), Postdoc. Harvard Medical School (Prof. R. R. Rando, 2000-2002), Postdoc. Harvard Univ. (Prof. E. J. Corey, 2002-2005), Assistant, Associate, Full Prof. Sungkyunkwan Univ. (2005-present). [Field of research] Asymmetric catalyst, Synthetic methodology, Total synthesis of natural products and functional organic materials

Copper-Catalyzed Asymmetric Coupling of Enynes with Unsaturated Diesters to Construct C(sp^3)–C(sp^3) Bonds

Jaesook Yun* Wan Seok Yoon, Won Jun Jang
Department of Chemistry, Sungkyunkwan University, Suwon, 16419
E-mail: jaesook@skku.edu

Transition metal-catalyzed reductive coupling of unsaturated π-substrates is considered as a potent tool to expediently develop the molecular complexity with high atom efficiency. However, such an asymmetric and intermolecular process has yet to be developed fully. Hence, the development of asymmetric catalytic methods that employ two prochiral alkenes to form C(sp^3)–C(sp^3) bonds with concomitant stereocontrol is a worthwhile research target.[1]

In this study, we established such coupling processes using enynes and Michael acceptors in the presence of a copper catalyst and bis(pinacolato)diboron.[2] Through this process, asymmetric construction of C(sp^3)–C(sp^3) bond with good stereocontrol of the two connecting carbon centers retaining all carbon or hydrogen substituents was achieved. We were able to incorporate a wide range of terminal and internal enynes as coupling partners and to facilitate highly diastereo- and enantioselective synthesis of organoboron derivatives with multiple adjacent stereocenters in a single operation.



[Asymmteric Olefin Reductive Cross Coupling]

References

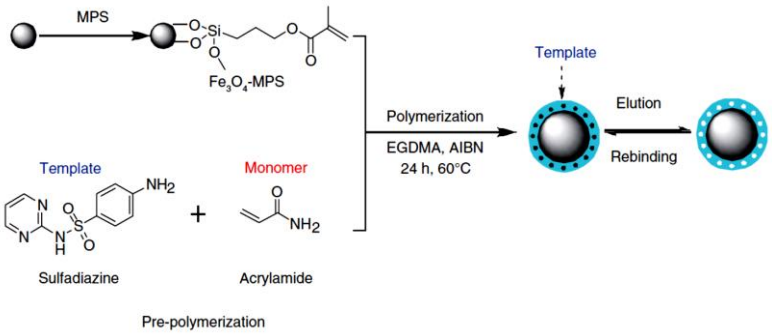
1. (a) Lo, J. C.; Gui, J.; Yabe, Y.; Pan, C. M.; Baran, P. S. *Nature* **2014**, *516*, 343; (b) Nguyen, K. D.; Park, B. Y.; Luong, T.; Sato, H.; Garza, V. J.; Krische, M. J. *Science* **2016**, *354*, aah5133.
2. Yoon, W. S.; Jang, W. J.; Yoon, Y.; Yun, H.; Yun, J. *Nat. Commun*. **2022**, *13*, 2570

Jaesook Yun (윤재숙). MIT (Ph. D, 2001). Ajou University, Assistant Professor (2002~2005). Sungkyunkwan University, Associate Professor (2005~2012), Professor (2012~present). [Field of research] Organic Chemistry.

Acrylamide-based Magnetic Molecularly Imprinted Polymer (MION-MNP): Synthesis, Characterisation, and Adsorption Studies for The Sulfonamide Drug Recognitions

Yean Kee Lee[a*] , Lei Chen[a], Yanawut Manmana[b], Kheng Soo Tay[a], Vannajan Sanghiran Lee[a] and Noorsaadah Abd Rahman[a]
a: Department of Chemistry, Faculty of Science, Universiti Malaya, K.L., Malaysia.
b: Department of Chemistry, Faculty of Science, Prince of Songkla University, Songkhla, Thailand
*E-mail: yeankee@um.edu.my

In this work, a magnetic molecularly imprinted polymer (MION-MNP) was prepared in the purpose of the recognition and extraction of sulfadiazine (SDZ). The acrylamide was used to imprint directly onto the surface of 3-(trimethoxysilyl) propyl methacrylate-modified magnetic iron oxide nanoparticles. The synthesized material was characterized by FTIR, DSC and SEM. It was found to have a diameter of about 100 nm. The MION-MNP possesses fast adsorption kinetics and high adsorption capacity (775 μg g^{-1}). The Langmuir adsorption isotherm model was found to describe well the equilibrium adsorption data. The competitive binding experiment showed that the particle was not only selective toward SDZ, the adsorption of sulfamerazine was equally high. Both SDZ and sulfamerazine have similar substructure where only an additional methyl group on sulfamerazine.



MIOP-MNP synthesis

References:

1. Lei Chen, Yean Kee Lee, Yanawut Manmana, Kheng Soo Tay, Vannajan Sanghiran Lee, Noorsaadah Abd Rahman. *E-Polymers* **2015**;15: 141-150.
2. Bakas I, Oujji NB, Istamboulié G, Piletsky S, Piletska E, Ait-Addi E, Ait Ichou I, Noguer T, Rouillon R. *Talanta* **2014**; 125: 313–318.
3. Cheng W, Ma H, Zhang L, Wang Y. Talanta. **2014**; 120: 255–261.

Lee Yean Kee (李衍奇), Universiti Malaya (Ph.D., 2011).
Current position: Research Officer (2009-now).
Field of research :1. Organic synthesis, 2. Molecular modelling, 3. Drug design and synthesis

Cobalt-Catalyzed Selective Multi-Borylation of Unsaturated Hydrocarbons

Shaozhong Ge,* Ming Hu, Xiaoxu Yang, Yinsong Zhao, and Wei Jie Teo
Department of Chemistry, Faculty of Science, National University of Singapore,
E-mail: chmgsh@nus.edu.sg

Organoboron compounds are versatile building blocks for synthetic organic chemistry due to their stability, low toxicity, and diverse reactivity. As a unique family of organoboronates, polyborylated alkanes have gained increasing attention, particularly because the multiple boron groups in these polyborylated alkanes have different reactivity that allows stepwise and selective functionalization of these borylated alkanes. During our effort in developing hydroboration of unsaturated hydrocarbons catalyzed by cheap, abundant, and non-toxic base catalysts,[1] we have discovered that cobalt-hydride and cobalt boryl intermediates ligated bisphosphine ligands co-exist in these borylation reactions. In addition, thse cobalt-hydride and cobalt-boryl species can be interconverted in the presence activated alkenes as hydrogen acceptors. By taking the advantage of the co-existence of these two cobalt intermediates, we have developed several cobalt catalysts that are very effective in diborylation and triborylation of alkenes, alkynes, allylic ethers or double hydroboration of 1,n-dienes (Scheme 1).[2] These diborylation, chain-walking double hydroboration, and triborylation reactions provide convenient access to synthetically versatile *gem*-bis(boryl)alkanes and 1,1,3-tri(boryl)alkanes. The reaction scope, synthetic utilities, and detailed mechanism on these cobalt-catalyzed multi-borylation reactions will be discussed.

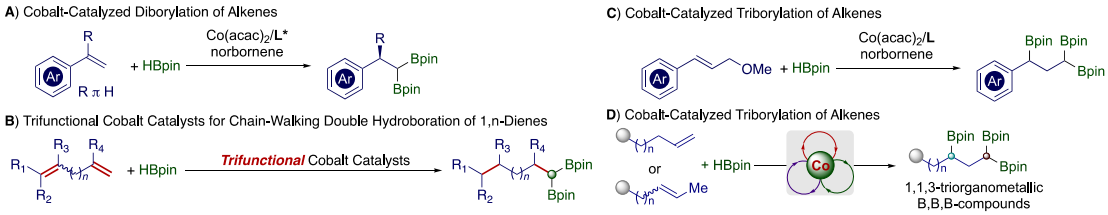


Figure 1. Cobalt-Catalyzed Multi-borylation of unsaturated hydrocarbons

References

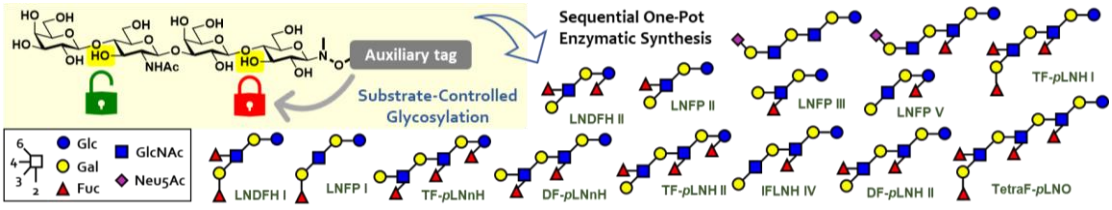
1. (a) Yu, S.; Wu, C.; Ge, S.* *J. Am. Soc. Chem.* **2017**, *139*, 6526; (b) Wang, C.; Ge, S.* *J. Am. Soc. Chem.* **2018**, *140*, 10687; (c) Wu, C.; Liao, J.; Ge, S.* *Angew. Chem. Int. Ed.* **2019**, *58*, 8882.
2. (a) Teo, W. J.; Ge, S.* *Angew. Chem. Int. Ed.* **2018**, *57*, 1654; (b) Teo, W. J.; Ge, S.* *Angew. Chem. Int. Ed.* **2018**, *57*, 1654; (c) Hu, M.; Ge, S.* *Nat. Commun.* **2020**, *11*, 765; (d) Teo, W. J.; Yang, X. Poon, Y. Y.; Ge, S.* *Nat. Commun.* **2020**, *11*, 5193; (e) Zhao, Y.; Ge, S.* *Angew. Chem. Int. Ed.* **2022**, *61*, e202116133; (f) Yang, X.; Ge, S.* *Organometallics* **2022**, *41*, doi: 10.1021/acs.organomet.2c00053.

Shaozhong Ge (葛少中). University of Groningen, the Netherland (PhD, 2009). Postdoc at University of California, Berkeley and University of Illinois at Urbana Champaign (2010-2014). Assistant (2015-2021) and Associate (2021-present) Professor at National University of Singapore.
Field of research: Base Metal Catalysis, Asymmetric Catalysis, Synthetic Organometallic Chemistry

Sulfo-Fluorous Tagging Strategy for Site-Selective Enzymatic Glycosylation of *para*-Human Milk Oligosaccharides

Ching-Ching Yu,* Yu-Ting Huang, Yi-Chia Su, Hsin-Ru Wu, Hsin-Hui Huang, Eugene C. Lin, Teng-Wei Tsai, Hsien-Wei Tseng, and Jia-Lin Fang
Department of Chemistry and Biochemistry, National Chung Cheng University, Chiayi 62102, Taiwan
E-mail: checcyu@ccu.edu.tw

In this study, we developed an efficient fluorous tagging strategy for site-selective enzymatic fucosylation/sialylation in which appending a readily removable auxiliary tag (**SF_{17}**) to the reducing end of an acceptor provided the regioselectivity control of a given wild-type fucosyltransferase/sialyltransferase. By combining this strategy with the sequential one-pot enzymatic system of HMO production, various fucosylated *para*-HMOs, such as LNFP I, LNFP II, LNFP III, LNFP V, LNDFH I, LNDFH II, TF-LNT, F-*p*LNH I, F-*p*LNH IV, DF-*p*LNH I isomer, DF-*p*LNH II, TF-*p*LNH I, TF-*p*LNH II, F-*p*LNnH, F-*p*LNnH I, DF-*p*LNnH, TF-*p*LNnH, and TetraF-*p*LNO, were synthesized. Furthermore, the SF_{17}-tagged acceptors improved the reaction rates of the enzymatic glycan chain extension. Terminal α2,6-sialylation on **SF_{17}**-tagged *p*LNnH was directly achieved using wild-type α2,6-sialyltransferase from *Photobacterium damsela* (Pd26ST). Moreover, enzyme kinetics revealed that the catalytic efficiency (k_{cat}/K_M) of α1,4-fucosylation of Bf13FT (α1,3/4-fucosyltransferase from *Bacteroides fragilis*) on **SF_{17}**-tagged LNFP V acceptors could be enhanced by 55 times compared with tagging with an azidohexyl aglycone. We developed an efficient and reliable strategy for generating complex and diverse natural HMO libraries for functional gut microbiome studies. This **SF_{17}**-assisted glycosylation strategy provides a practical approach to harness the extreme substrate flexibility offered by readily available bacterial glycosyltransferases, which enables the site-selective fucosylation/sialylation on *para*-HMOs.[1]



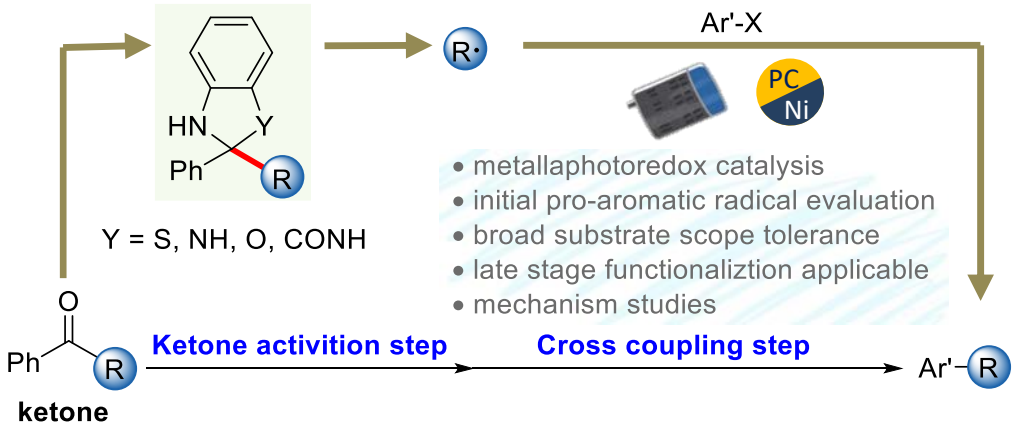
Reference
1. Huang, Y.-T.; Su, Y.-C.; Wu, H.-R.; Huang, H.-H.; Lin, E. C.; Tsai, T.-W.; Tseng, H.-W.; Fang, J.-L.; Yu, C.-C. *ACS Catal.* **2021**, *11*, 2631−2643.

Ching-Ching Yu (游景晴). National Chang Hua University of Education (BS, 2005), National Tsing Hua University (MS, 2007), National Tsing Hua University (PhD, 2012), National Tsing Hua University (PDF, 2013-2014), University of British Columbia (PDF, 2014-2015), National Chung Cheng University (Assist. Prof., 2015-2020; Assoc. Prof., 2020-present). [Field of research] Carbohydrate Chemistry, Enzyme Chemistry, Protein Chemistry, Directed Evolution of Enzymes.

Aromatization as an Impetus to Harness Ketones for Metallaphoto-redox-Catalyzed Benzoylation/Benzylation of (Hetero)arenes

Hsuan-Hung Liao,* Li-Yun Li, Zong-Nan Tsai
Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan, R.O.C.
E-mail: hsuan-hung.liao@mail.nsysu.edu.tw

Herein, we report ketones as feedstock materials in radical cross-coupling reactions under Ni/photoredox dual catalysis. In this approach, simple condensation first converts ketones into pre-aromatic intermediates that then act as activated radical sources for cross-coupling with aryl halides. Our strategy enables the direct benzylation/benzoylation of (hetero)arenes under mild reaction conditions with high functional group tolerance.



References

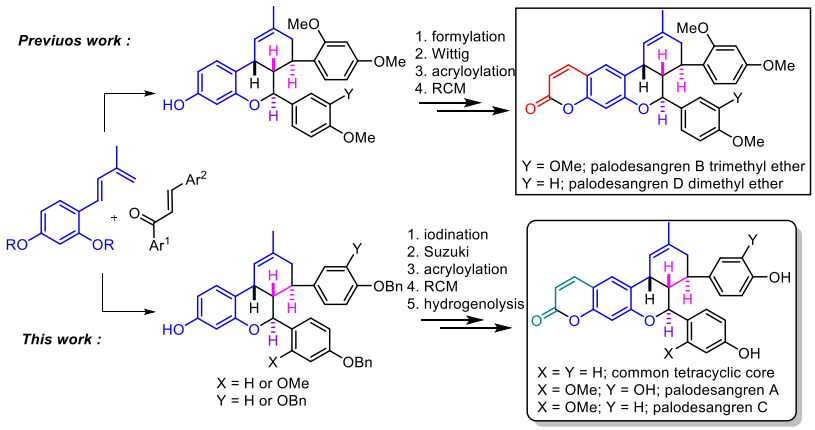
1. Lee, S. C.; Li, L. L.; Tsai, Z. N.; Lee, Y. H.; Tsao, Y. T.; Huang, P. G.; Cheng, C. K.; Lin, H. B.; Chen, T. W.; Yang, C. H.; Chiu, C. C.; Liao, H. H. *Org. Lett.* **2022**, *24*, 85–89.

Hsuan-Hung Liao (廖軒宏). RWTH Aachen University, Germany (PhD in Organic Chemistry, 2012–2016). Marie Skłodowska-Curie individual fellow with Prof. Varinder K. Aggarwal at the University of Bristol, UK (2017–2019). Assistant professor in Chemistry, National Sun Yat-sen University, Taiwan (2019–present). [Field of research] Organo Photochemistry/ Asymmetric Synthesis.

Total Synthesis of Palodesangrens A and C

Poramate Songthammawat,* Kassrin Tangdenpaisal, Somsak Ruchirawat, Poonsakdi Ploypradith*
Laboratory of Medicinal Chemistry, Chulabhorn Research Institute, 54 Kamphaeng Phet 6 Road, Laksi, Bangkok 10210, Thailand and *Program in Chemical Sciences, Chulabhorn Graduate Institute, Chulabhorn Royal Academy, 906 Kamphaeng Phet 6 Road, Laksi, Bangkok 10210, Thailand*
E-mail: poramate@cri.or.th

Palodesangrens A and C, unlike other related natural Diels−Alder adducts possess a tetracyclic benzo[*c*]pyranochromenone core and C2′-OMe arising biosynthetically from the chalcone moieties. Thus, previously reported methodologies, which have mostly hinged upon the use of the corresponding 2′-hydroxy chalcones as dienophiles for the intermolecular Diels−Alder reaction, would be synthetically infeasible. Further developed from our previous work, total synthesis of palodesangrens A and C has been accomplished for the first time in 10 longest linear sequence which featured bioinspired Diels–Alder reaction, $LiAlH_4$-mediated isomerization, stereoselective chroman formation, regioselective iodination/vinyl Suzuki reaction, acryloylation and ring-closing metathesis (RCM) forming the 2*H*-pyran-2-one. Overall, the desired palodesangrens A and C could be obtained in 6.1% and 6.4% yields, respectively.



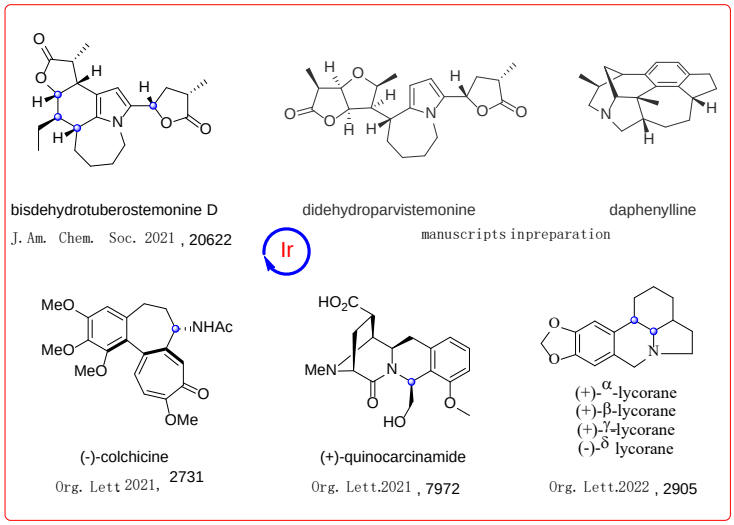
References
1. Tangdenpaisal, K.; Songthammawat, P.; Akkarasereenon, K.; Chuayboonsong, K.; Ruchirawat, S.; Ploypradith, P. *J. Org. Chem*. **2019**, *84*, 13410−13429.
2. Tangdenpaisal, K.; Songthammawat, P.; Ruchirawat, S.; Ploypradith, P. *J. Org. Chem*. **2022**, *87*, 386–398.

Poramate Songthammawat (ปรเมธ ทรงธรรมวัฒน์). Silpakorn University (BSc 2010 and MSc 2013), Chulabhorn Graduate Institute (PhD, 2020). Research Scientist, PTT Global Chemical Co. Ltd. (2014-2015), Visiting Scholar, Colorado State University (2019-2020), Research Scientist, Chulabhorn Research Institute (2020-present). Field of research: total synthesis and synthetic methodology

Ir-Catalyzed Asymmetric Total Syntheses of Alkaloids

Yu-Rong Yang*
E-mail: yangyurong@mail.kib.ac.cn

Polycyclic alkaloids are the long-standing popular targets in total synthesis for their notable bioactivities and complex chemical structures. My laboratory has recently devoted itself to the asymmetric catalytic total syntheses of diverse alkaloids by enlisting the unique catalytic process of transition-metal iridium catalyzed allylic substitution.[1] Through the innovation of the synthetic strategies, the step economy can be significantly increased for some of the alkaloids, such as pyrrole-containing *stemona* alkaloids[2] and colchicine.[3]



References

1. (a) Liang, X.; Jiang, S.-Z.; Wei, K.; Yang, Y.-R. *JACS* **2016**, *138*, 2560; (b) Jiang, S.-Z.; Zeng, X.-Y.; Liang, X.; Lei, T.; Wei, K.; Yang, Y.-R. *ACIE* **2016**, *55*, 4044; (c) Liang, X.; Zhang, T.-Y.; Zeng, X.-Y.; Zheng, Y.; Wei, K.; Yang, Y.-R. *JACS* **2017**, 139, 3364.
2. Deng, Y.; Liang, X.; Wei, K.; Yang, Y.-R. *JACS* **2021**, *143*, 20622.
3. Liang, X.; Li, Lei, Wei, K.; Yang, Y.-R. *Org. Lett.* **2021**, *23*, 2731.

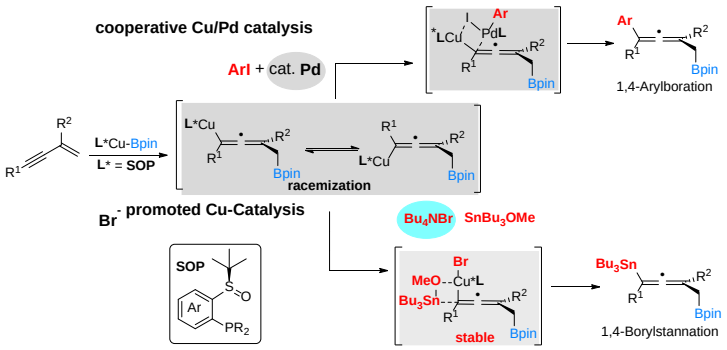
Yu-Rong Yang (杨玉荣). Lanzhou University (PhD, 2005). Harvard University (Postdoc, 2005-2007). Kunming Institute of Botany (2008-). Natural Product Synthetic Chemistry.

Stereocontrolled transformations of chiral copper-allenyl species

Jian Liao,* Yang Liao, Jialin Ye, Ming Wang
Chengdu Institute of Biology, CAS, Chengdu 610041, China
E-mail: jliao@cib.ac.cn

Transition metal-catalyzed 1,4-functionalizations of unactivated 1,3-enynes is a valuable and straightforward strategy to reach allenes.[1] Recently, Cu-catalyzed 1,4-functionalization of unactivated 1,3-enynes has attracted significant attention with respect to the synthesis of axially chiral allenes.[2] The protocol involves trapping enantioenriched copper allenyl species, which generated by the addition of chiral Cu-Bpin species to 1,3-enynes, is one of the most effective methods to synthesis chiral allenes but remains a challenging task. The key issue of this protocol is the easy racemization of chiral copper-allenyl species.

To fix the above-mentioned issue, recently, by employing chiral sulfoxide phosphines (SOP) as ligands, we developed a cooperative Cu/Pd-catalyzed enantioselective 1,4-borylarylation and halogenated salt promoted Cu-Catalyzed asymmetric 1,4-borylstannation of 1,3-enynes, chiral multisubstituted allenes were readily afforded with excellent yields and enantioselecities (Scheme 1), in addition, mechanism was investigated via control experiment and density functional theory (DFT) calculations.[3]



Scheme 1

References

1. (a) L. Fu, S. Greßies, P. Chen, G. Liu, *Chin. J. Chem.* **2020**, *38*, 91.
2. (a) Hoveyda, et al. *J. Am. Chem. Soc.* **2018**, *140*, 2643; (b) Ge, et al. *Org. Chem. Front.* **2018**, *5*, 1284; (c) Engle, et al. *ACS Catal.* **2018**, *8*, 3650; (d) Ge, et al. *Commun. Chem.* **2018**, *1*, 64; (e) Buchwald, et al. *J. Am. Chem. Soc.* **2019**, *141*, 13788.
3. (a) Y. Liao, J. Liao, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 1176. (b) J. Ye, J. Liao, et al. *Chem. Sci.* **2021**, *12*, 3032. (c) unpublished results.

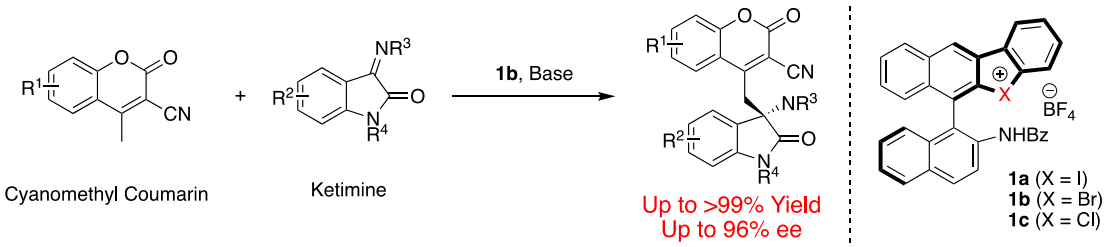
Jian Liao (廖建). University of Chinese Academy of Sciences (PhD, 2002). PostDoc. The Pennsylvania State University, USA (2003-2006). Professor, Chengdu Institute of Organic Chemistry, CAS (2006-2010). Professor, Chengdu Institute of Biology, CAS (2010- now). Field of Research-Organic Chemistry.

Halogen-bonding Catalysis by Chiral Halonium Salt

Yasushi Yoshida,* Tappei Fujimura, Takashi Mino, Masami Sakamoto
Graduate School of Engineering, Chiba University
1-33, Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan
E-mail: yoshiday@chiba-u.jp

The halogen-bonding, which is formed between electron-deficient halogen atoms and Lewis bases, has been focused as a unique interaction in organic synthesis. Although, the catalysts with halogen-bonding have been widely researched in these years, the asymmetric catalysis by chiral halogen-bonding catalyst have been limited to date.[1] In this presentation, we would like to talk about the development of chiral halonium salts, which works in the enantioselective reactions as a halogen-bonding catalyst to form the products in high enantioselectivities.

The chiral halonium salts **1** were prepared from commercially available BINAM in 7 steps, which were applied to the enantioselective reactions. The vinylogous-Mannich reaction of cyanomethyl coumarins with isatin-derived ketimines was conducted using 0.5 mol% of **1** under the basic condition. The catalyst screening revealed that the halonium salt moiety was essential to the asymmetric induction to the products, and the bromonium salt **1b** was found to be optimal. The substrate scope was conducted with **1b** and the products were obtained in high yields with high enantioselectivities.[2a] Furthermore, our chiral halonium salts could be applied to the addition reaction thiols to the ketimines. The catalyst screening was conducted using the *tert*-butyl thiol and the isatin-derived ketimine, which demonstrated the iodonium salt **1a** showed the highest outcome.[2b] We also would like to discuss about the details on this reaction.



References

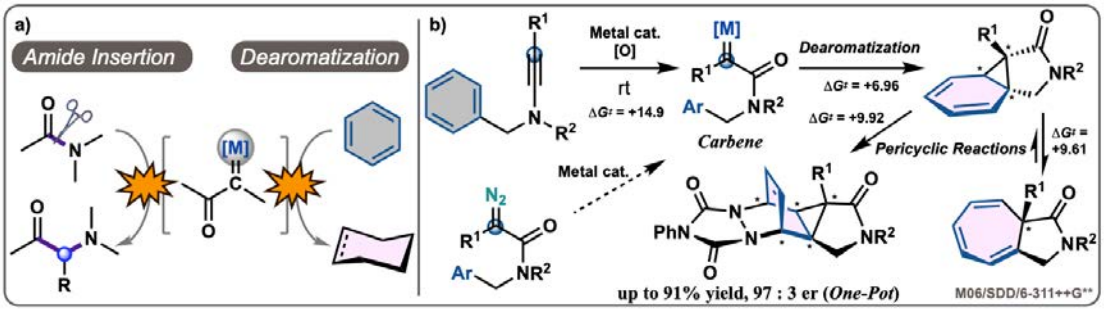
1. (a) Kuwano, S.; Suzuki, T.; Hosaka, Y.; Arai, T. *Chem. Commun.* **2018**, *54*, 3847–3850; (b) Sutar, R. L.; Engelage, E.; Stoll, R.; Huber, S. M. *Angew. Chem., Int. Ed.* **2020**, *59*, 6806–6810.
2. (a) Yoshida, Y.; Mino, T.; Sakamoto, M. *ACS Catal.* **2021**, *11*, 13028–13033; (b) Yoshida, Y.; Fujimura, T.; Mino, T.; Sakamoto, M. *Adv. Synth. Catal.* **2022**, *364*, 1091–1098.

Yasushi Yoshida (吉田泰志). Osaka University (Ph.D, 2015, Prof. Hiroaki Sasai), California Institute of Technology (Postdoc, 2015, Prof. Gregory C. Fu), Chiba University (Assistant Professor, 2015-present).
[Field of research] Asymmetric Catalysis

Asymmetric Dearomatization of Nonactivated Arenes based on Diazo-free Generation of Chiral Metal-Carbene

Shingo Harada,1* Tsubasa Ito,1 Haruka Homma,1 Hiroki Takenaka,1 Shumpei Hirose,1 Tetsuhiro Nemoto1*
Chiba University, 1-8-1, Inohana, Chuo-ku, Chiba 260-8675, Japan
E-mail: Sharada@chiba-u.jp

Metal-carbenes are highly active carbon species with divergent reactivity. Numerous natural products and pharmaceutical candidates have been synthesized on the basis of the metal-carbene reactions. In continuation of our research for expanding metal-carbene chemistry and dearomatization reactions, we reported a silver-catalyzed asymmetric dearomatization of phenols and indoles bearing a diazo functionality as a carbene precursor.[1)] In our previous method, however, improvements were required to address the following issues: (a) use of diazo compounds, which are often unstable and potentially explosive; (b) installation of the functionality into substrates requires an additional step count; and (c) reacting aromatics must be electron-rich, consequently compromising the overall synthetic competence of the strategy. To overcome these challenges, we pondered over a method for diazo-free generation of silver-carbene, which could contribute to promoting sustainability in chemical science. In our presentation, we would like to report the dearomative functionalization of non-activated arenes based on the diazo-free methodology.[2,3)]



(a) Our ongoing work (b) Overview of this presentation

References

1. Nakayama, H., **Harada, S.***, Kono, M., Nemoto, T.* *J. Am. Chem. Soc.* **2017**, *139*, 10188.
2. Recent review; **Harada, S.*** *Chem. Pharm. Bull.* **2021**, *69*, 1170.
3. Ito, T., **Harada, S.***, Homma, H., Takenaka, H., Hirose, S., Nemoto, T.* *J. Am. Chem. Soc.* **2021**, *143*, 604.

Shingo Harada (原田　慎吾). Kyoto University (Ph.D. 2013). Assistant Professor in Chiba University (2013). Visiting Scientist in Bielefeld University (Germany) (2017). Visiting Scientist in Yale University (USA) (2019). Lecturer in Chiba University (2020). [Field of research] Organic Chemistry, Computational Chemistry. Synthetic Chemistry. Natural Product Chemistry.

High Carbon Utilization Efficiency for Electrochemical CO_2 Reduction Reaction

Ying Wang*
The Chinese University of Hong Kong, Shatin, N.T., Hong Kong S.A.R.
E-mail: ying.b.wang@cuhk.edu.hk

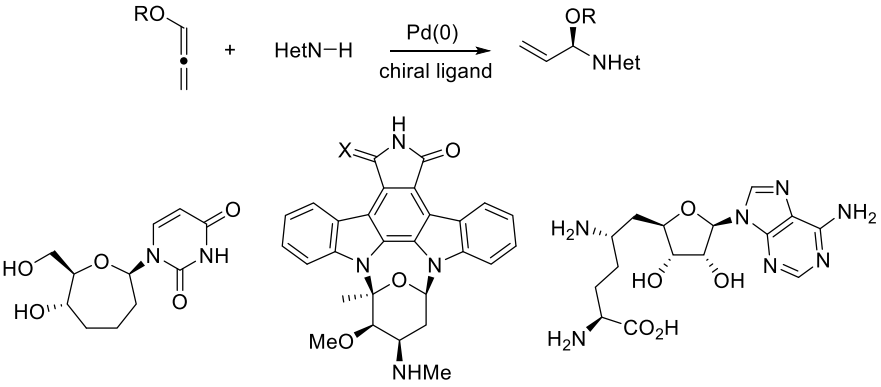
Developing high-efficiency carbon dioxide capture, storage, and conversion technologies has received extensive attention. Renewable electricity-powered CO_2 conversion offers an attractive means to produce low-carbon-footprint fuels and chemicals. Various carbon-based compounds, C_1 (methane, methanol, and CO) to C_3 (n-propanol), have been reported for electrochemical CO_2 reduction reaction (CO_2RR). Significant progress has been made in the field of CO2RR under industrial relevant current densities (> 100 mA/cm^2). One of the critical challenges for further development of CO2RR technology is how to achieve high selectivity under commercial relevant conditions. Mechanistic studies have revealed the key intermediates, such as *CO and *HCO, for multi-electron/multi-carbon products from CO_2. Steering the adsorption energy of key intermediates through catalysts design are crucial for highly selective CO_2RR. In our work, we introduced different metals, such as Ag, Au and Pd, into Cu catalyst to achieve high selectivity and activity to multi-electron transfer products, acetate, methane, and ethanol.

Another significant challenge remaining for CO_2RR is the low carbon utilization rate. Due to the produced hydroxide ion at the electrode interface during electrolysis, a significant amount of CO_2 will be converted to carbonate rather than being reduced to targeted products. It is suggested that the maximum carbon conversion efficiency of CO_2-to-CO is only at 50% for the current neutral/alkaline CO_2RR electrolyser. This efficiency will further drop for multi-electron transfer products, such as ethylene (25%) and ethanol (25%). To probe this, we developed an acidic CO2RR electrolyser with optimized catalysts showing a high carbon conversion efficiency to multicarbon products.

A *De Novo* Synthetic Approach towards *N*-Heterocyclic glycosides Natural Products

Young Ho Rhee,* Seok Hyeon Jang, Dong-Jin Jang, Kyeongdeok Seo
Department of Chemistry, Pohang University of Science and Technology, Nam-gu Pohang, Kyungbook, Korea 37673
E-mail: yhrhee@postech.ac.kr

N-heterocyclic glycosides are found in numerous bioactive natural products, and play pivotal roles in physiological processes. Despite these significances, efficient synthetic methods towards *N*-heterocyclic glycosides are limited, mostly due to the poor reactivity of the *N*-heterocycle precursors. Over the last decades, we have been working on the development of a *de novo* synthetic approach towards *N*-heterocyclic glycosides based upon the use of sequential metal catalysis. A key feature of this method is the Pd-catalyzed asymmetric addition reaction of various *N*-heterocycles to alkoxyallene. Notably, various *N*-heterocycles exhibited high reactivity in this reaction with no need of additives. Upon combination with other metal-catalyzed reaction (such as ring-closing-metathesis and olefin migration), this new method successfully gave an access to highly challenging targets such as 7-membered oxepine pyrimidine nucleosides, staurosporine, and sinefungin.



References

1. Kim, S. Kim, Y. J. Rhee, Y. H. *Org. Lett.* **2018,** *4,* 979.
2. Kang, S. Jang, S. H. Lee, J. Kim, D.G. Kim, M. Jeong, W. Rhee, Y. H. *Org. Lett.* **2017**, *19*, 4684.
3. Seo, K. Jang, S. H. Rhee, Y. H. *Angew. Chem. Int. Ed.* **2021**, *61*, e202112524

Young Ho Rhee (이 영호). Stanford University Ph. D, 2003). Pohang University of Science and Technology 2005~current. [Field of research] methodology development, total synthesis of natural products.

Chemical strategy for targeted protein degradation

Hyun-Suk Lim

Department of Chemistry, Pohang University of Science & Technology, Pohang, Republic of Korea.

Abstract. The proteolysis targeting chimeras (PROTACs) have emerged as a powerful, new therapeutic modality. PROTACs are chimeric molecules capable of recruiting a target protein to an E3 ligase, thereby leading to ubiquitination and subsequent degradation of the target protein by the 26S proteasome. In contrast to conventional drugs that generally function by inhibiting target proteins, PROTACs induce the degradation of a protein of interest in cells. While PROTACs hold great promise as a versatile therapeutic modality, current PORTAC technology has limitations. When targeting tissues or cells do not sufficiently express the E3 ligase, such as cereblon, it is impossible to generate a PROTAC molecule. It is necessary to identify a new E3 ligase and discover a potent and selective ligand for the E3 ligase. However, this process requires a huge amount of time and effort. To circumvent such obstacles, we have developed a novel targeted protein degradation strategy that can remove a protein via the N-degron pathway. Specifically, we designed ligands based on the crystal structure of the E3 ligases of the N-degron pathway and showed that the resulting chimeric molecules were able to efficiently degrade target proteins. Given that these new E3 ligases are ubiquitously expressed in most cells, our strategy can be generally applicable for developing PROTACs in various diseases.

Hit-to-Lead Short Peptides against Dengue Type 2 Envelope Protein

Rozana Othman[1,*], Abdullah Al Hadi Ahmad Fuaad[2], Norburhanuddin Johari Zaidi[2] and Choon Han Heh[1]

[1]*Department of Pharmaceutical Chemistry, Faculty of Pharmacy*
[2]*Department of Chemistry, Faculty of Science*
Universiti Malaya, 50603 Kuala Lumpur Malaysia
*E-mail: rozanaothman@um.edu.my

In this study, a library of 11,699 short chain peptides (6 to 10 residues) was constructed based on the peptides yielded in our previous work [1]. Virtual screening of these peptides against dengue type 2 (DEN2) envelope (E) protein yielded candidates with promising binding affinity and shown to be stable in the DI-DIII binding pocket of the protein. Selected peptides were synthesised using conventional Fmoc solid-phase peptide chemistry, purified using RP-HPLC, and characterised using LCMS. *In vitro* studies followed, to test for the peptide toxicity and efficacy in inhibiting the DENV2 growth cycle. Our studies identified the electrostatic interactions to be the driving stabilising force for the E protein–peptide interactions. The peptide coded as DN58opt_8-13 showed the best inhibitory activity, ~ 63% DENV2 plague reduction compared with no treatment. This correlates well with the *in silico* studies in which this peptide exhibited the lowest binding energy (-9.0 kcal/mol) and was maintained steadily within the binding pocket of DENV2 E protein during the MD simulations [2]. This study demonstrates the use of computational studies to expand research on lead optimisation of antiviral peptides, thus explaining the inhibitory potential of the designed peptides.

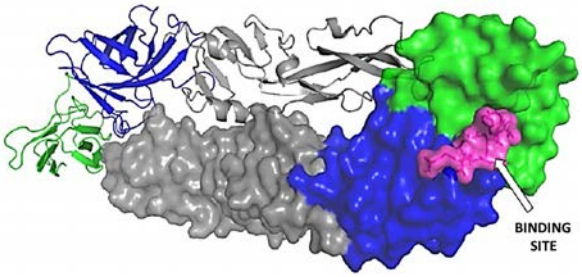


Figure illustrating the position of the peptide-binding site on DENV2 E protein (magenta) positioned at the DI-DIII hinge (DI in green and DIII in blue).

Reference:

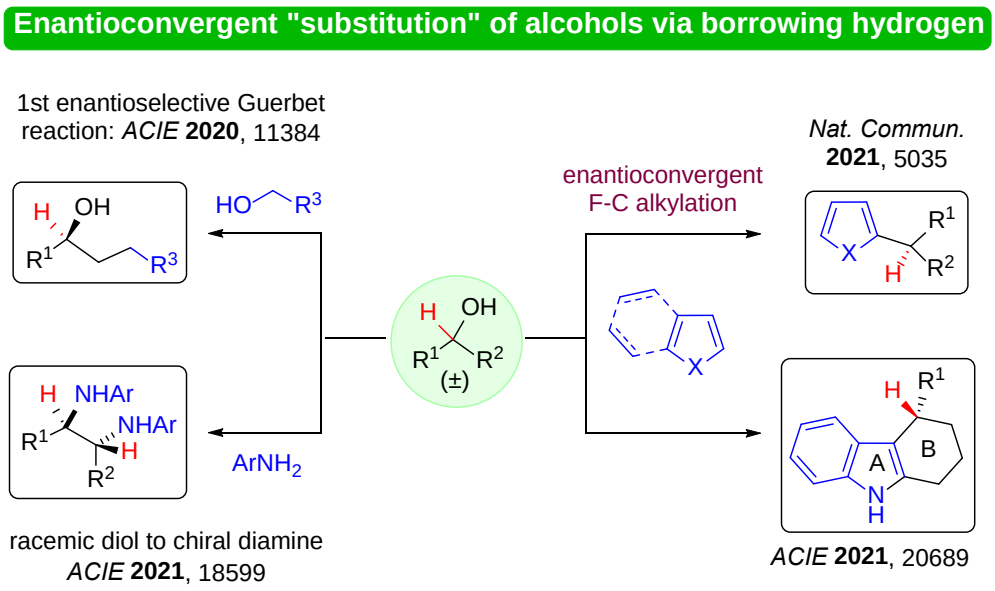
[1] Xu, Y.; Rahman, N.A.; Othman, R.; Hu, P.; Huang, M. *Proteins* **2012,** *80,* 2154-2168.
[2] Zaidi, N.J.; Abdullah, A.A.; Heh, C.H.; Lin, C.-H.; Othman, R.; Ahmad Fuaad, A.A.H. *Molecules* **2022**, *27*, 3233- 3249.

Rozana OTHMAN. Universiti Malaya (PhD, 2010). Lecturer (1999). Associate Professor (2016 - present). [Field of research] Computational Chemistry, Medicinal Chemistry, Natural Product Chemistry.

Catalytic Enantioselective Redox-Neutral Processes for Efficient Chemical Synthesis

Yu ZHAO group
Department of Chemistry, National University of Singapore, Singapore, 117544
E-mail: zhaoyu@nus.edu.sg

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 focuses on the identification of catalytic enantioselective redox-neutral transformations to access valuable chiral building blocks in organic synthesis. In particular, the stereo-convergent chiral amine[1] and higher-order alcohol synthesis[2] from readily available racemic alcohols as well as enantioselective heterocycle functionalization[3] via borrowing hydrogen will be discussed in details.



References

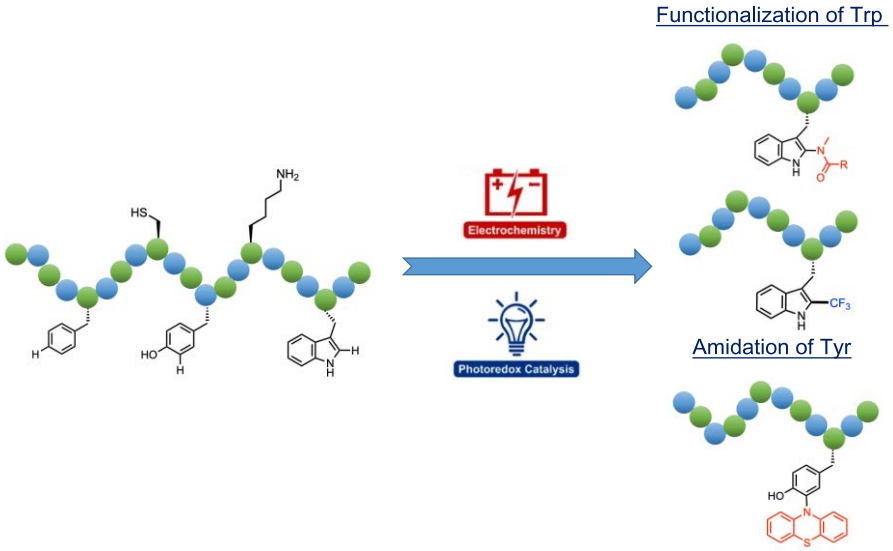
1. Pan, H.-J.; Lin, Y.; Gao, T.; Lau, K. K.; Feng, W.; Yang, B.; Zhao, Y. *Angew. Chem. Int. Ed.* **2021**, *60*, 18599-18604.
2. Ng, T. W.; Liao, G.; Lau, K. K.; Pan, H.-J.; Zhao, Y. *Angew. Chem. Int. Ed.* **2020**, *59*, 11384–11389.
3. (a) Liu, Y.; Tao, R.; Lin, Z.-K.; Yang, G.; Zhao, Y. *Nat. Commun*. **2021**, *12*, 5035; (b) Yang, G.; Pan, J.; Ke, Y.-M.; Liu, Y.; Zhao, Y. *Angew. Chem. Int. Ed.* **2021**, *60*, 20689-20694.

Yu Zhao (赵宇)
Peking University (B.S. 2002)
Boston College (Ph.D. 2008)
Postdoctoral Associate (MIT, 2008-2011)
Assistant Professor (NUS, 2011-2017)
Associate Professor (NUS, 2017-)
[Field of research] Organic Chemistry

Single Electron Transfer-based Aromatic Amino Acid Containing-Peptide/protein Bioconjugations

Chien-Wei Chiang*
Department of Chemistry, Soochow University
No.70, Linhsi Road, Shihlin District, Taipei 111002, Taiwan
E-mail: cwchiang@scu.edu.tw

The growing interest in peptides and antibody-drug conjugates as drug candidates in current therapeutics has stimulated increased interest in new bioconjugation strategies. Therefore, introducing new late-stage modification methods has become essential and attractive to researchers. Herein, we report on the mild biomolecule modifications with a single electron transfer (SET) process through the photoredox and electrolysis technologies, achieving the transformation of tryptophan and tyrosine, respectively. These protocols would be expected to provide new toolkits for the late-stage modification labeling and peptide–drug bioconjugation.



References
1. Weng, Y.; Ding, B.; Liu, Y.; Song, C.; Chan, L.-Y.; Chiang, C.-W.. *Org. Lett.*, **2021**, *23*, 2710-2714.
2. Ding, B.; Weng, Y.; Liu, Y.; Song, C.; Yin, L.; Yuan, J.; Ren, Y.; Lei, A.; Chiang, C.-W.. *Eur. J. Org. Chem.*, **2019**, *46*, 7596-7605.
3. Song, C.; Liu, K.; Wang, Z.; Ding, B.; Wang, S.; Weng, Y.; Chiang, C.-W.; Lei, A. *Chem. Sci*., **2019**, *10*, 7982-7987.

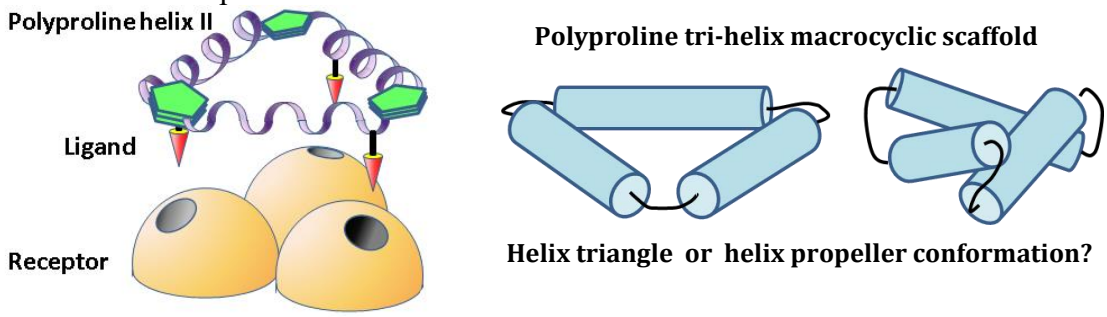
Chien-Wei Chiang (江建緯).

National Taiwan Normal University (Ph.D., 2008-2012).
Postdoctoral Fellow, Academia Sinica, Taiwan (2013-2015).
Postdoctoral Fellow, University of Cambridge, UK (2015-2016).
Associate Researcher, Wuhan University, PRC (2016-2020).
Assistant Professor, Department of Chemistry,
Soochow University, Taiwan (2021-now).
[Field of research] Bioorganic Chemistry.

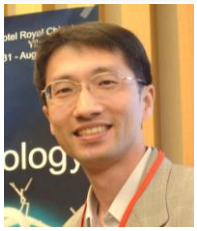
Polyproline macrocyclic nanoscaffolds: Applications in protein interactions and the structure analysis

Sheng-Kai Wang,* Cin-Hao Lin, Hsin-Chuan Wen, Chia-Lung Tsai
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan
E-mail: skwang@mx.nthu.edu.tw

Multivalent binding plays essential roles in biology, especially on recognition and signal transduction. Whereas the precise control of ligand presentation would provide enhanced binding avidity and additional spatial selectivity against cross-reactivity observed in ligand-protein binding, this poses a challenge to synthetic chemists as the distance between binding sites on protein oligomers are typically few nanometers.
We employed polyproline peptides as scaffolds to present ligands for their unique secondary structure that allows the distance and direction of the conjugated ligands to be precisely controlled. When the peptide helices were connected into a macrocycle, the pattern of the conjugated ligand on the cyclic scaffold can be manipulated. We demonstrated that the controlled ligand patterns recognized protein receptor oligomers based on their arrangements.[1] We exploited the scaffold to discriminate two human lectins langerin and DC-SIGN, both bind to high mannose of HIV but lead to different outcomes. By controlling oligomannose ligand pattern on cyclic scaffold to match the tetrameric receptor arrangement of DC-SIGN, a strong selectivity was observed to favor the application as promising selective anti-viral agents.[2] We further investigated the structure of polyproline tri-helix macrocyclic nanoscaffolds with CD spectroscopy, ion-mobility spectrometry and other approaches.[3] The results provide better understanding for the ligand positions on the nanoscaffold for future applications toward other receptors.



References
1. Lin CH, Wen HC, Chiang CC, Huang JS, Chen Y, Wang SK* *Small* **2019**, *15*, e1900561
2. Wen HC, Lin CH, Huang JS, Tsai CL, Chen TF, Wang SK* *Chem Commun* **2019**, *55*, 9124-9127
3. Tsai CL, Wu SY, Hsu HK, Huang SB, Lin CH, Chan YT,* Wang SK* *Nanoscale* **2021**, 13, 4592-4601

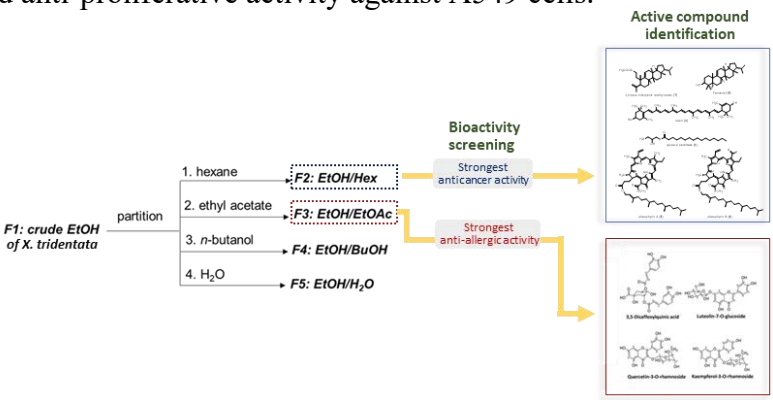


Sheng-Kai Wang (王聖凱). National Tsing Hua University, Hsinchu, Taiwan (BS, 1999), The Scripps Research Institute, La Jolla, USA (Ph.D, 2008). Assistant professor (2013-2019). Associate professor (2019-). Glycoscience and peptide nanotechnology.

Identification of active compounds responsible for the bioactivities of *Xenostegia tridentata*

Jaruwan Chatwichien[1,2]
[1]*Program in Chemical Biology, Chulabhorn Graduate Institute, Chulabhorn Royal Academy, Laksi, Bangkok, Thailand*
[2]*Center of Excellence on Environmental Health and Toxicology (EHT), OPS, Ministry of Higher Education, Science, Research and Innovation, Bangkok, Thailand*
E-mail: jaruwanc@cgi.ac.th

Xenostegia tridentata (L.) D.F. Austin & Staples has been used since ancient times, especially in India and Africa, as a medicinal plant for treatment of various diseases. Studies have shown that the plant possesses broad range of bioactivities including antioxidant, antimicrobial, wound healing, anti-diabetic, anti-inflammatory, and anti-arthritic activities. Despite extensive phytochemical analysis, knowledge on the chemical components and the active compounds responsible for the bioactivities of the plant is still limited. Recently, our group has reported that 3,5-dicaffeoylquinic acid, quercetin-3-O-rhamnoside, kaempferol-3-O-rhamnoside and luteolin-7-O-glucoside, isolated from the ethyl acetate subfraction of the ethanol extract of *X. tridentata*, are the compounds important for its anti-allergic property. This work, anticancer activity of *X. tridentata* was studied. Unlike in the case of anti-allergic activity, the hexane subfraction was found to be the most toxic to A549 human lung cancer cells. Both the crude ethanol extract and the hexane subfraction, as compared to the control, could inhibit cancer cell migration. Moreover, they could synergize with cisplatin to inhibit the cancer cell proliferation. The activities corresponded to the intracellular ROS induction. To identify the active compounds responsible for the anticancer activity of *X. tridentata*, the hexane subfraction was then further isolated, yielding six compounds that possessed anti-proliferative activity against A549 cells.



References

1. Suntivich, R., Songjang, W., Jiraviriyakul, A., Ruchirawat, S., Chatwichien, J. *PLoS ONE* **2022**, *17*(4), e0265505.
2. Krishnappan, AL. Seetharaman, TR. *Fitoterapia* **1992**, *63*(2), 190.
3. Austin, DF. *Ethnobot. Res. Appl*. **2014**, *12*, 433.

Jaruwan Chatwichien (จารุวรรณ ฉัตรวิเชียร). University of Pennsylvania (Ph.D. 2016). Naresuan University: Lecturer (2016-2019). Chulabhorn Graduate Institute: Lecturer (2020-present). [Field of Research] Natural product chemistry and Medicinal chemistry.

Chiral Aldehyde-Involved Ternary Catalysis

Qi-Xiang Guo,* Wei Wen, Lei Chen, Fang Zhu, Jian-Hua Liu
Southwest University, Chongqing, China, 400715
E-mail: qxguo@swu.edu.cn

Since the first chiral aldehyde-catalyzed asymmetric α–functionalization of aminomethyl compounds has been reported by us in 2014,[1] this novel organocatalytic strategy has gradually become a powerful strategy for the preparation of optically active nonproteinogenic α–amino acids and amines. Besides as organocatalysts, chiral aldehyde also can coordinate with other catalytic systems for achieving challenging organic transformations. Especially, the ternary catalytic system comprising a chiral aldehyde, a palladium, and a Lewis acid exhibited powerful catalytic activation and stereoselective control abilities (Figure 1a). With the utilization of this ternary catalytic system, we reported an asymmetric α–allylation[2] and an asymmetric α–benzylation[3] of *N*-unprotected amino acids in 2019 and 2022, respectively, and the asymmetric α–allylation of *aza*-aryl methylamines in 2021.[4] These works indicated that this ternary catalysis is potentially applicable in more and more asymmetric reactions (Figure 1b).

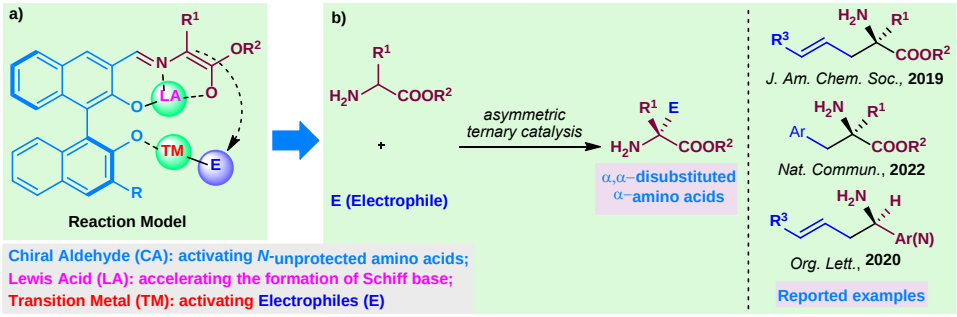


Figure 1. Chiral aldehyde-involved ternary catalysis. a) Reaction model; b) Reported reactions.

References

1. Xu, B.; Shi, L.-L.; Zhang, Y.-Z.; Wu, Z.-J.; Fu, L.-N.; Luo, C.-Q.; Zhang, L.-X.; Peng, Y.-G.; Guo, Q.-X.* *Chem. Sci.* **2014**, *5*, 1988-1991.
2. Chen, L.; Luo, M-J.; Zhu, F.; Wen, W.; Guo, Q.-X.* *J. Am. Chem. Soc.* **2019**, *141*, 5159-5163.
3. Liu, J.-H.; Wen, W.*; Liao, J.; Shen, Q.-W.; Lin, Y.; Wu, Z.-L.; Cai, T.; Guo, Q.-X.* *Nat. Commun.* **2022**, *13*, 2509.
4. Zhu, F.; Shen, Q.-W.; Wang, W.-Z.; Wu, Z.-L.; Cai, T.; Wen, W.*; Guo, Q.-X.* *Org. Lett.* **2021**, *23*, 1463-1467.

Qi-Xiang Guo (郭其祥). Graduate School of Chinese Academy of Sciences (PhD, 2007). Southwest University (Professor, 2008). [Field of research] Asymmetric Synthesis.

Enantiodivergence Enabled by the Development of Acyclic Chiral Secondary Aminocatalysts

Zhihui Shao*
Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, School of Chemical Science and Technology, Yunnan University
E-mail: zhihui_shao@hotmail.com

The development of enantiodivergent catalysis for the preparation of both enantiomers of a chiral compound is of importance in pharmaceutical and bioorganic chemistry. With the design of a class of reactive and stereoselective organocatalysts, acyclic chiral secondary amines, a method for achieving the enantiodivergence has been developed simply by changing the secondary *N*-*i*-Bu- to *N*-Me-group within the catalyst architecture while maintaining the same absolute configuration of the catalysts (Figure 1). This catalyst-controlled enantiodivergent method not only enables challenging and previously unknown asymmetric transformations to occur in an enantiodivergent manner but also features high level of stereocontrol and broad scope that is demonstrated in eight different reactions (90 examples), all delivering both enantiomers of a range of structurally diverse products including hitherto less accessible yet important compounds in good yields with high stereoselectivities.

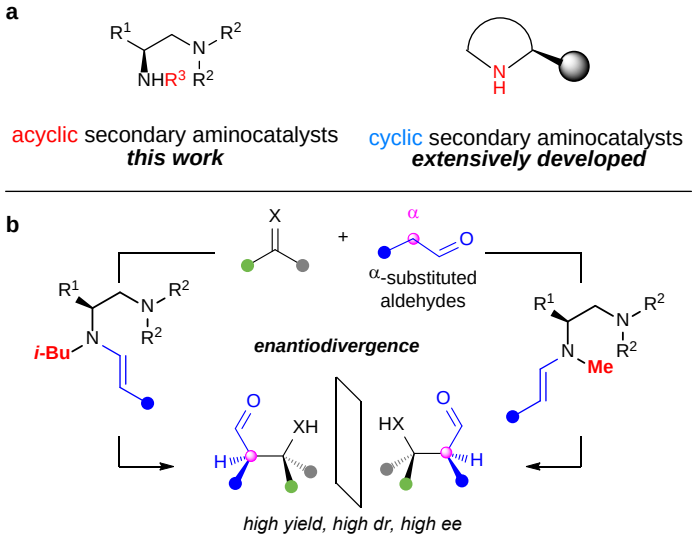


Figure 1. Enantiodivergence by Minimal Modification of an Acyclic Chiral Secondary Aminocatalyst

References

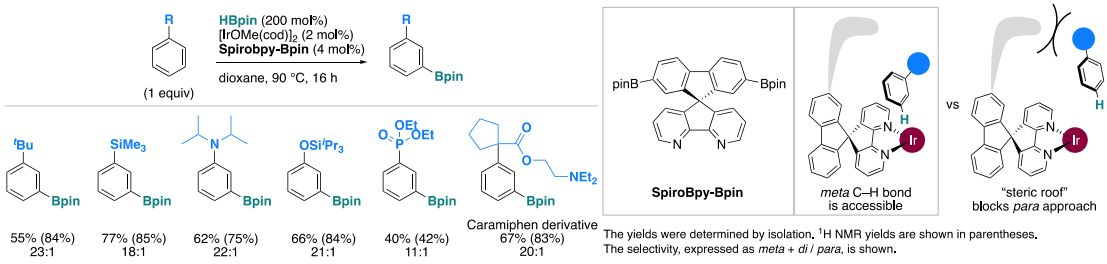
1. Dai, J.; Wang, Z.; Deng, Y.; Zhu, L.; Peng, F.; Lan, Y.; Shao, Z. *Nat. Commun.* **2019**, *10*, 5182.

Zhihui Shao (邵志会). Lanzhou University (PhD, 2004). University of Montreal (2004-2006), The Hong Kong Polytechnic University (2006-2007). Yunnan University (2007-now). [Field of research] Asymmetric catalysis and synthesis.

Spirobipyridine Enables Remote Steric Control and Rate Enhancement in Iridium-Catalyzed C–H Borylation of Arenes

Sobi Asako,* Yushu Jin, Boobalan Ramadoss, Laurean Ilies*
RIKEN Center for Sustainable Resource Science
Wako, Saitama 351-0198, Japan
E-mail: sobi.asako@riken.jp

Transition-metal-catalyzed regioselective C–H functionalization of arenes has been achieved by the use of "directing groups" with various attractive interactions or by electronically or sterically biasing the substrate. However, the regioselective functionalization of simple arenes such as alkylbenzenes, lacking in such interactions has remained challenging. We report herein a conceptually new ligand, SpiroBpy-Bpin, that sterically protects a *para* site to achieve *meta*-selective C–H activation in the iridium-catalyzed borylation. Thus, the rigid Bpin group functions as a steric "roof" to create a molecular pocket that allows the substrate to approach the catalytic center only in the *meta* orientation. The strategy proved general, and a variety of monosubstituted arenes including alkylbenzenes, anilines, phenols, and drug molecules could be selectively borylated at the *meta* position. We also found that the iridium/SpiroBpy catalyst accelerates the C–H borylation reaction and the reactions of reluctant electron-rich arenes with SpiroBpy proceeded more efficiently than with commonly used ligands such as dtbpy and tmphen.



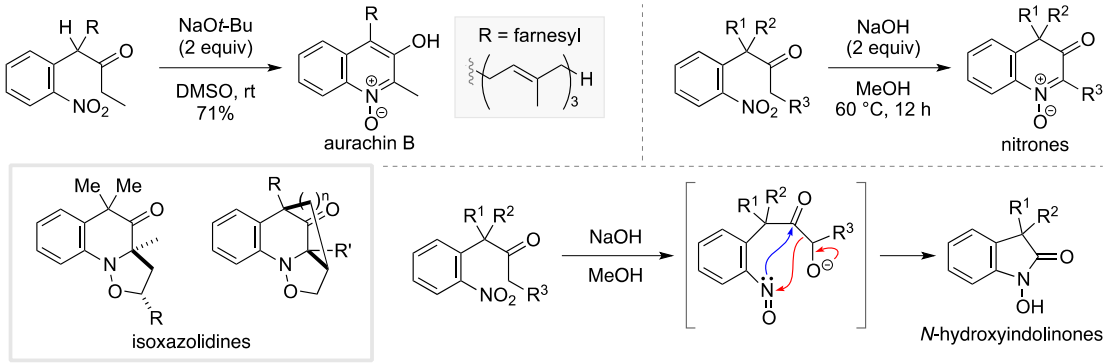
References
1. Ramadoss, B.; Jin, Y.; Asako, S.; Ilies, L. *Science* **2022**, *375*, 658.
2. *Synform* **2022/06**, A92 (doi: 10.1055/s-0040-1720561).

Sobi Asako (浅子壮美).
The University of Tokyo (Ph.D., 2014). Assistant Professor, Okayama University (2014–2019). Senior Scientist, RIKEN Center for Sustainable Resource Science (2019–present). Visiting Researcher, Okinawa Institute of Science and Technology Graduate University (2021–present).
[Field of research] synthetic organic chemistry, organometallic chemistry, molecular catalysis, computational chemistry.

Reactions of Ketones Having a 2-Nitrophenyl Group at the α-Position

Satoshi Yokoshima,* Hiroaki Shimizu, Kohei Yoshinaga, Shinnosuke Kitayama
Graduate School of Pharmaceutical Sciences, Nagoya University
Nagoya 464-8601, Japan
E-mail: yokosima@ps.nagoya-u.ac.jp

Aurachin B, a natural product having a quinoline *N*-oxide core, was synthesized from a ketone via cyclization by treatment with sodium *tert*-butoxide in DMSO at room temperature.[1] Considering the reaction mechanism of the cyclization, we tried the same reaction by using substrates that cannot be aromatized. The requisite substrates having a quaternary carbon at the benzylic position were prepared. By treatment with sodium hydroxide in methanol at 60 °C, the cyclization reaction proceeded to afford nitrones in good yield.[2] Inter- and intramolecular 1,3-dipolar cycloaddition of the resulting nitrones occurred to give a variety of isoxazolidines. During optimization of the nitrone formation, we obtained *N*-hydroxyindolinones as the major product under some conditions. The reaction might involve formation of α-hydroxyketone by an intramolecular reaction of an enolate with the nitro group, followed by attack of the resulting nitroso group to the α-hydroxyketone moiety.



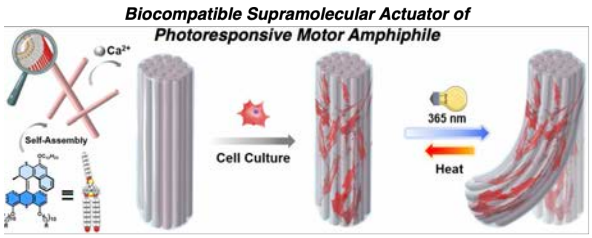
References
1. Haruhiko Hattori, Satoshi Yokoshima, Tohru Fukuyama, *Angew. Chem. Int. Ed.* **2017**, *56*, 6980-6983.
2. Hiroaki Shimizu, Kohei Yoshinaga, Satoshi Yokoshima, *Org. Lett.* **2021**, *23*, 2704-2709.

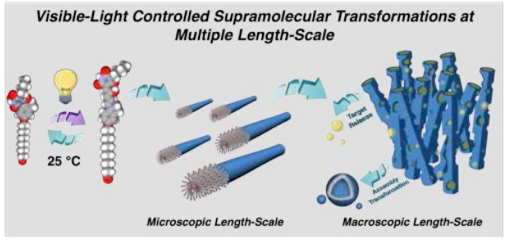
YOKOSHIMA Satoshi (横島　聡). He received his Ph.D. in 2002 from the University of Tokyo. After working for Mitsubishi Pharma Corporation as a medicinal chemist (2002-2004), he joined Professor Fukuyama's group at The University of Tokyo as an assistant professor. He was promoted to lecturer in 2008 and to associate professor in 2011. In 2012 he moved to Nagoya University as an associate professor, and was promoted to professor in 2017. [Field of research] Synthetic Organic Chemistry, Natural Products Chemistry.

Controlled Supramolecular Assemblies of Photoresponsive Molecular Amphiphiles at Multiple Length-Scale

Franco King-Chi Leung*
State Key Laboratory of Chemical Biology and Drug Discovery, Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University
E-mail: kingchifranco.leung@polyu.edu.hk

Advancements in supramolecular chemistry and soft 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, *e.g.*, azobenzenes, molecular motors, and stiff stilbenes, 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.[1a] Some of these photoresponsive molecular amphiphiles are capable to assemble across multiple length-scale, fabricating photoresponsive soft materials or supramolecular actuators at macroscopic length-scale.[1b,1c] 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 motor amphiphile[2] and visible-light controlled supramolecular soft materials.[3]





References

1. (a) Leung, F. K.-C.; Feringa, B. L. *et al. Nat. Chem.* **2018**, *10*, 132; (b) Leung, F. K.-C.; Feringa, B. L. *et al. J. Am. Chem. Soc.* **2018**, *140*, 17724; (c) Leung, F. K.-C.; Feringa, B. L. *et al. Angew. Chem. Int. Ed.* **2019**, *58*, 10985.
2. Chen, S.; Leung, F. K.-C.; Feringa, B. L. *et al. J. Am. Chem. Soc.* **2022**, *144*, 3543.
3. Cheung, L.-H; Kajitani, T.; Leung, F. K.-C. **2022**, *Under Review*.

Franco King-Chi Leung (梁敬池).
The Hong Kong Polytechnic University (B.Sc., 2011) (MPhil., 2013)
Tokyo Institute of Technology (Ph.D., 2017)
University of Groningen (Postdoc, 2017–2019, Prof. Ben L. Feringa)
Assistant Professor (PolyU, 2019–now)
Research Interests: Supramolecular Assembly and Molecular Machine.

Synergistic bimetallic catalysts for selective organic reactions

B. Moon Kim,* Jin Hee Cho, Ahra Cho, Jayoon Choi
Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul, 088826, Republic of Korea
E-mail: kimbm@snu.ac.kr

Heterogeneous catalysts offer several advantages over homogeneous ones including the possibility of mixing more than one metals to introduce new catalytic properties, which are not found in monometallic systems.[1] In this regards, we have been investigating several bimetallic alloy nanoparticle catalysts for efficient organic transformations. An example of bimetallic alloy catalytic systems include a new catalytic, one-pot synthesis of unsymmetrical secondary amines via the reductive amination of aryl nitriles with nitroalkanes using a PdPt–Fe_3O_4 nanoparticle catalyst. The use of a bimetallic catalyst resulted in increased reactivity and selectivity compared to the employment of either monometallic Pd–or Pt–Fe_3O_4 catalyst. With this bimetallic catalytic, synthesis of many unsymmetrical secondary amines was possible under mild conditions.[2]
Use of methanol as a sustainable C1 building block continues to attract attention. Methylation of amines using methanol as a C1 source can be atom-economical and simple one-pot protocol. So far, studies of methylation on heterogeneous systems have been restricted to noble monometallic catalysts such as Ir, Pd, and Pt. A bimetallic catalyst containing a non-noble metal can be an ideal tool to modify the reactivity of the catalyst. A new bimetallic PdCu– Fe_3O_4 nanoparticle catalyst is reported here for the selective *N*-methylation of aniline with methanol via a "hydrogen borrowing strategy". The PdCu catalyst system showed synergistic activity, which is superior to that of monometallic Pd and Cu catalyst. The best catalytic activity for *N*-methylation of aniline was studied with variation of metal compositions on Fe_3O_4 support. The electronic properties of the catalytic surface of Pd_xCu_y on Fe_3O_4 NPs were studied through the density functional theory (DFT) to decipher the synergistic effect according to the metal composition. The DFT calculation together with kinetic studies successfully explained the observed catalytic activities of *N*-methylation depending upon varying Pd/Cu ratios. Highly efficient monomethylations of a wide range of aromatic amines were converted to their corresponding *N*-methylamines through optimally chosen Pd_xCu_y catalyst system.

References

1. Cho, J. H.; Ha, Y.; Cho, A.; Choi, J.; Won, Y.; Kim, H.; Kim, B.M. *Cat. Sci. Technol.* **2022** in press (*DOI: 10.1039/D2CY00065B*).
2. Cho, J.H.; Byun, S.; Cho, A.; Kim, B.M. *Sci. Technol.* **2020**, 8, 7632-7651.

B. Moon Kim (김병문). M.I.T. (PhD, 1988). Dept. of Chemistry, Merck Research Laboratories (1990~1995). Seoul National University (1995~).
[Field of research] Synthetic organic chemistry, heterogeneous catalysis, and medicinal chemistry

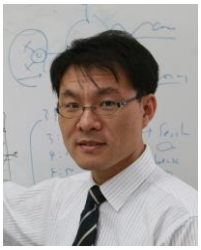
Self-assemblies formed by of expanded π-aromatic molecules

Woo-Dong Jang*, Jeong Heon Lee, Younghun Kim
[1]*Department of Chemistry, Yonsei University, Korea*
E-mail: wdjang@yonsei.ac.kr

Organic molecules with expanded π-aromatic electronic structures, including porphyrins, phthalocyanine, pyrene, and so on, have unique chemical and physical properties to attract attention in synthetic organic as well as physical chemists. Porphyrins and chlorophylls are often self-assembled into nanoscale superstructures to perform many essential functions, such as light harvesting and electron transport. The crystal structure of the light-harvesting antenna complexes in purple photosynthetic bacteria shows the presence of a highly symmetric wheel-like supramolecular architecture involving many bacteriochlorophyll pigments. From the inspiration of the natural light harvesting systems, a variety of porphyrin-based nanoarchitectures, such as nanofibers, nanosheets, nanoparticles, and nanorings have been fabricated for applications in various research fields including photonics, catalysis, and electronics. Depending on the coordination of metal ions into the center of porphyrin derivatives, optical, electrochemical, magnetic properties, and oxidation states can be varied. Since the skeletons of porphyrin and phthalocyanine have a C4 symmetry, they can be utilized as excellent building blocks to form various supramolecular structures. By introducing various functional groups to expanded π-aromatic compounds, the function of the molecule itself can be controlled, and various applications using photochemical and electrochemical characteristics are expected. In this context, we recently designed molecular building blocks composed of expanded π-aromatic organic molecules to obtain various types of supramolecular assemblies by introducing structural motifs to form hydrogen bonds, coordination bonds, and π-π interactions. In this symposium, we would like to report recent results of the supramolecular assemblies formed by expanded π-aromatic compounds

References

1. Park, J. M.; Hong, K.-I.; Lee, H.; Jang, W.-D. *Acc. Chem. Res.* **2021**, 54, 2249-2260.
2. Lee. H.; Lee, D.; Kim, I.; Lee, E.; Jang W.-D. *Macromolecules*, **2020**, 53, 8060-8067.
3. Oh, I.; Lee, H., Kim, T. W.; Kim, C. W.; Jun S.; Kim C.; Choi E. H.; Rhee, Y. M.; Kim, J., Jang W.-D.; Ihee, H. *Adv. Sci.* **2020**, 7, 2001623.
4. Jin, E.; Lee, I. S.; Kim D.; Lee, H., Jang W.-D.; Lah M. S., Min, S. K.; Choe, W. *Sci. Adv.* **2019**, 5, EAAV4119.
5. Yim D.; Sung J., Kim, S.; Oh, J.; Yoon, H.; Sung, Y. M.; Kim, D.; Jang, W.-D. *J. Am. Chem. Soc.* **2017**, 139, 993-1002.



Woo-Dong Jang (張祐銅) Kyungpook Nat'l Univ. (Bs, 1997), The Univ. Tokyo (Ph.D., 2003), Postdoc. JST CREST The Univ. Tokyo (2003-2005), Assistant Prof. Dept. Materials Eng. The Univ. Tokyo (2005-2006), Prof. Yonsei Univ. Dept. Chem. (2006-present), [Field of research] Supramolecular chemistry, Stimuli-responsive polymers

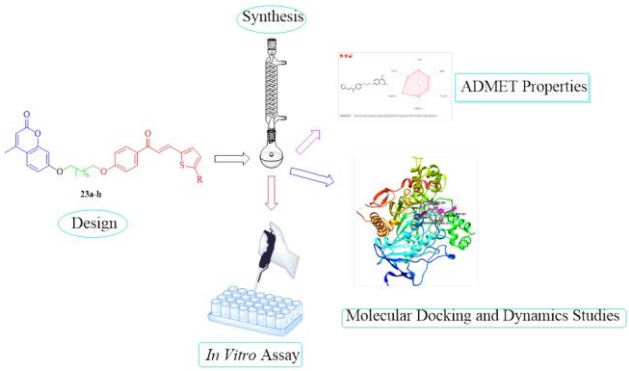
PA-43

Novel Thiophene Chalcones-Coumarin as Acetylcholinesterase Inhibitors: Design, Synthesis, Biological Evaluation, Molecular Docking, ADMET Prediction and Molecular Dynamics Simulation

Aso Hameed Hasan[a,b], Sankaranarayanan Murugesan[c], Syazwani Itri Amran[d], Subhash Chander[e], Mohammed M. Alanazi[f], Taibi Ben Hadda[g], Sonam Shakya[h], Mohammad Rizki Fadhil Pratama[i,j], Basundhara Das[k], Subhrajit Biswas[k], Joazaizulfazli Jamalis[a,*]

*[a] Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia. [b] Department of Chemistry, College of Science, University of Garmian, Kalar 46021, Kurdistan Region-Iraq, Iraq. [c] Medicinal Chemistry Research Laboratory, Birla Institute of Technology & Science Pilani (BITS Pilani), Pilani Campus, Pilani-333031, Rajasthan, India. [d] Department of Biosciences, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia. [e]Amity Inst Phytomedicine and Phytochemistry, Amity University, Amity Univ Uttar Pradesh, Noida 201313, India. [f] Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, Riyadh 11451, Saudi Arabia. [g] Umm Al Qura University Umm Al Qura Univ, Fac Pharm, Dept Pharmaceut Chem, Mecca 21955, Almukkarramah, Saudi Arabia. [h] Department of Chemistry, Faculty of Science Aligarh Muslim University, Aligarh 202002, India. [i] Doctoral Program of Pharmaceutical Sciences, Universitas Airlangga, Jl Dr Ir Soekarno Kampus C UNAIR Mulyorejo, Surabaya, East Java 60115, Indonesia. [j] Department of Pharmacy, Universitas Muhammadiyah Palangkaraya, Jl RTA Milono Km 1.5 Pahandut, Palangka Raya, Central Kalimantan 73111, Indonesia. [k]Amity Institute of Molecular Medicine and Stem Cell Research (AIMMSCR), Translational Cancer & Stem Cell Research Laboratory, Research Laboratory 101, J3 Block, Amity University, NOIDA, Uttar Pradesh, India. * E-mail: joazaizulfazli@utm.my*

A series of around eight novel chalcone based coumarin derivatives (**10a-h**) was designed, subjected to *in-silico* ADMET prediction, synthesized, characterized by IR, NMR, Mass analytical techniques and evaluated as acetylcholinesterase (AChE) inhibitor for the treatment of Alzheimer's disease (AD). The results of predicted ADMET study demonstrated the drug-likeness properties of the titled compounds with developmental challenges in lipophilicity and solubility parameters. The *in vitro* assessment of the synthesized compounds revealed that all of them showed significant activity (IC_{50} ranging from 0.42 to 1.296 µM) towards AChE compared to the standard drug, galantamine (IC_{50} = 1.142 ± 0.027 µM). Among these, compound **10e** displayed the most potent inhibitory activity with IC_{50} value of 0.42 ± 0.019 µM. Cytotoxicity of all compounds was tested on normal human hepatic (THLE-2) cell lines at three different concentrations using the MTT assay, in which none of the compound showed significant toxicity at the highest concentration of 1000µg/ml compared to the control group. Based on the docking study against AChE, the most active derivative **10e** was orientated towards the active site and occupied both catalytic anionic site (CAS) and peripheral anionic site (PAS) of the target enzyme. *In-silico* studies revealed tested showed better inhibition activity of AChE compared to Butyrylcholinesterase (BuChE). Molecular dynamics simulation explored the stability and dynamic behavior of compound **10e**, AChE complex.

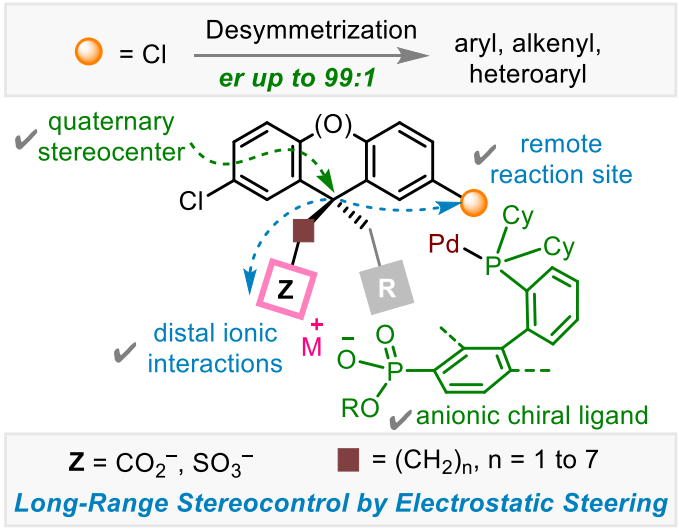


Joazaizulfazli Jamalis. University of Bristol, UK (PhD, 2011). Previous positions (year). Senior lecturer (2011-current). Organic Chemistry, Medicinal Chemistry.

Remote Quaternary Stereocenters Through Distal Ionic Interactions-Directed Desymmetrizing Suzuki–Miyaura Reaction

Ye Zhu,* Yazhou Lou, Junqiang Wei, Mingfeng Li
Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543
E-mail: chmzhu@nus.edu.sg

Catalytic construction of a chiral molecule relies on seamless communication between chirality of catalyst and prochirality of substrate. Spatial separation of a prostereogenic center from either the reaction sites or the prochirality-revealing groups (i.e., points of difference between geminal substituents) presents a universal hurdle in asymmetric catalysis. Here, we report an enantioselective, catalytic transformation where both the enantiotopic reaction sites and the prochirality-revealing groups are distant from a prostereogenic quaternary carbon. We addressed the challenges arising from the twofold spatial separations by innovating a unique anionic, axially chiral catalyst and developing a general strategy employing distal electrostatic interactions. This study demonstrates that, contrary to general expectation, it is viable to achieve precise long-range enantioinduction by engaging electrostatic interactions at a remote position, even as distant as 12 connecting atoms away from the reaction site.



Distal Ionic Substrate–Catalyst Interactions Enable Long-Range Stereocontrol

Reference
Lou, Y., Wei, J., Li, M., and Zhu, Y. *J. Am. Chem. Soc.* **2022**, *144*, 123–129.

Ye ZHU (朱烨). 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 (current). [Field of research] Organic Chemistry.

Concise Synthesis of (–)-Negamycin from a Chiral Advanced Epoxide

Cheng-Kun Lin* and Po-Yu Tseng
Department of Chemistry, National Chung Hsing University, 145 Xingda Rd., South Dist., Taichung City 402, Taiwan
E-mail: cklin93@nchu.edu.tw

(+)-Negamycin, an unusual antibiotic containing a hydrazine peptide linkage was originally isolated from *Streptomyces purpeofuscus* strains, exhibits strong inhibitory activity against Gram-positive and Gram-negative bacteria including *Pseudomonas aeruginosa* and *Klebsiella pneumonia*.[1] Its potent antibacterial activity make (+)-negamycin an attractive synthetic target. For instance, Davies[2] and Hayashi[3] independently used a chiral amine to react with an oxazolidine containing α,β-unsaturated ester to insert the second nitrogen of (+)-negamycin via asymmetric aza-Michael addition. In this work, we converted **epoxide A**, that its enantiomer was prepared during our study toward the synthesis of citreochlorol monochloro analogs.[4] to natural product antibiotic (–)-negamycin (**Figure 1**). Since this advanced intermediate has the main carbon chain required for the target and subsequent functional group conversions can be performed to furnish the total synthesis of (–)-negamycin as shown in **Figure 1**.

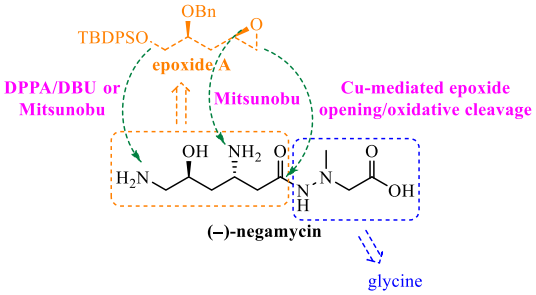


Figure 1. The transformations of designed intermediate to the target

References

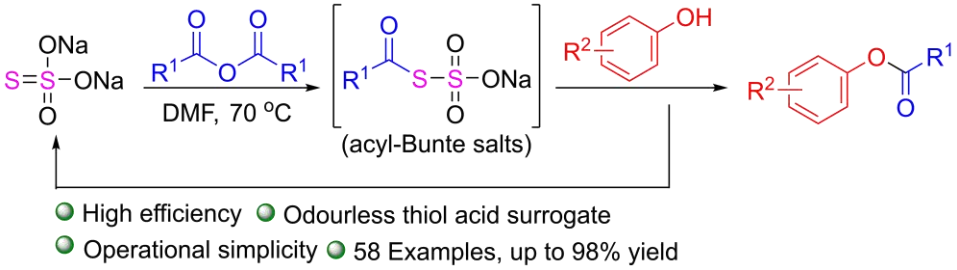
1. Hamada, M.; Takeuchi, T.; Kondo, S.; Ikeda, Y.; Naganawa, H.; Maeda, K.; Okami, Y.; Umezawa, H. *J. Antibiot.* **1970**, *23*, 170−171.
2. Davies, S. G.; Ichihara, O. *Tetrahedron: Asymmetry* **1996**, *7*, 1919−1922.
3. Hayashi, Y.; Regnier, T.; Nishiguchi, S.; Sydnes, M. O.; Hashimoto, D.; Hasegawa, J.; Katoh, T.; Kajimoto, T.; Shiozuka, M.; Matsuda, R.; Node, M.; Kiso, Y. *Chem. Commun.* **2008**, 2379–2381.
4. Lin, C. K.; Hsieh, B. H.; Wu, C. F. *Synthesis* **2022**, *54*, 1321−1328.

Cheng-Kun Lin (林正坤) obtained his organic chemistry Ph.D. degree from Department of Chemistry, National Chung-Hsing University in 2011 and did his postdoctoral research at Genomics Research Center, Academia Sinica (2011–2018). He became an Assistant Professor (2018-present) at Department of Chemistry, National Chung-Hsing University. The major research efforts are directed toward the development of new synthetic strategies for biologically interesting natural products. Research interests include: Asymmetric synthesis, Total synthesis of natural products, and Synthesis of potential inhibitors/antibiotics inspired from natural sources.

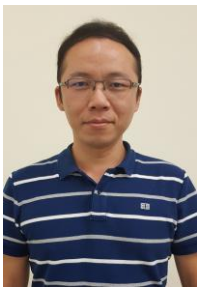
An Acyl Bunte salt as a Nucleophilic Catalyst for Selective Phenol Acylation

Chien-Fu Liang,* Wei-Jr Liao, Sih-Yu Lin, Yu-Shan Kuo
Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
E-mail: lcf0201@dragon.nchu.edu.tw

Although thioacid as an acylating agent to synthesize amide bonds has been successfully verified, few studies have attempted to use thioacids to form ester bonds by directly acylating a hydroxyl group.[1-2] In this study, we presented an efficient method for synthesizing phenolic esters from anhydrides and phenols through sodium thiosulfate catalysis under transition metal-free and oxidant-free conditions. In term of overall design, our strategy uses catalytic amounts of sodium thiosulfate as the sulfur source for acylation with aryl anhydrides to produce corresponding acyl-Bunte salts as an intermediate,[3] which can be considered an analogue of thioacid and be used as a nucleophilic acylating agent. Furthermore, we applied this proposed method for the site-selective acylation of the phenolic hydroxyl group in the presence of other alcoholic groups. Finally, the practical potential of acyl-Bunte salts for site-selective phenol acylation was demonstrated through the structural modification of pharmaceutical natural compounds.



References
1. Liu, H.-X.; Dang, Y.-Q.; Yuan, Y.-F.; Xu, Z.-F.; Qiu, S.-X.; Tan, H.-B. *Org. Lett.* **2016**, *18*, 5584.
2. Shi, L.; Liu, H.; Hou, L.; Dang, Y.; Wang, Y.; Yang, B.; Qiu, S.; Tan, H. *Org. Chem. Front*. **2018**, *5*, 1312.
3. Liao, Y.-S.; Liang, C.-F.* *Org. Biomol. Chem*. **2018**, *16*, 1871.
4. Liao, W.-J.; Lin, S.-Y.; Kuo, Y.-S.; Liang, C.-F.* *Submitted*.



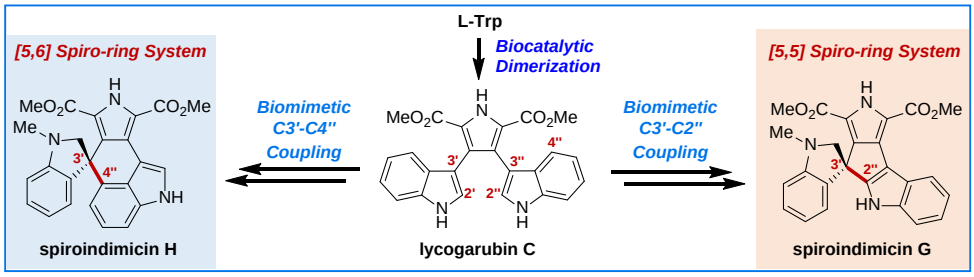
Chien-Fu Liang (梁健夫) received his B.Sc. (2003) in chemistry from NCHU, and earned his M.Sc. (2005) and Ph.D. (2009) in Chemistry from NTHU in Taiwan under the supervision of Professor Chin-Kang Sha and Chun-Cheng Lin. After a post-doc with Professor Chun-Cheng Lin at NTHU (2010-2012), Professor Peter H. Seeberger at MPI, Germany (2012-2014) and Professor Po-Chiao Lin at NSYSU (2014-2015), he joined National Chung Hsing University (assistant professor, 2015-2019; associate professor, 2019~). His research interests are primarily in the areas of organic synthesis.

Biomimetic Total Synthesis of Spiroindimicin Family of Natural Products

Zhengren Xu,* Xikang Zheng, Yan Li
State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, 38 Xueyuan Road, Haidian, Beijing 100191, China
E-mail: zhengrenxu@bjmu.edu.cn

First isolated from deep-sea-derived *Streptomyces* strains, the spiroindimicin family of natural products with either [5,6] or [5,5] spiro-ring systems represent a unique group of tryptophan dimers that are derived from the oxidative dimerization of two tryptophan molecules.[1] While a planar indolocarbazole skeleton was found in most of the members of tryptophan dimers including staurosporine and rebeccamycin, the two indole planes of spiroindimicins positioned perpendicular to each other, forming a T-shaped non-planar skeleton. The intriguing structure have accumulated two reports on the total synthesis of spiroindimicin family of natural products, including the first total synthesis of [5,5] spiro-ring members by Sperry and co-workers, and the first total synthesis of [5,6] spiro-ring members by Smith and co-workers, respectively.[2]

We herein reported our unified strategy for the total synthesis of both [5,6] and [5,5] spiro-ring members of the spiroindimicin family of natural products. We have developed a two-enzyme-catalyzed process for the preparation of the key intermediate lycogarubin C from the oxidative dimerization of L-tryptophan. On the other hand, biomimetic oxidative C3′-C2″ and C3′-C4″ couplings converted the suitably protected lycogaruin C to two skeletally different natural products, including spiroindimicin G with a [5,5] spiro-ring system, and spiroindimicin H with a [5,6] spiro-ring system, respectively.



References

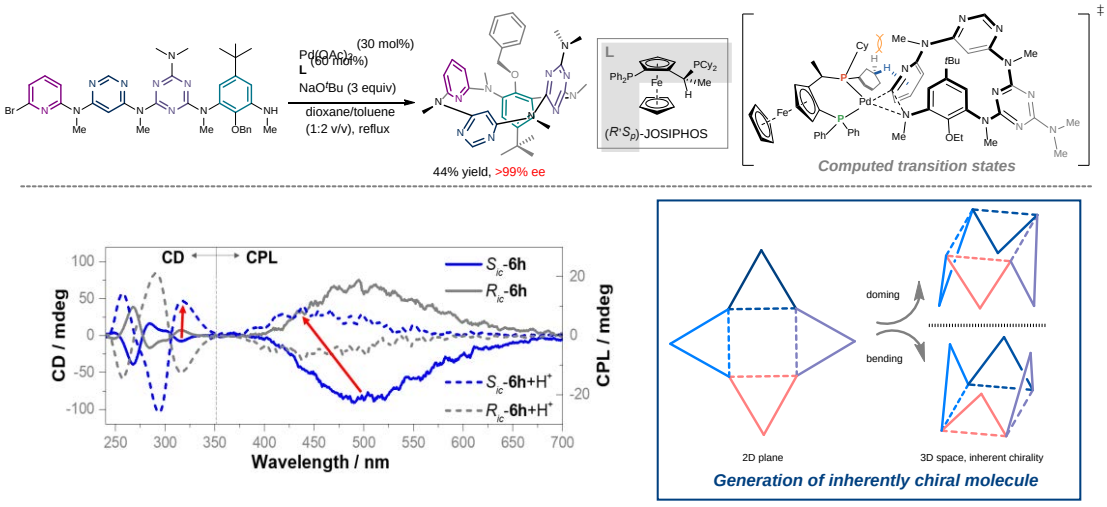
1. (a) Zhang, C. et al. *Org. Lett.* **2012**, *14*, 3364-3367; (b) Luzhetskyy, A. et al. *Sci. Rep.* **2017**, *7*, 42382; (c) Zhang, C. et al. *Org. Biomol. Chem.* **2019**, *17*, 1053-1057.
2. (a) Blair, L. M.; Sperry, J. *Chem. Commun.* **2016**, *52*, 800-802; (b) Smith, M. W. et al. *Chem. Sci.* **2021**, *12*, 10388-10394.

Zhengren Xu (徐正仁). Peking University (Ph. D., 2011). Postdoctoral Associate (2011-2014, in EPFL with Prof. Jieping Zhu). Postdoctoral Associate (2014-2018, in Scripps Florida with Prof. Ben Shen). Assistant Professor (2018-now). [Field of research] Natural Product Chemistry.

Catalytic Enantioselective Synthesis and Switchable Chiroptical Property of Inherently Chiral Macrocycles

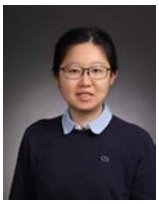
Shuo Tong,* Mei-Xiang Wang
Department of Chemistry, Tsinghua University, Beijing, P. R. China
E-mail: tongshuo@mail.tsinghua.edu.cn

Molecular chirality is classified generally into point, axial, planar, and helical chirality based on stereogenic elements. In 1994, Böhmer coined inherent chirality to describe macrocycles devoid of any symmetry elements except a C_1 asymmetry axis. Inherently chiral macrocycles have drawn growing attention owing to their unique chiral structures and chiral recognition properties. However, it is noteworthy that while synthesis and application of conventional types of chiral molecules have reached a highly sophisticated level, catalytic synthesis of enantiomerically pure inherently chiral molecules remains a formidable challenge. We report herein a strategy to construct enantiopure inherently chiral macrocycles through a catalytic enantioselective intramolecular C-N bond forming reaction.[1] A chiral ligand-palladium complex was found to efficiently induce the inherent chirality of molecules during the macrocyclization process with *ee* values up to >99%. The resulting inherent chiral macrocycles displayed excellent and pH-triggered switchable electronic circular dichroism (ECD) and circularly polarized luminescence (CPL) properties.



Reference

1. Shuo Tong,* Jiang-Tao Li, Dong-Dong Liang, Yan-E Zhang, Qi-Yun Feng, Xin Zhang, Jieping Zhu, Mei-Xiang Wang*, *J. Am. Chem. Soc.* **2020**, *142*, 14432-14436; and unpublished results.



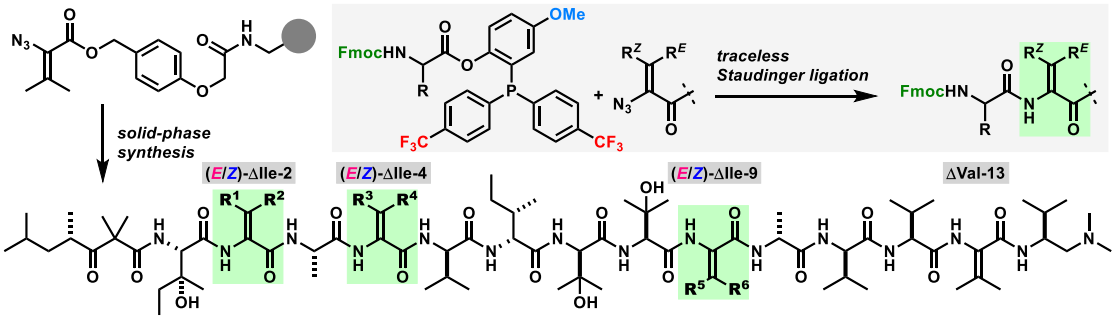
Shuo Tong (佟硕). Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing, P. R. China (Ph.D. 2007-2013). Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland (Postdoc. 2013-2018). Associate Prof. (since 2018). Organic synthesis and supramolecular chemistry.

Solid-Phase Total Synthesis and Functional Analysis of Yaku'amide B and Its Analogues

Hiroaki Itoh, Masayuki Inoue
Graduate School of Pharmaceutical Sciences, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
E-mail: itoh@mol.f.u-tokyo.ac.jp

Yaku'amide B (**1**) is a structurally complex natural peptide isolated from the rare deep-sea sponge *Ceratopsion* sp. The unique structure of **1** characterized by four β,β-dialkylated α,β-unsaturated amino acids and N- and C-terminal groups exerts potent growth inhibitory activity against multiple cancer cell lines. Despite its important biological activity, the lack of efficient synthetic methods had hampered the detailed biological investigation and structure-function relationship study on **1**.

In this presentation, solid-phase total synthesis and biological evaluation of **1** and its analogues will be reported.[1,2] The efficient construction of β,β-dialkylated α,β-unsaturated amino acid residues was achieved by optimized stereoselective traceless Staudinger ligation. The solid-phase strategy successfully generated **1** and its seven *E*/*Z* isomers **2**-**8**, which enabled to conduct the functional evaluation. Biological assays proved the importance of the *E*/*Z* stereochemistries of three dehydroisoleucines (ΔIle) for inhibition of cancer cell growth and ATP production by F_oF_1-ATP synthase.[3]



compounds	R^1 R^2	R^3 R^4	R^5 R^6
yaku'amide B (**1**, *ZEZ*)	Et Me	Me Et	Et Me
2 (*EEZ*)	Me Et	Me Et	Et Me
3 (*ZZZ*)	Et Me	Et Me	Et Me
4 (*EZZ*)	Me Et	Et Me	Et Me

compounds	R^1 R^2	R^3 R^4	R^5 R^6
5 (*ZEE*)	Et Me	Me Et	Me Et
6 (*EEE*)	Me Et	Me Et	Me Et
7 (*ZZE*)	Et Me	Et Me	Me Et
8 (*EZE*)	Me Et	Et Me	Me Et

References

1. Itoh, H.; Miura, K.; Kamiya, K.; Yamashita, T.; Inoue, M. *Angew. Chem., Int. Ed.* **2020**, *59*, 4564.
2. Kamiya, K.; Miura, K.; Itoh, H.; Inoue, M. *Chem. Eur. J.* **2021**, *27*, 1088.
3. Kitamura, K.; Itoh, H.; Sakurai, K.; Dan, S.; Inoue, M. *J. Am. Chem. Soc.* **2018**, *140*, 12189.

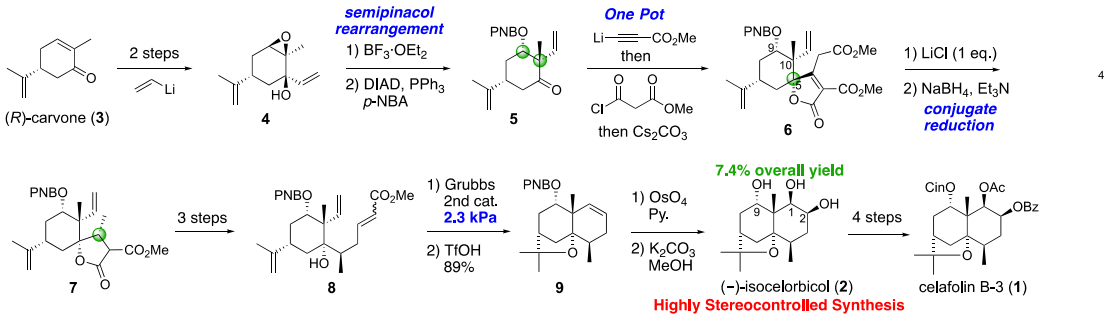
Hiroaki Itoh (伊藤寛晃). The University of Tokyo (Ph.D., 2013). FUJIFILM Corporation (2013-2015). Graduate School of Pharmaceutical Sciences, The University of Tokyo: Assistant Professor (2015-present). [Field of research] Synthetic Organic Chemistry, Bioorganic Chemistry.

Total Syntheses of Celafolins B-1, B-2, and B-3 Enabled by the Highly Stereocontrolled Synthesis of (–)-Isocelorbicol

Yusuke Ogura,* Tomoyo Mohri
Graduate School of Agricultural and Life Sciences, The University of Tokyo
1-1-1 Yayoi, Bunkyo-ku, Tokyo, 113-8657, Japan
E-mail: ayskogura@g.ecc.u-tokyo.ac.jp

The highly stereocontrolled total synthesis of isocelorbicol (**2**), an alkaline hydrolysis product of the seed oil of *Celastrus orbiculatus*,[1] has been accomplished in 7.4% overall yield from (*R*)-carvone (**3**) through a concise 14-step sequence. The structure of isocelorbicol (**2**) futures a tricyclic basic skeleton known as dihydro-β-agarofuran, seven densely packed stereocenters, and six axially oriented substituents of the decalin ring. The scalable synthesis of **2** enabled the first total syntheses of its naturally occurring and bioactive ester derivatives, celafolins B-1, B-2, and B-3 (**1**).[2] This synthesis features (1) stereoselective installation of the C10 quaternary asymmetric carbon by the semipinacol rearrangement (**4**→**5**); (2) one-pot transformation of **5** to **6** in an excellent yield of 93%; (3) complete diastereofacial selectivity in the construction of the methyl-bearing C4 chiral center based on the difference in the steric environment between the α and β faces of the butenolide ring in **6** (**6**→**7**); (4) ring-closing metathesis under vacuum to promote the formation of the decalin ring system (**8**→**9**); and (5) manipulation of the three hydroxy groups of **2** to obtain celafolin Bs.[3]

There are proper negligible discrepancies between the spectroscopic data of our synthetic sample of **2** and those of previous synthesis. Therefor, the structure of our synthetic **2** was unambiguously confirmed by X-ray crystallographic analysis.



References
1. Smith, C.R. *et. al. J. Org. Chem.* **1976**, *41*, 3264–3269.
2. Iwashima, A. *et. al. J. Nat. Prod.* **1993**, *56*, 815–824.
3. Mohri, T.; and Ogura, Y. *et. al. Org Lett.* **2020**, *22*, 9234–9238.

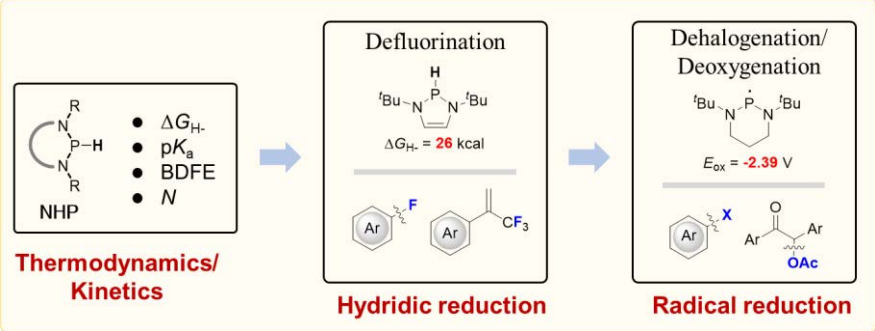
Yusuke Ogura (小倉由資). The University of Tokyo (Ph.D., 2012). Oxford University (Postdoctoral fellow, 2012-2014). Tohoku University (Assistant Professor, 2014-2019), The University of Tokyo (Assistant Professor, 2019; Associate Professor, 2020). [Field of research] Natural Product Chemistry, Synthetic Organic Chemistry, Natural Product Synthesis.

Reactivity Studies and Synthetic Applications of *N*-Heterocyclic Phosphines

Jingjing Zhang, Jin-Dong Yang,* Jin-Pei Cheng
CBMS, Department of Chemistry, Tsinghua University, Beijing, China.
E-mail: jdyang@mail.tsinghua.edu.cn

N-heterocyclic phosphines (**NHP**s), represented by diazaphospholenes, have emerged as a promising class of hydride reagents since their unique hydridic reactivity was revealed in 2000. Their super-hydricity, presumably stronger than most metal hydrides, yet with common features of organic reagents makes synthetic applications of P-H hydrides a burgeoning field in recent years. However, the lack of a quantitative understanging of the structure-reactivity relationship hampers their promising potential to find new reductions or new efficient P-H reagents. Moreover, their synthetic applications were limited to hydridic reduction, other reaction patterns (e.g., serving as hydrogen-atom or electron donors) are undeveloped and largely overlooked.

In the past several years, we have evaluated the thermodynamic and kinetic property of representative **NHP**s,[1] based on which we designed a new versatile **NHP** which could serve as the hydride, hydrogen-atom and proton donors,[2] and further exploited their selectively reductive defluorination via a hydridic mechanism[3] as well as opened up their synthetic applications in radical chemistry,[4] e.g., dehalogenation and deoxygenation (Scheme 1).[5]



Scheme 1. Reactivity studies and synthetic applications of **NHP**s.

References

1. Zhang J., Yang J.-D., Cheng J.-P. *Angew. Chem. Int. Ed.* **2019**, *58*, 5983-5987.
2. Zhang J., Yang J.-D., Cheng J.-P. *Chem. Sci.* **2020**, *11*, 3672-3679.
3. (a) Zhang J., Yang J.-D., Cheng J.-P. *Nat. Commun.* **2021**, *12*, 2835; (b) Zhang J., Zhao X., Yang J.-D., Cheng J.-P. *J. Org. Chem.* **2022**, *87*, 294-300.
4. (a) Zhang J., Yang J.-D., Cheng J.-P. *Chem. Sci.* **2020**, *11*, 4786-4790; (b) Zhang J., Yang J.-D., Cheng J.-P. *Chem. Sci.* **2020**, *11*, 8476-8481.
5. Zhang J., Yang J.-D., Cheng J.-P. *Natl. Sci. Rev.* **2021**, *8*, nwaa253.

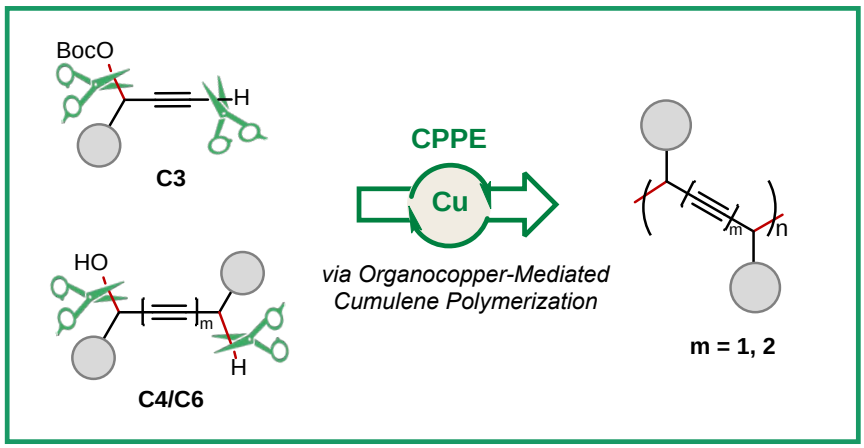
Yang Jin-Dong (杨金东). Nankai University (PhD., 2009-2014). Nankai University (postdoctor, 2014-2017). Tsinghua University (2017-now). Physical Organic Chemistry.

Copper-Catalyzed Condensation Polymerization of Propargylic Electrophiles

Bin Wu, Han-Li Sun, Qianyi Liu, Rong Zhu*
College of Chemistry and Molecular Engineering, Peking University
E-mail: rongzhu@pku.edu.cn

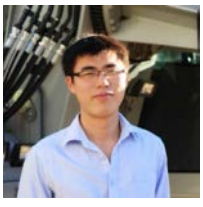
Polymers with alkyne-rich backbones are interesting synthetic targets. Current methods for the synthesis of alkyne polymers typically involve either polycouplings and metathesis, which utilizes the acetylenic bonds and carbon–carbon triple bonds, respectively.

Recently, we introduced a new strategy based on propargylic bond activation: copper-catalyzed condensation polymerization of propargylic electrophiles (CPPE).[1,2] In the presence of a copper catalyst and an electron-rich phosphine ligand, simple C3, C4 and C6 were polymerized in high efficiency and with exclusive regioselectivity, forging a unique "head-to-head" all carbon alkyne-rich backbone. Mechanistic studies revealed a new pathway for the *in situ* formation and chain-growth polymerization of [n]cumulenes, both mediated by copper. The isomerization of these polymers provided new conjugated polymers with interesting electrical properties.



References

1. Wu, B.; Su, H.-Z.; Wang, Z.-Y.; Yu, Z.-D.; Sun, H.-L.; Yang, F.; Dou, J.-H.; Zhu, R. *J. Am. Chem. Soc*., **2022**, *144*, 4315-4320.
2. Sun, H.-L.; Wu, B.; Liu, D.-Q.; Yu, Z.-D.; Wang, J.-J.; Liu, Q.; Liu, X.; Niu, D.; Dou, J.-H.; Zhu, R. *J. Am. Chem. Soc*., **2022**, *144*, 8807-8817.

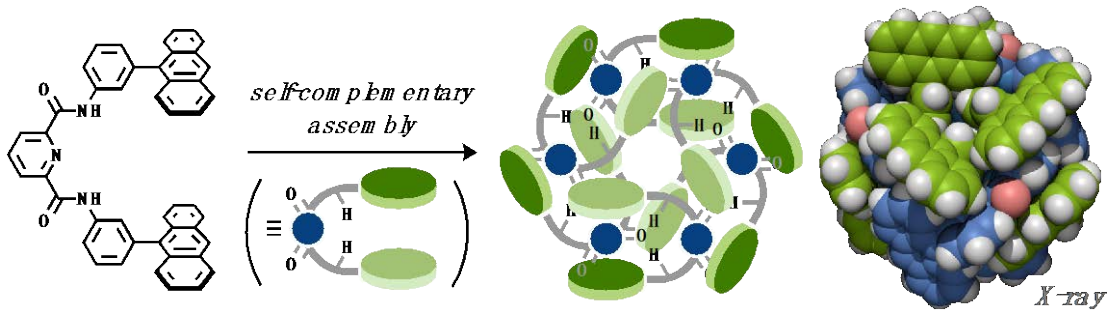


Rong Zhu (朱戎), Peking University (B.S., 2010), MIT (Ph.D., 2015, PostDoc, 2015-2018), Peking University (Assistant Prof. 2018-). Transition metal catalysis, polymer chemistry, functional organic materials.

Construction of a Self-Complementary Macrocycle by Dual Interaction System

Masahiro Yamashina,* Yuta Sawanaka, Hiroyoshi Ohtsu, Shinji Toyota*
Department of Chemistry, School of Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan.
E-mail: yamashina@chem.titech.ac.jp

Self-complementary assembly[1] is one of the most promising phenomena for the formation of discrete assemblies, e.g., proteins and capsids. However, self-complementary assembly based on multiple host-guest systems has been scarcely reported due to the difficulty in controlling each assembly.[2] Herein, we report a dual interaction system in which the key assembly direction is regulated by both π-π stacking and hydrogen bonding to construct a self-complementary macrocycle. Continuous host-guest behavior of anthracene-based molecular tweezers led to successful construction of an unprecedented cyclic hexamer, as confirmed by single crystal and powder X-ray analyses. The dual interaction system consisting of intermolecular π-π interactions and hydrogen bonds in concert provides exclusive formation of a cyclic hexamer in a triple-layered fashion among at least 32 types of possible linear isomers. The discrete and tight packing of the hexamer was well-reflected in its fluorescent property and thermal stability. Furthermore, the cyclic hexamers transformed into both a giant spherical cuboctahedron composed of 108 molecular tweezers and rhombohedral grid assemblies upon simple addition of TFA as a result of hierarchical assembly.[3]



References

1. Rebek, J., Jr. *Chem. Soc. Rev.* **1996**, *25*, 255–264.
2. (a) Rotzler, J., Mayor, M. *Chem. Soc. Rev.* **2013**, *42*, 44–62; (b) Yang, X., Wang, R., Kermagoret, A., Bardelang, D. *Angew. Chem. Int. Ed.* **2020**, *59*, 21280–21292.
3. Sawanaka, Y., Yamashina, M., Ohtsu, H., Toyota, S. *submitted*.

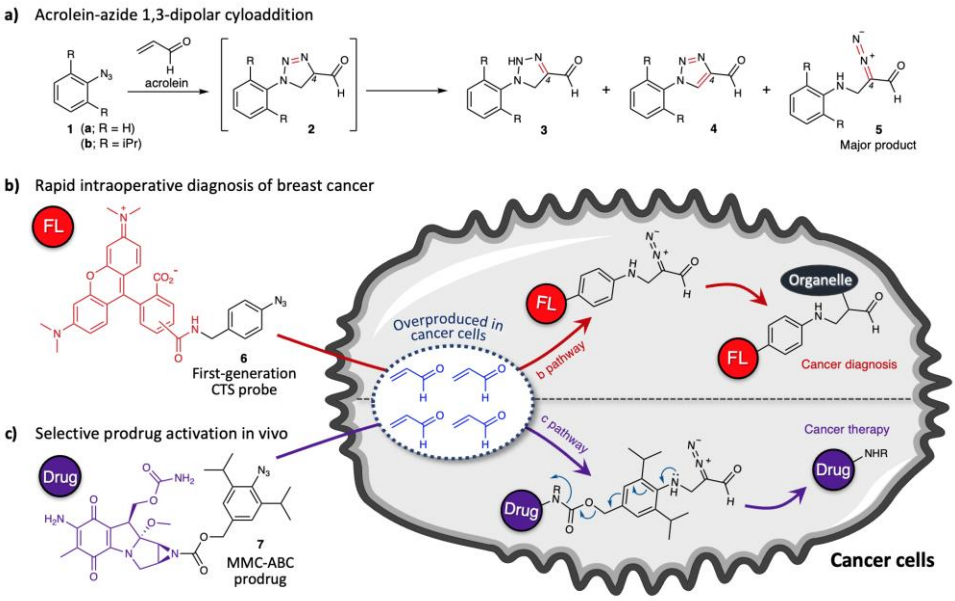
Masahiro Yamashina (山科雅裕). Tokyo Institute of Technology (Ph.D. in Engineering, 2016). Postdoctoral researcher at the University of Cambridge (2017). Assistant professor at the Tokyo Institute of Technology (2019). [Field of research] Supramolecular chemistry, organic chemistry, and coordination chemistry.

Biofunctional chemistry and reactivity of biogenic acrolein for cancer diagnosis and therapy

Ambara R. Pradipta,[a,b,*] Katsunori Tanaka [a,b]
[a]Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, 152-8552, Tokyo, Japan; [b]Biofunctional Synthetic Chemistry Laboratory, Cluster for Pioneering Research, RIKEN, 2-1 Hirosawa, Wako, 351-0198, Saitama, Japan;
E-mail: pradipta.a.aa@m.titech.ac.jp

Previously, we discovered [2+3] cycloaddition reaction between aryl azide **1a** and acrolein, which proceeds without a catalyst to give α-diazocarbonyl **5a** as the major product. The reaction proceeds with high reactivity and selectivity even under physiological conditions. We have successfully utilized the CTS probe **4** as a robust method for detecting and visualizing acrolein generated by live cells.[1] Furthermore, we found that a high level of acrolein is expressed in cancer cells, whereas only a negligible amount is expressed in healthy cells. We utilized the azide-acrolein click reaction to discriminate breast cancer lesions from the normal breast gland, which was resected from breast cancer patients.[2] This method can be used to visualize the cancer tissues rapidly and to distinguish the morphology of the resected tissues. Thus, it has a potential clinical application for breast-conserving surgery.

More recently, we found that the reaction rate of a bulky 2,6-diisopropylphenyl azide **1b** with acrolein is about ten times faster than the rate observed for the reaction between the simple phenyl azide **1a** with acrolein. Also, we observed that acrolein presence in cancer tissues is higher than in cultured cancer cells. Accordingly, we designed MMC-ABC prodrug **7** to target acrolein in cancer tissue of xenograft mouse models.[3] The method successfully treats cancer in mouse models without inducing any side effects caused by the off-target reaction.



(a) Aryl azide **1** reacts with acrolein to give **5** as the primary product. (b) CTS probe for cancer diagnosis. (c) MMC-ABC prodrug to target acrolein for prodrug activation.[4]

References

(1) Pradipta, A. R., Tanaka, K., et al., *ACS Sens.* **2016**, 1, 623.; (2) Pradipta, A. R., Tanaka, K., et al., *Adv. Sci.* **2019**, *6*, 1801479.; (3) Pradipta, A. R., Tanaka, K., et al., *Chem. Sci.* **2021**, *12*, 5438.;(4) Pradipta, A. R., Tanaka, K., *Chem. Commun.* **2021**, 57, 9798.

Ambara R. Pradipta. Osaka University (Ph.D., 2011). RIKEN, Researcher (2012-2020). Tokyo Institute of Technology, Assistant Professor (2020~present). [Field of research] Bioorganic Chemistry, Organic Synthesis Chemistry, Natural Product Chemistry.

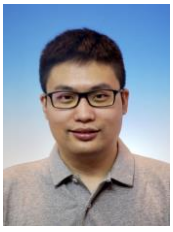
Photoinduced Dehydrogenative Borylation via Dihydrogen Bond Bridged Electron Donor and Acceptor Complexes

Yangjian QUAN,* Zhiyong WANG
The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong
E-mail: chyjquan@ust.hk

Despite the versatile applications of organoboron compounds ranging from synthons to pharmaceuticals, their preparation still suffers from limitations of relatively low boron-atom economy and/or rigorous reaction conditions.[1] The use of air stable boranes as the feedstocks brings a mild and compatible route to organoboron compounds.[2] We very recently discovered that tetracoordinated boranes could work as competent donors to generate photoactive electron-donor-acceptor (EDA) complexes. Our experimental results and DFT calculations suggested a dihydrogen bond bridging the donor and acceptor. Illuminating the corresponding EDA complex enabled an intramolecular single electron transfer to give boron-centered radical for dehydrogenative borylation. This investigation is anticipated to pave a convenient avenue towards more efficient borylation with functional group compatibility.

References

1. (a) Mkhalid, I. A. I.; Barnard J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*. 890-931. (b) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández E. *Chem. Soc. Rev*. **2017**, *46*, 415-430.
2. Curran, D. P.; Solovyev, A.; Makhlouf Brahmi, M.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem. Int. Ed*. **2011**, *50*, 10294-10317.

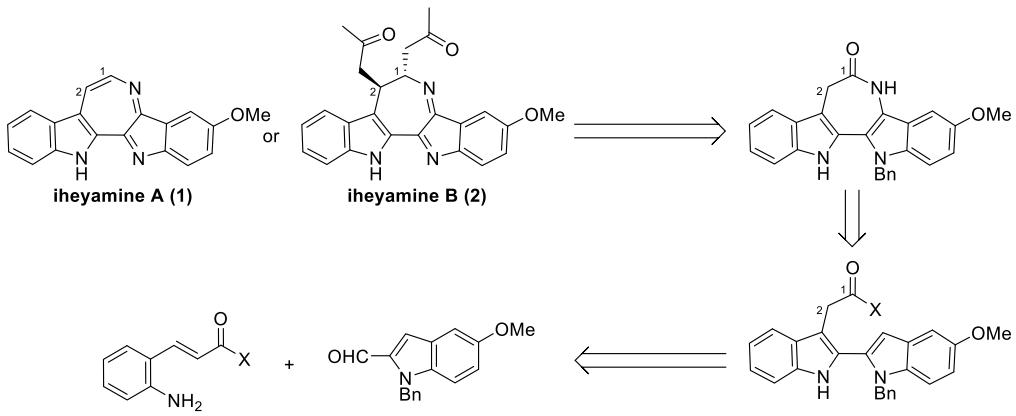


Yangjian QUAN (全杨健). Nanjing University (BS, 2011), The Chinese University of Hong Kong (PhD, 2015; Research Assistant Professor 2015-2019), University of Chicago (2019-2021). Assistant Professor (2021). [Field of interest] Boron Chemistry, Organic Synthesis, Metal-Organic Framework.

Total Syntheses of Iheyamines A and B

Cheol-Hong Cheon,* Jiye Jeon
Department of Chemistry, Korea University, Seoul, Republic of Korea
E-mail: cheon@korea.ac.kr

Iheyamines A (**1**) and B (**2**) were isolated in 1999 from a colonial ascidian *Polycitorilla* sp. collected off the coast of Iheya, Okinawa.[1] Iheyamine A and B possesses a unique azepino-2,2'-bisindole subunit as its basic scaffold, and iheyamine B has additional vicinal 2-oxopropyl groups in a *trans*-configuration on the azepine scaffold located at the C-1 and 2 positions. In addition to its distinct structural features, these two alkaloids display cytotoxicity against several cancer cell lines. The unique structural features and beneficial biological activities, along with its very low bioavailability, have prompted the chemical community to develop a total synthesis of this natural product. Although the total synthesis of iheyamine A has been previously reported,[2] there have been no reports on the total synthesis of iheyamine B. As iheyamines A and B are isolated from the same source in nature and possess structural similarities, we envisioned that iheyamines A and B may be synthesized from the same intermediate in their biosynthetic pathway. Herein, we present the first divergent total syntheses of iheyamines A and B from bisindoloazepinone.



References
1. Sasaki, T.; Ohtani, I. I.; Tanaka, J.; Higa, T. *Tetrahedron Lett.* **1999**, *40*, 303−306.
2. (a) Lindsay, A. C.; Leung, I. K. H.; Sperry, J. *Org. Lett.* **2016**, *18*, 5404−5407. (b) Abe, T.; Yamada, K. *Org. Lett.* **2018**, *20*, 1469−1472. (c) Jeon, J.; Kim, H. J.; Cheon, C.-H. *J. Org. Chem.* **2020**, *85*, 8149-8156.
3. Jeon, J.; Cheon, C.-H. *Manuscript in Preparation.*

Cheol-Hong Cheon (천철홍, 千喆洪). University of Chicago (PhD, 2010). Korea University, Assistant, Associate, and Full Professor (2011 ~ present). [Field of research] Organic Synthesis, Total Synthesis of Natural Products, Umpolung Chemistry.

CuBr-Catalyzed One-Pot Three-Component Synthesis of Novel 2-(Carbazolyl)benzothiazoles

Ramu Meesala*[a], Yean Kee Lee[a], Ahmad Saifuddin Mohamad Arshad[b], Iskandar Abdullah[a], Mohd Nizam Mordi[b], Noorsaadah Abd. Rahman[a].

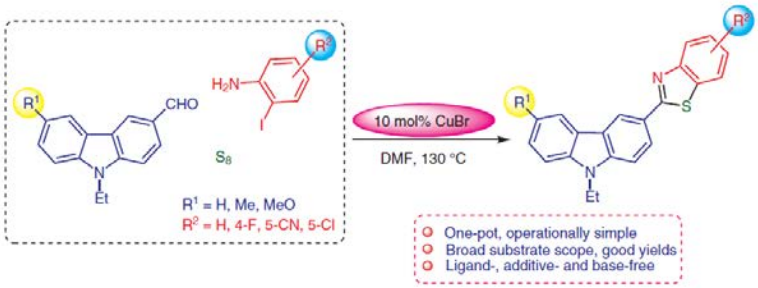
[a] *Drug Design and Development Research Group, Department of Chemistry, Faculty of Science, Universiti Malaya, 50603, Kuala Lumpur, Malaysia*

[b] *Centre for Drug Research, Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia*

meesalaramu@gmail.com; iskandar.a@um.edu.my

A facile synthesis of various 2-(carbazolyl)benzothiazoles has been developed by one-pot CuBr-catalyzed three-component reactions of 2-iodoanilines, arylaldehydes, and elemental sulfur. Unlike traditional approach, this reaction exhibited a good functional group tolerance to produce the corresponding 2-(carbazolyl)benzothiazoles in good yields in the absence of any additive.

Keywords: 2-(carbazolyl)benzothiazoles, 2-iodoanilines, arylaldehydes, elemental sulfur



Copper bromide catalysed reaction for the preparation of various 2-(carbazolyl)benzothiazoles in DMF as solvent.

References

1. Fontana, G. *Curr. Bioact. Compd.* **2010**, *6*, 284.
2. (a) Meesala, R.; Arshad, A. S. M.; Pichika, M. R.; Mordi, M. N.; Mansor, S. M. *Synlett* **2018**, *29*, 1084. (b) Meesala, R.; Arshad, A. S. M.; Mordi, M. N.; Mansor, S. M. *Tetrahedron Lett.* **2014**, *55*, 7023. (c) Meesala, R.; Ezzat, M. O.; Mordi, M. N.; Mansor, S. M. *Synlett* **2014**, *25*, 2176. (d) Meesala, R.; Nagarajan, R. *Synlett* **2010**, 2808. (e) Meesala, R.; Nagarajan, R. *J. Chem. Sci.* **2009**, *121*,183. (f) Meesala, R.; Nagarajan, R. *Tetrahedron* **2009**, *65*, 6050. (g) Meesala, R.; Nagarajan, R. *Tetrahedron Lett.* **2006**, *47*, 7557.
3. (a) Liu, C.; Yuan, J.; Gao, M.; Tang, S.; Li, W.; Shi, R.; Lei, A. *Chem. Rev.* **2015**, *115*, 12138. (b) Zhao, D. B.; You, J. S.; Hu, C. W. *Chem. Eur. J.* **2011**, *17*, 5466. (c) Bugaut, X.; Glorius, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 7479.

ISKANDAR ABDULLAH. Universiti Malaya (Ph.D, 2015). PostDoc (University of Manchester, 2015-2016). Senior Lecturer (2016-current) | Deputy Director Graduate Employability, Entrepreneurship & Student Development Centre, Student Affairs Division (2020-current). Organic Synthesis & Drug Design.

Synthesis of a Fully Conjugated Zigzag Carbon Nanobelt

Chunyan Chi,* Yi Han
Department of chemistry, National University of Singapore
E-mail: chmcc@nus.edu.sg

Single-walled carbon nanotubes (SWCNTs) are regarded as one of the most promising materials for the next generation microelectronics. The length, diameter, and edge structure determine their electronic properties and applications. However, atomic precise synthesis of SWCNTs seems to be almost impossible. Fully conjugated, double-stranded carbon nanobelts (CNBs) as sidewall fragments of CNTs were regarded as the "laurel" for synthetic chemists because of their unique electronic structures, aesthetic beauty, and synthetic difficulties. However, pioneering synthetic attempts toward CNBs only led to partially saturated or cross-conjugated counterparts of CNBs. In recent years, there has been a revival of interest in the bottom-up organic synthesis of CNBs. Sidewall segments of SWCNTs with arm-chaired edges and chiral edges have been synthesized. However, synthesis towards the fragments of zigzag edged CNTs remained elusive before 2020. In this poster, the synthesis and physical properties of a fully conjugated carbon nanobelt with zigzag edges (See Figure 1) will be reported. Strain analysis by DFT calculations reveals the phenyl substituents at the zigzag edges are crucial to the successful synthesis of the CNB with zigzag edges. We hope to open the gate to zigzag CNBs and inspire more work in this exciting and challenging field.

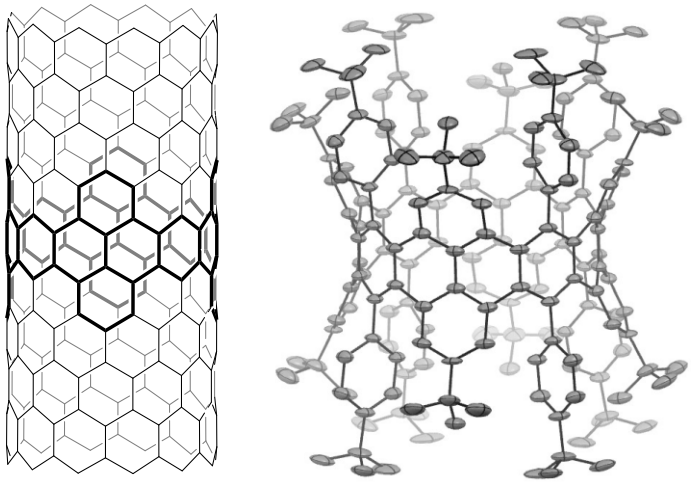


Figure 1. The structure of octabenzo[12]cyclacene.

References

1. Han, Y.; Dong, S.; Shao, J.; Fan, W.; Chi, C.* *Angew. Chem. Int. Ed*. **2021**, *60*, 2658-2662.

Chunyan CHI (池春彦). Max-Planck Institute for Polymer Research (PhD, 2004), University of California at Santa Barbara (Postdoc. 2005-2007). National University of Singapore (Assistant Professor, 2011-2017, Associate Professor, 2017-present). [Field of research] Organic Chemistry (on pi-conjugated systems), Materials Chemistry, Physical Organic Chemistry.

Syntheses of Glycoprobes as Tools to Interrogate Biological Systems

Pei-Jhen Li,[a] Chun-Cheng Lin*,[b]
[a]Department of Chemistry and Biochemistry, National Chung Cheng University, Chiayi 621301, Taiwan
[b]Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan
E-mail: chepjli@ccu.edu.tw and cclin66@mx.nthu.edu.tw

Investigations of protein-protein interactions (PPIs) are crucial for uncovering molecular mechanisms and the physiological basis of diseases and developing next-generation therapies. However, PPI elucidations have remained challenging and poorly characterized. Lectin-glycoprotein interactions are especially difficult to study due to their low affinities and transient interactions. To overcome these limitations, recently, we developed ligand-assisted imprinting probes (LIP)[1]. The LIP-based approaches are used to build different kinds of lectin probes for further interrogating lectin-glycoprotein interactions in biological systems. LIPs were designed with dual photoactivatable groups for construction of an alkyne handle proximal to the carbohydrate-binding pocket of lectins, Ricinus communis agglutinin 120 (RCA120), recombinant human Siglec-2/7 protein (rSiglec-2/7). Moreover, the azide-containing functional groups including photoreactive diazirine crosslinker, environment-sensitive fluorophore, anti-cancer agent doxorubicin (Dox) can be conjugated to alkynylated lectins via the bioorthogonal click chemistry (Figure **1**). The modified RCA120 or rSiglec-2 was used for detecting the interaction with target glycoprotein in solution or endogenously expressed glycoproteins on live HeLa cells. In addition, rSiglec-7 can serve as a drug carrier and Dox-rSiglec-7 conjugate can be transported to Siglec-ligand-expressing HeLa cells. We expect that LIP labeling method can be a general strategy to achieve the discovery of novel PPIs.

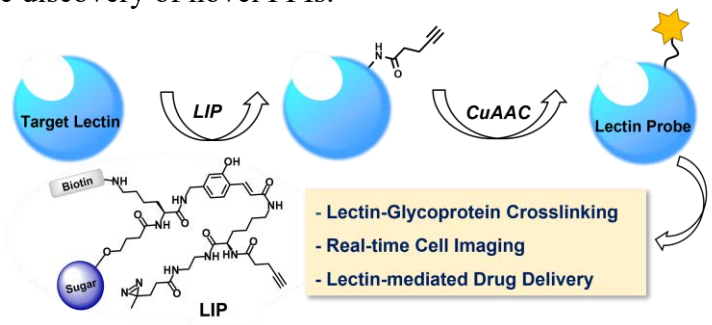


Figure **1**. The construction of a lectin probe from the glycoprobe via the LIP strategy.

References

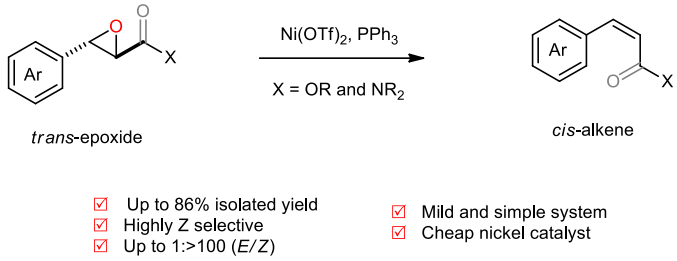
1. P.-J. Li, M. T. Anwar, C.-Y. Fan, D. S. Juang, H.-Y. Lin, T.-C. Chang, S. K. Kawade, H.-J. Chen, Y.-J. Chen, K.-T. Tan, C.-C. Lin, *Biomacromoles* **2020**, *21*, 815–824.

Pei-Jhen Li (李珮甄). National Chung Cheng University. Assistant professor (2021-present). Organic Chemistry and Carbohydrate Chemisrty.

Nickel-Catalyzed Stereoinvertive Deoxygenation of *trans*-Epoxides to *cis*-Alkenes

Sunisa Akkarasamiyo[a],* Saranya Chitsomkhuan[a], Supawadee Buakaew[a], Joseph S.M. Samec[b], Pitak Chuawong[a], Punlop Kuntiyong[c]
[a]*Department of Chemistry, Faculty of Science, Kasetsart University, Thailand.*
[b]*Department of Organic Chemistry, Stockholm University, Sweden.*
[c]*Department of Chemistry, Faculty of Science, Silpakorn University, Thailand*
E-mail: sunisa.a@ku.ac.th

Alkenes are versatile building blocks in organic synthesis. Both *trans*- and *cis*-isomers of alkenes interact with reagents or biomolecular targets differently. *cis*-Alkenes, which are less thermodynamically stable than *trans*-isomers, are also less abundant in nature. Furthermore, stereoselective methods for synthesis of *cis*-alkenes have been less developed nowadays. We report a stereoinvertive deoxygenation of *trans*-epoxides to access *cis*-alkenes using nickel triflate with triphenyl phosphine. High functional group tolerance was observed where *cis*-cinnamate esters, *cis*-cinnamamides and *cis*-cinnamyl ethers contained methoxy, halogent and nitro groups were obtained in high yields with moderate to high *E/Z* ratios.



Scheme 1 Deoxygenation of *trans*-epoxides to *cis*-alkenes using nickel catalyst

References

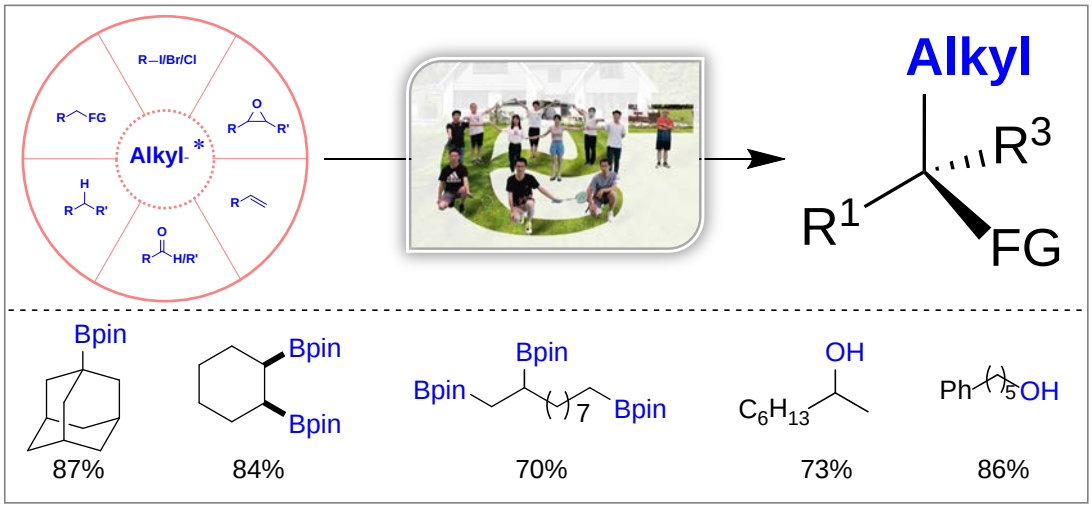
1. Lamb, J.R.; Hubbell, A.K.; MacMillan, S.N.; Coates, G.W. *J. Am. Chem. Soc.* **2020**, *142*, 8029−8035
2. Asako, S.; Sakae, T.; Murai, M.; Takai, K. *Adv. Synth. Catal.* **2016**, *358*, 3966-3970
3. Akkarasamiyo, S.; Chitsomkhuan, S.; Buakaew, S.; Samec, J.S.M.; Chuawong, P.; Kuntiyong, P. *Synlett* **2022**, DOI : 10.1055/s-0040-1719911 (Cluster : Organic Chemistry in Thailand)

Sunisa Akkarasamiyo (สุนิสา อัคคะรัสมิโย). Kasetsart University (Ph.D. (Chemistry) 2014). Post-doc (2014-2020). Lecturer (2020-present). [Organic Synthesis] Organic Chemistry.

Organic Electroreduction: Construction of Alkyl-Based Structures

Qingquan Lu*
The Institute for Advanced Studies (IAS), Wuhan University, Wuhan 430072, P. R. China
E-mail: gci2011@whu.edu.cn

Electrosynthesis utilize an electron as a sustainable and inherently safe redox reagent, which migrates the use of reactive (even dangerous) and sthochiometric oxidants and reductants, representing an environmentally benign, atomically economical and easy-to-operate method. Moreover, reaction selectivity in eletrochemistry can be perfectly tuned by the external potential or current density via precisely controlling the desired reaction sequences. Recently, various alkyl-based molecules, such as alkyl alcohols and alkyl boronic esters, have been constructed efficiently in our group via electrosynthesis.



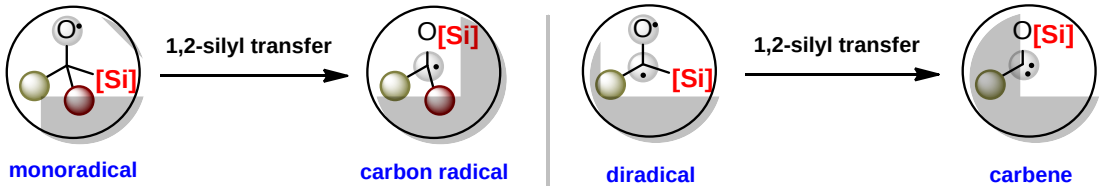
References
1. Huang, C.; Ma, W.; Zheng, X.; Xu, M.; Qi, X.;* **Lu, Q.,*** *J. Am. Chem. Soc.* **2022**, *144*, 1389.
2. Wang, B.; Peng, P.; Ma, W.; Liu, Z.; Huang, C.; Cao, Y.; Hu, P.; Qi, X.;* **Lu, Q.,*** *J. Am. Chem. Soc.* **2021**, *143*, 12985.

Prof. Qingquan Lu
The Institute for Advanced Studies (IAS), Wuhan University
Homepage: http://qingquanlu.whu.edu.cn/
Research Area: Electroorganic Synthesis, Transition Metal Catalysis, Radical Chemistry, AI Chemistry

Selective Transformations Enabled by C-Si Bond Activation with Alkoxy Radicals

Xiao Shen*
Institute for Advanced Studies, Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, Wuhan University, 299 Bayi Road, Wuhan, Hubei 430072, China
E-mail: xiaoshen@whu.edu.cn

Compared with that of C-H bond, the ionic bond property of the C-Si bond increases, so it is more prone to undergo heterolysis, rather than homolysis. Therefore, the activation of C-Si bond mainly depends on the two-electron activation modes such as Lewis base activation and transition metal insertion. The mode of single-electron activation of C-Si bond will provide different reactivity from that of two-electron activation mode, thus would expand the synthetic application value of organosilicon compounds. Considering that alkoxy radical is a kind of highly active free radical and can form a stable O-Si bond with silicon, our group have utilized the strategy of "**alkoxy radical C-Si bond activation**" to achieve selective transformations of organosilicon compound. Various radical and carbene reaction have been developed based on this strategy.[1~3]



Intramolecular C-Si bond activation with alkoxy radicals

References

1. (a) Chen, X.; Gong, X.; Li, Z.; Zhou, G.; Zhang, W.; Liu, S.; Shen, X. *Nat. Commun.* **2020**, *11*, 2756; (b) Zhu, Z.; Chen, X.; Liu, S.; Zhang, J.; Shen, X. *Eur. J. Org. Chem.* **2021**, 4927; (c) Chen, X.; Zhu, Z.; Liu, S.; Chen, Y.-H.; Shen. X. *Chin. Chem. Lett.* **2022**, *33*, 2931.
2. (a) Yang, Z.; Niu, Y.; He, X.; Chen, S.; Liu, S.; Li, Z.; Chen, X.; Zhang, Y.; Lan, Y.; Shen, X. *Nat. Commun.* **2021**, *12*, 2131; (b) Zhang, Y.; Zhang, Y.; Shen, X. *Chem Catal.* **2021**, *1*, 423; (c) He, X.; Zhao, Y.; Zhang, Z.; Shen, X. *Org. Lett.* **2022**, *24*, 1991.
3. (a) Zhou, G.; Shen, X. *Angew. Chem. Int. Ed.* **2022**, *61*, e202115334; (b) Zhang, Y.; Zhou, G.; Gong, X.; Guo, Z.; Qi, X.; Shen, X. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202175.

Xiao Shen (沈晓). Shanghai Institute of Organic Chemistry (PhD, 2008~2013, advisor: Professor Jinbo Hu). Harvard University (Postdoc, 2014~2015, advisor: Professor Tobias Ritter). Boston College (Postdoc, 2015~2017, Advisor: Professor Amir H. Hoveyda). Wuhan University (Professor, 2017~now). Field of research: organosilicon chemistry and catalysis.

Synthesis of Sequence-Controlled Supramolecular Terpolymers

Takeharu Haino*
Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University
E-mail: haino@hiroshima-u.ac.jp

Supramolecular polymeric assemblies represent an emerging, promising class of molecular assemblies with enormous versatility compared with their covalent polymeric counterparts. We have been developing supramolecular polymers that are formed through the molecular recognition of host molecules based on calix[5]arenes[1,2,3] and bisporphyrins[4,5,6]. In this presentation, I will describe the development of sequence-controlled supramolecular terpolymer.[7] Complementary biscalix[5]arene-C_{60}, bisporphyrin-trinitrofluorenone (TNF) and Hamilton's bis(acetamido pyridinyl)isophthalamide-barbiturate hydrogen-bonding host-guest complexes are completely orthogonal. Thus, the combinations of the mismatched host-guest complexes were incorporated into heteroditopic monomers **1**, **2**, and **3**. Their host-guest association generated the ABC-sequence-controlled supramolecular terpolymer poly-**1•2•3**.

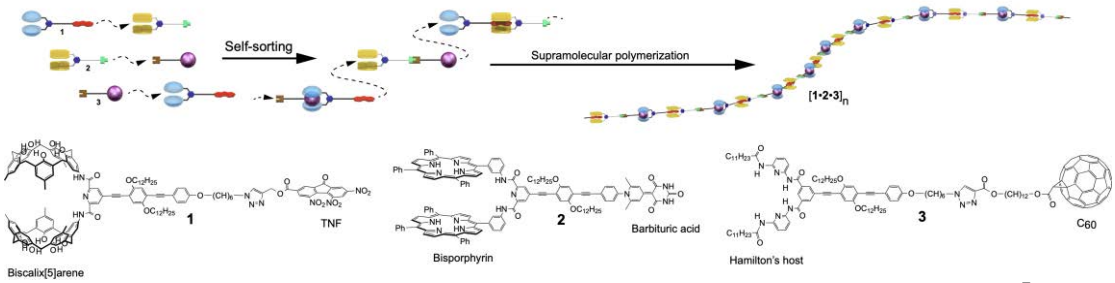


Figure 1. Schematic representation of supramolecular terpolymerization.[7]

References

1. Hirao, T.; Iwabe, Y.; Fujii, N.; Haino, T. *J. Am. Chem. Soc.* **2021**, *143*, 4339-4345.
2. Nitta, N.; Takatsuka, M.; Kihara, S.-i.; Hirao, T.; Haino, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 16690-16697.
3. Tsunoda, Y.; Takatsuka, M.; Sekiya, R.; Haino, T. *Angew. Chem. Int. Ed.* **2017**, *56*, 2613-2618.
4. Nadamoto, K.; Maruyama, K.; Fujii, N.; Ikeda, T.; Kihara, S.-i.; Haino, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 7028 - 7033.
5. Haino, T.; Watanabe, A.; Hirao, T.; Ikeda, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 1473-1476.
6. Haino, T.; Fujii, T.; Watanabe, A.; Takayanagi, U. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10477-10481.
7. Hirao, T.; Kudo, H.; Amimoto, T.; Haino, T. *Nat. Commun.* **2017**, *8*, 634.

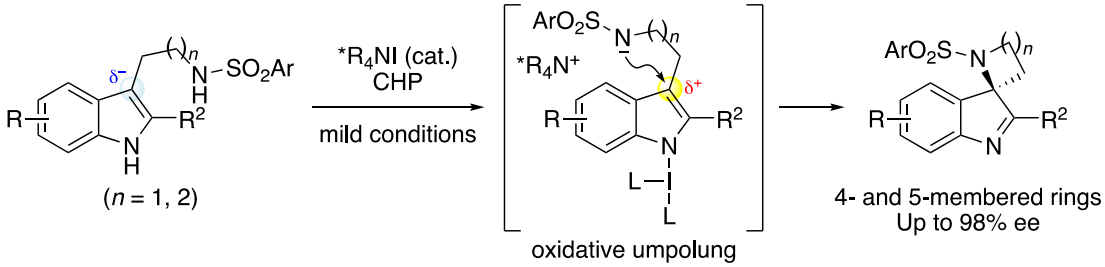
Takeharu Haino (灰野岳晴). Hiroshima University (PhD, 1992). Sagami Chemical Research Center (Post Doctorial Fellow, 1992-93), Assistant Professor, Department of Chemistry, Hiroshima University (1993-2000), The Scripps Research Institute (Post Doctorial Fellow, 1999-2000), Associate Professor (2000-2007), Full professor (2007-2021), Distinguished professor (2021-). Research Interests: Supramolecular Chemistry, Polymer Chemistry, and Graphene Chemistry.

Enantioselective Ammonium Hypoiodite Catalysis for Oxidative Umpolung of Indoles

Muhammet Uyanik,* Hiroki Tanaka, Naoya Ukegawa, Kazuaki Ishihara*
Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
E-mail: muha@chembio.nagoya-u.ac.jp; ishihara@cc.nagoya-u.ac.jp

The dearomatization of the structurally planar indoles into enantio-enriched three-dimensional indoline or indolenine structures has emerged as a powerful tool for the asymmetric synthesis of indole-derived alkaloids.[1] Dearomatization reactions of indoles often proceed by the addition of electrophiles at the C3 position due to the inherent nucleophilicity of the indoles, especially at the C3 position.

Here, we report an oxidative umpolung strategy for dearomatization of indoles.[2,3] Chiral ammonium hypoiodite-catalyzed enantioselective dearomative aza-spirocyclization of homotryptamine derivatives gave the corresponding aza-spiroindolenines with high enantioselectivity. Mechanistic studies revealed the unusual umpolung reactivity of the C3 position of indoles by N1-iodination. Moreover, the introduction of pyrazole as an electron-withdrawing auxiliary group at C2 suppressed a competitive dissociative racemic pathway, and enantioselective spirocyclization proceeded to give not only spiropyrrolidines but also four-membered spiroazetidines that are otherwise difficult to access. Furthermore, to demonstrate the synthetic utility, 2-alkyl- and pyrazole-substituted spiroindolenines were readily converted to various valuable and unique structures. These results demonstrate the high potential of hypoiodite catalysis[4,5] for oxidative umpolung of indoles towards the synthesis of polycyclic indole-derived alkaloids.



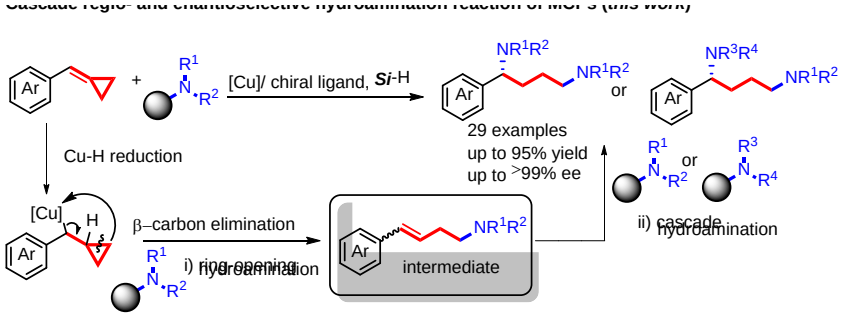
References
1. Zheng, C.; You, S.-L. *Nat. Prod. Rep.* **2019**, *36*, 1589.
2. Tanaka, H.; Ukegawa, N.; Uyanik, M.; Ishihara, K. *J. Am. Chem. Soc.* **2022**, *144*, 5756.
3. (a) Uyanik, M.; Tanaka, H.; Ishihara, K. *Org. Lett.* **2020**, *22*, 8049. (b) Uyanik, M.; Tanaka, H.; Ishihara, K. *Asian J. Org. Chem.* **2021**, *10*, 164.
4. (a) Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K. *Science* **2010**, *328*, 1376. (b) Uyanik, M.; Hayashi, H.; Ishihara, K. *Science* **2014**, *345*, 291.
5. (a) Uyanik, M.; Ishihara, K. *ChemCatChem* **2012**, *4*, 177. (b) Chen, R.; Chen, J.; Zhang, J.; Wan, X. *Chem. Rec.* **2018**, *18*, 1292.

Muhammet Uyanik. Nagoya University (Ph.D. 2007, Prof. K. Ishihara), Nagoya University (Asst. Prof. 2007-2020), Nagoya University (Assoc. Prof. 2020-present). [Field of research] Halogen catalysis, asymmetric catalysis, oxidative transformations.

Enantio- and Regioselective Construction of 1,4-Diamines *via* Cascade Hydroamination of Methylene Cyclopropanes

Jian Zhou, Jun (Joelle) Wang*
Hong Kong Baptist University
E-mail: junwang@hkbu.edu.hk

Despite the widespread existence of chiral 1,4-diamines in bioactive molecules and their applications in asymmetric catalysis, the catalytic and asymmetric synthesis of such structures from readily accessible substrates remains a long-standing challenge. Here, we report a Cu-catalyzed asymmetric cascade hydroamination protocol to construct a wide range of chiral 1,4-diamine derivatives in high yields with excellent enatioselectivities (up to 95% yield and up to ＞99% ee). The use of two hydroxylamine esters containing different functionalized amino groups allowed us to increase the complexity of the final 1,4-diamine structures. The desired products could be easily transformed into chiral 1,4-diamines and chiral NH_2-Terfenadine. Mechanistic study demonstrates that this reaction proceeds through hydroamination ring-opening and cascade hydroamination sequence.



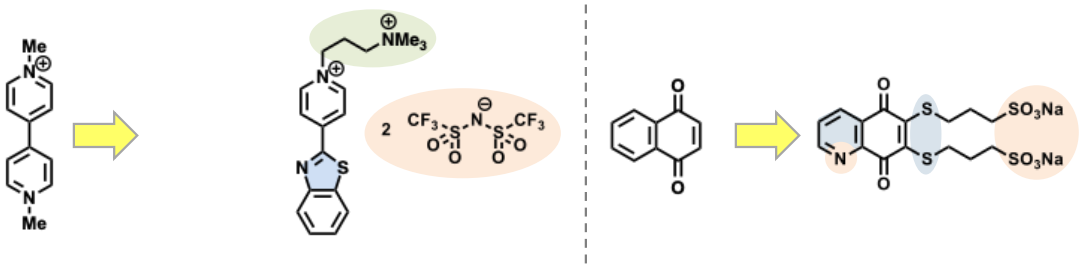
References
1. Zhou, J.; Yang, Q.; Lee, C. S.*; Wang, J.* *Angew. Chem. Int. Ed.* **2022**, *61*, doi.org/10.1002/anie.202202160.
2. Yang, Z.-P.; Wang, J.* *Angew. Chem. Int. Ed.* **2021**, *60*, 27288-27292.
3. Yang, Z.-P.; Du, Q.-W.; Jiang, Y.-X.; Wang, J.* *CCS Chem.* **2021**, *3*, 2507-2517.

Jun Wang (汪君，Joelle) Dr. Wang received her B.S. from Lanzhou University, M.S. from Shanghai Institute of Organic chemistry (SIOC), Chinese Academy of Science, and Ph.D. from Hong Kong Polytechnic University. She then pursued post-doctoral research at the University of Texas Southwestern Medical Center (UTSW). In 2012, she started her independent career at the Southern University of Science and Technology (SUSTech), before relocating her research program to Hong Kong Baptist University in 2020. Her current research interests include asymmetric catalysis, synthetic methodology, and cosmeceuticals.

Systematic Designs of New Redox-Active Heterocyclic Mediators

Jung Min Joo
Department of Chemistry, Pusan National University, Busan 46241, South Korea
E-mail: jmjoo@pusan.ac.kr

Organic redox-active materials are used in several electrochemical applications. Their application has expanded from conventional optoelectronic devices to new energy storage systems in recent years. Therefore, the design and synthesis of redox-active organic compounds are critical for modulating their redox potentials, stability, solubility, and related properties to achieve optimal performance. In collaboration with electrochemists, we have developed heterocycle-containing redox-active organic materials for the applications as redox-flow batteries and electrochemical biosensors. The incorporation of heterocycles facilitated by C–H functionalization reactions of heterocycles was critical to control redox potentials and stability in a systematic manner. In addition, pendant substituents and counterions were carefully selected to increase solubility.



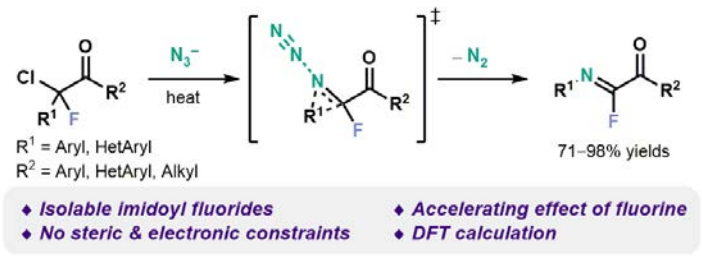
References
1. Jeong, S.; Joo, J. M., *Acc. Chem. Res.* **2021**, *54*, 4518-4529.
2. Ahn, S.; Jang, J. H.; Kang, J.; Na, M.; Seo, J.; Singh, V.; Joo, J. M.*; Byon, H. R.*, *ACS Energy Lett.* **2021**, *6*, 3390-3397.
3. Nandhakumar, P.; Lee, W.; Nam, S.; Bhatia, A.; Seo, J.; Kim, G.; Lee, N.-S.; Yoon, Y. H.; Joo, J. M.*; Yang, H.*, *Adv. Healthcare Mater.* **2022**, *11*, 2101819.

Jung Min Joo (주정민, 朱貞玟). Princeton University (PhD, 2004–2008, Prof. Chulbom Lee). Columbia University (Postdoc, 2008–2011, Prof. Dalibor Sames). Eli Lilly and Company (Research Scientist, 2011–2013). Pusan National University (Assistant & Associate Professor, 2013–present). [Field of research] Heterocyclic Chemistry.
https://sites.google.com/view/jmjoogroup

Synthesis of α-Ketoimidoyl Fluorides via Geminal Fluorine-Promoted Azide Rearrangement

Ha Eun Kim, Jun-Ho Choi,* Won-jin Chung*
Department of Chemistry, GIST, Buk-gu, Gwangju 61005, Korea
E-mail: wjchung@gist.ac.kr

Imidoyl fluorides are versatile functional groups that can undergo various synthetic transformations to give a diverse range of nitrogen- and/or fluorine-containing organic compounds. Despite the promising synthetic potential, the utilization of imidoyl fluorides has been hampered by the lack of broadly applicable preparative methods. We developed an efficient one-pot synthesis of α-ketoimidoyl fluorides from geminal chlorofluorides via the tandem azidation and rearrangement. This process afforded a variety of structurally and electronically diverse, bench-stable α-ketoimidoyl fluorides in high yields regardless of the steric and electronic environments. Moreover, the synthetic utility of the products was showcased via several derivatizations. Notably, the rearrangement was completely suppressed when the geminal fluorine substituent was absent. This phenomenon was explained through computational studies by invoking the electronegative fluorine-enabled hyperconjugative stabilization. The current work provides access to a formerly unavailable class of imidoyl fluorides, thereby broadening the synthetic potential significantly.



References
1. Kim, H. E.; Choi, J.-H; Chung, W.-j. *Org. Lett.* **2021**, *23*, 8810–8815.
2. Choi, G.; Kim, H. E.; Hwang, S.; Jang, H.; Chung, W.-j. *Org. Lett.* **2020**, *22*, 4190–4195.

Won-jin Chung (정원진). University of Illinois at Urbana-Champaign, (Ph.D., 2008). LG Chem Research Park (Research Scientist, 2008–2011), University of California, Irvine (Postdoctoral Associate, 2011–2014), Gwangju Institute of Science and Technology (GIST, Assistant, Associate Professor, 2014–present). [Field of research] Halogenation Chemistry, Synthetic Methodology, Total Synthesis of Natural Products.

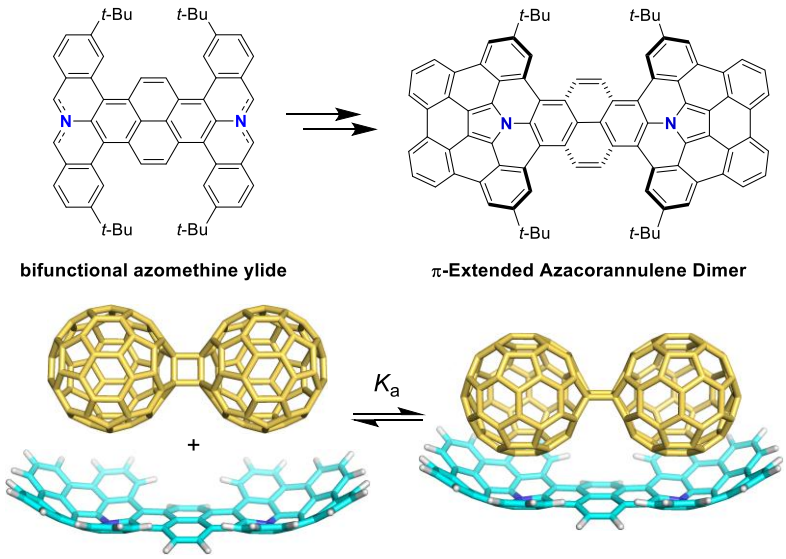
Synthesis and Properties of Fully Conjugated Azacorannulene Dimer

Shingo Ito,* Weifan Wang, Fiona Hanindita, Yosuke Hamamoto, Yongxin Li

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore

E-mail: sgito@ntu.edu.sg

Heterofullerenes are an important synthetic target for organic chemists, but their selective synthesis has long been challenging. Towards the selective synthesis of multiazafullerenes, we have developed the synthesis of a fully conjugated azacorannulene dimer starting from a bifunctional polycyclic aromatic azomethine ylide.[1] The molecular structure can be considered as the largest "diaza-C80" fragment molecule. The X-ray analysis of the azacorannulene dimer revealed its boat-shaped structure which can be viewed as the fusion of two bowl-shaped azacorannulenes linked by a fused pyrene unit. The unique molecular shape leads to preferable association with a dumbbell-shaped C_{60} dimer (C_{120}) through shape recognition.



References

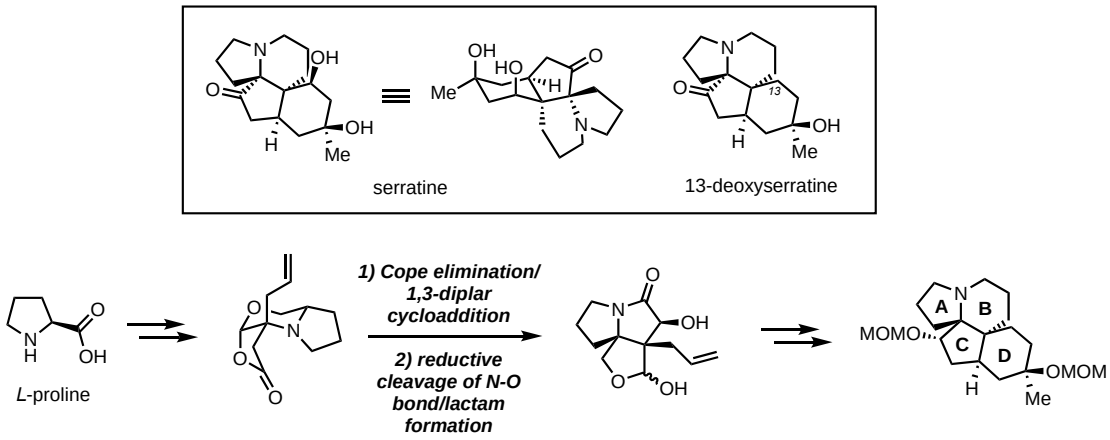
1. W. Wang, F. Hanindita, Y. Hamamoto, Y. Li, S. Ito, *Nat. Commun.* **2022**, *13*, 1498.

Shingo ITO (伊藤慎庫). The University of Tokyo (Ph.D, 2008). The University of Tokyo: Assistant Professor & Lecturer (2008–2018); Nanyang Technological University: Assistant Professor (2018–current). [Field of research] Organic Chemistry and Polymer Chemistry.

Synthetic Studies towards Serratine-Type Alkaloids

Hsiang-Yu Chuang*
National Chiayi University, No. 300 Syuefu Rd., Chiayi City
E-mail: hychaung@mail.ncyu.edu.tw

Serratine-type *Lycopodium* alkaloids have greatly intrigued synthetic chemists since their discovery because of the 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**. Starting from *L*-proline, our group have employed 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.[1,2] Moreover, ring closing metathesis in ring **D**, and iridium-catalyzed reductive Strecker reaction in ring **B** as key C-C bond forming reactions accomplished the skeleton of serratine-type alkaloids (**Scheme 1**.).



(**Scheme 1**.)

References
1. Li, Y. -J.; Chang, Y. -K.; Ho, G. -M.; Huang, H. -Ming. *Org. Lett*. **2009**, *11*, 4227.
2. Li, Y. -J.; Chuang, H. -Y.; Yeh, S. -S.; Huang, W. -S. *Eur. J. Org. Chem*. **2011**, *10*, 1932.

Hsiang-Yu Chuang (莊翔宇). National Tsing Hua University (Ph. D., 2017). Postdoctoral Researcher at Vienna University (2019-2020). Assistant Professor at National Chiayi University (2021-present). Organic Chemistry, Natural Product Synthesis.

Synthesis of Dibenzopleiadiene-Embedded Polyaromatics via Palladium-Catalyzed [4+3] Decarbonylative/Decarboxylative Annulation

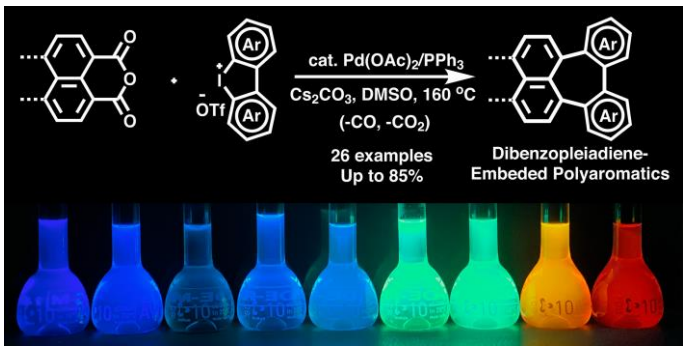
Pawaret Leowanawat,[a]* Kritchasorn Kantarod,[a] Thanapat Worakul,[a] Darunee Soorukram,[a] Chutima Kuhakarn,[a] Vichai Reutrakul,[a] Panida Surawatanawong,[a] and Worawat Wattanathana[b]

[a]Center of Excellence for Innovation in Chemistry (PERCH-CIC) and Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand.

[b]Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

E-mail: pawaret.leo@mahidol.edu

Heptagon-embedded polyaromatics have received considerable attention due to their unique structural and electronic properties. However, the incorporation of heptagons into polyarene frameworks remains a synthetic challenge. Herein, we report a palladium-catalyzed cascade [4+3] decarbonylative/decarboxylative annulation as a new strategy for the synthesis of dibenzopleiadiene-embedded polyaromatics from 1,8-naphthalic anhydride derivatives and cyclic diaryliodonium salts. The method provides access to diverse dibenzopleiadiene-embedded polyaromatics in moderate to high yields. The molecular structure, and their photophysical properties are also investigated by X-ray crystallography, UV-Vis and fluorescence spectroscopy, and DFT calculations.



Reference

Kantarod, K.; Worakul, T.; Soorukram, D.; Kuhakarn, C.; Reutrakul, V.; Surawatanawong, P.; Wattanathana, W.; Leowanawat, P. *Org. Chem. Front.* **2021**, 8, 522-530.

Pawaret Leowanawat (ปวเรศร์ เหลียววนวัฒน์). University of Pennsylvania, (Ph.D., 2013). Mahidol University: Lecturer (2015); Assistant Professor (2022). [Field of research] Synthetic Methodology.

Sulfonium Ylide in Glycosylation

Lingkui Meng, Peng Wu, Jing Fang, Jing Zeng, Qian Wan*
School of Pharmacy, Huazhong University of Science and Technology, Wuhan
E-mail: menglk@hust.edu.cn, wanqian@hust.edu.cn

Sulfonium ylides are among the most important and widely applied reagents within the realm of organic synthetic chemistry. However, in the past over 30 years application sulfonium ylides in carbohydrate synthesis received less attentions. Galvanized on the Kametani, Porter and Aggarwal's works, we devised a novel glycosylation reaction constitutes of successive Rh(II)-catalyzed sulfonium ylide formation and Brønsted acid catalyzed sulfonium formation which facilely affords the oxocarbenium ion susceptible for nucleophilic attack of acceptors.

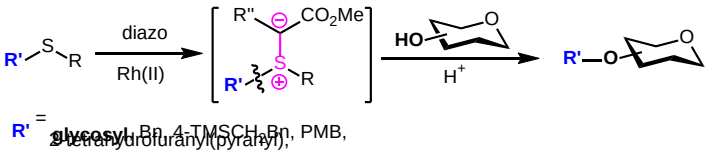
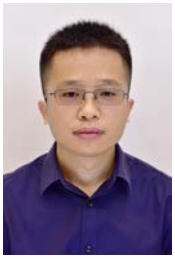


Figure. Rh(II)/H^+ catalyzed Glycosylation/alkylation

References
1. a) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.*, **1997**, *97* , 2341; b) Lu, L.-Q.; Li, T.-R.; Wang, Q.; Xiao, W.-J. *Chem. Soc. Rev.*, **2017**, *46*, 4135.
2. Kametani, T.; Kawamura, K.; Honda, T. *J. Am. Chem. Soc.* **1987**, *109*, 3010
3. Meng, L.; Wu, P.; Fang, J.; Xiao, Y.; Xiao, X.; Tu, G.; Ma, X.; Teng, S.; Zeng, J.; Wan, Q. *J. Am. Chem. Soc.* **2019**, *141*, 11775.
4. Fang, J.; Li, T.; Ma, X.; Sun, J.; Cai, L.; Chen, Q.; Liao, Z.; Meng, L.; Zeng, J.; Wan, Q. *Chin. Chem. Lett.* **2021**, *33*, 288.

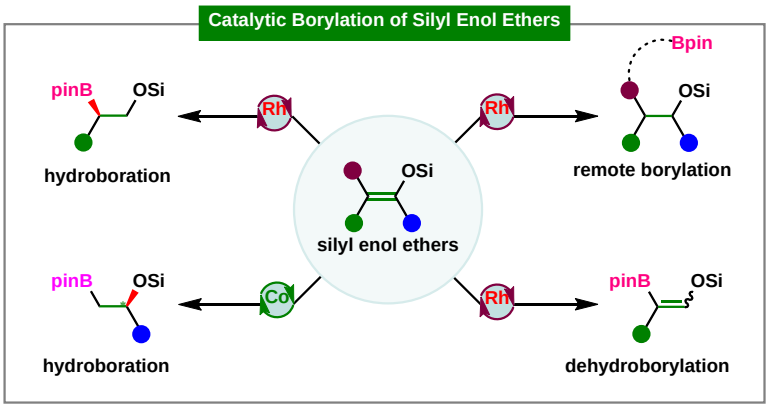


Lingkui Meng (孟令奎). Ph.D, Wuhan University (2009-2014). Postdoc, Nagoya University (2014-2016). Associate Professor, Huazhong University of Science and Technology (2016-current). [Field of research] Carbohydrate Chemistry.

Catalytic Borylation of Silyl Enol Ethers

Wanxiang, Zhao*
State Key Laboratory of Chemo/Biosensing and Chemometrics,
Advanced Catalytic Engineering Research Center of the Ministry of Education,
College of Chemistry and Chemical Engineering, Hunan University, Changsha,
Hunan 410082, P. R. China
E-mail: zhaowanxiang@hnu.edu.cn

Organoboron compounds are among the most coveted scaffolds in organic chemistry due to their abundance in biologically active molecules. Their ubiquity as versatile building blocks also makes them attractive in synthetic chemistry and materials science. Thus, the development of highly efficient methods for the synthesis of organoboron compounds are extremely desirable. Silyl enol ethers (SEEs) are readily available and useful synthons, but their borylation is rarely developed. Recently, we disclosed that the SEEs can undergo asymmetric Rh- or Co-catalyzed hydroboration to provide valuable enantiopure *β*-hydroxy boronic esters. The remote C(sp^3)−H borylation of SEEs via alkene isomerization and hydroboration was also explored. Noticeably, the dehydronative borylation was also achieved, providing a powerful platform for the construction of functionalized SEEs.



References

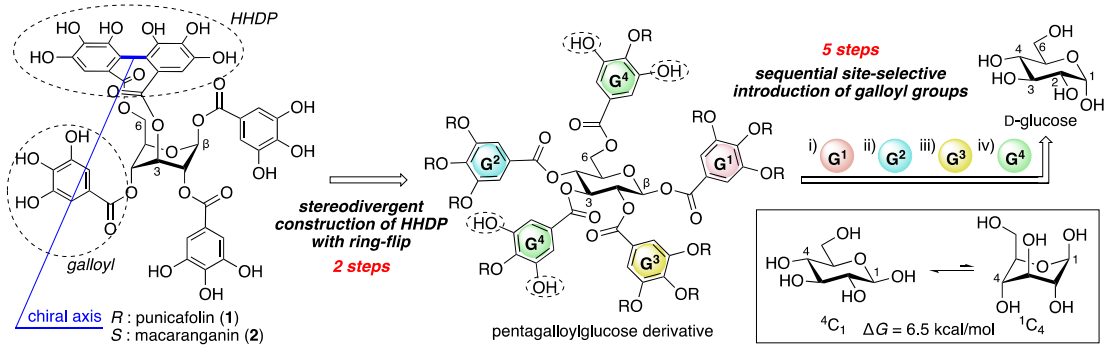
1. Dong, W.; Xu, X.; Ma, H.; Lei, Y.; Lin, Z.*; Zhao*, W. *J. Am. Chem. Soc.* **2021**, *143*, 10902-10909.
2. Dong, W.; Ye, Z.; Zhao, W.* *Angew. Chem. Int. Ed.* **2022**, e202117413.
3. Li, J.; Qu, S.; Zhao, W.* *Angew. Chem. Int. Ed.* **2020**, *59*, 2360-2364.
4. Li, J.; Zhao, P.; Li, R.; Yang, W.*; Zhao, W.* *Org. Lett.* **2021**, *23*, 9580-9585.

ZHAO, Wanxiang (赵万祥). The Hong Kong University of Science and Technology (PhD, 2014). Professor, Hunan University (2017-now). Organoboron Chemistry.

Seven-Step Stereodivergent Total Syntheses of Punicafolin and Macaranganin

Yoshihiro Ueda,*[1] Hiromitsu Shibayama,[1] Takeo Kawabata*[1,2]
[1] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
[2] Department of Pharmaceutical Science, International University of Health and Welfare, Okawa, Fukuoka 831-8501, Japan
E-mail: ueda.yoshihiro.4z@kyoto-u.ac.jp; kawabata@scl.kyoto-u.ac.jp

Punicafolin (**1**) and macaranganin (**2**) are ellagitannins isolated by Nishioka and each of them is an atropisomer of the other due to the stable axial chirality of the HHDP (hexahydroxy diphenoyl) group.[1)] Since the HHDP bridges the 3- and 6-oxygens of the glucose unit, the pyranose ring is in the axial-rich conformation such as flipped chair $^{1}C_4$ conformation. Because of the structural features, the following issues are required to be solved in the syntheses of **1** and **2**; 1) differentiation of C(1,2,4)-OHs and C(3,6)-OHs of the glucose units, and 2) construction (stereoselectively) of the HHDP group. The energy difference between $^{4}C_1$ and $^{1}C_4$ conformers of β-D-glucose (6.5 kcal/mol based on DFT study) suggests that the construction of HHDP group with ring-flip of the pyranose moiety should be difficult, which was supported by previous experimental trials.[2)] Here we report the first total syntheses of **1** and **2** in seven steps, respectively, from commercial α-D-glucose.[3)] The prominent features of the synthesis are 1) sequential site-selective introduction of the adequate galloyl groups into unprotected D-glucose in a catalyst-controlled manner and 2) stereodivergent construction of the 3,6-HHDP bridge by oxidative phenol coupling of a common intermediate via a ring-flipping process of the glucose core.



References

1. (a) Tanaka, T.; Nonaka, G.; Nishioka, I. *Phytochemistry* **1985**, *24*, 2075; (b) Lin, J.; Nonaka, G.; Nishioka, I. *Chem. Pharm. Bull.* **1990**, *38*, 1218.
2. (a) Yamada, H. *et al. Tetrahedron Lett.* **2004**, *45*, 487; (b) Spring, D. R. *et al. Synthesis* **2009**, *22*, 3880.
3. Shibayama, H.; Ueda, Y.; Tanaka, T.; Kawabata, T. *J. Am. Chem. Soc.* **2021**, *143*, 1428.

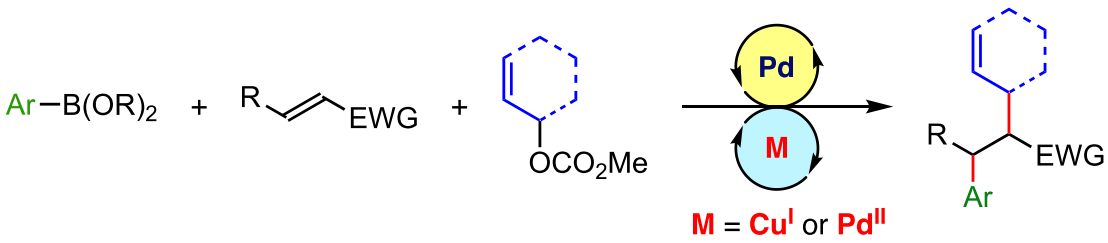
Yoshihiro Ueda (上田 善弘).
Kyoto University (Ph.D., 2013).
Postdoctoral Fellow, POSTECH, The University of Tokyo (2013-2014).
Assistant Professor, Kyoto University (2014-present).
[Field of Research] Synthetic Organic Chemistry, Natural Product Chemistry, Supramolecular Chemistry.

Carboallylation of Electron-Deficient Alkenes by Cooperative Metal Catalysis

Kazuhiko Semba*
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
E-mail: semba.kazuhiko.5n@kyoto-u.ac.jp

The transition-metal-catalyzed conjugate addition of organoboronic acids and esters across electron-deficient alkenes is powerful to construct C–C bonds thanks to the functional group compatibility, and wide availability and bench stability of organoboronic acids and esters. Hydroarylation is a typical reaction, where transition-metal enolates generated via 1,4-addition of organotransition-metals toward electron-deficient alkenes are protonated. Dicarbofunctionalization of alkenes can be achieved by trapping these enolates with carbon electrophiles, which is highly useful to build-up complex carbon skeletons. In this context, Krische has developed an intermolecular arylative aldol reaction to afford cyclic products.[1a] In contrast, intermolecular variants are rare. Although Nakamura reported the Pd-catalyzed diallylation of alkenes with potassium allyltrifluoroborate,[1b] the method suffers from a narrow alkene scope, which is limited to highly electron-deficient alkenes conjugated with two electron-withdrawing groups.

Herein, we report the allylarylation of electron-deficient alkenes with allylic carbonates and arylboronates.[2] Cooperative Pd/Cu or Pd/Pd catalysis are indispensable to achieve the reaction. These methods can be applied to a wide variety of electron-deficient alkenes, organoboron reagents, and allylic carbonates, which allows rapid access to complex carbon skeletons by these methods.



References

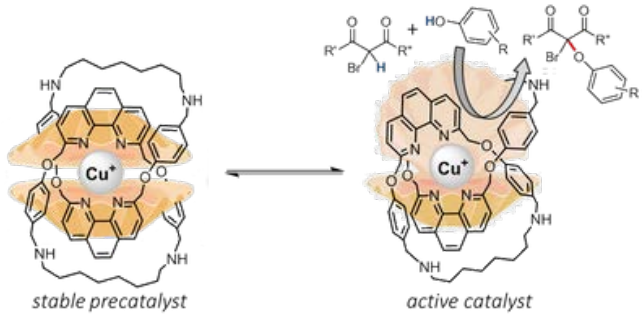
1. (a) Cauble, D. F.; Gipson, J. D.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 1110; (b) Nakamura, H.; Shimizu, K. *Tetrahedron Lett.* **2011**, *52*, 426.
2. (a) Semba, K.; Ohta, N.; Nakao, Y. *Org. Lett.* **2019**, *21*, 4407; (b) Semba, K.; Ohta, N.; Paulus, F.; Ohata, M.; Nakao, Y. *Chem. Eur. J.* **2021**, *27*, 5035.

Kazuhiko Semba (仙波一彦). Kyoto University (Ph.D., 2013). He received his PhD degree from Kyoto University under the supervision Prof. Yasushi Tsuji. During his PhD study, he worked with Prof. Cathleen M. Crudden at Queen's University in Canada. From 2013, he joined the Department of Material Chemistry, Graduate School of Engineering, Kyoto University, as an Assistant Professor. [Field of research] Synthetic Organic Chemistry and Organometallic Chemistry.

Copper Catalyzed C-O and C-C Cross Coupling Reactions: Effects of Mechanical Interlocking in the Ligand Framework

Ho Yu Au-Yeung,* Lihui Zhu, Man Pang Tang
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong
E-mail: hoyuay@hku.hk

Catenane is a representative class of mechanically interlocked molecules (MIMs) composed of interlocked macrocycles.[1,2] When employed as a coordination ligand, the mechanical interlocking in a catenane kinetically stabilizes the metal from ligand exchange and yet co-conformational changes of the catenane would enable the coordination site to be transiently approachable to substrates for reactions.[3] In this presentation, our efforts towards exploiting the unusual kinetic and dynamic features of catenane ligands in transition metal catalysis will be discussed.



References
1. Au-Yeung, H. Y.; Deng, Y. *Chem. Sci.* **2022**, *13*, 3315
2. Ng, A. W. H.; Lai, S. K.-M.; Yee, C.-C.; Au-Yeung, H. Y. *Angew. Chem. Int. Ed.* **2022**, *61*, e202110200
3. Zhu, L.; Li, J.; Yang, J.; Au-Yeung, H. Y. *Chem. Sci.* **2020**, *11*, 13008

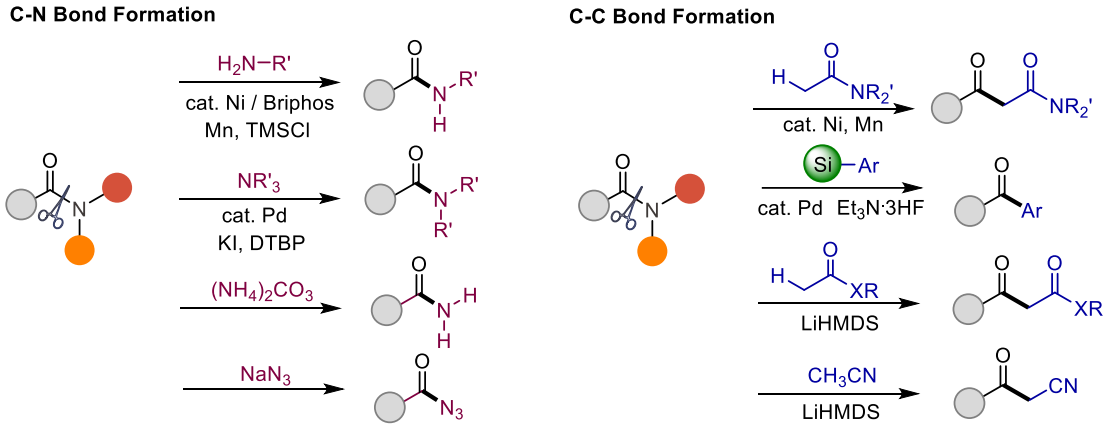
Ho Yu Au-Yeung (歐陽灝宇). Chinese University of Hong Kong (BSc and MPhil), University of Cambridge (PhD 2010). University of California, Berkeley (Postdoc). University of Hong Kong (2013-present). Current position: Associate Professor.
Field of research: Supramolecular Chemistry, Mechanically Interlocked Molecules: Synthesis and Applications in Catalysis, Molecular Recognition and Materials

Transformation of Amides using C-N Bond Activation

Sunwoo Lee*
Department of Chemistry, Chonnam National University,
77 Yongbongro, Gwangju 61186, Republic of Korea
E-mail: sunwoo@chonnam.ac.kr

The amide functionality is one of the key structural motifs found in biological compounds such as peptides, proteins, and alkaloids. It is also widely used to prepare agrochemicals, pharmaceuticals, polymers, and materials. Therefore, a number of synthetic routes to amides have been reported. We developed the transformation of amides to another amides and acyl azides using nitrogen nucleophiles.[1] In addition, we developed the coupling reaction of amides and enolizable carbon nucleophiles such ketone, ester, amides and acetonitrile to give the corresponding acylated products.[2]

In this post, the details about our recent findings of the C-N bond activations of amides for the synthesis of different type of acylated products will be presented.



References

1. (a) Yu, S. Shin, T.; Zhang, M.; Xia, Y.; Kim, H.; Lee, S. *Org. Lett*. **2018**, *20*, 7563 (b) Chen, J.; Xia, Y.; Lee, S. *Org. Lett.* **2020**, *22*, 3504. (c) Idris, M. A.; Lee, S. *Org. Chem. Front.* **2020**, *7*, 2737.
2. (a) Chen, J.; Xu, M.; Yu, S.; Xia, Y.; Lee, S. *Org. Lett.* **2020**, *22*, 2287-2292. (b) Chen, J.; Xia, Y.; Lee, S. *Org. Chem. Front.* **2020**, *7*, 2931. (c) Idris, M. A.; Lee, S. *Org. Lett.* **2020**, *22*, 9190. (d) Chen, J.; Joseph, D.; Xia, Y.; Lee, S. *J. Org. Chem.* **2021**, *86*, 5943. (e) Joseoph, D.; Oh, M. S.; Jayaraman, A.; Lee, S. *Bull. Korean Chem. Soc*. **2021**, *42*, 1293

Sunwoo Lee (이선우). POSTECH (Ph.D, 1999, Prof. Jaiwook Park). Yale University (Postdoc, 1999-2001, Prof. John F. Hartwig) LG Chem (Senior Researcher, 2001-2004), UC Berkeley (Visiting Scholar, 2014-2015) Chonnam National University (Assistant & Associate & Full Professor, 2004-present) [Field of Research] Decarboxylative coupling reactions, transformation of amides

Highly Chemoselective Deoxygenation of N-Heterocyclic *N*-Oxides Using Hantzsch Esters as

Jun Hee Lee*
Department of Advanced Materials Chemistry, Dongguk University WISE Campus, Gyeongju, Korea
E-mail: leejunhee@dongguk.ac.kr

Chemoselective strategies represent a powerful synthetic skill in organic synthesis, which can provide access to valuable scaffolds that are otherwise too difficult to synthesize by other methods. For example, given the importance of the N-oxide moiety of N-heteroaromatics as a superb directing group for various regioselective C−H functionalizations, the development of efficient protocols for the chemoselective removal of the oxygen atom from densely functionalized oxygenated heterocycles under mild and eco-friendly conditions is highly desirable in organic synthesis.

As part of our ongoing research program to develop selective transformations via visible-light-mediated photoredox catalysis, we recently disclosed a highly chemoselective room-temperature deoxygenation protocol applicable to a diverse range of functionalized N-heteroaryl *N*-oxides using Hantzsch esters as the photoreductant. This scalable and operationally simple protocol encompasses a wide range of synthetically fruitful functional groups, such as amides, carbamates, esters, ketones, nitrile groups, nitro groups, and halogens, which provide access to the corresponding deoxygenated N-heterocycles in good to excellent yields. Further details of this protocol will be presented in the poster presentation.

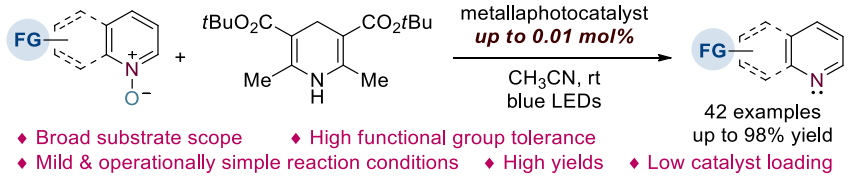


Figure. Hantzsch Ester-Mediated Deoxygenation of N-Heterocyclic *N*-Oxides

References

1. (a) Lee, J. H.; Mho, S.-i. *J. Org. Chem.* **2015**, *80*, 3309–3314. (b) Kim, K. D.; Lee, J. H. *Org. Lett.* **2018**, *20*, 7712–7716. (c) Kim, S. H.; An, J. H.; Lee, J. H. *Org. Biomol. Chem.* **2021**, *19*, 3735–3742.
2. An, J. H.; Kim, K. D.; Lee, J. H. *J. Org. Chem.* **2021**, *86*, 2876–2894.

Jun Hee Lee (이준희). Dongguk University (B.S. 1995). Sogang University (M.S. 1995 & Ph.D. 2001). Yonsei University (Postdoc 2001-03). Sogang University (Postdoc 2003-05). UC Berkeley (Postdoc 2005-08). Columbia University (Postdoc 2008-11). Ewha Womans University (2010-13). Ajou University (2013-14). Institute for Basic Science (2014-15). Dongguk University Wise Campus (Assist. Prof. 2016-2022. Associate Prof. 2022-present.). [Field of research] Organic Synthesis, Organometallic Chemistry, Visible Light Photoredox Catalysis.

Photoredox Catalysis by Metal Halide Perovskites and Vanadium Complexes

Yonghao XIAO, Chenfei LI, Xin ZHAO, Xin Ying KONG, Adisak THANETCHAIYAKUP, Han Sen SOO*
Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, 21 Nanyang Link, Nanyang Technological University, Singapore 637371
E-mail: hansen@ntu.edu.sg

Photoredox catalysis is a powerful and elegant way to achieve novel transformations in organic syntheses under exceptionally mild, often ambient conditions. In this poster, I will discuss some of the latest groundbreaking examples from my team. In one instance, I will discuss the applications of metal halide perovskites for effective charge separation and photocatalytic decarboxylation reactions.[1] In addition, I will also present our efforts at using vanadium complexes for selective photocatalytic C-C bond cleavage reactions under ambient, aerobic conditions. We conducted detailed kinetic measurements and other experiments to identify the fastest catalyst and the vital functional groups in the substrates. We then applied the vanadium photocatalysts for the C-C bond cleavage and oxygenation of over 30 substrates, including unactivated aliphatic alcohols and even non-biodegradable plastics.[2] In the future, we plan to integrate these vanadium coordination complexes into artificial photosynthetic systems to upcycle a broad range of plastics (**Figure 1**).[3]

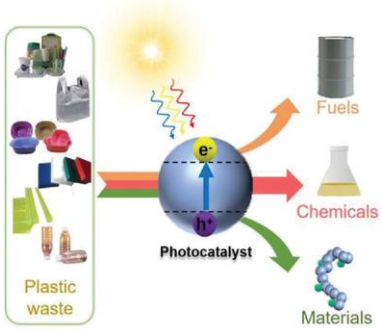


Figure 1. Photoredox catalytic upcycling of plastics to value-added products.

References

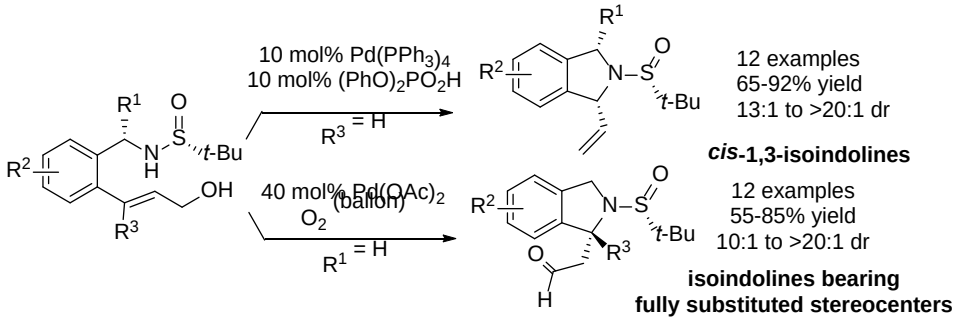
1. Hong, Z.; Chong, W. K.; Ng, A. Y. R.; Li, M.; Ganguly, R.; Sum, T. C.; Soo, H. S. *Angew. Chem. Int. Ed.* **2019**, *58*, 3456-3460.
2. Gazi, S.; Dokić, M.; Chin, K. F.; Ng, P. R.; Soo, H. S. *Adv. Sci.* **2019**, *6*, 1902020.
3. (a) Zhao, X.; Boruah, B.; Chin, K. F.; Dokić, M.; Modak, J. M.; Soo, H. S. *Adv. Mater.* **2021**, e2100843; (b) Chu, S.; Zhang, B.; Zhao, X.; Soo, H. S.; Wang, F.; Xiao, R.; Zhang, H. *Adv. Energy Mater*. **2022**, e2200435.

Han Sen Soo (苏汉昇). U.C. Berkeley (Ph.D., 2005-2009). MIT (S.B. & S.M., 1999-2003). Nanyang Assistant Professor (2012-2020). Associate Professor (2020-). Artificial Photosynthesis, Catalysis, and Photochemistry.

Palladium/Brønsted-Acid-Catalyzed Diastereoselective Cyclization with Chiral Sulfinamides as Nucleophiles

Cheng-Che Tsai*
Department of Chemistry, Tunghai University, Taichung City 40704
E-mail: chengchetsai@thu.edu.tw

Chiral *N*-*tert*-butyl sulfinamides (Ellman's reagents) are versatile auxiliaries in many asymmetric transformations.[1] In contrast to nucleophilic addition to chiral sulfinyl imine, methods for stereoselective reactions with *N*-*tert*-butyl sulfinamide derivatives as chiral nucleophiles remain limited.[2] Herein, we report diastereoselective cyclization with chiral sulfinamides in two reaction pathways: (1) intramolecular allylic substitution and (2) sequential aerobic oxidation with aza-Michael addition. These reactions were enabled by synergistic palladium and Brønsted acid catalysis and produced chiral isoindolines with good yields of 55−92% and high diastereoselectivities of 10:1 to >20:1 dr.[3]



Diastereoselective Cyclization with Tethered Chiral Sulfinamide Nucleophiles

References

1. Robak, M. T.; Herbage, M. A.; Ellman, J. A. *Chem. Rev*. **2010**, *110*, 3600–3740.
2. (a) Redford, J. E.; McDonald, R. I.; Rigsby, M. L.; Wiensch, J. D.; Stahl, S. S. *Org. Lett.* **2012**, *14*, 1242−1245. (b) Fustero, S.; Monteagudo, S.; Sánchez-Roselló, M.; Flores, S.; Barrio, P.; Del Pozo, C. *Chem. Eur. J*. **2010**, *16*, 9835−9845.
3. Hung, C.-T.; Lu, C.-W.; Huang, S.-H.; Lu, Y.-F.; Chou, H.-C.; Tsai, C.-C. *J. Org. Chem.* **2021**, *86*, 12354−12366.

Cheng-Che Tsai (蔡政哲). National Tsing Hua University (PhD, 2016). Assistant Professor (2019-present). [Organic Chemistry] Asymmetric Catalysis.

Glycosylation of *n*-Pentenyl Glycosides Activated by Bromodiethylsulfonium Salt

Panuwat Padungros* and Supanat Buntasana
Green Chemistry for Fine Chemical Production and
Environmental Remediation Research Unit, Department of Chemistry,
Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: panuwat.p@chula.ac.th

n-Pentenyl glycosides (NPGs) are one of the important classes of glycosyl donors. The *n*-pentenyl moiety can be considered both protecting groups of the anomeric hydroxyl during protecting group manipulations and leaving group upon activation with a halonium activator. Conventionally, halonium activators such as *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS) were used; however, the activation for less reactive glycosyl donors was not very effective due to the slow activation.[1] Recently, bromodiethylsulfonium bromopentachloroantimonate (BDSB) was reported as a highly efficient brominating reagent. It can be prepared in a simple procedure and purified by crystallization. Herein, we investigated the application of BDSB as the halonium activator for NPGs in chemical glycosylation. Surprisingly, glycosyl chloride was observed as an intermediate generated by chloride ion transfer from $SbCl_5Br$ anion.[2] The BDSB-activated glycosylations between NPGs and primary, secondary, and tertiary alcohols were most efficient with the sequential addition of AgOTf as Lewis acid. The BDSB/AgOTf glycosylation was mild, highly stereoselective, and provided the desired products in moderate to good yields. This work represents BDSB as an effective activator for NPGs by virtue of *in situ* generations of the glycosyl chloride intermediate, which mitigates the equilibration during activation of the olefinic group by the bromonium ion.

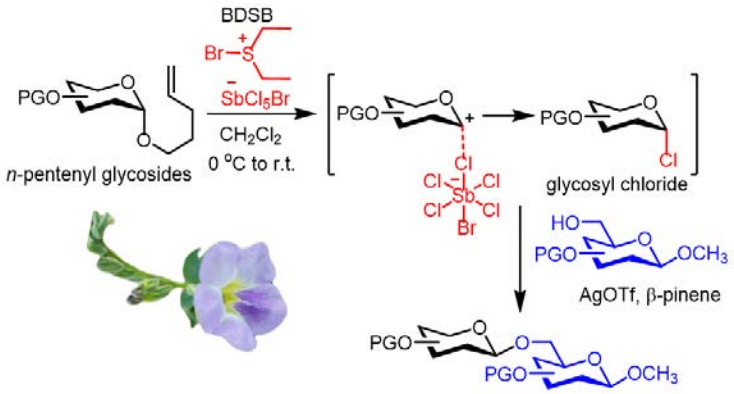


Figure 1. BDSB/AgOTf-mediated glycosylation of NPGs

References

1. Ratthachag, T.; Buntasana, S.; Vilaivan, T.; Padungros, P. *Org. Biomol. Chem.* **2021**, 19, 822–836
2. Chooppawa, T.; Janprasert, P.; Padungros, P., *Synlett* **2022**, *in press*.

Panuwat Padungros (ภาณุวัฒน์ ผดุงรส). Purdue University (Ph.D., 2012). Assistant Professor (2016–present). [Field of research] Carbohydrate Chemistry, Green Chemistry

Synthesis and Properties of Monoazadichalcogenasumanenes

Jihai Shang, Xiangfeng Shao*
State Key Laboratory of Applied Organic Chemistry, Lanzhou University, China
E-mail: shaoxf@lzu.edu.cn

Buckybowls possess unique properties that can be tailored by embedding main group elements into their π-scaffolds. Herein, a synthetic approach is developed for producing monoazadichalcogenasumanenes (**4a/4b, 6a/6b, 7a/7b**) derived from sumanene by replacing its three benzylic carbons with one nitrogen and two chalcogen atoms (S for **4a/4b**, Se for **6a/6b**, Te for **7a/7b**). Monoazadichalcogenasumanenes are deeper π-bowls than trichalcogensumanenes as C–N bond is much shorter than C–X (X = S, Se, Te). Particularly, bowl-depth of **4b** (0.95 Å) is greater than that of corannulene (0.85 Å). The nitrogen atom donates electron density to the entire π-system that makes monoazadichalcogenasumanenes electron-rich. Monoazadichalcogenasumanenes undergo ring reconstruction of chalcogenophene ring *via* transferring a chalcogen atom from one molecule to another under acidic conditions (Figure 1). It is found that both nitrogen and chalcogen atoms play crucial role on this reaction, including conversion rate and relative ratio of ring reconstruction products.

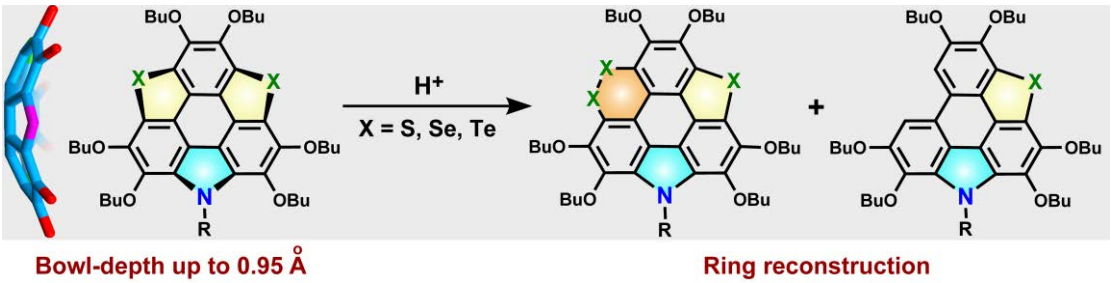


Figure 1. Protonation-induced ring reconstruction of monoazadichalcogenasumanenes

References

1. J. Shang, R. Wang, C. Yuan, Z. Liu, H.-L. Zhang, X. Shao, *Angew. Chem. Int. Ed.,* **2022**, *61*, e202117504.

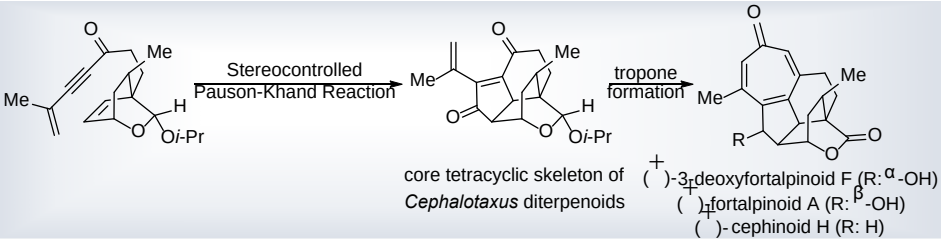
Xiangfeng Shao（邵向锋）
Department of Chemistry, Lanzhou University (B.S., 1998)
College of Chemistry and Chemical Engineering (M.S., 2001)
Institute of Chemistry, Chinese Academy of Science (Ph. D., 2004)
Postdoc., Japan Science and Technology Agency (JST) (2004-2005)
Postdoc., Kyoto University (2005–2008)
Research Associate, Osaka Prefecture University (2008-2009)
Professor, Lanzhou University (since 2009)
Field of Research: Physical Organic Chemistry

Total Synthesis of (+)-3-Deoxyfortalpinoid F, (+)-Fortalpinoid A, and (+)-Cephinoid H

Zhiqiang Ren,[+] Zhongliu Sun,[+] Yifei Li, Xin Fan, Mingda Dai, Yunxia Wang, Xiangdong Hu*
College of Chemistry & Materials Science, Northwest University, China
E-mail: xiangdonghu@nwu.edu.cn

3-Deoxyfortalpinoid F, fortalpinoid A, and cephinoid H are three *Cephalotaxus* diterpenoids isolated in recent years. 3-Deoxyfortalpinoid F showed significant antitumor activity. Cephinoid H exhibited intriguing biological features, including excellent inhibition of the NF-κB signaling pathway, strong cytotoxicity against human tumor cell lines, and distinct anti-inflammatory activities. Furthermore, in a zebrafish xenograft assay, cephinoid H displayed 49.0% inhibition of proliferation and metastasis of human lung cancer cells at a dose of 60.0 ng/mL, compared with 22.4% inhibition from cisplatin at 15.0 μg/mL. Therefore, cephinoid H seemed to be a promising lead candidate for anticancer therapeutics.

Structurally, 3-deoxyfortalpinoid F, fortalpinoid A, and cephinoid H share same core tetracyclic skeleton and a tropone unit. We proposed that the combination of construction of the tetracyclic skeleton and a later-stage formation of the tropone unit could be a feasible strategy. Herein, we have developed a stereocontrolled Pauson–Khand reaction as an effective approach to the tetracyclic skeleton. And the formation of the tropone unit was enabled by a ring-closing metathesis/elimination protocol. As the result, total synthesis of (+)-3-deoxyfortalpinoid F, (+)-fortalpinoid A, and (+)-cephinoid H was accomplished for the first time.



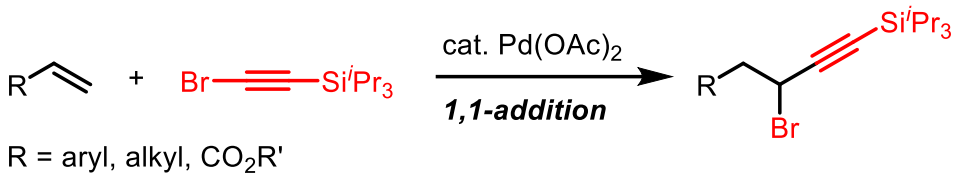
References
1. (a) Ni, L.; Zhong, X.-H.; Chen, X.-J.; Zhang, B.-J.; Bao, M.-F.; Cai, X.-H. *Phytochem.* **2018**, *151,* 50. (b) Ge, Z.-P.; Liu, H.-C.; Wang, G.-C.; Liu, Q.-F.; Xu, C.-H.; Ding, J.; Fan, Y.-Y.; Yue, J.-M. *J. Nat. Prod.* **2019**, *82,* 1565.
2. Ren, Z.; Sun, Z.; Li, Y.; Fan, X.; Dai, M.; Wang, Y.; Hu, X. *Angew. Chem. Int. Ed.* **2021**, *60*, 18572.

Xiangdong Hu (胡向东).
Lanzhou University (Ph.D., 2006).
University of South Florida (Postdoc. 2006-2009).
Northwest University (Prof., 2009-present).
[Field of research] Natural product synthesis, Synthetic methodology.

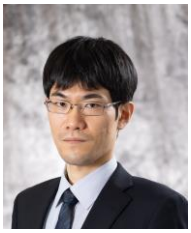
Palladium-Catalyzed 1,1-Alkynylbromination of Alkenes

Yusuke Ano,* Natsuki Kawai, Naoto Chatani
Department of Applied Chemistry, Graduate School of Engineering, Osaka University
2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
E-mail: ano@chem.eng.osaka-u.ac.jp

The catalytic carbohalogenation of alkenes involving the addition of carbon–halogen bonds is an efficient and straightforward approach to providing synthetically useful alkyl halides.[1] In 2011, Lautens[2a] and Tong[2b] independently reported the palladium-catalyzed intramolecular 1,2-carboiodination of alkenes tethered with aryl or alkenyl iodides. For the success of these reaction, the use of alkenes lacking any suitable β-hydrogen for the elimination is important, which enables the suppression of the undesirable Mizoroki-Heck type reaction. Although the palladium-catalyzed 1,1-carbohalogenation of alkenes has been achieved by employing both arylation and halogenation reagents,[3] the use of organohalides for 1,1-carbohalogenation is still a challenging issue in the palladium-catalyzed reaction. Herein, we will present the palladium-catalyzed 1,1-addition of alkynyl bromides to terminal alkynes.[4]



References
1. Jones, D. J.; Lautens, M.; McGlacken, G. P. *Nat. Catal.* **2019**, *2*, 843.
2. (a) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, 1778. (b) Liu, H.; Li, C.; Qiu, D.; Tong, X. *J. Am. Chem. Soc.* **2011**, *133*, 6187.
3. (a) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z.-i. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 735; (b) Kalyani, D.; Sanford, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2150; (c) He, Y.; Yang, Z.; Thornbury, R. T.; Toste, F. D. *J. Am. Chem. Soc.* **2015**, *137*, 12207.
4. Ano, Y.; Kawai, N.; Chatani, N. *Chem. Sci.* **2021**, *12*, 12326.

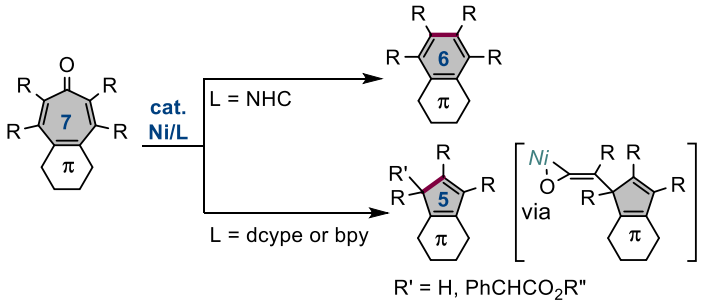


Yusuke Ano (阿野 勇介). Osaka University (Ph D., 2012). Postdoctoral Fellow, Chubu University (2012–2013), Research Fellowship for Young Scientists, JSPS (2013–2014). Designated Assistant Professor, Kyushu University (2014–2017). Assistant Professor, Osaka University (2017–). [Field of research] Organic Chemistry, Organometallic Chemistry.

Nickel-catalyzed skeletal transformation of tropone derivatives via C–C bond activation: catalyst-controlled access to diverse ring systems

Takuya Kodama, Kanako Saito, Mamoru Tobisu*
Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
E-mail: kodama@chem.eng.osaka-u.ac.jp

Transition metal-catalyzed carbon–carbon bond cleavage is a reaction that is of fundamental research interest.[1] However, both the kinetic and thermodynamic stability of C–C bonds renders their cleavage a daunting challenge. Our group previously reported that a nickel/N-heterocyclic carbene (NHC) complex can mediate the decarbonylation of simple, unstrained ketones.[2] We envisioned that tropone derivatives would be suitable substrates for catalytic decarbonylation because the process involves the formation of a benzene ring which would be expected to drive the otherwise difficult C–C bond cleavage reaction. We report herein on nickel-catalyzed C–C bond cleavage reactions of tropone derivatives.[3] When a Ni/NHC catalyst is used, decarbonylation proceeds with the formation of a benzene ring, while the use of bidentate ligands in conjunction with an alcohol additive results in a two-carbon ring contraction with the generation of cyclopentadiene derivatives. The latter reaction involves a nickel–ketene complex as an intermediate, which was characterized by X-ray crystallography. The choice of an appropriate ligand allows for selective synthesis of four different products via the cleavage of a seven-membered carbocyclic skeleton.



Nickel-catalyzed C–C bond cleavage of tropone derivatives

References
1. Review: Song, F.; Gou, T.; Wang, B.-Q.; Shi, Z.-J. *Chem. Soc. Rev.* **2018**, *47*, 7078.
2. Morioka, T.; Nishizawa, A.; Furukawa, T.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2017**, *139*, 1416.
2. Kodama, T.; Saito, K.; Tobisu, M. *Chem. Sci.* **2022**, *13*, 4922.

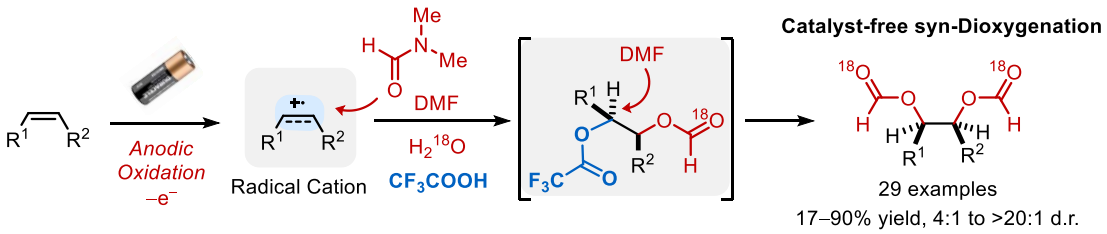
Takuya Kodama (兒玉 拓也). Osaka University (PhD in Science, 2018). Assistant Professor at Osaka University (2018~). [Field of research] Structural Organic Chemistry, Organometallic Chemistry.

Electrochemically Driven Stereoselective Approach to syn-1,2-Diol Derivatives from Vinylarenes and DMF

Steve H Park, Da Sol Chung, Sang-gi Lee and Hyunwoo Kim*
Ewha Womans University, Seoul 03760
E-mail: khw7373@ewha.ac.kr

Due to the unique reactivity of open-shell intermediates, the development of catalytic transformations driven by single-electron transfer (SET) has been an area of intense research in organic chemistry. In particular, the employment of unconventional means of activation, including photoredox catalysis and electrochemistry, has provided unique entry to single-electron reactivities and led to new solutions to challenging synthetic problems that are not readily addressed using existing tools.

An electrochemically driven radical-polar crossover strategy for the stereo- or regioselective alkene functionalization reactions will be discussed. Compared to the precedent examples, the newly developed system obviates the need for external oxidizing agents, thus providing an operationally simple and efficient route to an array of synthetically valuable organic products.



[Electrochemically driven syn-diastereoselective deoxygenation of vinylarenes]

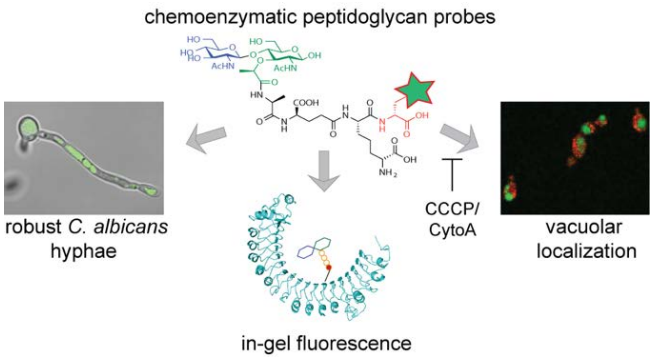
References
1. (a) Zhang, N.; Samanta, S. R.; Rosen, B. M.; Percec, V. Single Electron Transfer in Radical Ion and Radical-Mediated Organic, Materials and Polymer Synthesis. *Chem. Rev.* **2014**, *114*, 5848−5958. (b) Broggi, J.; Terme, T.; Vanelle, P. Organic Electron Donors as Powerful Single-Electron Reducing Agents in Organic Synthesis. *Angew. Chem., Int. Ed.* **2014**, *53*, 384−413.
2. Chung, D. S.; Park, S. H.; Lee, S.-g.; **Kim, H**. *Chem. Sci.* **2021**, *12*, 5892-5897

Hyunwoo Kim (김현우). KAIST (B.S., 2013). KAIST (Ph.D., 2018, Advisor: Sukbok Chang) Cornell Univ. (Postdoc, 2019-2020, Advisor: Song Lin & Tristan Lambert). Ewha Womans University (Assistant Professor, 2020-2022). [Synthetic Organic Methodology: Organic Electrosynthesis].

Chemoenzymatic probes reveal peptidoglycan recognition and uptake mechanisms in *Candida albicans*

Yuan Qiao,* Lanxin Li, Allan Ng, Christopher Adamson, Hirohito Hayashi
Nanyang Technological University, 21 Nanynang Link, Singapore 637371
E-mail: yuan.qiao@ntu.edu.sg

Candida albicans, the major fungal pathogen in humans, is under the strong influence of bacterial peptidoglycan fragments to undergo the yeast-to-hyphae transition, a key virulent step in *C. albicans* pathogenesis and infections. However, due to the synthetic difficulties of obtaining peptidoglycan fragments for biological studies, mechanistic details of how *C. albicans* recognizes and uptakes these peptidoglycan fragments have not been well-elucidated. Notably, previous works have solely focused on the synthetic peptidoglycan ligand, muramyl dipeptide (MDP), despite its poor hyphal-inducing activity in *C. albicans*. In this work, we isolated and purified natural peptidoglycan fragments via enzymatic degradation of bacteria cell wall sacculi, and chemoenzymatically installed a series of functional D-amino acids into the natural muropeptide, creating peptidoglycan probes that bear photoaffinity, bio-orthogonal, or fluorescent functionality. Using these chemoenzymatic peptidoglycan probes, we established that natural peptidoglycan fragments, which are potent hyphal-inducers, interact with the *C. albicans* Cyr1 sensor protein in the in-gel fluorescence assay as well as in *in vitro* pull-down studies. Moreover, we established that bacterial peptidoglycan probes enter *C. albicans* cells via an energy-dependent endocytic process.



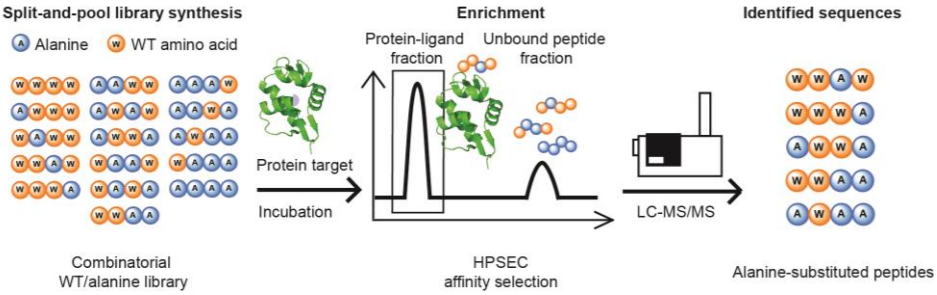
References
1. (a) Li et al. *ACS Chem Biol.* **2022** (In revision)

QIAO Yuan (乔媛). Harvard University (PhD, 2016). Nanyang Assistant Professor (2019-present). [Chemical Biology].

Combinatorial alanine scanning reveals potent protein-protein interaction inhibitors

Yen-Chun Lee,[†[a,b]] Xiyun Ye,[†[a]] Bradley Pentelute*[a]
[a]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[b]Department of Chemistry, National Cheng Kung University, Tainan, Taiwan
E-mail: z11008019@ncku.edu.tw

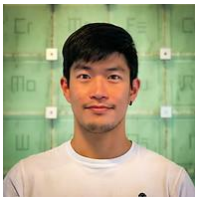
Protein-protein interactions (PPIs) form the molecular basis of processes that sustain life and cause disease. These interactions can be disrupted/promoted by peptide ligands. For ligand optimization, alanine scanning has been proven as a useful strategy to understand the interaction between the protein and ligand side chains. To enable rapid identification of multiple site tolerance of the ligand, we developed a label-free combinatorial alanine scanning platform. In this approach, we use an affinity selection-mass spectrometry workflow and applied it to peptides that inhibit the oncogenic p53-MDM2 interaction. After confirming that the single point mutagenesis agrees with the reported data, high pairwise alanine substitution frequencies reveal the tolerance of peptide binders for two simultaneous substitutions. While increasing the selecting stringency, the potent linear multi-substituted peptide binders were identified as novel MDM2 inhibitors with sub-nanomolar affinity. This platform is also applicable to other protein targets, such as the 12CA5 and 14-3-3 proteins, to reveal the mutational tolerance and binding 'hotspots' of peptide ligands. Combinatorial alanine scanning is a useful method for understanding the next level of structure-activity of peptides and for developing peptide therapeutics.



A label-free affinity selection of combinatorial alanine scanning

References

1. Ye, X; Lee, Y-C; Gates, Z. P.; Ling, Y.; Mortensen, J.; Yang, F.-S.; Lin, Y.-S.; Pentelute, B. *ChemRxiv* **2021**, https://doi.org/10.26434/chemrxiv.13609499.v1.

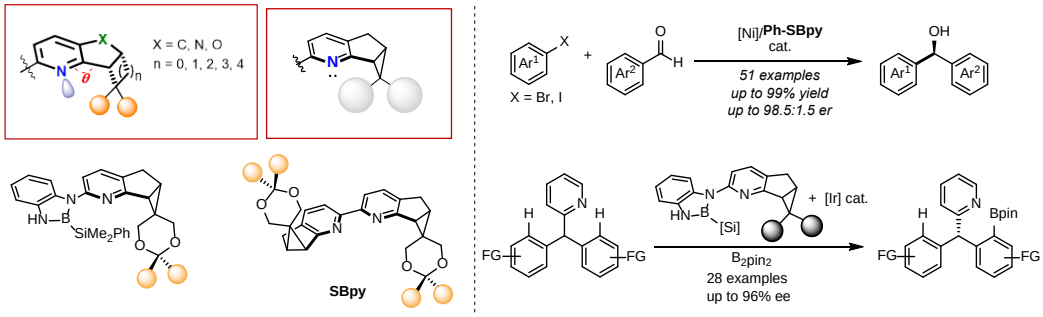


Yen-Chun Lee (李彥君). TU Dortmund, Dortmund, NRW, Germany (PhD, 2013-2018). MIT, Cambridge, MA, USA (DFG postdoctoral fellow, 2018-2021). Assistant professor at NCKU, Tainan, Taiwan (2021). Organic Chemistry, peptide chemistry, and transition metal catalysis.

A New Chiral Pyridine Unit for Asymmetric Catalysis

Pengfei Li,* Shuai Zhang, Peidong Song, Saima Perveen, Linghua Wang, Yizhao Ouyang
Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an, China
E-mail: lipengfei@mail.xjtu.edu.cn

Chiral ligands are the key structural components for tuning the activity and stereoselectivity of metal catalysts in enantioselective transformations. Pyridine is among the most widely used structural units of ligands in homogeneous catalysis. However, development of the asymmetric versions of these catalytic reactions have been significantly retarded because a chiral pyridine skeleton that is generally effective as ligands for asymmetric catalysis is still lacking. The major challenges for this gap include the difficulty to introduce chiral elements for a planar structure, local substituents' steric hindrance-induced paradox between activity and stereoselectivity, the poor flexibility in structural modification and the challenges for modular synthesis. In this work, a new strategy for ligand design is proposed as "double-sphere steric control". According to this strategy, a general skeleton of chiral pyridine ligands featuring a novel rigid polycyclic framework is designed by detailed configurational, conformational and strain analyses. The steric hindrance of both local sites and distal sites can be readily tuned. Recently, mechanistically distinct enantioselective reactions have been developed by employing this new chiral pyridine unit as the key stereochemical controlling element.



References
1. Song, P.; Hu, L.; Yu, T.; Jiao, J.; He, Y.; Xu, L.; Li, P. *ACS Catal.* **2021**, *11*, 7339-7349.
2. Zhang, S.; Perveen, S.; Ouyang, Y.; Xu, L.; Yu, T.; Zhao, M.; Wang, L.; Song, P.; Li, P. *Angew. Chem. Int. Ed.* **2022**, *61*, doi.org/10.1002/anie.202117843.

Pengfei Li (李鹏飞). University Heidelberg (Dr. 2010). Massachusetts Institute of Technology (Postdoctoral Associate 2010-2011), Xi'an Jiaotong University (Principal Investigator & Professor 2011-present). [Field of research] Organometallic Catalysis, Organoboron Chemistry, Natural Product Synthesis.

Highly Efficient Total Syntheses of Galanthamine and Lycoramine via a Two-Stage Strategy

Yu-Ming Zhao,* Ya-Ping Chang, Xia Ma
School of Chemistry and Chemical Engineering
Shaanxi Normal University, 620 West Chang'an Ave, Xi'an, 710119, China
E-mail: ymzhao@snnu.edu.cn

Herein, we report the highly efficient total syntheses of galanthamine and lycoramine from a common tetracyclic intermediate. This concise synthetic route features a two-phase strategy, which includes the early-stage rapid construction of a tetracyclic skeleton followed by the late-stage selective reorganization of the tetracyclic skeleton. Key to the success of this strategy are a palladium-catalyzed carbonylative cascade annulation, a DDQ-mediated intramolecular regioselective oxidative lactamization, as well as a $BF_3 \cdot Et_2O$-promoted reorganization of the bridged tetracyclic skeleton.

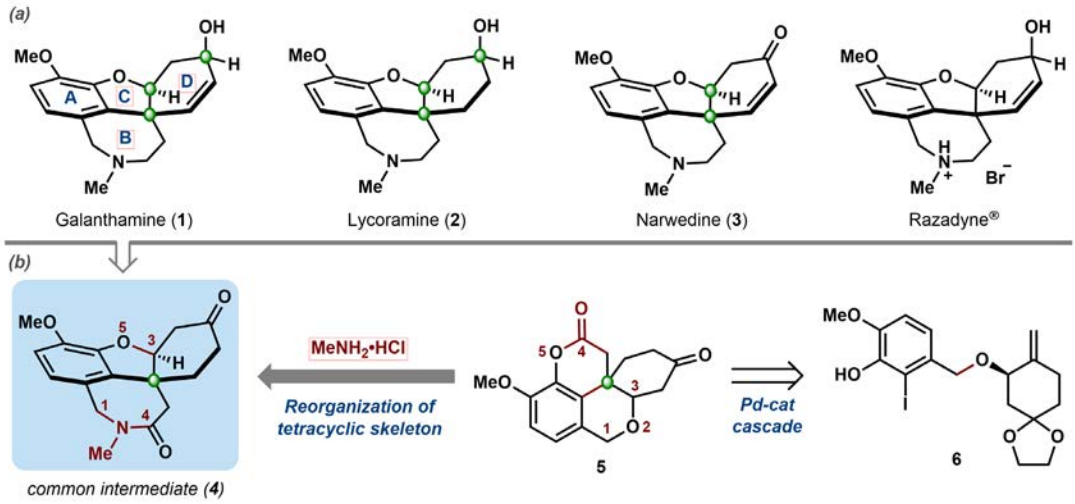


Figure 1. Structure of targeted molecules and our retrosynthetic analysis.

References

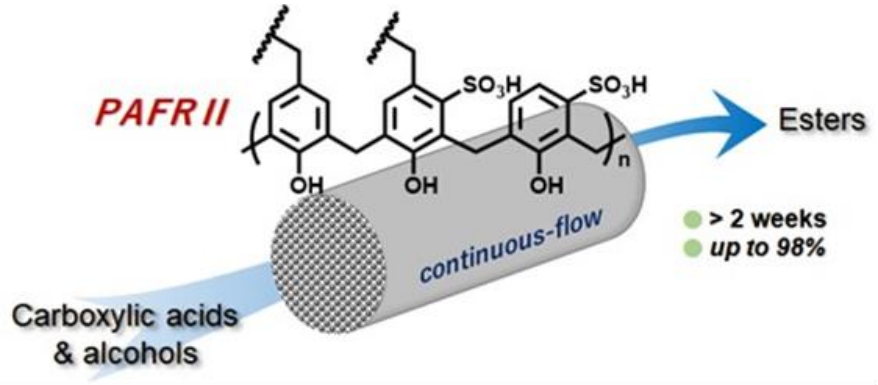
1. For a recent review of galanthamine, see: (a) Marco-Contelles, J.; do Carmo Carreiras, M.; RodrÍguez, C.; Villarroya, M.; GarcÍa, A. G. *Chem. Rev.*, **2006**, *106*, 116-133; (b) Rinner, U.; Dank, C.; Hudlicky, T. *Targets in Heterocyclic Systems*, **2016**, ***20***, 283-315. (c) Janssen, B.; Schäfer, B. *ChemTexts*, **2017**, *3*, 7.
2. Chang, Y.-P.; Ma, X.; Shao, H.; Zhao, Y.-M. *Org. Lett.*, **2021**, *23*, 9659-9663.

Yu-Ming Zhao (赵玉明). Lanzhou University (BS, 2005; Ph.D., 2010, Prof. Yong-Qiang Tu), The Hong Kong University of Science and Technology (Postdoc, 2011-2012, Prof. Jianwei Sun), University of California at Berkeley (Postdoc, 2012-2014, Prof. Tom Maimone), Shaanxi Normal University (2015-present). [Field of research] Total synthesis of complex natural products, Target directed synthetic methodology.

Second Generation Phenolsulfonic Acid-Formaldehyde Resin Catalyst (PAFR II) for Continuous Flow Esterification

Yoichi M. A. YAMADA,[1]* Hao HU,[1] Heeyoel BAEK,[1] Toshiaki MASE,[2] Yasuhiro UOZUMI[2]
1 RIKEN Center for Sustainable Resource Science, Wako, Saitama 351-0198, Japan
2 Institute for Molecular Science, Okazaki, Aichi 444-8787, Japan
E-mail: ymayamada@riken.jp

We have reported the development of porous *p*-phenolsulfonic acid-formaldehyde resin catalyst (PAFR) as a first-generation acid catalyst for direct esterification and transesterification without any removal of water or alcohols.[1-3] Although PAFR showed the high catalytic activity under batch and continuous flow conditions (less than 1 mol% SO_3H of PAFR), its reusability was not satisfied. Herein, I would like to introduce a more active, robust, stable, and reusable second-generation *m*-phenolsulfonic acid-formaldehyde resin catalyst (PAFR II) and its application to Fischer-Speier esterification under batch and continuous-flow conditions.[4]
PAFR II promoted the direct esterification of various carboxylic acids and alcohols under batch and continuous flow conditions without any removal of water to afford the corresponding ester compounds in high yield. PAFR II showed high stability to produce biodiesel fuels from wasting cooking oils like oleic acid or linoleic acid with methanol for over 2 weeks without loss of its catalytic activity.



References
1) M. Minakawa, H. Baek, Y. M. A. Yamada, J-W. Han, and Y. Uozumi, *Org. Lett.* **2013**, *15*, 5798. 2) H. Baek, M. Minakawa, Y. M. A. Yamada, J-W. Han, Y. Uozumi, *Sci. Rep.* **2016**, *6*, 25925. 3) Y. -M. Kim, J. Han, B. Y. Jung, H. Baek, Y. M. A. Yamada, Y. Uozumi, and Y. -S. Lee, *Synlett,* **2016**, *27*, 29. 4) H. Hu, H. Ota, H. Baek, K. Shinohara, T. Mase, Y. Uozumi and Y. M. A. Yamada, *Org. Lett.,* **2020**, *22*, 160-163.

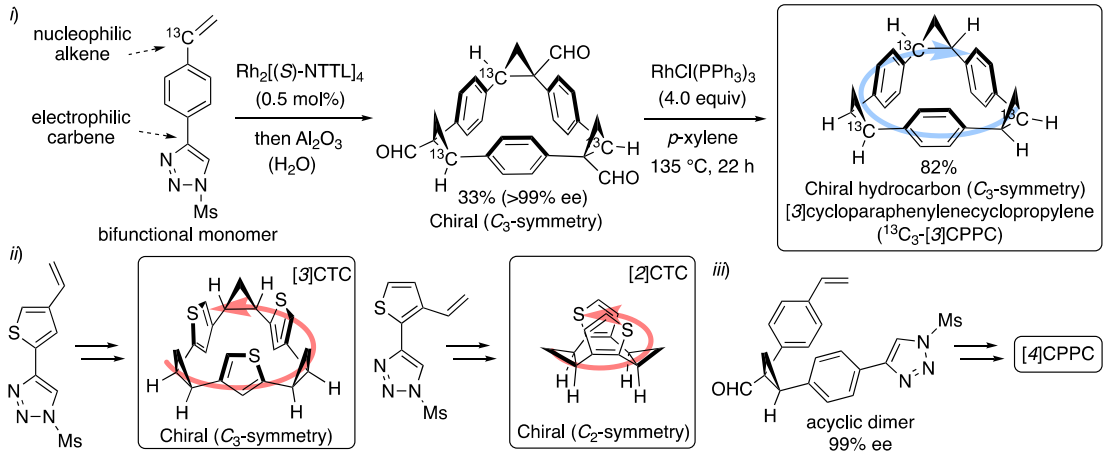
Yoichi M. A. YAMADA (山田陽一).

The University of Tokyo (Ph. D.1999).
Team Leader, RIKEN Center for Sustainable Resource Science (2018-current).
[Field of research] Organic and Catalytic Chemistry, Nano Chemistry

Synthesis, Structure, and Dynamics of Chiral Macrocycles with Arylene and 1,2-*cis*-Cyclopropylene Units Alternatively Connected

Tomoya Miura*
Graduate School of Natural Science and Technology, Okayama University
Tsushimanaka, Okayama 700-8530, Japan
E-mail: tmiura@okayama-u.ac.jp

Chiral macrocycles are of great interest in the fields of asymmetric synthesis, molecular recognition, and materials science. In 2017, we reported the asymmetric synthesis of chiral macrocycle ([*3*]cycloparaphenylenecyclopropylene-1-carbaldehyde, [*3*]CPPC-CHO) starting from a bifunctional monomer possessing triazolyl and vinyl groups at the *para* positions on a benzene ring.[1] Here, subsequent progress will be presented: *i*) the synthesis of chiral C_3-symmetric hydrocarbons ($^{13}C_3$-[*3*]CPPC) with asymmetric distribution of $^{12}C/^{13}C$ isotopes,[2] *ii*) the asymmetric synthesis of [*3*]- and [*2*]cyclothienylenecyclopropylenes ([*n*]CTCs) using a thiophene ring as a spacer,[3] and *iii*) the synthesis of [*4*]CPPC-CHO and [*4*]CPPC using a pre-organized acyclic dimer.



References

1. Miura, T.; Nakamuro, T.; Stewart, S. G.; Nagata, Y.; Murakami, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 3334.
2. Miura, T.; Nakamuro, T.; Nagata, Y.; Moriyama, D.; Stewart, S. G.; Murakami, M. *J. Am. Chem. Soc.* **2019**, *141*, 13342.
3. (a) Miura, T.; Nakamuro, T.; Ishihara, Y.; Nagata, Y.; Murakami, M. *Angew. Chem. Int. Ed.* **2020**, *59*, 20475. (b) Miura, T.; Ishihara, Y.; Nakamuro, T.; Moritani, S.; Nagata, Y.; Murakami, M. *Chem. Eur. J.* **2022**, *28*, e2021103962.

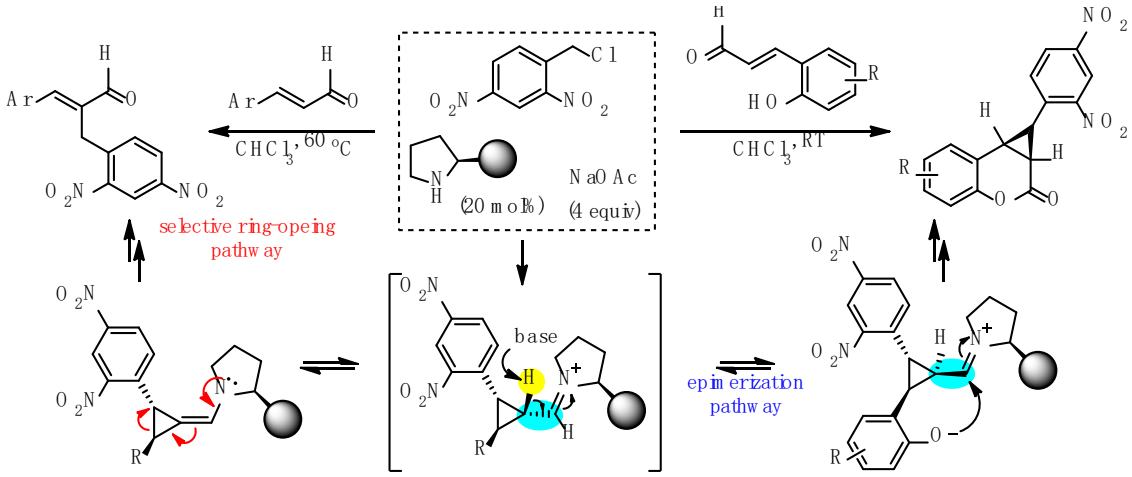
Tomoya Miura (三浦 智也). Tokyo Institute of Technology (DSc, 2003, Nobuharu Iwasawa Lab.). The University of Pennsylvania (Postdoc, 2003, Amos B. Smith, III Lab.). Kyoto University (Assistant Prof., 2003-2008; Senior Lecture, 2008-2011; Associate Prof., 2012-2021, Masahiro Murakami Lab.), Okayama University (Full Prof., 2021-present). [Field of research] Synthetic Organic Chemistry (Development of new synthetic methods, in particular transition-metal-catalyzed reactions).

Substrate-Controlled Chemo-/Enantioselective Synthesis of α-Benzylated Enals and Chiral Cyclopropane-Fused 2-Chromanones

Jung Woon Yang*
Department of Energy Science, Sungkyunkwan University
2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 16419, South Korea
E-mail: jwyang@skku.edu

The research area of asymmetric organocatalysis has rapidly grown to become a third pillar in asymmetric catalysis,[1] complementing enzymes and synthetic transition metal complexes.

I will present our recent research topics on organocatalytic chemo-/enantioselective reactions for the construction of α-benzylated enals and chiral cyclopropane-fused 2-chromanone derivatives utilizing iminium and enamine dual activations (Scheme 1).[2] The applications to biologically active molecule synthesis and the elucidation of reaction mechanism will be discussed.



Scheme 1. Synthesis of α-benzylated enals and chiral cyclopropane-fused 2-chromanones

References

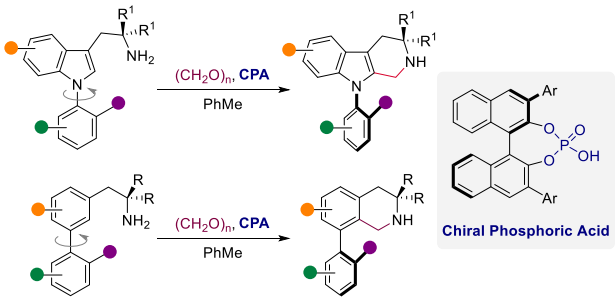
1. (a) List, B. Yang, J. W. *Science* **2006**, *313*, 1584; (b) MacMillan, D. W. C. *Nature* **2008**, 455, 304.
2. Byeon, H. Ryu, S. Yoo, E. J. Yang, J. W. *Adv. Synth. Catal*. **2021**, *363*, 5085.

Jung Woon Yang (양정운) Korea Institute of Science and Technology & Korea University (Ph.D., 2003). Max-Planck-Institut für Kohlenforschung (Post-Doc, Senior Scientist and Group Leader, 2003-2009). Sungkyunkwan University (Full Professor, 2009-present). [Field of research] Biomass Conversions and Synergistic & Enantioselective Organocatalysis.

Catalytic Atroposelective Pictet-Spengler Cyclization

Yongseok Kwon*
Sungkyunkwan University (SKKU), School of Pharmacy
2066 Seobu-ro, Jangan-gu, Suwon, 16419, Republic of Korea
E-mail: y.kwon@skku.edu

Heterocycles containing nitrogen atoms are of interest as an important scaffold in the pharmaceutical and material science. Particularly, *N*-heterocyclic biaryls are frequently found in bioactive natural products and their usefulness are appreciated in the field of asymmetric catalysis utilizing inherent axial chirality. Herein, we report chiral phosphoric acid catalyzed Pictet-Spengler cyclization to control the axial chirality around the C−N and C−C bond via dynamic kinetic resolution.
At the outset of our work, we designed two substrates based on *N*-arylindole and biphenyl which can undergo dynamic racemization around the stereogenic C−N and C−C bond. We envisioned that chiral phosphoric acids would give the cyclized products which have high enough rotational barrier. It was found that the *ortho*-substituent having hydrogen-bond donor ability was necessary in the bottom aromatic ring to form favorable interactions with the chiral phosphoric acid. Further screening of reaction parameters led to the optimized reaction conditions which were applicable with a variety of substrates with up to 97% e.e. With biaryl substrates, enantiodivergence depending on substituents on the aryl ring of chiral phosphoric acid has been observed.



References
1. Kim, A.; Kim, A.; Park, S.; Kim, S.; Jo, H.; Ok, K. M.; Lee, S. K.; Song, J.; Kwon, Y.* *Angew. Chem. Int. Ed.* **2021**, *60*, 12279−12283.
2. Kim, A.; Moon, J.; Lee, C.; Song, J.; Kim, J.; Kwon, Y.* *Org. Lett.* **2022**, *24*, 1077–1082.
3. Kim, A.; Kwon, Y.* *Synlett* **2022**, *33*, 201–206.

Yongseok Kwon (권용석).
Chungbuk National University (B.S., 2009), Seoul National University (M.S., 2011; Ph.D., 2016).
Yale University, Department of Chemistry (Postdoctoral associate, 2016–2019), Sogang University, Department of Chemistry (Assistant professor, 2019–2021). Sungkyunkwan University, School of Pharmacy (Assistant professor, 2021–). Organic chemistry, Asymmetric catalysis

NHC Catalysis: Beyond New Activation Modes

Yonggi Robin Chi,* Zhichao Jin, Pengcheng Zheng
School of Chemistry, Chemical Engineering, and Biotechnology, Nanyang Technological University, Singapore; MOE Key Laboratory of Green Pesticide and Agricultural Bioengineering, Guizhou University, China
E-mail: robinchi@ntu.edu.sg

The Chi laboratory is committed to the state-of-art original chemistry research that addresses problems of both fundamental and practical significance. A key objective is to develop green and efficient synthetic methods to make functional molecules, and to understand the principles guiding the bong breaking and formation events. We focus on the development of fundamentally novel basic catalytic activation modes with useful synthetic applications for the preparation of pharmaceuticals, agriculture chemicals, fine chemicals, and for efficient assembly and/or modification of polymers, biomolecules, and other functional molecules. Over the past years, we have developed new activation modes and synthetic transformations enabled by N-Heterocyclic Carbene (NHC) as the key organic catalyst.

Recent focus in the lab involves both curiosity-driven and user-inspired research with fundamental and/or industrial significance. Active projects are in three directions: chemical synthesis, agricultural chemicals, and medicinal molecules. Presented with this poster are examples of recent studies on catalytic chemo-selective reactions on sophisticated molecules such as saccharides. Our efforts on functional molecule development and manufacturing will also be briefed.

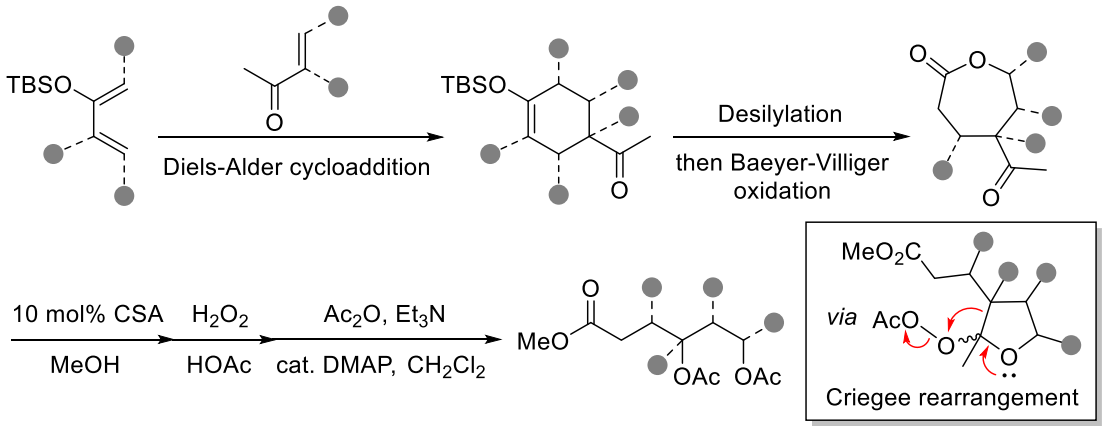
References:
Chi. et. al.
Chem. **2022**, *8*, 1518-1534; J. *Am. Chem. Soc*. 2022, *144*, 5441-5449; *Nature Commun*. 2022, 13, 84. *Nature Commun.* 2022, *13*, 36; *J. Agric. Food Chem.* **2022**, DOI: 10.1021/acs.jafc.2c01407; *Nature Commun.* **2022**, *13,* 2846.

Robin Chi. University of Wisconsin-Madison, USA (PhD, 2007). Full Professor, Chair Professor, Nanyang Technological University; Distinguished Professor, Guizhou University. [Field of research] Chemical Synthesis, Agricultural Chemicals, and Medicinal Molecules; fundamental and applied research.

Diastereodivergent Synthesis of *syn*,*syn*,*syn*-, *syn*,*anti*,*syn*- and *anti*,*syn*,*syn*-Stereotetrads

Guo-Ming Ho*, Hao-Lin Yang, and Yung-Chi Chang
Department of Chemistry, National Kaohsiung Normal University,
No.62, Shenjhong Rd., Yanchao District, Kaohsiung City 82446, Taiwan (R.O.C.)
E-mail: gmh@nknu.edu.tw

Stereotetrads with four contiguous stereogenic centres are important segments of many natural products possessing useful pharmacological properties. Synthetic access to these structures has been a longstanding interest in the synthesis community. Herein, we report a diastereodivergent strategy to stepwise synthesis of stereotetrad structures through a six-step Diels–Alder cycloaddition/Baeyer–Villiger oxidation/Criegee rearrangement relay process. The highly substrate-controlled Diels–Alder reaction enabled the establishment of the necessary cyclohexene ring featuring the silylenol ether and four stereogenic centres. Following an acid hydrolysis and Baeyer–Villiger oxidation formed the seven-membered lactones. Having the desired stereochemistry and the necessary carbon atoms of the target subunit, the lactones were subjected to transesterification and ketal formation utilizing catalytic camphorsulfonic acid in methanol. Subsequently, the ketals were converted to a mixture of hydroperoxy ketals upon exposure to 30% H_2O_2 and acetic acid. Final acetylation of the crude hydroperoxides and Criegee rearrangement, the *syn*,*syn*,*syn*-, *syn*,*anti*,*syn*- and *anti*,*syn*,*syn* stereotetrad stereoisomers with substantial skeletal diversity were accessed, respectively.



References
1. Ho, G.-M.; Zulueta, M. M.; Hung, S.-C. *Nat. Commun.* **2017**, *8*, 679 – 685.
2. Ziegler, F. E.; Kneisley, A.; Thottathil, J. K.; Wester. R. T. *J. Am. Chem. Soc*. **1988**, *110*, 5434 – 5442.
3. Ho, G.-M.; Huang, C.-J.; Li, E.; Hsu, S.-K.; Wu, T. ; Zulueta, M. M.; Wu, K.; Hung, S.-C. *Sci. Rep.* **2016**, *6*, 35147 – 35156.

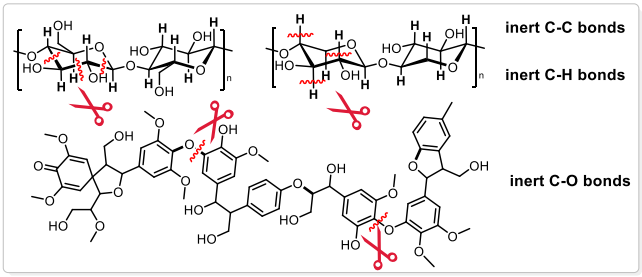
[Insert photo] Guo-Ming Ho (何國銘). Name in English (Name in your language). xxx University (degree, year). Previous positions (year). Current position (year). [Field of research] xxx Chemistry.

Cleavage of inert chemical bonds related biomass for green H_2 and chemicals by photoredox catalysis and transition-metal catalysis

Yang Li*
Frontier Institute of Science and Technology (FIST), Xi'an Jiaotong University
E-mail: liyang79@mail.xjtu.edu.cn

Utilization of waste non-food biomass for green hydrogen and chemicals is one of important pathways for the sustainable development. Highly efficient and selective cleavage of the inert chemical bonds in biomass is the key scientific issue in this field.

We realized efficient and selective cleavage of inert C–C bonds in biomass. The forming hydrogen-bonds between DMSO and the gem-diol, generated by the reaction of the aldehyde group of intermediates in the hydrolysis-oxidation of biomass, with water, stabilize the aldehyde group and inhibit cleavage of the C–H bonds connected with aldehyde group, to increase the selectivity of C–C bonds cleavage in biomass. Based on selective cleavage of C-C bonds, highly efficient H_2 production from various biomass was obtained by a one-pot two-step reaction.[1] Cleavage of multiple C–H bonds of N-Heterocycles at ambient temperature was triggered by using visible-light induced nitrogen radical cation to form more stable heteroaromatic ring. Acceptorless dehydrogenation reaction was developed. A new route for green H_2 storage was indicated.[2] Cleavage of the lignin 4-O-5 type inert C–O bonds was also realized at ambient temperature by using visible-light induced aryl carboxyl radical to trigger forming more stable ester-aryl ether C-O bonds. A new method for renewable aromatic phenol compounds from biomass was indicated.[3]



Efficient and selective cleavage of the inert chemical bonds in biomass

References

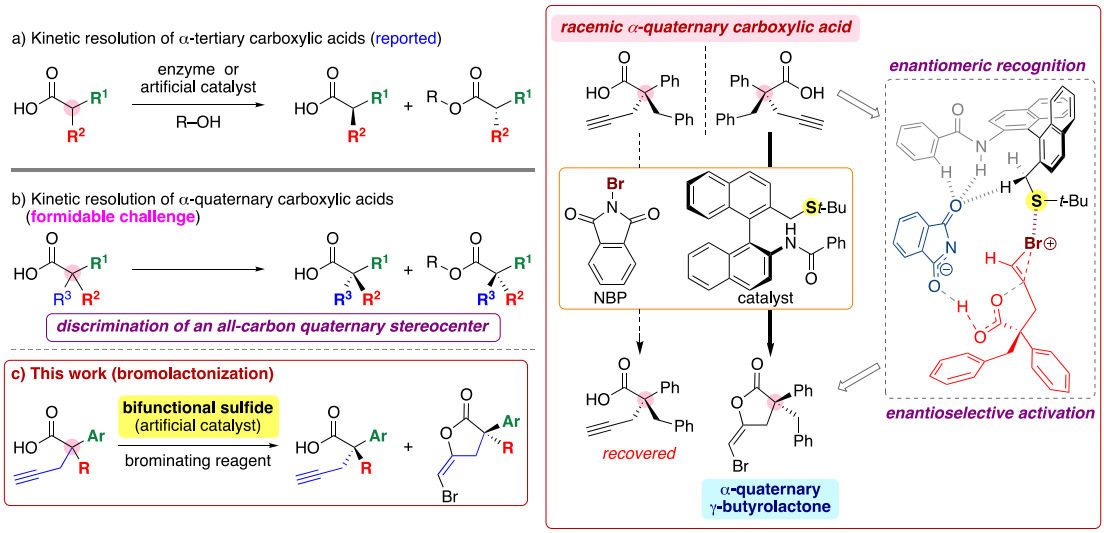
1. (a) Zhang, P.; Guo, Y.-J.; Chen, J.; Zhao, Y.-R.; Chang, J.; Junge, H; Beller, M.; Li, Y. *Nat. Catal.* **2018**, *1*, 332. (b) Guo, Y.-J.; Li, S-J.; Sun, Y.-L.; Wang, L.; Zhang, W.-M.; Zhang, P.; Lan, Y.; Li, Y. *Green Chem.* **2021**, 23, 7041.
2. He, K.-H.; Tan, F.-F.; Zhou, C.-Z.; Zhou, G.-J.; Yang, X.-L.; **Li, Y.*** *Angew. Chem. Int. Ed.* **2017**, *56*, 3080.
3. (a) Wang, S.-F.; Cao, X.-P.*; **Li, Y.*** *Angew. Chem. Int. Ed.* **2017**, *56*, 13809. (b) Tan, F.-F.; He, X.-Y.; Tian, W.-F.; **Li, Y.*** *Nat. Commun.* **2020**, *11*, 6126.

Yang Li (李洋), work in Frontier Institute of Science and Technology (FIST), Xi'an Jiaotong University since 2014, and supported by "Young Talent Support Plan" of Xi'an Jiaotong University since 2016. Our current research focus on the cleavage of inert bonds in biomass for green H_2 and green chemicals by photoredox catalysis and transition-metal catalysis.

Kinetic Resolution of α-Quaternary Carboxylic Acids via Chiral Bifunctional Sulfide-Catalyzed Bromolactonization

Seiji Shirakawa*
Department of Environmental Science, Nagasaki University
1-14, Bunkyo-machi, Nagasaki 852-8521, Japan
E-mail: seijishirakawa@nagasaki-u.ac.jp

Kinetic resolution of racemic carboxylic acids is a reliable method to enantioselectively prepare chiral carboxylic acids. Although efficient catalytic kinetic resolutions of chiral α-tertiary carboxylic acids have been reported, the kinetic resolution of α-quaternary carboxylic acids bearing an all-carbon quaternary stereocenter has remained a formidable challenge. Herein, we report a precious example of a kinetic resolution of α-quaternary carboxylic acids via a chiral bifunctional sulfide-catalyzed bromolactonization of alkynes. The ability of chiral bifunctional sulfides to recognize α-quaternary carboxylic acids was evaluated via the catalytic enantioselective desymmetrizing bromolactonization of achiral α,α-dipropargyl carboxylic acids, which is a reaction that is relative to the target kinetic resolution. The optimum bifunctional sulfide was successfully applied to the efficient kinetic resolution of α-propargyl carboxylic acids that bear an all-carbon quaternary stereocenter.[1]



References

1. Okuno, K.; Hiraki, M.; Chan, B.; Shirakawa, S. *Bull. Chem. Soc. Jpn.* **2022**, *95*, 52.

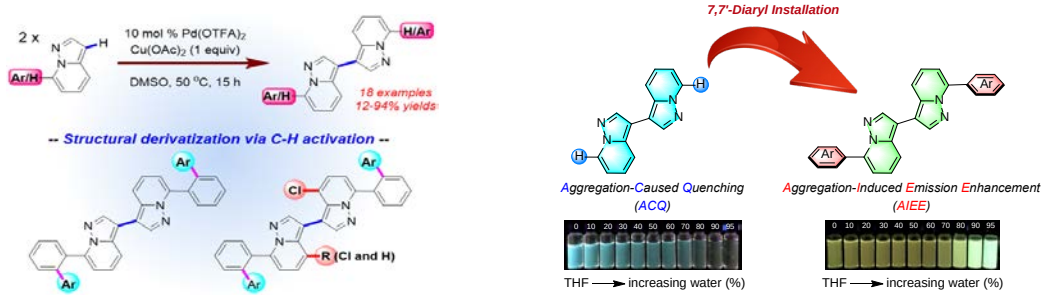
Seiji Shirakawa (白川誠司). Kyoto University (PhD, 2004). Columbia University (Posdoc, 2004–2005), University of Tokyo (Posdoc, 2005–2007), Nihon University (Assistant Professor, 2007–2009), Kyoto University (Associate Professor, 2009–2014). Nagasaki University (Associate Professor [PI], 2014–). [Field of research] Organocatalysis, Asymmetric Synthesis, Green Chemistry.

Synthesis of Novel Bipyrazolo[1,5-*a*]pyridine as Aggregation-Induced Emission Enhancement Luminogens

Jean-Ho Chu,*[a] Pu-Yen Hsiao,[a] Rong Chang,[b] Andrew C.-H. Sue,[b] Yi-Hsin Lee,[a] and Jui-Yang Huang[a]

[a]*Department of Applied Science, National Taitung University, Taitung, Taiwan 95092*
[b]*College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China 361005*
E-mail: j_hchu@nttu.edu.tw

A novel 3,3′-bipyrazolo[1,5-*a*]pyridine molecular scaffold was obtained as a product of serendipity *via* palladium-mediated direct cross-dehydrogenative coupling of pyrazolo[1,5-*a*]pyridine. The synthesis of a range of 7,7′-diaryl-3,3′-bipyrazolo[1,5-*a*]pyridines is successfully optimized based on this serendipitous discovery. This simple and efficient methodology shows good functional group tolerance and product yields. Through the mechanistic insights gained from both kinetic isotope effect experimental studies and density functional theory calculations, a plausible reaction mechanism is outlined. For 7,7′-diaryl-3,3′-bipyrazolo[1,5-*a*]pyridines, both photophysical characterizations and HOMO-LUMO theoretical calculations indicate its potential as a promising fluorophore with notable intramolecular charge transfer. This series of tailor-made luminogens with twisted π-structures display aggregation-induced emission enhancement properties, showing great promise for organic luminescent material applications.



References

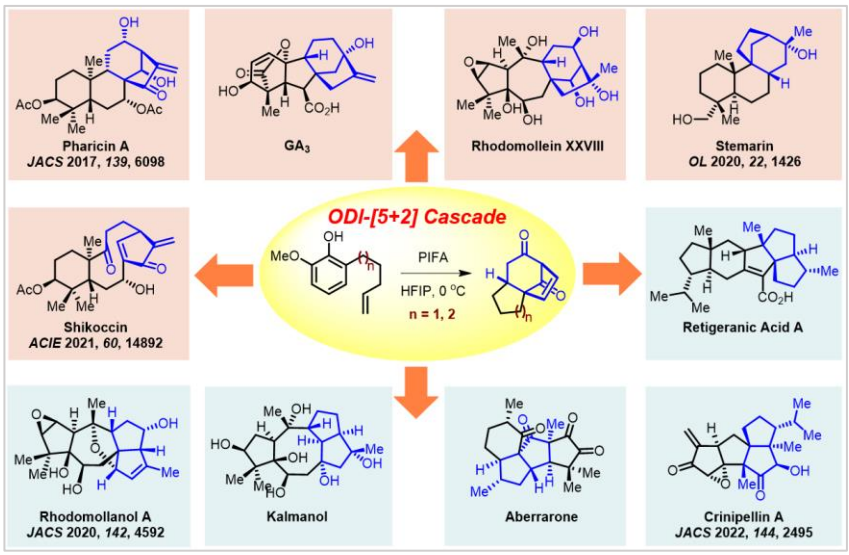
1. (a) Hsiao, P.-Y.; Chu, J.-H. *Chem. Commun.* **2021**, *57*, 12281-12284. (b) Hsiao, P.-Y.; Chang, R.; Sue, A. C.-H.; Chu, J.-H.; Lee, Y.-H.; Huang, J.-Y. *J. Org. Chem.* **2022** (under review).

Jean-Ho Chu (朱見和). Department of Applied Chemistry, National Yang-Ming Chiao-Tung University, Taiwan (PhD & MS, 2007 & 1999). Department of Chemistry, Tunghai University, Taiwan (BS, 1997). Postdoc. of Kaohsiung Medical University & National Sun Yat-sen University, Taiwan (2007-2011). Assistant Research Scholar of MOST, Taiwan (2011-2016). Guest Research Scholar of Kyoto University, Japan (Jan-Feb 2013). Assistant Professor (2016-2021) & Associate Professor (2021-present), Department of Applied Science, National Taitung University, Taiwan. Area of specialization: Organic Chemistry. Research interests: C-H activation strategy applied in organic synthesis and design of novel AIE luminogens.

Tetracyclic Diterpenoid Synthesis Facilitated by an ODI-[5+2] Cascade

Hanfeng Ding*
Department of Chemistry, Zhejiang University, 866 Yuhangtang Road, 310058 Hangzhou, China
E-mail: hfding@zju.edu.cn

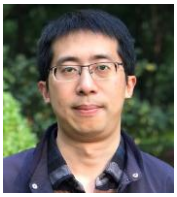
Tetracyclic diterpenoids (C20) mainly refer to the plant terpenoids bearing biogenetically related carbon skeletons that derived from copalyl diphosphates (*ent*-CPP and *syn*-CPP). This large family contains over 1600 known members. Among them, more than three-quarters share a common bicyclo[3.2.1]octane subunit. Combined with the significance of its stereochemical importance in biological activity, the assembly of the bicyclo[3.2.1]octane skeletons is critical to the success of the whole synthesis blueprint toward tetracyclic diterpenoids. Recently, we have developed a new ODI-[5+2] cascade reaction, which led to the rapid and efficient construction of bicyclo[3.2.1]octane skeletons. Herein, we summarize our methodology development, as well as its application in tetracyclic diterpenoid synthesis during the past few years in our lab (Scheme 1).



Scheme 1. ODI-[5+2] Cascade and Its Synthetic Application

References

1. (a) Sun, H.-D.; Huang, S.-X.; Han, Q.-B. *Nat. Prod. Rep.* **2006**, *23*, 673; (b) Liu, M.; Wang, W.-G.; Sun, H.-D.; Pu, J.-X. *Nat. Prod. Rep.* **2017**, *34*, 1090.
2. Gao, K.; Hu, J.; Ding, H. *Acc. Chem. Res.* **2021**, *54*, 875.



Hanfeng Ding (丁寒锋). Zhejiang University (Ph.D., 2008). A-STAR, Singapore (Postdoc 2008-2011). Zhejiang University (Professor, 2011). [Field of research] Natural product synthesis.

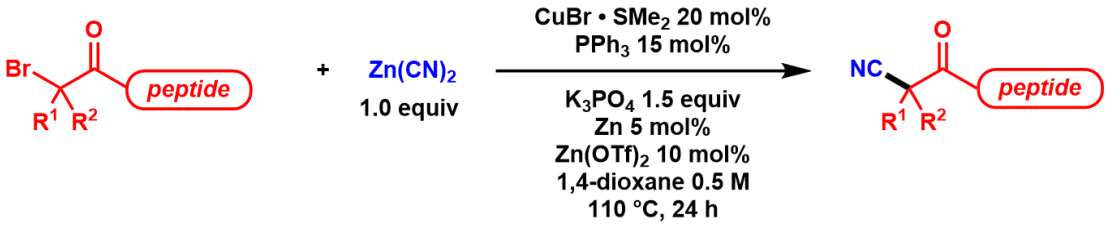
Cu catalyzed sterically congested C(sp3)-CN bond formations

Takashi Nishikata*
Yamaguchi University, 2-16-1 tokiwadai, Ube, Yamaguchi, 755-8611, Japan
E-mail: nisikata@ yamaguchi-u.ac.jp

α-Bromocarbonyls (Br-RR'CCOR") generate α-radicals in the presence of a copper catalyst. The resulting α-radicals can be used for atom-transfer radical polymerizations to produce long chain polymers. α-Bromocarbonyls are also attractive to synthesize quaternary carbons, in which α-bromocarbonyls are used as a tertiary alkyl source. In this context, we have started to study various transformations of α-bromocarbonyls in substitution and addition reactions. As the result, we found that α-bromocarbonyls react with alkene, alkyne, fluorine, and amine in the presence of copper catalyst. The chemistry of α-Bromocarbonyl is also applicable to electron catalyzed system, in which the reaction occurs without any metal catalyst.

In this presentation, we will introduce our recent results on the synthesis of small unnatural peptide derivatives via cyanations[1].

[One-column figure and caption here]



References
1. N. Miwa, C. Tanaka, S. Ishida, G. Hirata, J. Song, T. Torigoe, Y. Kuninobu, T. Nishikata *J. Am. Chem. Soc*., **2020**, *142*, 1692-1697.

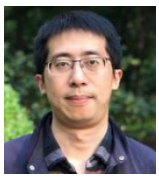
Takashi Nishikata (西形　孝司). Hokkaido University (PhD, 2005). Following the completion of his doctoral degree, he worked as a Podoc at Hokkaido University. In 2008-2010, he spent two years as a postdoctoral fellow at the University of California, Santa Barbara In 2010-2012, he worked as an assistant professor at Kyushu University. In 2012-2020, he worked as an associate professor at Yamaguchi University (PI).
[Field of research] Synthetic Organic Chemistry.

Author Index

China (27)

Ying-Chun CHEN
Sichuan University
IL-10 p10

Hanfeng DING
Zhejiang University
PB-49 p121



Qi-Xiang GUO
Southwest University
PA-36 p58

Chuan HE
Southern University of Science and Technology
PA-1 p23

Xiangdong HU
Northwest University
PB-32 p104

Yanxing JIA
Peking University
IL-21 p21

Chuang-Chuang LI
Southern University of Science and Technology
IL-1 p1

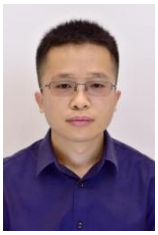
Pengfei LI
Xi'an Jiaotong University
PB-38 p110

Yang LI
Xi'an Jiaotong University
PB-46 p118

Jian LIAO
Chengdu Institute of Biology
PA-25 p47

Qingquan LU
Wuhan University
PB-11 p83

Lingkui MENG
Huazhong University of Science and Technology
PB-21 p93



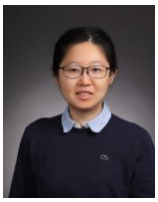
Xiangfeng SHAO
Lanzhou University
PB-31 p103

Zhihui SHAO
Yunnan University
PA-37 p59

Xiao SHEN
Wuhan University
PB-12 p84

Xing-Zhong SHU
Lanzhou University
IL-17 p17

Shuo TONG
Tsinghua University
PA-48 p70



Xinfang XU
Sun Yat-Sen University
PA-2 p24

Zhengren XU
Peking University
PA-47 p69

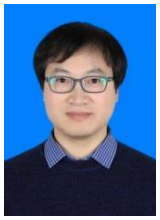
Jin-Dong YANG
Tsinghua University
PB-1 p73

Yu-Rong YANG
Kunming Institute of Botony
PA-24 p46

Guoyin YIN
Wuhan University
IL-15 p15

Wanxiang ZHAO
Hunan University
PB-22 p94

Yu-Ming ZHAO
Shanxi Normal University
PB-39 p111



Jianrong Steve ZHOU
Peking University Shenzhen Graduate School
PA-12 p34

Rong ZHU
Peking University
PB-2 p74

Shifa ZHU
South China University of Technology
PA-13 p35

Ho Yu AU-YEUNG
University of Hong Kong
PB-25 p97

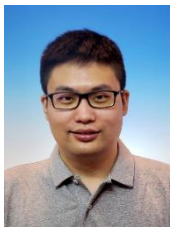
Zhongxing HUANG
University of Hong Kong
IL-3 p3

Guochen JIA
The Hong Kong University of Science and Technology
IL-14 p14

Franco King-Chi LEUNG
The Hong Kong Polytechnic University
PA-40 p62

Yudai MATSUDA
City University of Hong Kong
PA-5 p27

Yangjian QUAN
The Hong Kong University of Science and Technology
PB-5 p77

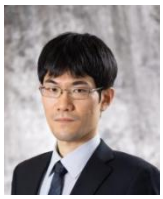


Gavin Chit TSUI
The Chinese University of Hong Kong
PA-16 p38

Ying WANG
The Chinese University of Hong Kong
PA-28 p50

Jun (Joelle) WANG
Hong Kong Baptist University
PB-15 p87

Yusuke ANO
Osaka University
PB-33 p105



Sobi ASAKO
Institute of Physical and Chemical Research
PA-38 p60

Nobutaka FUJIEDA
Osaka Metropolitan University
IL-13 p13

Takeharu HAINO
Hiroshima University
PB-13 p85

Shingo HARADA
Chiba University
PA-27 p49

Keisuke IIDA
Chiba University
IL-18 p18

Hiroaki ITOH
The University of Tokyo
PA-49 p71

Yoshiharu IWABUCHI
Tohoku University
PA-15 p37

Takuya KODAMA
Osaka University
PB-34 p106

Masahiro KOJIMA
Hokkaido University
PA-3 p25

Azusa KONDOH
Tohoku University
IL-9 p9

Yusuke MASUDA
Hokkaido University
IL-2 p2

Tomoya MIURA
Okayama University
PB-41 p113

Takashi NISHIKATA
Yamaguchi University
PB-50 p122

Yusuke OGURA
The University of Tokyo
PA-50 p72

Ambara R. PRADIPTA
Tokyo Institute of Technology
PB-4 p76

Kazuhiko SEMBA
Kyoto University
PB-24 p96

Seiji SHIRAKAWA
Nagasaki University
PB-47 p119

Hidetoshi T0KUYAMA
Tohoku University
PA-14 p36

Yoshihiro UEDA
Kyoto University
PB-23 p95

Muhammet UYANIK
Nagoya University
PB-14 p86

Yoichi M. A. YAMADA
Institute of Physical and Chemical Research
PB-40 p112

Masahiro YAMASHINA
Tokyo Institute of Technology
PB-3 p75

Makoto YAMASHITA
Nagoya University
IL-22 p22

Satoshi YOKOSHIMA
Nagoya University
PA-39 p61

Yasushi YOSHIDA
Chiba University
PA-26 p48

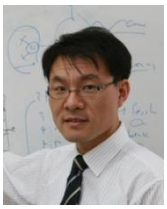
Taiga YURINO
Hokkaido University
PA-4 p26

Cheol-Hong CHEON
Korea University
PB-6 p78

Won-jin CHUNG
Gwangju Institute of Science and Technology
PB-17 p89

Sukwon HONG
Gwangju Institute of Science and Technology
IL-6 p6

Woo-Dong Jang
YONSEI University
PA-42 p64



Jung Min JOO
Pusan National University
PB-16 p88

B. Moon KIM
Seoul National University
PA-41 p63

Hyunwoo KIM
Korea Advanced Institute of Science and Technology
PA-6 p28

Hyunwoo KIM
Ewha Womans University
PB-35 p107

Min KIM
Chungbuk National University
PA-7 p29

Yongseok KWON
Sungkyunkwan University
PB-43 p115

Jun Hee LEE
Dongguk University
PB-27 p99

Sunwoo LEE
Chonnam National University
PB-26 p98

Sarah Yunmi LEE
Yonsei University
IL-11 p11

Hyun-Suk LIM
Pohang University of Science and Technology
PA-30 p52

Sun-Joon MIN
Hanyang University
IL-19 p19

Young Ho RHEE
Pohang University of Science and Technology
PA-29 p51

Do Hyun RYU
Sungkyunkwan University
PA-17 p39

Jung Woon YANG
Sungkyunkwan University
PB-42 p

Jaesook YUN
Sungkyunkwan University
PA-18 p40

Iskandar Abdullah
University of Malaya
PB-7 p79

Muhammad Kumayl ABDULWAHAB
University of Malaya
PA-8 p30

Joazaizulfazli JAMALIS
Universiti Teknologi Malaysia
PA-43 p65

Yean Kee LEE
University of Malaya
PA-19 p41

Aimi Suhaily SAAIDIN
Universiti Teknologi Mara
IL-5 p5

Rozana OTHMAN
University of Malaya
PA-31 p53

Chunyan CHI
National University of Singapore
PB-8 p80

Robin CHI
Nanyang Technological University
PB-44 p116

Shaozhong GE
National University of Singapore
PA-20 p42

Ming Joo KOH
National University of Singapore
IL-4 p4

Shingo ITO
Nanyang Technological University
PB-18 p90

Cheuk-Wai SO
Nanyang Technological University
IL-16 p16

Han Sen SOO
Nanyang Technological University
PB-28 p100

Jie WU
National University of Singapore
PA-9 p31

Yuan QIAO
Nanyang Technological University
PB-36 p108

Yu ZHAO
National University of Singapore
PA-32 p54

Ye ZHU
National University of Singapore
PA-44 p66

Chien-Wei CHIANG
Soochow University
PA-33 p55

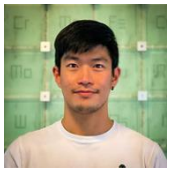
Chih-Ming CHOU
National University of Kaohsiung
IL-20 p20

Jean-Ho CHU
National Taitung University
PB-48 p120

Hsiang-Yu CHUANG
National Chiayi University
PB-19 p91

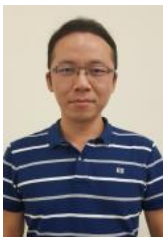
Guo-Ming HO
National Kaohsiung Normal University
PB-45 p117

Yen-Chun LEE
National Cheng Kung University
PB-37 p109



Pei-Jhen LI
National Chung Cheng University
PB-9 p81

Chien-Fu LIANG
National Chung Hsing University
PA-46 p68



Hsuan-Hung LIAO
National Sun Yat-sen University
PA-22 p44

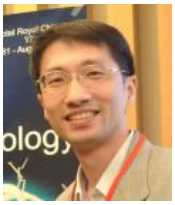
Cheng-Kun LIN
National Chung Hsing University
PA-45 p67

Cheng-Che TSAI
Tunghai University
PB-29 p101

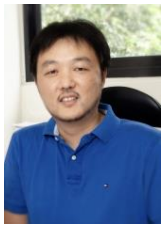
Cheng-Chung WANG
Academia Sinica
IL-12 p12

Tsung-Shing Andrew WANG
National Taiwan University
PA-10 p32

Sheng-Kai WANG
National Tsing-Hua University
PA-34 p56



Yen-Ku WU
National Yang Ming Chiao Tung University
IL-8 p8



Ching-Ching YU
National Chung Cheng University
PA-21 p43

Sunisa AKKARASAMIYO
Kasetsart University
PB-10 p82

Jaruwan CHATWICHIEN
Chulabhorn Graduate Institute
PA-35 p57

Pawaret LEOWANAWAT
Mahidol University
PB-20 p92

Aurapat NGAMNITHIPORN
Chulabhorn Research Institute
PA-11 p33

Panuwat PADUNGROS
Chulalongkorn University
PB-30 p102

Satapanawat SITTIHAN
Chulabhorn Graduate Institute
IL-7 p7

Poramate SONGTHAMMAWAT
Chulabhorn Research Institute
PA-23 p45

List of Participants

Last Name	First Name	Affiliation	country	Email	No.
Abdullah	Iskandar	University of Malaya	Malaysia	iskandar.a@um.edu.my	PB-7
Abdulwahab	Muhammad Kumayl	University of Malaya	Malaysia	kumaylabdul@um.edu.my	PA-8
Akkarasamiyo	Sunisa	Kasetsart University	Thailand	fscisia@ku.ac.th	PB-10
Ano	Yusuke	Osaka University	Japan	ano@chem.eng.osaka-u.ac.jp	PB-33
Asako	Sobi	Institute of Physical and Chemical Research	Japan	sobi.asako@riken.jp	PA-38
Au-Yeung	Ho Yu	University of Hong Kong	Hong Kong	hoyuay@hku.hk	PB-25
Chatwichien	Jaruwan	Chulabhorn Graduate Institute	Thailand	jaruwanc@cgi.ac.th	PA-35
Chen	Yingchun	Sichuan University	China	ycchen@scu.edu.cn	IL-10
Cheon	Cheol-Hong	Korea University	Korea	cheon@korea.ac.kr	PB-6
Chi	Chunyan	National University of Singapore	Singapore	chmcc@nus.edu.sg	PB-8
Chi	Robin	Nanyang Technological University	Singapore	robinchi@ntu.edu.sg	PB-44
Chiang	Chien-Wei	Soochow University	Taiwan	cwchiang@scu.edu.tw	PA-33
Chou	Chih-Ming	National University of Kaohsiung	Taiwan	cmchou@nuk.edu.tw	IL-20
Chu	Jean-Ho	National Taitung University	Taiwan	j_hchu@nttu.edu.tw	PB-48
Chuang	Hsiang-Yu	National Chiayi University	Taiwan	hychuang@mail.ncyu.edu.tw	PB-19
Chung	Won-jin	Gwangju Institute of Science and Technology	Korea	wjchung@gist.ac.kr	PB-17
Ding	Hanfeng	Zhejiang University	China	hfding@zju.edu.cn	PB-49
Fujieda	Nobutaka	Osaka Metropolitan University	Japan	fujieda@biochem.osakafu-u.ac.jp	IL-13
Ge	Shaozhong	National University of Singapore	Singapore	chmgsh@nus.edu.sg	PA-20
Guo	Qixiang	Southwest University	China	qxguo@swu.edu.cn	PA-36
Haino	Takeharu	Hiroshima University	Japan	haino@hiroshima-u.ac.jp	PB-13

Harada	Shingo	Chiba University	Japan	Sharada@chiba-u.jp	PA-27
He	Chuan	Southern University of Science and Technology	China	hec@sustech.edu.cn	PA-1
Ho	Guo-Ming	National Kaohsiung Normal University	Taiwan	gmh@nknu.edu.tw	PB-45
Hong	Sukwon	Gwangju Institute of Science and Technology	Korea	shong@gist.ac.kr	IL-6
Hu	Xiang-Dong	Northwest University	China	xiangdonghu@nwu.edu.cn	PB-32
Huang	Zhongxing	University of Hong Kong	Hong Kong	huangzx@hku.hk	IL-3
Iida	Keisuke	Chiba University	Japan	kiida@chiba-u.jp	IL-18
Ito	Shingo	Nanyang Technological University	Singapore	sgito@ntu.edu.sg	PB-18
Itoh	Hiroaki	The University of Tokyo	Japan	itoh@mol.f.u-tokyo.ac.jp	PA-49
Iwabuchi	Yoshiharu	Tohoku University	Japan	y-iwabuchi@tohoku.ac.jp	PA-15
Jamalis	Joazaizulfazli	Universiti Teknologi Malaysia	Malaysia	joazaizulfazli@utm.my	PA-43
Jang	Woo-Dong	Yonsei University	Korea	wdjang@yonsei.ac.kr	PA-42
Jia	Yanxing	Peking University	China	yxjia@bjmu.edu.cn	IL-21
Jia	Guochen	The Hong Kong University of Science and Technology	Hong Kong	chjiag@ust.hk	IL-14
Joo	Jung Min	Pusan National University	Korea	jmjoo@pusan.ac.kr	PB-16
Kim	Hyunwoo	Korea Advanced Institute of Science and Technology	Korea	hwk34@kaist.ac.kr	PA-6
Kim	Min	Chungbuk National University	Korea	minkim@chungbuk.ac.kr	PA-7
Kim	Byeong Moon	Seoul National University	Korea	kimbm@snu.ac.kr	PA-41
Kim	Hyunwoo	Ewha Womans University	Korea	khw7373@ewha.ac.kr	PB-35
Kodama	Takuya	Osaka University	Japan	kodama@chem.eng.osaka-u.ac.jp	PB-34
Koh	Ming Joo	National University of Singapore	Singapore	chmkmj@nus.edu.sg	IL-4
Kojima	Masahiro	Hokkaido University	Japan	m-kojima@pharm.hokudai.ac.jp	PA-3
Kondoh	Azusa	Tohoku University	Japan	kondoha@tohoku.ac.jp	IL-9
Kwon	Yongseok	Sungkyunkwan University	Korea	y.kwon@skku.edu	PB-43

Lee	Sarah Yunmi	Yonsei University	Korea	sarahyunmi@yonsei.ac.kr	IL-11
Lee	Sunwoo	Chonnam National University	Korea	sunwoo@chonnam.ac.kr	PB-26
Lee	Jun Hee	Dongguk University	Korea	leejunhee@dongguk.ac.kr	PB-27
Lee	Yean Kee	University of Malaya	Malaysia	yeankee@um.edu.my	PA-19
Lee	Yen-Chun	National Cheng Kung University	Taiwan	yenchunlee.chem@gmail.com	PB-37
Leowanawat	Pawaret	Mahidol University	Thailand	pawaret.leo@mahidol.ac.th	PB-20
Leung	Franco King-Chi	The Hong Kong Polytechnic University	Hong Kong	kingchifranco.leung@polyu.edu.hk	PA-40
Li	Chuang-Chuang	Southern University of Science and Technology	China	ccli@sustech.edu.cn	IL-1
Li	Pengfei	Xi'an Jiaotong University	China	lipengfei@mail.xjtu.edu.cn	PB-38
Li	Yang	Xi’an Jiaotong University	China	liyang79@mail.xjtu.edu.cn	PB-46
Li	Pei-Jhen	National Chung Cheng University	Taiwan	chepjli@ccu.edu.tw	PB-9
Liang	Chien-Fu	National Chung Hsing University	Taiwan	lcf0201@dragon.nchu.edu.tw	PA-46
Liao	Jian	Chengdu Institute of Biology	China	jliao@cib.ac.cn	PA-25
Liao	hsuan-hung	National Sun Yat-sen University	Taiwan	hsuan-hung.liao@mail.nsysu.edu.tw	PA-22
Lim	Hyun-Suk	Pohang University of Science and Technology	Korea	hslim@postech.ac.kr	PA-30
Lin	Cheng-Kun	National Chung Hsing University	Taiwan	cklin93@nchu.edu.tw	PA-45
Lu	Qingquan	Wuhan University	China	gci2011@whu.edu.cn	PB-11
Masuda	Yusuke	Hokkaido University	Japan	ymasuda@sci.hokudai.ac.jp	IL-2
Matsuda	Yudai	City University of Hong Kong	Hong Kong	ymatsuda@cityu.edu.hk	PA-5
Meng	Lingkui	Huazhong University of Science and Technology	China	menglk@hust.edu.cn	PB-21
Min	Sun-Joon	Hanyang University	Korea	sjmin@hanyang.ac.kr	IL-19
Miura	Tomoya	Okayama University	Japan	tmiura@okayama-u.ac.jp	PB-41
Ngamnithiporn	Aurapat	Chulabhorn Research Institute	Thailand	aurapat@cri.or.th	PA-11
Nishikata	Takashi	Yamaguchi University	Japan	nisikata@yamaguchi-u.ac.jp	PB-50

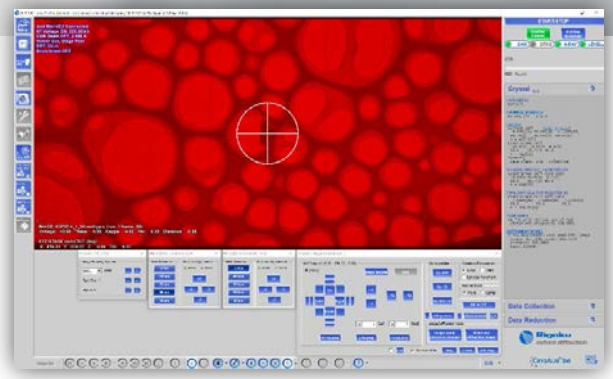
Ogura	Yusuke	The University of Tokyo	Japan	ayskogura@g.ecc.u-tokyo.ac.jp	PA-50
Othman	Rozana	University of Malaya	Malaysia	rozanaothman@um.edu.my	PA-31
Padungros	Panuwat	Chulalongkorn University	Thailand	Panuwat.P@chula.ac.th	PB-30
Pradipta	Ambara R.	Tokyo Institute of Technology	Japan	pradipta.a.aa@m.titech.ac.jp	PB-4
Quan	Yangjian	The Hong Kong University of Science and Technology	Hong Kong	chyjquan@ust.hk	PB-5
Rhee	Young Ho	Pohang University of Science and Technology	Korea	yhrhee@postech.ac.kr	PA-29
Ryu	Do Hyun	Sungkyunkwan University	Korea	dhryu@skku.edu	PA-17
Saaidin	Aimi Suhaily	Universiti Teknologi MARA	Malaysia	aimisuhaily@uitm.edu.m	IL-5
Semba	Kazuhiko	Kyoto University	Japan	semba.kazuhiko.5n@kyoto-u.ac.jp	PB-24
Shao	Zhihui	Yunnan University	China	zhihui_shao@hotmail.com	PA-37
Shao	Xiang-Feng	Lanzhou University	China	shaoxf@lzu.edu.cn	PB-31
Shen	Xiao	Wuhan University	China	xiaoshen@whu.edu.cn	PB-12
Shirakawa	Seiji	Nagasaki University	Japan	seijishirakawa@nagasaki-u.ac.jp	PB-47
Shu	Xing-Zhong	Lanzhou University	China	shuxingzh@lzu.edu.cn	IL-17
Sittihan	Satapanawat	Chulabhorn Graduate Institute	Thailand	satapanawat@cgi.ac.th	IL-7
So	Cheuk Wai	Nanyang Technological University	Singapore	CWSo@ntu.edu.sg	IL-16
Songthammawat	Poramate	Chulabhorn Research Institute	Thailand	poramate@cri.or.th	PA-23
Soo	Han Sen	Nanyang Technological University	Singapore	hansen@ntu.edu.sg	PB-28
Tokuyama	Hidetoshi	Tohoku University	Japan	hidetoshi.tokuyama.d4@tohoku.ac.jp	PA-14
Tong	Shuo	Tsinghua University	China	tongshuo@mail.tsinghua.edu.cn	PA-48
Tsai	Cheng-Che	Tunghai University	Taiwan	chengchetsai@thu.edu.tw	PB-29
Tsui	Gavin Chit	the Chinese University of Hong Kong	Hong Kong	gctsui@cuhk.edu.hk	PA-16
Ueda	Yoshihiro	Kyoto University	Japan	ueda.yoshihiro.4z@kyoto-u.ac.jp	PB-23
Uyanik	Muhammet	Nagoya University	Japan	muha@chembio.nagoya-u.ac.jp	PB-14

Wang	Cheng-Chung	Academia Sinica	Taiwan	wangcc@chem.sinica.edu.tw	IL-12
Wang	Tsung-Shing Andrew	National Taiwan University	Taiwan	wangts@ntu.edu.tw	PA-10
Wang	Sheng-Kai	National Tsing-Hua University	Taiwan	skwang@mx.nthu.edu.tw	PA-34
Wang	Ying	the Chinese University of Hong Kong	Hong Kong	ying.b.wang@cuhk.edu.hk	PA-28
Wang	Jun	Hong Kong Baptist University	Hong Kong	junwang@hkbu.edu.hk	PB-15
Wu	Jie	National University of Singapore	Singapore	chmjie@nus.edu.sg	PA-9
Wu	Yen-Ku	National Yang Ming Chiao Tung University	Taiwan	yenkuwu@nycu.edu.tw	IL-8
Xu	Xing-Fang	Sun Yat-Sen University	China	xuxinfang@mail.sysu.edu.cn	PA-2
Xu	Zhengren	Peking University	China	zhengrenxu@bjmu.edu.cn	PA-47
Yamada	Yoichi M. A.	Institute of Physical and Chemical Research	Japan	ymayamada@riken.jp	PB-40
Yamashina	Masahiro	Tokyo Institute of Technology	Japan	yamashina@chem.titech.ac.jp	PB-3
Yamashita	Makoto	Nagoya University	Japan	makoto@oec.chembio.nagoya-u.ac.jp	IL-22
Yang	Jung Woon	Sungkyunkwan University	Korea	jwyang@skku.edu	PB-42
Yang	Yurong	Kunming Institute of Botony	China	yangyurong@mail.kib.ac.cn	PA-24
Yang	Jin-Dong	Tsinghua University	China	jdyang@mail.tsinghua.edu.cn	PB-1
Yin	Guoyin	Wuhan University	China	yinguoyin@whu.edu.cn	IL-15
Yokoshima	Satoshi	Nagoya University	Japan	yokosima@ps.nagoya-u.ac.jp	PA-39
Yoshida	Yasushi	Chiba University	Japan	yoshiday@chiba-u.jp	PA-26
Yu	Ching-Ching	National Chung Cheng University	Taiwan	checcyu@ccu.edu.tw	PA-21
Yuan	Qiao	Nanyang Technological University	Singapore	yuan.qiao@ntu.edu.sg	PB-36
Yun	Jaesook	Sungkyunkwan University	Korea	jaesook@skku.edu	PA-18
Yurino	Taiga	Hokkaido University	Japan	tyurino@eng.hokudai.ac.jp	PA-4
Zhao	Yu	National University of Singapore	Singapore	zhaoyu@nus.edu.sg	PA-32
Zhao	Wanxiang	Hunan University	China	zhaowanxiang@hnu.edu.cn	PB-22

Zhao	Yu-Ming	Shaanxi Normal University	China	ymzhao@snnu.edu.cn	PB-39
Zhou	Jian-Rong	Peking University Shenzhen Graduate School	China	jrzhou@pku.edu.cn	PA-12
Zhu	Ye	National University of Singapore	Singapore	chmzhu@nus.edu.sg	PA-44
Zhu	Shi-Fa	South China University of Technology	China	zhusf@scut.edu.cn	PA-13
Zhu	Rong	Peking University	China	rongzhu@pku.edu.cn	PB-2

INTRODUCING OUR NEW ELECTRON DIFFRACTOMETER:
XtaLAB Synergy-ED

- HyPix technology inside
- CrysAlis^{Pro} for easy instrument control and data processing
- Study submicron samples with ease



Fully controllable from CrysAlis^{Pro}: find, center and collect data on samples with our intuitive control and data processing software.

Features a Rigaku HyPix detector for high-quality electron diffraction data.

We wanted to lower the barrier to entry to the emerging field of single-crystal electron diffraction, so we joined forces with JEOL to bring the expertise of both companies to one fantastic product.

With JEOL's expertise in generation and control of electron beams and Rigaku's expertise in HPC detectors and crystallographic software, we bring you our new electron diffractometer, the XtaLAB Synergy-ED.

Rigaku | JEOL

© 2022 Rigaku Corporation and its Global Subsidiaries. All rights reserved | info@rigaku.com | rigaku.com

SHIMADZU
Excellence in Science

Liquid Chromatograph Mass Spectrometer

LCMS-2050

SIMPLY EFFORTLESS

The LCMS-2050 provides both high speed and high sensitivity analysis even in a small design. We have achieved the utmost in both miniaturization and high performance with Shimadzu's technology cultivated over many years of MS development. A single platform, a single solution for LC detection, the LCMS-2050 has the power to deliver better results with incredible simplicity and unparalleled robustness. It may be small but the design and capability of the new single quadrupole LC/MS will change the productivity of any analytical laboratory.

Seamless integration with LC by design

Superior detection for added confidence

Streamlined operation for cost efficiency

Configuration example with Nexera series

www.shimadzu.com

Learn more about LCMS-2050