Academic Program [Oral A] | 10. Organic Chemistry -Organometallic Compounds-：Oral A

Wed. Mar 26, 2025 3:55 PM - 5:15 PM JST | Wed. Mar 26, 2025 6:55 AM - 8:15 AM UTC
[F]2101(2101, Bldg. 2, Area 4 [1F])

[[F]2101-1vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takashi Kurogi, Yoichiro Kuninobu

English
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[[F]2101-1vn-01]
Cobalt-catalyzed C-H borylation of simple arenes activated through π-coordination

○Akash Tathe[1], Yuichiro Mutoh[1], Laurean Ilies[1] (1. RIKEN Center for sustainable resource science)

English
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[[F]2101-1vn-02]
One-pot Synthesis of Azo Compounds from Nitroarenes Using a Cobalt Catalyst Bearing a Tetradentate PNNP Ligand

○HENG ZHANG[1], Yumiko Nakajima[1,2] (1. Institute of Science Tokyo, 2. National Institute of Advanced Industrial Science and Technology)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[[F]2101-1vn-03]
Hydrogen Bond-Controlled Site-selective C–H Borylation at the Remote-Position of Naphthalene Derivatives

○Lu Xu[1], Genki YOSHINO[1], Shiho INOMATA[1], Yoichiro KUNINOBU[1] (1. Kyushu University)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[[F]2101-1vn-04]
Rhodium/Chiral Diene-Catalyzed Stereoselective 1,4-Addition of Arylboron Compounds to Glycals Derivatives

○Akimasa Takahashi[1], Nishimura Takahiro[1] (1. Osaka Metropolitan University)

4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
Break

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[[F]2101-1vn-05]
Iridium-Catalyzed Linear Selective Addition of C–H Bond of Glycals to Terminal Alkenes

○Motoki Tatara[1], Katsumasa Tanaka[1], Takahiro Nishimura[1] (1. Osaka Metropolitan University)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[[F]2101-1vn-06]
Iridium-Catalyzed Enantioselective Allylation of α-Ketoesters and α-Diketones

Natsuki Suzuki[1], Kana Takahashi[1], Yuta Goto[1], Kazunori Miyashita[1], Takahiro Sawano[2], ○Ryo Takeuchi[1] (1. Aoyama Gakuin University, 2. Shimane University)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[[F]2101-1vn-07]

γ-heteroarylation of α,β-unsaturated amides via isomerization of alkene moiety

○Shoki Asai[1], Hirotsgu Suzuki[1] (1. University of fukui)

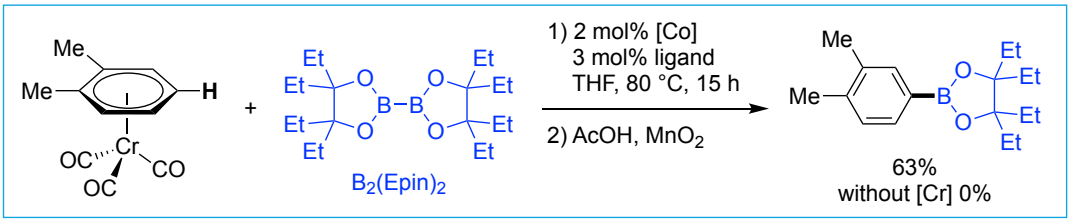
Cobalt-catalyzed C–H Borylation of Simple Arenes Activated through π-Coordination

([1]*RIKEN Center for Sustainable Resource Science*) ○Akash Tathe,[1] Yuichiro Mutoh,[1] Laurean Ilies[1]

Keywords: Cobalt catalyst; C–H activation; Borylation; π-coordination; Arenes

Direct C–H functionalization of an organic substrate has the potential to streamline organic synthesis, but reactive or toxic, expensive metal complexes and sophisticated ligands are often required. To introduce a new and more general approach, we focused on π-coordination strategy for the C–H activation and functionalization of simple arenes. This strategy relies on π-coordination of an arene substrate to a metal center such as chromium, which decreases the electron density on the arene and facilitates oxidative addition and C–H activation process.[1] We demonstrated this strategy for the cobalt-catalyzed C–H borylation[2] of electron-neutral and rich simple arenes under mild reaction conditions. Thus, the reaction of a preactivated simple arene, for example an *o*-xylene chromium complex with $B_2(Epin)_2$ in the presence of 2 mol% cobalt catalyst and 3 mol% terpyridine ligand in THF at 80 ºC for 15 h provided the borylated arene in 63% yield after demetallation (Scheme 1). Notably, without coordination to chromium, *o*-xylene did not react at all under these reaction conditions, highlighting the importance of activation through π-coordination.

This research is a part of our efforts in using the π-coordination strategy for the activation of strong bonds for organic synthesis, for example the use of chloroarenes as substrates for radical coupling reactions.[3]



Scheme 1: Cobalt-catalyzed borylation of arenes

1) J. W. Walton, L. A. Wilkinson, *Organomet. Chem*. **2019**, *42*, 125–171.
2) N. G. Leónard, M. J. Bezdek, P. J.Chirik, *Organometallics* **2017**, *36*, 142−150.
3) M. Nagata, K. Itonaga, Y. Mutoh, K. Endo, L. Ilies, *Chem. Lett*. **2024**, 53, upae233.

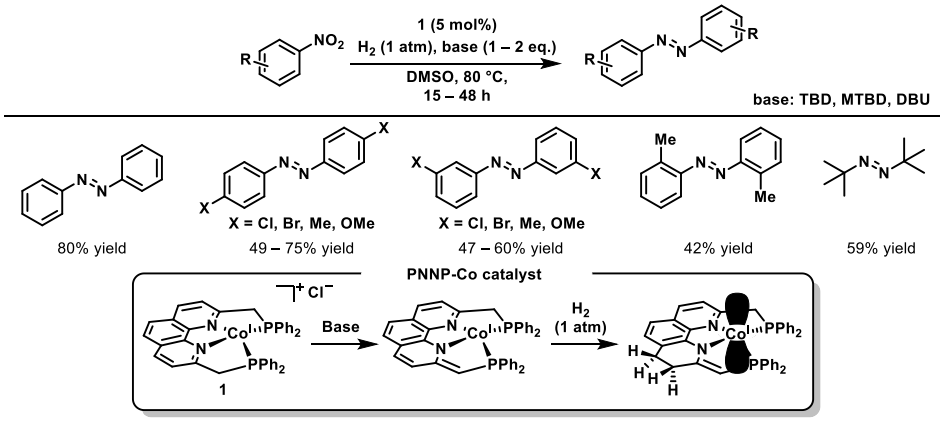
One-pot Synthesis of Azo Compounds from Nitroarenes Using a Cobalt Catalyst Bearing a Tetradentate PNNP Ligand

([1]*Graduate School of Materials and Chemical Technology, Institute of Science Tokyo*, [2]*National Institute of Advanced Industrial Science and Technology*) ○ Heng Zhang,[1] Yumiko Nakajima[1,2]

Keywords: Azo Compounds; Reduction; Cobalt(I); Tetradentate Phenanthroline-based PNNP Ligand

Aromatic azo compounds are important chemicals widely used in chemical industry as organic dyes, colorants, pigments and therapeutic agents. Traditional syntheses of aromatic azo compounds mainly depend on diazonium coupling reaction. However, this method needs a complicated reaction protocol, produces explosive intermediates, and generates large amounts of inorganic wastes. An attracting alternative approach is direct synthesis of aromatic azo compounds from nitroarenes, although precedent methods often demand excessive amounts of reductants or using noble metal catalyst.[1]

In this study, we revealed that direct synthesis of aromatic azo compounds from nitroarenes could be achieved using PNNP-cobalt catalyst bearing a phenanthroline-based PNNP ligand (2,9-bis-((diphenylphosphanyl)methyl)-1,10-phenanthroline). The PNNP-cobalt catalyst can activate 1 atm H_2 and at the same time bears electron-rich cobalt(I) center, which efficiently conducts charge electron to substrates.[2] The properties enable the production of various azobenzene derivatives using H_2 as a reductant at 80 °C without the need for sacrificial reagents. The method was applicable for halogenated azobenzenes from 47 to 70% yields, which are important synthetic building blocks. In addition, 2,2'-dimethylazobenzene and aliphatic azo compounds, which are difficult to be synthesized *via* conventional diazonium coupling reaction, are successfully synthesized in 42% and 59% yields.



1) E. Merino, *Chem. Soc. Rev.* **2011**, *40*, 3835. 2) a) N.-Y. Jheng, Y. Ishizaka, Y. Naganawa, A. Sekiguchi, Y. Nakajima, *Dalton Trans.* **2020**, *49*, 14592. b) N.-Y. Jheng, Y. Ishizaka, Y. Naganawa, Y. Minami, A. Sekiguchi, K. Iizuka, Y. Nakajima, *ACS Catal.* **2022**, *12*, 2320.

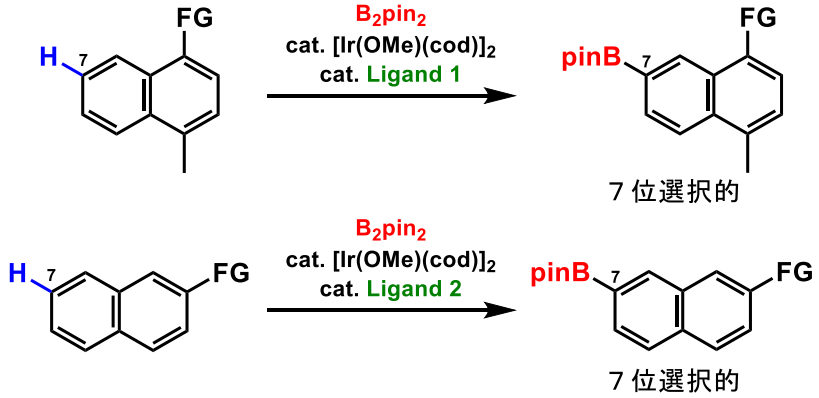
水素結合によるナフタレン誘導体の遠隔位における位置選択的なC–H ホウ素化反応の開発

(九大先導研[1]、九大院総理工[2]) ○盧 旭[2]、吉野 元規[2]、猪股 志帆[2]、國信 洋一郎[1,2]
(*[1]Institute for Materials Chemistry and Engineering, Kyushu University; [2]Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Xu Lu,[2] Genki Yoshino,[2] Shiho Inomata,[2] Yoichiro Kuninobu[1,2]

We succeeded in the development of site-selective C–H borylation at the remote position (7-position) of naphthalene derivatives controlled by hydrogen bond between the substrate recognition site of the catalyst and the functional group of substrates. By changing the catalysts, the site-selective remote C–H borylation can be achieved using naphthalene derivatives with the functional group at different positions (1- and 2-positions).
Keywords: Hydrogen Bonding; Remote-Position; Site-selectivity; C–H Borylation; C–H Transformation

芳香族化合物の遠隔位での位置選択的な C–H 変換反応の開発は困難であり、特に多環式芳香族化合物の遠隔位での位置選択的な C–H 変換反応の報告例はほとんどない。今回我々は、独自に開発した配位子を有するイリジウム触媒を利用することで、１位に官能基を有するナフタレン誘導体の７位選択的な C–H ボリル化反応の開発に成功した（Scheme 1）。また、別の構造を有する配位子を有するイリジウム触媒を用いることで、２位に官能基を有するナフタレン誘導体の７位選択的に C–H ボリル化反応が進行することも併せて見出した（Scheme 1）。本反応では、水素結合供与部位を有する触媒と基質の官能基（水素結合受容体）との間に働く水素結合により、高い位置選択性が発現したものと考えている。

Scheme 1. ナフタレン誘導体の遠隔位での位置選択的なC–Hホウ素化反応

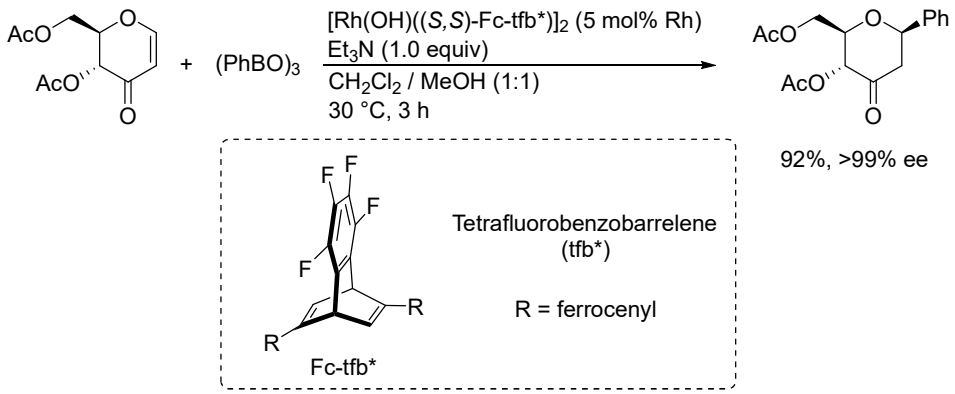


ロジウム/キラルジエン触媒を用いたアリールホウ素化合物のグリカール誘導体への立体選択的 1,4-付加反応

（阪公大院理）○高橋 明雅・西村 貴洋
Rhodium/Chiral Diene-Catalyzed Stereoselective 1,4-Addition of Arylboron Compounds to Glycals Derivatives (*Graduate School of Science, Osaka Metropolitan University*) ○Akimasa Takahashi, Takahiro Nishimura

C-Glycosyl arenes refer to sugar derivatives, whose sugar moiety is connected to an aromatic ring at the anomeric position via a stable carbon-carbon bond, and the structural motif is important in organic chemistry, medicinal chemistry, and natural product synthesis. Two isomers, α- and β-forms, are available for the *C*-glycosyl arenes based on the stereoconfiguration at the anomeric position. There have been several reports on the stereoselective synthesis of α-*C*-glycosyl arenes based on the substrate specificity from glycals, which have a characteristic C–C double bond between C1 and C2 in their cyclic form. In contrast, direct transformation of glycals into β-*C*-glycosyl arenes is quite limited. Here we report rhodium/chiral diene-catalyzed stereoselective 1,4-addition of arylboron compounds to glycals derivatives. We succeeded in the synthesis of the β-*C*-glycosyl arenes by use of the chiral diene ligand having an appropriate absolute configuration.
Keywords : Rhodium; 1,4-Addition; Glycal

C-グリコシルアレーンは、糖部分が安定な炭素-炭素結合によってアノマー位で芳香環に結合した糖誘導体であり、その構造モチーフは有機化学、医薬化学、天然物合成において重要である。*C*-グリコシルアレーンには、アノマー位の立体配座に基づくα体とβ体の 2 つの異性体が存在する。α-*C*-グリコシルアレーンの合成については、C1-C2 間に炭素-炭素二重結合を持つ不飽和糖であるグリカールから、その基質特異性に基づく立体選択的合成の報告がいくつかある。一方、グリカールから β-*C*-グリコシルアレーンへの直接変換は極めて限られている。本講演では、ロジウム/キラルジエン触媒を用いたアリールボロン化合物のグリカール誘導体への立体選択的 1,4-付加反応についてのべる。適切な絶対配置を持つキラルジエン配位子を用いることで、様々なアリール基を持つ β-C-グリコシルアレーンの合成に成功した。



イリジウム触媒を用いたグリカール C–H 結合の直鎖選択的アルキル化反応

(阪公大院理)○多田羅 元暉、田中 克昌、西村 貴洋

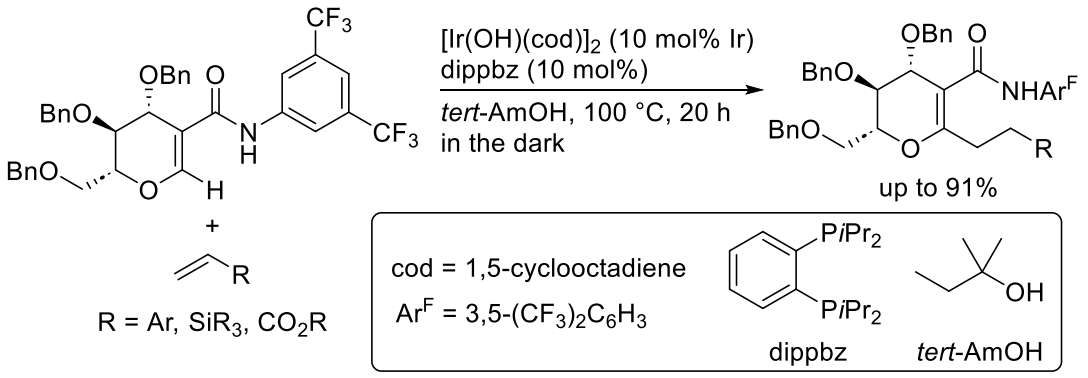
Iridium-Catalyzed Linear Selective Addition of C–H Bond of Glycals to Terminal Alkenes

(*Graduate School of Science, Osaka Metropolitan University*) ○Motoki Tatara, Katsumasa Tanaka, Takahiro Nishimura

C-glycoside compounds, which have a glycosidic linkage structure with the oxygen replaced by carbon, are generally resistant to hydrolysis from acids and enzymes. *C*-glycoside compounds are applied as medicines like diabetes drugs, and there has been much interest in the development of efficient synthesis of *C*-glycoside compounds. One of the methods of anomeric C–H bond functionalization is the direct transformation of the C–H to a C–C bond of glycals. Although arylation and alkenylation by using transition-metal catalysts have been reported, linear-selective alkylation by use of alkenes as coupling partner has been underdeveloped. Here we report that a hydroxoiridium(I) catalyst coordinated with diphosphine ligand can catalyze the direct C–H alkylation of glycals, which have an amide group, with terminal alkenes. The reaction proceeded with high linear selectivity to give the corresponding adducts in high yields.

Keywords : Iridium; C–H Activation; Alkylation; Glycal

酸素が炭素に置き換わったグリコシド結合構造を持つ *C*-グリコシド化合物は、一般に酸や酵素による加水分解を受けにくい。*C*-グリコシド化合物は糖尿病治療薬などの医薬品として応用されており、*C*-グリコシド化合物の効率的な合成法の開発が注目されている。アノマー位 C–H 結合の官能基化法の一つとして、グリカールの C–H 結合を C–C 結合に直接変換する方法があげられる。遷移金属触媒を用いたグリカールのアリール化やアルケニル化は報告されているが、アルケンをカップリングパートナーとして用いた直鎖選択的アルキル化は未開発であった。本講演では、ジホスフィン配位子をもつヒドロキソイリジウム(I)触媒を用いた、アミド基を有するグリカールの末端アルケンによる直鎖選択的 C–H アルキル化について述べる。



日本化学会 第105春季年会 (2025)

イリジウム触媒によるα−ケトエステルおよびα−ジケトンのエナンチオ選択的アリル化反応

（青山学院大理工[1]・島根大材エネ[2]）鈴木 菜月[1]・高橋 奏[1]・後藤 祐汰[1]・宮下 和典[1]・澤野 卓大[2]・○武内 亮[1]

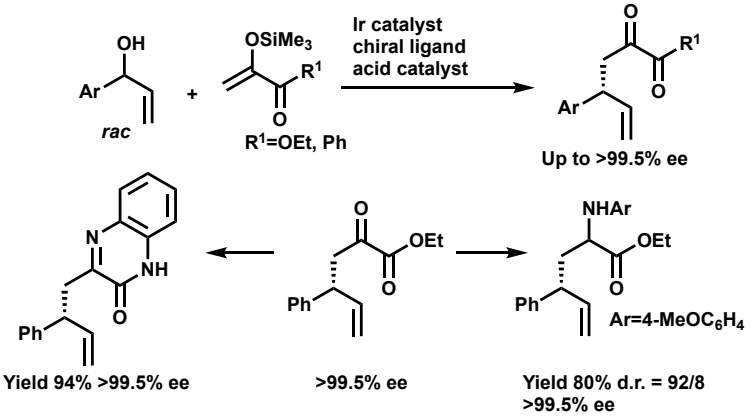
Iridium-Catalyzed Enantioselective Allylation of α-Ketoesters and α-Diketones

([1] *Faculty of Science and Engineering, Aoyama Gakuin University*, [2] *Faculty of Materials for Energy, Shimane University*) Natsuki Suzuki,[1] Kana Takahashi,[1] Yuta Goto,[1] Kazunori Miyashita,[1] Takahiro Sawano,[2] Ryo Takeuchi[1]

Enantioselective allylation of carbonyl compounds has been extensively studied in asymmetric synthesis. However, enantioselective allylation of 1,2-dicarbonyl compounds has not been studied. We wish to report enantioselective allylation of α-ketoesters and α-diketones with racemic secondary allylic alcohols by the cooperative effect of an iridium/chiral phosphoramidite catalyst and an acid catalyst. The product could be transformed to synthetically useful compounds such as chiral heterocycles or a chiral α-amino acid without a loss of optical purity.

Keywords : Iridium Catalysis; Enantioselective Allylation; α-Ketoester; α-Diketone; Phosphoramidite Ligand

イリジウム触媒による不斉アリル化反応は、精力的に研究されている[1)]。カルボニル化合物を炭素求核剤とする不斉アリル化反応はこれまで研究されてきたが、α-ヒドロキシ酸や α-アミノ酸などの有用な化合物へ変換可能な 1,2-ジカルボニル化合物を炭素求核剤とする不斉アリル化反応は未だ達成されていない。本発表では、イリジウム/キラルホスホラアミダイト触媒と酸触媒による協働作用によってα-ケトエステルやα-ジケトンのエナンチオ選択的アリル化反応が進行し、高収率かつ高エナンチオ選択的に生成物が得られること見出したので、報告する。これら光学活性生成物を光学活性複素環化合物や光学活性α-アミノ酸誘導体に導いた。これらの過程でラセミ化は全く進行しなかった。



1) Review on Ir-catalyzed allylation; T. Sawano, R. Takeuchi *Catal. Sci. Tech.* **2022**, *12*, 4100.

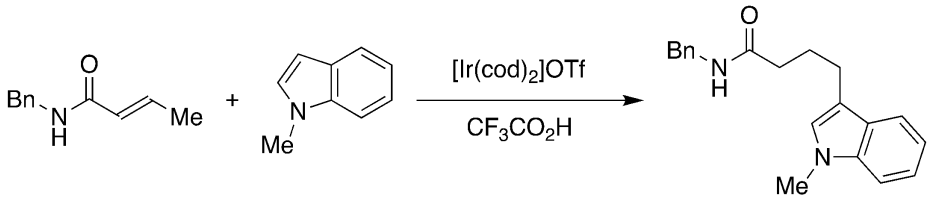
イリジウム触媒によるα,β-不飽和アミドに対するγ位選択的ヘテロアリール化

（福井大工）・○浅井 翔喜・鈴木 弘嗣
Iridium-Catalyzed γ-Heteroarylation of α,β-Unsaturated Amides (*School of Engineering, University of Fukui*)○Shoki Asai, Hirotsugu Suzuki

α,β-Unsaturated carbonyl compounds are widely recognized as key intermediates in synthetic organic chemistry due to their versatile reactivity. These compounds generally undergo a nucleophilic addition at the β-position (1,4-addition reactions), which is the most electrophilic site on the alkene moiety. In contrast, γ-selective addition reactions remain underexplored, with only a single reported example to date. In this study, we proposed a novel approach for γ-selective addition, involving isomerization of the alkene moiety followed by γ-selective heteroarylation under redox-neutral reaction conditions. Herein, we successfully developed a γ-selective addition reaction of indoles to α,β-unsaturated carbonyl compounds with the assistance of a carboxamide directing group. The preliminary mechanistic investigations revealed that the reaction proceeds via the isomerization of the alkene moiety, enabling the γ-selective addition.
Keywords: *Iridium; Hereroaryl; α,β-Unsaturated Carbonyl Compounds*

α,β-不飽和カルボニル化合物は、有機合成化学において重要な合成中間体として広く認知され、古くから分子骨格の構築に利用されてきた。これらの化合物はアルケン部位の電子的偏りにより、主にβ位への求核付加反応（1,4-付加反応）を経て変換されてきた。一方で、γ位選択的な付加反応についてはほとんど研究が進んでおらず、これまでに一例が報告されているのみである[1]。そこで本研究では、α,β-不飽和カルボニル化合物のアルケン部位を異性化させた後に、γ位選択的なヘテロアリール化を行う連続的な反応プロセスに着目し、酸化還元中性条件下でのγ位選択的付加反応の実現を目指した。

実際に、カルボン酸アミドを単座配向基とする2-ブテン酸アミドに対して、1-メチルインドールをイリジウム触媒とBrønsted酸触媒の共存下で作用させると、高いγ位選択性で目的物が得られることを明らかにした。



1) Wang, Z.-X.; Bai, X.-Y.; Yao, H.-C.; Li, B.-J. *J. Am. Chem. Soc.* **2016**, 138, 14872.