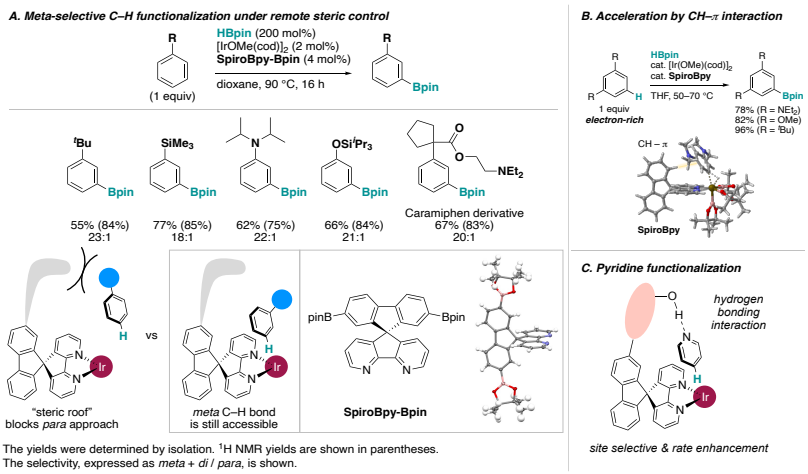
Spirobipyridine Ligands for Molecular Recognition and Selective Catalysis via Noncovalent Interactions

Sobi Asako

RIKEN Center for Sustainable Resource Science
E-mail: sobi.asako@riken.jp

We present our recent efforts toward the development of efficient and selective catalysis based on spirobipyridine (**SpiroBpy**) ligands, which are three-dimensionally extended analogues of conventional planar bipyridines. Our first design in this category is the conceptually novel ligand **SpiroBpy-Bpin**,[1] which sterically protects the furthest *para* site in addition to the *ortho* site, enabling *meta*-selective C–H activation in iridium-catalyzed borylation. The rigid Bpin group attached to **SpiroBpy** functions as a "remote steric roof", creating a molecular pocket that accommodates substrate approaching the metal center exclusively in the *meta* orientation. Further investigations revealed that the iridium/**SpiroBpy** catalyst also accelerates C–H borylation reactions.[2] We identified a CH–π interaction between the ligand backbone and the arene substrate as the key contributor in this enhanced reactivity. More recently, we developed **SpiroBpy** ligands bearing hydroxy groups as substrate recognition units, enabling control over selectivity and reactivity in the functionalization of pyridines and quinolines.[3] We anticipate that **SpiroBpy** derivatives, capable of recognizing substrates through noncovalent interactions, will serve as versatile ligands in transition metal catalysis and provide solutions to challenges that remain unresolved with conventional planar bipyridines.[4]



The yields were determined by isolation. ^{1}H NMR yields are shown in parentheses.
The selectivity, expressed as *meta* + *di* / *para*, is shown.

References

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2. Jin, Y.; Ramadoss, B.; Asako, S.; Ilies, L. *Nat. Commun.* **2024**, *15*, 2886.
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Sobi Asako

Affiliation
RIKEN Center for Sustainable Resource Science
2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Education
2011 – 2014 D. Sc., The University of Tokyo (Prof. Eiichi Nakamura)
2009 – 2011 M. Sc., The University of Tokyo (Prof. Eiichi Nakamura)
2005 – 2009 B. Sc., The University of Tokyo (Prof. Eiichi Nakamura)

Professional Career
2021 – present: Visiting Researcher, Okinawa Institute of Science and Technology Graduate University
2019 – present: Senior Scientist, RIKEN Center for Sustainable Resource Science
2014 – 2019: Assistant Professor, Okayama University
2011 – 2014: Research Fellow (JSPS, DC1), Japan Society for the Promotion of Science

Awards and Honors
- The Chemical Society of Japan Award for Young Chemists, 2023
- Thieme Chemistry Journals Award, 2023
- RIKEN BAIHO Award (RIKEN Excellent Achievement Award), 2023
- JSPC award, the Japanese Society for Process Chemistry, 2021
- Synthetic Organic Chemistry Award (Technology), The Society of Synthetic Organic Chemistry, Japan, 2020
- Young Scholar Lectures of Chemical Society of Japan, 2020

Selected Publications
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