



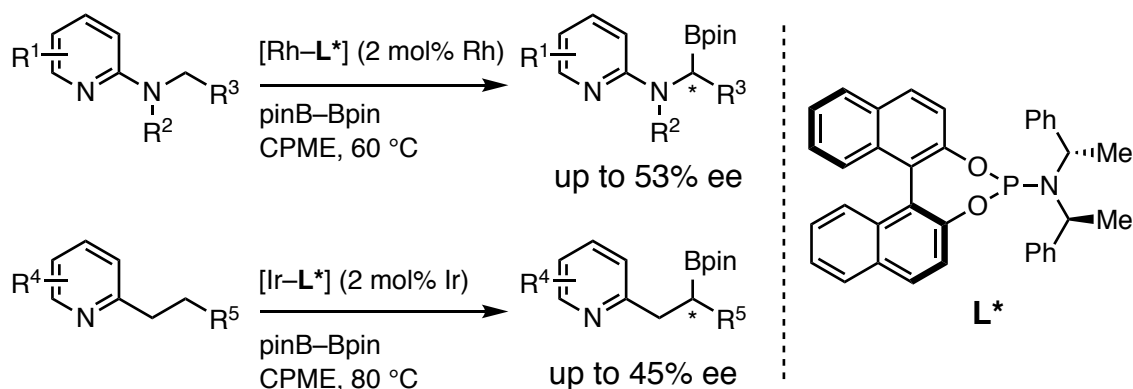
## Catalytic Enantioselective C(sp<sup>3</sup>)-H Borylation Reactions using Chiral Monophosphine Ligands

Ronald L. Reyes, Tomoya Harada, Tomohiro Iwai, and Masaya Sawamura  
(Department of Chemistry, Faculty of Science, Hokkaido University)

C-H bond activation strategies in transition metal catalysis have become one of the most straightforward and powerful tools in organic synthesis. While there has been a significant progress in the direct transformation of C(sp<sup>2</sup>)-H bonds, the functionalization of the C(sp<sup>3</sup>)-H bonds remains challenging due to both the absence of  $\pi$ -orbitals that can interact with a transition metal and the sterically demanding nature of C(sp<sup>3</sup>)-H bonds compared to planar C(sp<sup>2</sup>)-H bonds. Moreover, enantioselective C(sp<sup>3</sup>)-H functionalization contributing to an efficient access to optically active molecules is underdeveloped.

Recently, our group described a heteroatom-directed borylation of C(sp<sup>3</sup>)-H bonds with Rh- or Ir-catalyst systems based on immobilized, silica-supported bridgehead monophosphine, such as Silica-SMAP and Silica-TRIP.<sup>1,2</sup> This strategy allowed site-selective borylation of the *N*-adjacent or unactivated C(sp<sup>3</sup>)-H bonds located  $\gamma$  to N or O atoms on the directing groups due to the proximity effect by the heteroatom-to-metal coordination. Along these lines, we found that several soluble monophosphine ligands also promoted these transformations.

This presentation reports the Rh- or Ir-catalyzed site-selective C(sp<sup>3</sup>)-H borylation of 2-aminopyridines and 2-alkylpyridines providing an innovative example of a homogenous catalytic system using commercially available chiral monophosphine ligands such as BINOL-based phosphoramidite **L\***. The utility of this method allows the direct synthesis of enantioenriched alkylboronates.



### <参考文献>

- 1) Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 12924.
- 2) Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2013**, *135*, 2947.

### 発表者紹介

氏名 Ronald L. Reyes (ロナルド・ラズ・レイス)  
 所属 Graduate School of Chemical Sciences and Engineering  
 Hokkaido University  
 学年 D2  
 研究室 Organometallic Chemistry Laboratory

