

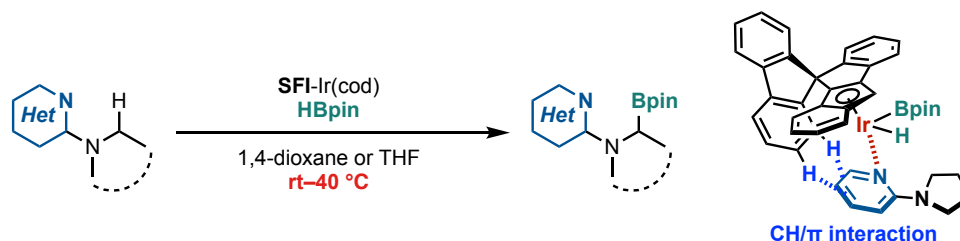
Spiro-Fluorene-Indenoindenyl-Ir(I)-Catalyzed, Nitrogen-Directed C(sp³)-H and C(sp²)-H Borylation

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Transition-metal catalyzed C–H borylation is an attractive strategy for synthesizing organoboron compounds. Starting with the pioneering works by Hartwig,¹ various transition metal catalysts have been developed for the non-directed C(sp³)-H borylation. In these catalytic systems, regioselectivity is controlled by the steric hindrance, and the primary C–H bonds are preferentially borylated. On the other hand, directing groups determines the regioselectivity by the distance to it, allowing the borylation of the sterically hindered C–H bonds. In 2012, Sawamura developed the silica-supported monophosphine-Rh² or Ir³ catalytic systems for nitrogen- or oxygen-directed C(sp³)-H borylation. These catalytic systems were applicable for broad substrates, but the borylation required high temperatures (up to 100 °C). From this report, the C(sp³)-H borylation has been developed by many research groups, but borylation still requires high temperature or light irradiation. Thus, a new catalytic system to facilitate the C(sp³)-H borylation under mild conditions is highly desired.

Herein we have synthesized the spiro-fluorene-indenoindenyl Iridium (SFI-Ir) catalyst as the highly active catalyst for the C–H borylation. The SFI-Ir(I) catalyst facilitated the nitrogen-directed C(sp³)-H borylation of 2-pyrrolidinopyridine derivatives to afford the corresponding alkylboronates with excellent yields. This catalytic system was applicable for broad cyclic amines such as azepane, morpholine, and piperidine. Besides these substrates, the SFI-Ir(I) catalyst showed high catalytic activity for the C(sp²)-H borylation of sterically demanding and less coordinative benzylamine derivatives at room temperature. To gain insights into the reaction mechanism, we performed experimental and theoretical mechanistic studies. The series of mechanistic studies indicated the CH/ π interactions between the C–H on the fluorene moiety and the π system of the substrate accelerated the nitrogen-directed C–H borylation.



- 1) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, 287, 1995.
- 2) Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, 134, 12924.
- 3) Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2013**, 135, 2947.
- 4) Inoue, T.; Sato, Y.; Nagashima, Y.; Tanaka, K. *ACS Catal.* **2025**, 15, in press.