

# Iron-Catalyzed C(sp<sup>3</sup>)–H Bond Activation/C–C Bond Formation through Hydrogen Atom Transfer: Remarkable Effect of Fluorinated Solvents in Chemical Yield

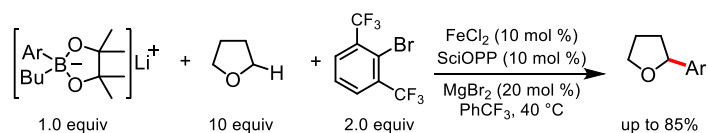
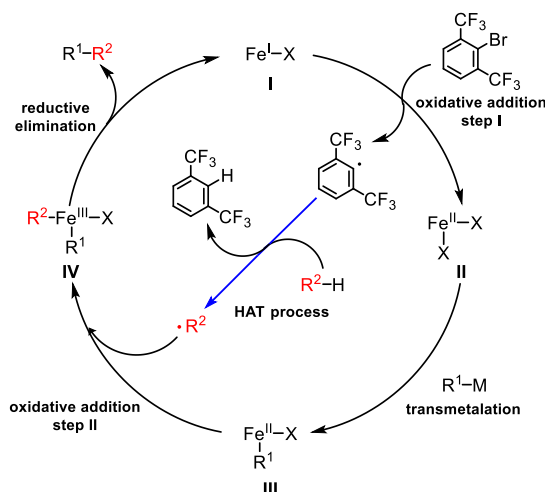
(<sup>1</sup>*Institute for Chemical Research, Kyoto University*, <sup>2</sup>*Graduate School of Engineering, Kyoto University*) ○Litian Chen,<sup>1,2</sup> Takahiro Doba,<sup>1,2</sup> Masaharu Nakamura<sup>1,2</sup>

**Keywords:** Iron Catalysis; C–H Activation; C–C Cross-Coupling; Hydrogen Atom Transfer; Radical Exchange

Functionalization of C(sp<sup>3</sup>)–H bonds is a useful but challenging tool in synthetic chemistry. A number of techniques such as directing group strategy<sup>1</sup> or hydrogen atom transfer (HAT)<sup>2</sup> strategy have been developed in the past few decades. However, these techniques require preinstalled directing group or irradiation of light with a certain energy to generate active radicals, respectively. Herein we report iron-catalyzed intermolecular cross-coupling of C(sp<sup>3</sup>)–H substrates with aryl boronates by merging Fe(II)/SciOPP catalytic system<sup>3</sup> with a HAT strategy.

In our previous studies using mesityl iodide as a sacrificial oxidant (HAT reagents) and *i*-Pr<sub>2</sub>O as a solvent, we obtained a promising result of 46% yield of the C(sp<sup>3</sup>)–H arylation product. After further attempts, we found that the fluorinated HAT reagents and solvents significantly improve the yield. The HAT reagent 2,6-bis(trifluoromethyl)bromobenzene<sup>4</sup> showed the best reactivity as high as 85% NMR yield. Unfortunately, due to the low molecular weight of the final products, unignorable loss happened during isolation. Besides, substrates other than THF showed lower reactivity toward this HAT reaction, which was possibly contributed to the coordination effect of Fe to O atom.

**Scheme 1.** Iron-catalyzed cross coupling through HAT-induced C(sp<sup>3</sup>)–H bond activation



- 1) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, 366, 529. 2) L. Capaldo, D. Ravelli, M. Fagnoni, *Chem. Rev.* **2022**, 122, 1875. 3) T. Hatakeyama, T. Hashimoto, Y. Kondo, Y. Fujiwara, H. Seike, H. Takaya, Y. Tamada, T. Ono, M. Nakamura, *J. Am. Chem. Soc.* **2010**, 132, 10674. 4) K. Yamada, K. P. S. Cheung, V. Gevorgyan, *J. Am. Chem. Soc.*, **2024**, 146, 27, 18218