Nickel-Catalyzed Suzuki-Miyaura Cross-Coupling Reaction Involving the Cleavage of the *ortho* C-F Bond in Aromatic Amide

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Over the past few decades, the Suzuki-Miyaura cross-coupling reaction with organoboron reagents has been recognized as one of the most powerful C-C bond forming reactions. In 2006, Radius reported the first example of a Ni-catalyzed Suzuki-Miyaura cross-coupling reaction of per-fluorinated arenes, such as octafluorotoluene and perfluorobiphenyl. Since then, several studies regarding this subject have appeared. In most cases, the reactions required a high temperature, over 100 °C. Our group recently reported the Ni-catalyzed reaction of ortho-fluoro-substituted aromatic amides with alkynes which results in C-F/N-H annulation to give 1(2H)-isoquinolinones. The reaction proceeded under mild reaction conditions, in the 40-60 °C range and under ligand-free conditions. We herein report the Ni-catalyzed Suzuki-Miyaura cross-coupling reaction of aryl fluorides with aryl boronic esters in which an amidate directing group is used even at lower reaction temperatures.

$$R = \begin{pmatrix} O \\ N \\ H \end{pmatrix} R' + Ar - B \\ O = \begin{pmatrix} Ni(cod)_2 / PPh_3 \\ KO^tBu, CsF \\ DMF, 60 °C \end{pmatrix} R = \begin{pmatrix} O \\ N \\ H \end{pmatrix} R'$$

- 1) For reviews on Suzuki-Miyaura cross-coupling reactions, see: Han, F.-S. *Chem. Soc. Rev.* **2013**, *42*, 5270-5298.
- 2) Schaub, T.; Backes, M.; Radius, U. J. Am. Chem. Soc. 2006, 128, 15964-15965.
- 3) Nohira, I.; Lu, S.; Bai, R.; Lan, Y.; Chatani, N. J. Am. Chem. Soc. 2020, 142, 17306-17311.