ジアミノナフタレン置換ボランをホウ素求電子剤とする遷移金属触媒フリーなホウ素化反応

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Transition Metal-free Borylation Reaction Using 1,8-Diaminonaphthalene-substituted Borane as a Boron Electrophile

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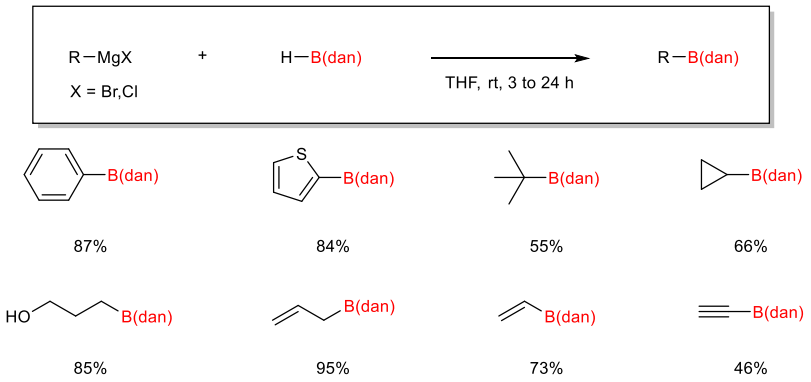
1,8-Diaminonaphthalene-substituted organoboron compounds with diminished Lewis acidity, R–B(dan), could directly be synthesized by the reaction of H–B(dan) and various Grignard reagents, where H–B(dan) serves as a B(dan) electrophile despite its highly diminished boron-Lewis acidity. A wide range of Grignard reagents were convertible into the respective C(sp/sp^2/sp^3)–B(dan) efficiently under transition metal-free conditions in one pot. Moreover, 2-pyridyl–B(dan) were also accessible as stable compounds by use of Turbo Grignard reagent, which can be purified by column chromatography and can be stored at room temperature in air. Successive cross-coupling of 5-bromo-2-pyridyl–B(dan), synthesized by the present method, was found to occur chemoselectively.

Keywords : Boron Electrophile; Grignard Reagent; 1,8-Diaminonaphthalene; Transition Metal-free

H–B(dan)と種々のグリニャール反応剤の反応により，遷移金属触媒を用いることなくルイス酸性抑制型 dan 置換有機ホウ素化合物を合成できる [1]．この反応では，H–B(dan)がホウ素求電子剤として機能する．さらに，ターボグリニャール反応剤を用いることで 2-pyridyl–B(dan)も得られ，カラムクロマトグラフィー精製が可能なうえ空気中室温で保存できる．本反応で合成できる 5-bromo-2-pyridyl–B(dan)の化学選択的な連続クロスカップリングも達成した [2]．



1) J. Li, M. Seki, S. Kamio, H. Yoshida, *Chem. Commun.* **2020**, *56*, 6388. 2) a) H. Yoshida, M. Seki, S. Kamio, H. Tanaka, Y. Izumi, J. Li, I. Osaka, M. Abe, H. Andoh, T. Yajima, T. Tani, T. Tsuchimoto, *ACS Catal.* **2020**, *10*, 346. b) J. Li, H. Yoshida, *Heterocycles* DOI: 10.3987/REV-20-949.

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