R. SHANG, L. ILIES,* E. NAKAMURA* (THE UNIVERSITY OF TOKYO, JAPAN) Iron-Catalyzed Directed C(sp²)–H and C(sp³)–H Functionalization with Trimethylaluminum *J. Am. Chem. Soc.* **2015**, *137*, 7760–7663.

Directed Iron-Catalyzed C-H Methylation



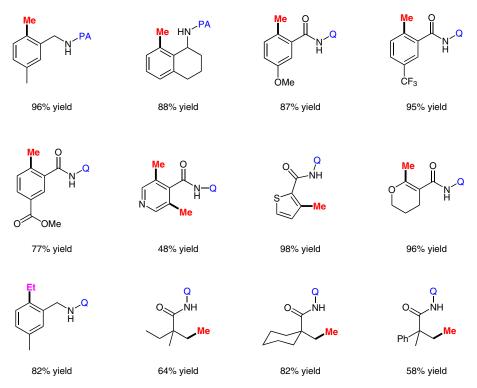
AlMe₃ (2.0 equiv, 2 M in hexanes)
Fe(acac)₃ (0.01–5 mol%)
dppen (Fe/ligand ratio = 1:1.1)
2.3-DCB (4.0 equiv)

2,3-DCB (4.0 equiv) THF (1.0–2.0 M), 70 °C, 24 h

> 32 examples up to 99% yield TON up to 6500

DG = picolinoyl (PA), 8-quinolyl (Q)

Selected examples:



Significance: The iron(III)-catalyzed directed functionalization of $C(sp^2)$ –H and $C(sp^3)$ –H bonds was achieved by Nakamura and co-workers. The methylation of anilides and carboxamides bearing a picolinoyl or 8-aminoquinolyl group with trimethylaluminum is tolerant of electron-withdrawing (CF₃, F, CI, Br, CO₂R) and electron-donating (OMe, NMe₂) groups, as well as heterocyclic amines.

Comment: The authors present an alternative to the use of AlMe₃ by isolating the air-stable diamine intermediate formed by complexation of AlMe₃ with the iron(III) salt and 1,2-bis(diphenyl-phosphino)ethane (dppen). This robust catalyst could be recovered and a turnover number of more than 6500 was reached.

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 Synfacts 2015, 11(9), 0969
 Published online: 18.08.2015

 DOI: 10.1055/s-0035-1560075; Reg-No.: P09415SF

Category

Metal-Mediated Synthesis

Key words

C-H functionalization

trimethylaluminum

iron

