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Nano-Fe₂O₃ Catalyzed Direct Borylation of Arenes

Chem. Commun. 2010, 46, 3170-3172.

Direct Borylation of Arenes Catalyzed by γ -Fe₂O₃

Typical results:					
Substrate	Product	Yield (%)	Substrate	Product	Yield (%)
	Bpin	75		Bpin	63
MeO	Bpin	70		(o/m/p = 71:20:9) Bpin	67
MeO	(o/m/p = 61:29:1) MeO Bpin OMe	32		Bpin	41

$$+ \text{ pinB-Bpin} \\ & \frac{1) \ \gamma \text{-Fe}_2 \text{O}_3 \ (20 \text{ mol}\% \text{ Fe})}{\text{t-BuOOt-Bu} \ (2 \text{ equiv}), \ K_2 \text{CO}_3 \ (2 \text{ equiv})}}{2) \ \text{Ar-I, PdCl}_2 (\text{dppf})_2 \ (3 \text{ mol}\%)} \\ & \text{$K_3 \text{PO}_4 \ (3 \text{ equiv}), DMF, 60 °C}} \\ & \text{up to 56\% yield} \\ & \text{(4 examples)} \\ \\ & \text{(4 examples)} \\ \\ & \text{(4 examples)} \\ \\ & \text{(5 \text{ equiv})} \\ & \text{(6 \text{ equiv})} \\$$

 $Ar = 4-O_2NC_6H_4$, $4-MeOC_6H_4$, $4-CIC_6H_4$, $4-MeC(O)C_6H_4$

Significance: γ-Fe₂O₃ magnetic nanoparticles (particle size 58 nm) catalyzed the borylation of arenes with bis(pinacolato)diborane in the presence of di-tert-butyl peroxide and potassium carbonate under air to give the corresponding borylated products in up to 75% yield (10 examples, eq. 1). A sequential reaction via γ-Fe₂O₃-catalyzed borylation of benzene and Suzuki-Miyaura coupling with iodoarenes gave the corresponding biaryls in up to 56% yield (4 examples, eq. 2).

Comment: The catalytic activity of γ -Fe₂O₃ was superior to that of the other iron catalysts, such as FeCl₃, FeBr₃, FeF₃, Fe(acac)₃, Fe₂(SO₄)₃, and Fe₂O₃. In the borylation of toluene and anisole, the ortho-borylated products were obtained as major regioisomers.

SYNFACTS Contributors: Yasuhiro Uozumi, Takao Osako Synfacts 2010, 8, 0959-0959 Published online: 22.07.2010

 $\textbf{DOI:}\ 10.1055/\text{s-}0030\text{-}1257795; \textbf{Reg-No.:}\ Y07610SF$

Category

Polymer-Supported Synthesis

Key words

maghemite

direct borylation

arenes

bis(pinacolato)diborane

