Direct Borylation of Arenes Catalyzed by \( \gamma \)-Fe\(_2\)O\(_3\)

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\begin{align*}
\text{Substrate} & \quad \text{Product} & \quad \text{Yield (\%)} & \quad \text{Substrate} & \quad \text{Product} & \quad \text{Yield (\%)} \\
\begin{array}{c|c|c}
\text{+ pinB} & \text{Bpin} & 75 \\
\end{array} & \begin{array}{c|c|c}
\text{MeO} & \text{MeO} & 70
\end{array} & \begin{array}{c|c|c}
\text{MeO} & \text{MeO} & 32
\end{array}
\]

Significance: \( \gamma \)-Fe\(_2\)O\(_3\) magnetic nanoparticles (particle size 58 nm) catalyzed the borylation of arenes with bis(pinacolato)diborane in the presence of di-\text{-}tert\text{-}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 \( \gamma \)-Fe\(_2\)O\(_3\)-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 \( \gamma \)-Fe\(_2\)O\(_3\) was superior to that of the other iron catalysts, such as FeCl\(_3\), FeBr\(_3\), Fe(acac)\(_3\), Fe\(_2\)(SO\(_4\))\(_3\), and Fe\(_2\)O\(_3\). In the borylation of toluene and anisole, the ortho-borylated products were obtained as major regioisomers.