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

\[
\text{R} + \text{pinB-Bpin} \rightarrow \text{R-Bpin} \quad \text{(5 mL)} \quad \text{(1 mmol)}
\]

\[
\gamma\text{-Fe}_2\text{O}_3 \quad \text{(20 mol\% Fe)} \quad \text{t-BuOOt-Bu} \quad \text{(2 equiv)} \quad K_2\text{CO}_3 \quad \text{(2 equiv)} \quad \text{air, 80 °C, 4–5 d}
\]

Typical results:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MeO} )</td>
<td>( \text{MeO} )</td>
<td>70</td>
<td>( \text{MeO} )</td>
<td>( \text{MeO} )</td>
<td>67</td>
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<tr>
<td>( \text{MeO} )</td>
<td>( \text{MeO} )</td>
<td>32</td>
<td>( \text{MeO} )</td>
<td>( \text{MeO} )</td>
<td>41</td>
</tr>
</tbody>
</table>

**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-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 \( \gamma\)-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\(_3\), FeF\(_3\), 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.