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

\[
\begin{align*}
R \quad (5 \text{ mL}) & \quad + \quad \text{pinB-Bpin} \quad (1 \text{ mmol}) \quad \xrightarrow{\gamma\text{-Fe}_2\text{O}_3 \quad (20 \text{ mol}\% \text{ Fe})} \quad \gamma\text{-Fe}_2\text{O}_3 & \quad \xrightarrow{\text{t-BuOOt-Bu \quad (2 equiv), K}_2\text{CO}_3 \quad (2 equiv)} \quad \text{air, 80 °C, 4–5 d} \quad \xrightarrow{} \quad \text{up to 75% yield} \quad (10 \text{ examples})
\end{align*}
\]

**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.

**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{R} \quad (5 \text{ mL}) )</td>
<td>( \text{Bpin} )</td>
<td>75</td>
<td>( \text{Bpin} )</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>MeO</td>
<td>MeO</td>
<td>70</td>
<td>(o/m/p = 71:20:9)</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>MeO</td>
<td>MeO-Bpin</td>
<td>32</td>
<td>(o/m/p = 61:29:1)</td>
<td>41</td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Ar} & \quad + \quad \text{pinB-Bpin} \quad \xrightarrow{\gamma\text{-Fe}_2\text{O}_3 \quad (20 \text{ mol}\% \text{ Fe})} \quad \gamma\text{-Fe}_2\text{O}_3 & \quad \xrightarrow{\text{t-BuOOt-Bu \quad (2 equiv), K}_2\text{CO}_3 \quad (2 equiv)} \quad \text{air, 80 °C, 5 d} \quad \xrightarrow{} \quad \text{up to 56% yield} \quad (4 \text{ examples})
\end{align*}
\]

\( \text{Ar} = 4\text{-O}_2\text{NC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-MeC(O)C}_6\text{H}_4 \)

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