Dual Copper- and Photoredox-Catalysed C(sp²)-C(sp³) Coupling

Euan B. McLean, Vincent Gauchot, Sebastian Brunen, David J. Burns and Ai-Lan Lee*

SUPPORTING INFORMATION

Contents

1- General Considerations 2
2- Selected Optimisation Tables 3
3- Mechanistic Investigations 14
4- Scale-up Procedure 17
5- Substrate Synthesis 17
6- General Procedure for the Dual Copper- and Photoredox-Catalysed C(sp²)-C(sp³) Cross-Coupling 20
7- Product Characterisation 21
8- NMR Spectra 31
9- References 57
General Considerations

$^1$H NMR spectra were recorded on a Bruker AV300 or AV400 spectrometer at 300 MHz or 400 MHz respectively and referenced to residual solvent. $^{13}$C NMR spectra were recorded using the same spectrometers at 75 MHz or 101 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks (CDCl$_3$ at $\delta_H$ 7.26 ppm and $\delta_C$ at 77.0 ppm). $^{19}$F NMR were recorded using the same spectrometers at 282 MHz or 376 MHz respectively. J values are given in Hz and s, d, t, q, dd, ddd and m are abbreviations corresponding to singlet, doublet, triplet, quartet, doublet of doublets, doublet of doublets of doublets and multiplet respectively. Mass spectra were obtained at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

Column chromatography was carried out using Matrix silica gel 60 from Fluorochem and TLC performed using Merck silica gel 60 F$_{254}$ pre-coated sheets and visualised by UV (254 nm) and/or aqueous acidic KMnO$_4$. Anhydrous solvents were obtained from a MBRAUN SPS-800 solvent purification system (SPS) and stored under an argon atmosphere until use. Arylboronic acids were bought from Sigma-Aldrich or Fluorochem and recrystallized from water prior to use unless otherwise stated. Arylborationes were obtained by dehydrating boronic acids by heating the corresponding boronic acid under vacuum. Benzyl bromides other than those whose syntheses are detailed here were obtained from a number of commercial sources and were used without further purification. Unless otherwise stated, photoredox reactions were carried out under argon atmosphere. The reaction mixture was sparged with argon for 5 min before use. Light irradiation was performed using blue LEDs (1.5 Watt/foot). The light source was placed ca 10 cm away from the reaction vessel, to prevent excess heating. We found that the reactions are most reproducible when only one reaction vessel is irradiated per setup, to allow maximum light penetration.
**Selected Optimisation Tables**

Unless otherwise stated, the reaction mixture was sparged with argon for 5 min before the reaction commenced and reactions were carried out in oven dried 1 dram screw cap vials. p-tolylboronic acid was recrystallized from water unless otherwise stated.

**Initial Screens**

**Solvent Optimisation**

![Chemical structure](image-url)

Reaction carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). Yield determined by $^1$H NMR analysis using mesitylene as an internal standard. Yields with respect to theoretical maximum formation of 7a. Reaction carried out at r.t. 30 mol% Cul, 1 mol% Ru(bpy)$_3$(PF$_6$)$_2$, 4 equiv. KF. Stoichiometry of benzyl bromide and boronic acid reversed. Not applicable as 4a is in excess.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>5aa (%)$^a$</th>
<th>4a (%)$^a$</th>
<th>7a (%)$^{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>Trace</td>
<td>N/A$^f$</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>8</td>
<td>N/A$^f$</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>23</td>
<td>N/A$^f$</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>8</td>
<td>N/A$^f$</td>
<td>41</td>
</tr>
<tr>
<td>5$^c$</td>
<td>MeCN</td>
<td>10</td>
<td>N/A$^f$</td>
<td>24</td>
</tr>
<tr>
<td>6$^{d,e}$</td>
<td>NMP</td>
<td>Trace</td>
<td>Trace</td>
<td>23</td>
</tr>
<tr>
<td>7$^{d,e}$</td>
<td>DMSO</td>
<td>8%</td>
<td>5%</td>
<td>26</td>
</tr>
<tr>
<td>8$^e$</td>
<td>Toluene</td>
<td>29</td>
<td>28</td>
<td>20</td>
</tr>
</tbody>
</table>

Reaction carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). Yield determined by $^1$H NMR analysis using mesitylene as an internal standard. Yields with respect to theoretical maximum formation of 7a. Reaction carried out at r.t. 30 mol% Cul, 1 mol% Ru(bpy)$_3$(PF$_6$)$_2$, 4 equiv. KF. Stoichiometry of benzyl bromide and boronic acid reversed. Not applicable as 4a is in excess.

Solvent screen showed toluene to be by far the best solvent.
Base Optimisation

\[ \text{Br} \quad \overset{\text{Kul (30 mol\%) \quad \text{Ru(bpy)}_3\text{(PF}_6)_2 \quad (2.5 \text{ mol\%)}}{\text{Toluene, 50 °C, 16 h \quad \text{Blue LEDs}}} \quad \text{NO}_2 \]

\[ \text{Br} \quad \overset{\text{N}}{\text{N}} \quad \text{NO}_2 \]

**Base**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Equiv.</th>
<th>5aa (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>4a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>7a (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3</td>
<td>29</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>KOtBu</td>
<td>3</td>
<td>19</td>
<td>24</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>DMAP</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>LiF</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>NaF</td>
<td>3</td>
<td>0</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>NH&lt;sub&gt;4&lt;/sub&gt;F</td>
<td>3</td>
<td>0</td>
<td>45</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>CsF</td>
<td>3</td>
<td>35</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>KF</td>
<td>3</td>
<td>37</td>
<td>13</td>
<td>22</td>
</tr>
<tr>
<td>10</td>
<td>KF</td>
<td>1</td>
<td>17</td>
<td>54</td>
<td>14</td>
</tr>
<tr>
<td>11</td>
<td>KF</td>
<td>6</td>
<td>45</td>
<td>0</td>
<td>28</td>
</tr>
</tbody>
</table>

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise).<sup>a</sup>Yield determined by <sup>1</sup>H NMR analysis using mesitylene as an internal standard. <sup>b</sup>Yields with respect to theoretical maximum formation of 7a.

Base screen identified KF to be the best base.

The increase in yield of 5aa when moving from LiF (0%) and NaF (0%) to CsF (35%) to KF (45%) indicates that ion pairing plays a role, with the tighter LiF/KF pairs showing no reactivity while the less tightly bound CsF and KF progressively show more reactivity.
Other parameters

![Chemical reaction diagram]

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Parameter</th>
<th>5aa (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>4a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>7a (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>37</td>
<td>13</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>1 mol% Ru</td>
<td>40</td>
<td>7</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>5 mol% Ru</td>
<td>31</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>1 equiv. KF</td>
<td>17</td>
<td>54</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>6 equiv. KF</td>
<td>45</td>
<td>0</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>5 equiv. of 1</td>
<td>44</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Half concentration</td>
<td>36</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>Half concentration</td>
<td>33</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Double concentration</td>
<td>35</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>100 °C instead of 50 °C</td>
<td>35</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>1 equiv. CuI</td>
<td>35</td>
<td>0</td>
<td>18</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yield determined by <sup>1</sup>H NMR analysis using mesitylene as an internal standard. <sup>b</sup>Yields with respect to theoretical maximum formation of 7a.

From these screens it was shown that the photocatalyst loading could be lowered to 1 mol% without any detriment to the reaction performance (entry 2).
Copper Catalyst Optimisation

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>5aa (%)</th>
<th>4a (%)</th>
<th>7a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuI</td>
<td>39</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>CuBr</td>
<td>41</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>PhenCu(PPh$_3$)Br</td>
<td>36</td>
<td>7</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OAc)$_2$</td>
<td>29</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OTf)$_2$</td>
<td>30</td>
<td>28</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>CuBr$_2$</td>
<td>36</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>7$^{c,d}$</td>
<td>Cu$_2$O</td>
<td><strong>55</strong></td>
<td><strong>0</strong></td>
<td><strong>20</strong></td>
</tr>
</tbody>
</table>

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). $^a$Yield determined by $^1$H NMR analysis using mesitylene as an internal standard. $^b$Yields with respect to theoretical maximum formation of 7a. $^c$4 equivalents of KF used. $^d$Ru(bpy)$_3$(PF$_6$)$_2$ (1 mol%)  

Cu$_2$O was identified as the best copper source.
Miscellaneous tests

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). Yield determined by $^1$H NMR analysis using mesitylene as an internal standard. Yields with respect to theoretical maximum formation of 7a. CFL= compact fluorescent lamp.

*Oxygen atmosphere reaction results in a large amount of aldehyde product deriving from oxidation of benzylic radical:

Up until this point, all optimisation had been carried out on recrystallised $p$-tolylboronic acid 1 as a model substrate. To our surprise, when the optimised reaction conditions for 1 (Entry 1, above) were applied to other arylboronic acids, either no coupling or low yields were obtained. We hypothesized that this difference in reactivity may be due to the different position of equilibrium between arylboronic acids and their corresponding arylboroxine for each arylboronic acid. This potentially leads to different reactivity as the arylboroxine is thought to be less efficient as a coupling partner. The reaction conditions would therefore need to be re-optimised in order to find a set of general conditions which would work for all arylboronic acids. We started by adding a known quantity of water to our reaction mixture in order to perturb the equilibrium towards the desired arylboronic acid.
Water Content Optimisation\textsuperscript{a}

\[ \text{B(OH)}_2 \text{ } \overset{3 \text{ equiv.}}{\text{1d}} \overset{p-\text{NO}_2\text{BnBr } 4\text{a} (1 \text{ equiv.)}}{\text{KF (4 equiv.)}} \overset{\text{Cu}_2\text{O} (15 \text{ mol\%})}{\text{Ru(bpy)}_3(\text{PF}_6)_2 (1 \text{ mol\%})} \overset{\text{H}_2\text{O} (x \text{ equiv.})}{\text{Toluene, 50 °C, 16 h}} \overset{\text{Blue LEDs}}{\text{5da \text{a}} \overset{\text{O}_2\text{N}}{\text{7a}} \text{b}} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equiv.</th>
<th>5da (%)\textsuperscript{b}</th>
<th>4a (%)\textsuperscript{b}</th>
<th>7a (%)\textsuperscript{b,c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>8</td>
<td>89</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>3</td>
<td>92</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>11</td>
<td>77</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>15</td>
<td>69</td>
<td>6</td>
</tr>
<tr>
<td>5\textsuperscript{d}</td>
<td>3</td>
<td>0</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>6\textsuperscript{d}</td>
<td>6</td>
<td>3</td>
<td>68</td>
<td>1</td>
</tr>
<tr>
<td>7\textsuperscript{d}</td>
<td>9</td>
<td>8</td>
<td>81</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>15</td>
<td>42</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>38</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>51</td>
<td>9</td>
<td>24</td>
</tr>
<tr>
<td>11\textsuperscript{d}</td>
<td>30</td>
<td>53</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>45</td>
<td>9</td>
<td>22</td>
</tr>
<tr>
<td>13</td>
<td>55</td>
<td>48</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td>14</td>
<td>60</td>
<td>44</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>42</td>
<td>14</td>
<td>16</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Phenylboronic acid 1d was used straight from the bottle without prior recrystallization unless otherwise stated. Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). \textsuperscript{b}Yield determined by \textsuperscript{1}H NMR analysis using mesitylene as an internal standard. \textsuperscript{c}Yields with respect to theoretical maximum formation of 7a. \textsuperscript{d}Arylborrowine (dehydrated from phenylboronic acid) used instead of arylboronic acid from bottle.

The addition of 30 equiv. of water was deemed to be optimal in order to gain consistent yields for a variety of arylboronic acids. The conditions in Entry 11 were therefore taken forward for further screening.
Temperature Screen

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp (°C)</th>
<th>5da (%)(^a)</th>
<th>4a (%)(^a)</th>
<th>7a (%)(^a, b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>45</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>53</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>51</td>
<td>0</td>
<td>32</td>
</tr>
</tbody>
</table>

Yield determined by \(^1\)H NMR analysis using mesitylene as an internal standard. \(^b\)Yields with respect to theoretical maximum formation of 7a.

Photocatalyst Screening

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>5aa (%)(^a)</th>
<th>4a (%)(^a)</th>
<th>7a (%)(^a, b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(bpy)(_3)(PF(_6))(_2)</td>
<td>59</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>Ir(ppy)(_2)(dtbbpy)(PF(_6))</td>
<td>51</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>Ir(ppy)(_3)</td>
<td>14</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>4(^c)</td>
<td>Eosin Y</td>
<td>21</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>5(^c)</td>
<td>Fluorescein</td>
<td>20</td>
<td>62</td>
<td>10</td>
</tr>
<tr>
<td>6(^c)</td>
<td>Fukuzumi’s catalyst</td>
<td>3</td>
<td>78</td>
<td>4</td>
</tr>
</tbody>
</table>

Yield determined by \(^1\)H NMR analysis using mesitylene as an internal standard. \(^b\)Yields with respect to theoretical maximum formation of 7a. \(^c\)Cu\(_2\)O (30 mol%) Fukuzumi’s Catalyst: 9-mesitylene-10-methylacridinium perchlorate.

Ru(bpy)\(_3\)(PF\(_6\))\(_2\) is the best photocatalyst for the reaction of the examples screened. Organic dyes such as Eosin Y and Fluorescein can also catalyse the reaction, but are far less efficient.
Testing more reducing catalyst for more electron-rich benzyl bromides:

The reaction using more electron-rich benzyl bromides (4k) was also attempted using the more reducing *fac*-Ir(ppy)$_3$ photocatalyst. However this resulted in only trace amounts of the desired product being detected by $^1$H NMR with large amounts of homocoupled benzyl bromide product 7k being detected (50%) and 11% of the benzyl bromide 4k starting material being recovered. Therefore, this result indicates that although the benzyl radical is forming from 4k with the more reducing photocatalyst, homocoupling predominates over the cross-coupling reaction.

![Chemical Diagram]

Reaction Using 4-Methoxypyridine as an Additive

In an attempt to improve the yields of product 5 and reduce reaction times, the reaction was carried out in the presence of a substoichiometric amount of 4-methoxypyridine which has been previously shown in the literature to activate benzyl bromides toward single electron reduction.\(^3\)

However, under our reaction conditions, the addition of 4-methoxypyridine resulted in a reduction in the yield of 5ak (14% vs. 42%) but with comparable amounts of remaining starting material 4d and homocoupling product 7k being observed when compared with the reaction without additive. Therefore, we hypothesise that this is caused by the 4-methoxypyridine coordinating to the copper catalyst and inhibiting the cross-coupling reaction.

Similarly, we also observe that no appreciable amount of cross-coupling product 5 is detected when a pyridyl moiety is present in either substrate 1 or 4, indicating that this type of motif is incompatible with our reaction conditions.
In both cases only traces of the desired products were observed and only traces of homocoupling product and left over starting material were detected.

**Stoichiometry Optimisation**

![Chemical structure](image1)

![Chemical structure](image2)

<table>
<thead>
<tr>
<th>Entry</th>
<th>x</th>
<th>y</th>
<th>5aa (%)</th>
<th>4a (%)</th>
<th>7a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3</td>
<td>59</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>54</td>
<td>24</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>27</td>
<td>69</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>32</td>
<td>N/A</td>
<td>8</td>
</tr>
</tbody>
</table>

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). aYield determined by 1H NMR analysis using mesitylene as an internal standard. bYields with respect to theoretical maximum formation of 7a. cNot applicable as 4a in excess.
Control Reactions

\[ \text{Br} \quad \begin{array}{c}
\text{NO}_2 \\
4a
\end{array} \quad \text{Br} \quad \begin{array}{c}
\text{NO}_2 \\
4a
\end{array} \rightarrow \begin{array}{c}
\text{NO}_2 \\
5aa
\end{array} \quad \begin{array}{c}
\text{NO}_2 \\
\text{O}_2 \text{N} \\
7a
\end{array} \]

\( p \)-Tolyboronic acid 1a (3 equiv.)

<table>
<thead>
<tr>
<th>Change</th>
<th>5aa (%(^{a,b}))</th>
<th>4a (%(^{a,b}))</th>
<th>7a (%(^{a,b}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Normal Conditions</td>
<td>59</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>No Ru(bpy)(_3)(PF(_6))(_2)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>No Cu(_2)O</td>
<td>21</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>No KF</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>In the dark</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>6(^{c})</td>
<td>Under Air</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). \(^{a}\)Yield determined by \(^{1}\)H NMR analysis using mesitylene as an internal standard. \(^{b}\)Yields with respect to theoretical maximum formation of 7a. \(^{c}\)No water, 20 mol% Cu\(_2\)O.

*Carrying out the reaction under air results 15% aldehyde SI-1 formation.

These control reactions confirm that both the photoredox and copper catalysts are required for the coupling reaction to proceed efficiently (Entries 2-3). Base (KF, Entry 3) and light (Entry 4) are also necessary.
Miscellaneous Optimisation

It was found that when the relative strength of the electron withdrawing effect from the benzyl bromide substituents was decreased, the reaction required extended reaction times to reach completion. It was also observed that in addition to increasing the yields of the reaction, increasing the copper loading from 15 to 30 mol% made the results of each reaction much more reproducible.

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). \(^a\)Yield determined by \(^1\)H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. \(^b\)Yields with respect to theoretical maximum formation of 7a. \(^c\)isolated yield.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>x</th>
<th>t</th>
<th>5a (%)(^a)</th>
<th>4 (%)(^a)</th>
<th>7 (%)(^{a,b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CN</td>
<td>15</td>
<td>16</td>
<td>42</td>
<td>41</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>CN</td>
<td>15</td>
<td>72</td>
<td>60</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>CN</td>
<td>15</td>
<td>120</td>
<td>60</td>
<td>5</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>CN</td>
<td>30</td>
<td>72</td>
<td>66(60)(^c)</td>
<td>trace</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>NO2</td>
<td>15</td>
<td>16</td>
<td>59</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>NO2</td>
<td>30</td>
<td>16</td>
<td>65(62)(^c)</td>
<td>0</td>
<td>28</td>
</tr>
</tbody>
</table>

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). \(^a\)Yield determined by \(^1\)H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. \(^b\)Yields with respect to theoretical maximum formation of 7a. \(^c\)isolated yield.
Mechanistic Investigations

Radical Trap Experiment

A oven-dried one dram vial was charged sequentially with 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol), 4-tolylboronic acid (40.8 mg, 0.3 mmol), KF (23.2 mg, 0.4 mmol), TEMPO (31.3 mg, 0.2 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.9 mg, 0.001 mmol) and Cu$_2$O (4.3 mg, 0.03 mmol) under an argon atmosphere. H$_2$O (54 mg, 54 µL, 3 mmol) was then added before all reagents were dissolved in anhydrous toluene (1 mL). The resulting solution was then sparged with an argon balloon for 5 minutes, before the vial was sealed and the resulting solution stirred at 50 °C under blue LED irradiation for 16 h. The reaction was then diluted with EtOAc (10 mL) and H$_2$O (10 mL). The organic and aqueous layers were then separated before the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were washed with saturated Na$_2$S$_2$O$_3$ solution (10 mL) followed by brine (10 mL). They were then dried over MgSO$_4$ and concentrated in vacuo to yield the crude product. Purification of the crude product by silica gel flash chromatography (49:1 to 19:1 petrol 40-60 °C: EtOAc, $R_f = 0.30$) followed by Kugelrohr distillation provided TEMPO-trapped adduct 8 as a yellow solid (18.7 mg, 0.064 mmol, 64%).

$R_f$; $v_{max}$/cm$^{-1}$ 3006 (C-H Ar), 2975 (C-H), 2931 (C-H), 1605 (NO$_2$), 1470 (C-C Ar), 1451 (C-C Ar), 1345 (NO$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$ 8.20 (d, $J = 8.9$ Hz, 2H, Ar-H), 7.50 (d, $J = 8.9$ Hz, 2H, Ar-H), 4.93 (s, 2H, OCH$_2$), 1.68 – 1.31 (m, 6H, 3xCH$_2$), 1.21 (s, 6H, 2xCH$_3$), 1.17 (s, 6H, 2xCH$_3$); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta_C$ 147.2 (C), 146.1 (C), 127.5 (CH), 123.7 (CH), 77.7 (CH$_2$), 60.3 (C), 39.8 (CH$_2$), 33.1 (CH$_3$), 20.4 (CH$_3$), 17.2 (CH$_2$); m.p. = 61-62 °C (lit.$^2$ 60-62 °C).

No formation of coupling product 5aa was detected in the presence of TEMPO. Isolation of the TEMPO trapped adduct of the benzylic radical originating from reduction of the benzyl bromide would suggest that the mechanism of the reaction is radical based with benzylic radicals serving as intermediates.
Quantum Yield Determination

The following model reaction was used in order to determine the quantum yield of the reaction (following the method used by Nicewicz and co-workers).³

\[
\begin{align*}
\textbf{4a} & \quad \text{Br} \quad \text{NO}_2 \\
\rightarrow & \quad \text{Toluene (0.1 M), 50 °C} \\
\text{Blue LEDs} & \\
\textbf{5aa} & \quad \text{NO}_2
\end{align*}
\]

In the dark, potassium ferrioxalate trihydrate (K₂Fe(C₂O₄)₃) was prepared by adapting a previously reported literature procedure and was purified by recrystallization from water prior to use.⁴ A 0.15 M aqueous solution of K₂Fe(C₂O₄)₃ was made up before 1 mL of the solution was irradiated under our standard reaction set up (Figure S1) for 30 seconds (a second measurement was also carried out irradiating for 15 seconds). After irradiation, the samples were kept in the dark as much as possible. After being irradiated for the appropriate amount of time, 0.5 mL of each sample was transferred to a 25 mL volumetric flask. To this 5 mL of a buffered 1,10-phenanthroline solution, previously prepared in accordance with the literature,⁵ was added and the flask made up to the mark with H₂O. The resulting solution was then stirred at room temperature for 30 minutes. 0.25 mL of the solution was then transferred to a cuvette and diluted to 2.75 mL with H₂O.

The moles of tris-phenanthroline-Fe²⁺ complex (ε₅₁₀ nm = 11110 M⁻¹ cm⁻¹)⁶ was then determined using UV/vis spectroscopy. The photon flux on the system was determined using the absolute quantum yield of 0.85 at 457.9 nm for the photodecomposition of K₂Fe(C₂O₄)₃. The photon flux averaged over the two experiments was determined to be 1.69×10⁻⁷ mol photons s⁻¹ (std. dev. 4.60×10⁻⁸ mol photons s⁻¹). The quantum yield of the reaction was then obtained by stopping the reaction at varying degrees of conversion, using the following relationship,

\[
\Phi_R = \frac{\text{moles of product}}{\text{moles of incident photons}}
\]

Three measurements were taken at 29%, 57% and 61% conversion. The average quantum yield of the reaction was \(\Phi = 0.012\) (std. dev. 0.0023).

(Sample calculation from 61% converted experiment, reaction time 8 h)

NMR yield = 47%

\[
\Phi_R = \frac{\text{moles of product}}{\text{moles of incident photons}}
\]

\[
\Phi_R = \frac{\text{moles of product}}{\text{Photon flux \times reaction time}}
\]

\[
\Phi_R = \frac{4.7 \times 10^{-5} \text{ mol}}{1.69 \times 10^{-7} \text{ mols}^{-1} \times 28800 \text{ s}}
\]
\[ \Phi_R = 0.0096 \]

(Sample calculation from 57% converted experiment, reaction time 5 h)

NMR yield = 39%

\[ \Phi_R = \frac{\text{moles of product}}{\text{moles of incident photons}} \]
\[ \Phi_R = \frac{\text{moles of product}}{\text{Photon flux } \times \text{reaction time}} \]
\[ \Phi_R = \frac{3.9 \times 10^{-5} \text{ mol}}{1.69 \times 10^{-7} \text{ mol s}^{-1} \times 18000 \text{ s}} \]
\[ \Phi_R = 0.013 \]

(Sample calculation from 29% converted experiment, reaction time 3 h)

NMR yield = 26%

\[ \Phi_R = \frac{\text{moles of product}}{\text{moles of incident photons}} \]
\[ \Phi_R = \frac{\text{moles of product}}{\text{Photon flux } \times \text{reaction time}} \]
\[ \Phi_R = \frac{2.6 \times 10^{-5} \text{ mol}}{1.69 \times 10^{-7} \text{ mol s}^{-1} \times 10800 \text{ s}} \]
\[ \Phi_R = 0.014 \]

Taking the average of the three experiments gives the average quantum yield of the reaction as \( \Phi = 0.012 \) (std. dev. 0.0023).
**Procedure for the 1 mmol Scale Reaction**

An oven-dried pyrex test tube was charged sequentially with the 4-nitrobenzyl bromide 4a (1 mmol), the p-tolyllboronic acid 1a (3 mmol), KF (232 mg, 4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (8.6 mg, 0.01 mmol) and Cu$_2$O (42.9 mg, 0.3 mmol) under an argon atmosphere. H$_2$O (540 mg, 540 µL, 30 mmol) was then added before all reagents were dissolved in anhydrous toluene which had previously been rigorously degassed by 3 consecutive freeze-pump-thaw cycles (10 mL). The resulting solution was then sparged vigorously with argon balloons for 45 minutes in the dark, before the test tube was sealed using a fresh rubber seal and parafilm. The solution was then stirred at 50 °C under blue LED irradiation for 96 h. The reaction was then diluted with EtOAc (20 mL) and H$_2$O (20 mL). The organic and aqueous layers were then separated, before the aqueous layer was extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO$_4$ and concentrated in vacuo to yield the crude product. Purification of the crude product by silica gel flash chromatography (7:3 petrol 40-60°C / toluene) yielded coupled product 5aa as a yellow crystalline solid (116.9 mg, 0.51 mmol, 51%).

**Starting Material Synthesis**

**Ammonia-borane (H$_3$N.BH$_3$)$^7$**

(NH$_4$)$_2$(SO$_4$) + NaBH$_4$ → THF, Ar, 40°C → H$_3$N.BH$_3$

Following a procedure by Zhang,$^7$ ammonium sulphate (3.30 g, 25 mmol) and sodium borohydride (0.95 g, 25 mmol) were dissolved in anhydrous THF (150 mL) under an argon atmosphere. The resulting solution was then vigorously stirred for 3 h at 40 °C. Upon completion of the reaction, the mixture was allowed to cool to room temperature before being filtered. Concentration of the solution under reduced pressure yielded the title compound (0.59 g, 19 mmol, 76%) as a white solid, with spectral data in accordance with the literature.

R$_f$; $v_{max}$/cm$^{-1}$; 3306 (N-H), 3248 (N-H), 2322, 2279, 1368, 1312 $^1$H NMR (300 MHz, DMSO) $\delta_H$ 4.40 (brs, 3H, NH$_3$), 2.08 – 0.40 (m, 3H, BH$_3$); $^{11}$B NMR (96 MHz, DMSO) $\delta_B$ -22.96; m.p. = 110-112 °C (lit.$^7$ 108.9-110 °C).
(2,4-Dinitrophenyl)methanol\(^7\) (SI-3)

![Chemical structure of SI-2 and SI-3](image)

Following a procedure by Zhang,\(^7\) 2,4-dinitrobenzaldehyde SI-2 (1.00 g, 5.1 mmol) and ammonia-borane (0.16 g, 5.1 mmol) were dissolved in H\(_2\)O (20 mL), the resulting solution was then stirred at room temperature for 4 h. Upon completion, the reaction mixture was extracted with EtOAc (3 x 40 mL). The combined organic layers were then washed with brine, dried over MgSO\(_4\), filtered and concentrated at reduced pressure to give the crude product. Purification by silica gel column chromatography (7:3 petrol 40-60 °C/EtOAc, R\(_f\): 0.29) yielded SI-3 (0.88 g, 4.4 mmol, 87%) as an orange solid with spectral data in accordance with the literature.\(^7\) Some impurities remained in the product but it was deemed pure enough to be taken to the next step.

1-(Bromomethyl)-2,4-dinitrobenzene\(^8\) (4l)

![Chemical structure of SI-3 and 4l](image)

N.B.: Reaction carried out under an argon atmosphere.

Adapting a procedure by Gheisari\(^9\) (2,4-dinitrophenyl)methanol SI-3 (500 mg, 2.52 mmol), potassium bromide (451 mg, 3.78 mmol) and phosphorus pentoxide (715 mg, 5.04 mmol) were dissolved in anhydrous acetonitrile (12.5 mL). The resulting solution was then stirred at 50 °C for 24 h. Upon completion of the reaction, the mixture was allowed to cool to room temperature before being extracted with EtOAc (3 x 20 mL). The combined organic layers were then washed with brine, dried over MgSO\(_4\) and filtered. Concentration of the solution under reduced pressure gave the crude product. Purification of the crude product by silica gel column chromatography (9:1 to 85:15 to 4:1 petrol 40-60 °C/EtOAc) yielded the title compound 4l (470 mg, 1.81 mmol, 72%) as a yellow solid.

R\(_f\) 0.21 (9:1 petrol 40-60 °C/EtOAc); \(v_{\text{max}}/\text{cm}^{-1}\) 3022 (C-H Ar), 2877 (C-H), 1606 (C-C Ar), 1537 (NO\(_2\)), 1440 (C-C Ar), 1346 (NO\(_2\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.89 (d, \(J = 2.4\) Hz, 1H, Ar-H), 8.46 (d, \(J = 8.5\), 2.4 Hz, 1H, Ar-H), 7.84 (d, \(J = 8.5\) Hz, 1H, Ar-H), 4.88 (s, 2H, CH\(_2\)); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 148.2 (C), 147.9 (C), 139.3 (C), 134.1 (CH), 127.8 (CH), 121.1 (CH), 27.0 (CH\(_2\)); m.p. = 43-46 °C (lit.\(^8\) 42-43 °C).
Following a procedure by Ishii, to a solution of sodium bromate (600 mg, 3.96 mmol) in H₂O (2 mL) a solution of 4-ethynitrobenzene (202 mg, 1.32 mmol) was added. A solution of sodium hydrogen sulphite (414 mg, 3.96 mmol) in H₂O (4 mL) was added dropwise over a period of 15 minutes. Once addition was complete, the resulting solution was then stirred at r.t. for 8 h. The crude mixture was then diluted with Et₂O (20 mL) before the organic and aqueous layers were separated. The aqueous layer was then washed with Et₂O (2×20 mL), the combined organic layers were then washed with saturated Na₂SO₃ solution (20 mL) dried over MgSO₄ filtered and concentrated at reduced pressure. Purification of the crude residue by silica gel flash column chromatography (19:1 petrol 40-60 °C/ EtOAc) afforded the product 4m (246.9 mg, 1.07 mmol) as yellow oil which crystallised on standing.

Rf 0.36 (19:1 petrol 40-60 °C/EtOAc; νmax/cm⁻¹ 3076 (C-H Ar), 2920 (C-H), 1596 (C-C Ar), 1513 (NO₂) 1492 (C-C Ar), 1452 (C-C Ar), 1339 (NO₂); ¹H NMR (CDCl₃, 400 MHz) δ H 8.20 (d, J = 8.6 Hz, 2H, Ar-H), 7.60 (d, J = 8.6 Hz, 2H, Ar-H), 5.20 (q, J = 6.9 Hz, 1H, ArCH), 2.05 (d, J = 6.9 Hz, 3H, CH₃); ¹³C NMR (CDCl₃, 101 MHz) δ C 150.2 (C), 147.7 (C), 128.0 (CH), 124.1 (CH), 46.5 (CH), 26.6 (CH₃); m.p. = 36-38 °C.
General Procedure for the Dual Copper- and Photoredox-Catalysed C(sp²)-C(sp³) Cross-Coupling

An oven-dried one dram vial was charged sequentially with the benzyl bromide 4 (0.1 mmol), the arylboronic acid 1 (0.3 mmol), KF (23.2 mg, 0.4 mmol), Ru(bpy)₃(PF₆)₂ (0.9 mg, 0.001 mmol) and Cu₂O (4.3 mg, 0.03 mmol) under an argon atmosphere. H₂O (54 mg, 54 µL, 3 mmol) was then added before all reagents were dissolved in anhydrous toluene (1 mL). The resulting solution was then sparged with an argon balloon for 5 minutes, before the vial was sealed. The solution was then stirred at 50 °C under blue LED irradiation for 16-96 h. The reaction was then diluted with EtOAc (10 mL) and H₂O (10 mL). The organic and aqueous layers were then separated, before the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄ and concentrated in vacuo to yield the crude product. Purification of the crude product by silica gel flash chromatography then yielded coupled products 5.

Figure S1
Product Characterisation

1-Methyl-4-(4-nitrobenzyl)benzene (5aa)

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) to yield product 5aa (14.1 mg, 0.062 mmol, 62%) as a yellow solid.

\[ R_f \] 0.26 (7:3 petrol 40-60 °C/toluene); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3048 (C-H Ar), 2929 (C-H), 2860 (C-H), 1601 (C-C Ar), 1592 (C-C Ar), 1511 (NO\(_2\)), 1339 (NO\(_2\)); \( ^{1}H \text{ NMR (CDCl}_3, 400 \text{ MHz}) \delta_H 8.14 (d, \ J = 8.9 \text{ Hz}, 2H, Ar-H), 7.33 (d, \ J = 8.9 \text{ Hz}, 2H, Ar-H), 7.13 (d, \ J = 7.9 \text{ Hz}, 2H, Ar-H), 7.06 (d, \ J = 7.9 \text{ Hz}, 2H, Ar-H), 4.04 (s, 2H, CH\(_2\)), 2.33 (s, 3H, CH\(_3\)); \( ^{13}C \text{ NMR (CDCl}_3, 100 \text{ MHz}) \) 149.3 (C), 146.7 (C), 136.5 (C), 136.3 (C), 136.0 (CH), 129.7 (CH), 129.6 (CH), 129.0 (CH), 123.9 (CH), 41.5 (CH\(_2\)), 21.1 (CH\(_3\)); m.p. = 74-75 °C.

1-Methyl-4-(2-nitrobenzyl)benzene (5ab)

Following the general procedure, 2-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (17:3→4:1→1:1 petrol 40-60 °C/toluene) to yield product 5ab (14.8 mg, 0.065 mmol, 65%) as a yellow oil.

\[ R_f \] 0.37 (9:1 petrol 40-60 °C/toluene); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3010 (C-H Ar), 2923 (C-H), 1578 (C-C Ar), 1525 (NO\(_2\)), 1514 (C-C Ar), 1445 (C-C Ar), 1349 (NO\(_2\)); \( ^{1}H \text{ NMR (CDCl}_3, 400 \text{ MHz}) \delta_H 7.91 (dd, \ J = 8.3, 1.3 \text{ Hz}, 1H, Ar-H), 7.50 (ddd, \ J = 7.5, 7.5, 1.3 \text{ Hz}, 1H, Ar-H), 7.39 – 7.34 (m, 1H, Ar-H), 7.29 – 7.27 (m, 1H, Ar-H), 7.10 (d, \ J = 8.0 \text{ Hz}, 2H, Ar-H), 7.04 (d, \ J = 8.0 \text{ Hz}, 2H, Ar-H), 4.27 (s, 2H, CH\(_2\)), 2.32 (s, 3H, CH\(_3\)); \( ^{13}C \text{ NMR (CDCl}_3, 101 \text{ MHz}) \) 149.6 (C), 136.3 (C), 136.2 (C), 135.8 (C), 133.0 (CH), 132.5 (CH), 129.5 (CH), 129.1 (CH), 127.4 (CH), 124.8 (CH), 38.0 (CH\(_2\)), 21.2 (CH\(_3\)); HRMS Found (TOF MS ASAP+) [M-H]\(^+\) 226.0870, C\(_{14}\)H\(_{12}\)NO\(_2\) requires 226.0868.
1-(4-Methylbenzyl)-3-nitrobenzene (5ac)\textsuperscript{12}

Following the general procedure, 3-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h, giving an NMR yield of 44%. Analysis of the crude \textsuperscript{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 44% with spectral data matching literature data.\textsuperscript{12} Due to co-ellution with the benzyl bromide starting material, an accurate isolated yield for the reaction could not be determined. The co-elluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed \textit{in vacuo}. The resulting residue was then subjected to silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) which yielded a pure sample of 5ac as a white solid which was then used for characterisation.

For the 3-nitrobenzyl bromide reactant, the following data was obtained:

- **Rf**: 0.33 (7:3 petrol 40-60 °C/toluene); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3010 (C-H Ar), 2922 (C-H), 1527 (NO\textsubscript{2}), 1514 (C-C Ar), 1479 (C-C Ar), 1442 (C-C Ar), 1350 (NO\textsubscript{2}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 8.08 – 8.03 (m, 2H, Ar-H), 7.49 – 7.49 (m, 1H, Ar-H), 7.47 – 7.41 (m, 1H, Ar-H), 7.13 (d, \textit{J} = 7.9 Hz, 2H, Ar-H), 7.08 (d, \textit{J} = 7.9 Hz, 2H, Ar-H), 4.04 (s, 2H, CH\textsubscript{2}), 2.33 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) \( \delta \) C 148.7 (C), 143.7 (C), 136.5 (C), 136.5 (C), 135.1 (CH), 129.7 (CH), 129.4 (CH), 128.9 (CH), 123.8 (CH), 121.4 (CH), 41.3 (CH\textsubscript{2}), 21.2 (CH\textsubscript{3}); m.p. = 61-63 °C.

4-(4-Methylbenzyl)benzonitrile (5ad)\textsuperscript{13}

Following the general procedure, 4-(bromomethyl)benzonitrile (19.6 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (1:1 petrol 40-60 °C/toluene) to yield product 5ad (12.4 mg, 0.060 mmol, 60%) as a white solid.

For the 4-(bromomethyl)benzonitrile reactant, the following data was obtained:

- **Rf**: 0.19 (1:1 petrol 40-60 °C/toluene); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3020 (C-H Ar), 2924 (C-H), 1527 (NO\textsubscript{2}), 1514 (C-C Ar), 1479 (C-C Ar), 1442 (C-C Ar), 1350 (NO\textsubscript{2}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 7.56 (d, \textit{J} = 8.3 Hz, 2H, Ar-H), 7.12 (d, \textit{J} = 8.3 Hz, 2H, Ar-H), 7.05 (d, \textit{J} = 7.9 Hz, 2H, Ar-H), 3.99 (s, 2H, CH\textsubscript{2}), 2.33 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) 147.2 (C), 143.7 (C), 136.5 (C), 136.5 (C), 135.1 (CH), 129.7 (CH), 129.4 (CH), 128.9 (CH), 123.8 (CH), 121.4 (CH), 41.3 (CH\textsubscript{2}), 21.2 (CH\textsubscript{3}); m.p. = 61-63 °C (lit.\textsuperscript{13} 65 °C).
Ethyl 4-(4-methylbenzyl)benzoate (5ae)\textsuperscript{14}

Following the general procedure, ethyl 4-\{(bromomethyl)benzoate (24.3 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. Analysis of the crude \textsuperscript{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 44% with spectral data matching literature data.\textsuperscript{14} Column chromatography was attempted but product 5ae co-eluted with unreacted benzyl bromide starting material under a number of solvent systems and could not be separated.

3-Bromo-4-(4-methylbenzyl)benzonitrile (5af)

Following the general procedure, 3-bromo-4-(bromomethyl)benzonitrile (27.5 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (1:1 petrol 40-60 °C/toluene) to yield product 5af (15.8 mg, 0.055 mmol, 55%) as a colourless oil.

\[ R_f \ 0.40 \ (1:1 \ petrol \ 40-60 \ °C/toluene); \nu_{\text{max}}/cm^{-1} \ 3023 \ (C-H \text{ Ar}), \ 2922 \ (C-H), \ 2231 \ (C≡N), \ 1597 \ (C-C \text{ Ar}), \ 1514 \ (C-C \text{ Ar}), \ 1479 \ (C-C \text{ Ar}); \textsuperscript{1}H \text{ NMR} \ (\text{CDCl}_3, \ 400 \ MHz) \ \delta_H \ 7.86 \ (d, \ J = 1.7 \ Hz, 1H, \text{Ar-H}), \ 7.50 \ (dd, \ J = 8.0, 1.7 \ Hz, 1H, \text{Ar-H}), \ 7.19 \ (d, \ J = 8.0 \ Hz, 1H, \text{Ar-H}), \ 7.14 \ (d, \ J = 7.9 \ Hz, 2H, \text{Ar-H}), \ 7.06 \ (d, \ J = 7.9 \ Hz, 2H, \text{Ar-H}), \ 4.11 \ (s, 2H, \text{CH}_2), \ 2.34 \ (s, 3H, \text{CH}_3); \textsuperscript{13}C \text{ NMR} \ (\text{CDCl}_3, \ 101 \ MHz) \ \delta_C \ 146.8 \ (C), \ 136.7 \ (C), \ 136.1 \ (CH), \ 134.9 \ (C), \ 131.5 \ (CH), \ 131.1 \ (CH), \ 129.6 \ (CH), \ 129.1 \ (CH), \ 125.3 \ (C), \ 117.5 \ (C), \ 111.9 \ (C), \ 41.7 \ (\text{CH}_2), \ 21.2 \ (\text{CH}_3); \textsuperscript{HRMS} \text{ Found} \ (\text{FTMS + p APCI}) \ [M+H]^+ \ 286.0225, \text{C}_{15}H_{13}NBr \text{ requires} \ 286.0226. \]
3-Fluoro-4-(4-methylbenzyl)benzonitrile (5ag)

Following the general procedure, 4-(bromomethyl)-3-fluorobenzonitrile (21.4 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 96 h. The crude was purified by silica gel flash column chromatography (9:11 petrol 40-60 °C/toluene) to yield product 5ag (13.4 mg, 0.060 mmol, 60%) as a colourless oil.

Rf 0.43 (2:3 petrol 40-60 °C/toluene); νmax/cm⁻¹ 3023 (C=H Ar), 2922 (C-H), 2233 (C≡N), 1607 (C=C Ar), 1571 (C=C Ar), 1498 (C=C Ar); ¹H NMR (CDCl₃, 400 MHz) δH 7.39 – 7.31 (m, 2H, Ar-H), 7.26 – 7.21 (m, 1H, Ar-H), 7.21 – 7.18 (m, 1H, (p-tolyl)), 7.09 – 7.03 (m, 1H, (p-tolyl)), 7.01 – 6.97 (m, 2H, Ar-H (p-tolyl)), 4.00 (s, 2H, CH₂), 2.33 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 101 MHz) δC 160.5 (d, J = 249.3 Hz, C), 138.7 (C), 138.1 (C), 134.7 (d, J = 16.0 Hz, C), 132.1 (d, J = 5.1 Hz, CH), 129.8 (CH), 128.9 (CH), 128.3 (d, J = 3.8 Hz, CH), 127.7 (CH), 126.0 (CH), 119.2 (d, J = 25.9 Hz, CH), 117.8 (d, J = 2.7 Hz, C), 111.7 (d, J = 9.4 Hz, C), 34.9 (d, J = 2.8 Hz, CH₂), 21.5 (CH₃); ¹⁹F NMR (CDCl₃, 376 MHz) δF -114.37 (dd, J = 7.9 Hz, 7.9 Hz); HRMS Found (TOF MS ASAP+) [M+H]+ 226.1035 C₁₅H₁₃NF requires 226.1032.

Note: The seemingly “extra” CH signals in the ¹³C NMR spectra are due to the 4 CHs on the p-tolyl ring being inequivalent. This is supported by HSQC NMR experiments. Spectra provided in Section 8.

1,2,3,4,5-Pentafluoro-6-(4-methoxybenzyl)benzene (5bh)

Following the general procedure, 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (26.1 mg, 0.1 mmol) was reacted with (4-methoxyphenyl)boronic acid (45.6 mg, 0.3 mmol) for 48 h. The crude was purified by silica gel flash column chromatography (1:0→99:1→19:1 petrol 40-60 °C/toluene) to yield product 5bh (14.8 mg, 0.051 mmol, 51%) as a colourless oil.

Rf 0.24 (99:1 petrol 40-60 °C/toluene); νmax/cm⁻¹ 3006 (C-H Ar), 2931 (C-H), 1504 (C=C Ar), 1465 (C=C Ar), 1422 (C=C Ar), 1247 (C-O-C); ¹H NMR (CDCl₃, 400 MHz) δH 7.16 (d, J = 8.8 Hz, 2H, Ar-H), 6.83 (d, J = 8.8 Hz, 2H, Ar-H), 3.96 (t, J = 1.9 Hz, 2H, CH₂), 3.78 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 101 MHz) δC 158.8 (C), 129.7 (C), 129.5 (CH), 114.4 (CH), 55.4 (CH₃), 27.5 (CH₂), 6 quaternary Cs (4 signals expected) on the pentafluorophenyl moiety are missing due to low intensity resulting from extensive coupling to fluorine but all other spectral and characterisation
data are consistent with literature data;\textsuperscript{15} \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 376 MHz) \(\delta_F\) -143.55 – -143.68 (m), -157.39 (t, \(J = 21.3\) Hz), -162.32 – -162.51 (m).

**Methyl 2-(4-methoxybenzyl)-3-nitrobenzoate (5bi)**

Following the general procedure, methyl 2-(bromomethyl)-3-nitrobenzoate (27.4 mg, 0.1 mmol) was reacted with (4-methoxyphenyl)boronic acid (45.6 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (1:3→1:5→1:7→1:10 petrol 40-60 °C/toluene) to yield product 5bi (16.2 mg, 0.054 mmol, 54%) as a yellow oil.

\(R_f\) 0.22 (1:7 petrol 40-60 °C/toluene); \(v_{\text{max}}/\text{cm}^{-1}\) 3026 (C-H Ar), 2925 (C-H), 2852 (C-H), 1727 (C=O), 1606 (C-C Ar), 1532 (NO\textsubscript{2}), 1435 (C-C Ar), 1347 (NO\textsubscript{2}), 1249 (C-O-C); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \(\delta_H\) 7.94 (dd, \(J = 7.9, 1.4\) Hz, 1H, Ar-H), 7.82 (dd, \(J = 7.9, 1.4\) Hz, 1H, Ar-H), 7.44 (dd, \(J = 7.9, 7.9\) Hz, 1H, Ar-H), 7.00 – 6.91 (m, 2H, Ar-H), 6.81 – 6.72 (m, 2H, Ar-H), 4.45 (s, 2H, CH\textsubscript{2}), 3.81 (s, 3H, CH\textsubscript{3}), 3.75 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) \(\delta_C\) 167.2 (C), 158.2 (C), 152.1 (C), 135.1 (C), 134.2 (C), 133.6 (CH), 130.9 (C), 129.7 (CH), 127.4 (CH), 126.9 (CH), 113.9 (CH), 55.3 (CH\textsubscript{3}), 52.8 (CH\textsubscript{3}), 32.8 (CH\textsubscript{2}); HRMS Found (TOF MS ASAP+) [M-CH\textsubscript{3}]\textsuperscript{+} 286.0714 C\textsubscript{15}H\textsubscript{12}NO\textsubscript{5} requires 286.0715.

**Methyl 3-chloro-4-(4-methylbenzyl)benzoate (5aj)**

Following the general procedure, methyl 2-(bromomethyl)-5-chlorobenzoate (26.4 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. Analysis of the crude \textsuperscript{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 47%. Due to co-elution with the benzyl bromide starting material an accurate isolated yield for the reaction could not be determined. 5aj was previously unknown in the literature therefore, the co-eluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed \textit{in vacuo}. The resulting residue was then subjected to silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) which yielded a pure sample of 5aj as a colourless oil which was then used for characterisation.

\(R_f\) 0.28 (7:3 petrol 40-60 °C/toluene); \(v_{\text{max}}/\text{cm}^{-1}\) 3023 (C-H Ar), 2952 (C-H), 2924 (C-H), 1721 (C=O), 1604 (C-C Ar), 1562 (C-C Ar), 1514 (C-C Ar), 1436 (C-C Ar); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta_H\)
8.04 (d, J = 1.7 Hz, 1H, Ar-H), 7.83 (dd, J = 8.0, 1.7 Hz, 1H, Ar-H), 7.20 (d, J = 8.0 Hz, 1H, Ar-H), 7.12 (d, J = 8.0 Hz, 2H, Ar-H), 7.07 (d, J = 8.0 Hz, 2H, Ar-H), 4.10 (s, 2H, CH₂), 3.91 (s, 3H, CH₃), 2.33 (s, 3H, CH₃); **¹³C NMR** (CDCl₃, 101 MHz) δc 166.1 (C), 144.3 (C), 136.3 (C), 135.7 (C), 134.6 (C), 131.0 (CH), 130.8 (CH), 129.9 (C), 129.5 (CH), 129.0 (CH), 128.0 (CH), 52.4 (CH₃), 39.1 (CH₂), 21.2 (CH₃); **HRMS** Found (TOF MS ASAP+) [M+H]⁺ 275.0840 C₁₆H₁₆O₂Cl requires 275.0839.

1-Methyl-4-(1-(4-nitrophenyl)ethyl)benzene (5am)¹⁶

Following the general procedure, 1-(1-bromoethyl)-4-nitrobenzene (23.0 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 16 h. Analysis of the crude **¹H NMR** spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 45%. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5am** (6.4 mg, 0.027 mmol, 27%) as a yellow solid.

Rf 0.33 (4:1 petrol 40-60 °C/toluene); νmax/cm⁻¹: 2970 (C-H Ar), 2925 (C-H), 1597 (C-C Ar), 1514 (NO₂), 1492 (C-C Ar), 1453 (C-C Ar), 1345 (NO₂); **¹H NMR** (CDCl₃, 400 MHz) δh 8.13 (d, J = 8.9 Hz, 2H, Ar-H), 7.36 (d, J = 8.9 Hz, 2H, Ar-H), 7.13 (d, J = 8.2 Hz, 2H, Ar-H), 7.08 (d, J = 8.2 Hz, 2H, Ar-H), 4.22 (q, J = 7.2 Hz, 1H, CH), 2.32 (s, 3H, Ar-CH₃), 1.66 (d, J = 7.2 Hz, 3H, CH₃); **¹³C NMR** (CDCl₃, 101 MHz) δc 154.5 (C), 146.6 (C), 141.7 (C), 136.5 (C), 129.6 (CH), 128.5 (CH), 127.6 (CH), 123.8 (CH), 44.6 (CH), 21.7 (CH₃), 21.1 (CH₃); m.p. = 69-71 °C.

1-Methyl-3-(4-nitrobenzyl)benzene (5ba)¹⁷

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 3-tolylboronic acid (40.8 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5ba** (13.0 mg, 0.057 mmol, 57%) as a yellow oil.

Rf 0.34 (4:1 petrol 40-60 °C/toluene); νmax/cm⁻¹: 3010 (C-H Ar), 2922 (C-H), 1605 (C-C Ar), 1515 (NO₂) 1492 (C-H Ar), 1345 (NO₂); **¹H NMR** (CDCl₃, 400 MHz) δh 8.14 (d, J = 8.8 Hz, 2H, Ar-H), 7.34 (d, J = 8.8 Hz, 2H, Ar-H), 7.25 – 7.18 (m, 1H, Ar-H), 7.09 – 7.03 (m, 1H, Ar-H), 7.00 – 6.95 (m, 2H, Ar-H), 4.04 (s, 2H, CH₂), 2.33 (s, 3H, CH₃); **¹³C NMR** (CDCl₃, 101 MHz) δc 149.1 (C), 146.7 (C), 139.3 (C), 138.7 (C), 129.9 (CH), 129.8 (CH), 128.9 (CH), 127.7 (CH), 126.1(CH), 123.9 (CH), 41.9 (CH₂), 21.5 (CH₃).
1-Methyl-2-(4-nitrobenzyl)benzene (5ca)\(^{18}\)

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 2-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. Analysis of the crude \(^1\)H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 51%. Due to co-elution with the benzyl bromide starting material an accurate isolated yield for the reaction could not be determined. 5ca was previously known in the literature but as part of a mixture of isomers, therefore, the co-eluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed in vacuo. The resulting residue was then subjected to silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) which yielded a pure sample of 5ca as a colourless oil which was then used for characterisation.

R\(_f\) 0.30 (7:3 petrol 40-60 °C/toluene); \(\nu_{\text{max}}/\text{cm}^{-1}\) 3013 (C-H Ar), 2925 (C-H), 1597 (C-C Ar), 1516 (NO\(_2\)), 1492 (C-C Ar), 1462 (C-C Ar), 1345 (NO\(_2\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta_H\) 8.13 (d, \(J = 8.8\) Hz, 2H, Ar-H), 7.26 (d, \(J = 8.8\) Hz, 2H, Ar-H), 7.22 – 7.17 (m, 3H, Ar-H), 7.12 – 7.08 (m, 1H, Ar-H), 4.09 (s, 2H, CH\(_2\)), 2.21 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta_C\) 148.5 (C), 146.7 (C), 137.3 (C), 136.7 (C), 130.8 (CH), 130.2 (CH), 129.5 (CH), 127.3 (CH), 126.5 (CH), 123.8 (CH), 39.6 (CH\(_2\)), 19.8 (CH\(_3\)).

1-Benzyl-4-nitrobenzene (5da)\(^{11}\)

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 2-tolyboronic acid (36.6 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product 5da (12.3 mg, 0.058 mmol, 58%) as a yellow oil.

R\(_f\) 0.30 (4:1 petrol 40-60 °C/toluene); \(\nu_{\text{max}}/\text{cm}^{-1}\) 3028 (C-H Ar), 2922 (C-H), 1605 (C-C Ar), 1595 (C-C Ar), 1516 (NO\(_2\)), 1495 (C-C Ar), 1453 (C-H), 1347 (NO\(_2\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta_H\) 8.15 (d, \(J = 8.7\) Hz, 2H, Ar-H), 7.37 – 7.30 (m, 4H, Ar-H), 7.28 – 7.22 (m, 1H, Ar-H), 7.17 (d, \(J = 8.7\) Hz, 2H, Ar-H), 4.08 (s, 2H, CH\(_2\)); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta_C\) 149.0 (C), 146.8 (C), 139.3 (C), 129.8 (CH), 129.1 (CH), 129.0 (CH), 126.9 (CH), 123.9 (CH), 41.9 (CH\(_2\)).
1-Methoxy-4-(4-nitrobenzyl)benzene (5ea)\textsuperscript{19}

```
O
\text{\textsuperscript{1}N} 3
\text{\textsuperscript{3}MeO} 1
```

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-methoxyphenyl)boronic acid (45.6 mg, 0.3 mmol) for 16 h. Analysis of the crude \textsuperscript{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 57\%, with spectral data matching literature data.\textsuperscript{19} Column chromatography was attempted but product 5ea co-elluted with homocoupling product under a number of solvent systems and could not be separated.

1-Chloro-4-(4-nitrobenzyl)benzene (5fa)\textsuperscript{21}

```
O
\text{\textsuperscript{1}N} 3
\text{\textsuperscript{3}Cl} 1
```

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-chlorophenyl)boronic acid (46.9 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (8:1:1 petrol 40-60 °C/toluene/ethyl acetate) to yield product 5fa (10.8 mg, 0.044 mmol, 44\%) as an orange solid. 

\textbf{R}\textsubscript{f} 0.51 (8:1:1 petrol 40-60 °C/toluene/ethyl acetate); \textit{v}\textsubscript{max}/cm\textsuperscript{-1} 3028 (C-H Ar), 2926 (C-H), 1606 (C-C Ar), 1519 (NO\textsubscript{2}), 1492 (C-C Ar), 1347 (NO\textsubscript{2}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \textdelta\textsubscript{H} 8.15 (d, J = 8.9 Hz, 2H, Ar-H), 7.32 (d, J = 8.9 Hz, 2H, Ar-H), 7.29 (d, J = 8.6 Hz, 2H, Ar-H), 7.10 (d, J = 8.6 Hz, 2H, Ar-H), 4.05 (s, 2H, CH\textsubscript{2}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) \textdelta\textsubscript{C} 148.3 (C), 146.9 (C), 137.8 (C), 132.9 (C), 130.4 (CH), 129.8 (CH), 129.1 (CH), 124.0 (CH), 41.2 (CH\textsubscript{2}); m.p. = 63-66 °C.

1-Fluoro-4-(4-nitrobenzyl)benzene (5ga)\textsuperscript{20}

```
O
\text{\textsuperscript{1}N} 3
\text{\textsuperscript{3}F} 1
```

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-fluorophenyl)boronic acid (42.0 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product 5ga (12.1 mg, 0.052 mmol, 52\%) as an off-white solid.

\textbf{R}\textsubscript{f} 0.25 (4:1 petrol 40-60 °C/toluene); \textit{v}\textsubscript{max}/cm\textsuperscript{-1} 3029 (C-H Ar), 2925 (C-H), 2853 (C-H), 1606 (C-C Ar), 1520 (NO\textsubscript{2}), 1510 (C-C Ar), 1492 (C-C Ar) 1347 (NO\textsubscript{2}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \textdelta\textsubscript{H} 8.15 (d, J = 8.8 Hz, 2H, Ar-H), 7.31 (d, J = 8.8 Hz, 2H, Ar-H), 7.19 - 7.07 (m, 2H, Ar-H), 7.07 - 6.94 (m, 2H, Ar-H), 4.05 (s, 2H, CH\textsubscript{2}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) \textdelta\textsubscript{C} 161.9 (d, J = 245.3 Hz, C), 148.7 (C), 146.8 (C), 135.0 (d, J = 3.2 Hz, C), 130.6 (d, J = 8.2 Hz, CH), 129.7 (CH), 129.1 (CH), 124.0 (CH), 121.1 (CH), 79.0 (CH), 41.2 (CH\textsubscript{2}).
115.8 (d, J = 21.5 Hz, CH), 41.0 (CH$_2$); $^{19}$F NMR (CDCl$_3$, 282 MHz) $\delta$ F -116.05 (tt, J = 9.3, 5.3 Hz); m.p. = 55-56 °C (lit. 58-60 °C).

1-Chloro-2-methyl-4-(4-nitrobenzyl)benzene (Sha)

Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-chloro-3-methylphenyl)boronic acid (51.1 mg, 0.3 mmol) for 96 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product Sha (13.0 mg, 0.050 mmol, 50%) as a colorless solid.

R$_f$ 0.30 (4:1 petrol 40-60 °C/toluene); $\nu_{max}$/cm$^{-1}$ 3027 (C-H Ar), 2925 (C-H), 2852 (C-H), 1606 (C=C Ar), 1597 (C=C Ar), 1517 (NO$_2$), 1480 (C=C Ar), 1346 (NO$_2$); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ H 8.15 (d, J = 8.8 Hz, 2H, Ar-H), 7.32 (d, J = 8.8 Hz, 2H, Ar-H), 7.28 (d, J = 8.2 Hz, 1H, Ar-H), 7.02 (d, J = 1.7 Hz, 1H, Ar-H), 6.93 (dd, J = 8.2, 1.7 Hz, 1H, Ar-H), 4.01 (s, 2H, CH$_2$), 2.34 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ C 148.5 (C), 146.9 (C), 136.6 (C), 133.0 (C), 131.7 (CH), 129.7 (CH), 129.6 (CH), 127.8 (CH), 124.0 (CH), 41.2 (CH$_2$), 20.2 (CH$_3$); HRMS Found (TOF MS ASAP+) [M+H]$^+$ 262.0640 C$_{14}$H$_{13}$NO$_2$Cl requires 262.0635; m.p. = 78-79 °C.

Methyl 2-(3-chloro-4-methoxybenzyl)-3-nitrobenzoate (5ib)

Following the general procedure, methyl 2-(bromomethyl)-3-nitrobenzoate (27.4 mg, 0.1 mmol) was reacted with (3-chloro-4-methoxyphenyl)boronic acid (55.9 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (1:2→1:3→1:5 petrol 40-60 °C/toluene) to yield product 5ib (16.8 mg, 0.050 mmol, 50%) as a yellow solid.

R$_f$ 0.30 (petrol 40-60 °C/toluene 1:3); $\nu_{max}$/cm$^{-1}$ 3022 (C=C Ar), 2954 (C-H), 1727 (C=O), 1606 (C=C Ar), 1532 (NO$_2$), 1501 (C-H Ar), 1463 (C=C Ar), 1441 (C-C Ar), 1359 (NO$_2$), 1286 (ester C-O) 1259 (C-O-C); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ H 7.99 (dd, J = 8.0, 1.4 Hz, 1H, Ar-H), 7.86 (dd, J = 8.0, 1.4 Hz, 1H, Ar-H), 7.48 (dd, J = 8.0 Hz, 1H, Ar-H), 7.07 (d, J = 2.2 Hz, 1H, Ar-H), 6.90 (dd, J = 8.4, 2.2 Hz, 1H, Ar-H), 6.79 (d, J = 8.4 Hz, 1H, Ar-H), 4.44 (s, 2H, CH$_2$), 3.84 (s, 3H, CH$_3$), 3.83 (s, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ C 166.9 (C), 153.7 (C), 152.1 (C), 134.4 (C), 134.1 (C), 133.9 (CH), 132.1 (C), 130.4 (CH), 127.9 (CH), 127.7 (CH), 127.1 (CH), 122.5 (C), 112.1 (CH), 56.3 (CH$_3$), 52.9 (CH$_3$), 32.6 (CH$_2$); HRMS Found (TOF MS ASAP+) [M-CH$_3$]$^+$ 304.0379 C$_{15}$H$_{12}$NO$_3$Cl requires 304.0377; m.p. = 80-81 °C.
1-ido-4-(4-nitrobenzyl)benzene (5la)

Adapting the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with tris(4-iodophenyl)boroxine (110.4 mg, 0.16 mmol) added in two portions at the start and halfway through the reaction time of 72 h. After the second addition the vial was sparged with argon. Analysis of the crude $^1$H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 44%. Due to co-elution with the benzyl bromide starting material an accurate isolated yield for the reaction could not be determined. 5la was previously unknown in the literature therefore, the co-elluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed in vacuo. The resulting residue was then subjected to silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) which yielded a pure sample of 5la as a white solid which was then used for characterisation.

Rf 0.22 (4:1 petrol 40-60 °C/toluene); ν$_{max}$/cm$^{-1}$ 3032 (C-H Ar), 2923 (C-H) 2855 (C-H), 1599 (C-C Ar), 1520 (NO$_2$), 1493 (C-C Ar), 1484 (C-C Ar), 1400 (C-C Ar), 1346 (NO$_2$); $^1$H NMR (CDCl$_3$, 400 MHz) δ$_H$ 8.15 (d, $J$ = 8.8 Hz, 2H, Ar-H), 7.64 (d, $J$ = 8.4 Hz, 2H, Ar-H), 7.31 (d, $J$ = 8.8 Hz, 2H, Ar-H), 6.92 (d, $J$ = 8.4 Hz, 2H, Ar-H), 4.02 (s, 2H, CH$_2$); $^{13}$C NMR (CDCl$_3$, 101 MHz) δ$_C$ 148.1(C), 146.9 (C), 139.0 (C), 138.1 (CH), 131.1 (CH), 129.8 (CH), 124.0 (CH), 92.2 (C), 41.4 (CH$_2$); HRMS Found (TOF MS ASAP+) [M+H]$^+$ 339.9834 C$_{13}$H$_{11}$NO$_2$I requires 339.9834; m.p. = 108-110 °C.
NMR Spectra

H$_3$N→BH$_3$

\[ \text{NH}_3 \rightarrow \text{BH}_3 \]

(pptm)

H$_3$N→BH$_3$

(pptm)
**1H NMR**

**4I**

- **A (δ)**: 8.90
- **B (δ)**: 8.44
- **C (δ)**: 7.54
- **D (δ)**: 4.98

---

**13C NMR**

**4I**

- **δ (ppm)**: 11 hours 54 min

---

**NMR characterization**
**NMR Spectra**


Chemical shifts in ppm.
O$_2$N

5ba

A (0) 8.44
B (0) 5.09
C (0) 7.21
D (0) 7.07

Carbon Characterisation:

13C 100.6 MHz, 6 h 33 min.

47
proton characterisation

\[
\text{8}
\]

E (6) 8.20
F (6) 7.90
G (8) 4.93

H (9) 1.52

\[
\text{8}
\]

C (7) 154.28
C (6) 142.65
C (5) 131.09
C (4) 123.50
C (3) 130.94
C (2) 27.68
C (1) 25.31

1H: 300 MHz; 13C: 75.5 MHz; m/z: 804.43; MS: elemental analysis; 25.0°C; 2 hours; 7 min

carbon characterisation
References