Electronic supplementary information

Phosphine Ligand Triggered Oxidative Decarbonylative 
Homocoupling of Aromatic Aldehydes: Selectively 
Generating Biaryls and Diarylketones 

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1. General information 

Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 
F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed 
chromatography was analyzed by UV lamp (254 nm). GCMS analysis was conducted 
on an Agilent GCMS-6890N instrument equipped with a HP-5 column (30 m × 0.25 
mm, Hewlett-Packard) and Agilent 5973 Mass Selective Detector. High-resolution 
mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). IR 
spectra were recorded by a Nexus 670 Avator FTIR spectrometer. Nuclear magnetic 
resonance (NMR) spectra were recorded on Varian MERCURY plus spectrometer (1H 
500 MHz, 13C 125 MHz or 13C 75 MHz) spectrometer. NMR yield was calculated 
based on the integration using nitromethane as internal standard. Chemical shifts for 
1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with
the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for $^{13}$C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl$_3$: δ 77.23 ppm). Data are reported as following: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $dd$ = doublet of doublets, $t$ = triplet, $q$ = quartet, $m$ = multiplet, $br$ = broad signal), coupling constant (Hz), and integration.

**Reagents:** Unless stated otherwise, liquid aromatic aldehydes were used after distillation under vacuum. Solid aromatic aldehydes, rhodium catalysts and phosphine ligands were used without further purification. Benzene was dried by sodium metal using benzophenone as the indicator.

2. The influence of solvents and concentrations to the homocoupling

**Table S1. Detailed Optimization of the Oxidative Decarbonylative Homocoupling**

<table>
<thead>
<tr>
<th>entry</th>
<th>Rh (mol%)</th>
<th>ligand (mol%)</th>
<th>Solvent/mL</th>
<th>Temp/°C</th>
<th>yield</th>
<th>ratio $^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>PPh$_3$ (6)</td>
<td>PhCl 0.4</td>
<td>150</td>
<td>55</td>
<td>52 : 48</td>
</tr>
<tr>
<td>2</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>PPh$_3$ (6)</td>
<td>dioxane 0.4</td>
<td>150</td>
<td>44</td>
<td>59 : 41</td>
</tr>
<tr>
<td>3</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>PPh$_3$ (6)</td>
<td>DCE 0.4</td>
<td>150</td>
<td>69</td>
<td>62 : 38</td>
</tr>
<tr>
<td>4</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>PPh$_3$ (6)</td>
<td>benzene 0.8</td>
<td>150</td>
<td>73</td>
<td>72 : 28</td>
</tr>
<tr>
<td>5</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>PPh$_3$ (6)</td>
<td>benzene 0.4</td>
<td>140</td>
<td>76</td>
<td>84 : 16</td>
</tr>
<tr>
<td>6</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>dppe (3)</td>
<td>PhCl 0.4</td>
<td>150</td>
<td>45</td>
<td>19 : 81</td>
</tr>
<tr>
<td>7</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>dppe (3)</td>
<td>dioxane 0.4</td>
<td>150</td>
<td>33</td>
<td>&lt;2 : 98</td>
</tr>
<tr>
<td>8</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>dppe (3)</td>
<td>benzene 0.8</td>
<td>150</td>
<td>44</td>
<td>&lt;2 : 98</td>
</tr>
<tr>
<td>9</td>
<td>[(CO)$_2$RhCl]$_2$ (1.25)</td>
<td>dppe (3)</td>
<td>benzene 0.4</td>
<td>140</td>
<td>56</td>
<td>&lt;2 : 98</td>
</tr>
<tr>
<td>10</td>
<td>[(CH$_2$=CH$_2$)$_2$RhCl]$_2$ (1.25)</td>
<td>PPh$_3$ (6)</td>
<td>benzene 0.4</td>
<td>150</td>
<td>65</td>
<td>71 : 29</td>
</tr>
<tr>
<td>11</td>
<td>[(CH$_2$=CH$_2$)$_2$RhCl]$_2$ (1.25)</td>
<td>dppe (3)</td>
<td>benzene 0.4</td>
<td>160</td>
<td>58</td>
<td>57 : 43</td>
</tr>
</tbody>
</table>

$^{a}$ Conditions: 1a (0.2 mmol), [Rh], phosphine ligand, TBP (0.5 mmol) and solvent, sealed and stirred for 12 h under argon, unless otherwise noted. $^{b}$ Determined by 1H NMR analysis of the crude reaction mixture using an internal standard.
3. General experimental procedure for the oxidative decarbonylative homocoupling of aromatic aldehydes and characterization data

A general experimental procedure for the decarbonylative coupling is described as following: An oven-dried reaction vessel was charged with [(CO)$_2$RhCl]$_2$ (0.9 mg, 0.0025 mmol, 1.25 mol%), PPh$_3$ (0.9 mg, 0.012 mmol, 6.0 mol%) and benzene (dried over Na) (0.4 mL). After stirring the mixture at r.t. for 12 h under argon, 4-methoxybenzaldehyde 1a (25 μL, 29.8 mg, 0.2 mmol) was added by syringe and the vessel was sealed and heated at 150 °C (oil bath temperature). After 12 h, the resulting mixture was cooled to room temperature, filtered through a short silica gel pad and washed by ethyl acetate. The above solution was evaporated under vacuum and the ratio of the two products was determined by $^1$H NMR using nitromethane as the internal standard. Then the mixture was transferred to silica gel column directly and eluted with hexanes and ethyl acetate (90:10) to give products 2a and 3a (36 mg, 82% yield).

\[ \text{H}_3\text{CO-} \begin{array}{c} \text{O} \\
\text{OCH}_3 \end{array} \]

\textit{2a}[1]: white solid, mp 160 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.48 (d, $J$=8.5 Hz, 4H), 6.96 (d, $J$=8.5 Hz, 4H), 3.85 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 158.9, 133.7, 128.0, 114.4, 55.6.

\[ \text{H}_3\text{CO-} \begin{array}{c} \text{O} \\
\text{OCH}_3 \end{array} \]

\textit{3a}[6]: white solid, mp 142 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.79 (dt, $J$=3.0, 8.5 Hz, 4H), 6.96 (dt, $J$=3.0, 8.5 Hz, 4H), 3.88 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 194.7, 163.0, 132.4, 131.0, 113.6, 55.7.

\[ \text{H}_3\text{CO-} \begin{array}{c} \text{O} \\
\text{OCH}_3 \end{array} \]

\textit{2b}[2]: colorless oil; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.35 (t, $J$=8.0 Hz, 2H),...
7.18 (ddd, J=1.0, 1.5, 8.0 Hz, 2H), 7.12 (t, J=2.5 Hz, 2H), 6.91 (ddd, J=1.0, 3.0, 8.0 Hz, 4H), 3.87 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 160.1, 142.9, 129.9, 119.9, 113.2, 113.0, 55.5.

![Structure of compound 3b](image)

3b$^{[10]}$: colorless oil; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.39-7.33 (m, 6H), 7.13 (ddd, J=1.5, 3.0, 8.0 Hz, 2H), 3.86 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 195.5, 159.8, 139.1, 129.4, 123.1, 119.1, 114.5, 55.7.

![Structure of compound 2e](image)

2e$^{[1]}$: white solid, mp 116 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.48 (dt, J=2.0, 8.0 Hz, 4H), 7.24 (dt, J=2.0, 8.0 Hz, 4H), 2.39 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 138.5, 136.9, 129.6, 127.0, 21.3.

![Structure of compound 3c](image)

3c$^{[6]}$: white solid, mp 92 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.70 (d, J=8.0 Hz, 4H), 7.28 (d, J=8.0 Hz, 4H), 2.44 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 196.3, 142.9, 135.2, 130.2, 128.9, 21.6.

![Structure of compound 2d](image)

2d$^{[4]}$: white solid, mp 150 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.55 (dt, J=2.5, 8.0 Hz, 4H), 7.16 (dt, J=2.5, 8.0 Hz, 4H), 2.33 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 169.8, 150.4, 138.4, 128.4, 122.1, 21.4.

![Structure of compound 2e](image)

2e$^{[1]}$: white solid, mp 70 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) δ (ppm) 7.59-7.61 (m, 4H), 7.43-7.46 (m, 4H), 7.34-7.37 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) δ (ppm) 141.5, 129.0, 127.5, 127.4.
3e \[^6\]: white solid, mp 48 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 7.80-7.82 (m, 4H), 7.57-7.61 (m, 2H), 7.47-7.50 (m, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 196.9, 137.8, 132.6, 130.2, 128.4.

\[
\begin{array}{c}
\text{F} \\
\text{O} \\
\text{F}
\end{array}
\]

2f \[^1\]: white solid, mp 86 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 7.48-7.50 (m, 4H), 7.10-7.14 (m, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 162.6 (d, \(J=245.0\) Hz), 136.6 (d, \(J=3.2\) Hz), 128.8 (d, \(J=7.9\) Hz), 115.9 (d, \(J=21.2\) Hz).

\[
\begin{array}{c}
\text{F} \\
\text{O} \\
\text{F}
\end{array}
\]

3f \[^7\]: white solid, mp 104 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 7.80-7.84 (m, 4H), 7.15-7.20 (m, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 194.0, 165.6 (d, \(J=253.5\) Hz), 133.9 (d, \(J=3.2\) Hz), 132.7 (d, \(J=9.2\) Hz), 115.8 (d, \(J=21.8\) Hz).

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl}
\end{array}
\]

2g \[^3\]: white solid, mp 145 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 7.56 (dt, \(J=2.0, 8.0\) Hz, 4H), 7.42 (dt, \(J=2.0, 8.0\) Hz, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 138.6, 134.0, 129.3, 128.4.

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl}
\end{array}
\]

3g \[^11\]: white solid, mp 144 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 7.73 (dt, \(J=2.0, 8.5\) Hz, 4H), 7.47 (dt, \(J=2.0, 8.5\) Hz, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 194.5, 135.7, 131.5, 129.0.

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Cl}
\end{array}
\]

2h \[^3\]: colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 7.55 (t, \(J=2.0\)Hz, 2H), 7.44 (dt, \(J=1.5, 8.0\) Hz, 2H), 7.38 (t, \(J=8.0\)Hz, 2H), 7.35 (dt, \(J=1.5, 8.0\) Hz, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\), TMS) \(\delta\) (ppm) 141.8, 135.0, 130.3, 128.1, 127.5, 125.5.
3h[8]: white solid, mp 170 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 7.74 (t, $J$=2.0Hz, 2H), 7.65 (dt, $J$=1.0, 8.0 Hz, 2H), 7.59 (ddd, $J$=1.0, 2.0, 8.0Hz, 2H), 7.35 (t, $J$=8.0 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 194.0, 138.8, 135.0, 133.0, 130.05, 130.0, 128.3.

2i[5]: white solid, mp 170 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 7.62 (d, $J$=2.5Hz, 2H), 7.52 (d, $J$=8.5 Hz, 2H), 7.36 (dd, $J$=3.0, 11.0Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 138.9, 133.4, 132.7, 131.2, 129.0, 126.3.

2j[1]: white solid, mp 220 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 7.78 (dt, $J$=2.0, 8.5Hz, 4H), 7.69 (dt, $J$=2.0, 8.5 Hz, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 143.7, 133.1, 128.2, 118.6, 112.7.

2k[2]: white solid, mp 80 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 7.74 (d, $J$=8.5Hz, 4H), 7.71 (d, $J$=8.5 Hz, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 143.5, 130.5 (d, $J$=32.3Hz), 127.9, 126.2 (q, $J$=3.6Hz), 124.3 (d, $J$=270.6Hz).

3k[10]: white solid, mp 110 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 7.91 (d, $J$=8.5Hz, 4H), 7.79 (d, $J$=8.5 Hz, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 194.6, 140.0, 134.6 (d, $J$=32.9Hz), 130.4, 125.8 (q, $J$=3.8Hz), 123.7 (d, $J$=271.1Hz).

2l[1]: white solid, mp 210 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$ (ppm) 8.13 (dt, $J$=2.0, 8.5Hz, 4H), 7.69 (dt, $J$=2.0, 8.5 Hz, 4H), 3.95 (s, 6H); $^{13}$C NMR (125 MHz,
$\text{CDCl}_3, \text{TMS}) \delta (\text{ppm}) 167.0, 144.6, 130.4, 129.9, 127.5, 52.4.$

\[
\text{O}
\quad \text{O}
\]

**3m**: colorless oil; $^1\text{H NMR (500 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 8.05 (dt, J=2.5, 9.5Hz, 4H), 6.93 (dt, J=2.5, 9.5 Hz, 4H), 4.03 (t, J=6.5 Hz, 4H), 1.80-1.84 (m, 4H), 1.37-1.47 (m, 8H), 0.94 (t, J=6.5 Hz, 6H); $^{13}\text{C NMR (125 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 170.8, 163.9, 132.5, 121.4, 114.4, 68.5, 29.0, 28.3, 22.6, 14.2.$ HRMS (ESI) m/z: [M+Na]$^+$ calcd for C$_{23}$H$_{30}$O$_3$Na, 377.2087; found: 377.2096.

\[
\text{O}
\quad \text{O}
\]

**3n**: colorless oil; $^1\text{H NMR (500 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 7.63 (s, 2H), 7.57 (d, J=7.5 Hz, 2H), 7.34-7.41 (m, 4H), 2.42 (s, 6H); $^{13}\text{C NMR (125 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 197.4, 138.3, 138.0, 133.3, 130.6, 128.2, 127.6, 21.6.$

\[
\text{O}
\quad \text{O}
\]

**3o**$^9$: white solid, mp 64 °C; $^1\text{H NMR (500 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 7.39 (td, J=1.5, 7.5 Hz, 2H), 7.31 (dd, J=1.5, 7.5 Hz, 2H), 7.28 (dd, J=1.0, 7.5 Hz, 2H), 7.20 (td, J=1.0, 7.5 Hz, 2H), 2.44 (s, 6H); $^{13}\text{C NMR (125 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 201.0, 139.2, 138.4, 131.6, 131.3, 130.5, 125.6, 20.9.$

\[
\text{O}
\quad \text{O}
\]

**3p**: colorless oil; $^1\text{H NMR (500 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 7.21 (d, J=2.5Hz, 2H), 7.08 (s, 2H), 6.99 (d, J=2.5 Hz, 2H), 2.41 (s, 6H), 2.36 (s, 6H); $^{13}\text{C NMR (125 MHz, CDCl}_3, \text{TMS}) \delta (\text{ppm}) 200.4, 141.3, 138.3, 136.5, 132.2, 130.6, 127.6.$ HRMS (ESI) m/z: [M+1]$^+$ calcd for C$_{17}$H$_{19}$O, 239.1430; found: 239.1433.
4. References


5. Copies of $^1$H and $^{13}$C NMR spectra of products 2a-6l, 3a-3c, 3d-3h, 3k, 3m-3p
2b

- Chemical structure
- NMR spectroscopy
- Mass spectrometry
Supplementary Material (ESI) for Chemical Communications
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F₃C-\(\text{C}_{6}\text{H}_{5}\)-CF₃

2k

1H NMR spectrum

31P NMR spectrum
3e

Supplementary Material (ESI) for Chemical Communications
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Supplementary Material (ESI) for Chemical Communications
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\text{CH}_3 \quad \text{CH}_3 \\
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\[3\alpha\]

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\text{6} \quad \text{7} \\
\text{1} \quad \text{2} \\
\text{p.p.m}
\]

\[
\text{60} \quad \text{120} \\
\text{180} \quad \text{240} \\
\text{p.p.m}
\]

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