Supporting Information for

A Versatile Approach for the Synthesis of para-Substituted Arenes via Palladium-Catalyzed C-H Functionalization and Protodecarboxylation of Benzoic Acids

Shulei Pan, Bo Zhou, Yanghui Zhang*, Changdong Shao, Guangfa Shi,

Shanghai Key Laboratory of Chemical Assessment and Sustain-ability, Department of Chemical, and UNEP-Tongji Institute of Environment for Sustainable Development, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. of China

Email: zhangyanghui@tongji.edu.cn

Table of Contents

I. General Information.................................................................S2
II. General Procedure for the Synthesis of para-Substituted Arenes.........S3
III. References and Notes...............................................................S5
IV. Characterization of Synthesized Compounds.................................S6
V. NMR Spectra..............................................................................S17
I. General Information

Pd(OAc)_2 and Pd(TFA)_2 were purchased from Strem Chemicals. The solvents and the inorganic salts were purchased from Tansoole. The solvents were purified by distillation prior to use. Unless otherwise noted, the other commercial chemicals were used without further purification. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were recorded with Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. \textsuperscript{1}H NMR spectra were recorded in CDCl\textsubscript{3} and referenced to residual CDCl\textsubscript{3} at 7.26 ppm, and \textsuperscript{13}C NMR spectra were referenced to the central peak of CDCl\textsubscript{3} at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance.

Table 1. Starting materials

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
</tr>
<tr>
<td>![ benzene with COOH ]</td>
<td>![ benzene with CF\textsubscript{3} ]</td>
<td>![ benzene with O ]</td>
<td>![ benzene with Ph ]</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
</tr>
<tr>
<td>![ benzene with CO\textsubscript{2}Me ]</td>
<td>![ benzene with COOH ]</td>
<td>![ benzene with F ]</td>
<td>![ benzene with Cl ]</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
</tr>
<tr>
<td>![ benzene with Br ]</td>
<td>![ benzene with OMe ]</td>
<td>![ benzene with OH ]</td>
<td>![ benzene with NO\textsubscript{2} ]</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
<td>COOH</td>
</tr>
<tr>
<td>![ benzene with NH\textsubscript{Ac} and F ]</td>
<td>![ benzene with Cl ]</td>
<td>![ benzene with COOH ]</td>
<td>![ benzene with COOH ]</td>
</tr>
</tbody>
</table>

The benzoic acids were purchased from Adamas-beta, Sigma-Aldrich, TCI or Alfa Aesar. \( \alpha \)-Oxocarboxylic acid(14-16) were prepared from oxidation of corresponding methyl ketones with SeO\textsubscript{2} according to the reported procedure.\textsuperscript{1}
II. General Procedure for the Synthesis of para-Substituted Arenes

The synthesis of para-arylated arenes

\[ \text{R} - \text{COOH} + \text{Arl} \rightarrow \text{Ar} - \text{R} \]

1) Pd(OAc)$_2$ (2 mmol %), Ag$_2$CO$_3$ (0.55 equiv), K$_2$CO$_3$ (0.50 equiv), AcOH (4.50 equiv), 120 °C, 24 h

2) Cu$_2$O (5 mmol %), Phen (10 mmol %), quinoline/NMP (1:3), 170 °C, 24 h, N$_2$

A mixture of benzoic acid (0.50 mmol), aryl iodide (1.50 mmol), Ag$_2$CO$_3$ (76.0 mg, 0.28 mmol), K$_2$CO$_3$ (35.0 mg, 0.25 mmol), and Pd(OAc)$_2$ (2.3 mg, 0.01 mmol) in acetic acid (130.0 µL) under an atmosphere of N$_2$ was heated at 120 °C for 24 h. After cooling down to room temperature, the reaction mixture was quenched by addition of 2.0 M aqueous HCl (10 mL), diluted with ethyl acetate (10 mL), and then filtered through a pad of Celite. The filtrate was washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo, yielding crude 2-phenylbenzoic acid derivatives. A mixture of the crude product, Cu$_2$O (3.6 mg, 0.025 mmol), and 1,10-phenanthroline (9.0 mg, 0.050 mmol) in a solution of NMP (1.5 mL) and quinoline (0.5 mL) under an atmosphere of N$_2$ was heated at 170 °C for 24 h. The reaction mixture was quenched by addition of 0.2 M aqueous HCl (10 mL), diluted with ethyl acetate (10 mL), and then filtered through a pad of Celite. The filtrate was washed with brine (10 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by silica gel preparative TLC to give the corresponding products.

The synthesis of para-benzoxylated arenes

\[ \text{R} - \text{COOH} + \text{ArCO}_{\text{OH}} \rightarrow \text{Ar} - \text{R} \]

1) Pd(TFA)$_2$ (10 mmol %), Ag$_2$CO$_3$ (3.00 equiv), DME, 150-165 °C, 24-48 h

2) Cu$_2$O (5 mmol %), Phen (10 mmol %), quinoline/NMP (1:3), 170 °C, 24 h, N$_2$

A mixture of benzoic acid (0.20 mmol), benzoyleformic acid (0.60 mmol), Pd(TFA)$_2$ (6.6 mg, 0.020 mmol), and Ag$_2$CO$_3$ (165.5 mg, 0.60 mmol) in DME (2 mL) was heated at 150-165 °C for 24-48 h. After cooling down to room temperature, the reaction mixture was diluted by addition of ethyl acetate (10 mL) and then filtered...
through a pad of Celite. The filtrate was concentrated \textit{in vacuo} to afford 2-benzoylbenzoic acid derivatives. A mixture of the crude product, Cu$_2$O (1.4 mg, 0.010 mmol), and 1,10-phenanthroline (3.6 mg, 0.020 mmol) in a solution of NMP (1.5 mL) and quinoline (0.5 mL) under an atmosphere of N$_2$ was heated at 170 °C for 24 h. The reaction mixture was quenched by addition of 0.2 M aqueous HCl (10 mL), diluted with ethyl acetate (10 mL), and then filtered through a pad of Celite. The filtrate was washed with brine (10 mL), dried over Na$_2$SO$_4$, and concentrated \textit{in vacuo}. The residue was purified by silica gel preparative TLC to give the corresponding products.

\textbf{The synthesis of para-hydroxylated arenes}\textsuperscript{2,5}

\[
\begin{align*}
R-\text{COOH} + O_2 & \quad \rightarrow \quad R-\text{OH} \\
1) \text{Pd(OAc)}_2 (10 \text{ mmol }\%), & \quad \text{KOAc} (2.00 \text{ equiv}), \\
& \quad \text{BQ (1.00 equiv), DMA,} \\
& \quad 115 \degree \text{C, 15 h}; \\
2) \text{Cu}_2\text{O} (5 \text{ mmol}%), & \quad \text{Phen} (10 \text{ mmol}%), \\
& \quad \text{quinoline/NMP (1:3),} \\
& \quad 220 \degree \text{C, 12 h, N}_2
\end{align*}
\]

A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) was charged with benzoic acid (0.50 mmol), benzoquinone (54.0 mg, 0.50 mmol), KOAc (98.0 mg, 1.00 mmol), Pd(OAc)$_2$ (11.2 mg, 0.050 mmol), and \textit{N,N}-dimethylacetamide (1.5 mL). The reaction tube was evacuated and back-filled with O$_2$ (3 times, ballon). After the reaction mixture was stirred at 115 °C for 15 h, it was allowed to cool down to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL), and then filtered through a pad of Celite. The filtrate was concentrated \textit{in vacuo} to yield crude 2-hydroxybenzoic acid. A mixture of the crude product, Cu$_2$O (3.6 mg, 0.025 mmol), and 1,10-phenanthroline (9.0 mg, 0.050 mmol) in a solution of NMP (1.5 mL) and quinoline (0.5 mL) under an atmosphere of N$_2$ was heated at 220 °C for 12 h. The reaction mixture was quenched by addition of 0.2 M aqueous HCl (10 mL), diluted with ethyl acetate (10 mL), and then filtered through a pad of Celite. The filtrate was washed with brine (10 mL), dried over Na$_2$SO$_4$, and concentrated \textit{in vacuo}. The residue was purified by silica gel preparative TLC to give the corresponding products.

\textbf{General Procedure for Hydroxylation Reactions with 5 atm O$_2$}

A 50 mL high pressure reactor was charged with benzoic acid substrate (0.50 mmol), KOAc (98.0 mg, 1.00 mmol), benzoquinone (54.0mg, 0.50mmol), Pd(OAc)$_2$ (11.2mg, 0.050 mmol), and \textit{N,N}-dimethylacetamide (1.5 mL). The reactor was filled with O$_2$ (20 atm), and then evacuated and back-filled with O$_2$ (5 atm, 2 times). After the reaction mixture was stirred at 115 °C for 15 h, it was allowed to cool to room
temperature. The reaction mixture was diluted with EtOAc (10 mL) and then filtered through a pad of Celite. The filtrate was concentrated *in vacuo* to yield crude 2-hydroxylbenzoic acid. A mixture of the crude sproduct, Cu₂O (3.6 mg, 0.025 mmol), and 1,10-phenanthroline (9.0 mg, 0.050 mmol) in a solution of NMP (1.5 mL) and quinoline (0.5 mL) under an atmosphere of N₂ was heated at 220 °C for 12 h. The reaction mixture was quenched by addition of 0.2 M aqueous HCl (10 mL), diluted with ethyl acetate (10 mL), and then filtered through a pad of Celite. The filtrate was washed with brine (10 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by silica gel preparative TLC to give the corresponding products.

III. References and Notes
IV. Characterization of the synthesized compounds

4-Methylbiphenyl (1a)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Ph} \\
\end{align*}
\]

\[^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.59 - 7.57 (m, 2H), 7.51 - 7.49 (m, 2H), 7.45 - 7.41 (m, 2H), 7.34 - 7.31 (m, 1H), 7.26 - 7.24 (m, 2H), 2.40 (s, 3H); \ ^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3): \delta 141.14, 138.34, 136.99, 129.45, 128.68, 126.97, 126.95, 21.08. \text{HRMS (ESI-TOF) } m/z: \text{calcld for C}_{13}\text{H}_{13}^+: 169.1012 (M + H)^+, \text{found: 169.0938.}
\]


1,4-Diphenylbenzene (2a)

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\[^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.69 - 7.65 (m, 8H), 7.49 - 7.46 (m, 4H), 7.39 - 7.36 (m, 2H); \ ^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3): \delta 140.69, 140.11, 128.80, 127.48, 127.32, 127.03. \text{HRMS (ESI-TOF) } m/z: \text{calcld for C}_{18}\text{H}_{14}\text{Na}^+: 253.0988 (M + Na)^+, \text{found: 253.0967.}
\]


4-Trifluoro-methylbiphenyl (3a)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{Ph} \\
\end{align*}
\]

\[^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.70 (s, 4H), 7.62 - 7.60 (m, 2H), 7.50 - 7.46 (m, 2H), 7.43 - 7.39 (m, 1H); \ ^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3): \delta 144.73, 139.76, 129.49 (q, J_{C-F} = 32.3 \text{ Hz}), 128.97, 128.16, 127.40, 127.26, 125.68 (q, J_{C-F} = 3.8 \text{ Hz}), 124.28 \text{ (q, } J_{C-F} = 270.2 \text{ Hz}). \text{HRMS (ESI-TOF) } m/z: \text{calcld for C}_{18}\text{H}_{14}\text{Na}^+: 253.0988 (M + Na)^+, \text{found: 253.0967.}
\]


4-Acetylbiphenyl (4a)

\[
\begin{align*}
\text{O} & \quad \text{Ph} \\
\end{align*}
\]

\[^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.05 - 8.03 (m, 2H), 7.70 - 7.68 (m, 2H), 7.66 - 7.62 \text{ ppm.} \]
(m, 2H), 7.50 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H), 2.64 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.75, 145.77, 139.86, 135.84, 128.94, 128.90, 128.21, 127.26, 127.21, 26.66. HRMS (ESI-TOF) \(m/z\): calc for C\(_{14}\)H\(_{12}\)NaO\(^+\): 219.0780 (M + Na\(^+\)), found: 219.0764.


**Methyl 4-Phenylbenzoate (5a)**

\[
\text{MeOOC-} \begin{array}{c}
\text{\textbullet} \\
\text{\textbullet} \\
\text{\textbullet} \\
\end{array} 
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.12 – 8.10 (m, 2H), 7.68 – 7.62 (m, 4H), 7.49 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H), 3.94 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.99, 145.63, 140.00, 130.08, 128.90, 128.88, 128.12, 127.26, 127.03, 52.11. HRMS (ESI-TOF) \(m/z\): calc for C\(_{14}\)H\(_{12}\)NaO\(^+\): 235.0730 (M + Na\(^+\)), found: 235.0744.


**2-Phenylnaphtalene (6a)**

\[
\begin{array}{c}
\text{\textbullet} \\
\text{\textbullet} \\
\text{\textbullet} \\
\text{\textbullet} \\
\end{array} 
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (s, 1H), 7.94 – 7.86 (m, 3H), 7.77 – 7.73 (m, 3H), 7.53 – 7.48 (m, 4H), 7.41 – 7.37 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.12, 138.55, 133.66, 132.60, 128.84, 128.39, 128.18, 127.62, 127.41, 127.33, 126.26, 125.91, 125.78, 125.58. HRMS (ESI-TOF) \(m/z\): calc for C\(_{16}\)H\(_{12}\)Na\(^+\): 227.0831 (M + Na\(^+\)), found: 227.0822.

The data are identical to: Budén, M. E.; Guastavino, J. F.; Rossi, R. A. Org. Lett. 2013, 15, 1174.

**4-Fluorobiphenyl (7a)**

\[
\text{F-} \begin{array}{c}
\text{\textbullet} \\
\text{\textbullet} \\
\text{\textbullet} \\
\end{array} 
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 – 7.54 (m, 4H), 7.46 – 7.42 (m, 2H), 7.37 – 7.34 (m, 1H), 7.16 – 7.11 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 162.44 (d, \(J_{C-F} = 244.7\) Hz), 140.24, 137.32 (d, \(J_{C-F} = 3.2\) Hz), 128.79, 128.66 (d, \(J_{C-F} = 8.0\) Hz), 127.23, 127.00, 115.58 (d, \(J_{C-F} = 21.3\) Hz). HRMS (ESI-TOF) \(m/z\): calc for C\(_{12}\)H\(_{10}\)F\(^+\): 173.0761 (M + H\(^+\)), found: 173.0807.

The data are identical to: Budén, M. E.; Guastavino, J. F.; Rossi, R. A. Org. Lett. 2013, 15, 1174.
4-Chlorobiphenyl (8a)

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 – 7.51 (m, 4H), 7.47 – 7.35 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.98, 139.65, 133.36, 128.89, 128.86, 128.37, 127.57, 126.97.


4-Bromobiphenyl (9a)

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 – 7.55 (m, 4H), 7.47 – 7.43 (m, 4H), 7.39 – 7.36 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.11, 139.98, 131.84, 128.88, 128.72, 127.62, 126.85, 121.51.


4-Methoxybiphenyl (10a)

\[
\begin{align*}
\text{MeO} & \quad \text{MeO} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 – 7.52 (m, 4H), 7.44 – 7.40 (m, 2H), 7.32 – 7.29 (m, 1H), 6.99 - 6.97 (m, 2H), 3.86 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.12, 140.81, 133.77, 128.70, 128.14, 126.72, 126.64, 114.18, 55.34. HRMS (ESI-TOF) \(m/z\): calcd for C\(_{13}\)H\(_{13}\)O\(^+\): 185.0961 (M + H\(^+\)), found: 185.0951.


1,1’-Biphenyl-4-ol (11a)

\[
\begin{align*}
\text{HO} & \quad \text{HO} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (d, \(J\) = 7.9 Hz, 2H), 7.49 (d, \(J\) = 8.3 Hz, 2H), 7.42 (t, \(J\) = 7.5 Hz, 2H), 7.31 (t, \(J\) = 7.3 Hz, 1H), 6.91 (d, \(J\) = 8.3 Hz, 2H), 4.90 (br, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 155.04, 140.73, 134.01, 128.70, 128.37, 126.70, 126.65, 115.62. HRMS (ESI-TOF) \(m/z\): calcd for C\(_{12}\)H\(_{10}\)NaO\(^+\): 193.0624 (M + Na\(^+\),

S8
found: 193.0653.

4-Nitro-1,1'-biphenyl (12a)

\[
\begin{align*}
\text{O}_2\text{N} & & \text{H} \\
\text{H} & & \text{H}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 7.7$ Hz, 2H), 7.52 – 7.45 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.49, 147.05, 138.73, 129.12, 128.88, 127.76, 127.35, 124.07. HRMS (ESI-TOF) $m/z$: calc'd for C$_{12}$H$_9$NNaO$_2^+$: 222.0525 (M + Na)$^+$, found: 222.0511.

4-Methoxy-4'-Methyl-1,1'-Biphenyl (14a)

\[
\begin{align*}
\text{H}_3\text{C} & & \text{H} \\
\text{H} & & \text{OMe}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 7.2$ Hz, 2H), 7.45 (d, $J = 6.8$ Hz, 2H), 7.23 (d, $J = 7.5$ Hz, 2H), 6.97 (d, $J = 7.3$ Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.93, 137.97, 136.34, 133.76, 129.42, 127.94, 126.57, 114.15, 55.34, 21.03.

The data are identical to: Patrick, S. H.; Matthias, S. O.; William, J. K. ACS Catal. 2015, 5, 5041.

4-Fluoro-4'-Methyl-1,1'-Biphenyl (15a)

\[
\begin{align*}
\text{H}_3\text{C} & & \text{F} \\
\text{H} & & \text{H}
\end{align*}
\]
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 – 7.49 (m, 2H), 7.44 (d, \(J = 8.1\) Hz, 2H), 7.24 (d, \(J = 8.1\) Hz, 2H), 7.11 (t, \(J = 8.7\) Hz, 2H), 2.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.29 (d, \(J_{\text{C-F}} = 245.8\) Hz), 137.39, 137.27 (d, \(J_{\text{C-F}} = 3.1\) Hz), 137.02, 129.51, 128.45 (d, \(J_{\text{C-F}} = 8.0\) Hz), 126.84, 115.52 (d, \(J_{\text{C-F}} = 21.3\) Hz), 21.05.

HRMS (ESI-TOF) \(m/z\): calcd for C\(_{13}\)H\(_{12}\)F\(_3\): 187.0918 (M+H\(^+\)), found: 187.0913.

The data are identical to: Patrick, S. H.; Matthias, S. O.; William, J. K. ACS Catal. 2015, 5, 5041.

4-Chloro-4'-Methyl-1,1'-Biphenyl (16a)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 8.6\) Hz, 2H), 7.45 (d, \(J = 8.1\) Hz, 2H), 7.39 (d, \(J = 8.5\) Hz, 2H), 7.25 (d, \(J = 7.9\) Hz, 2H), 2.40 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 139.58, 137.42, 137.09, 133.01, 129.57, 128.82, 128.16, 126.79, 21.09.

The data are identical to: Niu, L.; Hao, Y.; Fu, H. Synlett. 2014, 7, 995.

Phenyl(p-tolyl)methanone (1b)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J = 7.1\) Hz, 2H), 7.72 (d, \(J = 8.1\) Hz, 2H), 7.58 (t, \(J = 7.4\) Hz, 1H), 7.48 (t, \(J = 7.5\) Hz, 2H), 7.28 (d, \(J = 7.9\) Hz, 2H), 2.44 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 196.50, 143.22, 137.95, 134.87, 132.13, 130.29, 129.91, 128.95, 128.18, 21.64. HRMS (ESI-TOF) \(m/z\): calcd for C\(_{14}\)H\(_{12}\)NaO\(^+\): 219.0780 (M + Na\(^+\)), found: 219.0774.

The data are identical to: Li, M.; Wang, C.; Ge, H. Org. Lett. 2011, 13, 2062.

Phenyl(4-(trifluoromethyl)phenyl)methanone (2b)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 8.0\) Hz, 2H), 7.82 (d, \(J = 7.1\)Hz, 2H), 7.76 (d, \(J = 8.2\) Hz, 2H), 7.64 (t, \(J = 7.4\) Hz, 1H), 7.51 (t, \(J = 7.7\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 195.52, 140.72, 136.72, 133.72 (q, \(J_{\text{C-F}} = 32.5\) Hz), 133.07, 130.12, 130.09, 128.52, 125.34 (q, \(J_{\text{C-F}} = 3.7\) Hz), 123.66 (q, \(J_{\text{C-F}} = 271.1\) Hz). HRMS (ESI-TOF) \(m/z\): calcd for C\(_{14}\)H\(_{12}\)F\(_3\)NaO\(^+\): 273.0498 (M + Na\(^+\)), found: 273.0480.

The data are identical to: Li, M.; Wang, C.; Ge, H. Org. Lett. 2011, 13, 2062.

4-Phenylbenzophenone (4b)
\[ \text{Methyl 4-Benzoylbenzoate (5b)} \]

\[ \text{Naphthalen-2-yl(phenyl)methanone (6b)} \]

\[ \text{(4-Fluorophenyl)(phenyl)methanone (7b)} \]
132.64 (d, J_{C-F} = 9.1 Hz), 132.44, 129.85, 128.33, 115.86 (d, J_{C-F} = 21.7 Hz). HRMS (ESI-TOF) m/z: calc'd for C_{13}H_{9}FNaO^+: 223.0530 (M + Na)^+, found: 223.0521.

The data are identical to: Li, M.; Wang, C.; Ge, H. Org. Lett. 2011, 13, 2062.

(4-Chlorophenyl)(phenyl)methanone (8b)

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

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 – 7.75 (m, 4H), 7.61 (t, \(J = 7.4\) Hz, 1H), 7.48 (dd, \(J = 7.6\) Hz, \(J = 8.4\) Hz, 4H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 195.49, 138.89, 137.24, 135.86, 132.63, 131.45, 129.91, 128.62, 128.39. HRMS (ESI-TOF) m/z: calc'd for C_{13}H_{9}ClNaO^+: 239.0234 (M + Na)^+, found: 239.0218.

The data are identical to: Li, M.; Wang, C.; Ge, H. Org. Lett. 2011, 13, 2062.

(4-Bromophenyl)(phenyl)methanone (9b)

\[
\text{Br} \begin{array}{c}
\text{Ph} \\
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 – 7.76 (m, 2H), 7.69 – 7.67 (m, 2H), 7.64 – 7.59 (m, 3H), 7.49 (t, \(J = 7.6\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 195.62, 137.16, 136.29, 132.66, 131.60, 131.54, 129.92, 128.39, 127.49. HRMS (ESI-TOF) m/z: calc'd for C_{13}H_{9}BrNaO^+: 282.9729 (M + Na)^+, found: 282.9716.

The data are identical to: Li, M.; Wang, C.; Ge, H. Org. Lett. 2011, 13, 2062.

(4-Methoxyphenyl)(phenyl)methanone (10b)

\[
\text{MeO} \begin{array}{c}
\text{Ph} \\
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.83 (d, \(J = 8.8\) Hz, 2H), 7.76 (d, \(J = 7.0\) Hz, 2H), 7.57 (t, \(J = 7.4\) Hz, 1H), 7.47 (t, \(J = 7.5\) Hz, 2H), 6.97 (d, \(J = 8.8\) Hz, 2H), 3.89 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 195.56, 163.20, 138.27, 132.54, 131.86, 130.15, 129.71, 128.16, 113.53, 55.48. HRMS (ESI-TOF) m/z: calc'd for C_{14}H_{12}NaO_2^+: 235.0730 (M + Na)^+, found: 235.0722.

The data are identical to: Li, M.; Wang, C.; Ge, H. Org. Lett. 2011, 13, 2062.

4-Acetamidobenzophenone (13b)

\[
\text{AcHN} \begin{array}{c}
\text{Ph} \\
\end{array}
\]
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.78 (d, $J$ = 8.7 Hz, 2H), 7.74 (d, $J$ = 7.0 Hz, 2H), 7.66 (d, $J$ = 8.6 Hz, 2H), 7.57 (t, $J$ = 7.4 Hz, 1H), 7.46 (t, $J$ = 7.5 Hz, 2H), 7.20 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.01, 169.13, 142.25, 137.67, 132.66, 132.28, 131.51, 129.77, 128.25, 118.81, 24.58. HRMS (ESI-TOF) m/z: calc for C$_{15}$H$_{13}$NNaO$_2^+$: 262.0838 (M + Na)$^+$, found: 262.0826.


(4-Methoxyphenyl)(p-tolyl)methanone (14b)

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

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J$ = 8.8 Hz, 2H), 7.68 (d, $J$ = 8.1 Hz, 2H), 7.27 (d, $J$ = 9.1 Hz, 2H), 6.96 (d, $J$ = 8.8 Hz, 2H), 3.89 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.35 (s), 163.03 (s), 142.59 (s), 135.52 (s), 132.41 (s), 130.50 (s), 129.98 (s), 128.85 (s), 113.48 (s), 55.47 (s), 21.60 (s). HRMS (ESI-TOF) m/z: calc for C$_{15}$H$_{14}$NaO$_2^+$: 249.0886 (M+Na)$^+$, found: 249.0886.


(4-Fluorophenyl)(p-tolyl)methanone (15b)

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

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.79 (m, 2H), 7.69 (d, $J$ = 8.1 Hz, 2H), 7.29 (d, $J$ = 7.9 Hz, 2H), 7.15 (t, $J$ = 8.6 Hz, 2H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.04, 165.24 (d, $J_{C-F} = 253.5$ Hz), 143.31, 134.78, 134.14 (d, $J_{C-F} = 3.5$ Hz), 132.50 (d, $J_{C-F} = 9.1$ Hz), 130.12, 129.03, 115.35 (d, $J_{C-F} = 21.8$ Hz), 21.64. HRMS (ESI-TOF) m/z: calc for C$_{14}$H$_{12}$FO$^+$: 215.0867 (M+H)$^+$, found: 215.0877.

The data are identical to: Li, X.; Zou, G. J. Organomet. Chem. 2015, 794, 136.

(4-Chlorophenyl)(p-tolyl)methanone (16b)

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

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J$ = 8.5 Hz, 2H), 7.69 (d, $J$ = 8.1 Hz, 2H), 7.45 (d, $J$ = 8.5 Hz, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.24, 143.52, 138.59, 136.23, 134.54, 131.33, 130.16, 129.08, 128.55, 21.66. HRMS (ESI-TOF) m/z: calc for C$_{14}$H$_{12}$ClO$^+$: 231.0571 (M+H)$^+$, found: 231.0543.

**p-Cresol (1c)**

\[
\text{H}_3\text{C} \quad \text{\textbullet} \quad \text{OH}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.05 (d, $J = 8.3$ Hz, 2H), 6.75 (d, $J = 8.3$ Hz, 2H), 4.95 (br, 1H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.18, 130.03, 129.92, 115.06, 20.43. HRMS (ESI-TOF) $m/z$: calcd for C$_7$H$_9$O$: 109.0648$ (M + H)$^+$, found: 109.0657.


**4-(Trifluoromethyl)phenol (2c)**

\[
\text{F}_3\text{C} \quad \text{\textbullet} \quad \text{OH}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.5$ Hz, 2H), 5.24 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.26, 127.16 (q, $J_{C-F} = 3.7$ Hz), 124.36 (q, $J_{C-F} = 269.3$ Hz), 123.09 (q, $J_{C-F} = 32.5$ Hz), 115.44. HRMS (ESI-TOF) $m/z$: calcd for C$_{7}$H$_{6}$F$_{3}$O$: 163.0365$ (M + H)$^+$, found: 163.0335.


**1,1'-Biphenyl-4-ol (4c)**

\[
\text{Ph} \quad \text{\textbullet} \quad \text{OH}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.7$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 4.82 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.05, 140.74, 134.02, 128.70, 128.38, 126.71, 126.69, 115.61. HRMS (ESI-TOF) $m/z$: calcd for C$_{12}$H$_{10}$NaO$: 193.0624$ (M + Na)$^+$, found: 193.0580.


**Methyl 4-hydroxybenzoate (5c)**

\[
\text{MeOOC} \quad \text{\textbullet} \quad \text{OH}
\]

$^1$H NMR (400 MHz, DMSO) $\delta$ 10.40 (br, 1H), 7.80 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 3.77 (s, 3H). $^{13}$C NMR (100 MHz, DMSO): $\delta$ 167.04, 162.91, 132.38, 121.23, 116.31, 52.60. HRMS (ESI-TOF) $m/z$: calcd for C$_8$H$_8$NaO$_3$: 175.0366$ (M + Na)$^+$, found: 175.0393.

Naphthalen-2-ol (6c)

\[ \text{HO} \]

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.79 - 7.75 (m, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.45 - 7.42 (m, 1H), 7.35 - 7.31 (m, 1H), 7.15 (d, J = 2.0 Hz, 1H), 7.11 (dd, J = 8.8, 2.4 Hz, 1H), 5.04 (br, 1H); \[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 153.29, 134.55, 129.83, 128.92, 127.74, 126.51, 126.33, 123.60, 117.70, 109.46. \]

HRMS (ESI-TOF) m/z: calcd for C\(_{10}\)H\(_9\)O\(^+\): 145.0648 (M + H\(^+\)), found: 145.0641.


4-Fluorophenol (7c)

\[ \text{HO} \]

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 6.93 (t, J = 8.6 Hz, 2H), 6.79 - 6.75 (m, 2H), 4.73 (br, 1H); \[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 157.24 (d, J_{C-F} = 236.2 Hz), 151.50 (d, J_{C-F} = 1.8 Hz), 116.18 (d, J_{C-F} = 8.0 Hz), 115.95 (d, J_{C-F} = 23.1 Hz). \]

HRMS (ESI-TOF) m/z: calcd for C\(_6\)H\(_6\)FO\(^+\): 113.0397 (M + H\(^+\)), found: 113.0388.

The data are identical to: Inamoto, K.; Nozawa, K.; Yonemoto, M.; Kondo, Y. Chem. Commun. 2011, 47, 11775.

4-Chlorophenol (8c)

\[ \text{HO} \]

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.19 (d, J = 8.9 Hz, 2H), 6.77 (d, J = 8.9 Hz, 2H), 5.51 (br, 1H); \[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 154.01, 129.49, 125.60, 116.65. \]


4-Methoxyphenol (10c)

\[ \text{HO} \]

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 6.96 - 6.87 (m, 4H), 5.67 (s, 1H), 3.89 (s, 3H); \[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 153.48, 149.48, 116.13, 114.97, 55.88. \]

HRMS (ESI-TOF) m/z: calcd for C\(_7\)H\(_8\)NaO\(_2\)\(^+\): 147.0417 (M + Na\(^+\)), found: 147.0381.


4-Nitrophenol (12c)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J = 9.1$ Hz, 2H), 6.92 (d, $J = 9.0$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.27, 141.68, 126.25, 115.66. HRMS (ESI-TOF) $m/z$: calcd for C$_6$H$_6$NO$_3$+: 140.0342 (M + H)$^+$, found: 140.0340.

V. NMR spectra

Compound 1a.

$^1$H NMR

$^{13}$C NMR
Compound 2a.

$^1$H NMR

$^{13}$C NMR
Compound 3a.

$^1$H NMR

$^{13}$C NMR
Compound 4a.

$^1$H NMR

$^{13}$C NMR
Compound 5a.

$^1$H NMR

$^{13}$C NMR
Compound 6a.

\[^1\text{H} \text{ NMR}\]

\[^{13}\text{C} \text{ NMR}\]
Compound 7a.

$^1$H NMR

$^{13}$C NMR
Compound 8a.

$^1$H NMR

$^{13}$C NMR
Compound 9a.

$^1$H NMR

$^{13}$C NMR
Compound 10a.

$^1$H NMR

$^{13}$C NMR
Compound 11a.

$^1$H NMR

\[ \text{HO-} \]

11a

$^{13}$C NMR

\[ \text{HO-} \]

11a
Compound 12a.

$^1$H NMR

$^{13}$C NMR
Compound 13a.

$^1$H NMR

$^{13}$C NMR
Compound 14a.

$^1$H NMR

$^{13}$C NMR
Compound 15a.

$^1$H NMR

$^{13}$C NMR
Compound 16a.

$^1$H NMR

$^{13}$C NMR
Compound 1b.

$^1$H NMR

$^{13}$C NMR
Compound 2b.

$^1$H NMR

$^{13}$C NMR

S34
Compound 4b

$^1$H NMR

$^{13}$C NMR
Compound 5b.

$^1$H NMR

$^{13}$C NMR
Compound 6b.

$^1$H NMR

$^{13}$C NMR
Compound 7b.

$^1$H NMR

$^{13}$C NMR
Compound 8b.

$^1$H NMR

$^{13}$C NMR
Compound 9b.

$^1$H NMR

![$^1$H NMR spectrum of 9b]

$^{13}$C NMR

![$^{13}$C NMR spectrum of 9b]
Compound 10b.

$^1$H NMR

$^{13}$C NMR
Compound 13b

$^1$H NMR

$^{13}$C NMR
Compound 14b

$^1$H NMR

$^{13}$C NMR
Compound 15b

$^1$H NMR

$^{13}$C NMR
Compound 16b

$^1$H NMR

$^{13}$C NMR

16b
Compound 1c.

$^1$H NMR

$^{13}$C NMR
Compound 2c.

$^1$H NMR

$^{13}$C NMR
Compound 4c.

$^1$H NMR

![H NMR spectrum of 4c]

$^{13}$C NMR

![C NMR spectrum of 4c]
Compound 5c.

$^1$H NMR

$^{13}$C NMR
Compound 6c.

$^1$H NMR

$^{13}$C NMR
Compound 7c.

$^1$H NMR

$^{13}$C NMR
Compound 8c.

$^1$H NMR

$^{13}$C NMR
Compound 10c.

$^1$H NMR

$^{13}$C NMR
Compound 12c.

$^1$H NMR

$^{13}$C NMR