Supporting Information

Palladium-Catalyzed \textit{para}-Selective Arylation of Phenols with Aryl Iodides in Water

Zhiqing Wu,\textsuperscript{a} Feihua Luo,\textsuperscript{a} Si Chen,\textsuperscript{a} Zhengkai Li,\textsuperscript{a} Haifeng Xiang,\textsuperscript{a} and Xiangge Zhou\textsuperscript{*a,b}

\textsuperscript{a} Institute of Homogeneous Catalysis, College of Chemistry, Sichuan University, Chengdu 610064, China.
\textsuperscript{b} Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

Email: zhouxiangge@scu.edu.cn, Fax: +86-28-85412904.
1. General methods
Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Column chromatography was performed using silica gel (300-400 mesh) eluting with ethyl acetate, petroleum and acetic acid. All products were characterized by their NMR and HRMS. $^1$H NMR spectra were recorded at 400 MHz and $^{13}$C NMR spectra were recorded at 100 MHz (Bruker DPX) with CDCl$_3$ or DMSO-d$_6$ as solvent. Chemical shifts are reported in ppm using TMS as internal standard. HRMS was recorded on a commercial apparatus (ESI Source, TOF).

2. Table S1 Optimization of reaction conditions.$^[[a]]$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{Pd}]$</th>
<th>Additive</th>
<th>Time [h]</th>
<th>Yield [%]$^[[b]]$</th>
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<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)$_2$</td>
<td>AgOAc</td>
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<td>28</td>
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<tr>
<td>10</td>
<td>-</td>
<td>AgTFA</td>
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<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Pd(OAc)$_2$</td>
<td>-</td>
<td>24</td>
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<tr>
<td>12</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>24</td>
<td>84$^[[c]]$</td>
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</table>

$^[[a]]$ Reaction conditions: 1a (0.4 mmol), 2a (1 mmol), Pd(OAc)$_2$ (0.02 mmol), Ag salts (0.44 mmol), H$_2$O (0.8 mL), rt. $^[[b]]$ Yield of isolated product. $^[[c]]$ Reaction was performed at 50 °C. OTf = trifluoromethanesulfonate, TFA = trifluoroacetate.

3. Organic solvents screening
Table S2. Organic solvents screening for reaction between phenol and 2-iodobenzoic acid.$^[[a]]$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{Pd}]$</th>
<th>Additive</th>
<th>Solvent</th>
<th>Time [h]</th>
<th>Yield [%]</th>
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<tbody>
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<td>1</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>EtOH</td>
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<tr>
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<td>AgTFA</td>
<td>MeOH</td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>CH$_3$CN</td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>NMP</td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>EtOAc</td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>AcOH</td>
<td>24</td>
<td>trace</td>
</tr>
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<td>7</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>DCE</td>
<td>24</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>dioxane</td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>Tol</td>
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<td>25</td>
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<td>AgTFA</td>
<td>DMSO</td>
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<td>AgTFA</td>
<td>DMF</td>
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</table>
[a] Reaction conditions: 1a (0.4 mmol), 2a (1 mmol), Pd(OAc)$_2$ (0.02 mmol), Ag salts (0.44 mmol), Solvent (0.8 mL), rt.

Table S3. Organic solvents screening for oxidative C–H/C–H cross-coupling reaction.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Additive</th>
<th>Solvent</th>
<th>Time [h]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
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<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
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<td>0</td>
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<tr>
<td>2</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>MeOH</td>
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<td>0</td>
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<tr>
<td>3</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>CH$_3$CN</td>
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<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>NMP</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>EtOAc</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>AcOH</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>DCE</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>dioxane</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>Tol</td>
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<td>0</td>
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<tr>
<td>10</td>
<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
<td>DMSO</td>
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<td>trace</td>
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<tr>
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<td>Pd(OAc)$_2$</td>
<td>AgTFA</td>
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<td>trace</td>
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<td>AgTFA</td>
<td>Solvent-free</td>
<td>24</td>
<td>trace</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 5a (0.4 mmol), 2a (1 mmol), Pd(OAc)$_2$ (0.04 mmol), Ag salts (0.8 mmol), Solvent (1 mL), 100°C.

4. General experimental procedures

The general procedure for para-selective arylation of phenols:

Aryl iodides (0.4 mmol), phenols (1 mmol), Pd(OAc)$_2$ (0.02 mmol), and AgTFA (0.44 mmol) were combined in water (0.8 mL) in a 10 mL vial. The reaction mixture was stirred at the indicated temperature for 24 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:40:1) to afford the corresponding products.

The general procedure for the synthesis of dibenzopyranones:

Aryl iodides (0.4 mmol), para-substituted phenols (1 mmol), Pd(OAc)$_2$ (0.02 mmol), AgTFA (0.44 mmol), and TsOH (0.1 mmol) were combined in water (0.8 mL) in a 10 mL vial. The reaction mixture was stirred at 25 °C for 24 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:5:1) to afford the corresponding products.

The procedure for tandem C–H arylation/nitration:
\[ \text{Pd(OAc)}_2 (5 \text{ mol%) AgNO}_3 (2 \text{ equiv)} \]

\[ 1a + 2a \xrightarrow{\text{H}_2\text{O}, 25 \text{ oC, 24h}} 3y, 52\% \]

\[ \text{Pd(OAc)}_2 (10 \text{ mol%)} Ag\text{TFA} \]

\[ 5a + 2a \xrightarrow{\text{H}_2\text{O}, 100 \text{ oC, 24h}} 3h, 4f, 54\% (p:o = 2:1) \]

\( o\)-iodobenzoic acid (0.4 mmol), phenol (1 mmol), Pd(OAc)\(_2\) (0.02 mmol), and AgNO\(_3\) (0.8 mmol) were combined in water (0.8 mL) in a 10 mL vial. The reaction mixture was stirred at 25 oC for 24 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure (50 oC for 10 min). The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:40:1) to afford the corresponding product.

**The procedure for C–H/ C–H oxidative coupling:**

\( o\)-toluic acid (0.4 mmol), phenol (2 mmol), Pd(OAc)\(_2\) (0.04 mmol), and AgTFA (0.8 mmol) were combined in water (1 mL) in a 10 mL vial. The reaction mixture was stirred at 100 oC for 24 hours without an inert gas atmosphere. After cooled to room temperature, the mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:5:1 to 100:40:1) to afford the corresponding products.
5. Characterization data for products

2-(4-Hydroxyphenyl)benzoic acid (3a)[1]

\[ \text{COOH} \]

\[ \text{3a} \]

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 6.79\) (d, \(J = 8.8\) Hz, 2H), \(7.15\) (d, \(J = 8.8\) Hz, 2H), \(7.15\) (d, \(J = 7.6\) Hz, 1H), \(7.38\) (t, \(J = 7.6\) Hz, 1H), \(7.51\) (t, \(J = 7.6\) Hz, 1H), \(7.63\) (d, \(J = 7.6\) Hz, 1H), \(9.51\) (s, 1H), \(12.71\) (s, 1H).

\(^13\)C NMR (100 MHz, DMSO-\(d_6\)): 114.97, 126.44, 128.76, 129.36, 130.14, 130.55, 131.29, 132.33, 140.62, 156.80, 170.11.

ESI-MS: calculated \([\text{C}_{13}\text{H}_9\text{O}_3]^-\): 213.0552, found: 213.0552.

2-(4-Hydroxyphenyl)benzamide (3b)

\[ \text{NH}_2 \]

\[ \text{3b} \]

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 6.77\) (d, \(J = 8.4\) Hz, 2H), \(7.24\) (d, \(J = 8.4\) Hz, 2H), \(7.27\) (s, 1H), \(7.30\)–\(7.44\) (m, 4H), \(7.54\) (s, 1H), \(9.48\) (s, 1H).

\(^13\)C NMR (100 MHz, DMSO-\(d_6\)): 115.03, 126.23, 127.49, 129.08, 129.50, 129.64, 131.06, 137.14, 138.77, 156.82, 171.51.

ESI-MS: calculated \([\text{C}_{13}\text{H}_{11}\text{NO}_2\text{Na}]^+\): 236.0687, found: 236.0686.

2-(4-Hydroxyphenyl)-N-methylbenzamide (3c)

\[ \text{NHMe} \]

\[ \text{3c} \]

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 2.57\) (d, \(J = 4.4\) Hz, 3H), \(6.77\) (d, \(J = 8.0\) Hz, 2H), \(7.20\) (d, \(J = 8.0\) Hz, 2H), \(7.32\)–\(7.34\) (m, 3H), \(7.41\)–\(7.44\) (m, 1H), \(7.95\) (d, \(J = 4.8\) Hz, 1H), \(9.50\) (s, 1H).

\(^13\)C NMR (100 MHz, DMSO-\(d_6\)): 25.96, 115.08, 126.28, 127.61, 129.17, 129.37, 129.53, 130.85, 137.07, 138.83, 156.81, 170.04.

ESI-MS: calculated \([\text{C}_{14}\text{H}_{13}\text{NO}_2\text{Na}]^+\): 250.0844, found: 250.0848.

2-(4-Hydroxyphenyl)-N,N-dimethylbenzamide (3d)

\[ \text{NMe}_2 \]

\[ \text{3d} \]

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 2.39\) (s, 3H), \(2.77\) (s, 3H), \(6.80\) (d, \(J = 8.4\) Hz, 2H), \(7.20\) (d, \(J = 8.4\) Hz, 2H), \(7.26\) (d, \(J = 7.6\) Hz, 1H), \(7.34\)–\(7.38\) (m, 2H), \(7.43\)–\(7.47\) (m, 1H), \(9.58\) (s, 1H).

\(^13\)C NMR (100 MHz, DMSO-\(d_6\)): 33.98, 37.44, 115.30, 126.79, 127.11, 129.94, 129.12, 129.25, 130.30, 135.55, 138.02, 157.07, 170.25.

ESI-MS: calculated \([\text{C}_{15}\text{H}_{15}\text{NO}_2\text{Na}]^+\): 264.1000, found: 264.0995.
4-(2-Acetylphenyl)phenol (3e)

1H NMR (400 MHz, DMSO-d6): δ 2.07 (s, 3H), 6.71 (s, 1H), 6.89 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.37-7.40 (m, 2H), 7.48-7.54 (m, 2H). 13C NMR (100 MHz, DMSO-d6): 30.49, 115.80, 127.07, 127.79, 130.16, 130.25, 130.99, 132.72, 140.41, 140.62, 156.20, 207.06. ESI-MS: calculated [C14H11O2]−: 211.0759, found: 211.0765.

Methanone, (4'-hydroxy[1,1'-biphenyl]-2-yl)phenyl (3f)

1H NMR (400 MHz, DMSO-d6): δ 6.62 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.42-7.63 (m, 7H), 9.48 (s, 1H). 13C NMR (100 MHz, DMSO-d6): 115.25, 126.60, 128.26, 128.45, 129.36, 129.67, 129.86, 130.45, 133.14, 136.78, 138.28, 140.12, 156.84, 198.18. ESI-MS: calculated [C19H13O2]−: 273.0916, found: 273.0921.

6-Fluoro-2-(4-hydroxyphenyl)benzoic acid (3g)

1H NMR (400 MHz, DMSO-d6): δ 6.83 (d, J = 8.4 Hz, 2H), 7.21-7.27 (m, 4H), 7.47-7.52 (m, 1H), 9.69 (s, 1H), 13.34 (s, 1H). 13C NMR (100 MHz, DMSO-d6): 113.58 (d, JCF = 21.4 Hz), 115.36, 122.54 (d, JCF = 18.2 Hz), 125.36 (d, JCF = 2.4 Hz), 129.29, 129.37(d, JCF = 2.4 Hz), 130.78 (d, JCF = 9 Hz), 140.69 (d, JCF = 3.6 Hz), 157.43, 158.42 (d, JCF = 244.1 Hz), 166.74. ESI-MS: calculated [C13H9FO3]−: 231.0457, found: 231.0455.

6-Methyl-2-(4-hydroxyphenyl)benzoic acid (3h)

1H NMR (400 MHz, DMSO-d6): δ 2.31 (s, 3H), 6.79 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 7.6 Hz, 1H), 7.20-7.22 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H), 9.56 (s, 1H), 12.95 (s, 1H). 13C NMR (100 MHz, DMSO-d6): 19.25, 115.11, 126.85, 128.13, 128.61, 129.28, 131.06, 133.58, 134.70, 138.20, 156.88, 170.82. ESI-MS: calculated [C14H11O3]−: 227.0708, found: 227.0711.
5-Methoxy-2-(4-hydroxyphenyl)benzoic acid (3i)

\[
\begin{align*}
\text{5-Methoxy-2-(4-hydroxyphenyl)benzoic acid (3i)}
\end{align*}
\]

\[\begin{array}{c}
\text{MeO} \\
\text{COOH} \\
\text{3i}
\end{array}\]

\[\begin{align*}
^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta & \ 3.81 (s, 3\text{H}), 6.77 (d, J = 8.8 \text{ Hz}, 2\text{H}), 7.07-7.12 (m, 3\text{H}), 7.16 (d, J = 7 \text{ Hz}, 1\text{H}), 7.25 (d, J = 8.4 \text{ Hz}, 1\text{H}), 9.46 (s, 1\text{H}), 12.74 (s, 1\text{H}). \text{ } \\
{^{13}}\text{C NMR (100 MHz, DMSO-d}_6\text{): } 55.32, 113.66, 114.90, 116.32, 129.31, 131.07, 131.42, 133.07, 133.29, 156.43, 157.60, 169.82. \\
\text{ESI-MS: calculated [C}_{14}\text{H}_{11}\text{O}_4^- : 243.0657, found: 243.0660.}
\end{align*}\]

5-Methyl-2-(4-hydroxyphenyl)benzoic acid (3j)

\[\begin{align*}
\text{5-Methyl-2-(4-hydroxyphenyl)benzoic acid (3j)}
\end{align*}
\]

\[\begin{array}{c}
\text{COOH} \\
\text{3j}
\end{array}\]

\[\begin{align*}
^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta & \ 2.35 (s, 3\text{H}), 6.77 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.11 (d, J = 8.4 \text{ Hz}, 2\text{H}), 2.11 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.32 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.45 (s, 1\text{H}), 9.47 (s, 1\text{H}), 12.60 (s, 1\text{H}). \text{ } \\
{^{13}}\text{C NMR (100 MHz, DMSO-d}_6\text{): } 20.34, 114.92, 129.17, 129.30, 130.07, 131.13, 131.25, 132.12, 135.76, 137.84, 156.61, 170.18. \\
\text{ESI-MS: calculated [C}_{14}\text{H}_{11}\text{O}_3^- : 227.0708, found: 227.0710.}
\end{align*}\]

5-Chloro-2-(4-hydroxyphenyl)benzoic acid (3k)

\[\begin{align*}
\text{5-Chloro-2-(4-hydroxyphenyl)benzoic acid (3k)}
\end{align*}
\]

\[\begin{array}{c}
\text{Cl} \\
\text{COOH} \\
\text{3k}
\end{array}\]

\[\begin{align*}
^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta & \ 6.80 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.15 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.37 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.56-7.66 (m, 2\text{H}), 9.67 (s, 1\text{H}), 12.99 (s, 1\text{H}). \text{ } \\
{^{13}}\text{C NMR (100 MHz, DMSO-d}_6\text{): } 115.09, 128.23, 129.39, 129.97, 130.27, 131.11, 132.02, 134.15, 139.33, 157.10, 168.76. \\
\text{ESI-MS: calculated [C}_{13}\text{H}_{8}\text{ClO}_3^- : 247.0162, 249.0132, found: 247.0162, 249.0149.}
\end{align*}\]

5-Bromo-2-(4-hydroxyphenyl)benzoic acid (3l)

\[\begin{align*}
\text{5-Bromo-2-(4-hydroxyphenyl)benzoic acid (3l)}
\end{align*}
\]

\[\begin{array}{c}
\text{Br} \\
\text{COOH} \\
\text{3l}
\end{array}\]

\[\begin{align*}
^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta & \ 6.85 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.19 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.35 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.74-7.84 (m, 2\text{H}), 9.65 (s, 1\text{H}), 13.08 (s, 1\text{H}). \text{ } \\
{^{13}}\text{C NMR (100 MHz, DMSO-d}_6\text{): } 115.10, 119.39, 129.34, 129.99, 131.08, 132.28, 133.23, 134.35, 139.70, 157.13, 168.63. \\
\text{ESI-MS: calculated [C}_{13}\text{H}_{8}\text{BrO}_3^- : 290.9657, 292.9636, found: 290.9659, 292.9652.}
\end{align*}\]

5-Trifluoromethyl-2-(4-hydroxyphenyl)benzoic acid (3m)

\[\begin{align*}
\text{5-Trifluoromethyl-2-(4-hydroxyphenyl)benzoic acid (3m)}
\end{align*}
\]
\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 6.86 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 9.71 (s, 1H), 13.18 (s, 1H). \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): 115.21, 123.90 (q, J_{CF} = 270 Hz), 125.45 (q, J_{CF} = 4 Hz), 127.03 (q, J_{CF} = 32 Hz), 127.04 (q, J_{CF} = 4 Hz), 129.53, 129.75, 131.26, 133.11, 144.55, 157.57, 168.86.

ESI-MS: calculated [C_{14}H_{8}F_{3}O_{3}]^{-}: 281.0426, found: 281.0429.

2-(3-Methyl-4-hydroxyphenyl)benzoic acid (3n)

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 2.15 (s, 3H), 6.81 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 7.06 (s, 1H), 7.32-7.38 (m, 2H), 7.47-7.51 (m, 1H), 7.63 (d, J = 6.8 Hz, 1H), 9.43 (s, 1H), 12.65 (s, 1H). \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): 16.06, 114.32, 123.46, 126.31, 126.63, 128.65, 130.11, 130.44, 130.52, 131.25, 132.43, 140.73, 154.92, 170.27.

ESI-MS: calculated [C_{15}H_{11}O_{3}]^{-}: 227.0708, found: 227.0711.

2-(3,5-Dimethyl-4-hydroxyphenyl)benzoic acid (3o)

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 2.18 (s, 6H), 6.89 (s, 2H), 7.32-7.38 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 8.33 (s, 1H), 12.68 (s, 1H). \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): 16.69, 123.83, 126.30, 128.13, 128.57, 130.10, 130.39, 131.56, 132.43, 140.73, 152.71, 170.28.

ESI-MS: calculated [C_{15}H_{11}O_{3}]^{-}: 241.0865, found: 241.0867.

2-(3-Iodo-4-hydroxyphenyl)benzoic acid (3p)

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 6.92 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.60 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 10.46 (s, 1H), 12.83 (s, 1H). \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): 84.21, 114.54, 126.98, 128.98, 129.59, 130.26, 130.79, 132.09, 133.52, 138.15, 139.23, 156.02, 169.72.

ESI-MS: calculated [C_{13}H_{10}I]^{-}: 338.9518, found: 338.9508.
2-(3-Bromo-4-hydroxyphenyl)benzoic acid (3q)

$\text{COOH}$

$\text{Br}$

$\text{OH}$

$\text{H NMR (400 MHz, DMSO-}$d$_6$): $\delta$ 6.98 (d, $J = 8.4$ Hz, 1H), 7.14-7.17 (m, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.41-7.44 (m, 2H), 7.52-7.56 (m, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 10.39 (s, 1H), 12.83 (s, 1H).

$^{13}$C NMR (100 MHz, DMSO- $d_6$): 108.85, 115.96, 127.06, 128.76, 129.02, 130.30, 130.83, 132.08, 132.27, 133.06, 139.33, 153.41, 169.67.


2-(2-Fluoro-4-hydroxyphenyl)benzoic acid (3r)

$\text{COOH}$

$\text{F}$

$\text{OH}$

$\text{H NMR (400 MHz, DMSO-}$d$_6$): $\delta$ 6.54-6.58 (m, 1H), 6.64-6.67 (m, 1H), 7.13 (t, $J = 8.8$ Hz, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 1H), 10.08 (s, 1H), 12.37 (s, 1H).

$^{13}$C NMR (100 MHz, DMSO- $d_6$): 102.2 (d, $J_{CF} = 25$ Hz), 111.36, 119.4 (d, $J_{CF} = 16$ Hz), 127.35, 129.44, 130.98 (d, $J_{CF} = 6$ Hz), 131.21, 131.30, 135.49, 158.43 (d, $J_{CF} = 12$ Hz), 159.49 (d, $J_{CF} = 242$ Hz), 168.93.

ESI-MS: calculated [C$_{13}$H$_8$FO$_3$]$^-$: 231.0457, found: 231.0456.

2-(3-Phenyl-4-hydroxyphenyl)benzoic acid (3s)

$\text{COOH}$

$\text{3s}$

$\text{H NMR (400 MHz, DMSO-}$d$_6$): $\delta$ 7.00 (d, $J = 8.4$ Hz, 1H), 7.18-7.24 (m, 2H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.38-7.45 (m, 4H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.59 (d, $J = 7.2$ Hz, 2H), 7.65 (d, $J = 7.6$ Hz, 1H), 9.73 (s, 1H), 12.81 (s, 1H).

$^{13}$C NMR (100 MHz, DMSO- $d_6$): 115.21, 118.36, 126.38, 126.57, 127.79, 128.01, 129.01, 129.40, 130.11, 130.75, 131.15, 131.26, 136.84, 140.90, 141.82, 154.29, 169.07.

ESI-MS: calculated [C$_{19}$H$_{13}$O$_3$]$^-$: 289.0865, found: 289.0862.

2-(3-t-Butyl-4-hydroxyphenyl)benzoic acid (3t)

$\text{COOH}$

$\text{3t}$

$\text{H NMR (400 MHz, DMSO-}$d$_6$): $\delta$ 1.40 (s, 9H), 6.86 (d, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 7.19 (s, 1H), 7.35-7.40 (m, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 9.51 (s, 1H), 12.52 (s, 1H).

$^{13}$C NMR (100 MHz, DMSO- $d_6$): 29.26, 34.27, 116.01, 126.18, 126.43, 126.83,
128.54, 129.94, 130.37, 130.65, 132.62, 134.67, 140.81, 155.44, 170.58.

ESI-MS: calculated [C\textsubscript{17}H\textsubscript{17}O\textsubscript{3}]\textsuperscript{–}: 269.1178, found: 269.1180.

2-(3-Chloro-4-hydroxyphenyl)benzoic acid (3u)

![Structure of 3u](image)

\(^1\)H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) 7.05 (d, \(J = 8.4\) Hz, 1H), 7.16 (d, \(J = 8.0\) Hz, 1H), 7.32 (s, 1H), 7.41 (d, \(J = 7.6\) Hz, 1H), 7.47 (t, \(J = 7.6\) Hz, 1H), 7.59 (t, \(J = 7.6\) Hz, 1H), 7.74 (d, \(J = 7.6\) Hz, 1H), 10.35 (s, 1H), 12.88 (s, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\textit{d}_6): 116.29, 119.22, 127.06, 128.08, 129.02, 129.38, 130.28, 130.82, 132.11, 132.67, 139.44, 152.40, 169.67.

ESI-MS: calculated [C\textsubscript{13}H\textsubscript{8}ClO\textsubscript{3}]\textsuperscript{–}: 247.0162, 249.0132, found: 247.0162, 249.0154.

2-(3-Formyl-4-hydroxyphenyl)benzoic acid (3v)

![Structure of 3v](image)

\(^1\)H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) 7.04 (d, \(J = 8.4\) Hz, 1H), 7.38 (d, \(J = 7.6\) Hz, 1H), 7.43 - 7.51 (m, 2H), 7.55 - 7.60 (m, 2H), 7.74 (d, \(J = 7.6\) Hz, 1H), 10.31 (s, 1H), 10.84 (s, 1H), 12.82 (s, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\textit{d}_6): 117.14, 121.95, 127.29, 128.31, 129.37, 130.36, 131.11, 131.89, 132.11, 136.49, 139.91, 160.15, 169.52, 191.22.

ESI-MS: calculated [C\textsubscript{14}H\textsubscript{9}O\textsubscript{4}]\textsuperscript{–}: 241.0501, found: 241.0506.

2-(3-Acetyl-4-hydroxyphenyl)benzoic acid (3w)

![Structure of 3w](image)

\(^1\)H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) 2.72 (s, 3H), 7.06 (d, \(J = 8.4\) Hz, 1H), 7.49 - 7.55 (m, 3H), 7.64 (t, \(J = 7.6\) Hz, 1H), 7.81 (d, \(J = 8.0\) Hz, 1H), 7.88 (s, 1H), 12.00 (s, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\textit{d}_6): 27.81, 117.27, 120.12, 127.23, 129.28, 130.51, 130.65, 131.02, 131.74, 131.91, 136.34, 139.80, 159.98, 169.52, 204.14.

ESI-MS: calculated [C\textsubscript{15}H\textsubscript{11}O\textsubscript{4}]\textsuperscript{–}: 255.0657, found: 255.0661.

2-(3-Nitro-4-hydroxyphenyl)benzoic acid (3x)

![Structure of 3x](image)

\(^1\)H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) 7.17 (d, \(J = 7.6\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.47-7.52 (m, 2H), 7.60 (t, \(J = 7.6\) Hz, 1H), 7.78-7.81 (m, 2H), 11.14 (s, 1H), 12.91 (s, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\textit{d}_6): 118.75, 124.39, 127.67, 129.54, 130.51, 131.26, 131.64, 131.93, 135.30, 136.40,
ESI-MS: calculated \([\text{C}_{13}\text{H}_8\text{NO}_5]\) : 258.0402, found: 258.0400.

2-Methylbenzo[c]chromen-6-one (4a)\(^{[2]}\)

\[\text{H NMR (400 MHz, CDCl}_3\): } \delta = 2.47 (s, 3H), 7.26-7.31 (m, 2H), 7.58 (d, \(J = 8.0\) Hz, 1H), 7.82 (t, \(J = 8.0\) Hz, 1H), 7.86 (s, 1H), 8.13 (d, \(J = 8.0\) Hz, 1H), 8.41 (d, \(J = 8.0\) Hz, 1H).

\[\text{C NMR (100 MHz, CDCl}_3\): } 21.29, 117.66, 117.78, 121.43, 121.76, 122.90, 128.87, 130.75, 131.51, 134.25, 134.89, 134.99, 149.52, 161.56.

MS (EI, M/Z): 210 [M\(^+\)].

2,8-Dimethylbenzo[c]chromen-6-one (4b)\(^{[3]}\)

\[\text{H NMR (400 MHz, CDCl}_3\): } \delta = 2.44 (s, 3H), 2.48 (s, 3H), 7.22 (s, 2H), 7.60 (d, \(J = 8.0\) Hz, 1H), 7.77 (s, 1H), 7.96 (d, \(J = 8.0\) Hz, 1H), 8.17 (s, 1H).

\[\text{C NMR (100 MHz, CDCl}_3\): } 21.24, 21.39, 117.45, 117.85, 121.16, 121.69, 122.62, 130.44, 130.90, 132.35, 134.10, 136.04, 139.11, 149.16, 161.68.

MS (EI, M/Z): 224 [M\(^+\)].

2-Methyl-8-chlorobenzo[c]chromen-6-one (4c)

\[\text{H NMR (400 MHz, CDCl}_3\): } \delta = 2.37 (s, 3H), 7.12 (d, \(J = 8.4\) Hz, 1H), 7.19 (d, \(J = 8.4\) Hz, 1H), 7.62-7.65 (m, 2H), 7.91 (d, \(J = 8.4\) Hz, 1H), 8.22 (s, 1H).

\[\text{C NMR (100 MHz, CDCl}_3\): } 20.07, 115.73, 116.47, 121.43, 121.63, 122.25, 128.92, 130.67, 132.16, 133.42, 133.70, 133.93, 148.08, 159.12.

ESI-MS: calculated \([\text{C}_{14}\text{H}_{10}\text{ClO}_2]\) : 245.0369, 247.0340, found: 245.0366, 247.0357.

2-Methyl-8-trifluoromethylbenzo[c]chromen-6-one (4d)\(^{[4]}\)

\[\text{H NMR (400 MHz, CDCl}_3\): } \delta = 2.41 (s, 3H), 7.22 (d, \(J = 8.8\) Hz, 1H), 7.28 (d, \(J = 8.8\) Hz, 1H), 7.79 (s, 1H), 7.95 (d, \(J = 8.4\) Hz, 1H), 8.15 (d, \(J = 8.4\) Hz, 1H), 8.59 (s, 1H).

\[\text{C NMR (100 MHz, CDCl}_3\): } 20.08, 115.44, 116.73, 120.49, 121.56, 122.18, 127.01, 129.94, 131.75, 133.68, 136.64,
148.77, 159.24.
MS (EI, M/Z): 278 [M+].

3-Methylbenzo[c]chromen-6-one (4e)

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 2.46 (s, 3H), 7.16 (d, J = 8.4 Hz, 1H), 7.18 (s, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H).}
\]

\[
\text{C NMR (100 MHz, CDCl}_3\text{): } 21.60, 115.58, 118.05, 121.03, 121.59, 122.66, 125.83, 128.53, 130.70, 133.94, 135.15, 141.45, 151.42, 161.62.
\]

ESI-MS: calculated [C_{14}H_{11}O_2]^+: 211.0759, found: 211.0756.

7-Methylbenzo[c]chromen-6-one (4f)

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 2.87 (s, 3H), 7.29-7.34 (m, 2H), 7.39 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H).}
\]

\[
\text{C NMR (100 MHz, CDCl}_3\text{): } 24.06, 117.45, 118.43, 119.90, 123.17, 124.36, 130.39, 132.34, 134.09, 136.24, 144.56, 151.43, 160.61.
\]

ESI-MS: calculated [C_{14}H_{11}O_2]^+: 210 [M+].

References:
6. Kinetic isotope effect measurements:

\[
\text{Kinetic isotope effect measurements:}
\]

![Chemical structure](image)

**Experimental Procedure:**
2-Iodobenzoic acid (0.4 mmol), phenol-\(d_6\) (1 mmol), phenol-\(d_{10}\) (1 mmol), Pd(OAc)_2 (0.02 mmol), and AgTFA (0.44 mmol) were combined in water (1 mL) in a 10 mL vial. The reaction mixture was stirred at 25 °C for 12 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography to afford the corresponding product.
1. NMR spectra of products
2-(4-Hydroxyphenyl)benzoic acid (3a)
2-(4-Hydroxyphenyl)benzamide (3b)
2-(4-Hydroxyphenyl)-N-methylbenzamide (3c)
2-(4-Hydroxyphenyl)-N,N-dimethylbenzamide (3d)
4-(2-Acetylphenyl)phenol (3e)
Methanone, (4'-hydroxy[1,1'-biphenyl]-2-yl)phenyl- (3f)
6-Fluoro-2-(4-hydroxyphenyl)benzoic acid (3g)
6-Methyl-2-(4-hydroxyphenyl)benzoic acid (3h)
5-Methoxy-2-(4-hydroxyphenyl)benzoic acid (3i)
5-Methyl-2-(4-hydroxyphenyl)benzoic acid (3j)
5-Chloro-2-(4-hydroxyphenyl)benzoic acid (3k)
5-Bromo-2-(4-hydroxyphenyl)benzoic acid (3l)
5-Trifluoromethyl-2-(4-hydroxyphenyl)benzoic acid (3m)
2-(3-Methyl-4-hydroxyphenyl)benzoic acid (3n)
2-(3,5-Dimethyl-4-hydroxyphenyl)benzoic acid (3o)
2-(3-Iodo-4-hydroxyphenyl)benzoic acid (3p)
2-(3-Bromo-4-hydroxyphenyl)benzoic acid (3q)
2-(2-Fluoro-4-hydroxyphenyl)benzoic acid (3r)
2-(3-Phenyl-4-hydroxyphenyl)benzoic acid (3s)
2-(3-t-Butyl-4-hydroxyphenyl)benzoic acid (3t)
2-(3-Chloro-4-hydroxyphenyl)benzoic acid (3u)
2-(3-Formyl-4-hydroxyphenyl)benzoic acid (3v)
2-(3-Acetyl-4-hydroxyphenyl)benzoic acid (3w)
2-(3-Nitro-4-hydroxyphenyl)benzoic acid (3x)
2-Methylbenzo[c]chromen-6-one (4a)
2,8-Dimethylbenzo[c]chromen-6-one (4b)
2-Methyl-8-chlorobenzocchromen-6-one (4c)
2-Methyl-8-trifluoromethylbenzo[c]chromen-6-one (4d)
3-Methylbenzo[c]chromen-6-one (4e)
7-Methylbenzo[c]chromen-6-one (4f)