

## Supporting Information

### Pd(II)-Catalyzed Hydroxylation of Arenes with 1 atm O<sub>2</sub> or Air

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**General Information:** Unless otherwise noted, all commercial materials were used without further purification. Solvents were obtained from Acros or Sigma-Aldrich and used directly without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced to tetramethylsilane at 0.0 ppm and residue  $\text{CH}_3\text{COCH}_3$  at 205.0 or  $\text{CHCl}_3$  at 77.0 ppm respectively unless otherwise noted. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. High resolution mass spectra for new compounds were recorded at Mass Spectrometry Facilities, The Scripps Research Institute (TSRI).

**I. General procedure for screening of reaction conditions:** A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with  $\text{Pd}(\text{OAc})_2$  (11.2 mg, 0.05 mmol), followed by *m*-toluic acid (68.1 mg, 0.5 mmol), benzoquinone (the amount listed in the table), base (listed in the table) and solvent (1.5 mL). The reaction tube was evacuated and back-filled with  $\text{O}_2$  (3 times, balloon). After the reaction mixture was stirred at 115 °C for 15 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with aqueous HCl (1.0 N, 5 mL) and brine (5 mL, twice). The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. The yield was determined by  $^1\text{H}$  NMR analysis of crude product using  $\text{CH}_2\text{Br}_2$  as the internal standard.

**II. General procedure for Pd(II)-catalyzed *ortho*-hydroxylation with 1 atm  $\text{O}_2$ :** A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with  $\text{Pd}(\text{OAc})_2$  (11.2 mg, 0.05 mmol) followed by benzoic acid (0.5 mmol), benzoquinone (54.0 mg, 0.5 mmol), KOAc (98.0 mg, 1 mmol) and *N,N*-dimethylacetamide (1.5 mL). The reaction tube was evacuated and back-filled with  $\text{O}_2$  (3 times, balloon). After the

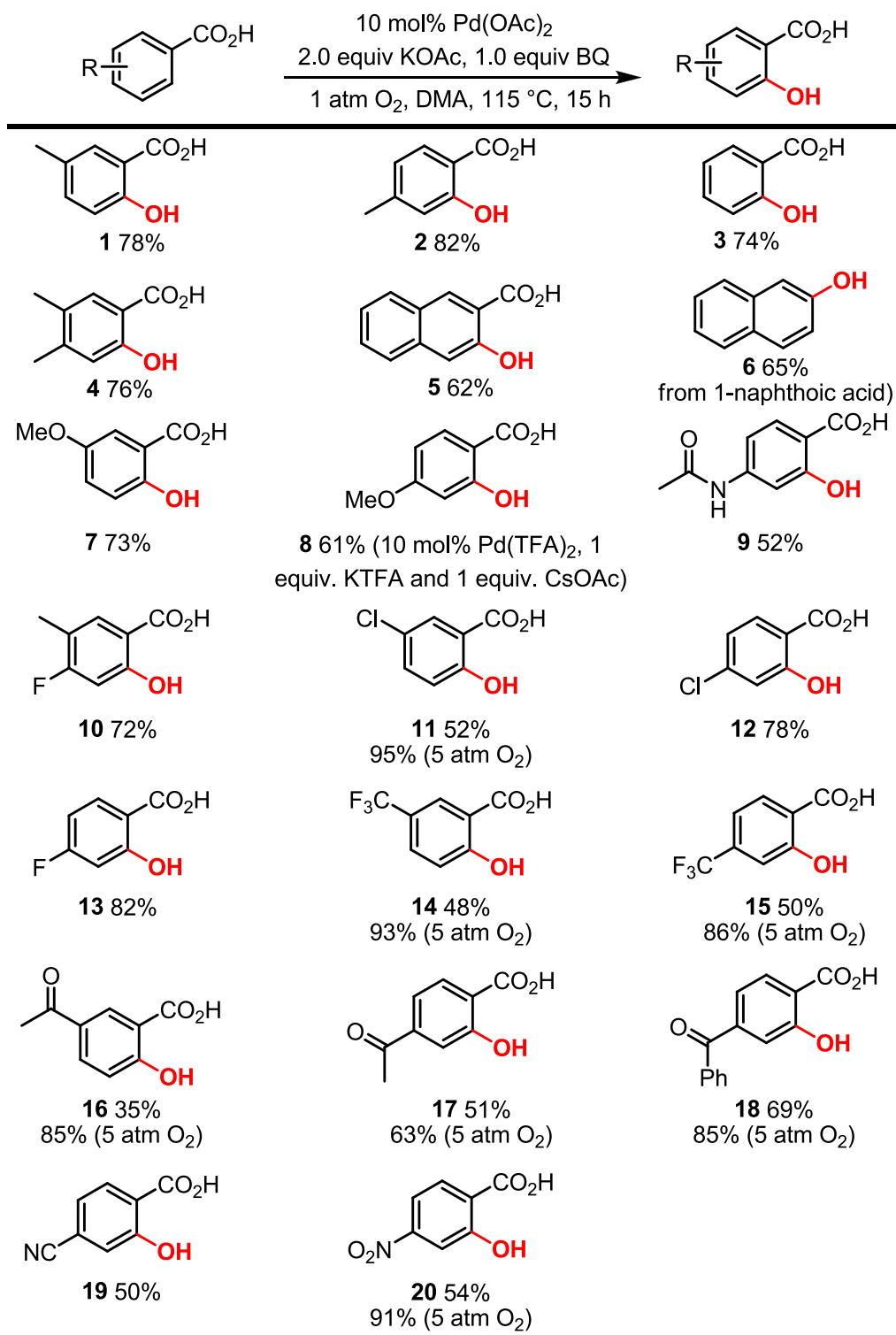
reaction mixture was stirred at 115 °C for 15 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with aqueous HCl (1.0 N, 5 mL) and brine (5 mL, twice). The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to give the corresponding product.

**Table 1.** Screening of Reaction Conditions

Entry	Solvent	Base	BQ (equiv)	%Yield <sup>a</sup>	% SM <sup>a</sup>
1	t-BuOH	KOAc (2 equiv)	0	0	100
2	THF	KOAc (2 equiv)	0	0	100
3	DMF	KOAc (2 equiv)	0	16	52
4	DMP	KOAc (2 equiv)	0	12	60
5	DMA	KOAc (2 equiv)	0	20	50
6	DMA	KOAc (2 equiv)	0	55 <sup>b</sup>	0
7	DMA	K <sub>2</sub> HPO <sub>4</sub> (3 equiv)	0	60 <sup>b</sup>	0
8	DMA	KOAc (2 equiv)	0.2	40	60
9	DMA	KOAc (2 equiv)	1	82	12
10	DMA	NaOAc (2 equiv)	1	25	70
11	DMA	CsOAc (2 equiv)	1	80	16
12	DMA	K <sub>2</sub> HPO <sub>4</sub> (3 equiv)	1	45	45
13	DMA	K <sub>2</sub> CO <sub>3</sub> (3 equiv)	1	33	65
14	DMA	KOAc (2 equiv)	1	62 <sup>c</sup>	30
15	DMA	KOAc (2 equiv)	1	0 <sup>d</sup>	100

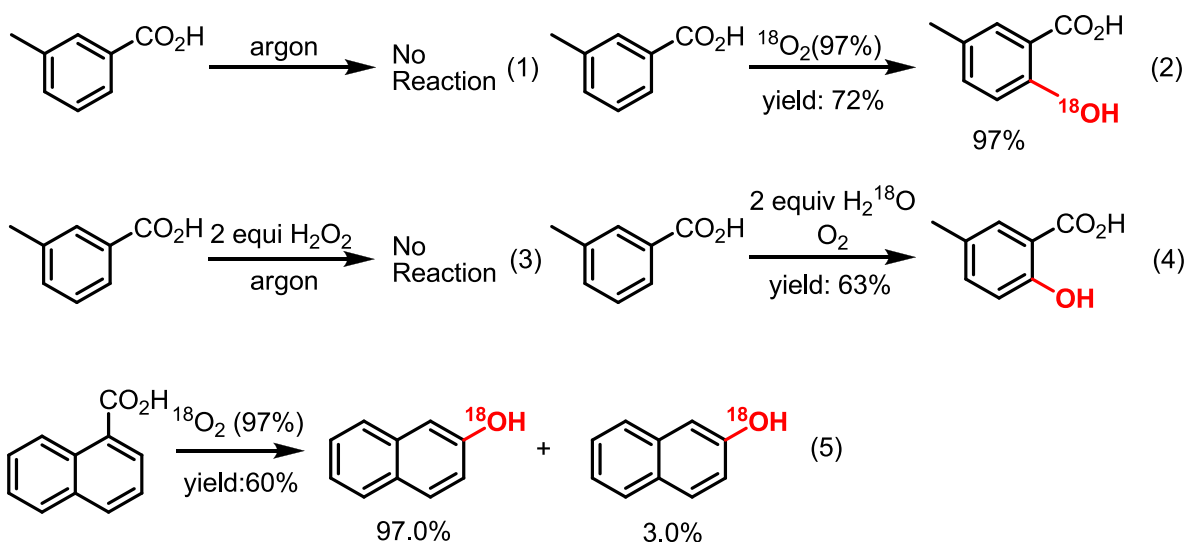
Note: <sup>a</sup> The yields were determined by <sup>1</sup>H NMR analysis of crude products using CH<sub>2</sub>Br<sub>2</sub> as the internal standard; <sup>b</sup> 5 atm. O<sub>2</sub>; <sup>c</sup> Air instead of O<sub>2</sub>; <sup>d</sup> Argon instead of O<sub>2</sub>. DMF: *N,N*-dimethylformamide; DMA: *N,N*-dimethylacetamide; DMP: *N,N*-dimethylpropionamide.

**Table 2.** Pd-Catalyzed *ortho*-hydroxylation with O<sub>2</sub><sup>a</sup>



Note: <sup>a</sup> Isolated yield.

**III. General procedure for Pd(II)-catalyzed *ortho*-hydroxylation with 5 atm O<sub>2</sub>:** A 50 mL high pressure reactor equipped with a magnetic stir bar was charged with Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol), followed by the benzoic acid substrate (0.5 mmol), benzoquinone (54.0 mg, 0.5 mmol), KOAc (98.0 mg, 1 mmol) and *N,N*-dimethylacetamide (1.5 mL). The reactor was filled with O<sub>2</sub> (20 atm), and then evacuated and backed-filled with O<sub>2</sub> (5 atm, 2 times). After the reaction mixture was stirred at 115 °C for 15 h, it was allowed to cool to ambient temperature. The reaction was worked up and the crude product was purified following the procedure described above for hydroxylation with 1 atm O<sub>2</sub>.



**Figure 1.** Preliminary mechanistic studies

**IV. Preliminary mechanistic studies: general procedure for the hydroxylation reaction in 1**

**atm Argon or <sup>18</sup>O:** A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol) followed by the benzoic acid substrate (0.5 mmol), benzoquinone (54.0 mg, 0.5 mmol), KOAc (98.0 mg, 1 mmol) and *N,N*-dimethylacetamide (1.5 mL). After the reaction mixture was cooled to -78 °C, the reaction tube was evacuated and back-filled with <sup>18</sup>O<sub>2</sub> or argon (3 times, balloon). The

reaction mixture was stirred at 115 °C for 15 h, and then it was allowed to cool to ambient temperature. The reaction was worked up and the crude product was purified following the procedure described above for hydroxylation with 1 atm O<sub>2</sub>.

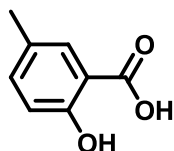
**Table 3.** Influence of benzoquinone on hydroxylation

Entry	BQ (equiv)	2 hours		15 hours	
		%Yield <sup>a</sup>	% SM <sup>a</sup>	%Yield <sup>a</sup>	% SM <sup>a</sup>
1	0	3	90	20	50
2	1	45	50	82	12

Note: <sup>a</sup> The yields were determined by <sup>1</sup>H NMR analysis of crude products using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

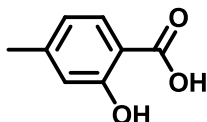
## V. Characterization of the synthesized compounds

### 2-Hydroxy-5-methylbenzoic acid **1**



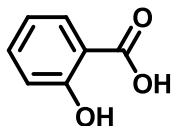
<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ 7.70 (s, 1 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 2.29 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ 171.48, 159.73, 136.36, 129.66, 127.78, 116.66, 111.52, 19.06. HRMS (ESI-TOF) *m/z*: calcd for C<sub>8</sub>H<sub>9</sub>O<sub>3</sub><sup>+</sup> 153.0546 (M+H)<sup>+</sup>, found 153.0543.

### 2-Hydroxy-4-methylbenzoic acid **2**



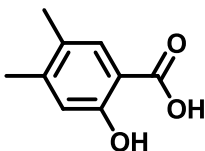
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.77 (d,  $J = 8.0$  Hz, 1 H), 6.78 (s, 1 H), 6.77 (d,  $J = 8.0$  Hz, 1 H), 2.34 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.47, 161.90, 146.87, 129.85, 119.94, 117.00, 109.32, 20.56. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_9\text{O}_3^+$  153.0546 ( $\text{M}+\text{H}$ ) $^+$ , found 153.0546.

### 2-Hydroxybenzoic acid **3**



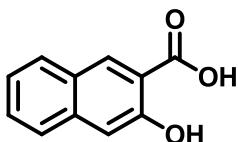
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.91 (d,  $J = 8.0$  Hz, 1 H), 7.54 (t,  $J = 8.0$  Hz, 1 H), 6.97–6.93 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.44, 161.78, 135.51, 129.99, 118.70, 116.81, 111.89. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_7\text{H}_7\text{O}_3^+$  139.0390 ( $\text{M}+\text{H}$ ) $^+$ , found 139.0389.

### 2-Hydroxy-4,5-dimethylbenzoic acid **4**



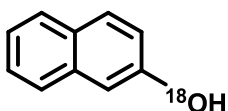
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.62 (s, 1H), 7.76 (s, 1 H), 2.26 (s, 3 H), 2.20 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.41, 160.06, 145.58, 129.91, 126.91, 117.46, 109.23, 19.05, 17.46. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_9\text{H}_{11}\text{O}_3^+$  167.0703 ( $\text{M}+\text{H}$ ) $^+$ , found 167.0703.

### 3-Hydroxy-2-naphthoic acid **5**



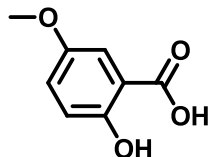
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.63 (s, 1 H), 7.96 (d,  $J = 8.0$  Hz, 1 H), 7.78 (d,  $J = 8.4$  Hz, 1 H), 7.55 (dd,  $J = 7.2$  Hz,  $J = 8.4$  Hz, 1 H), 7.37 (dd,  $J = 7.2$  Hz,  $J = 8.0$  Hz, 1 H), 7.33 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.08, 156.43, 137.61, 132.41, 128.82, 128.71, 126.62, 125.64, 123.41, 113.78, 110.64. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{11}\text{H}_7\text{O}_3^-$  187.0401 ( $\text{M}-\text{H}$ ) $^-$ , found 187.0394.

### Naphthalen-2-ol **6**



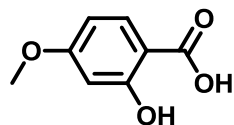
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77–7.73 (m, 2 H), 7.67 (d,  $J = 8.4$  Hz, 1 H), 7.42 (t,  $J = 7.6$  Hz, 1 H), 7.32 (t,  $J = 7.6$  Hz, 1 H), 7.15 (s, 1 H), 7.11 (d,  $J = 8.8$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.37, 134.56, 129.79, 128.85, 127.73, 126.47, 126.32, 123.54, 117.74, 109.43. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{10}\text{H}_9\text{O}^+$  147.0699 ( $\text{M}+\text{H}$ ) $^+$ , found 147.0693.

#### 2-Hydroxy-5-methoxybenzoic acid **7**



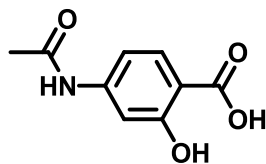
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.37 (s, 1 H), 7.16 (d,  $J = 8.8$  Hz, 1 H), 6.90 (d,  $J = 8.8$  Hz, 1 H), 3.79 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.20, 156.08, 151.73, 123.44, 117.81, 111.99, 111.54, 54.80. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_9\text{O}_4^+$  169.0495 ( $\text{M}+\text{H}$ ) $^+$ , found 169.0497.

#### 2-Hydroxy-4-methoxybenzoic acid **8**



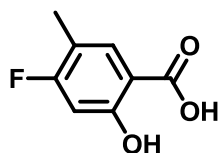
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  11.33 (s, 1H), 7.80 (d,  $J = 8.8$  Hz, 1 H), 6.51 (d,  $J = 8.8$  Hz, 1 H), 6.47 (s, 1 H), 3.86 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.31, 165.65, 164.11, 131.37, 106.81, 104.75, 100.22, 54.78. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_9\text{O}_4^+$  169.0495 ( $\text{M}+\text{H}$ ) $^+$ , found 169.0500.

#### 4-Acetamido-2-hydroxybenzoic acid **9**



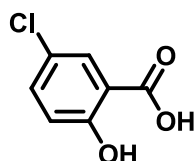
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  11.20 (s, 1H), 9.46 (s, 1 H), 7.80 (d,  $J = 8.8$  Hz, 1 H), 7.49 (s, 1 H), 7.10 (d,  $J = 8.8$  Hz, 1 H), 2.12 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  170.92, 168.33, 162.71, 145.61, 130.52, 109.49, 106.53, 105.52, 23.08. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_9\text{H}_{10}\text{NO}_4^+$  196.0604 ( $\text{M}+\text{H}$ ) $^+$ , found 196.0599.

#### 4-Fluoro-2-hydroxy-5-methylbenzoic acid **10**



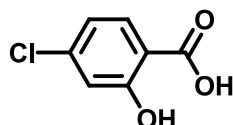
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.78 (d,  $J = 8.8$  Hz, 1 H), 6.65 (d,  $J = 11.2$  Hz, 1 H), 2.20 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  170.62, 164.86 (d,  $J_{\text{C-F}} = 250.8$  Hz), 161.63 (d,  $J_{\text{C-F}} = 4.0$  Hz), 132.46 (d,  $J_{\text{C-F}} = 8.2$  Hz), 115.36 (d,  $J_{\text{C-F}} = 18.5$  Hz), 108.20 (d,  $J_{\text{C-F}} = 2.0$  Hz), 102.77 (d,  $J_{\text{C-F}} = 25.3$  Hz), 12.11. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_6\text{FO}_3^-$  169.0306 (M-H) $^-$ , found 169.0307.

#### 5-Chloro-2-hydroxybenzoic acid **11**



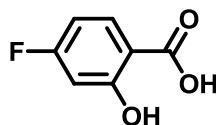
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.84 (s, 1 H), 7.52 (d,  $J = 8.4$  Hz, 1 H), 6.99 (d,  $J = 8.4$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  169.93, 159.95, 134.75, 128.58, 122.39, 118.36, 112.75. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_7\text{H}_4\text{ClO}_3^-$  170.9854 (M-H) $^-$ , found 170.9859.

#### 4-Chloro-2-hydroxybenzoic acid **12**



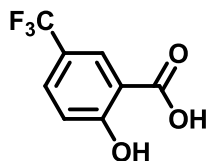
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.90 (d,  $J = 8.4$  Hz, 1 H), 7.02 (s, 1 H), 6.98 (d,  $J = 8.4$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  170.72, 162.21, 140.25, 131.31, 119.08, 116.59, 110.85. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_7\text{H}_4\text{ClO}_3^-$  170.9854 (M-H) $^-$ , found 170.9847.

#### 4-Fluoro-2-hydroxybenzoic acid **13**



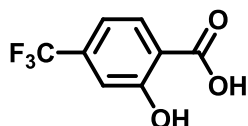
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.97 (t,  $J = 7.2$  Hz, 1 H), 6.76–2.71 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  170.60, 166.49 (d,  $J_{\text{C-F}} = 251.0$  Hz), 163.58 (d,  $J_{\text{C-F}} = 14.2$  Hz), 132.24 (d,  $J_{\text{C-F}} = 11.4$  Hz), 108.71 (d,  $J_{\text{C-F}} = 1.3$  Hz), 106.27 (d,  $J_{\text{C-F}} = 22.7$  Hz), 103.08 (d,  $J_{\text{C-F}} = 24.4$  Hz). HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_7\text{H}_4\text{FO}_3^-$  155.0150 (M-H) $^-$ , found 155.0156.

#### 2-Hydroxy-5-(trifluoromethyl)benzoic acid **14**



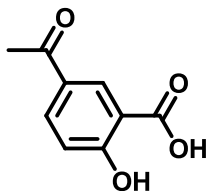
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.19 (s, 1 H), 7.84 (d,  $J = 8.8$  Hz, 1 H), 7.16 (d,  $J = 8.8$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  169.94, 163.77, 131.35 (q,  $J_{\text{C-F}} = 3.4$  Hz), 126.91 (q,  $J_{\text{C-F}} = 4.1$  Hz), 123.28 (q,  $J_{\text{C-F}} = 269.1$  Hz), 119.96 (q,  $J_{\text{C-F}} = 33.0$  Hz), 117.56, 111.65. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_4\text{F}_3\text{O}_3^-$  205.0118 ( $\text{M-H}^-$ ), found 205.0117.

#### 2-Hydroxy-4-(trifluoromethyl)benzoic acid **15**



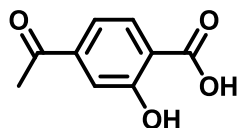
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.12 (d,  $J = 8.8$  Hz, 1 H), 7.29–7.27 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  171.06, 162.22, 136.40 (q,  $J_{\text{C-F}} = 32.2$  Hz), 131.89, 123.66 (q,  $J_{\text{C-F}} = 270.8$  Hz), 115.78, 115.52 (q,  $J_{\text{C-F}} = 3.7$  Hz), 114.46 (q,  $J_{\text{C-F}} = 4.0$  Hz). HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_4\text{F}_3\text{O}_3^-$  205.0118 ( $\text{M-H}^-$ ), found 205.0126.

#### 5-Acetyl-2-hydroxybenzoic acid **16**



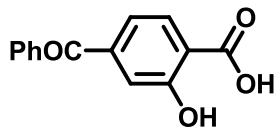
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.54 (s, 1 H), 7.16 (d,  $J = 8.8$  Hz, 1 H), 7.06 (d,  $J = 8.8$  Hz, 1 H), 2.58 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  194.48, 171.02, 165.06, 135.04, 131.02, 128.63, 117.03, 111.62, 25.01. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_9\text{H}_9\text{O}_4^+$  181.0495 ( $\text{M+H}^+$ ), found 181.0498.

#### 4-Acetyl-2-hydroxybenzoic acid **17**



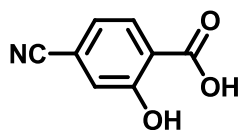
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1 H), 7.50 (d,  $J = 8.0$  Hz, 1 H), 7.49 (s, 1 H), 2.62 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  196.26, 170.78, 161.47, 142.48, 130.32, 117.66, 116.38, 115.21, 25.68. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_9\text{H}_8\text{O}_4\text{Na}^+$  203.0315 ( $\text{M+Na}^+$ ), found 203.0325.

4-Benzoyl-2-hydroxybenzoic acid **18**



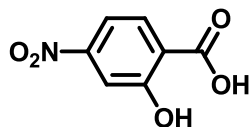
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.08 (d,  $J = 8.0$  Hz, 1 H), 7.83 (d,  $J = 7.6$  Hz, 2 H), 7.69 (t,  $J = 7.6$  Hz, 1 H), 7.58 (t,  $J = 7.6$  Hz, 1 H), 7.28–7.25 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  194.45, 171.05, 161.15, 143.58, 136.39, 132.53, 130.33, 129.36, 128.08, 119.12, 117.52, 115.14. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{11}\text{O}_4^+$  243.0652 ( $\text{M}+\text{H}$ ) $^+$ , found 243.0654.

4-Cyano-2-hydroxybenzoic acid **19**



$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  7.86 (br, 1 H), 7.34 (s, 1H), 7.24 (br, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  161.63, 132.23, 122.63, 121.46, 118.78, 116.99. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_8\text{H}_4\text{NO}_3^-$  162.0197 ( $\text{M}-\text{H}$ ) $^-$ , found 162.0199.

2-Hydroxy-4-nitrobenzoic acid **20**



$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.15 (d,  $J = 8.4$  Hz, 1 H), 7.76 (d,  $J = 8.4$  Hz, 1 H), 7.72 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  169.85, 161.62, 151.58, 131.39, 116.86, 112.76, 111.49. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_7\text{H}_4\text{NO}_5^-$  182.0095 ( $\text{M}-\text{H}$ ) $^-$ , found 182.0087.

# VI. NMR spectra

