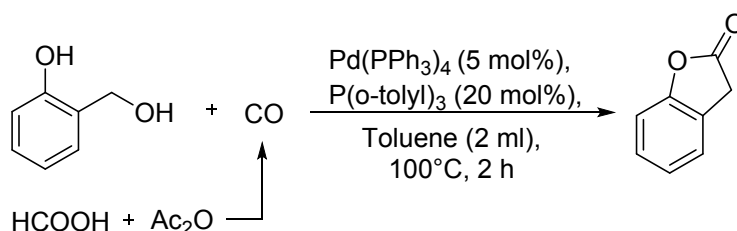


**Typical reaction procedure:** Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and P(*o*-tolyl) (20 mol %) were transferred into an oven-dried tube which was filled with nitrogen. Toluene (2.0 mL), 2-hydroxybenzyl alcohols (1.0 mmol) were added into the reaction tube. Then a mixture of formic acid (3.0 mmol) and acetic anhydride (3.0 mmol) was added to the reaction tube which was stirred for 1.5 h at 30 °C. The mixture was stirred for 2-3 h at 100 °C. After the reaction was complete, the reaction mixture was filtered and concentrated, column chromatography on silica gel (petroleum ether/ethyl acetate 20:1).



**Benzofuran-2(3H)-one:**<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.3 (t, J = 7.9 Hz, 2H), 7.1 (t, J = 7.5 Hz, 1H), 7.1 (d, J = 8.0 Hz, 1H), 3.7 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.0, 154.4, 128.6, 124.5, 123.9, 123.0, 110.5, 32.7; GC-MS (EI, 70 ev): m/z ( % ) = 134.1 ([M]<sup>+</sup>, 100), 106.1 (58), 78.1 (96), 51.1 (16).

**5-Bromobenzofuran-2(3H)-one:**<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.4 (d, J = 8.1 Hz, 2H), 6.9(d, J = 9.0 Hz, 1H), 3.7 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.1, 153.6, 132.0, 127.7, 125.1, 116.7, 112.4, 32.9; GC-MS (EI, 70 ev): m/z ( % ) = 211.8 ([M]<sup>+</sup>, 91), 183.8 (100), 155.8 (49), 77.0 (92), 51.0 (32).

**3-Ethylbenzofuran-2(3H)-one:**<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.2 (m, 2H), 7.1 (t, J = 7.5 Hz, 1H), 7.0(d, J = 8.0 Hz, 1H), 3.6 (t, J = 5.9 Hz, 1H), 2.0 – 1.9 (m, 2H), 0.9 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.0, 153.8, 128.6, 127.1, 124.1, 124.0, 110.5, 44.5, 24.2, 10.1; GC-MS (EI, 70 ev): m/z ( % ) = 162.0 ([M]<sup>+</sup>, 100), 134.0 (65), 119.0 (70), 105.0 (25), 91.0 (49), 77.0 (31), 51.0 (22).

**5-Methylbenzofuran-2(3H)-one:**<sup>4</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.1 – 7.0 (m, 2H), 7.0 – 6.9 (m, 1H), 3.6 (s, 2H), 2.3 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.4, 152.6, 133.7, 129.1, 125.2, 123.0, 110.2, 33.0, 21.0; GC-MS (EI, 70 ev): m/z ( % ) = 147.9 ([M]<sup>+</sup>, 100), 120.0 (70), 91.0 (95), 65.0 (14).

**5-Chlorobenzofuran-2(3H)-one:**<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.3 (m, 2H), 7.0 (d, J = 9.2 Hz, 1H), 3.7 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.2, 153.1, 129.3, 128.9, 124.9, 124.8, 111.9, 33.0; GC-MS (EI, 70 ev): m/z ( % ) = 167.9 ([M]<sup>+</sup>, 95), 139.9 (100), 111.9 (88), 77.0 (55), 51.0 (20).

**7-Methylbenzofuran-2(3H)-one:**<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.1 (m, 2H), 7.1 – 7.0 (m, 1H), 3.7 (s, 2H), 2.3 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 153.0, 130.0, 123.7, 122.5, 121.6, 120.8, 33.1, 14.8; GC-MS (EI, 70 ev): m/z( % ) = 148.0 ([M]<sup>+</sup>, 96), 120.0 (90), 91.0 (100), 65.0 (15).

**5-Methoxybenzofuran-2(3H)-one:**<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.0 (d, J = 8.7 Hz, 1H), 6.9 – 6.8 (m, 2H), 3.8 (s, 3H), 3.7 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.4, 156.4, 148.5, 124.1, 113.6, 111.0, 110.8, 55.8, 33.5; GC-MS (EI, 70 ev): m/z( % ) = 163.9 ([M]<sup>+</sup>, 85), 136.0 (100), 108.0 (48), 78.0 (23), 65.0 (25).

**5-(tert-Butyl)benzofuran-2(3H)-one:**<sup>6</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.3 (m, 2H), 7.0 (d, J = 8.8 Hz, 1H), 3.7 (s, 2H), 1.3 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.53, 152.52, 147.32, 125.61, 122.70, 121.73, 109.99, 34.63, 33.22, 31.56; GC-MS (EI, 70 ev): m/z( % ) = 190.0 ([M]<sup>+</sup>, 31), 175.0 (100), 147.0 (70).

**6-Methylbenzofuran-2(3H)-one:**<sup>7</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.1 (d, J = 7.6 Hz, 1H), 7.0 – 6.9 (m, 2H), 3.6 (s, 2H), 2.4 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.6, 154.8, 139.2, 124.7, 124.2, 120.0, 111.3, 32.8, 21.6; GC-MS (EI, 70 ev): m/z( % ) = 148.0 ([M]<sup>+</sup>, 100), 120.0 (56), 91.0 (85).

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