

Supplementary Data

Direct Palladium-Catalyzed C-4 Arylation of Tri-substituted Furans with Aryl Chlorides: An Efficient Access to Heteroaromatics

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Characterization Data for Desired Products

Diethyl 5-Methyl-4-phenylfuran-2,3-dicarboxylate (3a):

Yellowish viscous oil; IR (KBr) 1558, 1732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.14 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 7.22-7.34 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 12.6, 13.9, 14.2, 61.2, 61.6, 111.4, 22.7, 126.9, 127.7, 128.3, 128.8, 130.7, 131.7, 139.5, 152.6, 157.8, 164.1; MS (EI, 70 eV) *m/z* (%): 128, 185, 202, 229, 257, 302; C₁₇H₁₈O₅: Calcd. C, 67.54; H, 6.00; Found: C, 67.30; H, 6.04.

Diethyl 5-Methyl-4-m-tolylfuran-2,3-dicarboxylate (3b):

Yellowish viscous oil; IR (KBr) 1610, 1733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.16 (t, *J* = 6.8 Hz, 3H), 1.29 (t, *J* = 6.8 Hz, 3H), 2.30 (s, 3H), 2.34 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 7.02-7.09 (m, 3H), 7.19-7.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 12.6, 13.9, 14.9, 21.3, 61.2, 61.6, 122.7, 125.8, 126.7, 128.4, 128.5, 129.4, 130.6, 138.1, 139.4, 151.6, 157.8, 164.0; MS (EI, 70 eV) *m/z* (%): 91, 199, 243, 271, 316; C₁₈H₂₀O₅: Calcd. C, 68.34; H, 6.37; Found: C, 68.13; H, 6.40.

Diethyl 5-Methyl-4-o-tolylfuran-2,3-dicarboxylate (3c):

Yellowish viscous oil; IR (KBr) 1560, 1732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.08 (t, *J* = 8.0 Hz, 3H), 1.37 (t, *J* = 8.0 Hz, 3H), 2.15 (s, 3H), 2.21 (s, 3H), 4.14 (q, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 8.0 Hz, 2H), 7.11-7.26 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 12.3, 13.7, 14.2, 19.7, 60.6, 61.2, 111.3, 122.7, 125.5, 126.9, 128.3, 129.9, 130.4, 137.4, 140.0, 152.7, 157.9, 163.3; MS (EI, 70 eV) *m/z* (%): 91, 115, 170, 198, 242, 270, 316; C₁₈H₂₀O₅: Calcd. C, 68.34; H, 6.37; Found: C, 68.25; H, 6.34.

Diethyl 4-(4-Ethylphenyl)-5-methylfuran-2,3-dicarboxylate (3d):

Yellowish viscous oil; IR (KBr) 1600, 1728 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.18-1.25 (m, 6H), 1.33 (t, *J* = 6.8 Hz, 3H), 2.38 (s, 3H), 2.63 (q, *J* = 7.6 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 7.19 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 12.6, 13.9, 14.2, 15.3, 28.1, 61.2, 61.6, 122.6, 126.7, 127.9, 128.0, 128.7, 139.4, 143.8, 152.5, 157.8, 164.0; MS (EI, 70 eV) *m/z* (%): 77, 258, 285, 315, 330; C₁₉H₂₂O₅: Calcd. C, 69.07; H, 6.71; Found: C, 69.21;

H, 6.67.

Diethyl 4-(4-Methoxycarbonyl)phenyl-5-methylfuran-2,3-dicarboxylate (3e): Yellowish viscous oil; IR (KBr) 1612, 1729 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.19 (t, *J* = 8.0 Hz, 3H), 1.33 (t, *J* = 8.0 Hz, 3H), 2.39 (s, 3H), 3.90 (s, 3H), 4.26 (q, *J* = 8.0 Hz, 2H), 4.37 (q, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.6, 13.9, 14.1, 52.1, 61.3, 61.7, 121.8, 126.1, 128.8, 129.8, 135.5, 140.0, 152.9, 153.0, 157.6, 163.6, 166.6; MS (EI, 70 eV) *m/z* (%): 58, 128, 143, 211, 288, 315, 329, 360; C₁₉H₂₀O₇: Calcd. C, 63.33; H, 5.59; Found: C, 63.42; H, 5.57.

Diethyl 5-Methyl-4-(thiophen-2-yl)furan-2,3-dicarboxylate (3f): Yellowish viscous oil; IR (KBr) 1612, 1732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.28-1.37 (m, 6H), 2.49 (s, 3H), 4.30-4.39 (m, 4H), 7.05-7.06 (m, 2H), 7.33-7.34 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.0, 13.9, 14.2, 61.4, 61.9, 111.6, 116.1, 125.9, 126.9, 127.6, 132.9, 139.5, 153.2, 157.6, 163.7; MS (EI, 70 eV) *m/z* (%): 91, 135, 163, 208, 235, 263, 308; C₁₅H₁₆O₅S: Calcd. C, 58.43; H, 5.23; Found: C, 58.36; H, 5.21.

Diethyl 4-(4-Methoxyphenyl)-5-methylfuran-2,3-dicarboxylate (3g): Yellowish viscous oil; IR (KBr) 1606, 1737 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 3.82 (s, 3H), 4.27 (q, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 9.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.5, 13.9, 14.1, 55.2, 61.2, 61.6, 114.0, 122.2, 122.9, 126.7, 130.0, 139.3, 152.4, 157.8, 159.3, 164.0; MS (EI, 70 eV) *m/z* (%): 115, 187, 232, 259, 287, 304, 332; C₁₈H₂₀O₆: Calcd. C, 65.05; H, 6.07; Found: C, 65.24; H, 5.99.

Diethyl 4-(2-Methoxyphenyl)-5-methylfuran-2,3-dicarboxylate (3h): Yellowish viscous oil; IR (KBr) 1561, 1731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.03 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 2.20 (s, 3H), 3.72 (s, 3H), 4.09 (q, *J* = 6.8 Hz, 2H), 4.36 (q, *J* = 6.8 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 12.2, 13.6, 14.1, 52.1, 61.1, 61.2, 122.7, 126.1, 128.2, 130.5, 131.1, 131.6, 131.9, 140.4, 152.2, 158.1, 162.8,

167.1; MS (EI, 70 eV) *m/z* (%): 226, 242, 314, 332; C₁₈H₂₀O₂: Calcd. C, 65.05; H, 6.07; Found: C, 65.24; H, 5.97.

2-Methyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (3i): Colorless oil; IR (KBr): 1682, 1575 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.14 (m, 2H), 2.31 (s, 3H), 2.46 (m, 2H), 2.88 (m, 2H), 7.26-7.34 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 11.9, 22.4, 23.6, 38.5, 119.6, 125.2, 126.9, 127.8, 129.7, 131.6, 148.7, 165.9, 194.4; MS (EI, 70 eV): *m/z* 141, 155, 170, 183, 198, 211, 226; C₁₅H₁₄O₂: Calcd. C, 79.62; H, 6.24. Found: C, 79.66; H, 6.27.

2-Methyl-3-(thiophen-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (3j): Red solid; IR (KBr): 1684, 1577, 1615 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.17 (m, 2H), 2.42 (s, 3H), 2.51 (m, 2H), 2.87 (m, 2H), 7.05 (dd, 1H, *J* = 5.1 Hz), 7.30 (d, 1H, *J* = 5.1 Hz), 7.34 (d, 1H, *J* = 3.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 12.7, 22.3, 23.6, 38.5, 113.1, 119.4, 125.0, 126.8, 128.1, 136.8, 149.4, 166.1, 194.5; MS (EI, 70 eV): *m/z* 176, 204, 232; C₁₅H₁₂O₂S: Calcd. C, 67.21; H, 5.21. Found: C, 67.33; H, 5.23.

3-(2-Methoxyphenyl)-2-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (3k): Orange solid; IR (KBr): 1598, 1677 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.17 (m, 2H), 2.31 (s, 3H), 2.47 (m, 2H), 2.88 (m, 2H), 3.82 (s, 3H), 6.84 (m, 1H), 6.95 (m, 2H), 7.27 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 12.0, 22.4, 23.6, 38.5, 55.2, 112.8, 115.4, 119.6, 120.1, 122.4, 128.7, 132.9, 148.8, 158.9, 165.8, 194.2; MS (EI, 70 eV): *m/z* 200, 213, 225, 241, 256; C₁₆H₁₆O₃: Calcd. C, 74.98; H, 6.29. Found: C, 74.95; H, 6.33.

3-(3-Methoxyphenyl)-2-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (3l): Orange solid; IR (KBr): 1575, 1682 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.17 (m, 2H), 2.20 (s, 3H), 2.47 (m, 2H), 2.87 (m, 2H), 3.79 (s, 3H), 6.96 (m, 2H), 7.18 (d, 1H, *J* = 7.4 Hz), 7.33 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 11.9, 22.5, 23.5, 38.3, 55.4, 110.7, 114.7, 120.1, 120.6, 120.8, 128.1, 131.4, 149.1, 157.3, 165.3, 193.9; MS (EI, 70 eV): *m/z* 200, 256, 228; C₁₆H₁₆O₃: Calcd. C, 74.98; H, 6.29. Found: C, 74.74; H, 6.33.

3-(4-Methoxyphenyl)-2-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (3m): Orange solid; IR (KBr): 1577, 1682 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.15 (m, 2H), 2.31 (s, 3H), 2.44 (m, 2H), 2.86 (m, 2H), 3.85 (s, 3H), 6.92 (d, 2H, *J* = 8.2 Hz), 7.31 (d, 2H, *J* = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 11.9, 22.4, 23.6, 38.6, 55.1, 113.3, 118.7, 119.6, 123.9, 130.8, 148.1, 158.6, 165.7, 194.2; MS (EI, 70 eV): *m/z* 200, 228, 241, 256; C₁₆H₁₆O₃: Calcd. C, 74.98; H, 6.29. Found: C, 75.01; H, 6.22.

2-Methyl-3-(naphthalen-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (3n): Colorless oil; IR (KBr): 1588, 1681 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.21 (m, 2H), 2.36 (s, 3H), 2.52 (m, 2H), 2.91 (m, 2H), 7.55 (m, 3H), 7.83 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 12.0, 22.4, 23.6, 38.7, 119.1, 119.8, 125.8, 125.9, 127.2, 127.6, 127.8, 128.1, 128.2, 129.3, 132.5, 133.1, 149.2, 166.4, 195.0; MS (EI, 70 eV): *m/z* 233, 248, 276; C₁₉H₁₆O₂: Calcd. C, 82.58; H, 5.84. Found: C, 82.66; H, 5.89.

2,6,6-Trimethyl-3-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (3o): Yellow oil; IR (KBr): 1575, 1683 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.18 (s, 6H), 2.33 (s, 3H), 2.39 (s, 2H), 2.77 (s, 2H), 7.26-7.46 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 11.7, 28.2, 34.6, 37.3, 52.7, 118.4, 118.7, 126.7, 127.5, 129.4, 131.3, 148.7, 164.5, 193.1; MS (EI, 70 eV): *m/z* 170, 198, 239, 254; C₁₇H₁₈O₂: Calcd. C, 80.28; H, 7.13. Found: C, 80.33; H, 7.14.

3-(4-Methoxyphenyl)-2,6,6-trimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (3p): Orange solid; IR (KBr): 1586, 1689 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.18 (s, 6H), 2.33 (s, 3H), 2.39 (s, 2H), 2.48 (s, 2H), 3.83 (s, 3H), 6.94 (d, 2H, *J* = 8.5 Hz), 7.33 (d, 2H, *J* = 8.5 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 12.0, 28.3, 34.8, 37.6, 52.9, 55.2, 113.3, 118.4, 118.6, 123.8, 130.8, 148.5, 158.6, 164.8, 193.7; MS (EI, 70 eV): *m/z* 200, 228, 269, 284; C₁₈H₂₀O₃: Calcd. C, 76.03; H, 7.09. Found: C, 76.14; H, 7.14.

2,6,6-Trimethyl-3-(thiophen-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (3q): Red solid; IR (KBr): 1579, 1682 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.17 (s, 6H), 2.41 (s, 2H), 2.47 (s, 3H), 2.77 (s, 2H), 7.07 (dd, 1H, *J* = 5.2 Hz), 7.24-7.33 (d, 1H, *J* = 5.2 Hz), 7.46 (d, 1H, *J* = 3.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 12.6, 28.1, 34.4, 37.3, 52.8, 112.5, 118.0, 124.5, 126.7, 127.7, 132.1, 149.2, 164.5, 193.0; MS (EI, 70 eV): *m/z* 176, 204, 245, 260; C₁₅H₁₆O₂S: Calcd. C, 69.20; H, 6.19. Found: C, 69.01; H, 6.17.

Ethyl 2,5-Dimethyl-4-phenylfuran-3-carboxylate (3r): Yellow oil; IR (KBr): 1571, 1554, 1707 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 1.11 (t, 3H, *J* = 7.2 Hz), 2.15 (s, 3H), 2.54 (s, 3H), 4.17 (q, 2H, *J* = 7.2 Hz), 7.21-7.27 (m, 2H), 7.28-7.31 (m, 1H), 7.32-7.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 11.7, 13.9, 14.0, 59.7, 113.5, 126.7, 127.6, 130.3, 147.3, 157.1, 164.3; MS (EI, 70 eV): *m/z* 198, 215, 244; C₁₆H₁₆O₃: Calcd. C, 73.75; H, 6.60. Found: C, 73.84; H, 6.62.

Ethyl 4-(2-Methoxyphenyl)-2,5-dimethylfuran-3-carboxylate (3s): Yellow oil; IR (KBr): 1511, 1654, 1783 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.10 (t, 3H, *J* = 7.2 Hz), 2.13 (s, 3H), 2.55 (s, 3H), 4.11 (q, 2H, *J* = 7.2 Hz), 6.91 (d, *J* = 8.0 Hz, 1H), 6.97 (dt, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H) 7.29 (dt, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 11.8, 13.9, 14.0, 55.3, 59.7, 110.3, 113.5, 117.3, 120.1, 122.5, 127.6, 130.3, 147.1, 157.2, 158.3, 164.3; MS (EI, 70 eV): *m/z* 43, 213, 274; C₁₆H₁₈O₄: Calcd. C, 70.06; H, 6.61. Found: C, 70.42; H, 6.66.

Ethyl 2,5-Dimethyl-4-(naphthalen-2-yl)furan-3-carboxylate (3t): Red solid; IR (KBr): 1632, 1707 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.47 (t, 3H, *J* = 7.2 Hz), 2.14 (s, 3H), 2.65 (s, 3H), 3.70-3.85 (m, 2H), 7.30-7.48 (m, 4H), 7.65 (d, 1H, *J* = 8.4 Hz), 7.81 (d, 1H, *J* = 8.0 Hz), 7.84 (d, 1H, *J* = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 11.7, 13.1, 59.4, 119.1, 114.9, 125.1, 125.5, 125.7, 126.0, 127.6, 127.7, 128.4, 131.7, 133.3, 133.6, 147.1, 157.0, 164.3; MS (EI, 70 eV): *m/z* 317; C₁₉H₁₈O₃: Calcd. C, 77.53; H, 6.16. Found: C, 77.50; H, 6.12.