Supporting Information

Aerobic Oxidative α-Arylation of Furans with Boronic Acids via Pd(II)-Catalyzed C–C Bond Cleavage of Primary Furfuryl Alcohols: Sustainable Access to Arylfurans

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1 General experimental details

All chemicals and solvents were purchased from commercial vendors and used without further purification unless otherwise noted. Analytical TLC was performed with silica gel 60 F254 plates. Column chromatography was performed on silica gel 200-300 mesh and using appropriate solvents as eluent. Melting points were determined using a Stuart SMP10 melting point apparatus. NMR spectra were recorded on a Bruker AV-400 spectrometer (¹H NMR at 400 MHz and ¹³C NMR at 100 MHz). Proton chemical shifts were referenced relative to tetramethylsilane proton signals at $\delta = 0.00$ ppm. Carbon chemical shifts were referenced relative to CDCl₃ at $\delta = 77.16$ ppm. Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, dt = double triplet, dq = double quartet, br = broad), coupling constants (Hz), integration. Data for ¹³C NMR are reported in cm⁻¹. ESI technique was used for the high resolution mass (HRMS) measurements.

2 Synthesis of the starting materials

(5-Phenylfuran-2-yl)methanol (1a)



The syntheses of **1a** have been reported previously.¹ Analytical data were consistent with previously reported data.² Yellow solid (2.34 g, 85% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.64 (m, 2H), 7.42 – 7.34 (m, 2H), 7.28 – 7.23 (m, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 6.37 (d, *J* = 3.3 Hz, 1H), 4.66 (s, 2H), 1.83 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.2, 153.7, 130.8, 128.8, 127.6, 124.0, 110.1, 105.8, 57.8.

(5-(p-Tolyl)furan-2-yl)methanol (1b)



Compound **1b** was prepared in the same manner of **1a**, except that 4-tolylboronic acid was used instead of phenylboronic acid.¹ Analytical data were consistent with previously reported data.³ White solid (0.82 g, 94% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 3.2 Hz, 1H), 6.35 (d, *J* = 3.2 Hz, 1H), 4.65 (s, 2H), 2.35 (s, 3H), 1.89 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.4, 153.3, 137.5, 129.5, 128.1, 123.9, 110.1, 105.1, 57.8, 21.4.

(5-(4-Methoxyphenyl)furan-2-yl)methanol (1c)



Compound **1c** was prepared in the same manner of **1a**, except that 4-methoxyphenylboronic acid was used instead of phenylboronic acid.¹ Analytical data were consistent with previously reported data.³ White solid (0.91 g, 94% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 3.2 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 4.62 (s, 2H), 3.81 (s, 3H), 2.10 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 154.2, 153.0, 125.4, 123.9, 114.2, 110.1, 104.2, 57.7, 55.4.

(5-(4-Fluorophenyl)furan-2-yl)methanol (1d)



The syntheses of **1d** have been reported previously.³ Analytical data were consistent with previously reported data.³ Yellow solid (0.21 g, 24%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.58 (m, 2H), 7.09 – 7.02 (m, 2H), 6.51 (d, *J* = 3.3 Hz, 1H), 6.35 (d, *J* = 3.3 Hz, 1H), 4.64 (s, 2H), 2.05 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3 (d, *J*_{C-F} = 245.6 Hz), 153.7, 153.3, 127.2 (d, *J*_{C-F} = 3.3 Hz), 125.7 (d, *J*_{C-F} = 8.0 Hz), δ 115.8 (d, *J*_{C-F} = 21.8 Hz), 110.1, 105.5 (d, *J*_{C-F} = 1.3 Hz), 57.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.12.

(5-(4-Nitrophenyl)furan-2-yl)methanol (1e)



The syntheses of **1e** have been reported previously.³ Analytical data were consistent with previously reported data.³ Yellow solid (0.18 g, 17%). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 3.3 Hz, 1H), 6.46 (d, J = 3.3 Hz, 1H), 4.71 (s, 2H), 1.84 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 151.8, 146.6, 136.4, 124.5, 124.1, 110.7, 109.9, 57.7.

(5-(Thiophen-2-yl)furan-2-yl)methanol (1f)



Compound **1f** was prepared in the same manner of **1a**, except that 2-thiopheneboronic acid was used instead of phenylboronic acid.¹ White solid (0.32 g, 39% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.02 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.43 (d, *J* = 3.3 Hz, 1H), 6.33 (d, *J* = 3.3 Hz, 1H), 4.62 (s, 2H), 1.97 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 149.6, 133.7, 127.7, 124.4, 122.9, 110.1, 105.9, 57.6. IR (film) 3312, 3048, 2925, 1651, 1423, 1197, 1012, 845, 785 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₉H₈NaO₂S [M+Na]⁺: 203.0137, found: 203.0136.

(5-Methylfuran-2-yl)methanol (1g)



The syntheses of **1g** have been reported previously.⁴ Analytical data were consistent with previously reported data.⁴ Yellow oil (0.93 g, 84%). ¹H NMR (400 MHz, CDCl₃) δ 6.15 (d, *J* = 3.0 Hz, 1H), 5.90 (d, *J* = 3.0 Hz, 1H), 4.52 (s, 2H), 2.28 (s, 3H), 2.13 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 152.4, 108.8, 106.3, 57.5, 13.6.

(5-Ethylfuran-2-yl)methanol (1h)

The syntheses of **1h** have been reported previously.² Analytical data were consistent with previously reported data.² Yellow oil (0.72 g, 34% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 6.15 (d, J = 2.8 Hz, 1H), 5.91 (br, 1H), 4.51 (s, 2H), 2.67 – 2.50 (m, 3H), 1.22 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 152.3, 108.5, 104.7, 57.4, 21.4, 12.1.

Methyl 5-(hydroxymethyl)furan-2-carboxylate (1j)



To a DMSO solution of potassium hydroxide (100 mg potassium hydroxide in 5 mL DMSO) was added 5-(hydroxymethyl)furan-2-carboxylic acid (0.38 g, 2.7 mmol). After stirring at room temperature for 5 min, methyl iodide (0.25 g, 1.8 mmol) was added and the mixture stirred for 5 h. Water (30 mL) was added very carefully and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo, and then was purified by silica gel chromatography (petroleum ether/EtOAc =5:1) to give the title compound **1j** (0.23 g, 80 %) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.12 (d, *J* = 3.4 Hz, 1H), 6.41 (d, *J* = 3.4 Hz, 1H), 4.66 (s, 2H), 3.88 (s, 3H), 2.97 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 158.7, 143.9, 119.1, 109.5, 57.5, 52.1. Analytical data were consistent with previously reported data.⁵

1-(5-Phenylfuran-2-yl)ethan-1-ol (1k)

The syntheses of **1k** have been reported previously.⁶ Analytical data were consistent with previously reported data.⁶ Yellow oil (0.44 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 3.2 Hz, 1H), 6.31 (d, J

= 3.2 Hz, 1H), 4.99 – 4.87 (m, 1H), 2.10 (br, 1H), 1.59 (d, J = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 153.4, 130.9, 128.8, 127.5, 123.8, 107.4, 105.6, 63.9, 21.5.

1-(5-Phenylfuran-2-yl)propan-1-ol (11)

Compound **11** was prepared in the same manner of **1k**, except that ethylmagnesium bromide was used instead of methylmagnesium bromide.⁶ Yellow oil (0.47 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 3.3 Hz, 1H), 6.31 (d, *J* = 3.3 Hz, 1H), 4.65 (t, *J* = 6.7 Hz, 1H), 2.09 – 1.84 (m, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 153.4, 130.9, 128.8, 127.4, 123.8, 108.2, 105.6, 69.5, 28.8, 10.1. IR (film) 3353, 3068, 2969, 1605, 1455, 1381, 1018, 759 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₃H₁₄NaO₂ [M+Na]⁺: 225.0886, found: 225.0887.

2-Methyl-1-(5-phenylfuran-2-yl)propan-1-ol (1m)



Compound **1m** was prepared in the same manner of **1k**, except that *iso*-propylmagnesium bromide was used instead of methylmagnesium bromide.⁶ Yellow oil (0.38 g, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.61 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 3.3Hz, 1H), 6.30 (d, J = 3.3 Hz, 1H), 4.42 (d, J = 6.9 Hz, 1H), 2.17 (m, 1H), 2.05 (br, 1H), 1.05 (d, J= 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.9, 153.3, 131.0, 128.8, 127.4, 123.8, 108.8, 105.6, 73.8, 33.5, 18.9, 18.4. IR (film) 3446, 3021, 2961, 2843, 1611, 1543, 1353, 1019, 759 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₄H₁₆NaO₂ [M+Na]⁺: 239.1043, found: 239.1046.

2,2-Dimethyl-1-(5-phenylfuran-2-yl)propan-1-ol (1n)

Compound **1n** was prepared in the same manner of **1k**, except that *tert*-butylmagnesium chloride was used instead of methylmagnesium bromide.⁶ Yellow oil (0.27 g, 41%). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 3.3 Hz, 1H), 6.29 (d, J = 3.3 Hz, 1H), 4.41 (s, 1H), 2.04 (br, 1H), 1.01 (s, 9H). ¹³C NMR (100

MHz, CDCl₃) δ 155.6, 153.0, 131.0, 128.8, 127.3, 123.7, 109.4, 105.5, 76.7, 35.8, 26.0. IR (film) 3447, 3063, 2957, 1650, 1542, 1383, 1204, 1014, 760 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₅H₁₈NaO₂ [M+Na]⁺: 253.1199, found: 253.1196.

2-(5-Phenylfuran-2-yl)propan-2-ol (10)

Compounds **10** were prepared by additions of 5-lithio-2-phenylfuran, prepared by deprotonation of 2-phenylfuran with n-BuLi, to acetone.⁷ Yellow oil (0.44 g, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 1H), 6.55 (d, *J* = 3.1 Hz, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 2.16 (br, 1H), 1.64 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 153.0, 131.0, 128.8, 127.4, 123.8, 105.9, 105.6, 69.1, 28.9. IR (film) 3337, 3068, 2976, 1607, 1453, 1206, 1024, 759 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₃H₁₄NaO₂ [M+Na]⁺: 225.0886, found: 225.0884.

2-(Methoxymethyl)-5-phenylfuran (1p)



To a suspension of sodium hydride (60% in mineral oil, 0.19 g, 4.4 mmol) in 10 mL of anhydrous THF under N₂ was carefully added a solution of (5-phenylfuran-2-yl)methanol (**1a**, 0.5 g, 2.9 mmol) in 5 mL of anhydrous THF. After stirring at room temperature for 5 min, methyl iodide (0.82 g, 5.8 mmol) was added and the mixture stirred for 12 h. Water (15 mL) was added very carefully and the mixture concentrated in vacuo to remove the THF. The remaining aqueous mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo, and then was purified by silica gel chromatography (petroleum ether/EtOAc =20:1) to give the title compound **1p** (0.48 g, 93 %) as a red oil. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 6.39 (d, *J* = 3.3 Hz, 1H), 4.44 (s, 2H), 3.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 154.4, 151.4, 130.9, 128.7, 127.5, 124.0, 111.6, 105.7, 66.6, 57.9. Analytical data were consistent with previously reported data.⁸

3 General procedure for the synthesis of arylfurans **3**



General procedure: **1** (0.5 mmol) was added to an 25-mL dried Schlenk tube charged with aryl boronic acids (1.25 mmol), Pd(OAc)₂ (5 mol %, 5.6 mg), \mathbf{L}^7 (12 mol %, 11.0 mg), KF (1.0 mmol, 58.0 mg), and 1,2-dichloroethane (1.5 mL). The mixture was stirred at 70 °C for 15 h under O₂ atmosphere (in balloon), and then was cooled down to room temperature. The resultant mixture was evaporated in vacuum and further isolated by flash chromatography on silica gel with petroleum ether to give the pure product **3**.

4 Data for arylfurans 3

2,5-Diphenylfuran (3a)



White solid (76.1 mg, 69%), mp: 86-87 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.68 (m, 4H), 7.40 – 7.32 (m, 4H), 7.26 – 7.19 (m, 2H), 6.68 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.5, 130.9, 128.9, 127.5, 123.9, 107.4. IR (film) 3039, 1602, 1534, 1474, 1270, 1018, 794 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₆H₁₃O [M+H]⁺: 221.0961, found: 221.0963.

2-Phenyl-5-(m-tolyl)furan (3b)



White solid (80.5 mg, 68%), mp: 82-83 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.5 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.32 – 7.21 (m, 2H), 7.07 (d, J = 7.4 Hz, 1H), 6.77 – 6.64 (m, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.7, 153.4, 138.4, 131.0, 130.8, 128.8, 128.7, 128.3, 127.4, 124.5, 123.8, 121.0, 107.3, 107.2, 21.6. IR (film) 3046, 2959, 1602, 1533, 1478, 1271, 1022, 772 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₇H₁₅O [M+H]⁺: 235.1117, found: 235.1115.

2-Phenyl-5-(*p*-tolyl)furan (3c)



White solid (73.8 mg, 64%), mp: 109-110 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.70 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 3.5 Hz, 1H), 6.65 (d, *J* = 3.5 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 153.1, 137.3, 131.0, 129.5, 128.8, 128.3, 127.3, 123.8, 123.8, 107.3, 106.6, 21.4. IR (film) 3027, 2926, 1595, 1482, 1273, 1021, 791 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₇H₁₅O [M+H]⁺: 235.1117, found: 235.1113.

2-(3-Methoxyphenyl)-5-phenylfuran (3d)



White solid (86.6 mg, 70%), mp: 83-84 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.19 (m, 4H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.68 (br, 2H), 3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 153.4, 153.2, 132.1, 130.8, 129.9, 128.8, 127.5, 123.8, 116.5, 113.0, 109.4, 107.7, 107.3, 55.3. IR (film) 3122, 3067, 2956, 1596, 1476, 1284, 1219, 1031, 840, 766 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₇H₁₅O₂ [M+H]⁺: 251.1067, found: 251.1065.

2-(4-Methoxyphenyl)-5-phenylfuran (3e)

White solid (81.8 mg, 66%), mp: 121-122 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 8.5 Hz, 2H), 6.68 (d, J = 3.3 Hz, 1H), 6.56 (d, J = 3.3 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 153.6, 152.8, 131.0, 128.8, 127.2, 125.3, 124.0, 123.7, 114.3, 107.3, 105.8, 55.4. IR (film) 3123, 2961, 1607, 1533, 1490, 1246, 1023, 830, 756 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₇H₁₄O₂ [M]⁺: 250.0988, found: 250.0993.

2-(4-(tert-Butyl)phenyl)-5-phenylfuran (3f)



White solid (82.0 mg, 60%), mp: 105-107 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.24 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 3.4 Hz, 1H), 6.66 (d, J = 3.4 Hz, 1H), 1.33 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 153.7, 153.1, 150.6, 131.0, 128.8, 128.2, 127.3, 125.8, 123.8, 123.7, 107.3, 106.8, 34.8, 31.4. IR (film) 3118, 2964, 1604, 1490, 1408, 1269, 1022, 831, 795 cm⁻¹. HRMS (ESI) m/z Calcd for C₂₀H₂₁O [M+H]⁺: 277.1587, found: 277.1586.

2-Phenyl-5-(o-tolyl)furan (3g)



White solid (35.7 mg, 31%), mp: 49-51 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 7.4 Hz, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.30 – 7.19 (m, 4H), 6.77 – 6.72 (m, 1H), 6.64 – 6.60 (m, 1H), 2.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 153.1, 134.6, 131.4, 130.9, 130.2, 128.9, 127.6, 127.4, 127.0, 126.2, 123.8, 110.8, 107.1, 22.2. IR (film) 3064, 2962,

1604, 1481, 1204, 1029, 831, 791 cm⁻¹. HRMS (ESI) m/z Calcd for $C_{17}H_{15}O$ [M+H]⁺: 235.1117, found: 235.1113.

2-(3,5-Dimethylphenyl)-5-phenylfuran (3h)



White solid (88.6 mg, 71%), mp: 62-63 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 7.7 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.22 (t, J = 7.0 Hz, 1H), 6.88 (s, 1H), 6.69 – 6.66 (m, 1H), 6.66 – 6.64 (m, 1H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 153.2, 138.3, 131.0, 130.8, 129.3, 128.8, 127.3, 123.8, 121.7, 107.3, 107.1, 21.5. IR (film) 3034, 2920, 1602, 1533, 1475, 1273, 1026, 849, 794 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₈H₁₇O [M+H]⁺: 249.1274, found: 249.1280.

2-(3,5-Dimethoxyphenyl)-5-phenylfuran (3i)



White solid (91.9 mg, 66%), mp: 63-64 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.7 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 6.89 (s, 2H), 6.68 (s, 2H), 6.38 (s, 1H), 3.81 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 161.2, 153.4, 153.2, 132.5, 130.7, 128.8, 127.5, 123.8, 107.9, 107.3, 102.0, 99.7, 55.4. IR (film) 3119, 3070, 2948, 1603, 1470, 1210, 1058, 838, 795 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₈H₁₇O₃ [M+H]⁺: 281.1172, found: 281.1176.

2-(4-Fluorophenyl)-5-phenylfuran (3j)



White solid (65.2 mg, 55%), mp: 108-109 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.62 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 162.2 (d, *J*_{C-H} = 245.5 Hz), 153.5, 152.6, 130.8, 128.8, 127.5, 127.3 (d, *J*_{C-H} = 3.2 Hz), 125.5 (d, *J*_{C-H} = 8.0 Hz), 123.8, 115.8 (d, *J*_{C-H} = 21.8 Hz), 107.3, 107.0 (d, *J*_{C-H} = 1.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -114.1. IR (film) 3125, 3071, 1611, 1483, 1229, 1019, 836, 793 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₆H₁₂FO [M+H]⁺: 239.0867, found: 239.0862.

2-(4-Bromophenyl)-5-phenylfuran (3k)



White solid (85.6 mg, 58%), mp: 128-129 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.67 (br, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 152.3, 131.9, 130.6, 129.7, 128.8, 127.6, 125.2, 123.9, 121.1, 107.9, 107.4. IR (film) 3126, 3073, 1527, 1464, 1016, 826, 791 cm⁻¹. HRMS (ESI) m/z Calcd for C₁₆H₁₂BrO [M+H]⁺: 299.0066, found: 299.0066.

2-(4-Chlorophenyl)-5-phenylfuran (3l)



White solid (42.1 mg, 33%), mp: 126-128 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 3.5 Hz, 1H), 6.70 (d, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 152.4, 133.1, 130.7, 129.4, 129.1, 128.9, 127.7, 125.0, 123.9, 107.8, 107.4. IR (film) 3081, 1527, 1472, 1103, 1019, 831, 793 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₆H₁₂ClO [M+H]⁺: 255.0571, found: 255.0550.

Ethyl 4-(5-phenylfuran-2-yl)benzoate (3m)



Yellow solid (64.1 mg, 44%), mp: 86-88 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.04 (m, 2H), 7.75 (t, *J* = 7.9 Hz, 4H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 154.5, 152.4, 134.6, 130.5, 130.2, 129.6, 128.9, 127.9, 124.0, 123.3, 109.6, 107.6, 61.1, 14.5. IR (film) 3124, 2976, 1708, 1605, 1465, 1269, 1020, 854, 760 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₉H₁₇O₃ [M+H]⁺: 293.1172, found: 293.1170.

2-Phenyl-5-(4-(trifluoromethyl)phenyl)furan (3n)



White solid (30.2 mg, 21%), mp: 133-135 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 7.9 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.1 Hz, 1H), 6.83 (d, J = 3.4 Hz, 1H), 6.75 (d, J = 3.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.6, 151.9, 134.0, 130.5, 129.0 (q, J_{C-H} = 32.3 Hz), 128.9, 128.0, 125.9 (q, J_{C-H} = 3.8 Hz), 124.4 (q, J_{C-H} = 270.2 Hz), 124.1, 123.8, 109.4, 107.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.4. IR (film) 3124, 1608, 1527, 1330, 1163, 843, 795 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₇H₁₂F₃O [M+H]⁺: 289.0835, found: 289.0832.

4-(5-Phenylfuran-2-yl)benzaldehyde (30)



Yellow solid (21.5 mg, 18%), mp: 110-112 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.76 (d, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 191.6, 155.1, 151.9, 136.0, 134.9, 130.5, 130.3, 128.9, 128.1, 124.1, 123.8, 110.6, 107.8. IR (film) 3124, 2733, 1692, 1599, 1212, 1021, 832, 798 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₇H₁₃O₂ [M+H]⁺: 249.0910, found: 249.0908.

4-(5-Phenylfuran-2-yl)benzonitrile (3p)

Yellow solid (10.8 mg, 9%), mp: 122-125 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.7 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 3.5 Hz, 1H), 6.78 (d, J = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 155.2, 151.4, 134.6, 132.8, 130.2, 129.0, 128.3, 124.2, 123.9, 119.2, 110.6, 110.2, 107.8. IR (film) 3118, 2219, 1526, 1464, 1270, 1016, 837, 794 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₇H₁₁NNaO [M+Na]⁺: 268.0733, found: 268.0740.

2-(Naphthalen-1-yl)-5-phenylfuran (3r)

White solid (38.1 mg, 29%), mp: 40-42 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 8.2 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.81 (dd, J = 6.9, 6.1 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.57 – 7.47 (m, 3H), 7.40 (t, J = 7.7 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 3.4 Hz, 1H), 6.79 (d, J = 3.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.9, 153.1, 134.1, 131.0, 130.4, 128.9, 128.7, 128.7, 128.6, 127.5, 126.8, 126.2, 126.1, 125.7, 125.5, 123.9, 111.6, 107.1. IR (film) 3051, 1601, 1516, 1482, 1392, 1203, 1027, 782 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₂₀H₁₅O [M+H]⁺: 271.1117, found: 271.1121.

2-(Naphthalen-2-yl)-5-phenylfuran (3s)



White solid (68.5 mg, 52%), mp: 136-137 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 7.92 – 7.76 (m, 6H), 7.53 – 7.39 (m, 4H), 7.29 (t, J = 7.3 Hz, 1H), 6.86 (d, J = 3.3 Hz, 1H), 6.78 (d, J = 3.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 153.6, 133.7, 132.8, 130.9, 128.9, 128.6, 128.3, 128.2, 127.9, 127.6, 126.7, 126.0, 124.0, 122.4, 122.1, 108.1, 107.6. IR (film) 3121, 1601, 1526, 1463, 1269, 1017, 791 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₂₀H₁₅O [M+H]⁺: 271.1117, found: 271.1115.

2-(3,5-Dimethylphenyl)-5-(p-tolyl)furan (3t)



White solid (99.0 mg, 76%), mp: 123-124 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.59 (m, 2H), 7.35 (s, 2H), 7.18 (d, *J* = 7.0 Hz, 2H), 6.88 (s, 1H), 6.71 – 6.58 (m, 2H), 2.34 (br, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 153.5, 153.4, 138.3, 137.2, 130.8, 129.5, 129.1, 128.3, 123.8, 121.6, 107.1, 106.6, 21.5, 21.4. IR (film) 3119, 2920, 1602, 1492, 1209, 1022, 833, 779 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₉H₁₉O [M+H]⁺: 263.1430, found: 263.1429.

2-(3,5-Dimethylphenyl)-5-(4-methoxyphenyl)furan (3u)



White solid (113.1 mg, 82%), mp: 107-108 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.7 Hz, 2H), 7.34 (s, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.88 (s, 1H), 6.65 (d, J = 3.4 Hz, 1H), 6.55 (d, J = 3.4 Hz, 1H), 3.79 (s, 3H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 153.3, 153.1, 138.3, 130.9, 129.0, 125.2, 124.1, 121.5, 114.3, 107.1, 105.7, 55.4, 21.5. IR (film) 3126, 2953, 1604, 1491, 1291, 1030, 836, 781 cm⁻¹. HRMS (ESI) m/z Calcd for C₁₉H₁₉O₂ [M+H]⁺: 279.1380, found: 279.1378.

2-(3,5-Dimethylphenyl)-5-(4-fluorophenyl)furan (3v)



White solid (82.3 mg, 62%), mp: 91-93 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.64 (m, 2H), 7.33 (s, 2H), 7.10 – 7.03 (m, 2H), 6.89 (s, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.2 (d, *J*_{C-H} = 245.5 Hz), 153.9, 152.4, 138.4, 130.7, 129.4, 127.4 (d, *J*_{C-H} = 3.3 Hz), 125.5 (d, *J*_{C-H} = 8.0 Hz), 121.7, 115.8 (d, *J*_{C-H} = 21.8 Hz), 107.1, 107.0, 21.5; IR (film) 3115, 2919, 1605, 1494, 1233, 1024, 848, 790 cm⁻¹. HRMS (ESI) *m/z* Calcd for C₁₈H₁₅FO [M]⁺: 266.1107, found: 266.1105.

2-(3,5-Dimethylphenyl)-5-(4-nitrophenyl)furan (3w)



Yellow solid (94.0 mg, 63%), mp: 141-143 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.34 (s, 2H), 6.95 (s, 1H), 6.89 (d, *J* = 3.5 Hz, 1H), 6.72 (d, *J* = 3.5 Hz, 1H), 2.37 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 156.1, 150.8, 146.2, 138.5, 136.4, 130.2, 129.9, 124.4, 123.7, 122.0, 111.5, 107.8, 21.5. IR (film) 3113, 2919, 2842, 1596, 1464, 1335, 1027, 847, 782 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₈H₁₅NNaO₃ [M+Na]⁺: 316.0944, found: 316.0949.

2-(3,5-Dimethylphenyl)-5-(thiophen-2-yl)furan (3x)



White solid (59.2 mg, 47%), mp: 57-58 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (s, 2H), 7.30 (d, J = 3.5 Hz, 1H), 7.19 (d, J = 5.0 Hz, 1H), 7.02 (dd, J = 5.0, 3.5 Hz, 1H), 6.89 (s, 1H), 6.63 (d, J = 3.4 Hz, 1H), 6.53 (d, J = 3.4 Hz, 1H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 148.9, 138.3, 134.0, 130.5, 129.4, 127.8, 124.1, 122.6, 121.7, 107.3, 107.1, 21.5. IR (film) 3121, 2917, 1605, 1493, 1386, 1198, 1016, 846, 780 cm⁻¹. HRMS (ESI) m/z Calcd for C₁₆H₁₄OS [M]⁺: 254.0765, found: 254.0759.

2-(3,5-Dimethylphenyl)-5-methylfuran (3y)



Yellow oil (39.9 mg, 43%). ¹H NMR (400 MHz, CDCl₃) δ 7.25 (s, 2H), 6.84 (s, 1H), 6.48 (d, J = 3.1 Hz, 1H), 6.01 (d, J = 3.1 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 151.7, 138.2, 131.2, 128.7, 121.3, 107.7, 105.7, 21.5, 13.8. IR (film) 3110, 2920, 1603, 1451, 1381, 1212, 1023, 845, 780 cm⁻¹. HRMS (ESI) *m*/*z* Calcd for C₁₃H₁₅O [M+H]⁺: 187.1117, found: 187.1115.

2-(3,5-Dimethylphenyl)-5-ethylfuran (3z)



Yellow oil (26.9 mg, 27%). ¹H NMR (400 MHz, CDCl₃) δ 7.25 (s, 2H), 6.83 (s, 1H), 6.48 (d, J = 3.2 Hz, 1H), 6.01 (d, J = 3.2 Hz, 1H), 2.69 (q, J = 7.5 Hz, 2H), 2.30 (s, 6H), 1.26 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 152.6, 138.1, 131.3, 128.7, 121.3, 106.1, 105.5, 21.6, 21.4, 12.3. IR (film) 3108, 2926, 1602, 1551, 1376, 1203, 1014, 846, 781 cm⁻¹. HRMS (ESI) m/z Calcd for C₁₄H₁₇O [M+H]⁺: 201.1274, found: 201.1273.

5 Data for 4 and 5

5-Phenylfuran-2-carbaldehyde (4)

Yellow oil (4.8 mg, 5%). ¹H NMR (400 MHz, CDCl₃) δ 9.63 (s, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.46 – 7.35 (m, 3H), 7.31 (d, J = 3.7 Hz, 1H), 6.82 (d, J = 3.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 159.4, 152.0, 129.7, 128.9, 125.3, 107.7. Analytical data were consistent with previously reported data.⁹

5-Phenylfuran-2-carboxylic acid (5)



Compounds **5** were prepared by hydrolysis of methyl 5-phenylfuran-2-carboxylate, prepared by Suzuki coupling of methyl 5-bromofuran-2-carboxylate with phenylboronic acid. White solid (117.0 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 8.45 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.50 – 7.32 (m, 4H), 6.78 (d, *J* = 3.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 163.6, 158.9, 143.0, 129.4, 129.4, 129.0, 125.2, 122.3, 107.4. Analytical data were consistent with previously reported data.¹⁰

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¹³C NMR spectrum of **1b**



¹³C NMR spectrum of **1c**



¹³C NMR spectrum of 1d



¹H NMR spectrum of **1e**



¹H NMR spectrum of **1f**



¹H NMR spectrum of 1g



¹H NMR spectrum of **1h**



¹H NMR spectrum of **1j**



¹H NMR spectrum of **1k**







¹H NMR spectrum of 1m



¹H NMR spectrum of **1n**



¹H NMR spectrum of **10**



¹H NMR spectrum of **1p**





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¹³C NMR spectrum of **3a**



¹³C NMR spectrum of **3b**



¹³C NMR spectrum of **3c**



¹³C NMR spectrum of **3d**



¹³C NMR spectrum of **3e**



¹³C NMR spectrum of **3f**



¹³C NMR spectrum of **3g**



¹³C NMR spectrum of **3h**



¹³C NMR spectrum of **3i**



¹³C NMR spectrum of **3j**



¹H NMR spectrum of **3k**



¹H NMR spectrum of **3**l

~153.80 ~152.39 133.05 133.05 129.39 129.05 129.05 128.87 127.67 125.03 123.90 $<^{107.82}_{107.43}$ 120 110 100 90 80 fl (ppm) 180 140 130 60 190 170 160 150 70 50 40 30 20 10 0 ¹³C NMR spectrum of **3**l $\begin{bmatrix} 8.09\\ 8.07\\ 8.05\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.74\\ 7.73\\ 7.74\\ 7.74\\ 7.73\\ 7.74$ 7.74\\ 7.74\\ 7.74 7.74\\ 7.74 7.74 7.75 4.41 4.39 4.37 4.37 $\underbrace{ \bigwedge_{1.39}^{1.42} }$ [] COOEt 2.20⊣ 3.93⊣ 1.94 4 28 4 0.97 ¥ 0.96 ¥ 3.29 - $2.22 \pm$ 5.0 4.5 fl (ppm) 8.0 9.5 7.5 9.0 8.5 4.0 1.5 7.0 6.0 3.5 3.0 1.0 6.5 5.5 2.5 2.0 0.5 0.0

¹H NMR spectrum of **3m**



¹H NMR spectrum of **3n**



¹⁹F NMR spectrum of **3n**



¹³C NMR spectrum of **30**



¹³C NMR spectrum of **3p**



¹³C NMR spectrum of **3r**



¹³C NMR spectrum of **3s**



¹³C NMR spectrum of **3t**



¹³C NMR spectrum of **3u**



¹³C NMR spectrum of 3v



¹H NMR spectrum of **3w**

∼136.06 ∼136.080 √146.19 ~138.22 ~138.42 ~138.42 ~138.20 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~123.66 ~124.60~124.60 ~124.60 ~124.60~125.60 ~125.60 ~125.60~125.60 ~12



---21.46

¹H NMR spectrum of 3x

$= \frac{133.34}{123.45}$

---21.48



¹H NMR spectrum of **3**y



¹H NMR spectrum of 3z



