Electronic Supplementary Information

[2,2']Bifuranyl-5-carbaldehyde (3)

Conditions A: **2** (100 mg, 0.7 mmol), 2-bromofuran (99 mg, 0.7 mmol), tetrakis(triphenylphosphino)palladium (41 mg), DMF and Na_2CO_3 (1 M, 1.1 cm^3); reaction time 109 h; eluent DCM gave **3** as a yellow oil (37 mg, 34%). Conditions B: **2** (200 mg, 1.4 mmol), 2-bromofuran (165 mg, 1.4 mmol), $Pd(PPh_3)_2Cl_2$ (52 mg), 1,4-dioxane, and Cs_2CO_3 (1 M, 5.0 cm^3); reaction time 90 h; eluent DCM gave **3** as a yellow oil (139 mg, 64%); ^{1}H NMR (500 MHz, acetone-d_6) δ 9.66 (1H, CHO, s), 7.78 (1H, dd, *J* = 0.5 Hz, *J* = 1.0 Hz), 7.54 (1H, d, *J* = 3.5 Hz), 7.00 (1H, d, *J* = 3.5 Hz), 6.91 (1H, d, *J* = 3.5 Hz), 6.69-6.68 (1H, d, *J* = 3.5 Hz); ^{13}C NMR (125 MHz, acetone-d_6) δ 177.02, 152.23, 150.89, 145.11, 144.82, 124.03, 112.42, 109.63, 107.73; MS (EI) *m/z* 162 (M^+, 100%). HRMS(EI) calcd for $C_9H_6O_3$ (M^+) 162.0317, found 162.0319.

5-Thiophen-2-yl-furan-2-carbaldehyde (4)

Conditions A: **2** (100 mg, 0.7 mmol), 2-bromothiophene (102 mg, 0.6 mmol), tetrakis(triphenylphosphino)palladium (41 mg), DMF and Na_2CO_3 (1 M, 1.1 cm^3); reaction time 126 h; eluent DCM gave **4** as a yellow oil (34 mg, 30%). Conditions B: **2** (200 mg, 1.4 mmol), 2-bromothiophene (170 mg, 1.3 mmol), $Pd(PPh_3)_2Cl_2$ (52 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 5.0 cm^3); reaction time 91 h; eluent DCM gave **4** as a yellow oil (136 mg, 61%); ^{1}H NMR (500 MHz, acetone-d_6) δ 9.64 (1H, CHO, s), 7.68 (1H, dd, *J*= 1.5 Hz, *J*= 1.5 Hz), 7.66 (1H, dd, *J*= 1.0 Hz, *J*= 1.5 Hz), 7.53 (1H, d, *J*= 3.5 Hz), 7.23-7.21 (1H, m), 6.99 (1H, d, *J*= 3.5 Hz); ^{13}C NMR (125 MHz, acetone-d_6) δ 176.84, 154.57, 152.06, 131.83, 128.63, 128.14, 126.62, 124.46, 107.85; MS (EI) *m/z* 178 (M^+, 100%). HRMS(EI) calcd for $C_9H_6O_2S$ (M^+) 178.0089, found 178.0089.

5-(6-Methoxypyridin-3-yl)-furan-2-carbaldehyde (5)

Conditions A: **2** (100 mg, 0.7 mmol), 5-bromo-2-methoxypyridine (116 mg, 0.6 mmol), tetrakis(triphenylphosphino)palladium (41 mg), DMF and Na_2CO_3 (2 M, 1.5 cm^3); reaction time 112 h; eluent DCM:EtOAc (9:1 v/v) gave **5** as orange needles (20 mg, 16%). Conditions B: **2** (200 mg, 1.4 mmol), 5-bromo-2-methoxypyridine (247 mg, 1.3

mmol), $Pd(PPh_3)_2Cl_2$ (52 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 5.0 cm^3); reaction time 134 h; eluent DCM:EtOAc (9:1 v/v) gave **5** as orange needles (137 mg, 52%), mp 121-123 °C (from cyclohexane); ^{1}H NMR (400 MHz, acetone-d_6) δ 9.66 (1H, CHO, s), 8.71 (1H, dd, *J* = 0.8 Hz, *J* = 0.8 Hz), 8.14 (1H, dd, *J* = 2.4 Hz, *J* = 2.4 Hz), 7.54 (1H, d, *J* = 3.6 Hz), 7.13 (1H, d, *J* = 3.6 Hz), 6.92 (1H, dd, *J* = 0.8 Hz, *J* = 0.8 Hz), 3.96 (3H, OCH_3, s); ^{13}C NMR (100 MHz, acetone-d_6) δ 177.03, 164.88, 156.89, 152.59, 144.54, 135.74, 124.30, 119.51, 111.44, 107.68, 53.36; MS (EI) *m/z* 203 (M^+, 100%). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89%. Found: C, 65.07; H, 4.63; N, 6.93%.

5-(5-Trifluoromethylpyridin-2-yl)-furan-2-carbaldehyde (6)

Conditions A: **2** (100 mg, 0.7 mmol), 2-bromo-5-(trifluoromethyl)pyridine (110 mg, 0.6 mmol), tetrakis(triphenylphosphino)palladium (41 mg), DMF and Na_2CO_3 (2 M, 1.5 cm^3); reaction time 134 h; eluent DCM:EtOAc (9:1 v/v) gave **6** as orange needles (37 mg, 24%). Conditions B: **2** (239 mg, 1.7 mmol), 2-bromo-5-(trifluoromethyl)pyridine (354 mg, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (62 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 5.0 cm^3); reaction time 111 h; eluent DCM:EtOAc (9:1 v/v) gave **6** as orange needles (126 mg, 31%), mp 93-94 °C (from cyclohexane); ^{1}H NMR (300 MHz, acetone-d_6) δ 9.66 (1H, CHO, s), 8.87 (1H, s), 8.20 (1H, dd, *J* = 2.4 Hz, *J* = 2.4 Hz), 8.02 (1H, d, *J* = 8.4 Hz), 7.49 (1H, d, *J* = 3.9 Hz), 7.36 (1H, d, *J* = 3.6 Hz); ^{13}C NMR (125 MHz, acetone-d_6) δ 178.11, 156.56, 153.82, 151.30, 147.14, 135.06, 125.81(CF), 123.29, 119.76, 112.96; MS (EI) *m/z* 241 (M^+, 100%). Anal. Calcd for $C_{11}H_6F_3NO_2$: C, 54.78; H, 2.51; N, 5.81%. Found: C, 54.67; H, 2.48; N, 5.81 %.

5-Pyridin-2-yl-furan-2-carbaldehyde (7)

Conditions B: **2** (200 mg, 1.4 mmol), 2-bromopyridine (163 mg, 1.2 mmol), $Pd(PPh_3)_2Cl_2$ (52 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 5.0 cm^3); reaction time 110 h; eluent DCM:EtOAc (9:1 v/v) gave **7** as a yellow solid (121 mg, 57%), mp 88-90 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.73 (1H, CHO, s), 8.68-8.66 (1H, m), 7.98-7.92 (2H, m), 7.57 (1H, d, *J* = 3.6 Hz), 7.44-7.40 (1H, m), 7.32 (1H, d, *J* = 3.6 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 177.79, 158.30, 153.16, 150.40, 148.08, 137.42, 124.21, 123.65, 119.86,

110.83; MS (EI) *m/z* 173 (M^+, 100%). Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09%. Found: C, 69.17; H, 4.08; N, 8.14%.

5-(5-Cyanopyridin-3-yl-furan-2-carbaldehyde (8)

Conditions B: **2** (200 mg, 1.4 mmol), 3-bromo-5-cyanopyridine (238 mg, 1.3 mmol), $Pd(PPh_3)_2Cl_2$ (52 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 5.0 cm^3); reaction time 110 h; eluent DCM:EtOAc (7:3 v/v) gave **8** as an orange solid (39 mg, 15%), mp 219-220 °C (from CH_3CN); ^1H NMR (400 MHz, DMSO-d_6) δ 9.67 (1H, CHO, s), 9.04 (1H, d, *J* = 2.0 Hz), 9.31 (1H, d, *J* = 2.0 Hz), 8.78 (1H, t, *J* = 2.0 Hz), 7.71 (1H, d, *J* = 3.6 Hz), 7.56 (1H, d, *J* = 3.6 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 177.33, 152.25, 151.48, 151.13, 147.89, 134.67, 123.82, 123.52, 115.31, 110.65, 108.52; MS (EI) *m/z* 198 (M^+, 100%). Anal. Calcd for $C_{11}H_6N_2O_2$: C, 66.67; H, 3.05; N, 14.14%. Found: C, 66.40; H, 3.08; N, 14.19 %.

5-(6-Nitropyridin-3-yl)-furan-2-carbaldehyde (9)

Conditions B: **2** (50 mg, 0.4 mmol), 5-bromo-2-nitropyridine (81 mg, 0.4 mmol), $Pd(PPh_3)_2Cl_2$ (13 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 1.0 cm^3); reaction time 48 h; eluent DCM:EtOAc (9:1 v/v) gave **9** as an orange solid (35 mg, 44%), mp 162-164 °C; ^1H NMR (500 MHz, acetone-d_6) δ 9.83 (1H, CHO, s), 9.46 (1H, d, *J* = 3.0 Hz), 8.77 (1H, dd, *J* = 3.0 Hz, *J* = 2.5 Hz), 8.21 (1H, d, *J* = 8.5 Hz), 7.66 (1H, d, *J* = 4.0 Hz), 7.58 (1H, d, *J* = 4.0 Hz); ^{13}C NMR (125 MHz, acetone-d_6) δ 178.38, 156.01, 154.22, 152.28, 145.76, 143.97, 133.08, 123.25, 120.04, 114.30; MS (EI) *m/z* 218 (M^+, 100%). Anal. Calcd for $C_{10}H_6N_2O_4$: C, 55.05; H, 2.77; N, 12.84%. Found: C, 55.05; H, 2.89; N, 12.55%.

5-(5-Nitrothiophen-2-yl)-furan-2-carbaldehyde (10)

Conditions B: **2** (50 mg, 0.4 mmol), 5-bromo-2-nitrothiophene (90 mg, 0.4 mmol), $Pd(PPh_3)_2Cl_2$ (13 mg), 1,4-dioxane and Cs_2CO_3 (1 M, 1.0 cm^3); reaction time 41 h; eluent DCM:hexane (9:1 v/v) gave **10** as a yellow solid (43 mg, 54%), mp 150-152 °C; ^1H NMR (400 MHz, acetone-d_6) δ 9.73 (1H, CHO, s), 8.09 (1H, d, *J*= 4.4 Hz), 7.69 (1H, d, *J*= 4.4 Hz), 7.60 (1H, d, *J*= 4.0 Hz), 7.37 (1H, d, *J*= 3.6 Hz); ^{13}C NMR (400 MHz,

acetone-d_6) δ 177.71, 153.17, 151.46, 138.14(2C), 130.42, 125.45, 123.68, 111.98; MS (EI) *m/z* 223 (M^+, 100%). Anal. Calcd for $C_9H_5NO_4S$: C, 48.43; H, 2.26; N, 6.28%. Found: C, 48.42; H, 2.36; N, 6.24 %.

3-[5-(6-Methoxypyridin-3-yl)-furan-2-yl]-acrylic acid ethyl ester (11).

A solution of **5** (50 mg, 0.3 mmol) in acetonitrile (5 cm^3) was added with stirring to (ethoxycarbonylmethylene)triphenylphosphorane (91 mg, 0.3 mmol) in acetonitrile (5 cm^3). The mixture was heated at reflux for 18 h. Solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel: eluent DCM:EtOAc (9:1 v/v) gave **11** as a yellow powder (56 mg, 82%), mp 88-89 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 8.68 (1H, d, *J*=2.0 Hz), 8.13 (1H, dd, *J* =2.4 Hz, *J* = 2.4 Hz), 7.48 (1H, d, *J* = 15.6 Hz), 7.00-6.95 (2H, m), 6.87 (1H, dd, *J* = 0.6 Hz, *J* = 0.6 Hz), 6.41 (1H, d, *J* = 15.8 Hz), 4.21 (2H, q, *J* = 7.2 Hz), 3.94 (3H, OCH_3, s), 1.29 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 166.41, 164.21, 153.98, 150.58, 143.54, 135.14, 130.60, 120.19, 117.90, 115.30, 111.21, 107.76, 60.12, 53.21, 13.97; MS (EI) *m/z* 273 (M^+, 100%). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13%. Found: C, 65.83; H, 5.59; N, 5.11%.

3-[5-(5-Trifluoromethylpyridin-2-yl)-furan-2-yl]-acrylic acid ethyl ester (12)

Following the procedure for compound **11**, compound **6** (50 mg, 0.2 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (77 mg, 0.2 mmol); eluent DCM:EtOAc (9:1 v/v) gave **12** as a yellow powder (60 mg, 92%), mp 96-98 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.21 (1H, s), 7.53-7.44 (2H, m), 6.81 (1H, d, *J* = 16.0 Hz), 6.65 (1H, d, *J* = 3.6 Hz), 6.35 (1H, d, *J* = 3.6 Hz), 5.82 (1H, d, *J* = 15.6Hz), 3.50 (2H, q, *J* = 7.2 Hz), 0.57 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 166.10, 154.34, 152.72, 151.72, 146.96(2C), 134.73, 130.45, 122.80(CF), 118.94, 117.66, 113.58, 60.35, 13.93; MS (EI) *m/z* 311 (M^+, 40%). Anal. Calcd for $C_{15}H_{12}F_3NO_4$: C, 57.88; H, 3.89; N, 4.50%. Found: C, 57.76; H, 3.99; N, 4.45%.

3-(5-Pyridin-2-yl)-furan-2-yl)-acrylic acid ethyl ester (13)

Following the procedure for compound **11**, compound **7** (50 mg, 0.3 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (101 mg, 0.3 mmol); eluent DCM:EtOAc (7:3 v/v) gave **13** as a yellow powder (53 mg, 75%), mp 121-122 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.49-8.47 (1H, s), 7.84-7.73 (2H, m), 7.38 (1H, d, *J* = 16.0 Hz), 7.21-7.18 (1H, m), 7.08 (1H, d, *J* = 3.6 Hz), 6.90-6.88 (1H, m), 6.35 (1H, d, *J* = 15.2 Hz), 4.09 (2H, q, *J* = 7.2 Hz), 1.17 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 166.25, 155.92, 151.53, 150.16, 148.62, 137.16, 130.69, 123.22, 119.14, 117.72, 116.39, 111.19, 60.22, 13.95; MS (EI) *m/z* 243 (M^+, 52%). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76%. Found: C, 68.89; H, 5.51; N, 5.71%.

2-[5-(5-Trifluoromethylpyridin-2-yl)-furan-2-yl-methylene]-[1,3]-dithiol-4,5-dicarboxylic acid dimethyl ester (16)

To a solution of reagent **14** (127 mg, 0.3 mmol) in THF (5 cm^3) at –78 °C, nBuLi (1.6 M in hexane, 0.2 cm^3, 0.3 mmol) was added dropwise. The mixture was stirred for 10 min. A solution of **6** (60 mg, 0.3 mmol) in THF (5 cm^3) was added to the mixture at –78 °C. The mixture was allowed to warm to 25 °C, and then refluxed for 24 h. The solvent was removed *in vacuo*. The remaining residue was dissolved in DCM (20 cm^3) which was washed with water (20 cm^3) and dried with $MgSO_4$. The crude product was purified by silica gel column chromatography, eluent DCM:EtOAc (19:1 v/v) gave **16** as a red solid (56 mg, 51%), mp 135-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80-8.79 (1H, m), 7.97 (1H, dd, *J*= 2.4 Hz, *J*= 2.4 Hz), 7.78 (1H, d, *J*= 8.4 Hz), 7.27 (1H, d, *J*= 3.6 Hz), 6.42 (1H, s), 6.33 (1H, d, *J*= 4.0 Hz), 3.91 (3H, s, OCH_3), 3.88 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.98, 158.77, 151.71, 150.65, 150.46, 145.68, 133.05, 130.74, 129.67, 123.99-121.28(CF_3), 116.43, 112.42, 108.61(3C), 101.56, 52.48(2C); MS (EI) *m/z* 443 (M^+, 100%). HRMS Calcd for $C_{18}H_{12}F_3NO_5S_2$ 443.0109. Found: 443.0108

2-[5-(4,5-Dimethyl-[1,3]-dithiol-2-ylidenemethyl-furan-2-yl]-5-trifluoromethylpyridine (17)

To a solution of reagent **15** (100 mg, 0.3 mmol) in THF (5 cm^3) at –78 °C, nBuLi (1.6 M in hexane, 0.2 cm^3, 0.3 mmol) was added dropwise. The mixture was stirred for 10 min. A solution of **6** (60 mg, 0.3 mmol) in THF (5 cm^3) was added to the mixture at –78 °C.

The mixture was allowed to warm to 25 °C, and then refluxed for 24 h. Workup as described for **16** gave **17** as a yellow oil (12 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (1H, s), 7.86 (1H, d, *J*= 8.4 Hz), 7.70 (1H, d, *J*= 8.4 Hz), 7.07 (1H, d, *J*= 3.6 Hz), 6.36 (1H, d, *J* = 3.2 Hz), 4.72 (1H, t, *J*= 5.6 Hz), 1.86 (3H, s, CH_3), 1.32 (3H, s, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.82, 152.19, 150.88, 146.85, 137.24, 134.49, 134.46, 123.16-122.91(CF_3), 123.01, 122.01, 117.26, 114.08, 108.07, 99.23, 12.84, 12.24; MS (EI) *m/z* 355 (M^+, 2%), 242 (100%). HRMS Calcd for $C_{16}H_{12}F_3NOS_2$ 355.0312. Found: 355.0312.