Versatile Synthesis of Functionalised Dibenzothiophenes *via* Suzuki Coupling and Microwave-assisted Ring Closure

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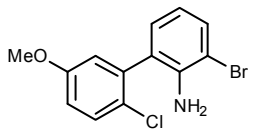
Supplementary Information

Experimental procedures for compounds 11b-f, 12b-f, 13c-f, 2c-f, 3c, 22b-f, 23a-c, 24

Chloro- and methoxy- substituted 3-bromo-biphenyl-2-amines (11a-f)

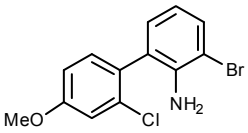
These compounds were prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **11a**.

3-Bromo-2'-chloro-5'-methoxy-[1,1'-biphenyl]-2-amine (11b)



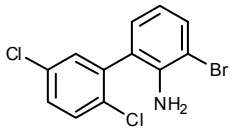
2,6-Dibromoaniline (1.35 g, 5.36 mmol), 2-chloro-5-methoxyphenylboronic acid (1.0 g, 5.36 mmol), $Pd(PPh_3)_4$ (0.16 g, 0.13 mmol), 2 M Na_2CO_3 (5.4 mL) and 1,4-dioxane (8 mL). The reaction mixture was heated under microwave irradiation at 100 °C for 1 h. The crude product was purified by medium pressure chromatography (DCM/petrol 1:4) to give the title compound as a white solid (1.28 g, 77%): R_f 0.46 (petrol/DCM, 1:1); mp: 84-85 °C; IR (cm^{-1}) 3442, 3369, 1611, 1550, 1448, 1444, 1392, 1365, 1345, 1299, 1207, 1178, 1017, 852, 823, 775; λ_{max} (EtOH)/nm 292; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (3H, s, OMe), 4.12 (2H, br. s, NH_2), 6.74 (1H, d, J = 7.6 Hz, H-Ar), 6.93-6.95 (2H, m, H-Ar), 7.08 (1H, d, J = 7.6 Hz, H-Ar), 7.45 (1H, d, J = 7.9 Hz, H-Ar), 7.52 (1H, d, J = 7.9 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0, 110.1, 116.0, 117.3, 119.0, 125.6, 130.0, 131.2, 132.8, 138.7, 142.2, 159.2; MS (EI) *m/z* = 311.0 $[M(^{35}Cl,^{79}Br)]^+$, 313.0 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 315.0 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{13}H_{11}BrClNO$ $[M(^{35}Cl,^{79}Br)]^+$ 310.9712, found 310.9706.

3-Bromo-2'-chloro-4'-methoxy-[1,1'-biphenyl]-2-amine (11c)



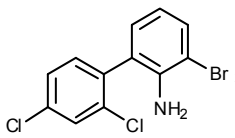
2,6-Dibromoaniline (4.6 g, 18.3 mmol), 2-chloro-4-methoxyphenylboronic acid (3.1 g, 16.6 mmol), $Pd(PPh_3)_4$ (1 g, 0.9 mmol), 3 M Na_2CO_3 (16.6 mL) and DME (10 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 80 min. The crude product was purified by medium pressure chromatography (DCM/petrol 3:2) to give the title compound as a yellow solid (2.70 g, 52%): R_f 0.38 (petrol/DCM, 13:7); mp: 84-85 °C; IR (cm^{-1}) 3441, 3354, 1603, 1496, 1442, 1280, 1211, 1060, 1029, 869, 842, 813; λ_{max} (EtOH)/nm 286; ^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (3H, s, OMe), 4.07 (2H, br. s, NH_2), 6.71 (1H, ap t, J = 7.6 Hz, H-Ar), 6.94 (1H, d, J = 8.5 Hz, H-Ar), 7.04 (1H, d, J = 7.6 Hz, H-Ar), 7.11 (1H, s, H-Ar), 7.25 (1H, d, J = 8.5 Hz, H-Ar), 7.49 (1H, d, J = 7.6 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.9, 109.9, 113.9, 115.8, 118.8, 126.3, 130.0, 130.3, 132.5, 134.9, 142.5, 160.5; MS (EI) m/z = 311.0 $[M(^{35}Cl,^{79}Br)]^+$, 313.3 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 315.1 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{13}H_{11}NClBrO$ $[M(^{35}Cl,^{79}Br)+H]^+$ 311.9785, found 311.9782.

3-Bromo-2',5'-dichloro-[1,1'-biphenyl]-2-amine (11d)



2,6-Dibromoaniline (2.5 g, 10 mmol), 2,5-dichlorophenylboronic acid (2.5 g, 13 mmol), $Pd(PPh_3)_4$ (0.5 g, 0.5 mmol), 4 M Na_2CO_3 (8 mL) and DME (8 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 50 min. The crude product was purified by medium pressure chromatography (DCM/petrol 1:5) to give the title compound as a colourless oil (3.01 g, 50%): R_f 0.22 (DCM/petrol 6:94); IR (cm^{-1}) 3383, 1609, 1446, 1379, 1255, 1092, 1055, 1020, 812; λ_{max} (EtOH)/nm 310; ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (2H, s, NH_2), 6.70 (1H, ap t, J = 7.5 Hz, H-Ar), 7.05 (1H, d, J = 7.5 Hz, H-Ar), 7.30-7.40 (2H, m, H-Ar), 7.50-7.60 (2H, m, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.9, 118.8, 124.8, 129.5, 129.7, 131.2, 131.8, 132.9, 139.1, 141.7; MS (EI) m/z = 314.9 $[M(^{35}Cl,^{79}Br)]^+$, 316.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 318.9 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{12}H_8NBrCl_2$ $[M(^{35}Cl,^{79}Br)+H]^+$ 315.9290, found 315.9287.

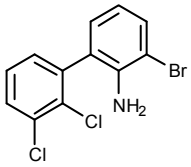
3-Bromo-2',4'-dichloro-[1,1'-biphenyl]-2-amine (11e)



2,6-Dibromoaniline (1.0 g, 4 mmol), 2,4-dichlorophenylboronic acid (1 g, 5.1 mmol), $Pd(PPh_3)_4$ (0.20 g, 0.2 mmol), 2 M Na_2CO_3 (8 mL) and DME (6 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 70 min. The crude product was purified by medium pressure chromatography (DCM/petrol 1:5) to

give the title compound as a colourless oil (0.580 g, 45%): R_f 0.77 (DCM/petrol 1:4)□; IR (cm^{-1}) 3381, 1608, 1554, 1449, 1371, 1282, 1099, 1056, 1008, 812, 729; λ_{max} (EtOH)/nm 309; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.99 (2H, s, NH_2), 6.72 (1H, ap t, *J* = 7.8 Hz, H-Ar), 7.02 (1H, d, *J* = 7.8 Hz, H-Ar), 7.29 (1H, d, *J* = 8.2 Hz, H-Ar), 7.39 (1H, d, *J* = 8.2 Hz, H-Ar), 7.52 (1H, d, *J* = 7.8 Hz, H-Ar), 7.59 (1H, s, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.1, 119.0, 125.2, 128.0, 129.9, 130.3, 132.9, 133.0, 135.1, 135.2, 136.4, 142.1; MS (EI) *m/z* = 315.0 [M(^{35}Cl,^{79}Br)]$^+$, 316.9 [M(^{35}Cl,^{81}Br; ^{37}Cl,^{79}Br)]$^+$, 319.0 [M(^{37}Cl,^{81}Br)]$^+$; HRMS calcd for $C_{12}H_8NBrCl_2$ [M(^{35}Cl,^{79}Br)+H]$^+$ 315.9290, found 315.9288.

3-Bromo-2',3'-dichloro-[1,1'-biphenyl]-2-amine (11f)

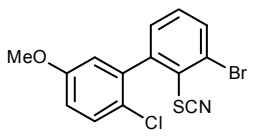


2,6-Dibromoaniline (2 g, 8 mmol), 2,3-dichlorophenylboronic acid (1.85 g, 9.5 mmol), $Pd(PPh_3)_4$ (0.5 g, 0.8 mmol), 4 M Na_2CO_3 (8 mL) and DME (5 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 50 min. The crude product was purified by medium pressure chromatography (DCM/petrol 1:5) to give the title compound as a colourless oil (1.01 g, 40%): R_f 0.33 (DCM/petrol 7:93); mp: 97-98 °C; IR (cm^{-1}) 3346, 3358, 1606, 1439, 1400, 1298, 1226, 1149, 1109, 1055, 902, 833, 786; λ_{max} (EtOH)/nm 303; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (2H, s, NH_2), 6.58 (1H, ap t, *J* = 7.6 Hz, H-Ar), 6.86 (1H, d, *J* = 7.5 Hz, H-Ar), 7.11 (1H, d, *J* = 7.6 Hz, H-Ar), 7.18 (1H, ap t, *J* = 7.7 Hz, H-Ar), 7.35-7.42 (2H, m, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.2, 119.0, 126.2, 128.0, 129.6, 130.2, 130.6, 132.9, 133.0, 134.4, 140.1, 141.9; MS (EI) *m/z* = 315.0 [M(^{35}Cl,^{79}Br)]$^+$, 316.9 [M(^{35}Cl,^{81}Br; ^{37}Cl,^{79}Br)]$^+$, 319.0 [M(^{37}Cl,^{81}Br)]$^+$; HRMS calcd for $C_{12}H_8NBrCl_2$ [M(^{35}Cl,^{79}Br)+H]$^+$ 315.9290, found 315.9292.

Chloro- and methoxy- substituted 3-bromo-2-thiocyanatobiphenyl (12a-f)

These compounds were prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **12a**.

3-Bromo-2'-chloro-5'-methoxy-2-thiocyanato-1,1'-biphenyl (12b)

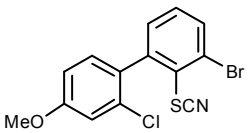


Following Method A: 3-bromo-2'-chloro-5'-methoxy-[1,1'-biphenyl]-2-amine **11b** (4.50 g, 14.4 mmol), MeOH (65 mL), conc. hydrochloric acid (30 mL), sodium nitrite (1.0 g, 14.4 mmol), potassium thiocyanate (3.90 g, 40.3 mmol), iron (III) chloride (1.60 g, 10.8 mmol) and water (50 mL). The crude product was purified by medium pressure chromatography (DCM/petrol 1:1) to give the title compound as a colourless oil

(2.50 g, 50%).

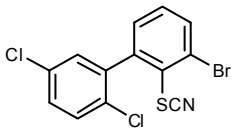
Following Method B: 3-bromo-2'-chloro-5'-methoxy-[1,1'-biphenyl]-2-amine **11b** (0.100 g, 0.32 mmol), 2,2,2-trifluoroethanol (2 mL), conc. hydrochloric acid (1 mL), sodium nitrite (0.022 g, 0.32 mmol), copper thiocyanate (0.062 g, 0.51 mmol), potassium thiocyanate (0.622 g, 6.4 mmol) and water (2 mL). The crude product was purified by medium pressure chromatography (DCM/petrol 1:1) to yield the title compound as a colourless oil (0.074 g, 66%): R_f 0.43 (DCM/petrol 1:1); IR (cm^{-1}) 2156, 1597, 1571, 1451, 1476, 1451, 1435, 1391, 1322, 1226, 1176, 1027, 825; λ_{max} (EtOH)/nm 288; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (3H, s, OMe), 6.84 (1H, s, H-Ar), 6.95 (1H, d, *J* = 8.8 Hz, H-Ar), 7.34 (1H, d, *J* = 7.9 Hz, H-Ar), 7.37-7.45 (2H, m, H-Ar), 7.80 (1H, d, *J* = 7.9 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.1, 109.5, 116.6, 124.8, 125.3, 130.2, 130.7, 130.8, 132.6, 134.5, 139.5, 146.9, 158.9; MS (EI) *m/z* = 353.0 $[M(^{35}Cl,^{79}Br)]^+$, 355.0 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 357.0 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{14}H_9NSBrClO$ $[M(^{35}Cl,^{79}Br)+NH_4]^+$ 370.9615, found 370.9612.

3-Bromo-2'-chloro-4'-methoxy-2-thiocyanato-1,1'-biphenyl (12c)



Following Method A: 3-bromo-2'-chloro-4'-methoxy-[1,1'-biphenyl]-2-amine **11c** (1.8 g, 5.8 mmol), MeOH (35 mL), conc. hydrochloric acid (15 mL), sodium nitrite (0.394 g, 5.7 mmol), potassium thiocyanate (1.85g, 19.0 mmol), iron (III) chloride (0.66 g, 4.1 mmol) and water (45 mL). The crude product was purified by medium pressure chromatography (DCM/petrol 1:1) to give the title compound as a colourless oil (1.57 g, 76%): R_f 0.50 (DCM/petrol 1:1); IR (cm^{-1}) 2454, 1603, 1550, 1498, 1434, 1392, 1287, 122, 1184, 1142, 1038, 868, 789; λ_{max} (EtOH)/nm 280; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (3H, s, OMe), 6.34 (1H, d, *J* = 8.5 Hz, H-Ar), 7.06 (1H, s, H-Ar), 7.22 (1H, d, *J* = 8.5 Hz, H-Ar), 7.32 (1H, d, *J* = 7.8 Hz, H-Ar), 7.41 (1H, ap t, *J* = 7.8 Hz, H-Ar), 7.80 (1H, d, *J* = 7.8 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0, 109.6, 113.5, 115.5, 126.0, 130.1, 131.0, 131.3, 131.7, 132.4, 134.0, 134.3, 146.7, 161.0; MS (EI) *m/z* = 353.0 $[M(^{35}Cl,^{79}Br)]^+$, 355.0 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 357.0 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{14}H_9BrClNOS$ $[M(^{35}Cl,^{79}Br)]^+$ 352.9276, found 352.9292.

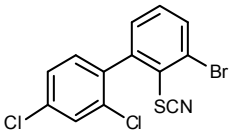
3-Bromo-2',5'-dichloro-2-thiocyanato-1,1'-biphenyl (12d)



Following Method A: 3-bromo-1',4'-dichloro-[1,1'-biphenyl]-2-amine **11d** (1.8 g, 6.3 mmol), MeOH (20 mL), conc. hydrochloric acid (15mL), sodium nitrite (0.45 g, 6.3 mmol), potassium thiocyanate (1.95 g, 20 mmol), iron (III)

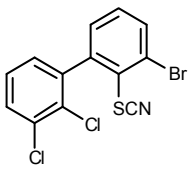
chloride (0.715 g, 4.4 mmol) and water (35 mL). The crude product was purified by medium pressure chromatography (DCM/petrol 2:3) to give the title compound as yellow needle-like crystals (1.6 g, 79%): R_f 0.72 (DCM/petrol 1:1); mp 95-96 °C; IR (cm^{-1}) 3061, 2156, 1546, 1439, 1376, 1135, 1093, 1018, 816; λ_{max} (EtOH)/nm 270; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.25 (2H, m H-Ar), 7.30-7.40 (3H, m, H-Ar), 7.75 (1H, d, *J* = 8.5 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.9, 125.4, 130.6, 131.0, 131.1, 132.0, 132.6, 133.4, 134.9, 140.1, 145.5; MS (EI) *m/z* = 356.9 $[M(^{35}Cl,^{79}Br)]^+$, 358.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 360.9 $[M(^{37}Cl,^{81}Br)]^+$.

3-Bromo-2',4'-dichloro-2-thiocyanato-1,1'-biphenyl (12e)



Following Method A: 3-bromo-4',6'-dichloro-[1,1'-biphenyl]-2-amine **11e** (0.55 g, 1.73 mmol), MeOH (12 mL), conc. hydrochloric acid (5 mL), sodium nitrite (0.12 g, 1.73 mmol), potassium thiocyanate (0.53 g, 5.5 mmol), iron (III) chloride (0.20 g, 1.2 mmol) and water (20 mL). The crude product was purified by medium pressure chromatography (DCM/petrol 2:3) to give the title compound as pale cream-yellow solid (0.44 g, 70%): R_f 0.55 (DCM/petrol 2:3); mp 135-137 °C; IR (cm^{-1}) 2146, 1589, 1550, 1477, 1433, 1369, 1141, 1099, 1070, 875, 813, 787; λ_{max} (EtOH)/nm 279; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (1H, d, *J* = 8.2 Hz, H-Ar), 7.32 (1H, d, *J* = 7.9 Hz, H-Ar), 7.40 (1H, d, *J* = 8.2 Hz, H-Ar), 7.45 (1H, ap t, *J* = 7.9 Hz, H-Ar), 7.55 (1H, s, H-Ar), 7.83 (1H, d, *J* = 7.9 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.1, 125.5, 127.8, 129.9, 130.8, 131.0, 131.9, 132.6, 134.4, 134.8, 135.9, 137.3, 145.8; MS (EI) *m/z* = 356.9 $[M(^{35}Cl,^{79}Br)]^+$, 358.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 360.9 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{13}H_6NSBrCl_2$ $[M(^{35}Cl,^{79}Br)]^+$ 356.8776, found 356.8778.

3-Bromo-2',3'-dichloro-2-thiocyanato-1,1'-biphenyl (12f)



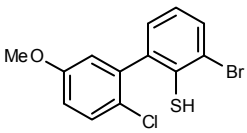
Following Method A: 3-bromo-5',6'-dichloro-[1,1'-biphenyl]-2-amine **11f** (0.920 g, 2.9 mmol), MeOH (10 mL), conc. hydrochloric acid (6 mL), sodium nitrite (0.225 g, 3.2 mmol), potassium thiocyanate (0.90 g, 9.3 mmol), iron (III) chloride (0.330 g, 2 mmol) and water (20 mL). The crude product was purified by medium pressure chromatography (DCM/petrol 1:1) to give the title compound as a colourless oil which crystallised on standing (0.637 g, 62%): R_f 0.61 (DCM/petrol 1:1); mp 119-121 °C; IR (cm^{-1}) 2157, 1548, 1433, 1408, 1195, 1151, 1043, 906, 827, 782, 723; λ_{max} (EtOH)/nm 279; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (1H, d, *J* = 7.6 Hz, H-Ar), 7.31-7.38 (2H, m, H-Ar), 7.46 (1H, ap t, *J* = 7.9 Hz, H-Ar), 7.59 (1H, d, *J* = 8.0 Hz, H-Ar), 7.85 (1H, d, *J* = 8.0 Hz, H-Ar); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 109.4, 125.5, 128.1, 129.5, 130.8, 131.3, 131.5, 132.4, 132.9, 134.4, 135.1, 141.1, 146.9; MS (EI) *m/z* = 356.9 $[M(^{35}Cl,^{79}Br)]^+$, 358.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 360.9 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{13}H_6NSBrCl_2$ $[M(^{35}Cl,^{79}Br)]^+$ 356.8776, found 356.8779.

Chloro- and methoxy- substituted 3-bromo-biphenyl-2-thiols (13a-f)

These compounds were prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **13a**.

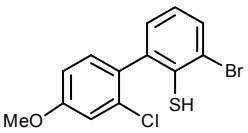
3-Bromo-2'-chloro-5'-methoxy-[1,1'-biphenyl]-2-thiol (13b)



Following Method C: 3-bromo-2'-chloro-5'-methoxy-2-thiocyanato-1,1'-biphenyl **12b** (1.0 g, 2.8 mmol), $LiAlH_4$ (1 M in THF, 3.1 mL, 3.1 mmol) and THF (25 mL). The title compound was obtained as an oil and used without further purification (0.810 g, 87 %).

Following Method D: potassium hydroxide (6.0 g, 0.11 mol) in EtOH (100 mL) was cooled to 0 °C, solid 3-bromo-2'-chloro-5'-methoxy-2-thiocyanato-1,1'-biphenyl **12b** (2.0 g, 5.63 mmol) was added portion-wise to the solution. The reaction mixture was stirred at room temperature for 30 min. Conc. H_2SO_4 (5 mL) in EtOH (50 mL) was added slowly, followed by water (50 mL). The reaction mixture was extracted with DCM (3 × 100 mL), the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The crude product was purified by medium pressure chromatography (DCM: petrol 1:4) to yield the title compound as a colourless oil (1.70 g, 91%): R_f 0.72 (DCM/petrol 1:1); IR (cm^{-1}) 1596, 1569, 1450, 1435, 1394, 1317, 1294, 1214, 1175, 119, 1051, 859, 718; λ_{max} (MeOH)/nm 285; ^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (3H, s, OMe), 4.00 (1H, s, SH), 6.85 (1H, s, H-Ar), 6.97 (1H, d, *J* = 8.8 Hz, H-Ar), 7.10 (1H, ap t, *J* = 7.6 Hz, H-Ar), 7.17 (1H, d, *J* = 7.6 Hz, H-Ar), 7.45 (1H, d, *J* = 8.8 Hz, H-Ar), 7.63 (1H, d, *J* = 7.6 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0, 155.9, 166.6, 122.9, 125.1, 125.9, 129.3, 131.0, 132.9, 134.9, 139.7, 140.7, 159.0; MS (EI) *m/z* = 328.0 $[M(^{35}Cl,^{79}Br)]^+$, 330.0 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 332 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{13}H_{10}BrClOS$ $[M(^{35}Cl,^{79}Br)]^+$ 327.9324, found 327.9326.

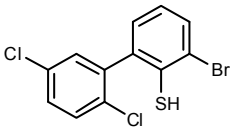
3-Bromo-2'-chloro-4'-methoxy-[1,1'-biphenyl]-2-thiol (13c)



Following Method C: 3-bromo-2'-chloro-4'-methoxy-2-thiocyanato-1,1'-biphenyl **12c** (1.72 g, 4.85 mmol), $LiAlH_4$ (1 M in THF, 5.30 mL, 5.3 mmol) and THF (30 mL). The title compound was obtained as an oil and used without further purification (1.45 g, 90%): R_f 0.42 (DCM/petrol 1:9); IR (cm^{-1}) 1598, 1551, 1496,

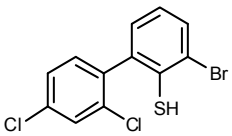
1434, 1394, 1282, 1222, 1060, 873, 848, 821, 777; λ_{max} (MeOH)/nm 288; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (3H, s, OMe), 3.97 (1H, s, SH), 6.92 (1H, d, *J* = 8.5 Hz, H-Ar), 7.02-7.08 (2H, m, H-Ar), 7.11 (1H, d, *J* = 7.6 Hz, H-Ar), 7.19 (1H, d, *J* = 8.5 Hz, H-Ar), 7.58 (1H, d, *J* = 7.6 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.9, 113.7, 115.6, 125.6, 129.9, 131.9, 132.4, 132.8, 134.5, 135.6, 135.6, 139.4, 160.7; MS (EI) *m/z* = 328.0 [M(^{35}Cl,^{79}Br)]$^{+}$, 330.0 [M(^{35}Cl,^{81}Br; ^{37}Cl,^{79}Br)]$^{+}$, 332.0 [M(^{37}Cl,^{81}Br)]$^{+}$; HRMS calcd for $C_{13}H_{10}BrClOS$ [M(^{35}Cl,^{79}Br)]$^{+}$ 327.9324, found 327.9321.

3-Bromo-2',5'-dichloro-[1,1'-biphenyl]-2-thiol (13d)



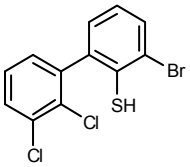
Following Method C: 3-bromo-2',5'-dichloro-2-thiocyanato-1,1'-biphenyl **12d** (0.35 g, 1.0 mmol), $LiAlH_4$ (1.8 M in THF, 0.62 mL, 1.1 mmol) and THF (10 mL). The title compound was obtained as an oil and used without futher purification (0.31 g, 97%): R_f 0.88 (DCM/petrol 2:3); IR (cm^{-1}) 1544, 1465, 1436, 1399, 1378, 1247, 1135, 1093, 1022, 883, 813; λ_{max} (EtOH)/nm 290; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (1H, s, SH), 6.90-7.00 (2H, m, H-Ar), 7.15-7.10 (1H, m, H-Ar), 7.30 (1H, d, *J* = 8.5 Hz, H-Ar), 7.40 (1H, d, *J* = 8.5 Hz, H-Ar), 7.53 (1H, d, *J* = 7.3 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.3, 126.1, 129.3, 130.1, 131.3, 132.3, 133.3, 134.7, 138.5, 141.4; MS (EI) *m/z* = 331.9 [M(^{35}Cl,^{79}Br)]$^{+}$, 333.9 [M(^{35}Cl,^{81}Br; ^{37}Cl,^{79}Br)]$^{+}$, 335.9 [M(^{37}Cl,^{81}Br)]$^{+}$; HRMS calcd for $C_{12}H_7BrSCl_2$ [M(^{35}Cl,^{79}Br)]$^{+}$ 331.8823, found 331.8823.

3-Bromo-2',4'-dichloro-[1,1'-biphenyl]-2-thiol (13e)



Following Method C: 3-bromo-2',4'-dichloro-2-thiocyanato-1,1'-biphenyl **12e** (0.43 g, 1.2 mmol), $LiAlH_4$ (1.8 M in THF, 0.73 mL, 1.32 mmol) and THF (10 mL). The title compound was obtained as an oil and used without futher purification (0.40 g, 99%): R_f 0.75 (DCM/petrol 1:4); IR (cm^{-1}) 1585, 1550, 1475, 1435, 1396, 1373, 1099, 1015, 815, 716; λ_{max} (EtOH)/nm 236; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (1H, s, SH), 7.03-7.10 (2H, m, H-Ar), 7.22 (1H, d, *J* = 8.2 Hz, H-Ar), 7.37 (1H, d, *J* = 8.2 Hz, H-Ar), 7.56 (1H, s, H-Ar), 7.61 (1H, d, *J* = 7.0 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.2, 126.1, 127.8, 129.4, 130.2, 132.2, 134.9, 138.9, 135.4, 138.5, 138.6; MS (EI) *m/z* = 331.9 [M(^{35}Cl,^{79}Br)]$^{+}$, 333.9 [M(^{35}Cl,^{81}Br; ^{37}Cl,^{79}Br)]$^{+}$, 335.9 [M(^{37}Cl,^{81}Br)]$^{+}$; HRMS calcd for $C_{12}H_7SBrCl_2$ [M(^{35}Cl,^{79}Br)]$^{+}$ 331.8823, found 331.8825.

3-Bromo-2',3'-dichloro-[1,1'-biphenyl]-2-thiol (13f)

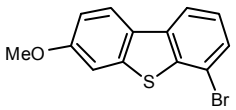


Following Method C: 3-bromo-2',3'-dichloro-2-thiocyanato-1,1'-biphenyl **12f** (0.560 g, 1.44 mmol), $LiAlH_4$ (1 M in THF, 1.6 mL, 1.59 mmol) and THF (10 mL). The title compound was obtained as an oil and used without futher purification (0.420 g, 87%): R_f 0.80 (DCM/petrol 2:3); IR (cm^{-1}) 1551, 1423, 1396, 1255, 1182, 1145, 1029, 812, 774; λ_{max} (EtOH)/nm 277; ^1H NMR (300 MHz, $CDCl_3$) δ 3.84 (1H, s, SH), 6.98-7.01 (2H, m, H-Ar), 7.10 (1H, d, *J* = 7.9 Hz, H-Ar), 7.23 (1H, ap t, *J* = 7.9 Hz, H-Ar), 7.46 (1H, d, *J* = 7.9 Hz, H-Ar), 7.53 (1H, d, *J* = 6.6 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.2, 126.1, 127.9, 129.2, 129.5, 130.8, 132.5, 133.2, 134.3, 134.7, 139.4, 142.0; MS (EI) *m/z* = 331.9 $[M(^{35}Cl,^{79}Br)]^+$, 333.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 335.9 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{12}H_7BrSCl_2$ $[M(^{35}Cl,^{79}Br)]^+$ 331.8823, found 331.8824.

1-, 2-, 3-, 4-Chloro or methoxy-6-bromo-dibenzo[*b,d*]thiophene derivatives (2c-f)

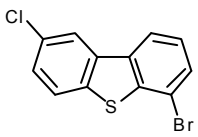
These compounds were prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **2a**.

6-Bromo-3-methoxydibenzo[*b,d*]thiophene (2c)



3-Bromo-2'-chloro-4'-methoxy-[1,1'-biphenyl]-2-thiol **13c** (0.500 g, 1.5 mmol), Cs_2CO_3 (0.72 g, 2.2 mmol), acetonitrile (15 mL). The reaction mixture was heated under microwave irradiation at 130 °C for 12 min. The title compound was obtained as a cream solid without futher purification (0.87 g, 98%): R_f 0.48 (DCM/petrol 1:4); mp 110-112 °C; IR (cm^{-1}) 1598, 1541, 1483, 1444, 1421, 1378, 1315, 1259, 1226, 1182, 1099, 1061, 1028, 817, 765; λ_{max} (EtOH)/nm 220, 268, 284; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82 (3H, s, OMe), 6.97 (1H, d, *J* = 8.5 Hz, H-Ar), 7.17-7.25 (2H, m, H-Ar), 7.44 (1H, d, *J* = 7.5 Hz, H-Ar), 7.86-8.89 (2H, m, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.1, 104.6, 112.3, 114.3, 117.8, 121.3, 124.2, 126.6, 128.1, 135.4, 139.0, 139.3, 158.1; MS (EI) *m/z* = 292.0 $[M(^{79}Br)]^+$, 294.0 $[M(^{81}Br)]^+$; HRMS calcd for $C_{13}H_9BrOS$ $[M(^{79}Br)]^+$ 291.9557, found 291.9566.

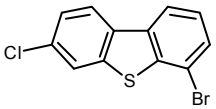
6-Bromo-2-chlorodibenzo[*b,d*]thiophene (2d)



3-Bromo-2',5'-dichloro-[1,1'-biphenyl]-2-thiol **13d** (0.7 g, 2.1 mmol), Cs_2CO_3 (1.1 g, 3.4 mmol), acetonitrile (15 mL). The reaction mixture was heated under microwave irradiation at 130 °C for 10 min. The title compound was obtained as a white solid without futher purification (0.59 g, 95%): R_f 0.65 (EtOAc/petrol 2:98); mp 166-168

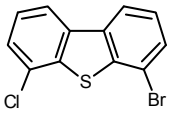
°C; IR (cm^{-1}) 1537, 1437, 1377, 1305, 1240, 1186, 1071, 1018, 852, 800; λ_{max} (EtOH)/nm 234, 289, 334; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (1H, ap t, *J* = 7.5 Hz, H-Ar), 7.35 (1H, d, *J* = 7.5 Hz, H-Ar), 7.55 (1H, d, *J* = 7.5 Hz, H-Ar), 7.70 (1H, d, *J* = 7.5 Hz, H-Ar), 7.85-7.80 (2H, m, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 116.8, 120.7, 122.4, 124.1, 126.3, 127.9, 130.4, 131.5, 137.7, 142.6; MS (EI) *m/z* = 295.9 $[M(^{35}Cl,^{79}Br)]^+$, 297.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$; HRMS calcd for $C_{12}H_6BrClS$ $[M(^{35}Cl,^{79}Br)]^+$ 295.9057, found 295.9055.

6-Bromo-3-chlorodibenzo[*b,d*]thiophene (2e)



3-Bromo-2',4'-dichloro-[1,1'-biphenyl]-2-thiol **13e** (0.380 g, 1.13 mmol), Cs_2CO_3 (0.550 g, 1.70 mmol), acetonitrile (8 mL). The reaction mixture was heated under microwave irradiation at 130 °C for 10 min. The title compound was obtained as a white solid without futher purification (0.315 g, 93%): R_f 0.77 (DCM/petrol 1:9); mp 162-163 °C; IR (cm^{-1}) 1577, 1239, 1465, 1429, 1369, 1306, 1240, 1095, 862, 815, 769; λ_{max} (EtOH)/nm 240, 290, 327; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (1H, ap t, *J* = 7.7 Hz, H-Ar), 7.37 (1H, d, *J* = 8.5 Hz, H-Ar), 7.55 (1H, d, *J* = 7.7 Hz, H-Ar), 7.78 (1H, s, H-Ar), 7.94 (1H, d, *J* = 8.5 Hz, H-Ar), 7.98 (1H, d, *J* = 7.7 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 116.7, 120.5, 122.9, 123.3, 125.8, 126.4, 130.0, 133.6, 134.9, 136.4, 140.7, 141.8; MS (EI) *m/z* = 296.0 $[M(^{35}Cl,^{79}Br)]^+$, 298.0 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 300.0 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{12}H_6BrClS$ $[M(^{35}Cl,^{79}Br)]^+$ 295.9057, found 295.9054.

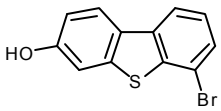
4-Bromo-6-chlorodibenzo[*b,d*]thiophene (2f)



3-Bromo-2',3'-dichloro-[1,1'-biphenyl]-2-thiol **13f** (0.40 g, 1.2 mmol), Cs_2CO_3 (0.585 g, 1.8 mmol) and acetonitrile (6 mL). The reaction mixture was heated under microwave irradiation at 130 °C for 10 min. Recrystallisation from ethanol gave the title compound as white needles (0.250 g, 70%): R_f 0.61 (DCM/petrol 1:9); mp 165-167 °C; IR (cm^{-1}) 1539, 1463, 1404, 1407, 1373, 1309, 1184, 1146, 1101, 1026, 837; λ_{max} (EtOH)/nm 274, 317, 329; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (1H, ap t, *J* = 7.8 Hz, H-Ar), 7.36-7.42 (2H, m, H-Ar), 7.56 (1H, d, *J* = 7.8 Hz, H-Ar), 7.92 (1H, d, *J* = 7.5 Hz, H-Ar), 7.98 (1H, d, *J* = 7.8 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 116.8, 120.7, 121.1, 126.3, 126.4, 127.1, 128.7, 130.3, 137.3, 137.9, 139.1, 141.8; MS (EI) *m/z* = 295.9 $[M(^{35}Cl,^{79}Br)]^+$, 297.9 $[M(^{35}Cl,^{81}Br;\ ^{37}Cl,^{79}Br)]^+$, 300.0 $[M(^{37}Cl,^{81}Br)]^+$; HRMS calcd for $C_{12}H_6ClBrS$ $[M(^{35}Cl,^{79}Br)]^+$ 295.9057, found 295.9056.

6-Bromodibenzo[*b,d*]thiophen-3-ol (3c)

This compound was prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **2a** and **2b**.



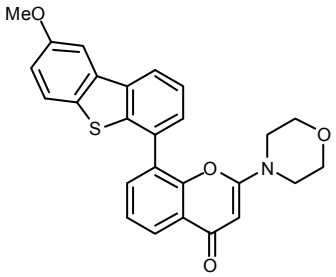
6-Bromo-3-methoxydibenzo[*b,d*]thiophene **2c** (1.0 g, 3.4 mmol), pyridine hydrochloride (5.0 g, 42.5 mmol). The crude product was purified by medium pressure chromatography (DCM/petrol 1:1) to give the title compound as a white solid (0.74 g, 78%).

Alternative procedure: 3-Bromo-2'-chloro-4'-methoxy-[1,1'-biphenyl]-2-thiol **13c** (0.10 g, 0.3 mmol), pyridine hydrochloride (1.0 g, 8.6 mmol). The mixture was heated to 150 °C for 28 h. The crude product was purified by medium pressure chromatography (DCM/petrol 4:1) to give the title compound as a white solid (0.03 g, 35%): R_f 0.41 (DCM/petrol 4:1); mp 210-212 °C; IR (cm^{-1}) 1603, 1562, 1501, 1456. 1431, 1384, 1251, 1228, 1182, 1061, 1033, 928, 854, 763; λ_{max} (EtOH)/nm 213, 246, 275, 298; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (1H, d, *J* = 8.5 Hz, H-Ar), 7.30-7.36 (2H, m, H-Ar), 7.55 (1H, d, *J* = 7.7 Hz, H-Ar), 7.97-8.01 (2H, m, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.9, 114.4, 116.6, 119.7, 123.5, 126.1, 128.7, 130.3, 134.3, 137.1, 141.3, 155.7; MS (EI) *m/z* = 278.0 $[M(^{79}Br)]^+$, 280.0 $[M(^{81}Br)]^+$; HRMS calcd for $C_{12}H_7BrOS$ $[M(^{79}Br)]^+$ 277.9401, found 277.9413.

Substituted dibenzothiophen-4-yl chromenone derivatives (22b-f, 23a-c, 24)

8-(8-Methoxydibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (22b)

This compound was prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **21.**

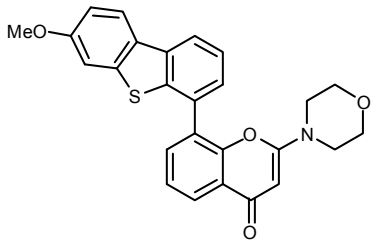


Following Method E: 6-bromo-2-methoxydibenzo[*b,d*]thiophene **2b** (0.025 g, 0.085 mmol), $PdCl_2$(dppf) (7.0 mg, 0.009 mmol), KOAc (0.050 g, 0.512 mmol) and bis(pinacolato)diboron (0.032 g, 0.128 mmol) in THF (5 mL) at reflux for 24 h. The crude product was purified by medium pressure chromatography (EtOAc/MeOH 95:5) to yield 4,4,5,5-tetramethyl-2-(8-methoxydibenzo[*b,d*]thiophen-4-yl)-1,3,2-dioxaborolane (0.028 g, 97%). The boronate (0.028 g, 0.082 mmol), 2-morpholino-4-oxo-4*H*-chromen-8-yl trifluoromethanesulfonate **19** (0.033 g, 0.086 mmol), $PdCl_2$(dppf) (7.0 mg, 0.009 mmol) and Cs_2CO_3 (0.080 g, 0.247 mmol) in THF (5 mL) was heated at reflux for 16 h. The crude product was purified by medium pressure chromatography (EtOAc/MeOH 9:1) to yield the title

compound as a white solid (0.010 g, 30%): R_f 0.12 (EtOAc); mp 193-195 °C; IR (cm^{-1}) 2978, 1616, 1553, 1467, 1396, 1219, 773; λ_{max} (EtOH)/nm 264; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.04 (4H, br. s, CH_2-morpholine), 3.44 (4H, br. s, CH_2-morpholine), 3.89 (3H, s, OMe), 5.23 (1H, s, H-3), 7.02 (1H, dd, *J* = 2.4 and 8.7 Hz, H-Ar), 7.39-7.52 (4H, m, H-Ar), 7.59-7.63 (1H, m, H-Ar), 7.71 (1H, d, *J* = 7.4 Hz, H-Ar), 8.10 (1H, d, *J* = 7.8 Hz, H-Ar), 8.21 (1H, d, *J* = 7.8 Hz, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.9, 56.1, 66.2, 88.2, 105.6, 116.6, 121.7, 123.8, 124.8, 125.3, 126.3, 128.4, 128.9, 131.5, 131.8, 133.7, 136.3, 136.9, 141.4, 150.9, 158.2, 162.4, 169.5; MS (ES+) *m/z* = 444.2 $[M+H]^+$; Anal. Calcd for $4C_{26}H_{21}NO_4S{\bullet}CH_2Cl_2$: C, 67.84, H, 4.66, N, 3.01. Found: C, 67.82, H, 4.73, N, 3.15%.

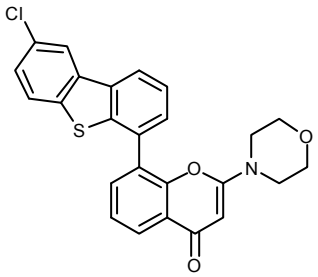
Compounds **22c-f**, **23a-c**, **24** were prepared using the typical procedure described in the Experimental section of the paper and exemplified there for **22a**.

8-(7-Methoxydibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (22c)



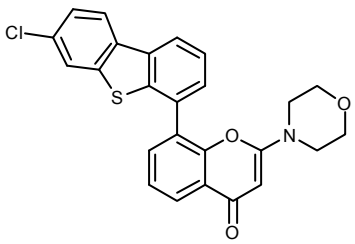
Following Method F: 2-morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.11 g, 0.31 mmol), 6-bromo-3-methoxydibenzo[*b,d*]thiophene **2c** (0.10 g, 0.34 mmol), $Pd(PPh_3)_4$ (0.018 g, 0.015 mmol), 3 M Na_2CO_3 (0.5 mL) and DME (4 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 35 min. The crude product was purified using medium pressure chromatography (MeOH/DCM 3:97) to give the title compound as a white solid (0.080 g, 58%): R_f 0.37 (MeOH/DCM 3:97); mp 245-247 °C; IR (cm^{-1}) 1612, 1556, 1471, 1427, 1406, 1307, 1244, 1112, 1039, 983, 860, 785; λ_{max} (EtOH)/nm 240, 275, 299; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02-3.05 (4H, m, CH_2-morpholine), 3.43-3.46 (4H, m, CH_2-morpholine), 3.86 (3H, s, OMe), 5.48 (1H, s, H-3), 7.01 (1H, d, *J* = 8.7 Hz, H-Ar), 7.20 (1H, s, H-6'), 7.33 (1H, d, *J* = 7.4 Hz, H-8'), 7.39-7.49 (2H, m, H-Ar), 7.69 (1H, d, *J* = 7.4 Hz, H-9'), 7.98-8.03 (2H, m, H-Ar), 8.20 (1H, d, *J* = 7.8 Hz, H-1'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.0, 56.0, 66.1, 87.4, 106.4, 114.0, 120.7, 122.8, 125.0, 125.1, 126.3, 127.1, 129.1, 129.5, 131.7, 133.5, 135.1, 139.6, 139.6, 141.63, 151.1, 159.9, 162.6; MS (ES+) *m/z* = 444.2 $[M+H]^+$; HRMS calcd for $C_{26}H_{21}NO_4S$ $[M+H]^+$ 444.1264, found 444.1265; Anal. Calcd for $C_{26}H_{21}NO_4S$: C, 68.98, H, 5.17, N, 2.87. Found: C, 68.75, H, 5.09, N, 2.79%.

8-(8-Chlorodibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (22d)



Following Method F: 2-morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.58 g, 1.6 mmol), 6-bromo-2-chlorodibenzo[*b,d*]thiophene **2d** (0.550 g, 1.7 mmol), $Pd(PPh_3)_4$ (0.100 g, 0.016 mmol), 2 M Na_2CO_3 (3.2 mL) and DME (10 mL). The reaction mixture was heated under microwave irradiation at 165 °C for 40 min. The crude product was purified using medium pressure chromatography (MeOH/DCM 3:97) to give the title compound as a pale cream solid (0.550 g, 75%): R_f 0.43 (MeOH/DCM 3:97); mp 240-244 °C; IR (cm^{-1}) 1618, 1559, 1438, 1408, 1380, 1242, 1117, 1071, 985, 858; λ_{max} (EtOH)/nm 236, 292; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.09-3.13 (4H, m, CH_2-morpholine), 3.50-3.55 (4H, m, CH_2-morpholine), 5.56 (1H, s, H-3), 7.40-7.56 (3H, m, H-Ar), 7.62 (1H, ap t, *J* = 8.1 Hz, H-Ar), 7.73 (2H, m, H-Ar), 8.18-8.21 (2H, m, H-Ar), 8.30 (1H, d, *J* = 8.1, H-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.0, 66.2, 87.4, 121.8, 122.1, 124.0, 125.1, 125.7, 126.6, 127.8, 128.6, 128.9, 131.4, 132.0, 133.4, 135.4, 137.3, 137.3, 137.8, 141.2, 151.0, 162.5, 177.1; MS (ES+) *m/z* = 448.2 $[M(^{35}Cl)+H]^+$, 450.2 $[M(^{37}Cl)+H]^+$; HRMS calcd for $C_{25}H_{18}NClO_3$ $[M(^{35}Cl)+H]^+$ 448.0769, found 448.0764; Anal. Calcd for $C_{25}H_{18}NClO_3$: C, 67.03, H, 4.05, N, 3.13%. Found: C, 66.81, H, 4.11, N, 3.10%.

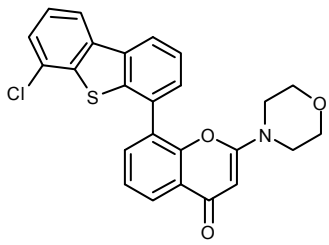
8-(7-Chlorodibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (22e)



Following Method F: 2-morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.275g, 0.76 mmol), 6-bromo-3-chlorodibenzo[*b,d*]thiophene **2e** (0.250 g, 0.084 mmol), $Pd(PPh_3)_4$ (0.050 g, 0.043 mmol), 2 M Na_2CO_3 (1.5 mL) and DME (5 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 70 min. The crude product was purified using medium pressure chromatography (MeOH/DCM 3:97) to give the title compound as a pale cream solid (0.136 g, 40%): R_f 0.45 (MeOH/DCM 5:95); mp 302 °C (decomp.); IR (cm^{-1}) 1620, 1563, 1471, 1408, 1244, 1113, 1029, 987, 864, 779; λ_{max} (EtOH)/nm 240, 293; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05-3.15 (4H, m, CH_2-morpholine), 3.50-3.60 (4H, m, CH_2-morpholine), 5.56 (1H, s, H-3), 7.40-7.60 (2H, m, H-Ar), 7.65 (1H, ap t, *J* = 7.9 Hz, H-6), 7.70-7.85 (3H, m, H-Ar), 8.15 (1H, d, *J* = 8.6 Hz, H-Ar), 8.20 (1H, d, *J* = 7.9 Hz, H-7), 8.30 (1H, d, *J* = 7.9 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.0, 66.0, 87.4, 121.6, 122.7, 122.9, 124.0, 125.2, 125.3, 125.7, 126.6, 126.8, 127.5, 128.6, 131.9, 133.5, 134.4, 135.6, 140.3, 140.8, 151.0, 162.5, 177.1; MS (ES+) *m/z* = 448.1 $[M(^{35}Cl)+H]^+$, 450.1

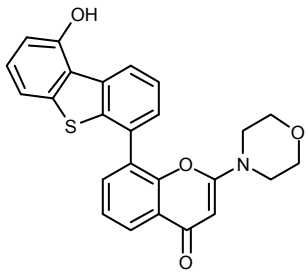
[M(^{37}Cl)+H]$^+$; HRMS calcd for $C_{25}H_{18}ClNO_3S$ [M(^{35}Cl)+H]$^+$ 448.0769, found 448.0763; Anal. Calcd for $C_{25}H_{18}ClNO_3S$: C, 65.45, H, 4.13, N, 3.00. Found: C, 65.52, H, 4.09, N, 2.77%.

8-(6-Chlorodibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (22f)



Following Method F: 2-morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.150 g, 0.42 mmol), 6-bromo-4-chlorodibenzo[*b,d*]thiophene **2f** (0.140 g, 0.46 mmol), $Pd(PPh_3)_4$ (4.5 mg, 0.004 mmol), 2 M Na_2CO_3 (0.8 mL) and DME (4 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 50 min. The crude product was purified using medium pressure chromatography (MeOH/DCM 3:97) and re-precipitated from EtOAc-petrol to give the title compound as a pale cream solid (0.065 g, 35%): R_f 0.32 (DCM/MeOH/petrol, 20:6:74); mp 205-206 °C; IR (cm^{-1}) 1617, 1558, 1404, 1361, 1242, 1110, 1065, 985, 858; λ_{max} (EtOH)/nm 305, 286; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05-3.15 (4H, m, CH_2-morpholine), 3.45-3.51 (4H, m, CH_2-morpholine), 5.52 (1H, s, H-3), 7.39-7.42 (4H, m, H-Ar), 7.54 (1H, ap t, *J* = 7.7 Hz, H-6), 7.70 (1H, d, *J* = 7.7 Hz, H-7), 7.04 (1H, d, *J* = 7.1 Hz, H-Ar), 8.13 (1H, d, *J* = 6.9 Hz, H-Ar), 8.22 (1H, d, *J* = 7.7 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.9, 66.1, 120.3, 121.6, 122.1, 124.9, 125.2, 125.4, 126.2, 126.8, 127.0, 127.5, 128.3, 128.5, 128.6, 128.9, 132.1, 133.5, 136.5, 137.5, 140.3, 151.1, 162.5; MS (ES+) *m/z* = 448.2 [M(^{35}Cl)+H]$^+$, 450.2 [M(^{37}Cl)+H]$^+$; HRMS calcd for $C_{25}H_{18}ClNO_3S$ [M(^{35}Cl)+H]$^+$ 448.0769, found 448.0774; Anal. Calcd for $C_{25}H_{18}ClNO_3S$: C, 65.91, H, 4.51, N, 2.85. Found: C, 65.95, H, 4.49, N, 2.60%.

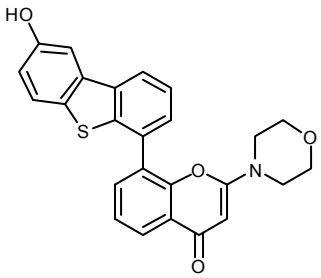
8-(9-Hydroxydibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (23a)



Following Method F: 2-morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.100 g, 0.28 mmol)), 6-bromo-dibenzo[*b,d*]thiophen-1-ol **3a** (0.085 g, 0.3 mmol), $Pd(PPh_3)_4$ (5.0 mg, 0.002 mmol), 2 M Na_2CO_3 (0.6 mL) and DME (4 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 45 min. The crude product was purified using medium pressure chromatography (MeOH/DCM 5:95) to give the title compound as a white solid (0.88 g, 73%): R_f 0.34 (MeOH/DCM 5:95); mp 336-338 °C; IR (cm^{-1}) 2391, 1643, 1574, 1431, 1381, 1255, 1125, 1052, 995, 929, 798; λ_{max} (EtOH)/nm 274, 288; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.11-3.18 (4H, m,

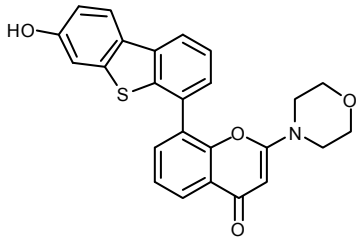
CH_2-morpholine), 3.41-3.45 (4H, m, CH_2-morpholine), 5.58 (1H, s, H-3), 6.95 (1H, d, J = 7.5 Hz, H-2'), 7.30-7.40 (2H, m, H-Ar), 7.55-7.65 (3H, m, H-Ar), 7.88 (1H, d, J = 6.9 Hz, H-Ar), 8.06 (1H, d, J = 6.9 Hz, H-Ar), 8.70 (1H, d, J = 7.5 Hz, H-1'), 10.73 (1H, s, OH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 44.7, 65.4, 86.4, 111.2, 113.5, 123.4, 123.7, 132.9, 125.1, 125.3, 125.4, 127.3, 128.3, 128.8, 130.0, 133.3, 136.0, 138.2, 170.1, 150.5, 155.6, 162.1, 175.2; MS (ES+) m/z = 430.1 $[M+H]^+$; HRMS calcd for $C_{25}H_{19}NO_4S$ $[M+H]^+$ 430.1108, found 430.1109; Anal. Calcd for $C_{25}H_{19}NO_4S$: C, 67.79, H, 4.38, N, 3.14. Found: C, 67.88, H, 4.43, N, 2.98%.

8-(8-Hydroxydibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (23b)



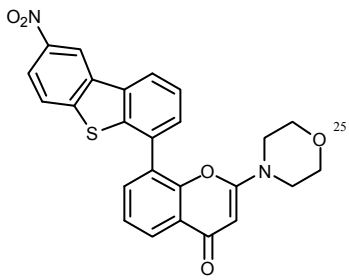
$PdCl_2$(dppf) (52.0 mg, 0.064 mmol), dppf (35.0 mg, 0.064 mmol) and potassium acetate (0.75 g, 7.65 mmol) were sequentially added to a degassed solution of 2-morpholino-4-oxo-4*H*-chromen-8-yl trifluoromethanesulfonate **19** (0.967 g, 2.55 mmol) and bis(pinacolato)diboron (0.668 g, 2.63 mmol) in anhydrous 1,4-dioxane (8 mL). The reaction mixture was heated under microwave irradiation at 150 °C for 1 h. To the reaction mixture 6-bromodibenzo[*b,d*]thiophen-2-ol **3b** (0.570 g, 2.04 mmol), $Pd(PPh_3)_4$ (59.0 mg, 0.051 mmol), 2 M Na_2CO_3 (5.1 mL, 10.2 mmol) were added sequentially. The reaction mixture was heated under microwave irradiation at 150 °C for 45 min. Upon cooling, the mixture was diluted with water (50 mL) and brine (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The crude product was triturated from MeOH to yield a light brown solid (0.820 g, 94% wrt **3b**): R_f 0.25 (MeOH/petrol/DCM 5:10:85); mp 298 °C (decomp.); IR (cm^{-1}) 2858, 1620, 1550, 1454, 1413, 1395, 1353, 1299, 1241, 1182, 1110, 1066, 987, 859; λ_{max} (EtOH)/nm 295; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.11-3.17 (4H, m, CH_2-morpholine), 3.41-3.43 (4H, m, CH_2-morpholine), 5.57 (1H, s, H-3), 7.03 (1H, d, J = 8.6 Hz, H-Ar), 7.54 (1H, ap t, J = 7.7 Hz, H-Ar), 7.60-7.61 (2H, m, H-Ar), 7.72-7.76 (2H, m, H-Ar), 7.88 (1H, d, J = 7.3 Hz, H-Ar), 8.06 (1H, d, J = 7.7 Hz, H-Ar), 8.31 (1H, ap t, J = 7.3 Hz, H-Ar), 9.73 (1H, s, OH); ^{13}C NMR (75 MHz, DMSO-d_6); δ 44.4, 65.3, 86.4, 108.1, 117.4, 122.0, 123.7, 124.9, 125.0, 125.4, 125.5, 128.4, 128.6, 128.8, 131.0, 133.2, 135.9, 136.8, 140.4, 150.4, 155.9, 162.1, 175.2; MS (ES+) m/z = 430.1 $[M+H]^+$; HRMS calcd for $C_{25}H_{19}N_SO_4$ $[M+H]^+$ 430.1108, found 430.1109.

8-(7-Hydroxydibenzo[*b,d*]thiophen-4-yl)-2-morpholino-4*H*-chromen-4-one (23c)



Following Method F: 2-morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.118 g, 0.33 mmol), 6-bromodibenzo[*b,d*]thiophen-3-ol **3c** (0.100 g, 0.36 mmol), $Pd(PPh_3)_4$ (0.020 g, 0.02 mmol), 2 M Na_2CO_3 (0.6 mL) and DME (4 mL). The reaction mixture was heated under microwave irradiation at 175 °C for 40 min. The crude product was purified recrystallisation from DCM/MeOH (1:1) to give the title compound as a beige solid (0.095 g, 62%): R_f 0.34 (MeOH/petrol/DCM 5:20:75); mp 283-286 °C; IR (cm^{-1}) 3013, 2936, 1614, 1548, 1469, 1413, 1384, 1354, 1282, 1238, 1221, 1105, 1064, 1028, 895, 850, 775; λ_{max} (EtOH)/nm 216, 240, 276, 300; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.10-3.13 (4H, m, CH_2-morpholine), 3.41-3.45 (4H, m, CH_2-morpholine), 5.57 (1H, s, H-3), 6.98 (1H, d, *J* = 8.6 Hz, H-Ar), 7.29 (1H, s, H-6'), 7.50-7.61 (3H, m, H-Ar), 7.86 (1H, d, *J* = 7.4 Hz, H-Ar), 8.05 (1H, d, *J* = 7.7 Hz, H-3'), 8.20 (1H, d, *J* = 8.6 Hz, H-Ar), 8.25 (1H, d, *J* = 7.7 Hz, H-1'), 9.95 (1H, s, OH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 44.7, 65.4, 86.4, 108.4, 114.7, 120.8, 123.4, 123.7, 125.1, 125.3, 125.4, 127.0, 127.7, 128.7, 130.8, 133.2, 136.2, 138.1, 140.8, 150.4, 157.7, 162.1, 175.2; MS (ES+) *m/z* = 430.1 $[M+H]^+$; HRMS calcd for $C_{25}H_{19}NO_4S$ $[M+H]^+$ 430.1108, found 430.1111. Anal. Calcd for $C_{25}H_{19}NO_4S$: C, 67.29, H, 4.36, N, 3.11. Found: C, 67.16, H, 4.49, N, 3.40%.

2-Morpholino-8-(8-nitrodibenzo[*b,d*]thiophen-4-yl)-4*H*-chromen-4-one (24)



2-Morpholino-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one **20** (0.068 g, 0.19 mmol), 6-chloro-2-nitrodibenzo[*b,d*]thiophene **4** (0.050 g, 0.19 mmol), $Pd(Pt\text{-}Bu_3)_2$ (5.0 mg, 0.010 mmol), K_2CO_3 (0.080 g, 0.57 mmol) and DMF (4 mL). The reaction mixture was heated under microwave irradiation at 150 °C for 10 min. The crude product was purified by medium pressure cromatography (MeOH/petrol/DCM 3:10:87) to give the title compound as white solid (0.026 g, 30%): R_f 0.44 (MeOH/DCM 4:96); mp 280-283 °C; IR (cm^{-1}) 1654, 1567, 1505, 1396, 1338, 1242, 1178, 1112, 1074, 981, 777; λ_{max} (EtOH)/nm 306, 247; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02-3.05 (4H, m, CH_2-morpholine), 3.44-3.47 (4H, m, CH_2-morpholine), 5.52 (1H, s, H-3), 7.44 (1H, d, *J* =

7.4 Hz, H-5), 7.55 (1H, d, *J* = 7.4 Hz, H-7), 7.60 (1H, ap t, *J* = 7.4 Hz, H-6), 7.69 (1H, d, *J* = 7.4 Hz, H-Ar), 7.86 (1H, d, *J* = 8.7 Hz, H-Ar), 8.22-8.29 (3H, m, H-Ar), 9.01 (1H, s, H-9'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.8, 65.8, 87.3, 117.5, 121.7, 122.0, 123.2, 123.8, 125.0, 125.7, 126.7, 127.9, 129.5, 132.1, 133.2, 135.3, 136.1, 141.1, 145.8, 146.1, 150.7, 162.3, 176.6; MS (ES+) *m/z* = 459.2 $[M+H]^+$; HRMS calcd for $C_{25}H_{18}N_2O_5S$ $[M+H]^+$ 459.1009, found 459.1009; Anal. Calcd $C_{25}H_{18}N_2O_5S$: C, 61.14, H, 3.82, N, 5.59. Found: C, 61.22, H, 3.72, N, 5.42%.