Supporting Information

Synthesis and Functionalization of 3-Bromo-2-(2-chlorovinyl)benzothiophenes as Molecular Tools

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General Information and Method. All glasswares were oven-dried at 140 °C and all reactions were conducted under an argon atmosphere. Solvents: cyclohexane, ethyl acetate (EtOAc), for chromatography, were technical grade. All new compounds were characterized by $^1$H NMR, $^{13}$C NMR, IR spectroscopy, HRMS and elemental analyses. $^1$H and $^{13}$C NMR spectra were measured in CDCl$_3$ with a Bruker Avance 300. $^1$H NMR chemical shifts are reported in ppm from an internal standard TMS or of residual chloroform (7.26 ppm). The following abbreviation are used: m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet). $^{13}$C chemical shifts are reported in ppm from the central peak of deuteriochloroform (77.14). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm$^{-1}$). High-resolution mass spectra were recorded on a Bruker Daltonics micrOTOF-Q instrument. Elemental analyses (C, H) were performed with a Perkin-Elmer 240 analyzer at the microanalyses Service of the Faculty of Pharmacy at Châtenay-Malabry (France) and were within 0.4% of the theoretical values otherwise stated. Analytical TLC was performed on Merck precoated silica gel 60 F-254 plates. Merck silica gel 60 (230-400 mesh) was used for column chromatography. The plates were visualized by either UV light (254 nm), or by a solution of phosphomolybdic acid in ethanol.

General Procedure for the Synthesis of (E)-Chloroenynes 5a, 5b and 18

To a solution of alkyne (10 mmol) in Et$_2$O (150 mL) was added successively (E)-1,2-dichloroethylene (8 mL, 100 mmol), PdCl$_2$(PPh$_3$)$_2$ (700 mg, 1 mmol), piperidine (2 mL, 20 mmol) and CuI in portions (190 mg, 1 mmol). After complete disappearance of starting material monitored by TLC, the solution was filtered through a pad of celite using EtOAc. The organic layer was washed successively with sat. NH$_4$Cl, sat. NaHCO$_3$ and HCl (1 M) solutions. After drying over MgSO$_4$ and evaporation in vacuo, the crude residue was purified by silica gel column chromatography.

(E)-(2-(4-Chlorobut-3-en-1-yn-1-l)phenyl)(methyl) sulfane (5a)
brown oil, yield 68%, 1.4 g.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.38 (d, $J = 7.8$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 1H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.68 (d, $J = 13.5$ Hz, 1H), 6.22 (d, $J = 13.5$ Hz, 1H), 2.48 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 141.6 (Cq), 132.3 (CH), 130.4 (CH), 129.1 (CH), 124.3
CH), 124.2 (CH), 120.7 (Cq), 113.8 (CH), 90.7 (Cq), 89.3 (Cq), 15.1 (CH). IR (neat): 3069, 2920, 2197, 1687, 1573, 1461, 1431, 1246, 1226, 1165, 1080, 1040, 908, 839, 786, 746, 717, 669 cm⁻¹. HRMS (APCI): m/z [M+H]+ calcd for C₁₁H₁₀₃₅ClS: 209.0186; found: 209.0195.

(E)-3-(4-Chlorobut-3-en-1-yn-1-yl)-2-(methylthio) pyridine (5b)
brown oil, yield 74%, 1.6 g.

¹H NMR (300 MHz, CDCl₃) δ = 8.38 (d, J = 4.8 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 6.94 (dd, J = 7.5 Hz, J = 4.8 Hz, 1H), 6.71 (d, J = 13.8 Hz, 1H), 6.21 (d, J = 13.8 Hz, 1H), 2.56 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 161.8 (Cq), 148.4 (CH), 138.6 (CH), 131.5 (CH), 118.3 (CH), 113.5 (CH), 93.1 (Cq), 87.1 (Cq), 13.2 (CH₃). IR (neat): 2926, 2853, 1756, 1587, 1565, 1547, 1385, 1244, 1227, 1137, 1096, 1061, 1029, 915, 848, 794, 774, 741, 664 cm⁻¹. HRMS (APCI): m/z [M+H]+ calcd for C₁₀H₉₃₅ClNS: 210.0139; found: 210.0137.

Procedure for the Synthesis of (Z)-5a

To a solution of alkyne (10 mmol) in Et₂O (150 mL) was added successively (Z)-1,2-dichloroethylene (8 mL, 100 mmol), PdCl₂(PPh₃)₂ (700 mg, 1 mmol), n-BuNH₂ (2 mL, 20 mmol) and CuI in portions (190 mg, 1 mmol). After complete disappearance of starting material monitored by TLC, the solution was filtered through a pad of celite using EtOAc. The organic layer was washed successively with sat. NH₄Cl, sat. NaHCO₃ and HCl (1 M) solutions. After drying over MgSO₄ and evaporation in vacuo, the crude residue was purified by silica gel column chromatography.

(Z)-(2-(4-Chlorobut-3-en-1-yn-1-yl)phenyl)(methyl) sulfane (5a)
brown oil, yield 56%, 1.2 g.

¹H NMR (300 MHz, CDCl₃) δ = 7.46 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.13 (m, 2H), 7.06 – 6.99 (m, 1H), 6.58 (d, J = 13.5 Hz, 1H), 6.11 (d, J = 13.5 Hz, 1H), 2.23 (s, 3H). IR (neat): 3069, 2928, 1732, 1588, 1509, 1458, 1424, 1277, 1243, 1223, 1161, 1063, 1030, 913, 844, 791, 749, 714, 656 cm⁻¹. HRMS (APCI): m/z [M+H]+ calcd for C₁₁H₁₀₃₅ClSe: 256.9628; found: 256.9635.
Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.47 (d, J = 7.5 Hz, 1H), 6.16 (d, J = 7.5 Hz, 1H), 2.50 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 141.8 (Cq), 132.7 (CH), 129.2 (CH), 128.6 (CH), 124.3 (2 CH), 120.9 (Cq), 112.0 (CH), 94.7 (Cq), 89.6 (Cq), 15.2 (CH$_3$). IR (neat): 3083, 2920, 2197, 1618, 1590, 1575, 1462, 1434, 1333, 1279, 1242, 1074, 1039, 966, 808, 750, 720, 671, 634 cm$^{-1}$. HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{11}$H$_{10}$Cl$_3$S: 209.0186; found: 209.0192.

**Procedure for the Synthesis of Dichloroenyne 5c**

Triethylamine (40 mL) was added to a stirred mixture of alkyne (3.0 g, 20.2 mmol), 2-bromo-1,1-dichloroethylene (5.7 g, 32.3 mmol), PdCl$_2$(PPh$_3$)$_2$ (60 mg, 0.085 mmol), CuI (27 mg, 0.14 mmol) and PPh$_3$ (53 mg, 0.2 mmol) under argon atmosphere. The mixture was heated under reflux for 4 h. The precipitated ammonium salt was filtered off, the solvent was evaporated and water (75 mL) was added to the residue. The mixture was extracted with Et$_2$O (3 x 50 mL), dried over MgSO$_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

**(2-(4,4-Dichlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (5c)**

yellow oil, yield 71%, 3.5 g.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.43 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.25 (s, 1H), 2.49 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 142.0 (Cq), 132.7 (CH), 131.9 (Cq), 129.5 (CH), 124.4 (CH), 124.3 (CH), 120.5 (Cq), 111.0 (CH), 95.1 (Cq), 89.5 (Cq), 15.2 (CH$_3$). IR (neat): 3029, 2920, 2198, 1591, 1573, 1462, 1434, 1291, 1264, 1164, 1131, 1079, 1041, 1016, 955, 922, 819, 748, 719, 672, 655 cm$^{-1}$. HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{11}$H$_9$Cl$_2$S: 242.9797; found: 242.9802.

**General Procedure for the Synthesis of (E)-6a, (Z)-6a, (E)-9, (E)-6b, 6c and (E)-19**

To a solution of chloroenyne substrate in CH$_2$Cl$_2$ (1 mmol) was added MPHT (1.2 equiv), and the resulting solution was stirred at room temperature until disappearance of the starting material (as judged by TLC). The reaction mixture was next treated with a saturated Na$_2$S$_2$O$_3$ solution. The organic layer was washed with 10 % HCl solution (3 x 10 ml) and dried with MgSO$_4$. Removal of the solvent yield a crude product, which was purified by silica gel chromatography.

**(E)-3-Bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a**

yellow solid, mp 97.8 - 98.3 °C, yield 88%, 240.1 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.81 - 7.73 (m, 2H), 7.48 - 7.39 (m, 2H), 7.26 (d, J = 13.5 Hz,
1H), 6.76 (d, J = 13.5 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 138.2 (Cq), 136.4 (Cq), 133.0 (Cq), 126.4 (CH), 126.0 (CH), 125.4 (CH), 123.4 (CH), 122.3 (2 CH), 108.7 (Cq). IR (neat): 3055, 1704, 1601, 1504, 1454, 1432, 1320, 1302, 1254, 1229, 1199, 1157, 1015, 920, 866, 786, 760, 746, 719 cm$^{-1}$. Anal. Calcd. for C$_{10}$H$_6$BrClS: C 43.90%, H 2.21%. Found C 43.58%, H 2.31%.

(Z)-3-Bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a

yellow solid, mp 70.9 - 71.8 °C, yield 85%, 232.5 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.87 - 7.80 (m, 2H), 7.48 - 7.40 (m, 2H), 7.26 (d, J = 7.8 Hz, 1H), 6.44 (d, J = 7.8 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 138.5 (Cq), 136.8 (Cq), 131.9 (Cq), 126.3 (CH), 125.3 (CH), 123.4 (CH), 122.7 (CH), 122.3 (CH), 119.8 (CH), 111.2 (Cq). IR (neat): 3076, 3055, 3024, 2924, 2851, 1940, 1908, 1819, 1787, 1733, 1641, 1607, 1556, 1483, 1453, 1431, 1338, 1307, 1260, 1242, 1147, 1018, 922, 867, 807, 767, 749, 721, 638 cm$^{-1}$. Anal. Calcd. for C$_{10}$H$_6$BrClS: C 43.90%, H 2.21%. Found C 43.63%, H 2.16%.

(E)-1-(4-(2-(3-Bromobenzo[b]thiophen-2-yl)vinyl) phenyl)ethanone (9)

yellow solid, mp 163.0 - 163.4 °C, yield 73%, 260.8 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.95 (d, J = 8.1 Hz, 2H), 7.80 - 7.73 (m, 2H), 7.63 - 7.55 (m, 3H), 7.45 - 7.35 (m, 2H), 7.07 (d, J = 15.9 Hz, 1H), 2.61 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 197.4 (Cq), 141.0 (Cq), 138.8 (Cq), 136.8 (Cq), 136.7 (Cq), 136.6 (Cq), 131.2 (CH), 129.0 (2 CH), 126.9 (2 CH), 126.5 (CH), 125.5 (CH), 123.4 (CH), 123.2 (CH), 122.4 (CH), 110.0 (Cq), 26.7 (CH$_3$). IR (neat): 1679, 1598, 1560, 1433, 1407, 1356, 1300, 1272, 1255, 1020, 961, 938, 923, 856, 812, 778, 753 cm$^{-1}$. HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{18}$H$_{14}$OSBr: 356.9949; found: 356.9955.

3-Bromo-2-(2,2-dichlorovinyl)benzo[b]thiophene (6c)

white solid, mp 113.1 - 113.5 °C, yield 80%, 246.4 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.85 - 7.78 (m, 2H), 7.49 - 7.41 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 138.1 (Cq), 137.0 (Cq), 131.1 (Cq), 126.7 (CH), 125.6 (CH), 123.6 (CH), 123.2 (Cq), 122.6 (CH), 122.4 (CH), 111.4 (Cq). IR (neat): 3030, 1747, 1621, 1481, 1452, 1426, 1368, 1325, 1306, 1252, 1220, 1184, 1086, 1059, 1047, 1034, 1016, 928, 913, 846, 810, 751, 734, 721, 680, 644 cm$^{-1}$. Anal. Calcd. for C$_{10}$H$_6$BrClS: C 38.99%, H 1.64%. Found C 39.20%, H 1.64%.

(E)-3-Bromo-2-(2-chlorovinyl)thieno[2,3-b]pyridine (6b)
light yellow solid, mp 131.9 - 132.4 °C, yield 65%, 178.5 mg.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.56 (d, J = 4.5 \text{ Hz}, 1H), 7.99 (d, J = 8.1 \text{ Hz}, 1H), 7.36 (dd, J = 8.1 \text{ Hz}, J = 4.5 \text{ Hz}, 1H), 7.21 (d, J = 13.5 \text{ Hz}, 1H), 6.81 (d, J = 13.5 \text{ Hz}, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 158.3 (Cq), 148.4 (CH), 133.8 (Cq), 132.6 (Cq), 130.8 (CH), 125.9 (CH), 124.0 (CH), 120.8 (CH), 106.0 (Cq).\) IR (neat): 3048, 2957, 2923, 1733, 1723, 1603, 1552, 1376, 1317, 1277, 1232, 1196, 966, 885, 791, 765, 672 cm\(^{-1}\). HRMS (APCI): m/z [M+H]\(^+\) calcd for C_{9}H_{6}BrClS: 273.9087; found: 273.9086.

(E)-3-Bromo-2-(2-chlorovinyl)benzo[b]selenophene 19

white solid, mp 87.7 - 87.9 °C, yield 93%, 298.1 mg.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.84 (d, J = 7.8 \text{ Hz}, 1H), 7.76 (d, J = 7.8 \text{ Hz}, 1H), 7.43 (t, J = 7.5 \text{ Hz}, 1H), 7.38 - 7.27 (m, 2H), 6.62 (d, J = 13.5 \text{ Hz}, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 140.2 (Cq), 136.8 (Cq), 134.6 (Cq), 128.5 (CH), 126.8 (CH), 125.9 (CH), 125.8 (CH), 125.4 (CH), 123.2 (CH), 110.8 (Cq).\) IR (neat): 3044, 1941, 1787, 1724, 1702, 1601, 1508, 1460, 1431, 1310, 1291, 1248, 1226, 1158, 1028, 938, 914, 865, 844, 788, 749, 712 cm\(^{-1}\). Anal. Calcd. for C_{10}H_{6}BrClSe: C 37.48%, H 1.89%. Found C 37.41%, H 1.91%.

General Procedure for the Synthesis of (E)-8a-g, (Z)-8a, (Z)-8b, 15

To a mixture of 3-bromobenzo[b]thiophene (1 mmol) in toluene (12 mL) and MeOH (6 mL) was successively added the desired boronic acid (1.3 mmol), K_{2}CO\(_3\) (276.4 mg, 2 mmol), and [PdCl(dmba)(IMes)] (70.2 mg, 0.1 mmol). The reaction mixture was heated at 90 °C under vigorous stirring and monitored by TLC until complete disappearance of starting material. The solvent was evaporated in vacuo and water (10 mL) was added. After extraction with EtOAc (3 x 10 mL), the combined organic layers were dried with MgSO\(_4\) and the solvent was removed under reduced pressure. The crude material was purified by column chromatography to afford the expected product.

(E)-1-(4-(2-(2-Chlorovinyl)benzo[b]thiophen-3-yl) phenyl)ethanone (8a)

eyellow solid, mp 148.7 - 149.3 °C, yield 90%, 281.6 mg.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.11 (d, J = 7.8 \text{ Hz}, 2H), 7.79 (d, J = 8.1 \text{ Hz}, 1H), 7.53 - 7.48 (m, 3H), 7.40 - 7.28 (m, 2H), 6.90 (d, J = 13.5 \text{ Hz}, 1H), 6.67 (d, J = 13.5 \text{ Hz}, 1H), 2.68 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 197.7 (Cq), 139.3 (Cq), 139.1 (Cq), 137.9 (Cq), 136.5 (Cq), 134.9 (2 Cq), 130.6 (2 CH), 128.8 (2 CH), 126.1 (CH), 125.8 (CH), 125.0 (CH), 123.1 (CH), 122.4 (CH),

**(E)-2-(2-Chlorovinyl)-3-(4-methoxyphenyl)benzo [b]thiophene (8b)**

Yellow solid, mp 93.3 - 93.6 °C, yield 74%, 222.6 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.79 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.39 - 7.28 (m, 4H), 7.06 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 13.5 Hz, 1H), 6.64 (d, J = 13.5 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 159.5 (Cq), 140.1 (Cq), 137.9 (Cq), 136.1 (Cq), 133.7 (Cq), 131.5 (2 CH), 126.8 (CH), 126.4 (Cq), 125.6 (CH), 124.7 (CH), 123.5 (CH), 122.3 (CH), 120.1 (CH), 114.3 (2 CH), 55.5 (CH₃). IR (neat): 3057, 3000, 2957, 2930, 2906, 2835, 1685, 1610, 1573, 1525, 1494, 1460, 1439, 1413, 1356, 1319, 1305, 1287, 1247, 1210, 1176, 1156, 1130, 1109, 1068, 1034, 1017, 924, 874, 834, 805, 788, 762, 733, 682, 659, 624 cm⁻¹. HRMS (APCI): m/z [M+H]+ calcd for C₁₇H₁₄O₃ClS: 301.0448; found: 301.0451.

**(E)-2-(2-Chlorovinyl)-3-(4-methoxyphenyl)benzo [b]thiophene (8c)**

Yellow solid, mp 105.9 - 106.5 °C, yield 88%, 277.0 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.78 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.39 - 7.29 (m, 2H), 7.02 - 6.84 (m, 4H), 6.65 (d, J = 13.5 Hz, 1H), 6.07 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ = 148.0 (Cq), 147.6 (Cq), 140.0 (Cq), 137.8 (Cq), 135.8 (Cq), 134.0 (Cq), 127.8 (Cq), 126.7 (CH), 125.6 (CH), 124.8 (CH), 124.1 (CH), 123.5 (CH), 122.3 (CH), 120.3 (CH), 110.6 (CH), 108.7 (CH), 101.4 (CH₂). IR (neat): 1518, 1501, 1479, 1440, 1425, 1367, 1314, 1272, 1239, 1205, 1117, 1094, 935, 898, 853, 813, 773, 761, 733 cm⁻¹. HRMS (APCI): m/z [M+H]+ calcd for C₁₇H₁₂O₃Cl₂S: 315.0241; found: 315.0240.

**(E)-4-(2-(2-Chlorovinyl)benzo[b]thiophen-3-yl)phenol (8d)**

Yellow solid, mp 153.0 - 153.7 °C, yield 59%, 169.2 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.81 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.41 - 7.28 (m, 4H), 7.09 - 6.95 (m, 3H), 6.65 (d, J = 13.5 Hz, 1H), 5.33 (br, 1H). ¹³C NMR (75 MHz, CDCl₃) δ = 155.5 (Cq), 140.1 (Cq), 137.9 (Cq), 136.0 (Cq), 133.8 (Cq), 131.7 (2 CH), 126.8 (CH), 126.7 (Cq), 125.6 (CH), 124.8 (CH), 123.5 (CH), 122.3 (CH), 120.1 (CH), 115.8 (2 CH). IR (neat): 3058, 1611, 1594, 1525, 1495, 1431, 1350, 1236, 1205, 1172, 1104, 1039, 1018, 908, 874, 837,
817, 761, 732 cm\(^{-1}\). HRMS (ESI): m/z [M-H]\(^-\) calcld for C\(_{16}H\(_{10}\)OS\(^{35}\)Cl: 285.0141; found: 285.0130.

\((E)\)-3-(3-Chlorophenyl)-2-(2-chlorovinyl)benzo[b] thiophene (8e)

yellow oil, yield 84%, 256.4 mg.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.82\) (d, \(J = 7.8\) Hz, 1H), 7.57 - 7.28 (m, 7H), 6.94 (d, \(J = 13.5\) Hz, 1H), 6.70 (d, \(J = 13.5\) Hz, 1H), 1.47 (cyclohexane). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 139.6\) (Cq), 137.9 (Cq), 136.0 (Cq), 134.8 (2 Cq), 134.6 (Cq), 130.2 (CH), 130.1 (CH), 128.6 (CH), 128.3 (CH), 126.2 (CH), 125.8 (CH), 125.0 (CH), 123.2 (CH), 122.3 (CH), 121.1 (CH), 27.0 (cyclohexane). IR (neat): 3058, 1595, 1564, 1517, 1470, 1455, 1432, 1403, 1353, 1317, 1288, 1271, 1234, 1208, 1159, 1132, 1094, 1078, 1019, 998, 953, 925, 894, 875, 846, 809, 785, 760, 731, 713, 693, 650 cm\(^{-1}\). Anal. Calcd. for C\(_{16}H\(_{10}\)Cl\(_2\)S: C 62.96%, H 3.30%. Found C 62.52%, H 3.37%.

\((E)\)-2-(2-Chlorovinyl)-3-(4-vinylphenyl)benzo[b] thiophene (8f)

yellow solid, mp 74.8 - 75.6 °C, yield 75%, 222.6 mg.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.80\) (d, \(J = 7.5\) Hz, 1H), 7.60 - 7.56 (m, 3H), 7.40 - 7.29 (m, 4H), 6.98 (d, \(J = 13.5\) Hz, 1H), 6.83 (dd, \(J = 17.7\) Hz, \(J = 10.8\) Hz, 1H), 6.66 (d, \(J = 13.5\) Hz, 1H), 5.87 (d, \(J = 17.7\) Hz, 1H), 5.36 (d, \(J = 10.8\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 139.8\) (Cq), 138.0 (Cq), 137.3 (Cq), 136.4 (CH), 135.9 (Cq), 134.1 (Cq), 133.7 (Cq), 130.5 (2 CH), 126.6 (3 CH), 125.7 (CH), 124.8 (CH), 123.5 (CH), 122.3 (CH), 120.5 (CH), 114.7 (CH\(_2\)). IR (neat): 3057, 1685, 1629, 1524, 1493, 1456, 1432, 1402, 1354, 1317, 1288, 1271, 1249, 1234, 1209, 1180, 1158, 1131, 1113, 1068, 1034, 1017, 989, 925, 907, 876, 844, 802, 787, 762, 731 cm\(^{-1}\). HRMS (APCI): m/z [M+H]\(^+\) calcld for C\(_{18}H\(_{14}\)Cl\(_2\)S: 297.0499; found: 297.0510.

\((E)\)-1-(4-(2-(2-Chlorovinyl)thieno[2,3-b]pyridin-3-yl)phenyl)ethanone (8g)

white solid, mp 166.9 - 167.1 °C, yield 85%, 267.5 mg.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.55\) (d, \(J = 3.9\) Hz, 1H), 8.12 (d, \(J = 7.8\) Hz, 2H), 7.77 (d, \(J = 8.1\) Hz, 1H), 7.49 (d, \(J = 7.8\) Hz, 2H), 7.30 - 7.23 (m, 1H), 6.93 (d, \(J = 13.5\) Hz, 1H), 6.75 (d, \(J = 13.5\) Hz, 1H), 2.68 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 197.5\) (Cq), 160.1 (Cq), 147.8 (CH), 138.2 (Cq), 136.9 (Cq), 135.0 (Cq), 133.2 (Cq), 132.3 (Cq), 130.4 (2 CH), 130.3 (CH), 129.0 (2 CH), 125.9 (CH), 123.0 (CH), 120.3 (CH), 26.8 (CH\(_2\)). IR (neat): 3056, 1682, 1605, 1552, 1518, 1486, 1424, 1404, 1384, 1357, 1264, 1234, 1211, 1183, 1017, 959, 928, 878, 839, 795, 753, 728 cm\(^{-1}\).
HRMS (ESI): m/z [M+H]^+ calcd for C_{17}H_{13}NOS^{35}Cl: 314.0406; found: 314.0400.

(Z)-1-(4-(2-Chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone (8a)
yellow solid, mp 179.1 - 179.8 °C, yield 86%, 240.9 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 8.10 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.56 - 7.50 (m, 3H), 7.44 - 7.31 (m, 2H), 6.84 (d, J = 8.1 Hz, 1H), 6.26 (d, J = 8.1 Hz, 1H), 2.68 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 197.7 (Cq), 140.0 (Cq), 139.9 (Cq), 137.9 (Cq), 137.4 (Cq), 136.6 (Cq), 133.8 (Cq), 130.8 (2 CH), 128.7 (2 CH), 125.7 (CH), 124.8 (CH), 123.1 (CH), 122.7 (CH), 122.3 (CH), 118.6 (CH), 26.8 (CH$_3$).

IR (neat): 1680, 1603, 1426, 1403, 1356, 1332, 1265, 1181, 1160, 1130, 1072, 1017, 958, 931, 908, 859, 823, 766, 729, 660, 643 cm$^{-1}$. HRMS (ESI): m/z [M+H]^+ calcd for C$_{18}$H$_{14}$OS$_{35}$Cl: 313.0454; found: 313.0448.

(Z)-2-(2-Chlorovinyl)-3-(4-methoxyphenyl)benzo[b] thiophene (8b)
yellow solid, mp 116.5 - 117.2 °C, yield 85%, 255.7 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.88 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.41 - 7.31 (m, 4H), 7.05 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 7.8 Hz, 1H), 6.22 (d, J = 7.8 Hz, 1H), 3.90 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 159.5 (Cq), 139.9 (Cq), 138.7 (Cq), 138.6 (Cq), 132.8 (Cq), 131.7 (2 CH), 127.1 (Cq), 125.5 (CH), 124.5 (CH), 123.5 (CH), 123.3 (CH), 122.2 (CH), 117.4 (CH), 114.2 (2 CH), 55.4 (CH$_3$).

IR (neat): 1743, 1685, 1609, 1521, 1484, 1459, 1426, 1332, 1287, 1245, 1175, 1129, 1108, 1033, 851, 825, 788, 765, 730, 663, 643, 622 cm$^{-1}$. HRMS (APCI): m/z [M+H]^+ calcd for C$_{17}$H$_{14}$OS$_{35}$Cl: 301.0448; found: 301.0449.

2-(2,2-Dichlorovinyl)-3-(4-methoxyphenyl)benzo[b] thiophene 15
yellow solid, mp 116.6 - 117.0 °C, yield 83%, 278.3 mg.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 7.86 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.42 - 7.30 (m, 4H), 7.08 - 7.02 (m, 3H), 3.91 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 159.6 (Cq), 139.6 (Cq), 138.8 (Cq), 138.7 (Cq), 131.7 (2 CH), 126.7 (Cq), 125.7 (CH), 124.7 (CH), 123.6 (CH), 123.1 (CH), 122.2 (CH), 120.6 (Cq), 114.4 (2 CH), 55.5 (CH$_3$), one C not seen. IR (neat): 2835, 1609, 1522, 1484, 1461, 1440, 1359, 1287, 1248, 1212, 1179, 1162, 1108, 1035, 912, 839, 813, 764, 735, 664, 645 cm$^{-1}$. HRMS (APCI): m/z [M+H]^+ calcd for C$_{17}$H$_{14}$OS$_{35}$Cl: 335.0059; found: 335.0057.

General Procedure for the Synthesis of (E)-1ab-ak, (E)-11, (Z)-1al, (Z)-1am
To a mixture of chloroenyne substrate (0.5 mmol) in toluene (6 mL) and MeOH (3 mL) was
successively added the desired boronic acid (0.6 mmol), K$_2$CO$_3$ (138.2 mg, 1 mmol) and Pd(PPh$_3$)$_4$ (28.9 mg, 0.025 mmol). The reaction mixture was heated at 90 °C, under vigorous stirring and monitored by TLC until complete disappearance of starting material. The solvent was evaporated in vacuo and water (10 mL) was added. After extraction with CH$_2$Cl$_2$ (3 x 10 mL), the combined organic layer were dried over MgSO$_4$, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel.

(E)-1-(4-(2-(3-(4-acetylphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one (1aa)

yellow solid, mp 199.5 – 199.7 °C.

$^1$H NMR (300 MHz, DMSO) $\delta$ = 8.18 (d, $J$ = 8.1 Hz, 2H), 8.05 (d, $J$ = 8.1 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 2H), 7.68 – 7.63 (m, 4H), 7.55 – 7.33 (m, 4H), 7.24 (d, $J$ = 15.9 Hz, 1H), 2.69 (s, 3H), 2.56 (s, 3H). $^{13}$C NMR (75 MHz, DMSO) $\delta$ = 198.0 (Cq), 197.6 (Cq), 191.0 (Cq), 139.7 (Cq), 138.9 (Cq), 138.7 (Cq), 138.0 (Cq), 136.7 (Cq), 136.5 (Cq), 135.9 (Cq), 131.3 (CH), 131.0 (2 CH), 129.3 (2 CH), 129.2 (2 CH), 127.3 (2 CH), 126.5 (CH), 125.8 (CH), 123.3 (CH), 123.2 (2 CH), 27.3 (CH$_3$), 27.1 (CH$_3$). IR (neat): 1678, 1599, 1561, 1561, 1456, 1432, 1407, 1357, 1306, 1266, 1223, 1182, 1159, 1112, 1073, 1016, 958, 876, 862, 839, 817, 764, 734, 675, 657, 612 cm$^{-1}$. HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{26}$H$_{21}$O$_2$S: 397.1262; found: 397.1272.

(E)-1-(4-(2-(4-Fluorostyryl)benzo[b]thiophen-3-yl) phenyl)ethanone (1ab)

yellow solid, mp 163.4 - 164.1 °C, yield 86%, 160.2 mg.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 8.14 (d, $J$ = 7.8 Hz, 2H), 7.82 (d, $J$ = 7.8 Hz, 1H), 7.59 - 7.53 (m, 3H), 7.40 - 7.29 (m, 4H), 7.15 - 6.98 (m, 4H), 2.71 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 197.8 (Cq), 162.6 (d, $J$ = 246.9 Hz, Cq), 140.0 (Cq), 139.9 (Cq), 139.3 (Cq), 138.0 (Cq), 136.4 (Cq), 134.6 (Cq), 132.8 (d, $J$ = 3.0 Hz, Cq), 130.8 (3 CH), 128.8 (2 CH), 128.3 (d, $J$ = 8.3 Hz, 2 CH), 125.5 (CH), 124.9 (CH), 122.8 (CH), 122.4 (CH), 120.6 (CH), 115.8 (d, $J$ = 21.6 Hz, 2 CH), 26.8 (CH$_3$). $^{19}$F NMR (188 MHz, CDCl$_3$): $\delta$ = -111.05. IR (neat): 3060, 1680, 1602, 1564, 1551, 1507, 1491, 1456, 1433, 1403, 1356, 1319, 1304, 1265, 1230, 1214, 1182, 1158, 1112, 1096, 1070, 1016, 951, 933, 907, 875, 854, 816, 778, 763, 731, 684, 656 cm$^{-1}$. HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{18}$H$_{15}$FClS: 297.0499; found: 297.0510.

(E)-2-(4-Fluorostyryl)-3-(4-methoxyphenyl)benzo[b] thiophene (1ac)

yellow solid, mp 108.2 - 108.9 °C, yield 85%, 153.2 mg.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.81 (d, $J$ = 8.4 Hz, 1H), 7.57 (d, $J$ = 7.2 Hz, 1H), 7.41 - 7.30 (m, 6H), 7.20 - 6.96 (m, 6H), 3.91 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 162.5 (d, $J$ = 246.2 Hz, Cq), 159.4 (Cq), 140.8 (Cq), 138.1 (2 Cq), 135.9 (Cq), 133.2 (d, $J$ = 2.9 Hz, Cq), 131.7 (2 CH), 121.2 (2 CH).
129.7 (CH), 128.2 (d, J = 7.9 Hz, 2 CH), 127.1 (Cq), 125.3 (CH), 124.6 (CH), 123.2 (CH), 122.3 (CH), 121.5 (CH), 115.8 (d, J = 21.7 Hz, 2 CH), 114.2 (2 CH), 55.5 (CH₃). ¹⁹F NMR (188 MHz, CDCl₃): δ = -111.66. IR (neat): 2835, 1610, 1528, 1510, 1494, 1460, 1436, 1287, 1248, 1231, 1177, 1157, 1034, 952, 856, 816, 789, 763, 735 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ calcd for C₂₃H₁₈OFS: 361.1062; found: 361.1075.

(Ε)-1-(4-(2-(3-(Benzo[d][1,3]dioxol-5-yl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one (1ad)

yellow solid, mp 148.3 - 148.7 °C, yield 85%, 169.4 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.91 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.40 - 7.29 (m, 3H), 7.07 - 6.69 (m, 4H), 6.08 (s, 2H), 2.59 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ = 197.5 (Cq), 148.1 (Cq), 147.6 (Cq), 141.6 (Cq), 140.5 (Cq), 138.3 (Cq), 137.9 (Cq), 137.0 (Cq), 136.2 (Cq), 129.7 (CH), 128.9 (2 CH), 128.2 (Cq), 126.7 (2 CH), 125.7 (CH), 124.8 (CH), 124.3 (CH), 124.2 (CH), 123.4 (CH), 122.4 (CH), 110.8 (CH), 108.8 (CH), 101.5 (CH₂), 26.7 (CH₃). IR (neat): 1753, 1679, 1599, 1503, 1482, 1367, 1271, 1237, 1220, 1085, 1038, 957, 916, 865, 816, 765, 735 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ calcd for C₂₅H₁₉O₃S: 399.1055; found: 399.1049.

(Ε)-5-(2-(3,4-Dichlorostyryl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole (1ae)
yellow solid, mp 162.2 - 163.1 °C, yield 79%, 168.0 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.81 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.48 (s, 1H), 7.39 - 7.19 (m, 5H), 7.01 - 6.87 (m, 4H), 6.09 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ = 148.1 (Cq), 147.6 (Cq), 140.6 (Cq), 138.2 (Cq), 137.7 (Cq), 137.1 (2 Cq), 136.7 (Cq), 132.9 (Cq), 131.5 (Cq), 130.7 (CH), 128.4 (CH), 128.2 (CH), 125.7 (CH), 125.6 (CH), 124.8 (CH), 124.2 (CH), 123.4 (CH), 123.3 (CH), 110.7 (CH), 108.8 (CH), 101.5 (CH₂). IR (neat): 1754, 1680, 1552, 1502, 1483, 1439, 1367, 1314, 1236, 1218, 1132, 1093, 1039, 937, 908, 884, 810, 763, 733, 674 cm⁻¹. HRMS (APCI): m/z [M+H]⁺ calcd for C₂₃H₁₅Cl₂O₂S: 425.0164; found: 425.0156.

(Ε)-4-(2-(3,4-Dichlorostyryl)benzo[b]thiophen-3-yl)phenol (1af)
yellow solid, mp 153.3 - 154.0 °C, yield 92%, 182.8 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.81 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.46 (s, 1H), 7.39 - 7.17 (m, 7H), 7.02 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 15.9 Hz, 1H), 5.24 (br, 1H). ¹³C NMR (75 MHz, CDCl₃) δ = 155.5 (Cq), 140.6 (Cq), 138.2 (Cq), 137.4 (Cq), 137.2 (Cq), 136.8 (Cq), 131.5 (Cq), 130.7 (CH), 128.4 (CH), 128.2 (CH), 125.7 (CH), 125.6 (CH), 124.8 (CH), 124.2 (CH), 123.4 (CH), 123.3 (CH), 110.7 (CH), 108.8 (CH), 101.5 (CH₂). IR (neat): 1754, 1680, 1552, 1502, 1483, 1439, 1367, 1314, 1236, 1218, 1132, 1093, 1039, 937, 908, 884, 810, 763, 733, 674 cm⁻¹. HRMS (APCI): m/z [M+H]⁺ calcd for C₂₅H₁₇Cl₂O₄S: 450.0156; found: 450.0156.
132.9 (Cq), 131.9 (2 CH), 131.4 (Cq), 130.6 (CH), 128.2 (CH), 127.1 (Cq), 125.7 (CH), 125.6 (CH), 124.7 (CH), 123.4 (2 CH), 122.4 (CH), 115.8 (2 CH), 125.7 (CH), 125.6 (CH), 124.7 (CH), 123.4 (2 CH), 122.4 (CH), 115.8 (2 CH), 125.7 (CH), 125.6 (CH), 124.7 (CH), 123.4 (2 CH), 122.4 (CH), 115.8 (2 CH). IR (neat): 1611, 1583, 1552, 1527, 1496, 1471, 1433, 1393, 1355, 1317, 1266, 1219, 1172, 1129, 1101, 1029, 941, 906, 880, 846, 810 cm⁻¹. HRMS (ESI): m/z [M-H]⁻ calcd for C₂₂H₁₃OS₂Cl₂: 395.0064; found: 395.0064.

(E)-3-(4-Methoxyphenyl)-2-(3-methoxystyryl)benzo[b]thiophene (1ag)
yellow oil, yield 89%, 165.8 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.84 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.44 - 7.24 (m, 6H), 7.12 - 6.97 (m, 5H), 6.84 (d, J = 8.1 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ = 159.9 (Cq), 159.4 (Cq), 140.8 (Cq), 138.5 (Cq), 138.1 (2 Cq), 136.0 (Cq), 131.7 (2 CH), 130.8 (CH), 129.7 (CH), 127.1 (Cq), 125.3 (CH), 124.6 (CH), 123.2 (CH), 122.3 (CH), 122.1 (CH), 119.3 (CH), 114.2 (2 CH), 113.4 (CH), 112.3 (CH), 55.5 (CH₃), 55.4 (CH₃). IR (neat): 2834, 1734, 1608, 1597, 1575, 1527, 1498, 1460, 1435, 1347, 1287, 1246, 1209, 1176, 1156, 1108, 1034, 949, 908, 846, 815, 782, 762, 734, 687 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ calcd for C₂₄H₂₁O₂S: 373.1262; found: 373.1254.

(E)-3-(4-Methoxyphenyl)-2-(3,4,5-trimethoxystyryl)benzo[b]thiophene (1ah)
yellow solid, mp 167.4 - 167.7 °C, yield 87%, 188.2 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.81 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.43 - 7.29 (m, 4H), 7.17 - 6.94 (m, 4H), 6.64 (s, 2H), 3.91 - 3.85 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ = 159.4 (Cq), 153.5 (2 Cq), 140.8 (Cq), 138.1 (Cq), 138.0 (Cq), 135.6 (Cq), 132.8 (Cq), 131.7 (2 CH), 131.1 (CH), 127.2 (Cq), 125.2 (CH), 124.6 (CH), 123.2 (CH), 122.3 (CH), 121.2 (CH), 114.2 (2 CH), 104.0 (2 CH), 61.1 (CH₃), 56.4 (2 CH₃), 55.5 (CH₃), one C not seen. IR (neat): 2834, 1734, 1608, 1597, 1575, 1527, 1498, 1460, 1435, 1347, 1287, 1246, 1209, 1176, 1153, 1126, 1104, 1034, 942, 908, 845, 812, 788, 764 cm⁻¹. HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₆H₂₄O₄S·Na: 455.1293; found: 455.1302.

(E)-4-(2-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)pyridine (1ai)
yellow oil and solid, yield 75%, 128.8 mg.

¹H NMR (300 MHz, DMSO) δ = 8.51 (d, J = 5.7 Hz, 2H), 8.00 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.48 - 7.35 (m, 7H), 7.16 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 16.2 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ = 159.6 (Cq), 150.6 (2 CH), 143.8 (Cq), 140.1 (Cq), 138.1 (Cq), 137.8 (Cq), 136.8 (Cq), 131.9 (2
CH), 128.7 (CH), 126.5 (Cq), 126.0 (CH), 125.5 (CH), 125.4 (CH), 125.3 (CH), 123.6 (CH), 123.1 (CH), 121.2 (2 CH), 114.9 (2 CH), 55.7 (CH).


(E)-1-(4-(2-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-3-yl)phenyl)ethan-1-one (1aj)
yellow solid, mp 206.9 – 207.2 °C, yield 80%, 164.2 mg.

¹H NMR (300 MHz, DMSO) δ = 8.19 (d, J = 7.8 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.81 – 7.76 (m, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.59 – 7.33 (m, 7H), 7.01 (d, J = 15.9 Hz, 1H), 2.69 (s, 3H).

¹³C NMR (75 MHz, DMSO) δ = 198.1 (Cq), 141.8 (Cq), 140.3 (Cq), 139.6 (Cq), 138.9 (Cq), 138.8 (Cq), 138.2 (Cq), 137.9 (Cq), 136.7 (Cq), 135.5 (Cq), 131.0 (2 CH), 129.3 (2 CH), 126.5 (CH), 126.0 (CH), 125.9 (CH), 125.8 (CH), 125.7 (CH), 124.4 (CH), 123.2 (CH), 123.1 (CH), 122.9 (CH), 122.4 (CH), 27.3 (CH₃).


(E)-1-(4-(3-(4-Fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone (1ak)
yellow solid, mp 144.3 – 144.5 °C, yield 82%, 152.7 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.93 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 7.5 Hz, 1H), 7.57 – 7.24 (m, 10H), 7.08 (d, J = 16.9 Hz, 1H), 2.61 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 197.4 (Cq), 162.7 (d, J = 246.2 Hz, Cq), 141.4 (Cq), 140.4 (Cq), 138.3 (Cq), 138.2 (Cq), 136.3 (Cq), 136.2 (Cq), 132.2 (d, J = 8.0 Hz, 2 CH), 130.6 (d, J = 3.1 Hz, Cq), 130.1 (CH), 129.0 (2 CH), 126.7 (2 CH), 125.8 (CH), 124.9 (CH), 123.8 (CH), 123.2 (CH), 122.4 (CH), 115.9 (d, J = 21.4 Hz, 2 CH), 26.7 (CH₃).

¹⁹F NMR (188 MHz, CDCl₃): δ = -111.67. IR (neat): 1679, 1599, 1561, 1526, 1492, 1433, 1409, 1358, 1269, 1258, 1223, 1182, 1158, 1095, 1015, 958, 943, 908, 861, 842, 815, 764 cm⁻¹. HRMS (ESI): m/z [M+H]^+ calcd for C₂₄H₁₈OF: 373.1062; found: 373.1067.

(E)-1-(4-(2-(methylthio)phenyl)but-3-yn-1-yl)phenyl)ethanone 11
white solid, mp 80.1 – 80.3 °C, yield 71%, 103.8 mg.

¹H NMR (300 MHz, CDCl₃) δ = 7.92 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.18 – 7.06 (m, 3H), 6.57 (d, J = 16.2 Hz, 1H), 2.59 (s, 3H), 2.51 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 197.4 (Cq), 141.8 (Cq), 140.8 (Cq), 140.1 (CH), 136.8 (Cq), 132.5 (CH), 129.1 (CH), 128.9 (2 CH), 126.5 (2 CH), 124.4 (CH), 124.2 (CH), 121.2 (Cq),
111.0 (CH), 95.0 (Cq), 90.9 (Cq), 26.7 (CH$_3$), 15.2 (CH$_3$). IR (neat): 1677, 1598, 1506, 1463, 1409, 1357, 1308, 1270, 1262, 1241, 1182, 1114, 1076, 1040, 1014, 959, 945, 860, 812, 751 cm$^{-1}$. HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{19}$H$_{17}$O:S: 293.1000; found: 293.0992.

**(Z)-1-(4-(2-(4-Methoxystyryl)benzol[b]thiophen-3-yl)phenyl)ethanone (1a)**

Yellow solid, mp 143.7 - 144.1 °C, yield 89%, 171.1 mg.

$^1$H NMR (300 MHz, DMSO) δ = 8.11 (d, J = 8.1 Hz, 2H), 7.90 - 7.86 (m, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.54 - 7.50 (m, 1H), 7.39- 7.28 (m, 4H), 6.90 (d, J = 8.1 Hz, 2H), 6.72 (d, J = 12.0 Hz, 1H), 6.47 (d, J = 12.0 Hz, 1H), 3.77 (s, 3H), 2.64 (s, 3H), 1.38 (cyclohexane). $^{13}$C NMR (75 MHz, DMSO) δ = 198.0 (Cq), 159.6 (Cq), 139.6 (Cq), 139.0 (Cq), 138.4 (Cq), 136.9 (Cq), 136.4 (Cq), 135.5 (Cq), 133.4 (CH), 130.8 (2 CH), 130.7 (2 CH), 129.0 (2 CH), 128.6 (Cq), 125.8 (CH), 125.3 (CH), 123.0 (CH), 122.7 (CH), 121.0 (CH), 114.3 (2 CH), 55.6 (CH$_3$), 27.3 (CH$_3$), 26.8 (cyclohexane). IR (neat): 1735, 1680, 1603, 1510, 1457, 1435, 1404, 1356, 1305, 1266, 1245, 1175, 1143, 1101, 1032, 1018, 951, 907, 875, 850, 819, 764, 728 cm$^{-1}$. HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{25}$H$_{21}$O$_2$S: 385.1262; found: 385.1260.

**(Z)-1-(4-(2-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone (1am)**

Yellow solid, mp 123.2 – 123.6 °C, yield 83%, 159.6 mg.

$^1$H NMR (300 MHz, DMSO) δ = 7.94 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 4.8 Hz, 1H), 7.54 - 7.51 (m, 3H), 7.41 - 7.34 (m, 4H), 7.11 (d, J = 8.1 Hz, 2H), 6.78 (d, J = 12.0 Hz, 1H), 6.65 (d, J = 12.0 Hz, 1H), 3.84 (s, 3H), 2.59 (s, 3H). $^{13}$C NMR (75 MHz, DMSO) δ = 197.8 (Cq), 159.5 (Cq), 141.6 (Cq), 139.0 (Cq), 138.8 (Cq), 137.8 (Cq), 136.4 (Cq), 134.3 (Cq), 131.8 (2 CH), 131.2 (CH), 129.7 (2 CH), 128.8 (2 CH), 126.6 (Cq), 125.9 (CH), 125.1 (CH), 124.6 (CH), 123.1 (CH), 122.9 (CH), 114.7 (2 CH), 55.7 (CH$_3$), 27.1 (CH$_3$). IR (neat): 1675, 1612, 1595, 1559, 1525, 1503, 1491, 1410, 1357, 1288, 1269, 1246, 1181, 1153, 1108, 1060, 1033, 958, 941, 907, 863, 838, 813, 769, 728 cm$^{-1}$. HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{25}$H$_{21}$O$_2$S: 385.1262; found: 385.1261.

**Procedure for the Synthesis of 1ca and 16**

In a round-bottomed flask, under an argon atmosphere, containing the chlorovinylic substrate (0.5 mmol) and Fe(acac)$_3$ (0.05 mmol) was added THF (6 mL). The reaction mixture was cooled to -30 °C and EtMgBr (0.75 mmol of typically 1 M solution in THF) was added dropwise (for the synthesis of 18 the quantity of EtMgBr was 1.5 mmol). The red colored solution turned dark brown to black (depending on the Grignard reagent quantity). The reaction mixture was stirred...
until the disappearance of starting material as judged by TLC. A 1 M aq HCl solution (5.0 mL) was then added, and the two layers were separated. After extraction using Et₂O (2 × 20 mL), the combined organic layers were washed three times with H₂O, then dried over MgSO₄, filtered, and concentrated under vacuum. The crude residue was then purified by silica gel column chromatography.

**(E)-2-(But-1-en-1-yl)-3-(4-methoxyphenyl) benzo[b]thiophene (1ca)**

Yellow solid, mp 73.6 - 73.9 °C, yield 84 %, 123.7 mg.

$^1$H NMR (300 MHz, CDCl₃) δ = 7.80 (d, $J = 6.9$ Hz, 1H), 7.55 (d, $J = 6.9$ Hz, 1H), 7.40 - 7.29 (m, 4H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.59 (d, $J = 15.6$ Hz, 1H), 6.33 - 6.23 (m, 1H), 3.93 (s, 3H), 2.29 - 2.19 (m, 2H), 1.10 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl₃) δ = 159.1 (Cq), 140.9 (Cq), 138.6 (Cq), 137.8 (Cq), 135.7 (CH), 133.5 (Cq), 131.6 (2 CH), 127.4 (Cq), 124.7 (CH), 124.3 (CH), 122.9 (CH), 122.2 (2 CH), 114.1 (2 CH), 55.4 (CH₃), 26.4 (CH₂), 13.6 (CH₃). IR (neat): 1751, 1682, 1610, 1529, 1499, 1458, 1434, 1381, 1356, 1287, 1246, 1206, 1181, 1132, 1107, 1083, 1034, 955, 910, 841, 812, 762, 732 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ calcd for C₁₉H₁₉OS: 295.1157; found: 295.1160.

**(E)-2-(2-Ethylbut-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b] thiophene (16)**

Colorless oil, yield 74 %, 119.3 mg.

$^1$H NMR (300 MHz, CDCl₃) δ = 7.83 - 7.80 (m, 1H), 7.59 - 7.55 (m, 1H), 7.37 - 7.28 (m, 4H), 7.02 (d, $J = 7.8$ Hz, 2H), 6.27 (s, 1H), 3.89 (s, 3H), 2.50 (q, $J = 7.5$ Hz, 2H), 2.17 (q, $J = 7.5$ Hz, 2H), 1.12 (t, $J = 7.5$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl₃) δ = 158.8 (Cq), 148.6 (Cq), 139.7 (Cq), 138.8 (Cq), 136.1 (Cq), 134.2 (Cq), 131.6 (2 CH), 127.9 (Cq), 124.1 (CH), 124.0 (CH), 122.7 (CH), 121.8 (CH), 116.3 (CH), 113.8 (2 CH), 55.3 (CH₃), 30.4 (CH₂), 25.0 (CH₂), 12.9 (2 CH₃). IR (neat): 2965, 1610, 1524, 1492, 1460, 1431, 1352, 1287, 1247, 1176, 1157, 1108, 1069, 1035, 936, 870, 830, 801, 764, 734 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ calcd for C₂₁H₂₁OS: 321.1313; found: 321.1323.

**General procedure for the Synthesis of (E)-12, (E)-13**

To a solution of PdCl₂(PhCN)₂ (9.6 mg, 0.025 mmol), (E)-chlorovinylic substrate (0.5 mmol), CuI (9.5 mg, 0.05 mmol) in 3 mL of piperidine was added the required 1-alkyne (0.6 mmol) in 1 mL of piperidine. The stirring was continued at 60 °C until TLC analysis indicated complete consumption of the chloroenyne. The reaction mixture was hydrolyzed with H₂O (10 mL) and...
HCl 0.5M (10 mL) and extracted with diethylether (3 x 10 mL). The organic layers were dried over MgSO₄ and the solvent was removed in vacuo. Purification by column chromatography afforded the expected \((E)\)-enynes. 

\((E)\)-3-(4-Methoxyphenyl)-2-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)benzo[b]thiophene (12)

brown oil, yield 91%, 187.7 mg.

\(^1\)H NMR (300 MHz, CDCl₃) δ = 7.83 (d, \(J = 8.1\) Hz, 1H), 7.60 (d, \(J = 7.5\) Hz, 1H), 7.44 - 7.26 (m, 6H), 7.21 - 7.08 (m, 5H), 6.43 (d, \(J = 15.9\) Hz, 1H), 3.93 (s, 3H), 2.51 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl₃) δ = 159.5 (Cq), 141.6 (Cq), 140.5 (Cq), 138.4 (Cq), 137.3 (Cq), 136.9 (Cq), 134.1 (CH), 132.4 (CH), 131.7 (2 CH), 128.9 (CH), 126.7 (Cq), 125.8 (CH), 124.7 (CH), 124.4 (CH), 124.3 (CH), 123.6 (CH), 122.3 (CH), 121.5 (Cq), 114.3 (2 CH), 109.7 (CH), 95.4 (Cq), 90.8 (Cq), 55.5 (CH₃). IR (neat): 1680, 1609, 1599, 1576, 1549, 1494, 1462, 1433, 1357, 1320, 1287, 1246, 1209, 1178, 1160, 1130, 1097, 1035, 936, 908, 844, 814, 765, 751 cm\(^{-1}\). HRMS (APCI): m/z [M+H]⁺ calcd for C\(_{26}\)H\(_{21}\)O\(_2\)S\(_2\): 413.1028; found: 413.1017.

\((E)\)-N-(2-(4-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)but-3-en-1-yn-1-yl)phenyl)-N,4-dimethylbenzenesulfonylamine (13)

yellow solid, mp 80.9 - 81.2 °C, yield 75 %, 206.1 mg.

\(^1\)H NMR (300 MHz, CDCl₃) δ = 7.82 (d, \(J = 8.1\) Hz, 1H), 7.61 - 7.57 (m, 3H), 7.42 - 7.27 (m, 8H), 7.17 - 7.08 (m, 4H), 6.89 (d, \(J = 15.9\) Hz, 1H), 5.91 (d, \(J = 15.9\) Hz, 1H), 3.92 (s, 3H), 3.30 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl₃) δ = 159.7 (Cq), 143.5 (Cq), 142.2 (Cq), 140.4 (Cq), 138.3 (Cq), 137.4 (Cq), 136.5 (Cq), 136.2 (Cq), 133.9 (CH), 133.5 (CH), 131.6 (2 CH), 131.4 (CH), 129.6 (2 CH), 129.1 (CH), 128.0 (CH), 127.8 (2 CH), 126.5 (Cq), 126.0 (CH), 124.8 (CH), 123.7 (CH), 122.6 (Cq), 122.4 (CH), 114.3 (2 CH), 109.3 (CH), 93.8 (Cq), 90.0 (Cq), 55.5 (CH₃), 38.1 (CH₃), 21.6 (CH₃). IR (neat): 1610, 1525, 1495, 1482, 1443, 1348, 1288, 1248, 1210, 1176, 1155, 1109, 1090, 1070, 1036, 938, 910, 891, 867, 845, 815, 765, 732, 710, 696, 676, 650 cm\(^{-1}\). HRMS (ESI): m/z [M+H]⁺ calcd for C\(_{33}\)H\(_{28}\)NO\(_3\)S\(_2\): 550.1511; found: 550.1503.

**Procedure for the Synthesis of 14**

Toluene (3 mL) was added to a mixture of AuBr\(_3\) (21.8 mg, 0.05 mmol) and 13 (274.9 mg, 0.5 mmol) at rt and the mixture was warmed immediately to 80 °C. After complete consumption of the starting material, as monitored by TLC, the reaction mixture was cooled to rt and filtered
through a short SiO₂ pad, and the filtrate was concentrated. The residue was purified by silica-gel column chromatography.

(E)-2-(2-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)-1-methyl-3-tosyl-1H-indole (14)

brown solid, mp 169.5 - 169.7 °C, yield 90 %, 247.4 mg.

¹H NMR (300 MHz, CDCl₃) δ = 8.29 - 8.25 (m, 1H), 7.92 - 7.84 (m, 3H), 7.74 (d, J = 16.5 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.46 - 7.26 (m, 8H), 7.20 - 7.15 (m, 2H), 7.11 - 7.05 (m, 2H), 3.91 (s, 3H), 3.73 (s, 3H), 2.33 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ = 159.6 (Cq), 143.1 (Cq), 141.3 (Cq), 140.4 (Cq), 140.3 (Cq), 138.9 (Cq), 138.3 (Cq), 137.7 (Cq), 137.1 (Cq), 131.6 (2 CH), 130.7 (CH), 129.6 (2 CH), 126.6 (Cq), 126.5 (2 CH), 126.1 (CH), 125.2 (Cq), 124.9 (CH), 124.1 (CH), 123.7 (CH), 122.8 (CH), 122.6 (CH), 120.5 (CH), 117.1 (CH), 114.3 (2 CH), 113.5 (Cq), 110.0 (CH), 55.5 (CH₃), 32.4 (CH₃), 21.6 (CH₃). IR (neat): 2957, 1732, 1609, 1531, 1505, 1458, 1437, 1393, 1317, 1287, 1249, 1213, 1179, 1159, 1141, 1109, 1082, 1033, 1017, 976, 909, 843, 811, 765, 737, 724, 705 cm⁻¹. HRMS (ESI): m/z [M+H]+ calcd for C₃₃H₂₈NO₃S₂: 550.1511; found: 550.1503.

References

Fig. 1 $^1$H NMR of (E)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane 5a

Fig. 2 $^{13}$C NMR of (E)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane 5a
Fig. 3 $^1$H NMR of (Z)-(2-(4-chloro-but-3-en-1-yn-1-yl)phenyl)(methyl)sulfane 5a

Fig. 4 $^{13}$C NMR of (Z)-(2-(4-chloro-but-3-en-1-yn-1-yl)phenyl)(methyl)sulfane 5a
Fig. 5 $^1$H NMR of (E)-3-(4-chlorobut-3-en-1-yn-1-yl)-2-(methylthio)pyridine 5b

Fig. 6 $^{13}$C NMR of (E)-3-(4-chlorobut-3-en-1-yn-1-yl)-2-(methylthio)pyridine 5b
Fig. 7 $^1$H NMR of (2-(4,4-dichlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane 5c

Fig. 8 $^{13}$C NMR of (2-(4,4-dichlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane 5c
**Fig. 9** $^1$H NMR of (E)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a

**Fig. 10** $^{13}$C NMR of (E)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a
Fig. 11 $^1$H NMR of (Z)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a

Fig. 12 $^{13}$C NMR of (Z)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a
Fig. 13 $^1$H NMR of (E)-3-bromo-2-(2-chlorovinyl)thieno[2,3-b]pyridine 6b

Fig. 14 $^1$H NMR of (E)-3-bromo-2-(2-chlorovinyl)thieno[2,3-b]pyridine 6b
Fig. 15 $^1$H NMR of 3-bromo-2-(2,2-dichlorovinyl)benzo[b]thiophene 6c

Fig. 16 $^{13}$C NMR of 3-bromo-2-(2,2-dichlorovinyl)benzo[b]thiophene 6c
Fig. 17 $^1$H NMR of $(E)$-1-(4-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone 8a

Fig. 18 $^{13}$C NMR of $(E)$-1-(4-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone 8a
Fig. 19 $^1$H NMR of (E)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene 8b

Fig. 20 $^{13}$C NMR of (E)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene 8b
Fig. 21 $^1$H NMR of (E)-5-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole 8c

Fig. 22 $^{13}$C NMR of (E)-5-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole 8c
Fig. 23 $^1$H NMR of (E)-4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenol 8d

Fig. 24 $^{13}$C NMR of (E)-4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenol 8d
Fig. 25 $^1$H NMR of (E)-3-(3-chlorophenyl)-2-(2-chlorovinyl)benzo[b]thiophene 8e

Fig. 26 $^{13}$C NMR of (E)-3-(3-chlorophenyl)-2-(2-chlorovinyl)benzo[b]thiophene 8e
Fig. 27 $^1$H NMR of (E)-2-(2-chlorovinyl)-3-(4-vinylphenyl)benzo[b]thiophene 8f

Fig. 28 $^{13}$C NMR of (E)-2-(2-chlorovinyl)-3-(4-vinylphenyl)benzo[b]thiophene 8f
Fig. 29 $^1$H NMR of (E)-1-(4-(2-(2-chlorovinyl)thieno[2,3-b]pyridin-3-yl)phenyl)ethanone 8g

Fig. 30 $^{13}$C NMR of (E)-1-(4-(2-(2-chlorovinyl)thieno[2,3-b]pyridin-3-yl)phenyl)ethanone 8g
Fig. 31 $^1$H NMR of (E)-1-(4-(2-(3-(4-acetylphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one 1aa

Fig. 32 $^{13}$C NMR of (E)-1-(4-(2-(3-(4-acetylphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one 1aa
Fig. 33 $^1$H NMR of (E)-1-(4-(2-(4-fluorostyryl)benzo[b]thiophen-3-yl)phenyl)ethanone 1ab

Fig. 34 $^{13}$C NMR of (E)-1-(4-(2-(4-fluorostyryl)benzo[b]thiophen-3-yl)phenyl)ethanone 1ab
Fig. 35 $^{19}$F NMR of (E)-1-(4-(2-fluorostyryl)benzo[b]thiophen-3-yl)phenyl)ethanone $1_{\text{ab}}$

Fig. 36 $^1$H NMR of (E)-2-(4-fluorostyryl)-3-(4-methoxyphenyl)benzo[b]thiophene $1_{\text{ac}}$
Fig. 37 $^{13}$C NMR of (E)-2-(4-fluorostyryl)-3-(4-methoxyphenyl)benzo[b]thiophene 1ac

Fig. 38 $^{19}$F NMR of (E)-2-(4-fluorostyryl)-3-(4-methoxyphenyl)benzo[b]thiophene 1ac
Fig. 39 the $^1$H NMR of

$$(E)-1-(4-(2-(3-(benzo[d][1,3]dioxol-5-yl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1\text{-}one$ $1\text{ad}$$

Fig. 40 $^{13}$C NMR of

$$(E)-1-(4-(2-(3-(benzo[d][1,3]dioxol-5-yl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1\text{-}one$ $1\text{ad}$$
Fig. 41 ¹H NMR of (E)-5-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole 1ae

Fig. 42 ¹³C NMR of (E)-5-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole 1ae
Fig. 43 $^1$H NMR of (E)-4-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)phenol 1af

Fig. 44 $^{13}$C NMR of (E)-4-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)phenol 1af
**Fig. 45** $^1$H NMR of (E)-3-(4-methoxyphenyl)-2-(3-methoxystyryl)benzo[b]thiophene 1ag

**Fig. 46** $^{13}$C NMR of (E)-3-(4-methoxyphenyl)-2-(3-methoxystyryl)benzo[b]thiophene 1ag
Fig. 47 $^1$H NMR of (E)-3-(4-methoxyphenyl)-2-(3,4,5-trimethoxystyryl)benzo[b]thiophene 1aH

Fig. 48 $^{13}$C NMR of (E)-3-(4-methoxyphenyl)-2-(3,4,5-trimethoxystyryl)benzo[b]thiophene 1aH
**Fig. 49** $^1$H NMR of $(E)$-4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)pyridine 1ai

**Fig. 50** $^{13}$C NMR of $(E)$-4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)pyridine 1ai
Fig. 51 $^1$H NMR of $(E)$-1-(4-(2-(2-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-3-yl)phenyl)ethan-1-one 1aj

Fig. 52 $^{13}$C NMR of $(E)$-1-(4-(2-(2-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-3-yl)phenyl)ethan-1-one 1aj
**Fig. 53** $^1$H NMR of (E)-1-(4-(2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone 1ak

**Fig. 54** $^{13}$C NMR of (E)-1-(4-(2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone 1ak
Fig. 55 $^{19}$F NMR of (E)-1-(4-(2-(4-fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone 1ak

Fig. 56 $^1$H NMR of (E)-1-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)phenyl)ethanone 11
Fig. 57 $^{13}$C NMR of (E)-1-(4-(4-(methylthio)phenyl)but-1-en-3-yn-1-yl)phenyl)ethanone

Fig. 58 $^1$H NMR of (E)-1-(4-((3-bromobenzo[b]thiophen-2-yl)vinyl)phenyl)ethanone
Fig. 59 $^{13}$C NMR of (E)-1-(4-(2-(3-bromobenzo[b]thiophen-2-yl)vinyl)phenyl)ethanone

Fig. 60 $^1$H NMR of

(E)-3-(4-methoxyphenyl)-2-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)benzo[b]thiophene
Fig. 61 $^{13}$C NMR of

$$(E)$-3-(4-methoxyphenyl)-2-(4-(2-methylthio)phenyl)but-1-en-3-yn-1-yl)benzo[b]thiophene

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Fig. 62 $^1$H NMR of

$$(E)\text{-N-(2-(4-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)but-3-en-1-yn-1-yl)phenyl)-N,4-dimethylbenzene sulfonamide}$$

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Fig. 63 $^1$H NMR of (E)-N-(2-(4-(3-(4-methoxyphenyl)benzo[|b|]thiophen-2-yl)but-3-en-1-yn-1-yl)phenyl)-N,4-dimethylbenzenesulfonamide 13

Fig. 64 $^1$H NMR of (E)-2-(2-(3-(4-methoxyphenyl)benzo[|b|]thiophen-2-yl)vinyl)-1-methyl-3-tosyl-1H-indole 14
**Fig. 65** $^{13}$C NMR of 

$$(E)-2-(2-(3-(4$-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)-1$-methyl-$3$-tosyl-$1$H-indole 14

**Fig. 66** $^1$H NMR of $(E)$-$2$-(but-1-en-1-yl)-$3$-(4$-$methoxyphenyl)benzo[b]thiophene 1ca
Fig. 67 $^1$H NMR of (E)-2-(but-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene 1ca

Fig. 68 $^1$H NMR of (Z)-1-(4-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone 8a
**Fig. 69** $^{13}$C NMR of (Z)-1-(4-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone 8a

**Fig. 70** $^1$H NMR of (Z)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene 8b
Fig. 71 $^{13}$C NMR of $\text{(Z)}$-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene 8b

Fig. 72 $^1$H NMR of $\text{(Z)}$-1-(4-(2-(4-methoxystyryl)benzo[b]thiophen-3-yl)phenyl)ethanone IaI
**Fig. 73** $^{13}$C NMR of (Z)-1-(4-(2-(4-methoxystyryl)benzo[b]thiophen-3-yl)phenyl)ethanone 1a

**Fig. 74** $^1$H NMR of (Z)-1-(4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone 1am
**Fig. 75** $^{13}$C NMR of (Z)-1-(4-(2-(4-(3-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone 1am

**Fig. 76** $^1$H NMR of 2-(2,2-dichlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene 15
Fig. 77 $^{13}$C NMR of 2-(2,2-dichlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene 15

Fig. 78 $^1$H NMR of 2-(2-ethylbut-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene 16
Fig. 79 $^{13}$C NMR of 2-(2-ethylbut-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene 16

Fig. 80 $^1$H NMR of (E)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)selane 18
Fig. 81 $^{13}$C NMR of (E)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)selane 18

Fig. 82 $^1$H NMR of (E)-3-bromo-2-(2-chlorovinyl)benzo[b]selenophene 19
Fig. 83 $^{13}$C NMR of (E)-3-bromo-2-(2-chlorovinyl)benzo[b]selenophene 29