Supporting Information

**Sulfoxide-directed metal-free cross-couplings in the expedient synthesis of benzothiophene-based components of materials**

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1. Experimental Section

General Procedure A – Condition A

1-(5-Methylbenzo[b]thiophen-2-yl)pentan-1-one S1

As described in general procedure A, (2-(hept-2-yn-1-y1)-4-methylphenyl)(methyl)sulfide (11.7 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (8.8 mg, 38.0 µmol, 76% yield) as a yellow solid (122 - 124 °C); ν\text{max} (neat)/cm\(^{-1}\) 2959, 2932, 2862, 1661, 1465, 1452, 1441, 1406, 1277, 1188, 1178, 1109, 904, 861, 799, 736, 726; δ\text{H} (400 MHz, CDCl\(_3\)) 0.98 (3H, t, J = 7.3, CH\(_3\)), 1.45 (2H, sxt, J = 7.4, CH\(_2\)CH\(_3\)), 1.78 (2H, quin, J = 7.5, CCH\(_2\)CH\(_3\)), 2.48 (3H, s, Ar-CH\(_3\)), 3.00 (2H, t, J = 7.5, CCH\(_2\)CH\(_3\)), 7.30 (1H, d, J 8.3, Ar-H), 7.68 (1H, s, Ar-H), 7.75 (1H, d, J 8.3, Ar-H), 7.88 (1H, s, Ar-H); δ\text{C} (100 MHz, CDCl\(_3\)) 13.9 (CH\(_2\)C\(_6\)H\(_5\)), 21.3 (Ar-CH\(_3\)), 22.5 (CH\(_2\)CH\(_3\)), 26.9 (CCH\(_2\)CH\(_3\)), 39.0 (CCH\(_2\)CH\(_3\)), 122.6 (Ar-CH), 125.5 (Ar-CH), 128.5 (Ar-CH), 129.4 (Ar-CH), 135.0 (Ar-C), 139.5 (Ar-C), 139.7 (Ar-C), 144.2 (Ar-C), 195.3 (C=O); m/z (El) M, 232; (Found: M, 232.0918. C\(_{14}\)H\(_{16}\)OS requires M, 232.0916).

1-(7-Methylbenzo[b]thiophen-2-yl)pentan-1-one S2

As described in general procedure A, (2-(hept-2-yn-1-y1)-6-methylphenyl)(methyl)sulfide (11.7 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (10.0 mg, 43.0 µmol, 86% yield) as a white solid (mp: 74 - 75 °C); ν\text{max} (neat)/cm\(^{-1}\) 2950, 2925, 2868, 1657, 1523, 1465, 1406, 1371, 1277, 1181, 1107, 870, 771, 722; δ\text{H} (400 MHz, CDCl\(_3\)) 0.98 (3H, t, J = 7.3, CH\(_3\)), 1.46 (2H, sxt, J = 7.4, CH\(_2\)CH\(_3\)), 1.79 (2H,
quin, $J = 7.5, \text{CCH}_2\text{CH}_2$, 2.58 (3H, s, Ar-CH$_3$), 3.02 (2H, t, $J = 7.5, \text{CCH}_2\text{CH}_2$), 7.24 - 7.30 (1H, m, Ar-H), 7.35 (1H, t, $J = 7.3, \text{Ar-H}$), 7.75 (1H, d, $J = 7.9, \text{Ar-H}$), 7.99 (1H, s, Ar-H); $\delta_C$ (100 MHz, CDCl$_3$) 13.9 (CH$_2$CH$_3$), 20.2 (Ar-CH$_3$), 22.5 (CH$_2$CH$_3$), 26.9 (CCH$_2$CH$_2$), 39.0 (CCH$_2$CH$_2$), 123.5 (Ar-CH), 125.4 (Ar-CH), 127.3 (Ar-CH), 129.4 (Ar-CH), 132.6 (Ar-C), 139.0 (Ar-C), 142.8 (Ar-C), 143.4 (Ar-C), 195.1 (C=O); m/z (EI) M, 232; (Found: M, 232.0929. C$_{14}$H$_{16}$OS requires M, 232.0916).

1-(5-Fluorobenzo[b]thiophen-2-yl)pentan-1-one S3

As described in general procedure A, (4-fluoro-2-(hept-2-yn-1-yl)phenyl)(methyl)sulfide (11.8 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (10.3 mg, 43.5 µmol, 87% yield) as a colourless solid (mp: 118 - 121°C); $\nu$$_{\text{max}}$ (neat)/cm$^{-1}$ 2954, 2926, 2854, 1670, 1521, 1437, 1274, 1264, 1191, 1182, 895, 806, 764, 736, 718, 705, 668; $\delta_H$ (400 MHz, CDCl$_3$) 0.98 (3H, t, $J = 7.3, \text{CH}_3$), 1.45 (2H, sxt, $J = 7.4, \text{CH}_2\text{CH}_3$), 1.78 (2H, quin, $J = 7.5, \text{CCH}_2\text{CH}_2$), 3.01 (2H, t, $J = 7.4, \text{CCH}_2\text{CH}_2$), 7.24 (1H, td, $J = 8.8, 2.5, \text{Ar-H}$), 7.55 (1H, dd, $J = 9.0, 2.4, \text{Ar-H}$), 7.82 (1H, dd, $J = 8.9, 4.7, \text{Ar-H}$), 7.90 (1H, s, Ar-H); $\delta_C$ (100 MHz, CDCl$_3$) 13.9 (CH$_2$CH$_3$), 22.4 (CH$_2$CH$_3$), 26.7 (CCH$_2$CH$_2$), 39.1 (CCH$_2$CH$_2$), 110.8 (d, $J = 22.7, \text{Ar-CH}$), 116.5 (d, $J = 24.9, \text{Ar-CH}$), 124.3 (d, $J = 9.5, \text{Ar-CH}$), 128.0 (d, $J = 4.4, \text{Ar-CH}$), 137.9 (d, $J = 1.5, \text{Ar-C}$), 140.0 (d, $J = 9.5, \text{Ar-C}$), 146.2 (Ar-C), 160.9 (d, $J = 243.6, \text{Ar-CF}$), 194.8 (C=O); m/z (EI) M, 236; (Found: M, 236.0671. C$_{13}$H$_{13}$OFS requires M, 236.0666).

1-(5-Chlorobenzo[b]thiophen-2-yl)pentan-1-one S4

As described in general procedure A, (4-chloro-2-(hept-2-yn-1-yl)phenyl)(methyl)sulfide (12.6 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (10.6 mg, 42.0 µmol, 84% yield) as a yellow solid (mp: 132 - 136 °C); $\nu$$_{\text{max}}$
As described in general procedure A, (2-(hept-2-yn-1-yl)-4-nitrophenyl)(methyl)sulfide (13.2 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (9.9 mg, 37.5 μmol, 75% yield) as a yellow solid (mp: 116 - 119 °C); ν_{\text{max}} (neat)/cm\(^{-1}\) 3071, 2967, 2947, 2930, 2850, 1659, 1599, 1576, 1531, 1517, 1467, 1405, 1349, 1268, 1177, 924, 826, 740, 735; δ_H (400 MHz, CDCl\(_3\)) 0.99 (3H, t, J = 7.5, CH\(_3\)), 1.80 (2H, quin, J = 7.5, CCH\(_2\)CH\(_2\)), 3.05 (2H, t, J = 7.4, CCH\(_2\)CH\(_2\)), 8.01 (1H, d, J = 9.0, Ar-H), 8.08 (1H, s, Ar-H), 8.31 (1H, dd, J = 8.9, 2.1, Ar-H), 8.81 (1H, d, J = 2.0, Ar-H); δ_C (100 MHz, CDCl\(_3\)) 14.1 (CH\(_2\)CH\(_3\)), 22.6 (CH\(_2\)CH\(_3\)), 26.8 (CCH\(_2\)CH\(_2\)), 39.3 (CCH\(_2\)CH\(_2\)), 121.4 (Ar-CH), 121.7 (Ar-CH), 124.0 (Ar-CH), 128.9 (Ar-CH), 139.1 (Ar-C), 146.1 (Ar-C), 147.7 (Ar-C), 147.8 (Ar-C), 194.7 (C=O); m/z (El) M, 263; (Found: M, 263.0612. C\(_{13}\)H\(_{13}\)O\(_3\)NS requires M, 263.0616).

1-(5-Methoxybenzo[b]thiophen-2-yl)pentan-1-one S6

As described in general procedure A, (2-(hept-2-yn-1-yl)-4-methoxyphenyl)(methyl)sulfide (12.4 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by...
preparative thin-layer chromatography on silica gel eluting with 15% EtOAc in n-hexane, gave the product (9.6 mg, 38.5 µmol, 77% yield) as a yellow solid (mp: 103 - 107 °C); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2963, 2953, 2864, 1657, 1598, 1515, 1456, 1441, 1407, 1374, 1336, 1275, 1268, 1232, 1201, 1178, 1158, 1148, 1071, 1031, 879, 812, 764, 749, 720; $\delta_H$ (400 MHz, CDCl$_3$) 0.98 (3H, t, $J = 7.4$, CH$_3$), 1.45 (2H, sxt, $J = 7.3$, CH$_2$CH$_3$), 1.78 (2H, quin, $J = 7.5$, CCH$_2$CH$_2$), 2.99 (2H, t, $J = 7.5$, CCH$_2$CH$_2$), 3.89 (3H, s, OCH$_3$), 7.13 (1H, dd, $J = 8.8$, 2.5, Ar-H), 7.30 (1H, d, J = 2.3, Ar-H), 7.74 (1H, d, $J = 9.0$, Ar-H), 7.88 (1H, s, Ar-H); $\delta_C$ (100 MHz, CDCl$_3$) 14.1 (CH$_2$CCH$_3$), 22.7 (CCH$_2$CH$_3$), 27.1 (CCH$_2$CH$_2$), 39.3 (CCH$_2$CH$_2$), 55.8 (OCH$_3$), 107.0 (Ar-CH), 118.6 (Ar-CH), 123.9 (Ar-CH), 128.6 (Ar-CH), 135.4 (Ar-C), 140.4 (Ar-C), 145.1 (Ar-C), 158.0 (Ar-C), 195.2 (C=O); m/z (El) M, 248; (Found: M, 248.0857. C$_{14}$H$_{16}$O$_2$S requires M, 248.0866).

1-(7-Methoxybenzo[b]thiophen-2-yl)pentan-1-one S7

As described in general procedure A, (2-(hept-2-yn-1-yl)-6-methoxyphenyl)(methyl)sulfide (12.4 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 15% EtOAc in n-hexane, gave the product (10.1 mg, 41.0 µmol, 82% yield) as a yellow solid (mp: 67 - 69 °C); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2957, 2930, 2870, 1661, 1567, 1526, 1469, 1438, 1404, 1347, 1322, 1260, 1218, 1191, 1167, 1093, 967, 918, 846, 800, 771, 716, 658, 602; $\delta_H$ (400 MHz, CDCl$_3$) 0.97 (3H, t, $J = 7.3$, CH$_3$), 1.45 (2H, sxt, $J = 7.4$, CH$_2$CH$_3$), 1.78 (2H, quin, $J = 7.5$, CCH$_2$CH$_2$), 3.00 (2H, t, J = 7.4, CCH$_2$CH$_2$), 4.01 (3H, s, OCH$_3$), 6.87 (1H, d, J = 7.8, Ar-H), 7.36 (1H, t, J = 7.9, Ar-H), 7.50 (1H, d, J = 8.0, Ar-H), 7.95 (1H, s, Ar-H); $\delta_C$ (100 MHz, CDCl$_3$) 13.9 (CH$_2$CH$_3$), 22.5 (CH$_2$CH$_3$), 26.8 (CCH$_2$CH$_2$), 39.1 (CCH$_2$CH$_2$), 55.7 (OCH$_3$), 106.3 (Ar-CH), 118.1 (Ar-CH), 126.2 (Ar-CH), 128.9 (Ar-CH), 131.8 (Ar-C), 140.7 (Ar-C), 144.2 (Ar-C), 154.6 (Ar-C), 195.0 (C=O); m/z (El) M, 248; (Found: M, 248.0857. C$_{14}$H$_{16}$O$_2$S requires M, 248.0866).
1-(7-(Trifluoromethyl)benzo[b]thiophen-2-yl)pentan-1-one S8

As described in general procedure A, (2-(hept-2-yn-1-yl)-6-(trifluoromethyl)phenyl)(methyl)sulfide (14.3 mg, 0.050 mmol), iodine (8.9 mg, 0.035 mmol) in toluene (2.0 mL), after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (13.0 mg, 45.5 µmol, 91% yield) as a yellow solid (mp: 57 - 59 °C); ν\text{max} (neat)/cm\textsuperscript{-1} 2970, 2945, 1662, 1341, 1300, 1275, 1203, 1172, 1131, 1089, 949, 873, 764, 750, 725; δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 0.98 (3H, t, J = 7.3, CH\textsubscript{3}), 1.45 (2H, sxt, J = 7.6, CH\textsubscript{2}CH\textsubscript{3}), 1.79 (2H, quin, J = 7.6, CCH\textsubscript{2}CH\textsubscript{2}), 3.03 (2H, t, J = 7.6, CCH\textsubscript{2}CH\textsubscript{2}), 7.52 (1H, t, J = 8.1, Ar-H), 7.77 (1H, d, J = 7.6, Ar-H), 8.01 (1H, s, Ar-H), 8.07 (1H, t, J = 8.1, Ar-H); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 13.9 (CH\textsubscript{2}C\textsubscript{H}\textsubscript{3}), 22.4 (CH\textsubscript{2}CH\textsubscript{3}), 26.7 (C\textsubscript{CH\textsubscript{2}}C\textsubscript{H}\textsubscript{2}), 39.1 (C\textsubscript{C}C\textsubscript{H}\textsubscript{2}CH\textsubscript{2}), 123.8 (q, J = 272.9, CF\textsubscript{3}), 124.7 (Ar-CH), 124.9 (q, J = 4.4, Ar-CH), 125.4 (q, J = 33.7, Ar-C), 127.8 (Ar-CH), 129.3 (Ar-C), 138.3 - 138.4 (m, Ar-C), 140.8 (Ar-C), 145.1 (Ar-C), 194.6 (C=O); m/z (EI) M, 286; (Found: M, 286.0632. C\textsubscript{14}H\textsubscript{13}OF\textsubscript{3}S requires M, 286.0639).

1-(5-(Trifluoromethyl)benzo[b]thiophen-2-yl)pentan-1-one S9

As described in general procedure A, (2-(hept-2-yn-1-yl)-4-(trifluoromethyl)phenyl)(methyl)sulfide (28.6 mg, 0.100 mmol), iodine (17.8 mg, 0.070 mmol) heated in toluene (4.0 mL) at 80 °C for 36 h, after purification by preparative thin-layer chromatography on silica gel eluting with 10% EtOAc in n-hexane, gave the product (22.6 mg, 79.0 µmol, 79% yield) as a white solid (mp: 99 - 101 °C); ν\text{max} (neat)/cm\textsuperscript{-1} 2982, 2937, 2856, 1663, 1607, 1525, 1470, 1456, 1446, 1406, 1338, 1326, 1276, 1186, 1112, 1078, 1053, 920, 862, 821, 732; δ\textsubscript{H} (500 MHz, CDCl\textsubscript{3}) 0.98 (3H, t, J = 7.4, CH\textsubscript{3}), 1.46 (2H, sxt, J = 6.9, CH\textsubscript{2}CH\textsubscript{3}), 1.80 (2H, quin, J = 7.6, CCH\textsubscript{2}CH\textsubscript{2}), 3.03 (2H, t, J = 7.6, CCH\textsubscript{2}CH\textsubscript{2}), 7.68 (1H, dd, J = 8.5, 1.3, Ar-H), 7.96 - 8.03 (2H, m, 2 × Ar-H), 8.18 (1H, s, Ar-H); δ\textsubscript{C} (125 MHz, CDCl\textsubscript{3}) 13.9 (CH\textsubscript{2}CH\textsubscript{3}), 22.4 (CH\textsubscript{2}CH\textsubscript{3}), 26.7 (CCH\textsubscript{2}CH\textsubscript{2}), 39.1 (CCH\textsubscript{2}CH\textsubscript{2}), 123.0 (q, J = 4.3, Ar-CH), 123.3 (q, J
Methyl(2-(pent-1-yn-3-yl)phenyl)sulfide (0.02 g, 0.1 mmol), O₂ sparged toluene (2 mL) and I₂ (0.017 g, 0.07 mmol) was added to an oven-dried tube fitted with a magnetic stirrer bar and under a nitrogen atmosphere. The resulting mixture was sparged with O₂ for a further 10 min before heating to 80 °C for 18 h. Saturated sodium thiosulfate solution (4 mL) was then added, the organic layer was separated and the aqueous layer extracted with Et₂O (3 x 2 ml). The combined organic layers were then washed with brine (2 mL), dried (MgSO₄), filtered and the solvent removed in vacuo. The resulting mixture was purified by column chromatography using hexanes to give the product as a white solid (0.009 g, 0.052 mmol, 52%). ν_max (neat)/cm⁻¹ 2967, 2918, 2832, 1651, 1560, 1524, 1448, 1350, 1247, 1163, 1088, 972, 850, 762, 709, 614, 544; δ_H (400 MHz, CDCl₃) 1.42 (3 H, t, J = 7.6 Hz, CH₃), 3.30 (2 H, q, J = 7.6 Hz, CH₂), 7.45 (1 H, t, J = 7.7 Hz, ArCH), 7.52 (1 H, t, J = 7.2 Hz, ArCH), 7.89 (1 H, d, J = 8.1 Hz, ArCH), 7.93 (1 H, d, J = 8.1 Hz, ArCH) 10.34 (1 H, s, CHO); δ_C (100 MHz, CHCl₃) 16.2 (CH₃), 20.0 (CH₂), 123.5 (ArCH), 123.9 (ArCH), 124.8 (ArCH), 128.3 (ArCH), 137.0 (ArC), 139.1 (ArC), 142.6 (ArC), 149.7 (ArC), 183.8 (CHO); m/z (GCMS) 190.0; (Found: M, 190.0446, C₁₁H₁₀O₁S₁ requires M, 190.0447).

**General Procedure B – Conditions B1**

**2-Pentylbenzo[b]thiophene S11**

Under an N₂ atmosphere a solution of iodine (17.8 mg, 0.07 mmol) in toluene (2.0 mL) was added to a solution of (2-(hept-2-yn-1-yl)phenyl)(methyl)sulfide (21.8 mg, 0.100 mmol) and
1,4-cyclohexadiene (20.0 mg, 0.25 mmol) in toluene (2.0 mL) at room temperature. The reaction mixture was stirred for 18 h at 80 °C before diluting with Et₂O (5 mL) and quenching with saturated aqueous Na₂S₂O₃ (5 mL). The aqueous layer was then extracted with Et₂O (2 × 5 mL) and the combined organic layers washed with brine (5 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude product was purified by preparative thin-layer chromatography on silica gel eluting with n-hexane to yield the product (17.9 mg, 88% yield) as a yellow oil; ν max (neat)/cm⁻¹ 2955, 2928, 2856, 1457, 1436, 1275, 1261, 1067, 1015, 855, 818, 764, 746, 726; δ H (500 MHz, CDCl₃) 0.89 - 0.95 (3H, m, CH₃), 1.34 - 1.43 (4H, m, 2 × CH₂), 1.73 - 1.81 (2H, m, CCH₂CH₂), 2.88 - 2.94 (2H, m, CCH₂CH₂), 7.00 - 7.02 (1H, m, Ar-H), 7.23 - 7.28 (1H, m, Ar-H), 7.31 (1H, td, J = 7.6, 1.1, Ar-H), 7.67 (1H, d, J = 7.6, Ar-H), 7.78 (1H, d, J = 7.6, Ar-H); δ C (125 MHz, CDCl₃) 14.0 (CH₃), 22.4 (CH₂), 30.8 (CCH₂CH₂), 31.3 (CH₂), 120.4 (Ar-CH), 122.1 (Ar-CH), 122.6 (Ar-CH), 123.3 (Ar-CH), 124.0 (Ar-CH), 139.3 (Ar-C), 140.2 (Ar-C), 146.9 (Ar-C); m/z (EI) M, 204; (Found: M, 204.0970. C₁₃H₁₈S requires M, 204.0967).

5-Methoxy-2-pentylenzo[b]thiophene S12

As described in general procedure B. (2-(hept-2-yn-1-yl)-4-methoxyphenyl)(methyl)sulfide (24.0 mg, 0.1 mmol), toluene (4 mL), I₂ (17.0 mg, 0.07 mmol) and 1,4-cyclohexadiene (0.014 mL, 0.15 mmol) were added to an oven-dried tube and the resulting mixture was heated at 80 °C for 18 h. The resulting mixture was purified by column chromatography using 10% EtOAc in hexanes to give the product as a yellow solid (14.0 mg, 0.069 mmol, 69%); ν max (neat)/cm⁻¹ 2955, 2918, 2849, 1596, 1568, 1457, 1377, 1269, 1198, 1154, 1069, 938, 854, 773, 694, 675, 579; δ H (400 MHz, CDCl₃) 0.92 (3 H, t, J = 6.8 Hz, CH₃), 1.35 - 1.42 (4 H, m, 2 x CH₂), 1.75 (2 H, quin, J = 7.3 Hz, CH₂), 2.88 (2 H, t, J = 7.5 Hz, CH₂), 3.86 (3 H, s, OCH₃), 6.88 - 6.95 (2 H, m, 2 × ArC-H), 7.15 (1 H, d, J = 2.2 Hz, ArC-H), 7.62 (1 H, d, J = 8.8 Hz, ArC-H); δ C (100 MHz, CDCl₃) 14.0 (CH₃), 22.4 (CH₂), 30.8 (CH₂), 30.8 (CH₂), 31.2 (CH₂), 55.5 (OCH₃). 105.2 (ArCH), 113.2 (ArCH), 120.3 (ArCH), 122.7 (ArCH), 131.5 (ArC), 141.2 (ArC), 148.3 (ArC), 157.3 (ArC); m/z (GCMS) 234.1; (Found: M, 234.1074, C₁₄H₁₈O₁S₁ requires M, 234.1073).
5-Chloro-2-pentylbenzo[b]thiophene S13

To an oven dried tube fitted with a magnetic stirrer bar and under a nitrogen atmosphere was added (2-(hept-2-yn-1-yl)-4-chlorophenyl)(methyl)sulfide (25.0 mg, 0.1 mmol), toluene (4 mL), I₂ (17.0 mg, 0.07 mmol) and 1,4-cyclohexadiene (0.014 mL, 0.15 mmol). The resulting mixture was heated at 80 °C for 18 h before the addition of saturated sodium thiosulfate solution (4 mL). The organic layer was separated and the aqueous layer extracted with Et₂O (3 x 2 mL). The combined organic layers were then washed with brine (2 mL), dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting mixture was purified by column chromatography using 10% EtOAc in hexanes to give the product as a yellow solid (17.5 mg, 0.075 mmol, 75%). νₘₐₓ (neat)/cm⁻¹ 2952, 2925, 2857, 1580, 1560, 1465, 1417, 1375, 1206, 1180, 1074, 903, 882, 803, 734, 667 597, 574; δ_H (400 MHz, CDCl₃) 0.9 (3 H, t, J = 6.8 Hz, CH₃), 1.3 - 1.4 (4 H, m, 2 x CH₂), 1.8 (2 H, quin, J = 7.3 Hz, CH₂), 2.9 (2 H, t, J = 7.5 Hz, CH₂), 6.9 (1 H, s, ArCH), 7.2 (1 H, dd, J = 8.6, 2.0 Hz, ArCH), 7.6 - 7.7 (2 H, m, 2 x ArCH); δ_C (100 MHz, CDCl₃) 14.0 (CH₃), 22.4 (CH₂), 30.7 (CH₂), 30.8 (CH₂), 31.2 (CH₂), 119.8 (ArCH), 122.2 (ArCH), 123.0 (ArCH), 123.7 (ArCH), 130.2 (ArC), 137.3 (ArC), 141.3 (ArC), 149.1 (ArC); m/z (GCMS) ; (Found: M, C₁₃H₁₅F₁S₁ requires M, ).

2-Pentyl-5-(trifluoromethyl)benzo[b]thiophene S14

As described in general procedure B. (2-(hept-2-yn-1-yl)-4-trifluoromethylphenyl)(methyl)sulfide (28.0 mg, 0.1 mmol), toluene (4 mL), I₂ (17.0 mg, 0.07 mmol) and 1,4-cyclohexadiene (0.014 mL, 0.15 mmol) were added to an oven-dried tube and the resulting mixture was heated at 80 °C for 18 h. The resulting mixture was purified by column chromatography using 10% EtOAc in hexanes to give the product as a yellow solid (20.7 mg, 0.076 mmol, 76%); νₘₐₓ (neat)/cm⁻¹ 2930, 1436, 1332, 1263, 1147, 1073, 911, 810, 761, 677, 609; δ_H (400 MHz, CDCl₃) 0.9 (1 H, t, J = 8.1 Hz, CH₃), 1.3 - 1.4 (4 H, m, 2 x CH₂), 1.8
(2 H, quin, J = 7.3 Hz, CH₂), 2.9 (2 H, t, J = 7.6 Hz, CH₂), 7.1 (1 H, s, ArCH), 7.5 (1 H, d, J = 8.3 Hz, ArCH), 7.9 (1 H, d, J = 8.4 Hz, ArCH), 7.9 (1 H, s, ArCH); δc (100 MHz, CDCl₃) 14.0 (CH₃), 22.4 (CH₂), 30.8 (CH₂), 30.8 (CH₂), 31.3 (CCH₂), 119.5 - 119.8 (m, 2 x ArCH), 120.5 (ArCH), 122.5 (ArCH), 126.6 (q, J = 13.5 Hz, ArCF₃), 127.0 (q, J = 271.2, CF₃), 139.8 (ArC), 142.4 (ArC), 149.3 (ArC); m/z (GCMS) 272.1; (Found: M, 272.0844, C₁₄H₁₅F₃S₁ requires M, 272.0841).

**7-Fluoro-2-pentybenzo[b]thiophene S15**

![Chemical structure](image)

As described in general procedure B. (2-(hept-2-yn-1-yl)-6-fluorophenyl)(methyl)sulfide (24.0 mg, 0.2 mmol), toluene (4 mL), I₂ (17.0 mg, 0.07 mmol) and 1,4-cyclohexadiene (0.014 mL, 0.15 mmol) were added to an oven-dried tube and the resulting mixture was heated at 80 °C for 18 h. The resulting mixture was purified by column chromatography using 10% EtOAc in hexanes to give the product as a yellow solid (14.0 mg, 0.069 mmol, 69%); νmax (neat)/cm⁻¹ 2929, 2857, 1603, 1573, 1542, 1467, 1249, 1214, 1193, 913, 847, 828, 731, 585; δₕ (500 MHz, CDCl₃) 0.93 (3 H, t, J = 6.0 Hz, CH₃), 1.39 (4 H, d, J = 2.4 Hz, 2 x CH₂), 1.75 (2 H, quin, J = 6.8 Hz, CH₂), 2.88 (2 H, t, J = 7.6 Hz, CCH₂), 6.96 (1 H, s, ArCH), 7.07 (1 H, t, J = 8.9 Hz, ArCH), 7.46 (1 H, d, J = 8.9 Hz, ArCH), 7.59 (1 H, dd, J = 8.4, 5.3 Hz, ArCH); δc (100 MHz, CDCl₃) 13.7 (CH₃), 22.1 (CH₂), 30.4 (CH₂), 30.5 (CH₂), 31.0 (CCH₂), 108.0 (dd, J = 25.4, 1.0 Hz, ArCH), 112.5 (d, J = 24.5 Hz, ArCH), 119.5 (ArCH), 123.2 (d, J = 9.1 Hz, ArCH), 136.4 (d, J = 1.8 Hz, ArC), 139.8 (d, J = 10.0 Hz, ArC), 146.2 (d, J = 3.6 Hz, ArC), 159.6 (d, J = 245.2 Hz, ArC-F); m/z (GCMS) 222.1; (Found: M, 222.0872, C₁₃H₁₅F₃S₁ requires M, 222.0873).

**General Procedure C – Conditions B2**

**2-Methyl-3-ethylbenzothiophene S16**

![Chemical structure](image)

S11
A microwave vial equipped with a magnetic stirrer, was charged with trimethyl(3-(2-methylsulfanyl)pent-1-yn-yl)silane (0.131 g, 0.5 mmol) and para-toluene sulfonic acid (95.1 mg, 0.5 mmol) and the mixture dissolved in EtOH (2.5 ml). The solution was then heated at 150 °C for 1 h 45 min in a microwave. The solution was quenched with aqueous saturated NaHCO$_3$ (6 mL) and the aqueous layer was extracted with Et$_2$O (3 x 5 mL). The combined organic layer was dried (MgSO$_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel eluting with 100% n-hexane to yield the product (49.0 mg, 56%); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2964, 2869, 1456, 1432, 1374, 1319, 1174, 1152, 1134, 1104, 1062, 1021, 925, 907, 808, 757, 729, 709, 638, 573; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 1.23 (3 H, t, $J = 7.6$ Hz, CH$_2$C$_3$H), 2.82 (2 H, q, $J = 7.6$ Hz, CH$_2$CH$_3$), 7.28 (1 H, t, $J = 8.2$ Hz, Ar-H), 7.35 (1 H, t, $J = 7.9$ Hz, Ar-H), 7.64 (1 H, d, $J = 7.9$ Hz, Ar-H), 7.77 (1 H, d, $J = 7.8$ Hz, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 13.5 (CH$_3$), 19.5 (CH$_2$CH$_3$), 121.0 (Ar-C-H), 122.1 (Ar-C-H), 123.3 (Ar-C-H), 123.7 (Ar-C-H), 133.5 (Ar-C), 138.4 (Ar-C), 140.1 (Ar-C); m/z (GCMS) 176.1; (Found: M, 176.0655, C$_{14}$H$_{18}$O$_1$S$_1$ requires M, 176.0654).

2-Methyl-3-isopropylbenzothiophene S17

As in general procedure B2, Trimethyl(4-methyl-3-(2-methylsulfanyl)phenyl)pent-1-yn-1-yl)silane (64.9 mg, 0.36 mmol) and p-TSA (68.4 mg, 0.36 mmol) in EtOH (2 ml) were heated at 150 °C in a microwave. The crude product was purified by column chromatography on silica gel eluting with 100% n-hexane to yield the product (28.4 mg, 0.15 mmol, 42%); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2961, 2952, 2870, 1456, 1432, 1384, 1363, 1189, 1173, 1106, 1066, 947, 760, 729, 674, 648; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 1.46 (6 H, dd, $J = 7.3$, CH$_3$), 2.54 (3 H, s, CH$_3$), 3.42 (1 H, spt, $J = 7.2$ Hz, CH(CH$_3$)$_2$), 7.25 (1 H, t, $J = 7.6$ Hz, Ar-H), 7.32 (1 H, t, $J = 8.1$ Hz, Ar-H), 7.76 (1 H, d, $J = 7.8$ Hz, Ar-H), 7.83 (1 H, d, $J = 8.1$ Hz, Ar-H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 14.5 (CH$_3$), 21.5 (CH(CH$_3$)$_2$), 27.7 (CH(CH$_3$)$_2$), 122.1 (Ar-C-H), 122.2 (Ar-C-H), 122.9 (Ar-C-H), 123.3 (Ar-C-H), 132.9 (Ar-C), 136.7 (Ar-C), 138.5 (Ar-C), 139.6 (Ar-C); m/z (GCMS) 190.1; (Found: M, 190.0808, C$_{12}$H$_{14}$S$_1$ requires M, 190.0811).
2-Methyl-3-cyclohexylbenzothiophene S18

As in general procedure B2, (3-cyclohexyl-3-(2-methylsulfanyl)phenyl)prop-1-yn-1-yl)trimethylsilane (60.4 g, 0.2 mmol) and p-TSA (38.0 g, 0.2 mmol) in EtOH (2 ml) were heated at 150 °C in a microwave. The crude product was purified by column chromatography on silica gel eluting with 100% n-hexane to yield the product (37.2 mg, 0.16 mmol, 81%); ν<sub>max</sub> (neat)/cm<sup>-1</sup> 2923, 2849, 1447, 1431, 1173, 1150, 1136, 889, 757, 728, 641; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 1.33 - 1.53 (4 H, m, 2 x CH<sub>2</sub>), 1.76 - 2.07 (6 H, m, 3 x CH<sub>2</sub>), 2.56 (3 H, s, CH<sub>3</sub>), 3.01 (1H, tt, J = 12.4, 3.6 Hz, CH(CH<sub>2</sub>)<sub>2</sub>), 7.25 (1H, td, J = 7.0 Hz x 2, 1.26 Hz x 2, Ar-H), 7.32 (1H, td, J = 7.8 Hz x 2, 1.26 Hz x 2, Ar-H), 7.76 (1 H, d, J = 6.6 Hz), 7.88 (1 H, d, J = 8.1 Hz); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 14.8 (CH<sub>3</sub>), 26.3 (2 x CH<sub>2</sub>), 27.3 (CH<sub>2</sub>), 31.3 (2 x CH<sub>2</sub>), 38.8 (CH), 122.1 (ArC-H), 122.3 (ArC-H), 122.8 (ArC-H), 123.3 (ArC-H), 133.2 (ArC), 136.0 (ArC), 138.4 (ArC), 139.9 (ArC); m/z 230.2; (Found: M, 230.1127, C<sub>14</sub>H<sub>18</sub>O<sub>1</sub>S<sub>1</sub> requires M, 230.1124).

General Procedure D – Conditions C

(E)-2-(Pent-1-en-1-yl)benzo[b]thiophene S19

Under an Ar atmosphere, a solution of iodine (55.6 mg, 0.22 mmol) in Ar flushed 1,2-dichloroethane (2 mL) was added to a solution of (2-(hept-2-yn-1-yl)phenyl)(methyl)sulfide (43.6 mg, 0.2 mmol) in Ar flushed 1,2-dichloroethane (18 mL) at room temperature. The reaction mixture was stirred for 18 h at 80 °C before quenching with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL). The aqueous layer was then extracted with EtOAc (3 x 5 mL) and the combined organic layers washed with brine (5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo. The crude product was purified by preparative thin-layer chromatography on silica
gel eluting with n-hexane to yield the product (37.5 mg, 0.18 mmol, 92 % yield) as a yellow solid (mp 38-40 °C); νmax (neat)/cm⁻¹ 2957, 2926, 2871, 1456, 1436, 1224, 1148, 1012, 950, 839, 839, 743, 725; δH (500 MHz, C₆D₆) 0.82 (3H, t, J = 7.3, CH₃), 1.29 (2H, sxt, J = 7.3, CH₂CH₃), 1.95 (2H, qd, J = 7.2, 1.4, CHCH₂), 6.14 (1H, dt, J = 15.7, 7.0, CCH=CH), 6.44 (1H, dt, J = 15.7, 1.2, CCH=CH), 6.81 (1H, s, Ar- H), 7.03 (1H, td, J = 7.6, 1.3, Ar-H), 7.12 (1H, td, J = 7.5, 1.2, Ar-H), 7.45 - 7.52 (2H, m, 2 × Ar-H); δC (125 MHz, C₆D₆) 14.1 (CH₃), 22.9 (C₆H₁₃), 35.6 (CHCH₂), 122.1 (Ar-CH), 122.8 (Ar-CH), 123.9 (Ar-CH), 124.9 (CCH=CH), 125.0 (2 × Ar-CH), 134.1 (CCH=CH), 139.5 (Ar-C), 141.2 (Ar-C), 143.9 (Ar-C); m/z (EI) M, 202; (Found: M, 202.0802. C₁₃H₁₄S requires M, 202.0811).

(欧盟)5-Methyl-2-(pent-1-en-1-yl)benzo[b]thiophene S20

As described in general procedure C, (2-(hept-2-yn-1-yl)-4-methylphenyl)(methyl)sulfide (46.4 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting with n-hexane, gave the product (34.7 mg, 0.16 mmol, 80 % yield) as a yellow solid (mp: 47-50 °C); νmax (neat)/cm⁻¹ 3012, 2954, 2924, 2867, 1443, 1378, 1301, 1259, 1230, 1209, 1169, 1138, 1065, 1044, 1008, 951, 889, 803, 744, 725, 694; δH (400 MHz, CDCl₃) 0.98 (3 H, t, J = 7.3 Hz, CH₃), 1.53 (2 H, sxt, J = 7.4 Hz, CH₂CH₃), 2.22 (2 H, qd, J = 7.2, 1.5 Hz, CHCH₂), 2.44 (3 H, s, CH₃), 6.15 (1 H, dt, J = 15.4, 7.0 Hz, CCH=CH), 6.60 (1 H, dd, J = 15.4, 0.5 Hz, CCH=CH), 6.98 (1 H, s, Ar- H), 7.10 (1 H, dd, J = 8.2, 1.1 Hz, Ar-H), 7.46 (1 H, s, Ar-H), 7.62 (1 H, d, J = 8.1 Hz, Ar-H); δC (100 MHz, CDCl₃) 13.4 (CH₃), 21.0 (CH₂CH₃), 22.0 (CH₃), 34.7 (CHCH₂), 120.6 (Ar-CH), 121.4 (Ar-CH), 122.8 (Ar-CH), 123.7 (CCH=CH), 125.6 (Ar-CH), 133.2 (Ar-C), 133.6 (CCH=CH), 135.2 (Ar-C), 140.2 (Ar-C), 143.1 (Ar-C); m/z (GCMS) M, 216.1; (Found: M, 217.1051. C₁₄H₁₇S requires M, 217.1050).

(欧盟)2-(3-Methylbut-1-en-1-yl)-5-(trifluoromethyl)benzo[b]thiophene S21
As described in general procedure C, (2-(hept-2-yn-1-yl)-4-trifluoromethylphenyl)(methyl)sulfide (57.2 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting with 1% EtOAc in n-hexane, gave the product (18.0 mg, 0.09 mmol, 47 % yield) as a yellow oil; \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 2959, 2929, 1607, 1528, 1433, 1332, 1262, 1217, 1169, 1144, 1120, 1073, 1054 953, 892, 812, 729, 709, 668, 650; \( \delta \)\(_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.99 (3 H, t, \( J = 7.4 \) Hz, \( \text{CH}_3 \)), 1.54 (2 H, sxt, \( J = 7.3 \) Hz, \( \text{CH}_2\text{CH}_3 \)), 2.18 - 2.29 (2 H, q, \( J = 6.9 \) Hz, \( \text{CHCH}_2 \)), 6.18 - 6.28 (1 H, m, \( \text{CHCH} = \text{CH} \)), 6.62 (1 H, d, \( J = 15.8 \) Hz, \( \text{CCCH} = \text{CH} \)), 7.10 (1 H, s, ArC\(-\text{H} \)), 7.48 (1 H, d, \( J = 8.5 \) Hz, ArC-\( \text{H} \)), 7.83 (1 H, d, \( J = 8.5 \) Hz, ArC-\( \text{H} \)), 7.91 (1 H, s, ArC-\( \text{H} \)); \( \delta \)\(_{\text{C}} \) (100 MHz, CDCl\(_3\)) 13.8 (\( \text{CH}_3 \)), 22.2 (\( \text{CH}_2\text{CH}_3 \)), 35.1 (\( \text{CHCH}_2 \)), 120.1 (q, \( J = 4.2 \) Hz, ArC-\( \text{H} \)), 120.4 (q, \( J = 3.7 \) Hz, ArC-\( \text{H} \)), 120.8 (ArC-\( \text{H} \)), 122.5 (ArC-\( \text{H} \)), 123.5 (CHC=CH), 124.5 (q, \( J = 272.9 \) Hz, CF\(_3 \)), 126.9 (q, \( J = 32.3 \) Hz, ArC-CF\(_3 \)), 135.3 (CHC=CH), 139.9 (Ar-C), 141.6 (Ar-C), 145.4 (Ar-C); m/z (GCMS) M, 270.0; (Found: M, 270.0685). C\(_{14}\)H\(_{13}\)F\(_3\)S requires M, 270.0685.

\( \text{E} \)-5-Fluoro-2-(3-methylbut-1-en-1-yl)benzo[b]thiophene S22

As described in general procedure C, (2-(hept-2-yn-1-yl)-4-fluorophenyl)(methyl)sulfide (47.2 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting with n-hexane, gave the product (30.4 mg, 0.13 mmol, 65 % yield) as a yellow solid (mp 55-58 °C); \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 2954, 2925, 1595, 1443, 1379, 1230, 1209, 1170, 1121, 1066, 1045, 951,889,836, 803, 725, 715; \( \delta \)\(_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.98 (3 H, t, \( J = 7.4 \) Hz, CH\(_3\)), 1.47 - 1.58 (2 H, m, CH\(_2\)CH\(_3\)), 2.18 - 2.26 (2 H, m, CHCH\(_2\)), 6.19 (1 H, dt, \( J = 15.5 \), 7.0 Hz, CHC=CH), 6.59 (1 H, d, \( J = 15.7 \) Hz, CHC=CH), 6.99 - 7.05 (2 H, m, ArC-\( \text{H} \)), 7.32 (1 H, dd, \( J = 9.5 \), 2.4 Hz, ArC-\( \text{H} \)), 7.65 (1 H, dd, \( J = 8.8 \), 4.9 Hz, ArC-\( \text{H} \)), 7.75 (1 H, d, \( J = 8.8 \) Hz, ArC-\( \text{H} \)), 7.85 (1 H, dd, \( J = 8.8 \), 4.9 Hz, ArC-\( \text{H} \)); \( \delta \)\(_{\text{C}} \) (100 MHz, CDCl\(_3\)) 13.7 (CH\(_3\)), 22.2 (CH\(_2\)CH\(_3\)), 35.0 (CHCH\(_2\)), 108.6 (d, \( J = 23.5 \) Hz, ArC-\( \text{H} \)), 112.7 (d, \( J = 29.3 \) Hz, ArC-\( \text{H} \)), 120.7 (d, \( J = 4.4 \) Hz, ArC-\( \text{H} \)), 123.1 (d, \( J = 9.5 \) Hz, ArC), 123.7 (CHC=CH), 133.7 (Ar-C), 134.6 (CHC=CH), 141.2 (d, \( J = 9.5 \) Hz, ArC), 145.7 (Ar-C), 160.8 (dd, \( J = 248.7 \), 1.0 Hz, ArC-F); m/z (GCMS) M, 220.1; (Found: M, 220.0719. C\(_{13}\)H\(_{13}\)F\(_{3}\)S\(_1\) requires M, 220.0717).
(E)-4-Fluoro-2-(3-methylbut-1-en-1-yl)benzo[b]thiophene S23

As described in general procedure C, (2-(hept-2-yn-1-yl)-5-fluorophenyl)(methyl)sulfide (47.2 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting with n-hexane, gave the product (40.3 mg, 0.18 mmol, 92 % yield) as a yellow solid (mp 64-65 °C); v_max (neat)/cm⁻¹ 2958, 2929, 2872, 1589, 1520, 1464, 1401, 1378, 1248, 1233, 1188, 1146, 1111, 1046, 957, 938, 851, 819, 807, 718, 586; δ_H (400 MHz, CDCl₃) 0.97 (3 H, t, J = 7.4 Hz, C₃H₃), 1.45 -1.58 (2 H, m, C₂H₂CH₃), 2.21 (2 H, qd, J = 7.2, 1.5 Hz, CHC₃H₂), 6.13 (1 H, dt, J = 15.6, 7.0 Hz, CCH=CH), 6.58 (1 H, d, J = 15.6 Hz, CCH=CH), 7.00 (1 H, s, ArC-H), 7.04 (1 H, td, J = 8.9, 2.4 Hz, ArC-H), 7.43 (1 H, dd, J = 8.8, 2.3 Hz, ArC-H), 7.58 (1 H, dd, J = 8.7, 5.2 Hz, ArC-H); δ_C (100 MHz, CDCl₃); 13.7 (C₃H₃), 22.3 (CH₂CH₃), 35.0 (CHCH₂), 108.3 (d, J = 24.9 Hz, ArC-H), 113.1 (d, J = 23.5 Hz, ArC-H), 120.3 (ArC-H), 123.6 (CH=CHCH₂), 123.9 (d, J = 8.8 Hz, ArC-H), 133.9 (d, J = 1.5 Hz, CH=CHCH₂), 136.7 (d, J = 1.5 Hz, ArC), 139.4 (d, J = 10.3 Hz, ArC), 143.0 (d, J = 3.7 Hz, ArC), 160.5 (d, J = 243.6 Hz, ArC-F); m/z (GCMS) M, 220.1; (Found: M, 220.0721. C₁₃H₁₃F₁S₁ requires M, 220.0717).

(E)-2-(3-Methylbut-1-en-1-yl)naphtho[2,1-b]thiophene S24

As described in general procedure C, (1-(hept-2-yn-1-yl)naphthalen-2-yl)(methyl)sulfide (53.6 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting with n-hexane, gave the product (40.3 mg, 0.16 mmol 80 % yield) as a white solid (mp 83-85 °C); v_max (neat)/cm⁻¹ 2950, 2962, 2869, 2833, 1555, 1502, 1465, 1406, 1340, 1253, 1200, 1159, 1092, 1062, 1025, 955, 868, 843, 770, 712; δ_H (400 MHz, CDCl₃) 1.01 (3 H, t, J = 7.4 Hz, CH₃), 1.57 (2 H, m, CH₂CH₃), 2.26 (2 H, m, CHCH₂), 6.25 (1 H, dt, J = 15.5, 7.0 Hz, CCH=CH), 6.72 (1 H, d, J = 15.5 Hz, CCH=CH),
7.52 (1 H, m, J = 6.8 Hz, ArC-H), 7.59 (1 H, t, J = 7.0 Hz, ArC-H), 7.73 (3 H, m, 3 x ArC-H), 7.92 (1 H, d, J = 7.9 Hz, ArC-H), 8.25 (1 H, d, J = 8.2 Hz, ArC-H); δC (100 MHz, CDCl₃) 13.8 (CH₃), 22.3 (CH₂CH₃), 35.0 (CHCH₂), 119.2 (ArC-H), 120.5 (ArC-H), 123.5 (ArC-H), 123.9 (CCH=CH), 124.8 (ArC-H), 125.1 (ArC-H), 126.3 (ArC-H), 128.5 (ArC-H), 128.9 (ArC), 131.0 (ArC), 133.0 (CCH=CH), 135.8 (ArC), 136.2 (ArC), 143.1 (ArC); m/z (GCMS) M, 252.1; (Found: M, 253.1056. C₁₇H₁₆S requires M, 253.1050).

(E)-5-Methoxy-2-(pent-1-en-1-yl)benzo[b]thiophene S25

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\text{MeO} \text{MeO} \quad \text{Pr}
\]

As described in general procedure C, (2-(hept-2-yn-1-yl)-4-methoxyphenyl)(methyl)sulfide (49.6 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting with 5% EtOAc in n-hexane, gave the product (35.2 mg, 0.15 mmol, 76 % yield) as a yellow solid (mp 79-81 °C); νmax (neat)/cm⁻¹ 2957, 2921, 2872, 2850, 1571, 1599, 1519, 1456, 1331, 1258, 1216, 1203, 1171, 1151, 1098, 1069, 1024, 1001, 951, 854, 806, 764, 751, 719, 680; δH (400 MHz, C₆D₆) 0.83 (3H, t, J = 7.4, CH₃), 1.30 (2H, sxt, J = 7.3, CH₂CH₃), 1.97 (2H, qd, J = 7.2, 1.3, CHCH₂), 6.17 (1H, dt, J = 15.6, 7.0, CCH=CH), 6.48 (1H, dt, J = 15.5, 1.2, CCH=CH), 6.81 (1H, s, Ar-H), 6.87 (1H, dd, J = 8.6, 2.5, Ar-H), 7.01 (1H, d, J = 2.5, Ar-H), 7.34 (1H, d, J = 8.8, Ar-H); δC (100 MHz, C₆D₆) 14.4 (CH₃), 22.9 (CH₂CH₃), 35.6 (CHCH₂), 55.4 (OCH₃), 106.4 (Ar-CH), 115.0 (Ar-CH), 122.0 (Ar-CH), 123.5 (Ar-CH), 125.1 (CCH=CH), 131.7 (Ar-C), 133.9 (CCH=CH), 142.3 (Ar-C), 145.2 (Ar-C), 158.6 (Ar-C); m/z (El) M, 232; (Found: M, 232.0915. C₁₄H₁₆OS requires M, 232.0916).

(E)-5-Chloro-2-(pent-1-en-1-yl)benzo[b]thiophene S26

\[
\text{Cl} \text{MeO} \quad \text{Pr}
\]

As described in general procedure C, (2-(hept-2-yn-1-yl)-4-chlorophenyl)(methyl)sulfide (49.7 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (2 mL), after purification by column chromatography on silica gel eluting with n-hexane, gave the product...
(19.0 mg, 0.08 mmol, 40 % yield) as a yellow solid (mp: 85 - 87 °C); \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \) 2960, 2928, 1582, 1438, 1416, 1275, 1262, 1145, 1077, 954, 906, 874, 799, 764, 749, 705; \( \delta \) \((400 MHz, C_6D_6) 0.81 (3H, t, J = 7.3, CH_3), 1.27 (2H, sxt, J = 7.3, CH_2CH_3), 1.93 (2H, qd, J = 7.2, 1.4, CHCH_2), 6.09 (1H, dt, J = 15.4, 7.1, CCH=CH), 6.34 (1H, dt, J = 15.6, 1.1, CCH=CH), 6.53 (1H, s, Ar-H), 6.98 (1H, dd, J = 8.6, 2.0, Ar-H), 7.10 (1H, d, J = 8.6, Ar-H), 7.42 (1H, d, J = 2.0, Ar-H); \( \delta \) \((100 MHz, C_6D_6) 14.1 (CH_3), 22.8 (CH_2CH_3), 35.5 (CHCH_2), 121.3 (Ar-CH), 123.4 (Ar-CH), 123.8 (Ar-CH), 124.6 (CCH=CH), 125.3 (Ar-CH), 131.3 (Ar-C), 134.9 (CCH=CH), 137.4 (Ar-C), 142.3 (Ar-C), 145.9 (Ar-CX); m/z (El) [M-Cl], 202; (Found: M, 202.0802. C_{13}H_{14}S requires M, 202.0811).

\( (E) - 4,6 \)-Dimethyl-2-(3-methylbut-1-en-1-yl)benzo[b]thiophene S27

\[ \text{As described in general procedure C, } (2-\text{hept-2-yn-1-yl})-3,5\text{-dimethylphenyl}(\text{methyl})\text{sulfide} \]

(49.2 mg, 0.2 mmol), iodine (55.6 mg, 0.22 mmol) in 1,2-dichloroethane (20 mL), after purification by column chromatography on silica gel eluting in n-hexane, gave the product (42.4 mg, 0.18 mmol, 92 % yield) as a yellow oil; \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \) 2957, 2924, 2869, 1671, 1600, 1567, 1504, 1454, 1376, 1301, 1221, 1204, 1160, 1113, 1032, 950, 843, 757, 657; \( \delta \) \((400 MHz, CDCl_3) 1.00 (3H, t, J = 7.4 Hz, CH_3), 1.54 (2H, sxt, J = 7.4 Hz, CH_2CH_3), 2.23 (2H, q, J = 6.9 Hz, CHCH_2), 2.43 (3H, s, CH_3), 2.52 - 2.55 (3H, s, CH_3), 6.14 (1H, dt, J = 15.4, 7.0 Hz, CCH=CH), 6.63 (1H, d, J = 15.5 Hz, CCH=CH), 6.94 (1H, s, ArC-H), 7.08 (1H, s, ArC-H), 7.40 (1H, s, ArC-H); \( \delta \) \((100 MHz, CDCl_3) 13.8 (CH_3), 19.4 (CH_2CH_3), 21.5 (CH_3), 22.3 (CH_3), 35.0 (CHCH_2), 119.3 (ArC-H), 119.5 (ArC-H), 124.1 (ArCH), 126.6 (CCH=CH), 132.0 (ArC), 132.9 (CCH=CH), 134.3 (ArC), 137.4 (ArC), 138.7 (ArC), 141.5 (ArC); m/z (GCMS) M, 230.1; (Found: M, 230.1119. C_{15}H_{18}S requires M, 230.1124).
General procedure E: Oxidation to bis-sulfoxide

1,5-bis(Hexylsulfinyl)naphthalene 8

To a solution of 1,5-bis(hexylthio)naphthalene (3.0 g, 8.32 mmol) in CH$_2$Cl$_2$ (42.0 mL) a solution of m-CPBA (2.05 g, 9.15 mmol) in CH$_2$Cl$_2$ (183 mL) was added at -78 °C over 30 min. The reaction was warmed to room temperature over 1 h before adding a second portion of m-CPBA (2.05 g, 9.15 mmol) in CH$_2$Cl$_2$ (183 mL) over 30 min at -78 °C. After allowing the reaction mixture to reach room temperature over 1 h it was stirred for a further 1 h before quenching with aqueous NaHCO$_3$ (100 mL) and extraction with CH$_2$Cl$_2$ (2 × 75 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (30% Et$_2$O in CHCl$_3$) to yield the product (2.98 g, 7.57 mmol, 91% yield) as a white solid (mp: 103 - 107 °C; $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2949, 2921, 2856, 1498, 1466, 1403, 1390, 1338, 1275, 1261, 1193, 1155, 1113, 1074, 1036, 970, 791, 764, 750, 724; $\delta_H$ (500 MHz, CDCl$_3$) 0.79 - 0.91 (6H, m, 2 × CH$_3$), 1.19 - 1.31 (8H, m, 4 × CH$_2$), 1.32 - 1.53 (4H, m, 2 × CH$_2$), 1.59 - 1.74 (2H, m, 2 × SCH$_2$CH$_2$CH$_3$), 1.79 - 1.95 (2H, m, 2 × SCH$_2$CH$_2$CH$_3$), 2.75 - 2.88 (2H, m, 2 × SCH$_2$CH$_2$CH$_3$), 2.94 - 3.07 (2H, m, 2 × SCH$_2$CH$_2$CH$_3$), 7.71 - 7.82 (2H, m, 2 × Ar-H), 8.03 - 8.13 (2H, m, 2 × Ar-H), 8.16 - 8.27 (2H, m, 2 × Ar-H); $\delta_C$ (125 MHz, CDCl$_3$) 14.1 (2 × CH$_3$), 22.5 (2 × SCH$_2$CH$_2$, 2 × CH$_2$), 28.4 (2 × SCH$_2$CH$_2$CH$_2$), 31.5 (2 × CH$_2$), 56.4 (2 × SCH$_2$), 123.9 (2 × Ar-CH), 124.5 (2 × Ar-CH), 127.1 (2 × Ar-CH), 129.1 (2 × Ar-C), 141.8 (2 × Ar-C); m/z (ES+) M + H, 393; (Found: M + Na, 415.1741. C$_{22}$H$_{32}$O$_2$S$_2$Na requires M, 415.1736).

2,6-bis(Hexylsulfinyl)naphthalene 7

S19
As described in general procedure E, 2,6-bis(hexylthio)naphthalene (6.70 g, 18.6 mmol), m-CPBA (9.25 g, 41.3 mmol) and CH₂Cl₂ (832 mL) after purification by column chromatography on silica gel (30% Et₂O in CHCl₃) gave the product (6.49 g, 16.5 mmol, 89% yield) as a white solid (mp: 155 - 157 °C); ν_max (neat)/cm⁻¹ 2955, 2925, 2857, 1458, 1379, 1076, 1061, 1030, 970, 909, 824, 749, 728, 706, 646, 638; δ_H major diastereoisomer (400 MHz, CDCl₃) 0.87 (6H, t, J = 7.1, 2 × C₆H₃), 1.21 - 1.34 (8H, m, 4 × C₆H₂), 1.36 - 1.53 (4H, m, 2 × C₆H₂), 1.58 - 1.71 (2H, m, 2 × SCH₂CH₃), 1.77 - 1.91 (2H, m, 2 × SCH₂CH₃), 2.80 - 2.97 (4H, m, 2 × SCH₂), 7.66 (2H, dd, J = 8.4, 1.4, 2 × Ar-H), 8.07 (2H, d, J = 8.6, 2 × Ar-H), 8.27 (2H, d, J = 1.5, 2 × Ar-H); δ_C (100 MHz, CDCl₃) 14.2 (2 × C₆H₃), 22.2 (2 × SCH₂CH₃), 22.6 (2 × C₆H₂), 28.6 (2 × SCH₂CH₂), 31.5 (2 × C₆H₂), 57.2 (2 × SCH₂), 121.6 (2 × Ar-CH), 124.8 (2 × Ar-CH), 130.0 (2 × Ar-CH), 134.1 (2 × Ar-C), 143.6 (2 × Ar-C); m/z (ES⁺) M + Na, 415; (Found: M + H, 393.1931. C₂₂H₃₃O₂S₂ requires M, 393.1916).

General Procedure F- 2D Propargylation

(2,6-Di(non-2-yn-1-yl)naphthalene-1,5-diylibis(hexylsulfide) 10b

A solution containing 1,5-bis(hexylsulfinyl)naphthalene (1.50 g, 3.82 mmol) and trimethyl(non-2-yn-1-yl)silane (2.25 g, 11.5 mol) in MeCN (180 mL) was added to an oven dried tube flushed with N₂. Triflic anhydride (1.93 mL, 11.5 mmol) and 2,6-lutidine (1.55 mL, 13.4 mmol) were added sequentially at room temperature and the reaction mixture was then heated for 24 h at 80 °C. After cooling to room temperature, the solution was quenched with aqueous saturated NaHCO₃ (100 mL) and the aqueous layer was extracted with EtOAc (3 × 75 mL). The combined organic layer was washed successively with aqueous HCl 1.0 M (2 × 20 mL) and brine (100 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel eluting with 2% EtOAc in n-hexane to yield the product (1.76 g, 2.90 mmol, 76% yield) as a brown solid (mp: 39 - 41 °C); ν_max (neat)/cm⁻¹ 2955, 2923, 2868, 2850, 1589, 1486, 1464, 1457, 1440, 1412, 1368,
1302, 1278, 1259, 1217, 1206, 1182, 956, 890, 813, 795, 764, 755, 726; δH (500 MHz, CDCl3) 0.84 - 0.92 (12H, m, 4 × CH3), 1.18 - 1.45 (24H, m, 12 × CH2), 1.54 (8H, m, 4 × CH2), 2.23 (4H, tt, J = 7.1, 2.5, 2 × CCH2H), 2.75 (4H, t, J = 7.6, 2 × SCH2), 4.14 (4H, t, J = 2.4, 2 × CCH2C), 7.85 (2H, d, J = 8.8, Ar-H), 8.74 (2H, d, J = 8.8, Ar-H); δC (125 MHz, CDCl3) 14.0 (4 × CH3), 18.9 (2 × CCH2), 22.5 (2 × CH2), 25.2 (2 × CCH2C), 28.6 (4 × CH2), 29.0 (2 × CH2), 29.8 (2 × CH2), 31.4 (4 × CH2), 36.9 (2 × SCH2), 78.1 (2 × C≡C), 82.7 (2 × C≡C), 127.7 (2 × Ar-CH), 128.0 (2 × Ar-CH), 131.0 (2 × Ar-C), 135.1 (2 × Ar-C), 140.7 (2 × Ar-C); m/z (ES+) M + H, 605; (Found: M, 604.4108. C40H60S2 requires M, 604.4131).

(1,5-Di(non-2-yn-1-yl)naphthalene-2,6-diyl)bis(hexylsulfide) 9

As described in general procedure F, 2,6-bis(hexylsulfinyl)naphthalene (29.4 mg, 0.075 mmol), trimethyl(non-2-yn-1-yl)silane (44.5 mg, 0.225 mol), triflic anhydride (38.0 µL, 0.225 mmol), 2,6-lutidine (31.0 µL, 0.263 mmol) and MeCN (7.50 mL), after purification by preparative thin-layer chromatography eluting with 2% EtOAc in n-hexane gave the product (34.8 mg, 0.17 mmol, 77% yield) as a yellow solid (mp: 56 - 57 °C); νmax (neat)/cm⁻¹ 2955, 2920, 2870, 2854, 1567, 1468, 1459, 1433, 1377, 1275, 1267, 1260, 1112, 941, 922, 798, 789, 764, 750, 722; δH (500 MHz, CDCl3) 0.82 - 0.92 (12H, m, 4 × CH3), 1.18 - 1.35 (20H, m, 10 × CH2), 1.37 - 1.48 (8H, m, 2 × SCH2CH2CH2, 2 × CCH2CH2), 1.64 (4H, quin, J = 7.5, 2 × SCH2CH2), 2.09 (4H, tt, J = 7.1, 2.2, 2 × CCH2H), 3.00 (4H, t, J = 7.3, 2 × SCH2), 4.22 (4H, t, J = 2.2, 2 × CCH2C), 7.62 (2H, d, J = 8.8, Ar-H), 8.06 (2H, d, J = 8.8, Ar-H); δC (125 MHz, CDCl3) 14.0 (4 × CH3), 18.9 (2 × CCH2), 20.5 (2 × CCH2C), 22.5 (2 × CH2), 22.6 (2 × CH2), 28.5 (4 × CH2), 28.9 (2 × CH2), 29.6 (2 × SCH2CH2), 31.3 (2 × CH2), 31.4 (2 × CH2), 35.2 (2 × SCH2), 77.9 (2 × C≡C), 81.6 (2 × C≡C), 124.2 (2 × Ar-CH), 129.5 (2 × Ar-CH), 131.5 (2 × Ar-C), 132.6 (2 × Ar-
2,7-Diheptylnaphtho[1,2-b:5,6-b']dithiophene 12

A solution containing 1,5-bis(hexylsulfinyl)naphthalene (29.4 mg, 0.075 mmol) and trimethyl(non-2-yn-1-yl)silane (44.2 mg, 0.225 mol) in MeCN (7.5 mL) was added. An oven-dried tube flushed with N₂. Triflic anhydride (38.0 µL, 0.225 mmol) was added at room temperature and the reaction mixture was then heated for 24 h at 80 °C. After cooling to room temperature, NaI (33.8 mg, 0.225 mmol) was added and the reaction mixture was heated for a further 2 h at 80 °C, before quenching with aqueous saturated NaHCO₃ (5 mL) and extracting the aqueous layer with EtOAc (3 × 5 mL). The combined organic layer was washed with brine (10 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude product was purified by thin-layer chromatography on silica gel eluting with 2% EtOAc in n-hexane to yield the product (18.3 mg, 0.12 mmol, 56% yield) as a white solid (mp 88 - 90 °C, toluene); ν max (neat)/cm⁻¹ 2950, 2921, 2849, 1541, 1466, 1460, 1363, 1306, 836, 818, 788, 688; δH (400 MHz, C₆D₆) 0.90 (6H, t, J = 7.0, 2 × CH₃), 1.17 - 1.34 (16H, m, 8 × CH₂), 1.67 (4H, quin, J = 7.3, 2 × CH₂), 2.75 (4H, t, J = 7.4, 2 × CH₂), 6.91 (2H, s, 2 × Ar-H), 7.60 (2H, d, J = 8.5, 2 × Ar-H), 8.05 (2H, d, J = 8.5, 2 × Ar-H); δC (100 MHz, C₆D₆) 14.7 (2 × CH₃), 23.4 (2 × CH₂), 29.8 (4 × CH₂), 31.4 (2 × CCH₂), 32.1 (2 × CCH₂CH₂), 32.5 (2 × CH₂), 121.6 (2 × Ar-CH), 122.8 (2 × Ar-CH), 122.8 (2 × Ar-CH), 126.6 (2 × Ar-C), 138.3 (2 × Ar-C), 138.4 (2 × Ar-C), 145.9 (2 × Ar-C); m/z (ES⁺) M + H, 437; (Found: M, 436.2259. C₂₈H₃₆S₂ requires M, 436.2253).
2,7-Diheptylnaphtho[2,1-b:6,5-b']dithiophene 11

As described in general procedure G, 2,6-bis(hexylsulfinyl)naphthalene (29.4 mg, 0.075 mmol), trimethyl(non-2-yn-1-yl)silane (44.2 mg, 0.225 mol), triflic anhydride (38.0 µL, 0.225 mmol), NaI (33.8 mg, 0.225 mmol) and MeCN (7.5 mL), after purification thin-layer chromatography on silica gel eluting with 2% EtOAc in n-hexane gave the product (14.1 mg, 96.7 µmol, 43% yield) as a white solid (mp 145 - 148 °C, toluene); ν<sub>max</sub> (neat)/cm<sup>-1</sup> 2950, 2923, 2843, 1520, 1464, 1429, 1361, 1317, 1243, 1207, 1181, 1158, 1121, 858, 834, 743, 726; δ<sub>H</sub> (400 MHz, C<sub>6</sub>D<sub>6</sub>) 0.90 (6H, t, J = 7.0, 2 × CH₃), 1.17 - 1.36 (16H, m, 8 × CH₂), 1.70 (4H, quin, J = 7.8, 2 × CH₂), 2.81 (4H, t, J = 7.5, 2 × CH₂), 7.52 (2H, s, 2 × Ar-H), 7.73 (2H, d, J = 8.5, 2 × Ar-H), 8.00 (2H, d, J = 8.8, 2 × Ar-H); δ<sub>C</sub> (100 MHz, C<sub>6</sub>D<sub>6</sub>) 14.7 (2 × CH₃), 23.4 (2 × CH₂), 29.8 (2 × CH₂), 29.9 (2 × CH₂), 31.6 (2 × CCH₂), 32.2 (2 × CCH₂CH₂), 32.5 (2 × CH₂), 120.1 (2 × Ar-CH), 120.8 (2 × Ar-CH), 121.3 (2 × Ar-CH), 127.2 (2 × Ar-C), 136.7 (2 × Ar-C), 137.9 (2 × Ar-C), 147.3 (2 × Ar-C); m/z (ES+) M + H, 437; (Found: M, 436.2249. C<sub>28</sub>H<sub>36</sub>S<sub>2</sub> requires M, 436.2253).

General Procedure H - Cyclisation to Ketone

1,1'-(Naphtho[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(heptan-1-one) 14
To a solution of (2,6-di(non-2-yn-1-yl)naphthalene-1,5-diyl)bis(hexylsulfide) (30.2 mg, 0.050 mmol) in O$_2$ flushed toluene (2.5 mL) was added a solution of iodine (17.8 mg, 0.070 mmol) in toluene (2.5 mL) at room temperature. The reaction mixture stirred for 18 h at 80 °C under an O$_2$ atmosphere before diluting with Et$_2$O (4 mL) and quenching with saturated aqueous Na$_2$S$_2$O$_3$ (4 mL). The aqueous layer was then extracted with Et$_2$O (2 × 2 mL) and the combined organic layers washed with brine (5 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude product was purified by preparative thin-layer chromatography on silica gel eluting with CH$_2$Cl$_2$ to yield the product (13.1 mg, 28.0 µmol, 56% yield) as a yellow solid (mp 166 - 169 °C, toluene); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2930, 2850, 1658, 1531, 1467, 1505, 1372, 1240, 1219, 1206, 1163, 1134, 1116, 919, 889, 849, 799, 789, 710, 652; $\delta$H (400 MHz, C$_6$D$_6$) 0.91 (6H, t, $J = 6.5$, 2 × CH$_3$), 1.21 - 1.36 (12H, m, 6 × CH$_2$), 1.76 (4H, quin, $J = 7.2$, 2 × CCH$_2$CH$_2$), 2.64 (4H, t, $J = 7.3$, 2 × CCH$_2$), 7.42 - 7.47 (4H, m, 4 × Ar-H), 7.87 (2H, d, $J = 8.5$, 2 × Ar-H); $\delta$C (100 MHz, C$_6$D$_6$) 14.7 (2 × CH$_3$), 23.3 (2 × CH$_2$), 25.0 (2 × CCH$_2$CH$_2$), 29.7 (2 × CH$_2$), 32.4 (2 × CH$_2$), 39.6 (2 × CCH$_2$), 122.7 (2 × Ar-CH), 124.7 (2 × Ar-CH), 127.8 (2 × Ar-C), 129.8 (2 × Ar-CH), 138.5 (2 × Ar-C), 142.8 (2 × Ar-C), 144.8 (2 × Ar-C), 193.7 (2 × C=O); m/z (ES+) M + H, 465; (Found: M, 464.1825. C$_{28}$H$_{32}$O$_2$S$_2$ requires M, 464.1838).

1,1'-[(Naphtho[2,1-b:6,5-b']dithiophene-2,7-diyl)bis(heptan-1-one) 13

As described in general procedure H, (1,5-di(non-2-yn-1-yl)naphthalene-2,6-diyl)bis(hexylsulfide) (30.2 mg, 0.050 mmol), iodine (17.8 mg, 0.070 mmol) and toluene (5.0 mL) after purification by thin-layer chromatography on silica gel eluting with CH$_2$Cl$_2$ gave the product (15.1 mg, 32.5 µmol, 65% yield) as a yellow solid (mp 144 - 147 °C, toluene); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2957, 2934, 2912, 2892, 2852, 1664, 1559, 1480, 1468, 1453, 1406, 1373, 1340, 1296, 1233, 1190, 1182, 1167, 1143, 1112, 962, 932, 876, 843, 822, 804, 793, 761, 744, 728;
δ\textsubscript{H} (400 MHz, CD\textsubscript{6}D\textsubscript{6}) 0.92 (6H, t, J = 6.5, 2 × CH\textsubscript{3}), 1.23 - 1.41 (12H, m, 6 × CH\textsubscript{2}), 1.81 (4H, quin, J = 7.2, 2 × CCH\textsubscript{2}CH\textsubscript{2}), 2.74 (4H, t, J = 7.3, 2 × CCH\textsubscript{2}), 7.51 (2H, d, J = 8.8, 2 × Ar-H), 7.81 (2H, d, J = 8.8, 2 × Ar-H), 8.17 (2H, s, 2 × Ar-H); δ\textsubscript{C} (100 MHz, CD\textsubscript{6}D\textsubscript{6}) 14.7 (2 × CH\textsubscript{3}), 23.3 (2 × CH\textsubscript{2}), 25.0 (2 × CCH\textsubscript{2}CH\textsubscript{2}), 29.7 (2 × CH\textsubscript{2}), 32.4 (2 × CH\textsubscript{2}), 39.7 (2 × CCH\textsubscript{2}), 122.4 (2 × Ar-C), 123.9 (2 × Ar-CH), 126.4 (2 × Ar-CH), 127.7 (2 × Ar-C), 137.1 (2 × Ar-C), 141.4 (2 × Ar-C), 145.3 (2 × Ar-C), 193.7 (C=O); m/z (ES+) M + H, 465; (Found: M + H, 465.1914. C\textsubscript{28}H\textsubscript{33}O\textsubscript{2}S\textsubscript{2} requires M, 465.1916).

**General Procedure I- Cyclisation to Alkene**

2,7-Di((E)-hept-1-en-1-yl)naphtho[1,2-b:5,6-b']dithiophene 16

![Diagram of 2,7-Di((E)-hept-1-en-1-yl)naphtho[1,2-b:5,6-b']dithiophene 16](image)

To a solution of (2,6-di(non-2-yn-1-yl)naphthalene-1,5-diyl)bis(hexylsulfide) (30.2 mg, 0.05 mmol) in Ar flushed 1,2-dichloroethane (8 mL) was added a solution of iodine (27.8 mg, 0.11 mmol) in 1,2-dichloroethane (2 mL) at room temperature with methanol (0.81 ml, 5 mmol) and stirred for 1 h at 80 °C before quenching with saturated aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (10 mL). The aqueous layer was then extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 × 10 mL), dried (MgSO\textsubscript{4}) and concentrated in vacuo. The crude product was purified by column chromatography on neutralised silica gel eluting with Hexane to yield the product (18.1 mg, 84% yield) as a white solid (mp 145-147 °C); ν\textsubscript{max} (neat)/cm\textsuperscript{-1} 2960, 2930, 2483, 1332, 1263, 1169, 1145, 1121, 1074, 1055, 953, 907, 893, 812, 729, 709, 669, 651; δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 0.90 - 0.99 (m, 2 × CH\textsubscript{3}), 1.29 - 1.45 (m, 2 × CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}) 1.47 - 1.61 (m, 2 × CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}) 2.27 (q, J = 6.89 Hz, 2 × CH=CHCH\textsubscript{3}) 6.26 (dt, J = 15.47, 7.00 Hz, 2 × CH=CH) 6.65 (d, J = 15.65 Hz, 2 × CH=CH) 7.18 (s, 2 × Ar-H) 7.75 (d, J = 8.56 Hz, 2 × Ar-H) 7.90 (d, J = 8.68 Hz, 2 × Ar-H); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 14.1 (2 × CH\textsubscript{3}), 22.6 (2 × CH\textsubscript{2}CH\textsubscript{3}), 28.9 (2 × CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 31.5 (2 × CHCH\textsubscript{2}CH\textsubscript{3}), 33.0 (2 × CH=CHCH\textsubscript{3}), 121.1 (2 × Ar-CH), 122.2 (2 × Ar-CH), 122.3 (2 × Ar-CH), 123.6 (2 × Ar-CH=CH),
125.8 (2 × Ar-C), 133.7 (2 × CCH=CH₂), 136.8 (2 × Ar-C), 137.6 (2 × Ar-C), 142.4 (2 × Ar-C);
m/z (AP+) M + H, 433.5; (Found: M + H, 433.2023. C₂₈H₃₂O₂S₂ requires M, 432.1945).

2,7-Di((E)-hept-1-en-1-yl)naphtho[2,1-b:6,5-b']dithiophene 15

As described in general procedure I, 2,7-di((E) hept-1-en-1-yl)naphtho[2,1-b:6,5-b']dithiophene (40.9 mg, 0.088 mmol), I₂ (55.7 mg, 0.022 mmol), 1,2-dichloroethane (20.0 mL) and methanol (0.40 mL, 8.8 mmol were heated for 1 h at 80 °C. Purification by column chromatography on neutralised silica gel (1 % Et₂O in hexanes) gave the product (24.6 mg, 65% yield) as a white solid (decomp. T > 235 °C); νmax (neat)/cm⁻¹ 2952, 2922, 2849, 1465, 1455, 1362, 1190, 1171, 955, 876, 837, 806, 796, 725, 677; δH (400 MHz,CDCl₃) 0.91 - 0.96 (m, 2 × CH₃), 1.37 (dq, J = 7.27, 3.57 Hz, 2 × CH₂CH₂CH₃), 1.49 - 1.57 (m, 2 × CH₂CH₂CH₃), 2.27 (q, J = 6.93 Hz, 2 × CH=CHCH₂), 6.26 (dt, J = 15.44, 7.02 Hz, 2 × CH=CH), 6.72 (d, J = 15.53 Hz, 2 × CH=CH), 7.72 (s, 2 × Ar-H), 7.87 (d, J = 8.80 Hz, 2 × Ar-H), 8.12 (d, J = 8.68 Hz, 2 × Ar-H); δc (100 MHz,CDCl₃) 14.4 (2 × CH₃), 22.9 (2 × CH₂CH₃), 29.1 (2 × CH₂CH₂CH₃), 31.8 (2 × CHCH₂CH₂), 33.3 (2 × CH=CHCH₂), 119.7 (2 × Ar-CH), 120.8 (2 × Ar-CH), 121.0 (2 × Ar-CH), 124.1 (2 × CCH=CH₂), 126.6 (2 × Ar-C), 134.1 (2 × CCH=CH₂), 135.5 (2 × Ar-C), 137.3 (2 × Ar-C), 143.8 (2 × Ar-C); m/z (AP+) M + H, 432.9; (Found: M + H, 433.2009. C₂₈H₃₂O₂S₂ requires M, 432.1945).
Methyl(4-(methylsulfinyl)phenyl)sulfide  

To a solution of 1,4-bis(methylthio)benzene (0.850 g, 5.0 mmol) in CH₂Cl₂ (60 mL) was added NaHCO₃ (0.460 g, 5.5 mmol) followed by a solution of m-CPBA (1.18 g, 5.25 mmol) in 15 mL CH₂Cl₂ at -78 °C. The reaction mixture was then allowed to warm to room temperature for 1 h before quenching with aqueous saturated NaHCO₃ (70 mL). The aqueous layer was then extracted with CH₂Cl₂ (3 x 70 mL) and the combined organic layers were washed with brine (70 mL), dried (MgSO₄) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (20% EtOAc in CH₂Cl₂) to yield the product (0.797 g, 4.3 mmol, 86%) as a white solid; δ (400 MHz, CDCl₃) 2.51 (3H, s, S(CH₃)), 2.70 (3H, s, S(O)CH₃), 7.35 (2H, d, J = 8.4, Ar-H), 7.55 (2H, d, J = 8.4, Ar-H); δ (100 MHz, CDCl₃) 124.1 (2 x ArCH), 126.5 (2 x ArCH), 141.8 (ArC), 143.3 (ArC).

(2-(Hept-2-yn-1-yl)-1,4-phenylene)bis(methylsulfide) S28

An oven-dried microwave tube was flushed with N₂ before adding a solution containing methyl(4-(methylsulfinyl)phenyl)sulfide (93.0 mg, 0.50 mmol) and hept-2-ynyltrimethylsilane (126.0 mg, 0.75 mol) in MeCN (2.5 mL). Triflic anhydride (100 µL, 0.60 mmol) and 2,6-lutidine (145 µL, 0.625 mmol) were added sequentially at room temperature and the reaction mixture was then heated in a microwave reactor for 15 min at 130 °C. After cooling to room temperature, the solution was quenched with aqueous saturated NaHCO₃ (10 mL) and the aqueous layers were extracted with EtOAc (3 x 10 mL). The combined organic layer was washed successively with aqueous HCl 1.0 M (10 mL) and brine (10 mL), dried (MgSO₄) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (20% EtOAc in CH₂Cl₂) to yield the product (0.797 g, 4.3 mmol, 86%) as a white solid; δ (400 MHz, CDCl₃) 2.51 (3H, s, S(CH₃)), 2.70 (3H, s, S(O)CH₃), 7.35 (2H, d, J = 8.4, Ar-H), 7.55 (2H, d, J = 8.4, Ar-H); δ (100 MHz, CDCl₃) 124.1 (2 x ArCH), 126.5 (2 x ArCH), 141.8 (ArC), 143.3 (ArC).

chromatography on silica gel (5% CH₂Cl₂ in hexane) to yield the product (0.103 g, 0.39 mmol, 78% yield) as a yellow oil; ν_max (neat)/cm⁻¹ 2955, 1921, 1434, 1113, 804; δ_H (400 MHz, CDCl₃) 0.93 (3H, t, J = 7.6, CH₃), 1.57 - 1.40 (4H, m, 2 × CH₂), 2.26 (2H, tt, J = 6.8, 2.4, CCH₂), 2.44 (3H, s, S-CH₃), 2.49 (3H, s, S-CH₃), 3.61 (2H, t, J = 2.4, Ph-CH₂), 7.17 - 7.12 (2H, m, ArH), 7.50 (1H, d, J = 0.8, ArH); δ_C (100 MHz, CDCl₃) 13.8 (CH₃), 16.4 (SCH₃), 16.6 (SCH₃), 18.7 (CCH₂), 22.2 (CH₂), 23.5 (PhCH₂), 31.2 (CH₂), 76.6 (C₃C), 84.0 (C₃C), 125.9 (ArCH), 127.0 (ArCH), 127.2 (ArCH), 133.6 (ArC), 135.6 (ArC), 136.9 (ArC); m/z (GCMS) 264.1; (Found: M, 265.1080, C₁₅H₂₁S₂ requires M, 265.1079).

5-(Methylsulfanyl)-2-pentylbenzo[b]thiophene 19

In a microwave tube was added (2-(hept-2-yn-1-yl)-1,4-phenylene)bis(methylsulfide) (396 mg, 1.5 mmol), para-toluene sulfonic acid (314 mg, 1.65 mmol) and EtOH (7.5 mL) and the reaction mixture was then heated in a microwave reactor for 105 min at 150 °C. After cooling to room temperature, the solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (2% CH₂Cl₂ in hexane) to yield the product (0.278 g, 1.11 mmol, 74% yield) as a yellow oil; ν_max (neat)/cm⁻¹ 2954, 2924, 1434, 1086, 796; δ_H (400 MHz, CDCl₃) 0.91 (3H, t, J = 6.8, CH₃), 1.39-1.36 (4H, m, 2 × CH₂), 1.78-1.71 (2H, m, HetAr-CH₂CH₂), 2.53 (3H, s, S(CH₃)), 2.88 (2H, t, J = 7.2, HetAr-CH₂), 6.93 (1H, s, ArH), 7.21 (1H, dd, J = 8.4, 1.6, ArH), 7.57 (1H, d, J = 1.6, ArH), 7.65 (1H, d, J = 8.4, ArH); δ_C (100 MHz, CDCl₃) 14.1 (CH₃), 17.2 (SCH₃), 22.6 (CH₂), 30.9 (CH₂), 31.4 (CH₂), 120.0 (ArCH), 121.4 (ArCH), 122.5 (ArCH), 123.7 (ArCH), 133.9 (ArC), 136.8 (ArC), 141.1 (ArC), 148.2 (ArC); m/z (ES+) (M), 250.2; m/z (GCMS) 250.1; (Found: M, 250.0845, C₁₄H₁₈S₂ requires M, 250.0844).

5-(Methylsulfinyl)-2-pentylbenzo[b]thiophene 20

5-(Methylsulfinyl)-2-pentylbenzo[b]thiophene
To a solution of 5-(methylthio)-2-pentylbenzo[b]thiophene (0.40 g, 1.6 mmol) in CH₂Cl₂ (20 mL) was added NaHCO₃ (0.147 g, 1.75 mmol) followed by a solution of m-CPBA (0.37 g, 1.68 mmol) in 5 mL CH₂Cl₂ at -78 °C. The reaction mixture was then allowed to warm to room temperature for 1 h before quenching with aqueous saturated NaHCO₃ (20 mL). The aqueous layer was then extracted with CH₂Cl₂ (3 x 20 mL) and the combined organic layers were washed with brine (20 mL), dried (MgSO₄) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (10% EtOAc in CH₂Cl₂) to yield the product (0.383 g, 1.44 mmol, 90% yield) as a pale yellow solid (mp 67-69 °C); ν_max (neat)/cm⁻¹: 2955, 2925, 1434, 1039, 810, 736; δ_H (400 MHz, CDCl₃) 0.91 (3H, t, J = 7.2, CH₃), 1.40-1.36 (4H, m, 2 × CH₂), 1.80-1.72 (2H, m, HetAr-CH₂CH₂), 2.76 (3H, s, SCH₃), 2.92 (2H, t, J = 7.6, HetAr-CH₂), 7.07 (1H, s, ArH), 7.44 (1H, dd, J 8.4, 1.2, ArH), 7.88 (1H, d, J 8.4, ArH), 8.00 (1H, d, J 1.2, ArH); δ_C (100 MHz, CDCl₃) 14.1 (CH₃), 22.5 (CH₂), 30.9 (CH₂), 31.0 (CH₂), 31.4 (CH₂), 44.5 (S(O)CH₃), 117.9 (ArCH), 118.2 (ArCH), 120.6 (ArCH), 123.2 (ArCH), 140.6 (ArC), 141.6 (ArC), 142.1 (ArC), 149.8 (ArC); m/z (ES+) (M + H), 267.2; (Found: M, 267.0877. C₁₄H₁₉S₂O requires M, 267.0877).

4-(3-Cyclohexylprop-2-yn-1-yl)-5-(methylthio)-2-pentylbenzo[b]thiophene

An oven-dried microwave tube was flushed with N₂, before adding a solution containing 5-(methylsulfinyl)-2-pentylbenzo[b]thiophene (133.0 mg, 0.50 mmol) and (3-cyclohexylprop-2-yn-1-yl)trimethylsilane (146.0 mg, 0.75 mol) in MeCN (2.5 mL). Triflic anhydride (100 µL, 0.60 mmol) and 2,6-lutidine (145 µL, 0.625 mmol) were added sequentially at room temperature and the reaction mixture was then heated in a microwave reactor for 15 min at 130 °C. After cooling to room temperature, the solution was quenched with aqueous saturated NaHCO₃ (10 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed successively with aqueous HCl 1.0 M (10 mL) and brine (10 mL), dried (MgSO₄) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (5% CH₂Cl₂ in hexane) to yield the product (0.140 g,
0.38 mmol, 76% yield) as a white solid (mp 50-52 °C); vmax (neat)/cm⁻¹ 2922, 2854, 1448, 1152, 945, 819; δ H (400 MHz, CDCl₃) 0.91 (3H, t, J = 7.2, CH₃), 1.28-1.19 (2H, m, CH₂), 1.45-1.33 (8H, m, CH₂), 1.66-1.62 (2H, m, CH₂), 1.78-1.70 (4H, m, CH₂), 2.34-2.26 (1H, m, CH), 2.48 (3H, s, SCH₃), 2.91 (2H, t, J = 7.2, HetAr-CH₂), 4.04 (2H, d, J = 2.4, Ph-CH₂C), 7.24 (1H, s, ArH), 7.33 (1H, d, J = 8.4, ArH), 7.60 (1H, d, J = 8.4, ArH); δ C (100 MHz, CDCl₃) 14.1 (CH₃), 19.2 (SCH₃), 21.4 (PhCH₂), 22.6 (CH₂), 25.0 (CH₂), 26.1 (CH₂), 29.3 (CH), 31.0 (PhCH₂), 31.1 (CH₂), 31.4 (CH₂), 33.0 (CH₂), 77.8 (C₆H), 85.6 (C₆H), 119.5 (ArCH), 121.2 (ArCH), 126.2 (ArCH), 131.7 (ArC), 132.7 (ArC), 138.5 (ArC), 140.1 (ArC), 147.7 (ArC); m/z

2-(Cyclohexylmethyl)-7-pentylbenzo[1,2-b:4,3-b′]dithiophene 21

In a microwave tube was added 4-(3-cyclohexylprop-2-yn-1-yl)-5-(methylthio)-2-pentylbenzo[b]thiophene (148.0 mg, 0.4 mmol), para-toluene sulfonic acid (84.0 mg, 0.44 mmol) and EtOH (2.5 mL) and the reaction mixture was then heated in a microwave reactor for 105 min at 150 °C. After cooling to room temperature, the solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (1% CH₂Cl₂ in hexane) to yield the product (0.124 g, 0.34 mmol, 87% yield) as a white solid (mp 67-68 °C); vmax (neat)/cm⁻¹ 2921, 2849, 1448, 1124, 830, 802; δ H (400 MHz, CDCl₃) 0.92 (3H, t, J = 6.8, CH₃), 1.05-0.97 (2H, m, CH₂), 1.30-1.15 (3H, m, CH+CH₂), 1.40-1.35 (4H, m, CH₂), 1.73-1.64 (4H, m, CH₂), 1.82-1.77 (4H, m, CH₂), 2.83 (2H, d, J = 7.2, HetAr-CH₂), 2.97 (2H, t, J = 7.6, HetAr-CH₂), 7.28 (1H, s, ArH), 7.31 (1H, s, ArH), 7.62 (2H, s, ArH); δ C (100 MHz, CDCl₃) 14.2 (CH₃), 22.6 (CH₂), 26.3 (2 x CH₂), 26.6 (CH₂), 31.0 (HetArCH₂), 31.2 (CH₂), 31.4 (CH), 33.2 (2 x CH₂), 38.9 (HetArCH₂), 40.1 (CH₂), 117.7 (ArCH), 117.7 (ArCH), 118.8 (ArCH), 119.7 (ArCH), 134.5 (ArC), 134.5 (ArC), 135.6 (ArC), 135.8 (ArC), 145.4 (ArC), 147.0 (ArC); m/z (ES+) (M + H), 357; (Found: M, 357.1699. C₂₂H₂₉S₂ requires M, 357.1711).

General Procedure J- Alkene Dimerisation
6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]benzothiophene 22

Under an Ar atmosphere, a solution of (E)-2-(pent-1-en-1-yl)benzo[b]thiophene (40.4 mg, 0.2 mmol) in Ar sparged 1,2-dichloroethane (2 ml) was added to a solution of iodine (506 mg, 2 mmol) in Ar sparged 1,2-dichloroethane (18 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching with saturated aqueous Na₂S₂O₃ (5 mL). The aqueous layer was then extracted with EtOAc (3 × 5 mL) and the combined organic layers washed with brine (5 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude product was washed with cold ethanol (3 ml) to yield the product (34.8 mg, 86.0 µmol, 86 % yield) as a white solid (mp: 151 - 155 °C); ν max (neat)/cm⁻¹ 2953, 2923, 2850, 1468, 1424, 1364, 1275, 1267, 1164, 1106, 1074, 1043, 927, 764, 751, 724, 670; δ H (400 MHz, CDCl₃) 1.09 (6 H, t, J = 7.3, 2 × CH₃), 1.69 (4 H, sxt, J = 7.1, 2 × CH₂CH₃), 1.93 (4 H, quin, J = 7.5, 2 × CH₂CH₂), 3.46 - 3.57 (4 H, m, 2 × CH₂), 7.44 - 7.57 (4 H, m, 4 × ArC-H), 7.88 - 7.97 (2 H, m, 2 × ArC-H), 8.25 - 8.37 (2 H, m, 2 × ArC-H); δ C (100 MHz, CDCl₃) 14.2 (2 × CH₃), 23.5 (2 × CH₂CH₂), 30.6 (2 × CCH₂CH₂), 33.9 (2 × CH₂), 123.1 (2 × Ar-CH), 124.7 (2 × Ar-CH), 125.1 (2 × Ar-CH), 126.3 (2 × Ar-CH), 131.3 (4 × Ar-C), 136.2 (2 × Ar-C), 139.1 (2 × Ar-C), 140.2 (2 × Ar-C); m/z (El) M, 402; (Found: M, 402.1483. C₂₆H₂₆S₂ requires M, 402.1470).

6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]5-methylbenzothiophene 23

As for general procedure J, (E)-5-methyl-2-(pent-1-en-1-yl)benzo[b]thiophene (43.2 mg, 0.2 mmol) in 1,2-dichloroethane (2 ml) was added to a solution of iodine (506 mg, 2 mmol) in 1,2-dichloroethane (18 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching. The crude product was washed with cold ethanol (3 ml) to yield the product (27.1 mg, 63.0 µmol, 63 % yield) as a white solid (mp: 260-262 °C); ν max (neat)/cm⁻¹ 2961,
1568, 1412, 1258, 1017, 861, 793, 687, 626, 613, 567; δH (400 MHz, CDCl3) 1.11 (6 H, t, J = 7.3 Hz, 2 x CH2CH3), 1.70 (4 H, sxt, J = 7.3 Hz, 2 x CH2CH3), 1.87 - 1.97 (4 H, dd, J = 8.0, 0.6 Hz, 2 x ArC-H), 7.80 (2 H, d, J = 8.0 Hz, ArC-H), 8.13 (2 H, s, ArC-H); δc (100 MHz, CDCl3) 14.0 (2 x CH3), 22.0 (2 x CH2CH3), 23.2 (2 x CH2CH3), 23.5 (2 x CCH2CH2), 122.4 (2 X ArC-H), 125.3 (2 X Ar-C), 127.4 (2 X Ar-C), 130.9 (2 X ArC), 131.0 (2 X ArC), 133.9 (2 X ArC), 136.2 (2 X ArC), 136.8 (2 X ArC), 139.2 (2 X ArC); m/z (APCI) M+H, 431.6; (Found: M, 431.1858. C28H30S2 requires M).  

6,12-Dibutylbenzo[1,2-b:4,5-b’]bis[b]5-methoxybenzothiophene 24

As in general procedure J, (E)-5-methoxy-2-(pent-1-en-1-yl)benzo[b]thiophene (49.6 mg, 0.2 mmol) in 1,2-dichloroethane (2 ml) was added to a solution of iodine (506 mg, 2 mmol) in 1,2-dichloroethane (18 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching. The crude product was washed with cold ethanol (3 ml) to yield the product (27.6 mg, 55.0 µmol, 55 % yield) as a white solid (mp: 175-177 °C); νmax (neat)/cm⁻¹ 2959, 2930, 2872, 1874, 1596, 1564, 1470, 1428, 1308, 1213, 1184, 1020, 894, 863, 794, 663; δH (500 MHz, CDCl3) 1.09 (6 H, t, J = 7.3 Hz, 2 x CH2CH3), 1.70 (4 H, sxt, J = 7.4 Hz, 2 x CH2CH3), 1.90 - 1.98 (4 H, m, 2 x CCH2CH2), 3.46 - 3.50 (4 H, m, 2 x CCH2CH2), 3.97 (6 H, s, 2 x OCH3), 7.14 (2 H, dd, J = 8.7, 2.3 Hz, 2 x Ar-C-H), 7.79 (2 H, d, J = 8.7 Hz, 2 x ArC-H), 7.84 (2 H, d, J = 2.3 Hz, 2 x Ar-C-H); δc (100 MHz, CDCl3) 14.1 (2 x CH3), 23.4 (2 x CH2CH3), 30.5 (2 x CCH2CH2), 33.7 (2 x CCH2CH2), 55.7 (2 x OCH3), 109.2 (2 x Ar-C-H), 114.6 (2 x Ar-C-H), 123.2 (2 x Ar-C-H), 131.1 (2 x ArC), 131.1 (2 x ArC), 131.8 (2 x ArC), 136.9 (2 x ArC), 139.9 (2 x ArC), 157.5 (2 x ArC-OCH3); m/z (APCI) M+H, 463.1; (Found: M, 463.1751. C28H30O2S2 requires M, 463.1765).  

6,12-Dibutylbenzo[1,2-b:4,5-b’]bis[b]5-fluorobenzothiophene 25
As for general procedure J, (E)-5-fluoro-2-(pent-1-en-1-yl)benzo[b]thiophene (44.0 mg, 0.2 mmol) in 1,2-dichloroethane (2 ml) was added to a solution of iodine (506 mg, 2 mmol) in 1,2-dichloroethane (18 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching. The crude product was washed with cold ethanol (3 ml) to yield the product (25.4 mg, 58.0 µmol, 58 % yield) as a white solid (mp: 209-211 °C); \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 2960, 2870, 1770, 1569, 1472, 1414, 1356, 1293, 1258, 1183, 1096, 1020, 939, 850, 793, 656, 613; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 1.09 (6 H, t, \( J = 7.34 \) Hz, 2 x CH\(_2\)CH\(_3\)), 1.69 (4 H, sxt, \( J = 7.3 \) Hz, 2 x CH\(_2\)CH\(_3\)), 1.84 - 1.94 (4 H, m, 2 x CH\(_2\)CH\(_3\)), 3.40 - 3.46 (4 H, m, 2 x CH\(_2\)CH\(_3\)), 7.26 (2 H, td, \( J = 8.5, 2.3 \) Hz, 2 x ArC-H), 7.84 (2 H, dd, \( J = 8.7, 5.2 \) Hz, 2 x ArC-H), 7.97 (2 H, dd, \( J = 11.0, 2.3 \) Hz, 2 x ArC-H); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 13.9 (2 x C\(_\text{H}_3\)), 23.1 (2 x CH\(_2\)CH\(_3\)), 30.3 (2 x CH\(_2\)CH\(_3\)), 33.3 (2 x CH\(_2\)CH\(_3\)), 111.0 (d, \( J = 28.2 \) Hz, 2 x ArC-H), 114.1 (d, \( J = 24.5 \) Hz, 2 x ArC-H), 123.6 (d, \( J = 9.1 \) Hz, 2 x ArC-H), 131.0 (d, \( J = 3.6 \) Hz, 2 x ArC), 131.4 (2 x ArC), 135.1 (2 x ArC), 136.9 (d, \( J = 9.1 \) Hz, 2 x ArC), 140.1 (2 x ArC), 158.9 (d, \( J = 240.7 \) Hz, 2 x ArC-F); \( m/z \) (APCI) M+Na+H,463.3; (Found: M, 439.1356. C\(_{26}\)H\(_{24}\)F\(_2\)S\(_2\) requires M, 439.1366).

6,12-Dibutylbenzo[1,2-b:4,5-b'bis[b]6-fluorobenzo[b]thiophene 26

![Diagram of 6,12-Dibutylbenzo[1,2-b:4,5-b'bis[b]6-fluorobenzo[b]thiophene](26)](image)

As in general procedure J, (E)-4-fluoro-2-(pent-1-en-1-yl)benzo[b]thiophene (32.8 mg, 0.14 mmol) in 1,2-dichloroethane (2 ml) was added to a solution of iodine (374 mg, 1.48 mmol) in 1,2-dichloroethane (12 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching. The crude product was washed with cold ethanol (3 ml) to yield the product (14.7 mg, 33.0 µmol, 43 % yield) as a white solid (mp: 213-215 °C); \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 2955, 2934, 2873, 2858, 1597, 1596, 1485, 1457, 1408, 1365, 1315, 1274, 1252, 1195, 1104, 1034,
925, 900, 842, 800, 767, 735, 720; δ_H (500 MHz, CDCl_3) 1.07 (6 H, t, J = 7.4 Hz, 2 x CH_3CH_2), 1.67 (4 H, sxt, J = 7.4 Hz, 2 x CH_2CH_3), 1.82 - 1.93 (4 H, m, 2 x CH_2CH_2), 3.38 - 3.48 (4 H, m, 2 x CCH_2CH_2), 7.23 (2 H, td, J = 8.8, 2.4 Hz, 2 x ArCH), 7.59 (2 H, dd, J = 8.4, 2.4 Hz, 2 x ArCH), 8.21 (2 H, dd, J = 9.0, 5.0 Hz, 2 x ArCH); δ_C (100 MHz, CDCl_3) 13.9 (2 x CH_3), 23.1 (2 x CH_2CH_3), 30.2 (2 x CCH_2CH_2), 33.3 (2 x CCH_2CH_2), 109.1 (d, J = 22.7 Hz, 2 x ArCH), 112.7 (d, J = 22.7 Hz, 2 x ArCH), 125.8 (d, J = 9.1 Hz, 2 x ArCH), 130.1 (2 x ArC), 130.4 (2 x ArC), 132.3 (2 x ArC), 138.9 (2 x ArC), 141.4 (d, J = 10.0 Hz, 2 x ArC), 161.1 (d, J = 248.0 Hz, 2 x ArC-F); m/z (APCI) M+H, 471.5; (Found: M, 471.0789. C_{26}H_{25}S_{2}Cl_{2} requires M, 471.0775).

6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]5-chlorobenzothiophene 27

![Chemical structure](image)

As in general procedure J, (E)-5-chloro-2-(pent-1-en-1-yl)benzo[b]thiophene) (33.7 mg, 0.14 mmol) in 1,2-dichloroethane (2 ml) was added to a solution of iodine (359 mg, 1.42 mmol) in 1,2-dichloroethane (12 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching. The crude product was washed with cold ethanol (2 ml) to yield the product (19.0 mg, 46.0 µmol, 64 % yield) as a white solid (mp: 196-198 °C); ν_{max} (neat)/cm^{-1} 2957, 2928, 2870, 2851, 1873, 1583, 1548, 1474, 1431, 1409, 1375, 1320, 1143, 1102, 1040, 865, 855, 812, 800, 783, 732; δ_H (500 MHz, CDCl_3) 1.11 (6 H, t, J = 7.4 Hz, 2 x CH_3CH_2), 1.70 (4 H, sxt, J = 7.3 Hz, 2 x CH_2CH_3), 1.85 - 1.96 (4 H, m, 2 x CCH_2CH_2), 3.39 - 3.51 (4 H, m, 2 x CCH_2CH_2), 7.47 (2 H, dd, J = 8.4, 1.9 Hz, 2 x ArCH), 7.83 (2 H, d, J = 8.3 Hz, 2 x ArCH), 8.27 (2 H, d, J = 1.8 Hz, 2 x ArCH); δ_C (100 MHz, CDCl_3) 13.9 (2 x CH_3), 23.1 (2 x CH_2CH_3), 30.1 (2 x CCH_2CH_2), 33.4 (2 x CCH_2CH_2), 123.6 (2 x ArCH), 124.8 (2 x ArCH), 126.4 (2 x ArCH), 130.6 (2 x ArC), 130.6 (2 x ArC), 131.4 (2 x ArC), 137.0 (2 x ArC), 138.1 (2 x ArC), 139.7 (2 x ArC-Cl); m/z (APCI) M+H, 471.5; (Found: M, 471.0789. C_{26}H_{25}S_{2}Cl_{2} requires M, 471.0775).
6,12-Dihexylbenzo[1,2-b:4,5-b’]bis[b]benzothiophene 28

As in general procedure J, (E)-2-(hex-1-en-1-yl)benzo[b]thiophene (41.2 mg, 0.17 mmol) in 1,2-dichloroethane (2 ml) was added to a solution of iodine (450 mg, 1.78 mmol) in 1,2-dichloroethane (15 ml). The reaction mixture was stirred for 18 h at 80 °C before quenching. The crude product was washed with cold ethanol (2 ml) to yield the product (30.7 mg, 69.0 µmol, 81 % yield) as a white solid (mp: 155-157 °C); ν\textsubscript{max} (neat)/cm\textsuperscript{-1} 2948, 2923, 2854, 1725, 1467, 1424, 1365, 1260, 1163, 1103, 1072, 1049, 927, 843, 801, 756, 723, 700, 660; δ\textsubscript{H} (500 MHz, CDCl\textsubscript{3}) 0.96 (6 H, t, J = 7.1 Hz, 2 x CH\textsubscript{3}C\textsubscript{H\textsubscript{3}}), 1.36 - 1.49 (8 H, m, 4 x CH\textsubscript{2}), 1.68 (4 H, quin, J = 7.4 Hz, 2 x CH\textsubscript{2}), 1.89 - 1.97 (4 H, m, 2 x CCH\textsubscript{2}CH\textsubscript{2}), 3.47 - 3.52 (4 H, m, 2 x CC\textsubscript{H}2CH\textsubscript{2}), 7.50 (4 H, quin, J = 6.5 Hz, 4 x ArC-H), 7.93 (2 H, d, J = 8.7 Hz, 2 x ArC-H), 8.30 (2 H, d, J = 7.5 Hz, 2 x ArC-H); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 14.1 (2 x CH\textsubscript{3}), 22.6 (2 x CH\textsubscript{2}CH\textsubscript{3}), 28.1 (2 x CH\textsubscript{2}), 29.7 (CH\textsubscript{3}), 31.6 (2 x CCH\textsubscript{2}CH\textsubscript{2}), 33.9 (2 x CCH\textsubscript{2}CH\textsubscript{2}), 122.8 (2 x ArC-H), 124.4 (2 x ArC-H), 124.8 (2 x ArC-H), 126.0 (2 x ArC-H), 131.0 (2 x ArC), 131.0 (2 x ArC), 135.9 (2 x ArC), 138.8 (2 x ArC), 139.9 (2 x ArC); m/z (APCI) M+H, 459.6; (Found: M, 459.2200. C\textsubscript{30}H\textsubscript{35}S\textsubscript{2} requires M, 459.2180).
$^1$H and $^{13}$C NMR Spectra

1-(5-Methylbenzo[b]thiophen-2-yl)pentan-1-one S1

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S36
S37

1-(7-Methylbenzo[b]thiophen-2-yl)pentan-1-one S2

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-{5-Fluorobenzo[b]thiophen-2-yl}pentan-1-one S3

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(5-Chlorobenzo[b]thiophen-2-yl)pentan-1-one S4

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(5-Nitrobenzo[b]thiophen-2-yl)pentan-1-one

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(5-Methoxybenzo[b]thiophen-2-yl)pentan-1-one S6

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(7-Methoxybenzo[b]thiophen-2-yl)pentan-1-one S7

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S42
1-(7-(Trifluoromethyl)benzo[b]thiophen-2-yl)pentan-1-one S8

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(5-(Trifluoromethyl)benzo[b]thiophen-2-yl)pentan-1-one S9

$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
3-Ethylbenzo[b]thiophene-2-carbaldehyde S10

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
2-Pentylbenzo[b]thiophene S11

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
5-Methoxy-2-pentylbenzo[b]thiophene S12

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5-Chloro-2-pentylbenzo[b]thiophene S13

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-Pentyl-5-(trifluoromethyl)benzo[b]thiophenes S14

$^1$H NMR (400 MHz, CDCl$_3$)

13C NMR (100 MHz, CDCl$_3$)
7-Fluoro-2-pentylbenzo[b]thiophene S15

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-Methyl-3-ethylbenzothiophene S16

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))
2-Methyl-3-isopropylbenzothiophene S17

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-Methyl-3-cyclohexylbenzothiophene S18

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-(Pent-1-en-1-yl)benzo[b]thiophenes S19

$^1$H NMR (500 MHz, C$_6$D$_6$)

$^{13}$C NMR (125 MHz, C$_6$D$_6$)
(E)-5-Methyl-2-(pent-1-en-1-yl)benzo[b]thiophene S20

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-2-(Pent-1-en-1-yl)-5-(trifluoromethyl)benzo[b]thiophene S21

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-5-Fluoro-2-(pent-1-en-1-yl)benzo[b]thiophene S22

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-4-Fluoro-2-(pent-1-en-1-yl)benzo[b]thiophene S23

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-2-(Pent-1-en-1-yl)naphtho[2,1-b]thiophene S24

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-5-Methoxy-2-(pent-1-en-1-yl)benzo[b]thiophene S25

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-5-Chloro-2-(pent-1-en-1-yl)benzo[b]thiophene S26

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-4,6-Dimethyl-2-(pent-1-en-1-yl)benzo[b]thiophene S27

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,6-bis(Hexylsulfinyl)naphthalene 7

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1,5-bis(Hexylsulfinyl)naphthalene 8

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(2,6-Di(non-2-yn-1-yl)naphthalene-1,5-diyl)bis(hexylsulfide) 10b

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(1,5-Di(non-2-yn-1-yl)naphthalene-2,6-diyl)bis(hexylsulfide) 9

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
2,7-Diheptylnaphtho[1,2-b:5,6-b']dithiophene 12

$^1$H NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (100 MHz, C$_6$D$_6$)
2,7-Diheptylnaphtho[2,1-b:6,5-b']dithiophene 11

$^1$H NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (100 MHz, C$_6$D$_6$)
1,1’-{Naphtho[1,2-b:5,6-b’]dithiophene-2,7-diyl}bis(heptan-1-one) 14

$^1$H NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (100 MHz, C$_6$D$_6$)
1,1'-(Naphtho[2,1-b:6,5-b']dithiophene-2,7-diyl)bis(heptan-1-one) 13

$^1$H NMR (400 MHz, C$_6$D$_6$)

$^{13}$C NMR (100 MHz, C$_6$D$_6$)
2,7-Di((E)-hept-1-en-1-yl)naphtho[2,1-b:6,5-b']dithiophene 15

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,7-Di((E)-hept-1-en-1-yl)naphtho[1,2-b:5,6-b']dithiophene 16

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(Hept-2-yn-1-yl)-1,4-phenylene)bis(methylsulfide) S28

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5-(Methylsulfanyl)-2-pentylenzo[b]thiophene 19

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5-(Methylsulfinyl)-2-pentylbenzo[b]thiophene 20

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(3-Cyclohexylprop-2-yn-1-yl)-5-(methylsulfanyl)-2-pentylbenzo[b]thiophene S29

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(Cyclohexylmethyl)-7-pentylbenzo[1,2-b:4,3-b']dithiophene 21

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6,12-Dibutylbenzo[1,2-\textit{b}:4,5-\textit{b}']bis[\textit{b}]benzothiophene 22

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6,12-Dibutylbenzo[1,2-\textit{b}:4,5-\textit{b}']bis[\textit{b}]5-methylbenzothiophene 23

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]5-methoxybenzothiophene 24

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

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S80
6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]5-fluorobenzothiophene 25

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]6-fluorobenzothiophene 26

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6,12-Dibutylbenzo[1,2-b:4,5-b']bis[b]5-chlorobenzothiophene 27

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
6,12-Dihexylbenzo[1,2-\(b:4,5-b'\)]bis[b]benzothiophene 28

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))
**Field Effect Transistors**

Field effect transistors were created for the compounds 22, 23, 11, 12, 13 and 14. Thin films were characterised by X-ray diffraction and atomic force microscopy and transistors were created and analysed using conventional thin film transistor techniques.

**Thin Film Deposition**

Heavily doped silicon (n++) with 300 nm of thermally grown silicon dioxide was used as the substrate and gate electrode for all following experiments. The substrates were cleaned by sonication in acetone, propan-2-ol and methanol followed by drying under a stream of nitrogen and subjected to a UV-Ozone treatment for approximately 20 minutes.

An octadecytrichlorosilane (OTS) monolayer was deposited in order to reduce the surface energy, passivate traps and improve thin film growth. OTS treatment was achieved by spin coating of a solution from chloroform as has been reported elsewhere.1 OTS treated substrates were all washed with organic solvents and dried with nitrogen before being transferred to the vacuum evaporation chamber for thin film deposition.

Evaporation of organic semiconductors was performed in a modified Edwards Auto306 vacuum evaporator with a base pressure of $7 \times 10^{-6} \text{ mbar}$. Nominally, between 30 and 40 nm of compounds was deposited onto substrates held at between 30 and 80 °C at a rate of 0.5 As$^{-1}$

To create thin film transistors the semiconductor coated substrates were transferred to a separate Edwards Auto500 vacuum evaporator (base pressure $1 \times 10^{-7} \text{ mbar}$) for gold evaporation. Nominally, 50 nm of gold was deposited on top of the organic layers at a rate of 1 As$^{-1}$ through a shadow mask, defining source and drain electrodes.

**Thin Film Characterisation**

![Optical microscopy images](image)

*Figure 1: Optical microscopy images of evaporated thin films of a) 22 on OTS, b) 23 on OTS, c) 22 on SiO2 and d) 22 on OTS, and gold electrodes more material was deposited during this evaporation.*
The thin films were characterised using a Park XE100 atomic force microscope in tapping mode and a Bruker D8 discover X-ray diffractometer for out-of-plane X-ray diffraction.

BDTs

Optical microscopy gives us an indication that the films are composed of small crystallites on both OTS treated surfaces and on bare SiO$_2$ (Figure 1). AFM topography, Figure 2, gives us further insight into the nature of the crystallisation. On the OTS treated substrates both compounds exhibit small needle like crystallites whereas when compound 22 is deposited on to SiO$_2$ it forms small nodule like structures and no thin film structure was observed in either case.

Thin film (out-of-plane) X-ray diffraction studies were conducted to look at the crystal structure of the samples. Figure 3 shows the X-ray diffraction of samples of 22 and 23 on OTS and 22 on SiO$_2$. On OTS both compounds show a single large peak representative of the highly crystalline nature of the needle like crystals. The reflections for compounds 22 and 23 on OTS correspond to a d-spacing of 12.2 A and 11.2 A respectively. The d-spacings for compound 22 on SiO$_2$ are 11.3 A and 9.6 A confirming the difference in crystal structure.
From the optical microscopy images (Figure 4) it is clear that the isomers 12 and 14 do not form complete films but instead forms small isolated crystals over the surface. However, for the isomers 11 and 13, both the heptyl (11) and the ketone (13) form complete, smooth films. Figure 5 confirms this incomplete coverage for isomers 12 and 13 via the AFM topography. Figure 5a and c show isomers 12 and 13 with large gaps separating crystalline material which hinders and percolation pathways for charge conduction. Figures 5b and d, however, show full crystalline thin films with little or no holes through to the substrate. As confirmation, of the thin film structure, Figure 6 shows the out-of-plane X-ray diffraction of all 4 thin films. For compounds 12 (black) and 14 (green) there are very sharp peaks represent the very crystalline nature of the small crystallites on the surface. In the case of compounds 11 (red) and 13 (blue) the peaks are broader, indicative of a thin film crystal structure.
Transistor Characterisation

Transistors were created via the evaporation of gold electrodes in a top contact bottom gate configuration. The devise were then tested in the saturation regime using the standard equation.

\[ I_D = C_i \frac{W}{2L} \mu_{sat} (V_G - V_T)^2 \]

Figure 5: AFM topography images of thin films of a) 12 b) 11, c) 14 and d) 13.

Figure 6: Out-of-plane X-ray diffraction of thin films. From bottom to top, 12 (black), 11 (red), 14 (green) and 13 (blue).
Where, $I_D$ is the source-drain current, $C_i$ is the capacitance, $W$ the channel width, $L$ the channel length, $\mu_{sat}$ is the saturation mobility, $V_G$ is the swept gate voltage and $V_T$ is the threshold voltage. The transistors had a channel width of 2000 $\mu$m and a channel length of 60 $\mu$m, the 300 nm silicon dioxide with OTS monolayer was calculated to have a capacitance of approximately 11.4 nFcm$^{-2}$.

**BDTs**

Only devices that were created on OTS substrates demonstrated transistor characteristics. Compound 22 showed a mobility of approximately $1 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ an on/off current ratio of $10^4$ and a very high threshold voltage. This can all be attributed to the poor percolation pathways of the needle like crystals, low coverage and poor interconnection between the grains which also meant that only 2 out of 9 devices were operational. Compound 23 demonstrated improved characteristics with and average mobility of approximately $5 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ an on off ratio of $10^5$ and threshold voltage around -20 V, 8 out of 9 devices exhibited transistor behaviour. Although exhibiting reasonable OFET characteristics the devices show poor reverse sweep performance as shown in Figure 7c.

It should be noted that during the deposition procedures a nominal value for the material density was used (1.23 g/cm$^3$). As such, in both cases the evaporation rate stated will not be an accurate representation of the actual rate. In fact, it is quite noticeable that the two compounds themselves have quite different densities as one is a hard powder (22) whilst the other is a more light weight solid (23). This leads to a mismatch even in the evaporation rate of the two compounds which would severely underestimate the rate of evaporation of compound 23, this fits with the observation of higher coverage of needles from AFM, Figure2b. This may be the reason for the increased number of working devices and improved performance. Hence, it was decided to increase the coverage of compound 22 to see if that would improve the performance. Figure 1d shows the image of an increased coverage sample of 22, Figure 2d is the AFM image of the same region showing a much increased number of needle crystals. Transfer characteristics are shown in Figure 7d, overall device performance is improved. A mobility of approximately $1 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ was achieved, a threshold voltage of -10 V and an on/off ration of $10^5$. Although improved performance only 2 of the 9 devices worked and reverse sweep behaviour is poor.

It should be noted that there was only enough material of 23 to do the one evaporation and more coverage was not obtained for this material.

**NDTs**

Compounds 12 and 14 showed no switching behaviour as expected from the incomplete films seen in Figure 4. Figure 8a shows a transfer curve for the compound 11. The device shows good p-type behaviour with an average mobility of $0.21 \pm 0.02$ cm$^2$Vs$^{-1}$, threshold voltage of -22 $\pm$ 4 and on/off ratio of $10^7$ over 9 devices. The devices do, however, show large hysteresis and memory behaviour as has been seen in similar materials before. Figure 8b shows a transfer curve for the compound 13, it does show limited p-type behaviour but only 10% of devices tested worked. This poor behaviour could be attributed to the poor alignment of the...
HOMO of the molecule and the work function of the gold electrodes. Devices made from compounds 14 and 13 were also tested under nitrogen as n-type devices but no switching behaviour was observed. The results from compounds 12 and 11 are consistent with that previously reported for these materials.

**Figure 8:** Transfer characteristics for a) compound 11, inset hysteresis, b) compound 13.

**References**


UV/Vis Spectra and Cyclic Voltammetry

Experimental Details

UV-Vis absorption spectra were recorded on a Varian Cary 5000 UV-Vis- NIR spectrophotometer in dichloromethane at room temperature.

Cyclic voltammetry was performed in dichloromethane solution scanning at 100 mV s\(^{-1}\) on a BASI Epsilon electrochemical workstation with a three-electrode cell, Ag/AgNO\(_3\) as reference electrode, platinum wire as counter electrode and working electrode, in nitrogen-purged, 0.1 M solution of tetrabutylammonium hexafluorophosphate as a supporting electrolye at room temperature.

Absorption spectra of Compound 11
Absorption spectra of Compound 12

Absorption spectra of Compound 13
Absorption spectra of Compound 14

Absorption spectra of Compound 15
Absorption spectra of Compound 16

Absorption spectra of Compound 22
Absorption spectra of Compound 23

Absorption / a.u.

Wavelength / nm

Absorption spectra of Compound 23
Absorption spectra of Compound 24
Absorption spectra of Compound 25
Absorption spectra of Compound 26

Absorption / a.u.

Wavelength / nm
Absorption spectra of Compound 27
Absorption spectra of Compound 28
Cyclic Voltammetry of Compound 11 in DCM

Cyclic Voltammetry of Compound 12 in DCM
Cyclic Voltammetry of Compound 13 in DCM
Cyclic Voltammetry of Compound 14 in DCM

Potential / V vs. Ag/AgNO₃

Current / μA

Cyclic Voltammetry of Compound 15 in DCM

Potential / V vs. Ag/AgNO₃

Current / μA
Cyclic Voltammetry of Compound 16 in DCM

Cyclic Voltammetry of Compound 16 (Fc/Fc⁺)
Cyclic Voltammetry of Compound 22 in DCM

Cyclic Voltammetry of Compound 23 in DCM
Cyclic Voltammetry of Compound 24 in DCM
Cyclic Voltammetry of Compound 25 in DCM

Cyclic Voltammetry of Compound 26 in DCM
Cyclic Voltammetry of Compound 27 in DCM
Cyclic Voltammetry of Compound 28 in DCM

[Cyclic Voltammetry Graph]

Potential / V vs. Ag/AgNO₃

Current / μA
X-Ray Structures and CCDC Numbers

Compound 11
CCDC 1415330

Compound 12
CCDC 1415331

Compound 13
CCDC 1415332

Compound 14
CCDC 1415333
Compound 22

CCDC 1415334