**Supplementary Information**

Sulfur-linked cyanobiphenyl-based liquid crystal dimers and the twist-bend nematic phase

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**1. Synthesis**

*1.1 4',4''-[1,ω-Alkanediylbis(thio)]bis-[1,1'-biphenyl]-4-carbonitriles (CBSnSCB)*

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***1.1.1 1,1'-(Alkane-1,ω-diyldithiodiyl)bis(4-bromobenzene)s (BrBSnSBBr) (1a)***

To a pre-dried flask, 4-bromothiophenol (2.10 eq) was added and kept under argon. Sodium hydroxide (2.53 eq) in ethanol (60 mL), sonicated to ensure all the solid was dissolved, was added. The reaction mixture was stirred for 2 h at room temperature. The appropriate 1,ω-dibromoalkane (1 eq) was syringed into the flask and the reaction mixture stirred at room temperature for a further 24 h. During this time a white precipitate formed, the sodium bromide salt. The ethanol was removed under vacuum and the residue was taken up in diethyl ether (120 mL). The sodium bromide solid was removed using vacuum filtration. The solvent was removed under vacuum to leave a white solid which was recrystallised from ethanol (150 mL).

**Table 1.1.1** Quantities of reagents used in the syntheses of BrBSnSBBr(**1**a).

|  |  |  |  |
| --- | --- | --- | --- |
| *n* | 1,ω-Dibromoalkane | 4-Bromothiophenol | Sodium hydroxide |
| 1 | 1.0 mL, 2.48 g, 1.43x10-2 mol | 5.65 g, 2.99x10-2 mol | 1.44 g, 3.60x10-2 mol |
| 3 | 1.2 mL, 2.36 g, 1.17x10-2 mol | 4.42 g, 2.34x10-2 mol | 1.12 g, 2.80x10-2 mol |
| 4 | 1.2 mL, 2.15 g, 1.00x10-2 mol | 3.97 g, 2.10x10-2 mol | 1.01 g, 2.52x10-2 mol |
| 5 | 2.2 mL, 3.72 g, 1.62x10-2 mol | 5.56g, 2.94x10-2 mol | 1.41 g, 3.53x10-2 mol |
| 6 | 1.5 mL, 2.38 g, 9.75x10-3 mol | 3.87 g, 2.05x10-2 mol | 0.99 g, 2.47x10-2 mol |
| 7 | 2.0 mL, 3.02 g, 1.17x10-2 mol | 4.65 g, 2.46x10-2 mol | 1.18 g, 2.96x10-2 mol |
| 9 | 2.5 mL, 3.52 g, 1.23x10-2 mol | 4.89 g, 2.58x10-2 mol | 1.24 g, 3.11x10-2 mol |
| 11 | 1.5 mL, 2.24 g, 7.13x10-3 mol | 2.83 g, 1.50x10-2 mol | 0.72 g, 1.80x10-2 mol |

**BrBS1SBBr**

Yield: 2.52 g, 90.4 %. MP: 76 °C

*vmax* /cm-1: 1473, 1401, 1385, 1203, 1087, 1065, 1006, 835, 807, 737, 493, 473

δ H/ppm (400 MHz, CDCl3): 7.44 (4 H, d, J 7.7, Ar-H), 7.27 (4 H, d, J 7.7, Ar-H), 4.28 (2 H, s, S-CH2-S)

δ C/ppm (100 MHz, CDCl3): 133.63, 132.53, 132.15, 121.56, 40.84

**BrBS3SBBr**

Yield: 3.02 g, 61.6 %. MP: 50 °C

*vmax* /cm-1: 2951, 2918, 1473, 1432, 1384, 1176, 1090, 1040, 823, 800, 749, 513, 475

δ H/ppm (400 MHz, CDCl3): 7.38 (4 H, d, J 8.3, Ar-H), 7.16 (4 H, d, J 8.3, Ar-H), 3.01 (4 H, t, J 7.0, S-CH2-CH2), 1.91 (2 H, quin, J 7.0, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 135.08, 132.00, 130.97, 120.05, 32.43, 28.02

**BrBS4SBBr**

Yield: 3.01 g, 69.7 %. MP: 100 °C

*vmax* /cm-1: 2950, 2862, 1473, 1459, 1385, 1320, 1091, 1069, 1003, 805, 514, 484.

δ H/ppm (400 MHz, CDCl3): 7.39 (4 H, d, J 8.5, Ar-H), 7.16 (4 H, d, J 8.5, Ar-H), 2.89 (4 H, t, J 6.1, S-CH2-CH2), 1.75 (4 H, t, J 6.1, CH2-CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 135.58, 131.94, 130.77, 119.79, 33.29, 27.88.

**BrBS5SBBr**

Yield: 2.37 g, 32.8 %. MP: 66 °C

*vmax* /cm-1: 2922, 2853, 1473, 1427, 1382, 1284, 1091, 1068, 1002, 800, 733, 509, 477, 451

δ H/ppm (400 MHz, CDCl3): 7.39 (4 H, d, J 8.0, Ar-H), 7.17 (4 H, d, J 8.0, Ar-H), 2.88 (4 H, t, J 7.1, S-CH2-CH2), 1.60 (6 H, m, CH2-CH2-CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 135.89, 131.90, 130.58, 119.63, 33.55, 28.48, 27.74

**BrBS6SBBr**

Yield: 3.13 g, 69.6 %. MP: 82 °C

*vmax* /cm-1: 2925, 2854, 1473, 1461, 1384, 1273, 1183, 1092, 1072, 1006, 809, 785, 727, 507, 484

δ H/ppm (400 MHz, CDCl3): 7.39 (4 H, d, J 8.2, Ar-H), 7.17 (4 H, d, J 8.2, Ar-H), 2.88 (4 H, t, J 7.3, S-CH2-CH2), 1.62 (4 H, quin, J 7.3, 7.0, CH2-CH2-CH2), 1.43 (4 H, quin, J 7.0, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 136.07, 131.87, 130.45, 119.51, 33.58, 28.82, 28.23

**BrBS7SBBr**

Yield: 2.28 g, 37.6 %. MP: 75 °C

*vmax* /cm-1: 2920, 2853, 1472, 1438, 1389, 1091, 1068, 1004, 804, 726, 510, 476

δ H/ppm (400 MHz, CDCl3): 7.39 (4 H, d, J 8.4, Ar-H), 7.17 (4 H, d, J 8.4, Ar-H), 2.88 (4 H, t, J 7.4, S-CH2-CH2), 1.61 (4 H, quin, J 7.4, 7.5, CH2-CH2-CH2), 1.41 (4 H, quin, J 7.5, 7.2, CH2-CH2-CH2), 1.31 (2 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 136.17, 131.85, 130.40, 119.44, 33.62, 28.87, 28.63, 28.56

**BrBS9SBBr**

Yield: 3.22 g, 52.1 %. MP: 68 °C

*vmax* /cm-1: 2920, 2851, 1472, 1430, 1387, 1090, 1003, 804, 724, 518, 477

δ H/ppm (400 MHz, CDCl3): 7.37 (4 H, d, J 8.1, Ar-H), 7.16 (4 H, d, J 8.1, Ar-H), 2.88 (4 H, t, J 7.4, S-CH2-CH2), 1.62 (4 H, quin, J 7.4, 6.9, CH2-CH2-CH2), 1.38 (4 H, quin, J 6.9, 6.8, CH2-CH2-CH2), 1.31 (6 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 136.23, 131.82, 130.34, 119.37, 33.64, 29.27, 29.01, 28.94, 28.69

**BrBS11SBBr**

Yield: 2.52 g, 66.7 %. MP: 69 °C

*vmax* /cm-1: 2919, 2850, 1467, 1430, 1386, 1283, 1179, 1094, 1070, 1003, 804, 772, 724, 513, 478

δ H/ppm (400 MHz, CDCl3): 7.37 (4 H, d, J 8.1, Ar-H), 7.16 (4 H, d, J 8.1, Ar-H), 2.88 (4 H, t, J 7.6, S-CH2-CH2), 1.63 (4 H, quin, J 7.6, 7.0, CH2-CH2-CH2), 1.40 (4 H, quin, J 7.0, 6.9, CH2-CH2-CH2), 1.27 (10 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 136.32, 131.82, 130.37, 119.37, 33.70, 29.43, 29.42, 29.10, 29.00, 28.76

***1.1.2 CBSnSCB (1b)***

To a pre-dried flask, **1a** (1 eq) was added under argon. 4-cyanophenylboronic acid (2.2 eq) and tetrakis(triphenylphosphine)palladium(0) (0.025 eq) were added and a condenser fitted under argon. A mixture of aqueous sodium carbonate (2 mol L-1, 10 mL), ethanol (5 mL) and toluene (40 mL) was added with stirring. The reaction mixture was heated to 85 °C for 24 hours. The mixture was allowed to cool to room temperature and 32% hydrochloric acid (5 mL) was added dropwise to neutralise the sodium carbonate. The resulting mixture was filtered using vacuum filtration to remove the palladium catalyst, and the solvents removed under vacuum. Water (100 mL) and dichloromethane (100 mL) were added to the solid obtained. The organic layer was washed with water (2 x 50 mL) and dried over anhydrous magnesium sulphate. The magnesium sulphate was then removed by vacuum filtration and the solvent removed under vacuum to give a brown solid. The crude product was purified using a silica gel column with the eluent being 10% 40:60 petroleum ether and 90% dichloromethane (RF values quoted in product data). The collected solvent was evaporated under vacuum to leave a white solid which was recrystallised from ethanol (50 mL).

**Table 1.1.2** Quantities of reagents used in the syntheses of CBS*n*SCB(**1b**).

|  |  |  |  |
| --- | --- | --- | --- |
| *n* | BrBS*n*SBBr (**1a)** | 4-Cyanophenylboronic acid | Tetrakis(triphenylphosphine) palladium(0) |
| 1 | 3.00 g, 7.69x10-3 mol | 2.49 g, 1.69x10-2 mol | 222 mg, 1.92x10-4 mol |
| 3 | 1.20 g, 2.87x10-3 mol | 0.928 g, 6.31x10-3 mol | 82.9 mg, 7.18x10-5 mol |
| 4 | 2.80 g, 6.48x10-3 mol | 2.10 g, 1.42x10-2 mol | 187 mg, 1.62x10-4 mol |
| 5 | 1.20 g, 2.69x10-3 mol | 0.870 g, 5.92x10-3 mol | 77.7 mg, 6.73x10-5 mol |
| 6 | 1.00 g, 2.17x10-3 mol | 0.703 g, 4.78x10-3 mol | 62.8 mg, 5.43x10-5 mol |
| 7 | 1.50 g, 3.16x10-3 mol | 1.02 g, 6.95x10-3 mol | 91.2 mg, 7.90x10-5 mol |
| 9 | 2.00 g, 3.98x10-3 mol | 1.29 g, 8.76x10-3 mol | 115 mg, 9.95x10-5 mol |
| 11 | 1.52 g, 2.87x10-3 mol | 0.928 g, 6.31x10-3 mol | 82.0 mg, 7.10x10-5 mol |

**CBS1SCB**

Yield: 2.67 g, 79.9 %. RF: 0.34. MP: 187 °C.

*vmax* /cm-1: 2224, 1606, 1595, 1485, 1394, 1315, 1195, 1181, 1093, 1003, 847, 797, 735, 558, 517.

δ H/ppm (400 MHz, CDCl3): 7.75 (4 H, d, J 8.1, Ar-H), 7.69 (4 H, d, J 8.1, Ar-H), 7.56 (8 H, m, Ar-H), 4.48 (2 H, s, S-CH2-S)

δ C/ppm (100 MHz, CDCl3): 144.65, 137.84, 135.84, 132.70, 130.76, 127.77, 127.50, 118.81, 111.18, 39.68.

Elemental Analysis: Calculated for: C = 74.62%, H = 4.18%, N = 6.45%, S = 14.75%. Found: C = 74.62%, H = 4.21%, N = 6.40%, S = 14.74%

**CBS3SCB**

Yield: 0.520 g, 17.8 %. RF: 0.37

TCr- 139 °C TNTBN (39 °C) TNI 79 °C.

*vmax* /cm-1: 2221, 1604, 1594, 1484, 1392, 1250, 1178, 1093, 833, 810, 759, 563, 524.

δ H/ppm (400 MHz, CDCl3): 7.75 (4 H, d, J 7.9, Ar-H), 7.69 (4 H, d, J 7.9, Ar-H), 7.56 (4 H, d, J 7.7, Ar-H), 7.43 (4 H, d, J 7.7, Ar-H), 3.16 (4 H, t, J 6.9, S-CH2-CH2), 2.08 (2 H, quin, J 7.0, 6.9, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.75, 137.41, 136.64, 132.65, 129.19, 127.62, 127.34, 118.81, 110.99, 31.93, 28.14.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C29H22N2S2Na: 485.1122; Found: 485.1128

**CBS4SCB**

Yield: 0.432 g, 14.0 %. RF: 0.31

TCr- 209 °C TNI (169 °C).

*vmax* /cm-1: 2917, 2231, 1596, 1485, 1456, 1436, 1392, 1182, 1093, 849, 809, 735, 563, 519.

δ H/ppm (400 MHz, CDCl3): 7.71 (4 H, d, J 8.1, Ar-H), 7.66 (4 H, d, J 8.1, Ar-H), 7.50 (4 H, d, J 8.3, Ar-H), 7.39 (4 H, d, J 8.3, Ar-H), 3.00 (4 H, t, J 6.3, S-CH2-CH2), 1.87 (4 H, t, J 6.3, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.83, 137.89, 136.45, 132.67, 128.99, 127.58, 127.35, 118.89, 110.90, 32.72, 27.99.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C30H24N2S2Na: 499.1279; Found: 499.1262

**CBS5SCB**

Yield: 0.434 g, 32.9 %. RF: 0.47

TCr- 147 °C TNTBN (76 °C)TNI 106 °C.

*vmax* /cm-1: 2221, 1593, 1486, 1394, 1179, 1096, 1001, 808, 728, 564, 521, 453

δ H/ppm (400 MHz, CDCl3): 7.71 (4 H, d, J 8.1, Ar-H), 7.65 (4 H, d, J 8.1, Ar-H), 7.50 (4 H, d, J 8.1, Ar-H), 7.39 (4 H, d, J 8.1, Ar-H), 2.98 (4 H, t, J 7.1, S-CH2-CH2), 1.73 (4 H, quin, J 7.1, 7.3, CH2-CH2-CH2), 1.64 (2 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.85, 138.19, 136.29, 132.66, 128.80, 127.95, 127.55, 127.33, 118.90, 110.85, 32.96, 28.53, 27.92.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C31H26N2S2Na: 513.1435; Found: 513.1403

**CBS6SCB**

Yield: 0.268 g, 24.5 %. RF: 0.42

TCr- 190 °C TNI (162 °C).

*vmax* /cm-1: 2930, 2857, 2229, 1592, 1485, 1432, 1393, 1271, 1185, 1098, 1002, 807, 727, 562, 519, 456

δ H/ppm (400 MHz, CDCl3): 7.71 (4 H, d, J 8.2, Ar-H), 7.65 (4 H, d, J 8.2, Ar-H), 7.50 (4 H, d, J 8.1, Ar-H), 7.39 (4 H, d, J 8.1, Ar-H), 2.98 (4 H, t, J 7.3, S-CH2-CH2), 1.72 (4 H, quin, J 6.9, 7.3, CH2-CH2-CH2), 1.50 (4 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.89, 138.36, 136.21, 132.65, 128.68, 127.53, 127.33, 118.91, 110.82, 32.99, 28.85, 28.33.

Elemental Analysis: Calculated for: C = 76.15%, H = 5.59%, N = 5.55%, S = 12.70%. Found: C = 75.86%, H = 5.84%, N = 5.30%, S = 12.58%

**CBS7SCB**

Yield: 0.783 g, 47.8 %. RF: 0.47

TCr- 109 °C TNTBN (85 °C) TNI 116 °C.

*vmax* /cm-1: 2925, 2850, 2224, 1592, 1485, 1434, 1392, 1181, 1094, 1001, 851, 815, 728, 562, 520, 447

δ H/ppm (400 MHz, CDCl3): 7.73 (4 H, d, J 8.1, Ar-H), 7.68 (4 H, d, J 8.1, Ar-H), 7.53 (4 H, d, J 8.2, Ar-H), 7.41 (4 H, d, J 8.2, Ar-H), 2.99 (4 H, t, J 7.3, S-CH2-CH2), 1.72 (4 H, quin, J 7.3, 7.2, CH2-CH2-CH2), 1.49 (4 H, quin, J 7.2, 7.2, CH2-CH2-CH2), 1.39 (2 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.90, 138.48, 136.14, 132.65, 128.62, 127.52, 127.32, 118.92, 110.81, 33.03, 28.89, 28.69, 28.65.

Elemental Analysis: Calculated for: C = 76.41%, H = 5.83%, N = 5.40%, S = 12.36%. Found: C = 76.28%, H = 5.82%, N = 5.24%, S = 12.27%

**CBS9SCB**

Yield: 1.47 g, 67.6 %. RF: 0.34

TCr- 94 °C TNTBN (89 °C) TNI 118 °C.

*vmax* /cm-1: 2923, 2850, 2226, 1605, 1595, 1466, 1393, 1182, 1095, 1003, 851, 807, 724, 563, 520

δ H/ppm (400 MHz, CDCl3): 7.71 (4 H, d, J 8.0, Ar-H), 7.65 (4 H, d, J 8.0, Ar-H), 7.50 (4 H, d, J 8.2, Ar-H), 7.38 (4 H, d, J 8.0, Ar-H), 2.97 (4 H, t, J 7.4, S-CH2-CH2), 1.69 (4 H, quin, J 7.4, 6.9, CH2-CH2-CH2), 1.44 (4 H, quin, J 6.9, 6.6, CH2-CH2-CH2), 1.31 (6 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.92, 138.58, 136.09, 132.65, 128.58, 127.50, 127.32, 118.93, 110.79, 33.05, 29.32, 29.06, 28.97, 28.80.

Elemental Analysis: Calculated for: C = 76.88%, H = 6.27%, N = 5.12%, S = 11.73%. Found: C = 77.02%, H = 6.09%, N = 5.32%, S = 11.49%

**CBS11SCB**

Yield: 0.685 g, 41.5 %. RF: 0.44

TCr- 108 °C TNI 116 °C.

*vmax* /cm-1: 2920, 2848, 2226, 1591, 1485, 1396, 1187, 1100, 849, 810, 720, 558, 520

δ H/ppm (400 MHz, CDCl3): 7.71 (4 H, d, J 8.1, Ar-H), 7.66 (4 H, d, J 8.1, Ar-H), 7.50 (4 H, d, J 8.0, Ar-H), 7.38 (4 H, d, J 8.0, Ar-H), 2.97 (4 H, t, J 7.4, S-CH2-CH2), 1.69 (4 H, quin, J 7.4, 7.5, CH2-CH2-CH2), 1.44 (4 H, quin, J 6.9, 7.5, CH2-CH2-CH2), 1.29 (10 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 144.94, 138.61, 136.06, 132.65, 128.56, 127.49, 127.32, 118.93, 110.77, 33.06, 29.48, 29.46, 29.15, 29.00, 28.85.

Elemental Analysis: Calculated for: C = 77.31%, H = 6.66%, N = 4.87%, S = 11.15%. Found: C = 77.38%, H = 6.66%, N = 4.99%, S = 11.27%

*1.2 4'-({ω-[(4'-Cyano[1,1'-biphenyl]-4-yl)oxy]alkyl}thio)[1,1'-biphenyl]-4-carbonitriles (CBOnSCB)*



***1.2.1 4'-[(ω-Bromoalkyl)oxy][1,1'-biphenyl]-4-carbonitriles (CBOnBr) (2a)***

To a pre-dried flask, 4′-hydroxy-4-biphenylcarbonitrile (1 eq) and potassium carbonate (2 eq) were added and kept under argon. Acetone (50 mL) was added and the mixture stirred. To this, the appropriate 1,ω -dibromoalkane (6 eq) was syringed in and the reaction mixture refluxed overnight. The reaction mixture was allowed to cool to room temperature, filtered and the residue washed with acetone (100 mL). The filtrate was concentrated under vacuum to give a yellow solution which was added to 40:60 petroleum ether (100 mL). The resulting white precipitate was collected and recrystallised from ethanol (250 mL).

**Table 1.2.1** Quantities of reagents used in the syntheses of CBO*n*Br(**2a**).

|  |  |  |  |
| --- | --- | --- | --- |
| *n* | 1,ω-Dibromoalkane | 4′-Hydroxy-4-biphenylcarbonitrile | Potassium carbonate |
| 3 | 8.0 mL, 15.0 g, 7.43x10-2 mol | 2.40 g, 1.23x10-2 mol | 3.34 g, 2.48x10-2 mol |
| 5 | 10.5 mL, 17.7 g, 7.68x10-2 mol | 2.50 g, 1.28x10-2 mol | 3.60 g, 2.56x10-2 mol |
| 6 | 7.0 mL, 11.1g, 4.55x10-2 mol | 1.48 g, 7.58x10-3 mol | 2.10 g, 1.52x10-2 mol |
| 7 | 6.62 mL, 10.0g, 3.90x10-2 mol | 1.17 g, 6.00x10-3 mol | 1.66 g, 1.20x10-2 mol |
| 9 | 7.0 mL, 9.85 g, 3.44x10-2 mol | 1.12 g, 5.74x10-3 mol | 1.59 g, 1.14x10-2 mol |
| 11 | 6.0 mL, 8.0 g, 2.50x10-2 mol | 0.81 g, 4.17x10-3 mol | 1.17 g, 8.49x10-3 mol |

**CBO3Br**

Yield: 3.34 g, 85.9 %. MP: 102 °C

*vmax* /cm-1: 2220, 1602, 1518, 1493, 1467, 1291, 1242, 1213, 1178, 1021, 851, 820, 645, 565, 532.

δ H/ppm (400 MHz, CDCl3): 7.70 (2 H, d, J 8.1, Ar-H), 7.64 (2 H, d, J 8.1, Ar-H), 7.54 (2 H, d, J 8.3, Ar-H), 7.01 (2 H, d, J 8.3, Ar-H), 4.17 (2 H, t, J 5.9, O-CH2-CH2), 3.63 (2 H, t, J 6.3, Br-CH2-CH2), 2.35 (2 H, quin, J 5.9, 6.3, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.32, 145.16, 132.59, 131.79, 128.42, 127.14, 119.08, 115.12, 110.19, 65.45, 32.27, 29.90.

**CBO5Br**

Yield: 3.52 g, 79.9 %

TCr-80°C TNI (68 °C)

*vmax* /cm-1: 2945, 2869, 1603, 1494, 1474, 1396, 1292, 1245, 1202, 1178, 1038, 997, 822, 802, 734, 629, 564, 531.

δ H/ppm (400 MHz, CDCl3): 7.72 (2 H, d, J 8.0, Ar-H), 7.66 (2 H, d, J 8.0, Ar-H), 7.56 (2 H, d, J 8.4, Ar-H), 7.02 (2 H, d, J 8.4, Ar-H), 4.05 (2 H, t, J 6.3, O-CH2-CH2), 3.48 (2 H, t, J 6.8, Br-CH2-CH2), 1.99 (2 H, quin, J 7.2, 6.8, CH2-CH2-CH2), 1.89 (2 H, quin, J 7.5, 6.3, CH2-CH2-CH2), 1.69 (2 H, quin, J 7.5, 7.2, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.62, 145.23, 132.58, 131.45, 128.36, 127.10, 119.11, 115.07, 110.10, 67.75, 33.57, 32.46, 28.41, 24.84.

**CBO6Br**

Yield: 1.82 g, 75.9 %

TCr- 67 °C TNI 69 °C

*vmax* /cm-1: 2938, 2862, 2227, 1601, 1578, 1493, 1468, 1393, 1245, 1199, 1030, 980, 817, 727, 644, 558, 529.

δ H/ppm (400 MHz, CDCl3): 7.69 (2 H, d, J 7.9, Ar-H), 7.64 (2 H, d, J 7.9, Ar-H), 7.53 (2 H, d, J 8.1, Ar-H), 6.99 (2 H, d, J 8.1, Ar-H), 4.02 (2 H, t, J 6.5, O-CH2-CH2), 3.43 (2 H, t, J 6.8, Br-CH2-CH2), 1.87 (4 H, m, CH2-CH2-CH2), 1.53 (4 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.70, 145.26, 132.57, 131.38, 128.35, 127.09, 119.11, 115.08, 110.07, 67.90, 33.79, 32.67, 29.05, 27.92, 25.30.

**CBO7Br**

Yield: 2.00 g, 89.5 %

TCr- 59 °C TNI 70 °C

*vmax* /cm-1: 2939, 2857, 2221, 1602, 1518, 1494, 1472, 1391. 1289, 1244, 1176, 1031, 997, 820, 803, 734, 638, 564, 531.

δ H/ppm (400 MHz, CDCl3): 7.69 (2 H, d, J 8.1, Ar-H), 7.64 (2 H, d, J 8.1, Ar-H), 7.53 (2 H, d, J 8.3, Ar-H), 6.99 (2 H, d, J 8.3, Ar-H), 4.01 (2 H, t, J 6.3, O-CH2-CH2), 3.41 (2 H, t, J 6.9, Br-CH2-CH2), 1.85 (4 H, m, CH2-CH2-CH2), 1.46 (6 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.74, 145.27, 132.57, 131.33, 128.34, 127.09, 119.12, 115.08, 110.07, 68.02, 33.92, 32.71, 29.12, 28.52, 28.08, 25.90.

**CBO9Br**

Yield: 1.97 g, 85.7 %

TCr- 70 °C TNI 71 °C

*vmax* /cm-1: 2921, 2852, 2223, 1602, 1496, 1476, 1289, 1251, 1181, 1013, 1000, 825, 802, 721, 644, 562, 530.

δ H/ppm (400 MHz, CDCl3): 7.69 (2 H, d, J 8.1, Ar-H), 7.64 (2 H, d, J 8.1, Ar-H), 7.53 (2 H, d, J 8.4, Ar-H), 6.99 (2 H, d, J 8.4, Ar-H), 4.01 (2 H, t, J 6.6, O-CH2-CH2), 3.41 (2 H, t, J 6.9, Br-CH2-CH2), 1.84 (4 H, m, CH2-CH2-CH2), 1.43 (10 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.79, 145.29, 132.57, 131.29, 128.33, 127.08, 119.12, 115.09, 110.06, 68.13, 34.03, 32.80, 29.35, 29.26, 29.21, 28.69, 28.14, 26.01.

**CBO11Br**

Yield: 1.47 g, 82.3 %

TCr-78 °CTNI (66 °C)

*vmax* /cm-1: 2917, 2849, 2223, 1604, 1521, 1495, 1470, 1291, 1243, 1181, 1033, 1000, 852, 821, 814, 719, 650, 562, 530.

δ H/ppm (400 MHz, CDCl3): 7.69 (2 H, d, J 8.1, Ar-H), 7.64 (2 H, d, J 8.1, Ar-H), 7.53 (2 H, d, J 8.4, Ar-H), 6.99 (2 H, d, J 8.4, Ar-H), 4.01 (2 H, t, J 6.4, O-CH2-CH2), 3.41 (2 H, t, J 7.2, Br-CH2-CH2), 1.84 (4 H, m, CH2-CH2-CH2), 1.32 (14 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.81, 145.29, 132.57, 131.26, 128.32, 127.07, 119.13, 115.09, 110.05, 68.17, 34.07, 32.84, 29.52, 29.46, 29.42, 29.36, 29.23, 28.77, 28.18, 26.04.

***1.2.2 CBOnSBBr (2b)***

To a pre-dried flask, 4-bromothiophenol (1.1 eq) was added and kept under argon. Sodium hydroxide (1.32 eq) dissolved in ethanol (50 mL) (sonicated to ensure all the solid was in solution) was added to the 4-bromothiophenol. The mixture was stirred for 2 h at room temperature. **2a** (1 eq) in tetrahydrofuran (5 mL) was added and the reaction mixture stirred at room temperature for 24 h. The resulting white precipitate was collected and recrystallised from ethanol (150 mL).

**Table 1.2.2** Quantities of reagents used in the syntheses of CBO*n*SBBr (**2b**).

|  |  |  |  |
| --- | --- | --- | --- |
| *n* | CBO*n*Br (**2a**) | 4-Bromothiophenol | Sodium hydroxide |
| 3 | 2.00 g, 6.33x10-3 mol | 1.32 g, 6.96x10-3 mol | 0.334 g, 8.35x10-2 mol |
| 5 | 2.50 g, 7.26x10-3 mol | 1.51 g, 7.99x10-3 mol | 0.384 g, 9.59x10-3 mol |
| 6 | 1.50 g, 4.19x10-3 mol | 0.871 g, 4.61x10-3 mol | 0.221 g, 5.53x10-3 mol |
| 7 | 1.60 g, 4.30x10-3 mol | 0.894 g, 4.73x10-3 mol | 0.227 g, 5.68x10-3 mol |
| 9 | 1.50 g, 3.75x10-3 mol | 0.779 g, 4.12x10-3 mol | 0.198 g, 494x10-3 mol |
| 11 | 1.45 g, 3.39x10-3 mol | 0.705 g, 3.73x10-3 mol | 0.179 g, 4.47x10-3 mol |

**CBO3SBBr**

Yield: 1.30 g, 44.0 %. MP: 106 °C

*vmax* /cm-1: 2227, 1601, 1492, 1473, 1436, 1387, 1285, 1244, 1117, 1089, 1034, 1006, 935, 822, 804, 563, 533, 482.

δ H/ppm (400 MHz, CDCl3): 7.69 (2 H, d, J 8.1, Ar-H), 7.64 (2 H, d, J 8.1, Ar-H), 7.51 (2 H, d, J 8.3, Ar-H), 7.39 (2 H, d, J 8.3, Ar-H), 7.22 (2 H, d, J 8.3, Ar-H), 6.97 (2 H, d, J 8.3, Ar-H), 4.12 (2 H, t, J 6.0, O-CH2-CH2), 3.13 (2 H, t, J 6.8, S-CH2-CH2), 2.13 (2 H, quin, J 6.8, 6.0, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.33, 145.17, 135.36, 132.59, 131.99, 131.69, 130.76, 128.39, 127.13, 119.89, 119.10, 115.07, 110.17, 65.94, 30.28, 28.79.

**CBO5SBBr**

Yield: 1.54 g, 46.9 %. MP: 101 °C

*vmax* /cm-1: 2923, 2859, 2223, 1603, 1494, 1472, 1461, 1431, 1381, 1293, 1244, 1171, 1094, 1028, 1012, 996, 854, 825, 803, 739, 563, 529, 481.

δ H/ppm (400 MHz, CDCl3): 7.69 (2 H, d, J 8.1, Ar-H), 7.63 (2 H, d, J 8.1, Ar-H), 7.53 (2 H, d, J 8.3, Ar-H), 7.38 (2 H, d, J 8.3, Ar-H), 7.19 (2 H, d, J 8.3, Ar-H), 6.97 (2 H, d, J 8.3, Ar-H), 4.01 (2 H, t, J 6.5, O-CH2-CH2), 2.93 (2 H, t, J 7.2, S-CH2-CH2), 1.83 (2 H, quin, J 7.1, 6.5, CH2-CH2-CH2), 1.72 (2 H, quin, J 7.2, 7.4, CH2-CH2-CH2), 1.63 (2 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.63, 145.24, 135.92, 132.58, 131.90, 131.43, 130.60, 128.36, 127.10, 119.61, 119.11, 115.07, 110.10, 67.77, 33.64, 28.74, 28.70, 25.27.

**CBO6SBBr**

Yield: 0.356 g, 18.2 %. MP: 115 °C

*vmax* /cm-1: 2933, 2858, 2226, 1602, 1493, 1474, 1466, 1387, 1290, 1266, 1247, 1179, 1089, 1061, 1002, 979, 823, 806, 564, 534, 479

δ H/ppm (400 MHz, CDCl3): ): 7.69 (2 H, d, J 8.2, Ar-H), 7.63 (2 H, d, J 8.2, Ar-H), 7.52 (2 H, d, J 8.3, Ar-H), 7.38 (2 H, d, J 8.3, Ar-H), 7.18 (2 H, d, J 8.3, Ar-H), 6.98 (2 H, d, J 8.3, Ar-H), 4.00 (2 H, t, J 6.5, O-CH2-CH2), 2.93 (2 H, t, J 7.2, S-CH2-CH2), 1.83 (2 H, quin, J 7.2, 6.5, CH2-CH2-CH2), 1.72 (2 H, quin, J 7.2, 7.4, CH2-CH2-CH2), 1.63 (4 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.70, 145.25, 136.10, 132.57, 131.87, 131.36, 130.44, 128.34, 127.08, 119.49, 119.11, 115.07, 110.08, 67.92, 33.60, 30.95, 28.91, 28.47, 25.64.

**CBO7SBBr**

Yield: 1.43 g, 69.2 %. MP: 88 °C

*vmax* /cm-1: 2940, 2853, 2224, 1603, 1495, 1471, 1432, 1387, 1294, 1269, 1174, 1094, 1029, 1003, 823, 806, 734, 661. 562, 528, 482.

δ H/ppm (400 MHz, CDCl3): ): 7.69 (2 H, d, J 8.2, Ar-H), 7.64 (2 H, d, J 8.2, Ar-H), 7.52 (2 H, d, J 8.5, Ar-H), 7.38 (2 H, d, J 8.5, Ar-H), 7.17 (2 H, d, J 8.5, Ar-H), 6.98 (2 H, d, J 8.5, Ar-H), 4.00 (2 H, t, J 6.4, O-CH2-CH2), 2.90 (2 H, t, J 7.6, S-CH2-CH2), 1.80 (2 H, quin, J 6.5, 6.4, CH2-CH2-CH2), 1.66 (2 H, quin, J 7.6, 7.2, CH2-CH2-CH2), 1.43 (6 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.74, 145.26, 136.19, 132.57, 131.85, 131.32, 130.39, 128.34, 127.08, 119.43, 119.12, 115.08, 110.07, 68.03, 33.64, 29.12, 28.89, 28.87, 28.65, 25.92.

**CBO9SBBr**

Yield: 0.569 g, 29.8 %. MP: 94 °C

*vmax* /cm-1: 2916, 2851, 2224, 1603, 1494, 1469, 1385, 1293, 1268, 1248, 1173, 1092, 1030, 1003, 822, 807, 727, 562, 529, 482.

δ H/ppm (400 MHz, CDCl3): ): 7.69 (2 H, d, J 8.1, Ar-H), 7.64 (2 H, d, J 8.1, Ar-H), 7.53 (2 H, d, J 8.4, Ar-H), 7.38 (2 H, d, J 8.4, Ar-H), 7.17 (2 H, d, J 8.4, Ar-H), 6.99 (2 H, d, J 8.4, Ar-H), 4.00 (2 H, t, J 6.4, O-CH2-CH2), 2.89 (2 H, t, J 7.4, S-CH2-CH2), 1.81 (2 H, quin, J 7.0, 6.4, CH2-CH2-CH2), 1.64 (2 H, quin, J 7.4, 7.5, CH2-CH2-CH2), 1.37 (10 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.78, 145.28, 136.26, 132.57, 131.84, 131.29, 130.35, 128.33, 127.08, 119.38, 119.12, 115.08, 110.06, 68.13, 33.66, 29.37, 29.27, 29.20, 29.05, 28.96, 28.73, 26.00.

**CBO11SBBr**

Yield: 1.44 g, 79.1 %. MP: 98 °C

*vmax* /cm-1: 2918, 2850, 2224, 1602, 1495, 1472, 1385, 1294, 1269, 1250, 1174, 1094, 1001, 815, 806, 737, 562, 530, 482.

δ H/ppm (400 MHz, CDCl3): ): 7.69 (2 H, d, J 8.2, Ar-H), 7.64 (2 H, d, J 8.2, Ar-H), 7.52 (2 H, d, J 8.4, Ar-H), 7.38 (2 H, d, J 8.4, Ar-H), 7.17 (2 H, d, J 8.4, Ar-H), 6.99 (2 H, d, J 8.4, Ar-H), 4.00 (2 H, t, J 6.6, O-CH2-CH2), 2.89 (2 H, t, J 7.4, S-CH2-CH2), 1.81 (2 H, quin, J 7.0, 6.6, CH2-CH2-CH2), 1.63 (2 H, quin, J 7.4, 7.5, CH2-CH2-CH2), 1.29 (14 H, m, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.80, 145.29, 136.30, 132.57, 131.83, 131.27, 130.33, 128.32, 127.07, 119.36, 119.12, 115.09, 110.05, 68.17, 33.66, 29.52, 29.47, 29.45, 29.37, 29.23, 29.12, 28.98, 28.77, 26.04.

***1.2.3 CBOnSCB (2c)***

To a pre-dried flask, **2b** (1eq) was added and kept under argon. 4-Cyanophenylboronic acid (1.1 eq) and tetrakis(triphenylphosphine)palladium(0) (0.025 eq) were added and a condenser fitted. A mixture of an aqueous solution of sodium carbonate (2 mol L-1, 10 mL), ethanol (5 mL) and toluene (40 mL) was added with stirring. The reaction mixture was heated to 85 °C for 24 hours. The reaction mixture was allowed to cool to room temperature and 32% hydrochloric acid (5 mL) was added dropwise to neutralise the sodium carbonate, and filtered to remove the palladium catalyst. The solvent was removed and water (100 mL) and dichloromethane (100 mL) added. The organic layer was washed with water (2 x 50 mL), dried over anhydrous magnesium sulphate and the solvent removed under vacuum. The crude brown solid was purified using a silica gel column with the eluent being 20% 40:60 petroleum ether and 80% dichloromethane (RF values quoted in product data). The collected solvent was evaporated under vacuum to give a white solid which was recrystallised from ethanol (50 mL).

**Table 1.2.3** Quantities of reagents used in the syntheses of CBO*n*SCB (**2c**).

|  |  |  |  |
| --- | --- | --- | --- |
| *n* | CBOnSBBr (**2b**) | 4-Cyanophenylboronic acid | Tetrakis(triphenylphosphine) palladium(0) |
| 3 | 0.650 g, 1.53x10-3 mol | 0.270 g, 1.84x10-3 mol | 44.0 mg, 3.83x10-5 mol |
| 5 | 1.40 g, 3.09x10-3 mol | 0.500 g, 3.40x10-3 mol | 89.0 mg, 7.73x10-5 mol |
| 6 | 0.300 g, 6.43x10-4 mol | 0.123 g, 8.36x10-4 mol | 18.6 mg, 1.61x10-5 mol |
| 7 | 1.30 g, 2.71x10-3 mol | 0.439 g, 2.99x10-3 mol | 78.3 mg, 6.78x10-5 mol |
| 9 | 0.550 g, 1.08x10-3 mol | 0.190 g, 1.30x10-3 mol | 31.2 mg, 2.7x10-5 mol |
| 11 | 1.25 g, 2.33x10-3 mol | 0.376 g, 2.56x10-3 mol | 67.3 mg, 5.83x10-5 mol |

**CBO3SCB**

Yield: 0.358 g, 52.4 %. RF: 0.23

TCr- 141 °CTNI (138 °C).

*vmax* /cm-1: 2223, 1602, 1493, 1395, 1289, 1246, 1178, 1096, 1030, 997, 821, 556, 525

δ H/ppm (400 MHz, CDCl3): 7.67 (8 H, m, Ar-H), 7.52 (4 H, m, Ar-H), 7.44 (2 H, d, J 7.8, Ar-H), 6.99 (2 H, d, J 8.3, Ar-H), 4.15 (2 H, t, J 6.1, O-CH2-CH2), 3.21 (2 H, t, J 6.7, S-CH2-CH2), 2.20 (2 H, quin, J 6.7, 6.1, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 159.37, 145.12, 144.80, 137.57, 136.53, 132.67, 132.60, 131.67, 129.03, 128.39, 127.64, 127.36, 127.10, 119.08, 118.90, 115.07, 110.89, 110.20, 66.00, 29.67, 28.82.

Elemental Analysis: Calculated for: C = 78.00%, H = 4.97%, N = 6.27%, S = 7.18%. Found: C = 78.15%, H = 4.92%, N = 6.40%, S = 7.19%

**CBO5SCB**

Yield: 0.314 g, 21.4 %. RF: 0.37

TCr- 127 °C TNTBN (81 °C) TNI 140 °C.

*vmax* /cm-1: 2941, 2857, 2222, 1602, 1494, 1472, 1395, 1288, 1247, 1180, 1096, 1043, 997, 811, 735, 566, 523.

δ H/ppm (400 MHz, CDCl3): 7.76 (8 H, m, Ar-H), 7.51 (4 H, m, Ar-H), 7.40 (2 H, d, J 8.1, Ar-H), 6.98 (2 H, d, J 8.3, Ar-H), 4.00 (2 H, t, J 6.5, O-CH2-CH2), 3.02 (2 H, t, J 7.2, S-CH2-CH2), 1.87 (2 H, quin, J 7.1, 6.5, CH2-CH2-CH2), 1.69 (2 H, quin, J 7.2, 7.4, CH2-CH2-CH2), 1.67 (2 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.64, 145.19, 144.88, 138.25, 136.25, 132.65, 132.59, 131.42, 128.81, 128.35, 127.55, 127.33, 127.07, 119.10, 118.92, 115.09, 115.07, 110.80, 110.10, 67.80, 33.03, 28.80, 28.75, 25.37.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C31H26N2SONa: 479.1664; Found: 497.1644

**CBO6SCB**

Yield: 0.131 g, 41.7 %. RF: 0.20

TCr- 185 °C TNI (184 °C).

*vmax* /cm-1: 2941, 2857, 2229, 1603, 1494, 1474, 1394, 1289, 1246, 1180, 1097, 1032, 1000, 851, 822, 810, 729, 560, 522.

δ H/ppm (400 MHz, CDCl3): 7.67 (8 H, m, Ar-H), 7.51 (4 H, m, Ar-H), 7.40 (2 H, d, J 8.0, Ar-H), 6.98 (2 H, d, J 8.3, Ar-H), 4.01 (2 H, t, J 6.4, O-CH2-CH2), 3.00 (2 H, t, J 7.2, S-CH2-CH2), 1.80 (4 H, m, CH2-CH2-CH2), 1.54 (4 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.70, 145.22, 144.90, 138.41, 136.18, 132.65, 132.58, 131.38, 128.68, 128.35, 127.53, 127.33, 127.08, 119.10, 118.92, 115.06, 110.81, 110.10, 67.94, 33.01, 29.11, 28.94, 28.58, 25.69.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C32H28N2SONa: 511.1820; Found: 511.1813

**CBO7SCB**

Yield: 0.596 g, 43.9 %. RF: 0.32

TCr- 118 °C TNTBN (88 °C)TNI 149 °C.

*vmax* /cm-1: 2936, 2854, 2225, 1602, 1494, 1393, 1290, 1244, 1178, 1096, 1030, 1000, 851, 809, 729, 563, 521.

δ H/ppm (400 MHz, CDCl3): 7.66 (8 H, m, Ar-H), 7.52 (4 H, t, J 8.0, Ar-H), 7.39 (2 H, d, J 8.0, Ar-H), 6.98 (2 H, d, J 8.0, Ar-H), 4.00 (2 H, t, J 6.2, O-CH2-CH2), 2.99 (2 H, t, J 7.3, S-CH2-CH2), 1.81 (2 H, quin, J 6.9, 6.2, CH2-CH2-CH2), 1.69 (2 H, quin, J 6.2, 7.3, CH2-CH2-CH2), 1.67 (6 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.74, 145.23, 144.91, 138.51, 136.12, 132.65, 132.58, 131.33, 128.63, 128.34, 127.52, 127.32, 127.07, 119.10, 118.92, 115.07, 110.80, 110.09, 68.04, 33.04, 29.15, 28.92, 28.90, 28.74, 25.94.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C33H30N2SONa: 525.1977; Found: 525.1992

**CBO9SCB**

Yield: 0.226 g, 39.4 %. RF: 0.26

TCr- 104 °C TNTBN (85 °C) TNI 143 °C.

*vmax* /cm-1: 2922, 2850, 2224, 1600, 1494, 1468, 1290, 1250, 1178, 1098, 1037, 1000, 854, 806, 723, 564, 520.

δ H/ppm (400 MHz, CDCl3): 7.67 (8 H, m, Ar-H), 7.52 (4 H, t, J 8.5, Ar-H), 7.39 (2 H, d, J 8.5, Ar-H), 6.98 (2 H, d, J 8.5, Ar-H), 4.00 (2 H, t, J 6.4, O-CH2-CH2), 2.98 (2 H, t, J 7.4, S-CH2-CH2), 1.80 (2 H, quin, J 7.1, 6.4, CH2-CH2-CH2), 1.69 (2 H, quin, J 6.9, 7.4, CH2-CH2-CH2), 1.67 (10 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.76, 145.25, 144.93, 138.58, 136.06, 132.66, 132.58, 131.29, 128.55, 128.34, 127.51, 127.32, 127.08, 119.14, 118.96, 115.07, 110.76, 110.05, 68.13, 33.03, 29.41, 29.31, 29.22, 29.10, 28.98, 28.83, 26.03.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C35H34N2SONa: 553.2290; Found: 553.2283

**CBO11SCB**

Yield: 0.447 g, 34.3 %. RF: 0.31

TCr- 114 °CTNI 137 °C.

*vmax* /cm-1: 2920, 2848, 2223, 1600, 1494, 1465, 1394, 1290, 1250, 1177, 1000, 854, 807, 722, 565, 520.

δ H/ppm (400 MHz, CDCl3): 7.67 (8 H, m, Ar-H), 7.51 (4 H, t, J 8.2, Ar-H), 7.38 (2 H, d, J 8.2, Ar-H), 6.99 (2 H, d, J 8.2, Ar-H), 4.00 (2 H, t, J 6.6, O-CH2-CH2), 2.95 (2 H, t, J 7.3, S-CH2-CH2), 1.87 (2 H, quin, J 7.0, 6.6, CH2-CH2-CH2), 1.69 (2 H, quin, J 7.3, 7.9, CH2-CH2-CH2), 1.67 (14 H, m, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 159.79, 145.27, 144.94, 138.63, 136.06, 132.65, 132.57, 131.28, 128.56, 128.32, 127.49, 127.32, 127.07, 119.11, 118.93, 115.08, 110.78, 110.06, 68.17, 33.06, 29.54, 29.50, 29.48, 29.38, 29.23, 29.16, 29.01, 28.87, 26.05.

MS (ESI+, m/z) = [M+Na]+ : Calculated for C37H38N2SONa: 581.2603; Found: 581.2599

*1.3 34-{6-[(4'-Cyano[1,1'-biphenyl]-4-yl)thio]hexyl}[11,21:24,31-terphenyl]-14-carbonitrile (CBS6CT)*



***1.3.1 6-Bromo-1-(4'-bromo[1,1'-biphenyl]-4-yl)hexan-1-one (3a)***

Aluminium trichloride (7.50 g, 0.056 mol) and dry dichloromethane (60 mL) was stirred under argon at 0˚C in a pre-dried flask wrapped in tin foil. A solution of 6-bromohexanoyl chloride (7.2 mL, 0.047 mol) and 4-bromobiphenyl (10.9 g, 0.047 mol) in dry dichloromethane (50 mL) was added dropwise. The temperature allowed to increase to room temperature and mixture stirred overnight. The reaction mixture was added to water (250 mL) and extracted using dichloromethane (100 mL). The organic fraction was washed using water (3 x 50 mL) and dried over anhydrous magnesium sulphate. The magnesium sulphate was removed by vacuum filtration and the solvent was removed under vacuum to give an off white/peach solid. The crude product was recrystallised from ethanol (250 mL) to give a white solid.

Yield: 10.15 g, 53.2%.. MP: 81 °C

*vmax* /cm-1: 2938, 1678, 1604, 1477, 1389, 1365, 1262, 1208, 1189, 1070, 1000, 969, 822, 794, 723, 664, 574

δ H/ppm (400 MHz, CDCl3): 8.02 (2 H, d, J 8.3, Ar-H), 7.65 (2 H, d, J 8.3, Ar-H), 7.59 (2 H, d, J 8.4, Ar-H), 7.49 (2 H, d, J 8.4, Ar-H), 3.44 (2 H, t, J 6.9, Br-CH2), 3.03 (2 H, t, J 7.2, C(=O)-CH2), 1.93 (2 H, quin, J 7.2, 6.9, CH2-CH2-CH2), 1.79 (2 H, quin, J 7.6, 7.2, CH2-CH2-CH2), 1.56 (2 H, quin, J 7.6, 7.2, CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 199.45, 144.40, 138.78, 135.94, 132.11, 128.82, 128.73, 127.07, 122.66, 38.37, 33.65, 32.64, 27.90, 23.37.

***1.3.2 4-Bromo-4'-(6-bromohexyl)-1,1'-biphenyl (3b)***

A mixture of **3a** (10.0 g, 0.024 mol), trifluoroacetic acid (100 mL) and dry dichloromethane (70 mL) was cooled to 0˚C with stirring under argon in a pre-dried flask. Triethylsilane (30 mL) was added via a syringe, the mixture allowed to warm to room temperature and stirred overnight. The reaction mixture was added to dichloromethane (100 mL) and water (300 mL), the organic layer was washed using water (3x 50 mL), dried over anhydrous magnesium sulphate, and the solvent was removed under vacuum to leave a peach solid. The crude product was recrystallised from ethanol (150 mL) to give a pale peach solid.

Yield: 6.77 g, 70.8%. MP: 76 °C

*vmax* /cm-1: 2931, 2856, 1479, 1465, 1390, 1235, 1189, 1077, 1000, 804, 726, 646, 503

δ H/ppm (400 MHz, CDCl3) 7.55 (2 H, d, J 8.2, Ar-H), 7.46 (4 H, t, J 8.2, Ar-H), 7.24 (2 H, d, J 8.2, Ar-H), 3.41 (2 H, t, J 6.8, Br-CH2), 2.66 (2 H, t, J 7.3, Ar-CH2), 1.87 (2 H, quin, J 7.3, 7.0, CH2-CH2-CH2), 1.67 (2 H, quin, J 7.5, 6.8, CH2-CH2-CH2), 1.48 (2 H, quin, J 7.4, 7.0 CH2-CH2-CH2), 1.40 (2 H, quin, J 7.4, 7.5 CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3) 142.18, 140.03, 137.42, 131.81, 128.96, 128.57, 126.82, 121.21, 35.44, 33.95, 32.73, 31.21, 28.40, 28.03.

***1.3.3 4-Bromo-4'-{6-[(4-bromophenyl)sulfanyl]hexyl}-1,1'-biphenyl (3c)***

4-Bromothiophenol (1.49 g, 7.89x10-3 mol) was placed in a pre-dried flask and kept under argon. To this was added sodium hydroxide (0.379 g, 9.47x10-3 mol) dissolved in ethanol (30 mL), sonicated to ensure all the solid was in solution, and the mixture stirred for 2 h at room temperature. **3b** (2.5 g, 6.31x10-3 mol) in tetrahydrofuran (5 mL) was added and the mixture stirred at room temperature for a further 24 h. A white precipitate, sodium bromide, was produced. The solvent was removed under vacuum, diethyl ether added (100 mL), and the sodium bromide removed using vacuum filtration. The solvent was removed under vacuum to leave a pale yellow solid which was recrystallised from ethanol (100 mL).

Yield: 2.04 g, mol, 64.2%. MP: 97 °C

*vmax* /cm-1: 2926, 2852, 1482, 1472, 1465, 1385, 1095, 1076, 1008, 1000, 801, 724, 508, 478.

δ H/ppm (400 MHz, CDCl3): 7.54 (2 H, d, J 8.4, Ar-H), 7.45 (4 H, t, J 8.5, 8.4, Ar-H), 7.38 (2 H, d, J 8.0, Ar-H), 7.23 (2 H, d, J 8.0, Ar-H), 7.17 (2 H, d, J 8.5, Ar-H), 2.89 (2 H, t, J 7.3, S-CH2), 2.64 (2 H, t, J 7.5, Ar-CH2), 1.64 (4 H, quin, J 7.5, 7.3, CH2-CH2-CH2), 1.47 (2 H, quin, J 7.3, CH2-CH2-CH2), 1.37 (2 H, quin, J 7.5, CH2-CH2-CH2)

δ C/ppm (100 MHz, CDCl3): 142.23, 140.02, 137.40, 136.20, 131.85, 131.81, 130.38, 128.95, 128.56, 126.81, 121.21, 119.42, 35.45, 33.63, 31.23, 28.88, 28.75, 28.58.

***1.3.4 CBS6CT (3d)***

To a stirred mixture of **3c** (1.5 g, 2.97x10-3 mol), 4-cyanophenylboronic acid (0.480 g, 3.27x10-3 mol) and tetrakis(triphenylphosphine)palladium(0) (0.086 g, 7.53x10-5 mol) in a pre-dried flask under argon, was added a mixture of aqueous sodium carbonate (2 mol L-1, 10 mL), ethanol (5 mL) and toluene (29 mL). The reaction mixture was heated to 85 °C for 24 h. The mixture was allowed to cool to room temperature and 32% hydrochloric acid (5 mL) was added dropwise. The mixture was filtered and the solvent removed to yield a mixture of a white and pale yellow solids. Water (100 mL) and dichloromethane (100 mL) were added. the organic layer was washed with water (2 x 50 mL), dried over anhydrous magnesium sulphate, and the solvent was removed under vacuum to give a brown solid. The crude product was purified using a silica gel column with the eluent being 10% 40:60 petroleum ether and 90% dichloromethane (RF: 0.43). The collected solvent was evaporated under vacuum to leave a yellow solid which was recrystallised from toluene (50 mL).

Yield: 0.335 g, 20.5 %

TCr- 132 °C TNTBN 144 °C TNI 238 °C.

*vmax* /cm-1: 2927, 2851, 2228, 1604, 1486, 1394, 1260, 1181, 1096, 1002, 808, 560, 519.

δ H/ppm (400 MHz, CDCl3): 7.69 (12 H, m, Ar-H), 7.55 (2 H, d, J 8.0, Ar-H), 7.50 (2 H, d, J 8.2, Ar-H), 7.39 (2 H, d, J 8.2, Ar-H), 7.27 (2 H, d, J 8.0, Ar-H), 2.98 (2 H, t, J 7.2, S-CH2-CH2), 2.66 (2 H, t, J 7.5, Ar-CH2-CH2), 1.69 (4 H, sept, J 7.4, 7.5, 7.2, CH2-CH2-CH2), 1.50 (2 H, quin, J 7.2, 7.4, CH2-CH2-CH2), 1.42 (2 H, quin, J 7.5, 7.4 CH2-CH2-CH2).

δ C/ppm (100 MHz, CDCl3): 145.16, 144.91, 142.37, 141.43, 138.51, 137.68, 137.57, 136.11, 132.66, 132.65, 128.99, 128.65, 127.58, 127.58, 127.53, 127.52, 127.32, 126.94, 118.98, 118.94, 110.88, 110.78, 35.49, 33.03, 31.25, 28.90, 28.79, 28.65.

Elemental Analysis: Calculated for: C = 83.17%, H = 5.88%, N = 5.11%, S = 5.84%. Found: C = 82.90%, H = 5.77%, N = 5.21%, S = 5.74%

**2. Phase Diagrams**

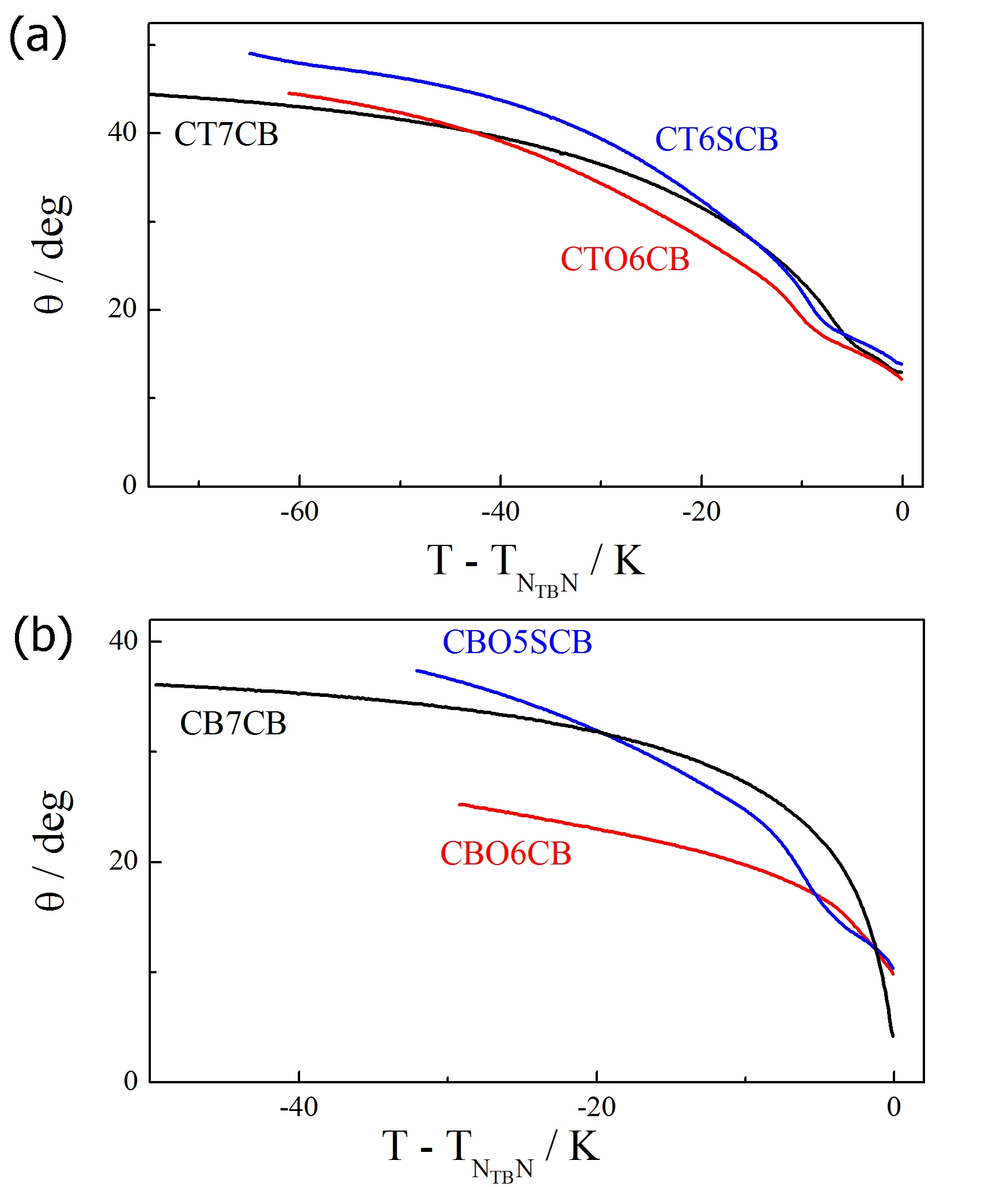
**Figure SI1.** Phase diagram constructed for binary mixtures of CBS1SCB and CB7CB. Open circles denote nematic-isotropic transitions, and filled circles twist-bend nematic-nematic transitions. The solid lines indicate trend lines drawn for the nematic-isotropic, and the twist-bend nematic-nematic transition temperatures. The broken line indicates the melting points.

**Figure SI2.** Phase diagram constructed for binary mixtures of CBS11SCB and CB7CB. Open circles denote nematic-isotropic transitions, and filled circles twist-bend nematic-nematic transitions. The solid lines indicate trend lines drawn for the nematic-isotropic, and the twist-bend nematic-nematic transition temperatures. The broken line indicates the melting points.

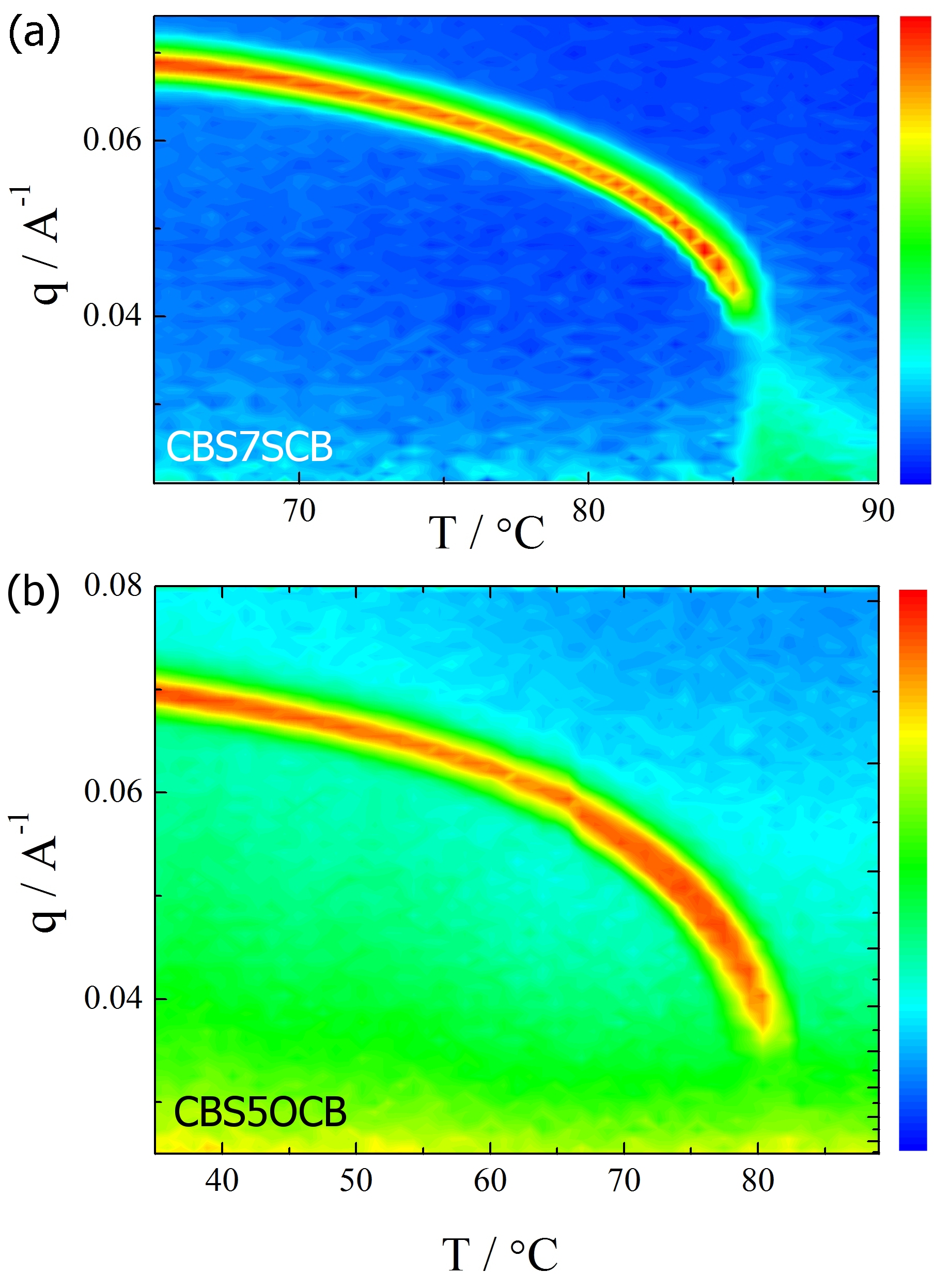
**Figure SI3.** Phase diagram constructed for binary mixtures of CBS5SCB and CB7CB. Open circles denote nematic-isotropic transitions, and filled circles twist-bend nematic-nematic transitions. The solid lines indicate trend lines drawn for the nematic-isotropic, and the twist-bend nematic-nematic transition temperatures. The broken line indicates the melting points.

**Figure SI4.** Phase diagram constructed for binary mixtures of CBS3OCB and CB7CB. Open circles denote nematic-isotropic transitions, and filled circles twist-bend nematic-nematic transitions. The solid lines indicate trend lines drawn for the nematic-isotropic, and the twist-bend nematic-nematic transition temperatures. The broken line indicates the melting points.

**Figure SI5.** Phase diagram constructed for binary mixtures of CBS11OCB and CB7CB. Open circles denote nematic-isotropic transitions, and filled circles twist-bend nematic-nematic transitions. The solid lines indicate trend lines drawn for the nematic-isotropic, and the twist-bend nematic-nematic transition temperatures. The broken line indicates the melting points.



**Figure SI6.** Dependence of the conical tilt angle on temperature.

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**Figure SI7.** Temperature evolution of the magnitude of wavevector related to heliconical pitch in the NTB phase of (a) CBS7SCB and (b) CBS5OCB determined by TReXS method.