Electronic Supplementary Information

A Triphenylene-based Small Molecule Compatibiliser using Incompatible Pendent Chains

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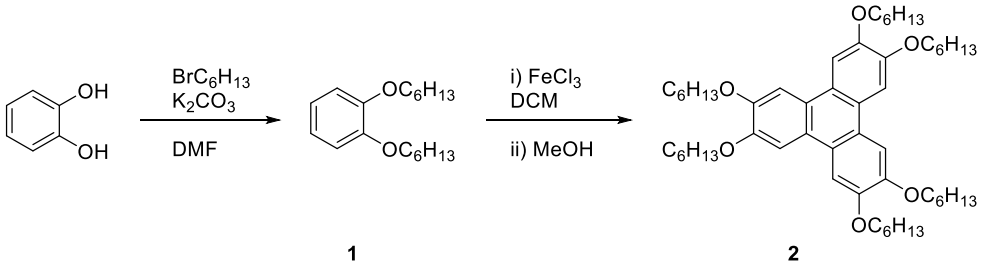


Scheme S1. Synthesis of TP6

Synthesis of 1,2-dihexyloxybenzene (1)

To a solution of K_2CO_3 (5.02 g, 36.4 mmol, 2 equiv.) and catechol (2.00 g, 18.2 mmol, 1 equiv.) in DMF (1 mL), was added dropwise 1-bromohexane (7.7 mL, 54.5 mmol, 3 equiv.). The mixture was stirred at 120 °C for 20 h. The solvent was evaporated *in vacuo* and resulting the solid was filtered through a pad of silica (eluent : ethyl acetate). Purification by chromatography (SiO_2, hexane/ethyl acetate = 20:1) afforded **1** as a colourless oil (3.69 g, 77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 4H, Ar*CH*), 3.99 (t, *J* = 6.7 Hz, 4H, Ar-O-*CH*$_2$-), 1.88 - 1.72 (m, 4H, -*CH*$_2$-), 1.52 - 1.23 (m, 6H, -*CH*$_2$-), 0.90 (t, *J* = 7.0 Hz, 3H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (Ar*C*), 121.2 (Ar*CH*), 114.3 (Ar*CH*), 69.5 (Ar-O-*CH*$_2$-), 31.8 (-*CH*$_2$-), 29.5 (-*CH*$_2$-), 25.9 (-*CH*$_2$-), 22.8 (-*CH*$_2$-), 14.2 (-*CH*$_3$). HRMS (TOF ES+): m/z $[M+H]^+$= 279.2250 (Calculated : 279.2246). IR : (neat)/cm^{-1} 2954, 2927, 2859, 1252 (Ar-O-R stretching), 836.

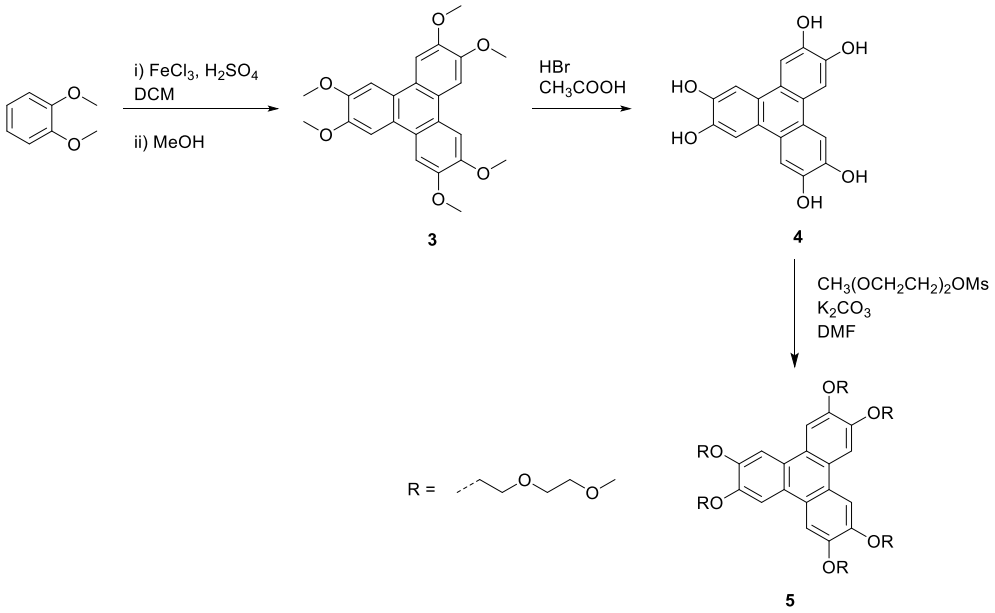
Synthesis of 2,3,6,7,10,11-hexahexyloxytriphenylene (2 - TP6)

To a vigorously stirred solution of $FeCl_3$ (3.5 g, 21.57 mmol, 9 equiv.) in CH_2Cl_2 (26 mL) was added sulphuric acid (2 drops) and 1,2-dihexyloxybenzene **1** (2.00 g, 7.19 mmol, 3 equiv.). The dark blue solution was stirred at room temperature for 1 h. The reaction mixture was then cooled down to 0 °C and methanol (90 mL) was slowly added until a precipitate was formed. After 2 h at 0 °C, the green solution was filtered and the precipitate was washed with cold methanol. The gray solid was dissolved in CH_2Cl_2 and purified through a pad of silica. The solvent was evaporated. Purification by column chromatography (SiO_2, hexane/CH_2Cl_2 = 1:1) afforded **2** as a white crystalline solid (1.220 g, 61%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 6H, Ar*CH*), 4.23 (t, *J* = 6.6 Hz, 12H, Ar-O-*CH*$_2$-), 2.04 - 1.80 (m, 12H, -*CH*$_2$-), 1.66 - 1.51 (m, 12H, -*CH*$_2$-), 1.49 - 1.30 (m, 24H, -*CH*$_2$-), 0.93 (t, *J* = 7.0 Hz, 18H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 (C), 123.8 (C), 107.6 (C), 69.9 (OCH_2), 31.8 (CH_2), 29.6 (CH_2), 26.0 (CH_2), 22.8 (CH_2), 14.2 (CH_3). HRMS (TOF ES+): m/z$[M+H]^+$= 828.6, m/z$[M+Na]^+$= 851.6169 (Calculated

: 851.6166), m/z[M+K]$^{+}$= 867.6. IR : (neat)/cm^{-1} 2923,2855 (alkanes); 1617, 1516, 1435 (aromatic ring stretch); 1257 (aromatic ether Ar-O-C); 1169, 836.

Synthesis of TP6EO2M



Scheme S2. Synthesis of TP6EO2M

Synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene (3)

To a suspension of $FeCl_3$ (36.96 g, 227.85 mmol, 9.3 equiv.) and conc. H_2SO_4 (0.5 mL) in CH_2Cl_2 (200 mL), was added dropwise a solution of veratrole (9.4 mL, 73.5 mmol, 3 equiv.) in CH_2Cl_2 (100 mL). The black mixture was stirred at room temperature for 3 h. The mixture was then cooled down to 0 °C and methanol (300 mL) was slowly added. The mixture was further stirred for 0.5 h. The precipitate was filtered, washed with methanol, and dried. The grey solid **3** (7.75 g, 78%) was used in the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 6H, Ar*H*), 4.13 (s, 18H, -O*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0 (Ar*C*), 123.4 (Ar*C*), 104.6 (Ar*CH*), 56.3 (-O*CH*$_3$). HRMS (TOF ES+): m/z[M+Na]$^{+}$= 431.1741 (Calculated : 431.1471). m.p.: 312-316 °C. IR : (neat)/cm^{-1} 1620, 1518 (aromatic ring stretch).

Synthesis of 2,3,6,7,10,11-Hexahydroxytriphenylene (4)

A solution of **3** (3.00 g, 7.2 mmol, 1 equiv.) in a mixture of glacial CH_3COOH (100 mL) and 48 wt% aqueous HBr (100 mL) was bubbled with argon for 0.5 h. The grey solution was stirred at reflux under argon for 12 h. The suspension was then filtered, washed with cold water and dried. The gray solid was recrystallised from hot CH_3COOH/H_2O solution (3:2, 200 mL) by treating with activated carbon, affording gray crystals (1.12 g, 48%), which were stored under argon.

^{1}H NMR (300 MHz, DMSO-d6) δ 9.31 (s, 6H, -O*H*), 7.59 (s, 6H, Ar*CH*). ^{13}C NMR (101 MHz, DMSO-d6) δ 145.2 (Ar*C*), 121.8 (Ar*C*), 107.7 (Ar*CH*). HRMS (TOF ES+): m/z$[M+Na]^{+}$= 347.0546 (Calculated : 347.0532). IR : (neat)/cm^{-1} 3389, 3273 (broad, O-H stretching); 1703,1531,1447 (Aromatic C=C-H stretching); 1388.

Synthesis of 2,5-dioxahept-7-yl methanesulfonate

To a solution of diethylene glycol monomethyl ether (3.1 mL, 25.8 mmol, 12 equiv.) in triethylamine (15 mL) and DCM (40 mL) at -5°C was added dropwise a solution of mesyl chloride (5 mL, 64.7 mmol, 15 equiv.) in DCM (30 mL). The solution was stirred at -5 °C for 3 h. The orange solution was washed with water, pre-dried with brine, dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. An orange oil was obtained. The crude product was used in the next step with no further purification.

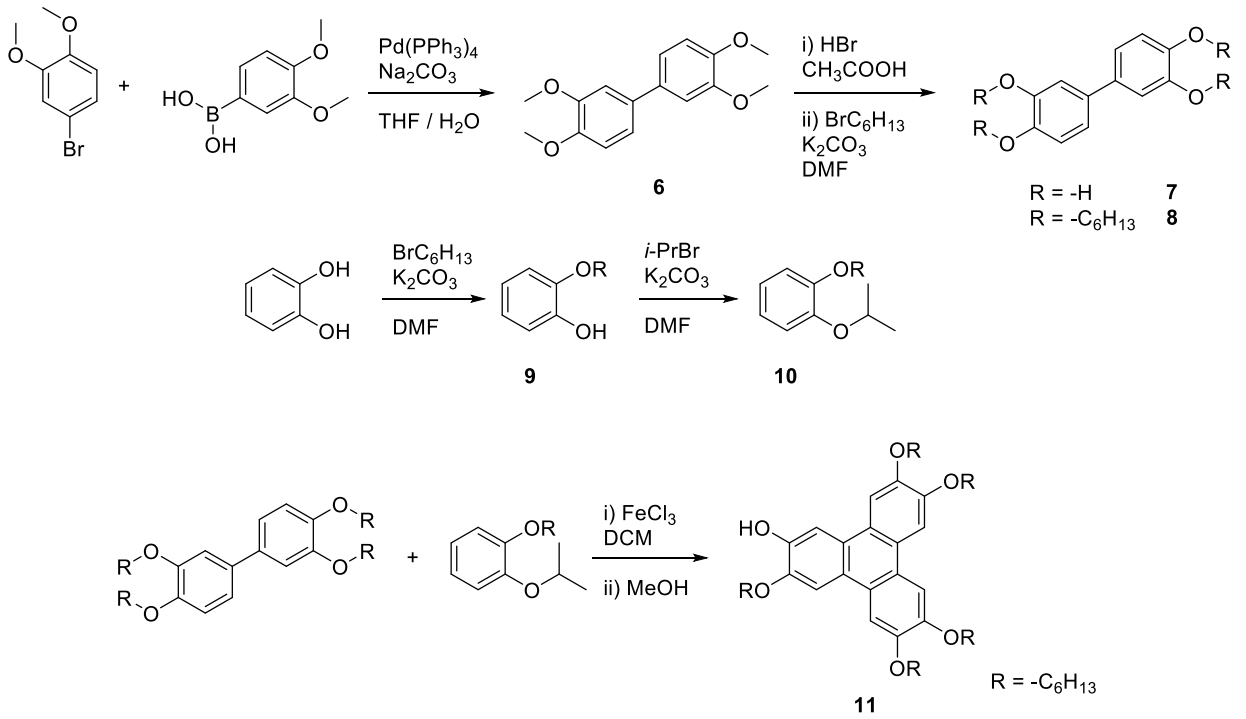
Synthesis of 2,3,6,7,10,11-hexa(1,4,7-trioxaoctyl)triphenylene - TP6EO2M (5)

A solution of **4** (700 mg, 2.15 mmol, 1 equiv.), K_2CO_3 (4.46 g, 32.25 mmol, 15 equiv.) and fresh 2-5-dioxahept-7-yl methanesulfonate (12 equiv.) in degassed DMF (100 mL) was stirred at reflux under argon for 65 h. The solvent was evaporated *in vacuo*. Filtration through a pad of silica (eluent : DCM/MeOH) followed by solvent evaporation afforded a brown oil which was purified by column chromatography (SiO_2 neat $CHCl_3$ to $CHCl_3$/MeOH = 95:5). A light brown crystalline solid (604 mg, 30%) was obtained. Additional purification by preparative HPLC using an isocratic mixture water and acetonitrile (40 vol%) as the eluent system, afforded HPLC pure TP6EO2M as a white crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 6H), 4.41 (t, *J* = 5.1 Hz, 12H), 4.00 (t, *J* = 5.0 Hz, 12H), 3.84 - 3.76 (m, 12H), 3.65 - 3.56 (m, 12H), 3.40 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.89 (C), 124.10 (C), 108.22 (CH), 72.19 (CH_2), 70.98 (CH_2), 70.06 (CH_2), 69.37 (CH_2), 59.22 (CH_3). HRMS (TOF ES+): m/z $[M+H]^{+}$= 937.4846 (Calculated : 937.4797). $[M+Na]^{+}$= 959.4614, $[M+Na]^{2+}$= 491.2. IR : (neat)/cm^{-1} 2926, 2874, 2826 (O-CH_3, CH stretch); 1618,1519,1436 (aromatic ring stretch); 1262 (aromatic ethers Ar-O-C); 1104 (aliphatic ether).

Synthesis of TP6Gall

Synthesis of the hydrophobic moiety



Scheme S3. Synthesis of the hydrophobic moiety of **TP6Gall**

Synthesis of 3,3',4,4'-tetramethoxybiphenyl (6)

$Pd(PPh_3)_4$ (428 mg, 0.37 mmol, 1 mol%) was dissolved in a mixture of degassed THF (200 mL) and water (90 mL) and the solution was bubbled with argon for 10 min. 4-Bromo-1,2-dimethoxybenzene (8.00 g, 37.04 mmol, 1 equiv.) and 3,4-dimethoxybenzeneboronic acid (8.09 g, 44.45 mmol, 1.2 equiv.) were added and the reaction mixture was stirred at reflux under argon overnight. The solvent was evaporated *in vacuo*, and recrystallisation from MeOH afforded **6** as a lightly brown solid (8.13 g, 80%)

^{1}H NMR (400 MHz, CDCl3) δ 7.12 - 7.05 (m, 4H, ArCH), 6.94 (s, 1H, ArCH), 6.92 (s, 1H, ArCH), 3.95 (s, 6H, Ar-O-CH3), 3.92 (s, 6H, Ar-O-*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (2 Ar*C*), 148.5 (2 Ar*C*), 134.4 (2 Ar*C*), 119.3 (2 Ar*CH*), 111.7 (2 Ar*CH*), 110.6 (2 Ar*CH*), 56.2 (4 Ar-O-*CH*$_3$). HRMS (TOF ES+): m/z$[M+H]^+$= 275.1191 (Calculated : 275.1283), m/z$[M+Na]^+$= 297.1, $[2M+Na]^+$= 571.3. IR : (neat)/cm^{-1} 2993,2932,2908 (alkane); 1602, 1574 (aromatic ring stretch); 1138, 1021 (ether); 809.

Synthesis of 3,3',4,4'-Tetrahydroxybiphenyl (7)

A solution of **6** (4,00 g, 14.58 mmol, 1 equiv.) in a previously degassed mixture of 48 wt% aqueous hydrobromic acid (120 mL) and glacial acetic acid (120 mL) was stirred overnight at reflux under argon. The reaction mixture was cooled down to room temperature and the product was extracted with diethyl ether (x5). The etherated phase was washed with a saturated solution of sodium hydrogenocarbonate, brine dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. **7** was obtained as a gray powder (3.14 g, 99 %) and was used in the next step with no further purification.

^{1}H NMR (400 MHz, DMSO) δ 8.87 (s, 4H, Ar-*OH*), 6.88 (d, *J* = 1.6 Hz, 2H, Ar*CH*), 6.80 - 6.71 (m, 4H, Ar*CH*). ^{13}C NMR (101 MHz, DMSO) δ 145.8 (Ar*C*), 144.7 (Ar*C*), 132.5 (Ar*C*), 117.3 (Ar*CH*), 116.4 (Ar*CH*), 113.9 (Ar*CH*). HRMS (TOF ES+): m/z$[M+H]^+$= 219.0651 (Calculated : 219.0657), m/z$[M+Na]^+$= 241.0. IR : (neat)/cm^{-1} 3404 (OH); 1608, 1514 (aromatic ring stretch), 1112, 850.

Synthesis of 3,3'-4,4'-tetrahexyloxybiphenyl (8)

A solution of **7** (3.14 g, 14.39 mmol, 1 equiv.), potassium carbonate (23.8 g, 172.7 mmol, 12 equiv.) and 1-bromohexane (16.2 mL, 115.1 mmol, 8 equiv.) in DMF (8 mL) was stirred overnight at 120 °C. The reaction mixture was cooled down to room temperature, the solvent was evaporated *in vacuo* and the resulting solid was filtered through a pad of silica (eluent : ethyl acetate). The solvent was evaporated and the product was recrystallised from acetonitrile to afford **8** as a light brown solid (4.71 g, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 - 7.03 (m, 4H, Ar*CH*), 6.92 (d, *J* = 8.0 Hz, 2H, Ar*CH*), 4.04 (m, 8H, Ar-O*CH*$_2$), 1.91 - 1.77 (m, 8H, -*CH*$_2$-), 1.54 - 1.43 (m, 8H, -*CH*$_2$-), 1.42 - 1.28 (m, 16H, -*CH*$_2$-), 0.99 - 0.84 (m, 12H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (2 Ar*C*), 148.7 (2 Ar*C*), 134.5 (2 Ar*C*), 119.5 (2 Ar*CH*), 114.4 (2 Ar*CH*), 113.4 (2 Ar*CH*), 69.7 (2 Ar-O-*CH*$_2$-), 69.6 (2 Ar-O-*CH*$_2$-), 31.8 (4 -*CH*$_2$-), 29.5 (2 -*CH*$_2$-), 29.5 (2 -*CH*$_2$-), 25.9 (4 -*CH*$_2$-), 22.8 (4 -*CH*$_2$-), 14.2 (4 -*CH*$_3$). HRMS (TOF ES+): m/z $[M+H]^+$= 555.4443 (calculated : 555.44083), $[2M+Na]^+$= 1131.8901. IR : (neat)/cm^{-1} 2952, 2932, 2872, 2859 (alkane); 1577, 1601, 1509, 1468 (Aromatic ring stretch); 1229 (ether); 793.

Synthesis of 2-hexyloxyphenol (9)

To a solution of K_2CO_3 (14.21 g, 103 mmol, 2 equiv.) and catechol (5.670 g, 51.5 mmol, 1 equiv.) in DMF (27 mL), 1-bromohexane (7.3 mL, 51.5 mmol, 1 equiv.) was added dropwise. The mixture was stirred overnight at 120 °C. The solvent was evaporated *in vacuo* and the resulting solid was filtered through a pad of silica (eluent : ethyl acetate). Purification by chromatography (SiO_2, hexane/ethyl acetate = 20:1) afforded **9** as a colourless oil (4.652 g, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (m, 1H, Ar*CH*), 6.85 (m, 3H, Ar*CH*), 5.64 (s, 1H, Ar-*OH*), 4.04 (t, *J* = 6.6 Hz, 2H, Ar-O-*CH*$_2$-), 1.81 (m, 2H, -*CH*$_2$-), 1.53 - 1.29 (m, 7H, -*CH*$_2$-), 0.91 (t, *J* = 7.1 Hz, 3H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.13 (Ar*C*), 146.98 (Ar*C*), 121.44 (Ar*CH*), 120.22 (Ar*CH*), 114.57 (Ar*CH*),

111.77 (Ar*CH*), 69.06 (Ar-O-*CH*$_2$-), 31.70 (-*CH*$_2$-), 29.37 (-*CH*$_2$-), 25.85 (-*CH*$_2$-), 22.73 (-*CH*$_2$-), 14.15 (-*CH*$_3$). HRMS (TOF ES+): m/z $[M+H]^+$= 195.1386 (Calculated : 195.1385).

Synthesis of 1-hexyloxy-2-isopropoxybenzene (10)

A solution of K_2CO_3 (1.07 g, 7.7 mmol, 1 equiv.), **9** (1.5 g, 7.7 mmol, 1 equiv.), and 2-bromopropane (2.16 mL, 23.2 mmol, 3 equiv.) in DMF (5.8 mL) was stirred at 55 °C and the reaction was monitored by TLC. After 44 h stirring, 2-bromopropane (0.72 mL, 7.7 mmol, 1 equiv.) was added and further reacted for 22 h. Water was added and the product was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. Purification by column chromatography (SiO_2, hexane/ethyl acetate = 20:1) afforded **10** as a colourless oil (1.240 g, 68%)

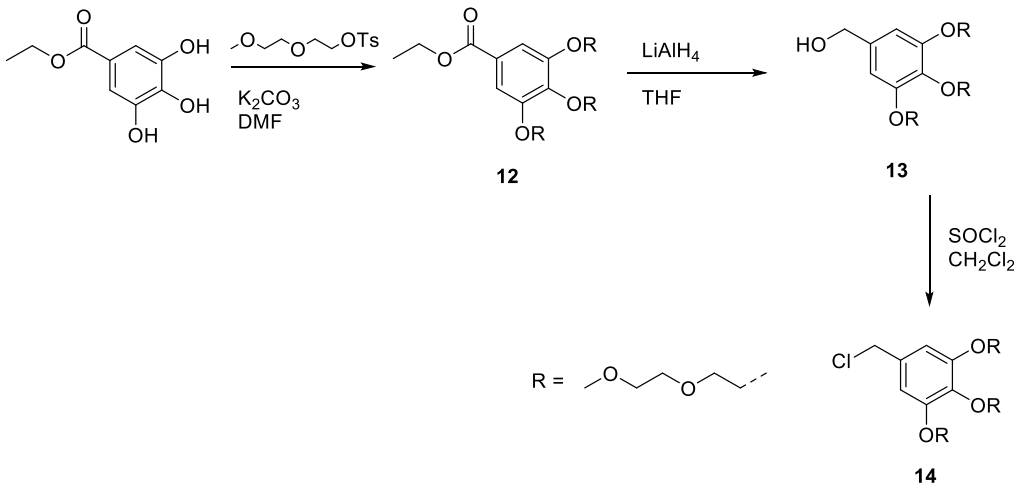
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 - 6.83 (m, 4H, Ar*CH*), 4.46 (hept, *J* = 6.1 Hz, 1H, Ar-O*CH*$(CH_3)_2$), 3.98 (t, *J* = 6.6 Hz, 2H, Ar-O-*CH*$_2$-), 1.81 (m, 2H, -*CH*$_2$-), 1.58 - 1.30 (m, 12H, -*CH*$_2$-), 0.91 (t, *J* = 7.1 Hz, 3H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (Ar*C*), 148.0 (Ar*C*), 122.2 (Ar*CH*), 121.0 (Ar*CH*), 118.7 (Ar*CH*), 114.5 (Ar*CH*), 72.6 (Ar-O*CH*$(CH_3)_2$), 69.3 (Ar-O-*CH*$_2$-), 31.7 (-*CH*$_2$-), 29.5 (-*CH*$_2$-), 25.9 (-*CH*$_2$-), 22.8 (-*CH*$_2$-), 22.4 (2 Ar-OCH(*CH*$_3$)$_2$), 14.2 (-*CH*$_3$). HRMS (TOF ES+): m/z 259.1665 (Calculated : 259.1669). HRMS (TOF ES+): m/z $[M+H]^+$= 236.1778 (Calculated : 236.1776). IR : (neat)/cm^{-1} 2958, 2930, 2863 (alkane); 1592,1497 (aromatic ring stretch); 1252 (Ar-O-R stretching).

Synthesis of 2-hydroxy-3,6,7,10,11-pentahexyloxytriphenylene (11)

To a solution of **10** (670 mg, 2.84 mmol, 1.7 equiv.) and **8** (943 mg, 1.70 mmol, 1 equiv.) in DCM (6 mL), $FeCl_3$ (1.38 g, 8.50 mmol, 5 equiv.) was slowly added. The dark blue solution was stirred overnight at room temperature. The mixture was then poured into cold methanol (40 mL) and stirred for 0.5 h. The solution was filtered and the gray precipitate was washed with cold methanol. Purification by column chromatography (SiO_2, petroleum ether/DCM = 7:3 to 4:6), followed by recrystallisation from ethanol afforded **11** as white crystals (360.8 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H, Ar*CH*), 7.86 - 7.80 (m, 4H, Ar*CH*), 7.77 (s, 1H, Ar*CH*), 5.91 (s, 1H,-*OH*), 4.29 (t, *J* = 6.4 Hz, 2H, Ar-O-*CH*$_2$), 4.26 - 4.17 (m, 8H, Ar-O-*CH*$_2$), 2.03 - 1.87 (m, 10H, -*CH*$_2$-), 1.57 (m, 10H, -*CH*$_2$-), 1.49 - 1.29 (m, 20H, -*CH*$_2$-), 1.01 - 0.83 (m, 15H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (Ar*C*), 149.2 (Ar*C*), 149.0 (Ar*C*), 148.9 (Ar*C*), 146.0 (Ar*C*), 145.4 (Ar*C*), 124.1 (Ar*C*), 123.8 (Ar*C*), 123.8 (Ar*C*), 123.7 (Ar*C*), 123.4 (Ar*C*), 123.1 (Ar*C*), 107.9 (Ar*CH*), 107.7 (Ar*CH*), 107.5 (Ar*CH*), 106.7 (Ar*CH*), 104.5 (Ar*CH*), 70.1 (Ar-O-*CH*$_2$), 70.0 (Ar-O-*CH*$_2$), 69.8 (Ar-O-*CH*$_2$), 69.3 (Ar-O-*CH*$_2$), 31.8 (-CH$_2$-), 31.8 (-*CH*$_2$-), 31.8 (-*CH*$_2$-), 29.6 (-*CH*$_2$-), 29.6 (-*CH*$_2$-), 29.5 (-*CH*$_2$-), 29.4 (-*CH*$_2$-), 26.0 (-*CH*$_2$-), 26.0 (-*CH*$_2$-), 22.8 (-*CH*$_2$-), 14.20 (5 -*CH*$_3$). HRMS (TOF ES+): m/z $[M+H]^+$= 745.5410 (Calculated : 745.5407), $[M+Na]^+$= 767.7. IR : (neat)/cm^{-1} 3551 (OH); 2951, 2924, 2856 (alkane); 1617, 1514, 1436 (aromatic ring stretch); 1257 (ether), 835.

Synthesis of the hydrophilic moiety



Scheme S4. Synthesis of the hydrophilic moiety of **TP6Gall**

Synthesis of ethyl 3,4,5-tris(1,4,7-trioxaoctyl) benzoate (12)

Synthesis of (3,6-dioxaheptyl) 4-methylbenzenesulfonate

To a solution of diethylene glycol monomethyl ether (11.61 g, 96.6 mmol, 1 equiv.) in THF (40 mL) at 0 °C was added a solution of potassium hydroxide (9.660 g, 214.5 mmol, 2.5 equiv.) in water (40 mL). A solution of tosyl chloride (27.63 g, 144.9 mmol, 1.5 equiv.) in THF (40 mL) was then added dropwise and stirred for 1 h at 0 °C. The reaction mixture was brought back to room temperature and further stirred for 1 h. Diethyl ether was added. The etherated phase was then washed with 1 M aqueous solution of potassium hydroxide, then water and brine, dried over $MgSO_4$ and the solvent was evaporated. The resulting oil was used in the next step with no further purification.

Synthesis of **12**

A solution of ethyl gallate (293 mg, 1.61 mmol, 1 equiv.), K_2CO_3 (2.23 g, 16. 1 mmol, 10 equiv.) and the freshly synthesised (3,6-dioxaheptyl)-4-methylbenzenesulfonate (4.5 equiv.) in degassed DMF (10 mL) was stirred at 80 °C for 20 h. The solvent was then removed *in vacuo* and the crude filtered through a pad of Celite. DCM was added and the organic phase was washed with a 1 M solution of HCl, brine, dried over $MgSO_4$ and the solvent was evaporated. The resulting yellow oil was purified by column chromatography (SiO_2, DCM/MeOH = 97:3) to afford **12** as a colourless oil (486 mg, 49%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H, Ar*CH*), 4.33 (q, *J* = 7.1 Hz, 2H, -*CH*$_2$OCOR), 4.26 - 4.17 (m, 6H, -*CH*$_2$-), 3.89 - 3.84 (m, 4H, -*CH*$_2$-), 3.82 - 3.78 (m, 2H, -*CH*$_2$-), 3.74 - 3.68 (m, 6H, -*CH*$_2$-), 3.58 - 3.50 (m, 6H, -*CH*$_2$-), 3.37 (s, 6H, -*CH*$_2$-), 3.36 (s, 3H, -*CH*$_3$), 1.36 (t, *J* = 7.1 Hz, 3H, *CH*$_3$CH$_2$OCOR). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 166.2 (*C*=*O*), 152.4 (2 Ar*C*), 142.6 (Ar*C*), 125.5 (Ar*C*) 109.1 (2 Ar*CH*), 72.6 (-*C*H_2-), 72.2 (-*C*H_2-), 72.1 (2 -*C*H_2-), 70.9 (2 -*C*H_2-), 70.7 (-*C*H_2-), 70.6 (-*C*H_2-), 69.8 (2 -*C*H_2-), 69.0 (2 -*C*H_2-), 61.1 (-*CH*$_2$OCOR), 59.2 (2 -*CH*$_3$), 59.1 (-*CH*$_3$), 14.5 (*CH*$_3$$CH_2$OCOR). HRMS (TOF ES+): m/z $[M+Na]^+$= 527.2479 (Calculated : 527.2468), $[M+K]^+$=543.5 .

Synthesis of 3,4,5-tris(1,4,7-trioxaoctyl) benzyl alcohol (13)

To a stirred suspension of $LiAlH_4$ (200 mg, 5.15 mmol, 1.3 equiv.) in dry THF (4 mL) was added a solution of **12** (2.00 g, 3.96 mmol, 1 equiv.) in dry THF (8 mL) at 0 °C under argon atmosphere. The mixture was brought back to room temperature, stirred for 3 h and was then quenched by successive addition of isopropyl alcohol (1 mL), cold water (3 mL) and a 30% aqueous solution of sodium hydroxide (1 mL). After filtration of the crude, the product was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and the solvent was evaporated *in vacuo* to afford **13** as a light yellow oil (1.137 g, 62%).

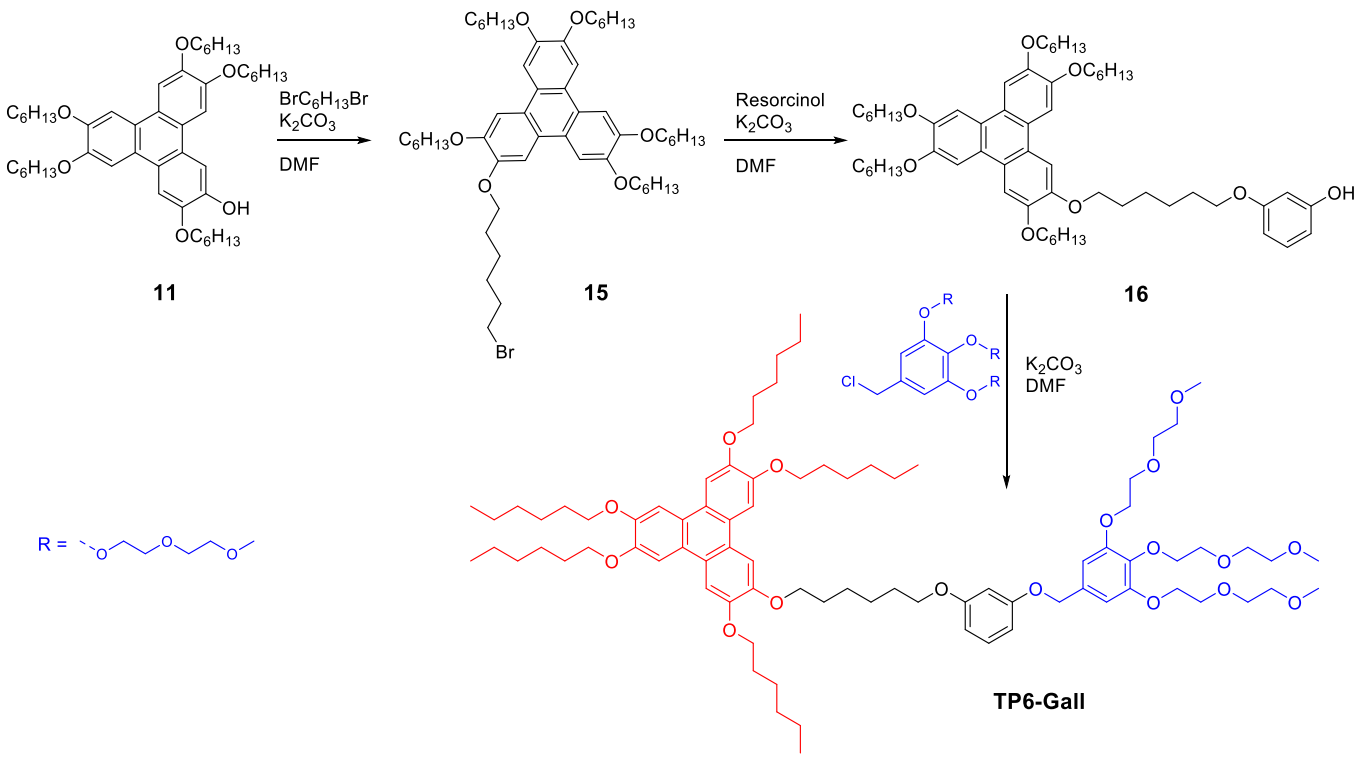
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 2H, Ar*CH*), 4.57 (s, 2H, Ar-*CH*$_2$-OH), 4.20 - 4.11 (m, 6H, Ar-O-*CH*$_2$-), 3.86 - 3.83 (m, 4H, -CH_2-), 3.82 - 3.77 (m, 2H, -CH_2-), 3.74 - 3.68 (m, 6H, -CH_2-), 3.58 - 3.53 (m, 6H, -CH_2-), 3.37 (s, 9H, O-*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9 (ArC), 137.9 (2 ArC), 136.7 (2 ArC), 106.6 (ArCH), 72.5 (-CH_2-), 72.2 (2 -CH_2-), 72.1 (2 -CH_2-),70.8 (-CH_2-), 70.7 (-CH_2-), 70.6 (-CH_2-), 70.0 (2 -CH_2-), 69.0 (2 -CH_2-), 65.5 (Ar-*CH*$_2$-OH), 59.2 (3 CH_3). HRMS (TOF ES+): m/z $[M+Na]^+$= 485.2368 (Calculated : 485.2363). IR : (neat)/cm^{-1} 3453 (OH); 2926, 2874, 2823; 1589,1435 (aromatic ring strech); 1299 (aromatic ether Ar-O-C); 1101 (aliphatic ether).

3,4,5-Tris(1,4,7-trioxaoctyl) benzyl chloride (14)

To a solution of **13** (200 mg, 0.43 mmol, 1 equiv.) in dry DCM (25 mL) at room temperature was added dropwise a solution of $SOCl_2$ (320 µL, 4.3 mmol, 10 equiv.) in dry DCM (10 mL). The solution was stirred at room temperature for 3 h. The solvent was evaporated *in vacuo*, affording **14** in a quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (s, 2H, Ar*CH*), 4.48 (s, 2H, Ar-*CH*$_2$-Cl), 4.21 – 4.12 (m, 6H, Ar-O-*CH*$_2$-), 3.89 – 3.83 (m, 4H, -*CH*$_2$-), 3.82 – 3.77 (m, 2H, -*CH*$_2$-), 3.74 – 3.69 (m, 6H, -*CH*$_2$-), 3.60 – 3.52 (m, 6H, -*CH*$_2$-), 3.38 (s, 6H, -*CH*$_3$), 3.38 (s, 3H, -*CH*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8 (3 Ar*C*), 132.9 (Ar*C*), 108.4 (2 Ar*CH*), 72.5 (-*CH*$_2$-), 72.2 (-*CH*$_2$-), 72.2 (2 -*CH*$_2$-), 70.9 (2 -*CH*$_2$-), 70.7 (-*CH*$_2$-), 70.6 (-*CH*$_2$-), 69.9 (2 -*CH*$_2$-), 69.1 (2 -*CH*$_2$-), 59.2 (3 -*CH*$_3$), 46.7 (Ar-*CH*$_2$-Cl).HRMS (TOF ES+): m/z $[M+Na]^+$= 503.2005 (Calculated : 503.2024). IR : (neat)/cm^{-1} 2925, 2876, 2823; 1591, 1504 (aromatic ring stretch); 1333 (aromatic ether Ar-O-C); 1101 (aliphatic ether).

Coupling of the two moieties



Scheme S5. Coupling of the two moieties

Synthesis of 2-(6-bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (15)

A solution of **11** (192 mg, 0.27 mmol, 1 equiv.), K_2CO_3 (75 mg, 0.54 mmol, 2 equiv.) and 1,6-dibromohexane (200 µL, 1.34 mmol, 5 equiv.) in degassed DMF (1 mL) was stirred at 120 °C for 21 h under argon. DMF was then evaporated *in vacuo* and the resulting dough was filtrated through a pad of Celite and washed with DCM. The solvent was evaporated and the resulting solid was recrystallised from ethanol to afford **15** as an off-white solid (140.3 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 6H, Ar*CH*), 4.23 (t, *J* = 6.6 Hz, 12H, Ar-O*CH*$_2$-), 3.45 (t, *J* = 6.8 Hz, 2H, -*CH*$_2$-Br), 2.00 - 1.86 (m, 14H, -*CH*$_2$-), 1.68 - 1.50 (m, 14H, -*CH*$_2$-), 1.49 -1.30 (m, 20H, -*CH*$_2$-), 1.00 - 0.87 (m, 15H, -*CH*$_3$-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 149.0, 123.9, 123.8, 123.7, 107.5, 107.4 , 69.9, 69.8, 69.6, 33.9, 32.9, 31.8, 31.1, 29.6, 29.5, 28.1, 26.0, 25.6, 22.8, 14.2. HRMS (TOF ES+): m/z $[M+H]^+$= 909.5374 (Calculated : 909.5373).

2-(6-(3-hydroxyphenyloxy)hexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (16)

A solution of **15** (246.1 mg, 0.27 mmol, 1 equiv.), resorcinol (149 mg, 1.35 mmol, 5 equiv.) and K_2CO_3 (75 mg, 0.54 mmol, 2 equiv.) in DMF (4 mL) was stirred at 120 °C and the reaction monitored by TLC

(Hexane/DCM = 3:6). After 20 h stirring, the reaction mixture was cooled down to room temperature and acidified with 1 M aqueous HCl. Extraction with ethyl acetate followed by solvent evaporation *in vacuo* afforded a orange solid which was purified by column chromatography (SiO_2, DCM). **16** was obtained as a white solid (105.9 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 6H, ArC*H*), 7.10 (t, *J* = 8.4 Hz, 1H, ArC*H*), 6.50 - 6.44 (m, 1H, ArC*H*), 6.43 - 6.37 (m, 2H, ArC*H*), 4.99 (s, 1H, -O*H*), 4.23 (t, *J* = 6.6 Hz, 12H, -OCH_2), 3.95 (t, *J* = 6.4 Hz, 2H, -OCH_2), 2.02 - 1.88 (m, 12H, -CH_2-), 1.88 - 1.77 (m, 2H, -CH_2-), 1.67 - 1.51 (m, 14H, -CH_2-), 1.47 - 1.32 (m, 20H, -CH_2-), 1.01 - 0.86 (m, 15H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 156.9, 149.2, 149.1, 149.1, 149.1, 130.2, 123.9, 123.9, 123.8, 107.8, 107.6, 107.1, 102.2, 69.9, 68.0, 31.8, 29.6, 29.3, 26.1, 26.0, 14.2. HRMS (TOF ES+): m/z [M]= 936.6451 (Calculated : 936.6479).

Synthesis of TP6Gall (017)

A solution of **14** (163 mg, 0.339 mmol, 3 equiv.), **16** (105.9 mg, 0.113 mg, 1 equiv.) and K_2CO_3 (47 mg, 0.339 mmol, 3 equiv.) in degassed DMF (5 mL) was stirred under argon at 120 °C for 24 h. The solvent was evaporated *in vacuo*. Water was added and the product was extracted with ethyl acetate (x3), dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. Purification by column chromatography (SiO_2, neat DCM to DCM /MeOH = 97.5:2.5) afforded **TP6Gall** as an off-white solid in a 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 6H), 7.19 - 7.13 (m, 1H), 6.65 (s, 2H), 6.56 - 6.50 (m, 3H), 4.90 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 12H), 4.20 - 4.13 (m, 6H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.88 - 3.83 (m, 4H), 3.83 - 3.78 (m, 2H), 3.74 - 3.68 (m, 6H), 3.58 - 3.53 (m, 6H), 3.38 (s, 3H), 3.37 (s, 6H), 2.01 - 1.89 (m, 12H), 1.89 - 1.81 (m, 2H), 1.63 - 1.53 (m, 12H), 1.44 - 1.33 (m, 22H), 0.97 - 0.89 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.1, 152.9, 149.1, 132.6, 130.0, 123.7, 107.7 - 106.9, 102.0, 72.8 - 68.0, 59.2, 31.8, 29.6,29.4,26.2, 26.0, 22.8, 14.2. HRMS (TOF ES+): m/z $[M+Na]^+$= 1403.8754 (Calculated : 1403.8736).

Analysis of pure compounds

Polarised Optical Microscopy

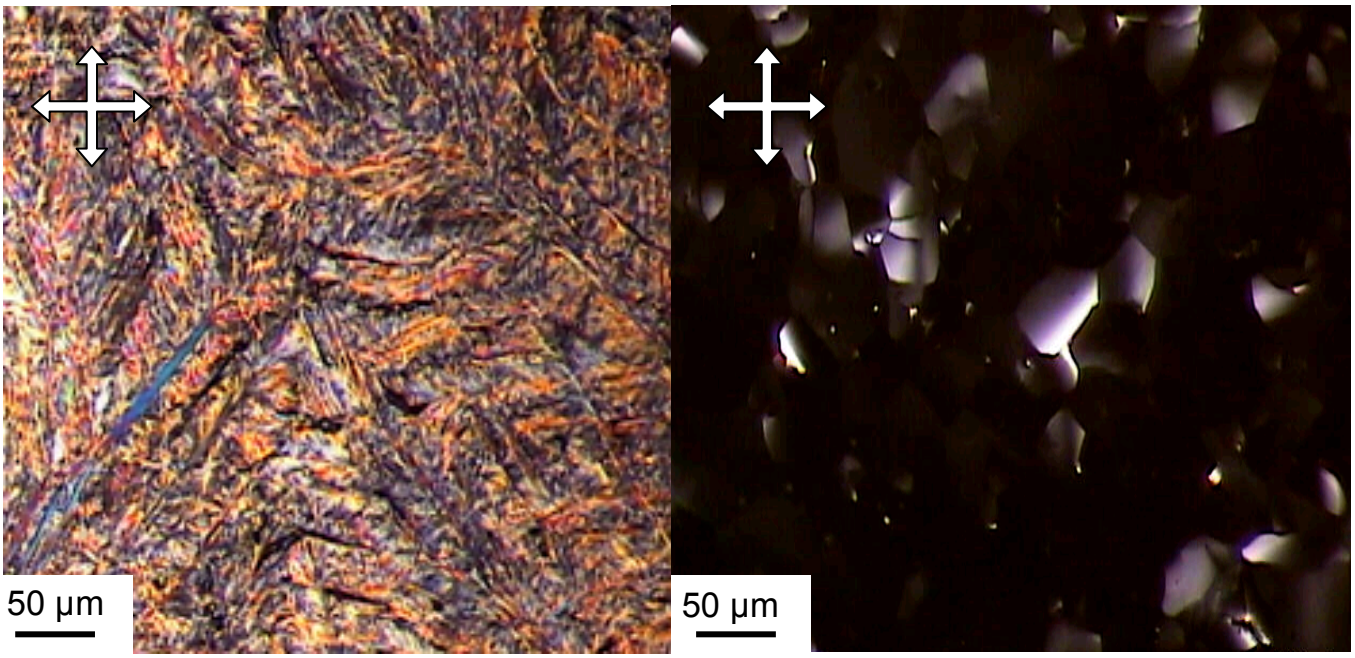


Fig. S1 POM image of **TP6** on heating stage. Left: room temperature, right: 70 °C.

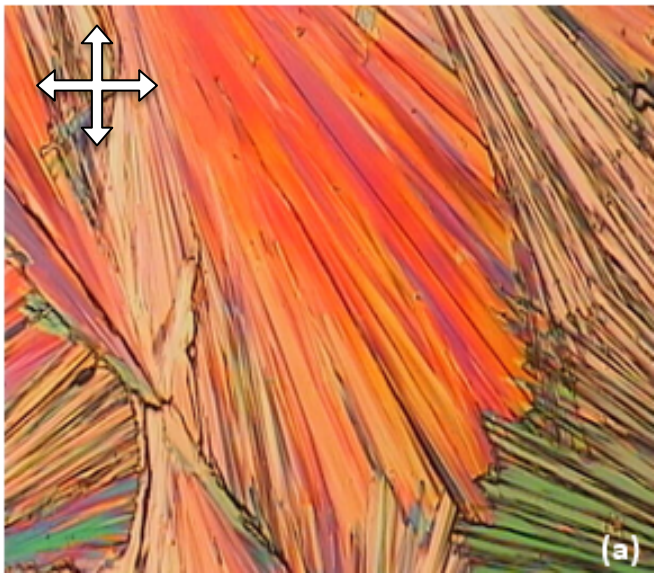


Fig. S2 POM image of **TP6EO2M** at room temperature.

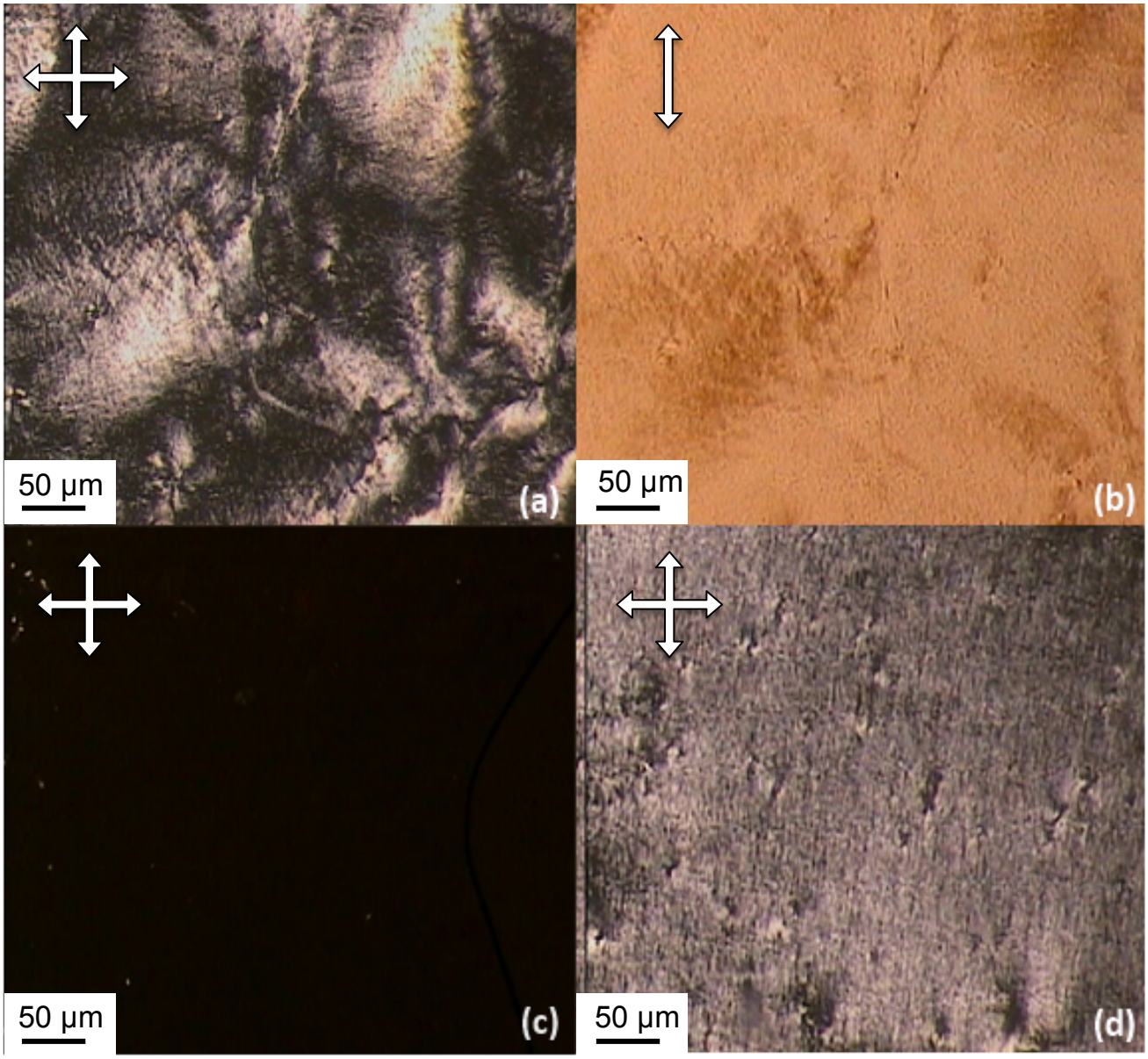


Fig. S3 POM image of **TP6Gall** on heating stage. (a) room temperature before heating, (b) RT without polarizer, (c) 34 °C, (d) room temperature on cooling.

Note: X-ray diffraction pattern for TP6Gall points to a cubic phase therefore a dark image should be observed in POM. We attribute the birefringence to the formation of a columnar phase enforced by the glass lid, which is not present during the Xray measurements (use of an open Mancor cup). This hypothesis is based on the columnar-like micelles (stacks of ~10 TP6Gall molecules), the ability of triphenylenes to form columnar phases, and the apparently more homogenous POM after cooling from the isotropic phase (Fig. S3d) compared to the POM before heating (Fig. 3a) supporting an effect of the glass lid.

Differential Scanning Calorimetry

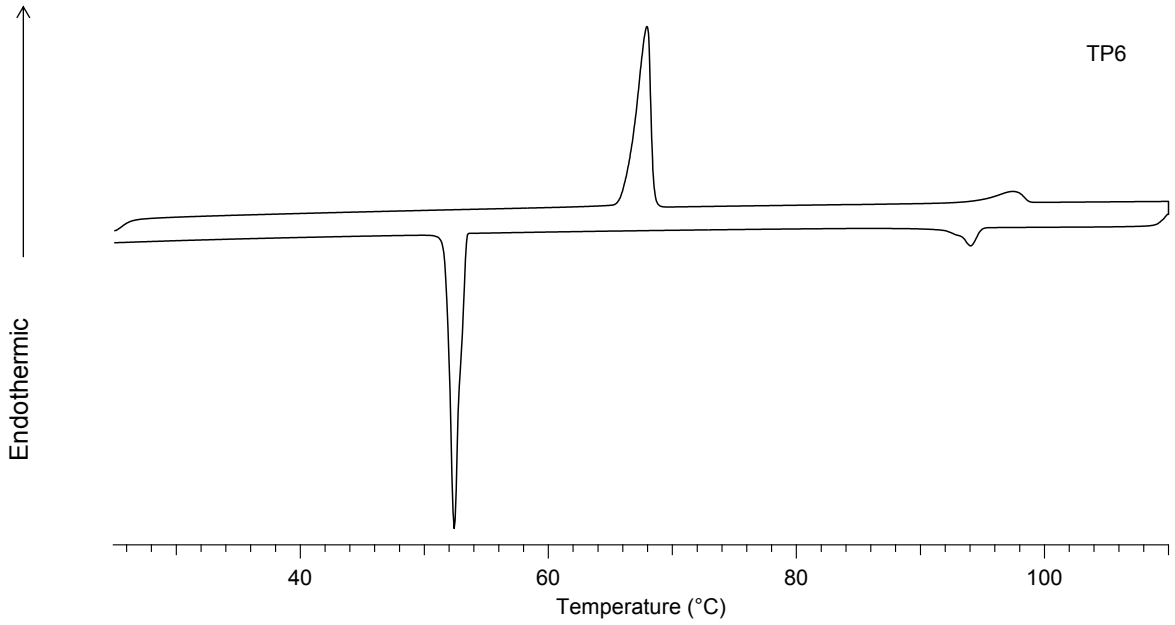


Fig. S4 DSC curve of **TP6** (10 ºC/min).

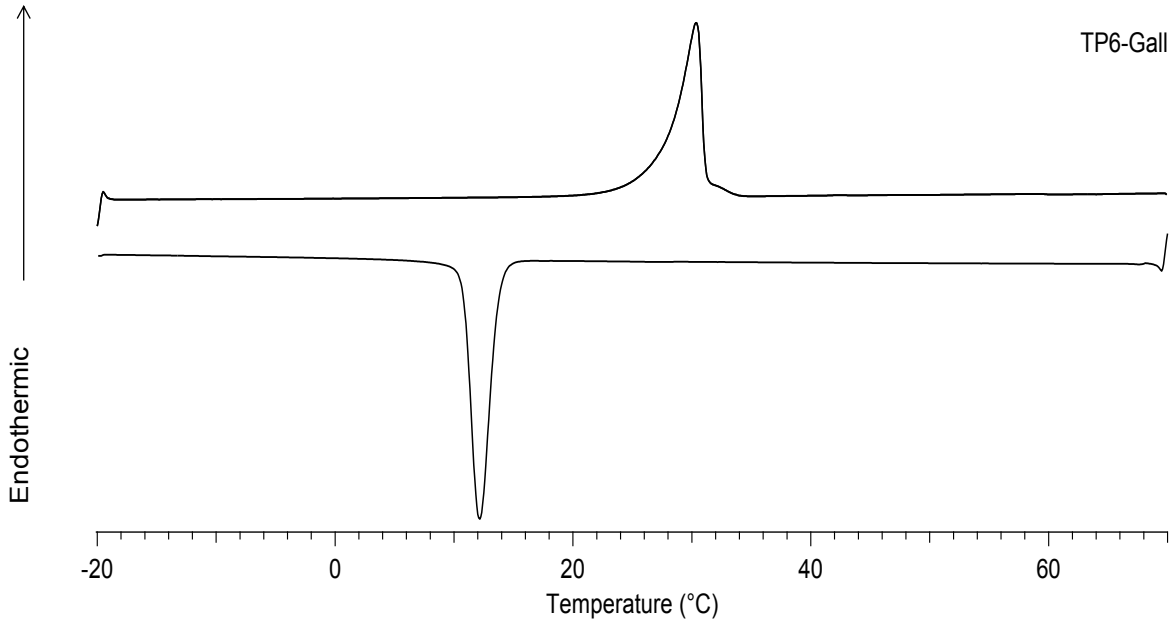


Fig. S5 DSC curve of **TP6Gall** (10 ºC/min).

Energy minimisation of TP6Gall

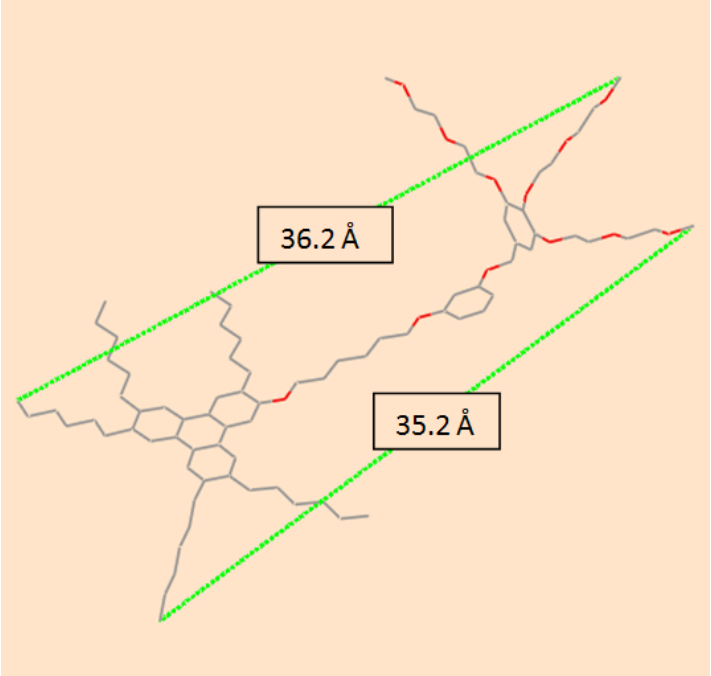


Fig. S6 MM2 energy minimisation of **TP6Galll** computed by Chem3D.

Small Angle X-ray scattering

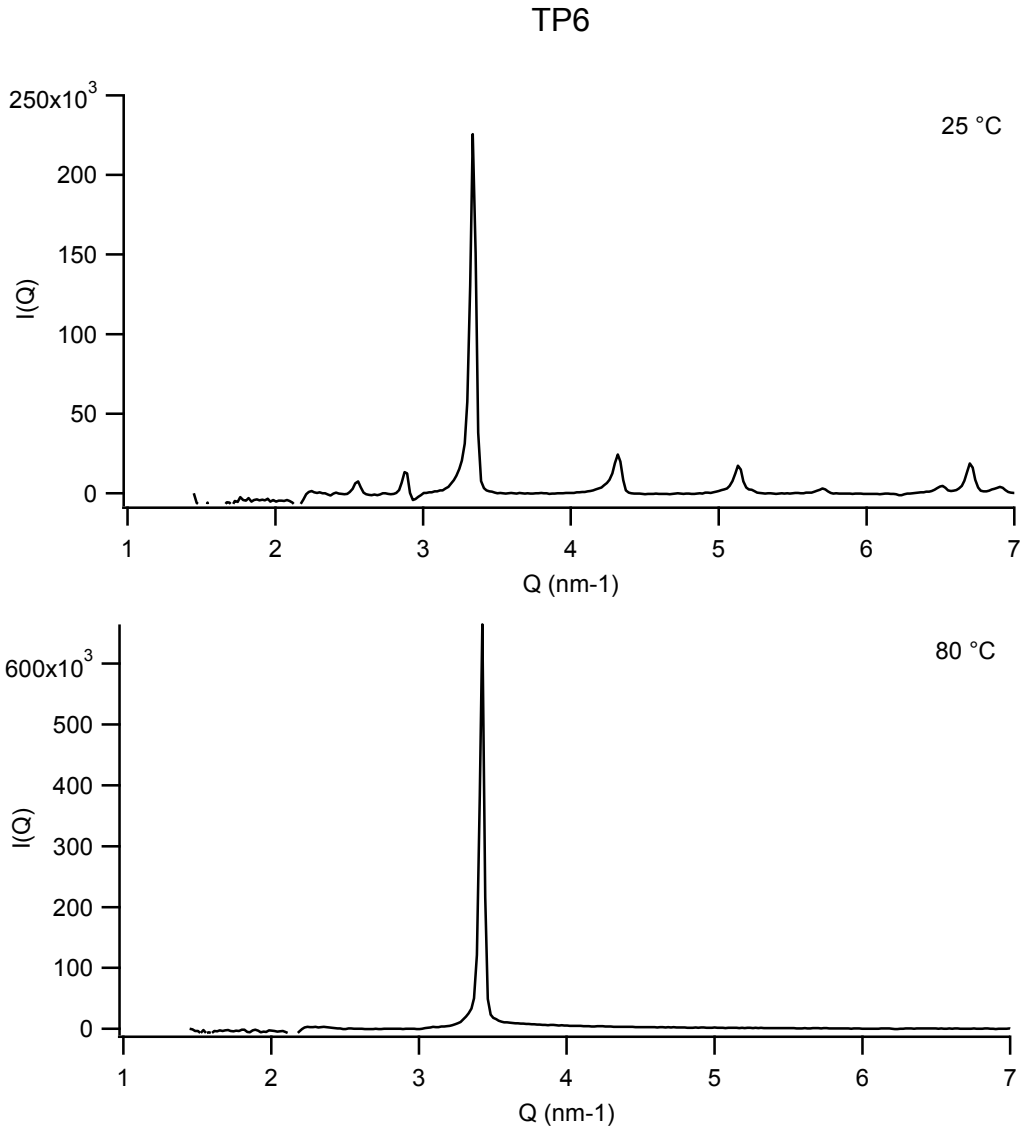


Fig. S7 SAXS pattern of **TP6**.

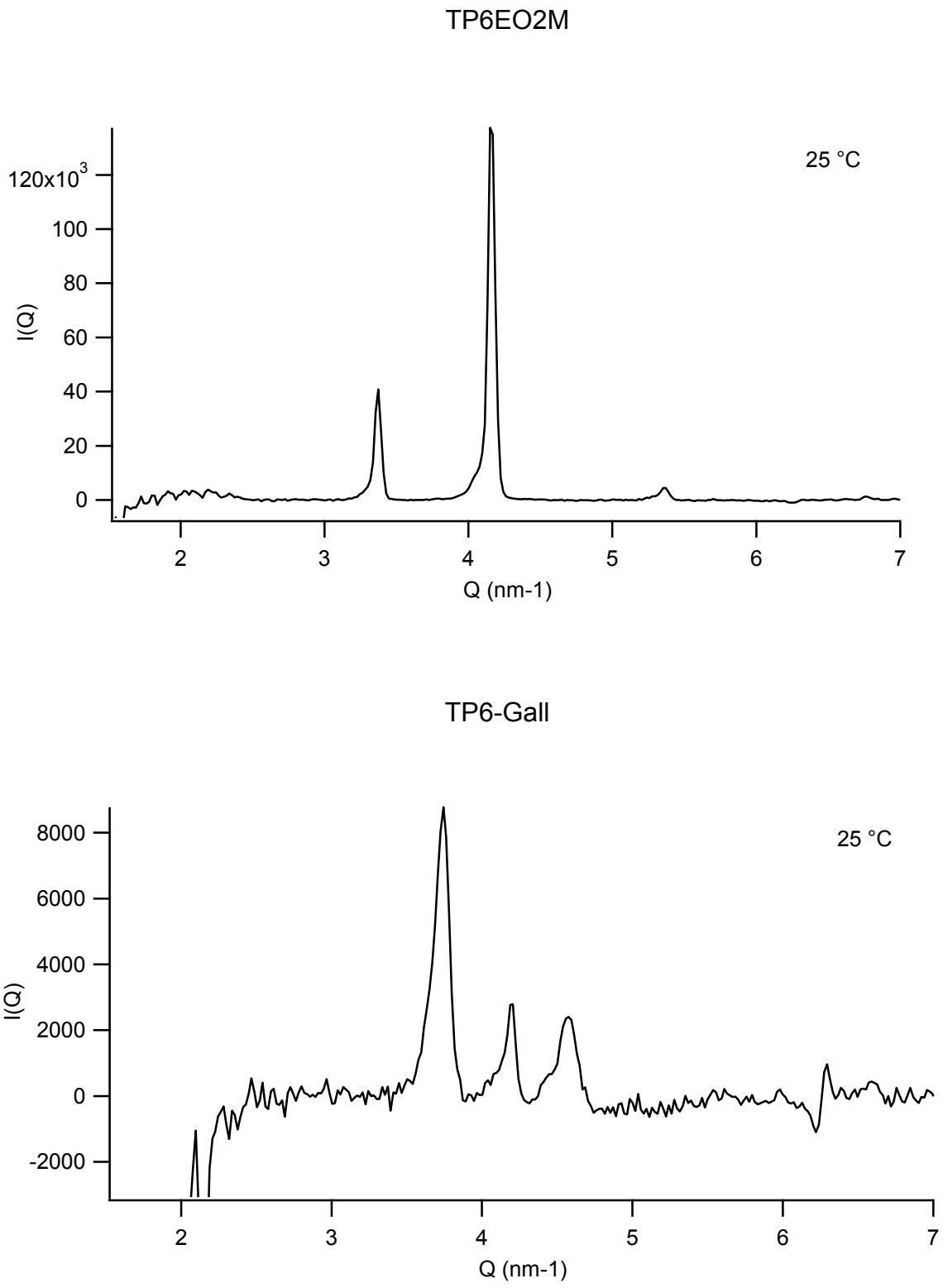


Fig. S8 SAXS pattern of **TP6EO2M** (top) and **TP6Gall** (bottom).

Morphology Study of the equimolar blend of TP6:TP6EO2M

Polarised Optical Microscopy

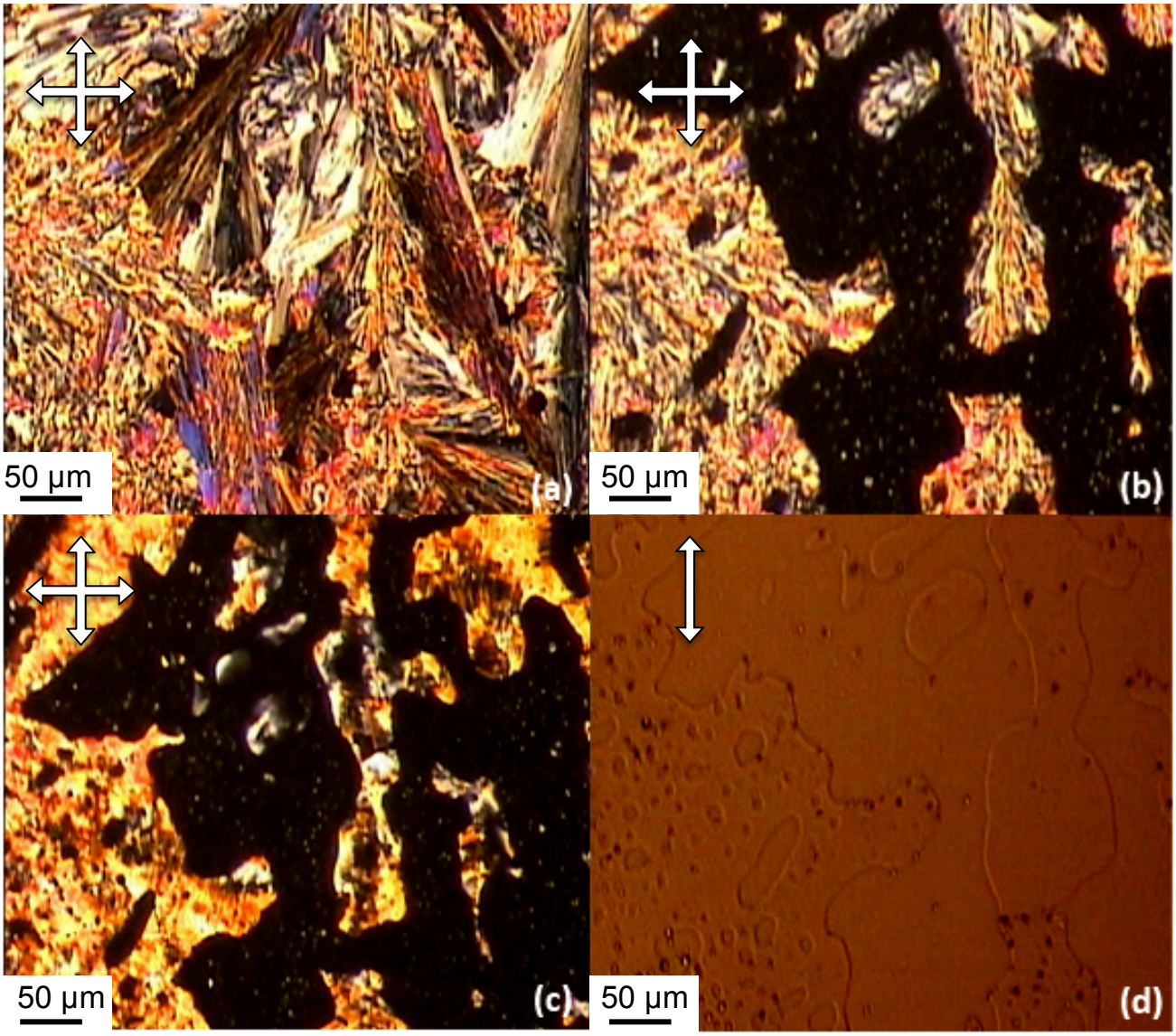


Fig. S9 POM image of a **TP6:TP6EO2M** 50 mol%:50 mol% mixture on heating stage. (a) room temperature, (b) 54 °C, (c) 67 °C, (d) 88 °C without polarizer.

Differential Scanning Calorimetry

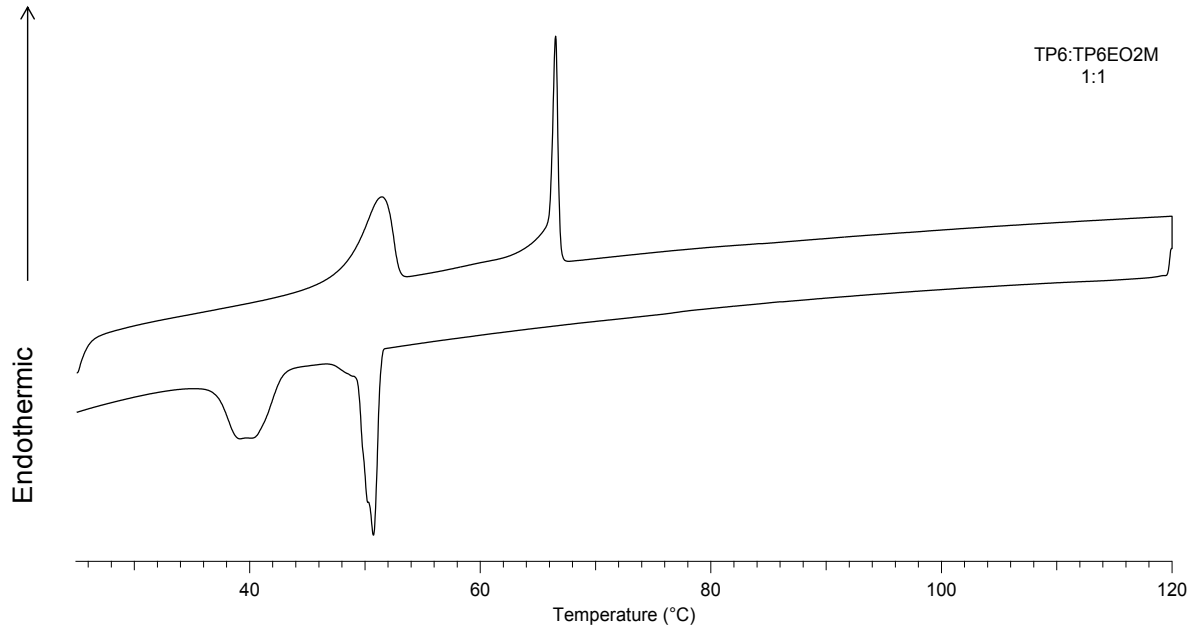


Fig. S10 DSC curve of a **TP6:TP6EO2M** 50mol%:50mol% mixture (10 ºC/min).

Small Angle X-ray scattering

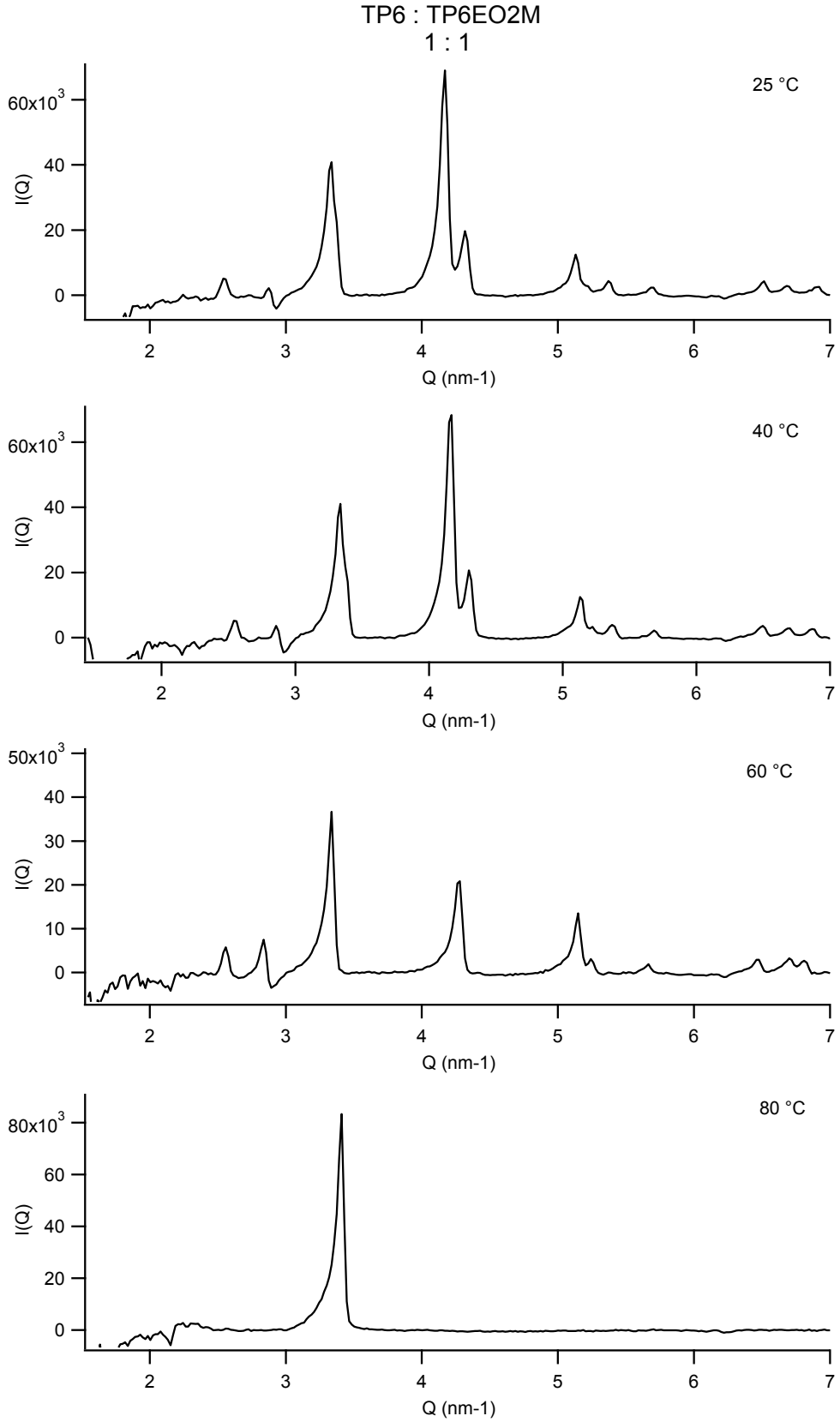


Fig. S11 SAXS patterns of a **TP6:TP6EO2M** 50mol%:50mol% mixture at different temperatures.

Morphology Study of the (TP6:TP6EO2M):TP6Gall = 95:5 mixture

Polarised Optical Microscopy

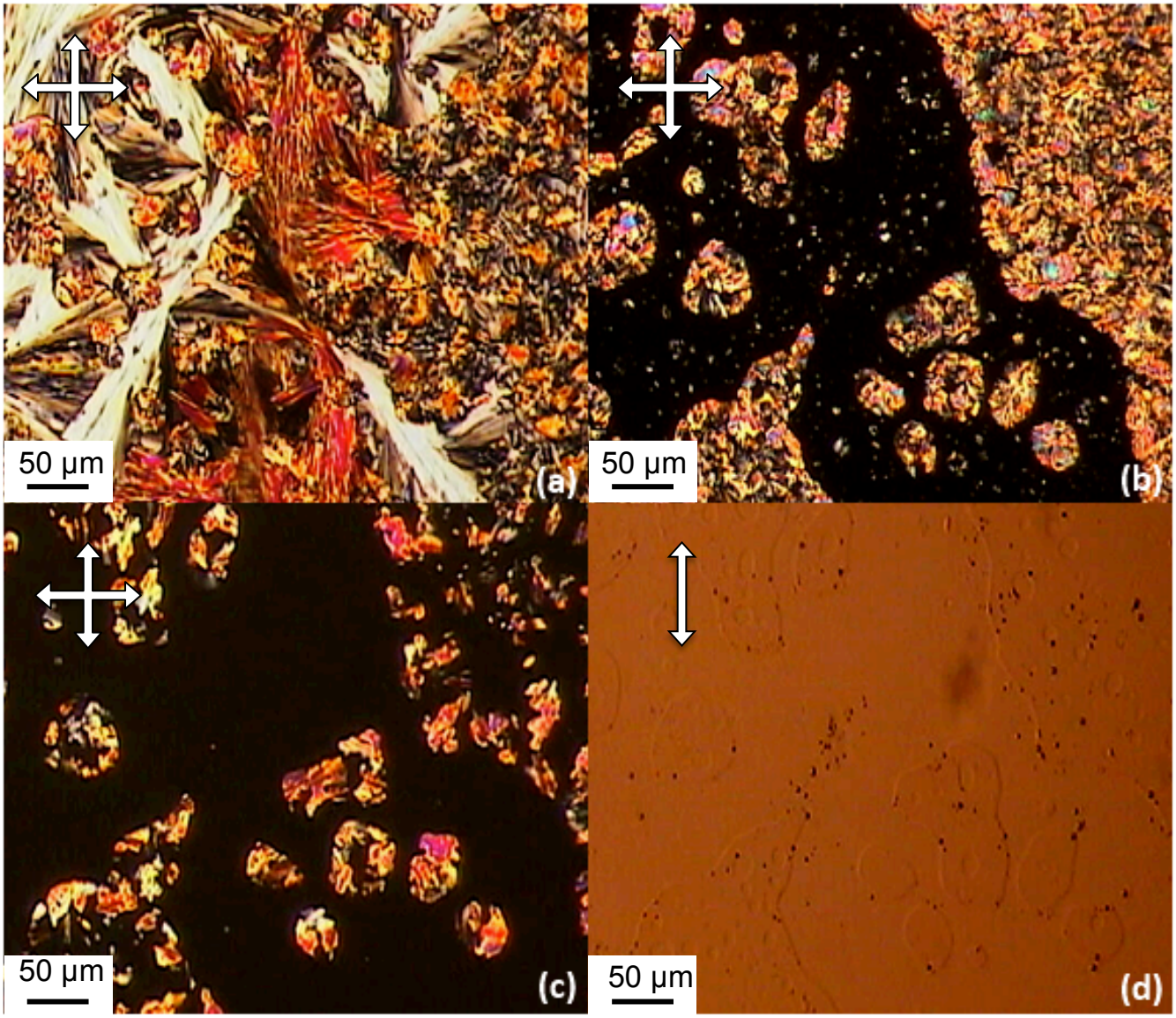


Fig. S12 POM image of a **(TP6:TP6EO2M):TP6Gall** 95mol%:5mol% mixture on heating stage. (a) room temperature, (b) 54 °C, (c) 67 °C, (d) 85 °C without polariser.

Differential Scanning Calorimetry

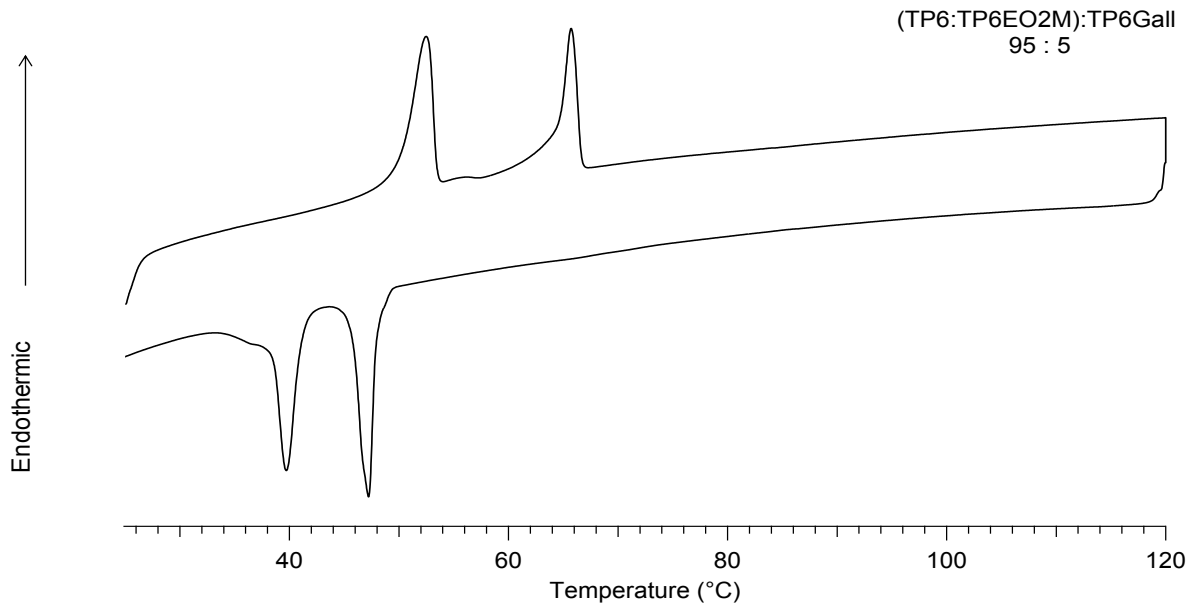


Fig. S13 DSC curve of a **(TP6:TP6EO2M):TP6Gall** 95mol%:5mol% mixture (10 ºC/min).

Small Angle X-ray scattering

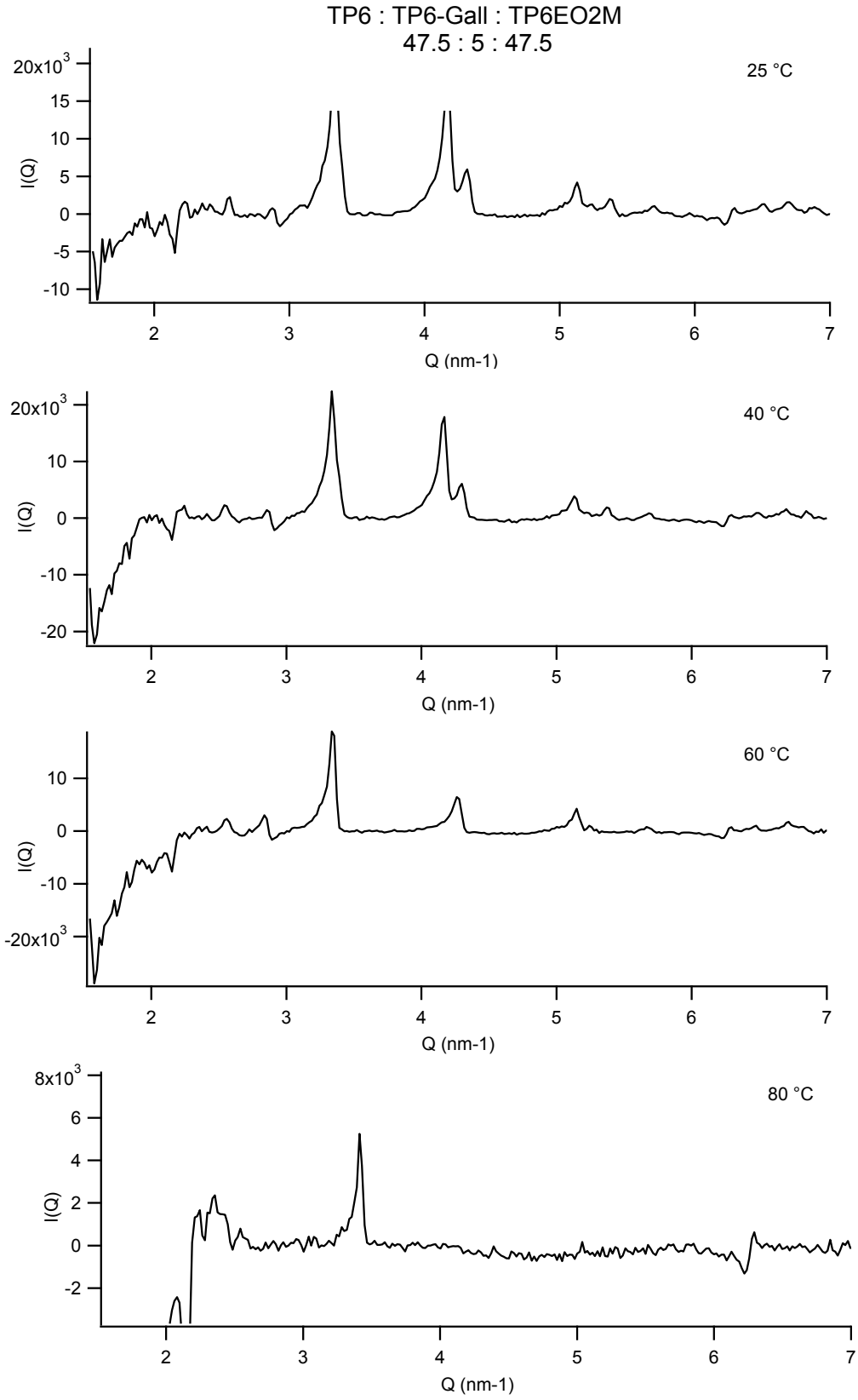


Fig. S14 SAXS patterns of a **(TP6:TP6EO2M):TP6Gall** 95mol%:5mol% mixture at different temperatures.

Morphology Study of the (TP6:TP6EO2M):TP6Gall = 80:20 mixture

Polarised Optical Microscopy

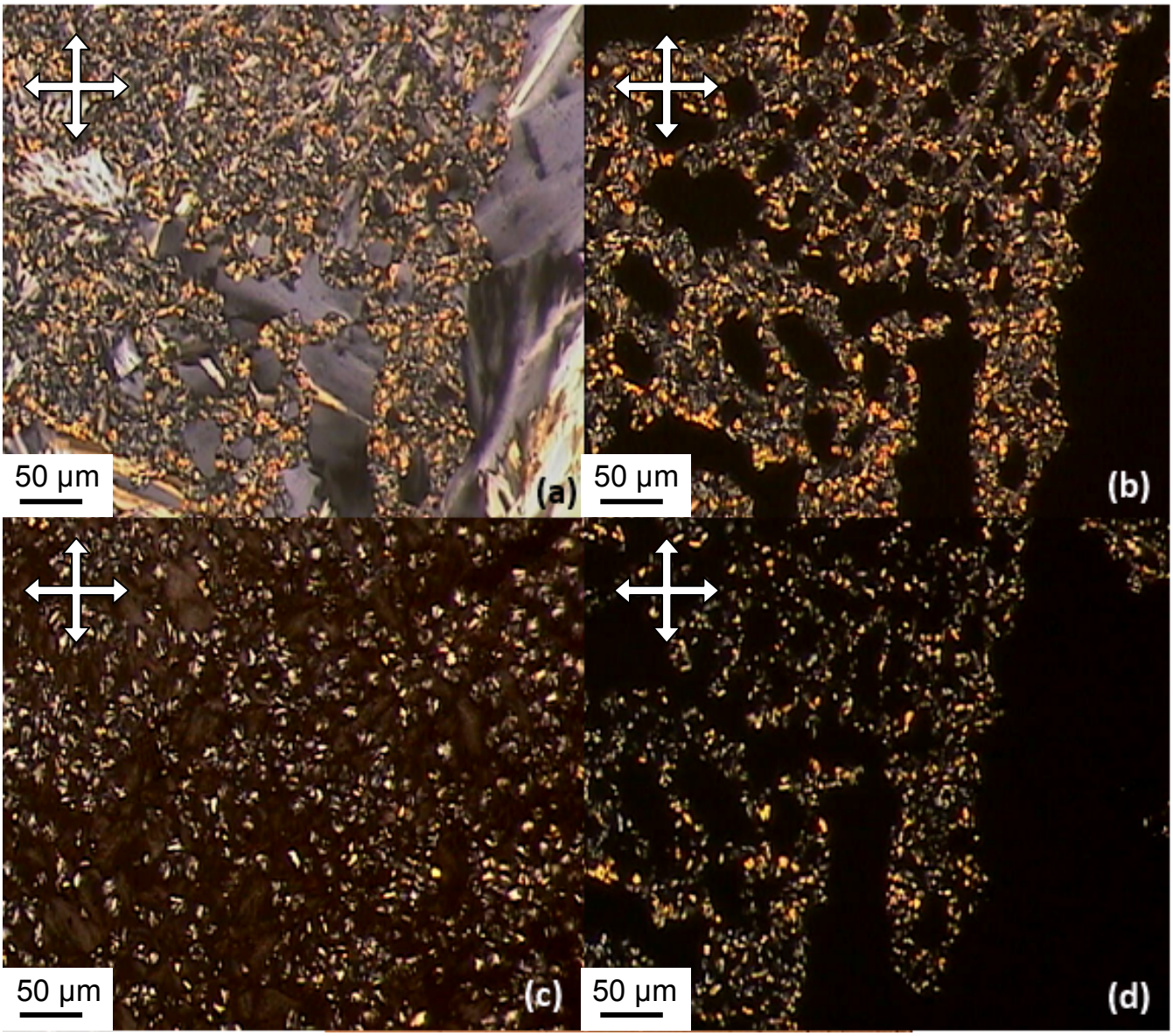


Fig. S15 POM image of a **(TP6:TP6EO2M):TP6Gall** 80mol%:20mol% mixture on heating stage. (a) room temperature, (b) 48 °C, (c) 54 °C, (d) 65 °C.

Differential Scanning Calorimetry

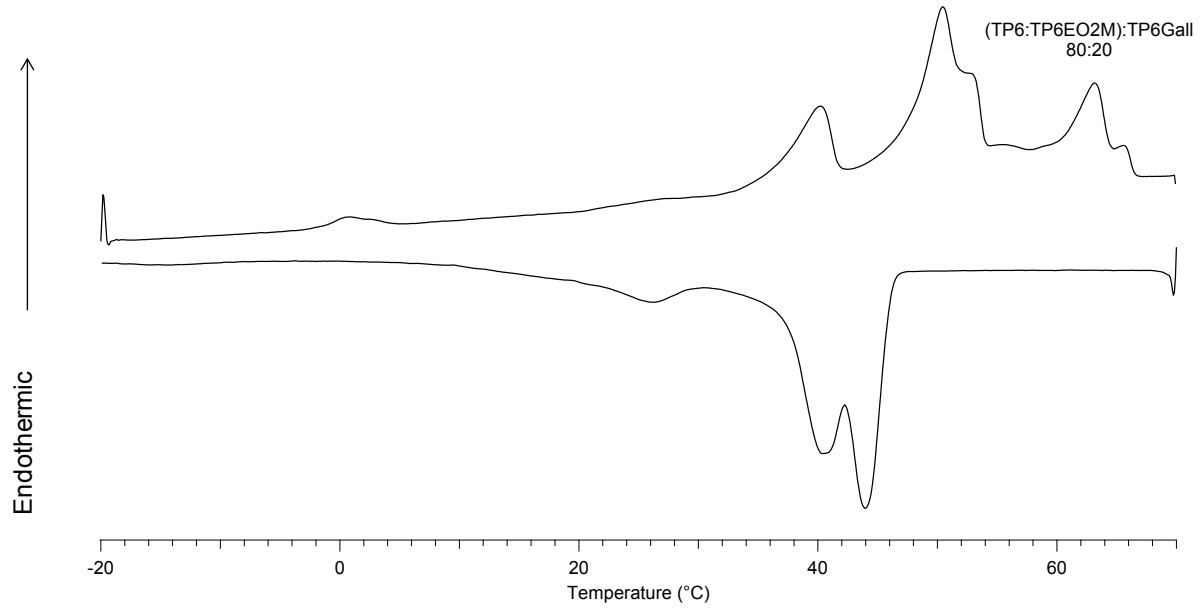


Fig. S16 DSC curve of a **(TP6:TP6EO2M):TP6Gall** 80mol%:20mol% mixture (10 ºC/min).

Small Angle X-ray scattering

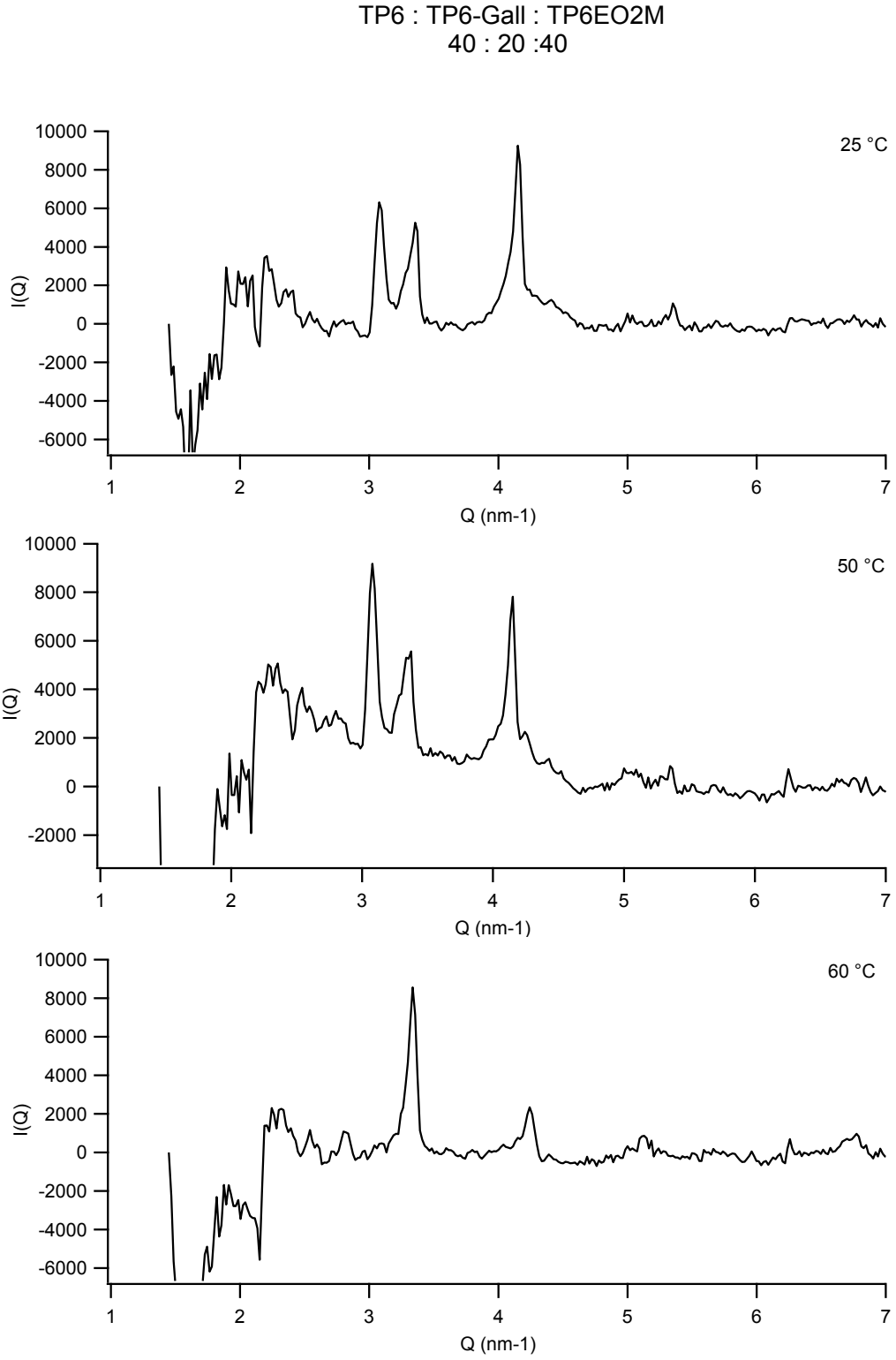


Fig. S17 SAXS patterns of a **(TP6:TP6EO2M):TP6Gall** 80mol%:20mol% mixture at different temperatures.

Morphology Study of the (TP6:TP6EO2M):TP6Gall = 50:50 mixture

Polarised Optical Microscopy

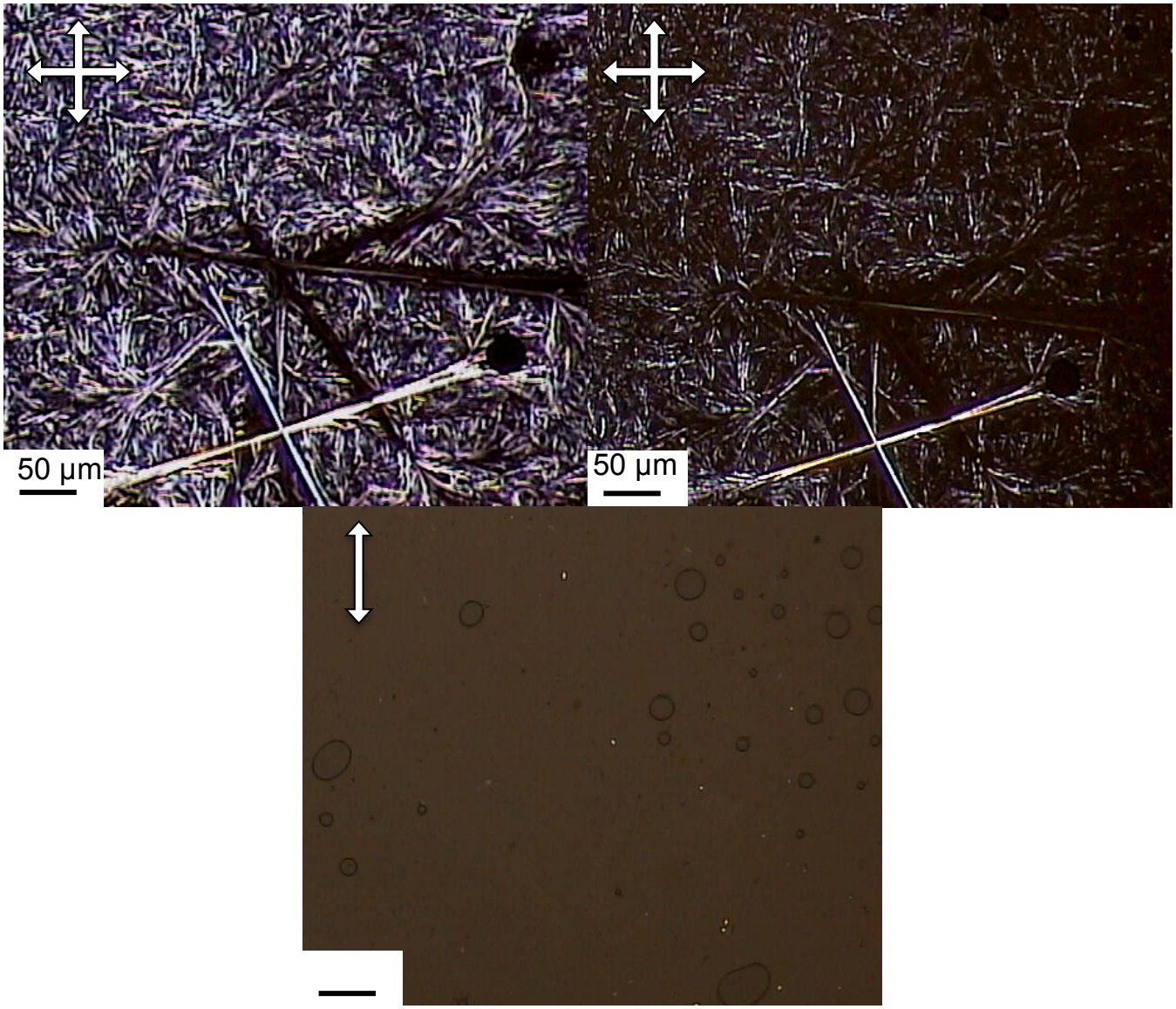


Fig. S18 POM image of a **(TP6:TP6EO2M):TP6Gall** 50mol%:50mol% mixture on heating stage. (a) 30 °C, (b) 50 °C, (c) 70 °C.

Differential Scanning Calorimetry

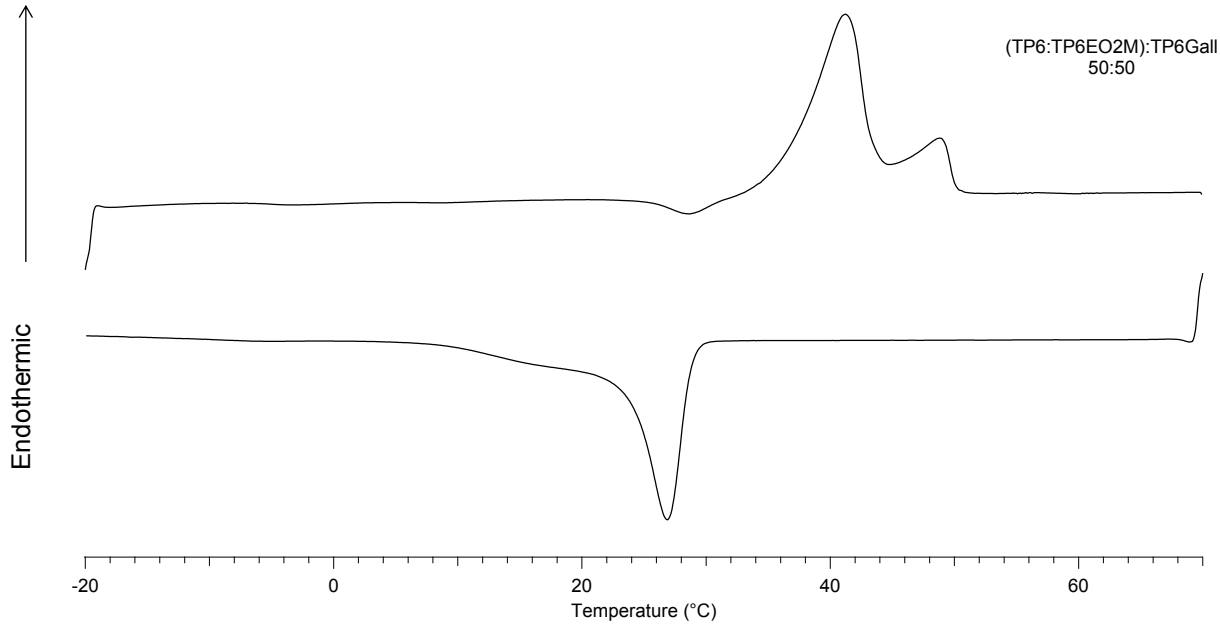


Fig. S19 DSC curve of a **(TP6:TP6EO2M):TP6Gall** 50mol%:50mol% mixture (10 ºC/min).

Small Angle X-ray scattering

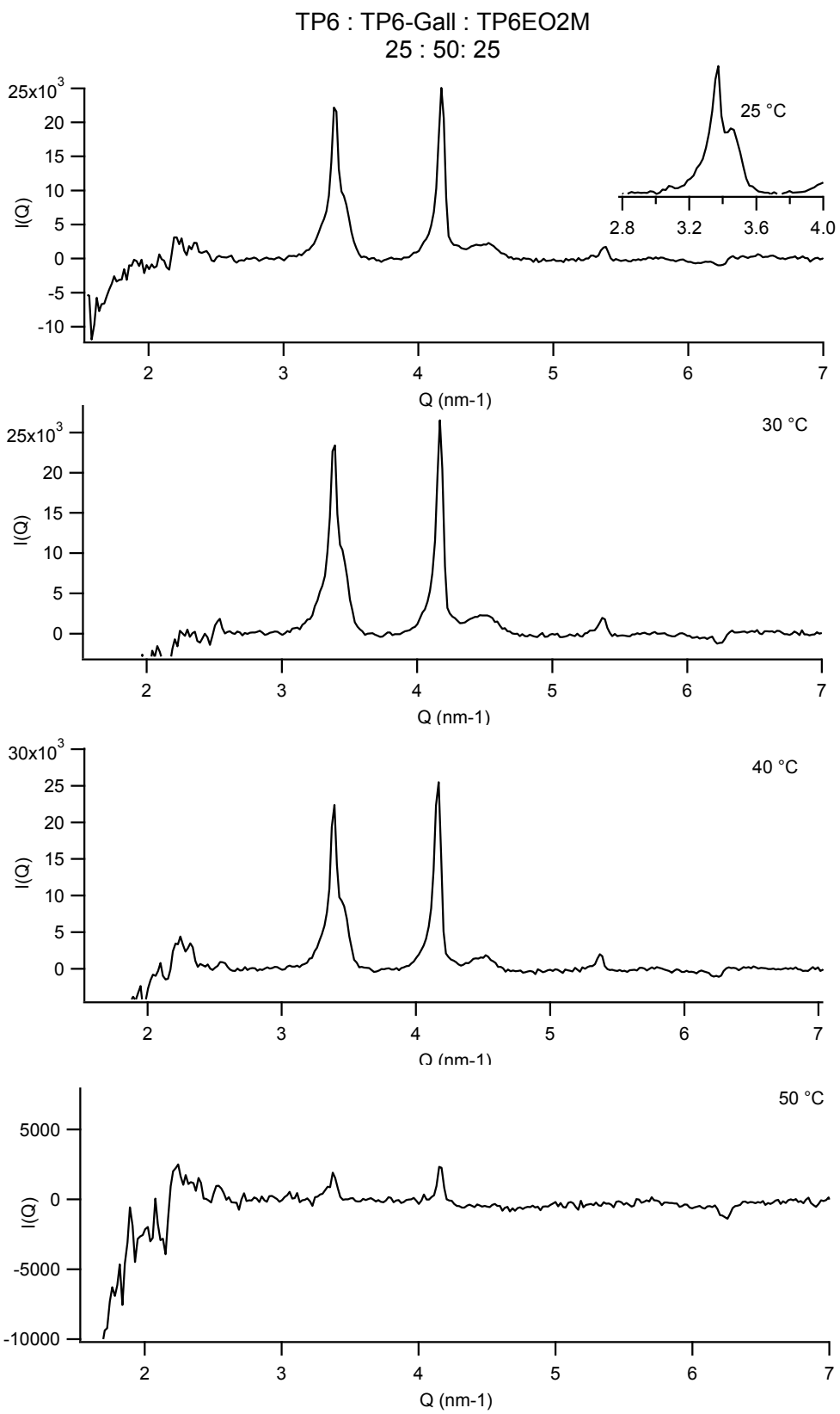


Fig. S20 SAXS patterns of a **(TP6:TP6EO2M):TP6Gall** 50mol%:50mol% mixture at different temperatures.

Morphology Study of the equimolar blend of TP6:TP6Gall

Polarised Optical Microscopy

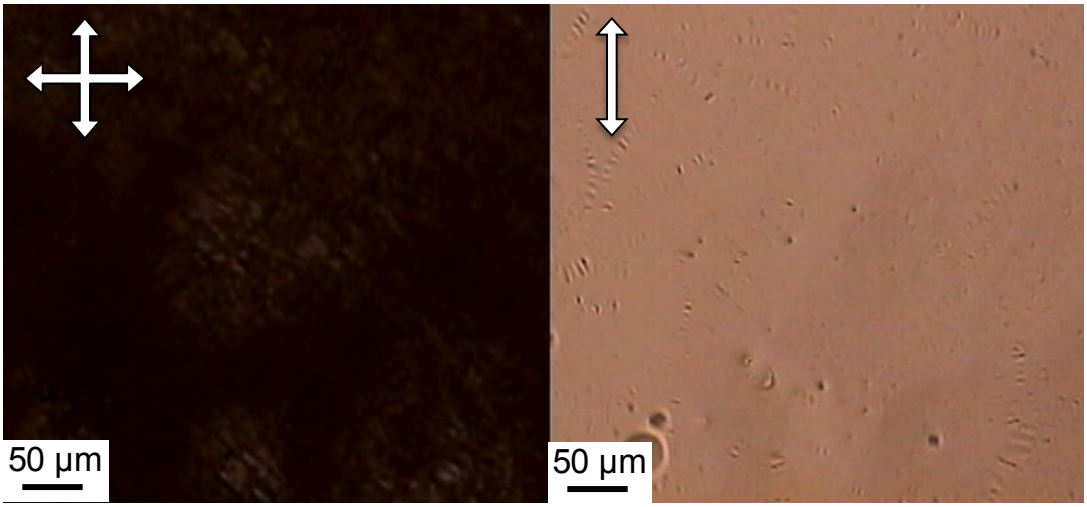


Fig. S21 POM image of a **TP6:TP6Gall** 50mol%:50mol% mixture on heating stage. From left to right: 22 °C, 52 °C without polariser.

Differential Scanning Calorimetry

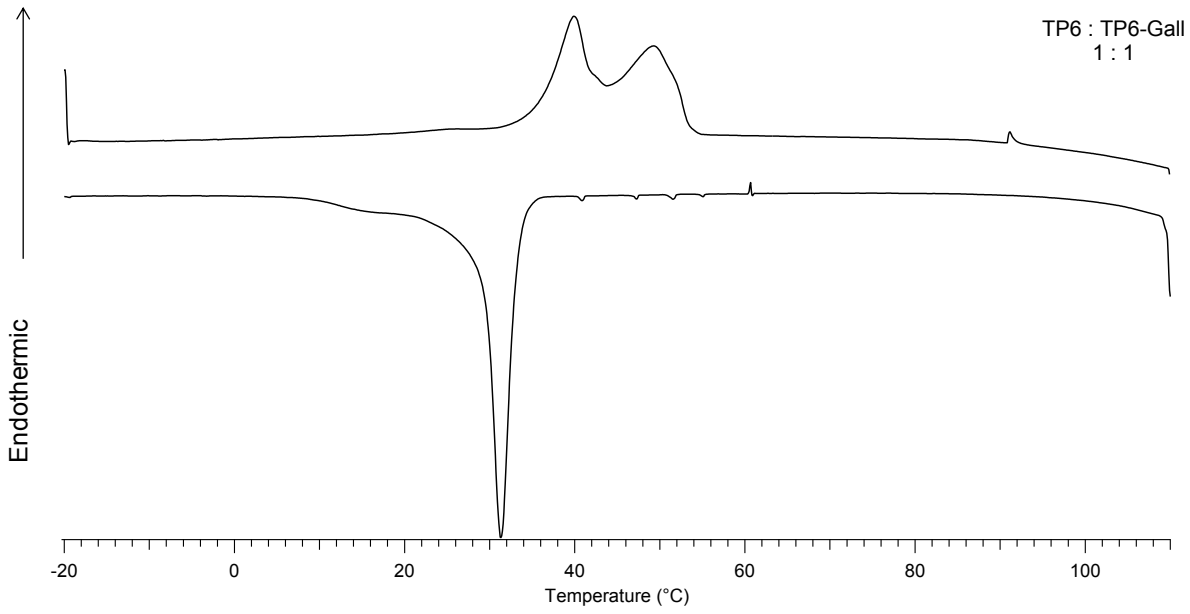


Fig. S22 DSC curve of a **TP6:TP6Gall** 50mol%:50mol% mixture (10 ºC/min).

Small Angle X-ray scattering

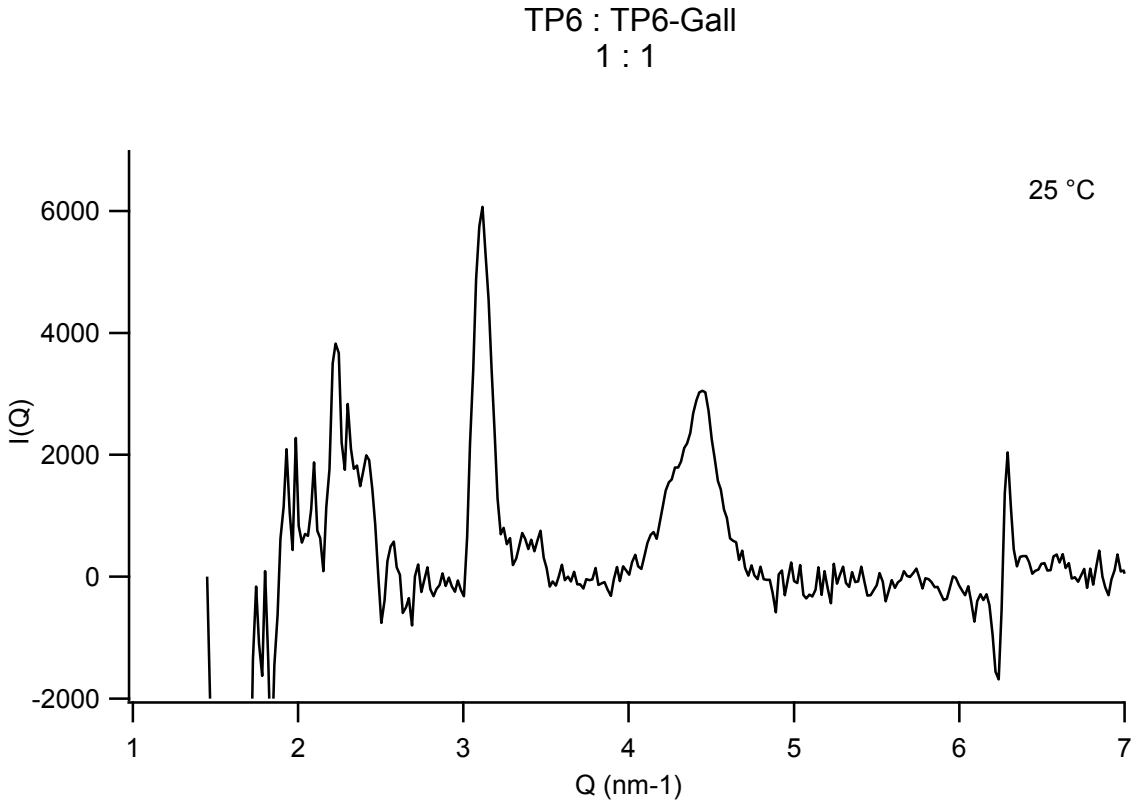


Fig. S23 SAXS pattern of a **TP6:TP6Gall** 50mol%:50mol% mixture.

^{1}H and ^{13}C NMR spectra

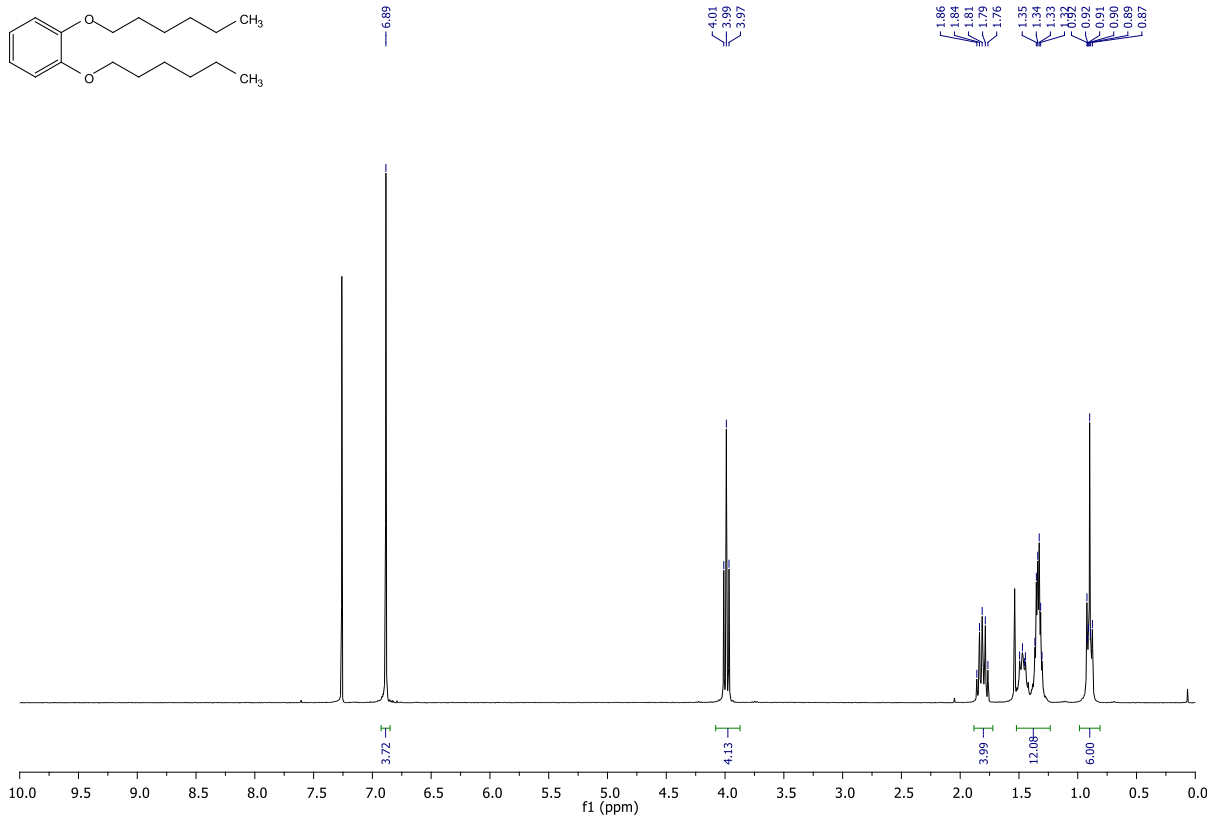


Fig. S24 ^{1}H NMR spectrum of **001** ($CDCl_3$).

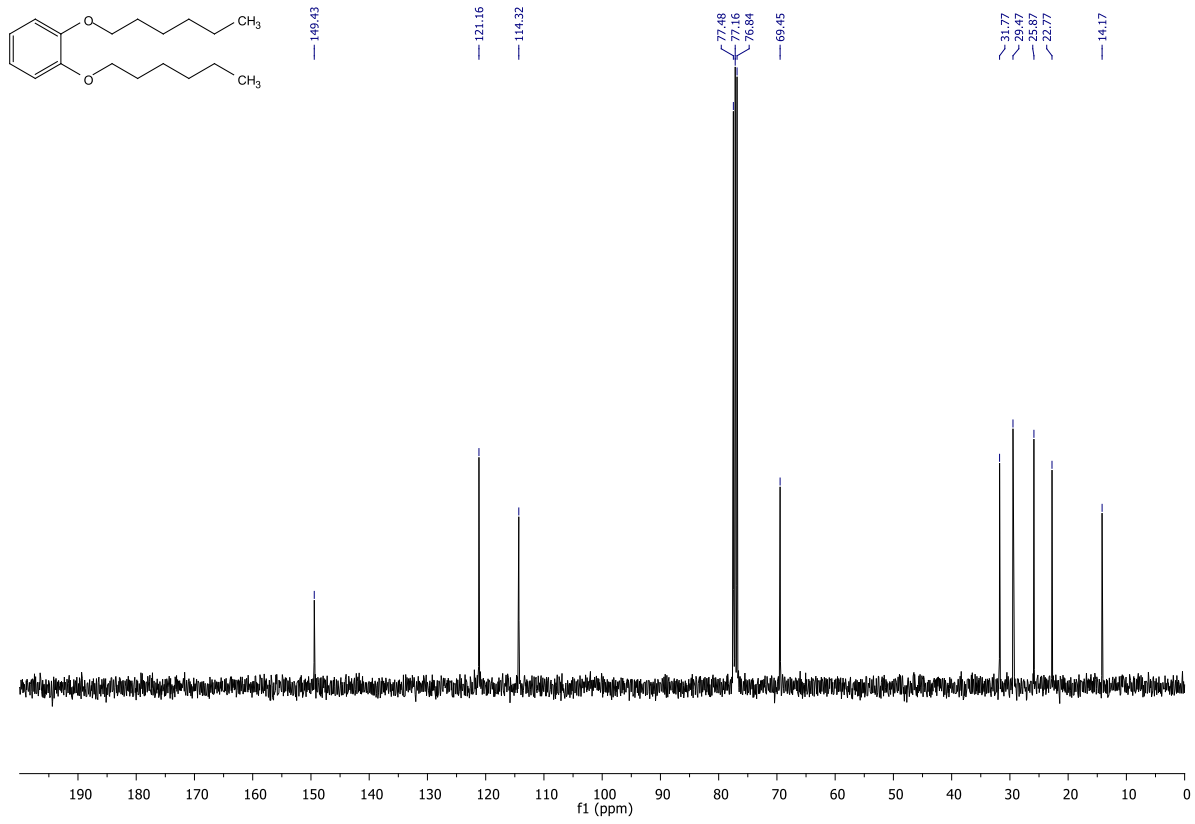


Fig. S25 ^{13}C NMR spectrum of **001** ($CDCl_3$).

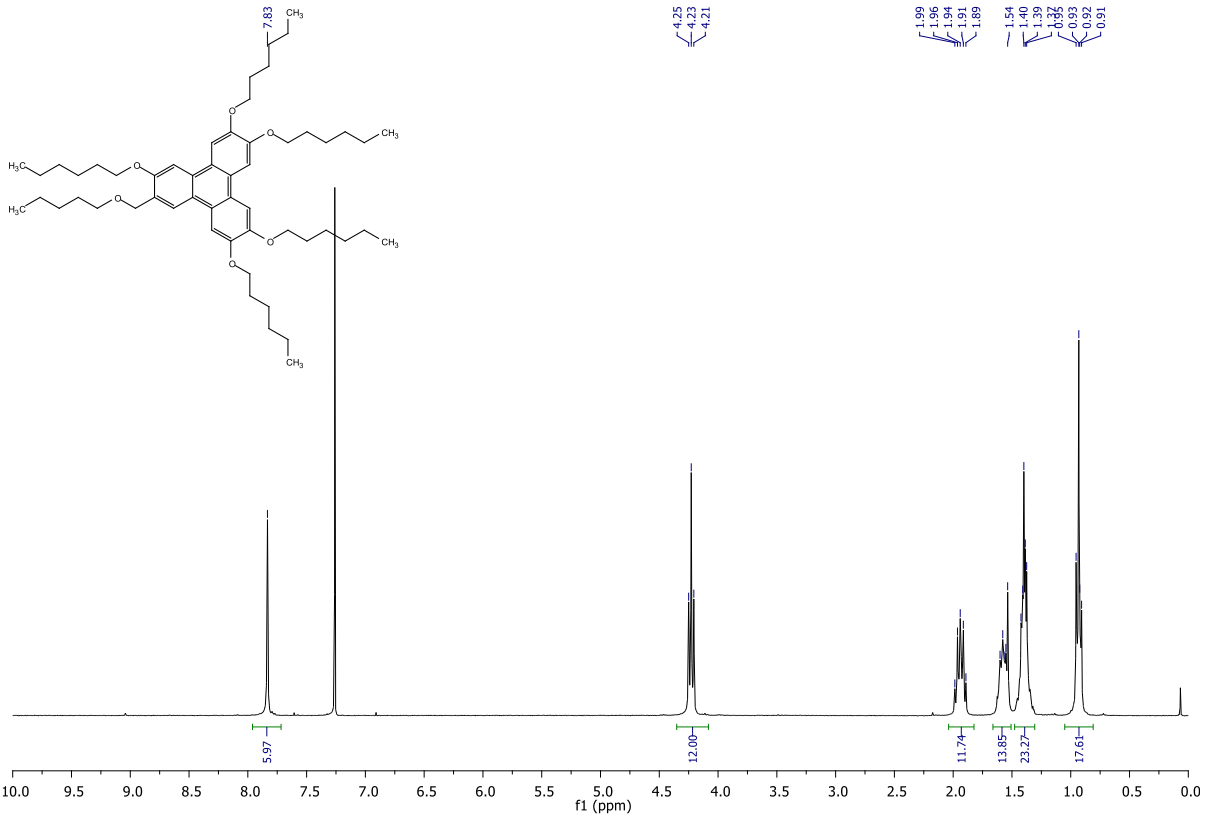


Fig. S26 ^{1}H NMR spectrum of **002** ($CDCl_3$).

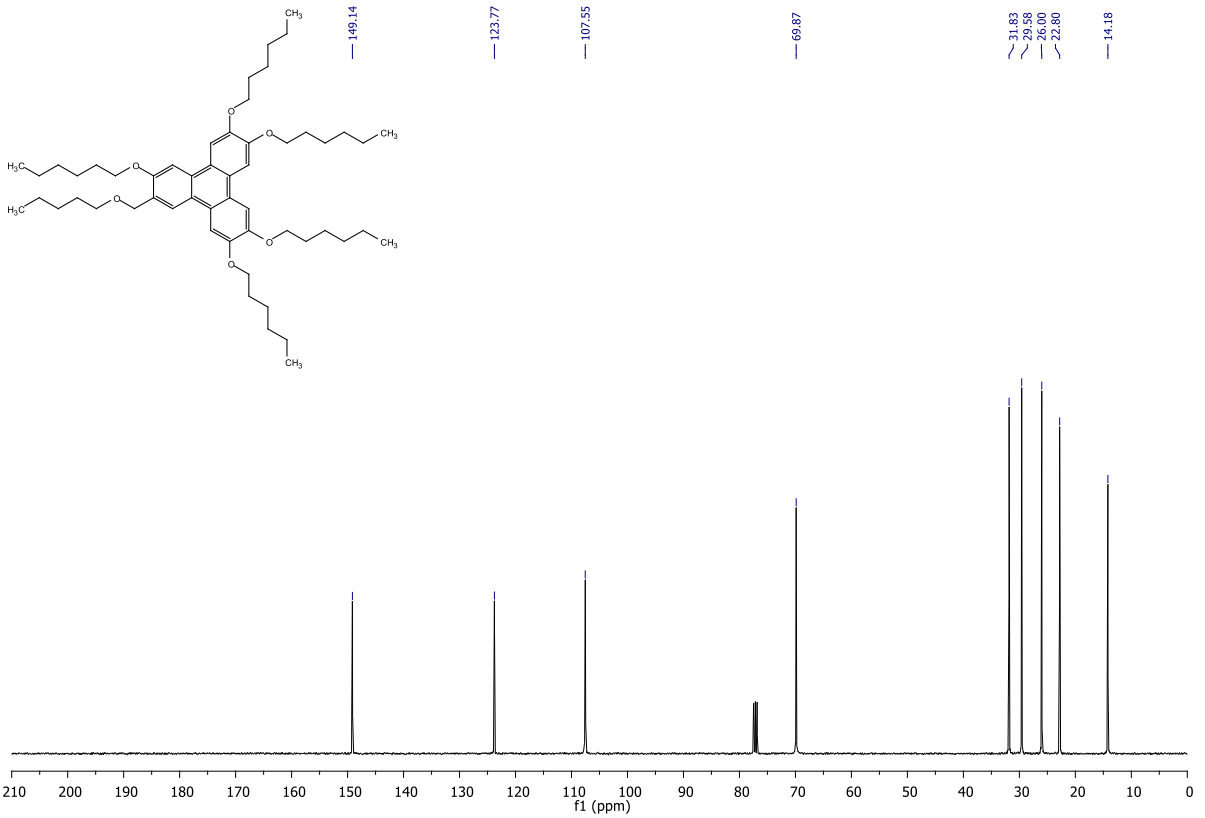


Fig. S27 ^{13}C NMR spectrum of **002** ($CDCl_3$).

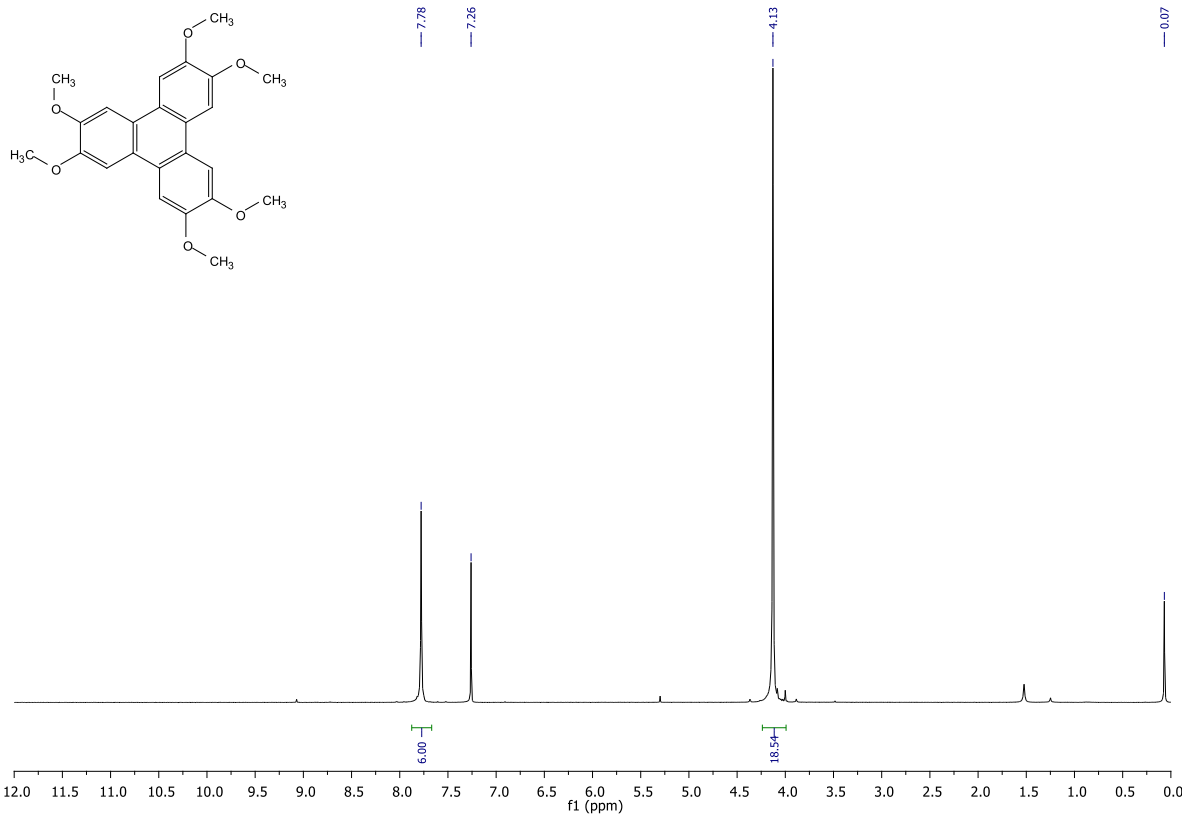


Fig. S28 ^{1}H NMR spectrum of **003** ($CDCl_3$).

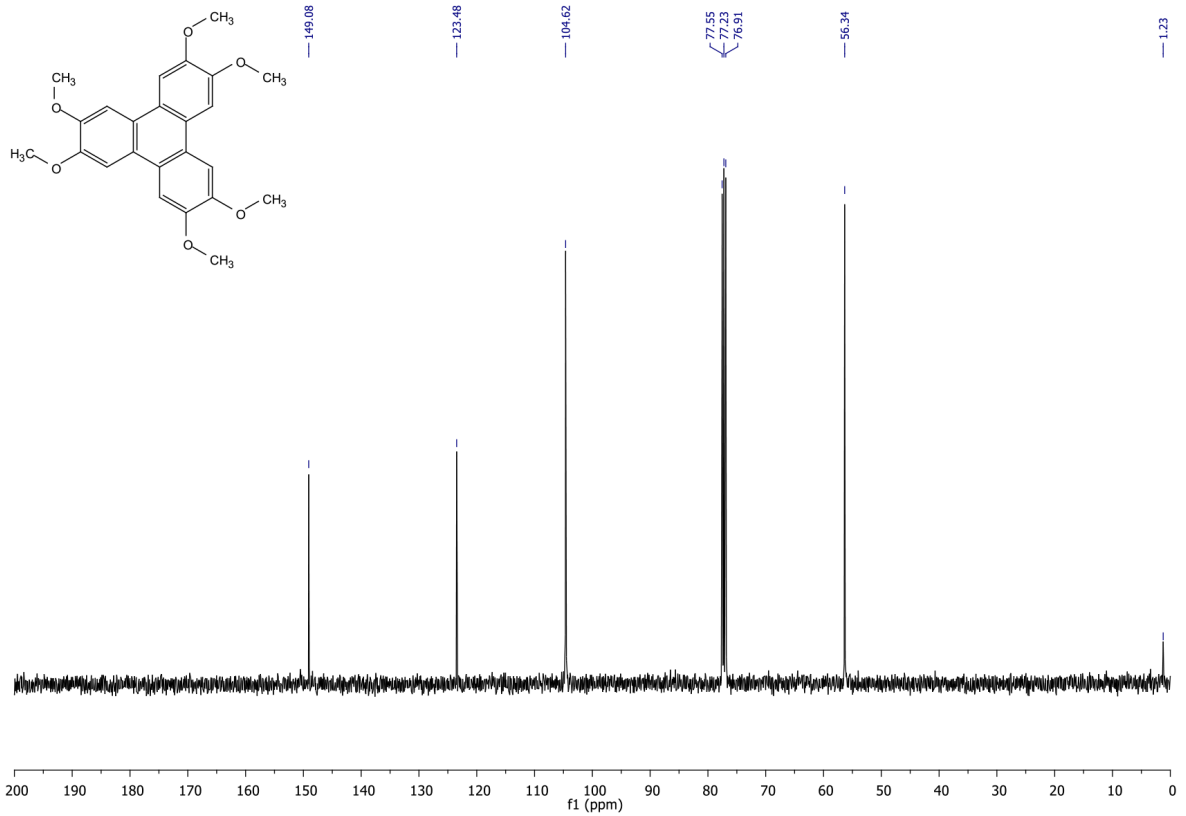


Fig. S29 ^{13}C NMR spectrum of **003** ($CDCl_3$).

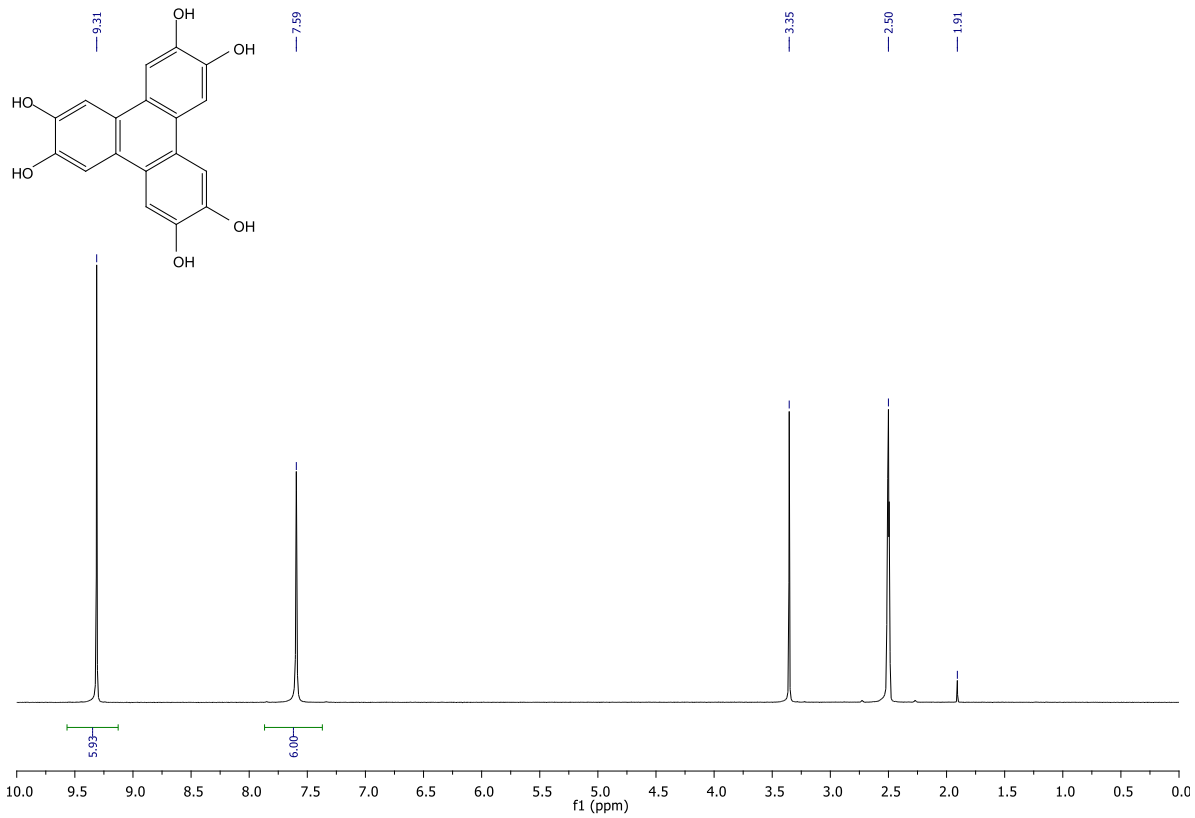


Fig. S30 ^{1}H NMR spectrum of **004** (DMSO-d6).

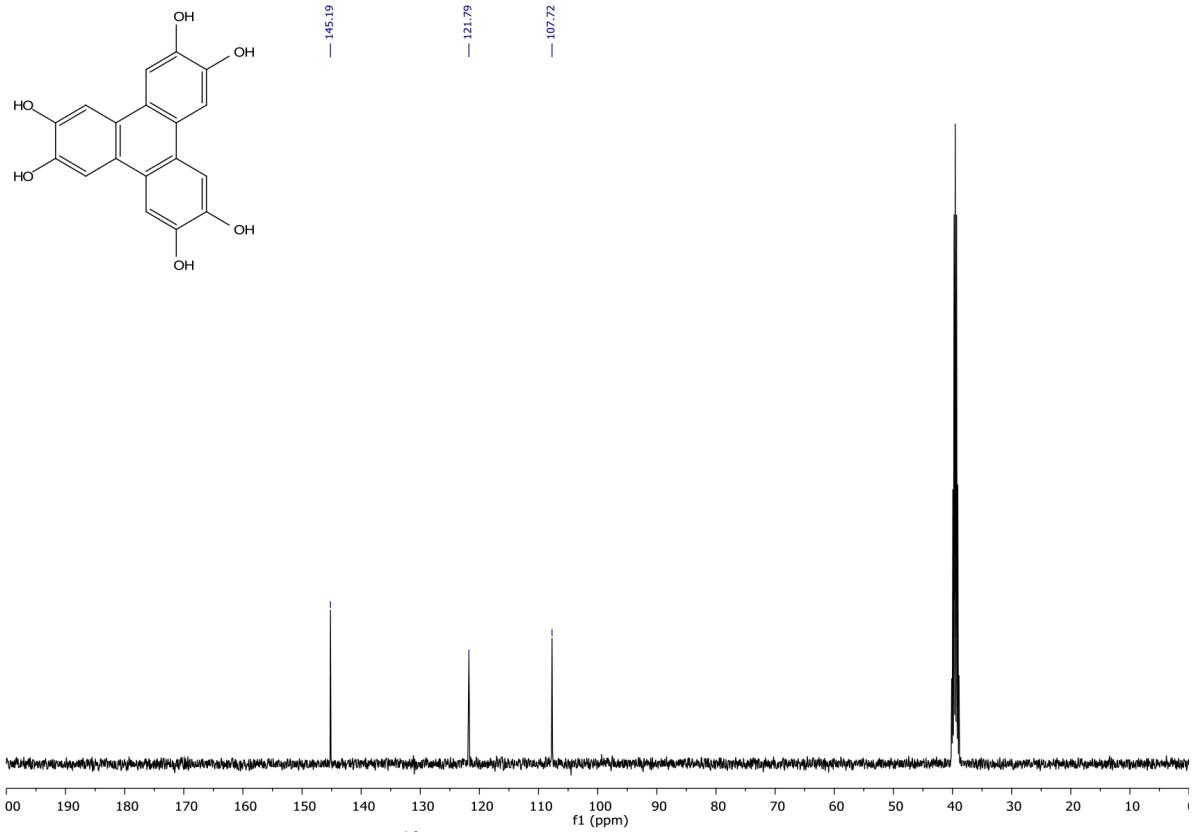
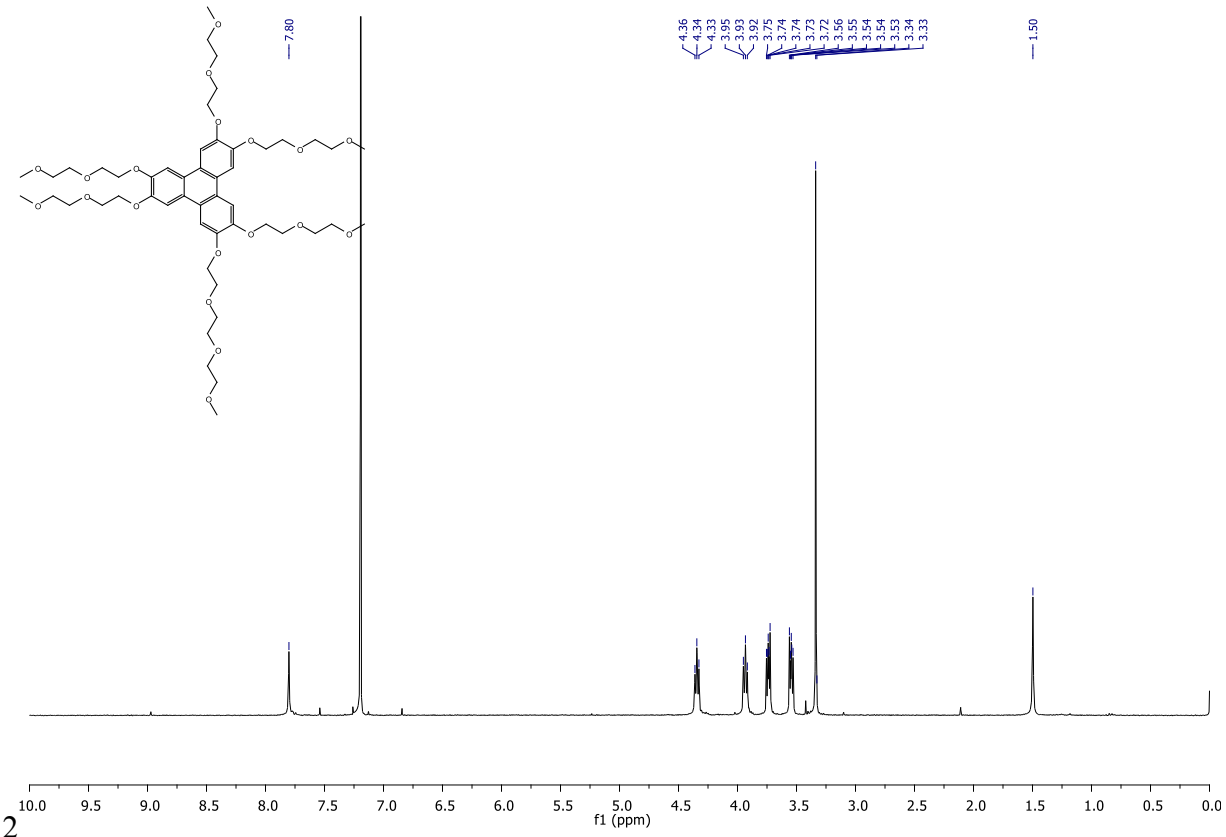


Fig. S31 ^{13}C NMR spectrum of **004** (DMSO-d6).



2

Fig. S32 ^{1}H NMR spectrum of **005** ($CDCl_3$).

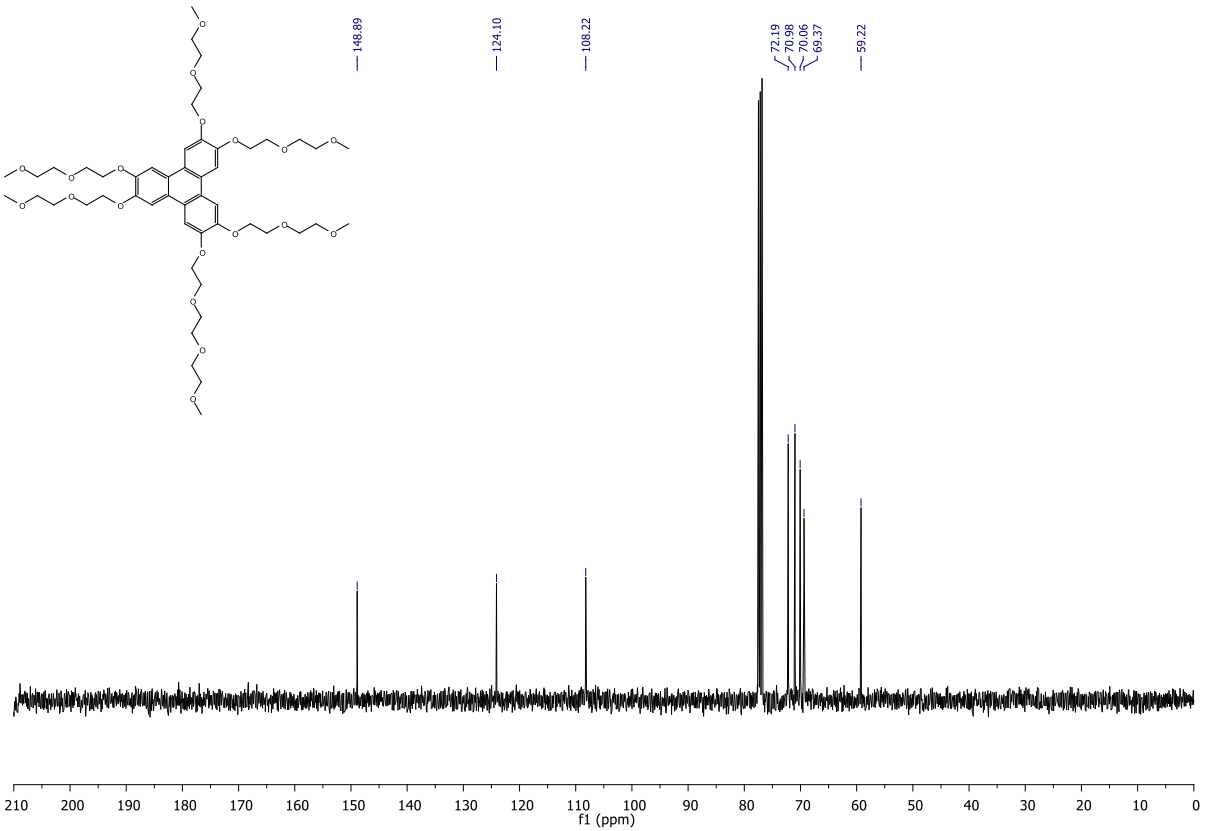


Fig. S33 ^{13}C NMR spectrum of **005** ($CDCl_3$).

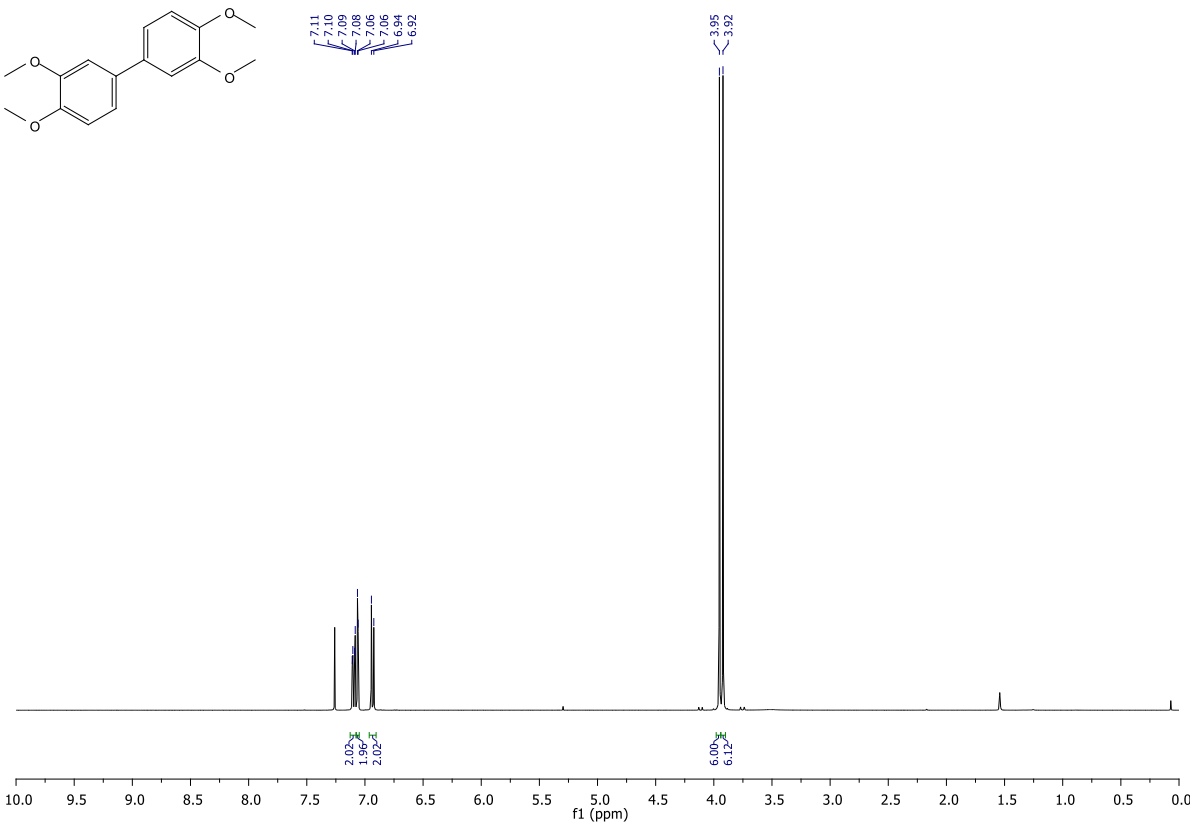


Fig. S34 ^{1}H NMR spectrum of **006** ($CDCl_3$).

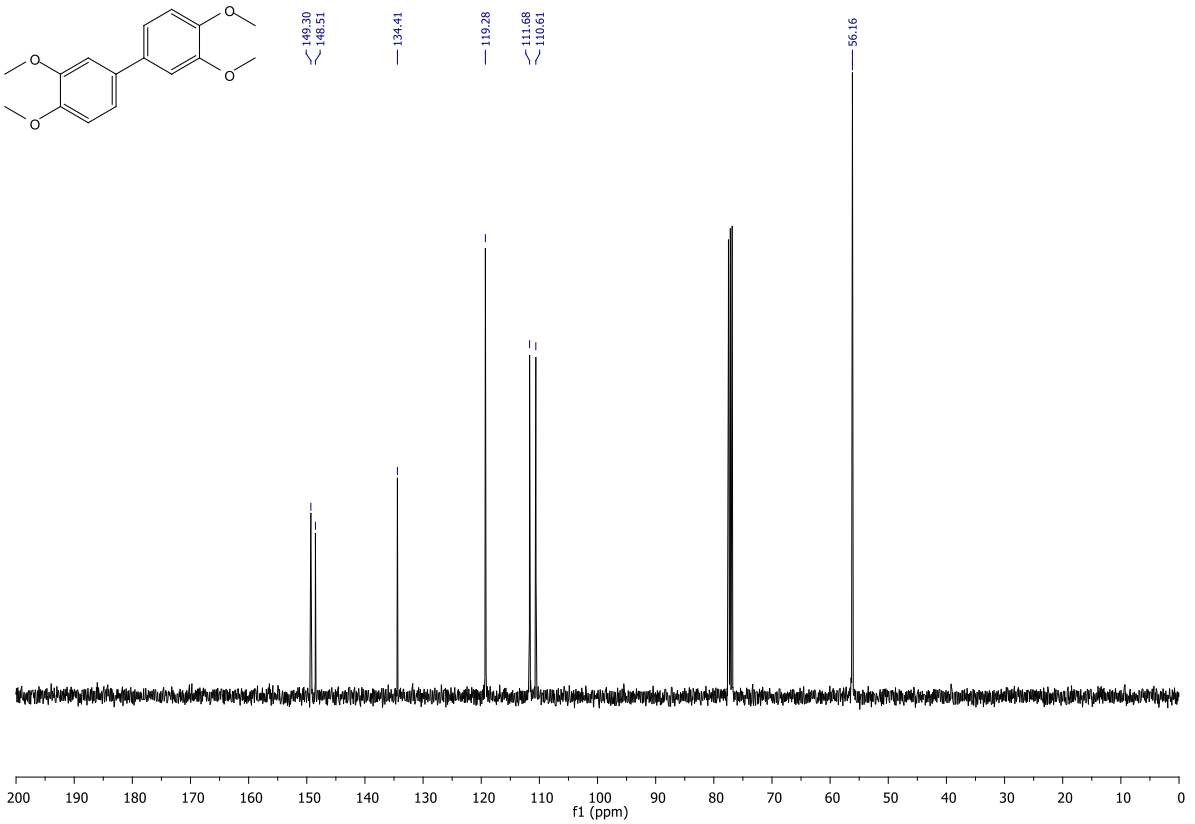


Fig. S35 ^{13}C NMR spectrum of **006** ($CDCl_3$).

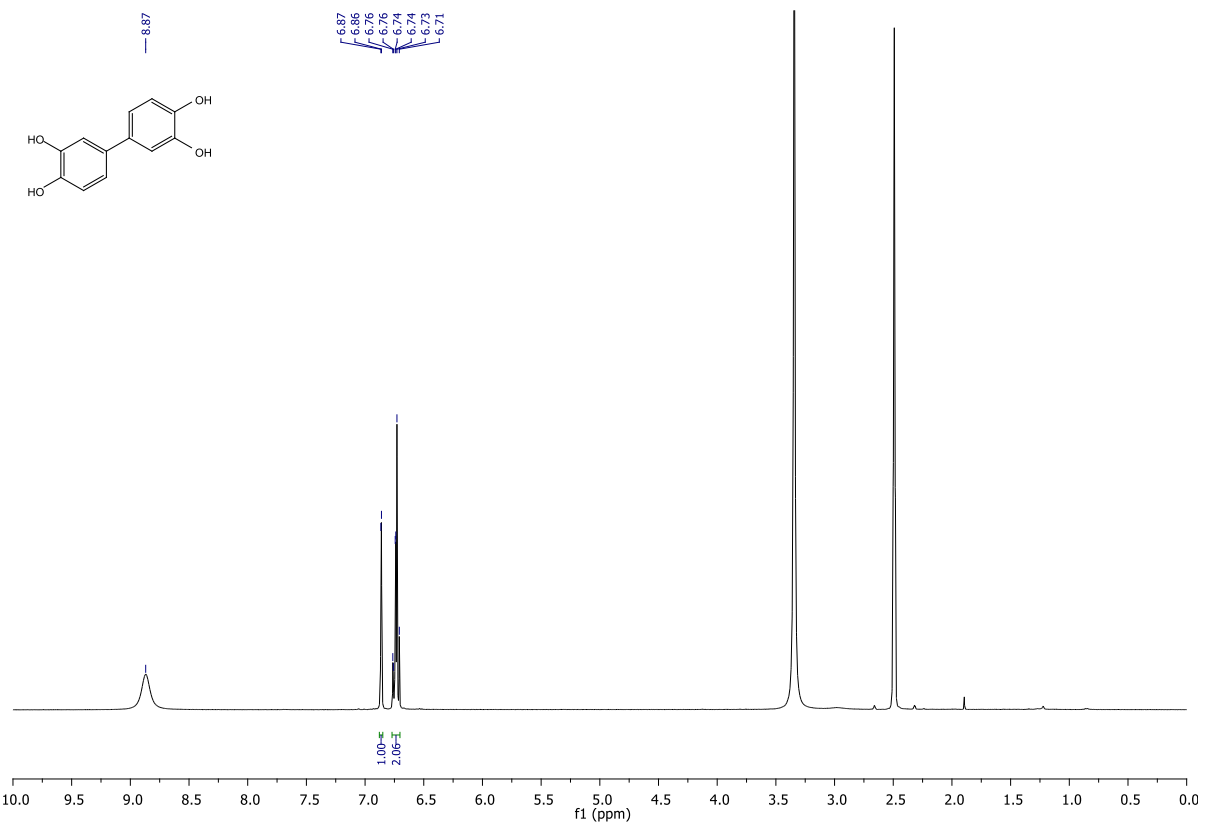


Fig. S36 ^{1}H NMR spectrum of **007** (DMSO-d6).

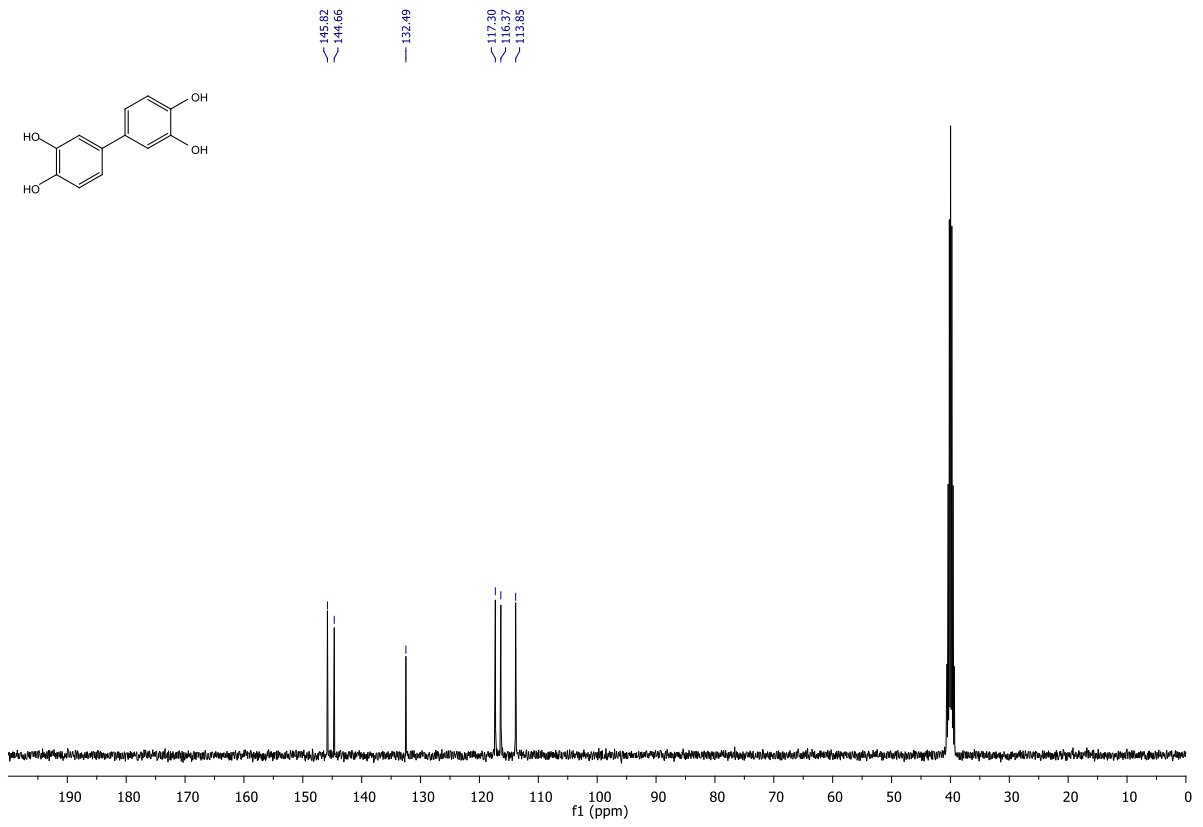


Fig. S37 ^{13}C NMR spectrum of **007** (DMSO-d6).

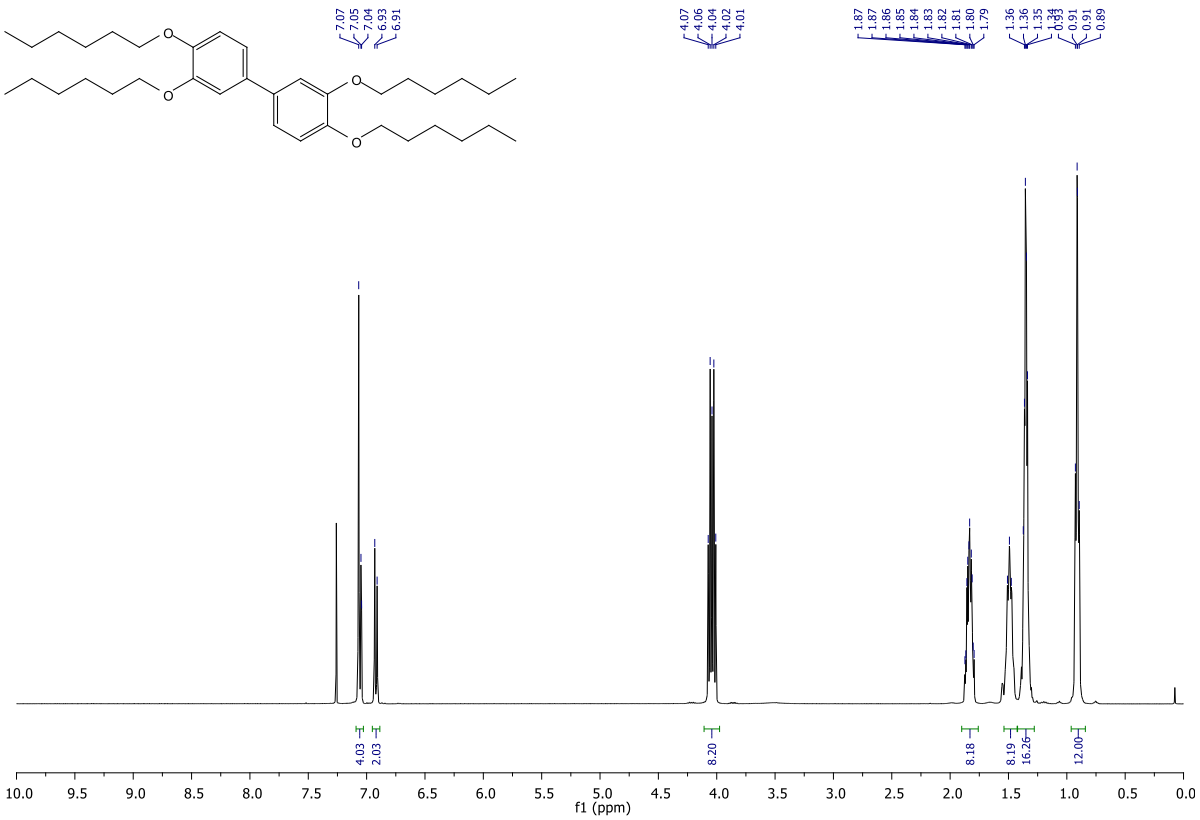


Fig. S38 ^{1}H NMR spectrum of **008** ($CDCl_3$).

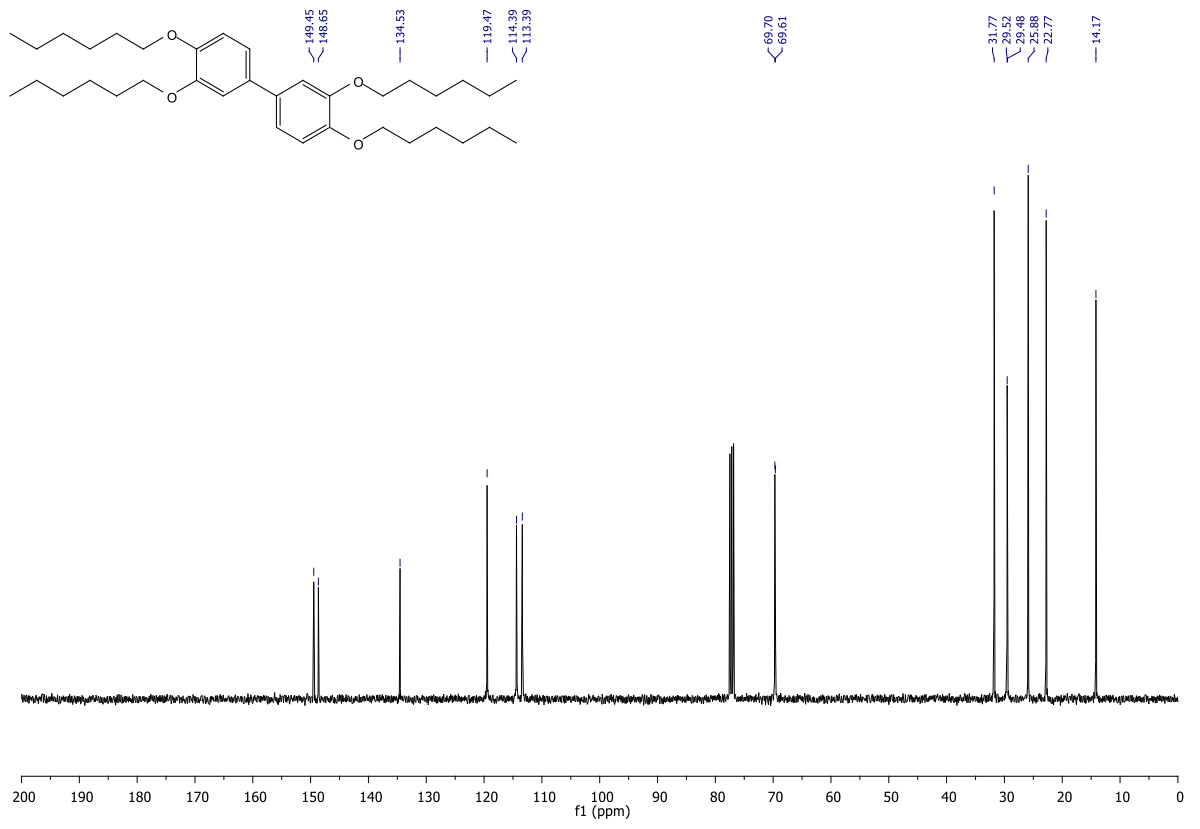


Fig. S39 ^{13}C NMR spectrum of **008** ($CDCl_3$).

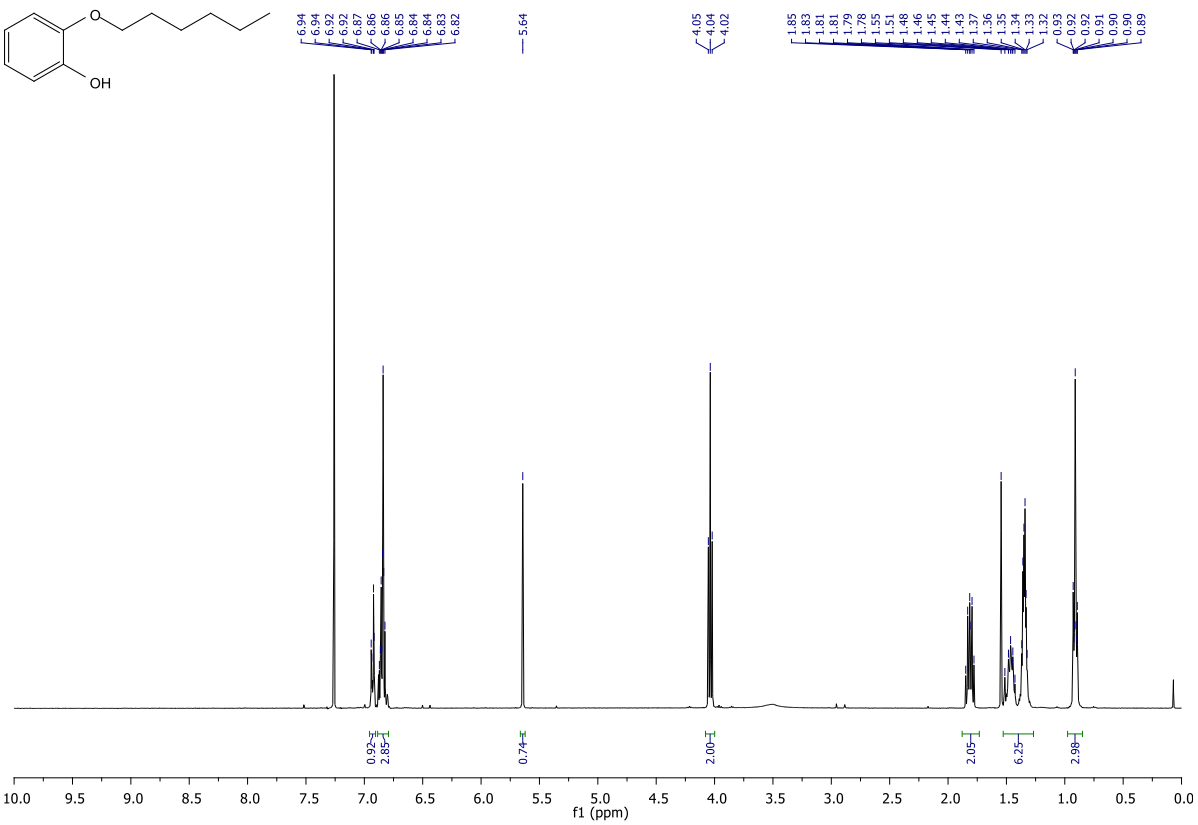


Fig. S40 ^{1}H NMR spectrum of **009** ($CDCl_3$).

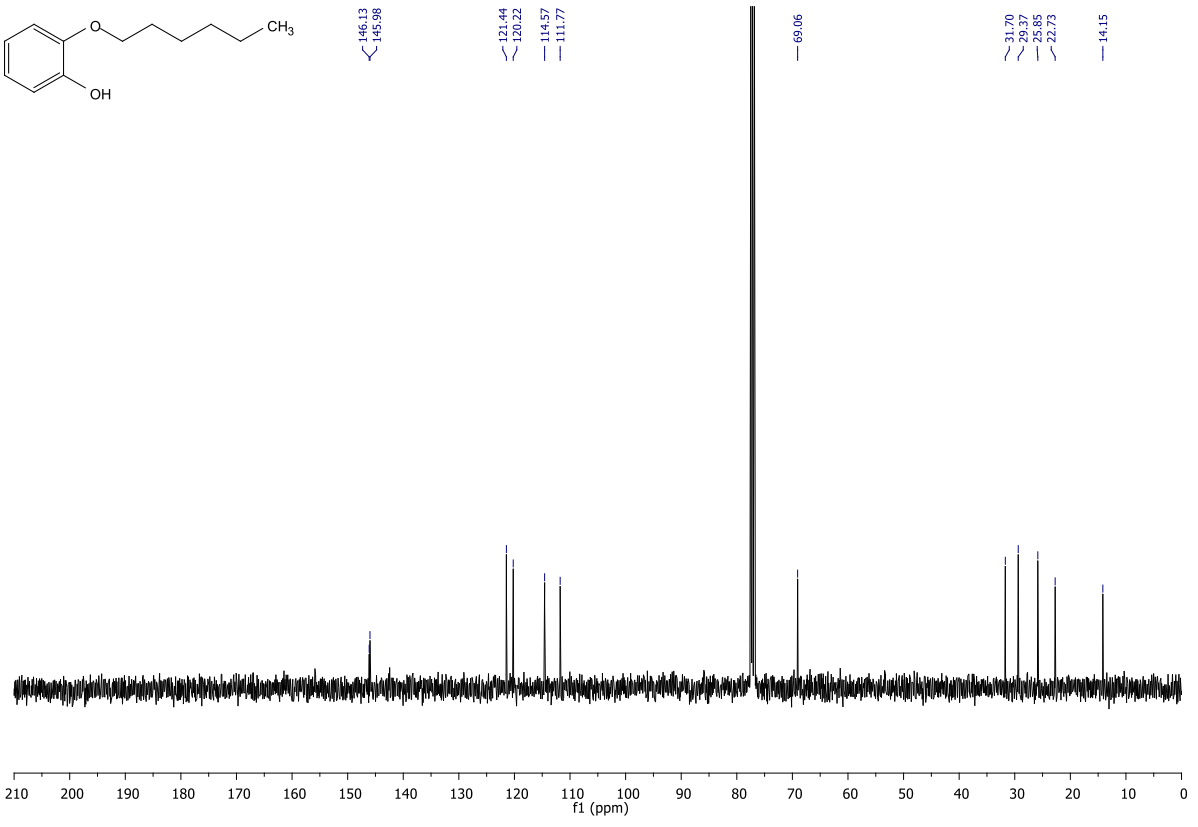


Fig. S41 ^{13}C NMR spectrum of **009** ($CDCl_3$).

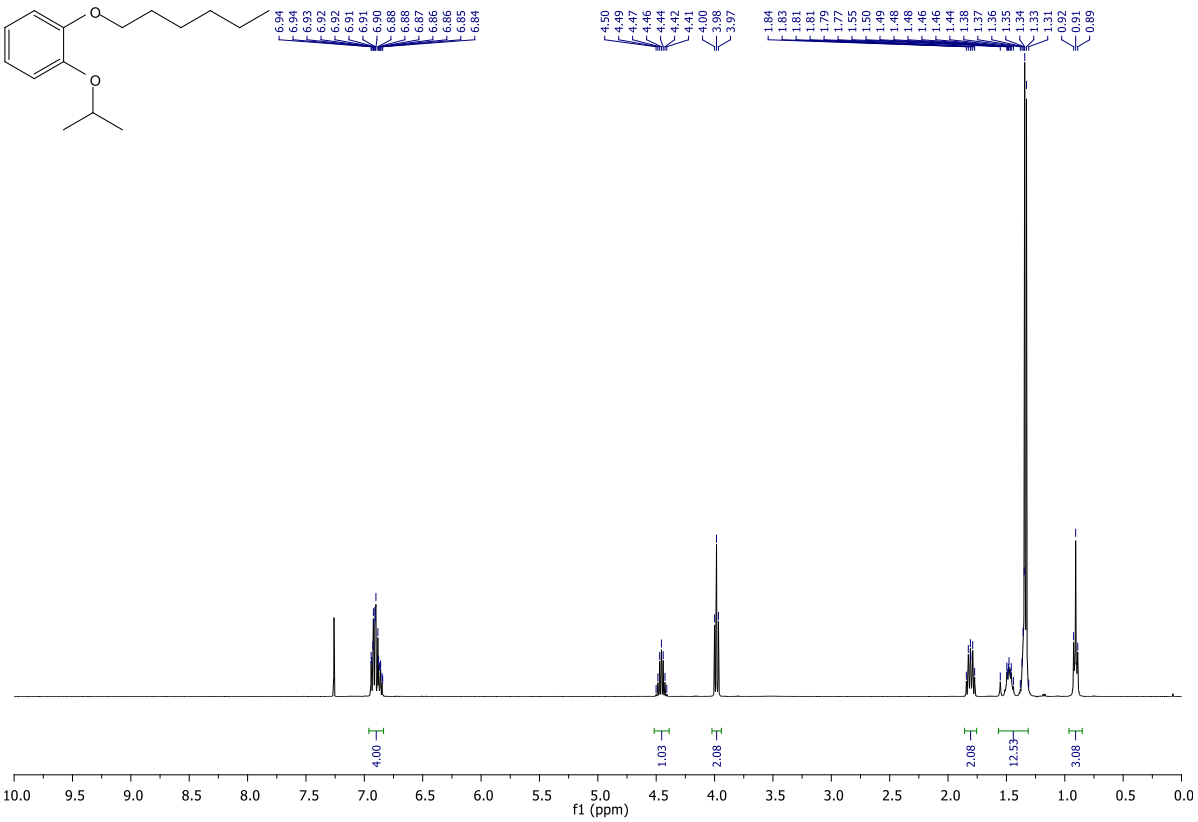


Fig. S42 ^{1}H NMR spectrum of **010** ($CDCl_3$).

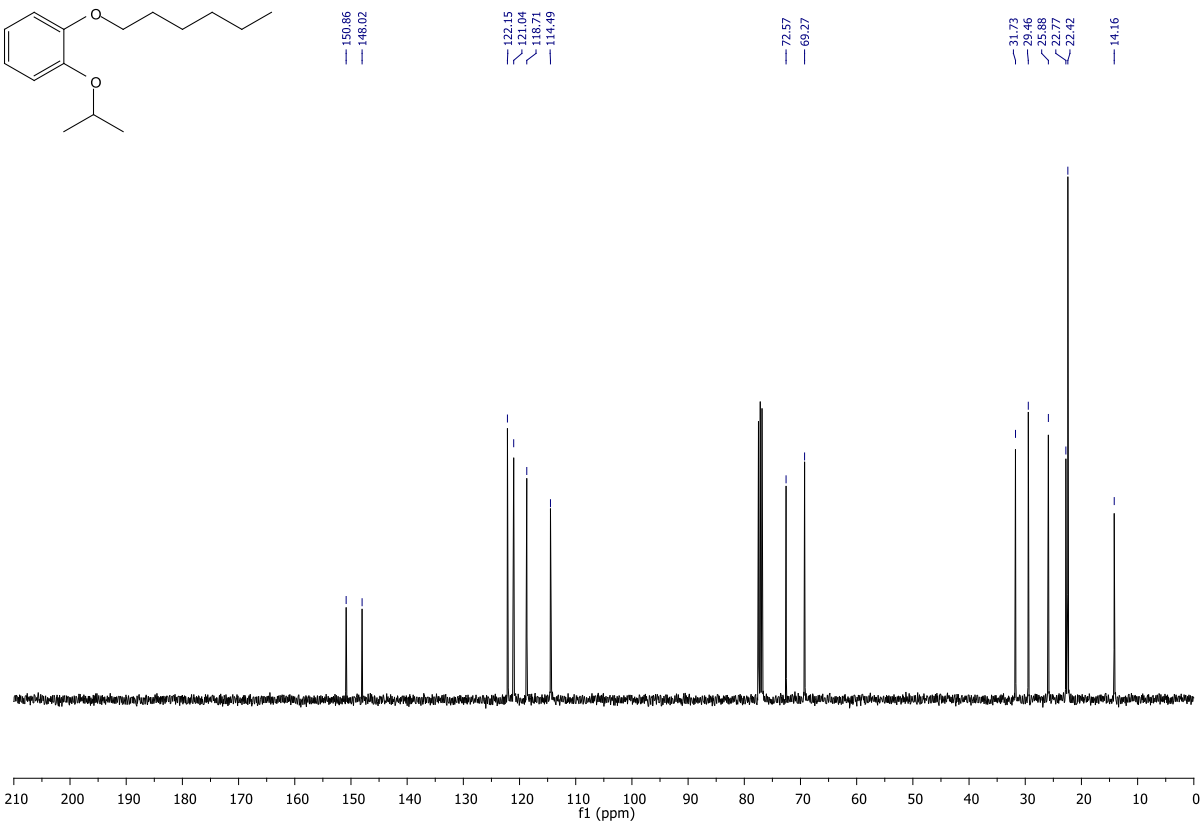


Fig. S43 ^{13}C NMR spectrum of **010** ($CDCl_3$).

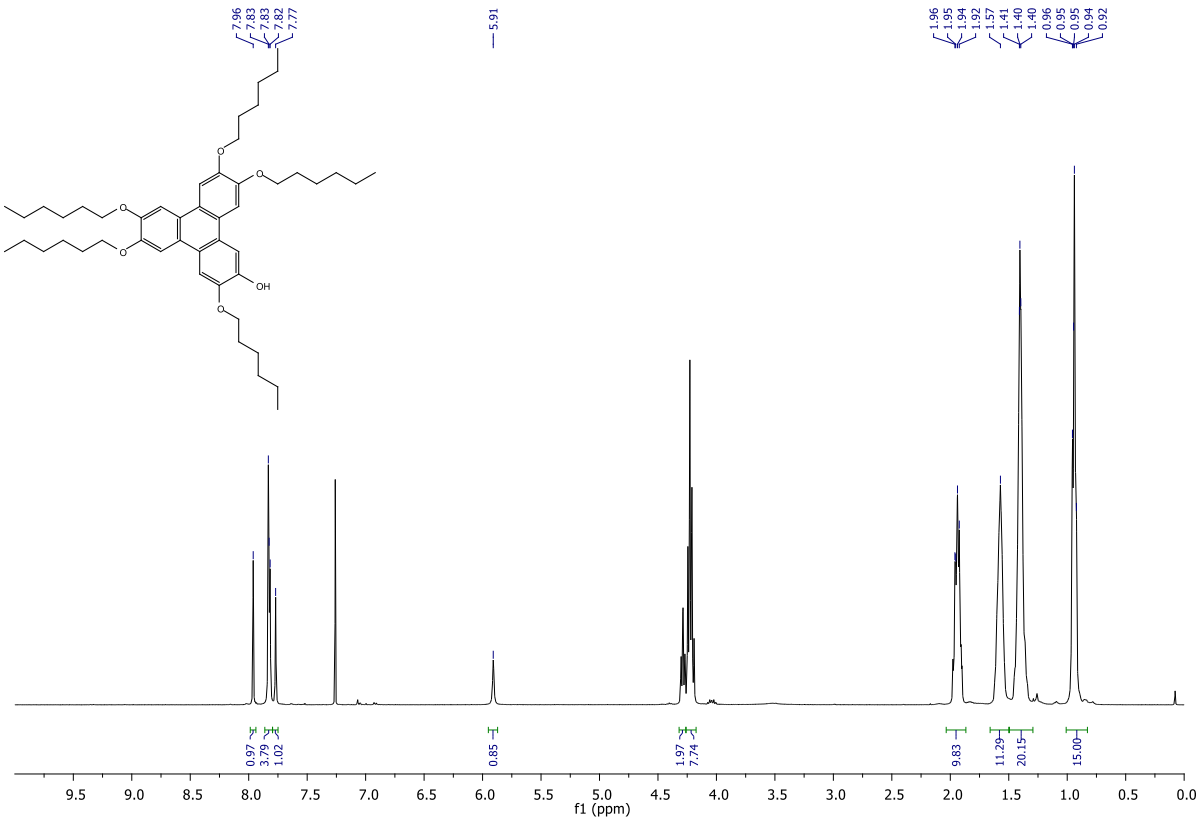


Fig. S44 ^{1}H NMR spectrum of **011** ($CDCl_3$).

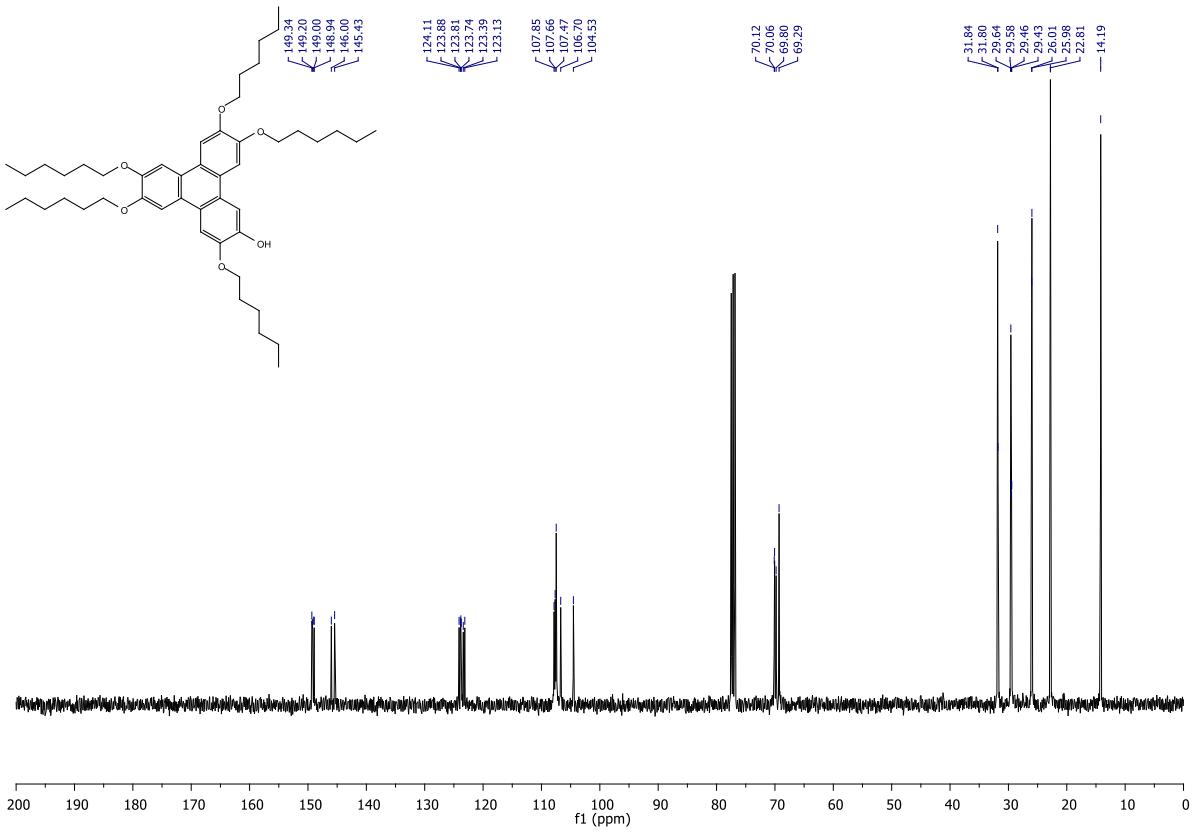


Fig. S45 ^{13}C NMR spectrum of **011** ($CDCl_3$).

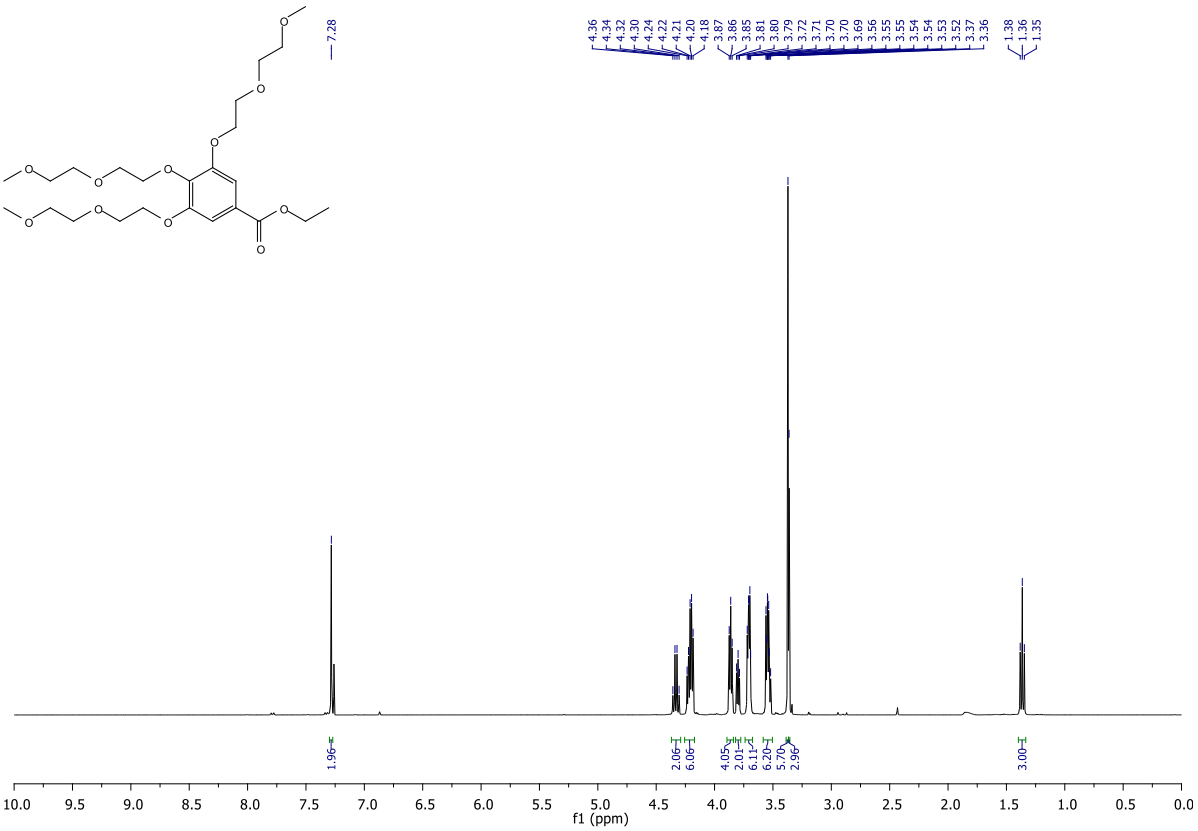


Fig. S46 ^{1}H NMR spectrum of **012** ($CDCl_3$).

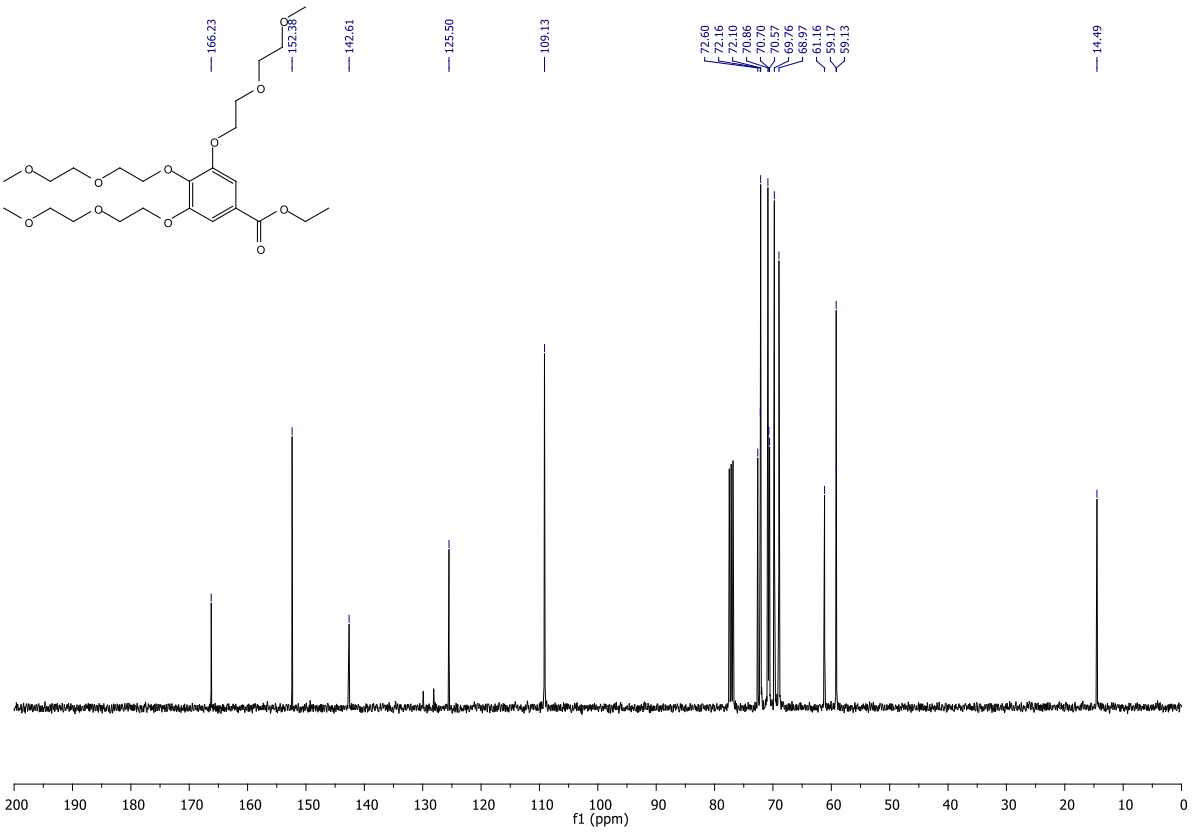


Fig. S47 ^{13}C NMR spectrum of **012** ($CDCl_3$).

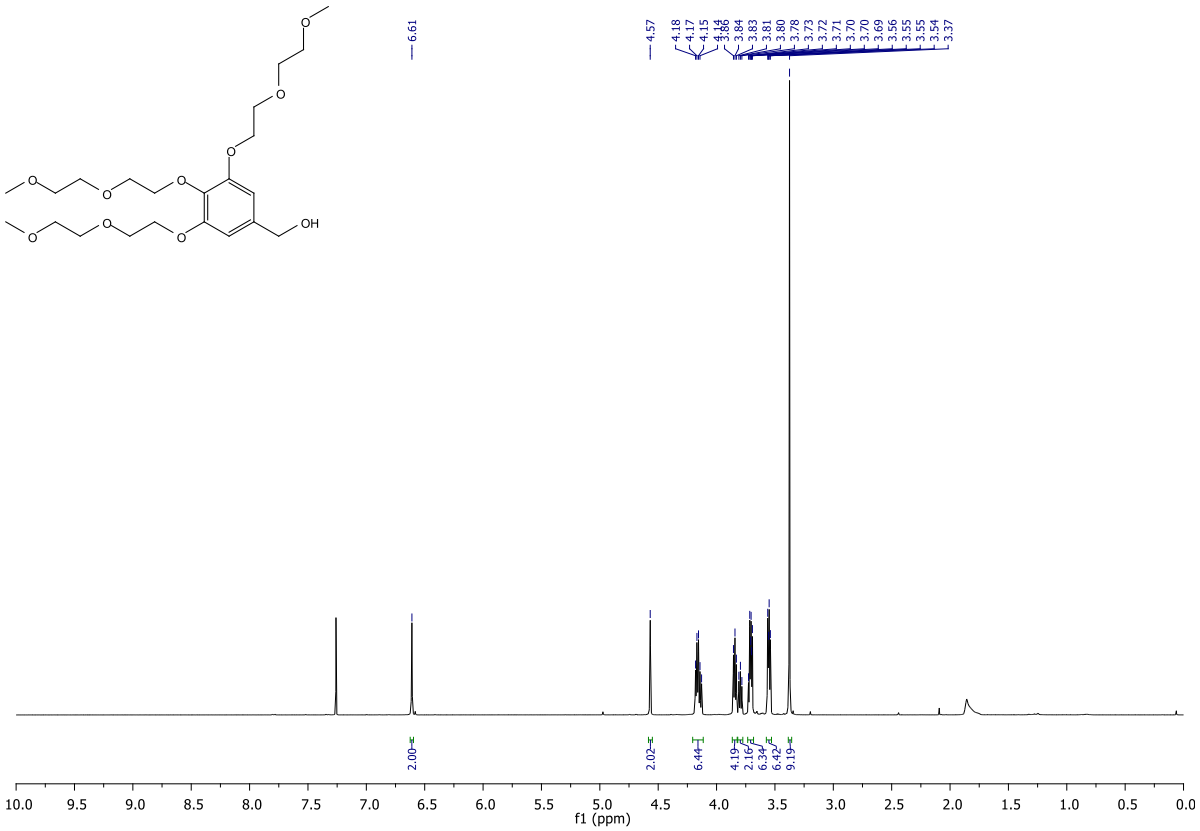


Fig. S48 ^{1}H NMR spectrum of **013** ($CDCl_3$).

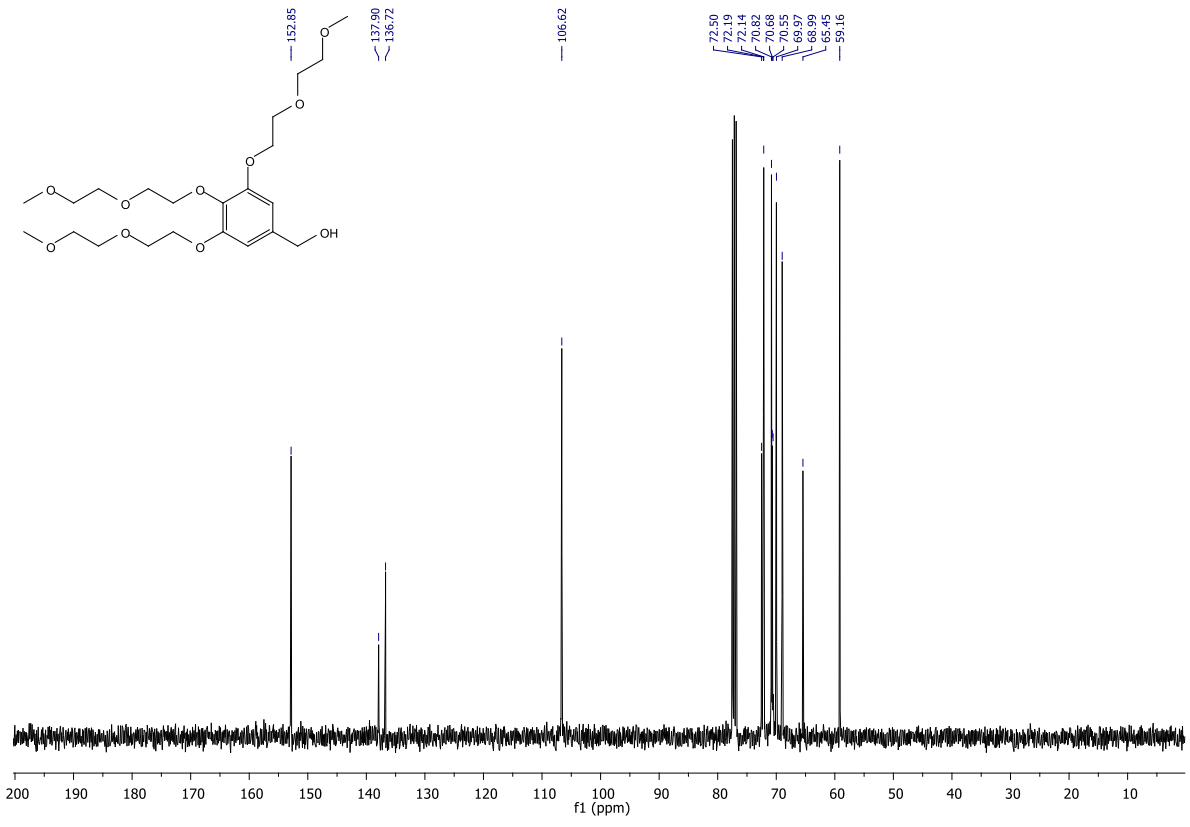


Fig. S49 ^{13}C NMR spectrum of **013** ($CDCl_3$).

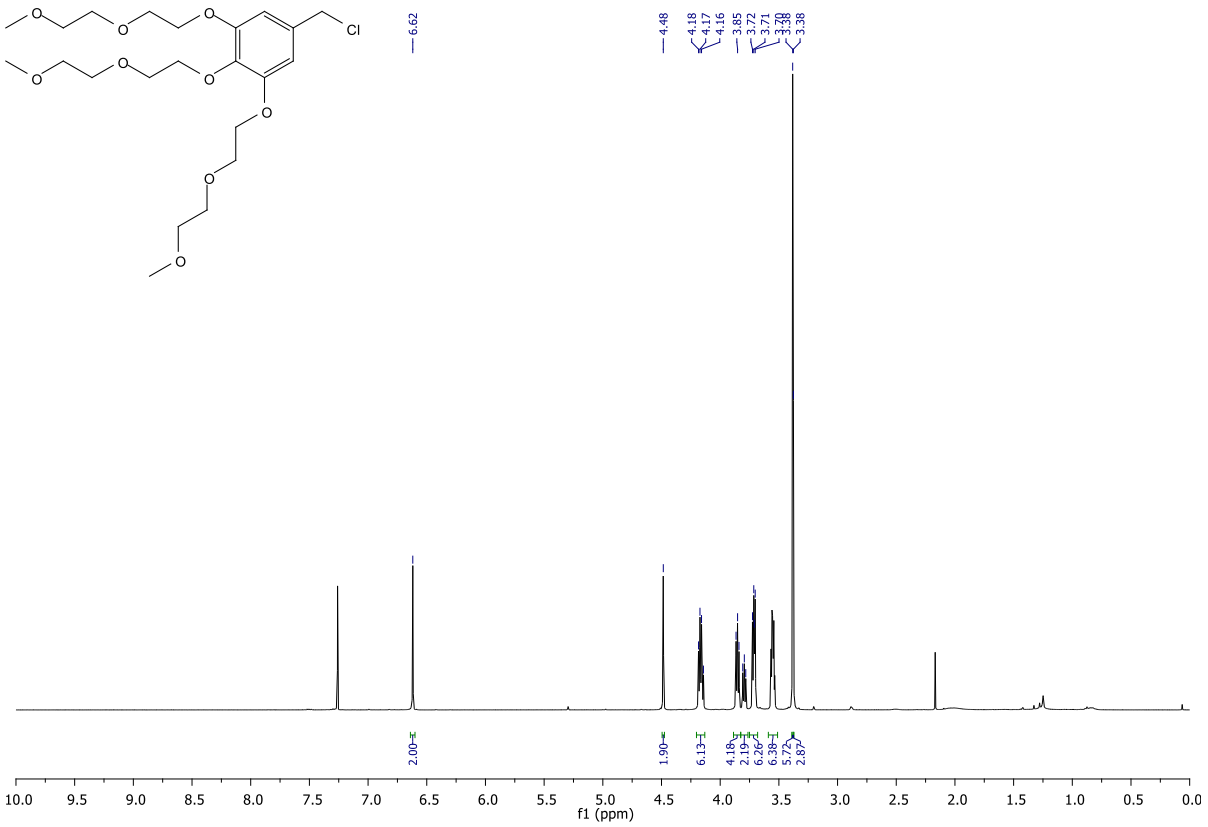


Fig. S50 ^{1}H NMR spectrum of **014** ($CDCl_3$).

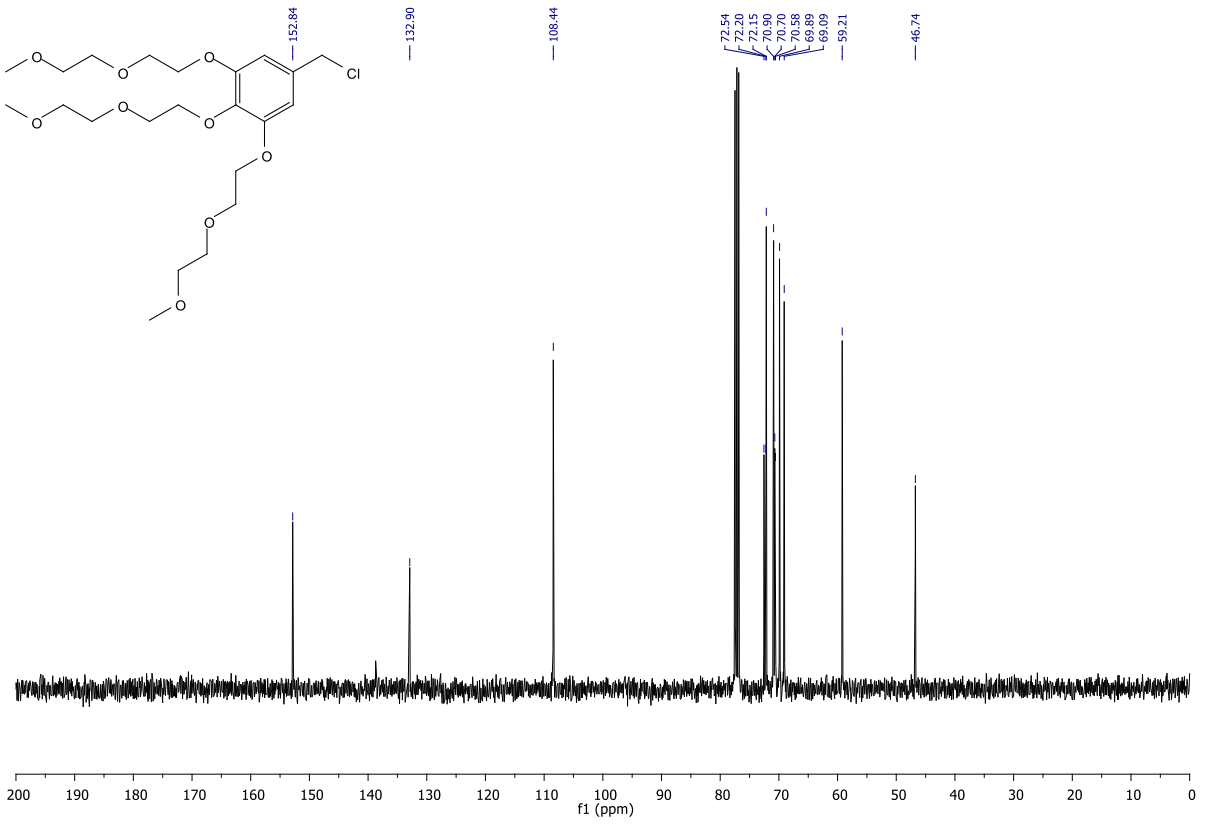


Fig. S51 ^{13}C NMR spectrum of **014** ($CDCl_3$).

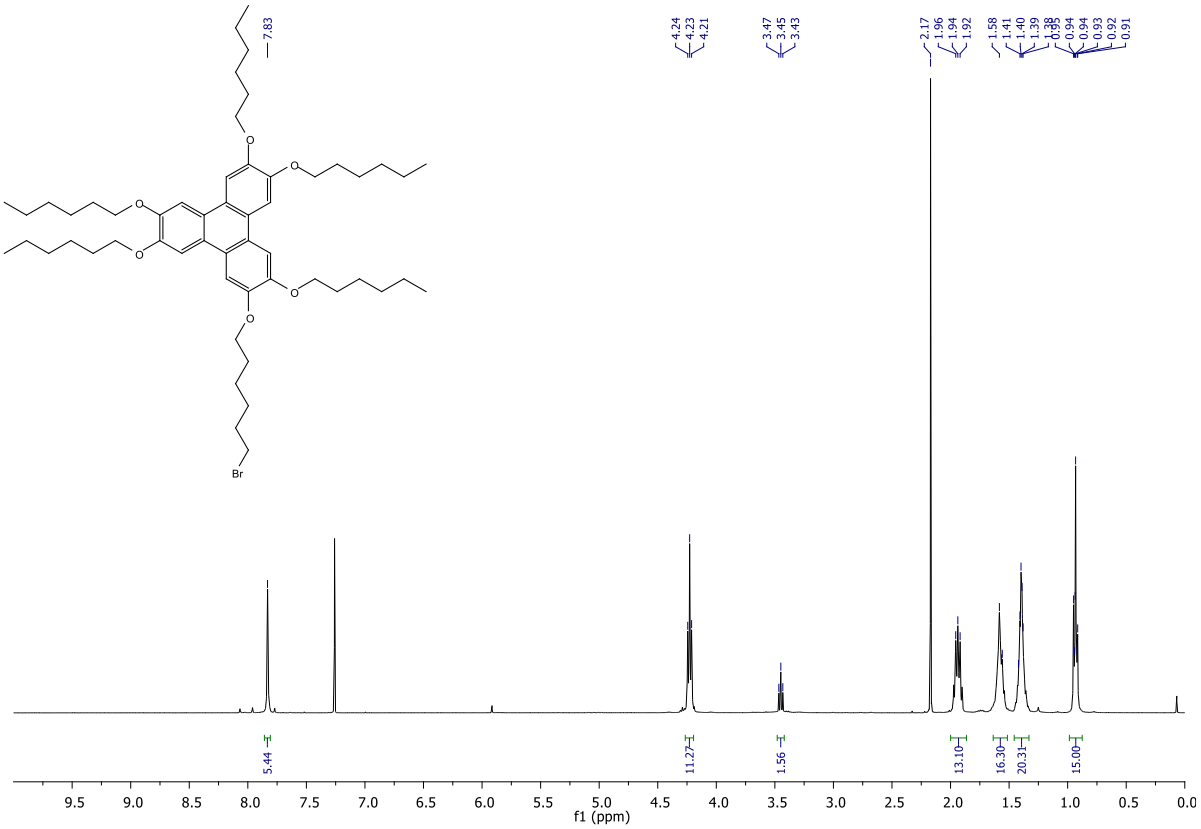


Fig. S52 ^{1}H NMR spectrum of **015** ($CDCl_3$).

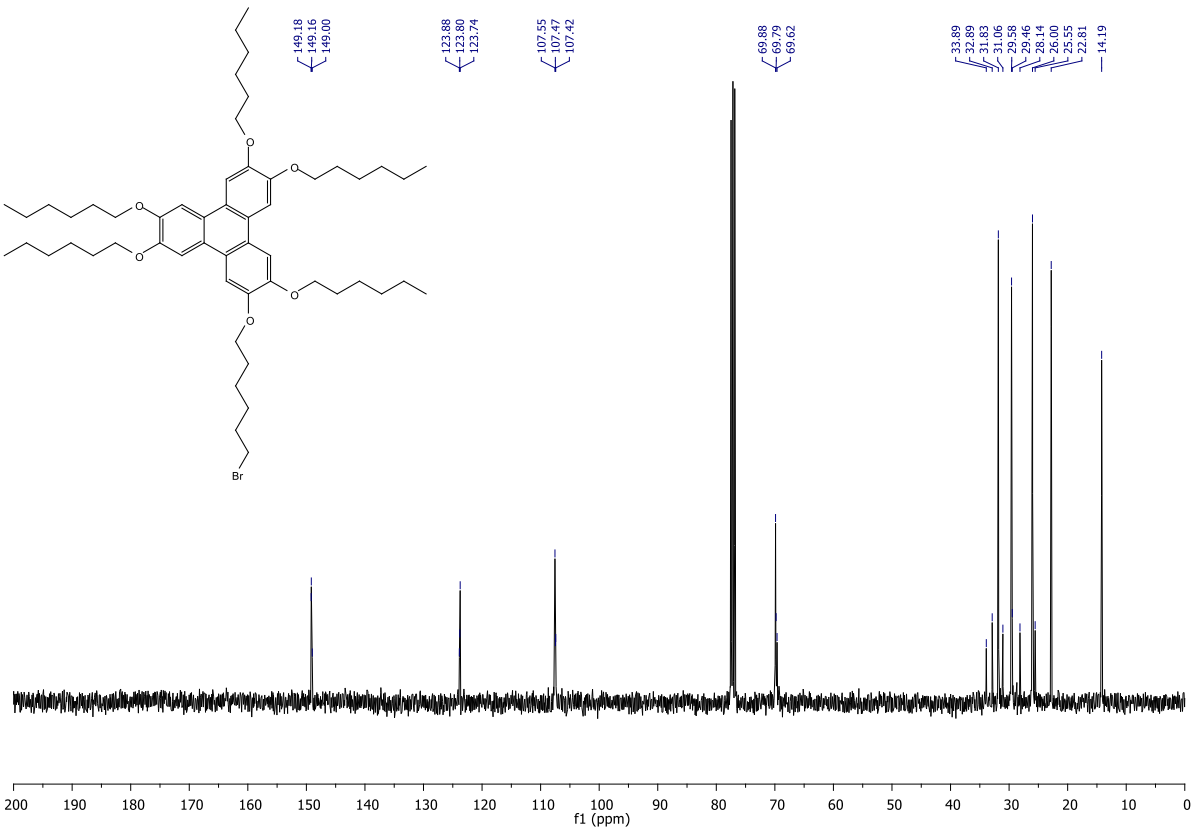


Fig. S53 ^{13}C NMR spectrum of **015** ($CDCl_3$).

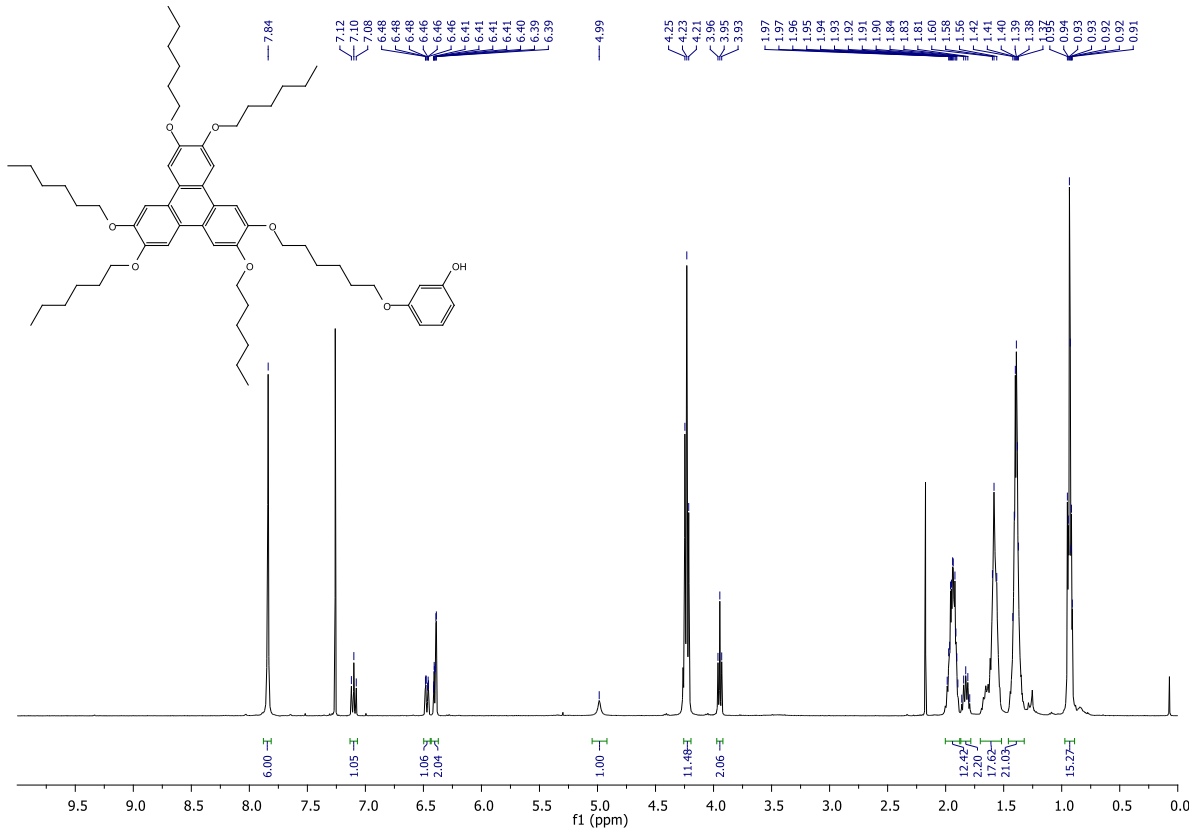


Fig. S54 ^{1}H NMR spectrum of **016** ($CDCl_3$).

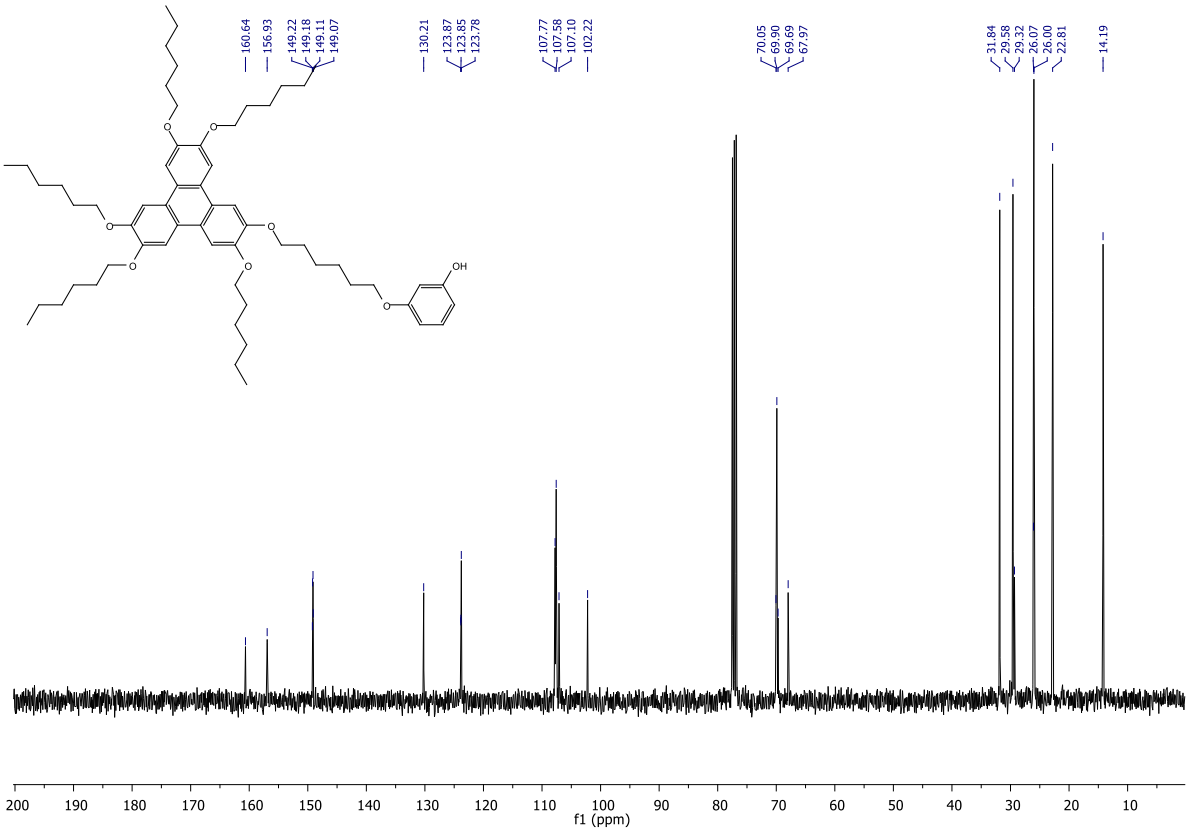


Fig. S55 ^{13}C NMR spectrum of **016** ($CDCl_3$).

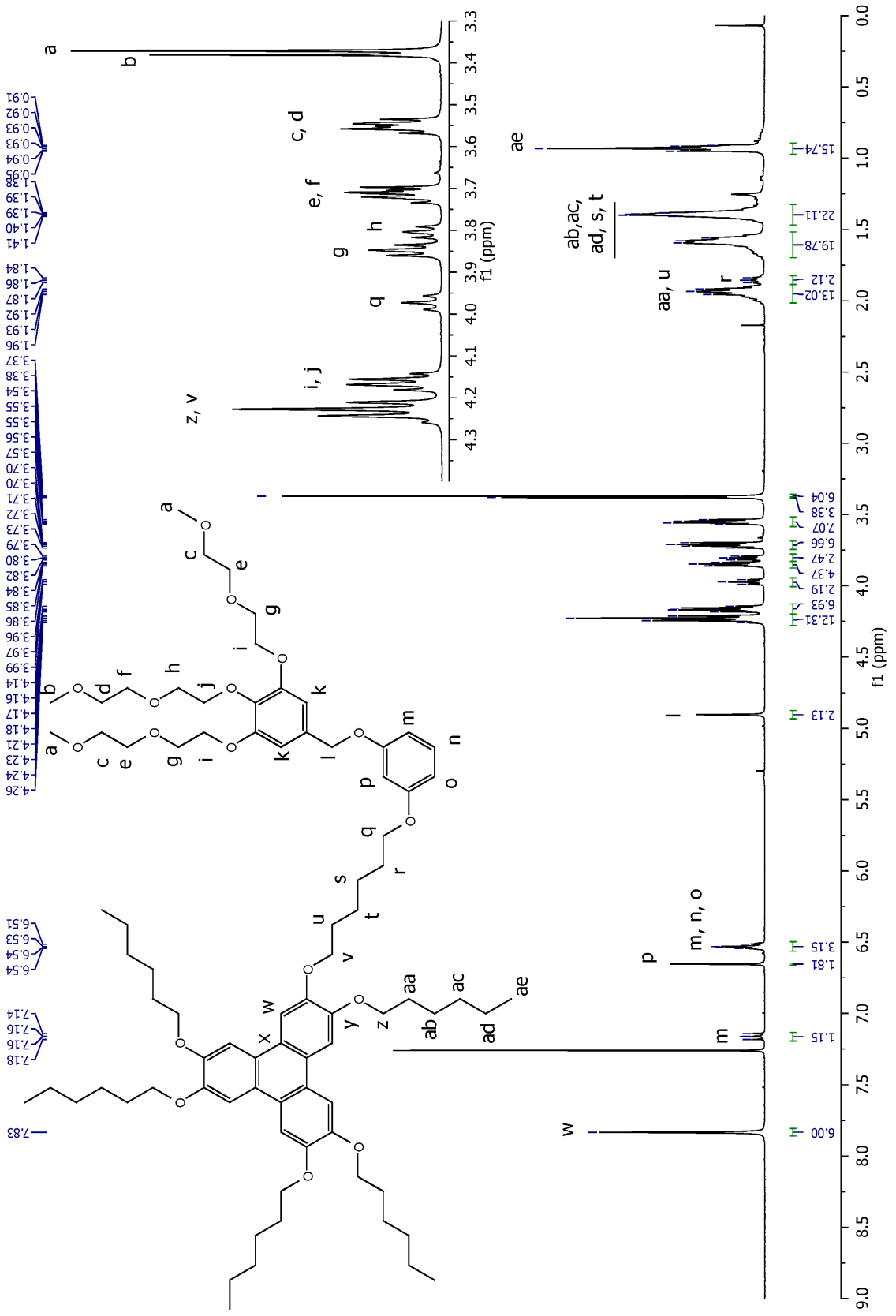


Fig. S56 ^{1}H NMR spectrum of TP6Gall ($CDCl_3$).

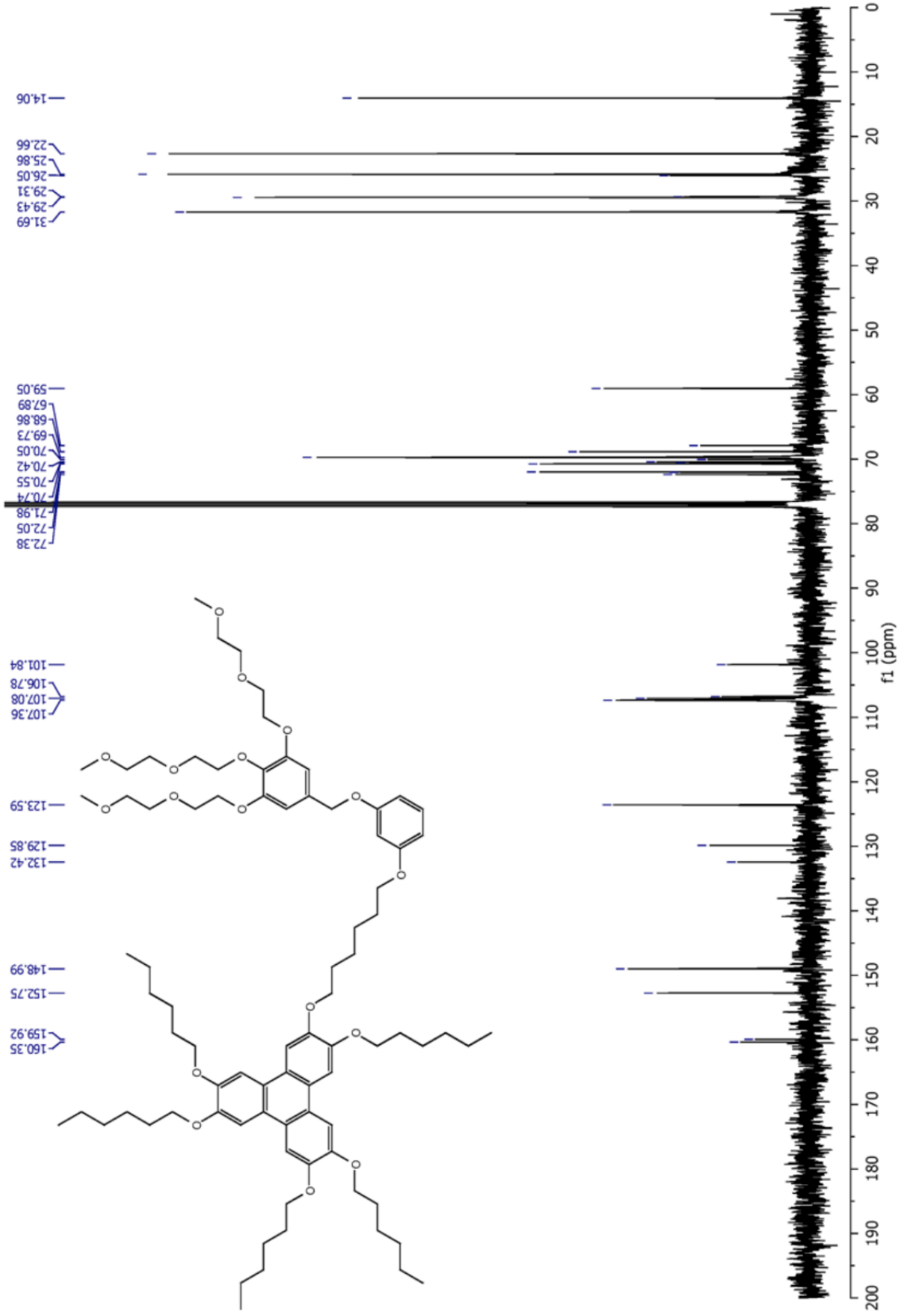


Fig. S57 ^{13}C NMR spectrum of **TP6Gall** ($CDCl_3$)