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Luminescent and photoconductive liquid crystalline lamellar and helical network phases of achiral polycatenars

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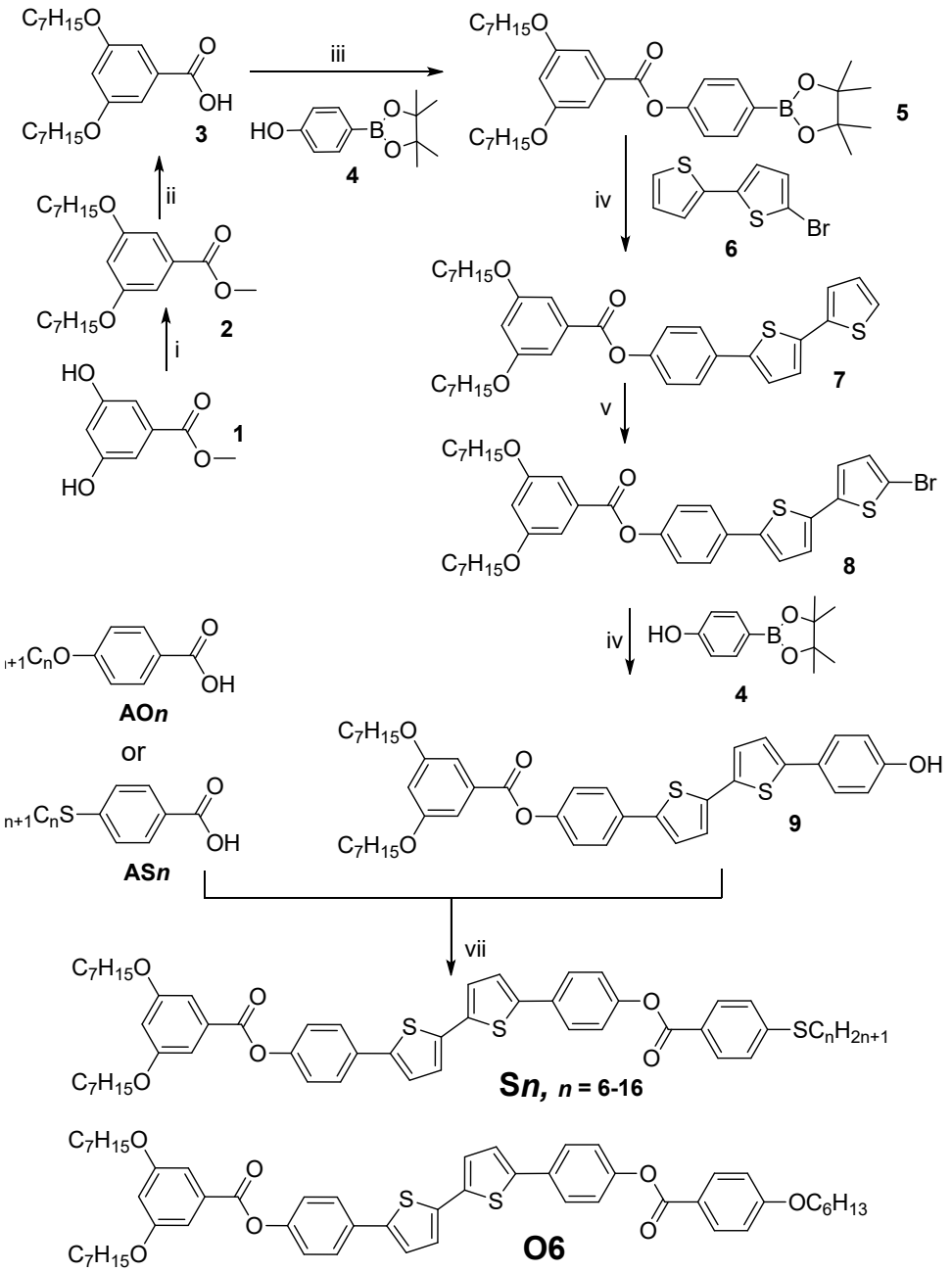
1. Synthesis



Scheme S1. Reagents and conditions: i) $C_7H_{15}Br$, K_2CO_3, Bu_4NI, 2-butanone, reflux; ii) 1) KOH, H_2O, EtOH, 2) HCl; iii) $SOCl_2$, pyridine, DMAP, DCM, reflux; iv) $[Pd(PPh_3)_4]$, THF/sat. $NaHCO_3$-solution, reflux; v) NBS, THF, RT, absence of light; vi) 1) absolute EtOH, KOH, $H_{2n+1}C_nBr$, 2) NaOH solution, reflux, 3) H^+; vii) 1) $SOCl_2$, 2) Triethylamine, pyridine, DCM, reflux.

The synthesis of the target materials is shown in Scheme S1. 5-Bromo-2,2'-bithiophene **6** was prepared according to reported standard procedures [S1] using tetrahydrofuran (THF) as solvent;[S2] 4-*n*-thioalkylbenzoic acids **AS*n*** were also prepared according to previously reported procedures.[S3,S4]

Methyl-3,5-bis(heptyloxy)benzoate, 2

A solution of methyl 3,5-dihydroxybenzoate **1** (7.5 g, 44.5 mmol, 1 equivalent), 1-bromoheptane (17.5 g, 98 mmol, 2.2 equivalent), potassium carbonate (61.5 g, 0.44 mol, 10 equivalent), tetrabutylammonium iodide (catalytic amount) and absolute 2-butanone (300 mL) was heated under reflux overnight. The reaction mixture was cooled to room temperature, and the remaining potassium carbonate was removed by filtration. The reaction was extracted three times with chloroform after adding water. The combined organic phases were dried over sodium sulfate. The solvent was distilled off under reduced pressure. The obtained oil was introduced to column chromatography, washed with *n*-hexane, and then eluted with methylene chloride. Colorless oil. 8.9 g (24.4 mmol, 55%), $C_{22}H_{36}O_4$; M = 364.51 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 2.4 Hz, 2H, Ar-H), 6.63 (t, *J* = 2.4 Hz, 1H, Ar-H), 3.97 (t, *J* = 6.8 Hz, 4H, OCH_2CH_2), 3.89 (s, 3H, $COOCH_3$), 1.83–1.72 (m, 4H, OCH_2CH_2), 1.51–1.24 (m, 16H, CH_2), 0.89 (t, *J* = 6.8 Hz, 6H, CH_3).

3,5-Bis(heptyloxy)benzoic acid, 3

Methyl 3,5-bis(heptyloxy)benzoate **2** (8.9 g, 24.4 mmol, 1 equivalent) was stirred in 200 mL ethanol until complete dissolution (one layer), then NaOH (9.8 g, 0.24 mol, 10 equivalent) dissolved in least amount of water was added. The reaction was refluxed for 1 h, and then left to cool. The reaction was then cooled in ice bath and added to HCl and ice with strong stirring. The obtained white precipitate was filtered off, washed with water several times, and then recrystallized from acetone/water. White powder. 5.9 g (17.0 mmol, 70%), m.p. = 48 ^{o}C, $C_{21}H_{34}O_4$; *M* = 350.49 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.4 Hz, 2H, Ar-H), 6.69 (t, *J* = 2.4 Hz, 1H, Ar-H), 3.98 (t, *J* = 6.4 Hz, 4H, OCH_2CH_2), 1.83–1.74 (m, 4H, OCH_2CH_2), 1.50–1.25 (m, 16H, CH_2), 0.90 (t, *J* = 6.8 Hz, 6H, CH_3).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl-3,5-bis(heptyloxy)benzoate, 5

3,5-Bis(heptyloxy)benzoic acid **3** (5 g, 14.3 mmol, 1 equivalent) and $SOCl_2$ (15 mL) were refluxed for 30 minutes, then $SOCl_2$ was removed under vacuum. Dry pyridine (10 mL), 4-

hydroxyphenylboronic acid pinacol ester **4** (3.2 g, 14.3 mmol, 1 equivalent), dichloromethane (DCM, 40 mL) and 4-dimethylaminopyridine (DMAP) as a catalyst were added, and the resulting mixture was stirred at room temperature overnight. The solvent was distilled off under reduced pressure, and the crude product was purified by column chromatography (eluent: chloroform). Colorless oil. 6.5 g (11.8 mmol, 83%), $C_{33}H_{49}BO_6$; *M* = 552.54 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.31 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.21 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.70 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.00 (t, *J* = 6.4 Hz, 4H, OC*H*$_2$CH$_2$), 1.83–1.74 (m, 4H, OCH$_2$*CH*$_2$), 1.50–1.21 (m, 16H, CH_2), 1.35 (s, 12H, CCH_3), 0.89 (t, *J* = 6.8 Hz, 6H, CH_3).

4-([2,2'-Bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, 7

A mixture of **5** (6.5 g, 11.8 mmol, 1 equivalent), 5-bromo-2,2'-bithiophene **6** (2.8 g, 11.8 mmol, 1 equivalent), THF (120 mL) and saturated $NaHCO_3$ solution (60 mL) was degassed with argon for 15 min. [$Pd(PPh_3)_4$] (0.7 g, 0.6 mmol, 0.05 equivalent) was added and the solution was refluxed for 4 h. The reaction mixture was cooled to room temperature, then it was extracted three times with $CHCl_3$. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and distilled off under reduced pressure. The crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane, 2:1), and then recrystallized from ethanol. Yellow-green crystals. 5.5 g (9.3 mmol, 79%), m.p. = 77 °C, $C_{35}H_{42}O_4S_2$; *M* = 590.83 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.25-7.19 (m, 5H, Ar-H & Th-H), 7.15 (d, *J* = 3.6 Hz, 1H, Th-H), 7.04 (dd, *J* = 5.2, 3.6 Hz, 1H, Th-H), 6.72 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.01 (t, *J* = 6.4 Hz, 4H, OC*H*$_2$CH$_2$), 1.89–1.73 (m, 4H, OCH$_2$*CH*$_2$), 1.52–1.21 (m, 16H, CH_2), 0.90 (t, *J* = 6.8 Hz, 6H, CH_3).

4-(5'-Bromo-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, 8

3,5-Bis(heptyloxy)benzoate derivative **7** (5.5 g, 9.3 mmol, 1 equivalent) was dissolved in dry THF (100 ml). *N*-bromosuccinimide (1.6 g, 9.3 mmol, 1 equivalent) was added to the solution in small portions at room temperature in the absence of light. The mixture was stirred for 3 h, and then quenched with saturated $Na_2S_2O_3$ solution (50 mL). The product was extracted three times with $CHCl_3$. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After filtration the solvents were removed under reduced pressure. The crude product was purified by column chromatography (eluent: $CHCl_3$/*n*-hexane 1:1) and then recrystallized from ethanol. Pale green crystals. 5.8 g (8.7 mmol, 94%), m.p. = 32 °C, $C_{35}H_{41}BrO_4S_2$; *M* = 669.73 g/mol; ^{1}H-NMR

(400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.23 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.19 (d, *J* = 4.0 Hz, 1H, Th-H), 7.08 (d, *J* = 4.0 Hz, 1H, Th-H), 6.99 (d, *J* = 4.0 Hz, 1H, Th-H), 6.94 (d, *J* = 4.0 Hz, 1H, Th-H), 6.72 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.01 (t, *J* = 6.4 Hz, 4H, OCH_2CH_2), 1.88–1.74 (m, 4H, OCH_2CH_2), 1.51–1.23 (m, 16H, CH_2), 0.90 (t, *J* = 6.8 Hz, 6H, CH_3).

4-(5'-(4-Hydroxyphenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, 9

A mixture of the bromo derivative **8** (5.8 g, 8.7 mmol, 1 equivalent), 4-hydroxyphenylboronic acid pinacol ester **4** (1.9 g, 8.7 mmol, 1 equivalent), THF (105 mL) and saturated $NaHCO_3$ solution (50 mL) were degassed with argon for 15 min. [$Pd(PPh_3)_4$] (0.5 g, 0.4 mmol, 0.05 equivalent) was added, and the solution was refluxed for 4 h. The reaction mixture was cooled to room temperature, and then extracted three times with $CHCl_3$. The organic phase was dried over anhydrous Na_2SO_4, filtered and distilled off under reduced pressure. The crude product was purified by column chromatography (eluent: methanol/dichloromethane, 1:1) then recrystallized from ethanol. Yellow crystals. 4.1 g (6.0 mmol, 69%), m.p. = 192 °C, $C_{41}H_{46}O_5S_2$; *M* = 682.93 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.47 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.23 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.21 (d, *J* = 3.6 Hz, 1H, Th-H), 7.13 (d, *J* = 4.0 Hz, 2H, Th-H), 7.10 (d, *J* = 3.6 Hz, 1H, Th-H), 6.83 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.72 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.92 (s, 1H, OH), 4.01 (t, *J* = 6.4 Hz, 4H, OCH_2CH_2), 1.86–1.75 (m, 4H, OCH_2CH_2), 1.52–1.25 (m, 16H, CH_2), 0.90 (t, *J* = 6.8 Hz, 6H, CH_3).

Synthesis of the target polycatenars S*n* and O*n*.

A solution of 4-*n*-thioalkylbenzoic acid **11** (1 equivalent) in 5 mL $SOCl_2$ and a catalytic amount of *N,N*-dimethylformamide (DMF) was refluxed for 1 hour. The excess thionyl chloride was removed under reduced pressure. The phenol **9** (1 equivalent) was added together with triethylamine (1.2 equivalent) and a catalytic amount of pyridine in 25 mL of dichloromethane to the obtained acid chloride. The reaction solution was refluxed for 6 hours. After the reaction completion, the crude product was extracted with dichloromethane (3 x 50 mL). The obtained organic layer was washed several times with water and dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The resulting solid material was chromatographed in a silica column using $CHCl_3$/*n*-Hexane 4:1 as an eluent followed by recrystallization from ethanol/chloroform mixture (2:1) to give the final compounds as yellow crystals.

4-(5'-(4-((4-(Hexylthio)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)-benzoate, S6

Yellow crystals. 196 mg (0.21 mmol, 87%); $C_{54}H_{62}O_6S_3$; *M* = 903.26 g/mol; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.65 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.35 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 3.5 Hz, 2H, Th-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.02–4.00 (m, 4H, OC*H*$_2$CH$_2$), 3.02 (t, 2H, *J* = 7.5 Hz, SC*H*$_2$CH$_2$), 1.83–1.69 (m, 6H, OCH$_2$C*H*$_2$ + SCH$_2$C*H*$_2$), 1.50–1.30 (m, 22H, CH$_2$), 0.92–0.88 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 164.98, 164.82, 160.32, 150.44, 145.83, 142.28, 136.78, 131.87, 131.02, 130.46, 126.69, 126.24, 125.56, 124.59, 124.03, 122.26, 122.23, 108.23, 107.23, 68.44, 31.99, 31.76, 31.32, 29.18, 29.02, 28.68, 28.58, 25.97, 22.59, 22.50, 14.06, 13.98; EA: calculated: C 71.80%, H 6.92%; found: C 71.71%, H 6.85%.

4-(5'-(4-((4-(Octylthio)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)-benzoate, S8

Yellow crystals. 186 mg (0.20 mmol, 80%); $C_{56}H_{66}O_6S_3$; *M* = 931.31 g/mol; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.35 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 4.0 Hz, 2H, Th-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.02–4.00 (m, 4H, OC*H*$_2$CH$_2$), 3.01 (t, 2H, *J* = 7.5 Hz, SC*H*$_2$CH$_2$), 1.83–1.69 (m, 6H, OCH$_2$C*H*$_2$ + SCH$_2$C*H*$_2$), 1.50–1.25 (m, 26H, CH$_2$), 0.91–0.87 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 164.98, 164.82, 160.31, 150.43, 145.84, 142.28, 136.78, 131.83, 131.02, 130.46, 126.69, 126.25, 125.55, 124.59, 124.03, 122.26, 122.23, 108.23, 107.23, 68.44, 31.99, 31.76, 29.18, 29.13, 29.10, 29.02, 28.90, 28.72, 25.97, 22.62, 22.59, 14.06; EA: calculated: C 72.22%, H 7.14%; found: C 72.15%, H 7.02%.

4-(5'-(4-((4-(Decylthio)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)-benzoate, S10

Yellow crystals. 203 mg (0.21 mmol, 85%); $C_{58}H_{70}O_6S_3$; *M* = 959.36 g/mol; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.35 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 3.5 Hz, 2H, Th-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.02–4.00 (m, 4H, OC*H*$_2$CH$_2$), 3.01 (t, 2H, *J* = 7.5 Hz, SC*H*$_2$CH$_2$), 1.83–1.69 (m, 6H, OCH$_2$C*H*$_2$ + SCH$_2$C*H*$_2$), 1.50–1.27 (m, 30H, CH$_2$), 0.91–0.87 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 164.98, 164.82, 160.31, 150.43, 145.84, 142.26, 136.79, 131.87, 131.02, 130.46, 126.69, 126.24, 125.55, 124.59, 124.03, 122.26, 122.23, 108.23,

107.23, 68.44, 31.98, 31.87, 31.76, 29.51, 29.47, 29.28, 29.18, 29.14, 29.02, 28.90, 28.71, 25.97, 22.66, 22.59, 14.09, 14.06; EA: calculated: C 72.61%, H 7.35%; found: C 72.53%, H 7.25%.

4-(5'-(4-((4-(Dodecylthio)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, S12

Yellow crystals. 195 mg (0.19 mmol, 79%); $C_{60}H_{74}O_6S_3$; *M* = 987.42 g/mol; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.35 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.32 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 3.5 Hz, 2H, Th-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.02–4.00 (m, 4H, OC*H*$_2$CH$_2$), 3.01 (t, 2H, *J* = 7.5 Hz, SC*H*$_2$CH$_2$), 1.83–1.69 (m, 6H, OCH$_2$C*H*$_2$ + SCH$_2$C*H*$_2$), 1.50–1.27 (m, 34H, CH$_2$), 0.91–0.87 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 164.98, 164.81, 160.32, 150.43, 145.85, 142.26, 136.78, 131.87, 131.83, 131.02, 130.46, 126.68, 126.24, 125.55, 124.58, 124.03, 122.26, 122.23, 108.23, 68.44, 31.98, 31.90, 31.76, 29.62, 29.61, 29.56, 29.47, 29.33, 29.18, 29.15, 29.02, 28.90, 28.72, 25.98, 22.67, 22.59, 14.10, 14.06; EA: calculated: C 72.98%, H 7.55%; found: C 72.83%, H 7.44%.

4-(5'-(4-((4-(Tetradecylthio)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, S14

Yellow crystals. 208 mg (0.20 mmol, 82%); $C_{62}H_{78}O_6S_3$; *M* = 1015.47 g/mol; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.66 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.36 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.33 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.25–7.23 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 3.5 Hz, 2H, Th-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.03–4.00 (m, 4H, OC*H*$_2$CH$_2$), 3.02 (t, 2H, *J* = 7.5 Hz, SC*H*$_2$CH$_2$), 1.84–1.70 (m, 6H, OCH$_2$C*H*$_2$ + SCH$_2$C*H*$_2$), 1.50–1.27 (m, 38H, CH$_2$), 0.92–0.87 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 164.98, 164.81, 160.32, 150.43, 145.85, 142.28, 142.26, 136.79, 131.87, 131.83, 131.02, 130.46, 126.68, 126.24, 125.55, 124.58, 124.03, 122.26, 122.23, 108.23, 107.23, 68.44, 31.98, 31.91, 31.77, 29.67, 29.65, 29.64, 29.63, 29.56, 29.47, 29.34, 29.18, 29.15, 29.03, 28.91, 28.72, 25.98, 22.68, 22.59, 14.10, 14.07; EA: calculated: C 73.33%, H 7.74%; found: C 73.25%, H 7.64%.

4-(5'-(4-((4-(Hexadecylthio)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, S16

Yellow crystals. 195 mg (0.18 mmol, 75%); $C_{64}H_{82}O_6S_3$; *M* = 1043.52 g/mol; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.35 (d, *J* = 8.5

Hz, 2H, Ar-H), 7.32 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 4.0 Hz, 2H, Th-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.02–4.00 (m, 4H, OCH_2CH$_2$), 3.01 (t, 2H, *J* = 7.5 Hz, SCH_2CH$_2$), 1.83–1.71 (m, 6H, OCH$_2$CH_2 + SCH$_2$CH_2), 1.50–1.26 (m, 42H, CH$_2$), 0.91–0.86 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, CDCl$_3$) δ 164.98, 164.81, 160.32, 150.44, 145.85, 142.26, 136.79, 131.87, 131.83, 131.02, 130.46, 126.68, 126.24, 125.55, 124.58, 124.03, 122.26, 122.23, 108.23, 107.23, 68.44, 31.98, 31.91, 31.76, 29.69, 29.67, 29.66, 29.64, 29.63, 29.56, 29.47, 29.35, 29.18, 29.15, 29.02, 28.90, 28.72, 25.97, 22.68, 22.59, 14.10, 14.06; EA: calculated: C 73.66%, H 7.92%; found: C 73.55%, H 7.86%.

4-(5'-(4-((4-(Hexyloxy)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl 3,5-bis(heptyloxy)benzoate, O6

Yellow crystals. 136 mg (0.15 mmol, 77%); $C_{54}H_{62}O_7S_2$; *M* = 887.19 g/mol; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.66-7.63 (m, 4H, Ar-H), 7.32 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 4.0 Hz, 2H, Th-H), 6.98 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.72 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.07–3.99 (m, 6H, OCH_2CH$_2$), 1.86–1.77 (m, 6H, OCH$_2$CH_2), 1.52–1.25 (m, 22H, CH$_2$), 0.94–0.88 (m, 9H, CH$_3$); ^{13}C-NMR (101 MHz, CDCl$_3$) δ 164.97, 164.83, 163.60, 160.30, 150.57, 150.42, 142.37, 142.22, 136.81, 136.70, 132.29, 131.87, 131.68, 131.01, 126.67, 126.65, 124.57, 124.55, 124.02, 123.96, 122.33, 122.22, 121.37, 114.31, 108.22, 107.22, 68.43, 68.34, 31.75, 31.53, 29.17, 29.05, 29.02, 25.97, 25.64, 22.58, 22.56, 14.06, 13.99; EA: calculated: C 73.10%, H 7.04%; found: C 73.01%, H 6.92%.

4-(5'-(4-((4-(Decyloxy)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, O10

Yellow crystals. 150 mg (0.16 mmol, 79%); $C_{58}H_{70}O_7S_2$; *M* = 943.30 g/mol; ^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.15 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.66-7.64 (m, 4H, Ar-H), 7.32 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.18 (d, *J* = 4.0 Hz, 2H, Th-H), 6.98 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.72 (t, *J* = 2.5 Hz, 1H, Ar-H), 4.06–4.00 (m, 6H, OCH_2CH$_2$), 1.84–1.77 (m, 6H, OCH$_2$CH_2), 1.49–1.28 (m, 30H, CH$_2$), 0.91–0.87 (m, 9H, CH$_3$); ^{13}C-NMR (126 MHz, CDCl$_3$) δ 164.98, 164.84, 163.62, 161.94, 160.31, 150.58, 142.38, 142.23, 136.71, 132.30, 131.68, 131.02,

126.69, 126.67, 124.58, 124.56, 124.03, 123.97, 122.34, 122.23, 121.37, 114.32, 108.23, 107.23, 68.44, 68.35, 31.88, 31.76, 29.54, 29.53, 29.35, 29.30, 29.18, 29.09, 29.02, 25.97, 22.66, 22.59, 14.09, 14.06; EA: calculated: C 73.85%, H 7.48%; found: C 73.80%, H 7.40%.

4-(5'-(4-((4-(Dodecyloxy)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, O12

Yellow crystals. 160 mg (0.16 mmol, 82%); $C_{60}H_{74}O_7S_2$; *M* = 971.35 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.66-7.63 (m, 4H, Ar-H), 7.32 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.25–7.21 (m, 6H, Ar-H + Th-H), 7.17 (d, *J* = 3.6 Hz, 2H, Th-H), 6.97 (d, *J* = 9.2 Hz, 2H, Ar-H), 6.72 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.06–3.99 (m, 6H, OC*H*$_2$CH$_2$), 1.84–1.77 (m, 6H, OCH$_2$C*H*$_2$), 1.49–1.28 (m, 34H, CH_2), 0.92–0.87 (m, 9H, CH_3); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.96, 164.82, 163.61, 160.31, 150.57, 150.42, 142.36, 142.20, 136.81, 136.70, 132.29, 131.87, 131.67, 131.02, 126.66, 126.64, 124.57, 124.55, 124.02, 123.96, 122.33, 122.22, 121.37, 114.31, 108.22, 107.21, 68.42, 68.34, 31.91, 31.76, 29.64, 29.62, 29.58, 29.55, 29.35, 29.33, 29.18, 29.09, 29.03, 25.97, 22.68, 22.59, 14.10, 14.06; EA: calculated: C 74.19%, H 7.68%; found: C 74.07%, H 7.60%.

4-(5'-(4-((4-(Tetradecyloxy)benzoyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)phenyl-3,5-bis(heptyloxy)benzoate, O14

Yellow crystals. 145 mg (0.14 mmol, 73%); $C_{62}H_{78}O_7S_2$; *M* = 999.40 g/mol; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.65-7.63 (m, 4H, Ar-H), 7.33 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.25–7.22 (m, 6H, Ar-H + Th-H), 7.17 (d, *J* = 3.6 Hz, 2H, Th-H), 6.97 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.72 (t, *J* = 2.4 Hz, 1H, Ar-H), 4.06–3.99 (m, 6H, OC*H*$_2$CH$_2$), 1.86–1.77 (m, 6H, OCH$_2$C*H*$_2$), 1.49–1.27 (m, 38H, CH_2), 0.92–0.87 (m, 9H, CH_3); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.96, 164.82, 163.61, 160.31, 150.57, 136.82, 132.29, 131.86, 131.66, 131.02, 126.66, 124.57, 124.02, 123.96, 122.33, 122.22, 121.37, 114.31, 108.22, 107.21, 68.42, 68.34, 31.91, 31.77, 29.68, 29.67, 29.65, 29.58, 29.55, 29.35, 29.18, 29.10, 29.03, 25.98, 22.68, 22.59, 14.10, 14.07; EA: calculated: C 74.51%, H 7.87%; found: C 74.38%, H 7.72%.

2. NMR Spectra

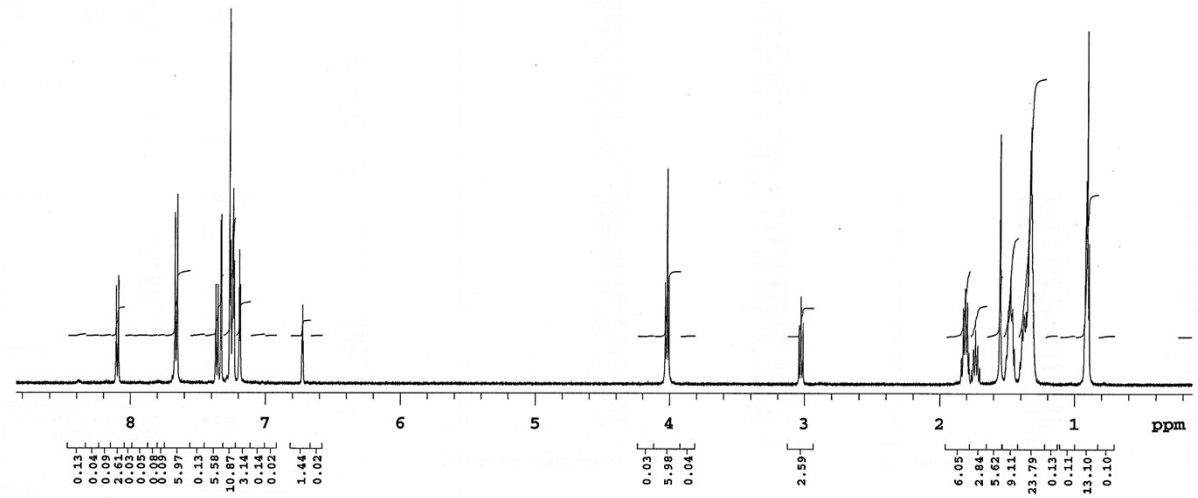


Figure S1. ^{1}H-NMR Spectrum of **S6** in $CDCl_3$.

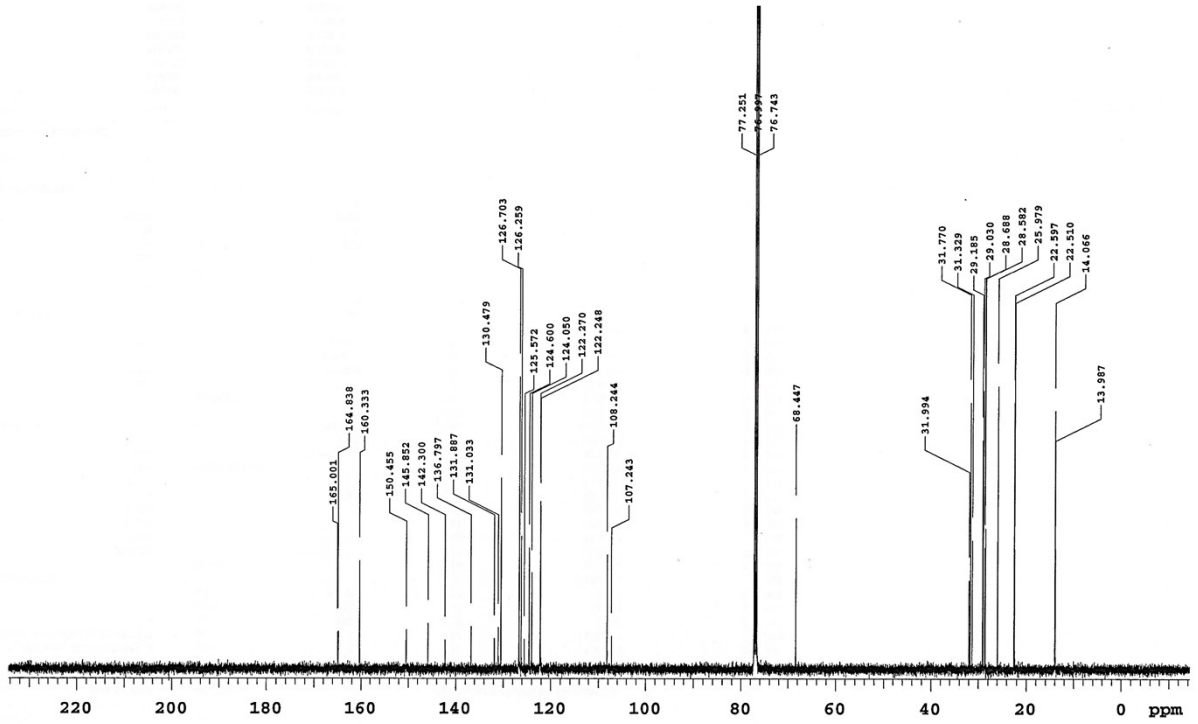


Figure S2. ^{13}C-NMR Spectrum of **S6** in $CDCl_3$.

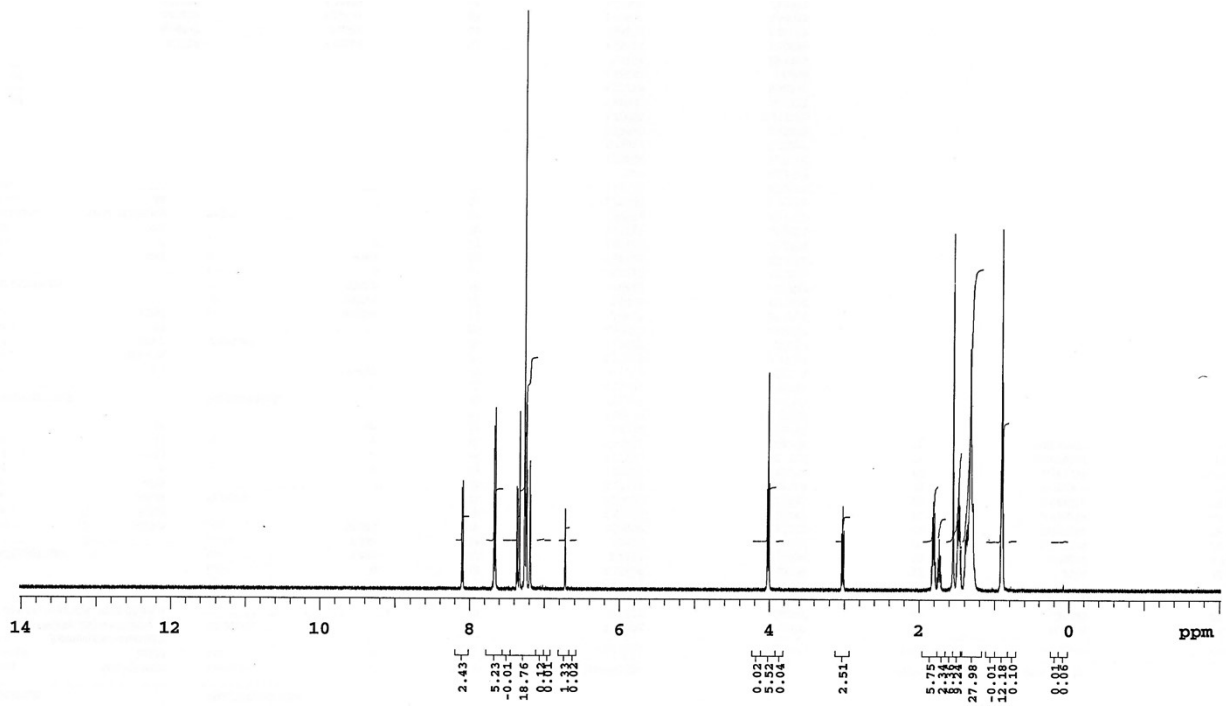


Figure S3. ^{1}H-NMR Spectrum of **S8** in $CDCl_3$.

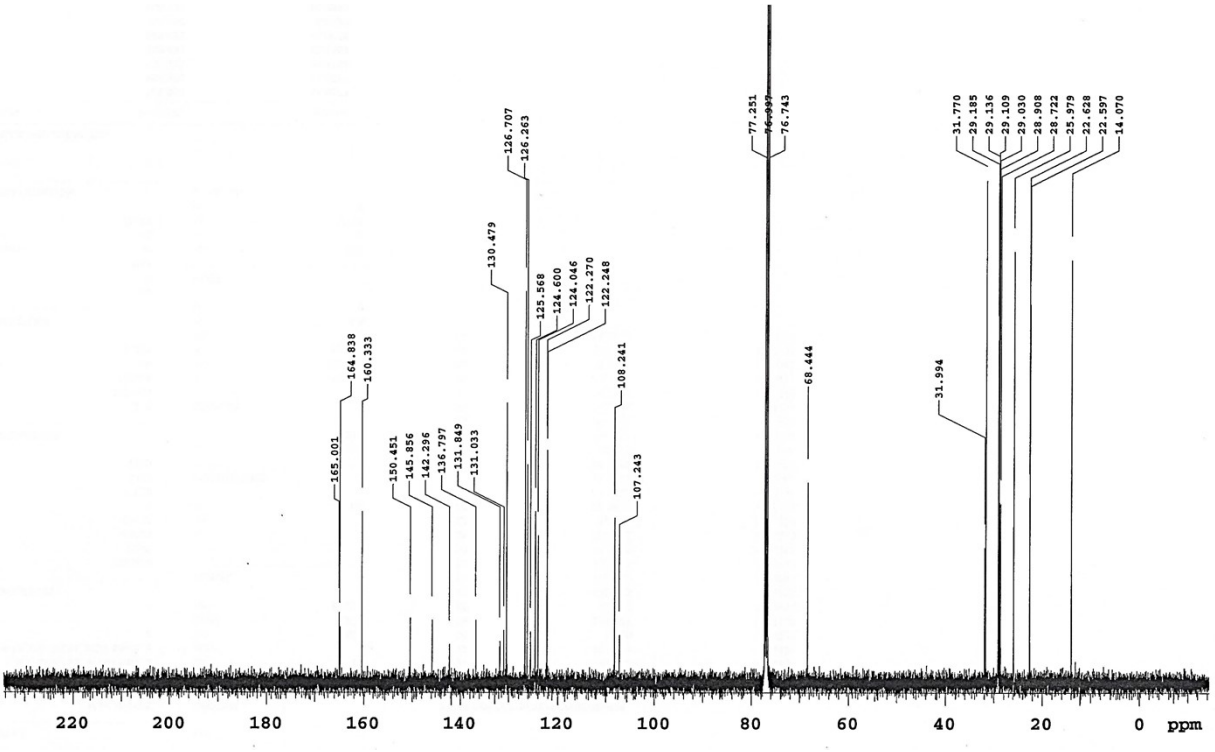


Figure S4. ^{13}C-NMR Spectrum of **S8** in $CDCl_3$.

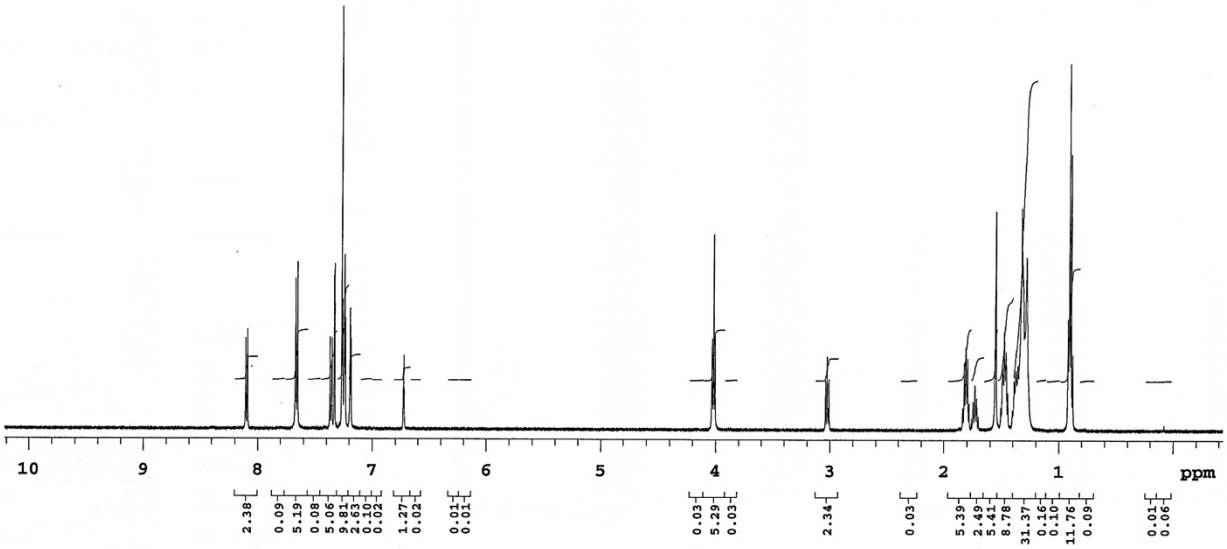


Figure S5. ^{1}H-NMR Spectrum of **S10** in $CDCl_3$.

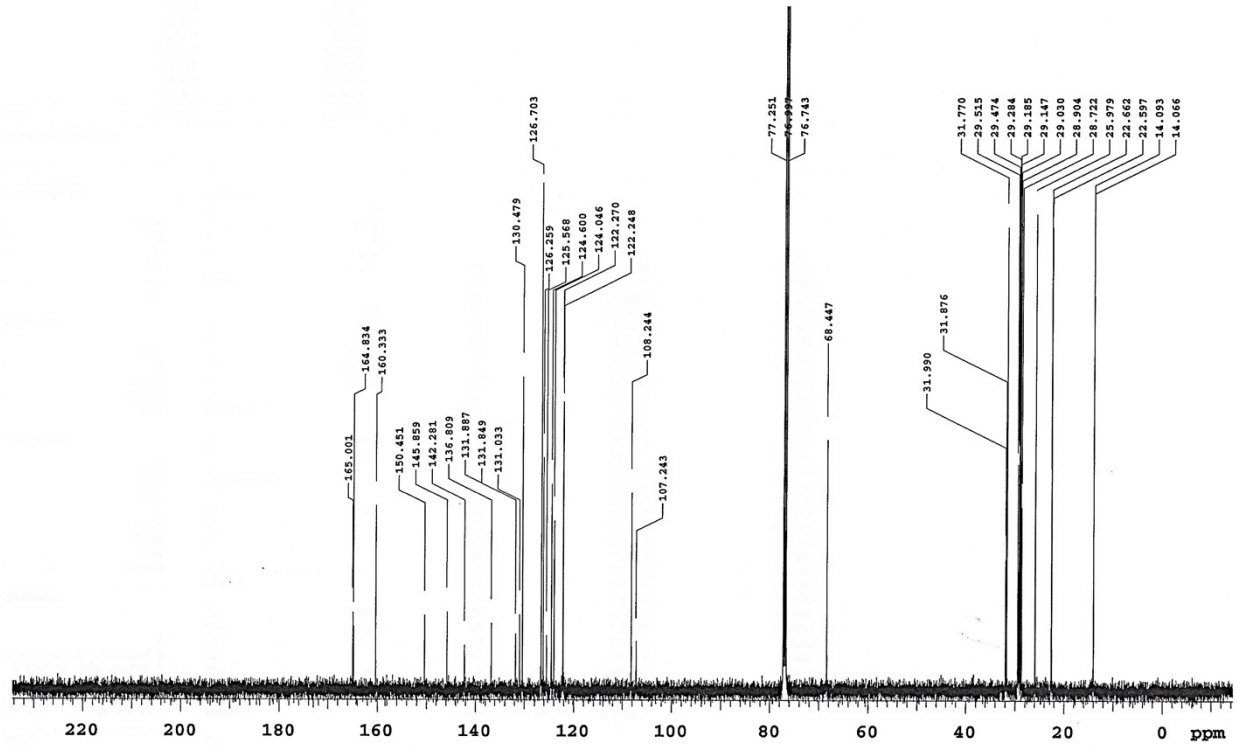


Figure S6. ^{13}C-NMR Spectrum of **S10** in $CDCl_3$.

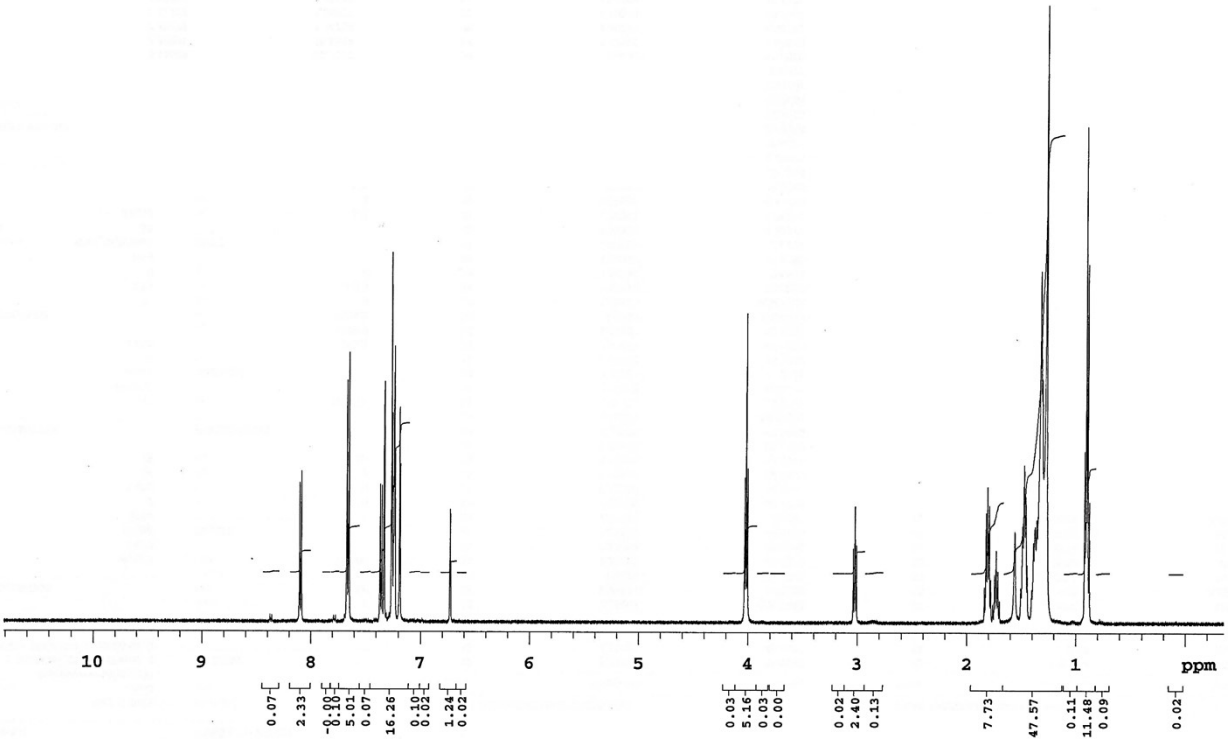


Figure S7. ^{1}H-NMR Spectrum of **S12** in $CDCl_3$.

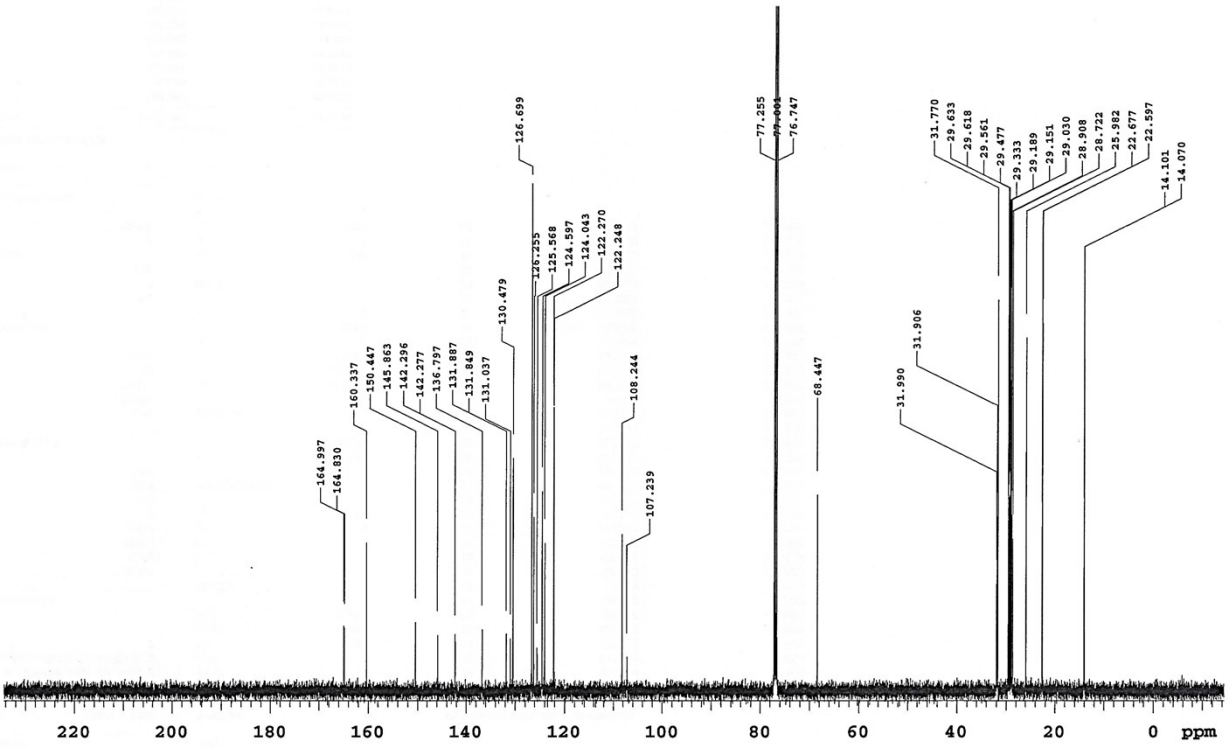


Figure S8. ^{13}C-NMR Spectrum of **S12** in $CDCl_3$.

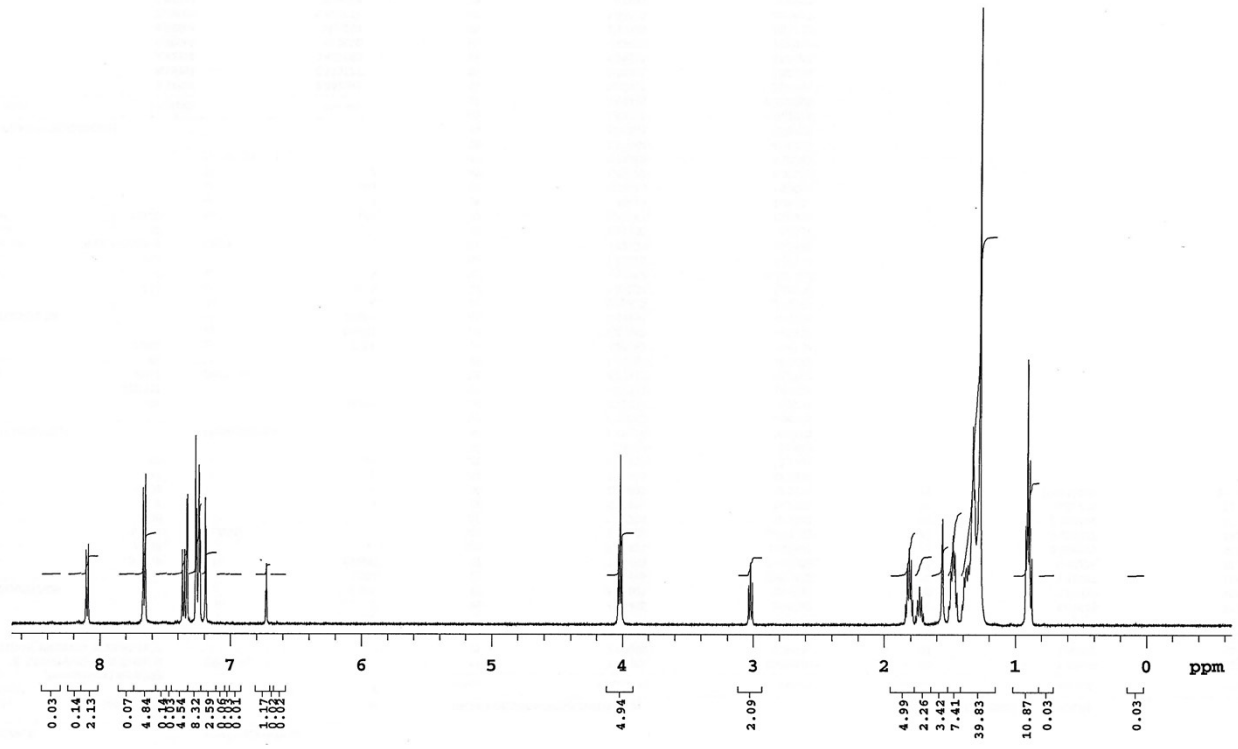


Figure S9. ^{1}H-NMR Spectrum of **S14** in $CDCl_3$.

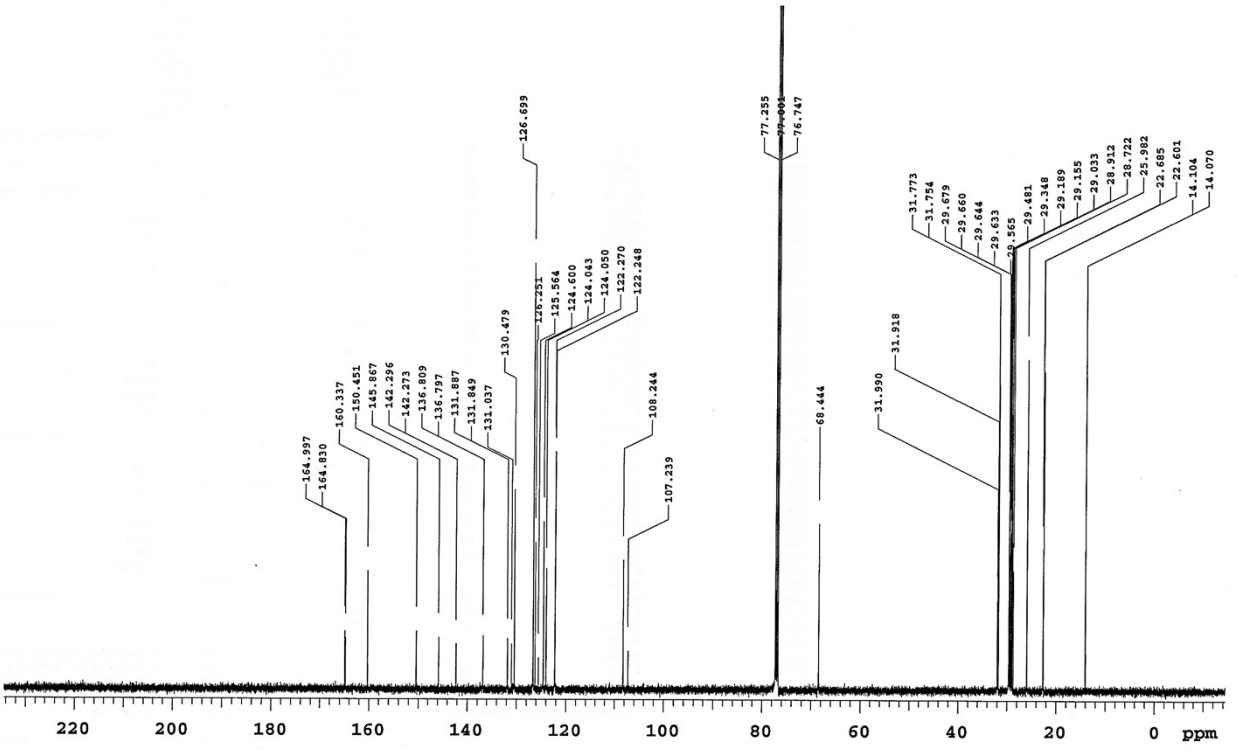


Figure S10. ^{13}C-NMR Spectrum of **S14** in $CDCl_3$.

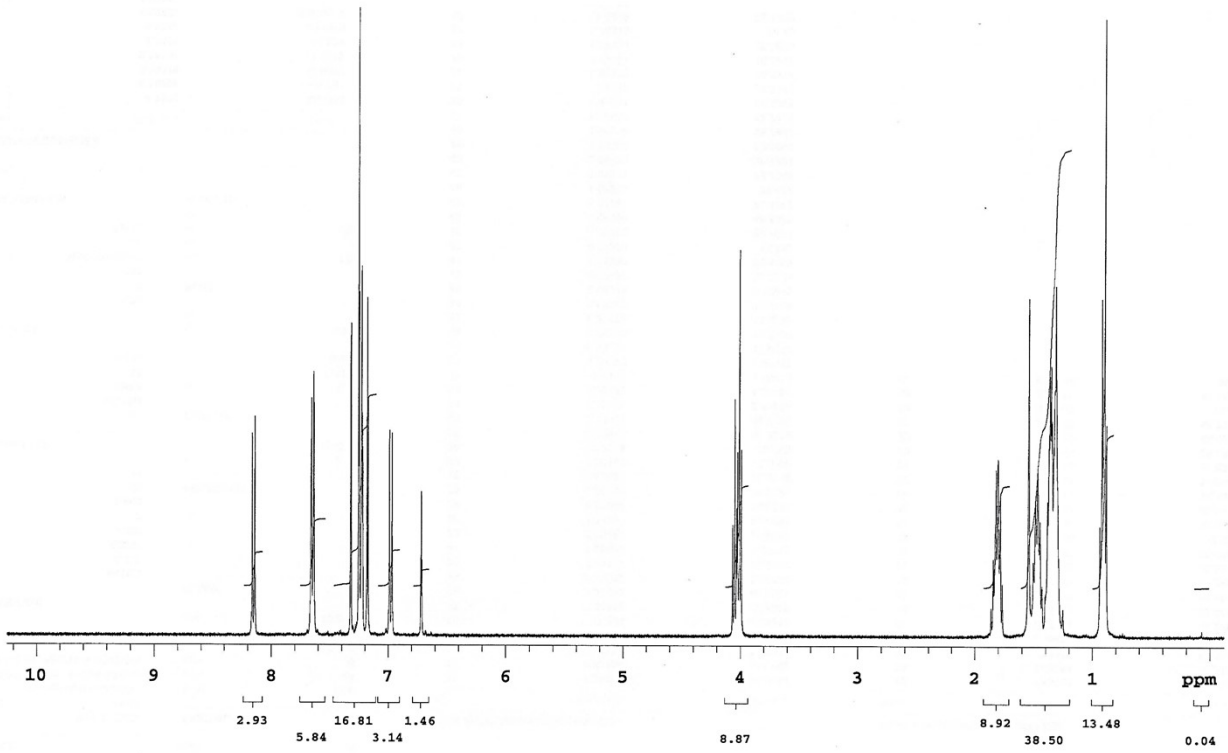


Figure S11. ^{1}H-NMR Spectrum of **O6** in $CDCl_3$.

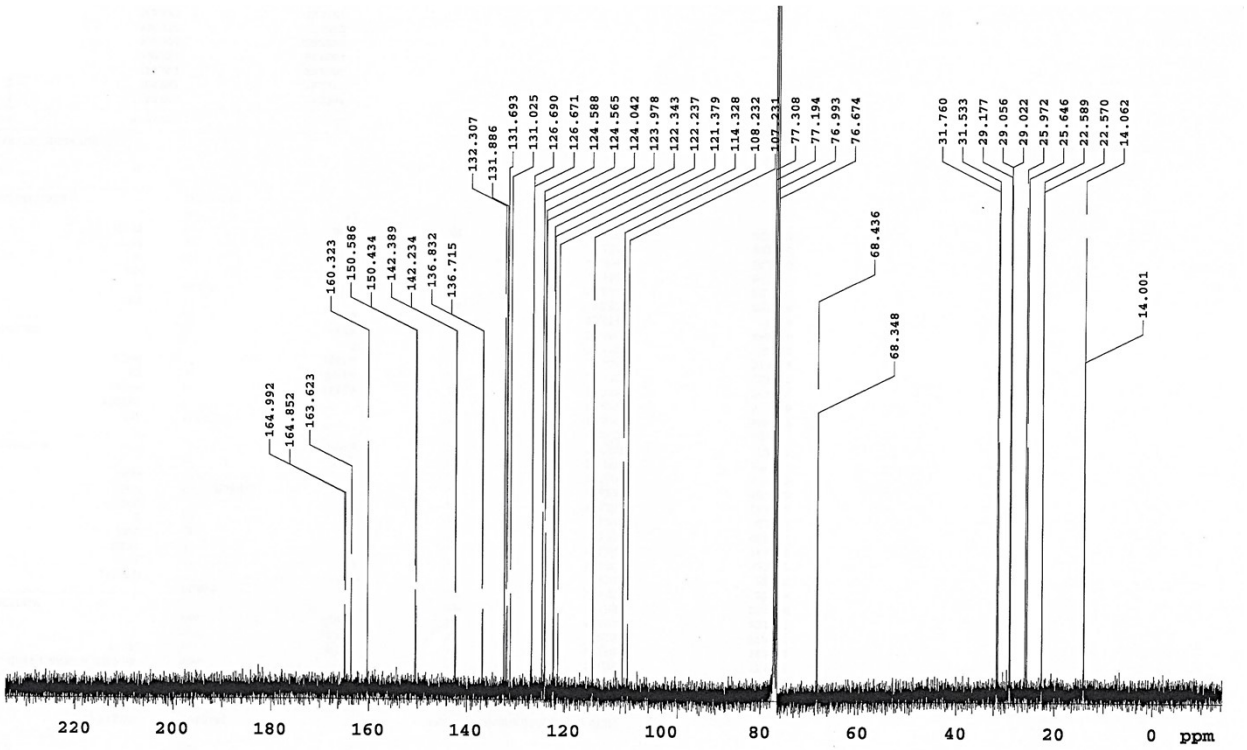


Figure S12. ^{13}C-NMR Spectrum of **O6** in $CDCl_3$.

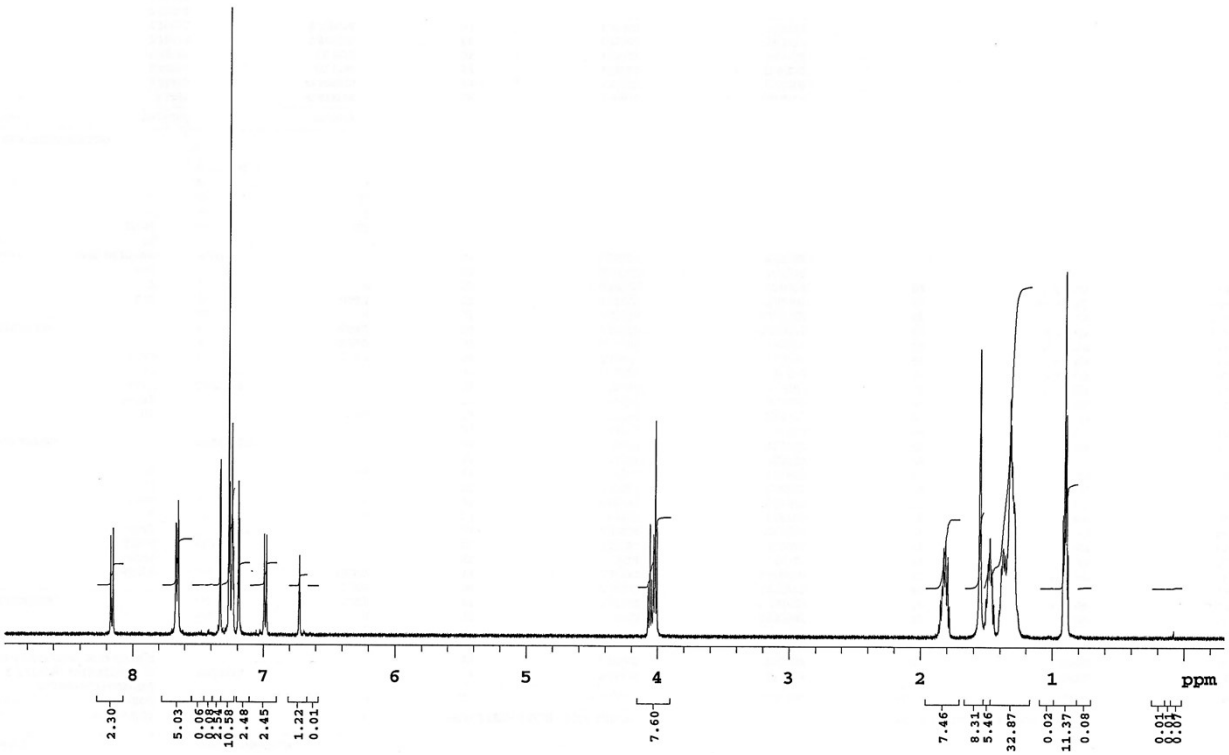


Figure S13. ^{1}H-NMR Spectrum of **O10** in $CDCl_3$.

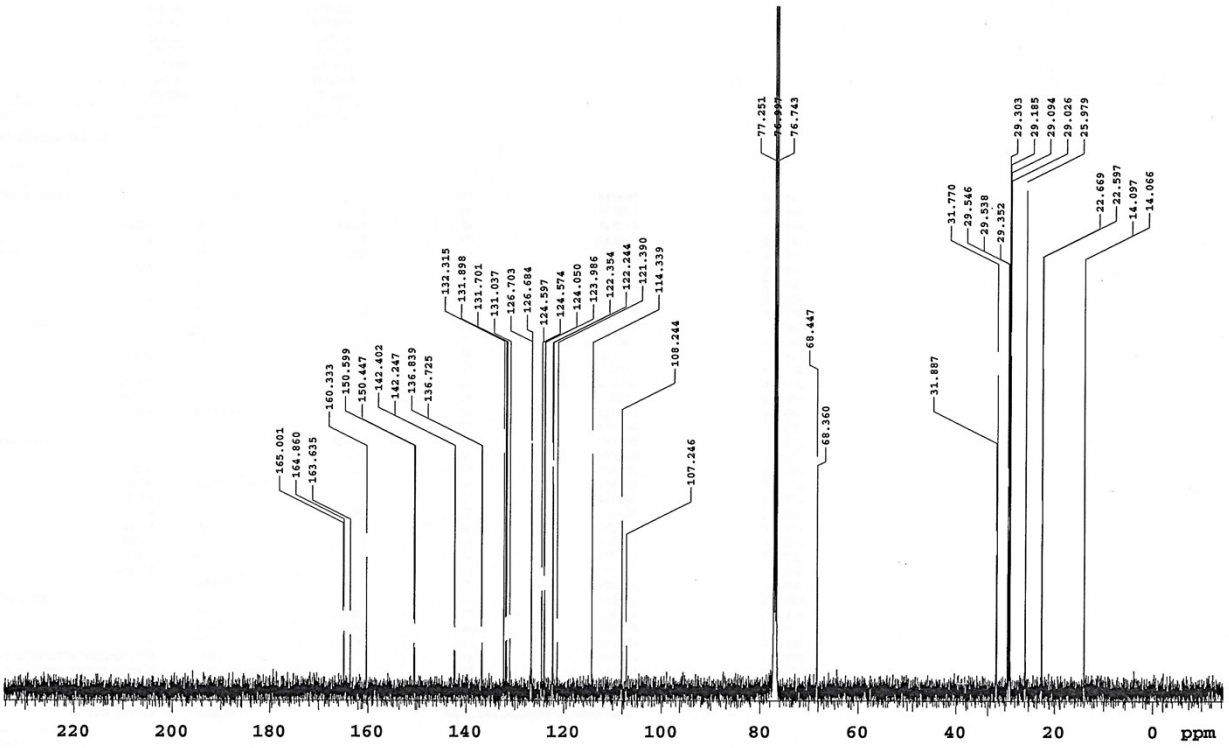


Figure S14. ^{13}C-NMR Spectrum of **O10** in $CDCl_3$.

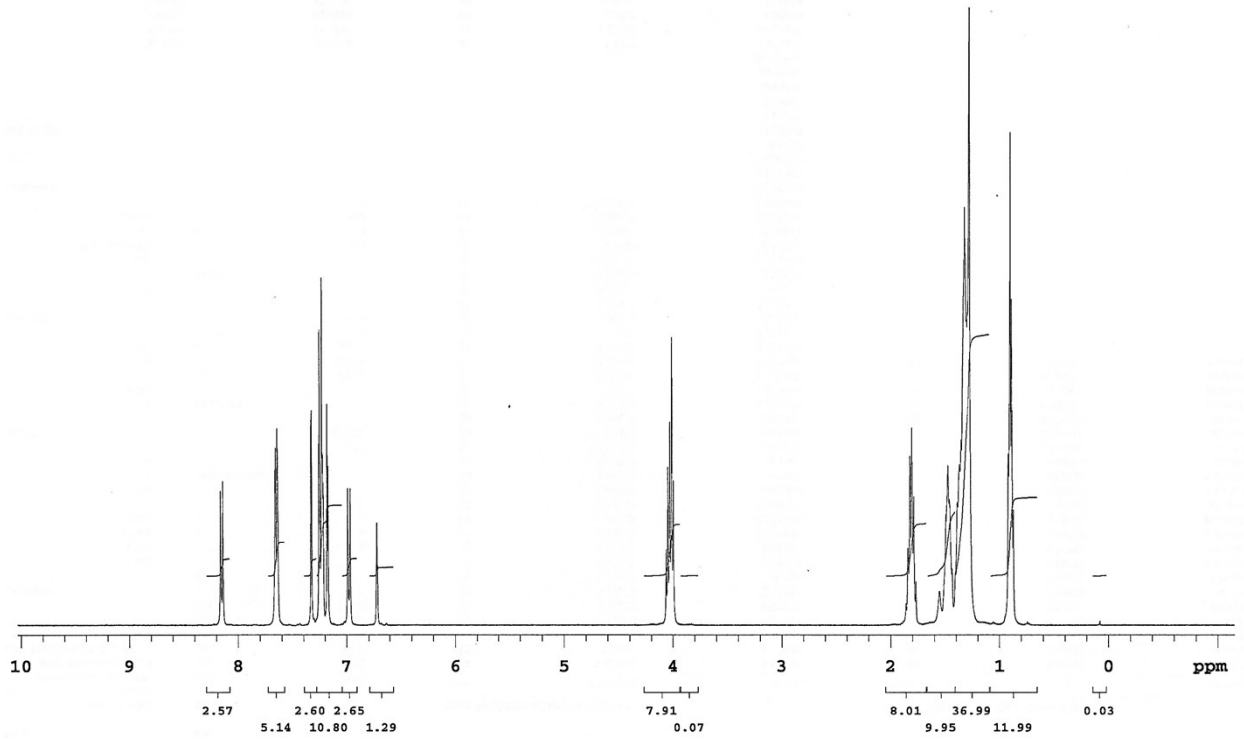


Figure S15. ^{1}H-NMR Spectrum of **O12** in $CDCl_3$.

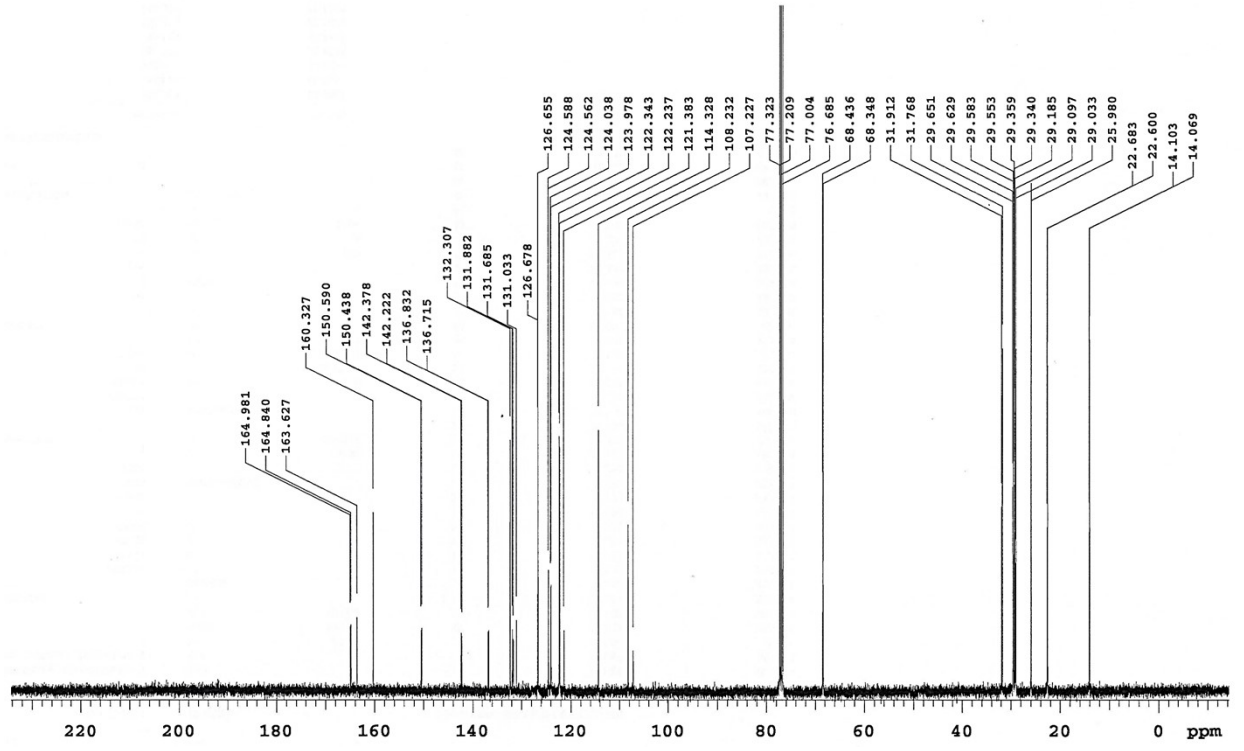


Figure S16. ^{13}C-NMR Spectrum of **O12** in $CDCl_3$.

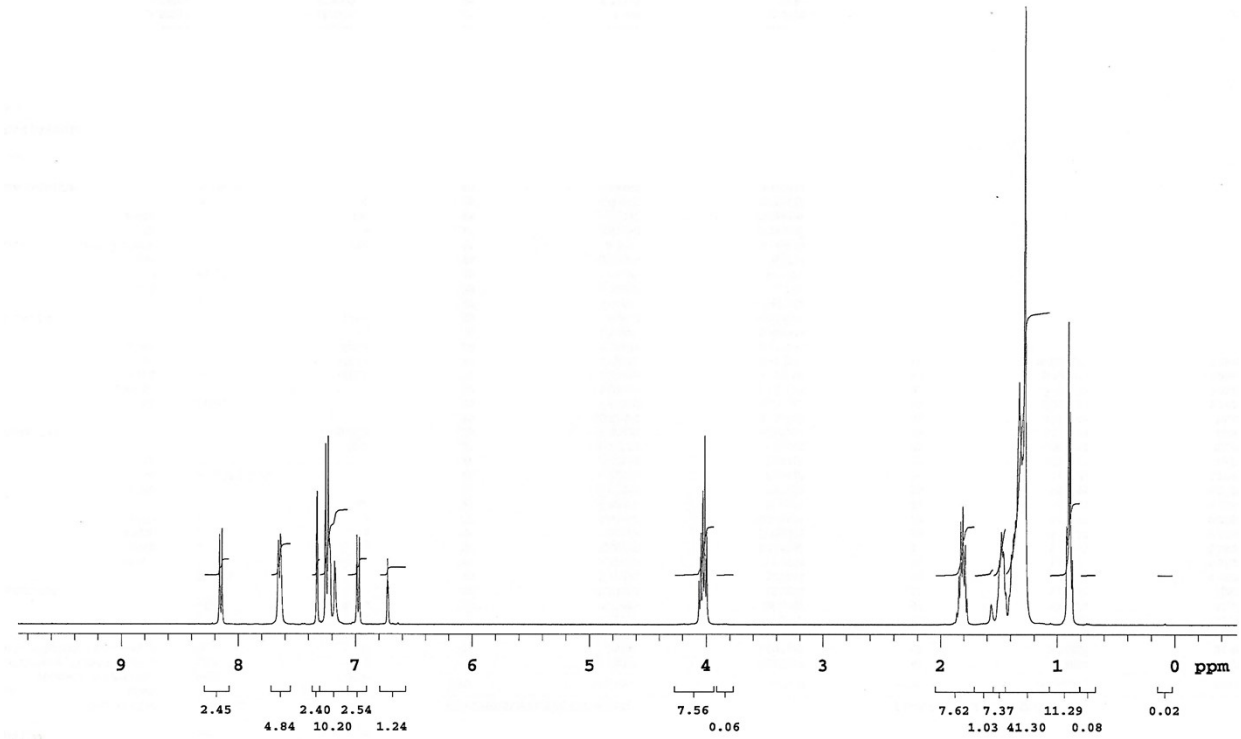


Figure S17. ^{1}H-NMR Spectrum of **O14** in $CDCl_3$.

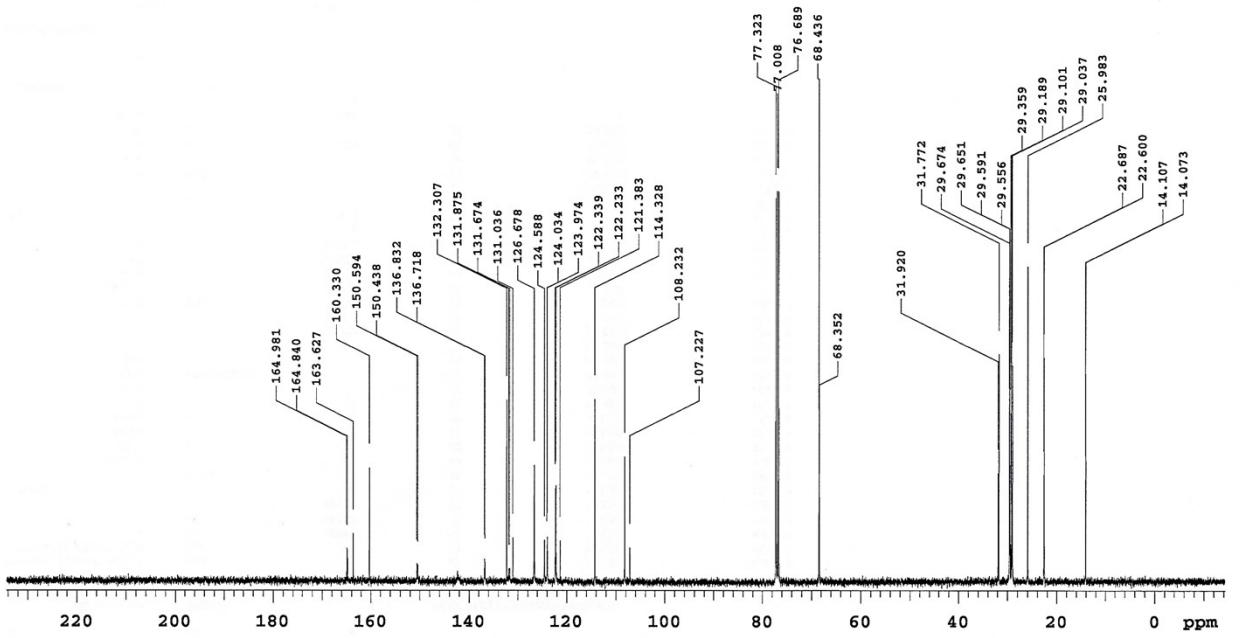


Figure S18. ^{13}C-NMR Spectrum of **O14** in $CDCl_3$.

3. DSC traces

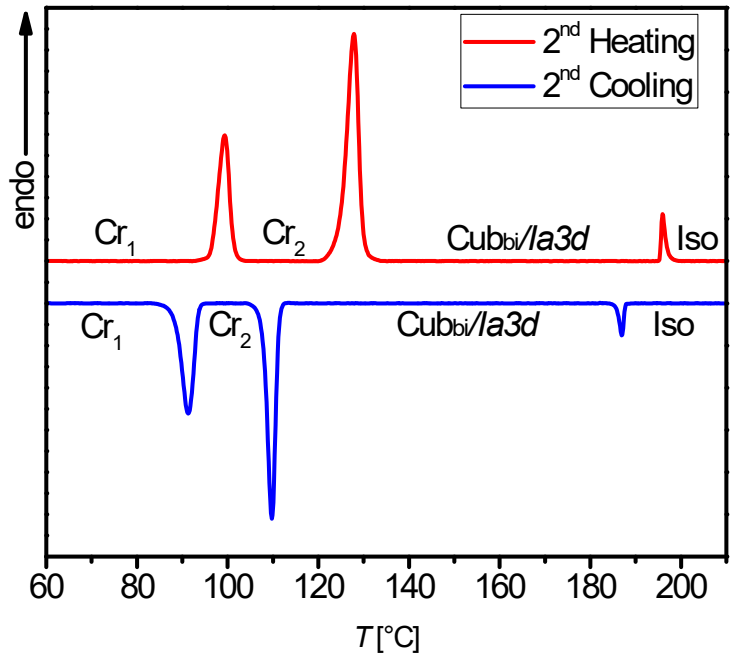


Figure S19. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **S8**.

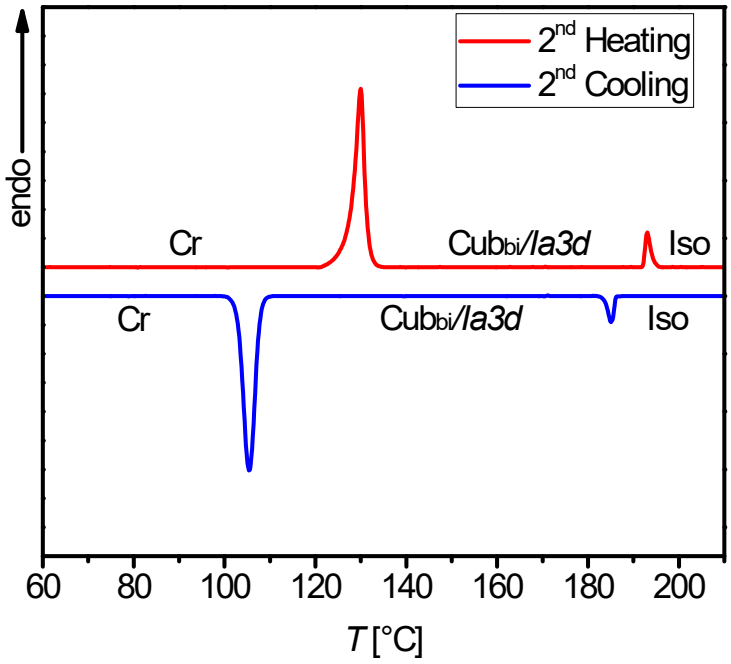


Figure S20. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **S10**.

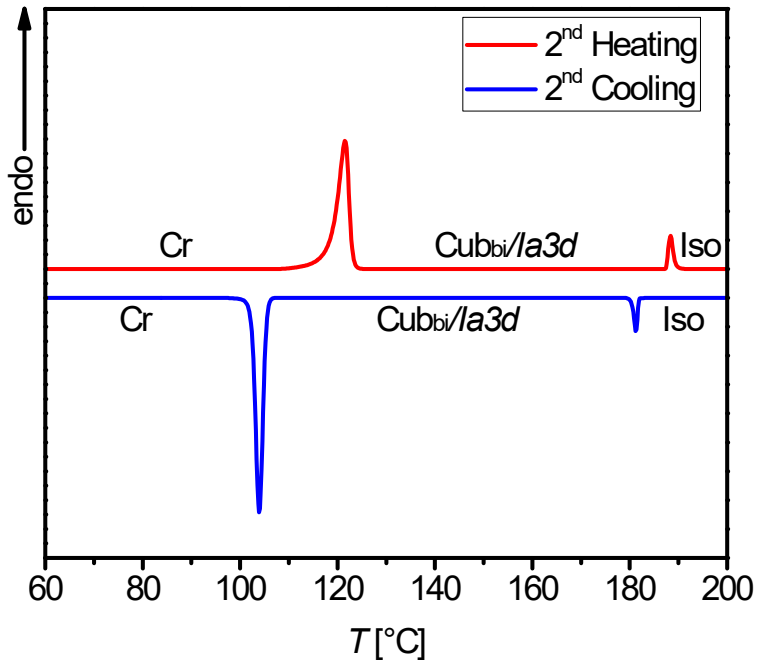


Figure S21. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **S12**.

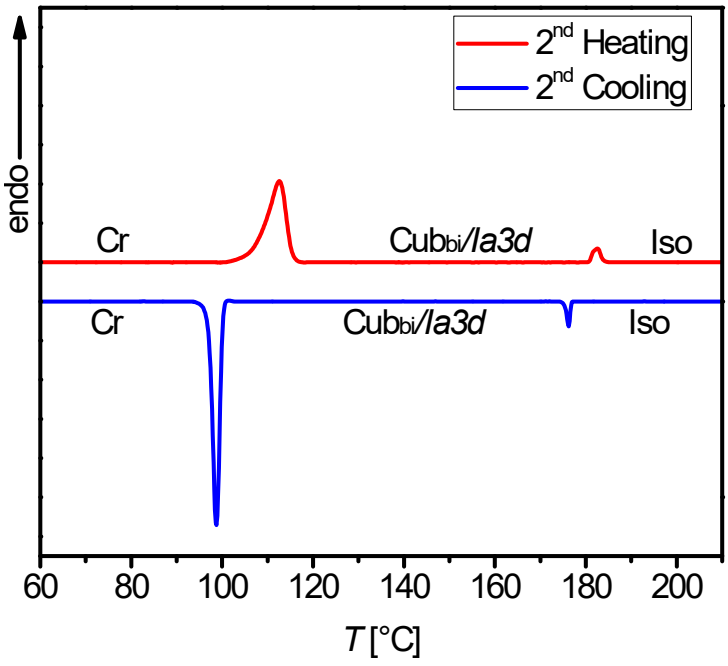


Figure S22. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **S14**.

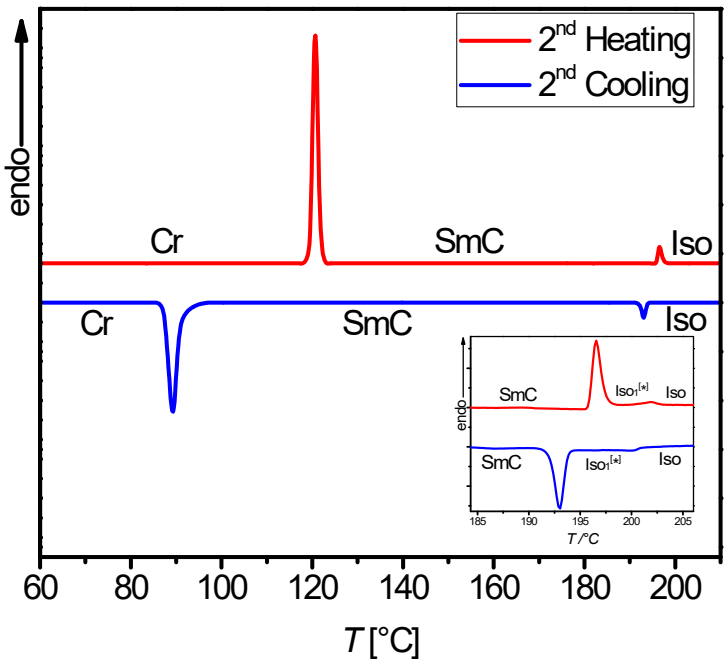


Figure S23. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **O6**. The insets zoom into the Iso-$Iso_1^{[*]}$-SmC transition.

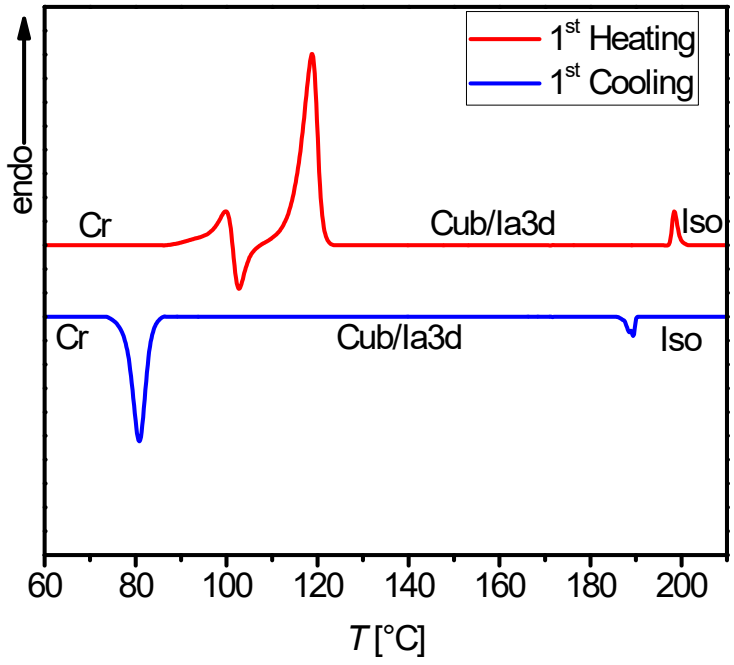


Figure S24. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **O10**.

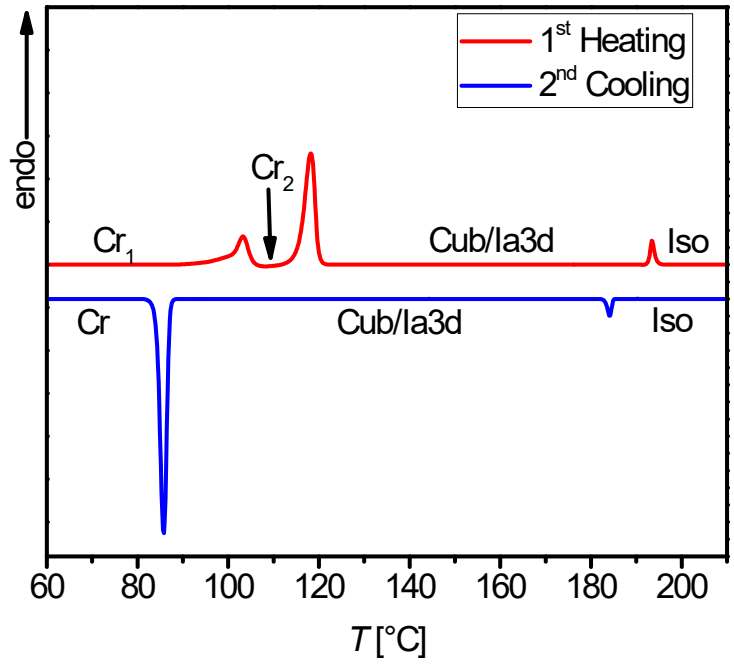


Figure S25. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **O12**.

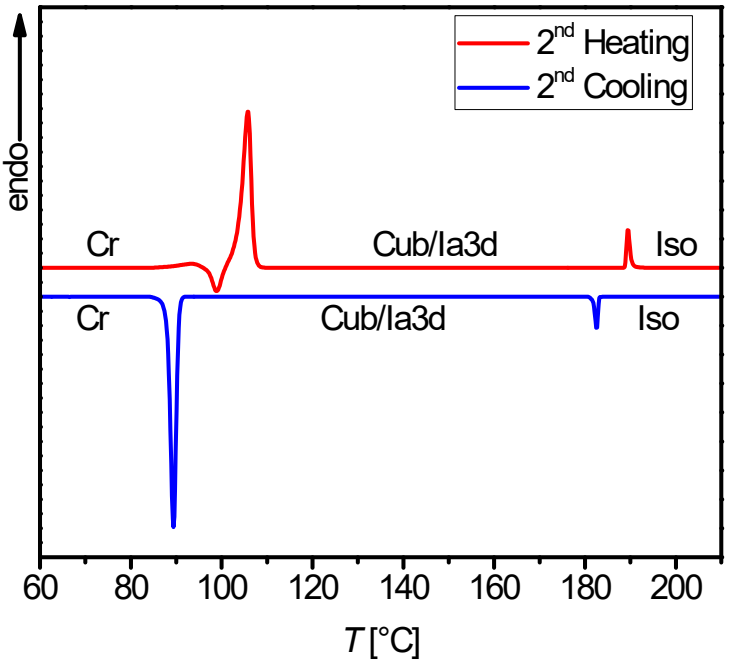


Figure S26. DSC heating and cooling traces recorded at 10 K min^{-1} for compound **O14**.

4. XRD data

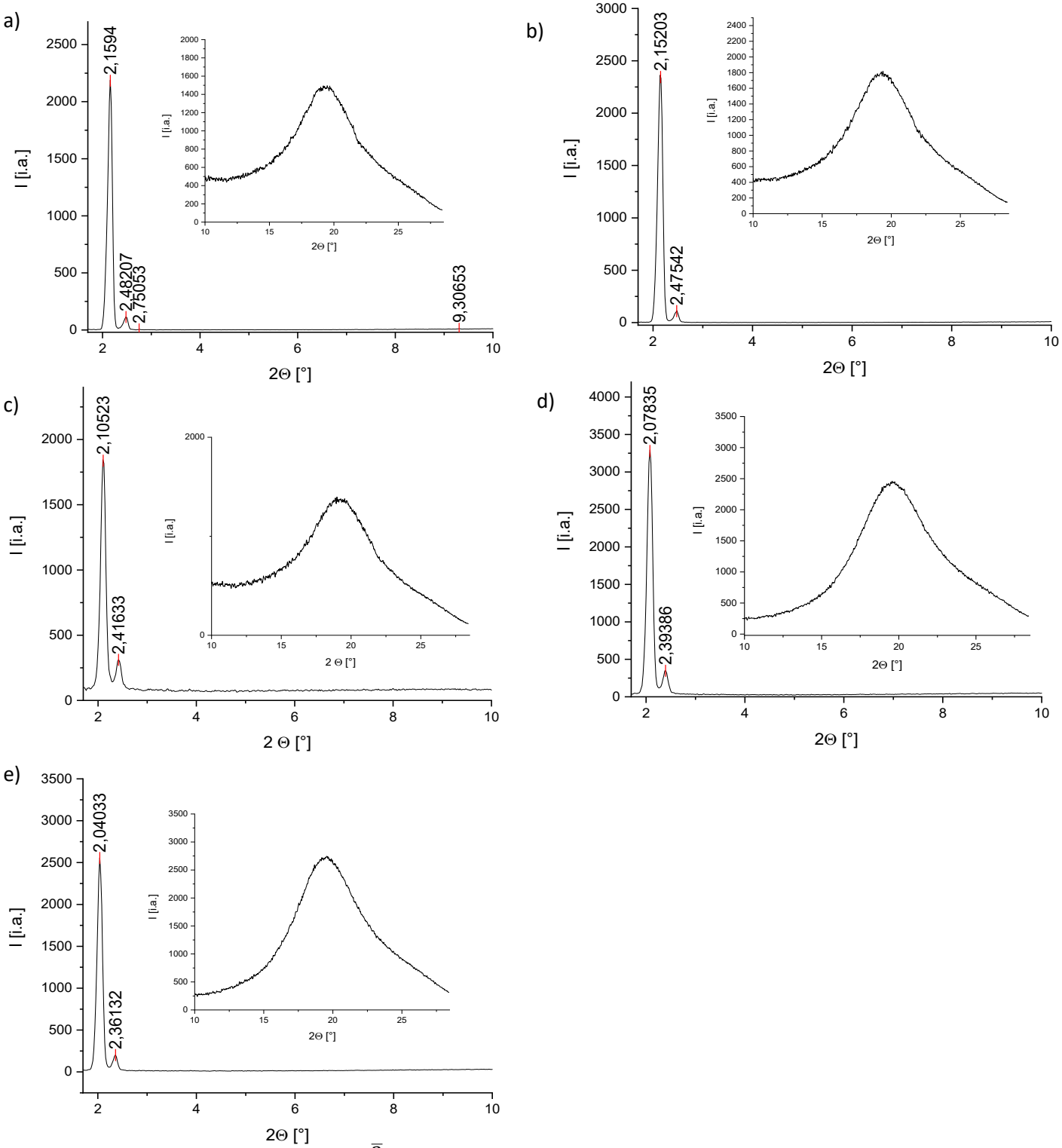


Figure S27. SAXS patterns in the $Cub_{bi}/Ia\bar{3}d$ phases of: a) **S8** at T = 140 °C; b) **S10** at T = 140 °C; c) **S12** at T = 140 °C; d) **S14** at T = 130 °C and e) **S16** at T = 130 °C. The insets show the corresponding WAXS patterns.

5. Additional textures

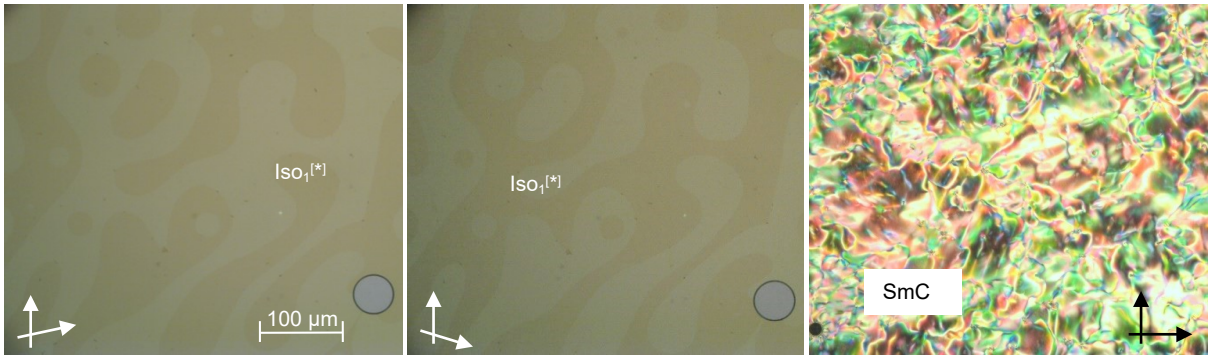


Figure S28. Optical micrographs observed for compound **O6** on cooling in: a,b) the chiral $Iso_1^{[*]}$ phase at 195 °C between slightly rotated polarizers in anti-clockwise or clockwise directions; c) the SmC phase at 185 °C between crossed polarizers.

Figure S29. Cross-polarized optical micrographs observed for aligned compounds **S6** and **O6**. Alignment was achieved by unidirectional flow of molten compound into a 2-µm-thick cell . Left: **S6** at 135 °C, middle: **O6** at 130 °C, right: **O6** at 30 °C. The kinks in the right image, combined with XRD data, suggest a monoclinic crystal structure with a ~ 5.55 nm, b ~ 1.75 nm and β~ 60°.

6. Gelation

We have succeeded in preparing gels from the studied compounds as follows. Powders were dissolved in dodecylbenzene at a concentration of 5-10 g/L. Then the solution was heated to 160 °C and cooled down to room temperature.

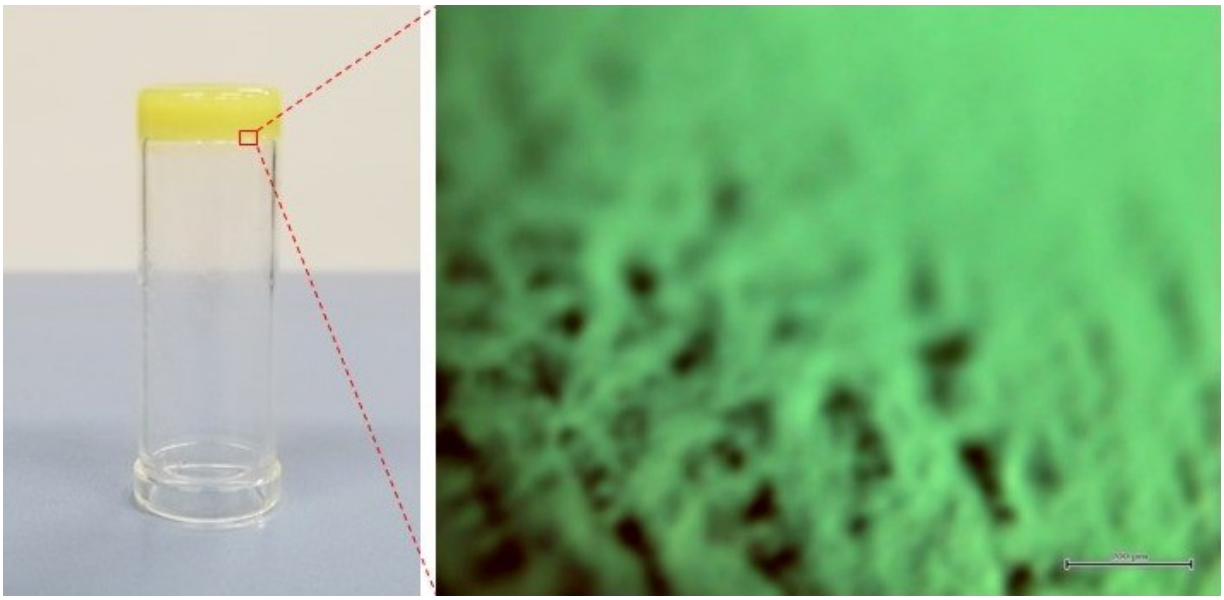


Figure S30. Left: photograph of **S12** gel. Right: gel texture viewed between crossed polarizers. Scale bar: 200 µm.

7. Luminescence mapping in coexisting smectic and cubic phases

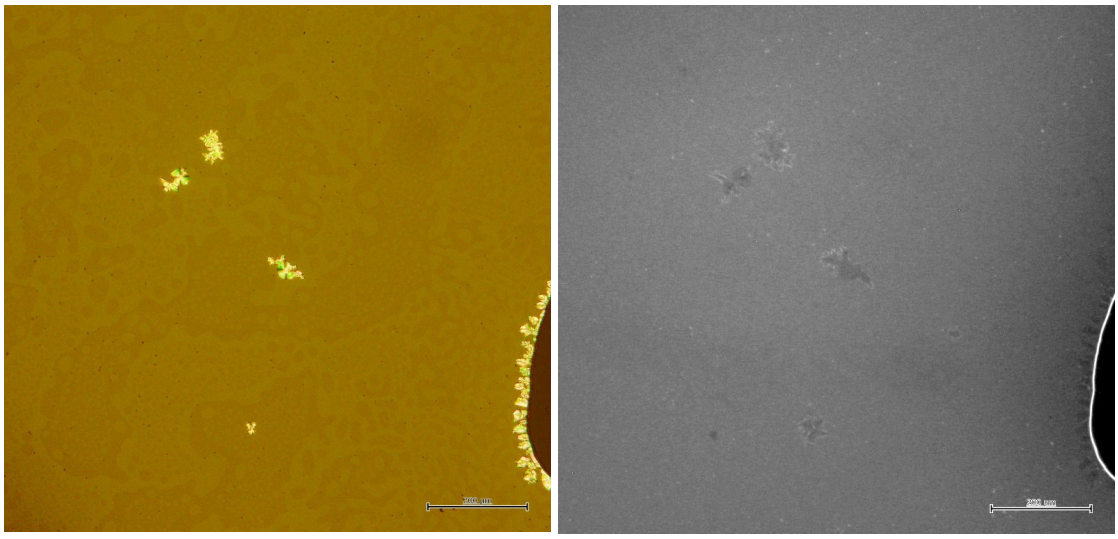


Figure S31. Compound **S6** in a 9-µm-thick cell viewed upon cooling, scale bars: 200 µm. Left: crossed polarizers. Right: photoluminescence (PL) intensity under unpolarized 350 nm excitation. In the left image, the dark contrast results from the cubic phase, while the bright contrast is the smectic phase. PL is relatively weak in the smectic phase, possibly due to the smaller intermolecular distance.

8. References

S1. R. Wu, J. S. Schumm, D. L. Pearson and J. M. Tour, *J. Org. Chem.,* 1996, **61**, 6906-6921.

S2. T. Yasuda, H. Ooi, J. Morita, Y. Akama, K. Minoura, M. Funahashi, T. Shimomura and T. Kato, *Adv. Funct. Mater.*, 2009, **19**, 411–419.

S3. Y. Arakawa, Y. Sasaki, K. Igawa and H. Tsuji, *New J. Chem.,* 2017, **41**, 6514–6522.

S4. M. Alaasar, A. F. Darweesh, X. Cai, Y. Cao, F. Liu and C. Tschierske, *Chem. Eur. J*., 2021, **27**, 14921–14930.