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Supporting Information

Extraordinary Magnetic Field Effects on the LC Phases of Homochiral and Racemic 4-Cyanoresorcinol-Based Diamagnetic Bent-Core Mesogens

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1. Synthesis and Analytical Data

1.1. General

The characterization of the synthesized compounds is based on ^{1}H-, ^{13}C-NMR (Bruker Avance III 500 spectrometer or Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions with tetramethylsilane as internal standard). Microanalyses were performed using a Leco CHNS-932 elemental analyzer. The optical rotation of compounds ((*S*)-**1/n** and ((*S*)-**2/n**) were determined using Anton Paar, Model MCP 100 Modular circular polarimeter. (S)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_D^{20}$ -6.3 ± 0.5°, c = 10 in EtOH), (*S*)-(-)-β-citronellol (Aldrich, ≥99.0%, $[\alpha]_D^{20}$ -5.3°, 4-benzyloxy-2-hydroxybenzaldehyde (ABCR, 99.0%), palladium 10 % on carbon (Alfa Aesar), oxalyl chloride (Merck), *N,N'*-dicyclohexylcarbodiimide (Merck) and 4-(dimethylamino)pyridine (Merck) were purchased commercially. THF (Merck 99%) was purchased commercially and used without further purification. Methylene chloride was dried over P_4O_{10} (Merck) and distilled under a N_2 atmosphere. Hexane, ethyl acetate, chloroform, dichloromethane and ethanol were distilled for use in crystallization and column chromatography. Analytical thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F254 (Merck). Column chromatography was performed using silica gel 60 (Merck, pore size 60 Å, 230-400 mesh particle size).

1.2. Intermediates

2-Cyano-5-benzyloxyphenyl 4-[4-((*S*)-2-methylbutoxy)benzoyloxy]benzoate [(*S*)-Bz-D], 2-cyano-5-benzyloxyphenyl 4-[4-((*S*)-3,7-dimethyloctyloxy)benzoyloxy]benzoate [(*S*)-Bz-E] and 2-cyano-5-benzyloxyphenyl 4-[4-(3,7-dimethyloctyloxy)benzoyloxy]benzoate [*rac*-Bz-E]

The synthesis of the (*S*)-**Bz-D**[S1], (*S*)-**Bz-E** and *rac*-**Bz-E** were carried out by the esterification of 4-benzyloxy-2-hydroxybenzonitrile **C** with alkoxybenzoyloxybenzoic acids (*S*)-**A**, (*S*)-**B** and *rac*-**B** respectively, using N,N'-dicyclohexylcarbodiimide (DCC)/DMAP. For the synthesis of the (*S*)-**Bz-D**, (*S*)-**Bz-E** and *rac*-**Bz-E**, the mixture 4-benzyloxy-2-hydroxybenzonitrile **C** (1.12 g, 5 mmol), (*S*)-**A** or (*S*)-**B** or *rac*-**B**, (5.0 mmol), N,N'-dicyclohexylcarbodiimide (DCC) (1.18 g, 5.8 mmol) and 4-(dimethylamino)pyridine (DMAP) as catalyst in dry dichloromethane (60 mL) was stirred at room temperature under an argon atmosphere for 24 h. The end of reaction was monitored by TLC (chloroform). The reaction mixture was filtered on silica gel with CH_2Cl_2 and the solvent was evaporated. The crude products were purified by column chromatography on silica gel using CH_2Cl_2 as eluent. Spectroscopic data (^{1}H-NMR, ^{13}C-NMR and MS) of (*S*)-**Bz-D** was previously reported in ref.S1.

2-Cyano-5-benzyloxyphenyl 4-[4-((*S*)-3,7-dimethyloctyloxy)benzoyloxy]benzoate [(*S*)-Bz-E]

Yield: 80%, m.p: 65 °C, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) =8.24 (d, J ≈ 8.6 Hz; 2 Ar-H), 8.08 (d, J ≈ 8.6 Hz; 2 Ar-H), 7.55 (d, J ≈ 8.6 Hz; 1 Ar-H), 7.36-7.31 (m, 7 Ar-H), 7.03 (d, J ≈ 2.1 Hz; 1 Ar-H), 6.92 (d, J ≈ 8.7 Hz, 2 Ar-H), 6.87 (dd, J ≈ 8.6 Hz and J ≈ 2.1 Hz; 1 Ar-H), 5.06 (s, 2H, OCH_2Ph), 4.06-3.99 (m, 2H, OCH_2), 1.86-1.77 (m, 1H, CH),

1.68-1.43, 1.36-1.08 (2m; 9H, CH, 4 CH_2), 0.89 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.81 (d, J ≈ 6.5 Hz; 6H, 2 CH_3).

2-Cyano-5-benzyloxyphenyl 4-[4-(3,7-dimethyloctyloxy)benzoyloxy]benzoate [*rac*-Bz-E]

Yield: 71%, m. p.: 64 °C, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.31 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.16 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.62 (d, J ≈ 8.7 Hz; 1 Ar-H), 7.42-7.37 (m, 7 Ar-H), 7.11 (d, J ≈ 2.4 Hz; 1 Ar-H), 6.99 (d, J ≈ 8.9 Hz, 2 Ar-H), 6.95 (dd, J ≈ 8.7 Hz and J ≈ 2.4 Hz; 1 Ar-H), 5.13 (s, 2H, OCH_2Ph), 4.14-4.06 (m, 2H, OCH_2), 1.93-1.84 (m, 1H, CH), 1.75-1.50, 1.39-1.15 (2m; 9H, CH, 4 CH_2), 0.96 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.88 (d, J ≈ 6.6 Hz; 6H, 2 CH_3).

2-Cyano-5-hydroxyphenyl 4-[4-((*S*)-2-methylbutoxy)benzoyloxy]benzoate (*S*)-D, 2-cyano-5-hydroxyphenyl 4-[4-((*S*)-3,7-dimethyloctyloxy)benzoyloxy]benzoate (*S*)-E and 2-cyano-5-hydroxyphenyl 4-[4-(3,7-dimethyloctyloxy)benzoyloxy]benzoate *rac*-E

The benzyl group of (*S*)-**Bz-D**, (*S*)-**Bz-E** and *rac*-**Bz-E** was removed by the catalytic hydrogenation according to procedures described in ref.[S2]. Spectroscopic data (^{1}H-NMR, APT-^{13}C-NMR and MS) of (*S*)-**D** was given in ref.S1. For the synthesis of (*S*)-**D**, (*S*)-**E** and *rac*-**E**, the benzylated compounds (*S*)-**Bz-D** or (*S*)-**Bz-E** or *rac*-**Bz-E** (2.0 mmol) were dissolved in THF (40 mL) and then catalytic amount of Pd/C-10% was added to this solution. The mixture was stirred in argon-flushed vessel of autoclave at 40 °C under 5 bar pressure of H_2 gas for 8-10 h. The end of reaction was monitored by TLC (chloroform). The resulting mixture was filtered on silica gel to remove the residue of catalyst and washed with THF. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with CH_2Cl_2.

2-Cyano-5-hydroxyphenyl 4-[4-((*S*)-3,7-dimethyloctyloxy)benzoyloxy]benzoate (*S*)-E:

Yield: 90%, m.p.: 166 °C, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) =8.29 (d, J ≈ 8.8 Hz; 2 Ar-H), 8.16 (d, J ≈ 8.8 Hz; 2 Ar-H), 7.55 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.38 (d, J ≈ 8.7 Hz; 2 Ar-H), 6.99 (d, J ≈ 8.7 Hz; 2 Ar-H), 6.96 (d, J ≈ 2.1 Hz; 1 Ar-H), 6.79 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 4.14-4.06 (m, 2H, OCH_2), 1.93-1.84 (m, 1H, CH), 1.80-1.50, 1.41-1.13 (2m; 9H, CH, 4 CH_2), 0.97 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.88 (d, J ≈ 6.6 Hz; 6H, 2 CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) =164.57, 163.31 (CO), 163.95, 155.91, 154.04, 125.63, 120.72, 115.69, 98.25 (Ar-C), 134.51, 132.54, 132.25, 122.41, 114.50, 110.73 (Ar-CH), 114.05 (CN), 66.78 (OCH_2), 39.23, 37.26, 35.99, 24.67 (CH_2), 29.83, 27.99 (CH), 22.72, 22.62, 19.65 (CH_3).

2-Cyano-5-hydroxyphenyl 4-[4-(3,7-dimethyloctyloxy)benzoyloxy]benzoate *rac*-E:

Yield: 44%, m.p.: 165 °C, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.30 (d, J ≈ 8.8 Hz; 2 Ar-H), 8.16 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.57 (d, J ≈ 8.6 Hz; 1 Ar-H), 7.38 (d, J ≈ 8.8 Hz; 2 Ar-H), 6.99 (d, J ≈ 8.9 Hz; 2 Ar-H), 6.97 (d, J ≈ 2.4 Hz; 1 Ar-H), 6.79 (dd, J ≈ 8.6 Hz and J ≈ 2.4 Hz; 1 Ar-H), 4.14-4.06 (m, 2H, OCH_2), 1.91-1.84 (m, 1H, CH), 1.72-1.50, 1.39-1.15 (2m; 9H, CH, 4 CH_2), 0.97 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.88 (d, J ≈ 6.6 Hz; 6H, 2 CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) =164.51, 163.27 (CO), 163.93, 155.91, 154.05, 125.60, 120.73, 115.62, 98.39 (Ar-C), 134.51, 132.51, 132.24, 122.39, 114.49, 110.71 (Ar-CH), 113.99 (CN), 66.77 (OCH_2), 39.22, 37.26, 35.98, 24.66 (CH_2), 29.82, 27.97 (CH), 22.70, 22.60, 19.64 (CH_3).

1.3 Compounds (*S*)-**1/*n***, (*S*)-**2/*n*** and *rac*-**2/12**

General procedure. A mixture of (*S*)-**D** or (*S*)-**E** (1.2 mmol) with the appropriate 4-(4-*n*-alkyloxybenzoyloxy)benzoic acids **F6 - F10** (1.2 mmol), DCC (0.28 g, 1.4 mmol) and DMAP (12 mg, 0.1 mmol) in dry dichloromethane (30 mL) was stirred at room temperature under an argon atmosphere for 24 h. The resulting mixture was filtered on silica gel and the solvent was evaporated. The crude products were purified by column chromatography on silica gel using chloroform as eluent and recrystallized from ethanol.
Compounds **(*S*)-2/12** and **rac-2/12** were obtained with the following procedure: 4-(4-*n*-dodecyloxybenzoyloxy)benzoic acid (**F*12)*** (0.22 mmol) was reacted with oxalyl chloride (5 mL) and this mixture was refluxed for 7h and then the excess of oxalyl chloride was removed by vacuum distillation. To the solution of the obtained product, ***(S)*-E** or ***rac*-E** (0.2 mmol) and dry pyridine (2 mL) in dry dichloromethane (10 mL) were added and this mixture was stirred for 24h at room temperature under argon atmosphere. The end of reaction was monitored by TLC (hexane:ethyl acetate/5:1). The mixture was poured into 10 mL of water and then the aqueous solution was neutralized to pH 7 by adding 1 N HCl. The mixture was extracted into CH_2C1_2 (x 3) and the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with chloroform: ethyl acetate/10:0.25. The product was recrystallized from ethanol.

All compounds form colorless crystals with phase transition temperatures collected in Table 1 of the main text.

4-{4-[4-(*n*-Hexyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-methylbutoxy)benzoyloxy] benzoyloxy}benzonitrile

***(S)*-1/6:** Yield: 38%, colorless crystals; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.20 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.08 (d, J ≈ 8.9 Hz; 2 Ar-H), 8.07 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.74 (d, J ≈ 8.6 Hz; 1 Ar-H), 7.47 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.33 (d; J ≈ 8.6 Hz; 2 Ar-H), 7.32 (d, J ≈ 8.6 Hz; 2 Ar-H), 7.26 (dd, J ≈ 8.6 Hz and J ≈ 2.1 Hz; 1 Ar-H), 6.93 (d; J ≈ 8.9 Hz; 2 Ar-H), 6.92 (d; J ≈ 8.9 Hz; 2 Ar-H), 3.99 (t; J ≈ 6.5 Hz, 2H, OCH_2), 3.85, 3.77 (2dd, J ≈ 8.9 Hz and J ≈ 6.1 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.87-1.81 (m, 1H, CH), 1.79-1.73, 1.55-1.39, 1.33-1.18 (3m, 10H, $5CH_2$), 0.98 (d, J ≈ 6.7 Hz; 3H, CH_3), 0.90 (t, J ≈ 7.4 Hz; 3H, CH_3), 0.85 (t, J ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.27, 164.22, 163.92, 163.88 (CO), 163.32, 162.94, 156.08, 155.93, 154.80, 153.49, 125.72, 125.33, 120.80, 120.06, 104.28 (Ar-C), 133.99, 132.47, 132.29, 132.04, 122.43, 122.38, 117.44, 114.47 (Ar-CH), 114.81 (CN), 73.19, 68.42 (OCH_2), 34.64 (CH), 31.55, 29.06, 26.09, 25.67, 22.60 (CH_2), 16.50, 14.04, 11.32 (CH_3). **$C_{46}H_{43}NO_{10}$** (769.83); Anal. Calc.: C, 71.77; H, 5.63; N, 1.82. Found: C, 72.00; H, 5.26; N, 1.96%. $[\alpha]_{589}^{25}$ = = -1.7° (c= 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Octyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-methylbutoxy)benzoyloxy] benzoyloxy}benzonitrile

***(S)*-1/8:** Yield: 35%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.20 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.08 (2d, J ≈ 8.9 Hz; 4 Ar-H), 7.74 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.47 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.34 (d; J ≈ 8.6 Hz; 2 Ar-H), 7.33 (d, J ≈ 8.6 Hz; 2 Ar-H), 7.26 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 6.93 (d; J ≈ 8.9 Hz; 2 Ar-H), 6.91 (d; J ≈ 8.9 Hz; 2 Ar-H), 3.99 (t; J ≈ 6.5 Hz, 2H, OCH_2), 3.85, 3.77 (2dd, J ≈ 8.9 Hz and J ≈ 6.0 Hz

each; 2H, OCH_2, (chiral alkyl chain)), 1.88-1.81 (m, 1H, CH), 1.79-1.73, 1.57-1.36, 1.33-1.18 (3m, 14H, $7CH_2$), 0.98 (d, J ≈ 6.7 Hz; 3H, CH_3), 0.90 (t, J ≈ 7.4 Hz; 3H, CH_3), 0.83 (t, J ≈ 6.5 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.27, 164.22, 163.91, 163.88 (CO), 163.32, 162.94, 156.07, 155.92, 154.79, 153.47, 125.71, 125.32, 120.81, 120.08, 104.27 (Ar-C), 134.01, 132.47, 132.29, 132.04, 122.44, 122.39, 117.45, 114.46 (Ar-CH), 114.82 (CN), 73.17, 68.42 (OCH_2), 34.64 (CH), 31.82, 29.34, 29.24, 29.09, 26.09, 26.00, 22.68 (CH_2), 16.51, 14.13, 11.33 (CH_3). $[\alpha]_{589}^{25}$ = = -2.8° (c= 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Decyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-methylbutoxy)benzoyloxy] benzoyloxy}benzonitrile

***(S)*-1/10:** Yield: 39%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; J ≈ 8.6 Hz; 2 Ar-H), 8.27 (d, J ≈ 8.6 Hz; 2 Ar-H), 8.16 (d, J ≈ 8.9 Hz; 2 Ar-H), 8.15 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.81 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.54 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.41 (d; J ≈ 8.6 Hz; 2 Ar-H), 7.39 (d, J ≈ 8.6 Hz; 2 Ar-H), 7.33 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 7.00 (d; J ≈ 8.9 Hz; 2 Ar-H), 6.99 (d; J ≈ 8.9 Hz; 2 Ar-H), 4.06 (t; J ≈ 6.5 Hz, 2H, OCH_2), 3.92, 3.84 (2dd, J ≈ 8.9 Hz and J ≈ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.95-1.89 (m, 1H, CH), 1.86-1.80, 1.64-1.45, 1.38-1.23 (3m, 18H, $9CH_2$), 1.05 (d, J ≈ 6.7 Hz; 3H, CH_3), 0.98 (t, J ≈ 7.4 Hz; 3H, CH_3), 0.89 (t, J ≈ 6.7 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.27, 164.23, 163.90, 163.87 (CO), 163.33, 162.94, 156.05, 155.90, 154.78, 153.46, 125.69, 125.31, 120.81, 120.08, 104.25 (Ar-C), 134.00, 132.46, 132.28, 132.03, 122.43, 122.38, 117.44, 114.45 (Ar-CH), 114.80 (CN), 73.16, 68.41 (OCH_2), 34.63 (CH), 31.90, 29.71, 29.55, 29.36, 29.32, 29.08, 26.07, 25.98, 22.69 (CH_2), 16.49, 14.13, 11.32 (CH_3). $[\alpha]_{589}^{25}$ = = -3.9° (c= 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Dodecyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-methylbutoxy)benzoyloxy] benzoyloxy}benzonitrile

***(S)*-1/12:** Yield: 28%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.36 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.29 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.19 (d, J ≈ 8.9 Hz; 2 Ar-H), 8.17 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.83 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.56 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.43 (d; J ≈ 8.7 Hz; 2 Ar-H), 7.42 (d, J ≈ 8.7 Hz; 2 Ar-H), 7.35 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 7.03 (d; J ≈ 8.7 Hz; 2 Ar-H), 7.01 (d; J ≈ 8.7 Hz; 2 Ar-H), 4.08 (t; J ≈ 6.5 Hz, 2H, OCH_2), 3.95, 3.86 (2dd, J ≈ 8.9 Hz and J ≈ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.98-1.91 (m, 1H, CH), 1.88-1.83, 1.67-1.48, 1.40-1.26 (3m, 22H, $11CH_2$), 1.07 (d, J ≈ 6.7 Hz; 3H, CH_3), 1.00 (t, J ≈ 7.4 Hz; 3H, CH_3), 0.91 (t, J ≈ 6.7 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.26, 164.23, 164.04, 163.92, (CO), 163.32, 162.94, 156.07, 155.93, 154.80, 153.48, 125.71, 125.32, 120.82, 120.08, 104.27 (Ar-C), 134.00, 132.47, 132.29, 132.04, 122.44, 122.38, 117.44, 114.47 (Ar-CH), 114.82 (CN), 73.17, 68.42 (OCH_2), 34.64 (CH), 31.94, 29.68, 29.65, 29.61, 29.57, 29.37, 29.09, 26.09, 25.99, 22.71 (CH_2), 16.51, 14.15, 11.33 (CH_3). **$C_{52}H_{55}NO_{10}$** (853.99); Anal. Calc.: C, 73.13; H, 6.49; N, 1.64. Found: C, 72.99; H, 6.16; N, 1.74%.

4-{4-[4-(*n*-Hexyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-3,7-dimethyloctyloxy) benzoyloxy]benzoyloxy}benzonitrile

***(S)*-2/6:** Yield: 34%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.20 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.09 (d, J ≈ 8.9 Hz; 2 Ar-H), 8.08 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.74 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.47 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.34 (d; J ≈ 8.7 Hz; 2

Ar-H), 7.32 (d, J ≈ 8.7 Hz; 2 Ar-H), 7.26 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 6.93 (d; J ≈ 8.9 Hz; 2 Ar-H), 6.92 (d; J ≈ 8.9 Hz; 2 Ar-H), 4.06-3.97 (m; 4H, 2 OCH_2), 1.84-1.73, 1.65-1.39, 1.33-1.06 (3m, 18H, 2CH, 8CH_2), 0.89 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.85 (t, J ≈ 7.0 Hz; 3H, CH_3), 0.81 (d, J ≈ 6.5 Hz; 6H, 2 CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.25, 164.20, 163.89, 163.83 (CO), 163.31, 162.92, 156.04, 155.90, 154.77, 153.45, 125.69, 125.30, 120.82, 120.07, 104.25 (Ar-C), 133.99, 132.45, 132.28, 132.03, 122.42, 122.37, 117.43, 114.43 (Ar-CH), 114.80 (CN), 68.40, 66.72 (OCH_2), 29.80, 27.97 (CH), 39.21, 37.24, 35.97, 31.54, 29.04, 25.65, 24.65, 22.71 (CH_2), 22.61, 22.59, 19.64, 14.04 (CH_3). **$C_{51}H_{53}NO_{10}$** (839.97); Anal. Calc.: C, 72.92; H, 6.36; N, 1.67. Found: C, 72.84; H, 6.01; N, 1.95%; $[\alpha]_{589}^{25}$ = -0.24° (c= 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Octyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-3,7-dimethyloctyloxy) benzoyloxy]benzoyloxy}benzonitrile

***(S)*-2/8:** Yield: 32%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.20 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.09 (d, J ≈ 8.9 Hz; 2 Ar-H), 8.08 (d, J ≈ 8.9 Hz; 2 Ar-H), 7.74 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.47 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.34 (d; J ≈ 8.7 Hz; 2 Ar-H), 7.32 (d, J ≈ 8.7 Hz; 2 Ar-H), 7.26 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 6.92 (2d; J ≈ 8.9 Hz; 4 Ar-H), 4.06-3.97 (m; 4H, 2 OCH_2), 1.84-1.73, 1.63-1.38, 1.32-1.08 (3m, 22H, 2CH, 10CH_2), 0.89 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.84-0.80 (m, 9H, 3CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.26, 164.21, 163.91, 163.88 (CO), 163.32, 162.94, 156.06, 155.92, 154.79, 153.48, 125.71, 125.32, 120.84, 120.07, 104.27 (Ar-C), 134.00, 132.47, 132.29, 132.04, 122.43, 122.38, 117.44, 114.46 (Ar-CH), 114.82 (CN), 68.42, 66.75 (OCH_2), 29.83, 27.99 (CH), 39.23, 37.27, 35.99, 31.82, 29.34, 29.24, 29.09, 26.00, 24.67, 22.73 (CH_2), 22.68, 22.63, 19.66, 14.13 (CH_3). **$C_{53}H_{57}NO_{10}$** (868.02); Anal. Calc.: C, 73.34; H, 6.62; N, 1.61. Found: C, 73.42; H, 6.35; N, 1.85%; $[\alpha]_{589}^{25}$ = -0.25° (c= 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Decyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-3,7-dimethyloctyloxy) benzoyloxy]benzoyloxy}benzonitrile

***(S)*-2/10:** Yield: 36%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.36 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.30 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.19 (d, J ≈ 8.8 Hz; 2 Ar-H), 8.17 (d, J ≈ 8.8 Hz; 2 Ar-H), 7.83 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.56 (d; J ≈ 2.0 Hz; 1 Ar-H), 7.43 (d; J ≈ 8.7 Hz; 2 Ar-H), 7.42 (d, J ≈ 8.7 Hz; 2 Ar-H), 7.35 (dd, J ≈ 8.5 Hz and J ≈ 2.0 Hz; 1 Ar-H), 7.02 (2d; J ≈ 8.8 Hz; 4 Ar-H), 4.16-4.07 (m; 4H, 2 OCH_2), 1.93-1.83, 1.70-1.48, 1.41-1.17 (3m, 26H, 2CH, 12CH_2), 0.99 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.93-0.90 (m, 9H, 3CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.26, 164.21, 163.92, 163.86 (CO), 163.32, 162.94, 156.07, 155.93, 154.80, 153.48, 125.71, 125.33, 120.86, 120.07, 104.27 (Ar-C), 134.00, 132.49, 132.29, 132.04, 122.43, 122.38, 117.44, 114.46 (Ar-CH), 114.82 (CN), 68.43, 66.75 (OCH_2), 29.83, 27.99 (CH), 39.23, 37.27, 36.00, 31.91, 29.72, 29.57, 29.37, 29.33, 29.09, 25.99, 24.67, 22.72 (CH_2), 22.70, 22.62, 19.66, 14.14 (CH_3). **$C_{55}H_{61}NO_{10}$** (896.07); Anal. Calc.: C, 73.72; H, 6.86; N, 1.56. Found: C, 73.51; H, 6.63; N, 1.70%; $[\alpha]_{589}^{25}$ = = -0.16° (c= 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Dodecyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-3,7-dimethyloctyloxy) benzoyloxy]benzoyloxy}benzonitrile

***(S)*-2/12:** Yield: 32%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.27 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.16 (d, J ≈ 8.9 Hz; 2 Ar-H), 8.15 (d, J ≈ 8.9

Hz; 2 Ar-H), 7.80 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.54 (d; J ≈ 2.1 Hz; 1 Ar-H), 7.41 (d; J ≈ 8.7 Hz; 2 Ar-H), 7.40 (d, J ≈ 8.7 Hz; 2 Ar-H), 7.33 (dd, J ≈ 8.5 Hz and J ≈ 2.1 Hz; 1 Ar-H), 7.00 (d; J ≈ 8.9 Hz; 2 Ar-H), 6.99 (d; J ≈ 8.9 Hz; 2 Ar-H), 4.14-4.04 (m; 4H, 2 OCH_2), 1.91-1.80, 1.67-1.45, 1.43-1.15 (3m, 30H, 2CH, 14CH_2), 0.97 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.90-0.87 (m, 9H, 3CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.25, 164.20, 163.91, 163.85 (CO), 163.31, 162.92, 156.06, 155.92, 154.79, 153.48, 125.71, 125.32, 120.86, 120.79, 120.06, 104.27 (Ar-C), 133.98, 132.48, 132.28, 132.03, 122.42, 122.37, 117.43, 114.46 (Ar-CH), 114.80 (CN), 68.42, 66.75 (OCH_2), 29.82, 27.98 (CH), 39.22, 37.26, 35.99, 31.92, 29.70, 29.66, 29.63, 29.59, 29.55, 29.35, 29.08, 25.97, 24.66 (CH_2), 22.70, 22.60, 19.64, 14.12 (CH_3). HRMS (m/z): $[M+Li]^+$ calcd. for $C_{57}H_{65}NO_{10}Li$ 930.4808, found 930.5081; Anal. Calc.: C, 74.08; H, 7.09; N, 1.52. Found: C, 74.14; H, 6.92; N, 1.64%. $[\alpha]_{589}^{25}$ = -0.15° (c = 1 mg/mL in $CHCl_3$ at 25 °C).

4-{4-[4-(*n*-Dodecyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-(*rac*-3,7-dimethyloctyloxy) benzoyloxy]benzoyloxy}benzonitrile

***rac*-2/12:** Yield: 35%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; J ≈ 8.7 Hz; 2 Ar-H), 8.27 (d, J ≈ 8.7 Hz; 2 Ar-H), 8.16 (d, J ≈ 8.8 Hz; 2 Ar-H), 8.15 (d, J ≈ 8.8 Hz; 2 Ar-H), 7.80 (d, J ≈ 8.5 Hz; 1 Ar-H), 7.54 (d; J ≈ 2.0 Hz; 1 Ar-H), 7.41 (d; J ≈ 8.6 Hz; 2 Ar-H), 7.40 (d, J ≈ 8.6 Hz; 2 Ar-H), 7.33 (dd, J ≈ 8.5 Hz and J ≈ 2.0 Hz; 1 Ar-H), 7.00 (d; J ≈ 8.9 Hz; 2 Ar-H), 6.99 (d; J ≈ 8.9 Hz; 2 Ar-H), 4.14-4.04 (m; 4H, 2 OCH_2), 1.91-1.80, 1.67-1.45, 1.43-1.15 (3m, 30H, 2CH, 14CH_2), 0.97 (d, J ≈ 6.5 Hz; 3H, CH_3), 0.90-0.87 (m, 9H, 3CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.24, 164.20, 163.91, 163.85 (CO), 163.31, 162.92, 156.06, 155.92, 154.79, 153.48, 125.71, 125.32, 120.86, 120.79, 120.05, 104.26 (Ar-C), 133.98, 132.46, 132.28, 132.03, 122.42, 122.36, 117.43, 114.46 (Ar-CH), 114.80 (CN), 68.42, 66.74 (OCH_2), 29.82, 27.98 (CH), 39.22, 37.26, 35.99, 31.92, 29.69, 29.66, 29.63, 29.59, 29.55, 29.35, 29.08, 25.97, 24.66 (CH_2), 22.70, 22.61, 19.65, 14.12 (CH_3). $C_{57}H_{65}NO_{10}$ (924.12); HRMS (m/z): $[M+Li]^+$ calcd. for $C_{57}H_{65}NO_{10}Li$ 930.4808, found 930.4764; Anal. Calc.: C, 74.08; H, 7.09; N, 1.52. Found: C, 73.81; H, 6.86; N, 1.36 %;

1.4 NMR Spectra

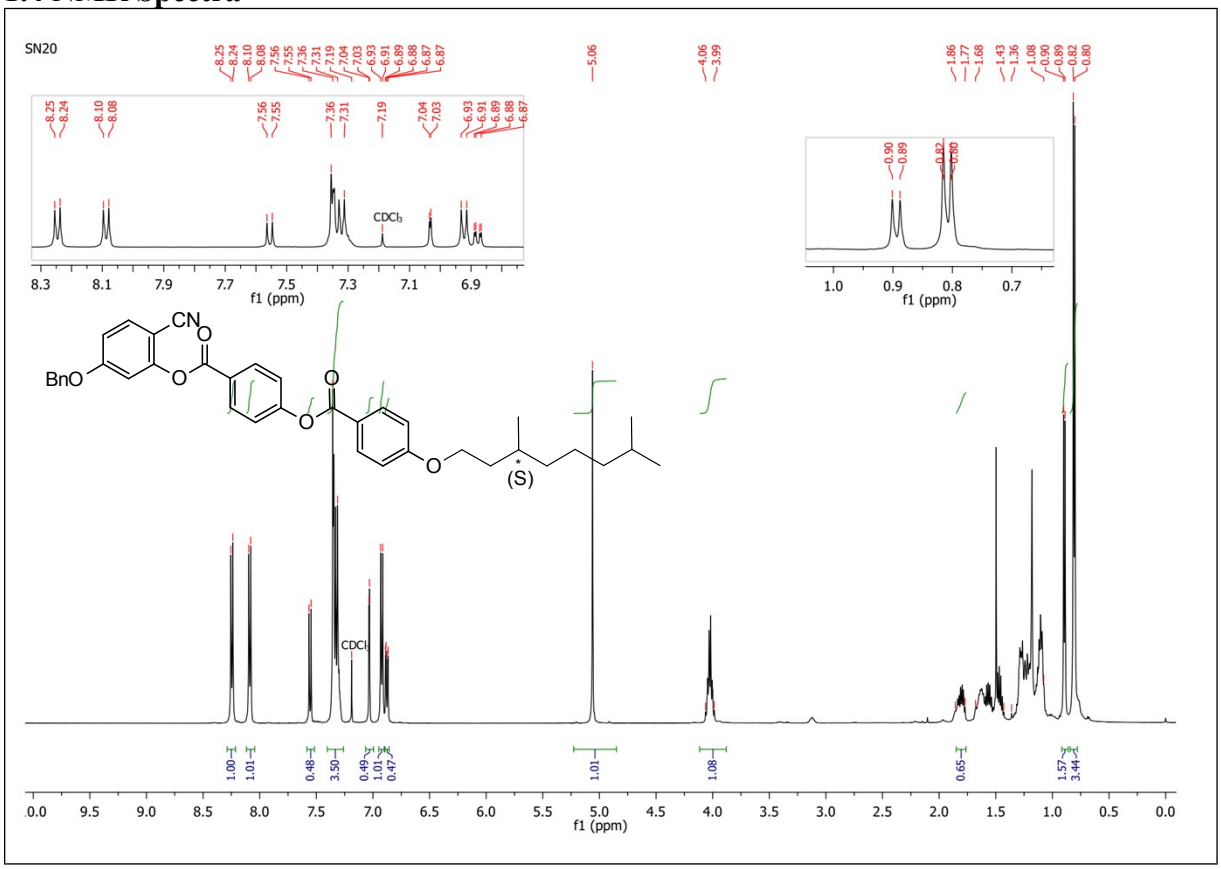


Figure S1. ^{1}H-NMR spectrum of compound (*S*)-**Bz-E** (500 MHz, $CDCl_3$).

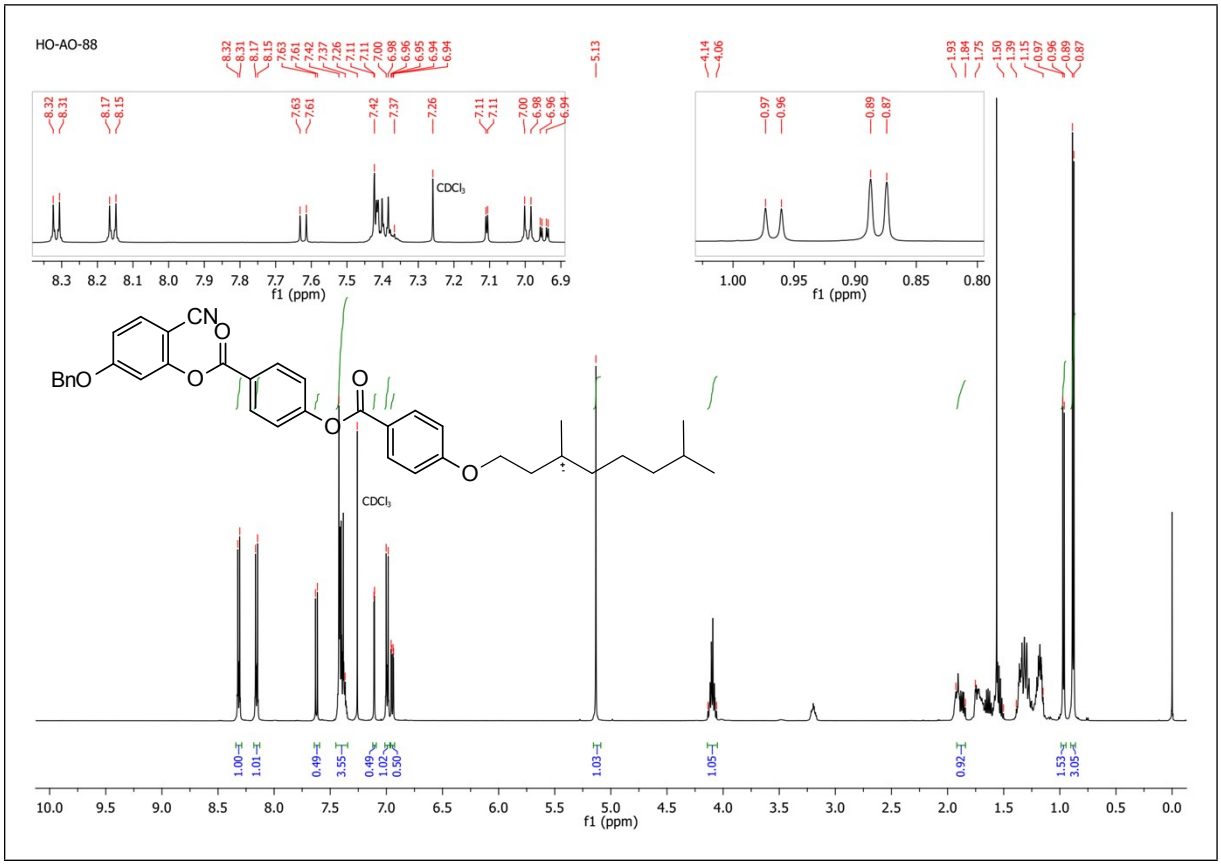


Figure S2. ^{1}H-NMR spectrum of compound *rac*-**Bz-E** (500 MHz, $CDCl_3$).

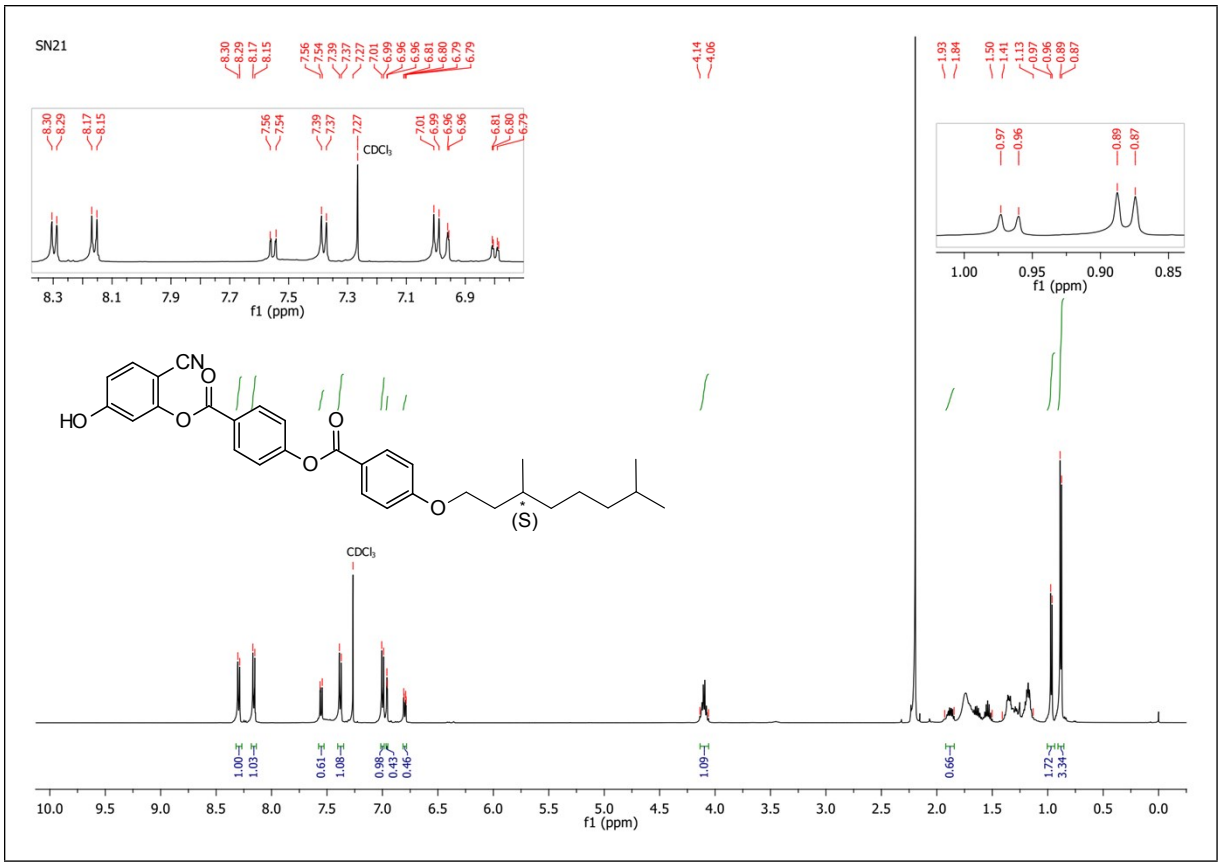


Figure S3. ^{1}H-NMR spectrum of compound (*S*)-**E** (500 MHz, $CDCl_3$).

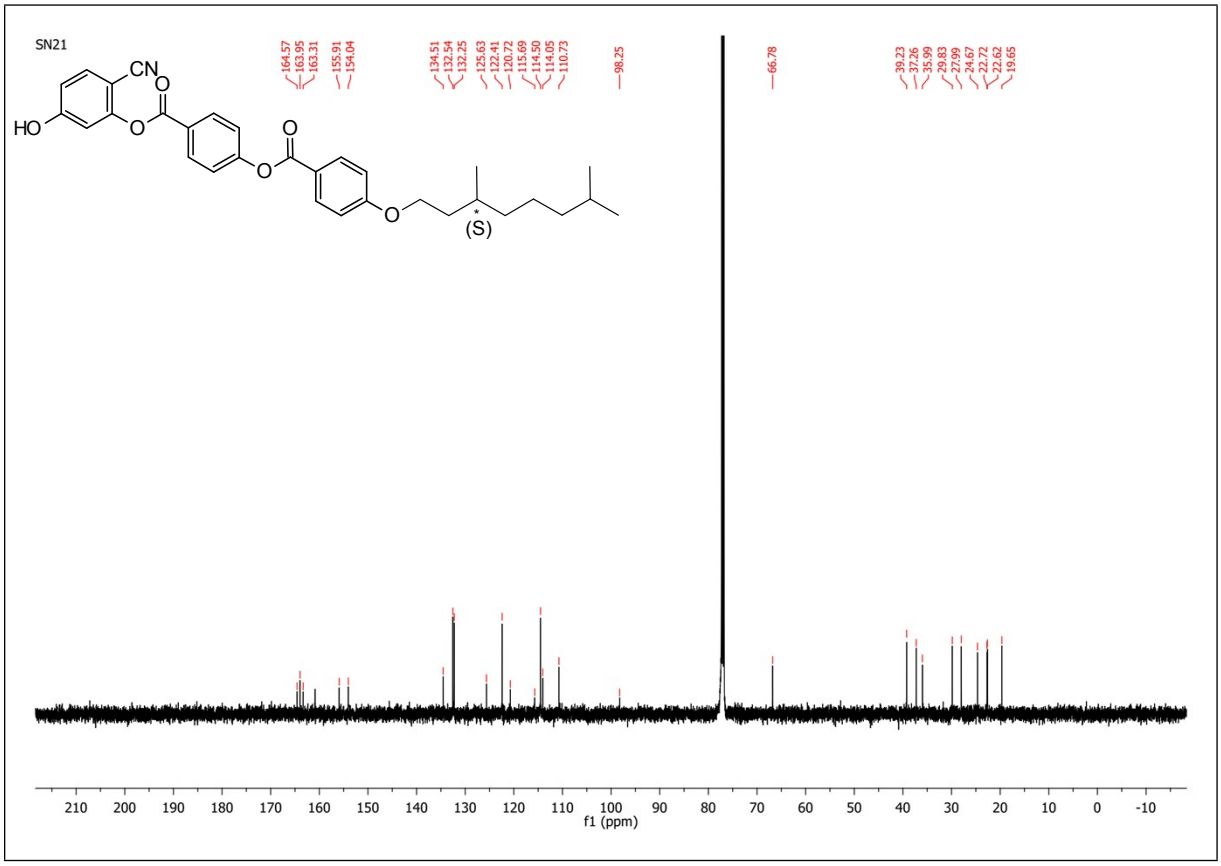


Figure S4. ^{13}C-NMR spectrum of compound (*S*)-**E** (125 MHz, $CDCl_3$).

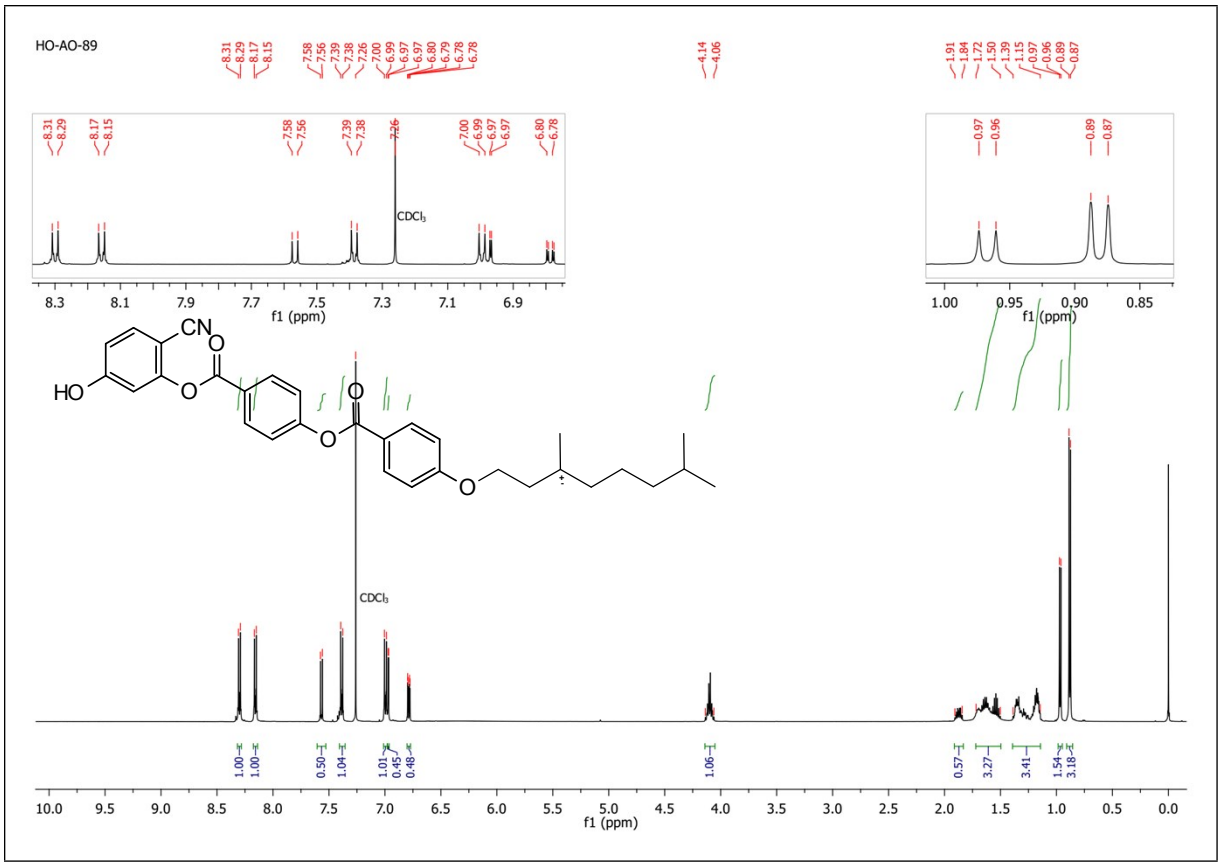


Figure S5. ^{1}H-NMR spectrum of compound *rac*-**E** (500 MHz, $CDCl_3$).

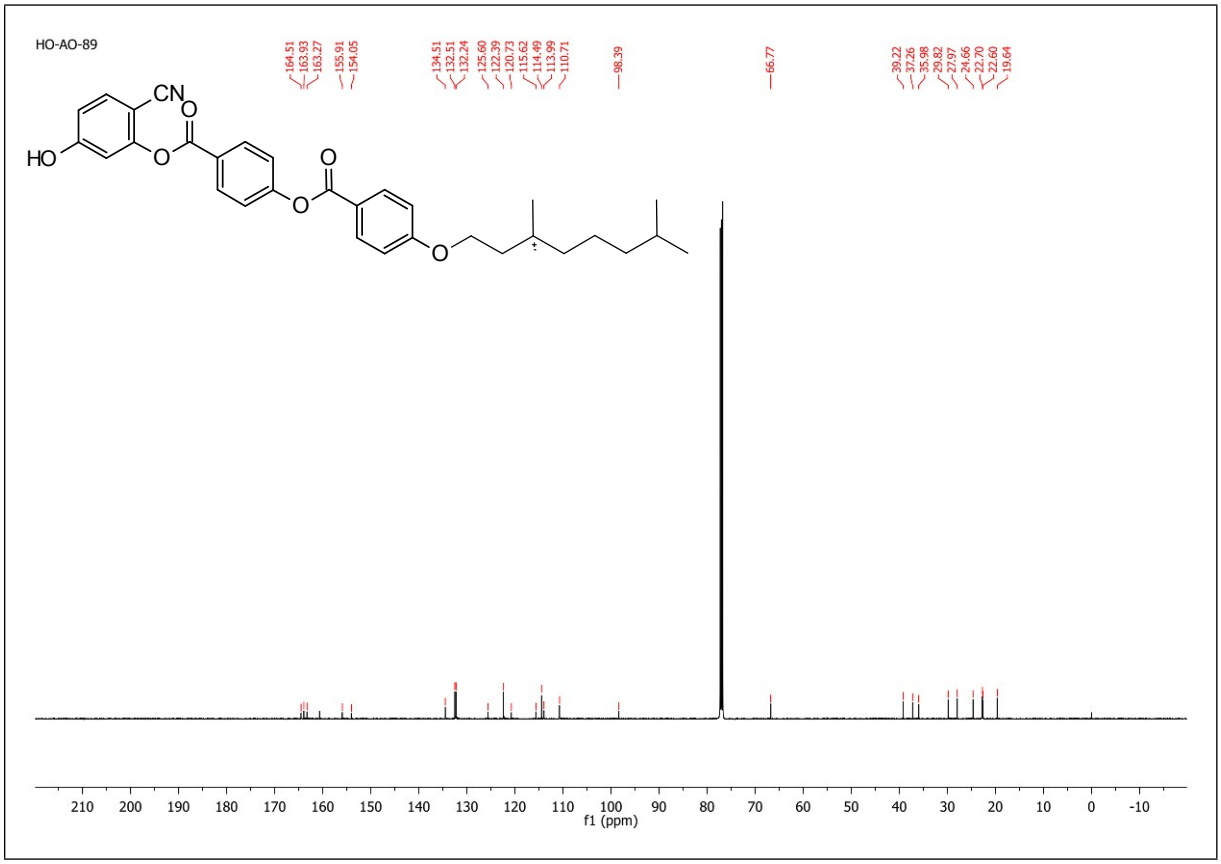


Figure S6. ^{13}C-NMR spectrum of compound *rac*-**E** (125 MHz, $CDCl_3$).

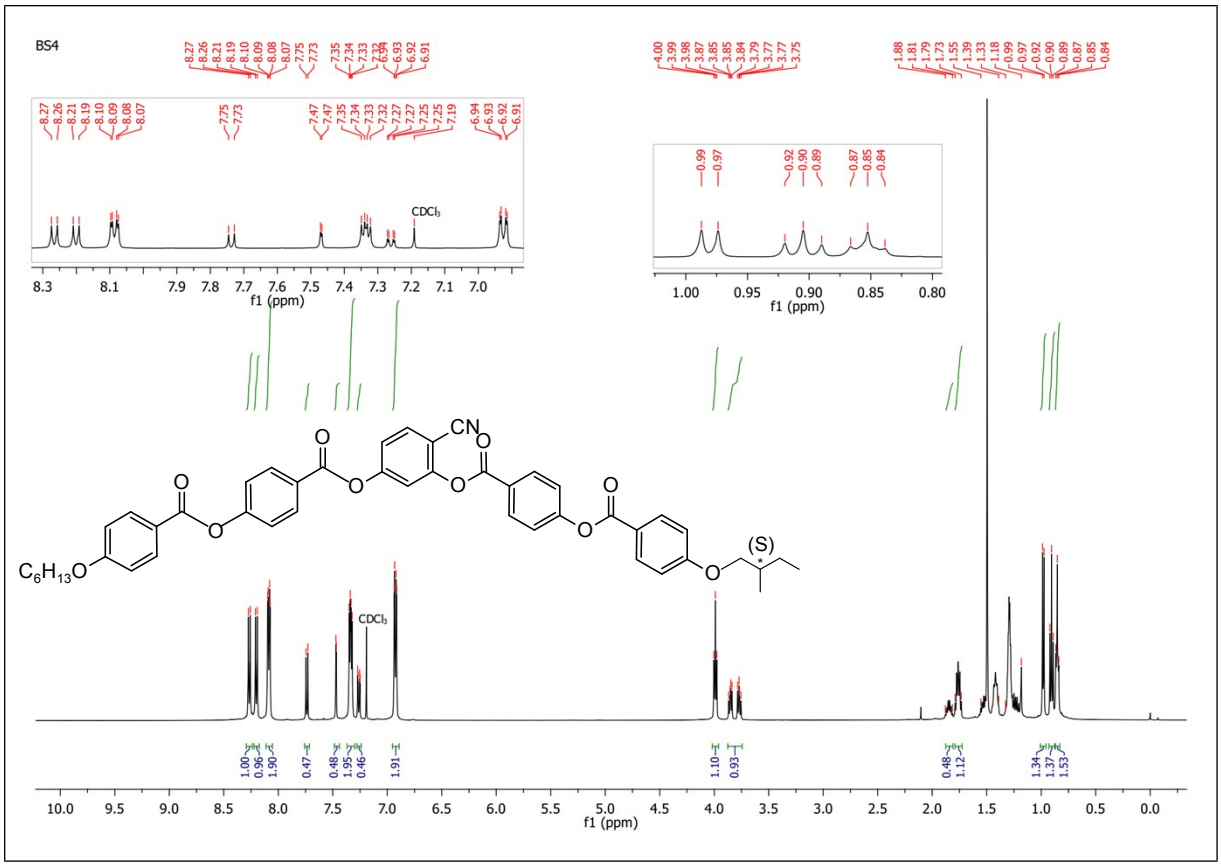


Figure S7. ^{1}H-NMR spectrum of compound *(S)*-**1/6** (500 MHz, $CDCl_3$).

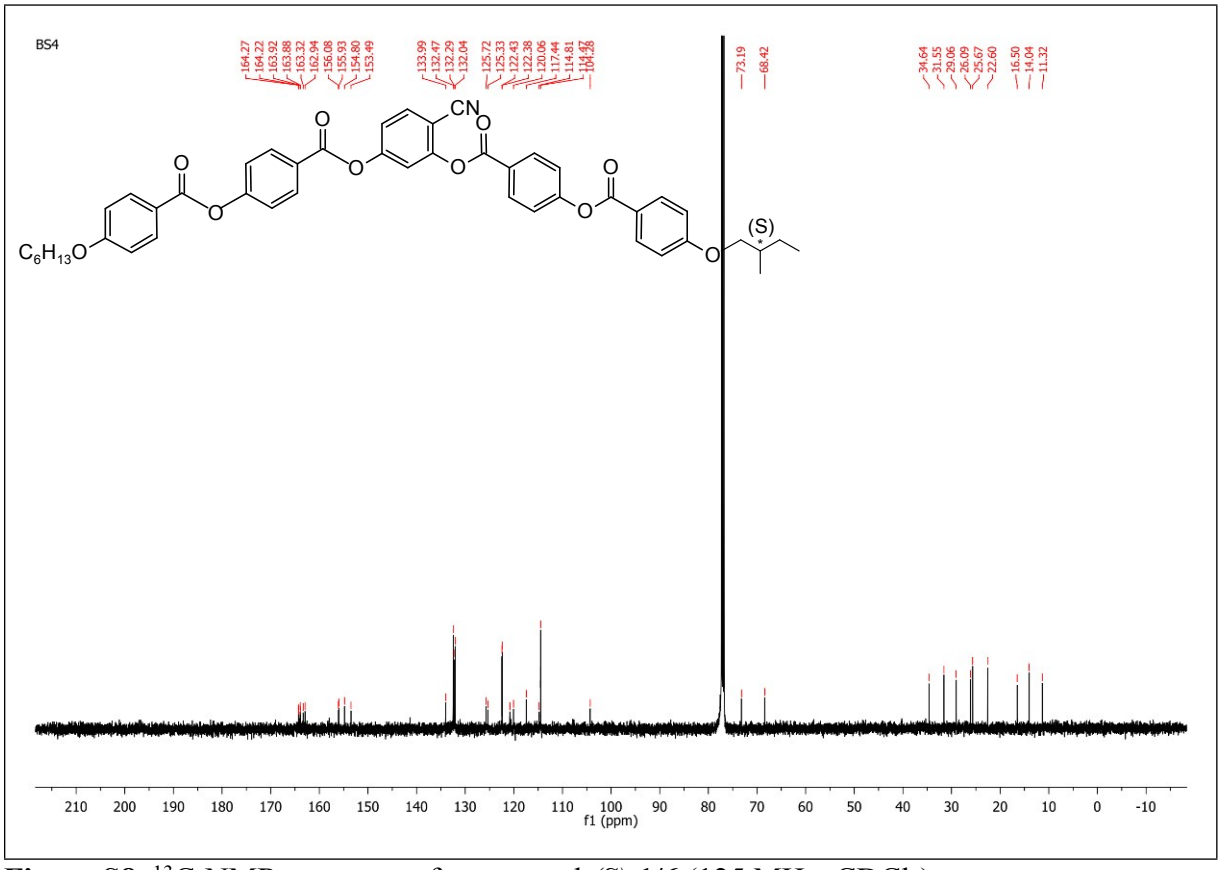


Figure S8. ^{13}C-NMR spectrum of compound *(S)*-**1/6** (125 MHz, $CDCl_3$).

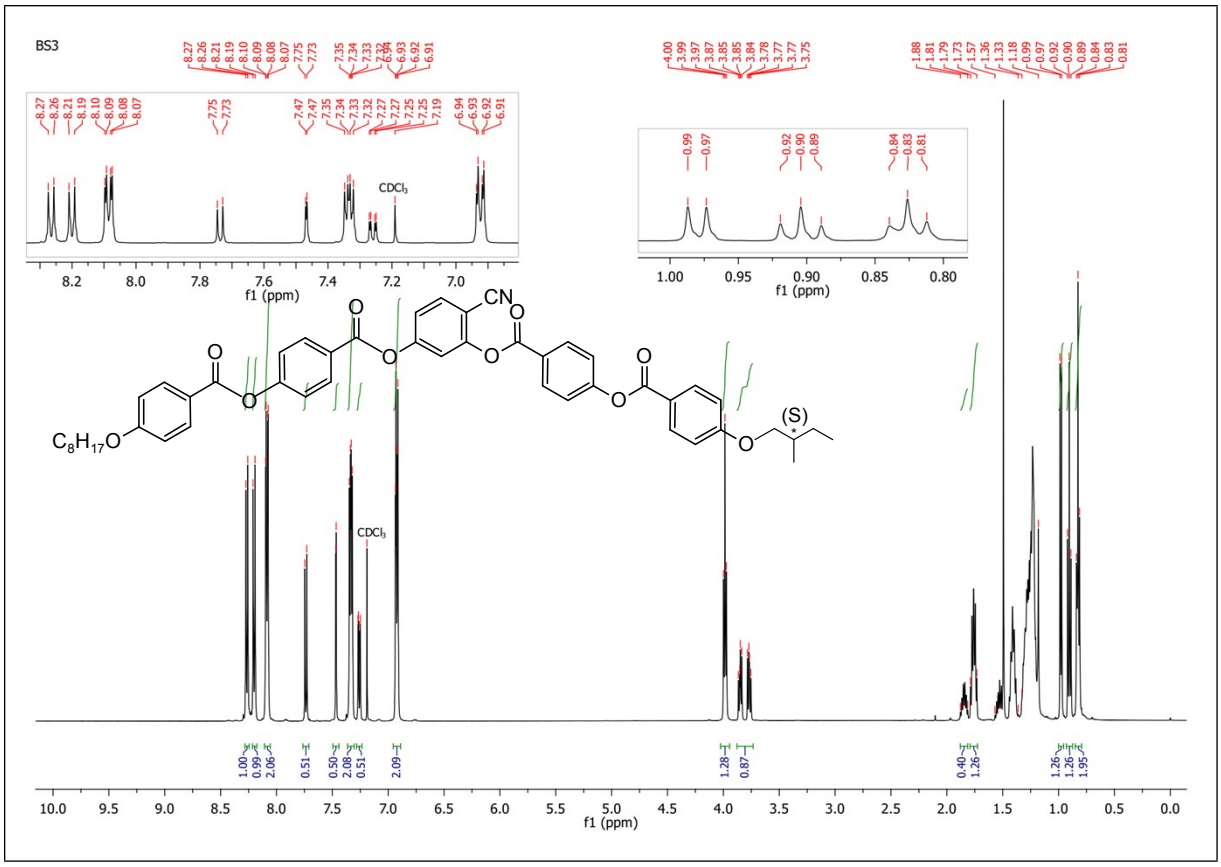


Figure S9. ^{1}H-NMR spectrum of compound *(S)*-**1/8** (500 MHz, $CDCl_3$).

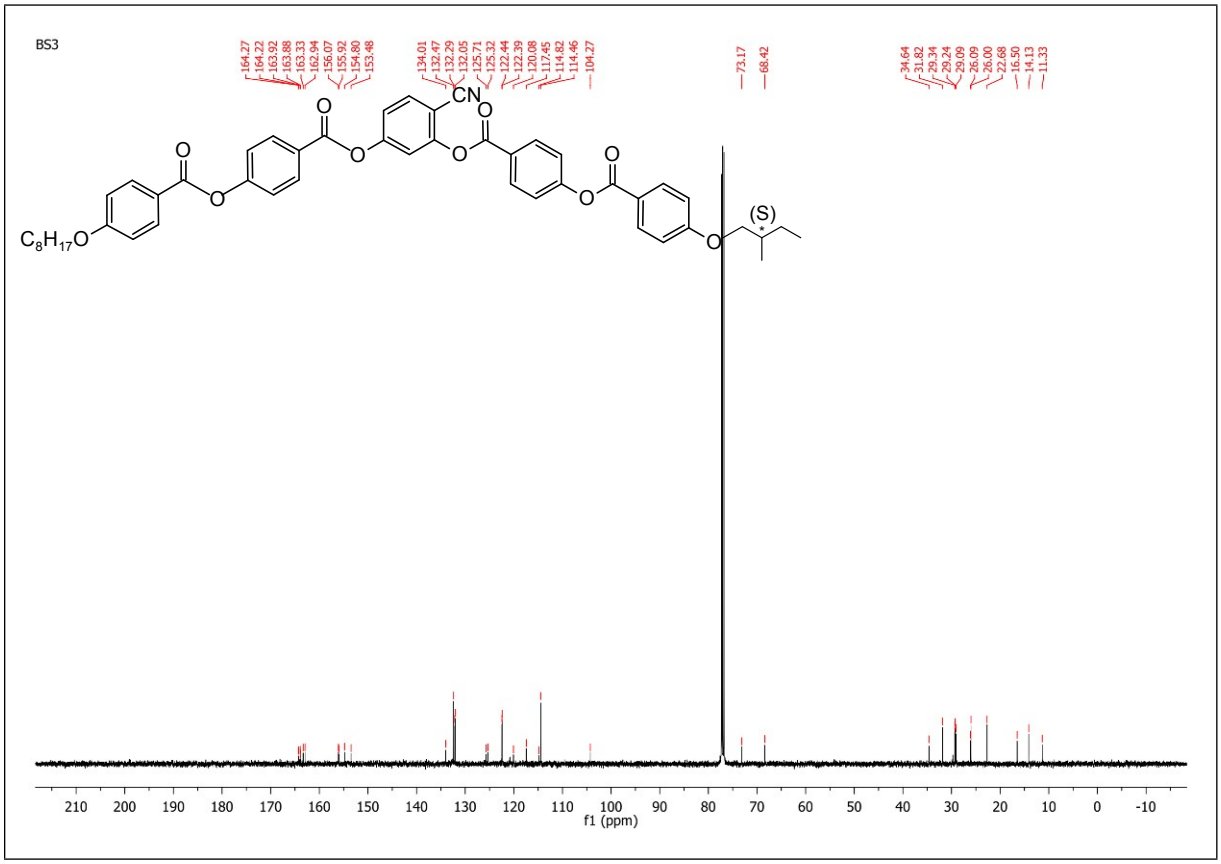


Figure S10. ^{13}C-NMR spectrum of compound *(S)*-**1/8** (125 MHz, $CDCl_3$).

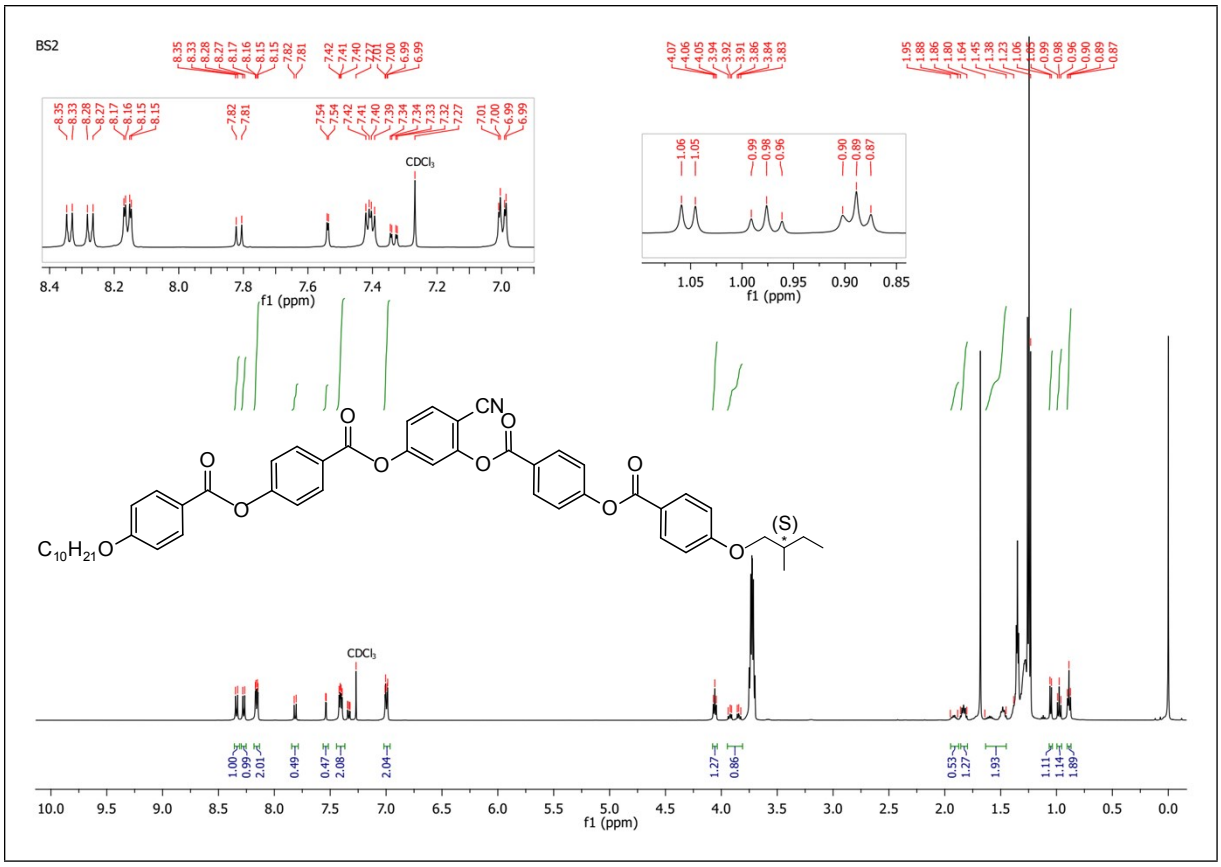


Figure S11. ^{1}H-NMR spectrum of compound *(S)*-**1/10** (500 MHz, $CDCl_3$).

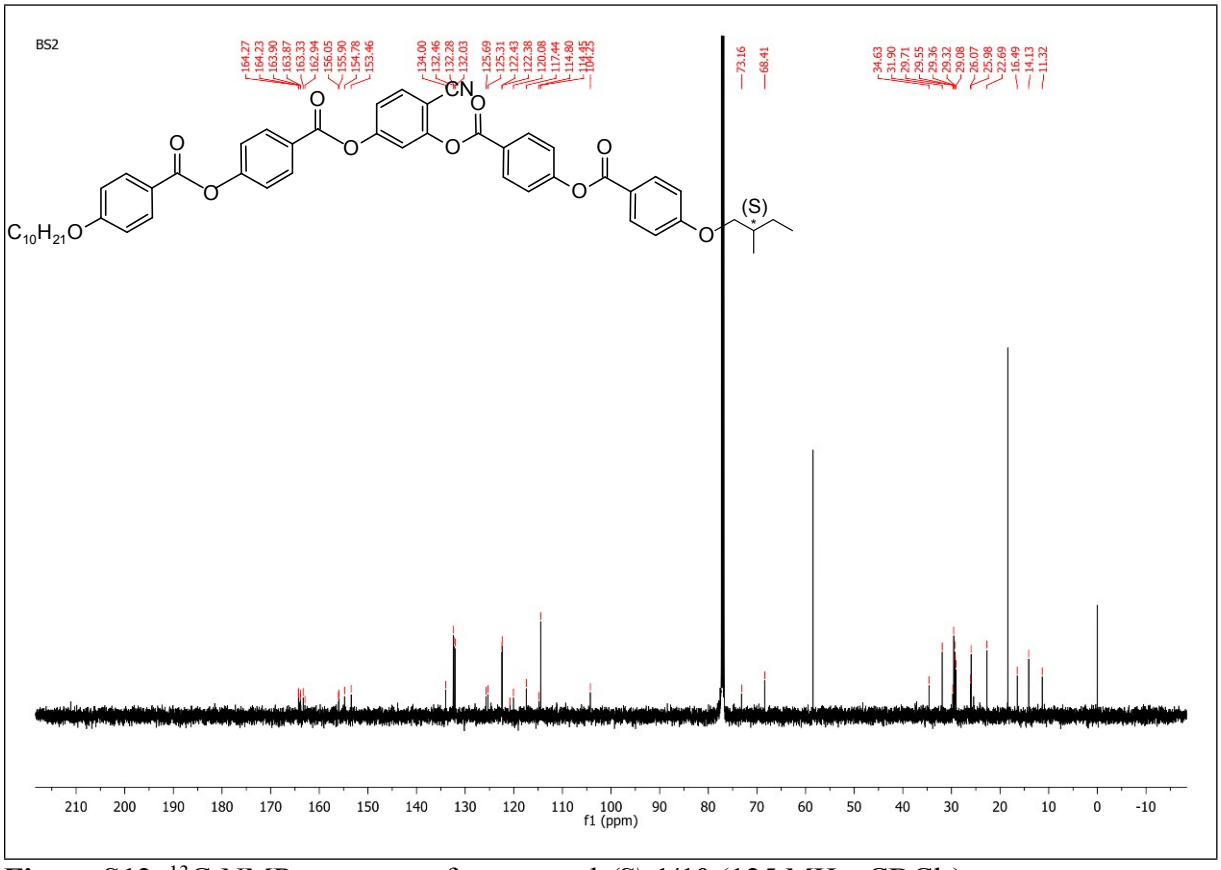


Figure S12. ^{13}C-NMR spectrum of compound *(S)*-**1/10** (125 MHz, $CDCl_3$).

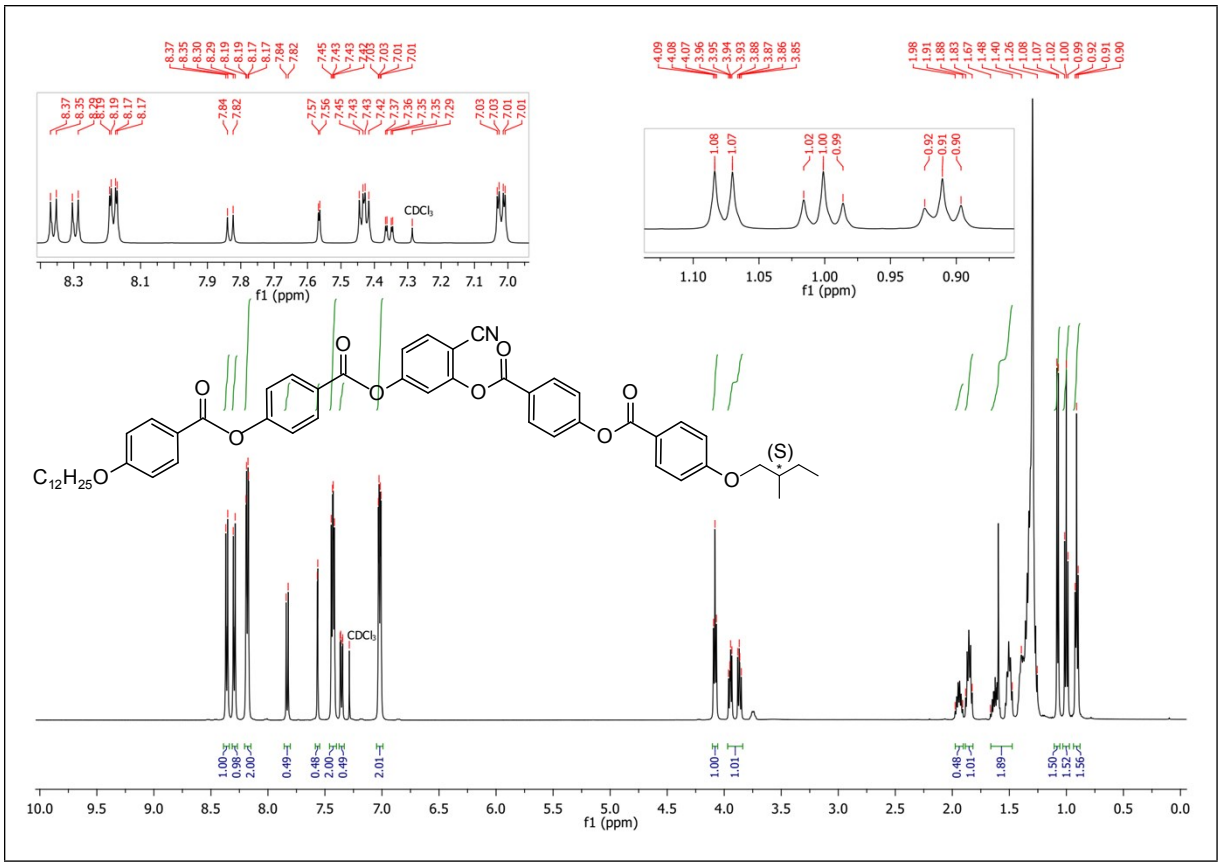


Figure S13. ^{1}H-NMR spectrum of compound *(S)*-**1/12** (500 MHz, $CDCl_3$).

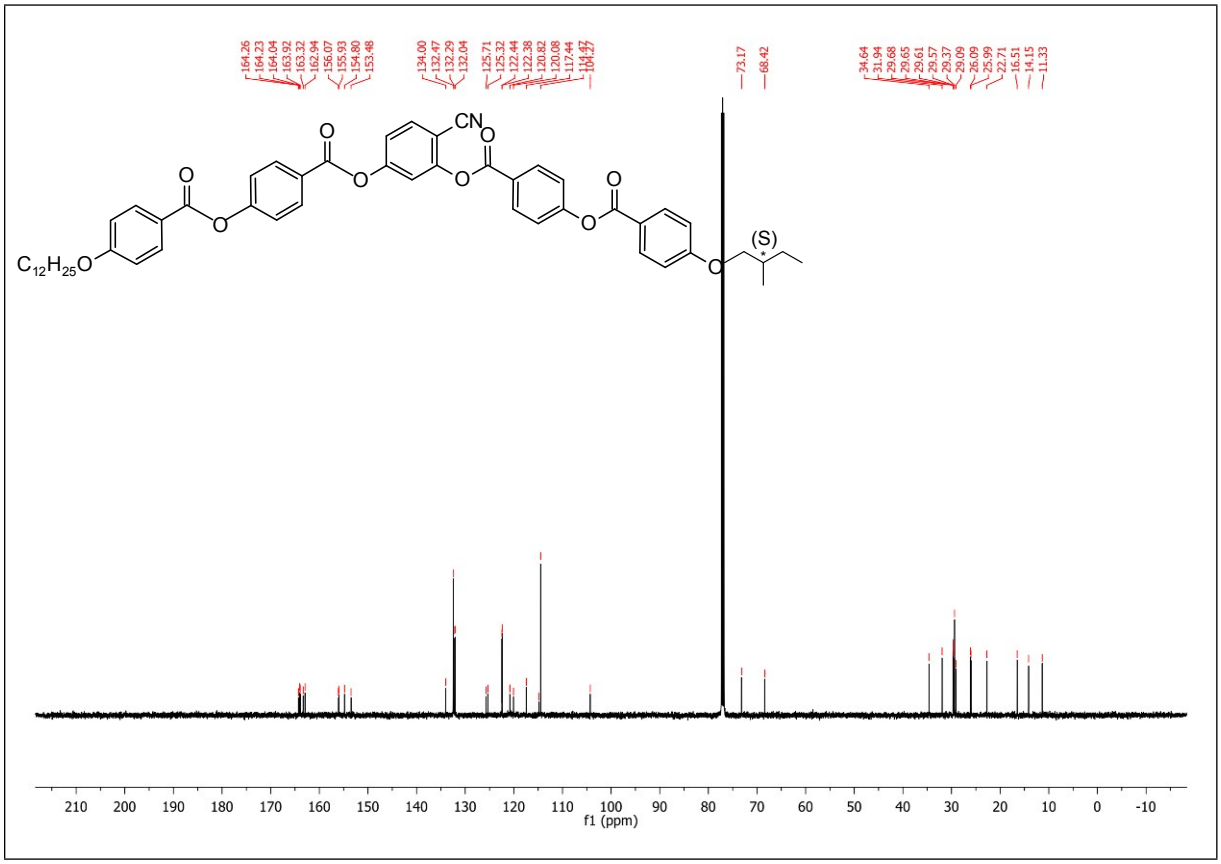


Figure S14. ^{13}C-NMR spectrum of compound *(S)*-**1/12** (125 MHz, $CDCl_3$).

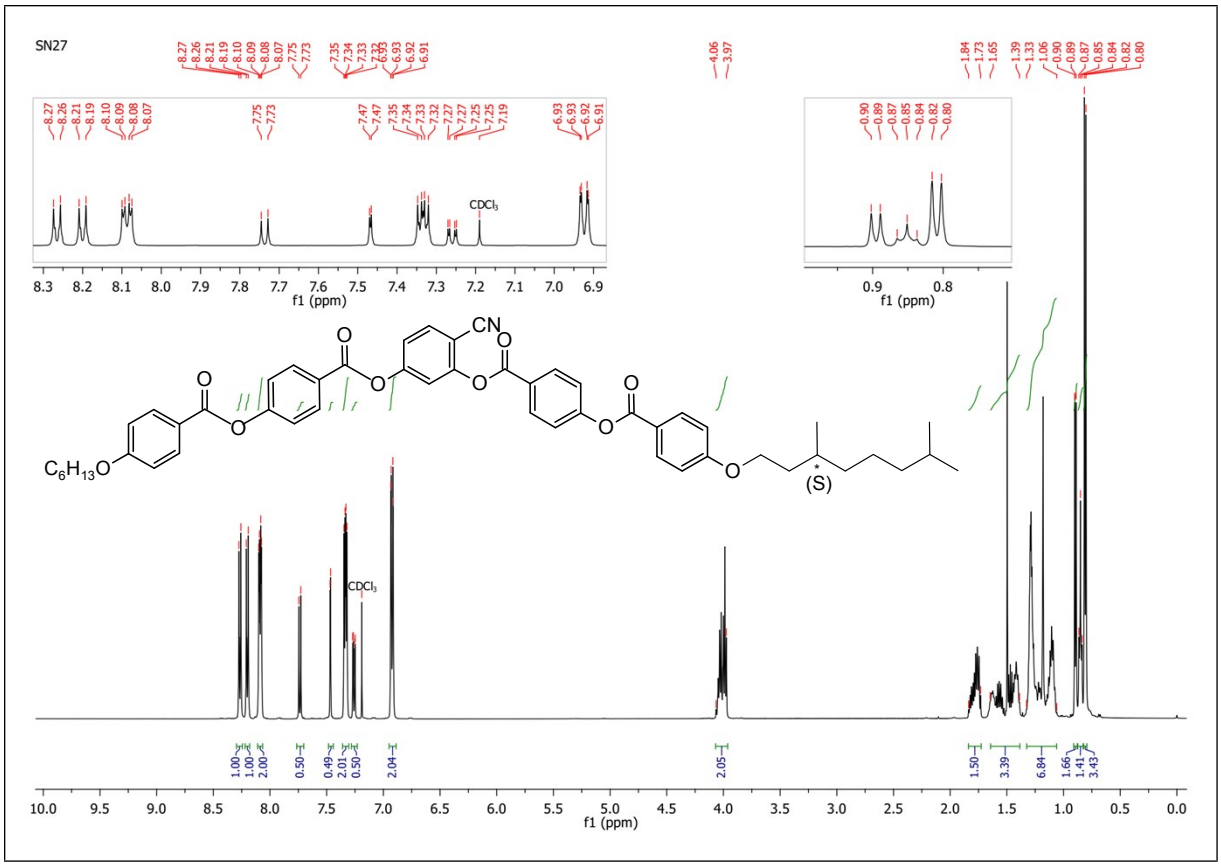


Figure S15. ^{1}H-NMR spectrum of compound *(S)*-**2/6** (500 MHz, $CDCl_3$).

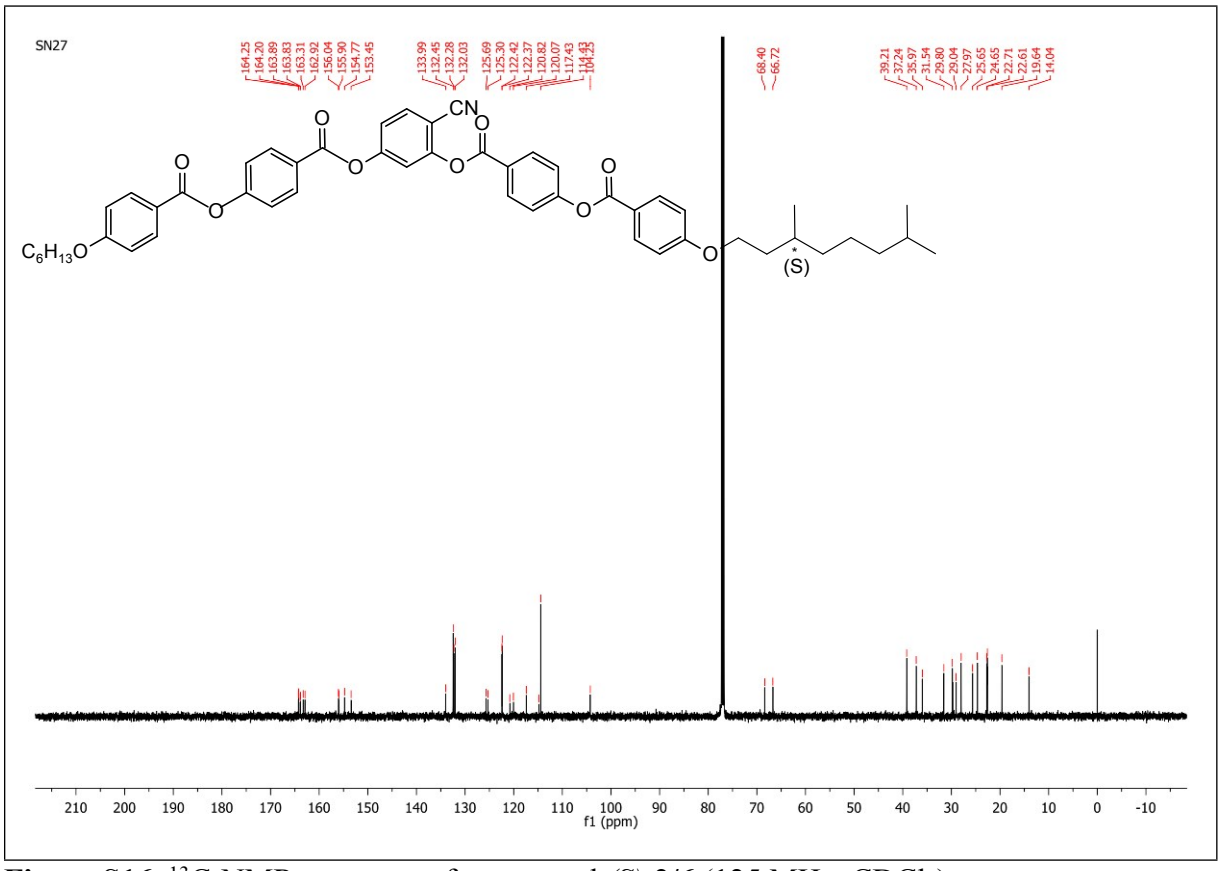


Figure S16. ^{13}C-NMR spectrum of compound *(S)*-**2/6** (125 MHz, $CDCl_3$).

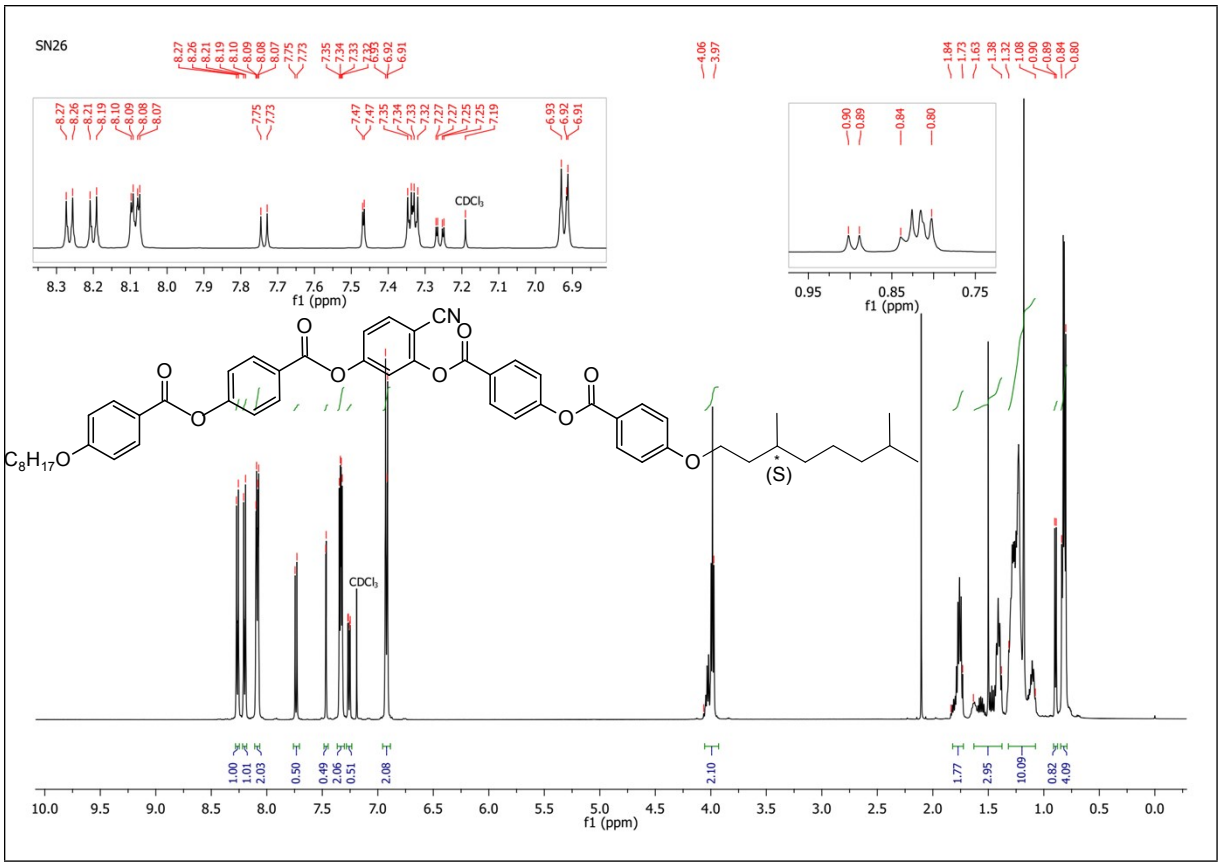


Figure S17. ^{1}H-NMR spectrum of compound *(S)*-**2**/**8** (500 MHz, $CDCl_3$).

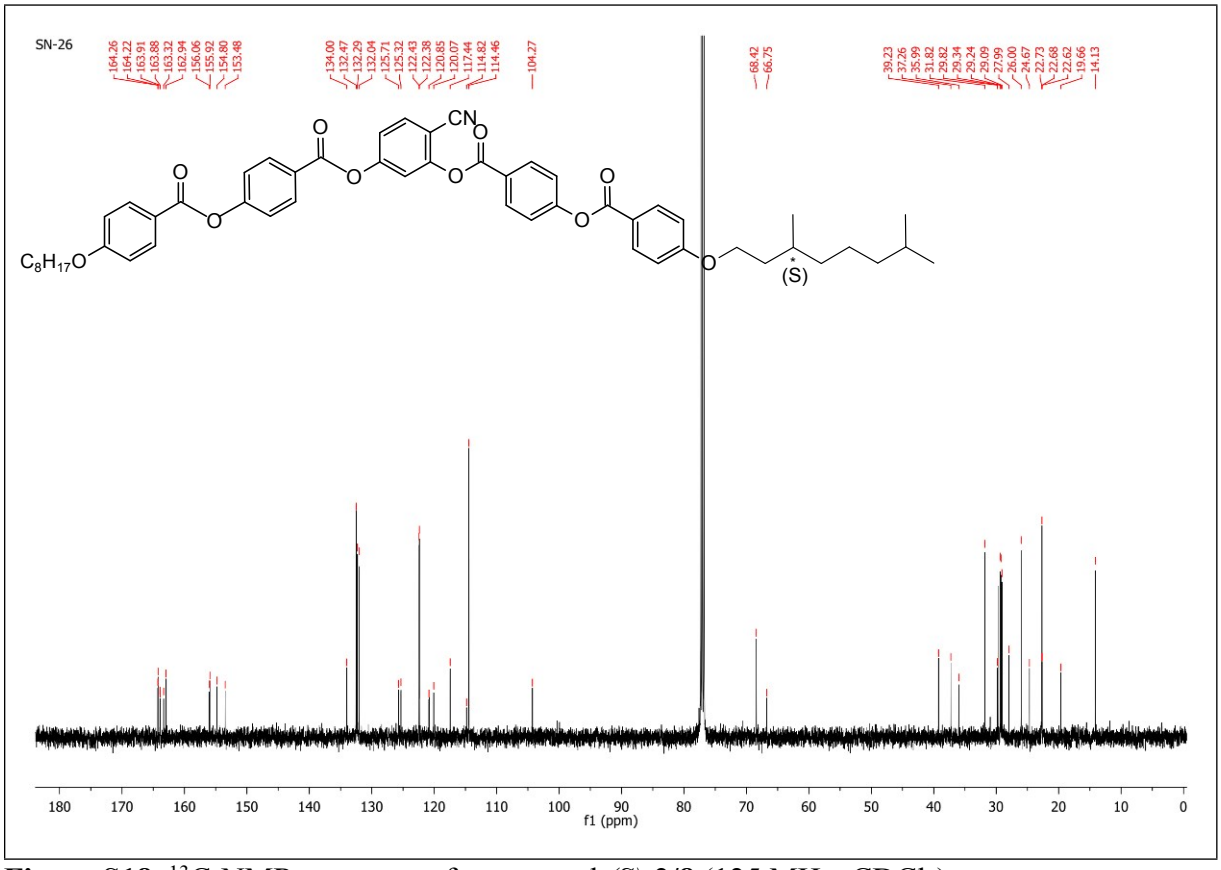


Figure S18. ^{13}C-NMR spectrum of compound *(S)*-**2**/**8** (125 MHz, $CDCl_3$).

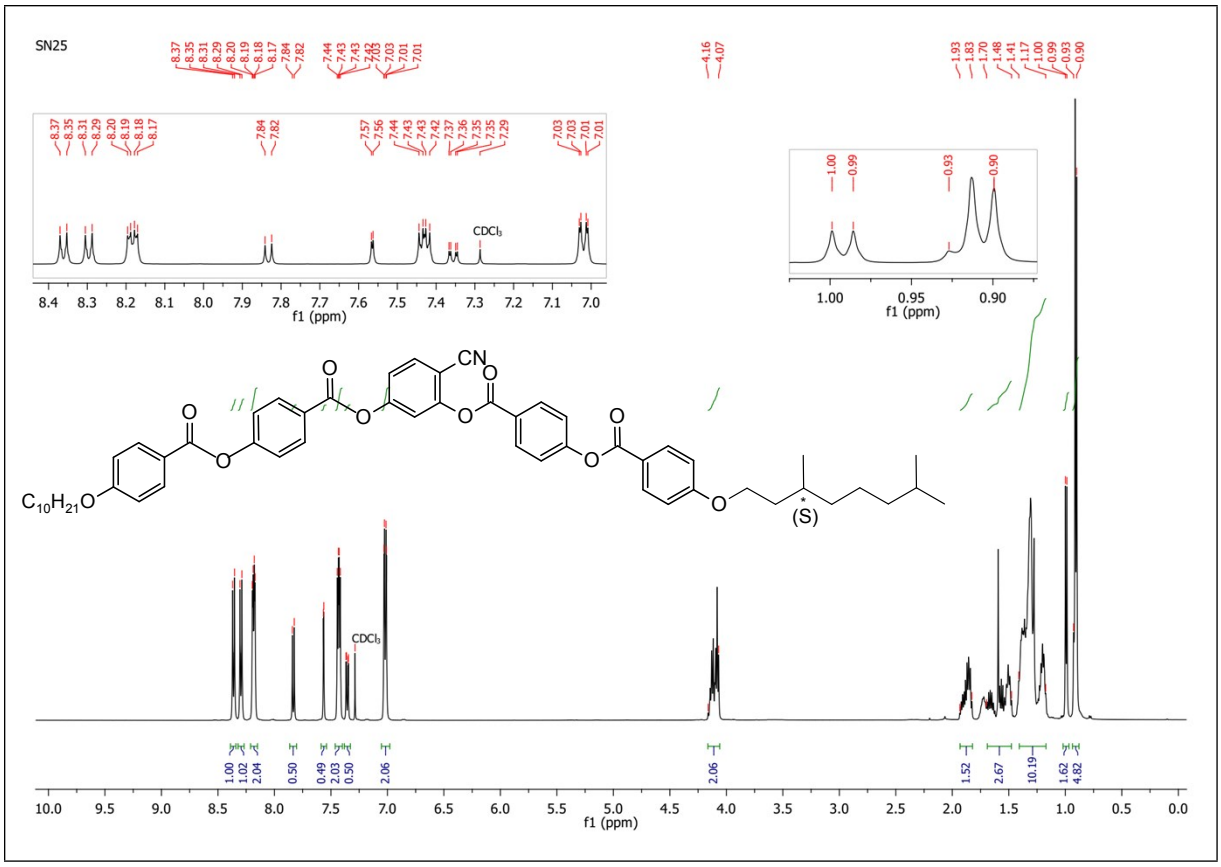


Figure S19. ^{1}H-NMR spectrum of compound *(S)*-**2**/**10** (500 MHz, $CDCl_3$).

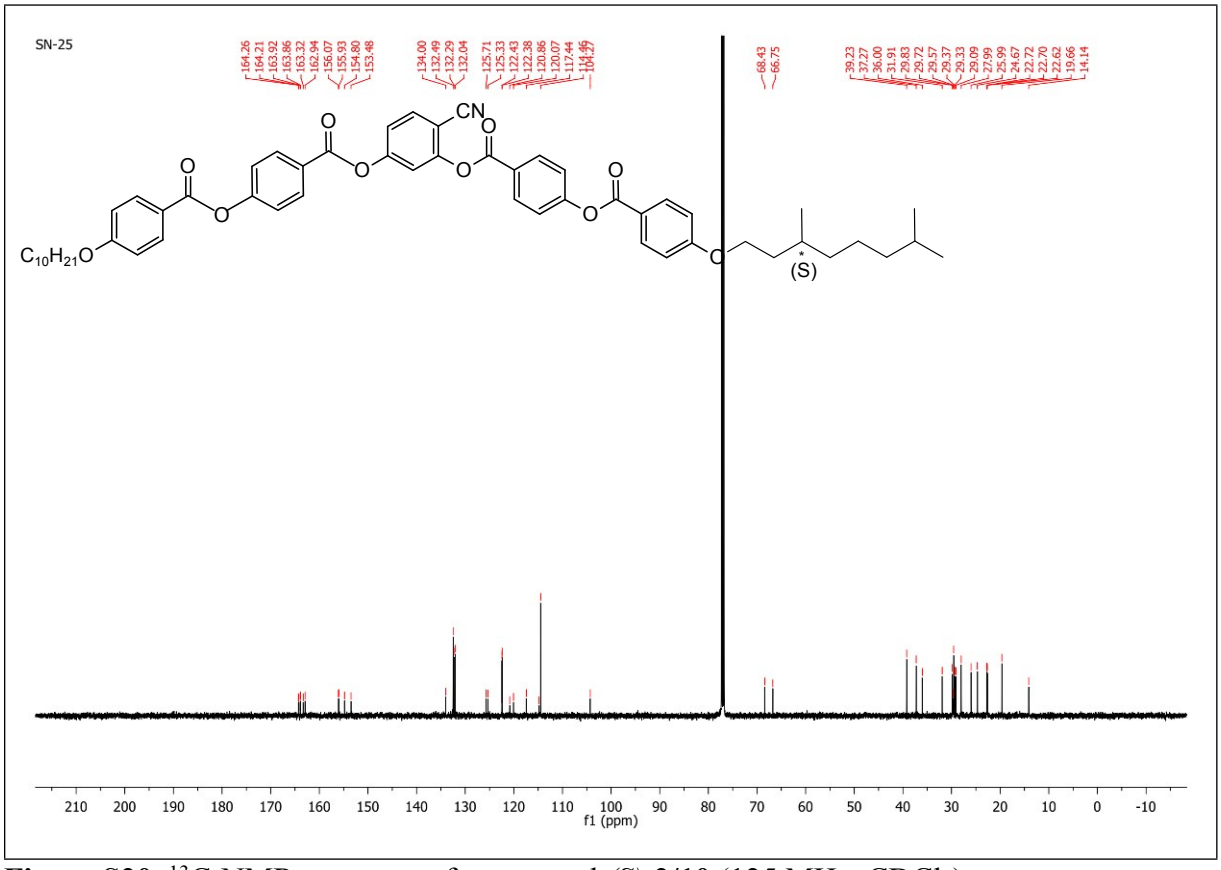


Figure S20. ^{13}C-NMR spectrum of compound *(S)*-**2**/**10** (125 MHz, $CDCl_3$).

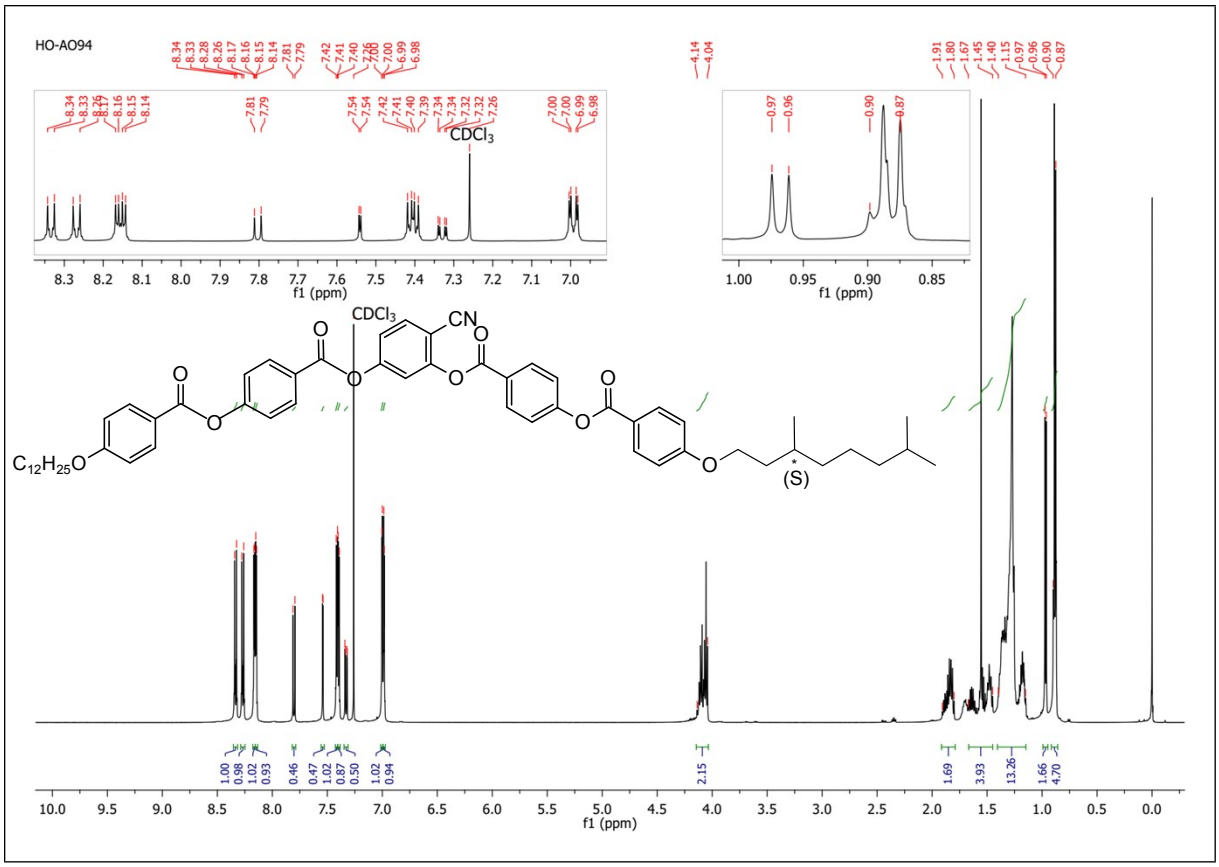


Figure S21. ^{1}H-NMR spectrum of compound *(S)*-**2**/**12** (500 MHz, $CDCl_3$).

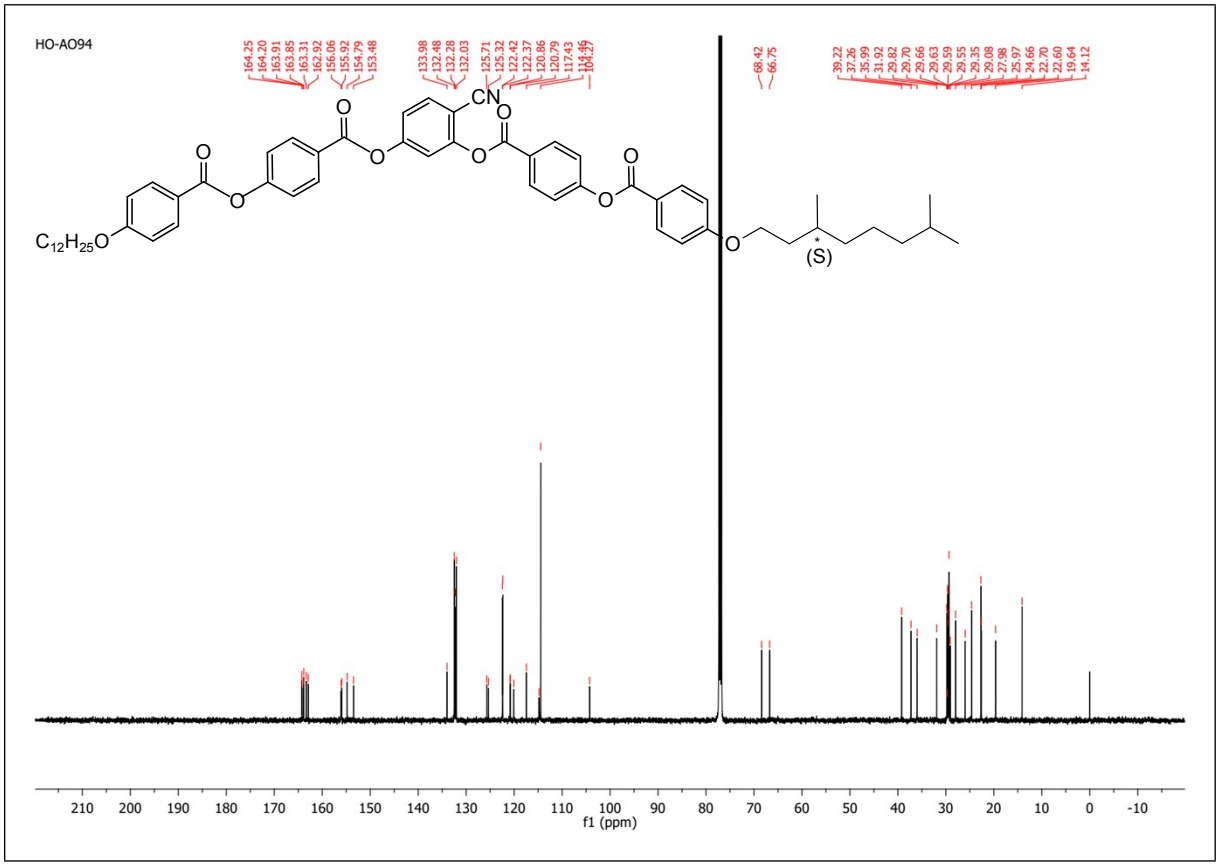


Figure S22. ^{13}C-NMR spectrum of compound *(S)*-**2**/**12** (125 MHz, $CDCl_3$).

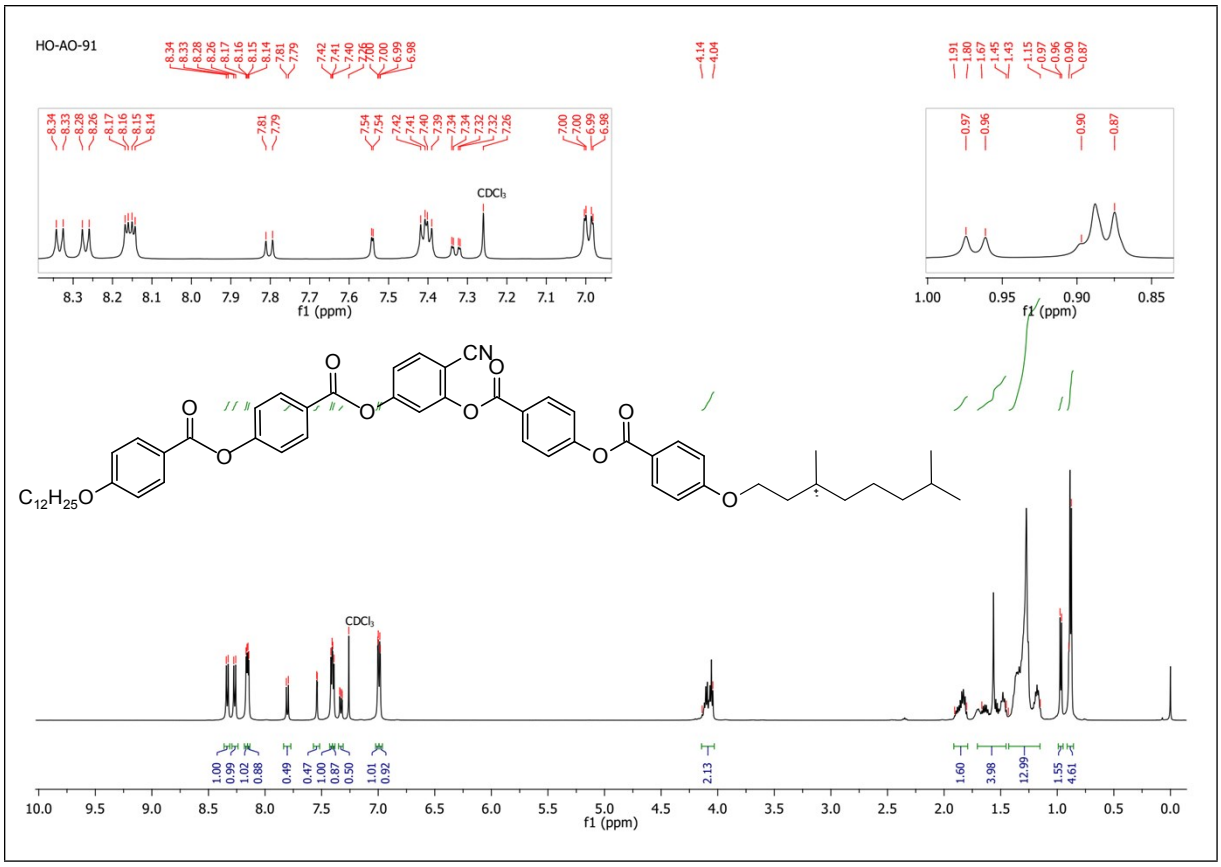


Figure S23. ^{1}H-NMR spectrum of compound *rac*-**2/12** (500 MHz, $CDCl_3$).

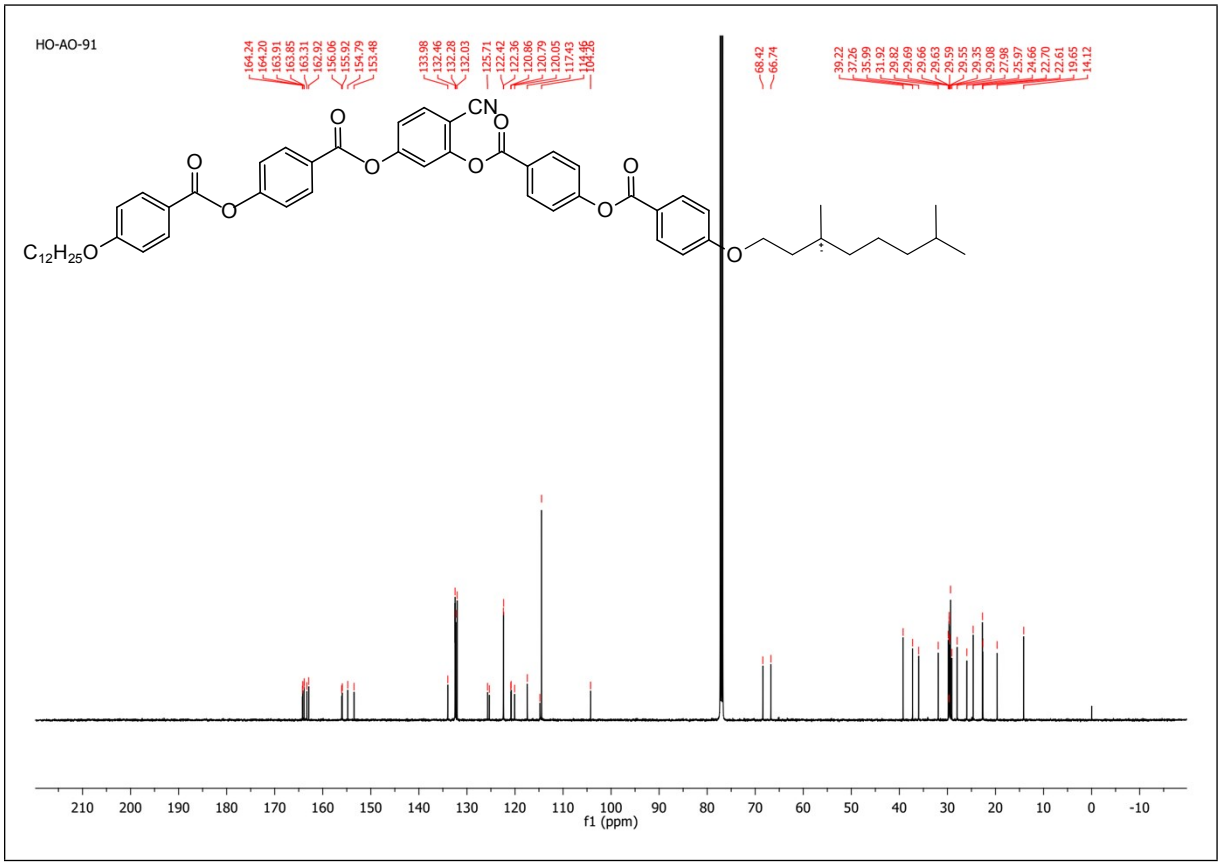


Figure S24. ^{13}C-NMR spectrum of compound *rac*-**2/12** (125 MHz, $CDCl_3$).

2. Additional Data

2.1 Molecular models

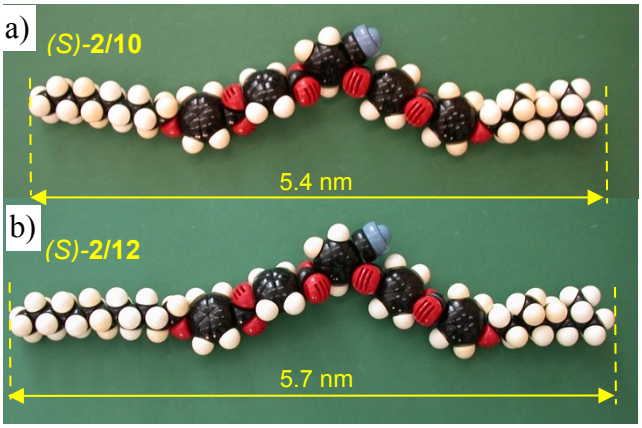


Figure S25. Space filling (CPK) models of compounds a) **2/10** and b) **2/12** with molecular lengths L_{mol}.

2.2 Additional XRD-data

Table S1. XRD data and calculated *d*-values of the mesophases of compound *(S)*-**2/10**.[a]

T/°C	Phase	*B* = 1 T				*B* = 0 T			
		2 θ/°	θ/°	*d*/nm	ζ / nm	2 θ/°	θ/°	*d*/nm	ζ / nm
90	N_{CybC}*	2.122	1.061	4.16	12	2.156	1.078	4.10	12
		19.610	9.805	0.45					
80	N_{CybC}*	2.054	1.027	4.30	17	2.050	1.025	4.31	17
		19.770	9.885	0.45					
70	N_{CybC}*	2.027	1.014	4.36	22	2.022	1.011	4.37	23
		19.770	9.885	0.45					
60	N_{CybC}*	2.096	1.048	4.22	34	2.081	1.040	4.25	45
		19.840	9.920	0.45					
50	SmC_s*	2.455	1.228	3.60	50	2.466	1.233	3.58	80
		19.870	9.935	0.45					

[a] ζ – domain size of the cybotactic SmC* clusters in the N* phase, determined by the Scherrer equation $\zeta = K \cdot \lambda / (\Delta(2\theta) \cdot \cos(\theta))$, with K = shape factor (~ 1), λ = wavelength of CuKα radiation (0.154 nm), $\Delta(2\theta)$·- full width at half maximum of the small angle peak.[S3]

Table S2. XRD data of compound (*S*)-**2/12** with and without application of a magnetic field.

T/°C	*B* = 1 T				*B* = 0 T			
	2 θ/°	θ/°	*d*/nm	*d*/nm	2 θ/°	θ/°	*d*/nm	*d*/nm
120	2.514	1.257	3.52	**3.52**	2.609	1.305	3.39	**3.39**
	18.997	9.499	0.467	**0.469**	18.851	9.425	0.471	**0.471**
	18.892	9.446	0.470		18.823	9.411	0.471	
110	2.457	1.228	3.60	**3.60**	2.490	1.245	3.55	**3.55**
	19.050	9.525	0.466	**0.467**	18.963	9.481	0.468	**0.469**
	18.983	9.491	0.468		18.915	9.458	0.469	
100	2.145	1.073	4.12	**4.12**	2.033	1.016	4.35	**4.35**
	19.177	9.589	0.463	**0.463**	19.095	9.547	0.465	**0.465**
	19.194	9.597	0.462		19.092	9.546	0.465	
90	2.056	1.028	4.30	**4.30**	1.940	0.970	4.55	**4.55**
	19.257	9.628	0.461	**0.460**	19.209	9.604	0.462	**0.462**
	19.336	9.668	0.459		19.222	9.611	0.462	
80	2.027	1.014	4.36	**4.36**	1.921	0.961	4.60	**4.60**
	19.413	9.707	0.457	**0.458**	19.357	9.678	0.459	**0.460**
	19.391	9.696	0.458		19.309	9.655	0.460	
70	2.112	1.056	4.18	**4.18**	1.921	0.960	4.60	**4.60**
	19.478	9.739	0.456	**0.457**	19.435	9.718	0.457	**0.457**
	19.415	9.708	0.457		19.436	9.718	0.457	
60	2.213	1.106	3.99	**3.99**	1.916	0.958	4.61	**4.61**
	19.559	9.779	0.454	**0.455**	19.487	9.744	0.456	**0.455**
	19.505	9.752	0.455		19.544	9.772	0.454	

Table S3. XRD data of compound *rac*-**2/12** with and without application of a magnetic field.

T/°C	*B* = 1 T				*B* = 0 T			
	2*θ*/°	*θ*/°	*d*/nm	*d*/nm	2*θ*/°	*θ*/°	*d*/nm	*d*/nm
120	2.469	1.235	3.58	**3.58**	2.469	1.234	3.58	**3.58**
	18.983	9.492	0.467	**0.468**	19.101	9.551	0.465	**0.470**
	18.928	9.464	0.469		18.719	9.359	0.474	
110	2.375	1.188	3.72	**3.72**	2.404	1.202	3.68	**3.68**
	19.063	9.532	0.466	**0.466**	19.267	9.633	0.461	**0.465**
	19.056	9.528	0.466		18.876	9.438	0.470	
100	2.019	1.010	4.39	**4.39**	2.228	1.114	3.97	**3.97**
	19.124	9.562	0.464	**0.465**	19.328	9.664	0.459	**0.463**
	19.105	9.552	0.465		19.036	9.518	0.466	
90	1.960	0.980	4.50	**4.50**	2.131	1.066	4.15	**4.15**
	19.190	9.595	0.462	**0.462**	19.435	9.718	0.457	**0.461**
	19.183	9.591	0.463		19.136	9.568	0.464	
80	2.042	1.021	4.33	**4.33**	2.107	1.054	4.19	**4.19**
	19.259	9.630	0.461	**0.461**	19.494	9.747	0.455	**0.459**
	19.315	9.657	0.460		19.223	9.612	0.462	
70	2.060	1.030	4.29	**4.29**	2.206	1.103	4.00	**4.00**
	19.386	9.693	0.458	**0.458**	19.606	9.803	0.453	**0.456**
	19.419	9.709	0.457		19.332	9.666	0.459	
60	2.180	1.090	4.05	**4.05**	2.334	1.167	3.79	**3.79**
	19.484	9.742	0.456	**0.456**	19.674	9.837	0.451	**0.454**
	19.508	9.754	0.455		19.434	9.717	0.457	
50	2.312	1.156	3.82	**3.82**	2.425	1.213	3.64	**3.64**
	19.591	9.795	0.453	**0.453**	19.799	9.900	0.448	**0.451**
	19.628	9.814	0.452		19.534	9.767	0.454	

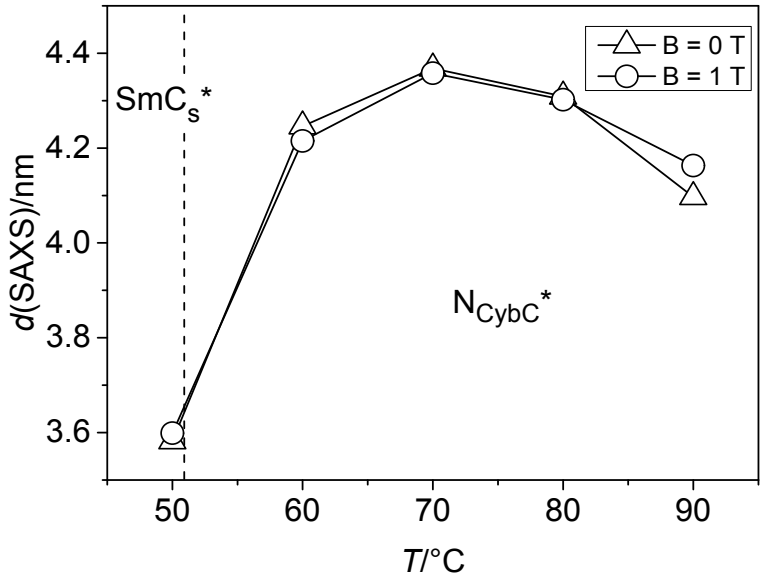


Figure S26. Influence of magnetic field on the SAXS *d*-spacing in the N* and SmC_S* phases of compound *(S)*-**1/10**.

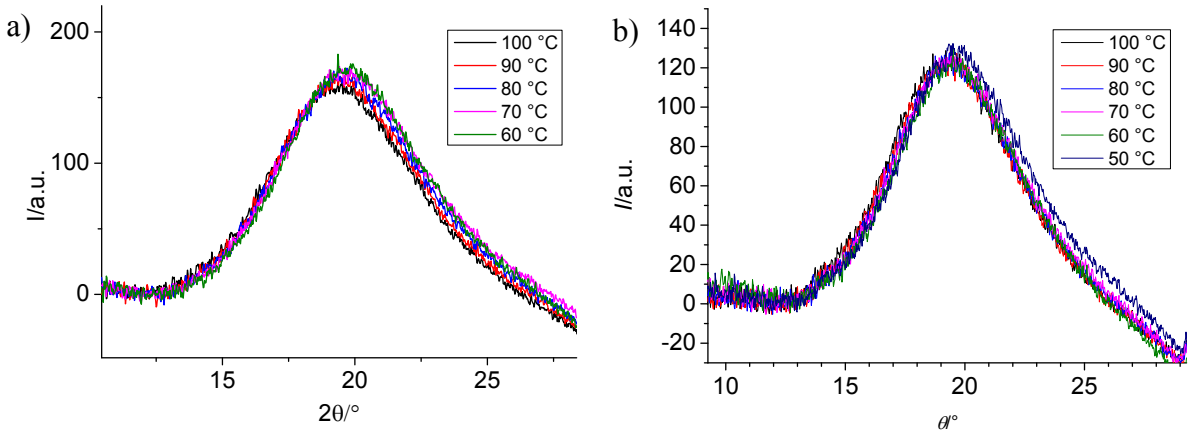
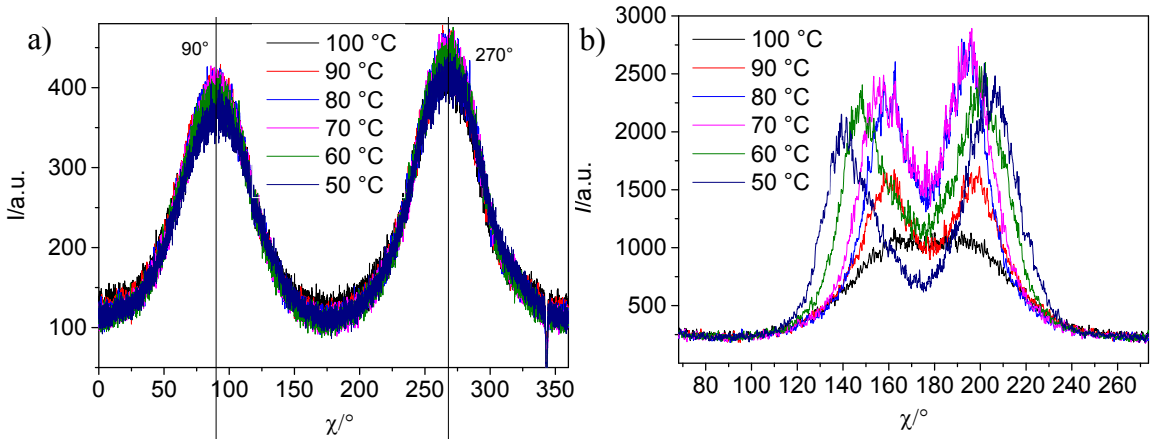


Figure S27. 2θ scans of WAXS region a) of (*S*)-**2/12** and b) of *rac*-**2/12**.



T/°C	Maximum 1 /°	Maximum 2 /°	Tilt/°	LC phase
100	160.1	197.8	19	N_{cybC}
90	160.2	197.1	19	SmC_s
80	161.5	193.1	16	SmC_s
70	159.0	194.2	18	SmC_s
60	149.9	199.1	25	SmC_s
50	140.9	204.8	32	SmC_s'

Figure S28. XRD data of compound *rac*-**2/12**: a) χ-scans over the wide angle range (15-25°) and b) over the small angle range (1-3°) of the diffraction patterns at the indicated temperatures with numerical values.

2.3 Additional DSC traces

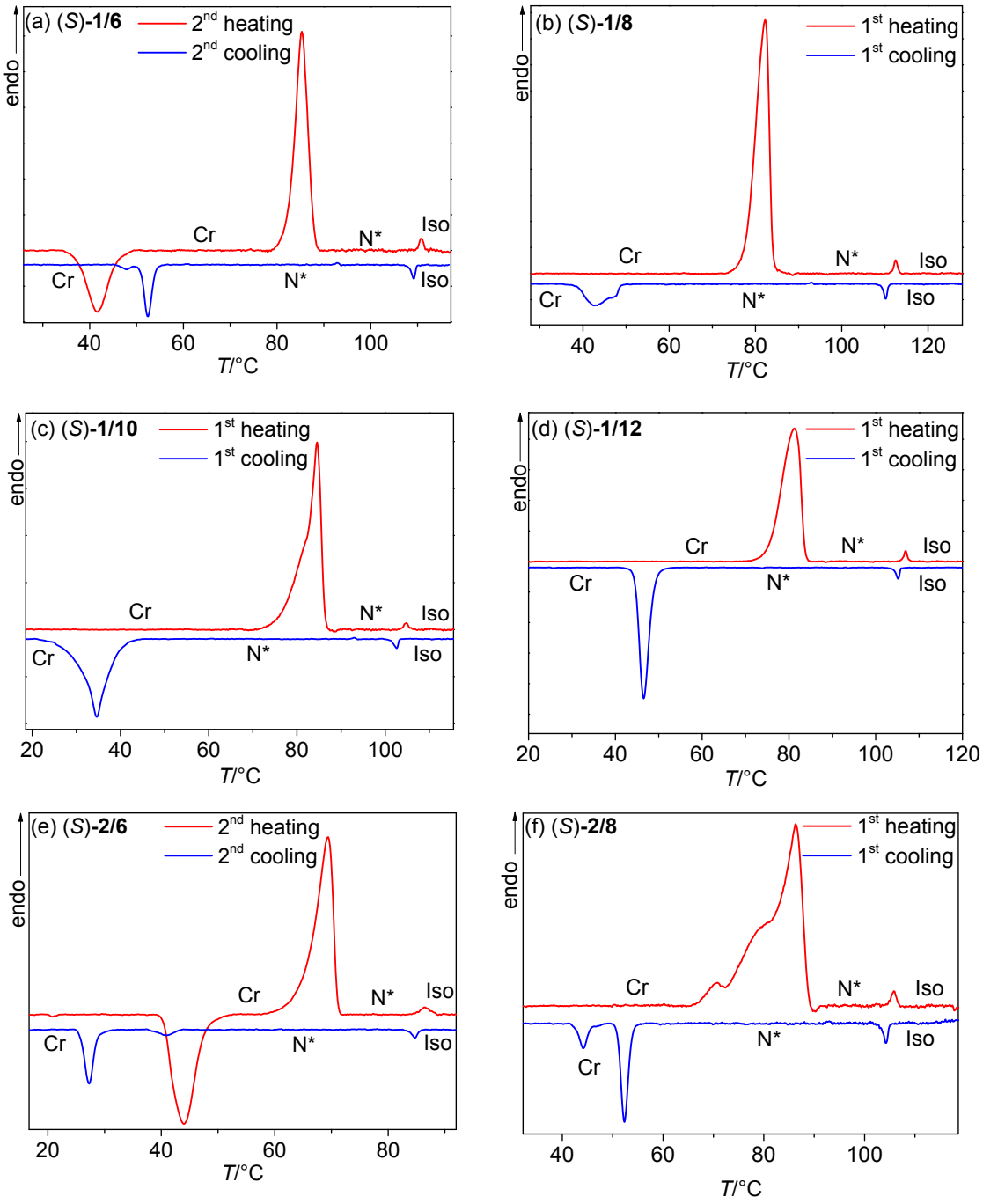


Figure S29. DSC thermograms of compounds **1/*n*** and **2/*n*** on heating and cooling (10 K min^{-1}).

2.4 Additional textures

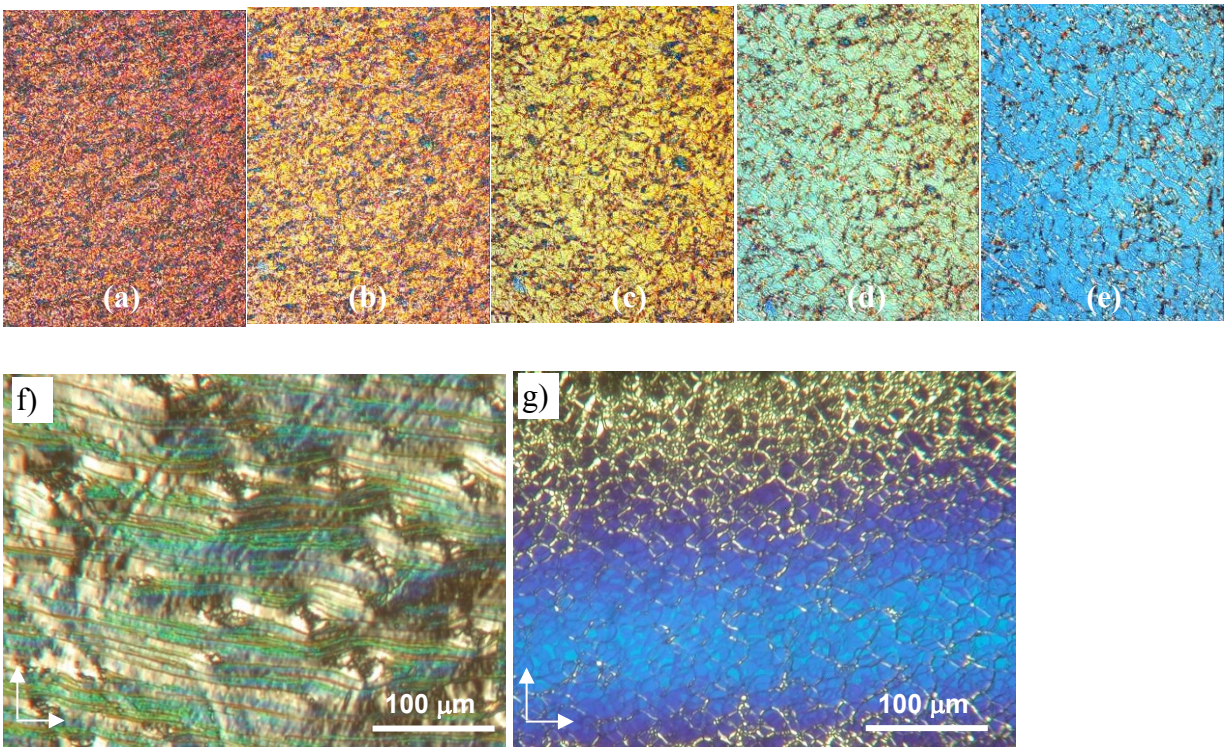
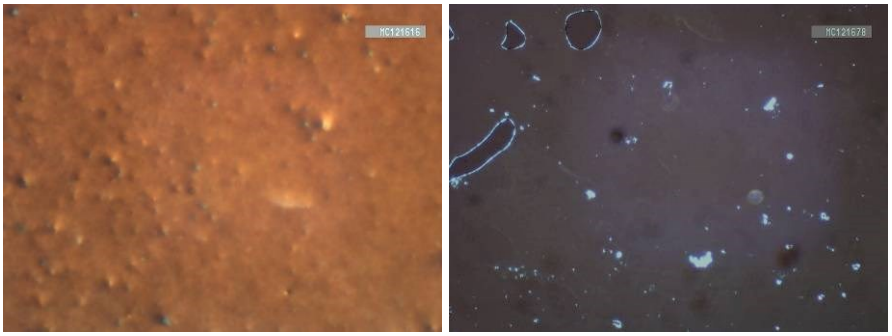
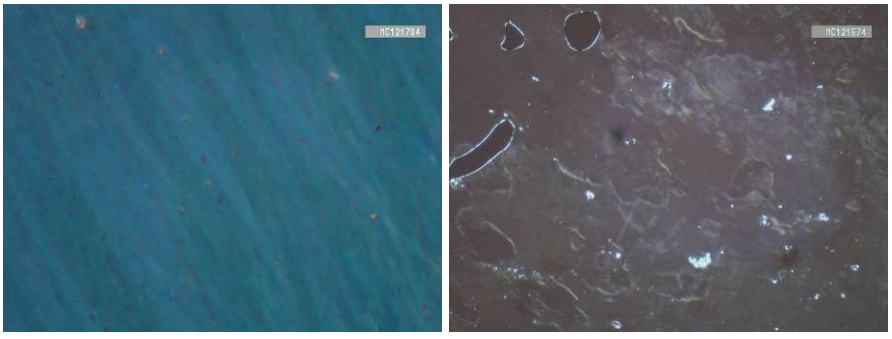


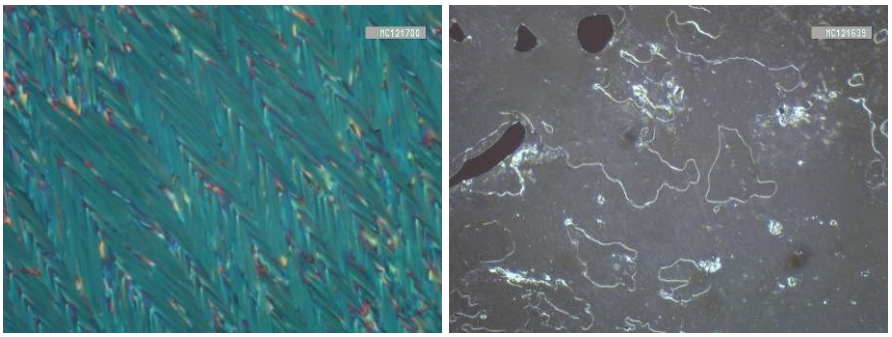
Figure S30. a-e) The change of the color in N* mesophase textures of compound (*S*)-**1/8** with increase in temperature as observed between crossed polarizers between nontreated microscopic glass slides on heating; (a) T = 85 °C; (b) T = 94 °C; (c) T = 100 °C; (d) T = 106 °C and (e) T = 110 °C; f, g) typical textures of the cybotactic N_{CybC}* phase of (*S*)-**2/10** as observed on cooling from Iso; f) thin sample at 70 °C and g) thick sample at 95 °C.



N_{CybC} 108 °C N_{CybC} 110 °C

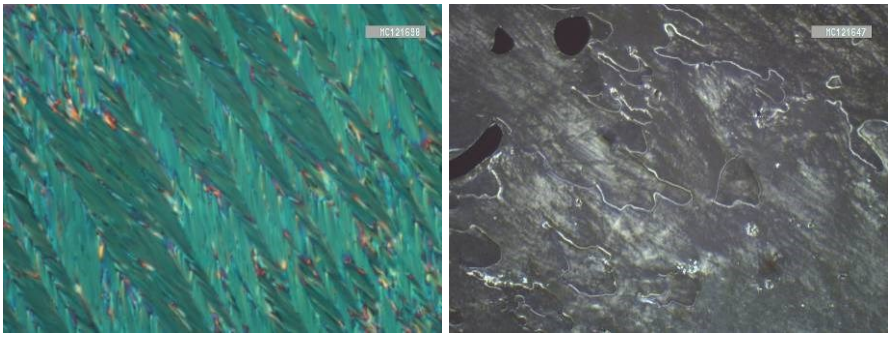


N_{CybC} 97 °C N_{CybC} 96 °C

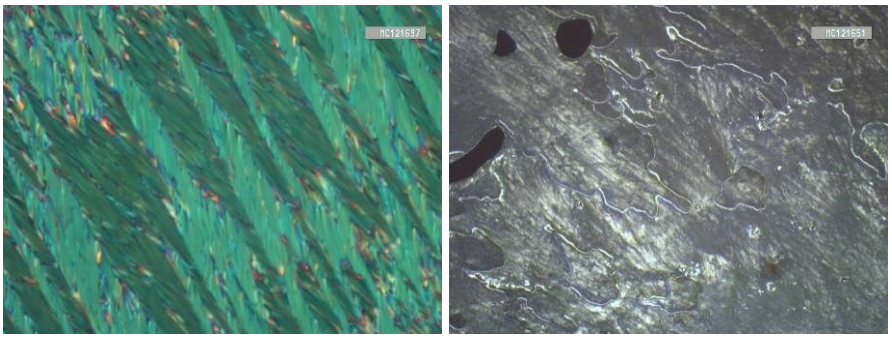


SmC 91 °C SmC 90 °C

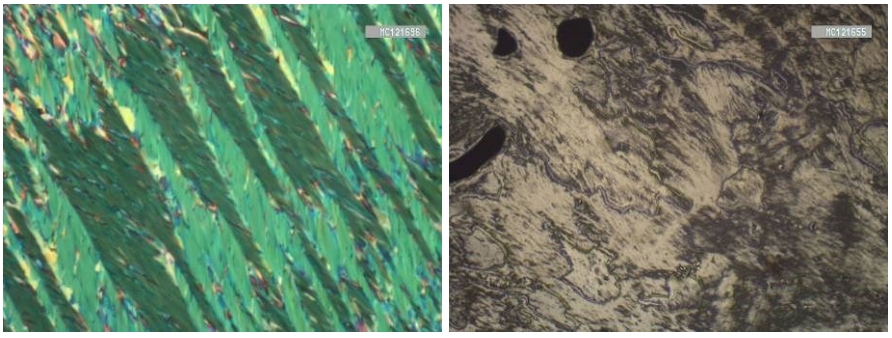
Figure S31. Textures of the planar aligned samples (left column, 6 μm ITO cell, PI coated) and homeotropic samples (right column, between non-trated microscopy glass plates) of *rac*-**2**/**12** as observed on slow cooling (5 K min^{-1}) from the isotropic liquid in the distinct phases at the indicated temperatures.



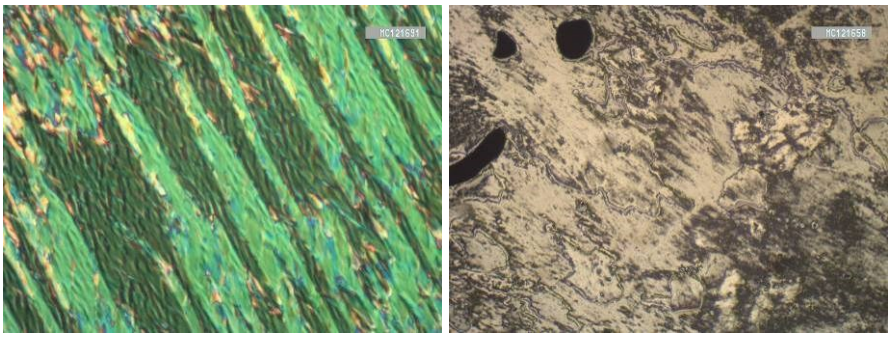
SmC 83 °C SmC 85 °C



SmC 67 °C SmC 65 °C

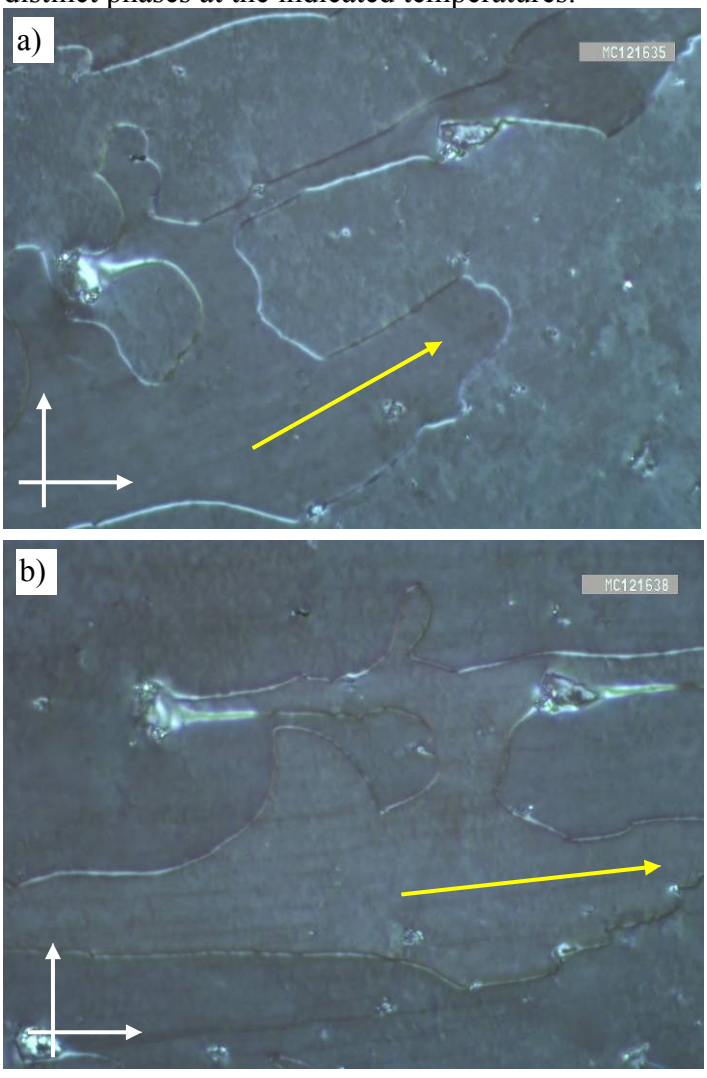


SmC 58 °C SmC 55 °C



SmC' 52 °C SmC' 45 °C

Figure S31. (continued) Textures of the planar aligned samples (left column, 6 μm ITO cell, PI coated) and homeotropic samples (right column, between non-trated microscopy glass plates) of *rac*-**2**/**12** as observed on slow cooling (5 K min^{-1}) from the isotropic liquid in the distinct phases at the indicated temperatures.



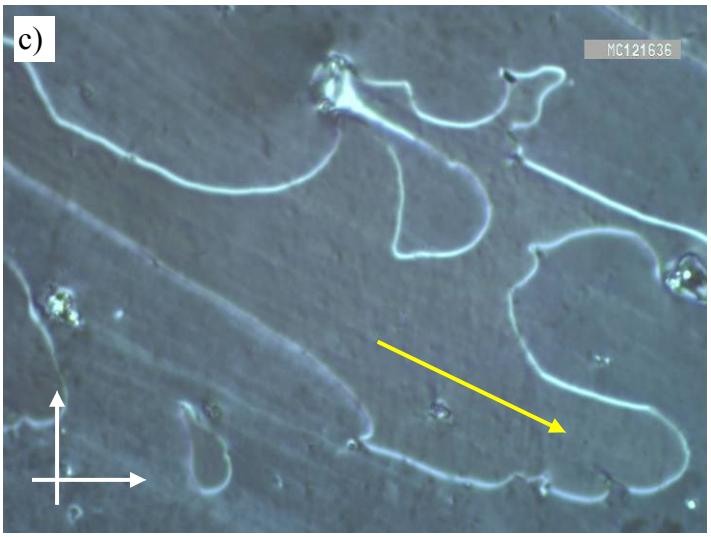
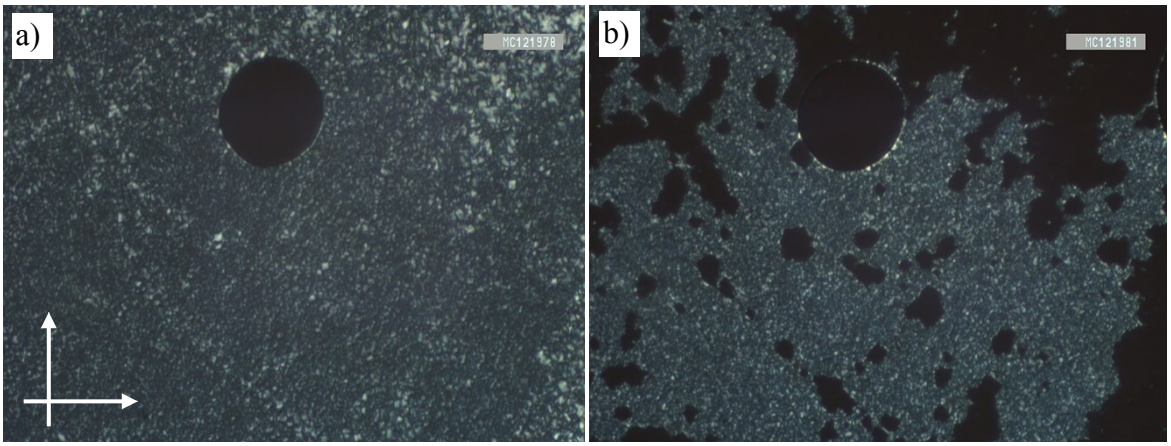
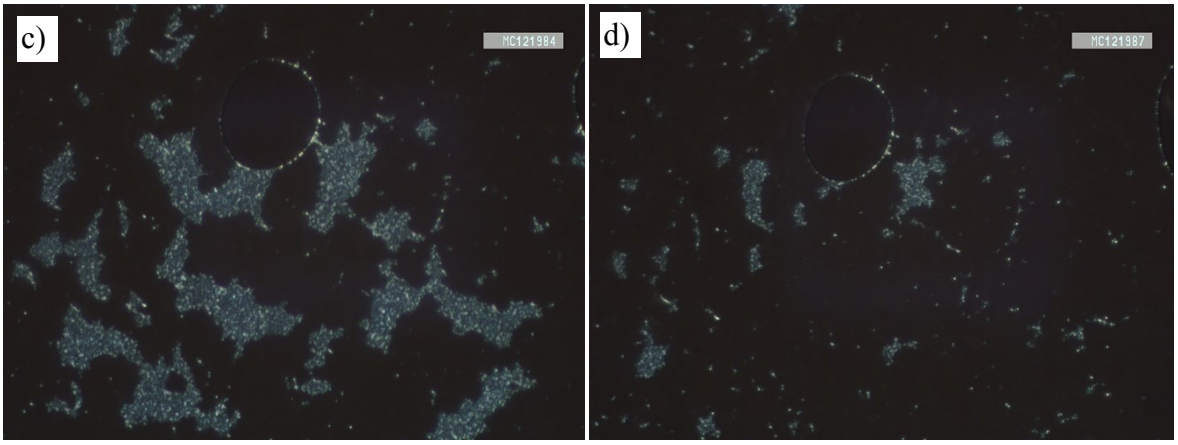


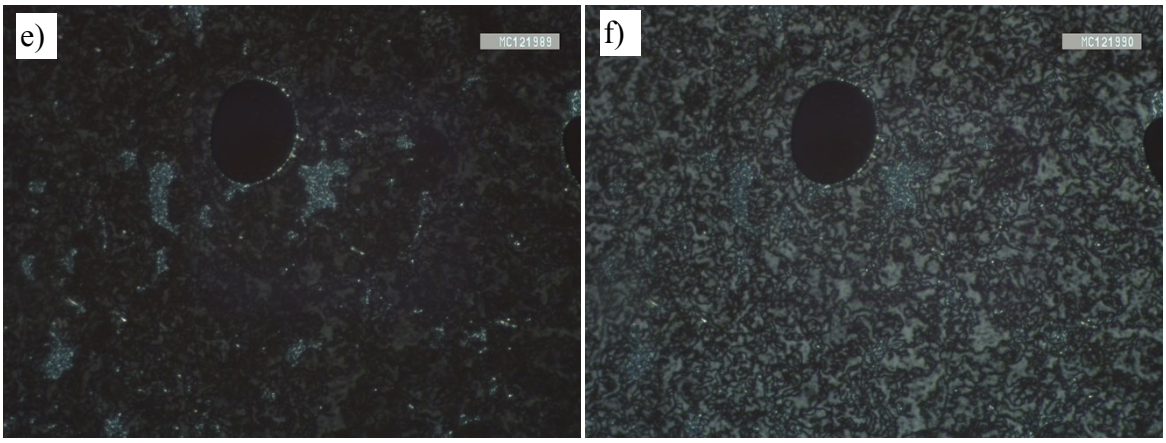
Figure S32. Chiral domains as observed in the SmC_s phase of *rac*-**2/12** at $T = 90$ °C between crossed polarizers by rotating the sample; the yellow arrow indicates the rubbing direction That the brightness of the domains does not change (compare with Fig. 7 in the main text) confirms that the dark bright contrast between the domains is due to optical activity and not to linear birefringence of tilt domains.



SmC_s*, 90 °C SmC_s*, 86 °C



SmC_s*, 86 °C SmC_s*, 86 °C



SmC_sP_{AR}*, 61 °C SmC_sP_A*, 52 °C

Figure S33. a-d) Development of the heliconical superstructure in the SmC_s* phase of *(S)*-**2/12** as observed at the indicated temperatures between two microscopy glass plates over 5 min.; the non-specific sandy texture of the non-helical SmC_s* phase slowly disappears and is replaced by the optical uniaxial texture (appearing isotropic in the developing homeotropic alignment with the layers parallel to the substrate surface and the heliconical axis perpendicular to the layer planes) of the heliconical SmC_s* phase; e, f) removal of the heliconical structure upon further cooling with developing polar order at the transition to the polar SmC_sP_A* phase via the SmC_sP_{AR}* range, finally leading to the typical B2-like Schlieren texture (homeotropic alignment is retained).

2.5. Electrooptical investigations

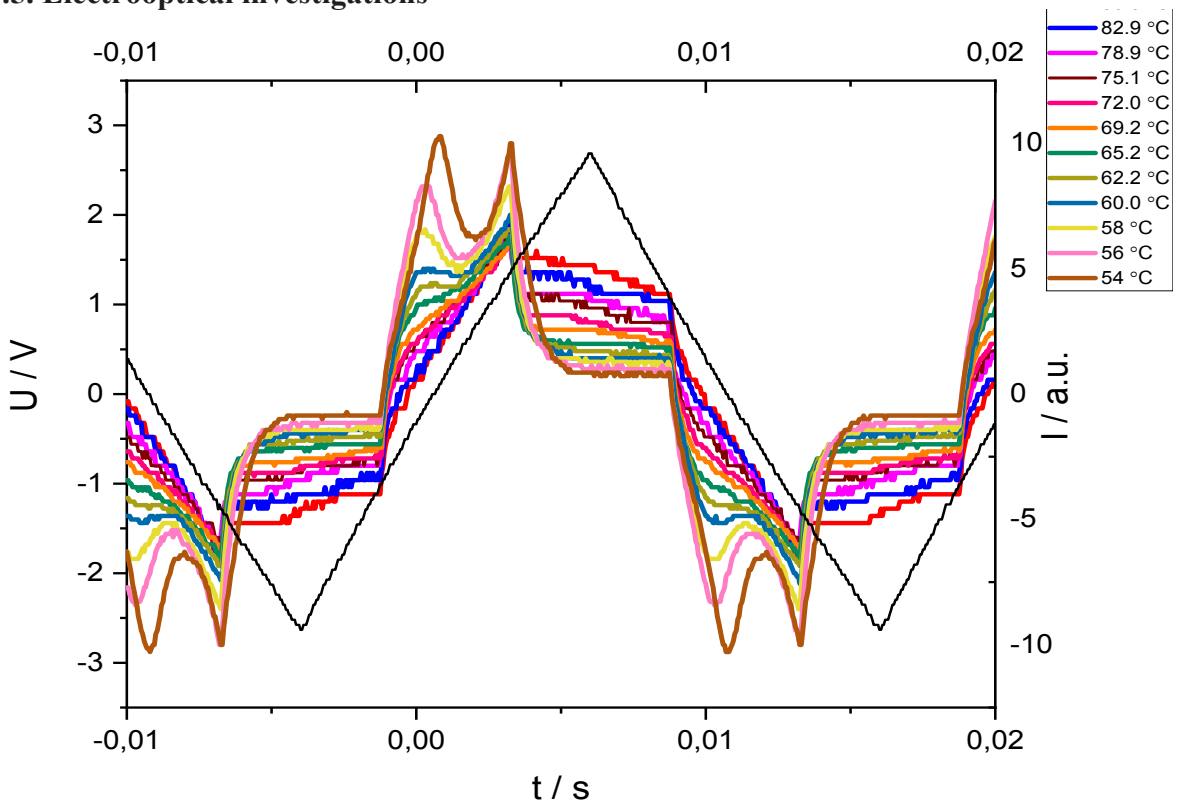


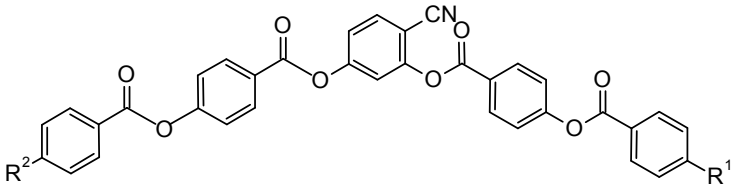
Figure S34. Polarization current response curves of *(S)*-**2/12** depending on temperature as measured on slow cooling in a 10 µm ITO cell at Vpp = 38 Vµm^{-1}.

3. Additional Discussion

Comparison with related bent-core systems. - The comparison of the compounds **2-4**, differing in the number of chiral chains (see Table S4) indicates that the increase of the number of branched chains, having in all cases the same length of 8 carbons, decreases the N-Iso transition temperature as expected. Moreover, there is a transition from N via N* to BPIII, with growing number of chiral chains. Similar to compounds **2** and **3** with branched chains the compound **4/8** with linear alkoxy chains forms a skewed cybotactic nematic phase (N_{CybC}). Replacing only one *n*-alkyl chain by a (*S*)-3,7-dimethyloctyloxy chain introduces a cholesteric phase N_{CybC}* with the helix formed in only one spatial direction. Introducing the second branched chiral group to the other ends (compound (*S*)-**3**) leads to an isotropic type III blue phase ($BPIII_{CybC}$*, blue fog phase), representing a highly chirality frustrated structure with short range helical order in all three directions[S4] That chiral groups at both ends of an aromatic core support the formation of chirality frustrated LC phases is known from previous work with rod-like mesogens and dimesogens,[S5,S6] but it requires chiral groups with a "high chirality", as provided by halogens or oxygen directly attached to the stereogenic centers.[S6] In contrast, in the series of the bent compounds **1/*n***, **2/*n*** and **3** the stereogenic center is substituted only by alkyl chains and H atoms which are known to produce only weak chirality effects. However, in this case the relatively long bent aromatic unit provides significant core-core interactions supporting the chirality induced helical twist. Therefore, even the weak chirality can in this case provide a significant effect. However, the packing density between the 4-cyanoresorcinol with phenylbenzoate wings is known to be still relatively small and

there is only weak hindrance of the rotation around the long axis.[S2] Therefore, relatively small chirality effects were observed and two stereogenic centers are required for BP formation.

Table S4. Influence of number of branched chains on the LC phases and phase transitions of representative 4-cyanoresorcinol bisbenzoates with identical length of the terminal chains.[a]



Compd.	R^1	R^2	*T* / °C
4/8[S7]	*n*-OC_8H_{17}	*n*-OC_8H_{17}	Cr 99 N_{CybC} 132 Iso
(*S*)-**2/8**	(*S*)-3,7-Dimethyloctyl-O-	*n*-OC_8H_{17}	Cr 83 N_{CybC}* 104 Iso
(*S*)-**3** [S4]	(*S*)-3,7-Dimethyloctyl-O-	(*S*)-3,7-Dimethyloctyl-O-	Cr 80 (BPIII 58) Iso
4/10[S7]	*n*-$OC_{10}H_{21}$	*n*-$OC_{10}H_{21}$	Cr 99 ($SmCP_A$' 66 $SmCP_A$ 77) N_{CybC} 128 Iso
5/9[S2,S8]	*n*-C_9H_{19}	*n*-C_9H_{19}	Cr 98 (SmC_sP_A 50 $CybC_s$ 58) N_{CybC} 104 Iso

[a]BPIII = isotropic blue phase; $CybC_s$ is considered as a LC phase composed of large cybotactic SmC clusters, but still short coherence length of the layer periodicity, being at the transition between N_{CybC} and SmC_s.

4. Additional Explanations

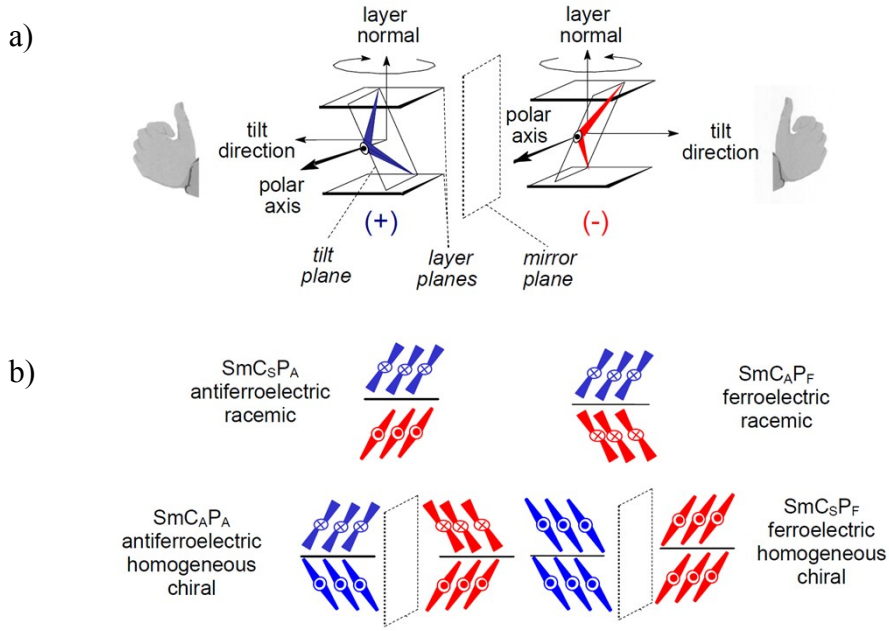


Figure S35. (a) Origin of the chirality of the polar smectic phases of achiral bent-core molecules (superstructural layer chirality). Layer normal, tilt direction and the polar axis define either a right handed ((+), shown in blue), or left handed system ((-), shown in red). Changing either polarization direction or tilt direction reverses the chirality sense of the layer, whereas changing polarization direction and tilt direction retains the sense of chirality. (b) shows the supramolecular arrangements resulting from the combination of the different tilt directions and polar directions (abbreviations: C_S = synclinic tilt, C_A = anticlinic tilt, P_F = "ferroelectric" polar order, P_A = "antiferroelectric" polar order). If the layer chirality changes from layer to layer, the phase is racemic. If the layer chirality is identical in adjacent layers the phase is homogeneous chiral and forms a conglomerate of the mirror images.

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