Supporting Information

Competition Between Helical and Heliconical Twist in the Development of Complex Soft Matter Structures

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1. Materials Synthesis

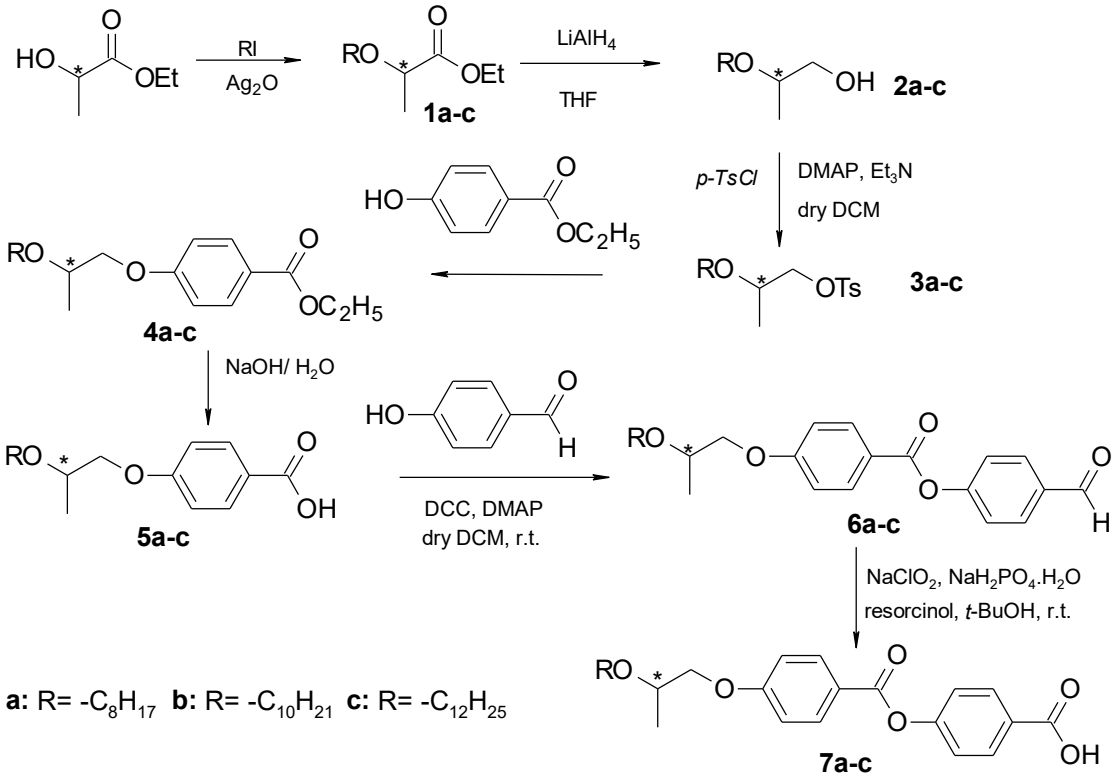
1.1 General remarks

1-Bromooctane (ABCR), 1-bromodecane (ABCR), 1-bromododecane (Merck), 1-iodooctane (Sigma-Aldrich), 1-iododecane (Sigma-Aldrich), 1-iododododecane (Sigma-Aldrich), 4-benzyloxy-2-hydroxybenzaldehyde (ABCR, 99.0%), (−)-ethyl L-lactate (Sigma-Aldrich ≥99.0%), ethyl 4-hydroxybenzoate (Alfa Aesar), sodium hydroxide pellets (Merck), lithium aluminium hydride (Sigma-Aldrich), N,N'-dicyclohexylcarbodiimide (Merck), 4-(dimetilamino)piridin (Merck), oxalyl chloride *(Merck),* 5 % palladium on carbon, dry (Sigma-Aldrich), potassium carbonate (Merck), *p*-toluene sulfonyl chloride (Merck), triethylamine (Merck), pyridine (Acros), resorcinol (Merck), cyclohexene (Merck), sodium dihydrogen phosphate monohydrate (Merck), sodium chlorite (Fluka) and resorcinol (ACS 99%) were purchased commercially. Silver (I) oxide was prepared by the reaction of commercially available silver nitrate (Merck) and sodium hydroxide. Solvents were purchased or distilled. *N*,*N*-Dimethylformamide (Merck), *ter*-butanol (Merck), ethanol (Merck), 2-butanone (Merck) and THF (Merck %99) were purchased commercially as dry solvents and were used without further purification. Anhydrous solvent CH_2Cl_2 was dried over P_4O_{10} (Merck) and distilled under a N_2 atmosphere. Solvents used in the purification step such as crystallization and column chromatography (hexane, ethyl acetate, chloroform, dichloromethane and ethanol) were distilled. 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).
The characterization of the synthesized compounds is based on ^{1}H-NMR, ^{13}C-NMR (Bruker Avance III 500 spectrometer, in $CDCl_3$-d_6 or DMSO-d_6 solutions with tetramethylsilane as internal standard). FT-IR analysis analysis was performed using a Perkin Elmer Spectrum One FT-IR spectrometer.

1.2. Synthesis and analytical data of intermediates

1.2.1 (*S*)-2-Alkyloxypropyl substituted 4-benzoyloxybenzoic acids 7a-c

The synthesis of **7a-c** was performed as shown in Scheme S1. It starts with an etherification reaction of (*S*)-ethyl lactate with the appropriate alkyl iodides (1-iodooctane, 1-iododecane and 1-iodododecane) in presence of Ag_2O.[1,2] Then, the corresponding O-alkyl substituted ethyl lactates were reduced to the (*S*)-2-alkyloxypropanols with $LiAlH_4$.[2] After tosylation[2] of the corresponding alcohols with *p*-TsCl in dry CH_2Cl_2 in the presence of DMAP and Et_3N,[2] the etherification reaction was carried out between 4-(*(S)*-2-alkyloxypropyloxy)tosylate and ethyl 4-hydroxybenzoate in DMF with K_2CO_3 as a base, followed by alkaline hydrolysis. The obtained 4-(*(S)*-2-alkyloxypropyloxy)benzoic acids were reacted with 4-hydroxybenzaldehyde in the presence of DCC and DMAP as a catalyst in dry DCM,[3] followed by $NaClO_2$ oxidation[4] to yield the benzoic acids **7a-c.**



Scheme S1. The synthesis of (*S*)-2-alkyloxypropyl substituted benzoate-based rod-like units (**7a-c**).

1.2.1.1 Ethyl (*S*)-2-(*n*-alkyloxy)propanoates (1a-c)[5,6,7]

To a solution of 30 mmol of commercially purchased (−)-ethyl L-lactate and 69 mmol of *n*-alkyl iodide in 15 mL of 2-butanone, 40 mmol of silver(I) oxide (Ag_2O) was added and the reaction mixture was refluxed under argon atmosphere at 100 °C for 20h. Then, silver precipitate was filtered and the solvent was removed under reduced pressure. The same amount of silver(I) oxide was added to the remaining liquid mixture and the reaction mixture was refluxed under argon atmosphere at 160 °C for 24h. The solution was filtered, washed with acetone and the solvent was removed under reduced pressure. The resulting product was purified by column chromatography on silica gel eluting with hexane : ethyl acetate/10:1.

^{1}H-NMR spectroscopic data of ethyl (*S*)-2-(*n*-dodecyloxy)propanoate (**1c**) was previously reported in ref.[5]

Ethyl (*S*)-2-(*n*-octyloxy)propanoate (1a) ($C_{13}H_{26}O_3$: 230.35 g/mol)
Yield: 47%, colorless liquid.**^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 4.25-4.13 (m; 2H, $OC\underline{H}_2CH_3$), 3.92 (q, $J \approx$ 6.8 Hz; 1H, CH), 3.53 (dd, $J \approx$ 15.7, 6.7 Hz; 1H, OCH_{2a}), 3.34 (dd, $J \approx$ 15.7, 6.8 Hz; 1H, OCH_{2b}), 1.62-1.54 (m; 2H, $OCH_2C\underline{H}_2$), 1.38 (d, $J \approx$ 6.9 Hz; 3H, $CHC\underline{H}_3$), 1.35-1.23 (m; 10H, $5CH_2$), 1.27 (t, 3H, $OCH_2C\underline{H}_3$), 0.86 (t, $J \approx$ 6.9 Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2926.18-2856.04 (C-H), 1750.29 (C=O), 1126.89 (C-O).

Ethyl (*S*)-2-(*n*-decyloxy)propanoate (1b) ($C_{15}H_{30}O_3$: 258.40 g/mol)
Yield: 44%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 4.25-4.13 (m; 2H, $OC\underline{H}_2CH_3$), 3.92 (q, $J \approx$ 6.8 Hz; 1H, CH), 3.54 (dd, $J \approx$ 15.7, 6.7 Hz; 1H, OCH_{2a}), 3.34 (dd, $J \approx$ 15.7, 6.8 Hz; 1H, OCH_{2b}), 1.62-1.55 (m; 2H, $OCH_2C\underline{H}_2$), 1.38 (d, $J \approx$ 6.9 Hz; 3H, $CHC\underline{H}_3$), 1.35-1.24 (m; 14H, $7CH_2$), 1.28 (t, 3H, $OCH_2C\underline{H}_3$), 0.87 (t, $J \approx$ 6.9 Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2923.59-2854.15 (C-H), 1750.51 (C=O), 1127.62 (C-O).

1.2.1.2 (*S*)-2-(*n*-Alkyloxy)propan-1-ols (2a-c)[2,8,9]
For the synthesis of (*S*)-2-(*n*-alkyloxy)propan-1-ols, THF (20 mL) was placed in a 100 mL three-necked reaction flask that has been cooled below 0 °C in an ice-salt bath and dried thoroughly, and 15 mmol of $LiAlH_4$ reagent was added and mixed under Ar gas for a few minutes. While 10 mmol of ethyl (*S*)-2-(*n*-alkyloxy)propanoate, which was diluted with 20 mL of THF, slowly added through the septum with a syringe, the temperature was controlled. After 2h, the ice-salt bath was removed and stirred at room temperature overnight. The end of reaction was monitored by TLC (hexane : ethyl acetate / 3:1, by using $KMnO_4$ indicator). The mixture was cooled to 0 °C by using an ice-salt bath, then approximately 4 mL of H_2O was added slowly and mixed at 0 °C for 30 min. The mixture was acidified by 20% HCl solution and then was extracted into ether (3 x). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo and the resulting product was purified by column chromatography on silica gel eluting with hexane : ethylacetate/3:1.

(*S*)-2-(*n*-Octyloxy)propan-1-ol (2a) ($C_{11}H_{24}O_2$; 188.31g/mol)
Yield: 94%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 3.58-3.47 (m; 3H, $C\underline{H}(CH_3)C\underline{H}_2OH$), 3.42 (dd, $J \approx$ 10.9, 7.0 Hz; 1H, OCH_{2a}), 3.36 (dd, $J \approx$ 15.9, 6.7 Hz; 1H, OCH_{2b}), 2.11 (s; 1H, OH), 1.61-1.52 (m; 2H, $OCH_2C\underline{H}_2$), 1.38-1.21 (m; 10H, $5CH_2$), 1.09 (d, $J \approx$ 6.1 Hz; 3H, $CHC\underline{H}_3$), 0.87 (t, $J \approx$ 6.9 Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 3424.20 (OH), 2924.21-2855.03 (CH), 1092.82-1045.59 (CO).

(*S*)-2-(*n*-Decyloxy)propan-1-ol (2b) ($C_{13}H_{28}O_2$; 216.37g/mol)
Yield: 90%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 3.59-3.48 (m; 3H, $C\underline{H}(CH_3)C\underline{H}_2OH$), 3.45-3.40 (m; 1H, OCH_{2a}), 3.36 (dd, $J \approx$ 15.9, 6.7 Hz; 1H, OCH_{2b}), 2.14 (m; 1H, OH), 1.61-1.53 (m; 2H, $OCH_2C\underline{H}_2$), 1.38-1.22 (m; 14H, $7CH_2$), 1.10 (d, $J \approx$ 6.1 Hz; 3H, $CHC\underline{H}_3$), 0.87 (t, $J \approx$ 6.9 Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 3423.04 (OH), 2922.41-2853.33 (CH), 1094.53-1046.27 (CO).

(*S*)-2-(*n*-Dodecyloxy)propan-1-ol (2c) ($C_{15}H_{32}O_2$; 244.42g/mol)
Yield: 86%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 3.60-3.49 (m; 3H, $C\underline{H}(CH_3)C\underline{H}_2OH$), 3.46-3.40 (m; 1H, OCH_{2a}), 3.37 (dd, $J \approx$ 15.9, 6.7 Hz; 1H, OCH_{2b}), 2.07 (m; 1H, OH), 1.60-1.53 (m; 2H, $OCH_2C\underline{H}_2$), 1.37-1.22 (m; 18H, $9CH_2$), 1.10 (d, $J \approx$ 6.1 Hz; 3H,

$CHC\underline{H}_3$), 0.88 (t, $J \approx 7.0$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 3385.59 (OH), 2921.73-2852.59 (CH), 1088.66-1046.93 (CO).

1.2.1.3 (*S*)-2-(*n*-Alkyloxy)propyl-4-methylbenzenesulfonates (3a-c)[2,10]

For the synthesis of (*S*)-2-(*n*-alkyloxy)propyl-4-methylbenzenesulfonates, 30 mmol of Et_3N and 4.5 mmol of DMAP were added respectively to the solution of 15 mmol of (*S*)-2-(*n*-alkyloxy)propan-1-ol compound in dry CH_2Cl_2, which was cooled below 0 °C in an ice-salt bath under Ar gas, and mixed for a few minutes. While the temperature was below 0 °C, 22.5 mmol of *p*-toluene sulfonyl chloride was added slowly and stirred overnight. The end of reaction was monitored by TLC ($CHCl_3$, by using $KMnO_4$ indicator). The reaction mixture was poured into ice and the pH was adjusted to around 5-6 with 1N HCl. The mixture was extracted with diethylether and washed with saturated brine solution. The organic phase was dried over Na_2SO_4 and the solvent was evaporated in a rotary evaporator. The crude product was purified by column chromatography (silica gel 60; $CHCl_3$).

(*S*)-2-(*n*-Octyloxy)propyl-4-methylbenzenesulfonate (3a) ($C_{18}H_{30}O_4S$, 342.49 g/mol)
Yield: 82%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 7.79 (d, $J \approx 8.3$ Hz; 2Ar-H), 7.33 (d, $J \approx 8.0$ Hz; 2Ar-H), 3.97-3.88 (m; 2H, $C\underline{H}_2OTs$), 3.64-3.57 (m; 1H, CH), 3.44-3.38 (m; 2H, OCH_{2a}), 3.37-3.31 (m; 2H, OCH_{2b}) 2.44 (s; 3H, CH_3), 1.49-1.42 (m; 2H, $OCH_2C\underline{H}_2$), 1.32-1.21 (m; 10H, $5CH_2$), 1.10 (d, $J \approx 6.4$ Hz; 3H, $CHC\underline{H}_3$), 0.87(t, $J \approx 7.0$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2926.12-2855.44 (CH), 1188.84-1176.10 (SO_2).

(*S*)-2-(*n*-Decyloxy)propyl-4-methylbenzenesulfonate (3b) ($C_{20}H_{34}O_4S$, 370.55 g/mol)
Yield: 83%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 7.79 (d, $J \approx 8.3$ Hz; 2Ar-H), 7.33 (d, $J \approx 8.0$ Hz; 2Ar-H), 3.98-3.88 (m; 2H, $C\underline{H}_2OTs$), 3.65-3.56 (m; 1H, CH), 3.45-3.37 (m; 2H, OCH_{2a}), 3.37-3.32 (m; 2H, OCH_{2b}) 2.44 (s; 3H, CH_3), 1.53-1.39 (m; 2H, $OCH_2C\underline{H}_2$), 1.32-1.22 (m; 14H, $7CH_2$), 1.10 (d, $J \approx 6.4$ Hz; 3H, $CHC\underline{H}_3$), 0.87(t, $J \approx 6.9$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2925.10-2854.23 (CH), 1189.05-1177.04 (SO_2).

(*S*)-2-(*n*-Dodecyloxy)propyl-4-methylbenzenesulfonate (3c) ($C_{22}H_{38}O_4S$, 398.60 g/mol)
Yield: 81%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 7.79 (d, $J \approx 8.3$ Hz; 2Ar-H), 7.33 (d, $J \approx 8.1$ Hz; 2Ar-H), 3.98-3.89 (m; 2H, $C\underline{H}_2OTs$), 3.64-3.56 (m; 1H, CH), 3.43-3.38 (m; 2H, OCH_{2a}), 3.38-3.32 (m; 2H, OCH_{2b}) 2.44 (s; 3H, CH_3), 1.49-1.42 (m; 2H, $OCH_2C\underline{H}_2$), 1.33-1.22 (m; 18H, $9CH_2$), 1.10 (d, $J \approx 6.4$ Hz; 3H, $CHC\underline{H}_3$), 0.87(t, $J \approx 6.9$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2922.70-2852.88 (CH), 1188.91-1176.61 (SO_2).

1.2.1.4 Ethyl 4-(*S*)-2-(*n*-alkyloxy)propoxybenzoates (4a-c)

For the synthesis of ethyl 4-(*S*)-2-(*n*-alkyloxy)propoxybenzoates, 19.5 mmol of ethyl 4-hydroxybenzoate and 33.75 mmol of K_2CO_3 were mixed into the 250 mL flask in 25 mL DMF and then 15 mmol of (*S*)-2-(*n*-alkyloxy)propyl 4-methylbenzenesulfonate was added to this mixture and refluxed at 150 °C under Ar atmosphere for 3h. The end of reaction was monitored by TLC ($CHCl_3$). The resulting mixture was filtered, washed with chloroform and the solvent was removed under reduced pressure. The resulting product was purified by column chromatography on silica gel 60 eluting with $CHCl_3$.

Ethyl 4-(*S*)-2-(*n*-octyloxy)propoxybenzoate (4a) ($C_{20}H_{32}O_4$; 336.47 g/mol)
Yield: 81%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 7.98 (d, $J \approx 8.8$ Hz; 2Ar-H), 6.91 (d, $J \approx 8.8$ Hz; 2Ar-H), 4.37 (q, $J \approx 7.1$ Hz; $OC\underline{H}_2CH_3$) 4.02 (dd, $J \approx 9.6$, 5.9 Hz; 1H, OCH_{2a}), 3.90 (dd, $J \approx 9.6$, 4.8 Hz; 1H, OCH_{2b}), 3.83-3.76 (m; 1H, CH), 3.59-3.48 (m; 2H,

$CHC\underline{H}_2O$) 1.60-1.53 (m; 2H, $OCH_2C\underline{H}_2$), 1.37 (t, $J \approx 7.1$ Hz; 3H, $OCH_2C\underline{H}_3$), 1.34-1.25 (m; 13H, $CHC\underline{H}_3$, $5CH_2$,), 0.87 (t, $J \approx 6.9$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2926.60-2855.32 (C-H), 1712.90 (C=O), 1272.96-1251.05 (CO).

Ethyl 4-(*S*)-2-(*n*-decyloxy)propoxybenzoate (4b) ($C_{22}H_{36}O_4$; 364.53 g/mol)
Yield: 60%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 7.98 (d, $J \approx 8.9$ Hz; 2Ar-H), 6.92 (d, $J \approx 8.9$ Hz; 2Ar-H), 4.34 (q, $J \approx 7.1$ Hz; $OC\underline{H}_2CH_3$), 4.02 (dd, $J \approx 9.6$, 5.9 Hz; 1H, OCH_{2a}), 3.91 (dd, $J \approx 9.6$, 4.8 Hz; 1H, OCH_{2b}), 3.84-3.76 (m; 1H, CH), 3.60-3.49 (m; 2H, $CHC\underline{H}_2O$) 1.60-1.53 (m; 2H, $OCH_2C\underline{H}_2$), 1.37 (t, $J \approx 7.1$ Hz; 3H, $OCH_2C\underline{H}_3$), 1.35-1.23 (m; 14H, $7CH_2$,), 1.27 (d, $J \approx 6.4$ Hz; 3H, $CHC\underline{H}_3$), 0.87 (t, $J \approx 7.0$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2923.87-2853.72 (CH), 1713.41 (C=O), 1273.00-1251.31 (CO).

Ethyl 4-(*S*)-2-(*n*-dodecyloxy)propoxybenzoate (4c) ($C_{24}H_{40}O_4$; 392.58 g/mol)
Yield: 65%, colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 7.98 (d, $J \approx 8.9$ Hz; 2Ar-H), 6.92 (d, $J \approx 8.9$ Hz; 2Ar-H), 4.34 (q, $J \approx 7.1$ Hz; $OC\underline{H}_2CH_3$), 4.02 (dd, $J \approx 9.6$, 5.9 Hz; 1H, OCH_{2a}), 3.91 (dd, $J \approx 9.6$, 4.8 Hz; 1H, OCH_{2b}), 3.83-3.76 (m; 1H, CH), 3.59-3.49 (m; 2H, $CHC\underline{H}_2O$) 1.60-1.53 (m; 2H, $OCH_2C\underline{H}_2$), 1.38 (t, $J \approx 7.1$ Hz; 3H, $OCH_2C\underline{H}_3$), 1.35-1.23 (m; 18H, $9CH_2$), 1.27 (d, $J \approx 6.3$ Hz; 3H, $CHC\underline{H}_3$), 0.88 (t, $J \approx 6.9$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2922.99-2853.01 (CH), 1714.10 (C=O), 1273.01-1251.49 (CO).

1.2.1.5 4-(*S*)-2-(*n*-Alkyloxy)propoxy benzoic acids (5a-c)[6]

For the synthesis of 4-(*S*)-2-(*n*-alkyloxy)propoxy benzoic acids, aqueous NaOH solution (20 mmol / 10 mL H_2O) was added to 8 mmol of ethyl 4-(*S*)-2-(*n*-alkyloxy)propoxybenzoate in ethanol and refluxed overnight. The end of reaction was monitored by TLC ($CHCl_3$). The resulting mixture was poured into water and the pH was adjusted to between 1-2 with using 1 N HCl. The precipitate was filtered and dried, then the crude product was purified by recrystallization with ethanol.

4-(*S*)-(2-(*n*-Octyloxy)propoxy)benzoic acid (5a) ($C_{18}H_{28}O_4$; 308.42 g/mol)
Yield: 91%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.05 (d, $J \approx 8.9$ Hz; 2Ar-H), 6.95 (d, $J \approx 8.9$ Hz; 2Ar-H), 4.05 (dd, $J \approx 9.6$, 5.9 Hz; 1H, OCH_{2a}), 3.93 (dd, $J \approx 9.6$, 4.7 Hz; 1H, OCH_{2b}), 3.85-3.77 (m; 1H, CH), 3.60-3.49 (m; 2H, $CHC\underline{H}_2O$) 1.61-1.54 (m; 2H, $OCH_2C\underline{H}_2$), 1.39-1.19 (m; 10H, $5CH_2$,), 1.28 (d, $J \approx 6.3$ Hz; 3H, $CHC\underline{H}_3$) 0.87 (t, $J \approx 7.0$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2916.97-2850.22 (CH), 2560.64 (OH), 1672.72 (C=O), 1253.33 (CO).

4-(*S*)-(2-(*n*-Decyloxy)propoxy)benzoic acid (5b) ($C_{20}H_{32}O_4$; 336.47 g/mol)
Yield: 93%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.05 (d, $J \approx 8.9$ Hz; 2Ar-H), 6.95 (d, $J \approx 8.9$ Hz; 2Ar-H), 4.05 (dd, $J \approx 9.6$, 5.9 Hz; 1H, OCH_{2a}), 3.93 (dd, $J \approx 9.6$, 4.8 Hz; 1H, OCH_{2b}), 3.85-3.77 (m; 1H, CH), 3.61-3.50 (m; 2H, $CHC\underline{H}_2O$) 1.61-1.54 (m; 2H, $OCH_2C\underline{H}_2$), 1.40-1.18 (m; 14H, $7CH_2$,), 1.28 (d, $J \approx 6.3$ Hz; 3H, $CHC\underline{H}_3$) 0.87 (t, $J \approx 7.0$ Hz; 3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2915.10-2849.44 (CH), 2562.88 (OH), 1671.73 (C=O), 1254.34 (CO).

4-(*S*)-(2-(*n*-Dodecyloxy)propoxy)benzoic acid (5c) ($C_{22}H_{36}O_4$; 364.53 g/mol)
Yield: 92%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.05 (d, $J \approx 8.9$ Hz; 2Ar-H), 6.95 (d, $J \approx 8.9$ Hz; 2Ar-H), 4.05 (dd, $J \approx 9.6$, 5.9 Hz; 1H, OCH_{2a}), 3.93 (dd, $J \approx 9.6$, 4.7 Hz; 1H, OCH_{2b}), 3.86-3.76 (m; 1H, CH), 3.62-3.49 (m; 2H, $CHC\underline{H}_2O$) 1.61-1.53 (m; 2H, $OCH_2C\underline{H}_2$), 1.41-1.17 (m; 18H, $9CH_2$,), 1.28 (d, $J \approx 6.3$ Hz; 3H, $CHC\underline{H}_3$) 0.88 (t, $J \approx 6.9$ Hz;

3H, CH_3). **FT-IR** (ATR, cm^{-1}): 2914.69-2849.22 (CH), 2562.93 (OH), 1672.95 (C=O), 1254.79 (CO).

1.2.1.6 4-Formylphenyl 4-(*S*)-(2-(*n*-alkyloxy)propoxy)benzoates (6a-c)

For the synthesis of 4-Formylphenyl 4-(*S*)-(2-(*n*-alkyloxy)propoxy)benzoates, to a mixture of 4-(*S*)-(2-(*n*-alkyloxy)propoxy)benzoic acid (3.0 mmol) and 4-hydroxybenzaldehyde (3.0 mmol) in dry CH_2Cl_2 (25 mL), *N*,*N'*-dicyclohexylcarbodiimide (DCC) (4.48 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.24 mmol) 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/3:1). The reaction mixture was filtered on silica gel with CH_2Cl_2 and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel, eluting with hexane:ethylacetate/3:1.

4-Formylphenyl 4-(*S*)-(2-(*n*-octyloxy)propoxy)benzoate (6a) ($C_{25}H_{32}O_5$; 412.53 g/mol)
Yield: 57%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 10.01 (s; 1H, CHO), 8.14 (d, *J* ≈ 8.9 Hz; 2Ar-H), 7.96 (d, *J* ≈ 8.6 Hz; 2Ar-H), 7.39 (d, *J* ≈ 8.5 Hz; 2Ar-H), 7.00 (d, *J* ≈ 8.9 Hz; 2Ar-H), 4.07 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHC$\underline{H}_{2a}$O), 3.96 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHC$\underline{H}_{2b}$O), 3.86-3.78 (m; 1H, C$\underline{H}$), 3.61-3.49 (m; 2H, OCH_2), 1.61-1.54 (m; 2H, $OCH_2C\underline{H}_2$), 1.43-1.18 (m; 10H, $5CH_2$), 1.29 (d, *J* ≈ 6.3 Hz; 3H, CHC$\underline{H}_3$), 0.87 (t, *J* ≈ 7.0 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 191.13 ($\underline{C}$HO), 164.31 (CO), 163.74, 156.00, 134.01, 121.23 (Ar-$\underline{C}$), 132.53, 131.35, 122.72, 114.69 (Ar-$\underline{C}$H), 73.66 (O$\underline{C}$H), 71.98, 69.81 (O$\underline{C}H_2$), 31.94, 30.17, 29.54, 29.39, 26.24, 22.77 (CH_2), 17.32, 14.22 (CH_3). **FT-IR** (ATR, cm^{-1}): 2926.71-2854.08 (CH), 1735.27-1700.90 2(C=O).

4-Formylphenyl 4-(*S*)-(2-(*n*-decyloxy)propoxy)benzoate (6b) ($C_{27}H_{36}O_5$; 440.58 g/mol)
Yield: 53%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 10.02 (s; 1H, CHO), 8.14 (d, *J* ≈ 8.9 Hz; 2Ar-H), 7.97 (d, *J* ≈ 8.6 Hz; 2Ar-H), 7.40 (d, *J* ≈ 8.5 Hz; 2Ar-H), 7.01 (d, *J* ≈ 8.9 Hz; 2Ar-H), 4.07 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHC$\underline{H}_{2a}$O), 3.96 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHC$\underline{H}_{2b}$O), 3.86-3.79 (m; 1H, C$\underline{H}$), 3.61-3.50 (m; 2H, OCH_2), 1.62-1.55 (m; 2H, $OCH_2C\underline{H}_2$), 1.37-1.22 (m; 14H, $7CH_2$), 1.29 (d, *J* ≈ 6.3 Hz; 3H, CHC$\underline{H}_3$), 0.87 (t, *J* ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 191.17 ($\underline{C}$HO), 164.35 (CO), 163.77, 156.04, 134.05, 121.27 (Ar-$\underline{C}$), 132.56, 131.40, 122.75, 114.72 (Ar-$\underline{C}$H), 73.69 (O$\underline{C}$H), 72.01, 69.86 (O$\underline{C}H_2$), 32.05, 30.21, 29.77, 29.72, 29.61, 29.47, 26.27, 22.83 (CH_2), 17.37, 14.27 (CH_3). **FT-IR** (ATR, cm^{-1}): 2917.21-2850.34 (CH), 1725.06-1698.69 2(C=O).

4-Formylphenyl 4-(*S*)-(2-(*n*-dodecyloxy)propoxy)benzoate (6c) ($C_{29}H_{40}O_5$; 468.63 g/mol)
Yield: 69%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 10.02 (s; 1H, CHO), 8.14 (d, *J* ≈ 8.9 Hz; 2Ar-H), 7.97 (d, *J* ≈ 8.6 Hz; 2Ar-H), 7.40 (d, *J* ≈ 8.5 Hz; 2Ar-H), 7.01 (d, *J* ≈ 8.9 Hz; 2Ar-H), 4.07 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHC$\underline{H}_{2a}$O), 3.96 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHC$\underline{H}_{2b}$O), 3.87-3.79 (m; 1H, C$\underline{H}$), 3.63-3.50 (m; 2H, OCH_2), 1.63-1.55 (m; 2H, $OCH_2C\underline{H}_2$), 1.42-1.18 (m; 18H, $9CH_2$), 1.29 (d, *J* ≈ 6.3 Hz; 3H, CHC$\underline{H}_3$), 0.87 (t, *J* ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 191.17 ($\underline{C}$HO), 164.34 (CO), 163.77, 156.04, 134.05, 121.27 (Ar-$\underline{C}$), 132.56, 131.39, 122.75, 114.72 (Ar-$\underline{C}$H), 73.69 (O$\underline{C}$H), 72.01, 69.86 (O$\underline{C}H_2$), 32.06, 30.21, 29.82, 29.79, 29.77, 29.61, 29.50, 26.27, 22.83 (CH_2), 17.37, 14.27 (CH_3). **FT-IR** (ATR, cm^{-1}): 2916.59-2849.75 (CH), 1725.37-1698.93 2(C=O).

1.2.1.7 4-((4-(*S*)-(2-(*n*-Alkyloxy)propoxy)benzoyloxy)benzoic acids (7a-c)

For the synthesis of 4-formylphenyl 4-(*S*)-(2-(*n*-alkyloxy)propoxy)benzoate (3.2 mmol) and resorcinol (4.11 mmol) were dissolved in *tert*-butyl alcohol (35 mL). Then, the aqueous solution of $NaClO_2$ (23.10 mmol) and $NaH_2PO_4.H_2O$ (11.99 mmol) was added dropwise with stirring to

this mixture. The mixture was stirred at room temperature for 24h. The end of reaction was monitored by TLC (hexane : ethyl acetate/5:1). After removing the solvent in vacuo, the residue was poured into 60 mL of water and then the aqueous solution was acidified to pH 2 by adding 1 N HCl. The obtained precipitate was filtered and washed with water. The crude product was purified by crystallization from ethanol.

4-((4-(*S*)-(2-(*n*-Octyloxy)propoxy)benzoyl)oxy)benzoic acid (7a) ($C_{25}H_{32}O_6$; 428.53 g/mol)
Yield: 80%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.19 (d, *J* ≈ 8.7 Hz; 2Ar-H), 8.15 (d, *J* ≈ 8.9 Hz; 2Ar-H), 7.33 (d, *J* ≈ 8.7 Hz; 2Ar-H), 7.01 (d, *J* ≈ 8.9 Hz; 2Ar-H), 4.08 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHC$\underline{H}_{2a}$O), 3.97 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHC$\underline{H}_{2b}$O), 3.89-3.79 (m; 1H, C$\underline{H}$), 3.63-3.51 (m; 2H, OCH_2), 1.62-1.55 (m; 2H, $OCH_2C\underline{H}_2$), 1.41-1.24 (m; 10H, $5CH_2$), 1.29 (d, *J* ≈ 6.3 Hz; 3H, CHC$\underline{H}_3$), 0.88 (t, *J* ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 170.71 (C$\underline{O}$OH), 164.44 (CO), 163.69, 155.58, 126.87, 121.42 (Ar-$\underline{C}$), 132.54, 132.00, 122.13, 114.69 (Ar-$\underline{C}$H), 73.72 (O$\underline{C}$H), 71.98, 69.87 (O$\underline{C}H_2$), 31.97, 30.19, 29.57, 29.43, 26.26, 22.80 (CH_2), 17.37, 14.25 (CH_3). **FT-IR** (ATR, cm^{-1}): 2924.96-2850.35 (CH), 1727.70-1682.44 2(C=O).

4-((4-(*S*)-(2-(*n*-Decyloxy)propoxy)benzoyl)oxy)benzoic acid (7b) ($C_{27}H_{36}O_6$; 456.58 g/mol)
Yield: 85%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.19 (d, *J* ≈ 8.7 Hz; 2Ar-H), 8.15 (d, *J* ≈ 8.9 Hz; 2Ar-H), 7.34 (d, *J* ≈ 8.7 Hz; 2Ar-H), 7.01 (d, *J* ≈ 8.9 Hz; 2Ar-H), 4.08 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHC$\underline{H}_{2a}$O), 3.96 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHC$\underline{H}_{2b}$O), 3.87-3.80 (m; 1H, C$\underline{H}$), 3.63-3.51 (m; 2H, OCH_2), 1.63-1.55 (m; 2H, $OCH_2C\underline{H}_2$), 1.38-1.21 (m; 14H, $7CH_2$), 1.30 (d, *J* ≈ 6.3 Hz; 3H, CHC$\underline{H}_3$), 0.88 (t, *J* ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 170.35 (C$\underline{O}$OH), 164.43 (CO), 163.70, 155.61, 126.73, 121.42 (Ar-$\underline{C}$), 132.55, 132.02, 122.15, 114.69 (Ar-$\underline{C}$H), 73.71 (O$\underline{C}$H), 71.99, 69.87 (O$\underline{C}H_2$), 32.05, 30.21, 29.78, 29.73, 29.62, 29.48, 26.27, 22.83 (CH_2), 17.38, 14.27 (CH_3). **FT-IR** (ATR, cm^{-1}): 2914.91-2848.84 (CH), 1735.45-1687.16 2(C=O).

4-((4-(*S*)-(2-(*n*-Dodecyloxy)propoxy)benzoyl)oxy)benzoic acid (7c) ($C_{29}H_{40}O_6$; 484.63 g/mol)
Yield: 82%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.19 (d, *J* ≈ 8.5 Hz; 2Ar-H), 8.15 (d, *J* ≈ 8.7 Hz; 2Ar-H), 7.34 (d, *J* ≈ 8.5 Hz; 2Ar-H), 7.01 (d, *J* ≈ 8.7 Hz; 2Ar-H), 4.08 (dd, *J* ≈ 9.5, 6.0 Hz; 1H, CHC$\underline{H}_{2a}$O), 3.97 (dd, *J* ≈ 9.6, 4.6 Hz; 1H, CHC$\underline{H}_{2b}$O), 3.88-3.78 (m; 1H, C$\underline{H}$), 3.63-3.49 (m; 2H, OCH_2), 1.63-1.55 (m; 2H, $OCH_2C\underline{H}_2$), 1.41-1.17 (m; 18H, $9CH_2$), 1.30 (d, *J* ≈ 6.3 Hz; 3H, CHC$\underline{H}_3$), 0.88 (t, *J* ≈ 6.8 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 170.84 (C$\underline{O}$OH), 164.43 (CO), 163.69, 155.62, 126.79, 121.41 (Ar-$\underline{C}$), 132.55, 132.02, 122.14, 114.69 (Ar-$\underline{C}$H), 73.72 (O$\underline{C}$H), 71.98, 69.87 (O$\underline{C}H_2$), 32.07, 30.20, 29.82, 29.79, 29.77, 29.62, 29.50, 26.26, 22.84 (CH_2), 17.37, 14.27 (CH_3). **FT-IR** (ATR, cm^{-1}): 2914.89-2848.91 (CH), 1736.73-1686.40 2(C=O).

1.2.2 4-[4-(*n*-Alkyloxy)benzoyloxy]benzoic acids and their chlorides (Cl-8a-c):

For the synthesis of 4-[4-(*n*-alkyloxy)benzoyloxy]benzoic acids[11] (**8**), the procedure which were reported on our previous studies was carried out[12]. Ethyl 4-hydroxybenzoate was firstly alkylated with the appropriate alkyl bromides (*n*-octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide), followed by hydrolysis of the ester group. The procedures of esterification with commecially available 4-hydroxybenzaldehyde and then $NaClO_2$ oxidation, which are the following steps starting from 4-*n*-alkyloxybenzoic acids, are the same as for the synthesis of the rod-like units **7a-c.** Spectroscopic data (^{1}H-NMR and ^{13}C-NMR) of the obtained compounds 4-(4-*n*-alkyloxybenzoyloxy)benzoic acids (**8**) are in aggrement with the expected structure as

well as those given in the literature[11]. 4-[4-(*n*-Alkyloxy)benzoyloxy]benzoic acids (**8**), (1.0 mmol) was reacted with oxalyl chloride (1.5 mL) and this mixture was refluxed for 4h. The end of reaction is checked by TLC ($CHCl_3$:MeOH/9:1) and then the excess of oxalyl chloride was removed by vacuum distillation.

4-[4-(*n*-Octyloxy)benzoyloxy)benzoyl chloride (Cl-8a) ($C_{22}H_{25}ClO_4$: 388.89 g/mol)[13]
Yield: 87 %, colorless crystal. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.21 (d; $J \approx 8.8$ Hz; 2Ar-H), 8.13 (d; $J \approx 8.8$ Hz; 2Ar-H), 7.39 (d; $J \approx 8.8$ Hz; 2Ar-H), 6.99 (d; $J \approx 8.8$ Hz; 2Ar-H), 4.05 (t; $J \approx 8.7$ Hz; OCH_2), 1.85-1.80 (m; 2H, $OCH_2C\underline{H}_2$), 1.51-1.45 (m; 2H, $OCH_2CH_2C\underline{H}_2$), 1.38-1.25 (m; 8H, $4CH_2$), 0.90 (t; $J \approx 6.9$ Hz; 3H, CH_3).

4-[4-(*n*-Decyloxy)benzoyloxy)benzoyl chloride (Cl-8b) ($C_{24}H_{29}ClO_4$: 416.94 g/mol)[13]
Yield: 83 %, colorless crystal. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.20 (d; $J \approx 8.8$ Hz; 2Ar-H), 8.13 (d; $J \approx 8.8$ Hz; 2Ar-H), 7.39 (d; $J \approx 8.8$ Hz; 2Ar-H), 6.98 (d; $J \approx 8.8$ Hz; 2Ar-H), 4.05 (t; $J \approx 8.7$ Hz; OCH_2), 1.85-1.82 (m; 2H, $OCH_2C\underline{H}_2$), 1.49-1.44 (m; 2H, $OCH_2CH_2C\underline{H}_2$), 1.34-1.28 (m; 12H, $6CH_2$), 0.88 (t; $J \approx 6.9$ Hz; 3H, CH_3).

4-(4-(*n*-Dodecyloxy)benzoyloxy)benzoyl chloride (Cl-8c) ($C_{26}H_{33}ClO_4$: 445.00 g/mol)[13]
Yield: 81 %, colorless crystal. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.20 (d; $J \approx 8.8$ Hz; 2Ar-H), 8.14 (d; $J \approx 8.8$ Hz; 2Ar-H), 7.39 (d; $J \approx 8.8$ Hz; 2Ar-H), 6.99 (d; $J \approx 8.8$ Hz; 2Ar-H), 4.05 (t; $J \approx 8.7$ Hz; OCH_2), 1.85-1.80 (m; 2H, $OCH_2C\underline{H}_2$), 1.50-1.45 (m; 2H, $OCH_2CH_2C\underline{H}_2$), 1.35-1.27 (m; 16H, $8CH_2$), 0.88 (t; $J \approx 6.9$ Hz; 3H, CH_3).

1.2.3 2,4-Dihydroxybenzonitrile and 4-benzyloxy-2-hydroxybenzonitrile

2,4-Dihydroxybenzonitrile was synthesized from commercially available 2,4-dihydroxybenzaldehyde by the formation of the oxime, followed by dehydration as described in Ref.[14]. **Yield:** 72%, colorless crystals.**^{1}H-NMR** (500 MHz, DMSO-d_6): δ (ppm) = 10.81 (s; 1Ar-OH), 10.37 (s; 1Ar-OH), 7.36 (d, $J \approx 8.6$ Hz; 1Ar-H), 6.40 (d, $J \approx 2.1$ Hz; 1Ar-H), 6.31 (dd, $J \approx 8.6$ Hz and $J \approx 2.2$ Hz; 1Ar-H).**^{13}C-NMR** (125 MHz, DMSO-d_6): δ (ppm) = 162.85, 161.88, 89.49 (Ar-$\underline{C}$), 134.48, 108.14, 102.37 (Ar-$\underline{C}$H), 117.79 ($\underline{C}$N).

4-Benzyloxy-2-hydroxybenzonitrile (9)[15]
The synthesis of 4-benzyloxy-2-hydroxybenzonitrile (**9**) was carried out by the similar method[15] which is mentioned for 2,4-dihydroxybenzonitrile. Commercially available 4-benzyloxy-2-hydroxybenzaldehyde was reacted with aqueous solution of hydroxylamine hydrochloride ($NH_2OH.HCl$) at room temperature to yield the formation of the oxime firstly and then followed by acetylation and dehydration. Spectroscopic data (^{1}H-NMR and ^{13}C-NMR) of the obtained compounds are in agreement with the expected structure as well as those previously reported in Ocak et al.[16,17]. **Yield:** 66%, colorless crystals.**^{1}H-NMR** (500 MHz, DMSO-d_6): δ (ppm) = 11.09 (s, 1H, OH), 7.52 (d, $J \approx 8.7$ Hz; Ar-H), 7.45-7.39, 7.37-7.33 (2m; 5 Ar-H), 6.61 (dd, $J \approx 8.7$ Hz and $J \approx 2.4$ Hz; Ar-H), 6.57 (d, $J \approx 2.3$ Hz; Ar-H), 5.13 (s, 2H, OCH_2). **^{13}C-NMR** (125 MHz, DMSO-d_6): δ (ppm) = 163.03, 161.76, 136.19, 91.41 (4 Ar-$\underline{C}$), 134.37, 128.49, 128.06, 127.78, 107.22, 101.91 (8 Ar-$\underline{C}$H), 117.29 ($\underline{C}$N), 69.50 (O$\underline{C}H_2$).

1.2.4 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoates (10a-c)

For the synthesis of 2-cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoates (**10a-c**), the mixture of 4-benzyloxy-2-hydroxybenzonitrile (**9**) (5 mmol), (*S*)-4-((4-(2-(*n*-alkyloxy)propoxy)benzoyl)oxy)benzoic acid (**7**) (5.0 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (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 ($CHCl_3$). The reaction mixture was filtered on silica gel with CH_2Cl_2 and the solvent was evaporated. The crude product was purified by column chromatography on silica gel 60 using $CHCl_3$ as eluent.

2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate ($C_{39}H_{41}NO_7$; 635.74 g/mol) (10a)
Yield: 63%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.32 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.17 (d; $J \approx 8.9$ Hz; 2Ar-H), 7.63 (d; $J \approx 8.7$ Hz; Ar-H), 7.42–7.37 (m; 5 Ar-H), 7.40 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.11 (d; $J \approx 2.4$ Hz; Ar-H), 7.02 (d; $J \approx 8.7$ Hz; 2 Ar-H), 6.95 (dd; $J \approx$ 8.7 Hz and 2.4 Hz; Ar-H), 5.13 (s; 2H, O$\underline{CH_2}$Ph), 4.08 (dd, $J \approx 9.7$, 6.0 Hz; 1H, CHC$\underline{H_{2a}}$O), 3.97 (dd, $J \approx 9.7$, 4.7 Hz; 1H, CHC$\underline{H_{2b}}$O), 3.86-3.80 (m; 1H, CH), 3.61-3.51 (m; 2H, O$\underline{CH_2}$CH), 1.58-1.51 (m; 2H, OCH$_2$C$\underline{H_2}$), 1.34-1.25 (m; 10H, 5CH$_2$), 1.25 (d; $J \approx 6.9$ Hz; 3H, CHC$\underline{H_3}$), 0.88 (t; $J \approx 6.9$ Hz; 3H, CH$_3$). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.34, 163.74 ($\underline{C}$OO), 163.35, 163.17, 156.03, 154.25, 135.33, 125.70, 121.32, 115.72, 98.95 (Ar-$\underline{C}$), 134.37, 132.59, 132.35, 128.96, 128.71, 127.75, 122.49, 114.71, 113.51, 109.98 (Ar-$\underline{C}$H), 73.70 (CH), 72.00, 70.89, 69.86 (O$\underline{C}$H$_2$), 31.98, 30.21, 29.57, 29.43, 26.27, 22.81 ($\underline{C}$H$_2$), 17.38, 14.25 ($\underline{C}$H$_3$).

2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate ($C_{41}H_{45}NO_7$; 663.81 g/mol) (10b)
Yield: 67%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.18 (d; $J \approx 8.9$ Hz; 2Ar-H), 7.65 (d; $J \approx 8.7$ Hz; Ar-H), 7.45–7.41 (m; 5 Ar-H), 7.43 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.13 (d; $J \approx 2.4$ Hz; Ar-H), 7.04 (d; $J \approx 8.7$ Hz; 2 Ar-H), 6.97 (dd; $J \approx$ 8.7 Hz and 2.4 Hz; Ar-H), 5.16 (s; 2H, O$\underline{CH_2}$Ph), 4.10 (dd, $J \approx 9.7$, 6.0 Hz; 1H, CHC$\underline{H_{2a}}$O), 3.99 (dd, $J \approx 9.7$, 4.7 Hz; 1H, CHC$\underline{H_{2b}}$O), 3.89-3.83 (m; 1H, CH), 3.64-3.54 (m; 2H, O$\underline{CH_2}$CH), 1.64-1.61 (m; 2H, OCH$_2$C$\underline{H_2}$), 1.36-1.28 (m; 14H, 7CH$_2$), 1.31 (d; $J \approx 6.9$ Hz; 3H, CHC$\underline{H_3}$), 0.90 (t; $J \approx 6.9$ Hz; 3H, CH$_3$). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.20, 163.61 (2 $\underline{C}$OO), 163.22, 163.04, 155.90, 154.12, 135.30, 125.67, 121.17, 115.59, 98.82 (9 Ar-$\underline{C}$), 134.24, 132.46, 132.18,128.80, 128.58, 127.62, 122.35, 114.57, 113.38, 109.85 (10 Ar-$\underline{C}$H), 73.56 (CH), 71.87, 70.76, 69.73 (3 O$\underline{C}$H$_2$), 31.92, 30.08, 29.64, 29.59, 29.48, 29.34, 26.14, 22.70 (8 $\underline{C}$H$_2$), 17.25, 14.16 (2 $\underline{C}$H$_3$).

2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate ($C_{43}H_{49}NO_7$; 691.85 g/mol) (10c)
Yield: 84%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.33 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.16 (d; $J \approx 8.9$ Hz; 2Ar-H), 7.63 (d; $J \approx 8.7$ Hz; Ar-H), 7.43–7.37 (m; 5 Ar-H), 7.40 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.11 (d; $J \approx 2.4$ Hz; Ar-H), 7.02 (d; $J \approx 8.7$ Hz; 2 Ar-H), 6.95 (dd; $J \approx$ 8.7 Hz and 2.4 Hz; Ar-H), 5.13 (s; 2H, O$\underline{CH_2}$Ph), 4.08 (dd, $J \approx 9.7$, 6.0 Hz; 1H, CHC$\underline{H_{2a}}$O), 3.97 (dd, $J \approx 9.7$, 4.7 Hz; 1H, CHC$\underline{H_{2b}}$O), 3.86-3.80 (m; 1H, CH), 3.61-3.52 (m; 2H, O$\underline{CH_2}$CH), 1.61-1.59 (m; 2H, OCH$_2$C$\underline{H_2}$), 1.33-1.26 (m; 18H, 9CH$_2$), 1.29 (d; $J \approx 6.9$ Hz; 3H, CHC$\underline{H_3}$), 0.88 (t; $J \approx 6.9$ Hz; 3H, CH$_3$). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.20, 163.61 ($\underline{C}$OO), 163.22, 163.04, 155.90, 154.12, 135.31, 125.65, 121.19, 115.99, 98.83 (Ar-$\underline{C}$), 134.24, 132.46,

132.22, 128.83, 128.58, 127.62, 122.36, 114.58, 113.38, 109.85 (Ar-CH), 73.56 (CH), 71.87, 70.76, 69.74 (OCH_2), 31.94, 30.08, 29.69, 29.66, 29.64, 29.49, 29.45, 29.37, 26.14, 22.71 (CH_2), 17.18, 14.14 (CH_3).

1.2.5 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoates (11-OHa-c)

For the synthesis of 2-cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoates (**11-OHa-c**), 2-cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoates (**10a-c**) (2.5 mmol) was dissolved in THF (40 mL) and a catalytic amount of Pd/C-5% and a few drops of cyclohexene were added to this solution. The mixture was stirred in previously argon-flushed flask at 40 °C under H_2 gas for 8h. The end of reaction was monitored by TLC ($CHCl_3$). 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 60, eluting with $CHCl_3$:EA/10:1.

2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate ($C_{32}H_{35}NO_7$: 545.62 g/mol) (11-OHa)
Yield: 82%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.28 (d; *J* ≈ 8.7 Hz; 2Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 2Ar-H), 7.56 (d; *J* ≈ 8.7 Hz; Ar-H), 7.38 (d; *J* ≈ 8.7 Hz; Ar-H), 7.00 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 2.4 Hz; Ar-H), 6.79 (dd; *J* ≈ 8.7 Hz and 2.4 Hz; Ar-H), 4.08 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHCH_{2a}O), 3.99 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHCH_{2b}O), 3.88-3.82 (m; 1H, CH), 3.63-3.54 (m; 2H, OCH_2CH), 1.61-1.58 (m; 2H, OCH_2CH_2), 1.35-1.26 (m; 10H, $5CH_2$), 1.30 (d; *J* ≈ 6.9 Hz; 3H, CHCH_3), 0.88 (t; *J* ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.53, 163.74 (COO), 163.37, 161.08, 155.99, 154.16, 125.78, 121.24, 115.83, 98.29 (Ar-C), 134.64, 132.63, 132.37, 122.49, 114.70, 114.19, 110.81 (Ar-CH), 73.81 (CH), 71.88, 69.94 (OCH_2), 31.97, 30.15, 29.56, 29.42, 26.25, 22.81 (CH_2), 17.33, 14.26 (CH_3).

2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate ($C_{34}H_{39}NO_7$: 573.69 g/mol) (11-OHb)
Yield: 89%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.31 (d; *J* ≈ 8.7 Hz; 2Ar-H), 8.16 (d; *J* ≈ 8.9 Hz; 2Ar-H), 7.57 (d; *J* ≈ 8.7 Hz; Ar-H), 7.40 (d; *J* ≈ 8.7 Hz; Ar-H), 7.03 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.99 (d; *J* ≈ 2.4 Hz; Ar-H), 6.80 (dd; *J* ≈ 8.7 Hz and 2.4 Hz; Ar-H), 4.09 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHCH_{2a}O), 4.01 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHCH_{2b}O), 3.91-3.85 (m; 1H, CH), 3.65-3.57 (m; 2H, OCH_2CH), 1.65-1.59 (m; 2H, OCH_2CH_2), 1.34-1.28 (m; 14H, $7CH_2$), 1.32 (d; *J* ≈ 6.9 Hz; 3H, CHCH_3), 0.90 (t; *J* ≈ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.42, 163.60 (2 COO), 163.26, 161.08, 155.85, 154.02, 125.67, 121.10, 115.73, 98.07 (8 Ar-C), 134.49, 132.50, 132.23, 122.36, 114.57, 114.08, 110.67 (7 Ar-CH), 73.69 (CH), 71.73, 69.79 (2 OCH_2), 31.91, 30.00, 29.63, 29.58, 29.47, 29.34, 26.11, 22.70 (8 CH_2), 17.20, 14.14 (2 CH_3).

2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate ($C_{36}H_{43}NO_7$: 601.73 g/mol) (11-OHc)
Yield: 88%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.29 (d; *J* ≈ 8.7 Hz; 2Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 2Ar-H), 7.56 (d; *J* ≈ 8.7 Hz; Ar-H), 7.39 (d; *J* ≈ 8.7 Hz; Ar-H), 7.01 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 2.4 Hz; Ar-H), 6.79 (dd; *J* ≈ 8.7 Hz and 2.4 Hz; Ar-H), 4.07 (dd, *J* ≈ 9.7, 6.0 Hz; 1H, CHCH_{2a}O), 3.98 (dd, *J* ≈ 9.7, 4.7 Hz; 1H, CHCH_{2b}O), 3.88-3.82 (m; 1H, CH), 3.63-3.54 (m; 2H, OCH_2CH), 1.63-1.57 (m; 2H, OCH_2CH_2), 1.31-1.26 (m;

18H, 9CH_2), 1.30 (d; $J \approx$ 6.9 Hz; 3H, CHC$\underline{H}_3$), 0.88 (t; $J \approx$ 6.9 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.39, 163.59 (C$\underline{O}$O), 163.25, 161.02, 155.85, 154.02, 125.65, 121.11, 115.71, 98.11 (Ar-$\underline{C}$), 134.49, 132.50, 132.23, 122.36, 114.57, 114.07, 110.68 (Ar-$\underline{C}$H), 73.68 (CH), 71.74, 69.82 (O$\underline{C}H_2$), 31.94, 30.01, 29.69, 29.66, 29.63, 29.47, 29.45, 29.37, 26.07, 22.71 ($\underline{C}H_2$), 17.21, 14.14 ($\underline{C}H_3$).

1. 3 Synthesis of compounds I and II

For the synthesis of 4-cyano-1,3-phenylene bis(4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoates (**Ia-c**), 1.2 mmol of (*S*)-4-((4-(2-(*n*-alkyloxy)propoxy)benzoyl)oxy)benzoic acids (**7a-c**) was refluxed with 7 mL of oxalyl chloride for 7 hours and then the excess of oxalyl chloride was removed by vacuum distillation. To the solution of the obtained product, 2,4-Dihydroxybenzonitrile (0.55 mmol), dry pyridine (4 mL) and 4-(dimethylamino)pyridine (DMAP) (0.19 mmol) in dry dichloromethane (25 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/3:1). The mixture was poured into 10 mL of water and then the aqueous solution was neutralized to pH 7 by adding 1 N HCl. Adjust the reaction mixture to pH around 7 with 1 N HCl. The mixture was extracted into CH_2Cl_2 (x 3) and the combined organic phases were washed with saturated aqueous $NaHCO_3$ solution and 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 and crystallized from CH_2Cl_2-EtOH solvent pair.
The synthesis and purification steps of 4-{4-[4-(*n*-alkyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-alkyloxypropoxy)benzoyloxy]benzoyloxy}benzonitriles (**IIa-c**) were carried out in a similar procedure to those of **Ia-c**. The mixture of 0.6 mmol of 2-cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-alkyloxypropoxy)benzoyl)oxy)benzoate) (**11-OHa-c**) with 1.2 mmol of 4-(4-*n*-alkyloxybenzoyloxy)benzoyl chlorides (**Cl-8a-c**), that are acylated derivatives obtained by the reaction of the corresponding acids **8a-c** with oxalyl chloride, dry pyridine (5 mL) and catalytic amount of 4-(dimethylamino)pyridine (DMAP) in dry dichloromethane (20 mL) were stirred at room temperature under an argon atmosphere for 24 h. The procedure for the end of the reaction and purification steps are the same with those of compounds **Ia-c**.

4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (Ia)
Yield: 60%, colorless crystals.**^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.33 (d, $J \approx$ 8.7 Hz; 2Ar-H), 8.27 (d, $J \approx$ 8.7 Hz; 2Ar-H), 8.17 (d, $J \approx$ 2.7 Hz; 2Ar-H), 8.15 (d, $J \approx$ 2.7 Hz; 2Ar-H), 7.80 (d, $J \approx$ 8.5 Hz; 1Ar-H), 7.54 (d, $J \approx$ 2.0 Hz; 1Ar-H), 7.40 (2d, $J \approx$ 8.6, 5.1 Hz; 4Ar-H), 7.33 (dd, $J \approx$ 8.5, 2.1 Hz; 1Ar-H), 7.02 (d, $J \approx$ 8.8 Hz; 4Ar-H) 4.08 (dd, $J \approx$ 9.6, 6.0 Hz; 2H, 2CHC$\underline{H}_{2a}$O), 3.97 (dd, $J \approx$ 9.6, 4.7 Hz; 2H, 2CHC$\underline{H}_{2b}$O), 3.87-3.79 (m; 2H, 2CH), 3.62-3.50 (m; 4H, 2OCH_2), 1.63-1.55 (m; 4H, 2O$CH_2C\underline{H}_2$), 1.41-1.19 (m; 20H, 10CH_2), 1.30 (d, $J \approx$ 6.3 Hz; 6H, 2CHC$\underline{H}_3$), 0.88 (t, $J \approx$ 6.8 Hz; 6H, 2CH_3).**^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 164.33, 164.29, 163.78, 163.74 (C$\underline{O}$), 163.44, 163.06, 156.16, 156.02, 154.92, 153.60, 125.86, 125.48, 121.30, 121.24, 104.40 (Ar-$\underline{C}$), 134.13, 132.59, 132.57, 132.42, 132.17, 122.55, 122.50, 120.20, 117.57, 114.73, 114.71 (Ar-$\underline{C}$H), 114.94 ($\underline{C}$N), 73.69 (O$\underline{C}$H), 72.01, 69.85 (O$\underline{C}H_2$), 31.97, 30.20, 29.57, 29.42, 26.27, 22.80 ($\underline{C}H_2$), 17.38, 17.36 (CH$\underline{C}H_3$), 14.25 ($\underline{C}H_3$). **FT-IR** (ATR, cm^{-1}): 2925.30-2854.26 (C-H), 2232.40 (C≡N), 1734.63 (C=O), 1247.27 (C-O).

4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (Ib)
Yield: 42%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.33 (d, $J \approx$ 8.7 Hz; 2Ar-H), 8.27 (d, $J \approx$ 8.7 Hz; 2Ar-H), 8.17 (d, $J \approx$ 2.7 Hz; 2Ar-H), 8.15 (d, $J \approx$ 2.8 Hz; 2Ar-H), 7.80 (d, $J \approx$ 8.5 Hz; 1Ar-H), 7.54 (d, $J \approx$ 2.2 Hz; 1Ar-H), 7.40 (2d, $J \approx$ 8.7, 5.0 Hz; 4Ar-

H), 7.33 (dd, $J \approx 8.5, 2.2$ Hz; 1Ar-H), 7.01 (d, $J \approx 8.9$ Hz; 4Ar-H) 4.08 (dd, $J \approx 9.5, 5.9$ Hz; 2H, 2CHC$\underline{H_{2a}}$O), 3.97 (dd, $J \approx 9.7, 4.7$ Hz; 2H, 2CHC$\underline{H_{2b}}$O), 3.87-3.79 (m; 2H, 2CH), 3.62-3.50 (m; 4H, 2OCH_2), 1.63-1.54 (m; 4H, 2OCH_2C$\underline{H_2}$), 1.39-1.20 (m; 28H, 14CH_2), 1.30 (d, $J \approx 6.3$ Hz; 6H, 2CHC$\underline{H_3}$), 0.88 (t, $J \approx 6.9$ Hz; 6H, 2CH_3).**^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 164.34, 164.29, 163.79, 163.75 (C=O), 163.45, 163.06, 156.17, 156.03, 154.93, 153.61, 125.87, 125.48, 121.31, 121.25, 104.41 (Ar-C), 134.14, 132.60, 132.58, 132.43, 132.18, 122.55, 122.50, 120.21, 117.58, 114.73, 114.71 (Ar-CH), 114.94 (CN), 73.69 (OCH), 72.01, 69.87 (O$\underline{C}H_2$), 32.05, 30.21, 29.77, 29.72, 29.62, 29.48, 26.27, 22.83 ($\underline{C}H_2$), 17.39, 17.37 (CH$\underline{C}H_3$), 14.27 ($\underline{C}H_3$). **FT-IR** (ATR, cm^{-1}): 2920.43-2851.52 (C-H), 2232.52 (C≡N), 1731.89 (C=O), 1248.96 (C-O).

4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (Ic)
Yield: 47%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm)= 8.34 (d, $J \approx 8.7$ Hz; 2Ar-H), 8.27 (d, $J \approx 8.7$ Hz; 2Ar-H), 8.17 (d, $J \approx 2.7$ Hz; 2Ar-H), 8.15 (d, $J \approx 2.8$ Hz; 2Ar-H), 7.81 (d, $J \approx 8.5$ Hz; 1Ar-H), 7.54 (d, $J \approx 2.1$ Hz; 1Ar-H), 7.40 (2d, $J \approx 8.7, 5.0$ Hz; 4Ar-H), 7.33 (dd, $J \approx 8.5, 2.1$ Hz; 1Ar-H), 7.02 (d, $J \approx 8.9$ Hz; 4Ar-H) 4.08 (dd, $J \approx 9.6, 6.0$ Hz; 2H, 2CHC$\underline{H_{2a}}$O), 3.97 (dd, $J \approx 9.7, 4.7$ Hz; 2H, 2CHC$\underline{H_{2b}}$O), 3.87-3.79 (m; 2H, 2CH), 3.62-3.50 (m; 4H, 2OCH_2), 1.62-1.54 (m; 4H, 2OCH_2C$\underline{H_2}$), 1.40-1.19 (m; 36H, 18CH_2), 1.30 (d, $J \approx 6.3$ Hz; 6H, 2CHC$\underline{H_3}$), 0.88 (t, $J \approx 6.9$ Hz; 6H, 2CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm)= 164.33, 164.29, 163.79, 163.75 (C=O), 163.45, 163.07, 156.17, 156.03, 154.93, 153.61, 125.87, 125.49, 121.32, 121.25, 104.41 (Ar-C), 134.14, 132.60, 132.58, 132.43, 132.18, 122.56, 122.50, 120.21, 117.58, 114.73, 114.71 (Ar-CH), 114.95 (CN), 73.69 (OCH), 72.01, 69.87 (O$\underline{C}H_2$), 32.07, 30.22, 29.82, 29.77, 29.77, 29.62, 29.51, 26.28, 22.83 ($\underline{C}H_2$), 17.39, 17.38 (CH$\underline{C}H_3$), 14.27 ($\underline{C}H_3$). **FT-IR** (ATR, cm^{-1}): 2916.09-2850.22 (C-H), 2232.43 (C≡N), 1731.83 (C=O), 1249.15 (C-O).

4-{4-[4-(*n*-Octyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-octyloxypropoxy) benzoyloxy]benzoyloxy}benzonitrile (IIa)
Yield: 55%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.27 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.17 (d; $J \approx 4.5$ Hz; 2Ar-H), 8.15 (d; $J \approx 4.5$ Hz; 2Ar-H), 7.81 (d; $J \approx 8.7$ Hz; Ar-H), 7.54 (d; $J \approx 8.7$ Hz; Ar-H), 7.42 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.40 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.33 (dd; $J \approx 8.7$ Hz and 2.4 Hz; Ar-H), 7.02 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.99 (d; $J \approx 8.9$ Hz; 2 Ar-H), 4.09-4.04 (m; 3H, OC$\underline{H_2}$CH_2, CHC$\underline{H_{2a}}$O), 3.97 (dd, $J \approx 9.7, 4.7$ Hz; 1H, CHC$\underline{H_{2b}}$O), 3.85-3.81 (m; 1H, CH), 3.60-3.53 (m; 2H, OC$\underline{H_2}$CH_2), 1.84-1.80 (m; 2H, OCH_2C$\underline{H_2}$), 1.50-1.45 (m; 2H, OCH_2C$\underline{H_2}$), 1.35-1.28 (m; 20H, 10CH_2), 1.29 (d; $J \approx 6.9$ Hz; 3H, CHC$\underline{H_3}$), 0.88 (t; $J \approx 6.9$ Hz; 6H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.27, 164.17, 163.92, 163.62 (COO), 163.33, 162.94, 156.04, 155.93, 154.80, 153.48, 125.71, 125.35, 121.18, 120.79, 104.27 (Ar-C), 134.01, 132.47, 132.30, 132.04, 122.42, 122.38, 120.08, 117.44, 114.60, 114.46 (Ar-CH), 114.81 (CN), 73.56 (CH), 71.88, 69.73, 68.43 (O$\underline{C}H_2$), 31.85, 31.81, 30.08, 29.44, 29.33, 29.30, 29.23, 29.09, 26.14, 25.99, 22.67 ($\underline{C}H_2$), 17.26, 14.12 ($\underline{C}H_3$). **FT-IR** (ATR, cm^{-1}): 2921.52-2852.26 (C-H), 2232.52 (C≡N), 1733.33 (C=O), 1247.58 (C-O).

4-{4-[4-(*n*-Decyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-decyloxypropoxy) benzoyloxy]benzoyloxy}benzonitrile (IIb)
Yield: 49%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.27 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.17 (d; $J \approx 4.5$ Hz; 2Ar-H), 8.15 (d; $J \approx 4.5$ Hz; 2Ar-H), 7.81 (d; $J \approx 8.7$ Hz; Ar-H), 7.54 (d; $J \approx 8.7$ Hz; Ar-H), 7.42 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.34 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.32 (dd; $J \approx 8.7$ Hz and 2.4 Hz; Ar-H), 7.02 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.99 (d; $J \approx 8.9$ Hz; 2 Ar-H), 4.10-4.04 (m; 3H, OC$\underline{H_2}$CH_2, CHC$\underline{H_{2a}}$O), 3.97 (dd, $J \approx 9.7, 4.7$ Hz; 1H, CHC$\underline{H_{2b}}$O), 3.86-3.82 (m; 1H, CH), 3.61-3.52 (m; 2H, OC$\underline{H_2}$CH_2), 1.86-1.80 (m; 2H,

$OCH_2C\underline{H}_2$), 1.58 (d; $J \approx 6.9$ Hz; 3H, $CHC\underline{H}_3$), 1.51-1.45 (m; 2H, $OCH_2C\underline{H}_2$), 1.30-1.26 (m; 28H, $14CH_2$), 0.88 (t; $J \approx 6.9$ Hz; 6H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.26, 164.16, 163.92, 163.61 (4 $\underline{C}OO$), 163.33, 162.93, 156.04, 155.93, 154.80, 153.48, 125.71, 125.35, 121.18, 120.79, 104.27 (11 Ar-$\underline{C}$), 134.00, 132.47, 132,30, 132.04, 122.42, 122.38, 120.08, 117.44, 114.58, 114.46 (10 Ar-$\underline{C}H$), 114.81 ($\underline{C}N$), 73.56 ($\underline{C}H$), 71.88, 69.73, 68.43 (3 $O\underline{C}H_2$), 31.91, 30.08, 30.08, 29.64, 29.59, 29.57, 29.57, 29.49, 29.37, 29.34, 29.33, 29.09, 29.09, 26.14, 25.99, 22.70 (16 $\underline{C}H_2$), 17.26, 14.14, 14.14 (3 $\underline{C}H_3$). **FT-IR** (ATR, cm^{-1}): 2921.53-2852.32 (C-H), 2232.49 (C≡N), 1732.88 (C=O), 1247.94 (C-O).

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

Yield: 52%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.27 (d; $J \approx 8.7$ Hz; 2Ar-H), 8.17 (d; $J \approx 4.5$ Hz; 2Ar-H), 8.15 (d; $J \approx 4.5$ Hz; 2Ar-H), 7.81 (d; $J \approx 8.7$ Hz; Ar-H), 7.54 (d; $J \approx 8.7$ Hz; Ar-H), 7.42 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.40 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.35 (dd; $J \approx 8.7$ Hz and 2.4 Hz; Ar-H), 7.02 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.99 (d; $J \approx 8.9$ Hz; 2 Ar-H), 4.10-4.04 (m; 3H, $OC\underline{H}_2CH_2$, $CHC\underline{H}_{2a}O$), 3.97 (dd, $J \approx 9.7$, 4.7 Hz; 1H, $CHC\underline{H}_{2b}O$), 3.85-3.82 (m; 1H, CH), 3.60-3.53 (m; 2H, $OC\underline{H}_2CH_2$), 1.86-1.80 (m; 2H, $OCH_2C\underline{H}_2$), 1.50-1.46 (m; 2H, $OCH_2C\underline{H}_2$), 1.34-1.26 (m; 36H, $18CH_2$), 1.29 (d; $J \approx 6.9$ Hz; 3H, $CHC\underline{H}_3$), 0.88 (t; $J \approx 6.9$ Hz; 6H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.26, 164.16, 163.92, 163.61 ($\underline{C}OO$), 163.33, 162.93, 156.04, 155.93, 154.80, 153.48, 125.71, 125.35, 121.18, 120.79, 104.27 (Ar-$\underline{C}$), 134.01, 132.47, 132.30, 132.04, 122.42, 122.38, 120.08, 117.48, 114.58, 114.46 (Ar-$\underline{C}H$), 114.81 ($\underline{C}N$), 73.56 ($\underline{C}H$), 71.87, 69.74, 68.43 ($O\underline{C}H_2$), 31.93, 30.08, 29.69, 29.67, 29.64, 29.60, 29.57, 29.49, 29.37, 29.09, 26.14, 25.99, 22.71 ($\underline{C}H_2$), 17.26, 14.07 ($\underline{C}H_3$). **FT-IR** (ATR, cm^{-1}): 2921.53-2852.32 (C-H), 2232.49 (C≡N), 1732.88 (C=O), 1247.94 (C-O).

1.4. NMR Spectra of Intermediates

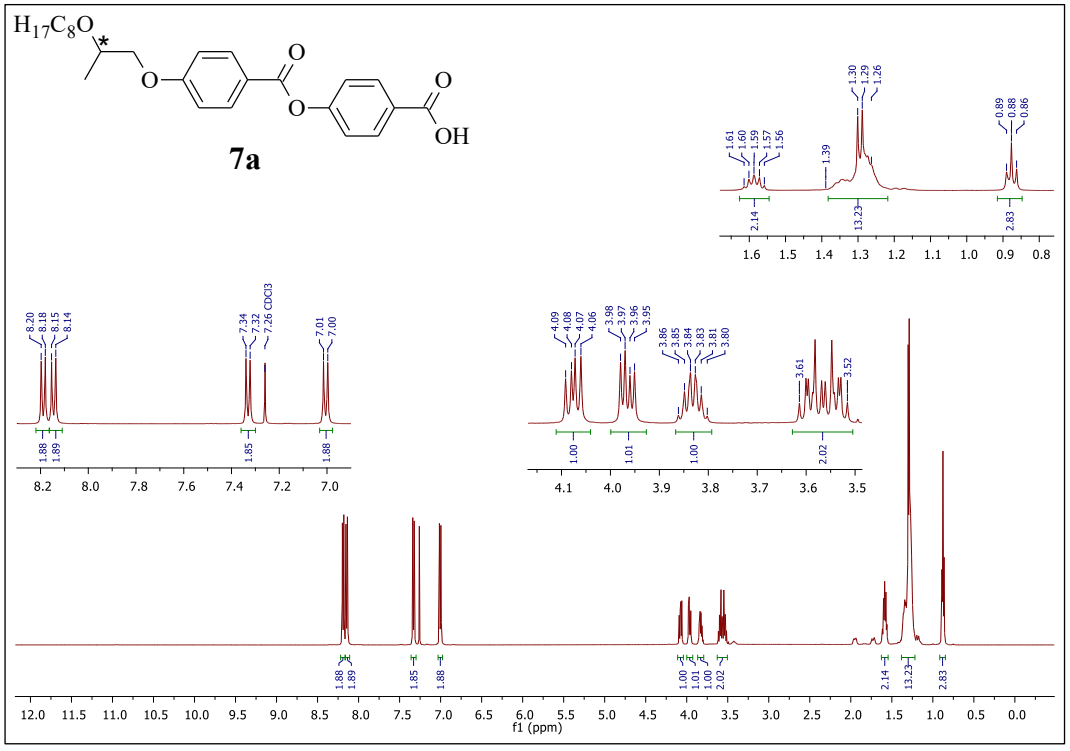


Figure S1. ^{1}H-NMR spectrum of 4-((4-(*S*)-(2-(*n*-Octyloxy)propoxy)benzoyl)oxy)benzoic acid (**7a**).

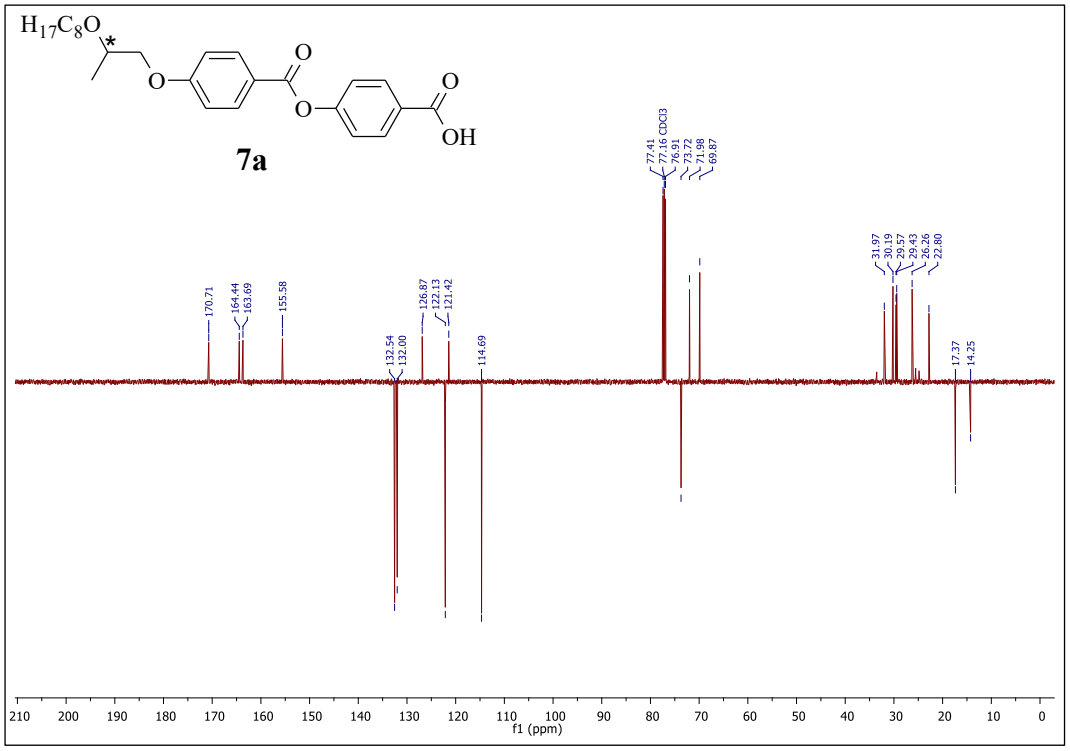


Figure S2. ^{13}C-NMR (APT) spectrum of 4-((4-(*S*)-(2-(*n*-Octyloxy)propoxy)benzoyl)oxy)benzoic acid (**7a**).

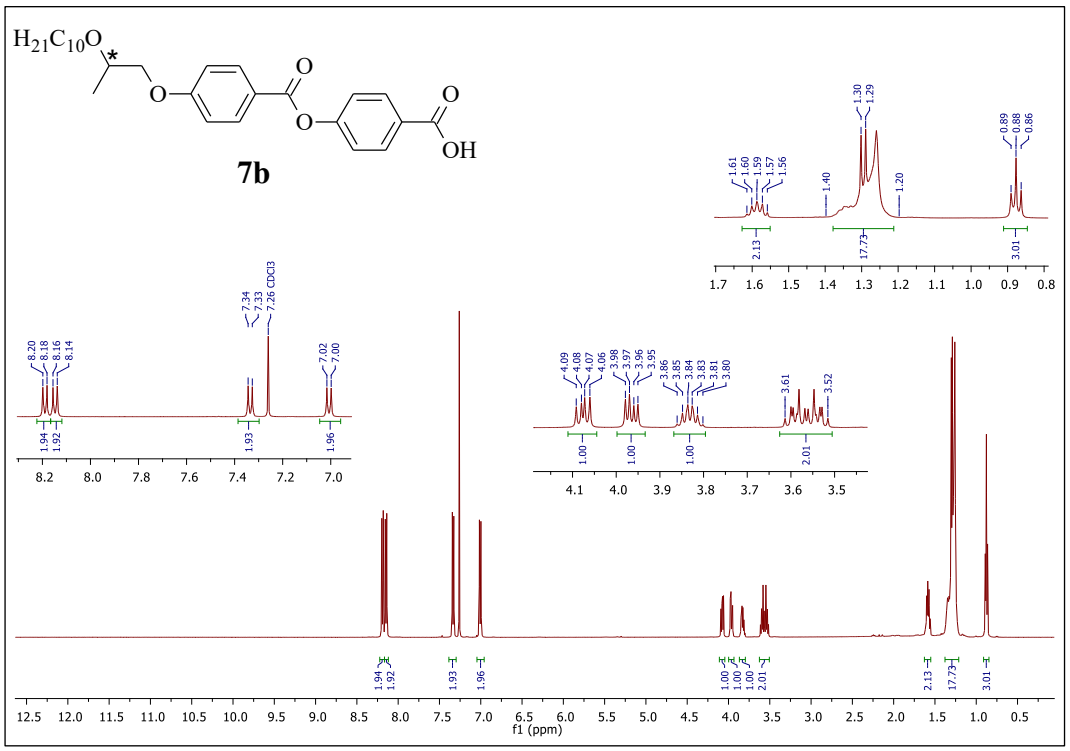


Figure S3. ^{1}H-NMR spectrum of 4-((4-(*S*)-(2-(*n*-Decyloxy)propoxy)benzoyl)oxy)benzoic acid (**7b**).

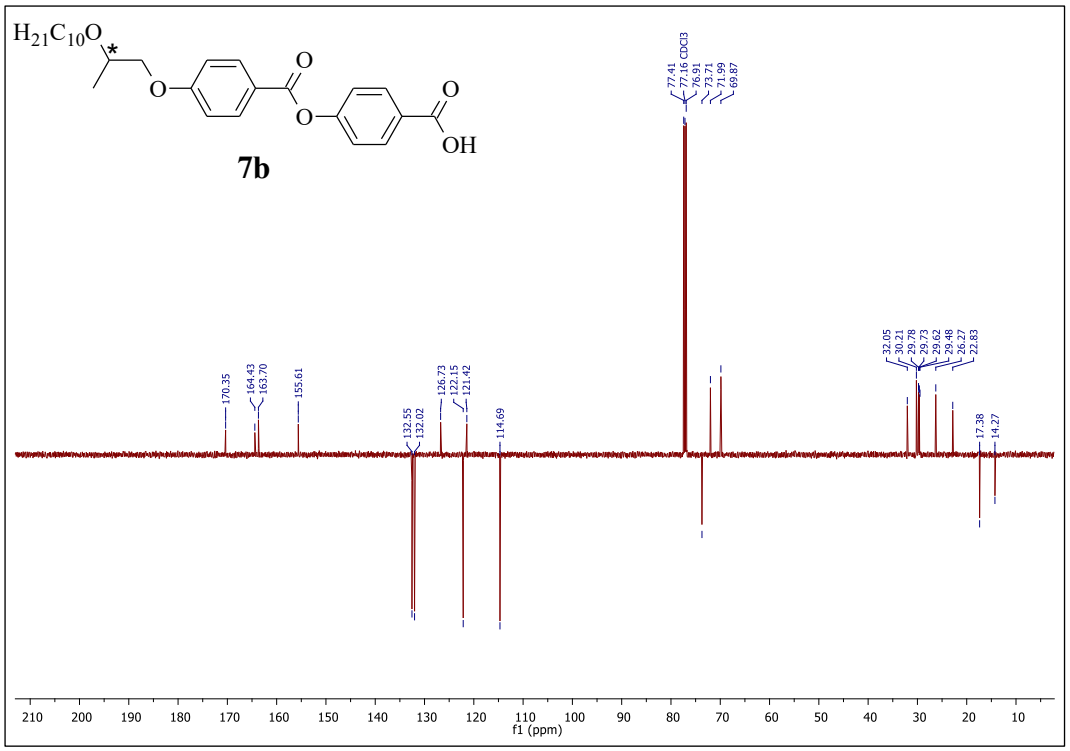


Figure S4. ^{13}C-NMR (APT) spectrum of 4-((4-(*S*)-(2-(*n*-Decyloxy)propoxy)benzoyl)oxy)benzoic acid (**7b**).

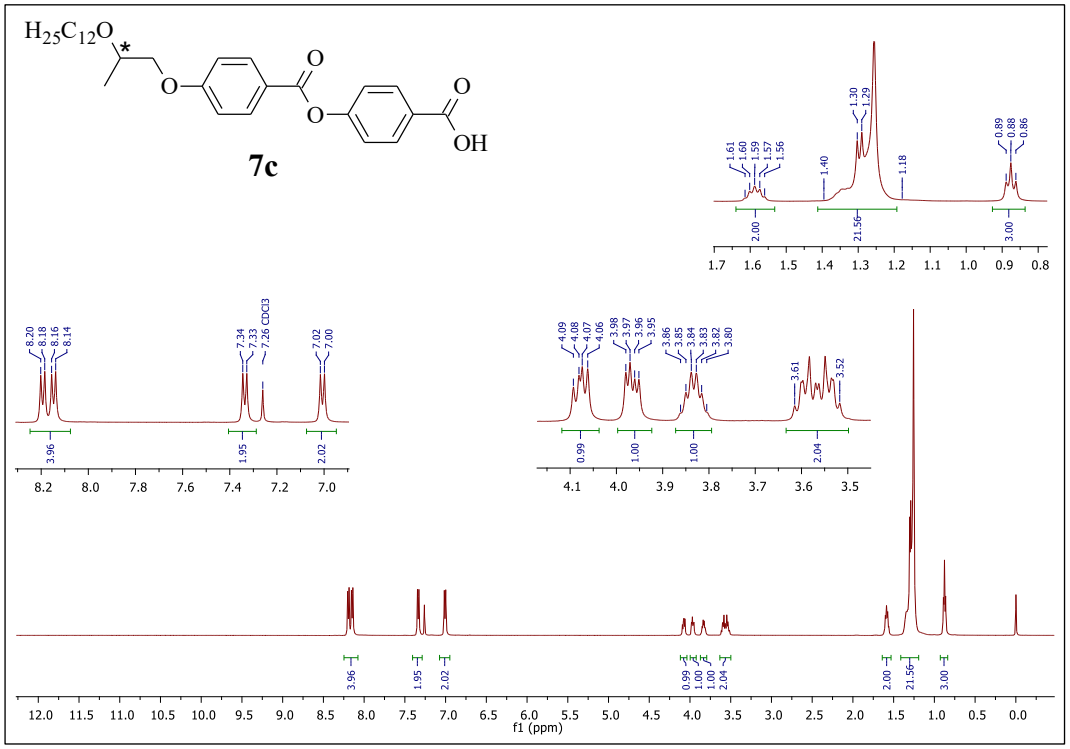


Figure S5. ^{1}H-NMR spectrum of 4-((4-(*S*)-(2-(*n*-Dodecyloxy)propoxy)benzoyl)oxy)benzoic acid (**7c**).

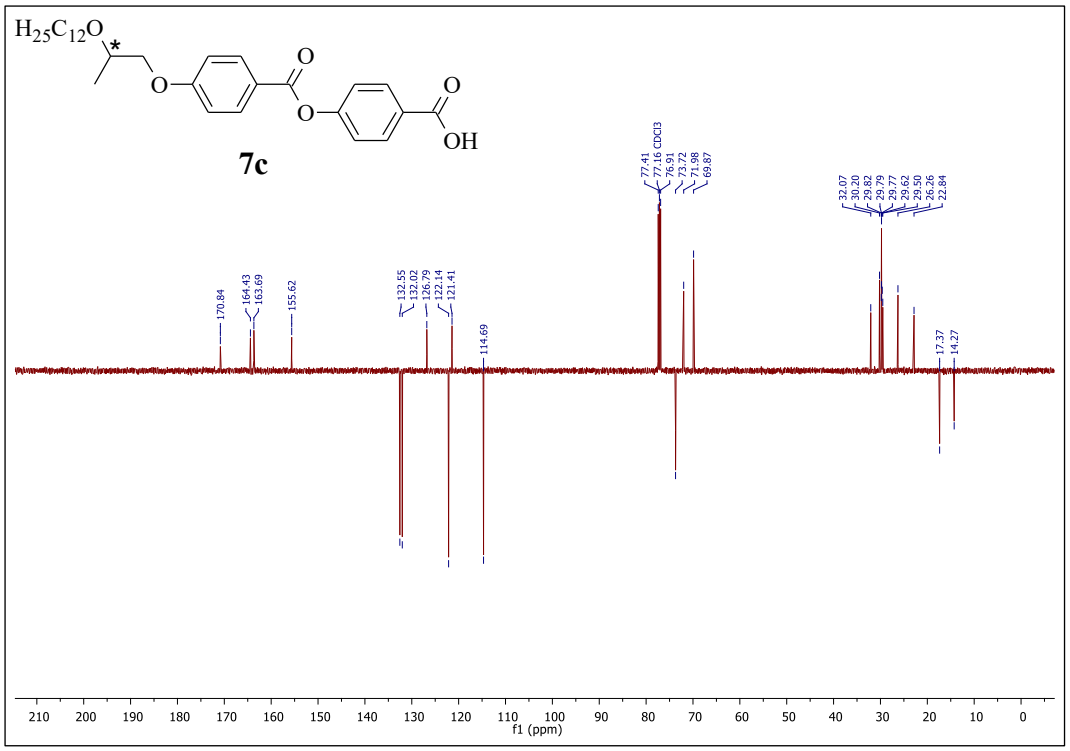


Figure S6. ^{13}C-NMR (APT) spectrum of 4-((4-(*S*)-(2-(*n*-Dodecyloxy)propoxy)benzoyl)oxy)benzoic acid (**7c**).

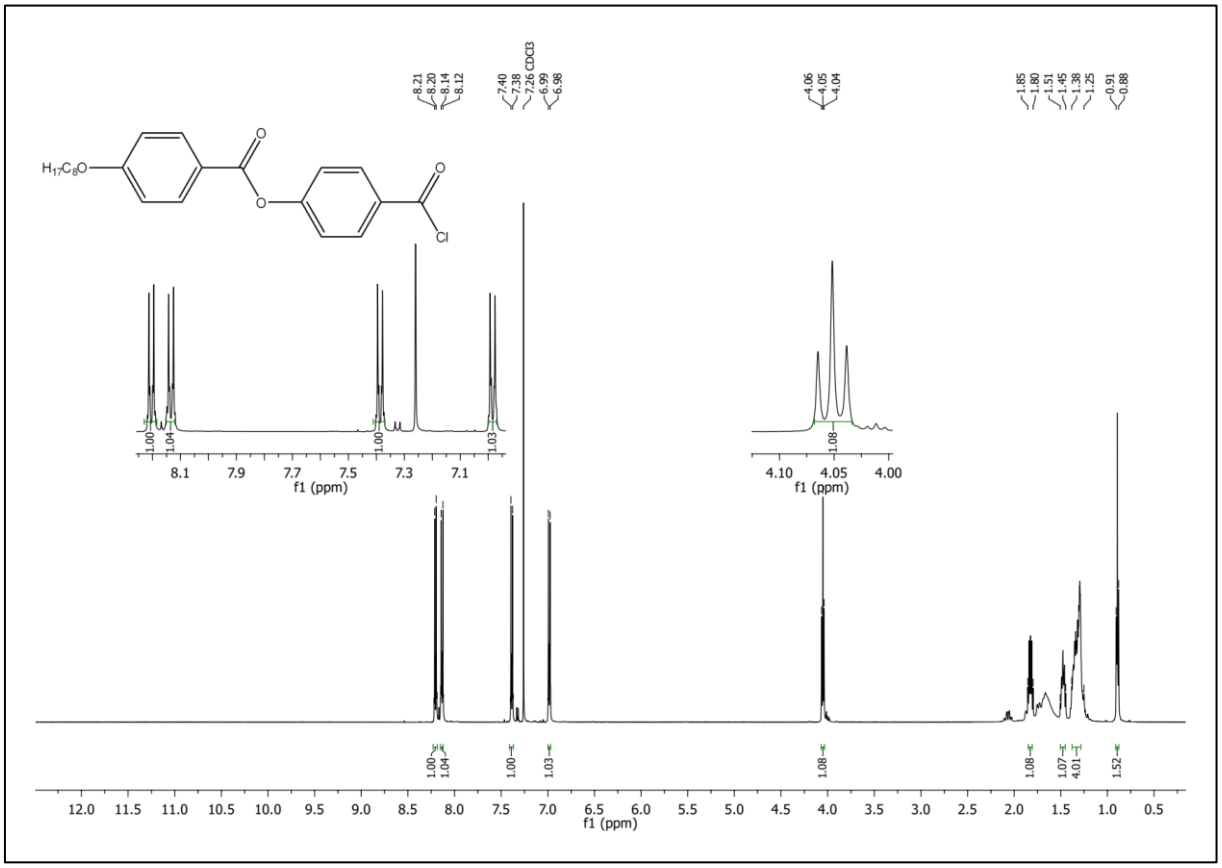


Figure S7. ^{1}H-NMR spectrum of 4-[4-(*n*-Octyloxy)benzoyloxy)benzoyl chloride (**Cl-8a**).

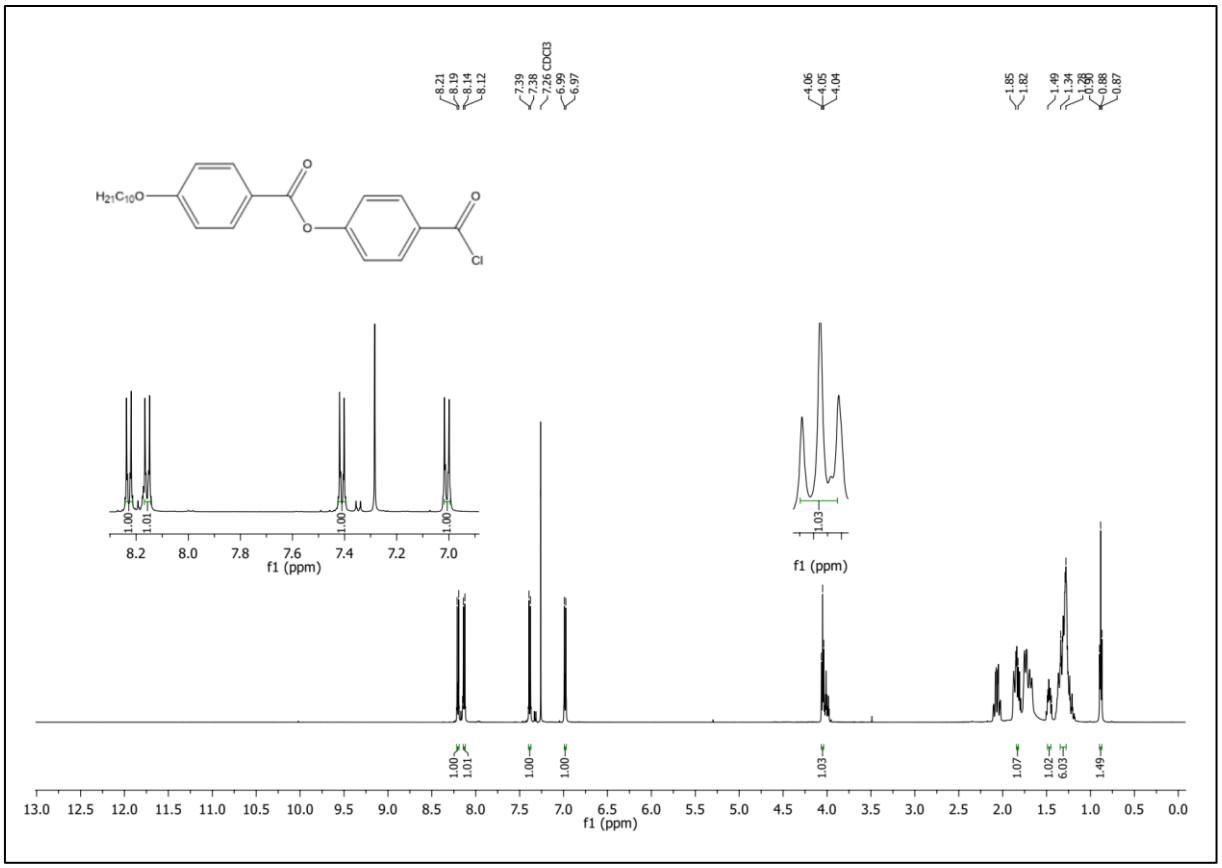


Figure S8. ^{1}H-NMR spectrum of 4-[4-(*n*-Decyloxy)benzoyloxy)benzoyl chloride (**Cl-8b**).

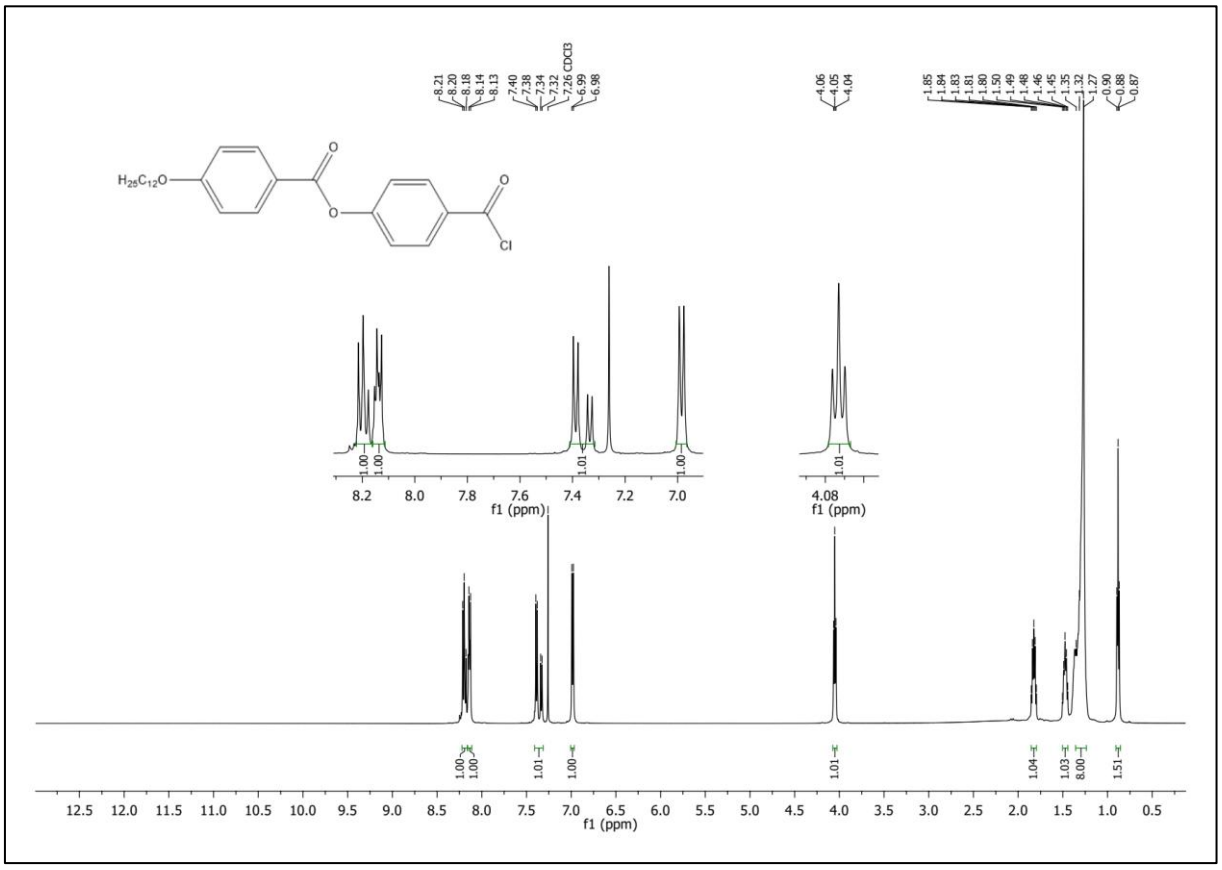


Figure S9. ^{1}H-NMR spectrum of 4-(4-(*n*-Dodecyloxy)benzoyloxy)benzoyl chloride (**Cl-8c**).

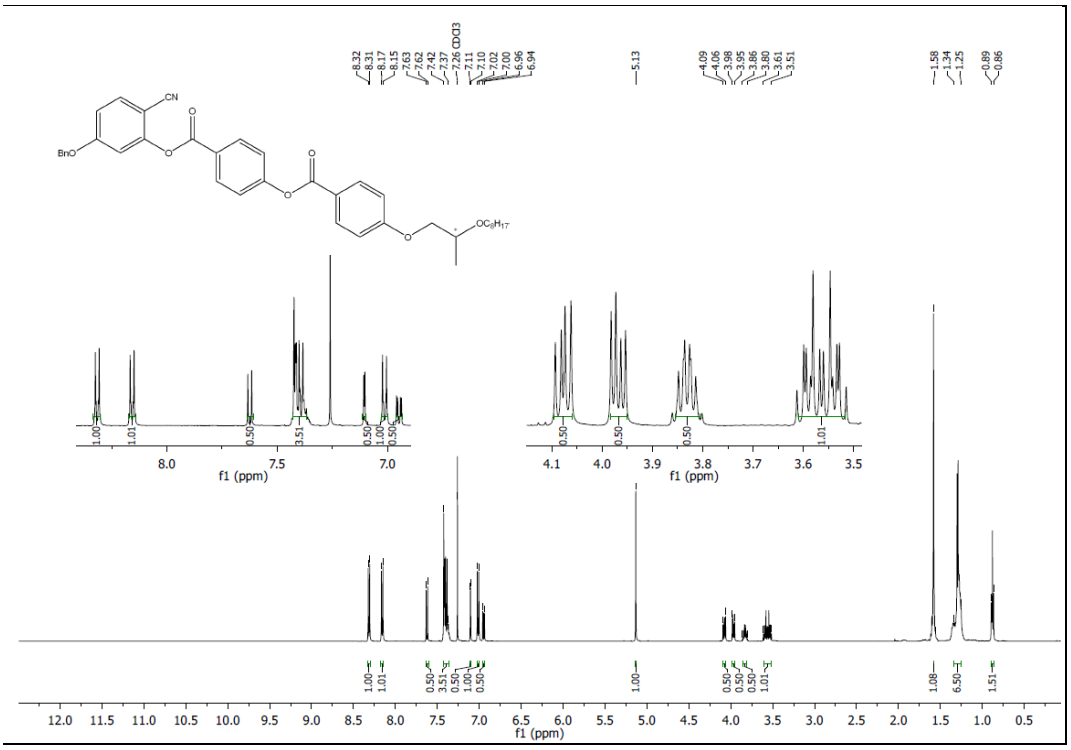


Figure S10. ^{1}H-NMR spectrum of 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**10a**).

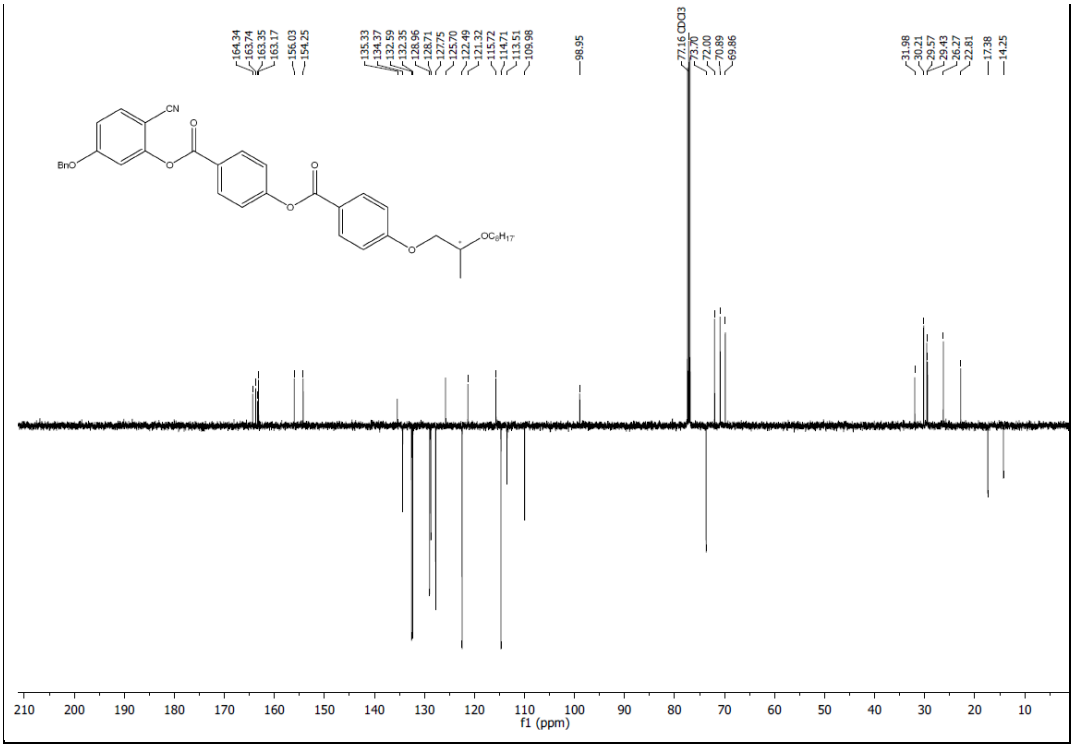


Figure S11. ^{13}C-NMR (APT) spectrum of 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**10a**).

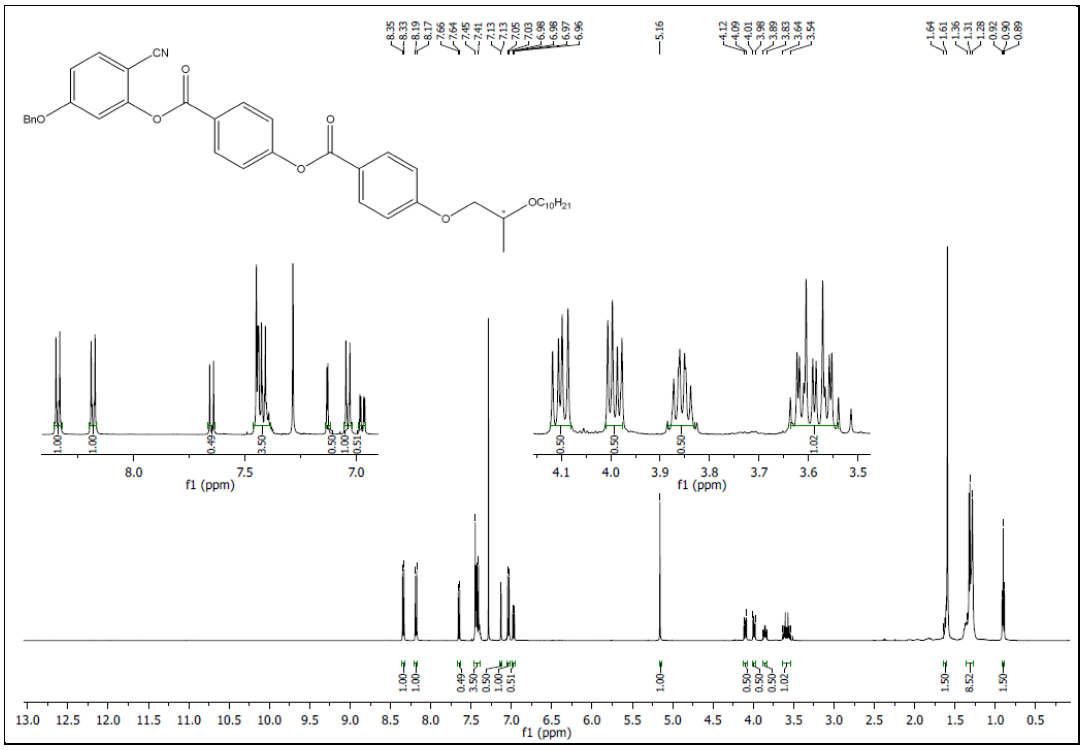


Figure S12. ^{1}H-NMR spectrum of 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**10b**).

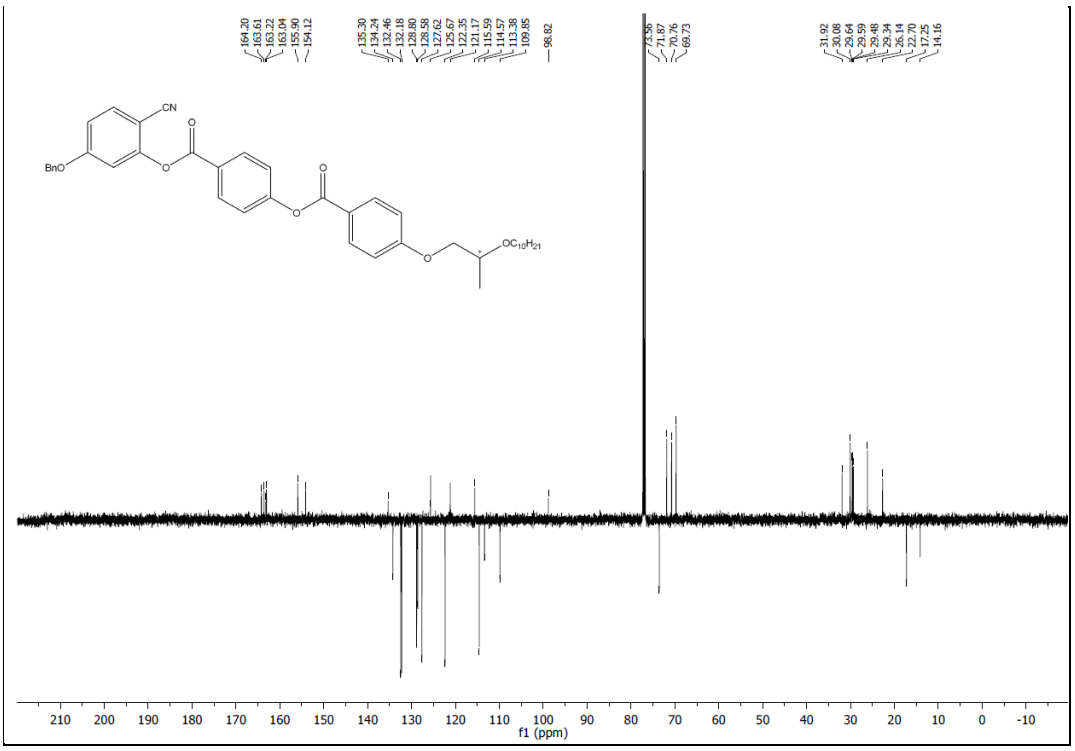


Figure S13. ^{13}C-NMR (APT) spectrum of 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**10b**).

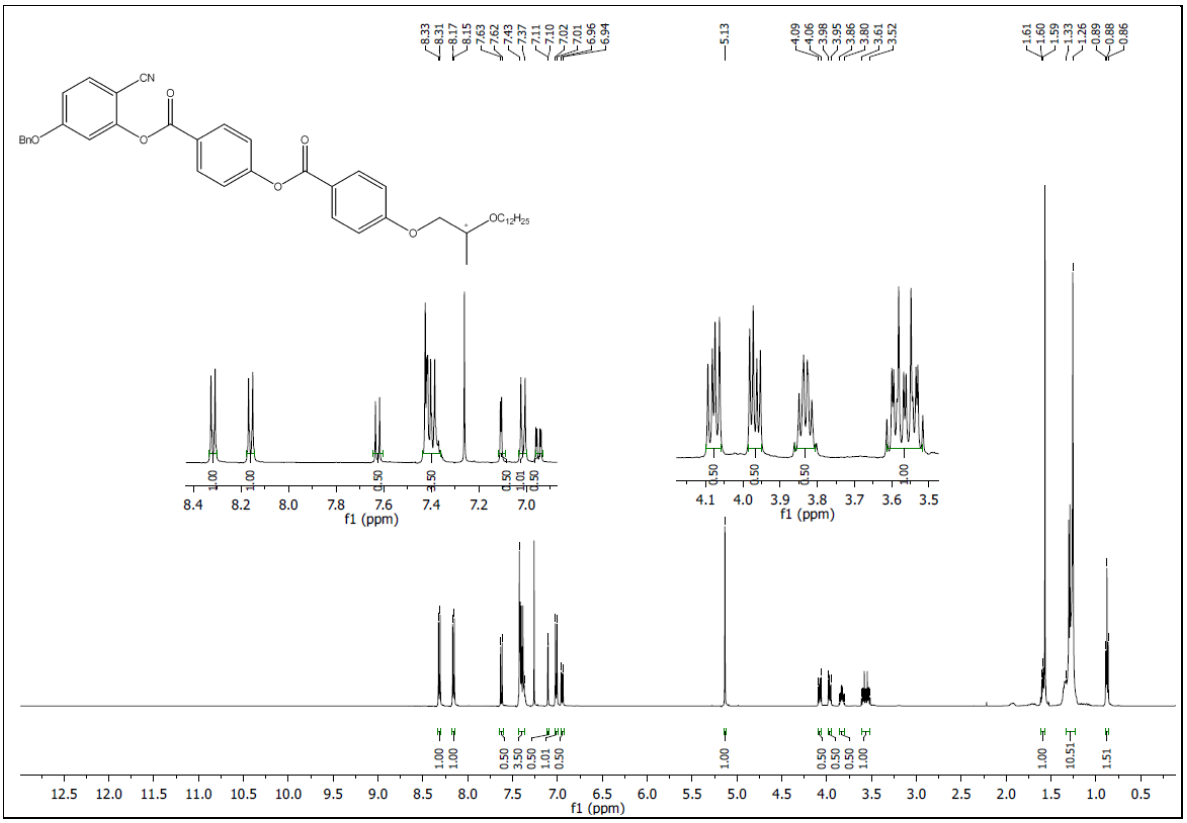


Figure S14. ^{1}H-NMR spectrum of 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**10c**).

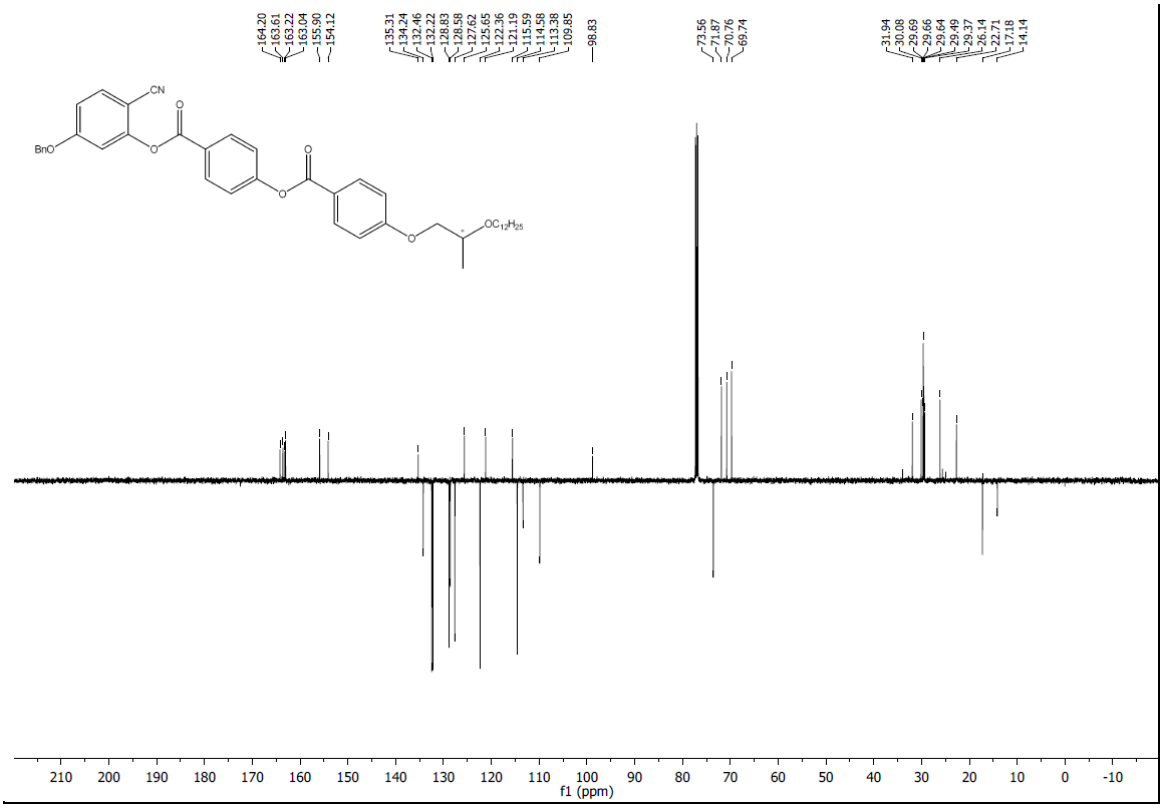


Figure S15. ^{13}C-NMR spectrum of 2-Cyano-5-benzyloxyphenyl 4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**10c**).

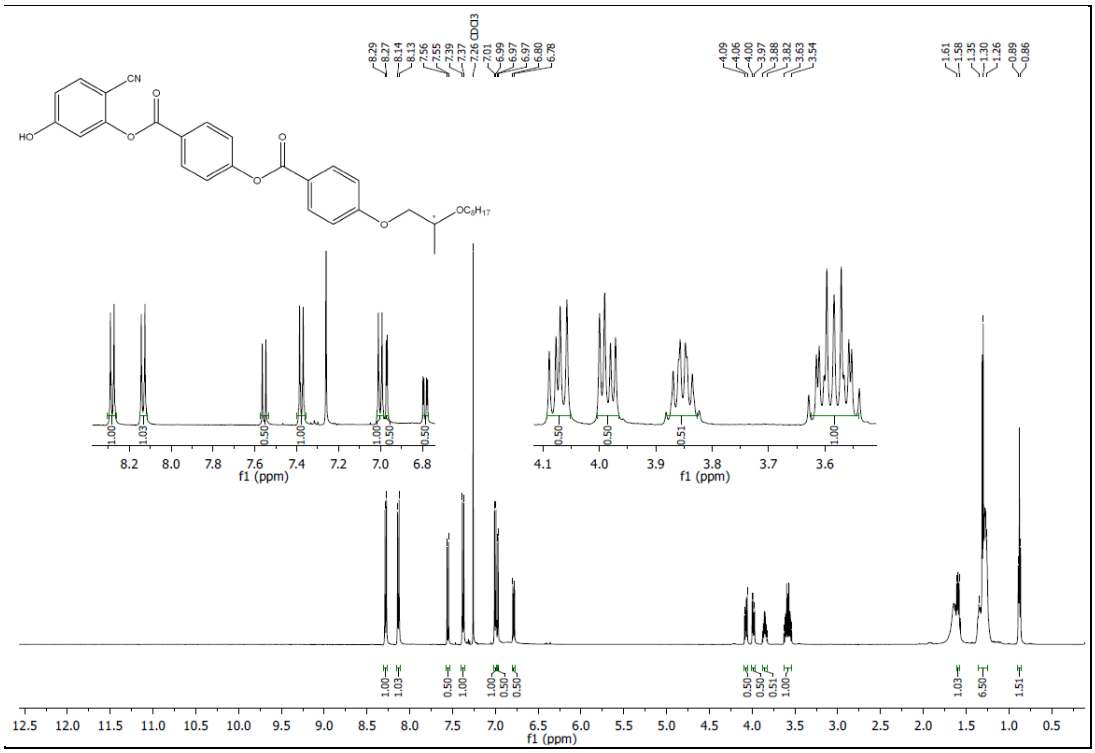


Figure S16. ^{1}H-NMR spectrum of 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**11-OHa**).

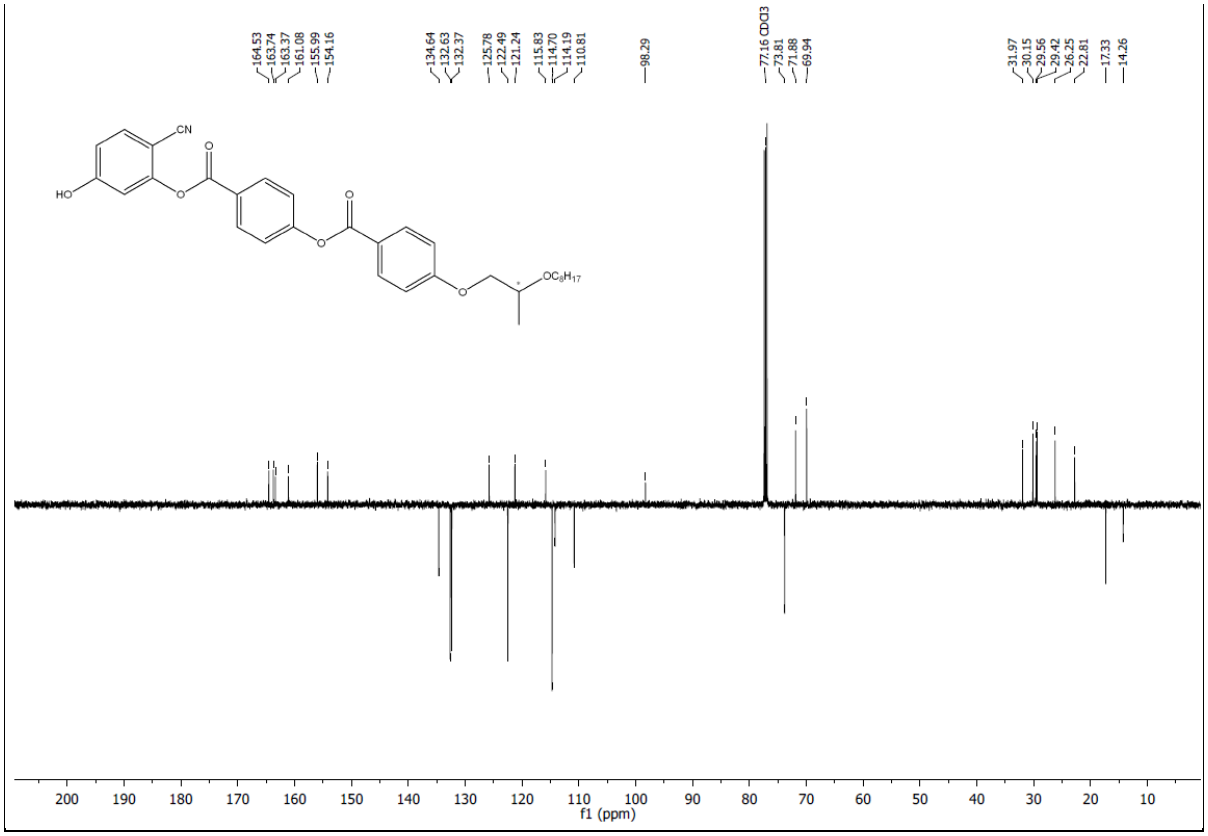


Figure S17. ^{13}C-NMR spectrum of 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**11-OHa**).

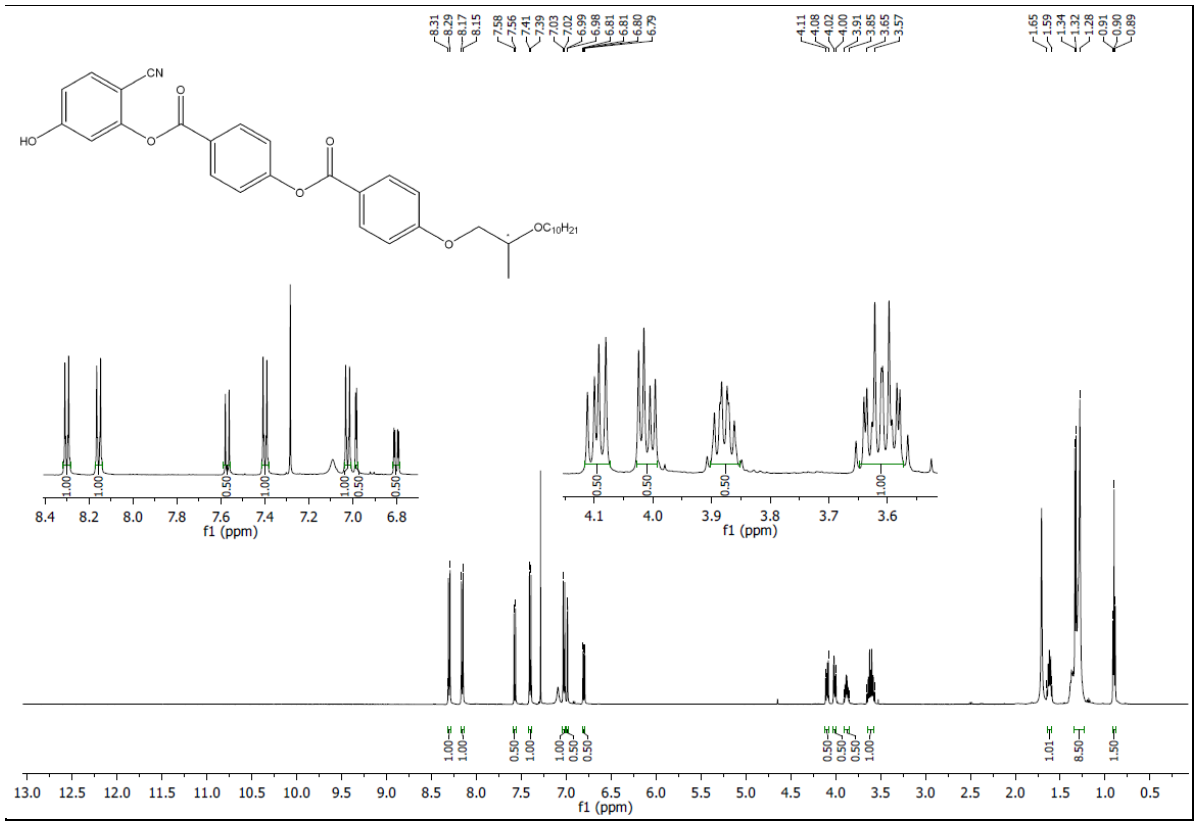


Figure S18. ^{1}H-NMR spectrum of 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**11-OHb**).

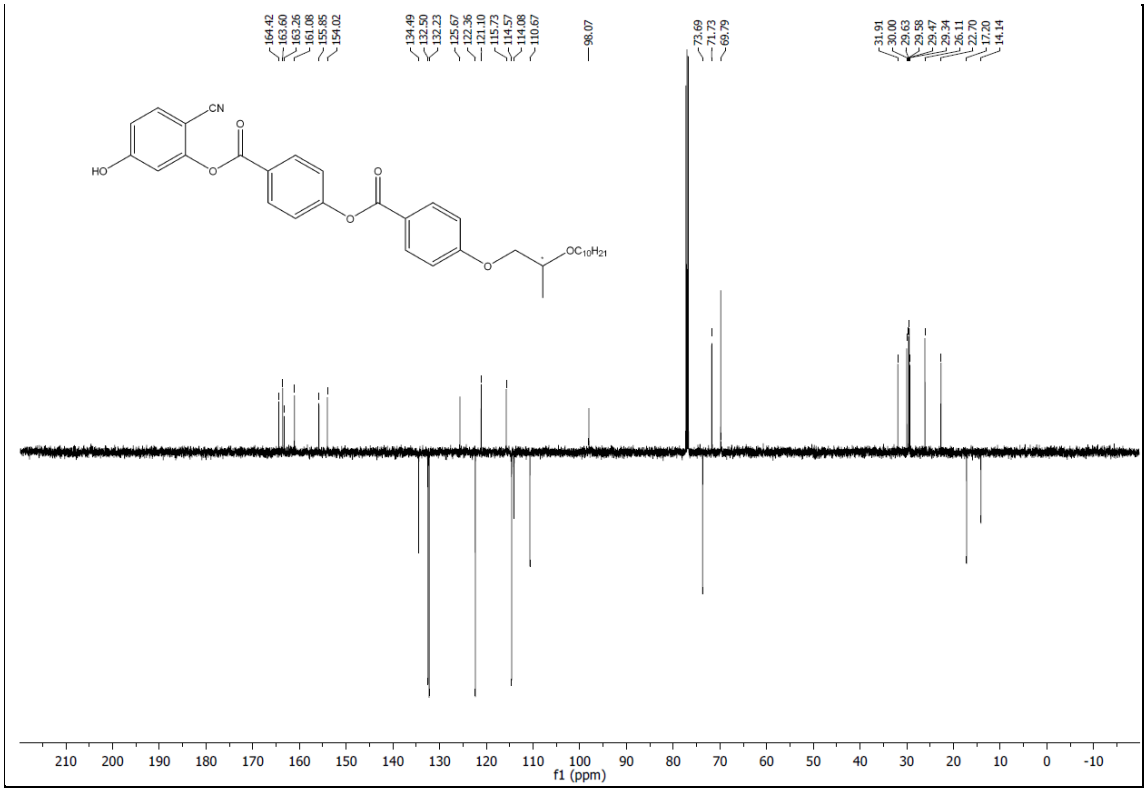


Figure S19. ^{13}C-NMR spectrum of 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**11-OHb**).

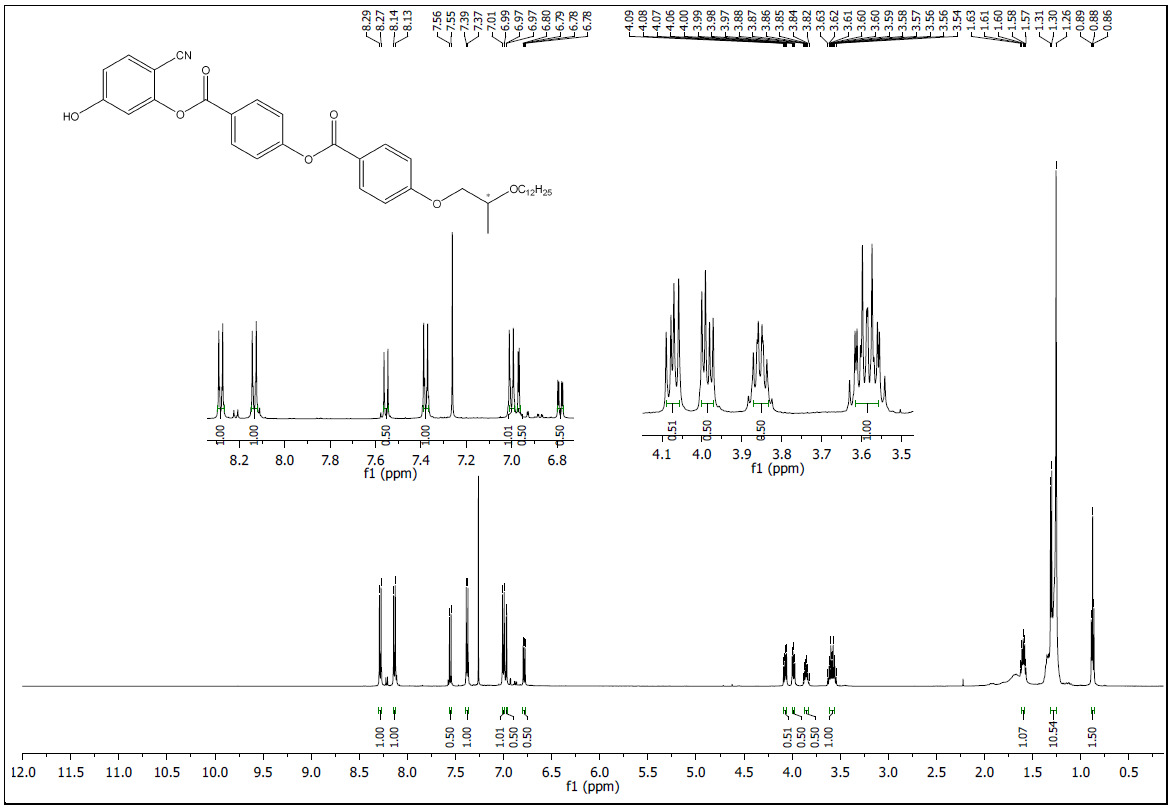


Figure S20. ^{1}H-NMR spectrum of 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**11-OHc**).

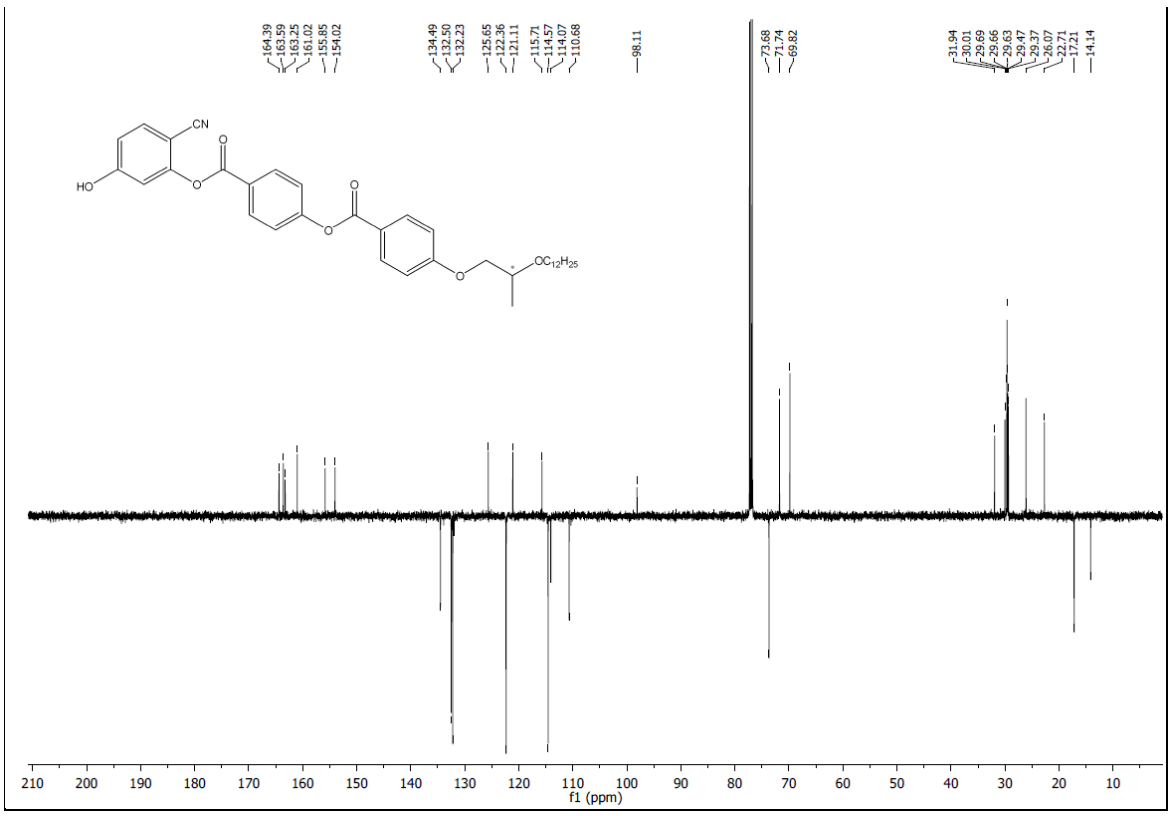


Figure S21. ^{13}C-NMR spectrum of 2-Cyano-5-hydroxyphenyl 4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**11-OHc**).

1. 5. NMR and FT-IR spectra of compounds Ia-c and IIa-c.

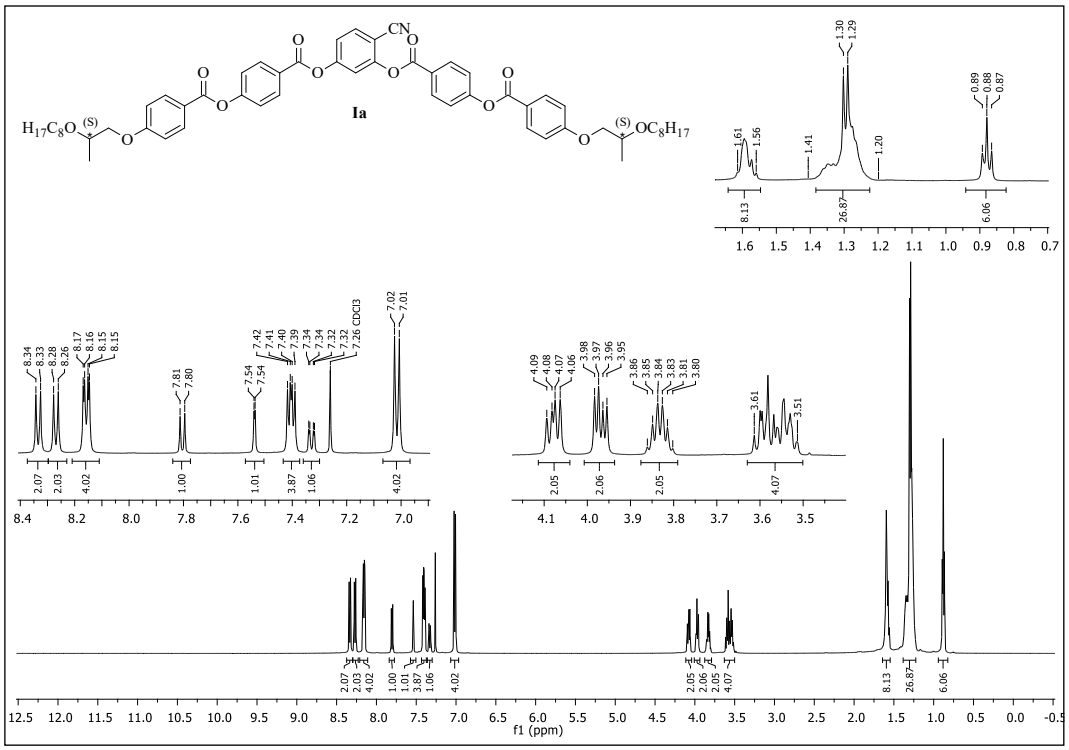


Figure S22. ^{1}H-NMR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**Ia**).

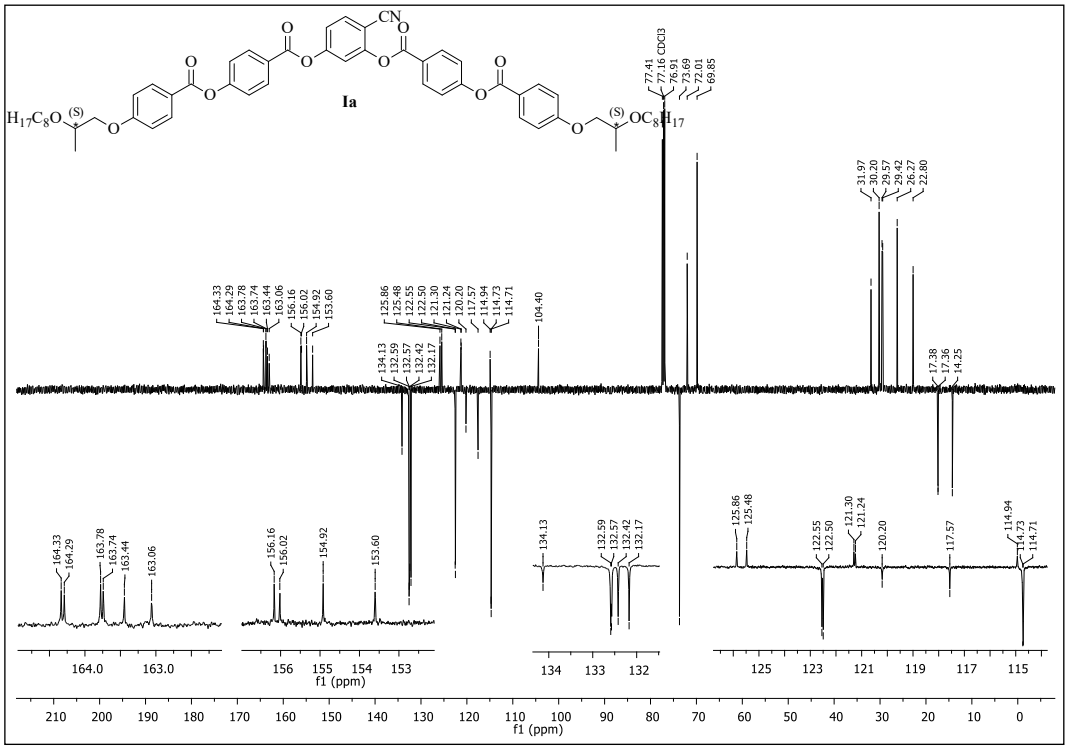


Figure S23. ^{13}C-NMR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**Ia**).

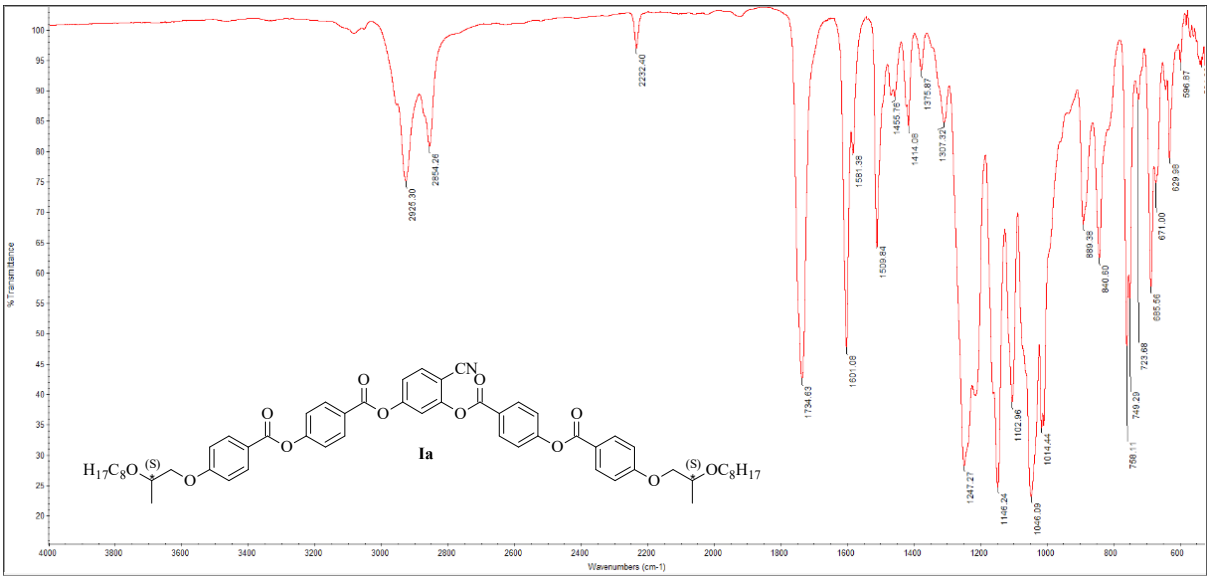


Figure S24. FT-IR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-octyloxypropoxy)benzoyl)oxy)benzoate (**Ia**).

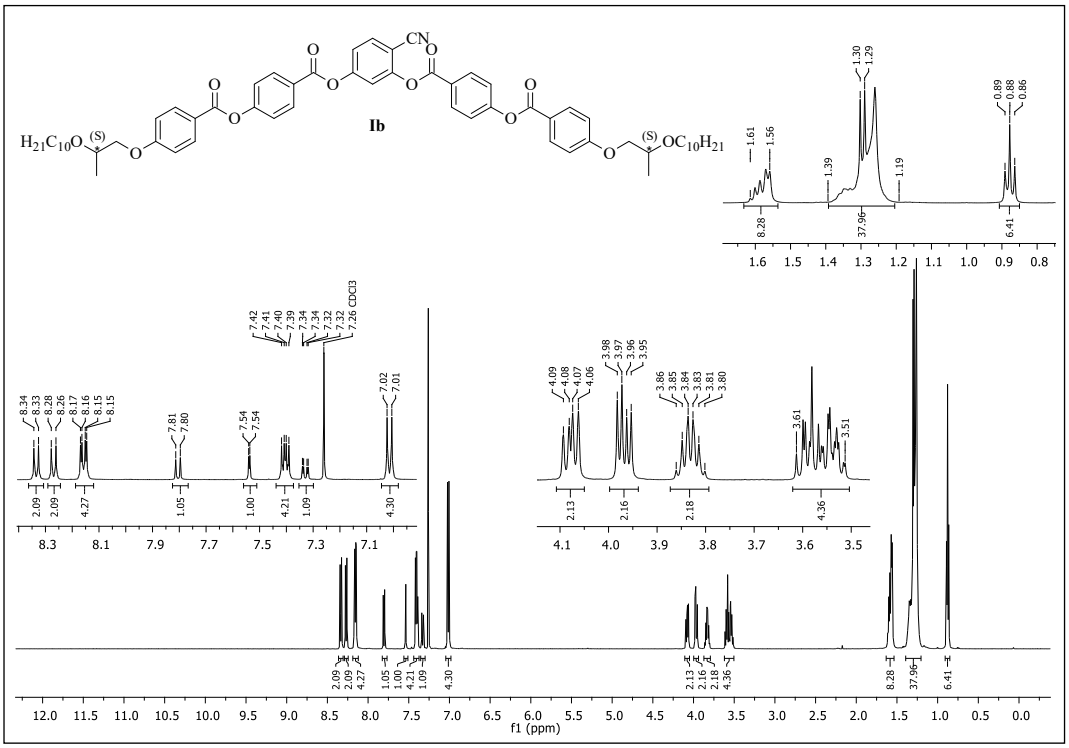


Figure S25. ^{1}H-NMR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**Ib**).

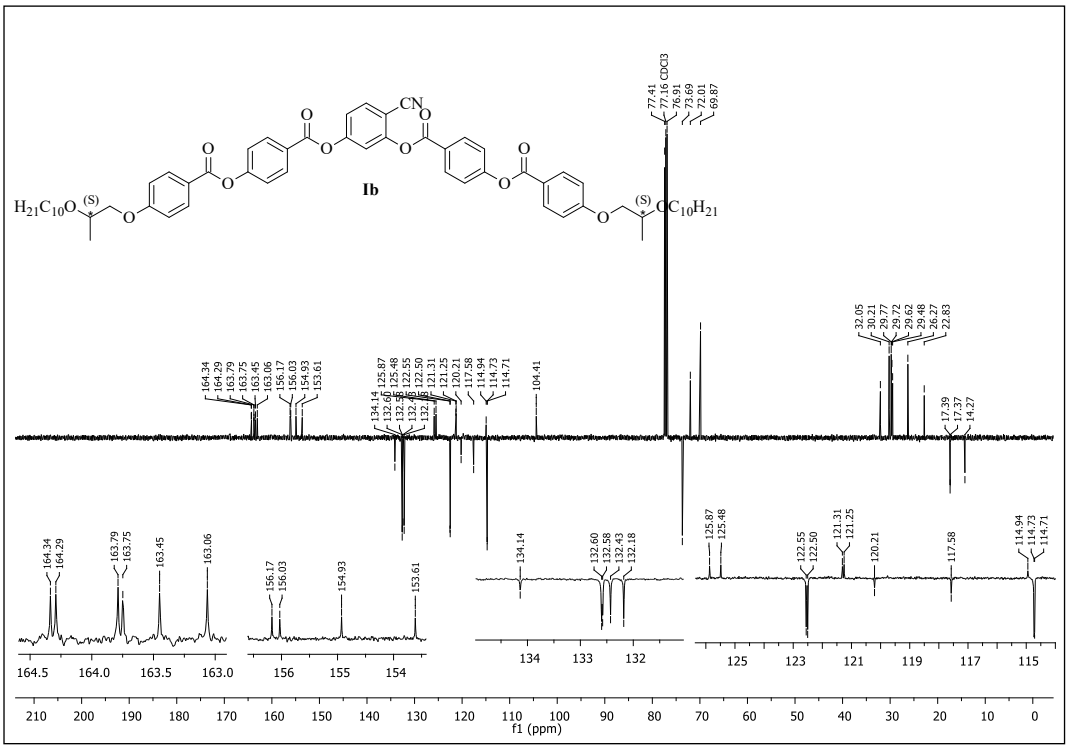


Figure S26. ^{13}C-NMR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**Ib**).

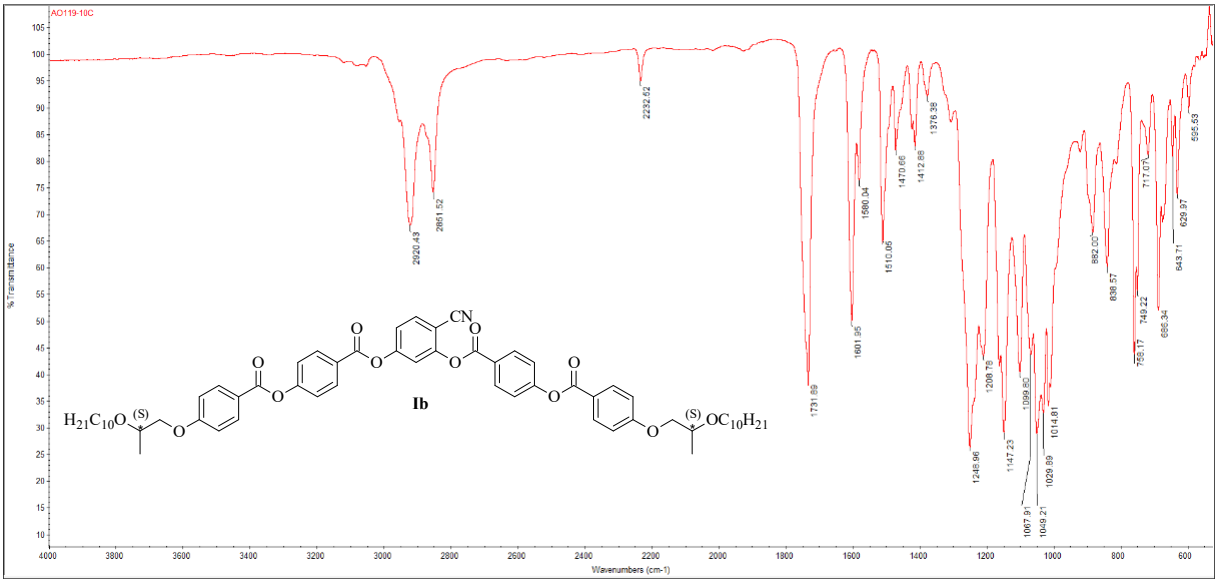


Figure S27. FT-IR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-decyloxypropoxy)benzoyl)oxy)benzoate (**Ib**).

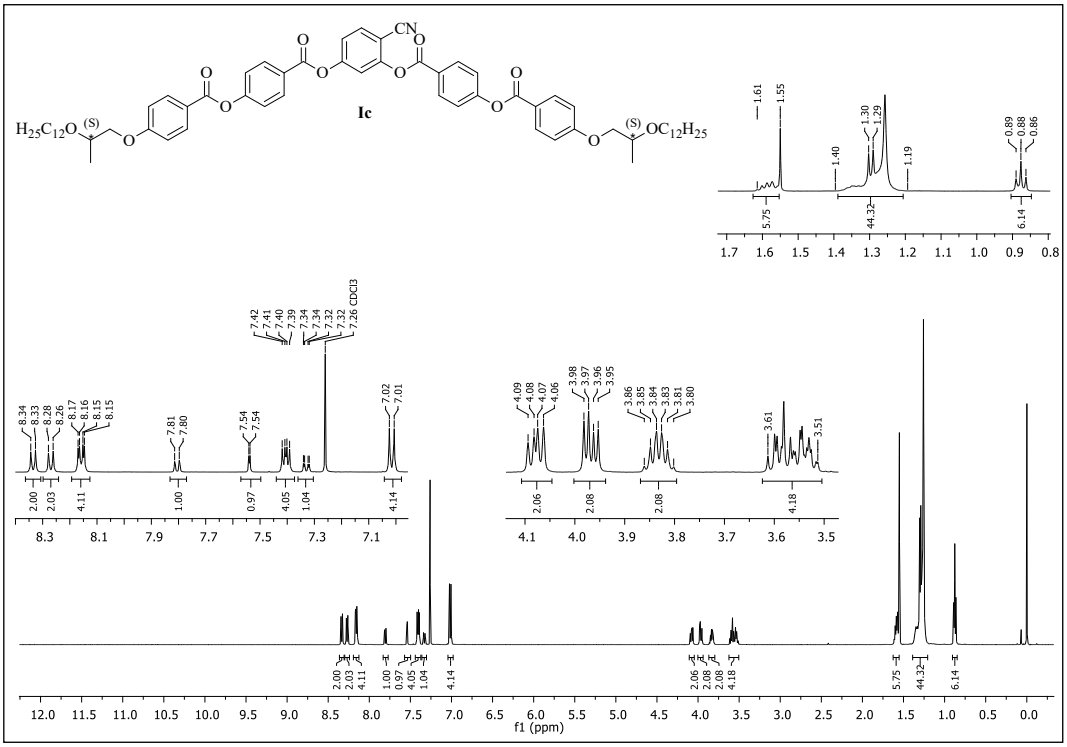


Figure S28. ^{1}H-NMR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**Ic**).

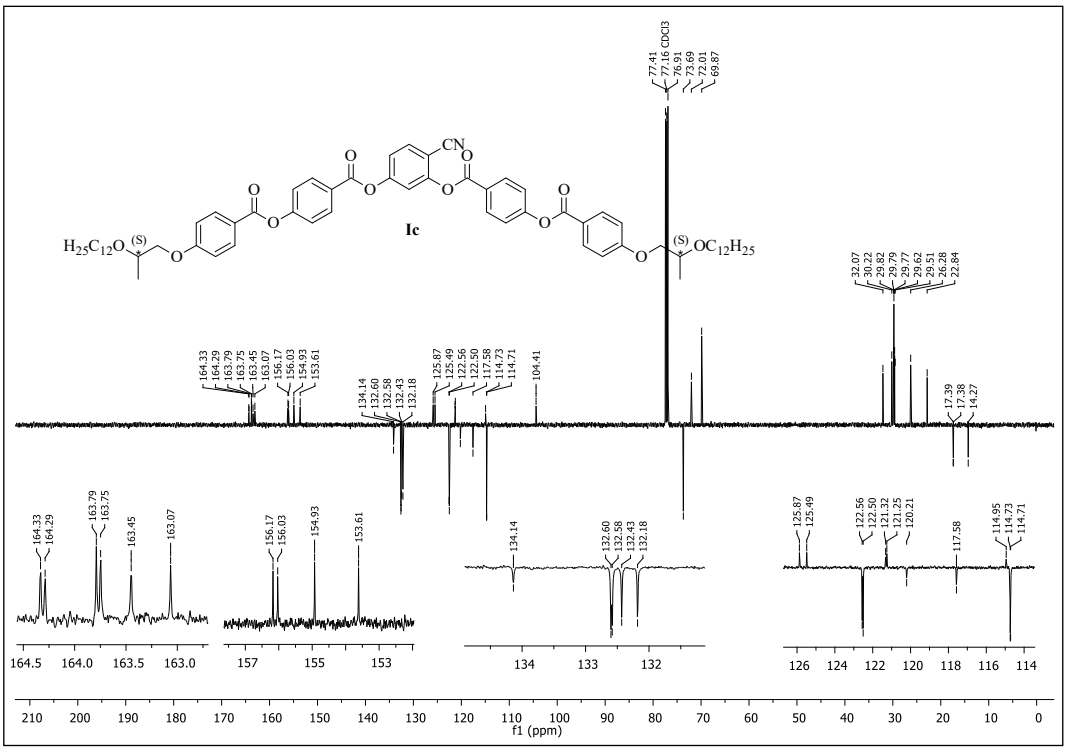


Figure S29. ^{13}C-NMR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**Ic**).

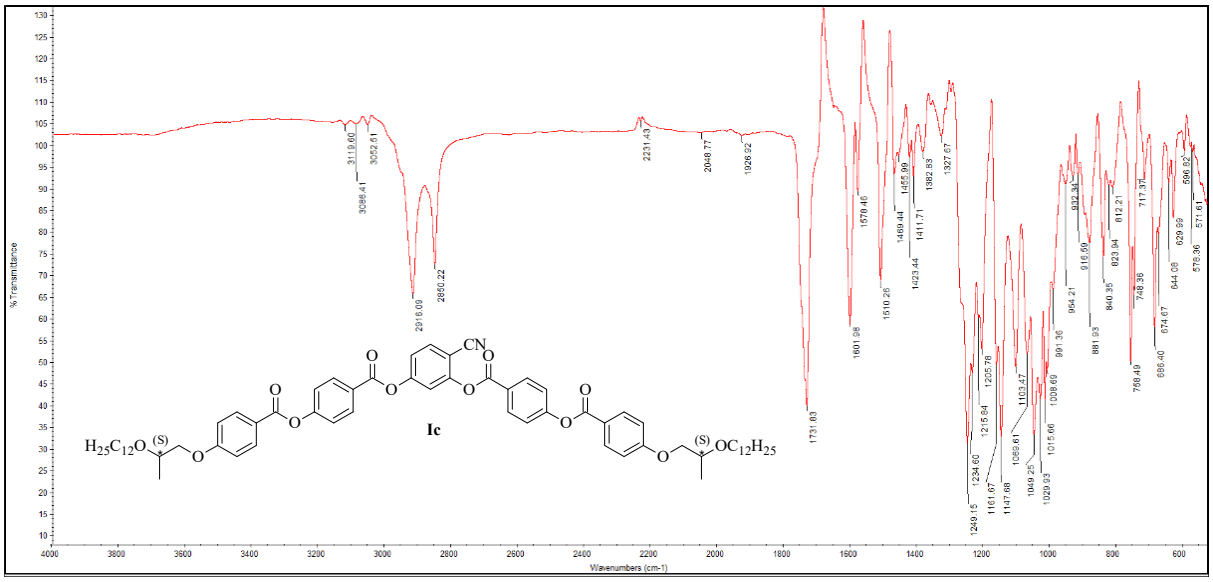


Figure S30. FT-IR spectrum of 4-Cyano-1,3-phenylenebis(4-((4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyl)oxy)benzoate (**Ic**).

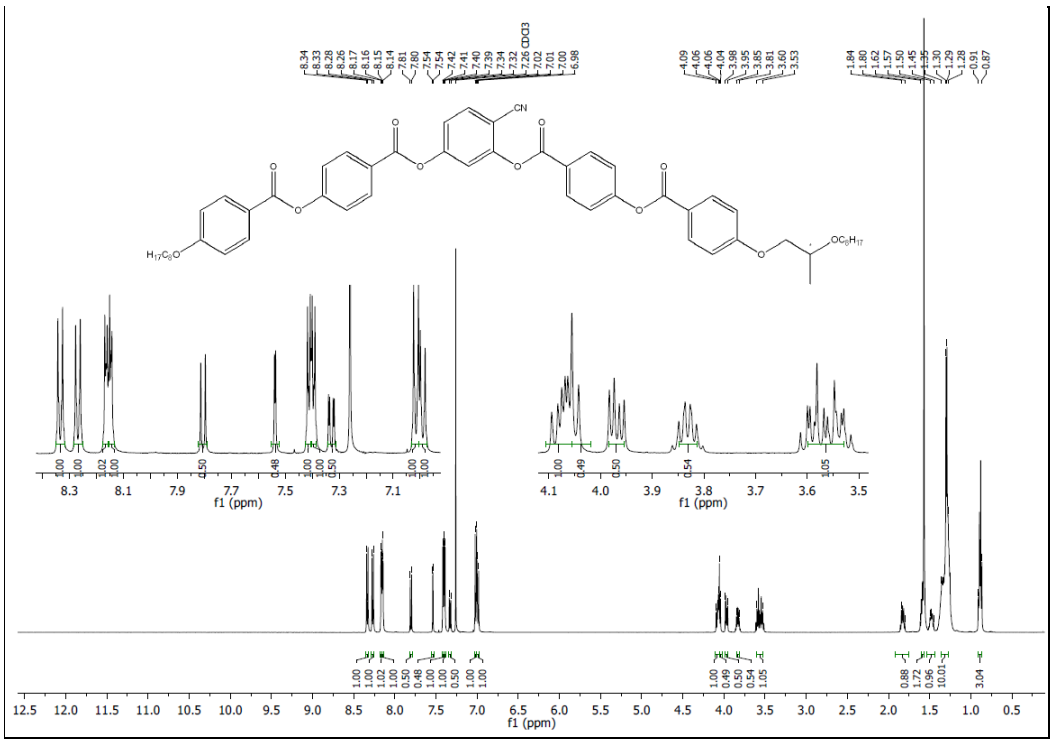


Figure S31. ^{1}H-NMR spectrum of 4-{4-[4-(*n*-Octyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-octyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIa**).

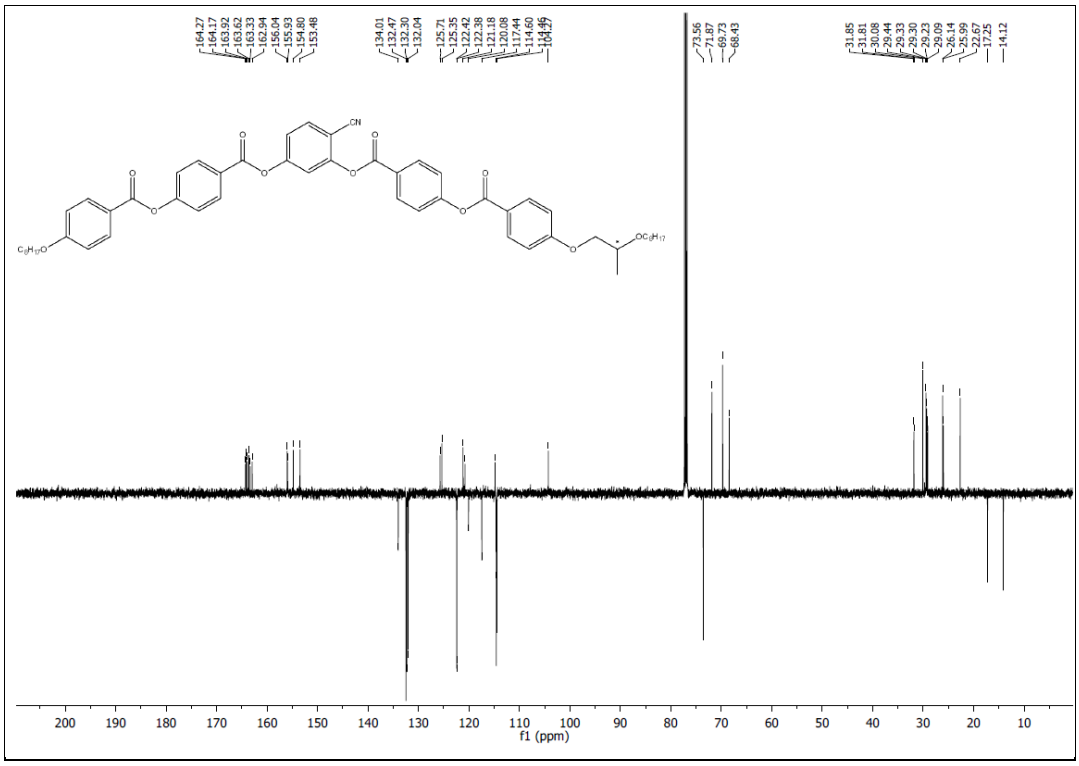


Figure S32. ^{13}C-NMR spectrum of 4-{4-[4-(*n*-Octyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-octyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIa**).

Figure S33. FT-IR spectrum of 4-{4-[4-(*n*-Octyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-octyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIa**).

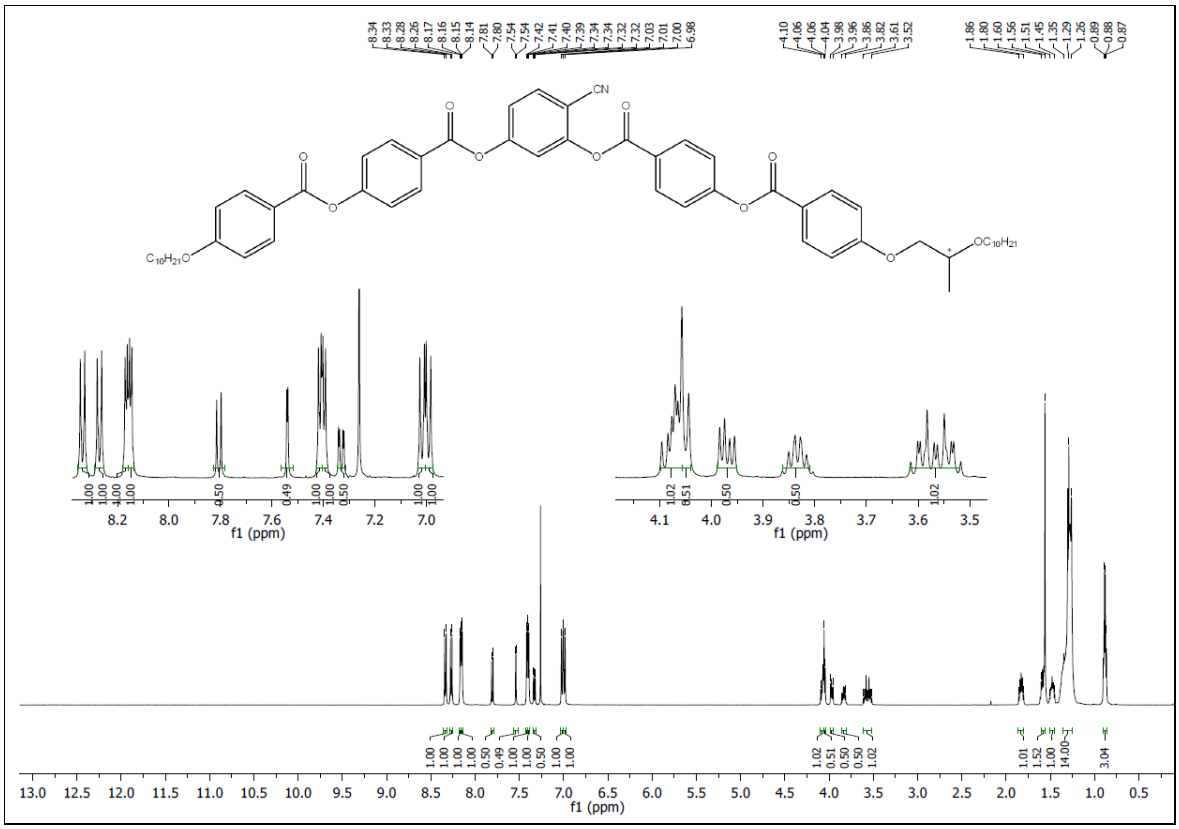


Figure S34. ^{1}H-NMR spectrum of 4-{4-[4-(*n*-Decyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)- 2-*n*-decyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIb**).

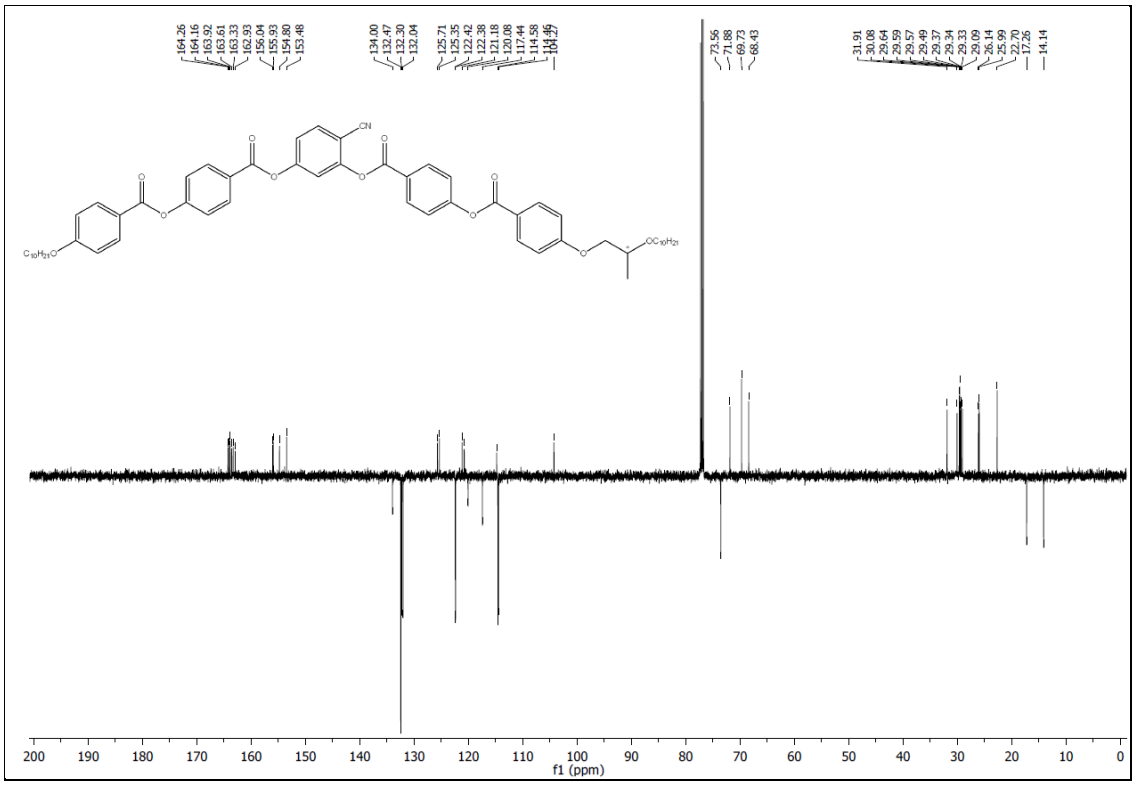


Figure S35. ^{13}C-NMR spectrum of 4-{4-[4-(*n*-Decyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)- 2-*n*-decyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIb**).

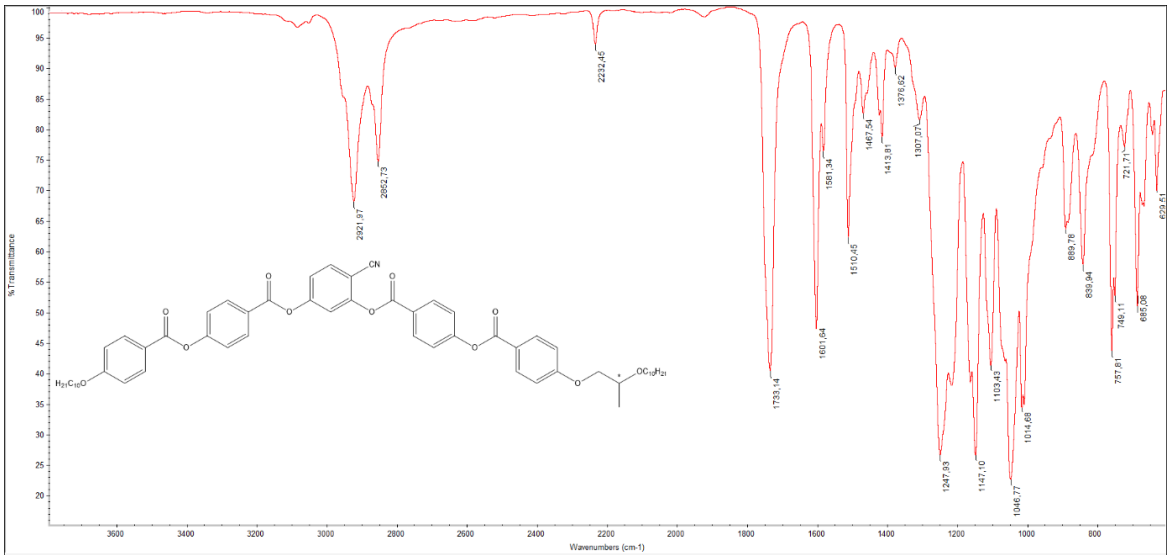


Figure S36. FT-IR spectrum of 4-{4-[4-(*n*-Decyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-decyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIb**).

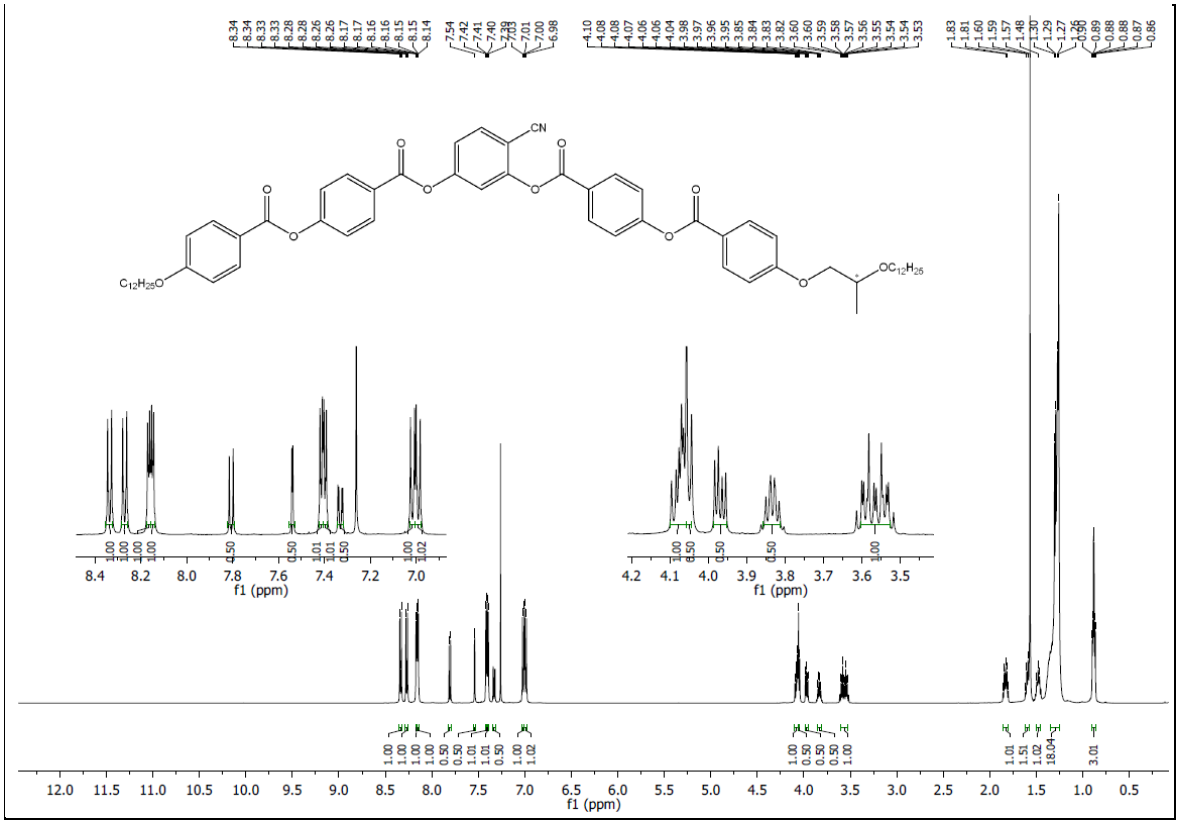


Figure S37. ^{1}H-NMR spectrum of 4-{4-[4-(*n*-Dodecyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIc**).

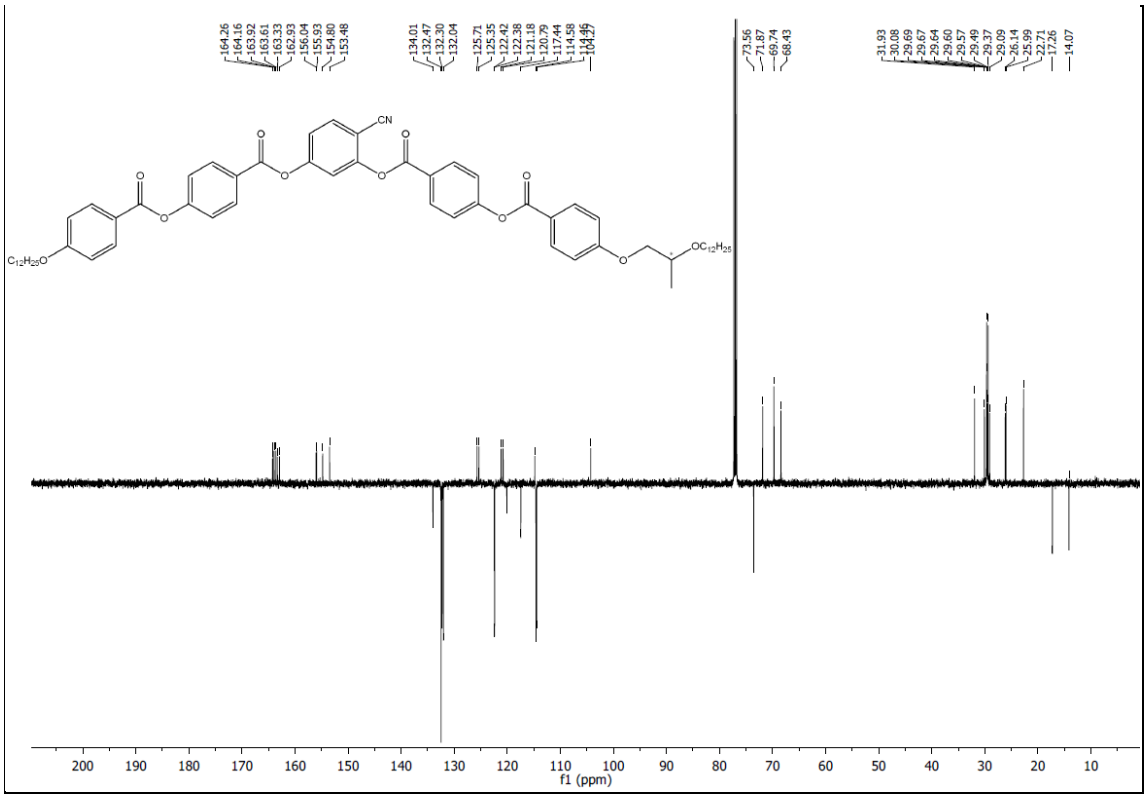


Figure S38. ^{13}C-NMR spectrum of 4-{4-[4-(*n*-Dodecyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIc**).

Figure S39. FT-IR spectrum of 4-{4-[4-(*n*-Dodecyloxy)benzoyloxy]benzoyloxy}-2-{4-[4-((*S*)-2-*n*-dodecyloxypropoxy)benzoyloxy]benzoyloxy}benzonitrile (**IIc**).

2. Investigation Methods

Transition temperatures were measured using a Linkam LTS420E hot stage and a T95-HS control unit in conjunction with an Olympus BX51-P polarizing microscope. The associated enthalpies were obtained from DSC-thermograms, which were recorded on a Perkin Elmer DSC-8000 (heating and cooling rate: 10 K min^{-1}) in a nitrogen atmosphere.

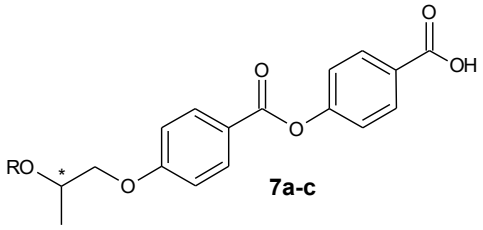
POM investigations were conducted using a Mettler FP-82 HT hot stage and a control unit in conjunction with a Nikon Optiphot-2 polarizing microscope. Investigation of compounds was carried out in a 10 µm PI-coated ITO cell (electrooptical studies) or between ordinary glass plates (investigation of the textures, used for all textures shown in this manuscript).
XRD measurements were done at Cu-Kα line (λ = 1.54 Å) using a standard Coolidge tube source with a Ni-filter. Investigations of oriented samples were performed using a 2D-detector (Vantec 500, Bruker)
Electro-optical investigations were performed in a 10 µm polyimide (PI) coated ITO cell (EHC, Japan) with a measuring area of 1 cm^2. Switching experiments were carried out with the triangular-wave method using a combination of a function synthesizer (Agilent, model 33220A, load was set to 10 kΩ), an amplifier (Tabor electronics, model 9400), and the current response traces were recorded using an oscilloscope (Agilent, model DSO3202A) across a 5kΩ resistance.

3. Additional Data

3.1. Data of the 4-((4-(*S*)-(2-(*n*-alkyloxy)propoxy)benzoyloxy)benzoic acids 7a-c

The liquid crystalline phases and transition temperatures of the 4-((*S*)-2-alkyloxypropyl)-4-benzoyloxybenzoic acids (**7a-c**) are presented in Table S1, while the DSC thermograms, POM textures are given in Figs. S40-43.

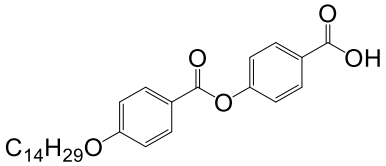
Table S1. Mesophases, phase transition temperatures, and corresponding transition enthalpies of the chiral benzoic acids **7a-c**.[a]



7a-c

Comp.	R	*T*/°C [Δ*H* /kJ mol^{-1}]
7a	OC_8H_{17}	**H**: Cr 85 [*4.9*] SmX* 124 [*10.0*] SmC* 136 [-][b] N* 150 [-][b] Iso
		C: Iso 145[-][b] N* 133 [-][b] SmC* 115 [*-2.7*] SmX* 90 [*-6.4*] Cr_2 63 [*-1.4*] Cr_1
7b	$OC_{10}H_{21}$	**H**: Cr 72 [*6.4*] SmC* 137 [*3.9*] N* 145 [-][b] Iso
		C: Iso 139 [*-0.5*] N* 130 [*-1.8*] SmC* 58 [*-6.1*] Cr
7c	$OC_{12}H_{25}$	**H**: Cr 87 [*17.1*] SmC* 143 [*3.6*] N* 146 [-][b] Iso
		C: Iso 142 [-][b] N* 139 [*-3.0*] SmC* 69 [*-17.4*] Cr

[a]Peak temperatures as recorded from the 2nd heating (**H**) and cooling (**C**) scans at a rate of 10 K min^{-1}; Abbreviations: Cr = crystalline, SmX* = unknown chiral smectic mesophase, SmC* = chiral smectic C phase, N* = chiral nematic phase, Iso = isotropic liquid phase. [b]These transitions were determined by POM.



B

Effect of chain branching on LC phases of rod-like LC. - The benzoic acids **7a-c** form hydrogen-bonded linear dimers with a rod length being comparable with the core length of the bent compounds **I** and **II**. The benzoic acids **7a-c** form chiral nematic (N*) and chiral SmC phases (SmC*) as the main LC phases (Table 1). Compared with related benzoic acids having linear alkyl chains with *n*+4 carbon atoms instead of the branched (*S*)-2-alkyloxypropyl group, significantly lower LC-Iso transition temperatures are observed for **7a-c**. For example, compared with 4-(4-*n*-tetradecyloxy-4-benzoyloxy)benzoic acid (**B**: Cr 118 °C SmC 209 °C N 214 °C Iso)[18] the N(*)-SmC(*) as well as the N(*)-Iso transition temperatures of **7b**, having almost the same total end-chain volume, are reduced by around 70 K. This shows that the chain branching in the (*S*)-2-alkyloxypropyl chains leads to a significant reduction of all transition temperatures including those of the LC phases if ompared with linear alkyl chains. In addition, in the case of the linear benzoic acid dimers **7**, the homogeneous chiral center replaces the N and SmC phases of **B** by the respective chiral cholesteric (N*) and SmC* phases, i.e. the branching has no effect on the observed phase type in this case.

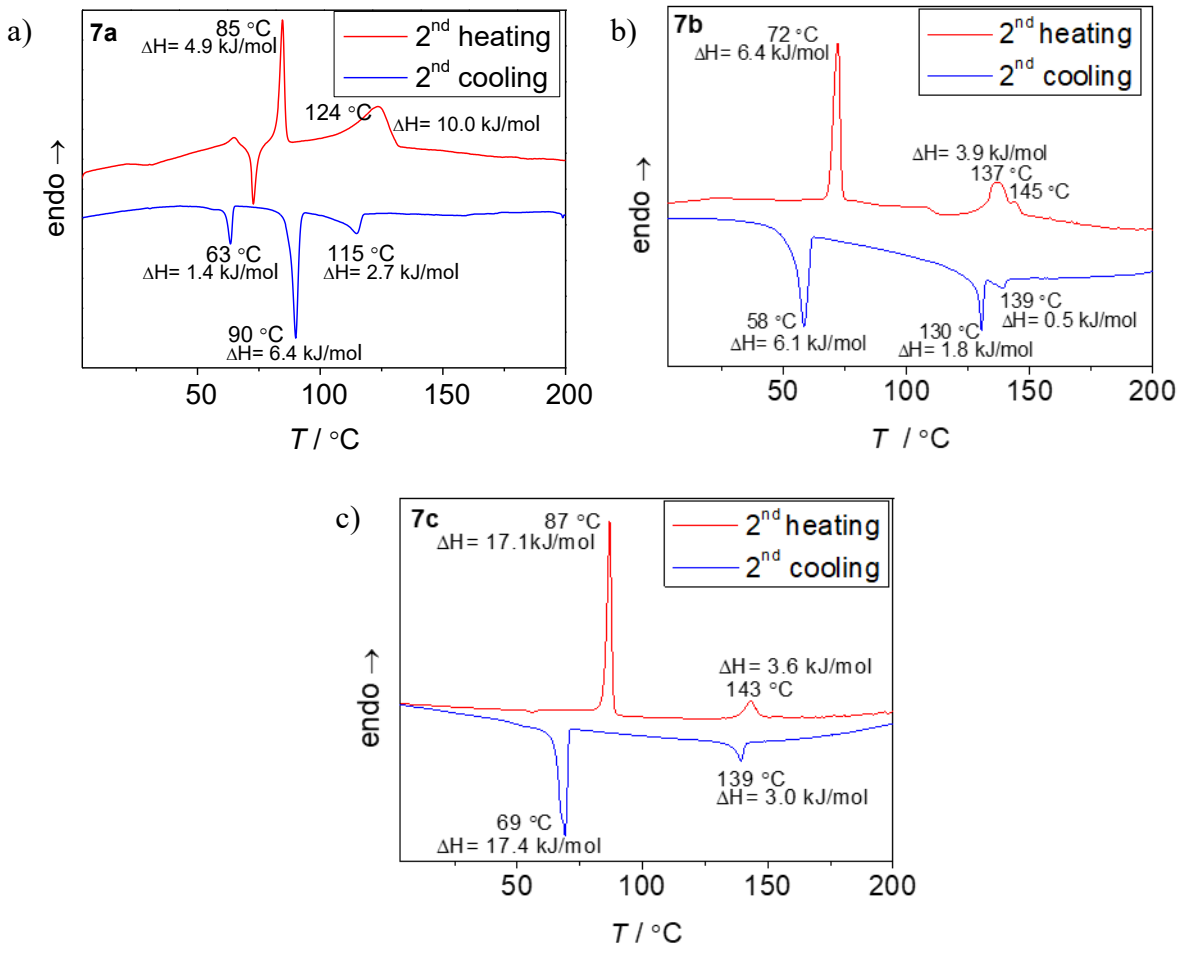


Figure S40. DSC thermograms of compounds **7a-c** on heating and cooling (10 K min^{-1}).

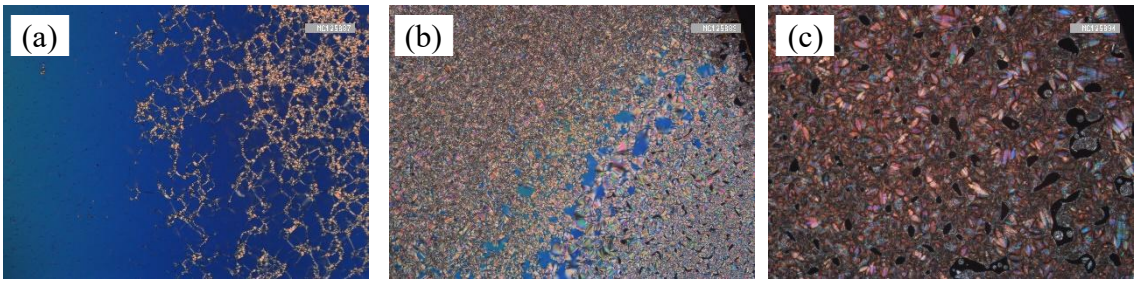


Figure S41. Optical textures of mesophases of compound **7a** as observed between crossed polarizers (indicated by arrows) in ordinary glass plates on cooling; (a) oily streaks texture of N* at T= 138.6 °C; (b) transition N* phase to SmC* phase at T= 133.0 °C; (c) SmX mesophase at T= 102.6 °C.

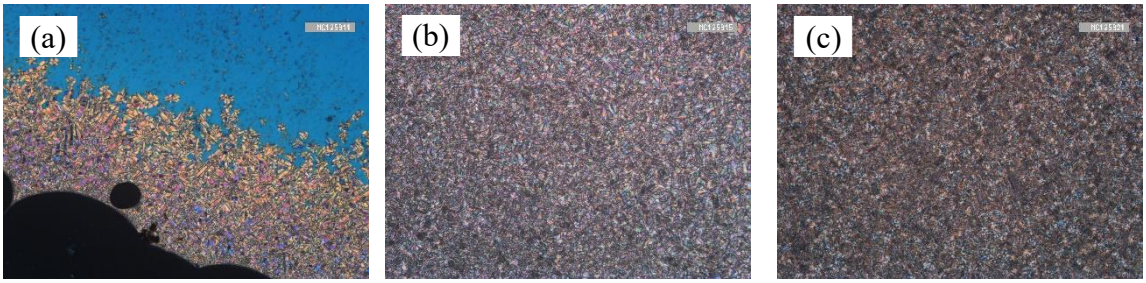


Figure S42. Optical textures of mesophases of compound **7b** as observed between crossed polarizers (indicated by arrows) in an ordinary glass plate on cooling; (a) N* at T= 139.0 °C; (b) finger-print texture of SmC* phase at T= 128.3 °C; (c) crystal state at T= 58.0 °C.

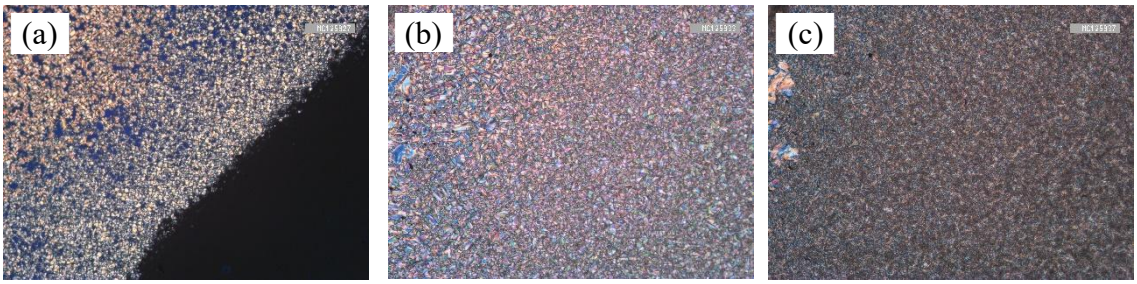


Figure S43. Optical textures of mesophases of compound **7c** as observed between crossed polarizers (indicated by arrows) in ordinary glass plates on cooling; (a) N* phase at T= 141.5 °C; (b) finger-print texture of SmC* phase at T= 97.5 °C; (c) crystal state at T= 69.

3.2 Additional data of compounds I and II

3.2.1 Additional DSC thermograms

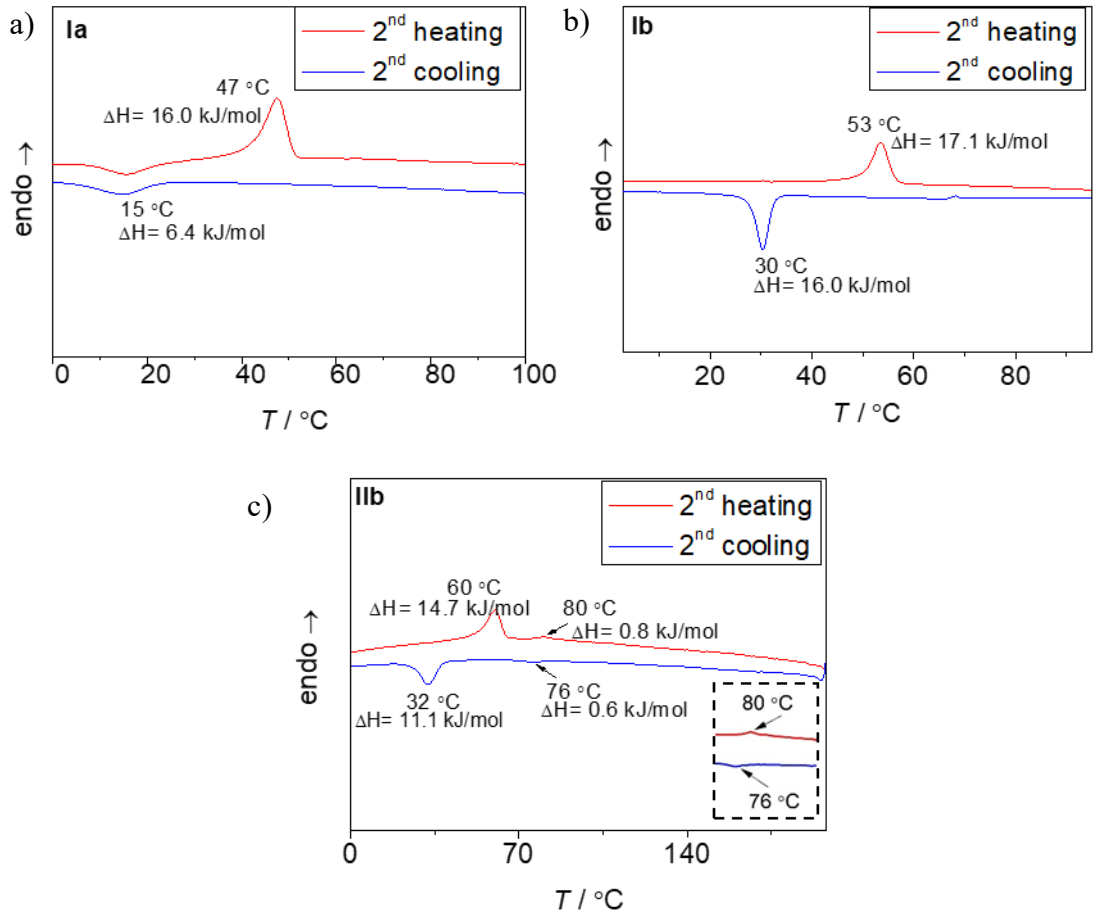


Fig. S44. DSC thermograms on 2nd heating and cooling (10 K min^{-1}) of **Ia**, **Ib** and **IIb**.

3.2.2 Additionall textures

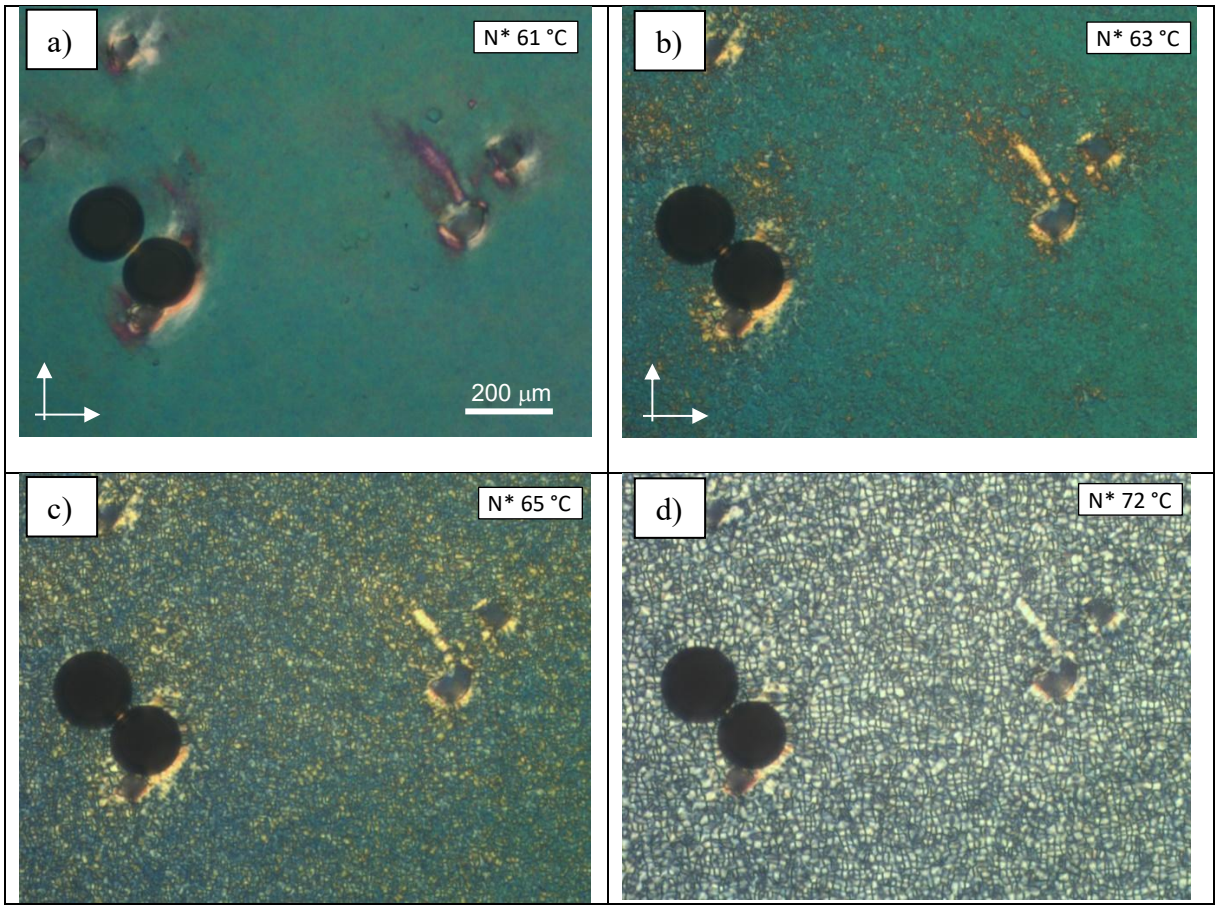


Figure S45. Textures of the N_{CybC}* phase of **IIb** depending on temperature as observed by POM between crossed polarizers upon heating; the textural changes are reversible, i.e., the inverted sequence is observed upon cooling without applying any shear force.

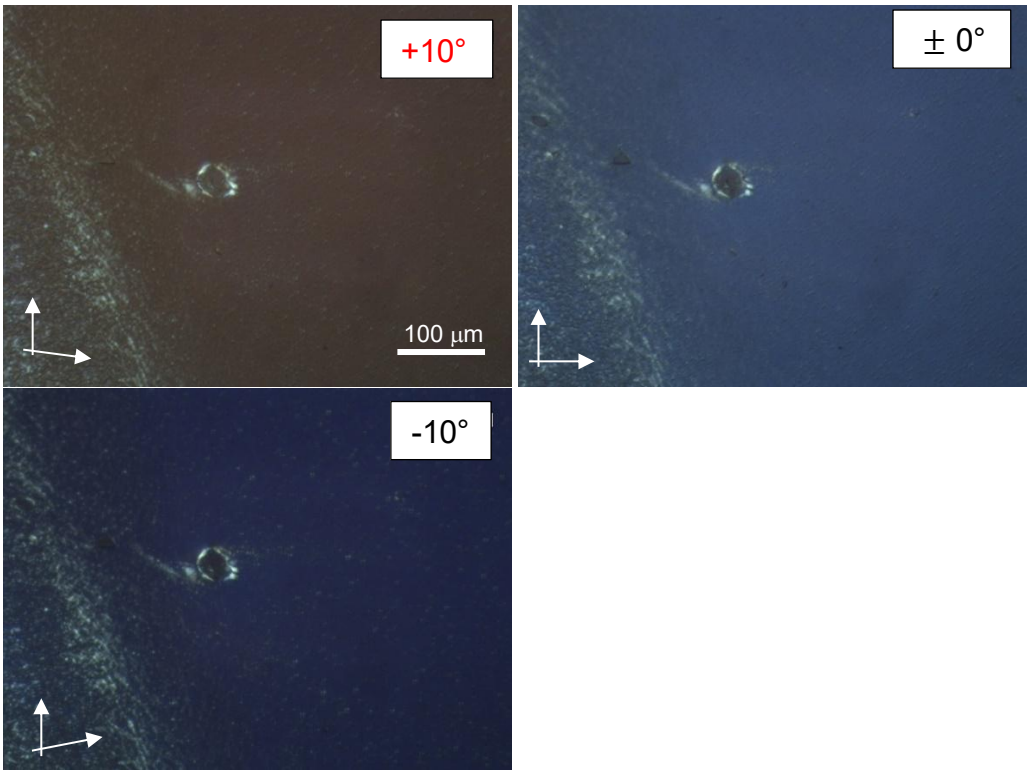


Figure S46. Textures of the N_{CybC}* phase of **IIb**, as observed at 72 °C by POM and rotating the analyzer by the given angles out of the 90° orientation, maximum darkness is achieved at +10; rotating the sample between crossed polarizers leads to no change.

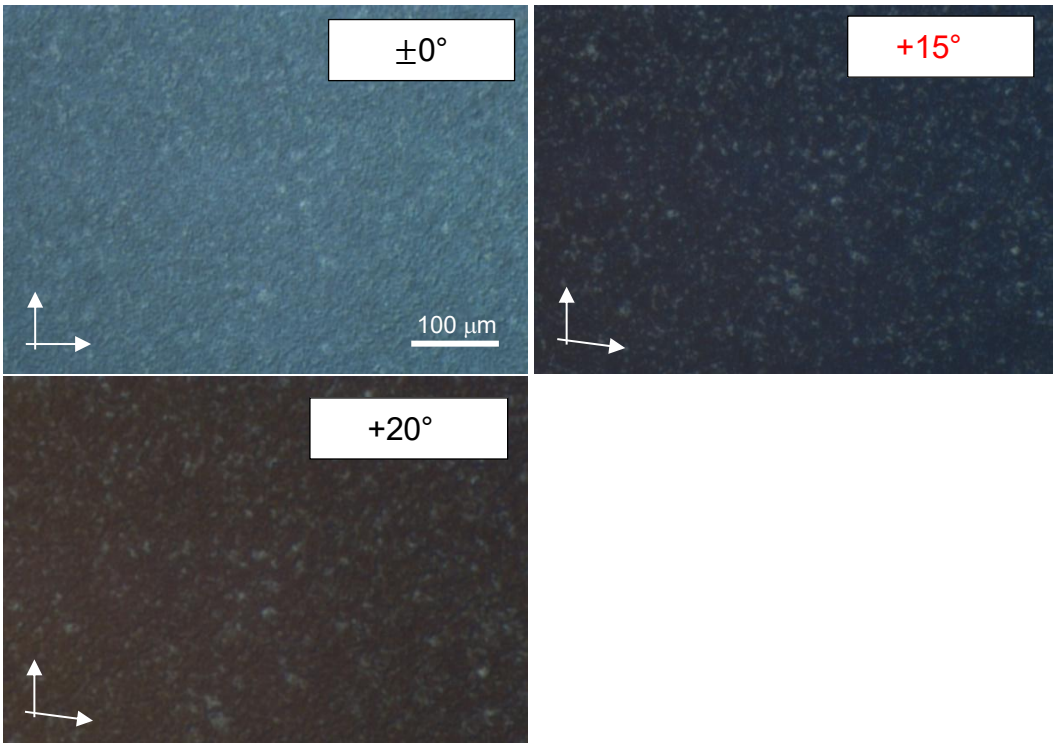


Figure S47. Textures of the SmC* phase of **IIc,** as observed at 49 °C by POM and rotating the analyzer by the given angles out of the 90° orientation, maximum darkness is achieved at +15; rotating the sample between crossed polarizers leads to no change.

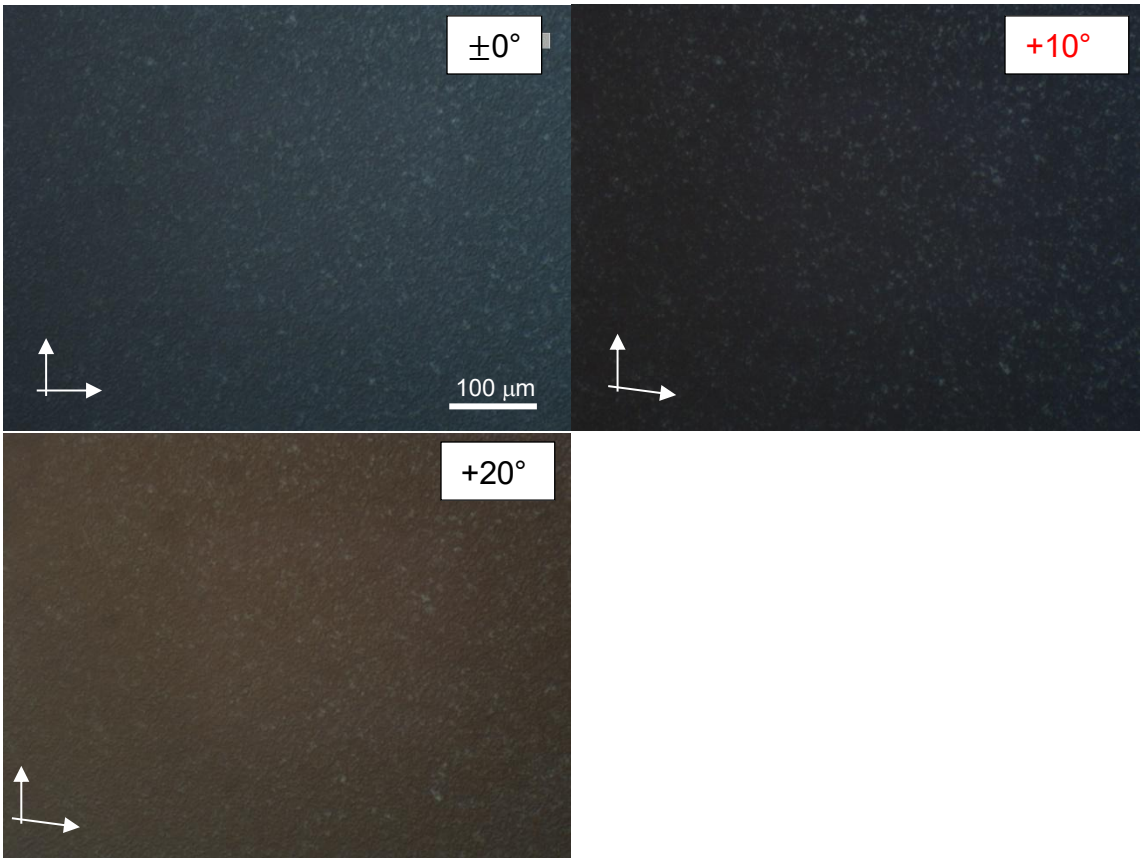


Figure S48. Textures of the M_L* phase of **IIc,** as observed at 30 °C by POM and rotating the analyzer by the given angles out of the 90° orientation, maximum darkness is achieved at +10; rotating the sample between crossed polarizers leads to no change.

3.2.3 Additional XRD-Data

Table S2. Numerical SAXS data and estimated correlation lengths of compounds **I** and **II**.[a]

Compd.	L_{mol} /nm [b]	T /°C	Phase	2θ/°	d/nm	FWHM (Δ2θ) /°	Δθ /°	Δθ/rad	ΔQ/ nm^{-1}	L_ζ/nm
Ia cooling	5.0	60	Iso	2.736	3.23	1.445	0.728	0.013	1.035	6.1
		50	Iso	2.698	3.28	1.289	0.645	0.011	0.917	6.9
		40	Iso	2.633	3.36	1.204	0.602	0.011	0.856	7.3
		30	M_{Iso}	1.990	4.44	0.901	0.451	0.008	0.641	9.8
Ia heating		60	Iso	2.712	3.26	1.421	0.711	0.012	1.011	6.2
		50	Iso	2.654	3.33	1.412	0.706	0.012	1.004	6.3
		40	M_{Iso}	2.007	4.40	0.863	0.432	0.008	0.614	10.2
		30	M_{Iso}	1.973	4.48	0.875	0.438	0.008	0.622	10.1
Ib	5.5	29	M_{Iso}	2.201	4.01	0.811	0.406	0.007	0.577	10.9
Ic	6.0	30	M_{Iso}	2.068	4.27	0.705	0.353	0.006	0.501	12.5
		40[b]	Cr	2.224	3.97	0.159	0.080	0.001	0.113	55.6
IIa cooling	4.6	70	Iso	2.496	3.54	2.027	1.014	0.018	1.442	4.4
		50	BPIII	2.200	4.02	1.251	0.626	0.011	0.890	7.1
		40	BPIII	1.963	4.50	0.541	0.271	0.005	0.385	16.3
		29(H)	M_{Iso}	1.999	4.42	0.719	0.360	0.006	0.511	12.3
IIb cooling	5.1	70	N_{CybC}*	1.927	4.58	0.687	0.344	0.006	0.489	12.9
		50	N_{CybC}*	1.911		0.344	0.172	0.003	0.245	25.7
		30	M_L*	1.884	4.69	0.457	0.229	0.004	0.325	19.3
IIc cooling	5.6	88	Iso	1.860	4.75	0.450	0.225	0.004	0.320	19.6
		80	N_{CybC}*	1.742	5.07	0.349	0.175	0.003	0.248	25.3
		70	SmC*	1.766	5.00	0.161	0.081	0.001	0.115	54.9
		60	SmC*	1.790	4.94	0.157	0.079	0.001	0.112	56.3
		50	SmC*	1.751	5.05	0.298	0.149	0.003	0.212	29.6
		40	M_L*	1.712	5.16	0.428	0.214	0.004	0.304	20.6
		35	M_L*	1.705	5.18	0.449	0.225	0.004	0.319	19.7

[a] $\Delta Q = (4\pi/\lambda)*\mathrm{Sin}(\Delta\theta)$; $L = 2\pi/\Delta\theta = \lambda / (\mathrm{FWHM} * \cos(\theta))$ with θ in rad. [b] Measured with space-filling CPK models with 120 ° bend of the polyaromatic core and maximally stretched alkyl chains. [c] Measured after storage for 3 months, see Fig. S48b, only the first strong scattering is considered.

Table S3. Numerical WAXS data of compounds **Ia-c** and **IIa-c**.

Compd.	*T* /°C	*phase*	*2θ/°*	*d/nm*
Ia	50	Iso	19.374	0.46
	28	M_{Iso}	14.066	0.63
			19.395	0.46
			23.475	0.38
Ib	28	M_{Iso}	14.315	0.62
			19.502	0.46
			24.804	0.36
Ic	30	M_{Iso}	14.254	0.62
			19.454	0.46
			24.518	0.36
IIa	50	BPIII	19.543	0.45
	29	M_{Iso}	13.815	0.64
			19.524	0.46
			24.876	0.36
IIb	70	N_{CybC}*	19.530	0.46
	30	M_L*	13.934	0.64
			19.293	0.46
			24.978	0.36
IIc	90	Iso	19.630	0.45
	78	N_{CybC}*	19.649	0.45
	60	SmC*	19.609	0.45
	35	M_L*	14.055	0.63
			19.431	0.46
			24.919	0.36

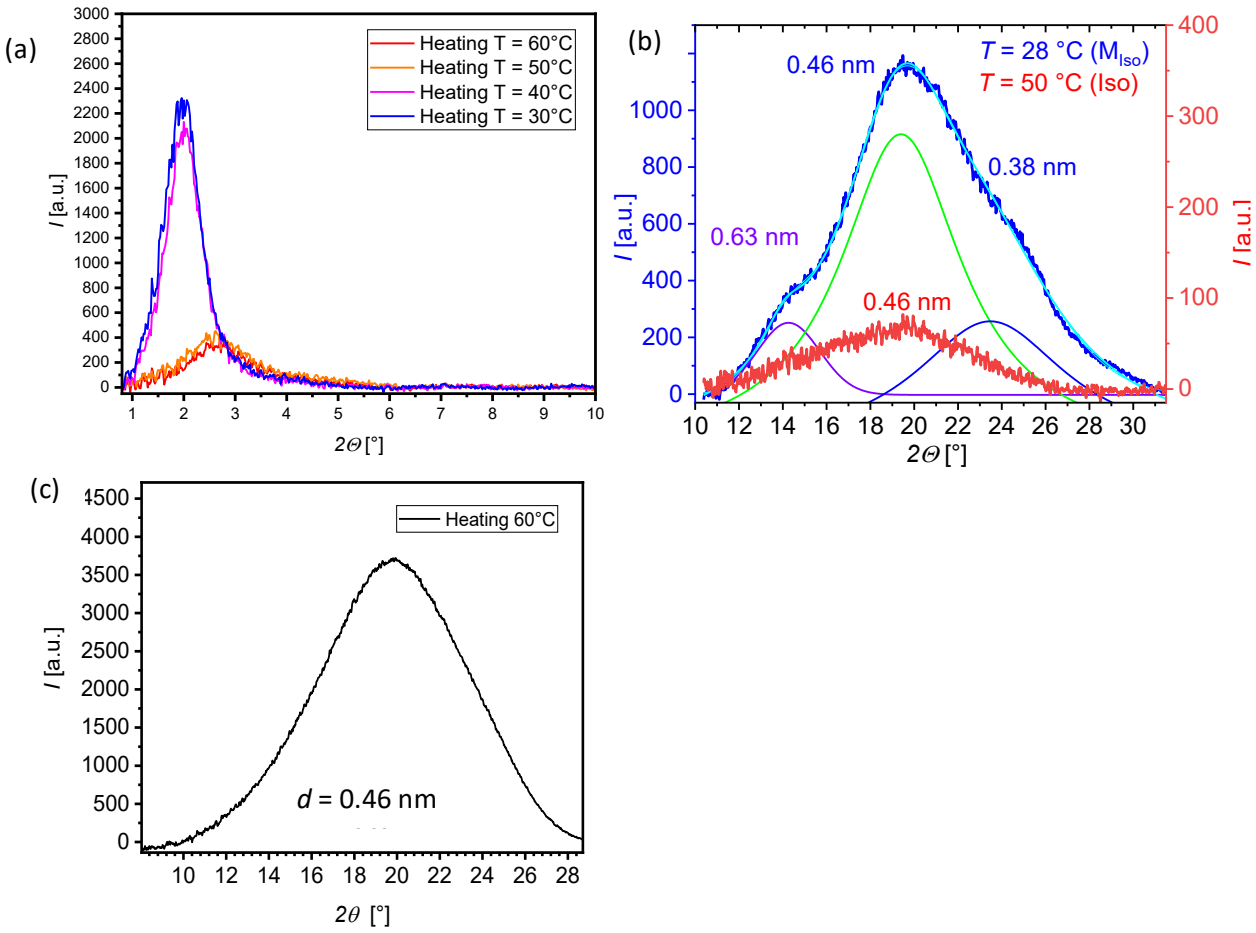


Figure S49. a) SAXS patterns of compound **Ia** on heating, (b) WAXS pattern in the M_{Iso} phase at 28 °C and in the Iso phase at 50°C, and (c) in the Iso phase at T = 60 °C

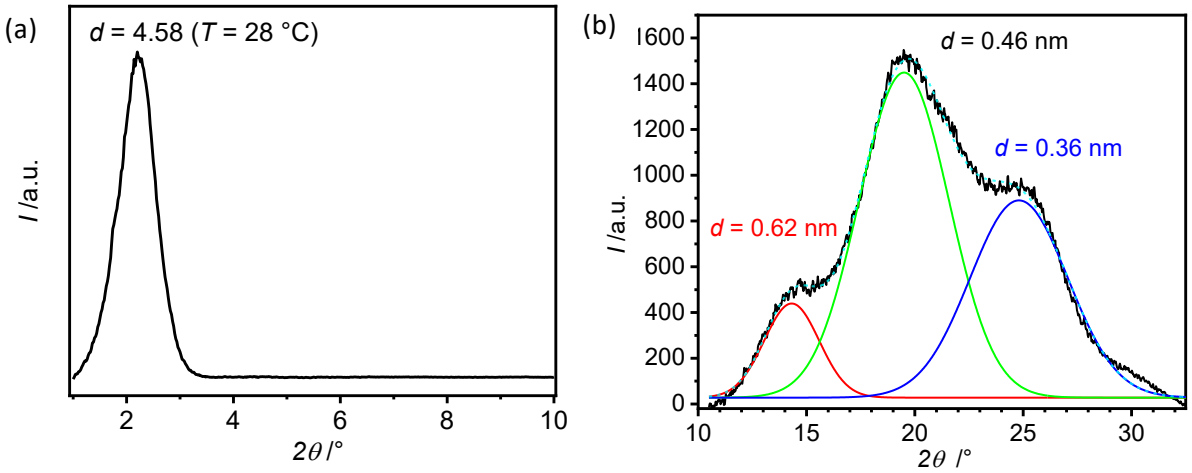


Figure S50. a) SAXS patterns of compound **Ib** on and (b) WAXS pattern in the M_{Iso} phase at 28°C, both measured on cooling.

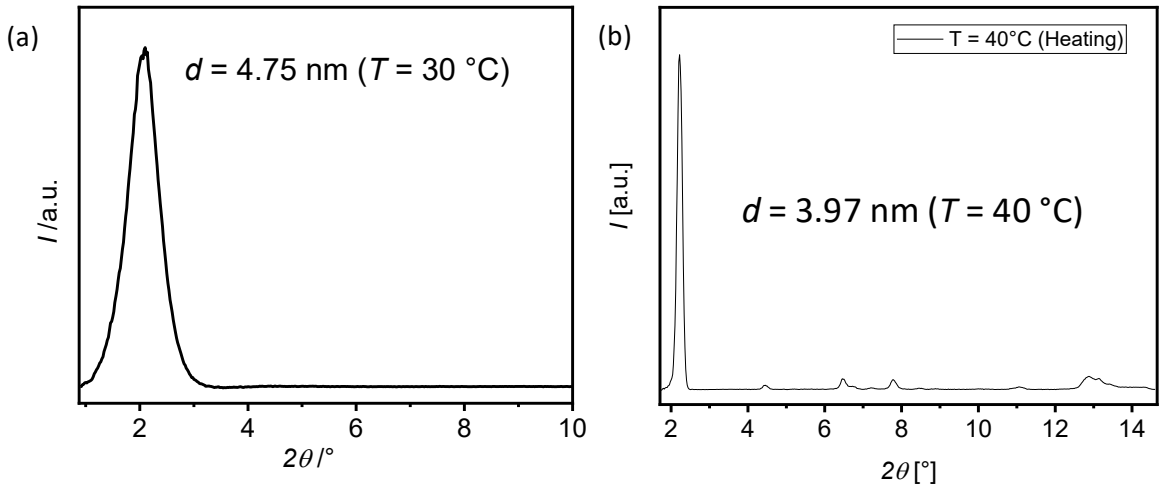


Figure S51. a) SAXS patterns of compound **Ic** a) in the M_{Iso} phase at 30 °C immediately after cooling from Iso and b) of the crystallized sample at 40 °C after 3 months storage at 25 °C.

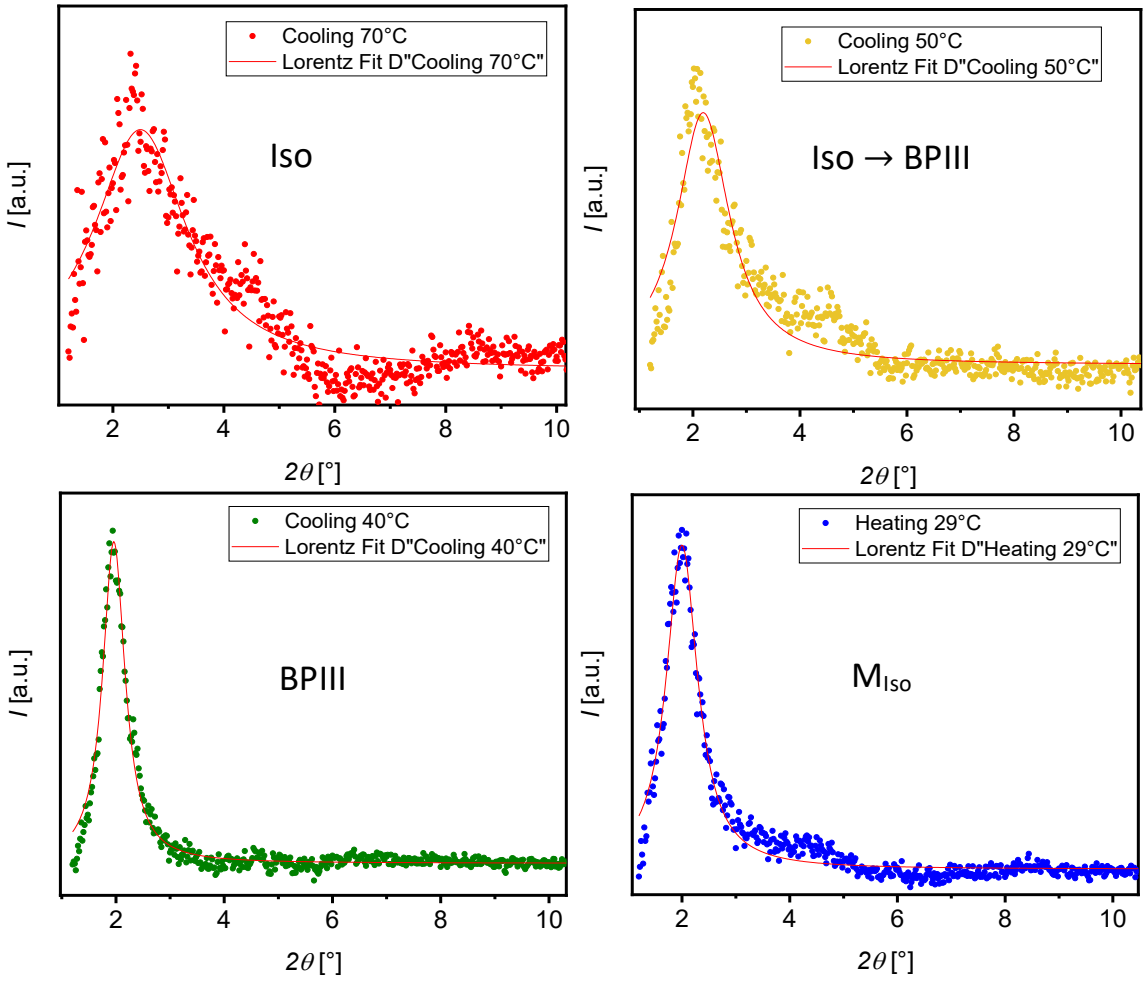


Figure S52. SAXS patterns of compound **IIa** at the indicated temperatures (individual curves used in Figure 5); the scattering around 4-5° is due to absorption by air.

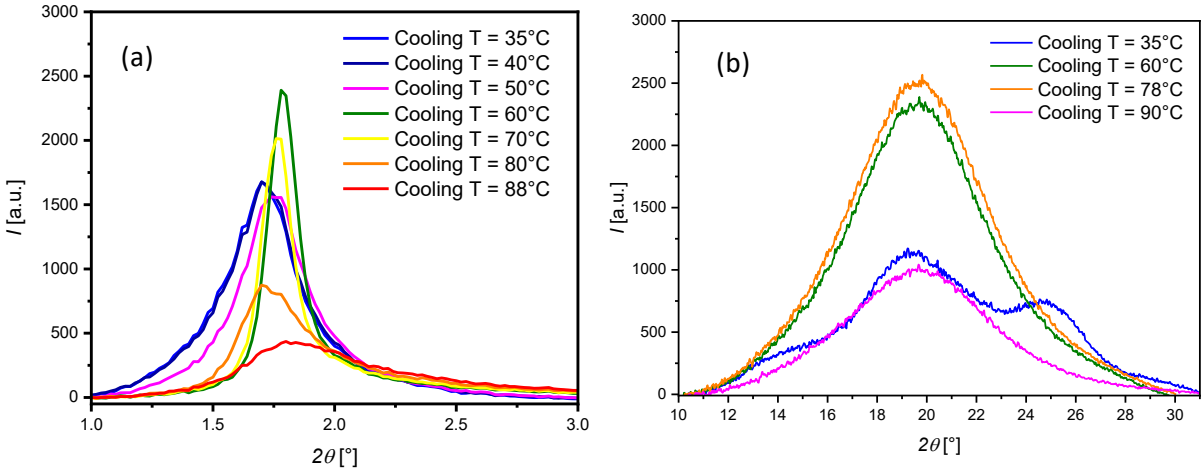


Figure S53. a) SAXS patterns of compound **IIc** as observed on cooling at the distinct temperatures and b) WAXS patterns, including all measured temperatures.

4. Mixtures with 5-CB

Though there is no detectable superstructural chirality in the mesophases of compounds **Ia-c**, if compound **Ib**, as example, was mixed with *4'-pentyl-4-biphenylcarbonitrile* (**5CB:** Cr 24 °C N 35 °C Iso) in different ratios 1:1, 1:4, 1: 9 (Fig. 3a, b) and 3: 97 (Fig. 3c) chiral nematic phases (N*) can efficiently be induced. In all cases, even at very small concentrations of **Ib** (3 : 97), the occurrence of the characteristic focal conic and oily-streaks texture of the induced N* phase indicates a significant helical twisting power of compound **Ib**. The predominance of focal conic textures indicates some tendency of the alignment of the helix axis parallel to the substrate surfaces in the induced cholesteric phase dominated by 5-CB self-assembly.

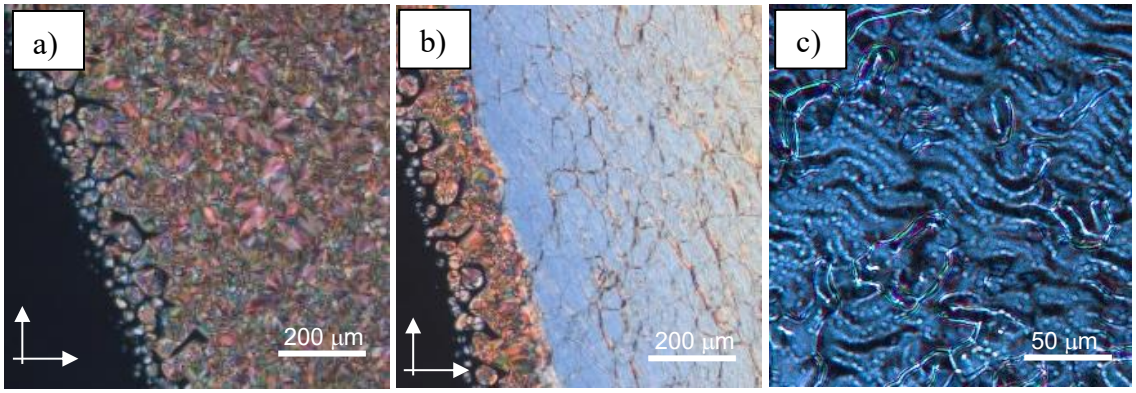


Figure S54. Optical textures of **Ib:5CB / 1:9** mixture at 28 °C between ordinary glass plates under crossed polarizers (indicated by arrows) showing the induced cholesteric phase, a) focal-conic texture and b) oily-streaks texture after shearing; c) cholesteric fingerprint texture of **Ib:5CB / 3:97** mixture at 25 °C. Note that the preferred organization is with the cholesteric helix lying parallel to the substrate surfaces (a,c), only after shearing does it become aligned perpendicular to the surfaces (b).

5. POM investigation of conglomerate textures and uniform chirality due to superstructural chiralty in isotropic mesophases

Superstructural chirality is commonly identified by POM with an angle ≠ 90° between analyzer and polarizer, where a conglomerate of bright and dark areas, representing areas with opposite optical rotation, can be observed. The brightness of these opposite chiral domains is inverted by reversing the twist sense between the polarizer and analyzer. In the case of enantiomerically enriched compounds, often only a single sense of optical rotation is found, i.e. the complete area becomes brighter or darker by inverting the twist direction (see Figs. S46-S48). It is important to note that in the thin samples (10-50 μm) used for these investigations, the much smaller optical rotation resulting from the chirality of the individual molecules (usually the specific rotation $[\alpha]_D$ is only a few degrees for decimeter thick samples in solution) is too small to be detected. Thus, in the case of optically isotropic systems, the superstructural chirality of self-assembly (in most cases helical) can easily be identified and distinguished from the much smaller intrinsic molecular optical rotation of the homochiral molecules themselves by this method.

6. Reference compounds

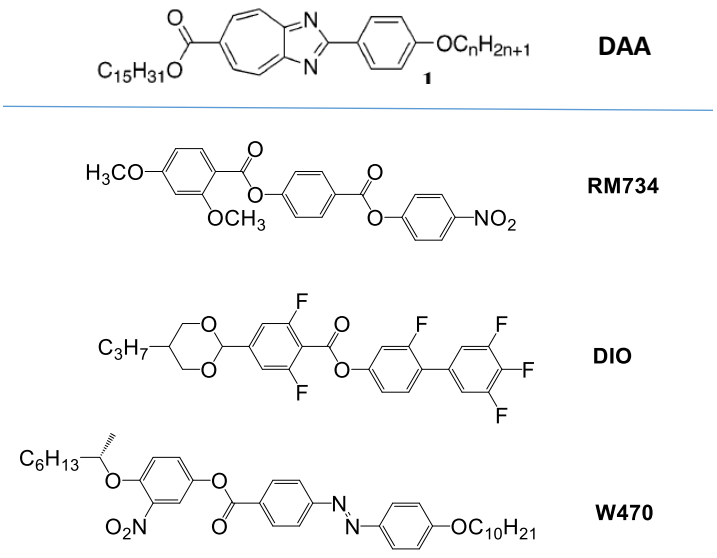


Figure S55. Formula of the chemical structures of **DAA**, **RM734**, **DIO**, and **W470**.

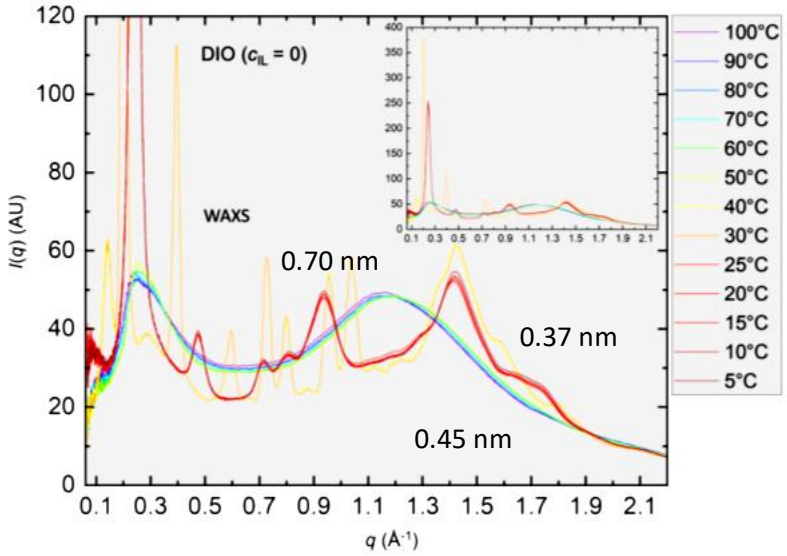


Figure S56. WAXS vs. *T* scans of DIO (I_{re} = red curve) with added *d-values for* the major WAXSs; reproduced from ref. 19 © 2025 by the authors (CC BY) license https://creativecommons.org/licenses/by/3.0/.

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