SUPPLEMENTARY INFORMATION

Chiral Cyanobiphenyl Dimers – Significance of the Linking Group for Mesomorphic Properties and Helical Induction

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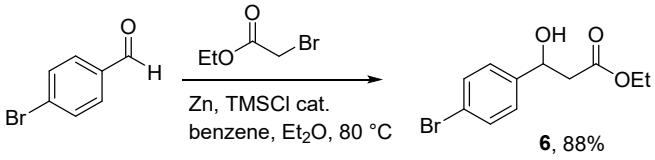
Synthetic methods

General Methods. All reactions were conducted under an argon atmosphere unless stated otherwise. Toluene, benzene, and Et_2O were dried following standard methods. Commercial grade reagents and solvents were used without further purification. (1*S*,2*S*)-(+)-*N*-*p*-Tosyl-1,2-diphenylethylenediamine and $[RuCl_2(mesitylene)]_2$ were obtained from commercial sources. TLC was performed on aluminum-baked silica plates (60 F254, Merck) and visualized using either UV light (254 nm) or phosphomolybdic acid reagent. Column chromatography was performed on silica gel (Silicagel 60, 70–230 mesh, Merck) or flash silica gel (Silicagel 60, 230-400 mesh, Merck). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV 300 and 600 spectrometers in $CDCl_3$ or d_6-DMSO. Chemical shifts (δ) are given in ppm and are referenced to TMS or the internal protic solvent. Coupling constants are given in Hz. Chemical purity and reaction progress were monitored by HPLC on a Shimadzu 10A VP HPLC system with a DAD detector. The stationary phase was a Nucleosil 100-5 C18, 250 mm x 4.6 mm column. The following solvent systems were used as mobile phases, either: H_2O, MeOH, H_3PO_4 (85%) = 90:10:0.5 (A); MeOH (B); Gradient method: 50/100/100/50 %B in 0/20/25/27 min, 1 mL/min. The optical purity of the formed products was determined by chiral HPLC analysis on an Agilent 1260 Infinity instrument using a Daicel Chiralpak IA (4.6 × 250 mm, 5 μm) column as the stationary phase. Optical rotation was measured using an Optical Activity AA-10 automatic polarimeter. High-resolution mass spectrometry (HRMS) was performed on Agilent 6546 LC/Q-TOF coupled with Agilent 1290 Infinity II HPLC instrument (+ESI). Compounds **2a** and **2b** were prepared according to literature procedure.[1]

1.1 Preparation of cyanobiphenyl acids

*Ethyl 3-(4-bromophenyl)-3-hydroxypropanoate (**6**)*

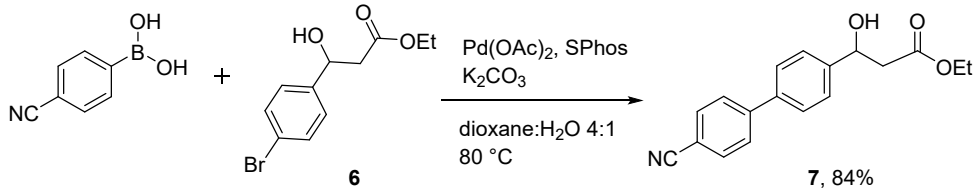


6, 88%

Powdered zinc (< 10 μm) (3.50 g, 54.0 mmol) was placed in a dry three necked flask under argon, and the flask was fitted with a reflux condenser and a dropping funnel. A solution of ethyl bromoacetate (1.2 mL, 10.8 mmol), 4-bromobenzaldehyde (2.01 g, 10.8 mmol) and TMSCl (80 μL) in a mixture of dry benzene (35 mL) and dry diethyl ether (3 mL) was placed in a dropping funnel. The reaction was initiated by adding 1 mL of this solution to the zinc, and heating under reflux. The rest of the solution was added dropwise and the mixture was refluxed for another 30 min. After cooling, the mixture is diluted with MTBE and 10% aqueous solution of H_3PO_4 is added. Layers were separated and the water layer was extracted with MTBE (2 x). Combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Crude ester was purified using silica gel column chromatography (DCM to DCM/MeOH = 50:1) to obtain product **6** (2.62 g, 88%) as a white

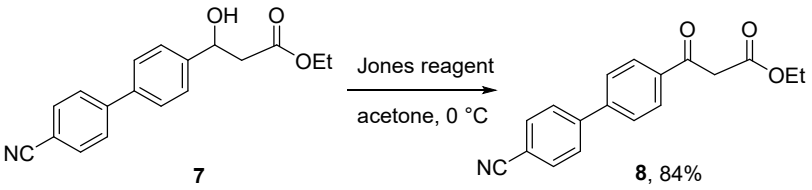
solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 5.15 – 5.02 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.38 (d, J = 3.5 Hz, 1H), 2.79 – 2.59 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.24, 141.51, 131.64, 127.42, 121.59, 69.67, 61.01, 43.12, 14.14.

*Ethyl 3-(4'-cyano-[1,1'-biphenyl]-4-yl)-3-hydroxypropanoate (**7**)*



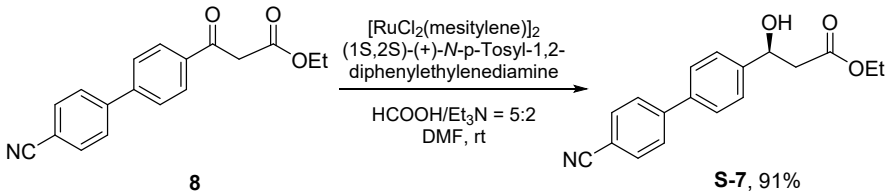
Compound **6** (505 mg, 1.8 mmol), 4-cyanophenylboronic acid (350 mg, 2.4 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (49 mg, 0.12 mmol), palladium (II) acetate (17 mg, 0.08 mmol) and K_2CO_3 (756 mg, 5.5 mmol) were placed in a 2-neck round bottom flask under nitrogen atmosphere. A degassed solvent mixture dioxane-H_2O (4:1) (20 mL) was then added to the reaction flask. The reaction mixture was stirred at 80 °C for 24 hours. After cooling down to room temperature, the reaction mixture was diluted with water and extracted with EtOAc (3x). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography in DCM/MeOH = 50:1 to yield product **7** as a white solid (461 mg, 84 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 5.25 – 5.15 (m, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.41 (d, J = 3.4 Hz, 1H), 2.86 – 2.69 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.35, 145.22, 143.10, 138.63, 132.63, 127.67, 127.41, 126.47, 118.90, 111.00, 69.88, 61.03, 43.17, 14.16.

*Ethyl 3-(4'-cyano-[1,1'-biphenyl]-4-yl)-3-oxopropanoate (**8**)*



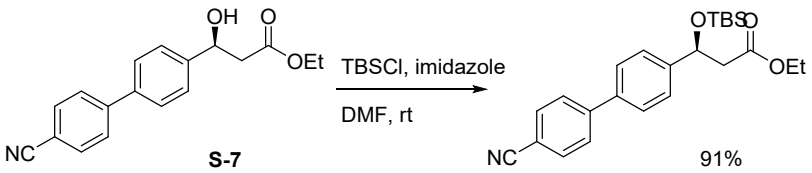
To a solution of hydroxyester **7** (472 mg, 1.60 mmol) in acetone (10 mL), cooled to 0 °C, Jones reagent was added dropwise until red-brown color persisted. The mixture was stirred for another 30 min. Solvent was evaporated, water was added (20 mL), and the mixture was extracted with DCM (3x). Organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Crude ketoester was purified using silica gel column chromatography (DCM/MeOH = 50:1) to obtain product **8** (392 mg, 84%) as a white solid. ^{1}H NMR (600 MHz, DMSO) δ 8.03 – 8.00 (m, 2H), 7.93 – 7.91 (m, 4H), 7.90 – 7.87 (m, 2H), 4.18 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 193.07, 167.63, 143.13, 143.00, 135.57, 132.94, 129.21, 127.97, 127.49, 118.65, 111.01, 60.63, 45.60, 13.97.

Ethyl (S)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)-3-hydroxypropanoate (**S-7**)



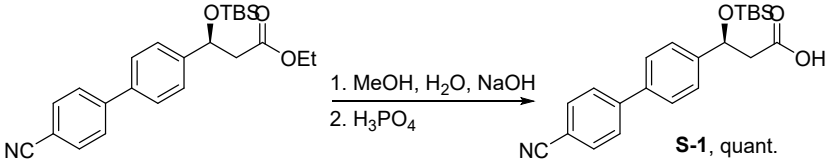
A mixture of [($RuCl_2$(mesitylene)]$_2$ (15 mg, 0.03 mmol, 2 mol%) and the chiral ligand (1*S*,2*S*)-(+)-*N*-*p*-Ts-1,2-DPEN (15 mg, 0.04 mmol, 3 mol%) was heated in DMF (1.5 mL) at 80 °C for 30 min under argon. The solution was cooled to room temperature. A mixture of HCO_2H and Et_3N, 5:2 molar ratio (1 mL) followed by the solution of ketone **8** (392 mg, 1.34 mmol) in DMF (2 mL) were added. The reaction mixture was stirred at room temperature for 24 h. The mixture was partitioned between water (10 mL) and MTBE (15 mL). Organic layer was washed with water (10 mL), and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Crude ester was purified using silica gel column chromatography (DCM/MeOH = 50:1) to obtain of product **S-7** (361 mg, 91%) as white solid. NMR given above for the racemic compound **7**.

Ethyl (S)-3-((tert-butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)propanoate



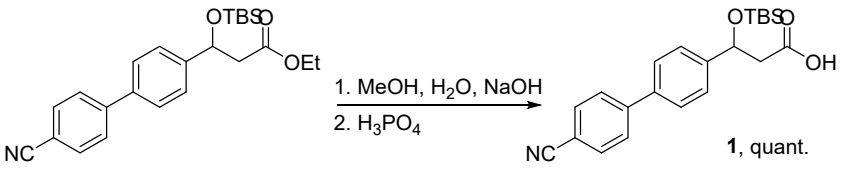
Compound **S-9** (361 mg, 1.2 mmol), TBDMSCl (318 mg, 2.1 mmol), and imidazole (149 mg, 2.2 mmol) in DMF (10 ml) were stirred overnight at room temperature. The reaction solution was partitioned between 5% aqueous solution of NH_4Cl (20 mL) and MTBE (20 mL); the two layers were separated, and the aqueous layer further extracted with MTBE (2 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified using silica gel column chromatography (DCM) to obtain the title compound (456 mg, 91%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.71 – 7.67 (m, 2H), 7.58 – 7.54 (m, 2H), 7.46 (d, J = 8.2 Hz, 2H), 5.21 (dd, J = 9.0, 4.3 Hz, 1H), 4.20 – 4.08 (m, 2H), 2.75 (dd, J = 14.7, 9.0 Hz, 1H), 2.58 (dd, J = 14.7, 4.3 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.87 (s, 9H), 0.05 (s, 3H), -0.13 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.97, 145.29, 144.87, 138.25, 132.60, 127.61, 127.15, 126.61, 118.95, 110.88, 71.79, 60.58, 46.40, 25.67, 18.07, 14.20, -4.63, -5.24. According to same procedure, racemic compound was prepared starting from 1.3 g of **7** in 95% yield.

*(S)-3-((tert-Butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)propanoic acid (**S-1**)*



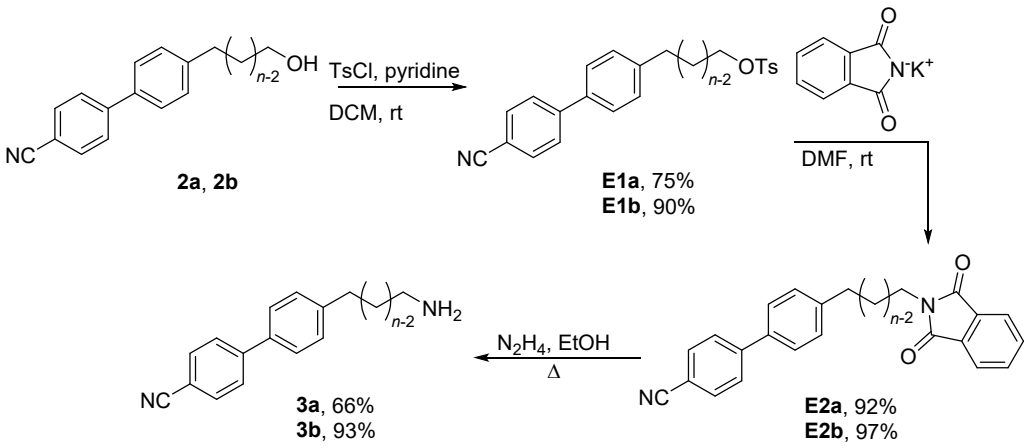
The TBS protected ester (456 mg, 1.1 mmol) was dissolved in a MeOH (25 mL) and water (5 mL) was added to the solution. NaOH (890 mg, 22 mmol) was added and the mixture was stirred at room temperature for 2 - 4 h. After completion of reaction as indicated by HPLC, solvent was evaporated and MTBE (20 mL) was added, followed by 10% aqueous solution of H_3PO_4 (20 mL). Layers were separated, and the water layer was extracted with MTBE (2 x 20 mL). Combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Crude product **S-1** (423 mg, quant.) was used directly in the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.71 – 7.67 (m, 2H), 7.59 – 7.55 (m, 2H), 7.47 (d, J = 8.2 Hz, 2H), 5.22 (dd, J = 8.7, 4.2 Hz, 1H), 2.80 (dd, J = 15.1, 8.7 Hz, 1H), 2.68 (dd, J = 15.1, 4.2 Hz, 1H), 0.88 (s, 9H), 0.07 (s, 3H), -0.11 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.38, 145.17, 144.19, 138.52, 132.60, 127.63, 127.28, 126.55, 118.88, 110.98, 71.51, 45.67, 25.67, 18.07, -4.64, -5.26. $[\alpha]_D^{25}$ = -58.2 (*c* 0.98, MeOH).

*3-((tert-Butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)propanoic acid (**1**)*



According to the same procedure described for (**S-1**), racemic compound **1** was prepared starting from 1.80 g of racemic TBS protected ester in a quantitative yield. ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum are the same as for the **S-1**.

1.2. Synthesis of amines 3a & 3b



General reaction procedure A. Cyanobiphenyl alcohol **2a**/**2b** (1 equiv.) and tosyl chloride (2 equiv.) were dissolved in DCM and pyridine (3 equiv.) was added to a solution. The reaction mixture was stirred at room temperature overnight and extracted with an aqueous solution of NH_4Cl. The water layer was extracted twice with DCM. Combined organic layers were dried over Na_2SO_4, filtered, and

concentrated under reduced pressure. Crude tosyl ester was purified using silica gel column chromatography (DCM) to obtain the product **E1a**/**E1b** as a colorless oil.

*5-(4'-Cyano-[1,1'-biphenyl]-4-yl)pentyl 4-methylbenzenesulfonate (**E1a**).* According to the general procedure A, starting from 4'-(5-hydroxypentyl)-[1,1'-biphenyl]-4-carbonitrile (2.72 g, 10.2 mmol), after silica gel column chromatography (DCM/hexane = 9:1 to DCM) the product **E1a** (3.22 g, 75%) was obtained as colorless viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.74 – 1.66 (m, 2H), 1.65 – 1.58 (m, 2H), 1.43 – 1.36 (m, 2H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 145.52, 144.68, 142.99, 136.69, 133.21, 132.58, 129.82, 129.14, 127.88, 127.50, 127.16, 119.01, 110.63, 70.40, 35.31, 30.62, 28.73, 25.03, 21.64.

*7-(4'-Cyano-[1,1'-biphenyl]-4-yl)heptyl 4-methylbenzenesulfonate (**E1b**).* According to the general procedure A, starting from 4'-(7-hydroxyheptyl)-[1,1'-biphenyl]-4-carbonitrile (1.58 g, 5.4 mmol), after silica gel column chromatography (DCM) the product **E1b** (2.18 g, 90%) was obtained as colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.64 (m, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 2.69 – 2.59 (m, 2H), 2.44 (s, 3H), 1.71 – 1.57 (m, 4H), 1.41 – 1.21 (m, 6H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 145.59, 144.64, 143.51, 136.54, 133.25, 132.57, 129.80, 129.16, 127.88, 127.49, 127.11, 119.04, 110.56, 70.60, 35.51, 31.17, 28.99, 28.81, 28.78, 25.28, 21.63.

General reaction procedure B. The compound **E1a**/**E1b** (1 equiv.) was dissolved in DMF and potassium phthalimide (1.5 equiv.) was added. The reaction mixture was stirred at 60 °C for 2 h. After cooling to room temperature, the mixture was diluted with water and extracted with Et_2O (3x). Combined organic layers were washed with an aqueous solution of $NaHCO_3$ and water, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain the compound **E2a**/**E2b** as a white solid.

*4'-(5-(1,3-Dioxoisoindolin-2-yl)pentyl)-[1,1'-biphenyl]-4-carbonitrile (**E2a**).* According to the general procedure B, starting from **E1a** (3.09 g, 7.4 mmol), product **E2a** (2.65 g, 92%) was obtained as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.77 – 7.59 (m, 6H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.69 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.82 – 1.63 (m, 4H), 1.51 – 1.32 (m, 2H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 168.44, 145.59, 143.23, 136.57, 133.88, 132.54, 132.16, 129.18, 127.49, 127.12, 123.17, 119.03, 110.55, 37.87, 35.34, 30.79, 28.36, 26.37.

*4'-(7-(1,3-Dioxoisoindolin-2-yl)heptyl)-[1,1'-biphenyl]-4-carbonitrile (**E2b**).* According to the general procedure B, starting from **E1b** (2.17 g, 4.8 mmol), product **E2b** (1.98 g, 97%) was obtained as a white

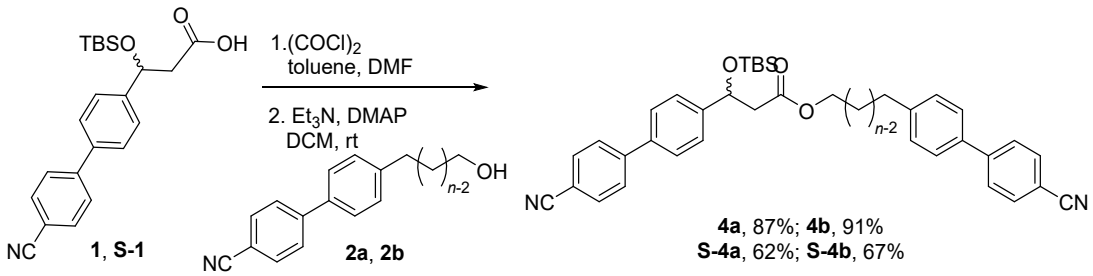
solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.75 – 7.64 (m, 6H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.60 (m, 4H), 1.46 – 1.26 (m, 6H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 168.50, 145.64, 143.64, 136.46, 133.88, 132.55, 132.17, 129.19, 127.49, 127.08, 123.17, 119.06, 110.51, 38.02, 35.53, 31.22, 29.07, 29.01, 28.56, 26.76.

General reaction procedure C. The crude product **E2a**/**E2b** (1 equiv.) was suspended in EtOH and hydrazine hydrate (0.15 mL per 1 mmol **E2a**/**E2b**) was added. The reaction mixture was refluxed for 2 h and cooled to room temperature and EtOH was evaporated. The resulting white solid was washed with Et_2O (3x). The filtrate was evaporated to white solid **3a**/**3b** and used without further purification.

*4'-(5-Aminopentyl)-[1,1'-biphenyl]-4-carbonitrile (**3a**).* According to the general procedure C, starting from **E2a** (1.04 g, 2.6 mmol), product **3a** (460 mg, 66%) was obtained as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.69 – 7.65 (m, 2H), 7.53 – 7.48 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.73 – 2.63 (m, 4H), 1.71 – 1.64 (m, 2H), 1.53 – 1.46 (m, 2H), 1.44 – 1.35 (m, 2H), 1.28 (br. s, 2H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 145.58, 143.47, 136.55, 132.56, 129.18, 127.48, 127.11, 119.03, 110.57, 41.98, 35.55, 33.29, 31.19, 26.53.

*4'-(7-Aminoheptyl)-[1,1'-biphenyl]-4-carbonitrile (**3b**).* According to the general procedure C, starting from **E2b** (1.97 g, 4.7 mmol), product **3b** (1.27 g, 93%) was obtained as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.61 (m, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.76 – 2.58 (m, 4H), 1.75 – 1.56 (m, 2H), 1.58 – 1.20 (m, 10H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 145.62, 143.69, 136.49, 132.56, 129.18, 127.48, 127.08, 119.04, 110.54, 42.09, 35.60, 33.44, 31.33, 29.33, 29.26, 26.80.

1.3. Preparation of TBS protected esters and amides

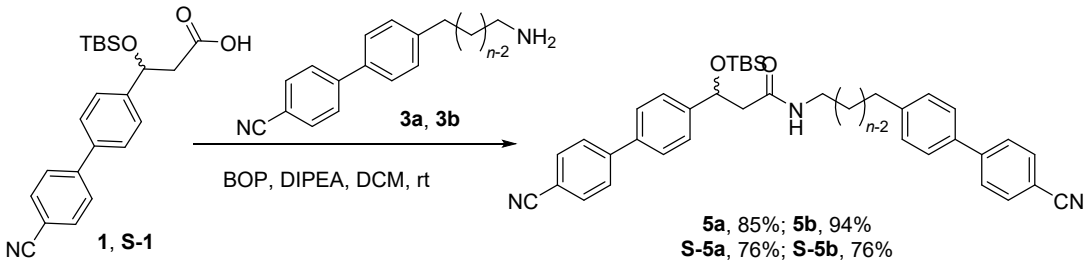


General procedure D – Esterification. Corresponding acid (1.5 equiv.) was suspended in anhydrous toluene (3 mL) under argon. Oxalyl chloride (1.5 – 2 equiv.) was added followed by DMF (1 drop). The mixture was stirred for 1-2 h at room temperature. The solvent was evaporated, and the residue dissolved in DCM (5 mL). This solution was added to a premixed solution of alcohol (1 equiv.), Et_3N (10 equiv.) and DMAP (cat.) in DCM (3 mL). The reaction mixture was stirred overnight at room temperature. Water (10 mL) was added, and the mixture was extracted with MTBE (3 × 10 mL). Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure.

The crude compound was purified using silica gel column chromatography to obtain the product as a colorless oil.

*5-(4'-Cyano-[1,1'-biphenyl]-4-yl)pentyl 3-((tert-butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)propanoate (**4a**, **S-4a**).* According to the general procedure D, starting from **2a** (107 mg, 0.40 mmol), product **4a** (219 mg, 87%) was obtained as a colorless viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.69 – 7.65 (m, 4H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.20 (dd, *J* = 8.9, 4.4 Hz, 1H), 4.13 – 4.02 (m, 2H), 2.76 (dd, *J* = 14.7, 8.9 Hz, 1H), 2.69 – 2.63 (m, 2H), 2.58 (dd, *J* = 14.7, 4.4 Hz, 1H), 1.72 – 1.62 (m, 4H), 1.45 – 1.36 (m, 2H), 0.87 (s, 9H), 0.05 (s, 3H), -0.13 (s, 3H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 171.02, 145.52, 145.21, 144.80, 143.19, 138.26, 136.66, 132.60, 132.58, 129.15, 127.58, 127.49, 127.14, 127.13, 126.62, 119.00, 118.91, 110.92, 110.63, 71.77, 64.57, 46.30, 35.42, 30.93, 28.44, 25.69, 25.58, 18.07, -4.63, -5.20. According to the same procedure, chiral compound **S-4a** was prepared starting from 100 mg of **2a** in 62% yield.

7-(4'-cyano-[1,1'-biphenyl]-4-yl)heptyl 3-((tert-butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)propanoate. According to the general procedure D, starting from **2b** (169 mg, 0.58 mmol), product **4b** (347 mg, 91%) was obtained as a colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.60 (m, 8H), 7.59 – 7.42 (m, 6H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.20 (dd, *J* = 8.7, 4.4 Hz, 1H), 4.14 – 3.99 (m, 2H), 2.76 (dd, *J* = 14.6, 8.8 Hz, 1H), 2.70 – 2.49 (m, 3H), 1.75 – 1.56 (m, 4H), 1.43 – 1.28 (m, 6H), 0.86 (s, 9H), 0.05 (s, 3H), -0.13 (s, 3H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 171.05, 145.58, 145.24, 144.83, 143.58, 138.25, 136.54, 132.60, 132.57, 129.16, 127.59, 127.48, 127.13, 127.11, 126.62, 119.02, 118.92, 110.90, 110.58, 71.78, 64.73, 46.32, 35.57, 31.28, 29.15, 29.11, 28.56, 25.85, 25.69, 18.07, -4.63, -5.21. According to the same procedure, chiral compound **S-4b** was prepared starting from 188 mg of **2b** in 67% yield.

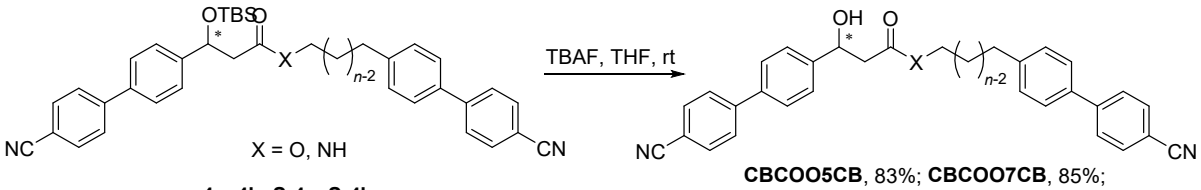


General procedure E – Coupling of amines and acids using BOP. Corresponding acid (1 equiv.) and BOP (1.1 equiv.) were dissolved in DCM. After 30 min, the solution of the corresponding amine (1.1 equiv.) and DIPEA (1.3 equiv.) in DCM was added. The reaction mixture was stirred overnight at room temperature. The mixture was diluted with DCM and extracted with an aqueous solution of NH_4Cl. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude compound was purified using silica gel column chromatography.

3-((tert-Butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)-N-(5-(4'-cyano-[1,1'-biphenyl]-4-yl)pentyl)propanamide. According to the general procedure E, starting from **1** (199 mg, 0.52 mmol), product **5a** (277 mg, 85%) was obtained as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 8H), 7.58 – 7.48 (m, 4H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 5.92 – 5.82 (m, 1H), 5.20 (t, *J* = 5.8 Hz, 1H), 3.39 – 3.23 (m, 1H), 3.23 – 3.06 (m, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.54 (d, *J* = 5.8 Hz, 2H), 1.74 – 1.43 (m, 4H), 1.43 – 1.28 (m, 2H), 0.91 (s, 9H), 0.07 (s, 3H), -0.09 (s, 3H). ^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 170.04, 145.51, 145.17, 144.67, 143.20, 138.16, 136.65, 132.61, 132.59, 129.13, 127.57, 127.49, 127.15, 127.14, 126.38, 119.01, 118.91, 110.91, 110.63, 71.82, 48.17, 39.42, 35.43, 30.95, 29.49, 26.57, 25.79, 18.12, -4.70, -5.12. According to the same procedure, chiral compound **S-5a** was prepared starting from 101 mg of **S-1** in 76% yield.

3-((tert-Butyldimethylsilyl)oxy)-3-(4'-cyano-[1,1'-biphenyl]-4-yl)-N-(7-(4'-cyano-[1,1'-biphenyl]-4-yl)heptyl)propenamide. According to the general procedure E, starting from **1** (199 mg, 0.52 mmol), product **5b** (322 mg, 94%) was obtained as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.69 – 7.66 (m, 4H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.89 – 5.83 (m, 1H), 5.20 (t, *J* = 5.9 Hz, 1H), 3.29 (td, *J* = 13.5, 7.2 Hz, 1H), 3.13 (td, *J* = 12.7, 7.1 Hz, 1H), 2.66 – 2.61 (m, 2H), 2.56 – 2.52 (m, 2H), 1.66 – 1.60 (m, 2H), 1.49 – 1.42 (m, 2H), 1.35 – 1.24 (m, 6H), 0.90 (s, 9H), 0.07 (s, 3H), -0.09 (s, 3H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 170.05, 145.58, 145.20, 144.68, 143.57, 138.14, 136.53, 132.60, 132.57, 129.16, 127.58, 127.48, 127.15, 127.10, 126.38, 119.03, 118.91, 110.90, 110.57, 71.83, 48.19, 39.51, 35.56, 31.28, 29.58, 29.17, 29.14, 26.88, 25.78, 18.11, -4.71, -5.13. According to the same procedure, chiral compound **S-5b** was prepared starting from 101 mg of **S-1** in 76% yield.

1.4. Synthesis of final compounds



4a, **4b**, **S-4a**, **S-4b**
5a, **5b**, **S-5a**, **S-5b**

CBCOO5CB, 83%; **CBCOO7CB**, 85%;
S-CBCOO5CB, 83%; **S-CBCOO7CB**, 83%
CBCONH5CB, 84%; **CBCONH7CB**, 75%;
S-CBCONH5CB, 77%, **S-CBCONH7CB**, 93%

General procedure F. To the solution of TBS protected esters and amides (0.2 mmol) in THF (5 mL) TBAF (1M solution in THF, 0.05 mmol) was added. The reaction mixture was stirred at room temperature overnight and monitored by TLC (DCM/MeOH = 50:1). The solvent was evaporated and the crude product purified using silica gel column chromatography (DCM/MeOH = 50:1) to obtain product as a white solid or a white wax.

5-(4'-Cyano-[1,1'-biphenyl]-4-yl)pentyl 3-(4'-cyano-[1,1'-biphenyl]-4-yl)-3-hydroxypropanoate (**CBCOO5CB**). According to the general procedure F, starting from **4a** (152 mg, 0.24 mmol), product **CBCOO5CB** (103 mg, 83%) was obtained as a white solid. According to the same procedure, chiral compound **S-CBCOO5CB** was prepared starting from 138 mg of **S-4a** in 83% yield. $[\alpha]_D^{25}$ = - 15.1 (*c* 0.86, $CHCl_3$). ν_{max}/cm^{-1} 3391, 2937, 2857, 2227, 1698, 1604, 1493, 800. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.70 – 7.63 (m, 4H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.46 (m, 4H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.18 (dt, *J* = 8.2, 4.1 Hz, 1H), 4.15 (td, *J* = 6.7, 1.7 Hz, 2H), 3.32 (d, *J* = 3.6 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.73 – 1.64 (m, 4H), 1.45 – 1.37 (m, 2H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 172.34, 145.48, 145.13, 143.11, 143.04, 138.65, 136.68, 132.65, 132.58, 129.16, 127.64, 127.48, 127.40, 127.16, 126.45, 118.99, 118.87, 111.05, 110.64, 69.89, 64.92, 43.15, 35.38, 30.84, 28.40, 25.46. HRMS (+ESI) *m/z*, ($[M+Na]^+$): calcd. for $C_{34}H_{30}N_2O_3Na$: 537.2154, found: 537.2155, Mass accuracy: 0.19 ppm.

7-(4'-Cyano-[1,1'-biphenyl]-4-yl)heptyl 3-(4'-cyano-[1,1'-biphenyl]-4-yl)-3-hydroxypropanoate (**CBCOO7CB**). According to the general procedure F, starting from **4b** (148 mg, 0.23 mmol), product **CBCOO7CB** (104 mg, 85%) was obtained as a white viscous resin. According to the same procedure, chiral compound **S-CBCOO7CB** was prepared starting from 284 mg of **S-4b** in 83% yield. $[\alpha]_D^{25}$ = - 14.3 (*c* 1.05, $CHCl_3$). ν_{max}/cm^{-1} 3539, 2922, 2858, 2227, 1706, 1607, 1495, 800. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.70 – 7.63 (m, 4H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.19 (dt, *J* = 8.1, 4.0 Hz, 1H), 4.14 (td, *J* = 6.8, 2.2 Hz, 2H), 3.38 (d, *J* = 3.6 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.68 – 2.62 (m, 2H), 1.68 – 1.61 (m, 4H), 1.39 – 1.31 (m, 6H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 172.40, 145.56, 145.17, 143.54, 143.07, 138.63, 136.54, 132.63, 132.57, 129.16, 127.65, 127.48, 127.40, 127.11, 126.46, 119.02, 118.88, 111.02, 110.58, 69.89, 65.11, 43.14, 35.55, 31.25, 29.12, 29.06, 28.52, 25.78. HRMS (+ESI) *m/z*, ($[M+Na]^+$): calcd. for $C_{36}H_{34}N_2O_3Na$: 565.2467, found: 565.2466, Mass accuracy: 0.18 ppm.

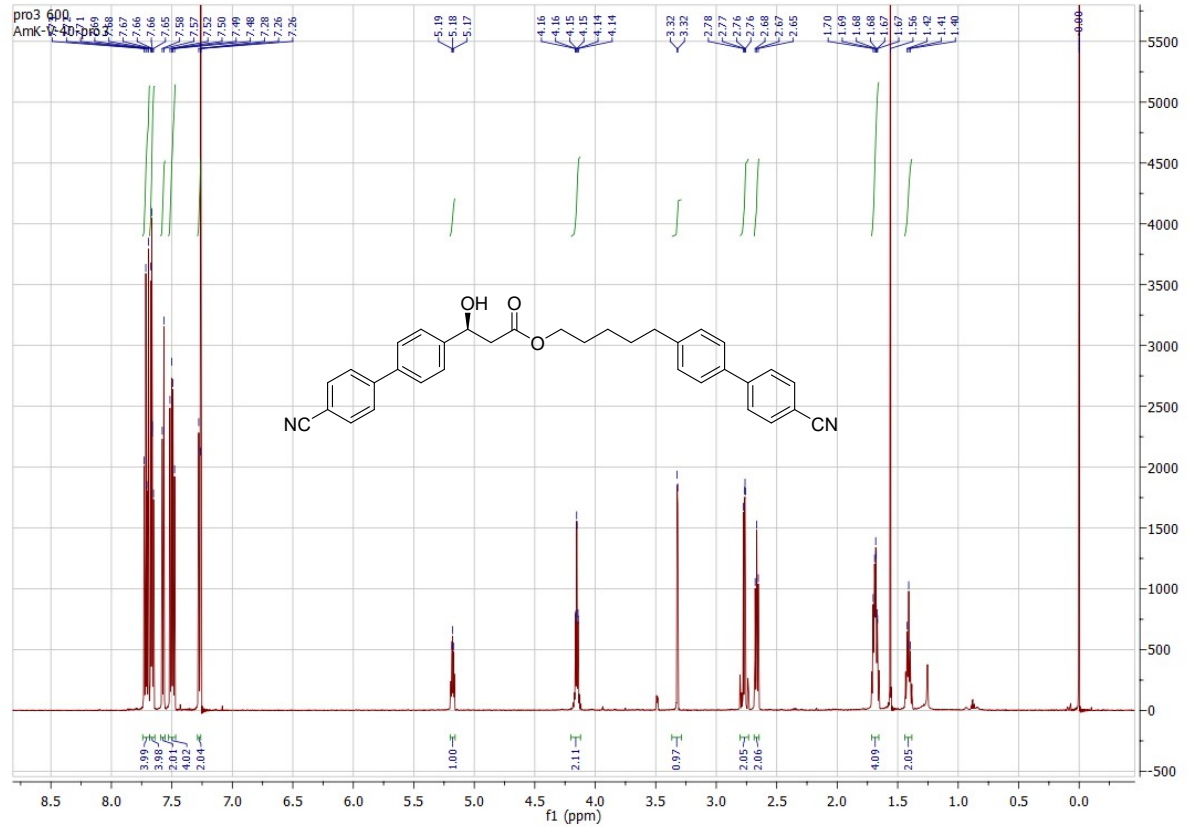
*3-(4'-Cyano-[1,1'-biphenyl]-4-yl)-N-(5-(4'-cyano-[1,1'-biphenyl]-4-yl)pentyl)-3-hydroxypropanamide (***CBCONH5CB***)*. According to the general procedure F, starting from **5a** (272 mg, 0.43 mmol), product **CBCONH5CB** (188 mg, 84%) was obtained as a white solid. The product was recrystalized from i-PrOH. According to the same procedure, chiral compound **S-CBCONH5CB** was prepared starting from 126 mg of **S-5a** in 77% yield. $[\alpha]_D^{25}$ = - 23.0 (*c* 1, $CHCl_3$). ν_{max}/cm^{-1} 3300, 2929, 2853, 2231, 1638, 1551, 1494, 825. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 4H), 7.67 – 7.64 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.73 – 5.69 (m, 1H), 5.15 (t, *J* = 6.2 Hz, 1H), 4.30 (s, 1H), 3.34 – 3.22 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.57 (d, *J* = 6.1 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.58 – 1.51 (m, 2H), 1.40 – 1.32 (m, 2H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 171.58, 145.46, 145.16, 143.67, 143.13, 138.44, 136.65, 132.64, 132.57, 129.17, 127.60, 127.47, 127.33, 127.14, 126.37, 118.99, 118.89, 110.98, 110.61, 70.53, 44.44, 39.39, 35.39, 30.82,

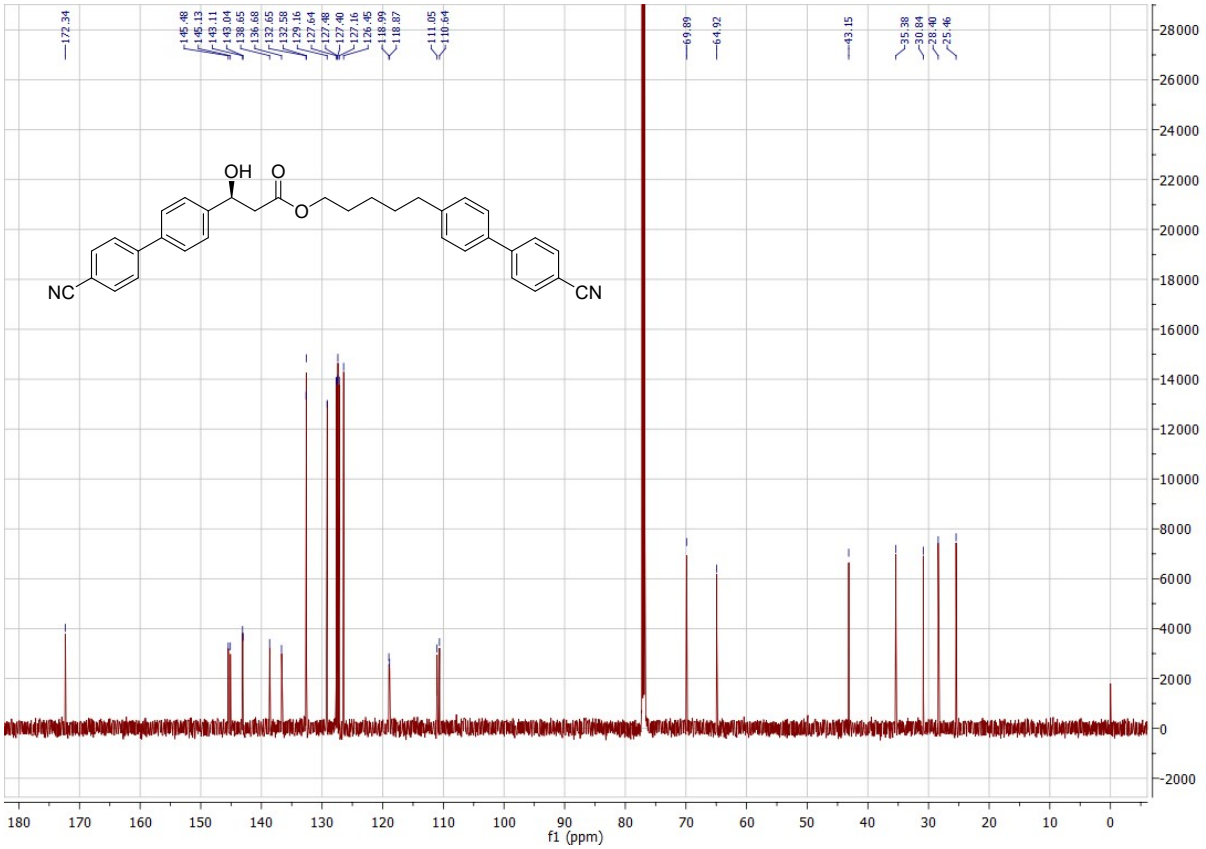
29.40, 26.36. HRMS (+ESI) *m/z*, ([M+H]$^+$): calcd. for $C_{34}H_{32}N_3O_2$: 514.2495, found: 514.2493, Mass accuracy: 0.39 ppm.

*3-(4'-Cyano-[1,1'-biphenyl]-4-yl)-N-(7-(4'-cyano-[1,1'-biphenyl]-4-yl)heptyl)-3-hydroxypropanamide (***CBCONH7CB***)*. According to the general procedure F, starting from **5b** (187 mg, 0.29 mmol), product **CBCONH7CB** (115 mg, 75%) was obtained as a white solid. The product was recrystalized from i-PrOH. According to the same procedure, chiral compound **S-CBCONH7CB** was prepared starting from 127 mg of **S-5b** in 93% yield. $[\alpha]_D^{25}$ = - 19.7 (*c* 0.71, $CHCl_3$). ν_{max}/cm^{-1} 3290, 2928, 2853, 2229, 1634, 1553, 1494, 825. ^{1}H NMR (600 MHz, CDCl3) δ 7.73 – 7.68 (m, 4H), 7.68 – 7.64 (m, 4H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.46 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.74 – 5.67 (m, 1H), 5.17 (td, *J* = 6.0, 3.0 Hz, 1H), 4.39 (d, *J* = 3.0 Hz, 1H), 3.26 (td, *J* = 7.1, 1.7 Hz, 2H), 2.69 – 2.61 (m, 2H), 2.58 (d, *J* = 6.1 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.55 – 1.45 (m, 2H), 1.38 – 1.26 (m, 6H). ^{13}C{1H} NMR (151 MHz, $CDCl_3$) δ 171.58, 145.56, 145.20, 143.68, 143.55, 138.43, 136.53, 132.62, 132.57, 129.16, 127.61, 127.47, 127.34, 127.11, 126.39, 119.03, 118.89, 110.96, 110.56, 70.53, 44.41, 39.53, 35.54, 31.26, 29.51, 29.15, 29.09, 26.77. HRMS (+ESI) *m/z*, ([M+H]$^+$): calcd. for $C_{36}H_{36}N_3O_2$: 542.2808, found: 542.2805, Mass accuracy: 0.55 ppm.

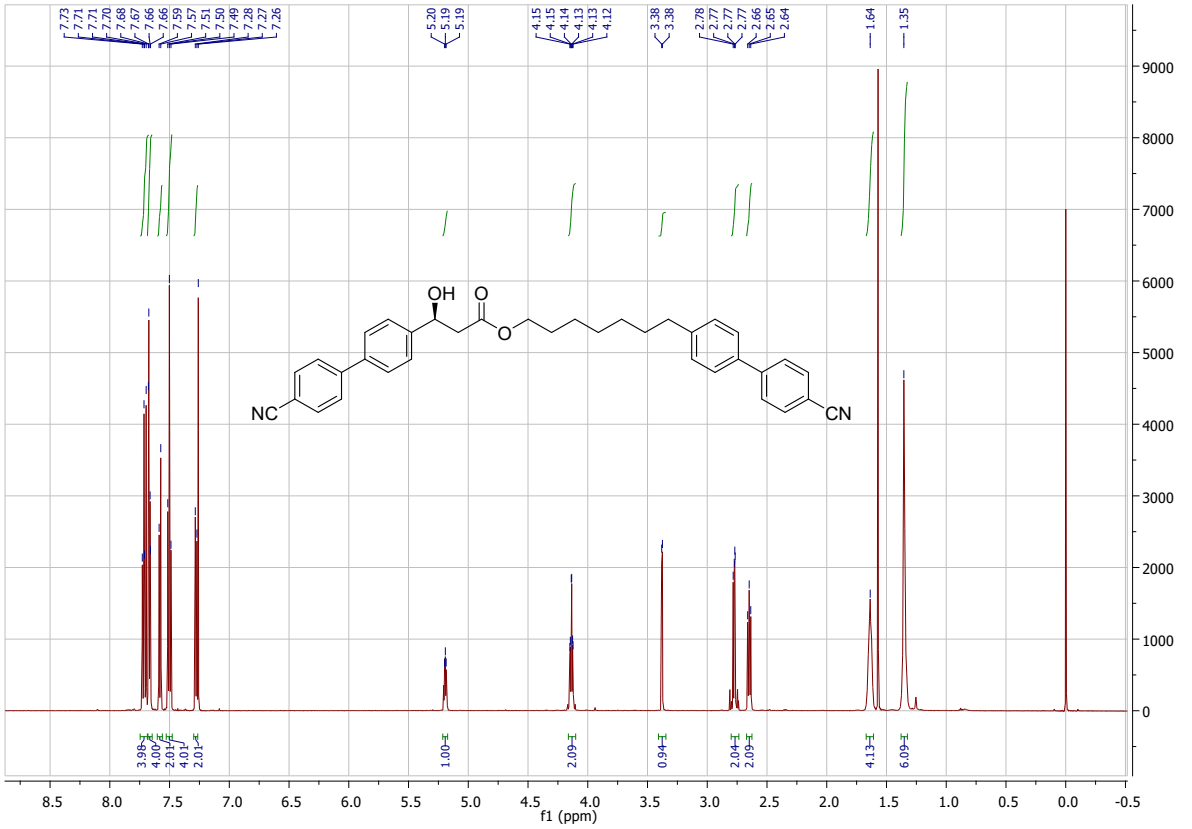
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of the final compounds

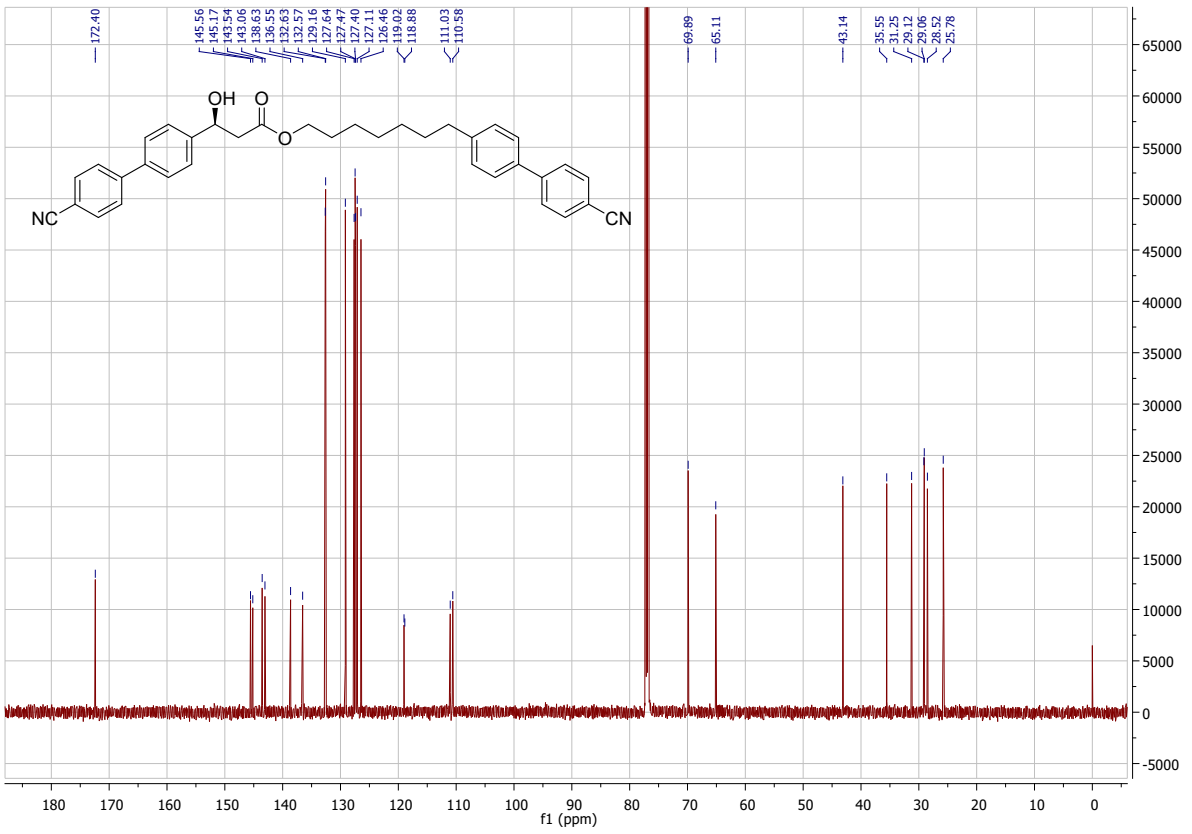
CBCOO5CB and **S-CBCOO5CB**



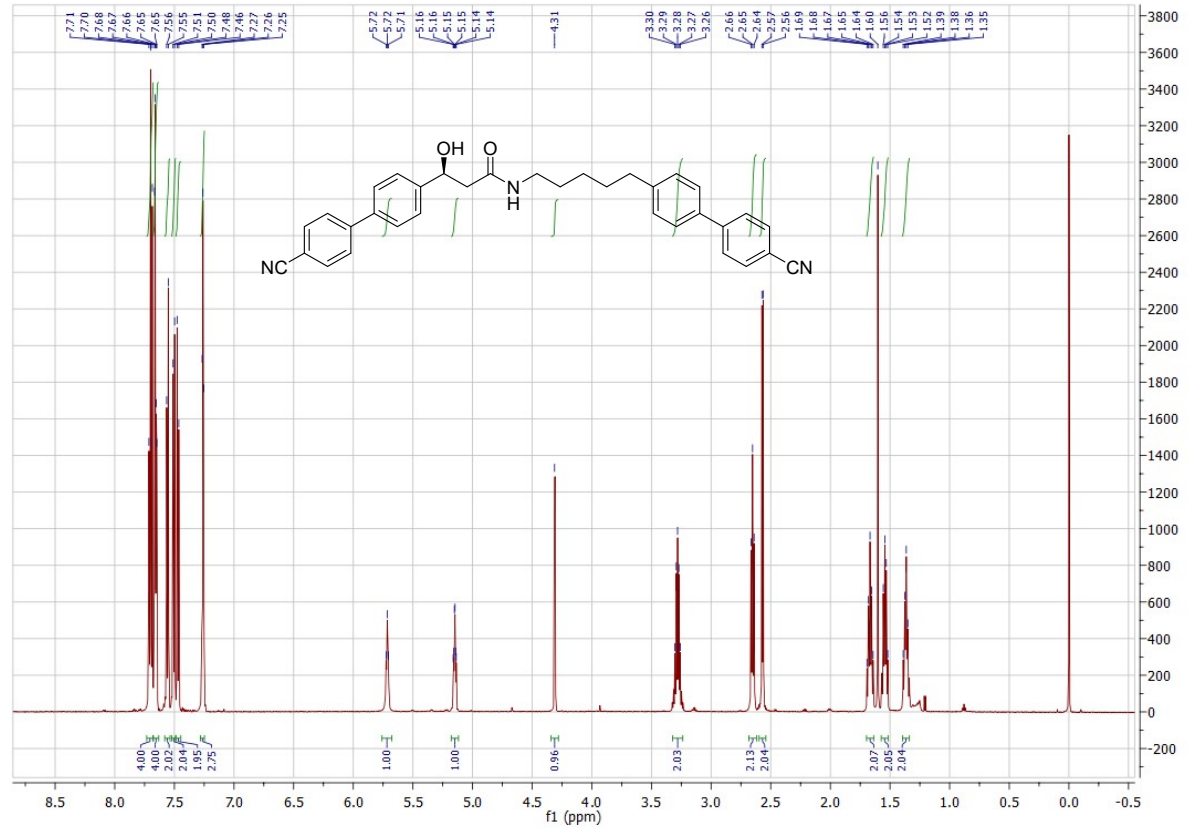


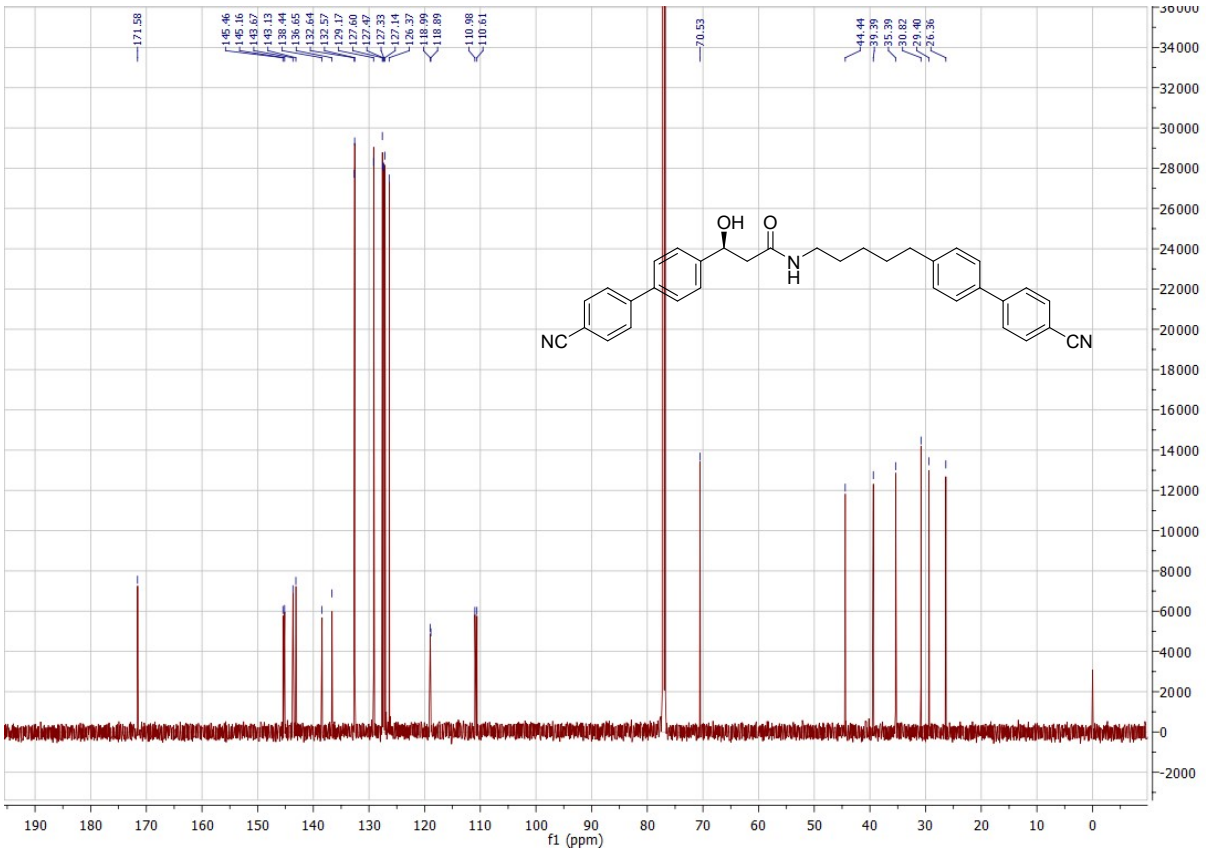
CBCOO7CB and **S-CBCOO7CB**



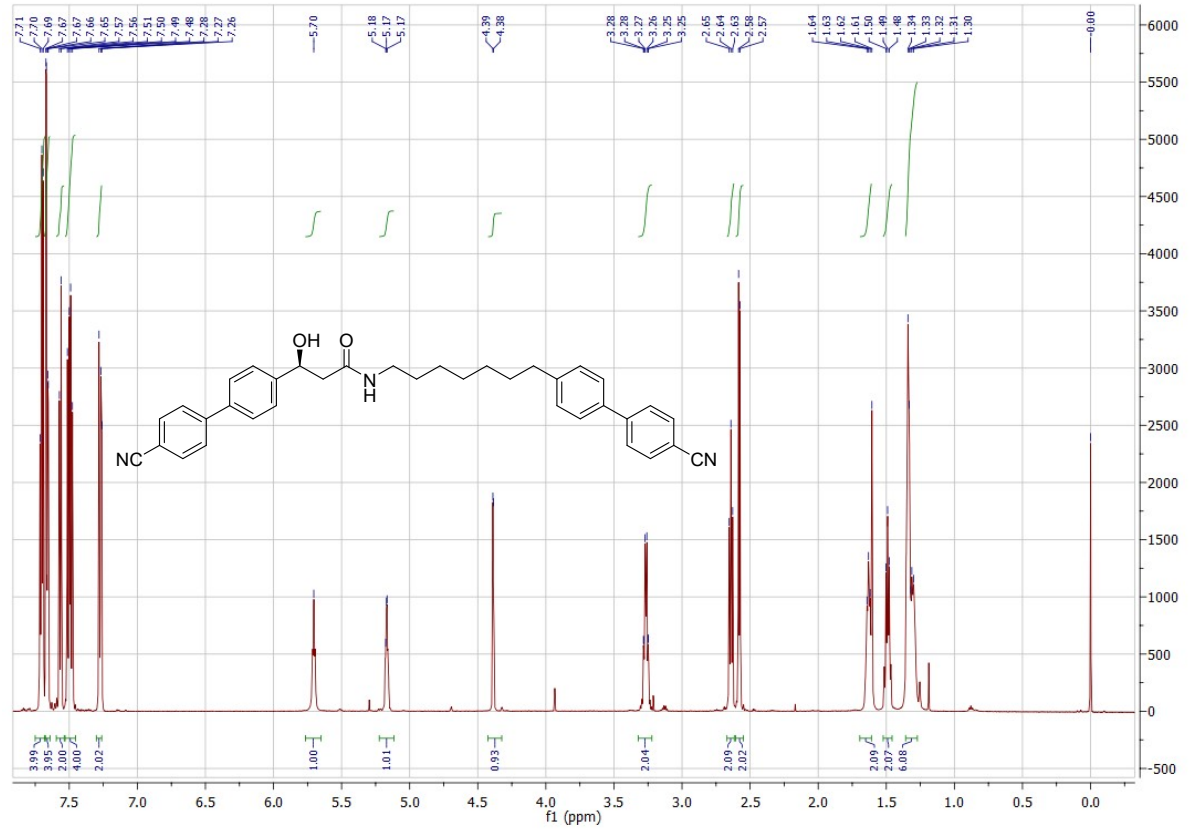


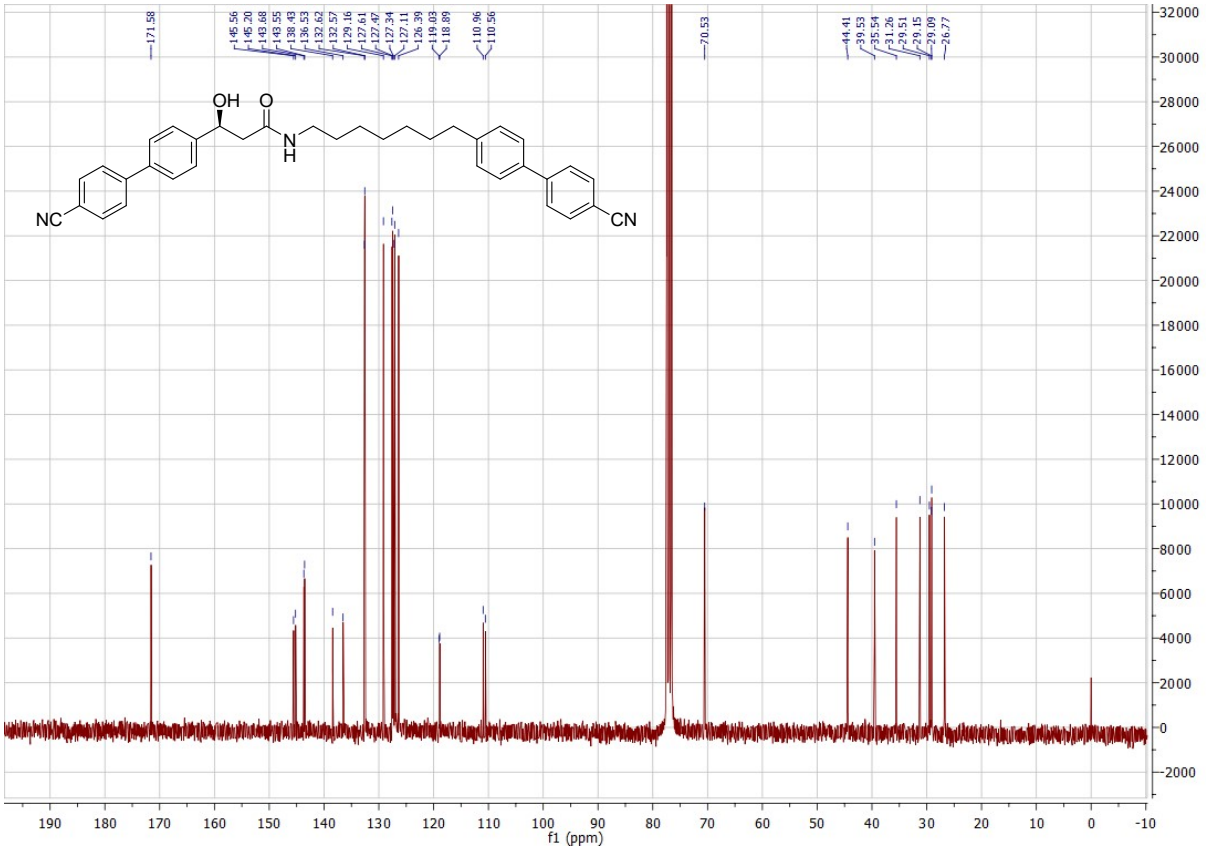
CBCONH5CB and **S-CBCONH5CB**





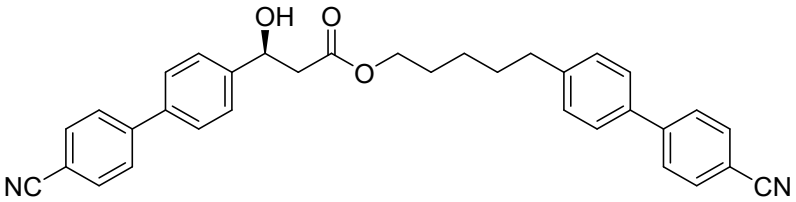
CBCONH7CB and **S-CBCONH7CB**



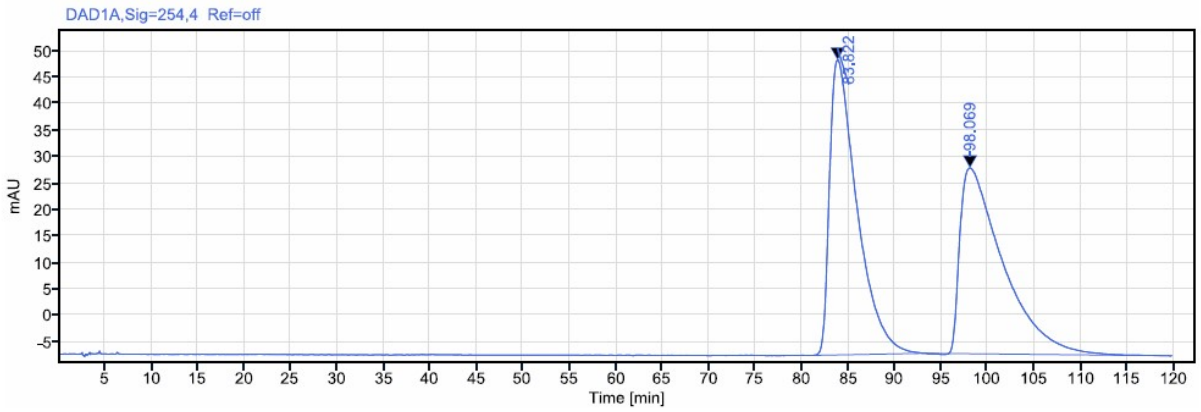


HPLC chromatograms for the determination of enantiomeric excess

CBCOO5CB and **S-CBCOO5CB**

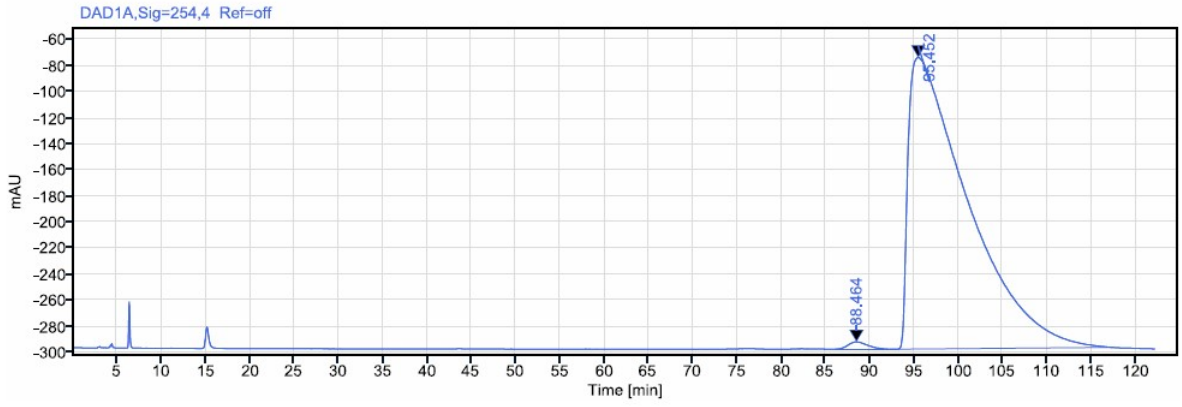


ee = 98%, Chiralpak IA, *n*-hexane/ethanol = 7:3, 254 nm, 1 ml/min



Signal: DAD1A,Sig=254,4 Ref=off

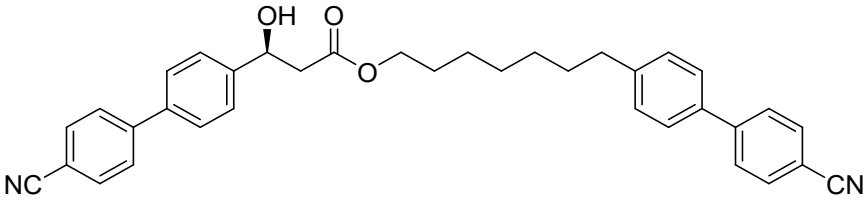
RT [min]	Type	Width [min]	Area	Height	Area%	Name
83.822	MM m	12.85	11421.31	55.76	50.28	
98.069	MM m	23.61	11292.64	35.13	49.72	
		Sum	**22713.94**			



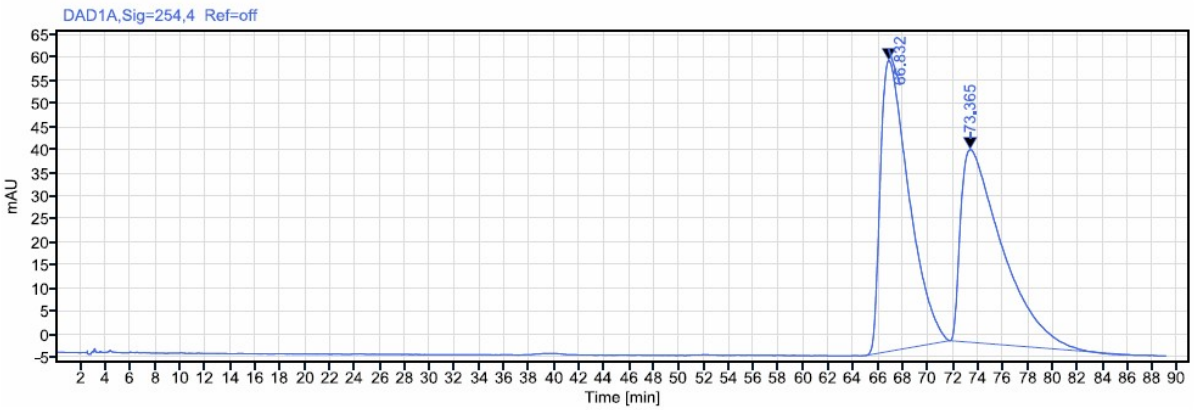
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
88.464	MM m	6.21	853.68	5.57	0.81	
95.452	MM m	25.18	104811.79	223.70	99.19	
		Sum	**105665.47**			

CBCOO7CB and **S-CBCOO7CB**

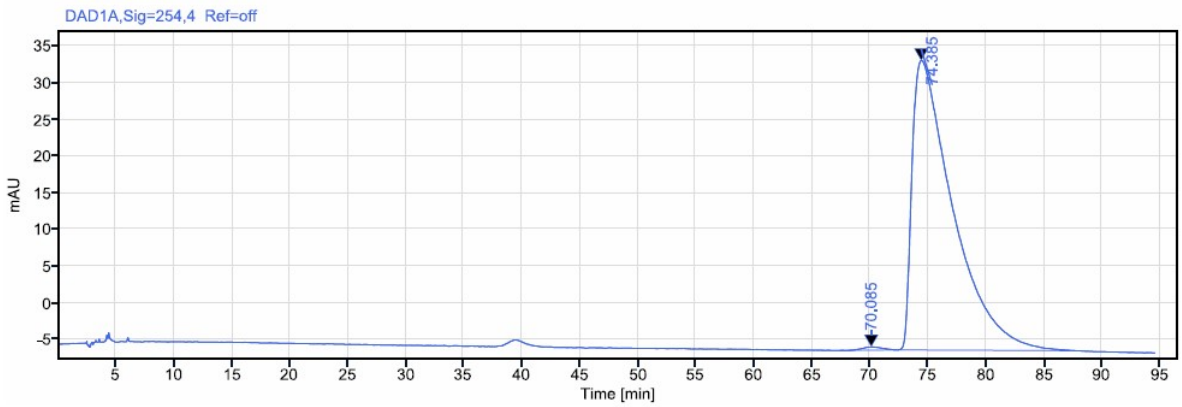


ee = 99%, Chiralpak IA, *n*-hexane/ethanol = 7:3, 254 nm, 1 ml/min



Signal: DAD1A,Sig=254,4 Ref=off

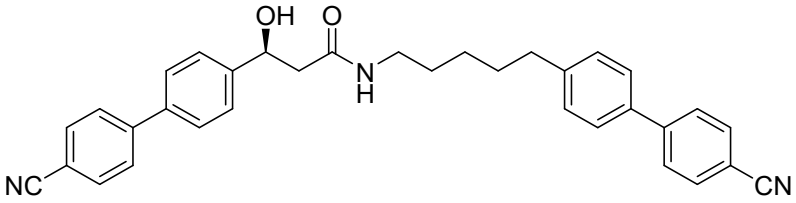
RT [min]	Type	Width [min]	Area	Height	Area%	Name
66.832	MM m	6.71	10032.27	63.02	50.80	
73.365	MM m	14.70	9716.73	41.77	49.20	
		Sum	**19749.00**			



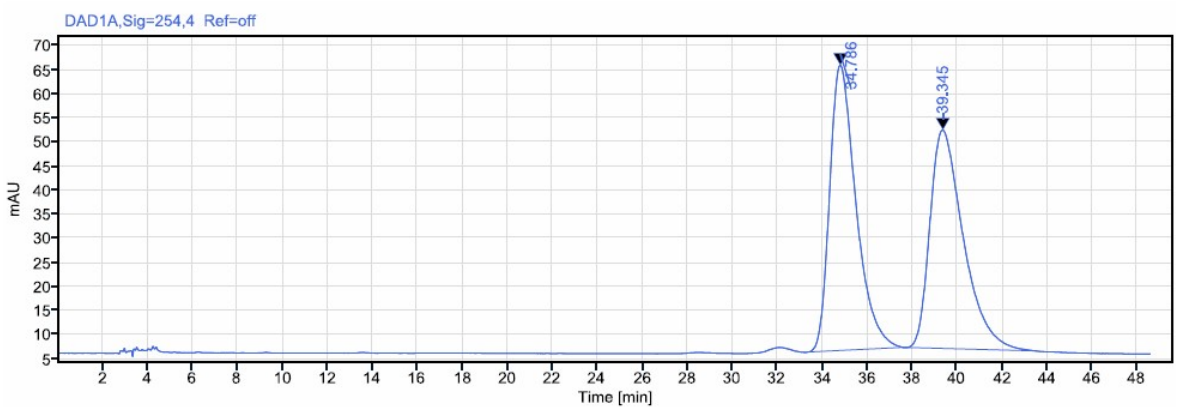
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
70.085	MM m	4.99	50.89	0.44	0.52	
74.385	MM m	15.70	9654.54	39.41	99.48	
		Sum	**9705.43**			

CBCONH5CB and **S-CBCONH5CB**

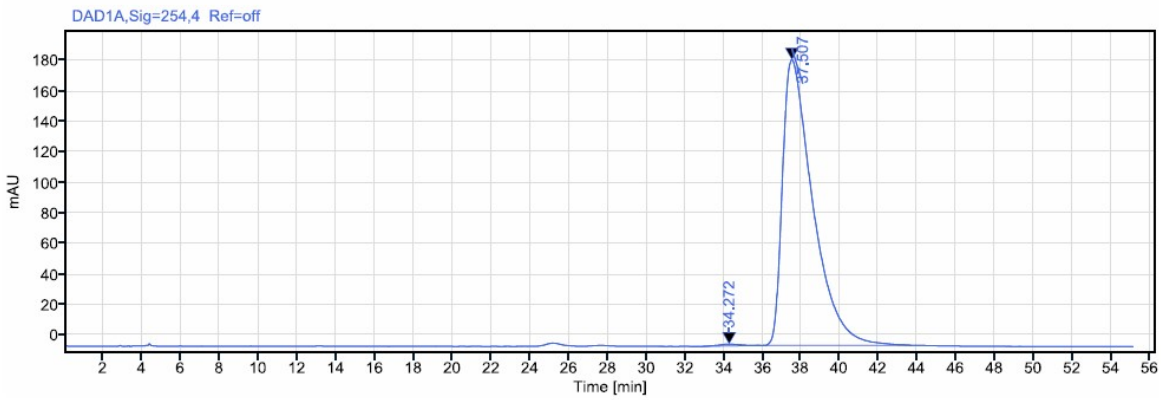


ee = 99%, Chiralpak IA, *n*-hexane/ethanol = 7:3, 254 nm, 1 ml/min



Signal: DAD1A,Sig=254,4 Ref=off

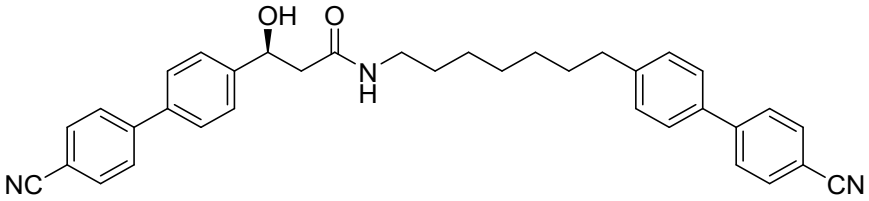
RT [min]	Type	Width [min]	Area	Height	Area%	Name
34.786	MM m	4.20	4817.21	59.20	50.70	
39.345	MM m	5.95	4684.33	45.33	49.30	
		Sum	**9501.55**			



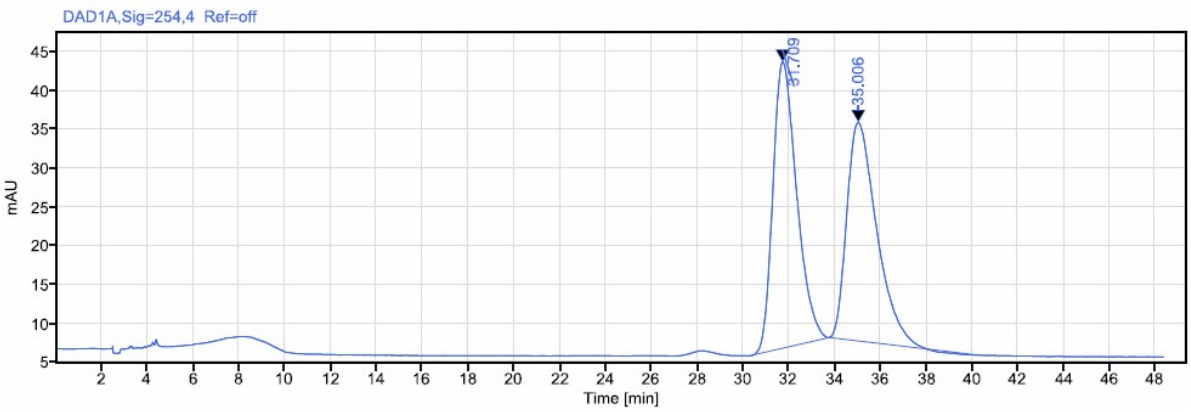
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
34.272	MM m	3.39	87.14	1.16	0.43	
37.507	MM m	7.97	20359.51	187.35	99.57	
		Sum	**20446.65**			

CBCONH7CB and **S-CBCONH7CB**

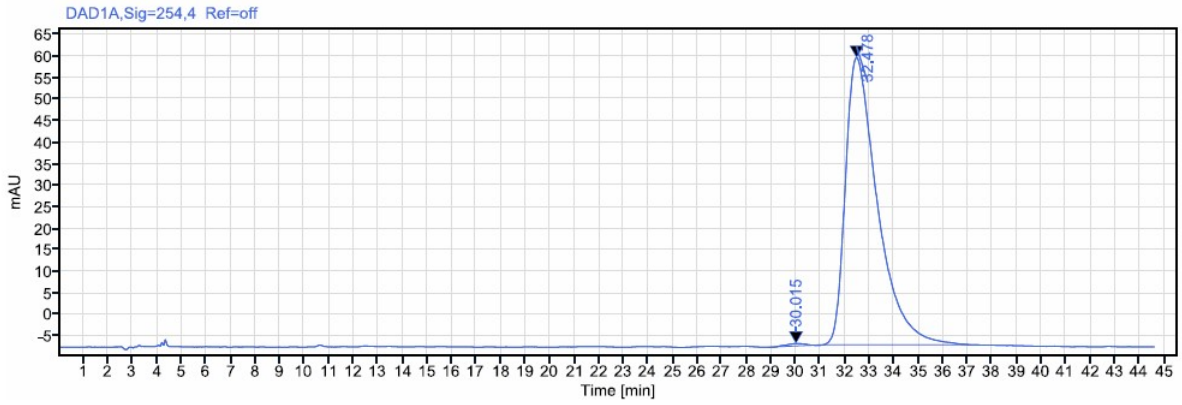


ee = 99%, Chiralpak IA, *n*-hexane/ethanol = 7:3, 254 nm, 1 ml/min



Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
31.709	MM m	3.40	2662.86	36.92	51.11	
35.006	MM m	6.49	2547.64	28.19	48.89	
		Sum	**5210.50**			



Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
30.015	MM m	2.22	28.02	0.57	0.46	
32.478	MM m	6.55	6060.44	66.63	99.54	
		Sum	**6088.45**			

Characterization of the LC properties

The liquid crystalline behavior of all final materials was examined by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction. Optical textures were determined using an Olympus BX51 polarizing microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller and Olympus camera EP50. The phase transition temperatures and corresponding enthalpies were determined from thermograms recorded on Perkin-Elmer Diamond DSC, operated at scanning rates of 10 °C min^{-1}. X-ray scattering measurements, both small angle (SAXS) and wide angle (WAXS) where recorded using an Anton Paar SAXSpoint 5.0 beamline machine comprising a primux 100 Cu X-ray source (λ = 0.154 nm) with a 2D EIGER2 R detector. Samples were filled into either thin-walled quartz capillaries or held between Kapton tape. Temperature was controlled using an Anton Paar heated sampler with a range of -10 ° C to 120 °C and the samples held in a chamber with an atmospheric pressure of < 1mbar. Samples were initially held at 120 °C to allow for temperature equilibration across the sample and then slowly cooled while stopping to record the scattering patterns. Subtraction of both the general background and any contributions from the Kapton tape was conducted by measuring scattering from an empty Kapton tape sample holder. Both this background and the sample were normalized for sample transmission and corrected to absolute scattering intensity in order to directly subtract the background scattering.

Table S1. Transition temperatures (°C), enthalpies (kJ mol^{-1}) in italics and the dimensionless value of ΔS/R in [ ] for the synthesized compounds obtained in cooling at a rate of 10 °C min^{-1}.

	Phase	*T* (°C)	Phase	*T* (°C)	Phase	*T* (°C)	Phase
CBCOO5CB	Gl	13	N_{TB}	41 -0.23[0.09]	N	57 -0.14[0.05]	I
CBCOO7CB	Gl	8	N_{TB}	56 -0.19[0.07][a]	N	76 -0.48[0.16][a]	I
CBCONH5CB	Gl	37	N_{TB}	77 -0.71[0.25]	N	84 -0.17[0.06]	I
CBCONH7CB	Cr	99 -27.80[8.98]			N	108 -0.23[0.07]	I
S-CBCOO5CB			N_{TB}*	42[b]	N*	53 -0.08[0.03][c]	I
S-CBCOO7CB	Gl	8	N_{TB}*	56 -0.42[0.15]	N*	77 -0.52[0.18]	I
S-CBCONH5CB	Cr	89 -27.45[9.11]					I
S-CBCONH7CB	Cr	118 -33.09[10.18]					I

N, nematic phase; N*, chiral nematic phase; N_{TB}, twist-bend nematic phase; N_{TB}*, chiral twist-bend nematic phase; I, isotropic liquid; [a]: The values are taken at a rate of 20 °C min^{-1}; [b]: observed by POM; [c]: The values are taken at a rate of 30 °C min^{-1}.

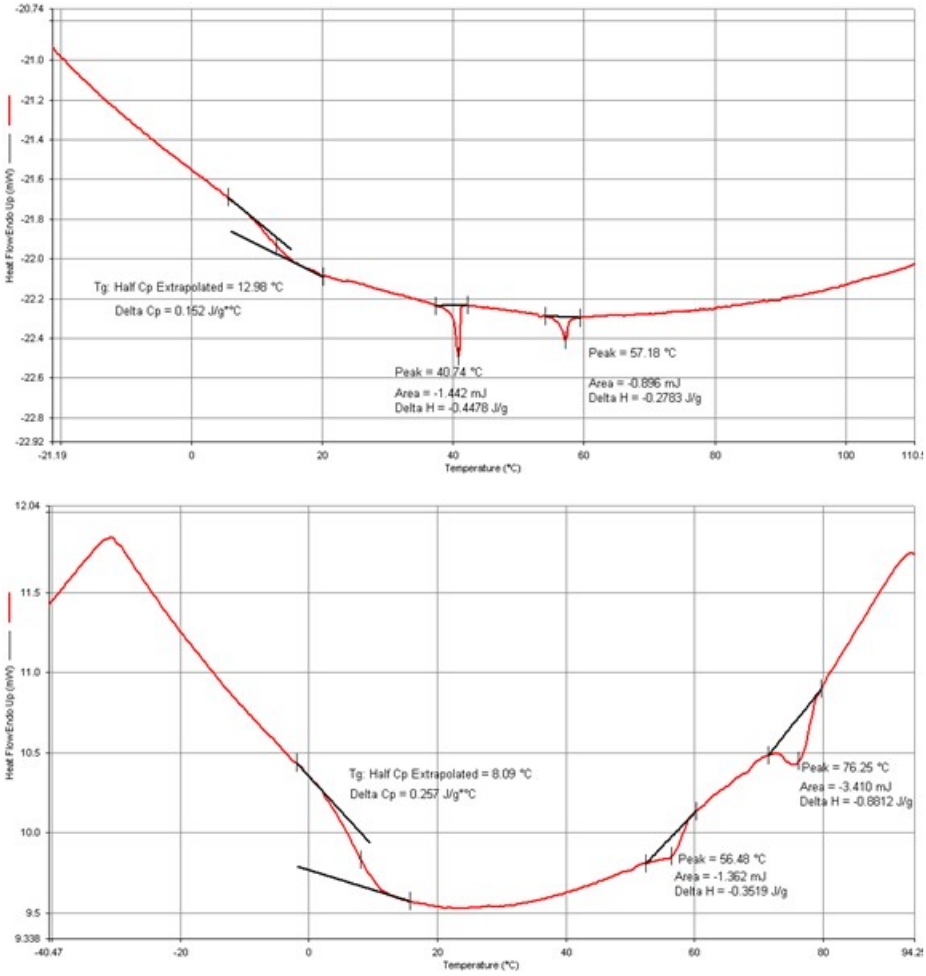


Figure S1. DSC thermograms of **CBCOO5CB** (upper) and **CBCOO7CB** (lower) upon cooling, 10 °C/min for **CBCOO5CB** and 20 °C/min for **CBCOO7CB**.

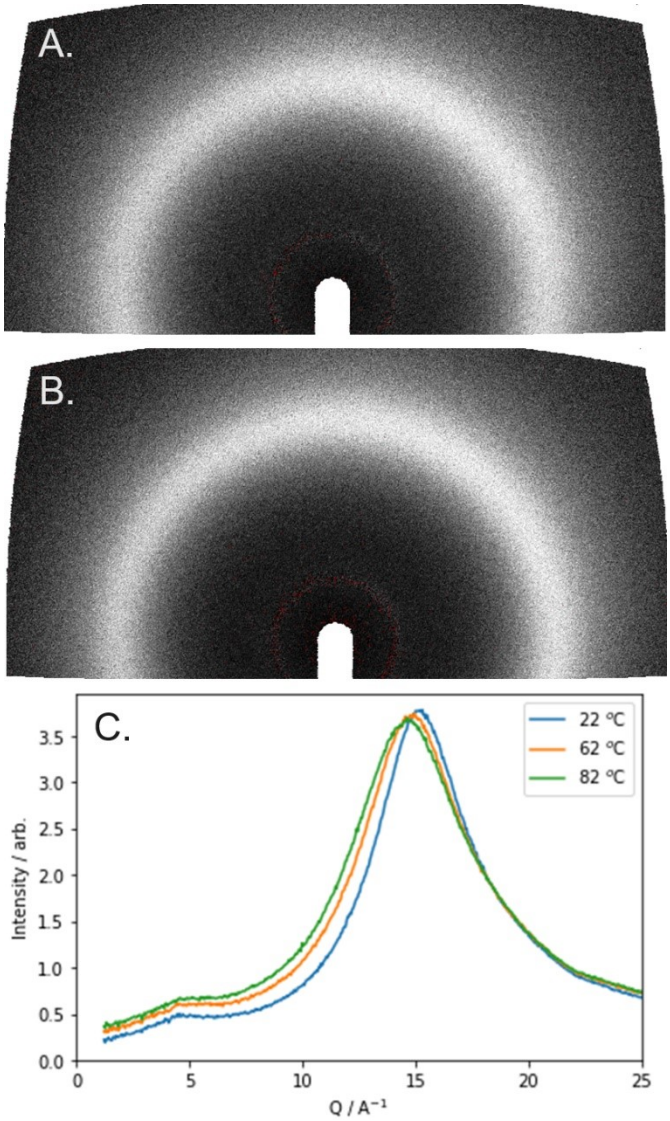


Figure S2. 2D SAXS patterns for a) **S-CBCOO7CB** in the N* phase at 70 °C; b) **CBCOO7CB** in the N_{TB}* phase at 30 °C. C) plot of integrated scattering intensity versus Q at the temperatures listed.

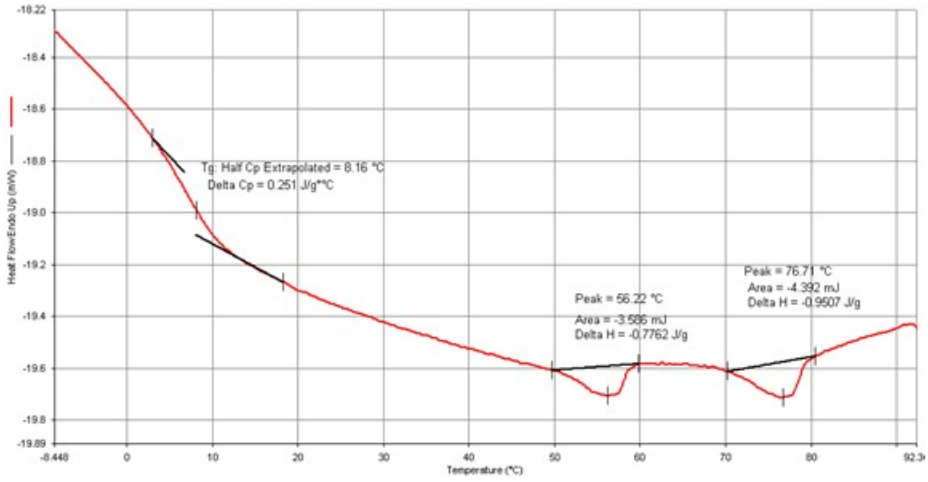


Figure S3. DSC thermogram of **S-CBCOO7CB** upon cooling, 10 °C/min.

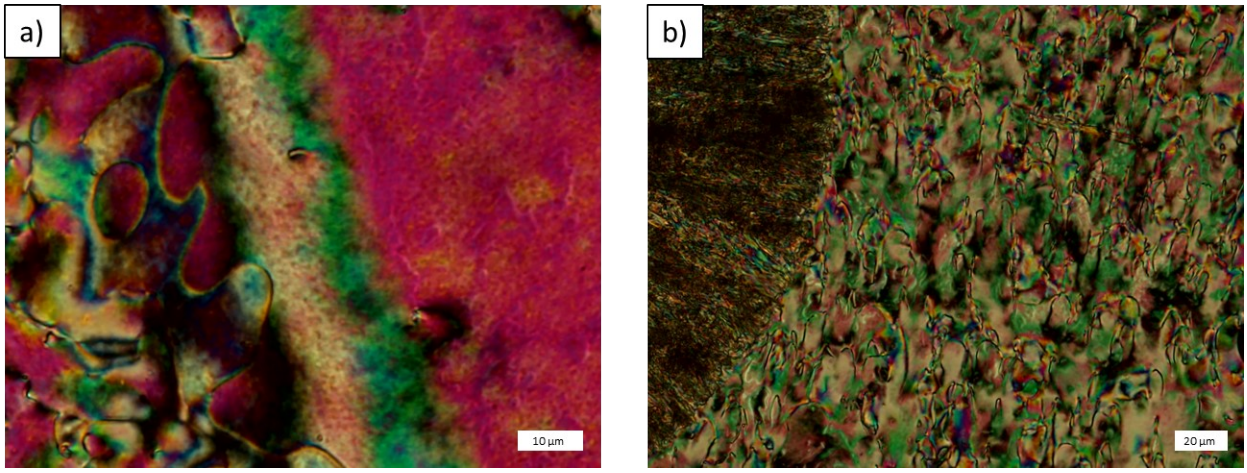


Figure S4. Optical textures of **CBCONH7CB** obtained on cooling. a) The schlieren texture of the N phase at 108 °C. b) Crystallization of the N phase at 108 °C upon standing.

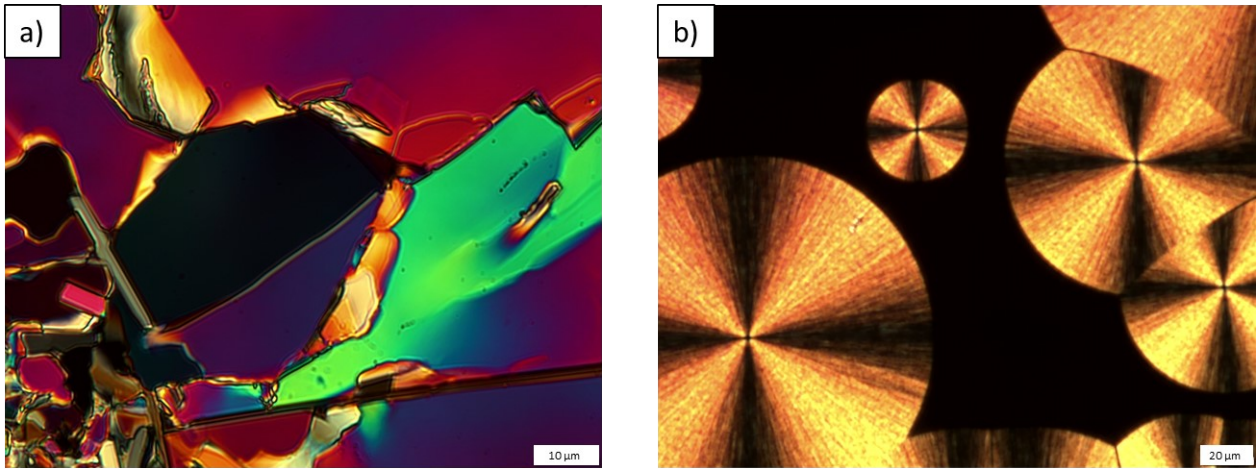
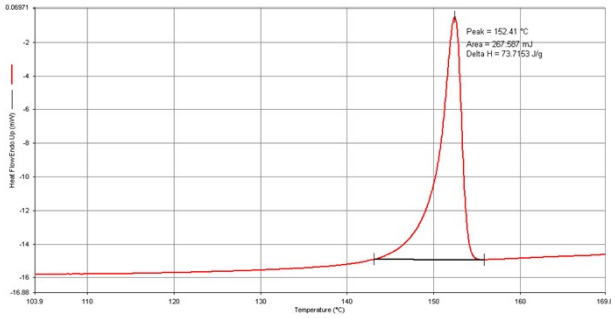
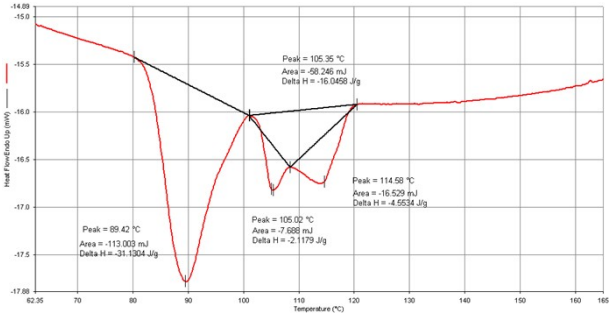


Figure S5. Optical textures of **S-CBCONH5CB** obtained on cooling. a) Crystallization from the isotropic melt at 109 °C, cooling rate 5 °C/min. b) Crystallization from the isotropic melt at 99 °C, cooling rate 10 °C/min.

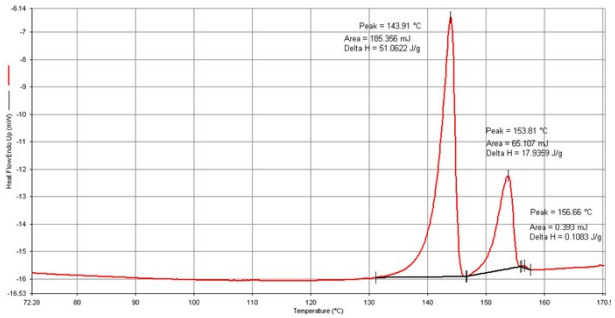
1st heating



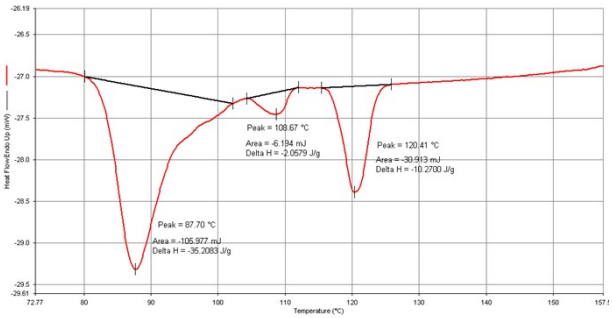
1st cooling



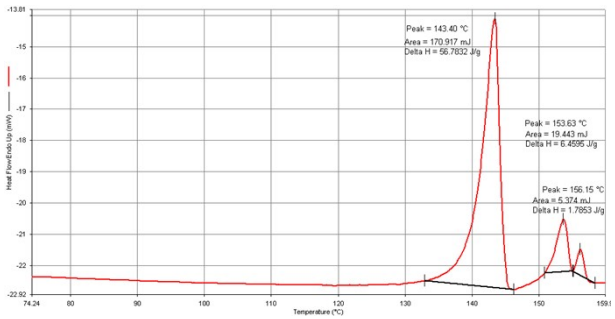
2nd heating



2nd cooling



3rd heating



3rd cooling

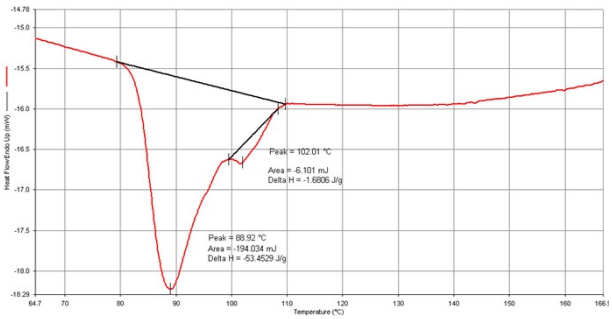


Figure S6. DSC thermograms of **S-CBCONH5CB** upon several heating and cooling cycles, m = 3.63 mg, 10 °C/min

Determination of the Helical Twisting Power

Determination of the helical pitch: The helical pitch of prepared mixtures of the chiral compounds in three nematic hosts, namely 4-cyano-4'-pentylbiphenyl (5CB), 4′-hexyloxy-4-cyanobipheny (6OCB) and 1,7-bis(6-(4-hexyloxybenzoyloxy)naphthalene-2-yl)heptane (BNA-76)[2] was determined by the Cano-wedge method using commercial EHC cells (KCRS-5, tanθ = 0.0192) at reduced temperature (T_R = T_I – 4 °C). The helical twist sense was determined directly from the wedge cells by applying Gerber's rule.[3]

Table S2. Determination of the helical twisting power (μm^{-1}) of prepared CB LC dimers in the nematic hosts 5CB, 6OCB, and BNA-76. $T_{R,}$ reduced temperature; *d*, the distance between two lines in the Cano-wedge cell; *P*, pitch

5CB	**S-CBCOO5CB**	**S-CBCOO7CB**	**S-CBCONH5CB**	**S-CBCONH7CB**
mol%	12	13	1,6	1,6
T_R/°C	34	39	31	32
d/μm	53,1	63,4	48,65	53,984
P/μm	2,04	2,43	1,87	2,07
HTP/μm^{-1}	4,17	3,19	33,79	30,45
Helical sense	**RH**	**RH**	**LH**	**LH**
6OCB	**S-CBCOO5CB**	**S-CBCOO7CB**	**S-CBCONH5CB**	**S-CBCONH7CB**
mol%	7	11	2,5	2,1
T_R/°C	74	76	67	76
d/μm	585,68	334	44,235	52,075
P/μm	22,22	12,83	1,70	2,00
HTP/μm^{-1}	0,65	0,72	23,79	24,05
Helical sense	**LH**	**LH**	**LH**	**LH**
BNA-76	**S-CBCOO5CB**	**S-CBCOO7CB**	**S-CBCONH5CB**	**S-CBCONH7CB**
mol%	7	8	6,7	4,3
T_R/°C	158	159	158	157
d/μm	175	124,98	45,76	62,66
P/μm	6,72	4,80	1,76	2,41
HTP/μm^{-1}	2,17	2,63	8,58	9,76
Helical sense	**LH**	**LH**	**LH**	**LH**

Table S3. Temperature dependence of the measured pitch of prepared CB LC dimers in 6OCB. T_1, isotropization temperature, *d*, the distance between two lines in the Cano-wedge cell; *P*, pitch.

6OCB	**S-CBCOO5CB**	**S-CBCOO7CB**	**S-CBCONH5CB**	**S-CBCONH7CB**
T_1/°C	77	80,7	77	80
d/μm	340,76	177	43,8	50,74
P/μm	13,09	6,80	1,68	1,95
T_2/°C	75,5	79,5	76	79
d/μm	443,62	215	43,7	53,39
P/μm	17,04	8,26	1,68	2,05
T_3/°C	74,6	78	74	78
d/μm	530,71	278	44,4	54,63
P/μm	20,38	10,68	1,70	2,1
T_4/°C	73,6	76	73	75
d/μm	585,68	334	44,71	56,1
P/μm	22,22	12,83	1,71	2,15

Computational methods

Conformational preferences of compounds **S-CBCOO7CB** and **S-CBCONH7CB** were studied by generating 2048 conformers for each system using the ETKDGv3 (Experimental-Torsion with Knowledge Distance Geometry version 3) as implemented in RDkit.[4–7] The geometry of each conformer was then optimized with the PM7 semi-empirical method[8] as implemented in Gaussian G16.[9] After removing duplicate entries, e.g. cases where the optimization of two different conformers converge to identical geometries, the bend-angle of each unique conformer was calculated as the angle between the vectors defined by the two nitrile C-N bonds. From the energy of each conformer, the probability weighted bend-angle calculated at a temperature of 298 K was obtained.

Relaxed scans about the dihedral angle were performed using a 10 degree step size and using the B3LYP hybrid functional with GD3BJ dispersion correction and the 6-31G(d,p) basis set as implemented in Gaussian G16.[9] The OPT=TIGHT flag was used to ensure convergence. Scans were performed both forwards and backwards, with the result of each averaged to give the presented data.

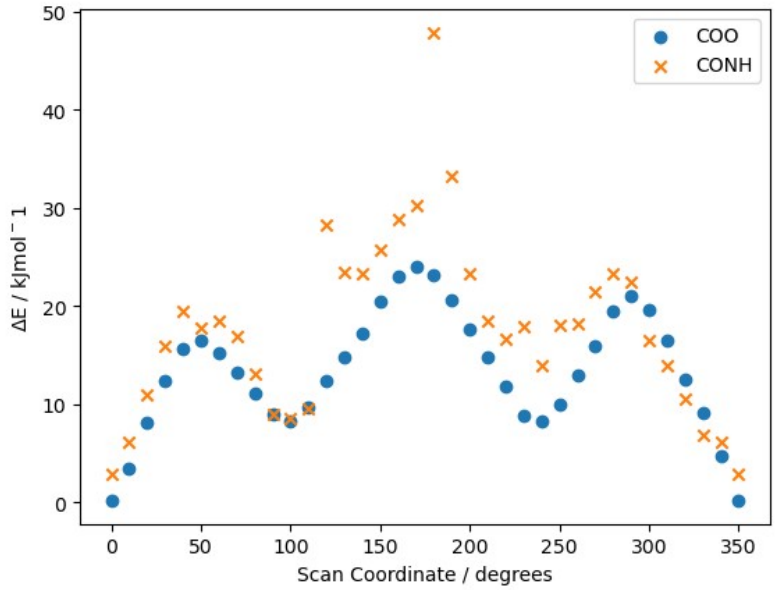


Figure S7. Relaxed potential energy surface scan for dihedral angles of **S-CBCOO7CB** (blue dot) and **S-CBCONH7CB** (orange cross) on B3LYP/GD3BJ level of theory

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