SUPPORTING INFORMATION

Cyanostilbene Bent-core Molecules: A Route to Functional Materials

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1. Experimental section

Materials and General Techniques. All chemical reagents were purchased from Aldrich and were used as received. Dichloromethane was purchased from Scharlab and was dried using a Pure Solv system from Innovative Technology, Inc. The final compounds were synthesized by following the synthetic procedures described in Schemes 1 and 2. Compounds **3** and **4** were prepared according to procedures already reported in the literature[1] and the characterization data are in agreement with those previously reported; As a consequence the experimental details are not included. All of the compounds that contain the cyanostilbene unit are photosensitive and, for this reason, great care had to be taken to exclude light during their synthesis and purification.

In order to confirm the molecular structures of the synthesized compounds the following analytical methods were applied. ^{1}H NMR spectra were recorded on spectrometers operating at 300.13 MHz (ARX-300 and AV-300) and 400.17 MHz (AV-400), whereas ^{13}C NMR spectra were recorded at 75.47 MHz and 100.62 MHz. Chemical shifts are given in ppm relative to TMS. The compositions of the synthesized compounds were determined by elemental analysis performed on a PERKIN-ELMER 240C CHNS elemental analyzer. FT-IR spectra were obtained using a THERMONICOLET Avatar 360 with KBr pellets. Mass spectrometry studies ($MALDI^{+}$) were performed with a Microflex (MALDI-ToF) apparatus. The preliminary mesophase identification was based on microscopic examination of the textures formed by samples between two glass plates. NIKON and OLYMPUS BH-2 polarizing microscopes equipped with a LINKAM THMS600 hot stage were used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements with a DSC TA Instrument Q-20 system. Thermogravimetric analysis (TGA) was performed using a TA Q5000IR instrument at a heating rate of 10 ºC min^{-1} under a nitrogen atmosphere. Molecular dimensions were estimated by molecular modeling (ChemSketch3D). The X-ray investigations on non-oriented samples were carried out in Lindemann capillary tubes (diameter 0.9 mm) using a PINHOLE (ANTON-PAAR) film camera. EFISH studies were performed in a SOPRA

1. (a) Gimeno, N.; Ros, M. B.; Serrano, J. L.; de la Fuente, M. R., Hydrogen-bonded banana liquid crystals. *Angewandte Chemie-International Edition* **2004,** *43*, 5235-5238; (b) Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C., Molecular design of nonchiral bent-core liquid crystals with antiferroelectric properties. *Journal of the American Chemical Society* **2000,** *122*, 1593-1601.

instrument with Nd:YAG laser. Absorption and fluorescence spectroscopy were carried out using ATI-Unicam UV4-200 and PERKIN-ELMER LS50B instrument, respectively.

Measurements of the complex dielectric permittivity in the range 10^0-10^8 Hz were performed using two impedance analyzers (Novocontrol Alpha-A and Agilent 4294A) and two type of cells: cell with gold-plated brass electrodes 50μm thick, and ITO coated transparent cells 8μm thick from Instec cells. A modified HP16091A coaxial test fixture was used as the sample holder for the high frequency measurements. It was held in a cryostat from Novocontrol and both temperature and dielectric measurements were computer-controlled. For measurements with the Instec cells the temperature was controlled with a Linkam THMSG-600 hot stage and a Linkam TMS-94 temperature controller. In order to characterize the relaxation processes, for each temperature the results were fitted to

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_k \frac{\Delta\varepsilon_k}{(1 + (i\omega\tau_k)^{\alpha_k})^{\beta_k}} - \frac{i\sigma_{dc}}{\omega\varepsilon_0}$$

where $\Delta\varepsilon_k$ is the dielectric strength of each relaxation mode, τ_k the relaxation time related to the frequency of maximum dielectric loss, α_k and β_k are parameters that describe the shape of the relaxation spectra($\alpha_k = \beta_k = 1$ correspond to Debye relaxation) and σ_{dc} is the dc conductivity. The summation is extended over all relaxation modes and each one is fitted to the Havriliak-Negami function.

Synthesis of the bent-core compounds and their cyanostilbene precursors:

Compound 1:[2] 4-Hydroxybenzaldehyde (4.00 g, 32.7 mmol) and anhydrous potassium carbonate (6.79 g, 49.1 mmol) were stirred in dry N,N-dimethylformamide (DMF) (120 mL). The solution was heated at 120 ºC under an argon atmosphere and 1-bromo-*n*-tetradecane (8.9 ml, 9.08 g, 32.7 mmol) was slowly added. After 15 h the reaction mixture was cooled to room temperature and poured into distilled water (100 mL). The product was extracted with dichloromethane and the organic fraction was washed with water, saturated brine, and dried over anhydrous magnesium sulfate. After evaporating the solvent, the solid was purified by chromatography using dichloromethane as the eluent to give a white solid in 72% yield. **M.p.** 36-37 ºC; **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 9.88 (s, 1H), 7.87-7.89 (m, 2H), 7.03-6.95 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 1.88-1.74 (m, 2H), 1.53-1.18 (m, 22H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):**190.9, 164.2, 132.3, 129.8, 114.8, 68.6, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 26.0, 22.7, 14.1; **IR, ν (KBr, cm^{-1}):** 2918, 2848, 1686, 1601, 1578, 1509, 1469, 1254, 1168.

Compound α-A: Potassium hydroxide (0.55 g, 9.4 mmol) was dissolved in absolute ethanol (13 mL) and methyl 4-(cyanomethyl)benzoate and compound **1** (0.60 g, 1.8 mmol) were added to the solution. To increase the solubility of the products a mixture of tetrahydrofuran (THF)/ethanol 2:1 (25 mL) was added and the stirred mixture was heated at 50 ºC for 24 h. The mixture was cooled to 0º C and hydrochloric acid (6 M) was added dropwise to give pH = 1. The resulting solid was filtered off and recrystallized from acetic acid to give a yellow solid (74% yield). **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm):** 8.10 (s, 1H), 8.06-8.00 (m, 2H), 8.00-7.93 (m, 2H), 7.88-7.80 (m, 2H), 7.12-7.05 (m, 2H), 4.05 (t, J = 6.5Hz, 2H), 1.81-1.65 (m, 2H), 1.46-1.19 (m, 22H), 0.84 (t, J = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm):** 166.7, 161.0, 144.2, 138.2, 131.5, 130.6, 130.0, 125.8, 125.5, 118.1, 114.9, 105.9, 67.8, 31.3, 29.0, 29.0, 29.0, 28.9, 28.7, 28.5, 25.4, 22.1, 13.9; **IR, ν (KBr, cm^{-1}):** 3400-2600, 2917, 2849, 2219, 1686, 1653, 1612, 1293, 1187; **MS (MALDI$^+$) m/z:** 484.3 $[M + Na]^+$.

[2] Brun, A.; Etemad-Moghadam, G., New Double-Chain and Aromatic (α-Hydroxyalkyl)phosphorus Amphiphiles. *Synthesis* **2002,** *2002*, 1385-1390.

Compound α-E: A solution of compound **1** (0.50 g, 1.57 mmol) and methyl 4-(cyanomethyl)benzoate (0.28 g, 1.57 mmol) in a mixture of THF/*tert*-butanol (*t*-BuOH) (5 mL/11 mL) was stirred and heated at 50 ºC for 1 h in the dark. Tetrabutylammonium hydroxide (1M) in methanol (0.16 mL, 0.16 mmol) was added and the mixture was heated for 1 h. When the reaction was complete, the resulting solid was washed with methanol (60% yield). **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):**8.14-8.04 (m, 2H), 7.97-7.85 (m, 2H), 7.77-7.68 (m, 2H), 7.56 (s, 1H), 7.03-6.92 (m, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.94 (s, 3H), 1.86-1.75 (m, 2H), 1.52-1.19 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 166.6, 161.7, 143.7, 139.3, 131.7, 130.4, 130.1, 125.9, 125.7, 118.3, 115.1, 107.3, 68.4, 52.4, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.2, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2920, 2851, 2214, 1724, 1609, 1590, 1471, 1438, 1287, 1274, 1263, 1186, 1110; **MS ($MALDI^+$) m/z**: 498.4 $[M + Na]^+$.

Compound 2[3]**:** Sodium hydroxide (0.25 g, 6.3 mmol) was dissolved in ethanol (5 mL). (4-Hydroxyphenyl)acetonitrile (0.80 g, 5.9 mmol) was added. The mixture was stirred for 15 min and the solvent was evaporated. The residue was dissolved in DMF (45 mL) at 0 ºC and 1-bromo-*n*-tetradecane (1.65 g, 1.76 ml, 5.9 mmol) was added. After 16 h the mixture was poured into distilled water (50 mL) and the product was extracted with ether. The organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the product was purified by chromatography using dichloromethane/hexane (1:1) as eluent (62% yield). **M.p.** 63-66 ºC; **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 7.24-7.19 (m, 2H), 6.92-6.86 (m, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 3.68 (s, 2H), 1.83-1.73 (m, 2H), 1.50-1.19 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):** 159.1, 129.2, 121.6, 118.3, 115.2, 68.3, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.2, 23.0, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2917, 2849, 2243, 1517, 1472, 1256.

[3] Dong, C.-Z.; Ahamada-Himidi, A.; Plocki, S.; Aoun, D.; Touaibia, M.; Meddad-Bel Habich, N.; Huet, J.; Redeuilh, C.; Ombetta, J.-E.; Godfroid, J.-J.; Massicot, F.; Heymans, F., Inhibition of secretory phospholipase A2. 2-Synthesis and structure–activity relationship studies of 4,5-dihydro-3-(4-tetradecyloxybenzyl)-1,2,4-4H-oxadiazol-5-one (PMS1062) derivatives specific for group II enzyme. *Biorg. Med. Chem.* **2005,** *13*, 1989-2007.

Compound β-A: An experimental procedure similar to that used for the synthesis of compound **α-A** was followed, using in this case potassium hydroxide (0.22 g, 3.9 mmol), methyl 4-formylbenzoate (0.30 g, 1.8 mmol). The purification was carried out by recrystallization from acetic acid (71% yield). **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, DMSO-*d*$_6$), δ (ppm):** 8.09-8.03 (m, 2H), 8.00 (s, 1H), 8.00-7.95 (m, 2H), 7.75-7.69 (m, 2H), 7.10-7.04 (m, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 1.78-1.67 (m, 2H), 1.46-1.18 (m, 22H), 0.84 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (75 MHz, THF-*d*$_8$), δ (ppm):** 164.1, 158.6, 136.4, 136.0, 129.9, 128.0, 136.8, 125.3, 124.6, 115.3, 112.9, 112.6, 66.0, 33.1, 30.8, 30.8, 30.7, 30.5, 30.5, 30.4, 27.2, 23.7, 14.6; **IR, ν (KBr, cm^{-1}):** 3260-2500, 2918, 2850, 2220, 1690, 1606, 1508, 1435, 1427, 1290, 1260, 1194; **MS (MALDI$^+$) m/z:** 484.3 $[M + Na]^+$.

Compound β-E: The synthetic method used for the preparation of this compound was analogous to that described for compound **α-E**, using compound **2** (0.50 g, 1.52 mmol) and methyl-(4-formylbenzoate) (0.25 g, 1.52 mmol) in a mixture of THF/*t*-BuOH (5/11 mL). The resulting solid was filtered off and washed with methanol, giving a yellow solid with 64% yield. **M.p.** See Table 1; **^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm):** 8.15-8.07 (m, 2H), 7.95-7.87 (m, 2H), 7.67-7.58 (m, 2H), 7.44 (s, 1H), 7.00-6.91 (m, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.95 (s, 3H), 1.86-1.74 (m, 2H), 1.53-1.23 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm):** 166.7, 160.6, 138.3, 138.3, 131.1, 130.2, 129.0, 127.6, 126.3, 117.8, 115.2, 113.7, 68.4, 52.5, 32.1, 29.8, 29.7, 29.7, 29.5, 29.3, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2918, 2850, 2220, 1725, 1605, 1473, 1446, 1435, 1286, 1257, 1182, 1111; **MS (MALDI$^+$) m/z:** 498.4 $[M + Na]^+$.

Compound α-B: The carboxylic acid **α-A** (0.25 g, 0.5 mmol), compound **3** (0.31 g, 0.5 mmol) and DPTS (0.12 g, 0.4 mmol) were dissolved in dichloromethane and cooled at 0 ºC under inert atmosphere. DCC (0.19 g, 0.9 mmol) was added and the mixture was stirred for 30 minutes and then allowed to warm up to room temperature. The mixture was stirred for 24 h, filtered off through Celite® and the filtrate was evaporated to give a yellow solid. The solid was purified by chromatography using dichloromethane/hexane as eluent followed by recrystallization from ethyl acetate to give α-B in 86% yield. **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm):** 8.35-8.24 (m, 4H), 8.19-8.12 (m, 2H), 7.97-7.90 (m, 2H), 7.85-7.77 (m, 2H), 7.72-7.64 (m, 2H), 7.61 (s, 1H), 7.52 (d, *J* = 5.0 Hz, 2H), 7.49-7.45 (m, 1H), 7.43-7.35 (m, 2H), 7.35-7.30 (m, 2H), 7.25-7.20 (m, 1H), 7.03-6.95 (m, 4H), 4. 06 (t, *J* = 6.7 Hz, 2H), 4.04 (t, *J* = 6.7 Hz, 2H), 1.89-1.75 (m, 4H), 1.52-1.19 (m, 44), 0.88 (t, *J* = 6.7 Hz, 6H); **^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm):** 164.7,

164.6, 164.5, 164.0, 161.9, 155.6, 151.5, 150.8, 144.1, 142.2, 140.1, 138.3, 132.6, 132.0, 131.9, 131.0, 130.0, 129.5, 128.5, 127.0, 126.0, 125.9, 124.9, 122.3, 122.2, 121.1, 120.8, 120.6, 118.3, 115.2, 114.6, 107.3, 68.6, 68.5, 32.1, 29.8, 29.8, 29.8, 29.7, 29.5, 29.3, 29.3, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2918, 2850, 2217, 1733, 1604, 1540, 1473, 1268, 1171, 1073; **MS (MALDI^{+}) m/z:** 1088.5 [M + Na]$^{+}$; **Elemental analysis:** Calcd. for $C_{70}H_{83}NO_8$: C 78.84, H 7.85, N 1.31; found C 79.01, H 8.07, N 1.55.

Compound β-B: The experimental procedure used was analogous to that described for compound **α-B**, using **β-A** (0.25 g, 0.54 mmol), compound **3** (0.31 g, 0.50 mmol), DPTS (0.12 g, 0.41 mmol) and DCC (0.19 g, 0.91 mmol) dissolved in dichloromethane (50 mL). After 24 h the reaction was complete and the mixture was filtered through Celite®. The solvent was evaporated and the solid was purified by chromatography using dichloromethane as eluent followed by recrystallization from ethyl acetate (81% yield). **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.35-8.26 (m, 4H), 8.21-8.13 (m, 2H), 8.03-7.96 (m, 2H), 7. 72-7.62 (m, 4H), 7.52 (d, *J* = 5.0 Hz, 2H), 7.49 (s, 1H), 7.48-7.45 (m, 1H), 7.43-7.36 (m, 2H), 7.36-7.30 (m, 2H), 7.25-7.20 (m, 1H), 7.04-6.94 (m, 4H), 4. 06 (t, *J* = 6.6 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 1.90-1.74 (m, 4H), 1.54-1.23 (m, 44), 0.88 (t, *J* = 6.7 Hz, 6H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 164.6, 164.6, 164.5, 164.0, 160.7, 155.6, 151.5, 150.7, 142.2, 139.0, 138.2, 138.0, 132.6, 132.0, 130.8, 130.4, 130.0, 129.2, 128.5, 127.7, 127.0, 126.3, 124.9, 122.3, 122.2, 121.1, 120.8, 120.6, 117.8, 115.2, 114.6, 114.3, 68.5, 68.4, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.3, 29.2, 26.2, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2918, 2850, 2217, 1733, 1604, 1540, 1473, 1268, 1171, 1073; **MS (MALDI^{+}) m/z:** 1088.5 [M + Na]$^{+}$; **Elemental analysis:** Calcd. for $C_{70}H_{83}NO_8$: C 78.84, H 7.85, N 1.31; found C 79.09, H 8.05, N 1.55.

Compound α,α-B: DCC (0.21 g, 1.04 mmol) was added to a cooled (0 ºC) mixture of **α-A** (0.40 g, 0.9 mmol), compound **4** (0.08 g, 0.45 mmol) and DPTS (0.13 g, 0.4 mmol) in dry dichloromethane (40 mL) under argon. After 48 hours the mixture was filtered through Celite® and the solvent was evaporated. The solid was purified by chromatography using dichloromethane/hexane 9:1 as eluent followed by a recrystallization from dichloromethane and then from ethyl acetate (51% yield). **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.32-8.24 (m, 4H), 8.00-7.90 (m, 4H), 7.85-7.77 (m, 4H), 7.73-7.65 (m, 2H), 7.61 (s, 2H), 7.48 (d, *J* = 5.1 Hz, 2H), 7.50-7.45 (m, 1H), 7.38-7.29 (m, 2H), 7.25-7.19 (m, 1H), 7.05-6.95 (m, 4H), 4.04 (t, *J* = 6.5 Hz, 4H), 1.92-1.78 (m, 4H), 1.52-1.21 (m, 44H), 0.88 (t, *J* = 6.6 Hz, 6H); **^{13}C NMR**

(75 MHz, $CDCl_3$), δ (ppm): 164.7, 161.8, 151.4, 150.8, 144.1, 142.2, 140.1, 138.2, 131.8, 131.0, 130.1, 129.5, 129.4, 128.5, 125.9, 124.9, 122.2, 120.8, 120.6,118.3, 115.2, 107.2, 68.5, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.3, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2917, 2849, 2222, 1740, 1731, 1600, 1514, 1468, 1258, 1176, 1074; **MS (MALDI$^+$) m/z:** 1095.7 $[M + Na]^+$; **Elemental analysis:** Calcd. for $C_{72}H_{84}N_2O_6$: C 80.56, H 7.89, N 2.61; found C 80.72, H 8.10, N 2.61.

Compound β,β-B: The synthetic method was similar to that used for the synthesis of compound **α,α-B**, using **β-A** (0.40 g, 0.9 mmol), compound **4** (0.08 g, 0.45 mmol), DPTS (0.13 g, 0.4 mmol) and DCC (0.21 g, 1.0 mmol) in dichloromethane (40 mL). The resulting solid was purified by chromatography using dichloromethane/hexane as eluent followed by two recrystallizations from ethyl acetate (69% yield). **M.p. (ºC):** See Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.35-8.26 (m, 4H), 8.04-7.94 (m, 4H), 7.72-7.60 (m, 6H), 7.53 (d, *J* = 5.0 Hz, 2H), 7.49 (s, 2H), 7.49-7.45 (m, 1H), 7.38-7.30 (m, 2H), 7.25-7.20 (m, 1H), 7.02-6.93 (m, 4H), 4.02 (t, *J* = 6.5 Hz, 4H), 1.89-1.75 (m, 4H), 1.53-1.20 (m, 44H), 0.88 (t, *J* = 6.7 Hz, 6H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 164.6, 160.7, 151.5, 150.8, 142.2, 139.1, 138.2, 138.1, 130.8, 130.5, 130.4, 130.1, 129.2, 128.5, 127.7, 126.3, 124.9, 122.2, 120.7, 120.6, 117.8, 115.2, 114.3, 68.5, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.2, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2918, 2850, 2220, 1733, 1605, 1513, 1472, 1255, 1161; **MS (MALDI$^+$) m/z:** 1095.7 $[M + Na]^+$; **Elemental analysis:** Calcd. for $C_{72}H_{84}N_2O_6$: C 80.56, H 7.89, N 2.61; found C 80.73, H 8.01, N 2.85.

2. NMR spectra of the bent-core compounds.

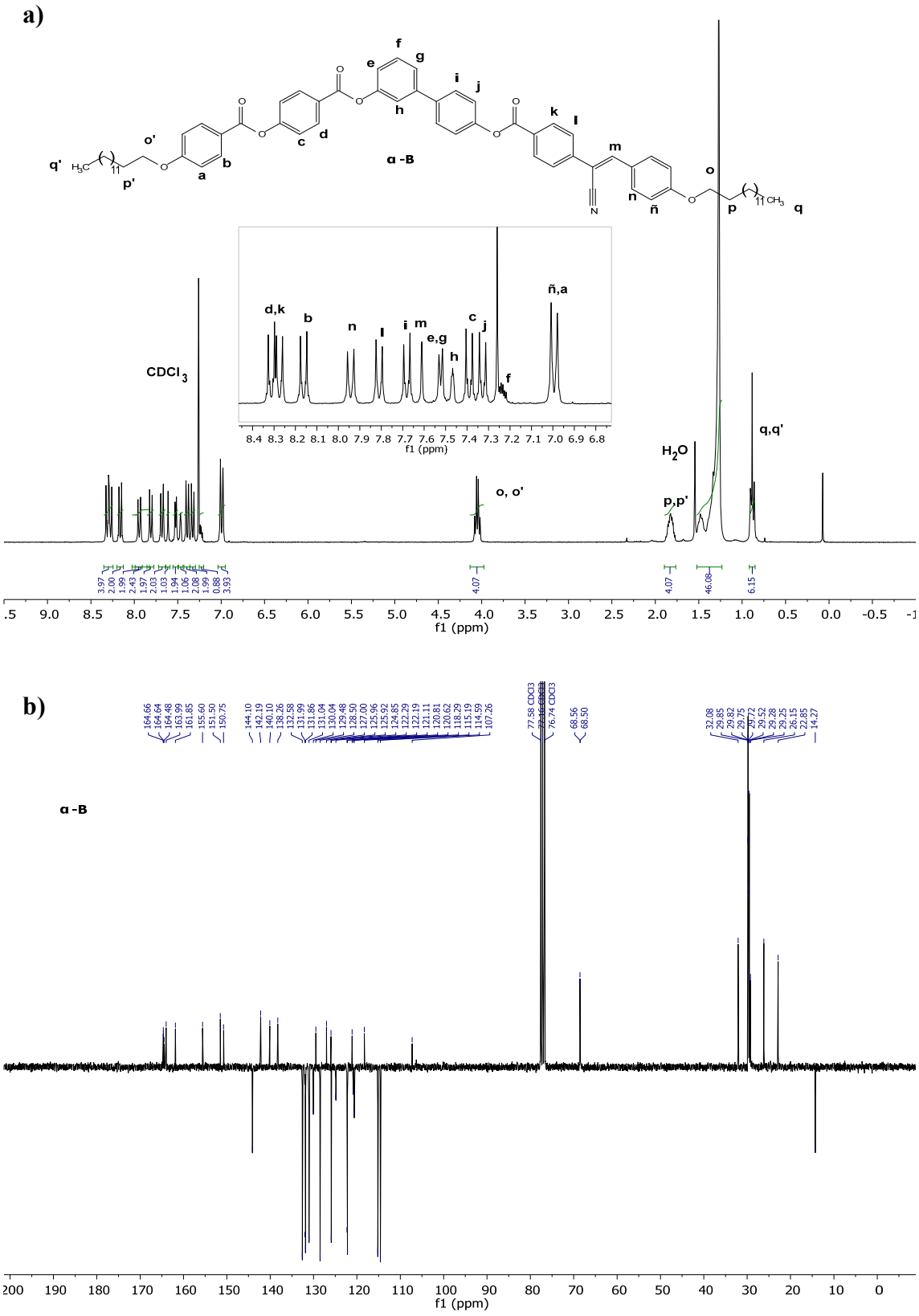

Figure S1. a) ^{1}H NMR (300 MHz) and b) ^{13}C NMR (75 MHz) in $CDCl_3$ at 25 ºC of **α-B**.

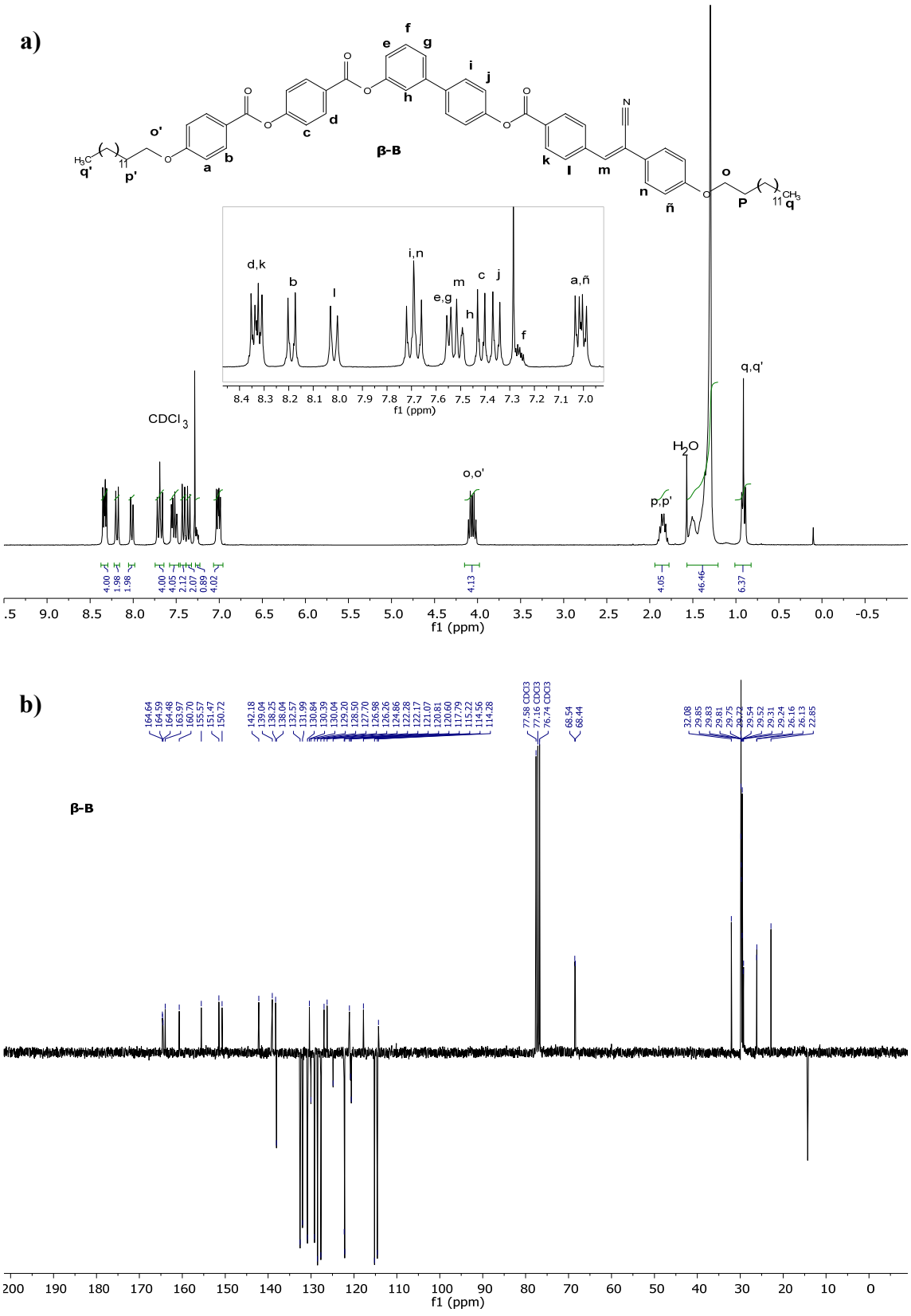

Figure S2. a) ^{1}H NMR (300 MHz) and b) ^{13}C NMR (75 MHz) in $CDCl_3$ at 25 ºC of **β-B**.

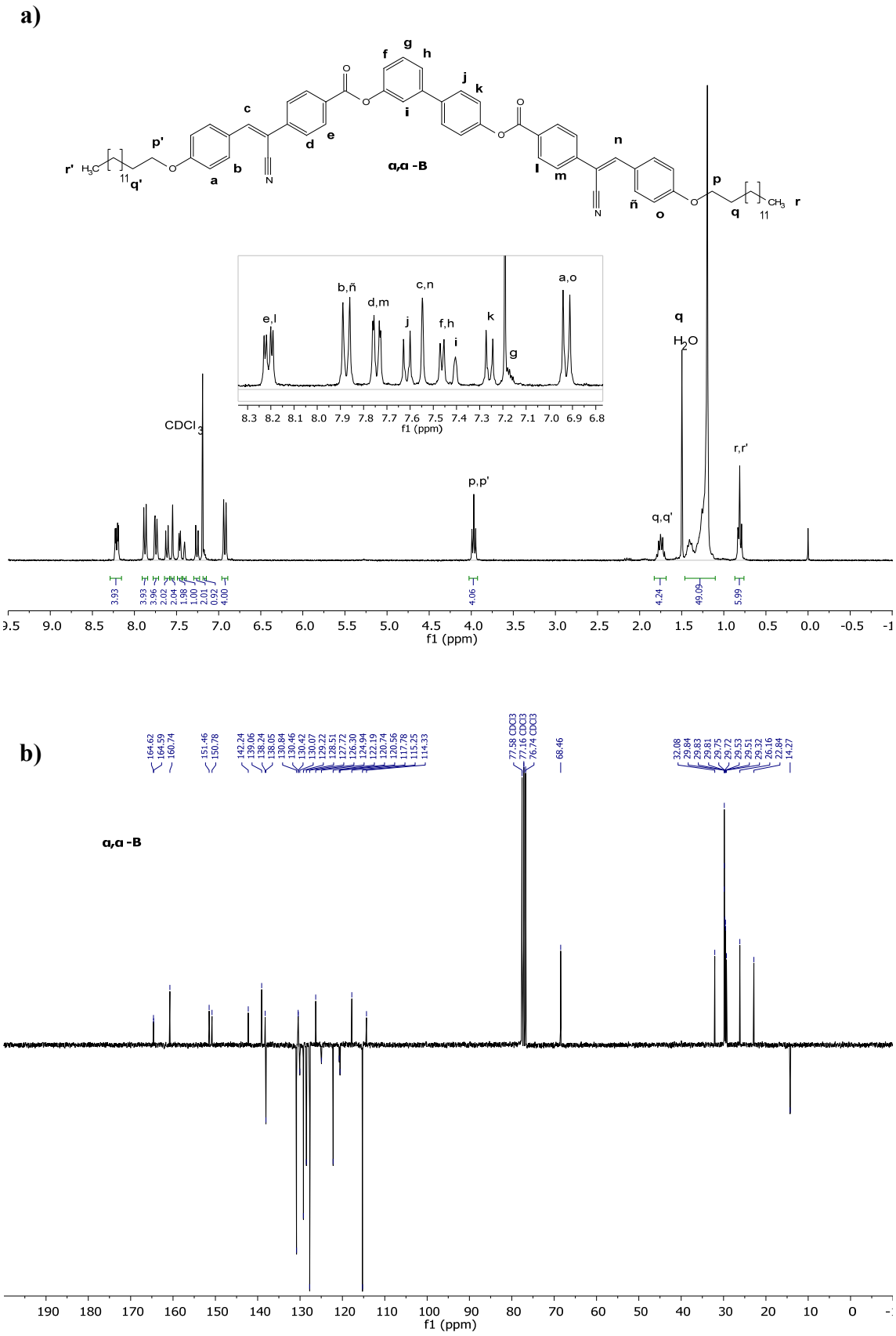

Figure S3. a) ^{1}H NMR (300 MHz) and b) ^{13}C NMR (75 MHz) in $CDCl_3$ at 25 ºC of **α,α-B**.

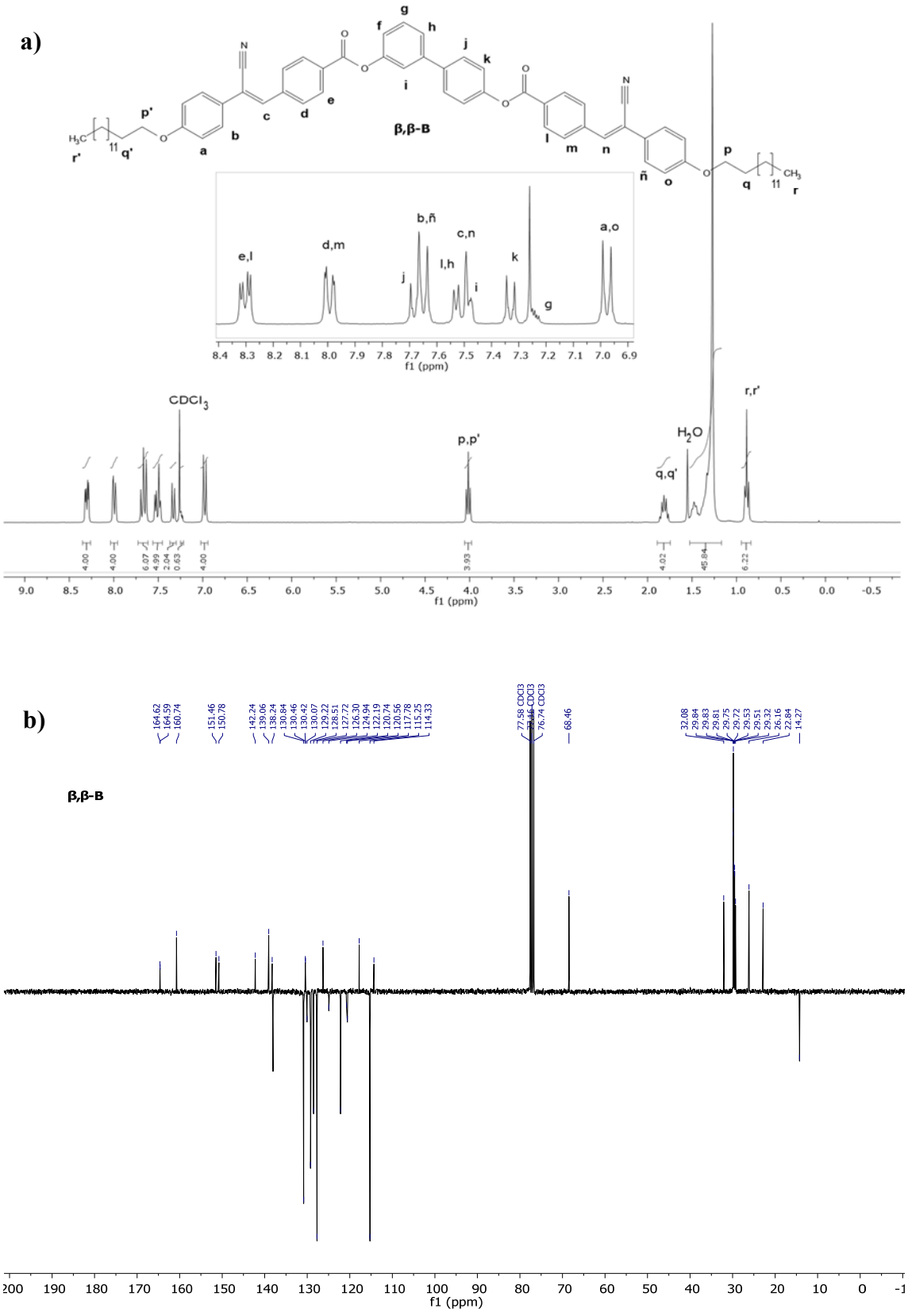

Figure S4. a) ^{1}H NMR (300 MHz) and b) ^{13}C NMR (75 MHz) in $CDCl_3$ at 25 ºC of **β,β-B**.

3. DSC thermograms

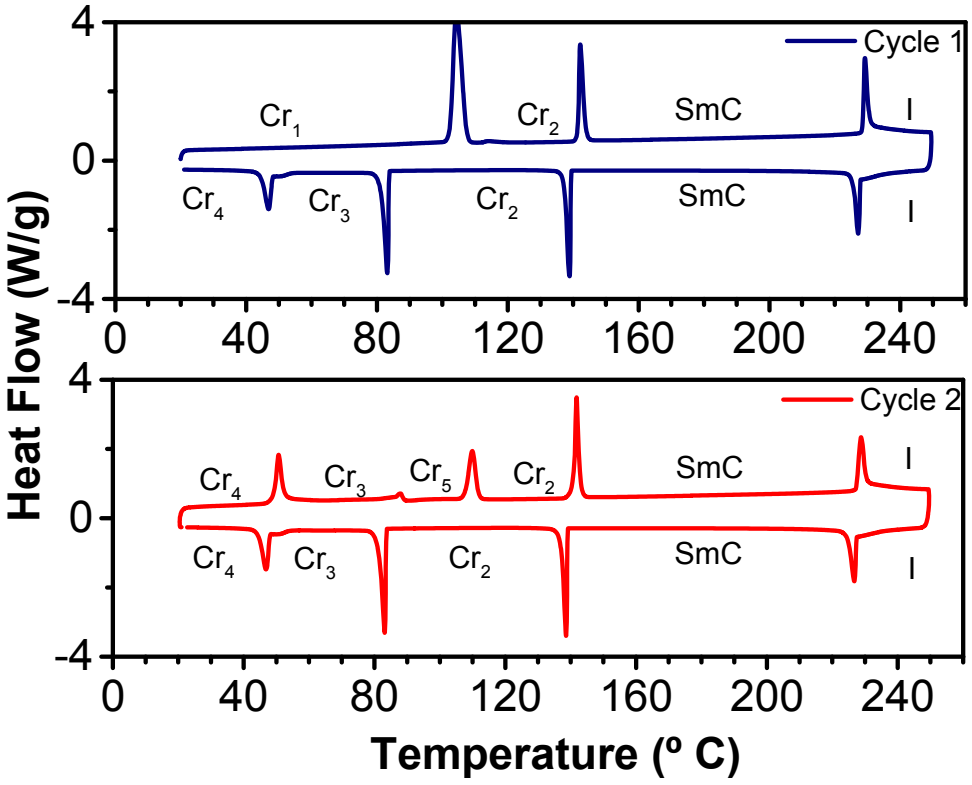

Figure S5. DSC thermograms, first and second heating/cooling cycles of **α-A**.

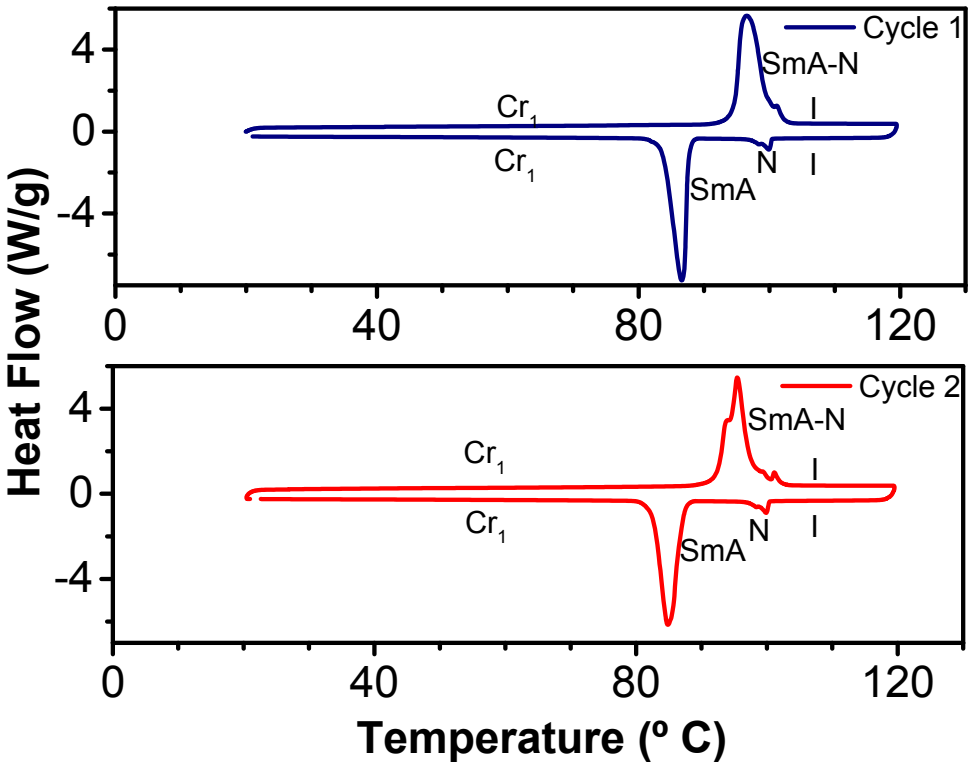

Figure S6. DSC thermograms, first and second heating/cooling cycles of **α-E**.

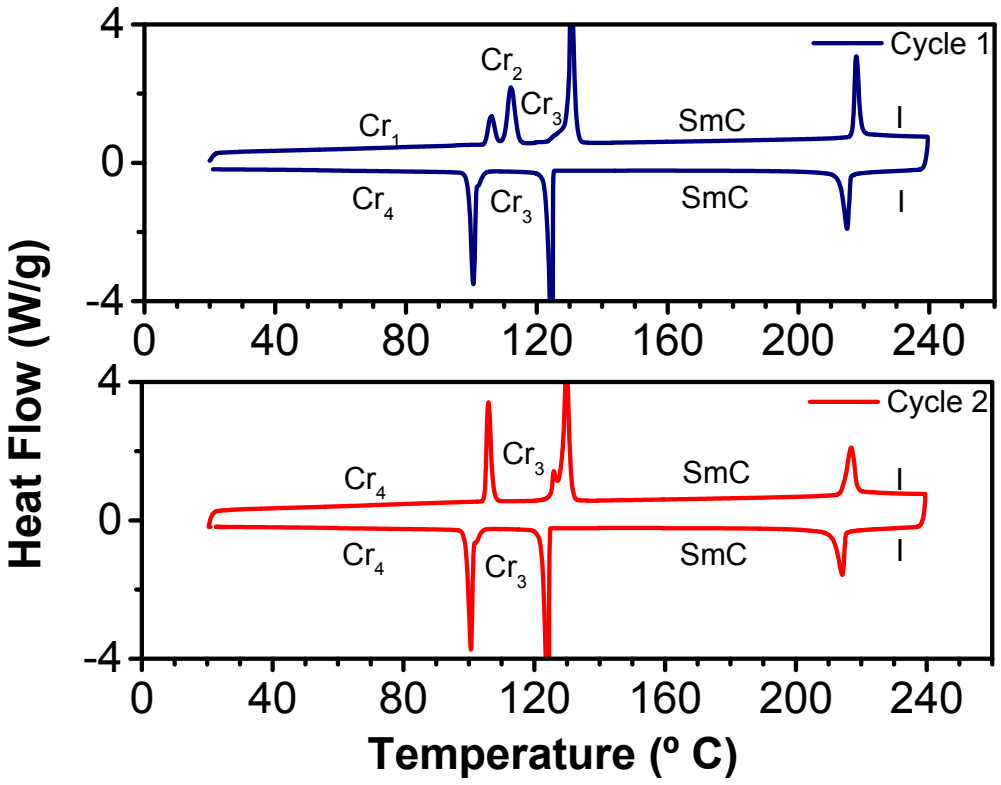

Figure S7. DSC thermograms, first and second heating/cooling cycles of **β-A**.

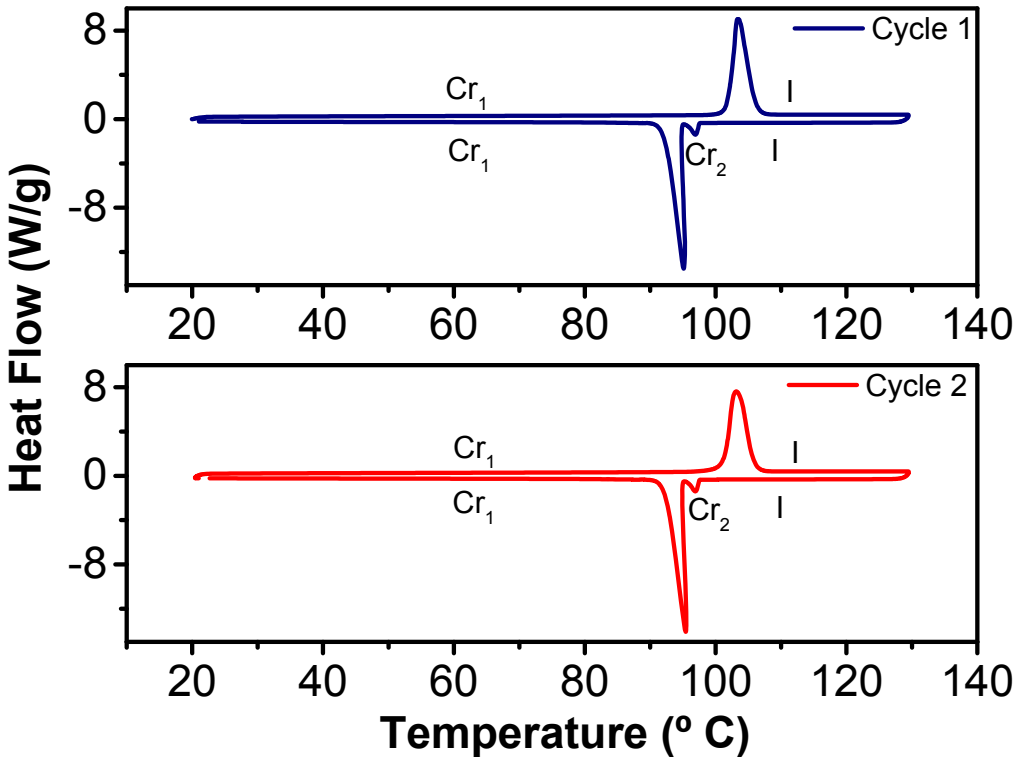

Figure S8. DSC thermograms, first and second heating/cooling cycles of **β-E**.

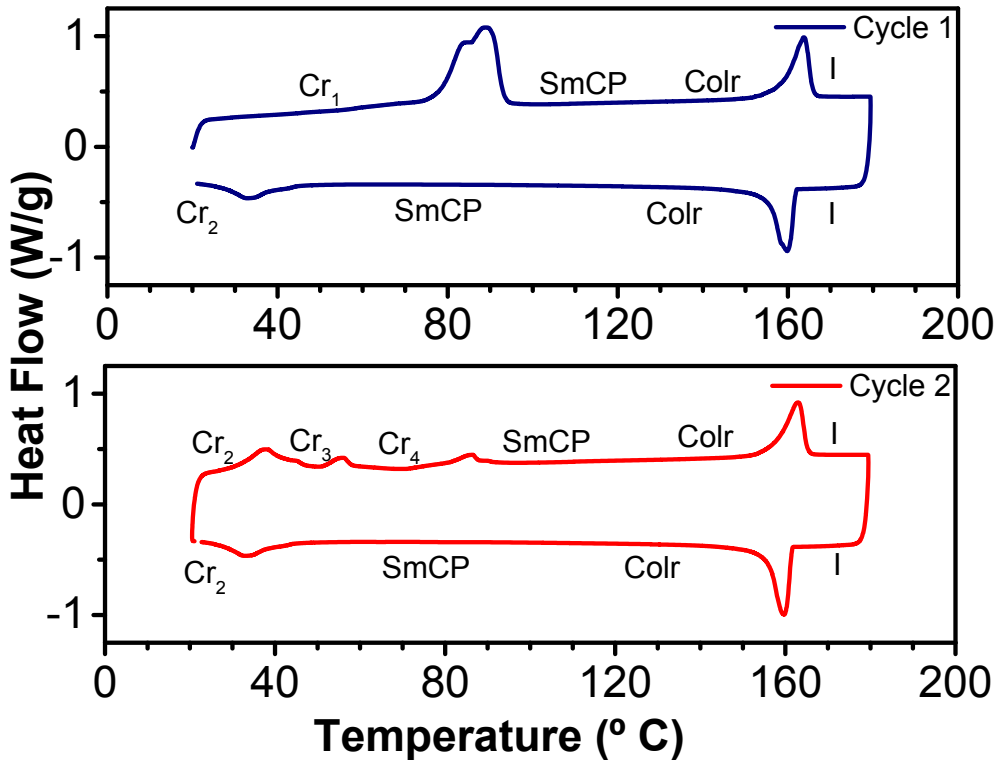

Figure S9. DSC thermograms, first and second heating/cooling cycles of **α-B**.

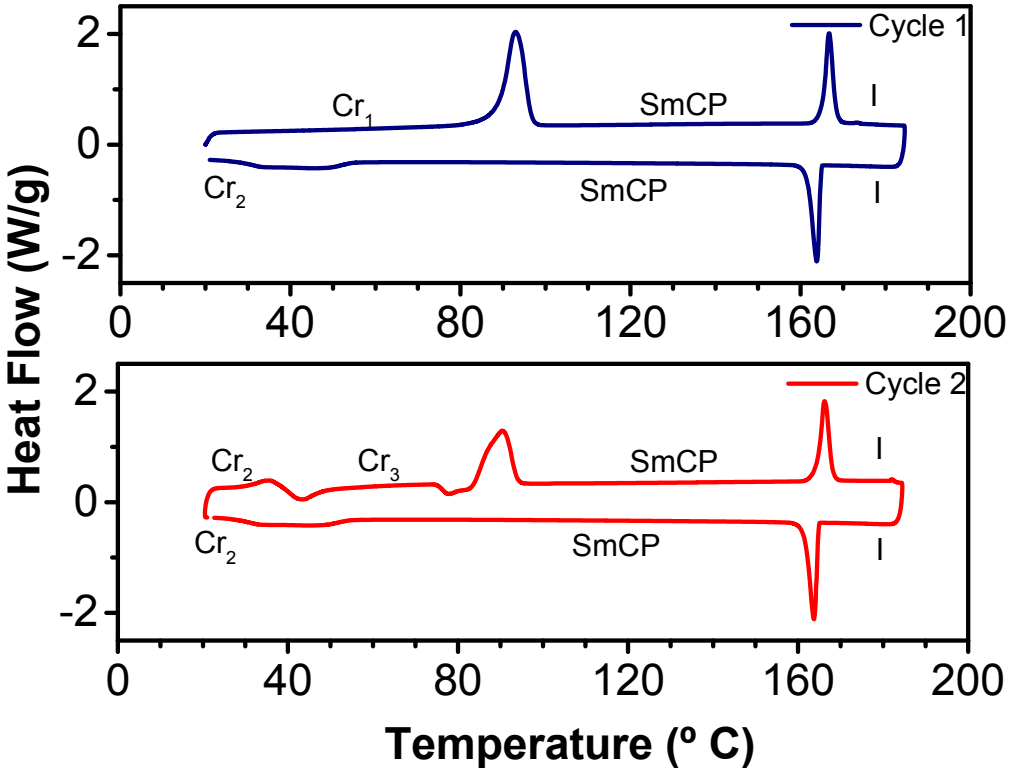

Figure S10. DSC thermograms, first and second heating/cooling cycles of **β-B**.

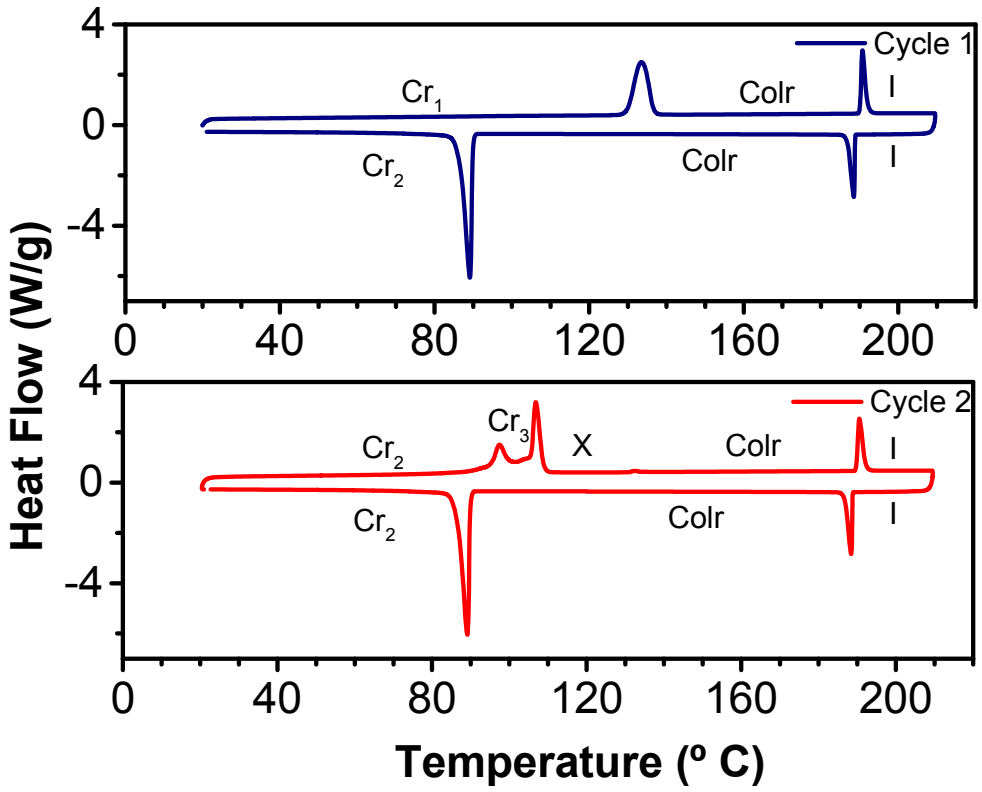

Figure S11. DSC thermograms, first and second heating/cooling cycles of **α,α-B**.

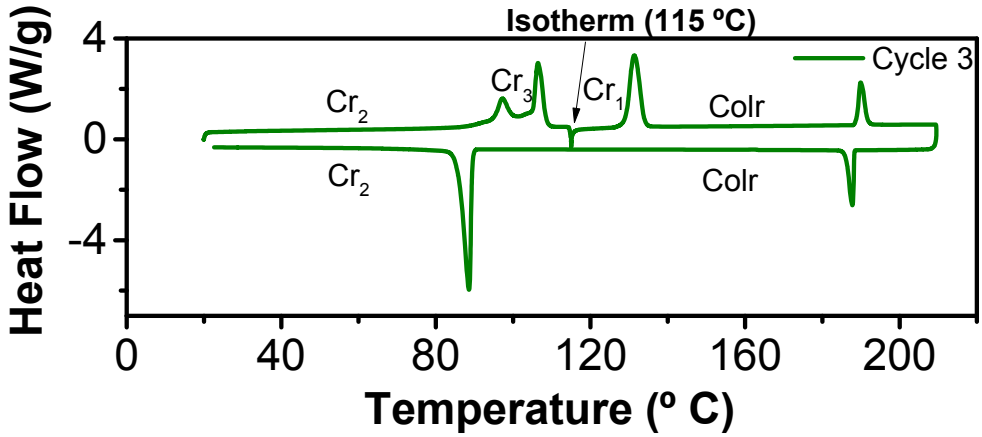

Figure S12. DSC thermogram of **α,α-B**, heating/cooling cycle including an isotherm at 115 ºC

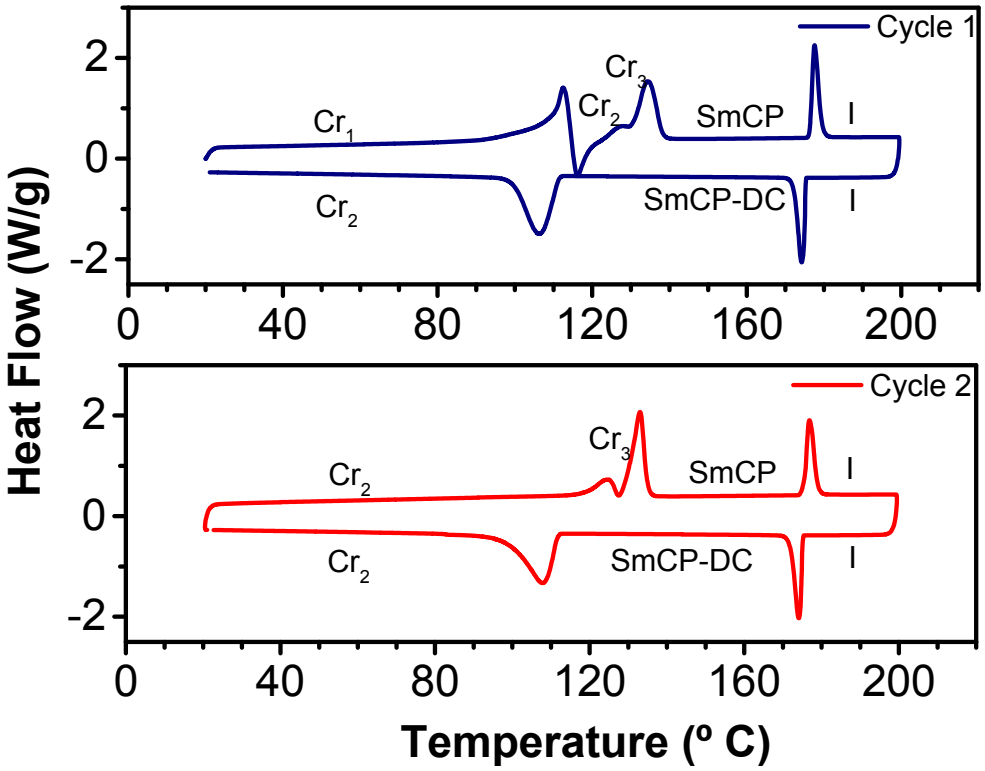

Figure S13. DSC thermograms, first and second heating/cooling cycles of **β,β-B**.

4. X-ray Diffraction

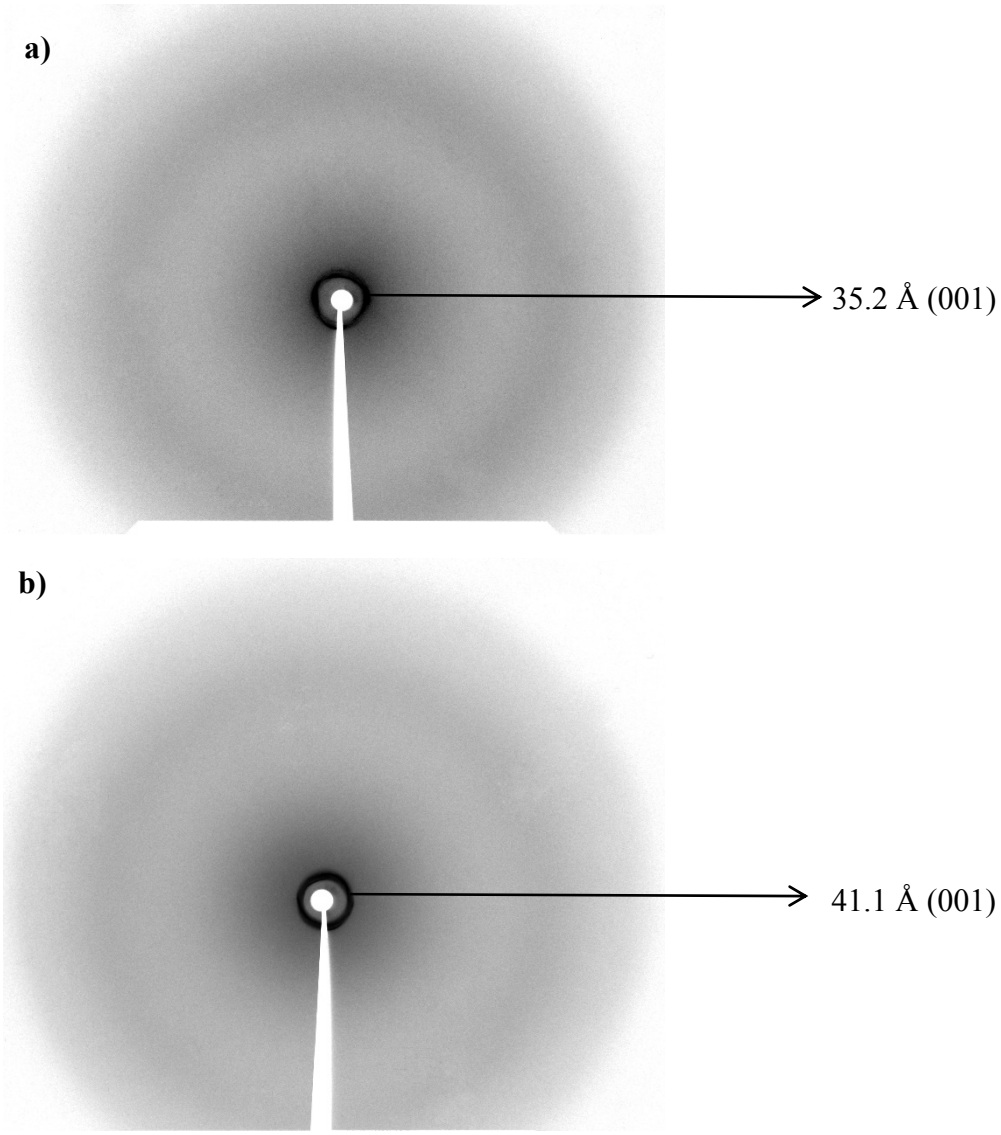

Figure S14. XRD patterns of the representative mesophases of the rod-like cyanostilbenes, a) **α-E**, SmA phase at 104 ºC; b) **β-A**, SmC phase at 145 ºC.

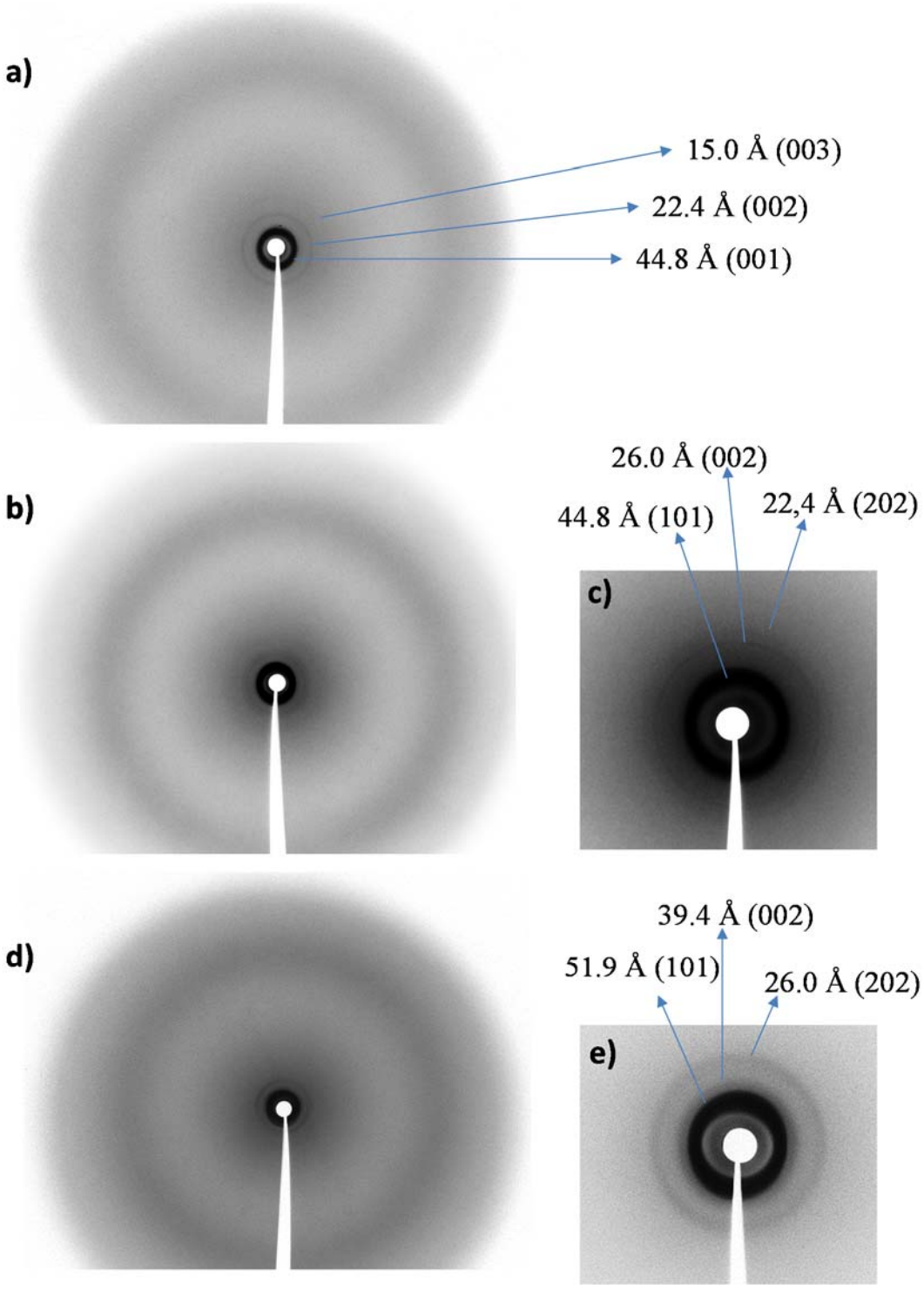

Figure S15. XRD patterns of the representative bent-core mesophases: a) **β-B**, SmCP phase at 131 ºC or **α-B**, SmCP at 110 ºC; b, c) **α-B**, Col_r phase at 152 ºC; d, e) **α,α-B**, Col_r phase at 147 ºC.

5. Absorption and fluorescence studies of the bent-core compounds.

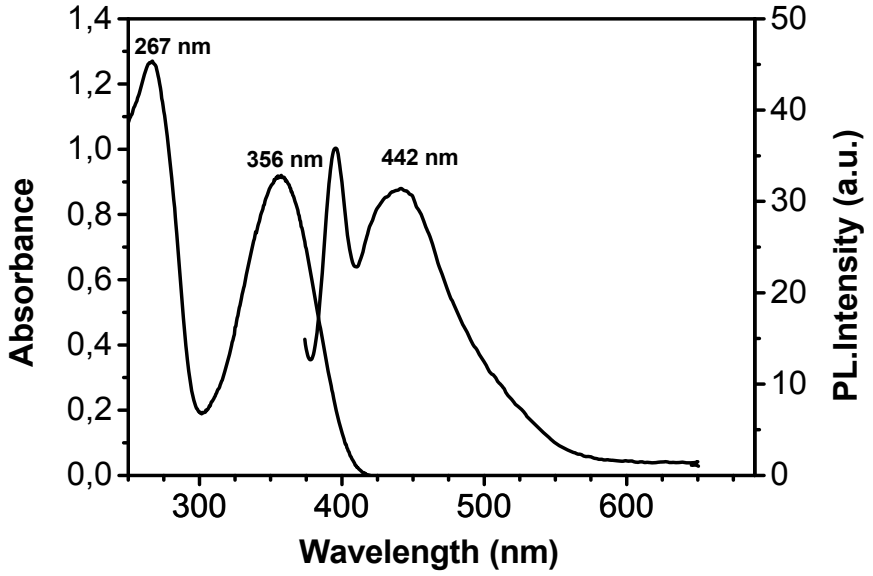

Figure S16. Absorption and fluorescence spectra in dichloromethane of **α-B** (2.43 x 10^{-5} M and 2.41 x 10^{-6} M, respectively).

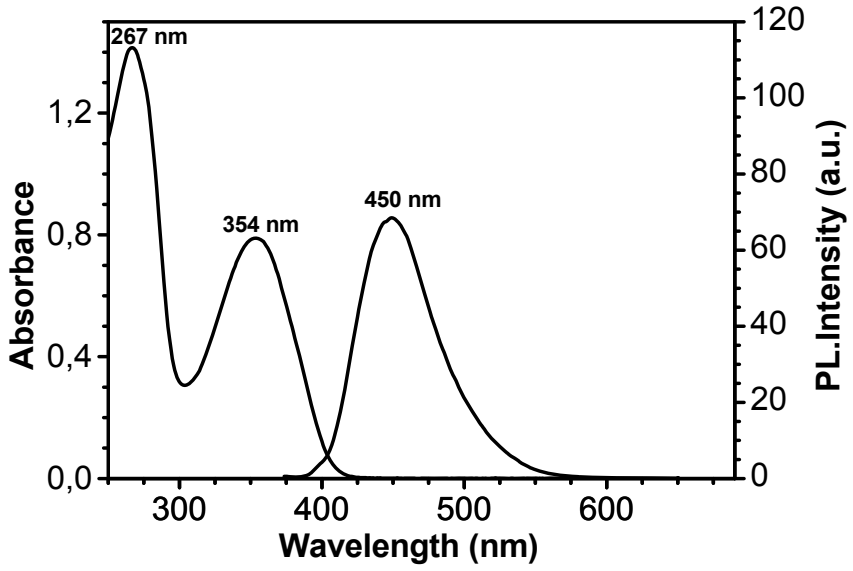

Figure S17. Absorption and fluorescence spectra in dichloromethane of **β-B** (2.57 x 10^{-5} M and 7.94 x 10^{-7} M, respectively).

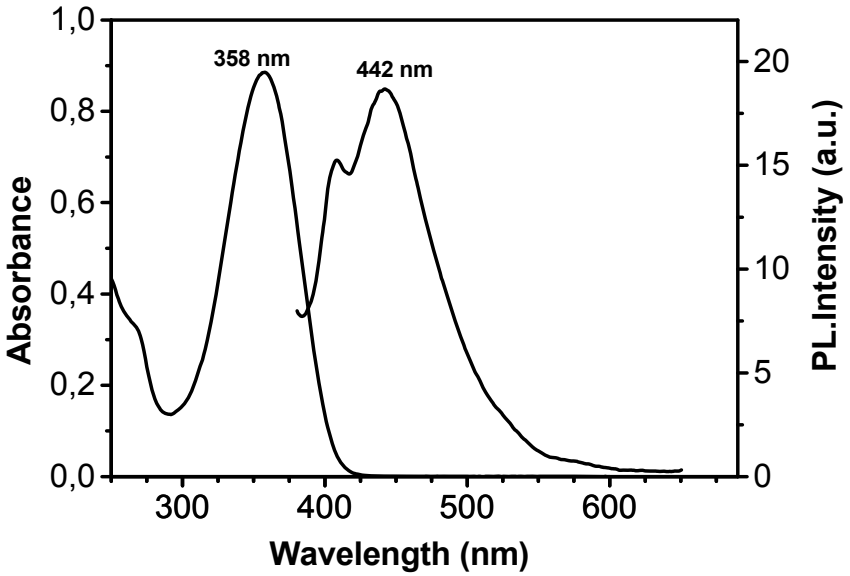

Figure S18. Absorption and fluorescence spectra in dichloromethane of **α,α-B** (2.50 x 10^{-5} M and 1.26 x 10^{-6} M, respectively).

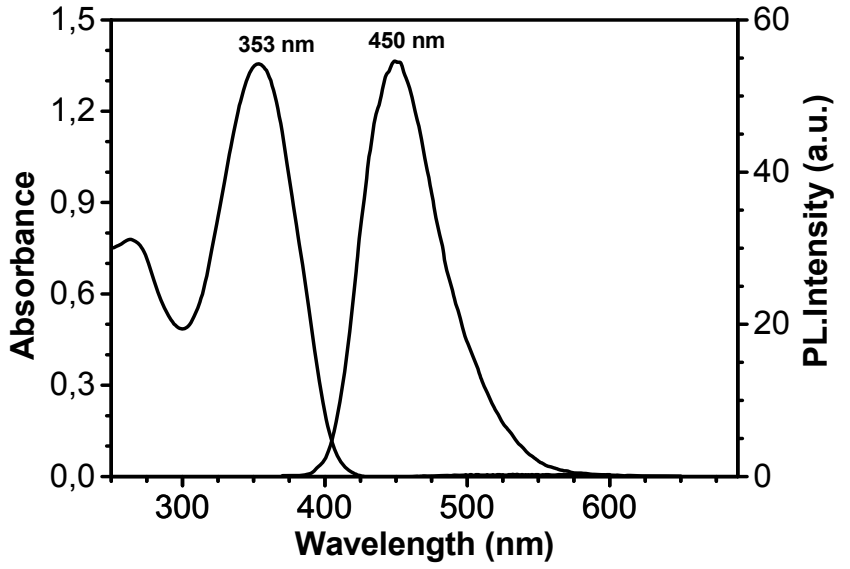

Figure S19. Absorption and fluorescence spectra in dichloromethane of **β,β-B** (2.46 x 10^{-5} M and 1.72 x 10^{-7} M, respectively).

6. Dielectric and electrooptic studies of compound α,α-B

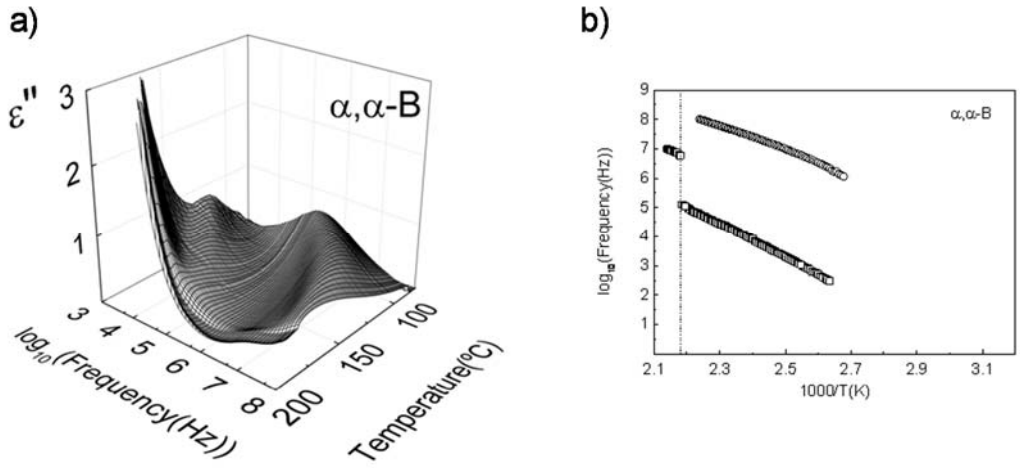

Figure S20. Dielectric studies for **α,α-B** compound on cooling, in order to characterize the columnar mesophase. a) Three-dimensional plot of the dielectric losses vs. temperature and frequency. b) Arrhenius plot of the frequency of the relaxation modes.

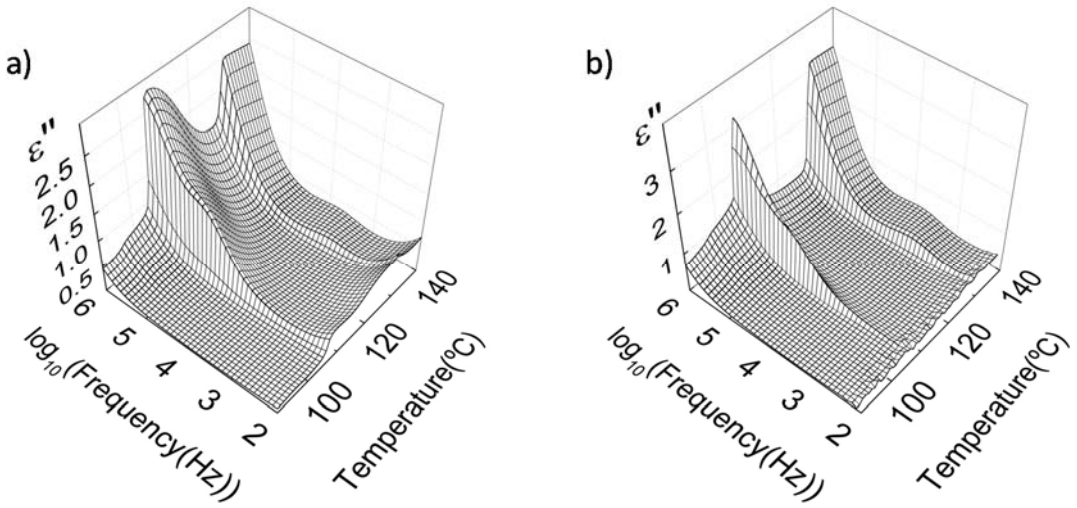

Figure S21. Dielectric studies for **α,α-B** compound on heating, in order to characterize the X phase. a) Three-dimensional plot of the dielectric losses vs. temperature and frequency on heating with a ramp of temperature from 90 ºC to 140 ºC. b) Three-dimensional plot of the dielectric losses vs. temperature and frequency on heating stepwise from 90 ºC to 140 ºC.

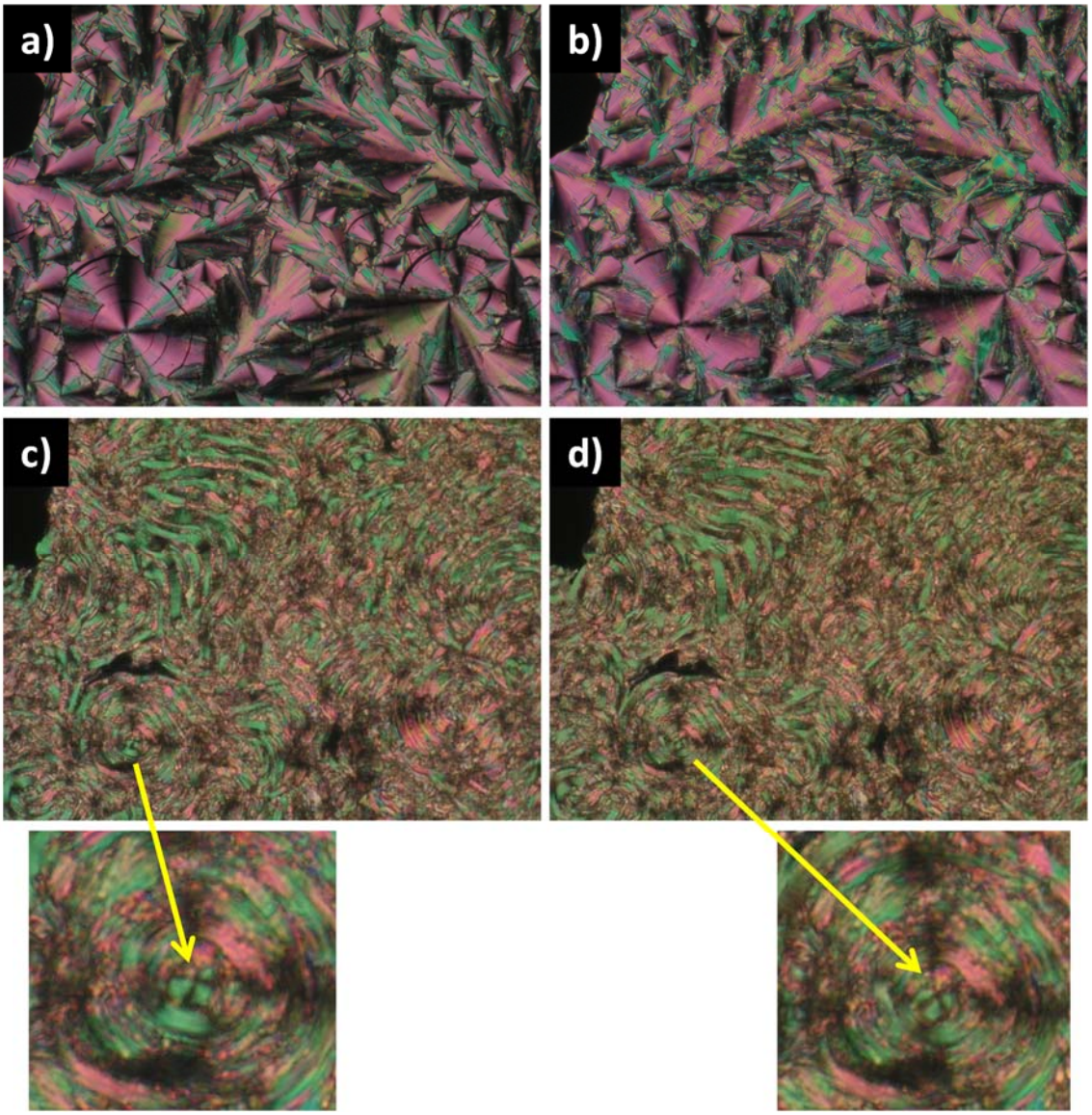

Figure S22. Electroptic studies with compound **α,α-B**. a) 90 ºC, Cr'' phase, b) 110 ºC, X phase, c) and d) 110 ºC, X phase, triangular field 5 Hz, 50 V_{pp} μm^{-1}