Supplemental information

Liquid crystalline derivatives exhibiting smectic phases with ferro and antiferroelectric properties

Natalia Podoliak,[1] Vladimíra Novotná,[1] Terézia Jurkovičová,[1] Věra Hamplová,[1] Damian Pociecha[2] and Martin Cigl[1]

[1] Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 18221, Prague, Czech Republic

[2] Chemistry Department, Warsaw University, Al. Zwirki i Wigury Warsaw, Poland

1. General scheme of synthesis

All starting materials and reagents were purchased from Sigma-Aldrich, Acros Organics or Lach:Ner with purity "For synthesis" or better. All solvents used for the synthesis were "p.a." grade. ^{1}H NMR spectra were recorded using Varian VNMRS 300 instrument, deuteriochloroform ($CDCl_3$) and hexadeuteriodimethyl sulfoxide (DMSO-d_6) were used as solvents and signals of the solvent serving as internal standards. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. Signals were identified with the help of homonuclear and heteronuclear correlation experiments. Elemental analyses were carried out on Elementar vario EL III instrument. The purity of all final compounds was checked by HPLC analysis (high-pressure pump ECOM Alpha; column WATREX Biospher Si 100, 250 × 4 mm, 5 μm; detector WATREX UVD 250) and were found to be >95.0 %. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm or 40–60 μm). Enantiomeric purity of chiral compounds was confirmed by chiral HPLC system, see section 2 in SI.

*(S)-2-Methylbutyl 4-hydroxybenzoate (***3a***)*

4-(Benzyloxy)-benzoic acid (2.50 g, 10.95 mmol) in dry dichloromethane (50 ml) was treated dropwise with oxalyl chloride (3.5 mL, 40.80 mmol) in the presence of DMF (cat.)

under anhydrous conditions. After 30 min of stirring, the clear solution was evaporated under reduced pressure, new portion of dichloromethane was added and the solution evaporated to dryness again to remove the residual oxalyl chloride. Solid was dissolved in toluene (50 mL) and added dropwise to the stirred mixture of (*S*)-2-methylbutanol (0.97 g, 10.97 mmol) and pyridine (2.0 mL) in toluene (40 mL) at 20 °C. The reaction mixture was stirred overnight under anhydrous conditions ($CaCl_2$ tube). The resulting mixture was diluted with toluene (30 mL), washed with HCl (1 : 15), brine and the separated organic layer was dried with anhydrous magnesium sulphate. After evaporation of the solvent, the residue was dissolved in ethyl acetate and pumped three times to degas the solution. Then palladium on carbon (0.30 g, 10%, unreduced) was added, the mixture was pumped again, and hydrogen gas was introduced from a rubber balloon. Reaction mixture was stirred vigorously for 5 h and then pumped to remove residual hydrogen gas. The resulting suspension was filtered through a pad of diatomite and the filtrate evaporated giving the crude product, which was purified by column chromatography on silica in dichloromethane-acetone (97: 3). Yield 1.89 g (83%). ^{1}H NMR ($CDCl_3$): 7.95 (2 H, d, *J*=9.4 Hz), 6.91 (2 H, d, *J*=8.8 Hz), 5.92 (2 H, br. s.), 4.05 - 4.27 (2 H, m), 1.76 - 1.92 (1 H, m), 1.43 - 1.60 (1 H, m), 1.18 - 1.37 (1 H, m), 0.85 - 1.07 (6 H, m).

*(rac)-2-Methylbutyl 4-hydroxybenzoate (**3a-rac**)*

Racemic analogue was synthesised by the same reaction protocol as described for **3a**. 4-(Benzyloxy)-benzoic acid (2.50 g, 10.95 mmol) was transformed to its chloride and reacted with (*S*)-2-methylbutanol (0.97 g, 10.97 mmol) in the presence of pyridine and subsequent hydrogenolysis yielded 1.93 g (84 %). ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 7.95 (2 H, d, *J*=9.4 Hz), 6.91 (2 H, d, *J*=8.8 Hz), 5.90 (2 H, br. s.), 4.04 - 4.27 (2 H, m), 1.77 - 1.92 (1 H, m), 1.42 - 1.61 (1 H, m), 1.16 - 1.37 (1 H, m), 0.83 - 1.06 (6 H, m).

*(S)-1-[((rac)-2-Methylbutoxy)-1-oxopropan-2-yl] 4-(benzyloxy)benzoate (**3b-S,rac**)*

4-(Benzyloxy)-benzoic acid (5.0 g, 21.91 mmol) in dry dichloromethane (100 ml) was treated dropwise with oxalyl chloride (7.0 mL, 81.60 mmol) in the presence of DMF (cat.) under anhydrous conditions. After 30 min of stirring, the clear solution was evaporated under reduced pressure, new portion of dichloromethane was added and the solution

evaporated to dryness again to remove the residual oxalyl chloride. Solid was dissolved in dry dichloromethane (50 mL) and added dropwise to the stirred mixture of (*S,rac*)-2-methylbutyl lactate (3.51 g, 21.91 mmol) and *N*,*N*-(dimethyamino)pyridine (DMAP, 2.67 g, 21.35 mmol) in dry dichloromethane (70 mL) at 0 °C. The reaction mixture was let to warm to room temperature while stirring overnight under anhydrous conditions ($CaCl_2$ tube). The resulting mixture was diluted with dichloromethane (30 mL), washed with HCl (1 : 15) and washed with brine. Separated organic layer was dried with magnesium sulphate. After evaporation of the solvent, the residue was dissolved in ethyl acetate and pumped three times to degas the solution. Then palladium on carbon (0.50 g, 10%, unreduced) was added, the mixture was pumped again, and hydrogen gas was introduced from a rubber balloon. Reaction mixture was stirred vigorously for 5 h and then pumped to remove residual hydrogen gas. The resulting suspension was filtered through a pad of diatomite and the filtrate evaporated giving the crude product which was purified by column chromatography on silica in dichloromethane-acetone (96 : 4). Yield 4.67 g (76 % - in two steps). ^{1}H NMR ($CDCl_3$): 7.91 (2 H, d, *J*=8.80), 6.80 (2 H, d, *J*=8.80), 5.30 (1 H, q, *J*=7.04), 3.93 - 4.14 (2 H, m), 1.52 - 1.83 (5 H, m), 1.31 - 1.49 (1 H, m), 1.06 - 1.28 (1 H, m), 0.80 - 0.99 (6 H, m)

*(S)-1-{[(S)-1-((rac)-2-Methylbutoxy)-1-oxopropan-2-yl]oxy}-1-oxopropan-2-yl 4-hydroxybenzoate (**3c-S,S,rac**)*

This compound was synthesised according to the same reaction protocol as described for **2b**. 4-(Benzyloxy)-benzoic acid (5.0 g, 21.91 mmol) was transformed to its chloride and reacted with (*rac*)-2-methylbutyl (*S*)-2-[((*S*)-2-hydroxypropanoyl)oxy]propanoate (5.09 g, 21.91 mmol) in the presence of DMAP (2.67 g, 21.35 mmol) and subsequent hydrogenolysis yielded 5.48 g (71 % - in two steps). 7.94 (2H, d, *J*=7.0), 6.82 (2H, d, *J*=8.8), 5.30 (1H, q, *J*=6.8), 5.15 (1H, q, *J*=7.2), 3.93 - 4.14 (2H, m), 1.50 - 1.75 (7H, m), 1.23 - 1.44 (2H, m), 0.88 - 0.99 (6H, m).

General procedure for DCC-mediated esterification of multichiral hydroxybenzoates

4′-(Dodecyloxy)biphenyl-4-carboxylic acid (**4**) and chiral hydroxybenzoate **3** were suspended in dry dichloromethane under anhydrous conditions and cooled in the ice-water bath to ca. 10 °C. Then solid DCC and 4-(*N,N*-dimethylamino)pyridine (DMAP) were added. The mixture was stirred in the cooling bath and let to warm to room temperature.

After cca. 8 h, the resulting suspension was filtered through a 5-cm pad of chromatographic silica gel, which was further washed with CH_2Cl_2-acetone (95 : 5). The filtrate was evaporated under reduced pressure and the residue purified by column chromatography on silica gel and recrystallised from *n*-hexane.

(S)-4-[(2-Methylbutoxy)carbonyl)] 4'-(dodecyloxy)biphenyl-4-carboxylate **Z12*(S)***

Reaction of 4′-(dodecyloxy)biphenyl-4-carboxylic acid (**4**, 1.50 g, 3.90 mmol) and hydroxybenzoate **3a** (0.82 g, 3.93 mmol) were suspended in the presence of DCC (0.89 g, 4.27 mmol) and DMAP (0.24 g, 1.85 mmol) in dry dichloromethane (30 mL) yielded 1.87 g (84 %) of **Z12(*S*)**. Chromatography: silica gel, CH_2Cl_2-acetone (99 : 1). ^{1}H NMR ($CDCl_3$): 8.24 (2 H, d, *J*=8.2 Hz), 8.15 (2 H, d, *J*=8.2 Hz), 7.70 (2 H, d, *J*=8.8 Hz), 7.60 (2 H, d, *J*=8.8 Hz), 7.33 (2 H, d, *J*=8.8 Hz), 7.01 (2 H, d, *J*=8.2 Hz), 4.08 - 4.35 (2 H, m), 4.02 (2 H, t, *J*=6.5 Hz), 1.73 - 1.99 (3 H, m), 1.11 - 1.62 (20 H, m), 1.04 (3 H, d, *J*=7.0 Hz), 0.98 (3 H, t, *J*=7.3 Hz), 0.85 - 0.94 (3 H, t, *J*=6.7 Hz). ^{13}C NMR ($CDCl_3$): 165.92 (s), 164.59 (s), 159.66 (s), 154.63 (s), 146.26 (s), 131.80 (s), 131.16 (s), 130.79 (s), 128.38 (s), 128.11 (s), 127.00 (s), 126.62 (s), 121.77 (s), 115.01 (s), 69.67 (s), 68.16 (s), 34.32 (s), 31.93 (s), 29.56 - 29.70 (m), 29.41 (s), 29.37 (s), 29.26 (s), 26.18 (s), 26.06 (s), 22.70 (s), 16.55 (s), 14.13 (s), 11.30 (s).

(S)-4-[(2-Methylbutoxy)carbonyl)] 4'-(dodecyloxy)biphenyl-4-carboxylate **Z12*(rac)***

Reaction of 4′-(dodecyloxy)biphenyl-4-carboxylic acid (**4**, 1.70 g, 4.44 mmol) and hydroxybenzoate **3a-rac** (0.93 g, 4.44 mmol) were suspended in the presence of DCC (1.02 g, 4.88 mmol) and DMAP (0.30 g, 2.38 mmol) in dry dichloromethane (35 mL) yielded 2.06 g (81 %) of **Z12(rac)**. Chromatography: silica gel, CH_2Cl_2-acetone (99 : 1). ^{1}H NMR ($CDCl_3$): 8.24 (2 H, d, *J*=8.2 Hz), 8.15 (2 H, d, *J*=8.2 Hz), 7.70 (2 H, d, *J*=8.8 Hz), 7.60 (2 H, d, *J*=8.8 Hz), 7.33 (2 H, d, *J*=8.8 Hz), 7.01 (2 H, d, *J*=8.2 Hz), 4.08 - 4.33 (2 H, m), 4.02 (2 H, t, *J*=6.5 Hz), 1.73 - 1.99 (3 H, m), 1.13 - 1.62 (20 H, m), 1.04 (3 H, d, *J*=7.0 Hz), 0.98 (3 H, t, *J*=7.3 Hz), 0.85 - 0.94 (3 H, t, *J*=6.7 Hz). ^{13}C NMR ($CDCl_3$): 165.89 (s), 164.56 (s), 159.64 (s), 154.60 (s), 146.23 (s), 131.78 (s), 131.13 (s), 130.76 (s), 128.36 (s), 128.08 (s), 126.98 (s), 126.59 (s), 121.75 (s), 114.99 (s), 69.64 (s), 68.14 (s), 34.30 (s), 31.90

(s), 29.54 - 29.68 (m), 29.38 (s), 29.35 (s), 29.23 (s), 26.15 (s), 26.04 (s), 22.67 (s), 16.52 (s), 14.10 (s), 11.28 (s).

*4-({[(S)-1-((S)-2-Methylbutoxy)-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4'-(dodecyloxy)-biphenyl-4-carboxylate (***ZL12*(S,S)*)**

Reaction of 4′-(dodecyloxy)biphenyl-4-carboxylic acid **1** (1.92 g, 5.0 mmol) and hydroxybenzoate **2a** (1.41 g, 5.0 mmol) were suspended in the presence of DCC (1.16 g, 5.45 mmol) and DMAP (0.40 g, 3.24 mmol) in dry dichloromethane (60 mL) yielded 2.61 g (79 %) of **ZL12/*(*S,S*)**. Chromatography: silica gel, CH_2Cl_2-acetone (99 : 1). ^{1}H NMR ($CDCl_3$): 8.23 (2 H, d, *J*=8.22), 8.18 (2 H, d, *J*=8.80), 7.70 (2 H, d, *J*=8.22), 7.60 (2 H, d, *J*=8.80), 7.34 (2 H, d, *J*=8.80), 7.01 (2 H, d, *J*=8.80), 5.36 (1 H, q, *J*=7.04), 3.91 - 4.15 (4 H, m), 1.53 - 1.92 (8 H, m), 1.07 - 1.53 (18 H, m), 0.84 - 0.95 (9 H, m). ^{13}C NMR ($CDCl_3$): 170.80 (s), 165.18 (s), 164.53 (s), 159.65 (s), 154.99 (s), 146.29 (s), 131.82 (s), 131.46 (s), 130.77 (s), 128.38 (s), 127.08 (s), 126.96 (s), 126.65 (s), 121.83 (s), 115.01 (s), 69.91 (s), 69.28 (s), 68.16 (s), 34.09 (s), 31.91 (s), 29.63 (br. s.), 29.57 (br. s.), 29.38 (s), 29.34 (s), 29.23 (s), 26.04 (s), 25.92 (s), 22.68 (s), 17.15 (s).

4-({[(S)-1-((rac)-2-Methylbutoxy)-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4'-(dodecyloxy)-biphenyl-4-carboxylate (**ZL12*(S,rac)***)

Reaction of 4′-(dodecyloxy)biphenyl-4-carboxylic acid 1.92 g (5.0 mmol) and hydroxybenzoate **2b** (1.41 g, 5.0 mmol) were suspended in the presence of DCC (1.17 g, 5.50 mmol) and DMAP (0.43 g, 3.48 mmol) in dry dichloromethane (60 mL) yielded 2.70 g (82 %) of **ZL12/*(*S*,rac)**. Chromatography: silica gel, CH_2Cl_2-acetone (99 : 1). ^{1}H NMR ($CDCl_3$): 8.23 (2 H, d, *J*=8.22), 8.18 (2 H, d, *J*=8.80), 7.70 (2 H, d, *J*=8.22), 7.60 (2 H, d, *J*=8.80), 7.34 (2 H, d, *J*=8.80), 7.01 (2 H, d, *J*=8.80), 5.36 (1 H, q, *J*=7.04), 3.90 - 4.13 (4 H, m), 1.53 - 1.93 (8 H, m), 1.05 - 1.53 (18 H, m), 0.85 - 0.96 (9 H, m). ^{13}C NMR ($CDCl_3$): 170.81 (s), 165.18 (s), 164.53 (s), 159.65 (s), 154.99 (s), 146.29 (s), 131.82 (s), 131.46 (s), 130.77 (s), 128.38 (s), 127.08 (s), 126.96 (s), 126.65 (s), 121.83 (s), 115.01 (s), 69.91 (s), 69.28 (s), 68.15 (s), 34.09 (s), 31.91 (s), 29.62 (br. s.), 29.58 (br. s.), 29.37 (s), 29.33 (s), 29.23 (s), 26.06 (s), 25.91 (s), 22.67 (s), 17.14 (s).

*4-{[((S)-1-{[(S)-1-((S)-2-Methylbutoxy)-1-oxopropan-2-yl]oxy}-1-oxopropan-2-yl)oxy]-carbonyl}phenyl 4'-(dodecyloxy)biphenyl-4-carboxylate (***ZLL12*(S,S,S)*)**

Synthesized using general DCC-mediated esterification from 1.91 g (4.97 mmol) of **1** and 1.76 g (4.98 mmol) **3a**, 1.10 g (5.17 mmol) DCC and 0.32 g (2.60 mmol) DMAP. Chromatography: CH_2Cl_2-acetone (98 : 2). Yield 2.64 g (76 %). ^{1}H NMR ($CDCl_3$): 8.22 (4 H, dd, *J*=14.67, 8.22), 7.71 (2 H, d, *J*=8.22), 7.61 (2 H, d, *J*=8.22), 7.35 (2 H, d, *J*=8.22), 7.02 (2 H, d, *J*=8.22), 5.34 - 5.47 (1 H, m), 5.23 (1 H, q, *J*=7.04), 3.90 - 4.12 (4 H, m), 1.15 - 1.91 (29 H, m), 0.85 - 0.99 (9 H, m).

*4-({[(S)-1-((rac)-2-Methylbutoxy)-1-oxopropan-2-yl]oxy}carbonyl)phenyl 4'-(dodecyloxy)-biphenyl-4-carboxylate (***ZL12*(S,S,rac)*)**

Quantities used for DCC-mediated esterification: 1.90 g (4.95 mmol) of **1**, 1.74 g (4.95 mmol) **3b** with 1.09 g (5.12 mmol) DCC and 0.32 g (2.60 mmol) DMAP. Chomatography: CH_2Cl_2-acetone (98 : 2). Yield 2.77 g (78 %). ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 8.22 (4 H, dd, *J*=14.67, 8.22), 7.71 (2 H, d, *J*=8.22), 7.61 (2 H, d, *J*=8.22), 7.35 (2 H, d, *J*=8.22), 7.02 (2 H, d, *J*=8.22), 5.35 - 5.47 (1 H, m), 5.23 (1 H, q, *J*=7.04), 3.90 - 4.11 (4 H, m), 1.14 - 1.93 (29 H, m), 0.80 - 0.99 (9 H, m).

Materials UPAC names and molecular lengths generated by the ChemDraw software.

2. Chemical and optical purity

Chemical purity was determined by the separation system Agilent 1260 Infinity II (Agilent Technologies, USA). It was equipped with a Poroshell 120 PFP column (i.d. 4.6 mm, length 150 mm) containing 4-particles under specific separation conditions. The mobile phase consisted of acetonitrile, water and methanol in a ratio of 85/10/5 (v/v/v), with a flow rate of 1 ml/min, a temperature of 40 °C, a sample injection volume of 5 µl and wavelength of detection 305 nm. The samples were prepared at a concentration of 0.2 mg/ml in 100% acetonitrile. A separation method was developed and optimised for determining the chemical purity of the studied materials and led to baseline separation. After post-separation material identification in chromatographs, the studied materials were of high chemical purity.

The studied materials were analysed by enantiomeric high-performance liquid chromatography (HPLC) to determine their optical purity. Enantiomer HPLC is an essential

method for determining optical purity of chiral materials. The studied racemic materials were separated into two enantiomers under specific conditions. This separation method is improved in case the racemic material is fully separated to the baseline. After the separation, it is necessary to compare the retention times of the racemic samples with those of the pure Z12(*S*)-, ZL12(*S,S*) or ZLL12(*S,S,S*)-enantiomers to check for the presence of the Z12(*R*)-, ZL12(*S,R*)- and ZLL12(*S,S,R*)-enantiomers, respectively, which are impurities in this case.

The enantiomer HPLC separation conditions for Z12(rac) were a Phenomenex LUX 3 µm i-amylose 3 column, and a mobile phase mixture of acetonitrile and methanol at a ratio of 95/5 (v/v), and a flow rate of 1 ml/min at a temperature of 40 °C. The separation conditions for ZL12(*S*,rac) were equal to Z12(rac), except the mobile phase mixture of acetonitrile, methanol and isopropyl alcohol in a ratio of 20/40/40 (v/v/v). The separation conditions for ZLL12(*S,S*,rac) material were chiral column Phenomenex 3u Lux Amylose-2, mobile phase isopropylalcohol with acetonitrile in ratio 95/5 (v/v), temperature 30 °C , flow rate 1 ml/min and sample injection 5µl.

Table S1. Optical purity of the studied materials under specific separation conditions.

Material	Optical purity [%]
Z12(*S*)	98.2
Z12(*rac*)	50/50
ZL12(*S,S*)	99.2
ZL12(*S,rac*)	50/50
ZLL12(*S,S,S*)	99.3
ZLL12(*S,S,rac*)	50/50

3. Additional experimental results

Texture observations under polarising light optical microscope

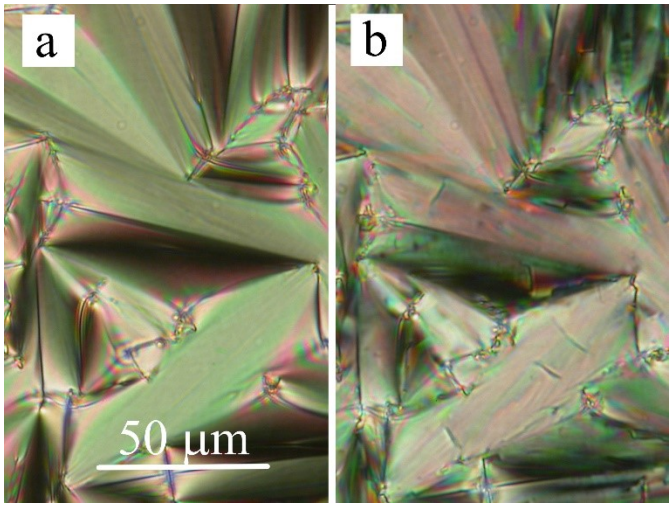

Fig. S1. Textures in (a) the SmA phase and (b) the SmC phase of Z12(*S*) in a 7-µm planar cell.

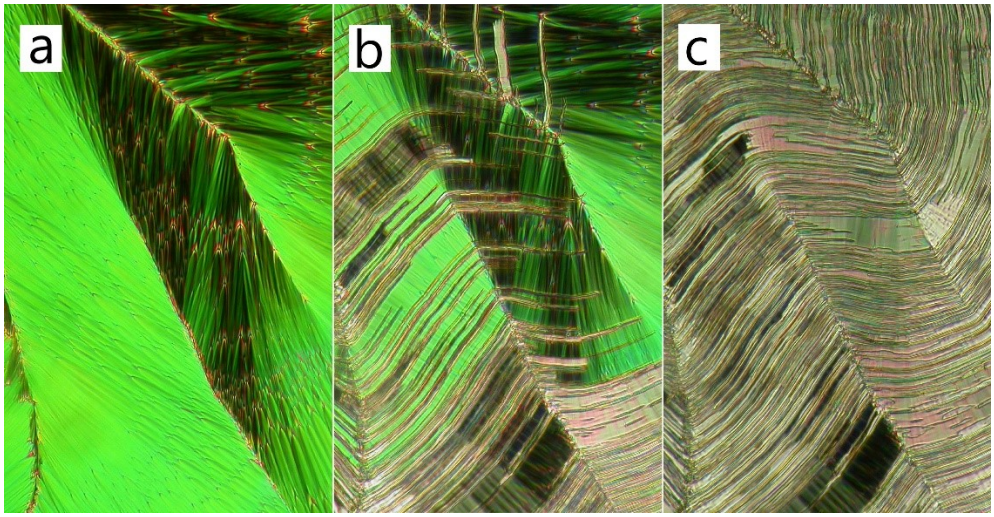

Fig. S2. Textures for ZLL12(*S,S*,rac) compound in 12-µm planar cell in the SmC* phase (a) without applied electric field; (b) under 2V/µm applied electric field; (c) under 10V/µm applied electric field.

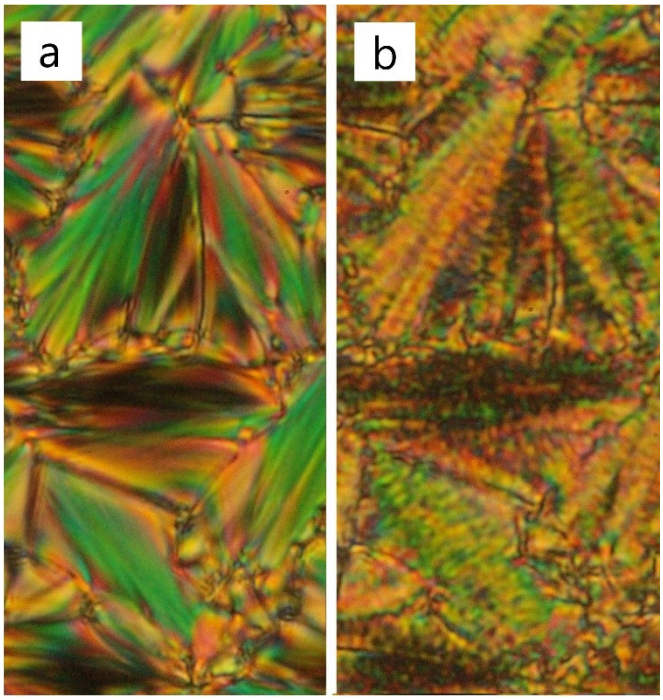

Fig. S3. Textures for ZLL12(*S,S,S*) in a 7-μm planar cell in (a) SmC* phase and (b) SmC^*_A phase.

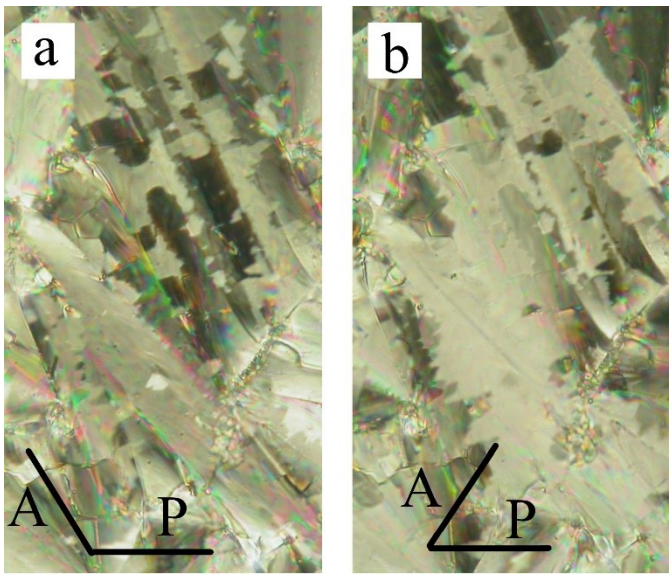

Fig. S4. Twisted domains observed in the SmC phase of a racemic compound Z12(rac) in a 7-μm planar cell. The positions of decrossed in opposite directions polariser and analyser are shown.

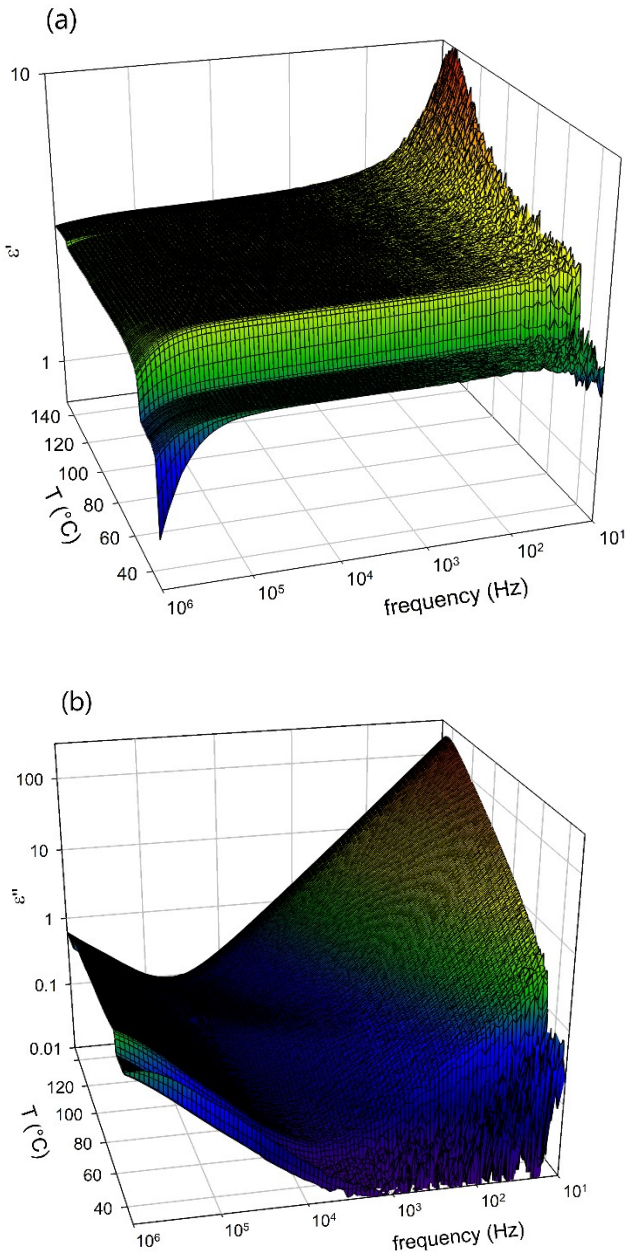

Fig. S5. For homologue Z12(rac), the 3-dimensional plots of (a) the real, ε', and (b) the imaginary, ε'', parts of permittivity in dependence on temperature, T, and frequency are plotted in logarithmic scale to show that for this compound no ferroelectric response was observed. Dielectric spectroscopy data were measured in a 7-μm HG cell.

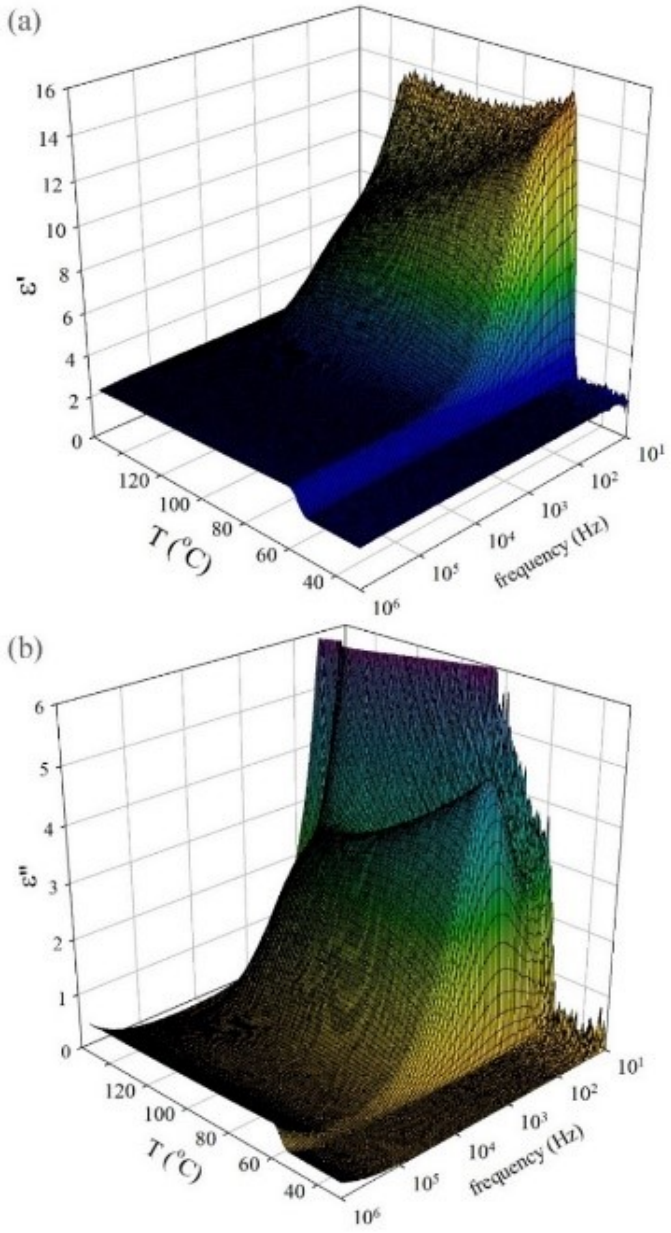

Fig. S6. For homologue Z12(*S*), the 3-dimensional plots of (a) the real, ε', and (b) the imaginary, ε'', parts of permittivity in dependence on temperature, *T*, and frequency are plotted. Dielectric spectroscopy data were measured in a 7-μm HG cell.

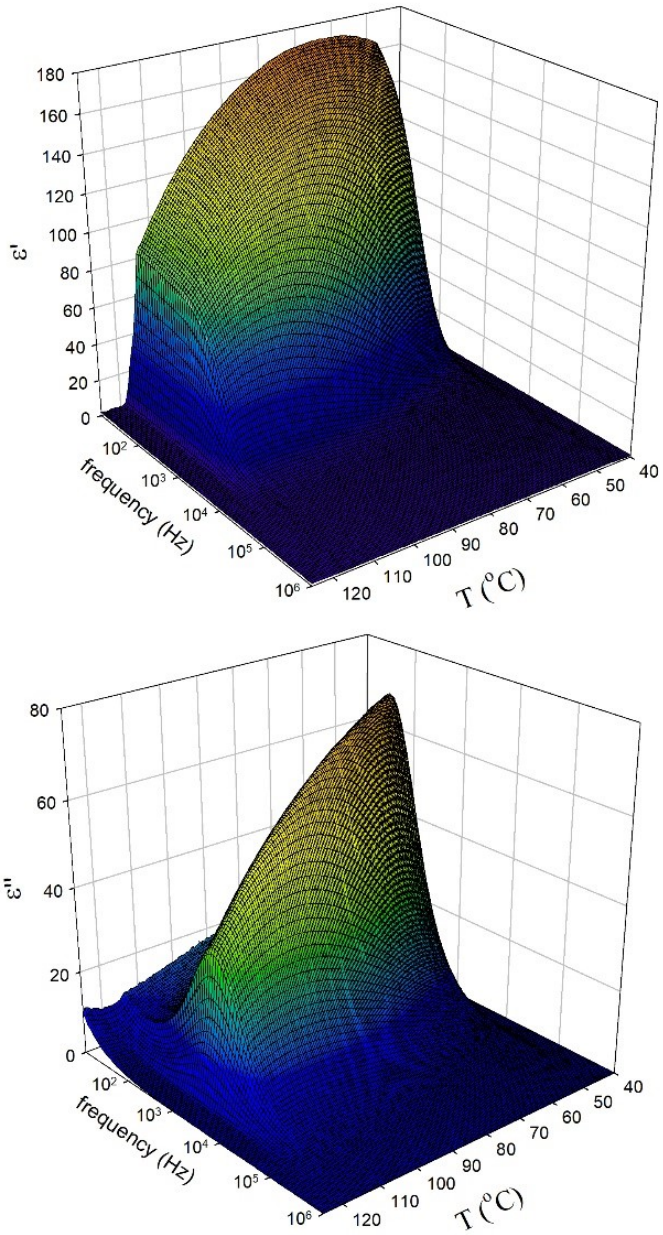

Fig. S7. For homologue ZL12(*S*,*S*), the 3-dimensional plots of (a) the real, ε', and (b) the imaginary, ε'', parts of permittivity in dependence on temperature, *T*, and frequency are plotted. Dielectric spectroscopy data were measured in a 7-μm HG cell.

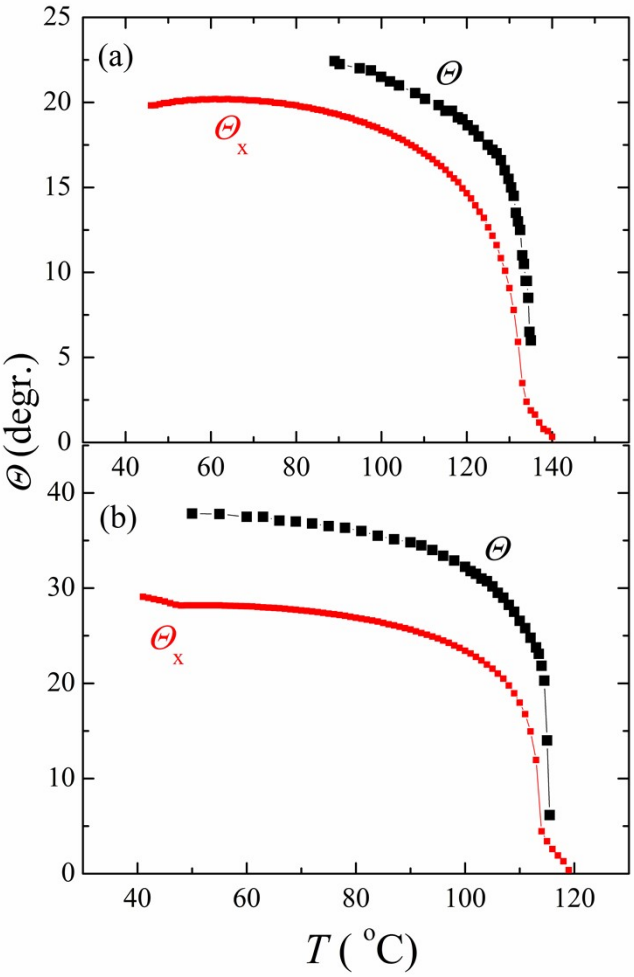

Fig. S8. The temperature dependences of the tilt angle measured optically, Θ, (black symbols), and calculated from the temperature dependences of the layer spacing measured by SAXS, Θ_X, (red symbols), for (a) Z12(*S*) and (b) ZL12(*S,S*).