

Electronic Supplementary Information for:

Tuning the Frustration Between SmA- and SmC-Promoting Elements in Liquid Crystals with 'de Vries-Like' Properties

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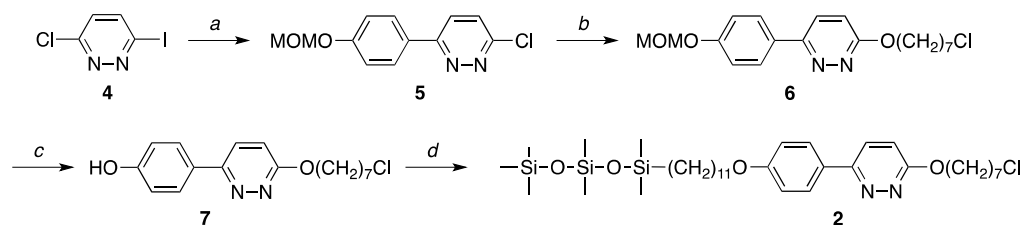
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A. EXPERIMENTAL

General. ¹H and ¹³C NMR spectra were recorded using a Bruker Avance 400 spectrometer; chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard. Mass spectra were recorded using Waters/Micromass GC-TOF (low- and high- resolution) and Applied Biosystems/MDS Sciex QSTAR XL QTOF (low-resolution) instruments in electron ionization (EI) mode. Differential scanning calorimetry (DSC) analyses were performed using a TA Instruments Q2000 instrument with a scanning rate of 3 K min⁻¹, unless otherwise noted. Texture analyses were performed using a Nikon Eclipse E600 POL polarized microscope fitted with a Linkam LTS 350 hot stage and TMS 93 temperature controller. Optical tilt angles were measured as a function of temperature by polarized microscopy as half the rotation between the two extinction positions corresponding to opposite signs of an applied electric field of 2 V μm^{-1} using the chiral dopant 2-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl)-5-((2*R*,3*R*)-difluorooctyloxy)pyrimidine (1-2 mol%).¹ The mixtures were introduced into ITO glass cells with a rubbed Nylon alignment layer (5 μm spacing, 0.25 cm² addressed area, AWAT PPW, Poland), and aligned by slow cooling from the isotropic phase to the chiral SmC* phase at 2 K min⁻¹ while applying a 6 V μm^{-1} triangular wave ac field. Small angle X-ray scattering data from unaligned samples (filled into Mark capillary tubes of 0.7 mm diameter) were obtained using a Kratky compact camera (A. Paar) equipped with a temperature controller (A. Paar) and a one-dimensional electronic detector (M. Braun). All chemicals were obtained from commercial sources under otherwise noted. 4-Methoxybenzohydrazide (**8**) was purchased from Alfa Aesar. 4-(Methoxymethoxy)phenylboronic acid,² 3-chloro-6-iodopyridazine (**4**),³ 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol,⁴ and 9-chlorononanoyl chloride^{5,6} were prepared according to literature procedures and shown to have the expected physical and spectral properties.



^a 4-(Methoxymethoxy)phenylboronic acid, Pd₂(dba)₃, Cy₃P, aq K₃PO₄; ^b Cl(CH₂)₇OH, NaH, THF; ^c aq 6 M HCl, IPA; ^d 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol, DIAD, Ph₃P, THF.

3-Chloro-6-(4-(methoxymethoxy)phenyl)pyridazine (5). A 50 mL Schlenk flask was charged with **4** (0.73 g, 3.0 mmol), 4-(methoxymethoxy)phenylboronic acid (0.70 g, 3.9 mmol), Pd₂(dba)₃ (27.6 mg, 0.030 mmol) and Cy₃P (20.1 mg, 0.072 mmol), then evacuated and filled with argon (5×). Degassed dioxane (15 mL) and aq K₃PO₄ (1.27 M, 4.0 mL, 5.08 mmol) were added by syringe, the Schlenk flask was sealed and heated in an oil bath at 100 °C for 18 h with vigorous stirring. The mixture was then filtered through a pad of silica gel and washed with EtOAc. The filtrate was concentrated and the aqueous residue extracted three times with EtOAc. The combined extracts were dried (MgSO₄), concentrated, and the residue purified by flash chromatography on silica gel (20% EtOAc/hexanes) to give **5** (0.52 g, 70%) as a white solid: mp 123-125 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.6 Hz, 2 H), 7.78 (d, *J* = 9.1 Hz, 1 H), 7.52 (d, *J* = 8.8 Hz, 1 H), 7.17 (d, *J* = 8.3 Hz, 2 H), 5.25 (s, 2 H), 3.51 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 158.1, 155.0, 128.6, 128.5, 128.4, 125.6, 116.7, 94.3, 56.2; LRMS (EI) *m/z* 250 (M⁺, 100), 222 (15), 220 (45), 192 (15), 149 (19), 132 (24), 117 (13), 89 (18); HRMS (EI) calcd for C₁₂H₁₁N₂O₂³⁵Cl 250.0509, found 250.0511.

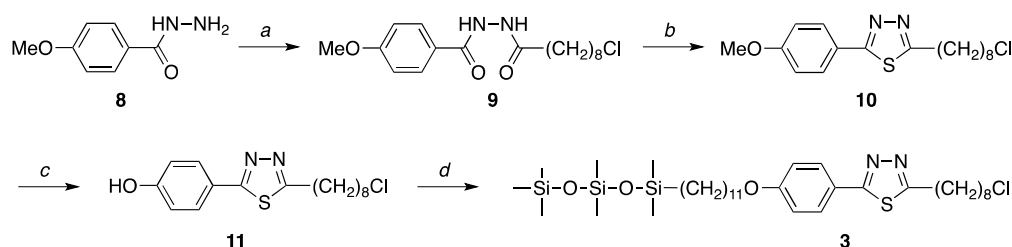
3-(7-Chloroheptyloxy)-6-(4-(methoxymethoxy)phenyl)pyridazine (6). A mixture of 7-chloro-1-heptanol (0.60 g, 4 mmol) and NaH (60% oil suspension, 0.16 g, 4 mmol) in dry THF (10 mL) was stirred for 1 hour, and a suspension of **5** (0.25 g, 1.0 mmol) in dry THF (20 mL) was added in one portion. The mixture was stirred overnight at room temperature and then slowly quenched with sat aq NH₄Cl. The mixture was poured into H₂O (30 mL) and extracted with CH₂Cl₂ (100 mL, then 3 × 10 mL). The combined extracts were washed with brine, dried (MgSO₄), concentrated, and the residue was purified by flash chromatography on silica gel (25% EtOAc/hexanes) to give **6** (0.22 g, 60%) as a white solid: mp 82-83 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.8 Hz, 2 H), 7.73 (d, *J* = 9.3 Hz, 1 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 7.00 (d, *J* = 9.3 Hz, 1 H), 5.24 (s, 2 H), 4.56 (t, *J* = 6.6 Hz, 2 H), 3.54 (t, *J* = 6.7 Hz, 2 H), 3.51 (s, 3 H), 1.70-1.95 (m, 4 H), 1.32-1.60 (m, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 158.4, 154.6, 130.0, 127.8, 126.7, 117.8, 116.5, 94.3, 67.4, 56.1, 45.1, 32.6, 28.8, 28.6, 26.8, 25.9; LRMS (EI) *m/z* 364 (M⁺, 19), 299 (22), 245(11), 233 (24), 232 (100), 202 (39), 200 (32), 189 (12), 188(55); HRMS (EI) calcd for C₁₉H₂₅N₂O₃³⁵Cl 364.1554, found 364.1552.

3-(7-Chloroheptyloxy)-6-(4-hydroxyphenyl)pyridazine (7). To a solution of **6** (0.2 g, 0.55 mmol) in isopropanol (20 mL) was added 6 M aq HCl (0.5 mL, 3.0 mmol). After stirring for 5 hours at 50 °C, the solution was concentrated and diluted with CH₂Cl₂ (20 mL) and H₂O (20 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined extracts were dried (MgSO₄), concentrated, and the residue was purified by flash chromatography on silica gel (33% EtOAc/hexanes) to give **7** (0.16 g, 91%) as a white solid: mp 102-103 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.6 Hz, 2 H), 7.74 (d, *J* = 9.3 Hz, 1 H), 6.92-7.05 (m, 3 H), 4.54 (t, *J* = 6.6 Hz, 2 H), 3.53 (t, *J* = 6.7 Hz, 2 H), 1.70-1.92 (m, 4 H), 1.33-1.54 (m, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 158.3, 155.2, 128.1, 127.7, 127.6, 118.5, 116.3, 67.6, 45.1, 32.5, 28.8, 28.6, 26.8, 25.9; LRMS (EI) *m/z* 320 (M⁺, 13), 279 (5), 255 (8), 189 (17), 188(100), 167 (6), 149 (8), 131 (5); HRMS (EI) calcd for C₁₇H₂₁N₂O₂³⁵Cl 320.1292, found 320.1290.

3-(7-Chloroheptyloxy)-6-(4-(11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl)pyridazine (2). Under an argon atmosphere, DIAD (202 mg, 0.20 mL, 1 mmol) was added to a solution of **7** (150 mg, 0.47 mmol), 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)-

undecanol (200 mg, 0.52 mmol) and triphenylphosphine (262 mg, 1.0 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc/hexanes) to give **2** (217 mg, 68%) as a yellow solid contaminated with traces of DIAD. Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.8 Hz, 2 H), 7.73 (d, J = 9.3 Hz, 1 H), 6.88–7.11 (m, 3 H), 4.56 (t, J = 6.6 Hz, 2 H), 4.02 (t, J = 6.6 Hz, 2 H), 3.55 (t, J = 6.7 Hz, 2 H), 1.72–1.98 (m, 6 H), 1.20–1.60 (m, 22 H), 0.54 (t, J = 7.4 Hz, 2 H), 0.09 (s, 9 H), 0.07 (s, 6 H), 0.03 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 158.5, 152.9, 126.8, 125.9, 124.7, 115.9, 113.0, 66.3, 65.5, 43.3, 31.6, 30.7, 27.8–27.4 (several overlapping peaks), 27.0, 26.8, 25.0, 24.2, 24.0, 21.4, 16.5, 0.0, -0.5, -1.6; LRMS (EI) m/z 694 (M^+ , 100), 681 (14), 680 (16), 679 (29), 562 (18), 561 (20), 473 (11), 333 (27), 322 (11), 320 (38), 222 (12), 221 (60); HRMS (EI) calcd for $\text{C}_{35}\text{H}_{63}\text{N}_2\text{O}_4\text{Si}_3^{35}\text{Cl}$ 694.3784, found 694.3781.

Anal. Calcd for $\text{C}_{35}\text{H}_{63}\text{N}_2\text{O}_4\text{Si}_3\text{Cl}$: C, 60.43; H, 9.13; N, 4.03. Found: C, 60.70; H, 9.28; N, 4.23.



^a 9-Chlorononanoyl chloride, Na_2CO_3 , DCM; ^b Lawesson's reagent, toluene; ^c BBr_3 , DCM; ^d 11-(1,1,1,3,3,3,5,5-heptamethyltrisiloxanyl)undecanol, DIAD, Ph_3P , THF.

N'-(9-Chlorononanoyl)-4-methoxybenzohydrazide (9). 9-Chlorononanoyl chloride was added dropwise to a solution of 4-methoxybenzohydrazide (1.4 g, 8.1 mmol) and Na_2CO_3 (3.4 g) in CH_2Cl_2 (60 mL) at 0 °C. The reaction mixture was stirred for 1 h, and then allowed to warm to room temperature. After 18 hours, the mixture was filtered and the solid residue washed with CH_2Cl_2 (100 mL) and EtOAc (100 mL). The filtrate was concentrated and the residue was purified by flash chromatography on silica gel (3:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$) to give **9** (1.2 g, 52%) as a white solid: mp 107–109 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.83 (d, J = 4.8 Hz, 1 H), 9.58 (d, J = 4.8 Hz, 1 H), 7.81 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 8.6 Hz, 2 H), 3.83 (s, 3 H), 3.51 (t, J = 6.7 Hz, 2 H), 2.29 (t, J = 7.6 Hz, 2 H), 1.54–1.73 (m, 4 H), 1.27–1.44 (m, 8 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 164.5, 162.8, 129.3, 123.6, 113.8, 55.4, 45.1, 34.1, 32.6, 29.1, 29.0, 28.7, 26.8, 25.4; LRMS (EI) m/z 340 (M^+ , 17), 322 (12), 166 (41), 135 (100); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}_3^{35}\text{Cl}$ 340.1554, found 340.1549.

2-(8-Chlorooctyl)-5-(4-methoxyphenyl)-1,3,4-thiadiazole (10). A mixture of **9** (1.1 g, 3.2 mmol) and Lawesson reagent (1.5 g, 3.7 mmol) in toluene (80 mL) was heated to reflux and stirred for 2 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water (60 mL) and extracted with CHCl_3 (3×30 mL). The combined extracts were washed with water, dried (MgSO_4), concentrated, and the crude product was purified by flash chromatography on silica gel (9:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$) to give **10** (0.65 g, 60%) as a white solid: mp 70–71 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.8 Hz, 2 H), 6.97 (d, J = 8.8 Hz, 2 H), 3.87

(s, 3 H), 3.53 (t, $J = 6.7$ Hz, 2 H), 3.11 (t, $J = 7.6$ Hz, 2 H), 1.67-2.00 (m, 4 H), 1.22-1.57 (m, 8 H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 168.1, 161.7, 129.4, 123.1, 114.5, 55.5, 45.1, 32.6, 30.2, 30.0, 29.0, 28.9, 28.7, 26.8; LRMS (EI) m/z 338 (M^+ , 32), 303 (14), 219 (40), 206 (100); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{OS}^{35}\text{Cl}$ 338.1220, found 338.1227.

2-(8-Chlorooctyl)-5-(4-hydroxyphenyl)-1,3,4-thiadiazole (11). A solution of BBr_3 in CH_2Cl_2 (1.0 M, 8.85 mL, 8.85 mmol) was added to a solution of **10** (0.60 g, 1.77 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The reaction mixture was warmed to 20 °C over 3 h, and then poured into 10% aq HCl and stirred for 30 min at 20 °C. The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O (4×30 mL). The combined organic layers were dried (MgSO_4), concentrated, and the residue was purified by flash chromatography on silica gel (2:1 hexane/ EtOAc) to give **11** (0.50 g, 87%) as a white solid: mp 77-79 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1 H), 7.81 (d, $J = 8.6$ Hz, 2 H), 7.10 (d, $J = 8.6$ Hz, 2 H), 3.52 (t, $J = 6.7$ Hz, 2 H), 3.12 (t, $J = 7.6$ Hz, 2 H), 1.63-1.92 (m, 4 H), 1.16-1.53 (m, 8 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 166.6, 157.4, 127.1, 119.1, 114.1, 42.6, 30.1, 27.6, 27.5, 26.5, 26.4, 26.2, 24.3; LRMS (EI) m/z 324 (M^+ , 13), 289 (13), 247 (11), 206 (11), 205 (49), 192 (100); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{OS}^{35}\text{Cl}$ 324.1063, found 324.1053.

2-(8-Chlorooctyl)-5-(4-(11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyloxy)phenyl)-1,3,4-thiadiazole (3). Under an argon atmosphere, DIAD (202 mg, 0.20 mL, 1 mmol) was added to a solution of **11** (195 mg, 0.60 mmol), 11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecanol (314 mg, 0.80 mmol) and triphenylphosphine (262 mg, 1.00 mmol) in dry THF (25 mL). The yellow solution was stirred overnight at room temperature, then concentrated and purified by flash chromatography on silica gel (10% EtOAc /hexanes) to give **3** (242 mg, 58%) as a yellow solid contaminated with traces of DIAD. Recrystallization from HPLC-grade acetonitrile (3×) gave a white solid with sharp phase transitions: ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.8$ Hz, 2 H), 6.96 (d, $J = 8.8$ Hz, 2 H), 4.01 (t, $J = 6.6$ Hz, 2 H), 3.53 (t, $J = 6.8$ Hz, 2 H), 3.11 (t, $J = 7.6$ Hz, 2 H), 1.69-1.92 (m, 6 H), 1.13-1.56 (m, 24 H), 0.54 (t, $J = 7.5$ Hz, 2 H), 0.09 (s, 9 H), 0.07 (s, 6 H), 0.03 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 166.4, 159.5, 127.5, 121.0, 113.1, 66.4, 43.3, 31.6, 30.8, 28.3, 28.2, 27.8-27.6 (several overlapping peaks), 27.4, 27.2, 27.0, 26.9, 25.0, 24.2, 21.4, 16.5, 0.0, -0.5, -1.6; LRMS (EI) m/z 698 (M^+ , 14), 683 (12), 324 (13), 223 (13), 222 (20), 221 (100), 207 (16), 205 (10), 73 (23); HRMS (EI) calcd for $\text{C}_{34}\text{H}_{63}\text{N}_2\text{O}_3\text{Si}_3\text{S}^{35}\text{Cl}$ 698.3556, found 698.3561.

Anal. Calcd for $\text{C}_{34}\text{H}_{63}\text{N}_2\text{O}_3\text{Si}_3\text{SCl}$: C, 58.37; H, 9.08; N, 4.00; S, 4.58. Found: C, 58.48; H, 9.23; N, 4.14; S, 4.74.

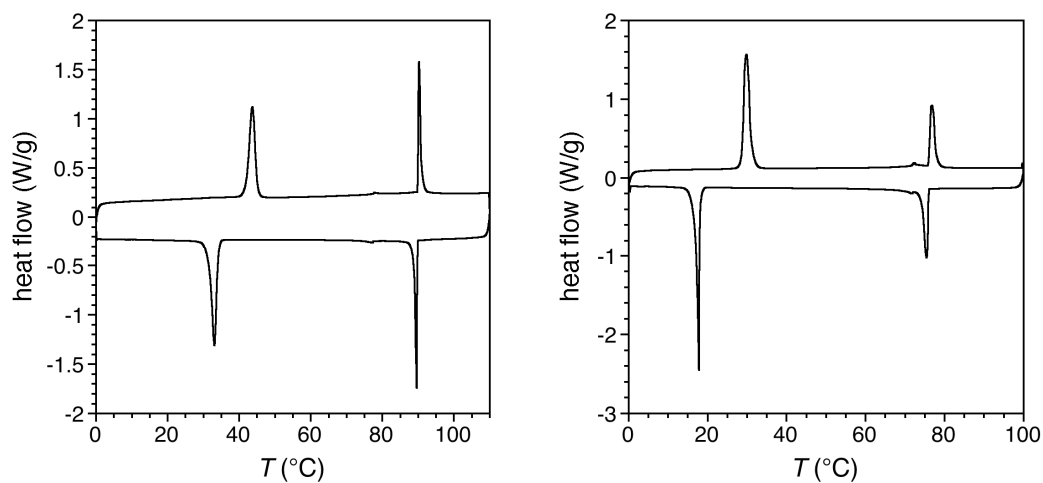


Fig S1. Differential scanning calorimetry scans for compounds **2** (left) and **3** (right).

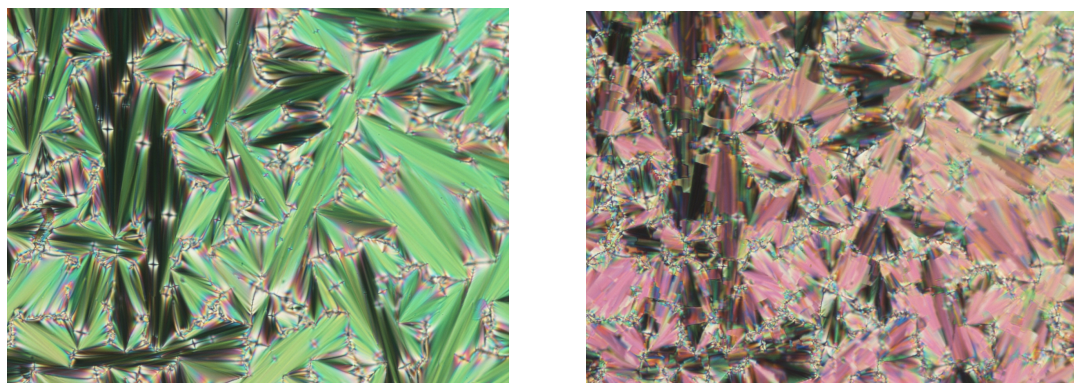


Fig S2. Polarized photomicrographs (200 $\times$) of compound **2** at 87 °C in the SmA phase (left) and at 73 °C in the SmC phase (right).

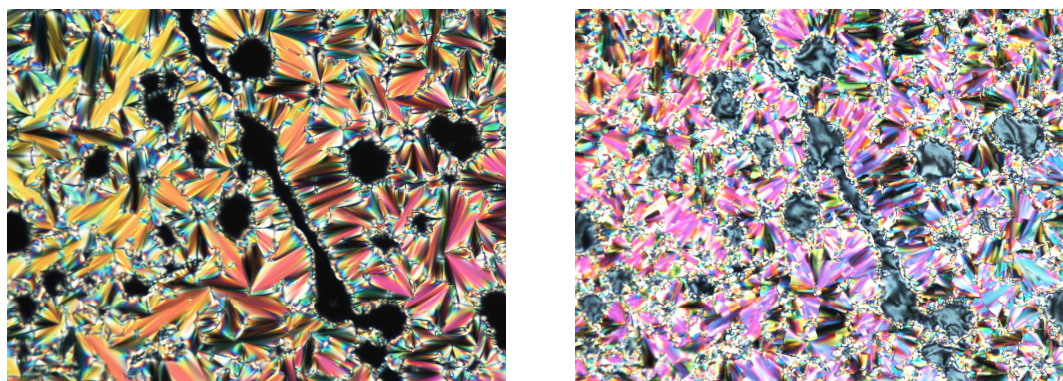


Fig S3. Polarized photomicrographs (200 $\times$) of compound **3** at 74 °C in the SmA phase (left) and at 71 °C in the SmC phase (right).

References

- (1) J. C. Roberts, N. Kapernaum, F. Giesselmann, M. D. Wand and R. P. Lemieux, *J. Mater. Chem.*, 2008, **18**, 5301-5306.
- (2) M. Miyakawa and T. Scanlan, *Synth. Commun.*, 2006, **36**, 891-902.
- (3) A. J. Goodman, S. P. Stanforth and B. Tarbit, *Tetrahedron*, 1999, **55**, 15067-15070.
- (4) J. Z. Vlahakis, K. E. Maly and R. P. Lemieux, *J. Mater. Chem.*, 2001, **11**, 2459-2464.
- (5) A. Schulze and A. Giannis, *Synthesis*, 2006, 257-260.
- (6) P. Perlmutter, W. Selajerern and F. Vounatsos, *Org. Biomol. Chem.*, 2004, **2**, 2220-2228.