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Electronic Supplementary Information

Novel achiral four-ring bent-shaped nematic liquid crystals with trifluoromethyl and methyl substituents in central molecular core: Unusual large Kerr constant in blue phase III of nematic-chiral dopant mixture.

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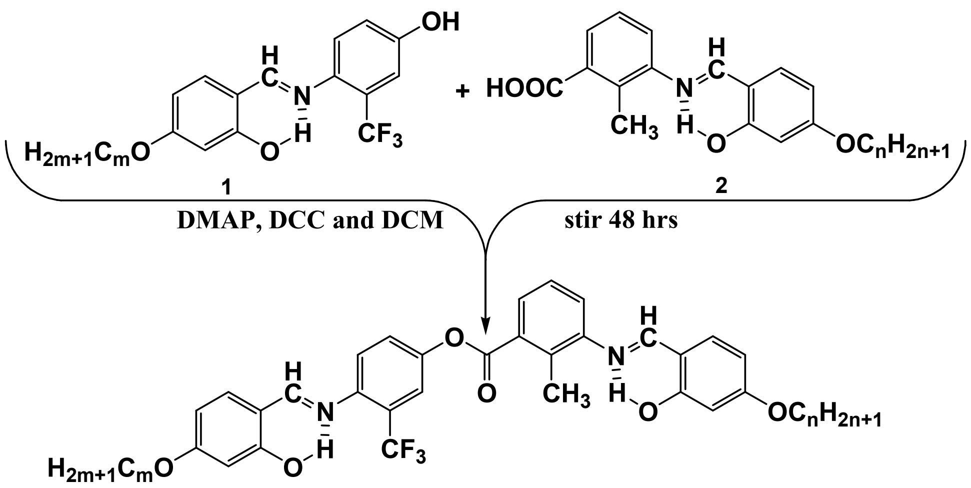
Procedure for the Synthesis of the compounds:



m-3CF$_3$-2Me-n

m = n = 5; m = 5, n = 12; m = 12, n = 5; m = n = 12

Scheme 1: Synthesis of m-3CF$_3$-2Me-n series

4-[N-(4′-(n-pentyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4′-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 5-3CF$_3$-2M-5:

3-[N-(4′-n-pentyloxy-2-hydroxybenzylidene)amino]- 2-methylbenzoicacid (0.68g; 2 mmol) was dissolved in dichloromethane, stirred on a magnetic stirrer and a catalytic amount of N,N/-dimethylaminopyridine (DMAP) was added to the solution. To the stirred reaction mixture a solution 4-[N-(4-n-pentyloxy-2-hydroxybenzylidene)amino]-3-trifluoromethyl phenol (0.73g, 2 mmol) was slowly added. To the resulting solution an equimolar quantity of dicyclohexylcarbodiimide (DCC) (0.412g, 2 mmol) was added and stirred for 48 hours. After the completion of stirring, the dicyclohexylurea thus formed in the reaction mixture was filtered off. Evaporation of the solvent gave the crude product which was then recrystallized several times from ethanol to obtain the pure product 4-[N-(4′-(n-pentyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4′-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, **5-3CF$_3$-2M-5**, as yellow solid. Yield: 0.96g, (70%); IR ν_{max} in cm^{-1}: 1619 ($\nu_{CH=N}$, imine); 1759 ($\nu_{C=O}$, ester), 3070(ν_{O-H}, H-bonded); ^{1}H NMR (CDCl$_3$, 400 MHz): 13.46 (s, 1H, -**OH**), 12.94 (s, 1H, -**OH**), 8.52 (s, 1H, -C**H**=N-), 8.45 (s, 1H, -C**H**=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, Ar**H**), 7.58 (d, 1H, J = 2.4 Hz, Ar**H**), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, Ar**H**), 7.39 (t, 1H, J = 8.0 Hz, Ar**H**), 7.31-7.27 (4H, Ar**H**), 6.52-6.50 (4H, **ArH**), 4.01 (t, 4H, J = 6.8 Hz, -**OCH$_2$**-), 2.67 (s, 3H, Ar-**CH$_3$**), 1.83-1.36 (m, 12H, -**(CH$_2$)**$_6$-), 0.94 (t, 6H, J = 7.6 Hz, 2x -**CH$_3$**), ^{19}F NMR 60.93. Elemental Analysis calculated for $C_{39}H_{41}F_3N_2O_6$: C, 67.81; H, 5.98 %, N = 4.06%; Found: C, 67.18; H, 5.89%, N = 4.00%.

Using the same procedure as described above, the other compounds of **n-3CF$_3$-2Me-m** series **(n = 5, m =12), (n = 12, m = 5)** and **(n = m =12),** with varying the number of carbon atoms (n) and (m) in the terminal alkyloxy chains using starting compounds in appropriate molar ratios were synthesized.

4-[N-(4′-(n-pentyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4′-n-dodecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 5-3CF$_3$-2M-12:

Yield: 1.19g, (76%); **IR** ν_{max} in cm^{-1}: 1622 ($\nu_{CH=N}$, imine); 1762 ($\nu_{C=O}$, ester), 3105(ν_{O-H}, H-bonded); **^{1}H NMR** (CDCl$_3$, 400 MHz): 13.48 (s, 1H, -**OH**), 12.96 (s, 1H, -**OH**), 8.54 (s, 1H, -C**H**=N-), 8.47 (s, 1H, -C**H**=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, Ar**H**), 7.58 (d, 1H, J = 2.4 Hz, Ar**H**), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, Ar**H**), 7.39 (t, 1H, J = 8.0 Hz, Ar**H**), 7.31-7.27 (4H, Ar**H**), 6.52-6.50 (4H, **ArH**), 4.03 (t, 4H, J = 6.8 Hz, -**OCH$_2$**-), 2.69 (s, 3H, Ar-**CH$_3$**), 1.84-1.29 (m, 26H, -**(CH$_2$)$_{13}$**-), 0.96 (t, 3H, J = 7.6 Hz, -**CH$_3$**), 0.90 (t, 3H, J = 7.6 Hz, -**CH$_3$**). Elemental Analysis calculated for $C_{46}H_{55}F_3N_2O_6$: C, 70.03; H, 7.03 %, N = 3.55%; Found: C, 69.37; H, 6.99 %, N = 3.55%.

4-[N-(4′-(n-dodecyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4′-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 12-3CF$_3$-2M-5:

Yield: 1.22g, (78%); **IR** ν_{max} in cm^{-1}: 1628 ($\nu_{CH=N}$, imine); 1749 ($\nu_{C=O}$, ester), 3103(ν_{O-H}, H-bonded); **^{1}H NMR** (CDCl$_3$, 400 MHz): 13.46 (s, 1H, -**OH**), 12.94 (s, 1H, -**OH**), 8.52 (s, 1H, -C**H**=N-), 8.45 (s, 1H, -C**H**=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, Ar**H**), 7.58 (d, 1H, J = 2.4 Hz, Ar**H**), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, Ar**H**), 7.39 (t, 1H, J = 8.0 Hz, Ar**H**), 7.31-7.27 (4H, Ar**H**), 6.52-6.50 (4H, **ArH**), 4.02 (t, 4H, J = 6.8 Hz, -**OCH$_2$**-), 2.67 (s, 3H, Ar-**CH$_3$**), 1.84-1.27 (m, 26H, -**(CH$_2$)$_{13}$**-), 0.94 (t, 3H, J = 7.2 Hz, -**CH$_3$**), 0.88 (t, 3H, J = 6.8

Hz, -**CH₃**). Elemental Analysis calculated for $C_{46}H_{55}F_3N_2O_6$: C, 70.03; H, 7.03 %, N = 3.55%; Found: C, 69.44; H, 6.88; N = 3.55%.

4-[N-(4′-(n-dodecyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4′-n-dodecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 12-3CF$_3$-2M-12:

Yield: 1.31g, (74%); **IR** ν_{max} in cm^{-1}: 1622 ($\nu_{CH=N}$, imine); 1761 ($\nu_{C=O}$, ester), 3114ν_{O-H}, H-bonded); **^{1}H NMR** ($CDCl_3$, 400 MHz): 13.46 (s, 1H, -**OH**), 12.94 (s, 1H, -**OH**), 8.52 (s, 1H, -C**H**=N-), 8.45 (s, 1H, -C**H**=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, Ar**H**), 7.58 (d, 1H, J = 2.4 Hz, Ar**H**), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, Ar**H**), 7.39 (t, 1H, J = 8.0 Hz, Ar**H**), 7.31-7.27 (4H, Ar**H**), 6.52-6.50 (4H, **ArH**), 4.01 (t, 4H, J = 6.8 Hz, -**OCH$_2$**-), 2.67 (s, 3H, Ar-**CH$_3$**), 1.83-1.27 (m, 40H, -**(CH$_2$)$_2$**-), 0.88 (t, 6H, J = 6.8 Hz, 2 x -**CH$_3$**). Elemental Analysis calculated for $C_{53}H_{69}F_3N_2O_6$: C, 71.76; H, 7.84 %, N = 3.16; Found: C, 71.01; H, 7.45 %, N = 3.15%.

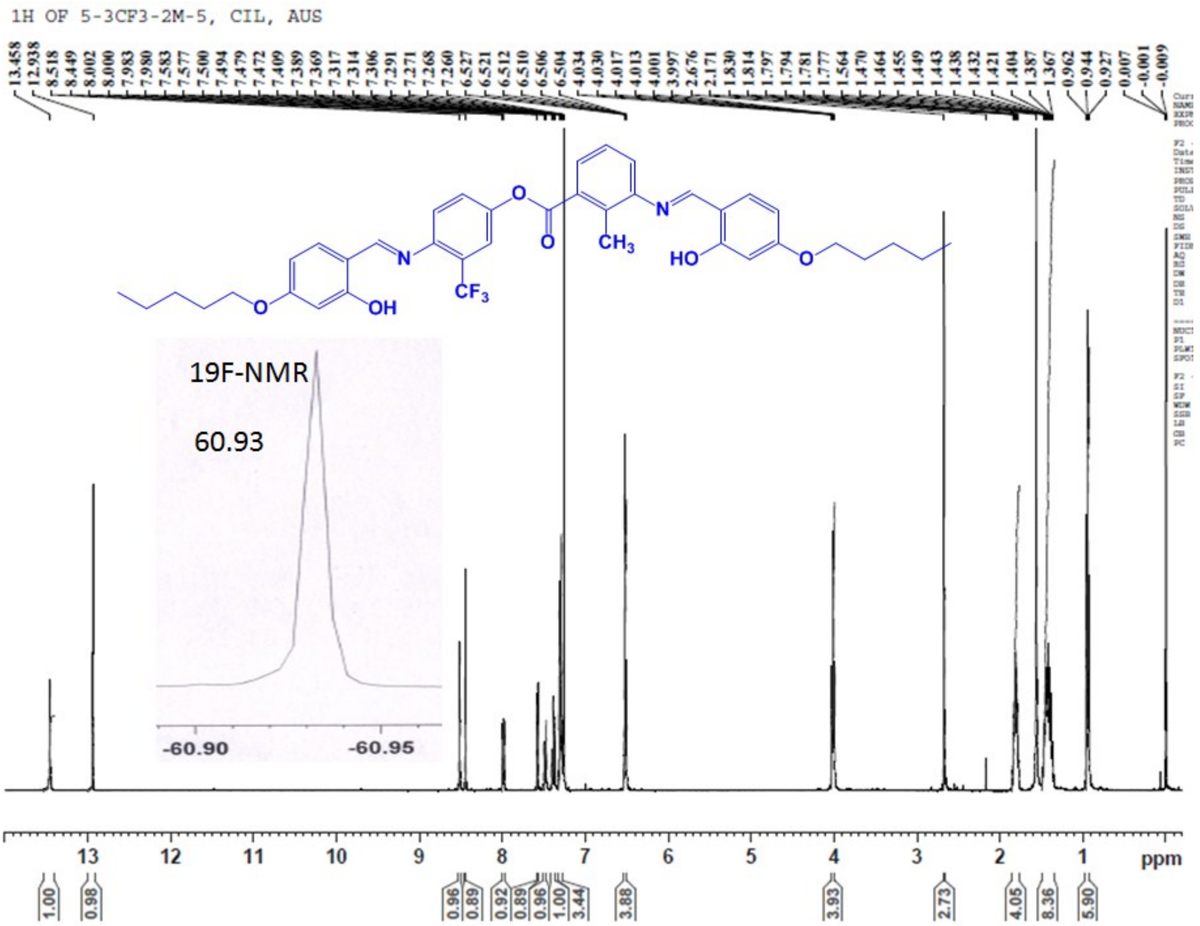


Figure 1a: ^{1}H-NMR and ^{19}F-NMR spectra of representative compound **5-3CF$_3$-2M-5**

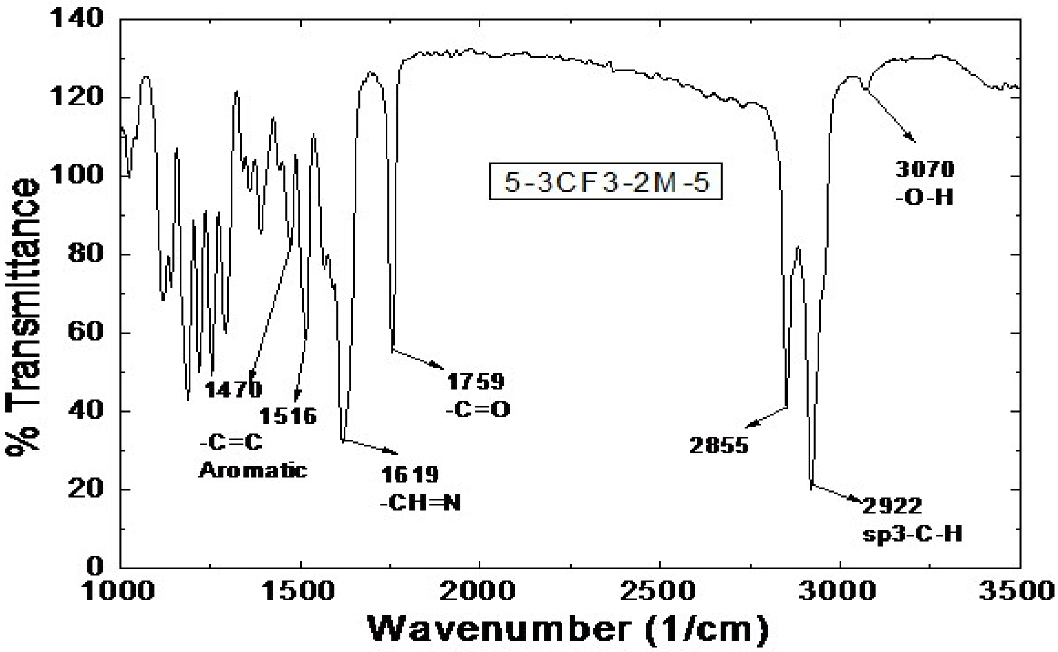


Figure 1b: FT-IR spectra of **5-3CF3-2M-5**

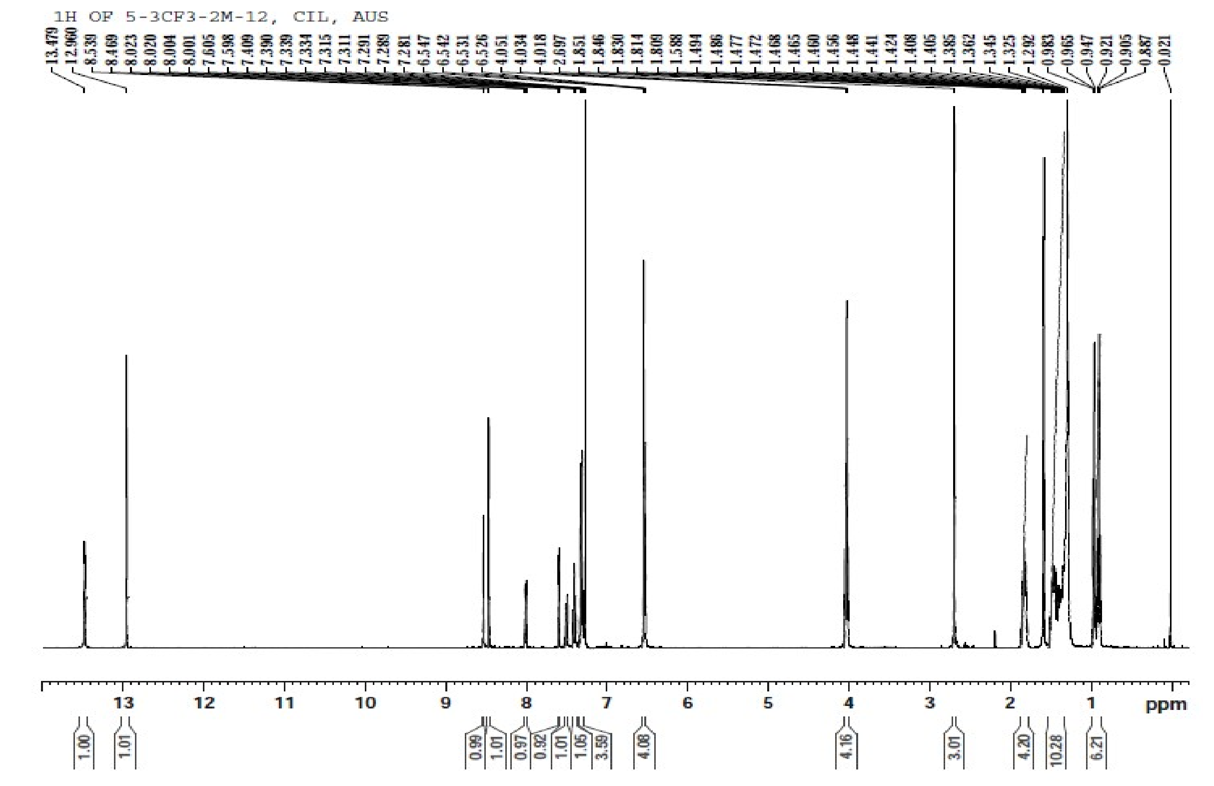


Figure 1c: ^{1}H-NMR and ^{19}F-NMR spectra of representative compound **5-3CF$_3$-2M-12**

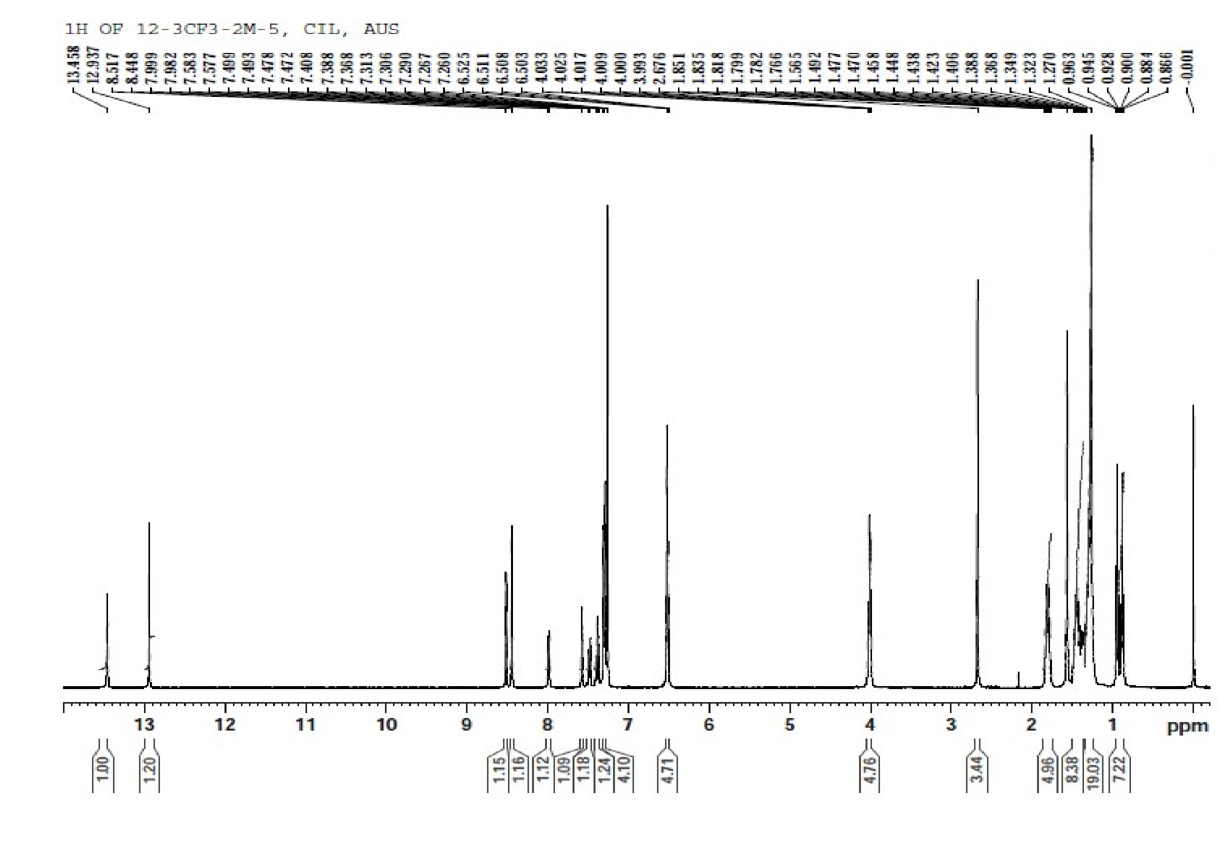


Figure 1d: ^{1}H-NMR spectra of representative compound **12-3CF$_3$-2M-5**

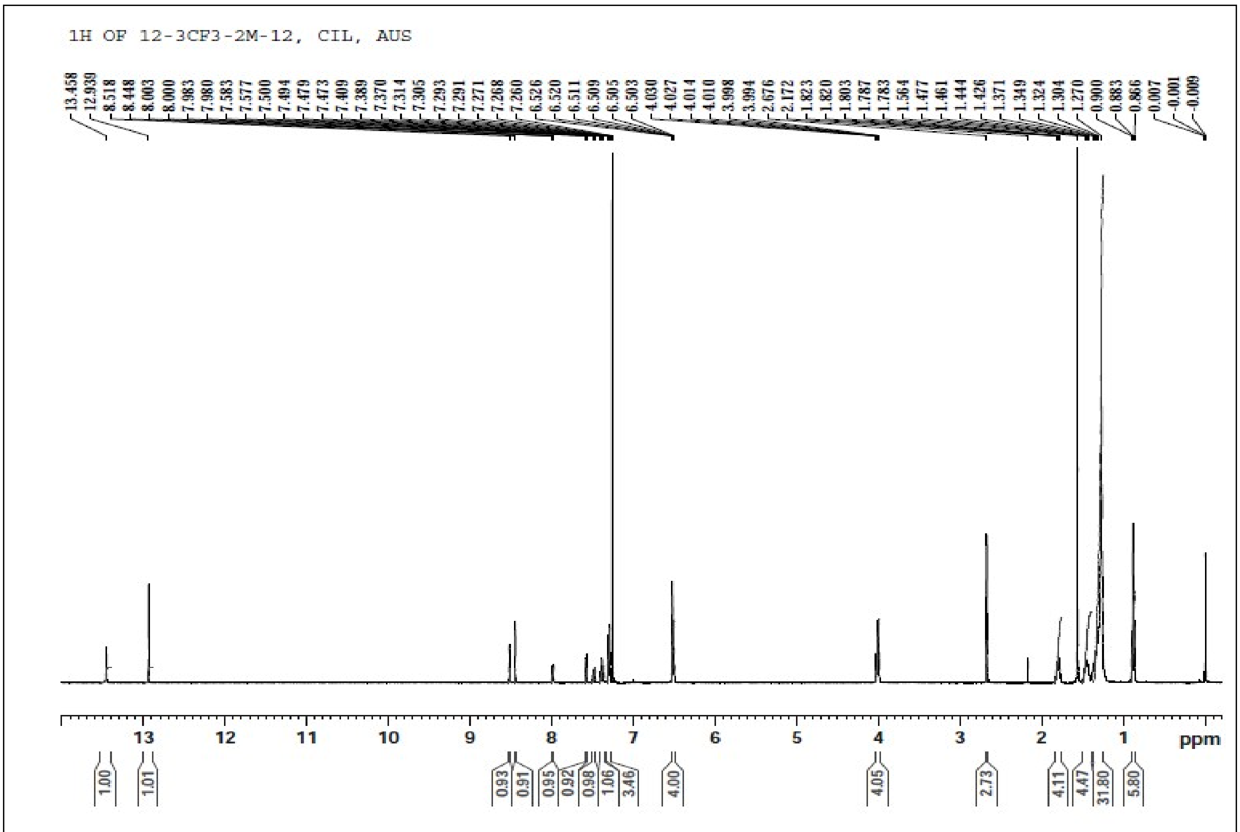


Figure 1e: ^{1}H-NMR spectra of representative compound **12-3CF$_3$-2M-12**

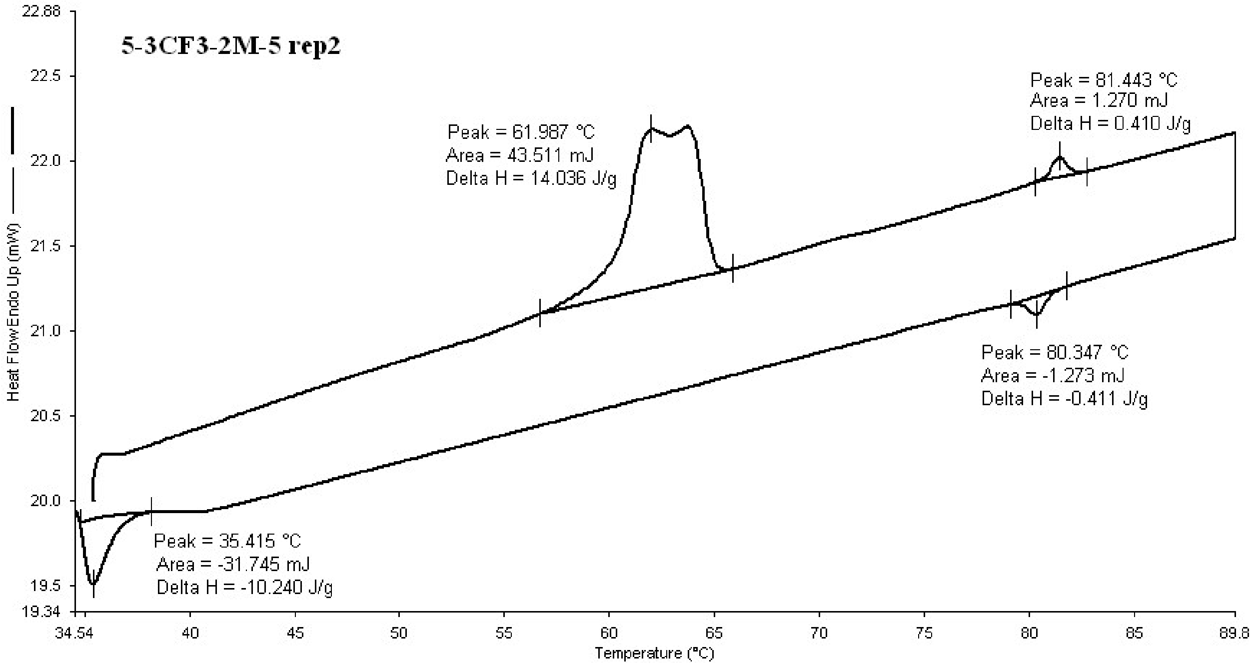


Figure 1a: Differential scanning calorimetry thermogram of of compound **5-3CF$_3$-2M-5** in the second heating and cooling at 5^{o}C/min.

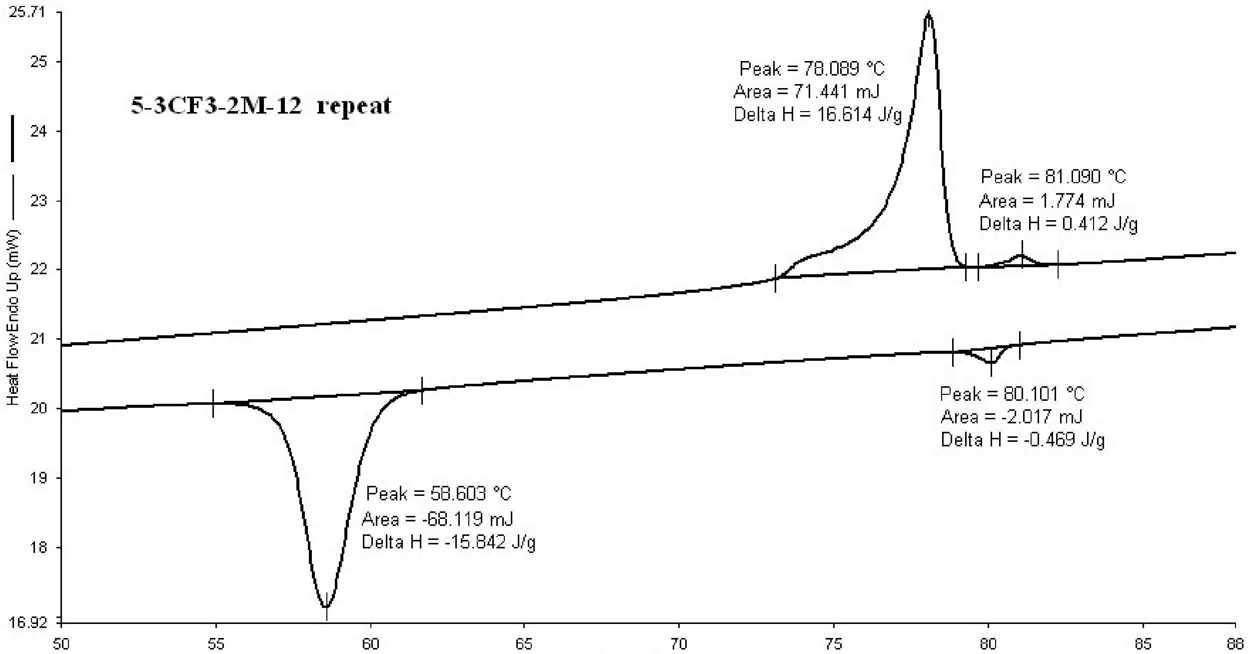


Figure 1b: Differential scanning calorimetry thermogram of of compound **5-3CF$_3$-2M-12** in the second heating and cooling at 5^{o}C/min.

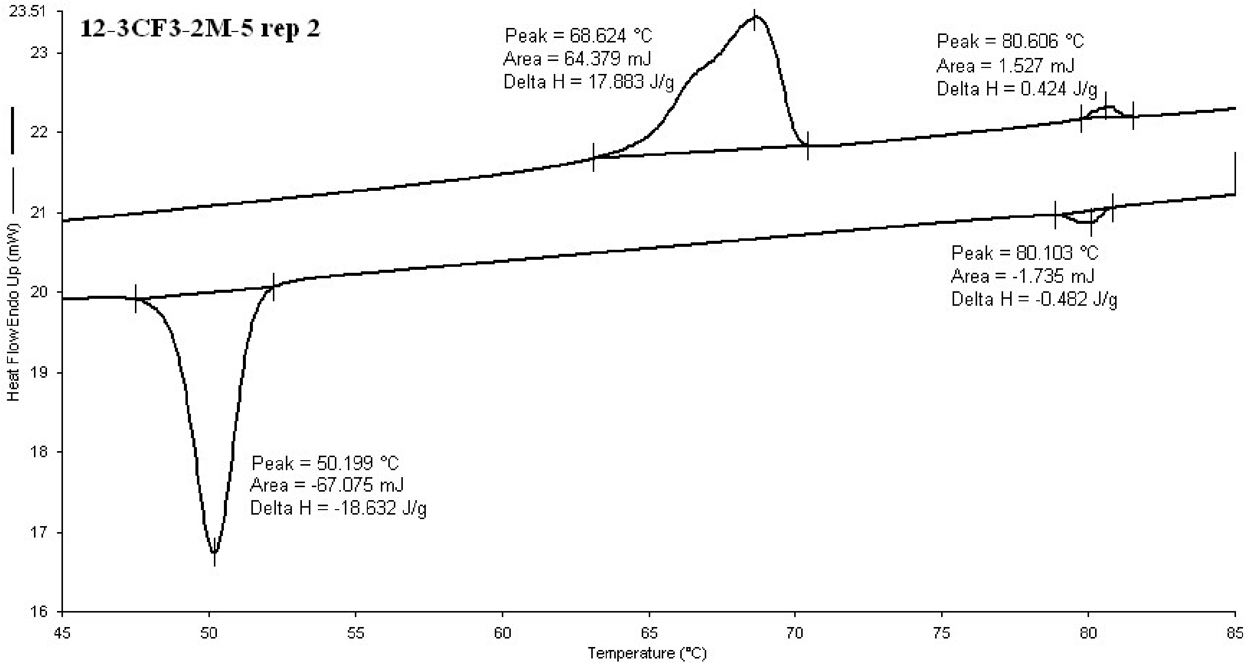


Figure 1c: Differential scanning calorimetry thermogram of compound **12-3CF$_3$-2M-5** in the second heating and cooling at 5^{o}C/min.

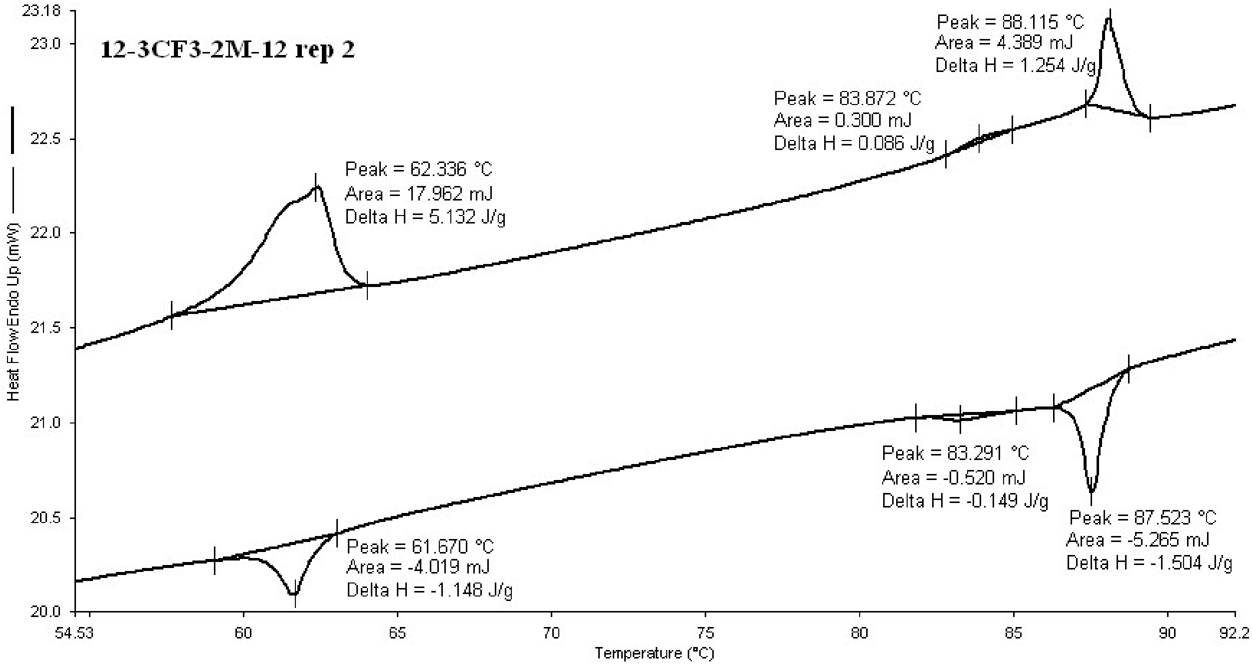


Figure 1d: Differential scanning calorimetry thermogram of of compound **12-3CF$_3$-2M-12** in the second heating and cooling at 5^{o}C/min.

2. Polarizing Optical micrographs of BPIII:

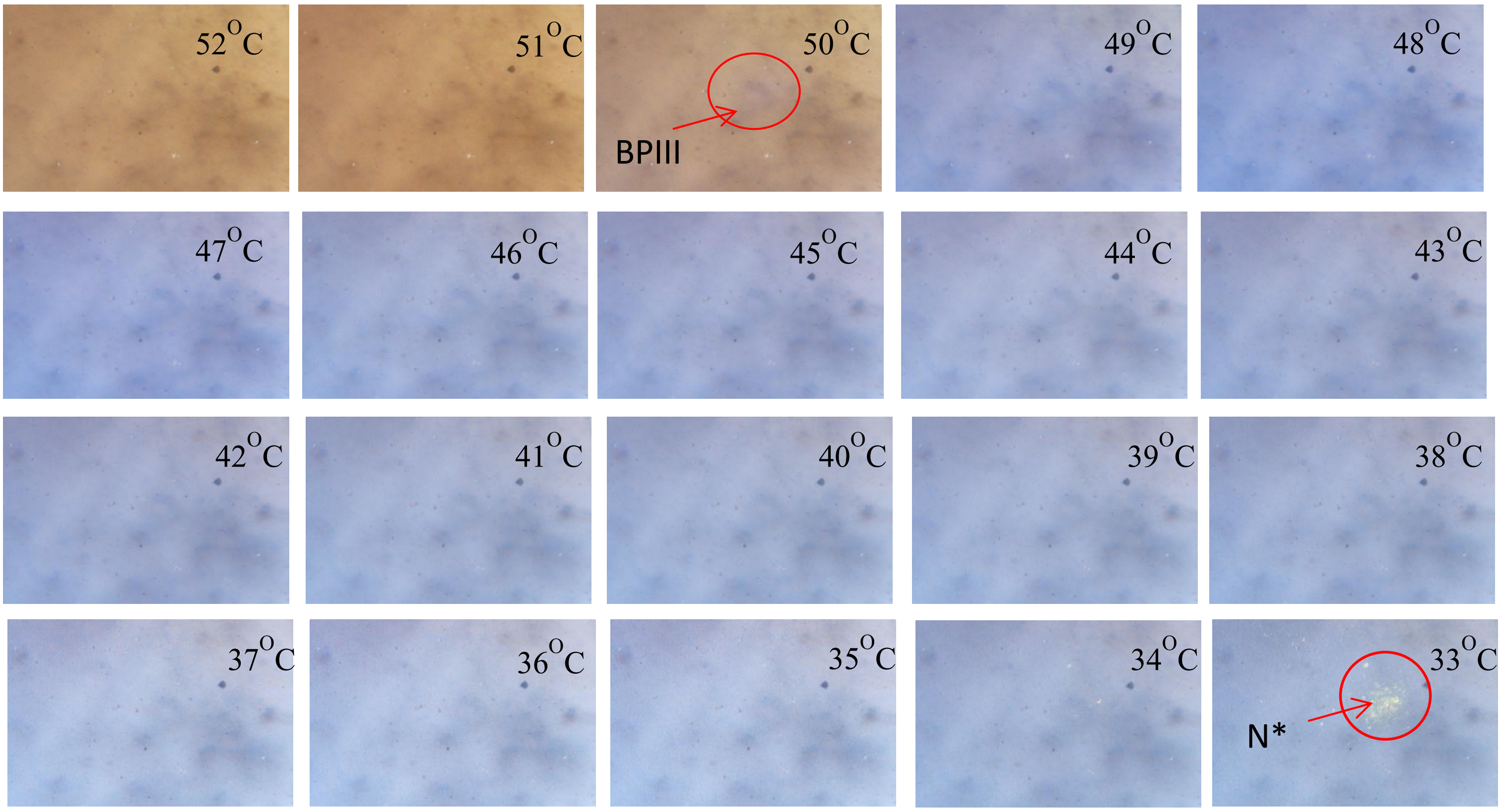


Figure 2a: POM images exhibiting Iso-BPIII-N* transition in a planar cell of thickness 4µm for the mixture 5-3CF3-2M-5 + 30% S811

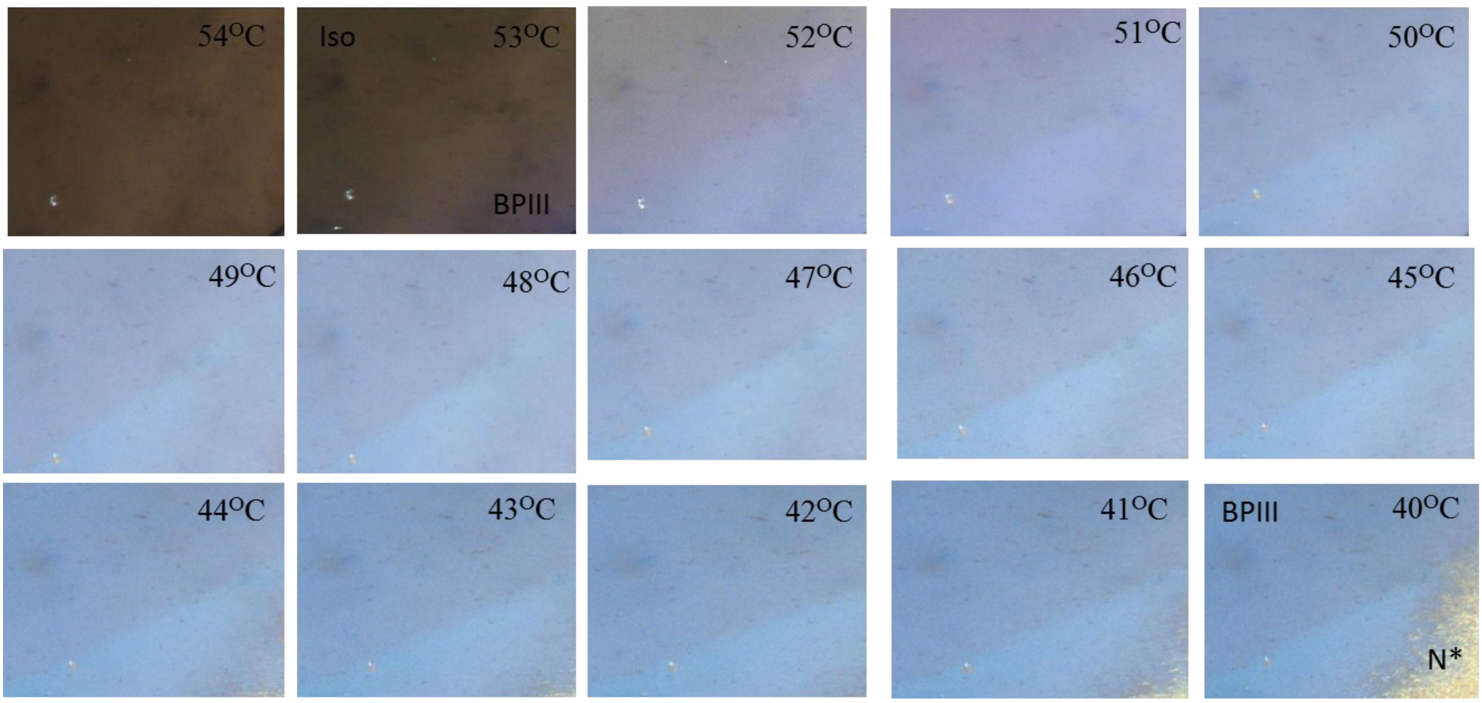


Figure 2b: POM images exhibiting Iso-BPIII-N* transition in a planar cell of thickness 4μm for the mixture 5-3CF3-2M-12 + 30% S811.