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Synthesis and mesomorphic characterization of novel amphotropic steroidal esters

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1. Experimental section:

1.1 Materials and method

All the chemicals and reagents employed were purchased from Sigma-Aldrich and Spectrochem. The solvents used for the reaction are dried and distilled using the standard protocols. Purification of the pre-final and the final compounds were carried out by column chromatography using silica gel (mesh size: 100-200) as adsorbent and recrystallization using suitable solvents. The chemical structures and the purity of synthesized compounds were determined using NMR spectroscopy and elemental analysis. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer using tetramethyl silane (TMS) as an internal standard and $CDCl_3$ as solvent. The chemical shift values are given in ppm and the solvent ($CDCl_3$) peak appears at δ = 7.26 ppm in ^{1}H NMR and at δ = 77 ppm in ^{13}C NMR. Peak multiplicities are indicated as s = singlet, d = doublet, t = triplet, dd = doublet of doublet and m = multiplet. The elemental analysis was carried out for all the intermediates and final compounds using Elementar Vario MICRO select elemental analyser. Mettler Toledo differential scanning calorimeter (DSC) was used to determine the transition temperatures and the associated enthalpy values for all the synthesized mesogenic compounds (by using 2-4 mg of sample at a scan rate of 5 °C/min). The mesophase textures were observed using an Olympus BX51 polarising optical microscope equipped with a Mettler FP82HT heating stage and a Mettler FP90 central processor. X-ray diffraction (XRD) measurements on powder samples were carried out using PANalytical, Empyrean diffractometer using Cu-K_α (λ = 1.54 Å) beam. The sample was filled in Lindemann capillaries (0.7 mm diameter). Specific rotation was measured by using a Jasco P-1020 automated Polarimeter by diluting the samples in chloroform solvent. The thermal stability of all the target compounds was established by Perkin Elmer TGA 4000 analyser.

Lyotropic samples were prepared in DMF (dimethyl formamide) by mixing 5 wt% of the compounds in 95 wt% of the solvent. Samples were sonicated to ensure the compound's homogeneous distribution and incubated at 40 °C for 15 days without any disturbance. After equilibration, the samples were taken for further characterization.

Cryo-SEM: For cryogenic scanning electron microscopy (Cryo-SEM) studies, the lyotropic samples were quenched in liquid nitrogen. The frozen samples were then transferred to a

PP3000T cryo unit (Quorum Technologies) which is maintained at a temperature of −180 °C, where they were fractured using a cold knife. The fractured samples were then subjected to sublimation at −90 °C for 5 min and then sputtered with platinum for 90 s to form a few nm thick coating on the fractured surface. Samples were imaged using a Zeiss Ultra Plus Cryo-SEM Samples were imaged using a Zeiss Ultra Plus Cryo-SEM.

1.2 Synthetic procedure

Compounds **2-5** were synthesized following the previous literature procedure with minor modifications[1–3]. The general procedure for the synthesis of intermediates (**2-4**) and the final compound (**5a**) are given below.

Procedure for tosylation of ethylene glycols (2): n=2; 3,6-dioxaheptyl-4-toluenesulfonate

A 500 mL round bottom flask with a magnetic stirrer was charged with diethylene glycol monomethyl ether (10 g, 1 eq) and 50 ml of tetrahydrofuran (THF). This reaction mixture was then cooled to 0 °C using ice bath and 5 eq of 6 M NaOH was added to it (around 70 ml). Tosyl chloride (2 eq) in 80 ml THF is added dropwise to this reaction mixture with the help of addition funnel under N_2 atmosphere. After stirring at 0°C for 1 h, the reaction mixture was allowed to attain room temperature and stirred for another 2 h. The resulting mixture was then extracted with diethyl ether (Et_2O) and the resulting organic layer was washed with 1 M NaOH and water. After drying over Na_2SO_4, the solvent was evaporated under vacuum and the crude product was purified by column chromatography to obtain the tosylated product as a colourless liquid (Yield = 70%).

Procedure for the synthesis of 3: **n=2; 4-(3,6-dioxaheptyloxy)benzoic acid ethyl ester**

Compound **3** (1 eq), 4-hydroxtybenzoic acid ethyl ester (1eq), K_2CO_3 (5 eq) and 18-crown-6 (0.1 eq) were taken in an RB and refluxed for 22 h using acetone (around 100 ml) as solvent. The progress of the reaction was monitored with the help of TLC. After the completion of the reaction, the reaction mixture was filtered to remove K_2CO_3 and the filtrate was concentrated. The mixture containing crude product was extracted with ethyl acetate. It is then washed with water and brine solution. The combined organic layer dried over anhydrous Na_2CO_3, was then evaporated under reduced pressure to obtain the crude product. It was then purified with the help of column chromatography employing silica gel

as adsorbent with chloroform as eluent to obtain pure final product (Yield: 75%).

General procedure for the synthesis of 4: n=2; 4-(3,6-dioxaheptyloxy)benzoic acid (4)

To a solution of **3a** (1 eq) in ethanol was added KOH (2 eq) in water (Ethanol:water = v/v) and refluxed overnight. After completion of the reaction, mixture is poured into an acidic water solution (pH=1, HCl). The precipitated acid is filtered and washed repeatedly with water and dried to obtain pure, colourless solid (Yield = 40 %).

Procedure for the synthesis of 5: (for n=2) [4-(3,6-dioxaheptyloxy)benzoyloxy] cholesterol

A mixture of 4-(3,6-dioxaheptyloxy)benzoic acid (0.31 g, 1 eq), cholesterol (0.50 g, 1eq), EDC.HCl (0.49 g, 2 eq), 4-N,N-(dimethylamino) pyridine/DMAP (12 mg, 0.05 eq) and dry DCM (25 ml) was stirred overnight at 45°C. The completion of the reaction was analyzed using TLC. The resultant solution was washed with water and brine solution. The required product is extracted with dichloromethane (3 x 25 ml), dried over anhydrous sodium sulphate (Na_2SO_4) and evaporated to dryness. The crude product was purified by column chromatography using a mixture of DCM and petroleum ether (20:80) as eluent. The solvent is evaporated from the resultant eluate to obtain the desired product as a white compound. This was further purified by re-precipitation using DCM-methanol solvent system (Yield : 45 %).

1.3 NMR spectral data and elemental analysis

Compound **5a**: (**4-[(3,6-dioxaheptyloxy)benzoyloxy]cholesterol)**

Molecular formula-$C_{39}H_{60}O_5$

Cholesterol (0.500 g, 1 eq), 4-(3,6-dioxaheptyloxy)benzoic acid (0.31 g, 1 eq), EDC.HCl (0.49 g, 2 eq), DMAP (12 mg, 0.05 eq) and dry DCM, yield: 55%.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 7.98 (d, J=8.5 Hz, 2H), 6.92 (d, J=8 Hz, 2H), 5.41 (s, 1H), 4.82 (m, 1H), 4.19 (t, J=4 Hz, 2H), 3.88 (t, J=4 Hz, 2H), 3.72 (t, J=4 Hz, 2H), 3.58 (t, J=4 Hz, 2H), 3.39 (s, 3H), 2.45 (2H), 1.55-2.10 (m, 9H), 0.95-1.55 (m, 20H), 0.8-0.95 (m, 9H), 0.60-0.80 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$), δ (ppm) = 165.76, 162.40, 139.78, 131.51, 123.44, 122.68, 114.10, 74.25, 71.95, 70.82, 69.59, 67.53, 59.10, 56.71, 56.15, 50.06, 42.33, 39.76, 39.53, 38.29, 37.06, 36.66, 36.19, 35.81, 31.94, 31.90, 28.24, 28.02, 27.94, 24.30, 23.84, 22.83, 22.57, 21.06, 19.39, 18.73, 11.87.

Elemental analysis: C, 76.93; H, 9.93 (calculated); C, 76.73; H, 9.60 (found).

Compound **5b**: (**4-(3,6,9-trioxadecyloxy)benzoyloxy]stigmasterol)**

Molecular formula-$C_{41}H_{62}O_5$

Stigmasterol (0.500 g, 1 eq), 4-(3,6-dioxaheptyloxy)benzoic acid (0.29 g, 1 eq), EDC.HCl (0.46 g, 2 eq), DMAP (7.4 mg, 0.05 eq) and dry DCM, yield: 50%.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 7.98 (d, J=8.5 Hz, 2H), 6.92 (d, J=8 Hz, 2H), 5.41 (s, 1H), 5.10-5.25 (m, 1H), 4.90-5.10 (m, 1H), 4.83 (m, 1H), 4.20 (t, J=4 Hz, 2H), 3.88 (t, J=4 Hz, 2H), 3.73 (t, J=4 Hz, 2H), 3.59 (t, J=4 Hz, 2H), 3.39 (s, 3H), 2.45 (2H), 1.65-2.10 (m, 9H), 0.95-1.65 (m, 20H), 0.75-0.95 (m, 9H), 0.60-0.80 (s, 3H). ^{13}C NMR (500 MHz, CDCl3), δ (ppm) = 165.76, 162.40, 139.77, 138.33, 131.51, 129.28, 123.43, 122.66, 114.10, 74.25, 71.94, 70.82, 69.59, 67.53, 59.10, 56.80, 55.94, 51.24, 50.08, 42.22, 40.51, 39.65, 38.29, 37.06, 36.68, 31.93, 31.89, 28.93, 27.94, 25.42, 24.37, 21.23, 21.10, 21.04, 19.39, 18.99, 12.26, 12.06.

Elemental analysis: C, 77.56; H, 9.84 (calculated); C, 77.46; H, 10.00 (found).

Compound **5c**: (**4-(3,6,9,12-trioxatridecyloxy)benzoyloxy]cholesterol)**

Molecular formula-$C_{41}H_{64}O_6$

Cholesterol (0.500 g, 1 eq), 4-(3,6,9,12-trioxatridecyloxy)benzoic acid (0.36 g, 1 eq), EDC.HCl (0.49 g, 2 eq), DMAP (12 mg, 0.05 eq) and dry DCM, yield: 45%.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 7.98 (d, J=8.5 Hz, 2H), 6.92 (d, J=9 Hz, 2H), 5.41 (s, 1H), 4.82 (m, 1H), 4.18 (t, J=4 Hz, 2H), 3.87 (t, J=4 Hz, 2H), 3.60-3.80 (m, 6H), 3.55 (t, 2H), 3.39 (s, 3H), 2.44 (2H), 1.55-2.10 (m, 9H), 0.95-1.55 (m, 20H), 0.80-0.95 (m, 9H), 0.60-0.80 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$), δ (ppm) = 165.75, 162.42, 139.77, 131.50, 123.43, 122.67, 114.10, 74.24, 71.93, 70.89, 70.65, 70.57, 69.57, 67.55, 59.03, 56.71, 56.15, 50.06, 42.33, 39.75, 39.52, 38.29, 37.06, 36.66, 36.19, 35.80, 31.94, 31.89, 28.24, 28.01, 27.94, 24.30, 23.84, 22.82, 22.57, 21.06, 19.39, 18.73, 11.87.

Elemental analysis: C, 75.42; H, 9.88 (calculated); C, 75.40; H, 9.79 (found).

Compound **5d**: (**4-(3,6,9,12-trioxatridecyloxy)benzoyloxy] stigmasterol)**

Molecular formula-$C_{43}H_{66}O_6$

Stigmasterol (0.500 g, 1 eq), 4-(3,6,9-trioxadecyloxy)benzoic acid (0.34 g, 1 eq), EDC.HCl (0.46 g, 2 eq), DMAP (7.4 mg, 0.05 eq) and dry DCM, yield: 55%.

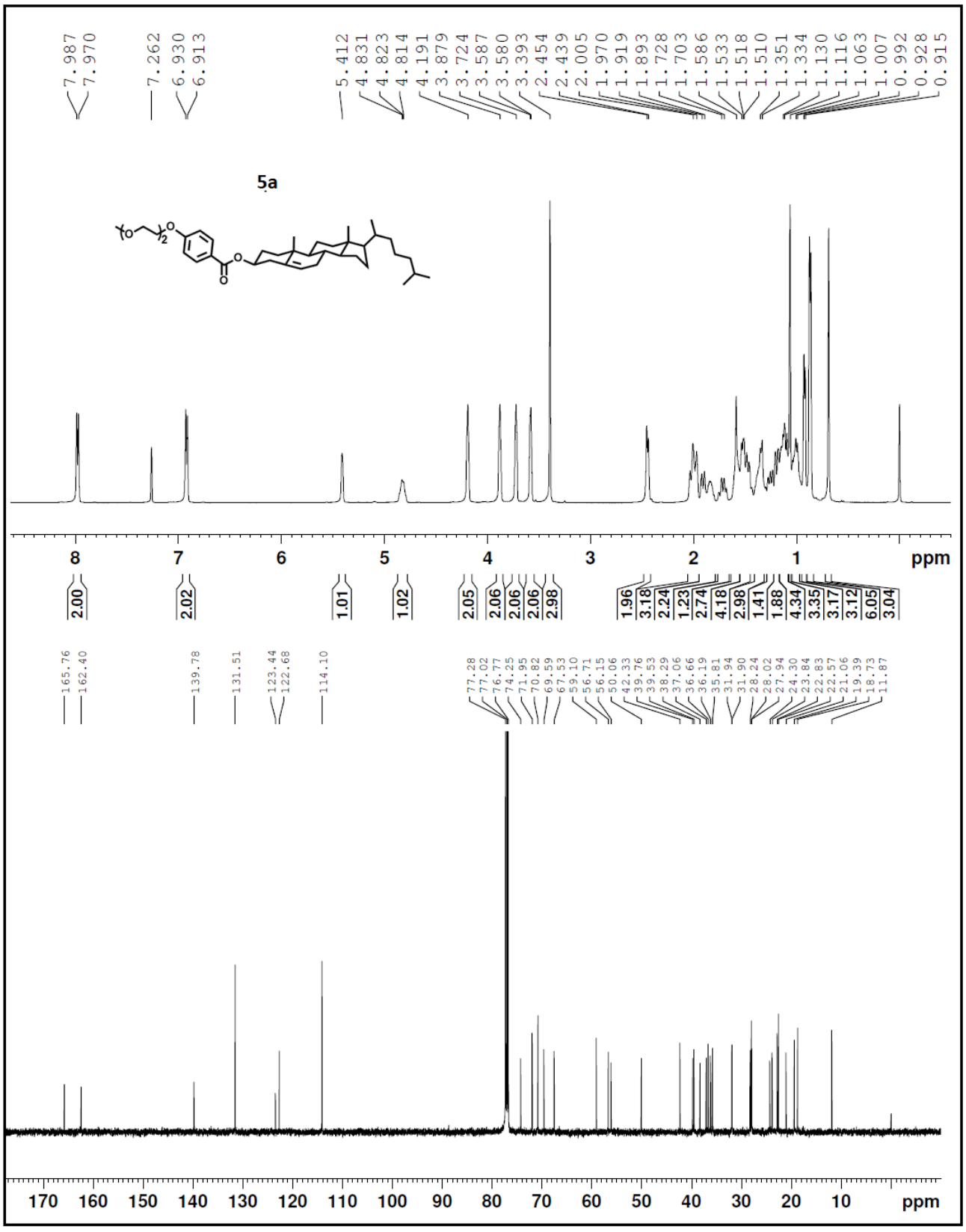
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 7.98 (d, J=8.5 Hz, 2H), 6.92 (d, J=8 Hz, 2H), 5.41 (s, 1H), 5.10-5.25 (m, 1H), 4.90-5.10 (m, 1H), 4.82 (m, 1H), 4.19 (t, J=4 Hz, 2H), 3.88 (t, J=4 Hz, 2H), 3.73 (t, J=4 Hz, 2H), 3.59-3.70 (t, J=4 Hz, 4H), 3.50-3.60 (t, J=4 Hz, 2H), 3.39 (s, 3H), 2.45 (2H), 1.65-2.10 (m,

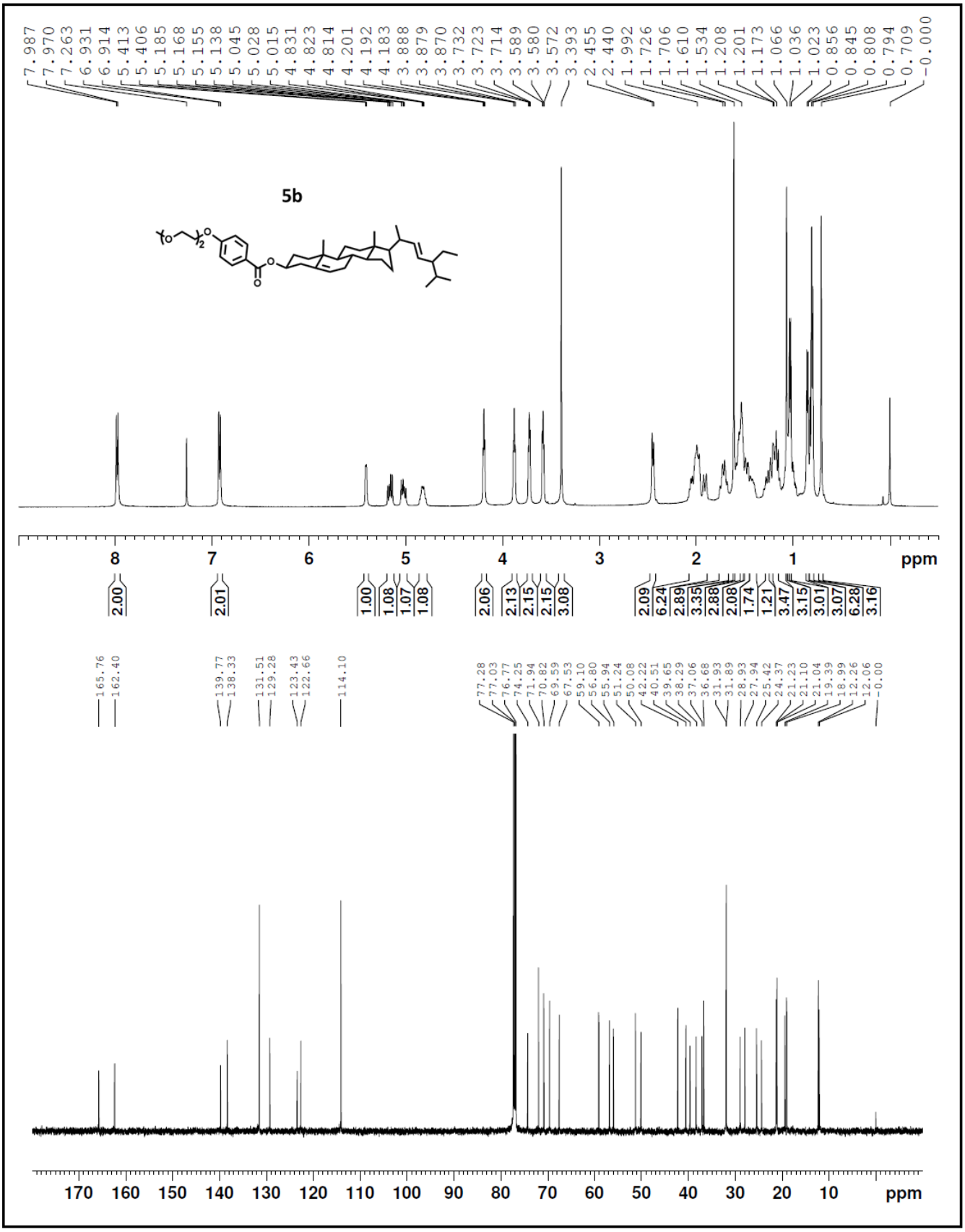
9H), 0.95-1.65 (m, 20H), 0.75-0.90 (m, 9H), 0.60-0.75 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$), δ (ppm) = 165.76, 162.43, 139.77, 138.34, 131.50, 129.28, 123.42, 122.67, 114.10, 74.24, 71.94, 70.90, 70.67, 70.59, 69.58, 67.55, 59.05, 56.80, 55.94, 51.24, 50.08, 42.22, 40.51, 39.65, 38.29, 37.06, 36.68, 31.89, 31.89, 28.93, 27.94, 25.42, 24.37, 21.23, 21.10, 21.05, 19.39, 18.99, 12.26, 12.06.
Elemental analysis: C, 76.06; H, 9.80 (calculated); C, 76.26; H, 9.74 (found).

Compound **5e**: (**4-(3,6,9,12-tetraoxatridecyloxy)benzoyloxy]cholesterol)**
Molecular formula-$C_{43}H_{68}O_7$
Cholesterol (0.500 g, 1 eq), 4-(3,6,9-trioxadecyloxy)benzoic acid (0.42 g, 1 eq), EDC.HCl (0.49 g, 2 eq), DMAP (12 mg, 0.05 eq) and dry DCM, yield: 40%.
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 7.98 (d, J=8 Hz, 2H), 6.92 (d, J=8 Hz, 2H), 5.41 (s, 1H), 4.82 (m, 1H), 4.18 (t, J=4 Hz, 2H), 3.88 (t, J=4 Hz, 2H), 3.60-3.80 (m, 10H), 3.55 (t, 2H), 3.39 (s, 3H), 2.44 (2H), 1.65-2.10 (m, 9H), 0.95-1.65 (m, 20H), 0.80-0.95 (m, 9H), 0.60-0.80 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$), δ (ppm) = 165.74, 162.43, 139.78, 131.50, 123.45, 122.66, 114.10, 74.25, 71.94, 70.88, 70.63, 70.61, 70.51, 69.56, 67.57, 59.01, 56.71, 56.16, 50.07, 42.34, 39.76, 39.52, 38.29, 37.07, 36.67, 36.20, 35.80, 31.94, 31.90, 28.23, 28.01, 27.94, 24.30, 23.84, 22.81, 22.55, 21.06, 19.38, 18.72, 11.86.
Elemental analysis: C, 74.10; H, 9.83 (calculated); C, 73.91; H, 10.08 (found).

Compound **5f**: (**4-(3,6,9,12-tetraoxatridecyloxy)benzoyloxy]stigmasterol)**
Molecular formula-$C_{45}H_{70}O_7$
Stigmasterol (0.500 g, 1 eq), 4-(**3,6,9,12-tetraoxatridecyloxy)benzoic acid** (0.39 g, 1 eq), EDC.HCl (0.46 g, 2 eq), DMAP (7.4 mg, 0.05 eq) and dry DCM, yield: 50%.
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) = 7.98 (d, J=8.5 Hz, 2H), 6.92 (d, J=8 Hz, 2H), 5.41 (s, 1H), 5.10-5.25 (m, 1H), 4.90-5.10 (m, 1H), 4.82 (m, 1H), 4.19 (t, J=4 Hz, 2H), 3.88 (t, J=4 Hz, 2H), 3.73 (t, J=4 Hz, 2H), 3.59-3.80 (t, J=4 Hz, 8H), 3.50-3.60 (t, J=4 Hz, 2H), 3.39 (s, 3H), 2.45 (2H), 1.65-2.10 (m, 9H), 0.95-1.65 (m, 20H), 0.80-0.95 (m, 9H), 0.60-0.80 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$), δ (ppm) = 165.74, 162.43, 139.77, 138.32, 131.50, 129.29, 123.44, 122.65, 114.10, 74.24, 71.94, 70.88, 70.63, 70.61, 70.51, 69.55, 67.56, 59.02, 56.81, 55.96, 51.24, 50.09, 42.23, 40.49, 39.65, 38.29, 37.07, 36.68, 31.93, 31.89, 28.91, 27.94, 25.40, 24.37, 21.23, 21.08, 21.05, 19.38, 18.99, 12.24, 12.06.
Elemental analysis: C, 74.75; H, 9.76 (calculated); C, 74.30; H, 9.47 (found).

2. ^{1}H NMR and ^{13}C NMR spectra

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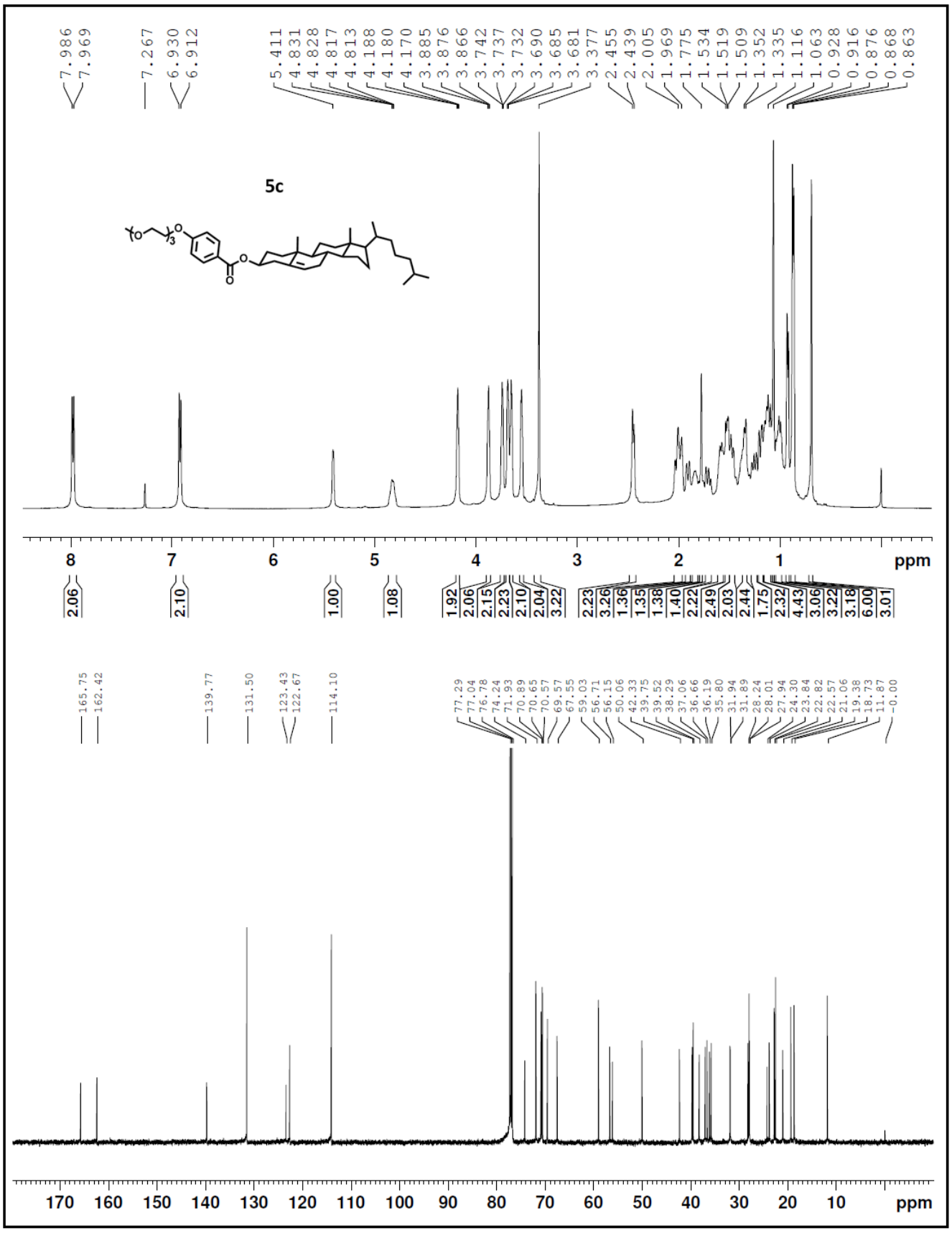
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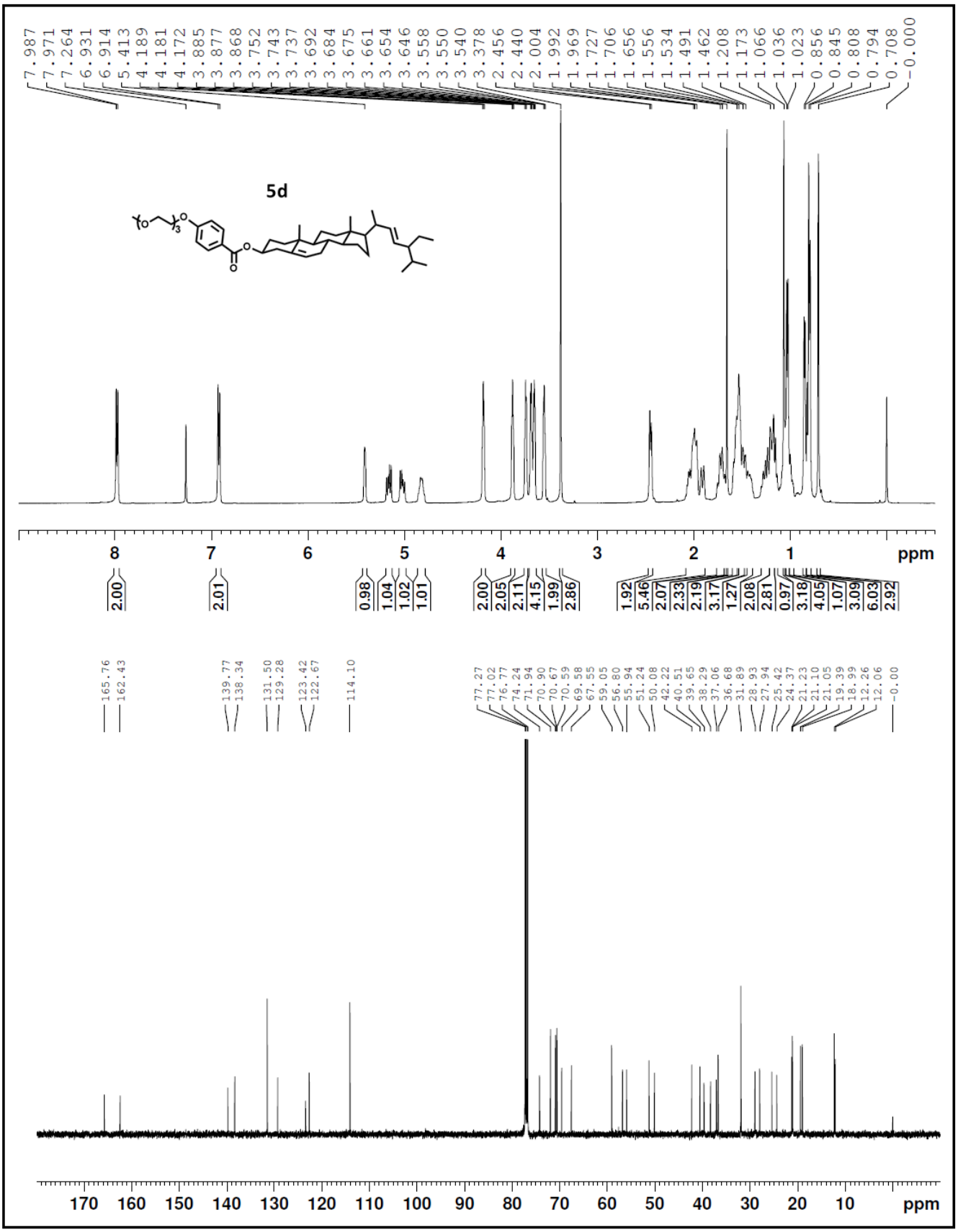
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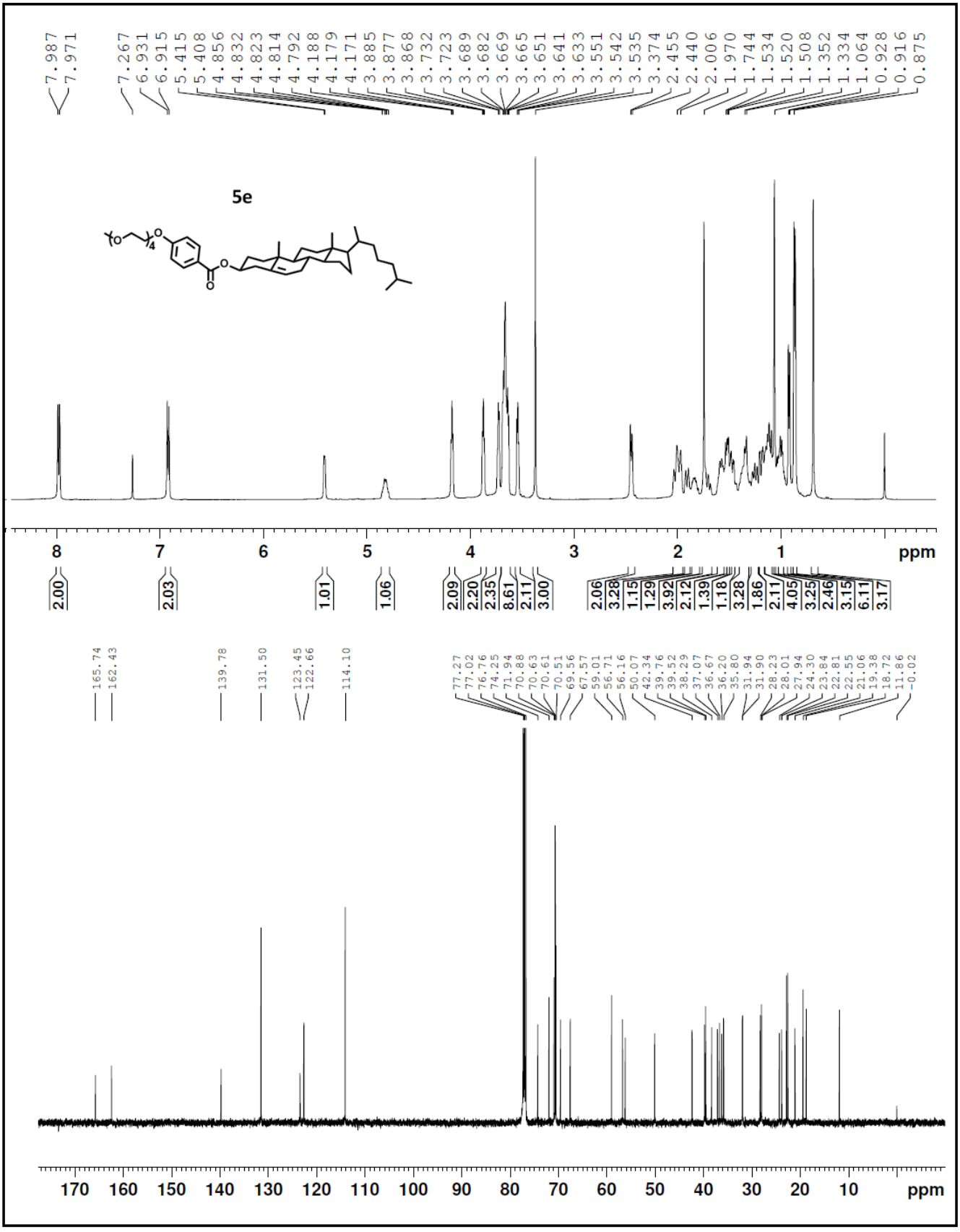
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1.18
3.28
1.86
2.11
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3.15
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3.17
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162.43
139.78
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76.76
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27.94
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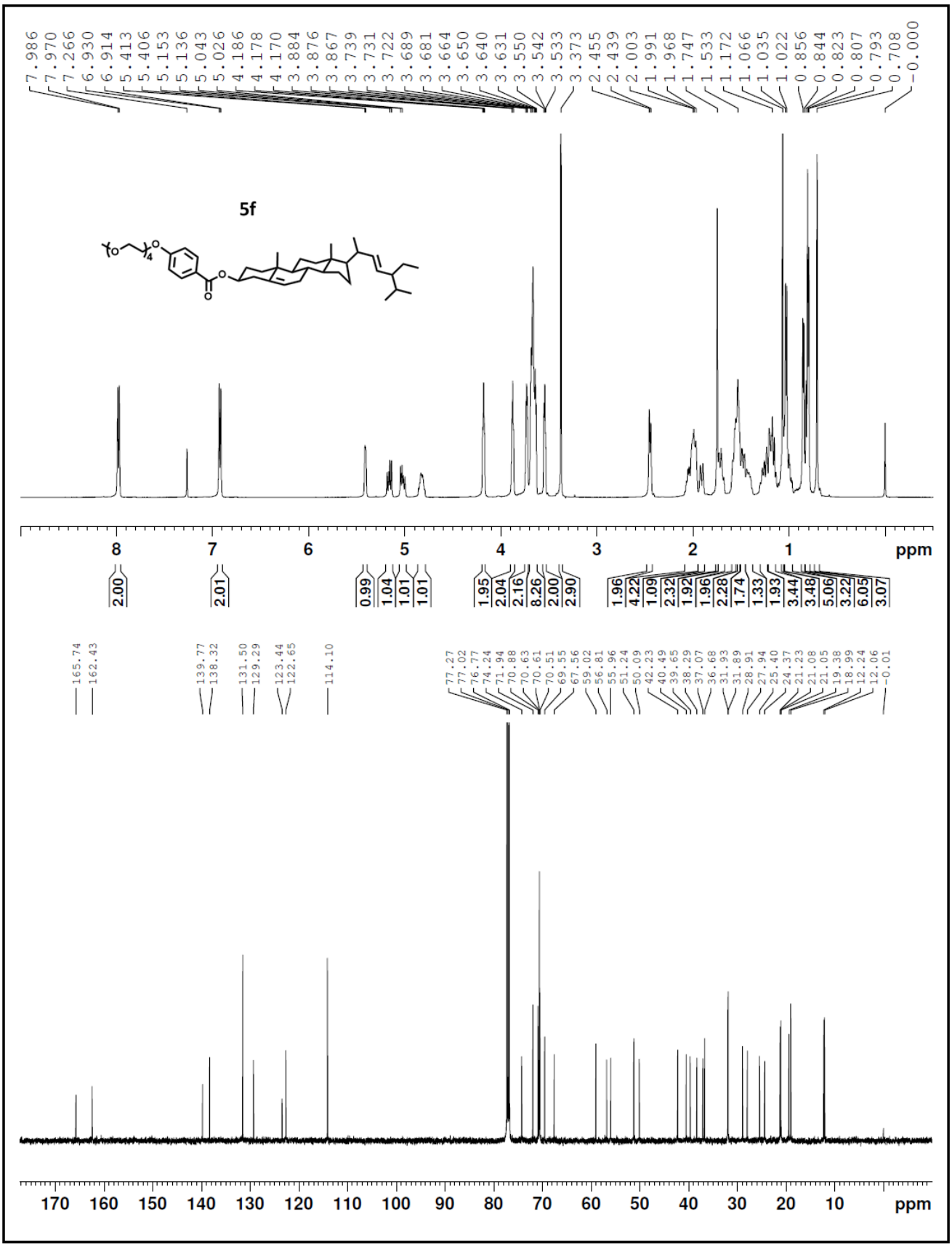
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3. Polarizing optical microscopy (POM) studies:

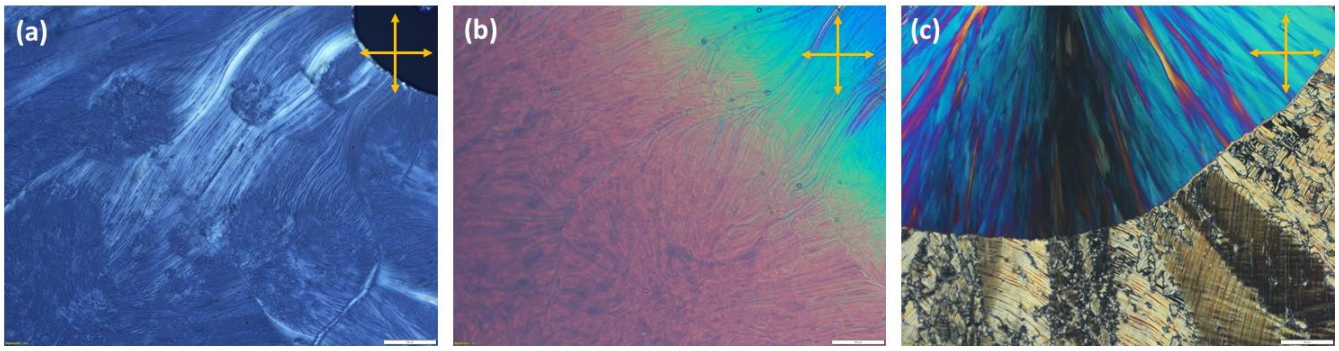

Fig. S1: POM micrographs of compound **5a** showing (a) Smectic (Sm) phase at 108 °C on heating, (b) Cholesteric phase at 117 °C on heating, (c) transition from smectic to crystal phase on cooling at 49 °C.

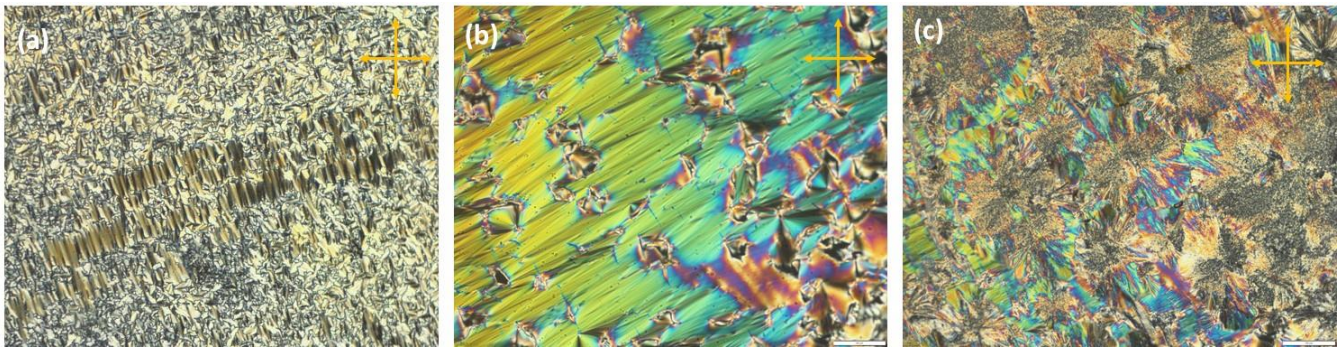

Fig. S2: POM micrographs of compound **5b** showing (a) Cholesteric phase at 146 °C on cooling, (b) focal conic texture of smectic A (SmA) phase at 80 °C on cooling, (c) transition from smectic A to crystal phase at 49.8 °C on cooling.

Fig. S3: POM micrographs of compound **5c** showing (a) smectic A phase at 77 °C on cooling, (b) Transition from TGB_A to smectic A phase at 132.5 °C on cooling, (c) Cholesteric phase at 176 °C on cooling.

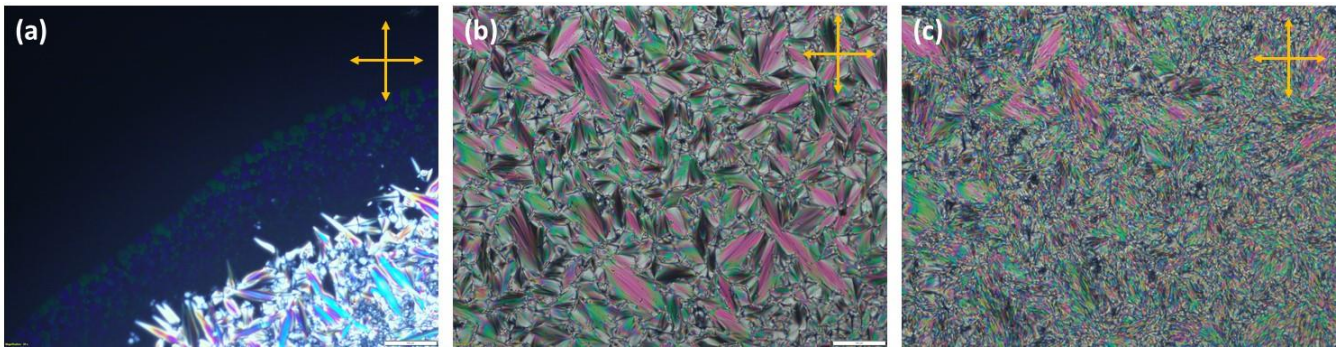

Fig. S4: POM micrographs of compound **5d** showing (a) Co-existence of BP, N* and SmA phase at 176 °C on cooling, (b) Smectic A phase at 51 °C on cooling, (c) Phase X at 47 °C on cooling.

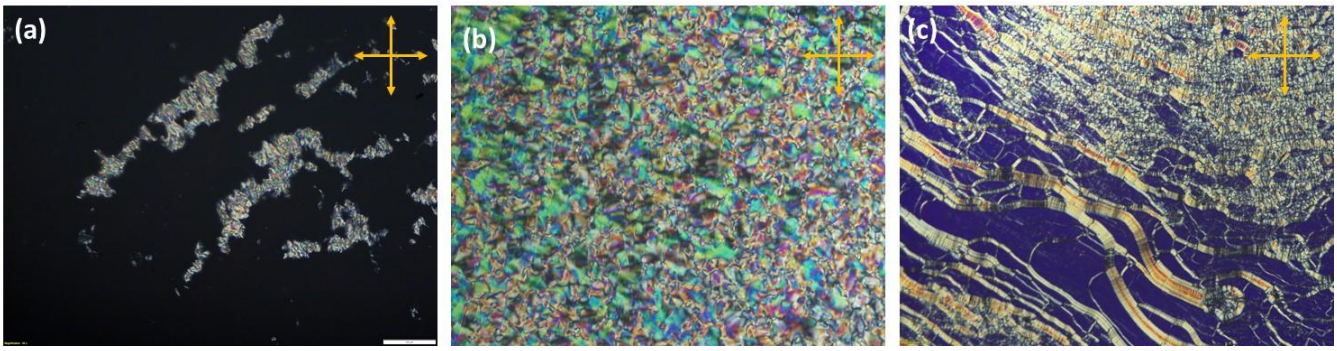

Fig. S5: POM micrographs of compound **5e** showing (a) SmA phase at 114 °C on heating, (b) TGB_A phase at 117 °C on heating, (c) Cholesteric phase at 129 °C on heating.

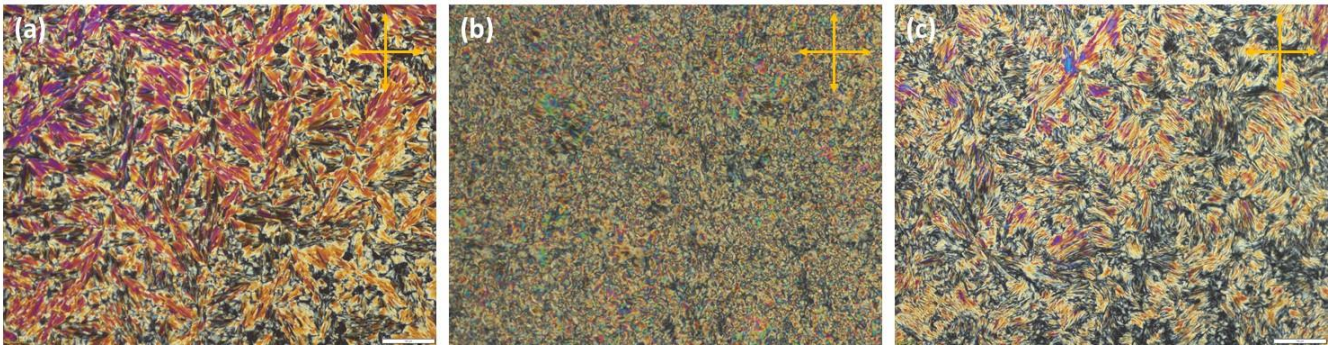

Fig. S6: POM micrographs of compound **5f** showing (a) Phase X at 56 °C on heating, (b) Phase X at 55 °C on cooling (after smearing), (c) Crystal phase at 40 °C on cooling.

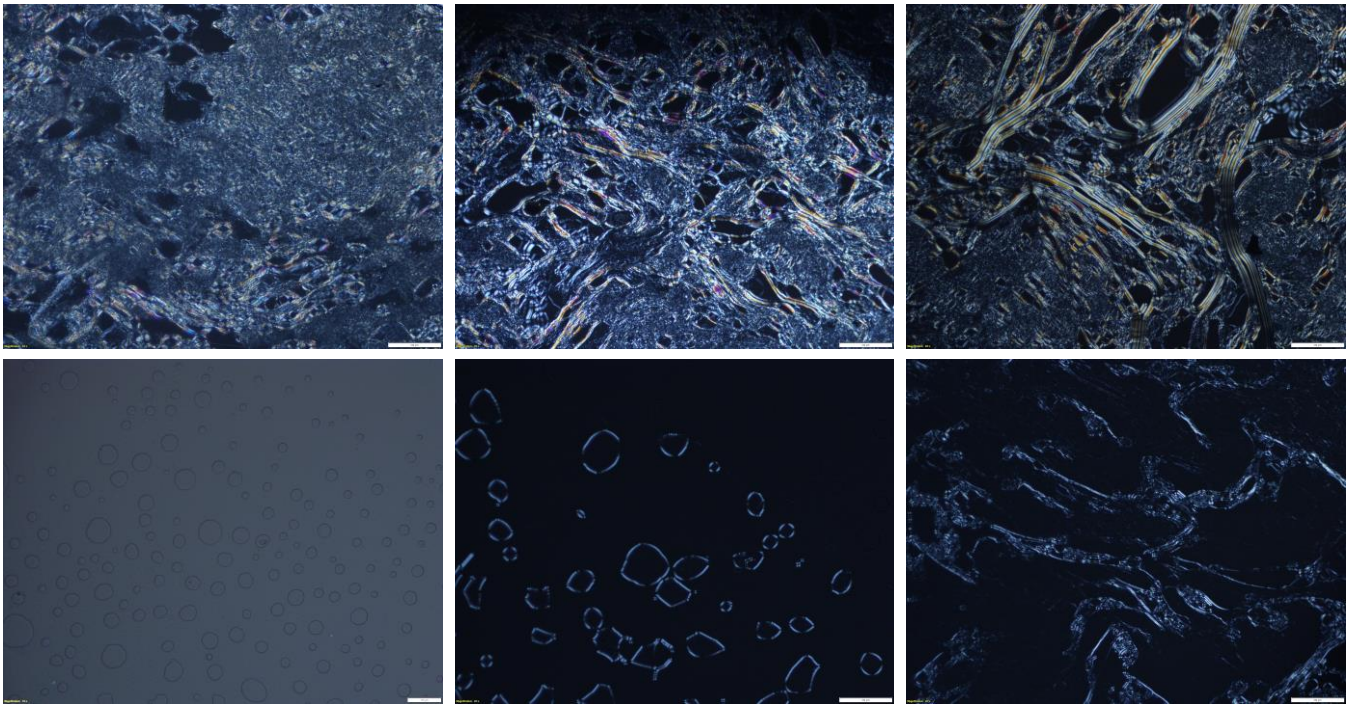

Fig. S7: POM images of lyotropic sample **5c** at (a) 30 °C on heating, (b) 45 °C on heating, (c)) 50 °C on heating, (d) 110 °C on heating (isotropic), (e) 106 °C on cooling, (f) 40 °C on cooling.

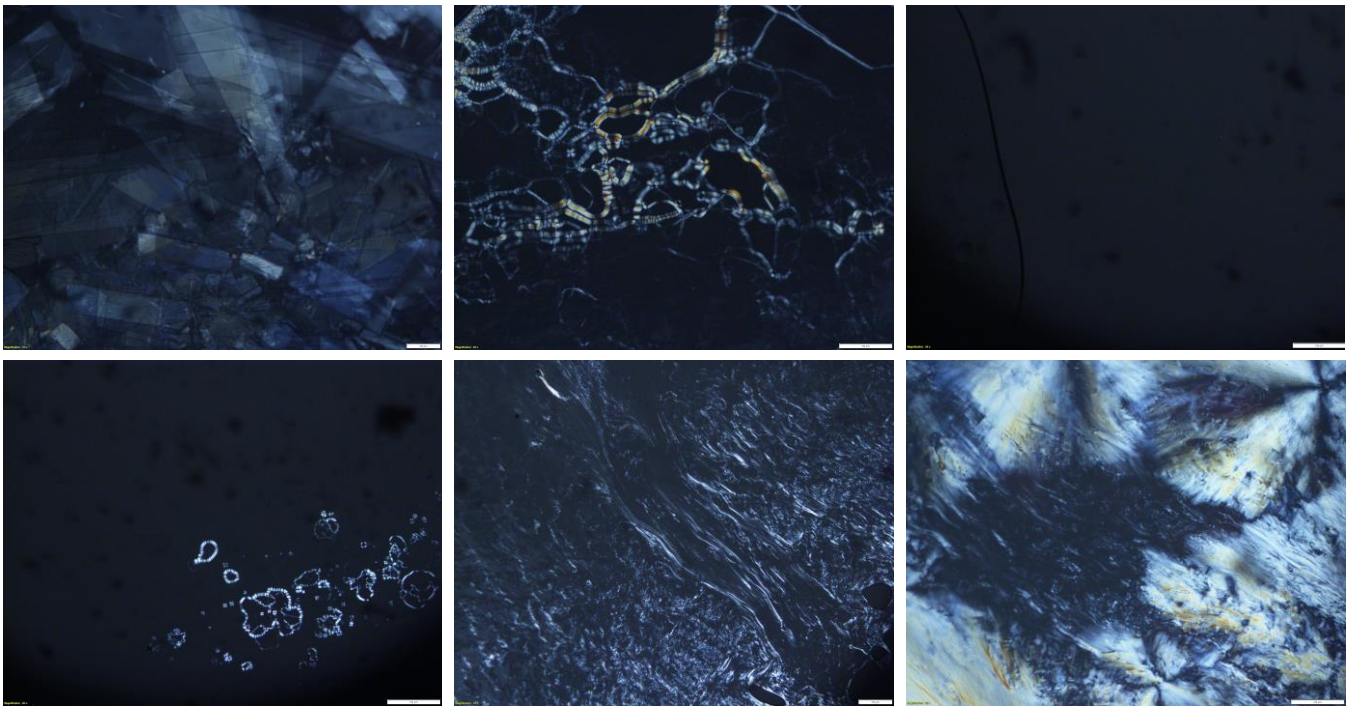

Fig. S8: POM images of lyotropic sample **5d** at (a) room temperature, (b) 67 °C on heating, (c)) 91 °C on heating (isotropic), (d) 83 °C on cooling, (e) 45 °C on cooling, (f) 31 °C on cooling.

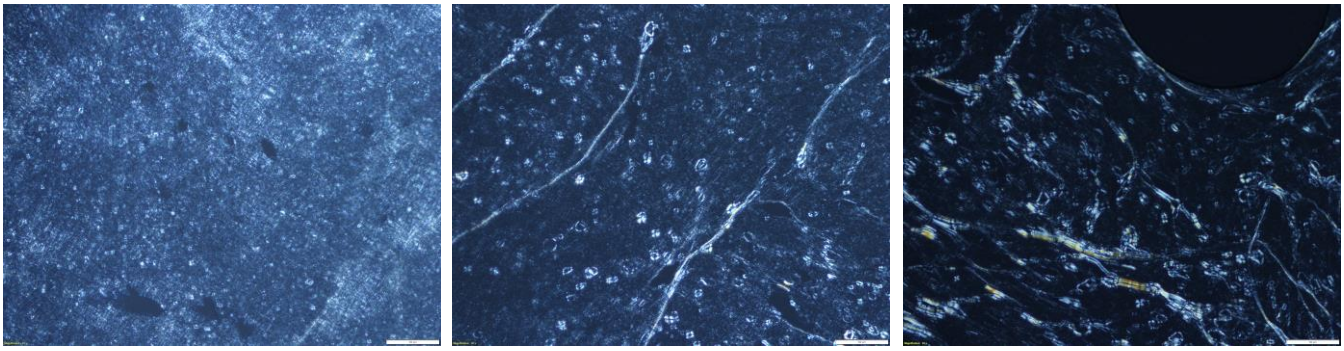

Fig. S9: POM images of lyotropic sample **5e** at (a) 50 °C on heating, (c)) 80 °C on heating, (d) 98 °C on heating.

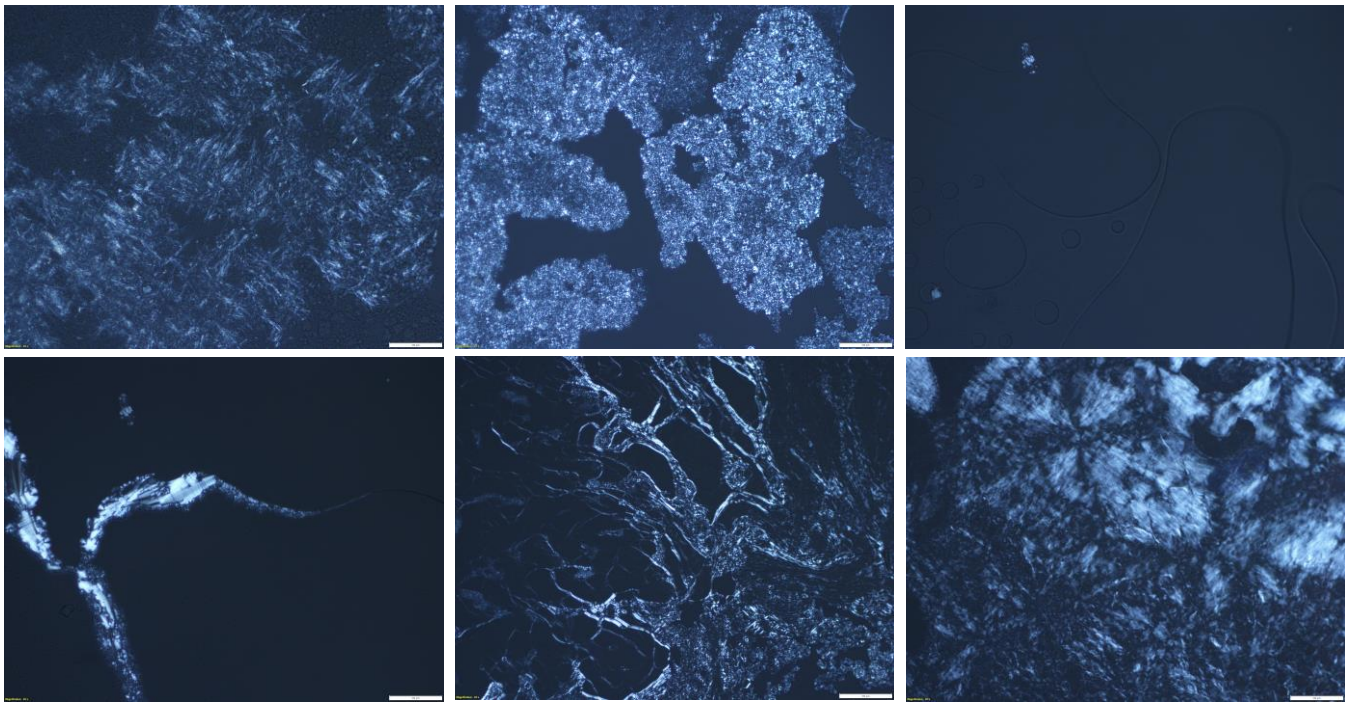

Fig. S10: POM images of lyotropic sample **5f** at (a) room temperature, (b) 62 °C on heating, (c) 89 °C on heating (isotropic), (d) 80 °C on cooling, (e) 35 °C on cooling, (f) 28 °C on cooling.

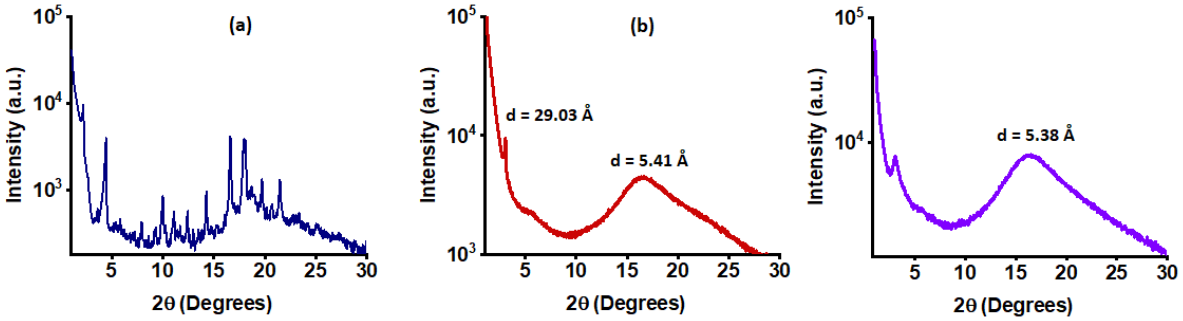

Fig. S11: X-ray diffractogram of **5a** indicating (a) Crystal phase at room temperature, (b) SmA phase at 110 °C on heating and (c) N* phase at 140 °C on heating.

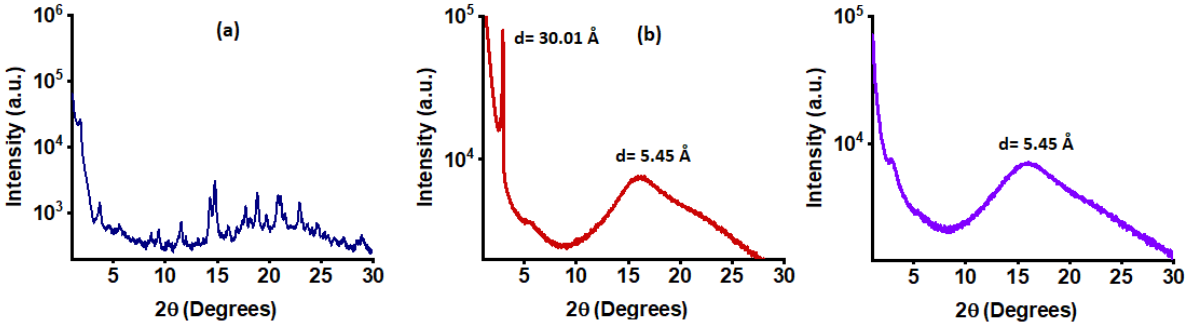

Fig. S12: X-ray diffractogram of **5b** indicating (a) Crystal phase at room temperature, (b) SmA phase at 135 °C on heating and (c) N* phase at 150 °C on heating.

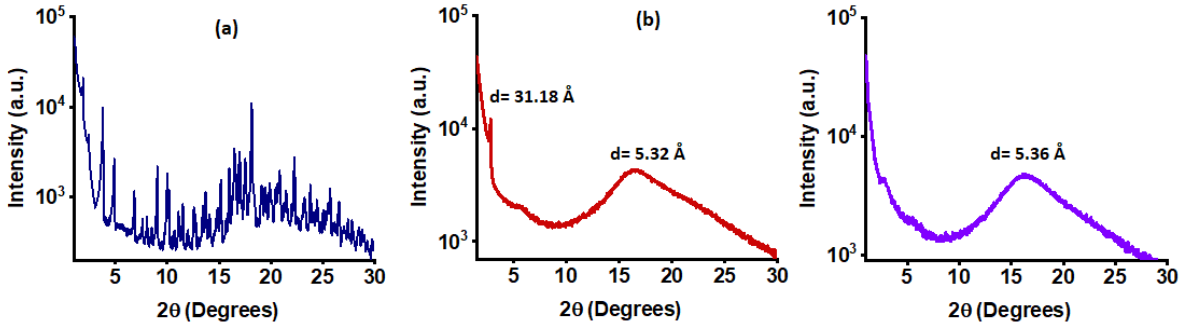

Fig. S13: X-ray diffractogram of **5c** indicating (a) Crystal phase at room temperature, (b) SmA phase at 120 °C on cooling and (c) N* phase at 145 °C on cooling.

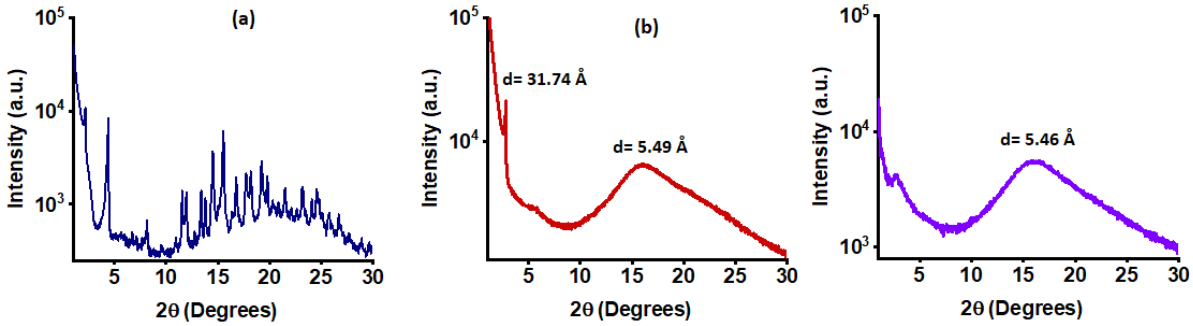

Fig. S14: X-ray diffractogram of **5d** indicating (a) Crystal phase at room temperature, (b) SmA phase at 123 °C on cooling and (c) N* phase at 133 °C on cooling.

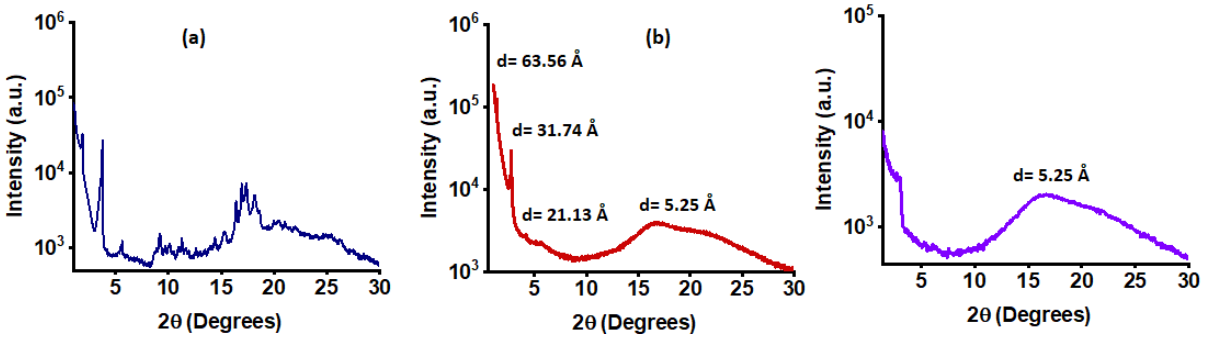

Fig. S15: X-ray diffractogram of **5e** indicating (a) Crystal phase at room temperature, (b) SmA_d phase at 65 °C on cooling and (c) N* phase at 135 °C on cooling.

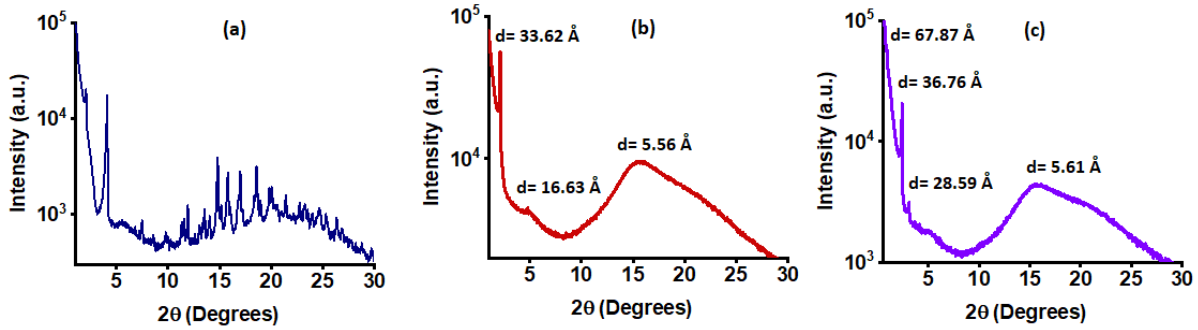

Fig. S16: X-ray diffractogram of **5f** indicating (a) Crystal phase at room temperature, (b) SmA phase at 100 °C on heating and (c) Phase X at 50 °C on cooling.

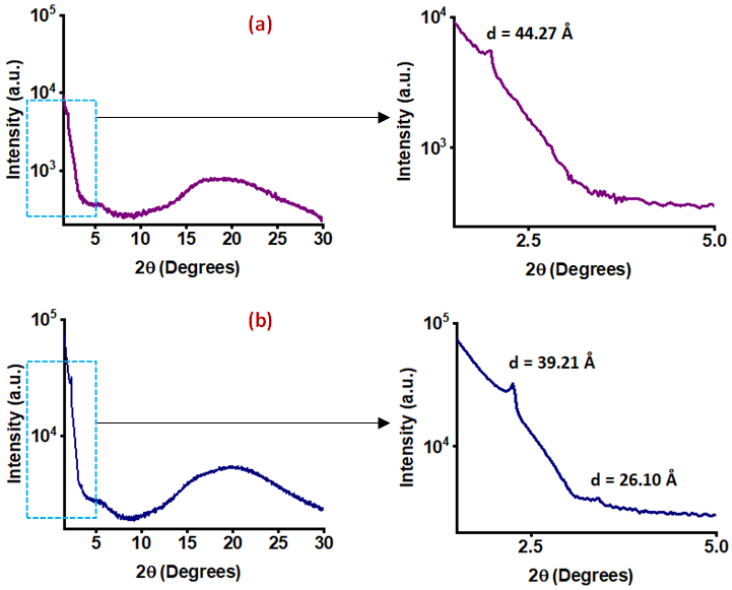

Fig. S17: X-ray diffractogram of lyotropic samples **5c** and **5f** indicating lamellar mesophase.

[Note: The first order peak was not observed as the periodicity is very large (e.g. around 78.40 Å for **5e**) which is beyond the capacity of the X-ray diffractometer in which the XRD data are recorded.]

4. References:

[1] S. Kohmoto, E. Mori, K. Kishikawa, Room-temperature discotic nematic liquid crystals over a wide temperature range: Alkali-metal-ion-induced phase transition from discotic nematic to columnar phases, J. Am. Chem. Soc. 129 (2007) 13364–13365. https://doi.org/10.1021/ja073962f.

[2] A. Gowda, L. Jacob, N. Joy, R. Philip, S. Kumar, Novel phenazine fused triphenylene discotic liquid crystals: synthesis, characterisation, thermal, optical and nonlinear optical properties, New J. Chem. 42 (2018) 19034–19042. https://doi.org/10.1039/c8nj03024c.

[3] K. Kubo, K. Tsuji, A. Mori, S. Ujiie, Synthesis and Properties of Cholesteryl Benzoate Derivatives: Liquid Crystals and Organogelators, J. Oleo Sci. 53 (2004) 467–470. https://doi.org/10.5650/jos.53.467.