

ChemistrySelect

Supporting Information

Functionalized Triphenylene Discotic Molecules: Synthesis and Mesomorphic Characterizations

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Electronic supplementary information

Experimental

Instrumentation

Chemicals and solvents (AR quality) were used as received without any further purification. Column chromatographic separations were performed on silica gel (Acme make, 100-200 mesh). Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). Chemical structure characterization of the compounds was carried out through a combination of ^1H NMR, ^{13}C NMR (Bruker AMX 400 spectrometer), and elemental analysis (Carlo-Erba 1106). ^1H NMR spectra were recorded using deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as an internal standard. The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (DSC; Perkin-Elmer, Model Pyris 1D) which was operated at a scanning rate of $5\text{ }^\circ\text{C}/\text{min}^{-1}$ both on heating and cooling cycles. The apparatus was calibrated using indium ($156.6\text{ }^\circ\text{C}$) as a standard. The textural observations of the mesophase were carried out using polarized light microscopy (Olympus BX51) provided with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). X-ray diffraction studies (XRD) were carried out on unoriented samples filled in a Lindemann capillary of diameter of 1 mm (Hampton Research) using Cu KR (λ) 1.54 \AA radiation from a PANalytical instrument (DY 1042-Empyrean) and a linear detector (PIXcel 3D). The sample temperature was controlled with the precision of $1^\circ\text{C}/\text{min}$ using a heater and a temperature controller (Linkam).

Synthesis and characterizations

Synthesis of key precursors: ω -Brominated triphenylene **2** was prepared by alkylation of monohydroxy triphenylene with 1,8-dibromooctane and 1,12-dibromododecane. The functionalized triphenylene alcohol **3** was prepared by simple etherification reaction of monohydroxy triphenylene with 11-bromoundecane-1-ol as shown in Schemes 1 and 2.

Synthetic procedure for compound (4a): A mixture of compound **2** (1 mmol), 4-benzyloxy phenol (1 mmol), and K_2CO_3 (1.2 mmol) was refluxed in butanone for overnight. Progress of the

reaction was monitored by TLC. After complete conversion of starting material **2** into protected benzyl ether, the reaction mixture was cooled, poured into an excess of distilled water, extracted into chloroform and dried over anhydrous sodium sulphate. Rotary evaporation of the organic solvent yielded the crude material.

The crude benzyl protected compound was taken in a dried round bottomed flask containing 1,4-dioxane (25 mL) and catalytic quantity of 5% Pd-C, under an atmosphere of hydrogen. The reaction mixture was stirred for overnight at room temperature. After completion of the reaction, the remaining Pd/C was filtered out and solvent removed under reduced pressure to isolate an off white solid compound. IR: 3468, 2924, 2852, 1614, 1504, 1433, 1261, 1037, 800; ¹H NMR (400 MHz, CDCl₃): δ : 7.83 (s, 8H, Ar-H), 6.75 (m, 2H, Ar-H), 4.40 (s, 1H, -OH), 4.42 (m, 12H, -OCH₂-), 3.92 (t, *J* = 6.5 Hz, 2H, -OCH₂-), 1.98-1.36 (m, 52H, -CH₂-), 0.94 (t, *J* = 6.5, 15H, -CH₃). ¹³C NMR: 149, 123.6, 116, 115.6, 107.4, 69.7, 68.5, 31.7, 29.4, 25, 28.8, 22.7, 14; Elemental analysis calculated for (Mol. Wt: 965.39) C, 77.14; H, 9.61; found C, 77.20; H, 9.71 %.

Compound (4b): Compound **2** is directly reacted with 4-hydroxybenzaldehyde (**3b**) to get target molecule **4b**. IR: 2955, 2858, 1666, 1600, 1504, 1435, 1263, 1039, 837; ¹H NMR (400 MHz, CDCl₃): δ: 9.86 (s, 1H, Ar-CHO), 7.83 (m, 8H, Ar-H), 6.98 (m, 2H, Ar-H), 4.24 (m, 12H, -OCH₂-), 4.0 (t, *J* = 6.5 Hz, 2H, -OCH₂-), 1.96-1.43 (m, 42H, -CH₂-), 0.97 (t, *J* = 6.5 Hz, 15H, -CH₃). Elemental analysis calculated for (Mol. Wt. 907.27) C, 76.78; H, 9.11; found C, 76.58. H, 9.19 %. MS analysis: 931 (Na⁺ ion).

Compound (4c): IR: 2920, 2854, 1685, 1608, 1518, 1458, 1377, 1261, 837; ¹H NMR (400 MHz, CDCl₃): δ: 7.93 (m, 8H, Ar-H), 6.90 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.24 (t, *J* = 6.4 Hz, 12H, -OCH₂-), 3.98 (t, *J* = 6.8 Hz, 2H, -OCH₂-), 1.97-1.32 (m, 60H, -CH₂-), 0.93 (t, *J* = 6.5 Hz, 15H, -CH₃). Elemental analysis calculated for (Mol. Wt. 1049.51) C, 76.68; H, 9.60; found C, 76.74; H, 9.67 %.

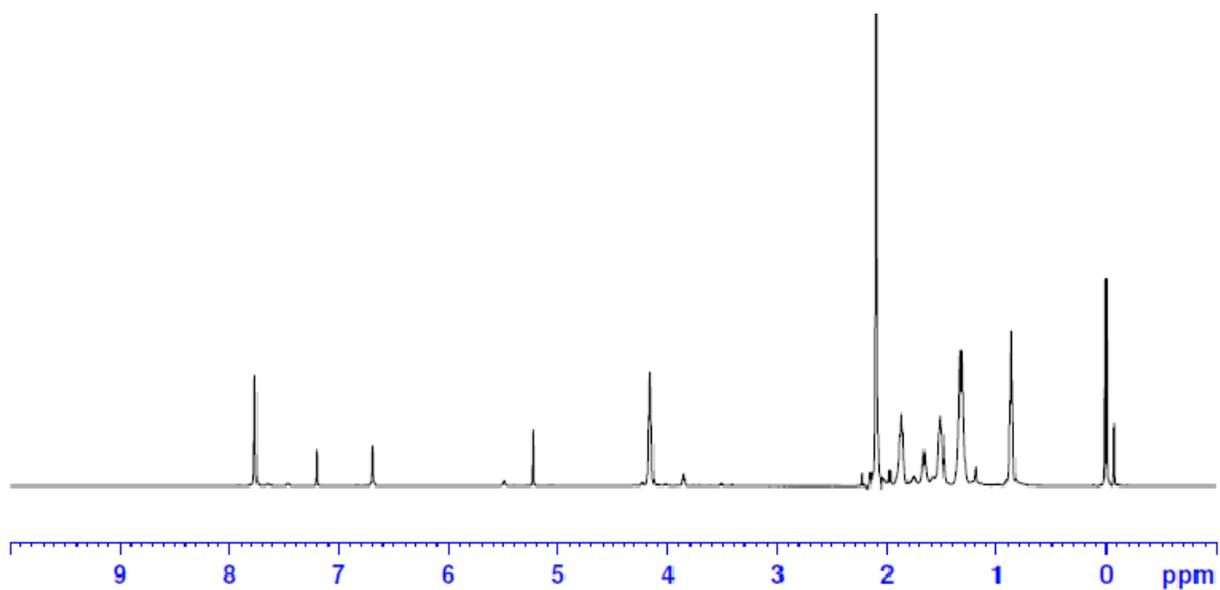
Synthetic procedure for (5a): To a solution of 4-(hexadecyloxy)benzoic acid (1 mmol), hydroxyl-functionalized triphenylene **3** (1 mmol), and *N,N'*-dicyclohexylcarbodiimide (DCC) (1.5 mmol) in

dry dichloromethane was added a catalytic amount of 4-dimethylaminopyridine (DMAP). The reaction mixture was stirred at room temperature for 48 h. After the completion of the reaction, as monitored by TLC, the solvent was evaporated and the crude product was purified by silica gel (100-200 mesh size) chromatography using 2% ethyl acetate in hexane as eluant. The final product was achieved by recrystallization from hexane. Yield: 66%. ^1H NMR (400 MHz, CDCl_3): δ : 7.98 (d, $J = 8.8\text{Hz}$, 2H, Ar-H), 7.84 (s, 6H, Ar-H), 6.88 (d, $J = 2\text{Hz}$, 2H, Ar-H), 4.29 (m, 14H, $-\text{OCH}_2-$), 3.38 (t, $J = 6.8\text{Hz}$, 2H, $-\text{COOCH}_2-$), 1.96-1.26 (m, 66H, $-\text{CH}_2-$), 1.04 (t, $J = 7.2\text{Hz}$, 18H, $-\text{CH}_3$). Elemental analysis calculated for $\text{C}_{72}\text{H}_{110}\text{O}_9$ (Mol. Wt.: 1119.64) C, 77.24; H, 9.90 %. Found C, 77.31; H, 9.97 %.

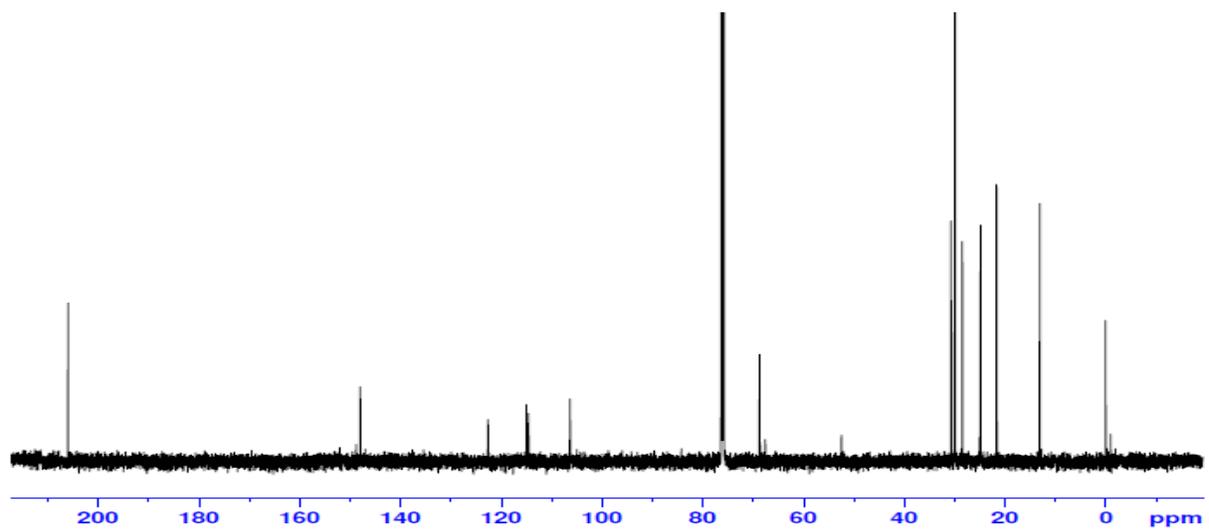
Compound (5b): IR: 2924, 2854, 1716, 1508, 1456, 1263, 1172, 837 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ : 8.08 (d, $J = 8.4\text{Hz}$, 2H, Ar-H), 7.83 (s, 6H, Ar-H), 7.62 (d, $J = 8.4\text{Hz}$, 2H, Ar-H), 7.51 (d, $J = 8.0\text{Hz}$, 2H, Ar-H), 7.23 (s, 2H, Ar-H), 4.34 (t, $J = 6.4\text{Hz}$, 2H, $-\text{COOCH}_2-$), 4.22 (t, $J = 6.4\text{Hz}$, 12H, $-\text{OCH}_2-$), 2.63 (t, $J = 7.6\text{Hz}$, 2H, Ar- CH_2-), 1.96-1.25 (m, 66H, $-\text{CH}_2-$), 0.93 (t, $J = 6.8\text{Hz}$, 18H, $-\text{CH}_3$). Elemental analysis calculated for $\text{C}_{78}\text{H}_{114}\text{O}_8$ (Mol Wt: 1179.73) C, 79.41; H, 9.74; Found C, 79.50; H, 9.85 %.

Compound (5c) ^[31]: IR: 2922, 2852, 1716, 1581, 1454, 1377, 1261, 1172, 721 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ : 8.12 (m, 2H, Ar-H), 7.84 (s, 6H, Ar-H), 7.68-7.38 (m, 10H, Ar-H), 4.35 (t, $J = 6.4\text{Hz}$, 2H, $-\text{COOCH}_2-$), 4.23 (t, $J = 6.4\text{Hz}$, 12H, $-\text{OCH}_2-$), 2.63 (t, $J = 7.6\text{Hz}$, 2H, Ar- CH_2-), 1.96-1.25 (m, 58H, $-\text{CH}_2-$), 0.93 (t, $J = 5.4\text{Hz}$, 18H, $-\text{CH}_3$). ^{13}C -NMR (100 MHz, CDCl_3): 149.05, 130.12, 128.86, 127.61, 127.07, 126.86, 123.67, 107.47, 69.77, 65.11, 31.71, 29.47, 29.36, 29.26, 28.78, 26.12, 26.02, 25.88, 22.68, 14.07; Elemental analysis calculated for $\text{C}_{80}\text{H}_{110}\text{O}_8$ (Mol Wt: 1199.72) C, 80.09; H, 9.24. Found C 76.19, H 9.77%.

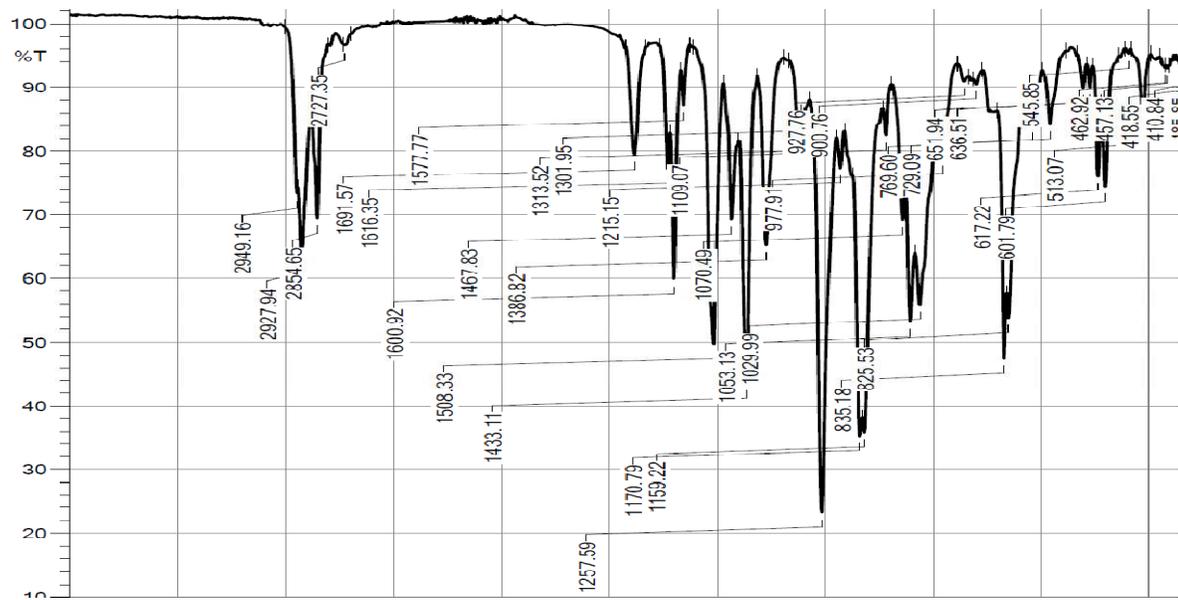
¹H-NMR of (4a)



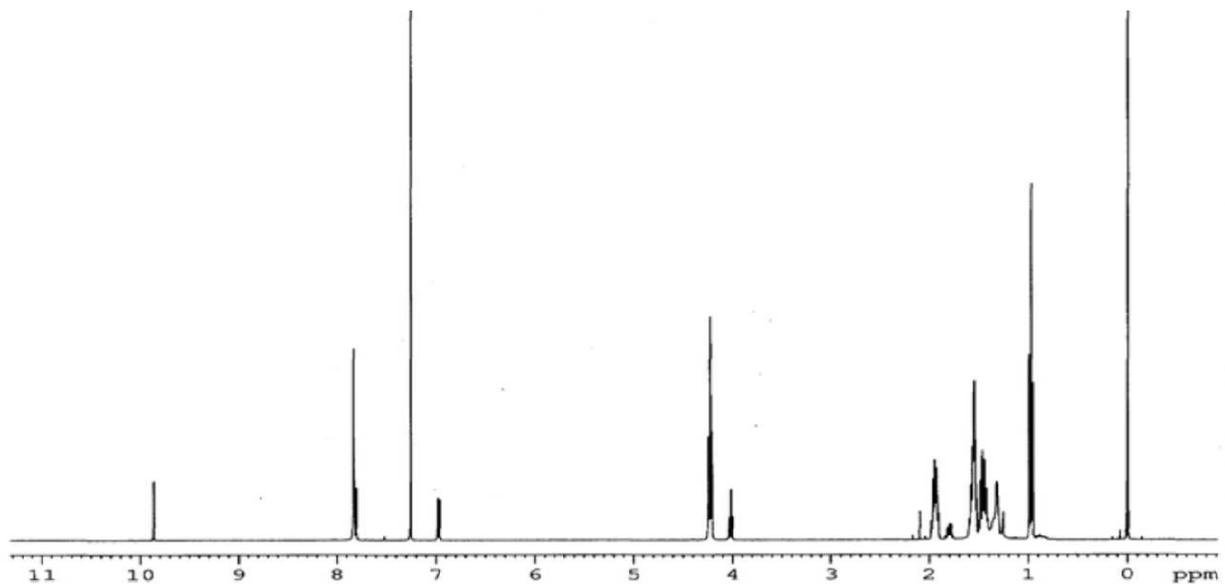
¹³C-NMR of (4a)



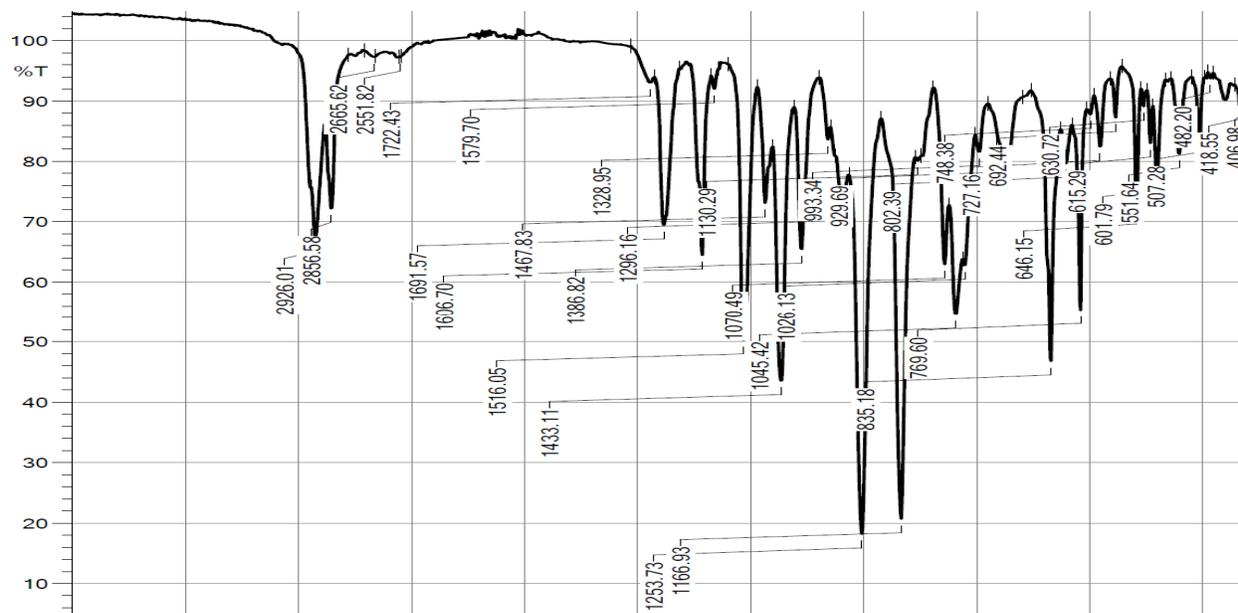
IR of (4b)



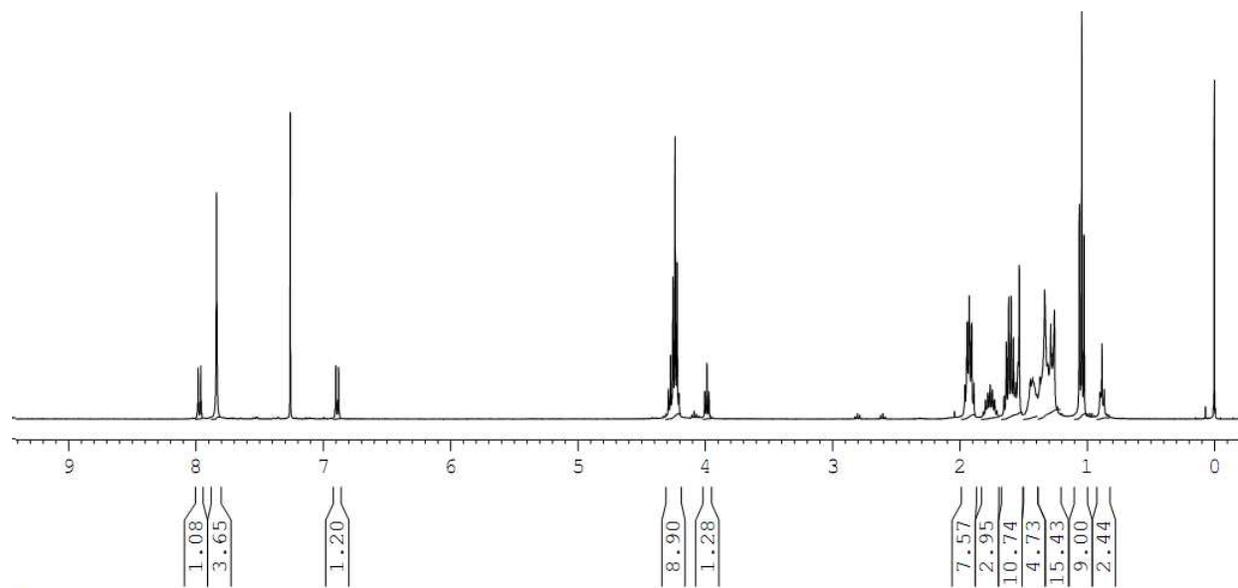
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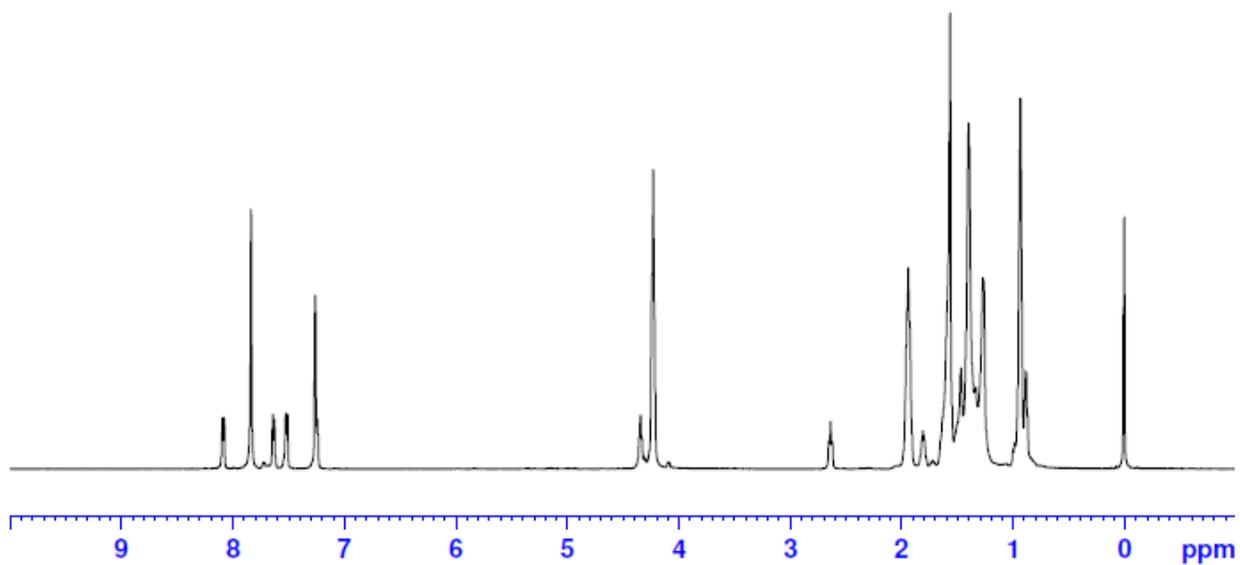
IR of (4c)



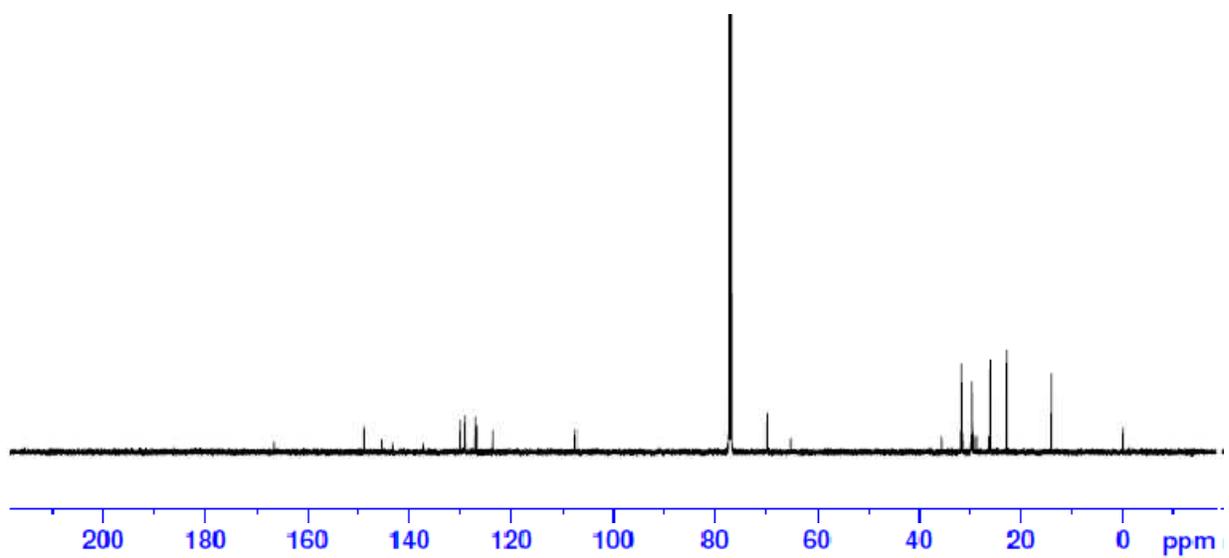
¹H NMR of (5a)



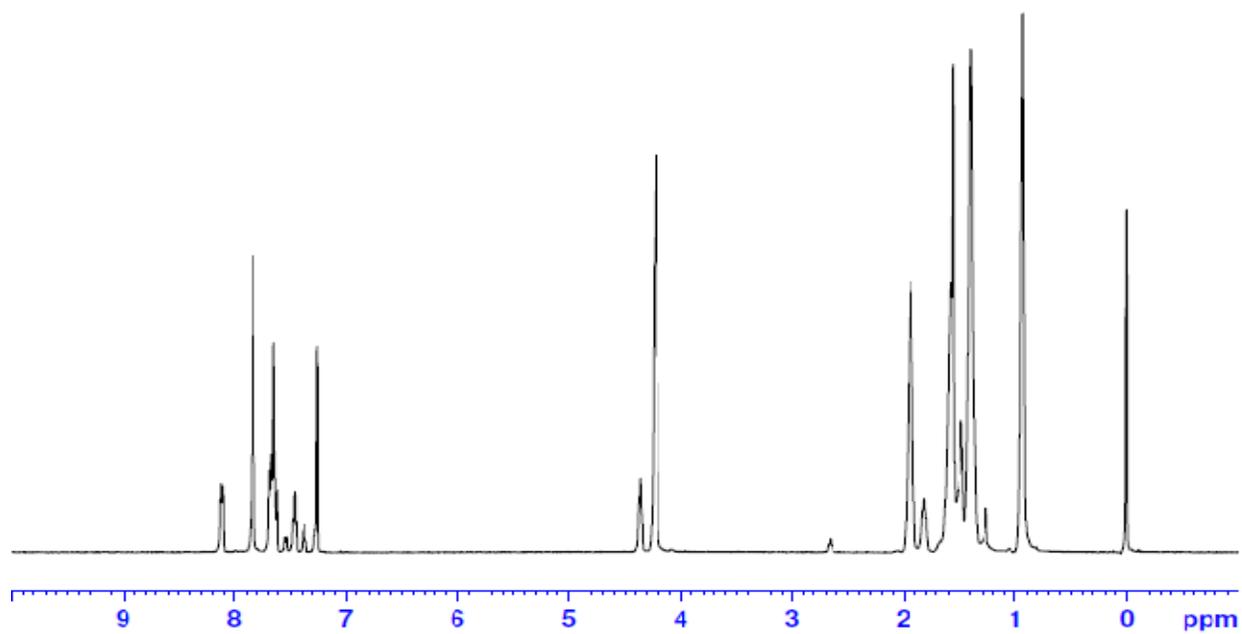
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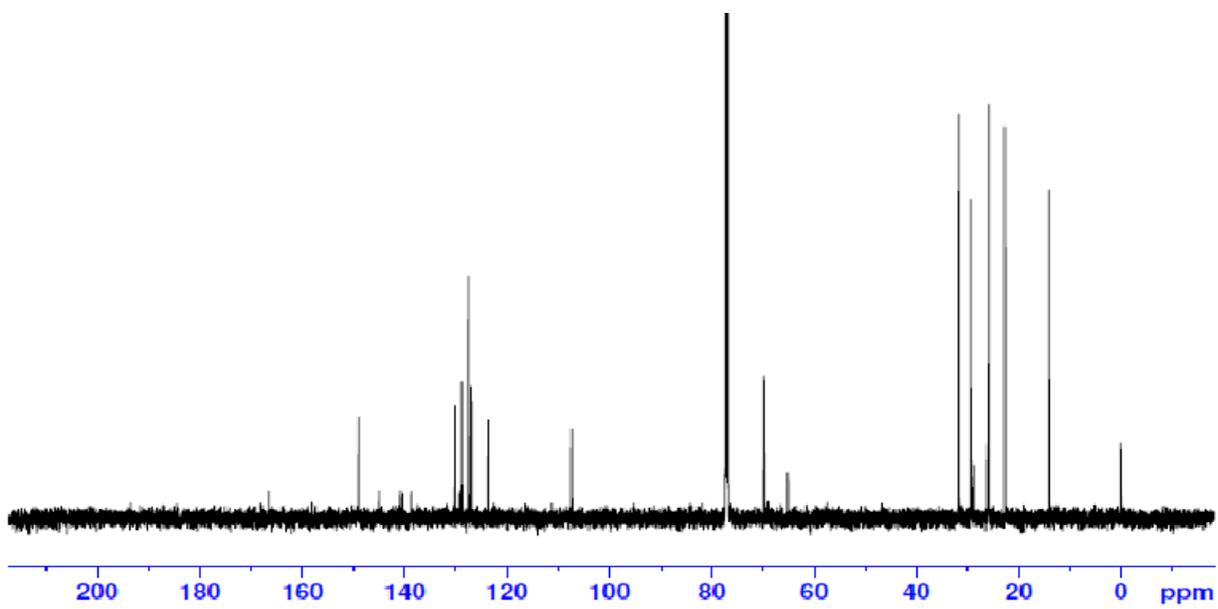
¹³C-NMR of (5b)



¹H-NMR of (5c)



¹³C-NMR of (5c)



[31] B. K. Sadashiva, G. S. R. Subba Rao. *Mol. Cryst. Liq. Cryst.* **1977**, 38, 345-352.