



Supporting Information

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Novel Annulated Triphenylene Discotic Liquid Crystals Generated by Pictet-Spengler Cyclization

Marichandran Vadivel, Irla Siva Kumar, K Swamynathan, V A Raghunathan, and
Sandeep Kumar*

Experimental details

All the chemicals and reagents were purchased from Sigma Aldrich and used directly. The AR grade solvents were distilled and dried using corresponding protocols before usage. The crude products were subjected to column chromatography using silica gel (100-200 mesh) and recrystallized using suitable solvents. All the intermediates and final products structure were confirmed by NMR, Mass, Elemental analysis. ^1H NMR and ^{13}C NMR (Nuclear magnetic resonance spectroscopy) were recorded on Bruker 500MHz instrument using CDCl_3 as solvent and trimethyl silane as internal standard. Chemical shift values are given in ppm and the solvent CDCl_3 peaks appear at ^1H NMR: $\delta = 7.23$ ppm and ^{13}C NMR $\delta = 77.0$ ppm. Peak multiplicity is given as s = singlet, d = doublet, t = triplet, m = multiplet, b = broad peak. Mass spectra were recorded on a MicroMassESI-TOF spectrometer. Elemental analysis was done by using Elementar Vario MICRO Select instrument. Samples were placed between the glass slides and kept inside Mettler FP82HT hot stage which is controlled by Mettler FP90 central processor and the liquid crystal textures were recorded using Olympus BX51 polarising optical microscope (Olympus, Tokyo, Japan). Mettler Toledo DSC instrument was used to record the phase transition temperatures of all the compounds. The peak temperatures are given in $^{\circ}\text{C}$ and corresponding enthalpy values are given in J g^{-1} . Panalytical (Empyrean) X-ray diffractometer was used to further confirm the mesophase structure of all compounds. Absorption studies were carried out by Perkin Elmer UV-Vis-lambda 35 double-beam spectrophotometer. Emission spectra obtained from fluoromax-4 spectrofluorometer. Thermal stability of all the compounds was studied using TGA 4000 thermo gravimetric analysis instrument.

Synthesis of 2: To the mixture of Catechol (10g, 90.8 mmol, 1 eq) Potassium carbonate (50.20g, 363.2 mmol, 4eq) in acetone (100 ml), was added 1-bromobutane (27.37g, 199.7 mmol, 2.2 eq). The mixture was refluxed for 48 hours and filtered upon cooling. The filtrate

was extracted with dichloromethane and the organic layer was washed with brine, dried over Na_2SO_4 and evaporated using vacuum to give a crude product. The crude was then purified by column chromatography using petroleum ether: dichloromethane (90 :10) as eluent to get desired product as colourless liquid (80%). ^1H NMR (500 MHz, CDCl_3), δ (ppm) = 6.92 (s, 4 H), 4.03 (t, J = 6.5 Hz, 4H), 1.83 (m, 4H), 1.54 (m, 4H), 1.01 (t, J = 7.5 Hz, 6H). ^{13}C NMR (500 MHz, CDCl_3), δ (ppm) = 149.3, 121.05, 114.3, 69.0, 31.4, 19.3, 13.9. Elemental analysis: C, 75.63; H, 9.97; (calcd.); C, 74.40; H, 10.11; (expt.).

Synthesis of 3: Compound 2 (10g, 44.9 mmol, 1eq) was added dropwise to a solution of Ferric chloride (21.84g, 134.7 mmol, 3eq) in dichloromethane (150 ml) and catalytic amount of Conc. H_2SO_4 . The mixture was stirred at room temperature for an hour and poured on to cold methanol (500 ml). The mixture then was kept inside the fridge for few hours and the crude solid product was filtered and washed with ethanol. The crude was purified by column chromatography using petroleum ether: dichloromethane (90:10) as eluent and recrystallized using ethanol to get white solid (72%). ^1H NMR (500 MHz, CDCl_3), δ (ppm) = 7.76 (s, 6H), 4.16 (s, 12H), 1.85 (m, 12H), 1.53 (m, 12H), 0.98 (m, J = 7.0 Hz, 18H). ^{13}C NMR (500 MHz, CDCl_3), δ (ppm) = 149.0, 123.6, 107.4, 69.4, 31.5, 19.4, 14.0. M. P = 148 °C. Elemental analysis: C, 76.33; H, 9.15; (calcd.); C, 76.15; H, 9.45; (expt.).

Synthesis of 4^[1]: 70% HNO_3 (0.6809g, 7.564 mmol, 1eq) was added slowly to a solution of compound 3 (5g, 7.564 mmol, 1eq) in dichloromethane/nitromethane (50ml /10ml) and stirred for 15 minutes at room temperature. Solution of sodium bicarbonate was added after 15 min and the mixture was extracted using dichloromethane. The organic layer was washed with brine, dried in Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude was purified using column chromatography using petroleum ether: dichloromethane (1:1) as eluent. Recrystallization using methanol to give yellow solid (76%). ^1H NMR (500 MHz,

CDCl₃), δ (ppm) = 7.93 (s, 1H), 7.82 (s, 1H), 7.79 (s, 2H), 7.51 (s, 1H), 4.25 (m, 12H), 1.8-2 (m, 12H), 1.5-1.7 (m, 12H), 1.0-1.1 (m, 18H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm) = 150.5, 150.3, 149.1, 149.0, 143.9, 140.6, 126.7, 124.8, 124.4, 122.0, 119.4, 114.4, 108.0, 107.5, 107.4, 107.1, 106.6, 75.0, 69.7, 69.4, 69.1, 69.0, 68.5, 32.1, 31.5, 31.4, 31.3, 31.1, 19.4, 19.35, 19.33, 19.31, 19.0, 13.94, 13.90, 13.86. M. P = 143 °C. Elemental analysis: C, 71.46; H, 8.42; N, 2.07 (calcd.); C, 71.44; H, 8.71; N, 1.89 (expt.).

Synthesis of 5^[2]: Raney Ni (4.98g, 84.99 mmol, 20 eq) was added to the solution of compound 4 (3g, 4.249 mmol, 1eq) in THF: Ethanol (1:1). The reaction mixture was stirred at room temperature and hydrogen atmosphere. The conversion from nitro to amine was monitored using TLC. After completion of the reaction, the catalyst was removed by filtration. The solvent was evaporated under reduced pressure and purified by column chromatography using dichloromethane as eluent. Recrystallization using methanol to give greyish white solid (90%). ¹H NMR (500 MHz, CDCl₃), δ (ppm) = 8.74 (s, 1H), 7.76 (s, 1H), 7.72 (s, 1H), 7.70 (s, 1H), 7.30 (s, 1H), 4.53 (broad peak, 2H), 4.1 (m, 12H), 1.80 (m, 12H), 1.52 (m, 12H), 0.96 (m, 18H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm) = 150.8, 149.4, 148.8, 147.9, 147.4, 138.2, 135.5, 126.9, 124.6, 124.4, 123.9, 123.8, 113.9, 110.2, 108.4, 108.1, 107.0, 97.3, 72.8, 69.6, 69.3, 69.0, 68.3, 32.6, 31.6, 31.5, 31.49, 31.46, 31.44, 19.5, 19.42, 19.39, 19.35, 14.00, 13.95, 13.93. M. P = 102 °C. Elemental analysis: C, 74.63; H, 9.10; N, 2.07 (calcd.); C, 74.58; H, 9.08; N, 1.86 (expt.)

General procedure for the synthesis of compound 6:

A mixture of compound 5 (1eq) and aldehyde (2eq) in dry DMF (10 ml) and 1% triflic acid were heated to 100 °C. The reaction was monitored using TLC. Water (20ml) was added to the reaction mixture after completion of the reaction. The mixture was alkalized with 15% NaOH solution and extracted using dichloromethane and washed with brine. The organic

layer was dried using anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography using petroleum ether: ethyl acetate (90:10) as eluent to give yellow solid (60%).

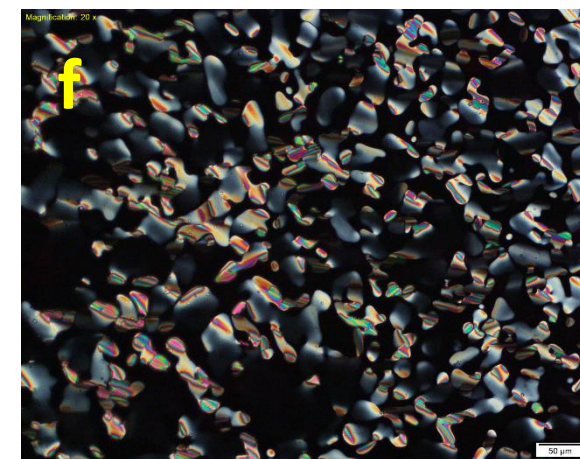
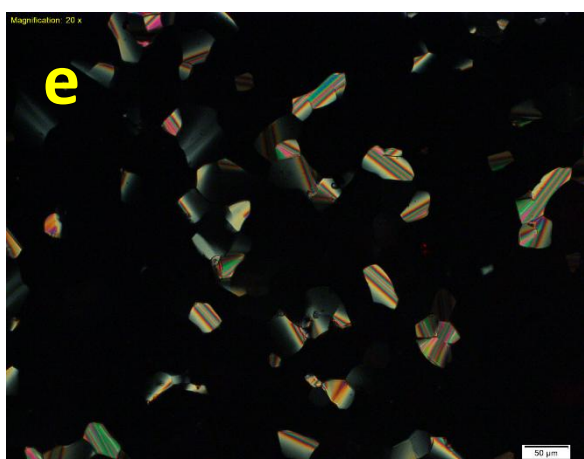
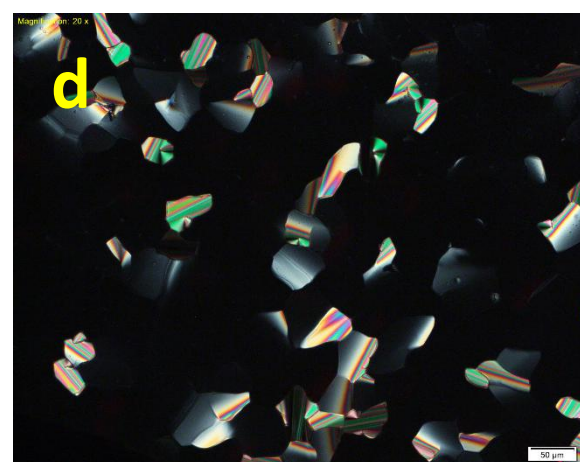
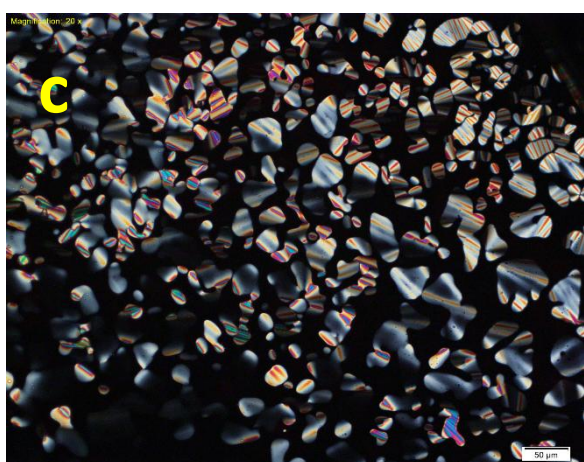
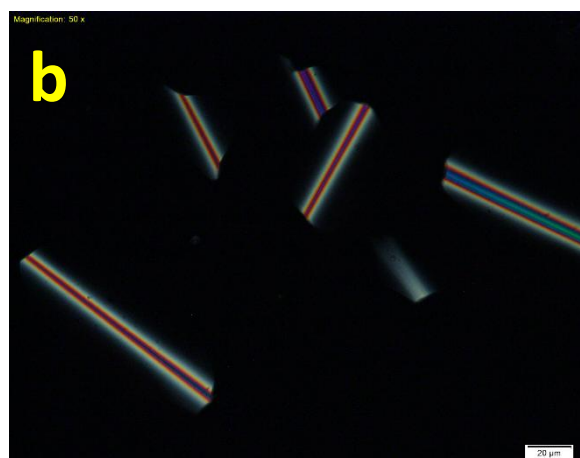
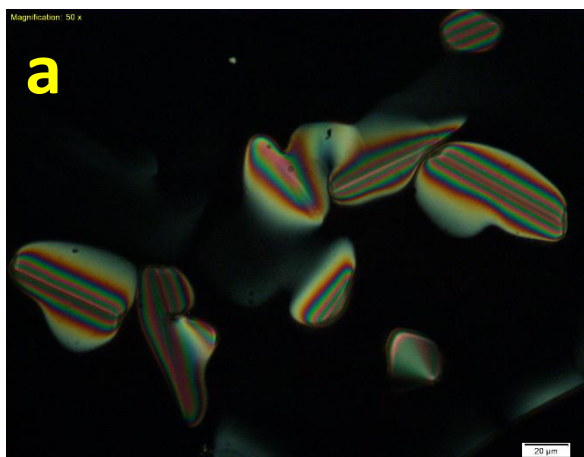
Compound 6a: **5** (0.500g, 0.739mmol, 1eq), benzaldehyde (0.156g, 1.479 mmol, 2eq), DMF 10 ml, 1% triflic acid, yield: 56%. ^1H NMR (500 MHz, CDCl_3), δ (ppm) = 8.35 (s, 1H), 8.16 (s, 1H), 7.94 (s, 2H), 7.68 (m, 2H), 7.36 (m, 3H), 4.41 (t, J = 6.0 Hz, 2H), 4.2-4.3 (m, 8H), 3.48 (t, J = 6 Hz, 2H), 1.8-1.9 (m, 10H), 1.56 (m, 12H), 0.87-1.05 (m, 18H), 0.70 (t, J = 6.7 Hz, 3H). ^{13}C NMR (500 MHz, CDCl_3), δ (ppm) = 158.5, 151.5, 150.9, 150.0, 149.5, 145.2, 144.4, 144.0, 136.3, 129.4, 127.4, 126.9, 124.5, 124.1, 123.3, 123.2, 122.6, 117.9, 113.7, 110.5, 108.7, 107.7, 107.0, 75.1, 74.4, 70.9, 69.5, 69.2, 32.5, 31.8, 31.6, 31.5, 31.4, 31.2, 19.4, 19.3, 19.3, 18.9, 13.9, 13.9, 13.8. ESI-MS: m/z calcd: 762.47, found: 762.47. M.P = 149 °C. Elemental analysis: C, 77.23; H, 8.33; N, 1.84 (calcd.); C, 76.82; H, 8.52; N, 1.74 (expt.).

Compound 6b: **5** (0.500g, 0.739mmol, 1eq), 4-methoxy benzaldehyde (0.201g, 1.479 mmol, 2eq), DMF 10 ml, 1% triflic acid, yield: 61%. ^1H NMR (500 MHz, CDCl_3), δ (ppm) = 8.43 (s, 1H), 8.23 (s, 1H), 8.04 (s, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 4.52 (t, J = 6.2 Hz, 2H), 4.33 - 4.42 (m, 8H), 3.93 (s, 3H), 3.59 (m, 2H), 1.91-1.99 (m, 10H), 1.68 (m, 11H), 1-1.17 (m, 19H), 0.81 (t, J = 6.5 Hz, 3H). ^{13}C NMR (500 MHz, CDCl_3), δ (ppm) = 159.5, 158.0, 151.5, 150.9, 150.0, 149.6, 145.3, 144.3, 136.6, 139.4, 131.0, 124.6, 124.2, 123.3, 123.2, 122.8, 117.8, 113.7, 112.5, 110.5, 108.6, 107.7, 107.1, 75.1, 74.6, 71.0, 69.6, 69.6, 69.2, 55.4, 32.6, 31.9, 31.6, 31.5, 31.4, 31.4, 19.4, 19.0, 14.0, 13.9, 13.8. ESI-MS: m/z calcd: 792.48, found: 792.48. M.P = 145 °C. Elemental analysis: C, 75.82; H, 8.27; N, 1.77 (calcd.); C, 75.43; H, 8.22; N, 1.85 (expt.).

Compound 6c: **5** (0.500g, 0.739mmol, 1eq), 3, 4-dimethoxy benzaldehyde (0.245g, 1.479 mmol, 2eq), DMF 10 ml, 1% triflic acid, yield: 59%. ^1H NMR (500 MHz, CDCl_3), δ (ppm) =

8.33 (s, 1H), 8.14 (s, 1H), 7.94 (s, 2H), 7.39 (s, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 4.42 (t, $J = 6.0$ Hz, 2H), 4.22 - 4.32 (m, 8H), 3.89 (d, $J = 4.5$ Hz, 6H), 3.53 (s, 2H), 1.8 - 1.9 (m, 10H), 1.52 - 1.59 (m, 11H), 1.0 (m, 4H), 0.95 - 1.01 (m, 12H), 0.88 - 0.91 (t, 3H), 0.71 (t, 3H). ^{13}C NMR (500 MHz, CDCl_3), δ (ppm) = 158.0, 151.5, 151.0, 150.1, 149.6, 149.1, 147.9, 145.5, 144.4, 136.8, 136.3, 124.5, 124.1, 123.3, 123.2, 122.9, 122.8, 117.8, 113.7, 113.3, 110.9, 110.1, 108.6, 107.7, 107.1, 75.0, 74.6, 71.0, 69.8, 69.6, 69.2, 56.1, 56.0, 32.7, 31.9, 31.7, 31.5, 31.4, 31.45, 19.4, 19.3, 19.0, 14.0, 13.9, 13.92, 13.8. ESI-MS: m/z calcd: 822.49, found: 822.49. M.P = 139 °C. Elemental analysis: C, 74.51; H, 8.22; N, 1.70 calculated (%): C, 74.21; H, 8.44; N, 1.56(expt. %)

Compound 6d: 5 (0.500g, 0.739mmol, 1eq), 3, 4, 5-trimethoxy benzaldehyde (0.29g, 1.479 mmol, 2eq), DMF 10 ml, 1% triflic acid, yield: 56%. ^1H NMR (500 MHz, CDCl_3), δ (ppm) = 8.34 (s, 1H), 8.16 (s, 1H), 7.94 (s, 2H), 6.93 (s, 2H), 4.41 (t, $J = 6.2$ Hz, 2H), 4.23 - 4.32 (m, 8H), 3.87 (s, 3H), 3.83 (s, 6H), 3.61 (s, 2H), 1.80 - 1.89 (m, 10H), 1.52 - 1.58 (m, 12H), 1.18 - 1.21 (m, 2H), 1.12 (m, 4H), 0.96 - 1.01 (m, 12H), 0.88 (m, 3H), 0.75 - 0.80 (m, 3H). ^{13}C NMR (500 MHz, CDCl_3), δ (ppm) = 158.1, 152.2, 151.6, 151.0, 150.1, 149.6, 145.5, 144.3, 139.8, 138.1, 136.2, 124.4, 124.1, 123.3, 122.8, 117.8, 113.8, 111.4, 108.8, 107.7, 107.2, 107.0, 75.0, 74.4, 71.0, 70.0, 69.6, 69.2, 61.0, 56.3, 32.6, 31.9, 31.7, 31.5, 31.4, 29.7, 19.43, 19.4, 19.0, 14.0, 13.9. ESI-MS: m/z calcd: 852.12, found: 852.61. M.P = 128°C. Elemental analysis: C, 73.30; H, 8.16; N, 1.64 calculated (%): C, 73.21; H, 8.13; N, 1.44 (expt. %).



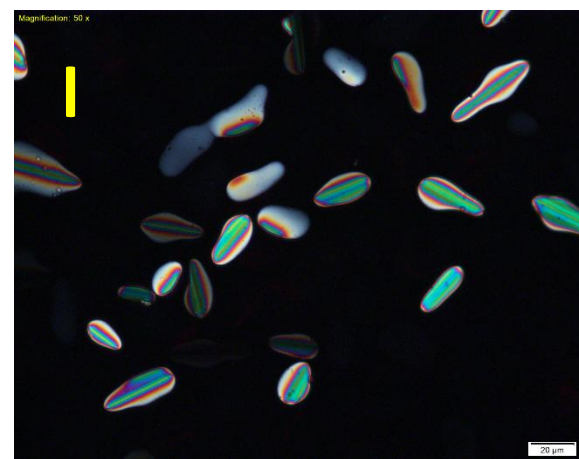
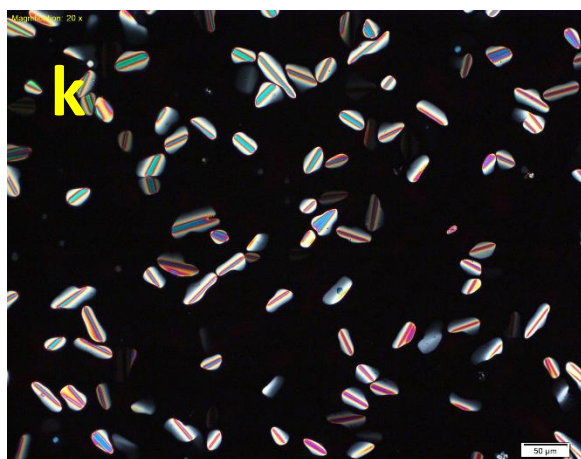
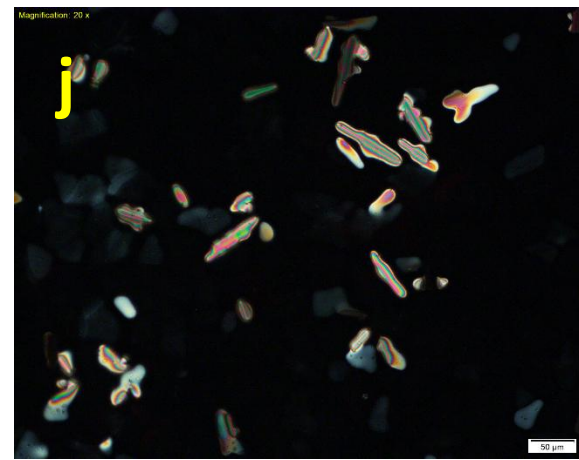
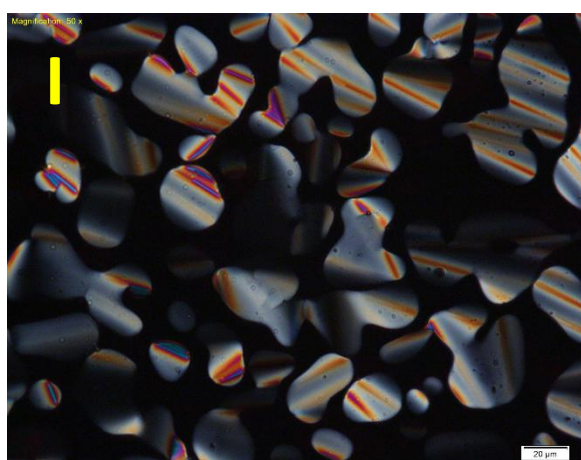
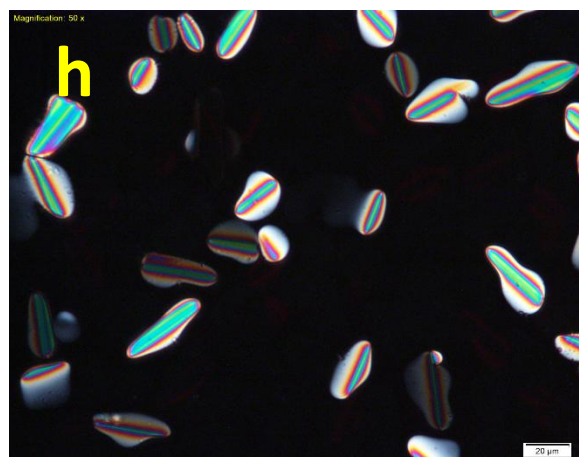
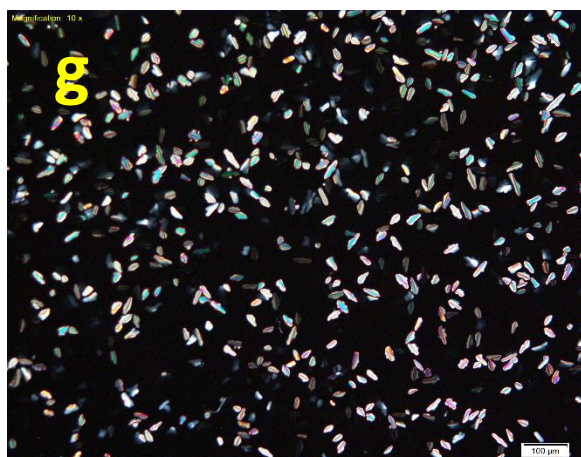
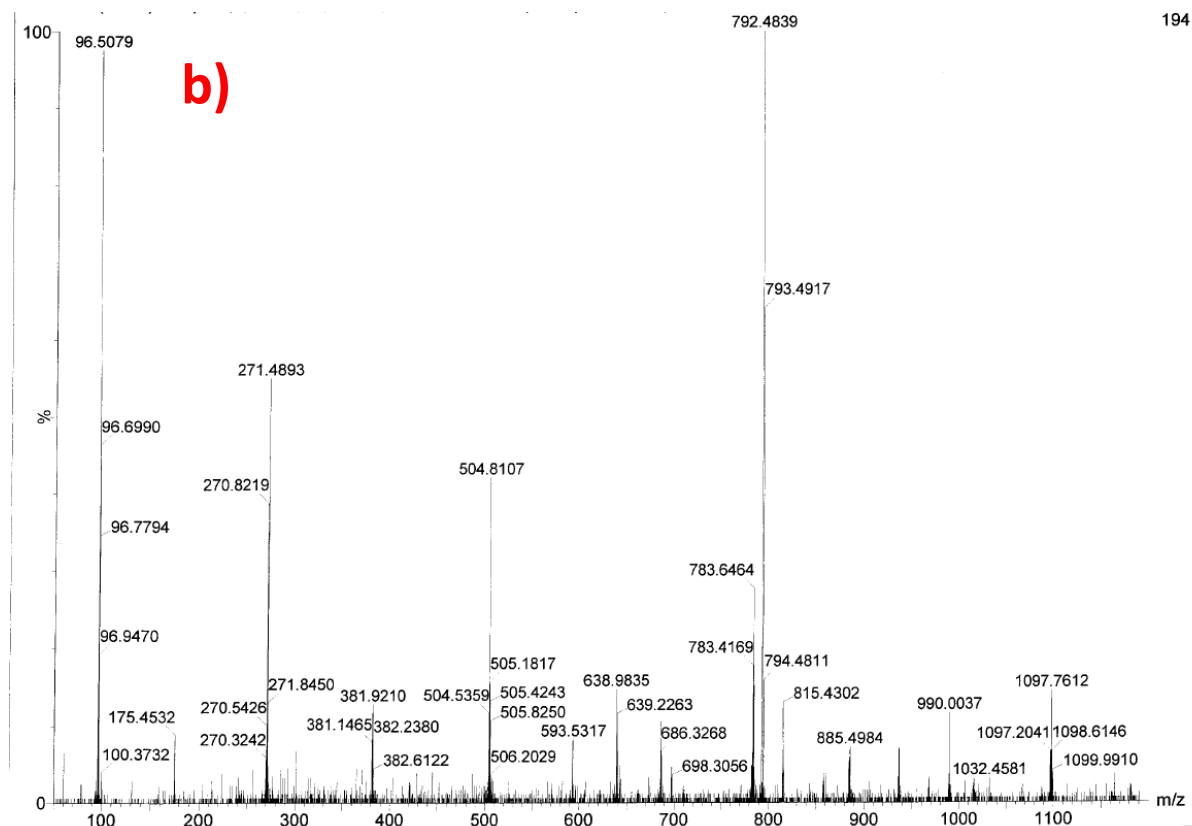
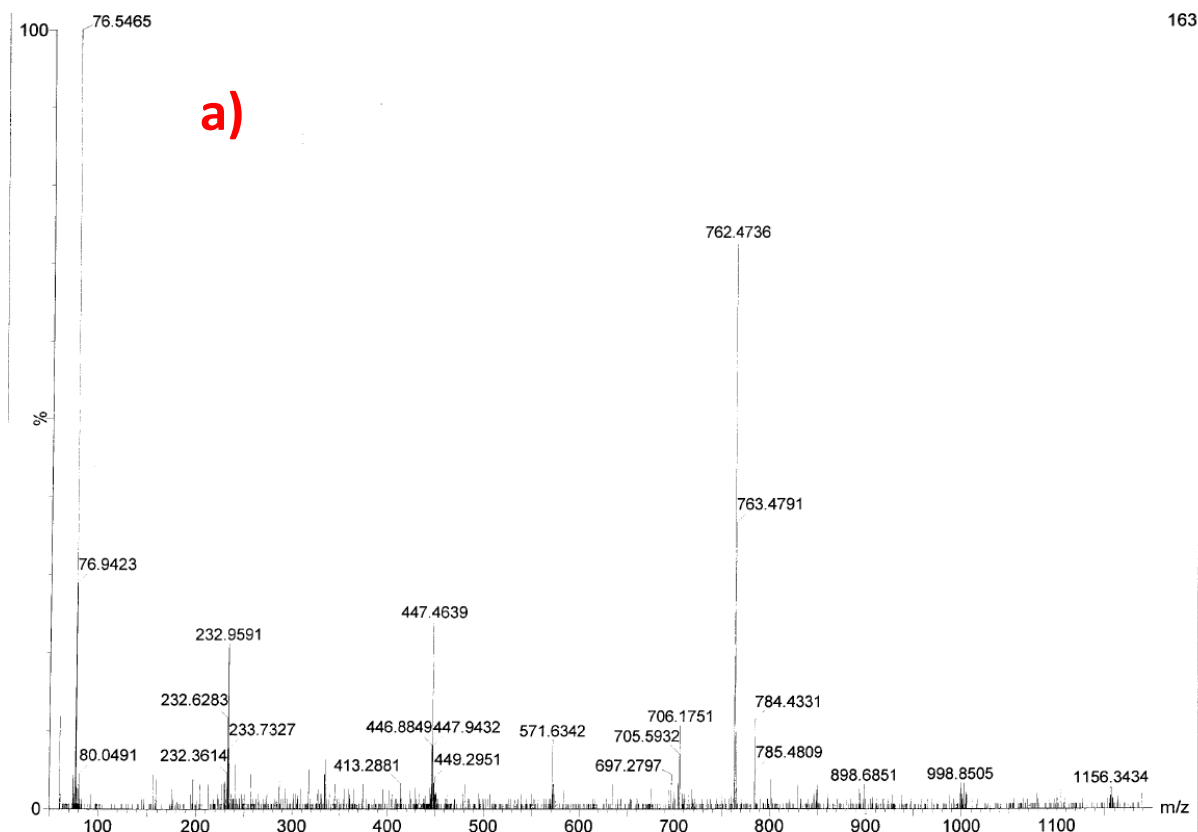


Figure S4: Mosaic texture was observed for four compounds under POM upon Colling from the isotropic phase: **a**, **b**, **c**, and **d** for compound **6a** at different temperatures. **e**, **f**, **g**, and **h** compound **6c**. **i**, **j**, **k** and **l** for compound **6d**.

d observed	d calculated	hkl	a=19.15Å c= 31.56Å
16.58	16.58	100	
14.42	14.69	101	
9.54	9.57	110	
8.26	8.29	200	
7.89	7.89	004	
7.56	7.36	202	
6.24	6.27	210	
4.28	4.50	007	
3.76	3.94	008	
3.52	3.50	009	
3.36	3.15	0010	

TableS1: Indexation of Col_{hp} XRD pattern of compound 6b



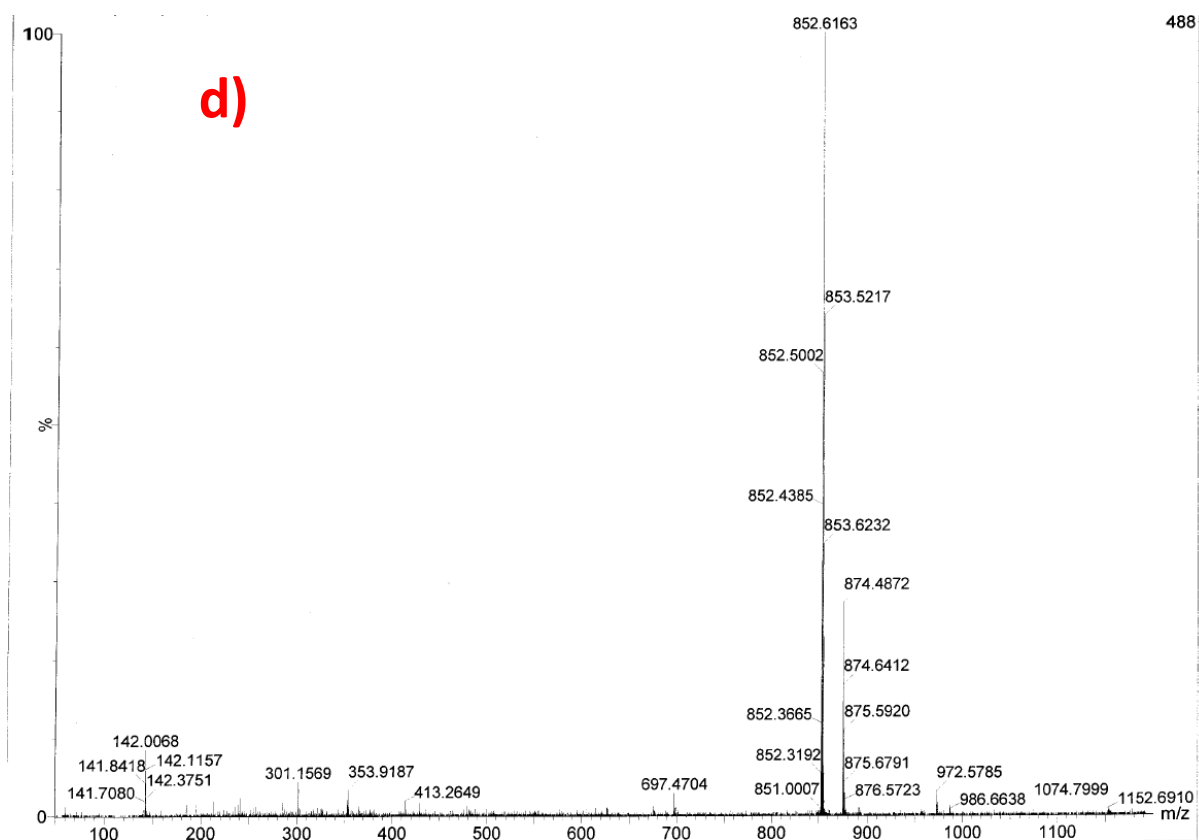
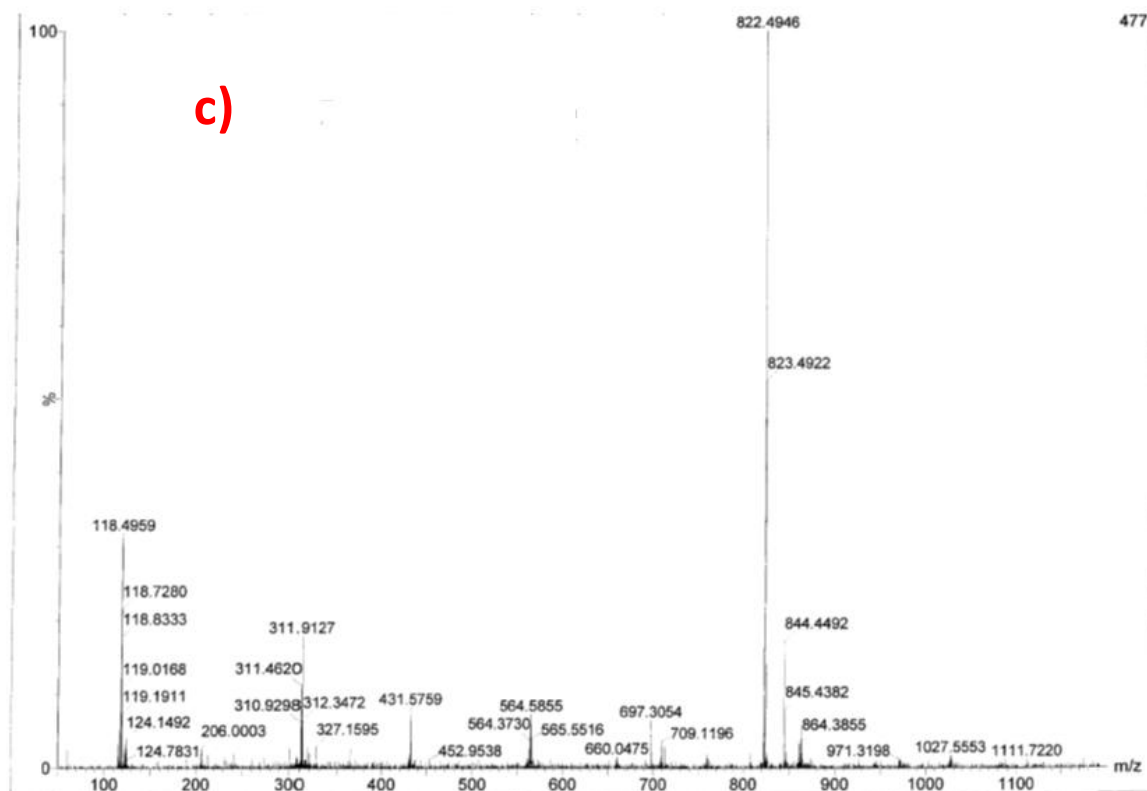


Figure S7: HR-MS Mass spectra of a) 6a, b) 6b, c) 6c and d) 6d

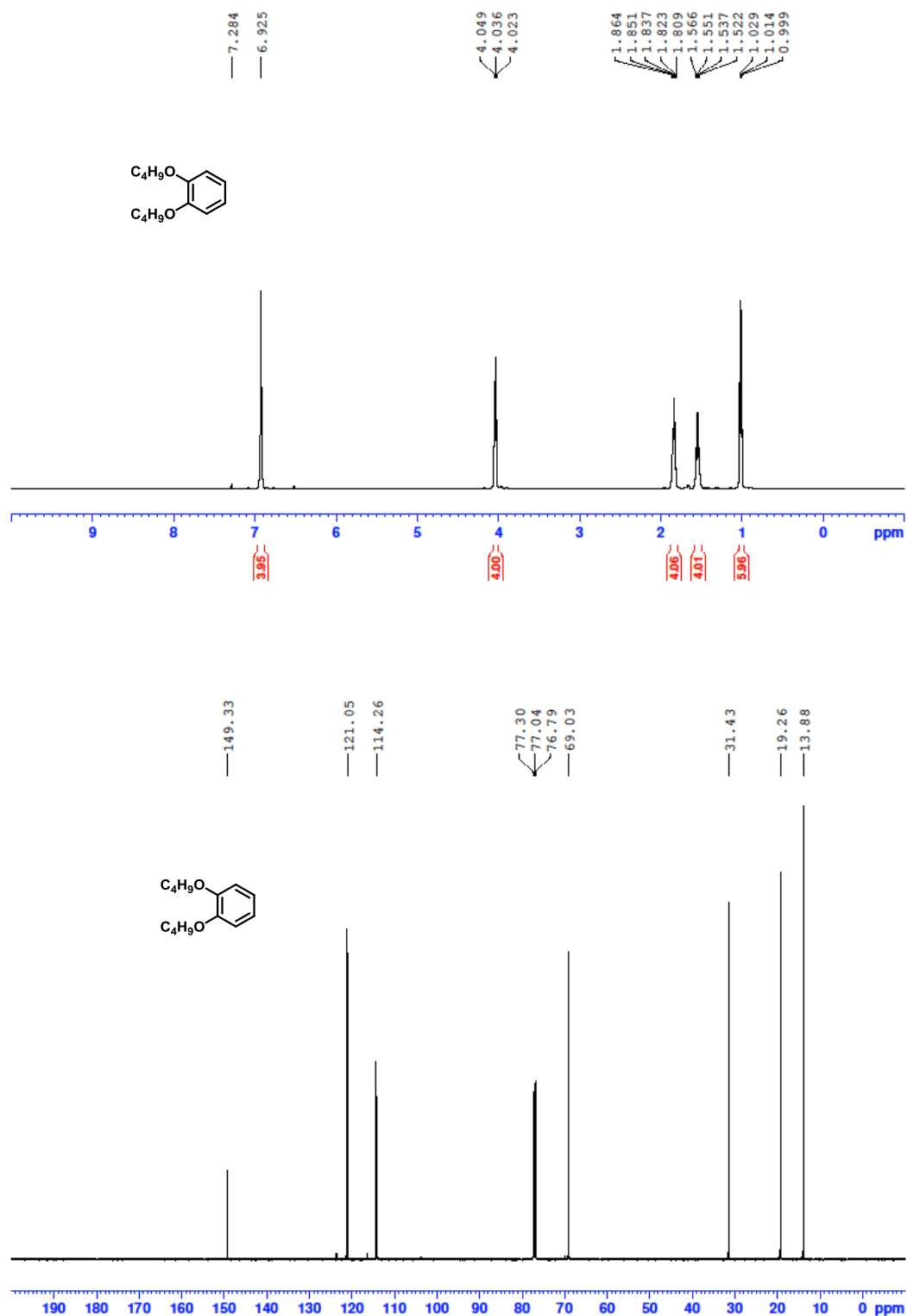
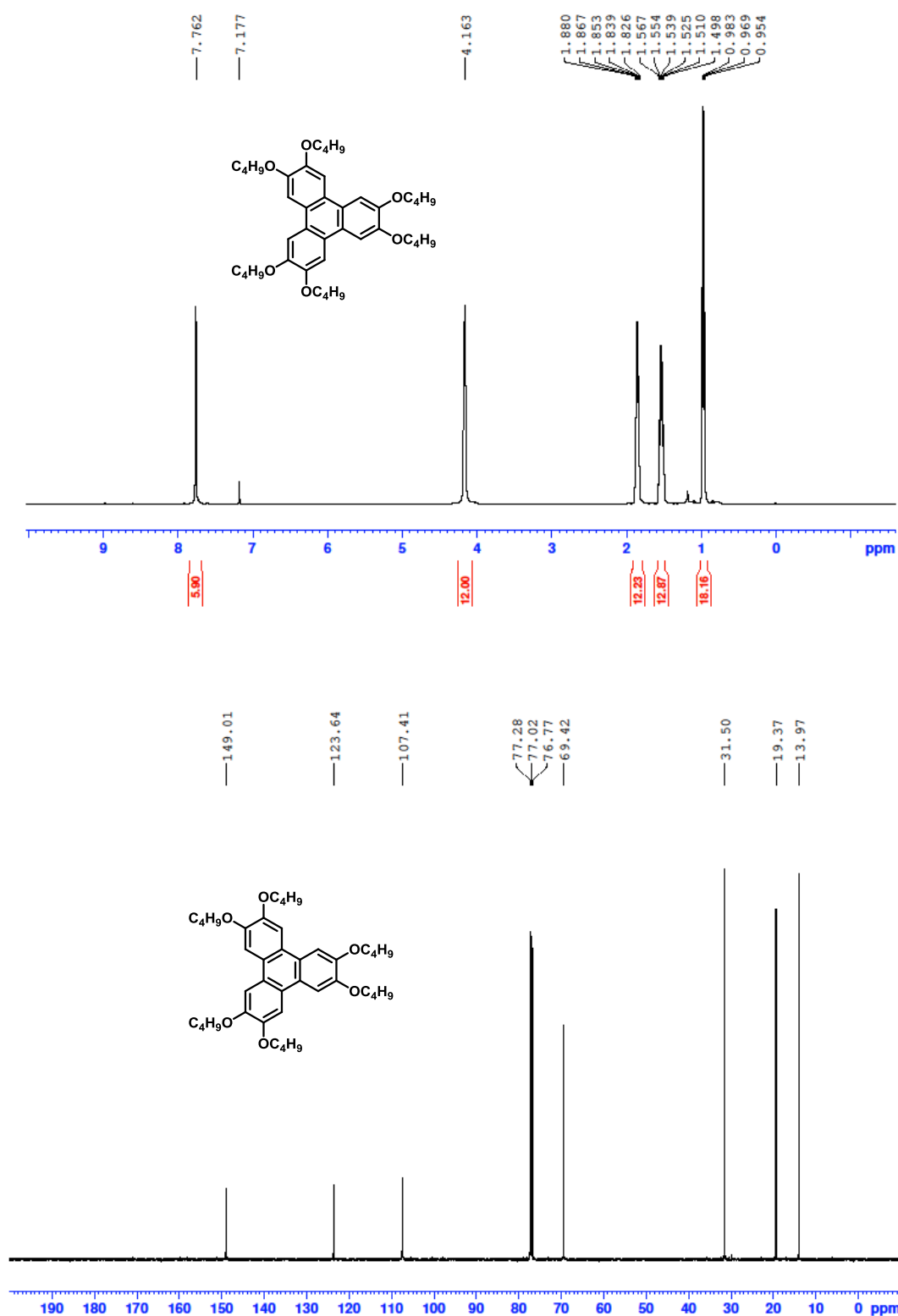
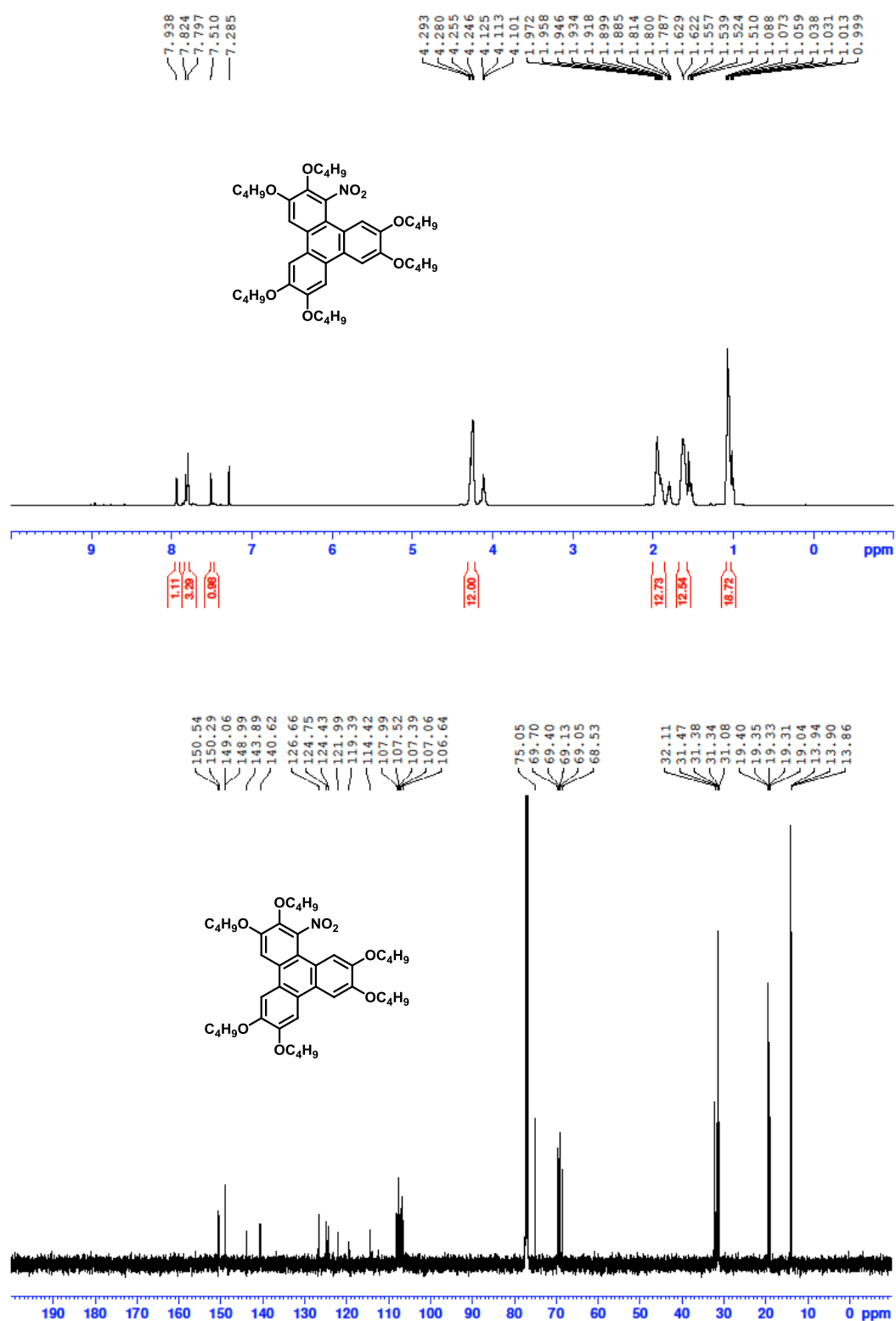


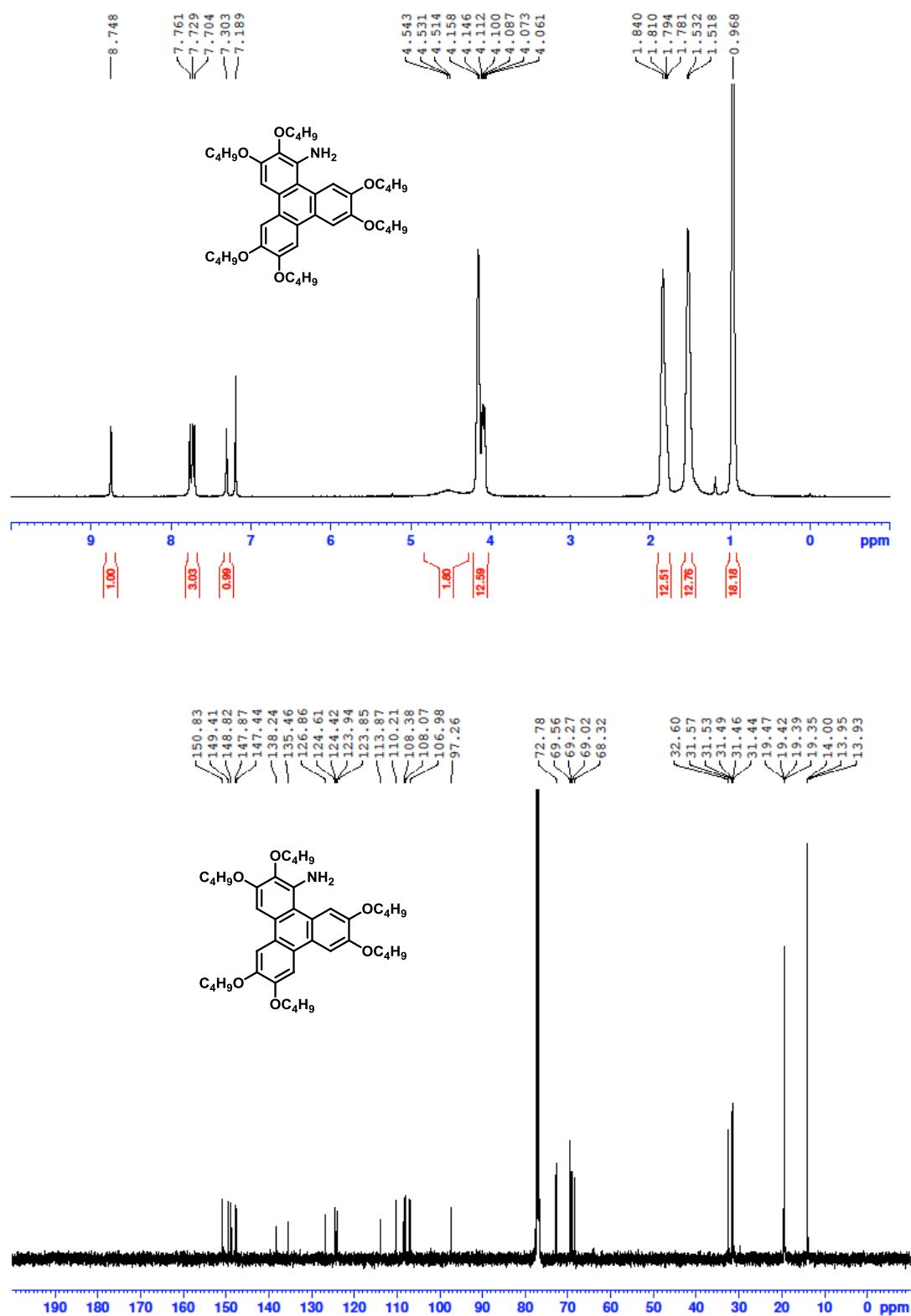
Figure S8: ^1H (top) and ^{13}C -NMR (bottom) spectra of **2**



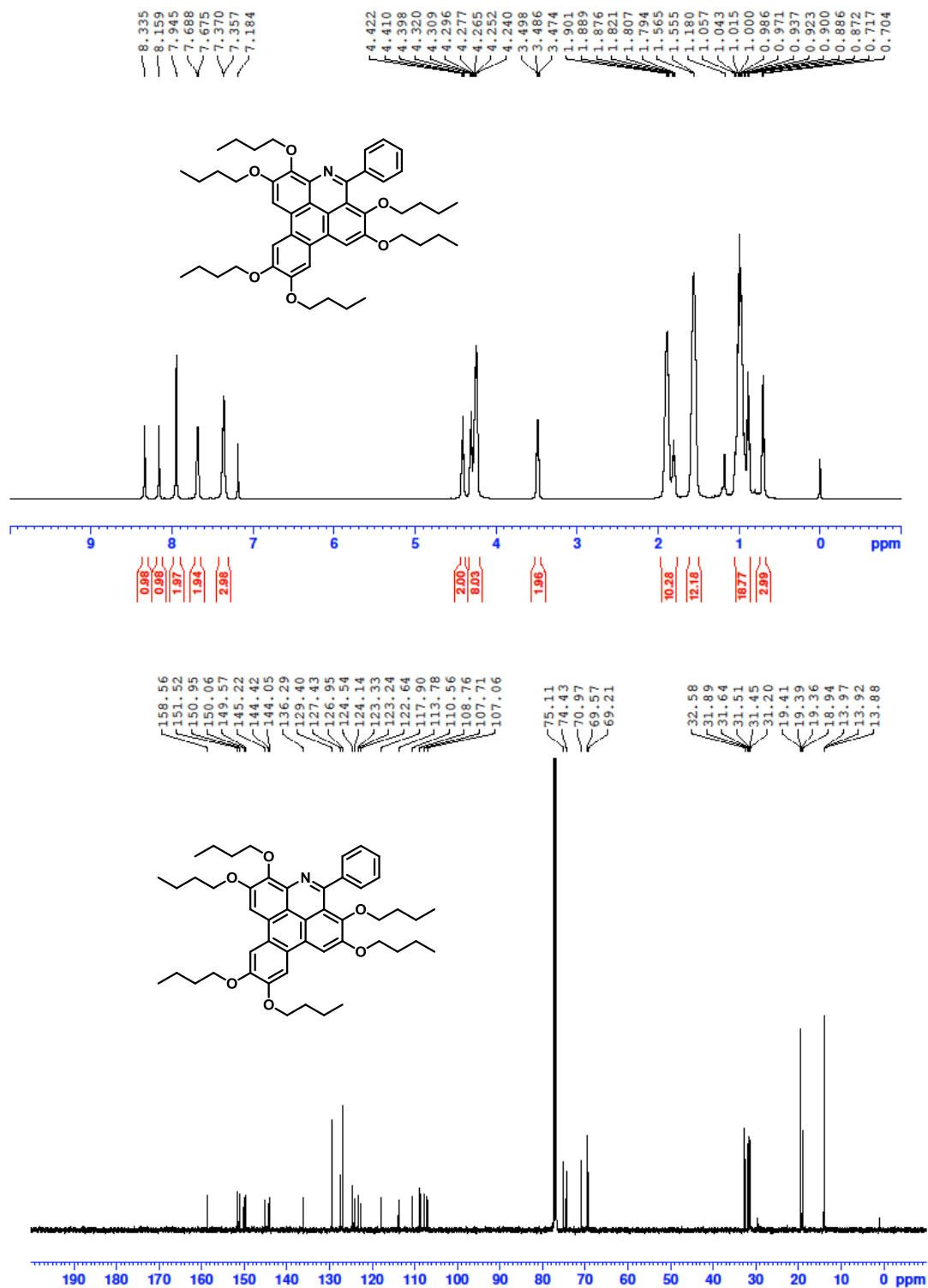
FigureS9: ^1H (top) and ^{13}C -NMR (bottom) spectra of **3**



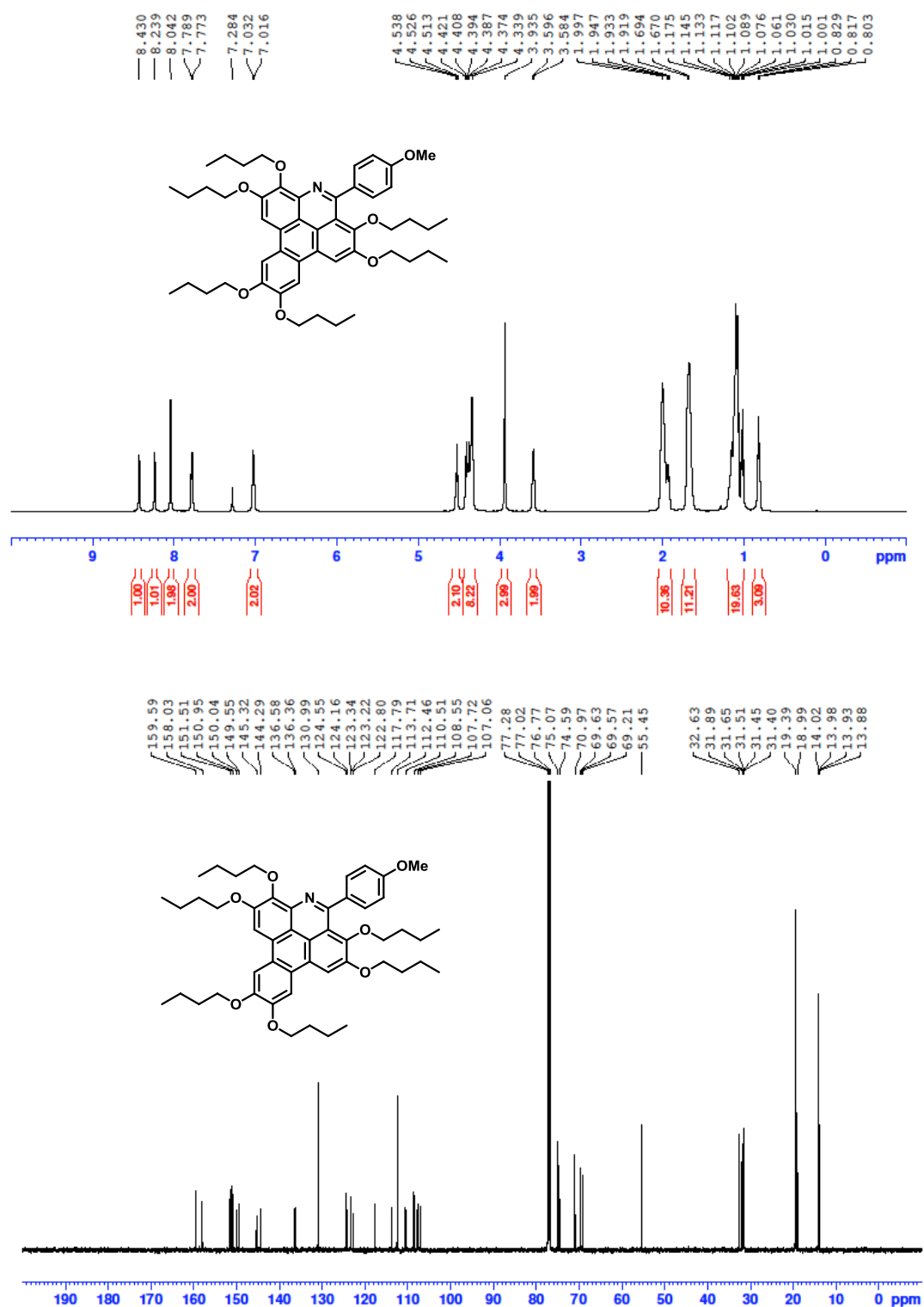
FigureS10: ^1H (top) and ^{13}C -NMR (bottom) spectra of 4



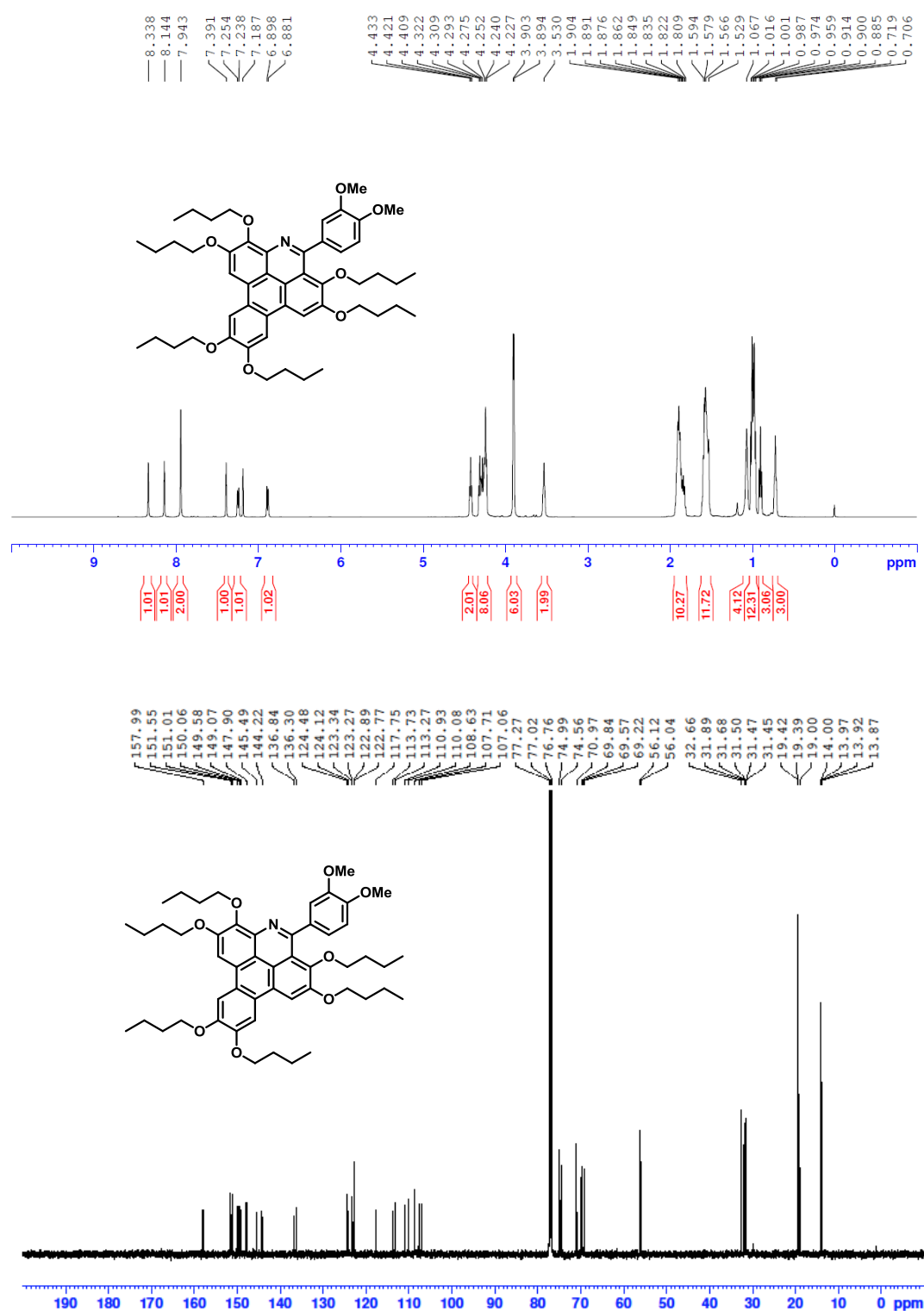
FigureS11: ¹H (top) and ¹³C-NMR (bottom) spectra of **5**



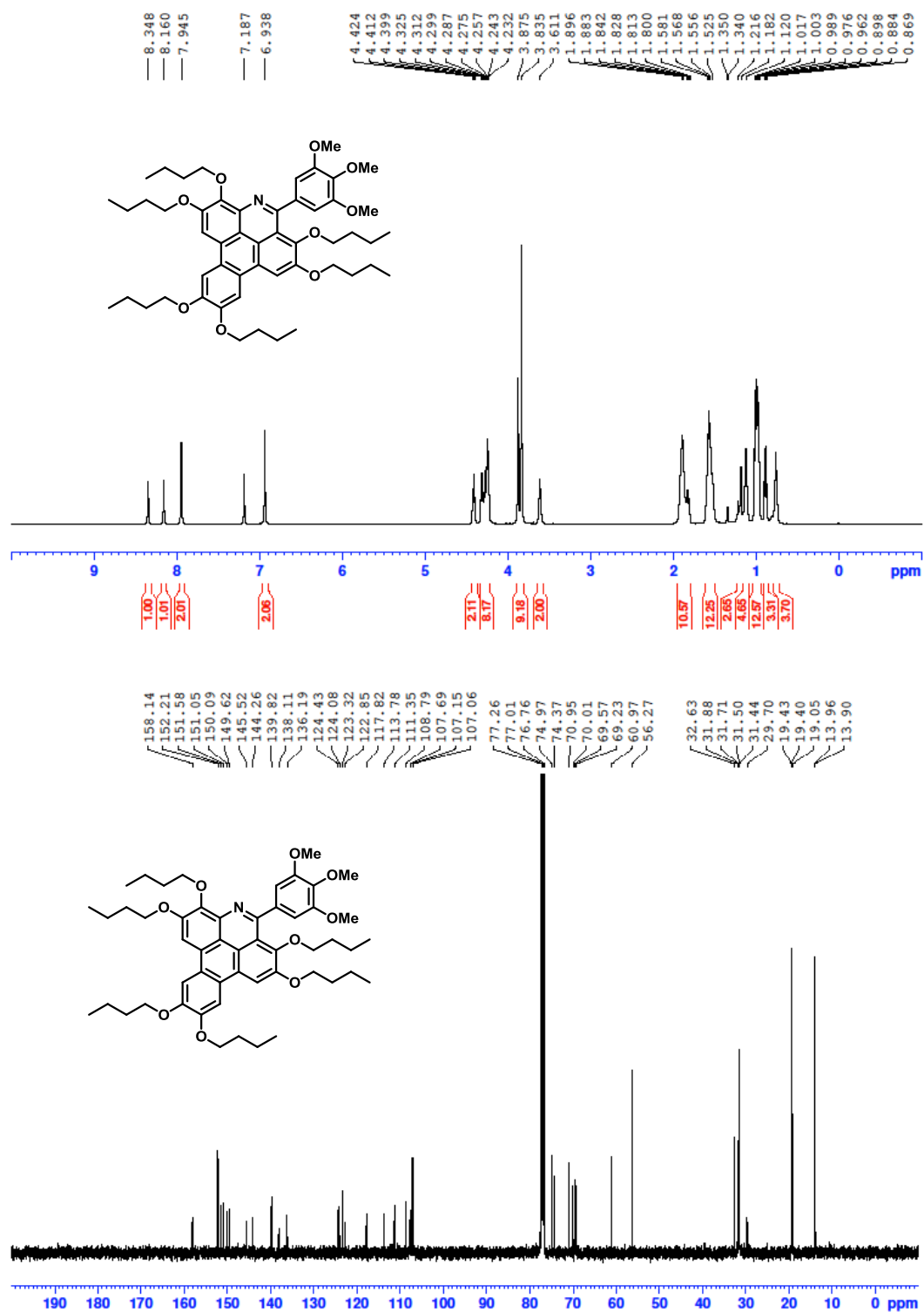
FigureS12: ^1H (top) and ^{13}C -NMR (bottom) spectra of **6a**



FigureS13: ¹H (top) and ¹³C-NMR (bottom) spectra of **6b**



FigureS14: ¹H (top) and ¹³C-NMR (bottom) spectra of 6c



FigureS15: ^1H (top) and ^{13}C -NMR (bottom) spectra of **6d**

References

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2. J. Wei, B. Han, Q. Guo, X. Shi, W. Wang and N. Wei, *Angew. Chemie - Int. Ed.*, **2010**, 49, 8209–8213.