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Synthesis of novel regioisomeric phenanthro [a] phenazine derivatives through S_NAr Strategy and their self-assembly into columnar phases

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1. Material and Instruments

All the chemicals and reagents are purchased from Sigma Aldrich and used directly. The solvents are AR grade and they 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 product structures were confirmed by NMR and elemental analysis. ^{1}H NMR and ^{13}C NMR (Nuclear magnetic resonance spectroscopy) were recorded by Bruker 500MHz instrument using $CDCl_3$ as the solvent and trimethyl silane as an internal standard. Chemical shift values are given in ppm and the solvent $CDCl_3$ peaks appear at ^{1}H NMR: δ = 7.23 ppm and ^{13}C NMR δ = 77.0 ppm. Peak multiplicity is given as s = singlet, d = doublet, t = triplet, m = multiplet, b = broad peak, dd = doublet of doublet. 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 polarizing 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 ^{o}C and corresponding enthalpy values are given in kJ mol^{-1}. Panalytical (Empyrean) Cu-Kα (1.54Å) X-ray diffractometer was used to further confirm the mesophase structures 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 thermogravimetric analysis instrument.

2. Synthetic procedure of intermediates

Synthesis of 2[1]**:** To the solution of catechol (5 g, 45.41 mmol, 1 eq) and potassium carbonate (25.10 g, 181.64 mmol, and 4 eq) in ethanol (55 ml), 1-bromododecane was added

(23.77 g, 95.361 mmol, 2.1 eq). The mixture was refluxed under an inert atmosphere for 36 hours and filtered upon cooling. The filtrate was concentrated by evaporating ethanol and then extracted with dichloromethane. The organic layer was washed with brine, dried over sodium sulphate and evaporated under vacuum to give a crude product which was purified by column chromatography using petroleum ether as eluent to get the desired product as white solid. (91%).

^{1}H NMR: 6.884 (s, 4H), 3.987 (t, 4H, *J* = 7 Hz), 1.837-1.780 (m, 4H), 1.490-1.261 (36 H), 0.881 (t, 6H, *J* = 6 Hz). ^{13}C NMR: 149.25, 121.00, 114.12, 69.29, 31.95, 29.98, 29.72, 29.68, 29.66, 29.47, 29.39, 29.37, 26.08, 22.71, 14.13. Elemental analysis($C_{30}H_{54}O_2$): C 8.65%, H 12.28%(Expected); C 80.18%, H 12.49%(Observed)

Synthesis of 3[2]**:** Compound **2** (10 g, 22.39 mmol, 1eq) was added dropwise to a solution of ferric chloride (12.695 g, 78.365 mmol, 3.5 eq) in dichloromethane (150 ml) and a catalytic amount of concentrated 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 maintaining 0 °C for a an hour and filtered. The crude product was purified by column chromatography using petroleum ether and dichloromethane in 95:5 ratio. (compound **3' (2,3,6,7,10,11-hexadodecyloxytriphenylene)**: 42%, compound **3 (2-hydroxy 3,6,7,10,11-pentadodecyloxytriphenylene)**: 22%). Compound **3** was used for the next oxidation step.

^{1}H NMR: 7.958 (s, 1H), 7.827-7.815 (m, 4H), 7.769 (s, 1H), 5.907 (s, 1H), 4.287 (t, 2H, *J* = 6 Hz), 4.235-4.190 (m, 8H), 1.938-1.269 (100H), 0.879 (t, 15H, *J* = 6.5 Hz). ^{13}C NMR: 149.16, 149.02, 148.82, 148.76, 145.85, 145.26, 123.95, 123.72, 123.65, 123.57, 123.22, 122.98, 107.66, 107.47,107.32, 107.28, 106.51, 104.35, 69.97, 69.91, 69.64, 69.15, 31.95, 29.75, 29.72, 29.70, 29.66, 29.64, 29.57, 29.51, 29.49, 29.40, 29.37, 26.24, 26.20, 26.16, 22.71, 14.13.

Elemental analysis($C_{78}H_{132}O_6$): C 80.35%, H 11.41% (Expected); C 80.20%, H 11.73% (Observed)

Synthesis of 4[3]**:** Ceric ammonium nitrate (1.34 g, 1.89 mmol, 2.2 eq) was added slowly to a solution of compound **3** (1 g, 0.857 mmol, 1 eq) in the tetrahydrofuran-dioxane mixture (3 ml – 10 ml) and stirred for 3 hours at room temperature. The reaction mixture was poured on cold ethanol and the precipitate was filtered. The crude product was purified by column chromatography using petroleum ether: ethyl acetate (95:5) as eluent. Recrystallization using methanol yields a violet solid (65%).

^{1}H NMR: 8.967 (s, 1H), 7.711 (s, 1H), 7.678 (s, 1H), 7.442 (s, 1H), 7.076 (s, 1H), 4.267 (t, 2H, *J* = 6 Hz), 4.222-4.182 (m, 6H), 4.103 (t, 2H, *J* = 6 Hz), 1.971- 1.267 (100H), 0.879 (t, 15H, *J* = 6 Hz). ^{13}C NMR: 181.07, 177.28, 152.94, 151.63, 150.30, 149.26, 149.14, 133.18, 130.43, 125.27, 124.66, 122.37, 119.29, 111.74, 107.80, 106.94, 105.29, 104.54, 69.71, 69.53, 69.05, 69.85, 69.59, 31.95, 29.75, 29.70, 29.66, 29.61, 29.55, 29.51, 29.47,29.40,29.38, 29.34, 29.16, 29.11, 28.84, 26.19, 26.11, 26.08, 22.71, 14.13. Elemental analysis($C_{78}H_{130}O_7$): C 79.40%, H 11.11% (expected); C 79.41%, H 11.45% (observed)

Synthesis of 5[4]**:** 4-Nitrobenzene-1,2-diamine (1.78 g, 1.2 eq) was added to the solution of compound **4** (5 g, 1 eq) in toluene and acetic acid mixture. The reaction mixture was refluxed under an inert atmosphere. After completion of the reaction, the solvent was evaporated under reduced pressure and dissolved in dichloromethane. The organic layer was washed with brine and dried using sodium sulphate. The solvent was evaporated under vacuum and the crude product having a mixture of compounds **5(a) (2,3,6,14,15-pentakis(dodecyloxy)-9-nitrophenanthro[9,10-a]phenazine)** and **5(b)** (**2,3,6,14,15-pentakis(dodecyloxy)-10-nitrophenanthro[9,10-a]phenazine)** was separated using gravitational column chromatography over silica gel using petroleum ether: ethyl acetate (90:10). The isolated

compounds were reprecipitated twice using DCM/MeOH to obtain reddish color solid compounds.

Compound 5(a): yield 51%, red solid, m.p. in Table 1, ^{1}H NMR: 10.489 (s, 1H), 9.277 (d, 1H, *J* = 1 Hz), 8.548-8.527 (dd, 1H, *J* = 9.5, 1 Hz), 8.214 (d, 1H, *J* = 9.5 Hz), 7.893 (s,1H), 7.852 (s,1H), 7.821 (s, 2H), 4.436 (t, 2H, *J* = 6.5 Hz), 4.358 (t, 2H, *J* = 7.5Hz), 4.297-4.243 (m, 6H), 2.164-1.281 (m, 100), 8.882 (t,15H, *J* = 6 Hz). ^{13}C NMR: 151.45, 151.23, 149.57, 148.87, 148.32, 147.24, 146.02, 142.36, 138.65, 137.96, 131.79, 130.38, 127.29, 126.58, 124.61,124.52, 122.93, 122.30, 117.49, 112.13, 107.97, 106.15,106.08, 105.37, 69.86, 69.61, 69.49, 69.19, 68.85, 31.96, 31.95, 29.83, 29.80, 29.76, 29.74, 29.67, 29.65, 29.61, 29.54, 29.51, 29.43, 29.37, 26.31,26.28, 22.72, 14.13.

Elemental analysis ($C_{84}H_{133}N_3O_6$): C 77.79%, H 10.34%, N 3.24% (expected); C 77.75%, H 9.88%, N 2.92% (observed)

Compound 5(b): yield 43%, red solid, m.p. in Table 1, ^{1}H NMR: 10.563 (s, 1H), 9.01 (d, 1H, *J* = 2 Hz), 8.542-8.520 (dd, 1H, *J* = 9, 2 Hz,), 8.476 (d, 1H, *J* = 9 Hz,), 7.998 (s, 1H), 7.873 -7.856 (m, 3H), 4.484 (t, 2H, *J* = 6.5 Hz), 4.384, 2H, *J* = 6.5 Hz), 4.312-4.262 (m, 6H), 2.183-1.259 (100H), 0.883(t, 15H, *J* = 6 Hz). ^{13}C NMR: 151.48, 151.28, 149.61, 148.90, 148.36, 147.27, 146.07, 142.41, 138.71, 138.01, 131.83, 130.42, 127.33, 126.62, 124.63, 124.56, 122.97, 122.34, 117.56, 112.17, 108.02, 106.21, 106.16, 105.43, 69.89, 63.83, 69.53, 69.20, 68.87, 31.96, 29.79, 29.75, 29.73, 29.66, 29.64, 29.60, 29.53, 29.50, 29.42, 29.37, 29.04, 26.40, 26.30, 26.27, 22.71, 14.13.

Elemental analysis($C_{84}H_{133}N_3O_6$): C 77.79%, H 10.34%, N 3.24% (Expected); C 77.82%, H 9.94%, N 3.21% (Observed)

3. Polarized Optical Microscopy Images

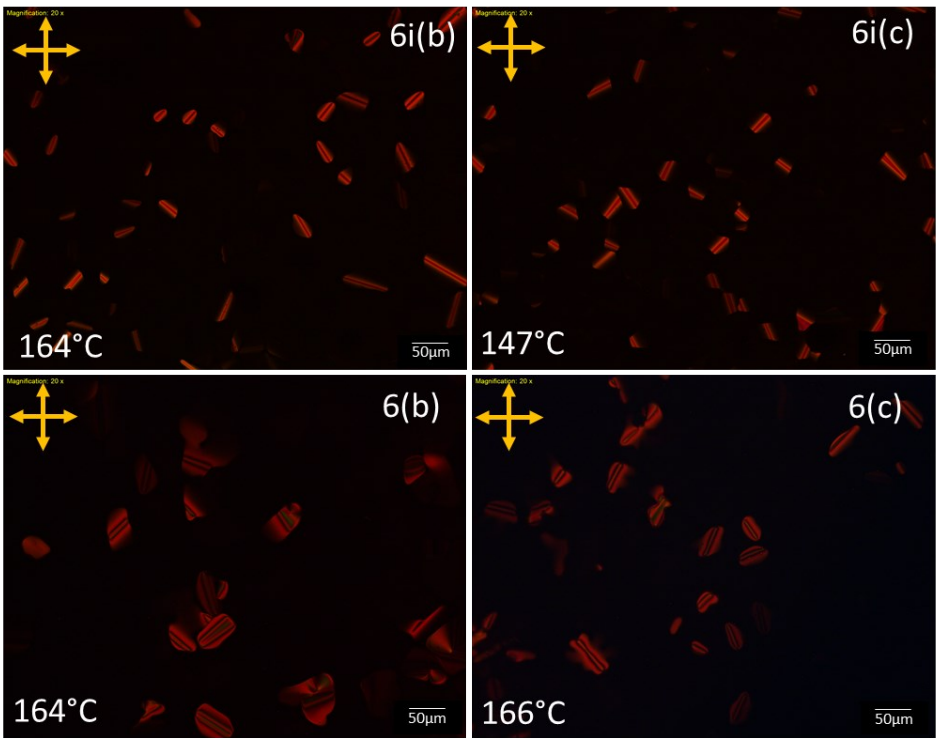

Fig S1: Polarising optical microscopy textures: **6ib** at 164 ºC**, 6ic** at 147 ºC**, 6b** at 164 ºC**, 6c** at 166 ºC, showing mosaic texture**,** all the POM textures were viewed at 20X magnification.

4. Thermal Gravimetric Analysis Curves

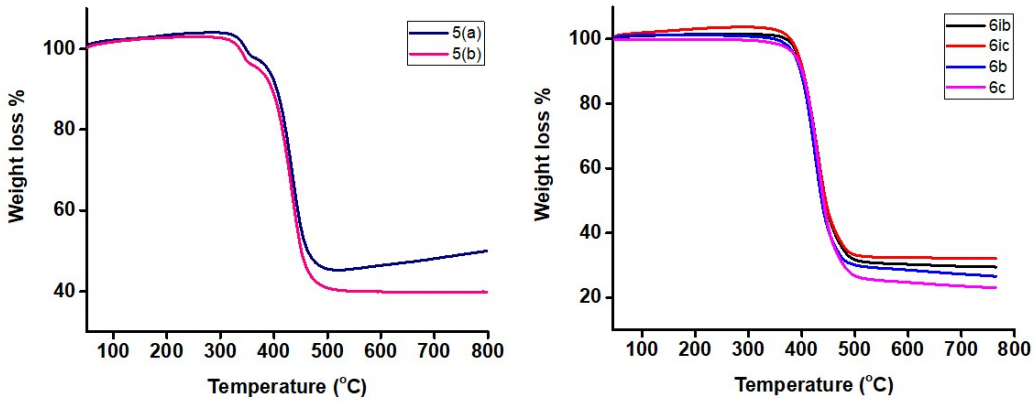

Fig S2: TGA themogram of **5a-b, 6ib, 6ic, 6b, 6c**

5. Differential Scanning Calorimetry Thermograms

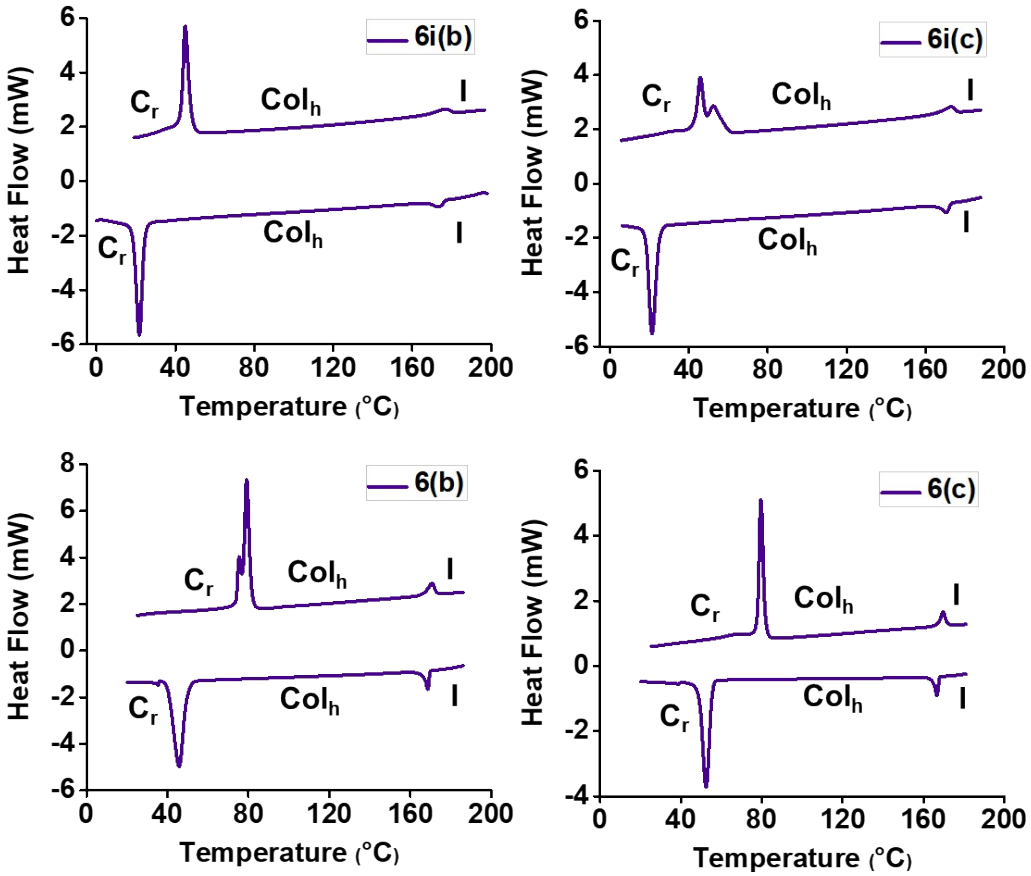

Fig S3: DSC thermograms of compound **6ib, 6ic, 6b, 6c;** phase transitions on heating and cooling cycles at a scan rate of 10 °C min^{-1}.

6. X-ray Diffractgrams

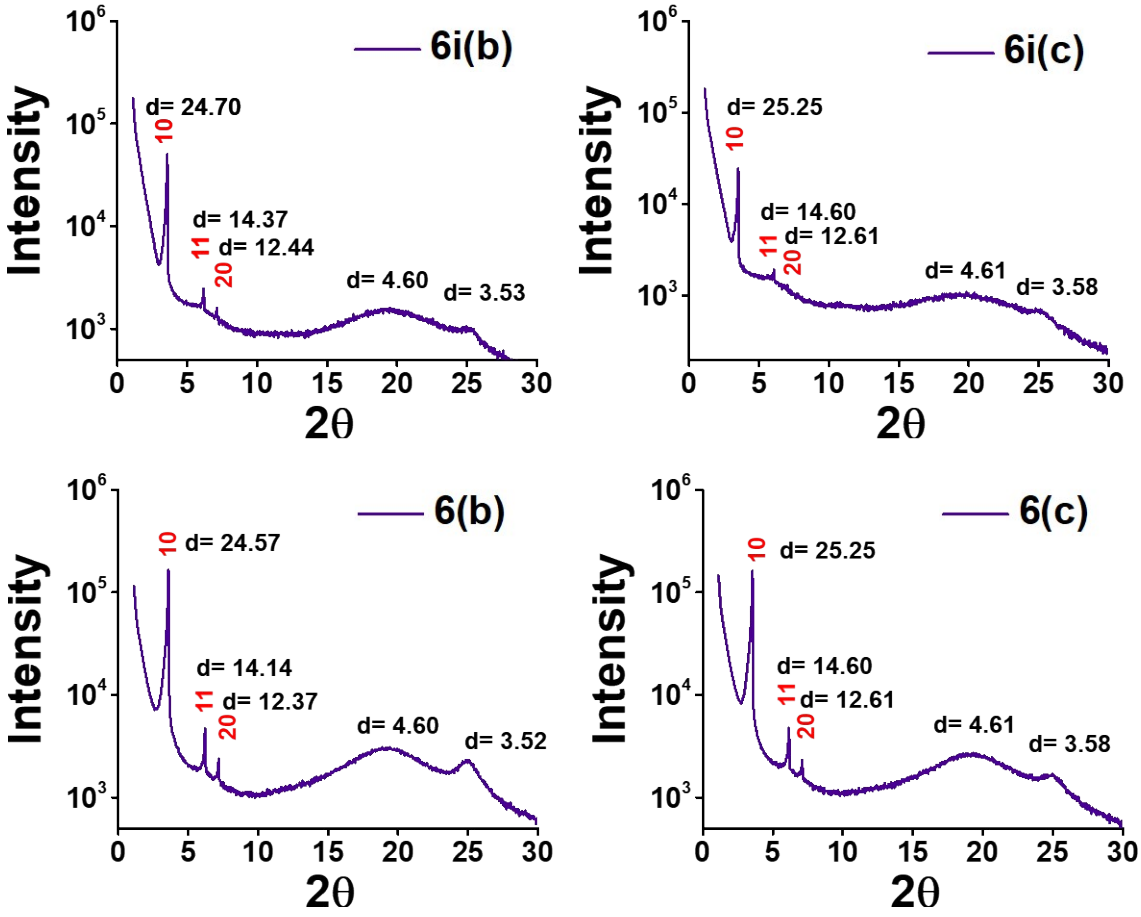

Fig S4: XRD diffractograms of **6ib** at 120 ºC, **6ic** 125 ºC, **6b** at 75 ºC, **6c** at 135 ºC (Intensity in arbitrary unit and d spacing in Å)

7. COSY and ROESY NMR Spectra of 6i(b) and 6(b)

7.1. COSY NMR Spectra

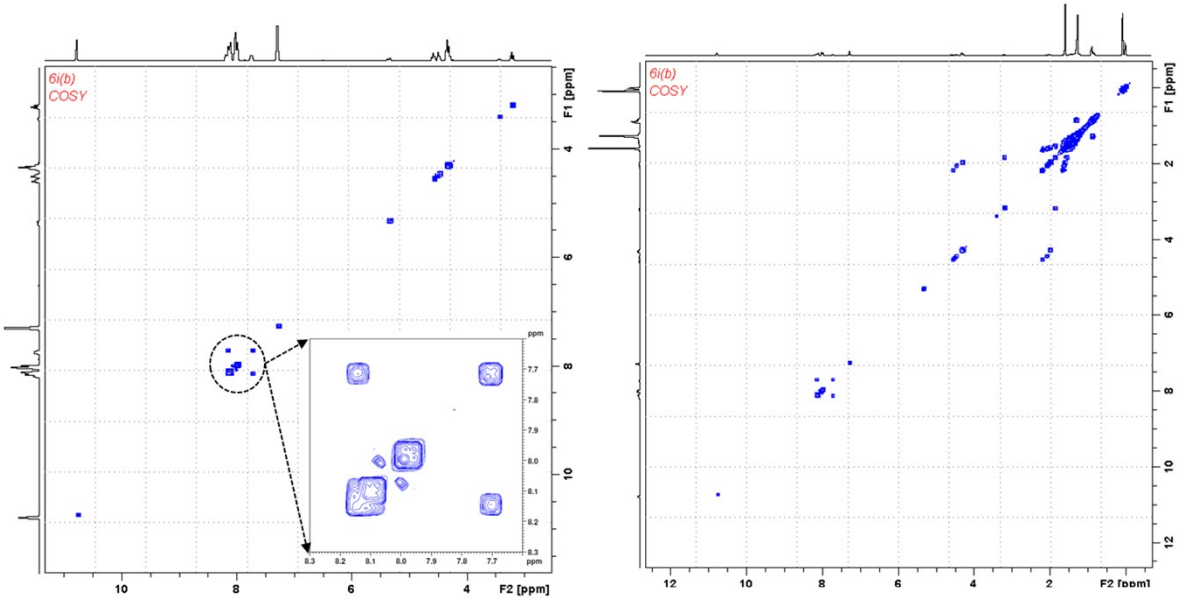

Fig S5: COSY spectra of **6i(b)** [Enlarged and full spectrum]

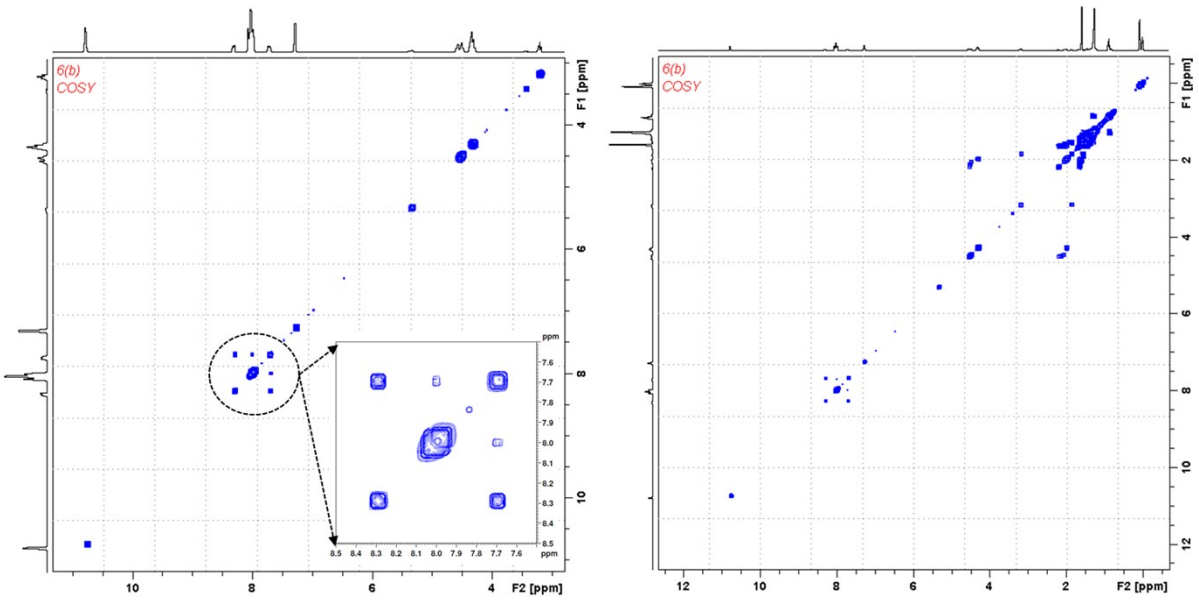

Fig S6: COSY spectra of **6(b)** [Enlarged and full spectrum]

7.2. ROESY NMR Spectra

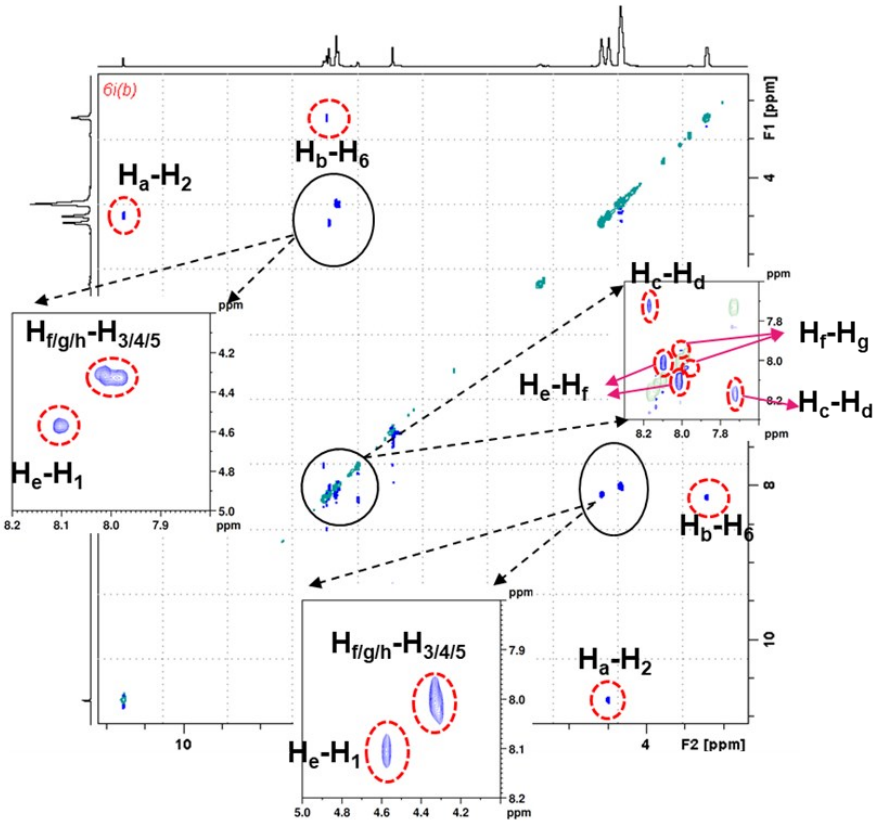

Fig S7: ROESY spectra of **6i(b)** (interactions other than H_a-H_c)

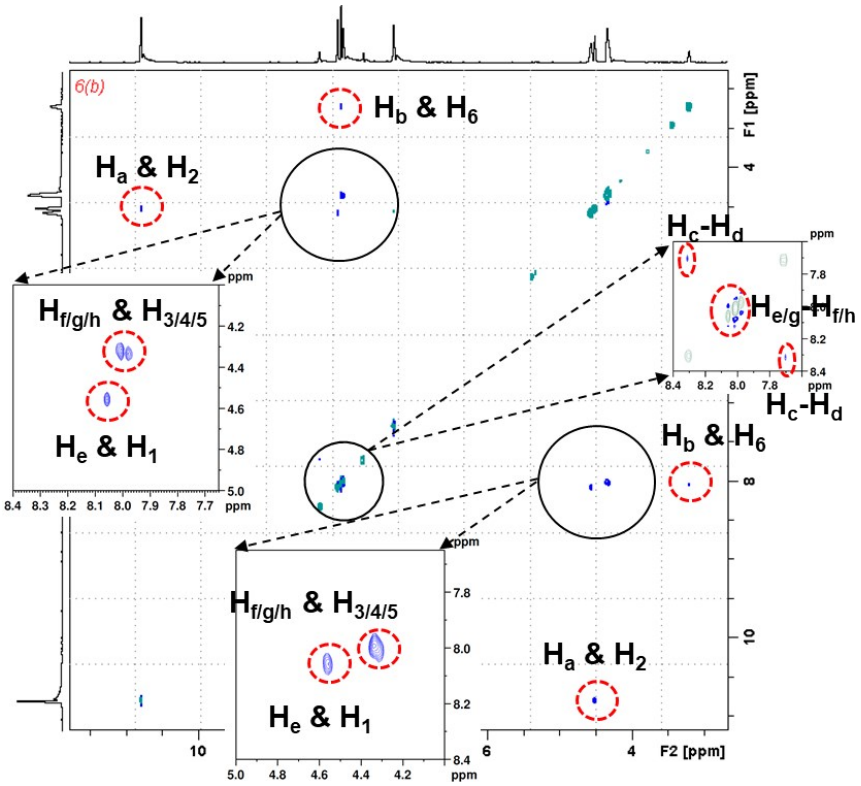

Fig S8: ROESY spectra of **6(b)** (interactions other than H_a-H_b)

8. ^{1}H and ^{13}C NMR Spectra of synthesized compounds

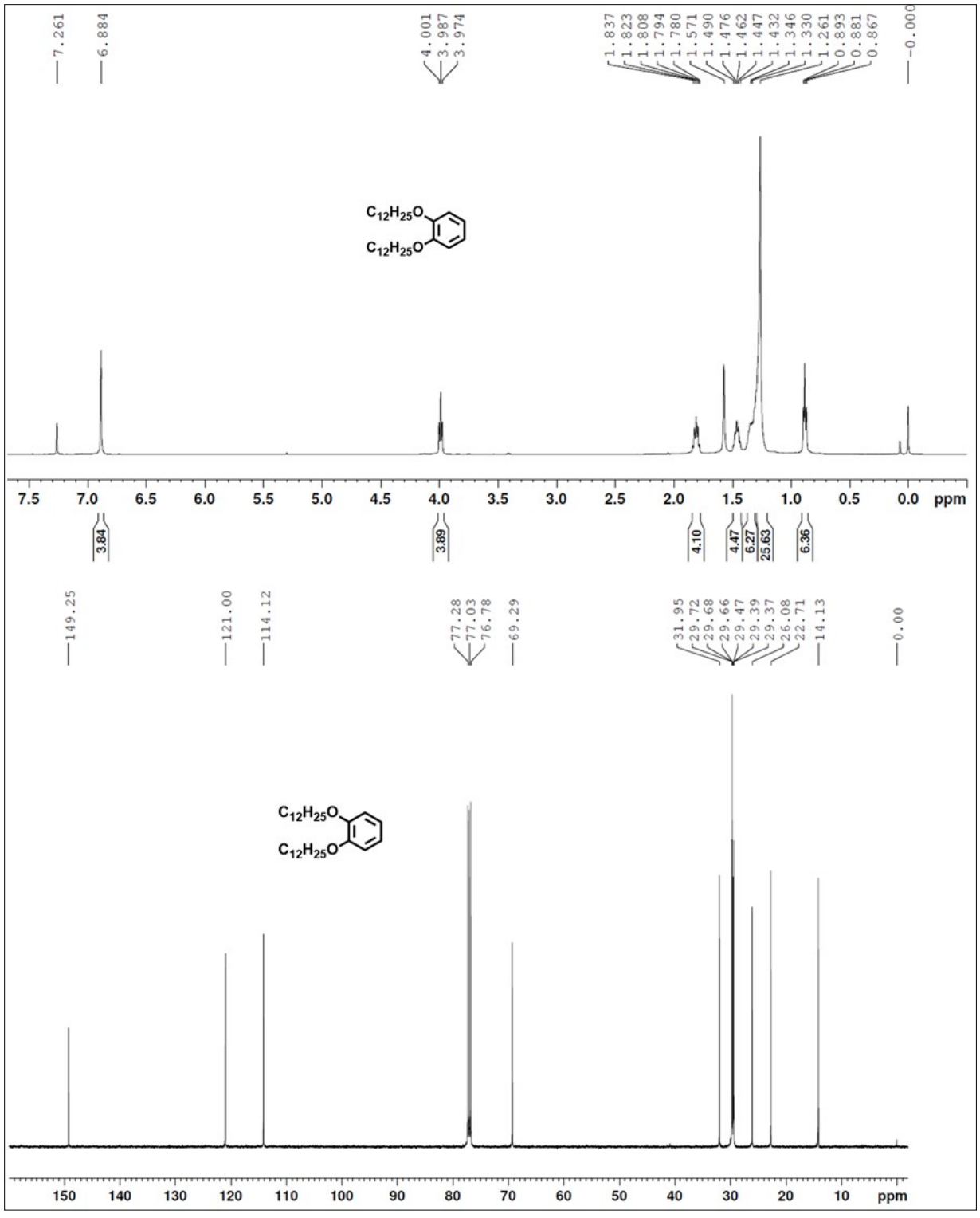

Fig S9: ^{1}H, ^{13}C NMR spectra of **2**

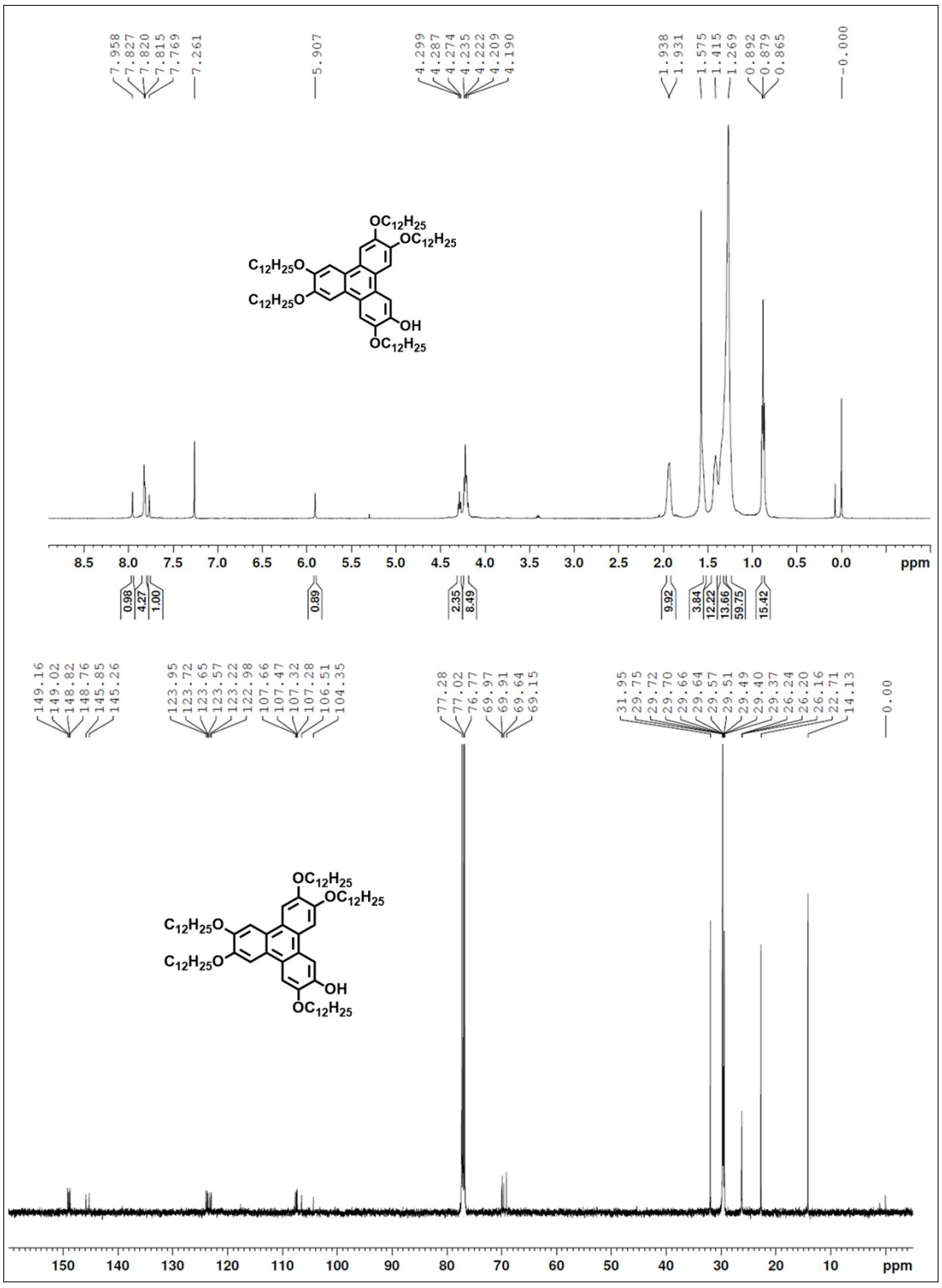

Fig S10: ^{1}H, ^{13}C NMR spectra of **3**

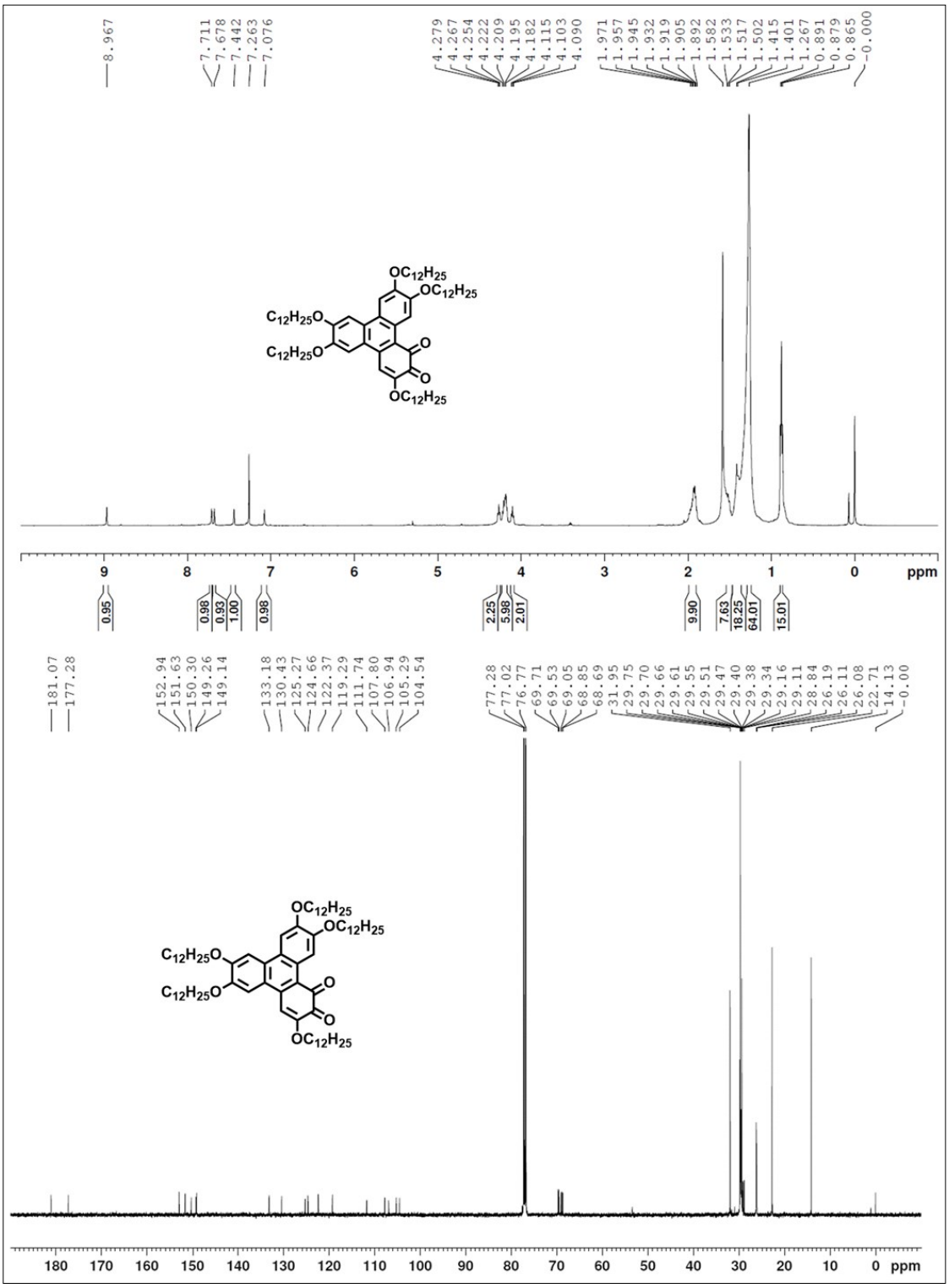

Fig S11: ^{1}H, ^{13}C NMR spectra of **4**

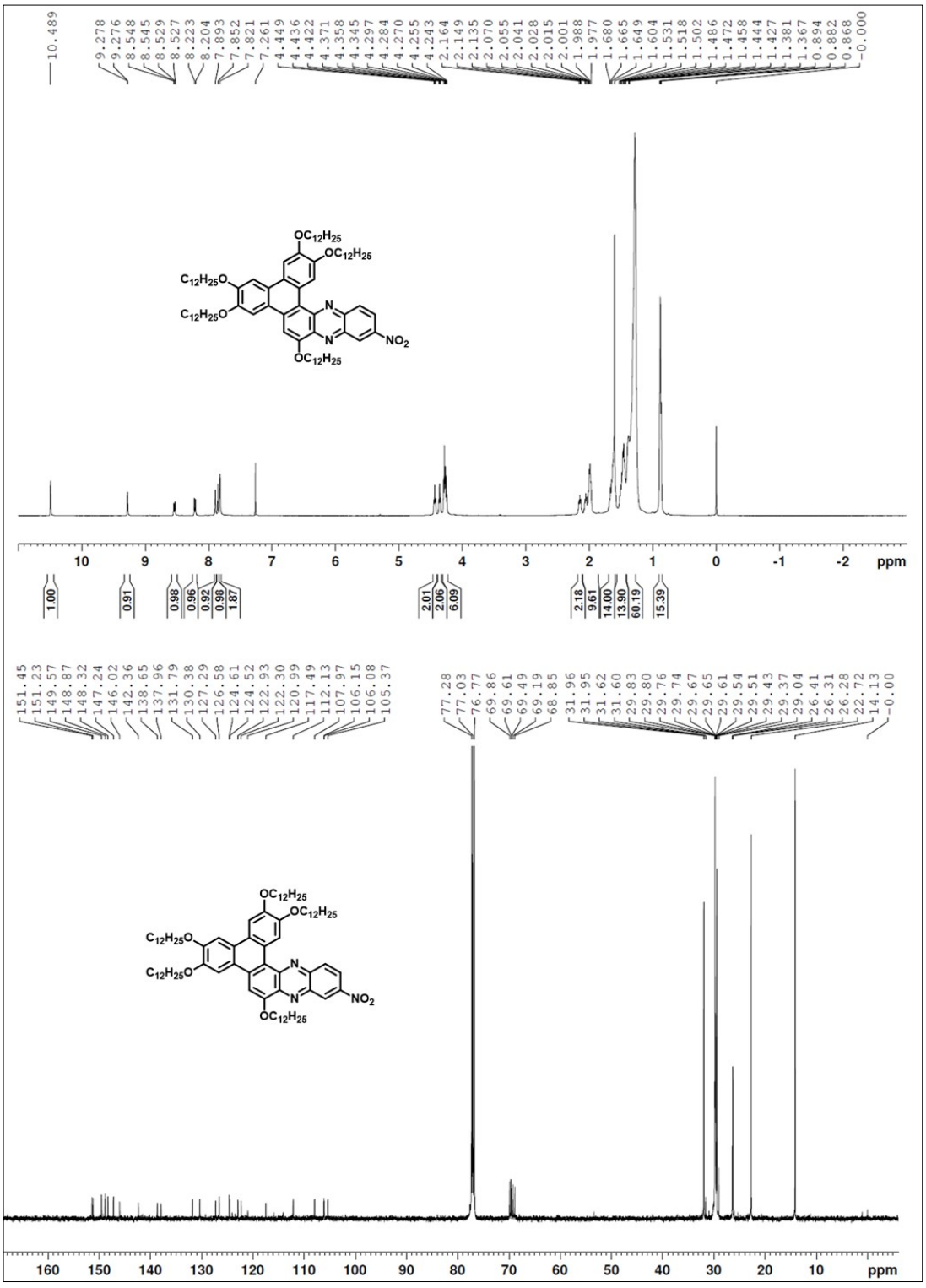

Fig S12: ^{1}H, ^{13}C NMR spectra of **5(a)**

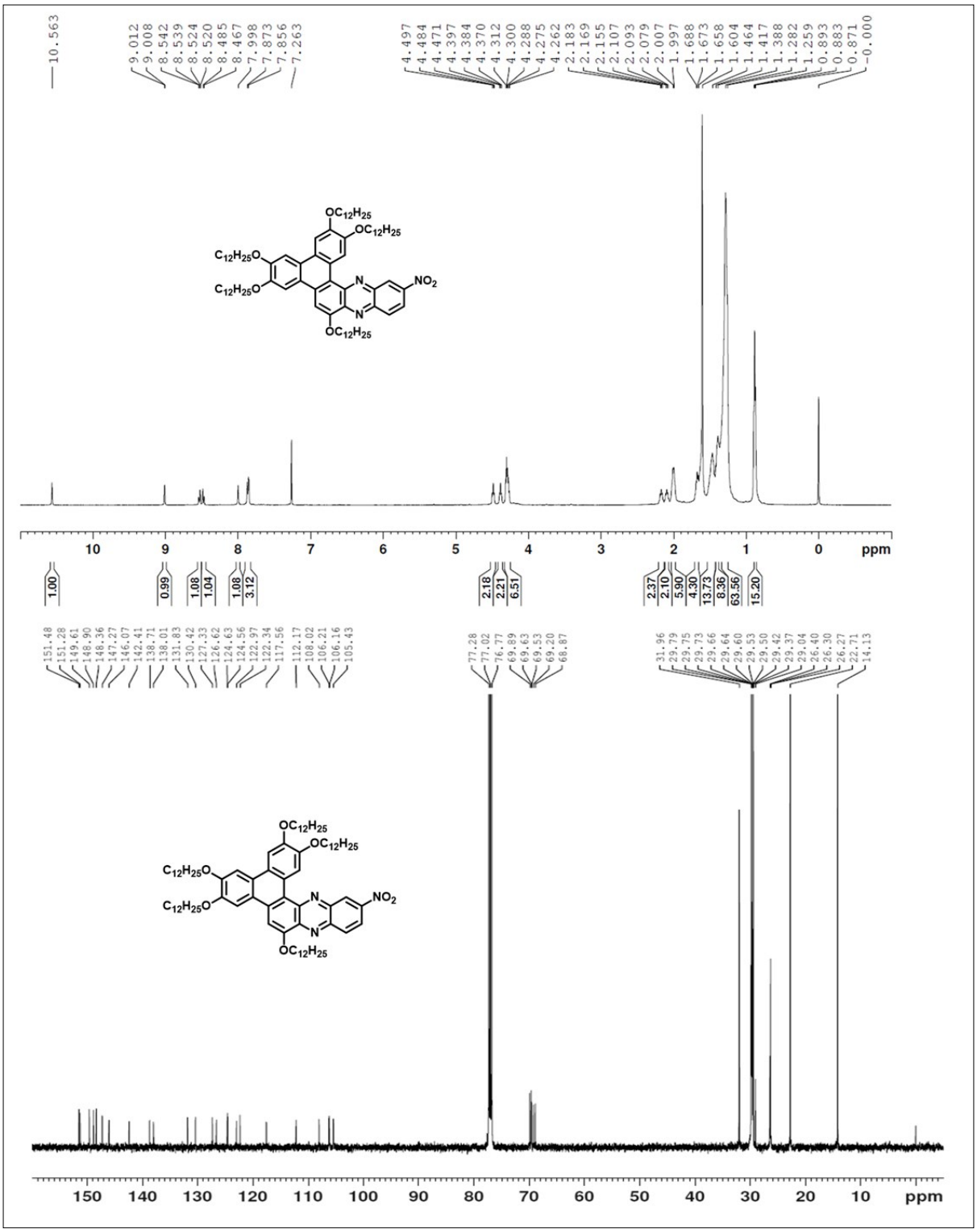

Fig S13: ^{1}H, ^{13}C NMR spectra of **5(b)**

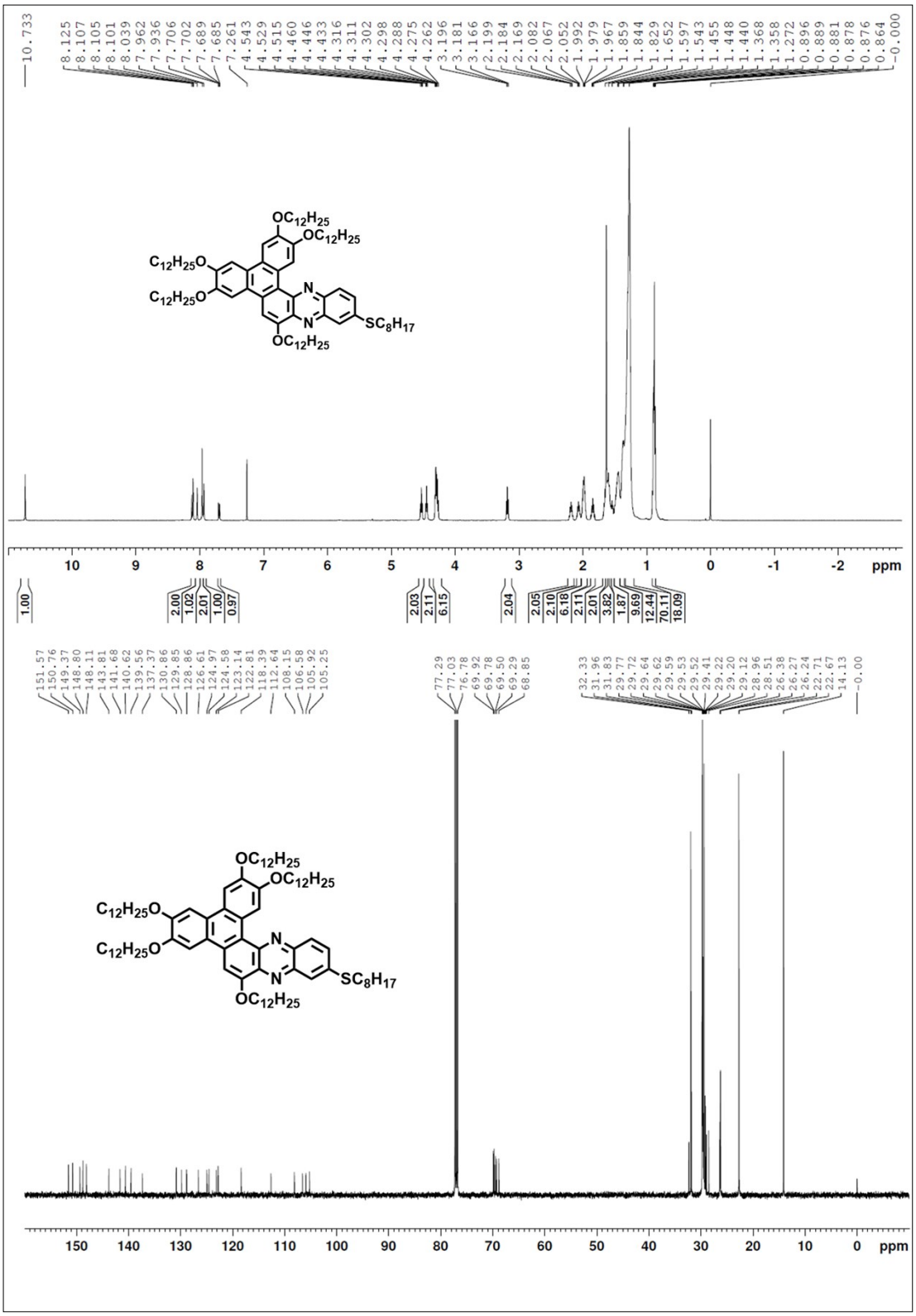

Fig S14: ^{1}H, ^{13}C NMR spectra of **6i(a)**

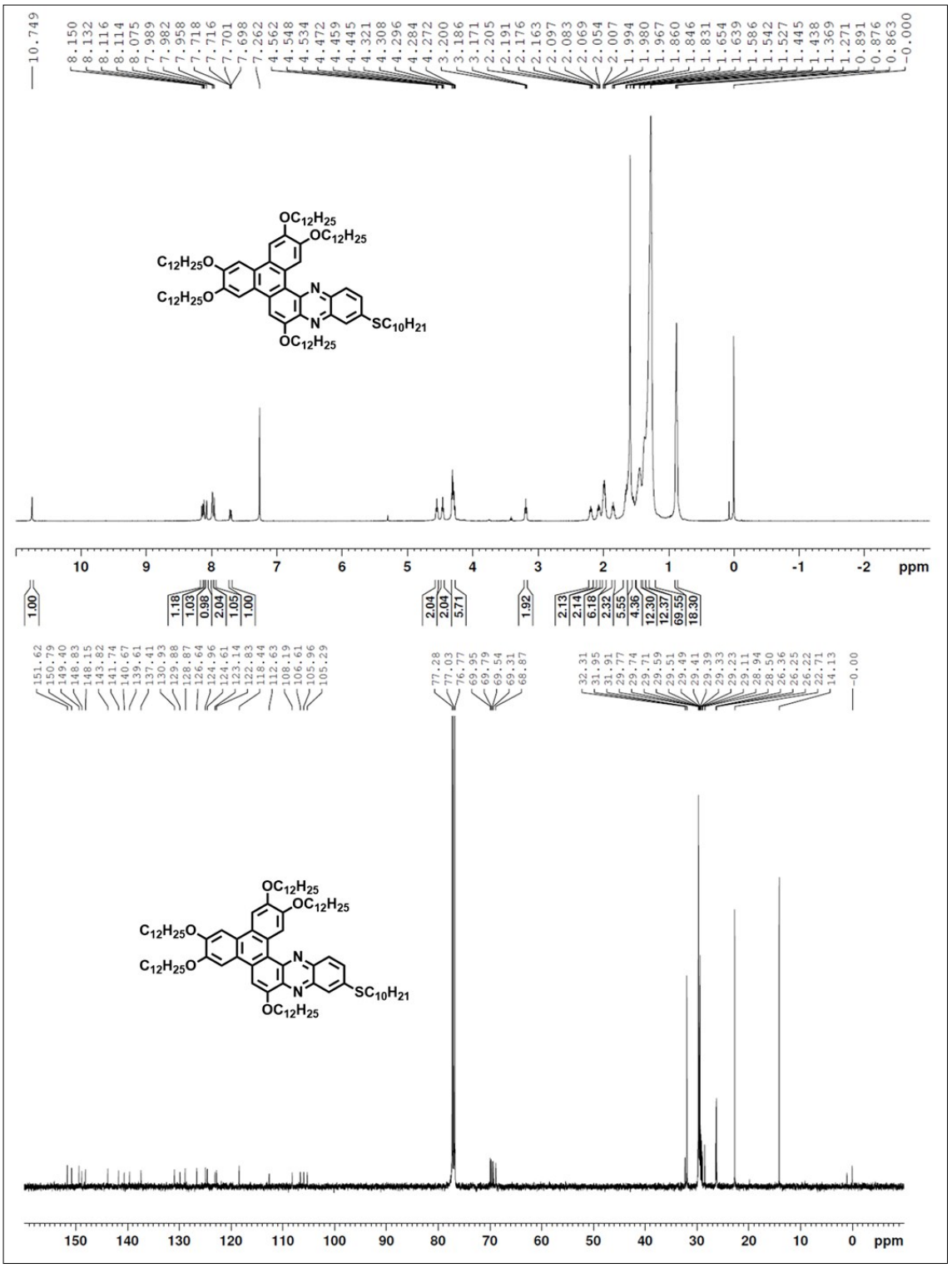

Fig S15: ^{1}H, ^{13}C NMR spectra of **6i(b)**

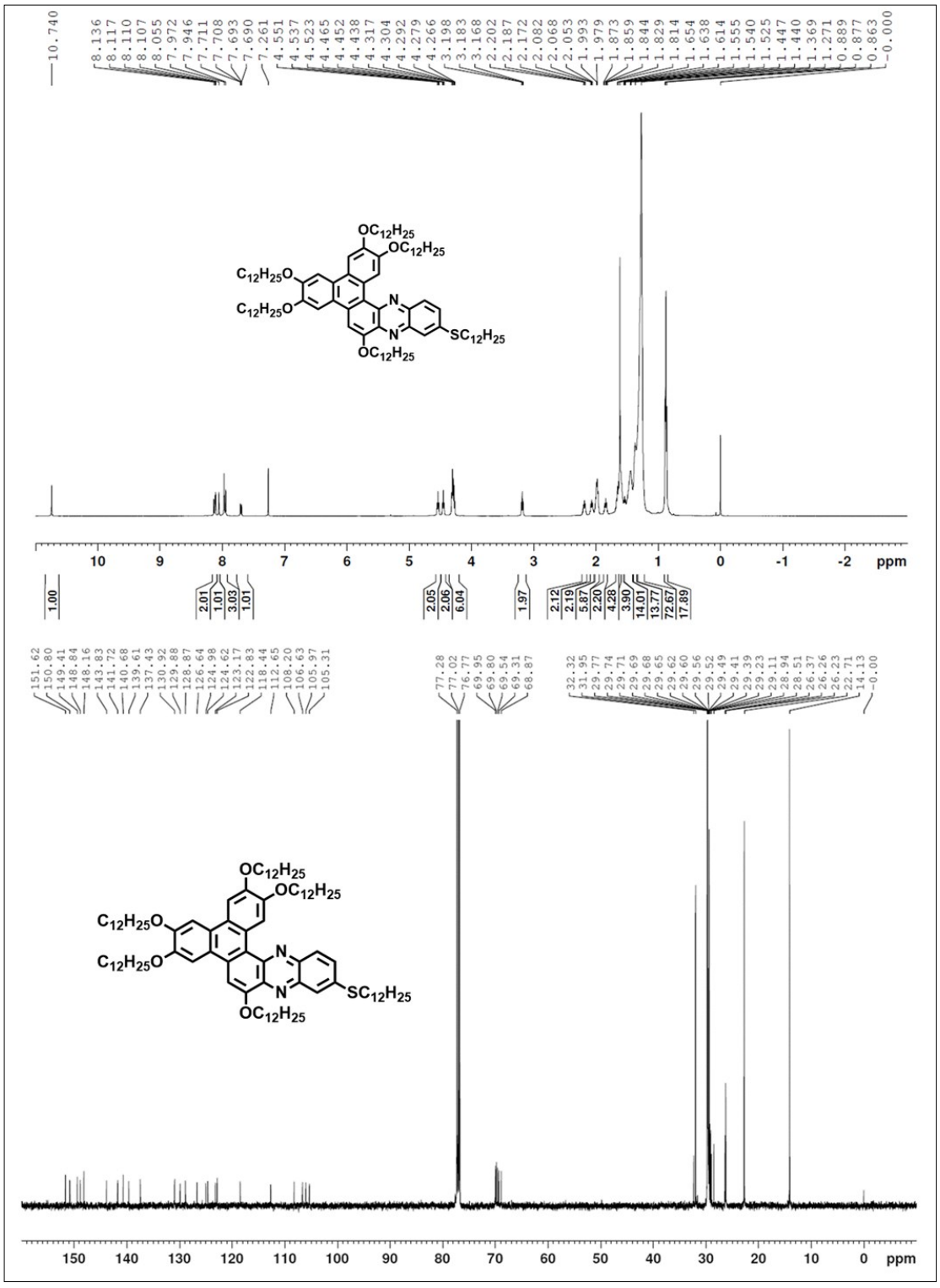

Fig S16: ^{1}H, ^{13}C NMR spectra of **6i(c)**

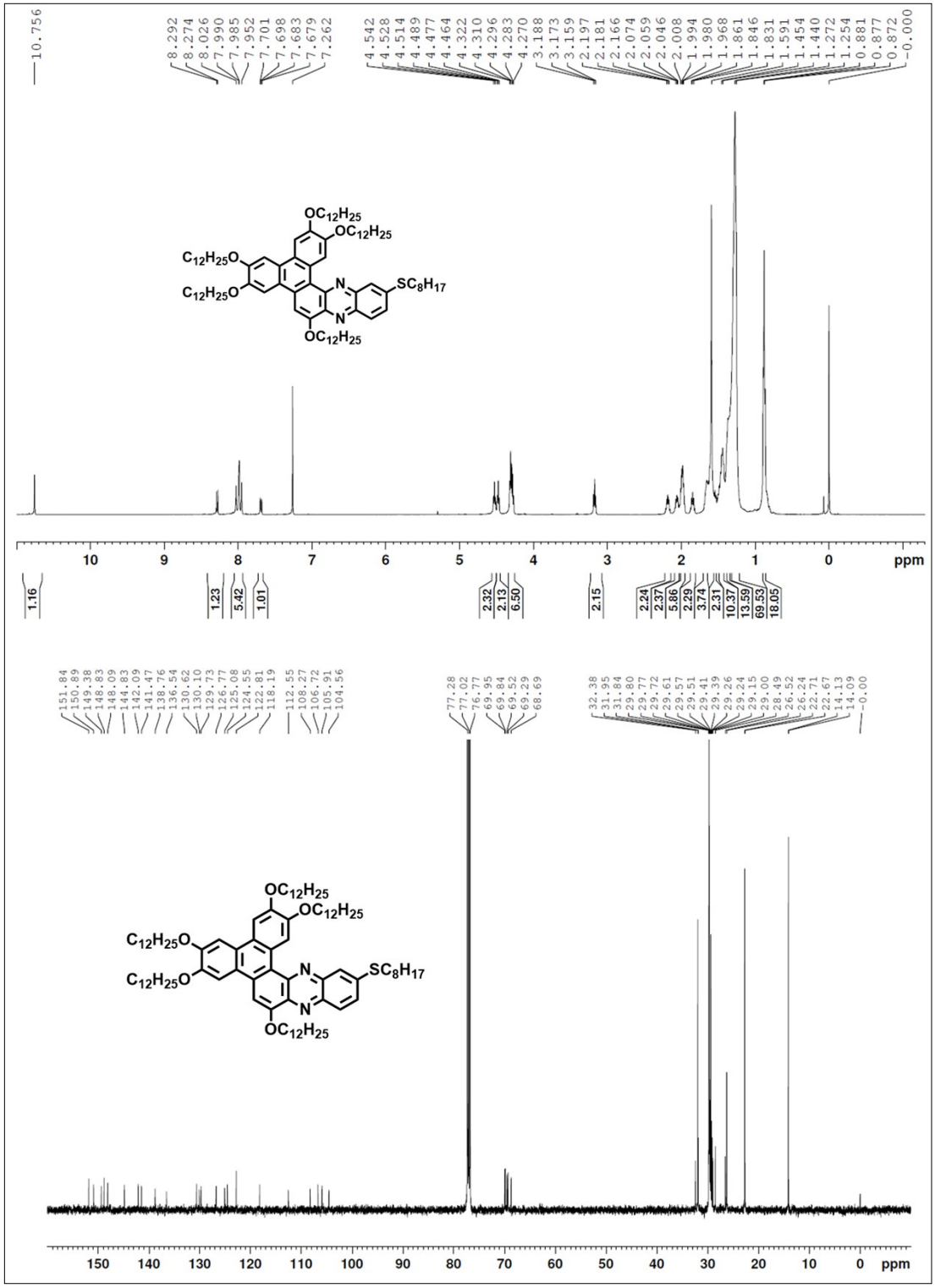

Fig S17: ^{1}H, ^{13}C NMR spectra of **6(a)**

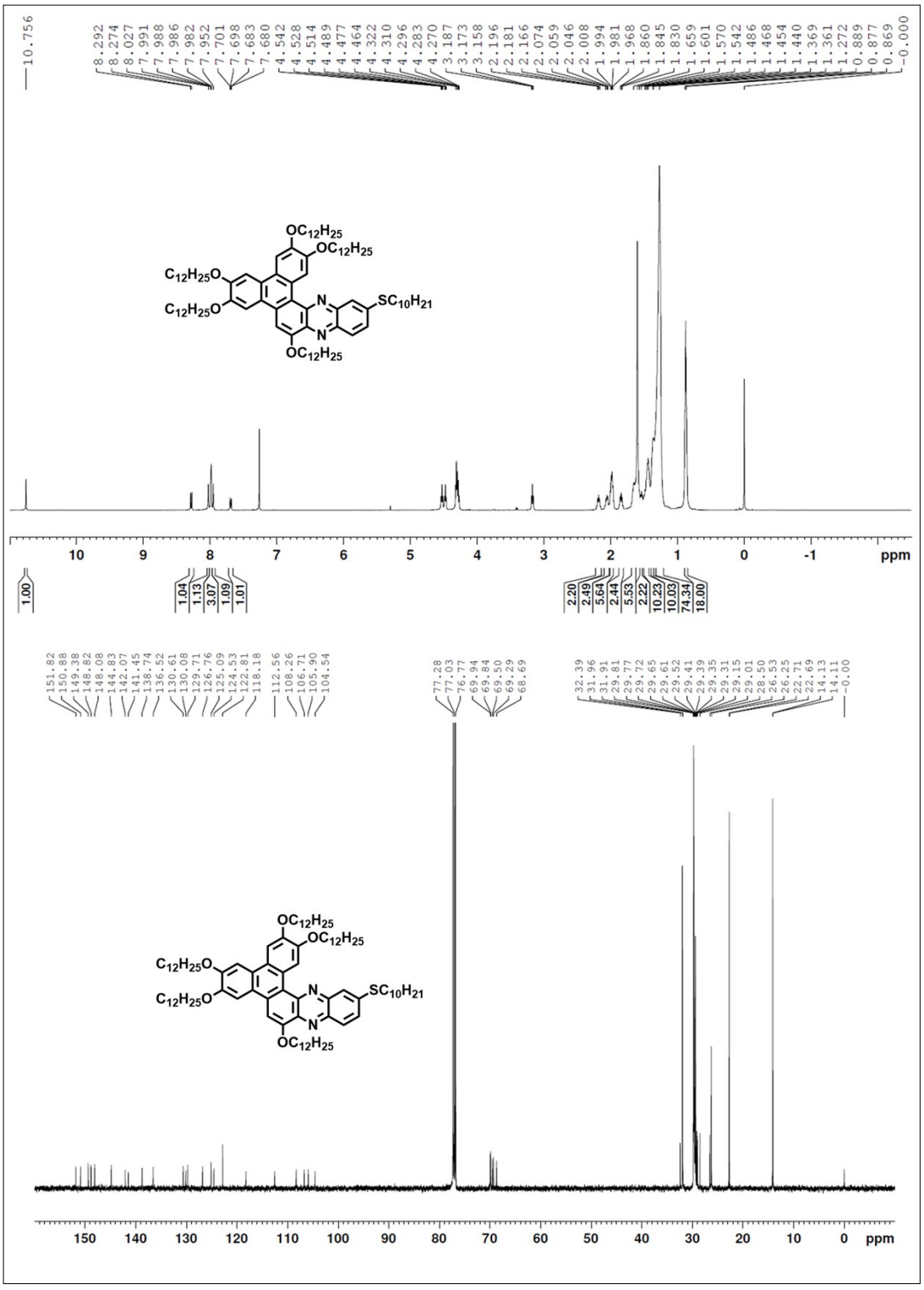

Fig S18: ^{1}H, ^{13}C NMR spectra of **6(b)**

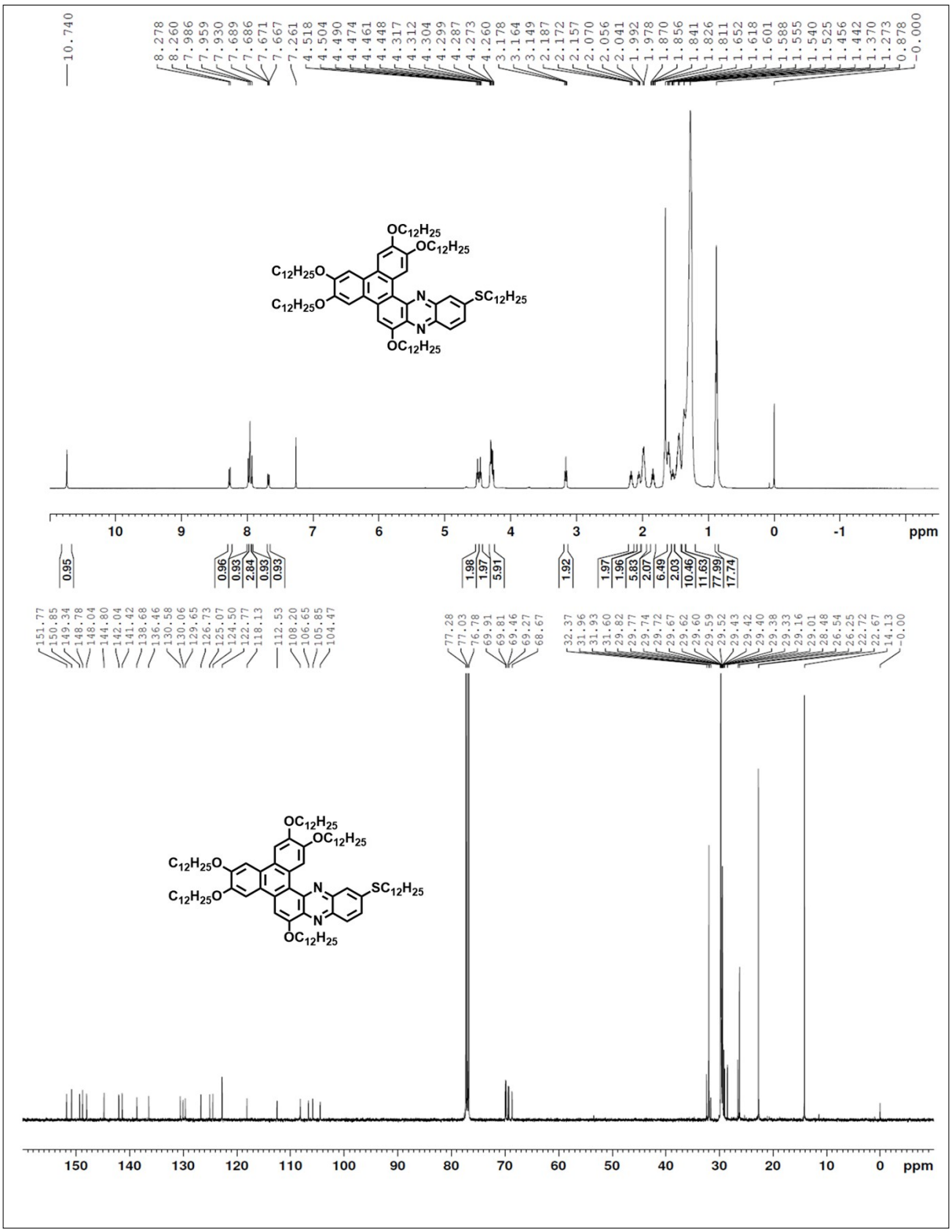

Fig S19: ^{1}H, ^{13}C NMR spectra of **6(c)**

9. References

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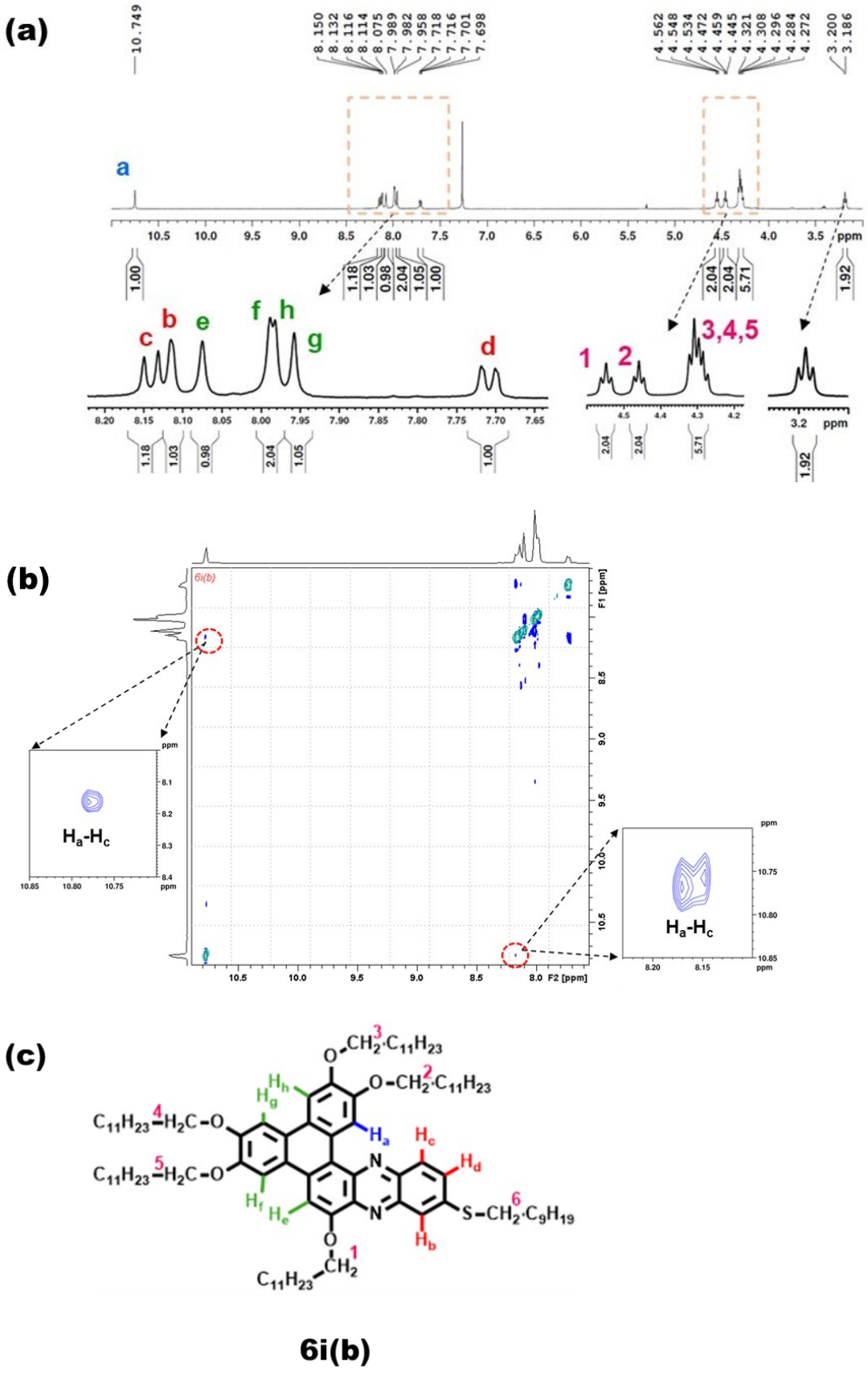

Fig 2. ^{1}H and ROESY NMR spectrum of compound **6i(b)** [Enlarged Images]

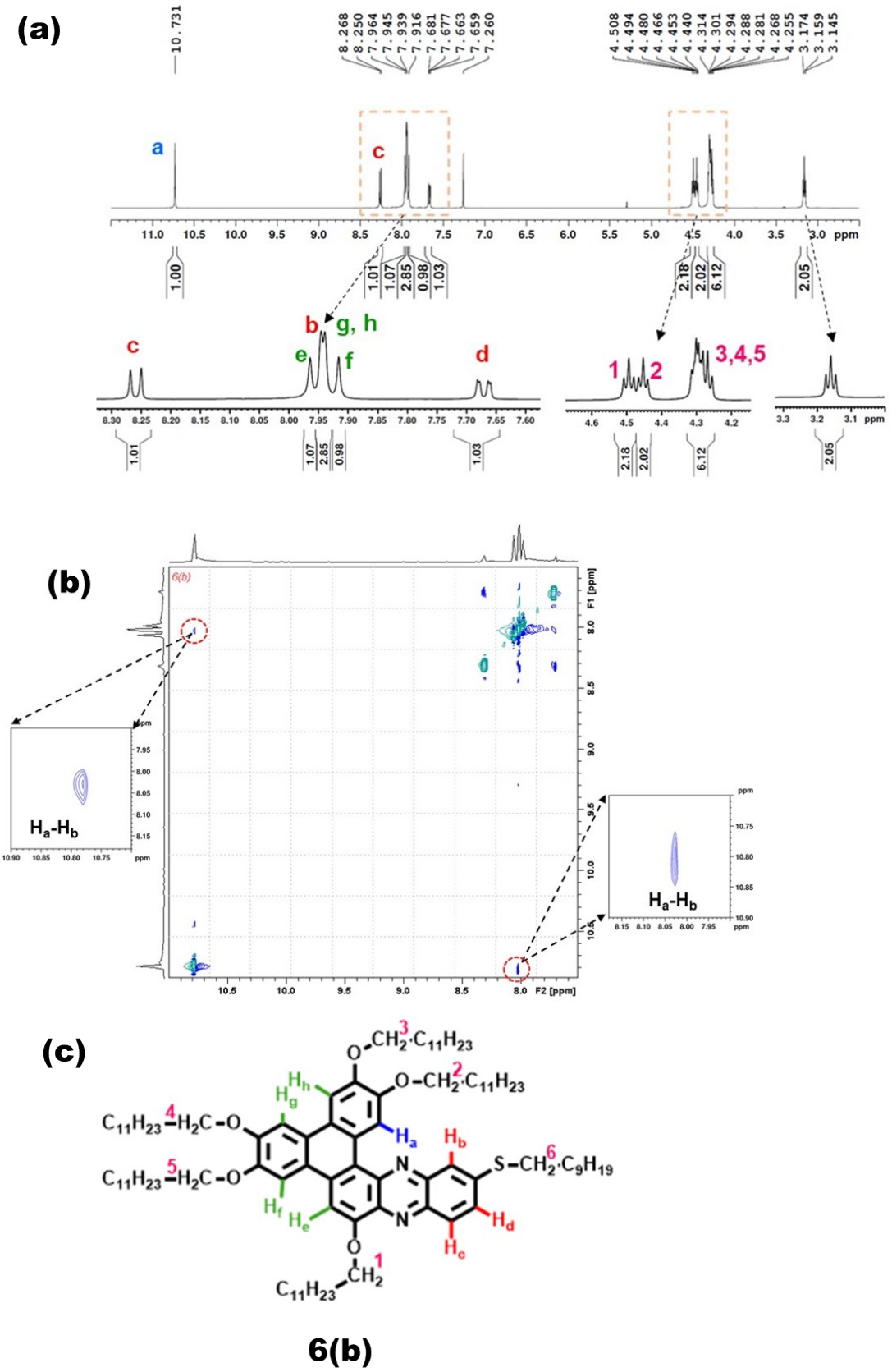

Fig 3. [1]H and ROESY NMR spectrum of compound **6(b)** [Enlarged Images]