Supporting Information for

Facile Transformation of Perylene Tetracarboxylic Acid Dianhydride into Strong Donor-Acceptor Chromophores

Yulian Zagranyarski,[†] Long Chen,[†] Yanfei Zhao,[†] Henrike Wonneberger,[‡] Chen Li,[†] Klaus Müllen*[,†]

[†]*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany*

[‡]*BASF SE, 67056 Ludwigshafen, Germany*
Email: *muellen@mpip-mainz.mpg.de*

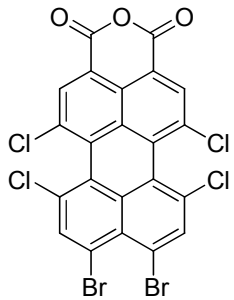
Table of Contents

Materials and Methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC300 NMR spectrometers using the residual proton or the carbon signal of the deuterated solvent as an internal standard. Chemical shifts are reported in parts per million. FD mass spectra were performed with a VG-Instrument ZAB 2-SE-FDP. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. Fluorescence emission spectra were recorded on a J&M Tidas spectrometer. The fluorescence quantum yield measurement was using Cresyl violet in ethanol as standard (54%). The absorbance of each sample in the 10 mm fluorescence cuvette was < 0.1 at the excitation wavelength. The elemental analyses were carried out by the Microanalytical Laboratory of Johannes Gutenberg University. Cyclic voltammetry (CV) measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a dichloromethane solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature, using gold discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker (The Fc^+/Fc's oxidation onset potential vs. the reference electrode AgCl/Ag is 0.32 V) for the calibration of potentials. All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified.. Column chromatography was performed with dichloromethane (Fisher Scientific), methanol, tetrahydrofuran, hexane or acetone (Sigma-Aldrich) on silica gel (Macherey-Nagel, Si60). 1,6,7,12-tetrachloro-3,4,9,10-perylentetracarboxilyc acid dianhydride was supplied from BASF-AG (Ludwigshafen). All reported yields are isolated yields.

Experimental Section

9,10-dibromo-1,6,7,12-tetrachloro-3,4-perylenedicarboxilyc acid anhydride (2)



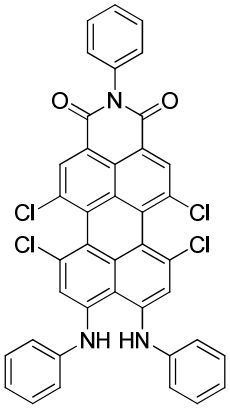
To a suspension of 1,6,7,12-tetrachloro-3,4,9,10-perylentetracarboxilyc acid dianhydride (2.65 g, 5.00 mmol) in 100 mL water was added 30 mL 1M NaOH and the mixture was stirred to obtained a limpid solution of tetra sodium salt. The mixture was heated to 80°C and 30 mmol acetic acid was added. Bromine (11mmol, 0.57 mL) was added in one portion and the reaction mixture was stirred at 80°C for 2 h. The resulted precipitate was filtered, washed with water and dried. The crude product was purified by redispersion in 50 mL methanol and 50 mL acetic acid and stirred at 100°C for 5h. The mixture was poured in methanol (200 mL) and precipitate was filtered, washed with methanol and dried. Yield 2.65 g (86%).

MALDI TOF Mass spectrum : *m/z* (%): calcd for 617.89; found: 617.9 (100)

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300K): 8.20 (s, 2H); 8.63 (s, 2H).

Elemental analysis calcd (%) for $C_{22}H_4Br_2Cl_4N_3O_3$: C 42.76, H 0.65; found: C 42.76, H 0.66.

5,6,11,12-tetrachloro-2-phenyl-8,9-bis(phenylamino)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (3)



A suspension of compound **2** (0.64 g, 2. 0 mmol) in 8 ml aniline was stirred at 180°C under argon for 5 h. The mixture was poured into 10 % hydrochloric acid and ice. The precipitate was filtered, washed with water and water/methanol 1:1. The crude product was purified by column chromatography using dichloromethane as eluent on silica. Yield 1.01 g (70%).

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300K): 7.17-7.22 (m, 6H); 7.33-7.35 (m, 4H); 7.40-7.46 (m, 4H); 7.52-7.63 (m, 3H); 7.86 (s, 2H, NH) 8.56 (s, 2H).

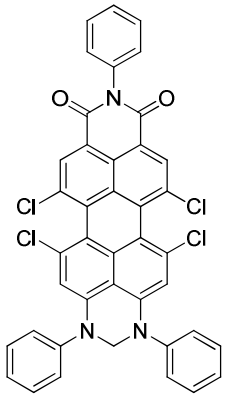
^{13}C NMR (75.0 MHz, $C_2D_2Cl_4$, 300K): 113.86 (1C); 116.13 (2C); 116.85 (2C); 119.37 (2C); 121.15 (4C); 123.61 (1C); 124.53 (2C); 128.76 (1C); 129.37 (2C); 129.90 (4C); 130.64 (2C); 131.64 (2C); 131.83 (1C); 132.55 (2C); 135.04 (1C); 135.86 (1C); 137.75 (2C); 140.53 (2C); 145.27 (2C); 163.07 (2C, CO).

MALDI TOF Mass spectrum (8 kV): *m/z* (%): calcd for 717.43; found: 717.6 (100) $[M]^+$.

Elemental analysis calcd (%) for $C_{40}H_{21}Cl_4N_3O_2$: C 66.97, H 2.95, N 5.86; found: C 66.41, H 3.08, N 5.86.

UV-Vis (CH_2Cl_2): λ_{max} = 615 (33 163) nm ($M^{-1}cm^{-1}$).

5,6,12,13-tetrachloro-1,3,9-triphenyl-2,3-dihydropyrido[3',4',5':6,7]phenaleno[1,2,3-gh]perimidine-8,10(1H,9H)-dione (4)



To a solution of compound **3** (0.72 g, 1.00 mmol) and paraformaldehyde (0.120 g, 4.0mmol) in 100 mL chloroform 0.10 ml trifluoroacetic acid was added and the reaction mixture was refluxed for 1.5 h under argon. The solvent was removed under vacuum and the crude solid was purified by column chromatography using dichloromethane as eluent on silica. Yield 0.70 g (96%).

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300K): 5.38 (s, 2H, CH_2); 6.91 (s, 2H); 7.33-7.45 (m, 8H); 7.53-7.62 (m, 7H); 8.56 (s, 2H).

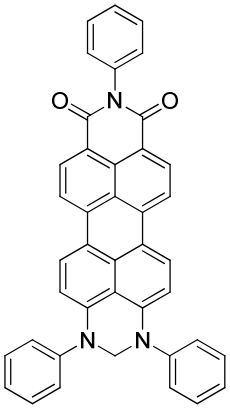
^{13}C NMR (75.0 MHz, $C_2D_2Cl_4$, 300K): 67.21 (1C, CH_2); 109.65 (1C); 109.87 (2C); 114.44 (2C); 118.65 (2C); 124.09 (1C); 124.75 (4C); 127.33 (2C); 128.68 (2C); 129.34 (2C); 129.52 (2C); 130.32 (4C); 131.77 (2C); 131.87 (1C); 132.55 (1C); 133.98 (1C); 135.20 (1C); 138.45 (2C); 142.02 (2C); 144.59 (2C); 163.15 (2C, CO).

FD mass spectrum (8 kV): *m/z* (%): calcd for 729.44; found: 729.5 (100) $[M]^+$.

Elemental analysis calcd (%) for $C_{41}H_{21}Cl_4N_3O_2$: C 67.51, H 2.90, N 5.76; found: C 67.44, H 2.83, N 5.79.

UV-Vis (CH_2Cl_2): λ_{max} = 635 (45 092) nm ($M^{-1}cm^{-1}$).

1,3,9-triphenyl-2,3-dihydropyrido[3',4',5':6,7]phenaleno[1,2,3-gh]perimidine-8,10(1H,9H)-dione (5)



A mixture of potassium hydroxide (3.0 g) and compound **4** (0.68 g, 1.08 mmol) in 30 mL 1,2-ethanediol was stirred an heated at 165°C for 4 h. The mixture was cooled and diluted with 50 mL 10% hydrochloric acid. The precipitate was filtered, washed with water and dried. The crude solid was purified by column chromatography using dichloromethane/acetone as eluent on silica. Yield 0.40 g (63%).

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300K): 5.37 (s, 2H, CH_2); 6.87 (d, 2H, $^3J_{HH}$ = 8.6 Hz); 7.25-7.39 (m, 8H); 7.45-7.55 (m, 7H); 7.83 (d, 2H, $^3J_{HH}$ = 8.5 Hz); 8.11 (d, 2H, $^3J_{HH}$ = 8.9 Hz); 8.29 (d, 2H, $^3J_{HH}$ = 8.2 Hz).

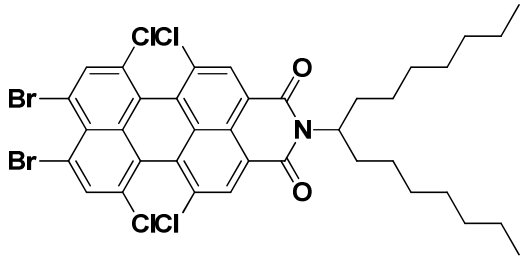
^{13}C NMR (75.0 MHz, $C_2D_2Cl_4$, 300K): 67.06 (1C, CH_2); 108.56 (2C); 114.10 (1C); 116.55 (1C); 116.77 (2C); 119.34 (2C); 124.60 (4C); 125.75 (1C); 126.31 (2C); 126.92 (2C); 128.13 (1C); 128.70 (2C); 128.84 (2C); 129.06 (2C); 129.94 (4C); 130.90 (1C); 131.32 (2C); 136.00 (1C); 138.66 (2C); 143.04 (2C); 144.83 (2C); 163.99 (2C, CO).

FD mass spectrum (8 kV): *m/z* (%): calcd for 591.66; found: 591.9 (100) $[M]^+$.

HRMS *m/z* calculated for $C_{41}H_{25}N_3O_2$ 591.1947 found 591.1932

UV-Vis (CH_2Cl_2): λ_{max} = 655 (45 398) nm ($M^{-1}cm^{-1}$).

8,9-dibromo-5,6,11,12-tetrachloro-2-(pentadecan-8-yl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (6)



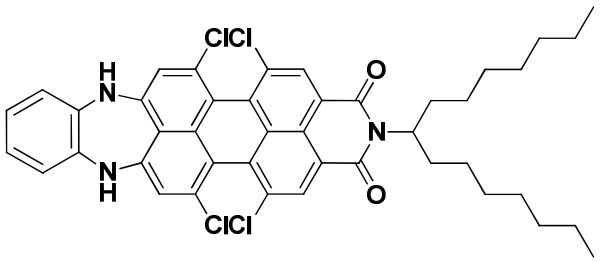
To a suspension of compound **2** (2.0 mmol, 1.24 g) in 20 mL NMP and 10 mL acetic acid, pentadecan-8-amine (4.0 mmol, 0.91 g) was added. The reaction mixture was stirred at 110°C for 15 h. After cooling down to room temperature the reaction mixture was poured in water. The precipitate was filtered, washed with methanol, dried and purified by column chromatography using hexane/dichloromethane as eluent on silica. Yield 0.80 g (48%).

MALDI TOF spectrum (8 kV): *m/z* (%): calcd for 827.30; found: 827.2 (100) $[M]^+$.

^{1}H-NMR (300 MHz, $CDCl_3$, 300K): 0.83 (t, 6H, CH_3, $^3J_{HH}$ = 7.3 Hz); 1.16-1.36 (m, 20H, CH_2); 1.77-1.88 (m, 2H, CH_2); 2.16-2.26 (m, 2H, CH_2); 5.11-5.21 (m, 1H, CHN); 8.13 (s, 2H); 8.55 (s, 1H); 8.58 (s, 1H).

^{13}C NMR (75.0 MHz, $CDCl_3$, 300K): 14.19 (2C, CH_3); 22.75 (2C, CH_2); 27.06 (2C, CH_2); 29.33 (2C, CH_2); 29.63 (2C, CH_2); 31.94 (2C, CH_2); 32.49 (2C, CH_2); 55.23 (1C, CHN); 122.58 (2C); 123.22 (2C); 124.46 (2C); 125.51 (2C); 129.42 (2C); 131.44 (2C); 132.71 (2C); 133.32 (2C); 133.82 (2C); 134.87 (2C); 135.59 (2C); 137.19 (2C).

5,6,15,16-tetrachloro-2-(pentadecan-8-yl)-8,13-dihydro-1H-benzo[b]pyrido-[3',4',5':9,10]peryleno[3,4-ef][1,4]diazepine-1,3(2H)-dione (7)



A mixture of compound **6** (0.83 g, 1.0 mmol), 1,2-diaminobenzene (0.54 g, 5.0 mmol) in 20 mL NMP was stirred at 180°C under argon for 5 h. The mixture was poured into 10 % hydrochloric acid and ice. The precipitate was filtered, washed with water and methanol. The crude product was purified by column chromatography using hexane/dichloromethane as eluent on silica. Yield 0.35 g (45%).

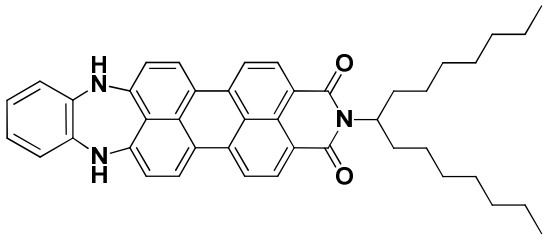
^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300K): 0.84 (t, 6H, CH_3, $^{3}J_{HH}$ = 6.9 Hz); 1.17-1.35 (m, 20H, CH_2); 1.80-1.90 (m, 2H, CH_2); 2.15-2.25 (m, 2H, CH_2); 5.10-5.20 (m, 1H, CHN); 6.35 (s, 2H, NH); 6.86-6.91 (m, 2H); 6.99-7.03 (m, 4H); 8.49 (s, 1H) 8.53 (s, 1H).

^{13}C NMR (75.0 MHz, $C_2D_2Cl_4$, 300K): 14.07 (2C, CH_3); 22.53 (2C, CH_2); 26.85 (2C, CH_2); 29.09 (2C, CH_2); 29.43 (2C, CH_2); 31.71 (2C, CH_2); 32.21 (2C, CH_2); 54.63 (1C, CHN); 109.07 (2C); 116.12 (2C); 116.20 (2C); 119.83 (2C); 120.18 (1C); 123.27 (2C); 123.99 (2C); 130.50 (2C); 130.69 (1C); 130.96 (1C); 131.05 (1C); 132.18 (1C); 132.84 (2C); 135.86 (2C); 136.75 (2C); 143.73 (2C); 162.92 (1C, CO); 164.03 (1C, CO).

UV-Vis (CH_2Cl_2): λ_{max} = 588 (36 654) nm ($M^{-1}cm^{-1}$).

HRMS *m/z* calculated for $C_{43}H_{41}Cl_4N_3O_2$ 771.1953 found 771.1982

2-(pentadecan-8-yl)-8,13-dihydro-1H-benzo[b]pyrido[3',4',5':9,10]peryleno[3,4-ef][1,4]diazepine-1,3(2H)-dione (8)



A mixture of potassium hydroxide (1.0 g) and compound **7** (0.22 g, 0.285 mmol) in 30 mL 1,2-ethanediol was stirred an heated at 165°C for 24 h. The mixture was cooled and diluted with 50 mL 10% hydrochloric acid. The precipitate was filtered, washed with water and dried. The crude solid was purified by column chromatography using dichloromethane as eluent on silica. Yield 0.038 g (21%).

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300K): 0.83 (t, 6H, CH_3, $^{3}J_{HH}$ = 6.2 Hz); 1.15-1.37 (m, 20H, CH_2); 1.80-1.95 (m, 2H, CH_2); 2.13-2.28 (m, 2H, CH_2); 5.10-5.22 (m, 1H, CHN); 6.27

(s, 2H, NH); 6.88-7.02 (m, 6H); 8.07 (d, 2H, $^{3}J_{HH}$ = 8.1 Hz); 8.21 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz); 8.42 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz).

^{13}C NMR (75.0 MHz, THF-*d8*, 300K): 14.54 (2C, CH_3); 23.66 (2C, CH_2); 27.97 (2C, CH_2); 30.38 (2C, CH_2); 30.69 (2C, CH_2); 32.96 (2C, CH_2); 33.45 (2C, CH_2); 54.17 (1C, CHN); 113.65 (2C); 115.84 (2C); 118.32 (2C); 120.13 (2C); 122.10 (2C); 123.37 (2C); 126.91 (2C); 127.39 (2C); 131.57 (1C); 131.87 (1C); 132.00 (1C); 132.55 (1C); 135.39 (2C); 139.64 (2C); 147.01 (2C); 164.71 (1C, CO); 165.62 (1C, CO).

UV-Vis (CH_2Cl_2): λ_{max} = 591 (30 187) nm ($M^{-1}cm^{-1}$).

HRMS *m/z* calculated for $C_{43}H_{45}N_3O_2$ 635.3512 found 635.3514

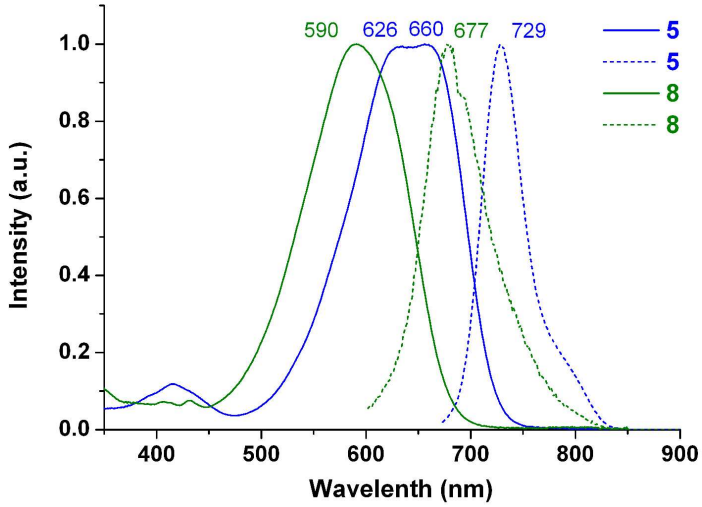
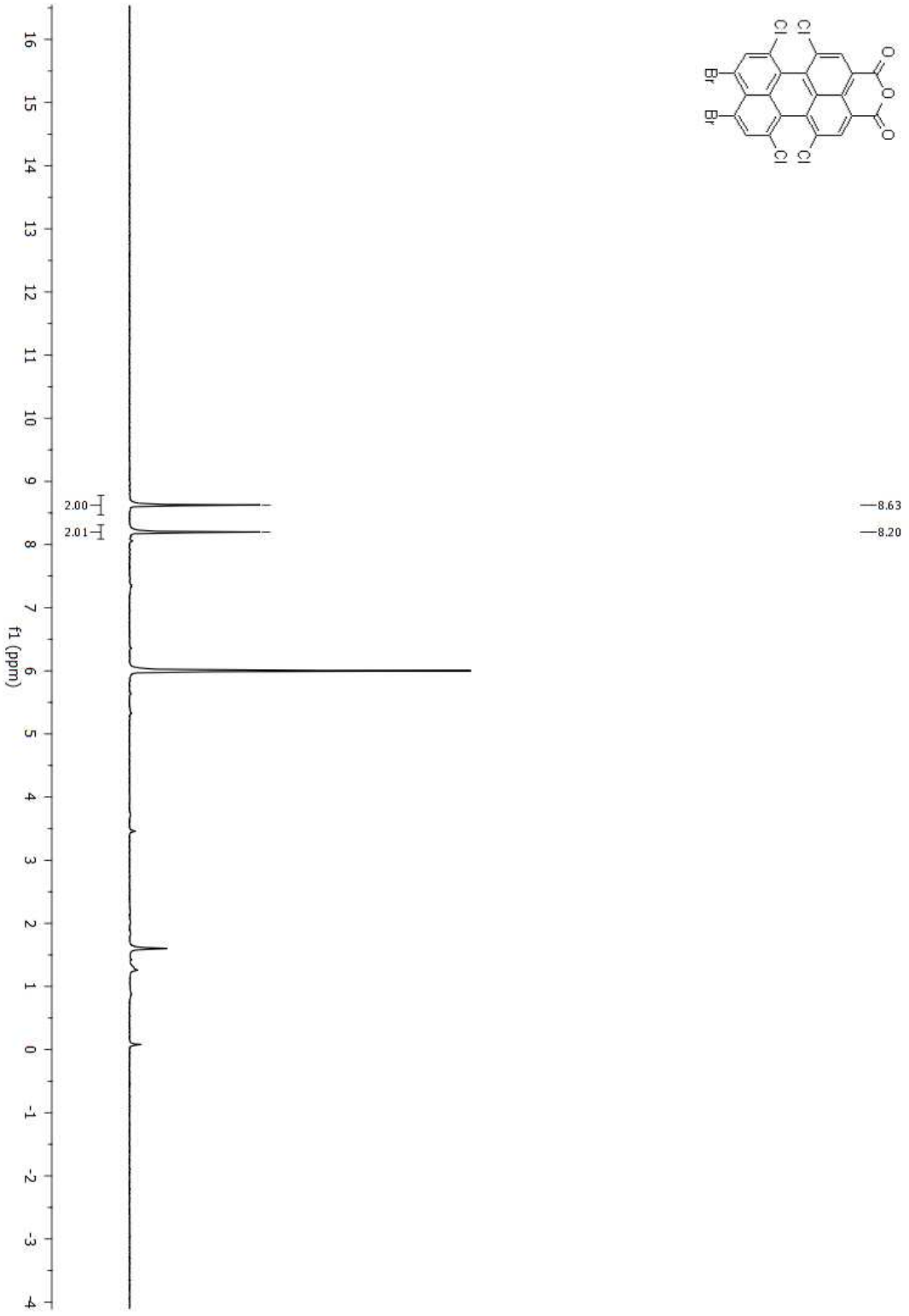


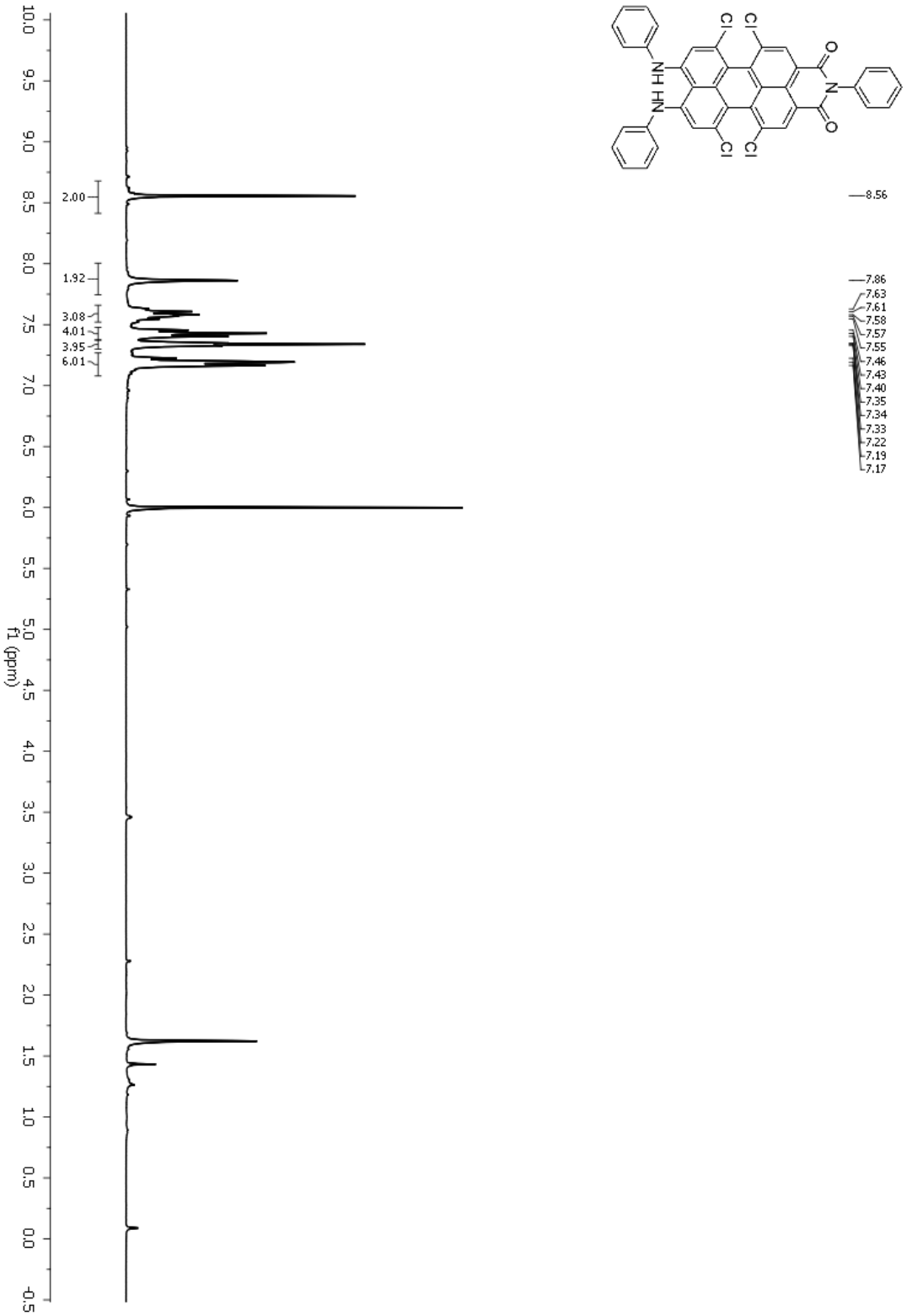
Figure S1. Normalized UV-Vis and Photoluminescence spectra of **5** and **8** in CH_2Cl_2.

^{1}H NMR and ^{13}C NMR Spectra

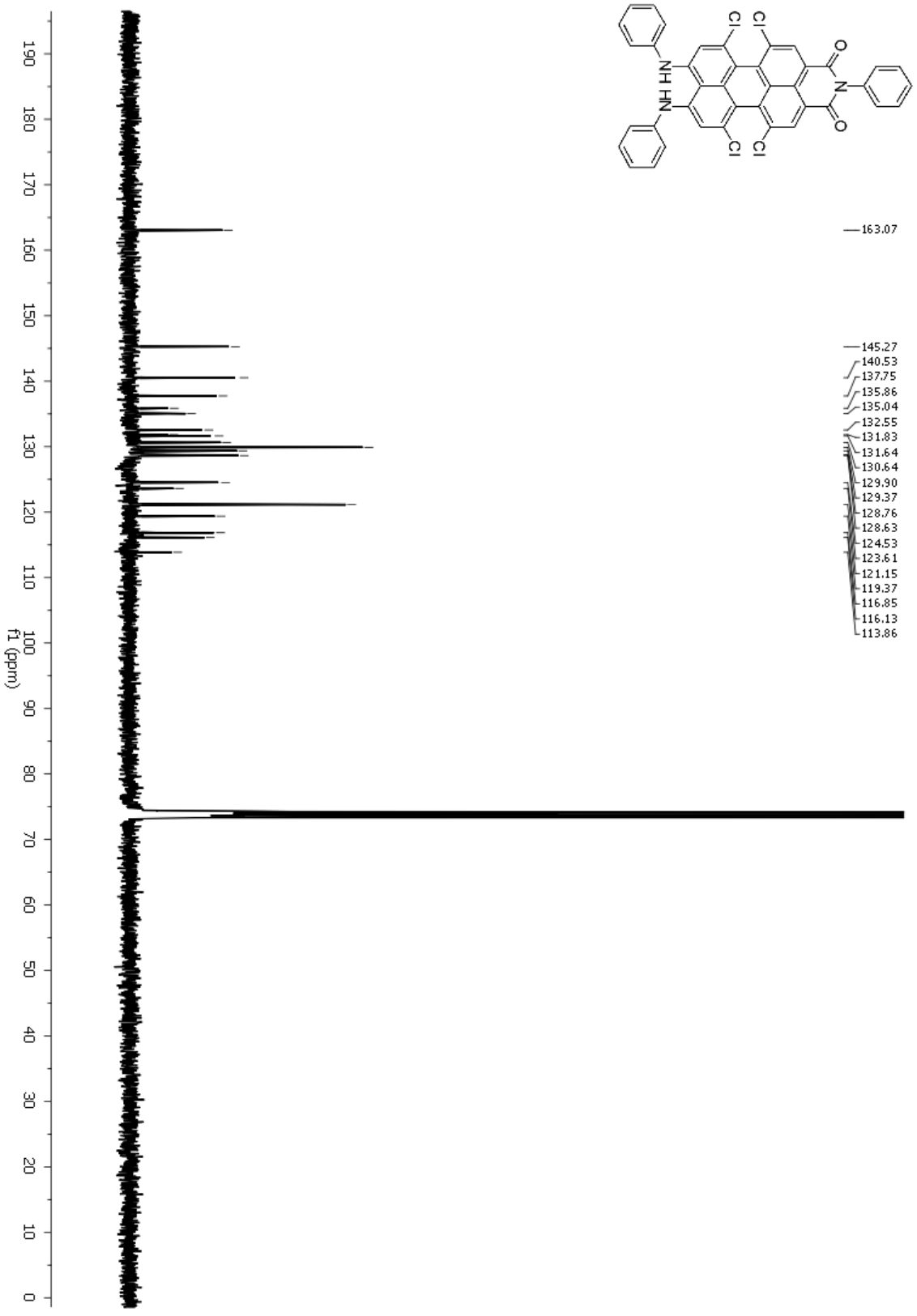
^{1}H NMR spectrum of Compound 2 in 1,1,2,2-tetrachloroethane-d_2 300 MHz



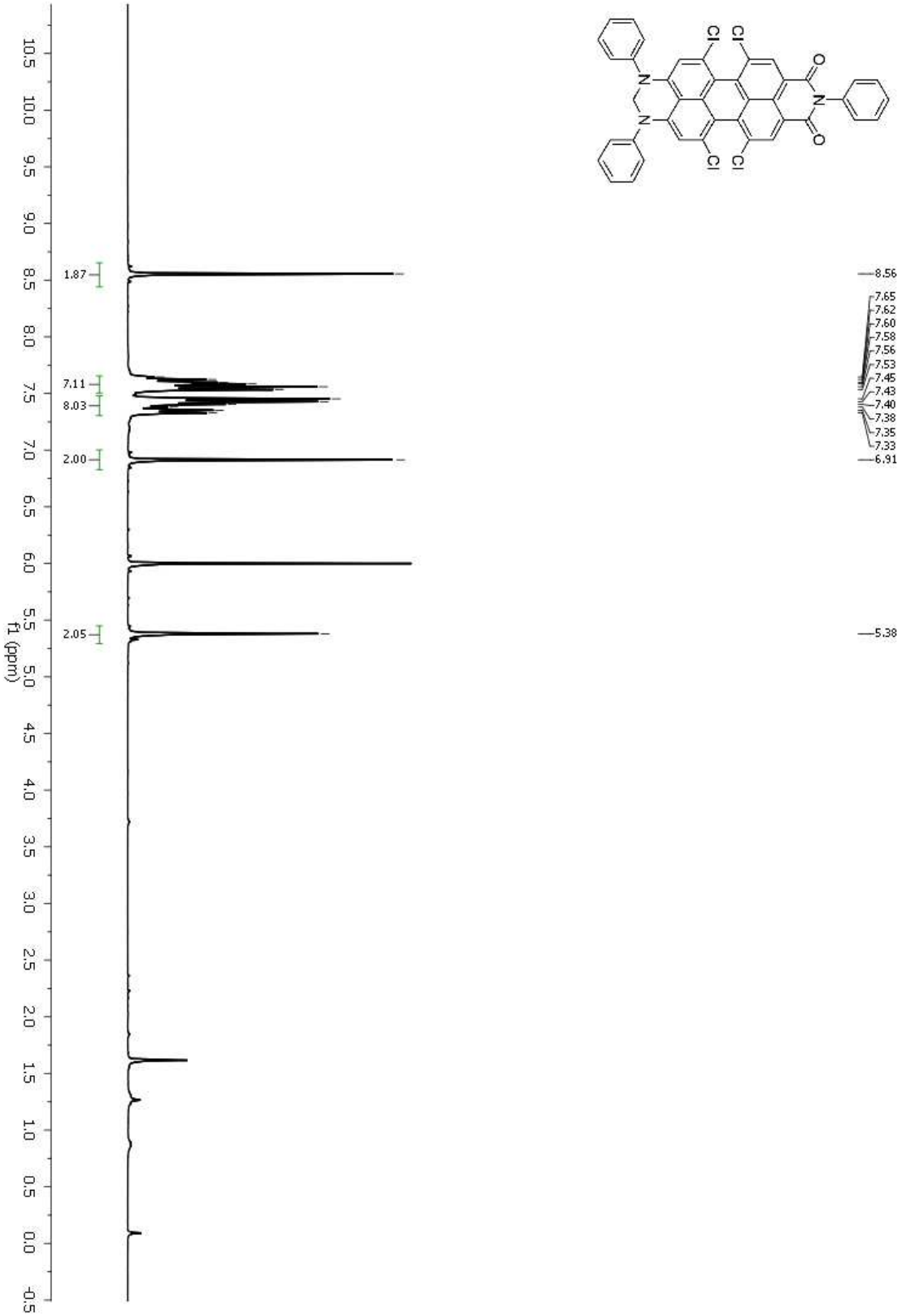
^{1}H NMR spectrum of Compound 3 in 1,1,2,2-tetrachloroethane-d_2 300 MHz



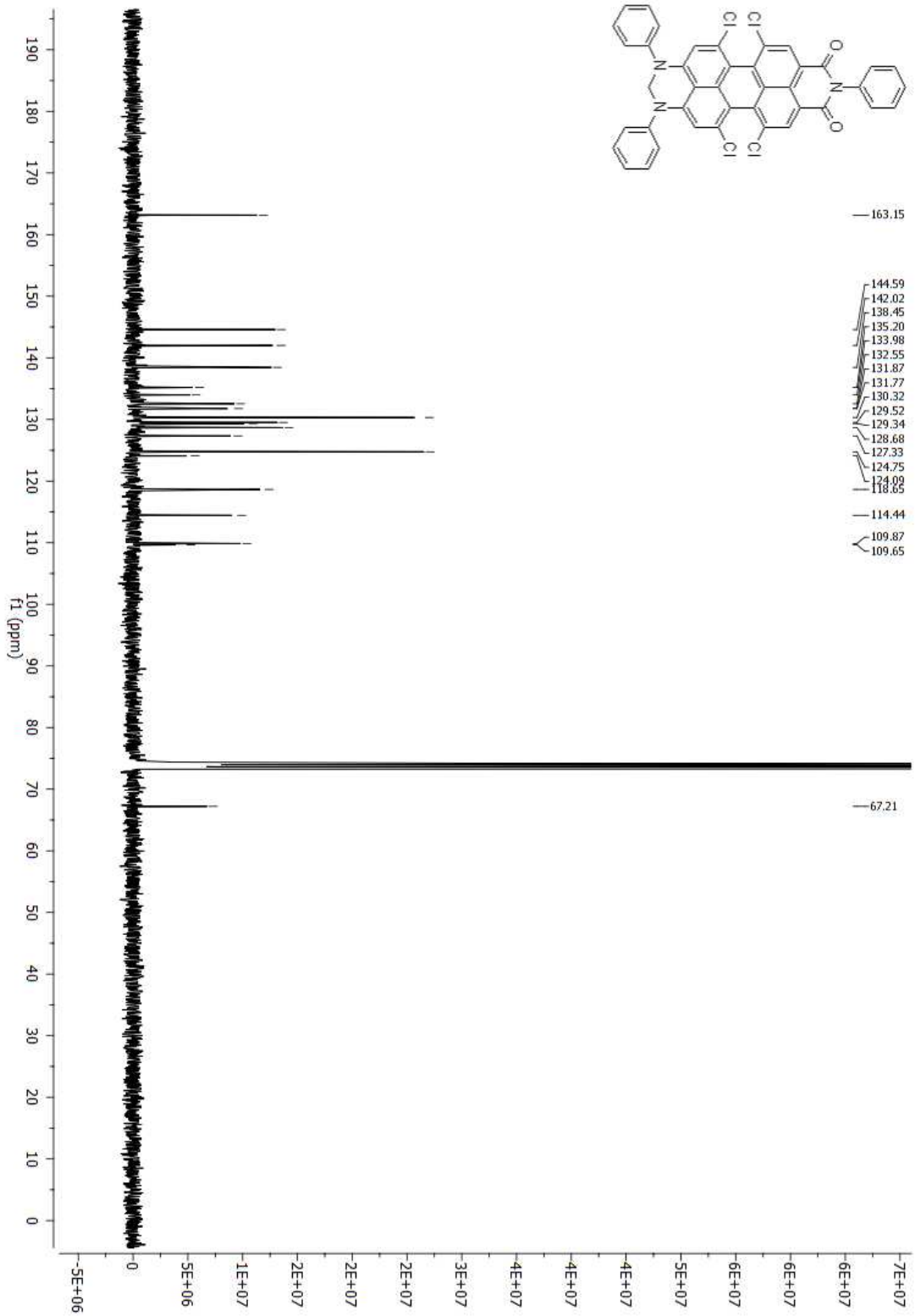
^{13}C NMR spectrum of Compound 3 in 1,1,2,2-tetrachloroethane-d_2 75MHz



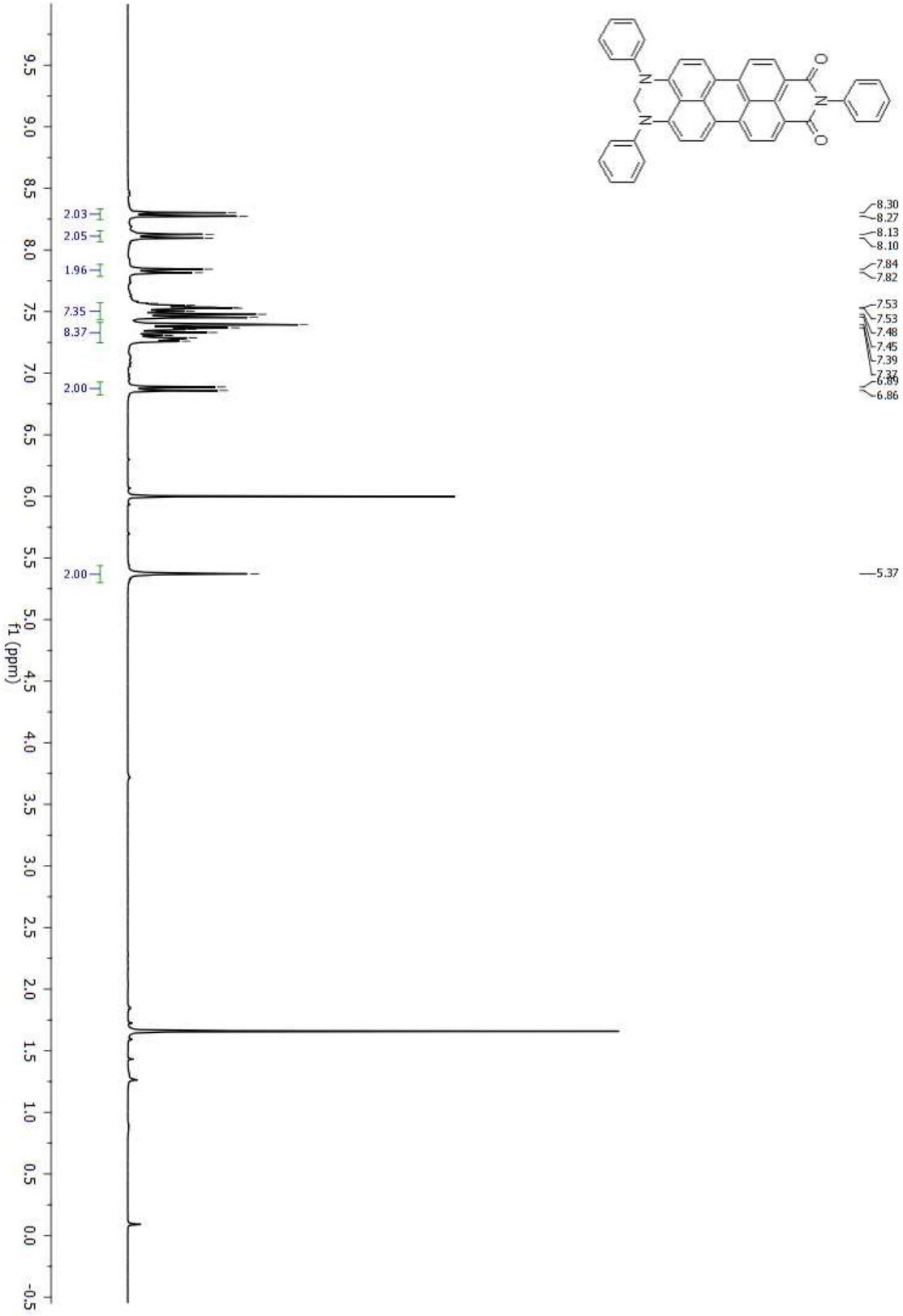
^{1}H NMR spectrum of Compound 4 in 1,1,2,2-tetrachloroethane-d_2 300 MHz



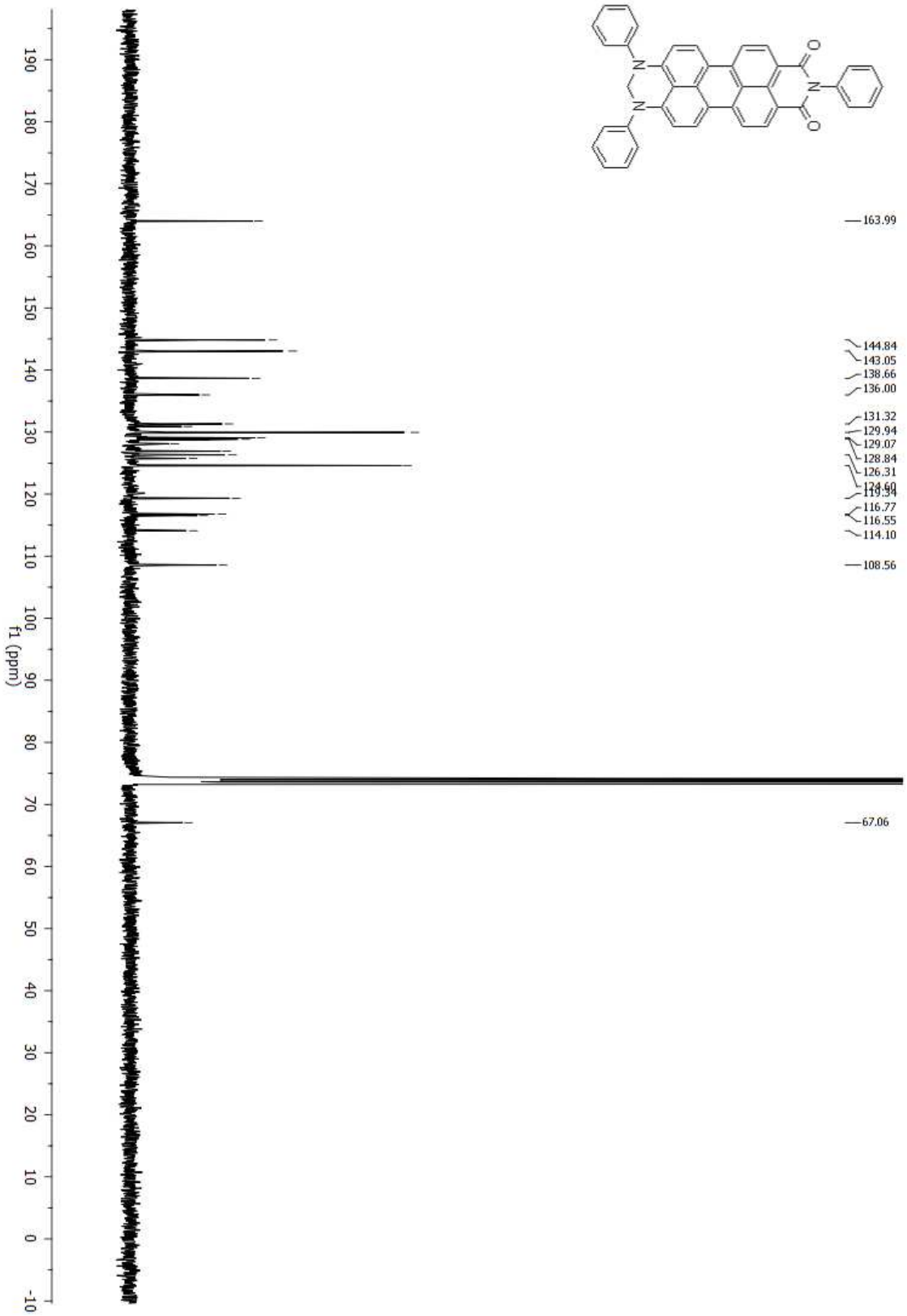
^{13}C NMR spectrum of Compound 4 in 1,1,2,2-tetrachloroethane-d_2 75 MHz



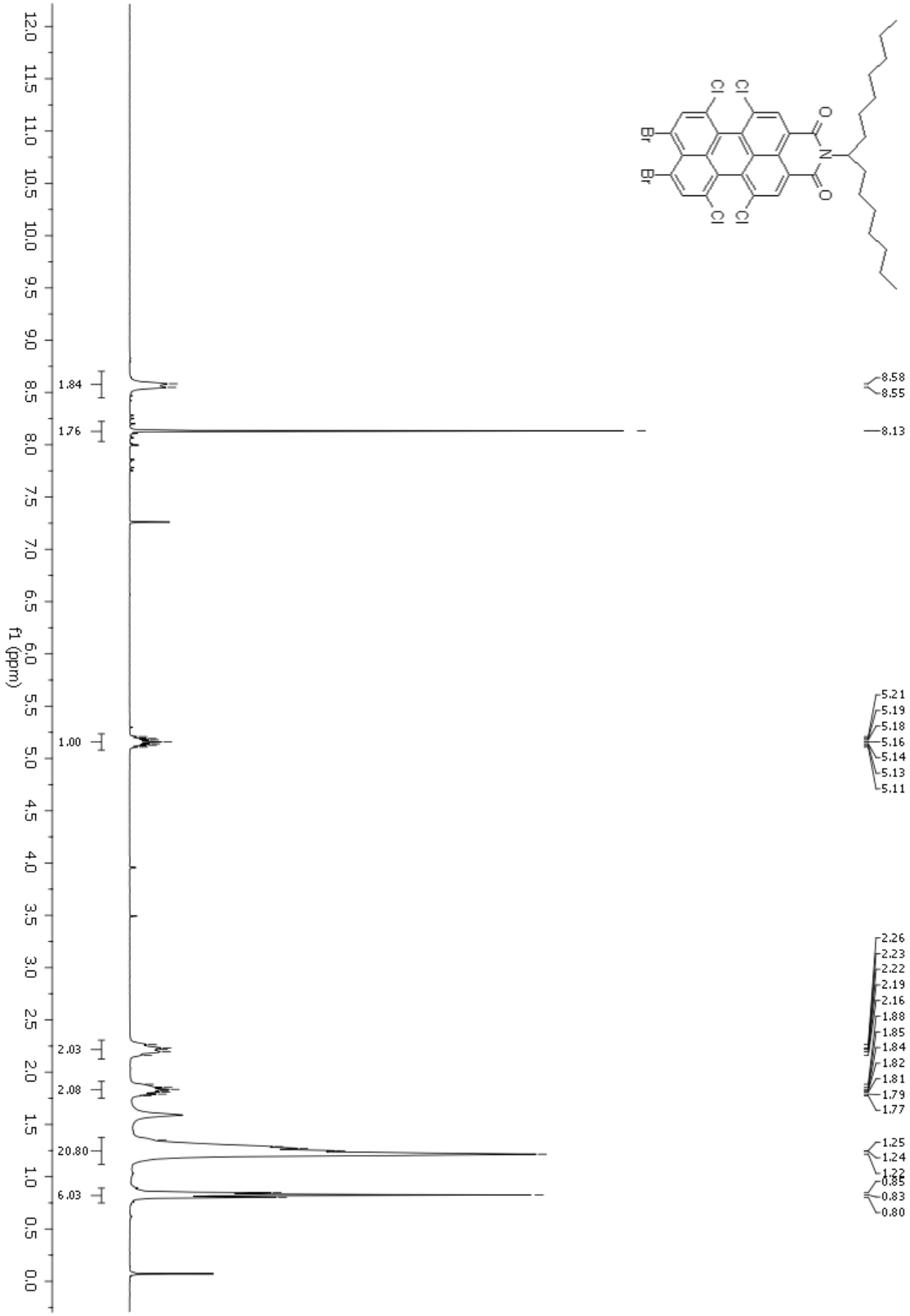
^{1}H NMR spectrum of Compound 5 in 1,1,2,2-tetrachloroethane-d_2 300 MHz



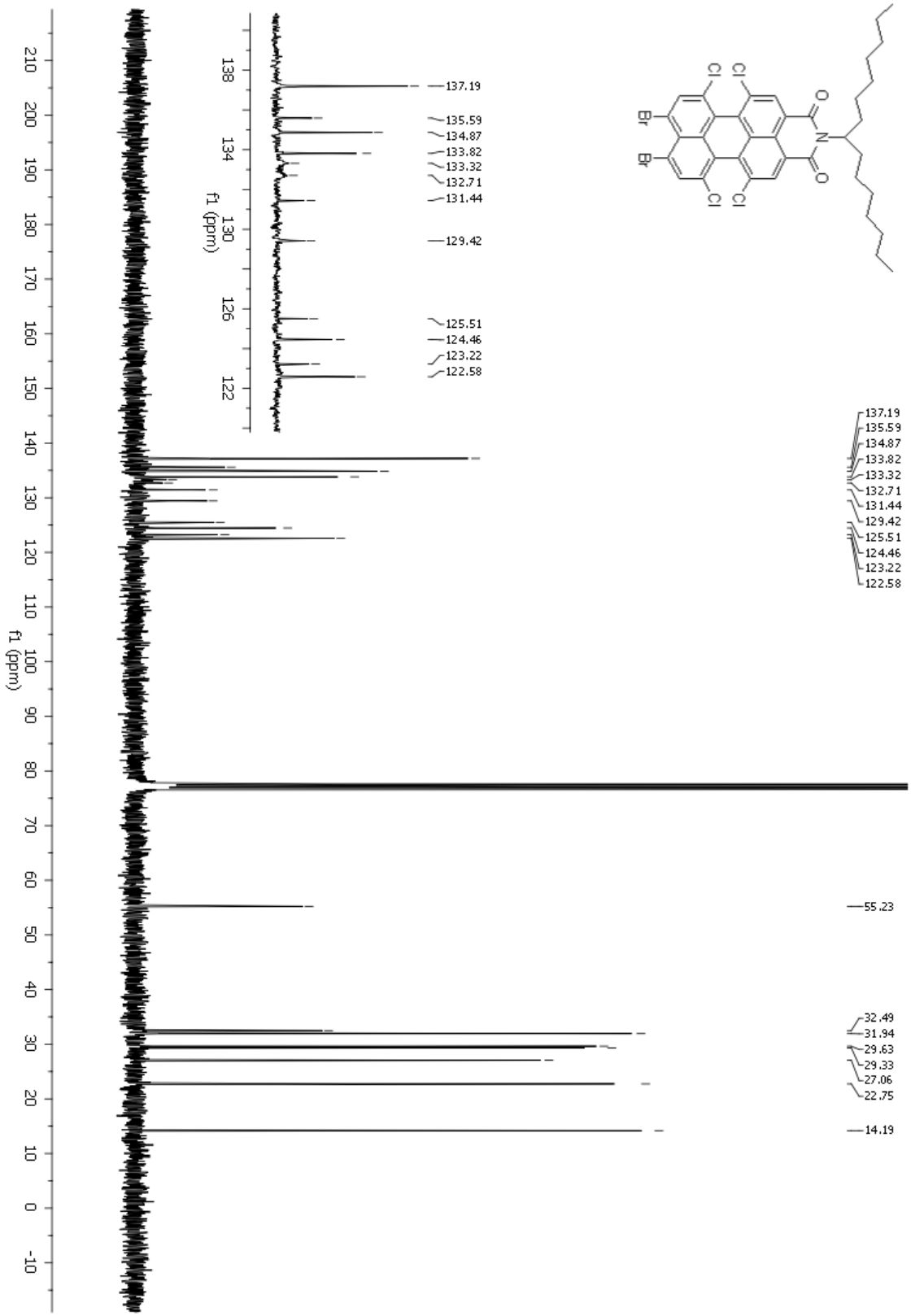
^{13}C NMR spectrum of Compound 5 in 1,1,2,2-tetrachloroethane-d_2 75 MHz



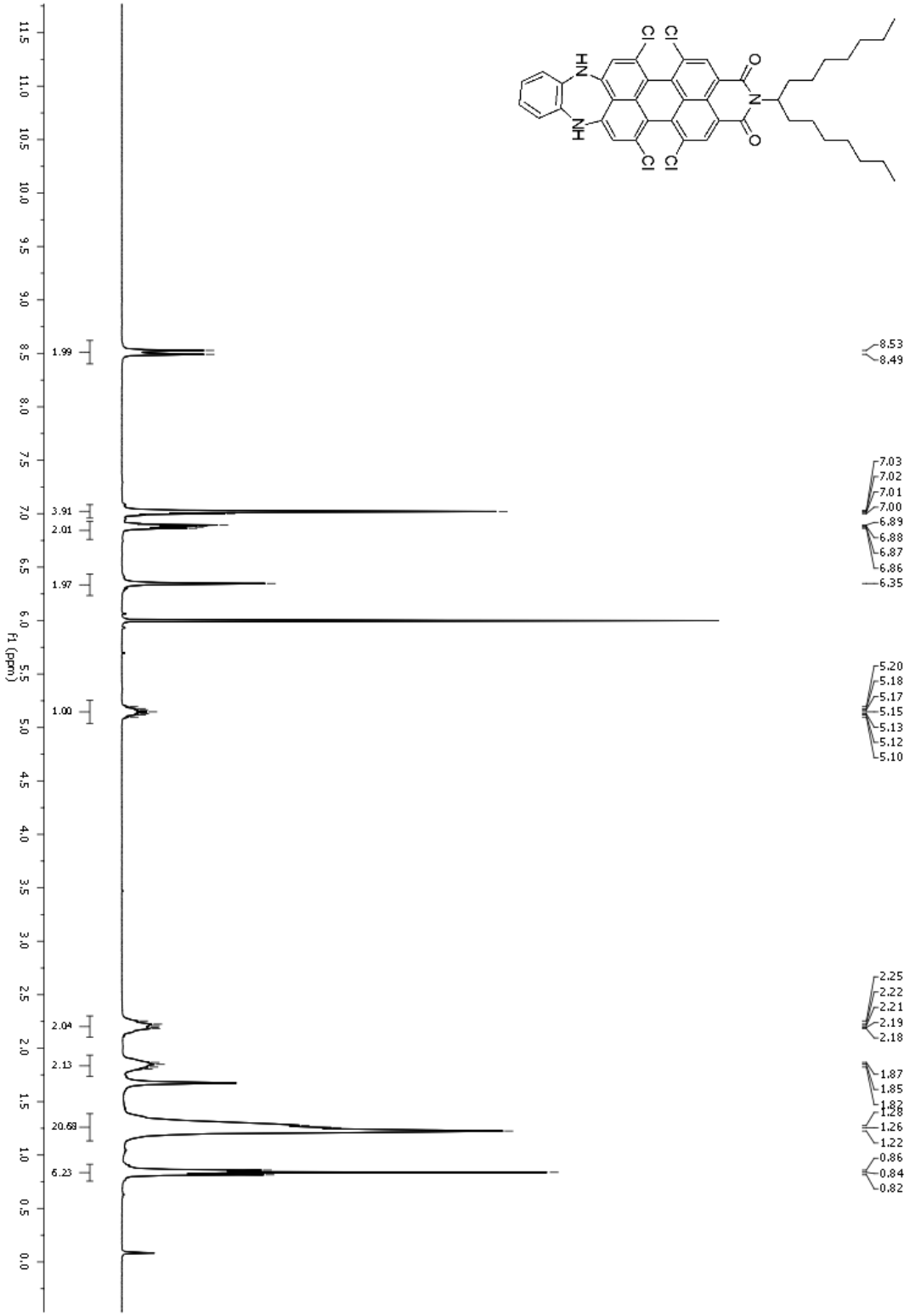
^{1}H NMR spectrum of Compound 6 in chloroform-d 300 MHz



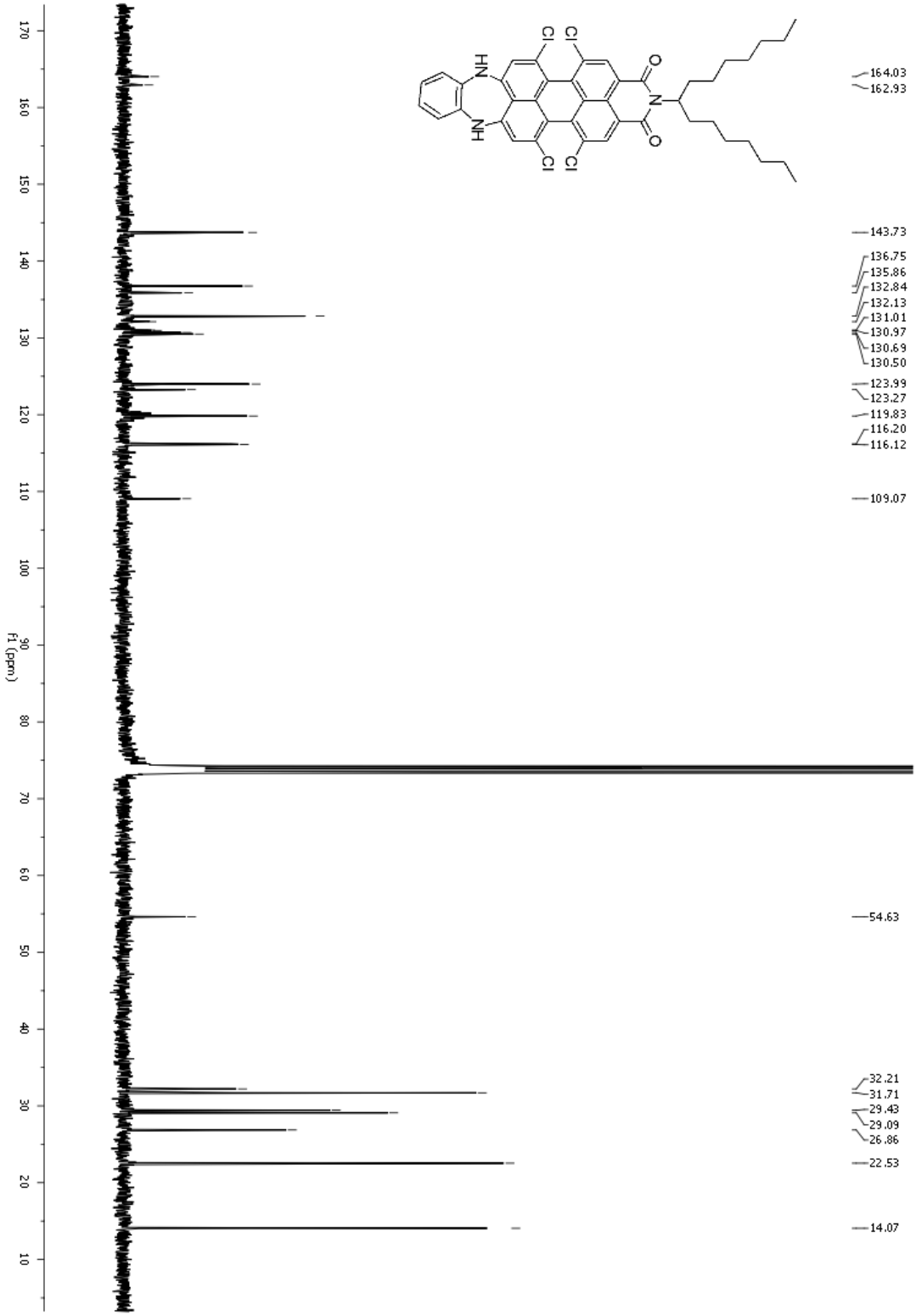
^{13}C NMR spectrum of Compound 6 in chloroform-d 75 MHz



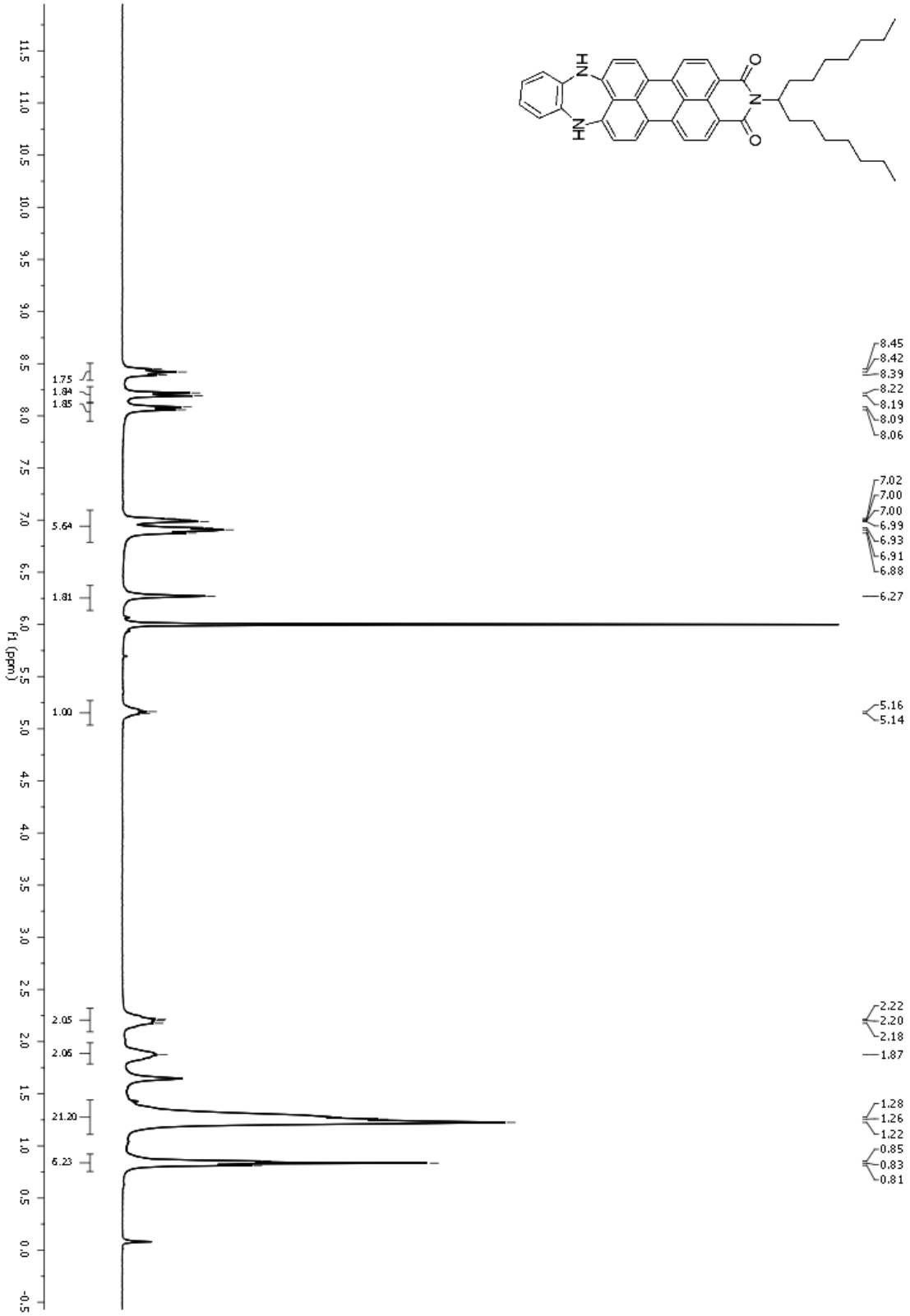
^{1}H NMR spectrum of Compound 7 in 1,1,2,2-tetrachloroethane-d_2 300 MHz



^{13}C NMR spectrum of Compound 7 in 1,1,2,2-tetrachloroethane-d_2 75 MHz



^{1}H NMR spectrum of Compound 8 in 1,1,2,2-tetrachloroethane-d_2 300 MHz



^{13}C NMR spectrum of Compound 8 in tetrahydrofurane-d_8 75 MHz