Supporting Information for

Columnar Liquid Crystalline Bis-N-annulated Quaterrylenes

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1. Materials and Methods:

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer and a Bruker ADVANCE 600 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer. Elemental analysis were determined on Flash EA 1112, and High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer and Bruker Apex IV FTMS. Absorption spectra were measured with Jasco V-570 UV/Vis/NIR spectrophotometer in a 1-cm quartz cell. Fluorescence spectra were measured with Jasco FP-6600 spectrofluorometer and all fluorescence spectra are corrected. The fluorescence quantum yields were determined by optical dilute method (A< 0.05) using Cresyl Violet (Φ_{st}=0.54 in Methanol) as reference.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Starting material 6 *H*-Phenanthro[1,10,9,8-*c,d,e,f,g*]carbazole was synthesized according to literature.[1]

2. Synthesis and characterization of compounds 3 to 8

The synthesis of compounds 3a to 8a are similar to that of compounds 3b to 8b, and here take compounds 3a to 8a for illustrations.

Compound 3a:

A mixture of 6*H*-Phenanthro[1,10,9,8-*c,d,e,f,g*]carbazole (500 mg, 1 equiv), NaH (68 mg, 1.5 equiv), 1-bromo-dodecane (705 mg, 1.5 equiv) in dry 50 ml THF was stirred at 66°C for 12 h under nitrogen. After cooling to room temperature, the mixture was stirred for 30 min at 0°C before 2 ml of water was added dropwise. The reaction mixture was then poured into water and the product was extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2, 3:1) to yield the yellow wax product (784 mg, 96 %).

3a: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.65 (d, 2H), 8.12 (d, 2H), 7.90 (d, 2H), 7.82-7.79 (m, 4H), 4.70 (t, 2H), 2.13-2.06 (m, 2H), 1.38-1.21 (m, 18H) , 0.87 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 131.8, 130.3, 128.7, 124.9, 124.8, 124.4, 123.5, 120.6, 117.3, 113.3, 45.7, 31.8, 31.2, 29.6, 29.5, 29.4, 29.3, 29.2, 27.1, 22.6, 14.1, 1.0. MS (MALDI-TOF): m/z (M^+) = 433.4 (calcd for $C_{32}H_{35}N$: 433.6), HRMS: calcd for $C_{32}H_{36}N$ $[M+H]^+$: 434.2842; found 434.2838.

3b: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.65 (d, 2H), 8.12 (d, 2H), 7.90 (d, 2H), 7.83-7.76 (m, 4H), 4.54 (d, 2H), 2.28-2.26 (m, 1H), 1.42-1.18 (m, 24H) , 0.89-0.81 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 132.1, 130.3, 128.7, 124.9, 124.8, 124.4, 123.5, 120.6, 117.2, 113.4, 50.0, 39.9, 31.9, 31.8, 31.7, 29.8, 29.6, 29.5, 29.2, 26.5, 22.7, 22.7, 22.6, 22.5, 14.1, 14.0, 1.0. MS (MALDI-TOF): m/z (M^+) = 489.4 (calcd for $C_{36}H_{43}N$: 489.3).

Compound 4a:

To the solution of compound **3a** (500 mg, 1 equiv) in 100 ml DMF added NBS (206 mg, 1 equiv), and the mixture was stirred at 25°C for 2 h. The reaction mixture was then poured into water and the product was extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2, 6:1) to yield the yellow

solid product (485 mg, 82%).

4a: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ = 8.64 (t, 2H), 8.31 (d, 1H), 8.12 (t, 2H), 7.93-7.85 (m, 2H), 7.81 (t, 1H), 7.74 (d, 1H), 4.61 (t, 2H), 2.06 (m, 2H), 1.34-1.21 (m, 18H), 0.86 (t, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 132.0, 131.3, 131.2, 130.3, 129.7, 129.6, 128.6, 127.8, 125.3, 125.2, 124.9, 124.6, 124.4, 124.3, 124.1, 121.3, 121.0, 117.4, 116.9, 116.8, 116.7, 116.6, 113.2, 45.8, 31.8, 31.1, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 27.1, 22.6, 14.1, 1.0. MS (MALDI-TOF): m/z (M^+) = 512.7 (calcd for $C_{32}H_{34}BrN$: 512.5) , HRMS: calcd for $C_{32}H_{35}BrN$ $[M+H]^+$: 512.1947; found 512.1942.

4b: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ = 8.64 (t, 2H), 8.31 (d, 1H), 8.12 (d, 1H), 8.02 (s, 1H), 7.91-7.85 (m, 2H), 7.81 (t, 1H), 7.68 (d, 1H), 4.40 (d, 2H), 2.21-2.19 (m, 1H), 1.39-1.18 (m, 24H) , 0.88-0.81 (m, 6H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 132.0, 131.3, 130.2, 129.6, 128.5, 127.6, 125.1, 125.0, 124.5, 124.2, 124.1, 123.9, 121.1, 120.8, 117.2, 116.9, 116.6, 116.3, 113.2, 49.8, 39.7, 31.8, 31.8, 31.7, 31.6, 29.8, 29.5, 29.5, 29.2, 26.4, 22.6, 22.6, 14.1, 14.0, 1.0. MS (MALDI-TOF): m/z (M^+) = 569.3 (calcd for $C_{36}H_{42}BrN$: 569.2).

Compound 5a:

A mixture of compound **4a** (300 mg, 1 equiv), 4- (Methoxycarbonyl)benzeneboronic acid (127 mg, 1.2 equiv), $Pd(PPh_3)_4$ (68 mg, 10% equiv), K_2CO_3 (404 mg, 5 equiv) in 50 ml THF (2 ml H_2O) was stirred at 66°C for 12 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water and the product was extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2, 1:1) to yield the yellow solid product (290 mg, 87 %).

5a: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.69 (t, 2H), 8.24 (d, 2H), 8.14 (d, 1H), 8.09 (d, 1H), 7.94 (d, 1H), 7.85-7.76 (m, 6H), 4.72 (t, 2H), 4.01 (s, 3H), 2.11 (m, 2H) , 1.40-1.20 (m, 18H), 0.86 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 167.1, 146.9, 136.1, 132.2, 131.6, 130.7, 130.3, 129.8, 128.8, 128.7, 127.4, 125.1, 125.0, 124.7, 124.6, 124.0, 123.7, 121.0, 120.9, 117.3, 114.2, 113.3, 52.2, 45.8, 31.9, 31.2, 29.6, 29.5, 29.5, 29.3, 29.2, 27.1, 22.6, 14.1, 1.0. MS (MALDI-TOF): m/z (M^+) = 568.0 (calcd for $C_{40}H_{41}NO_2$: 567.8) , HRMS: calcd for $C_{40}H_{41}NO_2$ [M]: 567.3132; found 567.3130.

5b: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.69 (t, 2H), 8.24 (d, 2H), 8.14 (d, 1H), 8.09 (d, 1H), 7.94 (d, 1H), 7.85-7.75 (m, 6H), 4.56 (d, 2H), 4.01 (s, 3H), 2.29 (s, 1H), 1.39-1.16 (m, 24H) , 0.84-0.81 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 167.2, 147.0, 136.1, 132.5, 131.9, 130.7, 130.3, 129.8, 128.8, 128.7, 127.4, 125.1, 125.0, 124.7, 124.5, 124.0, 123.7, 121.0, 120.9, 117.3, 114.4, 113.5, 52.2, 50.1, 39.9, 31.8, 31.7, 29.9, 29.6, 29.5, 29.2, 26.4, 22.5, 14.0, 1.0. MS (MALDI-TOF): m/z (M^+) = 624.0 (calcd for $C_{44}H_{49}NO_2$: 623.9) , HRMS: calcd for $C_{44}H_{49}NO_2$ [M]: 623.3758; found 623.3750.

Compound 6a:

A mixture of compound **5a** (300 mg, 1 equiv), $Sc(OTf)_3$ (260 mg, 1 equiv), DDQ (120 mg, 1 equiv) in 50 ml dichloromethane was stirred at 25°C for 10 min under nitrogen. The reaction mixture was poured into water and the product was extracted with dichloromethane. The solvent was evaporated under reduced pressure, and the product was washed with methanol two times to yield the yellow solid product (293 mg, 98 %).

6a: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ = 8.78-8.73 (m, 4H), 8.28 (d, 4H), 8.16 (d, 2H), 8.07 (s, 2H), 7.88-7.83 (m, 10H), 7.67 (t, 2H), 4.65 (d, 4H), 4.03 (s, 6H), 2.13-2.09 (m, 4H), 1.40-1.20 (m, 36H), 0.86 (t, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, 298K): δ = 167.2, 147.0, 136.8, 136.3, 132.6, 132.2, 130.8, 130.5, 130.4, 129.8, 129.4, 128.8, 127.5, 125.0, 124.9, 124.7, 124.7, 123.8, 121.1, 121.0, 117.5, 117.0, 115.6, 114.5, 52.2, 45.8, 31.9, 31.2, 29.6, 29.5, 29.5, 29.3, 29.2, 27.1, 22.6, 14.1, 1.0. MS (MALDI-TOF): m/z

(M^+) =1133.8 (calcd for $C_{80}H_{80}N_2O_4$: 1133.5), HRMS: calcd for $C_{80}H_{81}N_2O_4$ $[M+H]^+$: 1133.6191; found 1133.6164.

6b: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ = 8.78-8.73 (m, 4H), 8.28 (d, 4H), 8.16 (d, 2H), 8.07 (s, 2H), 7.88-7.83 (m, 10H), 7.67 (t, 2H), 4.65 (d, 4H), 4.03 (s, 6H), 2.35 (m, 2H), 1.41-1.11 (m, 48H), 0.76-0.72 (m, 12H); ^{13}C NMR ($CDCl_3$, 150 MHz, 298K): δ = 167.2, 147.0, 136.8, 136.3, 132.6, 132.2, 130.8, 130.5, 130.4, 129.8, 129.4, 128.8, 127.5, 125.0, 124.9, 124.7, 124.7, 123.8, 121.1, 121.0, 117.5, 117.0, 115.6, 114.5, 52.2, 50.2, 39.9, 31.8, 31.8, 31.7, 31.7, 30.0, 29.9, 29.7, 29.6, 29.5, 29.2, 26.4, 22.5, 14.0, 13.9, 1.0. MS (MALDI-TOF): m/z (M^+) =1246.1 (calcd for $C_{88}H_{96}N_2O_4$: 1245.8), HRMS: calcd for $C_{88}H_{96}N_2O_4$ [M]: 1244.7365; found 1244.7372.

Compound 7a:

A solution of 593 mg (30 equiv) KOH in 2 ml water/8 ml methanol was added to a 400 mg (1equiv) compound **6a** dissolved in 50 ml THF under an inert atmosphere and refluxed for 24 h. When the mixture was cooled to room temperature, 2 ml 25% hydrochloric acid was added dropwise and stirred for 30 min. The mixture was poured into water and the product was extracted with toluene and THF (1:3, v/v). The organic layer was separated, dried with sodium sulfate, and the solvent was removed under reduced pressure. The remaining precipitate was filtered, washed with hexane and dried under vacuum to get the intermediate product for 98% yield without any further purification for the second step. A mixture of 300 mg (1 equiv) the intermediate product, 965 mg (10 equiv) 2-Decyl-1-tetradecanol, 105 mg (2 equiv) 1-(3-Dimethylaminopropyl)-3-ethylcarbo diimide hydrochloride and catalytic amount of 4-(Dimethylamino)pyridine were stirred in 10 ml CH_2Cl_2 at 25°C for 12 h under argon. 2 ml methanol was added to quench the reaction and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2, 5:1) to yield the yellow solid product (304 mg, 63 %).

7a: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ = 8.76-8.72 (m, 4H), 8.28 (d, 4H), 8.18 (d, 2H), 8.11 (s, 2H), 7.89-7.83 (m, 10H), 7.68 (t, 2H), 4.79 (t, 4H), 4.34 (d, 4H), 2.16 (m, 4H), 1.86 (m, 2H) , 1.46-1.16 (m, 116H) , 0.88-0.80 (m, 18H); ^{13}C NMR ($CDCl_3$, 150 MHz, 298K): δ = 166.8, 146.8, 136.8, 136.3, 132.2, 131.8, 130.8, 130.5, 130.3, 129.7, 129.3, 129.2, 127.5, 125.0, 124.9, 124.7, 124.6, 123.9, 121.2, 121.1, 117.5, 117.1, 115.4, 114.3, 67.8, 45.9, 37.5, 31.9, 31.8, 31.5, 31.3, 30.0, 29.7, 29.5, 29.4, 29.3, 27.3, 26.8, 22.7, 22.6, 14.1, 14.0, 1.0. MS (MALDI-TOF): m/z (M^+) =1779.2 (calcd for $C_{126}H_{172}N_2O_4$: 1778.8), HRMS: calcd for $C_{126}H_{172}N_2O_4$ [M]: 1777.3312; found 1777.3315.

7b: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ = 8.79-8.73 (m, 4H), 8.28 (d, 4H), 8.18 (d, 2H), 8.08 (s, 2H), 7.89-7.83 (m, 10H), 7.68 (t, 2H), 4.65 (d, 4H), 4.34 (d, 4H), 2.36 (m, 2H), 1.87 (m, 2H) , 1.47-1.10 (m, 128H) , 0.90-0.86 (m, 12H), 0.76-0.75 (m, 12H); ^{13}C NMR ($CDCl_3$, 150 MHz, 298K): δ = 166.8, 146.8, 136.8, 136.3, 132.6, 132.2, 130.9, 130.6, 130.4, 129.8, 129.4, 129.3, 127.5, 125.0, 124.9, 124.8, 124.7, 123.9, 121.1, 121.0, 117.4, 117.0, 115.6, 114.5, 67.8, 50.3, 39.9, 37.6, 31.9, 31.8, 31.7, 31.5, 30.0, 29.7, 29.5, 29.4, 29.2, 26.8, 26.4, 22.7, 22.6, 14.1, 14.0, 1.0. MS (MALDI-TOF): m/z (M^+) =1891.2 (calcd for $C_{134}H_{188}N_2O_4$: 1891.0), HRMS: calcd for $C_{134}H_{188}N_2O_4$ [M]: 1889.4564; found 1889.4584.

Compound 8a:

A mixture of compound **7a** (300 mg, 1equiv), $Sc(OTf)_3$ (415 mg, 5equiv), DDQ (192 mg, 5equiv) in 50 ml toluene was stirred at 110°C for 8 h under nitrogen. After cooling to room temperature, the mixture was added 0.5 ml $N_2H_4 \cdot H_2O$ and stirred for 30 min. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (THF/CH_2Cl_2, 1:10) to yield the deep black solid product (186 mg, 62%).

8a: MS (MALDI-TOF): m/z (M^+) =1775.7 (calcd for $C_{126}H_{170}N_2O_4$: 1776.8); elemental analysis: calcd (%)

for $C_{126}H_{170}N_2O_4$: C 85.18, H 9.64, N 1.58; found C 84.69, H 9.68, N 1.62; HRMS: calcd for $C_{126}H_{171}N_2O_4^+$ $[M+H]^+$: 1776.3233; found 1776.3278.

8b: MS (MALDI-TOF): m/z (M^+) =1887.8 (calcd for $C_{134}H_{186}N_2O_4$: 1889.0); elemental analysis: calcd (%) for $C_{134}H_{186}N_2O_4$: C 85.20, H 9.93, N 1.48; found C 84.82, H 9.96, N 1.50; HRMS: calcd for $C_{134}H_{187}N_2O_4^+$ $[M+H]^+$: 1888.4485; found 1888.4517.

3. The fluorescence quantum yields (Φ_F):

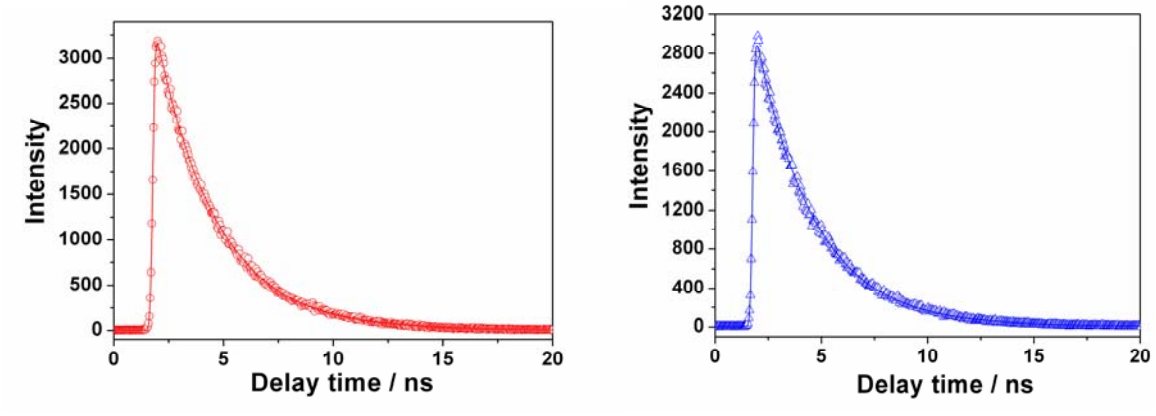
The fluorescence quantum yields (Φ_F) of compounds **8a** and **8b** were calculated by the steady-state comparative method using Cresyl Violet as a standard (Φ_{st}=0.54, methanol).

$$\Phi_F = \Phi_{st} \frac{S_u}{S_{st}} \frac{A_{st}}{A_u} \frac{n_{Du}^2}{n_{Dst}^2} \quad (1)$$

Where Φ_F is the emission quantum yield of the sample, Φ_{st} is the emission quantum yield of the standard, A_{st} and A_u represent the absorbance of the standard and sample at the excitation wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and sample, respectively, and n_{Dst} and n_{Du} the solvent refractive index of the standard and sample, u and st refer to the unknown and standard, respectively.

4. Fluorescence lifetime measurement

The fluorescence lifetime measurements were carried out on the ps time-resolved fluorescence spectrometer. The 800-nm laser pulses generated from a Ti:sapphire regenerative amplifier(Spitfire, Spectra Physics) were frequency doubled and used as the excitation pulses. The pulse energy was about 100 nJ/pulse at the sample. Fluorescence gathered with the 90-degree-geometry was dispersed by a polychromator (250is, Chromex) and collected with a photon-counting type streak camera (C5680, Hamamatsu Photonics). The data detected by digital camera (C4742-95, Hamamatsu) is rountinely transferred to PC for analysis with HPDTA software. The spectral resolution was 2 nm, and the temporal resolution was 2~100 ps depending on the delay-time-range setting.



(a) (b)

Fig. S1 Time profiles of fluorescence lifetime measurement of (a) **8a** and (b) **8b** (10^{-5} M) in THF.

5. Theoretical calculations method

The theoretical calculations method include time-depended density functional theory (TDDFT), complete active space self-consistent field theory (CASSCF/CASPT2), multireference configuration interaction

(MRCI)/Zerner's intermediate neglect of diatomic overlap (ZINDO), and MRCI/modified neglect of differential overlap. More details see reference[2].

6. Polarized optical microscopy (POM) and Wide-Angle X-ray Scattering (WAXS)

Polarized optical microscopy (POM)

The optical textures were investigated using a ZEISS West Germany polarizing optical microscope (POM), equipped with digital temperature control system UNKAM TMS 591.

Each sample was sandwiched between glass slides to form a thin film and was afterwards heated above the melting point using a Linkam heating stage. Then it was cooled to 30 °C at a rate of 1 °C/min. The images were recorded at 30 °C between cross-polarizers.

Wide-Angle X-ray Scattering (WAXS)

The 2D WAXS experiments were performed by means of rotating anode (Rigaku 18 kW) X-ray beam with pinhole collimation and two-dimensional Simens detector. A double graphite monochromator for the CrK_{α} radiation (λ=0.154) was used. The samples were prepared as a thin filament of 0.7 mm diameter by filament extrusion using a home built mini extruder. The sample was positioned perpendicular to the incident X-ray beam and vertical to the 2D detector. The 2D WAXS patterns were recorded at different temperatures upon heating and cooling.

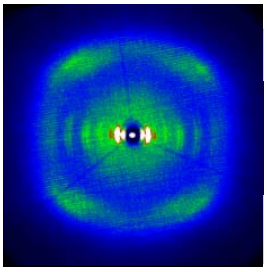
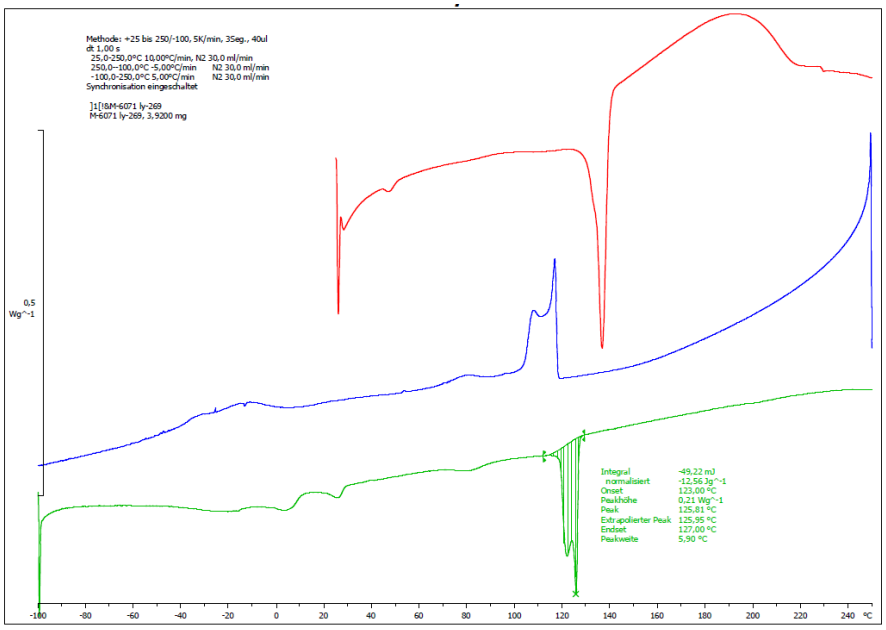
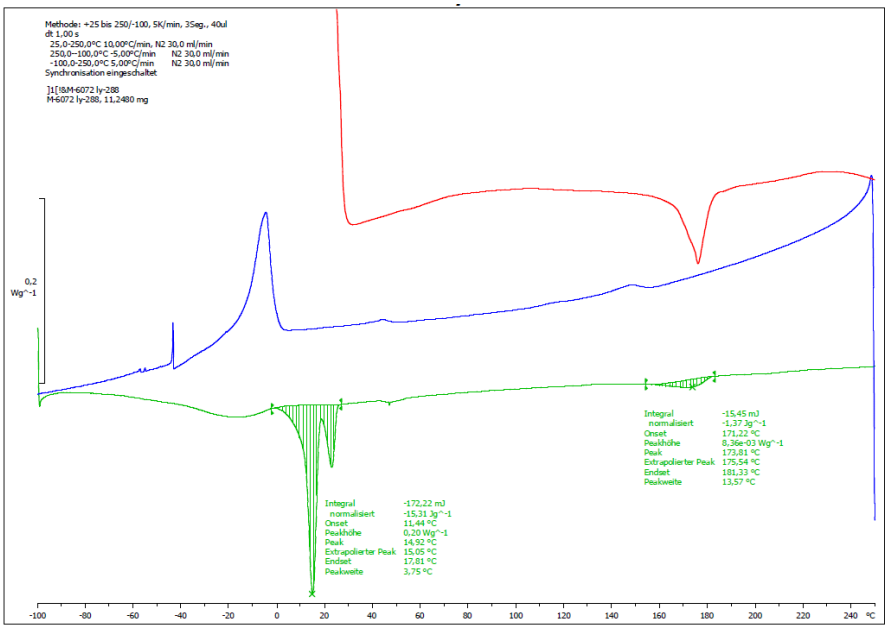


Figure S2. 2D WAXS of **8b** recorded at 30 °C.

7. Differential scanning calorimetry (DSC)



(a)



(b)

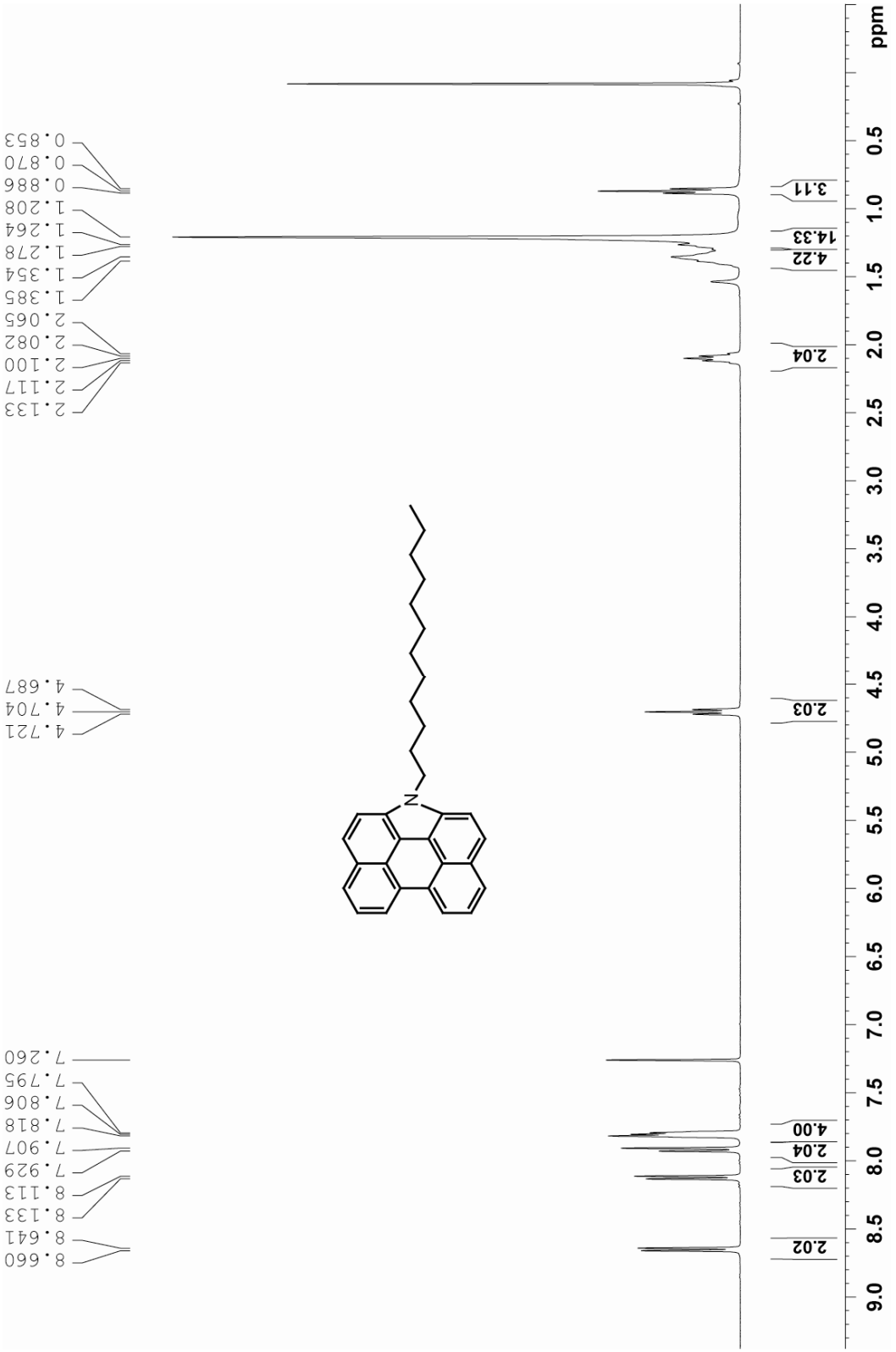
Figure S3. DSC of **8a** (a) and **8b** (b).

References:

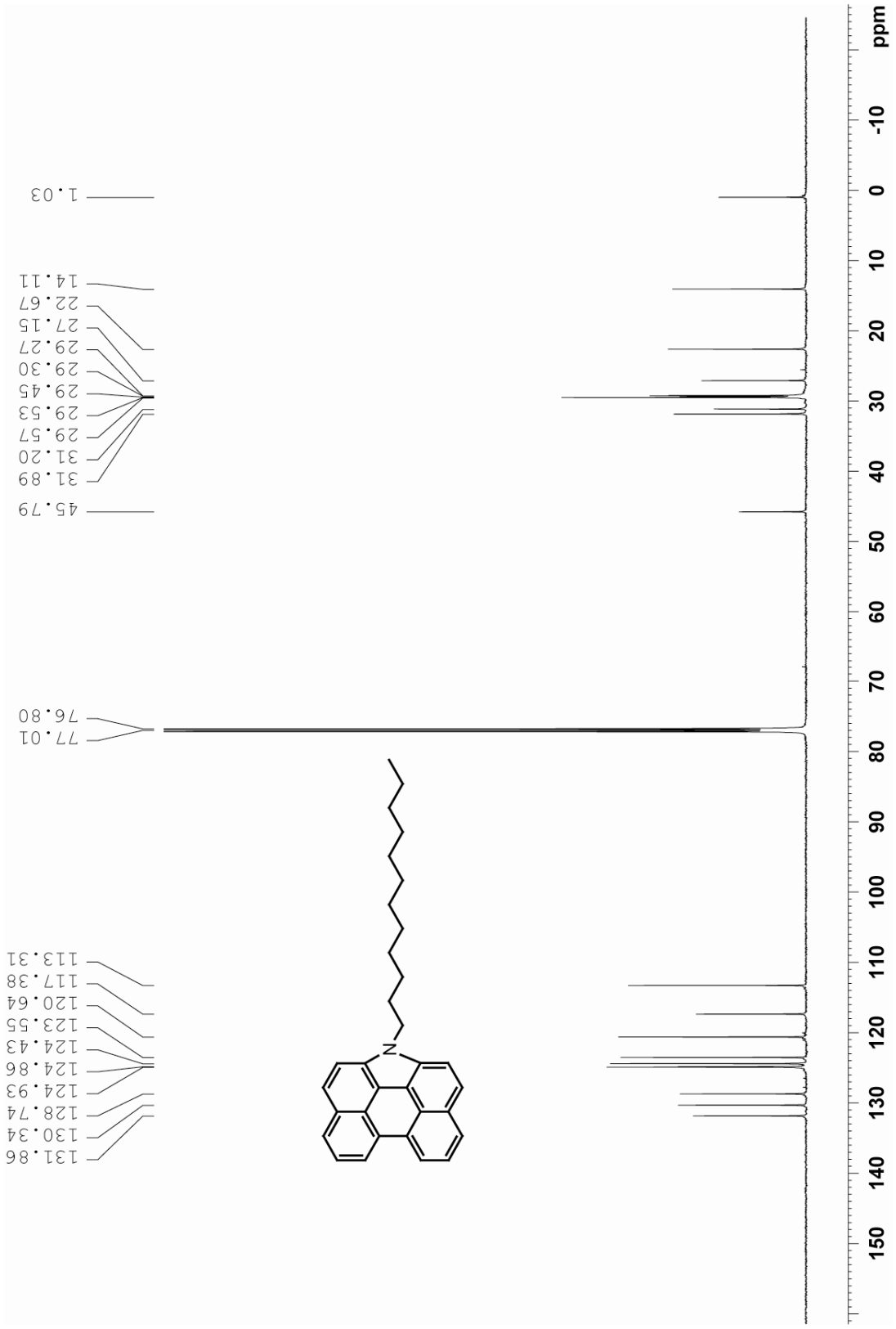
(1) Jiang, W.; Qian, H.; Li, Y.; Wang, Z. *J. Org. Chem.* 2008, 73, 7369.

(2) Q. Peng, Y. Niu, Z. Wang, Y. Jiang, Y. Li, Y. Liu and Z. Shuai, *J. Chem. Phys.*, 2011, 134, 074510.

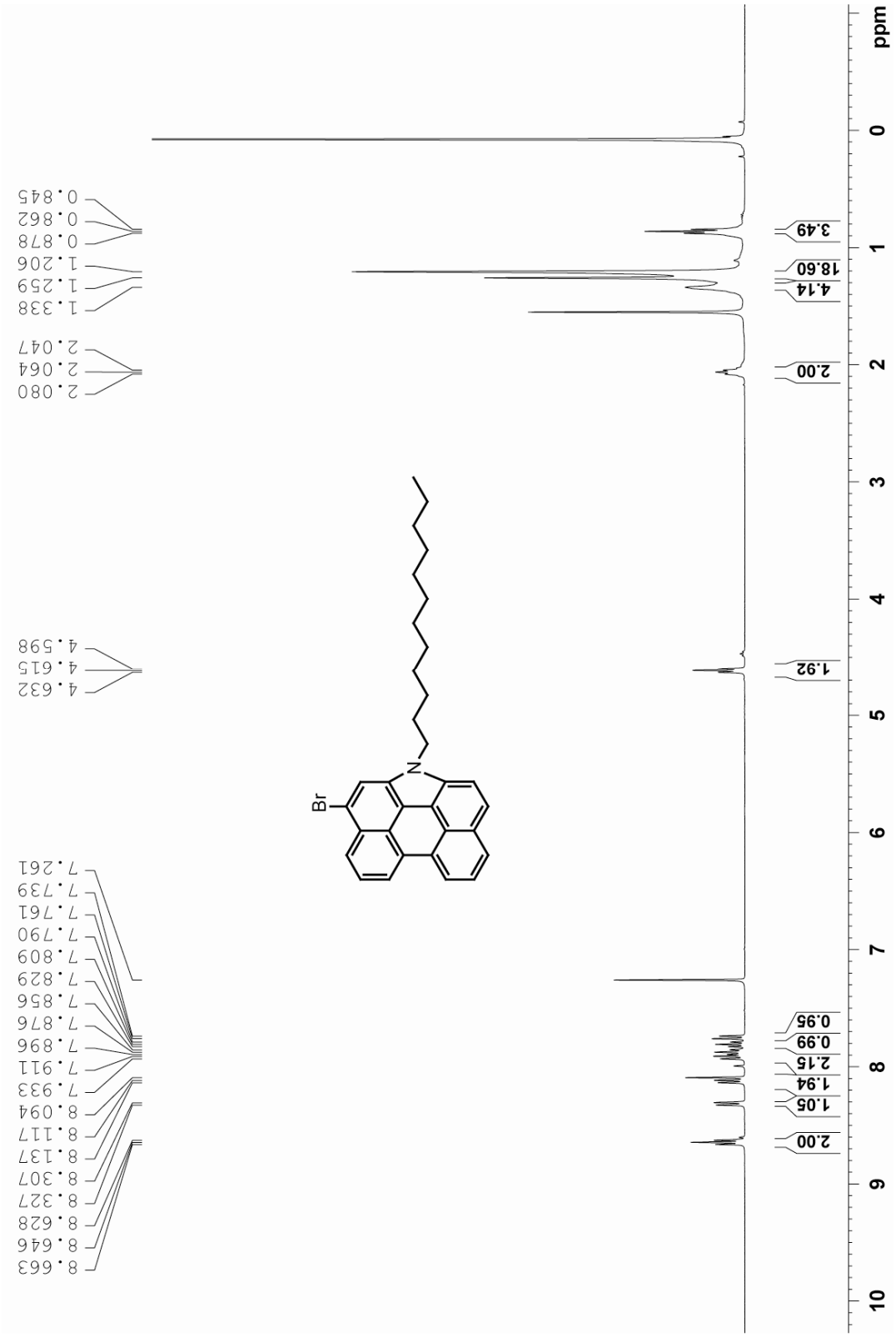
^{1}H NMR spectrum of **3a** in $CDCl_3$



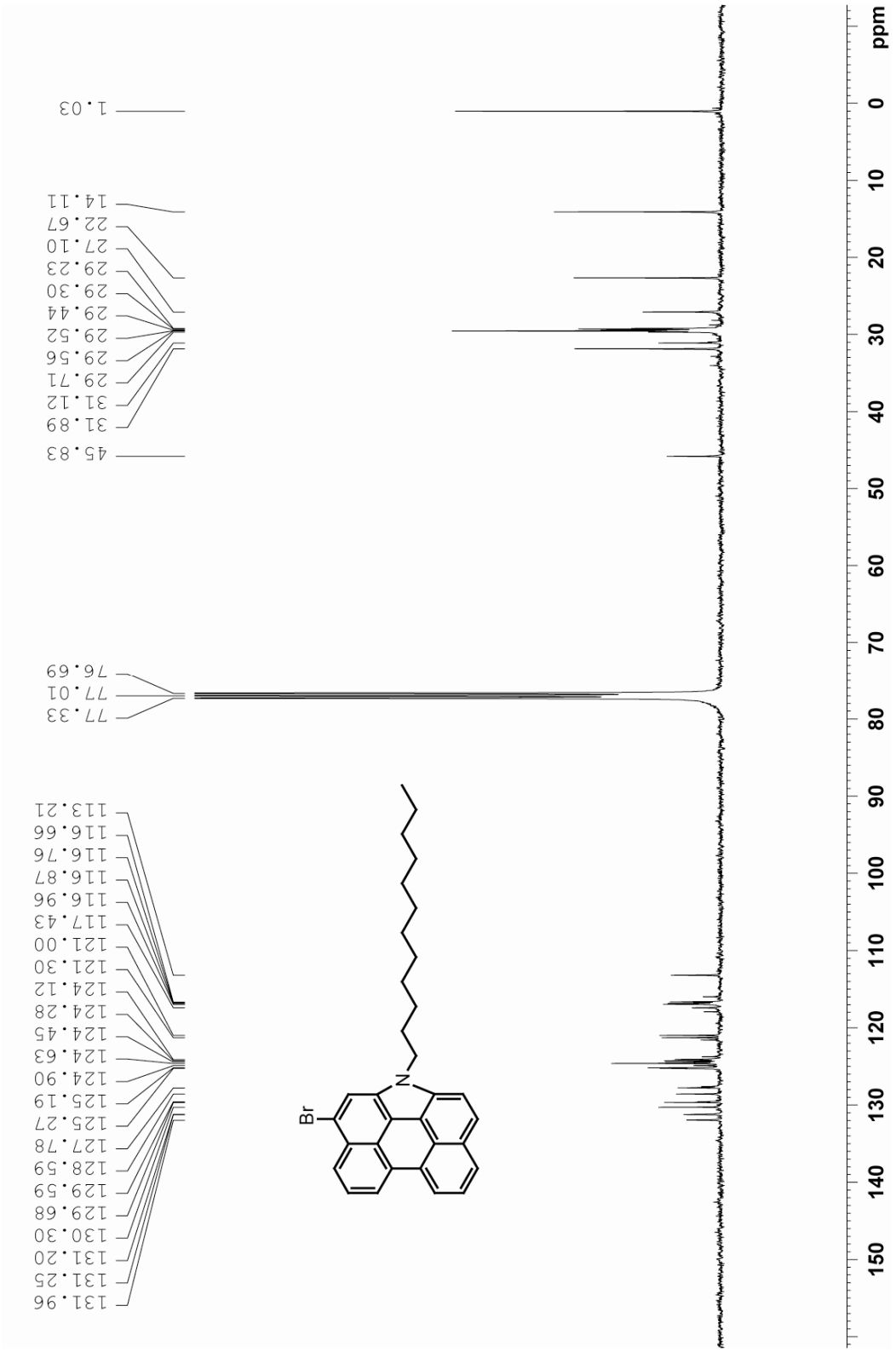
^{13}C NMR spectrum of **3a** in $CDCl_3$



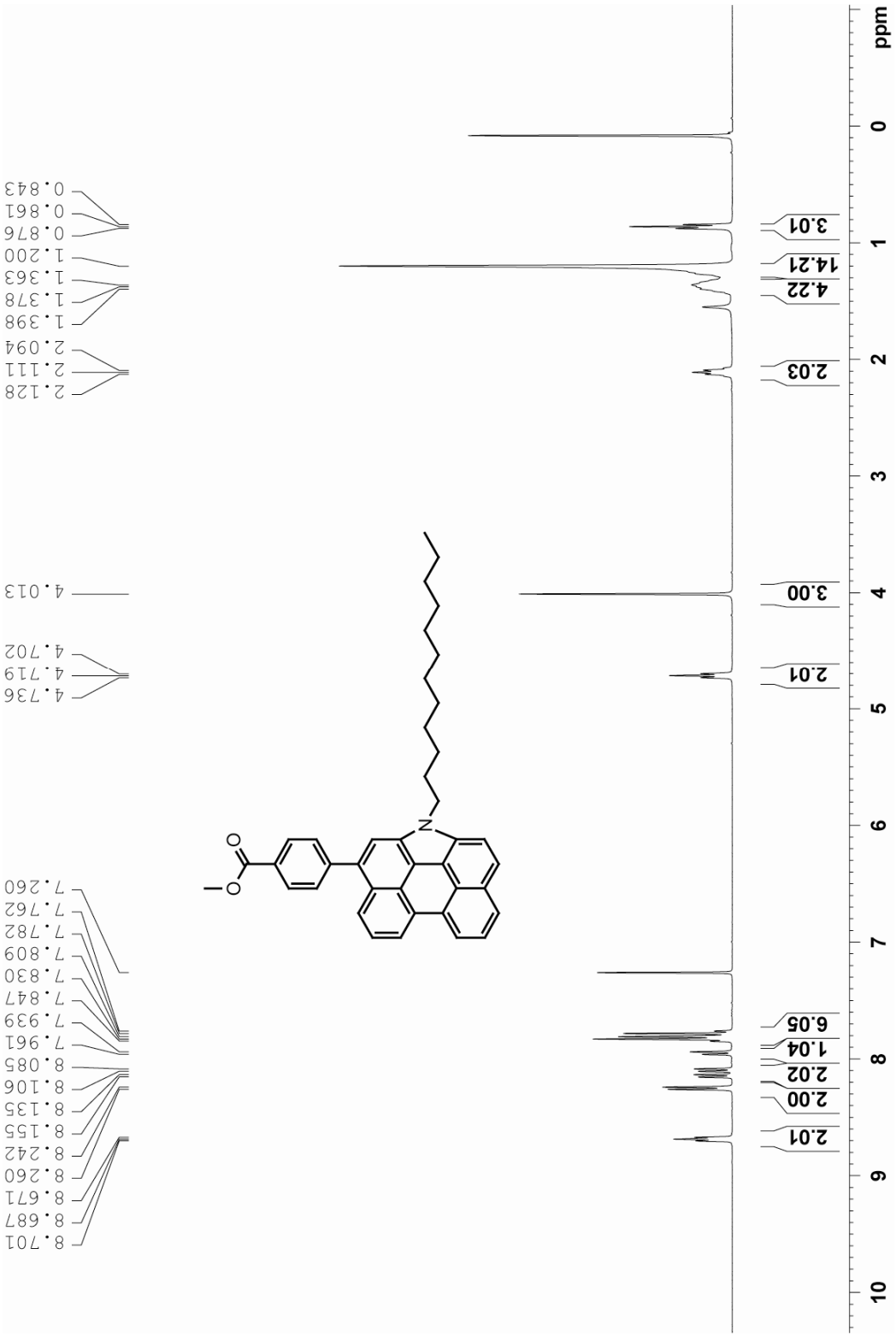
^{1}H NMR spectrum of **4a** in $CDCl_3$



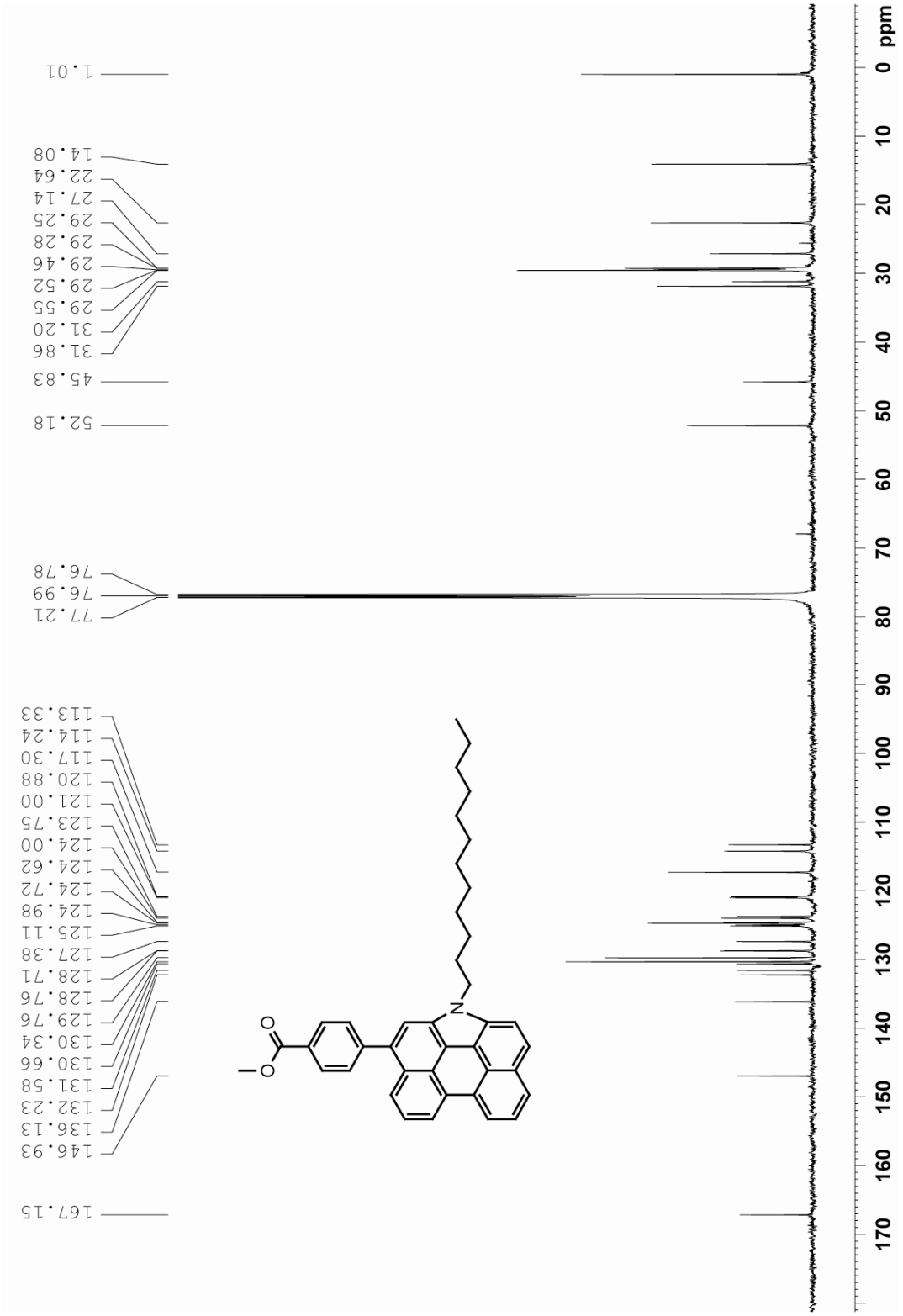
^{13}C NMR spectrum of **4a** in $CDCl_3$



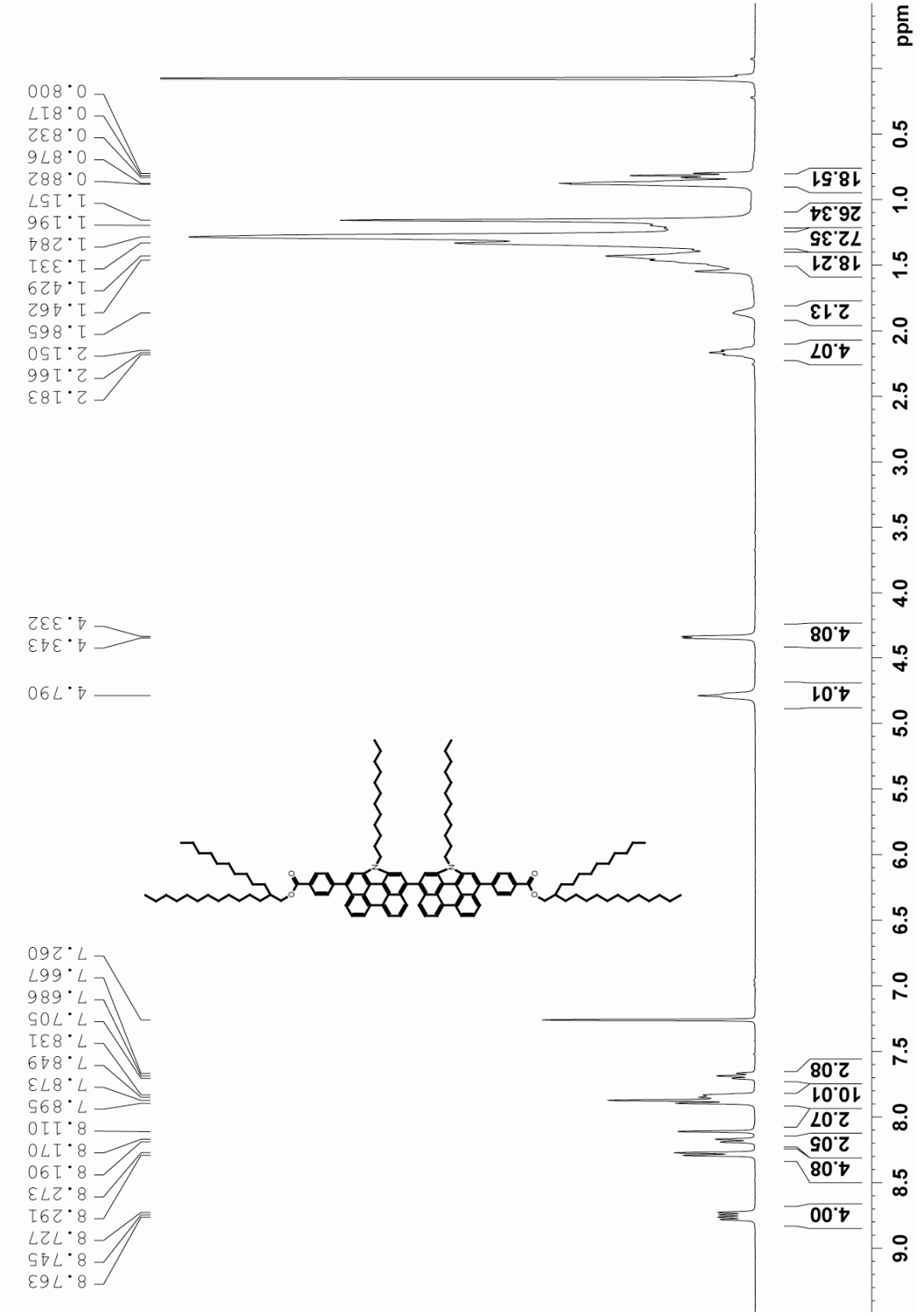
^{1}H NMR spectrum of **5a** in $CDCl_3$



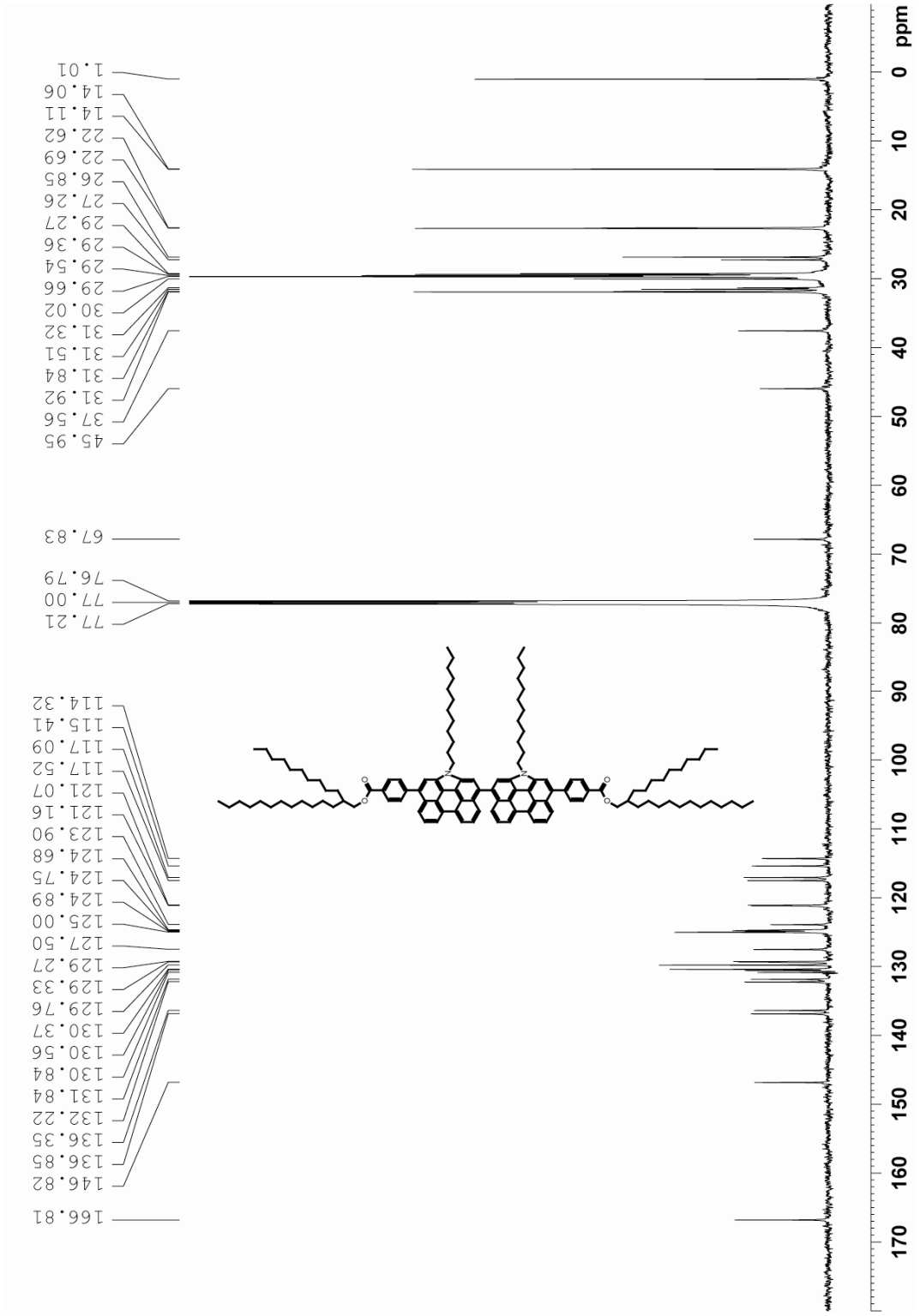
^{13}C NMR spectrum of **5a** in $CDCl_3$



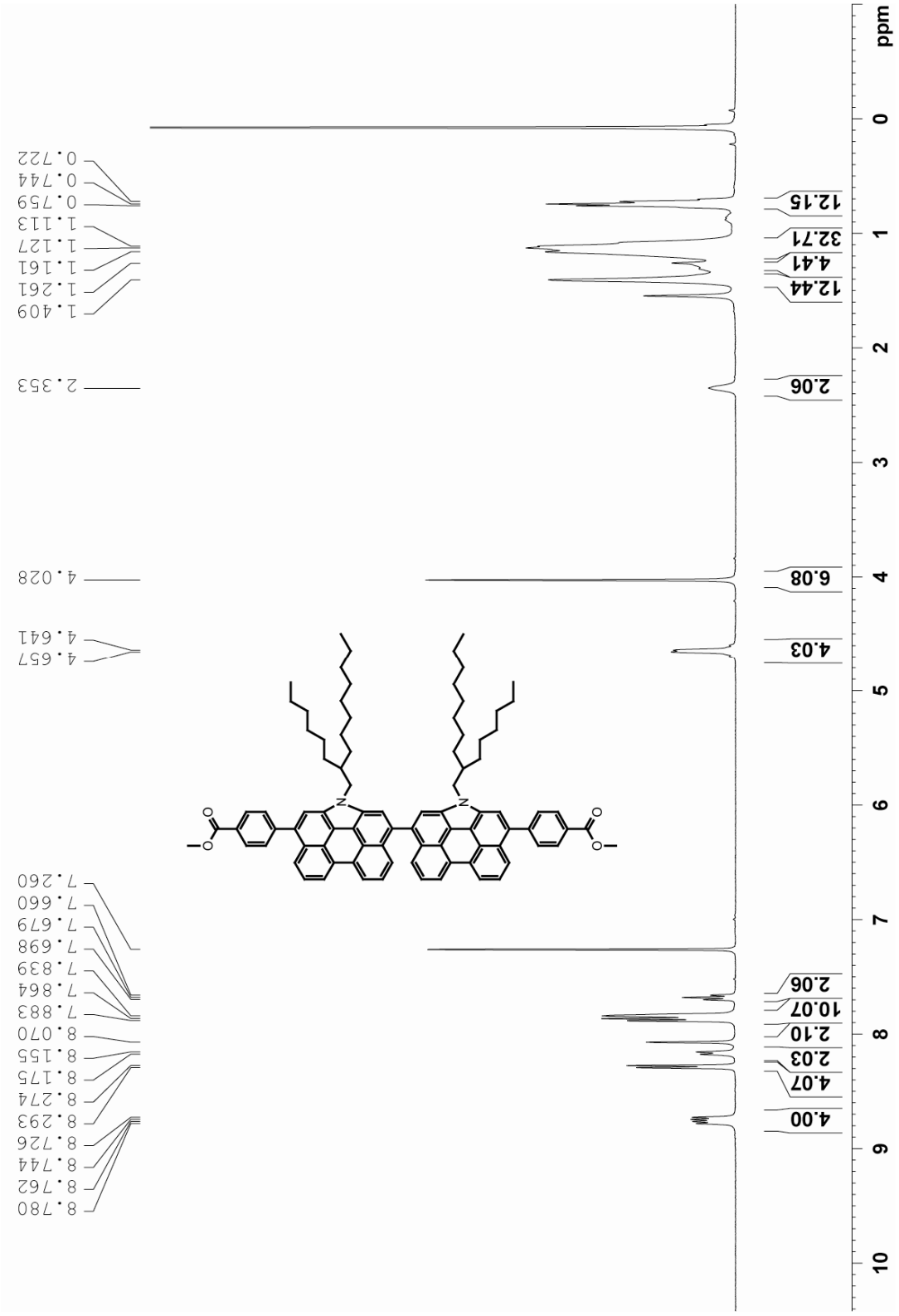
^{1}H NMR spectrum of **7a** in $CDCl_3$



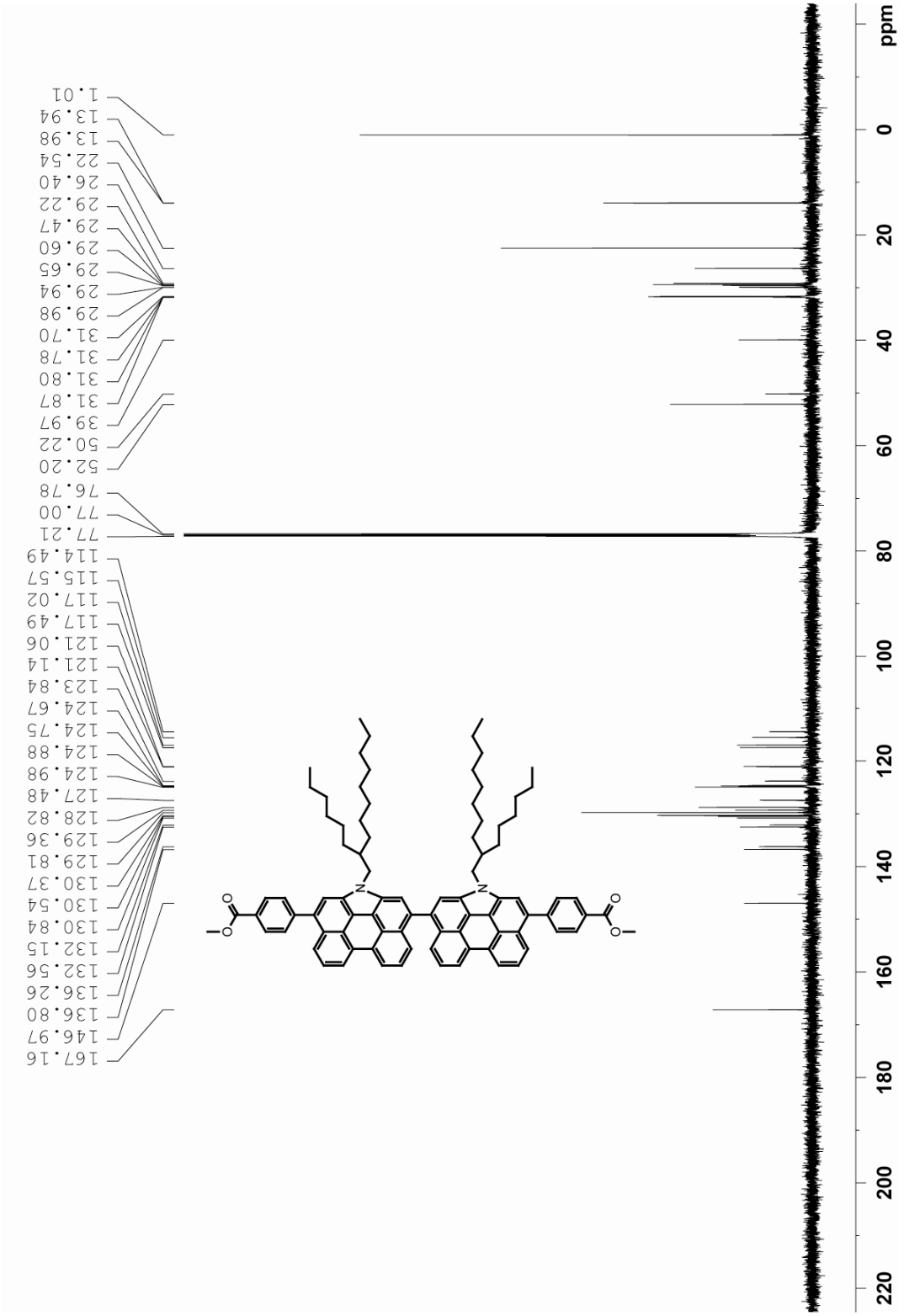
^{13}C NMR spectrum of **7a** in $CDCl_3$



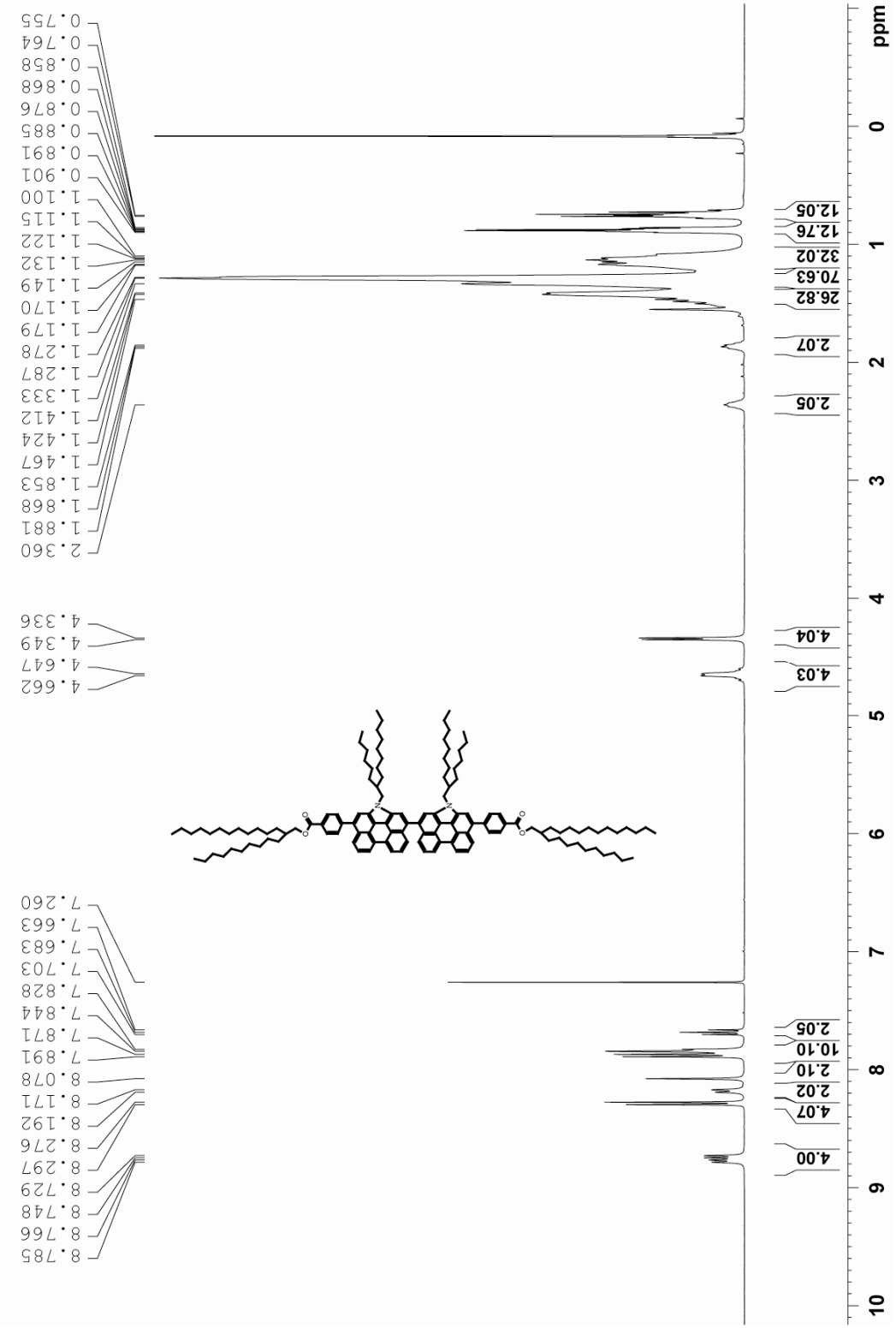
^{1}H NMR spectrum of **6b** in $CDCl_3$



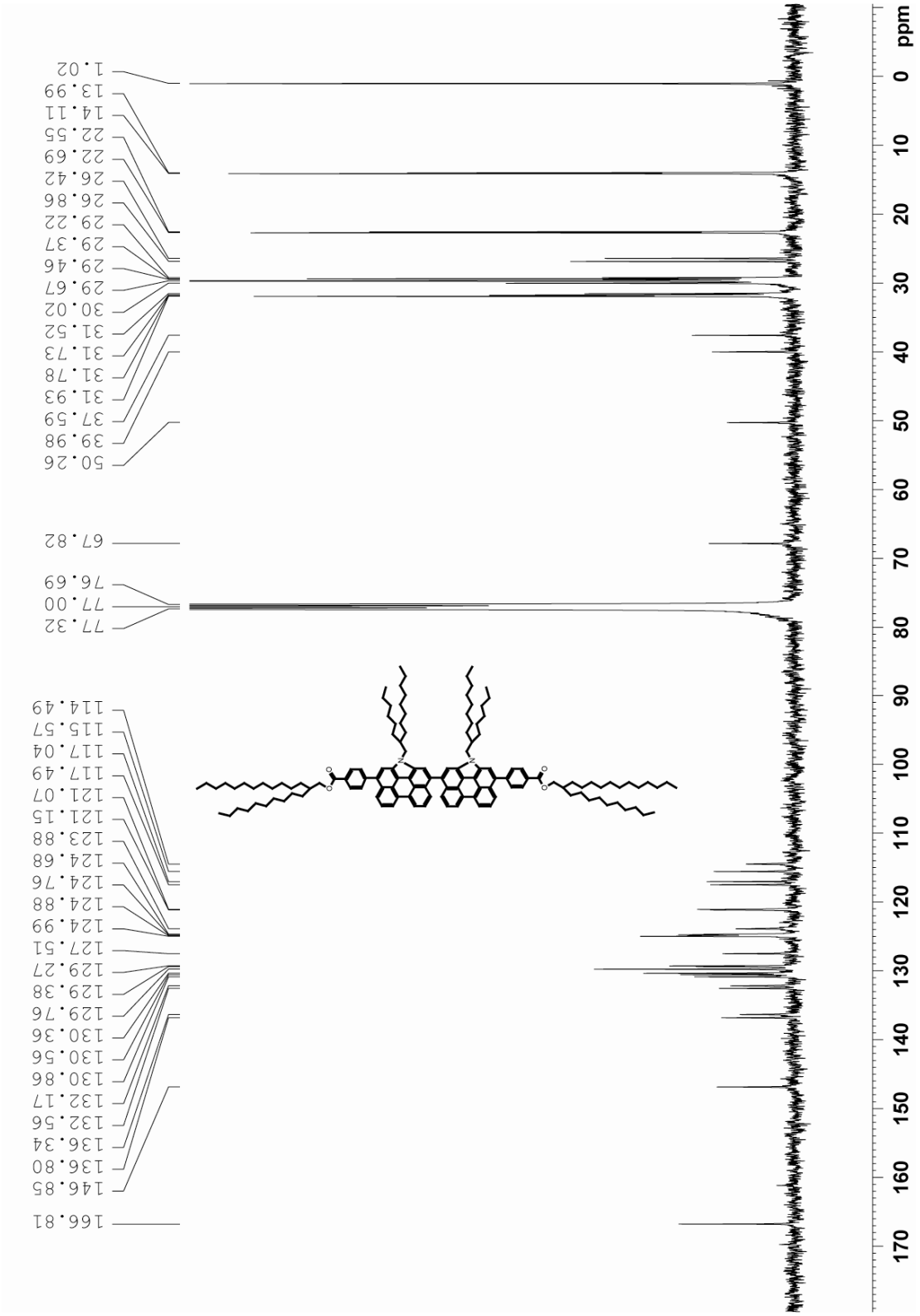
^{13}C NMR spectrum of **6b** in $CDCl_3$



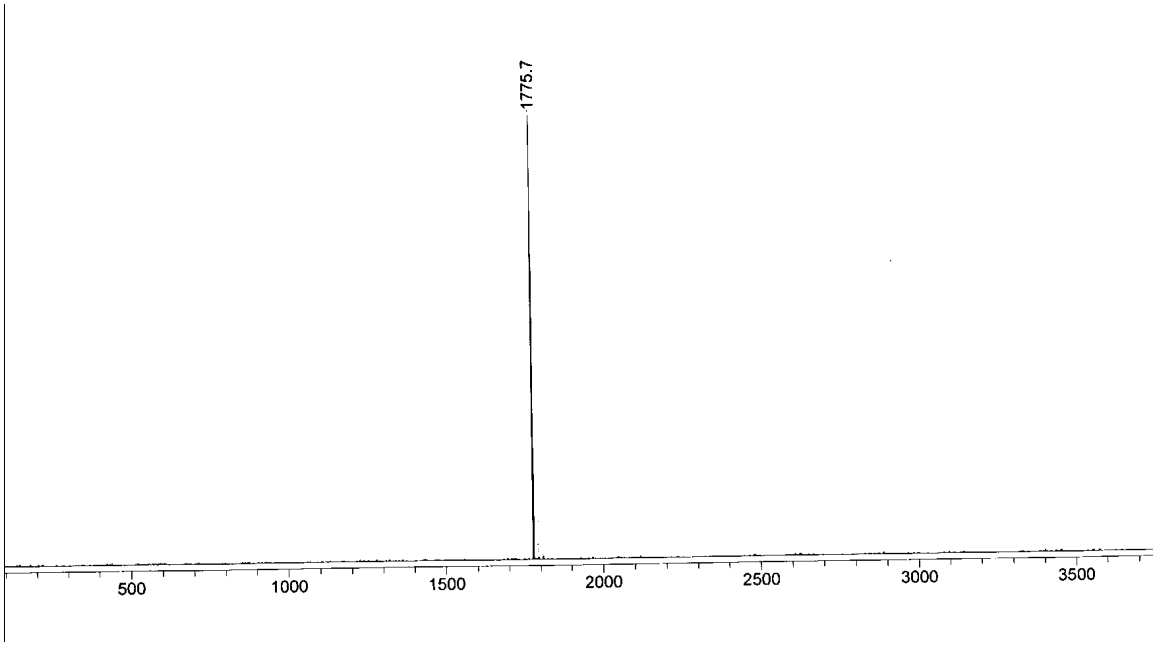
^{1}H NMR spectrum of **7b** in $CDCl_3$

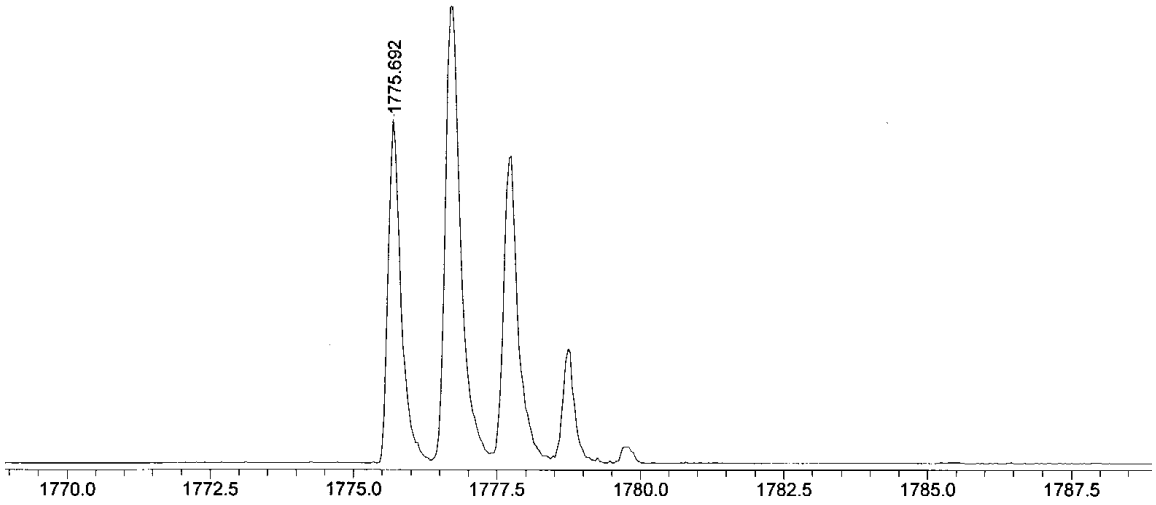


^{13}C NMR spectrum of **7b** in $CDCl_3$



MALDI-TOF mass spectrum of **8a**





MALDI-TOF mass spectrum of **8b**