

Supporting Information for:

π -Expanded Triple [5]Helicenes Bearing Dibenzocoronene Monoimide Subunits

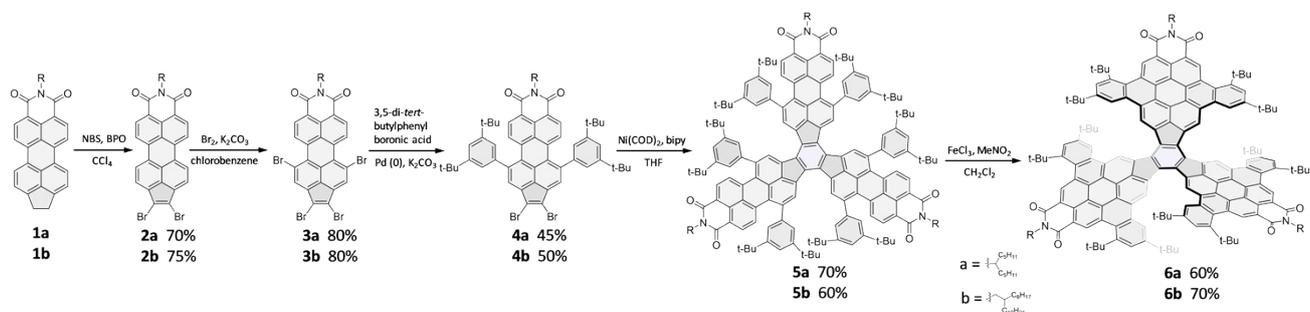
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1. Materials and Methods:

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. THF were freshly distilled prior to use. ^1H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on Bruker ADVANCE 400 NMR Spectrometer. ^1H NMR spectra were referenced to the signals of CDCl_3 ($\delta = 7.26$ ppm) or $\text{C}_2\text{D}_2\text{Cl}_4$ ($\delta = 6.00$ ppm). ^{13}C NMR spectra were referenced to the signals of CDCl_3 ($\delta = 77.20$ ppm). TOCSY and NOESY spectra were referenced to the signals of C_6D_6 ($\delta = 7.16$ ppm). High resolution mass spectra (HRMS) were determined on IonSpec 9.4 Tesla Fourier Transform Mass Spectrometer.

2. Synthesis and Characterization of Compounds



N-(1-Pentylhexyl)-1,2-dihydrocyclopenta[cd]perylene-7,8-dicarboximide (**1a**) and *N*-(2-Octyldodecyl)-1,2-dihydrocyclopenta[cd]perylene-7,8-dicarboximide (**1b**). **1a** and **1b** were prepared according to the literature.^[1]

1a: ^1H NMR (400 MHz, CDCl_3) δ 8.28 (s, 2H), 7.77 (t, $J = 7.2$ Hz, 4H), 7.10 (d, $J = 7.4$ Hz, 2H), 5.39–5.09 (m, 1H), 3.26 (s, 4H), 2.42–2.17 (m, 2H), 1.90 (m, 2H), 1.51–1.20 (m, 12H), 0.87 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.14, 164.24, 149.24, 139.18, 136.69, 131.30, 130.04, 126.77, 125.37, 125.29, 124.51, 120.65, 118.55, 54.25, 32.45, 31.88, 30.93, 26.82, 22.67, 14.12; HRMS (MALDI-TOF) m/z calculated for $\text{C}_{35}\text{H}_{35}\text{NO}_2$ 501.2667; found 501.2663.

1b: ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.9$ Hz, 2H), 7.38 (d, $J = 7.5$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 7.3$ Hz, 2H), 4.00 (d, $J = 7.1$ Hz, 2H), 3.13 (s, 4H), 2.09–1.84 (m, 1H), 1.47–1.17 (m, 32H), 0.98–0.78 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.93, 149.09, 138.75, 136.11, 130.14, 129.25, 126.09, 124.85, 124.59, 124.10, 120.30, 119.09, 118.14, 44.33, 36.85, 31.94, 31.77, 30.83, 30.20, 29.71, 29.69, 29.66, 29.38, 26.56, 22.69, 14.12. HRMS (MALDI-TOF) m/z : calculated for $\text{C}_{44}\text{H}_{54}\text{NO}_2$ 628.4154; found 628.4152.

N-(1-Pentylhexyl)-1,2-dibromocyclopenta[cd]perylene-7,8-dicarboximide (**2a**) and *N*-(2-Octyldodecyl)-1,2-dibromocyclopenta[cd]perylene-7,8-dicarboximide (**2b**). Compound **1a** or **1b** (1 mmol), NBS (4 mmol, 4 eq), BPO (75%, 0.1 mmol, 0.1 eq) were added in CCl_4 (20 ml). The mixture was refluxed with stirring for 4 h under N_2 atmosphere. After cooling, the reaction was quenched with saturated Na_2SO_3 , and then extracted with CH_2Cl_2 (3 \times). The combined organic fractions were then washed with water, dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography (CH_2Cl_2 /petroleum ether = 1/1, v/v) to yield the corresponding **2a** or **2b** as red solids.

2a: (0.46 g, 70%) ^1H NMR (400 MHz, CDCl_3) δ = 8.38 (s, 2H), 7.86 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 2H), 6.88 (d, $J = 7.4$ Hz, 2H), 5.24–5.14 (m, 1H), 2.40–2.21 (m, 2H), 2.07–1.85 (m, 2H), 1.51–1.31 (m, 12H), 0.89 (t, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ = 164.66, 136.57, 133.49, 130.52, 129.69, 129.14, 126.10, 124.28, 123.08, 122.17, 122.01, 121.56, 120.51, 54.61, 32.49, 31.86, 26.86, 22.70, 14.16; HRMS (MALDI-TOF) m/z : calculated for $\text{C}_{35}\text{H}_{32}\text{Br}_2\text{NO}_2$ 656.0799; found 656.0783.

2b: (0.59 g, 75%) ^1H NMR (400 MHz, CDCl_3) δ = 8.37 (d, $J = 7.8$ Hz, 2H), 8.05 (d, $J = 7.0$ Hz, 2H), 7.76 (d, $J = 5.4$ Hz, 2H), 7.28–7.22 (m, 2H), 4.08 (d, $J = 7.3$ Hz, 2H), 1.99–1.90 (m, 1H), 1.47–1.08 (m, 32H), 0.85 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ = 163.34, 136.51, 133.16, 130.44, 129.32, 128.51, 125.87, 123.86, 122.98, 122.45, 122.06, 121.67, 120.59, 44.60, 36.90, 31.96, 31.76, 30.21, 29.74, 29.72, 29.71, 29.68, 29.40, 26.54, 22.71, 14.15; HRMS (MALDI-TOF) m/z : calculated for $\text{C}_{44}\text{H}_{50}\text{Br}_2\text{NO}_2$ 784.2187; found 784.21848.

N-(1-Pentylhexyl)-1,2,4,11-tetrabromocyclopenta[cd]perylene-7,8-dicarboximide (**3a**) and *N*-(2-Octyldodecyl)-1,2,4,11-tetrabromocyclopenta[cd]perylene-7,8-dicarboximide (**3b**). To the solution of compound **2a** or **2b** (0.5 mmol) and K₂CO₃ (1.5 mmol, 3 eq) in chlorobenzene, Br₂ (1.5 mmol, 3 eq) was added and stirred at 80 °C for 24 h. After cooling, the reaction was quenched with saturated Na₂SO₃, and extracted with CH₂Cl₂ (3×). The combined organic fractions were washed with water, dried (Na₂SO₄), and concentrated in vacuo. The crude product was purified by column chromatography (CH₂Cl₂/petroleum ether = 1/2, v/v) to yield the corresponding **3a** or **3b** as red solids.

3a: (0.33 g, 80%) ¹H NMR (400 MHz, CDCl₃) δ = 9.37 (d, *J* = 8.2 Hz, 2H), 8.48 (d, *J* = 6.4 Hz, 2H), 7.37 (s, 2H), 5.41–4.99 (m, 1H), 2.43–2.19 (m, 2H), 1.94–1.84 (m, 2H), 1.46–1.21 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 164.44, 163.41, 135.91, 131.66, 131.15, 130.22, 129.50, 128.26, 127.87, 126.72, 125.18, 125.04, 124.25, 123.70, 123.43, 121.00, 120.68, 54.75, 32.43, 31.82, 26.77, 22.67, 14.13; HRMS (MALDI-TOF) *m/z*: calculated for C₃₅H₃₀Br₄NO₂ 811.9010; found 811.9004.

3b: (0.38 g, 80%) ¹H NMR (400 MHz, CDCl₃) δ = 9.63 (d, *J* = 8.2 Hz, 2H), 8.60 (d, *J* = 8.2 Hz, 2H), 7.90 (s, 2H), 4.14 (d, *J* = 7.4 Hz, 2H), 2.24–1.88 (m, 1H), 1.45–1.13 (m, 32H), 0.85 (t, *J* = 5.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 163.59, 136.74, 134.73, 132.40, 131.45, 129.94, 128.50, 128.13, 126.83, 123.25, 121.49, 121.21, 44.70, 36.71, 31.92, 31.90, 31.73, 30.09, 29.70, 29.65, 29.60, 29.35, 29.32, 26.54, 22.67, 14.11; HRMS (MALDI-TOF) *m/z*: calculated for C₄₄H₄₇Br₄NO₂ 941.0299; found 941.0299.

N-(1-Pentylhexyl)-1,2-dibromo-4,11-bis(3,5-di-*tert*-butylphenyl)-ocyclopenta[cd]perylene-7,8-dicarboximide (**4a**) and *N*-(2-Octyldodecyl)-1,2-dibromo-4,11-bis(3,5-di-*tert*-butylphenyl)-ocyclopenta[cd]perylene-7,8-dicarboximide (**4b**). The mixture solution of **3a** or **3b** (0.5 mmol), 3,5-di-*tert*-butylphenylboronic acid (1.1 mmol, 2.2 eq), Pd(PPh₃)₄ (0.05 mmol, 0.1 eq) in THF (15 ml) and 2 M K₂CO₃ (5 ml) was heated to 80 °C for 3 h under N₂ atmosphere. After cooling, the reaction was poured into water, and extracted with CH₂Cl₂ (3×). The combined organic fractions were washed with water, dried (Na₂SO₄), and concentrated in vacuo. The crude product was purified by column chromatography (CH₂Cl₂/petroleum ether = 1/4, v/v) to yield the corresponding **4a** or **4b** as red solids.

4a: (0.23 g, 45%) ¹H NMR (400 MHz, CDCl₃) δ = 8.03 (s, 2H), 7.67 (s, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.57 (s, 2H), 7.30 (s, 4H), 5.16–5.08 (m, 1H), 2.23–2.13 (m, 2H), 1.90–1.69 (m, 2H), 1.35 (s, 36H), 1.29–1.17 (m, 12H), 0.82–0.76 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 152.08, 151.78, 142.76, 141.75, 135.57, 133.96, 128.01, 127.84, 127.29, 125.90, 124.42, 124.21, 121.58, 120.85, 120.30, 53.21, 34.09, 31.24, 30.60, 30.44, 25.44, 21.47, 12.94; HRMS (MALDI-TOF) *m/z*: calculated for C₆₃H₇₁Br₂NO₂ 1031.3851; found 1031.3860.

4b: (0.29 g, 50%) ¹H NMR (400 MHz, CDCl₃) δ = 8.05 (d, *J* = 8.3 Hz, 2H), 7.67 (s, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.56 (s, 2H), 7.29 (d, *J* = 1.6 Hz, 4H), 4.03 (d, *J* = 7.2 Hz, 2H), 1.96–1.88 (m, 1H), 1.34 (s, 36H), 1.29–1.11 (m, 32H), 0.88–0.78 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 163.99, 153.11, 143.88, 142.70, 136.71, 135.18, 129.57, 129.01, 128.31, 127.05, 125.43, 125.25, 122.67, 121.90, 121.75, 121.41, 44.31, 36.57, 35.12, 31.91, 31.88, 31.71, 31.47, 30.03, 29.66, 29.64, 29.59, 29.54, 29.36, 29.31, 26.44, 22.67, 14.10. HRMS (MALDI-TOF) *m/z*: calculated for C₇₂H₉₀Br₂NO₂ 1158.5338; found 1158.5339.

N-(1-Pentylhexyl)-4,7,14,17,24,27-hept(3,5-di-*tert*-butylphenyl)-triaceperylene-1,10,11,20,21,30-hexacarboximide (**5a**) and *N*-(2-Octyldodecyl)-4,7,14,17,24,27-hept(3,5-di-*tert*-butylphenyl)-triaceperylene-1,10,11,20,21,30-hexacarboximide (**5b**). Ni(COD)₂ (2 mmol, 2 eq) was added to the solution of COD (2 mmol, 2 eq) and Bipy (2 mmol, 2 eq) in dried THF (30 ml) under N₂ atmosphere. **4a** or **4b** (1 mmol) was dissolved into the dried THF (80 ml) and added dropwise over 20 min. The mixture was heated to 70 °C and stirred overnight. After cooling, the reaction mixture was filtered, concentrated in vacuo, and purified by column chromatography (CH₂Cl₂/petroleum ether = 1/3, v/v) to yield the corresponding **5a** or **5b** as blue solids.

5a: (0.6 g, 70%) ¹H NMR (400 MHz, CDCl₃) δ = 8.79 (s, 6H), 7.95 (s, 6H), 7.49 (s, 6H), 7.21 (d, *J* = 1.6 Hz, 12H), 6.96 (d, *J* = 8.2 Hz, 6H), 5.19–4.96 (m, 3H), 2.34–2.10 (m, 6H), 1.86–1.71 (m, 6H), 1.25 (d, *J* = 3.4 Hz, 36H), 1.20 (s, 108H), 0.80 (t, *J* = 6.8 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃) δ = 152.83, 144.55, 142.52, 137.23, 136.96, 135.50, 133.37, 128.90, 128.63, 128.07, 128.03, 127.94, 127.42, 123.14, 121.81, 54.07, 34.96, 32.25, 31.89, 31.64,

31.50, 29.71, 26.42, 22.70, 22.54, 13.99; HRMS (MALDI-TOF) m/z : calculated for $C_{189}H_{213}N_3O_6$ 2622.6512; found 2622.6495.

5b: (0.6 g, 60%) 1H NMR (400 MHz, $CDCl_3$) δ = 8.80 (s, 6H), 7.98 (d, J = 8.2 Hz, 6H), 7.50 (s, 6H), 7.21 (d, J = 1.5 Hz, 12H), 6.97 (d, J = 8.2 Hz, 6H), 4.05 (d, J = 7.1 Hz, 6H), 2.10–1.81 (m, 3H), 1.34–1.15 (m, 204H), 0.88–0.81 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.12, 152.84, 144.63, 142.47, 137.31, 137.02, 135.68, 133.37, 129.56, 128.85, 128.51, 128.19, 127.97, 127.45, 123.14, 121.84, 120.54, 44.21, 36.56, 34.95, 31.92, 31.90, 31.50, 30.07, 30.06, 29.68, 29.65, 29.61, 29.56, 29.37, 29.34, 26.50, 22.68, 14.12; HRMS (MALDI-TOF) m/z : calculated for $C_{216}H_{267}N_3O_6$ 3001.07470; found 3001.07510.

N-(1-Pentylhexyl)-3,5,10,12,17,19,24,26,31,33-dodeca(3,5-di-*tert*-butylphenyl)-tridibenzo(*dm*)coronylene-1,14,15,28,29,42-hexacarboximide (**6a**) and *N*-(2-Octyldodecyl)-3,5,10,12,17,19,24,26,31,33-dodeca(3,5-di-*tert*-butylphenyl)-tridibenzo(*dm*)coronylene-1,14,15,28,29,42-hexacarboximide (**6b**). $FeCl_3$ (1.2 mmol, 60 eq) in CH_3NO_2 (3 ml) was added dropwise to **5a** or **5b** (0.02 mmol) in CH_2Cl_2 (30 ml) under N_2 atmosphere. The reaction mixture was stirred for 20 min at room temperature, then quenched with methanol, extracted with CH_2Cl_2 , purified by column chromatography (CH_2Cl_2 /petroleum ether = 1/2, v/v), followed by HPLC to yield the corresponding **6a** or **6b** as red solids.

6a: (0.031 g, 60%) 1H NMR (400 MHz, $CDCl_3$) δ = 11.47–10.86 (m, 6H), 10.66–9.82 (m, 6H), 9.61–8.89 (m, 6H), 8.7–8.35 (m, 6H), 5.45 (m, 3H), 2.80–2.15 (m, 12H), 2.15–1.95 (m, 36H), 1.91–1.03 (m, 108H), 0.95–0.60 (m, 18H); ^{13}C NMR (600 MHz, $CDCl_3$) δ 165.50, 164.28, 149.20, 148.94, 148.44, 148.17, 147.87, 147.64, 147.36, 139.38, 138.83, 136.88, 136.37, 136.28, 136.10, 135.99, 134.13, 133.81, 133.34, 133.09, 130.96, 130.59, 130.50, 130.23, 130.08, 128.76, 128.68, 128.18, 127.56, 127.36, 126.85, 126.79, 124.75, 124.37, 123.30, 121.68, 121.37, 121.29, 120.68, 120.34, 117.90, 117.62, 117.44, 117.07, 116.82, 116.68, 116.54, 53.70, 38.25, 34.13, 31.82, 31.53, 31.04, 30.92, 30.81, 30.71, 30.45, 30.23, 29.92, 28.63, 25.94, 25.78, 25.55, 21.61, 21.41, 13.14, 13.04, 12.87. HRMS (MALDI-TOF) m/z : calculated for $C_{189}H_{201}N_3O_6$ 2610.5582; found 2610.5565.

6b: (0.042 g, 70%) 1H NMR (400 MHz, $CDCl_3$) δ = 11.58–10.93 (m, 6H), 10.68–10.04 (m, 6H), 9.68–8.81 (m, 6H), 8.75–8.37 (m, 6H), 4.46 (M, 6H), 2.66–2.15 (m, 3H), 2.02 (d, J = 16.1 Hz, 50H), 1.53–0.97 (m, 154H), 0.79 (M, 18H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 165.91, 165.74, 150.28, 150.04, 149.55, 149.28, 149.02, 148.77, 148.51, 140.55, 139.98, 138.01, 137.50, 137.40, 137.23, 137.12, 134.84, 134.54, 134.48, 132.21, 132.07, 131.94, 131.77, 131.57, 131.33, 131.19, 129.82, 129.73, 129.24, 128.56, 127.87, 125.95, 125.76, 125.48, 124.23, 122.86, 122.35, 121.74, 118.99, 118.52, 117.95, 117.76, 45.02, 39.34, 36.67, 36.57, 35.35, 35.16, 35.06, 31.87, 31.69, 31.54, 31.28, 31.01, 30.19, 29.72, 29.65, 29.31, 26.55, 22.65, 14.10. HRMS (MALDI-TOF) m/z : calculated for $C_{216}H_{255}N_3O_6$ 2988.9808; found 2988.9777.

3. CV and UV Spectra of the Compounds

Cyclic voltammograms (CVs) were recorded on a 1000B model electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/Ag^+ electrode as the reference electrode, ferrocene/ferrocenium as an internal potential marker, and tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as the supporting electrolyte. UV/Vis absorption spectra were measured with Hitachi (model U-3010) spectrophotometer. Emission were measured in room temperature in $CHCl_3$ (10^{-5} M); Fluorescence measurements were carried out on a FLS980 Spectrometer and quantum yield was determined by a Quanta- ϕ integrating sphere.

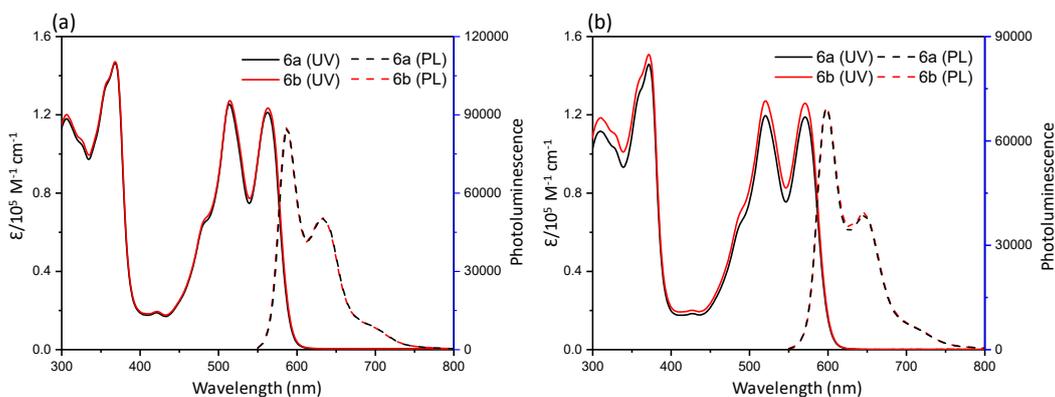


Fig. S1 UV-vis absorption (solid line, 10^{-5} M) and emission (dashed line, excitation at 520 nm) spectra of **6a** and **6b** in hexane (a) and toluene (b).

4. X-ray Crystallographic Data for Compounds

Single crystals of **6a** for X-ray diffraction analysis could be obtained by slow diffusion of methanol into a toluene solution at room temperature. The X-ray diffraction data were collected on a MM007HF Saturn724+ diffractometer with graphite monochromated Cu K α (1.54184 Å). **6a** were refined using the SHELXL-2014.

Table S1. Crystal data and structure refinement for **6a**.

Identification code	6a
Empirical formula	C ₁₈₉ H ₂₀₁ N ₃ O ₆
Formula weight	2608.5512
Crystal system	triclinic
Space group	P-1
Radiation type	Cu K α
Radiation wavelength(Å)	1.54184
T(K)	169.99(13)
a(Å)	10.23090(10)
b(Å)	30.6709(2)
c(Å)	32.1621(3)
α (deg)	81.0210(10)
β (deg)	83.8780(10)
γ (deg)	87.77700(10)
V(Å ³)	9909.11(15)
Z	2
ρ_{calc} (g cm ⁻³)	0.906
θ , range(°)	2.169 to 75.741
R(int)	3.49%
μ (mm ⁻¹)	0.406
F(000)	2908.0
Crystal size (mm ³)	0.04 × 0.04 × 0.02
Index ranges	-9 ≤ h ≤ 12, -38 ≤ k ≤ 38, -38 ≤ l ≤ 39
Reflections collected	111270
Independent reflections	38357 [R _{int} = 0.0349, R _{sigma} = 0.0371]
Absorption correction	spherical harmonics
Data / restraints / parameters	38357/784/2222
Goodness-of-fit on F ²	1.871
Final R indices [I > 2 σ (I)]	R1 = 0.0908, wR2 = 0.2517
R indices(all data)	R1 = 0.1092, wR2 = 0.2668
Largest diff. peak and hole(e.Å ⁻³)	0.88/-0.45

5. Dynamic NMR and the Thermal Interconversion

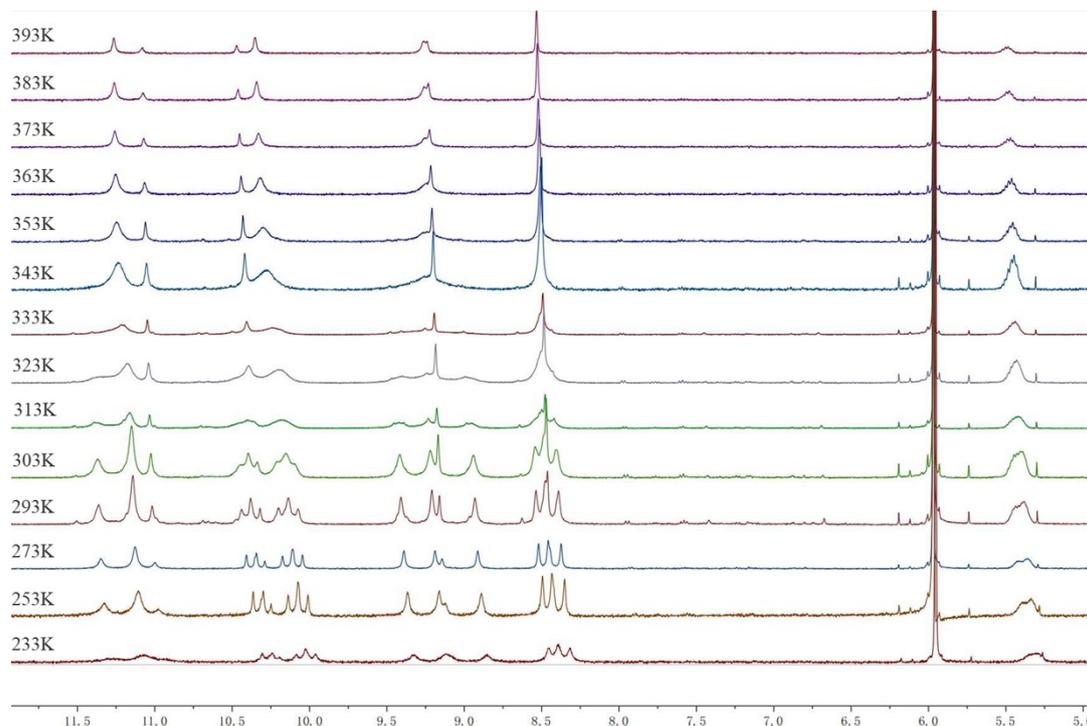


Fig. S2 Variable-temperature ^1H NMR spectrum of **6a** in 1,1,2,2-tetrachloroethane- d_2 .

The exchange rate constant (k) was determined using equation as follows:

- i) For the coalescence temperature k can be calculated using:

$$k = \frac{\pi\Delta V_0}{\sqrt{2}} \quad (1)$$

- ii) At fast exchange temperature

$$k = \frac{\pi\Delta V_0^2}{\sqrt{2}} \left[(\Delta v_e)_{\frac{1}{2}} - (\Delta v_0)_{\frac{1}{2}} \right]^{-1} \quad (2)$$

Combining with the variable-temperature ^1H NMR spectra of **6a** in 1,1,2,2-tetrachloroethane- d_2 and the above equations, we can obtain the Table S2, then fitting with Eyring equation (Figure S2):

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h} \quad (3)$$

and then the thermodynamic parameters can be derived from:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

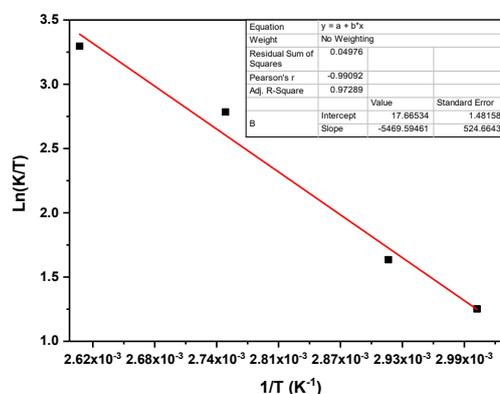


Fig. S3 Fitting of the exchange rate constants with temperature by Eyring equation for **6a** in 1,1,2,2-tetrachloroethane- d_2

giving thermodynamic parameters: $\Delta H^\ddagger = 45.47 \pm 4.4 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta S^\ddagger = -50.6 \pm 12.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $\Delta G^\ddagger_{T_c} = 61.8 \pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$ (14.8 kcal·mol⁻¹).

Table S2. Parameters obtained from the line-shape analysis based on the variable-temperature ¹H NMR spectra of **6a** in 1,1,2,2-tetrachloroethane-*d*₂.

T(K)	Peak width (Hz)	Peak separation(Hz)	Constant <i>k</i>	1/T(K)	Ln(<i>k</i> /T)
393	5.15		(Δ <i>v</i> ₀) _{1/2} for temperatures above <i>T</i> _c		
383	5.65		10347.480	0.002610	3.296072
363	6.03		5879.250	0.002754	2.784369
343	8.09		1759.776	0.002914	1.634774
333	9.59		1165.257	0.003002	1.252104
323	22.2	<i>T</i> _c	303.445	0.003095	-0.062916
293		48.2		Δ <i>V</i> ₀	

6. Density Functional Theory Results

DFT calculations were performed by using Gaussian 09. The geometry of compounds **6a** was optimized at the B3LYP level with the 6-31G(d, p) basis set. Time-dependent density functional theory (TD-DFT) were calculated at the B3LYP/6-31G(d, p) level in CHCl₃ with the SMD solvent model. For **6a**, 50 excited states were calculated. NICS values according to magnetic shielding values were calculated at the B3LYP/6-31G(d,p) level through the gauge-including atomic orbital (GIAO) method^[2,3]. NICS_{zz} values calculated 1 Å above the ring center (NICS(1)_{zz}) and 1 Å below the ring center (NICS(-1)_{zz}) and the results are the average of NICS(1)_{zz} and NICS(-1)_{zz}. UV-vis curves and NICS values of the compound were generated using Multiwfn 3.8 software^[4].

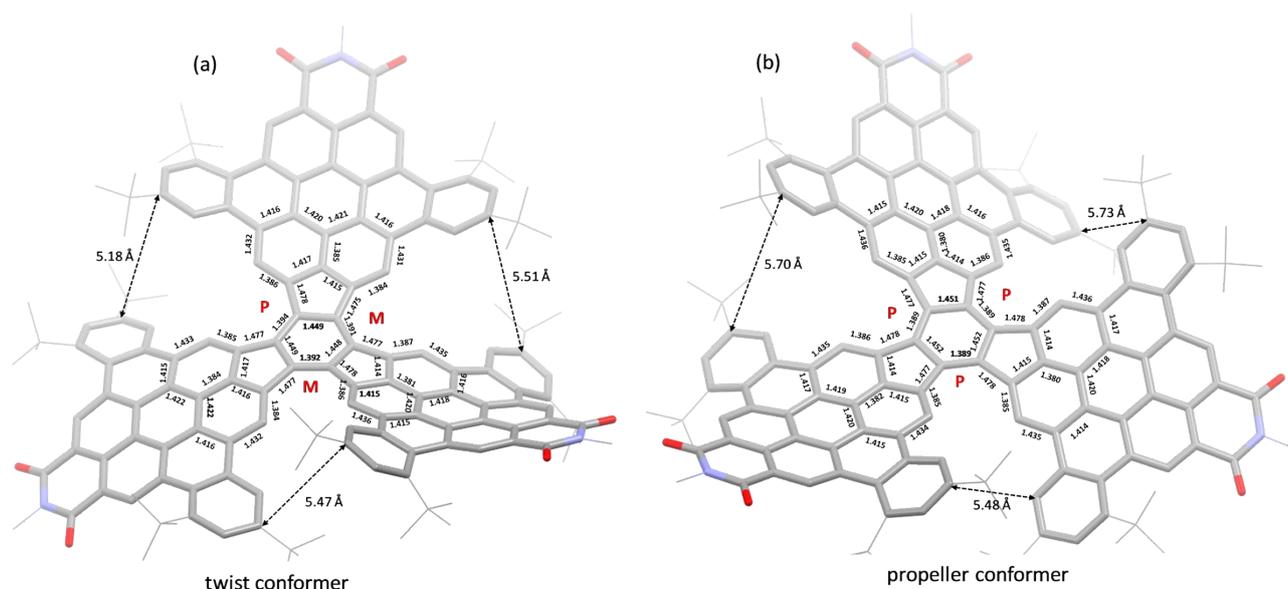


Fig. S4 Calculated structure **6a** with selected bond lengths and the handedness. (The branched alkyl chains are replaced by methyl groups.)

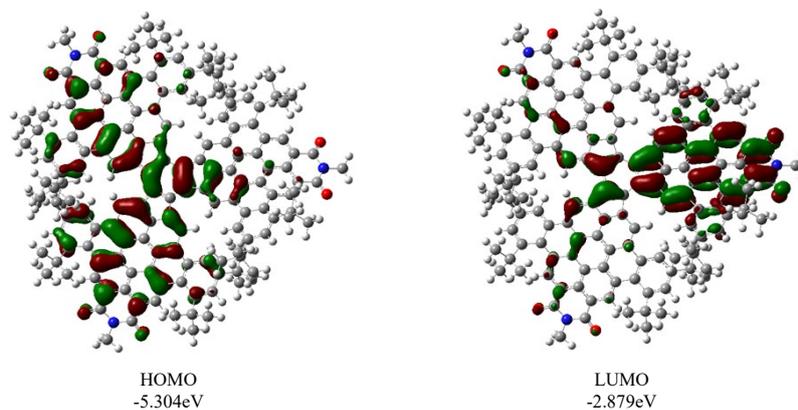


Fig. S5 Frontier orbitals and frontier orbital energies of **6a** at the optimized S_0 geometry at B3LYP/6-31G(d, p) level.

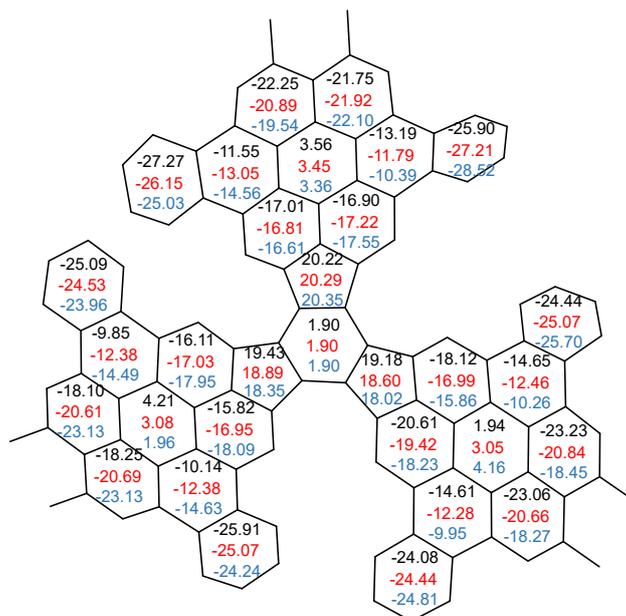


Fig. S6 Calculated NICS(1)_{zz} values (black), NICS(-1)_{zz} values (blue) of **6a** at B3LYP/6-31G(d,p) level and their average NICS values (red).

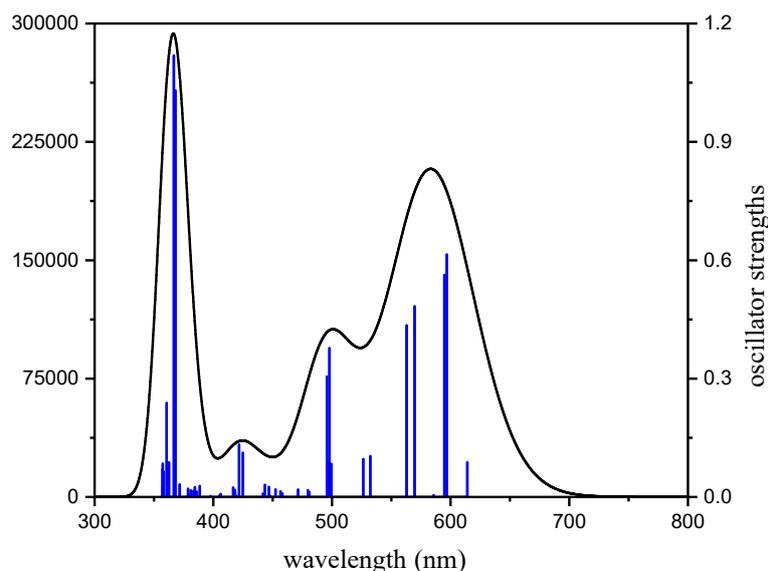


Fig. S7 Calculated UV-vis spectrum of **6a** at the B3LYP/6-31G(d) level in CHCl_3 solution.

Table S3. TD-DFT singlet excitation energies E , excitation wavelengths λ , oscillator strengths $f > 0.1$, and orbital contributions for **6a** at the optimized S_0 ground state geometry at the B3LYP/6-31G(d) level in CHCl_3 solution.

Excited state	Energy (eV)	Wavelength (nm)	Osc. Strength	contributions
S2	2.078	596.7	0.6144	HOMO→LUMO+1:51.5% HOMO-1→LUMO:41.3%
S3	2.085	594.7	0.5622	HOMO-1→LUMO+1:76.5% HOMO→LUMO:13.8% HOMO-1→LUMO:6.0%
S5	2.176	569.7	0.4831	HOMO→LUMO+2:95.7%
S6	2.203	562.9	0.4349	HOMO-1→LUMO+2:95.0%
S7	2.329	532.3	0.1036	HOMO-2→LUMO:93.8%
S10	2.490	497.9	0.3773	HOMO-3→LUMO+1:36.5% HOMO-4→LUMO:16.1% HOMO-2→LUMO+2:9.2%

S12	2.501	495.7	0.3051	HOMO-4→LUMO+2:8.9% HOMO-4→LUMO+1:8.7% HOMO-5→LUMO:64.0% HOMO-2→LUMO+2:12.4% HOMO-5→LUMO+2:8.0%
S23	2.917	425.0	0.1120	HOMO-8→LUMO:49.7% HOMO-7→LUMO:19.6% HOMO-6→LUMO+1:15.1% HOMO-8→LUMO+1:47.8% HOMO-6→LUMO:10.4% HOMO-6→LUMO+2:10.2% HOMO-7→LUMO+1:9.4%
S24	2.940	421.8	0.1328	HOMO-8→LUMO:7.5% HOMO→LUMO+5:63.4% HOMO→LUMO+6:8.8% HOMO-12→LUMO:5.8% HOMO-1→LUMO+5:67.2%
S42	3.367	368.2	1.0301	
S43	3.381	366.7	1.1185	

7. GIWAXS Patterns and AFM of the Thin Films

Grazing incidence wide-angle X-ray scattering characterization of the thin films were conducted with a XEUS SAXS/WAXS system. The scattering intensity was recorded on a 2-D image detector (Pilatus 300K) with a pixel size of $172 \times 172 \mu\text{m}$. The samples were exposed to an X-ray beam with the wavelength of 1.5418 \AA , and the detector was located at a distance of 133 mm from the sample center. The incidence angle was 0.18° to optimize the signal-to-background ratio.

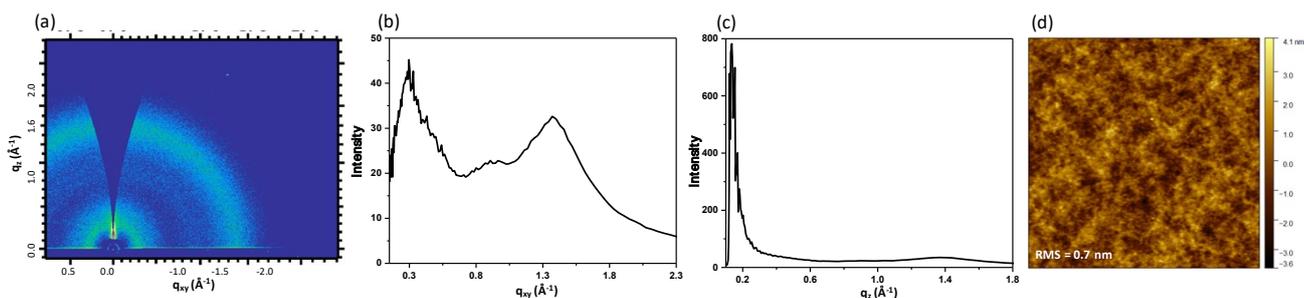


Fig. S8 (a) 2D GIWAXS scattering patterns of the thin films of **6b**; (b) In-plane and (c) out-of-plane diffraction plots from GIWAXS patterns; (d) AFM image of the thin films of **6b**.

8. OFET Fabrication and Characterization

Thin-film devices fabrication: OTFT devices were fabricated in bottom-gate/bottom-contact type, where heavily doped silicon substrates were employed as substrate gold as source and drain electrodes, which were prepared by photolithography. The substrates were cleaned with deionized water, piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2=7:3$), deionized water, isopropyl alcohol, and finally were blown dry with high-purity nitrogen gas. Treatment of the SiO_2/Si wafers with octadecyltrichlorosilane (OTS) was conducted by the vapor-deposition method. The clean substrates were dried under vacuum at 90°C for 0.5 h to eliminate the moisture. When the temperature decreased to approximately room temperature, a small drop of OTS was dropped onto the substrates. Subsequently, this system was heated to 120°C for 2 h under vacuum, after which the vacuum is maintained at approximately room temperature. After careful cleaning the substrates, the thin films were fabricated by spin-coating with 10 mg/ml chlorobenzene solution at 3000 rpm for 40 s, which was subsequently annealed at 110°C for 0.5 h under vacuum.

Devices characterization: All electrical characteristics of the devices were measured at room temperature using a semiconductor parameter analyser (Keithley 4200 SCS) in nitrogen atmosphere. The mobilities of the devices were calculated in the saturation regime. The equation is listed as follows:

$$I_{\text{DS}} = (W/2L)C_i\mu(V_{\text{GS}}-V_{\text{T}})^2$$

where W/L is the channel width/length, C_i is the insulator capacitance per unit area (10 nF/cm^2), and V_{GS} and V_{T} are

the gate voltage and threshold voltage, respectively.

9. ^1H NMR, ^{13}C NMR, and HRMS Spectra of Compounds

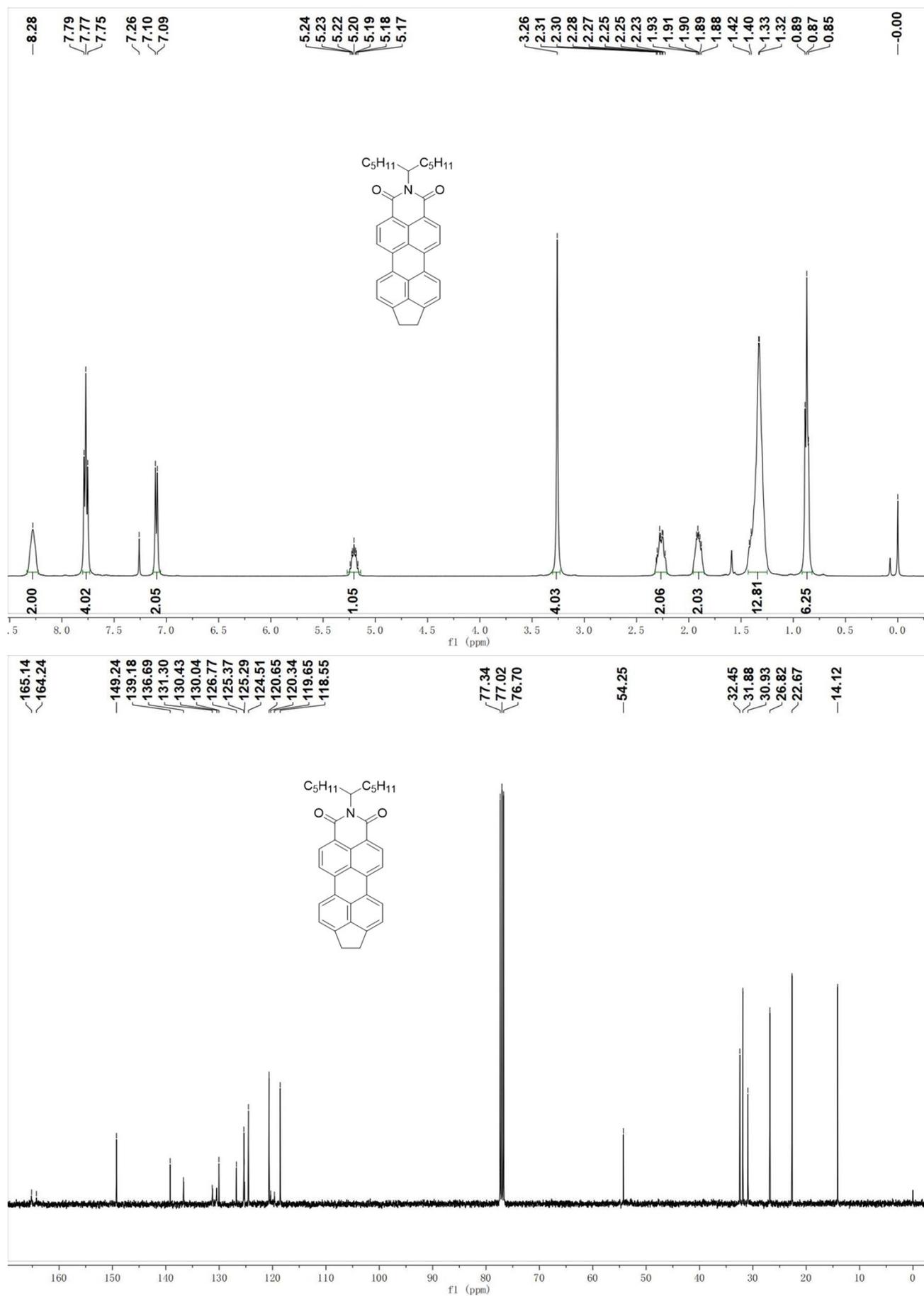


Fig. S9 ^1H NMR and ^{13}C NMR spectra of **1a** in CDCl_3 (400 MHz, 298 K).

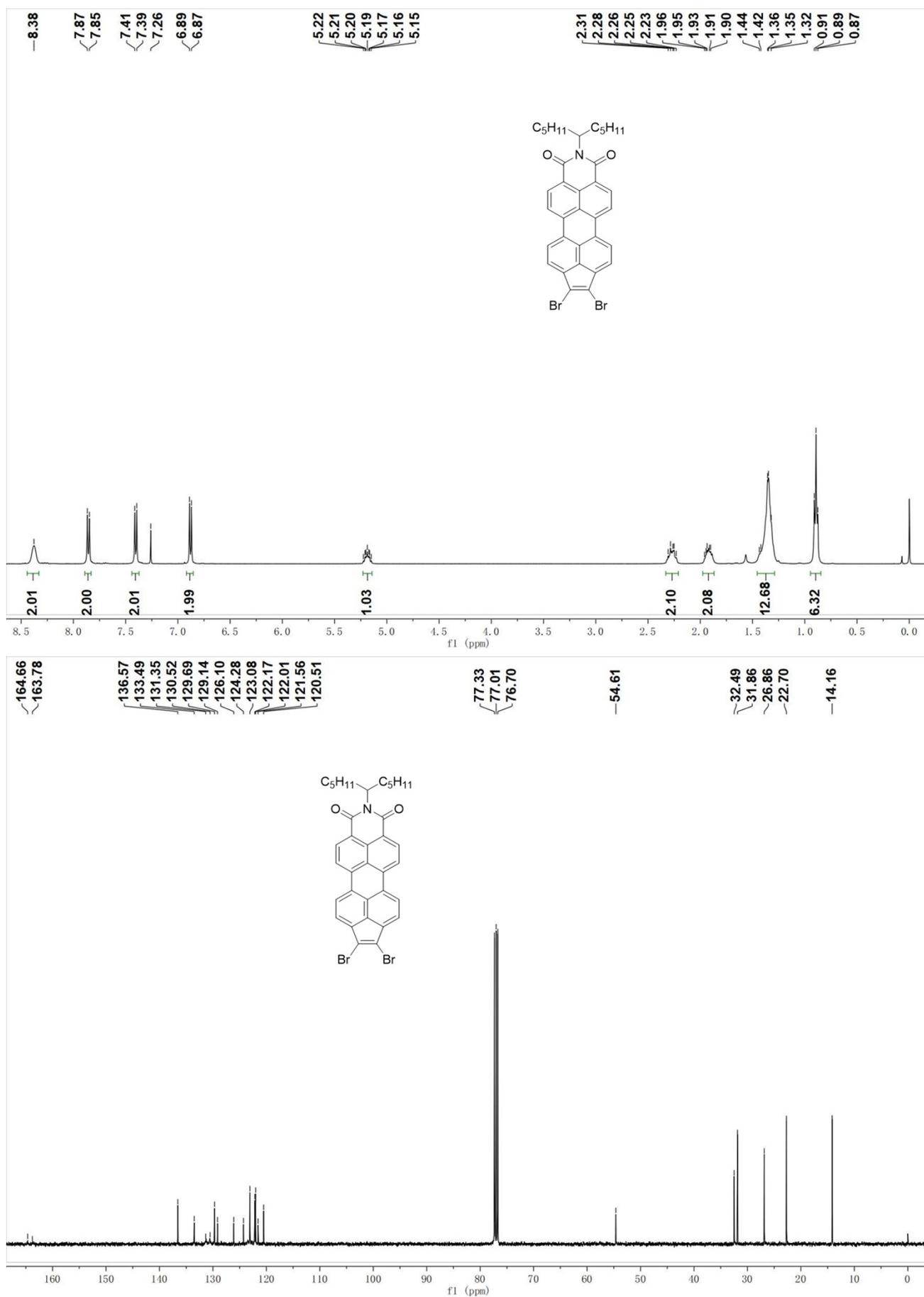


Fig. S10 ¹H NMR and ¹³C NMR spectra of **2a** in CDCl₃ (400 MHz, 298 K).

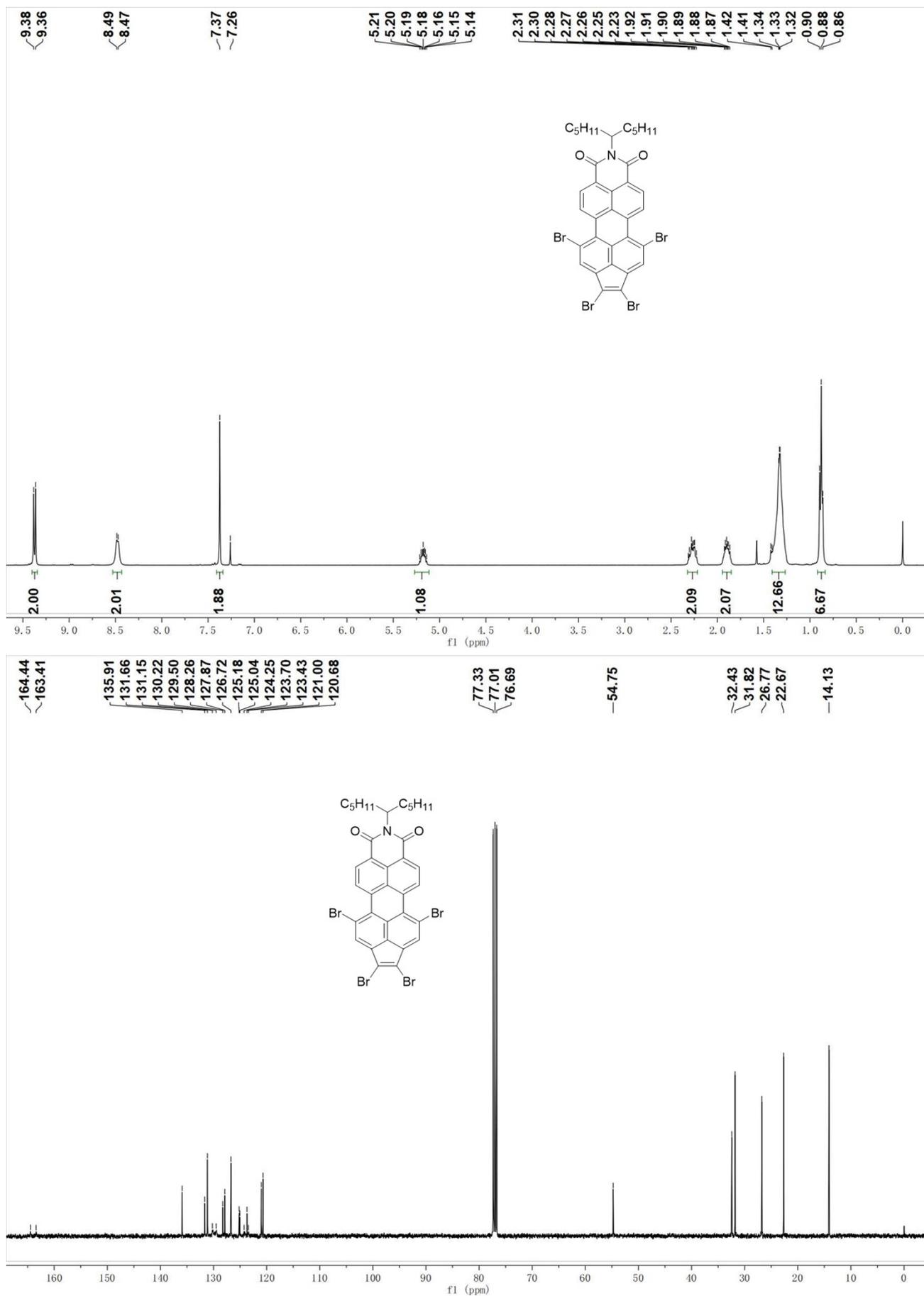


Fig. S11 ¹H NMR and ¹³C NMR spectra of **3a** in CDCl₃ (400 MHz, 298 K).

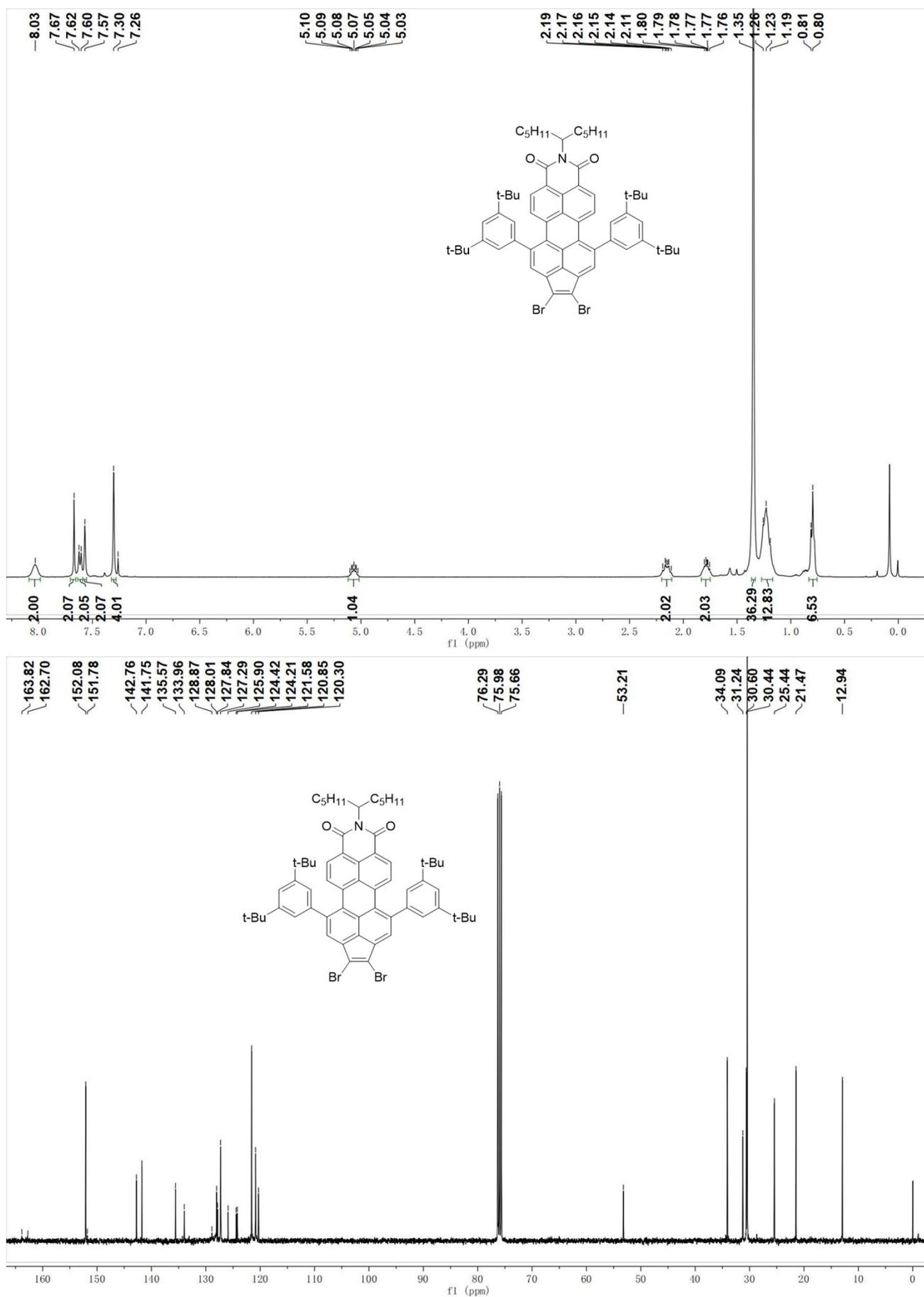


Fig. S12 ¹H NMR and ¹³C NMR spectra of **4a** in CDCl₃ (400 MHz, 298 K).

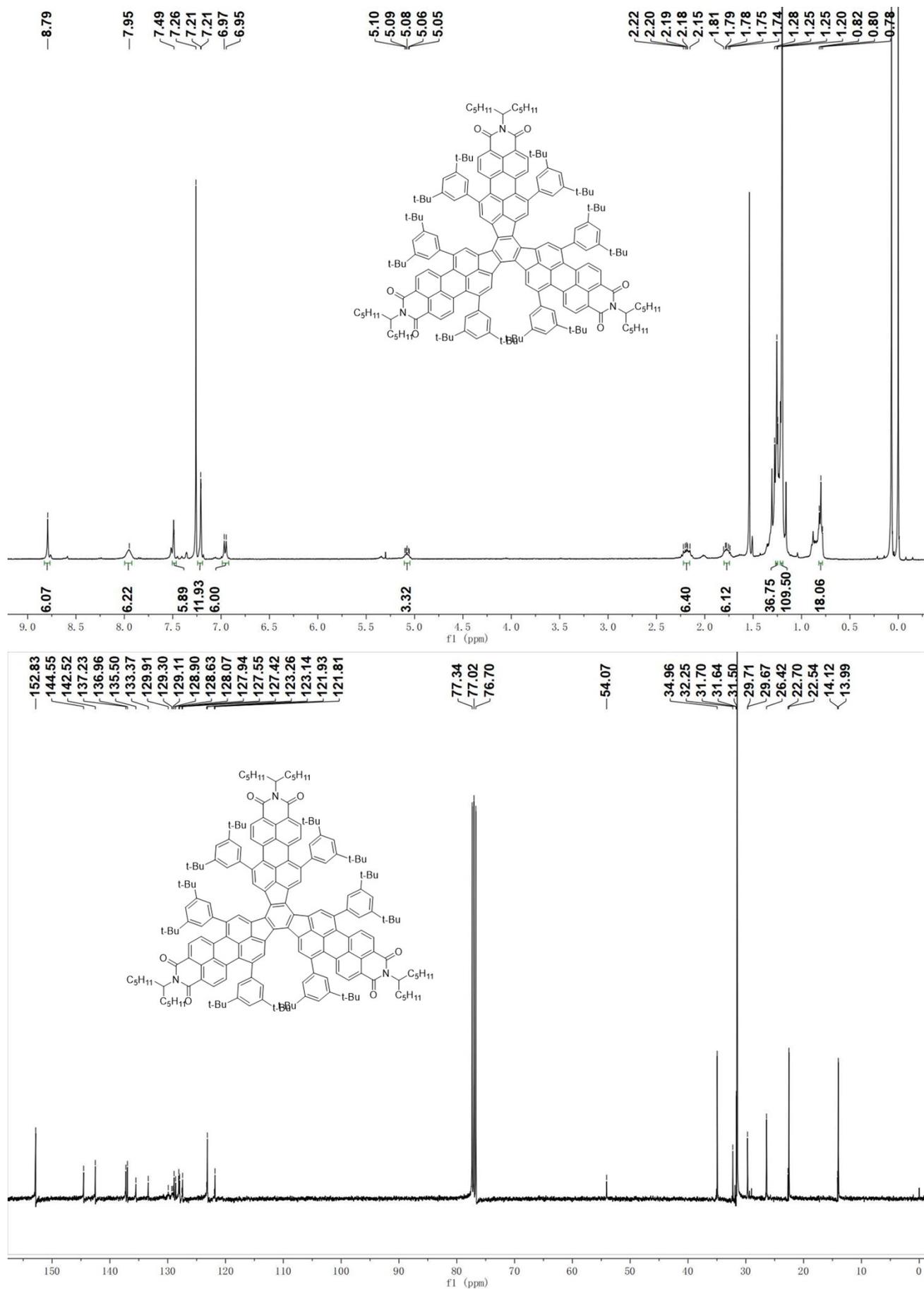


Fig. S13 ¹H NMR and ¹³C NMR spectra of **5a** in CDCl₃ (400 MHz, 298 K).

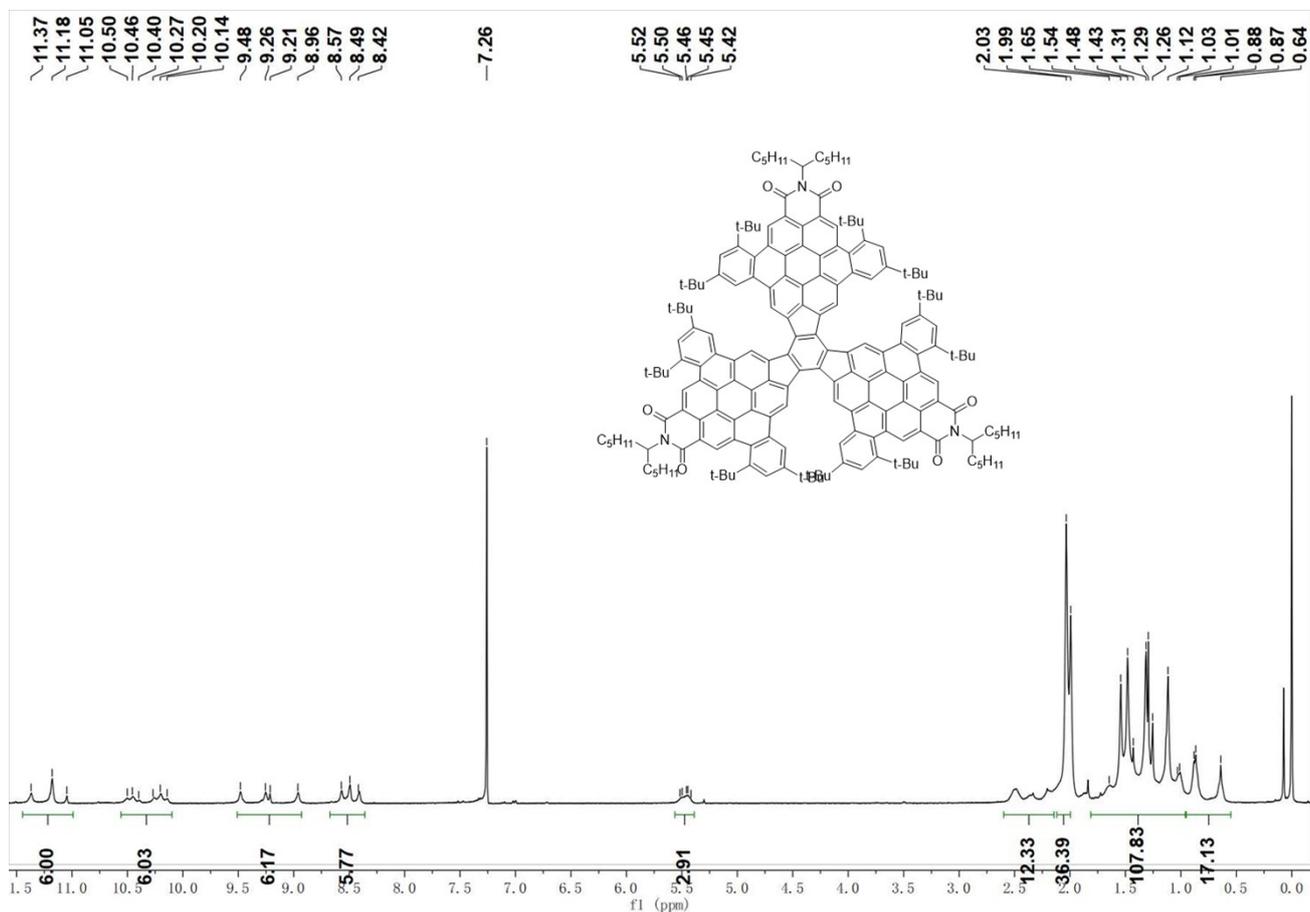


Fig. S14 ¹H NMR spectrum of **6a** in CDCl₃ (400 MHz, 298 K).

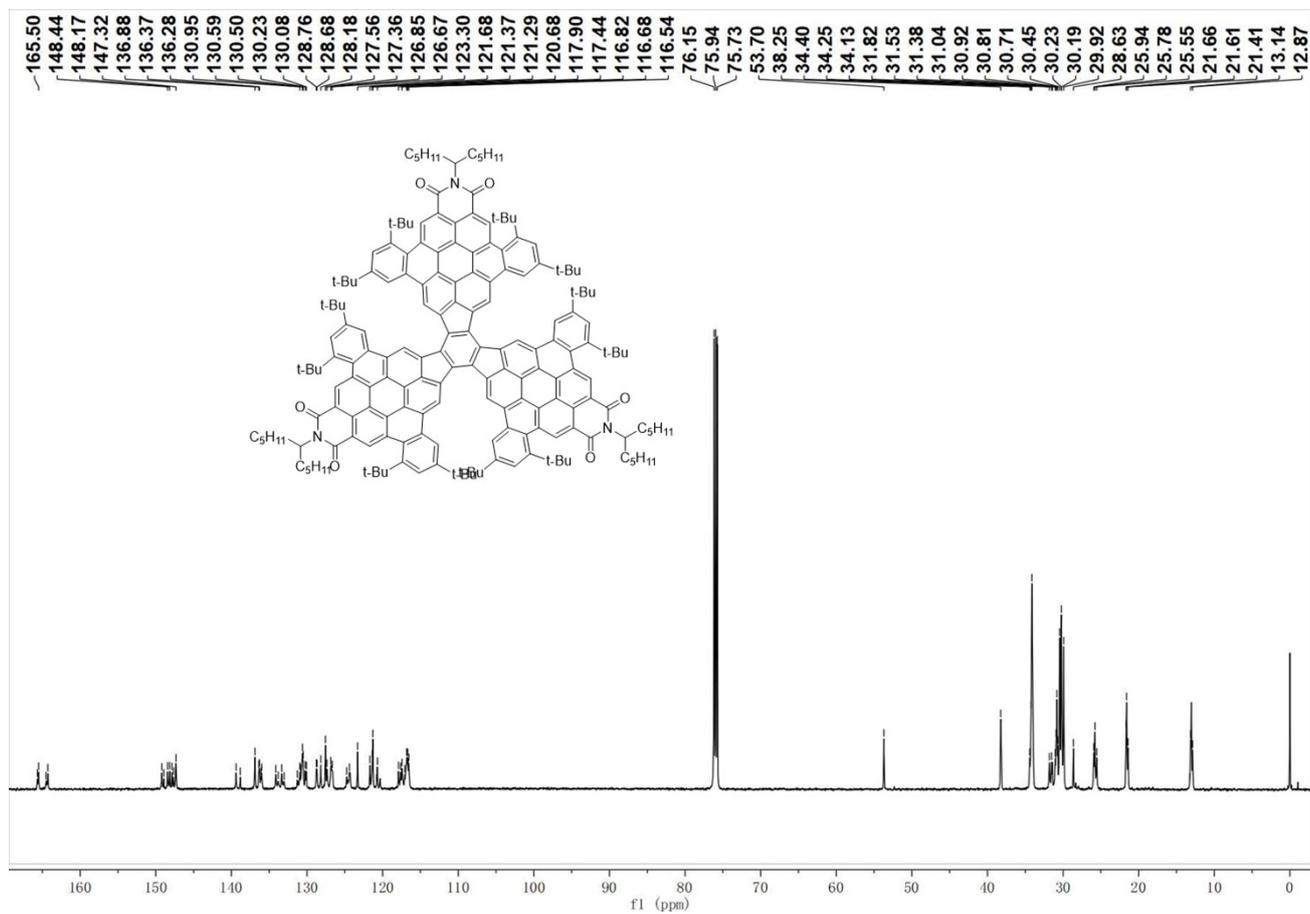


Fig. S15 ¹³C NMR spectrum of **6a** in CDCl₃ (600 MHz, 298 K).

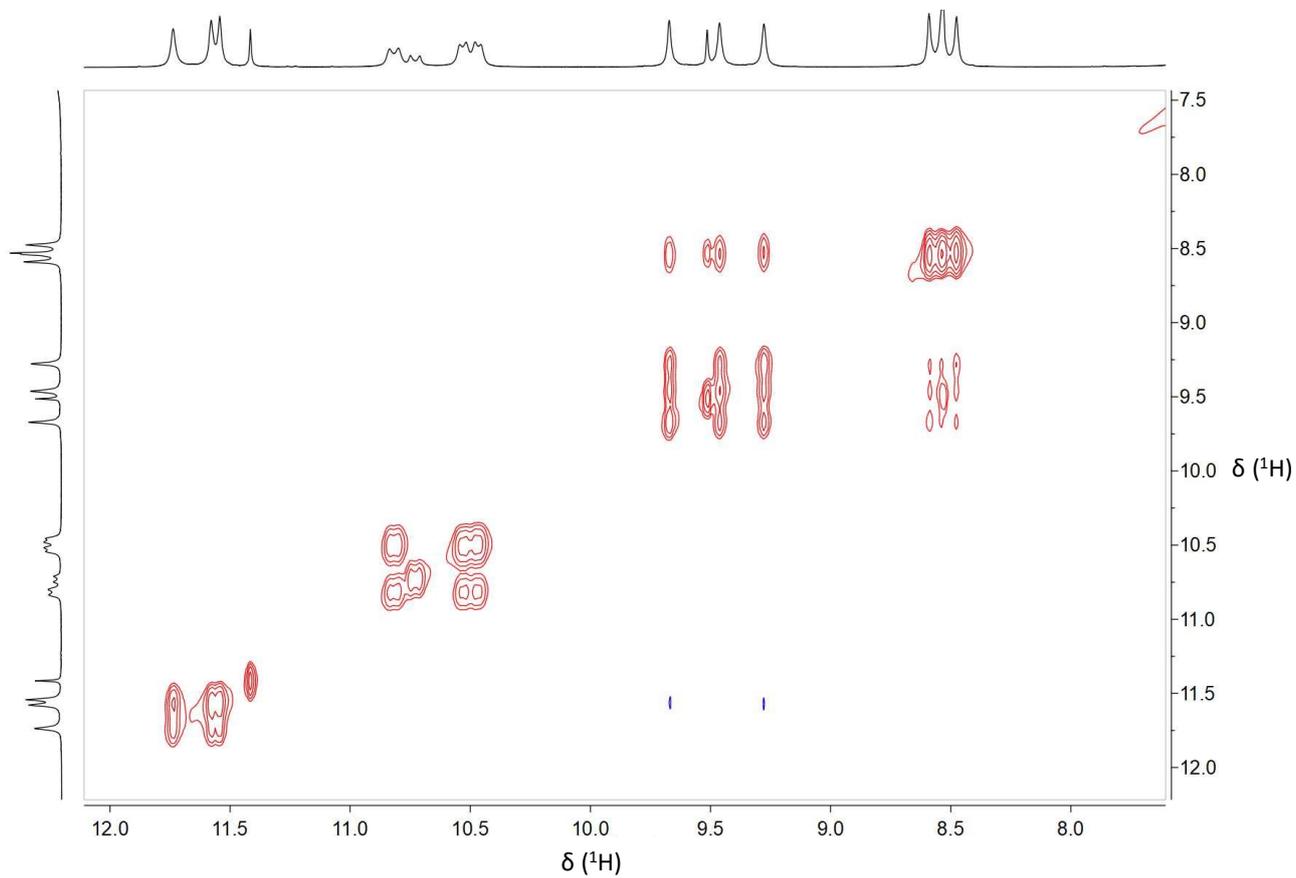


Fig. S16 TOCSY spectrum of **6a** in C_6D_6 (600 MHz, 298 K).

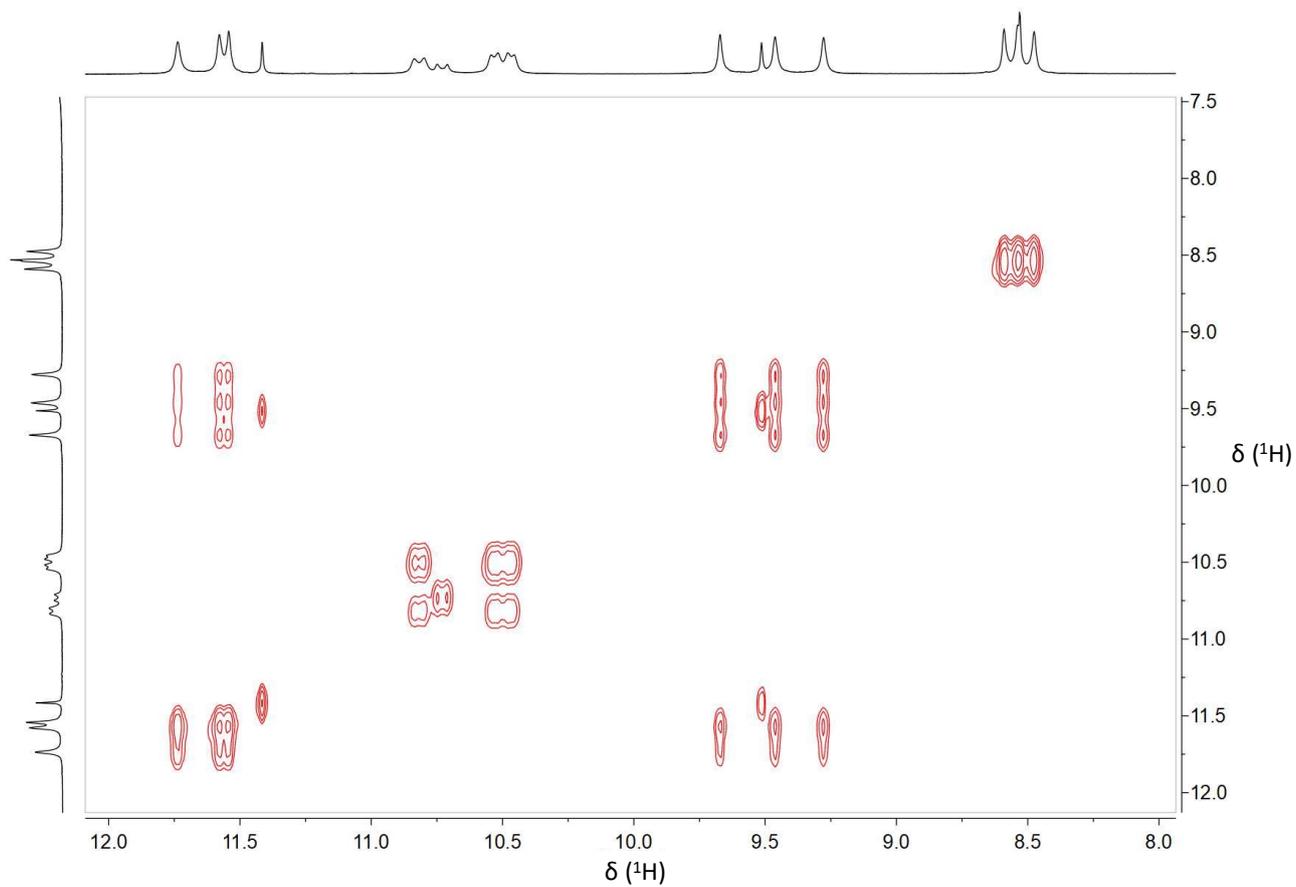


Fig. S17 NOESY spectrum of **6a** in C_6D_6 (600MHz, 298K).

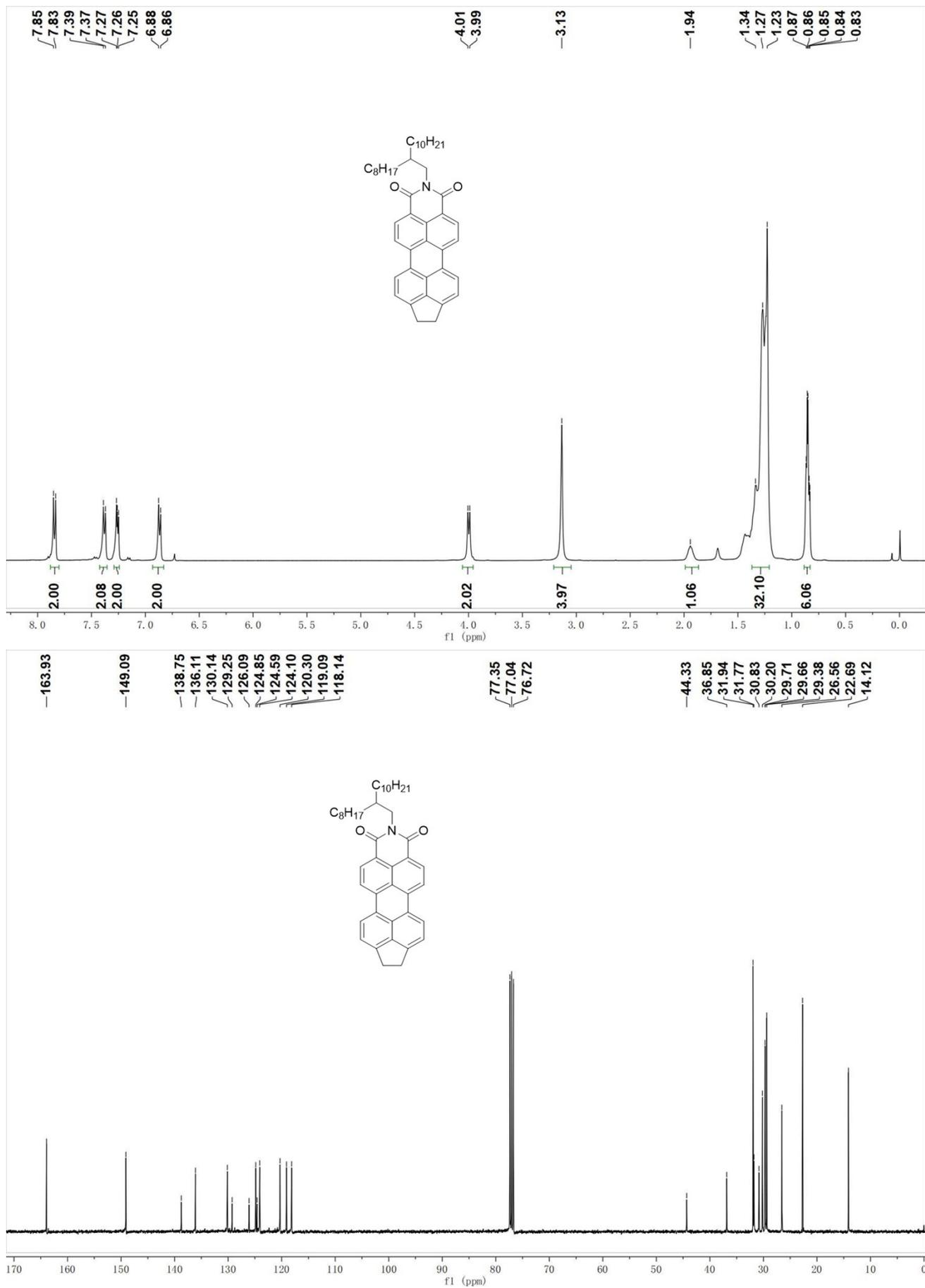


Fig. S18 ^1H NMR and ^{13}C NMR spectra of **1b** in CDCl_3 (400 MHz, 298 K).

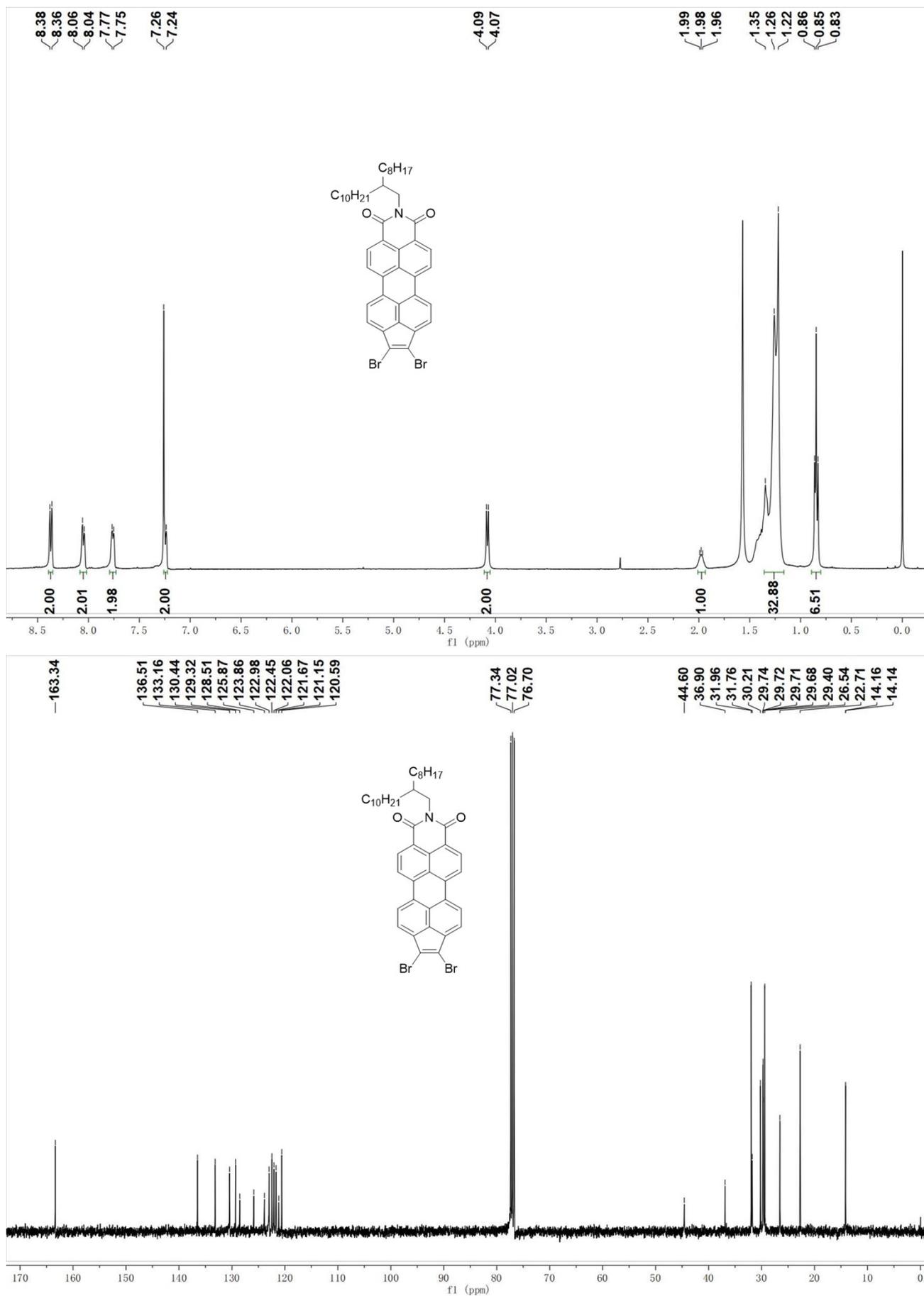


Fig. S19 ¹H NMR and ¹³C NMR spectra of **2b** in CDCl₃ (400 MHz, 298 K).

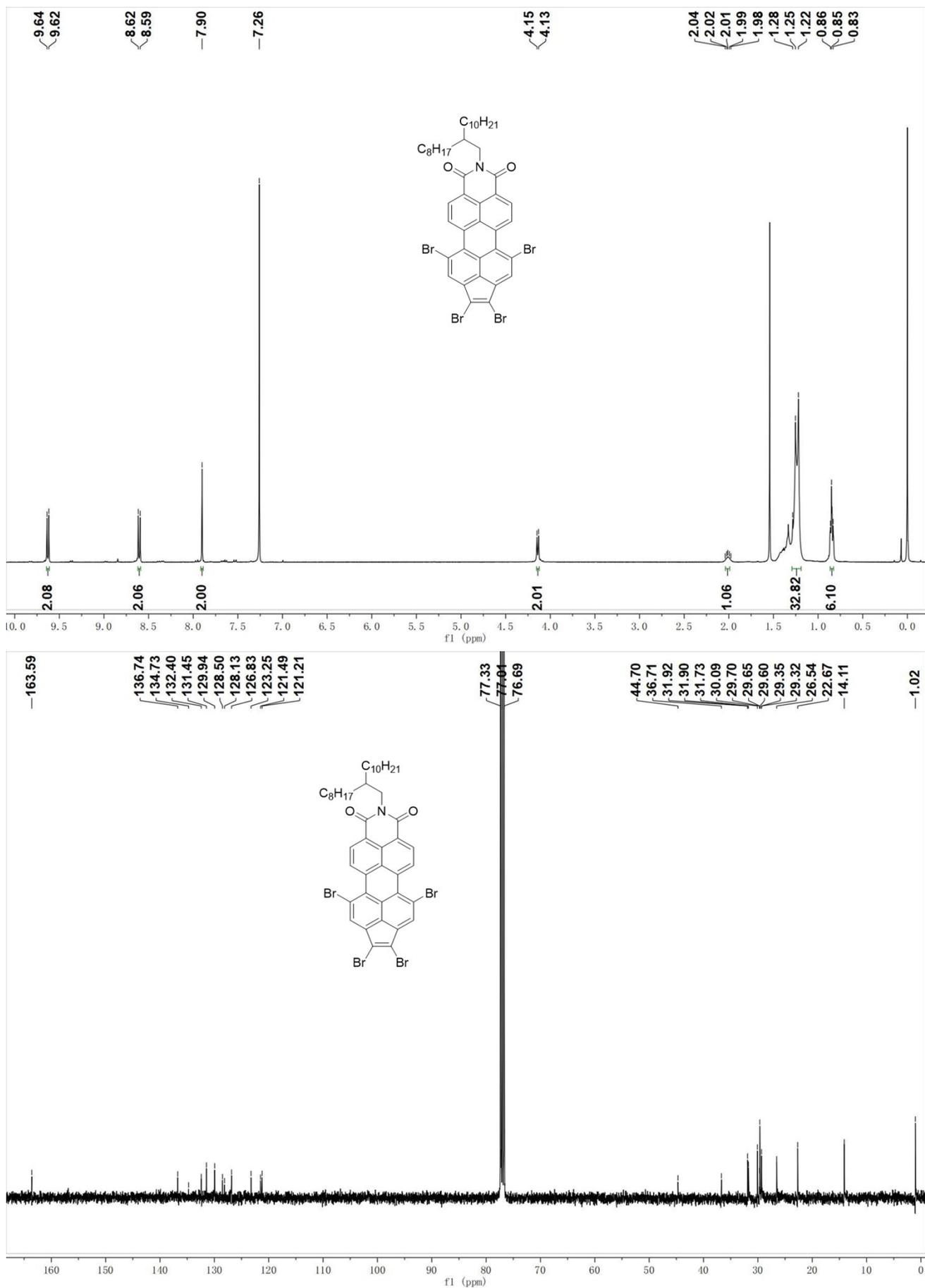


Fig. S20 ¹H NMR and ¹³C NMR spectra of **3b** in CDCl₃ (400 MHz, 298 K).

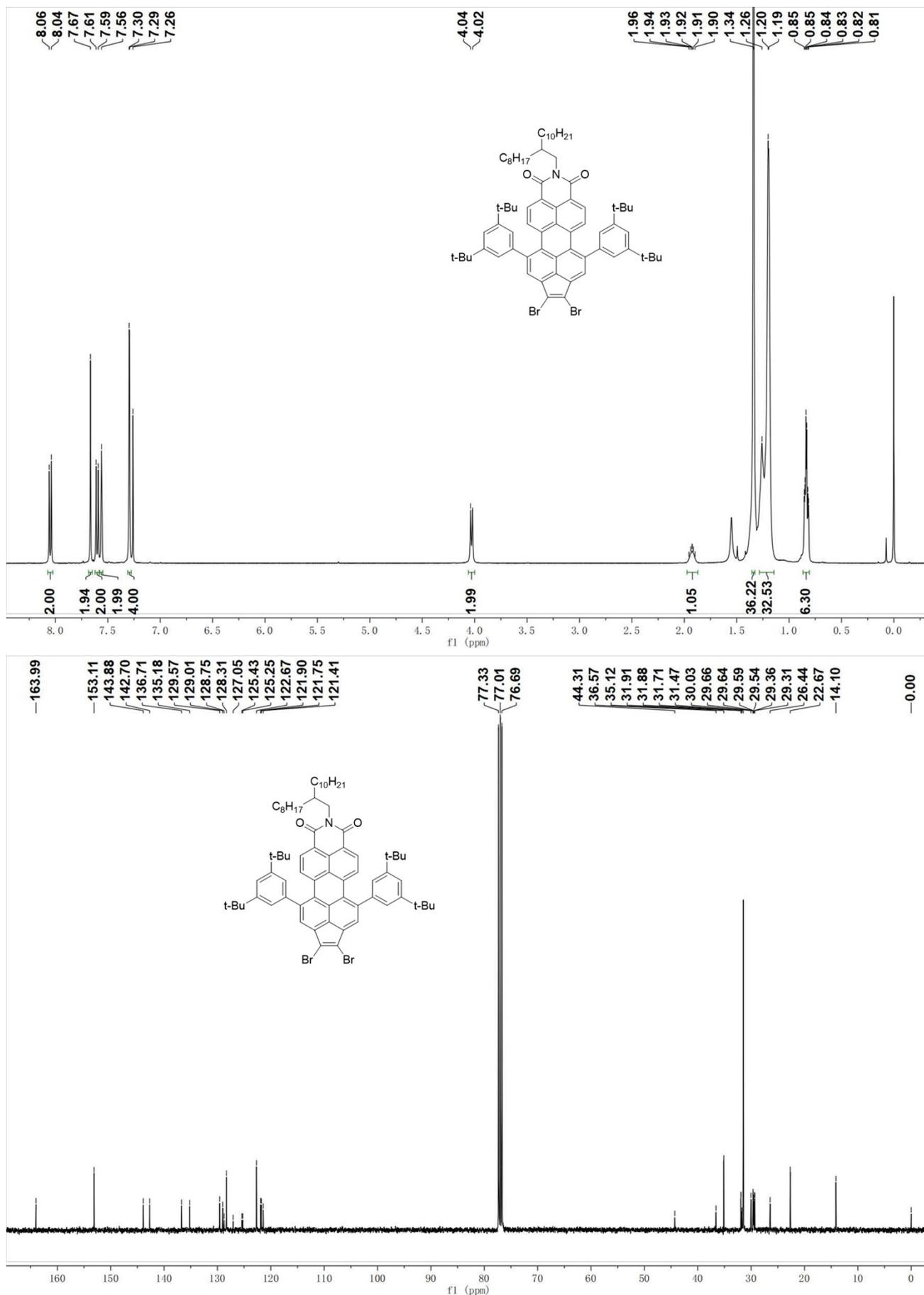


Fig. S21 ¹H NMR and ¹³C NMR spectra of **4b** in CDCl₃ (400 MHz, 298 K).

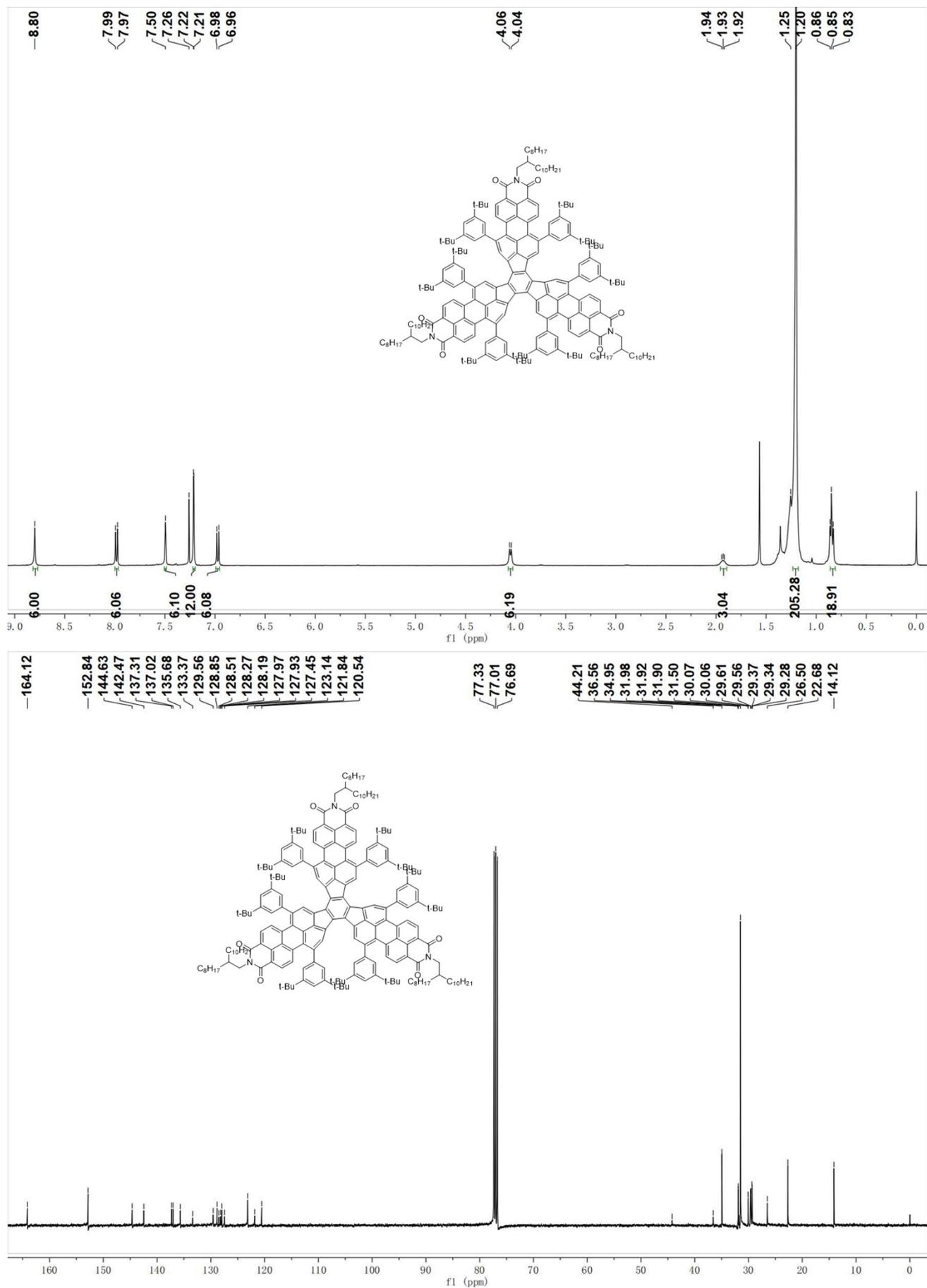


Fig. S22 ¹H NMR and ¹³C NMR spectra of **5b** in CDCl₃ (400 MHz, 298 K).

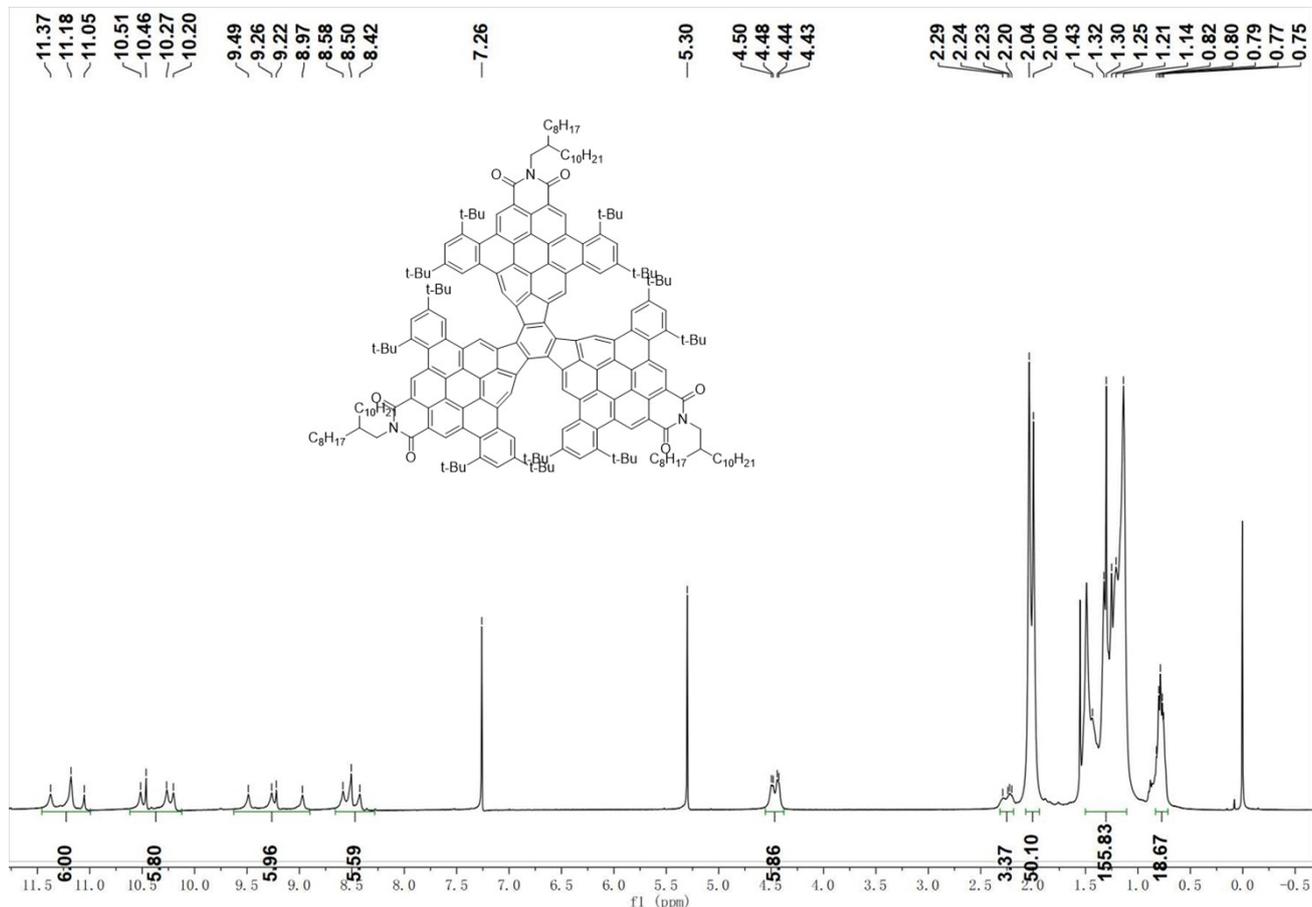


Fig. S23 ¹H NMR spectrum of **6b** in CDCl₃ (400 MHz, 298 K).

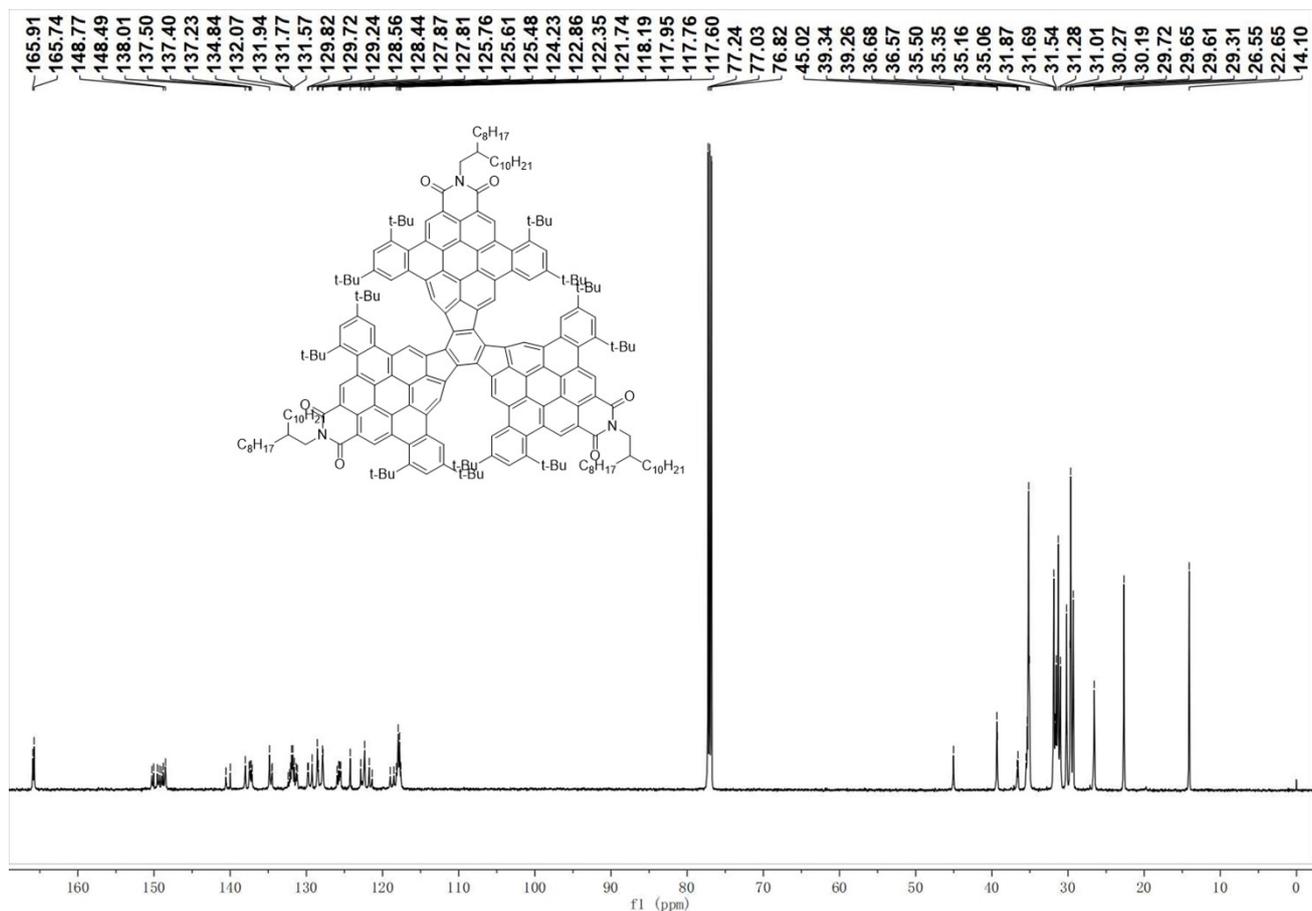


Fig. S24 ¹³C NMR spectrum of **6b** in CDCl₃ (600 MHz, 298 K).

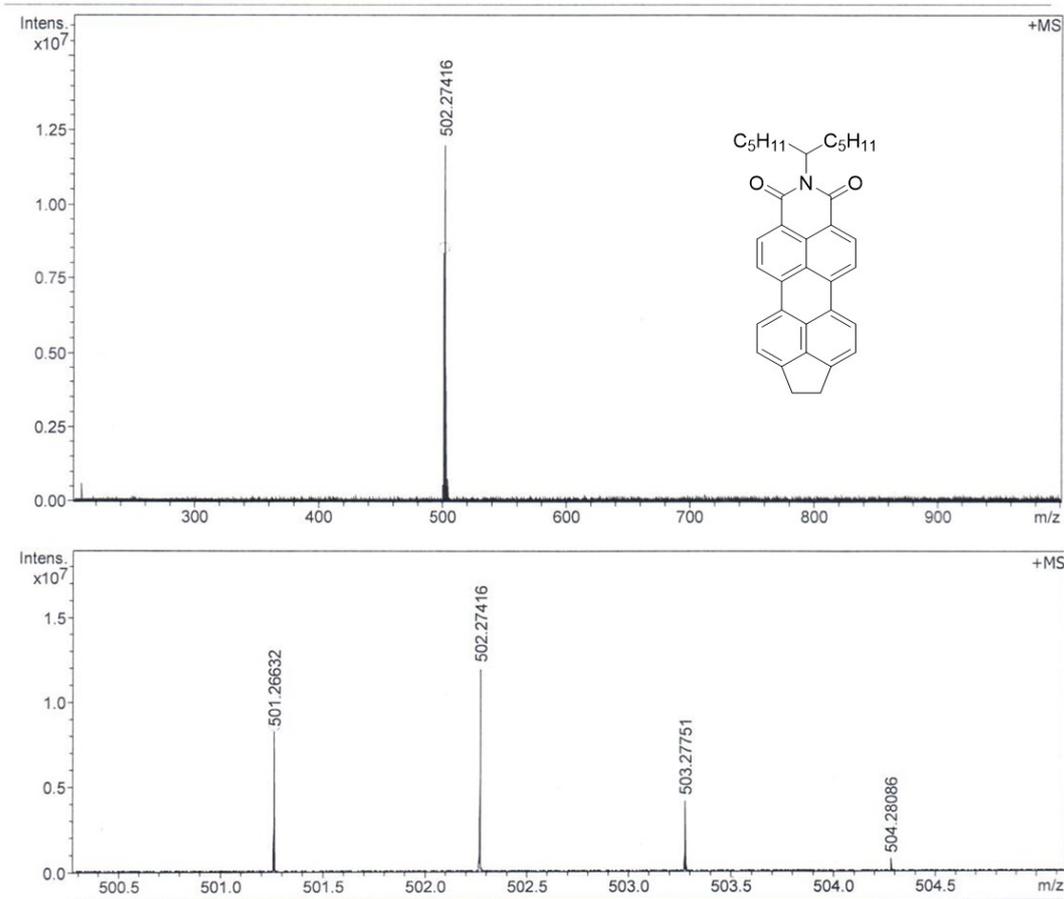


Fig. S25 HR-MALDI-TOF spectrum of **1a**.

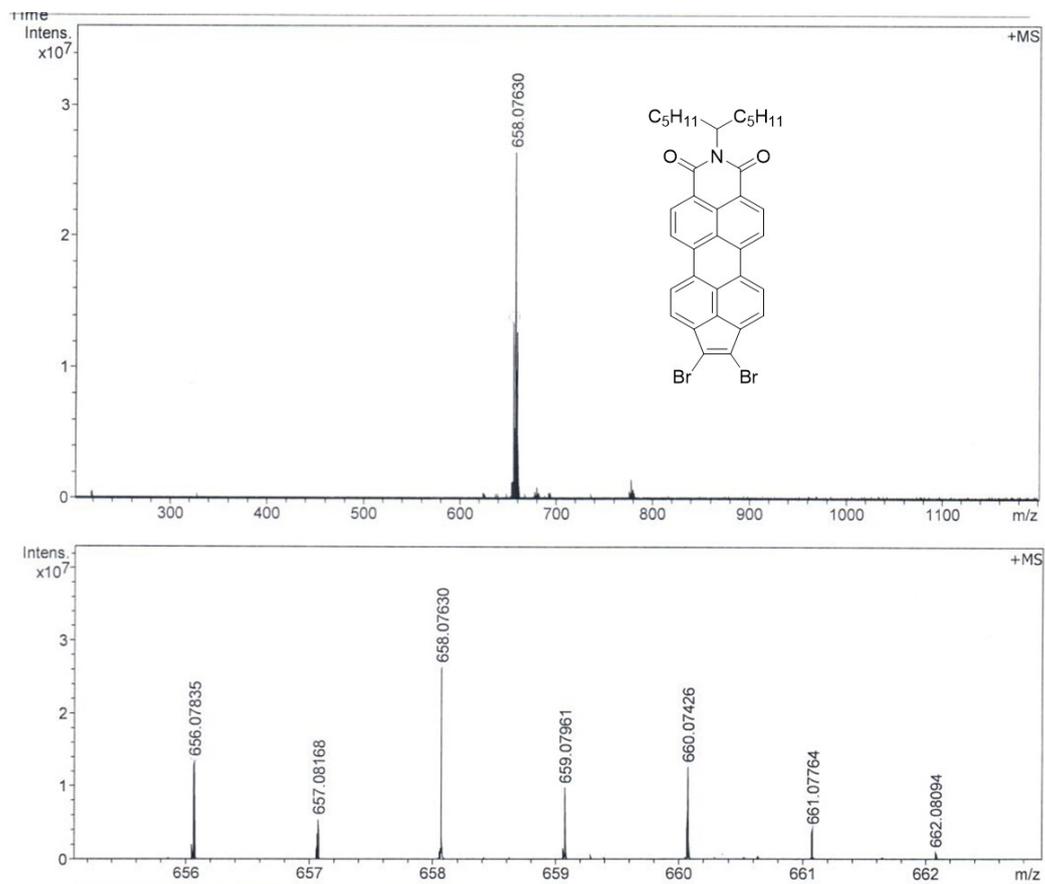


Fig. S26 HR-MALDI-TOF spectrum of **2a**.

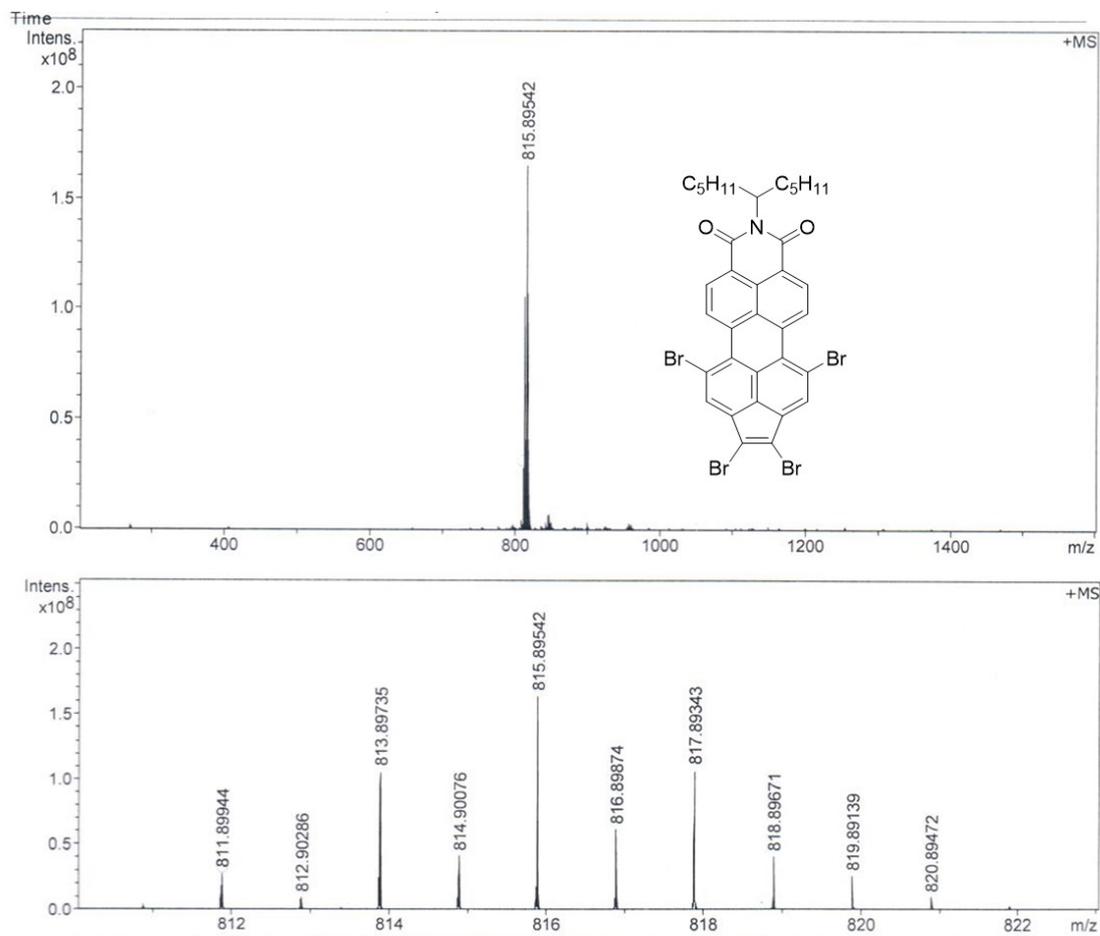


Fig. S27 HR-MALDI-TOF spectrum of 3a.

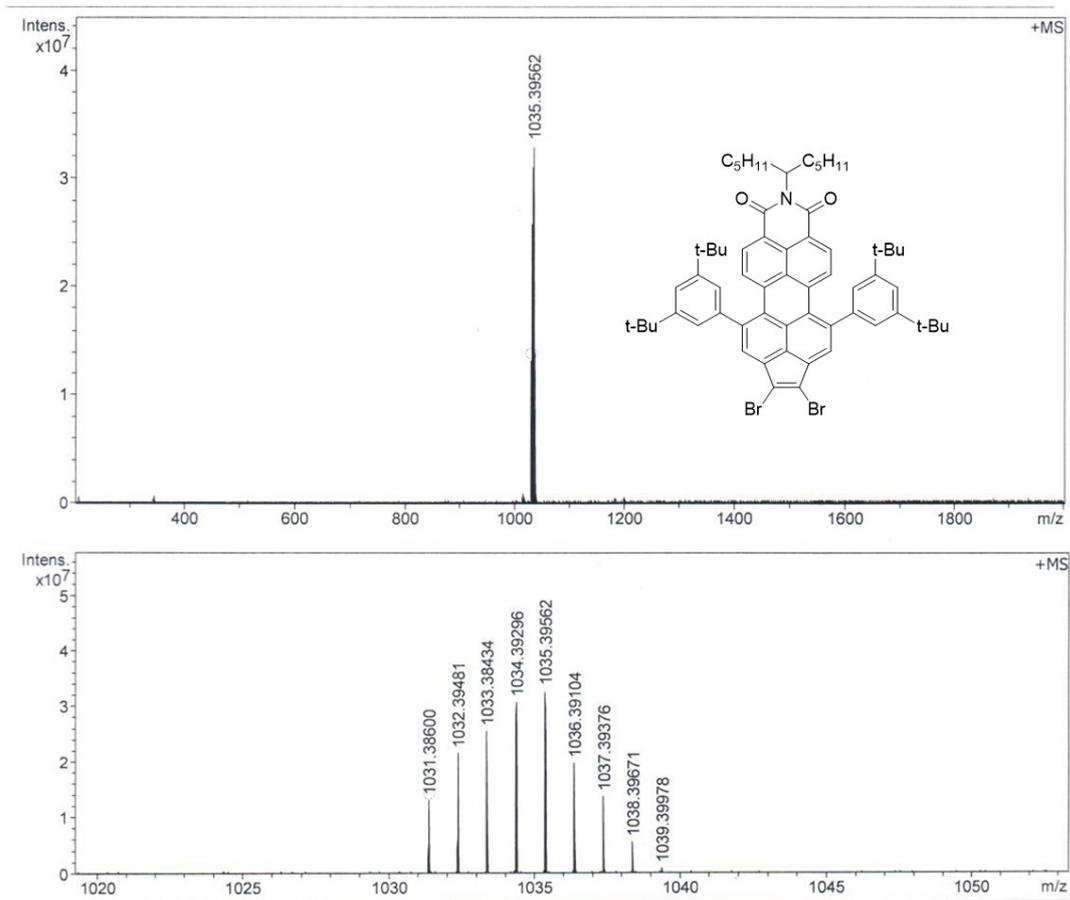


Fig. S28 HR-MALDI-TOF spectrum of 4a.

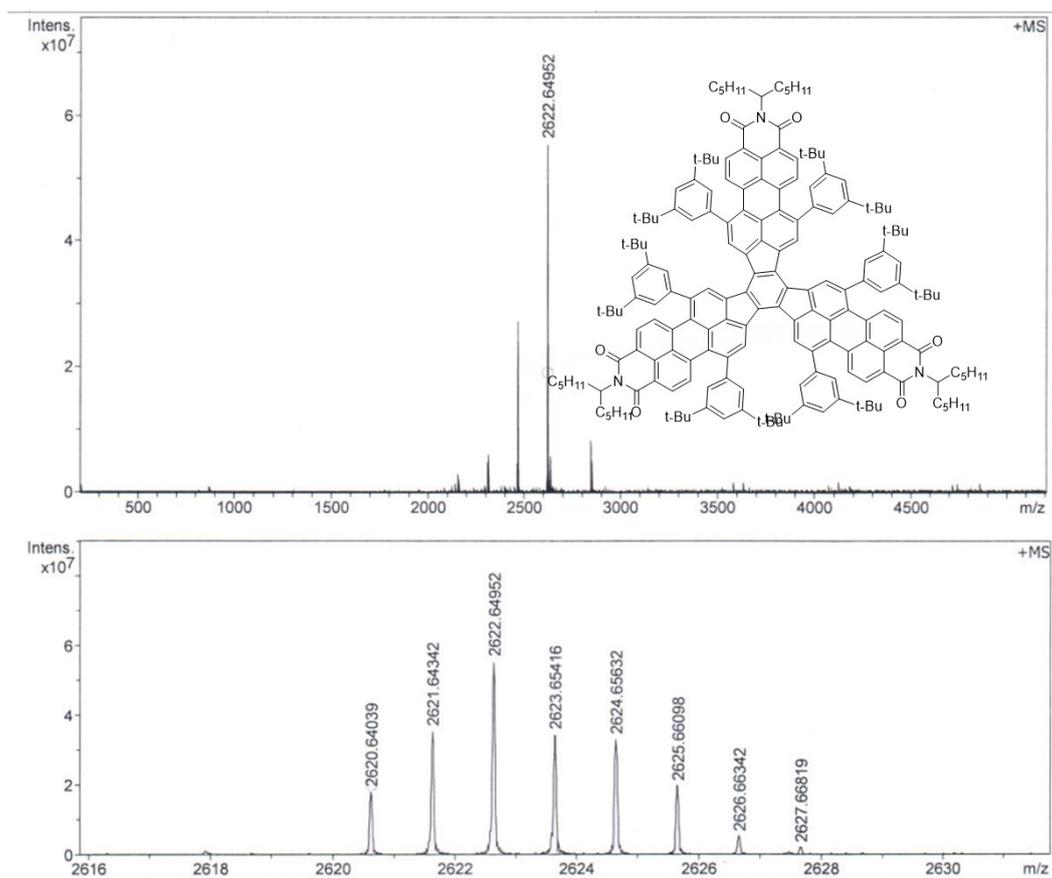


Fig. S29 HR-MALDI-TOF spectrum of **5a**.

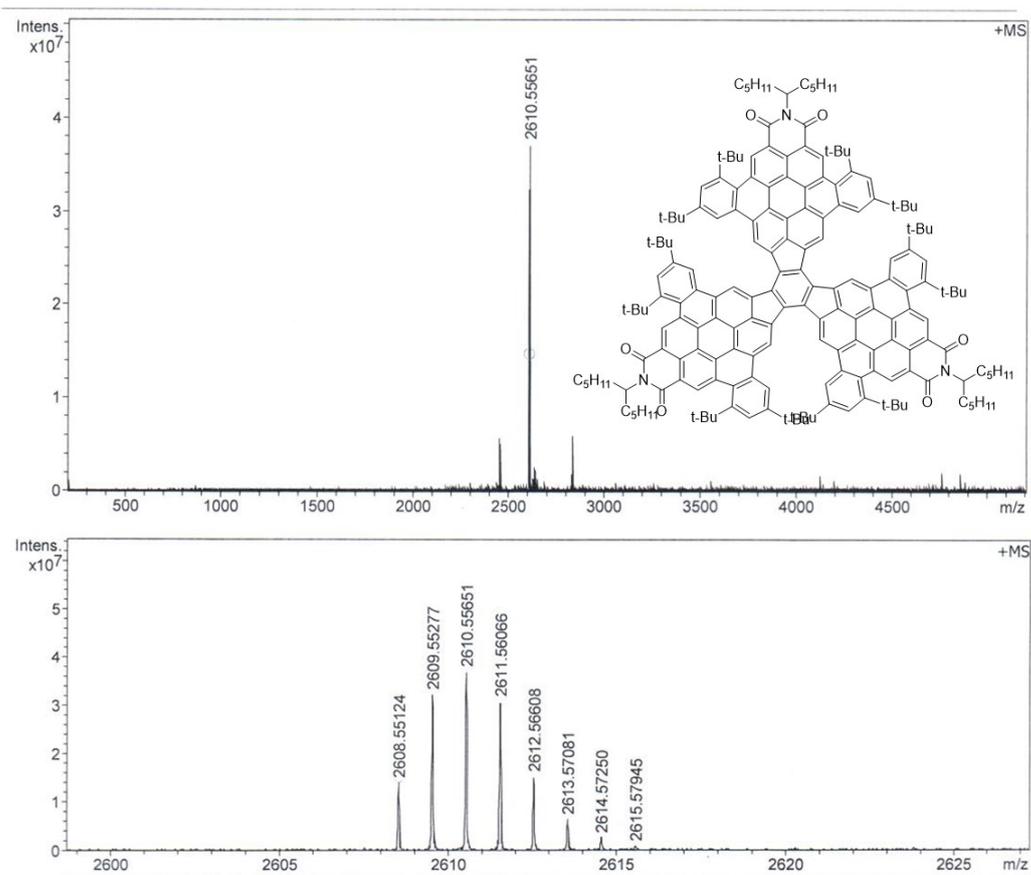


Fig. S30 HR-MALDI-TOF spectrum of **6a**.

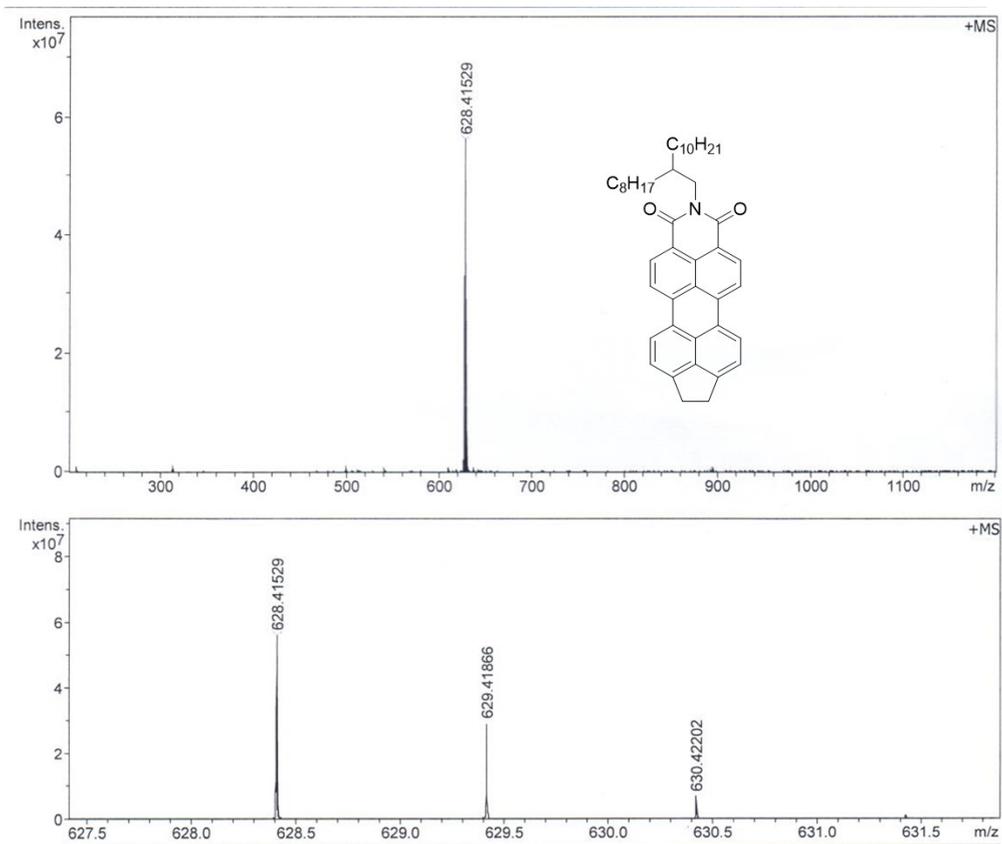


Fig. S31 HR-MALDI-TOF spectrum of **1b**.

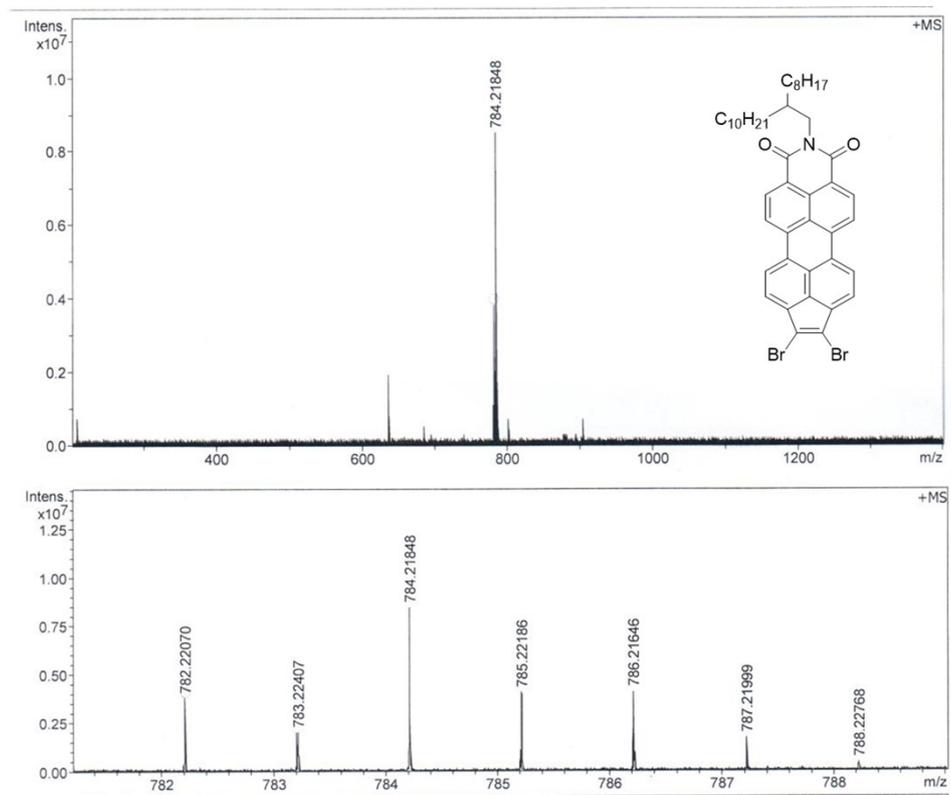


Fig. S32 HR-MALDI-TOF spectrum of **2b**.

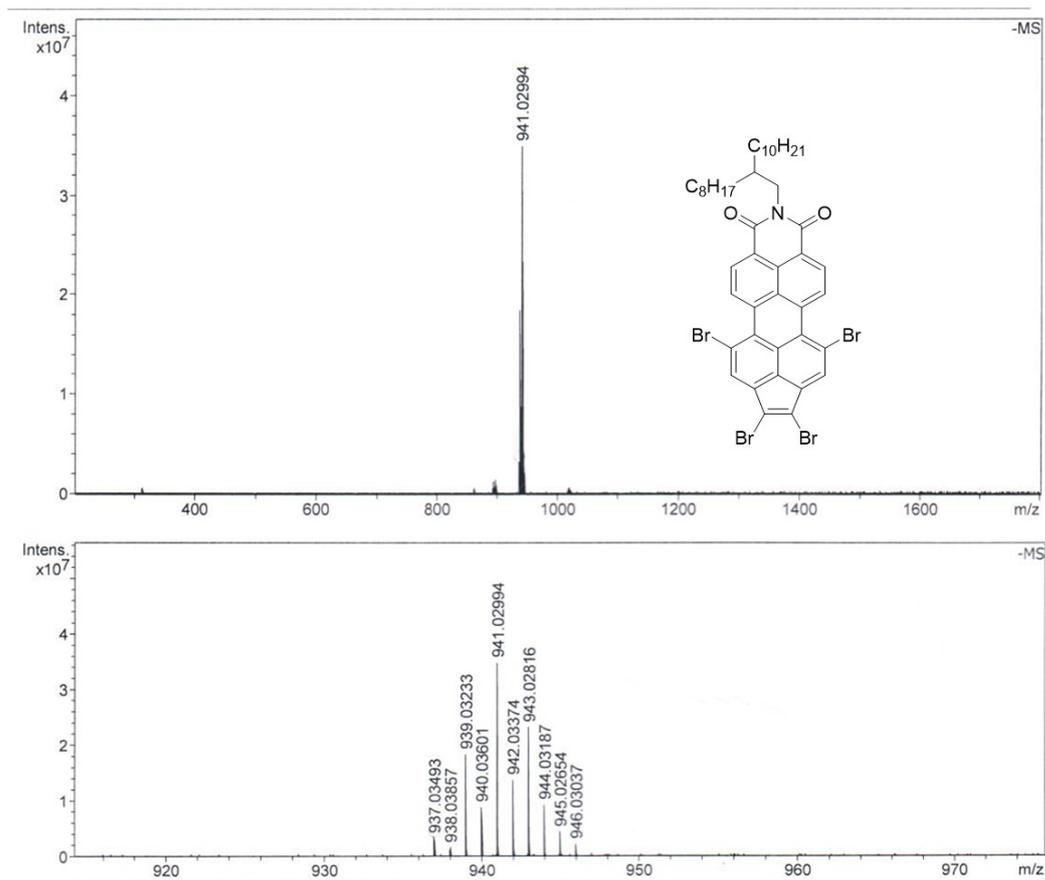


Fig. S33 HR-MALDI-TOF spectrum of **3b**.

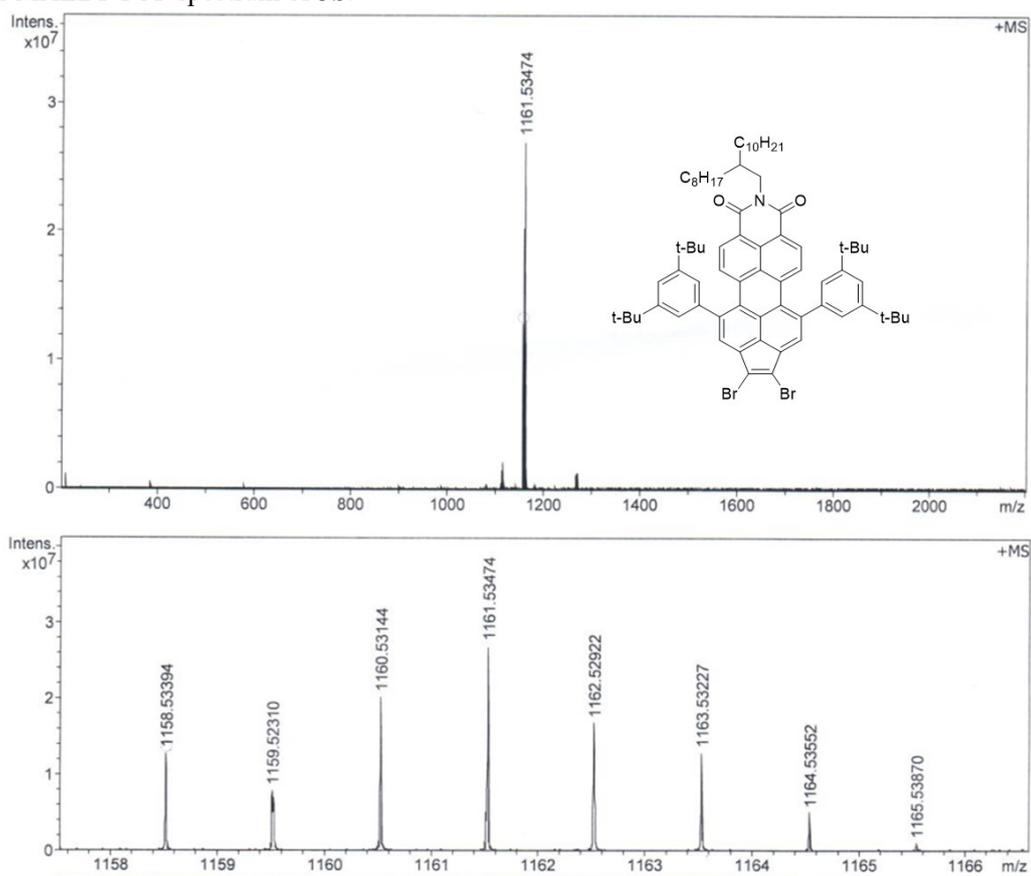


Fig. S34 HR-MALDI-TOF spectrum of **4b**.

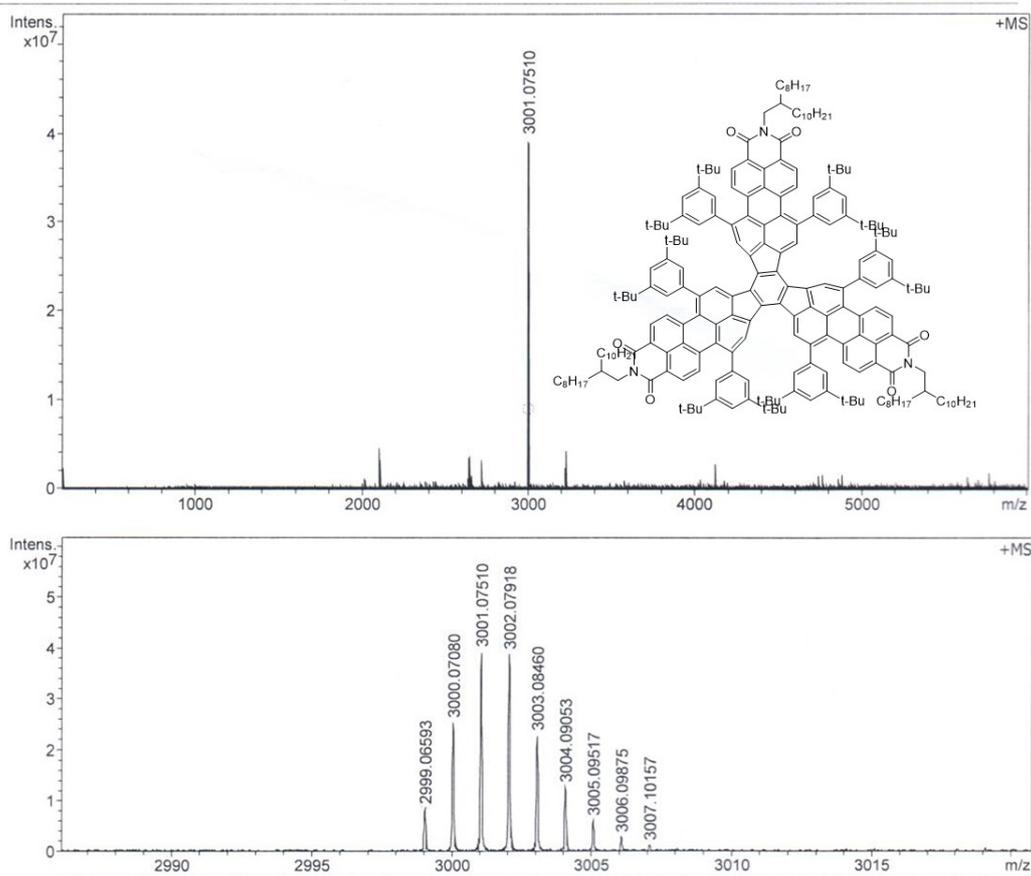


Fig. S35 HR-MALDI-TOF spectrum of **5b**.

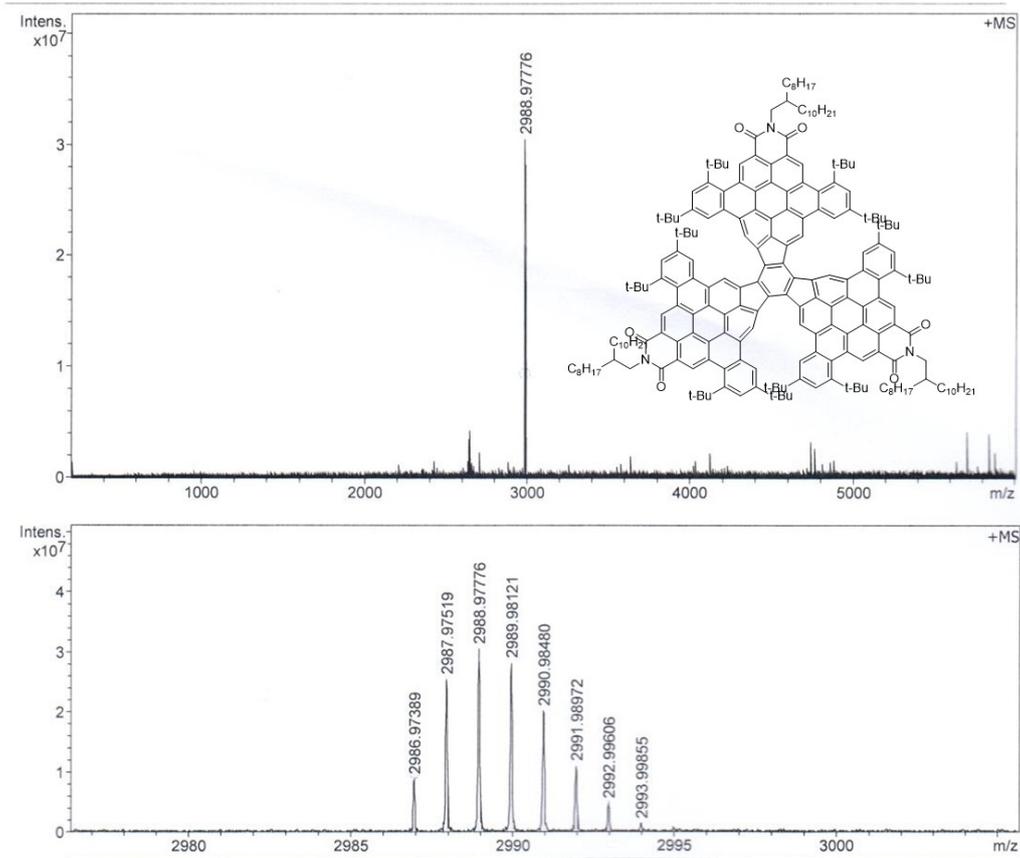


Fig. S36 HR-MALDI-TOF spectrum of **6b**.

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