Supporting Information

A Modular Approach toward 5,6,7,8-functionalized Acepleiadylene derivatives

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1. General Information

Unless otherwise noted, all materials including dry solvents were obtained from Energy Chemical, Adamas, or TCI chemicals, and used without further purification.

Newly synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy (HRMS). ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with a nuclear magnetic resonance (NMR) spectrometer. Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard, and coupling constants (*J*) in Hertz. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray ionization in Positive/Negative ion detection (ESI^+/ESI^-) mode. Significant fragments are reported in the following fashion: m/z (relative intensity).

The ultraviolet−visible (UV−Vis) spectra were obtained using UV-2700 220v CH. UV−Vis measurements were carried out using an anhydrous DCM solution at a sample concentration of 0.1 M. (Transparent cuvette on four sides: 1×1×5 cm^3).

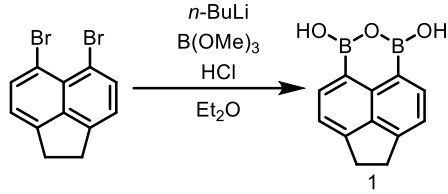
Crystal data were collected using a Rigaku-AFC7 equipped with a Rigakuj Saturn CCD area-detector system. The measurements were made using monochromatic Mo Kα radiation (λ = 0.71073 Å) under a cold nitrogen stream.

The electrochemical measurements were carried out in anhydrous DCM containing 0.1 M nBu_4NPF_6 as supporting electrolyte under argon atmosphere by CHI 660E electrochemical analyzer. A standard three-electrode system was used: Ag/AgCl (3.0 mol/L KCl solution) electrode reference electrode; Glassy carbon electrode working electrode (3 mm-diameter circular base with a geometric surface area of 0.071 cm^2); A platinum wire electrode is the opposite electrode. Prior to use, it was polished with alumina (Al_2O_3) suspension to reduce surface roughness. The cyclic voltammetry parameters with a scan rate of 100 mV/s. The potential was calibrated against ferrocene/ferrocenium couple.

The Gaussian 16W running on the Linux system was used for optimization (B3LYP/6-31G (d)). Structures were optimized in the gas phase without any symmetry assumptions. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary frequency). Visuali-zation of the results was performed by the use of GaussView 6.0 software, VMD software[1], and Multiwfn software[2].

2. The Experiment Method

2.1 Synthesis of **1**

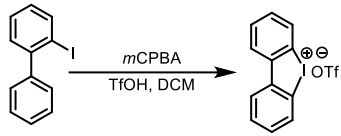


1

5,6-dibromo-1,2-dihydroacenaphthylene 3.12 g (10 mmol) was placed in a two-necked Schlenk flask equipped with two dropping funnels and dissolved in dry Et_2O (250 mL). The solution was cooled to 0°C and *n*-BuLi (1.6 M in n-hexane; 25 mL, 40 mmol, 4.0 equiv.) was added dropwise with stirring. After warming to room temperature, the solution was stirred for 20 mins and afterwards cooled to –78 °C. $B(OMe)_3$ (4.46 mL, 40 mmol, 4.0 equiv) was added dropwise. The solution was allowed to reach room temperature in the course of 12 h. HCl (2 M in H_2O; 25 mL) was added at room temperature and the mixture stirred for another 2 h. The two phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (4x15 mL). The organic phases were combined and compound 1 was extracted into aqueous. KOH (2M; 4x15 mL). The combined aqueous phases were washed with CH_2Cl_2. HCl (33 M in H_2O) was added to the aqueous phase until it was acidic, whereupon a colorless precipitate formed. The solid was collected on a frit, washed several times with H_2O, and dissolved in ethyl acetate. The

solution was dried over Na_2SO_4, filtered, and the filtrate evaporated to dryness under reduced pressure to obtain 1 as an off-white solid (1.20 g ,10 mmol, 54%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.04 (s, 2H), 8.10 (d, J = 6.9 Hz, 2H), 7.40 (d, J = 6.8 Hz, 2H), 3.40 (s, 4H). ^{13}C NMR (151 MHz, DMSO-D_6) δ 150.04, 140.22, 137.04, 135.62, 119.34, 30.36. HRMS (ESI): Exact mass calculated for $C_{12}H_{10}B_2O_3$ ([M+H]+): 225.0889, mass found: 224.0888. (Note: The color of **1** can vary between almost colorless and pale brown green, which is irrelevant for the success of the further conversion to compound **1**).

2.2 Synthesis of **2a**

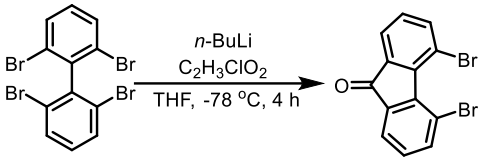


2a

To a solution of 2-iodo-biphenyl (280 mg, 0.176ml, 1 mmol, 1.0 equiv) in anhydrous DCM (11 mL) was added m-chloroperbenzoic acid (mCPBA, 276 mg, 1.6 mmol, 1.6 equiv) followed by the dropwise addition of TfOH (0.26 mL, 0.33 mmol, 3.3 equiv) with constant stirring in an ice bath. After additional stirring for 1.5 h at RT, the crude mixture was concentrated in vacuo at RT. The resulting residue was diluted with ether (~10 mL) and stirred for additional 30 min at RT. The solid precipitate was filtered and washed with ether several times and recrystallized from diethyl ether and methanol to afford the desired product 2a. White solid (370 mg, 90%). ^{1}H

NMR (600 MHz, chloroform-*d*) δ 8.40 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 2H), 7.68 – 7.63 (t, 2H). The ^{1}H NMR data are in full agreement with published data.[3]

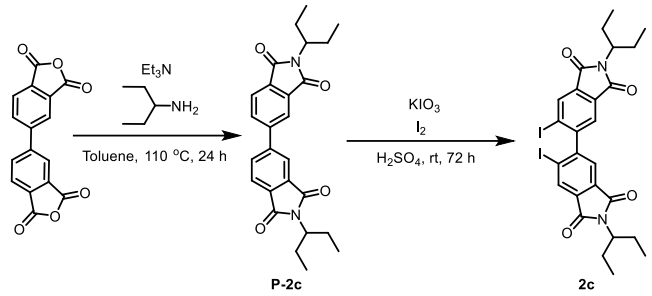
2.2 Synthesis of **2b**



2b

To a Schlenk tube equipped with a magnetic stir bar under an argon atmosphere, *n*-BuLi (2.5 M in hexane, 1.6 mL, 4.00 mmol, 2.00 equiv.) was added dropwise within 30 min under an argon atmosphere to a cooled (–78 °C) solution of **1** (940 mg, 2.00 mmol, 1.00 equiv.) in dry THF (24.0 mL) and the mixture was stirred for 40 minutes. Methyl chloroformate (465 μL, 6.00 mmol, 3.00 equiv.) was added in one portion at –78 °C and stirring was continued for 2 h. The mixture was allowed to warm to room temperature. Water (50.0 mL) was added, and stirring was continued for 10 minutes. The mixture was extracted with DCM (3 × 50.0 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, PE/CH_2Cl_2 = 3/1) to obtain **2** as a yellow solid (466 mg, 1.38 mmol, 72%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75–7.69 (m, 4H), 7.24–7.20 (m, 2H) The ^{1}H NMR data are in full agreement with published data.[4]

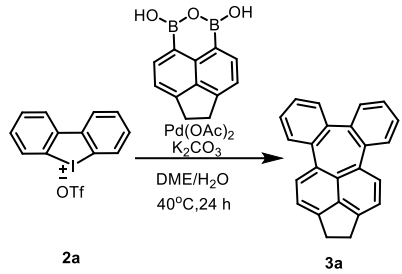
2.2 Synthesis of **2c**



To a dry Schlenk tube equipped with a magnetic stir bar under an argon atmosphere, (5.88 g, 20.00 mmol, 1.00 equiv.) and 120.0 mL toluene were added. After that, triethylamine (2.6 mL, 16.40 mmol, 0.82 equiv.) was then injected into the reaction mixture, followed by the addition of 3-aminopentane (4.0 mL, 20.00 mmol, 2.00 equiv.) under argon atmosphere. After stirring at 110 ℃ in the oil bath for 18 hours in the oil bath, the solvent including volatile reagents were removed under reduced pressure, and the residure was purified through silica gel column chromatography (PE/DCM = 2/1) to yield **P-2c** as obtained as a white solid (20 mmol, 6.31g, 73%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.07 (s, 1H), 7.95 (d, *J* = 1.3 Hz, 2H), 4.07 (tt, *J* = 10.2, 5.3 Hz, 2H), 2.13-2.03 (m, 3H), 1.87 – 1.77 (m, 3H), 0.89 (t, *J* = 7.4 Hz, 10H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 168.41, 168.39, 145.26, 135.42, 131.15, 125.77, 122.02, 54.42, 24.76, 20.01. Exact mass calculated for $C_{26}H_{28}N_2O_4$ ([M+H]+): 433.2122, mass found: 433.2143.

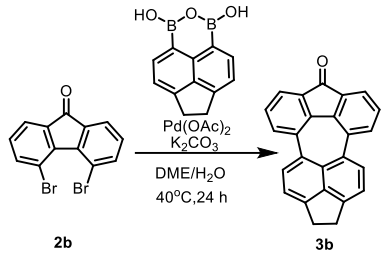
P-2c (2.16 g, 5 mmol) was added to concentrated H_2SO_4 (98 wt%, 30 mL) in a three-necked round-bottom flask under vigorously stirring. When the solid dissolved completely, KIO_3 (4.28 g, 20 mmol) and I_2 (2.54 g, 10 mmol) were added to the mixture, with vigorous stirring for 72 h. After the reaction finished the reaction mixture was poured into ice-water containing the previously dissolved Na_2SO_3 (fume hood). Filtration and the collected precipitate was filtrated and washed thoroughly by water then purified by recrystallization from ethanol to give **2c** as obtained as a yellow solid. (5 mmol, 2.12g, 62%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 9.27 (s, 2H), 8.66 (s, 2H), 4.13 (tt, *J* = 10.2, 5.4 Hz, 2H), 2.15-2.05 (m, 4H), 1.90-1.80 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 167.02, 166.10, 144.10, 134.80, 133.35, 133.16, 126.74, 120.63, 58.94, 25.29, 11.25. Exact mass calculated for $C_{26}H_{26}I_2N_2O_4$ ([M+H]+): 684.0054, mass found: 684.0055.

2.3 General Synthesis procedure of **3**



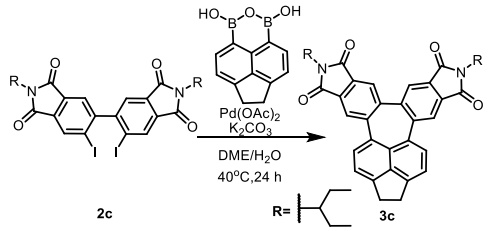
Under argon atmosphere, cyclic diphenyliodonium salt compound 2 (0.20 mmol), compound **1**(58.2mg, 0.26 mmol, 1.3 eq), Pd $(OAc)_2$ (4.49 mg, 0.02 mmol, 0.1 eq.), DME (4mL) and H_2O (0.8mL) were added to a 25 mL Schlenk tube. The reaction mixture was refluxed at 40 °C in the oil bath until complete consumption of starting material 1 was observed by thin-layer chromatography (TLC).

The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, petroleum ether) to obtain **3a** as yellow solid (yield: 37mg, 62%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.37 – 7.34 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.12 (m, 2H), 3.40 (s, 4H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 145.92, 142.09, 139.73, 139.33, 136.98, 134.39, 133.03, 131.89, 128.79, 127.59, 127.30, 120.16, 30.32. Exact mass calculated for $C_{24}H_{16}$ ([M+H]+): 305.1324, mass found: 305.1325.



2b 3b

The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2=5:1) to obtain **3b** as rufous solid (yield: 26mg, 39%) ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 6.2 Hz, 2H), 7.26 (dd, *J* = 13.8, 7.8 Hz, 44H), 3.36 (s, 4H). ^{13}C NMR (151 MHz, chloroform-*d*)) δ 195.07, 147.43, 143.34, 141.71, 137.70, 134.79, 134.50, 134.29, 130.83, 130.52, 128.50, 123.25, 120.12, 30.69. Exact mass calculated for $C_{25}H_{14}O$ ([M+H]+): 331.1113, mass found: 331.1117.

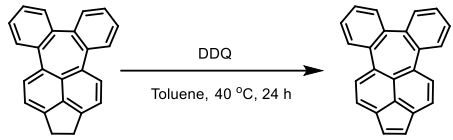


2c 3c

The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography

(silica gel, petroleum ether/CH_2Cl_2 =2:1) to obtain **3c** as yellow solid (60 mg, 52%) ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.97 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.56 (s, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 4.05 (tt, *J* = 10.1, 4.2 Hz, 2H), 3.44 (d, *J* = 23.3 Hz, 4H), 2.10-2.00 (m, 4H), 1.83 – 1.76 (m, 9H), 0.87 (t, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 168.96, 168.25, 148.24, 147.85, 143.94, 138.76, 136.88, 132.14, 131.57, 130.20, 129.93, 127.80, 127.00, 121.89, 56.41, 30.45, 24.80, 10.79. Exact mass calculated for $C_{38}H_{34}N_2O_4$([M+H]+): 583.2592, mass found:583.2591.

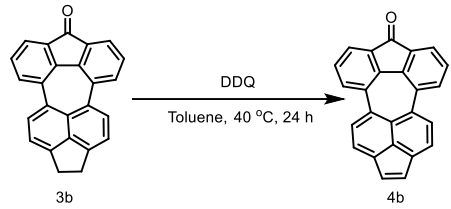
2.4 General Synthesis procedure of **4**



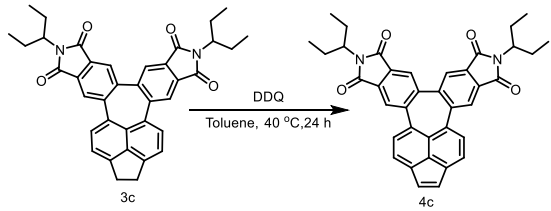
To a Schlenk flask charged with 3 (0.1 mmol), DDQ (45.4 mg, 0.2 mmol), was added toluene (2 mL). The mixture was stirred at 40 °C in the oil bath for 24h. After cooling down to room temperature, the mixture was filtered with diatomite.

The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, petroleum ether) to obtain **4a** as yellow solid (12 mg, 40%) ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.85 – 7.76 (m, 4H), 7.56 – 7.51 (m, 2H), 7.48 – 7.41 (m, 4H), 7.14 (s, 2H). ^{13}C NMR (151

MHz, chloroform-*d*)) δ 139.81, 138.18, 137.30, 137.13, 133.63, 132.54, 131.93, 128.77, 128.17, 127.62, 126.45, 124.63. Exact mass calculated for $C_{24}H_{14}$ ([M+H]+):303.1168, mass found: 303.1168



The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2=5:1) to obtain **4b** as yellow solid.(21.3 mg, 65%) ^{1}H NMR (600 MHz, chloroform-*d*) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.33 (s, 2H).^{13}C NMR (151 MHz, chloroform-*d*). ^{13}C NMR (151 MHz, Chloroform -*d*) δ 193.40, 141.77, 139.17, 135.18, 134.78, 134.61, 134.25, 129.86, 129.36, 128.83, 128.78, 127.16, 124.64, 123.71. Exact mass calculated for $C_{25}H_{12}O$ ([M+H]+):329.0963, mass found: 329.0961



The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2=2:1) to obtain **4c** as yellow solid.(34.8 mg, 60%) ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.22 (s, 2H), 8.14 (d, *J* = 7.2 Hz, 2H), 7.96 (s, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.20 (s, 2H), 4.08 (tt, *J* = 10.1, 5.3 Hz, 2H), 2.13 – 2.05 (m, 4H), 1.86 – 1.76 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 12H), ^{13}C NMR (151 MHz, chloroform-*d*) δ 168.98, 168.27, 148.68, 147.86, 143.95, 139.34, 136.69, 132.13, 131.57, 130.20, 129.94, 127.82, 127.02, 120.58, 52.68, 24.69, 10.67. Exact mass calculated for $C_{38}H_{32}N_2O_4$ ([M+H]+):581.2434, mass found: 581.2435

3. Cyclic voltammogram of **4a**, **4b** and **4c**

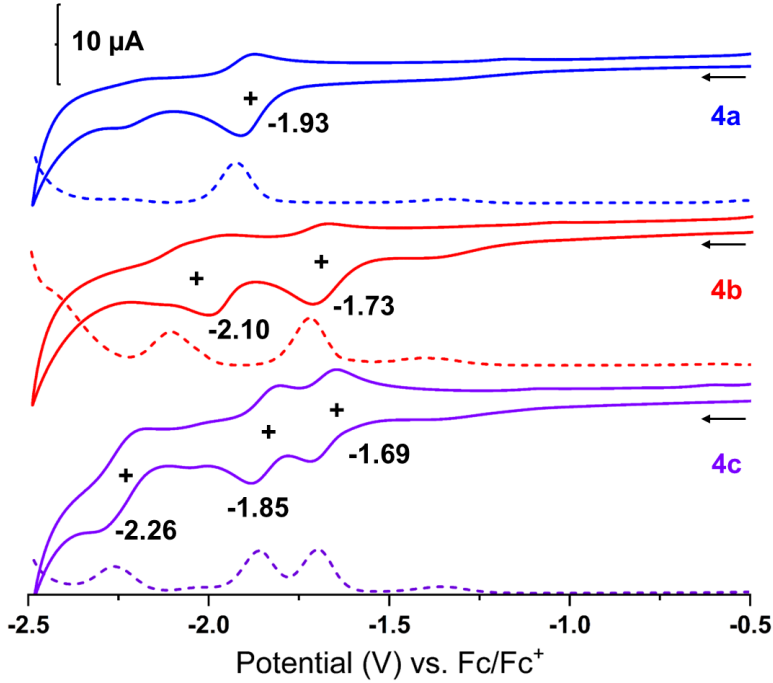


Figure S1. Cyclic voltammogram of **4a, 4b** and **4c** in DCM (c = 1 × 10^{-4} mol/L) solution containing 0.1 M [*n*-Bu_4N] [$BCH_3(C_6H_3(3,5\text{-}CF_3)_2)_4$] at room temperature at a scan rate of 0.1 V/s. IUPAC convention: Scan starts at 0 V vs. EAg/AgCl（V）and proceeds in the negative potential direction.

4. UV-Vis absorption spectra of **4a** and acenaphthylene

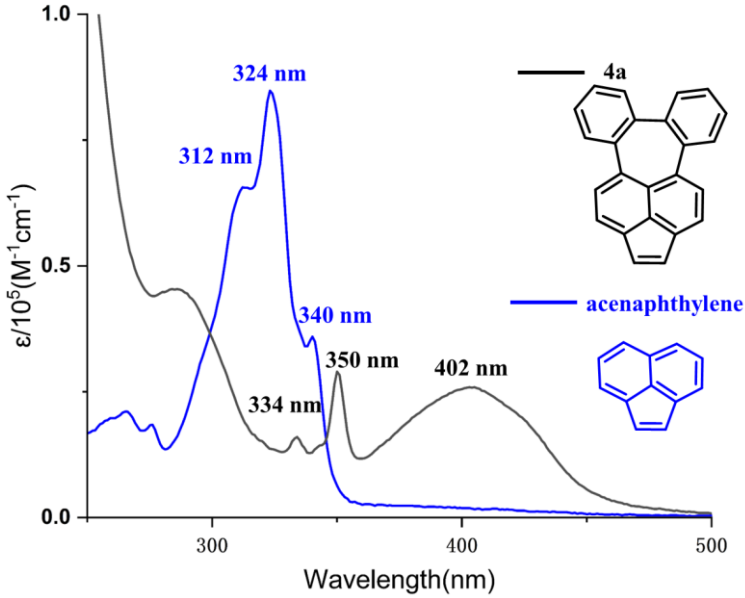


Figure S2. UV-Vis absorption spectra of **4a** and acenaphthylene in DCM ($c = 5 \times 10^{-5}$ mol/L).

5. Computational Study

5.1 The TD-DFT Calculation

Table S1. Major electronic transitions for **4a** by TD-DFT method using B3LYP/6-31G(d) after the structure first optimized at the same level. (f: Oscillator Strength)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Major Contributions
S1	2.6103 eV	474.98	0.03530	H→ L 98.1%
S2	2.9546 eV	419.63	0.24830	H-1→ L 89.7% H → L+1 9.1%
S3	3.6776eV	337.13	0.00700	H-2 → L 98.1%
S6	4.0789 eV	303.96	0.13000	H-3 → L 74.5% H-1→L+1 8.2% H-1→ L+3 5.8%
S9	4.6023 eV	269.40	0.17340	H → L+2 93.2%
S10	4.9367 eV	251.15	0.19380	H-2→L+149.2% H-1 → L+2 27.5 H-6 → L 8.0% H →L+4 7.7% H-4 → L 5.2%

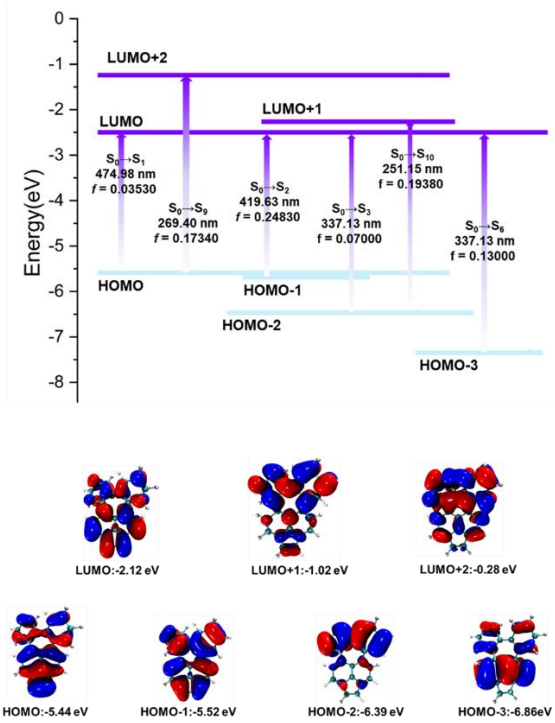


Figure S3: Energy diagrams and frontier molecular and orbitals of **4a** calculated at the B3LYP/6-31G(d) level of theory.

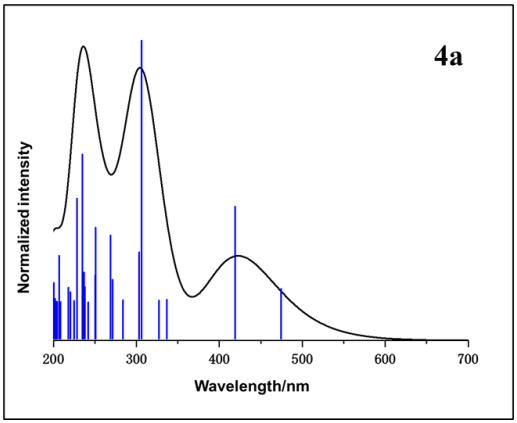


Figure S4. Calculated UV-Vis spectra for **4a** in dichloromethane by TDDFT (B3LYP/6-31G(d))

Table S2. Major electronic transitions for **4b** by TD-DFT method using B3LYP/6-31G(d) after the structure first optimized at the same level. (f: Oscillator Strength)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Major Contributions
S1	2.4539	505.25	0.0202	H→L (95.8%)
S2	2.6717	464.06	0.0016	H-1→L (79.1%) H→L+1 (18.9%)
S3	2.6907	460.79	0.0240	H-1→L+1 (97.5%)
S5	2.9821	415.76	0.3117	H→L+1 (68.3%) H-1→L (19.8%) H-1→L+2 (9.6%)
S7	3.6222	342.29	0.00030	H-2→L+1 (96.1%)

S8	3.6792	336.99	0.00370	H→L+2 (95.6%)
S11	4.1699	297.33	1.01490	H-1→L+2 (72.6%) H-4→L (15.5%) H→L+1 (9.9%)
S13	4.5122	274.78	0.03406	H-5→L+1 (60.2%) H-2→L+2 (18.9%) H→L+3 (18.9%)

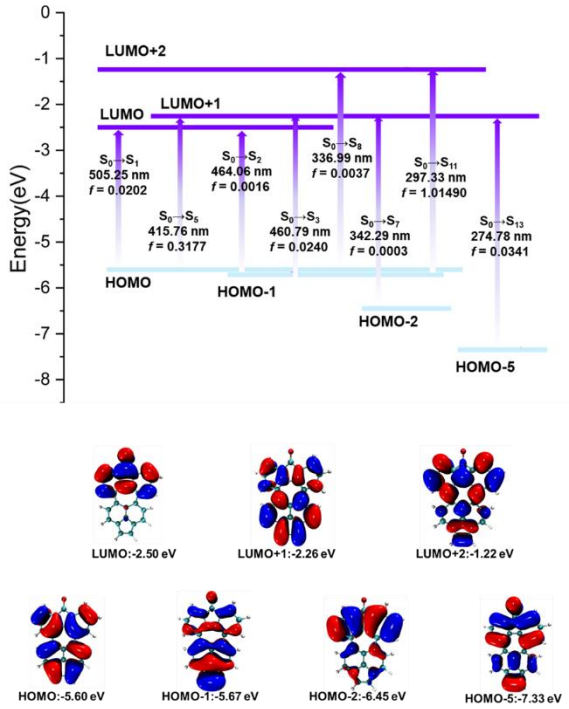


Figure S5: Energy diagrams and frontier molecular and orbitals of **4b** calculated at the B3LYP/6-31G(d) level of theory.

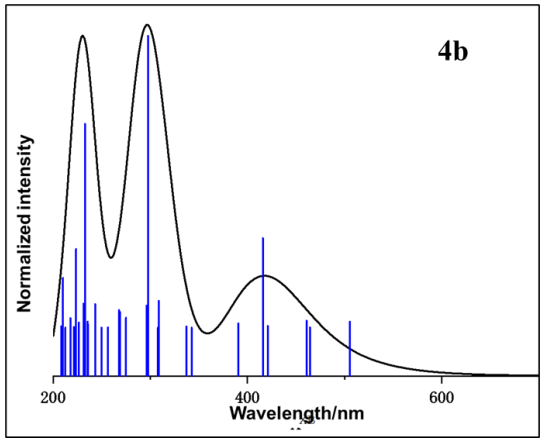


Figure S6. Calculated UV-Vis spectra for **4b** in dichloromethane by TDDFT (B3LYP/6-31G(d))

Table S3. Major electronic transitions for **4c** by TD-DFT method using B3LYP/6-31G(d) after the structure first optimized at the same level. (f: Oscillator Strength)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Major Contributions
S1	2.4233	511.63	0.03130	H→L+1 (81.6%) H-1→ L (15.9%)
S4	2.9666	417.93	0.68770	H-1→L+1 (67.8%) H →L (26.0%)
S6	3.4580	358.54	0.17750	H-1→L+2 (90.6%)

S9	3.6263	341.90	0.08630	H-2 → L (49.8%) H-6 → L 24.0% H-1→ L+3 8.8% H-5 → L+1 5.9%
S12	3.9128	316.87	0.29900	H-3→L+1 84.3%
S15	4.0101	309.18	0.17990	H → L+3 80.2% H-4→ L 9.5% H-2→ L+1 5.6%
S18	4.2208	293.75	0.36620	H-7→ L 46.3% H-1 → L+3 15.0% H-5→ L+1 9.8% H-4 → L+1 7.6% H-2→ L 5.4%
S19	4.2562	291.30	0.24290	H-4 → L+1 43.4% H-5 → L+1 19.5% H-1→ L+3 10.3% H-10→ L 7.9% H-2 → L 6.0%

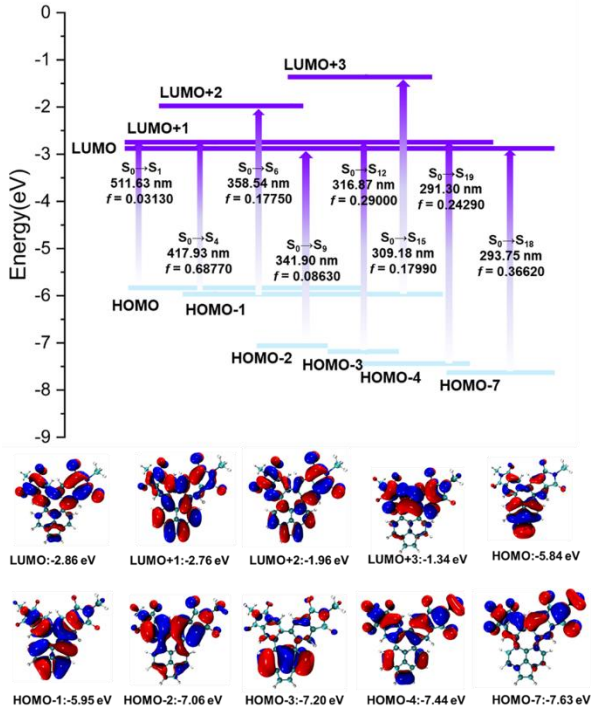


Figure S7: Energy diagrams and frontier molecular and orbitals of **4c** calculated at the B3LYP/6-31G(d) level of theory.

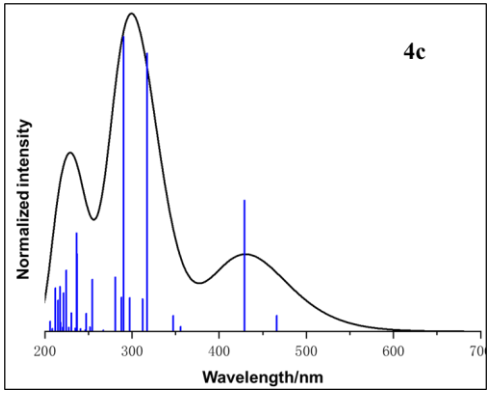
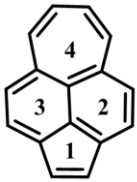


Figure S8. Calculated UV-Vis spectra for **4c** in dichloromethane by TDDFT (B3LYP/6-31G(d))

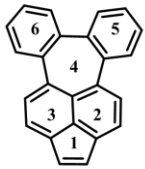
5.2 NICS

Table S4. The aromaticity values of APD by density functional theory (DFT) calculations based on B3LYP/6-31G(d).



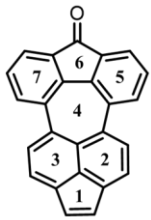
Ring	NICS(0)	NICS(+1)	NICS(-1)	$NICS(1)_{ZZ}$
1	-16.08	-18.03	-18.03	-47.08
2	-10.69	-12.84	-12.84	-32.52
3	-10.69	-12.84	-12.84	-32.52
4	-3.62	-6.53	-6.53	-15.10

Table S5. The aromaticity values of **4a** by density functional theory (DFT) calculations based on B3LYP/6-31G(d).



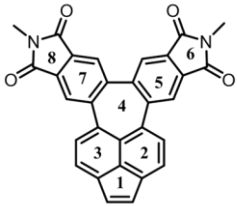
Ring	NICS(0)	NICS(+1)	NICS(-1)	$NICS(1)_{ZZ}$
1	-0.5286	-40481	-4.0480	5.5995
2	-11.0676	-11.0865	-10.6356	-19.8575
3	-11.0677	-10.6356	-11.8467	-17.2013
4	1.4917	-1.8910	-1.8910	9.6300
5	-13.0057	-13.4981	-12.1826	-24.5894
6	-13.0057	-12.1826	-13.4981	-22.0502

Table S6. The aromaticity values of **4b** by density functional theory (DFT) calculations based on B3LYP/6-31G(d).



Ring	NICS(0)	NICS(+1)	NICS(-1)	$NICS(1)_{ZZ}$
1	-2.6911	-5.6413	-5.6416	-0.9819
2	-11.6612	-12.7565	-11.6855	-20.2461
3	-11.6611	-11.6854	-12.7563	-20.1375
4	-0.2387	-2.2242	-2.2242	7.2668
5	-10.1233	-11.0439	-10.3436	-16.5834
6	8.3063	2.0900	2.0900	20.4540
7	-10.1232	-10.3437	-11.0441	-15.5377

Table S7. The aromaticity values of **4c** by density functional theory (DFT) calculations based on B3LYP/6-31G(d).



Ring	NICS(0)	NICS(+1)	NICS(-1)	$NICS(1)_{ZZ}$
1	2.8360	-1.0190	-1.0172	2.4765
2	-6.3857	-7.7912	-8.7950	-19.2680
3	-6.3833	-8.7903	-7.7926	-21.5918
4	4.9516	0.2267	0.2272	8.6616
5	-7.1719	-7.9182	-9.3321	-19.5040
6	3.8016	-0.0694	0.3478	6.4709
7	-7.1723	-9.3228	-7.9184	-21.789
8	3.8015	-0.0693	0.3577	6.4715

5.3AICD

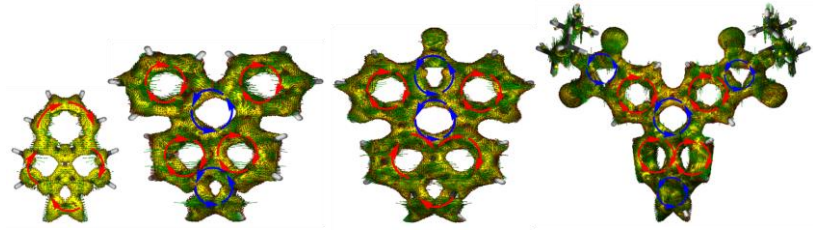


Figure S9. Calculated ACID plots of APD, **4a**, **4b** and **4c** at the GIAO-B3LYP/6-31G(d,p) level.

5.4 The Electrostatic Potential (ESP)

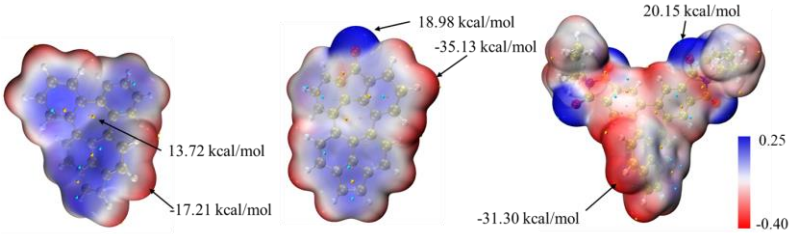


Figure S10. Calculated ESP plots of **4a**, **4b**, and **4c** at the B3LYP/6-31G(d) level.

5.5 Cartesian Coordinates of Optimized Structures

Table S8: Cartesian Coordinates of Optimized Structures calculated by B3LYP/6-31G(d).

4a

C	0.3447920	2.2432910	2.5452550	C	-0.3319240	1.4837070	-0.9101490
C	0.2545510	2.2890070	1.2073790	C	-0.8664830	2.7078650	-1.1636440
C	0.0000000	1.2343070	0.3839220	C	-1.3038150	3.1398150	-2.3519260
C	0.0000000	0.0000000	0.9449400	C	-1.2620570	2.2888050	-3.3735770
C	0.0000000	0.0000000	2.2922910	C	-0.7654240	1.0687460	-3.1436740
C	0.1523200	1.0512530	3.1006070	H	0.5299210	3.1388310	3.1596230
C	0.0000000	-1.2343070	0.3839220	H	0.4225440	3.3124210	0.8328820
C	-0.2545510	-2.2890070	1.2073790	H	-0.4225440	-3.3124210	0.8328820
C	-0.3447920	-2.2432910	2.5452550	H	-0.5299210	-3.1388310	3.1596230
C	-0.1523200	-1.0512530	3.1006070	H	0.2062360	1.3054980	5.2662920
C	0.1038030	0.6630460	4.3826580	H	-0.2062360	-1.3054980	5.2662920
C	-0.1038030	-0.6630460	4.3826580	H	1.0792890	-3.4633370	-0.3905960
C	0.8664830	-2.7078650	-1.1636440	H	0.8796150	-0.4298850	-4.0355090
C	0.3319240	-1.4837070	-0.9101490	H	1.6739320	-2.5746670	-4.3562020
C	0.2592020	-0.6283050	-1.9616580	H	1.7537850	-4.1391420	-2.4793400
C	0.7654240	-1.0687460	-3.1436740	H	-1.0792890	3.4633370	-0.3905960
C	1.2620570	-2.2888050	-3.3735770	H	-1.7537850	4.1391420	-2.4793400
C	1.3038150	-3.1398150	-2.3519260	H	-1.6739320	2.5746670	-4.3562020
C	0.3447920	2.2432910	2.5452550	H	-0.8796150	0.4298850	-4.0355090

4b

C	-0.5229400	-1.5714120	-0.0216720	C	3.5288910	-1.0437590	0.1083450
C	-0.9762800	-2.8495830	-0.1346840	C	0.7987850	1.2522040	-0.0565310
C	-2.2627120	-3.2335780	-0.1761250	C	1.6589140	2.2977510	-0.2179990
C	-3.2315030	-2.3182820	-0.1165390	C	2.9971960	2.2502820	-0.2472140
C	-2.8155220	-1.0519440	-0.0486800	C	3.5288720	1.0438880	-0.1086630
C	-1.5232130	-0.6706880	-0.0219760	C	4.8139920	-0.6659770	0.0724580
C	-1.5231630	0.6706960	0.0222550	C	4.8139470	0.6660060	-0.0734560
C	-2.8155890	1.0518490	0.0484270	H	-0.3341850	-3.7351170	-0.2347180
C	-3.2316700	2.3182530	0.1162060	H	-2.5361820	-4.2994940	-0.2677580
C	-2.2629060	3.2335710	0.1763740	H	-4.2939890	-2.6058050	-0.1454840
C	-0.9764460	2.8496100	0.1353330	H	-4.2941720	2.6057360	0.1447090
C	-0.5230440	1.5714520	0.0222100	H	-2.5364180	4.2994030	0.2680510
C	-3.6603530	-0.0000960	-0.0002900	H	-0.3343930	3.7351560	0.2357240
O	-4.8709120	-0.0001440	-0.0006190	H	3.6302520	-3.1435180	0.3755630
C	2.9972620	-2.2502860	0.2473490	H	1.3574970	-3.3417270	0.3712040
C	1.6589280	-2.2976790	0.2185450	H	1.3573910	3.3418260	-0.3705200
C	0.7989100	-1.2521830	0.0570100	H	3.6302240	3.1435390	-0.3756910
C	1.3491230	0.0000790	0.0002110	H	5.6954650	-1.3153160	0.1450230
C	2.7022280	0.0000510	-0.0000060	H	5.6955520	1.3151210	-0.1464870

4c

C	-1.8684940	3.9354560	-1.2884360	C	4.6852430	-1.2765150	0.0579530
C	-1.9516450	2.5978880	-1.2232080	C	-4.6856920	-1.2752000	-0.0587450
C	-1.1131550	1.7769030	-0.5321160	N	-4.5898940	-2.5982020	0.3309270

C	**0.0003560**	**2.3371060**	**0.0000990**	**C**	**-3.3013330**	**-3.0616210**	**0.5217940**
C	**0.0005850**	**3.6842280**	**0.0001200**	**O**	**2.9744900**	**-4.1767590**	**-0.8525570**
C	**-0.8796250**	**4.4915120**	**-0.5957740**	**O**	**5.7006250**	**-0.6653670**	**0.2858830**
C	**1.1137640**	**1.7766000**	**0.5321620**	**O**	**-2.9765360**	**-4.1757710**	**0.8530490**
C	**1.9525370**	**2.5973400**	**1.2231880**	**O**	**-5.7005730**	**-0.6635450**	**-0.2876160**
C	**1.8698080**	**3.9348850**	**1.2885630**	**C**	**5.7593240**	**-3.4503320**	**-0.4912230**
C	**0.8809260**	**4.4912230**	**0.5961200**	**C**	**-5.7595410**	**-3.4497150**	**0.4913200**
C	**-0.5505160**	**5.7733480**	**-0.3828220**	**H**	**-2.5942660**	**4.5492130**	**-1.8455220**
C	**0.5521310**	**5.7731580**	**0.3831270**	**H**	**-2.8021040**	**2.2192840**	**-1.8145780**
C	**2.8312330**	**0.2619920**	**0.3417320**	**H**	**2.8030760**	**2.2184330**	**1.8142850**
C	**1.4878530**	**0.4874290**	**0.3191360**	**H**	**2.5959850**	**4.5483990**	**1.8454410**
C	**0.6796320**	**-0.5656620**	**0.0164250**	**H**	**-1.0834340**	**6.6572690**	**-0.7553970**
C	**1.2712990**	**-1.7534890**	**-0.2900140**	**H**	**1.0852690**	**6.6569360**	**0.7555830**
C	**2.5901150**	**-1.9441350**	**-0.2425050**	**H**	**3.6009650**	**1.0351650**	**0.4828710**
C	**3.3769300**	**-0.9281220**	**0.0864020**	**H**	**0.7335430**	**-2.6409780**	**-0.6602840**
C	**-0.6799200**	**-0.5653900**	**-0.0160730**	**H**	**-3.6005360**	**1.0363550**	**-0.4832550**
C	**-1.4877840**	**0.4878860**	**-0.3191000**	**H**	**-0.7346270**	**-2.6404350**	**0.6615090**
C	**-2.8312090**	**0.2628250**	**-0.3419120**	**H**	**5.5698790**	**-4.2798770**	**-1.2082190**
C	**-3.3772740**	**-0.9271770**	**-0.0866950**	**H**	**6.6235920**	**-2.8741380**	**-0.8913640**
C	**-2.5908770**	**-1.9432440**	**0.2427890**	**H**	**6.0442100**	**-3.8875260**	**0.4925980**
C	**-1.2719480**	**-1.7529940**	**0.2906960**	**H**	**-6.6340840**	**-2.8693790**	**0.8616790**
C	**3.3001710**	**-3.0627860**	**-0.5214860**	**H**	**-6.0246500**	**-3.9130050**	**-0.4860930**
N	**4.5889730**	**-2.5996280**	**-0.3310580**	**H**	**-5.5778000**	**-4.2597340**	**1.2324880**

6. X-ray Single Crystal Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.2498031(**4a**), No.2498032(**4b**) and No.2503270 (**4c/3c**). The single crystal X-ray crystallographic data were summarized in Table S1, and Table S2.

Table S9. Crystal data and structure refinement for **4a**

Identification code CCDC 2498031	**4a**
Empirical formula	C24H14
Formula weight	302.35
Temperature/K	100.0(4)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.3890(3)
b/Å	12.4618(2)
c/Å	11.2831(3)
α/°	90
β/°	112.093(3)
γ/°	90
Volume/Å3	1483.80(7)
Z	4
ρcalcg/cm3	1.353
μ/mm-1	0.372
F(000)	632.0
Crystal size/mm3	? × ? × ?

Radiation	micro-focus metaljet (λ = 1.3405)
2Θ range for data collection/°	7.284 to 109.982
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -8 ≤ l ≤ 13
Reflections collected	9895
Independent reflections	2786 [Rint = 0.0222, Rsigma = 0.0204]
Data/restraints/parameters	2786/0/218
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0340, wR2 = 0.0830
Final R indexes [all data]	R1 = 0.0369, wR2 = 0.0853
Largest diff. peak/hole / e Å-3	0.24/-0.17

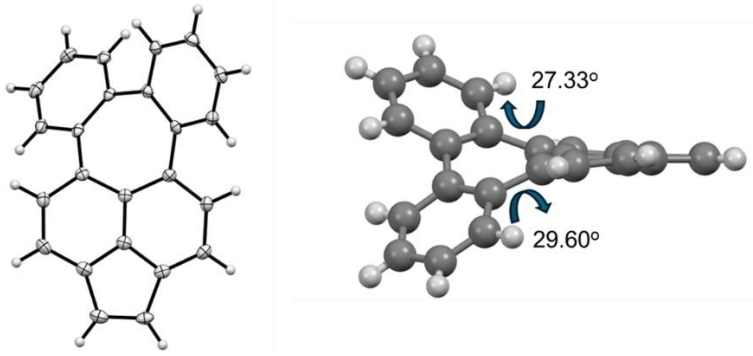


Figure 11: The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for **4a**. Solvent: $CH_3OH/CHCl_3$.

Table S10. Crystal data and structure refinement for **4b**

Identification code CCDC 2498032	**4b**
Empirical formula	$C_{25}H_{12}O$
Formula weight	328.35
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	21.1650(13)
b/Å	7.1531(4)
c/Å	21.5804(14)
α/°	90
β/°	109.878(7)
γ/°	90
Volume/Å^3	3072.5(3)
Z	8
ρ_{calc}g/cm^3	1.420
μ/mm^{-1}	0.085
F(000)	1360.0
Crystal size/mm^3	0.05 × 0.04 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.836 to 59.044
Index ranges	$-28 \le h \le 26$, $-9 \le k \le 8$, $-28 \le l \le 28$
Reflections collected	27432

Independent reflections	12950 [R_{int} = 0.0322, R_{sigma} = 0.0567]
Data/restraints/parameters	12950/1/939
Goodness-of-fit on F^2	0.998
Final R indexes [I>=2σ (I)]	R_1 = 0.0471, wR_2 = 0.0971
Final R indexes [all data]	R_1 = 0.0811, wR_2 = 0.1077
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.17
Flack parameter	0.9(9)

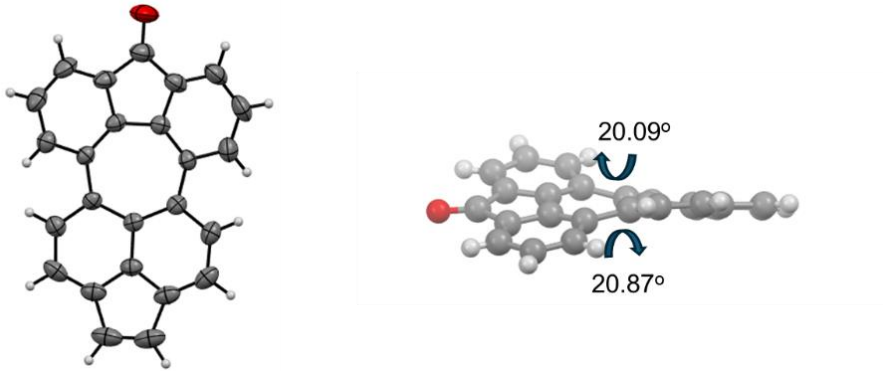


Figure 12: The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for **4b**. Solvent: $CH_3OH/CHCl_3$.

Table S11. Crystal data and structure refinement for **4c/3c**

Identification code CCDC 2503270	**4c/3c**
Empirical formula	$C_{38}H_{33.03}N_2O_4$
Formula weight	581.69
Temperature/K	150.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.5903(9)
b/Å	7.7865(4)
c/Å	27.3312(15)
α/°	90
β/°	94.747(2)
γ/°	90
Volume/Å^3	3306.5(3)
Z	4
ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.076
F(000)	1228.0
Crystal size/mm^3	0.12 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.006 to 50.746
Index ranges	$-18 \le h \le 18$, $-9 \le k \le 9$, $-32 \le l \le 32$
Reflections collected	45777

Independent reflections	6068 [R_{int} = 0.0484, R_{sigma} = 0.0323]
Data/restraints/parameters	6068/137/450
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0519, wR_2 = 0.1401
Final R indexes [all data]	R_1 = 0.0701, wR_2 = 0.1507
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.23

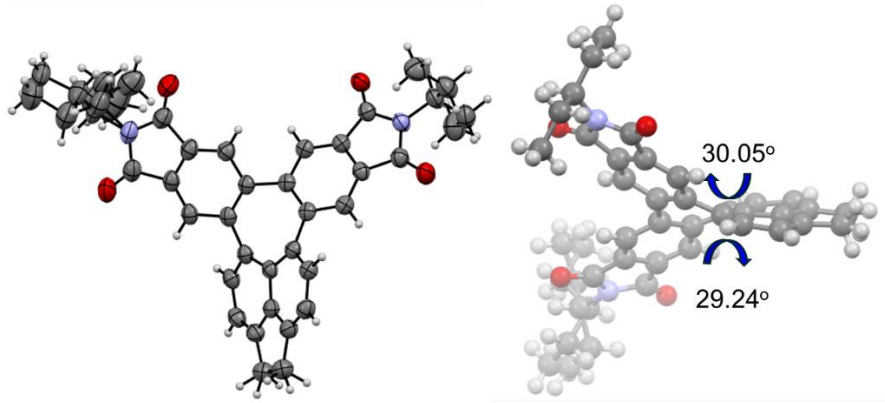


Figure 13: The thermal ellipsoid plot (left, at 50% probability) and dihedral angle (right) for **4c/3c**. Solvent: $CH_3OH/CHCl_3$.

7.Reference

(1) Lu, T.*; Chen, F.;* Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem* **2012**, *33*, 580–592.

(2) Humphrey, W.; Dalke, A.; Schulten, K., VMD: Visual Molecular Dynamics. *J. Mol. Graph* 14:33-38, 1996

(3) Lee, J. B.; Jeon, M. H.; Seo, J. K.; von Helden, G.; Rohde, J.-U.; Zhao, B. S.; Seo, J.; Hong, S. Y., Annulative π-Extension of Unactivated Benzene Derivatives through Nondirected C–H Arylation. *Org. Lett.* **2019,** *21*, 7004-7008.

(4) Herzog, S.; Hinz, A.; Breher, F.; Podlech, J., Cyclopenta-fused polyaromatic hydrocarbons: synthesis and characterisation of a stable, carbon-centred helical radical. *Org. Biomol. Chem* **2022,** *20*, 2873-2880.

8.NMR Spectra

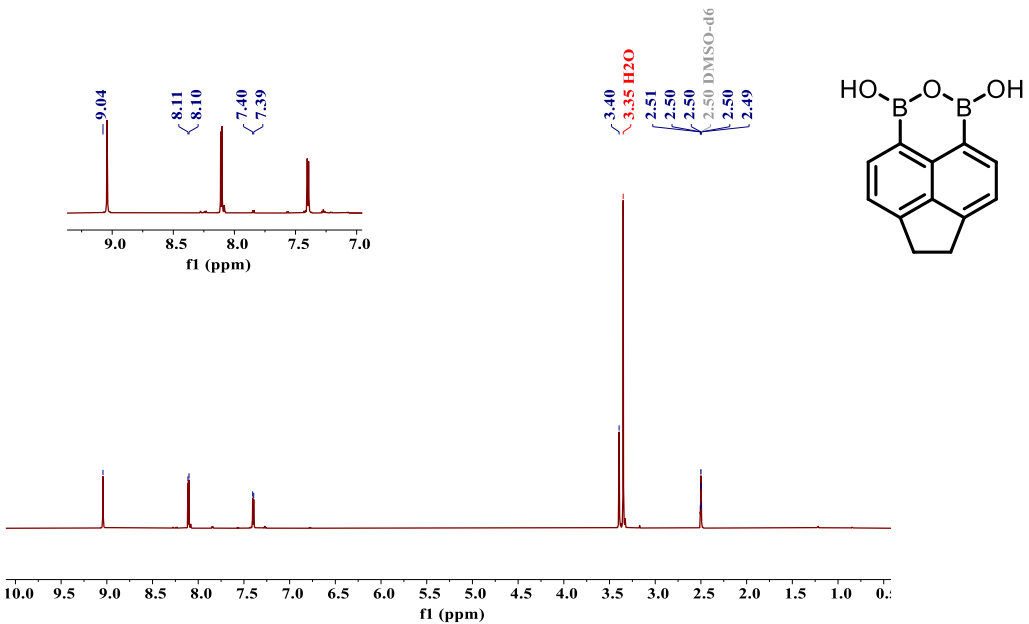


Figure S14. [1]H NMR Spectra of **1** in DMSO-d6 (600 MHz).

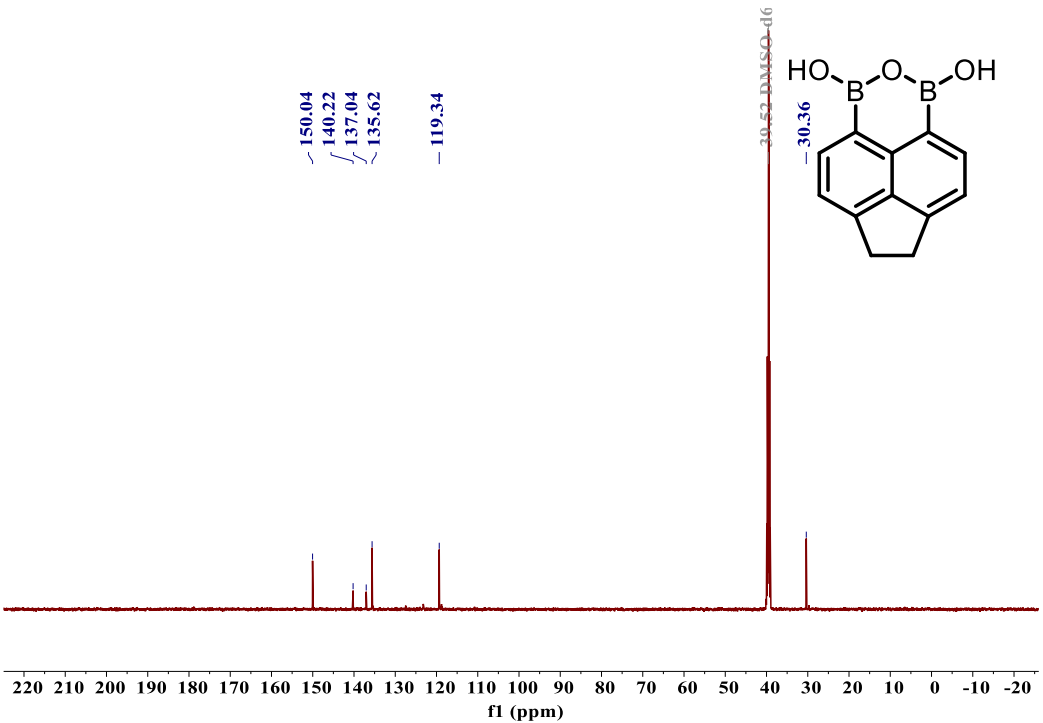


Figure S15. ^{13}C NMR Spectra of **1** in DMSO-d6 (600 MHz).

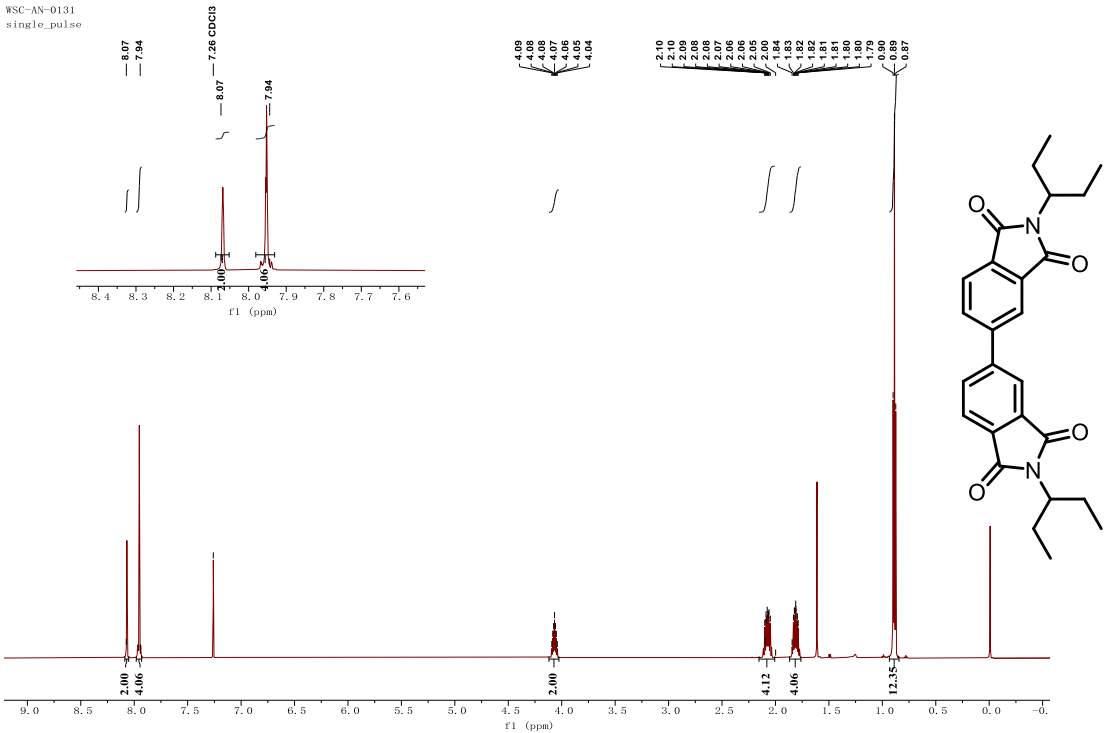


Figure S16. ^{1}H NMR Spectra of **p-2a** in $CDCl_3$ (600 MHz)

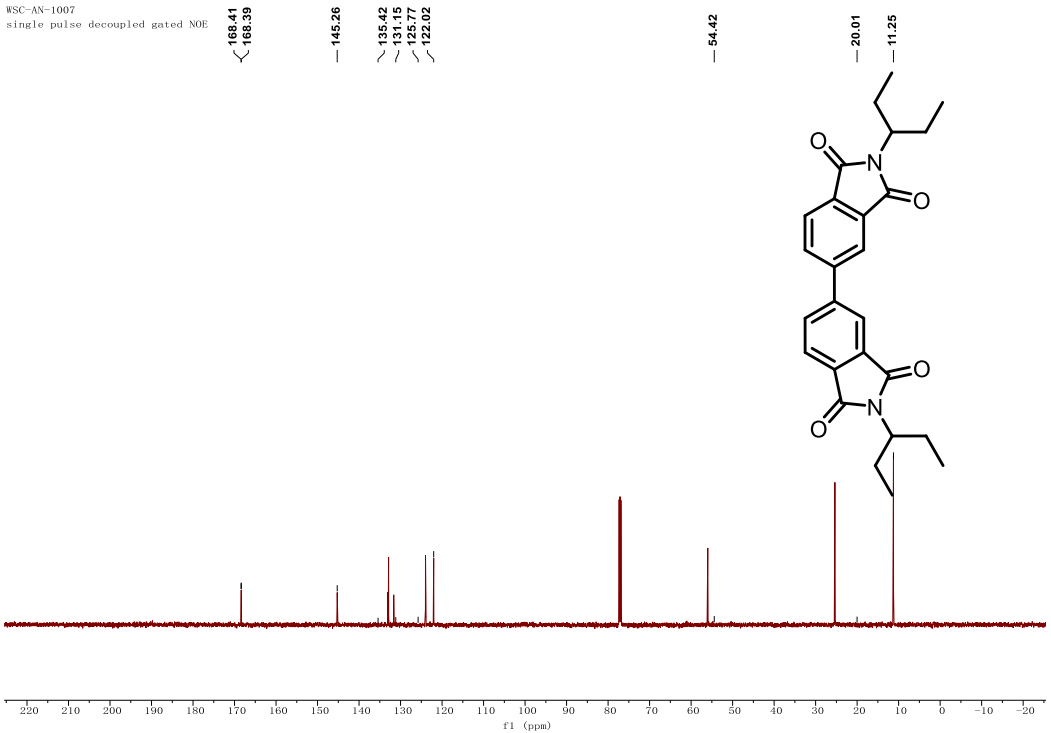


Figure S17. ^{13}C NMR Spectra of **p-2a** in $CDCl_3$ (600 MHz)

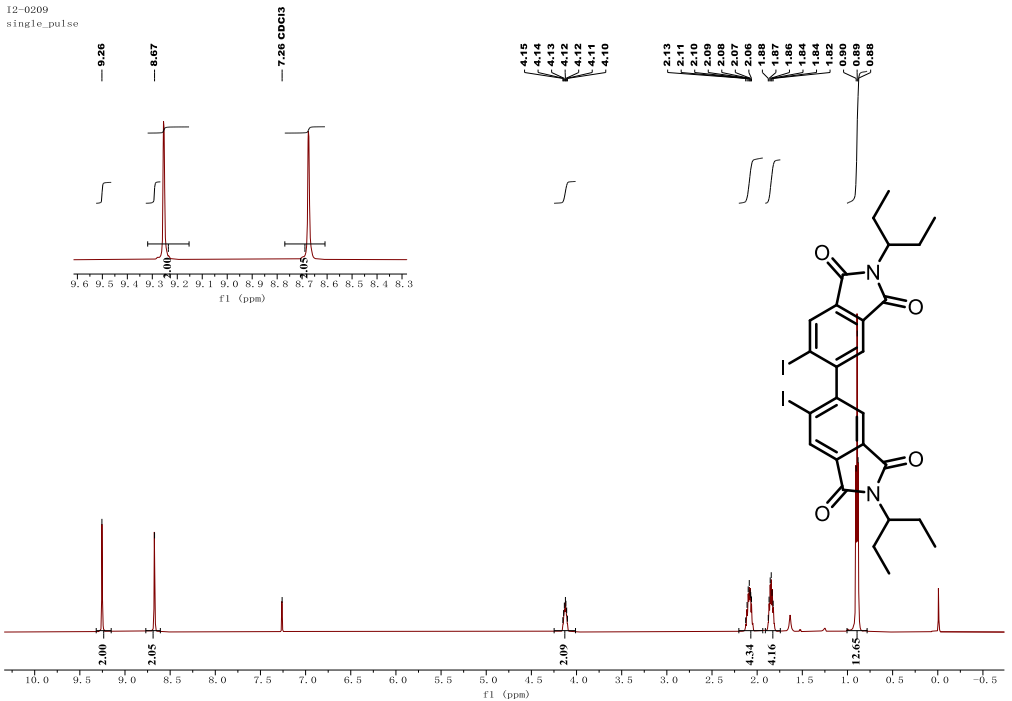


Figure S18.^{1}H NMR Spectra of **2c** in $CDCl_3$ (600 MHz)

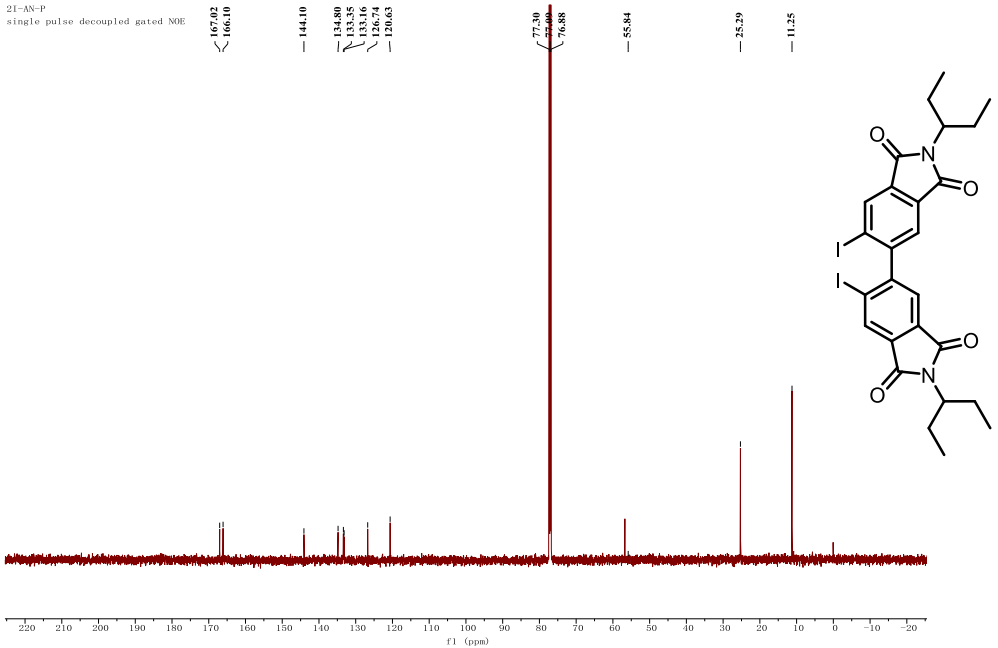


Figure S19.[13]C NMR Spectra of **2c** in $CDCl_3$ (600 MHz)

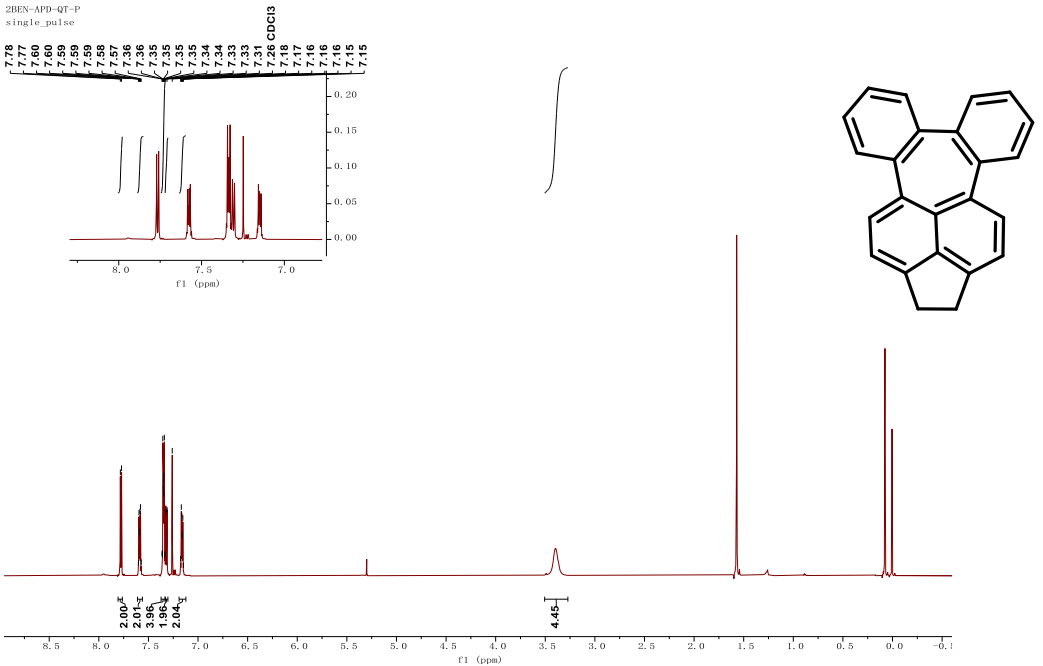


Figure S20.^{1}H NMR Spectra of **3a** in $CDCl_3$ (600 MHz)

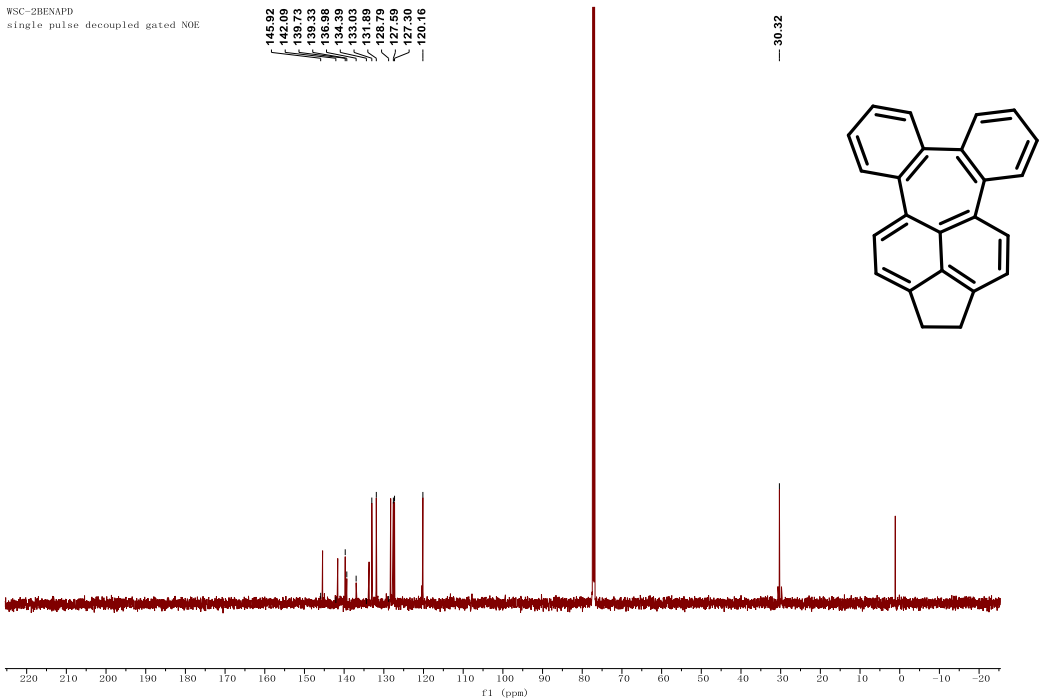


Figure S21.[13]C NMR Spectra of **3a** in $CDCl_3$ (600 MHz)

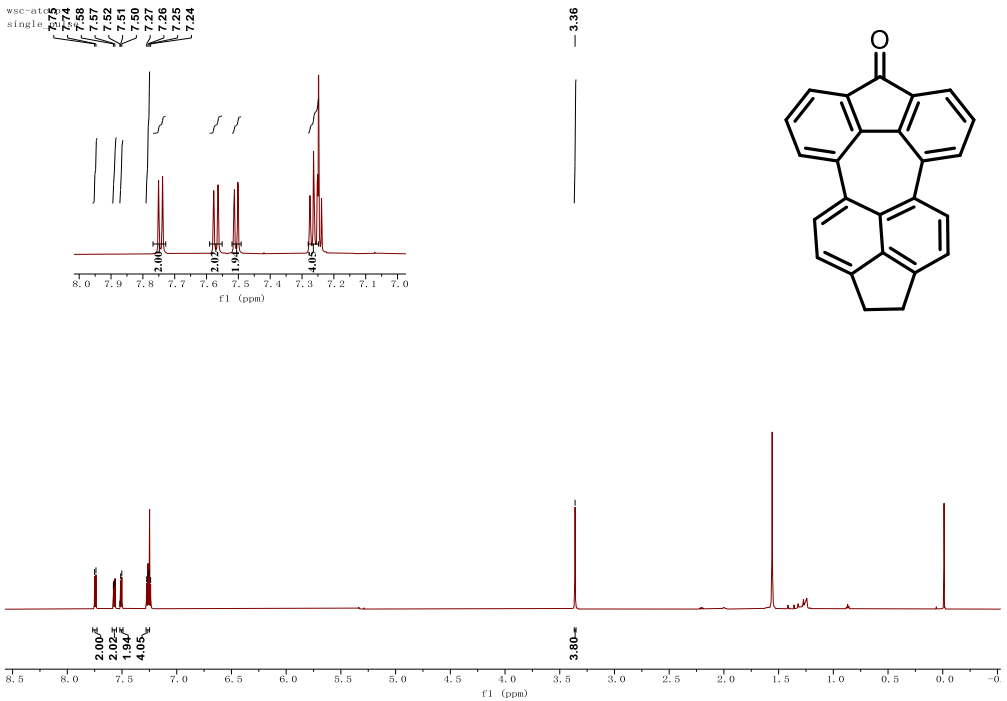


Figure S22.[1]H NMR Spectra of **3b** in $CDCl_3$ (600 MHz)

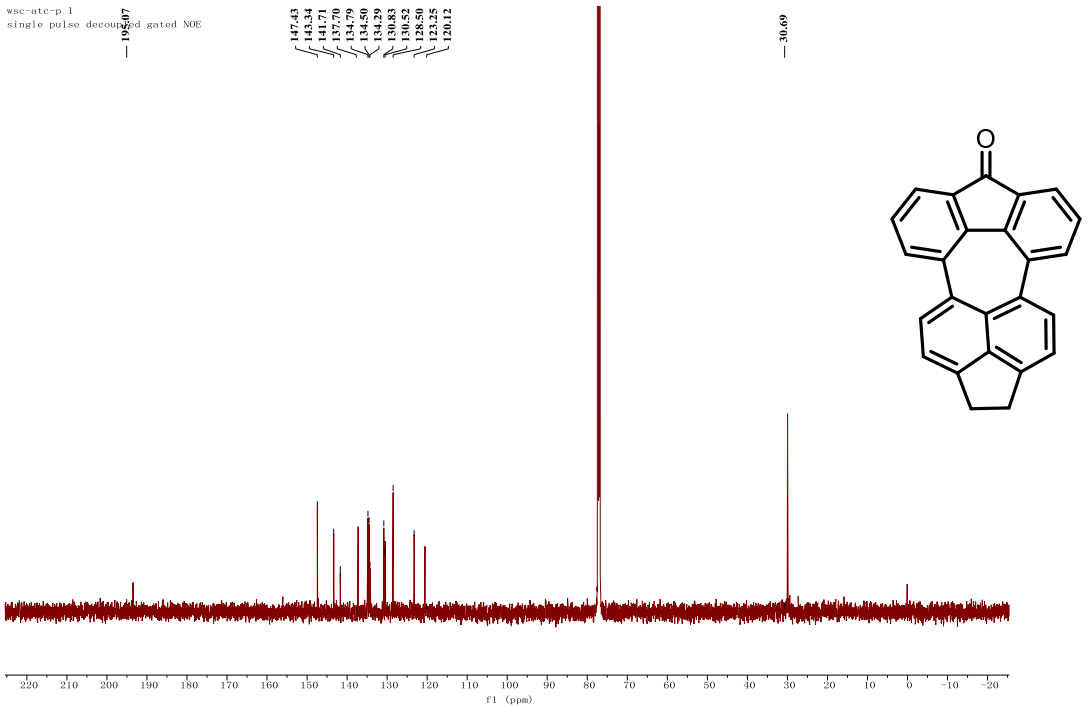


Figure S23.[13]C NMR Spectra of **3b** in $CDCl_3$ (600 MHz)

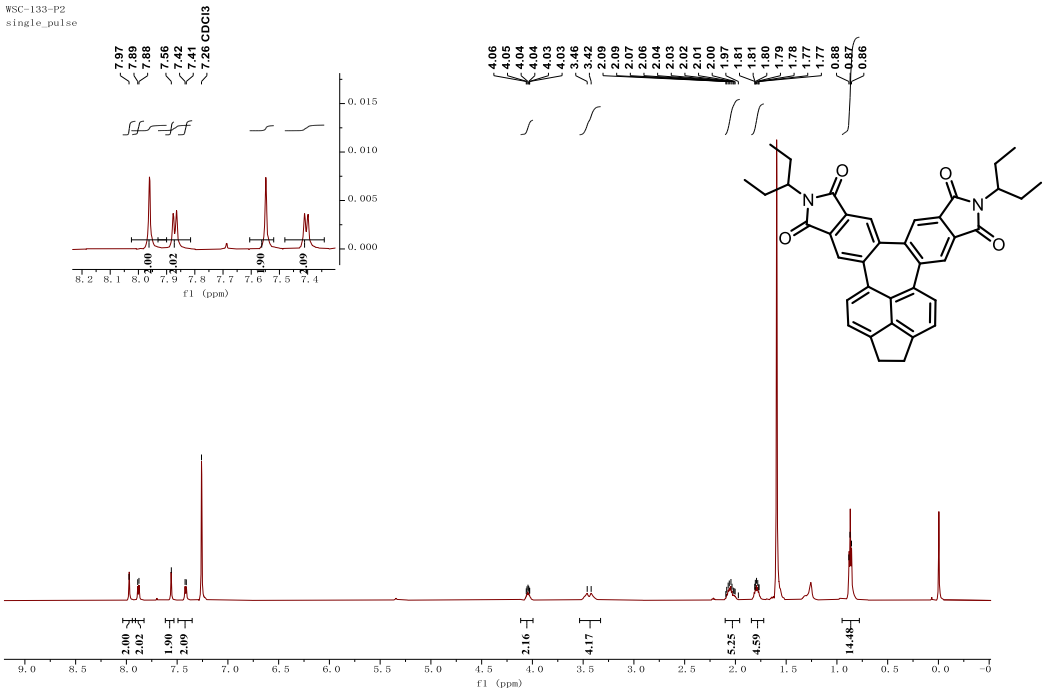


Figure S24.[1]H NMR Spectra of **3c** in $CDCl_3$ (600 MHz)

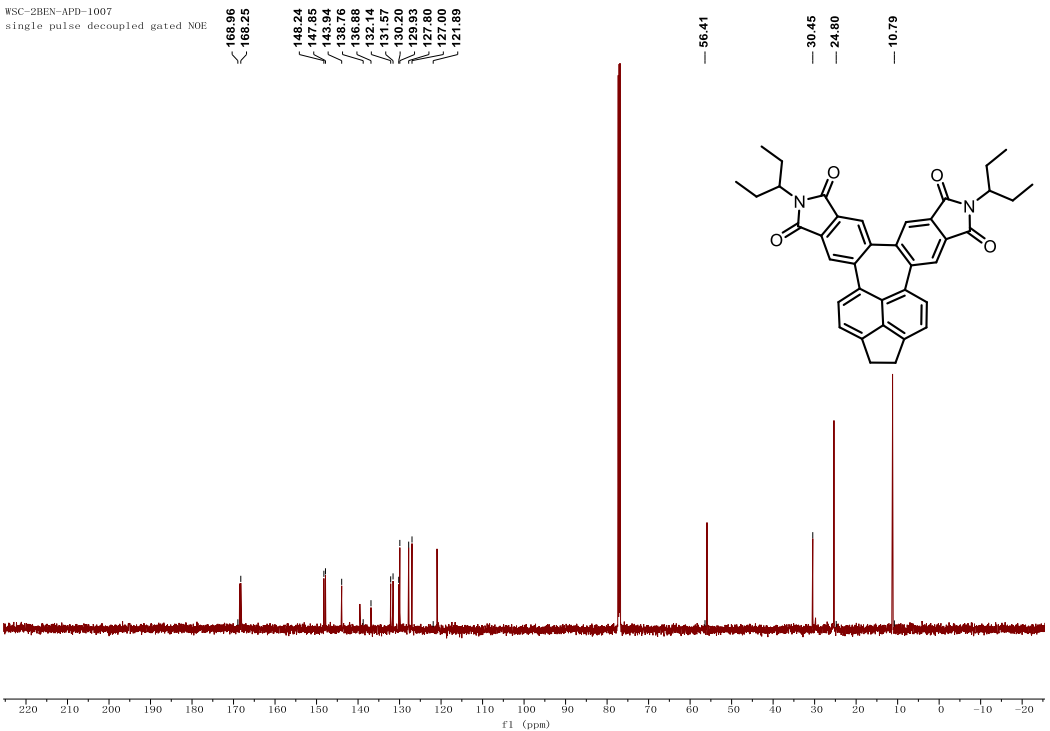


Figure S25.^{1}H NMR Spectra of **3c** in $CDCl_3$ (600 MHz)

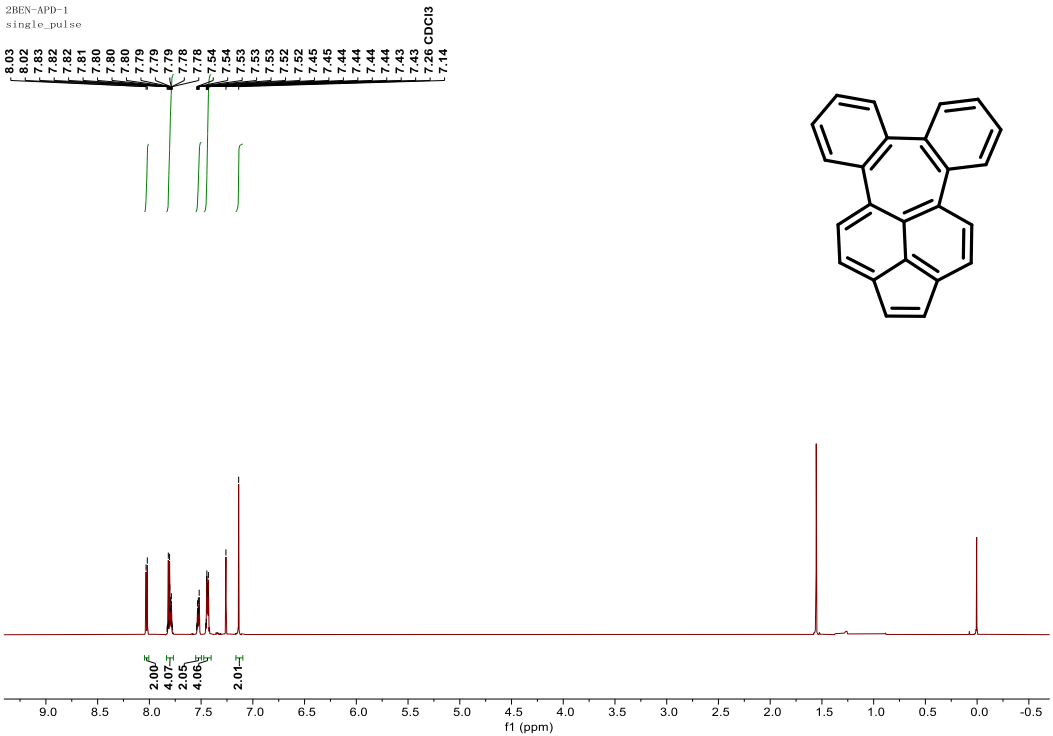


Figure S26.[1]H NMR Spectra of **4a** in $CDCl_3$ (600 MHz)

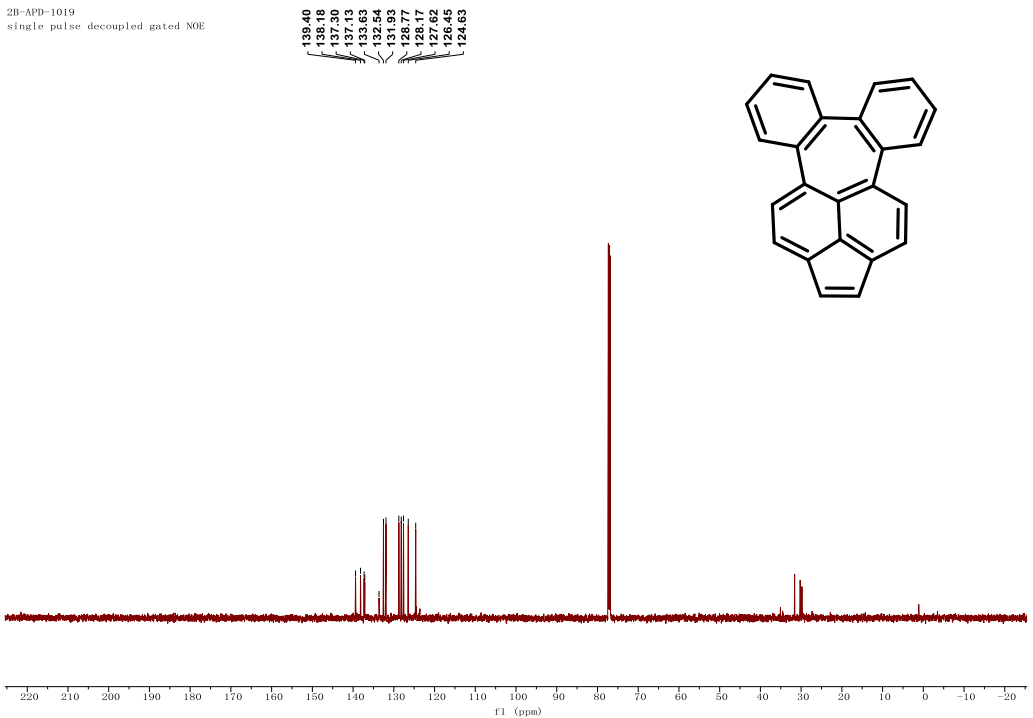


Figure S27.[13]C NMR Spectra of **4a** in $CDCl_3$ (600 MHz)

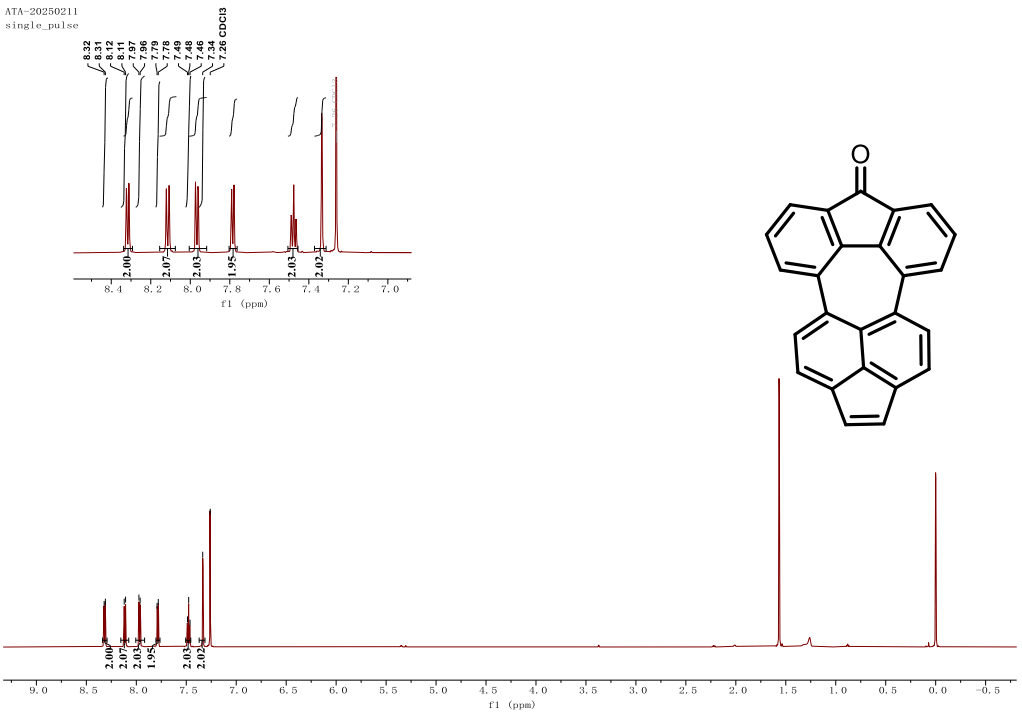


Figure S28.[1]H NMR Spectra of **4b** in $CDCl_3$ (600 MHz)

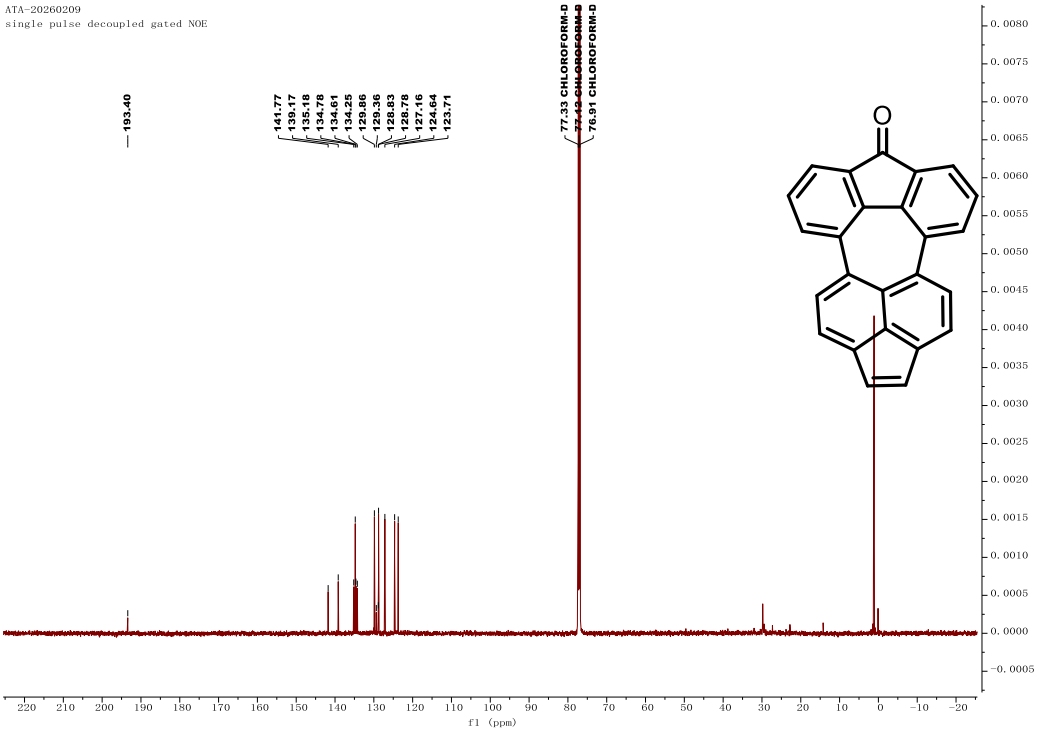


Figure S29.[13]C NMR Spectra of **4b** in $CDCl_3$ (600 MHz)

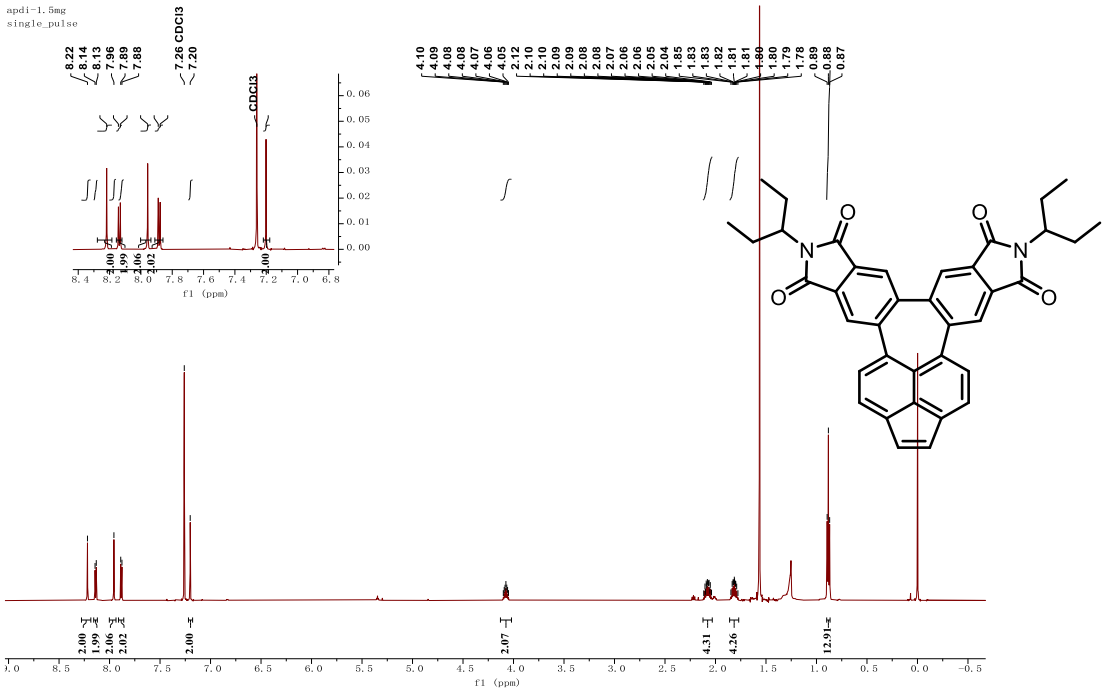


Figure S30.[1]H NMR Spectra of 4**c** in $CDCl_3$ (600 MHz)

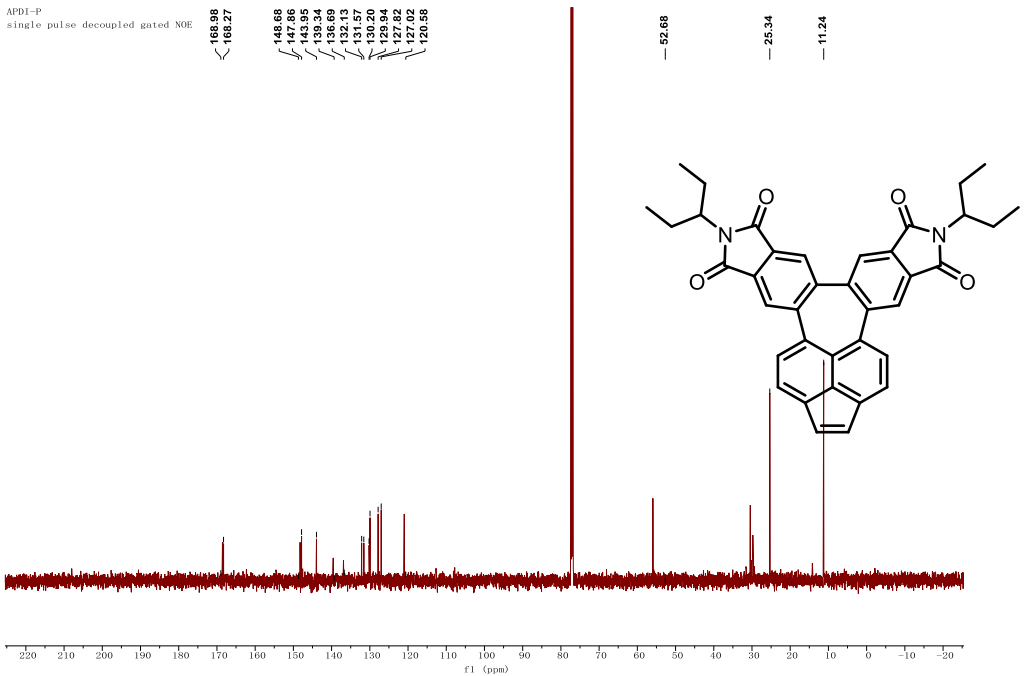


Figure S31.[13]C NMR Spectra of **4c** in $CDCl_3$ (600 MHz)

9.MS NMR Spectra

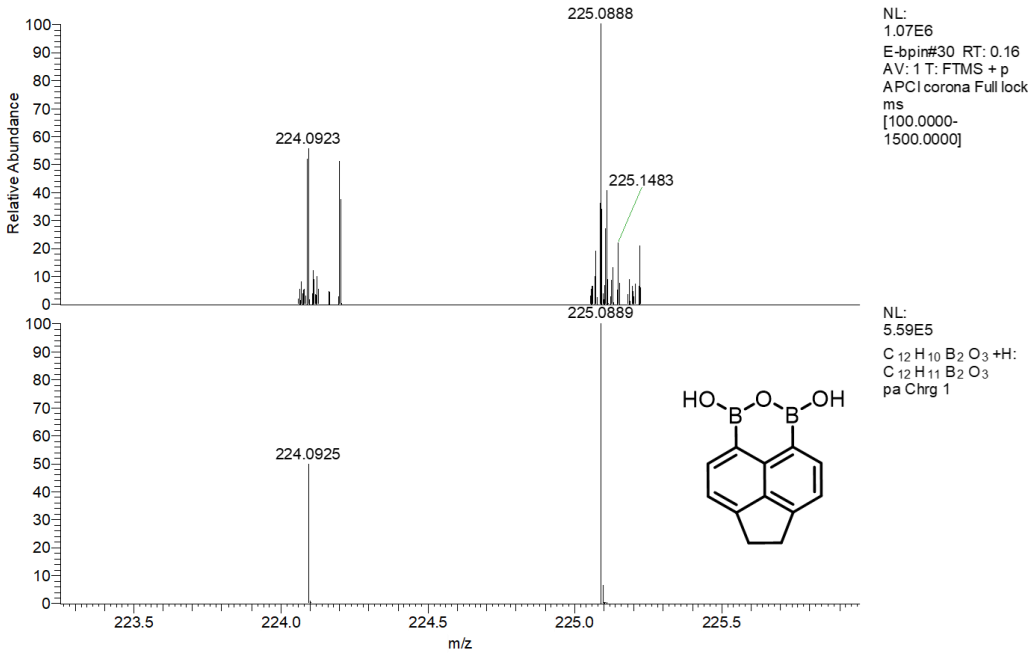


Figure S32.MS Spectra (positive ion mode) of **1**

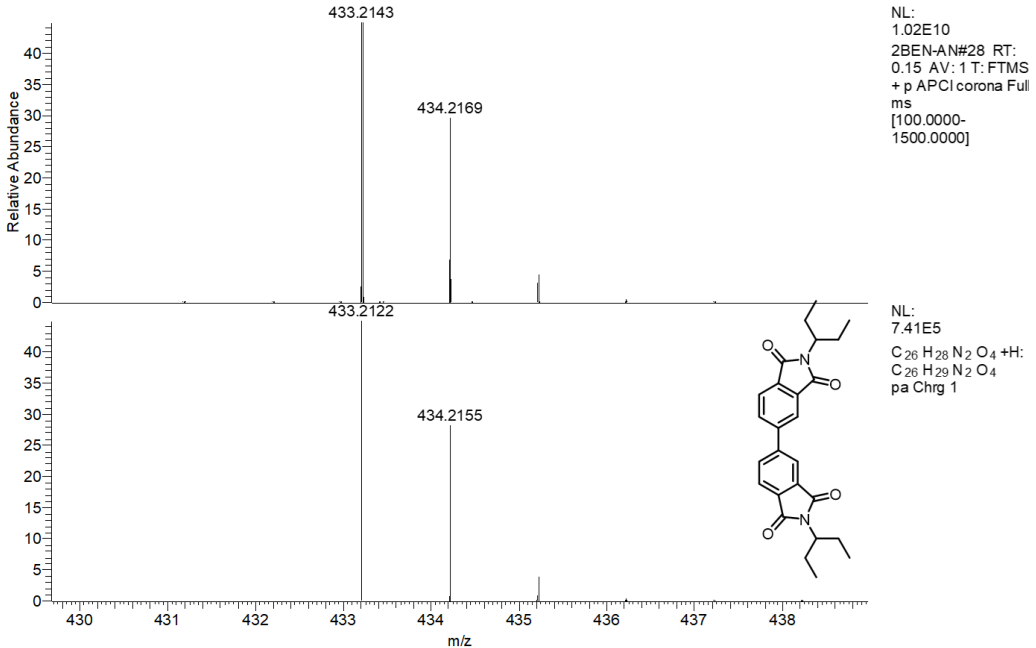


Figure S33.MS Spectra (positive ion mode) of **p-2c**

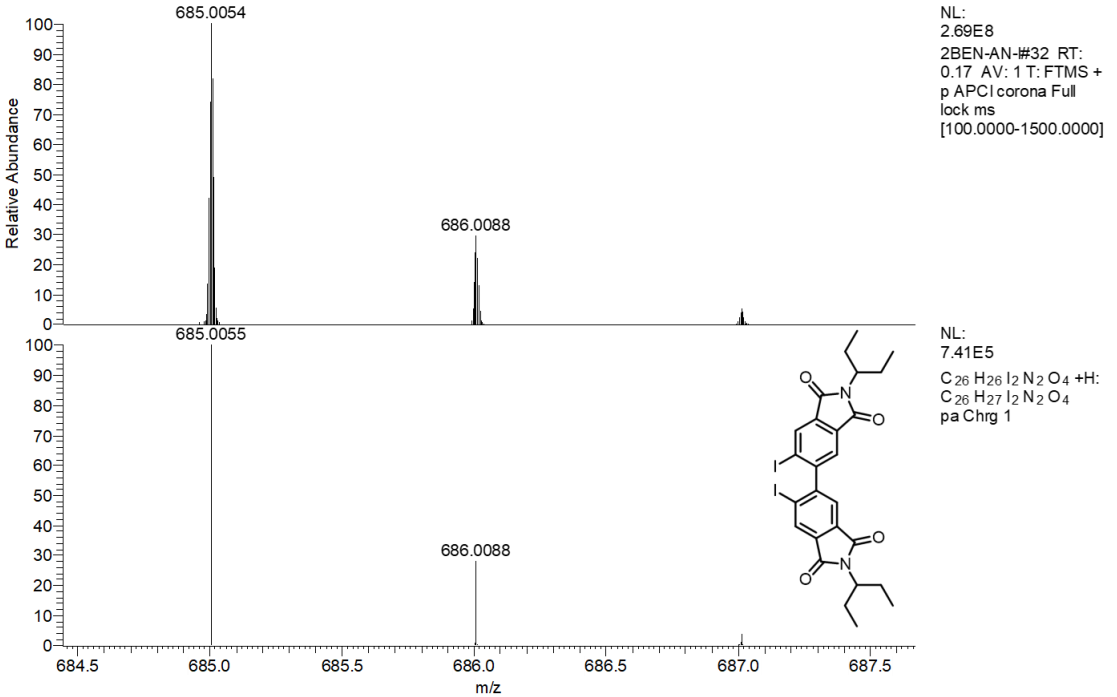


Figure S34.MS Spectra (positive ion mode) of **2c**

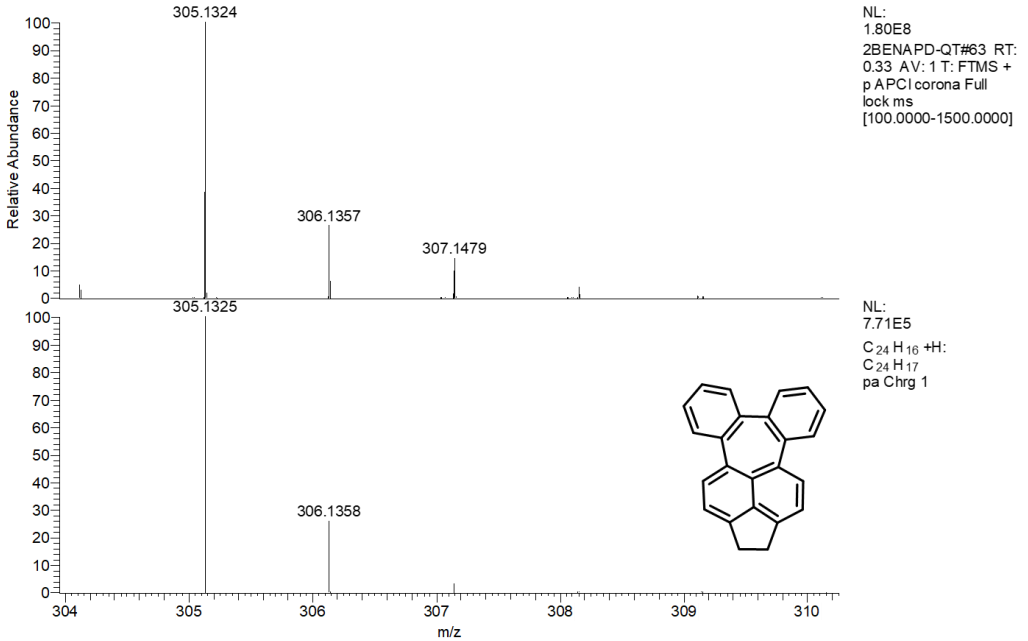


Figure S35.MS Spectra (positive ion mode) of **3a**

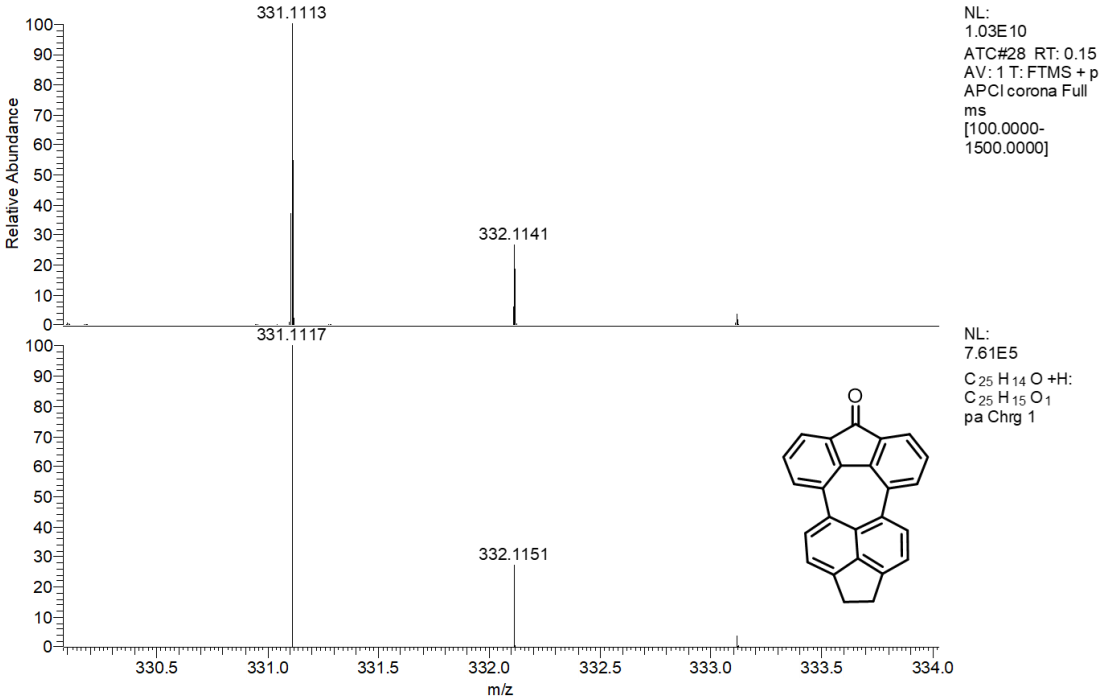


Figure S36.MS Spectra (positive ion mode) of **3b**

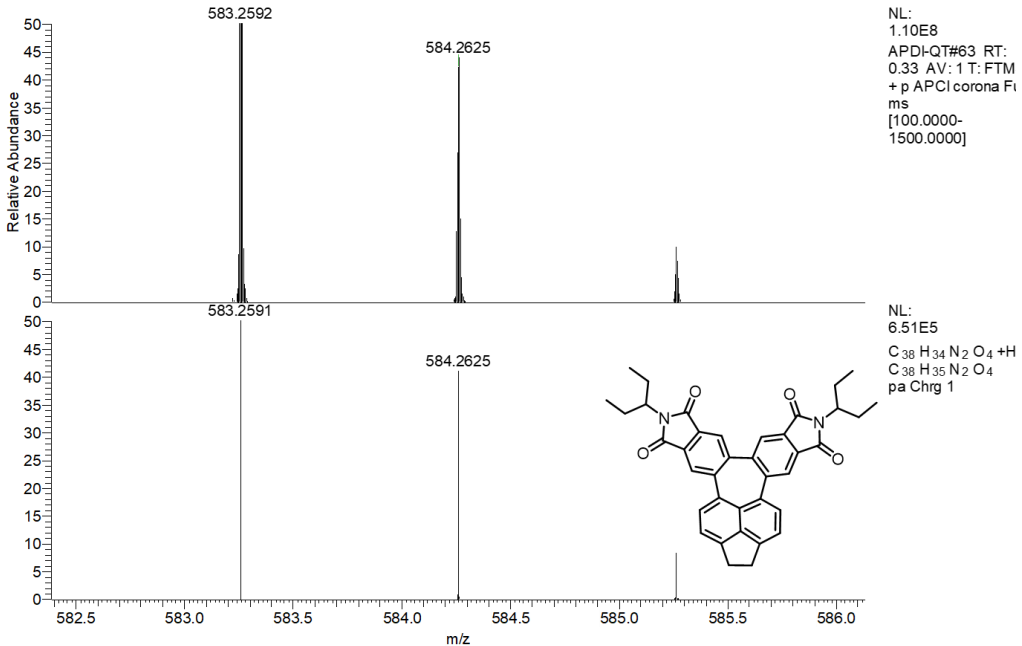


Figure S37.MS Spectra (positive ion mode) of **3c**

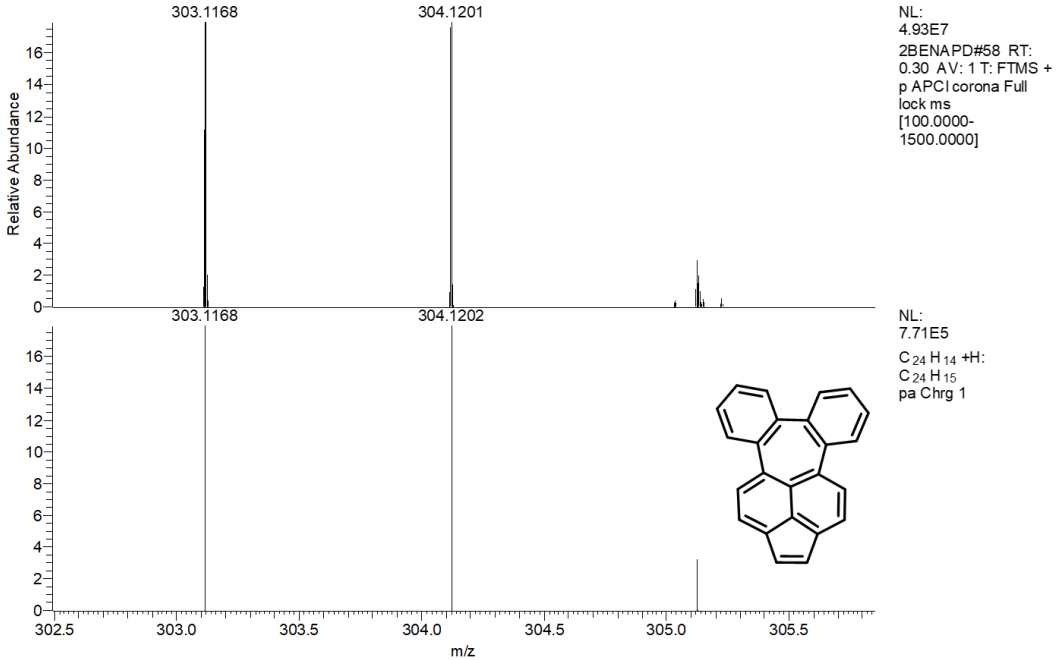


Figure S38.MS Spectra (positive ion mode) of **4a**

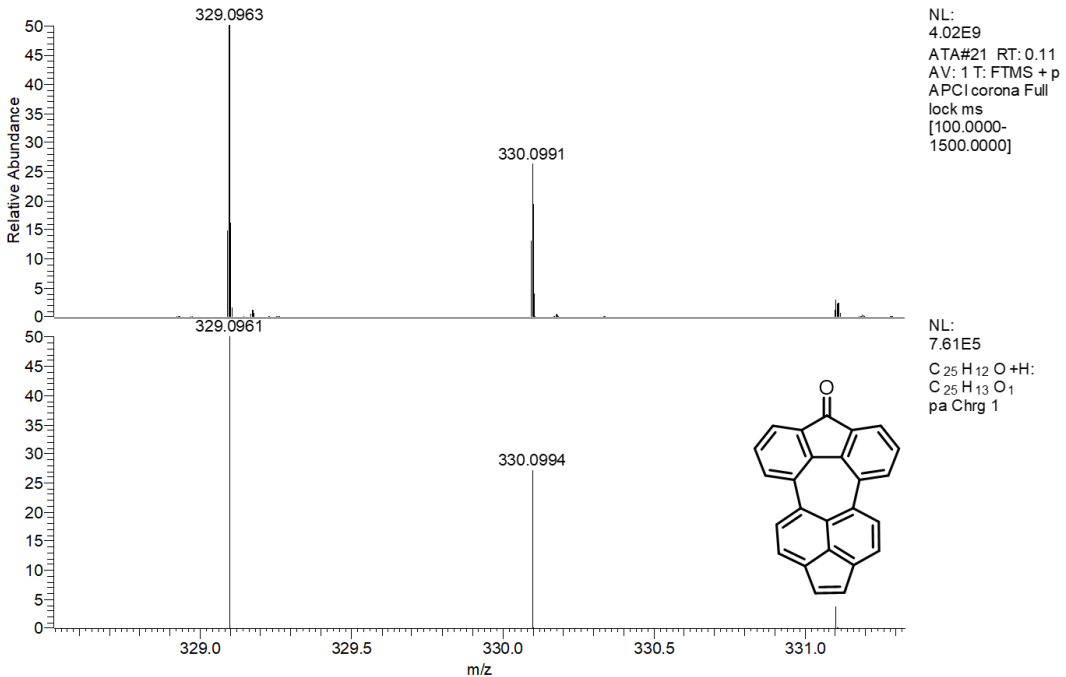


Figure S39.MS Spectra of (positive ion mode) **4b**

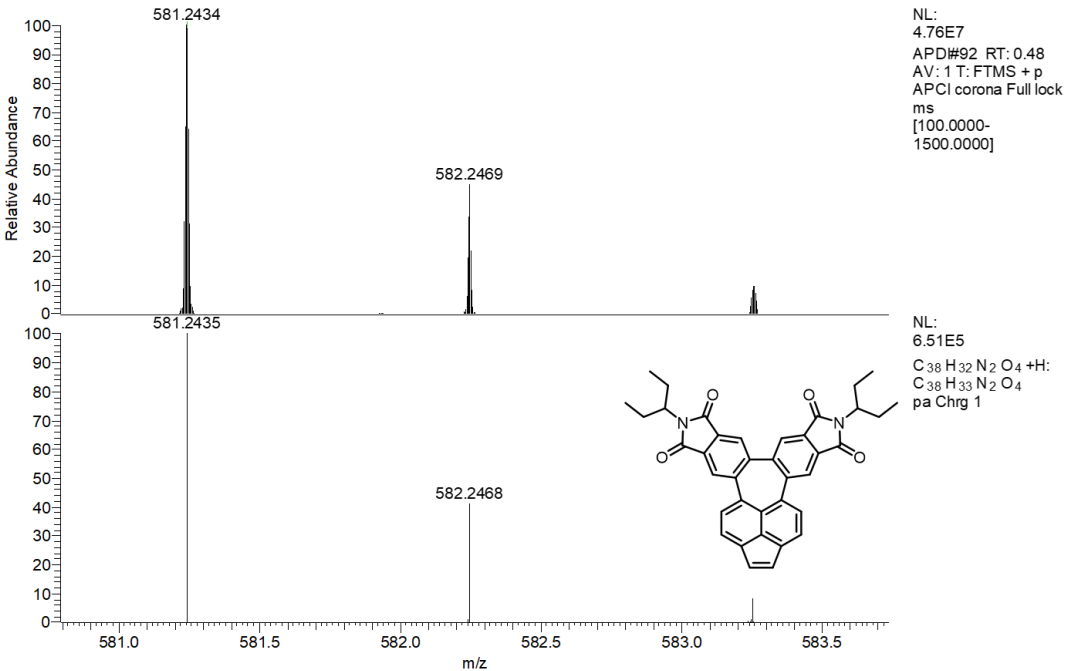


Figure S40.MS Spectra (positive ion mode) of **4c**