Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

The Synthesis, Property, and Applicationof *o*-carborane based π-Conjugated Macrocycles

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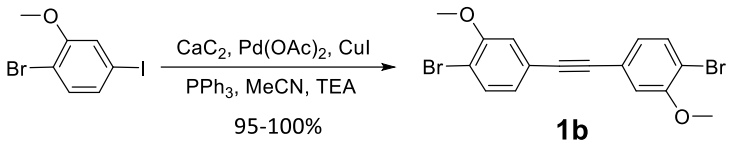
1. Materials and Methods

All commercially available reagents and solvents were used as received without further purification unless noted otherwise. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were measured at room temperature by using a JEOL JNM-ECZ500R/S1 or Bruker AVANCE NEO 400. HRMS were obtained on an Exactive plus LC-MS (ESI) mass spectrometer. UV-visible absorption spectra were recorded on a PerkinElmer Lambda750 UV-vis/NIR spectrophotometer. The instrument used for the fluorescence test in solution is a Hitachi F4600. Steady-state fluorescence and lifetime measurements were carried out on an Edinburgh Instruments (EI) FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe1). Photoluminescence quantum yield (Φ_{PL}) was obtained via “Integrated Sphere” using Spectrofluorometer FLS1000 equipped with a xenon lamp as the excitation source. Transmission electron microscope (TEM) images were acquired with an FEI-*/TECNAI G2 F20. Element analysis were acquired with an Elementar Vario EL Cube. X-ray single crystal diffraction data for the **4a** and **4b** in PE/THF mixture was collected on a Bruker Apex diffractometer and 1.5 kW graphite monochromated Mo-Kα (λ = 0.71073) and Cu-Kα radiation (λ = 1.54184 Å). The crystal was kept at 296.15 K during data collection. Using the Olex2 graphical program,[1] the structure was solved using SHELXT 2018. Structure solution and refinement of the structure have been done using SHELXL 2018.[2] Density functional theory (DFT) calculations were carried out using Gaussian 09(Revision C.01) program.[3] Molecular geometry was optimized using B3LYP/6-31G(d) basis set.

2. Synthesis Section

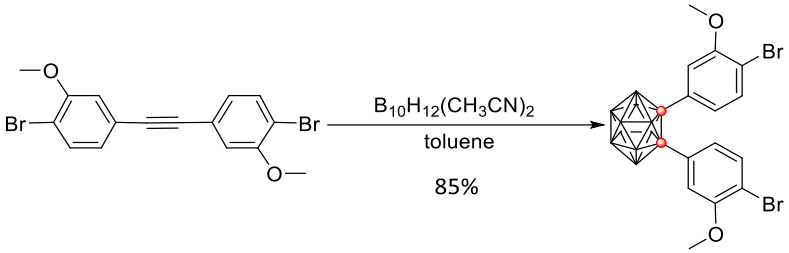
Synthesis of compound 1b



1b

A 250 mL round bottom flask with a magnetic stir bar was charged with 2-bromo-5-iodoanisole (1.25 g, 4mmol), CuI (76.2 mg, 0.4mmol), and $Pd(OAc)_2$ (45 mg, 0.1 mmol), CaC_2 (1.0 g, 12.0 mmol) and PPh_3(105.0 mg, 0.4 mmol). The flask was evacuated and refilled with nitrogen for 3 times. Then, EtN_3(30 mL) and acetonitrile(30 mL)were added. The mixturewas stirred at room temperature over night under nitrogen atmosphere. The reaction mixture was poured into water and then extracted with chloroform 3 times. The extract was washed with water, brine, and then dried over Na_2SO_4. After removed the solvent, the residue was then purified by silica gel column chromatography(PE:DCM = 4:1, R_f = 0.60) to give **1b** as a white solid (760.3 mg, 1.9 mmol) in 95% yield.^{1}H NMR (500 MHz, Chloroform-d) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 1.8 Hz, 2H), 7.01 (dd, *J* = 8.1, 1.8 Hz, 2H), 3.92 (s, 6H).^{13}C NMR (126 MHz, Chloroform-d) δ 155.8, 133.4, 125.1, 123.2, 114.7, 112.7, 89.4, 56.4. HR-MS (ESI)$[M+H]^+$ calcd for $C_{16}H_{13}O_2Br_2$, 396.9256; found 396.9256.

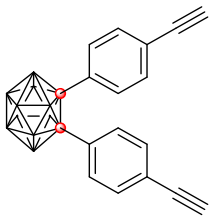
Synthesis of compound 2b



2b

Under nitrogen atmosphere, a mixture of **1b** (693 mg, 1.75 mmol) and $B_{10}H_{12}(CH_3CN)_2$ (530.8 mg, 2.625 mmol) in 50 mL distilled toluene was stirred at room temperature for 30 min. Then the system was heated to 110℃. After 18 h, the system was cooled down to room temperature. The residue was purified by silica gel column chromatography(PE:EA = 10:1, R_f = 0.65) to give **2b** as a white solid (774.3 mg, 1.5 mmol) in 85% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.94 (dd, *J* = 8.4, 2.3 Hz, 2H), 6.88 (d, *J* = 2.3 Hz, 2H), 3.76 (s, 6H), 3.63–0.97 (m, 10H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.8, 133.4, 125.1, 123.2, 114.7, 112.7, 89.4, 56.4. ^{11}B NMR (160 MHz, Chloroform-d) δ 0.09 – -5.13 (m), -8.51 – -13.16 (m). HR-MS (ESI) $[M]^+$ calcd for $C_{16}H_{22}B_{10}O_2Br_2$, 511.1013; found 511.1021.

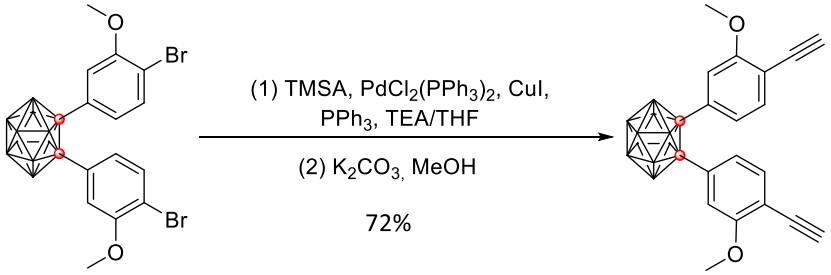
Synthesis of compound 3a



3a

3a was synthesized according to the procedures previously reported in the literature.[4,5]

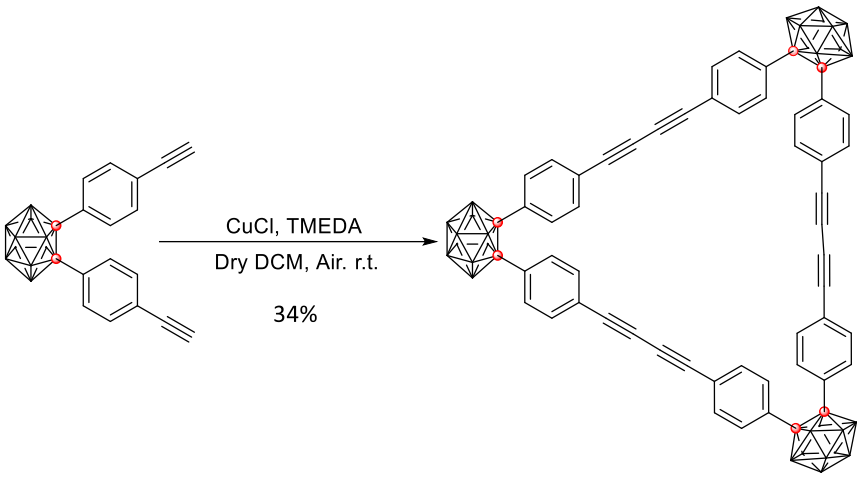
Synthesis of compound 3b



3b

Into an oven-dried round-bottom flask were added compound **2b** (454.2mg, 1.0mmol), $Pd(PPh_3)_2Cl_2$(14.0mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), PPh_3(5.3mg, 0.02mmol), degassed triethylamine (10 mL) and THF (30 mL), followed by injection of trimethylsilylacetylene (0.224 g, 2.4 mmol). The reaction mixture was refluxed for 36 h. After cooling to room temperature, the solid was filtered and the solvent was removed under vacuum.The mixture was added to a 250ml flask with proper amount of MeOH and K_2CO_3 and stirred at room temperature for 2h. The extract was washed with water and brine and dried over Na_2SO_4. Evaporation of solvent followed by silica gel column chromatography(PE:DCM = 4:1, R_f = 0.20) to give **3b** as a white solid (250.0 mg, 0.63 mmol) in 72% yield for the two steps. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.25 (d, *J* = 8.2 Hz, 2H), 7.03 (dd, *J* = 8.1, 2.0 Hz, 2H), 6.86 (d, *J* = 1.9 Hz, 2H), 3.74 (s, 6H), 3.35 (s, 2H), 3.28 – 1.65 (m, 10H). ^{13}C NMR (126 MHz, Chloroform-d) δ 160.0, 133.8, 132.4, 122.9, 113.9, 112.9, 84.5, 83.8, 56.0. ^{11}B NMR (160 MHz, Chloroform-d) δ -3.23 (d, J = 128.6 Hz), -8.46 – -21.98 (m). HR-MS (ESI) $[M+H]^+$ calcd for $C_{20}H_{24}B_{10}O_2$, 405.2852; found 405.2850.

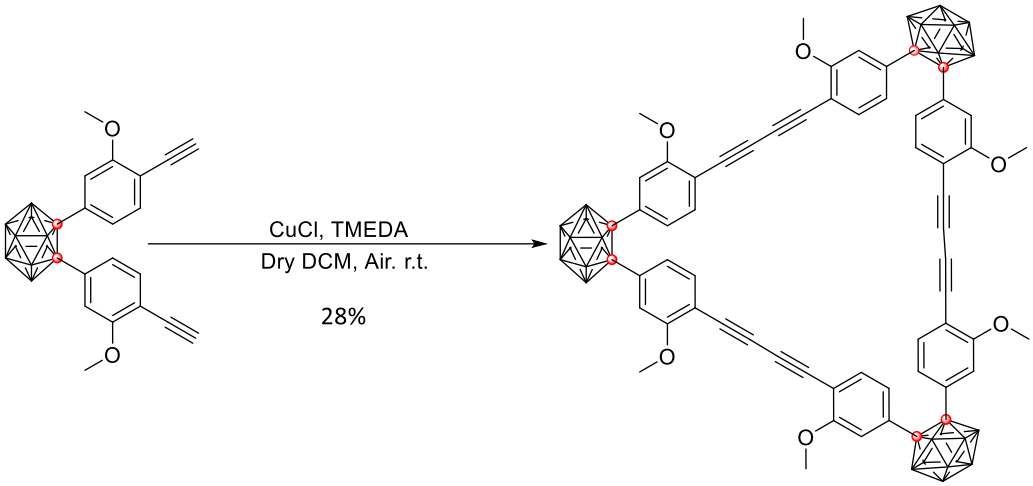
Synthesis of compound 4a



4a

A solution of the **3a**[4,5](172.0 mg, 0.5 mmol), CuCl (297.6 mg, 3 mmol), and N,N,N',N' -tetra-methylethylenediamine (TMEDA) (45 μL, 3 mmol) in dry CH_2Cl_2 (300 mL) was stirred for 24 h at room temperature. The reaction mixture was washed with water and brine and dried over anhydrous Na_2SO_4.Evaporation of the solvent followed by silica gel column chromatography(PE:THF = 5:1, R_f = 0.65) to give **4a**(58.1 mg, 0.057 mmol) as a white solidin 34% yield. Elemental Anal. Calcd for $C_{54}H_{54}B_{30}$: C, 63.13; H, 5.30. Found: C, 63.09; H, 5.29. M.p. > 300 ℃; 1H NMR (400 MHz, Chloroform-d) δ 7.41 (d, J = 8.2 Hz, 12H), 7.30 (d, J = 8.3 Hz, 12H), 2.85 (d, *J* = 284.2 Hz, 30H). ^{13}C NMR (101 MHz, Chloroform-d) δ 132.5, 131.3, 130.6, 123.9, 84.5, 80.8, 76.1. ^{11}B NMR (128 MHz, Chloroform-d) δ -1.73, -10.48. HR-MS (ESI) $[M+H]^+$ calcd for $C_{54}H_{54}B_{30}$, 1027.7308; found 1027.7316.

Synthesis of compound 4b



4b

A solution of the **3b**(202 mg, 0.5 mmol), CuCl(297.6 mg, 3 mmol), and *N*,*N*,*N*',*N*' -tetra-methylethylenediamine (TMEDA) (45 μL, 3 mmol) in dry CH_2Cl_2 (300 mL) was stirred for 24 h at room temperature. The reaction mixture was washed with water and brine and dried over anhydrous Na_2SO_4.Evaporation of the solvent followed by silica gel column chromatography(PE:THF = 10:1, R_f = 0.40) to give **4b**(47.9mg, 0.047mmol) as a white solidin 28% yield. Elemental Anal. Calcd for $C_{60}H_{61}B_{30}O_6$: C, 59.68; H, 5.51. Found: C, 59.68; H, 5.62. M.p. > 300 ℃. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.25 (d, *J* = 8.0 Hz, 6H), 7.01 (d, *J* = 7.9 Hz, 6H), 6.88 (s, 6H), 3.75 (s, 18H), 2.84 (d, *J* = 322.2 Hz, 30H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.7, 134.0, 132.6, 122.8, 113.7, 113.0, 84.6, 80.0, 78.0, 55.9.^{11}B NMR (128 MHz, Chloroform-d) δ -2.67, -9.59. HR-MS (ESI) $[M+H]^+$ calcd for $C_{60}H_{66}B_{30}O_6$, 1207.7903; found 1207.7942.

3. Crystal Data and DFT Calculations

Table S1. Crystal data and structure refinement for **4a** and **4b**

Identification code	**4a**	**4b**
Empirical formula	$C_{54}H_{54}B_{30}$	$C_{60}H_{66}B_{30}O_6$
Formula weight	1026.30	1207.42
Temperature/K	296.15	150.15
Crystal system	hexagonal	trigonal
Space group	$P6_3/m$	R-3c
a/Å	21.9777(18)	29.4352(4)
b/Å	21.9777(18)	29.4352(4)
c/Å	9.8702(15)	19.3133(3)
α/°	9.8702(15)	19.3133(3)
β/°	90	90
γ/°	120	120
Volume/Å^3	4128.8(9)	14491.8(5)
Z	121	6
ρ_{calc}g/cm^3	0.826	0.830
μ/mm^{-1}	0.041	0.352
F(000)	1056.0	3744.0
Crystal size/mm^3	0.12 × 0.11 × 0.1	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.706 to 50.044	9.794 to 145.396
Index ranges	26 ≤ h ≤ 22, -25 ≤ k ≤ 26, -11≤ l ≤ 11	-36 ≤ h ≤ 35, -36 ≤ k ≤ 33, -23 ≤ l ≤ 19
Reflections collected	23943	30382
Independent reflections	2587 [R_{int} = 0.1362, R_{sigma} = 0.0736]	3188 [R_{int}= 0.1042, R_{sigma} = 0.0398]
Data/restraints/parameters	2587/0/145	3188/0/146
Goodness-of-fit on F^2	1.0.35	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0797, wR_2 = 0.2325	R_1 = 0.0591, wR_2 = 0.1681
Final R indexes [all data]	R_1 = 0.1190, wR_2 = 0.2637	R_1 = 0.0713, wR_2 = 0.1787
CCDC number	2212259	2204374

DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian 09(Revision C.01).[3] Geometry optimizations were performed with C3 symmetries limit, using Single-crystal as starting geometries. The calculations were performed using the functional B3LYP and the 6-31G(d) basis set. Each structure was optimized to meet standard convergence criteria, and the existence of a local minimum was verified by a normal mode frequency calculation. Negative frequencies were not observed.

General results

reference	SCF E[hartree]	ZPV E[hartree]	lowest freq.[cm^{-1}]	H [hartree]	G [hartree]	E_{HOMO} [eV]	E_{LUMO} [eV]
4a	-2836.4005	1.0220	7.68	-2835.3144	-2835.4805	-6.38	-2.49
4b	-3523.5912	1.2198	7.77	-3522.2931	-3522.4855	-6.17	-2.17

Table S2. From left to right: reference, SCF electronic energy, zero-point vibrational energy, lowest vibrational frequency, sum of electronic and thermal enthalpies, sum of electronic and free energies, energy of the HOMO orbital, energy of the LUMO orbital.

Table S3 Atomic coordinates of **4a** after geometry optimization.

Atom	X (Å)	Y (Å)	Z (Å)
B	-1.86501600	-9.59207800	-1.41508500
B	-2.21640700	-11.31259100	-1.43774100
B	-1.58221500	-12.01544200	0.07513000
B	-0.68372500	-10.73467900	-0.75604100
C	-1.04818400	-9.29335100	0.07568700
B	-2.09393500	-9.54633300	1.41468200
C	-2.72474400	-8.94606600	-0.07519300
B	-3.49159400	-10.15428300	-1.01059000
B	-3.31554600	-11.65621600	-0.07752600
B	-2.45485900	-11.26486500	1.43603400
B	-3.63188200	-10.12502200	0.75497900
B	-0.82445100	-10.70781600	1.00956300
H	-4.63352800	-9.76788100	1.27304400
H	-4.38865100	-9.80110600	-1.69681200
H	-4.15040900	-12.49722800	-0.12913500
H	-2.66379000	-11.80917700	2.46884100
H	-2.04288300	-8.80903400	2.33077500
H	-1.61793700	-8.89390100	-2.32997900
H	-2.24072500	-11.89464100	-2.47084700
H	-1.14997800	-13.11888800	0.12515700
H	0.37732300	-10.80485100	-1.27412100
H	0.13906900	-10.74011100	1.69582400
C	-3.14120300	-7.50475600	-0.08618100
C	-0.09395900	-8.13562200	0.08782000
C	-2.90652000	-6.67708600	-1.19183800
C	-3.29664000	-5.34478700	-1.17949300
C	-3.94143700	-4.79825600	-0.05440800
C	-4.18000700	-5.63103400	1.05586500
C	-3.78352900	-6.96043800	1.03565300
C	0.71211800	-7.89151300	-1.03369800
C	1.60381800	-6.82878600	-1.05421000
C	1.71472500	-5.96898000	0.05536500
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C	0.01854600	-7.28205800	1.19308700
C	-4.35436800	-3.44127800	-0.04169300

C	2.63186800	-4.88692600	0.04214900
C	-4.72749700	-2.27933200	-0.02856200
C	3.43540700	-3.96840900	0.02771100
B	-7.37353100	6.42216600	-1.40942100
B	-8.68693400	7.58765700	-1.42455700
B	-9.61486800	7.37850400	0.08556800
B	-8.95443600	5.96633900	-0.75526900
C	-7.52506300	5.55419600	0.07479800
B	-7.22243900	6.57578100	1.42214500
C	-6.38560100	6.83260600	-0.06516300
B	-7.04675600	8.10841200	-0.99146400
B	-8.43625000	8.70076500	-0.05536600
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H	-10.78659700	7.55595500	0.13537900
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C	-7.00026700	4.14860100	0.07643600
C	-4.32825600	5.85791100	-1.18300800
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C	-2.18522300	5.81123700	-0.04232600
C	-2.78872900	6.43130500	1.06861500
C	-4.13811500	6.75310900	1.04710400
C	-7.19781000	3.33453700	-1.04842500
C	-6.72270900	2.03130500	-1.07860400
C	-6.02690800	1.49975000	0.02427100
C	-5.82768500	2.31751200	1.15209300
C	-6.30988200	3.61914800	1.17451200

C	-0.80361500	5.49021200	-0.02875400
C	-5.54910100	0.16434100	0.00288600
C	0.38912200	5.23178800	-0.01554200
C	-5.15500600	-0.99062500	-0.01294400
B	9.24380100	3.16801200	-1.41829700
B	10.90913600	3.72364900	-1.44195600
B	11.19679400	4.63867100	0.06325100
B	9.64064100	4.76844600	-0.77328200
C	8.57249700	3.74001000	0.06523900
B	9.31084000	2.97319200	1.41338600
C	9.11039200	2.11332400	-0.06891600
B	10.54249400	2.04427100	-0.99975700
B	11.75314800	2.95655400	-0.07228700
B	10.97948200	3.52061100	1.43396900
B	10.58309000	1.92482400	0.76695800
B	9.68288200	4.64981200	0.99386100
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H	9.17180500	5.71729800	-1.30163800
H	9.22699400	5.50657100	1.67095900
C	8.07059800	1.03177400	-0.07219300
C	7.09290400	3.98764700	0.07140200
C	7.23665800	0.81189700	-1.17624500
C	6.27799400	-0.19208000	-1.15535600
C	6.12726700	-1.01467000	-0.02342400
C	6.96751700	-0.79545000	1.08504400
C	7.92017200	0.21279900	1.05643800
C	6.48044000	4.55157100	-1.05734100
C	5.11415200	4.79152900	-1.08314500
C	4.31212700	4.46952800	0.02851400
C	4.92714900	3.90360300	1.16088800

C	6.29556800	3.67023700	1.17876100
C	5.15902400	-2.05114100	-0.00348300
C	2.91645400	4.72229900	0.01127500
C	4.33863500	-2.95461500	0.01230600
C	1.71887300	4.95725300	-0.00219100
H	-2.41529500	-7.07153000	-2.07077400
H	-3.10805900	-4.71511200	-2.04218500
H	-4.68088100	-5.22439500	1.92772200
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H	0.64667100	-8.54343900	-1.89596600
H	2.22505900	-6.65474900	-1.92606300
H	0.98148900	-5.56016600	2.04234600
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H	-4.91363400	5.63207400	-2.06382000
H	-2.52729400	5.05289200	-2.03250500
H	-2.18751300	6.65915500	1.94211000
H	-4.58055700	7.23454700	1.91043500
H	-7.73471600	3.72163300	-1.90564800
H	-6.88750700	1.41080900	-1.95277300
H	-5.29422300	1.92052000	2.00889500
H	-6.14414200	4.22428000	2.05524000
H	7.33204800	1.42713900	-2.06050100
H	5.63824500	-0.35083000	-2.01664200
H	6.86591600	-1.42514200	1.96226800
H	8.55976400	0.36059300	1.91777400
H	7.07917900	4.81241100	-1.92124800
H	4.65442500	5.23325600	-1.96057900
H	4.32145200	3.65245300	2.02479600
H	6.74199400	3.23736000	2.06358700

Table S4 Atomic coordinates of **4b** after geometry optimization.

Atom	X (Å)	Y (Å)	Z (Å)
O	1.18376900	4.72478600	-1.88191000
C	3.90811900	8.46645000	-0.13721200
C	2.64550100	7.65373600	-0.17883300
C	2.49246400	6.60986200	-1.09883800
H	3.27484800	6.41152100	-1.81404500

C	1.36836800	5.78556300	-1.06447000
C	0.33770300	6.03137800	-0.12184900
C	1.64188400	7.88744700	0.76799200
H	1.74997800	8.68241500	1.49382000
C	-1.87033000	4.59641100	-0.02869900
C	-0.82966900	5.23130300	-0.08928700
C	0.50082100	7.09544200	0.78117000
H	-0.28535700	7.28448400	1.50419800
B	3.97139800	9.97731100	0.64746000
H	2.96683900	10.41194900	1.09313900
B	5.94070300	9.84993700	-1.42790600
H	6.37360700	10.26455400	-2.45135500
C	2.25756300	4.33484700	-2.73251900
H	1.92013100	3.42631600	-3.23182800
H	3.16346300	4.12286400	-2.15213400
H	2.47200200	5.10598100	-3.48275400
B	5.05656800	8.33132700	-1.40894200
H	4.82788300	7.60999800	-2.31196900
B	4.19633800	9.84697500	-1.10476100
H	3.33286400	10.15805300	-1.85162900
B	5.27136800	10.88207200	-0.13914100
H	5.21107000	12.06300000	-0.23283000
O	-4.68491100	1.33826400	1.88484000
C	-9.28557100	0.84906900	0.13460600
C	-7.95031500	1.53603300	0.17769300
C	-6.97069900	1.14648600	1.09866100
H	-7.19074800	0.36950100	1.81339000
C	-5.69490300	1.70821200	1.06594900
C	-5.39150300	2.72378300	0.12366300
C	-7.64986700	2.52193700	-0.76885800
H	-8.39144200	2.82544300	-1.49577900
C	-3.04464100	3.91849200	0.03357400
C	-4.11499800	3.33493700	0.09299000
C	-6.39344000	3.11415400	-0.78071500
H	-6.16325600	3.88929300	-1.50373700
B	-10.62500900	1.55103200	-0.65066100
H	-10.49791800	2.63838200	-1.09585400

B	-11.50164000	-0.21730800	1.42433800
H	-12.07816300	-0.38488900	2.44720700
C	-4.88489900	0.21397700	2.73609700
H	-3.92981000	0.05231400	3.23636400
H	-5.15375200	-0.67705800	2.15631100
H	-5.66059400	0.41449200	3.48549400
B	-9.74469600	-0.21213800	1.40662200
H	-9.00569200	-0.37596900	2.30941100
B	-10.62557200	1.29112100	1.10141300
H	-10.46250500	2.19406000	1.84860200
B	-12.05950000	0.87863800	0.13513200
H	-13.05146500	1.52234700	0.22807600
O	3.50142600	3.38812000	1.88484000
C	5.37810100	7.61700600	0.13460600
C	5.30540100	6.11715900	0.17769300
C	4.47823500	5.46356000	1.09866100
H	3.91537100	6.04262000	1.81339000
C	4.32680700	4.07782500	1.06594900
C	5.05461700	3.30728800	0.12366300
C	6.00899500	5.36401000	-0.76885800
H	6.64262600	5.85448000	-1.49577900
C	4.91583500	0.67749100	0.03357400
C	4.94563900	1.89622400	0.09299000
C	5.89365600	3.97980400	-0.78071500
H	6.44985400	3.39289000	-1.50373700
B	6.65573800	8.42601200	-0.65066100
H	7.53386500	7.77227300	-1.09585400
B	5.56262600	10.06936700	1.42433800
H	5.70575800	10.65244000	2.44720700
C	2.62775900	4.12345800	2.73609700
H	2.01021000	3.37715800	3.23636400
H	1.99052600	4.80180900	2.15631100
H	3.18925700	4.69497200	3.48549400
B	4.68863100	8.54522300	1.40662200
H	4.17724700	7.98714300	2.30941100
B	6.43093000	8.55645400	1.10141300
H	7.13136400	7.96376500	1.84860200

B	6.79067300	10.00451400	0.13513200
H	7.84412400	10.54172700	0.22807600
O	-4.68366900	-1.33721900	-1.88191000
C	-9.28622000	-0.84869500	-0.13721200
C	-7.95108000	-1.53579700	-0.17883300
C	-6.97054100	-1.14639400	-1.09883800
H	-7.18996400	-0.36965900	-1.81404500
C	-5.69462900	-1.70773900	-1.06447000
C	-5.39217800	-2.72323000	-0.12184900
C	-7.65167200	-2.52181000	0.76799200
H	-8.39418100	-2.82568200	1.49382000
C	-3.04544400	-3.91795800	-0.02869900
C	-4.11560700	-3.33416600	-0.08928700
C	-6.39524300	-3.11399700	0.78117000
H	-6.16587000	-3.88936900	1.50419800
B	-10.62630300	-1.54932400	0.64746000
H	-10.50043200	-2.63661700	1.09313900
B	-11.50064700	0.21983100	-1.42790600
H	-12.07616800	0.38742900	-2.45135500
C	-4.88286900	-0.21231700	-2.73251900
H	-3.92734200	-0.05027500	-3.23182800
H	-5.15223600	0.67820700	-2.15213400
H	-5.65791000	-0.41217400	-3.48275400
B	-9.74342400	0.21345300	-1.40894200
H	-9.00439300	0.37607000	-2.31196900
B	-10.62589900	-1.28935200	-1.10476100
H	-10.46356400	-2.19268100	-1.85162900
B	-12.05983500	-0.87589700	-0.13914100
H	-13.05240000	-1.51858100	-0.23283000
O	3.49990000	-3.38756700	-1.88191000
C	5.37810100	-7.61775500	-0.13721200
C	5.30557900	-6.11793900	-0.17883300
C	4.47807700	-5.46346900	-1.09883800
H	3.91511600	-6.04186200	-1.81404500
C	4.32626000	-4.07782300	-1.06447000
C	5.05447500	-3.30814800	-0.12184900
C	6.00978800	-5.36563700	0.76799200

H	6.64420300	-5.85673300	1.49382000
C	4.91577300	-0.67845200	-0.02869900
C	4.94527500	-1.89713700	-0.08928700
C	5.89442200	-3.98144500	0.78117000
H	6.45122700	-3.39511500	1.50419800
B	6.65490500	-8.42798700	0.64746000
H	7.53359300	-7.77533200	1.09313900
B	5.55994400	-10.06976800	-1.42790600
H	5.70256100	-10.65198200	-2.45135500
C	2.62530600	-4.12253000	-2.73251900
H	2.00721100	-3.37604100	-3.23182800
H	1.98877400	-4.80107100	-2.15213400
H	3.18590900	-4.69380700	-3.48275400
B	4.68685600	-8.54478000	-1.40894200
H	4.17651000	-7.98606800	-2.31196900
B	6.42956100	-8.55762300	-1.10476100
H	7.13070000	-7.96537200	-1.85162900
B	6.78846600	-10.00617500	-0.13914100
H	7.84132900	-10.54441900	-0.23283000
O	1.18348500	-4.72638400	1.88484000
C	3.90747000	-8.46607500	0.13460600
C	2.64491400	-7.65319100	0.17769300
C	2.49246400	-6.61004500	1.09866100
H	3.27537700	-6.41212100	1.81339000
C	1.36809700	-5.78603700	1.06594900
C	0.33688700	-6.03107000	0.12366300
C	1.64087200	-7.88594800	-0.76885800
H	1.74881500	-8.67992300	-1.49577900
C	-1.87119300	-4.59598300	0.03357400
C	-0.83064100	-5.23116100	0.09299000
C	0.49978300	-7.09395800	-0.78071500
H	-0.28659800	-7.28218200	-1.50373700
B	3.96927100	-9.97704400	-0.65066100
H	2.96405300	-10.41065500	-1.09585400
B	5.93901500	-9.85205900	1.42433800
H	6.37240500	-10.26755200	2.44720700
C	2.25714000	-4.33743500	2.73609700

H	1.91960000	-3.42947200	3.23636400
H	3.16322500	-4.12475100	2.15631100
H	2.47133700	-5.10946400	3.48549400
B	5.05606400	-8.33308500	1.40662200
H	4.82844500	-7.61117400	2.30941100
B	4.19464200	-9.84757600	1.10141300
H	3.33114100	-10.15782500	1.84860200
B	5.26882700	-10.88315200	0.13513200
H	5.20734100	-12.06407400	0.22807600

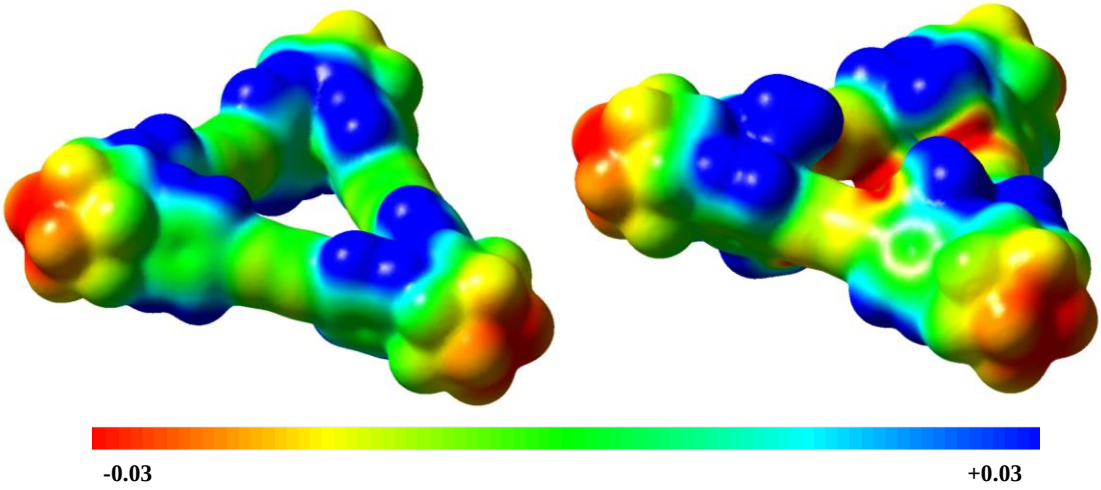

Figure S1 Electrostatic potential maps of **4a**(left) and **4b**(right).

4. Fluorescence Properties

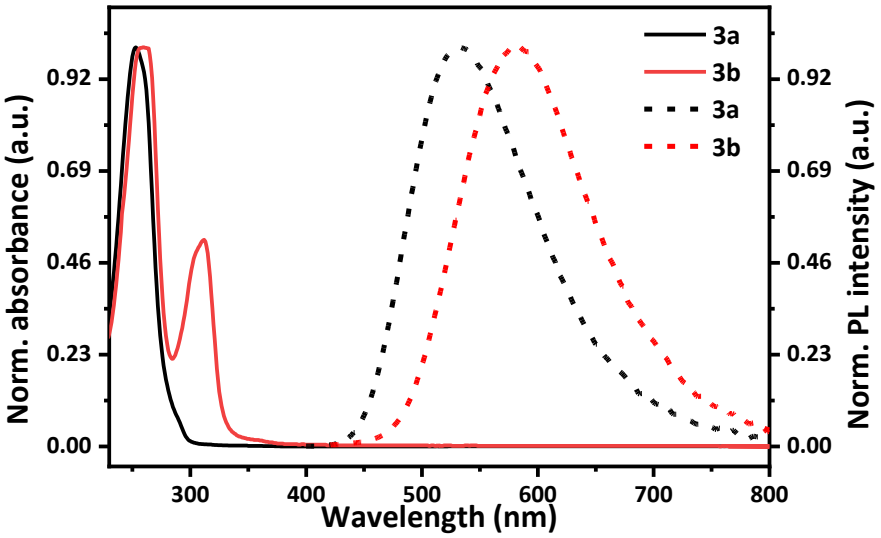

Figure S2 UV-vis absorption spectra of **3a** and **3b** in THF (1.0×10^{-5} M). Photoluminescence spectra of **3a** and **3b** in solid state. Excitation wavelength: 374 nm and 336 nm.

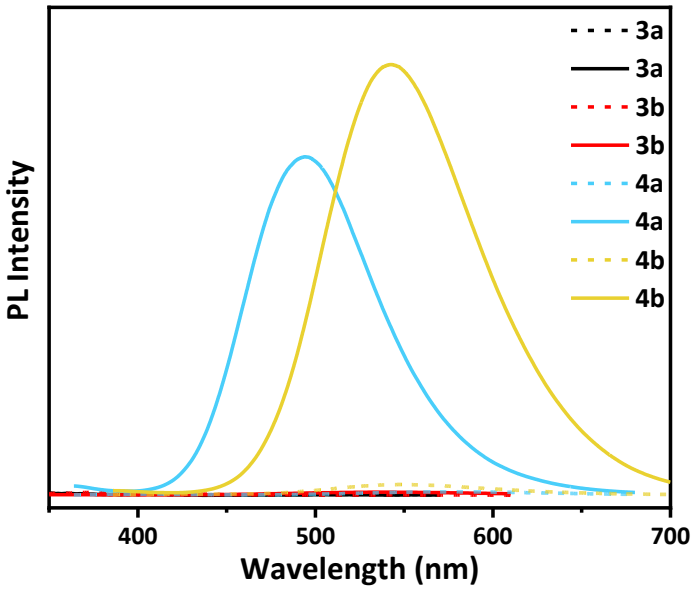

Figure S3. Fluorescence spectra of **3a**, **3b**, **4a** and **4b** in THF (1×10^{-5} mol/L, dashed line) and mixed solvent of THF/H_2O) 1/99 (v/v) (1×10^{-5}mol/L, solid line).

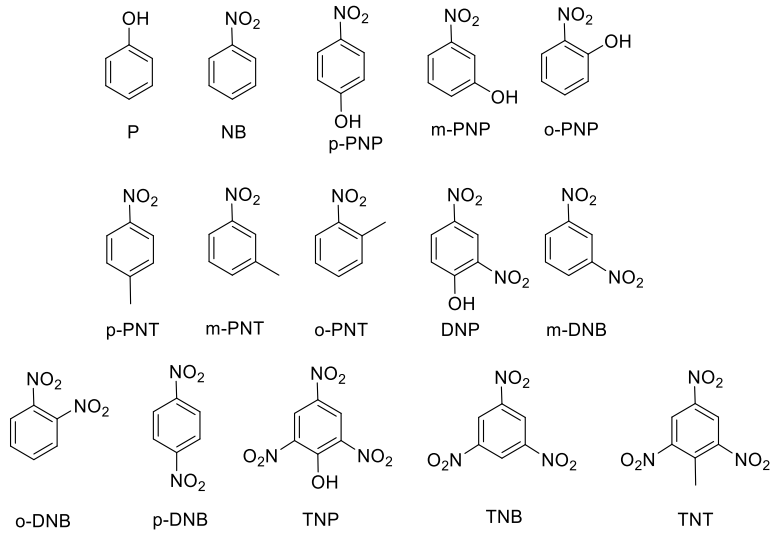

Figure S4 Structure and the abbreviation of guests

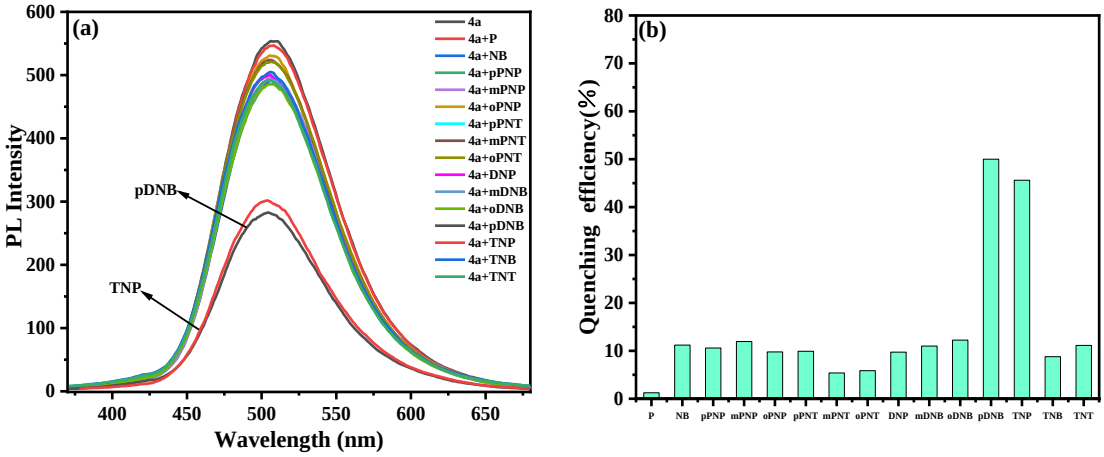

Figure S5 (a) Fluorescence spectra of 2 μM **4a** in 95:5 H_2O/THF by addition 10eq of different nitroaromatic compounds. Excitation at 354 nm. (b) Fluorescence quenching efficiencies ($(1-I/I_0)\times100$ %),where I and I_0 denote the fluorescence intensity of **4a** with and without analyte, respectively) of different analytes.

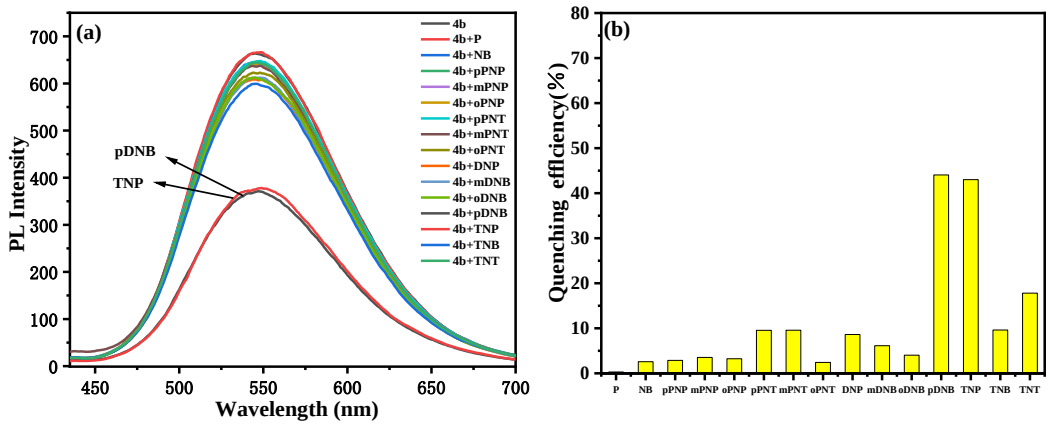

Figure S6 (a) Fluorescence spectra of 2 μM **4b** in 95:5 H_2O/THF by addition 10eq of different nitroaromatic compounds. Excitation at 376 nm. (b) Fluorescence quenching efficiencies ($(1-I/I_0)\times100$ %),where I and I_0 denote the fluorescence intensity of **4b** with and without analyte, respectively) of different analytes.

The fluorescent titration experiments of 4a for different quenchers.

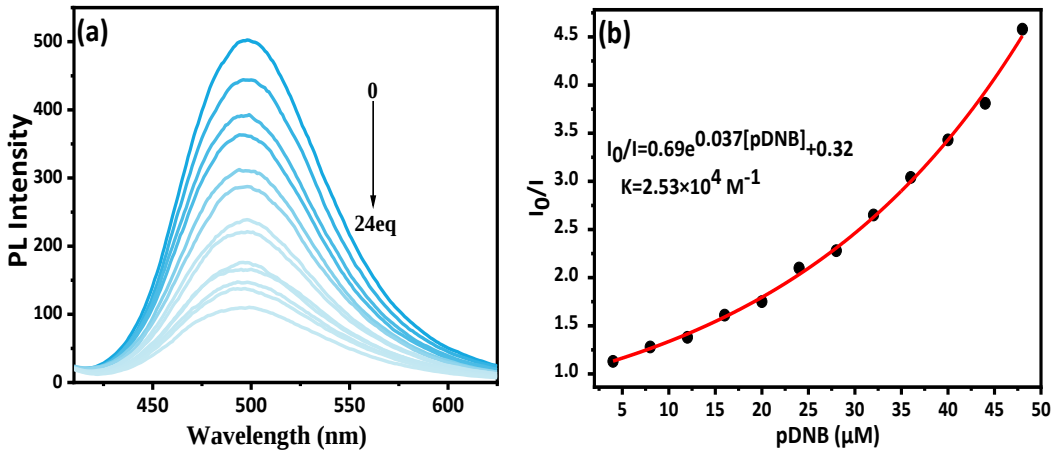

Figure S7 (a)Emission spectra (λ_{ex} =354nm) of 4a (2.0×10^{-6} M) in presence of p-DNB at various concentrations (from 0 to 24 equiv.). Solvent(95:5 H_2O/THF). (b) The nonlinear curve-fitting for the quenching constant of 4a with p-DNB.

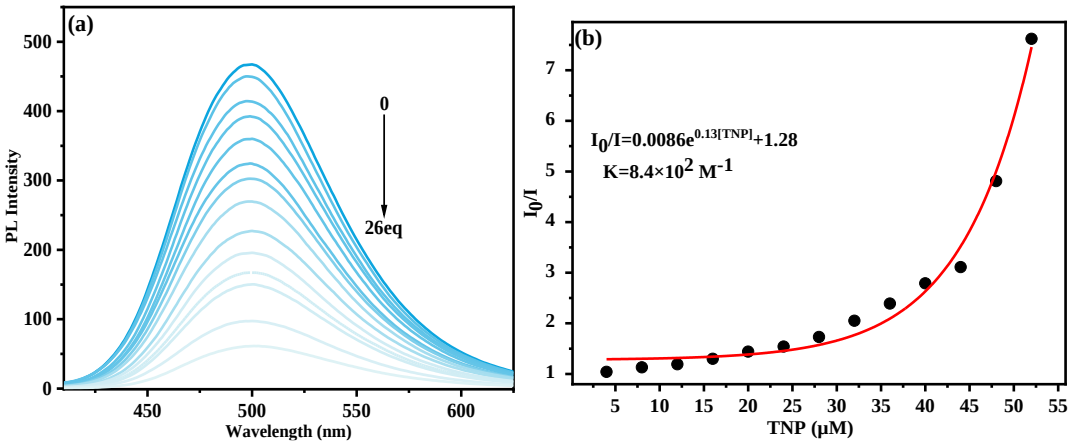

Figure S8 (a)Emission spectra (λ_{ex} = 354 nm) of **4a**(2.0×10^{-6} M) in presence of TNP at various concentrations (from 0 to26 equiv.). Solvent(95:5 H_2O/THF) (b) The nonlinear curve-fitting for the quenching constant of **4a** withTNP.

The fluorescent titration experiments of 4b for different quenchers.

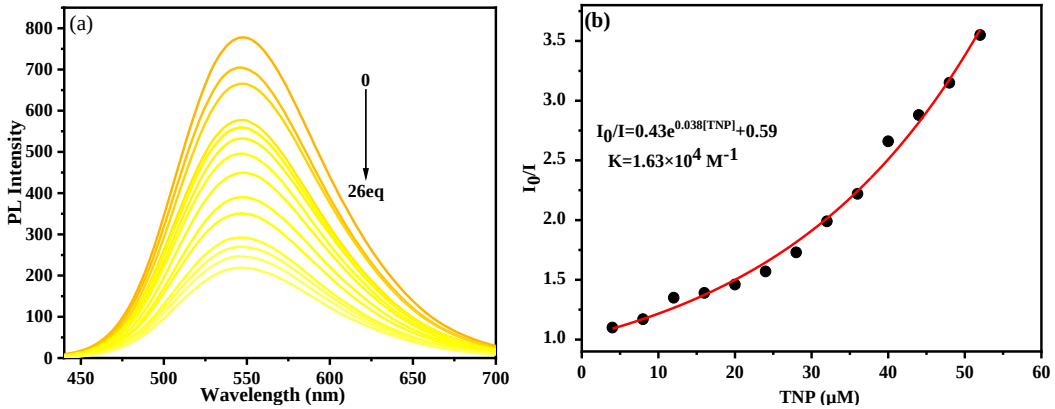

Figure S9 Emission spectra (λ_{ex} = 376 nm) of **4b**(2.0×10^{-6} M) in presence of p-TNP at various concentrations (from 0 to 26 equiv.). Solvent(95:5 H_2O/THF) (b) The nonlinear curve-fitting for the quenching constant of **4b** with TNP.

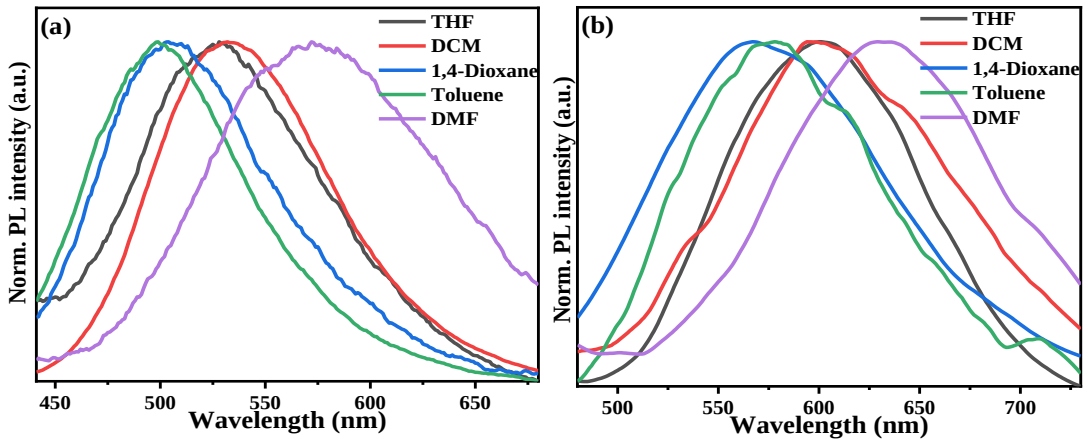

Figure S10 PL spectra of **4a** and **4b** in various solvents under excitation at 354 nm and 376 nm, respectively.

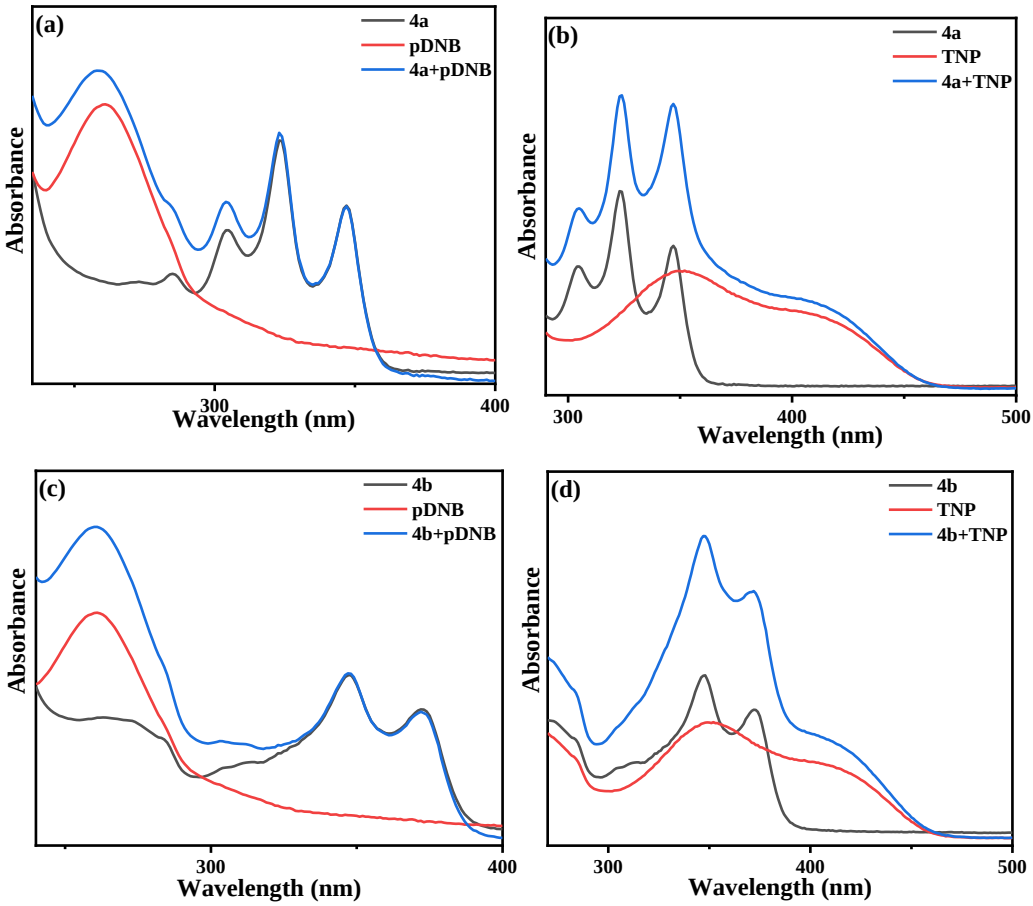

Figure S11. UV/Vis spectra of **4a**, **4b**, TNP, pDNB, and mixtures thereof in H_2O/THF (95:5) ([**4a**] = [**4b**] = 1×10^{-6} M， [TNP] = [pDNB] = 1×10^{-5} M).

Quantum yields determination:

Absolute quantum yields of all compounds in THF/water or in solid state were measured by employing an integrating sphere. The Principle of Absolute Quantum Yield Measurements. The absolute fluorescence quantum yield, η, is, by definition, the ratio of the number of photons emitted to the number of photons absorbed:

$$\eta = \frac{N^{em}}{N^{abs}} \quad \text{.....(1)}$$

There are two different methods for the measurement of the absolute fluorescence quantum yield: “Direct Excitation” measurements and “Direct & Indirect Excitation” measurements. With “Direct Excitation” measurements one records the scatter and the emission of the sample being directly exited by the radiation from the excitation monochromator only, whereas with “Direct and Indirect Excitation” one also records the emission of the sample while it is in a position where it is only indirectly excited by excitation radiation bouncing within the sphere.

“Direct Excitation” Method

This method only requires two experimental setups, see Figure S12. Note that with the “Direct Excitation” method the emission measurement actually contains the information of both direct and indirect excitation, as photons that pass the sample in the direct excitation beam may still be absorbed after scattering in the sphere.

Figure S12. Two different measurement configurations required for Direct Excitation measurements:(A) reference sample (solvent only) in sample

position (1); (B) test sample in position 1 (position 2 remains empty for both measurements.)

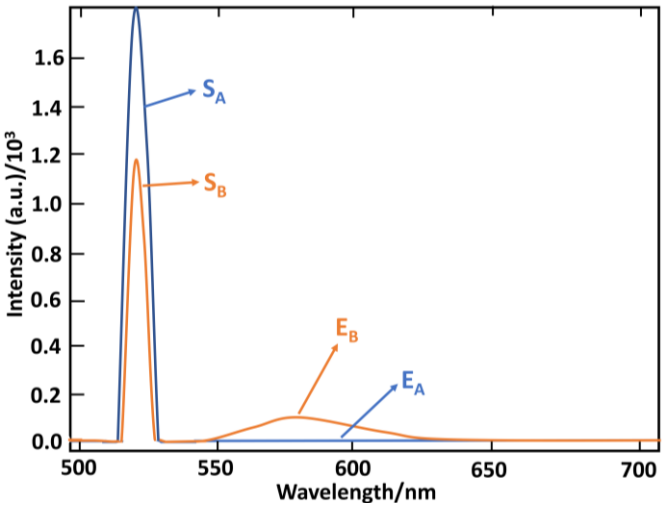

Figure S13. Spectral scans of the excitation scatter region or S-region (peaks on the left) and the emission region (E-region) of the sample and the solvent. The indices "A" and "B" refer to the experimental setup illustrated in Figure S12. Note that the quantities S_A, S_B, E_A, and E_B refer to the integral of the scans.

The absolute fluorescence quantum yield, calculated with the "Direct Excitation" method is calculated as follows:

$$\eta_{DExc} = \frac{E_B - E_A}{S_A - S_B} \quad \text{.....(2)}$$

$E_A(\lambda)$ and $S_A(\lambda)$, as well as $E_B(\lambda)$ and $S_B(\lambda)$ may be measured in four individual scans. However, it is often convenient to measure these spectra in two scans only. For the calculation of the integrals, the selection of the integral regions, and the final calculation of η_{DExc} use the quantum yield wizard that is supplied with the FLS980 software.

If the sphere background, $E_A(\lambda)$, is sufficiently low the measurement of this region may be omitted to save measurement time. In this case the equation degrades to:

$$\eta_{DExc} = \frac{E_B}{S_A - S_B} \quad \text{.....(3)}$$

The fluorescence quantum yield data

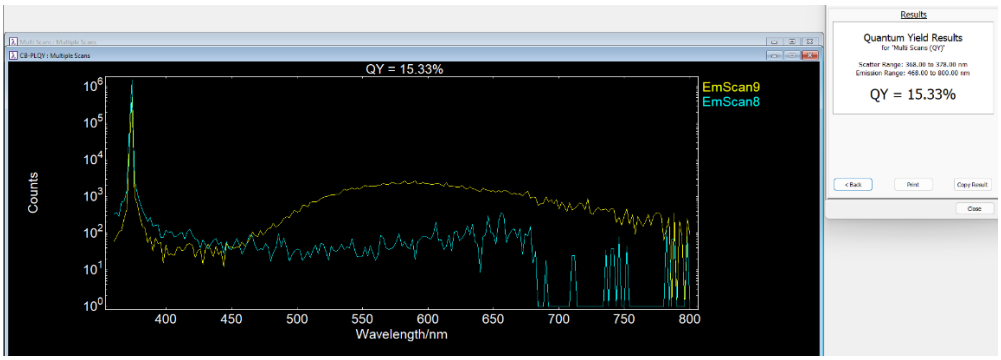

Figure S14 The fluorescence quantum yield data of **3a** in the powder state.

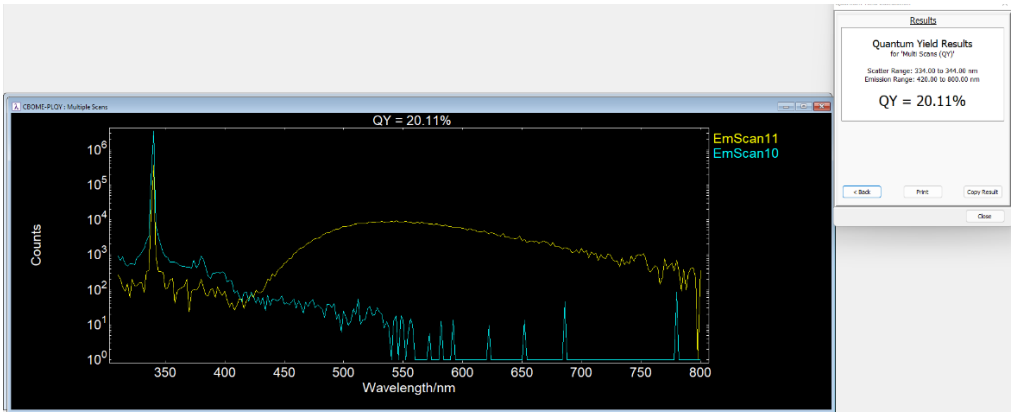

Figure S15 The fluorescence quantum yield data of **3b** in the powder state.

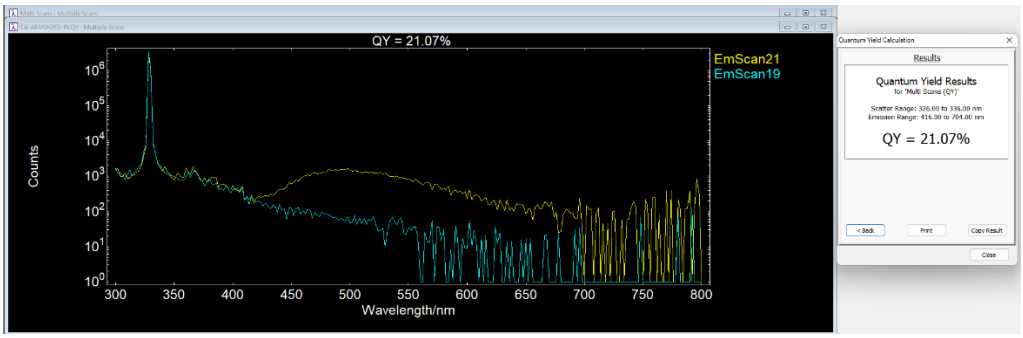

Figure S16 The fluorescence quantum yield data of **4a** in aggregation state, f_w = 99%(1.0×10^{-5} M) Water faction in THF solvent.

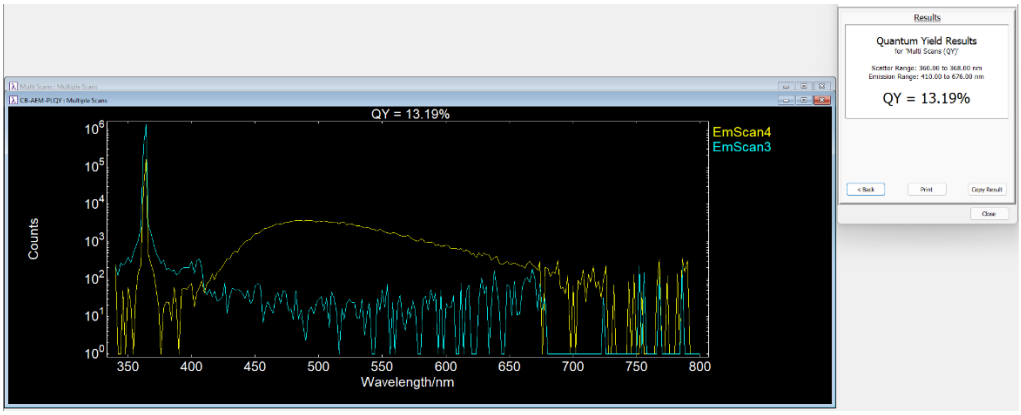

Figure S17 The fluorescence quantum yield data of **4a** in the powder state.

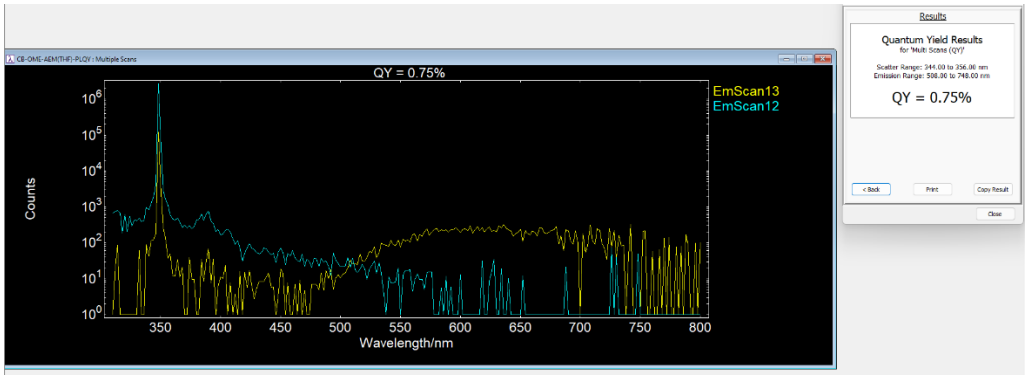

Figure S18 The fluorescence quantum yield data of **4b** in THF(1.0×10^{-5} M).

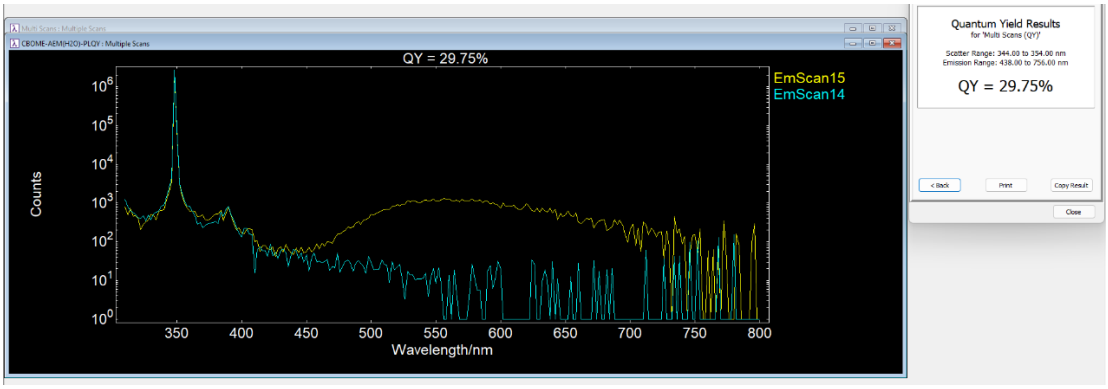

Figure S19 The fluorescence quantum yield data of **4b** in aggregation state, f_w = 99%(1.0×10^{-5} M) Water faction in THF solvent.

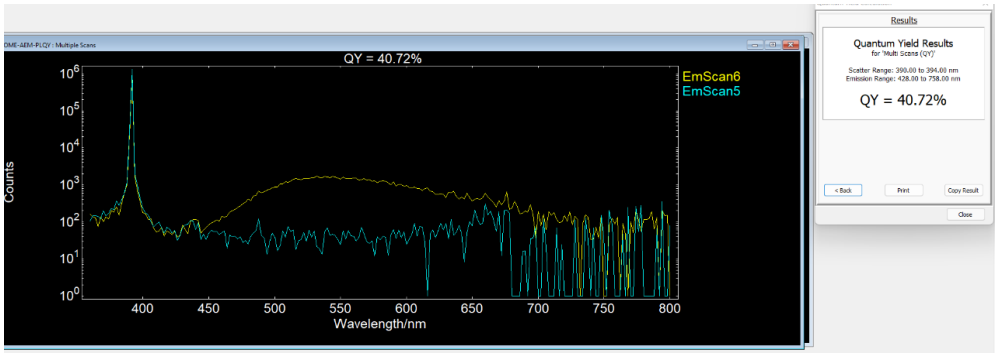

Figure S20 The fluorescence quantum yield data of **4b** in the powder state.

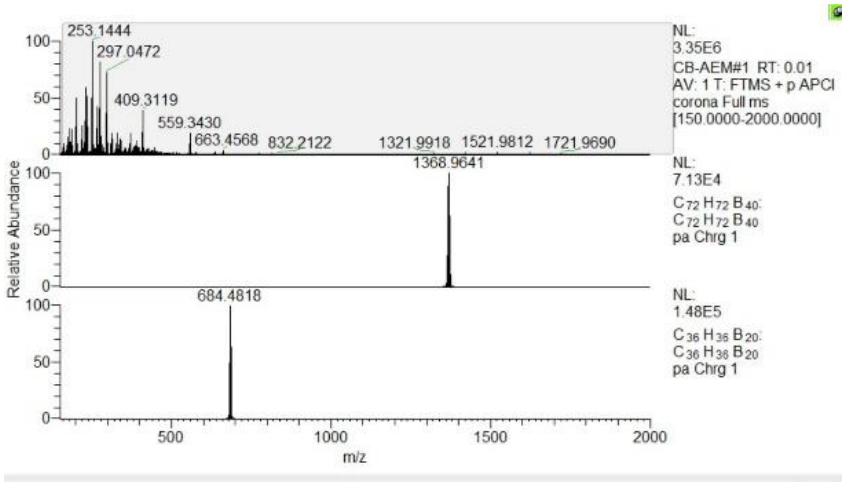

Figure S21 HRMS spectrum of **4a.** There didn't find the peaks of other dimers/tetramers in the final HRMS mass spectra.

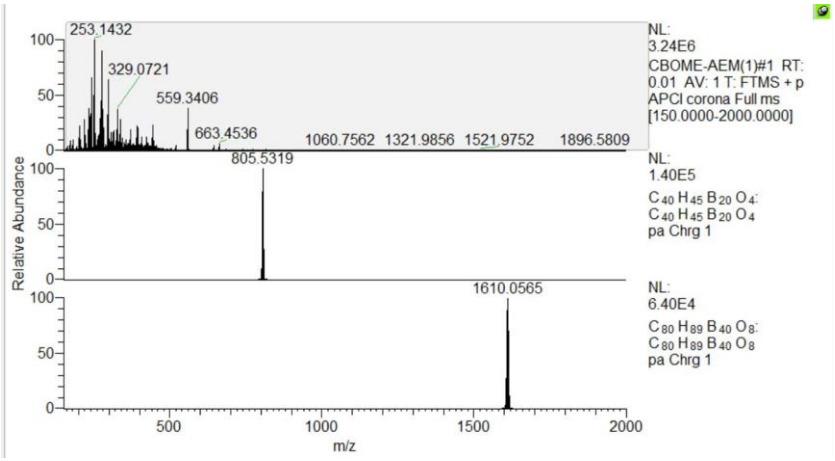

Figure S22 HRMS spectrum of **4b**. There didn't find the peaks of other dimers/tetramers in the final HRMS mass spectra.

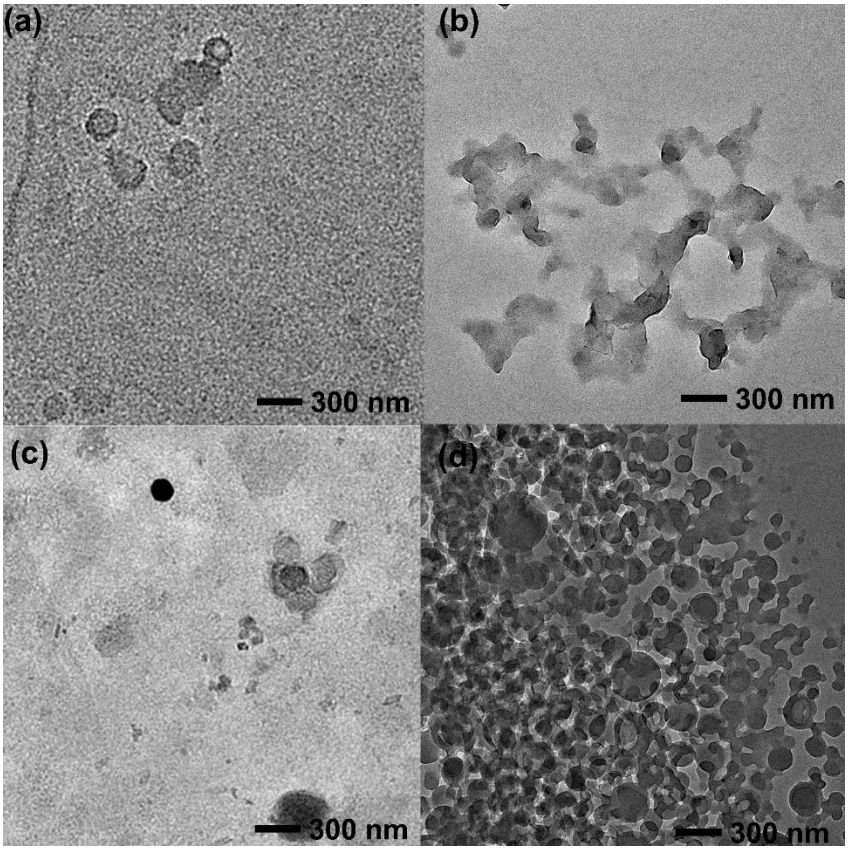

Figure S23 Transmission electron microscopic images of (a)-(b)**4a** and (c)-(d)**4b** aggregates under different water fractions(0, 99%).

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5. Structural Characterization

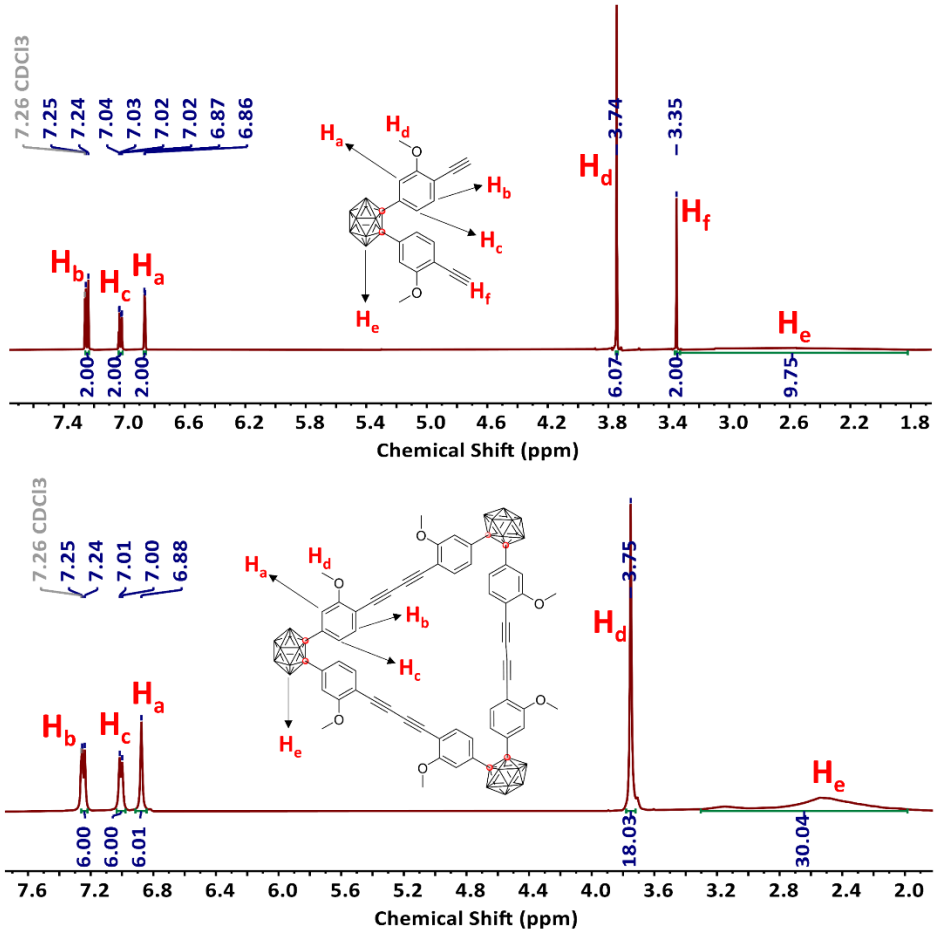

Figure S24 ^{1}H NMR spectrum of **3b** and **4b** in $CDCl_3$.

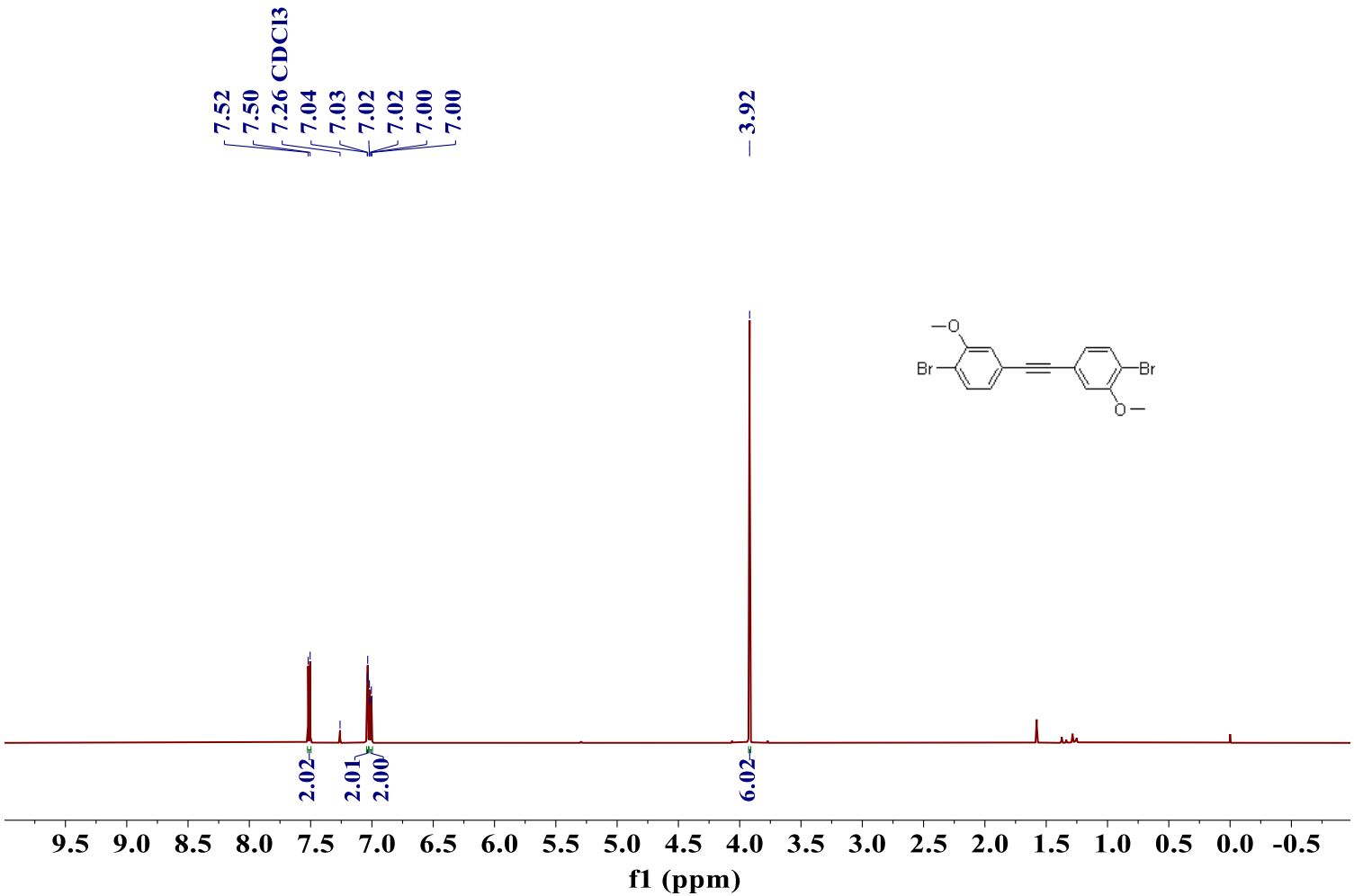

Figure S25 ^{1}H NMR spectrum of **1b** in $CDCl_3$.

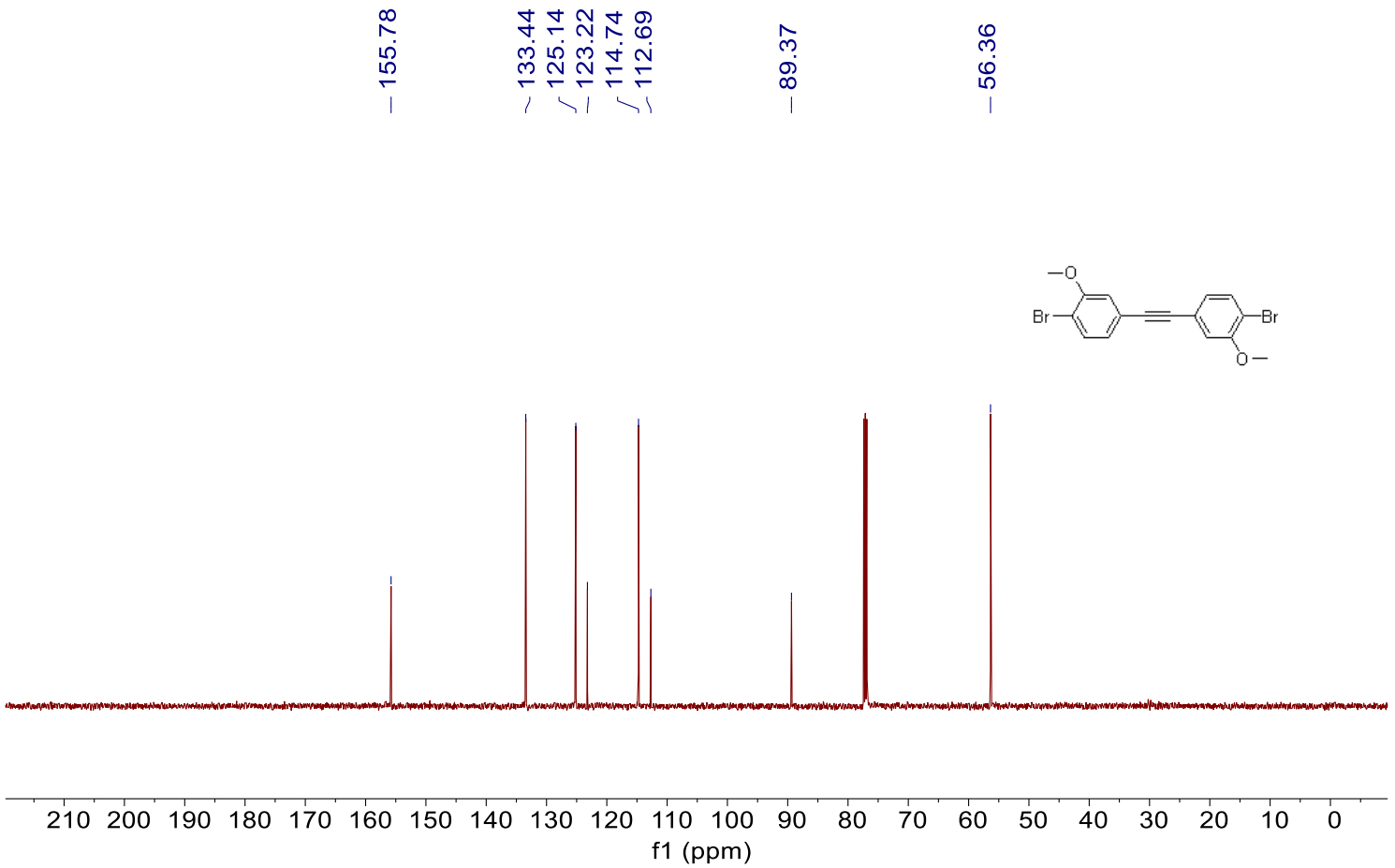

Figure S26 ^{13}C NMR spectrum of **1b** in $CDCl_3$.

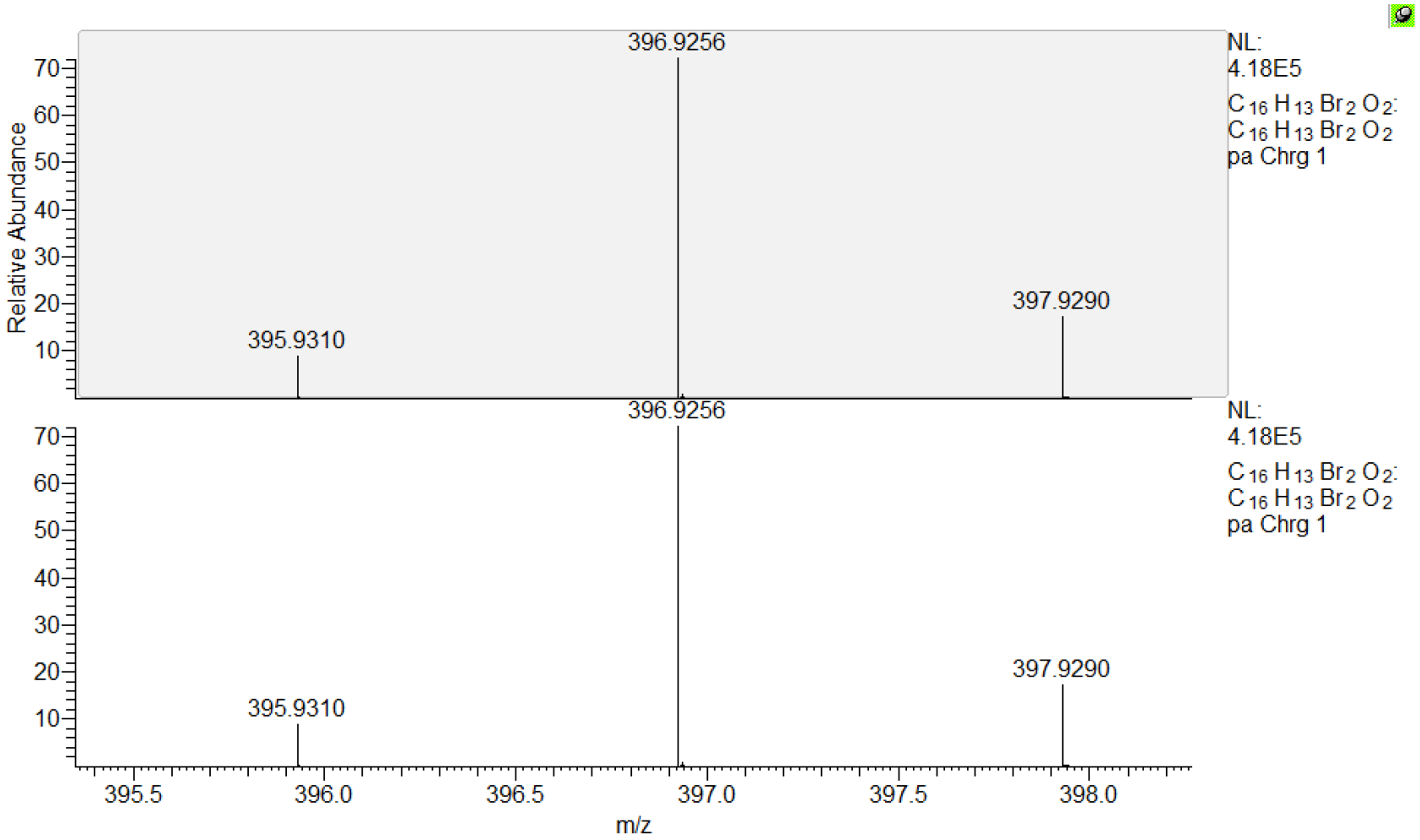

Figure S27 HRMS spectrum of **1b**.

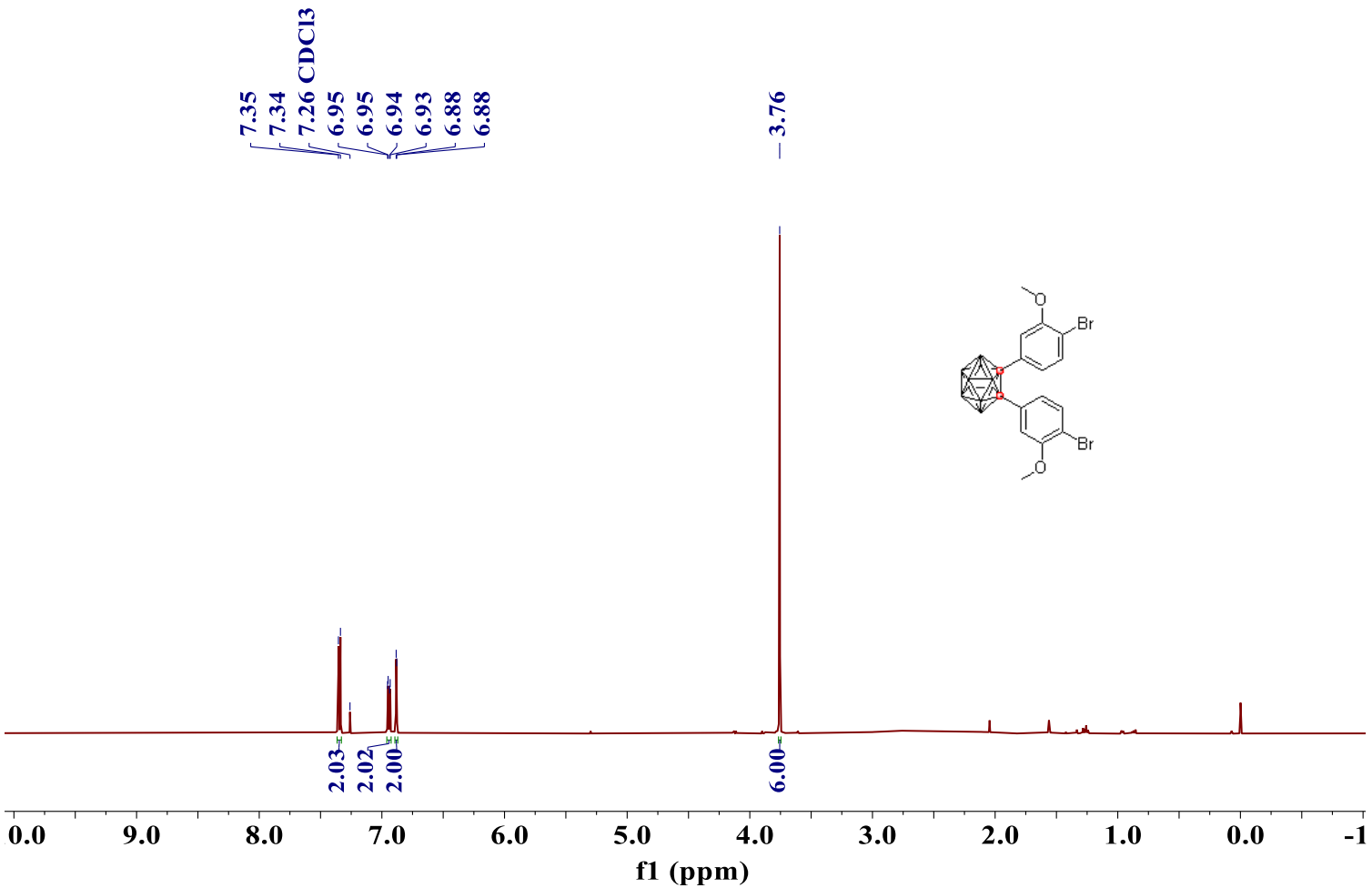

Figure S28 ^{1}H NMR spectrum of **2b** in $CDCl_3$.

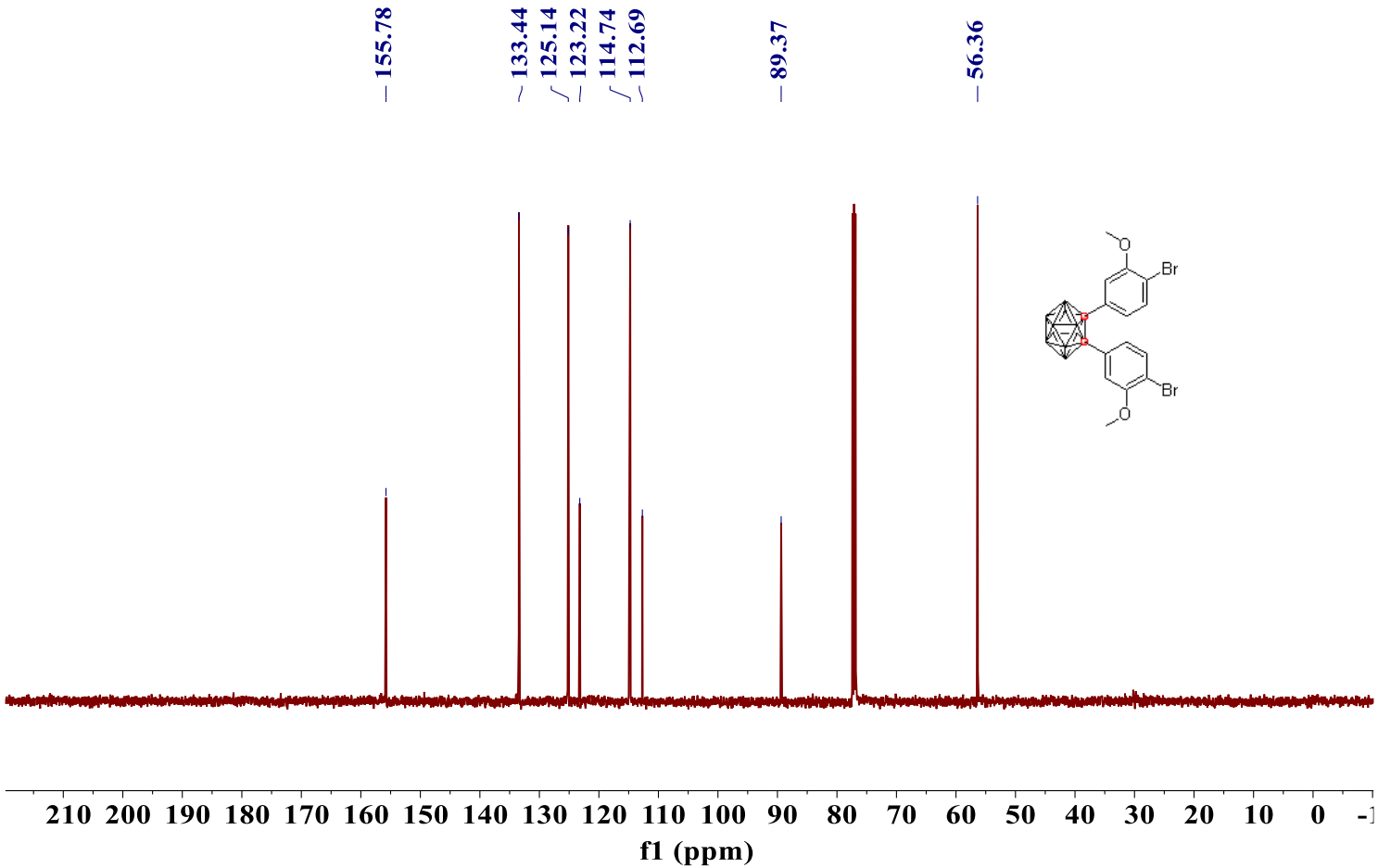

Figure S29 ^{13}C NMR spectrum of **2b** in $CDCl_3$.

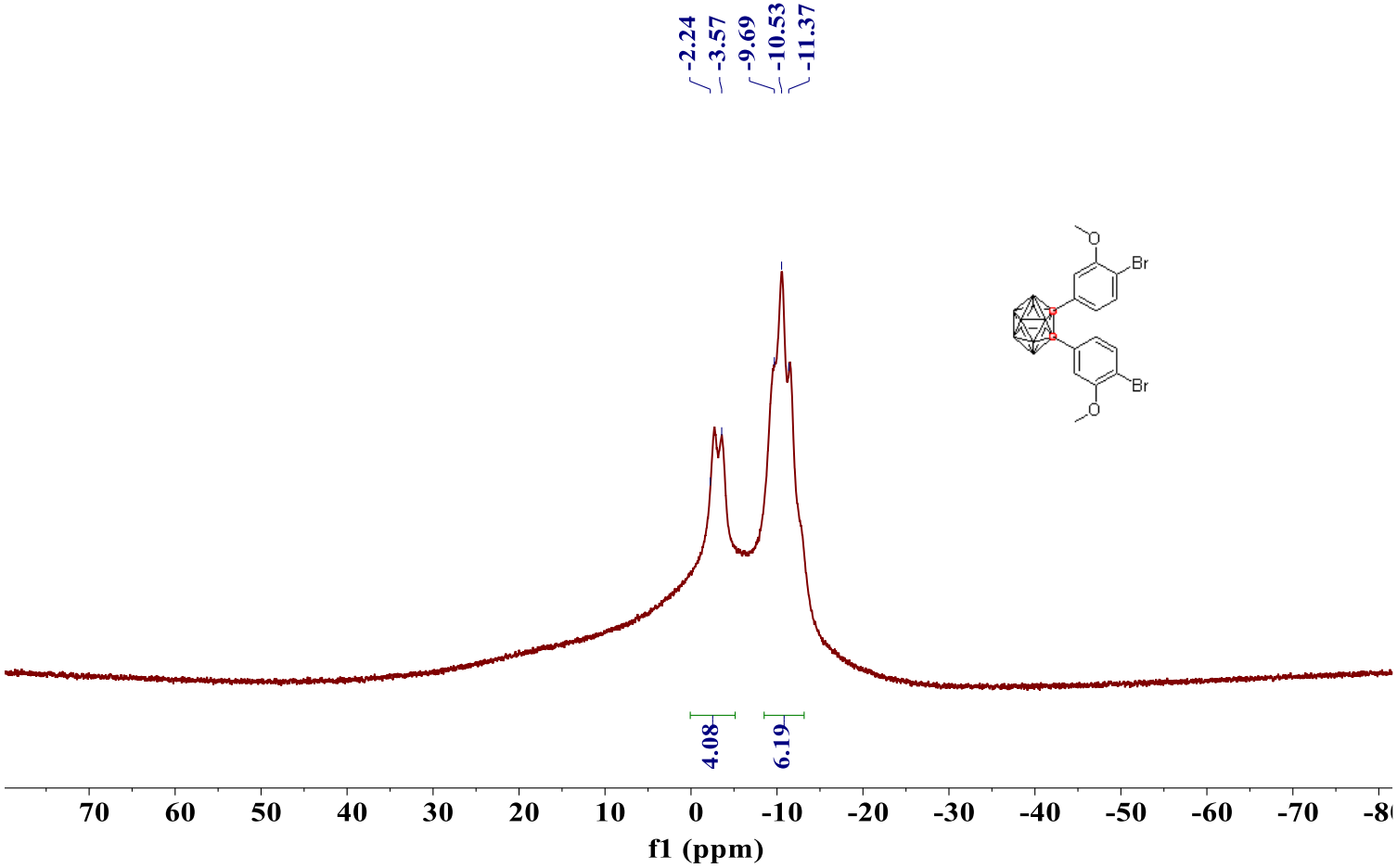

Figure S30 ^{11}B NMR spectrum of **2b** in $CDCl_3$.

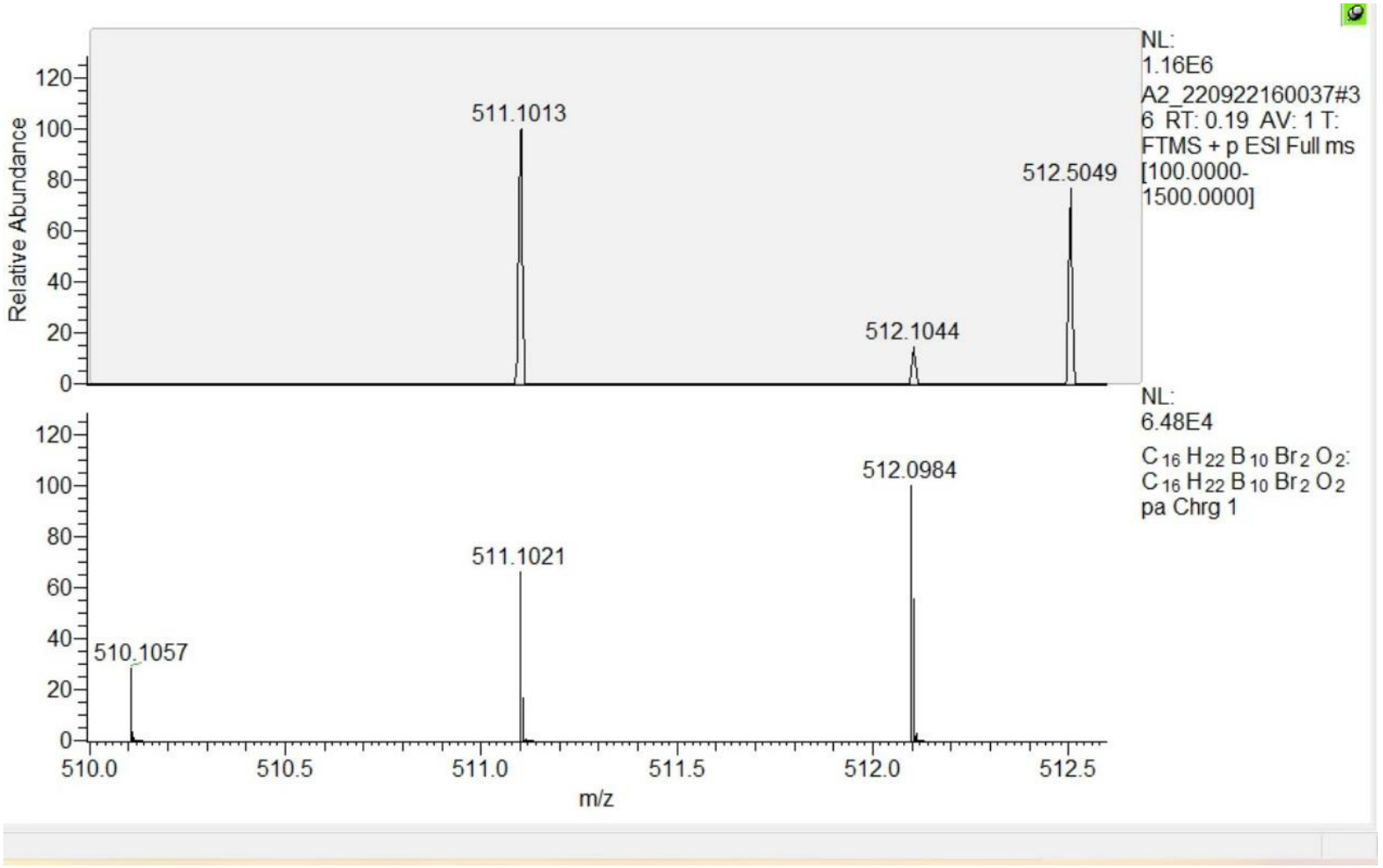

Figure S31 HRMS spectrum of **2b**.

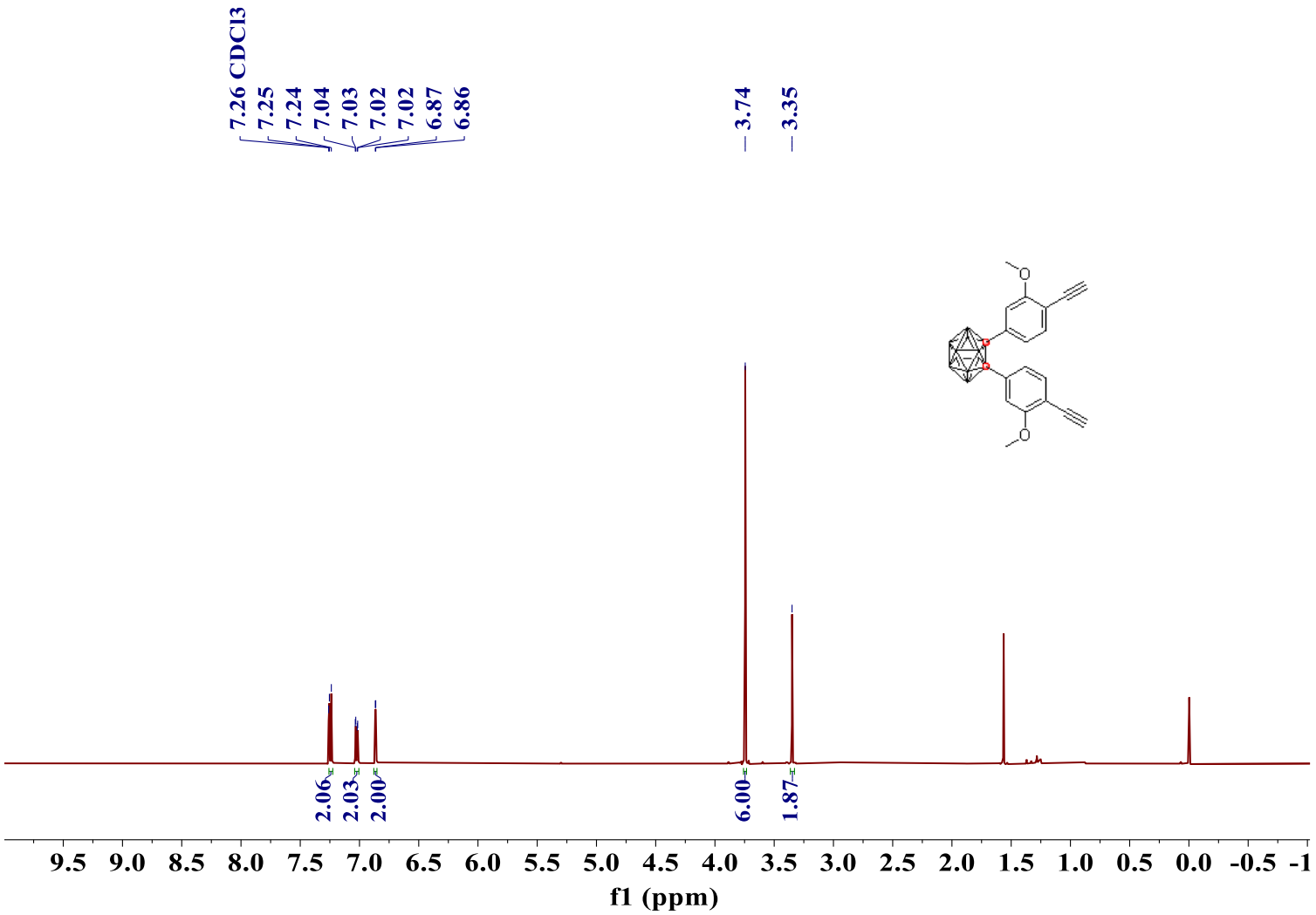

Figure S32 ^{1}H NMR spectrum of **3b** in $CDCl_3$.

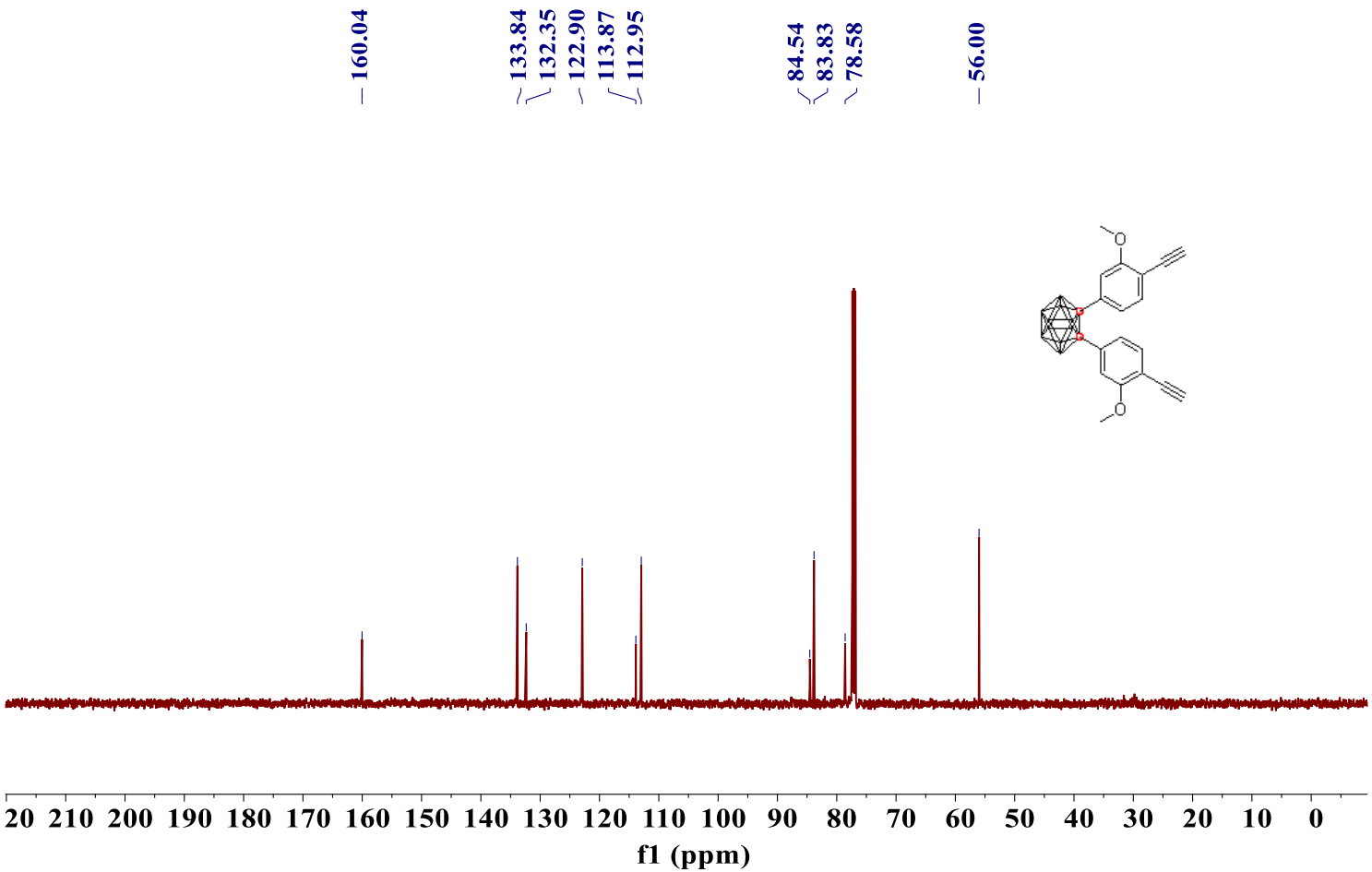

Figure S33 ^{13}C NMR spectrum of **3b** in $CDCl_3$.

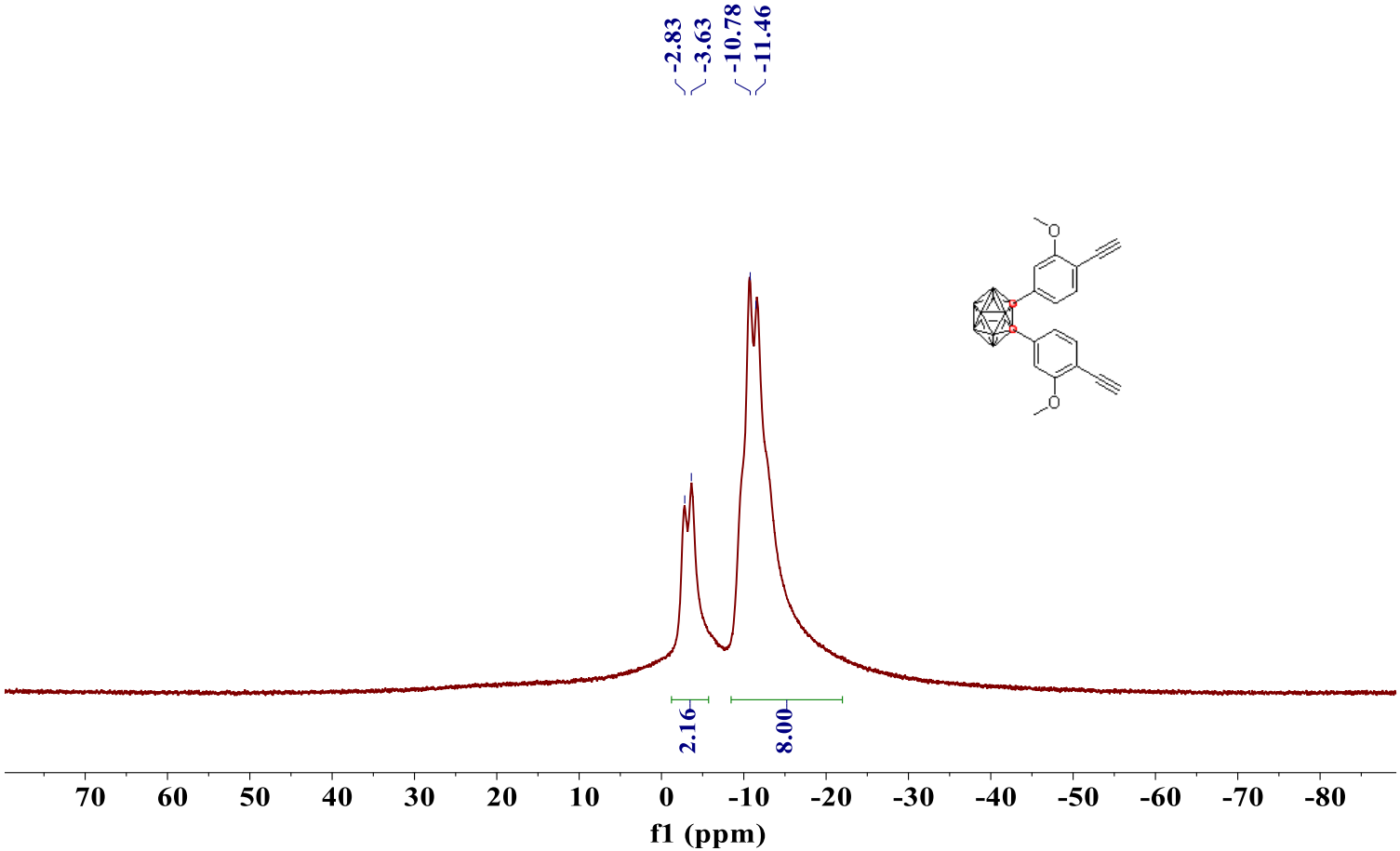

Figure S34 ^{11}B NMR spectrum of **3b** in $CDCl_3$.

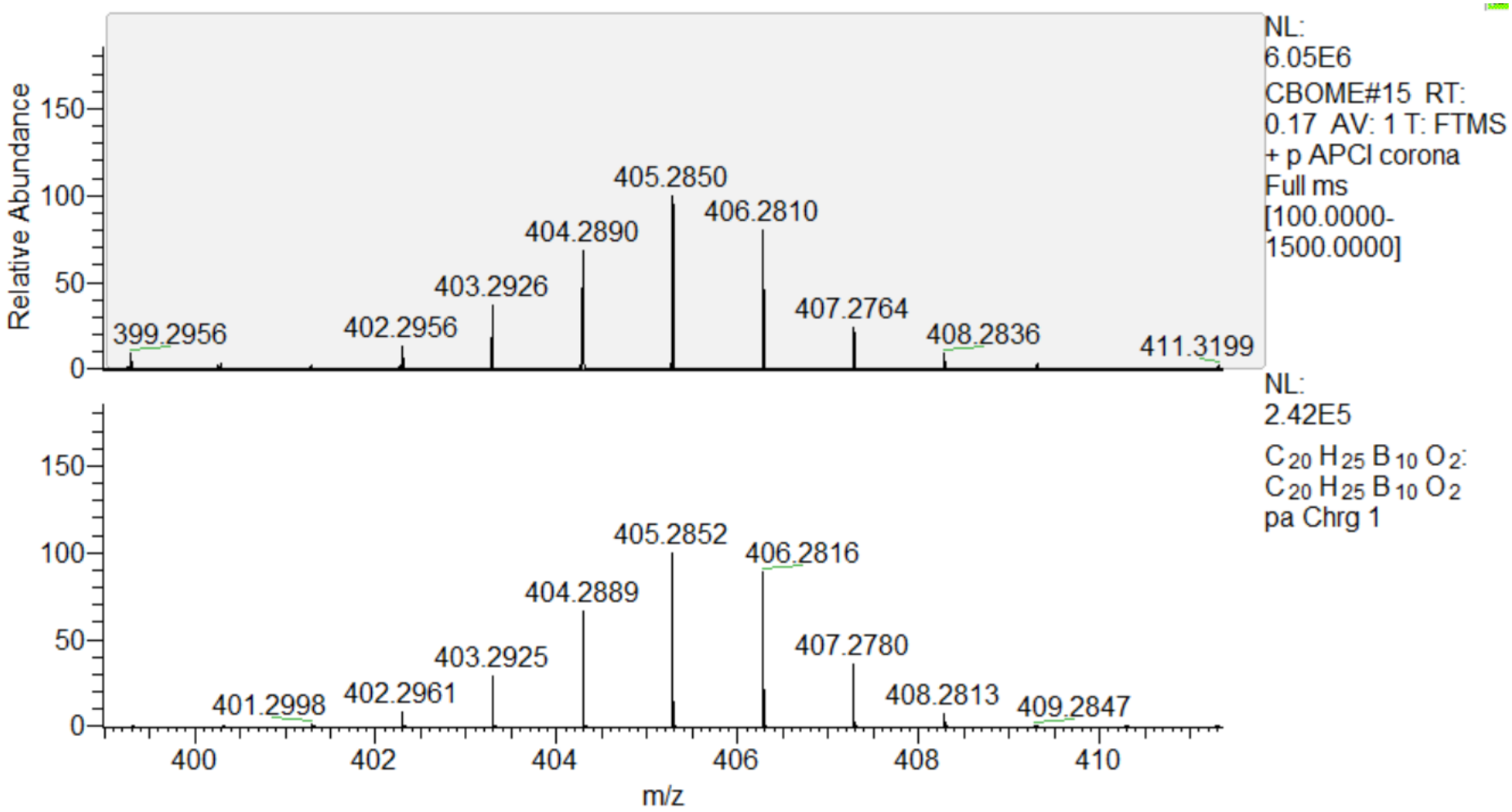

Figure S35 HRMS spectrum of **3b**.

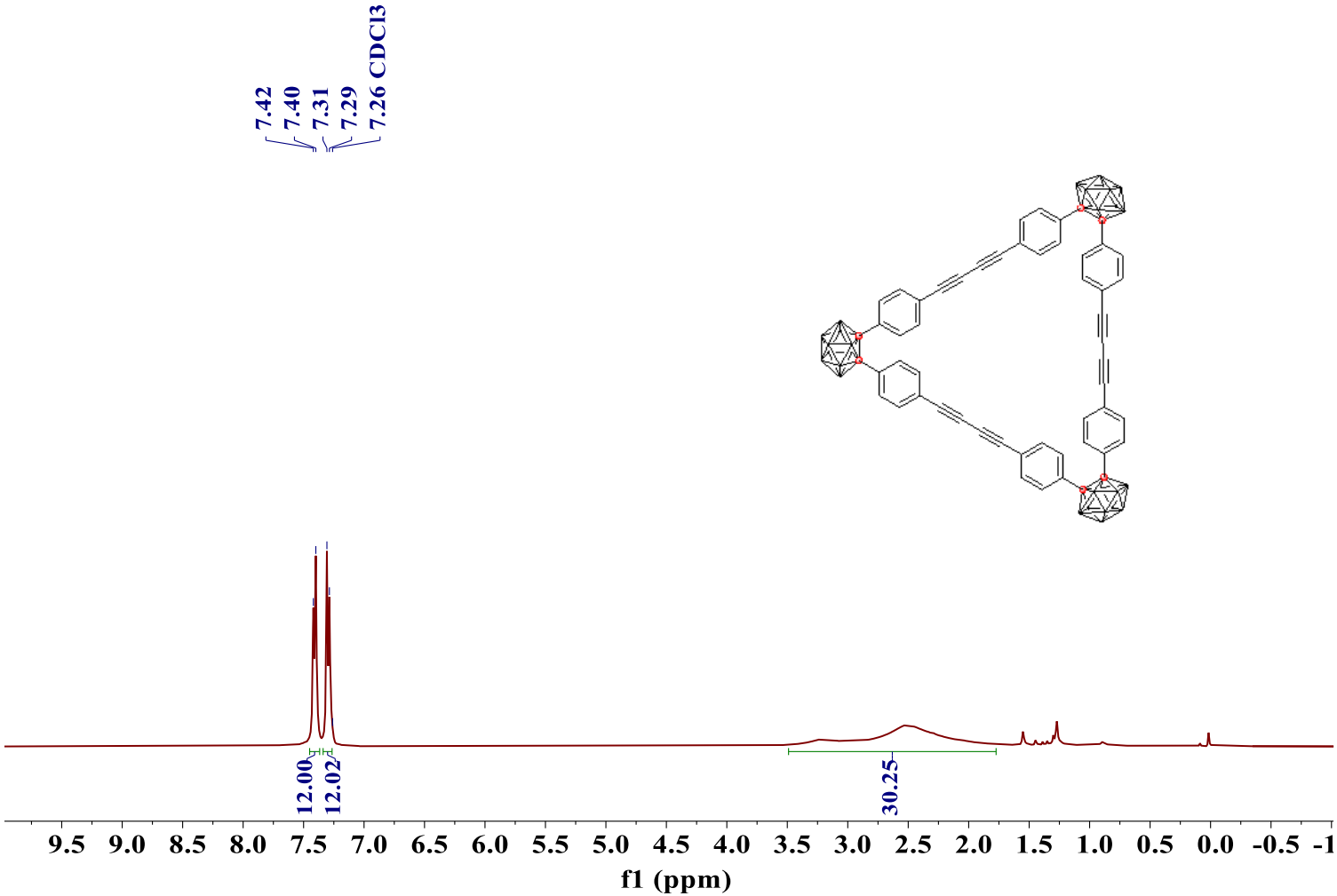

Figure S36 ^{1}H NMR spectrum of **4a** in $CDCl_3$.

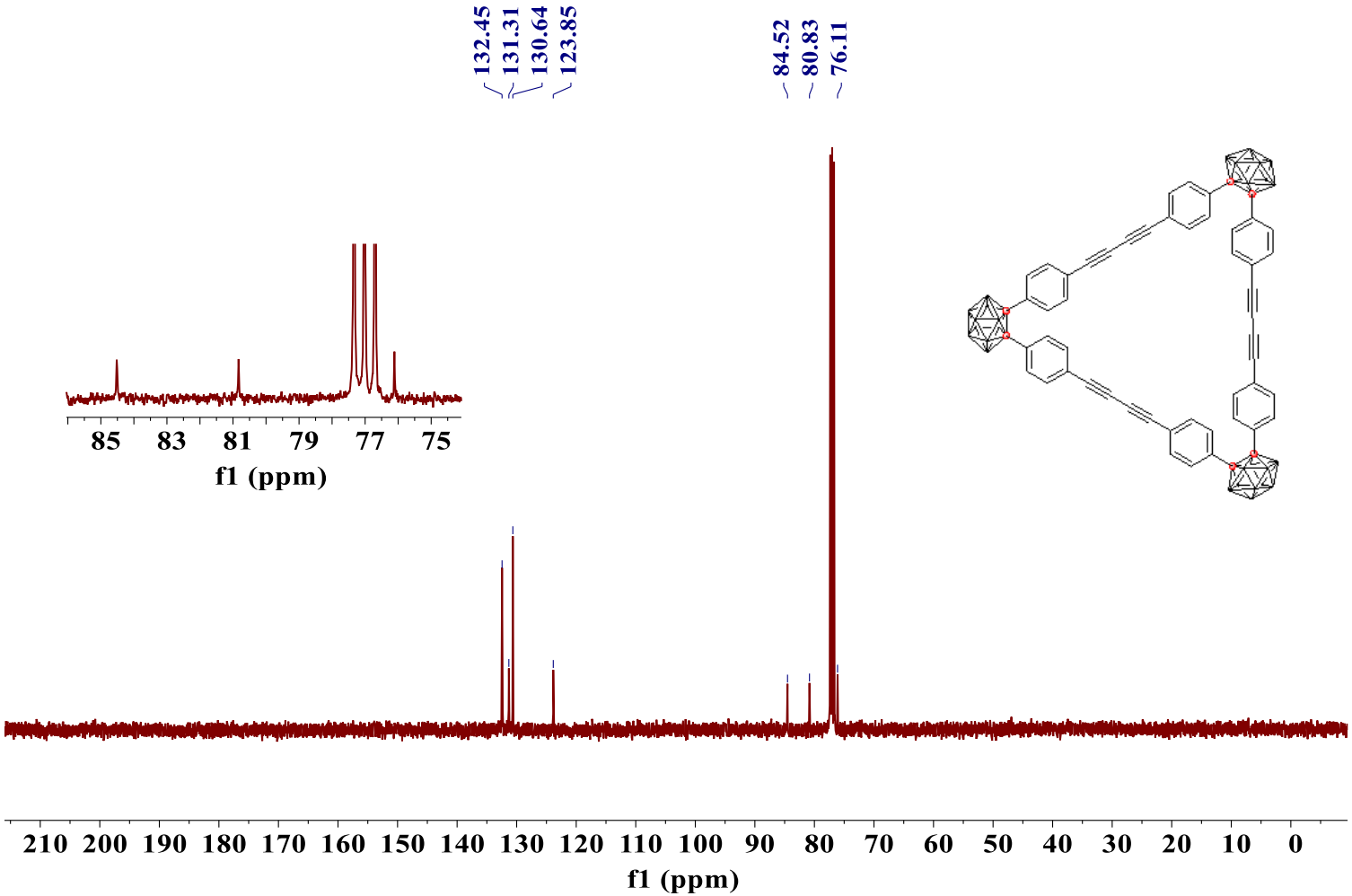

Figure S37 ^{13}C NMR spectrum of **4a** in $CDCl_3$.

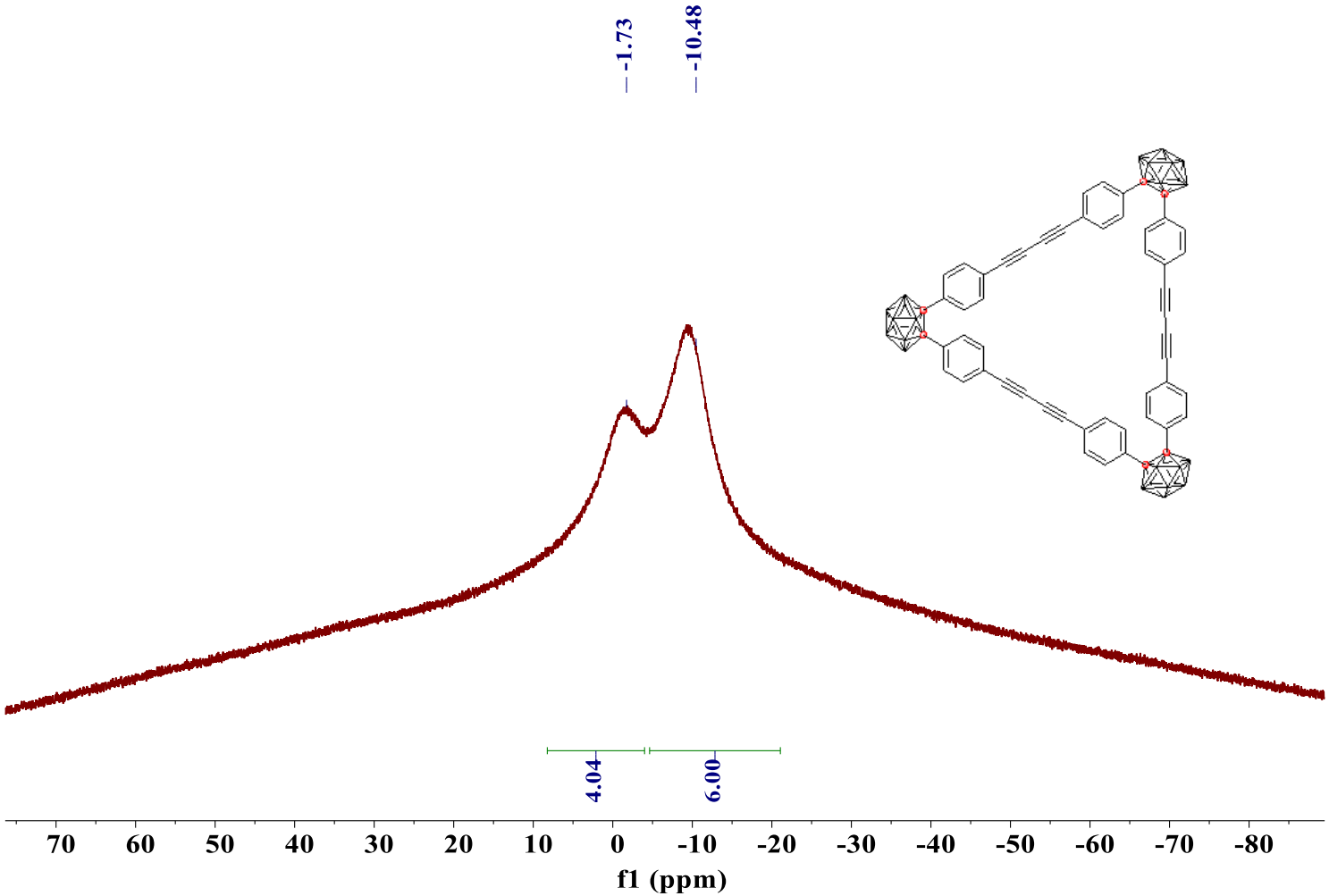

Figure S38 ^{11}B NMR spectrum of **4a** in $CDCl_3$.

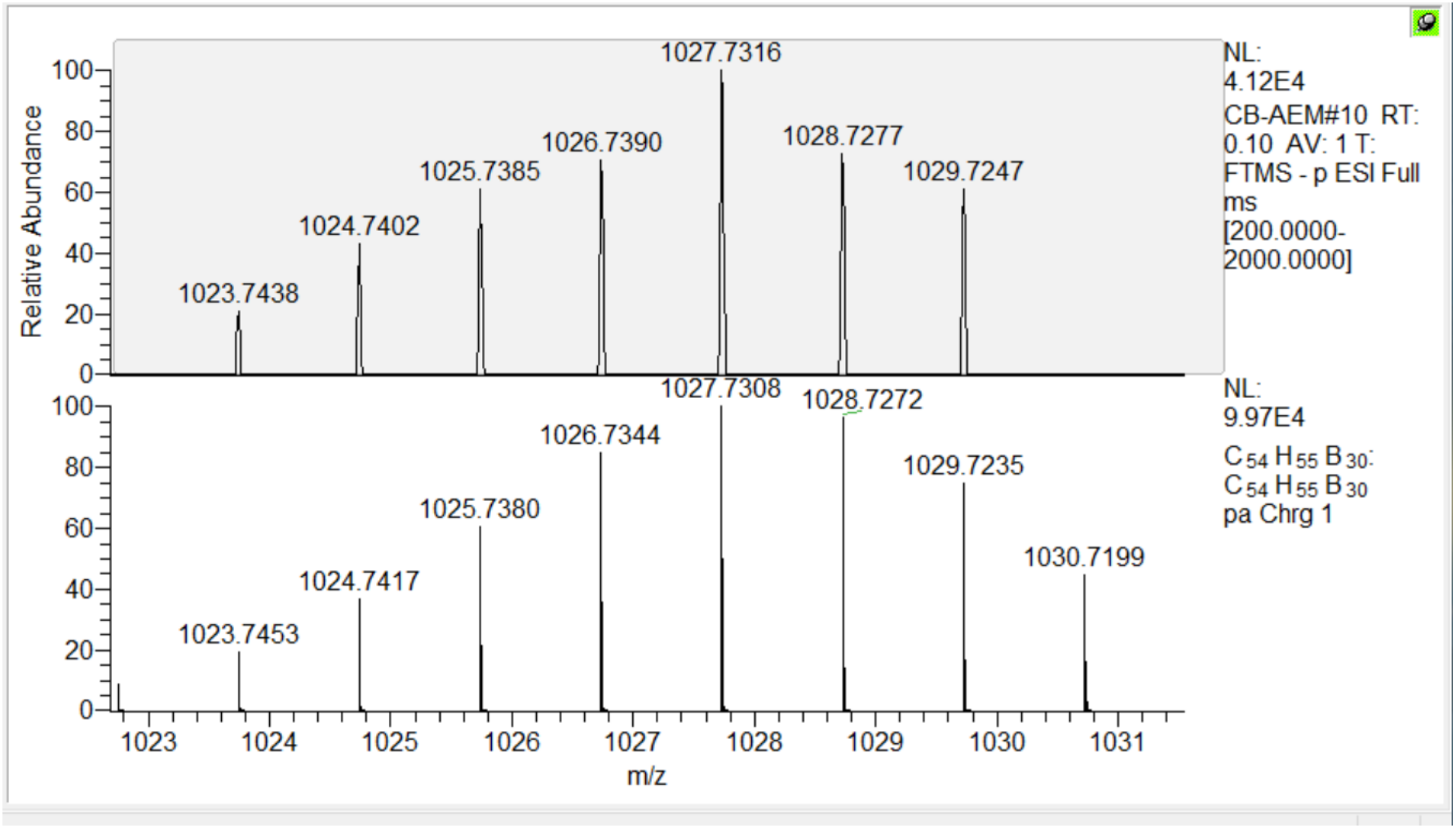

Figure S39 HRMS spectrum of **4a**.

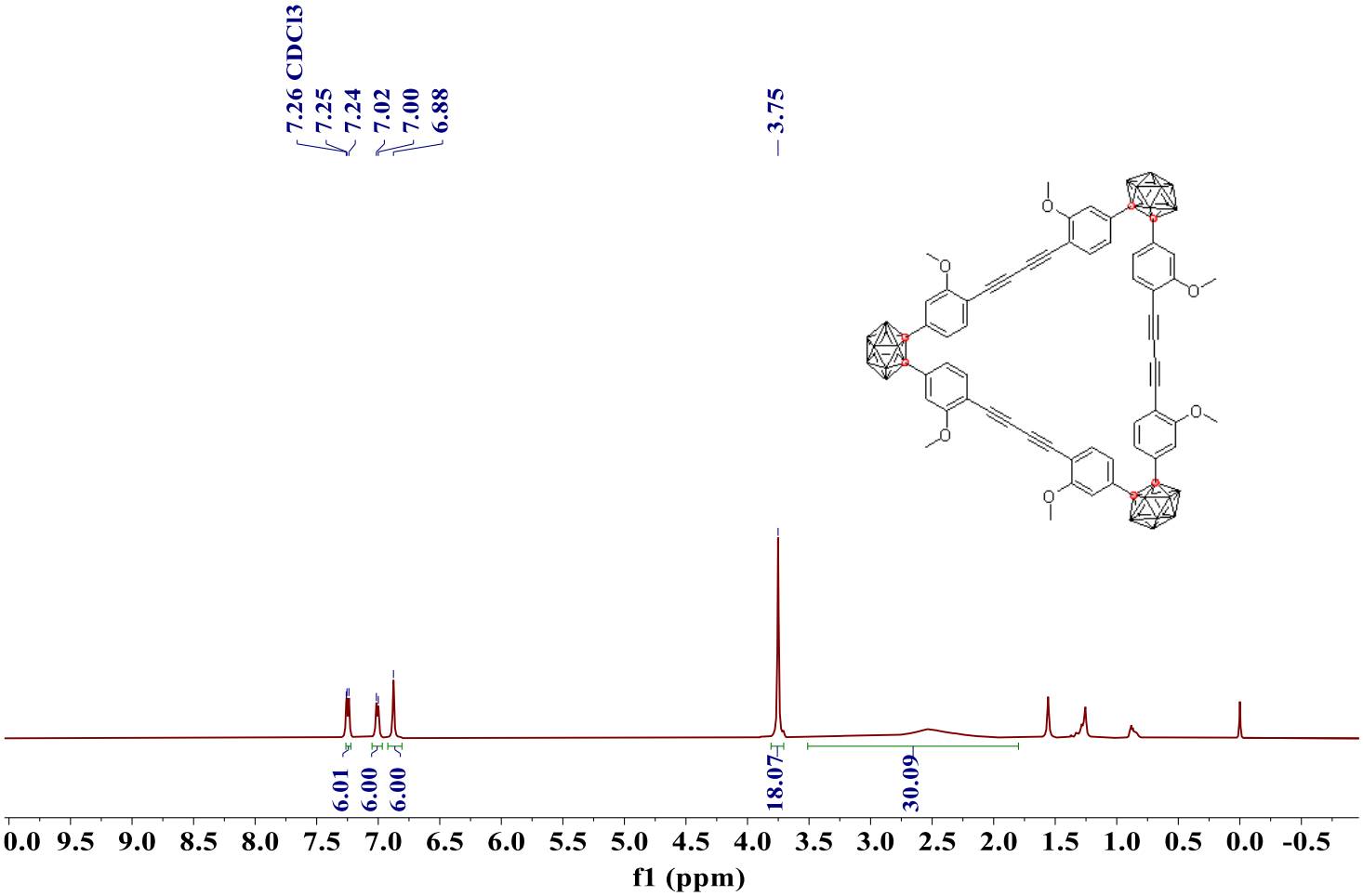

Figure S40 ^{13}C NMR spectrum of **4b** in $CDCl_3$.

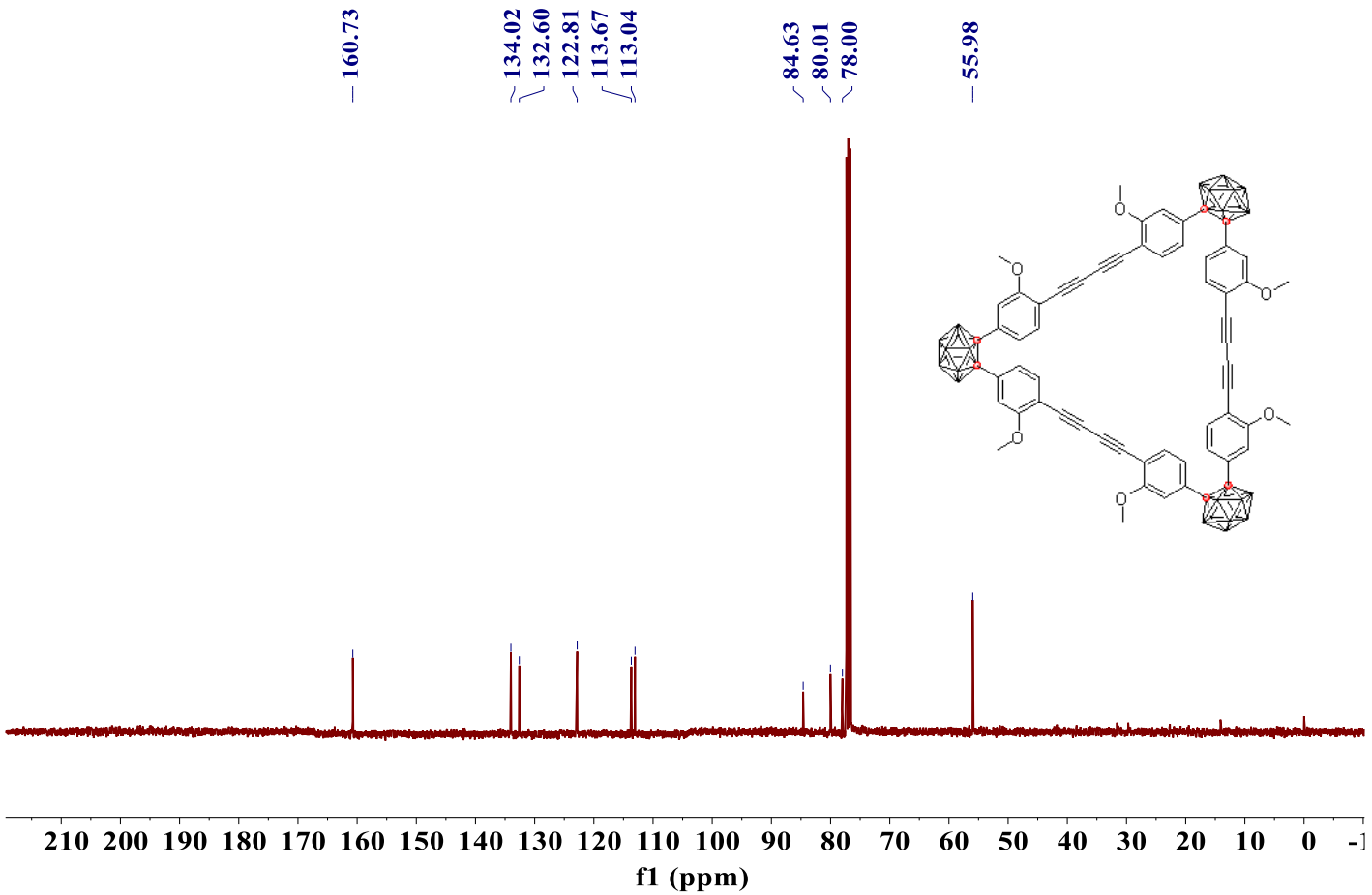

Figure S41 ^{1}H NMR spectrum of **4b** in $CDCl_3$.

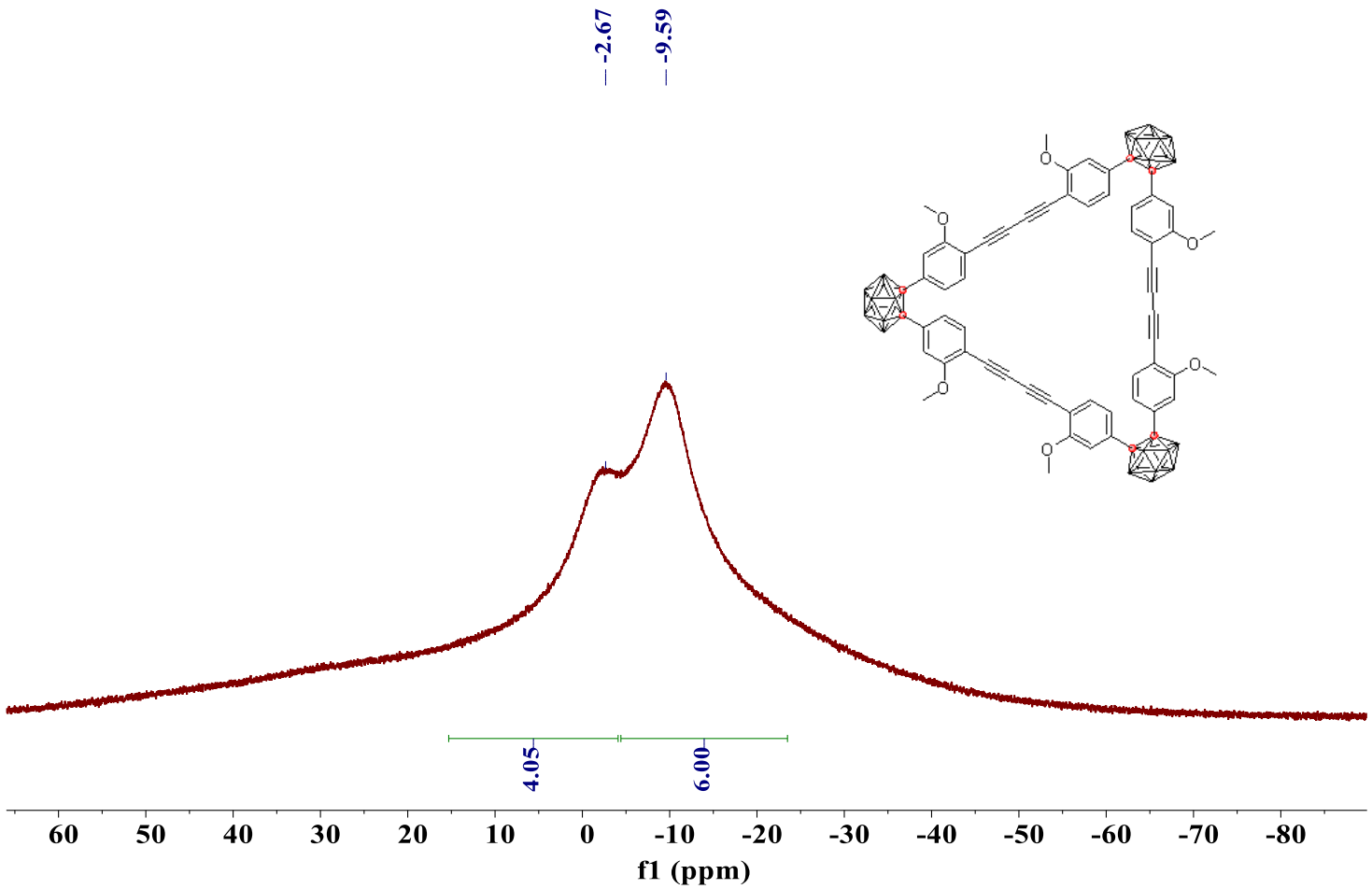

Figure S42 ^{11}B NMR spectrum of **4b** in $CDCl_3$.

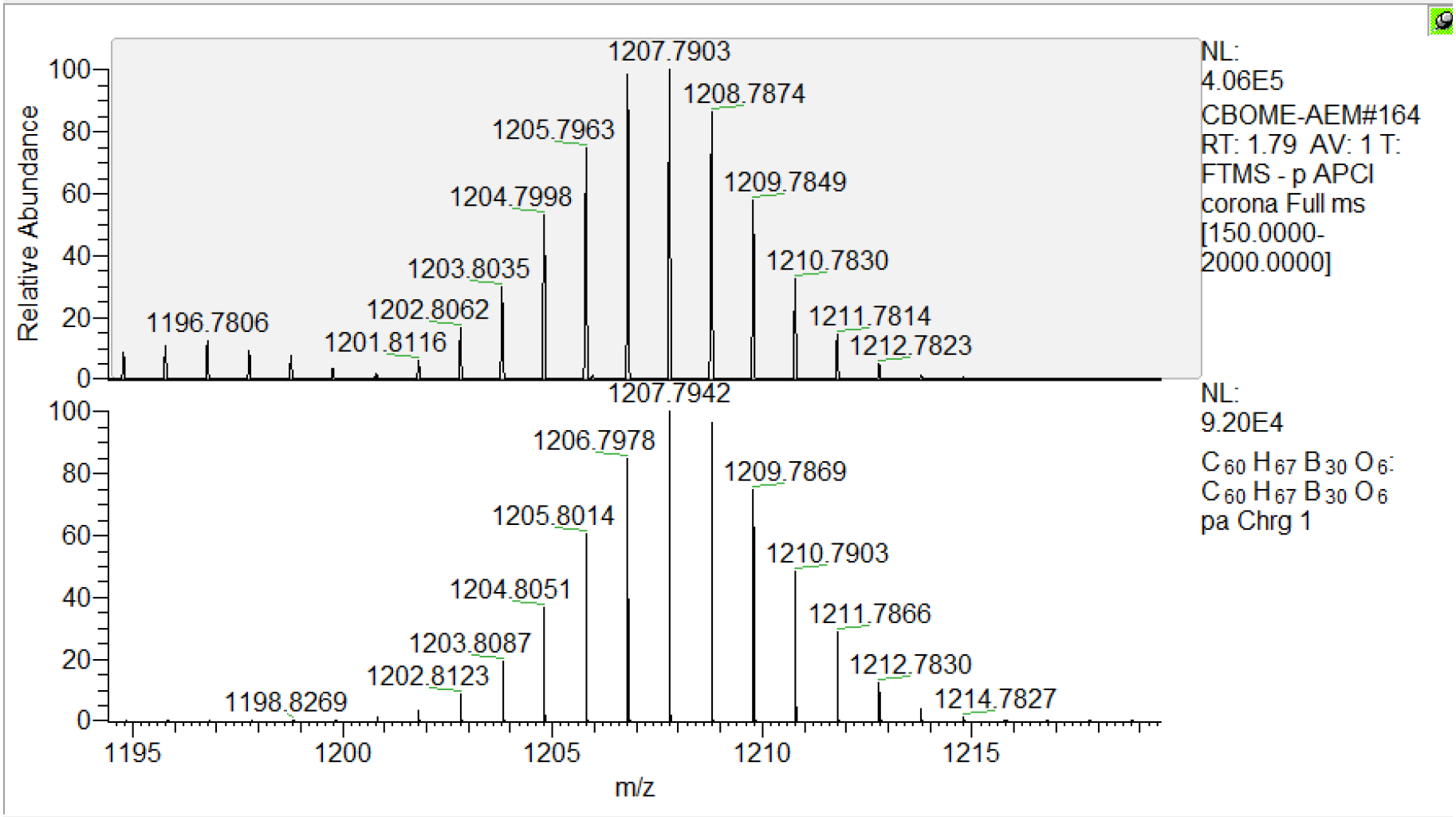

Figure S43 HRMS spectrum of **4b**.