Supporting Information

Rapid access to functionalized nanographenes through a palladium-catalyzed multi-annulation sequence

Takehisa Maekawa*[a] and Kenichiro Itami*[abc]

[a] *Institute of Chemistry, Academia Sinica, 128 Academia Road, Section 2, Nankang, Taipei 115201, Taiwan.*

[b] *Molecule Creation Laboratory, Cluster for Pioneering Research, RIKEN, Wako, Saitama 351-0198, Japan.*

[c] *Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya 464-8602, Japan.*

*E-mail: tmaekawa@gate.sinica.edu.tw (T.M.)

*E-mail: kenichiro.itami@riken.jp (K.I.)

Table of Contents

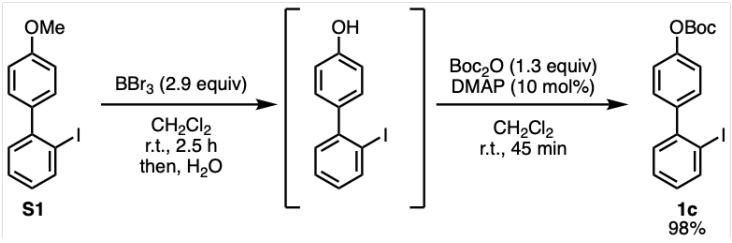
1	Material and methods	2
2.	Synthesis of starting materials	3–11
3.	Procedure for palladium-catalyzed multi-annulation sequence	12–21
4.	Further derivatization of **3ah'** and **3cm**	21–26
5.	Measurements of UV/vis absorption spectra	27–29
6.	Computational study	30–31
7.	Single crystal X-ray diffraction and structural analysis of **3ao'**	32–33
8.	Proposed reaction mechanism	34
9.	References	35
10.	^{1}H, ^{13}C and NOESY NMR spectra	36–152
11.	HRMS spectra	153-174

1. Material and methods

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. 2-Iodobiphenyl (**1a**) was purchased from Tokyo Chemical Industry (TCI). $Pd(OAc)_2$ was purchased from UniRegion Bio-Tech (UR). $P^tBu_2Me \cdot HBF_4$ was purchased from Combi-Blocks. 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU) was purchased from Alfa Aesar. Anhydrous KOAc was purchased from Sigma-Aldrich and stored in a glove box. Anhydrous N,N-dimethylformamide (DMF) was purchased from Thermo Fisher Scientific. 1,4-Diiodo-2,5-diphenylbenzene (**1b**)[S1], 2-iodo-4'-methoxy-1,1'-biphenyl (**S1**)[S2], 4-iodophenyl acetate (**S3**)[S3], 3-iodophenyl acetate (**S4**)[S4], 5-iodopyrimidine (**S5**)[S5], 3-iodoquinoline (**S6**)[S6], butyl 4-iodobenzoate (**S7**)[S7] were prepared according to previously reported literatures. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in heat-dried glassware with standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air. Analytical thin-layer chromatography (TLC) was performed using SiliaPlate™ glass-baked TLC plates (Silica gel, 250 μm thickness, F254 indicator). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). Flash column chromatography was performed with SiliaFlash® P60 40-63μm (230-400 mesh) 60Å irregular silica gels. Gel permeation chromatography (GPC) was performed with a JAI LaboAce 5060P instrument (Japan Analytical Industry) equipped with two JAIGEL-2H plus columns using chloroform with 1% ethanol as an eluent. High-resolution ESI mass spectra (HRMS) were conducted on a JMS-T100LP AccuTOF LC-plus 4G TOF mass spectrometer (JEOL). High-resolution EI and FAB mass spectra were conducted on a JMS-700 double-focusing magnetic sector mass spectrometer (JEOL) with a resolution of 8000 (5% valley definition). For FAB mass spectra, the source accelerating voltage was operated 10kV with Xe gun, using 3-nitrobenzyl alcohol(NBA) as a matrix. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVIII-400 (^{1}H: 400 MHz; ^{13}C: 101 MHz, NOESY: 400 MHz) spectrometer and a Bruker AV300 (^{1}H: 300 MHz, ^{13}C: 75M Hz). Chemical shifts in ^{1}H NMR spectra are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm), $CDCl_3$(δ 7.26 ppm), CD_2Cl_2 (δ 5.32 ppm), DMSO-d_6 (δ 2.50 ppm) or THF-d_8 (δ 3.58 ppm). Chemical shifts in ^{13}C NMR spectra are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm), CD_2Cl_2 (δ 53.84 ppm), DMSO-d_6 (δ 39.52 ppm) or THF-d_8 (δ 67.57 ppm). Chemical shift data are reported as follows: chemical shift (δ: ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, dt = doublet of triples, tt = triplet of triplets, m = multiplet, q = quartet, brd = broad), coupling constant (*J*: Hz), and integration. NOESY NMR spectra were recorded using a standard 'noesygpphpp' pulse sequence with 2.0 s relaxation delay and 800 ms mixing time.

2. Synthesis of starting materials

2.1 Synthesis of *tert*-butyl (2'-iodo-[1,1'-biphenyl]-4-yl) carbonate (1c)

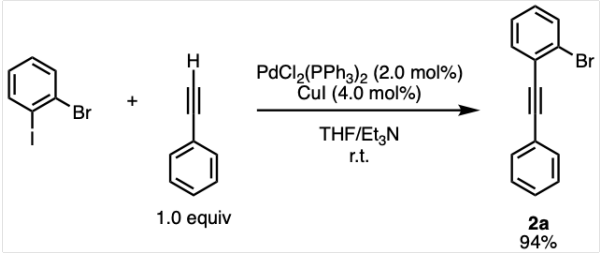


2-Iodo-4'-methoxy-1,1'-biphenyl (**S1**) (320 mg, 1.03 mmol, 1.00 equiv) was added to a heat-dried 25-mL Schlenk tube with a magnetic stirring bar. The Schlenk tube was repeatedly evacuated and backfilled with N_2 three times. Dry CH_2Cl_2 (10 mL) was added to the Schlenk tube and the mixture was cooled to 0 °C. A solution of 1.0 M BBr_3 in CH_2Cl_2 (3.0 mL, 3.00 mol, 2.91 equiv) was added dropwise to the mixture for over 10 minutes. After stirring at 0 °C for 30 minutes, the mixture was successively stirred at room temperature (27 °C) for 2 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was slowly poured into crushed ice and stirred for 30 minutes and the mixture was extracted with CH_2Cl_2 (20 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, and then filtered. The filtrate was concentrated under reduced pressure to afford the crude demethylated product.

The thus-obtained crude material was successively added to a 25-mL round bottom flask with a magnetic stirring bar. CH_2Cl_2 (5.0 mL) and 4-dimethylaminopyridine (DMAP) (13.0 mg, 0.107 mmol, 10.0 mol%) were added to the flask. Then, di-*tert*-butyl dicarbonate (Boc_2O) (285 mg, 1.31 mmol, 1.27 equiv) was added dropwise to the flask for over 5 min and the mixture was continuously stirred at room temperature for 45 minutes. After the completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 100:0 → 20:1) to afford *tert*-butyl (2'-iodo-[1,1'-biphenyl]-4-yl) carbonate (**1c**) (402 mg, 1.01 mmol, 98% yield) as a pale yellow viscous oil.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.97 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.38–7.31 (m, 3H), 7.21 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.06 (ddd, *J* = 7.9, 7.3, 1.8 Hz, 1H), 1.56 (s, 9H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 152.2, 151.2, 146.2, 142.1, 140.0, 130.8, 130.6, 129.4, 128.7, 121.3, 98.8, 83.9, 27.9. **HRMS** (EI, positive) *m/z* calcd for $C_{17}H_{17}IO_3$ $[M]^+$: 396.0222. Found: 396.0216.

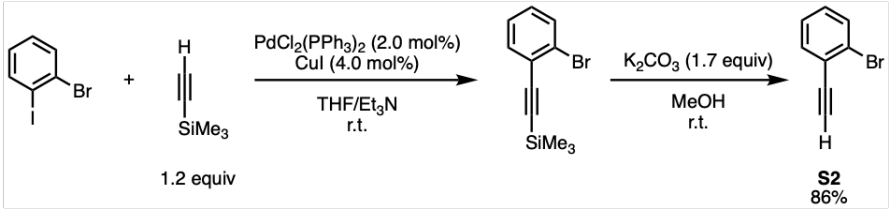
2.2 Synthesis of 1-bromo-2-(phenylethynyl)benzene (2a)



$PdCl_2(PPh_3)_2$ (280 mg, 0.399 mmol, 2.0 mol%) and CuI (152 mg, 0.798 mmol, 4.0 mol%) were added to a heat-dried 250-mL two-neck flask with a magnetic stirring bar. The flask was repeatedly evacuated and backfilled with N_2 three times. 1-Bromo-2-iodobenzene (5.59 g, 19.8 mmol, 1.00 equiv) and ethynylbenzene (2.07 g, 20.4 mmol, 1.02 equiv) were added to the flask. Anhydrous tetrahydrofuran (THF) (50 mL) and degassed triethylamine (50 mL) were added to the flask and the mixture was stirred at room temperature (27 °C) for 1 hour. After completion of the reaction (monitored by TLC), the reaction was quenched by saturated NH_4Cl aqueous solution (50 mL). The mixture was extracted with hexane (40 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by passing through a short silica gel plug (100% hexane) to afford 1-bromo-2-(phenylethynyl)benzene (**2a**) (4.76 g, 18.5 mmol, 94% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.54 (m, 4H), 7.40–7.33 (m, 3H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.18 (ddd, *J* = 7.9, 7.5, 1.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.4, 132.6, 131.8, 129.5, 128.8, 128.5, 127.2, 125.8, 125.6, 123.1, 94.1, 88.2. **HRMS** (EI, positive) *m/z* calcd for $C_{14}H_9Br$ $[M]^+$: 255.9888. Found: 255.9880.
Spectroscopic data are in accordance with those described in the literature.[S8]

2.3 Synthesis of 1-bromo-2-ethynylbenzene (S2)

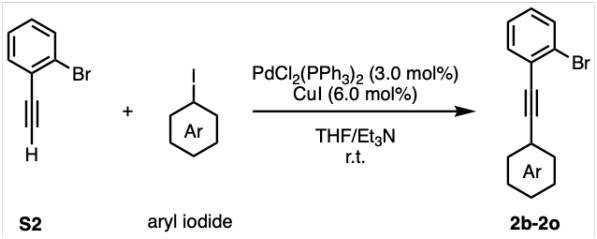


$PdCl_2(PPh_3)_2$ (140 mg, 0.199 mmol, 2.0 mol%) and CuI (76.6 mg, 0.402 mmol, 4.0 mol%) were added to a heat-dried 250-mL two-neck flask with a magnetic stirring bar. The flask was repeatedly evacuated and backfilled with N_2 three times. 1-Bromo-2-iodobenzene (2.85 g, 10.1 mmol, 1.00 equiv) and trimethylsilylacetylene (1.14 g, 11.6 mmol, 1.15 equiv) were added to the flask. Dry THF (30 mL) and degassed triethylamine (20 mL) were added to the flask and the mixture was stirred at room temperature (27 °C) for 10 hours. After completion of the reaction (monitored by TLC), the reaction was quenched by saturated NH_4Cl aqueous solution (30 mL). The mixture was extracted with hexane (20 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was roughly purified by passing through a short silica gel plug (100% hexane) to afford a yellow oil. Successively, the oil was added to a 250-mL round bottom flask with a magnetic stirring bar. MeOH (30 mL) and K_2CO_3 (2.34 g, 17.0 mmol, 1.69 equiv) were added to the flask and the mixture was vigorously stirred at room temperature for 3 hours. The reaction mixture was

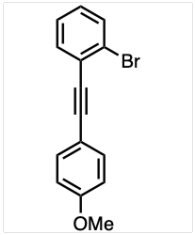
diluted with H_2O (30 mL) and extracted with hexane (30 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (100% hexane) to afford 1-bromo-2-ethynylbenzene (**S2**) (1.57 g, 8.67 mmol, 86% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.27 (td, *J* = 7.5, 1.3 Hz, 1H), 7.20 (td, *J* = 7.7, 1.8 Hz, 1H), 3.38 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.2, 132.5, 130.1, 127.1, 125.7, 124.4, 82.01, 81.96. Spectroscopic data are in accordance with those described in the literature.[S9]

2.4 General procedure for synthesis of diarylacetylenes (2b–2o)

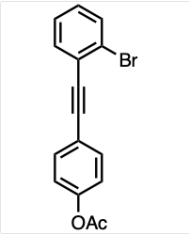


Aryl iodide (1.00 mmol, 1.00 equiv), $PdCl_2(PPh_3)_2$ (21.1 mg, 0.0300 mmol, 3.0 mol%) and CuI (11.4 mg, 0.0600 mmol, 6.0 mol%) were added to a heat-dried 25-mL Schlenk tube with a magnetic stirring bar. The tube was evacuated and backfilled with N_2 three times. 1-Bromo-2-ethynylbenzene (**S2**) (199 mg, 1.10 mmol, 1.10 equiv) were added to the Schlenk tube. Anhydrous THF (5.0 mL) and degassed triethylamine (5.0 mL) were added to the Schlenk tube and the mixture was stirred at room temperature (27 °C) for 2–10 hours. After completion of the reaction (monitored by TLC), the reaction was quenched by saturated NH_4Cl aqueous solution (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.



1-Bromo-2-((4-methoxyphenyl)ethynyl)benzene (2b) was prepared according to the general procedure. 4-Iodoanisole (233 mg, 1.00 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (208 mg, 1.16 mmol, 1.16 equiv), $PdCl_2(PPh_3)_2$ (20.8 mg, 0.0296 mmol, 3.0 mol%), CuI (12.3 mg, 0.0646 mmol, 6.5 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 10:1) to afford the product (265 mg, 0.921 mmol, 92% yield) as a white solid.

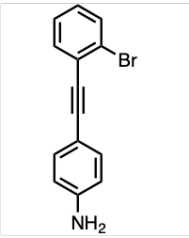
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.56–7.49 (m, 3H), 7.27 (td, *J* = 7.6, 1.3 Hz, 1H, overlapped with solvent peak), 7.15 (td, *J* = 7.8, 1.7 Hz, 1H), 6.89 (dt, *J* = 8.8, 2.4 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.1, 133.4, 133.2, 132.6, 129.1, 127.1, 125.9, 125.6, 115.2, 114.2, 94.3, 87.0, 55.5. **HRMS** (EI, positive) *m/z* calcd for $C_{15}H_{11}BrO$ $[M]^+$: 285.9996. Found: 285.9993. Spectroscopic data are in accordance with those described in the literature.[S8]



4-((2-Bromophenyl)ethynyl)phenyl acetate (2c) was prepared according to the general procedure. 4-Iodophenyl acetate (**S3**) (263 mg, 1.00 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (189 mg, 1.05 mmol, 1.05 equiv), $PdCl_2(PPh_3)_2$ (20.4 mg, 0.0291 mmol, 2.9 mol%), CuI (10.6 mg, 0.0559 mmol, 5.6 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford the product (226 mg, 0.717 mmol, 68% yield) as a white solid.

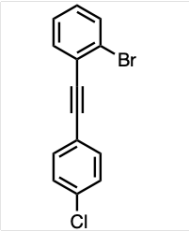
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.56 (m, 3H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.18 (ddd, *J* = 8.0, 7.6, 1.7 Hz, 1H), 7.11 (dt, *J* = 8.8, 2.3 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 150.9, 133.3, 133.0, 132.6, 129.6, 127.2, 125.8, 125.4, 121.9, 120.7, 93.2, 88.2, 21.2.

HRMS (EI, positive) *m/z* calcd for $C_{16}H_{11}BrO_2$ $[M]^+$: 313.9942. Found: 313.9947.



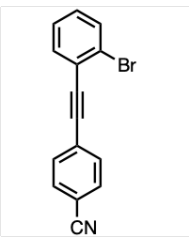
4-((2-Bromophenyl)ethynyl)aniline (2d) was prepared according to the general procedure. 4-Iodoaniline (219 mg, 0.991 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (215 mg, 1.19 mmol, 1.19 equiv), $PdCl_2(PPh_3)_2$ (20.9 mg, 0.0292 mmol, 2.9 mol%), CuI (13.0 mg, 0.0682 mmol, 6.8 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 5:1) to afford the product (246 mg, 0.905 mmol, 91% yield) as a red viscous oil.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.61 (ddd, *J* = 8.1, 1.2, 0.3 Hz, 1H), 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.36 (dt, *J* = 8.0, 2.3 Hz, 2H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 6.66 (dt, *J* = 8.6, 2.2 Hz, 2H), 3.96 (brd, 2H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 148.0, 133.4, 133.3, 132.8, 129.3, 127.5, 126.4, 125.5, 115.0, 112.1, 95.4, 86.4. **HRMS** (ESI, positive) *m/z* calcd for $C_{14}H_{11}NBr$ $[M+H]^+$: 282.00694. Found: 283.00660.



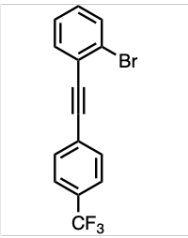
1-Bromo-2-((4-chlorophenyl)ethynyl)benzene (2e) was prepared according to the general procedure. 1-Chloro-4-iodobenzene (240 mg, 1.00 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (205 mg, 1.13 mmol, 1.13 equiv), $PdCl_2(PPh_3)_2$ (21.1 mg, 0.0300 mmol, 3.0 mol%), CuI (11.7 mg, 0.0614 mmol, 6.1 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (100% hexane) to afford the product (276 mg, 0.947 mmol, 94% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.51 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.34 (dt, *J* = 8.8, 2.1 Hz, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.9, 133.4, 133.0, 132.7, 129.7, 128.9, 127.2, 125.8, 125.3, 121.6, 92.9, 89.1. **HRMS** (EI, positive) *m/z* calcd for $C_{14}H_8ClBr$ $[M]^+$: 289.9498. Found: 289.9500. Spectroscopic data are in accordance with those described in the literature.[S10]



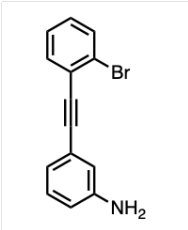
4-((2-Bromophenyl)ethynyl)benzonitrile (2f) was prepared according to the general procedure. 4-Iodobenzonitrile (229 mg, 1.00 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (199 mg, 1.10 mmol, 1.10 equiv), $PdCl_2(PPh_3)_2$ (20.1 mg, 0.0286 mmol, 2.9 mol%), CuI (11.9 mg, 0.0625 mmol, 6.3 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/$CHCl_3$ = 10:1) to afford the product (243 mg, 0.861 mmol, 86% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.61 (m, 5H), 7.57 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.24 (td, *J* = 7.4, 1.7Hz 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.6, 132.8, 132.3, 132.2, 130.4, 128.0, 127.3, 126.0, 124.6, 118.6, 112.1, 92.3, 92.1. Spectroscopic data are in accordance with those described in the literature.[S10]



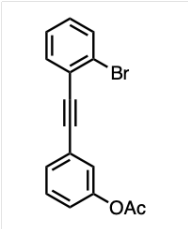
1-Bromo-2-((4-(trifluoromethyl)phenyl)ethynyl)benzene (2g) was prepared according to the general procedure. 1-Iodo-4-(trifluoromethyl)benzene (280 mg, 1.00 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (208 mg, 1.14 mmol, 1.14 equiv), $PdCl_2(PPh_3)_2$ (20.5 mg, 0.0292 mmol, 3.0 mol%), CuI (11.6 mg, 0.0609 mmol, 6.1 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (100% hexane) to afford the product (301 mg, 0.925 mmol, 93% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.60 (m, 5H), 7.57 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 (td, *J* = 7.8, 1.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.5, 132.7, 132.1, 130.5 (q, J_{CF} = 33 Hz), 130.1, 127.3, 126.9, 126.0, 125.5 (q, J_{CF} = 3.7 Hz), 125.0, 124.1 (q, J_{CF} = 273 Hz), 92.5, 90.4. Spectroscopic data are in accordance with those described in the literature.[S11]



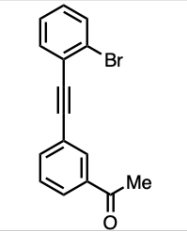
3-((2-Bromophenyl)ethynyl)aniline (2h) was prepared according to the general procedure. 3-Iodoaniline (502 mg, 2.29 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (454 mg, 2.51 mmol, 1.09 equiv), $PdCl_2(PPh_3)_2$ (40.3 mg, 0.0574 mmol, 2.5 mol%), CuI (23.2 mg, 0.122 mmol, 5.0 mol%), THF (10 mL) and triethylamine (10 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford the product (591 mg, 2.17 mmol, 95% yield) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.20–7.11 (m, 2H), 6.99 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.93–6.88 (m, 1H), 6.69 (ddd, *J* = 8.0, 2.4, 1.0 Hz, 1H), 3.71 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.4, 133.4, 132.6, 129.5, 129.4, 127.1, 125.8, 125.7, 123.8, 122.3, 118.0, 115.9, 94.4, 87.6. Spectroscopic data are in accordance with those described in the literature.[S12]



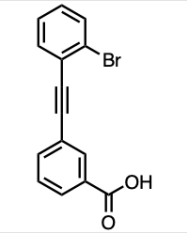
3-((2-Bromophenyl)ethynyl)phenyl acetate (2i) was prepared according to the general procedure. 3-Iodophenyl acetate (**S4**) (530 mg, 2.02 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (397mg, 2.19 mmol, 1.08 equiv), $PdCl_2(PPh_3)_2$ (42.1 mg, 0.0600 mmol, 3.0 mol%), CuI (20.2 mg, 0.106 mmol, 5.3 mol%), THF (10 mL) and triethylamine (10 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford the product (610 mg, 1.94 mmol, 96% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.45 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.33–7.27 (m, 2H), 7.19 (td, *J* = 7.7, 1.8 Hz, 1H), 7.10 (ddd, *J* = 8.1, 2.4, 1.1 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.3, 150.7, 133.4, 132.6, 129.7, 129.5, 129.3, 127.2, 125.8, 125.3, 124.9, 124.4, 122.3, 93.0, 88.9, 21.2. **HRMS** (EI, positive) *m/z* calcd for $C_{16}H_{11}BrO_2$ $[M]^+$: 313.9942. Found: 313.9947.



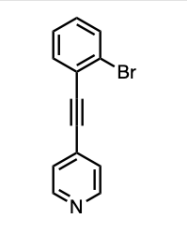
1-(3-((2-Bromophenyl)ethynyl)phenyl)ethan-1-one (2j) was prepared according to the general procedure. 3'-Iodoacetophenone (244 mg, 0.99 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (196 mg, 1.08 mmol, 1.09 equiv), $PdCl_2(PPh_3)_2$ (22.1 mg, 0.0315 mmol, 3.2 mol%), CuI (12.1 mg, 0.0635 mmol, 6.4 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford the product (286 mg, 0.955 mmol, 96% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (td, *J* = 1.7, 0.6 Hz, 1H), 7.94 (ddd, *J* = 7.9, 1.8, 1.2 Hz, 1H), 7.76 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.48 (td, *J* = 7.8, 0.5 Hz, 1H), 7.31 (td, *J* = 7.6, 1.3 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H), 2.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.4, 137.4, 136.1, 133.5, 132.7, 131.7, 129.9, 128.9, 128.3, 127.2, 125.8, 125.1, 123.7, 92.9, 89.1, 26.8. **HRMS** (EI, positive): *m/z* calcd for $C_{16}H_{11}BrO$ $[M]^+$: 297.9993. Found: 297.9989.



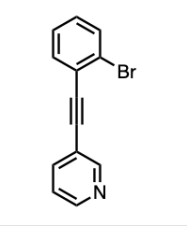
3-((2-Bromophenyl)ethynyl)benzoic acid (2k) was prepared according to the general procedure. 3-Iodobenzoic acid (504 mg, 1.99 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (383 mg, 2.11 mmol, 1.06 equiv), $PdCl_2(PPh_3)_2$ (42.0 mg, 0.598 mmol, 3.0 mol%), CuI (22.1 mg, 0.116 mmol, 6.0 mol%), THF (10 mL) and triethylamine (10 mL) were used. The crude mixture was purified by silica gel column chromatography ($CHCl_3$/MeOH = 10:1) to afford the product (496 mg, 1.65 mmol, 83% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 13.26 (brd, 1H), 8.08 (t, *J* = 1.5 Hz, 1H), 8.00 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.82 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.71 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (td, *J* = 7.8, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-*d*$_6$): δ 166.4, 135.3, 133.5, 132.5, 131.9, 131.5, 130.7, 129.8, 129.3, 127.8, 124.8, 123.8, 122.2, 92.5, 88.5. **HRMS** (EI, positive): *m/z* calcd for $C_{15}H_9BrO_2$ $[M]^+$: 299.9786. Found: 299.9785.



4-((2-Bromophenyl)ethynyl)pyridine (2l) was prepared according to the general procedure. 4-Iodopyridine (206.1 mg, 1.00 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (205.3 mg, 1.13 mmol, 1.13 equiv), $PdCl_2(PPh_3)_2$ (20.8 mg, 0.0296 mmol, 3.0 mol%), CuI (12.0 mg, 0.0630 mmol, 6.3 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford the product (253 mg, 0.979 mmol, 98% yield) as a brown semisolid.

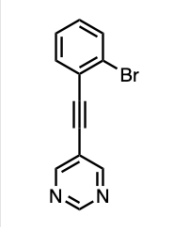
^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.68–8.54 (m, 2H), 7.66 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.47–7.40 (m, 2H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 150.3, 134.0, 133.0, 131.2, 130.9, 127.7, 126.1, 125.8, 124.7, 92.4, 91.3. **HRMS** (EI, positive): *m/z* calcd for $C_{13}H_8BrN$ $[M]^+$: 256.9840. Found: 256.9836.



3-((2-Bromophenyl)ethynyl)pyridine (2m) was prepared according to the general procedure. 3-Iodopyridine (206.5 mg, 1.01 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (208.8 mg, 1.15 mmol, 1.14 equiv), $PdCl_2(PPh_3)_2$ (20.4 mg, 0.0290 mmol, 2.9 mol%), CuI (10.7 mg, 0.0562 mmol, 5.5 mol%), THF (5.0 mL) and triethylamine (5.0 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford the product (254

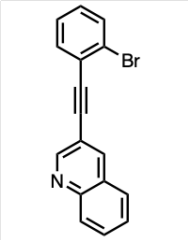
mg, 0.984 mmol, 98% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dd, *J* = 2.2, 0.9 Hz, 1H), 8.57 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.86 (ddd, *J* = 7.9, 2.2, 1.7 Hz, 1H), 7.64 (ddd, *J* = 8.0, 1.3, 0.4 Hz, 1H), 7.57 (ddd, *J* = 7.7, 1.8, 0.4 Hz, 1H), 7.35–7.27 (m, 2H), 7.22 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.4, 149.0, 138.6, 133.5, 132.7, 130.1, 127.2, 125.8, 124.9, 123.2, 120.3, 91.3, 90.5. Spectroscopic data are in accordance with those described in the literature.[S13]



5-((2-Bromophenyl)ethynyl)pyrimidine (2n) was prepared according to the general procedure. 5-Iodopyrimidine (**S5**) (1.04 g, 5.05 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (1.00 g, 5.54 mmol, 1.10 equiv), $PdCl_2(PPh_3)_2$ (70.5 mg, 0.10 mmol, 2.0 mol%), CuI (39.3 mg, 0.206 mmol, 4.1 mol%), THF (12 mL) and triethylamine (12 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1 → 7:1) to afford the product (1.19 g, 4.62 mmol, 91% yield) as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.13 (s, 1H), 8.89 (s, 2H), 7.67 (ddd, *J* = 8.0, 1.3, 0.5 Hz, 1H), 7.62 (ddd, *J* = 7.7, 1.8, 0.4 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.28 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 159.1, 157.5, 133.9, 133.1, 131.0, 127.8, 126.0, 124.6, 119.9, 94.7, 87.2. **HRMS** (EI, positive): *m/z* calcd for $C_{12}H_7BrN_2$ $[M]^+$: 257.9793. Found: 257.9789.

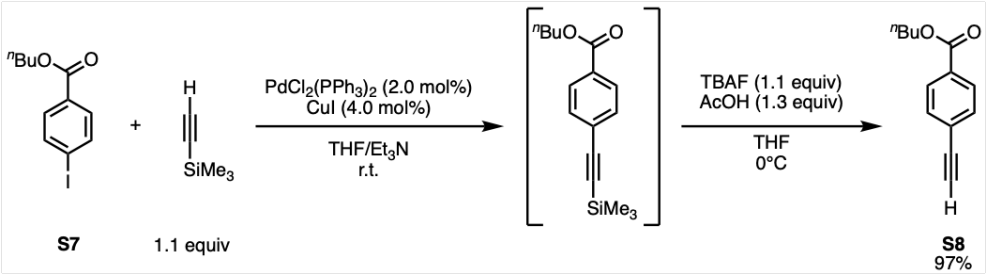


3-((2-Bromophenyl)ethynyl)quinoline (2o) was prepared according to the general procedure. 3-Iodoquinoline (**S6**) (2.26 g, 8.85 mmol, 1.00 equiv), 1-bromo-2-ethynylbenzene (**S2**) (2.03 g, 11.2 mmol, 1.27 equiv), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol, 2.3 mol%), CuI (77.9 mg, 0.409 mmol, 4.6 mol%), THF (25 mL) and triethylamine (25 mL) were used. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1 → 7:1) to afford the product (2.30 g, 7.46 mmol, 84% yield) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 2.1 Hz, 1H), 8.36 (d, *J* = 1.9 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.74 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.70–7.55 (m, 3H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (td, *J* = 8.0, 1.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.1, 147.2, 138.6, 133.5, 132.7, 130.4, 130.1, 129.6, 127.8, 127.5, 127.4, 127.3, 125.9, 125.0, 117.3, 91.3, 91.2. **HRMS** (EI, positive): *m/z* calcd for $C_{17}H_{10}BrN$ $[M]^+$: 306.9997. Found: 306.9996.

2.5 Synthesis of butyl 3-bromo-4-((4-(butoxycarbonyl)phenyl)ethynyl)benzoate (2p)

2.5.1 Synthesis of butyl 4-ethynylbenzoate (S8)

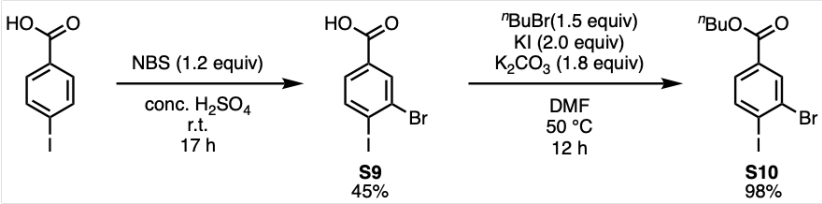


$PdCl_2(PPh_3)_2$ (140 mg, 0.199 mmol, 2.0 mol%) and CuI (76.5 mg, 0.402 mmol, 4.0 mol%) were added to a heat-dried 250-mL two-neck flask with a magnetic stirring bar. The flask was evacuated and backfilled with N_2

three times. Butyl 4-iodobenzoate (**S7**) (3.06 g, 10.1 mmol, 1.00 equiv) and trimethylsilylacetylene (1.08 g, 11.0 mmol, 1.09 equiv) were added to the flask. Dry THF (24 mL) and degassed triethylamine (24 mL) were added to the flask and the mixture was stirred at room temperature (27 °C) for 1 hour. After completion of the reaction (monitored by TLC), the reaction was quenched by saturated NH_4Cl aqueous solution (30 mL). The mixture was extracted with hexane (20 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was roughly purified by passing through a short silica gel plug (hexane/EtOAc = 20:1) to afford brownish oil. Successively, the oil was added to another 250-mL two-neck flask with a magnetic stirring bar. The flask was evacuated and backfilled with N_2 three times. Dry THF (50 mL) and AcOH (750 μL, 13.1 mmol, 1.3 equiv) were added to the flask and then the mixture was cooled at 0 °C on ice bath. A 1.0 M solution of tetrabutylammonium fluoride (TBAF) in MeOH (11.0 mL, 11.0 mmol, 1.10 equiv) was added dropwise to the mixture for over 15 minutes. After stirring at 0 °C for 1 hour, the reaction mixture was diluted with diethyl ether (50 mL) and washed with saturated NH_4Cl aqueous solution three times. The organic layer was further washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 100:0 → 20:1) to afford butyl 4-ethynylbenzoate (**S8**) (1.97 g, 9.75 mmol, 97% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.22 (s, 1H), 1.75 (quintet, *J* = 6.9 Hz, 2H), 1.48 (sextet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.1, 132.2, 130.7, 129.6, 126.8, 83.0, 80.1, 65.2, 30.9, 19.4, 13.9.
Spectroscopic data are in accordance with those described in the literature.[S14]

2.5.2 Synthesis of butyl 3-bromo-4-iodobenzoate (S10)



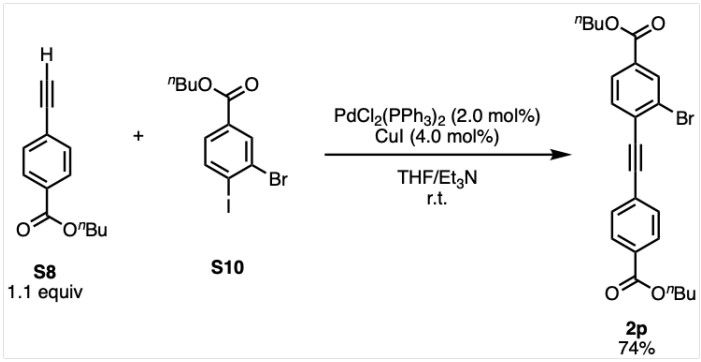
4-Iodobenzoic acid (2.51 g, 10.1 mmol, 1.00 equiv) and conc. H_2SO_4 (60 mL) were added to a 250-mL round bottom flask with a magnetic stirring bar. Recrystallized N-bromosuccinimide (NBS) (2.14 g, 12.0 mmol, 1.19 equiv) was added in one portion and the mixture was stirred at room temperature (27 °C) for 17 hours. The reaction mixture was carefully poured into crushed ice (ca. 300 g). The precipitate was collected by filtration, washed with H_2O and dried in an oven (100 °C) for 24 hours. The crude material was purified by recrystallization in hot ethanol to afford 3-bromo-4-iodobenzoic acid (**S9**) (1.48 g, 4.51 mmol, 45% yield)

3-Bromo-4-iodobenzoic acid (**S9**) (2.57 g, 7.88 mmol, 1.00 equiv), 1-bromobutane (1.30 mL, 12.1 mmol, 1.53 equiv), KI (2.63 g, 15.9 mmol, 2.02 equiv), K_2CO_3 (1.96 g, 14.2 mmol, 1.80 equiv) and N,N-dimethylformamide (DMF) (80 mL) were added to a 250-mL round bottom flask with a magnetic stirring bar. The mixture was stirred at 50 °C for 12 hours. The reaction was quenched by the addition of H_2O (60 mL) and the mixture was extracted with hexane/EtOAc = 10:1 (40 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford analytically pure butyl 3-bromo-4-iodobenzoate (**S10**) (2.95 g, 7.70 mmol, 98% yield) as a colorless oil. The product was directly used for the next step (**2.5.3**) without further purification.

3-Bromo-4-iodobenzoic acid (S9): **^{1}H NMR** (400 MHz, DMSO-d_6): δ 13.40 (brd, 1H), 8.11 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.60 (dd, J = 8.1, 2.0 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 165.7, 140.7, 132.6, 132.5, 129.3, 129.2, 108.3. Spectroscopic data are in accordance with those described in the literature.[S15]

Butyl 3-bromo-4-iodobenzoate (**S10**): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.62 (dd, J = 8.3, 2.0 Hz, 1H), 4.32 (t, J = 6.7 Hz, 2H), 1.74 (quintet, J = 6.4 Hz, 2H), 1.46 (sextet, J = 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.1, 140.6, 133.5, 132.1, 130.2, 129.1, 107.6, 65.6, 30.8, 19.3, 13.9. **HRMS** (EI, positive): *m/z* calcd for $C_{11}H_{12}BrIO_2$ $[M]^+$: 381.9065. Found: 381.9061.

2.5.2 Synthesis of butyl 3-bromo-4-((4-(butoxycarbonyl)phenyl)ethynyl)benzoate (2p)

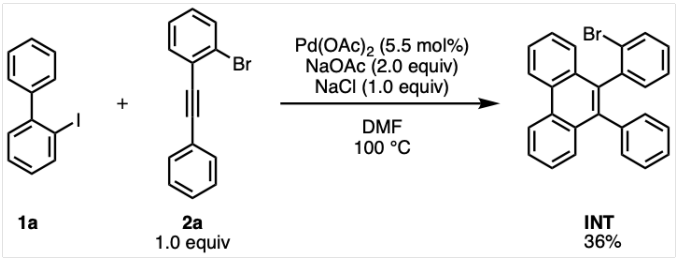


$PdCl_2(PPh_3)_2$ (102 mg, 0.145 mmol, 2.0 mol%) and CuI (54.5 mg, 0.286 mmol, 3.9 mol%) were added to a heat-dried 250-mL two-neck flask with a magnetic stirring bar. The flask was repeatedly evacuated and backfilled with N_2 three times. Butyl 4-ethynylbenzoate (**S8**) (1.68 g, 8.32 mmol, 1.12 equiv) and butyl 3-bromo-4-iodobenzoate (**S10**) (2.84 g, 7.41 mmol, 1.00 equiv) were added to the tube. Anhydrous THF (25 mL) and degassed triethylamine (25 mL) were added to the flask and the mixture was stirred at room temperature (27 °C) for 2 hours. After completion of the reaction (monitored by TLC), the reaction was quenched by saturated NH_4Cl aqueous solution (50 mL). The mixture was extracted with EtOAc (30 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 40:1). The resulting solid was washed with 100% hexane to remove remaining impurities to afford butyl 3-bromo-4-((4-(butoxycarbonyl)phenyl)ethynyl)benzoate (**2p**) (2.51 g, 5.50 mmol, 74% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 1.7 Hz, 1H), 8.05 (d, *J* = 8.7 Hz, 2H), 7.96 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 4.34 (t, *J* = 6.2 Hz, 4H), 1.83–1.71 (m, 4H), 1.54–1.41 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.1, 165.0, 133.6, 133.2, 131.9, 131.7, 130.9, 129.7, 129.3, 128.2, 127.0, 125.8, 95.9, 90.3, 65.6, 65.3, 30.91, 30.86, 19.42, 19.38, 13.9. **HRMS** (EI, positive): *m/z* calcd for $C_{24}H_{25}BrO_4$ $[M]^+$: 456.0936. Found: 456.0934.

3. Procedure for palladium-catalyzed multi-annulation sequence

3.1 Synthesis of 9-(2-bromophenyl)-10-phenylphenanthrene (INT) for crude ^{1}H NMR analysis

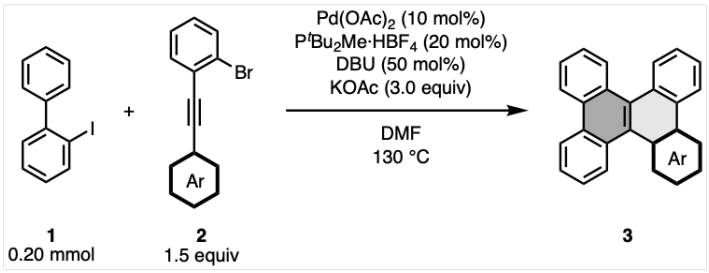


$Pd(OAc)_2$ (3.82 mg, 0.0170 mmol, 5.6 mol%), NaOAc (52.5 mg, 0.640 mmol, 2.09 equiv), and NaCl (12.8 mg, 0.303 mmol, 0.99 equiv) were added to a heat-dried test tube with a magnetic stirring bar. The test tube was sealed with an open-top screw cap with a silicone septum. Then, the test tube was evacuated and backfilled with N_2 three times. N,N-dimethylformamide (3.0 mL) was added to the test tube and the mixture was stirred at 100 °C for 20 hours. After completion of the reaction (monitored by TLC), the reaction mixture was cooled at room

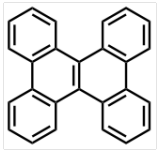
temperature and diluted with H_2O (5.0 mL). The mixture was extracted with CH_2Cl_2 (3.0 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 100:0 → 20:1) and recycling gel permeation chromatography (GPC) to afford 9-(2-bromophenyl)-10-phenylphenanthrene (**INT**) (45.4 mg, 0.111 mmol, 36% yield) as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.84 (d, *J* = 8.3 Hz, 2H), 7.75–7.65 (m, 2H), 7.59–7.45 (m, 4H), 7.42–7.37 (m, 1H), 7.36–7.10 (m, 8H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 141.0, 139.7, 137.7, 136.5, 133.4, 132.6, 132.4, 131.27, 131.23, 130.8, 130.3, 129.9, 129.1, 128.30, 128.27, 127.9, 127.5, 127.36, 127.35, 127.31, 127.2, 127.12, 127.06, 125.5, 123.1, 123.0. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{17}Br$ $[M]^+$: 408.0514. Found: 408.0515.

3.2 General procedure for palladium-catalyzed multi-annulation sequence

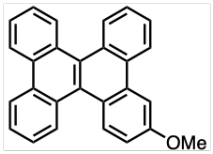


$Pd(OAc)_2$ (4.45 mg, 0.020 mmol, 10 mol%), P^{t}Bu$_2$Me·HBF_4 (9.96 mg, 0.040 mmol, 20 mol%), and diarylacetylene (**2**) (0.30 mmol, 1.50 equiv) were added to a heat-dried test tube with a magnetic stirring bar. Dry KOAc (58.9 mg, 0.60 mmol, 3.0 equiv) was added to the test tube in a glove box and the test tube was sealed with an open-top screw cap with a silicone septum. The test tube was repeatedly evacuated and backfilled with N_2 three times. 2-Iodobiphenyl (**1**) (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (15.0 μL, 0.100 mmol, 50 mol%) and anhydrous N,N-dimethylformamide (DMF) (2.0 mL) was added to the test tube *via* syringe and the mixture was stirred at 130 °C for 16 hours. After completion of the reaction (monitored by TLC), the reaction mixture was cooled at room temperature and diluted with H_2O (5.0 mL). The mixture was extracted with CH_2Cl_2 (3.0 mL, three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography and/or recycling gel permeation chromatography (GPC) to afford the corresponding functionalized dibenzo[*g*,*p*]chrysene.



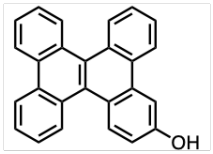
Dibenzo[*g*,*p*]chrysene (3aa) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2a** (77.6 mg, 0.302 mmol, 1.52 equiv), $Pd(OAc)_2$ (4.4 mg, 0.0196 mmol, 10 mol%), P^{t}Bu$_2$Me·HBF_4 (10.3 mg, 0.0415 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (58.1 mg, 0.592 mmol, 2.96 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/toluene = 100:1 → 10:1) to afford the product (43.6 mg, 0.133 mmol, 67% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (dd, *J* = 3.4, 1.5 Hz, 2H), 8.70 (dd, *J* = 3.5, 1.6 Hz, 2H), 7.69 (td, *J* = 6.8, 1.6 Hz, 2H), 7.64 (td, *J* = 7.6, 1.5 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 131.0, 129.4, 129.0, 127.6 (2C), 126.7, 123.7. Spectroscopic data are in accordance with those described in the literature.[S16]



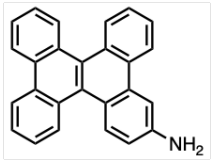
2-Methoxyldibenzo[*g*,*p*]chrysene (3ab) was prepared according to the general procedure. **1a** (56.7 mg, 0.202 mmol, 1.00 equiv), **2b** (86.4 mg, 0.301 mmol, 1.50 equiv), $Pd(OAc)_2$ (4.67 mg, 0.0208 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.4 mg, 0.0418 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (58.5 mg, 0.596 mmol, 2.95 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 10:1) and recycling gel permeation chromatography (GPC) to afford the product (50.4 mg, 0.141 mmol, 70% yield) as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.78–8.59 (m, 7H), 8.12 (d, *J* = 2.6 Hz, 1H), 7.75–7.60 (m, 6H), 7.28 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.07 (s, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 159.0, 132.9, 131.3, 130.9, 130.8 (2C), 129.9, 129.7, 129.5, 129.32, 129.28, 129.0, 128.0, 127.1, 127.00, 126.96, 126.93, 126.8, 126.6, 126.2, 124.1, 124.0 (2C), 123.9, 115.9, 106.2, 55.9. Spectroscopic data are in accordance with those described in the literature.[S16]



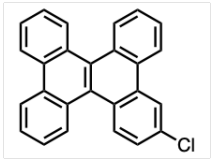
2-Hydroxydibenzo[*g*,*p*]chrysene (3ac) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2c** (98.8 mg, 0.313 mmol, 1.60 equiv), $Pd(OAc)_2$ (4.40 mg, 0.0196 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.0 mg, 0.0427 mmol, 22 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (59.8 mg, 0.609 mmol, 3.11 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 100:0 → 50:50 → 0:100) to afford the product (46.7 mg, 0.136 mmol, 69% yield) as a pale yellow semi-solid. *Note: The product is air sensitive and its color gradually turns to dark purple. It should be stored under an inert atmosphere at –20 °C.*

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75–8.66 (m, 4H), 8.66–8.55 (m, 3H), 8.08 (d, *J* = 2.6 Hz, 1H), 7.71–7.59 (m, 6H), 7.18 (dd, *J* = 8.8, 2.6 Hz, 1H), 5.18–5.12 (brd, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.4, 132.9, 131.03, 130.98, 130.6, 130.3, 129.7, 129.5, 129.3, 129.03, 129.01, 128.8, 127.7, 126.8, 126.7, 126.61, 126.59, 126.5, 126.3, 126.0, 123.9, 123.8, 123.73, 123.70, 116.0, 108.5. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{16}O$ $[M]^+$: 344.1201. Found: 344.1205.



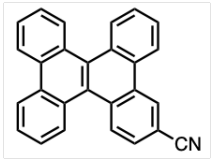
2-Aminodibenzo[*g*,*p*]chrysene (3ad) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2d** (82.8 mg, 0.301 mmol, 1.54 equiv), $Pd(OAc)_2$ (4.20 mg, 0.0187 mmol, 9.6 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.5 mg, 0.0423 mmol, 22 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (68.0 mg, 0.693 mmol, 3.53 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 5:1 → 1:1) to afford the product (20.3 mg, 0.0591 mmol, 30% yield) as a brown semi-solid. *Note: The product is air sensitive and its color gradually turns to dark brown. It should be stored under an inert atmosphere at –20 °C.*

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82–8.60 (m, 5H), 8.56 (dd, *J* = 7.4, 2.0 Hz, 1H), 8.50 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.77–7.45 (m, 6H), 7.03 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.05 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.3, 132.7, 131.1, 130.6, 130.44, 130.42, 129.8, 129.7, 129.4, 129.2, 129.0, 128.7, 128.2, 126.62, 126.58, 126.49, 126.46, 126.3, 126.0, 125.2, 123.8, 123.7(2C), 122.4, 116.2, 107.6. **HRMS** (FAB, positive): *m/z* calcd for $C_{26}H_{17}N$ $[M]^+$: 343.1361. Found: 343.1361.



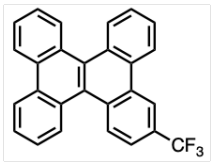
2-Chlorodibenzo[*g*,*p*]chrysene (3ae) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2e** (88.5 mg, 0.304 mmol, 1.55 equiv), $Pd(OAc)_2$ (4.50 mg, 0.0200 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.2 mg, 0.0411 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (65.7 mg, 0.669 mmol, 3.41 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 100:0 → 10:1) to afford the product (53.5 mg, 0.147 mmol, 75% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80–8.54 (m, 8H), 7.76–7.61 (m, 6H), 7.58 (dd, *J* = 8.9, 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 132.6, 132.3, 131.0 (2C), 130.5, 129.9, 129.7, 129.2, 129.1 (2C), 129.0, 128.8, 127.74, 127.69, 127.3, 127.0, 126.9–126.8 (brd, 4C), 126.82, 126.79, 123.8, 123.8, 123.7, 123.4. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{15}Cl$ $[M]^+$: 362.0862. Found: 362.0872.



2-Chlorodibenzo[*g*,*p*]chrysene (3af) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2f** (84.1 mg, 0.298 mmol, 1.52 equiv), $Pd(OAc)_2$ (4.40 mg, 0.0196 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.7 mg, 0.0431 mmol, 22 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (68.4 mg, 0.700 mmol, 3.56 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:0) to afford the product (43.7 mg, 0.124 mmol, 63% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, *J* = 1.3 Hz, 1H), 8.78–8.62 (m, 6H), 8.53 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.80 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.77–7.62 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 131.7, 131.5, 131.0, 130.6, 129.8, 129.6 (2C), 129.5, 129.2 (2C), 128.7, 128.6 (2C), 128.4, 128.1, 127.7, 127.6, 127.3, 127.2, 127.1, 126.9, 126.4, 123.9, 123.8, 123.6, 119.5, 109.6. Spectroscopic data are in accordance with those described in the literature.[S17]

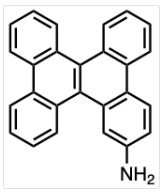


2-(Trifluoromethyl)dibenzo[*g*,*p*]chrysene (3ag) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2g** (98.5 mg, 0.303 mmol, 1.55 equiv), $Pd(OAc)_2$ (4.40 mg, 0.0196 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.5 mg, 0.0423 mmol, 22 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (60.9 mg, 0.621 mmol, 3.17 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (100% hexane) and recycling gel permeation chromatography (GPC) to afford the product (48.0 mg, 0.121 mmol, 62% yield) as a white solid.

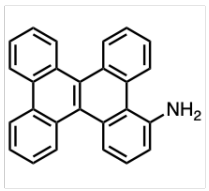
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.79 (d, *J* = 8.6 Hz, 1H), 8.76–8.66 (m, 5H), 8.61 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.78–7.61 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 131.42, 131.38, 131.1, 130.6, 130.4, 129.66, 129.63, 129.20, 129.16, 129.1, 129.0 (2C), 128.7, 128.2 (q, J_{CF} = 33 Hz), 127.5, 127.3, 127.2, 127.1, 127.0, 126.9, 126.7, 124.7 (q, J_{CF} = 273 Hz), 123.9, 123.8, 123.7, 122.6 (q, J_{CF} = 3.5 Hz), 121.0 (q, J_{CF} = 4.2 Hz). Spectroscopic data are in accordance with those described in the literature.[S18]

3-Aminodibenzo[*g*,*p*]chrysene (3ah) and **1-aminodibenzo[*g*,*p*]chrysene (3ah')** were prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2h** (83.7 mg, 0.304 mmol, 1.55 equiv), $Pd(OAc)_2$ (4.20 mg, 0.0187 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (9.40 mg, 0.0379 mmol, 19 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (58.8 mg, 0.599 mmol, 3.06 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:0 → 5:1) and recycling

gel permeation chromatography (GPC) to afford **3ah** (9.90 mg, 0.0144 mmol, 15% yield) and **3ah'** (31.5 mg, 0.0917 mmol, 45% yield) as a brown semi-solid and a yellow semi-solid, respectively.

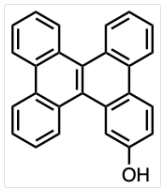


3ah: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.73–8.66 (m, 3H), 8.62 (dd, *J* = 8.2, 0.8 Hz, 1H), 8.55 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.50 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.74–7.57 (m, 5H), 7.52 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.10–3.70 (brd, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.2, 131.5, 130.9, 130.8, 130.7, 129.6, 129.5, 129.09, 129.06, 128.4, 128.3, 128.1, 127.2, 126.7, 126.55 (2C), 126.49, 126.45, 125.2, 125.0, 123.7, 123.6, 123.6, 122.8, 116.2, 112.6. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{17}N$ $[M]^+$: 343.1361. Found: 343.1360. NOESY NMR (400 MHz, $CDCl_3$) was further employed to confirm the position of the functional group (Figure S70).

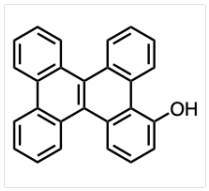


3ah': **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.09–9.00 (m, 1H), 8.76–8.63 (m, 4H), 8.63–8.57 (m, 1H), 8.10 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.71–7.51 (m, 6H), 7.42 (t, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 7.8, 1.1 Hz, 1H), 4.49 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.5, 131.7, 131.12, 131.09, 130.6, 130.2, 129.4, 129.0, 128.93, 128.90, 128.7, 128.4, 128.1, 127.5, 126.71, 126.65, 126.59, 126.5 (2C), 125.8, 125.6, 123.69, 123.65, 119.4, 118.8, 115.0. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{17}N$ $[M]^+$: 343.1361. Found: 343.1359. NOESY NMR (400 MHz, $CDCl_3$) was further employed to confirm the position of the functional group (Figure S73).

3-Hydroxydibenzo[*g*,*p*]chrysene (3ai) and **1-hydroxydibenzo[*g*,*p*]chrysene (3ai')** were prepared according to the general procedure. **1a** (34.0 µL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2i** (94.9 mg, 0.301 mmol, 1.53 equiv), $Pd(OAc)_2$ (4.20 mg, 0.0187 mmol, 9.5 mol%), $P^tBu_2Me{\cdot}HBF_4$ (9.21 mg, 0.0371 mmol, 19 mol%), DBU (15.0 µL, 0.100 mmol, 50 mol%), KOAc (59.0 mg, 0.601 mmol, 3.07 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/CH_2Cl_2= 10:0 → 1:1) and recycling gel permeation chromatography (GPC) to afford **3ai** (11.4 mg, 0.0331 mmol, 17% yield) and **3ai'** (33.6 mg, 0.0976 mmol, 50% yield) as a brownish semi-solid and a colorless semi-solid, respectively. *Note: Both products are air sensitive and their color gradually turns to dark purple or brown. It should be stored under an inert atmosphere at –20 °C.*



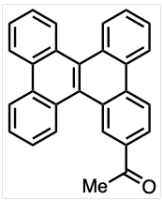
3ai: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76–8.57 (m, 7H), 8.12 (d, *J* = 2.6 Hz, 1H), 7.73–7.53 (m, 6H), 7.23 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.06 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.4, 131.14, 131.06, 130.92, 130.87, 129.4 (2C), 129.2 (2C), 128.6, 128.5, 128.4, 127.1, 126.9, 126.8, 126.72 (2C), 126.69, 125.8, 125.7, 125.3, 123.8, 123.7, 123.2, 116.0, 113.4. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{16}O$ $[M]^+$: 344.1201. Found: 344.1205. NOESY NMR (400 MHz, $CDCl_3$) was further employed to confirm the position of the functional group (Figure S76).



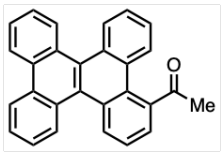
3ai': **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.39–9.32 (m, 1H), 8.76–8.59 (m, 5H), 8.28 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.75–7.55 (m, 6H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.1 Hz, 1H), 5.68 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.6, 132.2, 131.2, 131.0, 130.2, 129.41, 129.38, 129.04, 128.98 (2C), 128.6, 128.4, 128.1, 127.7, 126.9, 126.8, 126.7, 126.62, 126.56 (2C), 126.1, 123.7

(2C), 121.8, 119.6, 113.8. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{16}O$ $[M]^+$: 344.1201. Found: 344.1206. NOESY NMR (400 MHz, $CDCl_3$) was further employed to confirm the position of the functional group (Figure S79).

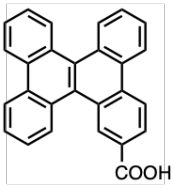
3-Acetyldibenzo[*g*,*p*]chrysene (3aj) and **1-acetyldibenzo[*g*,*p*]chrysene (3aj')** were prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2j** (89.4 mg, 0.319 mmol, 1.62 equiv), $Pd(OAc)_2$ (4.50 mg, 0.0200 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.4 mg, 0.0419 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (60.1 mg, 0.612 mmol, 3.12 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:0) to afford **3aj** (32.3 mg, 0.0871 mmol, 45% yield) and **3aj'** (11.4 mg, 0.0308 mmol, 16% yield) as a white solid and a pale yellow solid, respectively.



3aj: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (d, *J* = 1.8 Hz, 1H), 8.80–8.67 (m, 6H), 8.62 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.25 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.79–7.61 (m, 6H), 2.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 198.0, 135.0, 134.1, 131.1 (2C), 130.3, 130.2, 130.1, 129.1, 129.0 (2C), 128.93, 128.87, 128.7, 128.1, 127.8, 127.6, 127.09, 127.06, 127.0, 126.9, 126.8, 125.4, 124.3, 124.1, 123.9, 123.8, 26.9. **HRMS** (EI, positive): *m/z* calcd for $C_{28}H_{18}O$ $[M]^+$: 370.1358. Found: 370.1365. NOESY NMR (400 MHz, $CDCl_3$) was further employed to confirm the position of the functional group (Figure S82).

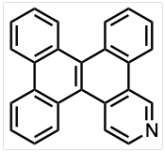


3aj': ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.76–8.64 (m, 4H), 8.60 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.77–7.54 (m, 8H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.5, 141.3, 131.3 (2C, quaternary sp^2 carbons), 130.7, 130.3 (2C, quaternary sp^2 carbons), 129.0, 128.9, 128.8 (2C, tertiary sp^2 carbons), 128.5, 128.1, 127.8, 127.2, 127.1, 127.0, 126.89, 126.87, 126.8, 126.3, 126.1, 123.9, 123.8, 31.3. The other three quaternary sp^2 carbons were overlapped. **HRMS** (EI, positive): *m/z* calcd for $C_{28}H_{18}O$ $[M]^+$: 370.1358. Found: 370.1353. NOESY NMR (400 MHz, $CDCl_3$) was further employed to confirm the position of the functional group (Figure S85).



Dibenzo[*g*,*p*]chrysene-3-carboxylic acid (**3ak**) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2k** (90.8 mg, 0.302 mmol, 1.54 equiv), $Pd(OAc)_2$ (4.50 mg, 0.0200 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.0 mg, 0.0403 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (61.2 mg, 0.629 mmol, 3.21 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography ($CHCl_3$/MeOH= 10:1) and then washed with MeOH to afford the product (27.1 mg, 0.0727 mmol, 37% yield) as a white solid. *Note: The crude material was poorly soluble in $CHCl_3$. ca. 50 mL of $CHCl_3$ is necessary to load into a silica gel column.*

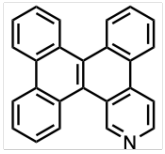
^{1}H NMR (400 MHz, DMSO-d_6): δ 13.24 (brd, 1H), 9.25 (d, *J* = 1.7 Hz, 1H), 8.97 (d, *J* = 8.7 Hz, 1H), 8.95–8.83 (m, 3H), 8.70–8.60 (m, 2H), 8.59–8.52 (m, 1H), 8.24 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.85–7.69 (m, 6H). **^{13}C NMR** (75 MHz, DMSO-d_6): δ 167.3, 133.1, 130.40 (2C), 130.1, 129.6, 129.1, 129.0, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.4, 127.42–127.35 (brd, 4C), 127.29, 127.16, 126.9, 126.6, 124.6, 124.4, 124.1, 124.0. One quaternary sp^2 carbon was overlapped. **HRMS** (ESI, negative): *m/z* calcd for $C_{27}H_{15}O_2$ $[M–H]^–$: 371.10775. Found: 371.10862.



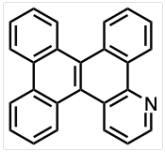
Benzo[*h*]phenanthro[9,10-*f*]isoquinoline (3al) was prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2l** (77.3 mg, 0.299 mmol, 1.53 equiv), $Pd(OAc)_2$ (4.20 mg, 0.0187 mmol, 9.6 mol%), $P^tBu_2Me{\cdot}HBF_4$ (9.98 mg, 0.0421 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (56.5 mg, 0.576 mmol, 3.21 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography ($CHCl_3$/EtOAc= 100:0 → 10:1) and then washed with MeOH to afford the product (47.5 mg, 0.144 mmol, 74% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.82 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.79–8.65 (m, 6H), 8.51 (d, *J* = 5.7 Hz, 1H), 7.79–7.64 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 147.2, 145.7, 133.6, 131.6, 130.9, 130.7, 129.5, 129.4, 129.2 (2C), 128.7, 128.6, 128.1, 127.6, 127.4, 127.3, 127.1, 127.0, 126.8, 125.23, 125.18, 123.8, 123.7, 122.9, 121.2. **HRMS** (EI, positive): *m/z* calcd for $C_{25}H_{15}N$ $[M]^+$: 329.1204. Found: 329.1198.

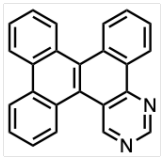
Benzo[*f*]phenanthro[9,10-*h*]isoquinoline (3am) and **benzo[*h*]phenanthro[9,10-*f*]quinoline (3am)** were prepared according to the general procedure. **1a** (34.0 μL, 55.0 mg, 0.196 mmol, 1.00 equiv), **2m** (77.1 mg, 0.299 mmol, 1.53 equiv), $Pd(OAc)_2$ (4.60 mg, 0.0205 mmol, 10.5 mol%), $P^tBu_2Me{\cdot}HBF_4$ (9.60 mg, 0.0387 mmol, 19.7 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (58.2 mg, 0.593 mmol, 3.03 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/$CHCl_3$/EtOAc= 50:50:0 → 0:100:0 → 0:10:1) and then washed with MeOH to afford **3am** (37.9 mg, 0.115 mmol, 59% yield) and **3am'** (10.0 mg, 0.030 mmol, 16%) as white solids.



3am: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.81 (d, *J* = 5.6 Hz, 1H), 8.79–8.63 (m, 6H), 8.48 (d, *J* = 5.6 Hz, 1H), 7.80–7.63 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.3, 145.3, 135.7, 131.2, 131.0, 130.6, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 127.2 (2C), 126.9, 126.8, 125.7, 124.5, 124.0, 123.81, 123.75, 116.5. The other two quaternary sp^2 carbons were overlapped. **HRMS** (EI, positive): *m/z* calcd for $C_{25}H_{15}N$ $[M]^+$: 329.1204. Found: 329.1198.



3am': ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43–9.37 (m, 1H), 9.05–8.96 (m, 2H), 8.81–8.69 (m, 4H), 8.54 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.81–7.63 (m, 6H), 7.58 (dd, *J* = 8.3, 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.4, 147.1, 136.3, 131.8, 131.2, 131.1, 130.7, 129.3, 129.2, 129.1, 128.6, 128.4, 128.2, 128.0, 127.2, 127.0 (2C), 126.9 (2C), 126.3, 125.4, 123.95, 123.89, 123.8, 121.4. **HRMS** (EI, positive): *m/z* calcd for $C_{25}H_{15}N$ $[M]^+$: 329.1204. Found: 329.1201.

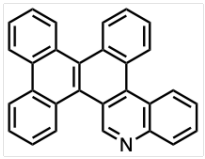


Benzo[*h*]phenanthro[9,10-*f*]quinazoline (3an) was prepared according to the general procedure. **1a** (56.3 mg, 0.201 mmol, 1.00 equiv), **2n** (78.0 mg, 0.301 mmol, 1.50 equiv), $Pd(OAc)_2$ (4.51 mg, 0.0201 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.8 mg, 0.0433 mmol, 22 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (58.1 mg, 0.592 mmol, 2.95 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (CH_2Cl_2/EtOAc = 100:0 → 10:1 → 5:1) and recycling gel permeation chromatography (GPC) to afford the product (30.8 mg, 0.933 mmol, 47% yield) as white solids.

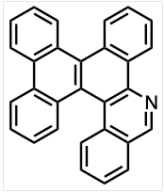
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 9.48 (s, 1H), 9.41 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.83–8.70 (m, 4H), 8.55–8.49 (m, 1H), 7.92–7.64 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.8, 155.0, 151.0, 132.1, 131.3, 131.1, 130.1,

129.8, 128.9, 128.8, 128.7, 128.6, 128.4, 127.8, 127.6, 127.5, 127.4, 127.3, 127.0, 125.6, 124.1, 123.9, 123.8, 120.8. **HRMS** (EI, positive): *m/z* calcd for $C_{24}H_{14}N_2$ $[M]^+$: 330.1157. Found: 330.1163.

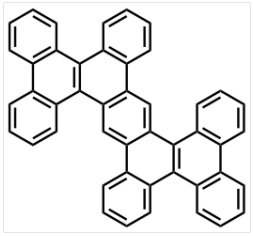
Benzo[*k*]phenanthro[9,10-*i*]phenanthridine (3ao) and **benzo[*c*]phenanthro[9,10-*a*]phenanthridine (3ao')** were prepared according to the general procedure. **1a** (57.5 mg, 0.205 mmol, 1.00 equiv), **2o** (92.8 mg, 0.301 mmol, 1.50 equiv), $Pd(OAc)_2$ (4.51 mg, 0.0200 mmol, 9.8 mol%), $P^tBu_2Me{\cdot}HBF_4$ (10.5 mg, 0.0423 mmol, 21 mol%), DBU (15.0 μL, 0.100 mmol, 50 mol%), KOAc (63.1 mg, 0.643 mmol, 3.13 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/$CHCl_3$/EtOAc = 3:1:0 → 3:1:1) to afford **3ao** (49.2 mg, 0.130 mmol, 63% yield) and **3ao'** (2.60 mg, 6.85 μmol, 3% yield) as pale yellow solids.



3ao: ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.21 (s, 1H), 9.11 (d, *J* = 7.9 Hz, 1H), 9.07–9.00 (m, 1H), 8.86–8.78 (m, 1H), 8.78–8.70 (m, 3H), 8.70–8.62 (m, 1H), 8.34 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.84 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.80–7.66 (m, 7H). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 150.9, 146.2, 131.7, 131.5, 131.3, 130.2, 129.6, 129.3, 128.74, 128.68, 128.5, 128.4, 128.1, 127.9, 127.3, 127.11 (2C), 127.05 (2C), 127.02, 126.3, 125.7, 123.9, 123.91, 123.85, 122.1. The other three quaternary sp^2 carbons were overlapped. **HRMS** (FAB, positive): *m/z* calcd for $C_{29}H_{18}N$ $[M+H]^+$: 380.1439. found: 380.1431.



3ao': ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.62–9.55 (m, 1H), 9.42 (s, 1H), 8.81–8.68 (m, 4H), 8.68–8.61 (m, 1H), 8.41 (d, *J* = 8.6 Hz, 1H), 8.05 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.90–7.58 (m, 8H). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 148.4, 147.1, 136.0, 132.1, 131.7, 131.21, 131.23, 130.0, 129.6, 129.3, 129.2, 128.92, 128.90, 128.7, 128.5, 128.3, 128.0, 127.3, 127.2, 127.1, 126.95, 126.91 (2C), 126.4, 126.2, 124.0, 123.8, 123.0. One quaternary sp^2 carbon was overlapped. **HRMS** (EI, positive): *m/z* calcd for $C_{29}H_{17}N$ $[M^+]$: 379.1361 found: 379.1353. The structure was confirmed by single crystal X-ray diffraction and structural analysis (Figure S8).



Tetrabenzo[*a*,*c*,*f*,*m*]phenanthro[9,10-*k*]tetraphene (3ba) was prepared according to the general procedure. **1b** (96.5 mg, 0.200 mmol, 1.00 equiv), **2a** (169 mg, 0.655 mmol, 3.28 equiv), $Pd(OAc)_2$ (9.00 mg, 0.0401 mmol, 20 mol%), $P^tBu_2Me{\cdot}HBF_4$ (19.6 mg, 0.0790 mmol, 40 mol%), DBU (21.0 μL, 0.141 mmol, 70 mol%), KOAc (116 mg, 1.18 mmol, 5.88 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was purified by silica gel column chromatography (hexane/$CHCl_3$ = 10:1 → 100% toluene) to afford the product (44.3 mg, 0.0765 mmol, 38% yield) as a yellow solid.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.94 (s, 2H), 9.09–9.05 (m, 2H), 8.85–8.74 (m, 6H), 8.72 (dd, *J* = 7.9, 2.4 Hz, 4H), 7.87–7.78 (m, 4H), 7.75–7.62 (m, 8H). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 131.42, 131.37, 131.1, 129.9, 129.75, 129.70, 129.39, 129.37, 129.0, 128.9, 128.1, 128.0, 127.15, 127.09, 126.96, 126.93, 126.84, 126.79, 124.2, 124.0 (2C), 123.8. The other two quaternary sp^2 carbons were overlapped. **HRMS** (ESI, positive): *m/z* calcd for $C_{46}H_{26}$ $[M^+]$: 578.20290. Found: 578.20331.

Tetrabutyl tetrabenzo[*a*,*c*,*f*,*m*]phenanthro[9,10-*k*]tetraphene-2,12,15,25-tetracarboxylate (3bp) was prepared according to the general procedure. **1b** (97.1 mg, 0.201 mmol, 1.00 equiv), **2p** (230 mg, 0.502 mmol, 2.49 equiv), $Pd(OAc)_2$ (8.96 mg, 0.0399 mmol, 20 mol%), $P^tBu_2Me{\cdot}HBF_4$ (19.6 mg, 0.0400 mmol, 40 mol%), DBU (30.0 μL, 0.200 mmol, 1.00 equiv), KOAc (117 mg, 1.19 mmol, 5.94 equiv) and DMF (2.0 mL) were used. The crude reaction mixture was roughly purified by silica gel column chromatography (CH_2Cl_2/EtOAc = 100:0 → 10:1) and then washed with hexane/EtOAc = 1:1 to afford the product (**3bp**) (28.2 mg, 0.0288 mmol, 14% yield) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.53–9.50 (m, 6H), 8.87 (d, *J* = 8.7 Hz, 2H), 8.59 (d, *J* = 8.7 Hz, 2H), 8.49 (t, *J* = 7.8 Hz, 4H), 8.36 (dd, *J* = 8.6, 1.7 Hz, 2H), 8.21 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.70–7.55 (m, 4H), 4.59–4.48 (m, 8H), 2.00–1.87 (m, 8H), 1.70–1.55 (m, 8H, partially overlapped with H_2O), 1.14–1.04 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.59, 166.56, 132.0, 131.5, 130.7, 130.2, 130.1, 129.1, 128.8 (2C), 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.5, 127.1, 126.9 (2C), 126.7, 125.9, 125.6, 123.8, 123.1, 65.46, 65.40, 31.1 (2C), 19.6 (2C), 14.0 (2C). One tertiary sp^2 carbon was overlapped. **HRMS** (FAB, positive): *m/z* calcd. for $C_{66}H_{58}O_8$ $[M]^+$: 978.4132. Found: 978.4123.

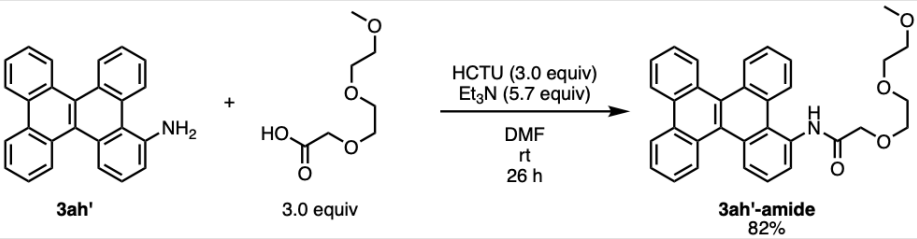
Benzo[*f*]phenanthro[9,10-*h*]isoquinolin-11-ol (3cm) and **benzo[*f*]phenanthro[9,10-*h*]isoquinolin-6-ol (3cm')** were prepared according to the general procedure. **1c** (794 mg, 2.00 mmol, 1.00 equiv), **2m** (790 mg, 3.16 mmol, 1.58 equiv), $Pd(OAc)_2$ (44.7 mg, 0.199 mmol, 10 mol%), $P^tBu_2Me{\cdot}HBF_4$ (106 mg, 0.428 mmol, 21 mol%), DBU (150 μL, 1.00 mmol, 0.502 equiv), KOAc (584 mg, 5.95 mmol, 2.98 equiv) and DMF (20.0 mL) were used. The crude reaction mixture was roughly purified by silica gel column chromatography (CH_2Cl_2/EtOAc = 100:0 → 10:1 → 1:1 → 0:100) and then washed with CH_2Cl_2 to afford **3cm** (114.4 mg, 0.331 mmol, 17% yield) and **3cm'** (132 mg, 0.383 mmol, 19% yield) as a pale yellow solid and a yellow solid, respectively.

3cm: ^{1}H NMR (400 MHz, THF-d_8): δ 9.91 (s, 1H), 8.90–8.80 (m, 2H), 8.80–8.71 (m, 2H), 8.70–8.64 (m, 2H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 5.5 Hz, 1H), 8.07 (d, *J* = 2.4 Hz, 1H), 7.77–7.69 (m, 2H), 7.69–7.63 (m, 1H), 7.63–7.55 (m, 1H), 7.22 (dd, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, THF-d_8): δ 158.0, 152.2, 146.6, 136.4, 132.7, 131.7, 131.5, 130.2, 130.0, 129.5, 129.2, 128.7, 128.2, 128.1, 127.8, 127.3, 126.6, 126.4, 125.5, 125.4, 125.1, 124.1, 118.0, 117.1, 113.6. **HRMS** (EI, positive): *m/z* calcd for $C_{25}H_{15}NO$ $[M]^+$: 345.1154. Found: 345.1149. NOESY NMR (400 MHz, THF-d_8) was further employed to confirm the position of functional groups (Figure S106).

3cm': ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.31–9.96 (brd, 1H), 9.92 (s, 1H), 8.98–8.91 (m, 1H), 8.81 (d, *J* = 5.5 Hz, 1H), 8.78–8.70 (m, 3H), 8.70–8.65 (m, 1H), 8.57 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 2.4 Hz, 1H), 7.90–7.77 (m, 2H), 7.72 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.62 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.28 (dd, *J* = 8.8, 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 156.9, 149.9, 145.4, 134.8, 131.0, 129.7, 129.0, 128.9, 128.6, 128.3, 128.1, 128.0, 127.5, 127.3, 126.9, 125.8, 125.7, 124.5, 124.4, 123.7, 123.2 (2C), 117.3, 116.8, 112.7. **HRMS** (EI, positive): *m/z* calcd for $C_{25}H_{15}NO$ $[M]^+$: 345.1154. Found: 345.1145. NOESY NMR (400 MHz, DMSO-d_6) was further employed to confirm the position of functional groups (Figure S109).

4. Further derivatization of 3ah' and 3cm

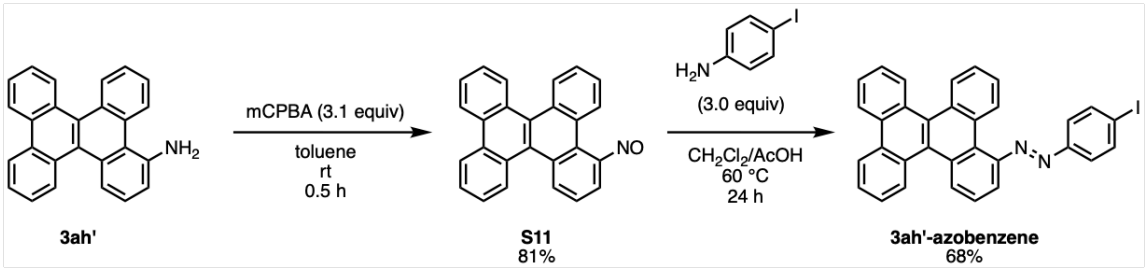
4.1 Synthesis of *N*-(dibenzo[*g*,*p*]chrysen-1-yl)-2-(2-(2-methoxyethoxy)ethoxy)acetamide (3ah'-amide)



[2-(2-Methoxyethoxy)ethoxy]acetic acid (53.9 mg, 0.303 mmol, 3.03 equiv), 2-(6-chloro-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethylaminium hexafluorophosphate (HCTU) (127 mg, 0.306 mmol, 3.07 equiv), triethylamine (Et_3N) (57.9 mg, 0.572 mmol, 5.74 equiv) and DMF (3.0 mL) were added to a heat-dried test tube with a magnetic stirring bar. After stirring at room temperature (27 °C) for 30 minutes, **3ah'** (34.2 mg, 0.0996 mmol, 1.00 equiv) was added to the mixture in one portion. The reaction mixture was stirred at the same temperature for 26 hours. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with H_2O (5.0 mL) and extracted with toluene (5.0 mL, three times). The combined organic layers were washed with H_2O (4.0 mL, twice), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was passed through a short silica gel plug eluting with 100% CH_2Cl_2. The crude material was purified by recycling gel permeation chromatography (GPC) to afford the corresponding product (**3ah'-amide**) (41.3 mg, 0.0820 mmol, 82% yield) as a yellow viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 8.80–8.73 (m, 1H), 8.73–8.67 (m, 2H), 8.67–8.58 (m, 3H), 8.54–8.47 (m, 1H), 8.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.73–7.52 (m, 7H), 4.35 (s, 2H), 3.91–3.84 (m, 2H), 3.72–3.63 (m, 2H), 3.50–3.41 (m, 2H), 3.28–3.20 (m, 2H), 3.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.4, 133.6, 131.4, 131.2, 131.1, 131.0, 128.9 (2C), 128.7, 128.6, 128.4, 128.0, 127.4, 127.3, 126.87, 126.84, 126.81, 126.77, 126.74, 125.9, 125.6, 123.77, 123.74, 123.6, 123.4, 71.9, 71.7, 71.5, 70.7, 70.4, 58.9. The other two quaternary carbons were overlapped. **HRMS** (ESI, positive): *m/z* calcd for $C_{33}H_{29}NO_4Na$ $[M+Na]^+$: 526.19888. Found: 526.198000.

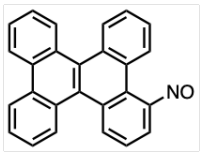
4.2 Synthesis of 1-(dibenzo[*g*,*p*]chrysen-1-yl)-2-(4-iodophenyl)diazene (3ah'-azobenzene)



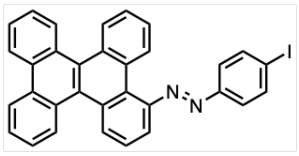
1-Aminodibenzo[*g*,*p*]chrysene (**3ah'**) (106 mg, 0.309 mmol, 1.00 equiv) and toluene (12.0 ml) were added to a 100-mL round bottom flask with a magnetic stirring bar. *m*-Chloroperoxybenzoic acid (mCPBA) (50% purity, 334 mg, 0.971 mmol, 3.14 equiv) was slowly added to the flask. The mixture was stirred at room temperature (27 °C) for 30 minutes. The reaction was quenched by the addition of saturated $NaHCO_3$ aqueous solution (10.0 mL) and $Na_2S_2O_3$ aqueous solution (5.0 mL). The mixture was extracted with EtOAc (20 mL, twice). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The

residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford 1-nitrosodibenzo[*g*,*p*]chrysene (**S11**) (89.8 mg, 0.251 mmol, 81% yield) as an orange solid.

S11 (36.5 mg, 0.102 mmol, 1.00 equiv), 4-iodoaniline (67.9 mg, 0.310 mmol, 3.03 equiv), CH_2Cl_2 (3.0 mL) and AcOH (1.0 mL) were added to a screw-capped test tube with a magnetic stirring bar. The mixture was stirred at 60 °C for 24 hours. After reaction completion (monitored by TCL), the reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution (5.0 mL) and extracted with CH_2Cl_2 (5.0 mL, twice). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 50:1) and recycling gel permeation chromatography (GPC) to afford 1-(dibenzo[*g*,*p*]chrysen-1-yl)-2-(4-iodophenyl)diazene (**3ah'-azobenzene**) (38.9 mg, 0.0697 mmol, 68% yield) as reddish orange solid.



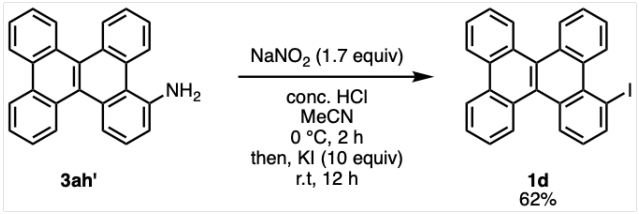
S11: ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.02 (dd, *J* = 8.0, 0.6 Hz, 1H), 8.87–8.67 (m, 4H), 8.53 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.23 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.87–7.48 (m, 7H), 6.31 (dd, *J* = 7.9, 1.2 Hz, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 165.2, 136.0, 135.4, 132.2, 131.8, 131.5 (2C), 131.3, 129.3, 129.1, 128.8 (2C), 128.4, 128.3, 127.8, 127.4, 127.2, 127.1, 127.0, 126.9, 126.5, 126.0, 124.0, 123.8, 104.6. One tertiary sp^2 carbon was overlapped. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{15}NO$: 357.1154. Found: 357.1160.



3ah'-azobenzene: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 7.4, 1.9 Hz, 1H), 8.77–8.67 (m, 4H), 8.64 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.02–7.93 (m, 2H), 7.89–7.82 (m, 2H), 7.78–7.62 (m, 7H), 7.56 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 152.5, 150.7, 138.8, 133.1, 131.4, 131.3 (2C), 131.23, 131.19, 129.1, 129.0 (2C), 128.9, 128.7, 128.6, 128.4, 128.1, 127.3, 127.2, 127.0, 126.9, 126.82, 126.77, 125.8, 125.3, 123.84, 123.77, 114.6, 98.1. One quaternary carbon was overlapped. **HRMS** (FAB, positive): *m/z* calcd. for *m/z* calcd for $C_{32}H_{20}IN_2$ $[M+H]^+$: 559.0671. Found: 559.0679.

Note: ***3ah'-azobenzene*** *isomerizes upon light irradiation at 365 nm and becomes a cis/trans mixture. This mixture returns to the trans isomer by heating at 60 °C for 1 hour. The photoisomerization profile was analyzed by* ^{1}*H NMR (Figure S116).*

4.3 Synthesis of 1-iododibenzo[*g*,*p*]chrysene (1d)

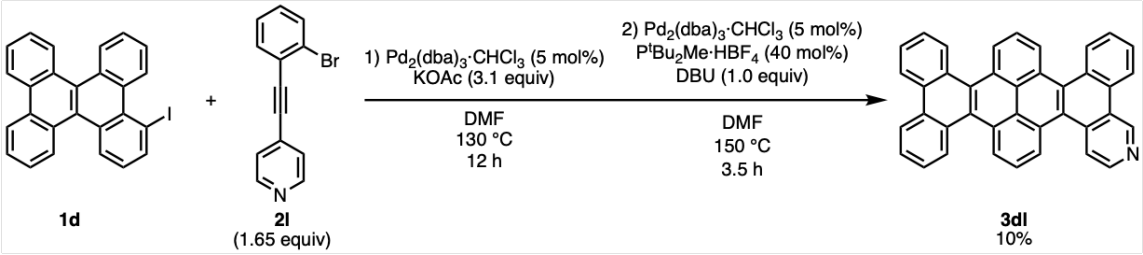


1-Aminodibenzo[*g*,*p*]chrysene (**3ah'**) (388 mg, 1.13 mmol, 1.00 equiv) and MeCN (2.0 mL) were added to a 25-mL Schlenk tube with a magnetic stirring bar. After cooling to 0 °C, conc. HCl aq (5.5 mL) was added to the Schlenk tube and stirred at the same temperature for 30 min. An aqueous solution (ca. 3.0 mL) of $NaNO_2$ (134 mg, 1.94 mmol, 1.71 mmol) was added to the Schlenk, keeping the temperature below 4 °C. The reaction mixture was stirred at 0°C for 2 hours. KI (1.92 g, 11.6 mmol, 10.3 equiv) was added to the dark red reaction mixture in

one portion and then further stirred at room temperature (27 °C) for 12 hours. The resulting reaction mixture was extracted with CH_2Cl_2 (10 mL, three times). The combined organic layers were washed with saturated $NaHCO_3$ aqueous solution (20 mL, twice) and subsequently washed with $Na_2S_2O_3$ aqueous solution (20 mL) to consume the remaining iodine. The resulting organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (hexane/$CHCl_3$ = 100:0 → 10:1) to afford the 1-iododibenzo[*g*,*p*]chrysene (**1d**) (317 mg, 0.698 mmol, 62%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.40–9.30 (m, 1H), 8.74–8.66 (m, 3H), 8.64 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.60–8.52 (m, 2H), 8.28 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.76–7.53 (m, 6H), 7.23 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.3, 132.5, 131.5, 131.3, 131.1, 130.8, 130.5, 128.9 (2C), 128.8, 128.7, 128.6 (2C), 128.5, 128.1, 128.0 (2C), 127.5, 127.1, 126.9, 126.69, 126.66, 124.0, 123.8, 123.7, 93.4. **HRMS** (EI, positive): *m/z* calcd for $C_{26}H_{15}I$: 454.0219. Found: 454.0216.

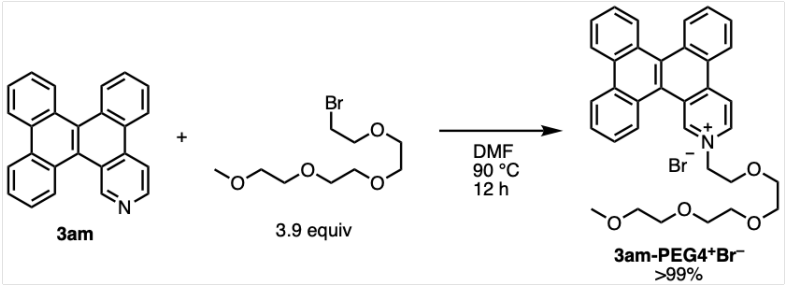
4.4 Synthesis of benzo[*h*]tribenzo[5,6:7,8:11,12]tetrapheno[9,10-*f*]isoquinoline (3dl)



1d (90.4 mg, 0.199 mmol, 1.00 equiv) and $Pd_2(dba)_3 \cdot CHCl_3$ (10.3 mg, 0.0100 mmol, 5.0 mol%) were added to a heat-dried test tube with a magnetic stirring bar. Dry KOAc (60.4 mg, 0.615 mmol, 3.09 equiv) was added to the test tube in a glove box and the test tube was sealed with an open-top screw cap with a silicone septum. The test tube was evacuated and backfilled with N_2 three times. N,N-dimethylformamide (DMF) (2.0 mL) was added to the test tube and the mixture was stirred at 130 °C for 12 hours. Subsequently, additional $Pd_2(dba)_3 \cdot CHCl_3$ (10.3 mg, 0.0100 mmol, 5.0 mol%), $P^tBu_2Me \cdot HBF_4$ (23.4 mg, 0.0943 mmol, 47.4 mol%), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (30.0 µL, 0.200 mmol, 1.00 equiv) were added to the reaction mixture as a DMF solution (1.5 mL) via syringe and the mixture was stirred at 150 °C for 3.5 hours. After cooling to room temperature, H_2O (6.0 mL) was added to the reaction mixture. The precipitate was filtered, washed with H_2O and collected by dissolving $CHCl_3$. The solution was concentrated under reduced pressure and dried *in vacuo*. The crude material was purified by silica gel column chromatography ($CHCl_3$/MeOH = 10:1) to afford benzo[*h*]tribenzo[5,6:7,8:11,12]tetrapheno[9,10-*f*]isoquinoline (**3dl**) (10.0 mg, 0.0199 mmol, 10 % yield) as an orange solid. *Note: The product was poorly soluble in general organic solvents. $CHCl_3$ (ca. 50 mL for 10 mg) was needed to dissolve completely.*

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (s, 1H), 9.09–8.99 (m, 3H), 8.99–8.76 (m, 8H), 8.70 (d, J = 5.8 Hz, 1H), 8.12 (td, J = 8.0, 2.9 Hz, 2H), 7.85–7.65 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 147.5, 146.1, 131.3, 130.1, 129.9, 129.6, 129.2, 128.8, 128.7, 128.6, 128.1, 128.0, 127.9, 127.8, 127.6, 127.2 (2C), 127.0, 126.57, 126.54, 126.03, 126.00, 125.88, 125.80, 125.7, 125.2, 123.9, 123.2, 121.2. (only detectable carbons were shown due to low solubility.) **HRMS** (ESI, positive): *m/z* calcd for $C_{39}H_{22}N$ $[M+H]^+$: 504.17468. Found: 504.17450.

4.5 Synthesis of 3-(2,5,8,11-tetraoxatridecan-13-yl)benzo[*f*]phenanthro[9,10-*h*]isoquinolin-3-ium bromide (3am-PEG4$^+$Br$^-$)

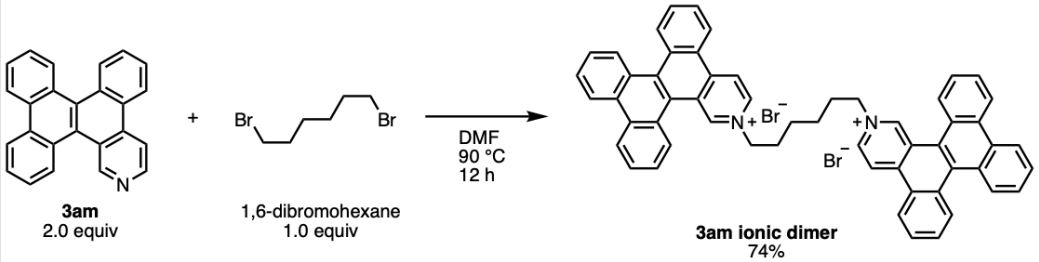


3am (33.4 mg, 0.101 mmol, 1.00 equiv), triethylene glycol 2-bromoethyl methyl ether (83 µL, 107 mg, 0.390 mmol, 3.90 equiv) and DMF (1.0 mL) were added to a screw-capped test tube. The mixture was stirred at 90 °C for 12 hours. After monitoring the consumption of **3am** by TLC, the reaction mixture was cooled at room temperature and concentrated under evacuation. The residue was purified by silica gel column chromatography

($CHCl_3$/MeOH = 100:0 → 10:1 → 5:1) to afford the product as a yellow gel-like solvent-containing product. The product was mixed with hexane (3.0 mL), sonicated for 5 minutes, concentrated under reduced pressure and dried under evacuation for 24 hours to afford the product (**3am-PEG4$^+$Br$^-$**) (60.6 mg, 0.101 mmol, >99% yield) as a yellow hygroscopic semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (d, *J* = 6.7 Hz, 1H), 9.94 (s, 1H), 9.21 (d, *J* = 6.7 Hz, 1H), 8.85 (d, *J* = 7.8 Hz, 1H), 8.79–8.73 (m, 3H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 7.9 Hz, 1H), 7.96–7.78 (m, 5H), 7.70 (t, *J* = 7.6 Hz, 1H), 5.41 (t, *J* = 4.5 Hz, 2H), 4.22 (t, *J* = 4.6 Hz, 2H), 3.75–3.68 (m, 2H), 3.58–3.51 (m, 2H), 3.43–3.31 (m, 8H), 3.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.1, 139.6, 138.8, 132.0, 131.8, 131.7, 130.9, 130.6, 129.2, 128.84, 128.78, 128.76, 128.5, 128.36, 128.32, 127.6, 127.3, 126.5, 126.4, 125.8, 124.9, 124.1, 124.0, 123.4, 122.2, 71.8, 70.8, 70.4 (2C), 70.3, 70.1, 69.8, 61.8, 58.9. **HRMS** (ESI, positive): *m/z* calcd for $C_{34}H_{34}NO_4$ [M–Br]$^+$: 520.24824. Found: 520.24748.

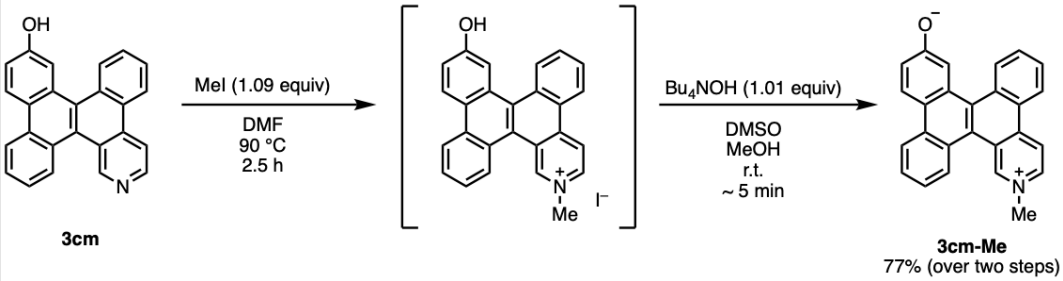
4.6 Synthesis of 3,3'-(hexane-1,6-diyl)bis(benzo[*f*]phenanthro[9,10-*h*]isoquinolin-3-ium) bromide (3am ionic dimer)



3am (36.4 mg, 0.111 mmol, 1.00 equiv), 1,6-dibromohexane (7.6 μL, 12.2 mg, 0.0506 mmol, 1.00 equiv) and DMF (1.0 mL) were added to a screw-capped test tube. The mixture was stirred at 90 °C for 30 minutes. After reaction completion, a yellow precipitate formed. After cooling to room temperature, the reaction mixture was diluted with acetone (4.0 mL). The precipitate was collected by filtration and washed with acetone (10 mL, three times). The collected solid was dried under evacuation to afford a yellow solid (36.8 mg, 0.0407 mmol, 74% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.12 (s, 2H), 9.50 (d, *J* = 6.9 Hz, 2H), 9.18 (d, *J* = 7.2 Hz, 4H), 9.03–8.89 (m, 4H), 8.81 (d, *J* = 8.2 Hz, 2H), 8.67 (d, *J* = 8.1 Hz, 2H), 8.53 (d, *J* = 7.7 Hz, 2H), 8.08 (td, *J* = 7.6, 1.0 Hz, 2H), 8.00 (td, *J* = 7.6, 0.8 Hz, 2H), 7.90 (td, *J* = 7.8, 1.2 Hz, 2H), 7.87–7.75 (m, 6H), 4.85 (t, *J* = 7.4 Hz, 4H), 2.10–1.95 (brd, 4H), 1.48–1.35 (brd, 4H). **^{13}C NMR** (101 MHz, DMSO-*d*$_6$): δ 146.5, 139.0, 137.9, 132.1, 131.3, 131.2, 130.5, 129.7, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 127.8, 127.3, 126.6, 126.5, 126.2, 124.8, 124.24, 124.15, 123.7, 122.0, 60.7, 30.6, 25.0. **HRMS** (ESI, positive): *m/z* calcd for $C_{56}H_{42}BrN_2$ [M–Br]$^+$: 821.25259. Found: 821.25179.

4.7 Synthesis of 3-methylbenzo[*f*]phenanthro[9,10-*h*]isoquinolin-3-ium-11-olate (3cm-Me)



3cm (35.0 mg, 0.101 mmol, 1.00 equiv) was added to a screw-capped test tube with a magnetic stirring bar. N,N-Dimethylformamide (DMF) (1.0 mL) and MeI (7.0 μL, 0.110 mmol, 1.09 equiv) were added to the test tube. The mixture was stirred at 90 °C for 2.5 hours. After cooling to room temperature, the resulting mixture was diluted with acetone (2.0 mL). The orange precipitate was collected by filtration, washed with acetone and dried under evacuation to afford the methylated product (41.9 mg, 0.0860 mmol, 91% yield) as a yellow solid. The afforded methylated product (41.9 mg) was dissolved in DMSO (1.0 mL) and MeOH (0.5 ml) mixture solvent. Bu_4NOH (225 mg, 10 % MeOH solution, 0.0868 mmol, 1.01 equiv) was added to the solution. A brown–orange precipitate was immediately formed. The precipitate was collected by filtration, washed with CH_2Cl_2 and acetone, and dried under evacuation to afford 3-methylbenzo[*f*]phenanthro[9,10-*h*]isoquinolin-3-ium-11-olate (**3cm-Me**) (28.2 mg, 0.0785 mmol, 77% yield over 2 steps) as a dark brown solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.99 (s, 1H), 9.35 (d, J = 6.8 Hz, 1H), 9.04–8.91 (m, 3H), 8.63 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 9.0 Hz, 1H), 8.42 (d, J = 8.2 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.75–7.64 (m, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 4.53 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6 with AcOH): δ 157.3, 147.3, 138.71, 138.65, 131.8, 131.5, 131.1, 129.3, 129.0, 128.9, 128.5, 128.3, 128.2, 126.9, 126.3, 126.2, 126.0, 125.4, 124.7, 124.0, 123.9, 123.4, 121.7, 118.7, 112.6, 48.1. **HRMS** (ESI, positive): *m/z* calcd for $C_{26}H_{18}NO$ $[M+H]^+$: 360.13829. Found: 360.13760.

5. Measurements of UV/vis absorption spectra

UV/vis absorption spectra of **3am** ($c = 7.50 \times 10^{-5}$ M), **3cm** ($c = 7.09 \times 10^{-5}$ M), **3am-PEG4^{+}Br^{-}** ($c = 6.67 \times 10^{-5}$ M) and **3cm-Me** ($c = 6.88 \times 10^{-5}$ M) in dry N,N-dimethylformamide (DMF) and **3cm-Me** in DMF/H_2O = 99:1 and DMF/AcOH = 99:1 were recorded on an Agilent Cary 8454 Spectrophotometer with a resolution of 1.0 nm.

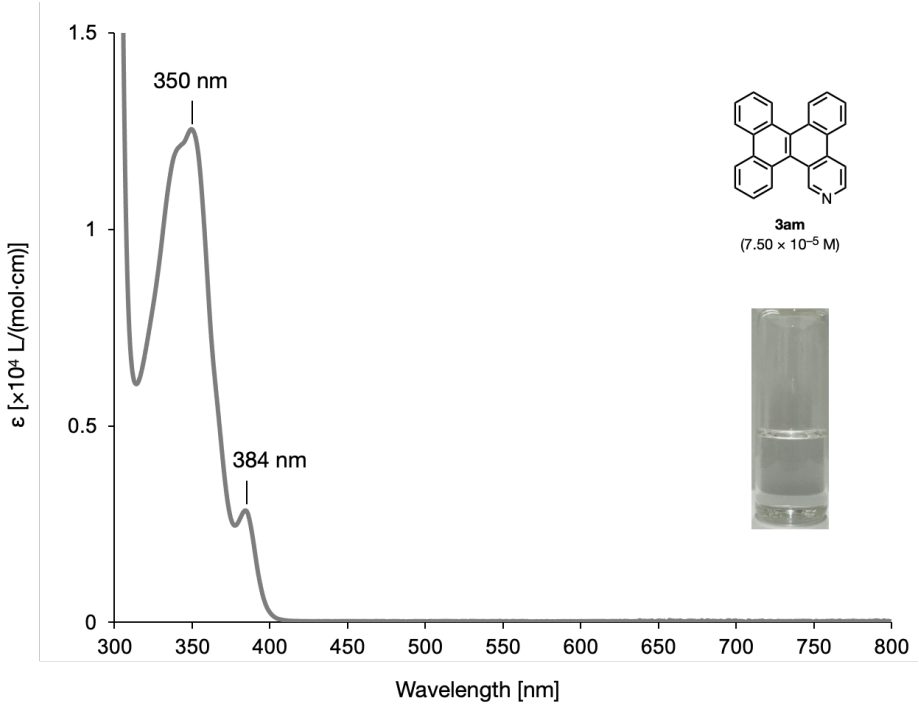


Figure S1. UV–vis absorption spectrum of dry DMF solution of **3am**.

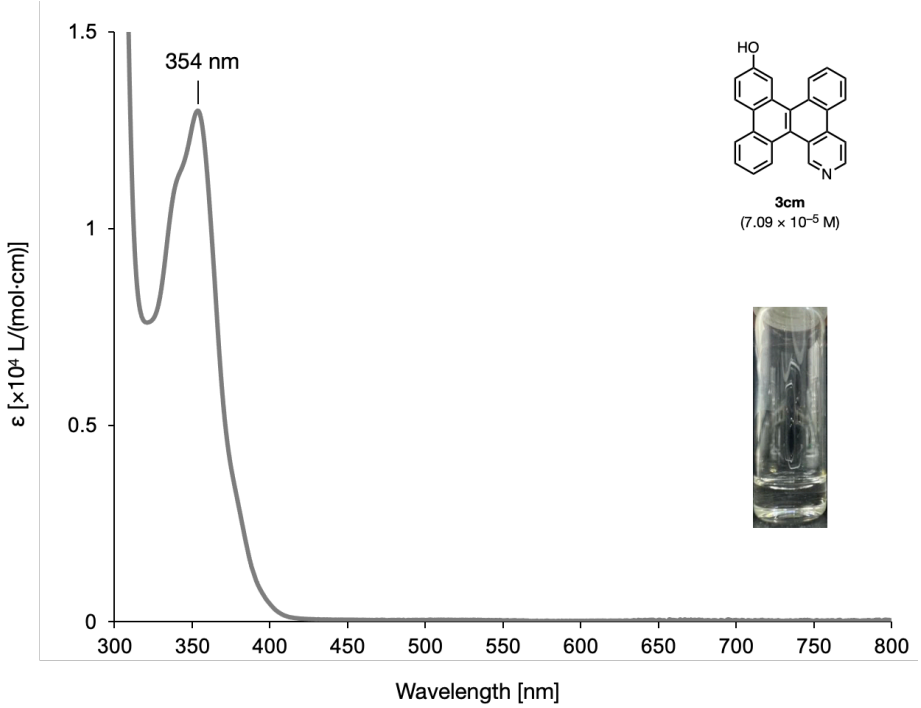


Figure S2. UV–vis absorption spectrum of dry DMF solution of **3cm**.

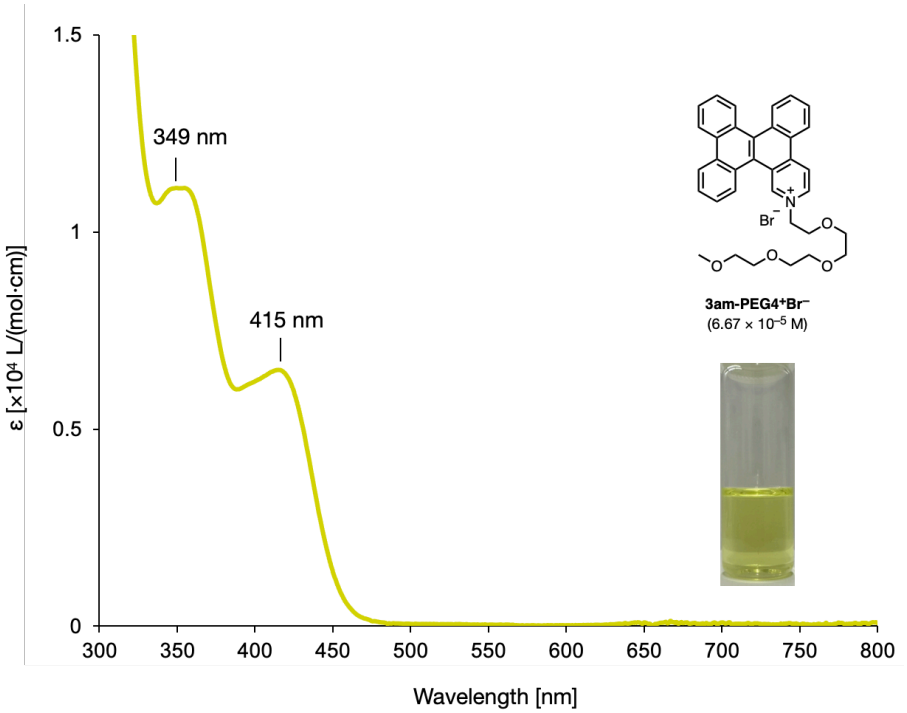


Figure S3. UV–vis absorption spectrum of dry DMF solution of **3am-PEG4^{+}Br^{-}**.

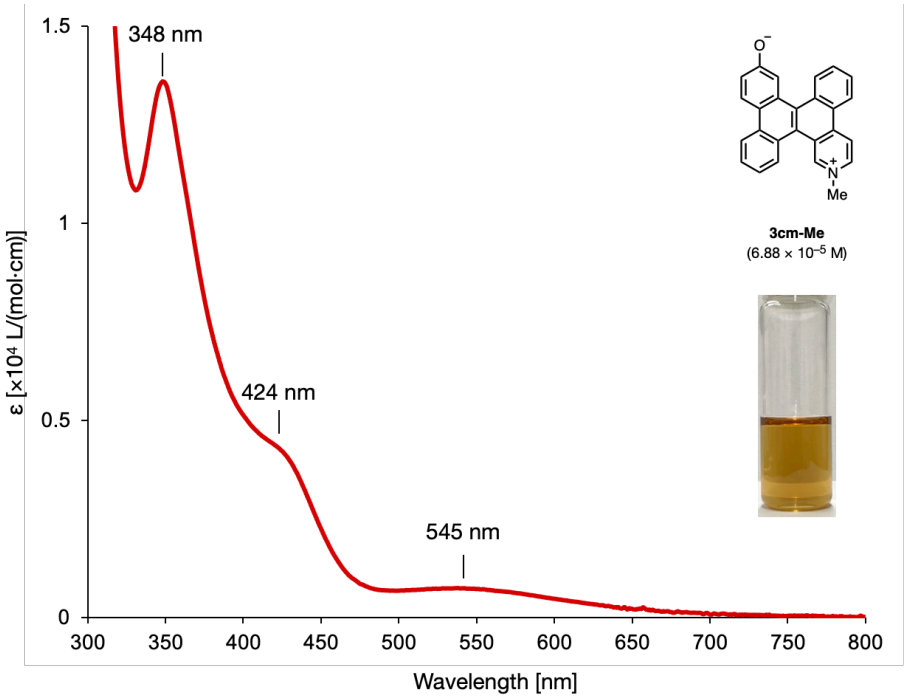


Figure S4. UV–vis absorption spectrum of dry DMF solution of **3cm-Me**.

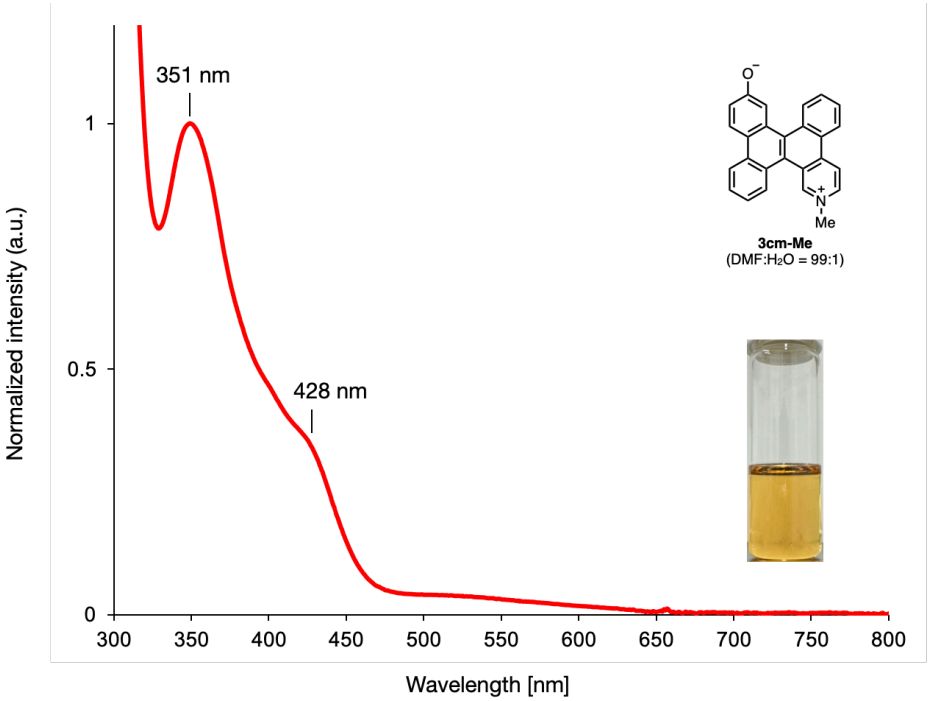


Figure S5. UV–vis absorption spectrum of DMF/H_2O = 99:1 solution of **3cm-Me**.

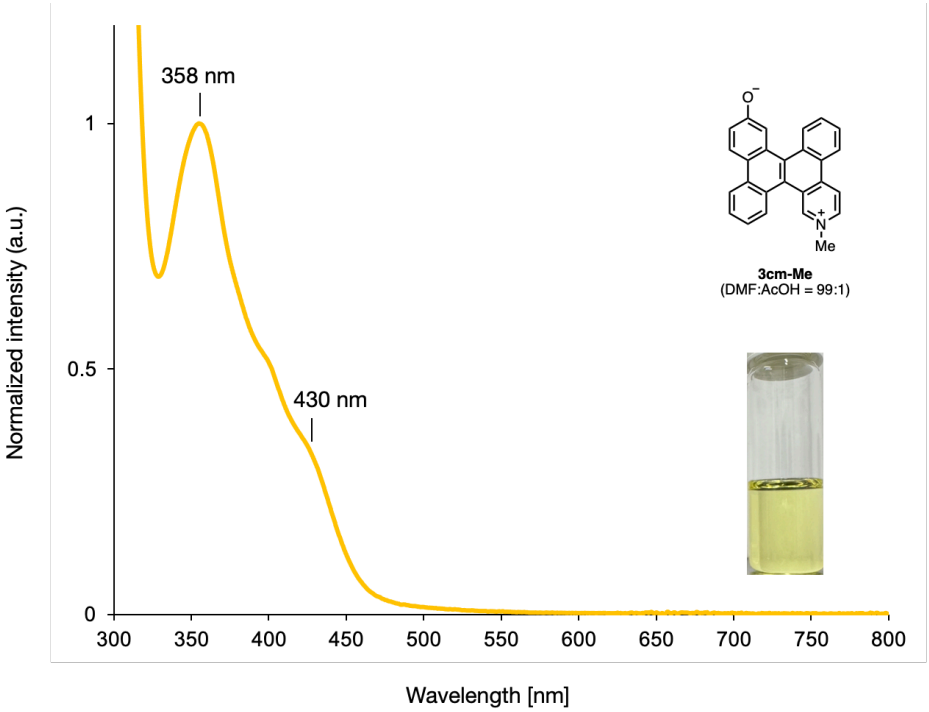


Figure S6. UV–vis absorption spectrum of DMF:AcOH = 99:1 solution of **3cm-Me**

6. Computational study

3am-Me^{+} was selected as a simplified model molecule of **3am-PEG4**$^{+}$**Br**$^{-}$ to reduce calculation time. Geometry optimizations and frequency calculations were performed with the Gaussian 16 programs[S19] at the B3LYP[S20]/6-31+G(d) level of theory for **3am, 3cm, 3am-Me**$^{+}$. Visualization of the results was performed by use of GaussView 6.1 software.[S21]

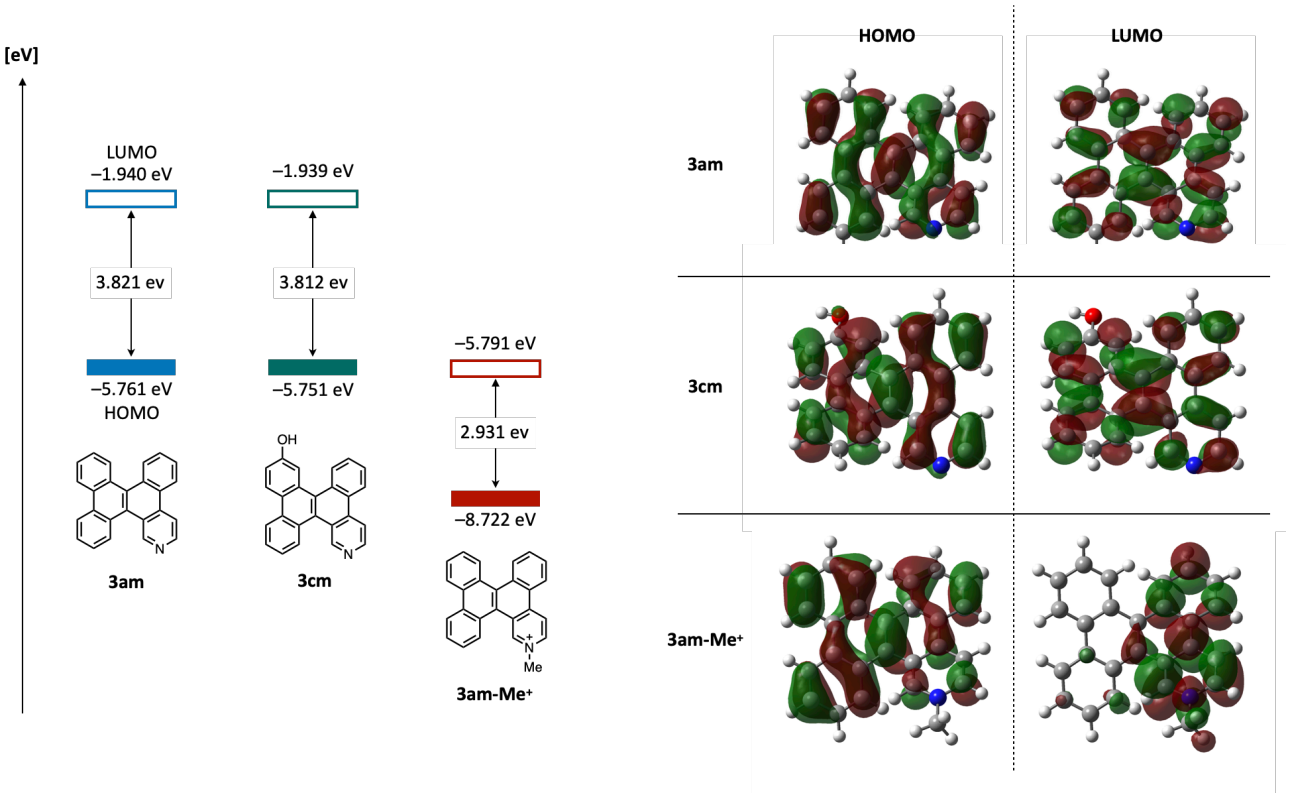


Figure S7. Energy diagram and pictorial representation of frontier MOs of **3am**, **3cm** and **3am-Me**$^{+}$.

Table S1. Cartesian coordinates of optimized structures.

3am

C	3.626544	2.695409	-1.081558	C	-1.304967	2.684367	0.850311
C	3.654585	1.393759	-0.608348	C	-1.253001	-2.706422	-0.867107
C	2.474644	0.720784	-0.220042	N	-2.345061	-3.358606	-1.244944
C	1.229489	1.409298	-0.298517	C	-3.525725	-2.724269	-1.095574
C	1.225252	2.723767	-0.830731	C	-3.635567	-1.425685	-0.631074
C	2.396252	3.358992	-1.21078	H	4.549234	3.183993	-1.383336
C	2.489991	-0.663922	0.238768	H	4.605516	0.873218	-0.571495
C	1.261912	-1.383592	0.300362	H	0.281143	3.226827	-1.001187
C	0.007123	-0.699748	-0.003761	H	2.354417	4.359718	-1.632863
C	-0.012273	0.69833	0.00128	H	4.620235	-0.766754	0.612421
C	3.68181	-1.310353	0.634925	H	4.611814	-3.085835	1.402044
C	3.680554	-2.617184	1.095025	H	2.445911	-4.321607	1.608137
C	2.466638	-3.314046	1.201367	H	0.351802	-3.234171	0.969605
C	1.283939	-2.703909	0.816578	H	-4.641179	0.755566	0.550119
C	-1.235929	-1.400411	-0.309427	H	-4.644833	3.065531	1.383099
C	-2.480183	-0.719241	-0.23808	H	-2.478201	4.285026	1.657826
C	-2.504078	0.661105	0.222674	H	-0.374838	3.210292	1.027579
C	-1.273325	1.374145	0.308256	H	-0.316762	-3.219513	-1.06199
C	-3.704204	1.300053	0.603589	H	-4.409537	-3.282611	-1.396792
C	-3.70978	2.598218	1.086246	H	-4.612784	-0.9554	-0.606505
C	-2.494119	3.286549	1.228609				

3cm

C	-4.213651	-1.127198	0.744483	C	0.490076	-2.766755	-1.050054
C	-3.753639	0.122586	0.365424	C	2.257788	2.195807	1.014934
C	-2.398666	0.358233	0.051647	N	3.490904	2.398306	1.461138
C	-1.485248	-0.735012	0.115537	C	4.379118	1.396949	1.295859
C	-1.96318	-1.993326	0.547992	C	4.046954	0.170967	0.747622
C	-3.301498	-2.189581	0.851362	O	-3.675938	-3.439931	1.275019
C	-1.90572	1.680386	-0.312027	H	-5.264011	-1.273752	0.989861
C	-0.50128	1.91834	-0.298487	H	-4.462382	0.943256	0.342388
C	0.413931	0.815871	-0.011646	H	-1.284906	-2.820549	0.712928
C	-0.059243	-0.496725	-0.108415	H	-3.84288	2.557572	-0.722766
C	-2.772319	2.730518	-0.688703	H	-2.978074	4.760346	-1.35379
C	-2.287419	3.974276	-1.059834	H	-0.507803	5.152117	-1.433746
C	-0.901957	4.197675	-1.095136	H	1.034593	3.354997	-0.824864
C	-0.03086	3.185115	-0.727085	H	4.274394	-2.156076	-0.552862
C	1.808802	1.012967	0.369683	H	3.50429	-4.272982	-1.531073
C	2.735952	-0.059085	0.281626	H	1.061091	-4.634869	-1.928957
C	2.293853	-1.331633	-0.268558	H	-0.556624	-2.923526	-1.279245
C	0.895912	-1.558605	-0.427556	H	1.553293	2.994826	1.222318
C	3.20933	-2.331806	-0.6625	H	5.388169	1.589565	1.654128
C	2.780581	-3.52171	-1.226633	H	4.796756	-0.612208	0.713996
C	1.408103	-3.728838	-1.439005	H	-4.619039	-3.443891	1.500381

3am-Me$^+$

C	-4.490354	1.223569	1.327563	N	3.273818	-2.064226	0.840491
C	-4.056327	0.036485	0.759635	C	4.163867	-1.032115	0.740034
C	-2.737281	-0.113149	0.280393	C	3.73249	0.213112	0.362174
C	-1.844853	0.996524	0.367315	C	3.752775	-3.371948	1.338928
C	-2.301896	2.18372	0.99397	H	-5.508696	1.306407	1.696273
C	-3.599614	2.29979	1.462694	H	-4.744041	-0.800407	0.716528
C	-2.262231	-1.371001	-0.288925	H	-1.611508	2.999778	1.168971
C	-0.862837	-1.564456	-0.469736	H	-3.916089	3.214311	1.955873
C	0.050171	-0.473	-0.155224	H	-4.214457	-2.264807	-0.567607
C	-0.451041	0.829902	-0.028596	H	-3.386835	-4.349481	-1.54427
C	-3.144861	-2.40179	-0.678629	H	-0.943611	-4.641274	-1.976546
C	-2.682281	-3.579409	-1.244017	H	0.624848	-2.866873	-1.37159
C	-1.308222	-3.75018	-1.473472	H	3.794973	2.693877	-0.647368
C	-0.419521	-2.755715	-1.097827	H	2.875211	4.86664	-1.307344
C	1.473341	-0.65578	0.075416	H	0.401791	5.168608	-1.469347
C	2.376578	0.45604	0.042535	H	-1.110745	3.339683	-0.886401
C	1.864257	1.757627	-0.304844	H	1.333664	-2.736561	0.683903
C	0.446962	1.945709	-0.319571	H	5.191855	-1.254042	0.999625
C	2.719117	2.833003	-0.647009	H	4.460566	1.014611	0.345506
C	2.206258	4.056419	-1.033717	H	4.548835	-3.737367	0.685961
C	0.812645	4.228424	-1.112653	H	2.926466	-4.082224	1.335926
C	-0.044593	3.19814	-0.763151	H	4.131365	-3.256231	2.357316
C	1.979066	-1.884099	0.523574				

7. Single crystal X-ray diffraction and structural analysis of 3ao'

Details of the crystal data and a summary of the intensity data collection parameters for **3ao'** were listed in Table S2 and Figure S8. A single crystal of **3ao'** was prepared by recrystallization using hot toluene. A suitable crystal was mounted with mineral oil on a MiTeGen MicroMounts and transferred to the kappa goniometer of a RIGAKU XtaLAB Synergy-S system with 1.2 kW MicroMax-007HF microfocus rotating anode (Graphitemonochromated Mo Kα radiation (l = 0.71073 Å)) and PILATUS200K hybrid photon-counting detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (RIGAKU, 2015). The structures were solved by direct methods with SIR-97[S22] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2016/6)[S23] by using Yadokari-XG 2009 software package.[S24] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC **2383473** contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S2. Crystallographic data and structure refinement details for **3ao'**.

CCDC deposition No.	**2383473**
formula	C29H17N
fw	379.44
T (K)	123(2) K
λ (Å)	0.71073 Å
cryst syst	monoclinic
space group	P21/n
a (Å)	10.4701(3)
b (Å)	8.8984(2)
c (Å)	19.6220(5)
α (deg)	90
β (deg)	99.531(3)
γ (deg)	90
V (Å^3)	1802.89(8)
Z	4
D_{calc} (g / cm^3)	1.398
μ (mm^{-1})	0.081
F(000)	792.0
cryst size (mm)	0.1 × 0.1 × 0.1
Theta range for data collection (deg)	2.519–25.000
reflns collected	19052
indep reflns/R_{int}	3183 /0.0286
params	271
GOF on F^2	1.049
R_1, wR_2 [$I>2\sigma(I)$]	0.0321, 0.0809
R_1, wR_2 (all data)	0.0382, 0.0843

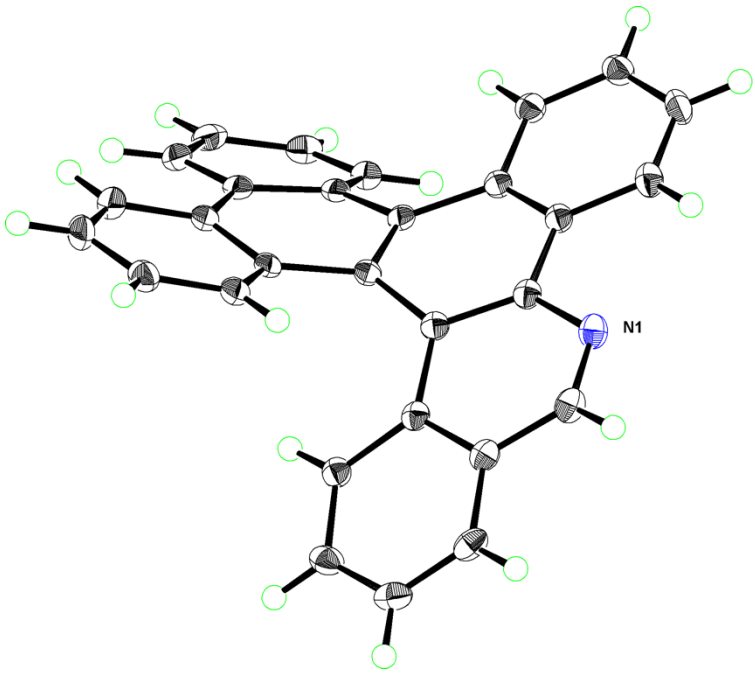


Figure S8. ORTEP drawing of **3ao'**. Displacement ellipsoids are shown at 50% probability level.

8. Proposed reaction mechanism

A proposed mechanism of our palladium-catalyzed multi-annulation sequence is described in Figure S9: (i) oxidative addition of 2-iodobiphenyl to Pd^0 catalyst, (ii) insertion of π-extending agent (**2a**), (iii) formation of seven-membered palladacycle *via* concerted metalation-deprotonation (CMD) process, (iv) reductive elimination to release the corresponding intermediate (**INT**) and regeneration of Pd^0 catalyst, (v) oxidative addition of bromophenyl moiety of **INT** to Pd^0 catalyst, (vi) formation of seven-membered palladacycle *via* CMD process, (vii) reductive elimination to release the final product (**3aa**) and regeneration of Pd^0 catalyst.

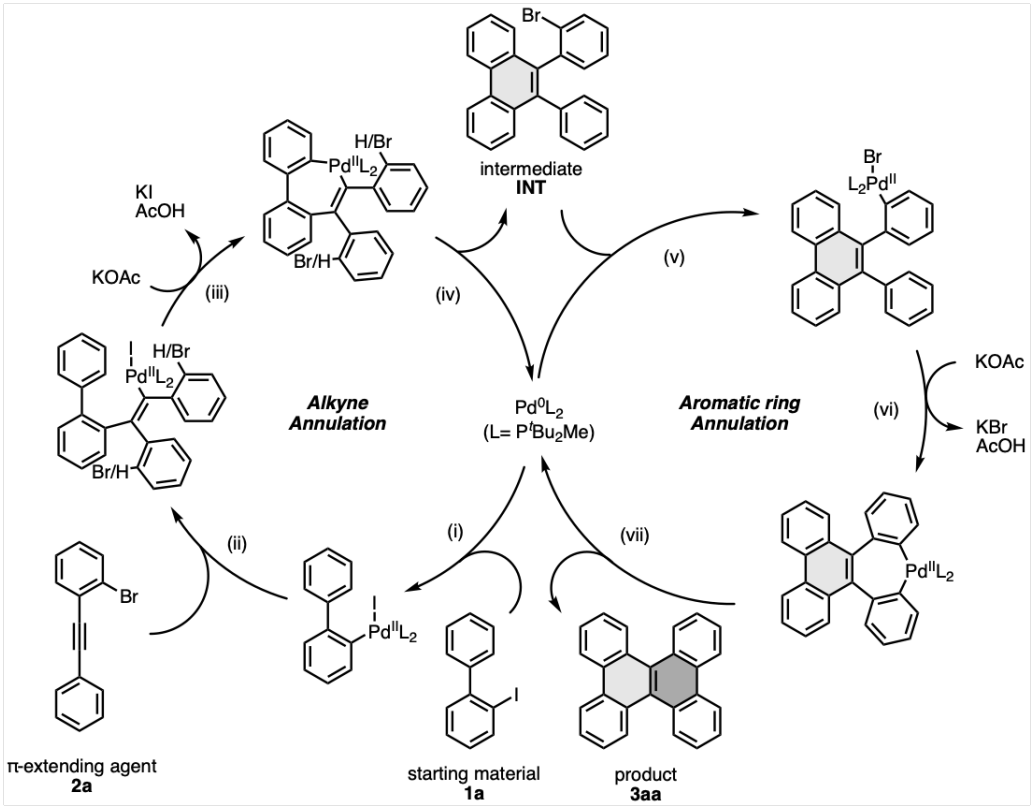


Figure S9. Proposed catalytic cycles of a palladium-catalyzed multi-annulation sequence.

9. References

S1 X. Feng, W. Pisula, K. Müllen, *J. Am. Chem. Soc.* 2007, **129**, 14116.

S2 Y. Wu, J. Li, Y. Fu, Z. Bo, *Org. Lett.* 2004, **6**, 3485.

S3 D. P. Flaherty, T. Kiyota, Y. Dong, T. Ikezu, J. L. Vennerstrom, *J. Med. Chem.* 2010, **53**, 7992.

S4 C. J. Bennett, S. T. Caldwell, D. B. McPhail, P. C. Morrice, G. G. Duthie, R. C. Hartley, *Biorg. Med. Chem.* 2004, **12**, 2079.

S5 G. Ranjani, R. Nagarajan, *Org. Lett.* 2017, **19**, 3974.

S6 M. Hapke, K. Kral, A. Spannenberg, *Synthesis*, 2011, **4**, 642.

S7 L. D. Tran, J. Ma, A. G. Wong-Foy, A. J. Matzger, *Chem. Eur. J.* 2016, **22**, 5509.

S8 S. K. Banjare, L. Lezius, E. S. Horst, D. Leifert, C. G. Daniliuc, F. A. Alasmary, A. Studer, *Angew. Chem., Int. Ed.* 2024, **63**, e202404275.

S9 A. Bakhoda, O. E. Okoromoba, C. Greene, M. R. Boroujeni, J. A. Bertke, T. H. Warren, *J. Am. Chem. Soc.* 2020, **142**, 18483.

S10 K. Naveen, P. T. Perumal, D.-H. Cho, *Org. Lett.* 2019, **21**, 4350.

S11 M. Chen, N. Su, T. Deng, D. J. Wink, Y. Zhao, T. G. Driver, *Org. Lett.* 2019, **21**, 1555.

S12 A. K. Verma, T. Kesharwani, J. Singh, V. Tandon, R. C. Larock, *Angew. Chem., Int. Ed.* 2009, **48**, 1138.

S13 D. C. Hamm, L. A. Braun, A. N. Burazin, A. M. Gauthier, K. O. Ness, C. E. Biebel, J. S. Sauer, R. Tanke, B. C. Noll, E. Bosch, N. P. Bowling, *Dalton Trans.* 2013, **42**, 948.

S14 R. H. Pawle, V. Eastman, S. W. Thomas, *J. Mater. Chem.* 2011, **21**, 14041.

S15 X. Xu, S. M. Rummelt, F. L. Morel, M. Ranocchiari, J. A. van Bokhoven, *Chem. Eur. J.* 2014, **20**, 15467.

S16 W. Matsuoka, H. Ito, K. Itami, *Angew. Chem., Int. Ed.* 2017, **56**, 12224.

S17 E. Heyer, R. Ziessel, *Tetrahedron Lett.* 2013, **54**, 3388.

S18 M. Shimizu, I. Nagao, Y. Tomioka, T. Kadowaki, T. Hiyama, *Tetrahedron* 2011, **67**, 8014.

S19 Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S20 (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.

S21 GaussView, Version 6.1, R. Dennington, T. A. Keith, and J. M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

S22 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 1999, **32**, 115.

S23 G. M. Sheldrick, *Acta Crystallogr. A.* 2008, **64**, 112.

S24 C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Cryst. Soc. Jpn.* 2009, **51**, 218.

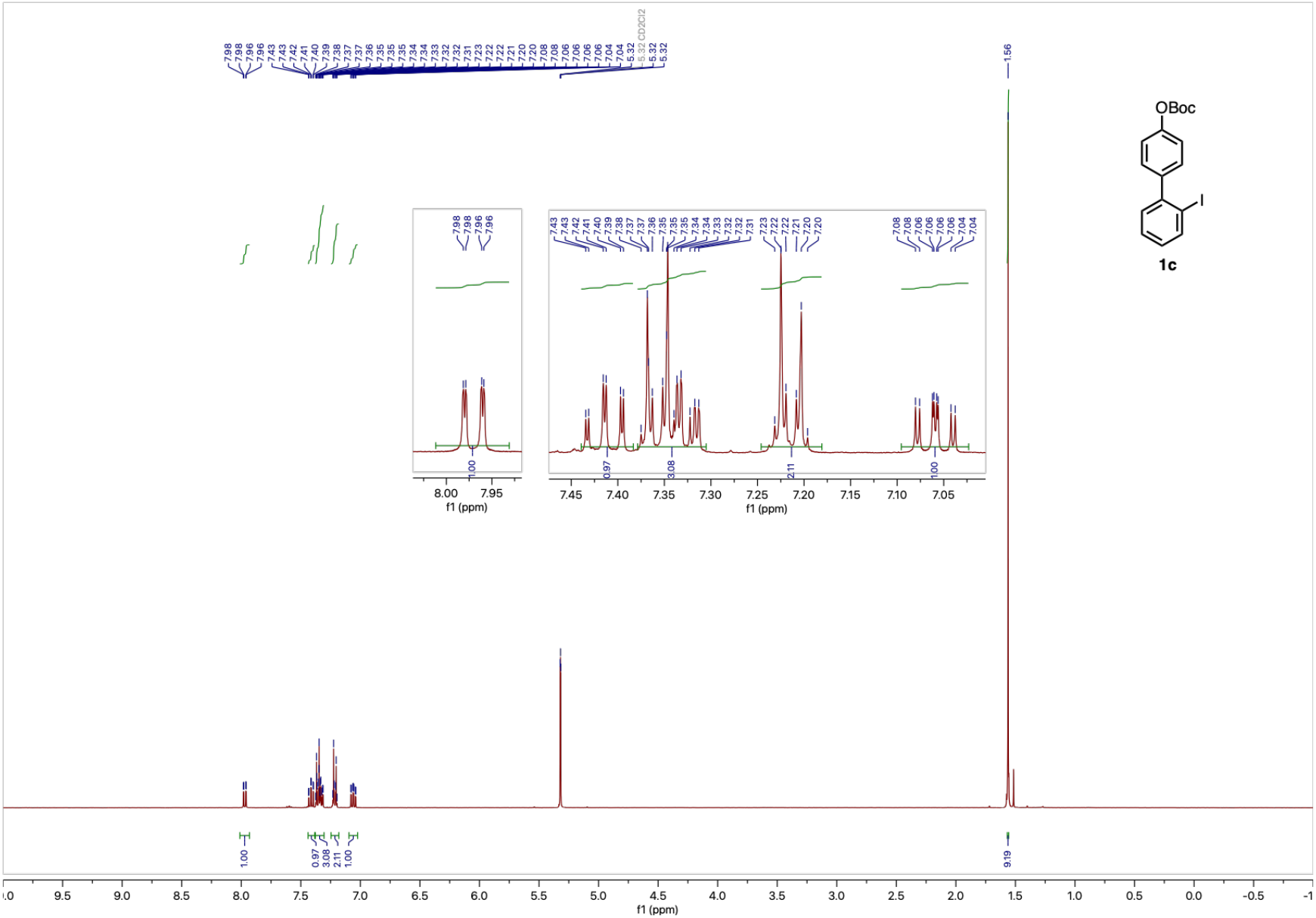


Figure S10. ^{1}H NMR of **1c**.

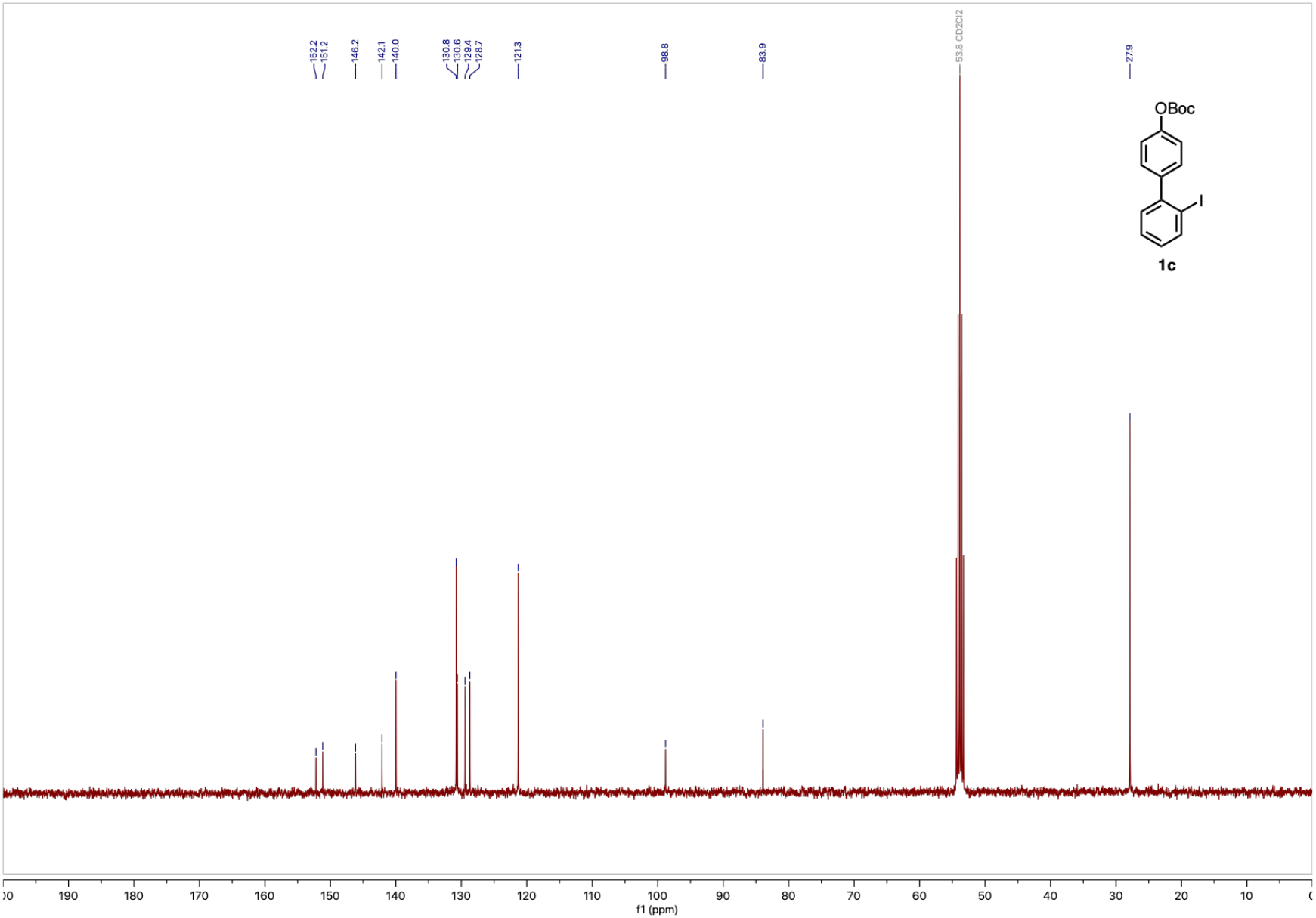


Figure S11. ^{13}C NMR of **1c**.

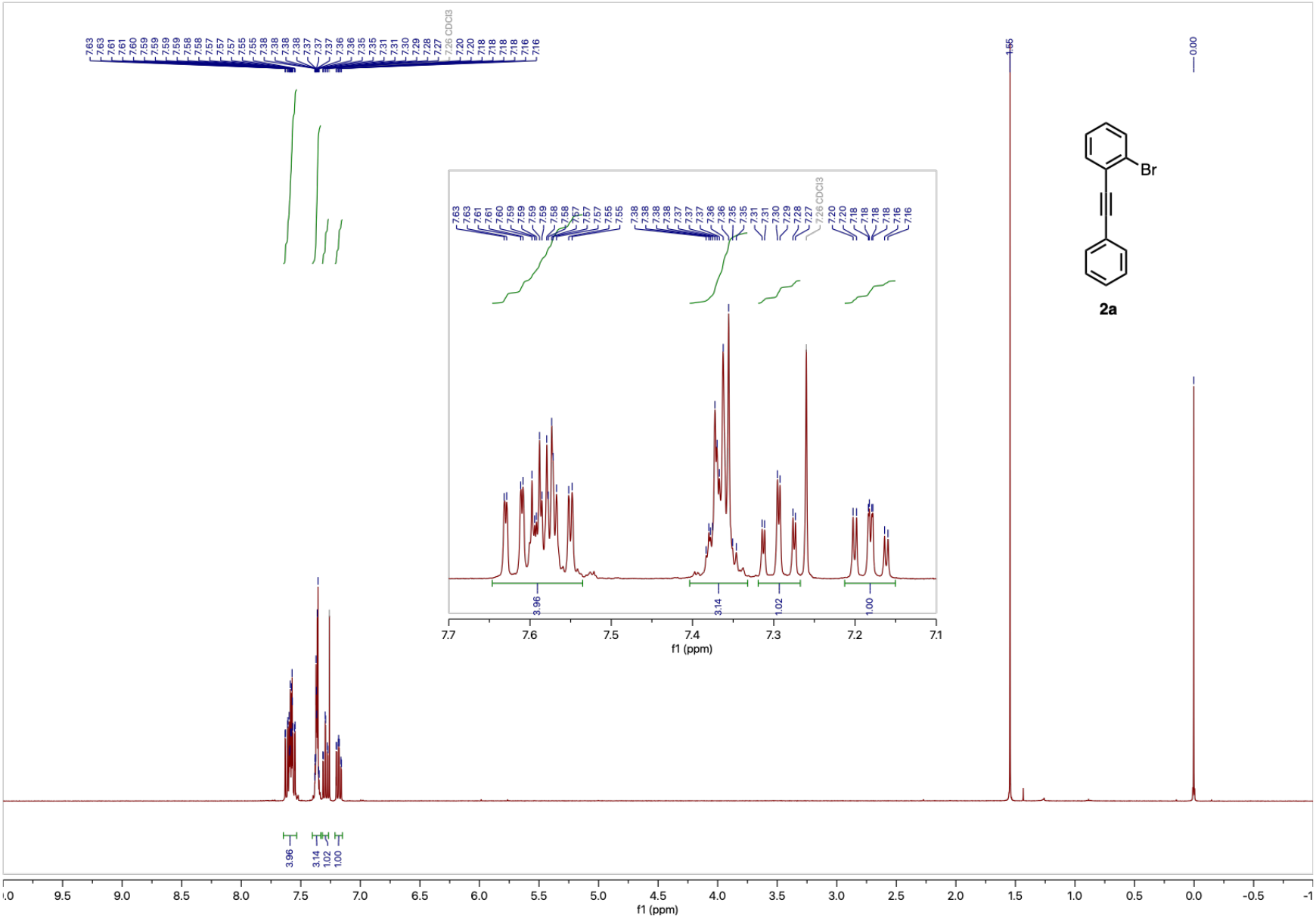


Figure S12. ^{1}H NMR of **2a**.

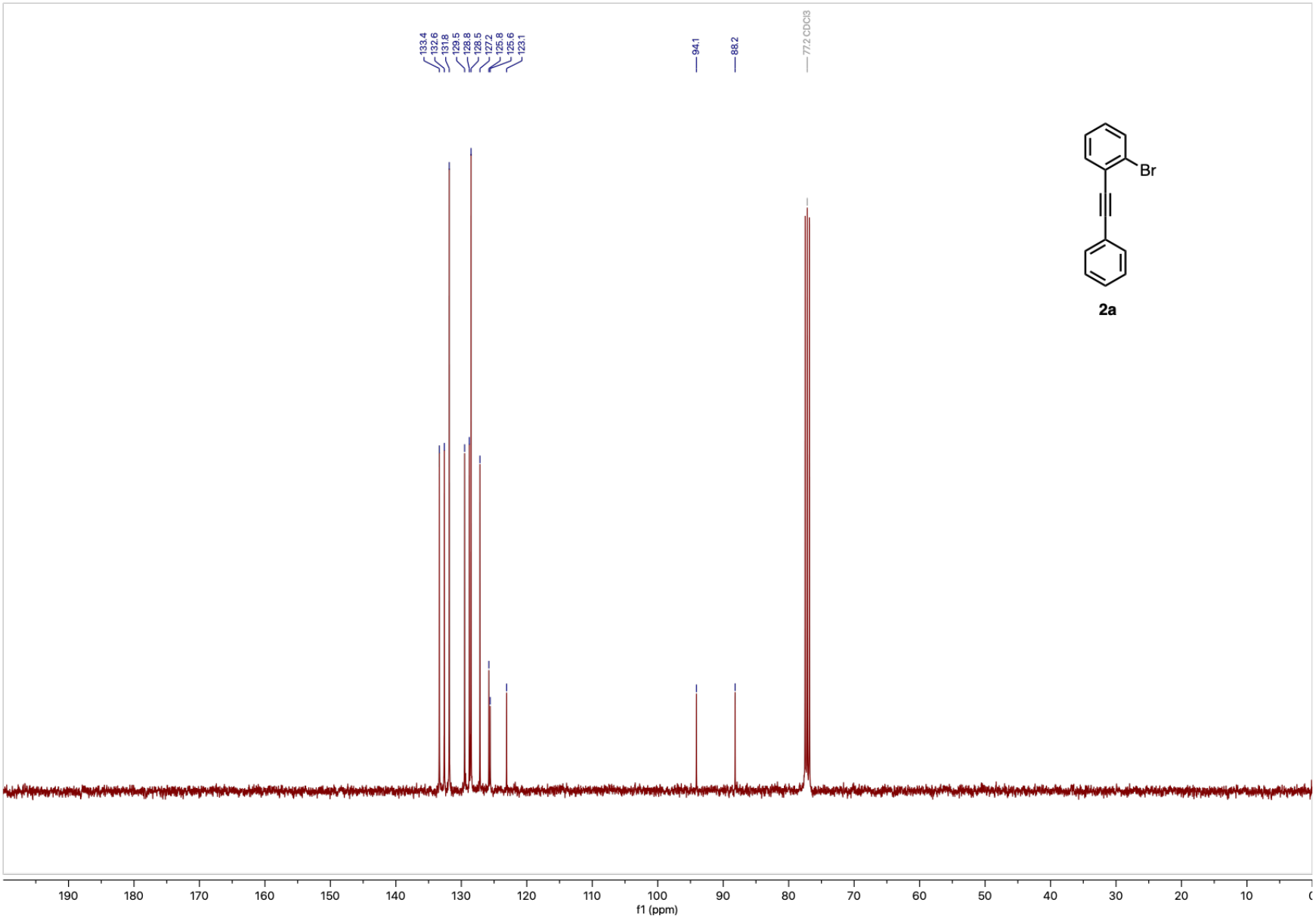


Figure S13. ^{13}C NMR of **2a**.

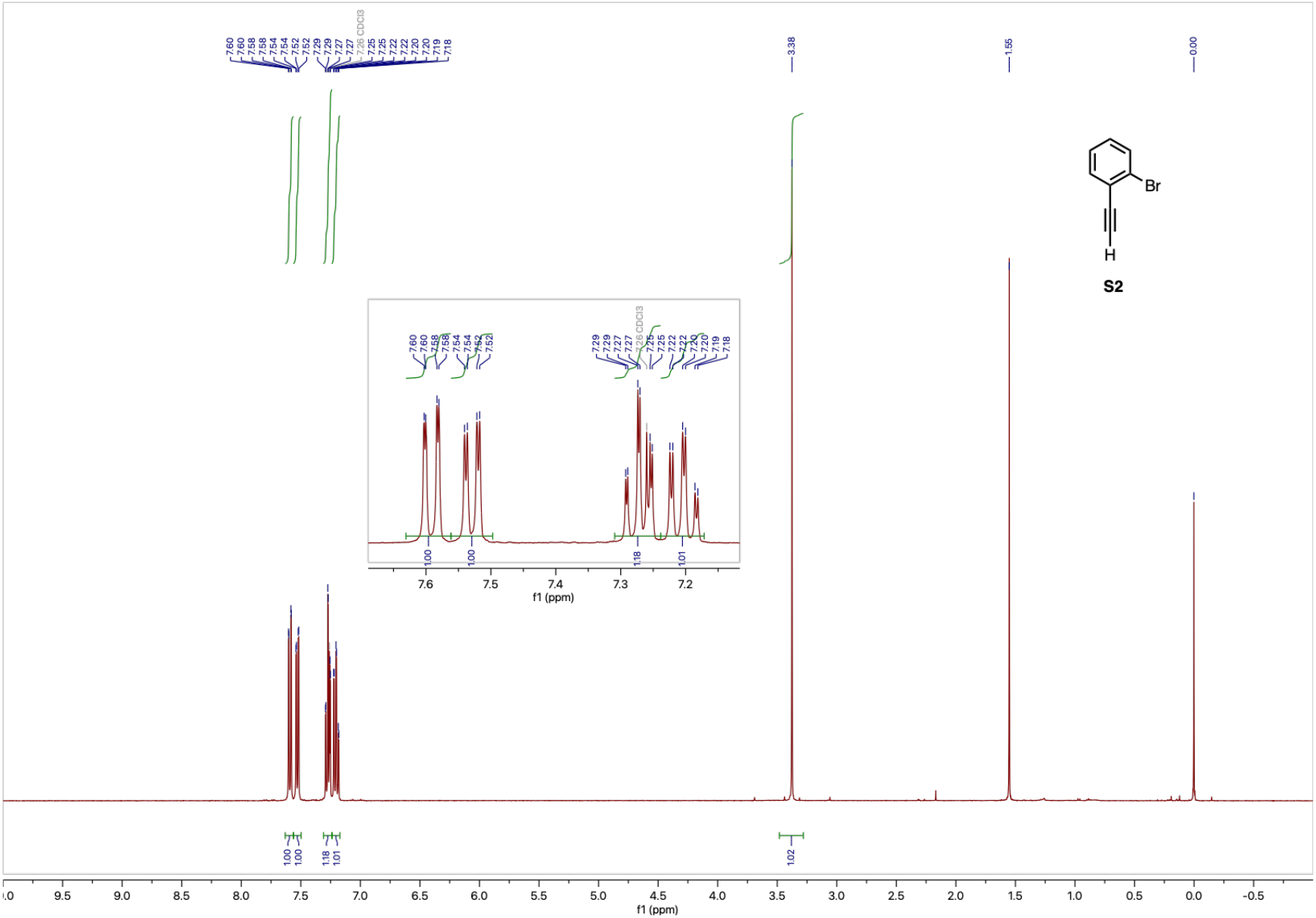


Figure S14. ^{1}H NMR of **S2**.

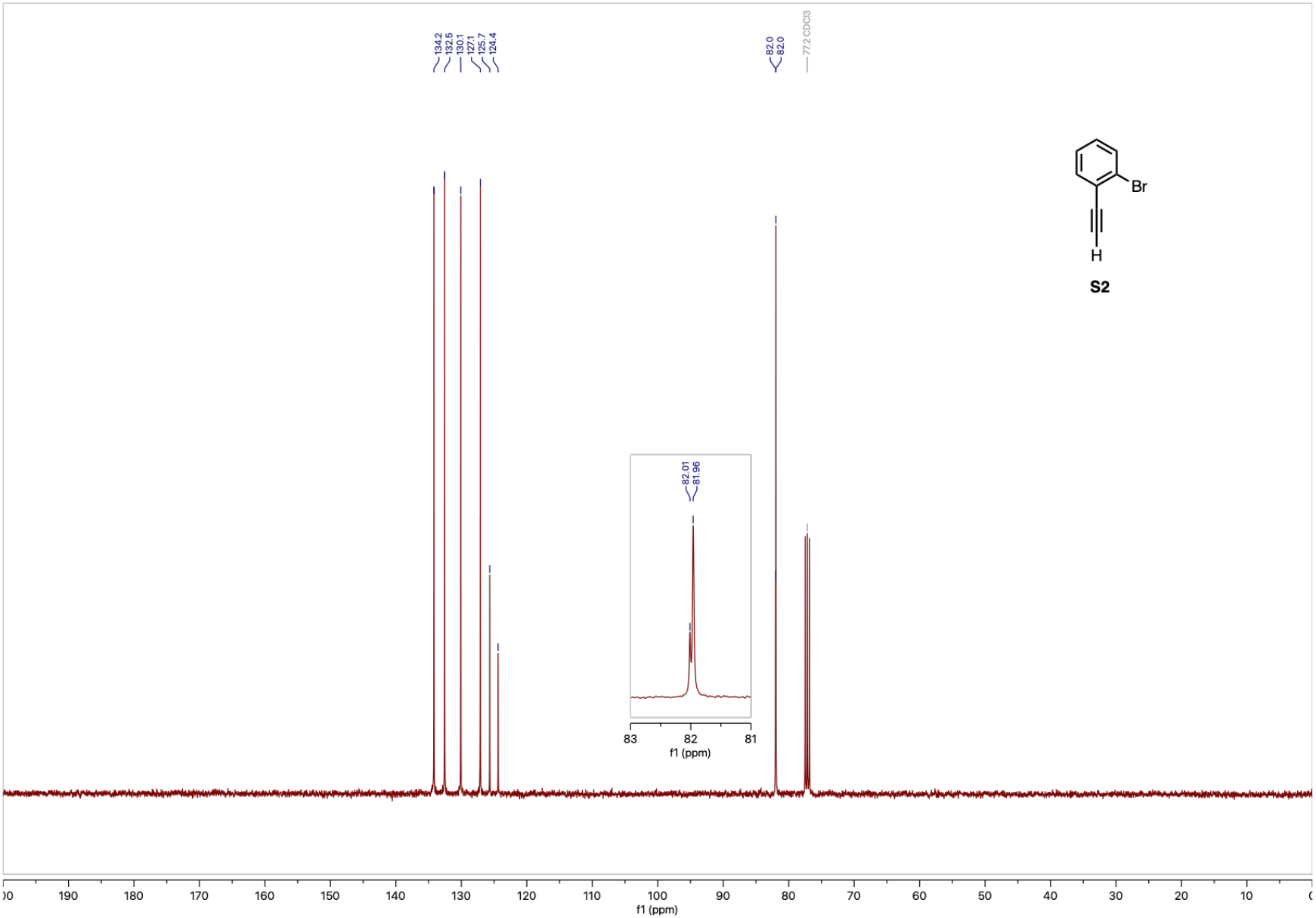


Figure S15. ^{13}C NMR of **S2**.

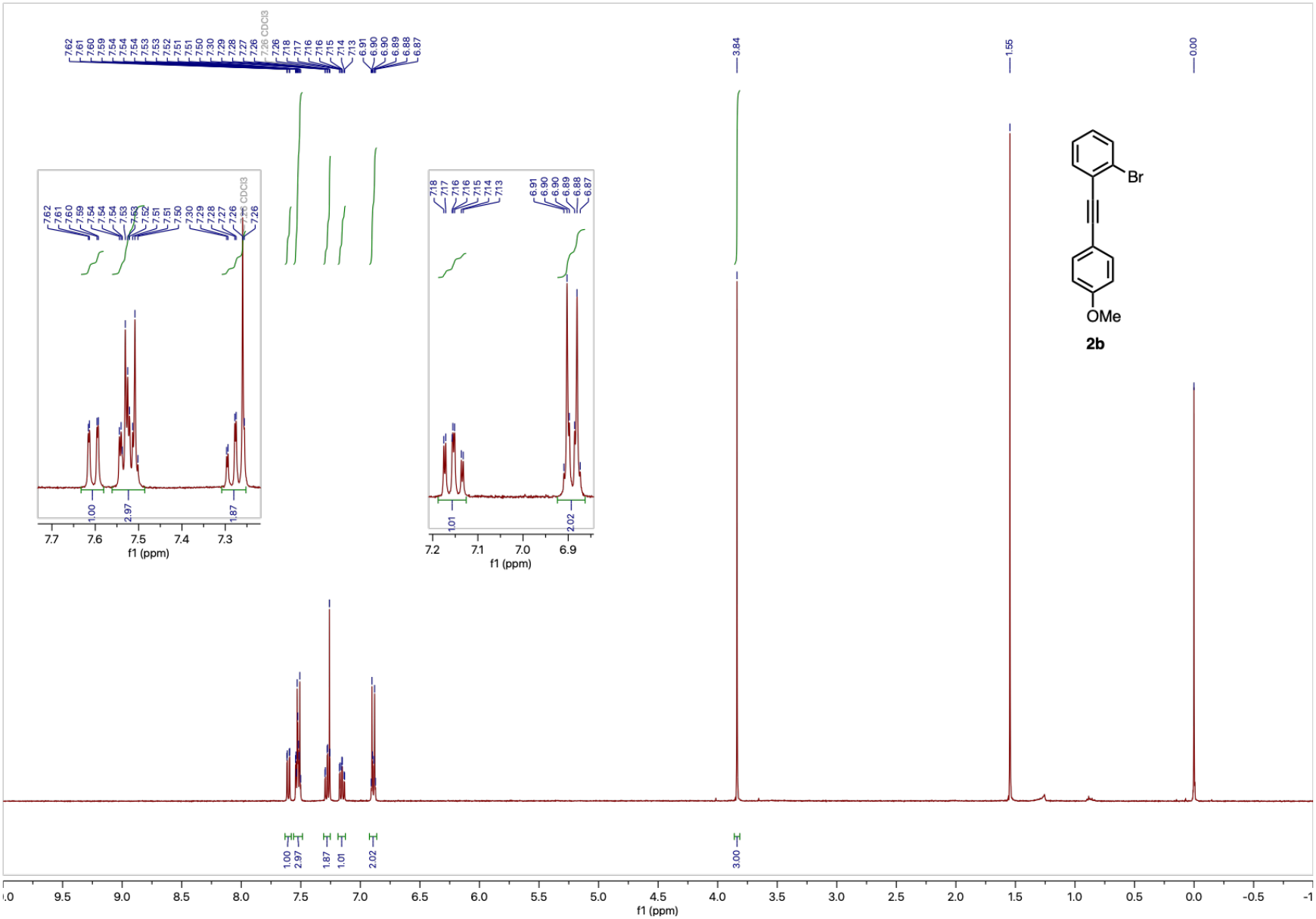


Figure S16. ^{1}H NMR of **2b**.

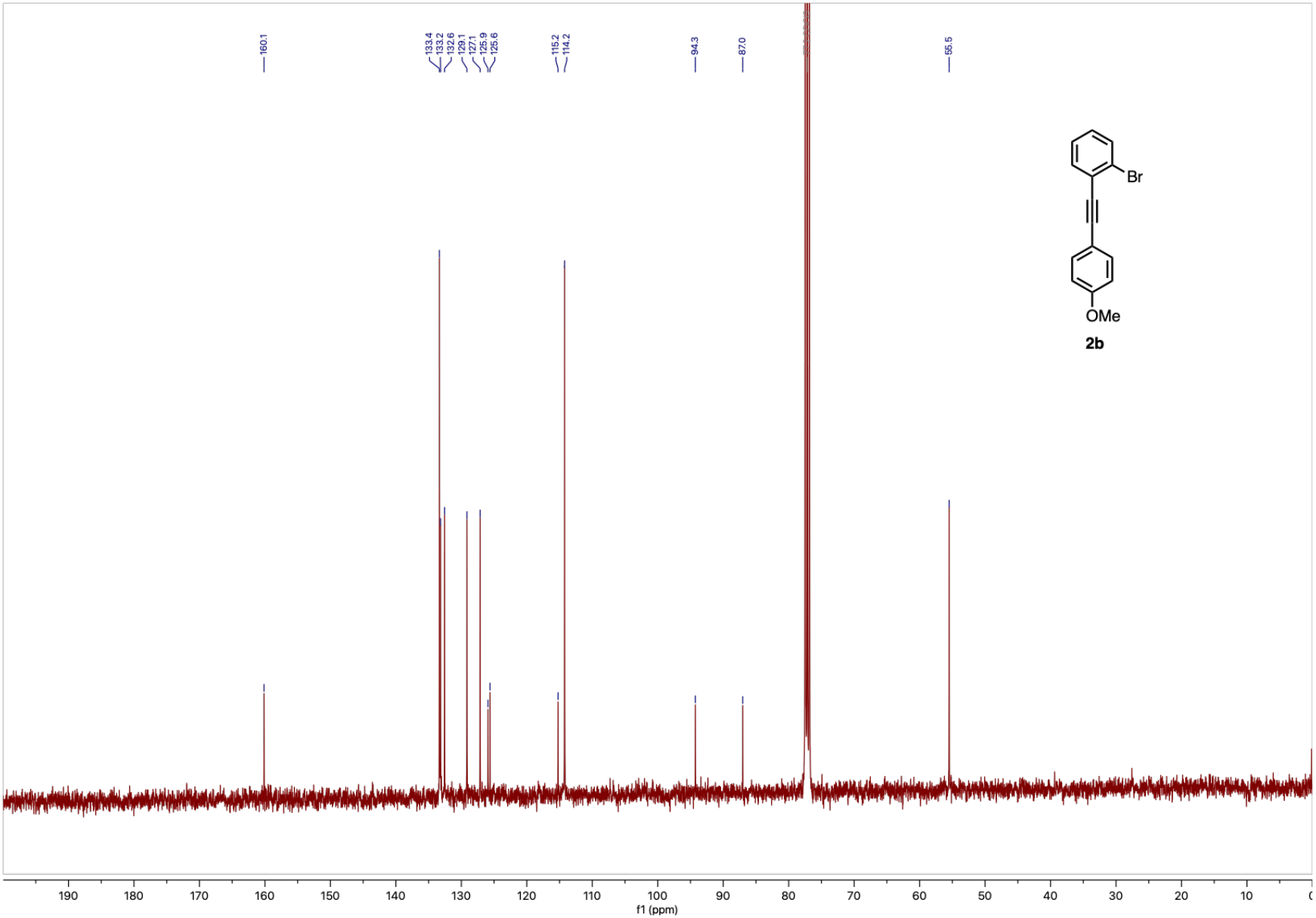


Figure S17. ^{13}C NMR of **2b**.

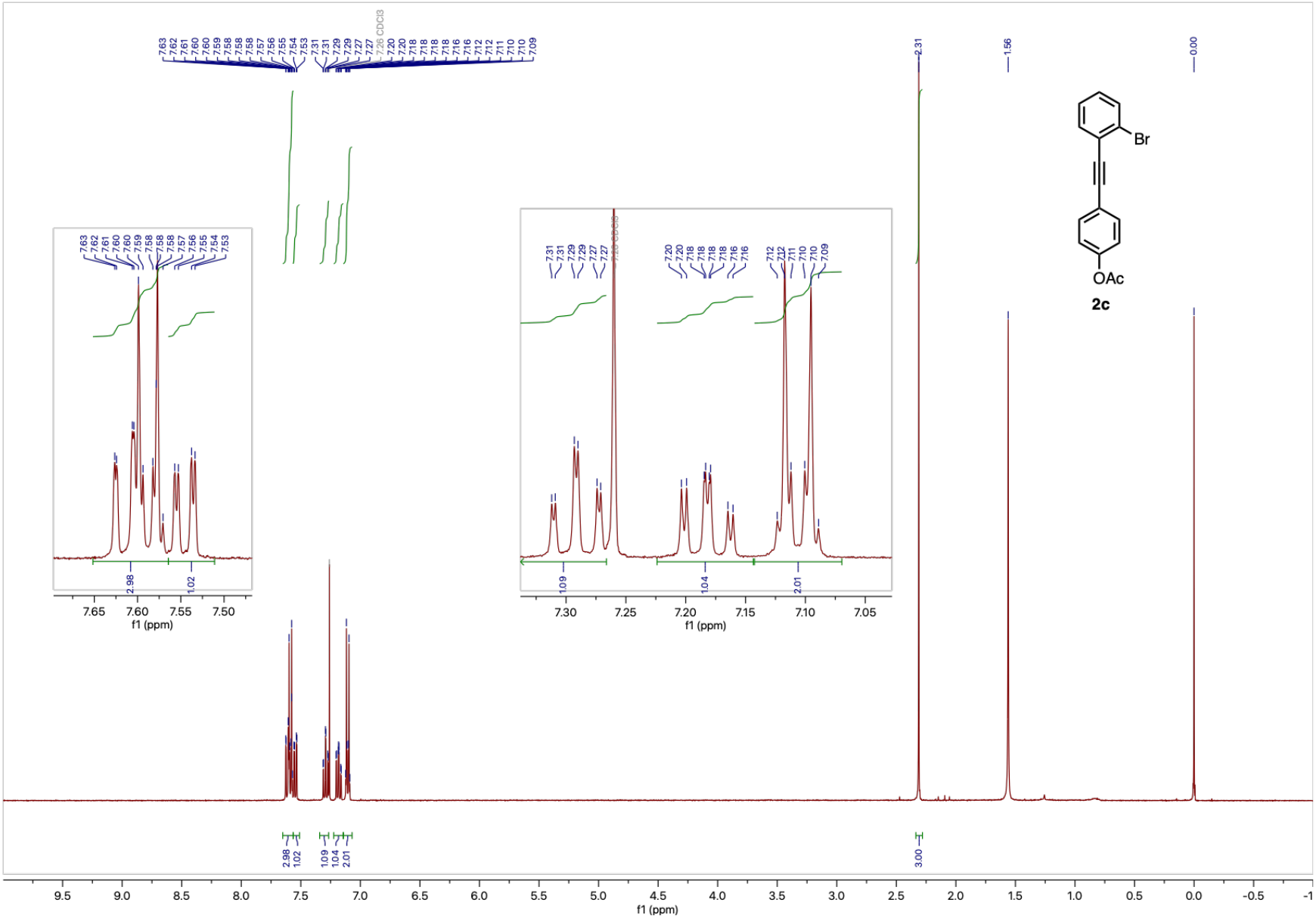


Figure S18. ^{1}H NMR of **2c**.

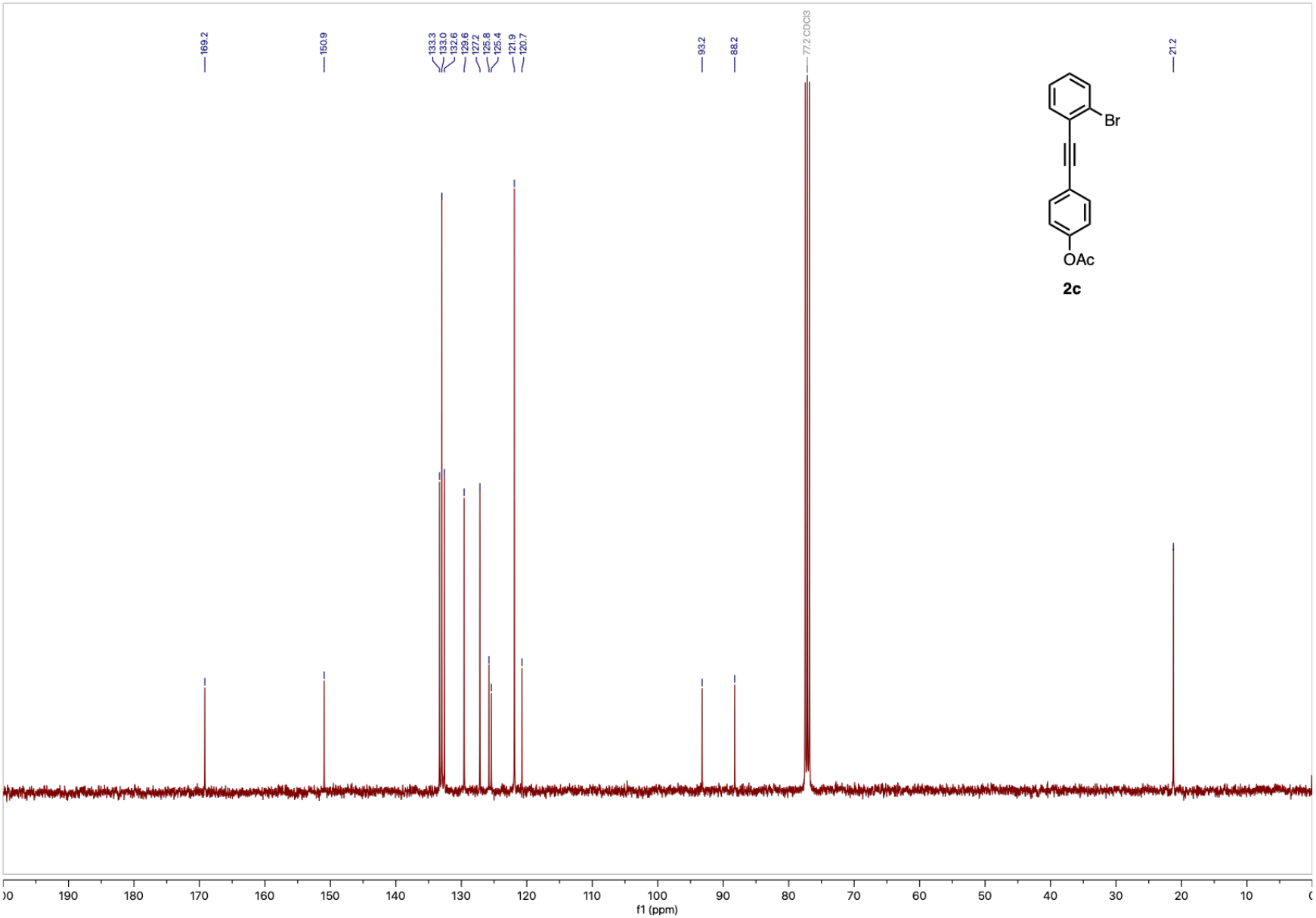


Figure S19. ^{13}C NMR of **2c**.

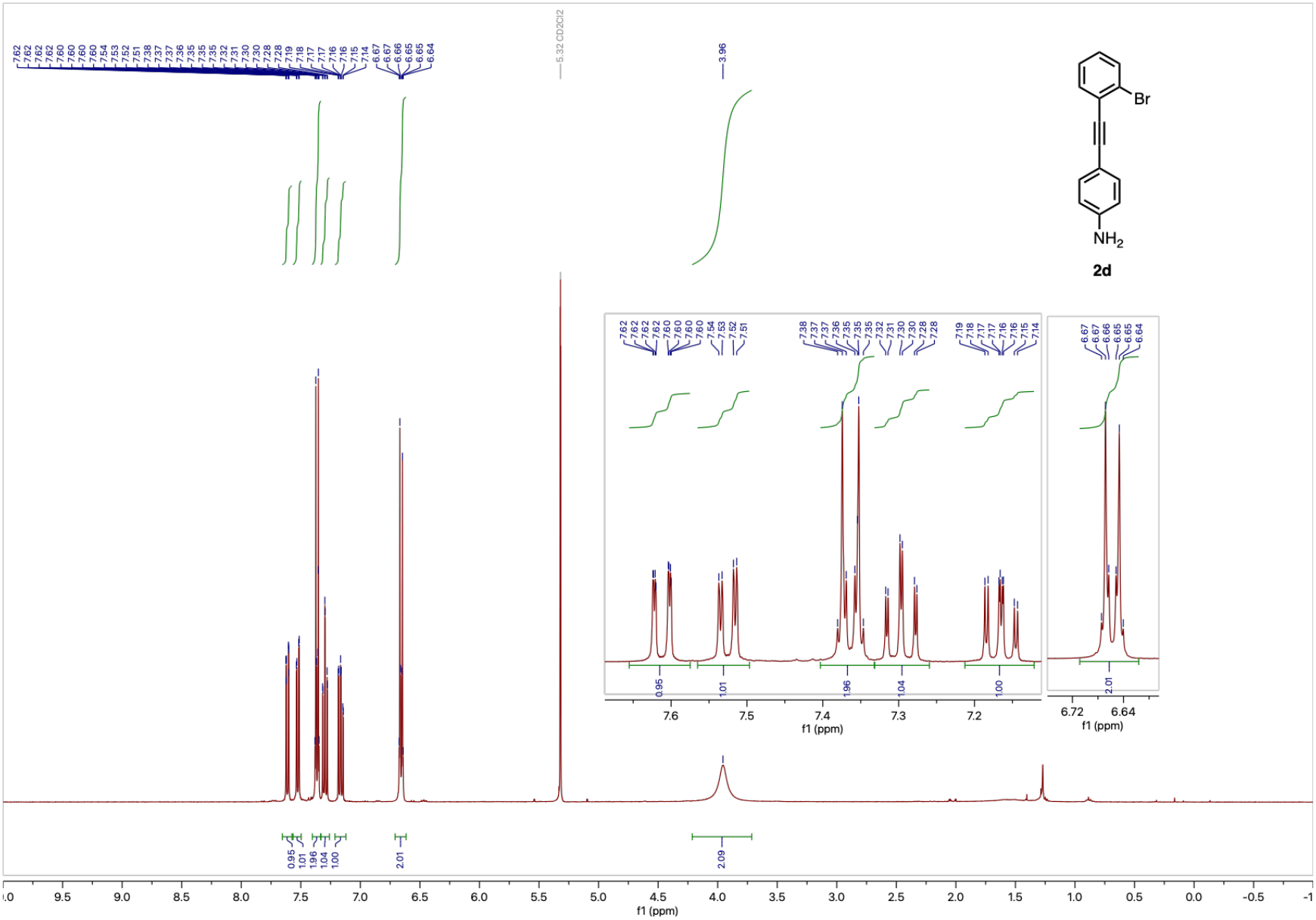


Figure S20. ^{1}H NMR of **2d**.

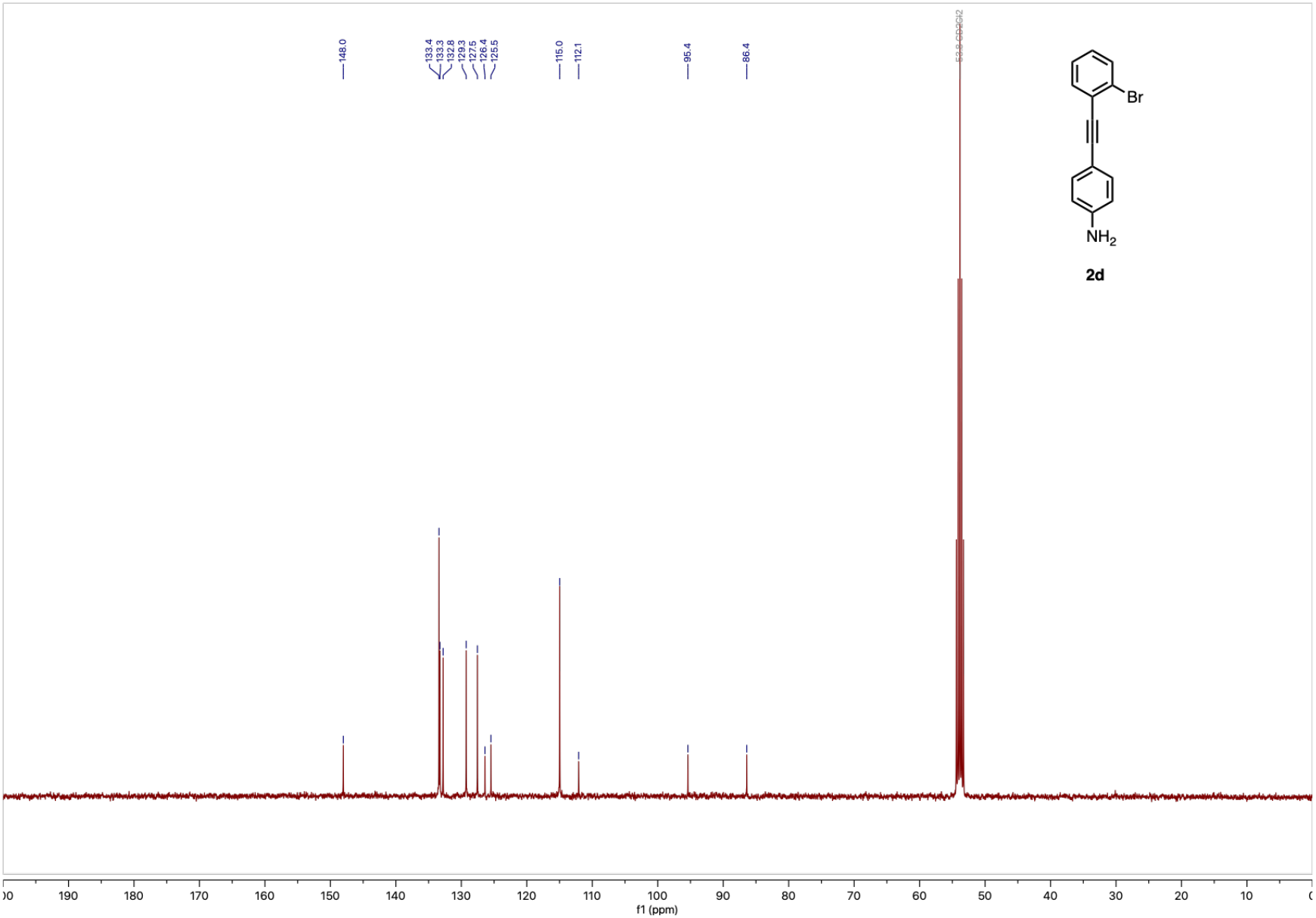


Figure S21. ^{13}C NMR of **2d**.

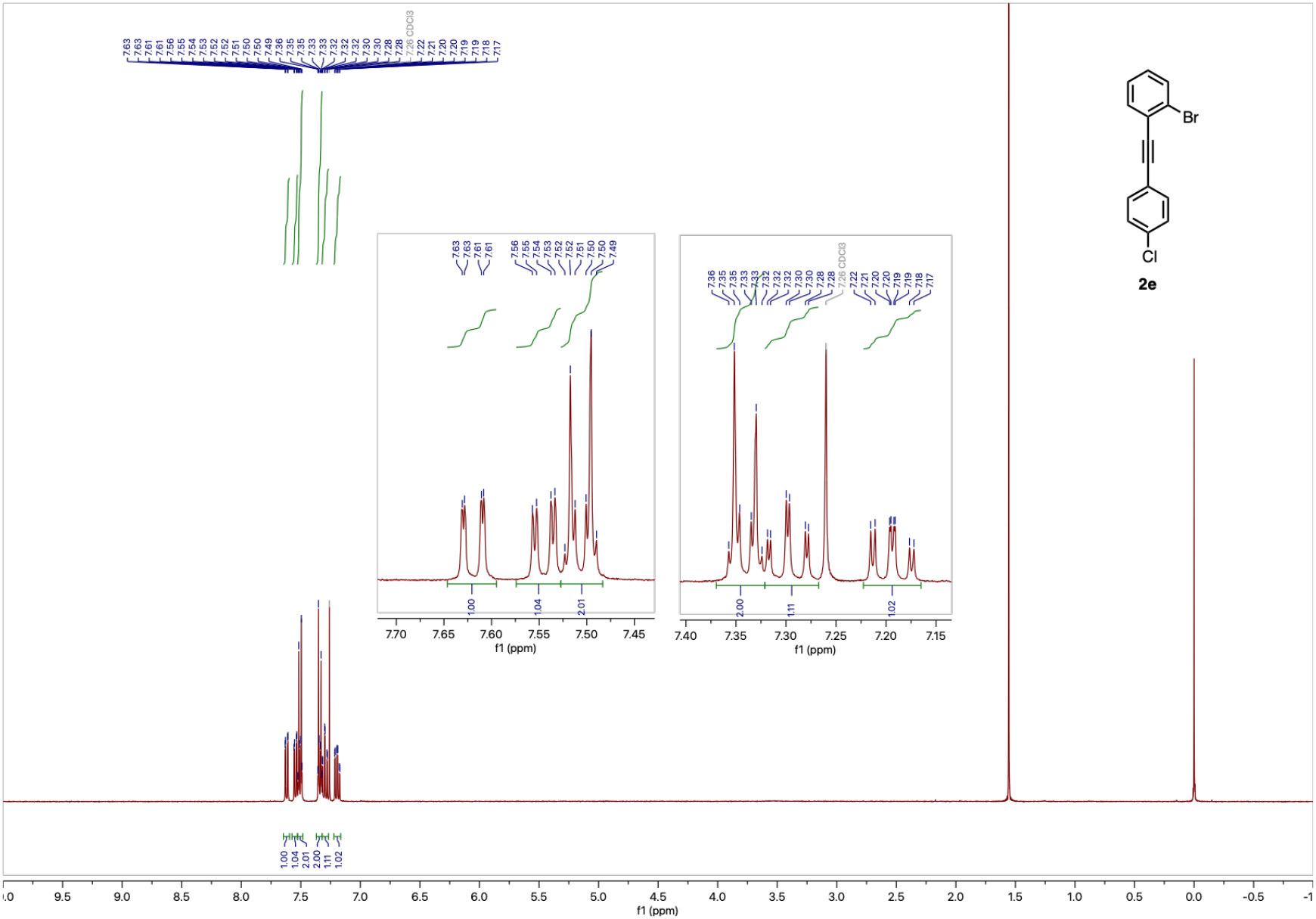


Figure S22. ^{1}H NMR of **2e**.

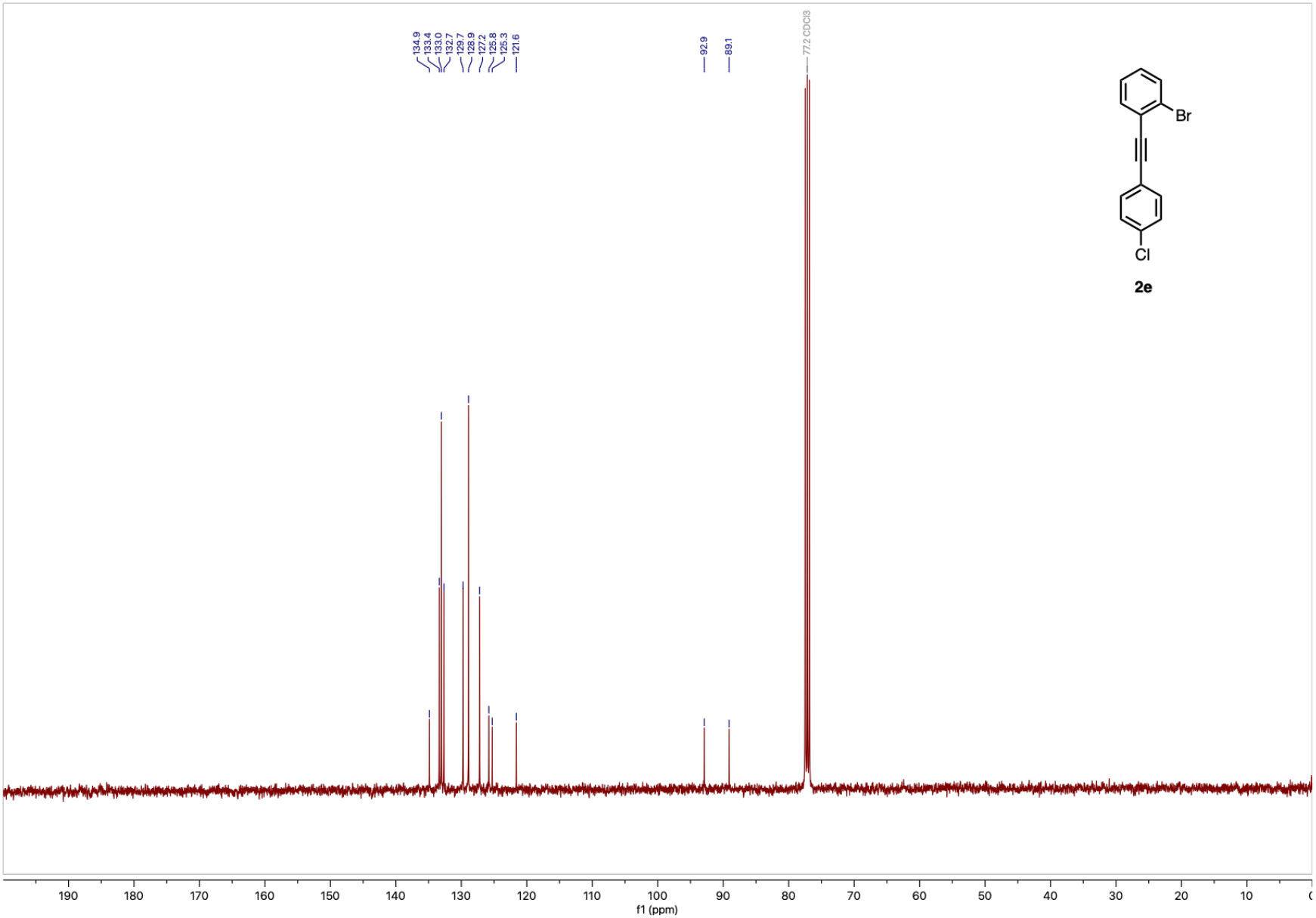


Figure S23. ^{13}C NMR of **2e**.

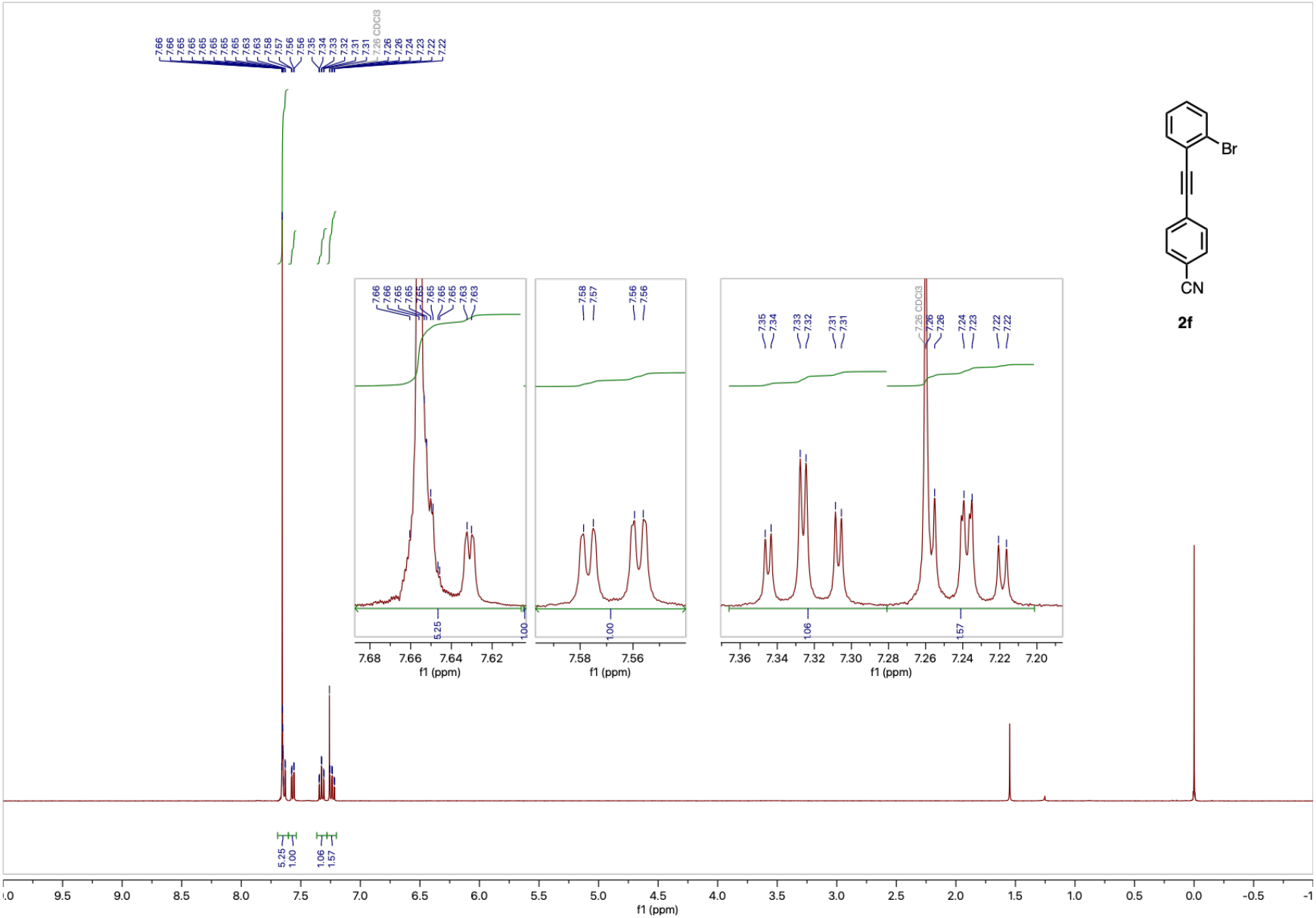


Figure S24. ^{1}H NMR of **2f**.

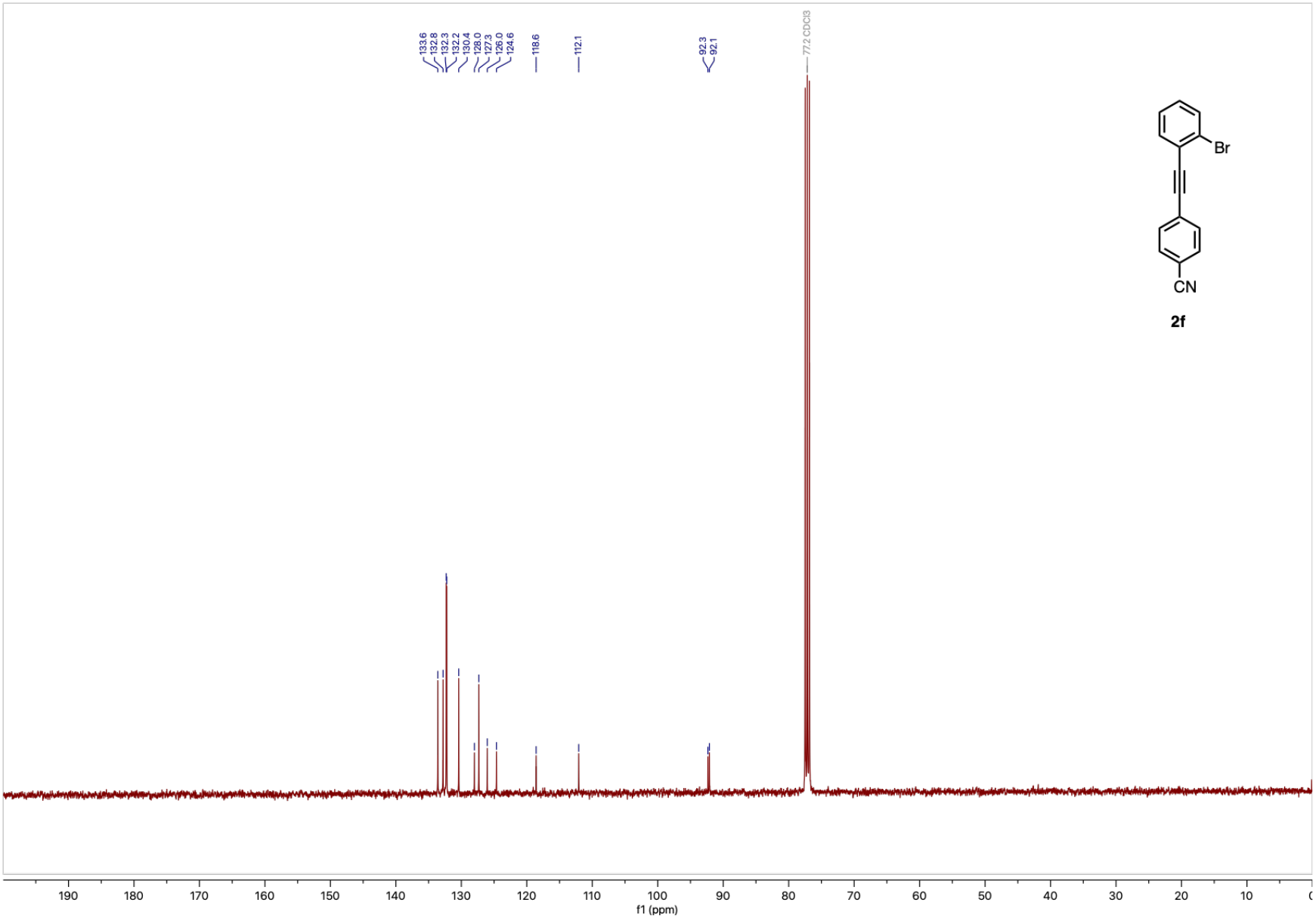


Figure S25. ^{13}C NMR of **2f**.

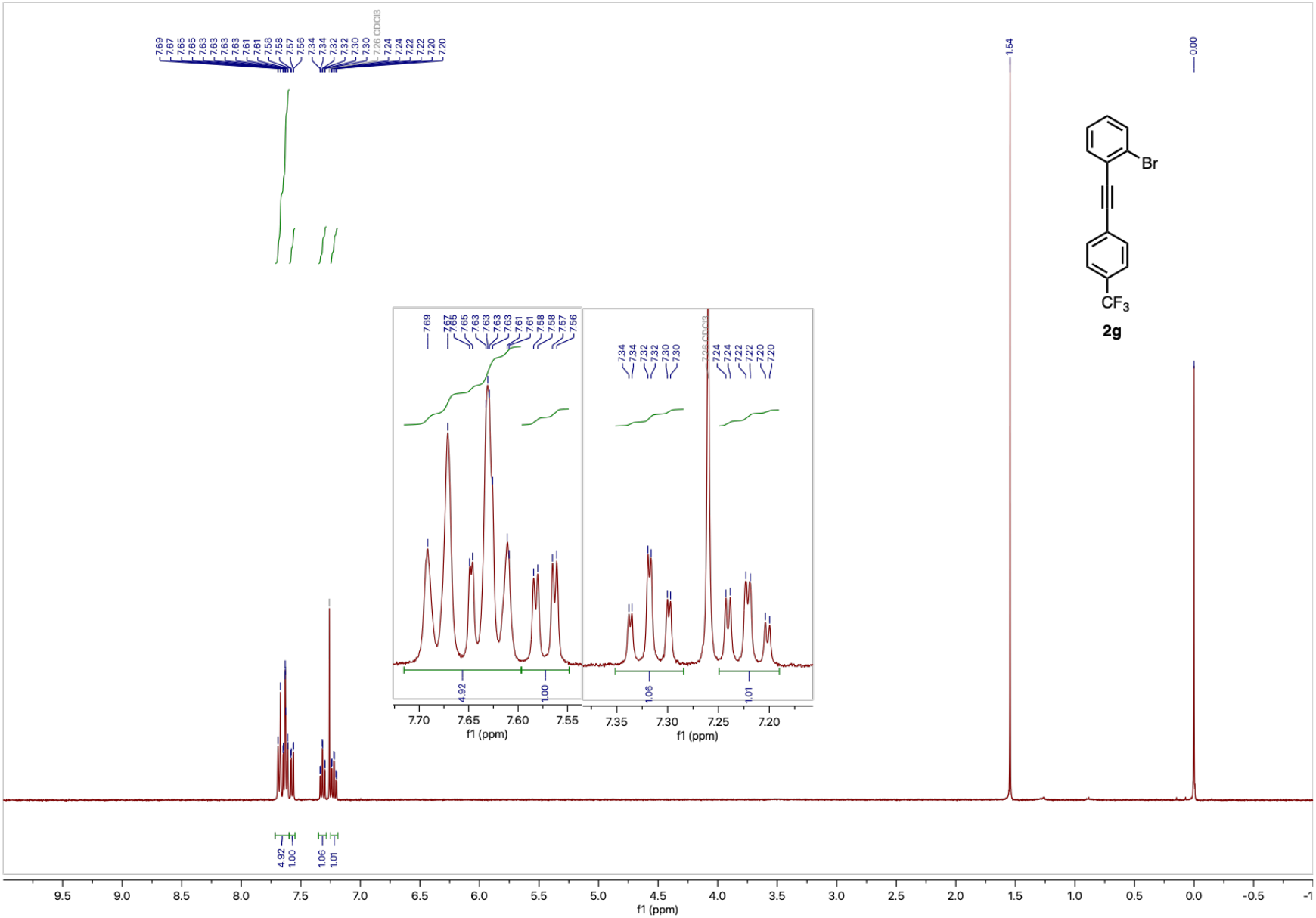


Figure S26. ^{1}H NMR of **2g**.

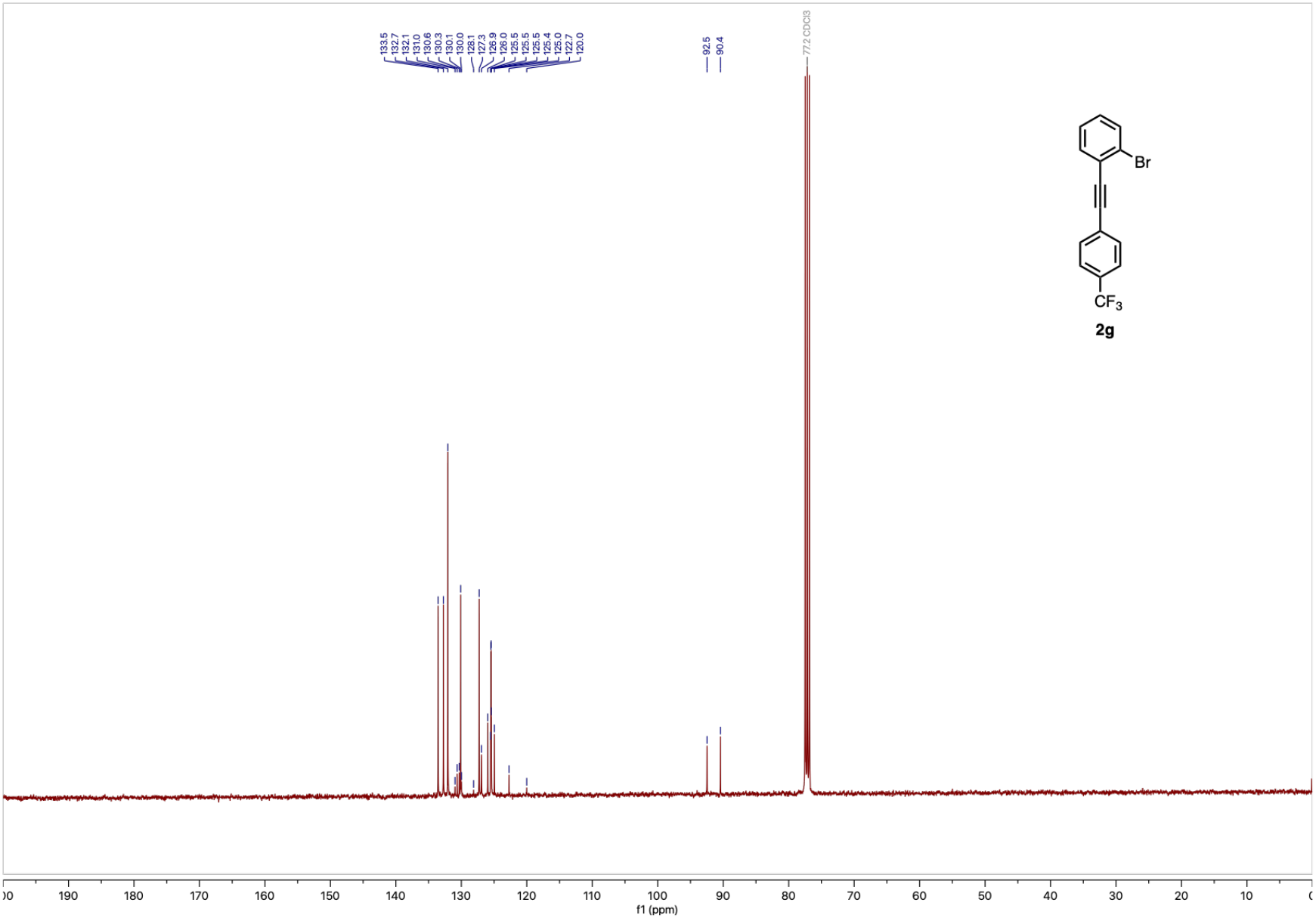


Figure S27. ^{13}C NMR of **2g**.

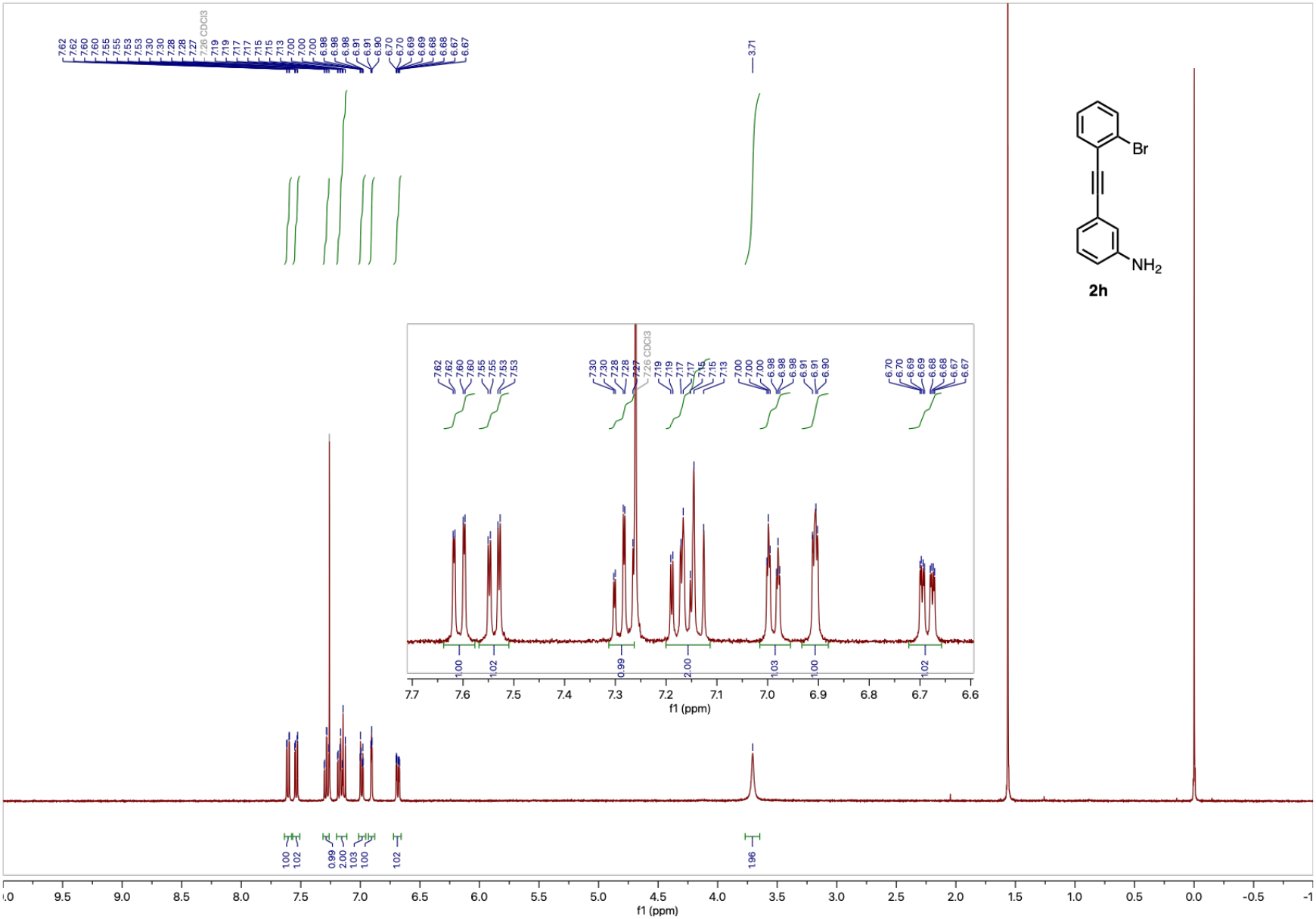


Figure S28. ^{1}H NMR of **2h**.

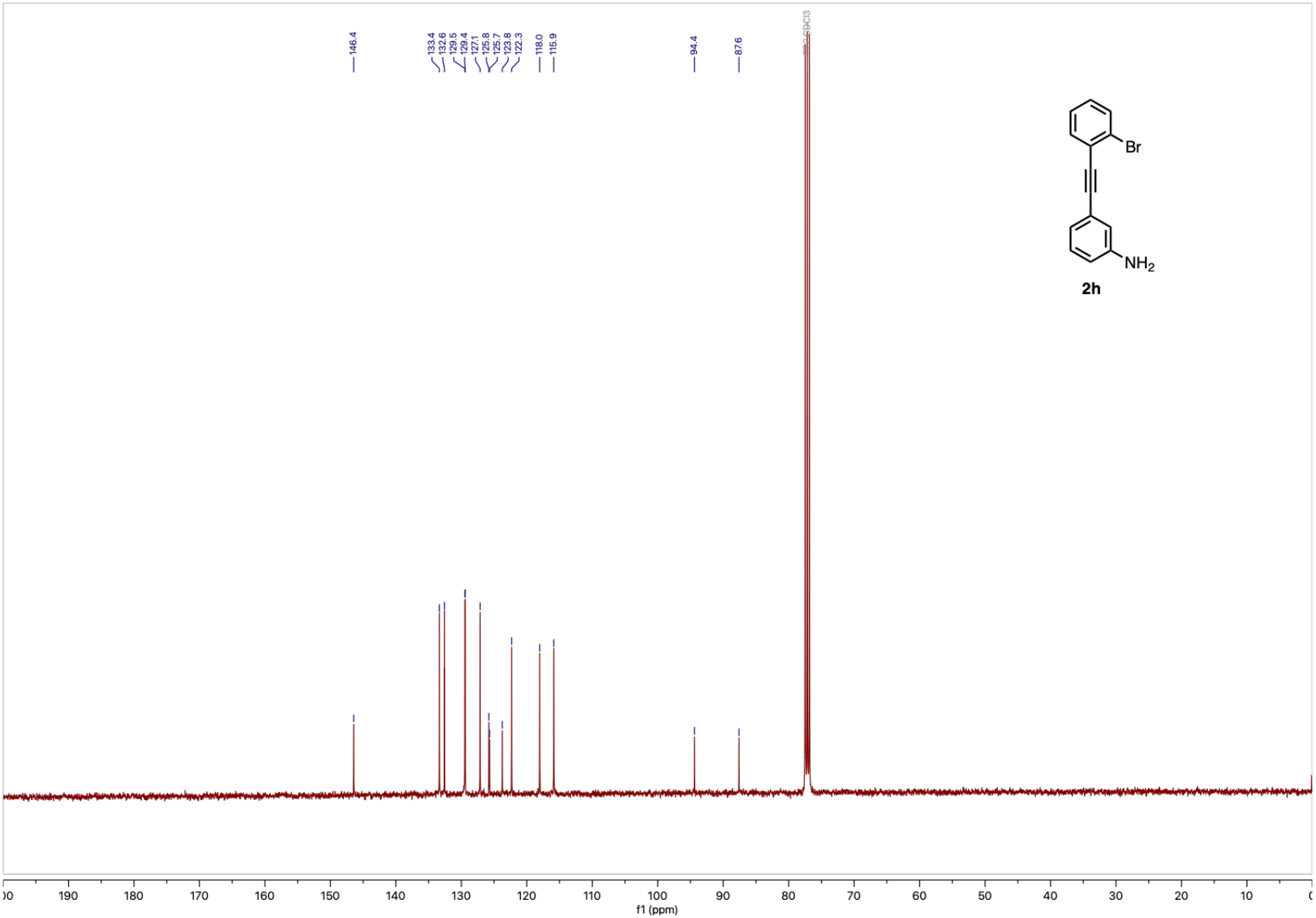


Figure S29. ^{13}C NMR of **2h**.

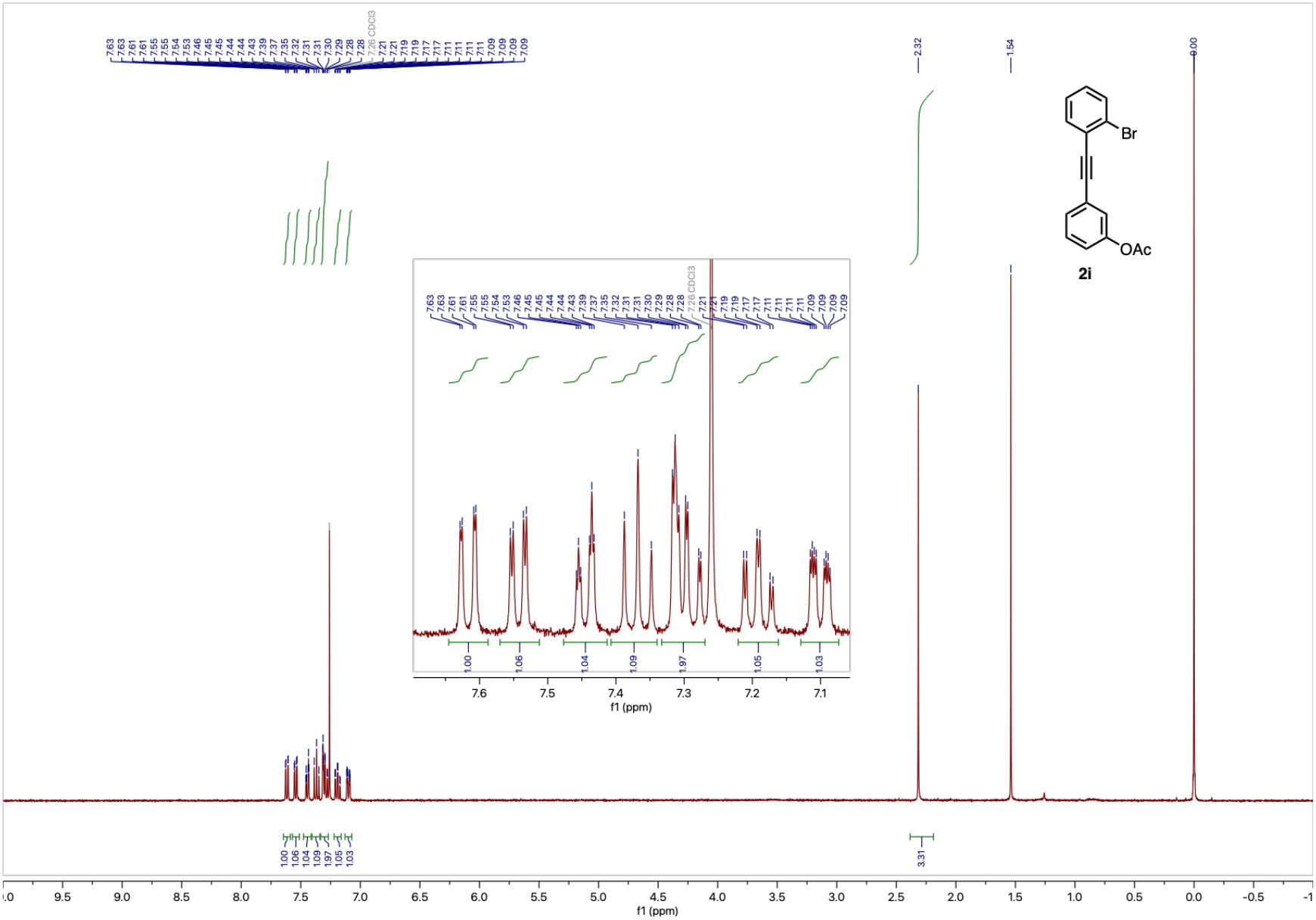


Figure S30. ^{1}H NMR of **2i**.

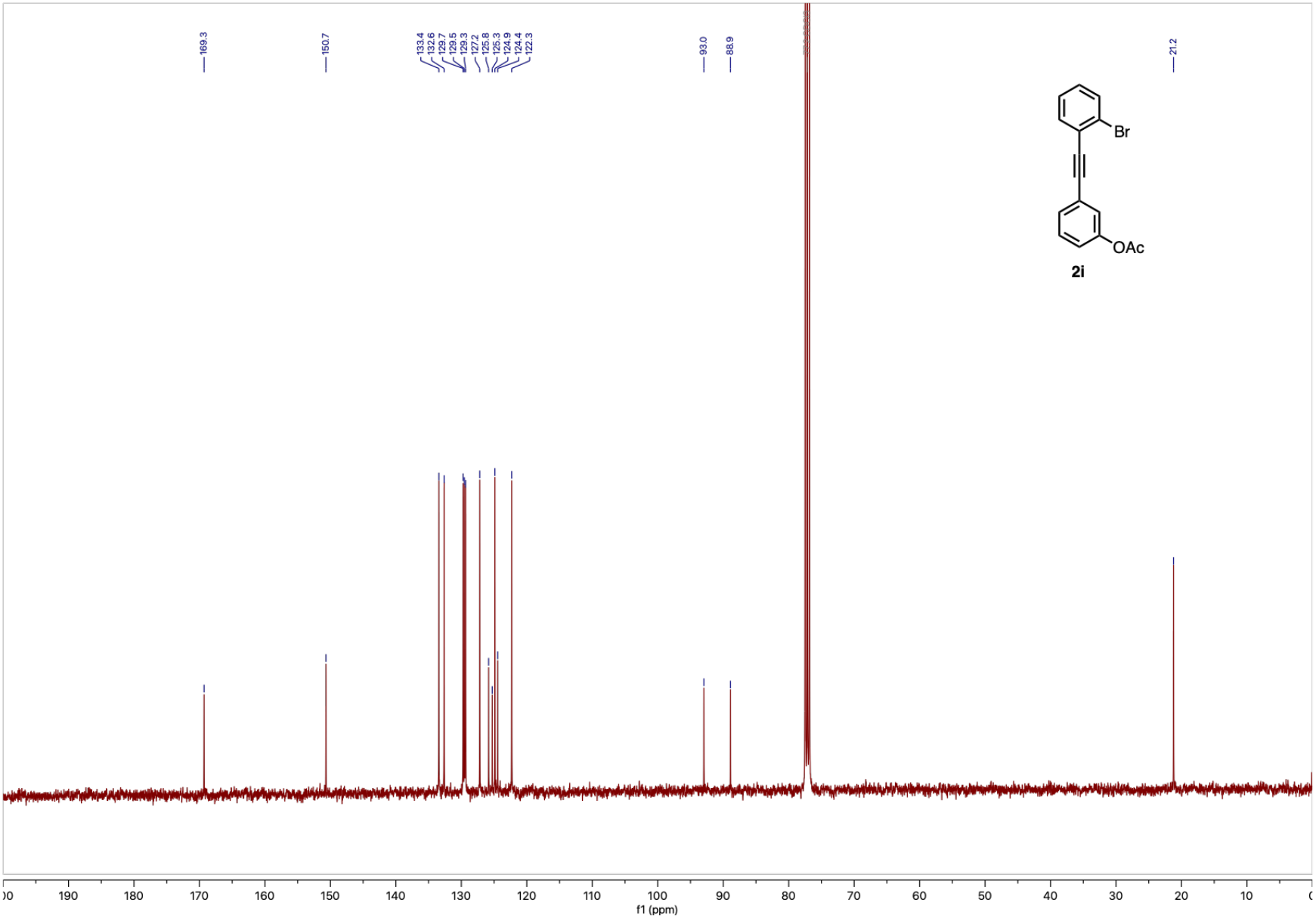


Figure S31. ^{13}C NMR of **2i**.

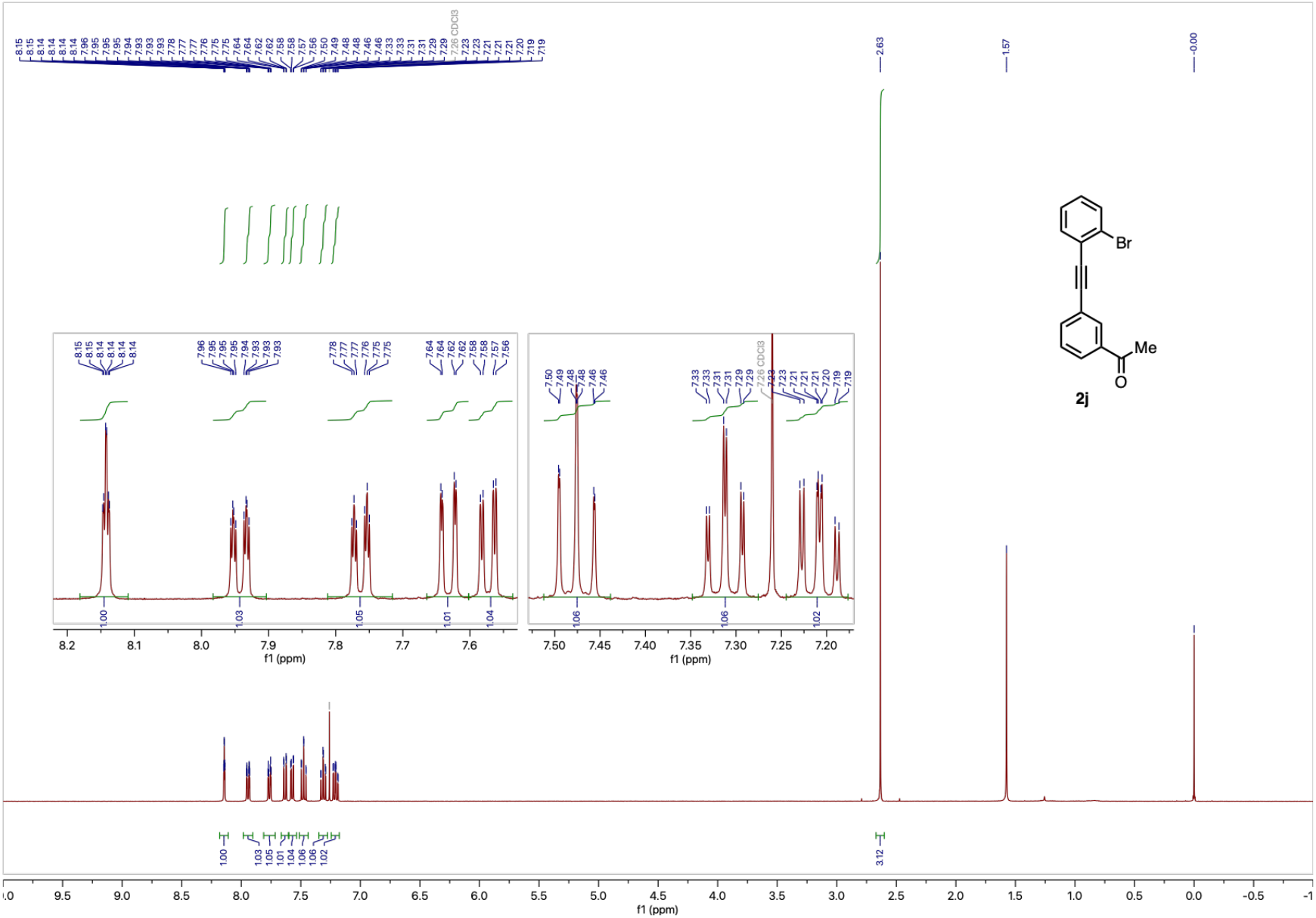


Figure S32. ^{1}H NMR of **2j**.

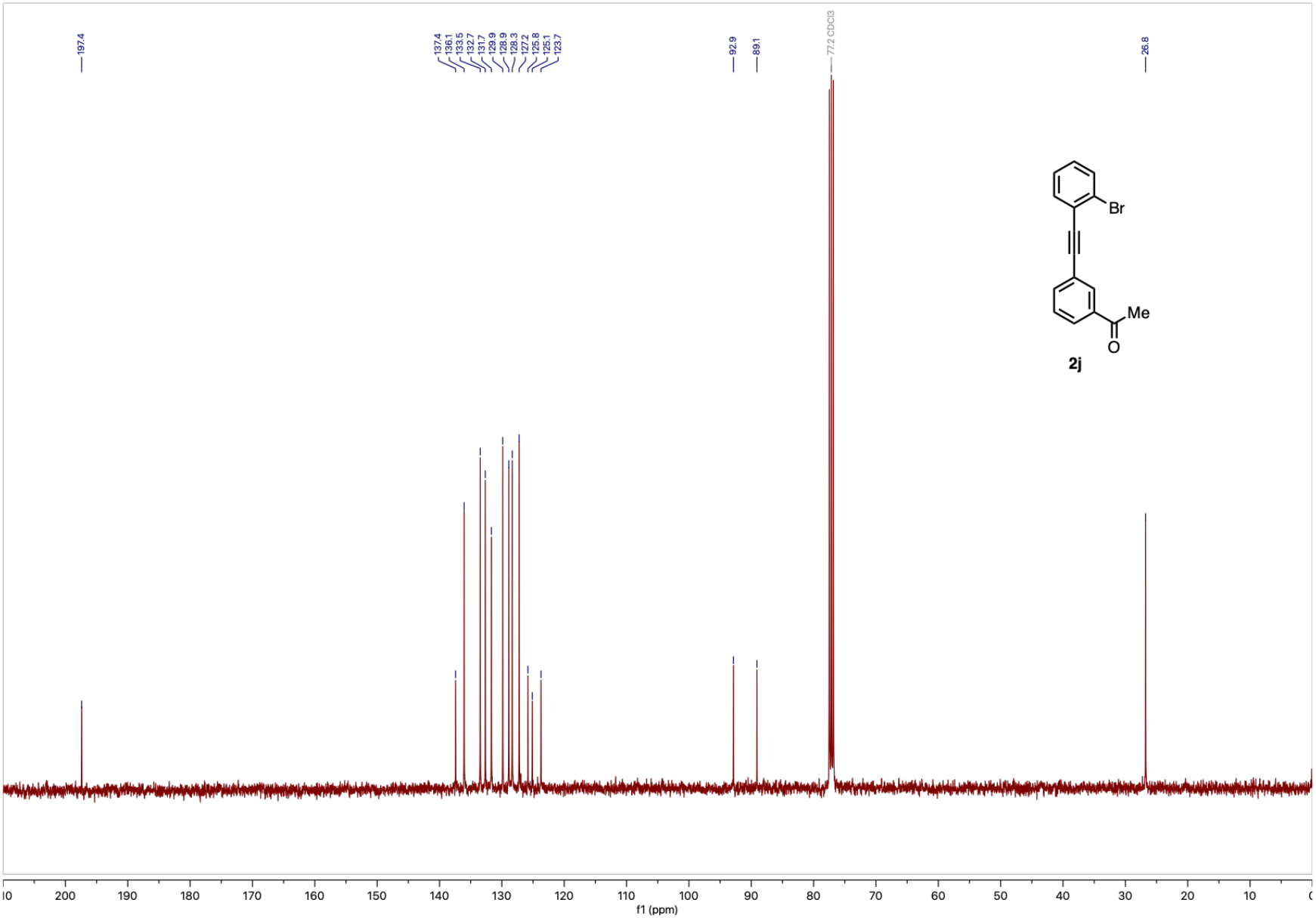


Figure S33. ^{13}C NMR of **2j**.

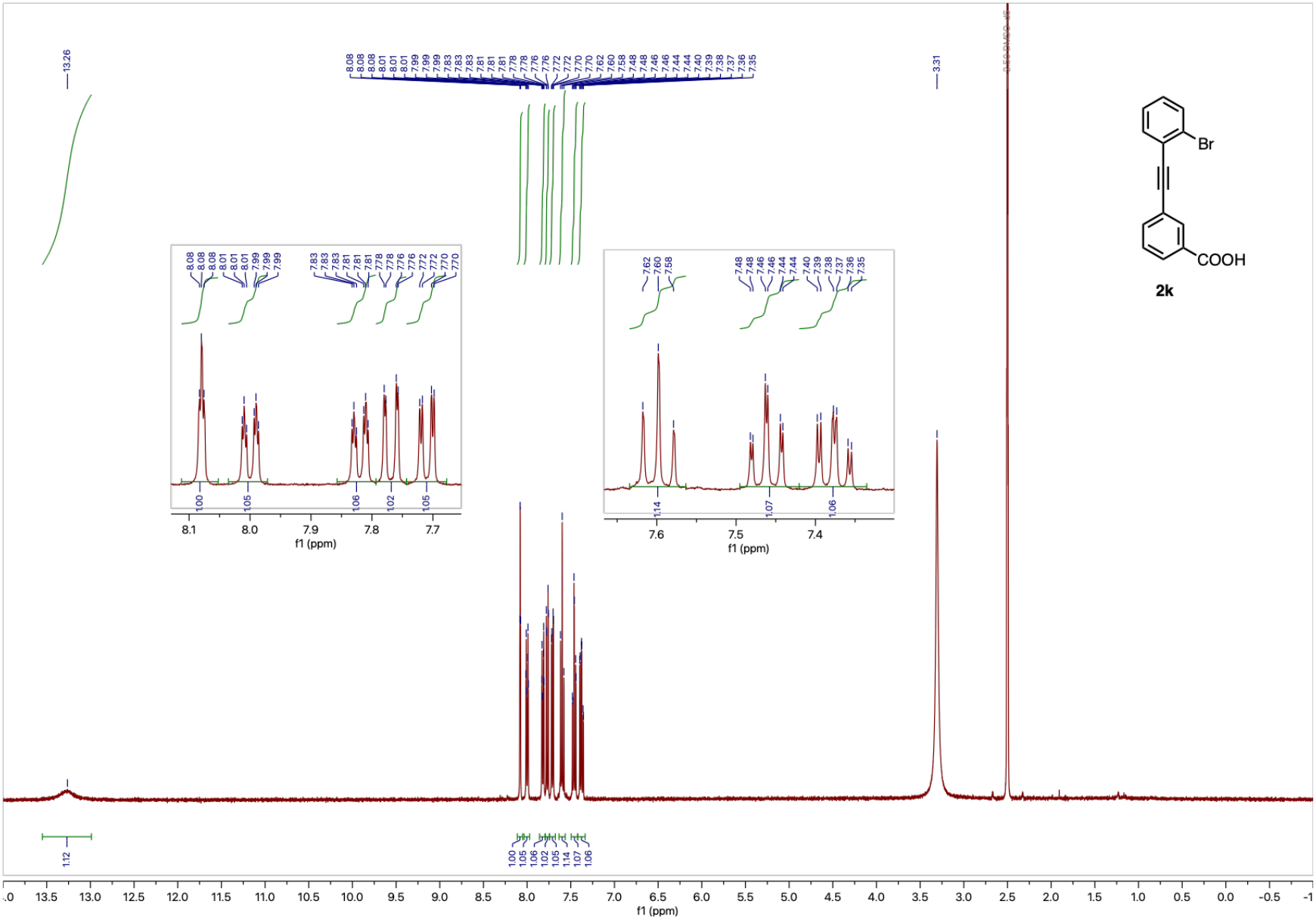


Figure S34. ^{1}H NMR of **2k**.

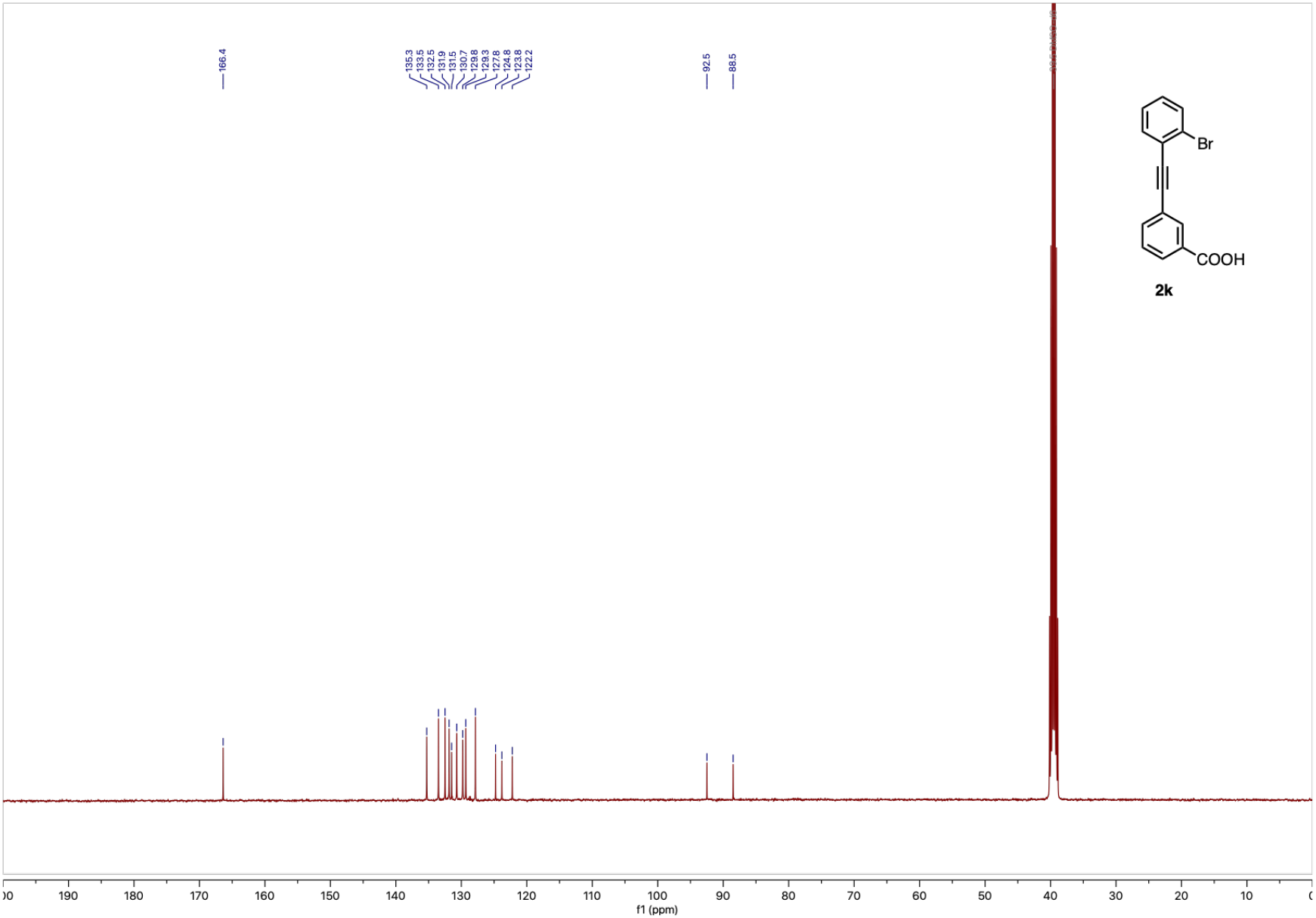


Figure S35. ^{13}C NMR of **2k**.

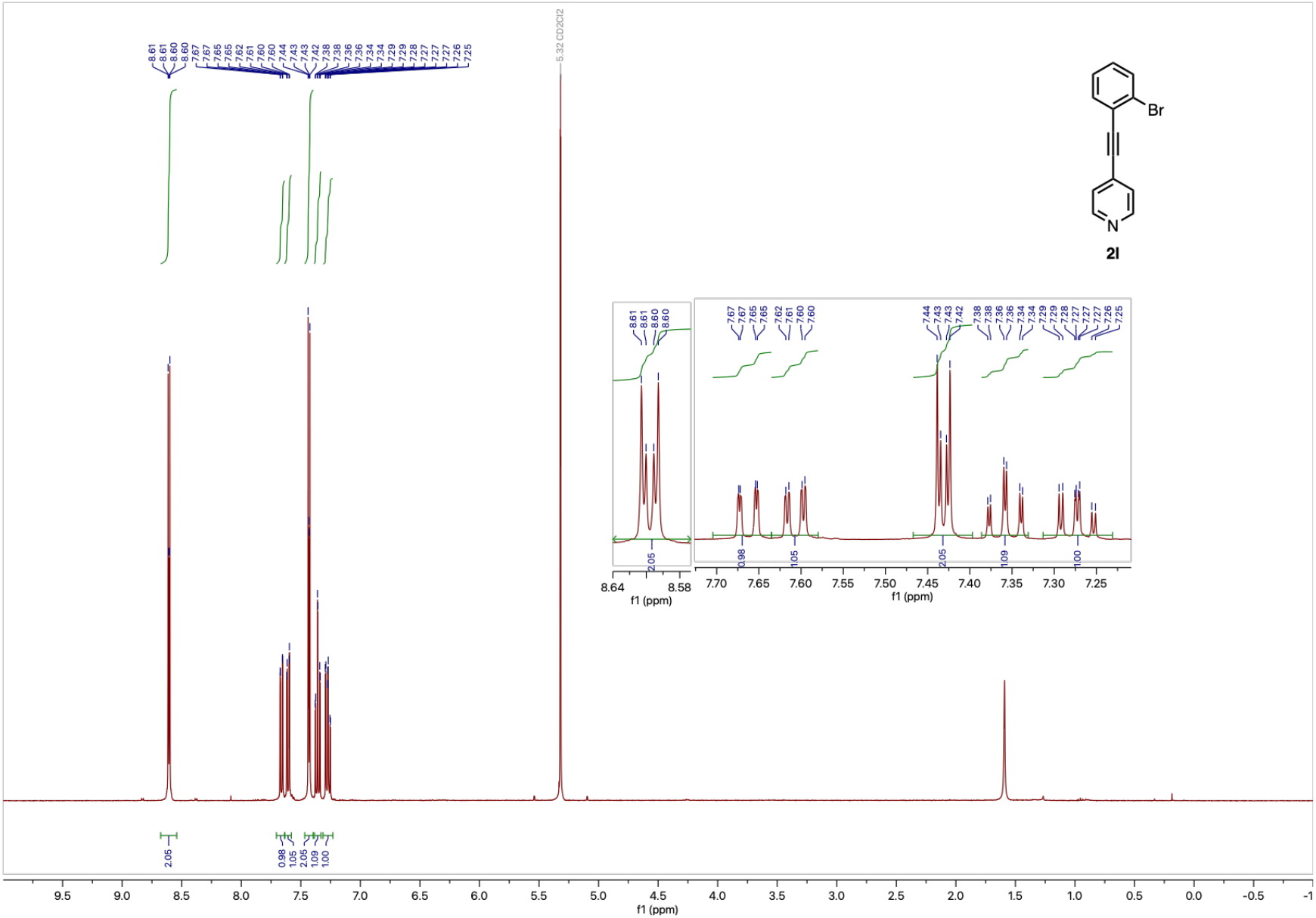


Figure S36. ^{1}H NMR of **2l**.

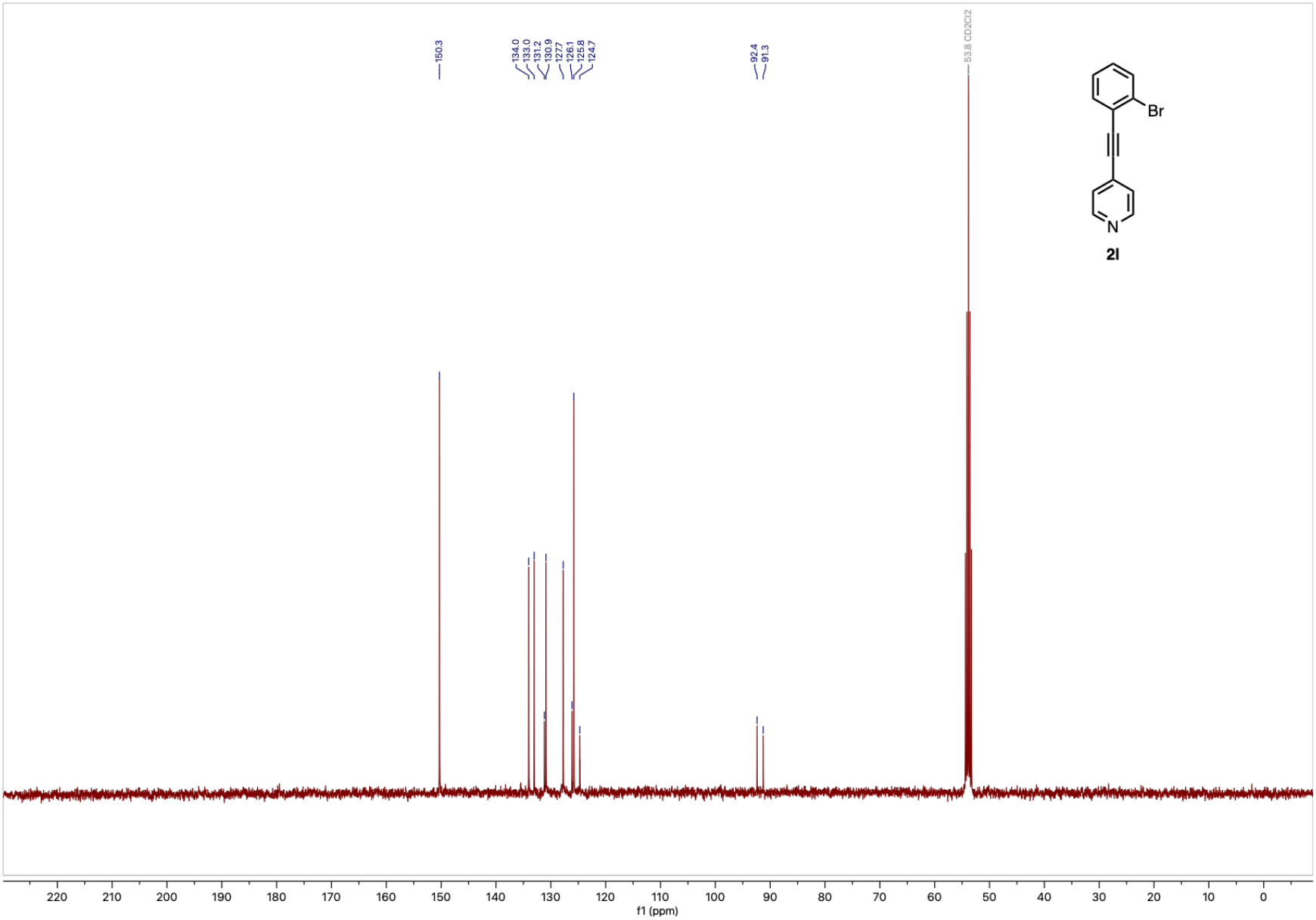


Figure S37. ^{13}C NMR of **2l**.

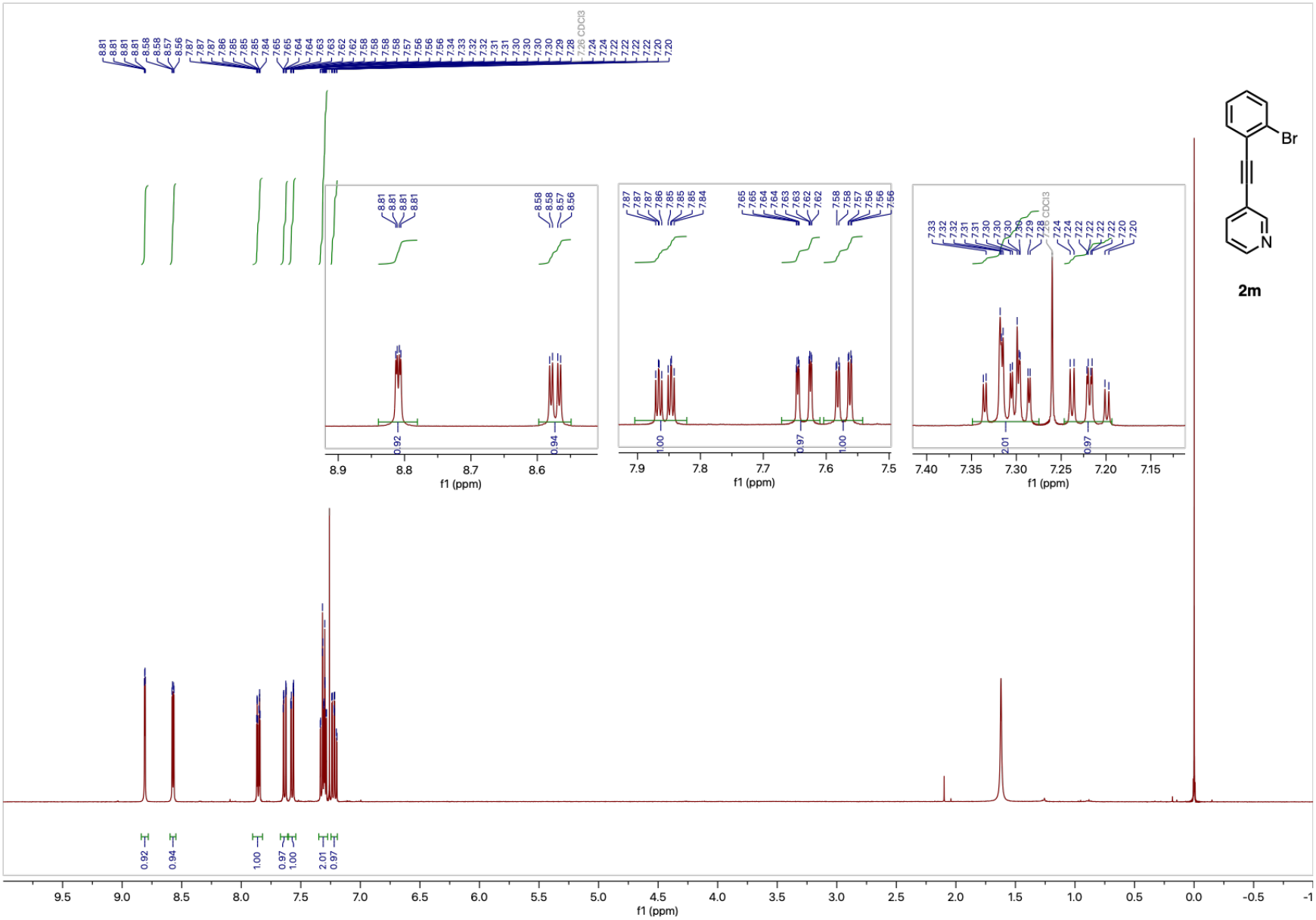


Figure S38. ^{1}H NMR of **2m**.

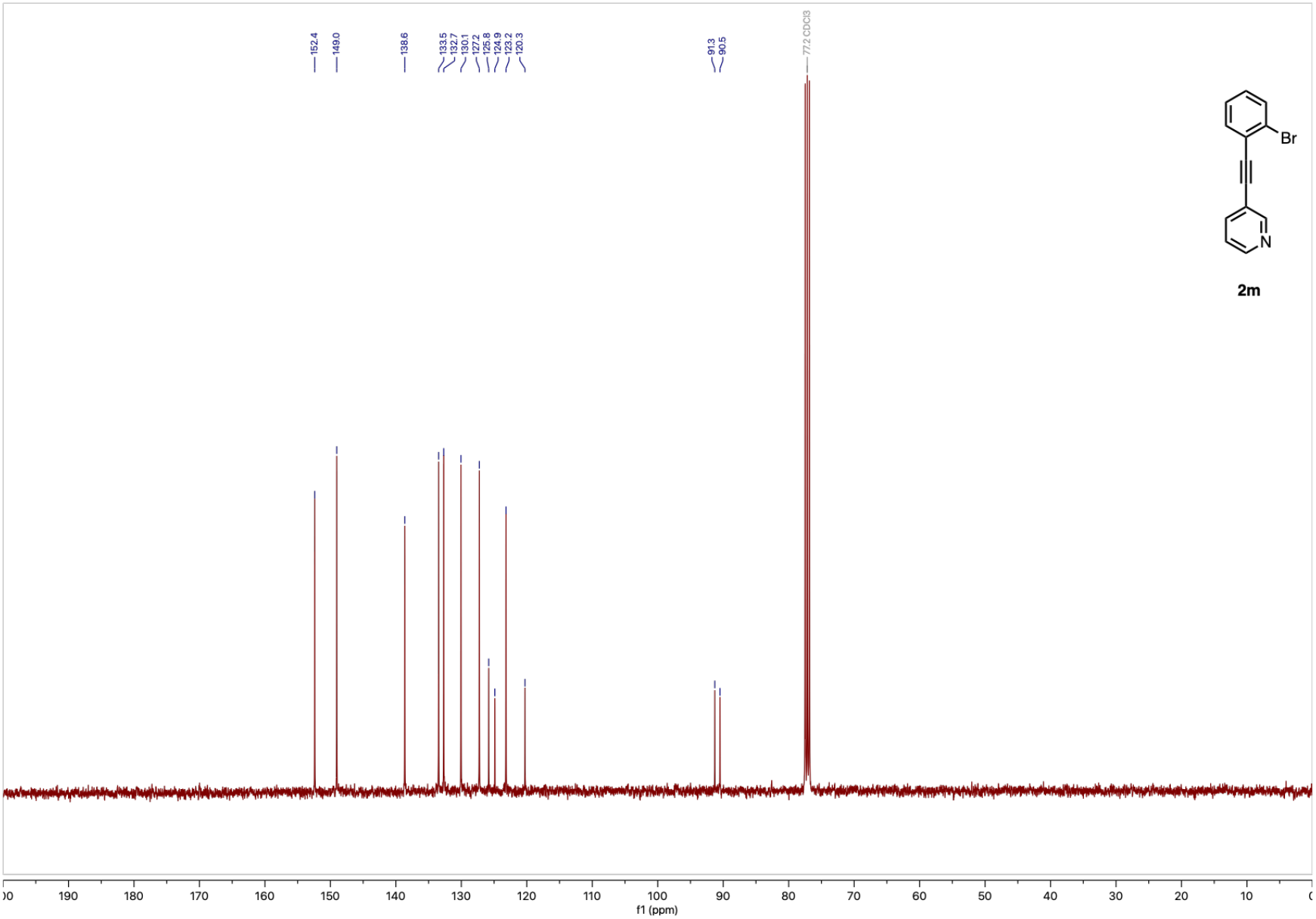


Figure S39. ^{13}C NMR of **2m**.

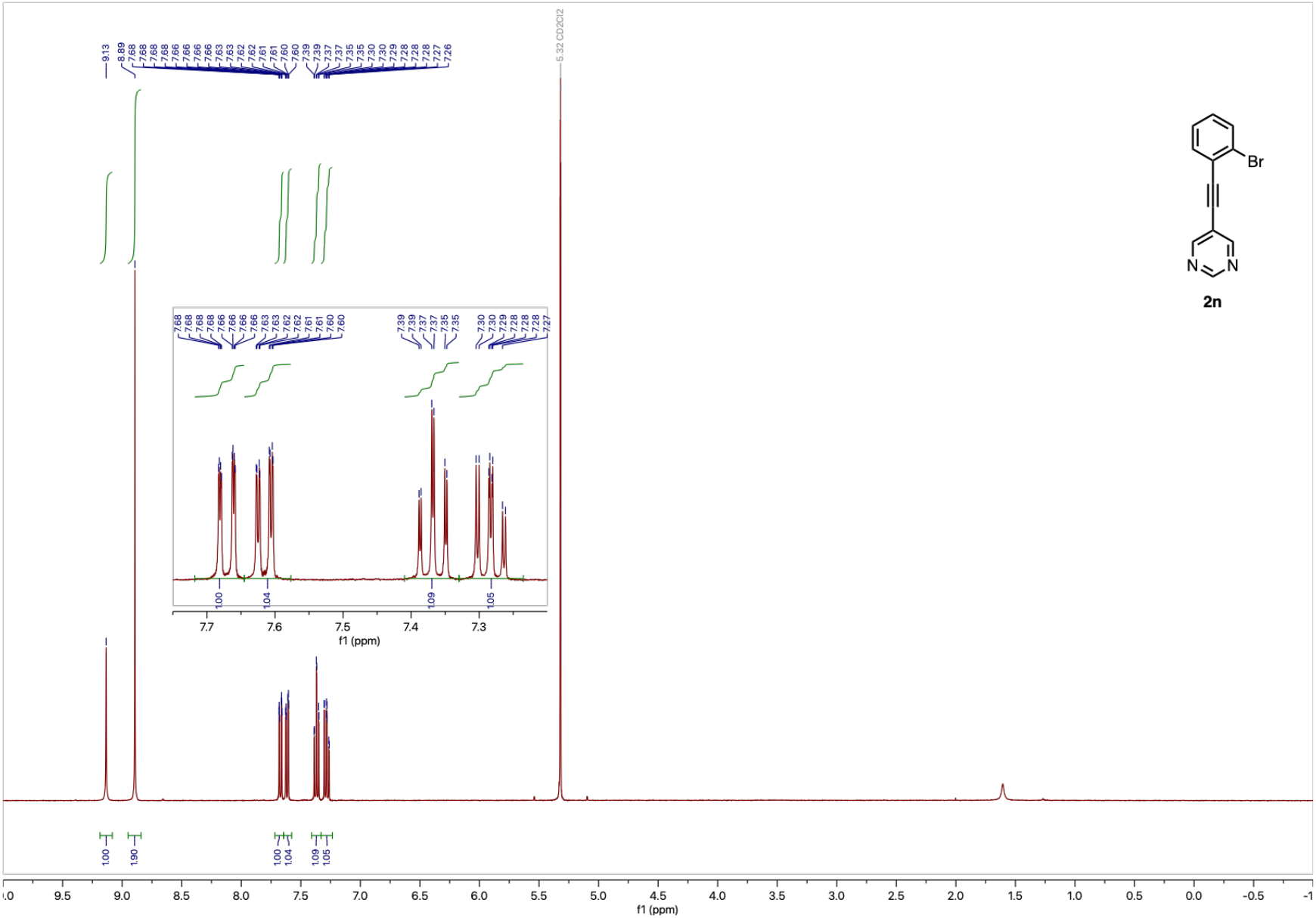


Figure S40. ^{1}H NMR of **2n**.

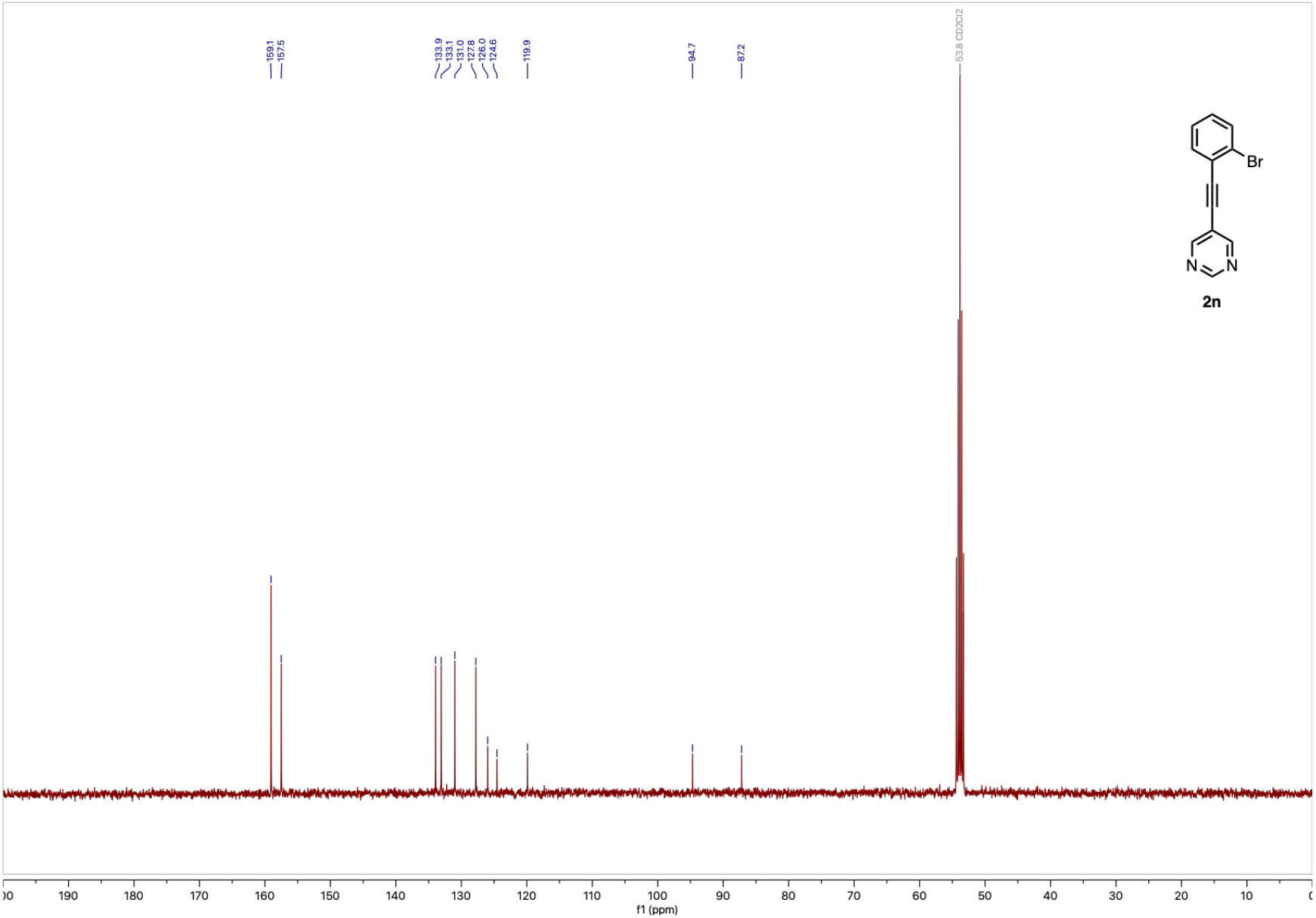


Figure S41. ^{13}C NMR of **2n**.

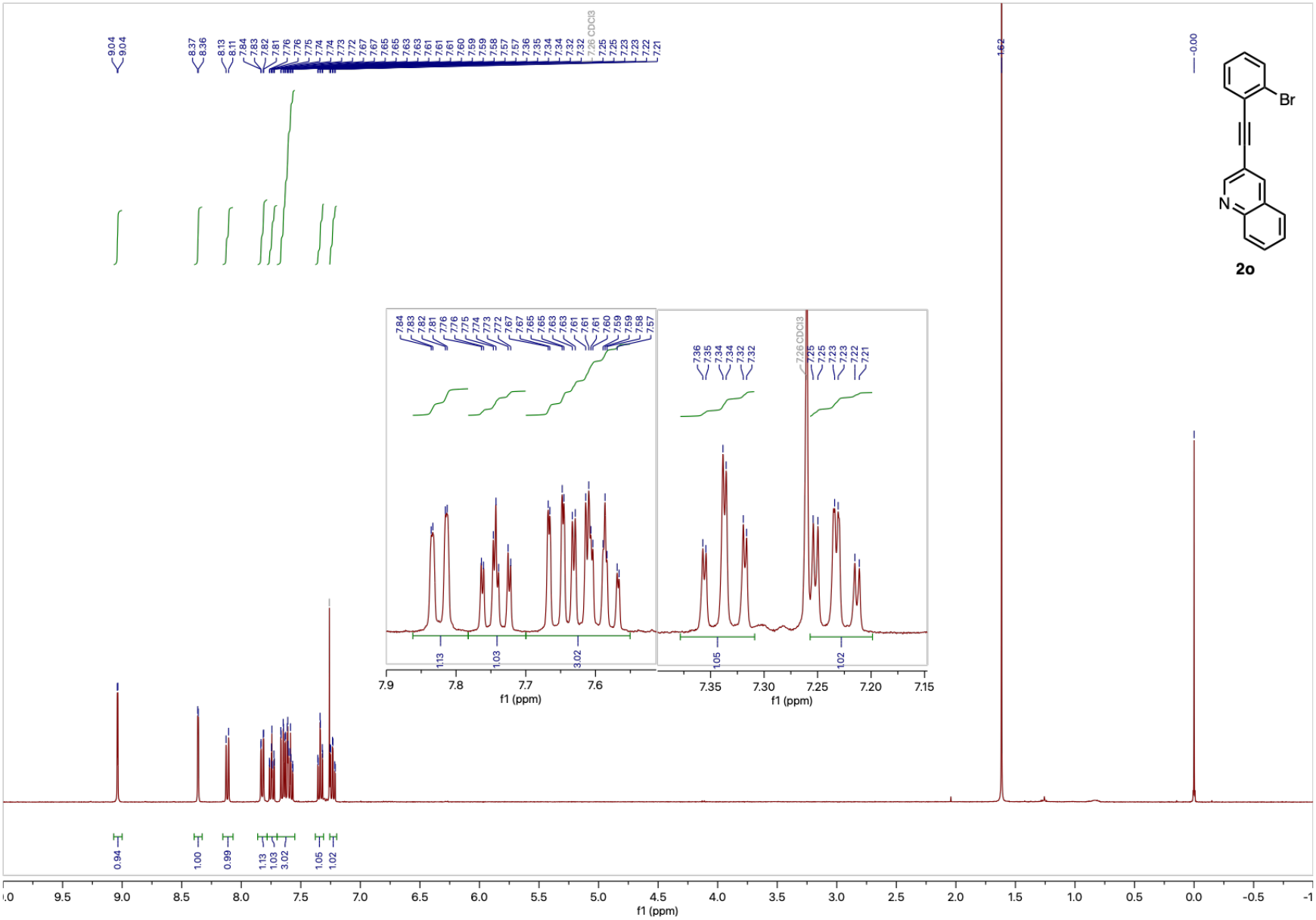


Figure S42. ^{1}H NMR of **2o**.

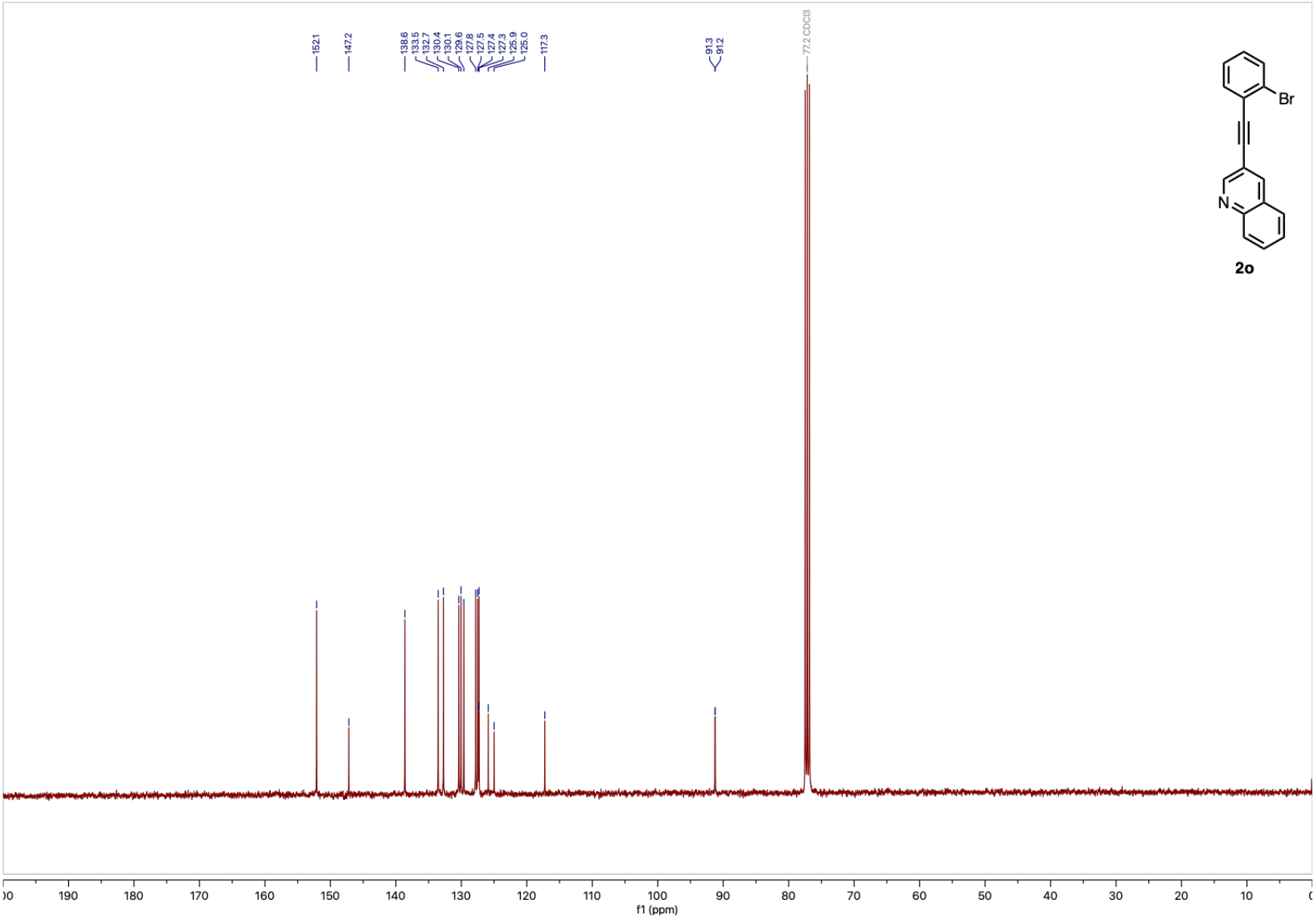


Figure S43. ^{13}C NMR of **2o**.

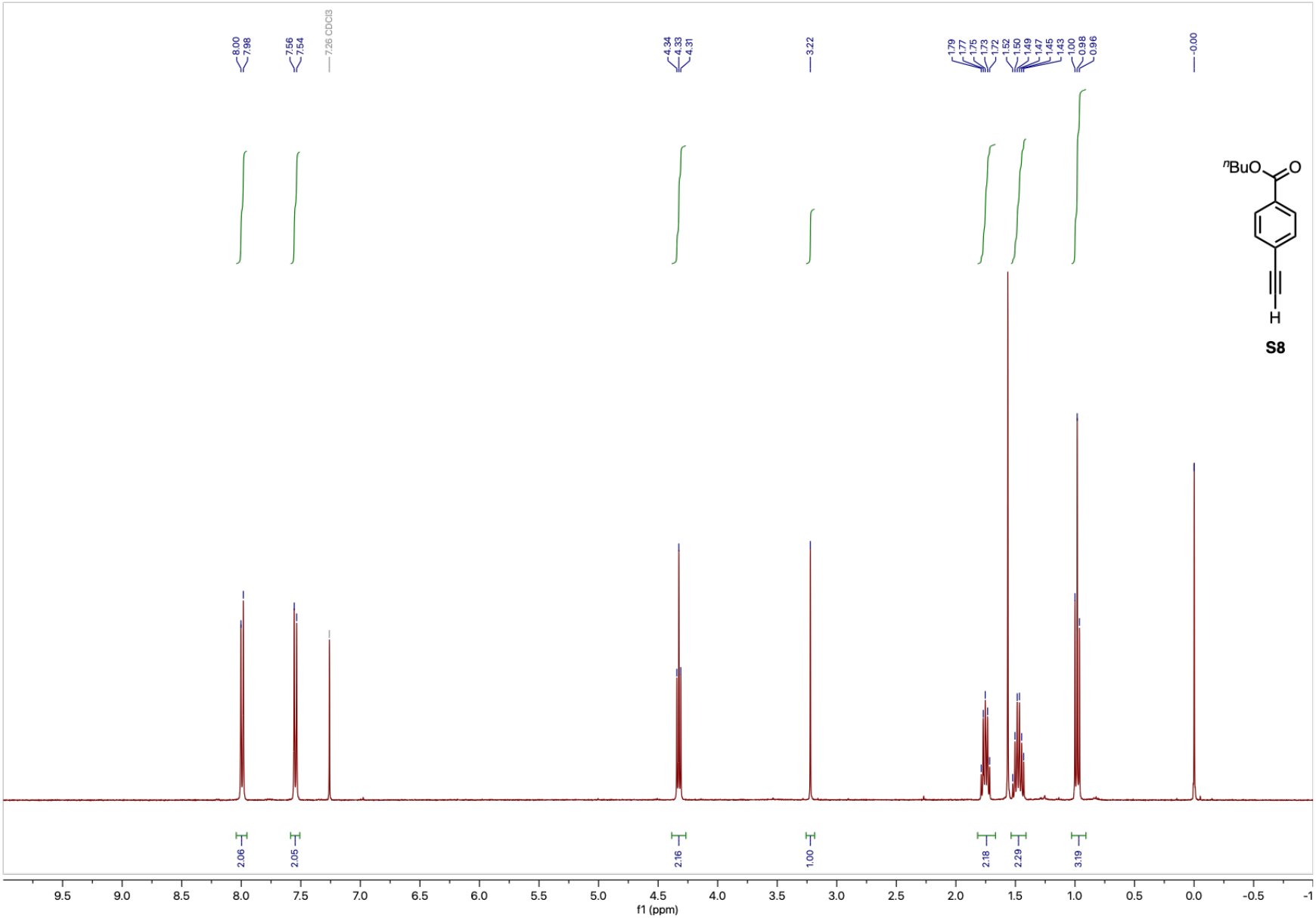


Figure S44. ^{1}H NMR of **S8**.

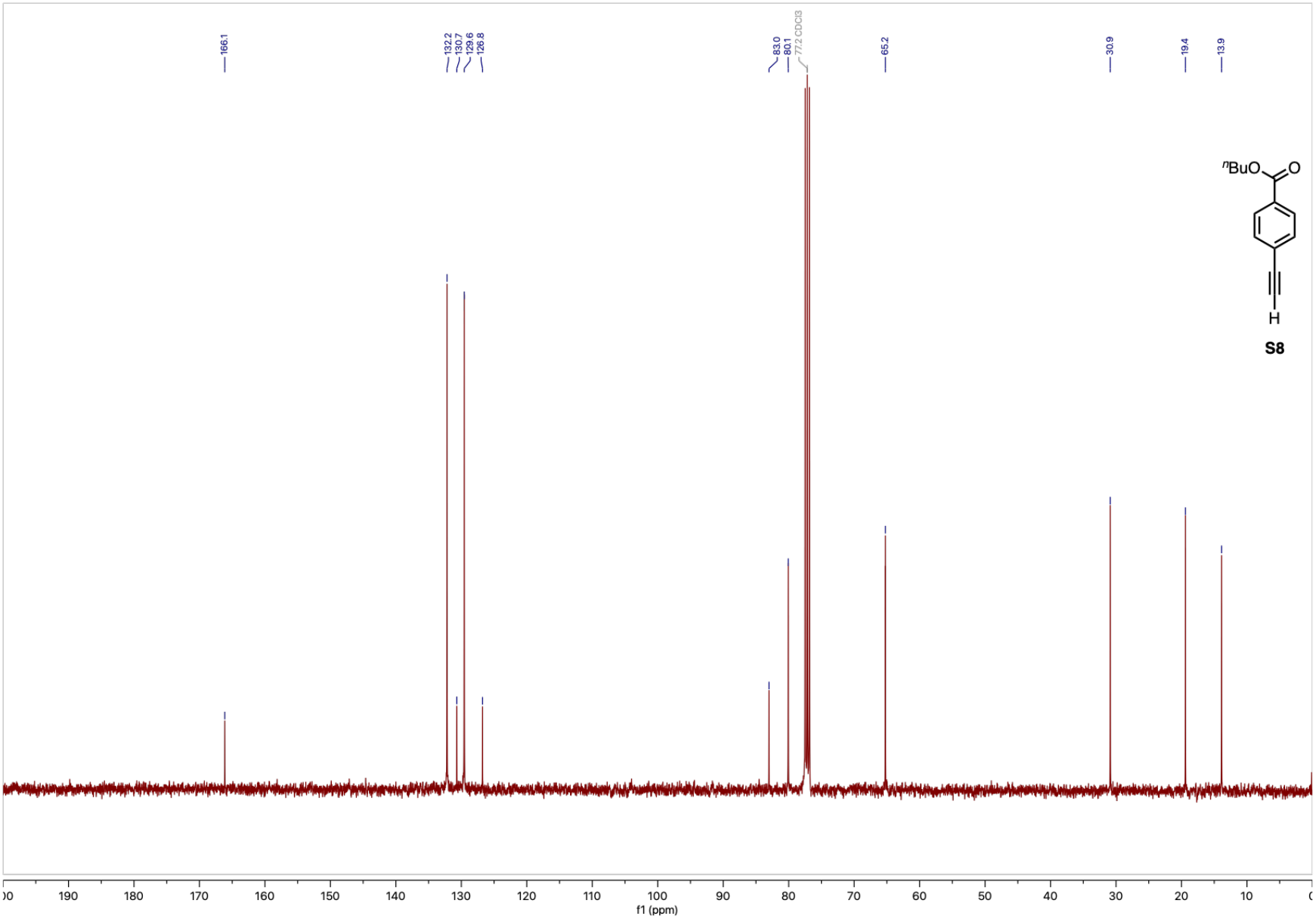


Figure S45. ^{13}C NMR of **S8**.

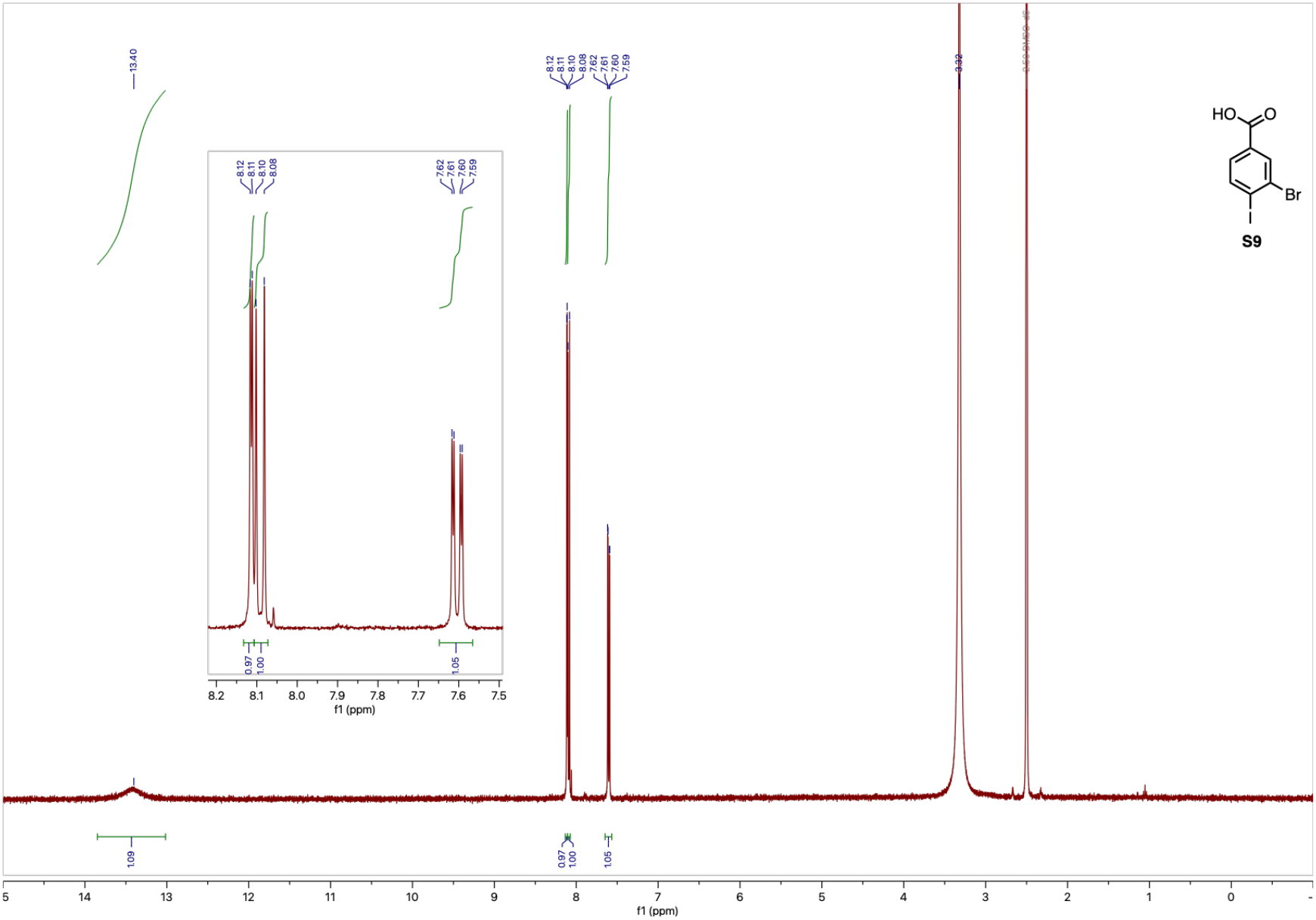


Figure S46. ^{1}H NMR of **S9**.

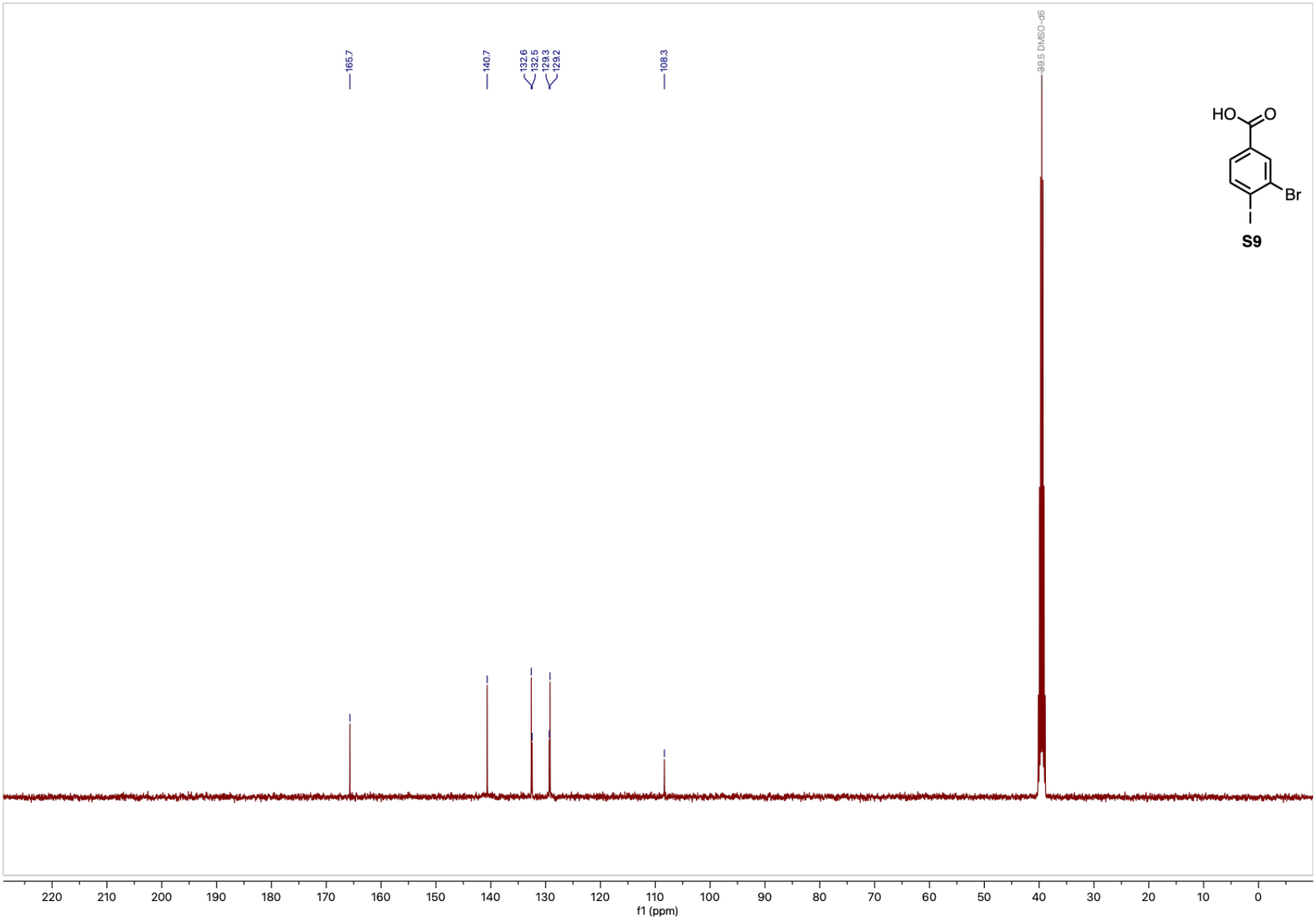


Figure S47. ^{13}C NMR of **S9**.

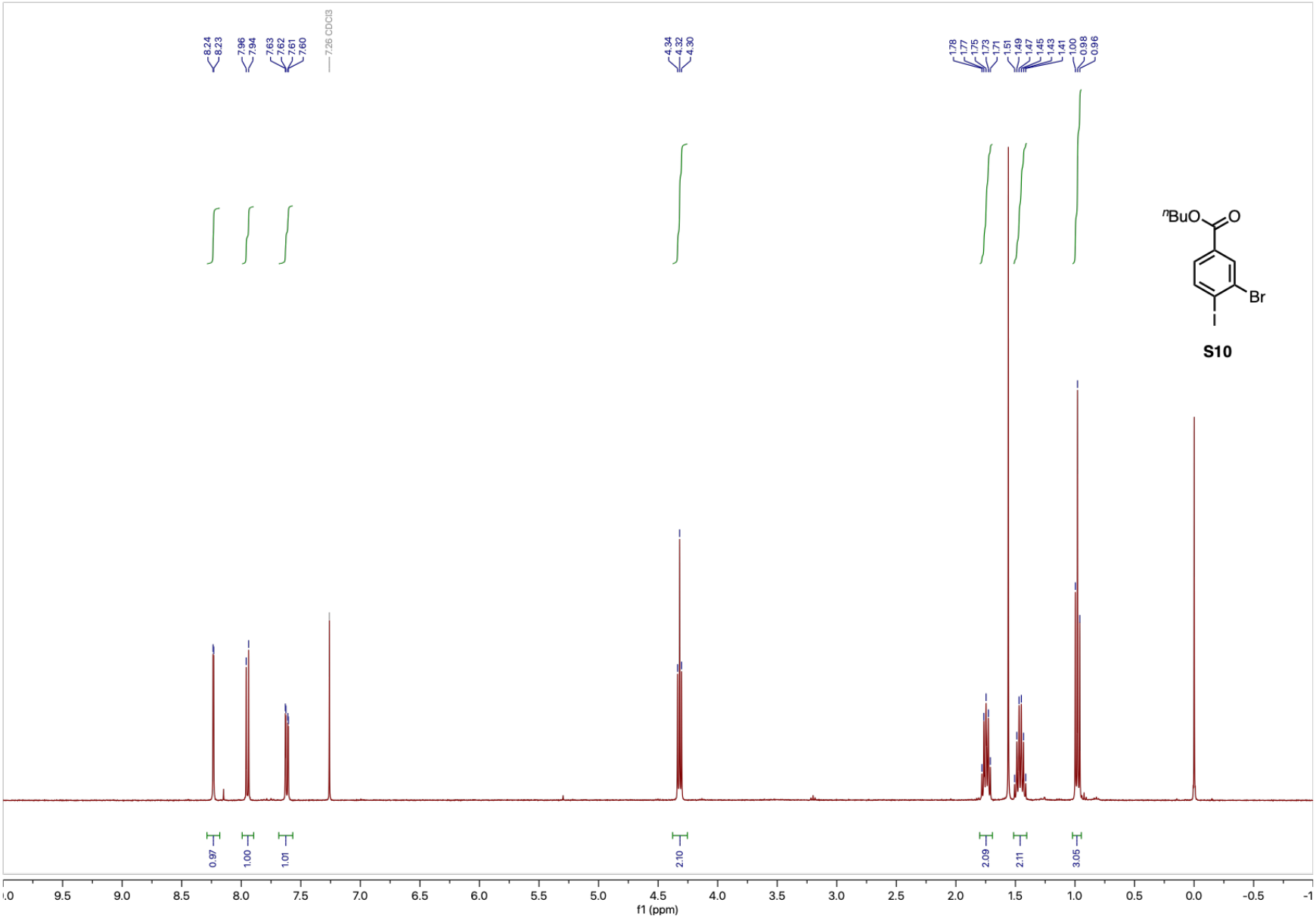


Figure S48. ^{1}H NMR of **S10**.

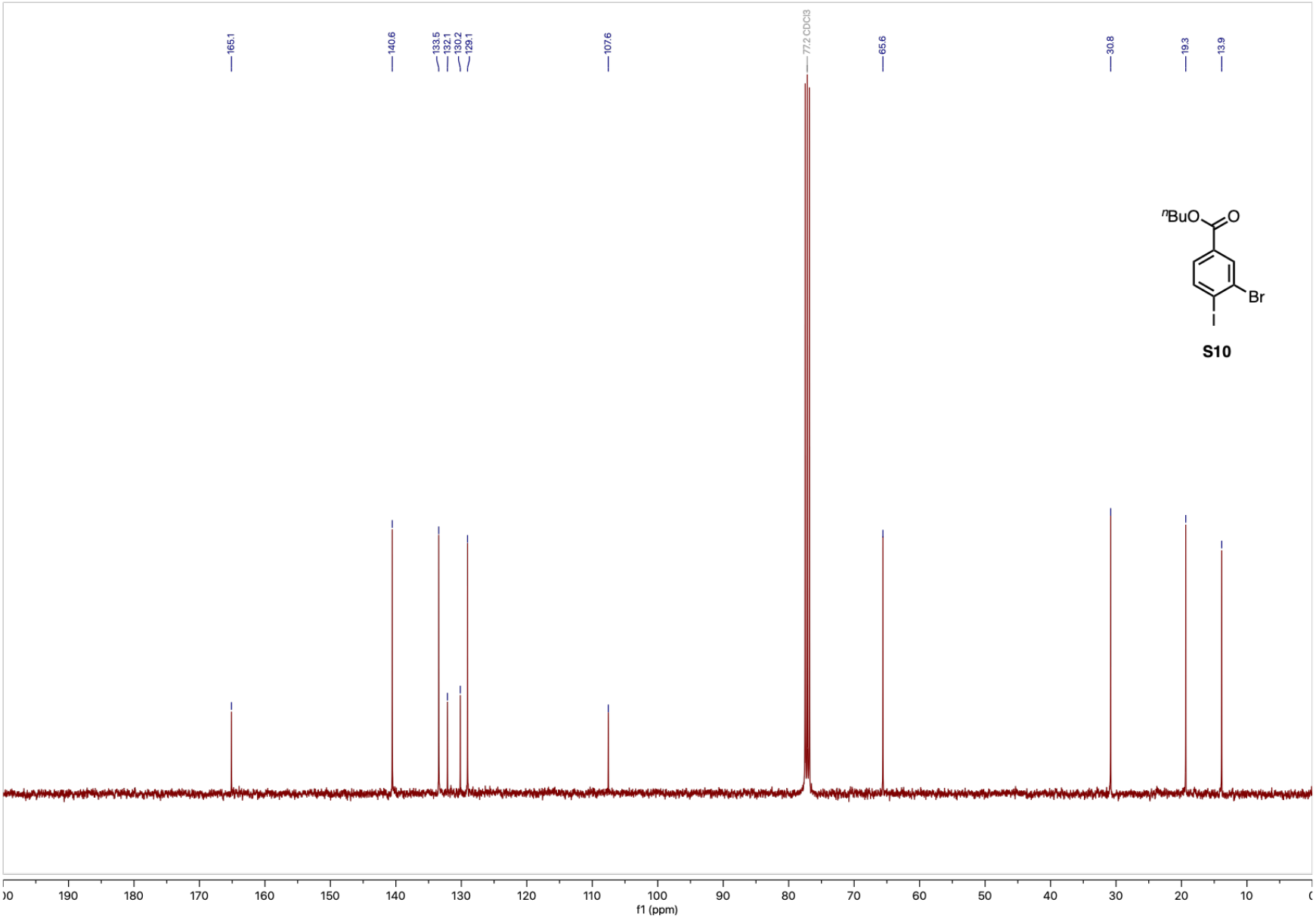


Figure S49. ^{13}C NMR of **S10**.

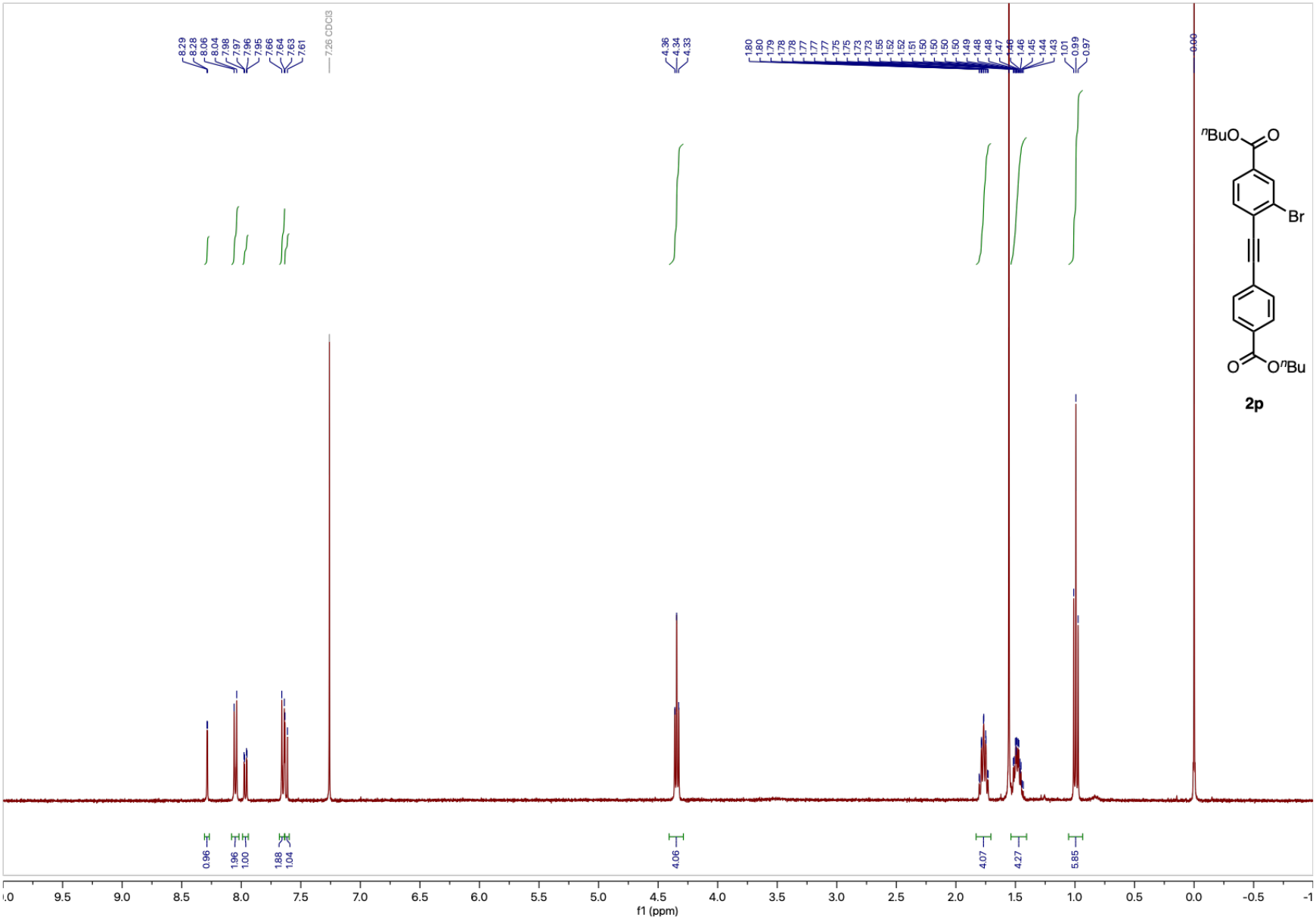


Figure S50. ^{1}H NMR of **2p**.

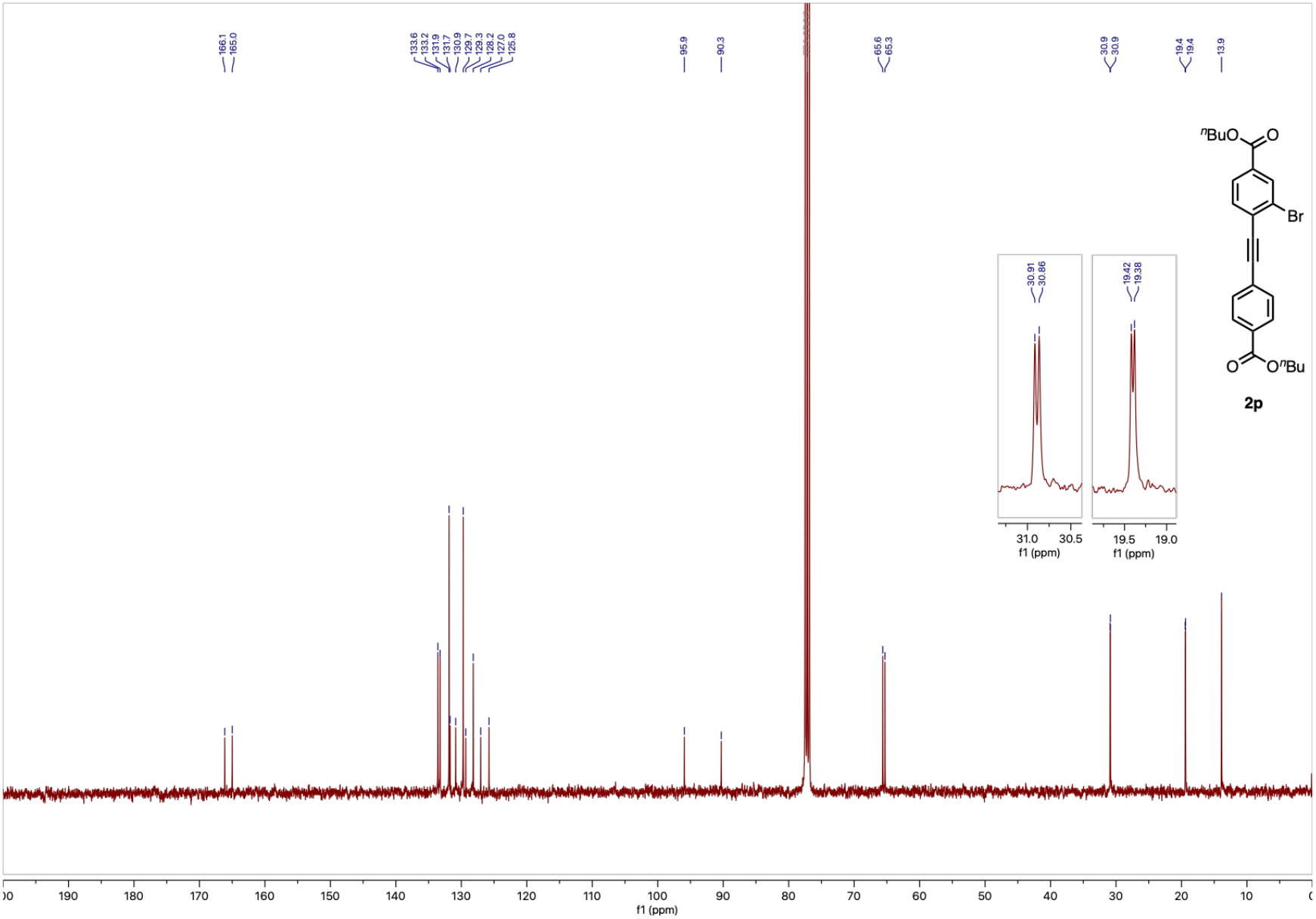


Figure S51. ^{13}C NMR of **2p**.

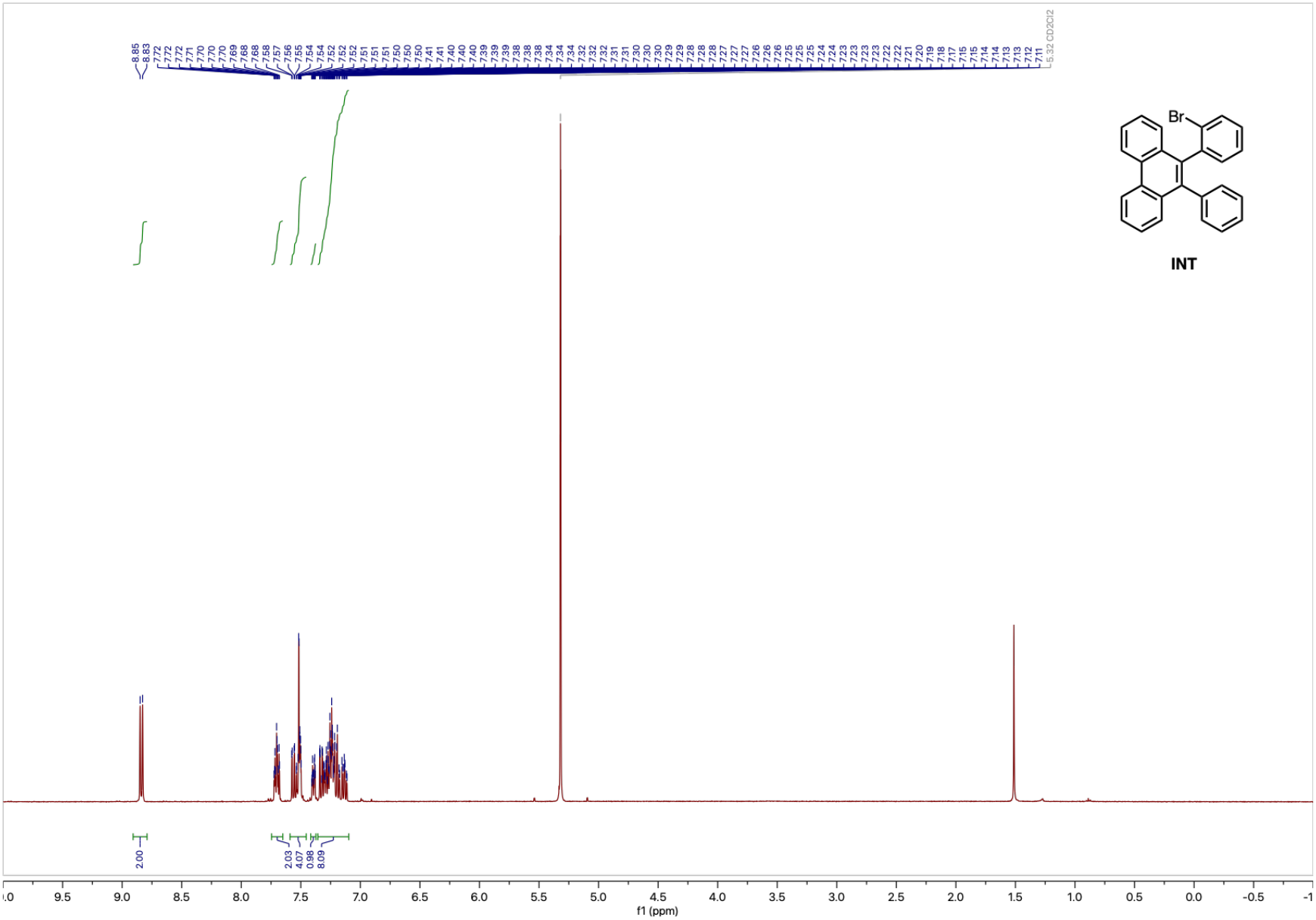


Figure S52. ^{1}H NMR of **INT**.

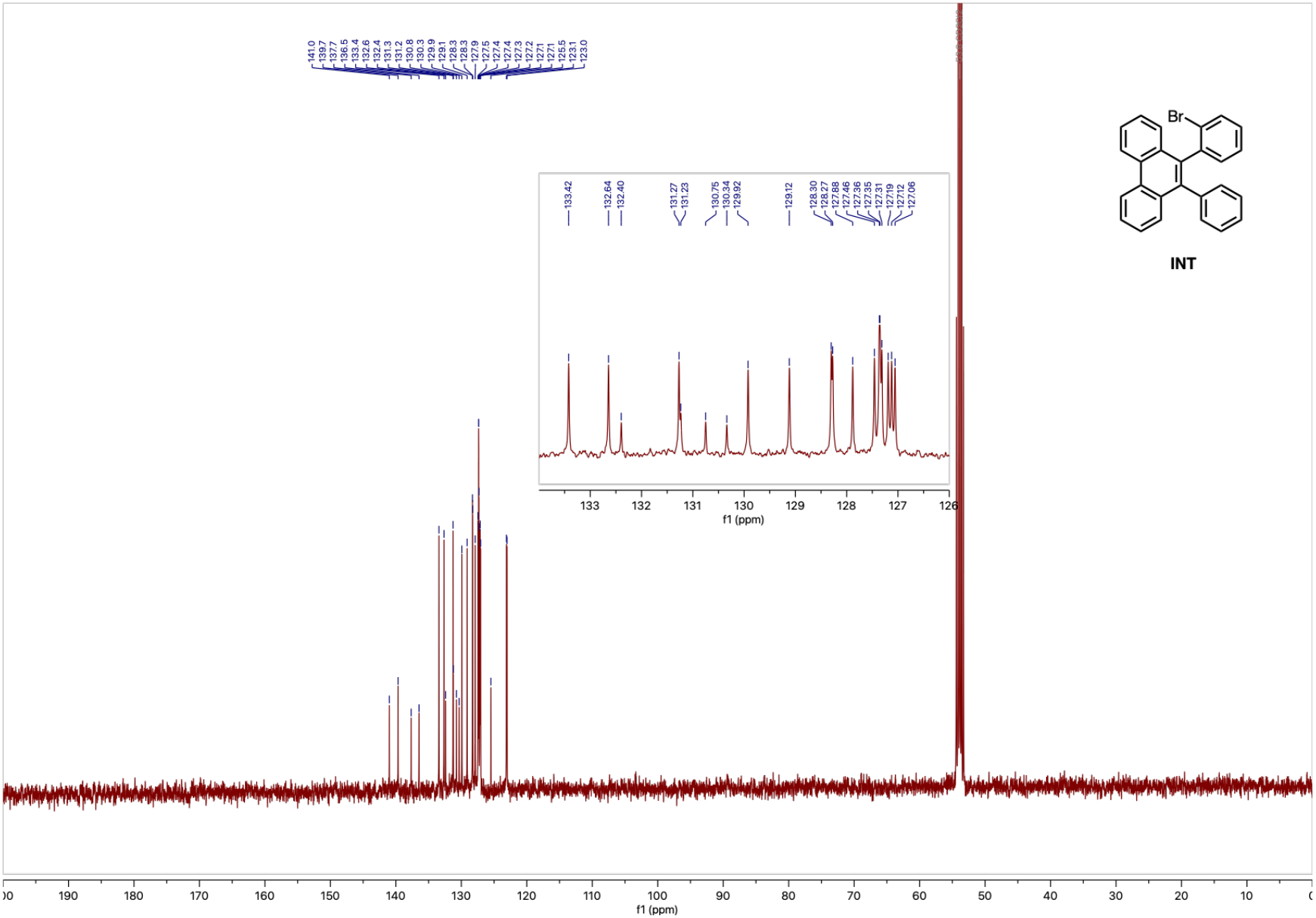


Figure S53. ^{13}C NMR of **INT**.

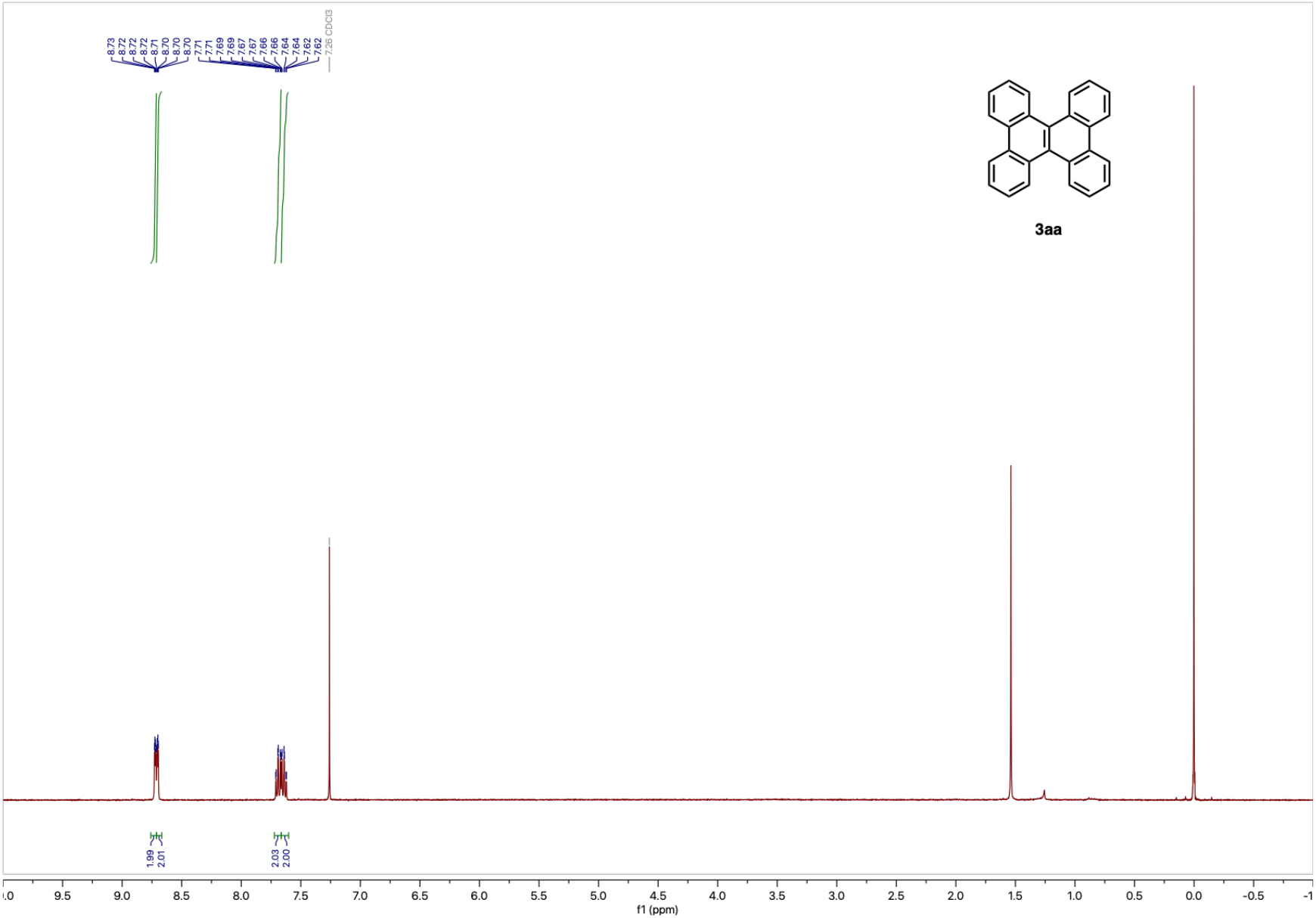


Figure S54. ^{1}H NMR of **3aa**.

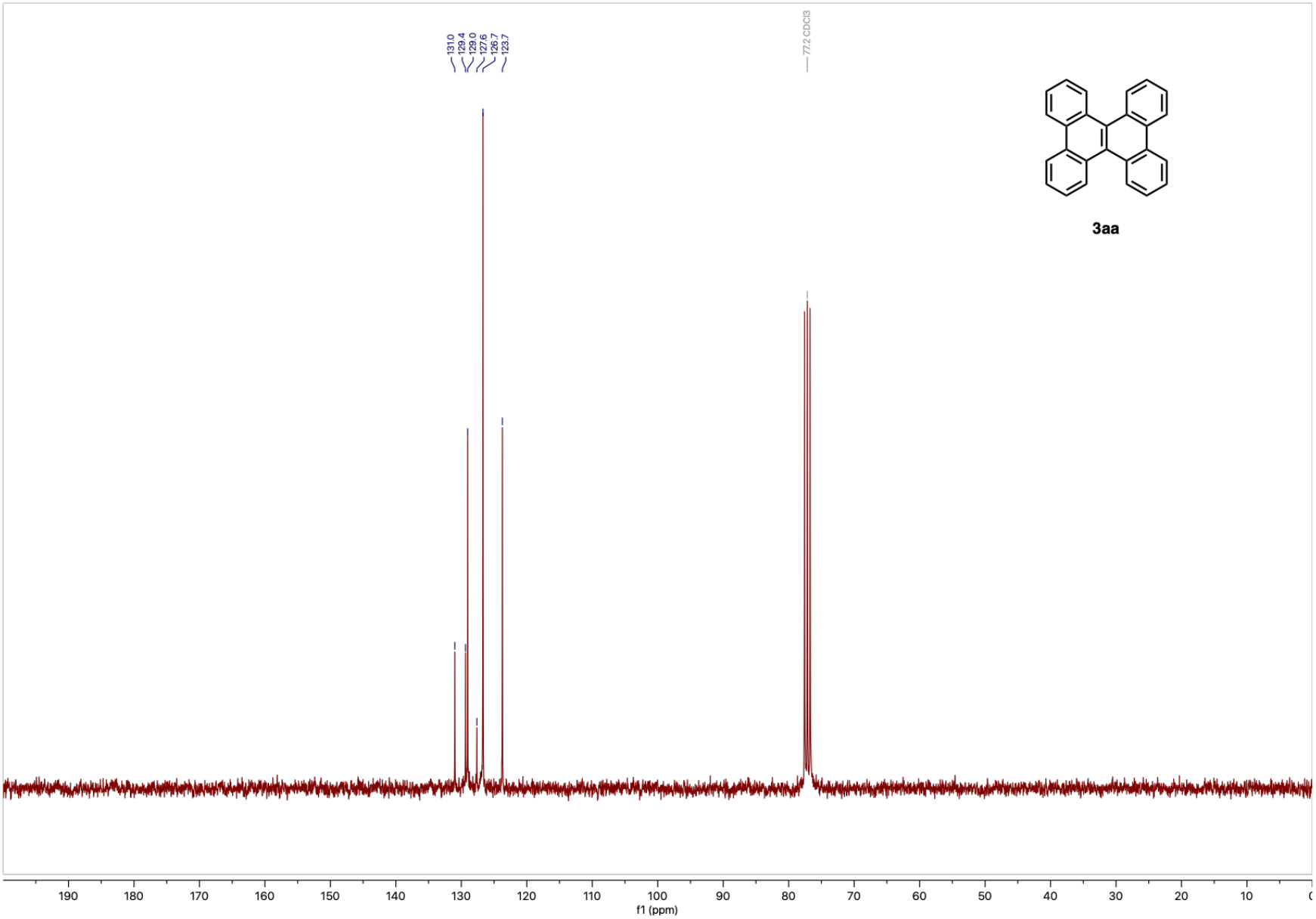


Figure S55. ^{13}C NMR of **3aa**.

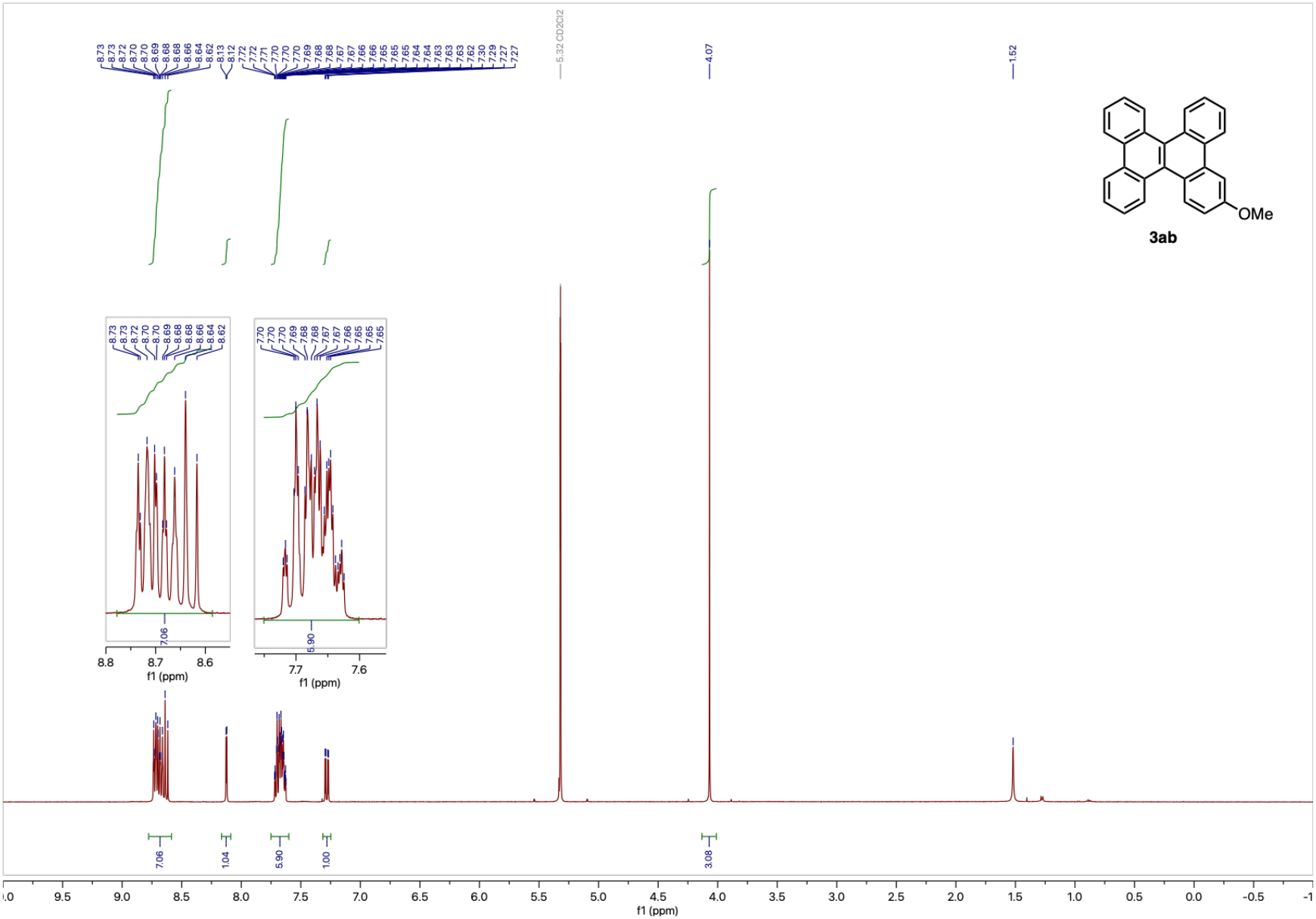


Figure S56. ^{1}H NMR of **3ab**.

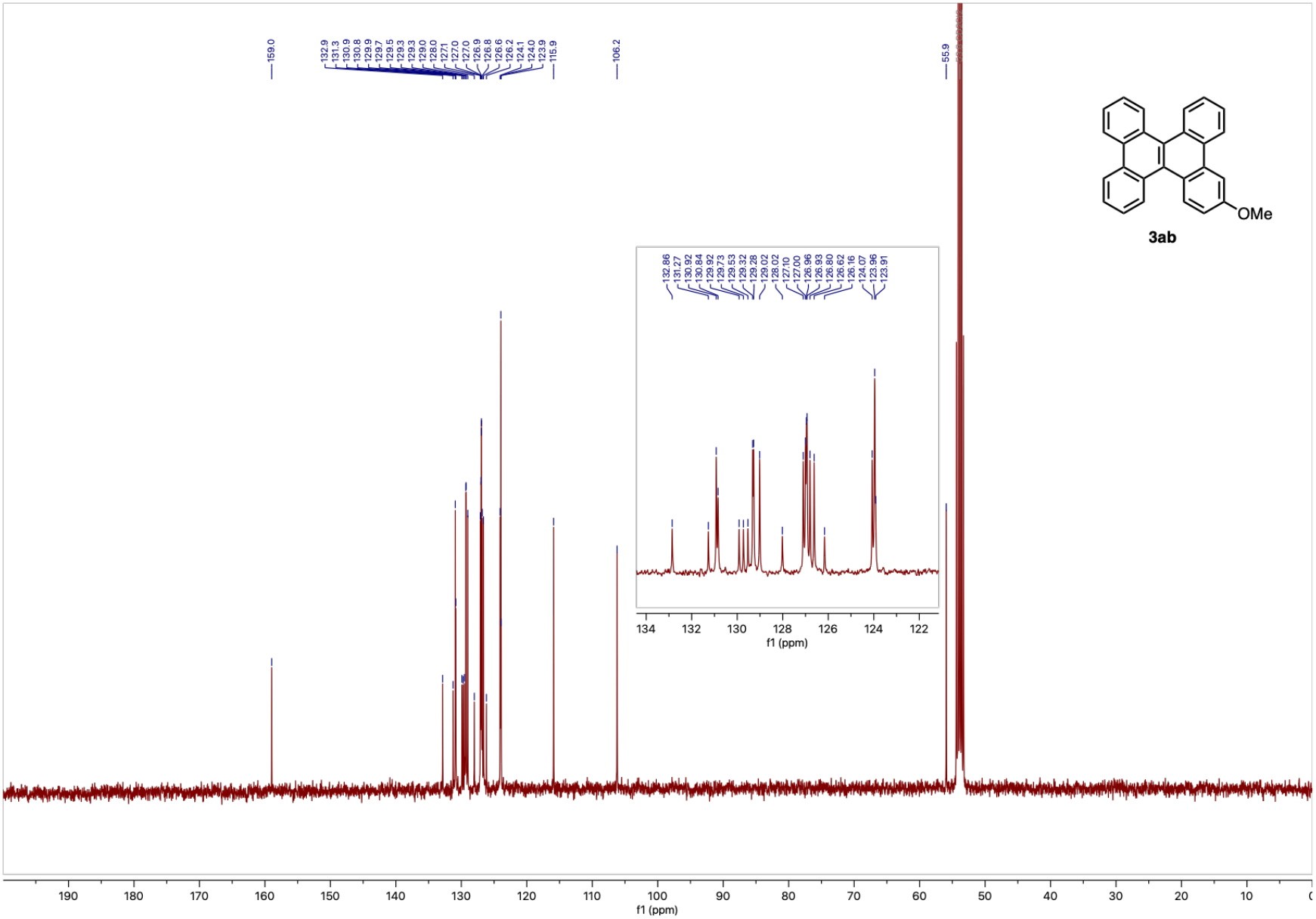


Figure S57. ^{13}C NMR of **3ab**.

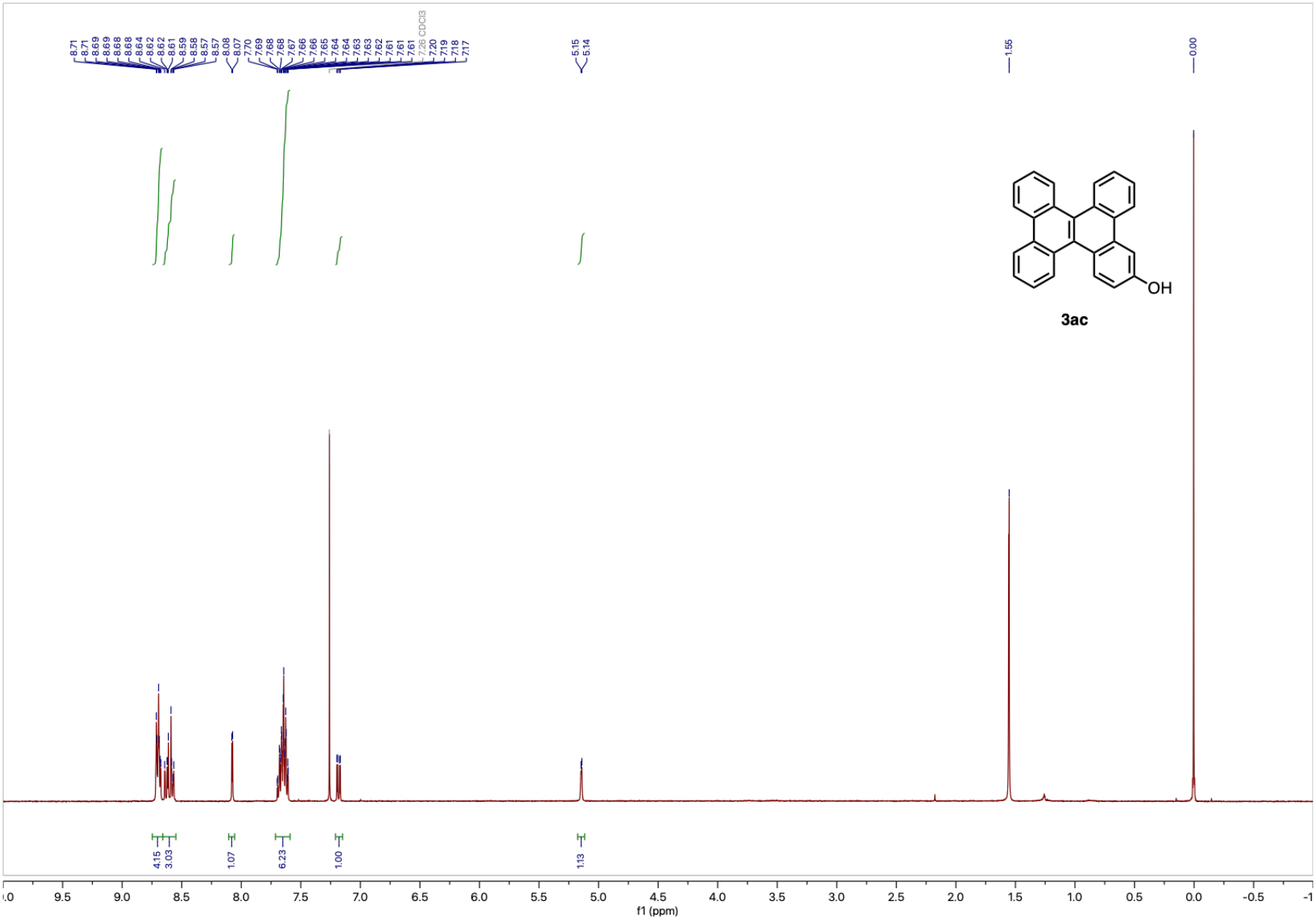


Figure S58. ^{1}H NMR of **3ac**.

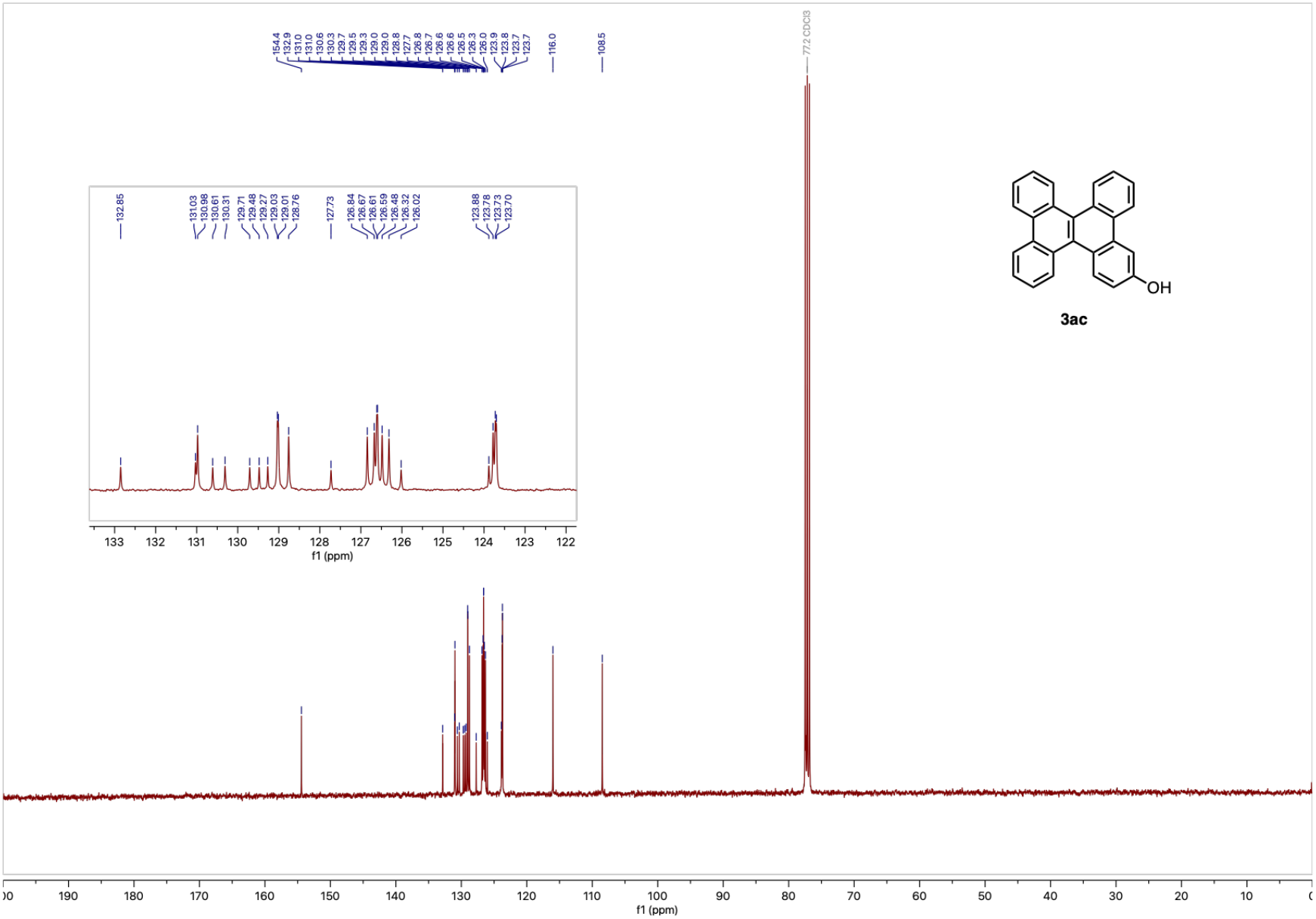


Figure S59. ^{13}C NMR of **3ac**.

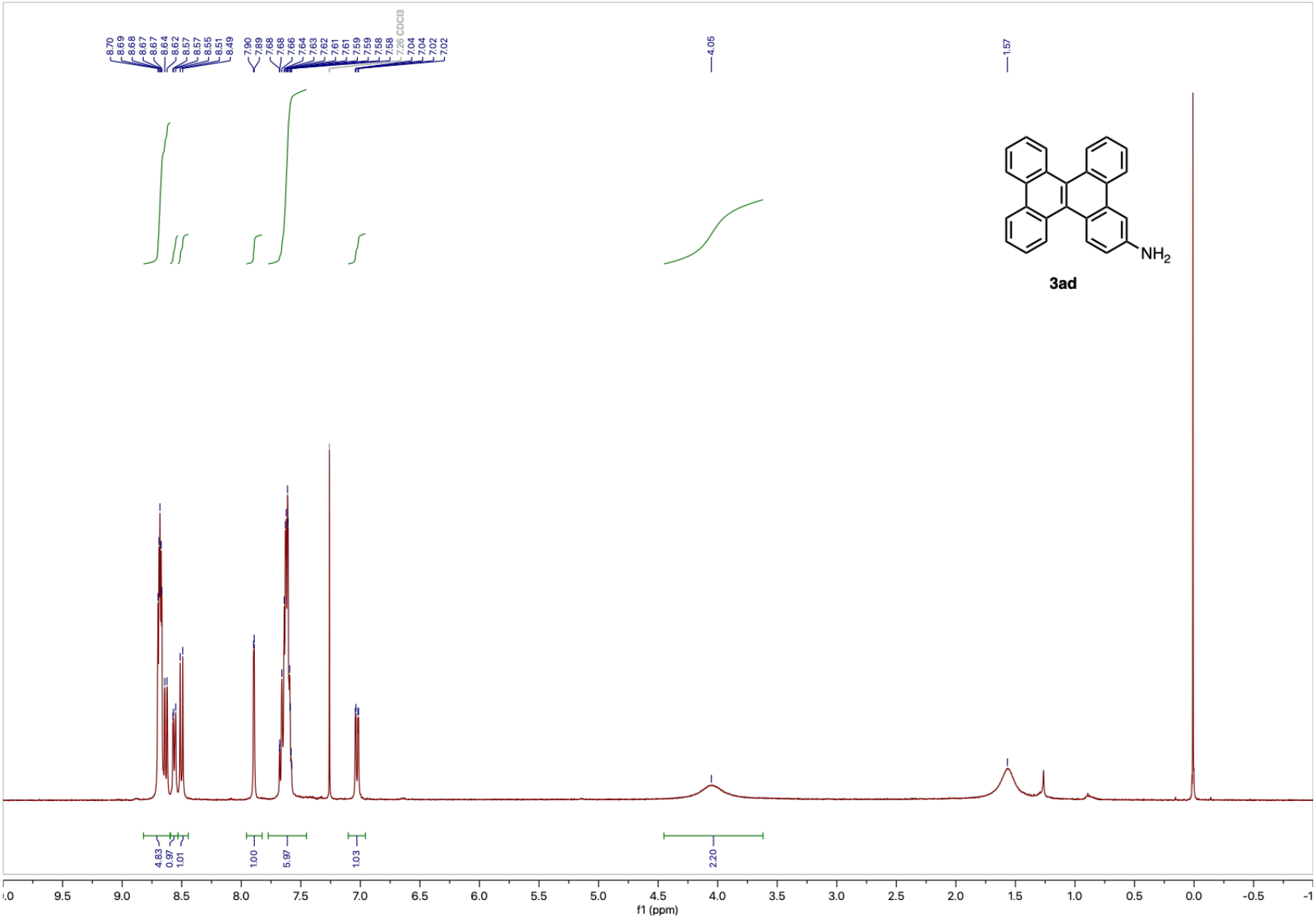


Figure S60. ^{1}H NMR of **3ad**.

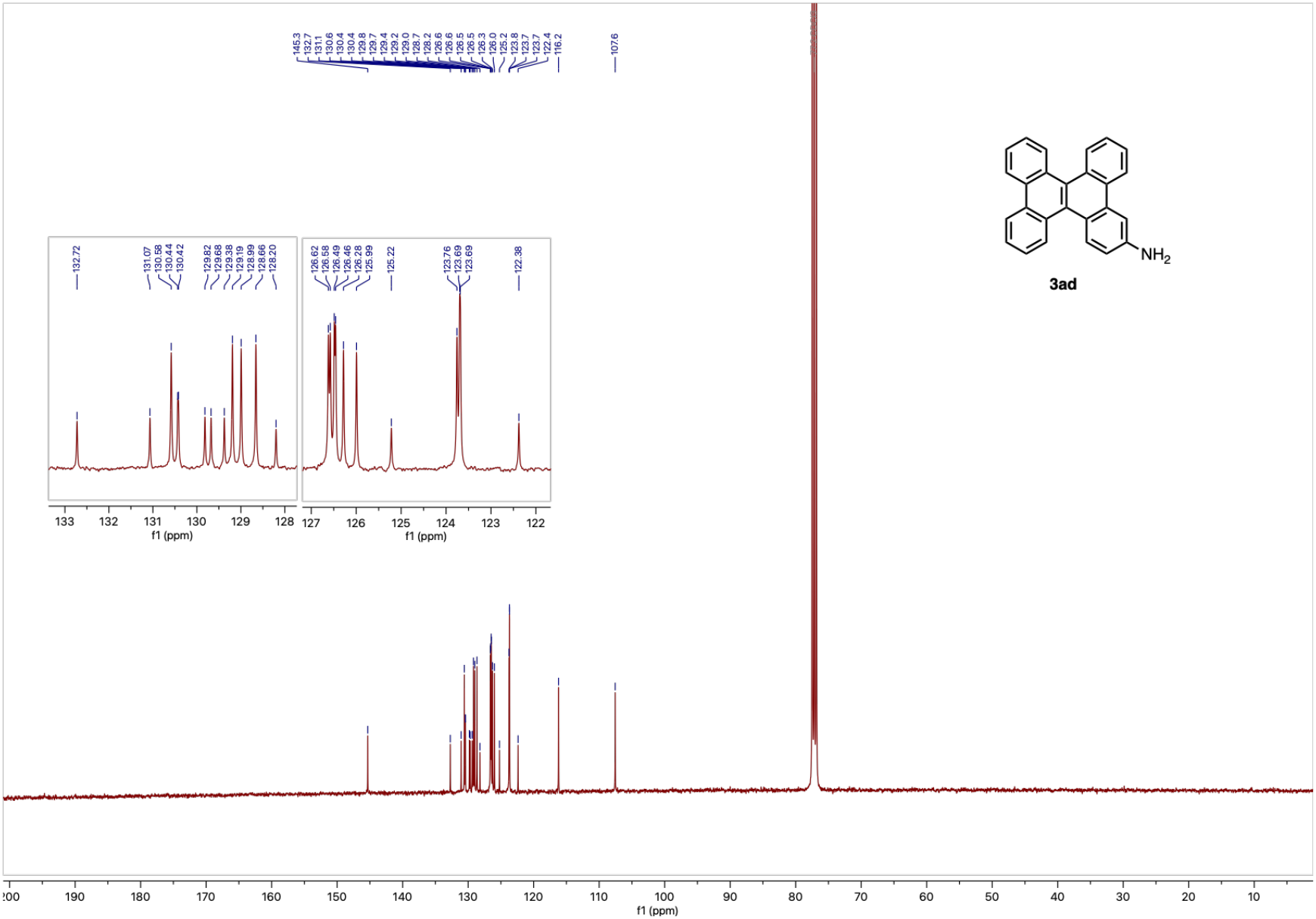


Figure S61. ^{13}C NMR of **3ad**.

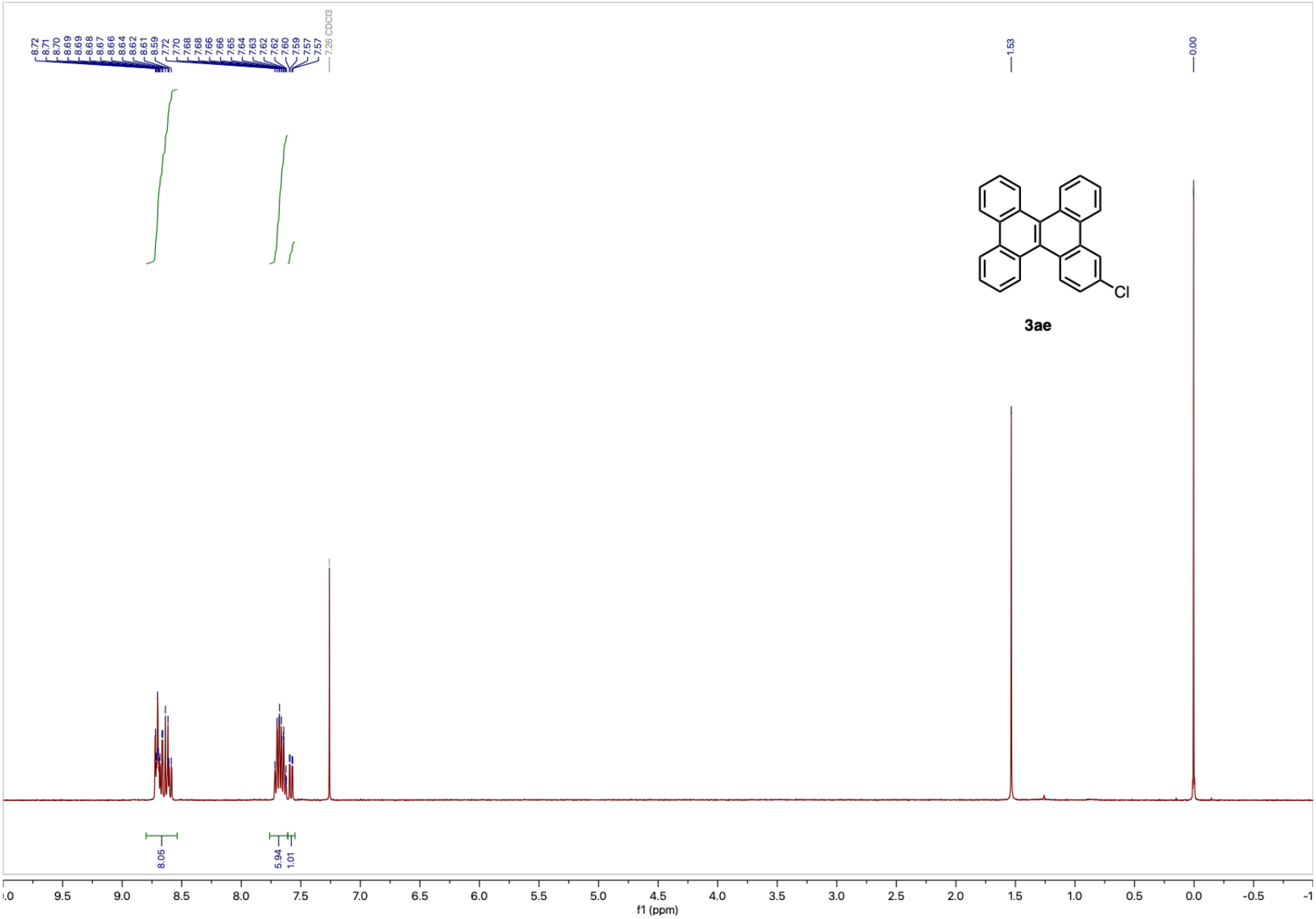


Figure S62. ^{1}H NMR of **3ae**.

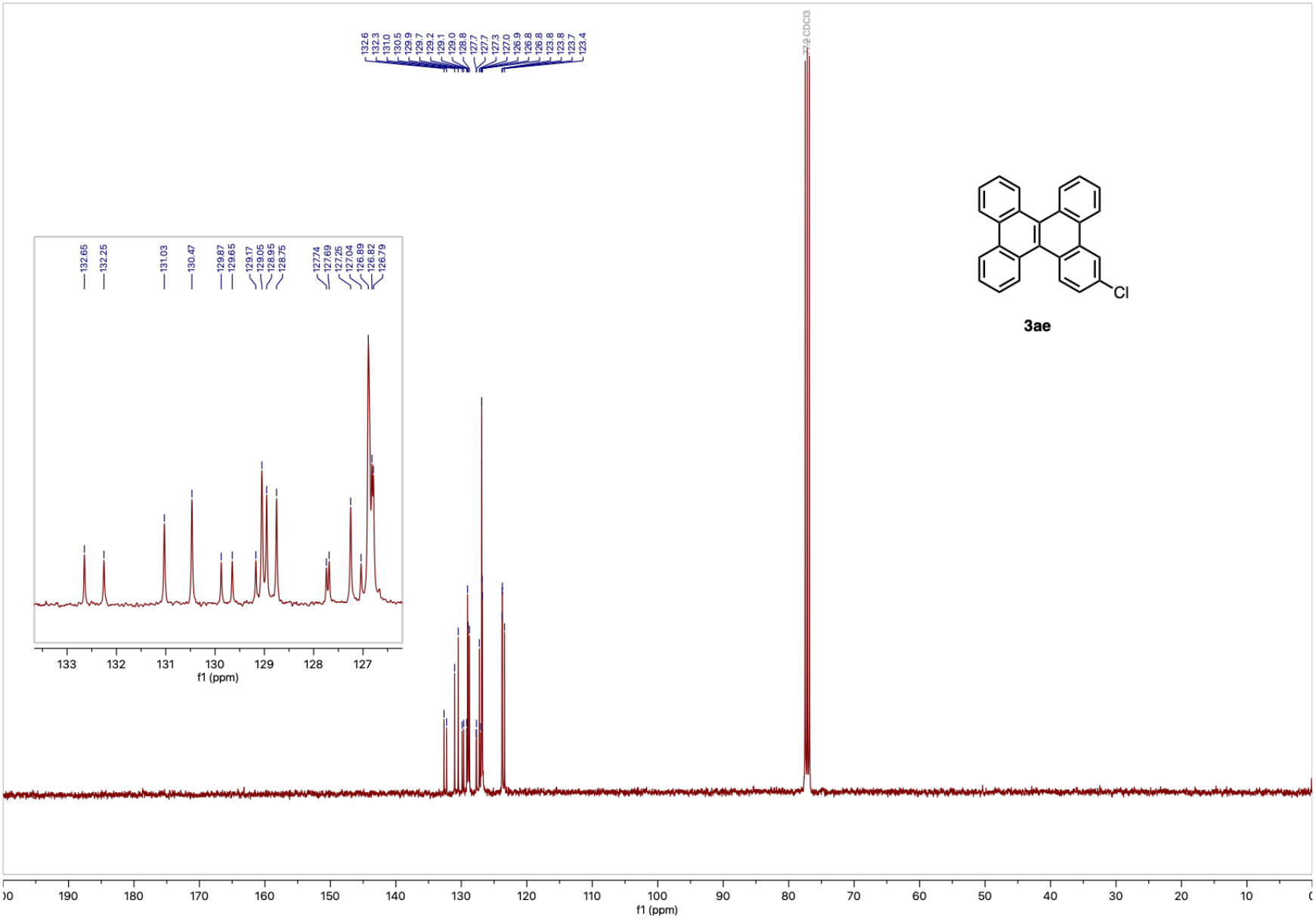


Figure S63. ^{13}C NMR of **3ae**.

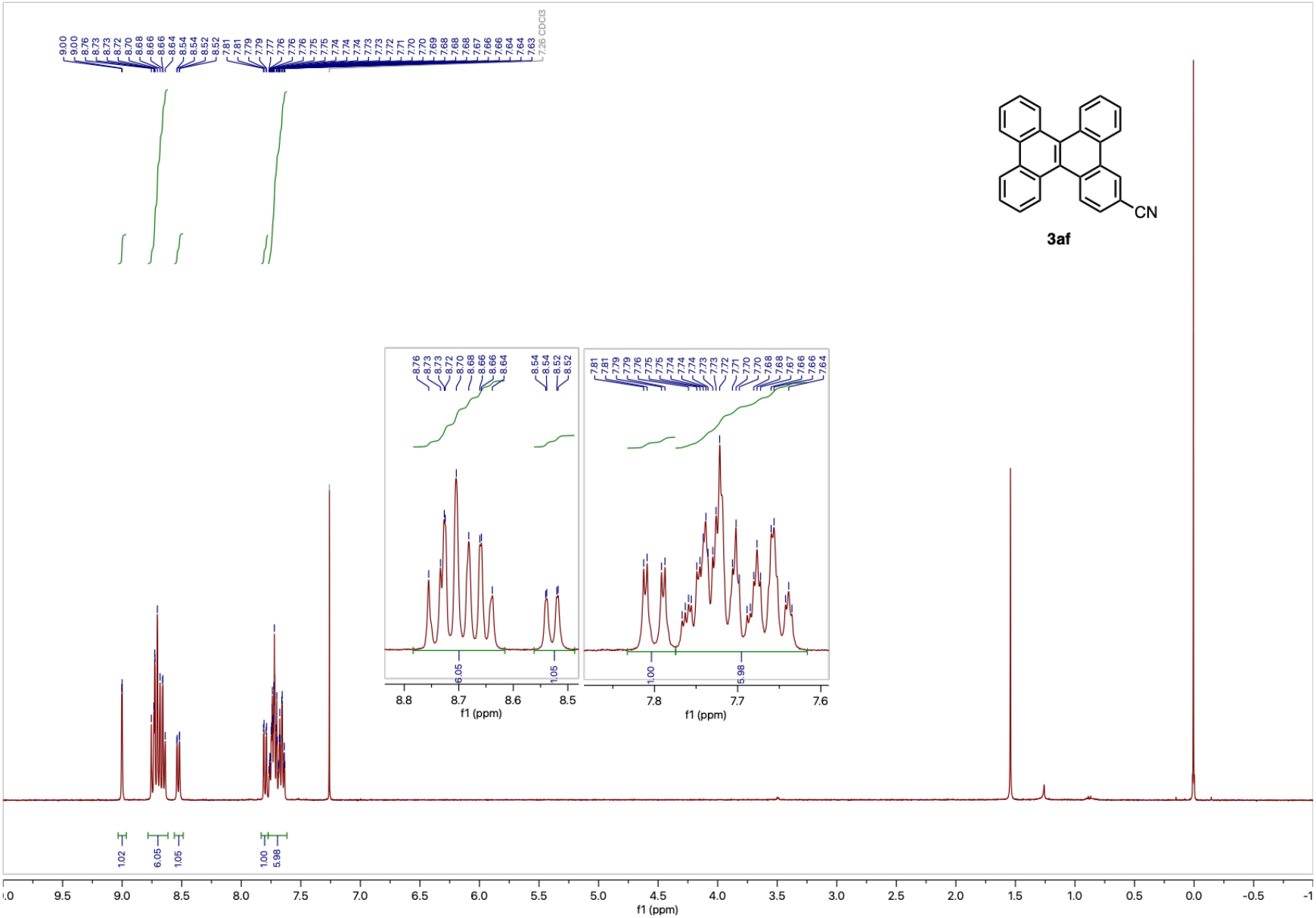


Figure S64. ^{1}H NMR of **3af**.

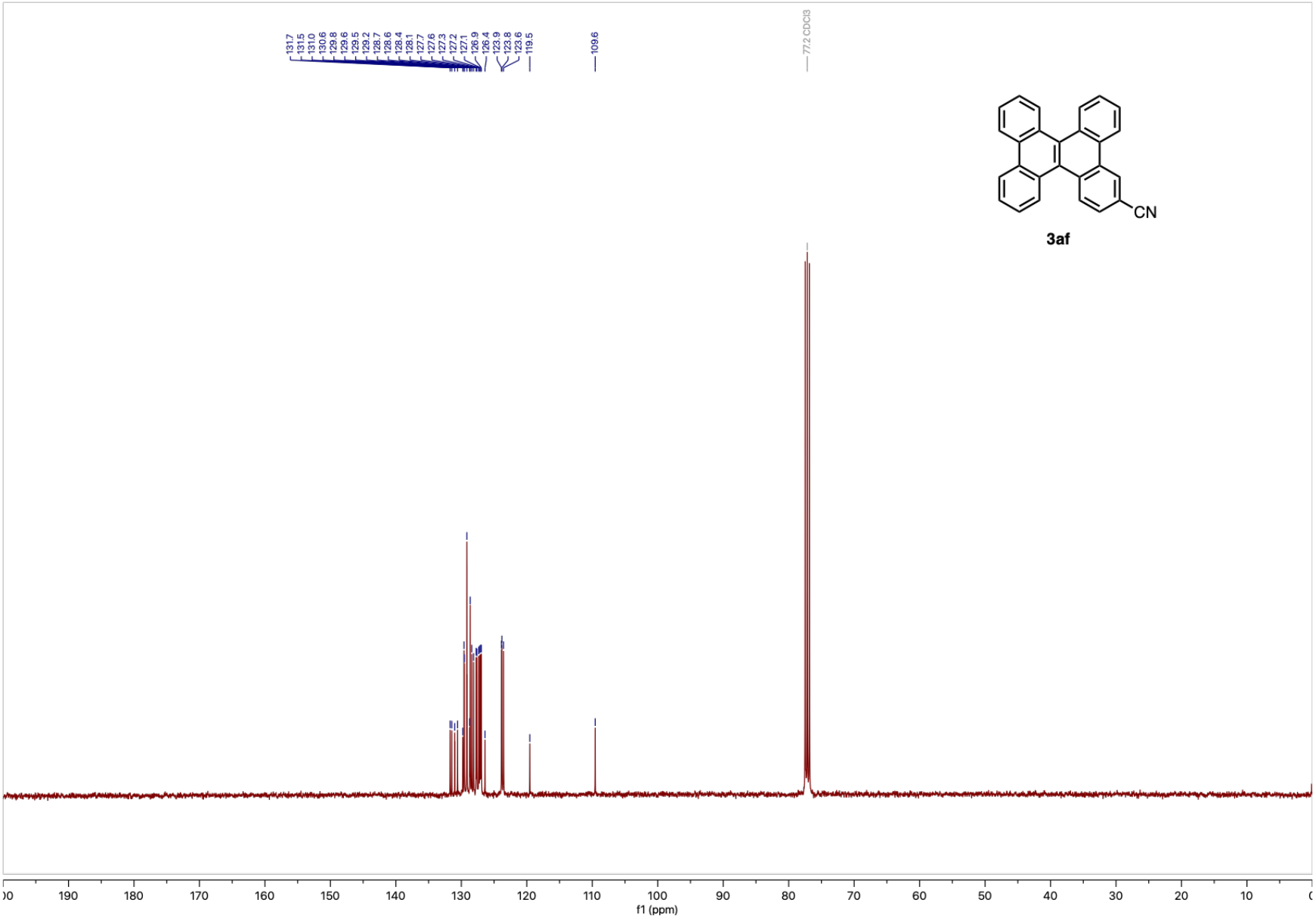


Figure S65. ^{13}C NMR of **3af**.

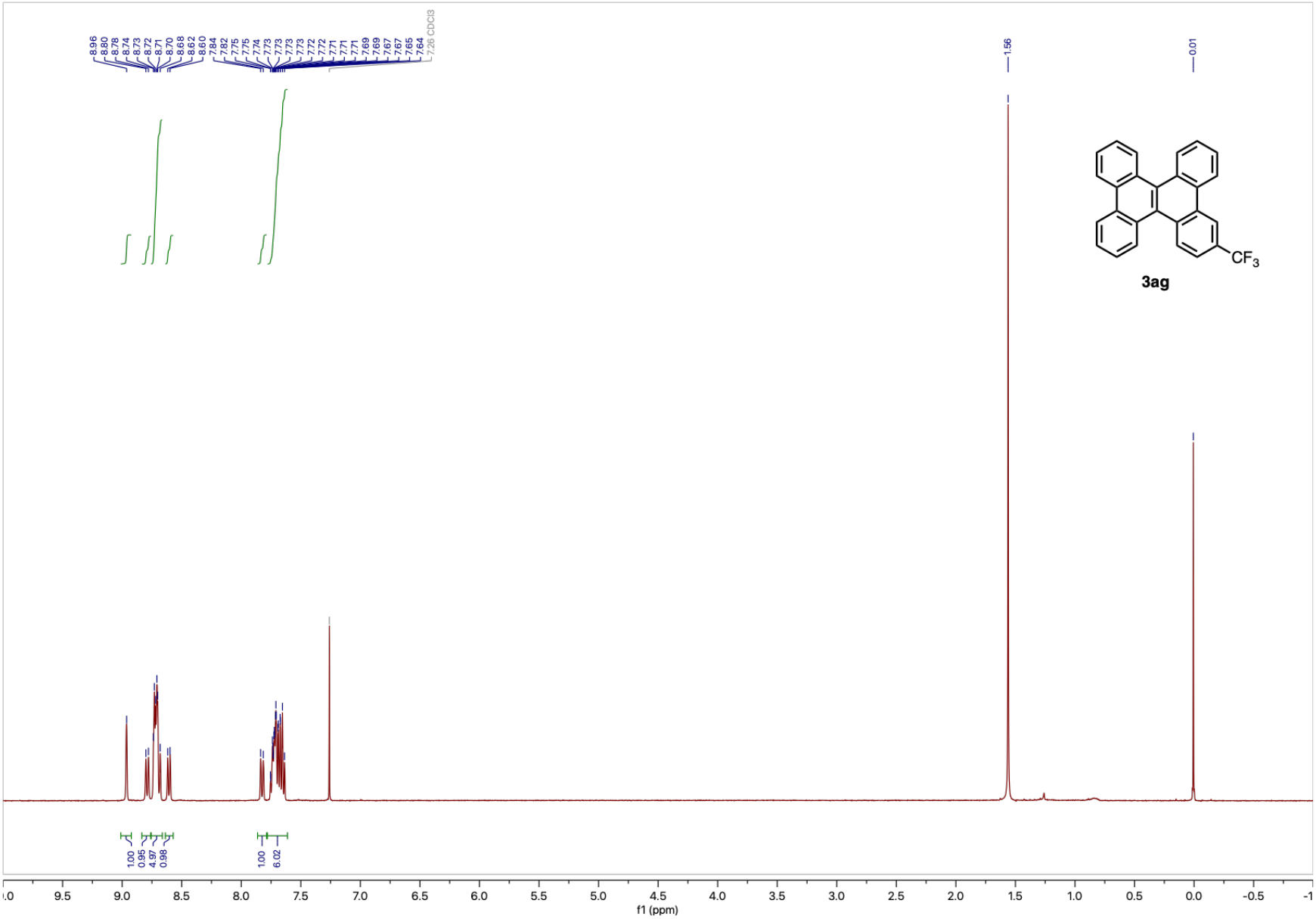


Figure S66. ^{1}H NMR of **3ag**.

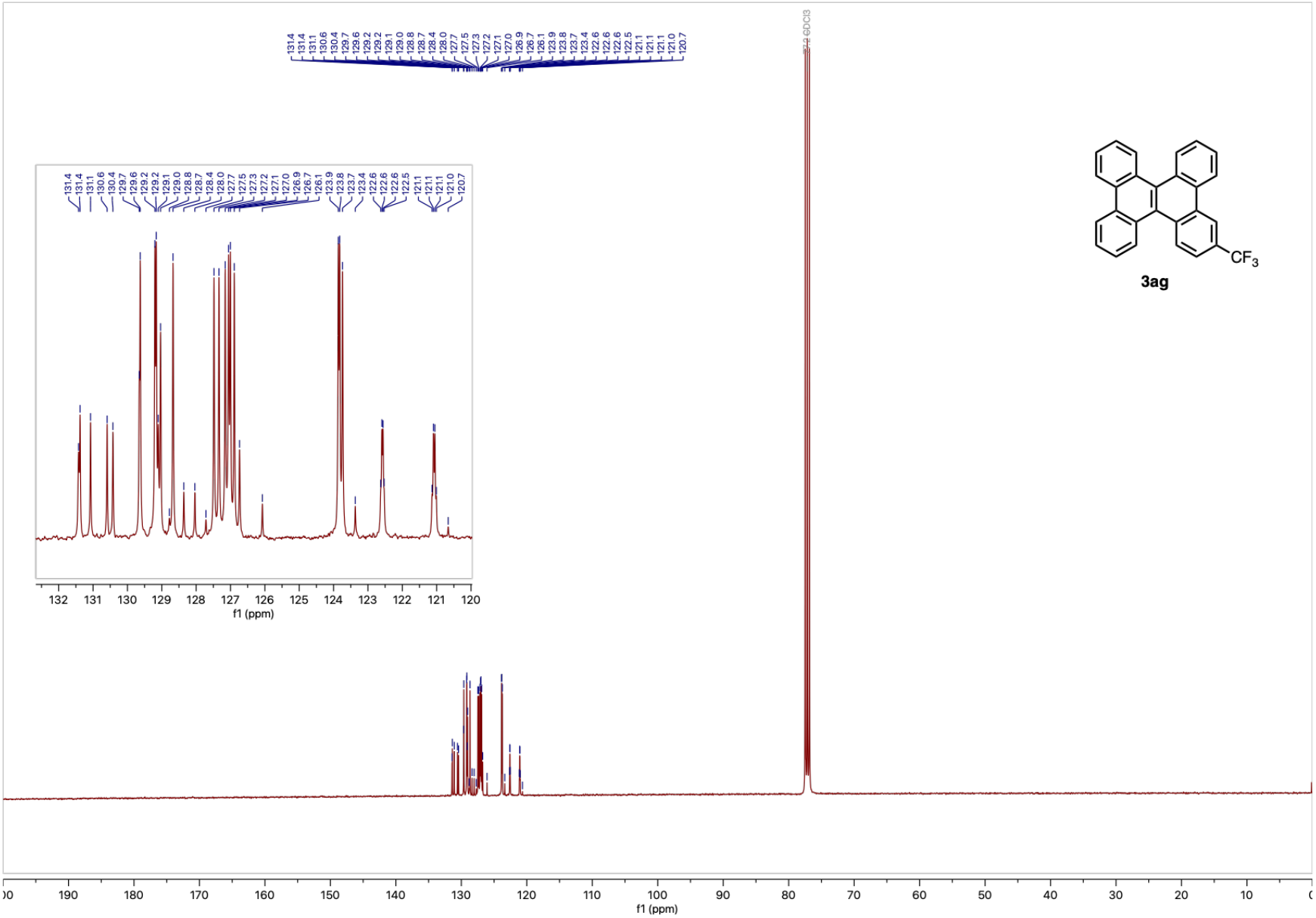


Figure S67. ^{13}C NMR of **3ag**.

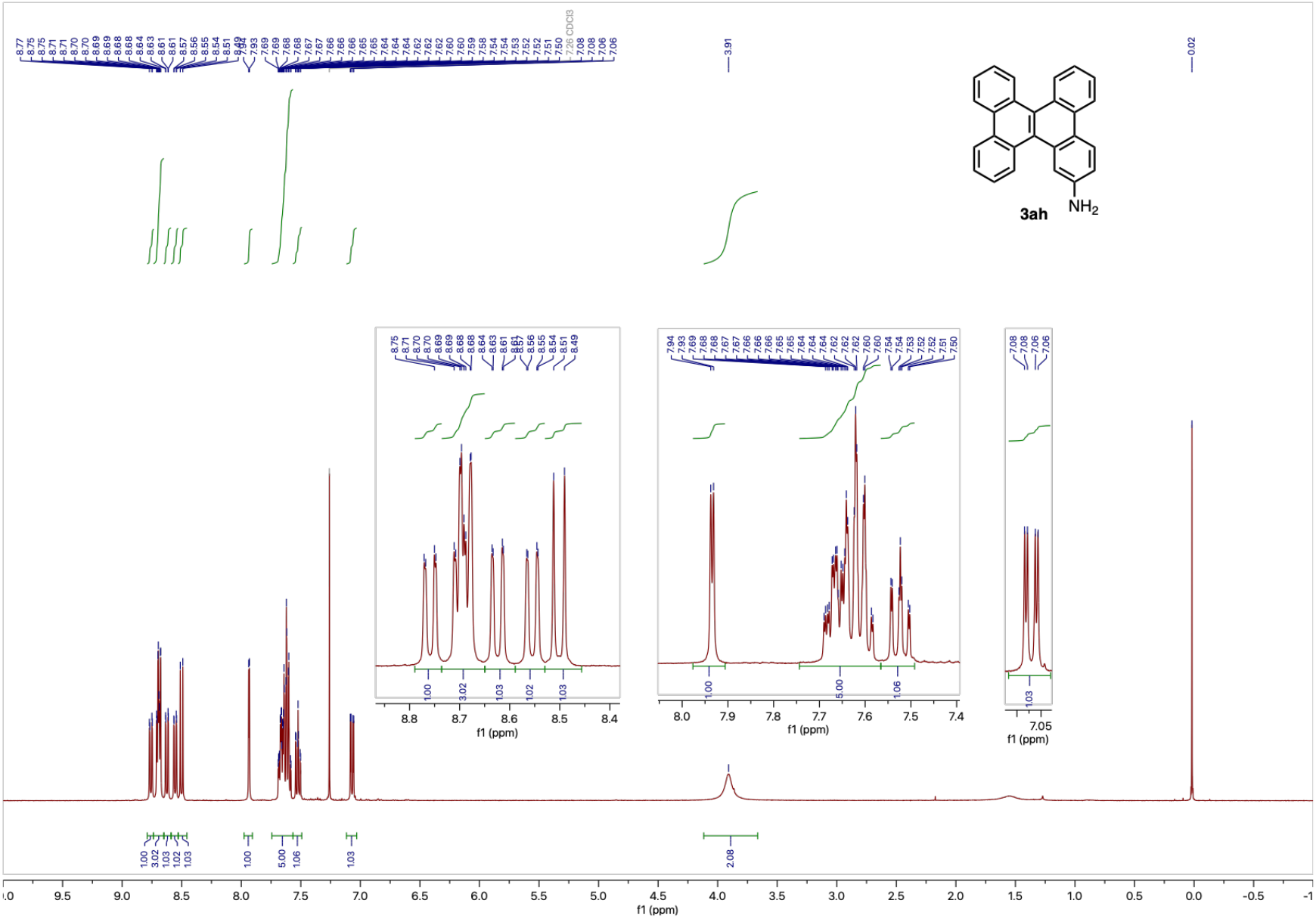


Figure S68. ^{1}H NMR of **3ah**.

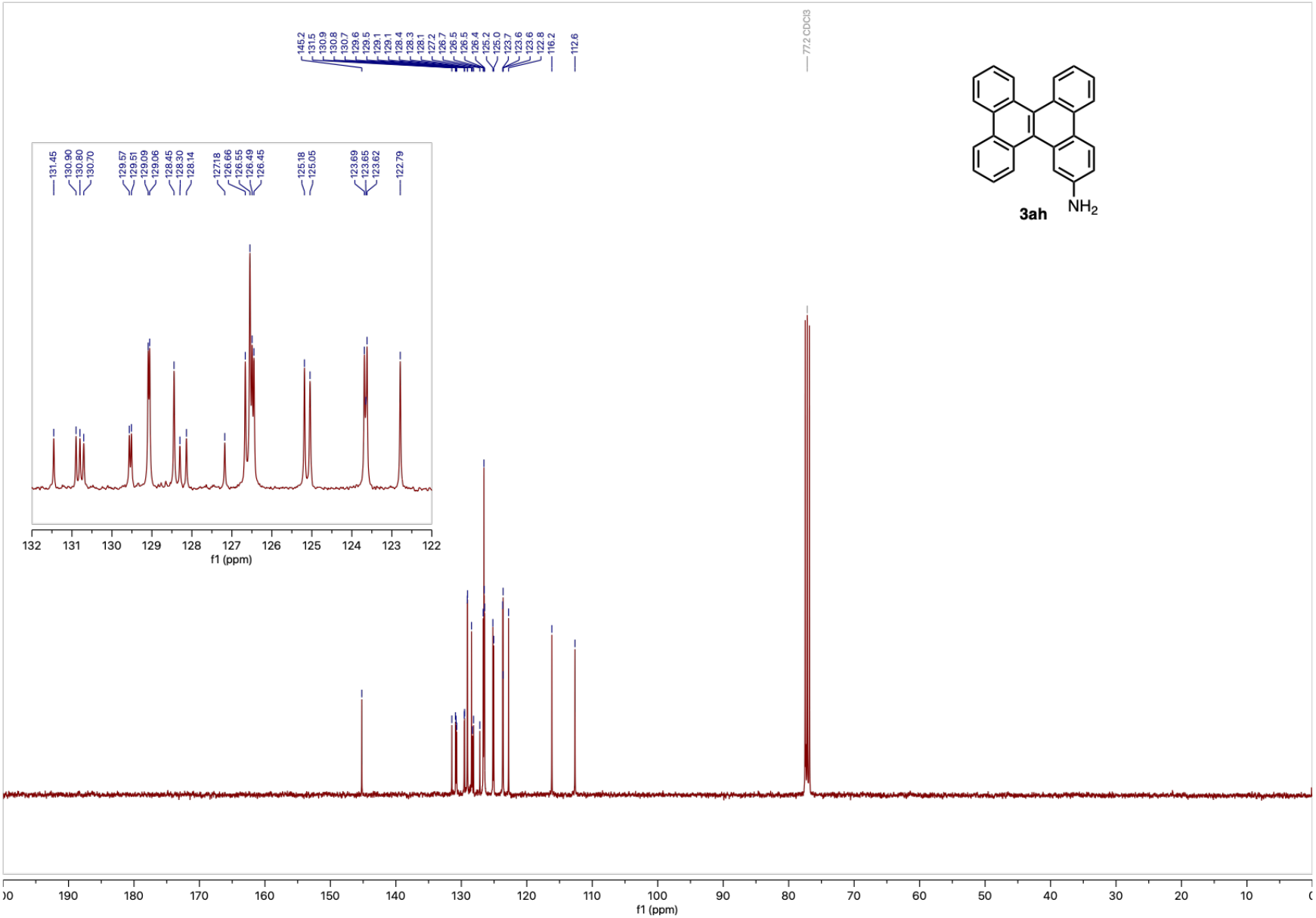


Figure S69. ^{13}C NMR of **3ah**.

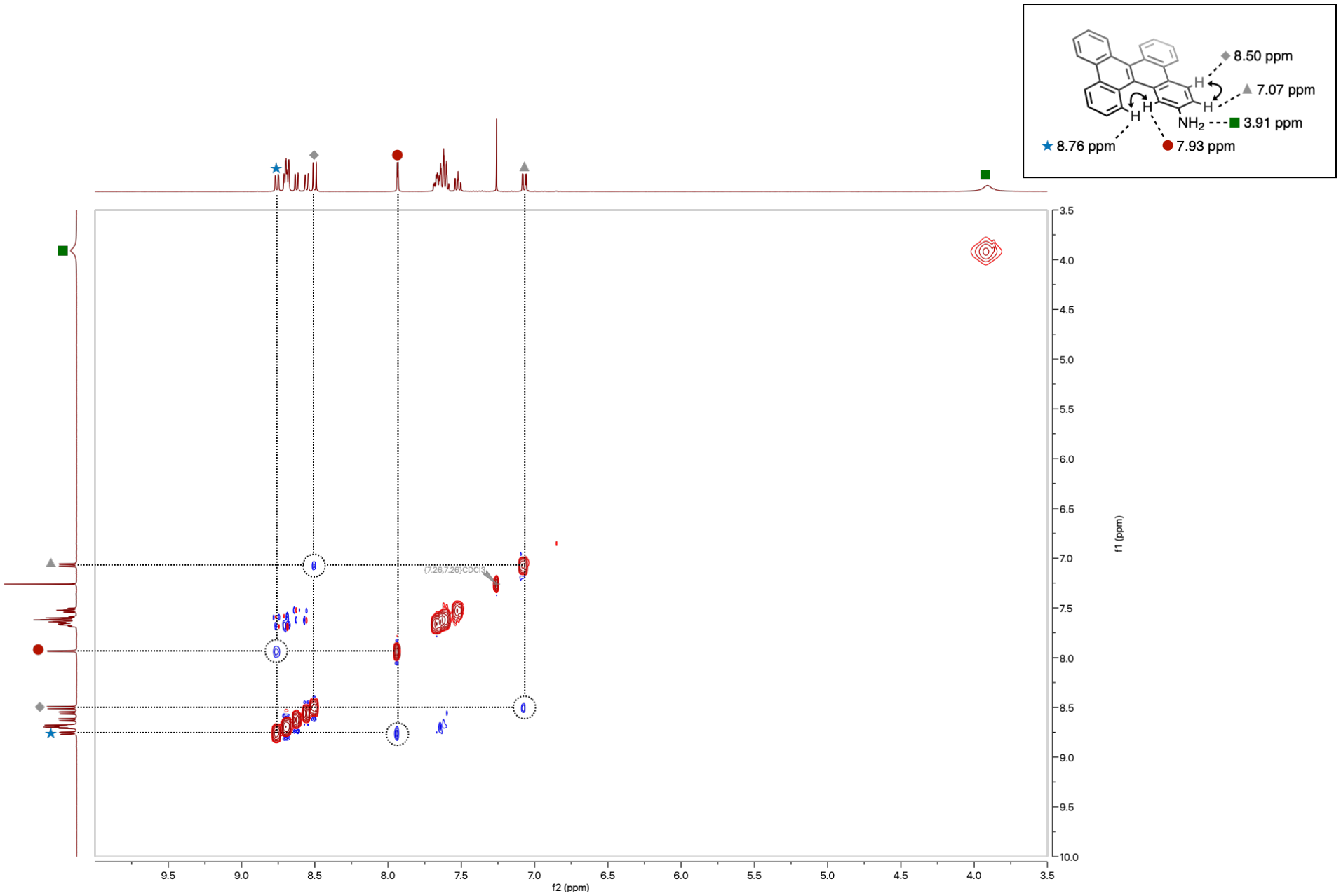


Figure S70. NOESY NMR of **3ah**.

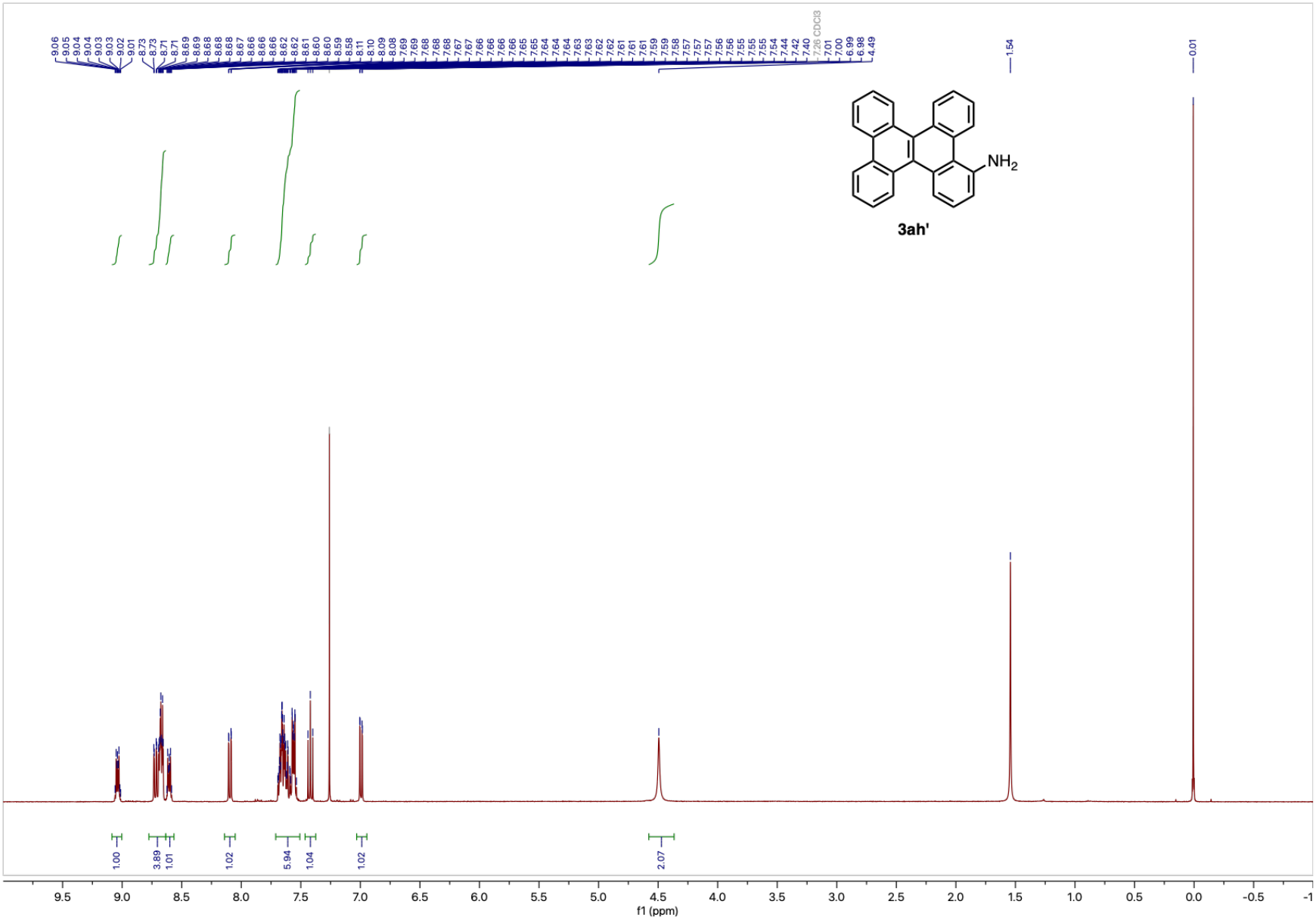


Figure S71. ^{1}H NMR of **3ah'**.

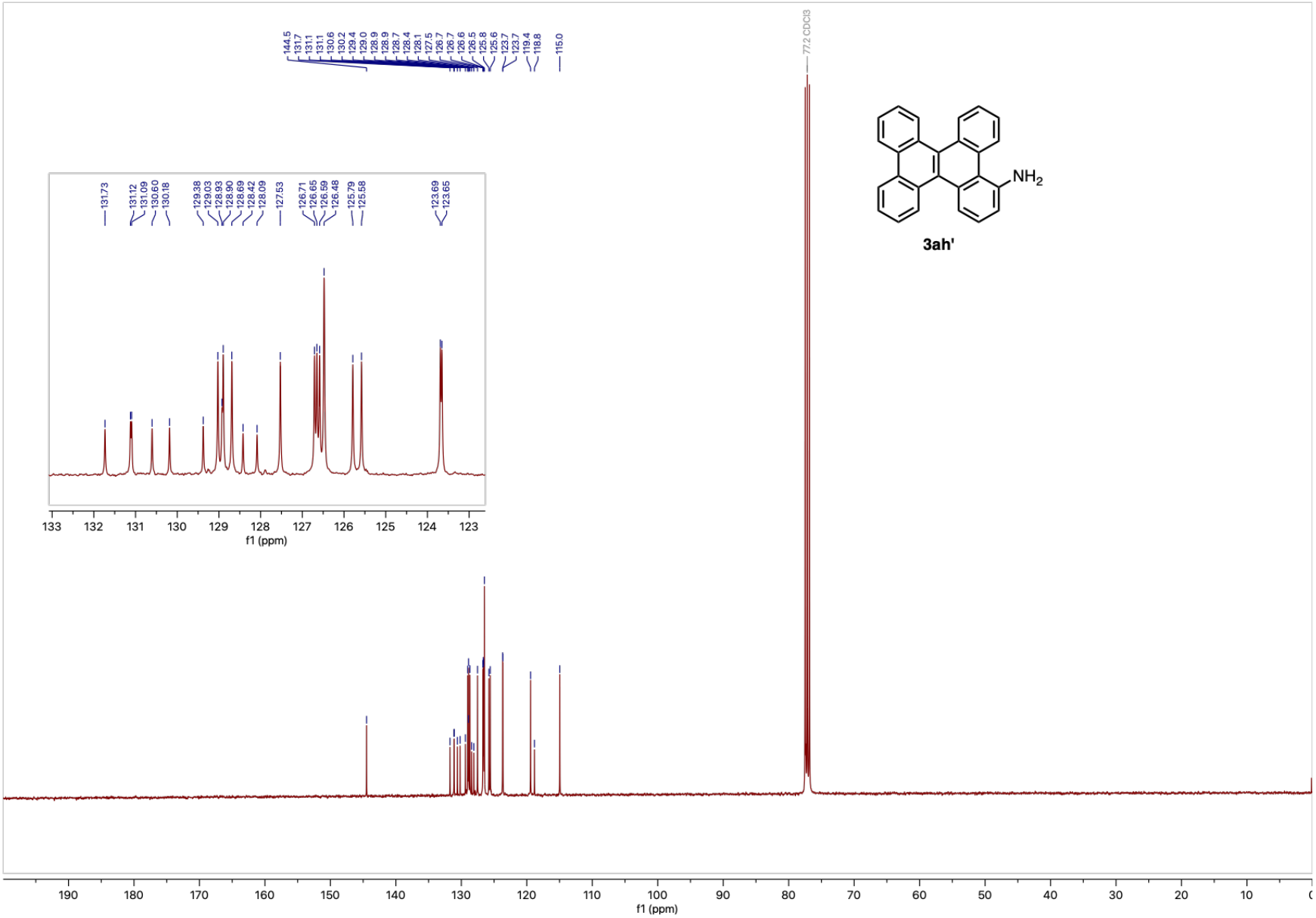


Figure S72. ^{13}C NMR of **3ah'**.

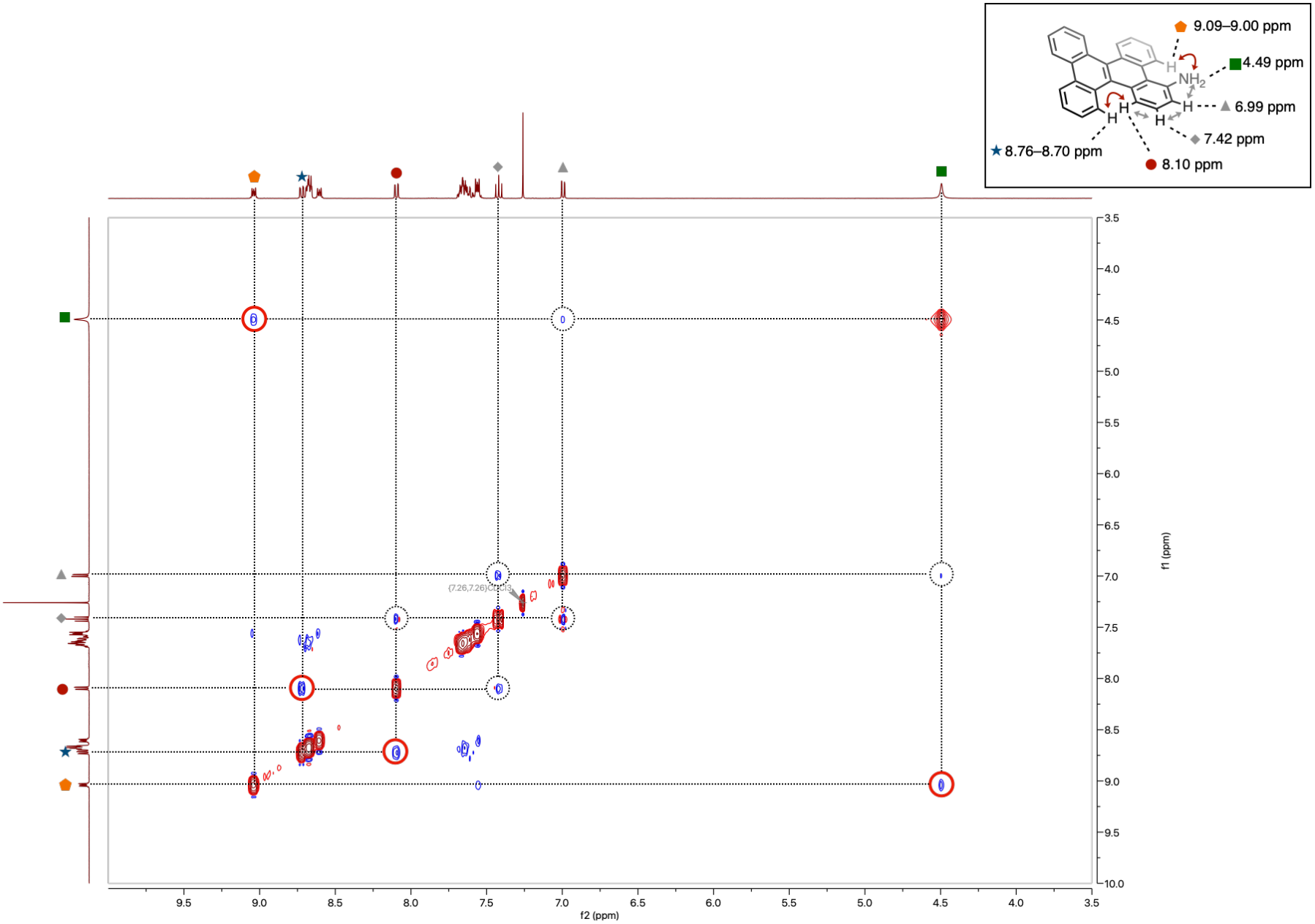


Figure S73. NOESY NMR of **3ah'**.

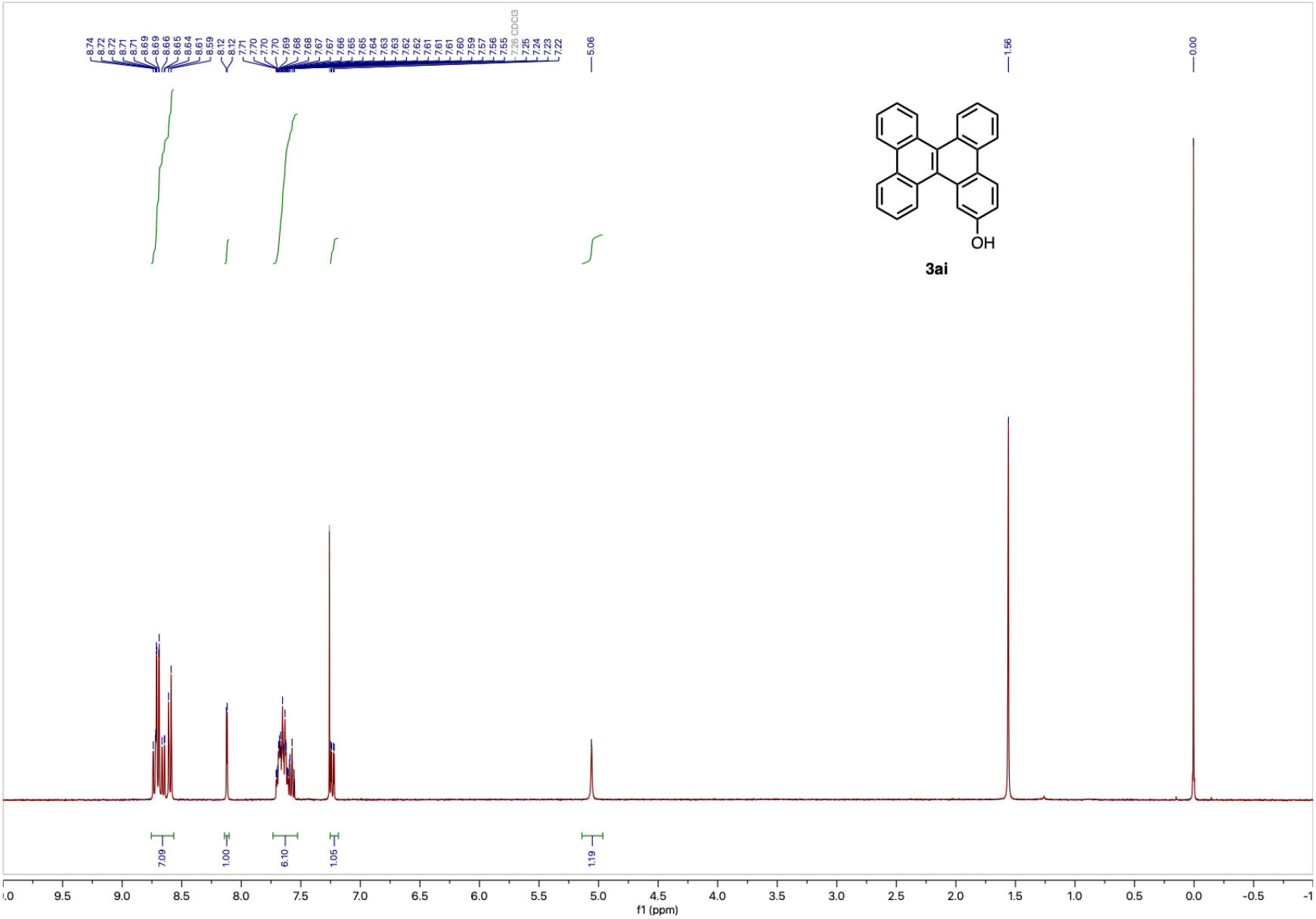


Figure S74. ^{1}H NMR of **3ai**.

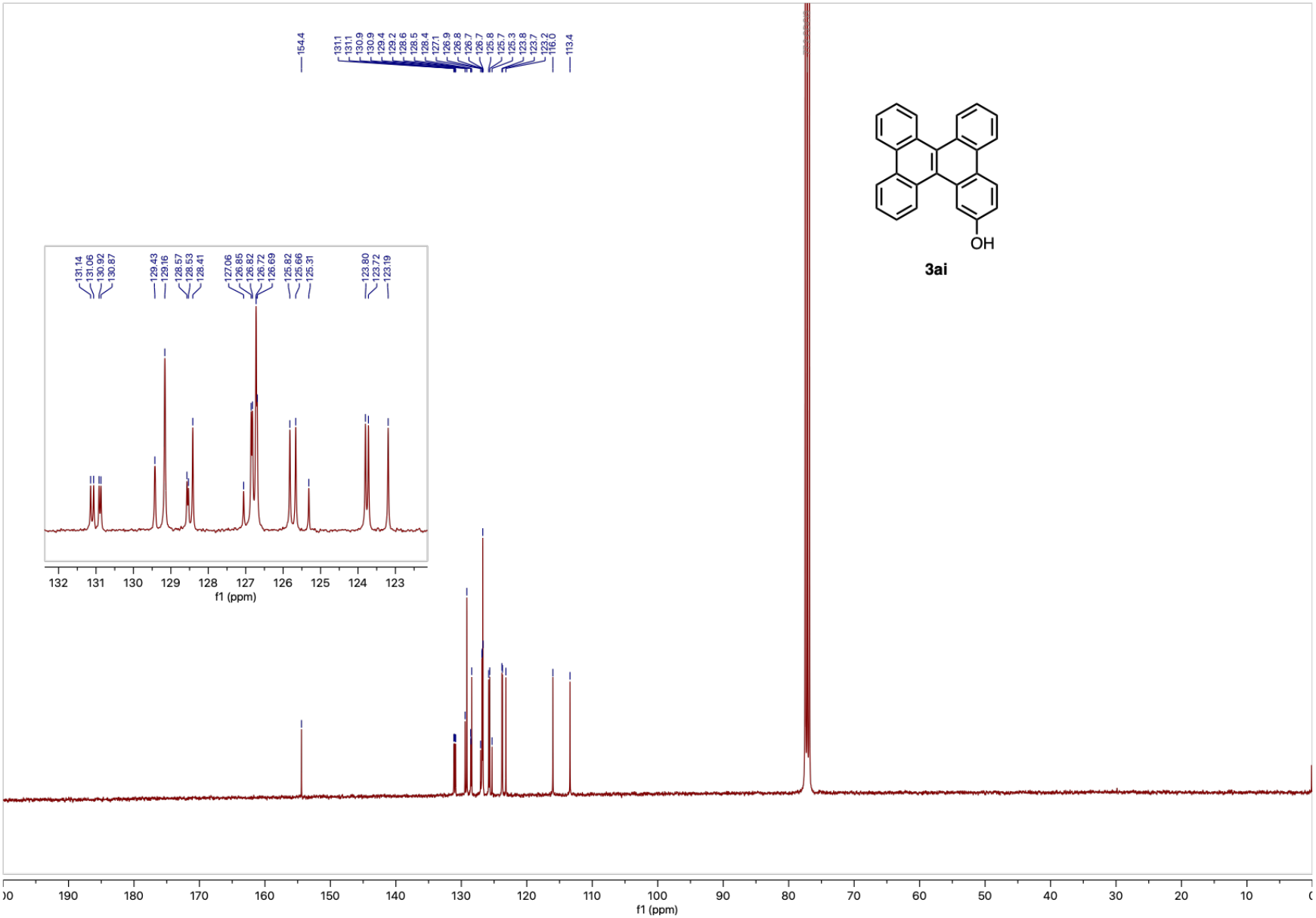


Figure S75. ^{13}C NMR of **3ai**.

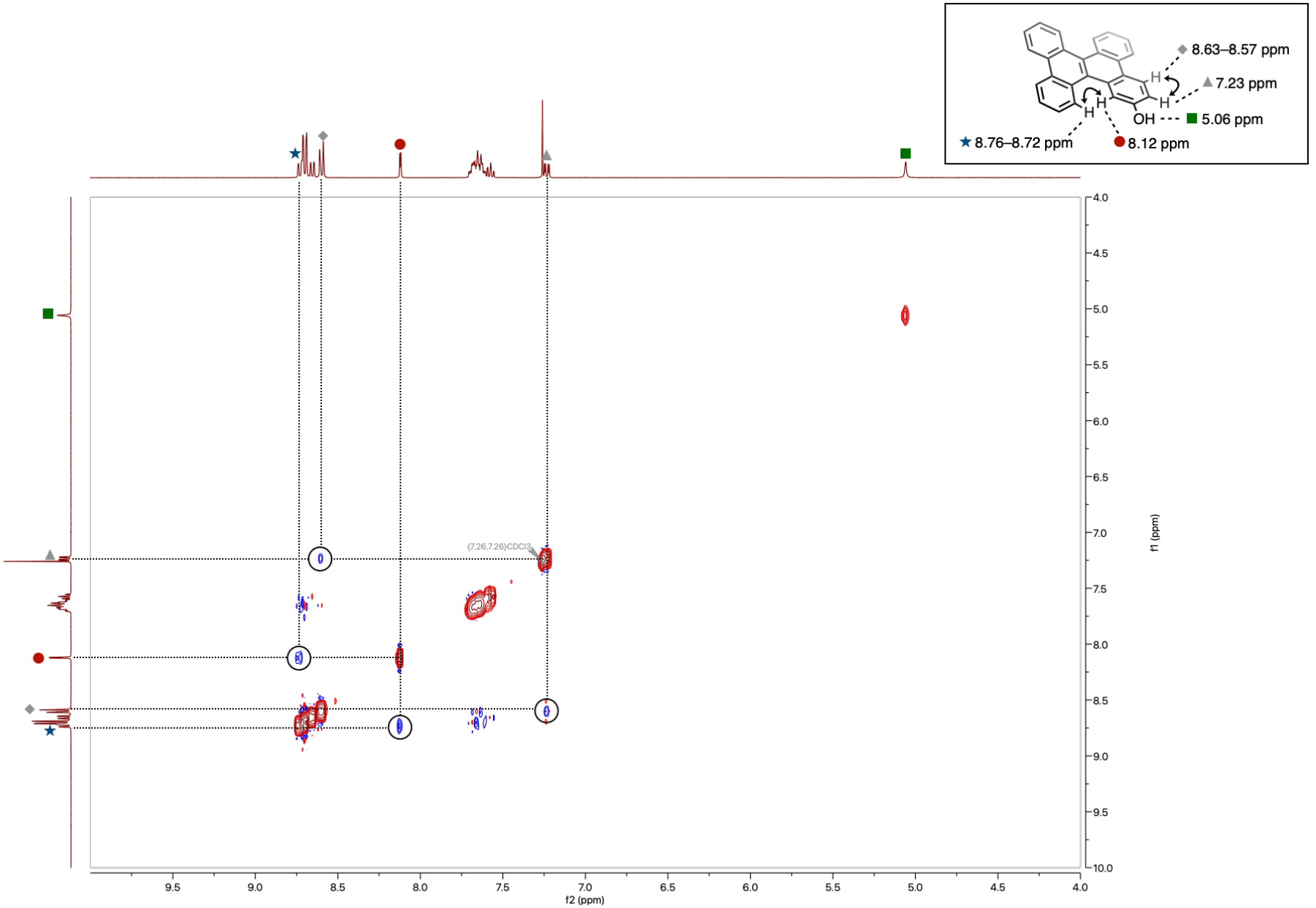


Figure S76. NOESY NMR of **3ai**.

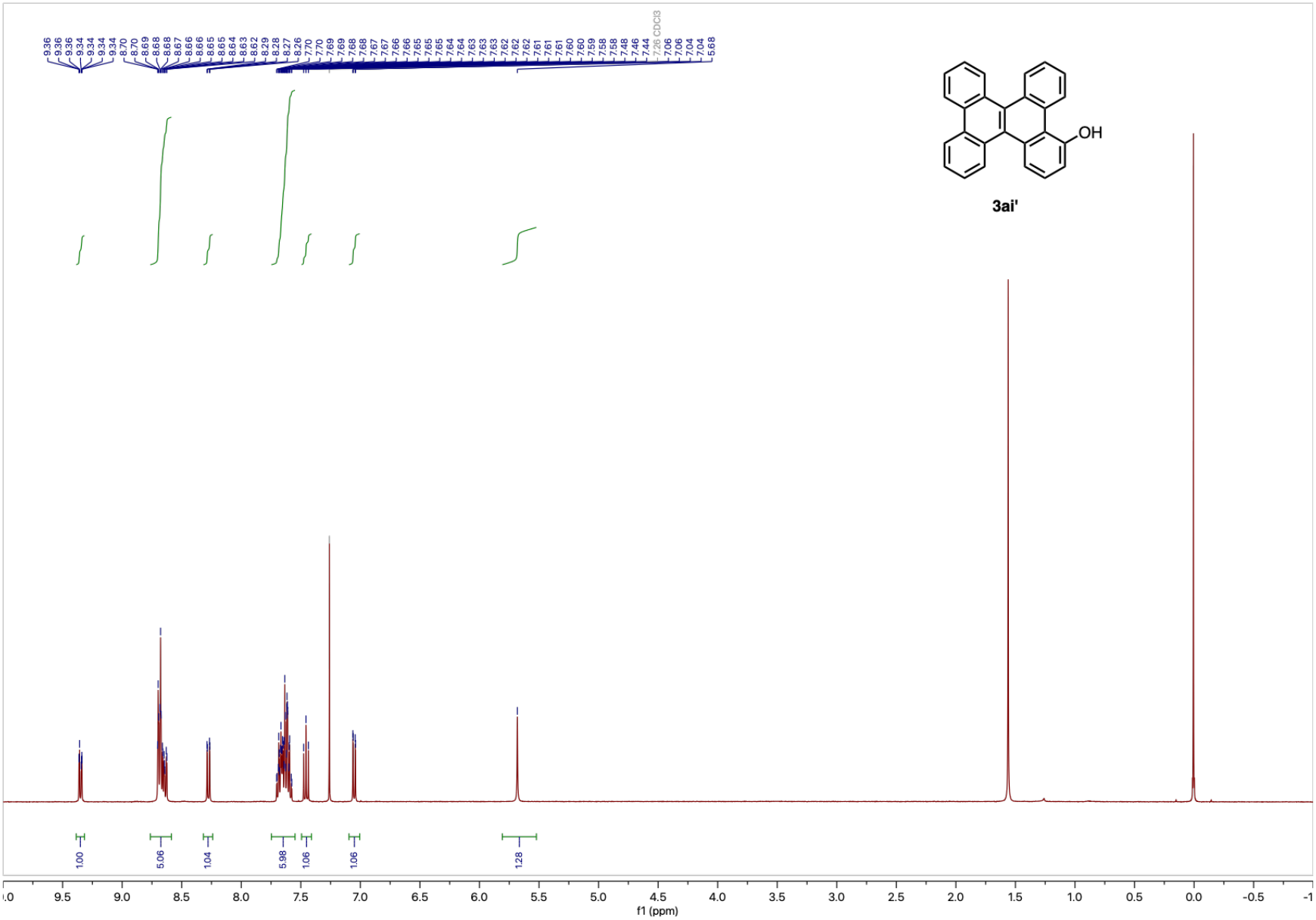


Figure S77. ^{1}H NMR of **3ai'**.

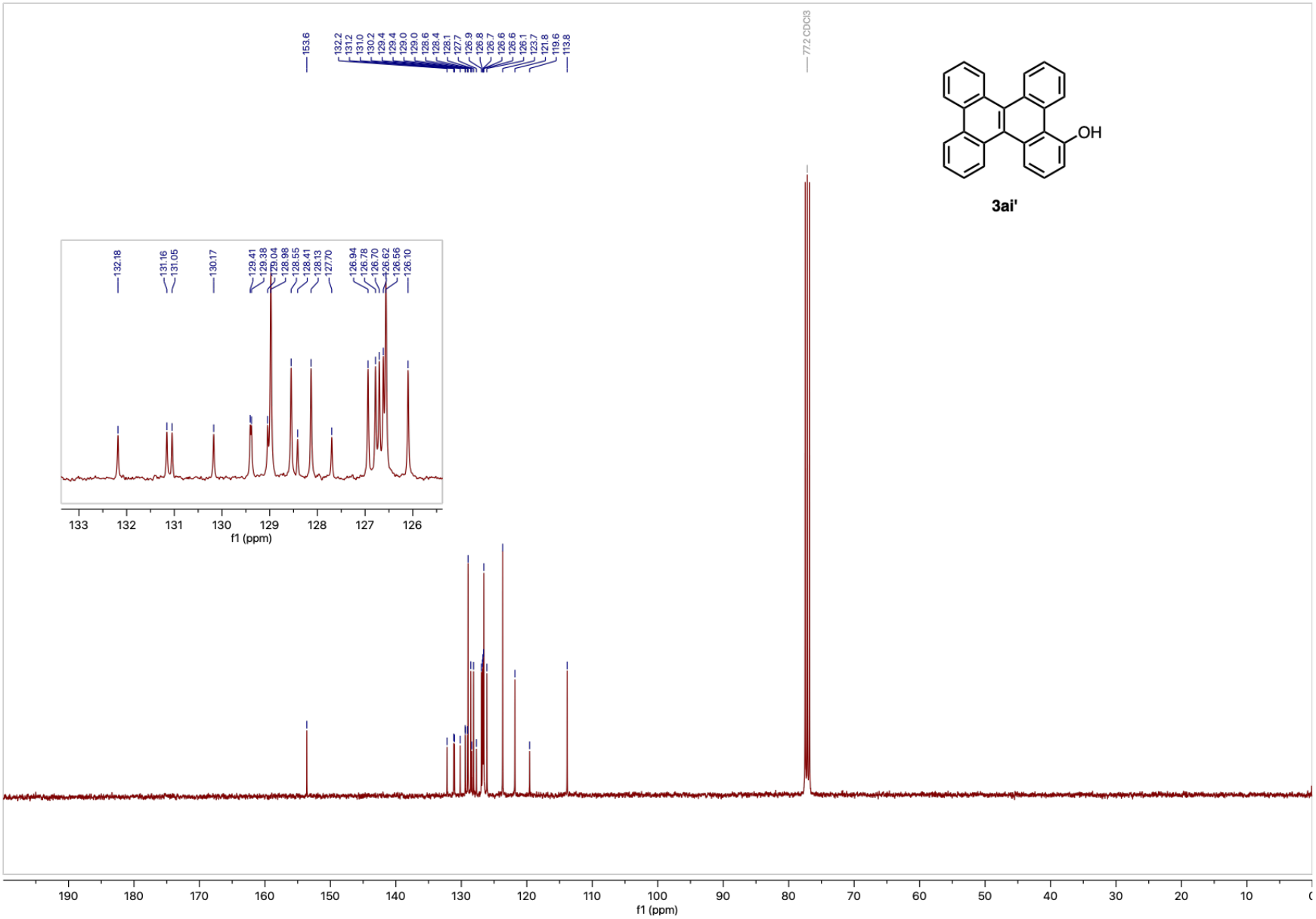


Figure S78. ^{13}C NMR of **3ai'**.

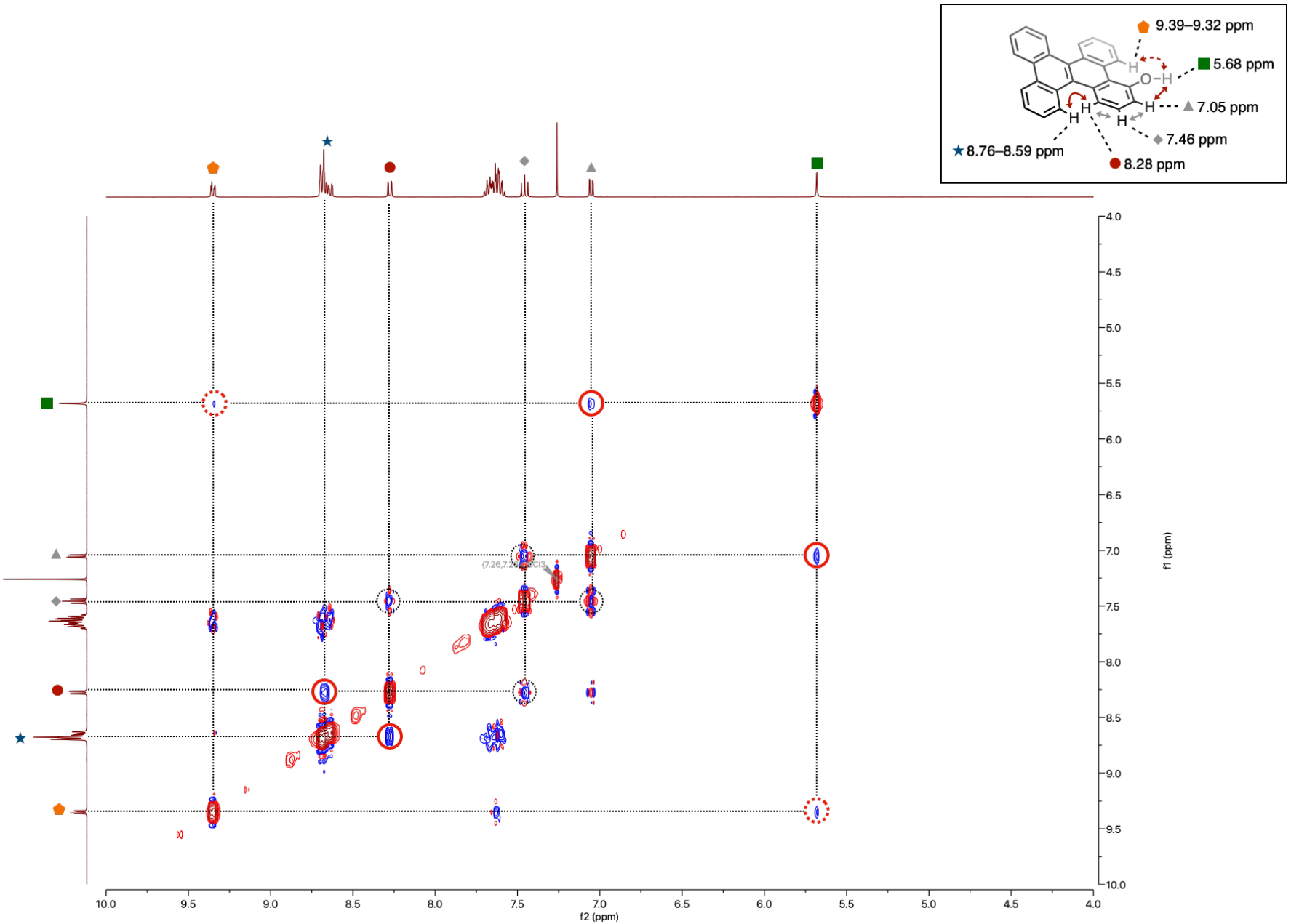


Figure S79. NOESY NMR of **3ai'**.

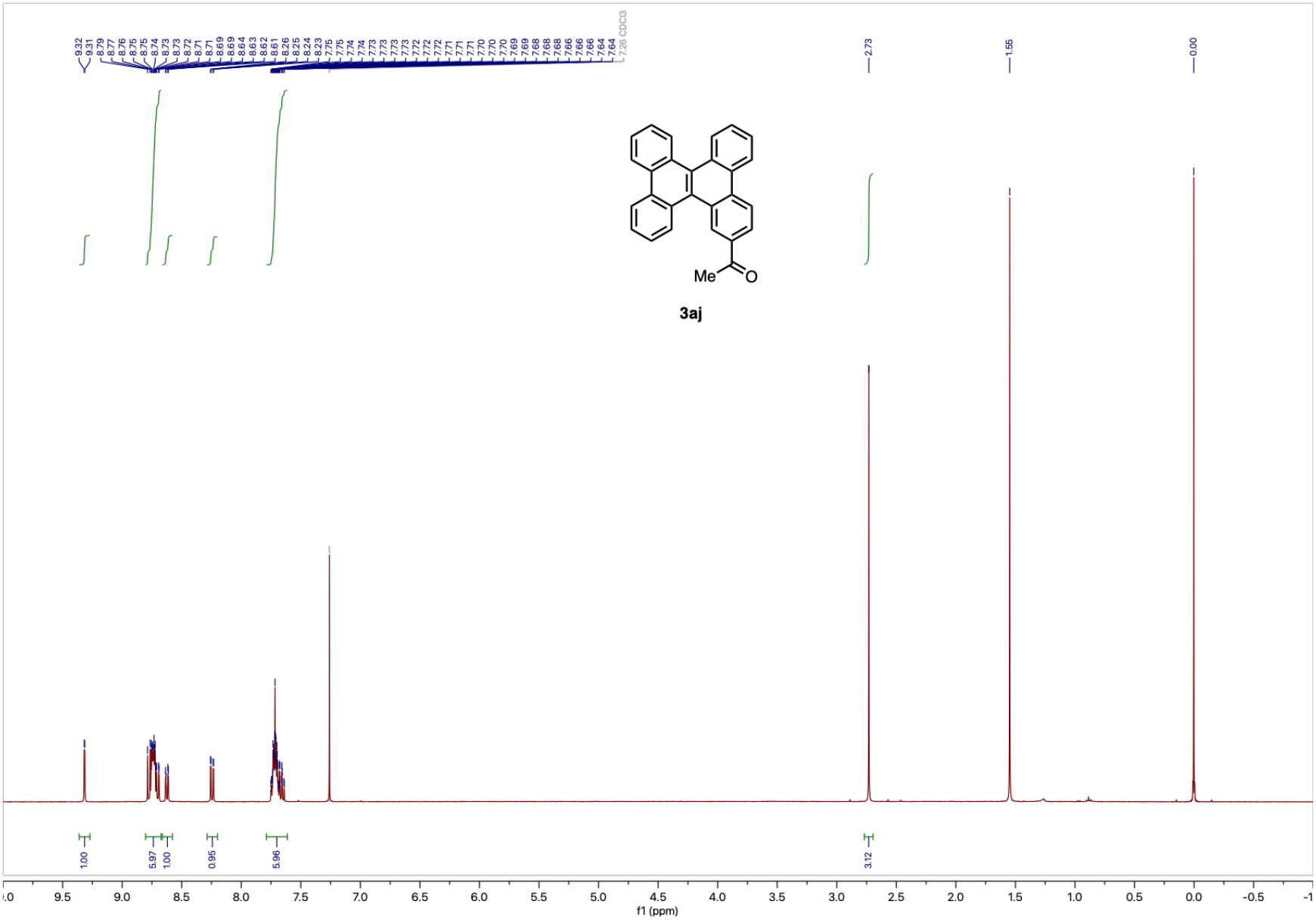


Figure S80. ^{1}H NMR of **3aj**.

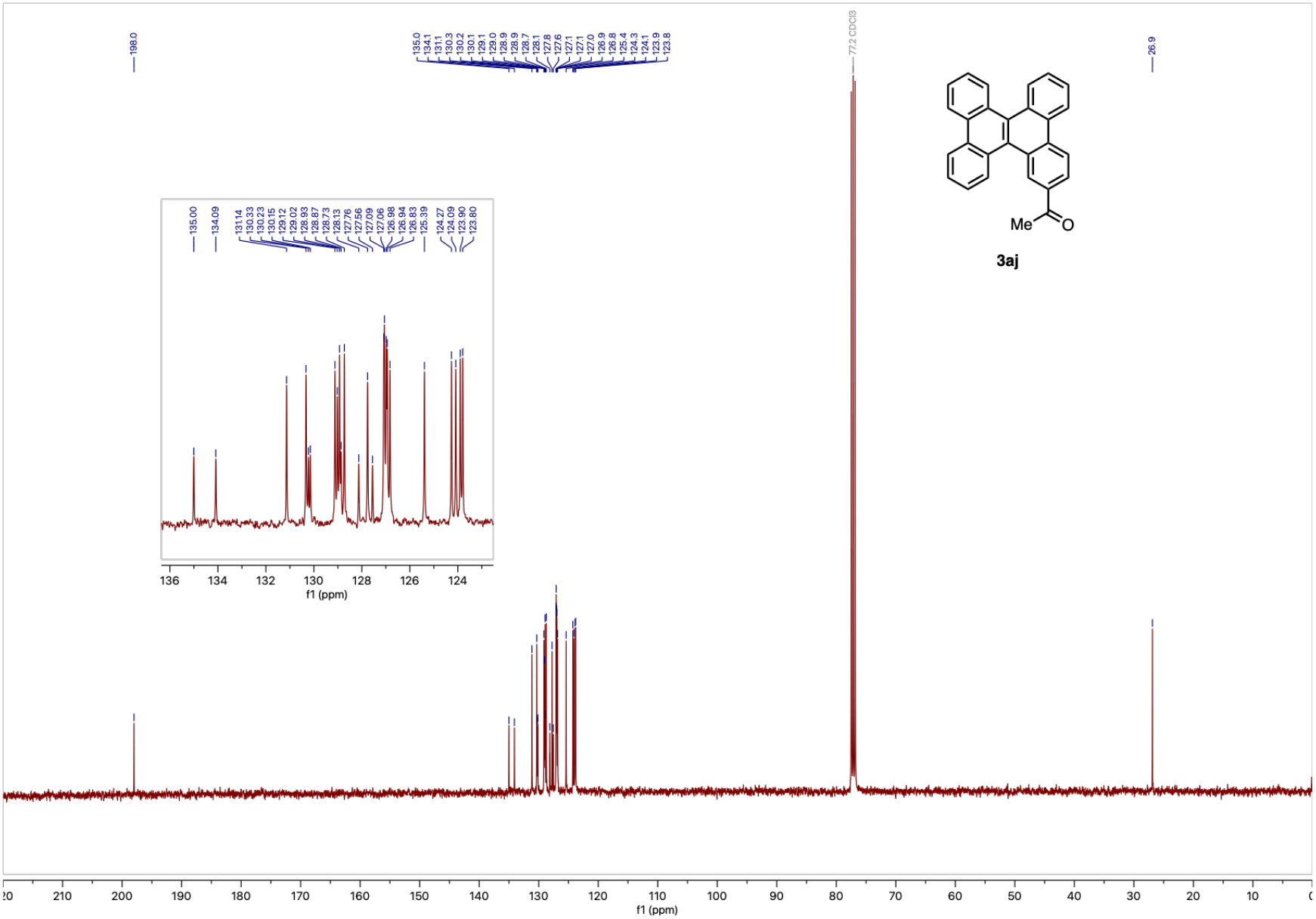


Figure S81. ^{13}C NMR of **3aj**.

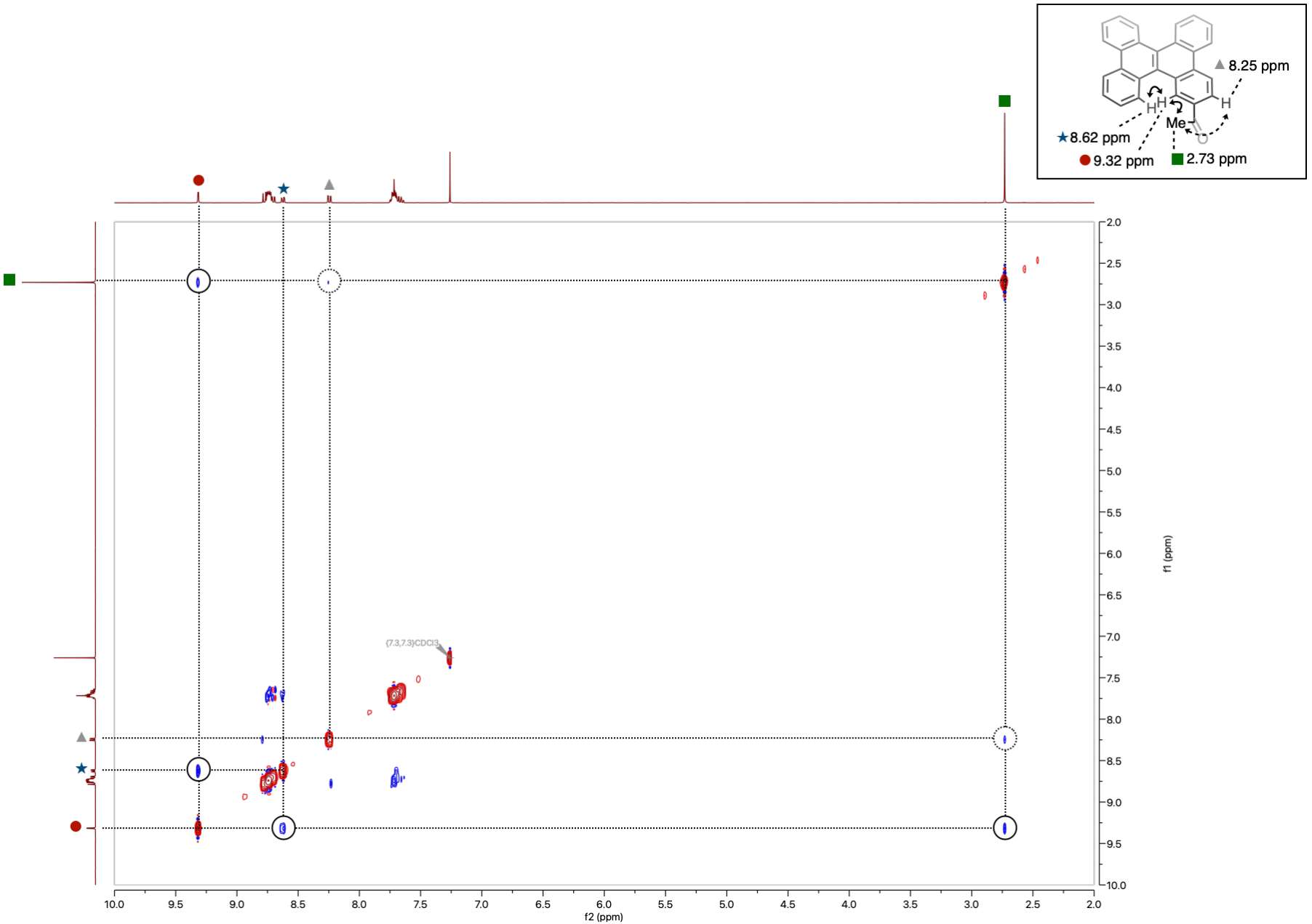


Figure S82. NOESY NMR of **3aj**.

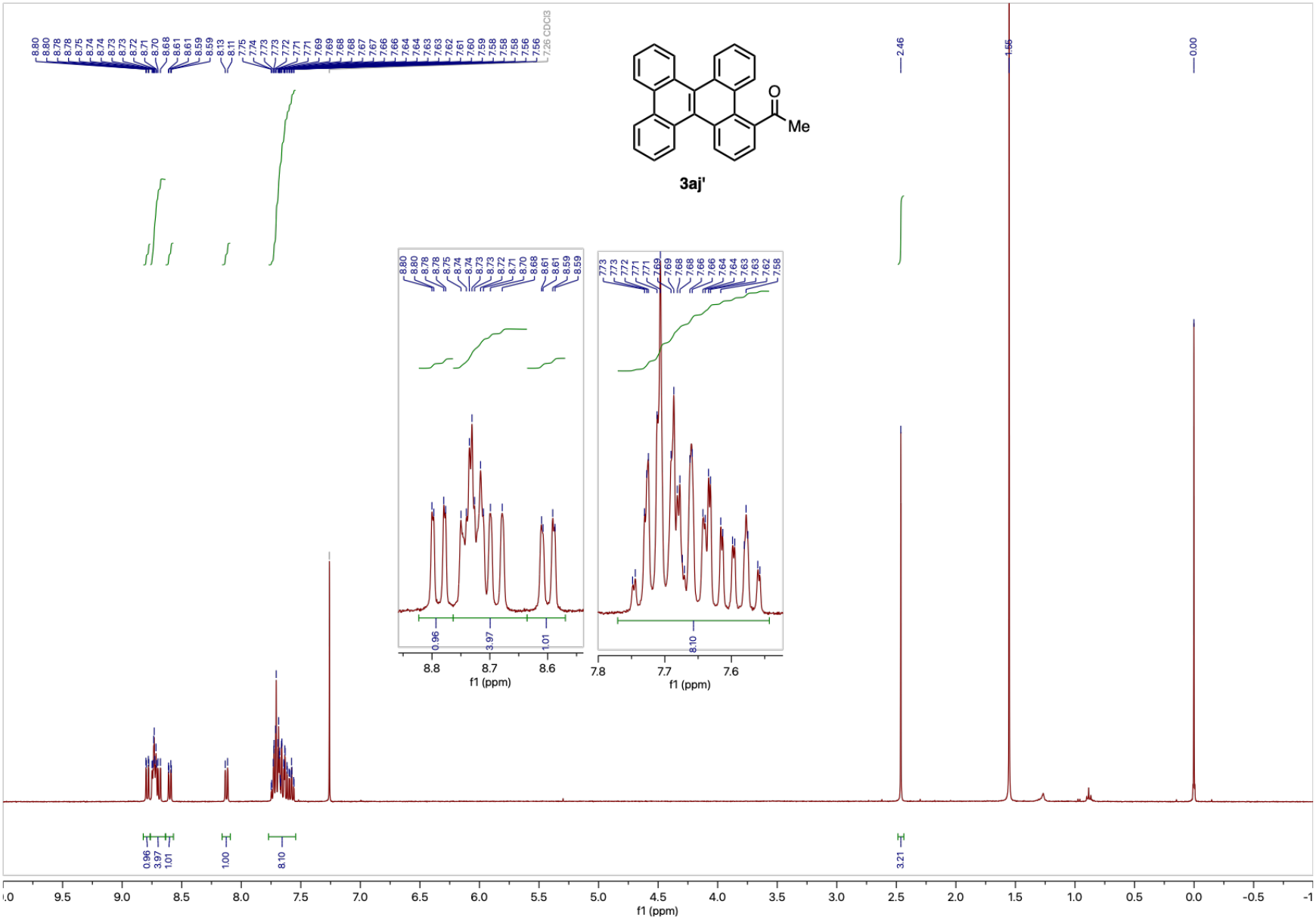


Figure S83. ^{1}H NMR of **3aj'**.

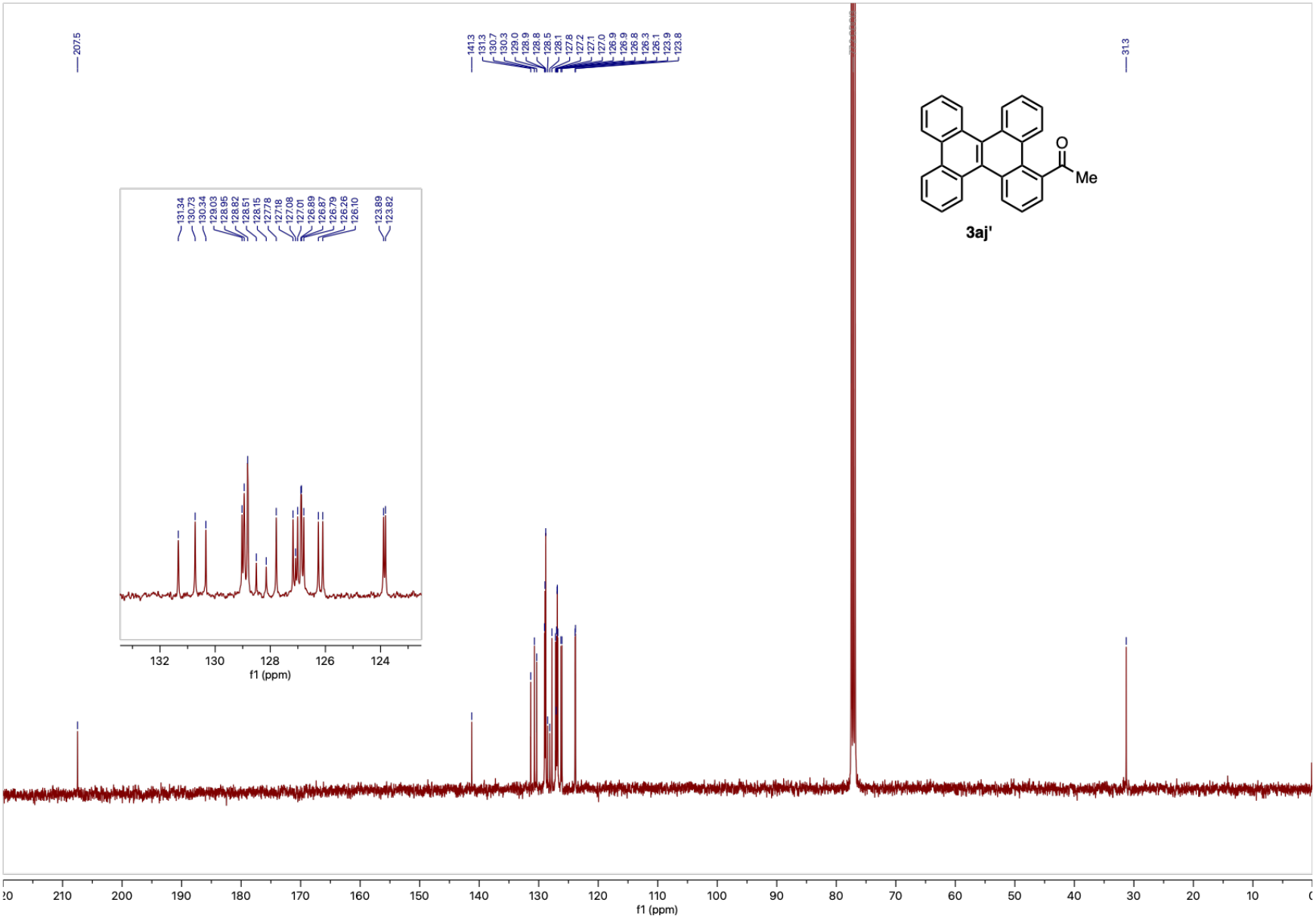


Figure S84. ^{13}C NMR of **3aj'**.

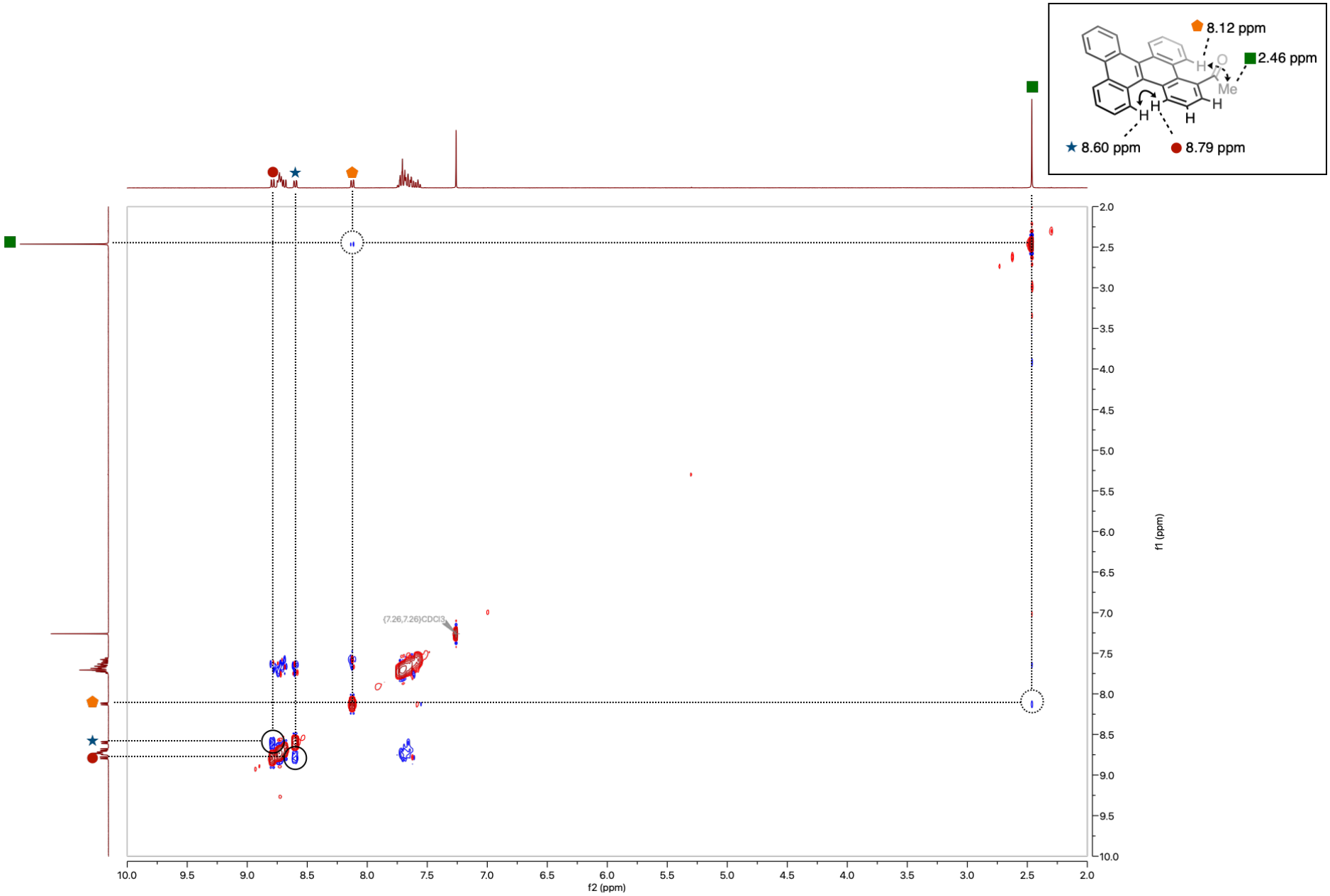


Figure S85. NOESY NMR of **3aj'**.

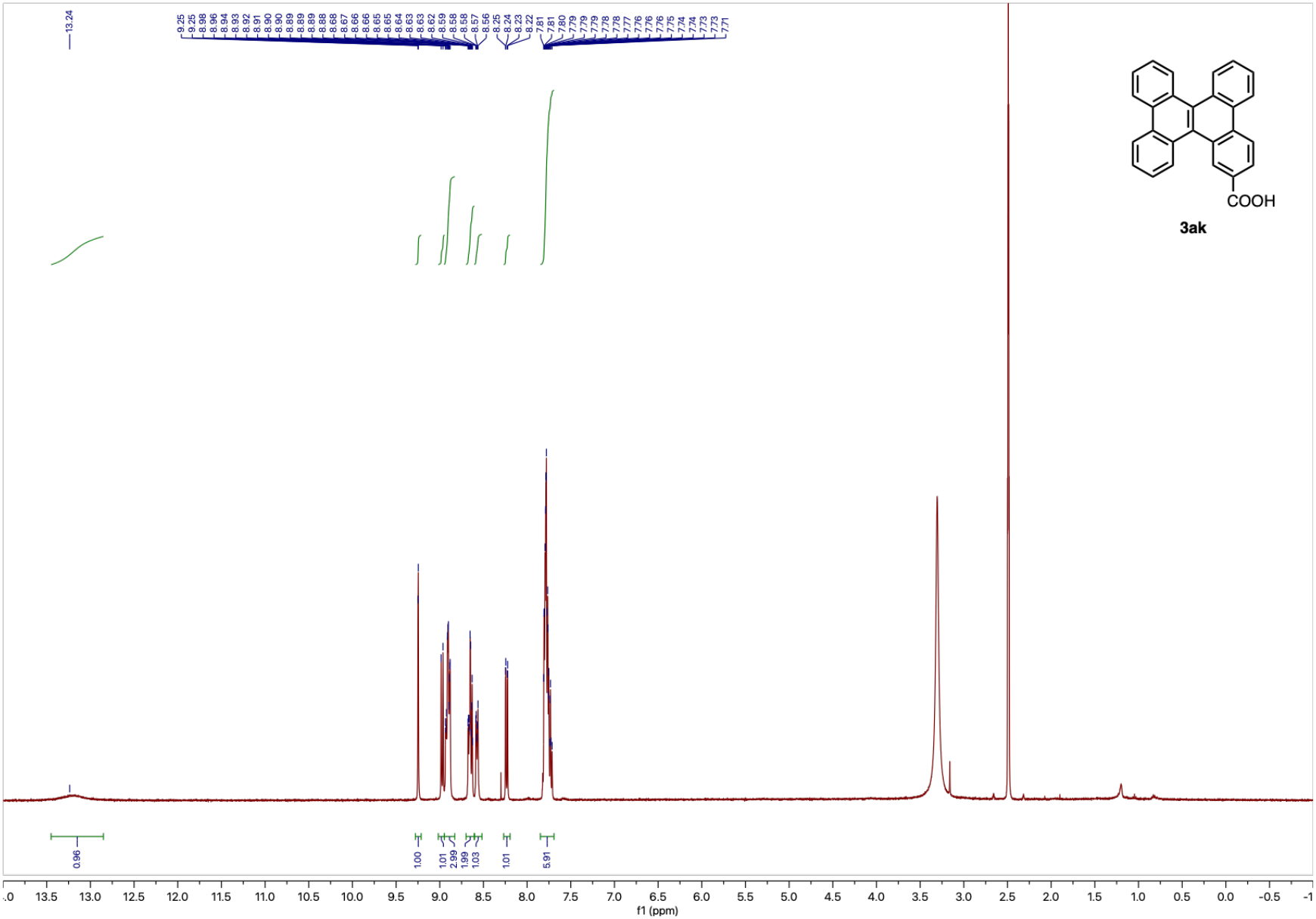


Figure S86. ^{1}H NMR of **3ak**.

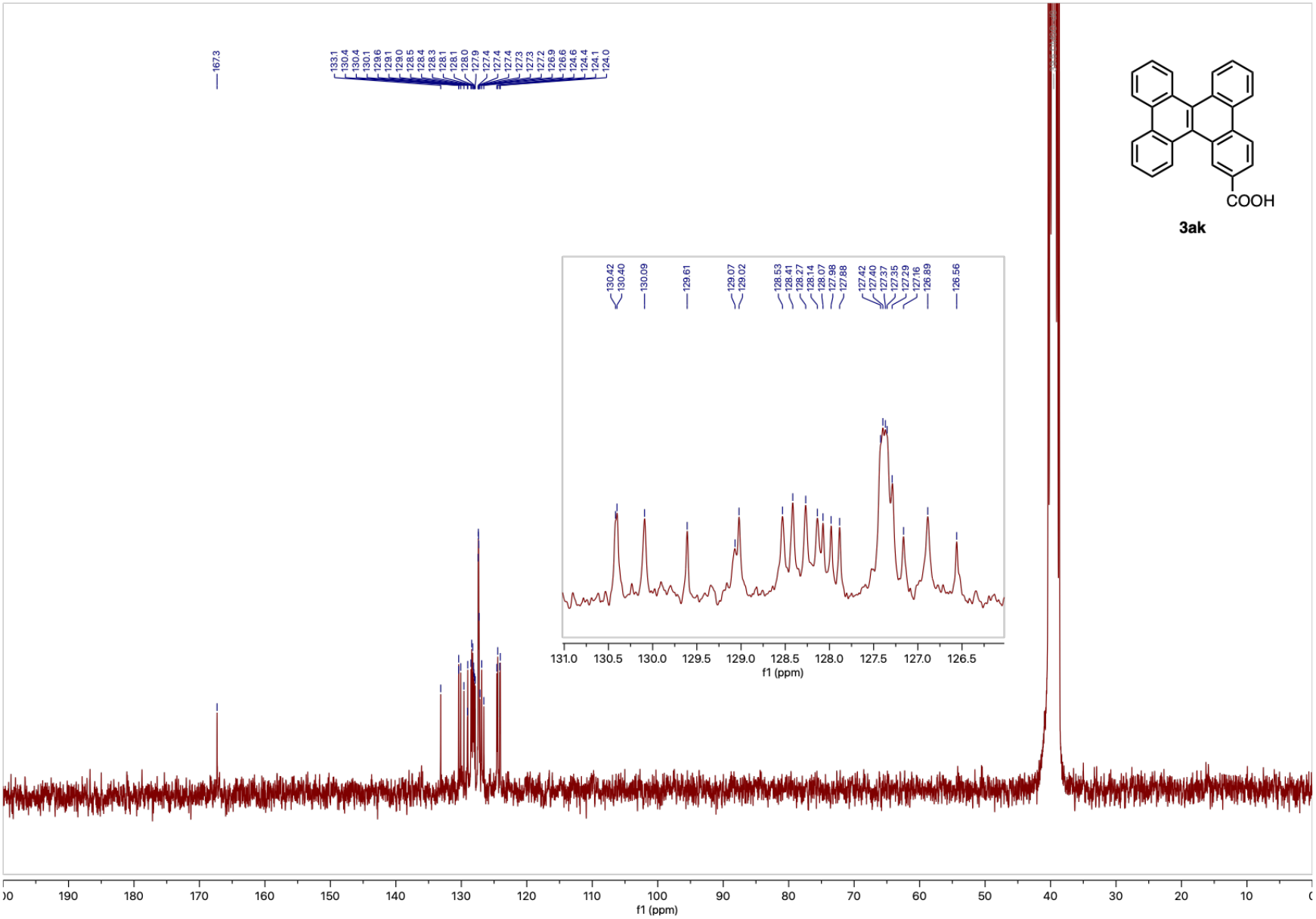


Figure S87. ^{13}C NMR of **3ak**.

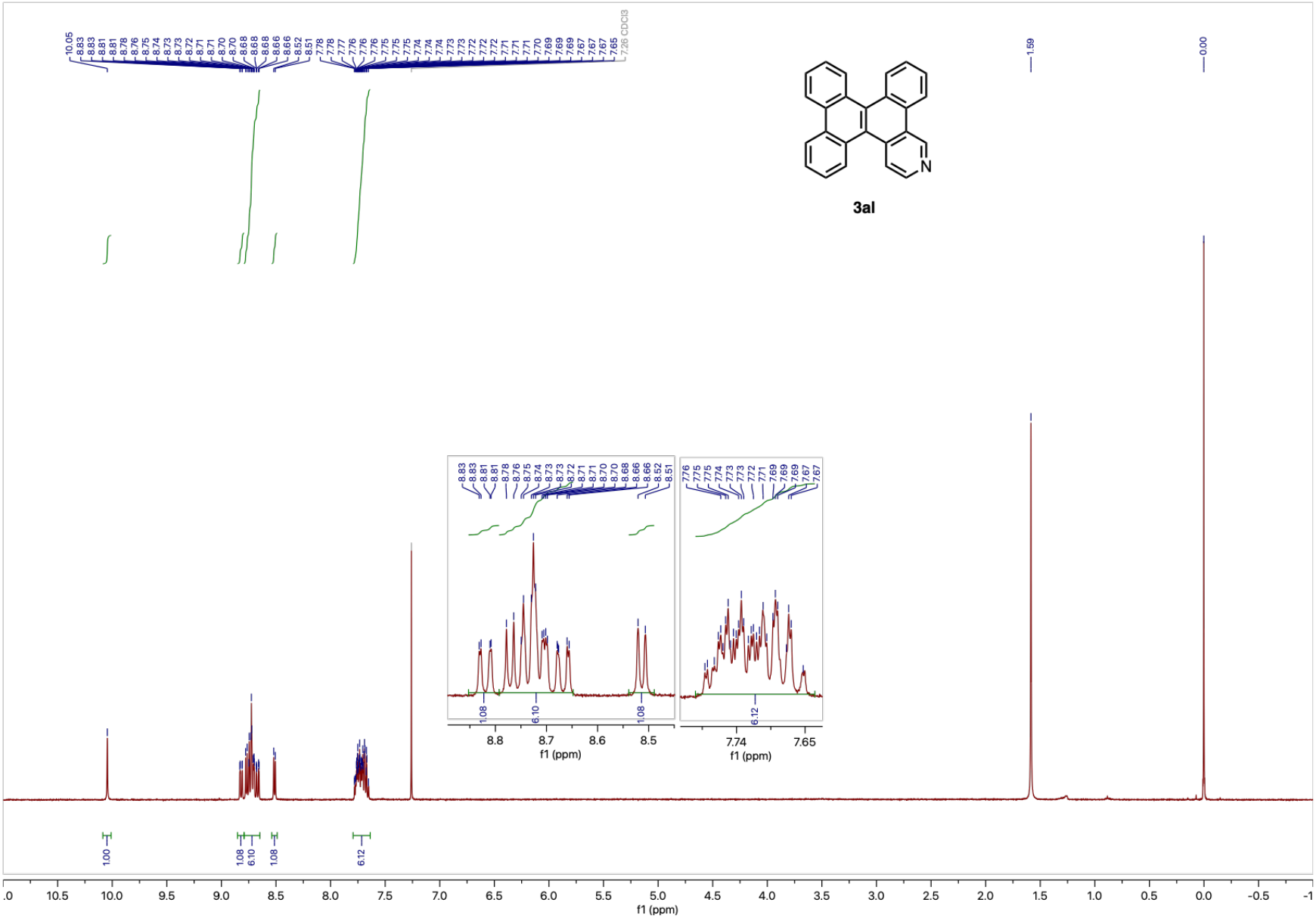


Figure S88. ^{1}H NMR of **3al**.

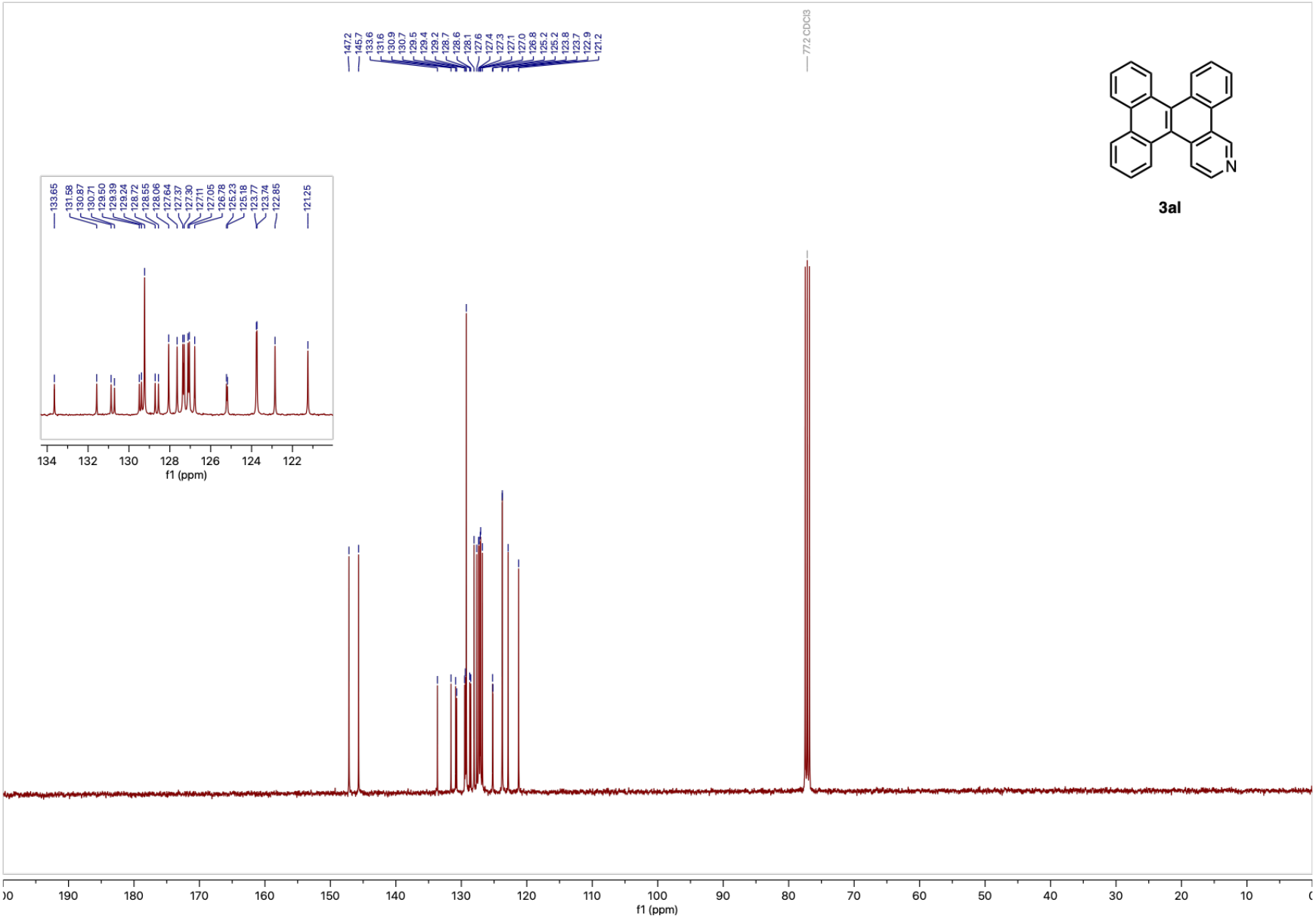


Figure S89. ^{13}C NMR of **3al**.

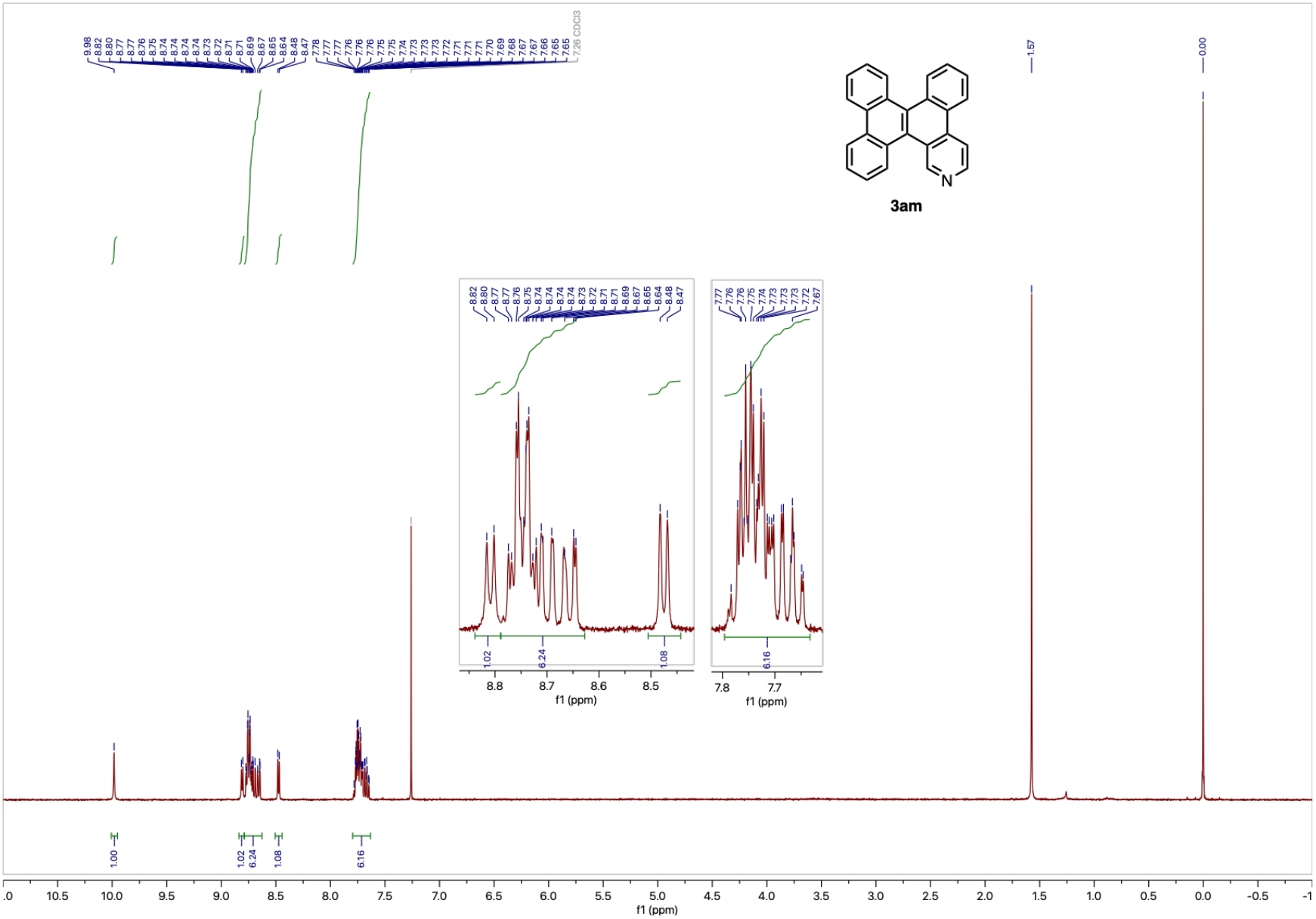


Figure S90. ^{1}H NMR of **3am**.

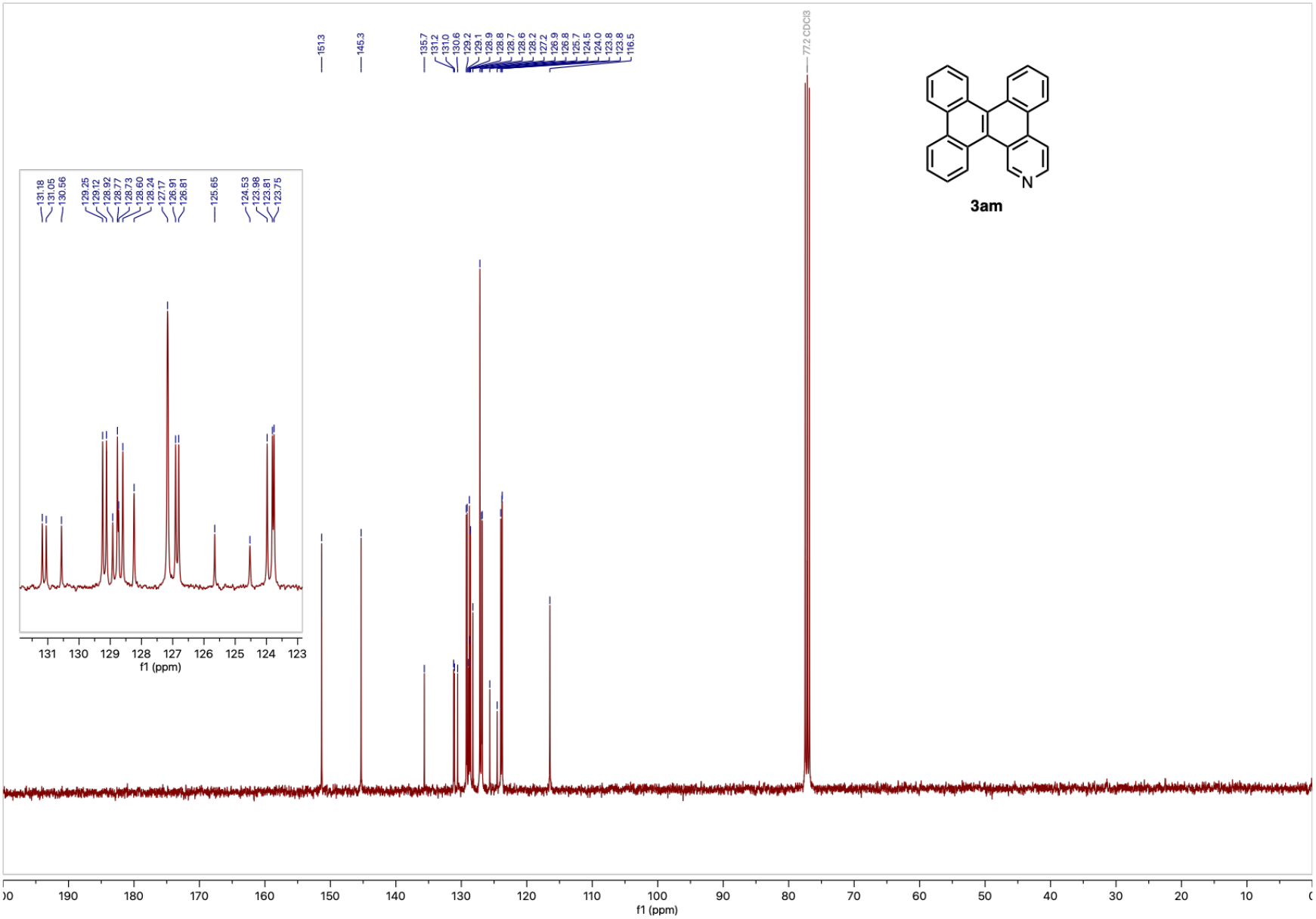


Figure S91. ^{13}C NMR of **3am**.

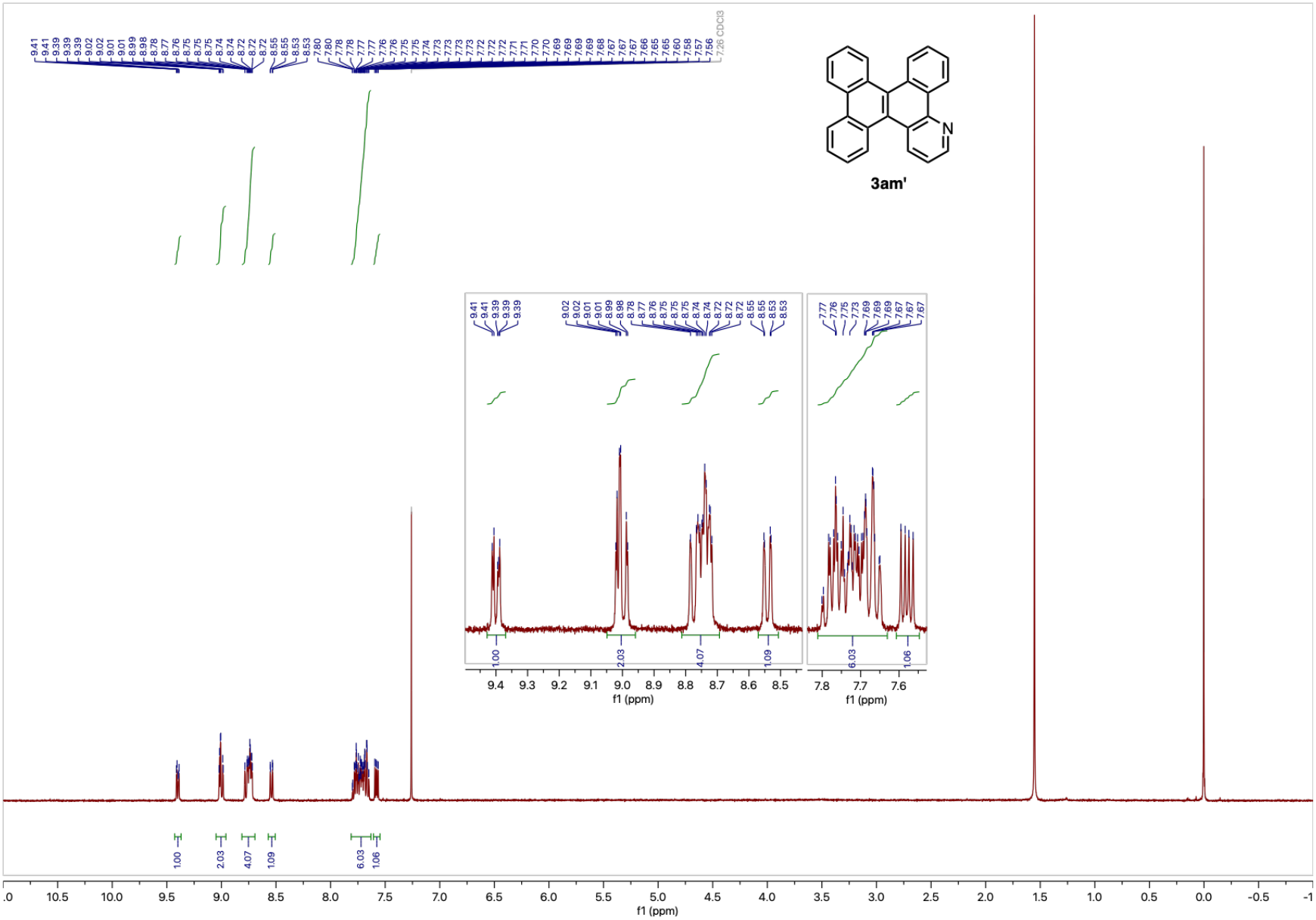


Figure S92. ^{1}H NMR of **3am'**.

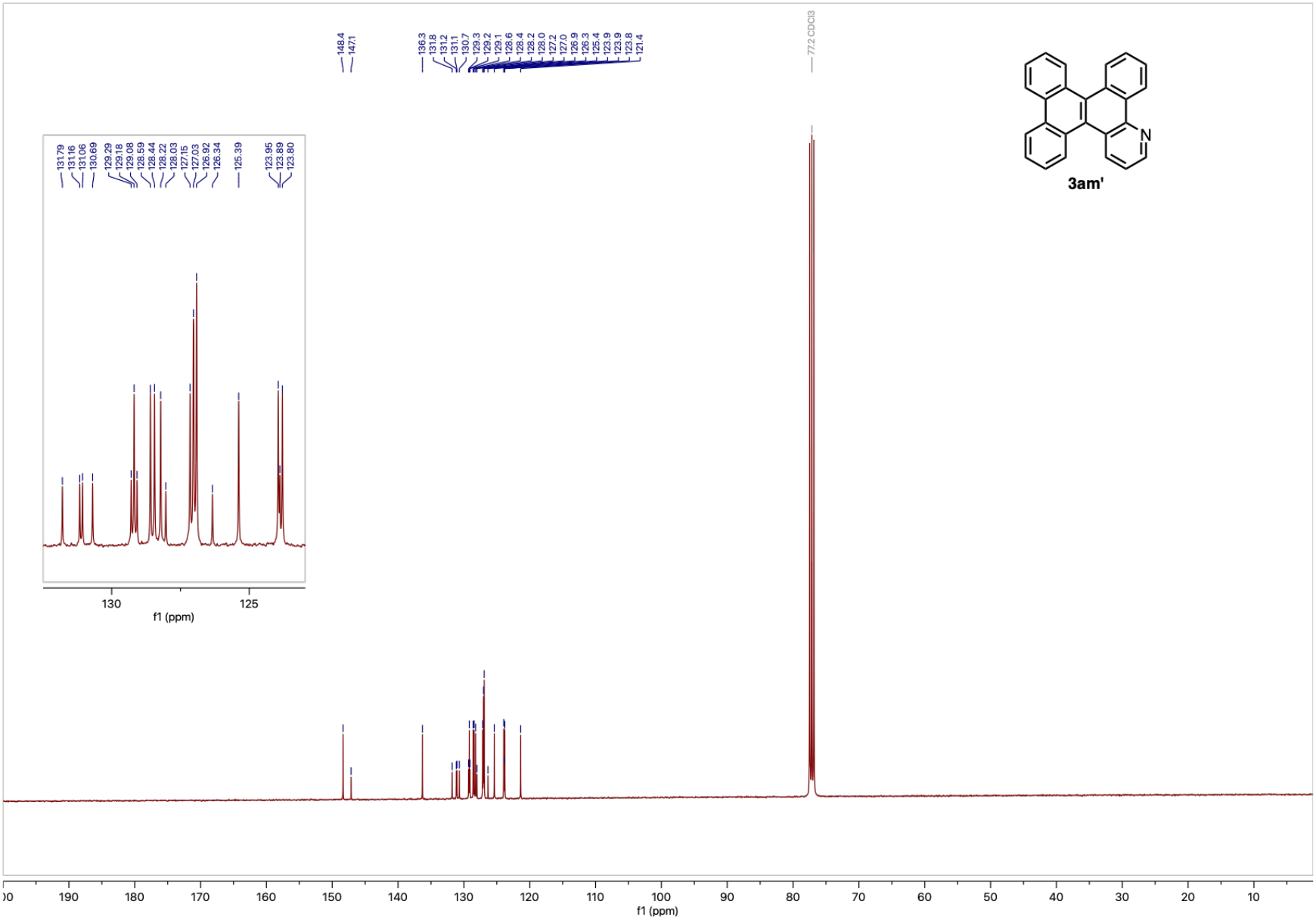


Figure S93. ^{13}C NMR of **3am'**.

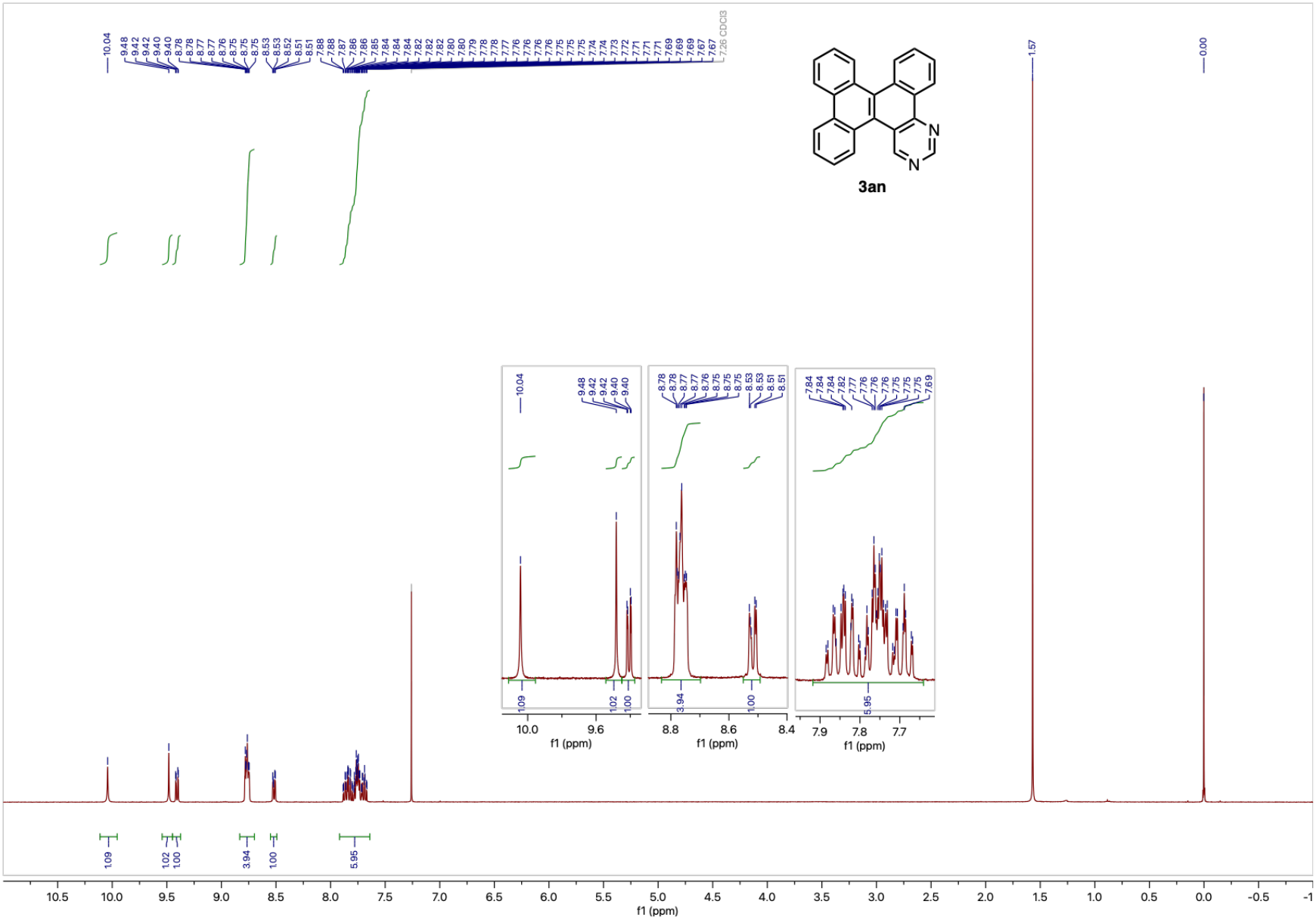


Figure S94. ^{1}H NMR of **3an**.

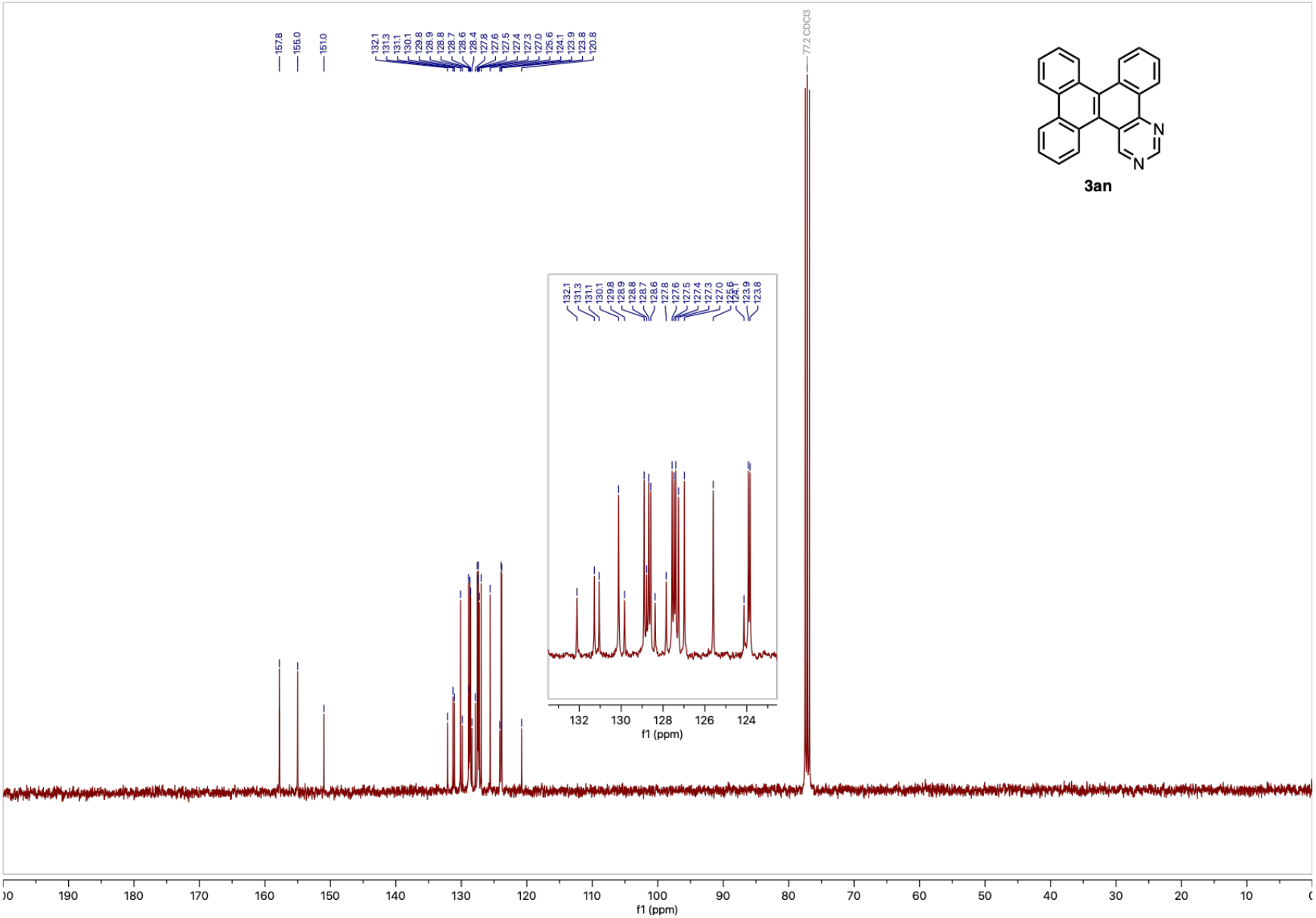


Figure 95. ^{13}C NMR of **3an**.

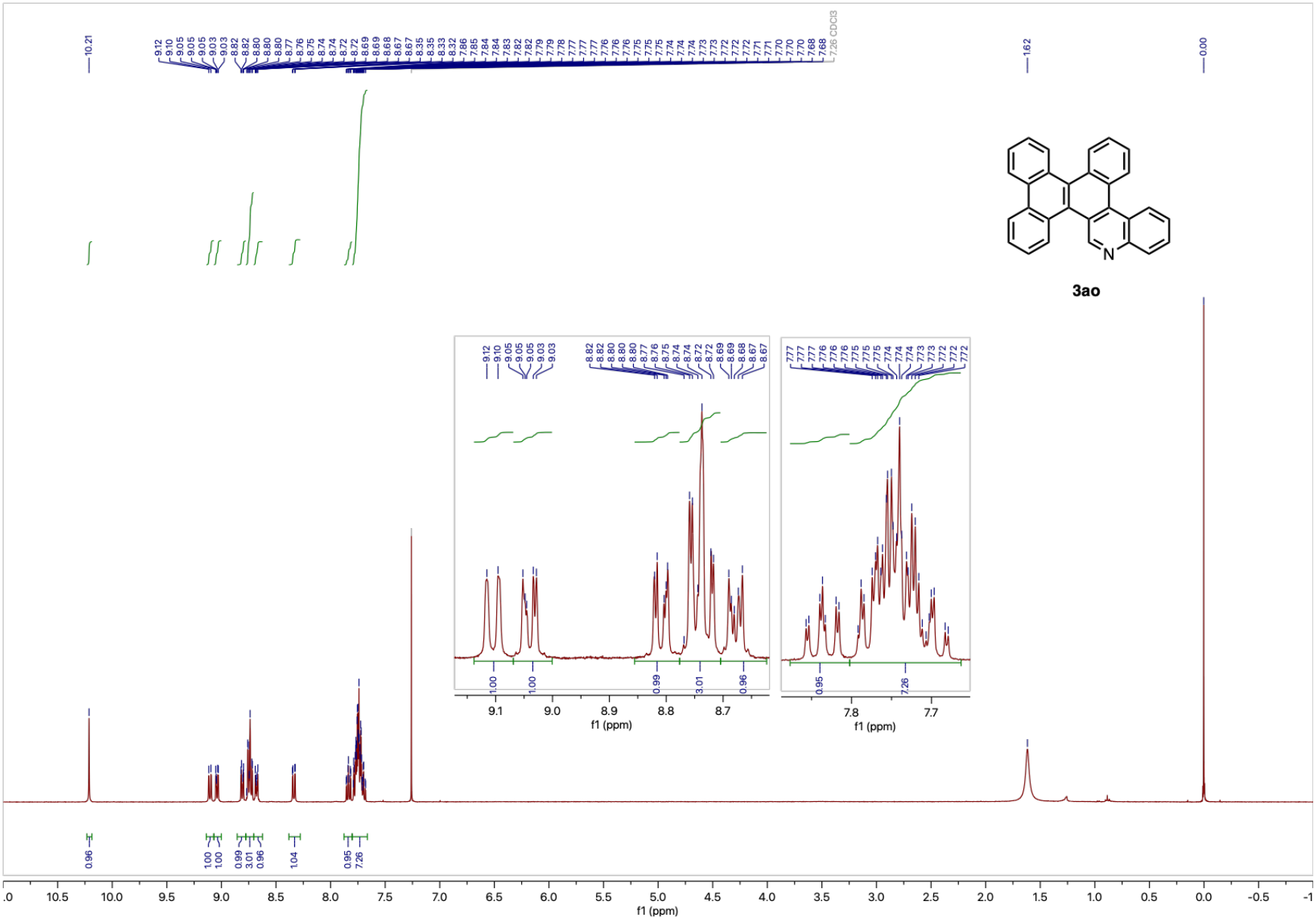


Figure S96. ^{1}H NMR of **3ao**.

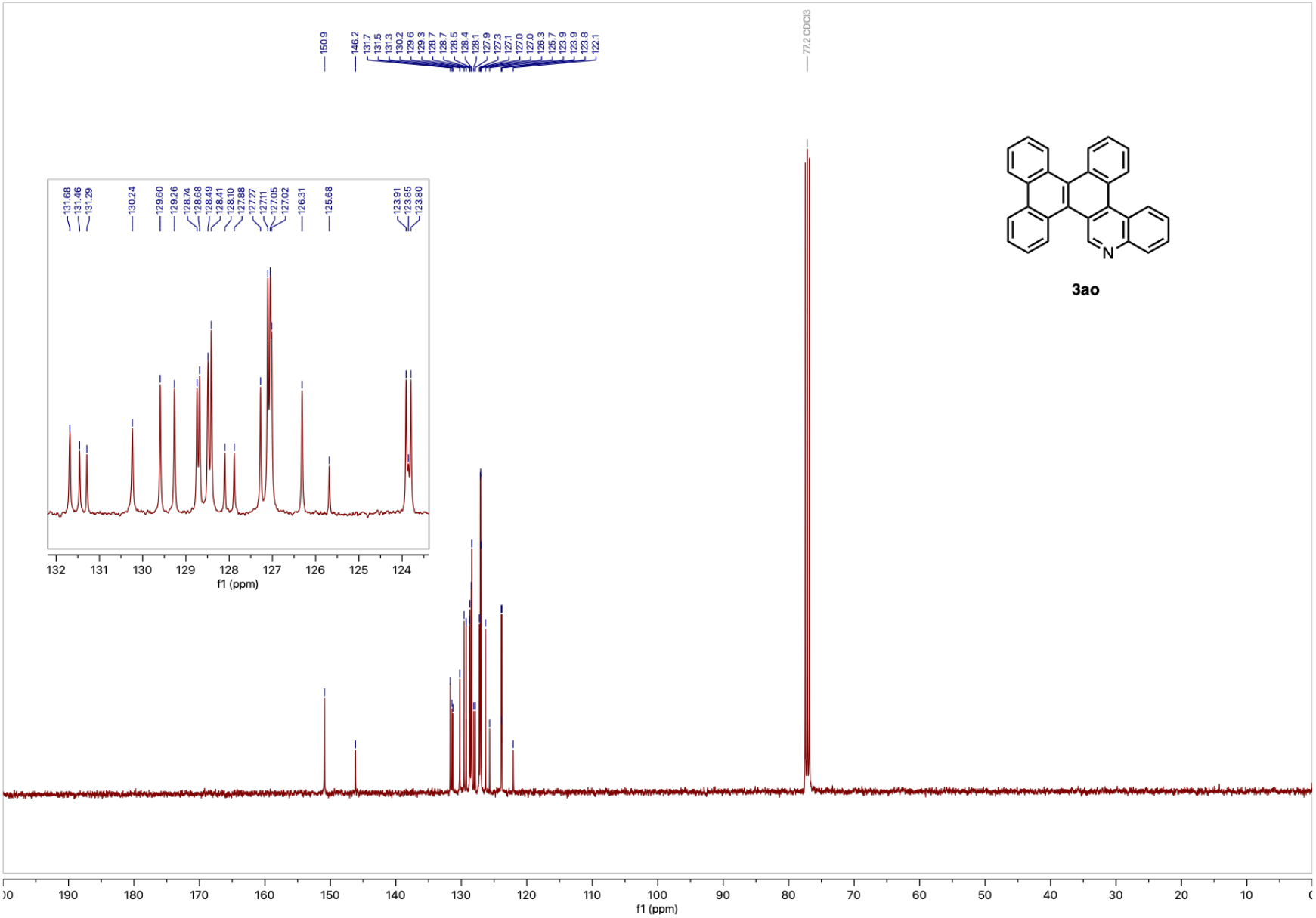


Figure S97. ^{13}C NMR of **3ao**.

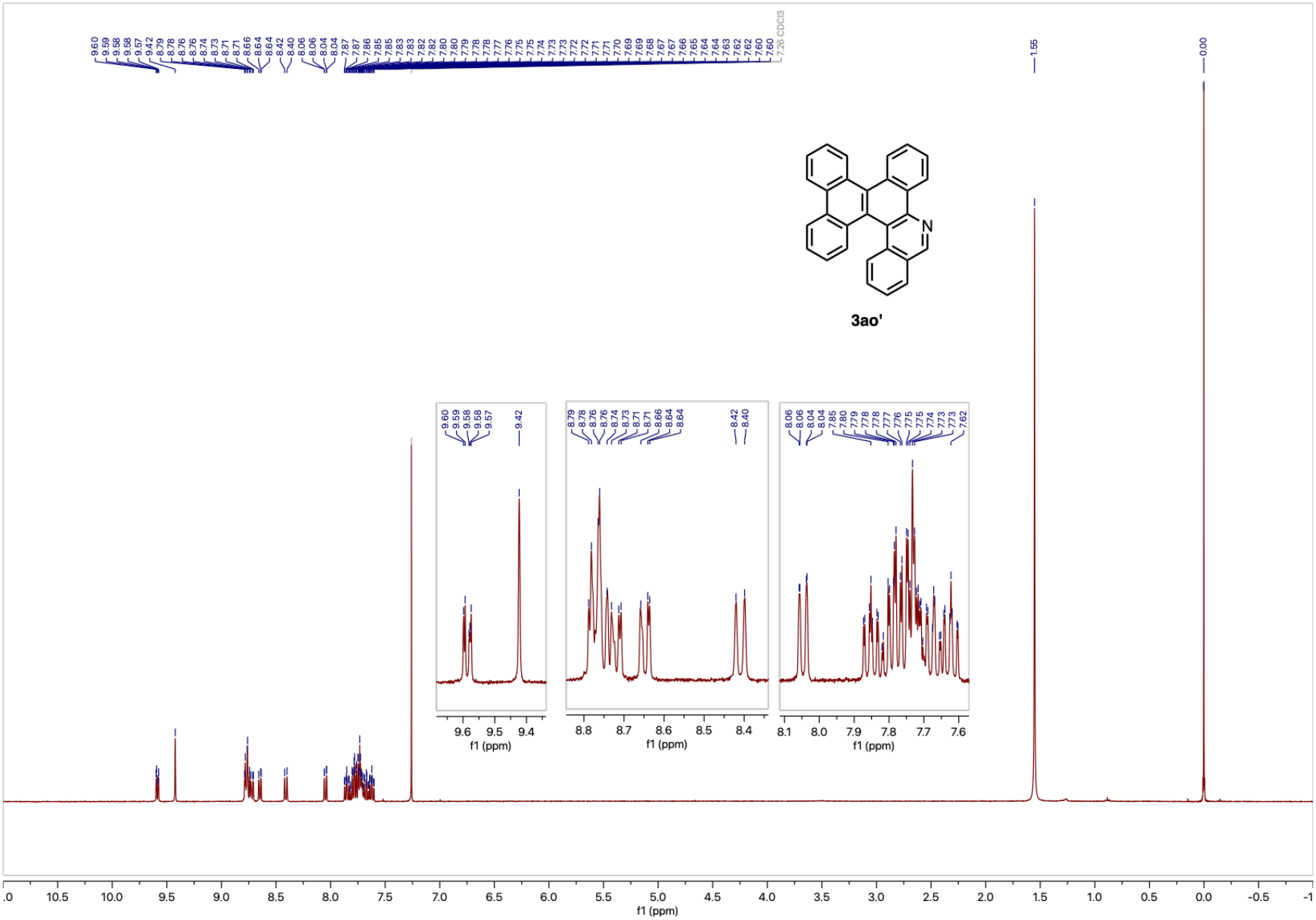


Figure S98. ^{1}H NMR of **3ao'**.

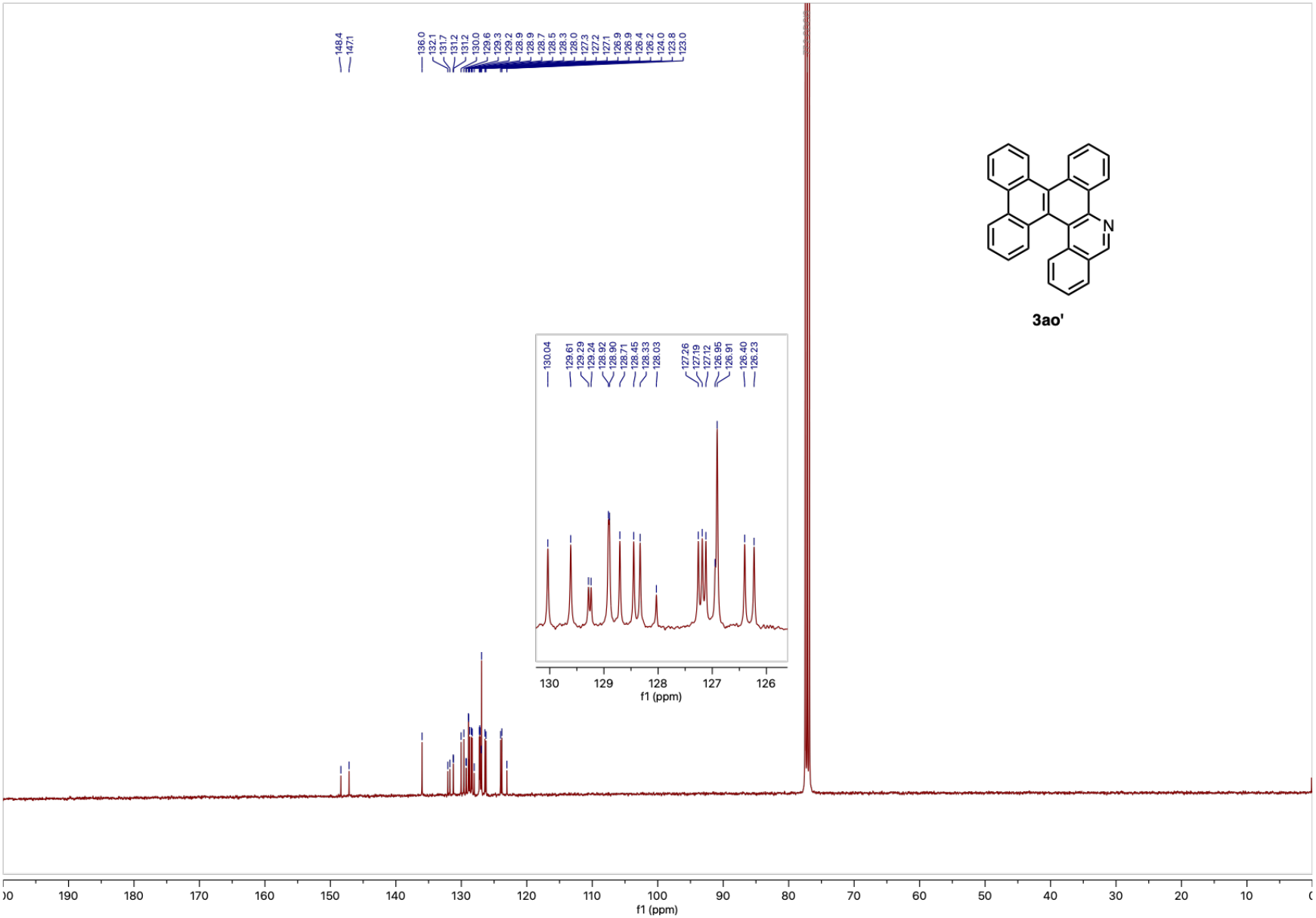


Figure S99. ^{13}C NMR of **3ao'**.

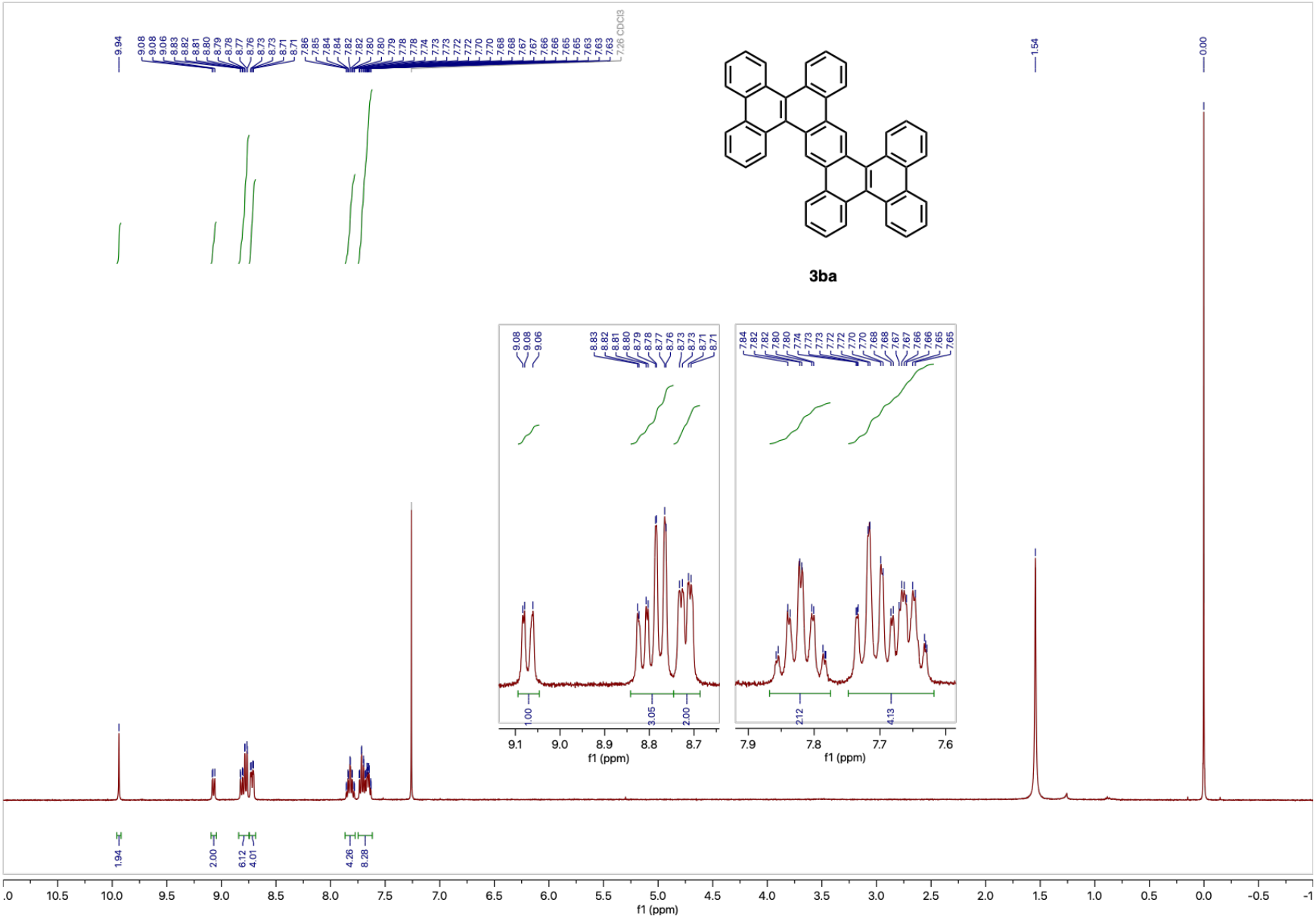


Figure S100. ^{1}H NMR of **3ba**.

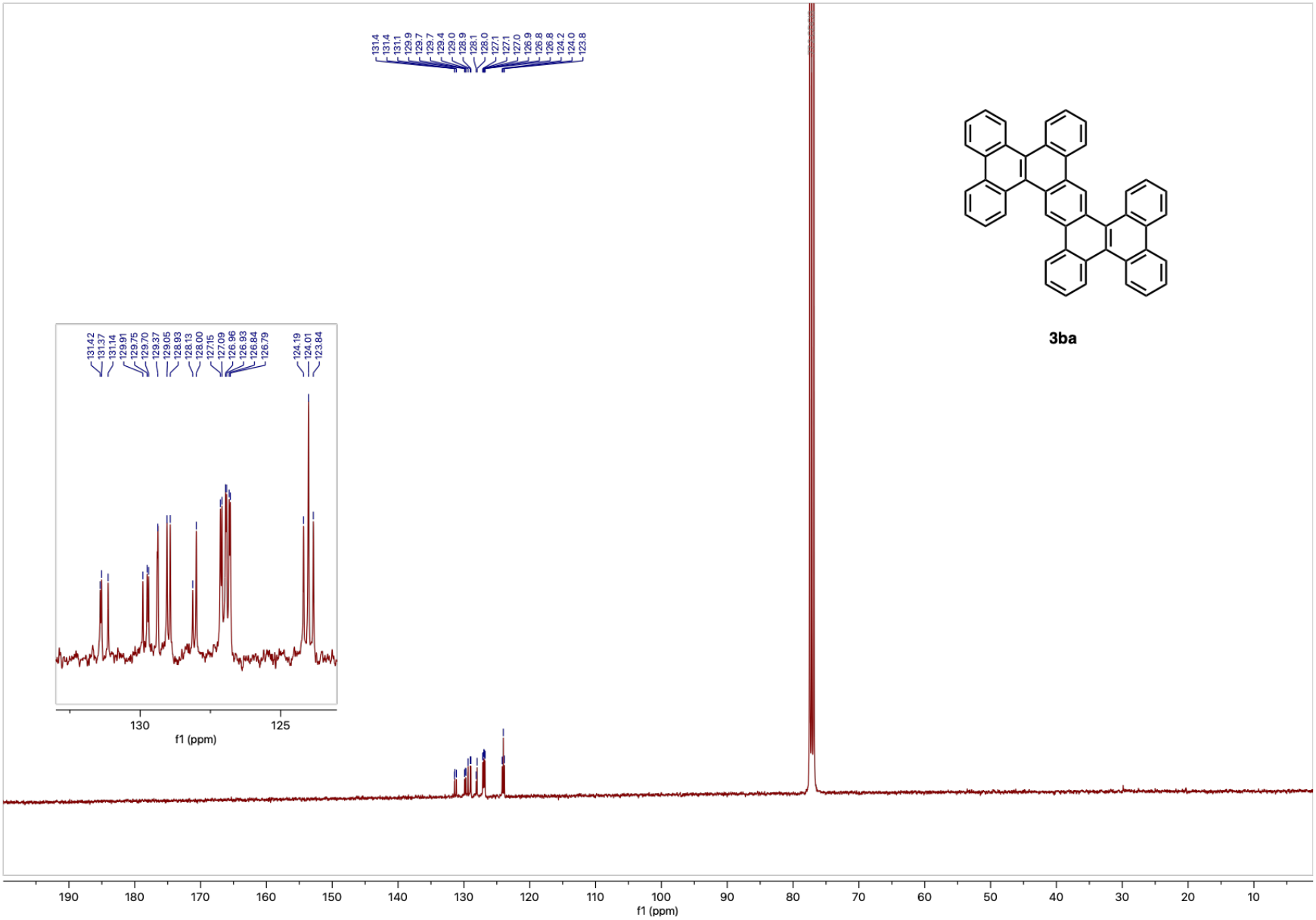


Figure S101. ^{13}C NMR of **3ba**.

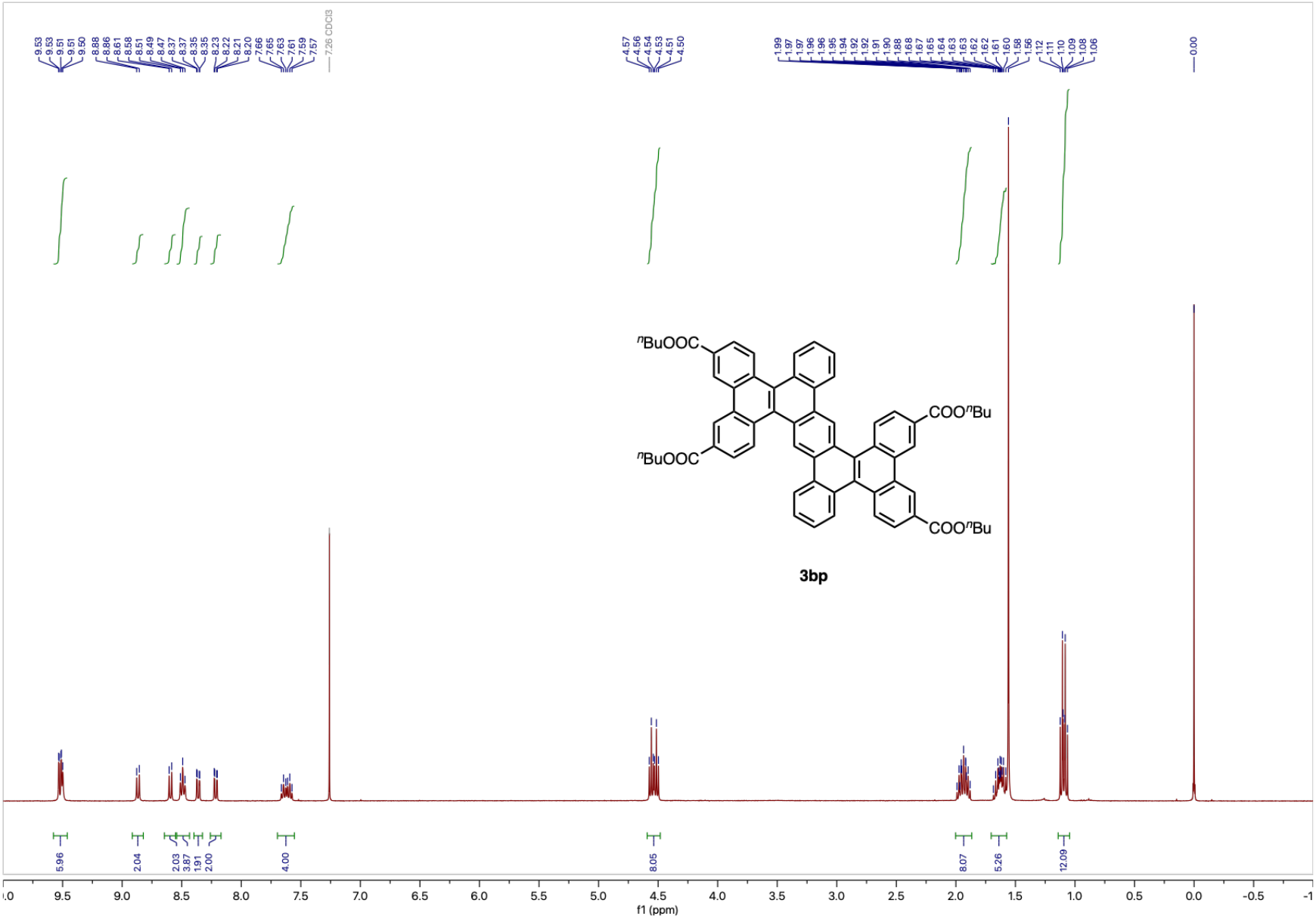


Figure S102. ^{1}H NMR of **3bp**.

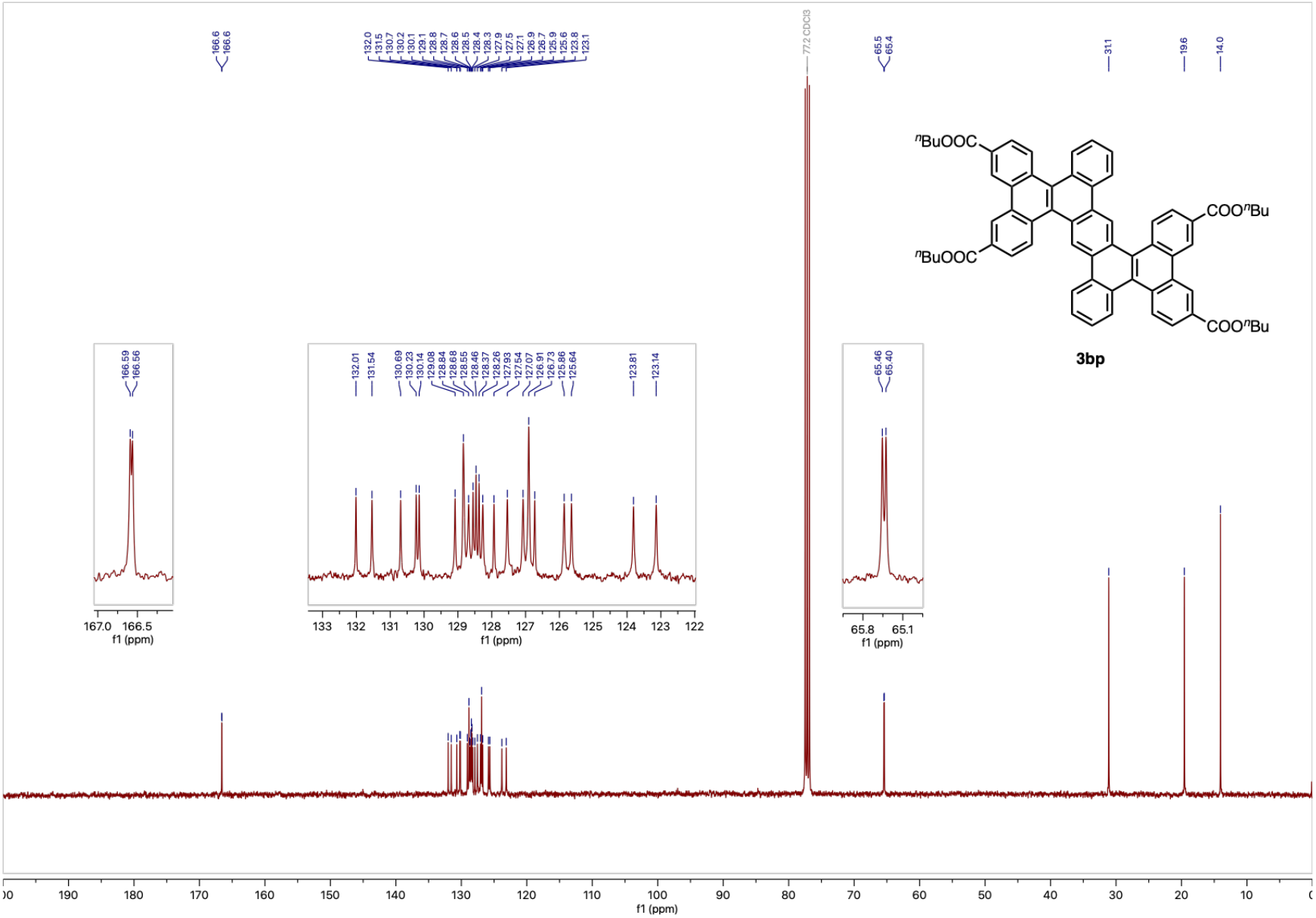


Figure S103. ^{13}C NMR of **3bp**.

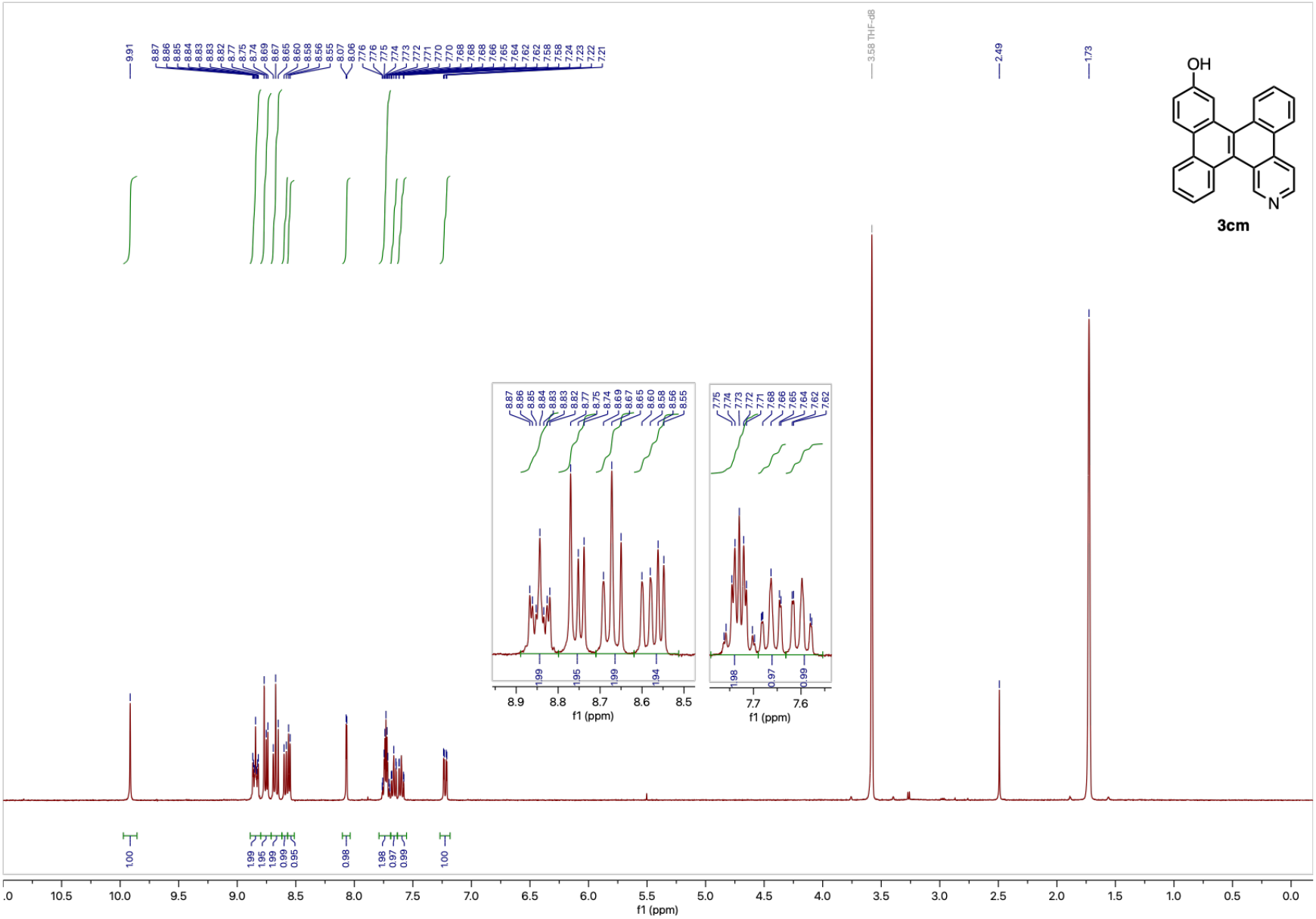


Figure S104. ^{1}H NMR of **3cm**.

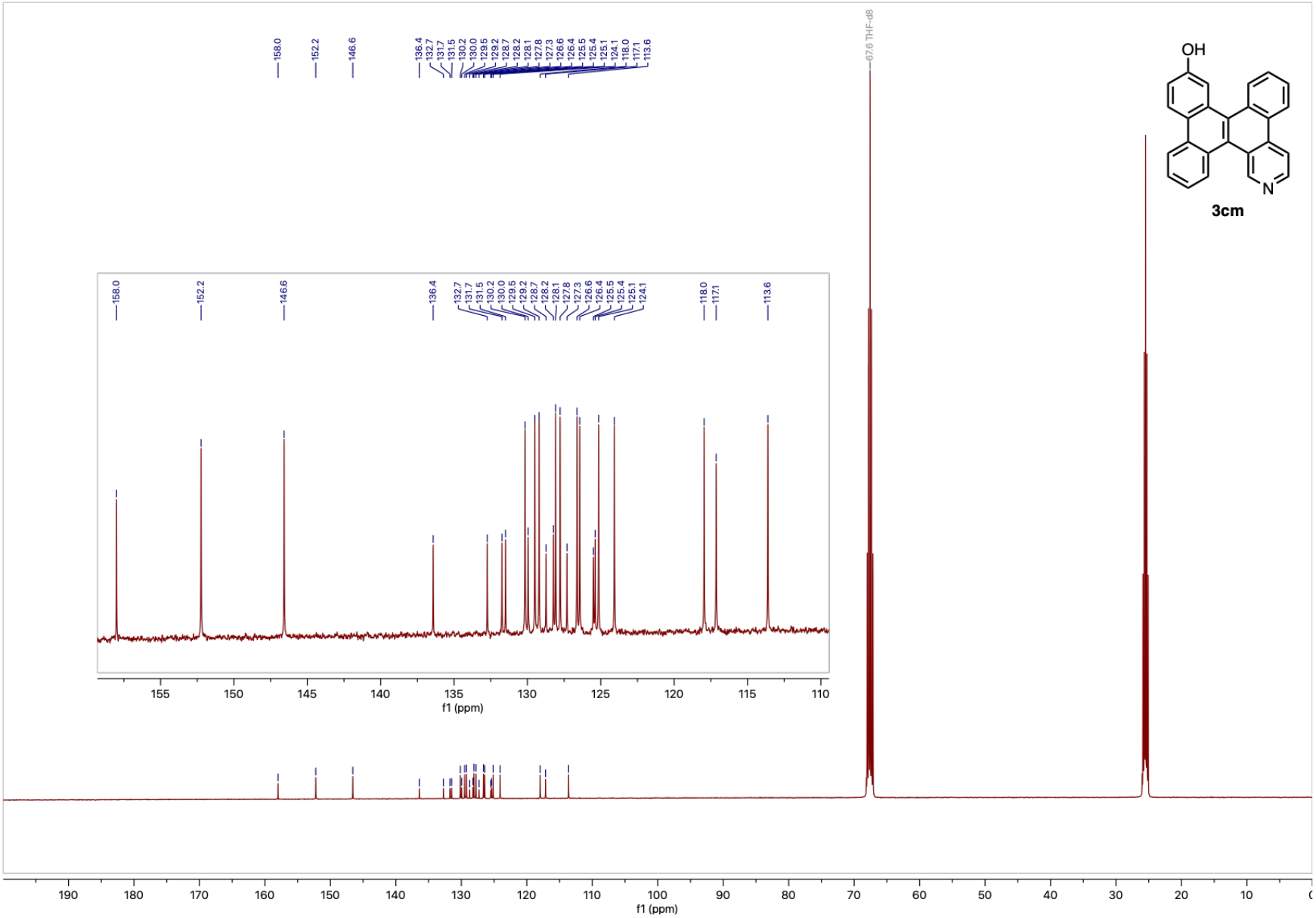


Figure S105. ^{13}C NMR of **3cm**.

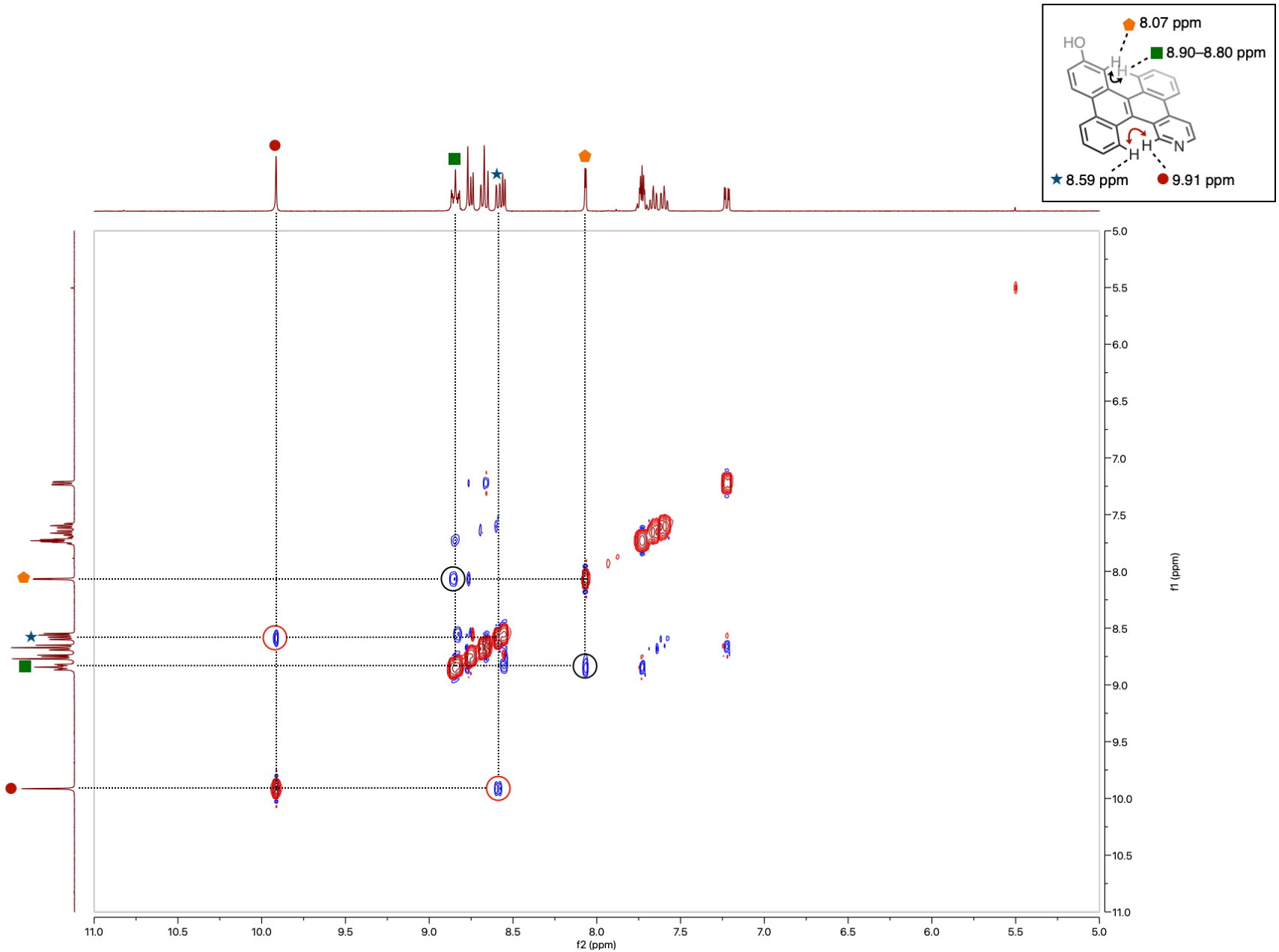


Figure S106. NOESY NMR of **3cm**.

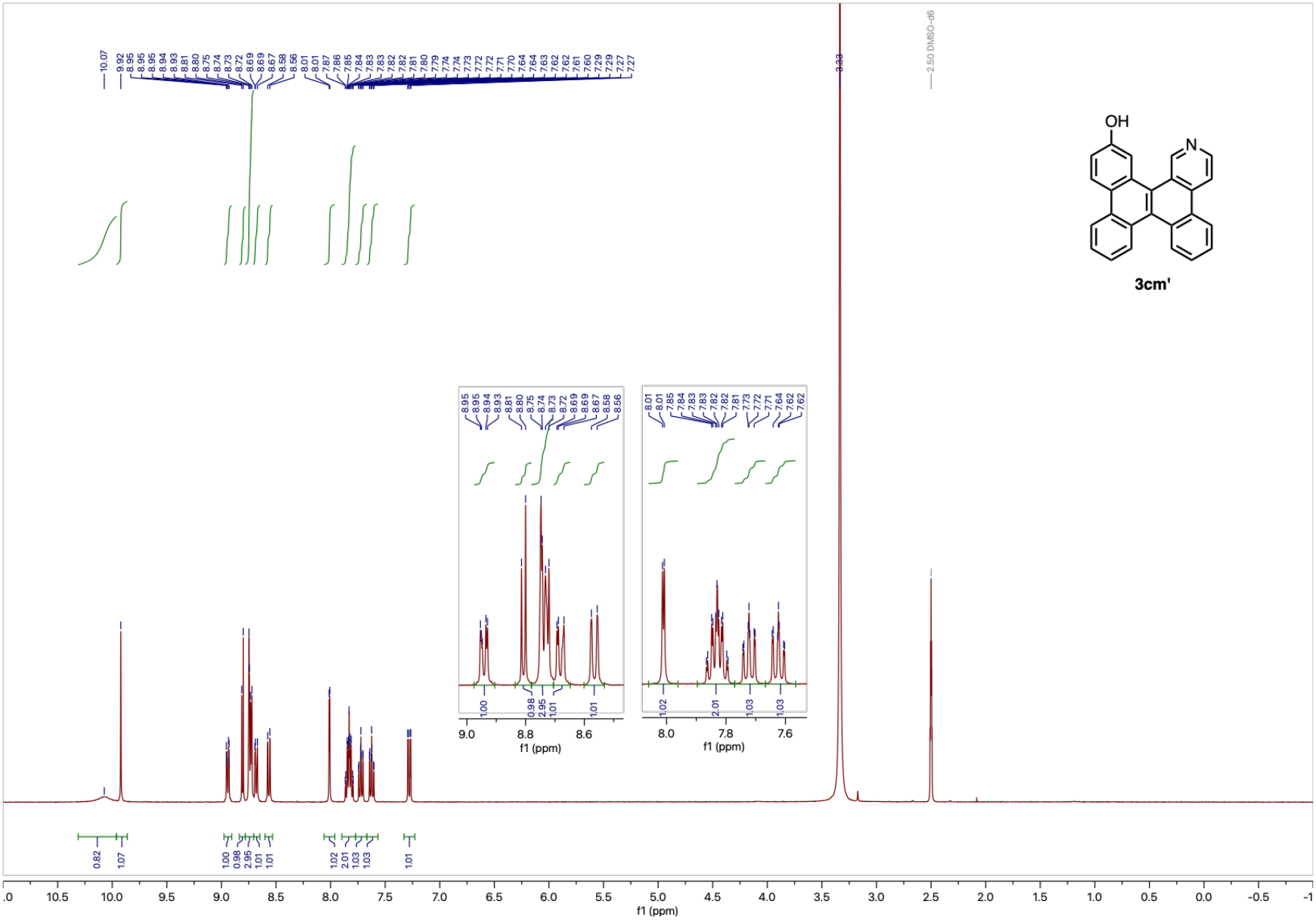


Figure S107. ^{1}H NMR of **3cm'**.

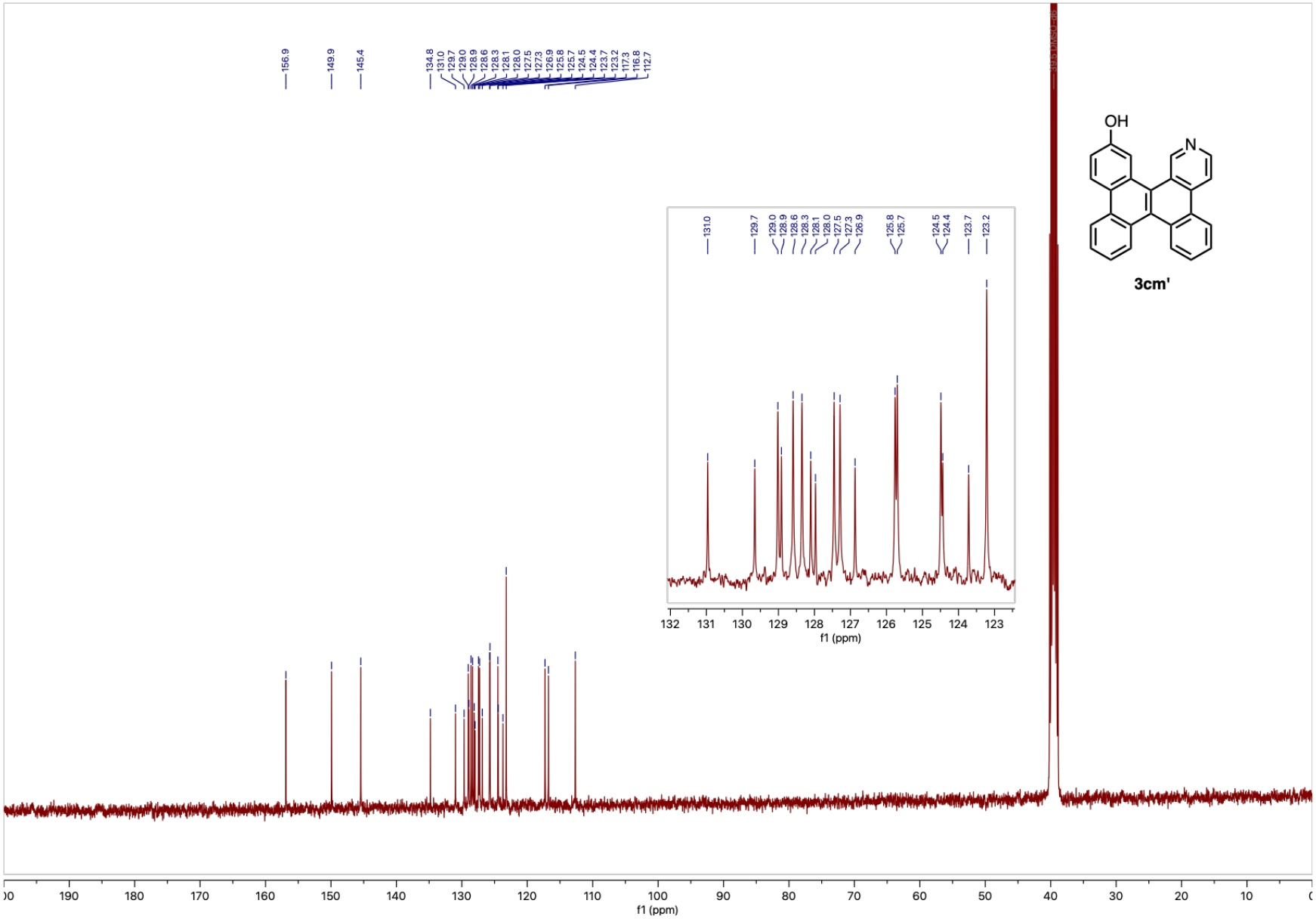


Figure S108. ^{13}C NMR of **3cm'**.

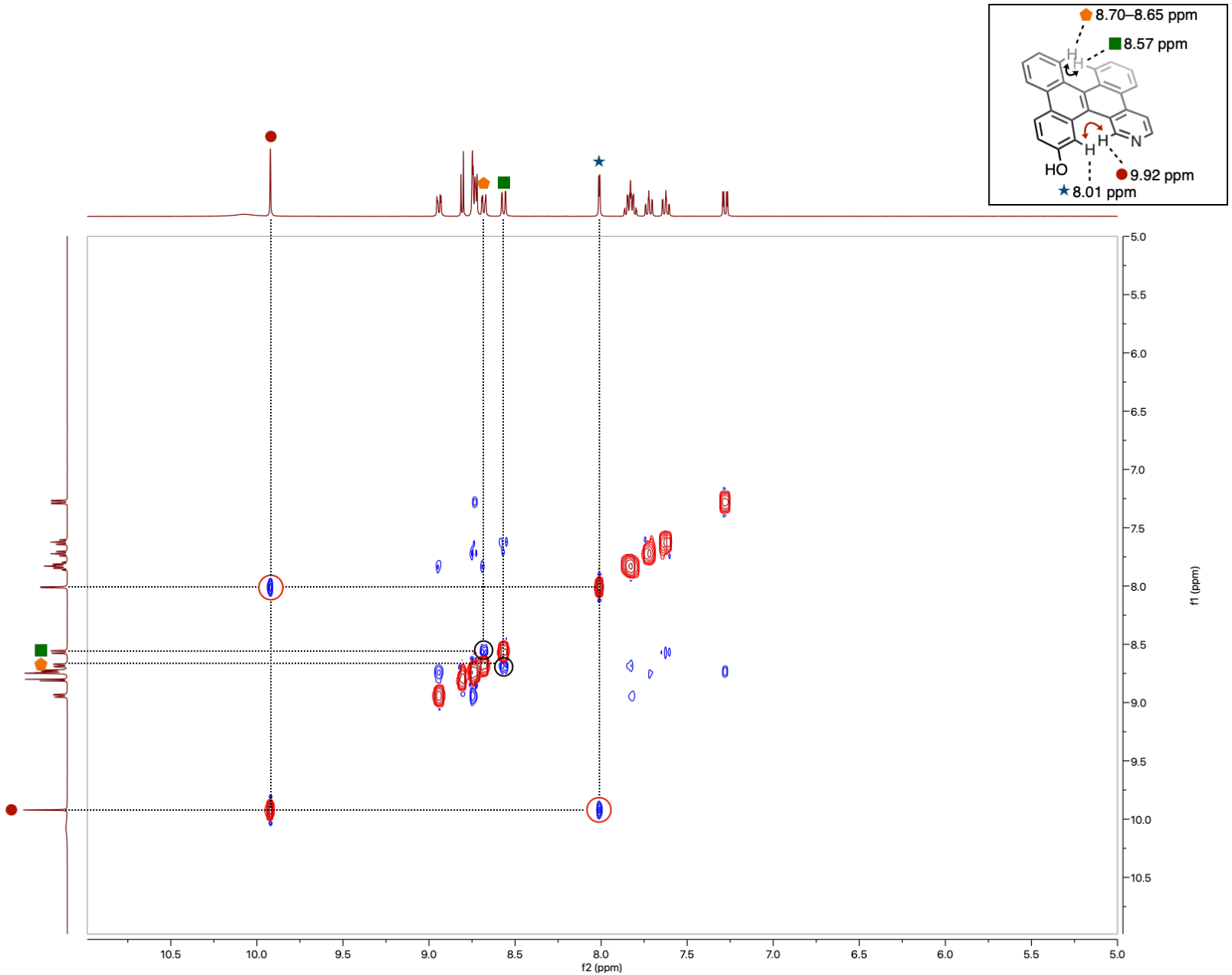


Figure S109. NOESY NMR of **3cm'**.

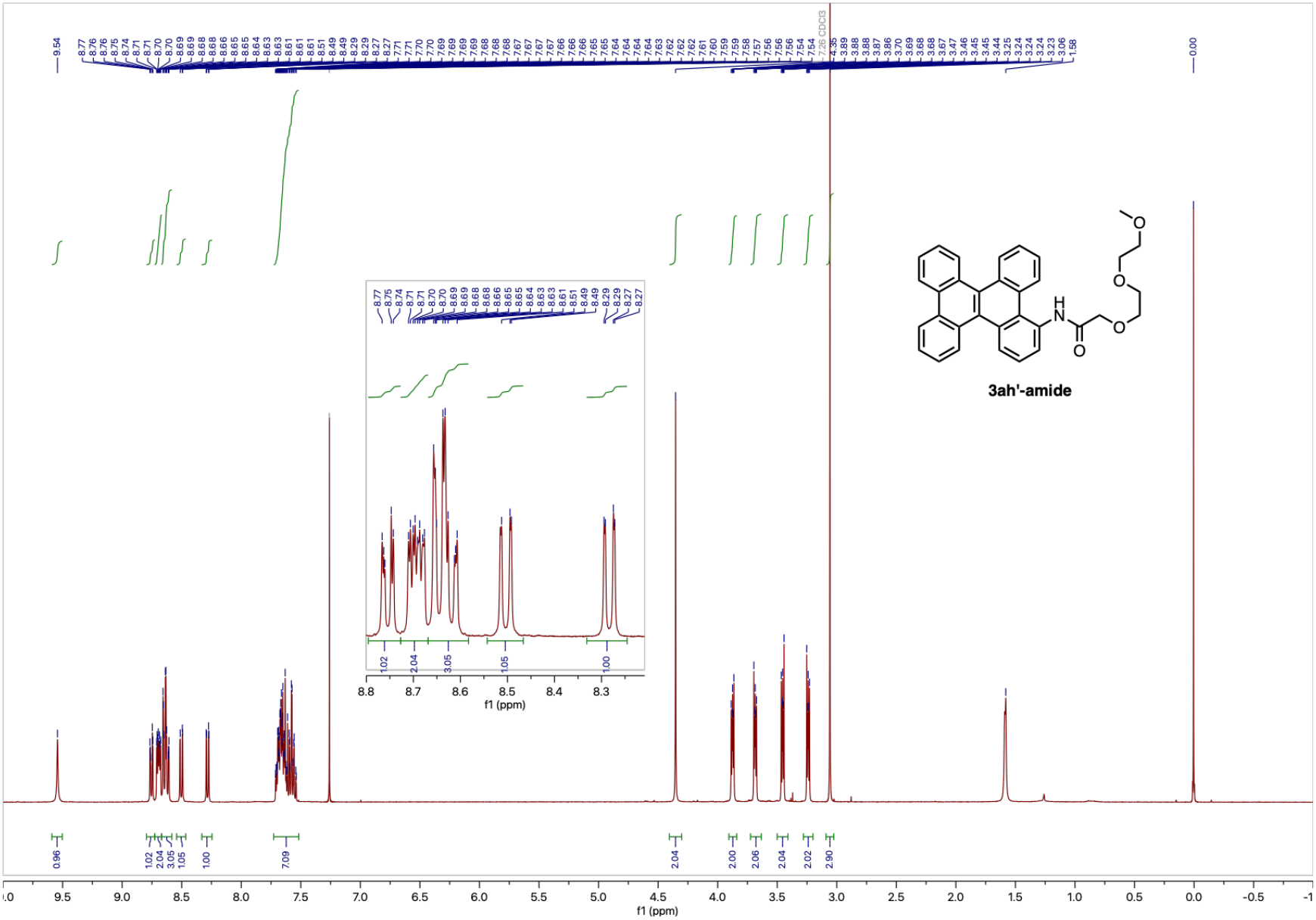


Figure S110. ^{1}H NMR of **3ah'-amide**.

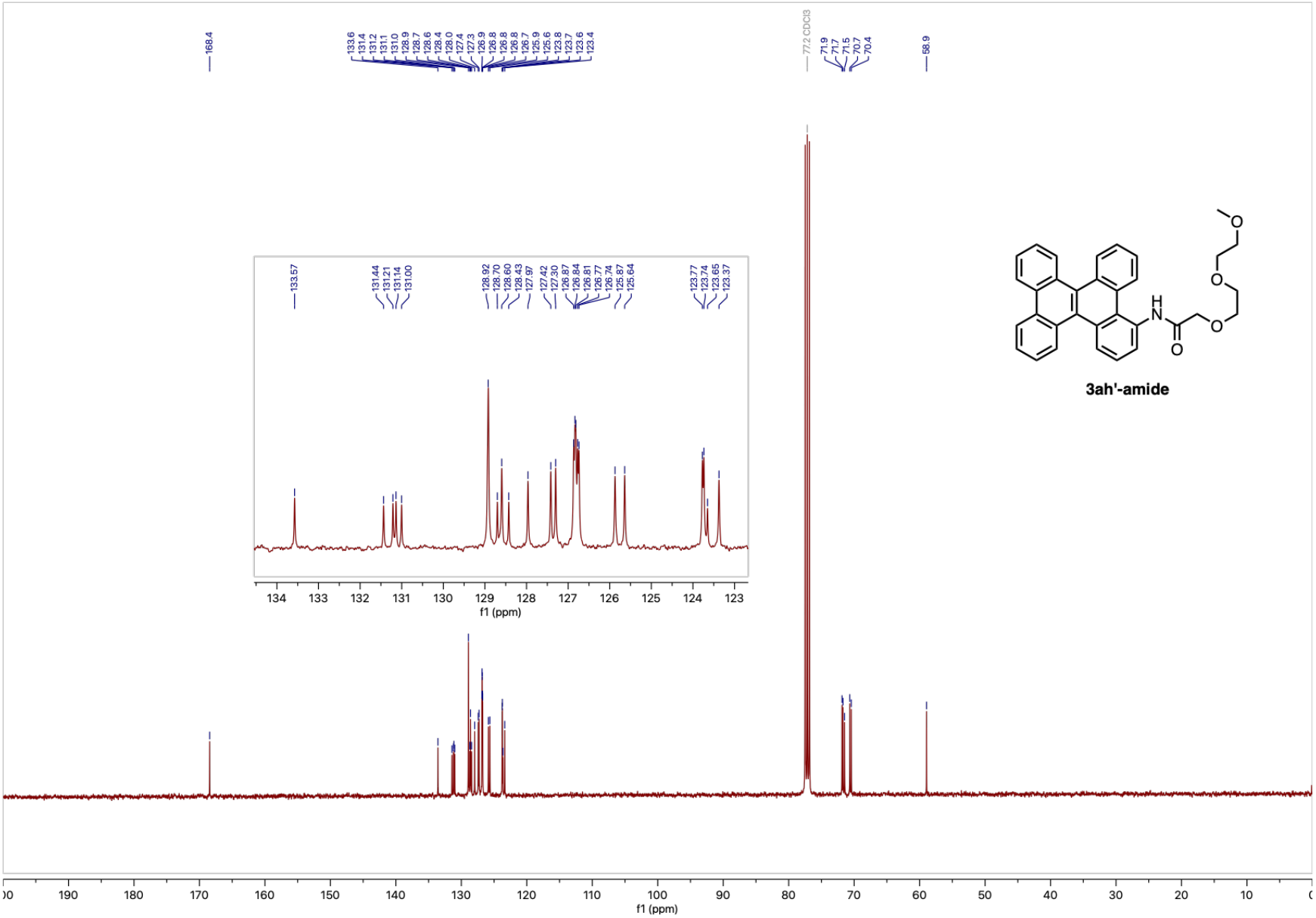


Figure S111. ^{13}C NMR of **3ah'-amide**.

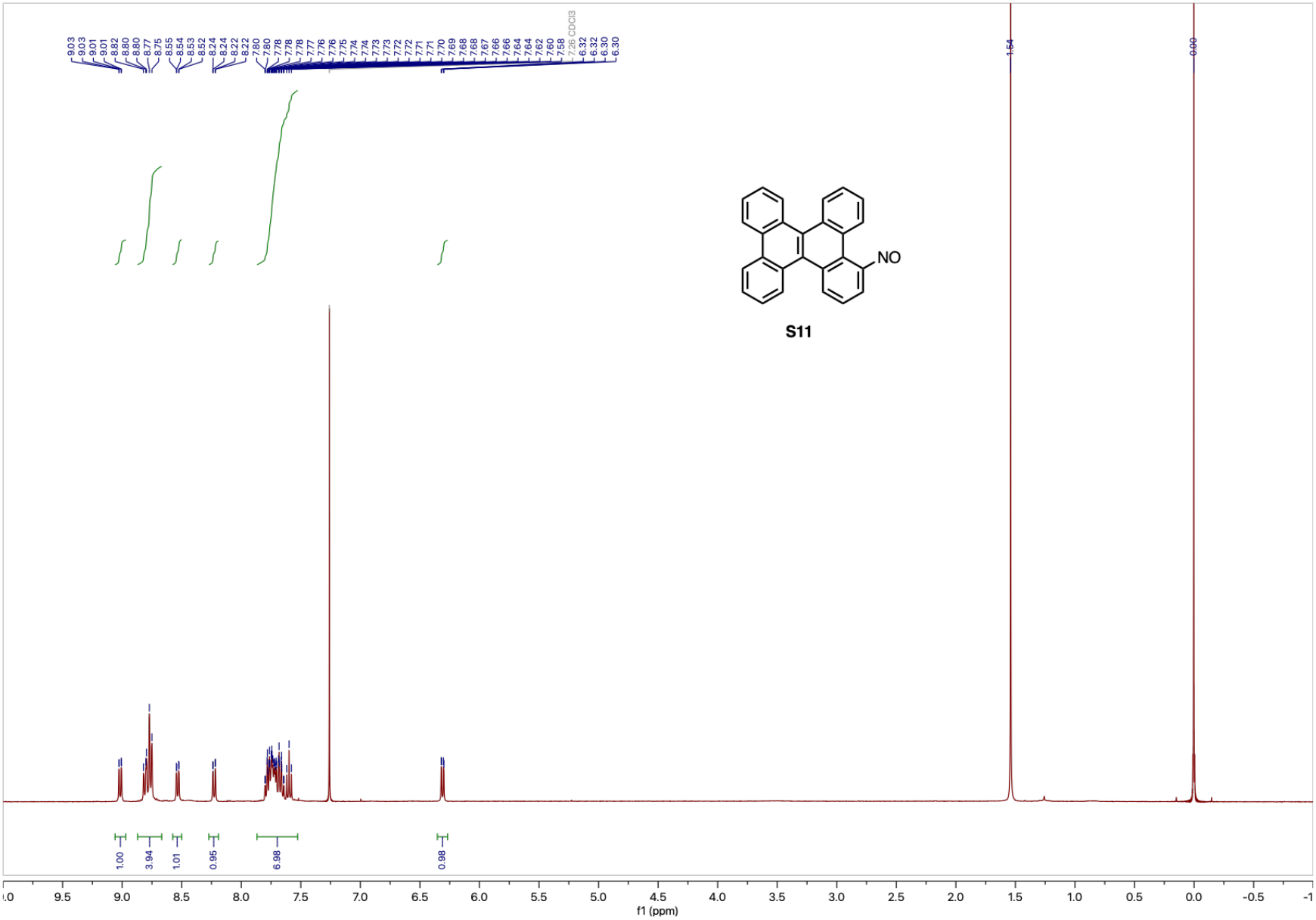


Figure S112. ^{1}H NMR of **S11**.

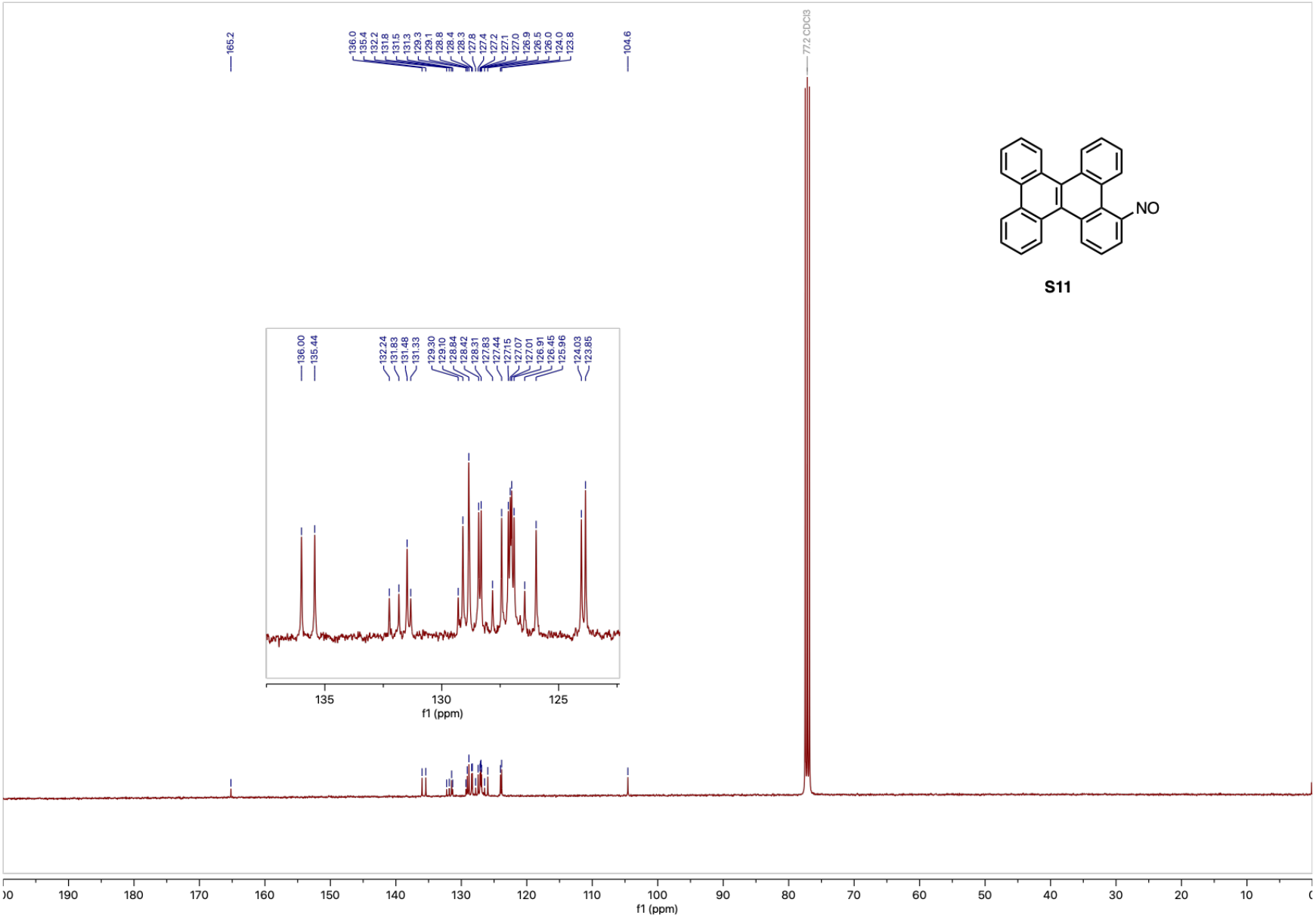


Figure S113. ^{13}C NMR of **S11**.

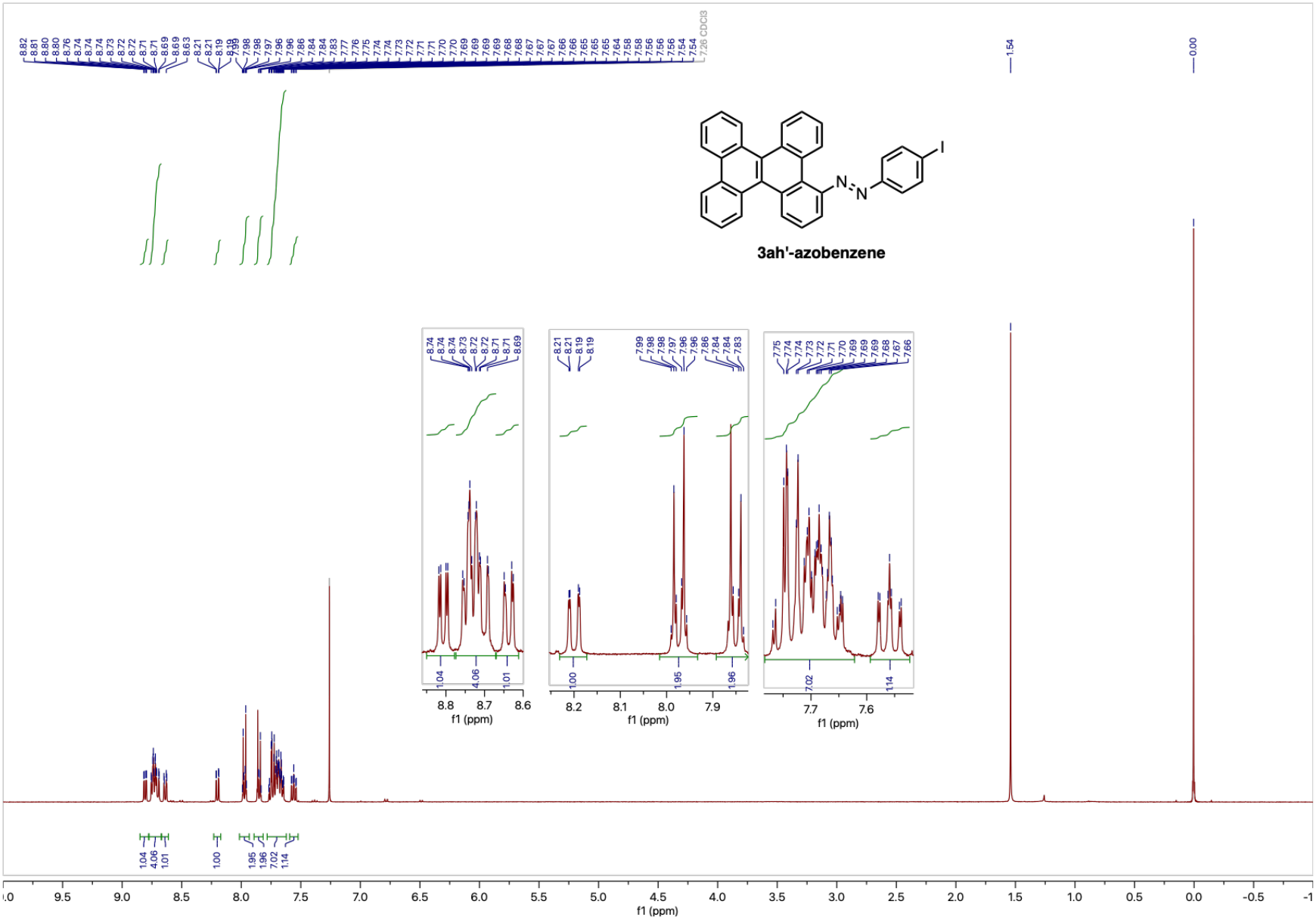


Figure S114. ^{1}H NMR of **3ah'-azobenzene**.

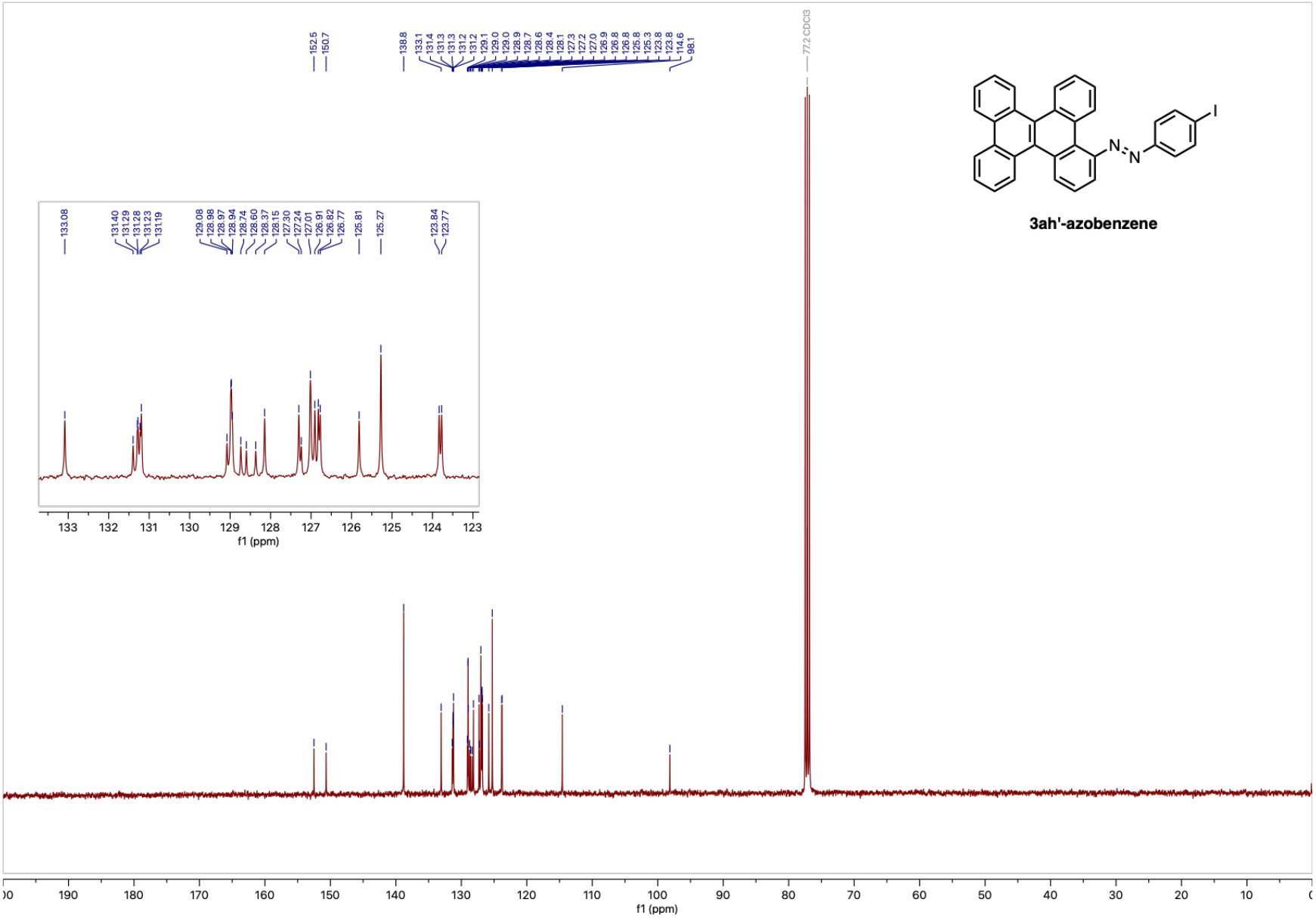


Figure S115. ^{13}C NMR of **3ah'-azobenzene**.

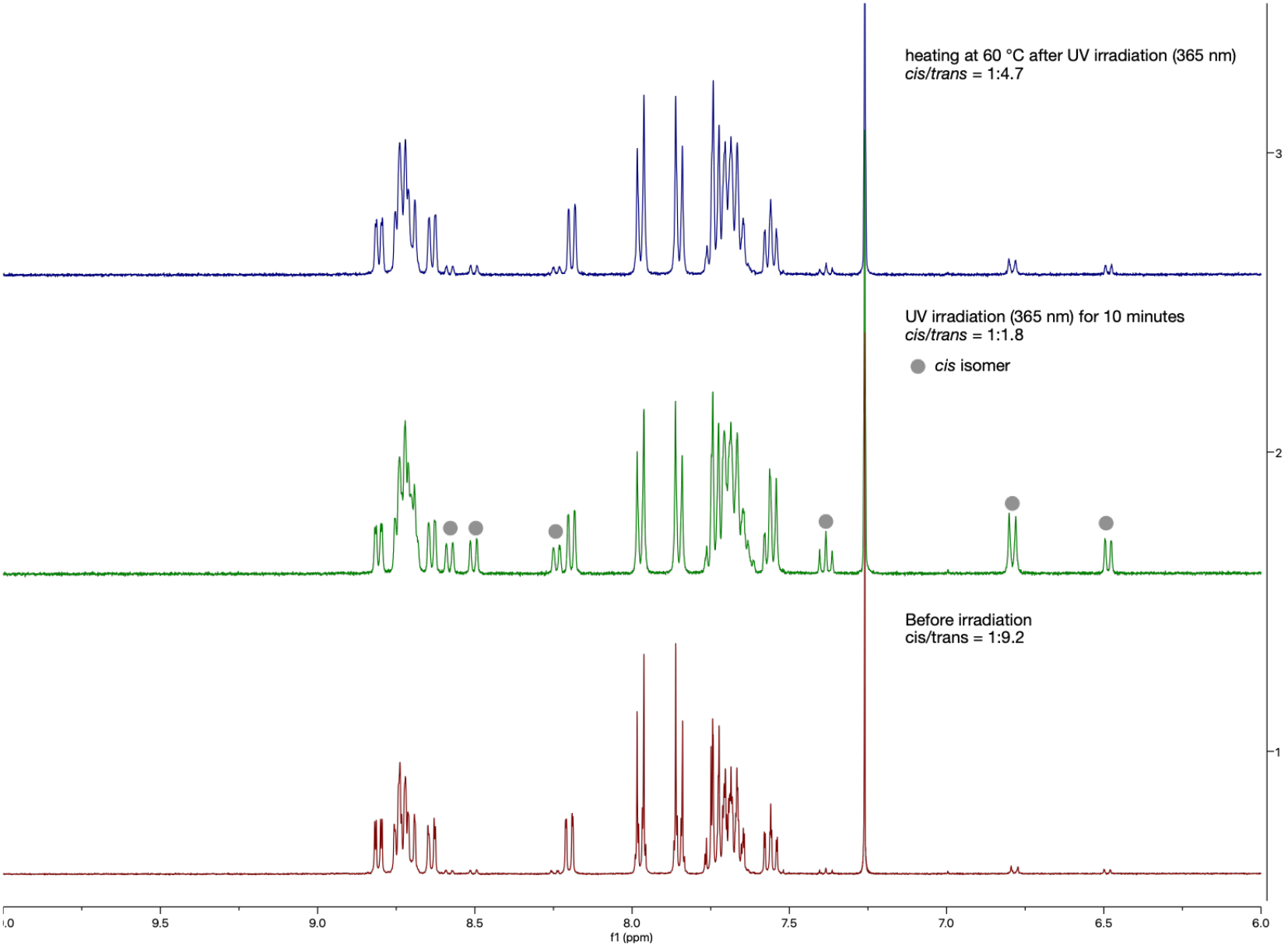


Figure S116. Photoisomerization profile of **3ah'-azobenzene**.

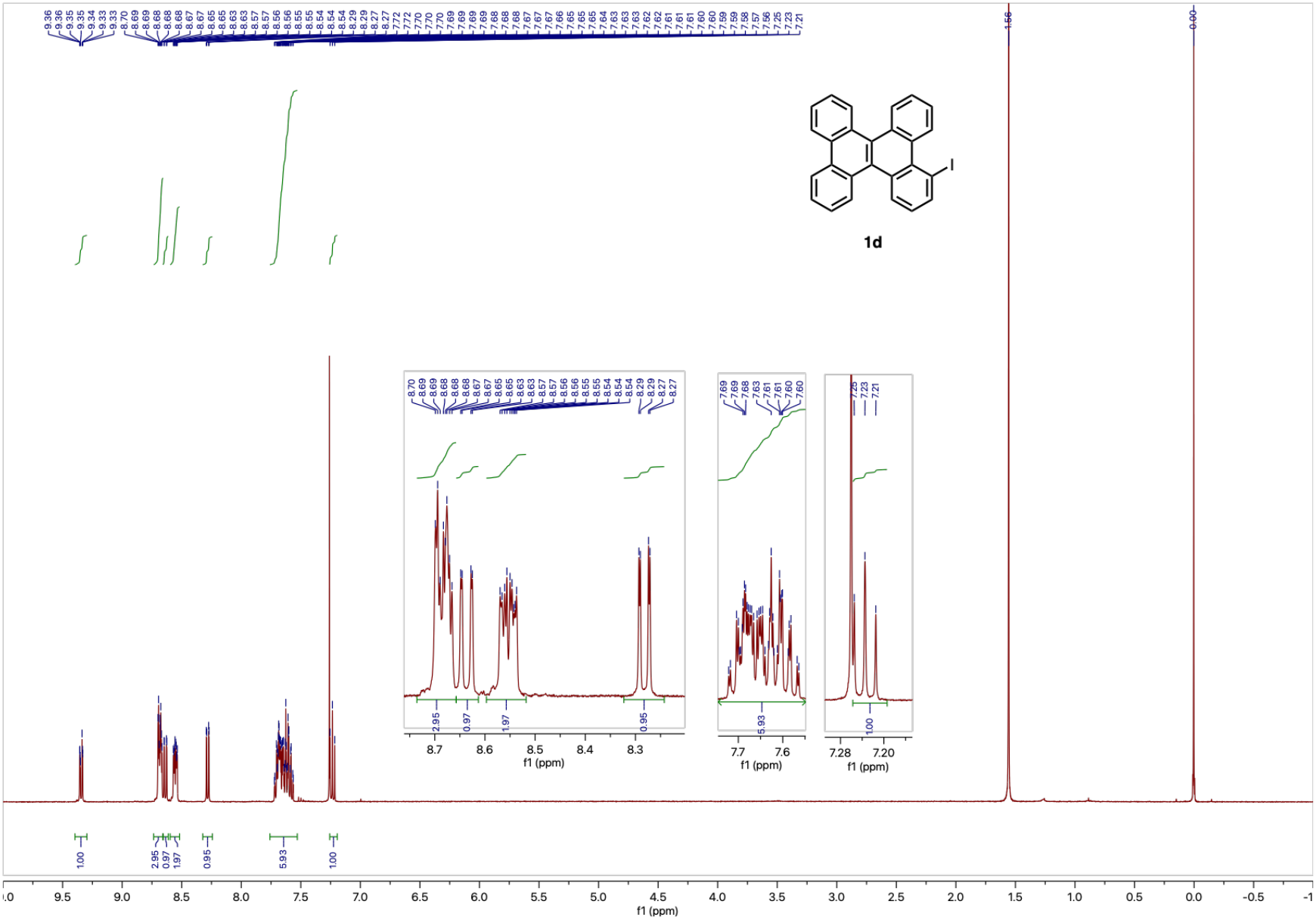


Figure S117. ^{1}H NMR of **1d**.

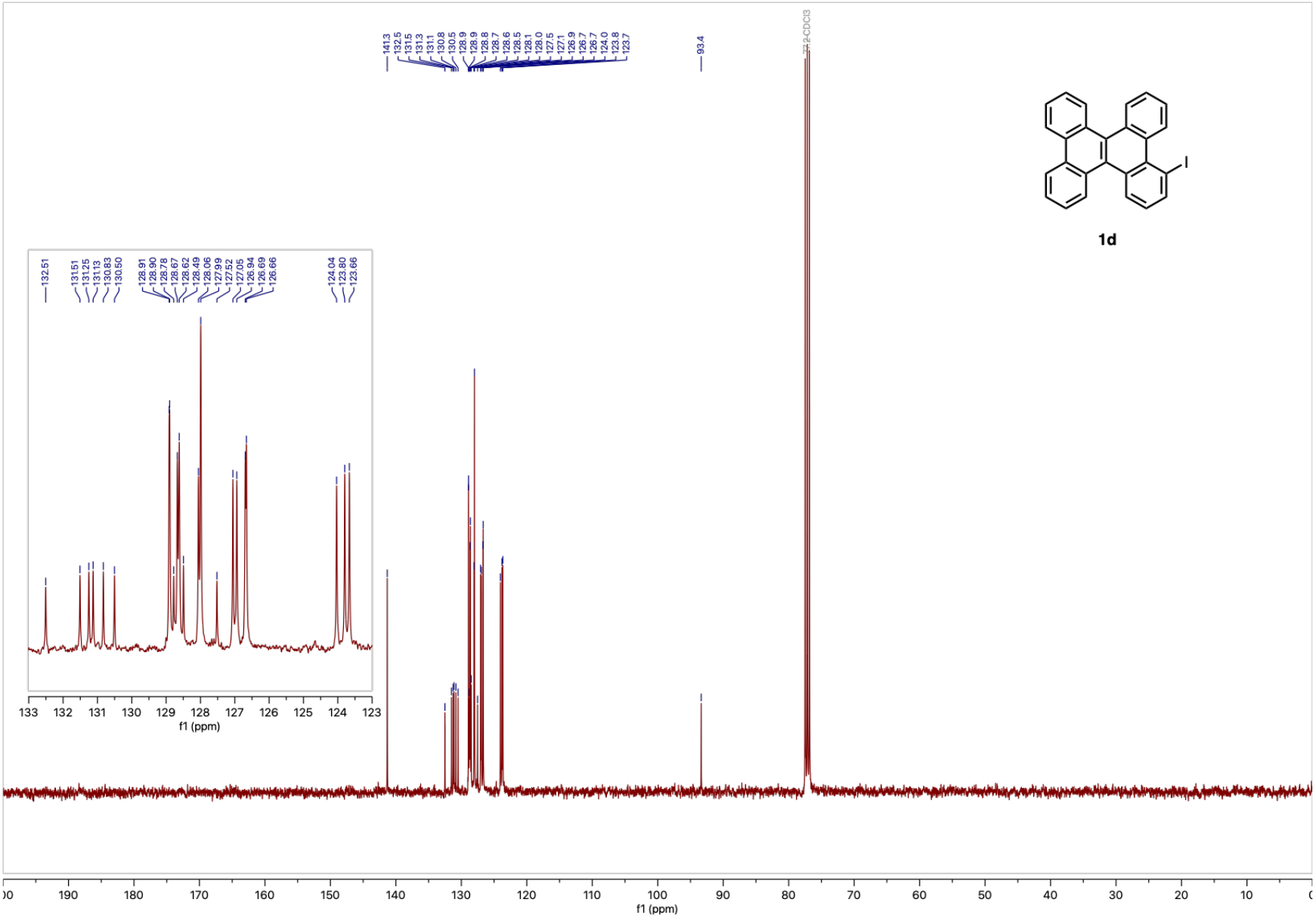


Figure S118. ^{13}C NMR of **1d**.

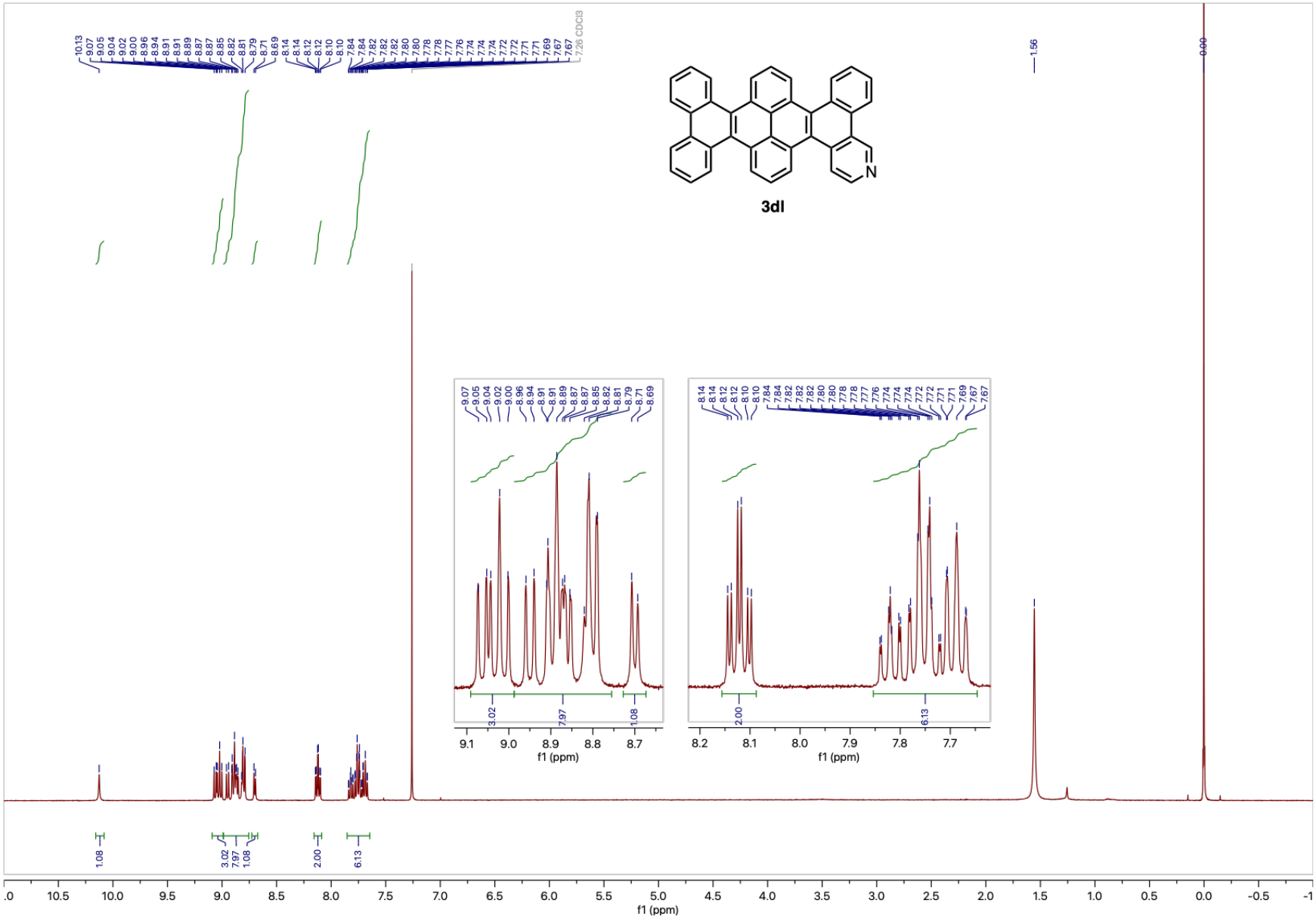


Figure S119. ^{1}H NMR of **3dl**.

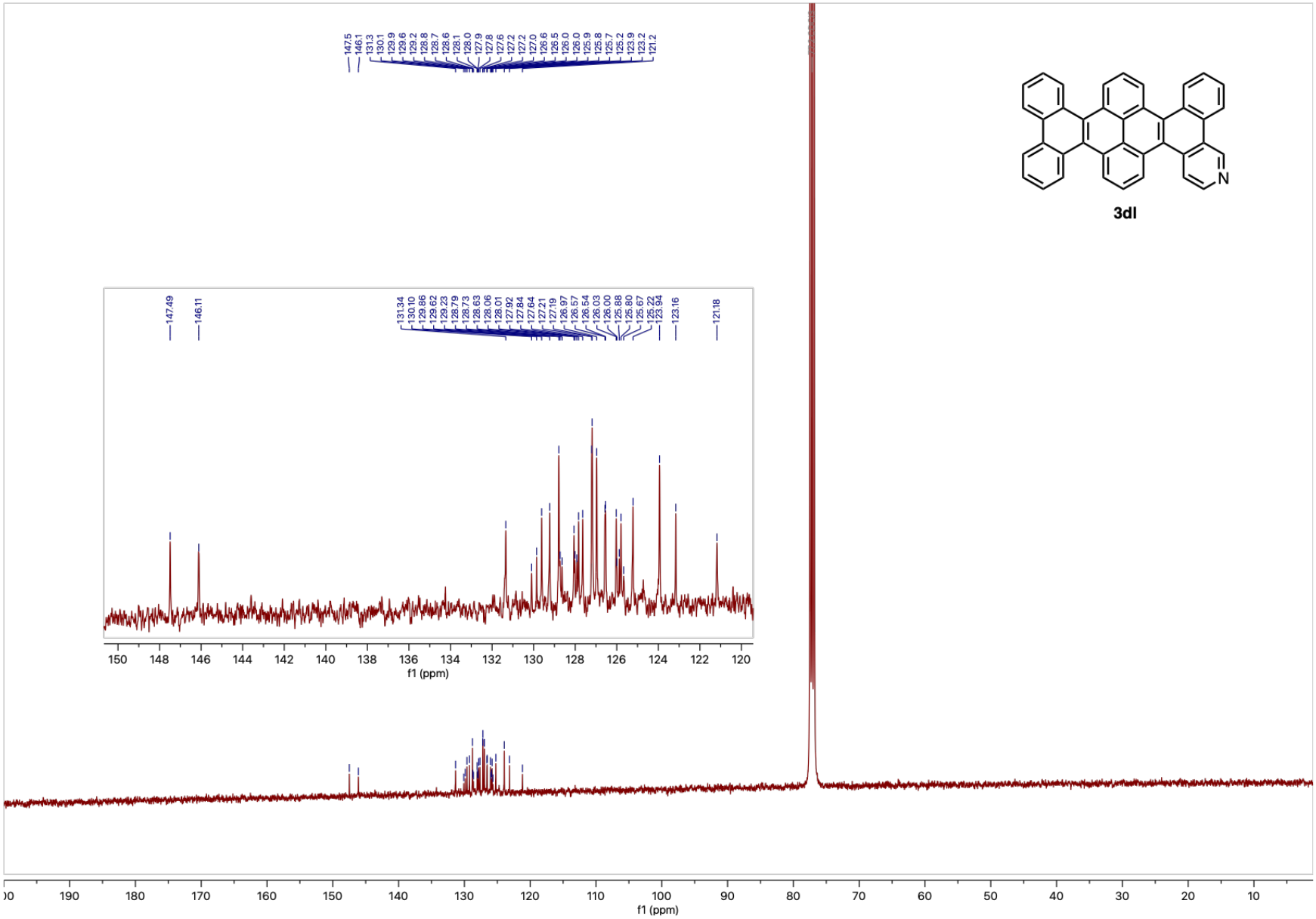


Figure S120. ^{13}C NMR of **3dl**.

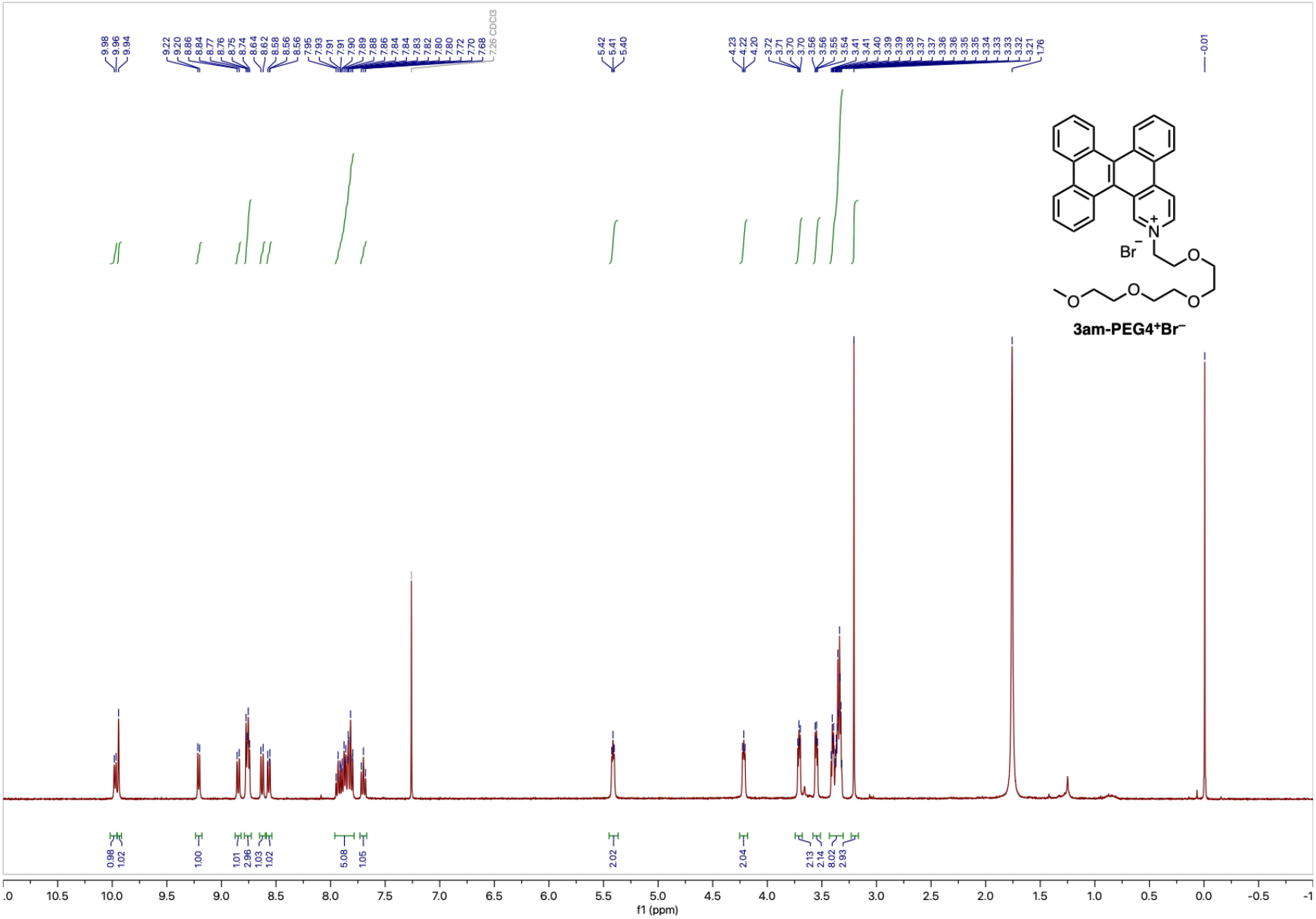


Figure S121. ^{1}H NMR of **3am-PEG4^{+}Br^{-}**.

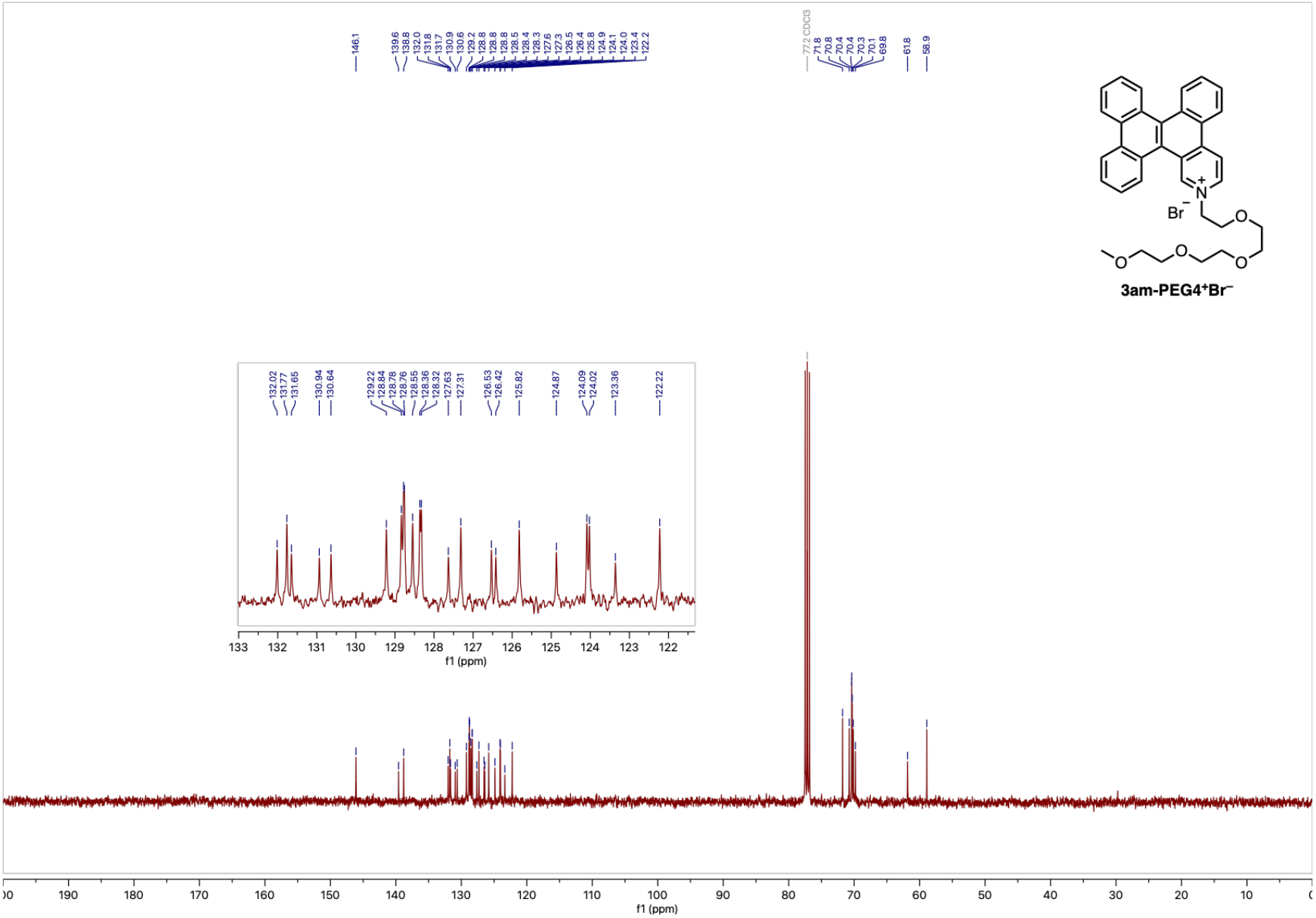


Figure S122. ^{13}C NMR of **3am-PEG4^{+}Br^{-}**.

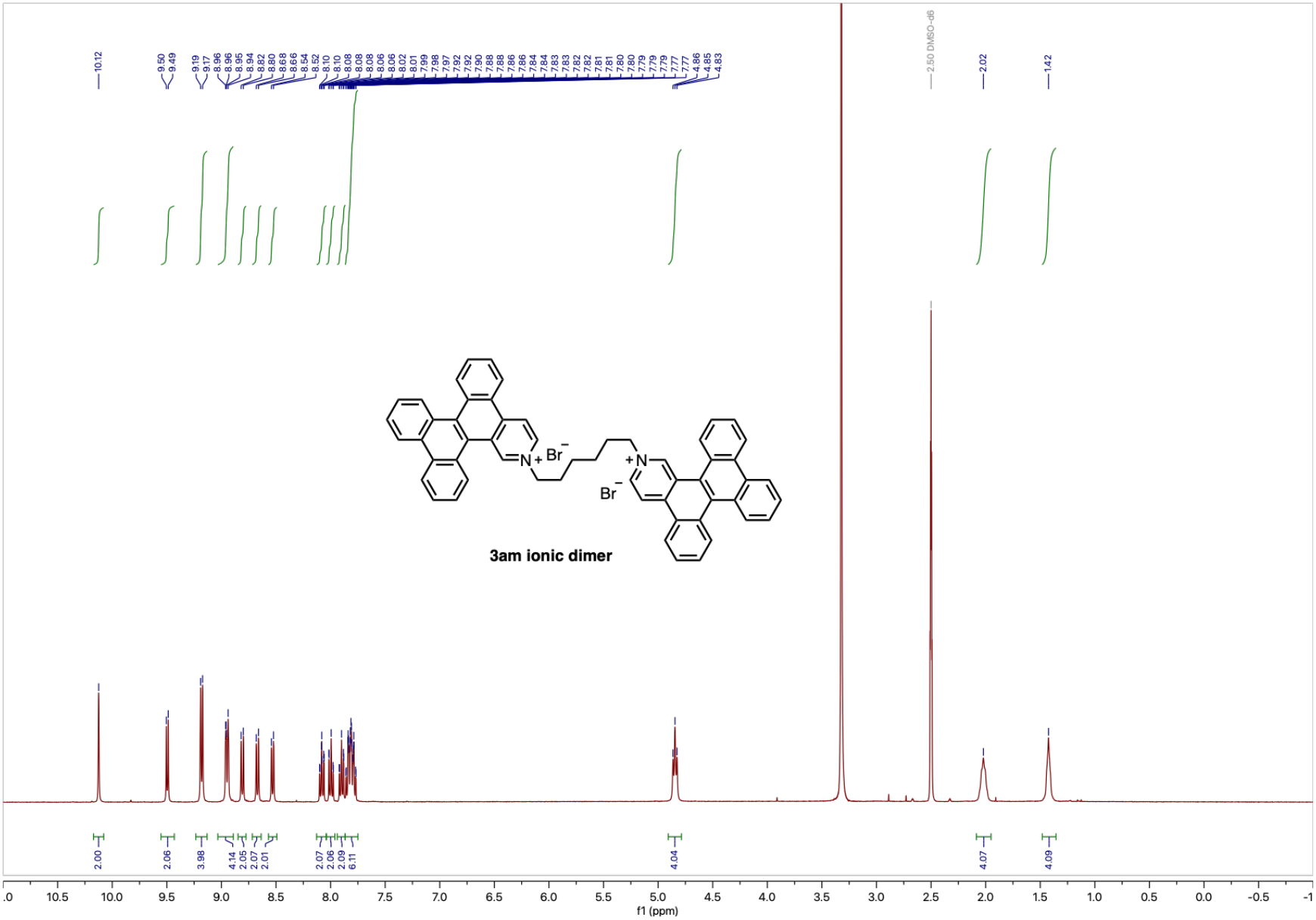


Figure S123. ^{1}H NMR of **3am ionic dimer**.

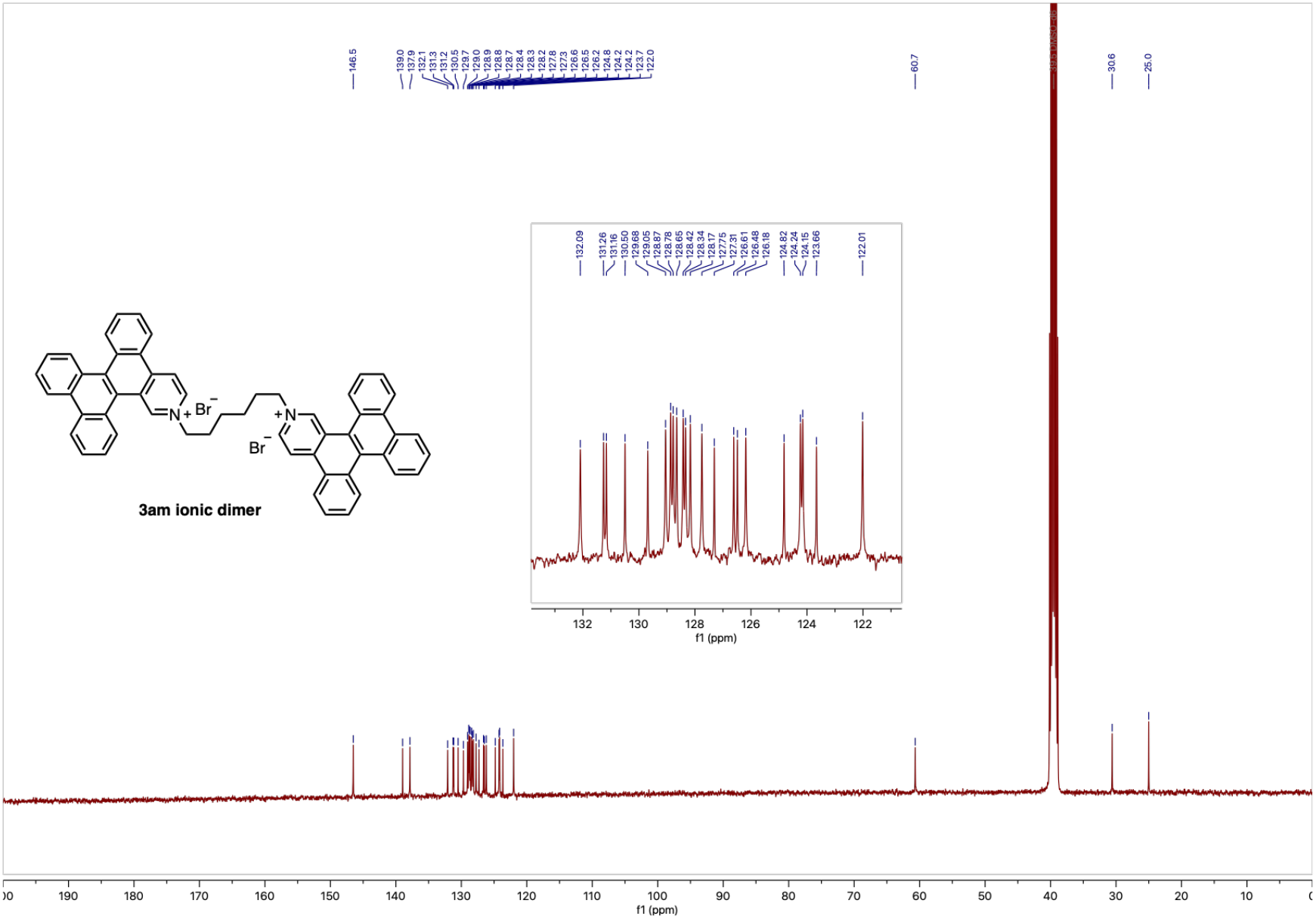


Figure S124. ^{13}C NMR of **3am ionic dimer**.

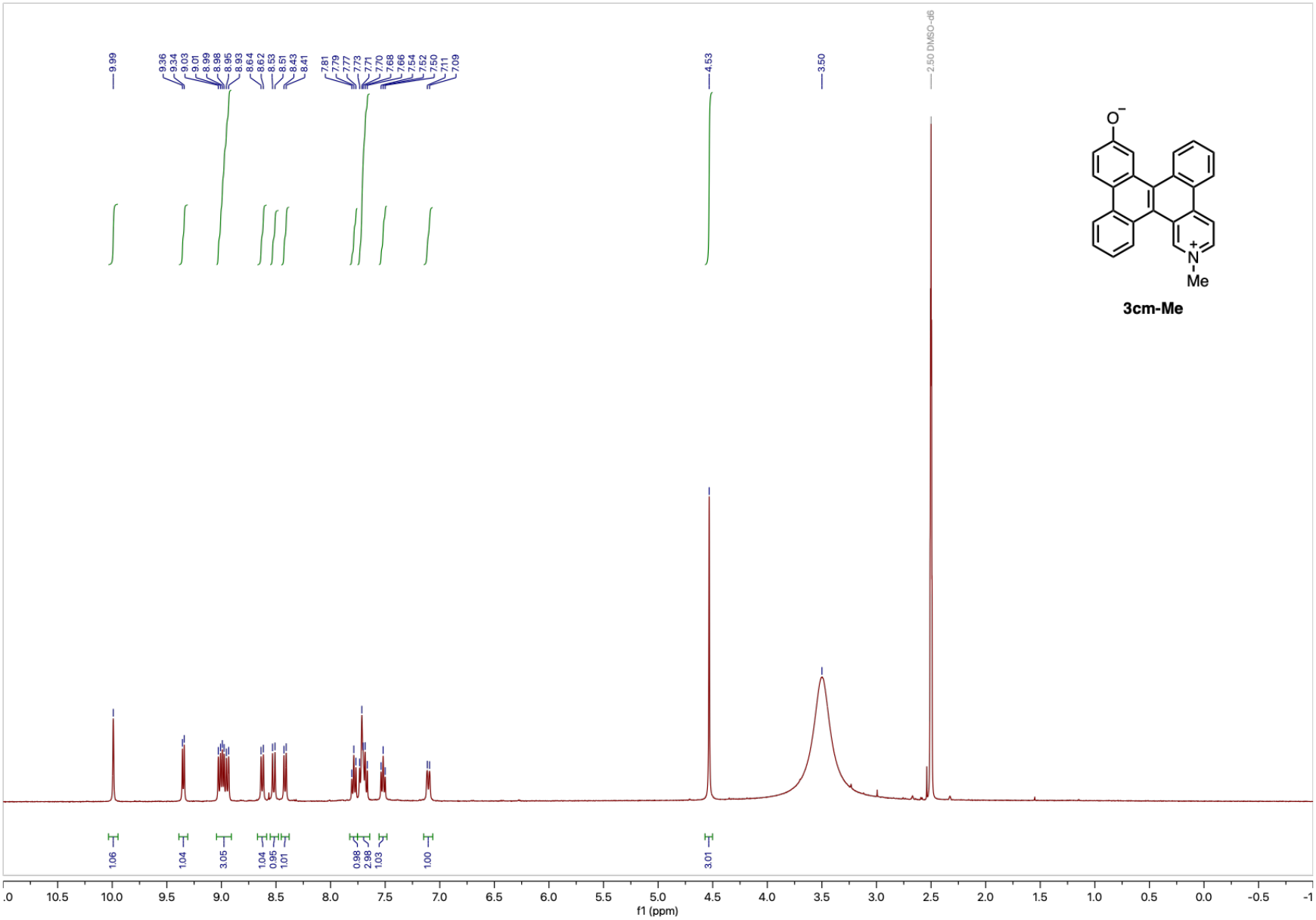


Figure S125. ^{1}H NMR of **3cm-Me**.

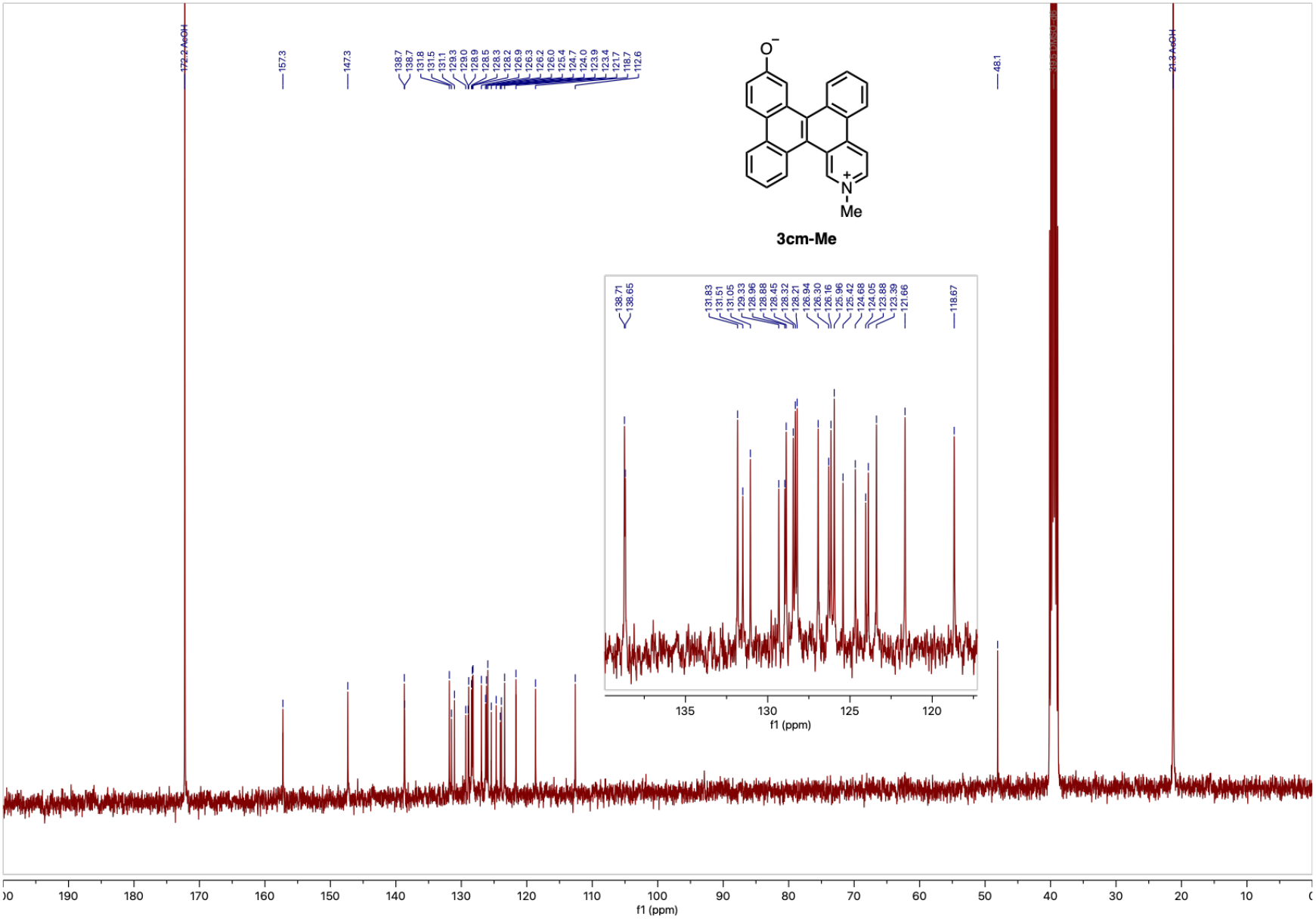


Figure S126. ^{13}C NMR of **3cm-Me**.

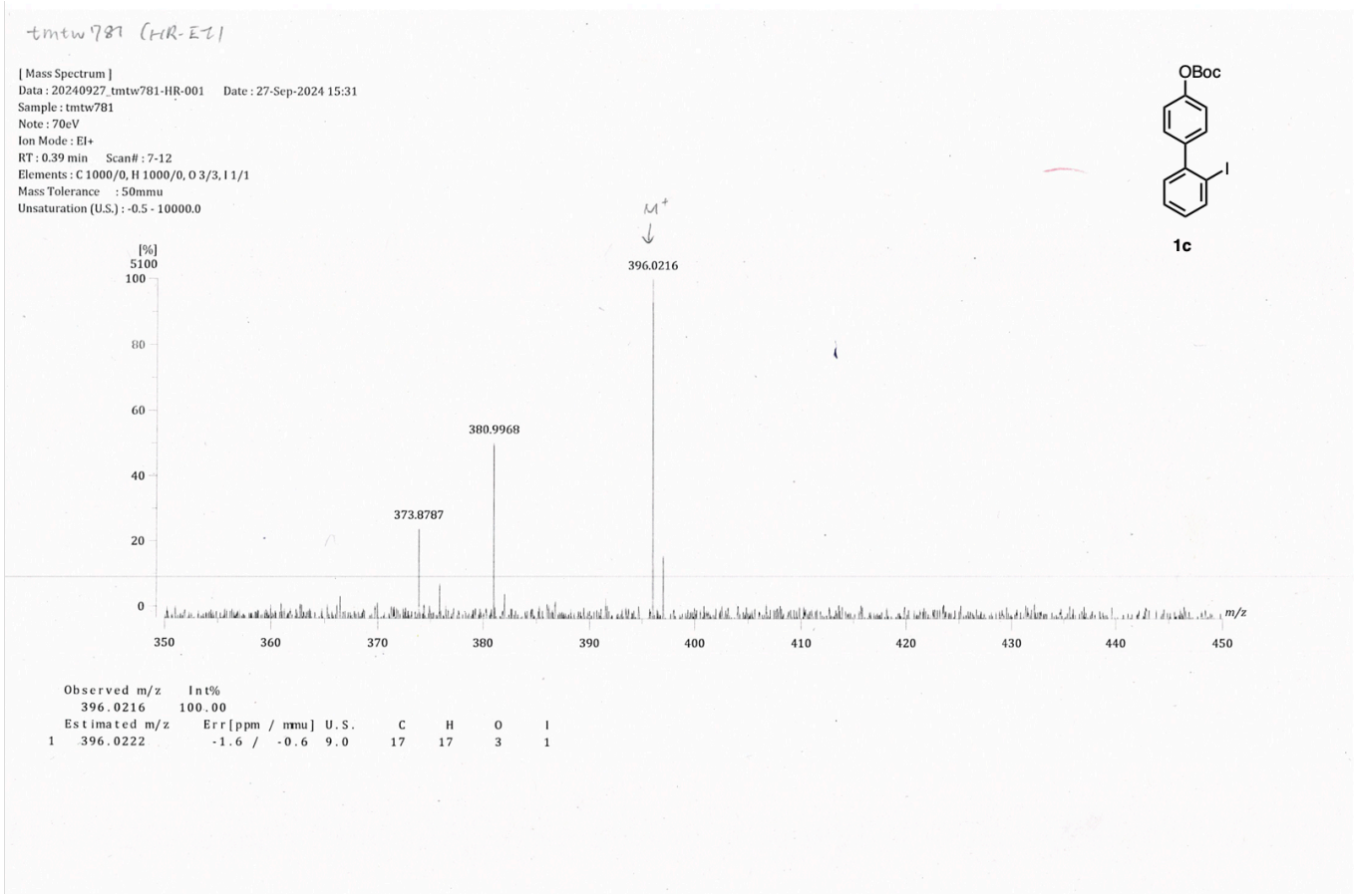


Figure S127. HRMS of **1c**.

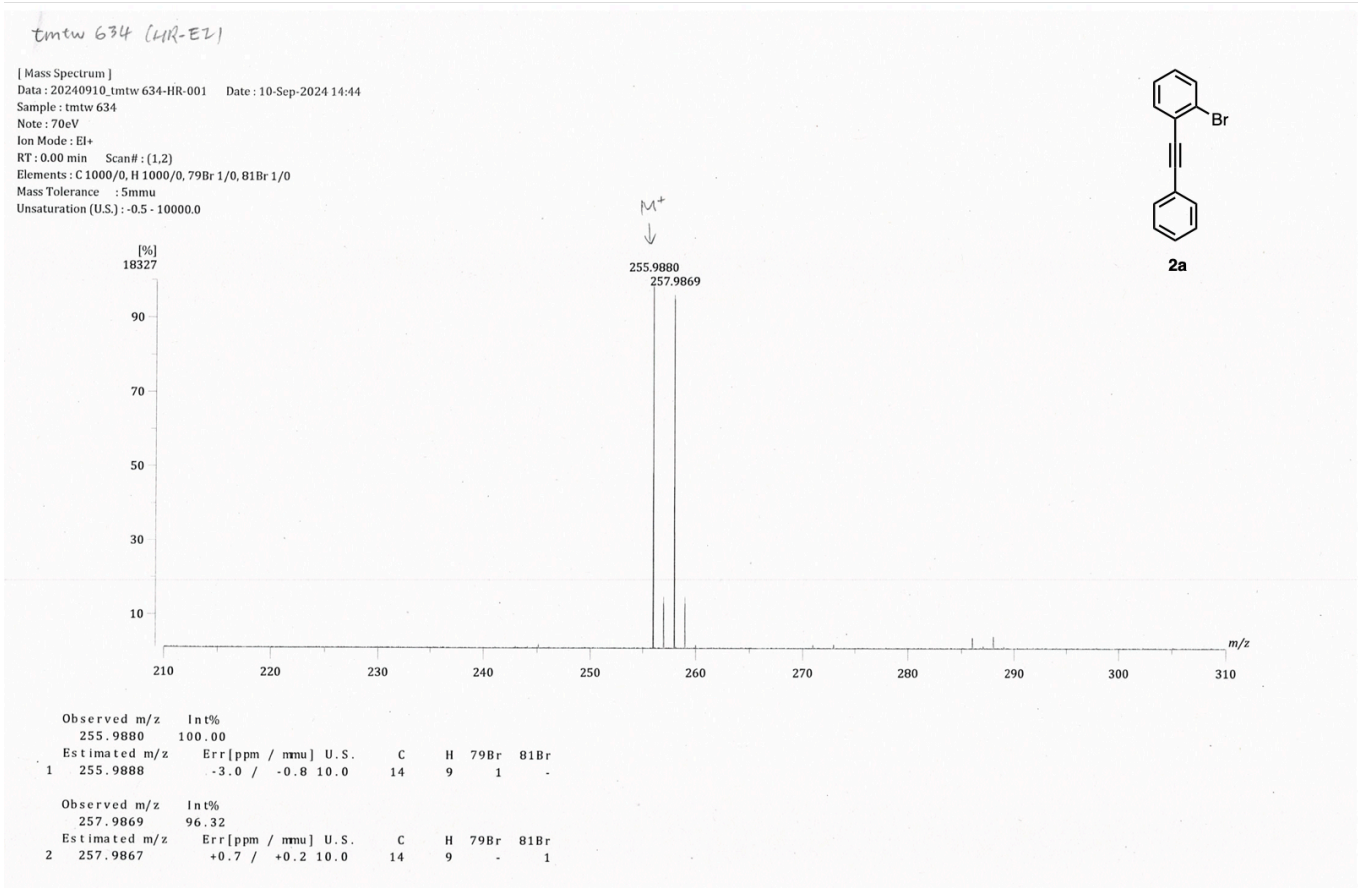


Figure S128. HRMS of **2a**.

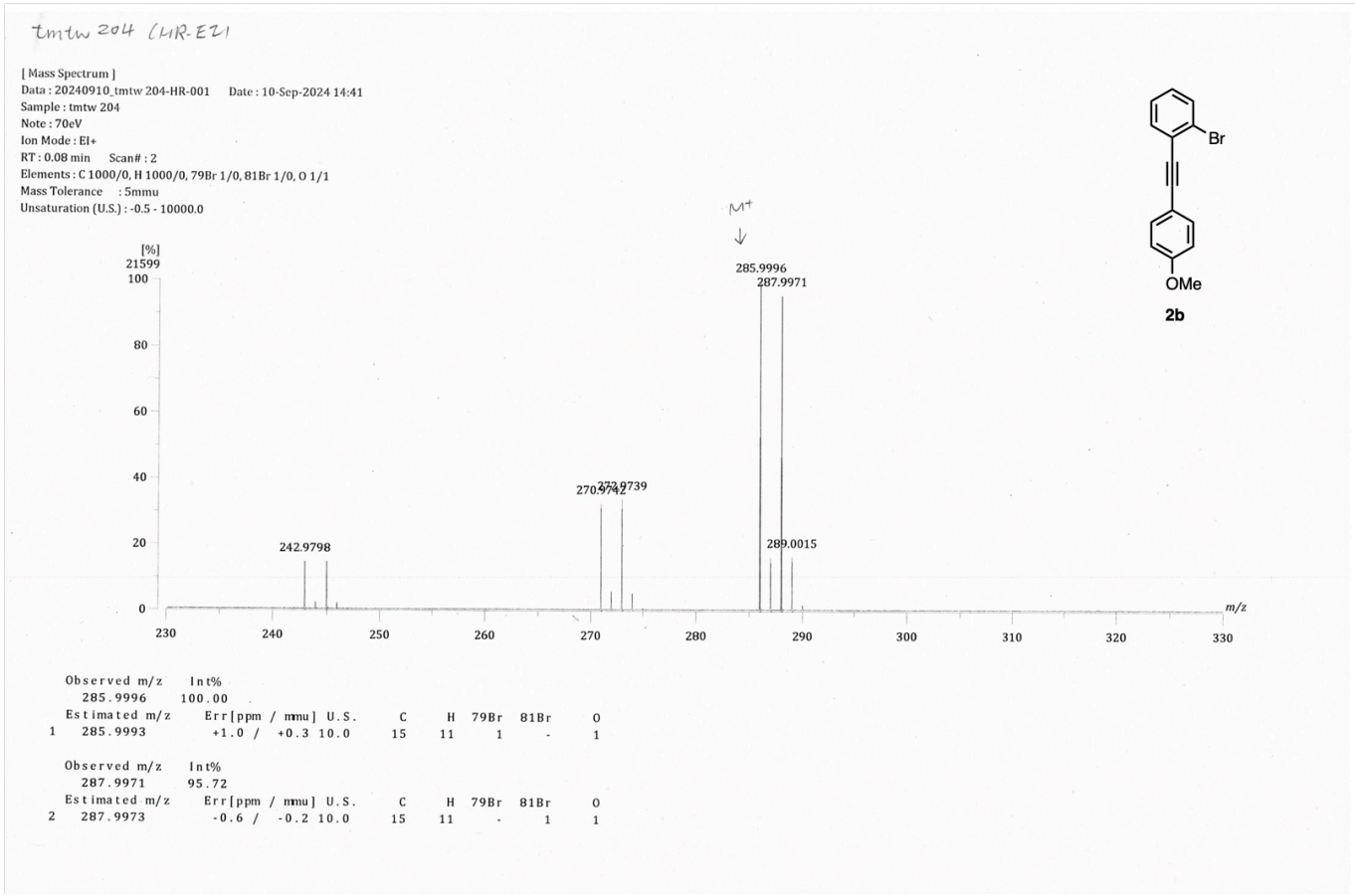


Figure S129. HRMS of **2b**.

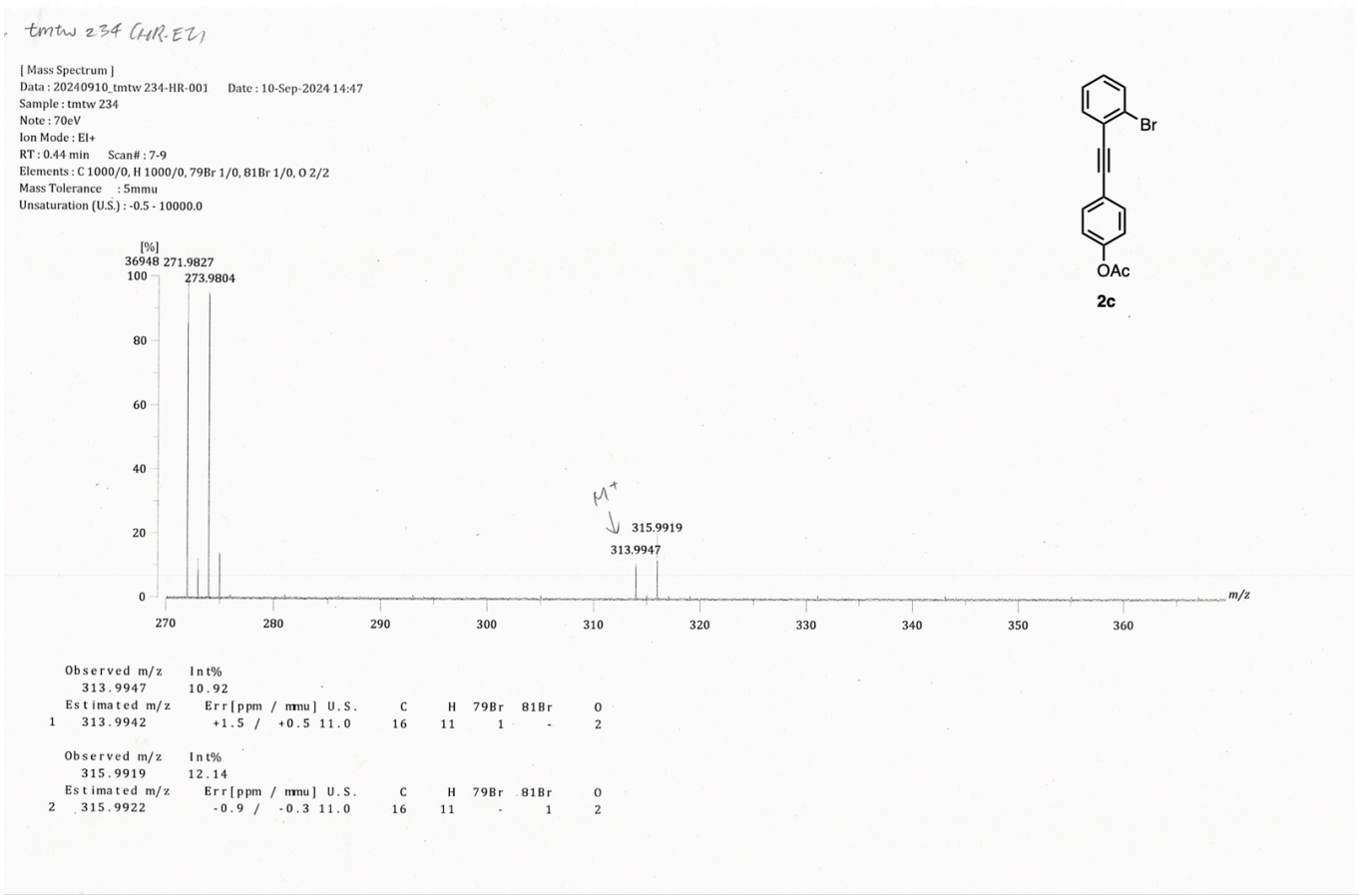


Figure S130. HRMS of **2c**.

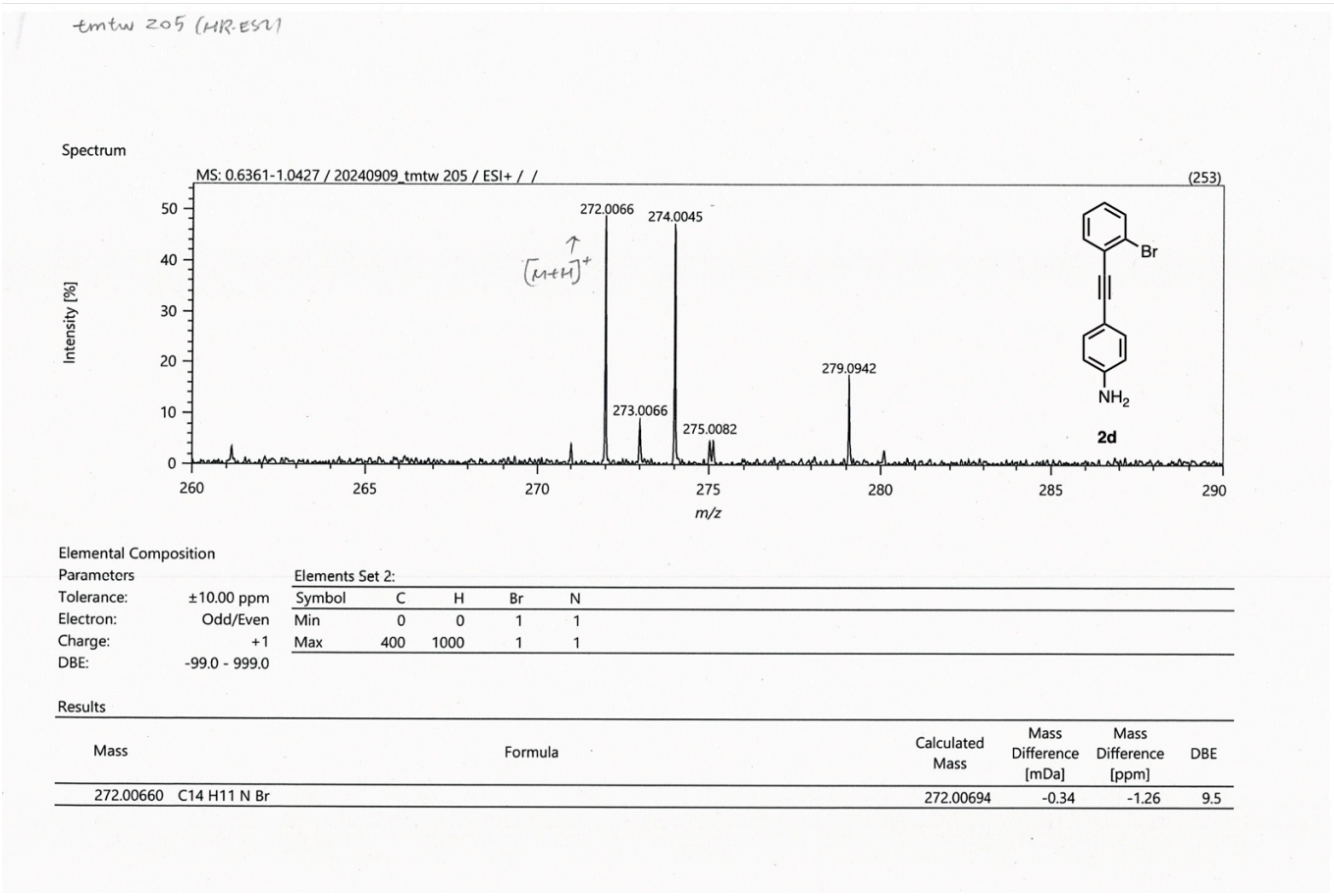


Figure S131. HRMS of **2d**.

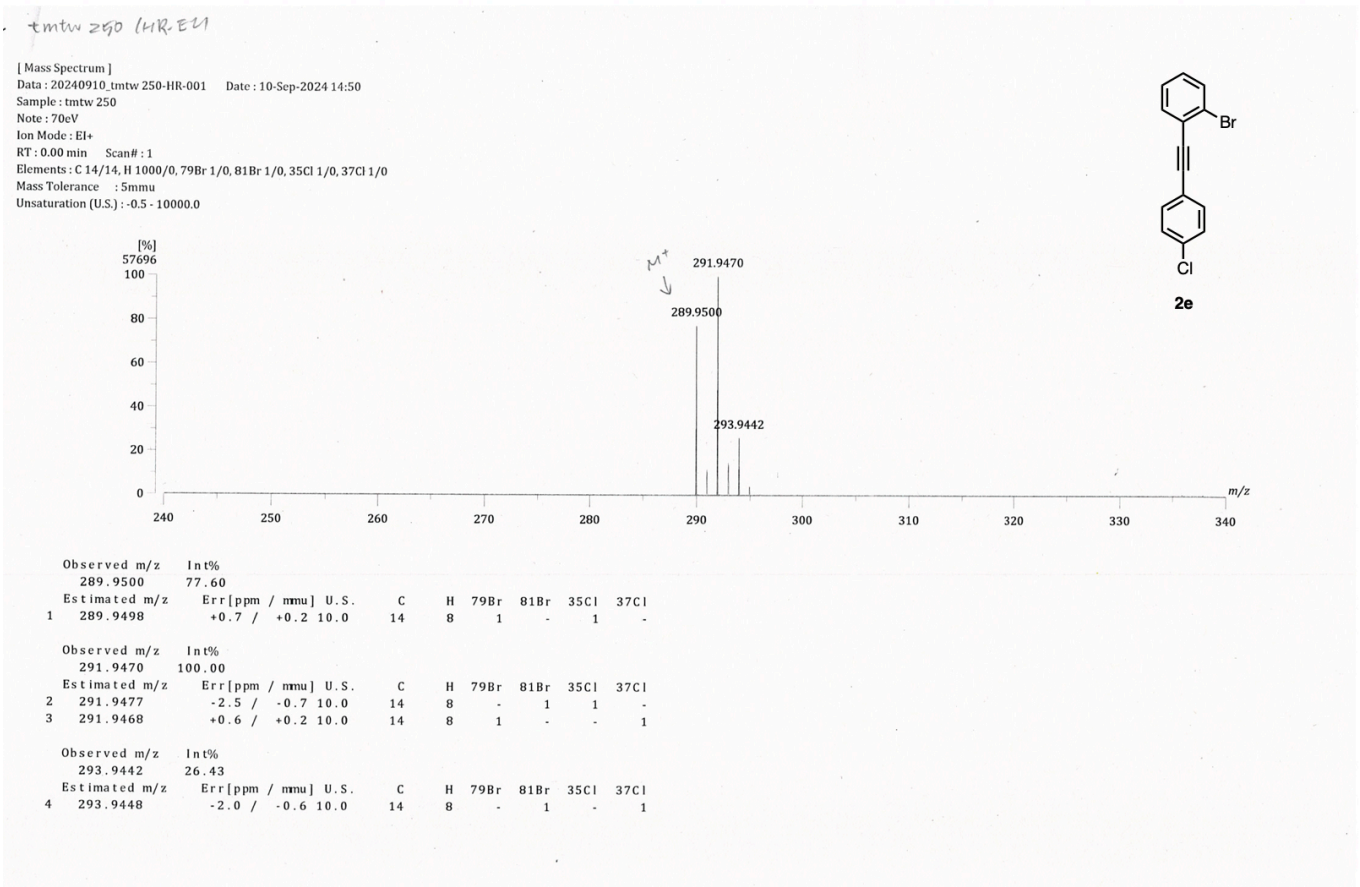


Figure S132. HRMS of **2e**.

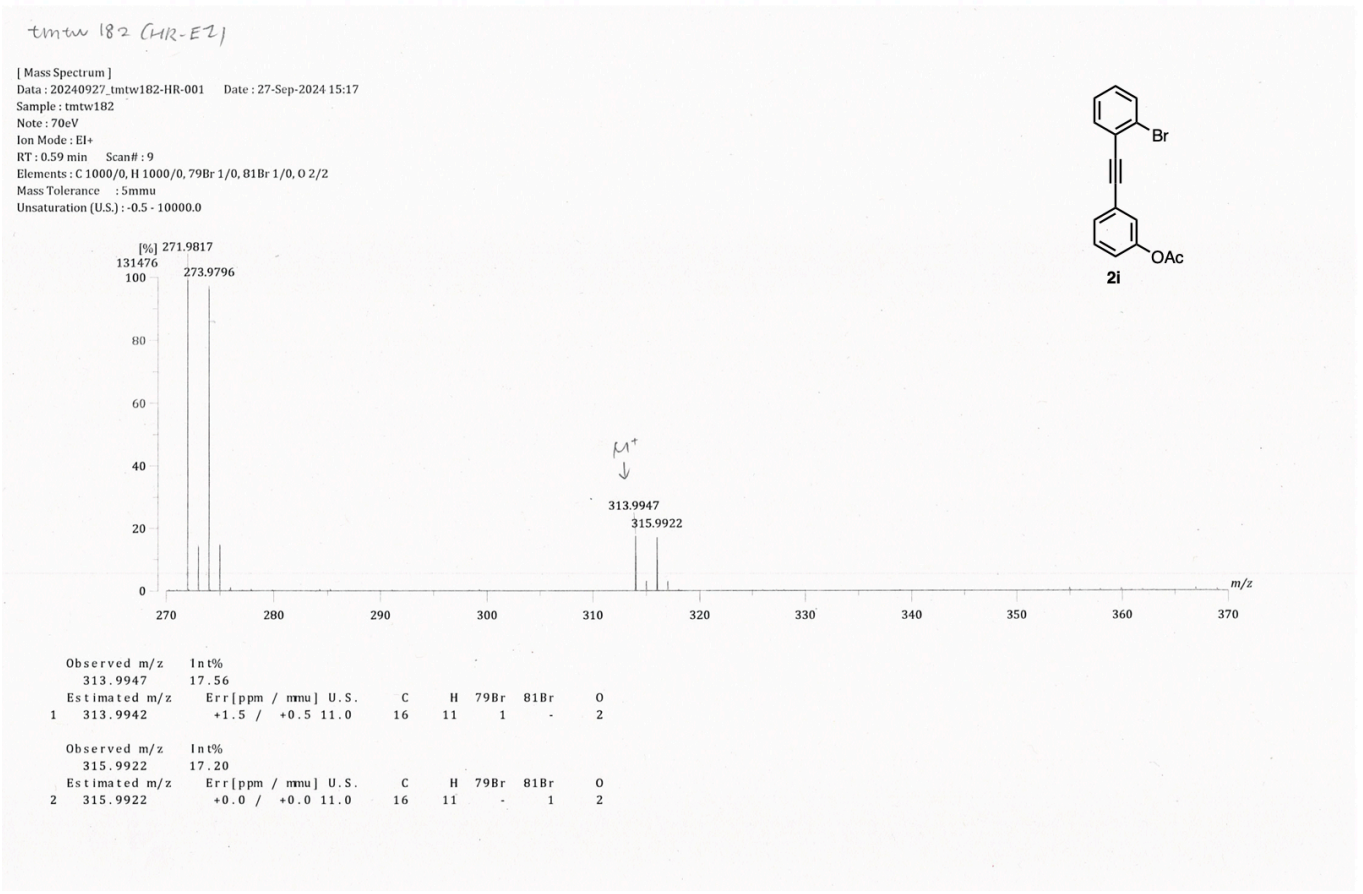


Figure S133. HRMS of **2i**.

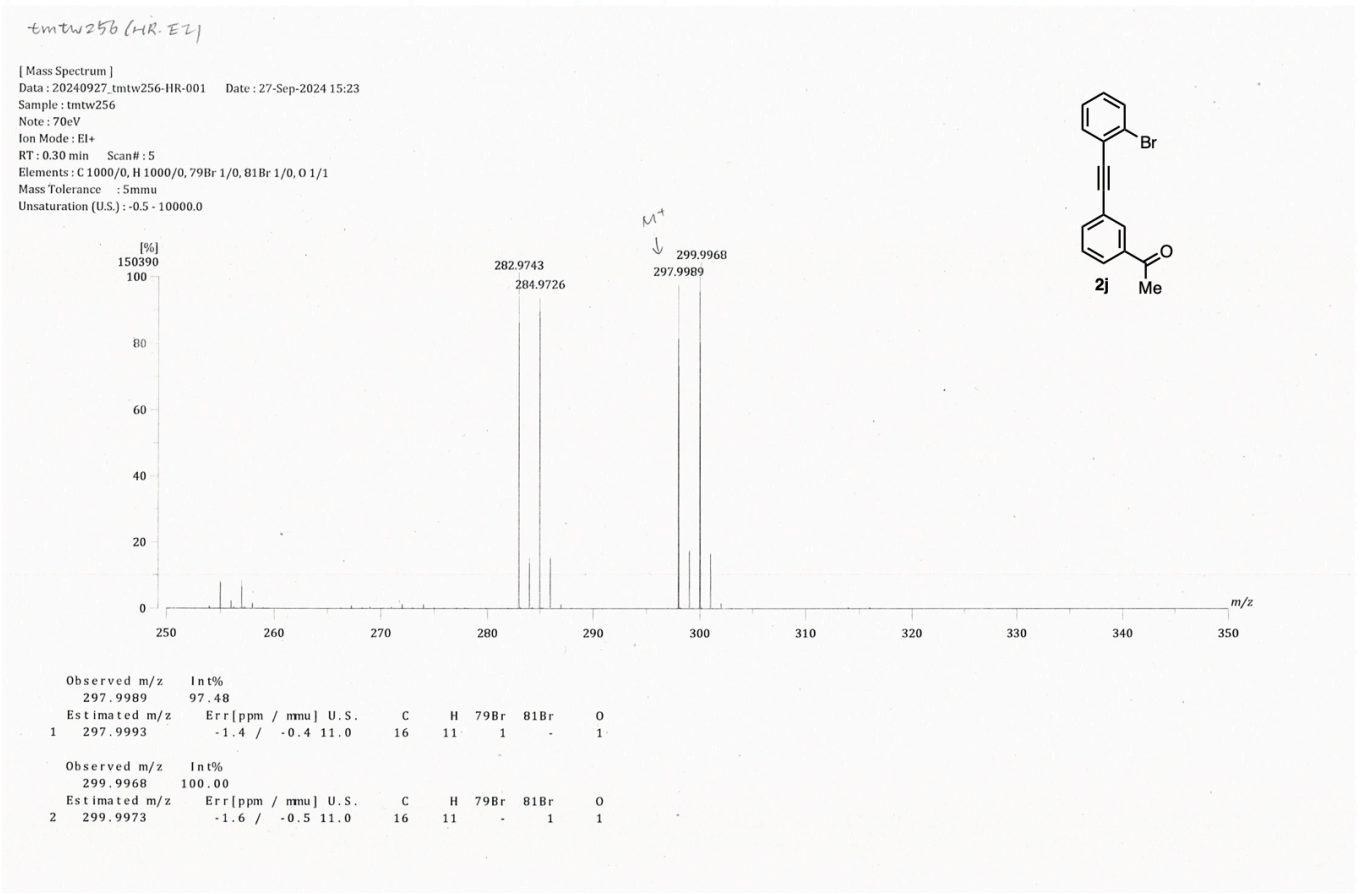


Figure S134. HRMS of **2j**.

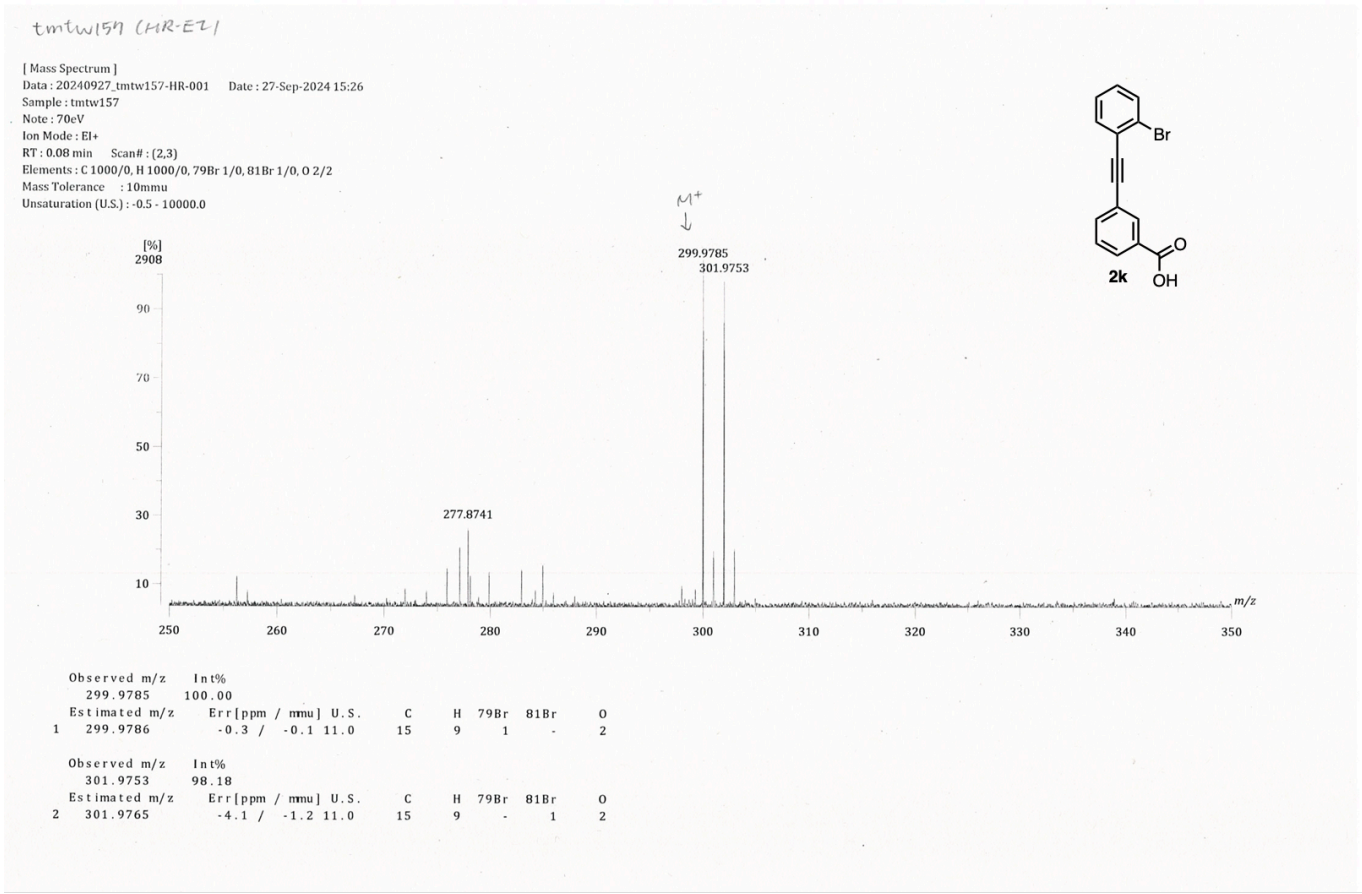


Figure S135. HRMS of **2k**.

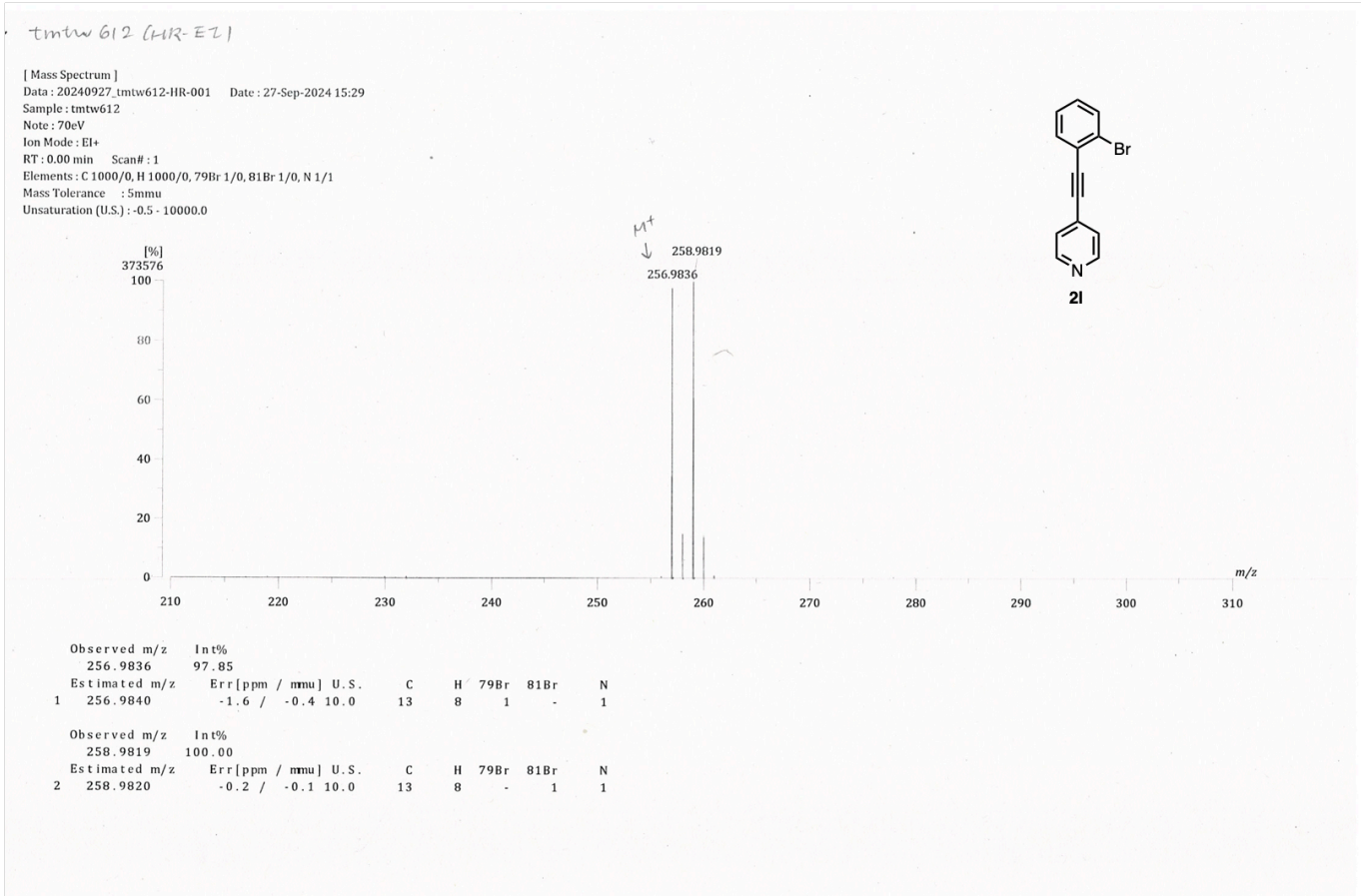


Figure S136. HRMS of **2l**.

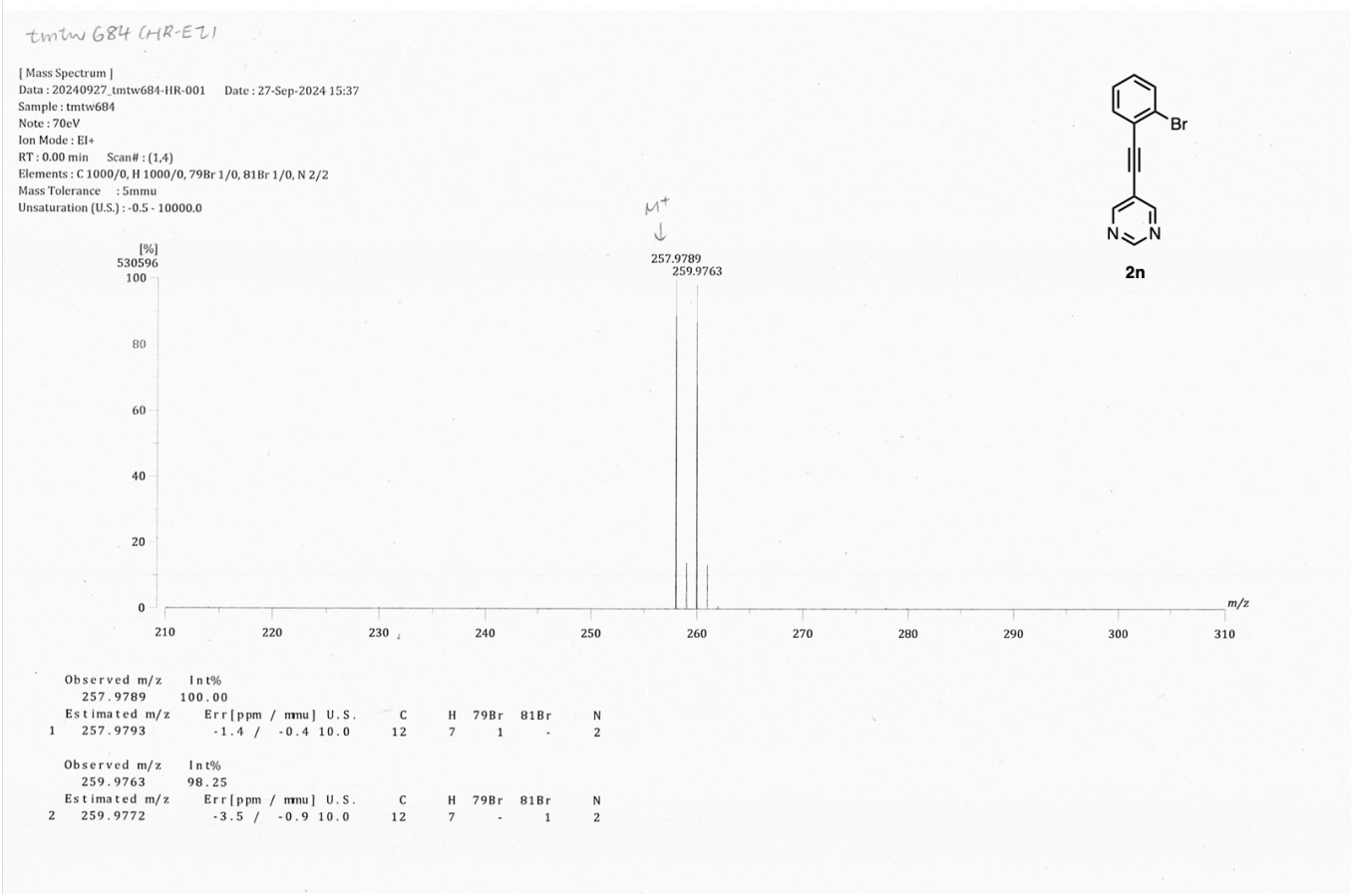


Figure S137. HRMS of **2n**.

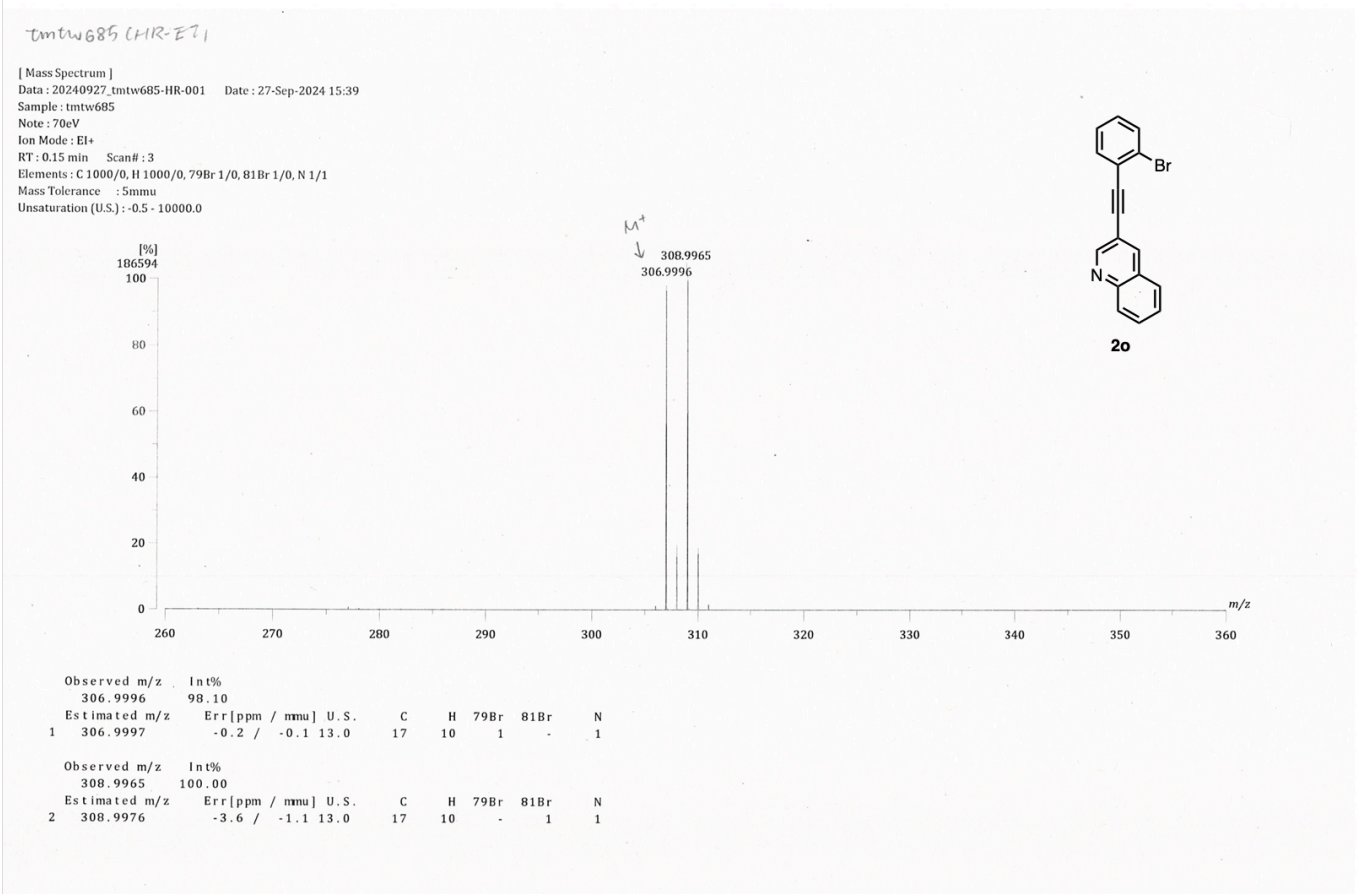


Figure S138. HRMS of **2o**.

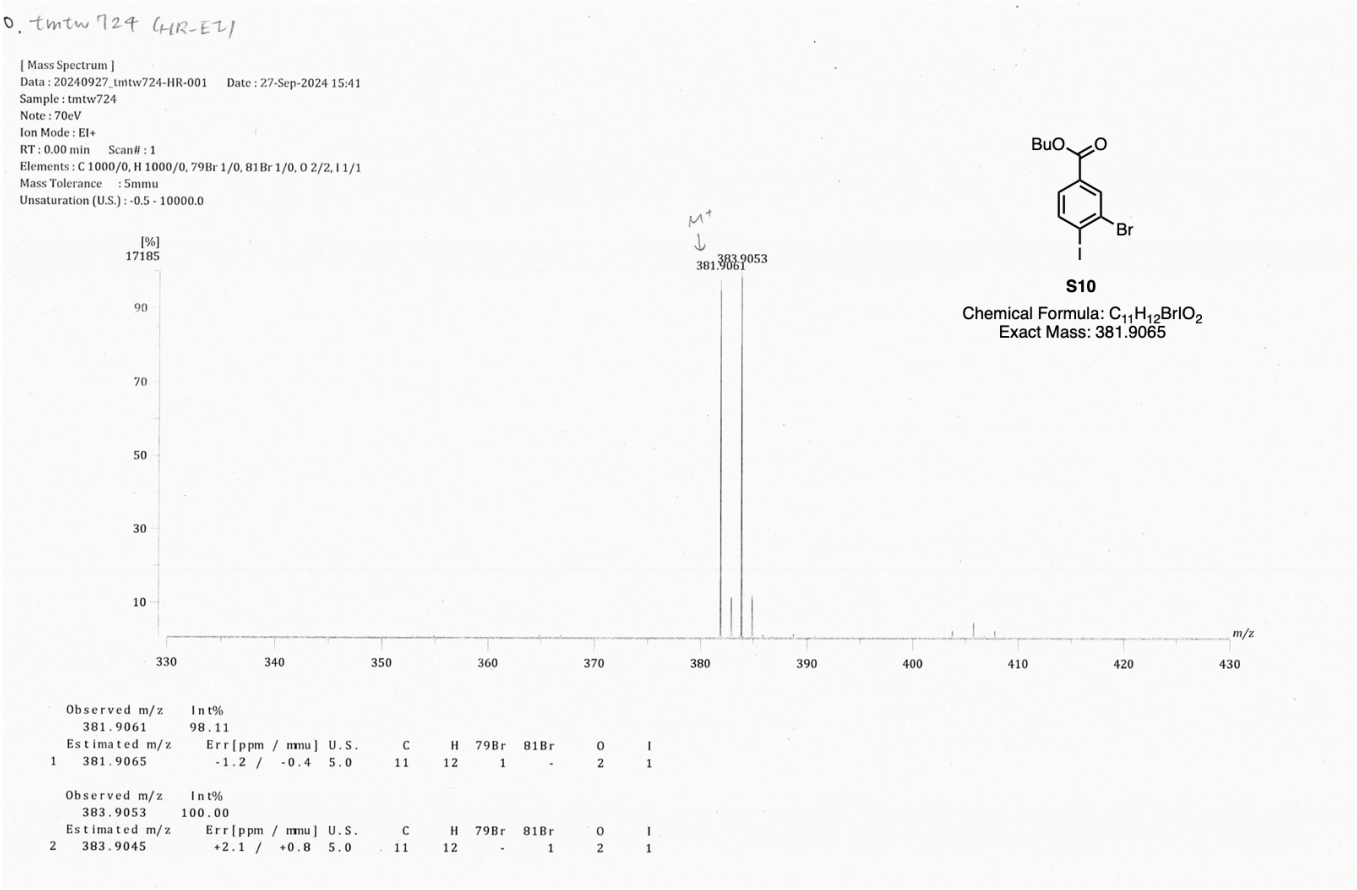


Figure S139. HRMS of **S10**.

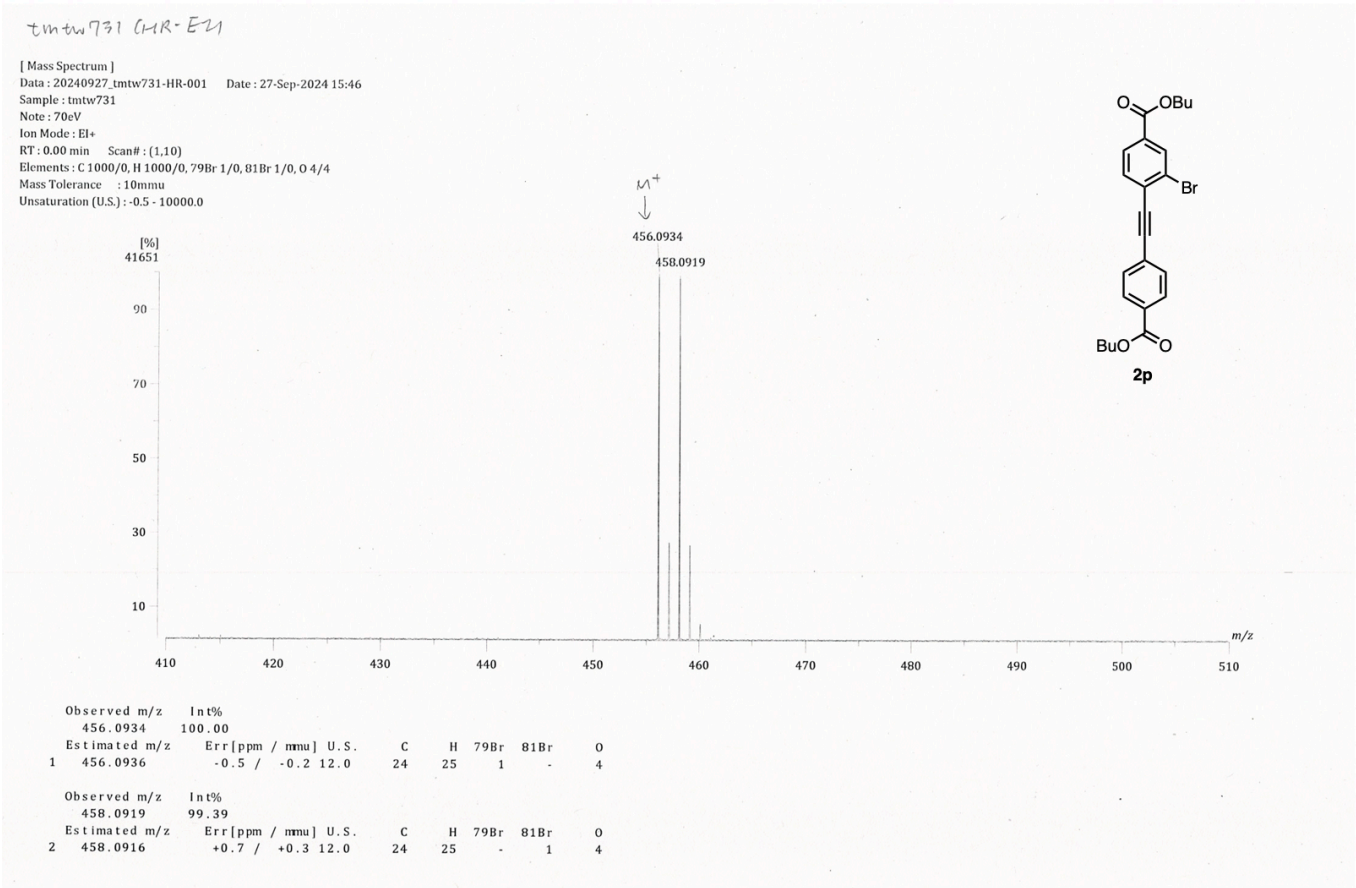


Figure S140. HRMS of **2p**.

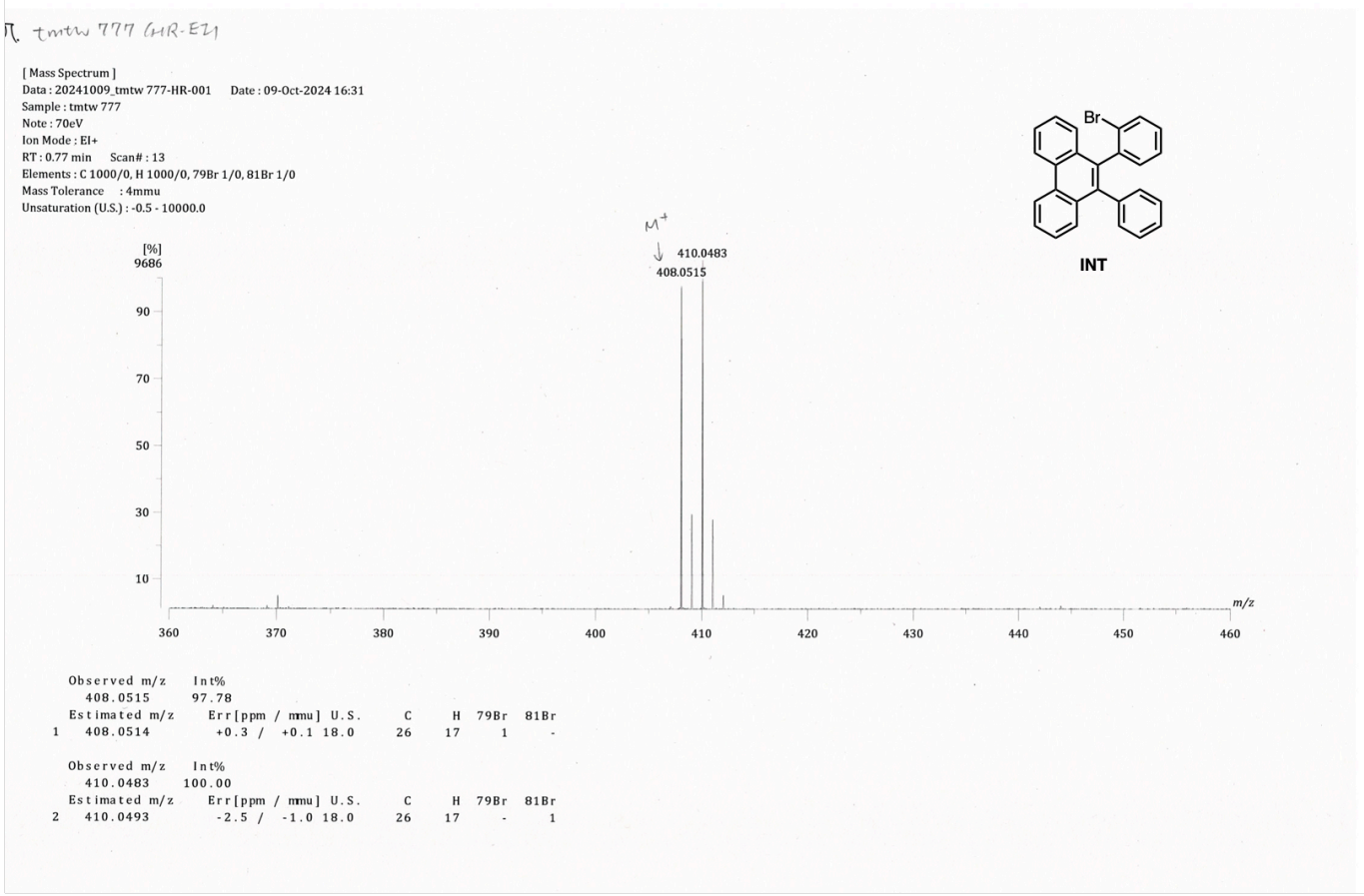


Figure S141. HRMS of **INT**.

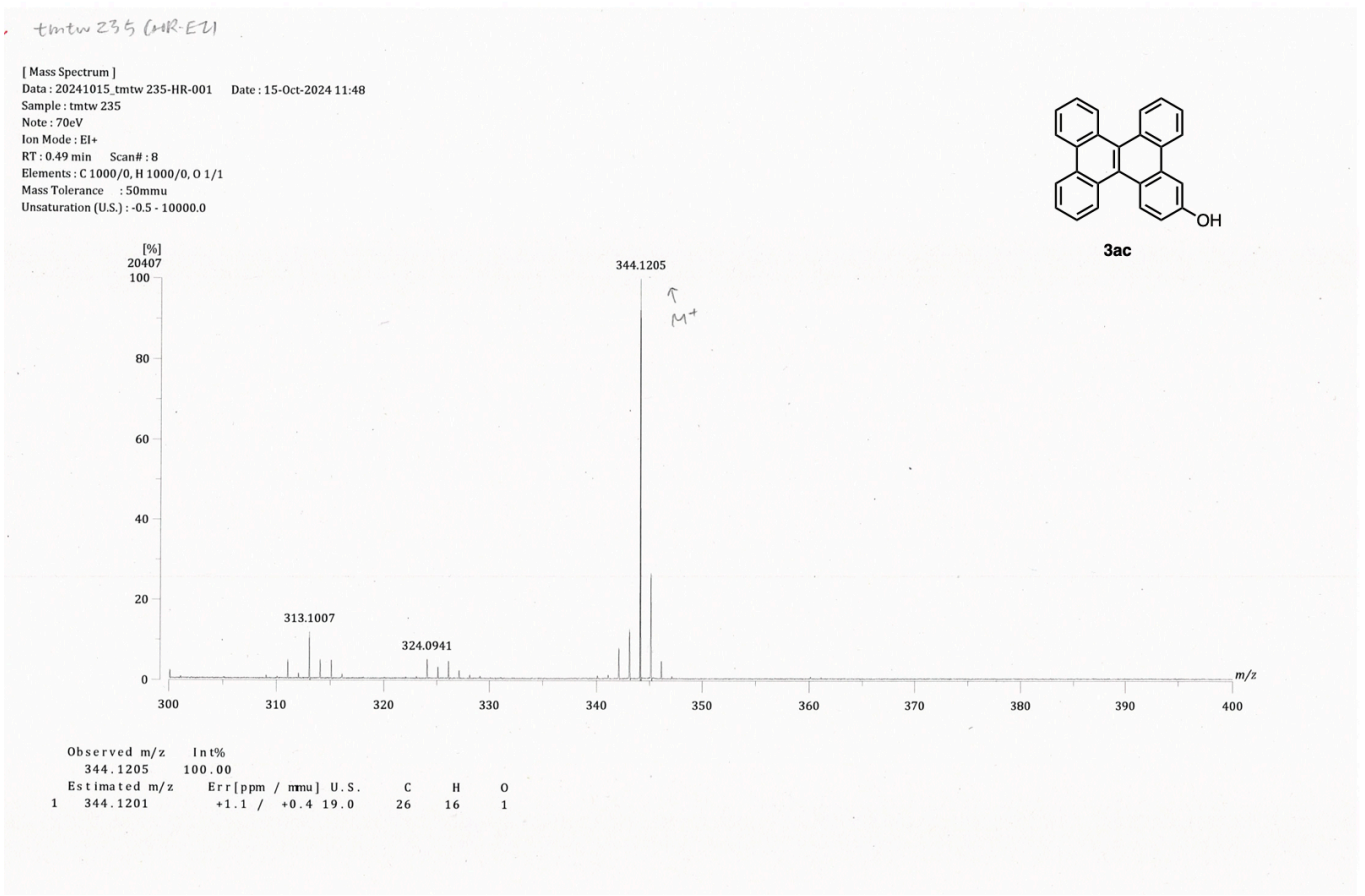


Figure S142. HRMS of **3ac**.

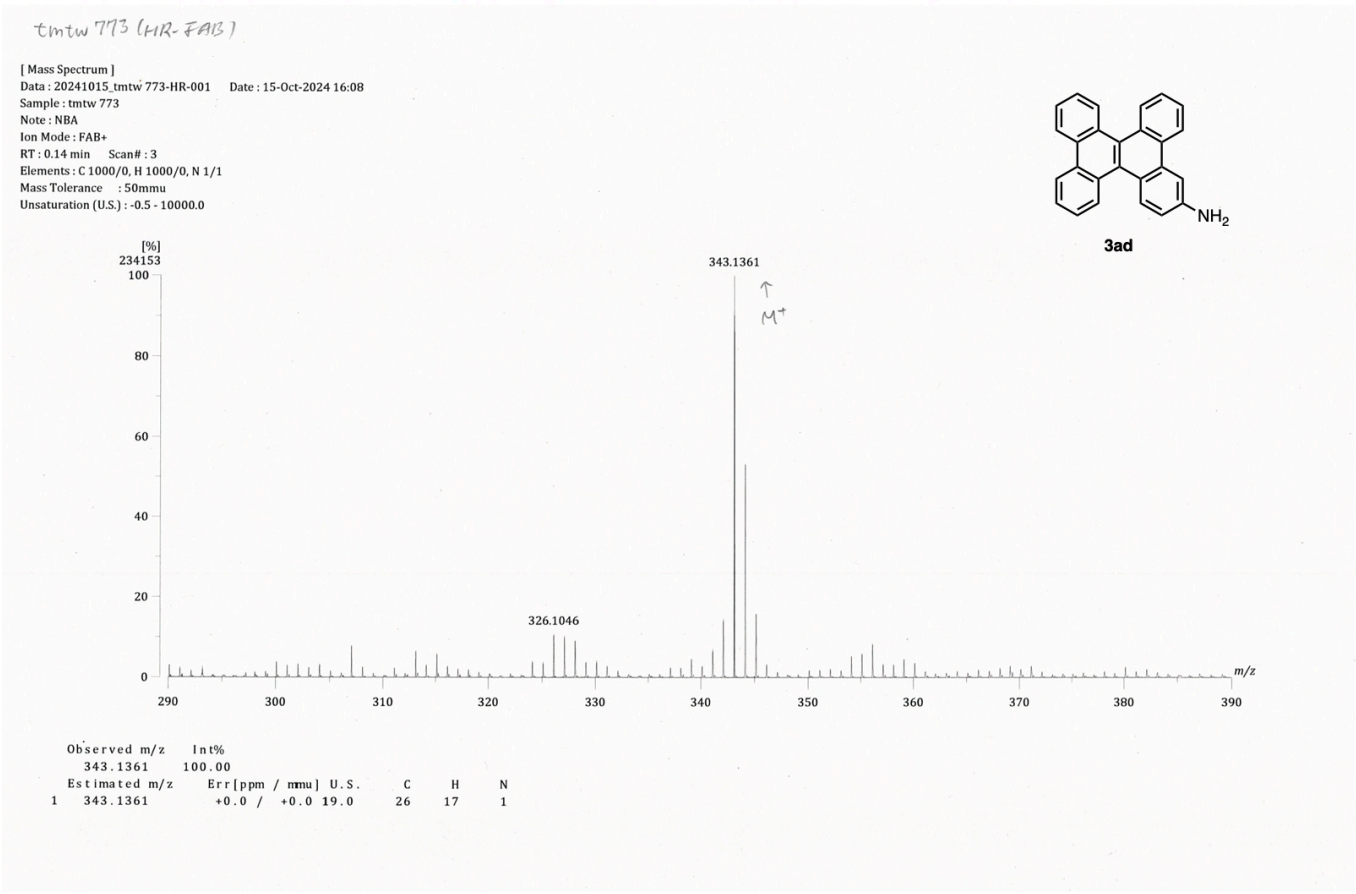


Figure S143. HRMS of **3ad**.

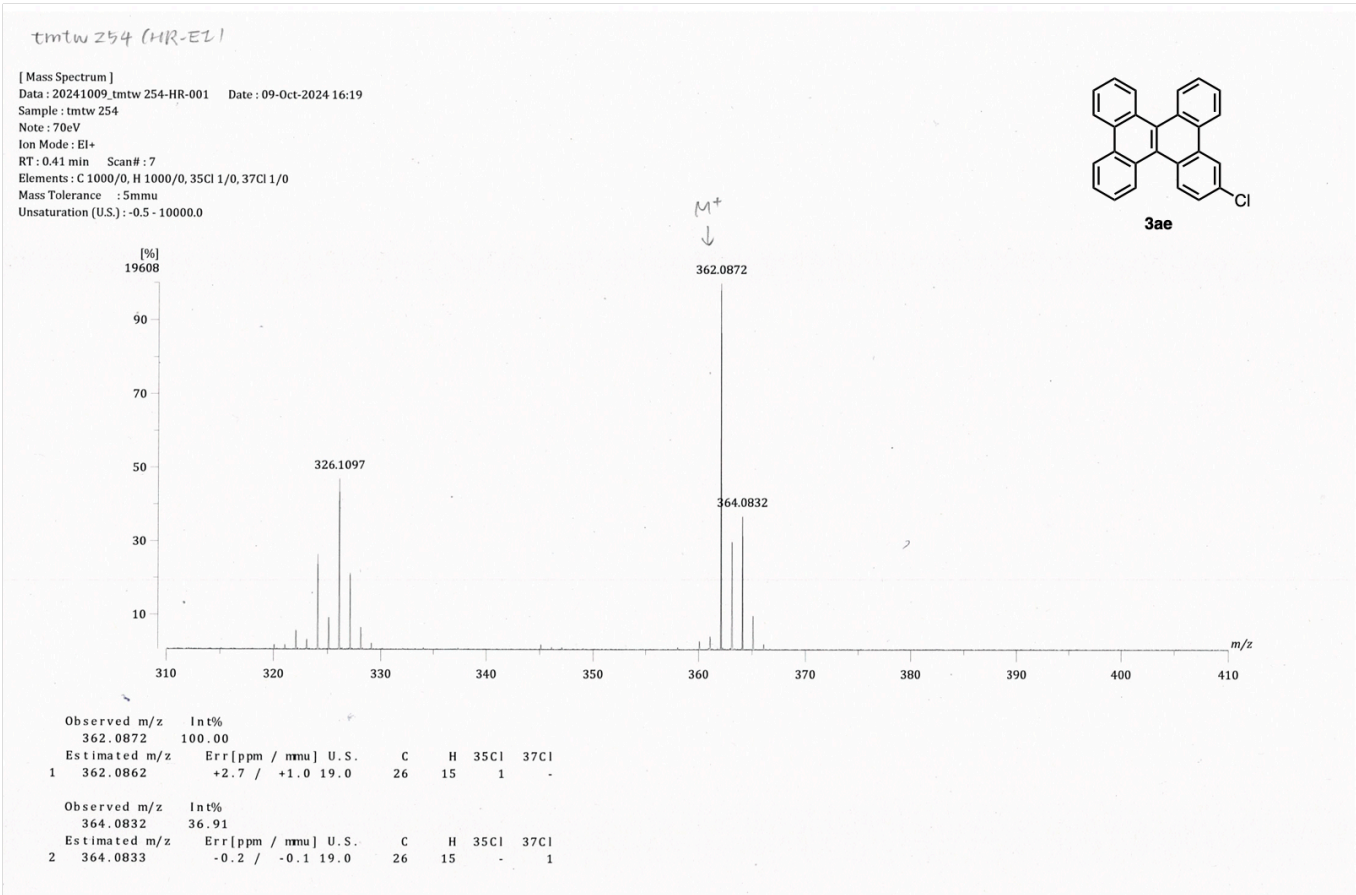


Figure S144. HRMS **of 3ae**.

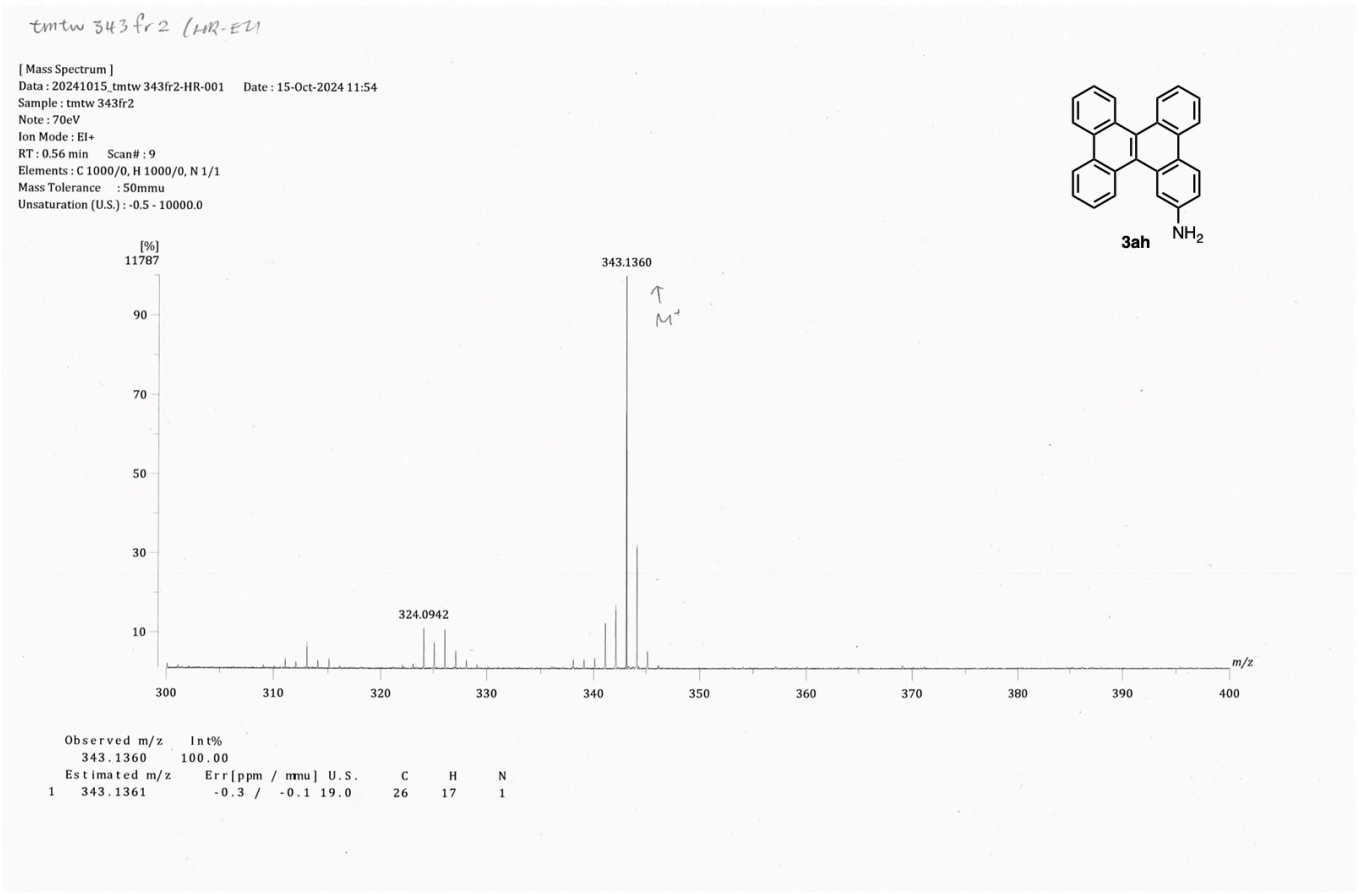


Figure S145. HRMS of **3ah**.

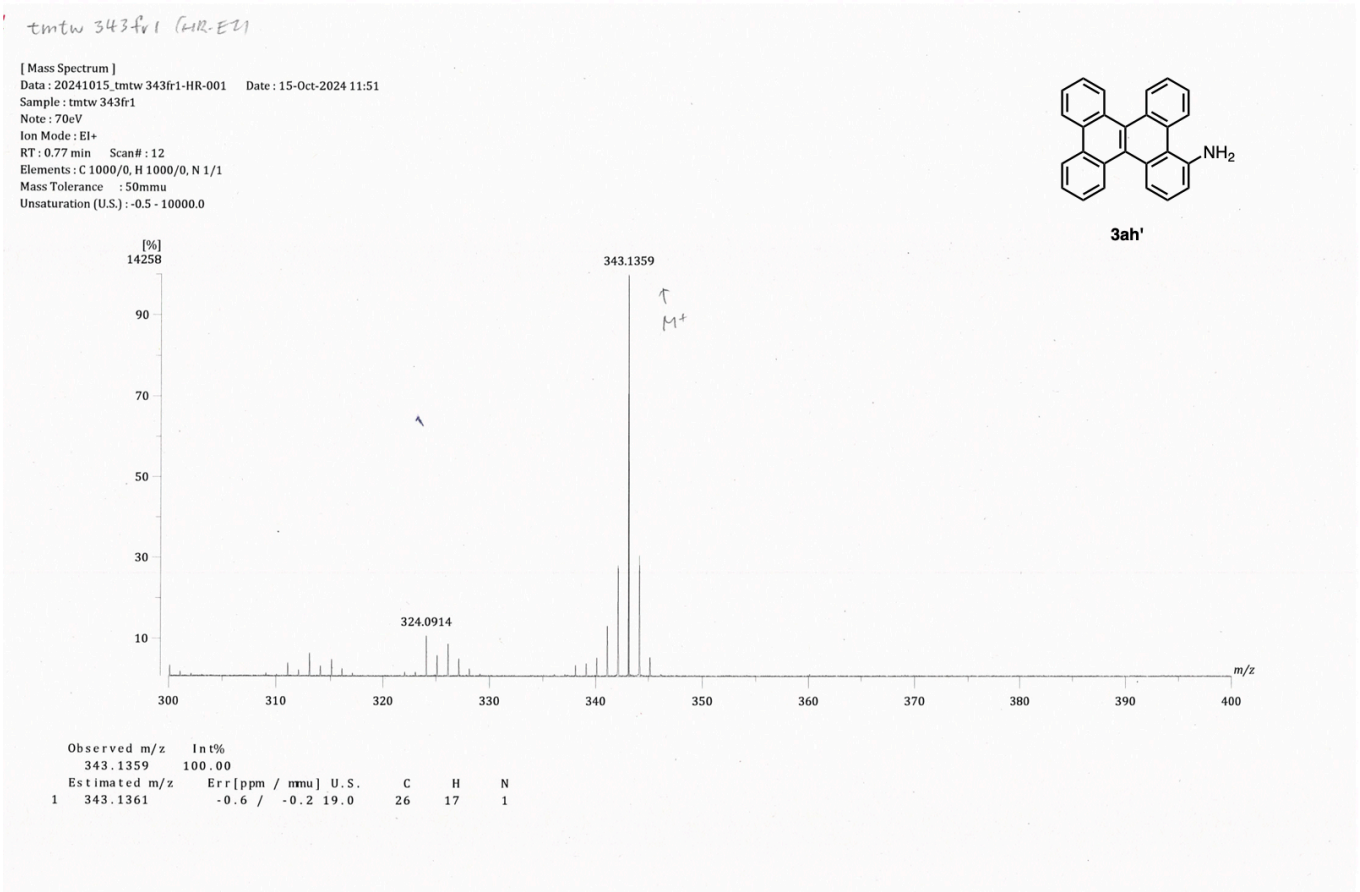


Figure S146. HRMS of **3ah'**.

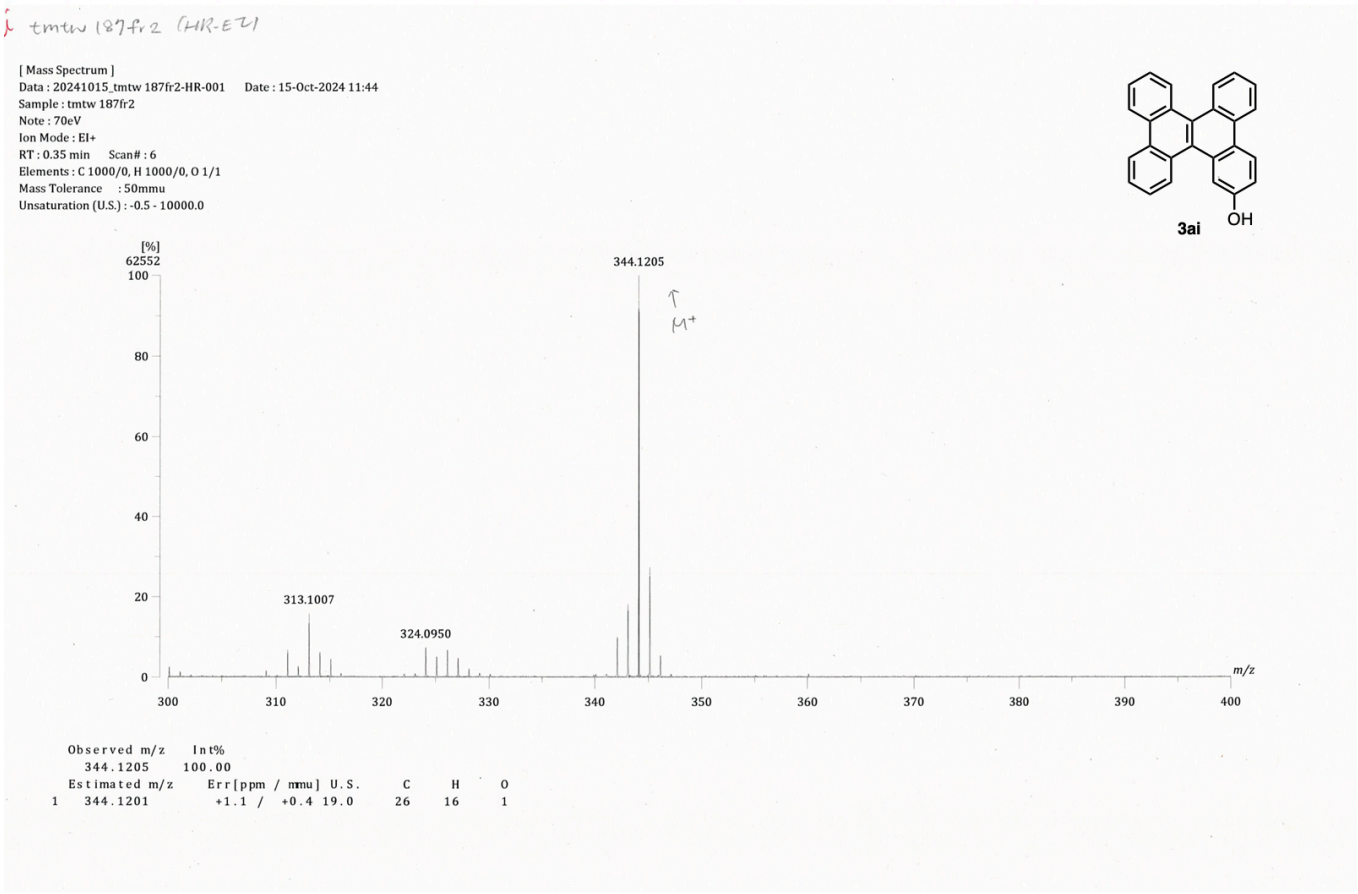


Figure S147. HRMS of **3ai**.

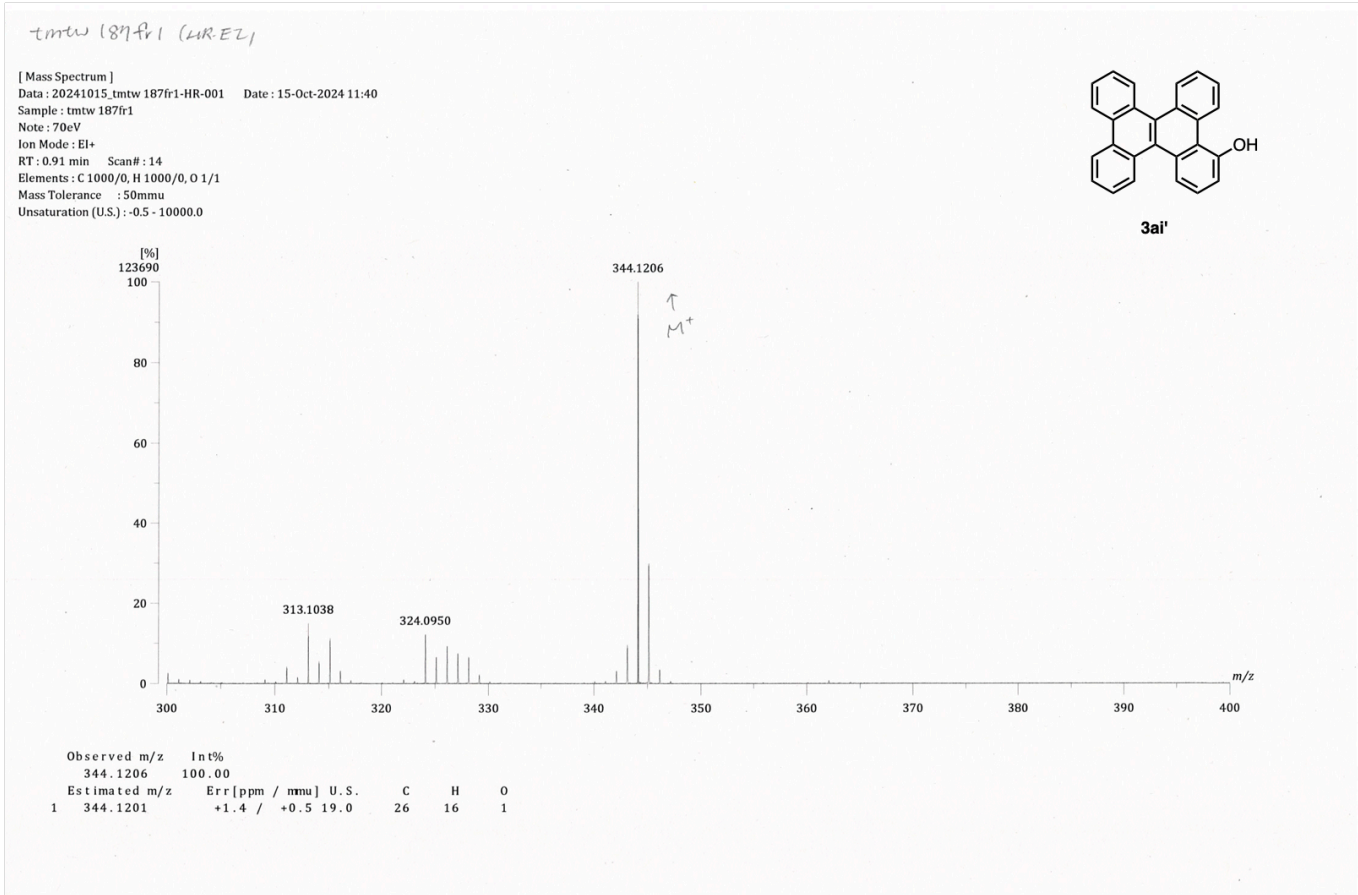


Figure S148. HRMS of **3ai'**.

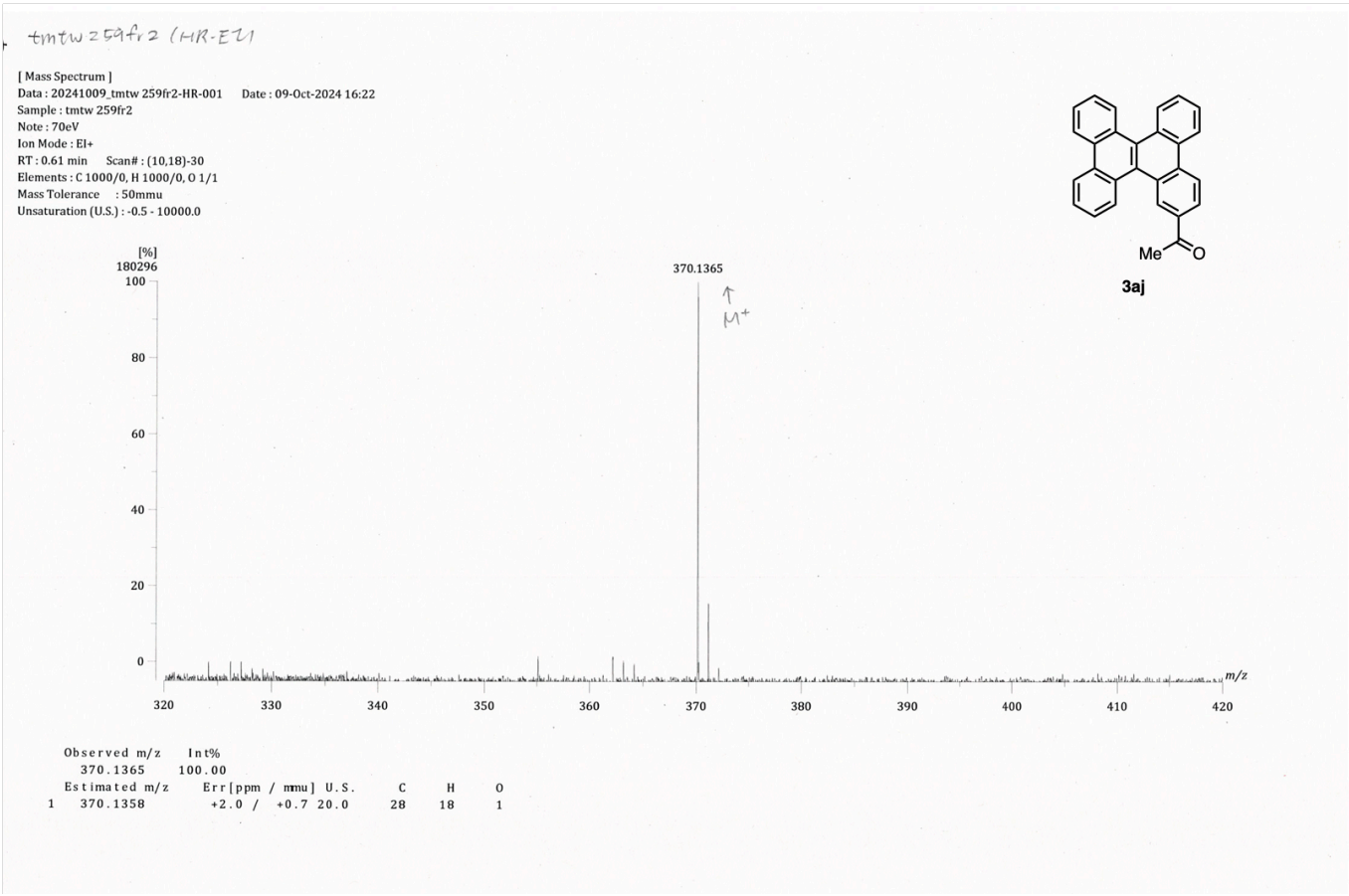


Figure S149. HRMS of **3aj**.

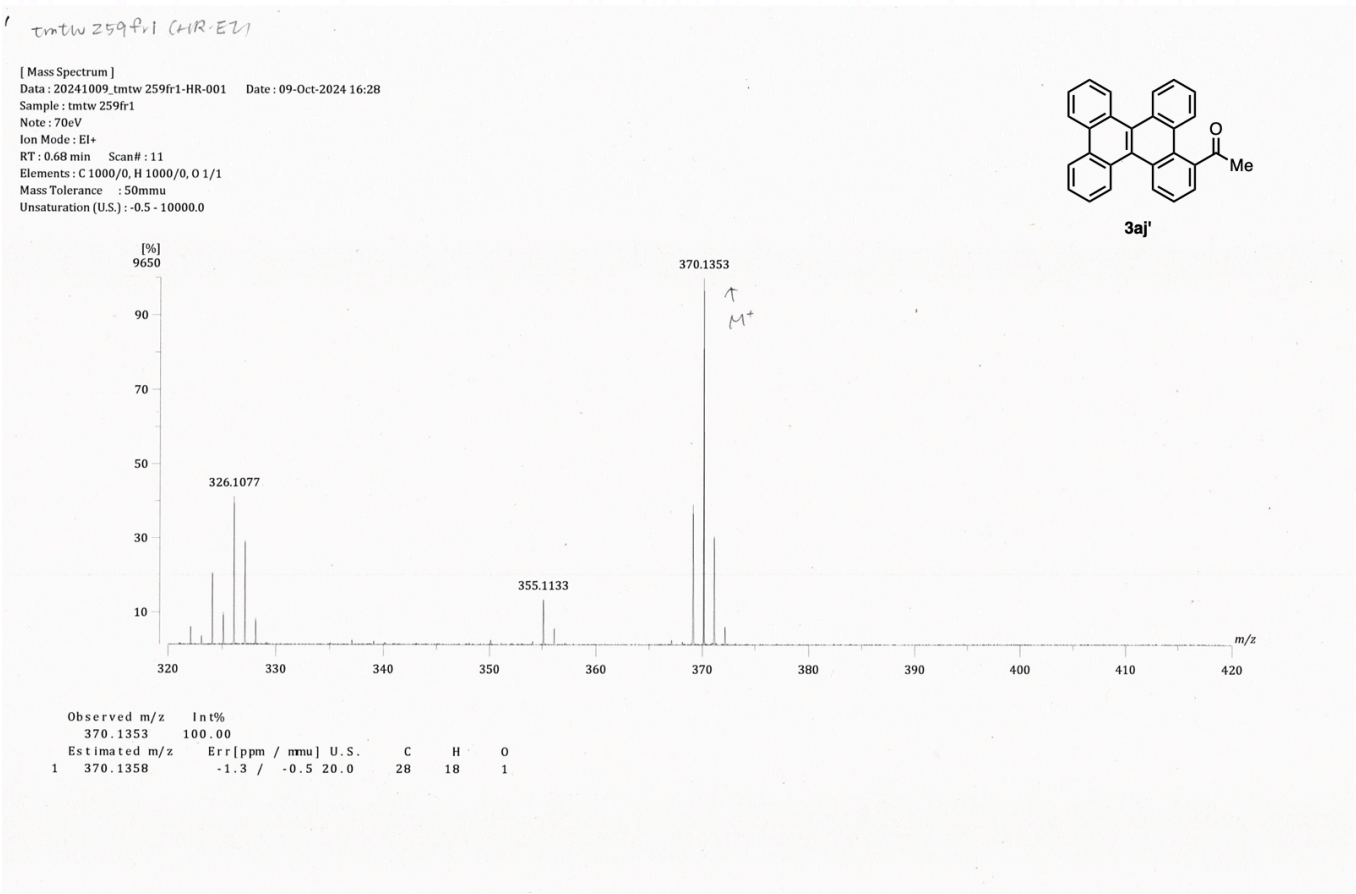


Figure S150. HRMS of **3aj'**.

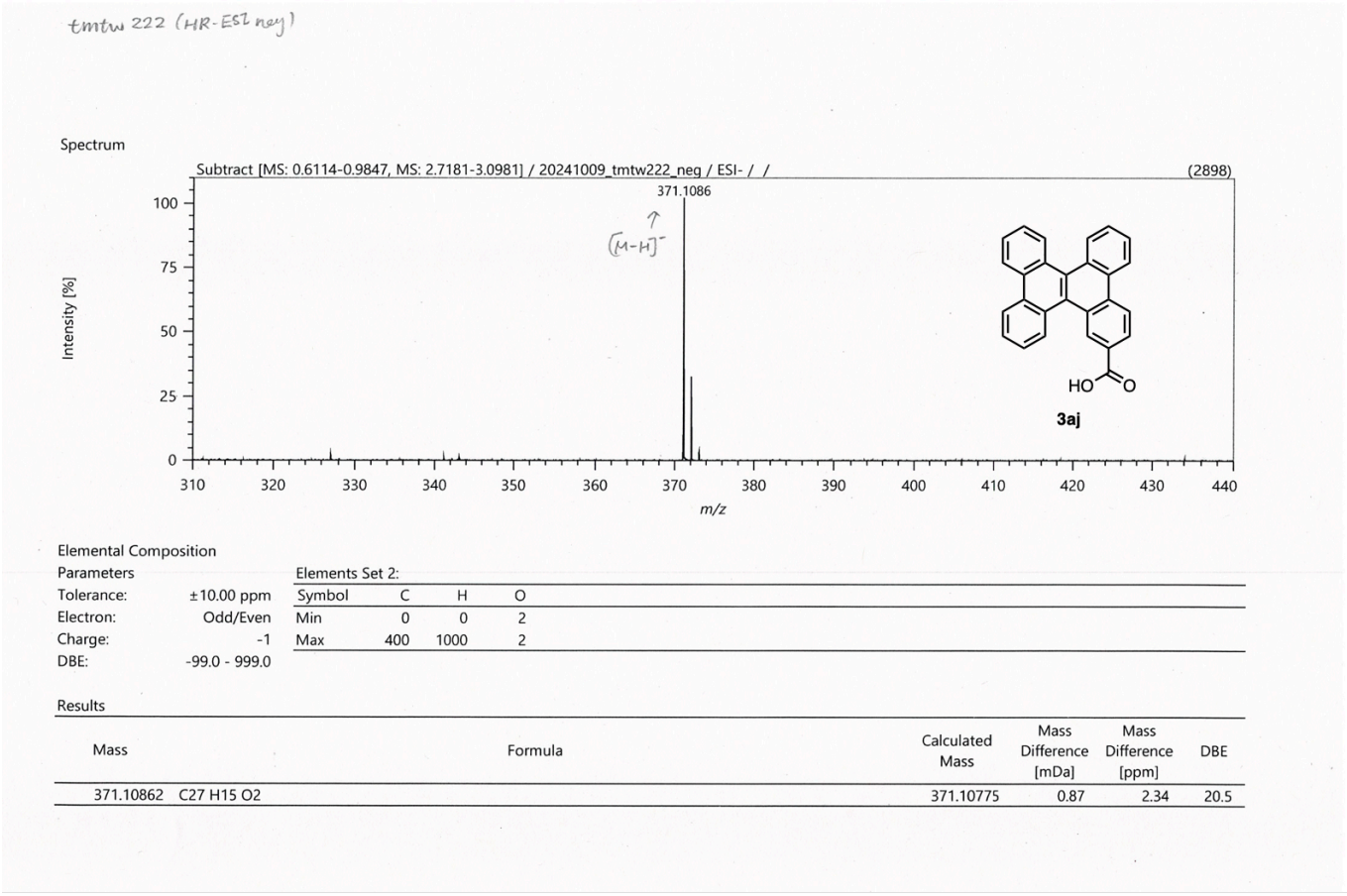


Figure S151. HRMS of **3ak**.

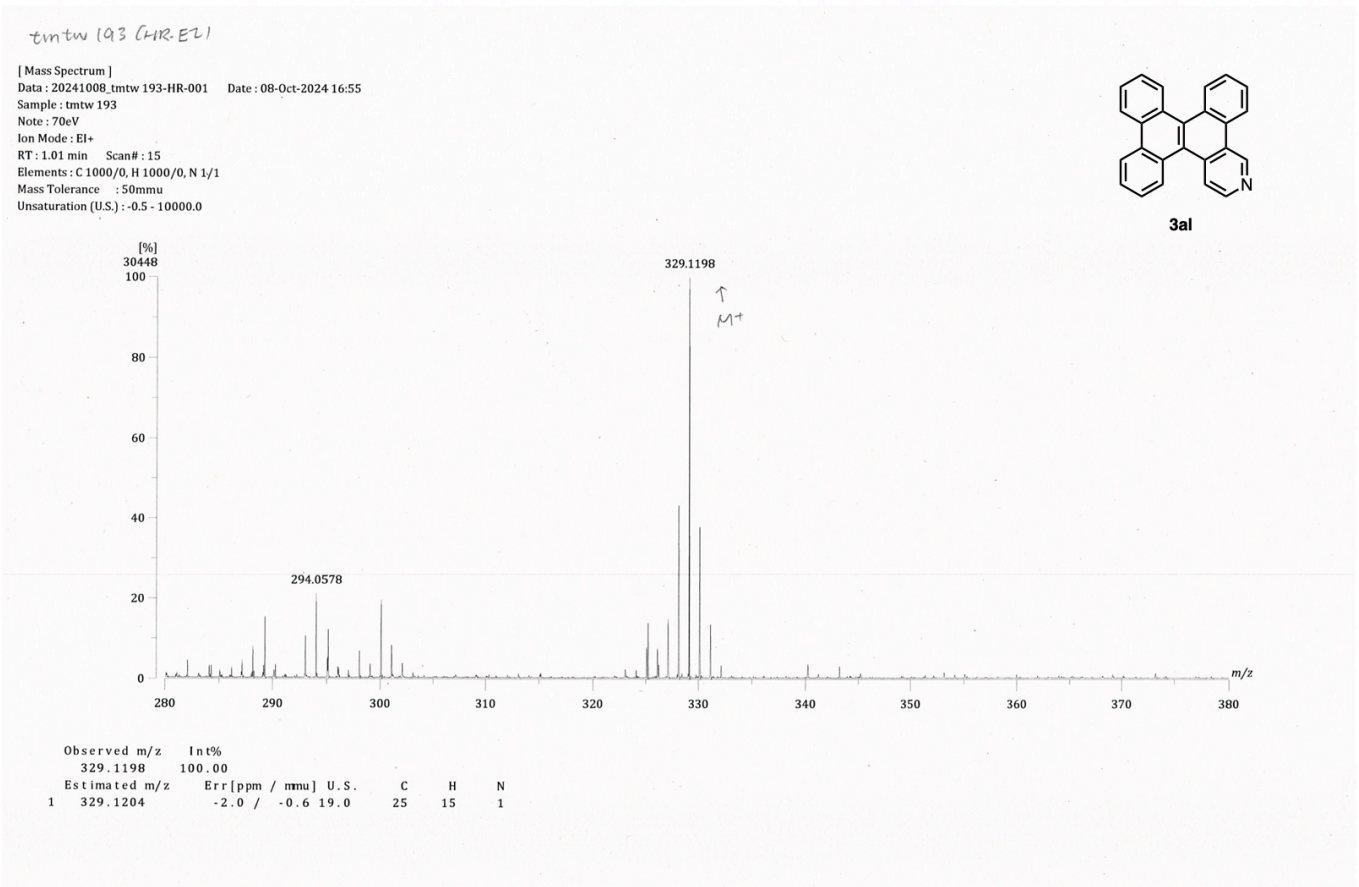


Figure S152. HRMS of **3al**.

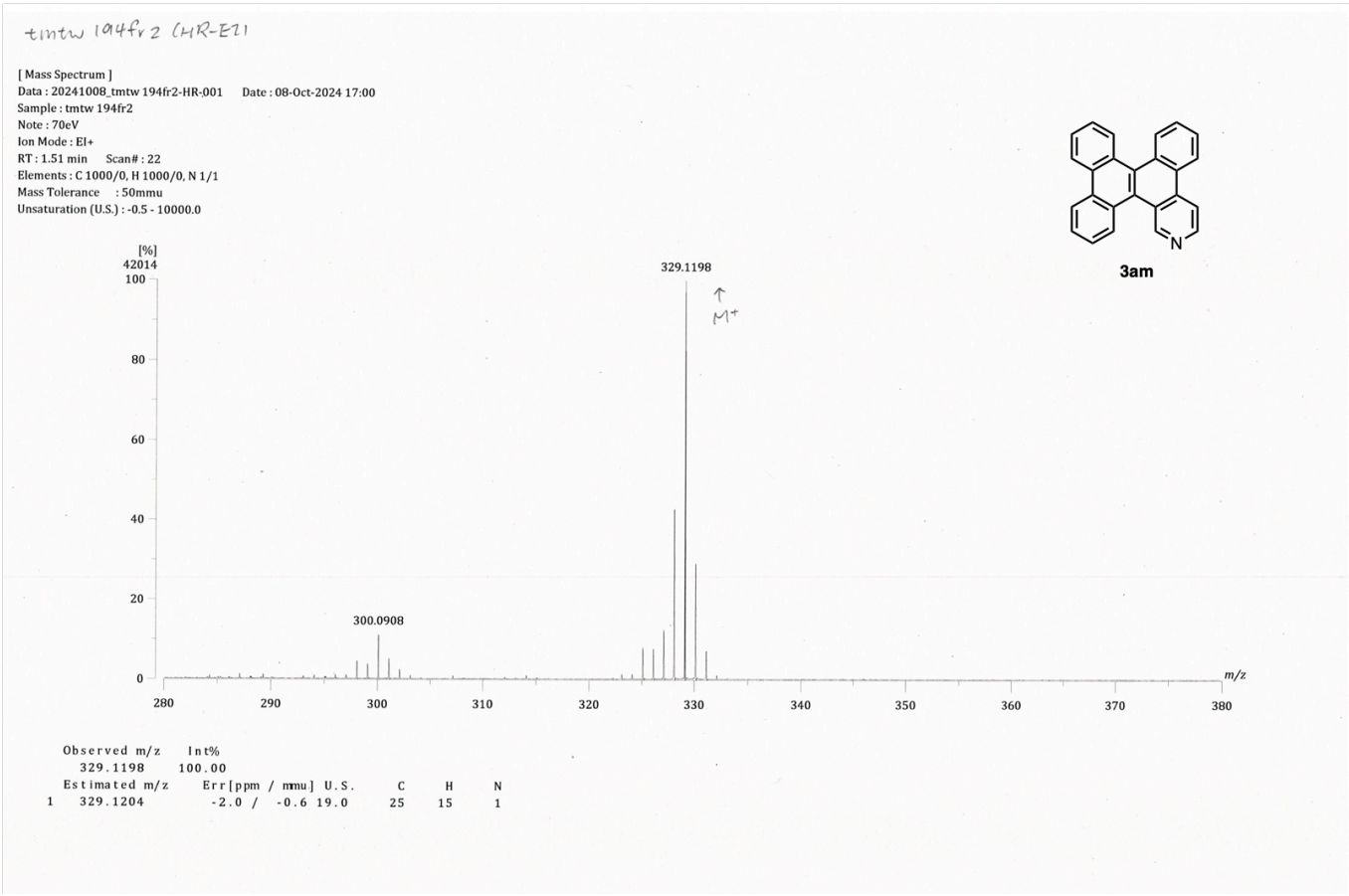


Figure S153. HRMS of **3am**.

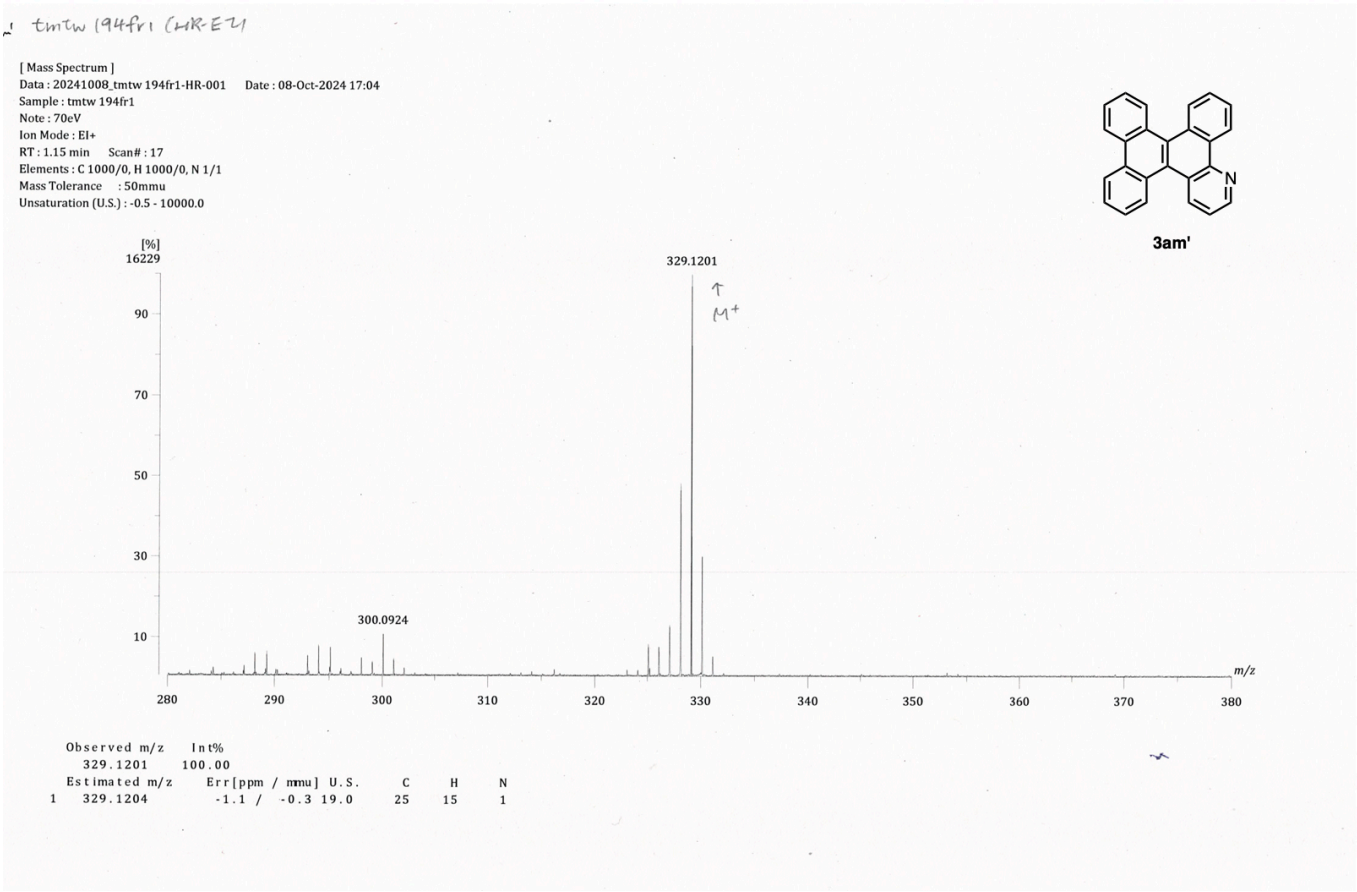


Figure S154. HRMS of **3am'**.

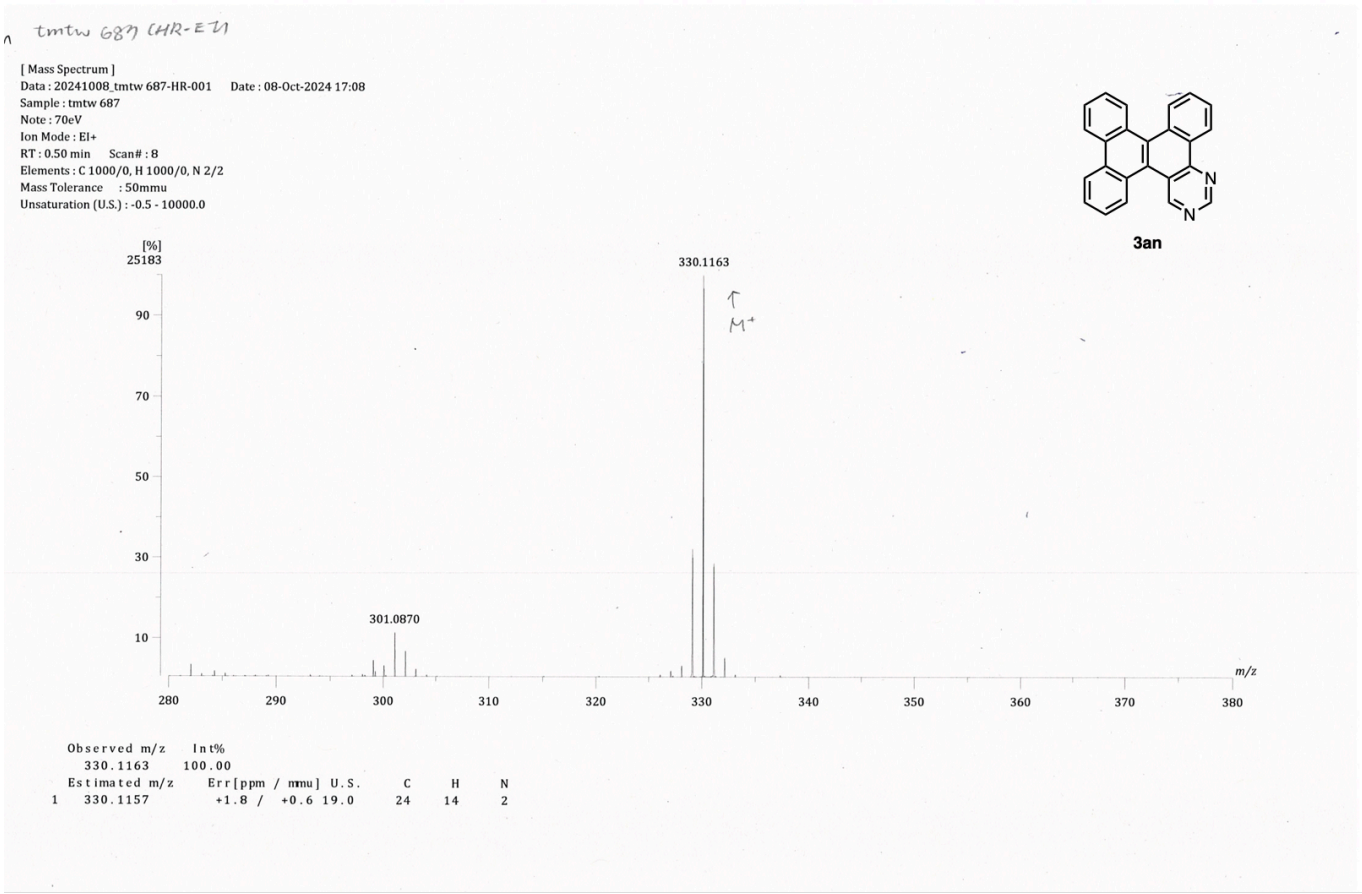


Figure S155. HRMS of **3an**.

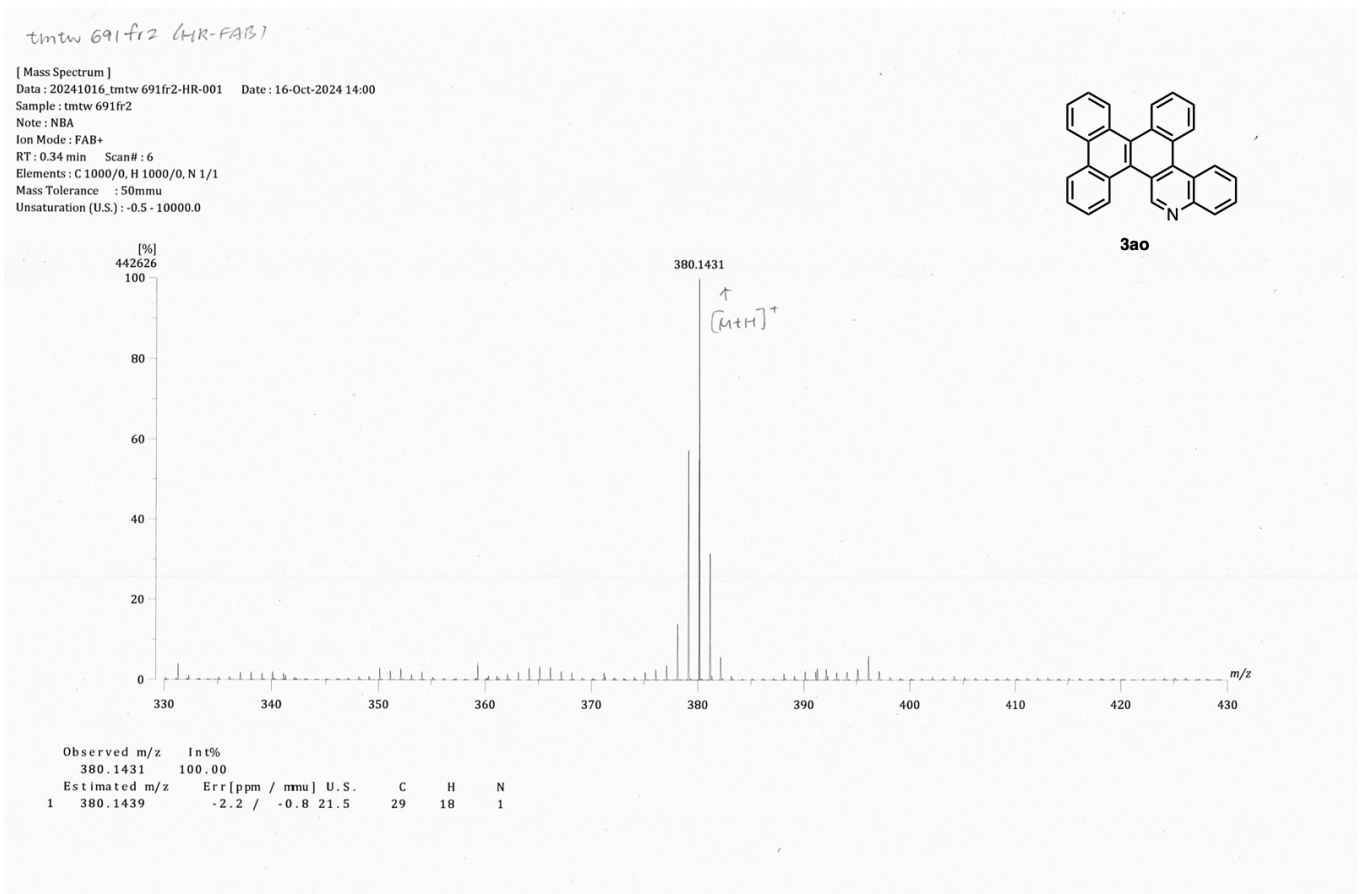


Figure S156. HRMS of **3ao**.

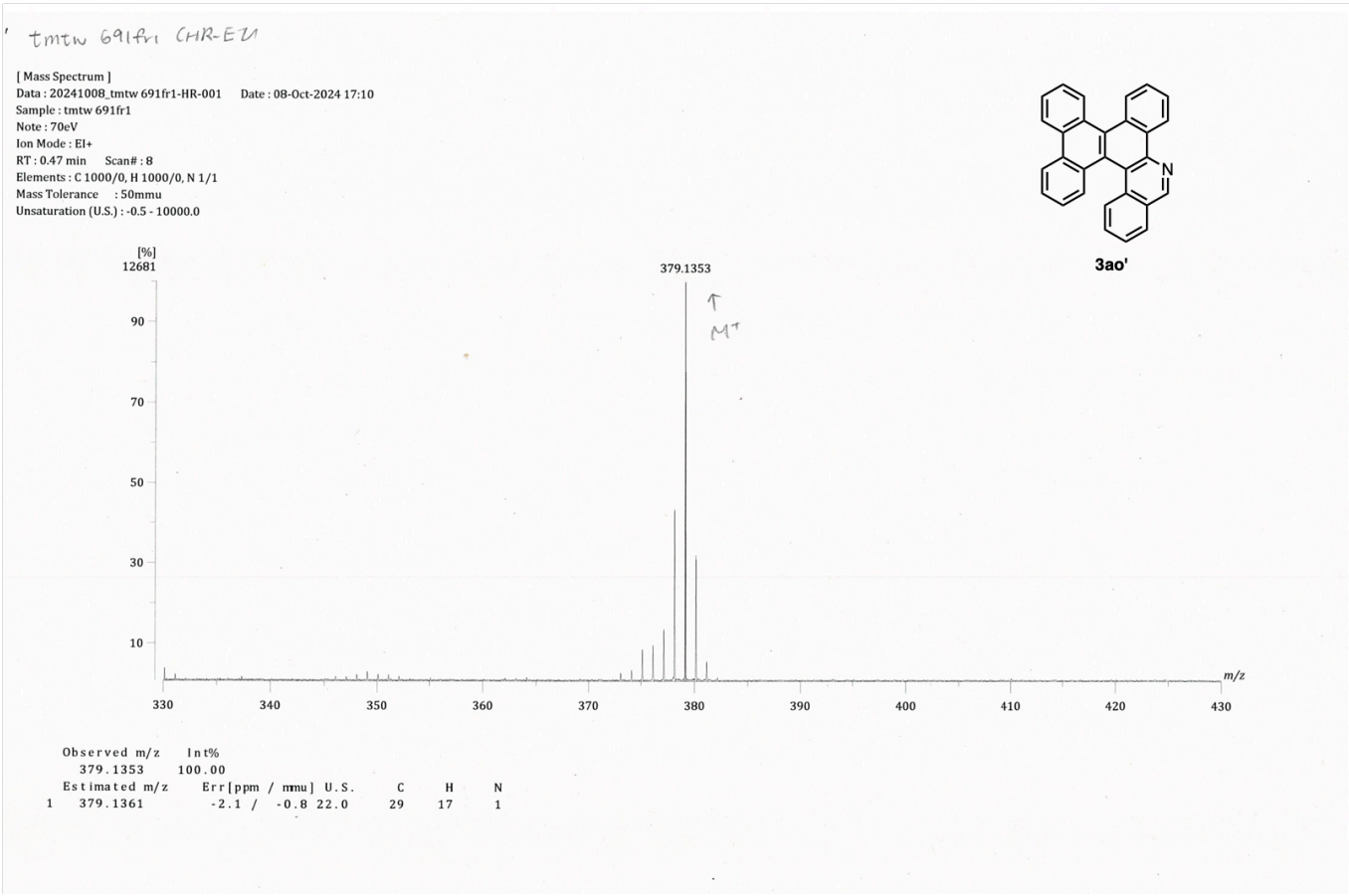


Figure S157. HRMS of **3ao'**.

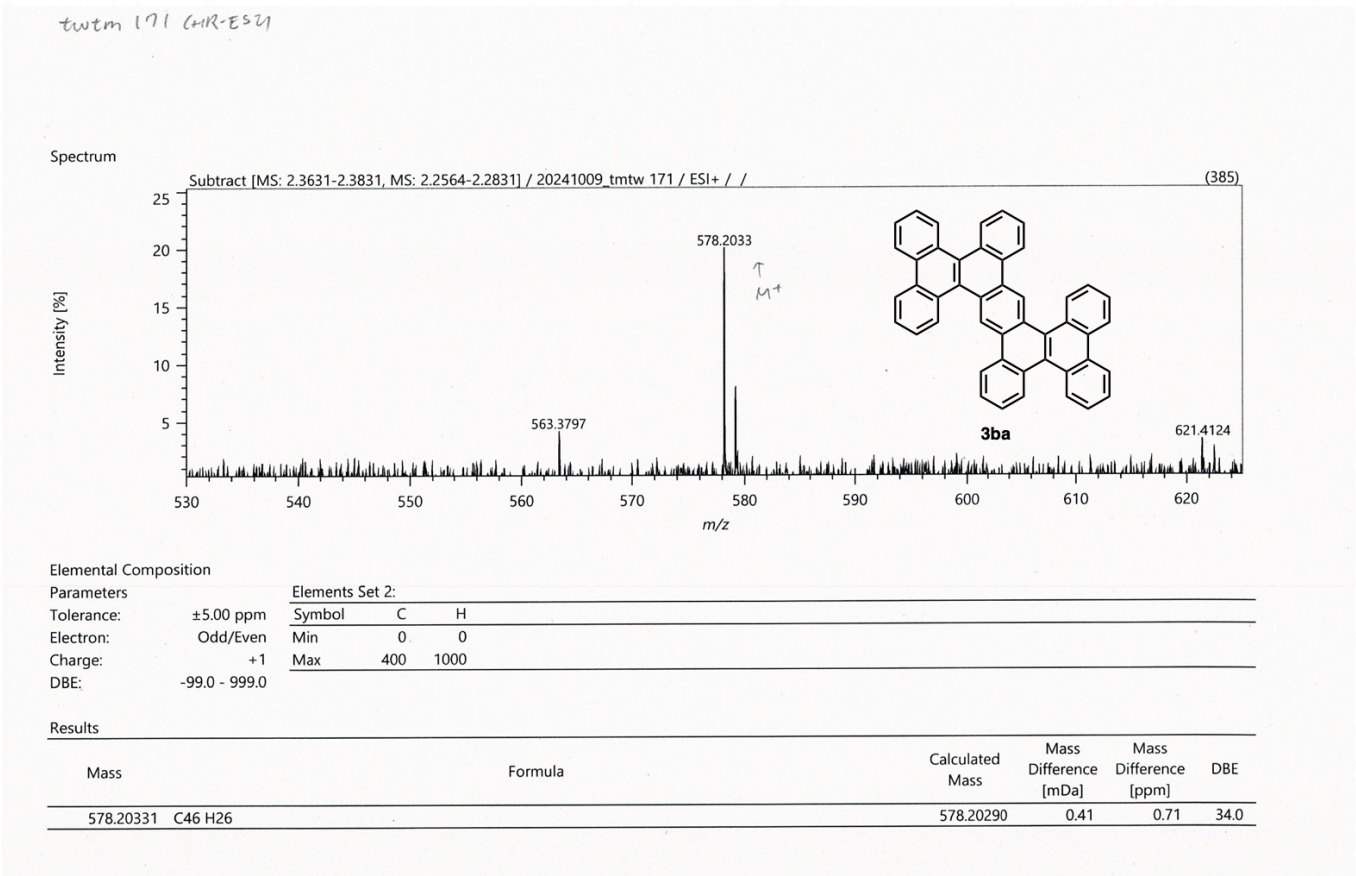


Figure S158. HRMS of **3ba**.

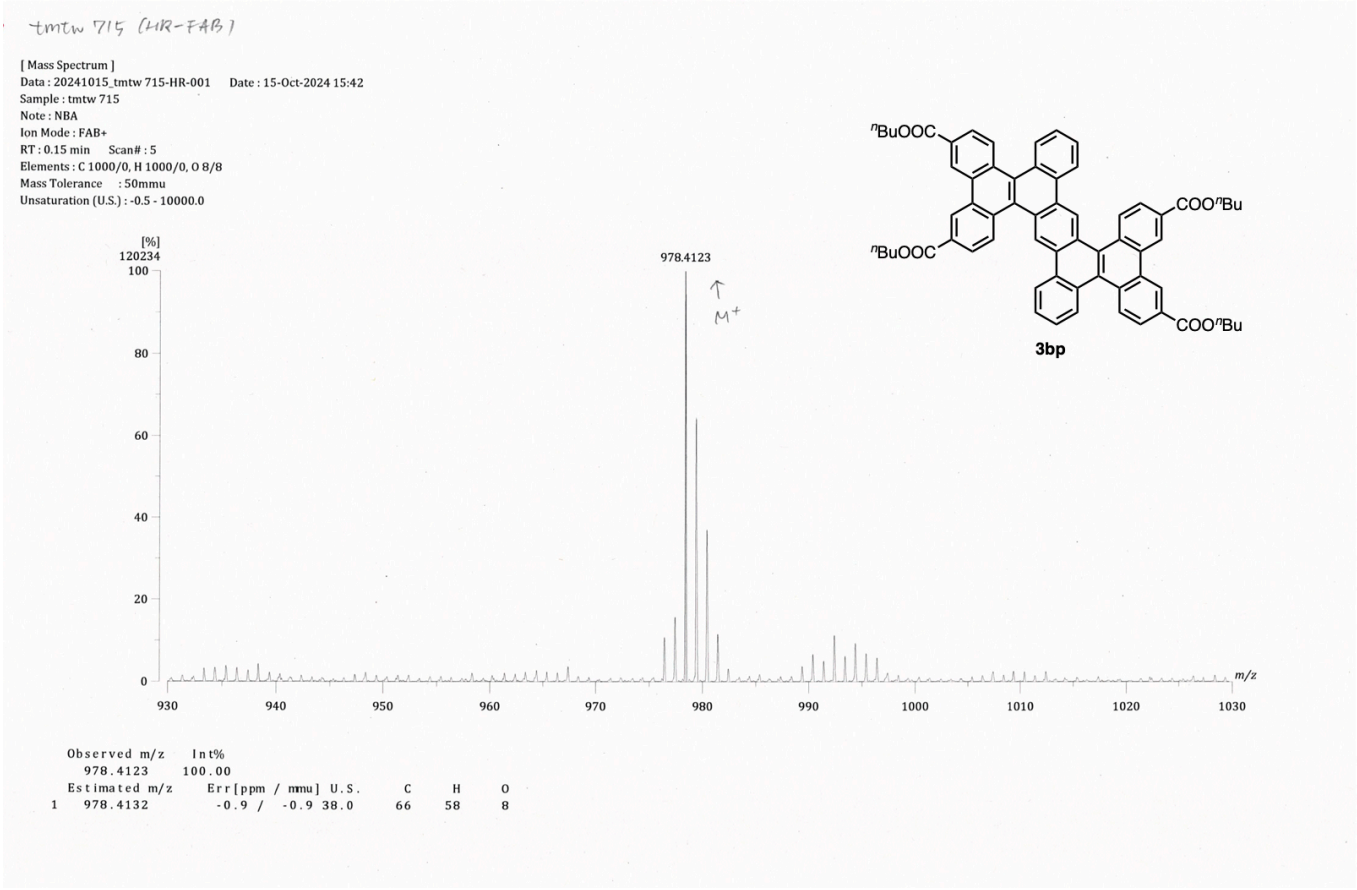


Figure S159. HRMS of **3bp**.

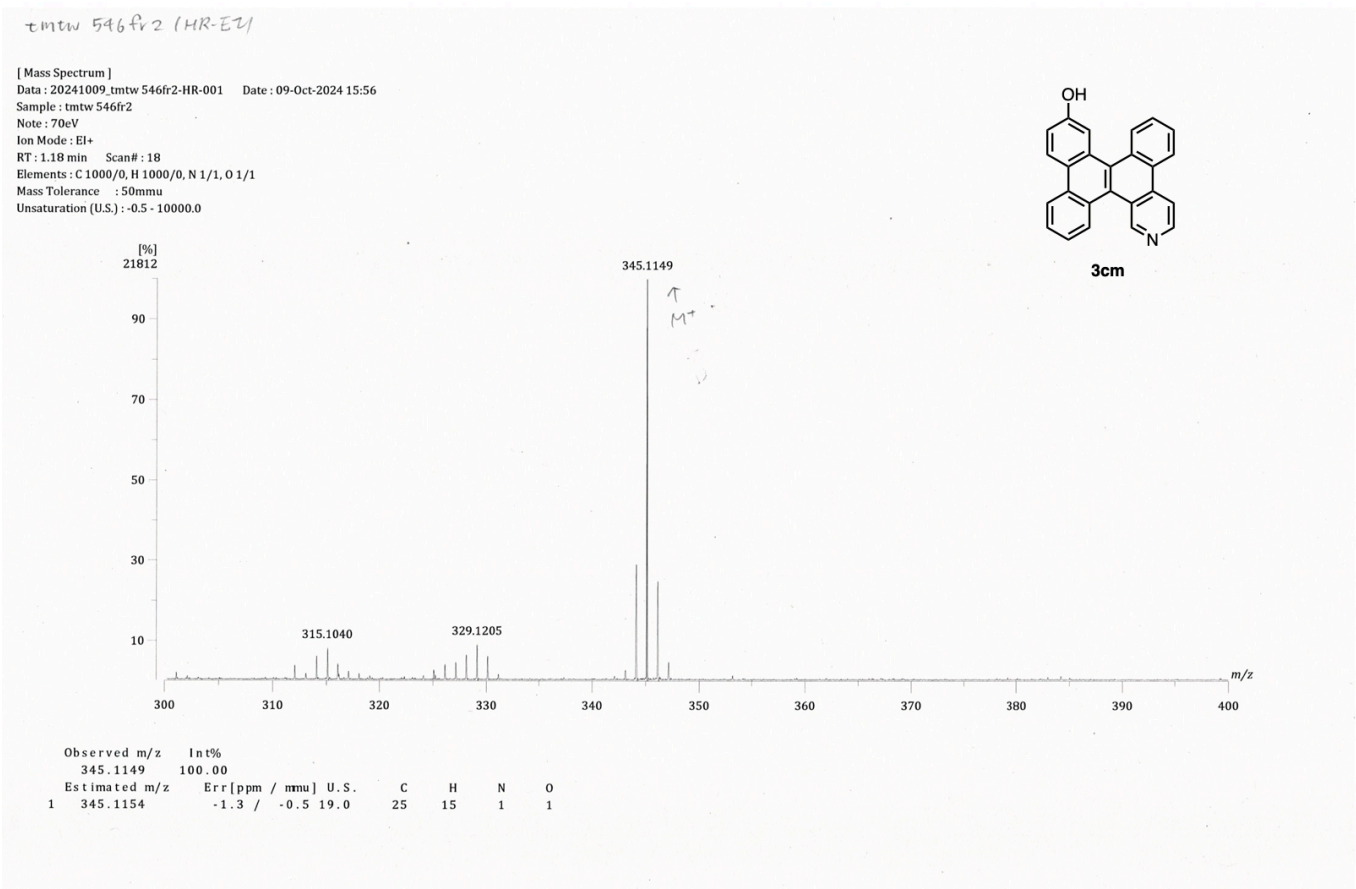


Figure S160. HRMS of **3cm**.

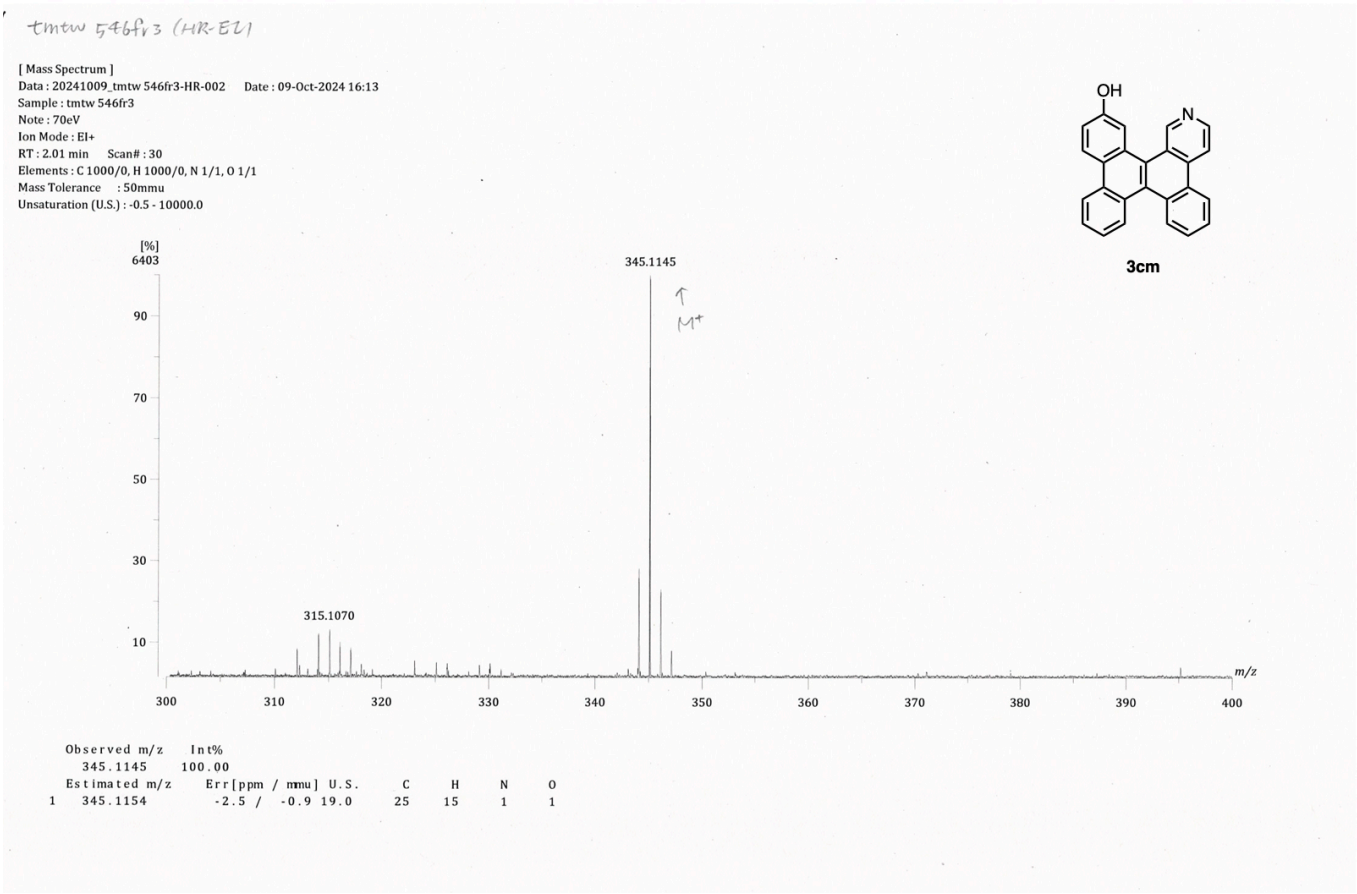


Figure S161. HRMS of **3cm'**.

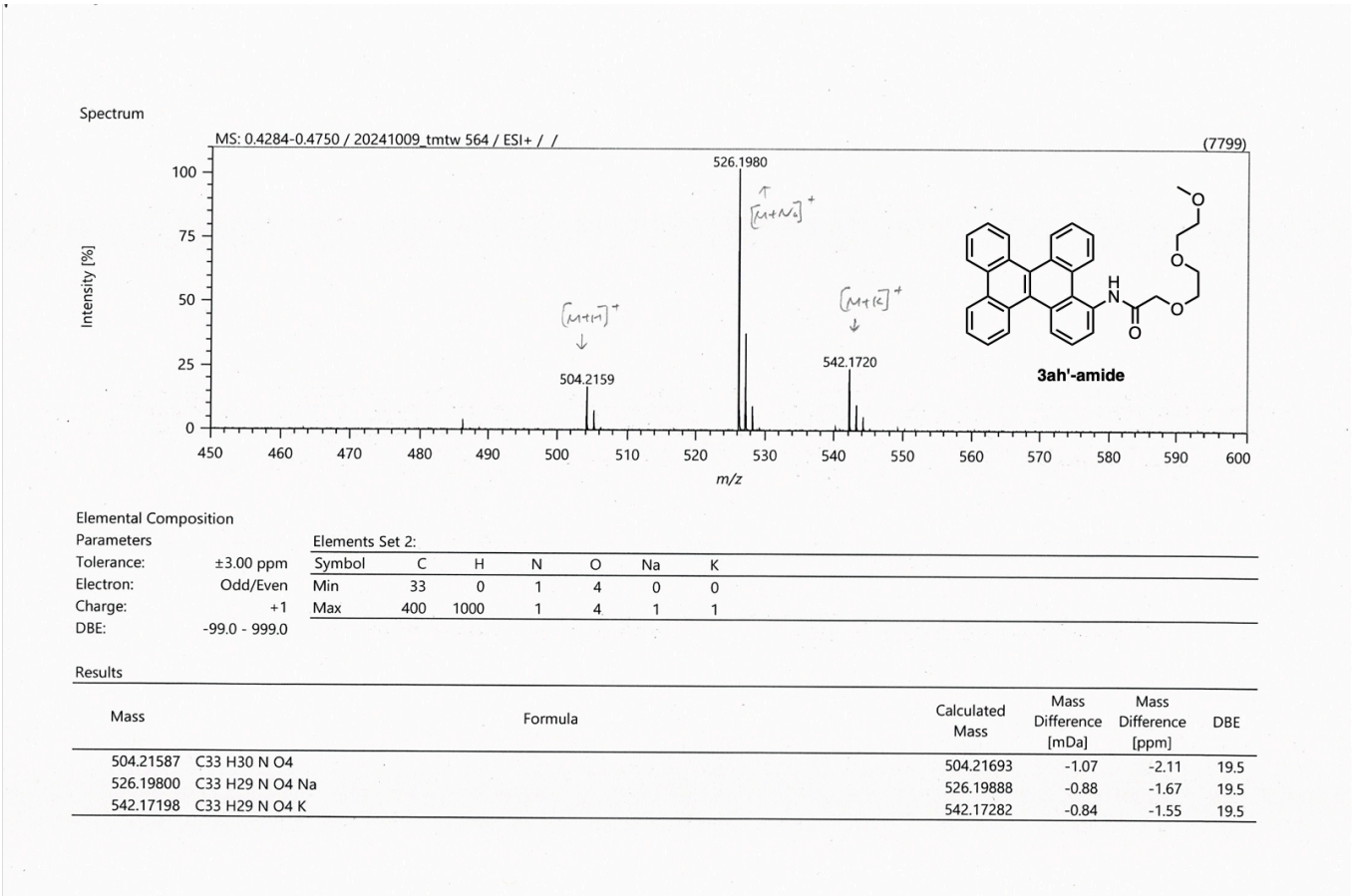


Figure S162. HRMS of **3ah'-amide**.

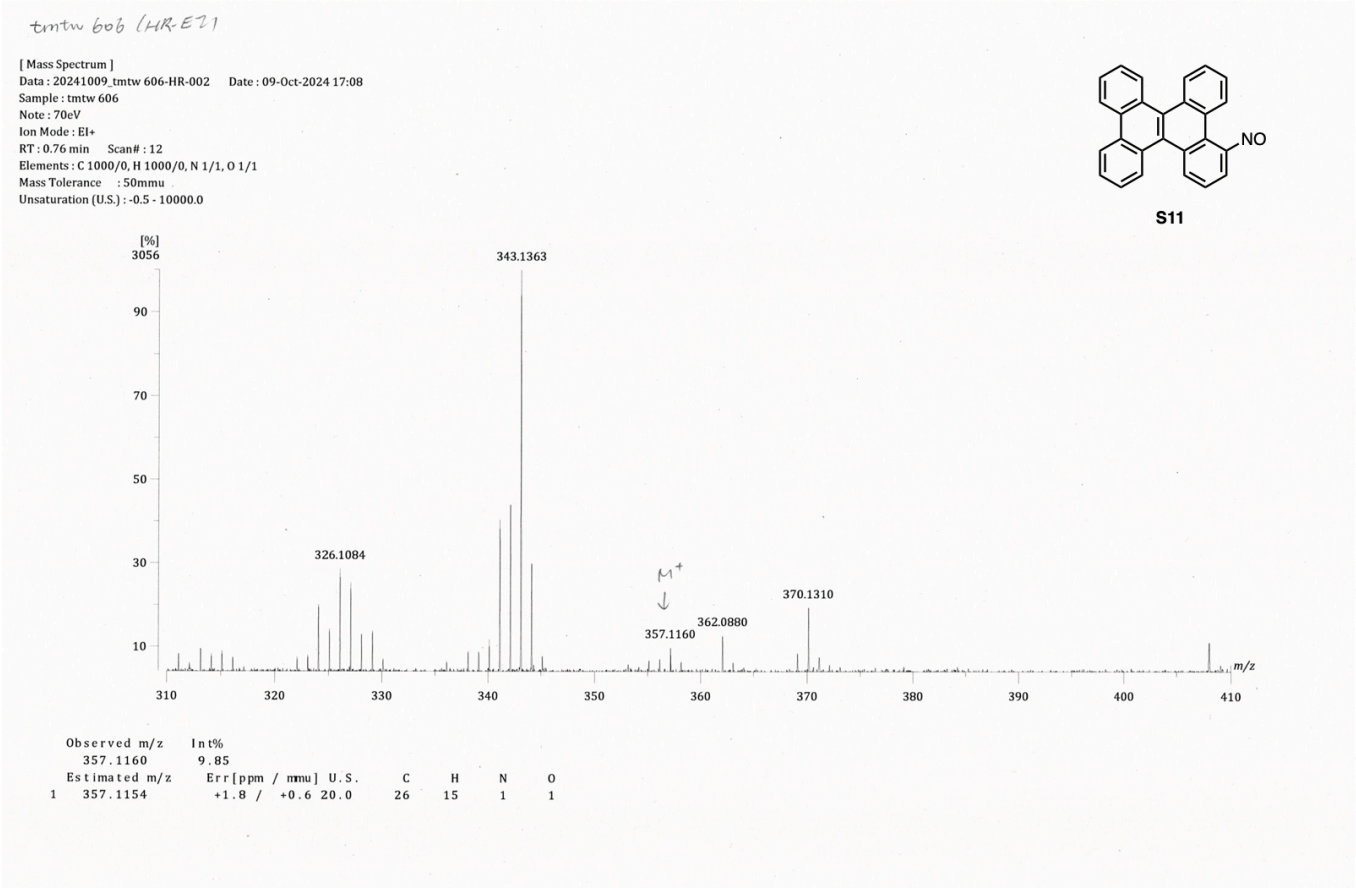


Figure S163. HRMS of **S11**.

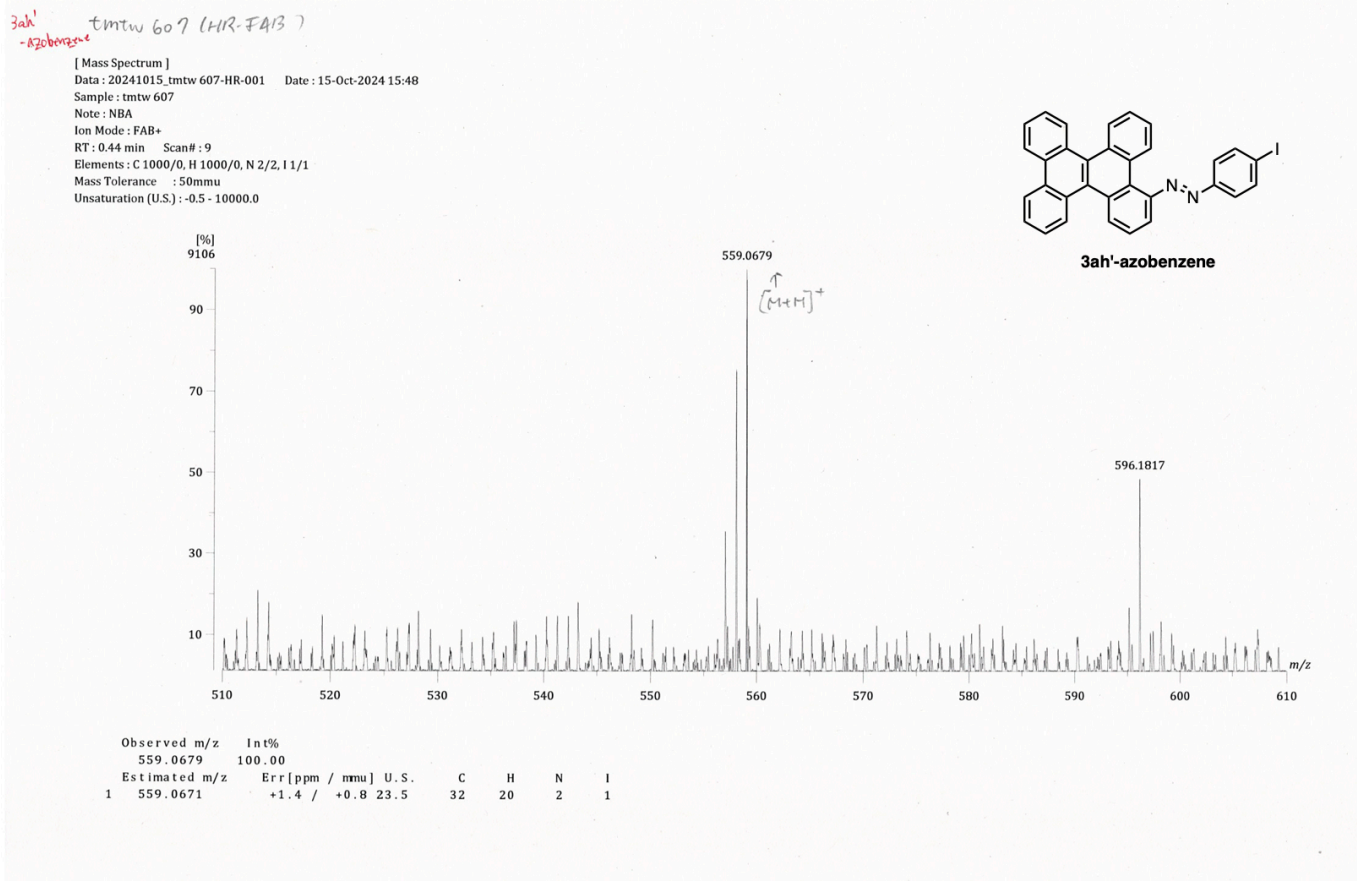


Figure S164. HRMS of **3ah'-azobenzene**.

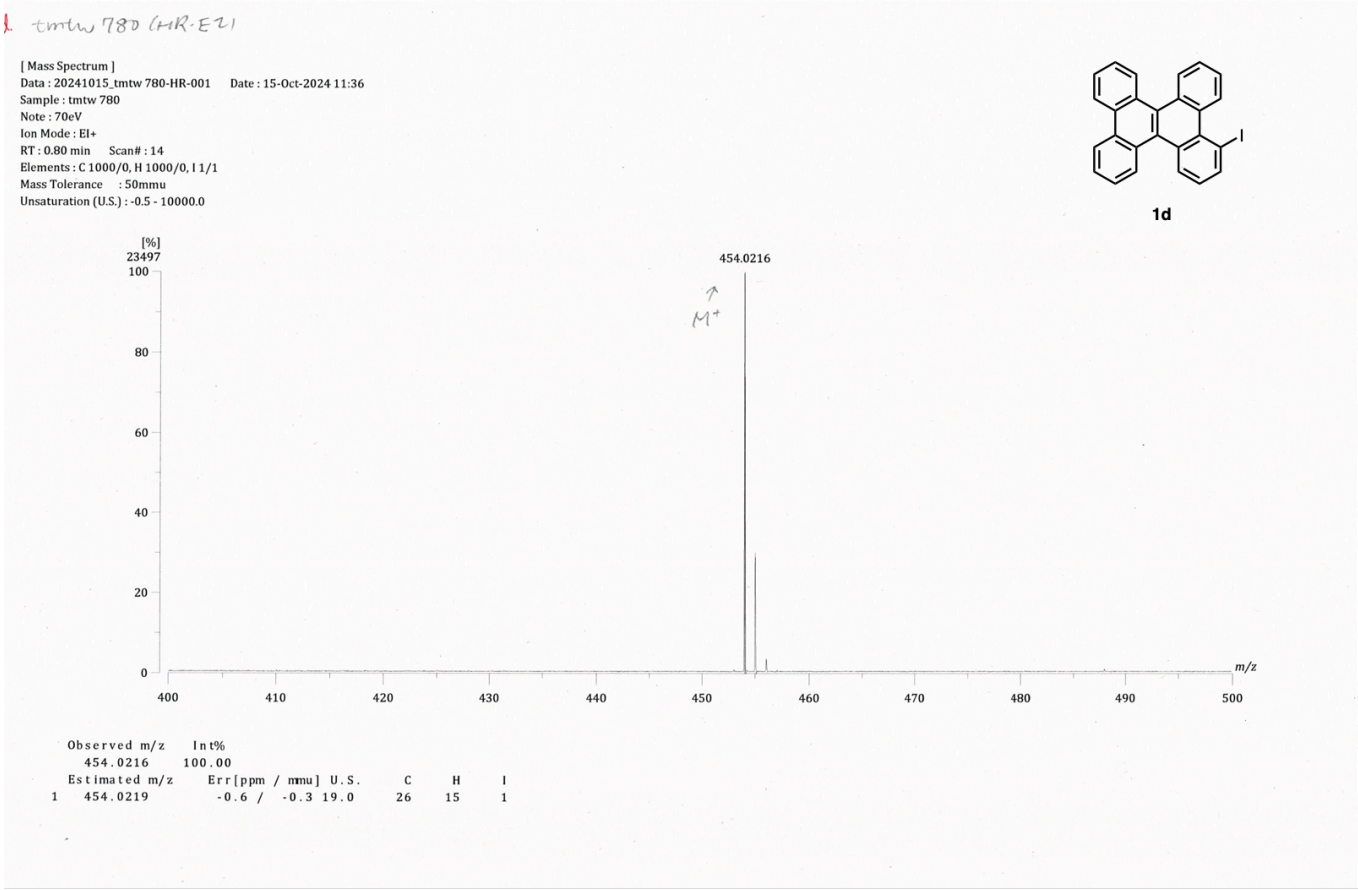


Figure S165. HRMS of **1d**.

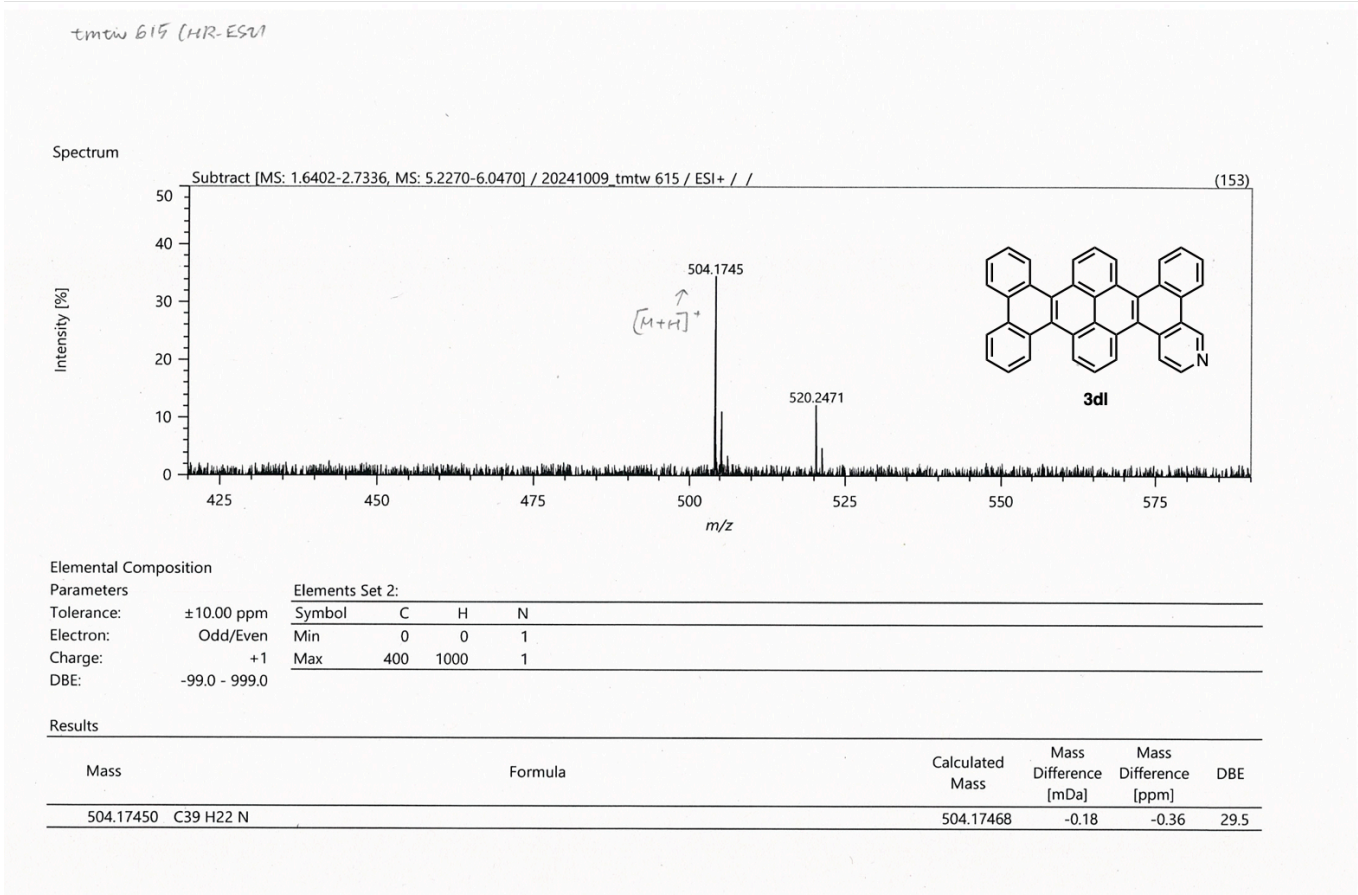
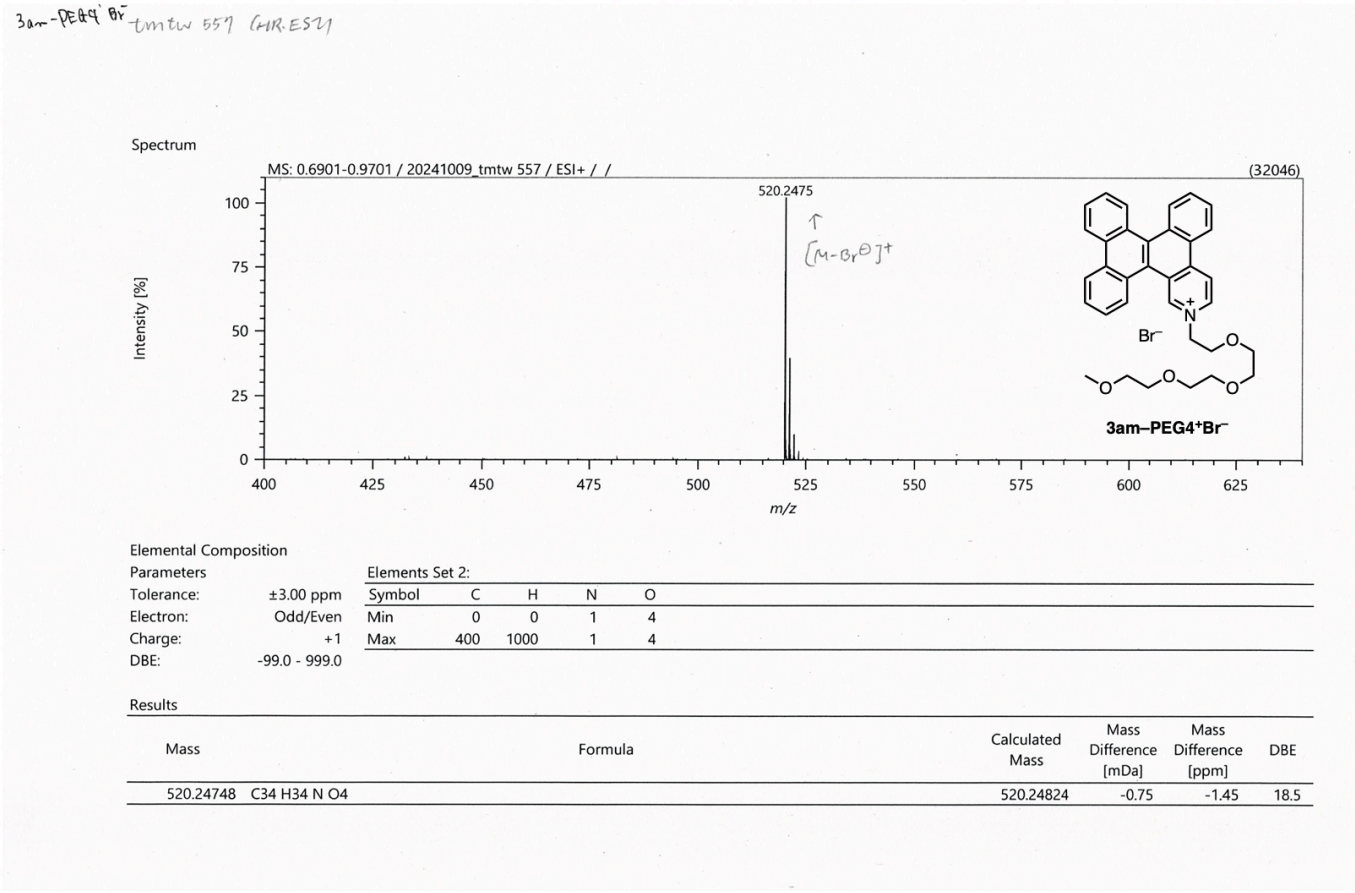


Figure S166. HRMS of **1dl**.



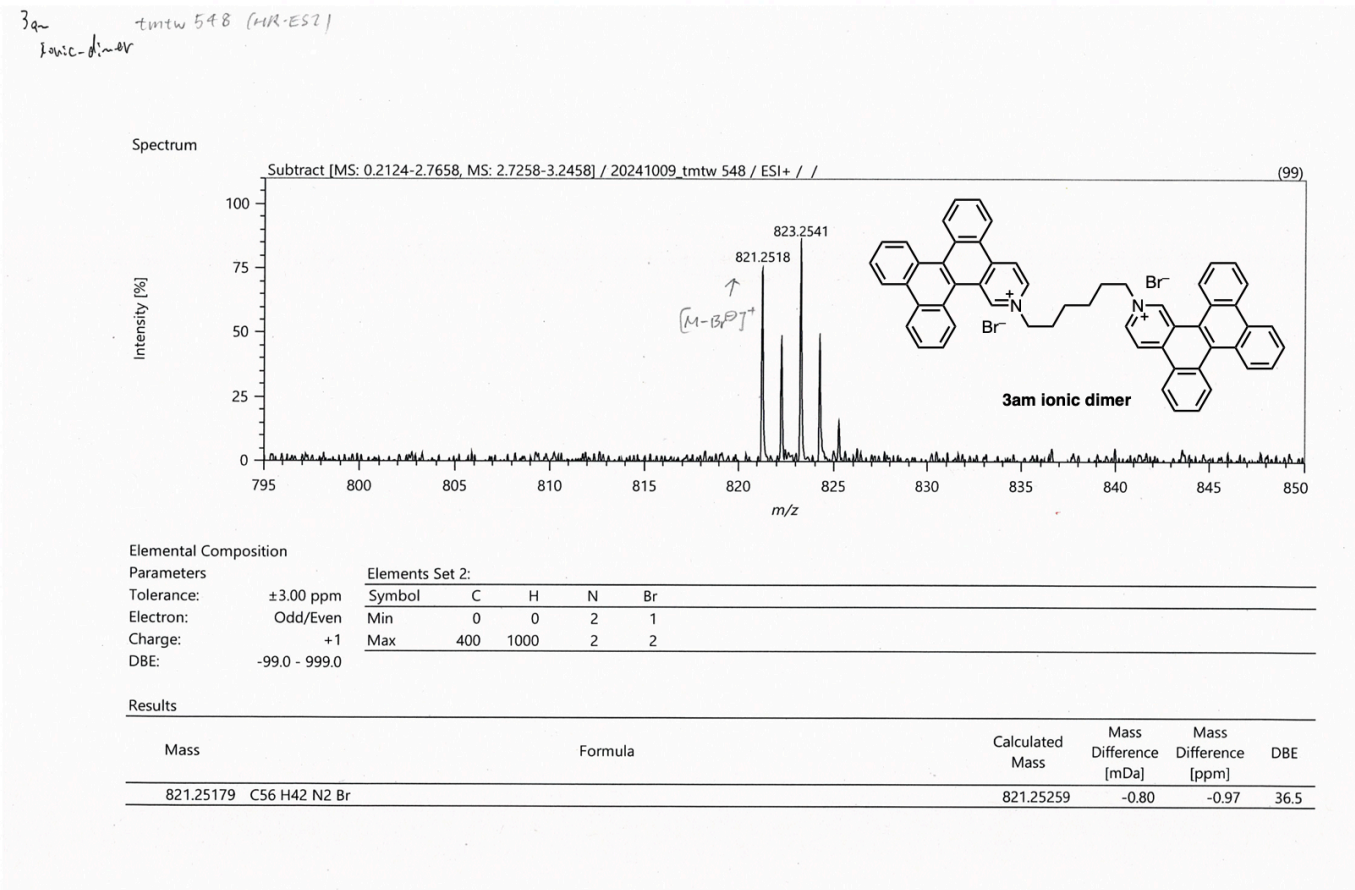
Elemental Composition

Parameters		Elements Set 2:				
Tolerance:	±3.00 ppm	Symbol	C	H	N	O
Electron:	Odd/Even	Min	0	0	1	4
Charge:	+1	Max	400	1000	1	4
DBE:	-99.0 - 999.0					

Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
520.24748	C34 H34 N O4	520.24824	-0.75	-1.45	18.5

Figure S167. HRMS of **3am-PEG4^{+}Br^{-}**.



Elemental Composition

Parameters		Elements Set 2:				
Tolerance:	±3.00 ppm	Symbol	C	H	N	Br
Electron:	Odd/Even	Min	0	0	2	1
Charge:	+1	Max	400	1000	2	2
DBE:	-99.0 - 999.0					

Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
821.25179	C56 H42 N2 Br	821.25259	-0.80	-0.97	36.5

Figure S168. HRMS of **3am ionic dimer**.

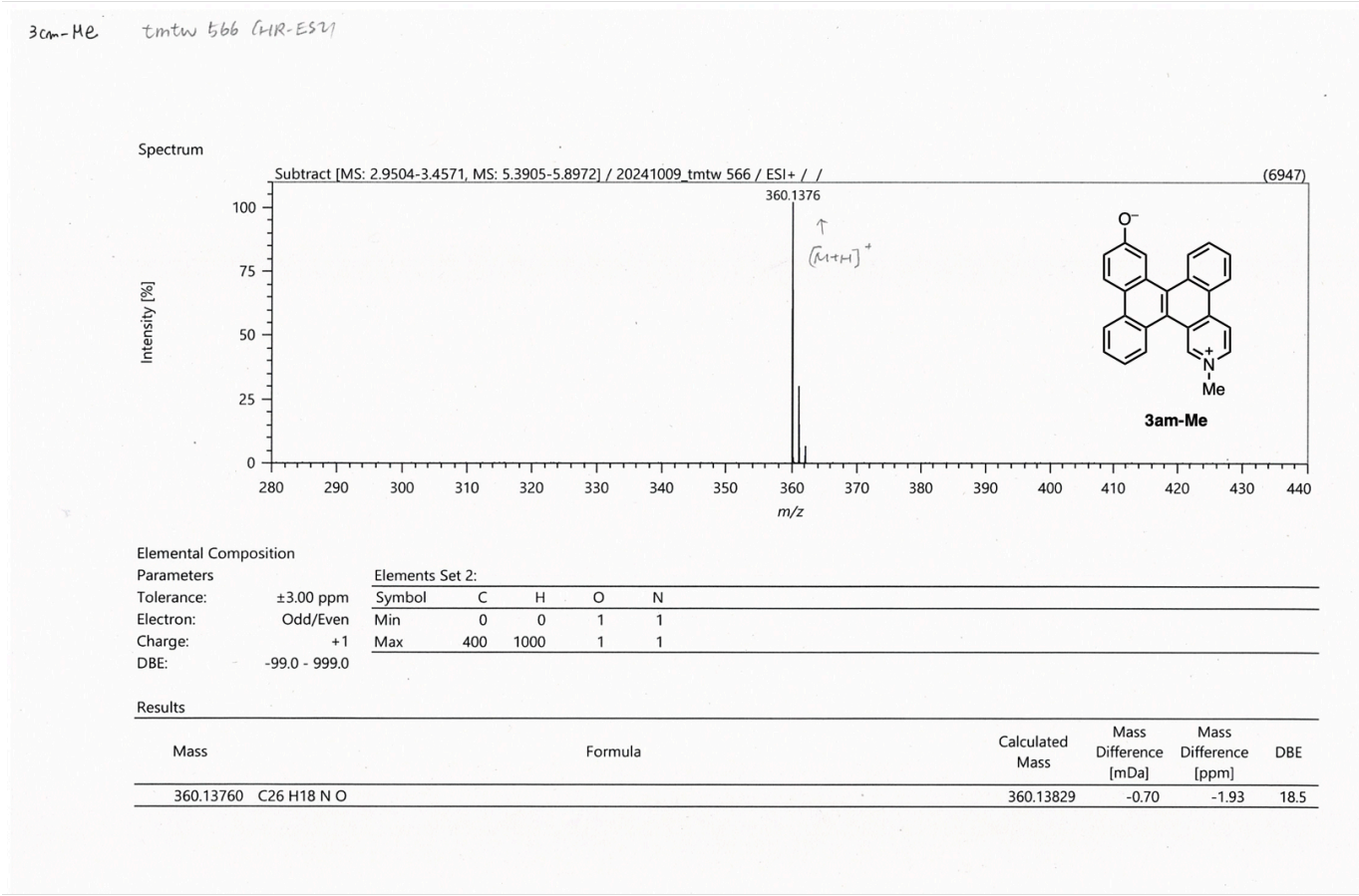


Figure S169. HRMS of **3am-Me**.