Supporting Information

Alkyne/Thio Umpolung Tactic Replacement: Synthesis of Alkynyl Sulfides via Capturing the in-situ Formed Alkynylthiolate Anion

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General Information

Reagents and Solvents

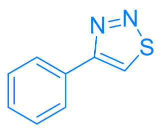
Unless otherwise noted, all chemicals used in the preparation of starting materials were commercially available and were used as received without further purifications. Metal catalysts and ligands were purchased from Acros, Laajoo, Energy Chemical, Bidepharm, and Accela. Other chemicals were purchased from Macklin, Adamas, and Innochem, and were directly used without further purifications.

Anhydrous THF and DMSO were purchased from Energy Chemical. Toluene was distilled from sodium/benzophenone and stored under nitrogen before use.

Analytical Methods

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using a Bruker DRX-400 spectrometer or a Bruker DRX-500 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants (J) are reported in Hertz. Melting points were measured using a melting point instrument. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. GC analyses were performed on an Agilent 7890B GC equipped with HP-5 columns (30 m × 320 μm × 0.25 μm), FID detectors, and hydrogen as the carrier gas. GC/MS analyses were performed on a Shimadzu GCMS-QP2010SE equipped with an RTX-5MS column (30 m × 0.25 mm × 0.25 μm) with a quadrupole mass analyzer using helium as the carrier gas. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm.

Part 1: General Procedures for the Synthesis of 1,2,3-thiadiazoles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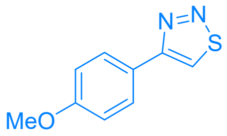
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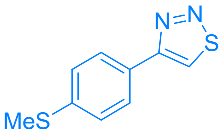
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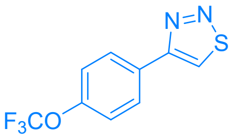
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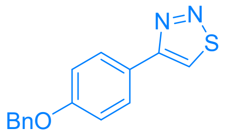
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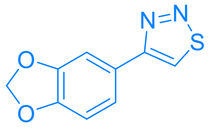
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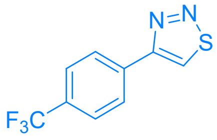
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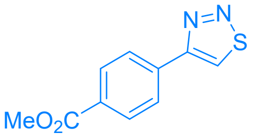
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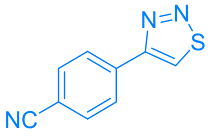
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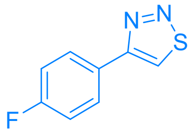
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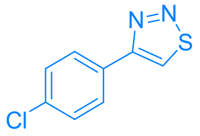
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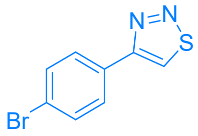
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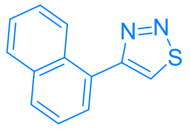
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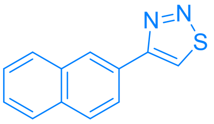
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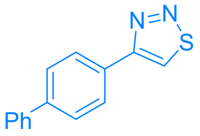
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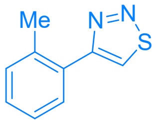
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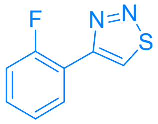
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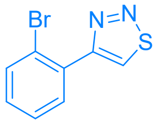
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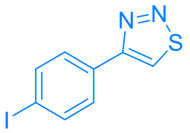
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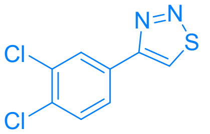
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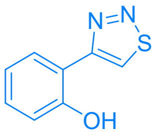
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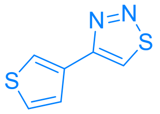
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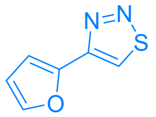
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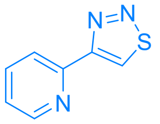
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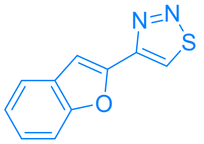
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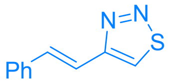
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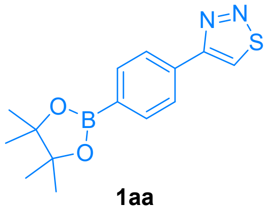
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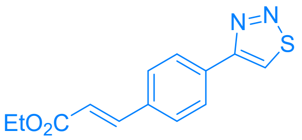
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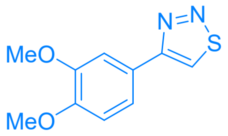
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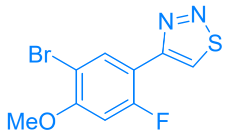
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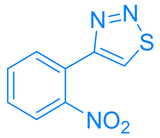
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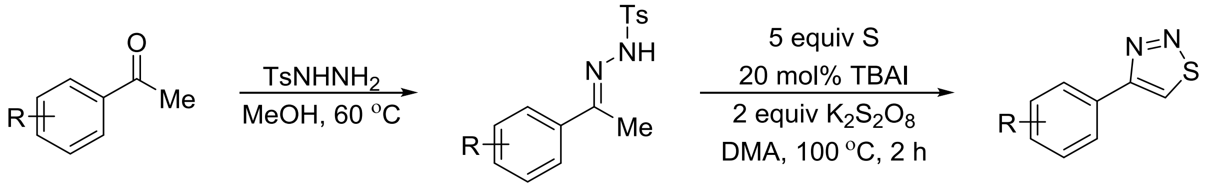
All compounds were synthesized following the reported methods. For the analysis data of 1,2,3-thiadiazoles, please refer to our previous article.[1-2]

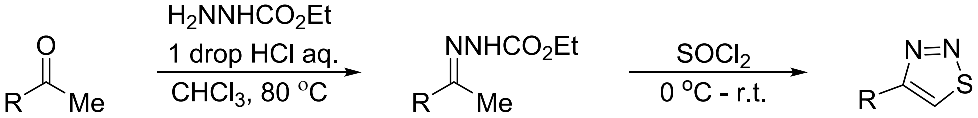
General Procedure A:[3]



p-Toluenesulfonylhydrazide (1.86 g, 10 mmol) was placed in a round-bottom boiling flask equipped with a reflux condenser in 10 mL of dry methanol; the ketone (10 mmol) was added slowly, and the mixture was heated in an oil bath at 60 °C. Within 5−60 min, N- tosylhydrazone began to precipitate. The mixture was cooled to 0 °C, and the product was collected on a Büchner funnel, washed with petroleum ether, and then dried in vacuo to afford the pure product quantatively.

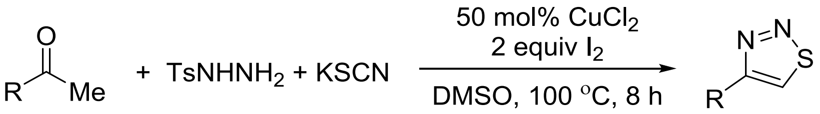
A sealed tube was charged with *N*-tosylhydrazone (3 mmol), sulfur (15 mmol), TBAI (0.6 mmol), $K_2S_2O_8$ (6 mmol), and DMAC (30 mL). The mixture was stirring under air at 100 °C for 2 h. The mixture was washed with water and extracted by ethyl acetate and then concentrated in vacuum, and the residue was purified by preparative TLC (petroleum ether /ethyl acetate) to afford the desired product.

General Procedure B:[4]



A mixture of acetophenone (1 equiv) and ethyl hydrazine carboxylate (1.2 equiv) was dissolved in dry, hot chloroform. When the reaction mixture started refluxing, one drop of concentrated hydrochloric acid were added and the mixture was then refluxed overnight with continuous removal of the water generated. The solvent was removed under vacuum and the residue was washed several times with diethyl ether or chloroform to remove excess reactants. Next, An excess amount of thionyl chloride was stirred at 0 ºC and the hydrazones were added in several portions. The mixtures were stirred at room temperature overnight until no more hydrogen chloride was produced. The remaining thionyl chloride was evaporated under vacuum and the residue was washed with diethyl ether to give good yields of the corresponding 1,2,3-thiadiazoles as fine powders. A recrystallization from chloroform or dimethylsulfoxide was carried out when necessary.

General Procedure C:[5]

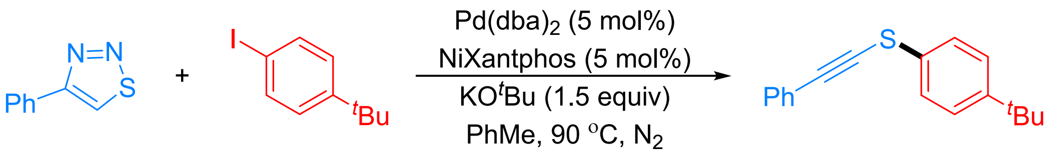


A sealed tube was charged with ketone (1.0 mmol), p-toluenesulfonylhydrazide (1.0 mmol), and potassiumthiocyanate (97.2 mg, 1.0 mmol), iodine (507.6mg, 2.0 mmol) at room temperature, and DMSO (3 mL) was added. The resulting mixture was stirred at 100 °C for 1h. After the reaction completed, the mixture was quenched with saturation $Na_2S_2O_3$ solution (50 mL), extracted with EtOAc (3×50 mL). The combined organiclayers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatographyonsilicagel (petroleum ether/EtOAc = 20:1) to give the product.

Part 2: Palladium-Catalyzed Cross-Coupling of Thiadiazoles with Aryl Iodides

2.1. Optimization of the Reaction Parameters

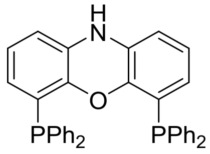
Table S1. Details of Optimization of the Reaction Conditions[a]

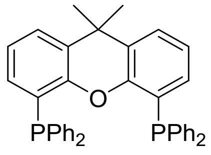


1a **2a** **3a**

Entry	Variation from the standard conditions	Yield of 3a (%)
1	none	84 (77)^b
2	K_3PO_4 instead of KO^{t}Bu	n.d.
3	K_2CO_3 instead of KO^{t}Bu	n.d.
4	Cs_2CO_3 instead of KO^{t}Bu	36
5	NaO^{t}Bu instead of KO^{t}Bu	70
6	LiO^{t}Bu instead of KO^{t}Bu	17
7	NEt$_3$ instead of KO^{t}Bu	n.d.
8	DIEPA instead of KO^{t}Bu	n.d.
9	without NiXantphos	n.d.
10	DPPP instead of NiXantphos	n.d.
11	Xantphos instead of NiXantphos	76
12	DPEphos instead of NiXantphos	21
13	Pd(PPh$_3$)$_4$ instead of Pd(dba)$_2$	73
14	Pd(OAc)$_2$ instead of Pd(dba)$_2$	66
15	PdCl$_2$(PPh$_3$)$_2$ instead of Pd(dba)$_2$	76
16	rt instead of 90 °C	trace
17	110 °C instead of 90 °C	36
18	THF instead of PhMe	16
19	Dioxane instead of PhMe	67
20	MeCN instead of PhMe	9
21	DMSO instead of PhMe	trace
22	DMF instead of PhMe	trace

[a]Conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), Pd(dba)$_2$ (5 mol%), NiXantphos (5 mol%), KO^{t}Bu (1.5 equiv) in PhMe (1 mL) at 90 ^{o}C for 16 h. Yield of **3a** was determined by GC using dodecane as the internal standard. n.d. = not detected. [b]Isolated yield.


NiXantPhos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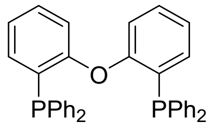
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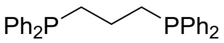
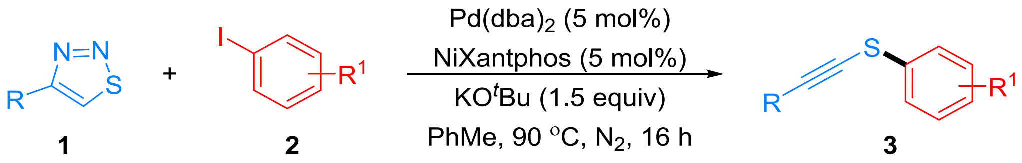

DPPP

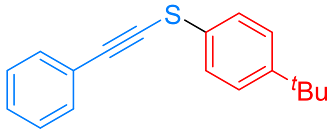
General Procedure for the Optimization Reactions: In glove box, palladium catalyst (5 mol%) and ligand (5 mol%) was stirred in solvent (0.5 ml) for 10 minutes in advance. A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, 4-phenyl-1,2,3-thiadiazole **1a** (0.12 mmol, 1.2 equiv.), 1-(tert-butyl)-4-iodobenzene **2a** (0.1 mmol, 1.0 equiv.) and base was added. Then the solvent (0.5 ml) was added and resulting mixture was stirred at specified temperature for 24 h. After the reaction completed, the mixture was cooled down to room temperature, several drops of solution were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was analyzed by GC to determine calibrated GC yields.

2.2. General Procedure for Palladium-catalyzed Alkynylthiolation of Aryl Iodides



In glove box, Pd(dba)$_2$ (5 mol%) and NiXantphos (5 mol%) was stirred in PhMe (1.5 ml) for 10 minutes in advance. A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, 1,2,3-thiadiazole **1** (0.36 mmol, 1.2 equiv.), iodobenzene **2** (0.3 mmol, 1.0 equiv.) and KO^{t}Bu (0.45 mmol, 1.5 equiv) was added. Then PhMe (1.5 ml) was added and resulting mixture was stirred at 90 °C for 16 h. After the reaction completed, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×20 mL), the combined organic phases were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products.

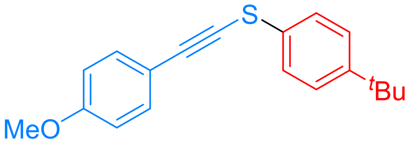
(4-(tert-butyl)phenyl)(phenylethynyl)sulfane



3a

According to the general procedure, the reaction gave **3a** in 77% yield (61 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 – 7.52 (m, 2H), 7.48 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.42 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.39 – 7.35 (m, 3H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.92, 131.62, 129.26, 128.45, 128.33, 126.35, 126.18, 123.03, 97.20, 76.13, 34.48, 31.24. Spectroscopic data for **3a** match those previously reported in the literature.[6]

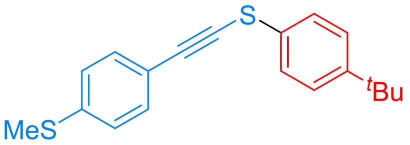
(4-(tert-butyl)phenyl)((4-methoxyphenyl)ethynyl)sulfane



3b

According to the general procedure, the reaction gave **3b** in 78% yield (69 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2960, 2164, 1602, 1501, 1252, 1027, 826 cm^{-1}**.** **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.52 – 7.37 (m, 6H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.97, 149.75, 133.63, 129.74, 126.28, 126.17, 115.11, 113.99, 97.18, 74.14, 55.26, 34.46, 31.24. **HRMS** (ESI) calculated 297.1308 for $C_{19}H_{21}OS$ $[M+H]^+$, found 297.1301.

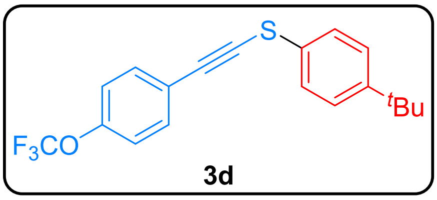
(4-(tert-butyl)phenyl)((4-(methylthio)phenyl)ethynyl)sulfane



3c

According to the general procedure, the reaction gave **3c** in 63% yield (71 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3469, 2959, 2164, 1591, 1488, 1088, 819 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.48 – 7.38 (m, 6H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.50 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.87, 139.81, 132.02, 129.29, 126.32, 126.27, 125.74, 119.17, 96.92, 76.00, 34.44, 31.21, 15.25. **HRMS** (ESI) calculated 313.1079 for $C_{19}H_{21}S_2$ [M+H]$^+$, found 313.1074.

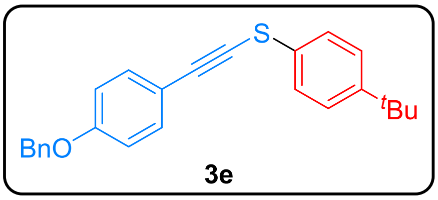
(4-(tert-butyl)phenyl)((4-(trifluoromethoxy)phenyl)ethynyl)sulfane



3d

According to the general procedure, the reaction gave **3d** in 52% yield (55 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3456, 2960, 2168, 1597, 1259, 1168, 830 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.18 (d, *J* = 8.3 Hz, 2H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.25, 149.00 (q, *J* = 2.2 Hz), 133.14, 128.83, 126.58, 126.46, 121.84, 120.87, 120.38 (q, *J* = 258.3 Hz), 95.55, 77.59, 34.54, 31.25. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.79. **HRMS** (ESI) calculated 351.1025 for $C_{19}H_{18}F_3OS$ [M+H]$^+$, found 351.1018.

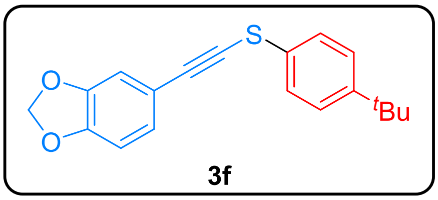
((4-(benzyloxy)phenyl)ethynyl)(4-(tert-butyl)phenyl)sulfane



3e

According to the general procedure, the reaction gave **3e** in 76% (85 mg) yield as a white solid (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3441, 2959, 2165, 1599, 1498, 1240, 827 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.38 (m, 11H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.11 (s, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.09, 149.70, 136.44, 133.61, 129.66, 128.58, 128.05, 127.40, 126.27, 126.13, 115.32, 114.86, 97.15, 74.25, 69.96, 34.43, 31.22. **HRMS** (ESI) calculated 373.1621 for $C_{25}H_{25}OS$ [M+H]$^+$, found 373.1615.

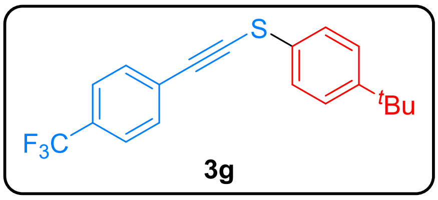
5-(((4-(tert-butyl)phenyl)thio)ethynyl)benzo[d][1,3]dioxole



3f

According to the general procedure, the reaction gave **3f** in 81% yield (75 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3450, 2960, 1598, 1489, 1250, 1039, 816 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 4H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.82, 148.23, 147.38, 129.48, 126.87, 126.30, 126.22, 116.20, 111.85, 108.42, 101.34, 97.03, 74.15, 34.45, 31.22. **HRMS** (ESI) calculated 311.1100 for $C_{19}H_{19}O_2S$ [M+H]$^+$, found 311.1096.

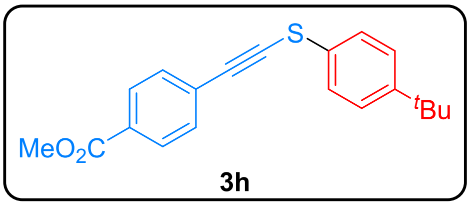
(4-(tert-butyl)phenyl)((4-(trifluoromethyl)phenyl)ethynyl)sulfane



3g

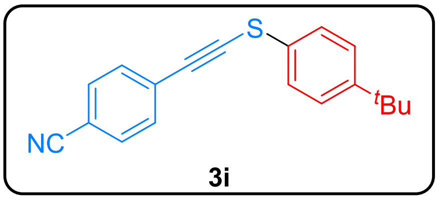
According to the general procedure, the reaction gave **3g** in 43% (mg) yield as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3432, 2960, 2166, 1607, 1322, 1123, 831 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 4H), 7.47 – 7.38 (m, 4H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.45, 131.43, 129.89 (q, *J* = 32.6 Hz), 128.45, 126.86, 126.74, 126.53, 125.30 (q, *J* = 3.8 Hz), 123.89 (q, *J* = 272.2 Hz), 95.74, 79.85, 34.57, 31.24. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.81. **HRMS** (ESI) calculated 335.1076 for $C_{19}H_{18}F_3S$ $[M+H]^+$, found 335.1069.

methyl 4-(((4-(tert-butyl)phenyl)thio)ethynyl)benzoate


3h

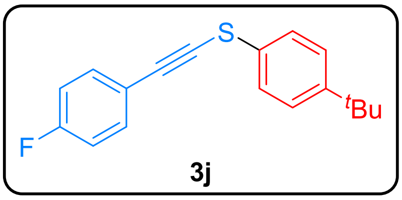
According to the general procedure, the reaction gave **3h** in 46% (46 mg) yield as a yellow solid (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3462, 2958, 2163, 1722, 1600, 1277, 823 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.39 (m, 4H), 3.92 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.48, 150.39, 131.01, 129.53, 129.39, 128.57, 127.72, 126.68, 126.51, 96.50, 80.35, 52.21, 34.56, 31.24. **HRMS** (ESI) calculated 325.1257 for $C_{20}H_{21}O_2S$ $[M+H]^+$, found 325.1255.

4-(((4-(tert-butyl)phenyl)thio)ethynyl)benzonitrile


3i

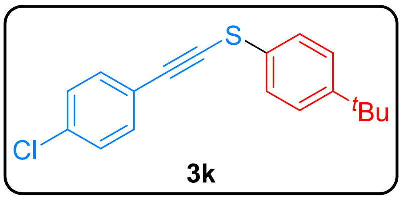
According to the general procedure, the reaction gave **3i** in 61% yield (53 mg) as a yellow solid (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3461, 2960, 2164, 1598, 1492, 1269, 830 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.42 (s, 4H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.65, 132.03, 131.41, 128.01, 127.87, 126.86, 126.57, 118.44, 111.25, 95.52, 82.56, 34.56, 31.20. **HRMS** (ESI) calculated 292.1154 for $C_{19}H_{18}NS$ $[M+H]^+$, found 292.1149.

(4-(tert-butyl)phenyl)((4-fluorophenyl)ethynyl)sulfane


3j

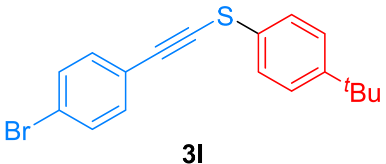
According to the general procedure, the reaction gave **3j** in 65% yield (55 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3479, 2961, 2166, 1599, 1498, 1233, 827 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.42 (q, *J* = 8.7 Hz, 4H), 7.04 (t, *J* = 8.7 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.65 (d, *J* = 250.1 Hz), 150.06, 133.76 (d, *J* = 8.4 Hz), 129.12, 119.15 (d, *J* = 3.5 Hz), 115.66 (d, *J* = 22.1 Hz), 95.94, 75.96, 34.50, 31.24. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -110.12 (tt, *J* = 8.6, 5.3 Hz). **HRMS** (ESI) calculated 285.1108 for $C_{18}H_{18}FS$ $[M+H]^+$, found 285.1103.

(4-(tert-butyl)phenyl)((4-chlorophenyl)ethynyl)sulfane


3k

According to the general procedure, the reaction gave **3k** in 71% yield (66 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3463, 2960, 2166, 1596, 1486, 1087, 822 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 6H), 7.31 (d, J = 8.4 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.16, 134.48, 132.79, 128.88, 128.69, 126.52, 126.43, 121.53, 95.89, 77.55, 34.52, 31.24. **HRMS** (ESI) calculated 301.0812 for $C_{18}H_{18}ClS$ $[M+H]^+$, found 301.0808.

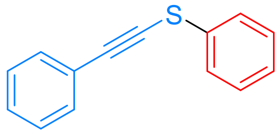
((4-bromophenyl)ethynyl)(4-(tert-butyl)phenyl)sulfane



3l

According to the general procedure, the reaction gave **3l** in 77% yield (73 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 2960, 2167, 1468, 1266, 1018, 822, 747 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.58 (d, J = 8.7 Hz, 1H), 7.48 (td, J = 8.2, 7.8, 1.7 Hz, 3H), 7.38 (d, J = 8.6 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.14 (td, J = 7.9, 1.6 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.06, 133.02, 132.40, 129.28, 128.75, 127.00, 126.37, 124.96, 95.91, 81.39, 34.51, 31.25. **HRMS** (ESI) calculated 345.0307 for $C_{18}H_{18}BrS$ $[M+H]^+$, found 345.0301.

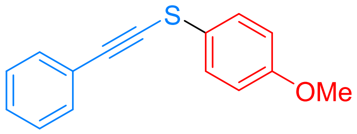
phenyl(phenylethynyl)sulfane



3m

According to the general procedure, the reaction gave **3m** in 79% yield (50 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.45 (m, 4H), 7.42 – 7.32 (m, 5H), 7.26 – 7.20 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 132.91, 131.72, 129.25, 128.62, 128.38, 126.50, 126.17, 122.87, 97.88, 75.39. Spectroscopic data for **3m** match those previously reported in the literature.[7]

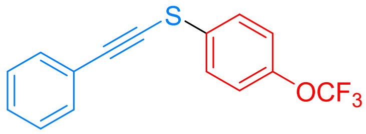
(4-methoxyphenyl)(phenylethynyl)sulfane



3n

According to the general procedure, the reaction gave **3n** in 51% yield as a yellow oil (flash column chromatography eluent, petrol ether). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.41 (m, 4H), 7.36 – 7.29 (m, 3H), 6.95 – 6.89 (m, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.00, 131.60, 128.89, 128.41, 128.32, 123.04, 122.99, 115.04, 96.24, 55.40. Spectroscopic data for **3n** match those previously reported in the literature.[7]

(phenylethynyl)(4-(trifluoromethoxy)phenyl)sulfane

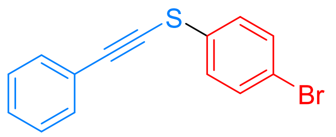


3o

According to the general procedure, the reaction gave **3o** in 76% yield (67 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3469, 2925, 1593, 1488, 1260, 1167, 753 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 4H), 7.38 – 7.31 (m, 4H), 7.24 – 7.18 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.89 (q, J = 1.7 Hz), 132.45, 131.81, 128.89, 128.43, 127.52, 122.55, 121.95, 120.42 (q, J = 258.6 Hz), 98.40, 74.68. **^{19}F**

NMR (376 MHz, Chloroform-*d*) δ -58.02. **HRMS** (ESI) calculated 295.0399 for $C_{15}H_{10}F_{3}OS$ $[M+H]^{+}$, found 295.0394.

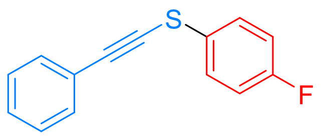
(4-bromophenyl)(phenylethynyl)sulfane



3p

According to the general procedure, the reaction gave **3p** in 71% yield (61 mg) as a colorless liquid (flash column chromatography eluent, petrol ether/EtOAc = 10/1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.48 – 7.46 (m, 1H), 7.46 – 7.44 (m, 1H), 7.37 – 7.31 (m, 5H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 132.27, 132.23, 131.77, 128.84, 128.41, 127.67, 122.55, 120.25, 98.50, 74.59. Spectroscopic data for **3p** match those previously reported in the literature.[7]

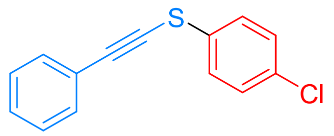
(4-fluorophenyl)(phenylethynyl)sulfane



3q

According to the general procedure, the reaction gave **3q** in 65% yield (44 mg) as a yellow oil (flash column chromatography eluent, petrol ether). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 4H), 7.36 – 7.34 (m, 3H), 7.11 – 7.04 (m, 2H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 161.84 (d, *J* = 246.5 Hz), 131.74, 128.73, 128.40, 128.33, 127.84 (d, *J* = 3.3 Hz), 122.71, 116.45 (d, *J* = 22.5 Hz), 97.52, 75.62. ^{19}**F NMR** (376 MHz, Chloroform-*d*) δ -115.35 – -115.46 (m). Spectroscopic data for **3q** match those previously reported in the literature.[8]

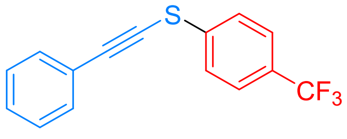
(4-chlorophenyl)(phenylethynyl)sulfane



3r

According to the general procedure, the reaction gave **3r** in 67% yield as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.30 (m, 5H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 132.49, 131.79, 131.55, 129.37, 128.85, 128.43, 127.45, 122.60, 98.37, 74.75. Spectroscopic data for **3r** match those previously reported in the literature.[9]

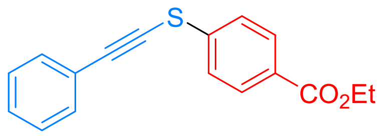
(phenylethynyl)(4-(trifluoromethyl)phenyl)sulfane



3s

According to the general procedure, the reaction gave **3s** in 53% yield (44 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.57 (m, 4H), 7.56 – 7.52 (m, 2H), 7.39 – 7.35 (m, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 138.37, 131.87, 130.98, 129.06, 128.48, 126.24 (q, *J* = 3.7 Hz), 126.03 (q, *J* = 3.8 Hz), 125.80, 123.97 (q, *J* = 272.7 Hz), 99.42, 73.56. Spectroscopic data for **3s** match those previously reported in the literature.[10]

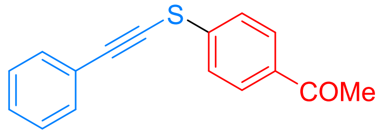
ethyl 4-((phenylethynyl)thio)benzoate



3t

According to the general procedure, the reaction gave **3t** in 65% yield (54 mg) as a yellow solid (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3460, 1715, 1594, 1274, 1108, 1017, 754 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 7.97 (m, 2H), 7.58 – 7.50 (m, 4H), 7.40 – 7.34 (m, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.96, 139.40, 131.80, 130.23, 128.94, 128.47, 128.43, 125.22, 122.43, 99.35, 73.76, 61.01, 14.26. **HRMS** (ESI) calculated 283.0787 for $C_{17}H_{15}O_2S$ $[M+H]^+$, found 283.0782.

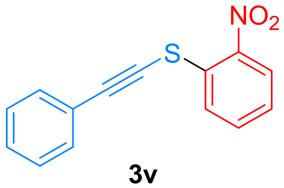
1-(4-((phenylethynyl)thio)phenyl)ethan-1-one



3u

According to the general procedure, the reaction gave **3u** in 76% yield (57 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3467, 1679, 1590, 1356, 1261, 1083, 753 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 2H), 7.58 – 7.51 (m, 4H), 7.41 – 7.33 (m, 3H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.93, 139.94, 135.10, 131.83, 129.06, 129.02, 128.45, 125.37, 122.36, 99.48, 73.55, 26.46. **HRMS** (ESI) calculated 253.0682 for $C_{16}H_{13}OS$ $[M+H]^+$, found 253.0678.

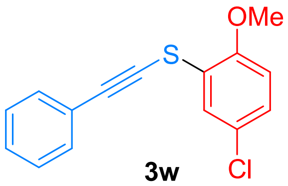
(2-nitrophenyl)(phenylethynyl)sulfane



3v

According to the general procedure, the reaction gave **3v** in 93% yield (74 mg) as a yellow solid (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3461, 2422, 2329, 1607, 1354, 1046, 739 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 – 8.30 (m, 1H), 8.22 – 8.16 (m, 1H), 7.72 – 7.65 (m, 1H), 7.60 – 7.54 (m, 2H), 7.42 – 7.36 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.24, 134.48, 134.33, 131.96, 129.30, 128.47, 128.44, 126.37, 126.01, 122.03, 101.29, 75.06. **HRMS** (ESI) calculated 255.0354 for $C_{14}H_{10}NO_2S$ $[M+H]^+$, found 255.0357.

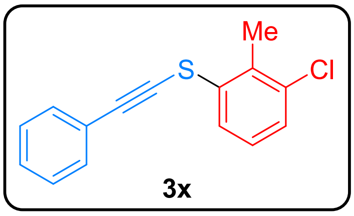
(4-chloro-2-methoxyphenyl)(phenylethynyl)sulfane



3w

According to the general procedure, the reaction gave **3w** in 81% yield (66 mg) as a yellow solid (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 2928, 1580, 1474, 1248, 1061, 1020, 751 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.5 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.39 – 7.35 (m, 3H), 7.18 – 7.13 (m, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.70, 131.78, 128.80, 128.42, 126.80, 126.67, 125.91, 123.79, 122.62, 111.20, 99.55, 74.07, 56.22. **HRMS** (ESI) calculated 275.0292 for $C_{15}H_{12}ClOS$ $[M+H]^+$, found 275.0286.

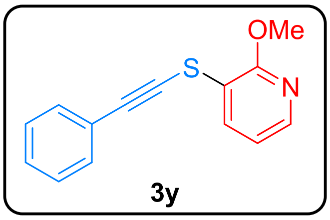
(4-chloro-2-methylphenyl)(phenylethynyl)sulfane



3x

According to the general procedure, the reaction gave **3x** in 68% yield (67 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3462, 3064, 2923, 2168, 1566, 1436, 760 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.42 – 7.37 (m, 3H), 7.32 – 7.28 (m, 1H), 7.24 – 7.17 (m, 1H), 2.46 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.97, 134.38, 132.65, 131.79, 128.81, 128.39, 127.35, 127.30, 125.03, 122.63, 98.41, 75.03, 16.51. **HRMS** (ESI) calculated 259.0343 for $C_{15}H_{12}ClS$ [M+H]$^+$, found 259.0337.

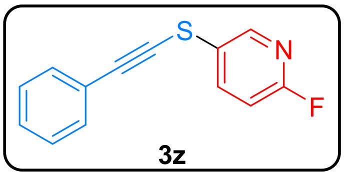
2-methoxy-3-((phenylethynyl)thio)pyridine



3y

According to the general procedure, the reaction gave **3y** in 62% yield (44 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 2935, 2353, 1563, 1462, 1400, 1247, 1021 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.90 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.40 – 7.33 (m, 3H), 6.96 (dd, *J* = 7.5, 5.0 Hz, 1H), 4.03 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.01, 143.88, 134.50, 131.82, 128.87, 128.42, 122.56, 117.70, 117.43, 99.27, 73.77, 53.88. **HRMS** (ESI) calculated 242.0634 for $C_{14}H_{12}NOS$ [M+H]$^+$, found 242.0630.

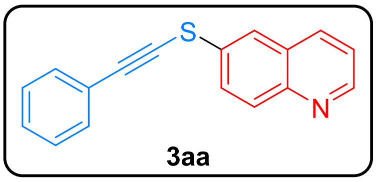
2-fluoro-5-((phenylethynyl)thio)pyridine



3z

According to the general procedure, the reaction gave **3z** in 56% yield as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3456, 1583, 1463, 1359, 1248, 748, 639 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 2.4 Hz, 1H), 7.94 – 7.85 (m, 1H), 7.50 – 7.44 (m, 2H), 7.35 – 7.30 (m, 3H), 6.93 (dd, *J* = 8.6, 3.0 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.81 (d, *J* = 240.0 Hz), 145.46 (d, *J* = 15.4 Hz), 139.80 (d, *J* = 7.9 Hz), 131.84, 129.09, 128.47, 127.32 (d, *J* = 4.8 Hz), 122.20, 110.35 (d, *J* = 38.4 Hz), 97.71, 73.75. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -70.49. **HRMS** (ESI) calculated 230.0434 for $C_{13}H_9FNS$ [M+H]$^+$, found 230.0430.

6-((phenylethynyl)thio)quinoline

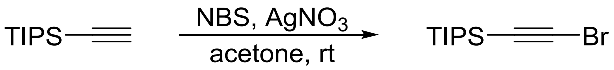


3aa

According to the general procedure, the reaction gave **3aa** in 49% yield (38 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3488, 3430, 3059, 2923, 1588, 1489, 745 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.93 – 8.84 (m, 1H), 8.16 – 8.04 (m, 2H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.60 – 7.53 (m, 2H), 7.42 – 7.34 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.24, 147.01, 135.07, 131.85, 131.66, 130.36, 128.90, 128.64, 128.43, 127.50, 123.90, 122.57, 121.85, 98.65, 74.67. **HRMS** (ESI) calculated 262.0685 for $C_{17}H_{12}NS$ [M+H]$^+$, found 262.0680.

Part 3: Copper-Catalyzed Cross-Coupling of Thiadiazoles with Bromoalkyne

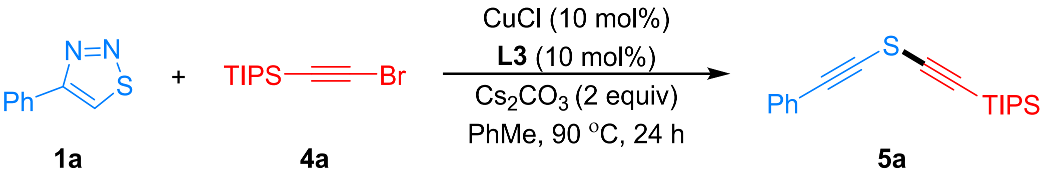
3.1. Synthesis of Bromoalkyne



According to the literature procedures,[11] Ethynyltriisopropylsilane (10 mmol, 1.0 equiv) was first dissolved in acetone (20 mL). Then, *N*-bromosuccinimide (1.2 equiv) and $AgNO_3$ (10 mol%) were added to the resulting solution sequently and the mixture was stirred at room temperature for 4 h. The crude product was filtered and the organic extracts were concentrated. The residue was dissolved in hexane (30 mL) and filtered again. The filtrate was concentrated under reduced pressure and the bromoalkyne was obtained as a colorless liquid (2.55 g, 98%) without further purification.

3.2. Optimization of the Reaction Parameters

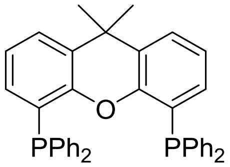
Table S2. Details of Optimization of the Reaction Conditions[a]



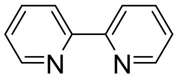
Entry	Variation from the standard conditions	Yield of 5a (%)
1	none	90 (84)[b]
2	Without CuCl	n.d.
3	$CuCl_2$ instead of CuCl	88
4	CuI instead of CuCl	77
5	$Cu(acac)_2$ instead of CuCl	41
6	Without **L3**	35
7	Xantphos instead of **L3**	9
8	bpy instead of **L3**	41
9	**L1** instead of **L3**	12
10	**L2** instead of **L3**	14
11	1,10-Phen instead of **L3**	84
12	**L4** instead of **L3**	68
13	Without Cs_2CO_3	n.d.
14	K_3PO_4 instead of Cs_2CO_3	trace
15	K_2CO_3 instead of Cs_2CO_3	trace
16	NEt_3 instead of Cs_2CO_3	n.d.
17	DIEPA instead of Cs_2CO_3	n.d.

18	THF instead of PhMe	50
19	Dioxane instead of PhMe	74
20	DMSO instead of PhMe	30
21	DMF instead of PhMe	25

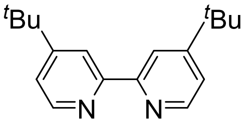
[a]Conditions: **1a** (0.1 mmol), **4a** (0.12 mmol), CuCl (10 mol%), **L3** (10 mol%), Cs_2CO_3 (2 equiv) in PhMe (1 mL) at 90 °C for 24 h. Yield of **5a** was determined by GC using dodecane as the internal standard. n.d. = not detected. [b]Isolated yield.



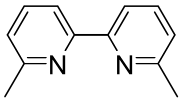
XantPhos
9%



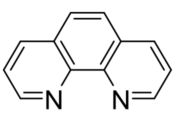
bpy
41%



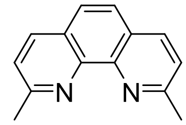
L1
12%



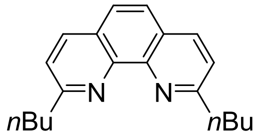
L2
14%



1,10-Phen
84%



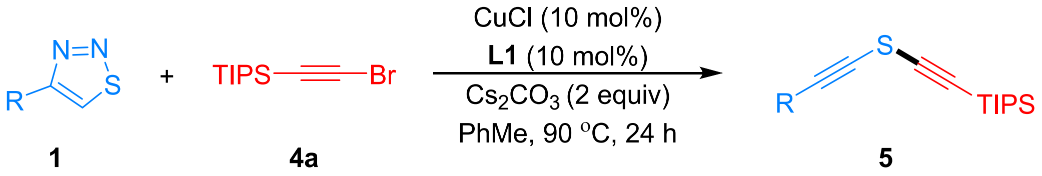
L3
90%



L4
68%

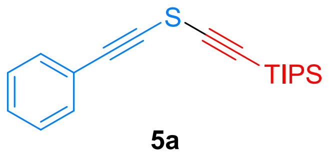
General Procedure for the Optimization Reactions. The procedure was conducted in a N_2-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Copper catalyst (10 mol%, 0.01 mmol), ligand (10 mol%, 0.01 mmol), base, 4-phenyl-1,2,3-thiadiazole **1a** (0.1 mmol, 1.0 equiv), (bromoethynyl)triisopropylsilane **4a** (0.12 mmol, 1.2 equiv) and solvent (1 ml). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at an appreciate temperature for 24 h. After the reaction completed, the mixture was cooled down to room temperature, several drops of solution were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was analyzed by GC to determine calibrated GC yields using n-dodecane as the internal standard.

3.3. General Procedure for Copper-catalyzed Alkynylthiolation of Bromoalkyne



In a N_2-filled glove box, to a reaction tube equipped with a magnetic stir bar was charged with CuCl (10 mol%), **L1** (10 mol%), Cs_2CO_3 (0.6 mmol, 2.0 equiv), 1,2,3-thiadiazole **1** (0.3 mmol, 1.0 equiv), (bromoethynyl)triisopropylsilane **4a** (0.36 mmol, 1.2 equiv) and PhMe (3 ml). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at an appreciate temperature for 24 h. After the reaction completed, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×20 mL), the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products.

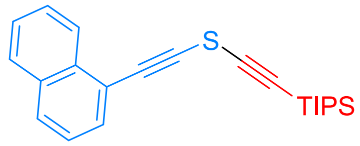
triisopropyl(((phenylethynyl)thio)ethynyl)silane



5a

According to the general procedure, the reaction gave **5a** in 84% yield (79 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2944, 2870, 2353, 2101, 1464, 842, 672 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 6.2 Hz, 2H), 7.31 (d, *J* = 6.3 Hz, 3H), 1.09 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 131.6, 128.8, 128.3, 122.3, 100.4, 94.9, 87.6, 72.2, 18.5, 11.2. **HRMS** (ESI) calculated 313.1452 for $C_{19}H_{27}SSi$ [M-H]$^+$, found 313.1449.

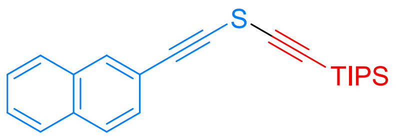
triisopropyl(((naphthalen-1-ylethynyl)thio)ethynyl)silane



5b

According to the general procedure, the reaction gave **5b** in 85% yield (93 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2099, 1586, 1461, 1392, 1014 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.18 (dd, J = 8.3, 1.4 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.55 (dd, J = 7.1, 1.2 Hz, 1H), 7.43 (dddd, J = 17.8, 8.2, 6.8, 1.5 Hz, 2H), 7.30 (dd, J = 8.3, 7.1 Hz, 1H), 1.03 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 133.20, 133.07, 130.35, 129.21, 128.27, 126.93, 126.52, 125.98, 125.09, 119.97, 100.53, 93.47, 87.65, 76.97, 18.56, 11.28. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{23}H_{29}SSi$ 365.1754; found: 365.1750.

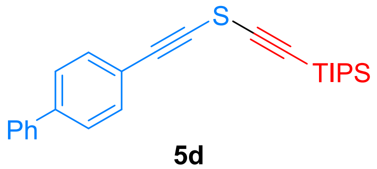
triisopropyl(((naphthalen-2-ylethynyl)thio)ethynyl)silane



5c

According to the general procedure, the reaction gave **5c** in 84% yield (91 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2359, 2341, 2099, 1461, 1382 cm^{-1}. ^{1}**H NMR** (400 MHz, Chloroform-d) δ 8.01 (d, J = 1.7 Hz, 1H), 7.83 (td, J = 8.7, 3.7 Hz, 3H), 7.53 (ddd, J = 10.1, 5.7, 2.4 Hz, 3H), 1.18 (s, 21H). ^{13}**C NMR** (101 MHz, Chloroform-d) δ 133.00, 132.79, 131.81, 128.03, 128.00, 127.81, 127.73, 126.96, 126.63, 119.59, 100.51, 95.37 (d, J = 1.7 Hz), 87.61 (d, J = 2.5 Hz), 72.51, 18.54, 11.27. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{23}H_{29}SSi$ 365.1754; found: 365.1760.

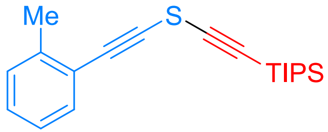
((([1,1'-biphenyl]-4-ylethynyl)thio)ethynyl)triisopropylsilane



5d

According to the general procedure, the reaction gave **5d** in 68% yield (80 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2359, 2101, 2099, 1458, 1394 cm^{-1}. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 4H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 1.13 (s, 21H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 141.59, 140.14, 132.10, 128.86, 127.75, 127.00, 121.19, 100.45, 94.82, 87.56, 72.82, 18.54, 11.25. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{25}H_{31}SSi$ 391.1910 found:391.1907.

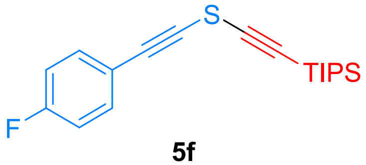
triisopropyl(((o-tolylethynyl)thio)ethynyl)silane



5e

According to the general procedure, the reaction gave **5e** in 70% yield (69 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2100, 1638, 1482, 1461, 1382 cm^{-1}. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 2.34 (s, 3H), 1.02 (s, 21H). ^{13}**C NMR** (126 MHz, Chloroform-d) δ 140.47, 131.65, 129.46, 128.71, 125.53, 122.17, 100.12, 94.06, 87.85, 75.72, 20.50, 18.52, 11.23. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{20}H_{29}SSi$ 329.1754; found: 329.1751.

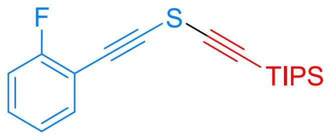
((((4-fluorophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5f

According to the general procedure, the reaction gave **5f** in 70% yield (70 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2100, 1652, 1600, 1540, 1505 cm^{-1}. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.05 – 6.99 (m, 2H), 1.10 (s, 21H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 162.84 (d, *J* = 250.7 Hz), 133.80 (d, *J* = 8.6 Hz), 118.46 (d, *J* = 3.5 Hz), 115.70 (d, *J* = 22.2 Hz), 100.50, 93.80, 87.36, 72.04, 18.52, 11.24. **HRMS-ESI (m/z):** [M+H]$^+$ Calcd. for $C_{19}H_{26}FSSi$ 333.1503; found: 333.1505.

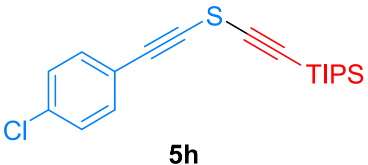
((((2-fluorophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5g

According to the general procedure, the reaction gave **5g** in 81% yield (81 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2101, 1489, 1452, 1249, 1212 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.3 Hz, 1H), 7.32 (q, *J* = 6.4 Hz, 1H), 7.13 – 7.05 (m, 2H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.78 (d, *J* = 252.8 Hz), 133.42, 130.57 (d, *J* = 7.9 Hz), 123.94 (d, *J* = 3.7 Hz), 115.56 (d, *J* = 20.7 Hz), 111.05 (d, *J* = 15.6 Hz), 100.77, 88.38, 86.92, 77.70 (d, *J* = 3.3 Hz), 18.50, 11.23. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -109.30 – -109.48 (m). **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{19}H_{26}FSSi$ 333.1503; found: 333.1506.

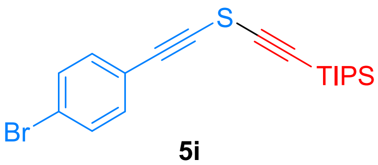
((((4-chlorophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5h

According to the general procedure, the reaction gave **5f** in 58% yield (61 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2100, 1683, 1652, 1540, 1488 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.95, 132.82, 128.71, 120.81, 100.70, 93.77, 87.09, 73.56, 18.52, 11.23. **HRMS-ESI (m/z):** [M+H]$^{+}$ Calcd. for $C_{19}H_{26}ClSSi$ 349.1135; found: 349.1201.

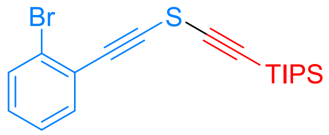
((((4-bromophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5i

According to the general procedure, the reaction gave **5j** in 74% yield (87 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2865, 2100, 1652, 1485, 1458, 1394 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.33 – 7.26 (m, 2H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 132.97, 131.64, 123.19, 121.26, 100.73, 93.84, 87.02, 73.79, 18.52, 11.23. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{19}H_{26}BrSSi$ 393.0702; found: 393.0710.

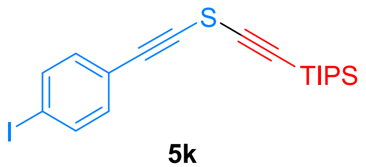
((((2-bromophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5j

According to the general procedure, the reaction gave **5k** in 75% yield (88 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2101, 1635, 1464, 1433, 1046 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (td, *J* = 7.8, 1.7 Hz, 1H), 1.02 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 133.02, 132.43, 129.68, 126.95, 125.12, 124.59, 100.79, 93.60, 86.72, 77.40, 18.54, 11.24. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{19}H_{26}BrSSi$ 393.0702 found:393.0695.

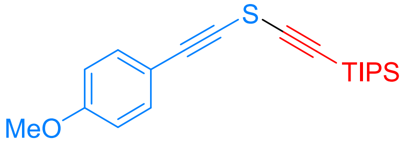
((((4-iodophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5k

According to the general procedure, the reaction gave **5l** in 58% yield (77 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2100, 1652, 1606, 1481, 1458 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 137.52, 132.94, 121.79, 100.74, 94.91, 93.98, 86.99, 74.08, 18.52, 11.22. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{19}H_{26}ISSi$ 441.0564; found: 441.0569.

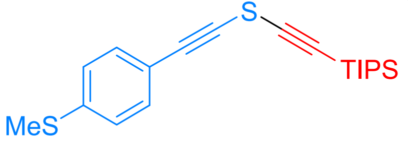
triisopropyl((((4-methoxyphenyl)ethynyl)thio)ethynyl)silane



5l

According to the general procedure, the reaction gave **5m** in 72% yield (74 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2359, 2098, 1603, 1540, 1507 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.18, 133.61, 114.43, 113.97, 99.97, 94.90, 88.10, 70.29, 55.27, 18.53, 11.25. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{20}H_{29}OSSi$ 345.1703; found: 345.1709.

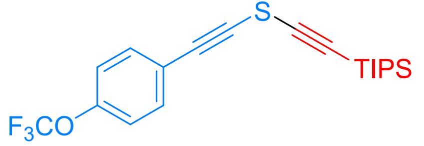
triisopropyl((((4-(methylthio)phenyl)ethynyl)thio)ethynyl)silane



5m

According to the general procedure, the reaction gave **5n** in 81% yield (87 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2864, 2099, 1683, 1652, 1540, 1488 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 2.48 (s, 3H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 140.38, 132.00, 125.58, 118.42, 100.29, 94.68, 87.62, 72.02, 18.50, 15.15, 11.21. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{20}H_{29}S_2Si$ 361.1474; found: 361.1476.

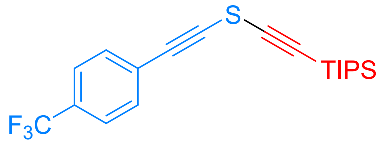
triisopropyl((((4-(trifluoromethoxy)phenyl)ethynyl)thio)ethynyl)silane



5n

According to the general procedure, the reaction gave **5o** in 60% yield (72 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2944, 2866, 2101, 1633, 1505, 1285, 1219 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.28, 133.21, 121.09, 120.83, 120.34 (q, *J* = 258.2 Hz), 100.79, 93.45, 87.00, 73.59, 18.52, 11.24. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.81. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{20}H_{26}F_3OSSi$ 399.1420; found:399.1412.

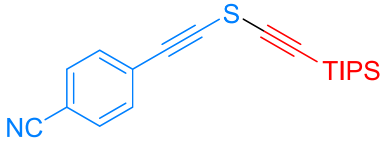
triisopropyl((((4-(trifluoromethyl)phenyl)ethynyl)thio)ethynyl)silane



5o

According to the general procedure, the reaction gave **5p** in 80% yield (92 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2944, 2866, 2102, 1615, 1463, 1322, 1169 cm^{-1}. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 1.11 (s, 21H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 131.56, 130.39 (q, *J* = 32.8 Hz), 126.12, 125.31 (q, *J* = 3.8 Hz), 123.80 (q, *J* = 272.3 Hz), 101.16, 93.64, 86.62, 75.77, 18.52, 11.27. **HRMS-ESI (m/z):** [M+H]$^+$ Calcd. for $C_{20}H_{26}F_3SSi$ 383.1471; found: 383.1470.

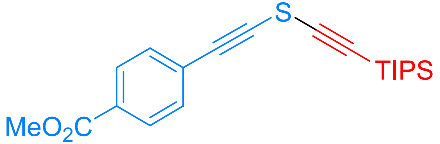
4-((((triisopropylsilyl)ethynyl)thio)ethynyl)benzonitrile



5p

According to the general procedure, the reaction gave **5q** in 47% yield (48 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2359, 2341, 2228, 2101, 1771 cm^{-1}. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 3H), 7.48 (d, *J* = 8.1 Hz, 2H), 1.10 (s, 21H). ^{13}**C NMR** (101 MHz, Chloroform-d) δ 132.05, 131.59, 127.07, 118.26, 111.91, 101.51, 93.44, 86.06, 78.27, 18.50, 11.21. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{20}H_{26}NSSi$ 340.1550; found: 340.1549.

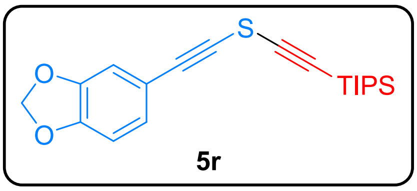
methyl 4-((((triisopropylsilyl)ethynyl)thio)ethynyl)benzoate



5q

According to the general procedure, the reaction gave **5r** in 52% yield (58 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2944, 2865, 2100, 1729, 1605, 1540, 1457 cm^{-1}. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 1.10 (s, 21H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 166.32, 131.12, 129.82, 129.48, 126.87, 101.01, 94.29, 86.70, 76.12, 52.23, 18.50, 11.21. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{21}H_{29}O_2SSi$ 373.1652; found: 373.1653.

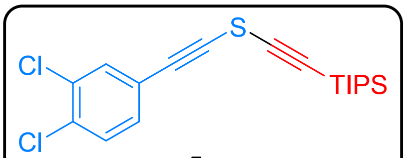
(((benzo[d][1,3]dioxol-5-ylethynyl)thio)ethynyl)triisopropylsilane



5r

According to the general procedure, the reaction gave **5s** in 71% yield (76 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2099, 1504, 1488, 1248, 1040 cm^{-1}. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 6.99 (dd, *J* = 8.0, 1.4 Hz, 2H), 6.89 (d, *J* = 1.3 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 1.09 (s, 21H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 148.51, 147.37, 126.97, 115.53, 111.76, 108.43, 101.40, 100.16, 94.78, 87.81, 70.27, 18.51, 11.23. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{20}H_{27}O_2SSi$ 359.1495; found: 359.1499.

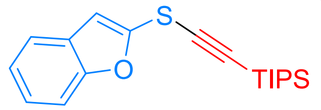
((((3,4-dichlorophenyl)ethynyl)thio)ethynyl)triisopropylsilane



5s

According to the general procedure, the reaction gave **5t** in 66% yield (76 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2944, 2866, 2101, 1633, 1505, 1285, 1219 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.24 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 133.30, 133.07, 132.66, 130.58, 130.40, 122.21, 101.12, 92.57, 86.48, 75.13, 18.52, 11.22. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{19}H_{26}Cl_2SSi$ 383.0818; found: 383.0828.

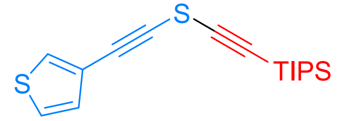
((benzofuran-2-ylthio)ethynyl)triisopropylsilane



5t

According to the general procedure, the reaction gave **5u** in 58% yield (57 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2865, 2100, 1635, 1462, 1445, 1252 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.79 (s, 1H), 1.01 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 156.46, 145.66, 128.33, 124.57, 123.14, 120.50, 111.08, 109.13, 101.19, 88.14, 18.54, 11.24. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{19}H_{27}OSSi$ 331.1546; found: 331.1551.

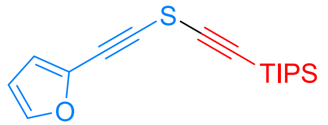
triisopropyl(((thiophen-3-ylethynyl)thio)ethynyl)silane



5u

According to the general procedure, the reaction gave **5v** in 77% yield (74 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2865, 2099, 1770, 1652, 1462, 1383 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.13 (d, *J* = 5.0 Hz, 1H), 1.10 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 130.37, 129.90, 125.40, 121.43, 100.33, 90.03, 87.48, 71.72, 18.53, 11.24. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{17}H_{25}S_2Si$ 321.1161; found: 321.1160.

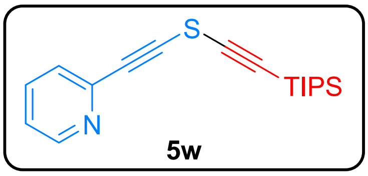
(((furan-2-ylethynyl)thio)ethynyl)triisopropylsilane



5v

According to the general procedure, the reaction gave **5w** in 67% yield (61 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2865, 2100, 1653, 1647,1458, 1206 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 1.2 Hz, 1H), 6.74 – 6.70 (m, 1H), 6.41 (dd, *J* = 3.4, 1.9 Hz, 1H), 1.08 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.70, 136.22, 118.28, 111.00, 100.60, 86.17, 85.11, 78.16, 18.21, 11.04. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{17}H_{25}OSSi$ 305.1390; found: 305.1398.

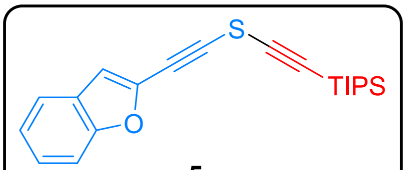
2-((((triisopropylsilyl)ethynyl)thio)ethynyl)pyridine



5w

According to the general procedure, the reaction gave **5f** in 45% yield (43 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2941, 2864, 2099, 1716, 1697, 1652, 1577 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.7 Hz, 1H), 7.65 (td, *J* = 7.8, 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.22 (m, 1H), 1.09 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.03, 142.45, 136.19, 126.97, 123.14, 101.29, 94.25, 86.04, 73.85, 18.51, 11.20. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{18}H_{26}NSSi$ 316.1550; found: 316.1552.

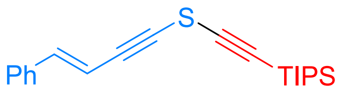
(((benzofuran-2-ylethynyl)thio)ethynyl)triisopropylsilane



5x

According to the general procedure, the reaction gave **5f** in 60% yield (64 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2943, 2866, 1764, 1743, 1658, 1553, 1540 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.33 (m, 1H), 7.28 – 7.23 (m, 1H), 7.06 (s, 1H), 1.10 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.08, 137.85, 127.22, 126.30, 123.43, 121.50, 114.19, 111.40, 101.41, 85.59, 85.51, 80.22, 18.51, 11.21. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{21}H_{27}OSSi$ 355.1546; found: 355.1551.

(E)-triisopropyl(((4-phenylbut-3-en-1-yn-1-yl)thio)ethynyl)silane

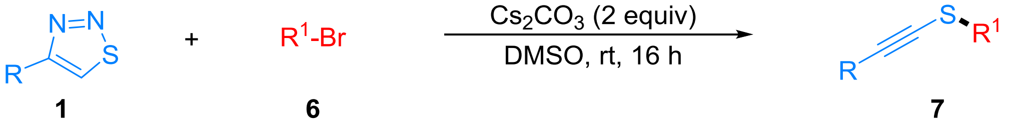


5y

According to the general procedure, the reaction gave **5z** in 50% yield (61 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2942, 2864, 2098, 1772, 1490, 1460, 1448 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.30 (m, 3H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.24 (d, *J* = 16.2 Hz, 1H), 1.11 (s, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.37, 135.83, 128.95, 128.74, 126.38, 107.19, 100.38, 94.61, 87.61, 73.96, 18.54, 11.26. **HRMS-ESI (m/z):** [M+H]+ Calcd. for $C_{21}H_{29}SSi$ 341.1754; found: 341.1753.

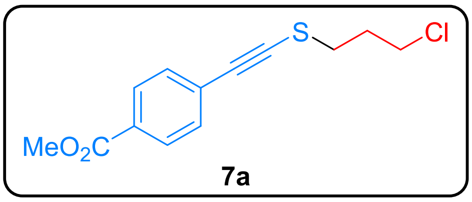
Part 4: Further Elaboration for Synthetic Potential of Thiadiazoles

4.1. Late-stage Alkynylthiolation of Unactivated Alkyl Bromide



General Procedure. Cs_2CO_3 (0.6 mmol, 2.0 equiv) and thiadiazoles (0.3 mmol, 1.0 equiv) in DMSO (3 mL) were added unactivated alkyl bromides (0.6 mmol, 2.0 equiv). After stirring under air for 16 h at room temperature, the mixture was quenched by 1 mL 1N-HCl. Then the reaction mixture was diluted with ethyl acetate (20.0 mL), washed with water (3×10 mL), the organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products.

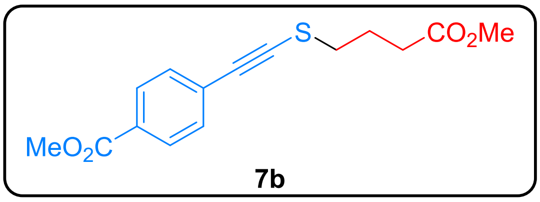
methyl 4-(((3-chloropropyl)thio)ethynyl)benzoate



7a

According to the general procedure, the reaction gave **7a** in 70% yield (56 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3486, 3428, 2952, 2161, 1718, 1601, 1274 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 3.73 (t, *J* = 6.1 Hz, 2H), 2.95 (s, 2H), 2.31 – 2.22 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.35, 130.77, 129.40, 129.04, 127.79, 92.96, 82.57, 52.11, 42.59, 32.44, 31.75. **HRMS** (ESI) calculated 269.0398 for $C_{13}H_{14}ClO_2S$ $[M+H]^+$, found 269.0392.

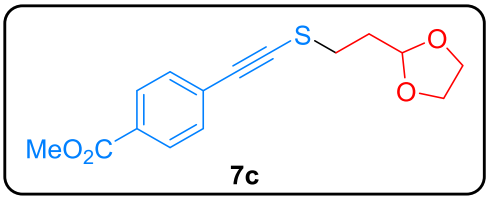
methyl 4-(((4-methoxy-4-oxobutyl)thio)ethynyl)benzoate



7b

According to the general procedure, the reaction gave **7b** in 65% yield (57 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3436, 2947, 2160, 1719, 1599, 1268, 757 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.66 (s, 3H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.17 – 2.09 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.05, 166.40, 130.78, 129.38, 128.96, 127.94, 92.83, 82.89, 52.10, 51.61, 34.79, 31.91, 24.38. **HRMS** (ESI) calculated 293.0842 for $C_{15}H_{17}O_4S$ $[M+H]^+$, found 293.0835.

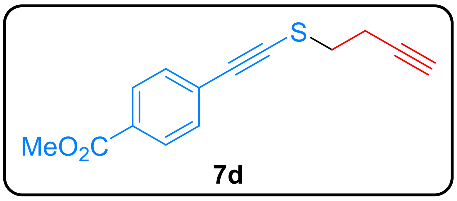
methyl 4-(((2-(1,3-dioxolan-2-yl)ethyl)thio)ethynyl)benzoate



7c

According to the general procedure, the reaction gave **7c** in 80% yield (70 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 2977, 2382, 2170, 1719, 1281, 1117, 765 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.02 (t, *J* = 4.4 Hz, 1H), 3.99 – 3.94 (m, 2H), 3.88 (s, 3H), 3.87 – 3.82 (m, 2H), 2.95 – 2.88 (m, 2H), 2.21 – 2.14 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.41, 130.76, 129.37, 128.90, 127.98, 102.50, 93.06, 83.15, 64.96, 52.09, 33.59, 29.94. **HRMS** (ESI) calculated 293.0842 for $C_{15}H_{17}O_4S$ [M+H]$^+$, found 293.0836.

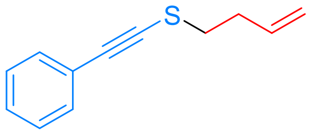
methyl 4-((but-3-yn-1-ylthio)ethynyl)benzoate



7d

According to the general procedure, the reaction gave **7d** in 85% yield (61 mg) as a white solid (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3486, 3272, 2161, 1713, 1601, 1278, 692 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.74 – 2.68 (m, 2H), 2.09 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.36, 130.86, 129.41, 129.11, 127.74, 93.59, 82.03, 81.31, 70.18, 52.13, 34.11, 19.42. **HRMS** (ESI) calculated 245.0631 for $C_{14}H_{13}O_2S$ [M+H]$^+$, found 245.0626.

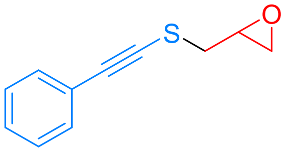
but-3-en-1-yl(phenylethynyl)sulfane



7e

According to the general procedure, the reaction gave **7e** in 82% yield (47 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3457, 2923, 2164, 1596, 916, 752, 689 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 5.97 – 5.80 (m, 1H), 5.24 – 5.08 (m, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.62 – 2.53 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.56, 131.38, 128.23, 127.98, 123.40, 116.78, 93.28, 79.10, 34.84, 33.41. **HRMS** (ESI) calculated 189.0732 for $C_{12}H_{13}S$ [M+H]$^+$, found 189.0729.

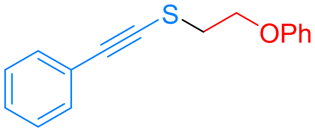
2-(((phenylethynyl)thio)methyl)oxirane



7f

According to the general procedure, the reaction gave **7f** in 76% yield (44 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3456, 2994, 2166, 1596, 1485, 1073, 754 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 3H), 3.41 – 3.32 (m, 1H), 3.04 – 2.97 (m, 1H), 2.94 (t, *J* = 4.4 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.77 – 2.73 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 131.31, 128.22, 128.20, 122.92, 93.09, 78.09, 50.61, 47.36, 37.68. **HRMS** (ESI) calculated 191.0525 for $C_{11}H_{11}OS$ [M+H]$^+$, found 191.0521.

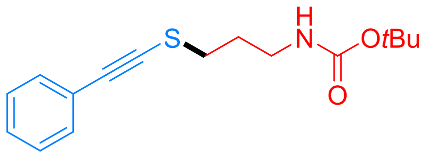
(2-phenoxyethyl)(phenylethynyl)sulfane



7g

According to the general procedure, the reaction gave **7g** in 76% yield (44 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 100/1). **IR** (KBr) ν_{max}: 2923, 2348, 2165, 1483, 1234, 1029, 750 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 – 7.35 (m, 2H), 7.33 – 7.15 (m, 5H), 7.00 – 6.87 (m, 3H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.11 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.22, 131.45, 129.47, 128.24, 123.04, 121.12, 114.59, 93.25, 78.31, 65.98, 34.37. **HRMS** (ESI) calculated 255.0838 for $C_{16}H_{15}OS$ [M+H]$^{+}$, found 255.0833.

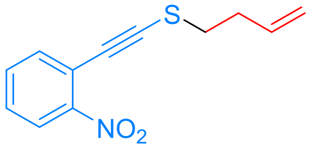
tert-butyl (3-((phenylethynyl)thio)propyl)carbamate



7h

According to the general procedure, the reaction gave **7h** in 85% yield (74 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 5/1). **IR** (KBr) ν_{max}: 3347, 2970, 2354, 1700, 1516, 1259, 1168 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.30 – 7.27 (m, 3H), 4.72 (s, 1H), 3.33 – 3.25 (m, 2H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.95 (m, 2H), 1.43 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.91, 131.37, 128.23, 128.05, 123.22, 93.21, 79.26, 78.96, 38.86, 32.92, 29.60, 28.33. **HRMS** (ESI) calculated 290.1220 for $C_{16}H_{22}NO_2S$ [M+H]$^{+}$, found 290.1214.

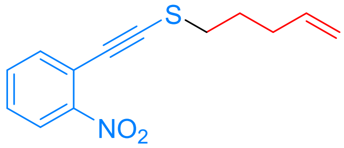
but-3-en-1-yl((2-nitrophenyl)ethynyl)sulfane



7i

According to the general procedure, the reaction gave **7i** in 93% yield (65 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 2829, 2353, 2153, 1603, 1354, 916, 766 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.40 – 7.33 (m, 1H), 5.93 – 5.81 (m, 1H), 5.24 – 5.06 (m, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.62 (q, *J* = 7.1 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.13, 135.31, 133.33, 132.93, 127.40, 124.66, 119.20, 117.04, 90.55, 90.40, 35.20, 33.28. **HRMS** (ESI) calculated 234.0583 for $C_{12}H_{12}NO_2S$ [M+H]$^{+}$, found 234.0576.

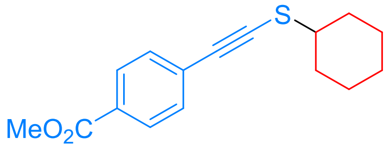
((2-nitrophenyl)ethynyl)(pent-4-en-1-yl)sulfane



7j

According to the general procedure, the reaction gave **7j** in 76% yield (56 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 2925, 2353, 2153, 1610, 1522, 1345, 744 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.40 – 7.32 (m, 1H), 5.86 – 5.76 (m, 1H), 5.11 – 4.97 (m, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.24 (q, *J* = 7.1 Hz, 2H), 2.03 – 1.94 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.14, 137.15, 133.35, 132.90, 127.35, 124.66, 119.26, 115.64, 90.81, 90.06, 35.31, 32.02, 28.21. **HRMS** (ESI) calculated 248.0740 for $C_{13}H_{14}NO_2S$ [M+H]$^{+}$, found 248.0732.

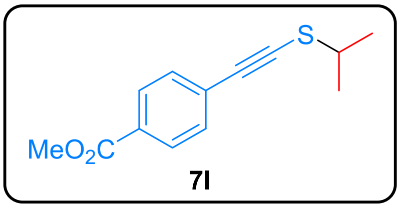
methyl 4-((cyclohexylthio)ethynyl)benzoate



7k

According to the general procedure, the reaction gave **7k** in 66% yield (54 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3432, 2932, 2855, 2160, 1722, 1277, 1107 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 3.11 – 2.97 (m, 1H), 2.18 – 2.06 (m, 2H), 1.90 – 1.78 (m, 2H), 1.61 – 1.51 (m, 2H), 1.43 – 1.25 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.57, 130.73, 129.43, 128.75, 128.42, 94.07, 82.92, 52.15, 47.83, 33.03, 25.98, 25.36. **HRMS** (ESI) calculated 275.1100 for $C_{16}H_{19}O_2S$ [M+H]$^+$, found 275.1094.

methyl 4-((isopropylthio)ethynyl)benzoate



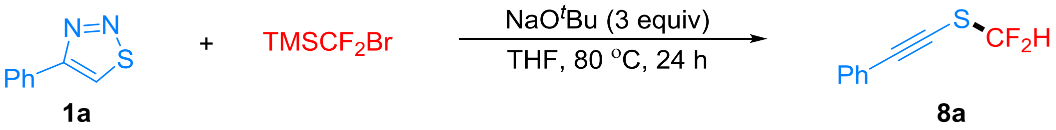
7l

According to the general procedure, the reaction gave **7l** in 78% yield (55 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3425, 2962, 2159, 1721, 1276, 1106, 765 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 3.32 – 3.21 (m, 1H), 1.43 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.47, 130.65, 129.40, 128.77, 128.29, 94.46, 82.84, 52.10, 39.98, 22.92. **HRMS** (ESI) calculated 235.0787 for $C_{13}H_{15}O_2S$ [M+H]$^+$, found 235.0782.

4.2. Concise Method for Synthesis of Difluoromethanethiated Alkyne from Thiadiazoles

4.2.1. Optimization of the Reaction Parameters

Table S3. Details of Optimization of the Reaction Conditions[a]

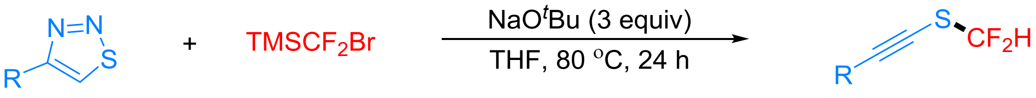


Entry	Variation from the standard conditions	Yield of 5a (%)
1	none	83(77)^b
2	K_3PO_4 instead of NaO*t*Bu	n.d.
3	K_2CO_3 instead of NaO*t*Bu	n.d.
4	Cs_2CO_3 instead of NaO*t*Bu	n.d.
5	NEt_3 instead of NaO*t*Bu	n.d.
6	DIEPA instead of NaO*t*Bu	n.d.
7	toluene instead of THF	14
8	Dioxane instead of THF	76
9	DMSO instead of THF	65
10	1 equiv of NaO*t*Bu	29
11	rt	trace

[a]Conditions: **1a** (0.1 mmol), $TMSCF_2Br$ (0.2 mmol), NaO*t*Bu (3 equiv) in THF (1 mL) at 80 °C for 24 h. Yield of **8a** was determined by GC using dodecane as the internal standard. n.d. = not detected. [b]Isolated yield.

General Procedure for the Optimization Reactions. The procedure was conducted in a N_2-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with 4-phenyl-1,2,3-thiadiazole **1a** (0.1 mmol, 1.0 equiv), $TMSCF_2Br$ (0.2 mmol, 2 equiv), base (0.3 mmol, 3 equiv) and solvent (1 ml). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at an appreciate temperature for 24 h. After the reaction completed, the mixture was cooled down to room temperature, several drops of solution were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was analyzed by GC to determine calibrated GC yields using n-dodecane as the internal standard.

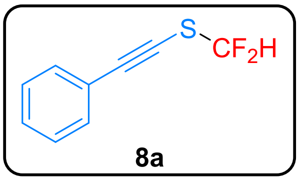
4.2.2 General Procedure for Alkynylthiolation with $TMSCF_2Br$



1 **8**

General Procedure. NaO^{t}Bu (0.9 mmol, 3.0 equiv) and thiadiazoles (0.3 mmol, 1.0 equiv) in THF (3 mL) were added $TMSCF_2Br$ (0.6 mmol, 2.0 equiv). After stirring under N_2 for 24 h at 80 °C, the mixture was quenched by 1 mL 1N-HCl. Then the reaction mixture was diluted with ethyl acetate (20.0 mL), washed with water (3×8 mL), the organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products.

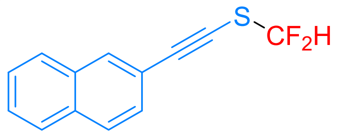
(difluoromethyl)(phenylethynyl)sulfane



8a

According to the general procedure, the reaction gave **8a** in 77% yield (43 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.29 (m, 3H), 6.95 (t, *J* = 56.9 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 131.98, 129.26, 128.40, 121.99, 119.62 (t, *J* = 281.3 Hz), 98.80 (t, *J* = 1.9 Hz), 68.95 (t, *J* = 6.5 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -92.8 (d, *J* = 57.0 Hz). Spectroscopic data for **8a** match those previously reported in the literature.[12]

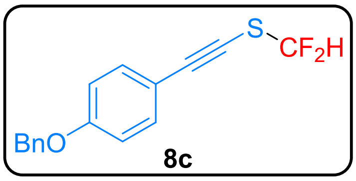
(difluoromethyl)(naphthalen-2-ylethynyl)sulfane



8b

According to the general procedure, the reaction gave **8b** in 85% yield (60 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3480, 3059, 2166, 1496, 1284, 1076, 741 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.86 – 7.79 (m, 3H), 7.57 – 7.50 (m, 3H), 7.01 (t, *J* = 56.9 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 133.15, 132.73, 132.33, 128.11, 128.10, 127.85, 127.74, 127.16, 126.71, 119.66 (t, *J* = 281.5 Hz), 119.22, 99.29, 69.22 (t, *J* = 6.4 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.7 (d, *J* = 56.9 Hz). **HRMS** (ESI) calculated 235.0388 for $C_{13}H_9F_2S$ [M+H]$^+$, found 235.0380.

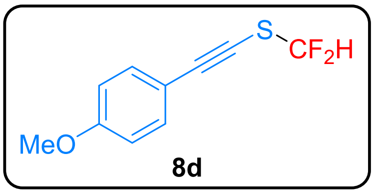
([1,1'-biphenyl]-4-ylethynyl)(difluoromethyl)sulfane



8c

According to the general procedure, the reaction gave **8c** in 81% yield (70 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3417, 2925, 2169, 1602, 1244, 1072, 739 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.5 – 7.2 (m, 7H), 7.0 – 6.7 (m, 3H), 5.0 (s, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.6, 136.3, 134.0, 128.6, 128.1, 127.4, 119.7 (t, *J* = 281.2 Hz), 114.9, 114.3, 98.8 (t, *J* = 1.9 Hz), 70.0, 67.4 (t, *J* = 6.5 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -93.0 (d, *J* = 56.9 Hz). **HRMS** (ESI) calculated 291.0650 for $C_{16}H_{13}F_2OS$ [M+H]$^+$, found 291.0644.

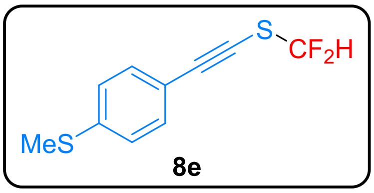
(difluoromethyl)((4-methoxyphenyl)ethynyl)sulfane



8d

According to the general procedure, the reaction gave **8d** in 48% yield (31 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 2927, 2349, 1628, 1505, 1256, 1072, 830 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.09 – 6.75 (m, 3H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.49, 134.03, 119.78 (t, *J* = 281.1 Hz), 114.02, 113.99, 98.86, 67.24 (t, *J* = 6.6 Hz), 55.27. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -93.07 (d, *J* = 57.0 Hz). **HRMS** (ESI) calculated 215.0264 for $C_{10}H_9F_2OS$ [M+H]$^+$, found 215.0268.

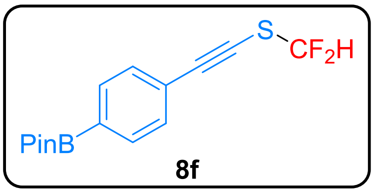
(difluoromethyl)((4-(methylthio)phenyl)ethynyl)sulfane



8e

According to the general procedure, the reaction gave **8e** in 72% yield (50 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3450, 2924, 2171, 1591, 1286, 1077, 819 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.93 (t, *J* = 56.9 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.01, 132.37, 125.56, 119.62 (t, *J* = 281.4 Hz), 118.02, 98.62, 68.84 (t, *J* = 6.4 Hz), 15.07. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.6 – -93.2 (m). **HRMS** (ESI) calculated 231.0108 for $C_{10}H_9F_2S_2$ [M+H]$^+$, found 231.0104.

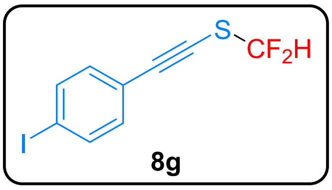
2-(4-(((difluoromethyl)thio)ethynyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



8f

According to the general procedure, the reaction gave **8f** in 65% yield (60 mg) as a white solid (flash column chromatography eluent, petrol ether/EtOAc = 10/1). **IR** (KBr) ν_{max}: 3490, 2980, 2927, 1606, 1362, 1146, 1080 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 56.9 Hz, 1H), 1.35 (s, 12H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.60, 130.84, 124.56, 119.58 (t, *J* = 281.4 Hz), 98.98, 84.04, 70.37 (t, *J* = 6.4 Hz), 24.83. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.7 (d, *J* = 57.3 Hz). **HRMS** (ESI) calculated 310.1119 for $C_{15}H_{18}BF_2O_2S$ [M+H]$^+$, found 310.1114.

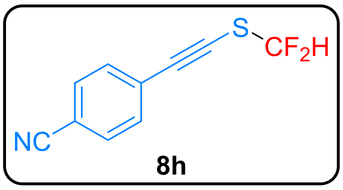
(difluoromethyl)((4-iodophenyl)ethynyl)sulfane



8g

According to the general procedure, the reaction gave **8g** in 63% yield (59 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3457, 2928, 2169, 1718, 1477, 1283, 1070 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 56.8 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 137.63, 133.26, 121.50, 119.37 (t, *J* = 281.7 Hz), 97.91 (t, *J* = 2.0 Hz), 95.44, 70.71 (t, *J* = 6.4 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.7 (d, *J* = 56.9 Hz). **HRMS** (ESI) calculated 308.9052 for $C_9H_4F_2IS$ [M-H]$^+$, found 308.9055.

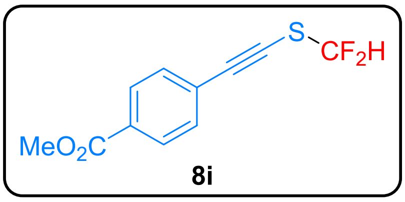
4-(((difluoromethyl)thio)ethynyl)benzonitrile



8h

According to the general procedure, the reaction gave **8h** in 46% yield (29 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.96 (t, *J* = 56.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 132.08, 131.89, 126.75, 119.03 (t, *J* = 282.4 Hz), 118.15, 112.29, 97.26 (t, *J* = 1.9 Hz), 74.44 (t, *J* = 6.2 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.46 (d, *J* = 56.6 Hz). Spectroscopic data for **8h** match those previously reported in the literature.[12]

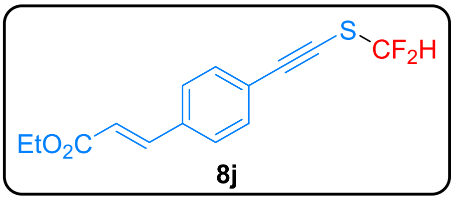
methyl 4-(((difluoromethyl)thio)ethynyl)benzoate



8i

According to the general procedure, the reaction gave **8i** in 56% yield (60 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.96 (t, *J* = 56.8 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.27, 131.46, 130.23, 129.52, 126.54, 119.31 (t, *J* = 282.0 Hz), 98.13 (t, *J* = 1.8 Hz), 72.50 (t, *J* = 6.3 Hz), 52.26. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.6 (d, *J* = 56.7 Hz). Spectroscopic data for **8i** match those previously reported in the literature.[12]

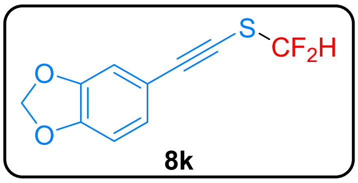
ethyl (E)-3-(4-(((difluoromethyl)thio)ethynyl)phenyl)acrylate



8j

According to the general procedure, the reaction gave **8j** in 63% yield (53 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3458, 2997, 2383, 1719, 1183, 1079, 744 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.50 – 7.44 (m, 4H), 6.95 (t, *J* = 56.8 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.61, 143.21, 135.07, 132.18, 127.91, 123.63, 119.53, 119.41 (t, *J* = 281.8 Hz), 98.38 (t, *J* = 1.9 Hz), 71.30 (t, *J* = 6.4 Hz), 60.61, 14.24. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.72 (d, *J* = 56.9 Hz). **HRMS** (ESI) calculated 283.0599 for $C_{14}H_{13}F_2O_2S$ $[M+H]^+$, found 283.0592.

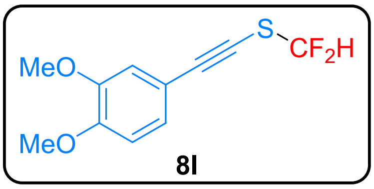
5-(((difluoromethyl)thio)ethynyl)benzo[d][1,3]dioxole



8k

According to the general procedure, the reaction gave **8k** in 74% yield (51 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3486, 2903, 2164, 1604, 1490, 1073, 815 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.08 – 6.71 (m, 4H), 5.99 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.85, 147.43, 127.51, 119.67 (t, *J* = 281.4 Hz), 115.11, 112.06, 108.47, 101.49, 98.72 (t, *J* = 1.7 Hz), 67.17 (t, *J* = 6.6 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -93.0 (d, *J* = 57.0 Hz). **HRMS** (ESI) calculated 229.0129 for $C_{10}H_7F_2O_2S$ $[M+H]^+$, found 229.0124.

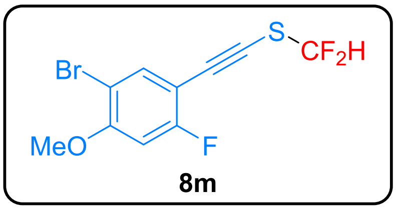
((3,4-dichlorophenyl)ethynyl)(difluoromethyl)sulfane



8l

According to the general procedure, the reaction gave **8l** in 61% yield (45 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1). **IR** (KBr) ν_{max}: 3469, 2926, 2163, 1590, 1254, 1065, 733 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 1.4 Hz, 1H), 7.05 – 6.78 (m, 3H), 3.89 (s, 3H), 3.87 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.46, 148.62, 126.10, 119.72 (t, *J* = 281.2 Hz), 114.84, 114.05, 110.91, 98.99 (t, *J* = 2.0 Hz), 67.20 (t, *J* = 6.5 Hz), 55.89, 55.87. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -93.02. **HRMS** (ESI) calculated 245.0442 for $C_{11}H_{11}F_2O_2S$ $[M+H]^+$, found 245.0438.

((5-bromo-2-fluoro-4-methoxyphenyl)ethynyl)(difluoromethyl)sulfane



8m

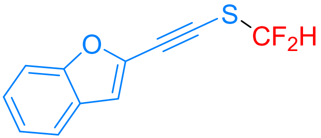
According to the general procedure, the reaction gave **8m** in 48% yield (67 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3457, 2921, 2166, 1605, 1491, 1074, 738 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 56.9 Hz, 1H), 6.66 (d, *J* = 10.7 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.50 (d, *J* = 253.9 Hz), 157.99 (d, *J* = 9.8 Hz), 137.11 (d, *J* = 2.2 Hz), 119.47 (t, *J* = 281.9 Hz), 105.89 (d, *J* = 3.5 Hz), 103.79 (d, *J* = 17.0 Hz), 100.15 (d, *J* = 26.4 Hz), 90.80 (t, *J* = 2.0 Hz), 74.24 – 73.77 (m), 56.65.**^{19}F NMR** (376 MHz, Chloroform-*d*) δ -92.72, -106.29. **HRMS** (ESI) calculated 310.9348 for $C_{10}H_7BrF_3OS$ $[M+H]^+$, found 310.9345.

(E)-(difluoromethyl)(4-phenylbut-3-en-1-yn-1-yl)sulfane

8n

According to the general procedure, the reaction gave **8n** in 65% yield (41 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3467, 2927, 2148, 1285, 1074, 953, 745 cm^{-1}. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 5H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.88 (t, *J* = 57.0 Hz, 1H), 6.24 (d, *J* = 16.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.30, 135.62, 129.17, 128.78, 126.46, 119.57 (t, *J* = 281.4 Hz), 106.91, 98.41 (t, *J* = 2.0 Hz), 70.66 (t, *J* = 6.4 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -92.9 (d, *J* = 56.9 Hz). **HRMS** (ESI) calculated 211.0388 for $C_{11}H_9F_2S$ [M+H]$^+$, found 211.0384.

2-(((difluoromethyl)thio)ethynyl)benzo[b]thiophene



8o

According to the general procedure, the reaction gave **8o** in 51% yield (34 mg) as a yellow oil (flash column chromatography eluent, petrol ether). **IR** (KBr) ν_{max}: 3444, 2922, 2161, 1602, 1292, 1076, 741 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.32 – 7.27 (m, 1H), 7.17 – 6.82 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.17, 137.47, 127.09, 126.60, 123.54, 121.66, 119.27, 116.45, 114.97, 111.45, 89.35 (t, *J* = 2.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -92.29 (d, *J* = 56.8 Hz). **HRMS** (ESI) calculated 225.0180 for $C_{11}H_7F_2OS$ [M+H]$^+$, found 225.0175.

Part 5: Product Derivatizations

(((3,3-difluoro-2-phenylcycloprop-1-en-1-yl)thio)ethynyl)triisopropylsilane (9a):

5a (0.3 mmol) (2.0 equiv) (2.2 equiv) **9a**, 82% yield

According to the literature procedures,[13] triisopropyl(((phenylethynyl)thio)ethynyl)silane (**5a**, 94.2 mg, 0.3 mmol), $TMSCF_3$ (85.2 mg, 0.6 mmol), NaI (98.9 mg, 0.66 mmol), and THF (1.0 mL) were mixed into a pressure tube at room temperature. Then the reaction mixture was heated at 110 ℃ for 2 h. The reaction was quenched by adding saturated Na_2CO_3 solution (5 mL), followed by extraction with Et_2O (20 mL x 2). The organic phase was dried over anhydrous K_2CO_3. After the removal of solvent under vacuum, the residue was subjected to silica gel column chromatography with petroleum ether. The product **9a** was obtained in 82% yield (89 mg) as a yellow oil (flash column chromatography eluent, petrol ether).

IR (KBr) ν_{max}: 3458, 2948, 2864, 2182, 2101, 1292, 1036 cm^{-1}.

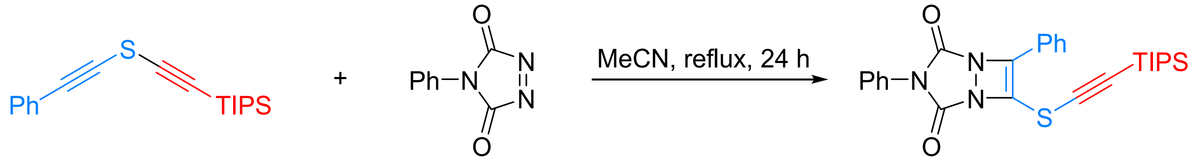
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 2H), 7.46 – 7.40 (m, 3H), 1.13 (s, 21H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 130.78, 130.39, 128.91, 127.35, 123.52, 118.06, 103.34, 102.72 (t, *J* = 268.7 Hz), 86.55, 18.49, 11.28.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.7.

HRMS (ESI) calculated 364.1493 for $C_{20}H_{27}F_2SSi$ $[M+H]^+$, found 364.1497.

3,6-diphenyl-7-(((triisopropylsilyl)ethynyl)thio)-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione (9b):



5a (0.39 mmol) (1.0 equiv) **9b**, 68% yield

According to the literature procedures,[14] to a flame dried round bottom flask equipped with a stir bar was added a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (52.5 mg, 0.3 mmol) in dry acetonitrile (1.5 mL). To this stirring solution was added dropwise a solution of **5a** (122.5 mg, 0.39 mmol) in dry acetonitrile (1 mL). Then the round bottom flask was attached to a water cooled condenser and the mixture was refluxed for 24 h. The resultant mixture was concentrated under reduced pressure and purified via flash chromatography to afford the corresponding product **9b** in 68% yield (100 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1).

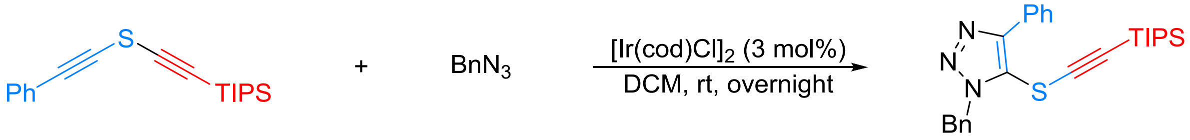
IR (KBr) ν_{max}: 2938, 2863, 2354, 1750, 1374, 1216, 681 cm^{-1}.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.52 – 7.43 (m, 8H), 1.03 (s, 21H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.44, 154.65, 146.69, 130.71, 129.32, 129.22, 128.83, 126.39, 125.56, 125.47, 121.72, 100.12, 86.08, 18.44, 11.13.

HRMS (ESI) calculated 490.1979 for $C_{27}H_{32}N_3O_2SSi$ $[M+H]^+$, found 490.1970.

1-benzyl-4-phenyl-5-(((triisopropylsilyl)ethynyl)thio)-1H-1,2,3-triazole (9c):



5a (0.3 mmol) (2 equiv) **9c**, 67% yield

According to the literature procedures,[15] in a glove box, to an oven-dried 5-mL vial was added **5a** (94.2 mg, 0.3 mmol), the azide (79.8 mg, 0.6 mmol), [Ir(cod)Cl]$_2$ (7 mg, 3 mol%), and DCM (3.0 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature overnight, and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **9c** in 67% yield (90 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1).

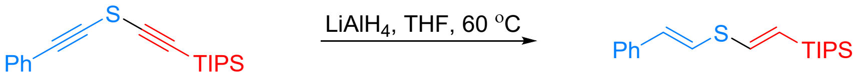
IR (KBr) ν_{max}: 3468, 2947, 2864, 2097, 1462, 841, 729 cm^{-1}.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.07 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.31 (m, 6H), 5.77 (s, 2H), 0.99 (s, 21H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.17, 134.44, 129.71, 128.83, 128.66, 128.47, 128.42, 127.86, 127.49, 120.65, 98.21, 88.41, 52.50, 18.38, 11.00.

HRMS (ESI) calculated 448.2237 for $C_{26}H_{34}N_3SSi$ [M+H]$^+$, found 448.2231.

triisopropyl((E)-2-(((E)-styryl)thio)vinyl)silane (9d):



5a (0.3 mmol) **9d**, 85% yield

According to the literature procedures,[16] **5a** (94.2 mg, 0.3 mmol) was dissolved in dry tetrahydrofuran (1 mL) and LiAlH$_4$ (0.6 mmol, 2.0 equiv.) was then added in one portion. The mixture was stirred at 60 °C for 2 hour. The crude mixture was cooled to 0 °C and 1M HCl was added dropwise until a neutral pH was obtained. Diethyl ether was added to the mixture and following extraction, the combined organic phases were dried with anhydrous magnesium sulfate. The resulting suspension was filtered and the filtrate was concentrated under vacuum to provide a crude reaction mixture which was purified by column chromatography. The product **9d** was obtained in 85% yield (81 mg) as a yellow oil (flash column chromatography eluent, petrol ether).

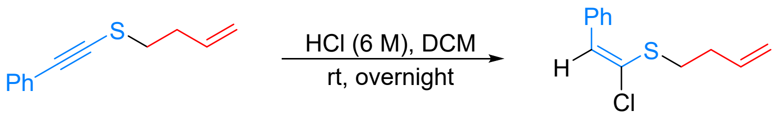
IR (KBr) ν_{max}: 3444, 2944, 2862, 1593, 947, 740, 659 cm^{-1}.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 4H), 7.31 – 7.26 (m, 1H), 6.93 – 6.88 (m, 1H), 6.78 – 6.69 (m, 2H), 5.96 (d, *J* = 18.3 Hz, 1H), 1.14 (s, 21H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.45, 136.57, 130.93, 128.65, 127.48, 125.94, 124.03, 121.70, 18.57, 10.94.

HRMS (ESI) calculated 319.1910 for $C_{19}H_{31}SSi$ [M+H]$^+$, found 319.1903.

(E)-but-3-en-1-yl(1-chloro-2-phenylvinyl)sulfane (9e):



7e (0.3 mmol) **9e**, 89% yield

According to the literature procedures,[17] to a solution of **7e** (56.4 mg, 0.3 mmol) in EtOAc (1 mL) was added HCl (0.3 mL, 6 M). The resulting solution was stirred at room temperature. Progress of the reaction was monitored periodically by TLC. The reaction mixture was quenched with saturated aqueous $NaHCO_3$-solution and then the solution was extracted with EtOAc three times, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **9e** in 89% yield (60 mg) as a yellow oil (flash column chromatography eluent, petrol ether).

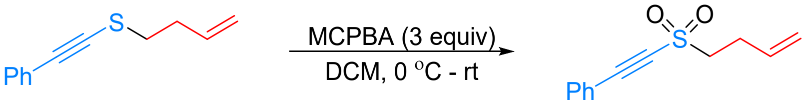
IR (KBr) ν_{max}: 3457, 2923, 1638, 1594, 915, 744, 691 cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.25 (m, 1H), 7.01 (s, 1H), 5.86 – 5.70 (m, 1H), 5.11 – 4.96 (m, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.42 – 2.35 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.82, 134.82, 134.70, 129.28, 129.15, 128.16, 127.85, 116.62, 33.61, 33.14.

HRMS (ESI) calculated 225.0499 for $C_{12}H_{14}ClS$ $[M+H]^+$, found 225.0498.

((but-3-en-1-ylsulfonyl)ethynyl)benzene (9f):



7e (0.3 mmol) **9f**, 78% yield

According to the literature procedures,[18] 3 equiv of *m*-CPBA acid was added to a solution of **7e** (56.4 mg, 0.3 mmol) in DCM (2 mL) cooled at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and then for 12 h at room temperature. Upon completion, the reaction mixture was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated. The residue was purified by silica gel flash column chromatograph to give the desired product **9f** in 78% yield (51 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1).

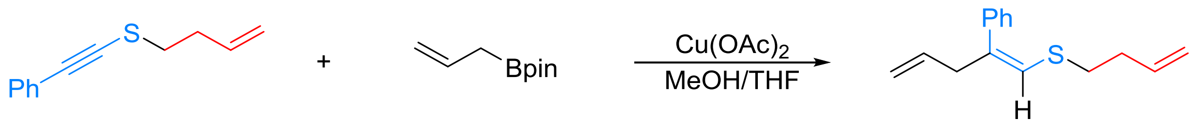
IR (KBr) ν_{max}: 3470, 2947, 2863, 1752, 1377, 1216, 684 cm^{-1}.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 2H), 7.56 – 7.49 (m, 1H), 7.46 – 7.38 (m, 2H), 5.92 – 5.80 (m, 1H), 5.24 – 5.11 (m, 2H), 3.39 – 3.32 (m, 2H), 2.77 – 2.68 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.19, 132.82, 131.74, 128.77, 117.62, 117.47, 92.61, 83.09, 57.35, 27.10.

HRMS (ESI) calculated 221.0631 for $C_{12}H_{13}O_2S$ $[M+H]^+$, found 221.0626.

(Z)-but-3-en-1-yl(2-phenylpenta-1,4-dien-1-yl)sulfane (9g):



7e (0.3 mmol) (2 equiv) **9g**, 72% yield

According to the literature procedures,[19] to a mixture of Cu(OAc)$_2$ (11.0 mg, 0.06 mmol) and **7e** (56.4 mg, 0.3 mmol) in 1.6 mL of MeOH/THF (v/v = 1:3) was added allylboronate (100.8 mg, 0.6 mmol) under a nitrogen atmosphere. After stirring at 25 °C for 12 h, the reaction mixture was concentrated and purified by column chromatography on silica gel. The product **9g** was obtained in 72% yield (50 mg) as a yellow oil (flash column chromatography eluent, petrol ether).

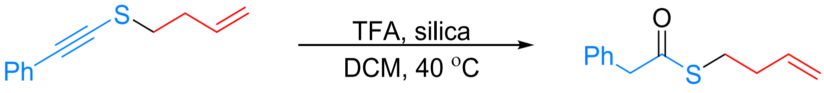
IR (KBr) ν_{max}: 3477, 3071, 2919, 2182, 1638, 1433, 915 cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 4H), 7.27 – 7.19 (m, 1H), 6.01 (s, 1H), 5.88 – 5.73 (m, 2H), 5.10 – 4.97 (m, 4H), 3.24 – 3.16 (m, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.40 – 2.32 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.88, 136.69, 136.31, 135.89, 128.03, 127.86, 127.08, 123.31, 116.47, 116.10, 42.64, 34.31, 34.01.

HRMS (ESI) calculated 231.1202 for $C_{15}H_{19}S$ [M+H]$^+$, found 231.1199.

S-(but-3-en-1-yl) 2-phenylethanethioate (9h):



7e (0.3 mmol) **9h**, 56% yield

According to the literature procedures,[20] to a 5-mL vial was added **7e** (56.4 mg, 0.3 mmol), 2.5 mL of DCM, TFA (51 mg, 0.45 mmol) and 0.2 g of silica. The resulting suspension was heated at 40 °C for 24 h, the reaction mixture was concentrated and purified by column chromatography on silica gel. The product **9h** was obtained in 56% yield (31 mg) as a yellow oil (flash column chromatography eluent, petrol ether/EtOAc = 20/1).

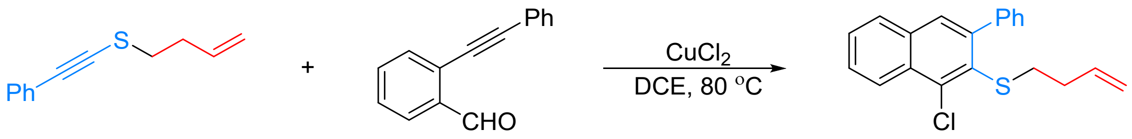
IR (KBr) ν_{max}: 3476, 2924, 1688, 1445, 999, 706, 606 cm^{-1}.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 5.82 – 5.70 (m, 1H), 5.10 – 5.00 (m, 2H), 3.82 (s, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.35 – 2.28 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.22, 135.94, 133.64, 129.48, 128.59, 127.33, 116.44, 50.49, 33.43, 28.43.

HRMS (ESI) calculated 207.0838 for $C_{12}H_{15}OS$ [M+H]$^+$, found 207.0835.

but-3-en-1-yl(1-chloro-3-phenylnaphthalen-2-yl)sulfane (9i):



7e (0.3 mmol) (1 equiv) **9i**, 66% yield

According to the literature procedures,[19] in a glove box, to an oven-dried 10-mL vial was added $CuCl_2$ (78 mg, 0.6 mmol), **7e** (56.4 mg, 0.3 mmol), 2-(phenylethynyl)benzaldehyde (61.8 mg, 0.3 mmol) and DCE (3.0 mL). The reaction mixture was stirred at 80 °C for 12 h, then the mixture was diluted with DCM (20 mL) and washed with saturated NH_4Cl (20 mL). The organic phase was separated, dried with $MgSO_4$, concentrated under vacuum and purified by column chromatography on silica gel. The product **9i** was obtained in 66% yield (64 mg) as a yellow oil (flash column chromatography eluent, petrol ether).

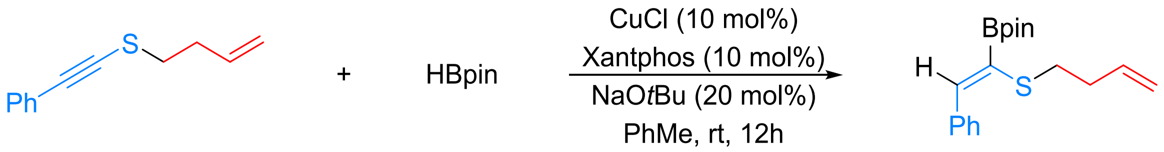
IR (KBr) ν_{max}: 3063, 2922, 1485, 1436, 1266, 900, 758 cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.73 (s, 1H), 7.65 – 7.51 (m, 4H), 7.49 – 7.41 (m, 3H), 5.71 – 5.54 (m, 1H), 4.97 – 4.85 (m, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.13 – 2.03 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.08, 141.44, 137.99, 136.30, 133.40, 130.98, 130.71, 129.69, 128.18, 128.00, 127.76, 127.41, 127.36, 127.31, 125.31, 115.79, 34.68, 33.54.

HRMS (ESI) calculated 325.0812 for $C_{20}H_{18}ClS$ $[M+H]^+$, found 325.0806.

(Z)-2-(1-(but-3-en-1-ylthio)-2-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9j):



7e (0.3 mmol) (2 equiv) **9j**, 68% yield

According to the literature procedures,[21] to a mixture of CuCl (3 mg, 10 mol%), Xantphos (17 mg, 10 mol%), and NaO*t*Bu (5.8 mg, 20 mol%) in 0.5 mL of toluene was added neat HBpin (90 μL, 0.6 mmol) under a nitrogen atmosphere. After stirring at 0 °C for 15 min, **7e** (0.3 mmol) was added at 0 °C, followed by stirring at 25 °C for 12 h, then the reaction mixture was concentrated and purified by column chromatography on silica gel. The product **9j** was obtained in 68% yield (64 mg) as a yellow oil (flash column chromatography eluent, petroleum ether/EtOAc = 20:1).

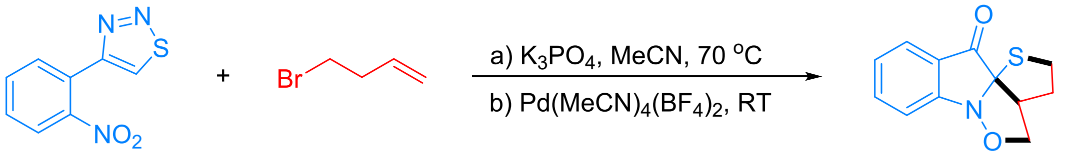
IR (KBr) ν_{max}: 3453, 2979, 2926, 1331, 1143, 993, 693 cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.24 (m, 1H), 5.87 – 5.71 (m, 1H), 5.05 – 4.94 (m, 2H), 3.01 – 2.96 (m, 2H), 2.33 – 2.26 (m, 2H), 1.33 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.53, 136.96, 136.64, 130.07, 127.87, 127.69, 115.70, 84.09, 34.75, 32.71, 24.71.

HRMS (ESI) calculated 316.1777 for $C_{18}H_{26}BO_2S$ $[M+H]^+$, found 316.1773.

2,3,3a,4-tetrahydro-11H-thieno[2',3':3,4]isoxazolo[2,3-a]indol-11-one (7i-a):



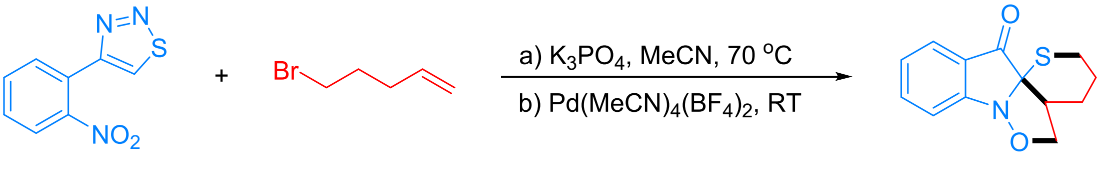
1ae **7i-a**, 69% yield

In a glove box, K_3PO_4 (0.6 mmol, 2.0 equiv) and **1ae** (0.3 mmol, 1.0 equiv) in MeCN (3 mL) were added 4-bromobut-1-ene (0.6 mmol, 2.0 equiv). After stirring under N_2 for 16 h at 70 °C, the mixture was cooled to room temperature. Then, to this mixture, $Pd(MeCN)_4(BF_4)_2$ (5 mol%) was added. After 3 hours of stirring at room temperature, full conversion of **1ae** was observed via TLC. The reaction was then quenched by the addition of water (20 mL) and extracted with ethyl acetate (3x20 mL). The organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product **7i-a** in 69% yield (48 mg) as a yellow solid. Spectroscopic data for **7i-a** match the previously reported in the literature.[22]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 3.88 (d, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.31 – 3.14 (m, 3H), 2.57 – 2.49 (m, 1H), 2.35 – 2.26 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.45, 160.23, 137.50, 126.17, 125.19, 123.82, 118.44, 93.37, 72.45, 57.82, 37.25, 35.94.

3,4,4a,5-tetrahydro-2H,12H-thiopyrano[2',3':3,4]isoxazolo[2,3-a]indol-12-one (7j-a):



1ae

7j-a, 55% yield

In a glove box, K_3PO_4 (0.6 mmol, 2.0 equiv) and **1ae** (0.3 mmol, 1.0 equiv) in MeCN (3 mL) were added 5-bromopent-1-ene (0.6 mmol, 2.0 equiv). After stirring under N_2 for 16 h at 70 °C, the mixture was cooled to room temperature. Then, to this mixture, $Pd(MeCN)_4(BF_4)_2$ (5 mol%) was added. After 3 hours of stirring at room temperature, full conversion of **1ae** was observed via TLC. The reaction was then quenched by the addition of water (20 mL) and extracted with ethyl acetate (3x20 mL). The organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product **7j-a** in 55% yield (41 mg) as a yellow solid.

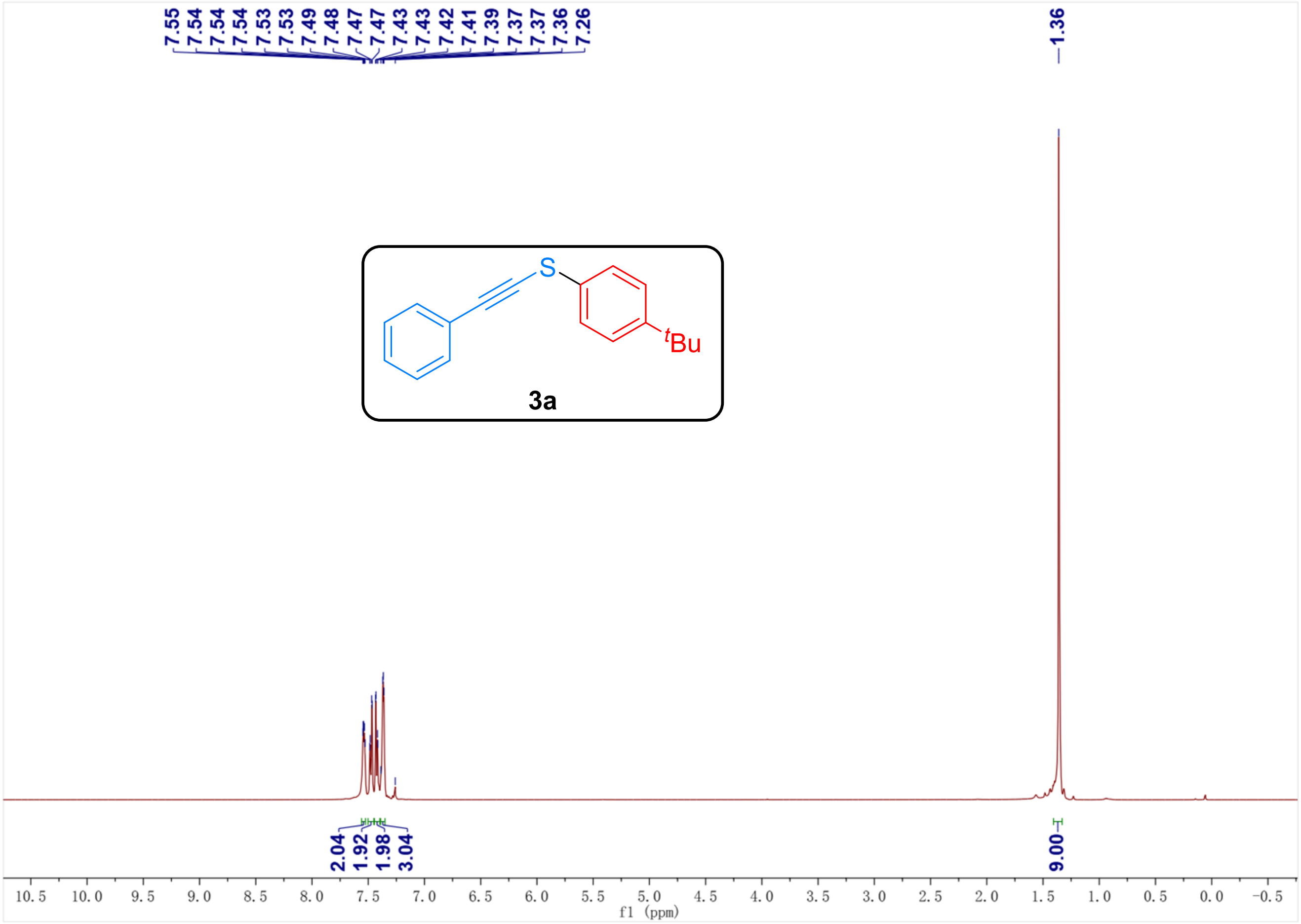
IR (KBr) ν_{max}: 2924, 2836, 2349, 1719, 1602, 1361, 769 cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 – 7.60 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 4.99 – 4.90 (m, 1H), 3.12 – 3.01 (m, 1H), 2.98 – 2.89 (m, 1H), 2.72 (d, *J* = 13.6 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.39 – 2.28 (m, 1H), 2.27 – 2.18 (m, 1H), 2.15 – 2.06 (m, 1H), 1.57 – 1.48 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.35, 162.41, 137.31, 125.37, 124.75, 120.89, 117.95, 83.86, 83.22, 41.58, 34.68, 29.72, 26.80.

HRMS (ESI) calculated 248.0740 for $C_{13}H_{14}NO_2S$ $[M+H]^+$, found 248.0734.

NMR Spectra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7.41
7.39
7.37
7.37
7.36
7.26
1.36
S
tBu
3a
2.04
1.92
1.98
3.04
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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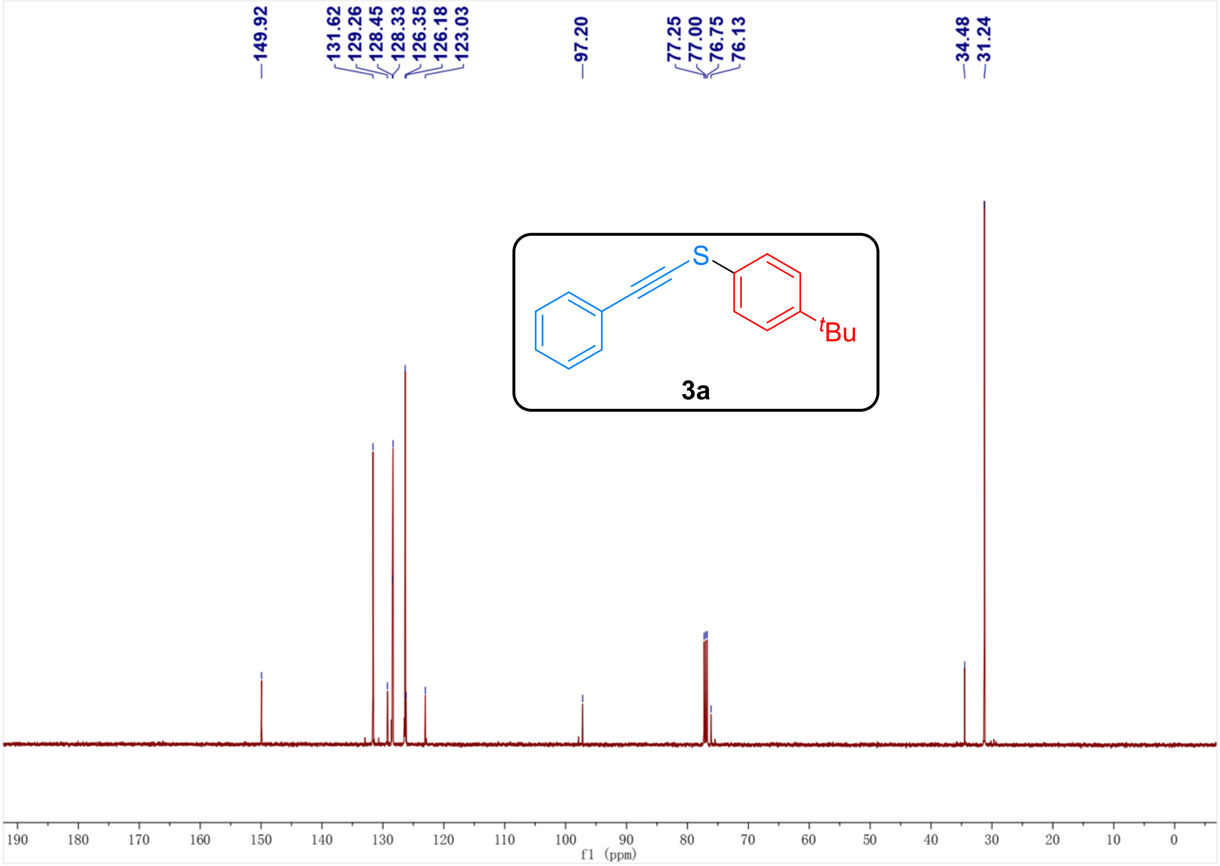
f1 (ppm)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3a
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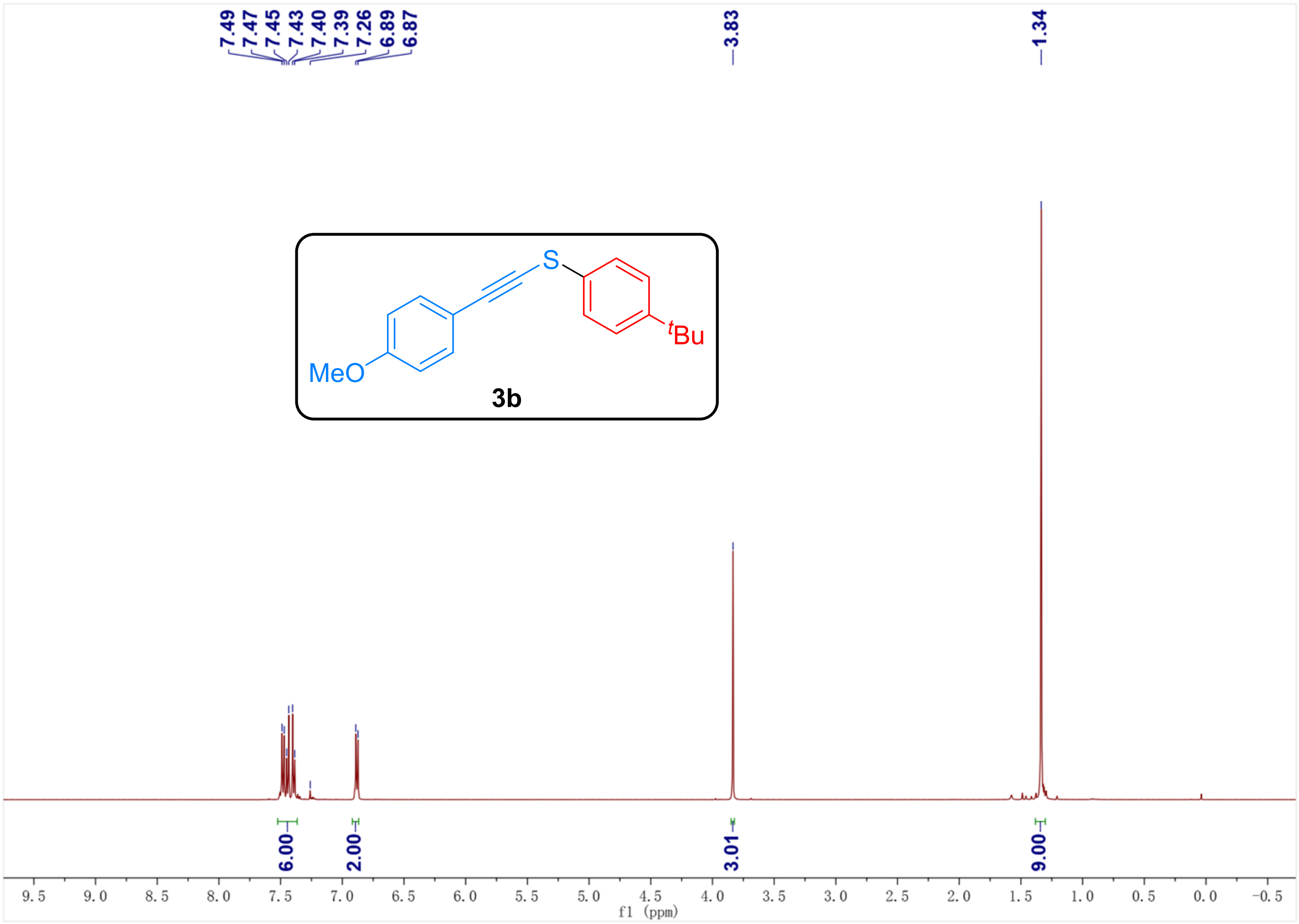
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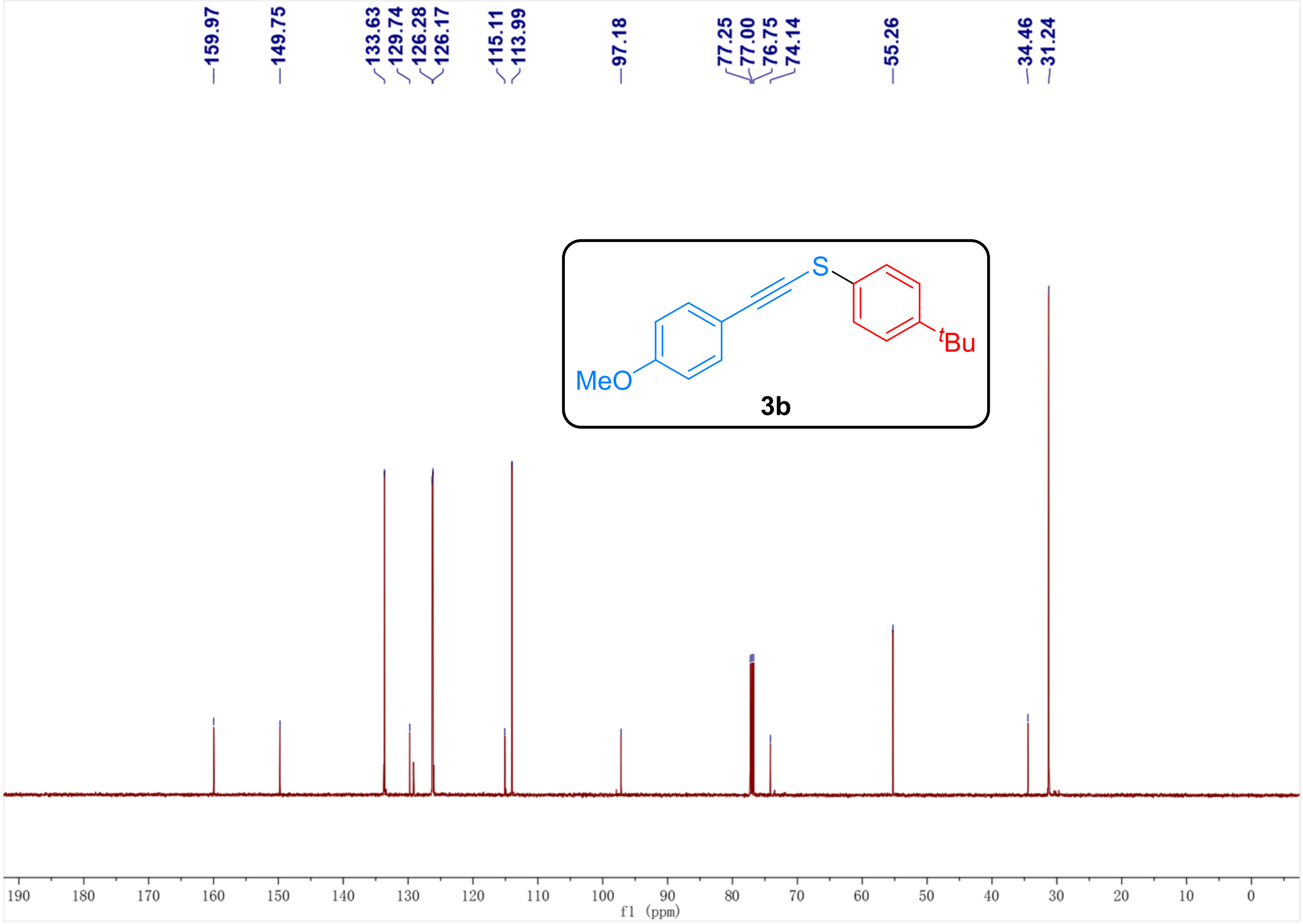
3b
6.00
2.00
3.01
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.00
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74.14
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31.24
S
MeO
tBu
3b
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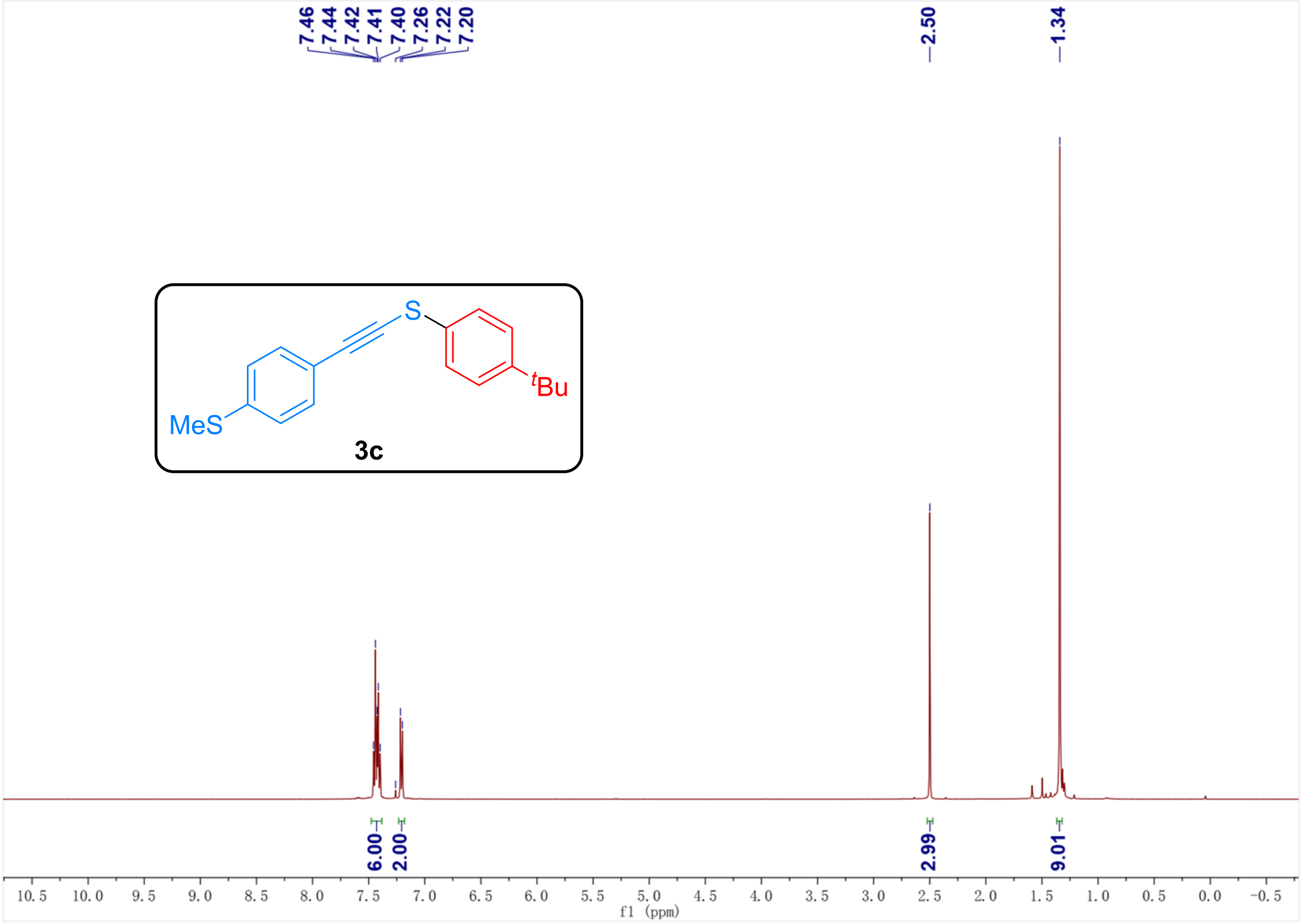
f1 (ppm)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3c
6.00
2.00
2.99
9.01
10.5
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8.0
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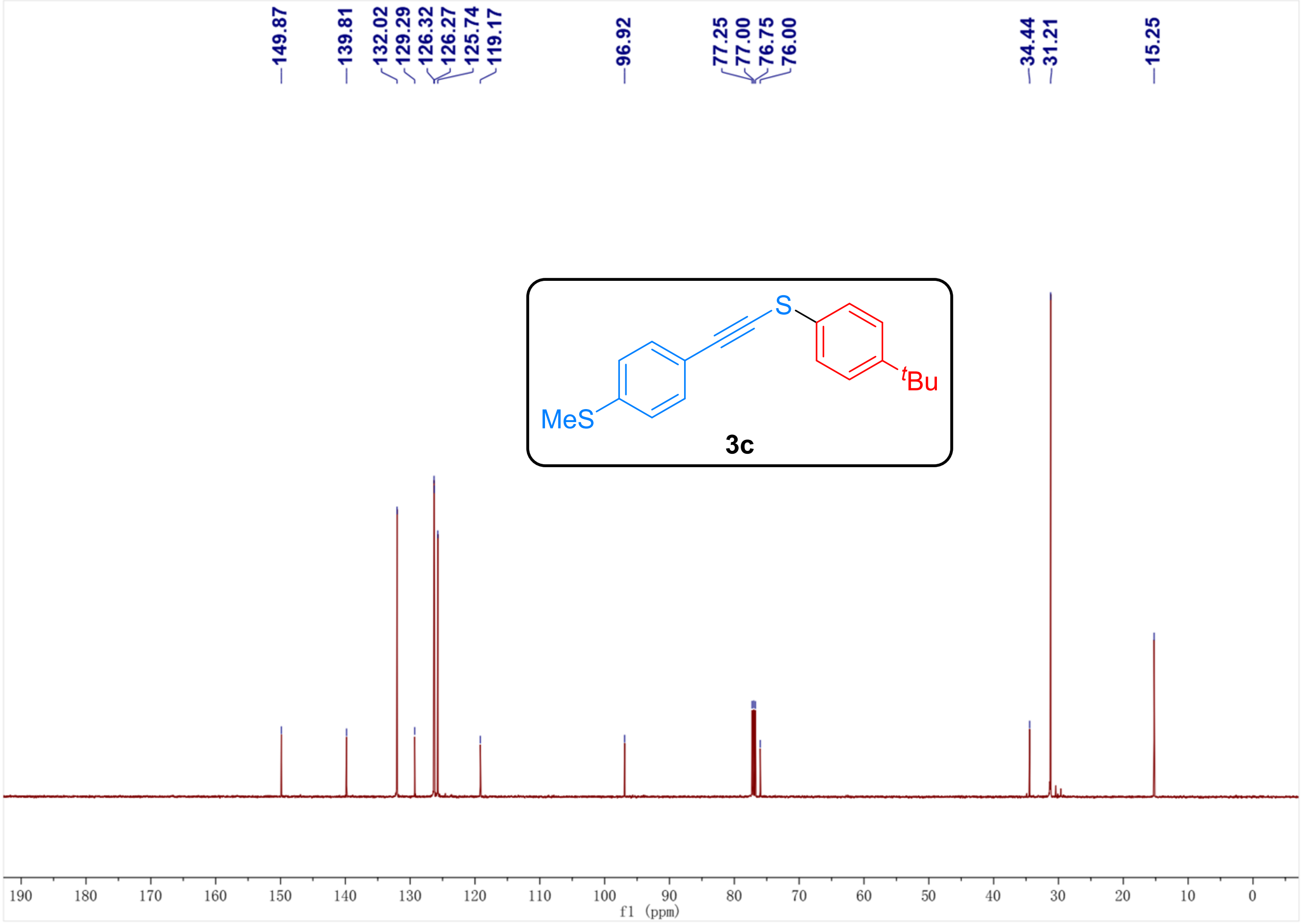
f1 (ppm)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3c
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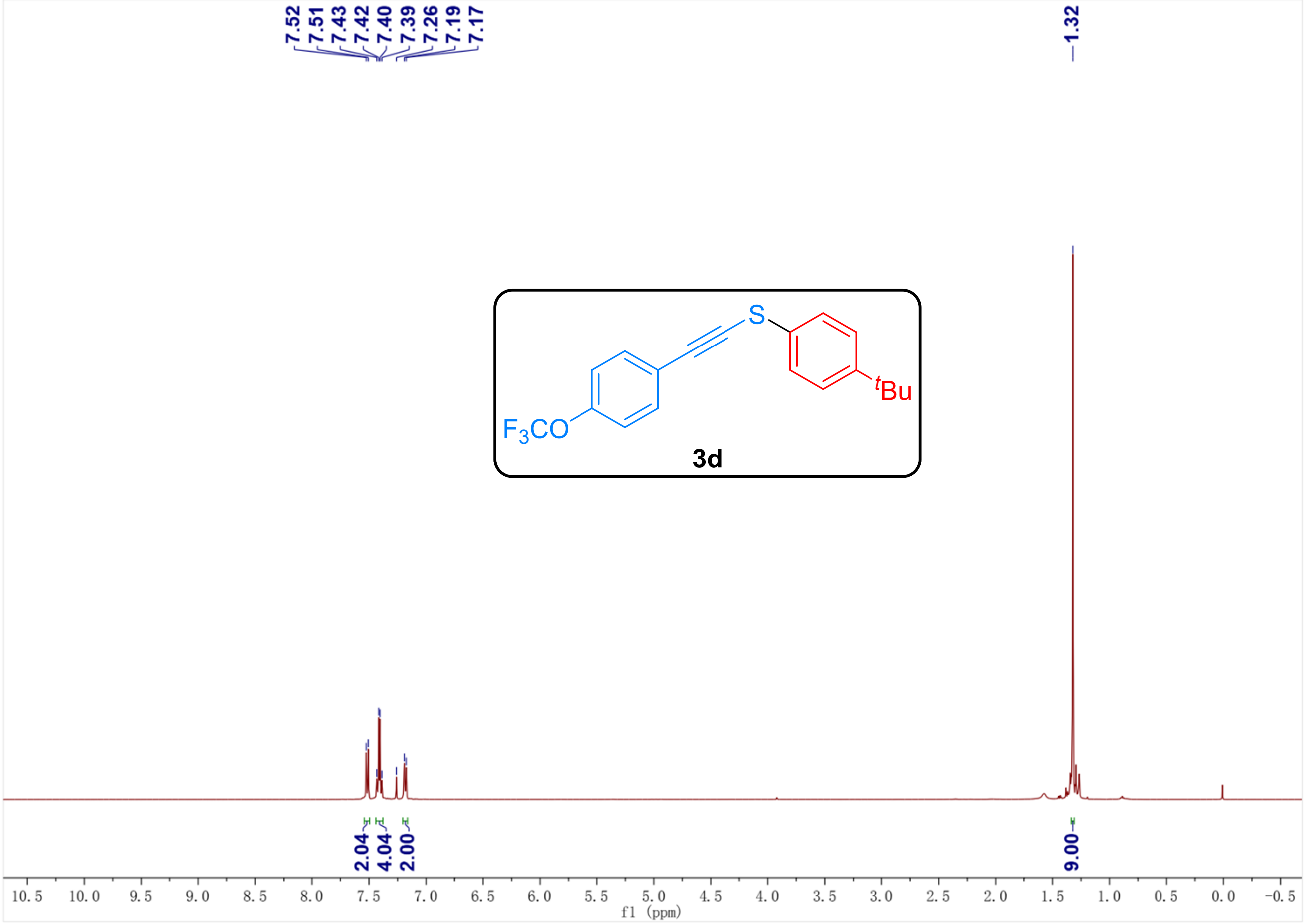
f1 (ppm)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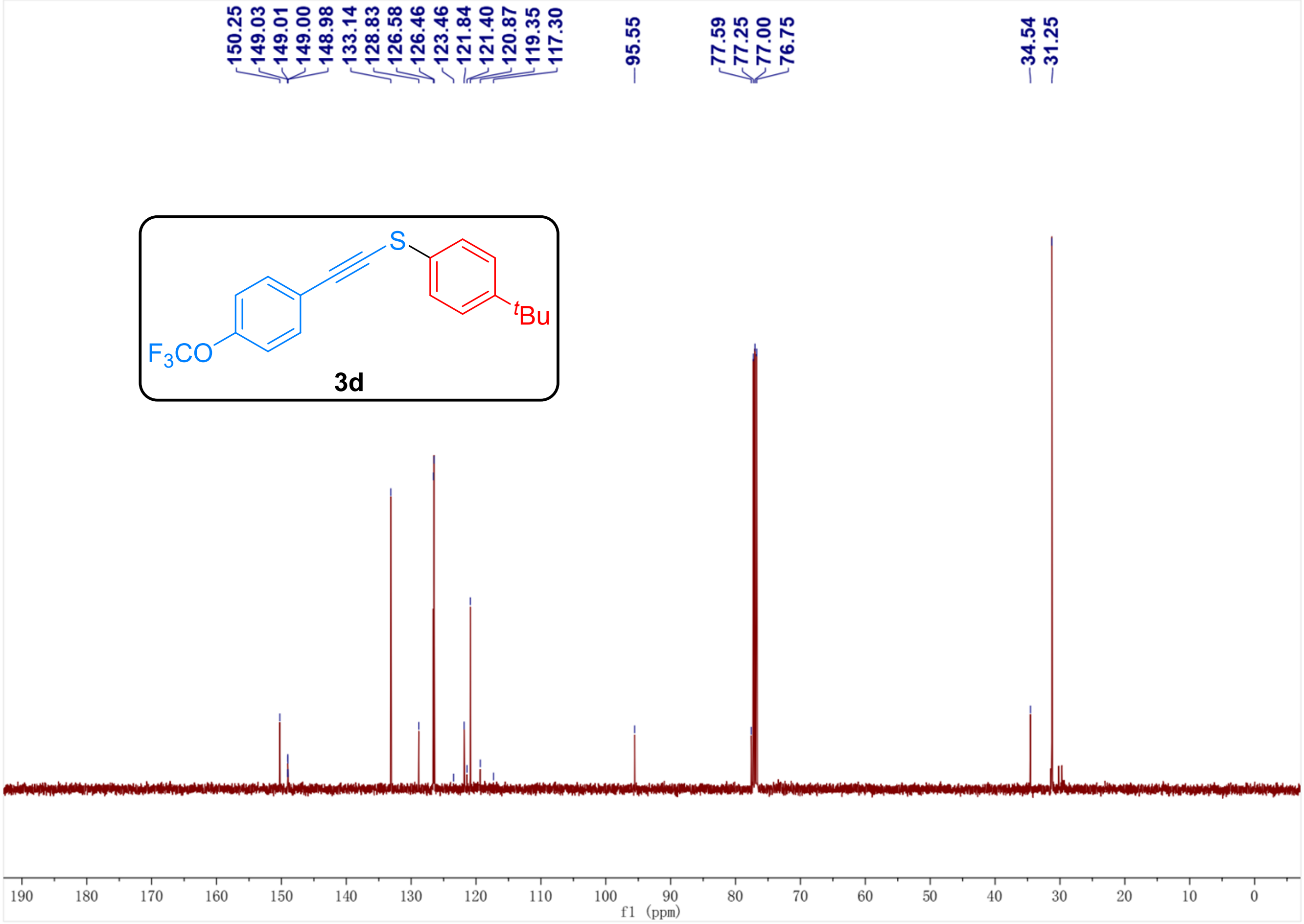
4.04
2.00
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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120.87
119.35
117.30
95.55
77.59
77.25
77.00
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34.54
31.25
F3CO
S
tBu
3d
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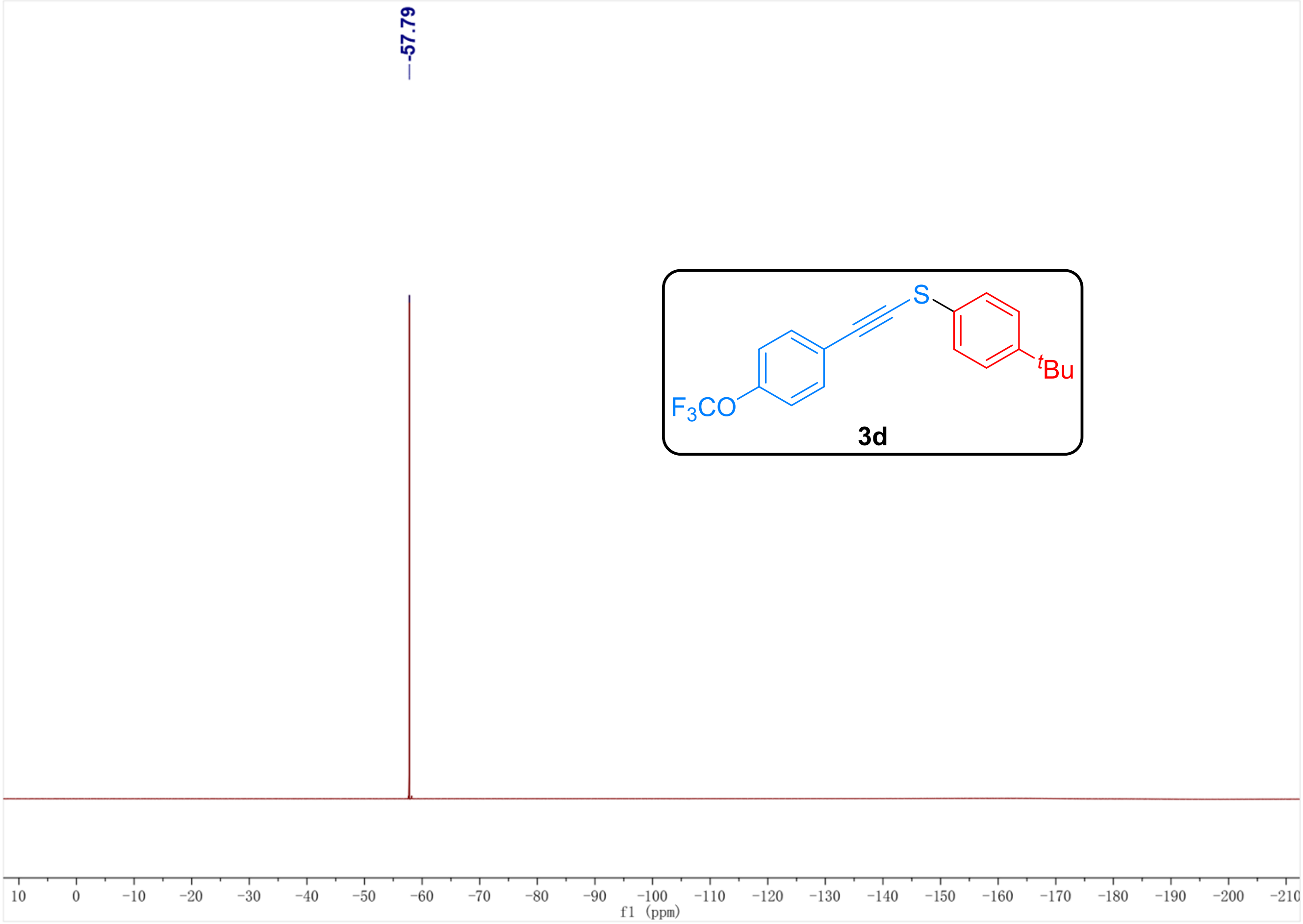
f1 (ppm)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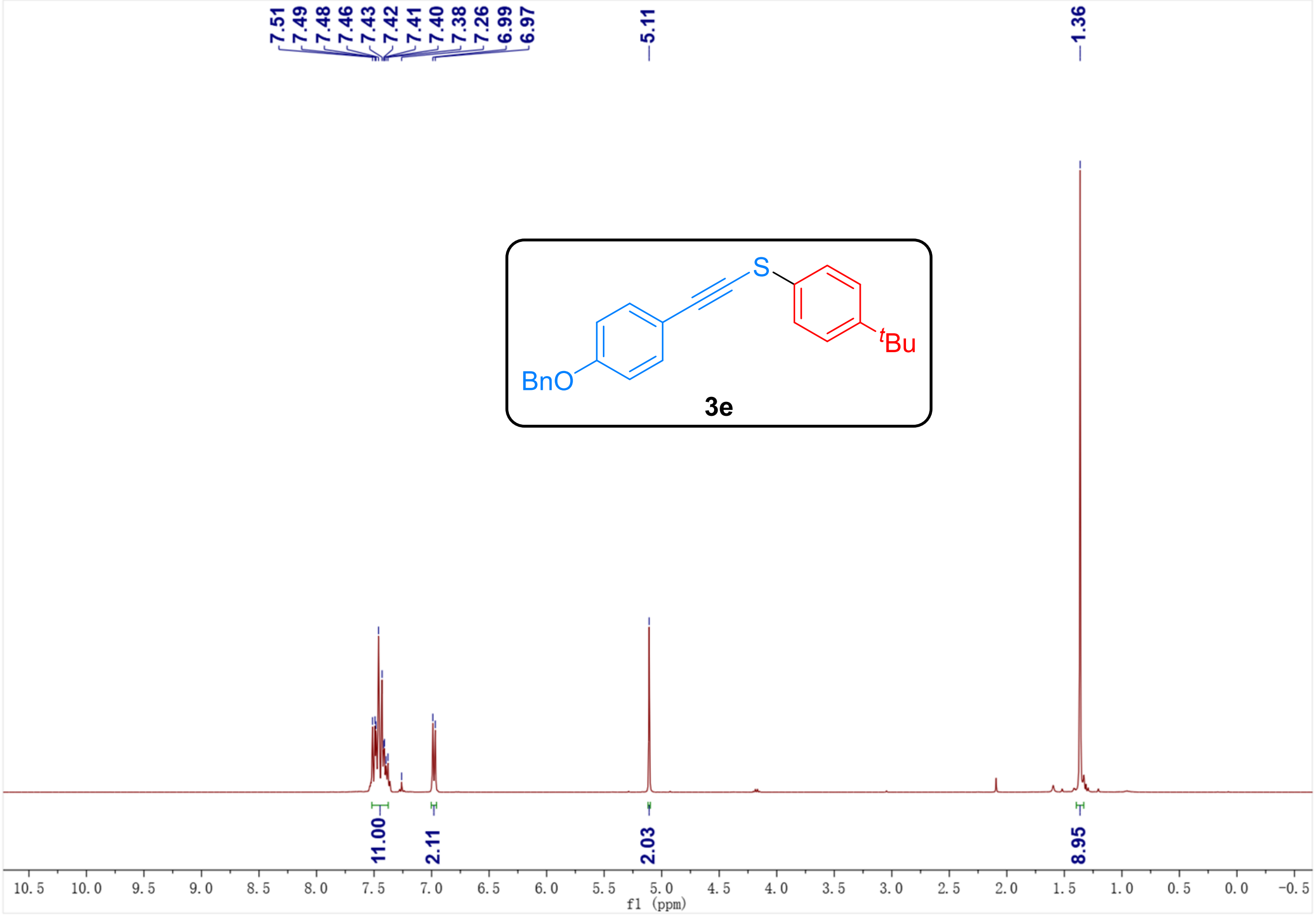
-210
f1 (ppm)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S
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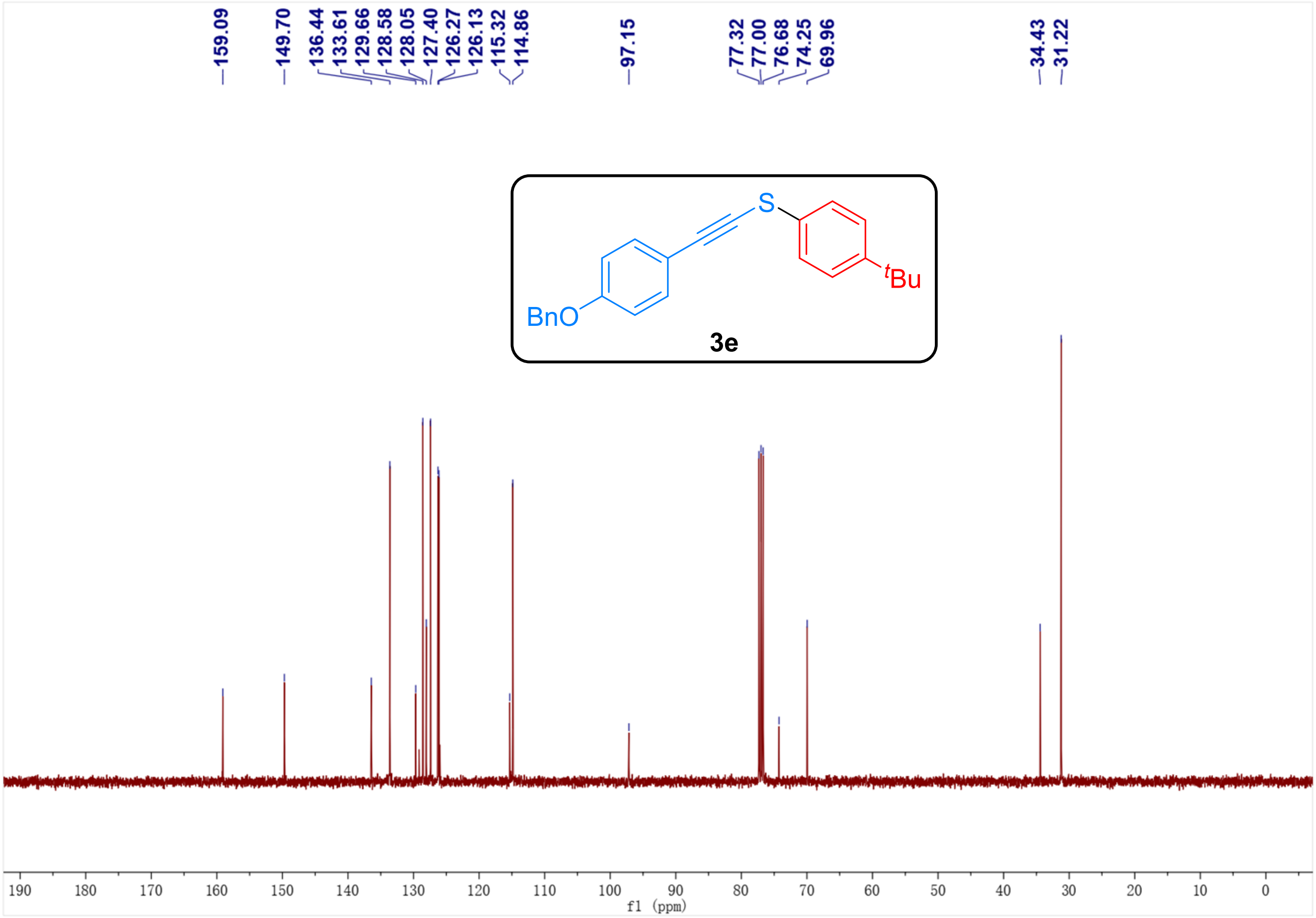
3e

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BnO
^{t}Bu
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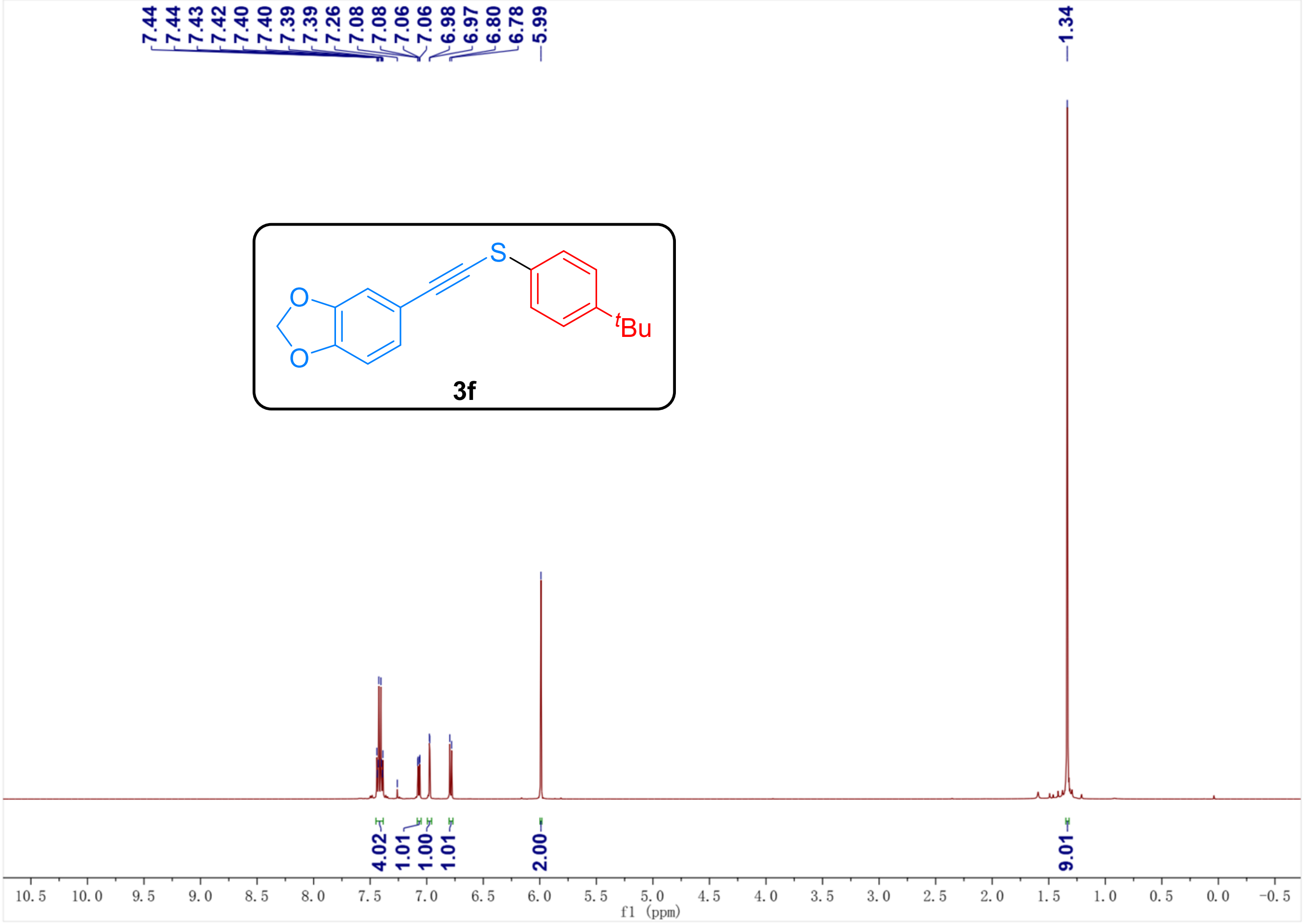
f1 (ppm)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O
S
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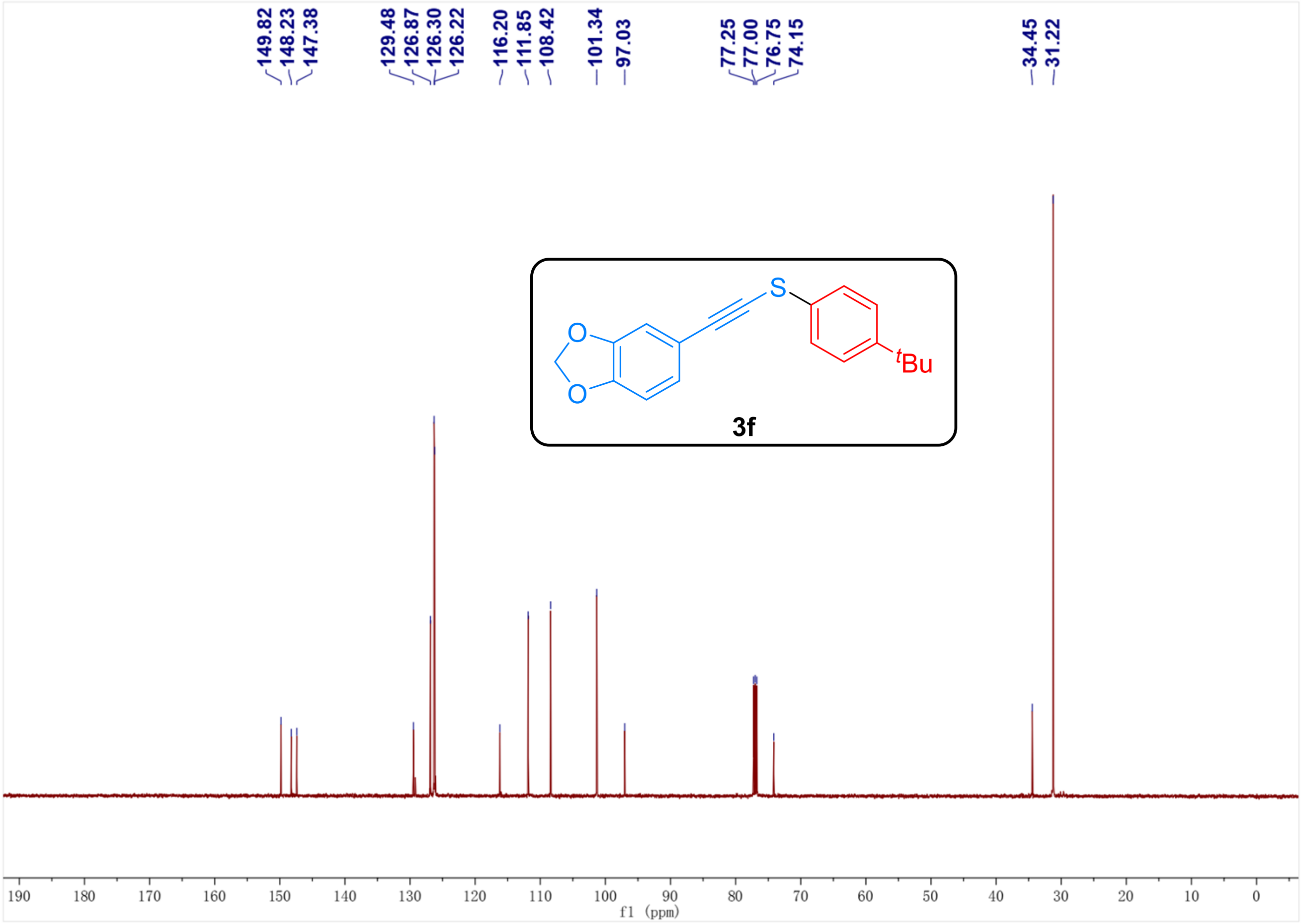
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O
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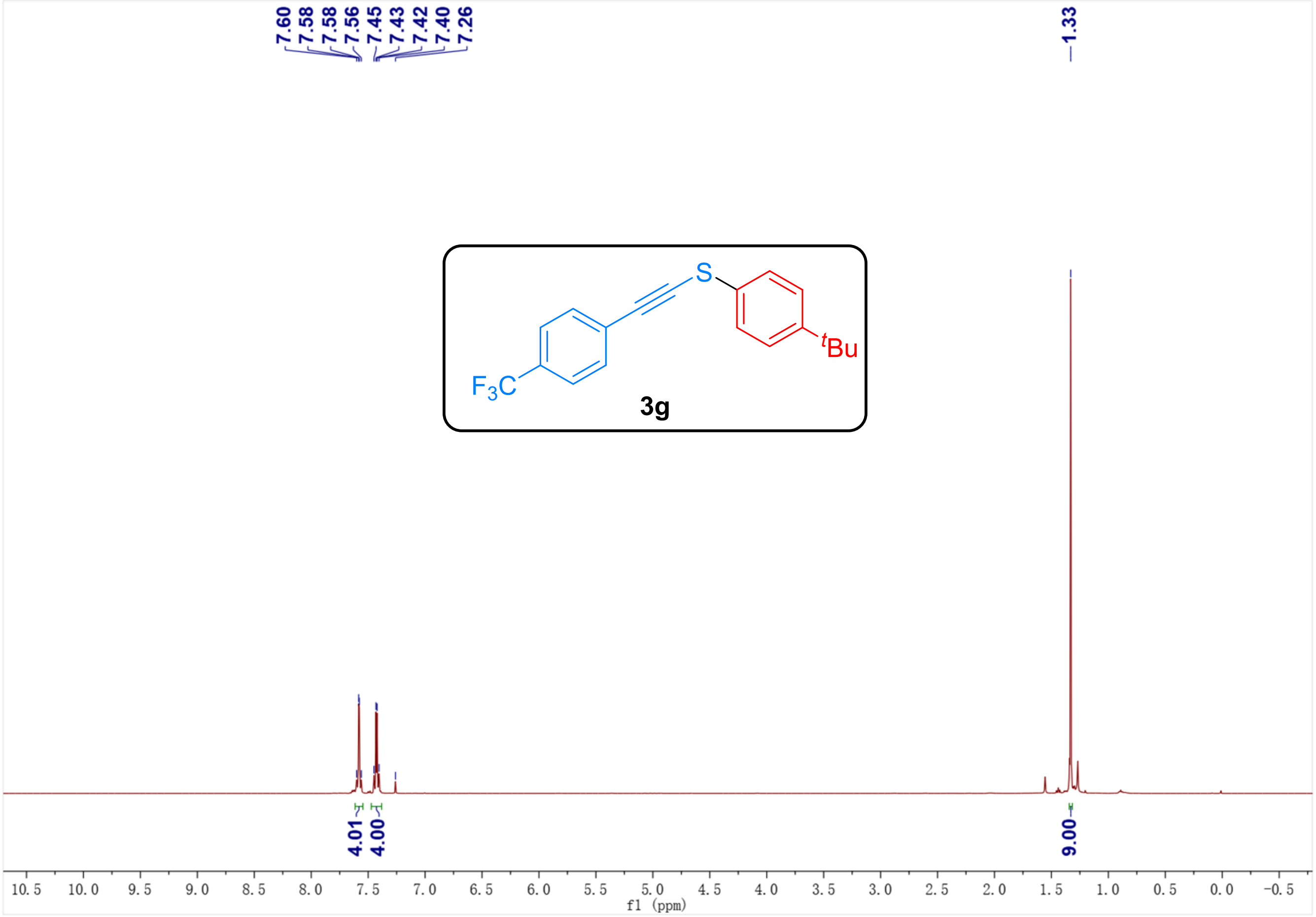
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3g
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4.00
9.00
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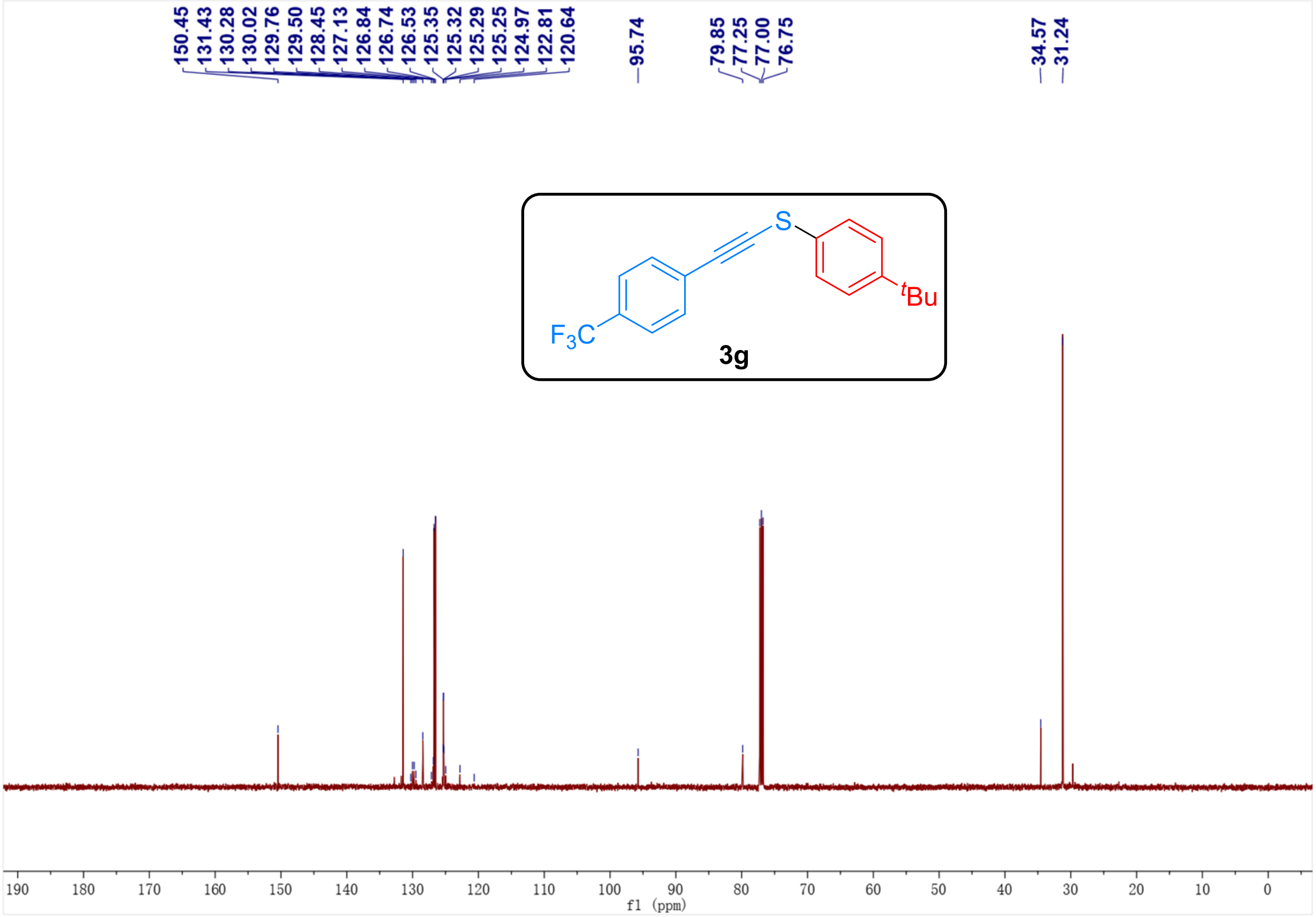
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79.85
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3g
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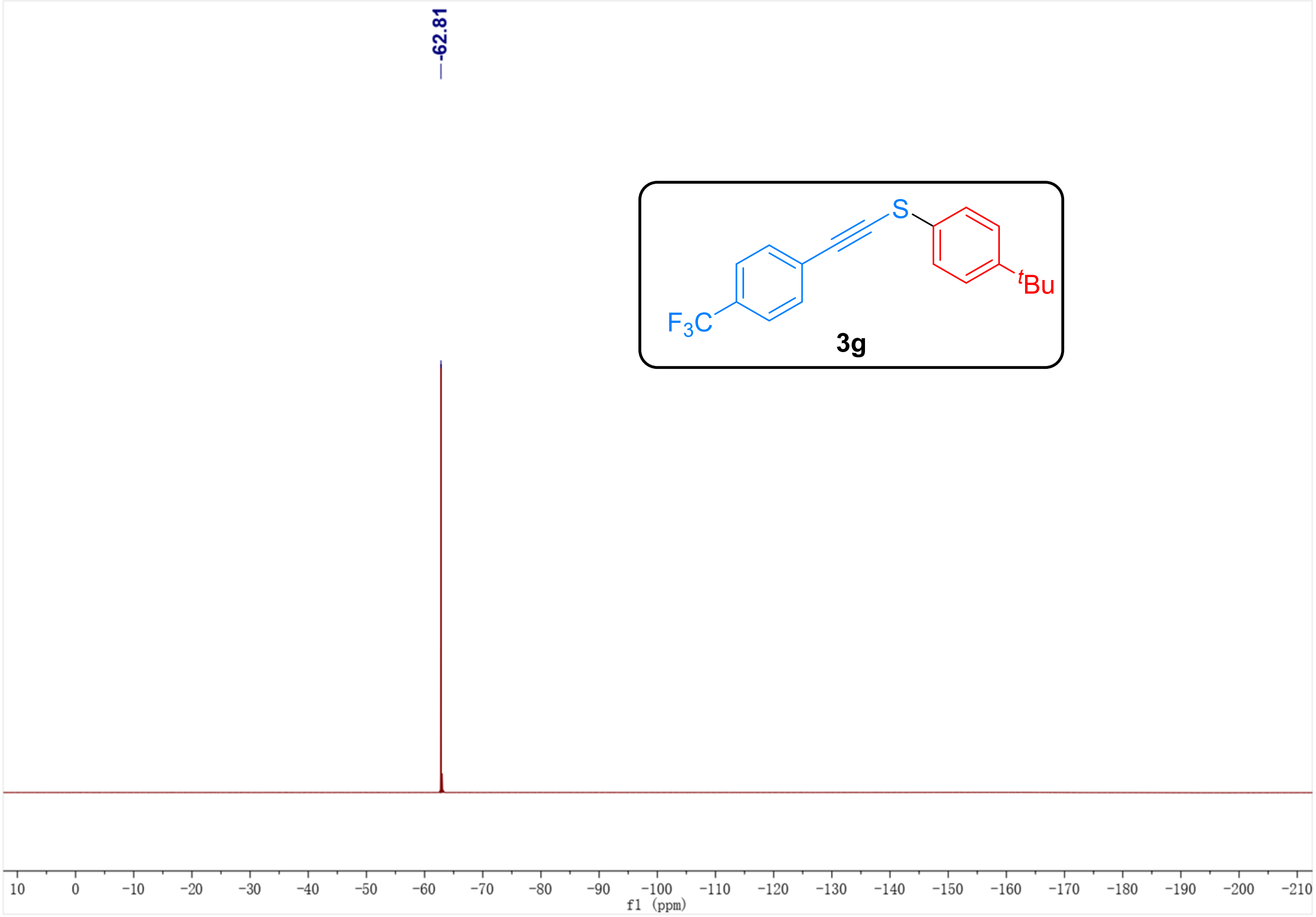
f1 (ppm)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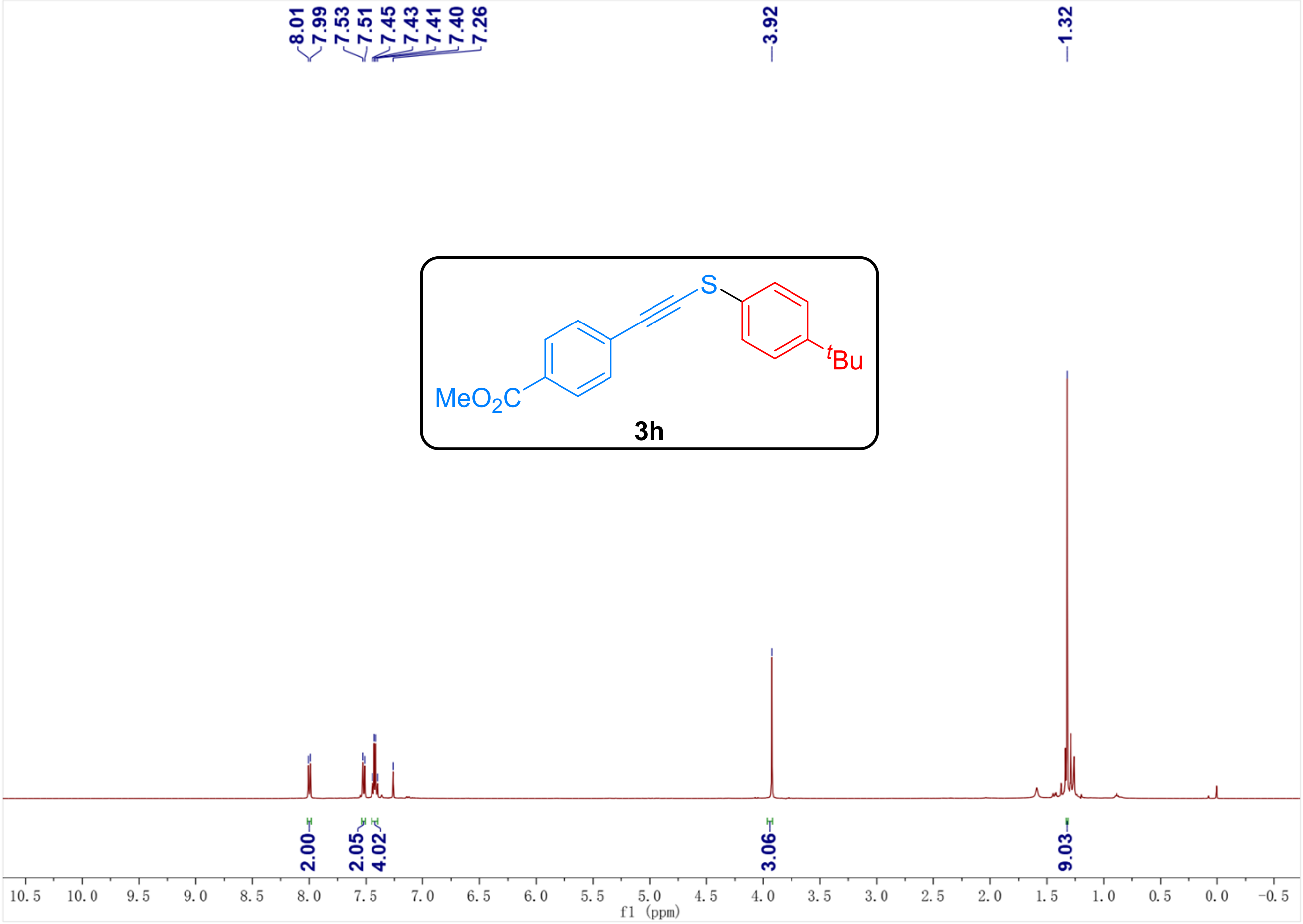
f1 (ppm)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tBu
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2.05
4.02
3.06
9.03
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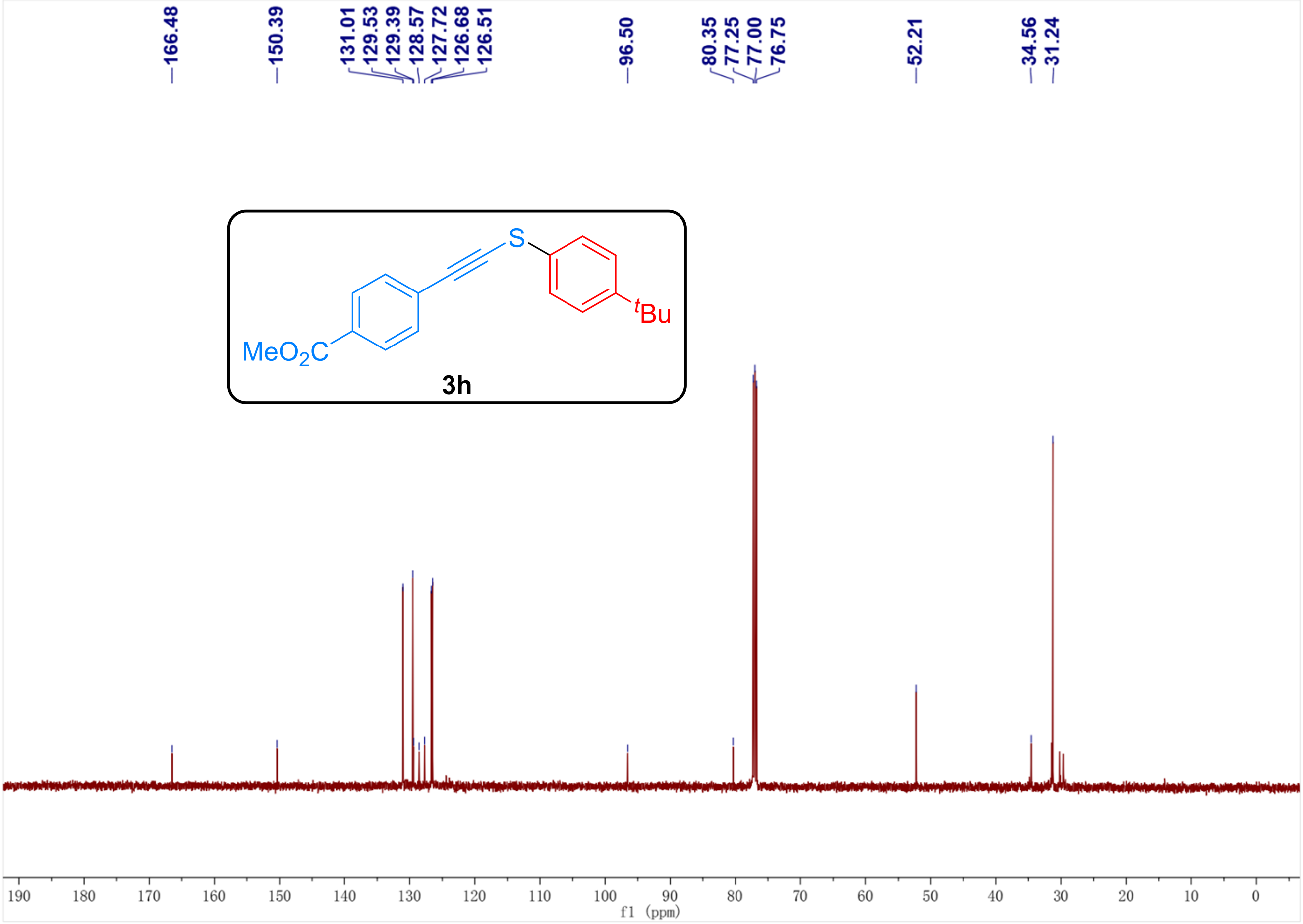
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tBu
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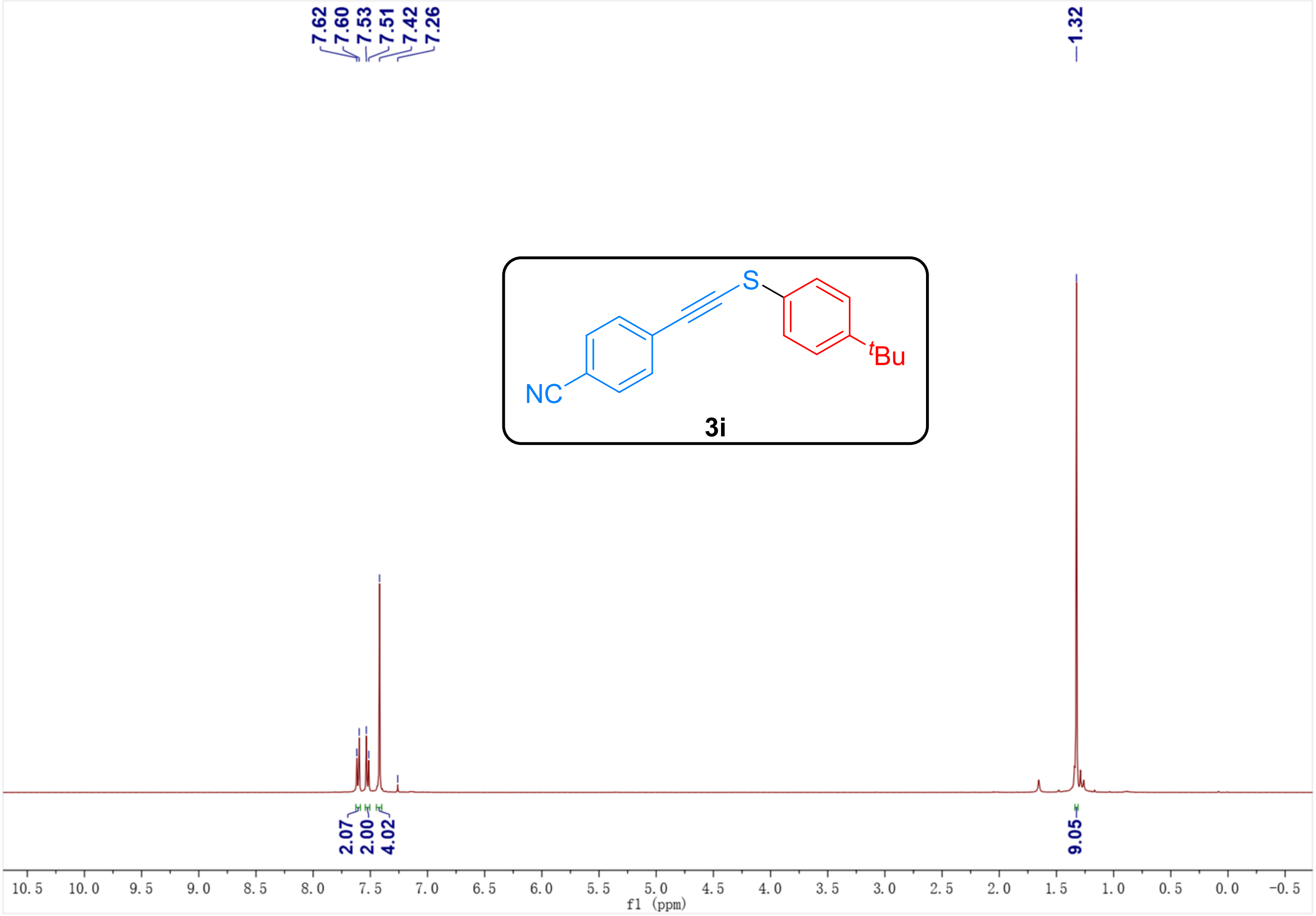
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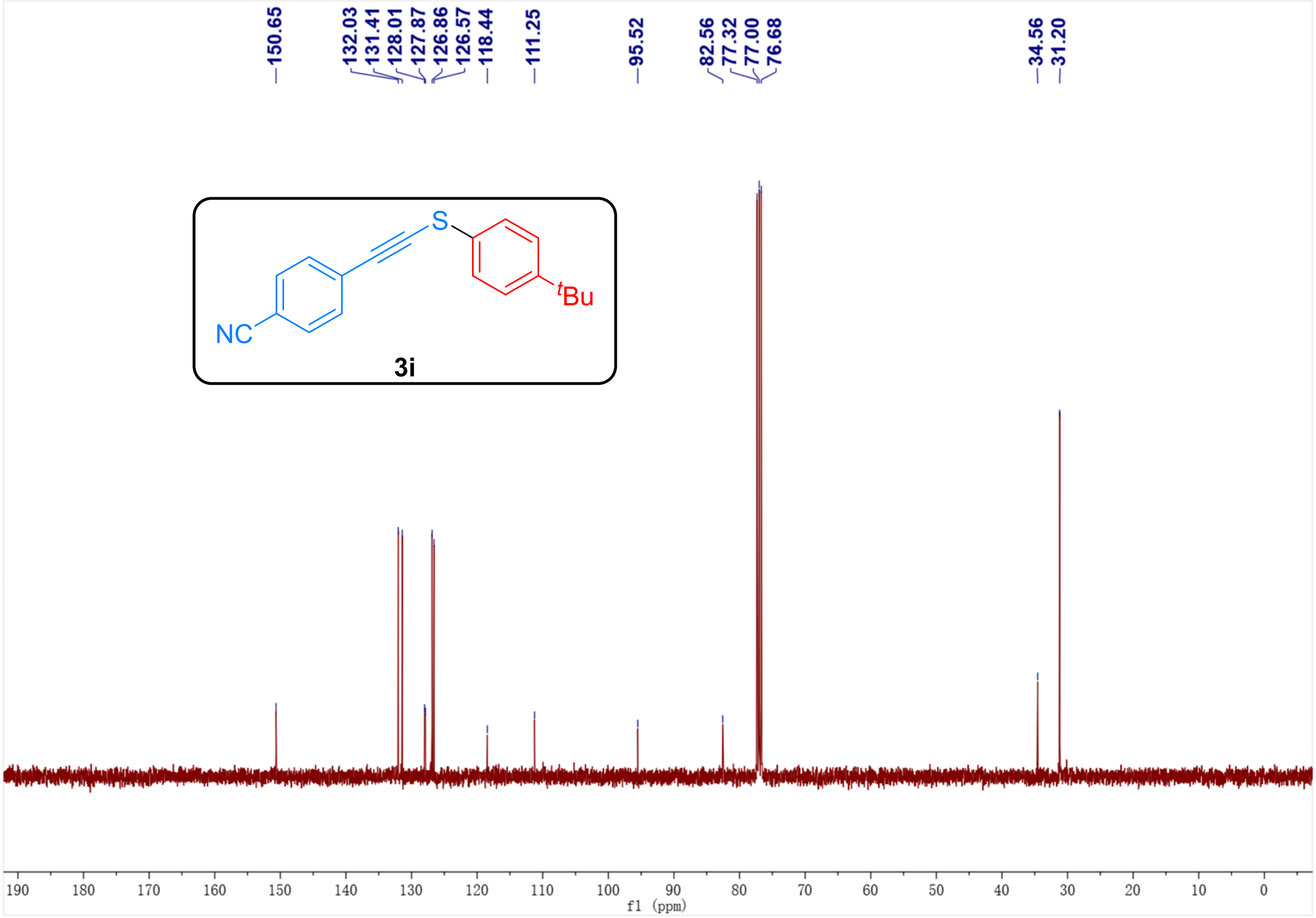
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3i
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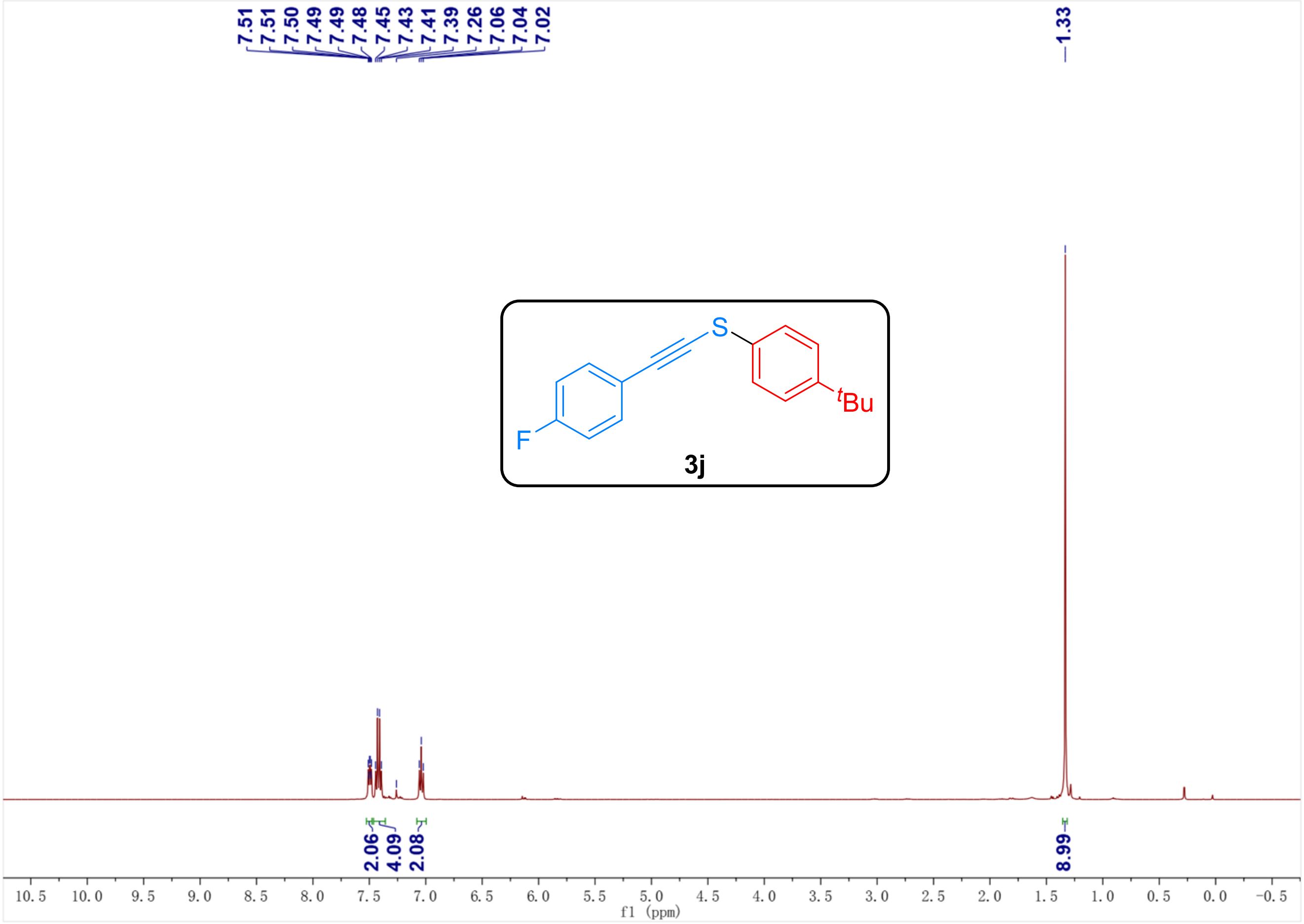
f1 (ppm)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F
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2.5
2.0
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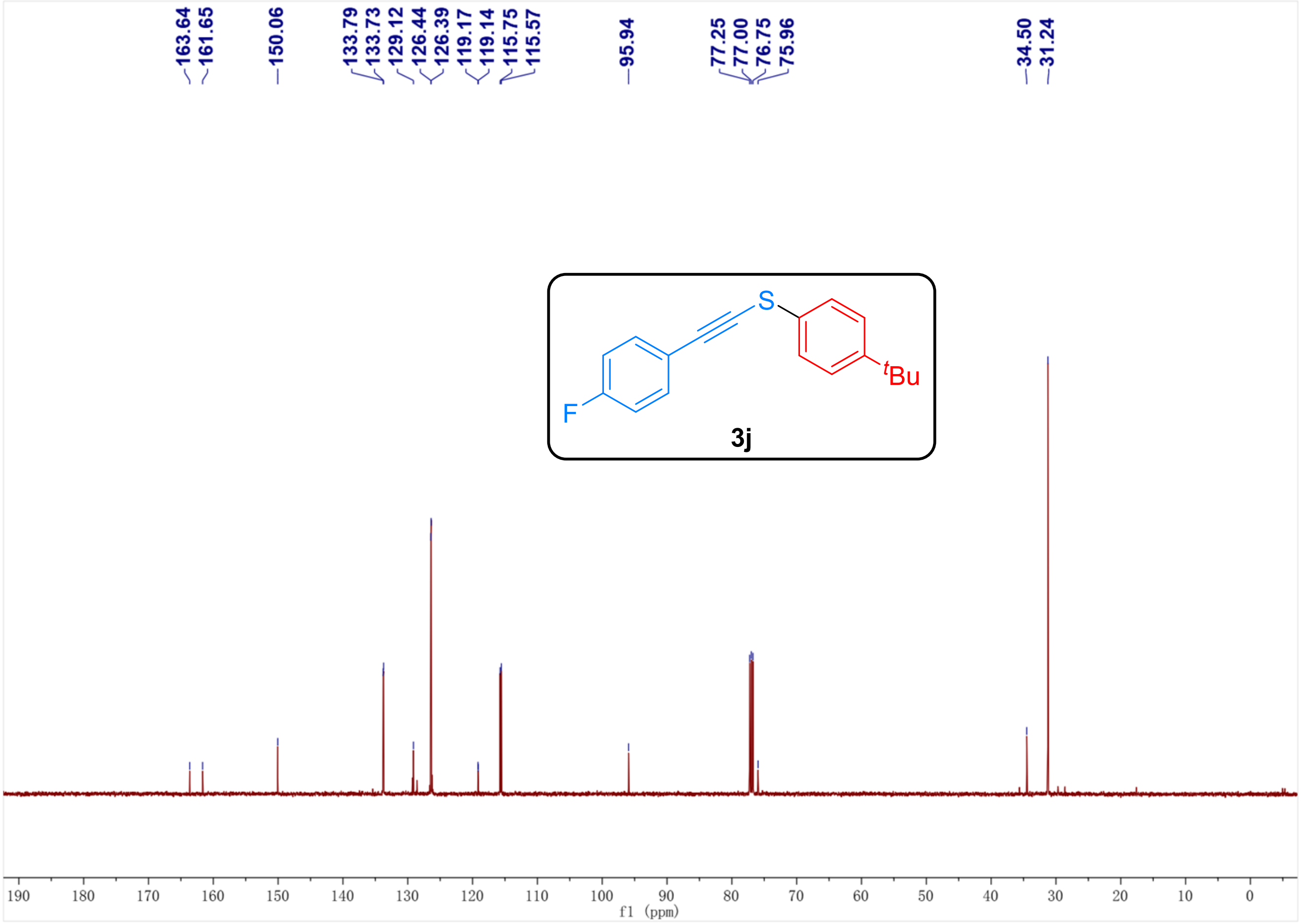
f1 (ppm)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50
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30
20
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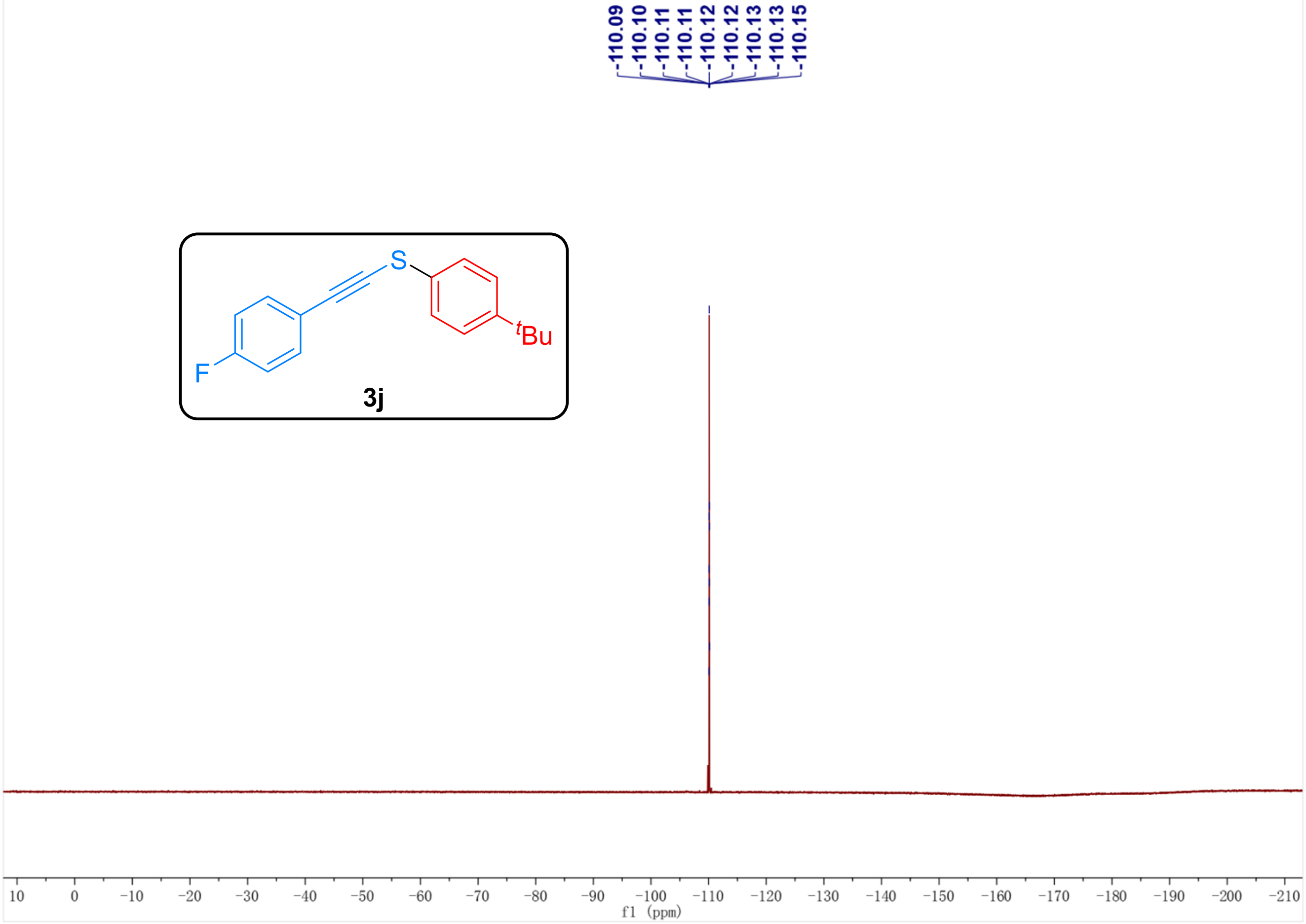
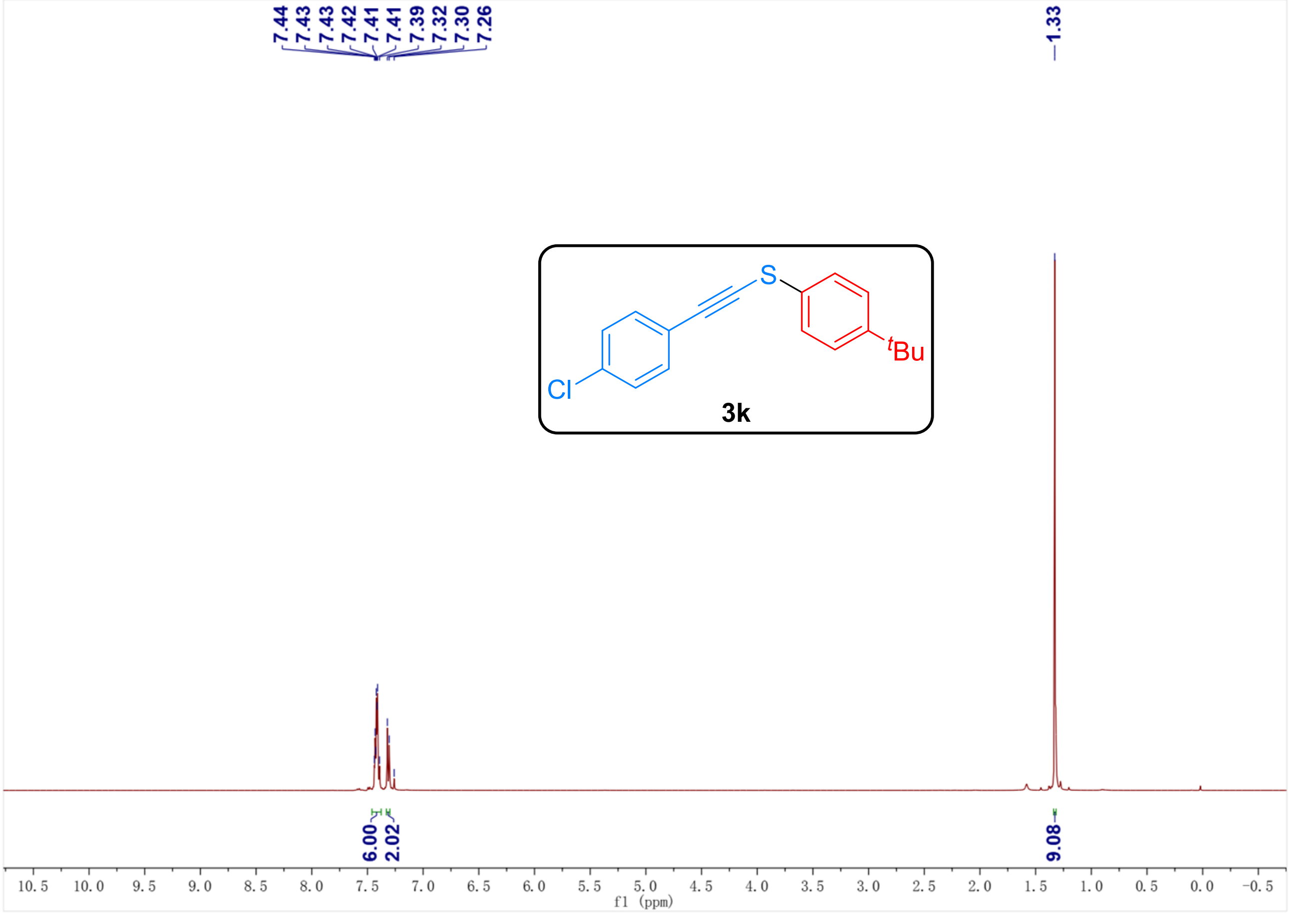
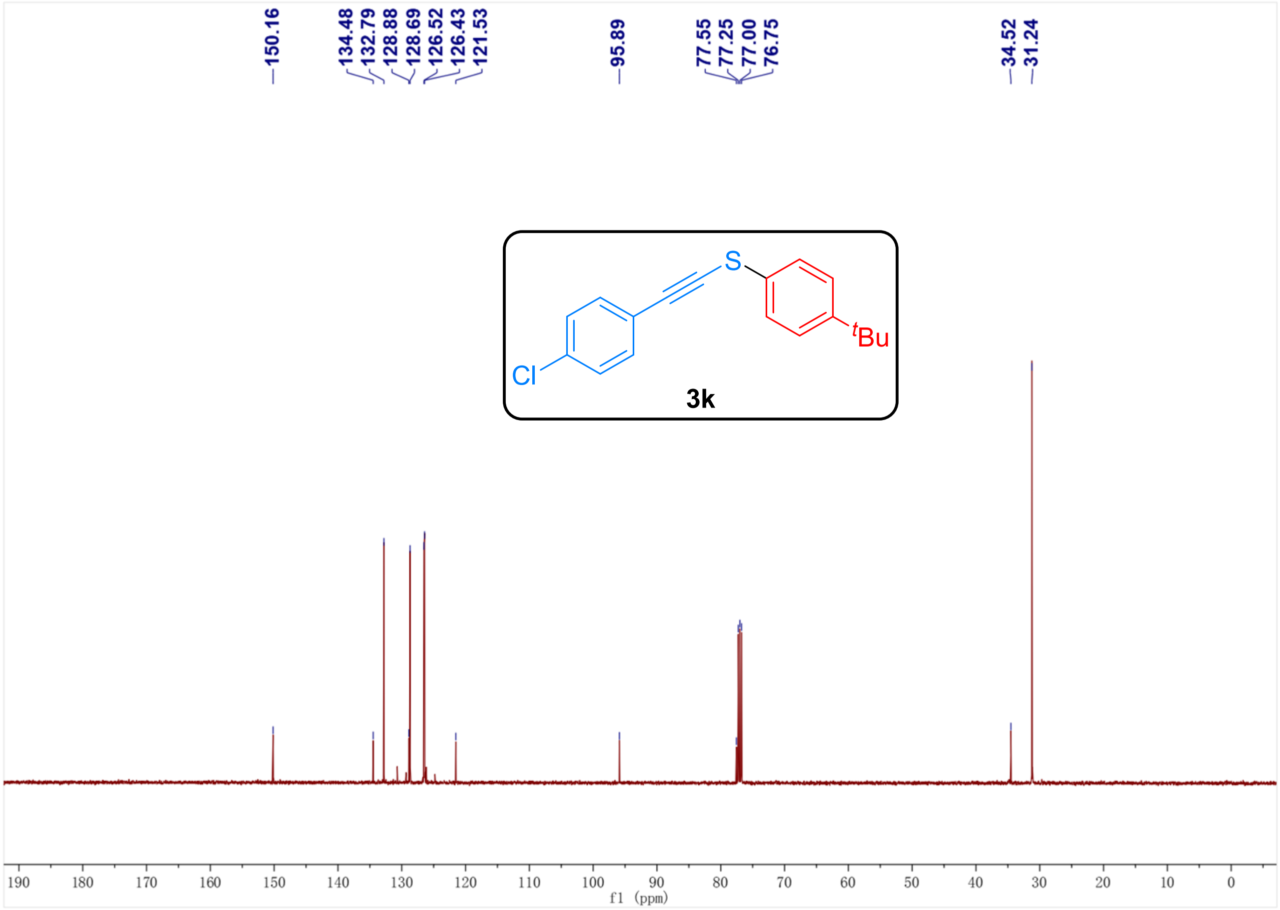
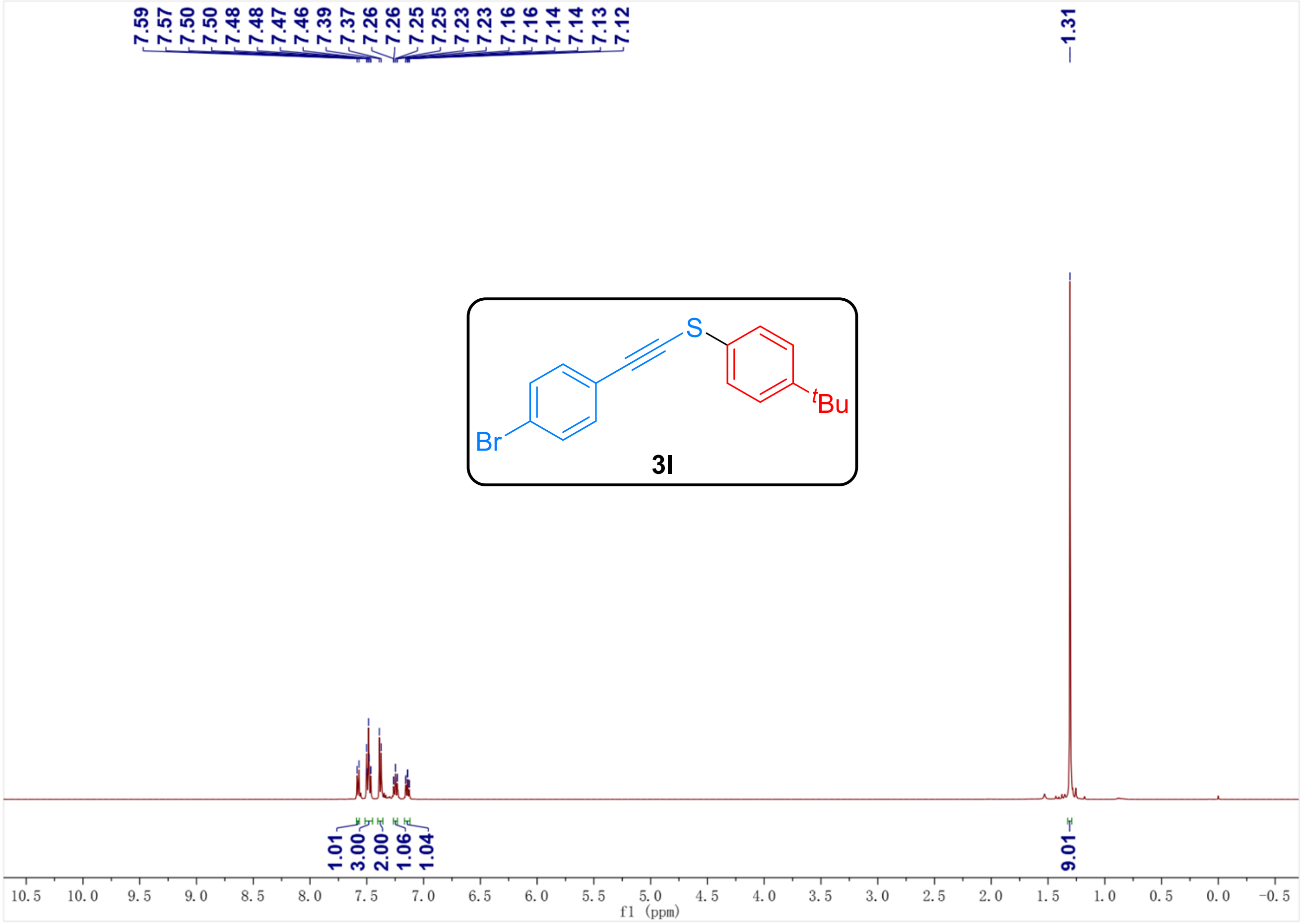
0
f1 (ppm)


-110.09
-110.10
-110.11
-110.11
-110.12
-110.12
-110.13
-110.13
-110.15
S
F
^{t}Bu
3j
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

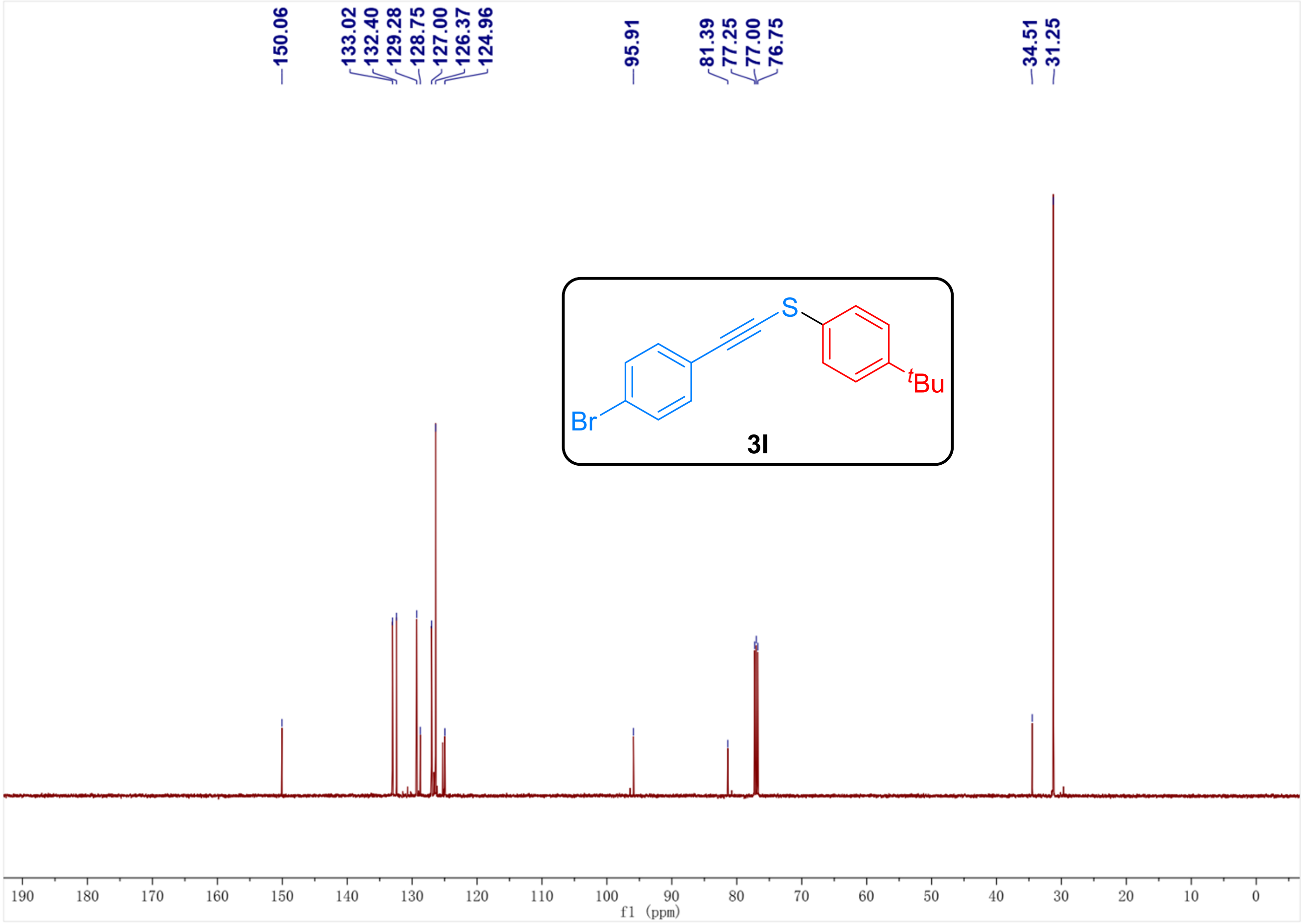

7.44
7.43
7.43
7.42
7.41
7.41
7.39
7.32
7.30
7.26
1.33
S
Cl
^{t}Bu
3k
6.00
2.02
9.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


150.16
134.48
132.79
128.88
128.69
126.52
126.43
121.53
95.89
77.55
77.25
77.00
76.75
34.52
31.24
Cl
S
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

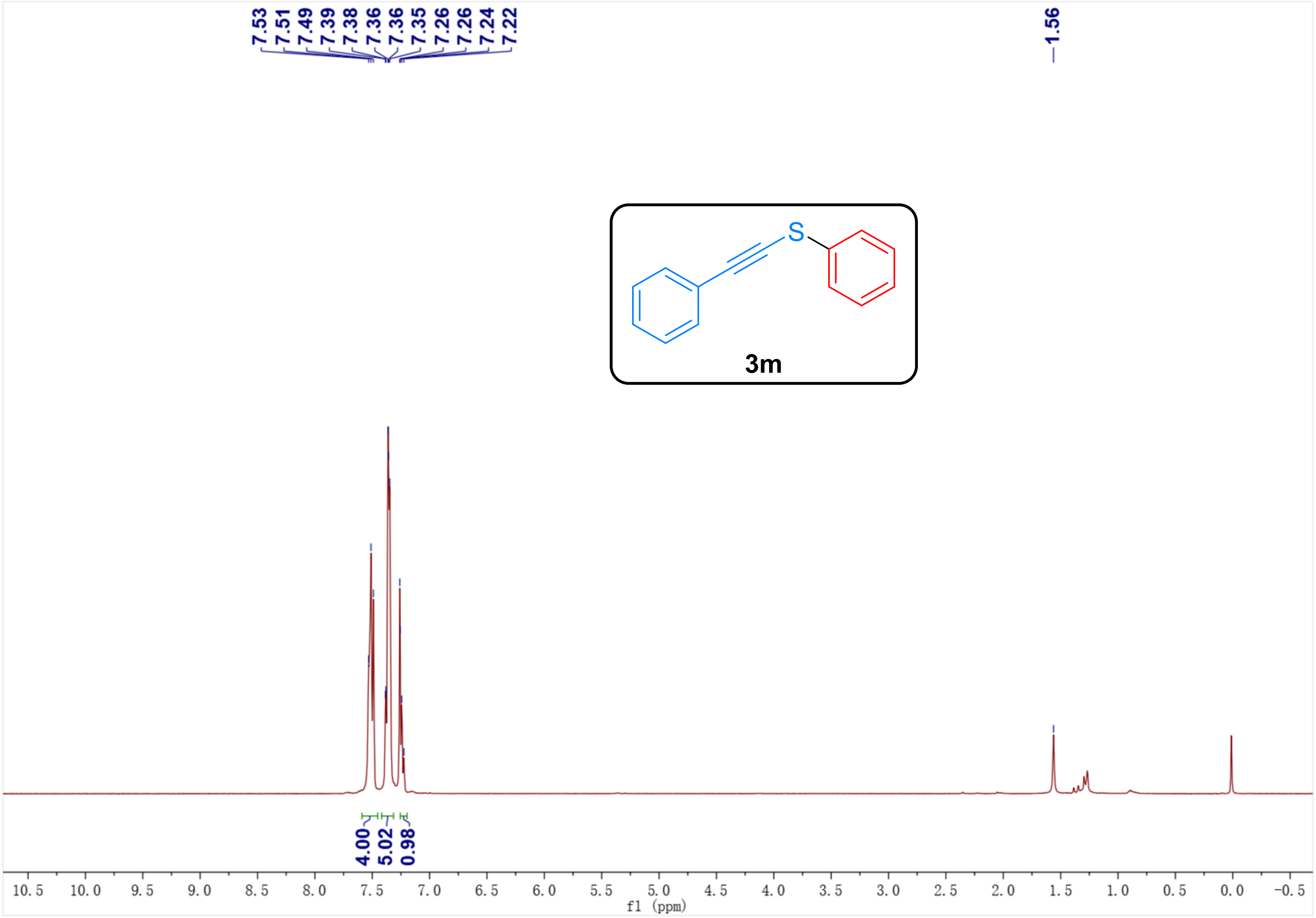
3k


7.59
7.57
7.50
7.50
7.48
7.48
7.47
7.46
7.39
7.37
7.26
7.26
7.25
7.25
7.23
7.23
7.16
7.16
7.14
7.14
7.13
7.12
1.31
Br
S
tBu
1.01
3.00
2.00
1.06
1.04
9.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

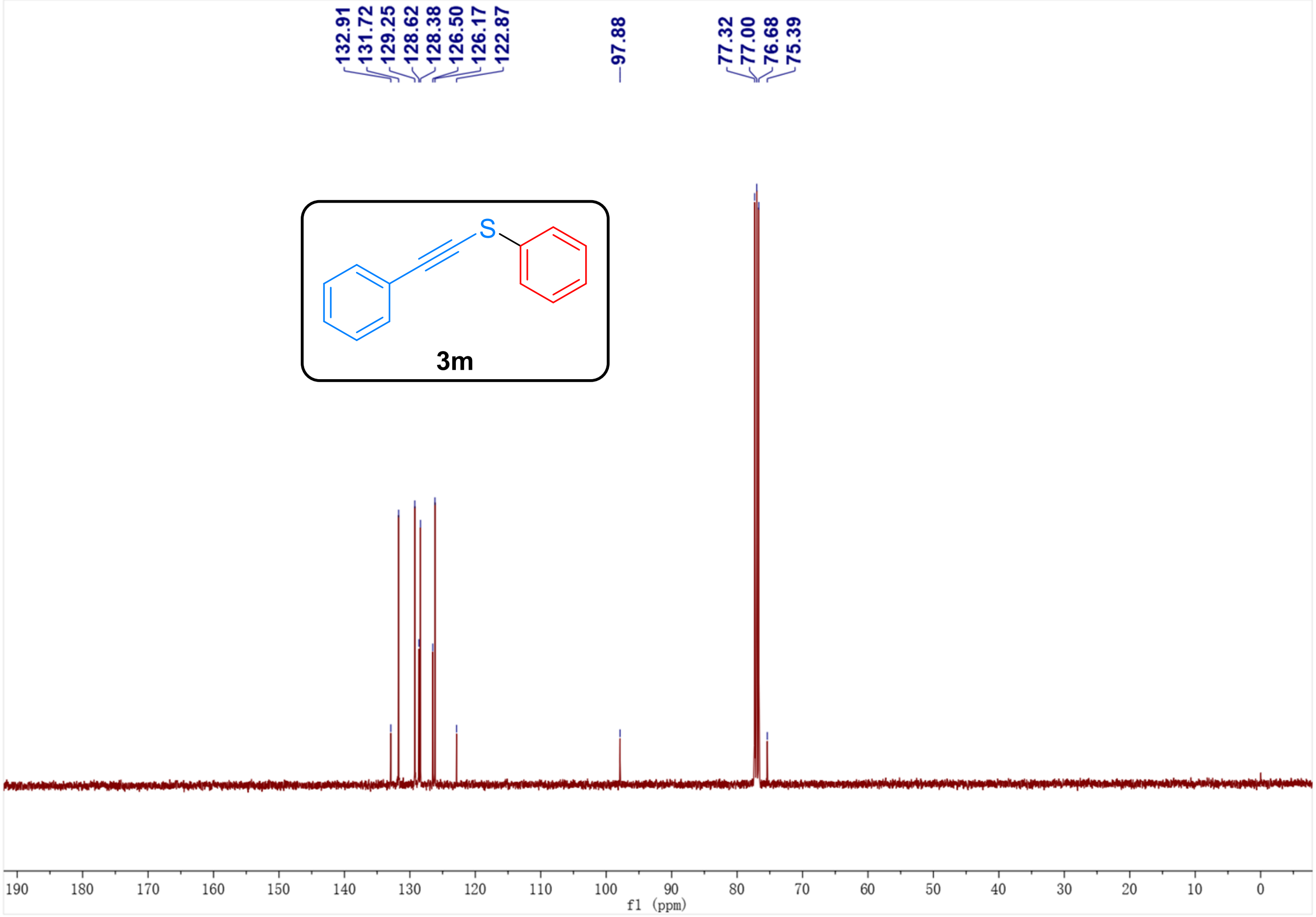
3l

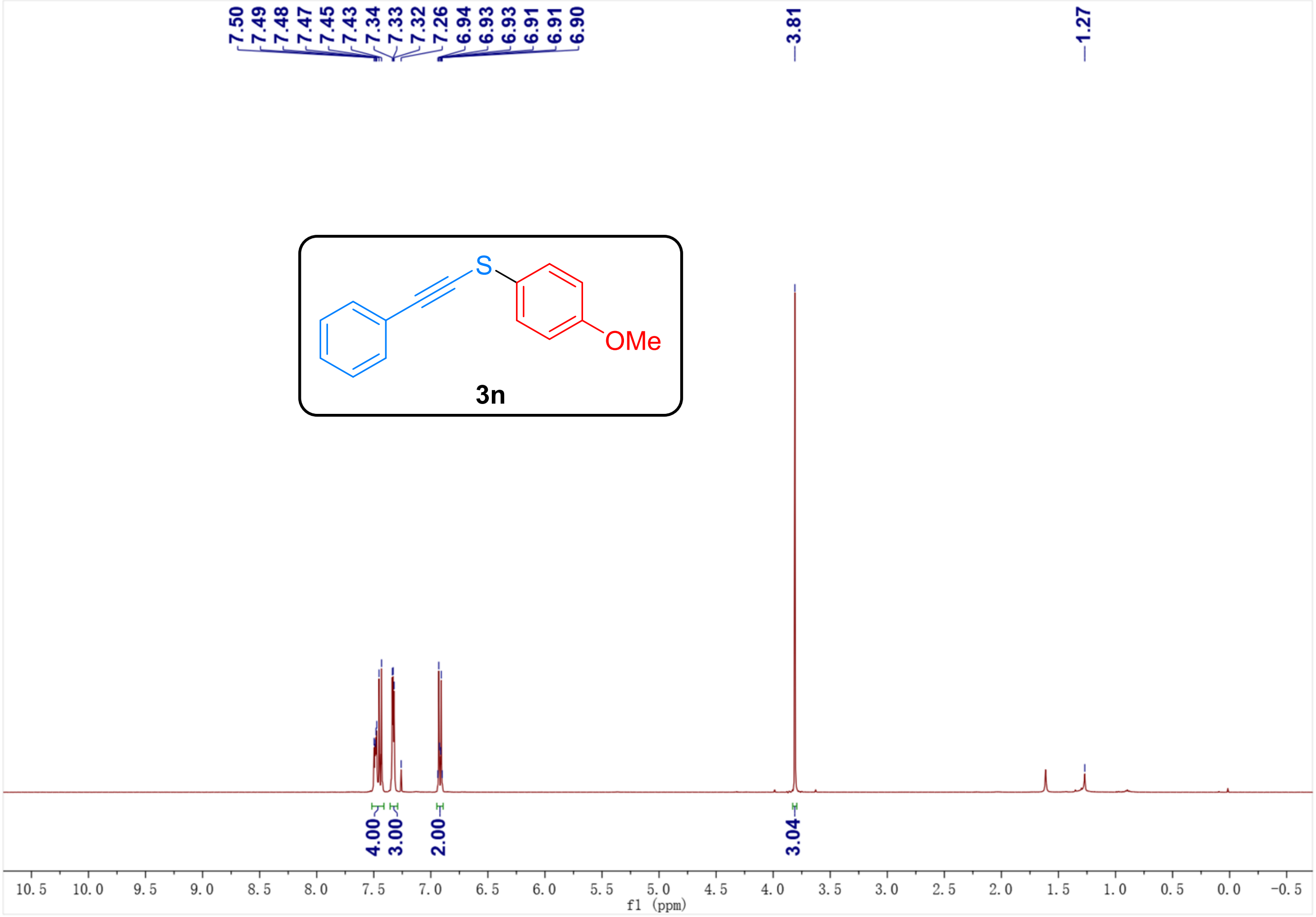

150.06
133.02
132.40
129.28
128.75
127.00
126.37
124.96
95.91
81.39
77.25
77.00
76.75
34.51
31.25
Br
S
tBu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

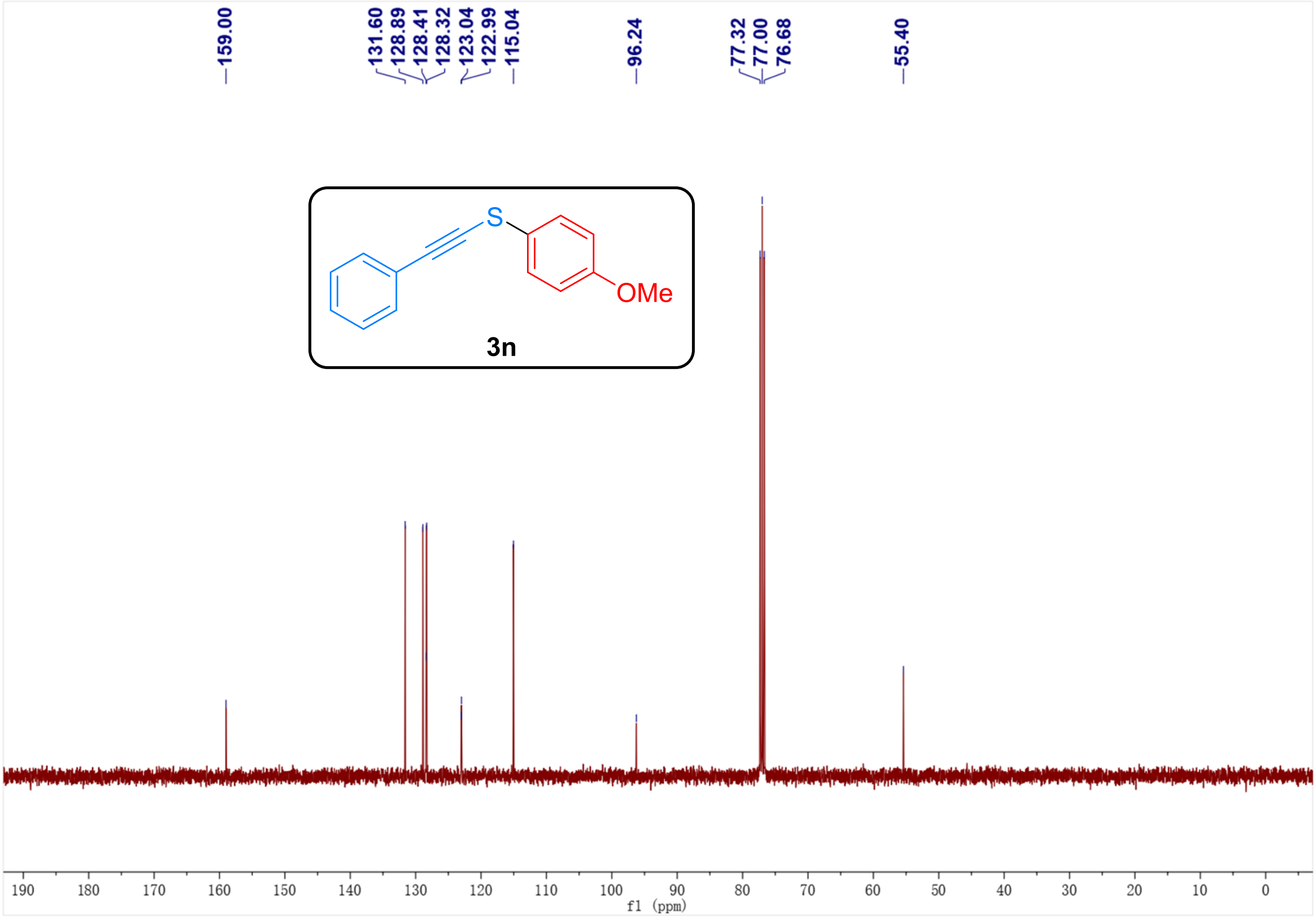
3l

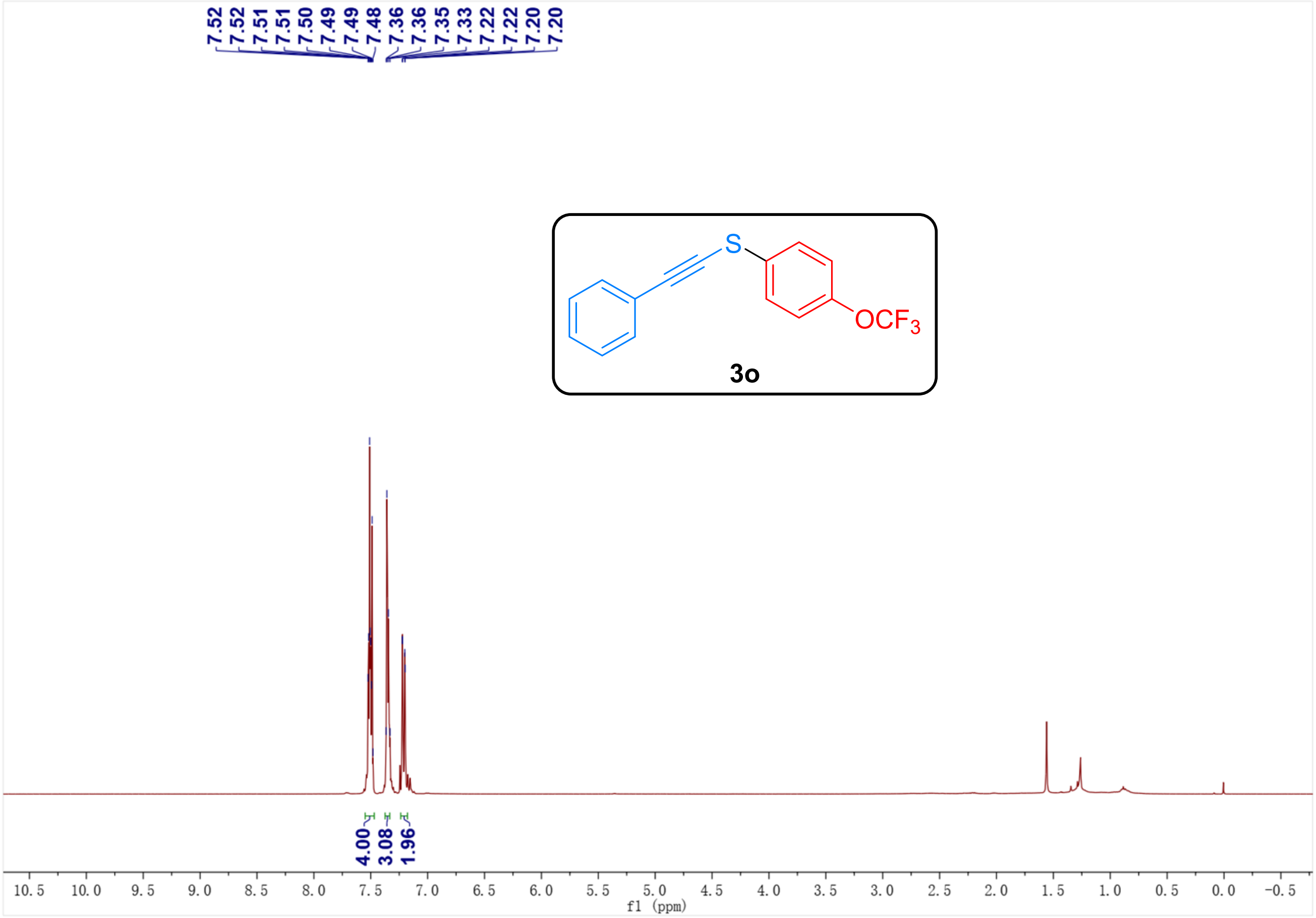

7.53
7.51
7.49
7.39
7.38
7.36
7.36
7.35
7.26
7.26
7.24
7.22
1.56
S
4.00
5.02
0.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

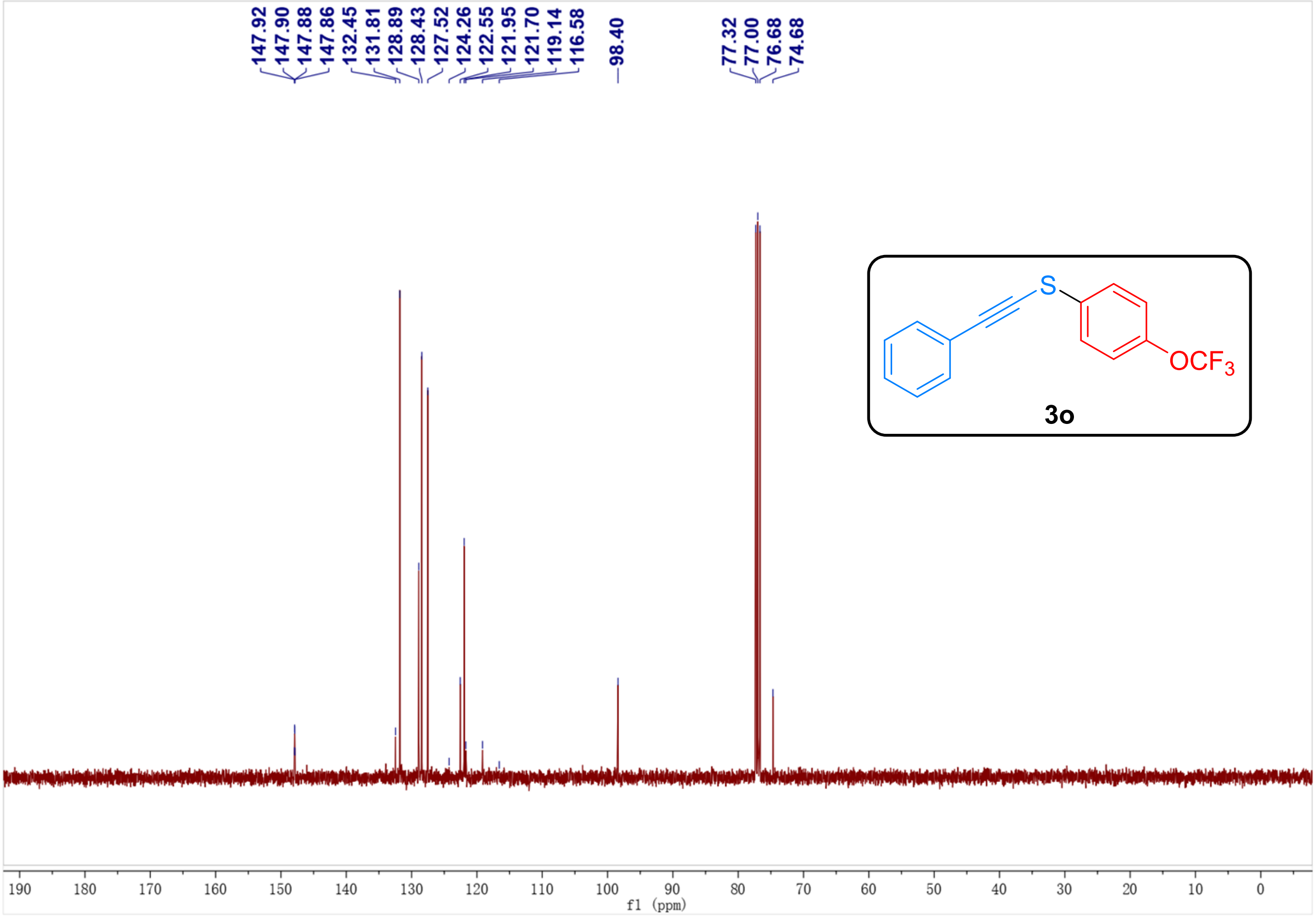
3m

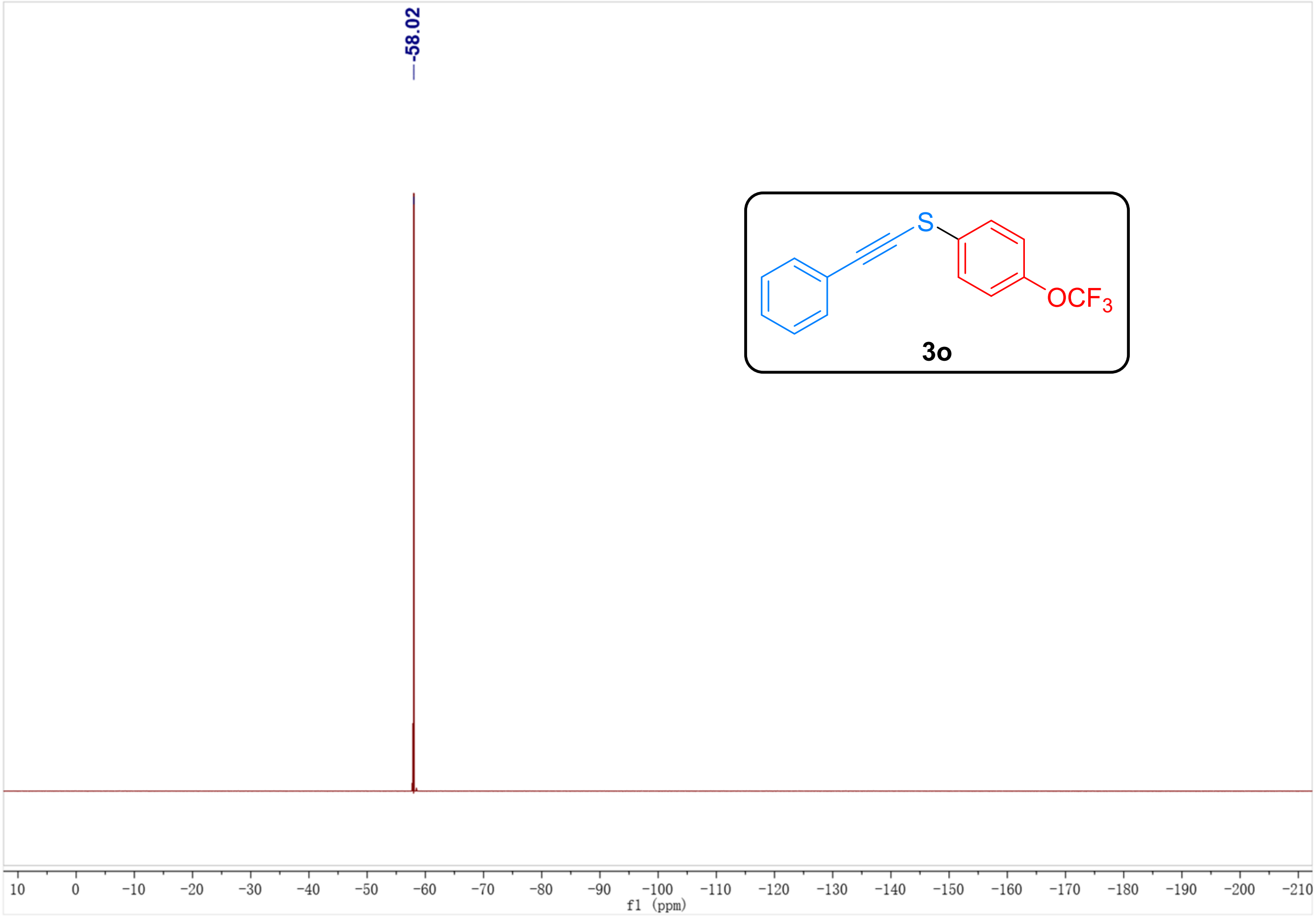

132.91
131.72
129.25
128.62
128.38
126.50
126.17
122.87
97.88
77.32
77.00
76.68
75.39
S
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

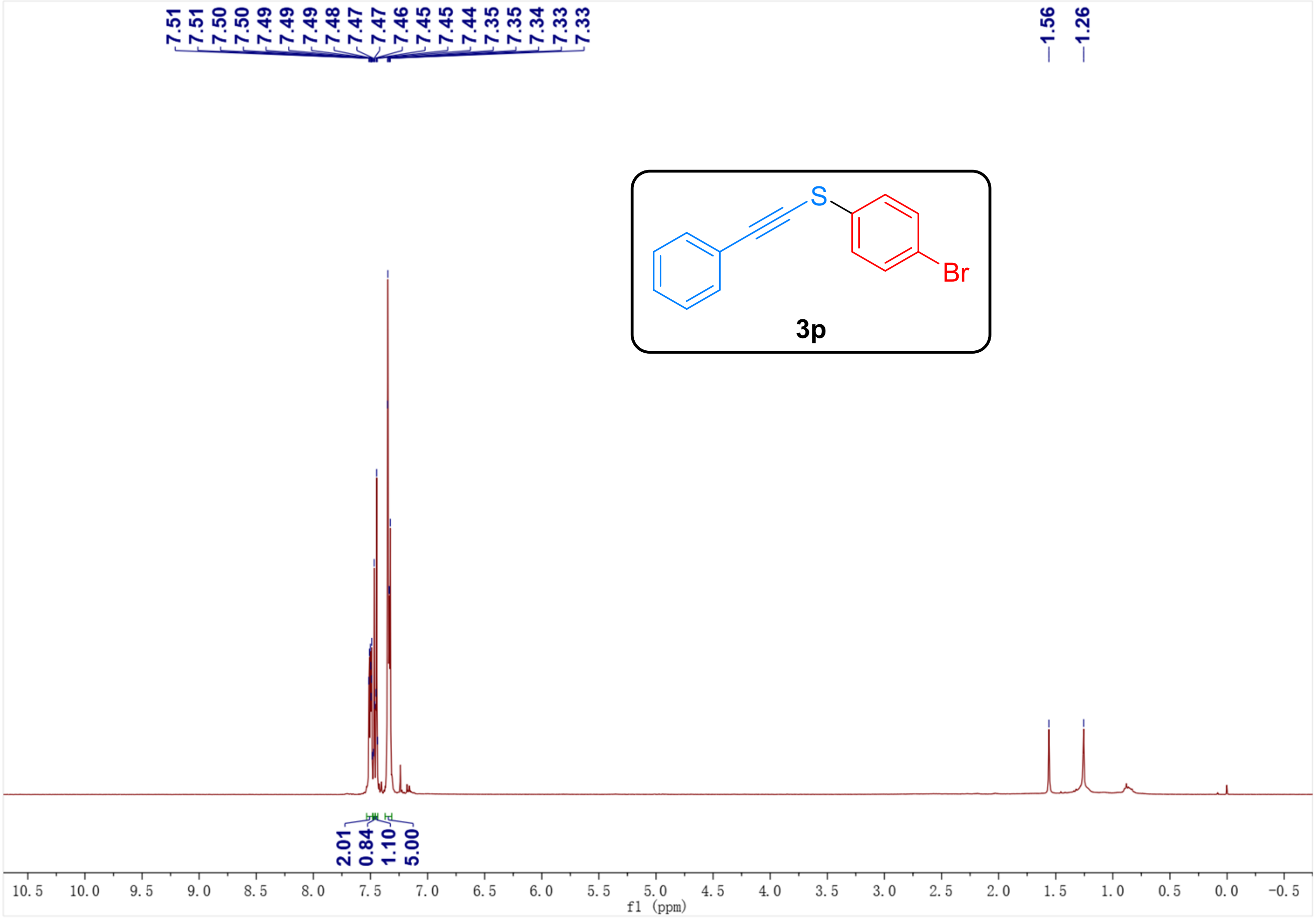

7.50
7.49
7.48
7.47
7.45
7.43
7.34
7.33
7.32
7.26
6.94
6.93
6.93
6.91
6.91
6.90
3.81
1.27
S
OMe
3n
4.00
3.00
2.00
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

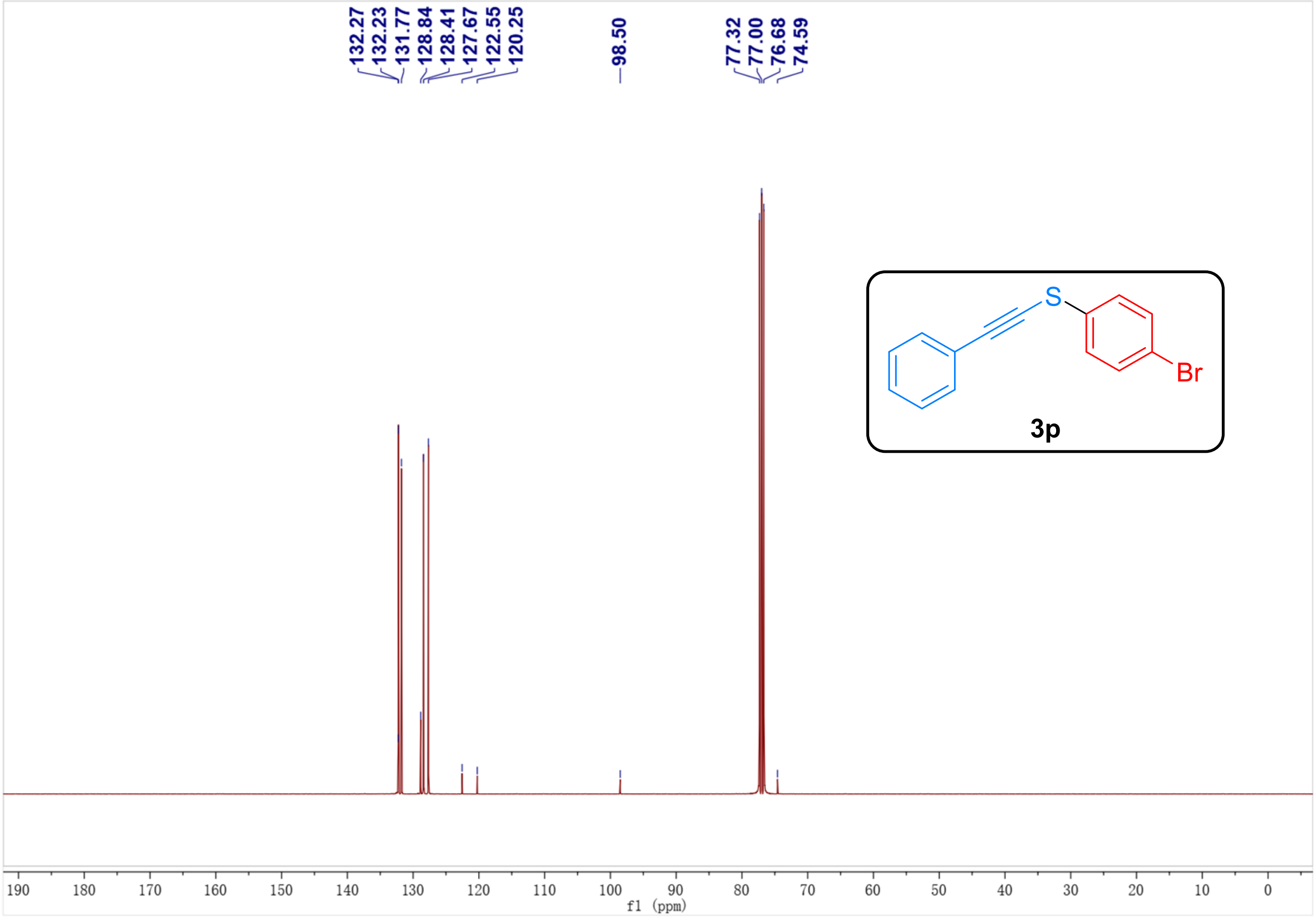

159.00
131.60
128.89
128.41
128.32
123.04
122.99
115.04
96.24
77.32
77.00
76.68
55.40
S
OMe
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

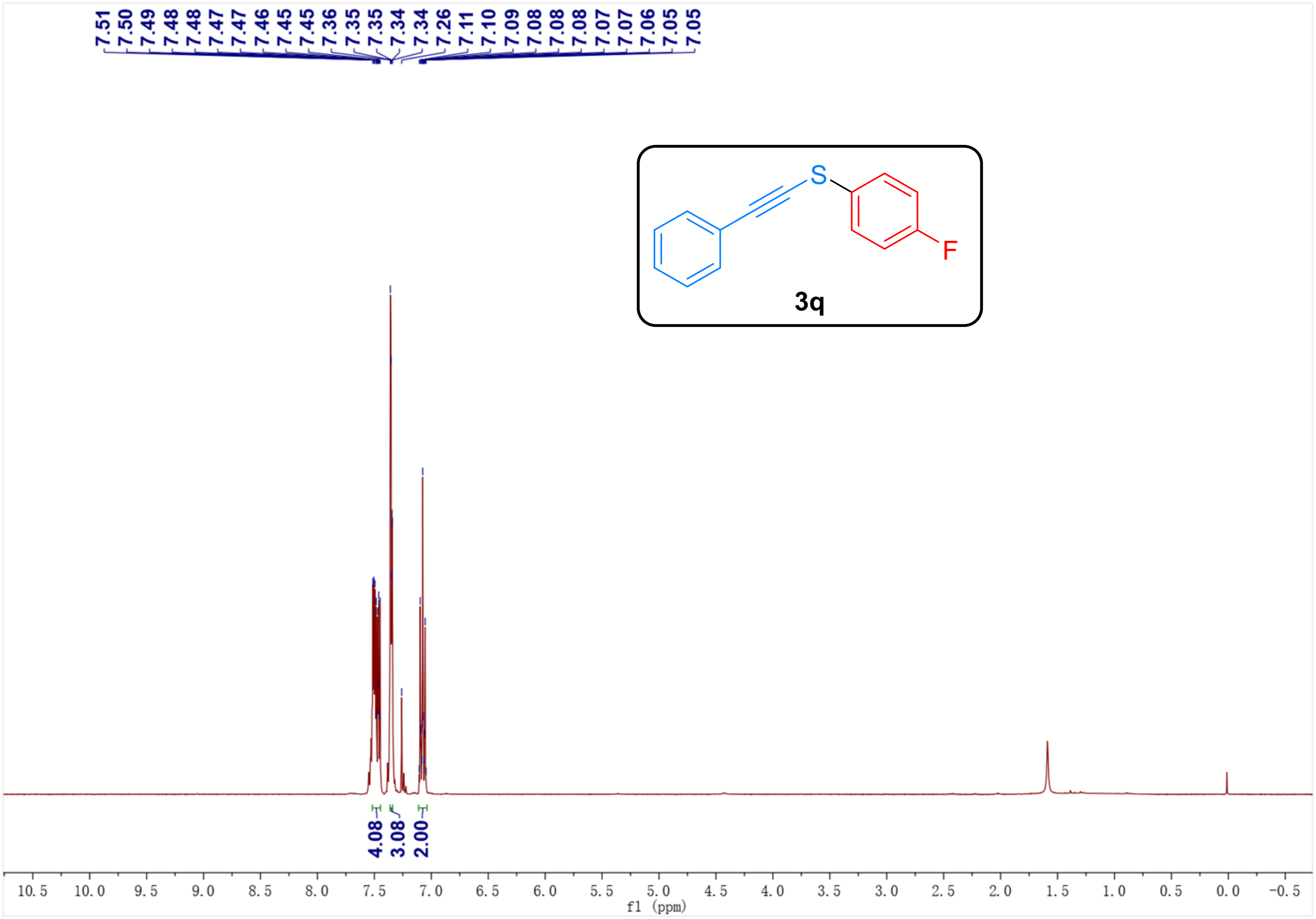

7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.36
7.36
7.35
7.33
7.22
7.22
7.20
7.20
S
OCF3
3o
4.00
3.08
1.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


147.92
147.90
147.88
147.86
132.45
131.81
128.89
128.43
127.52
124.26
122.55
121.95
121.70
119.14
116.58
98.40
77.32
77.00
76.68
74.68
S
OCF3
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-58.02
S
OCF3
3o
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.35
7.35
7.34
7.33
7.33
1.56
1.26
S
Br
3p
2.01
0.84
1.10
5.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


132.27
132.23
131.77
128.84
128.41
127.67
122.55
120.25
98.50
77.32
77.00
76.68
74.59
S
Br
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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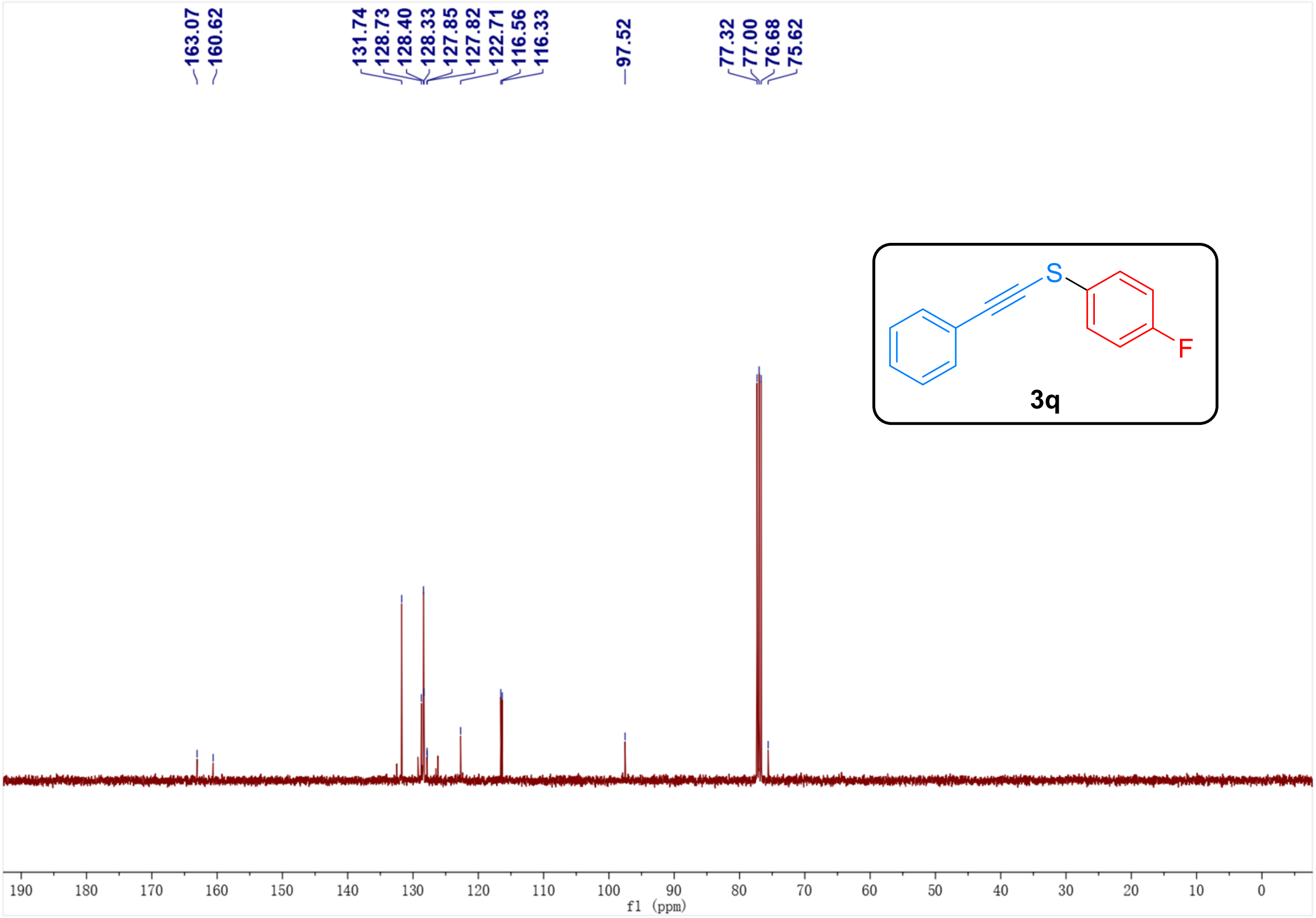
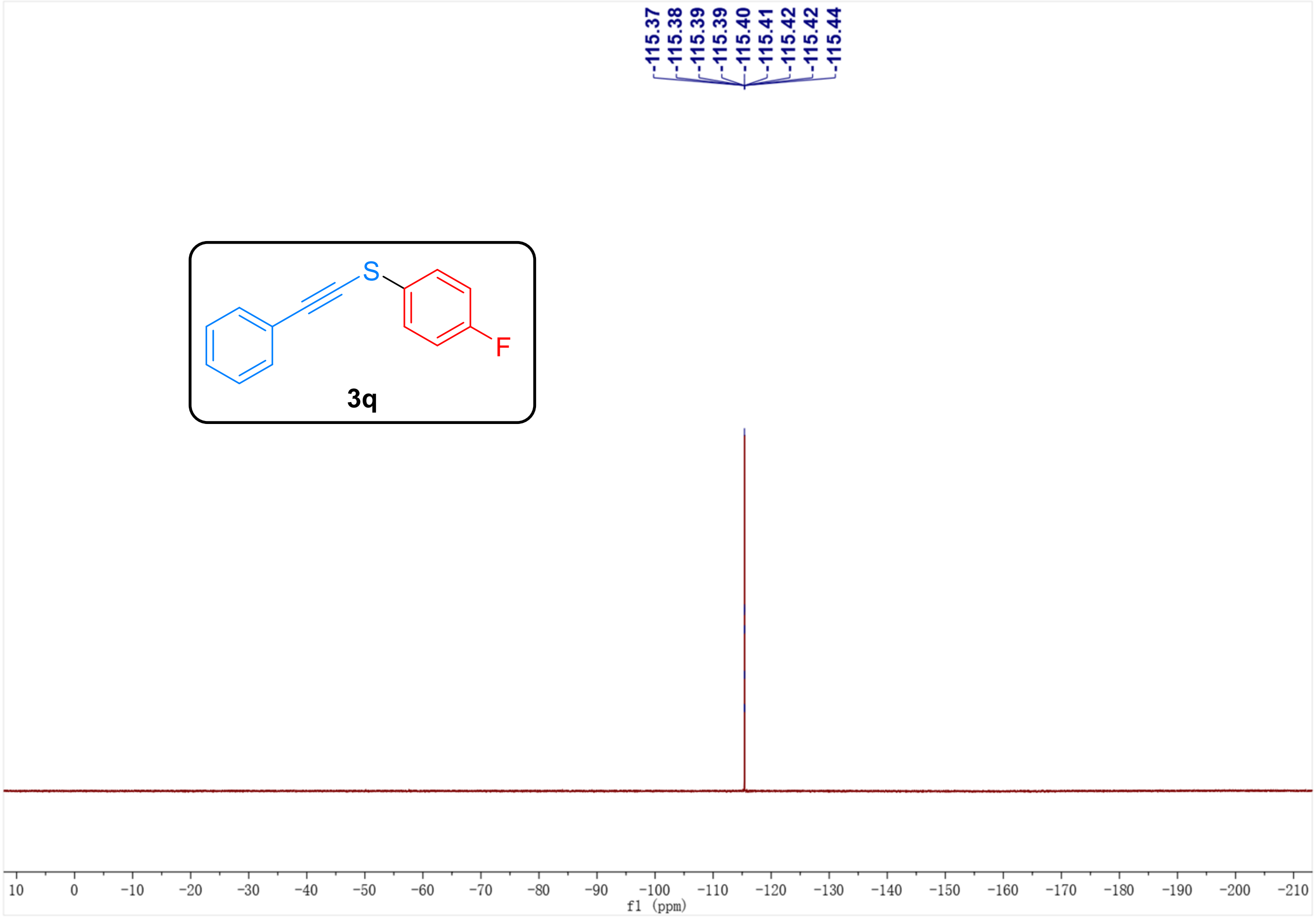
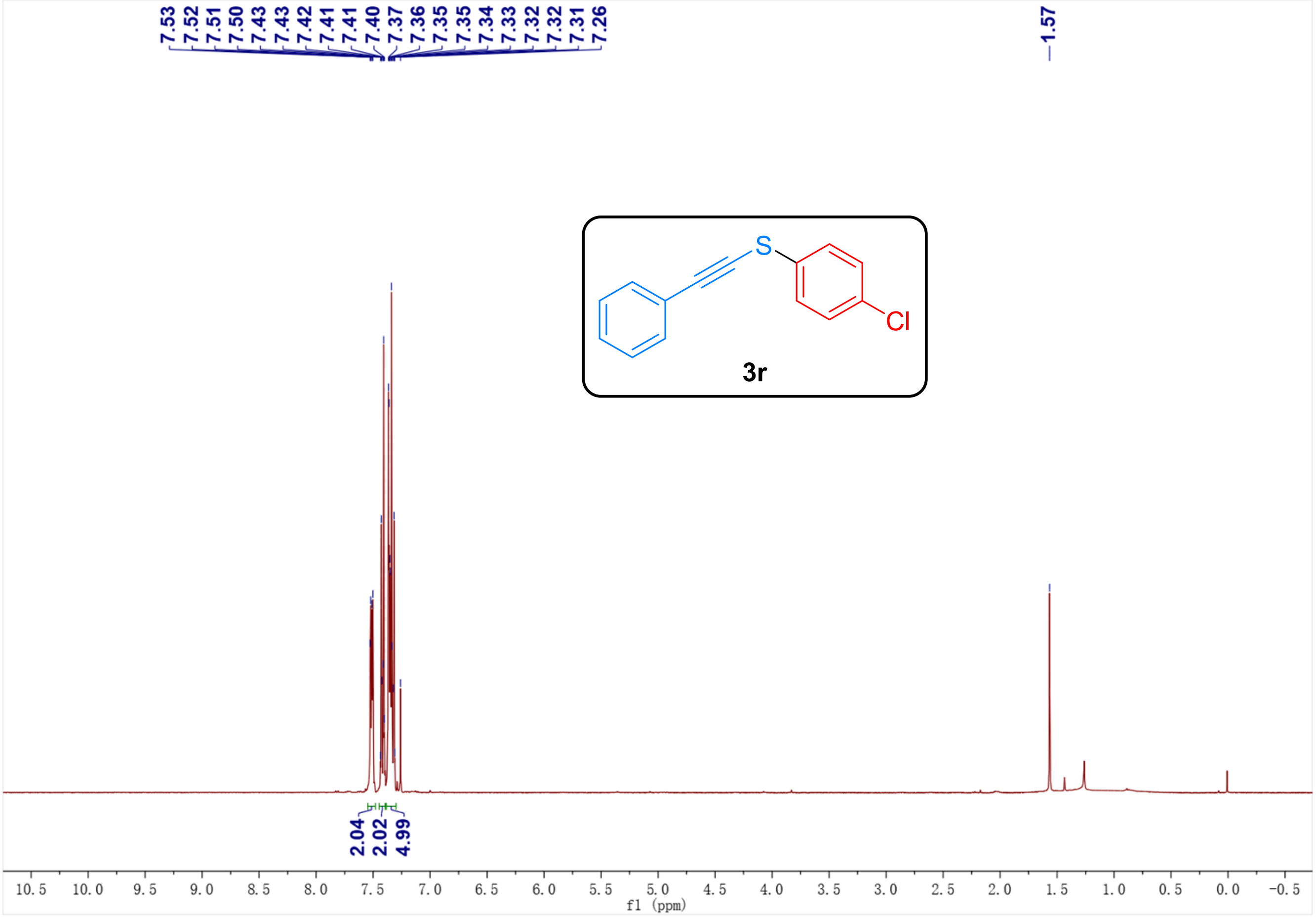
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.36
7.35
7.35
7.34
7.34
7.26
7.11
7.10
7.09
7.08
7.08
7.08
7.07
7.07
7.06
7.05
7.05
S
F
3q
4.08
3.08
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.07
160.62
131.74
128.73
128.40
128.33
127.85
127.82
122.71
116.56
116.33
97.52
77.32
77.00
76.68
75.62
S
F
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-115.37
-115.38
-115.39
-115.39
-115.40
-115.41
-115.42
-115.42
-115.44
S
F
3q
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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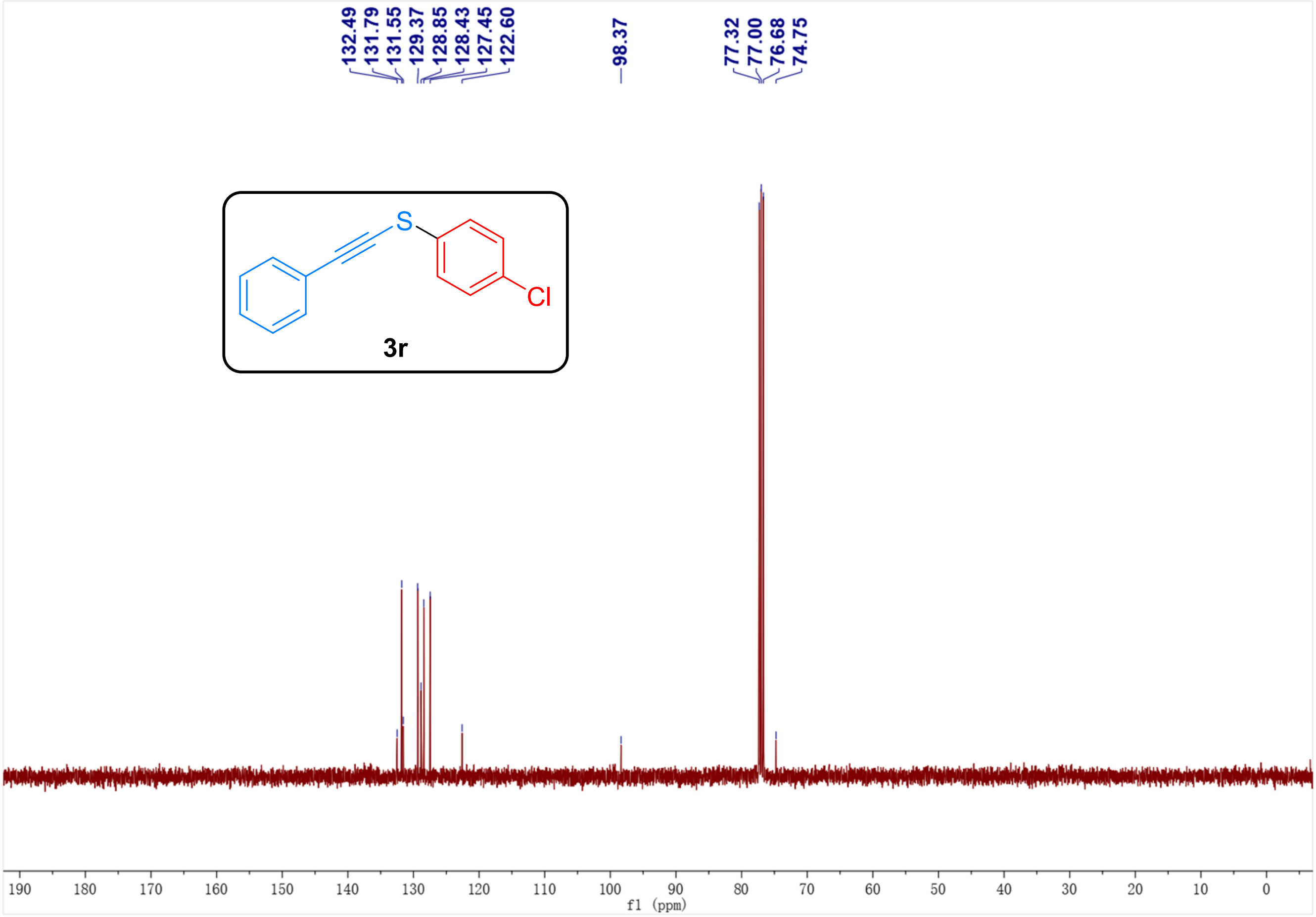
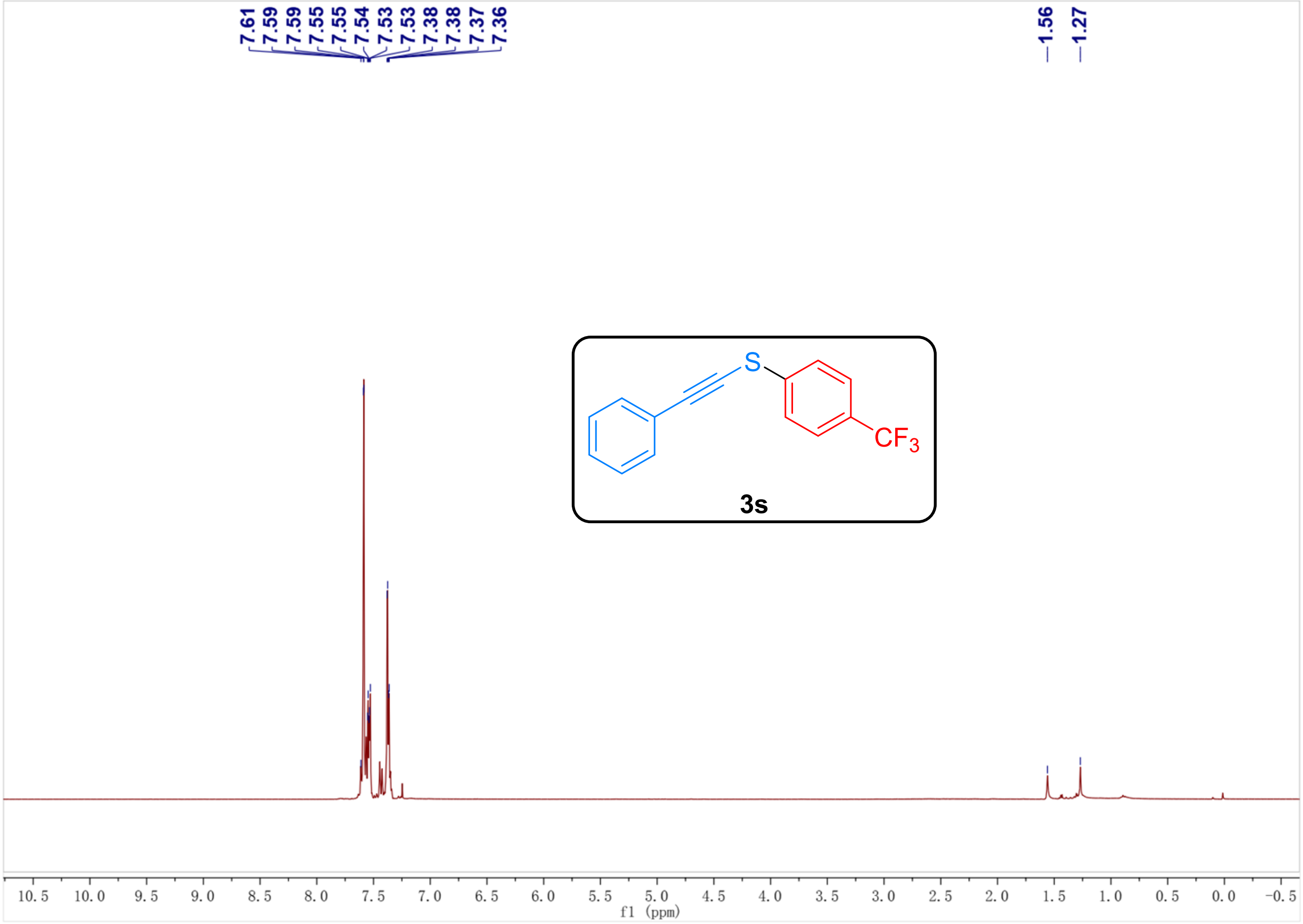
7.52
7.51
7.50
7.43
7.43
7.42
7.41
7.41
7.40
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.26
1.57
S
Cl
3r
2.04
2.02
4.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


132.49
131.79
131.55
129.37
128.85
128.43
127.45
122.60
98.37
77.32
77.00
76.68
74.75
S
Cl
3r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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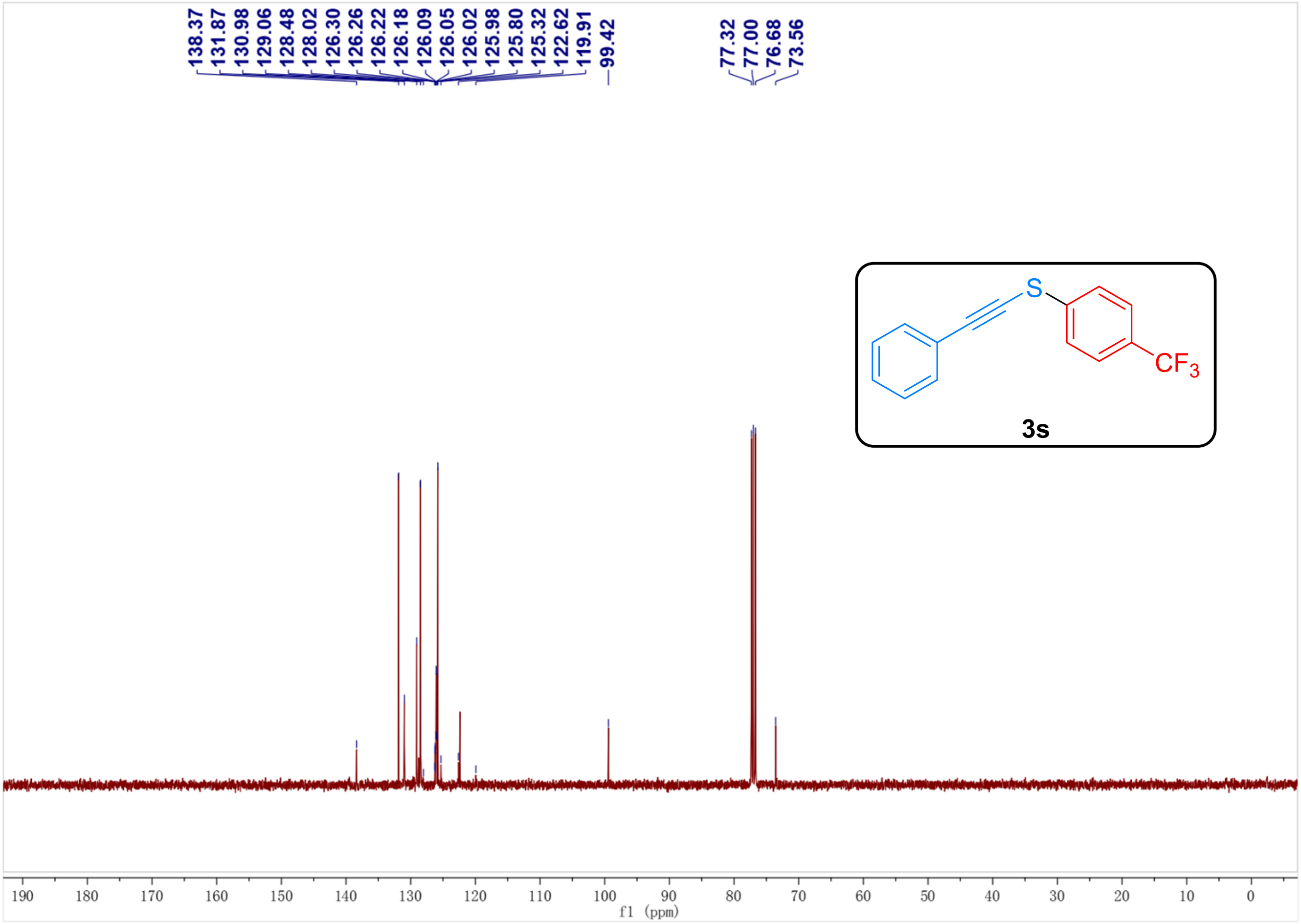
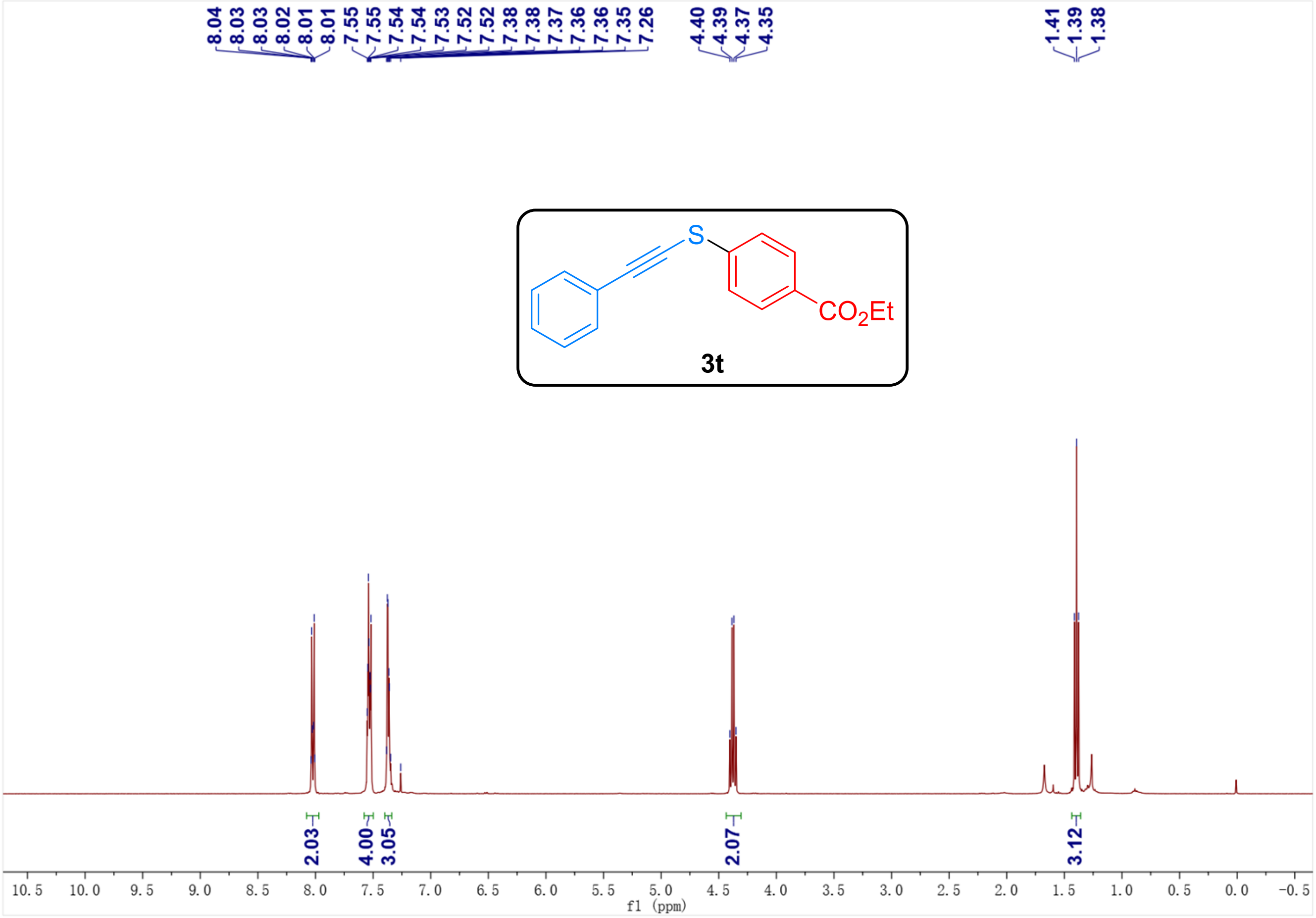
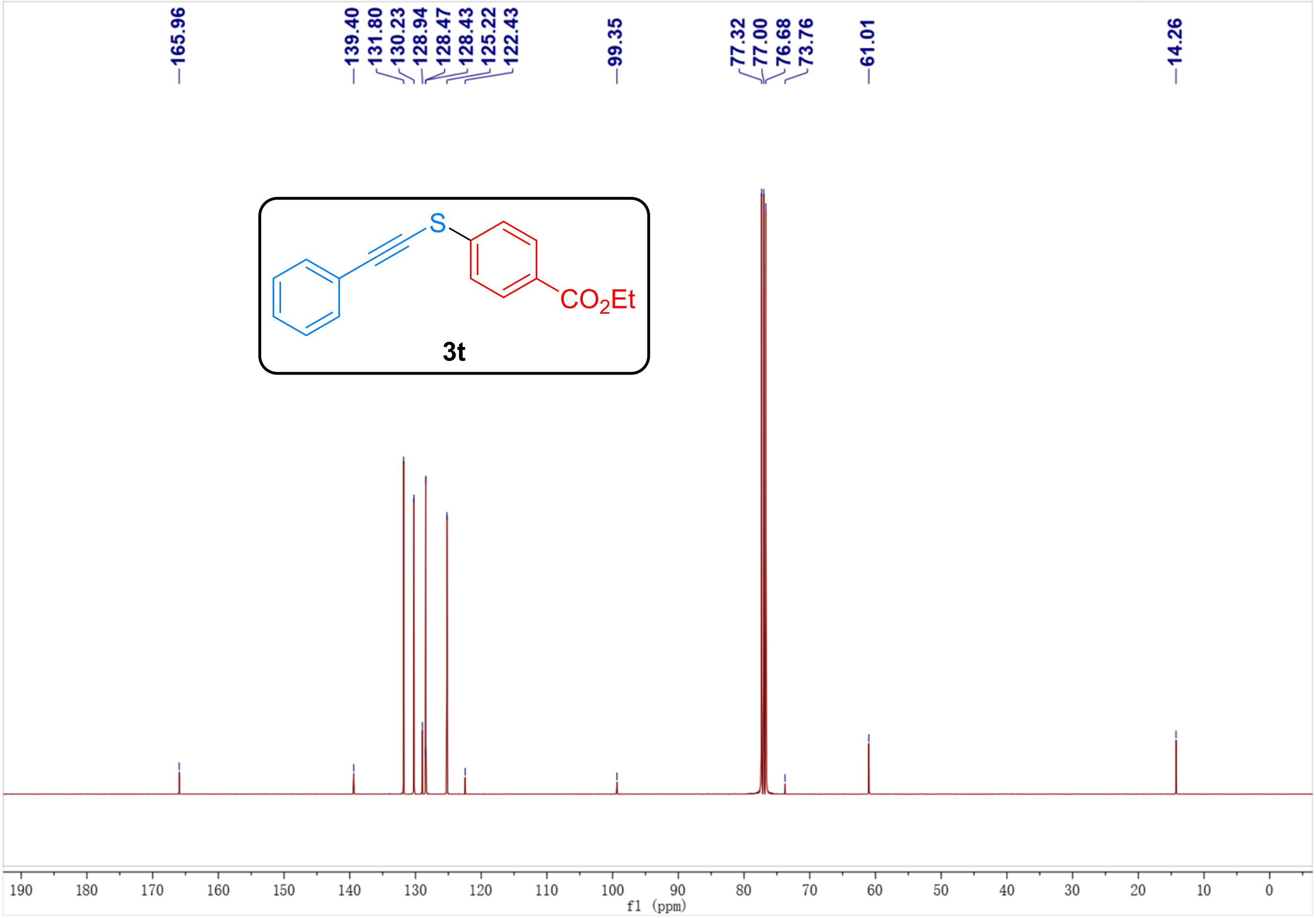
7.59
7.59
7.55
7.55
7.54
7.53
7.53
7.38
7.38
7.37
7.36
1.56
1.27
S
CF_3
3s
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

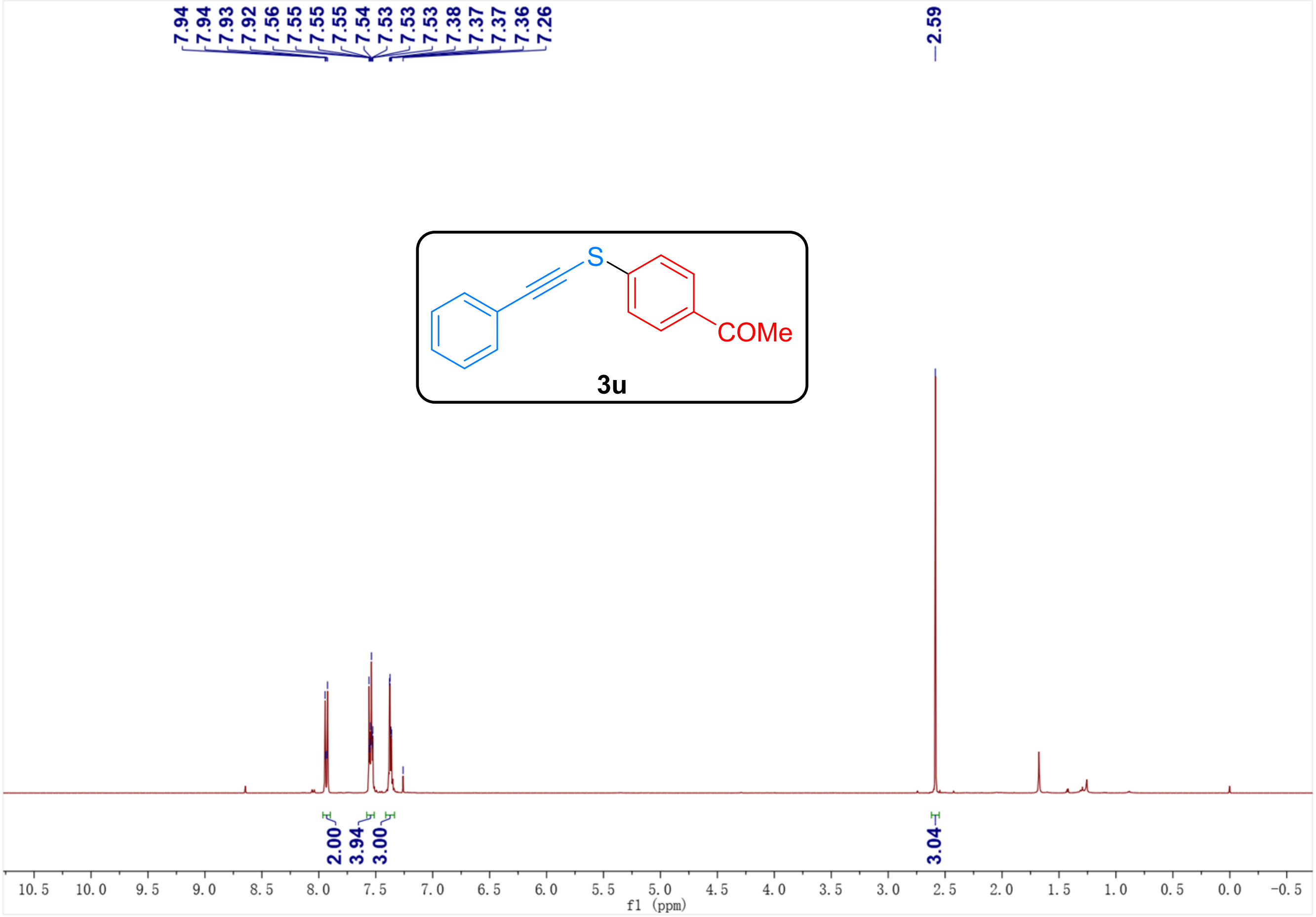

138.37
131.87
130.98
129.06
128.48
128.02
126.30
126.26
126.22
126.18
126.09
126.05
126.02
125.98
125.80
125.32
122.62
119.91
99.42
77.32
77.00
76.68
73.56
S
CF3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3s


8.04
8.03
8.03
8.02
8.01
8.01
7.55
7.55
7.54
7.54
7.53
7.52
7.52
7.38
7.38
7.37
7.36
7.36
7.35
7.26
4.40
4.39
4.37
4.35
1.41
1.39
1.38
S
CO2Et
2.03
4.00
3.05
2.07
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3t


165.96
139.40
131.80
130.23
128.94
128.47
128.43
125.22
122.43
99.35
77.32
77.00
76.68
73.76
61.01
14.26
S
CO_2Et
3t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.94
7.94
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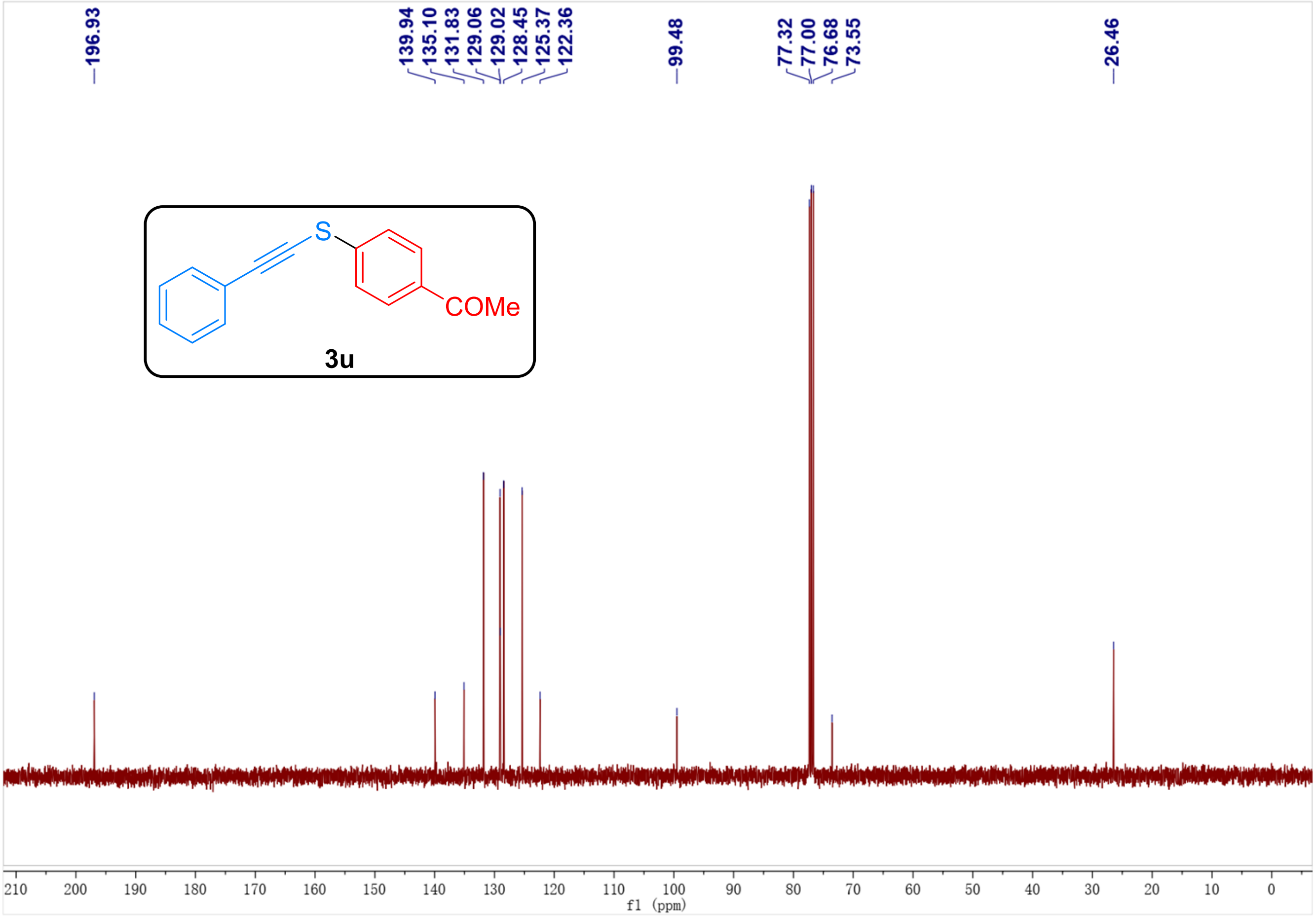
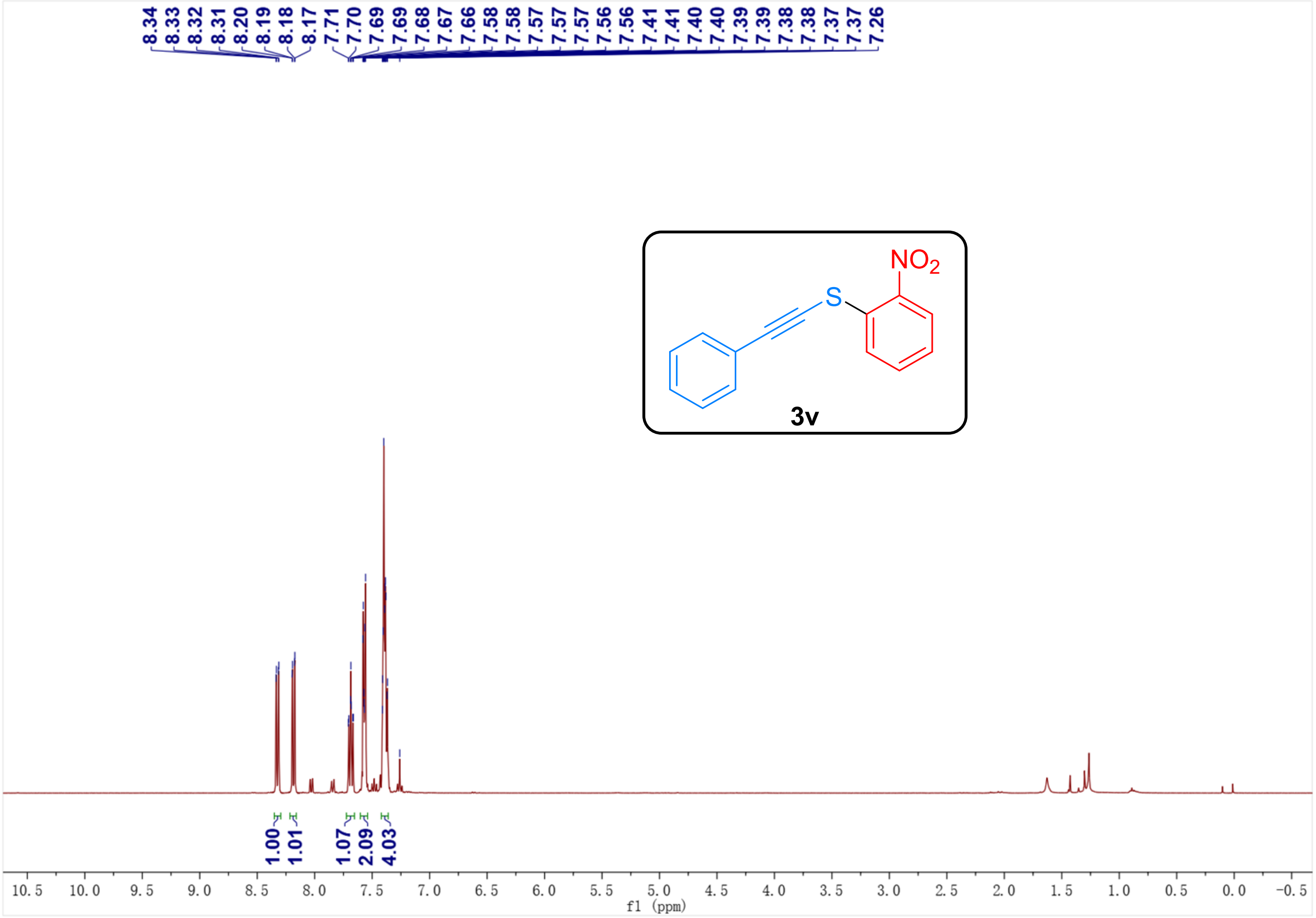
7.55
7.55
7.55
7.54
7.53
7.53
7.53
7.38
7.37
7.37
7.36
7.26
2.59
S
COMe
3u
2.00
3.94
3.00
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



196.93
139.94
135.10
131.83
129.06
129.02
128.45
125.37
122.36
99.48
77.32
77.00
76.68
73.55
26.46
S
COMe
3u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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8.19
8.18
8.17
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7.69
7.69
7.68
7.67
7.66
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7.58
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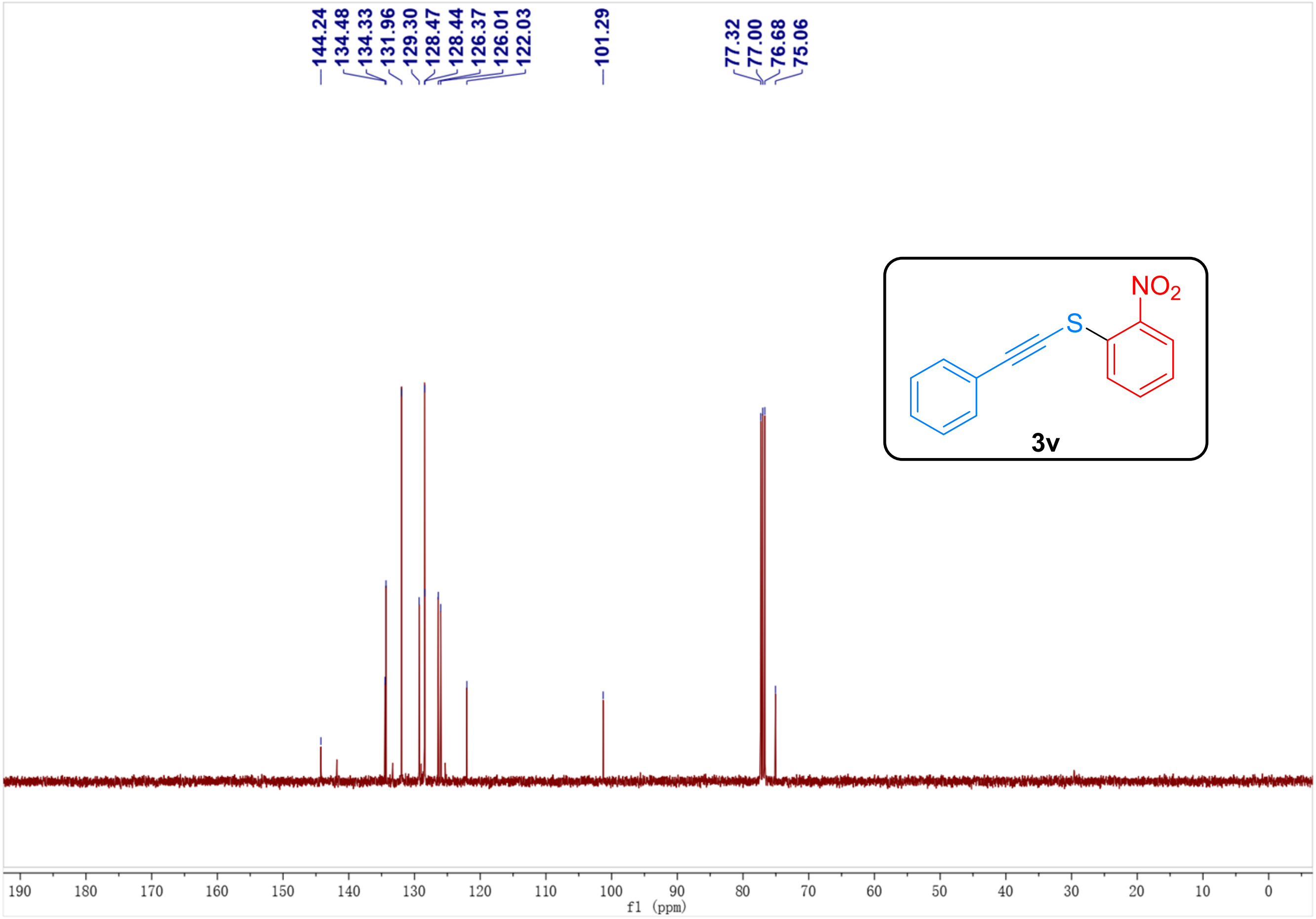
7.57
7.57
7.56
7.56
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.26
NO2
S
3v
1.00
1.01
1.07
2.09
4.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


144.24
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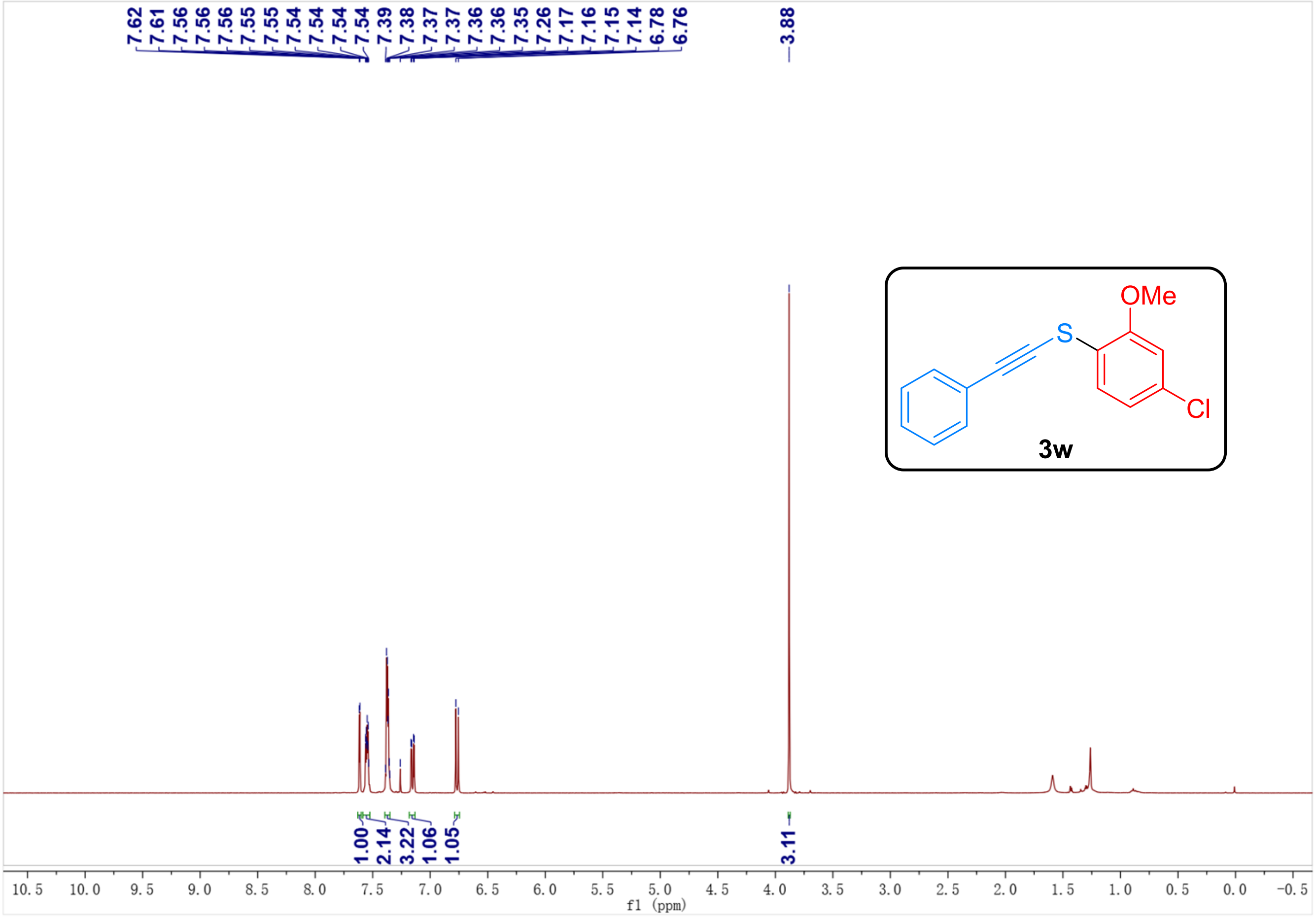
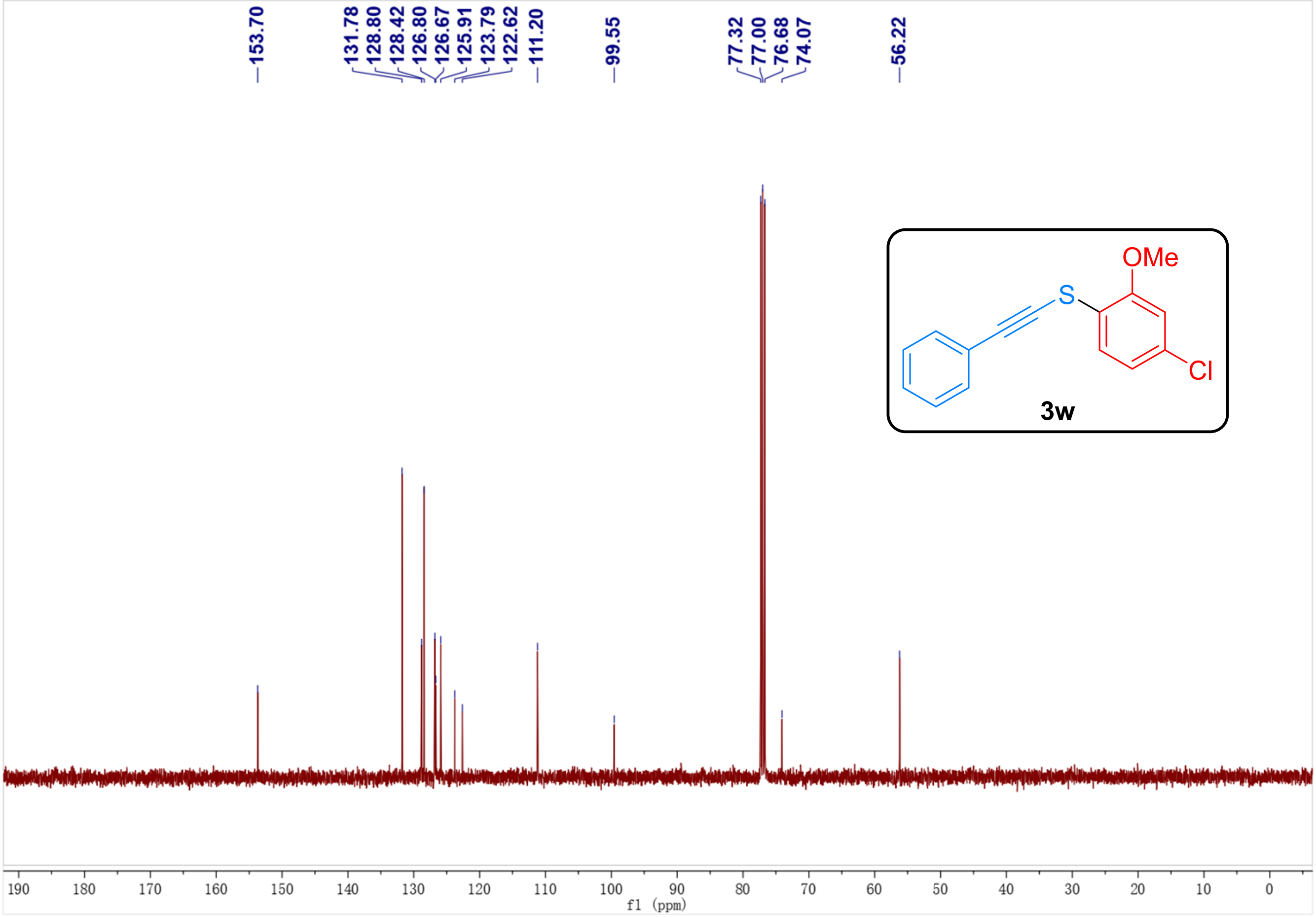
134.33
131.96
129.30
128.47
128.44
126.37
126.01
122.03
101.29
77.32
77.00
76.68
75.06
NO_2
S
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.62
7.61
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.54
7.54
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.26
7.17
7.16
7.15
7.14
6.78
6.76
3.88
OMe
S
Cl
3w
1.00
2.14
3.22
1.06
1.05
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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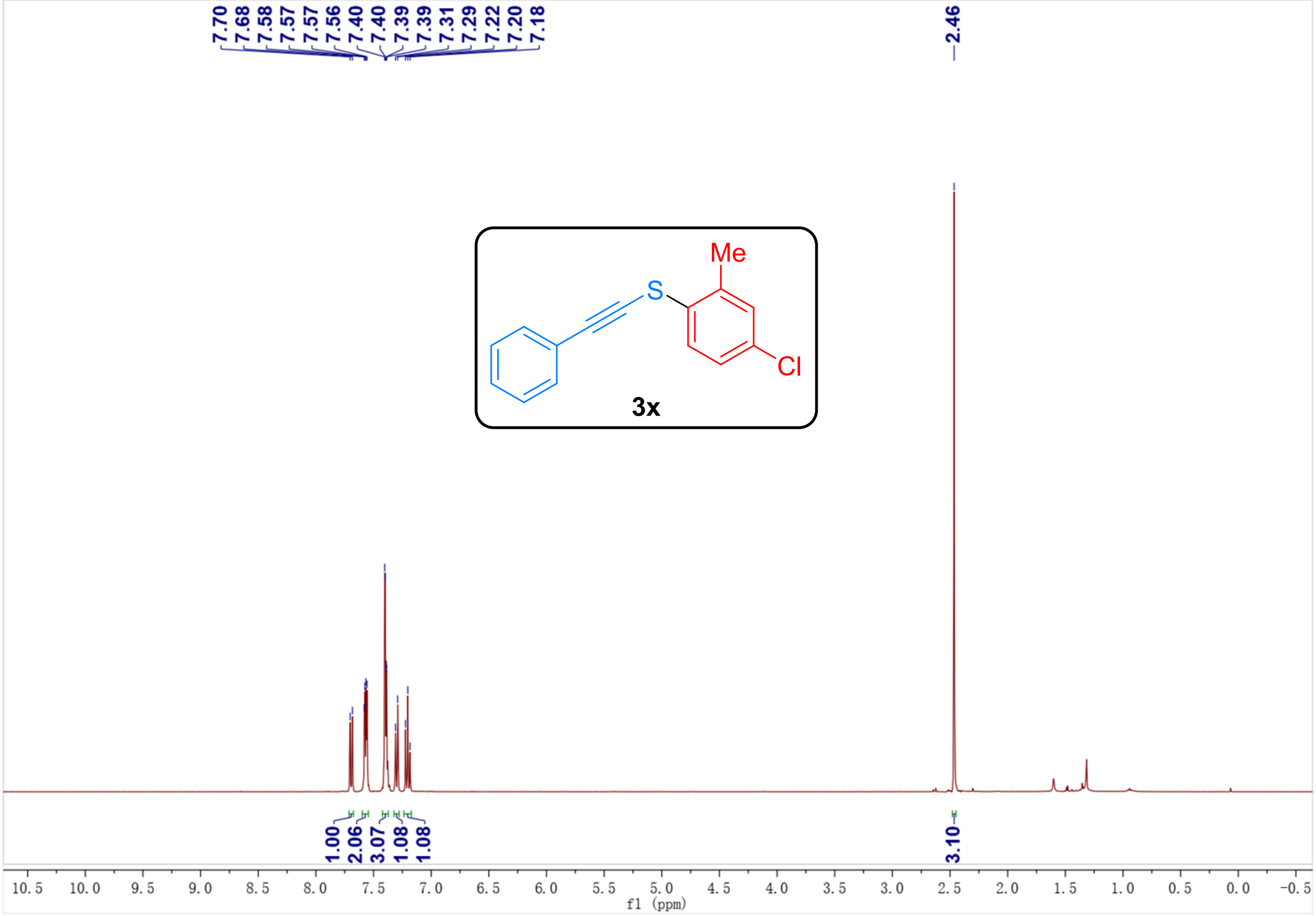
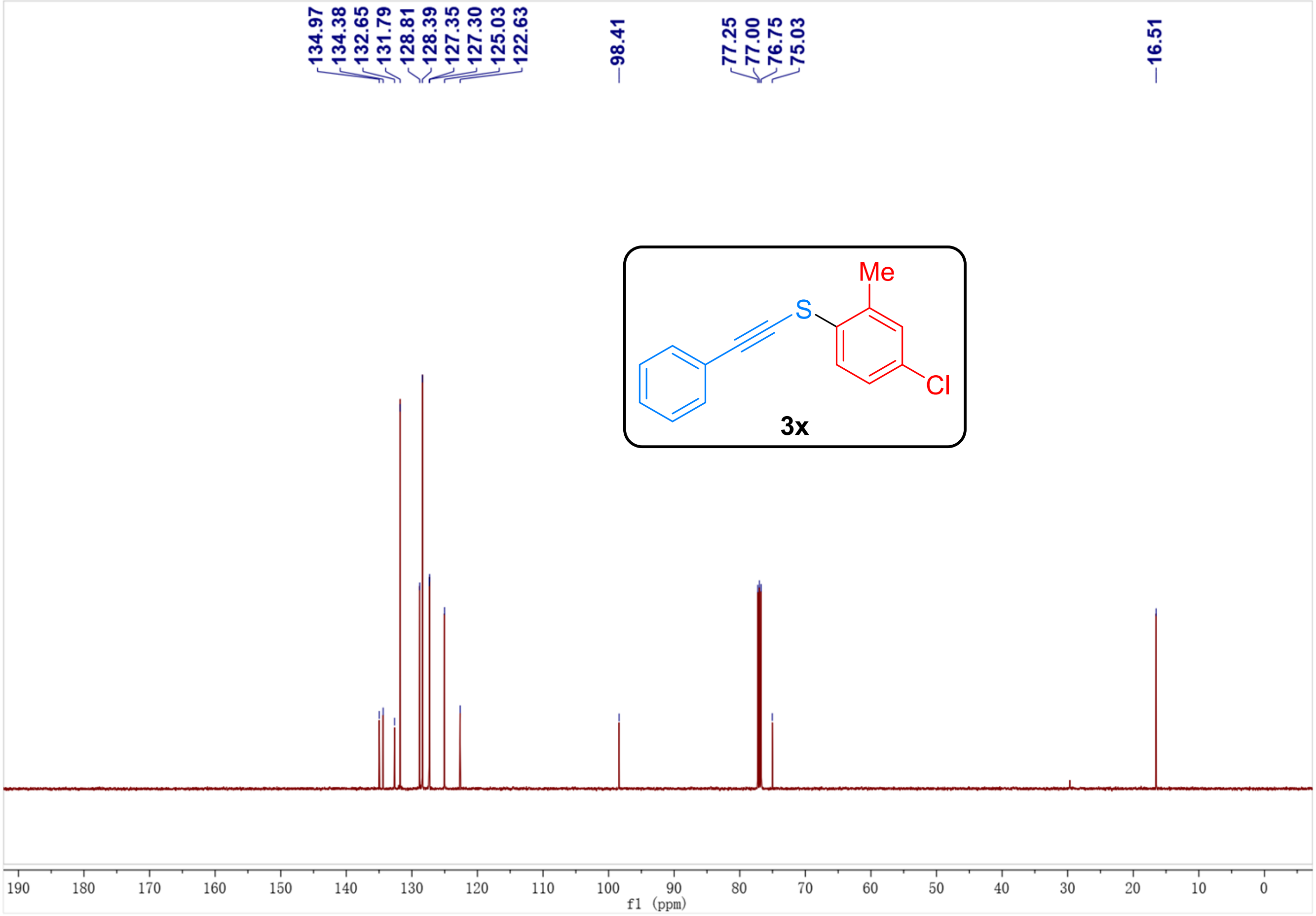
131.78
128.80
128.42
126.80
126.67
125.91
123.79
122.62
111.20
99.55
77.32
77.00
76.68
74.07
56.22
OMe
S
Cl
3w
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.70
7.68
7.58
7.57
7.57
7.56
7.40
7.40
7.39
7.39
7.31
7.29
7.22
7.20
7.18
2.46
Me
S
Cl
3x
1.00
2.06
3.07
1.08
1.08
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.63
98.41
77.25
77.00
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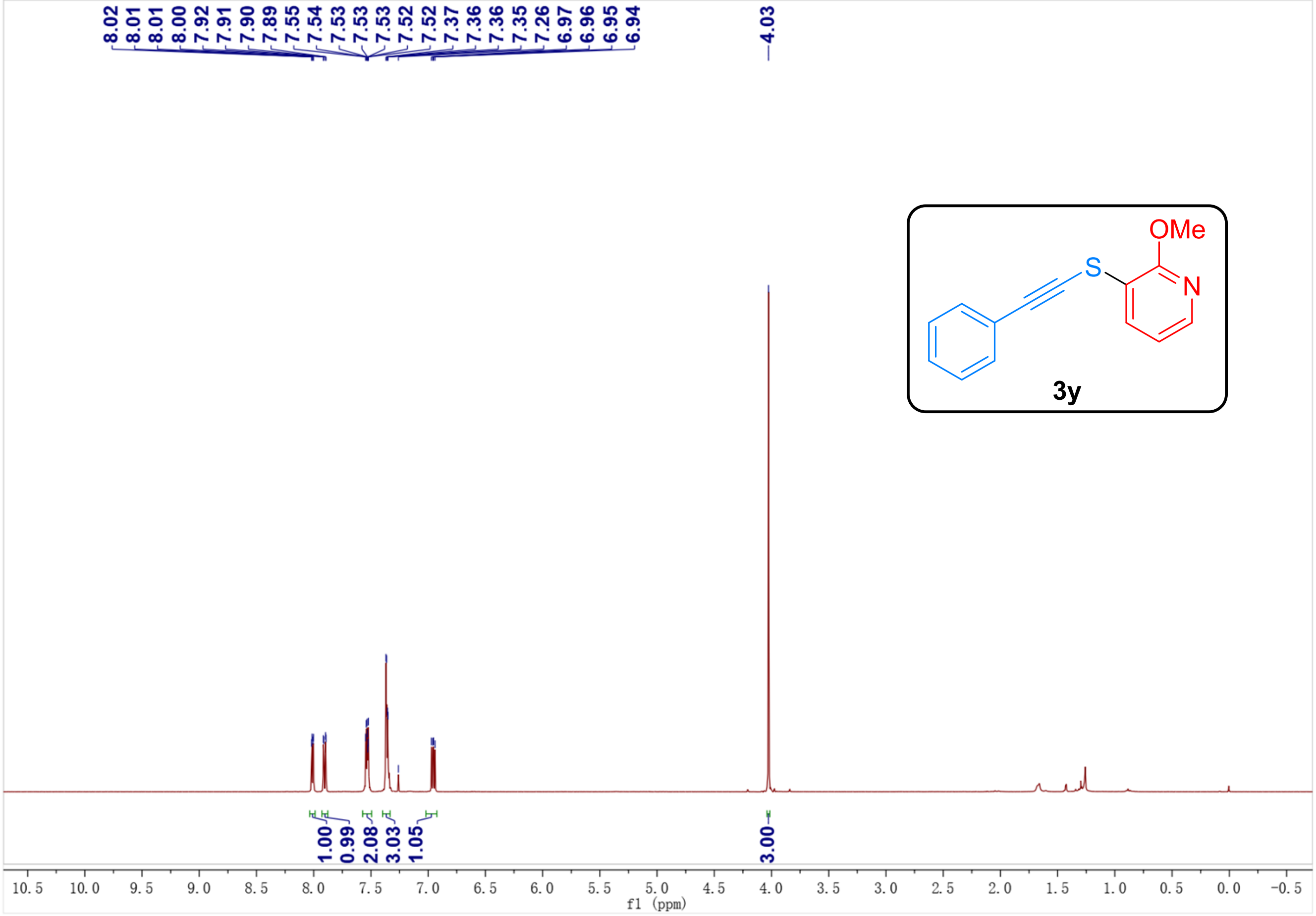
75.03
16.51
Me
S
Cl
3x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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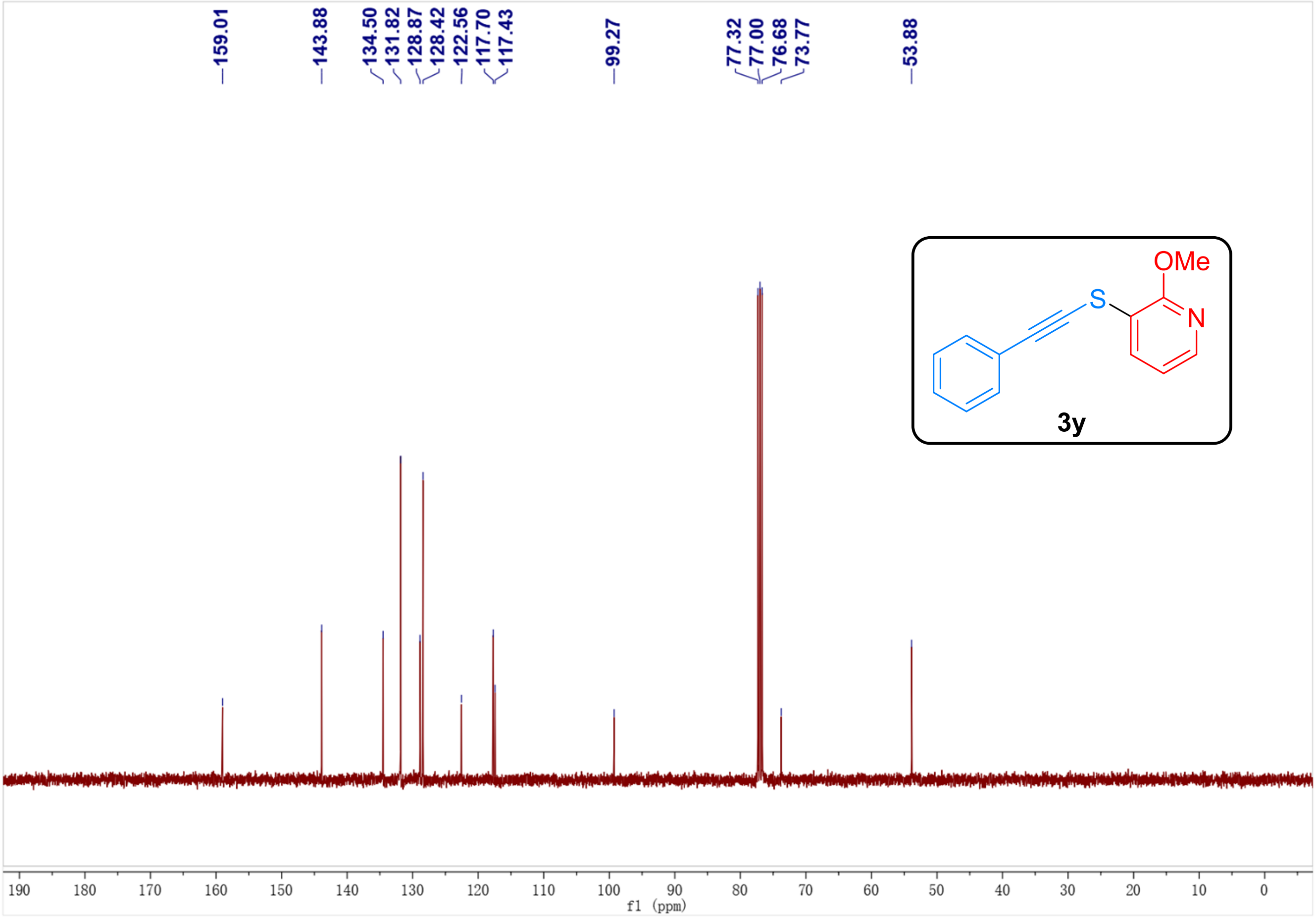
7.53
7.52
7.52
7.37
7.36
7.36
7.35
7.26
6.97
6.96
6.95
6.94
4.03
OMe
S
N
3y
1.00
0.99
2.08
3.03
1.05
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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76.68
73.77
53.88
OMe
S
N
3y
190
180
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140
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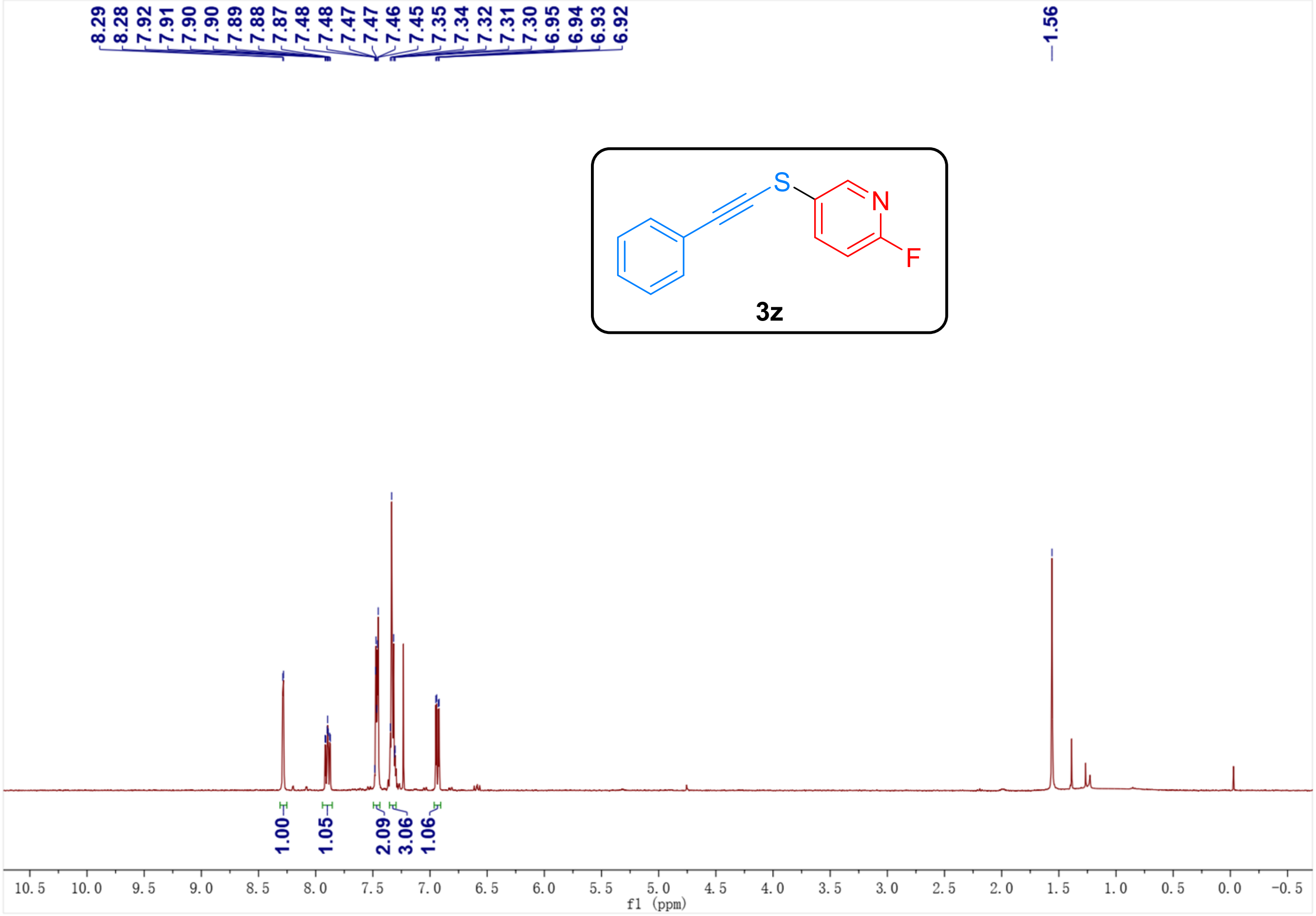
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.46
7.45
7.35
7.34
7.32
7.31
7.30
6.95
6.94
6.93
6.92
1.56
S
N
F
3z
1.00
1.05
2.09
3.06
1.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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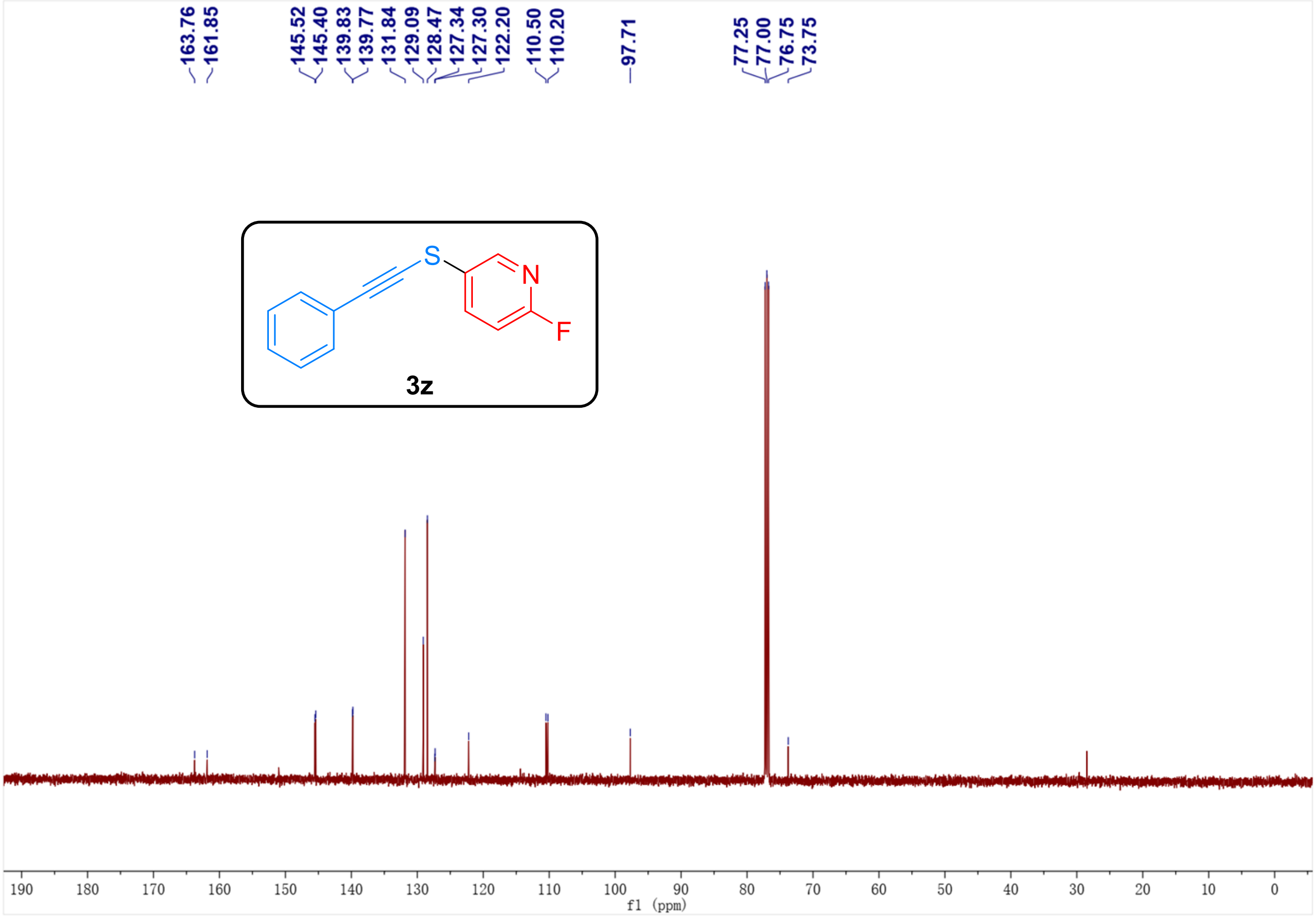
0.5
0.0
-0.5
f1 (ppm)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110.20
97.71
77.25
77.00
76.75
73.75
S
N
F
3z
190
180
170
160
150
140
130
120
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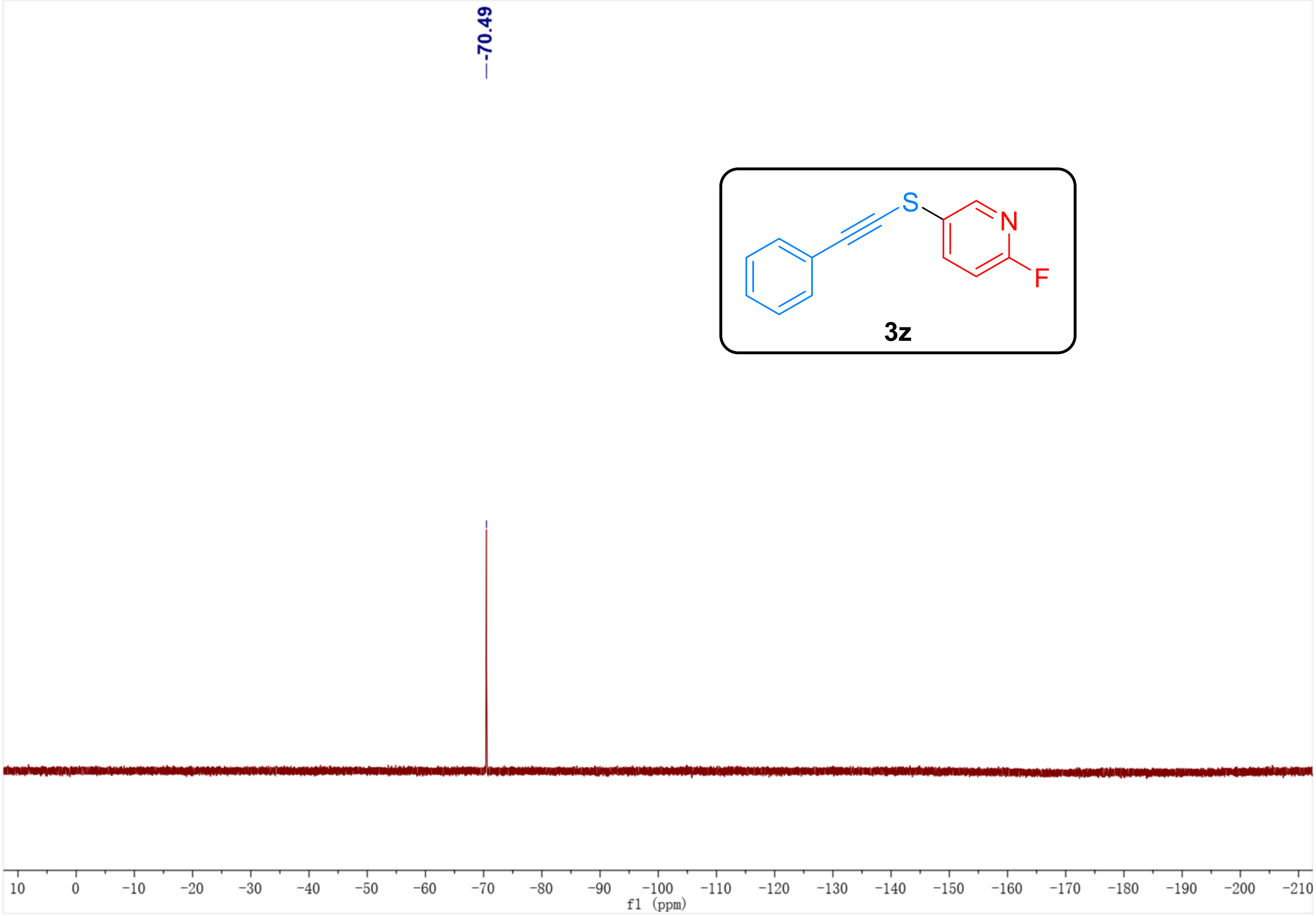
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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F
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-60
-70
-80
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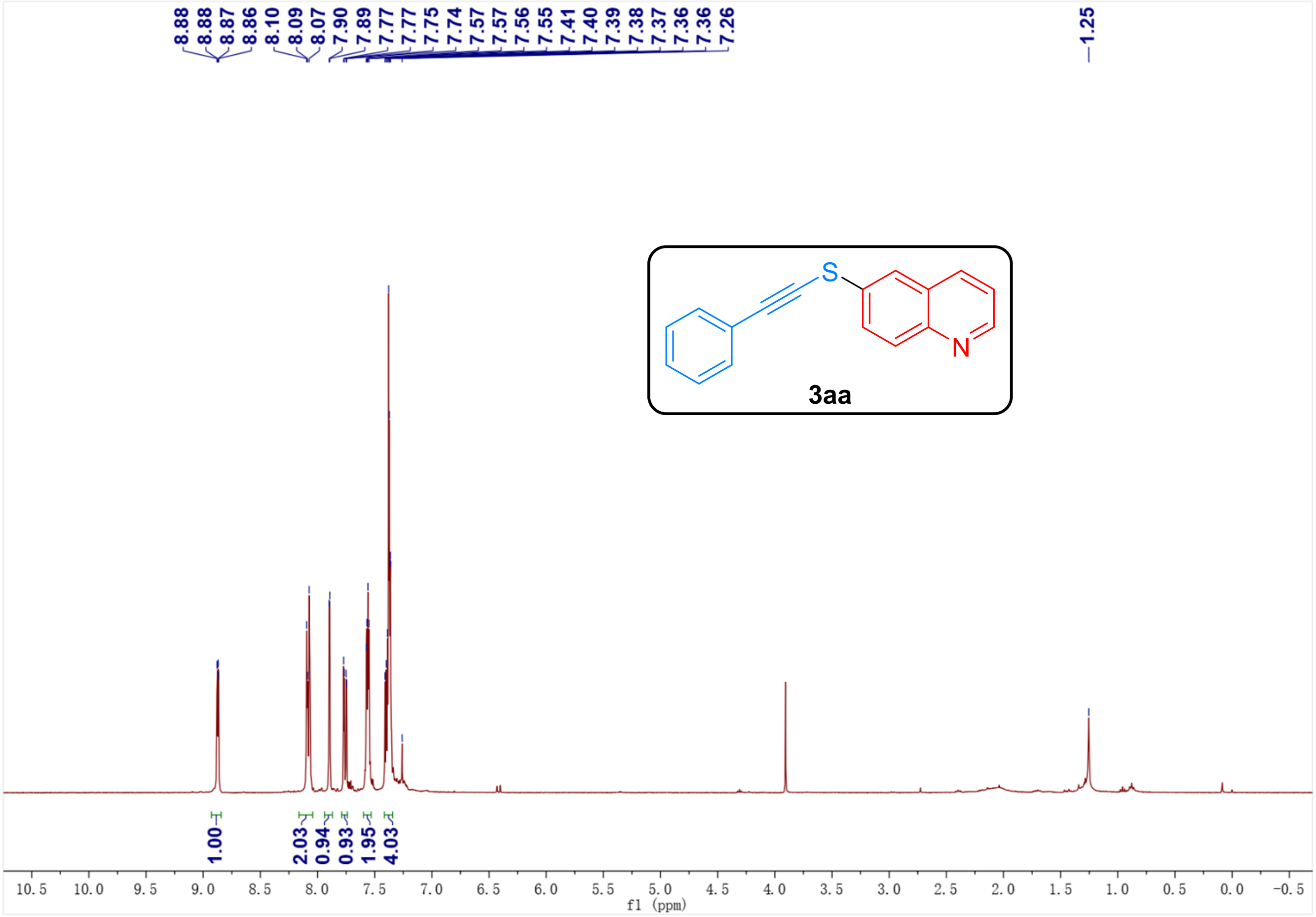
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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7.55
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.26
1.25
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2.03
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0.93
1.95
4.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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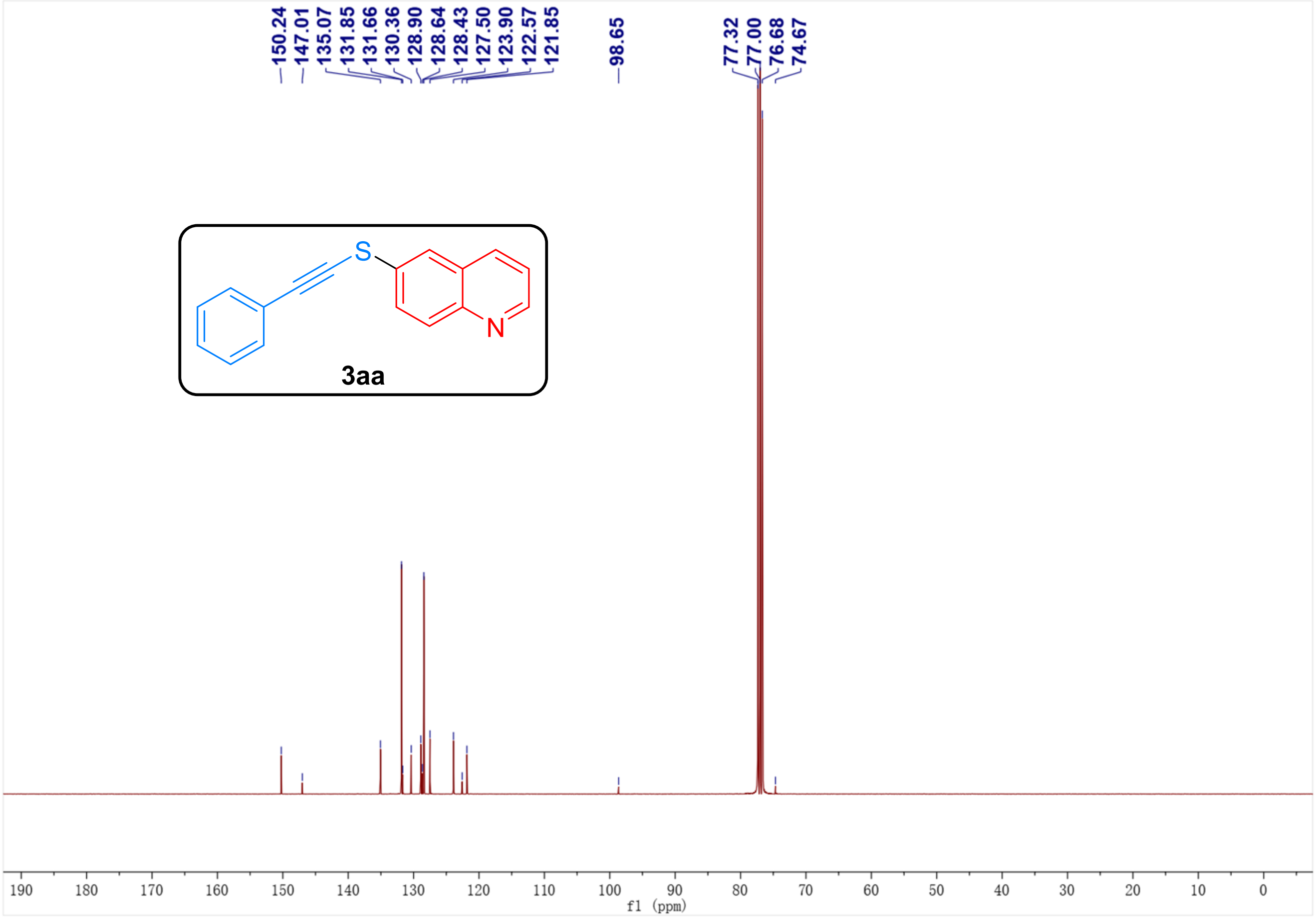
f1 (ppm)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128.64
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123.90
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121.85
98.65
77.32
77.00
76.68
74.67
3aa
190
180
170
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150
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130
120
110
100
90
80
70
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50
40
30
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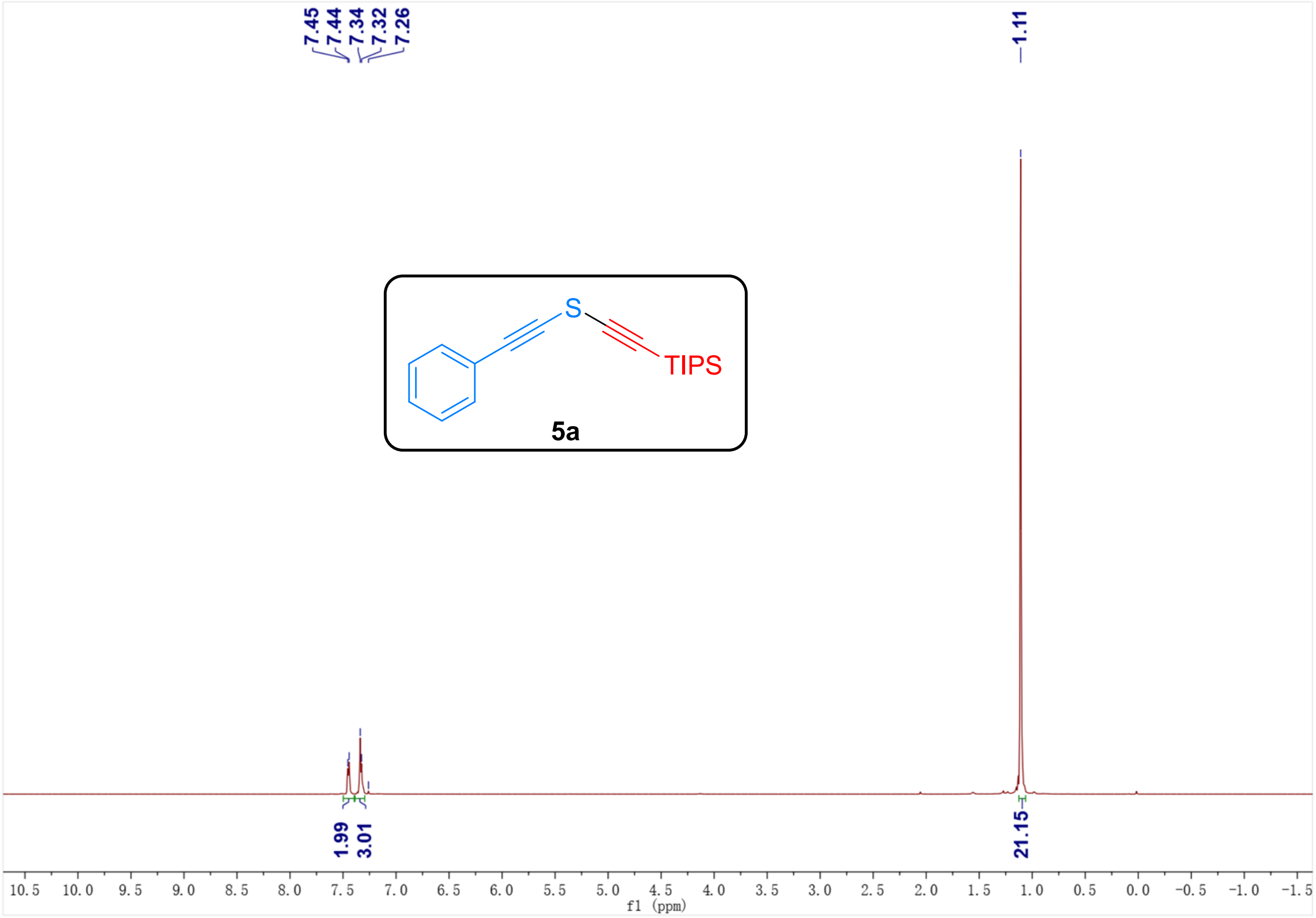
10
0
f1 (ppm)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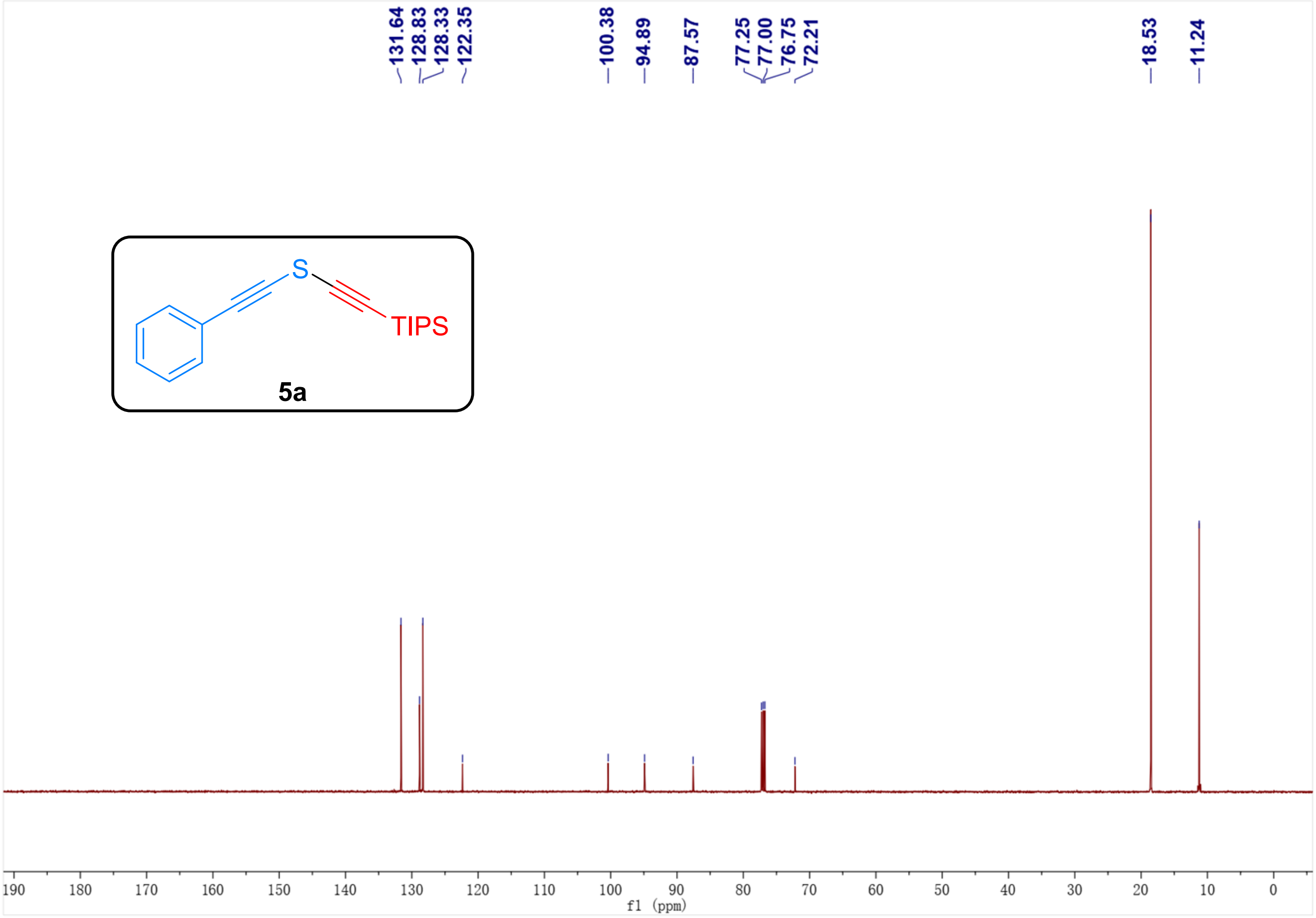
7.26
1.11
S
TIPS
5a
1.99
3.01
21.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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11.24
S
TIPS
5a
190
180
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160
150
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130
120
110
100
90
80
70
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50
40
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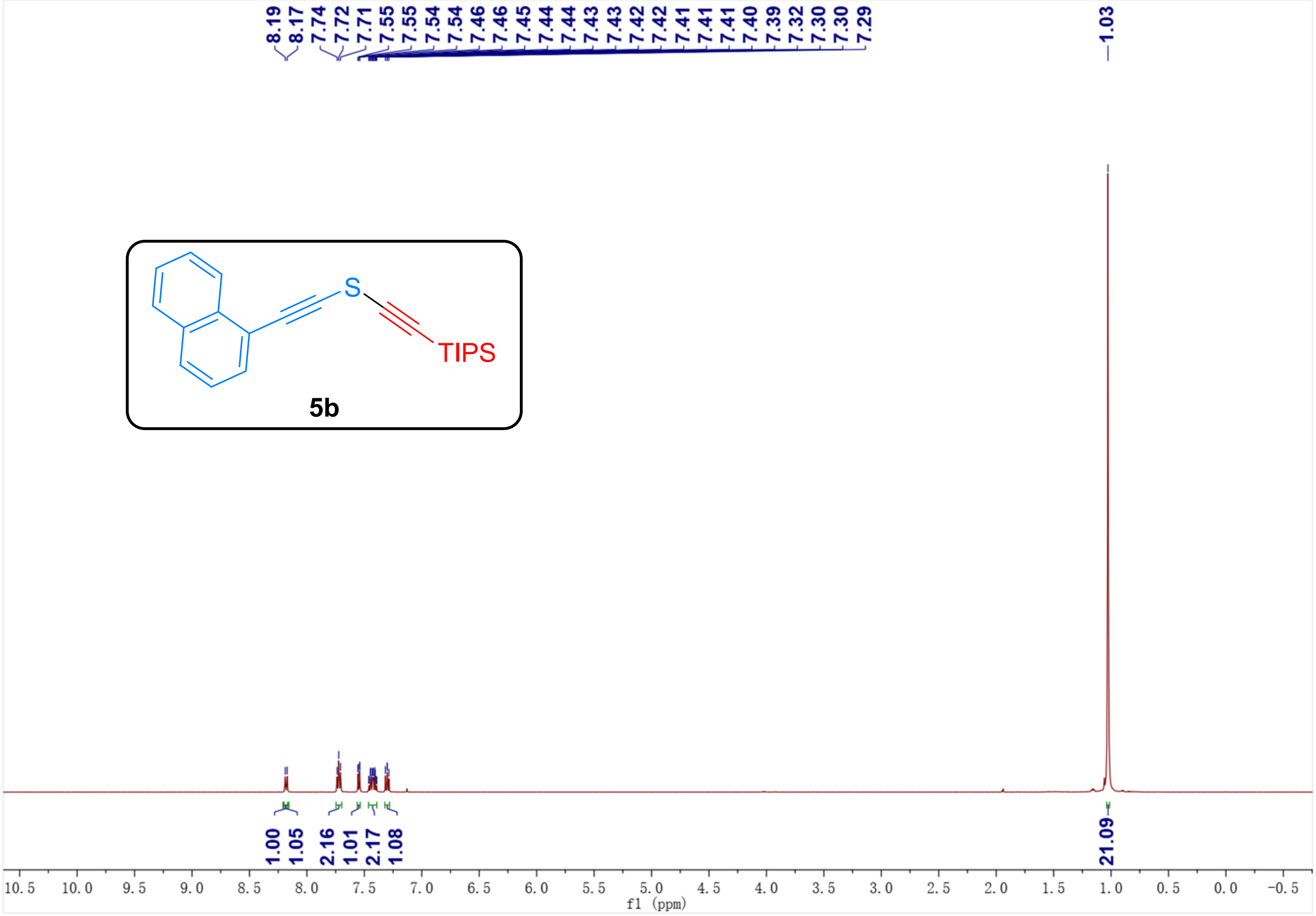
20
10
0
f1 (ppm)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7.54
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7.46
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7.45
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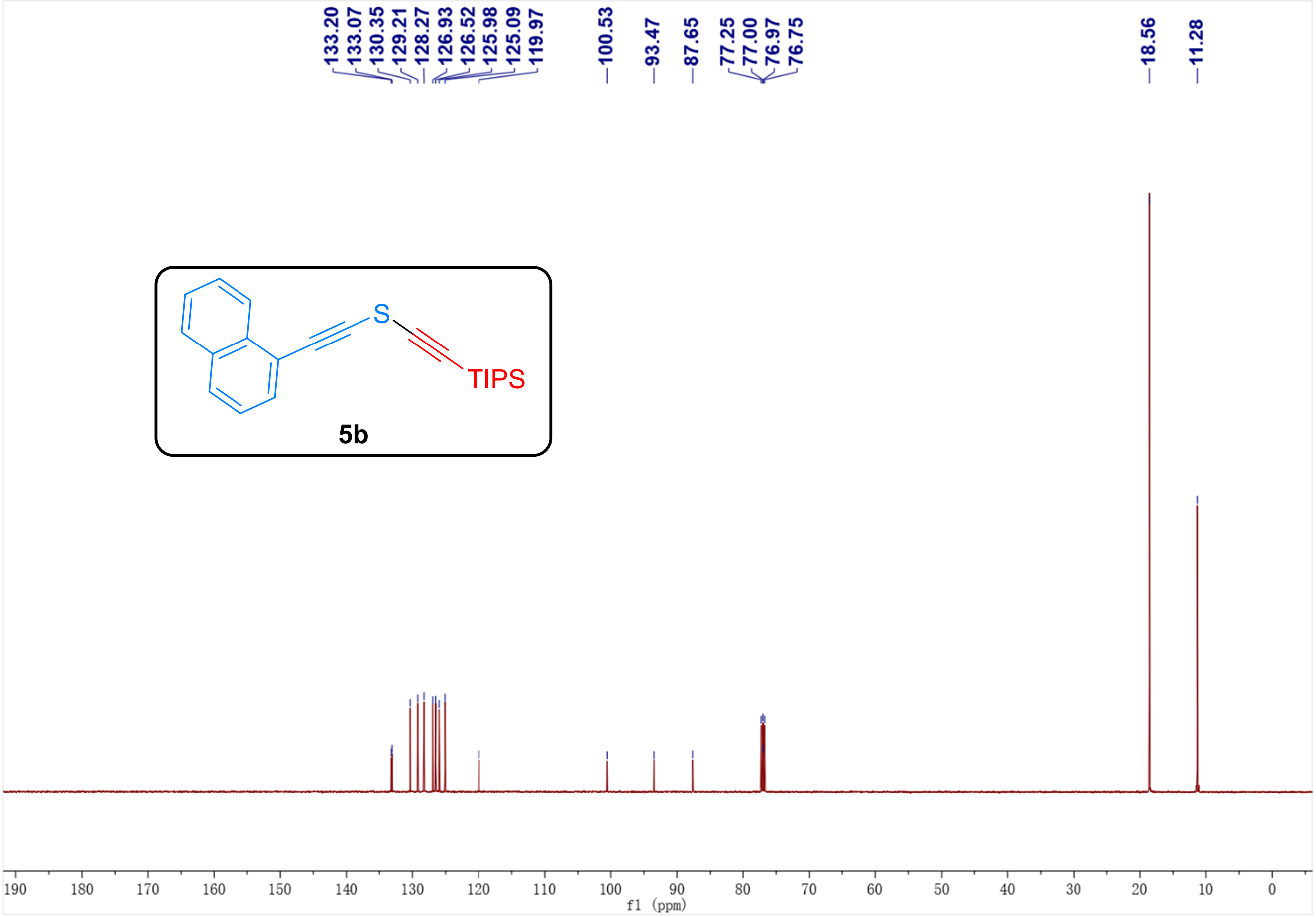
7.42
7.42
7.41
7.41
7.41
7.40
7.39
7.32
7.30
7.30
7.29
1.03
S
TIPS
5b
1.00
1.05
2.16
1.01
2.17
1.08
21.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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87.65
77.25
77.00
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11.28
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TIPS
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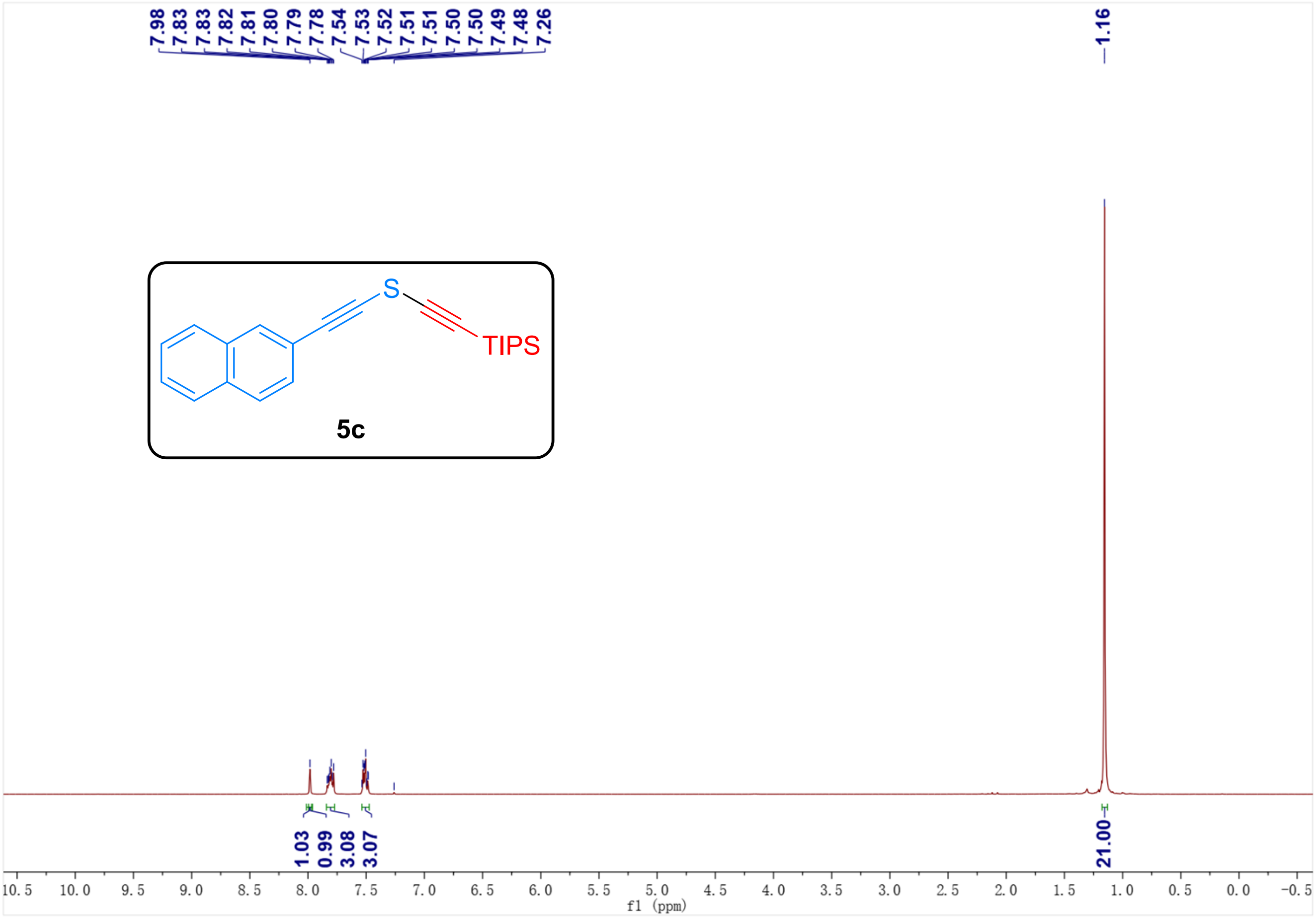
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.26
1.16
S
TIPS
5c
1.03
0.99
3.08
3.07
21.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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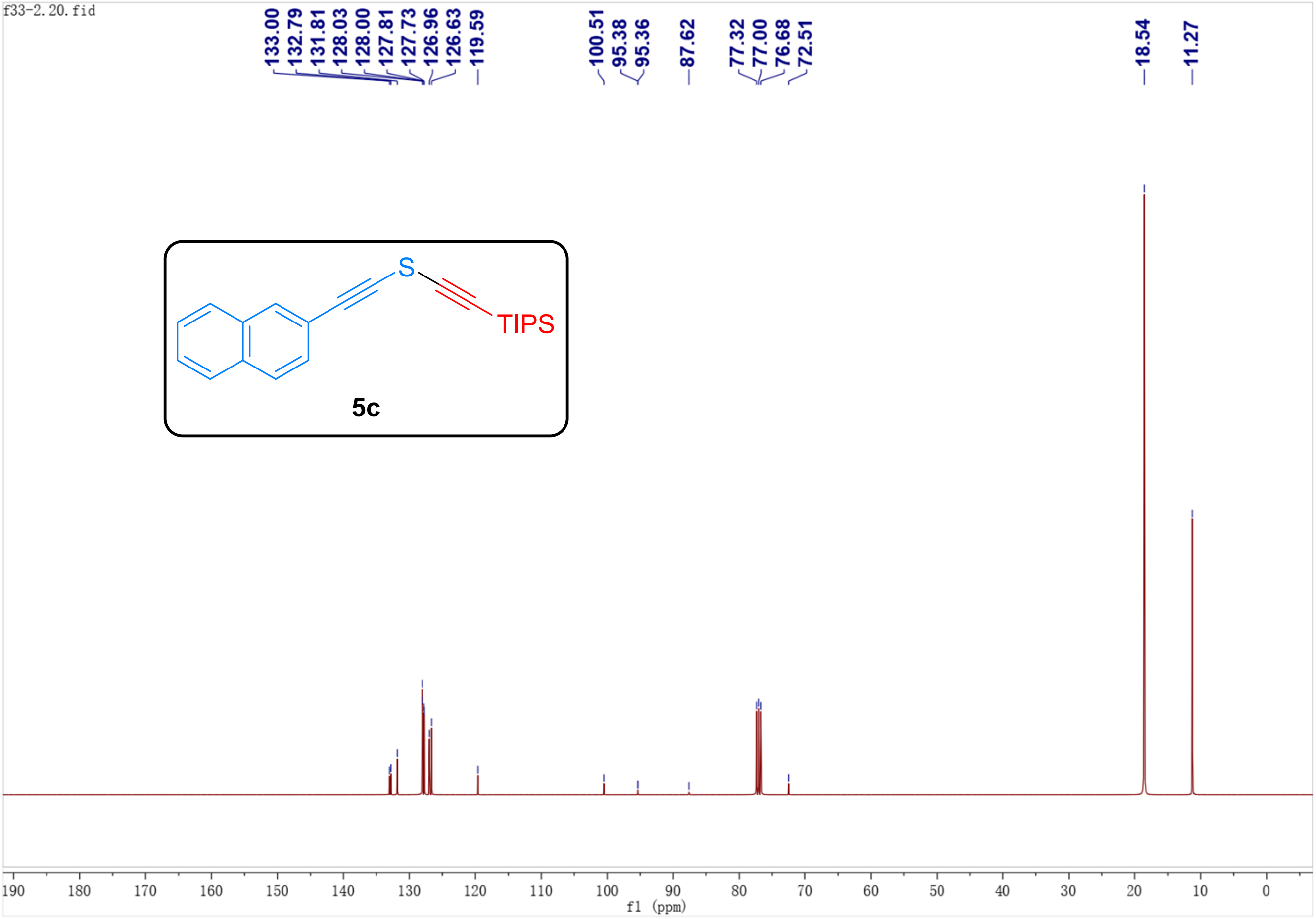
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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100.51
95.38
95.36
87.62
77.32
77.00
76.68
72.51
18.54
11.27
S
TIPS
5c
190
180
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130
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90
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40
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10
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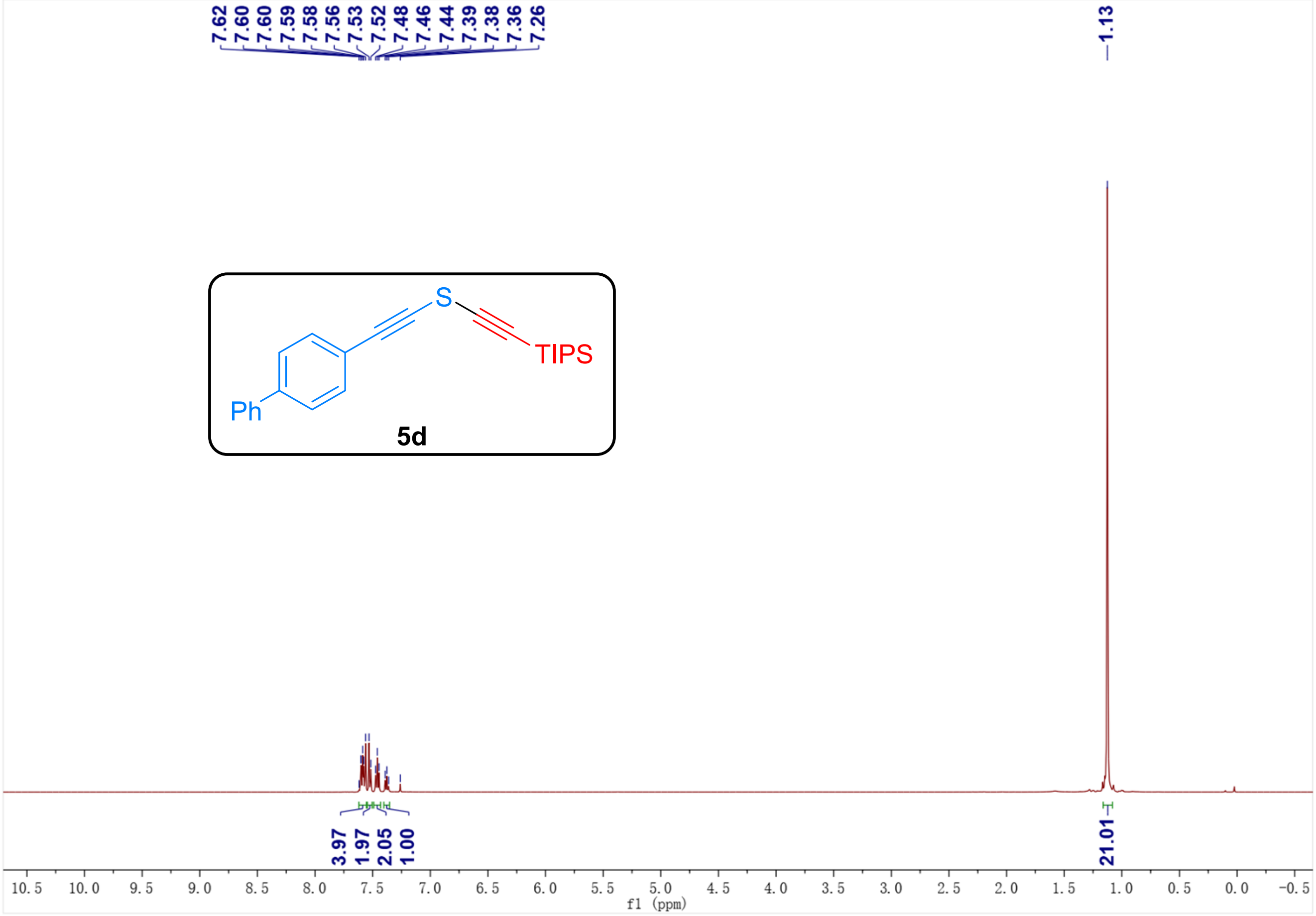
f1 (ppm)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7.46
7.44
7.39
7.38
7.36
7.26
1.13
S
TIPS
Ph
5d
3.97
1.97
2.05
1.00
21.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
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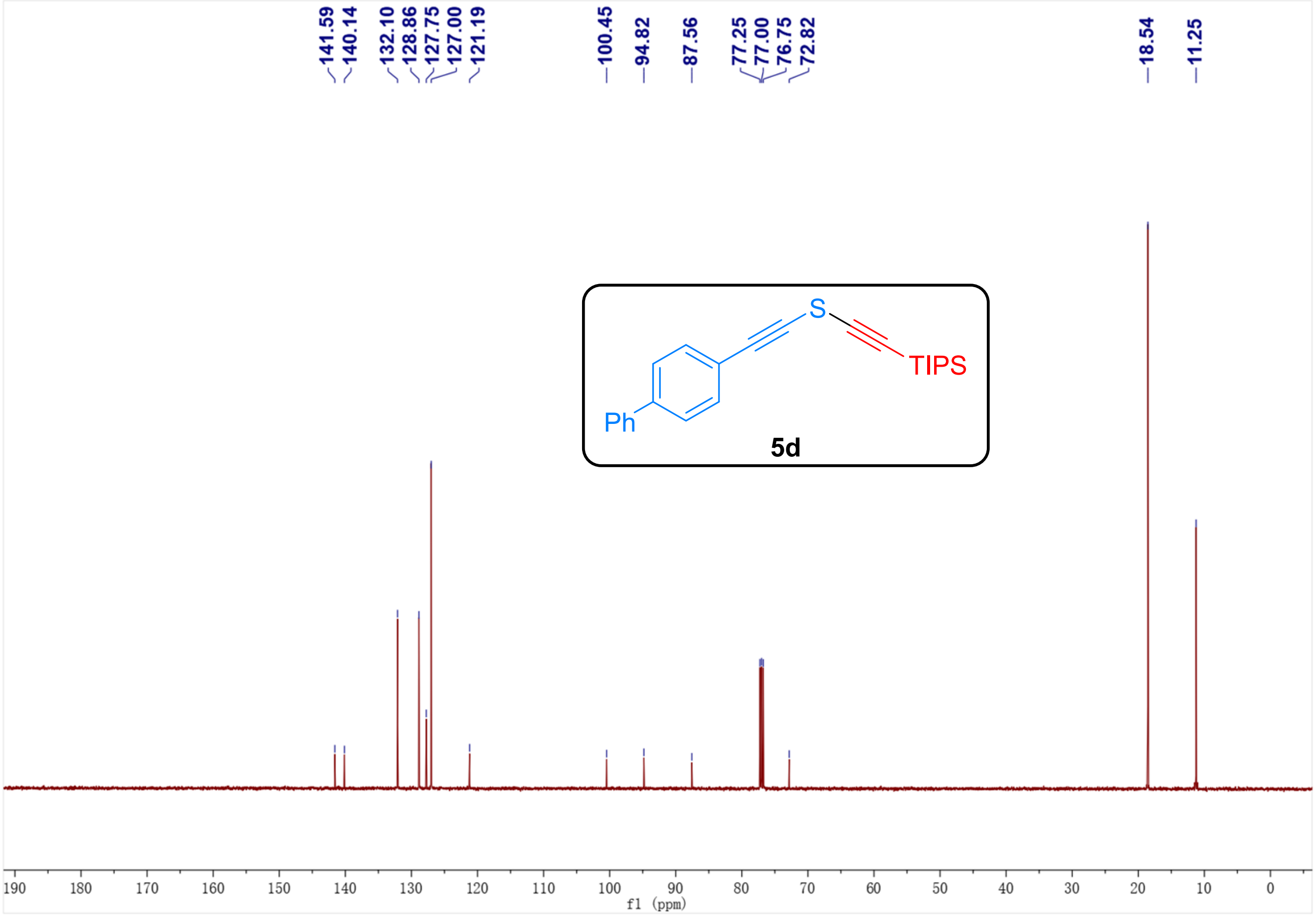
1.0
0.5
0.0
-0.5
f1 (ppm)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72.82
18.54
11.25
S
TIPS
Ph
5d
190
180
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150
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110
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90
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50
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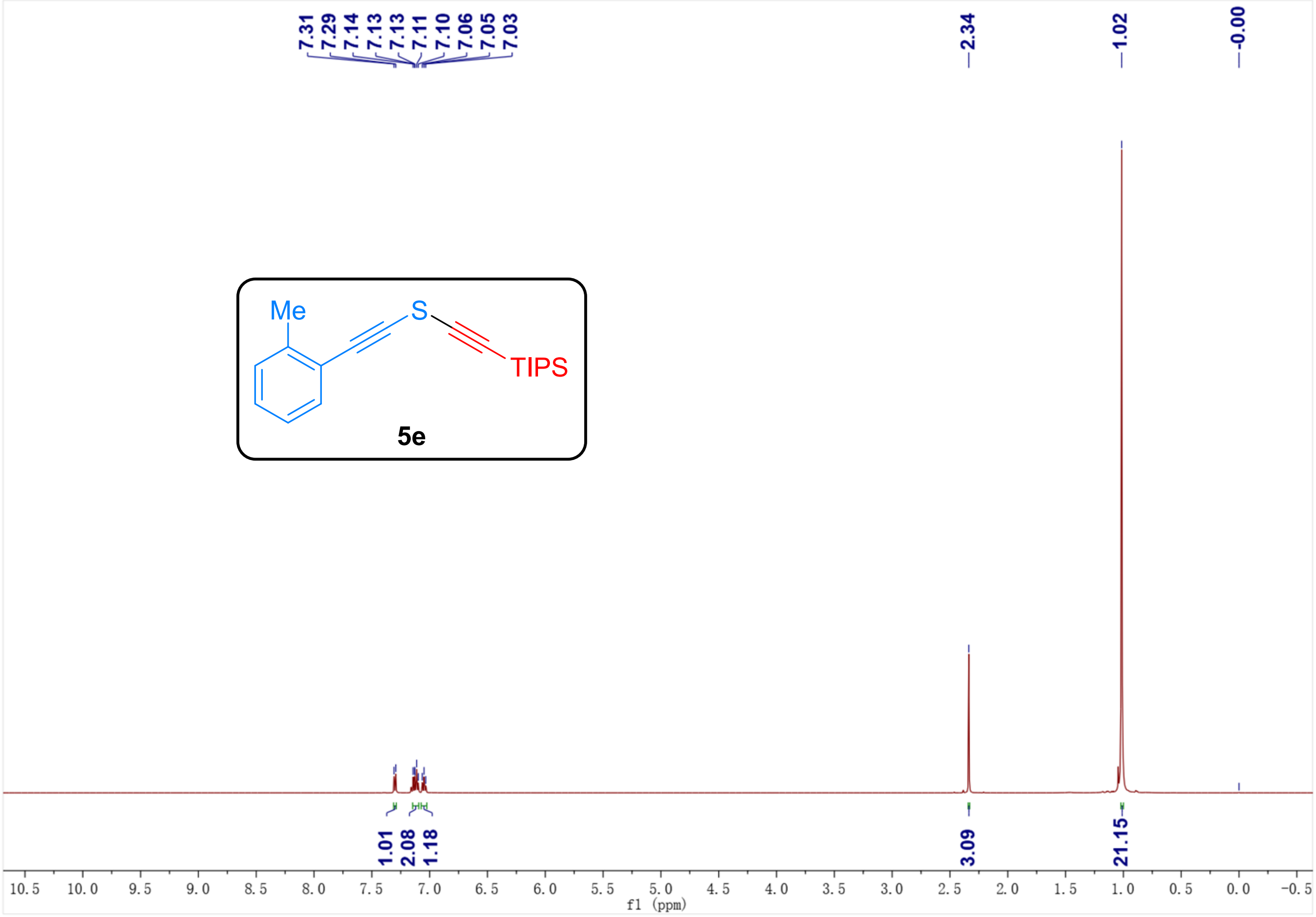
f1 (ppm)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7.06
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7.03
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-0.00
Me
S
TIPS
5e
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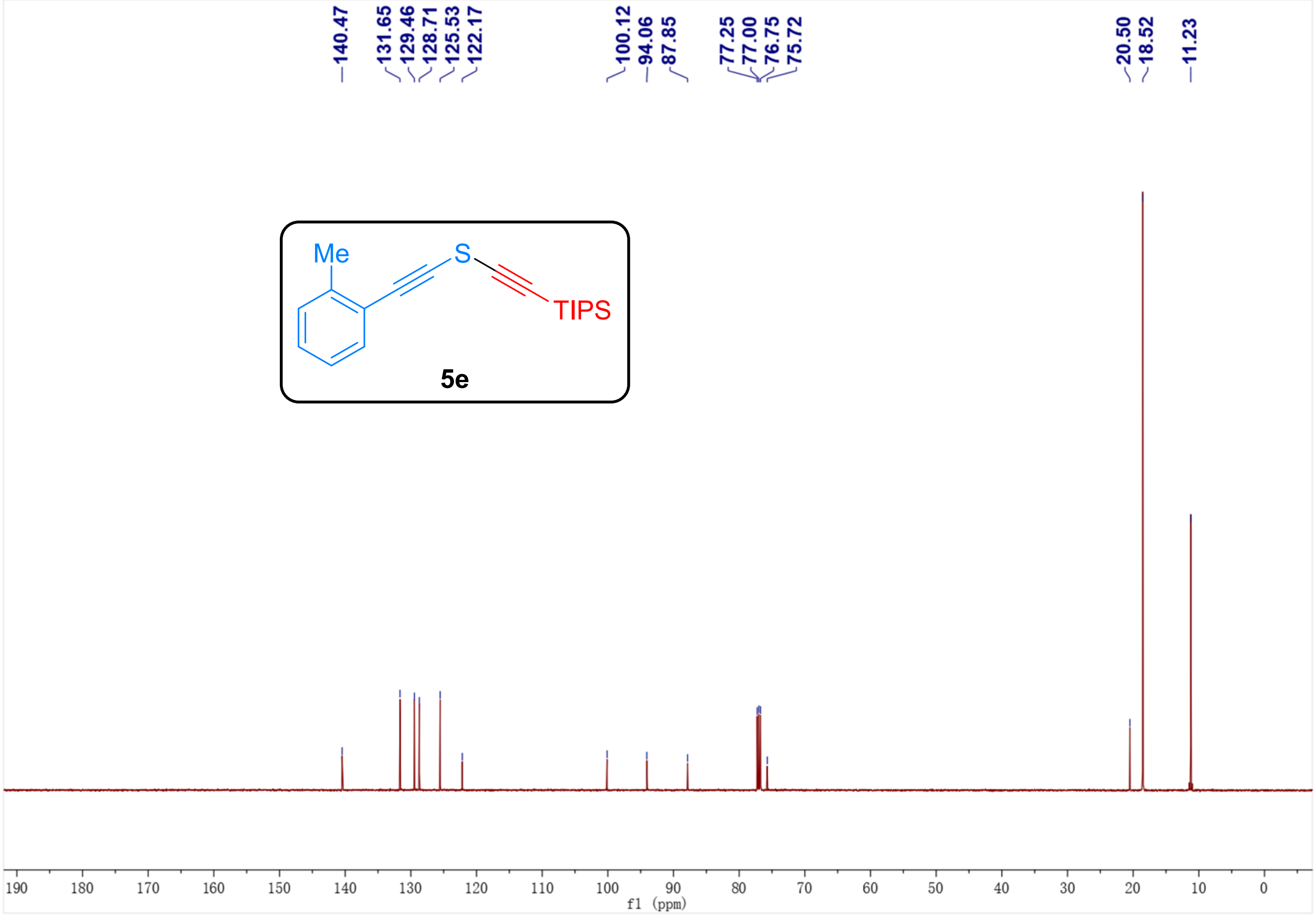
2.08
1.18
3.09
21.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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Me
S
TIPS
5e
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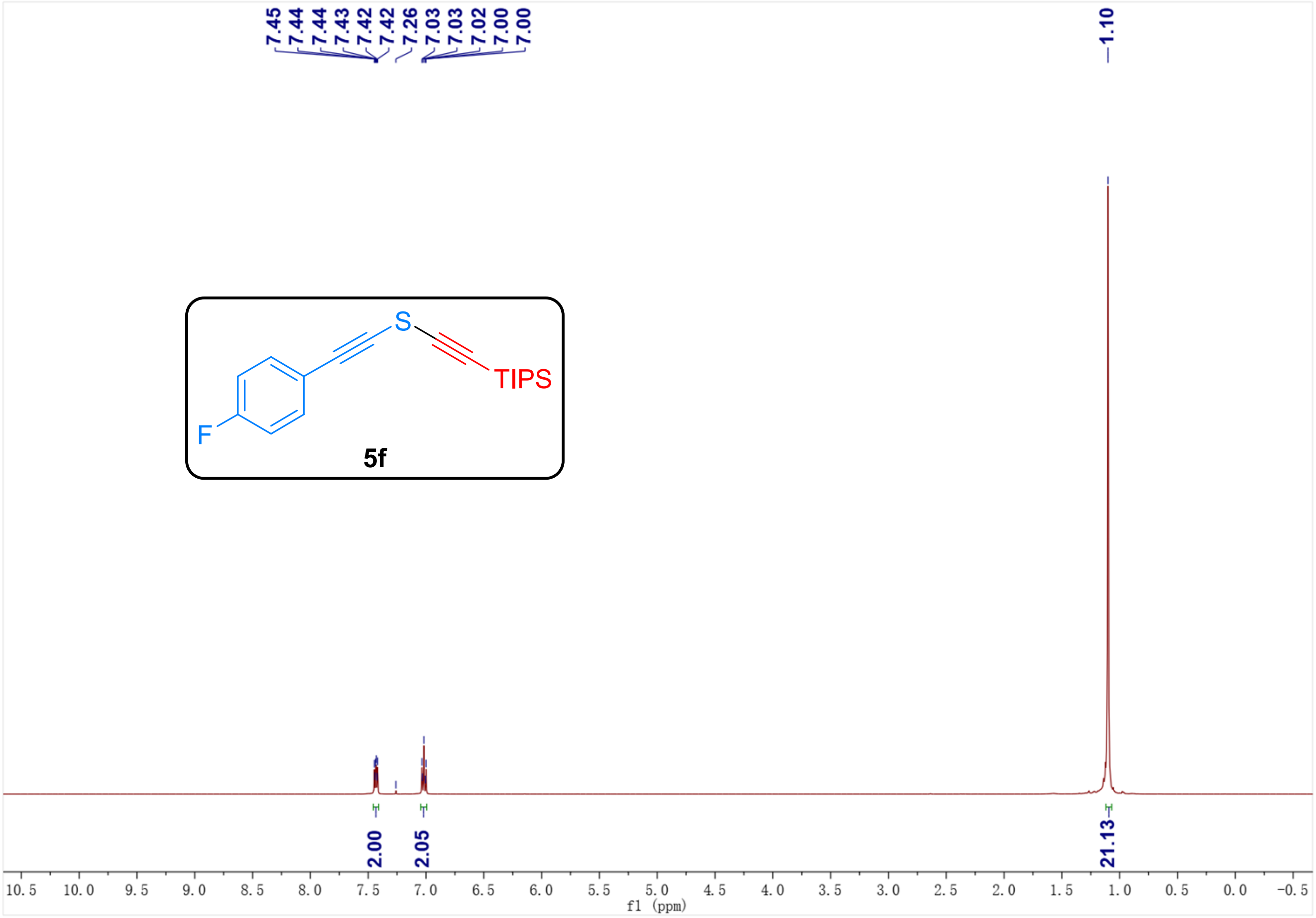
f1 (ppm)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7.00
1.10
S
TIPS
F
5f
2.00
2.05
21.13
10.5
10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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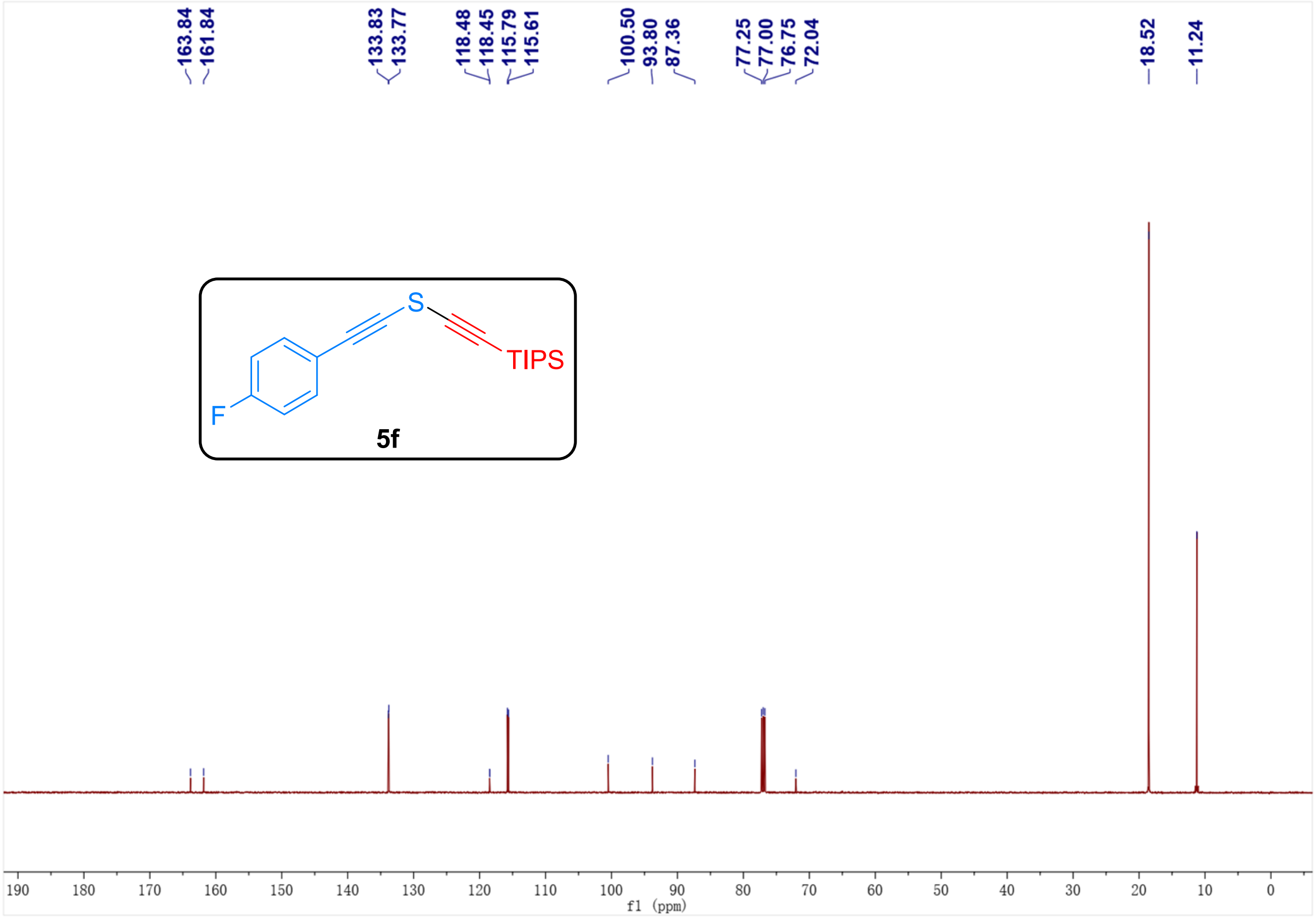
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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76.75
72.04
18.52
11.24
S
TIPS
F
5f
190
180
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100
90
80
70
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40
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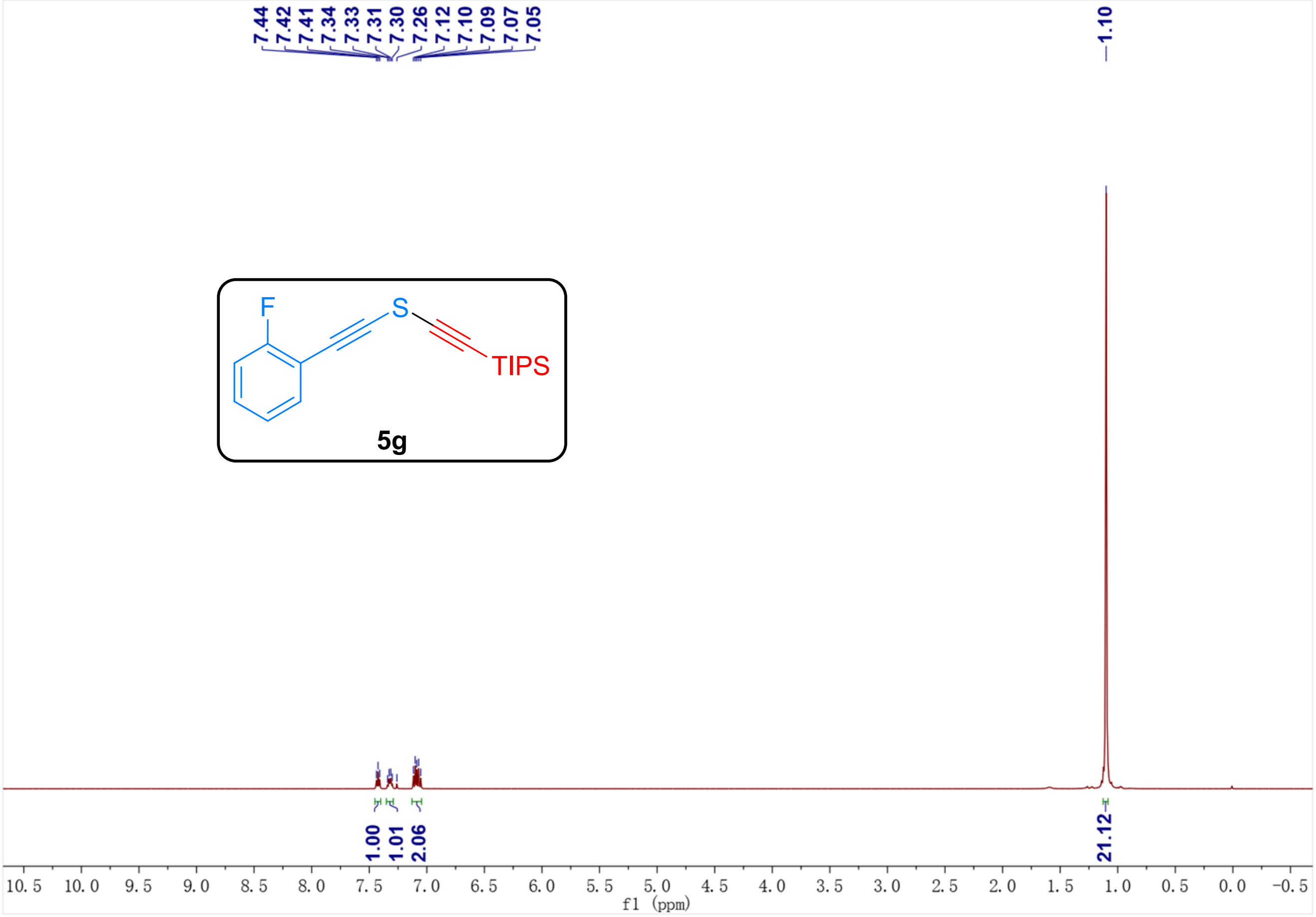
20
10
0
f1 (ppm)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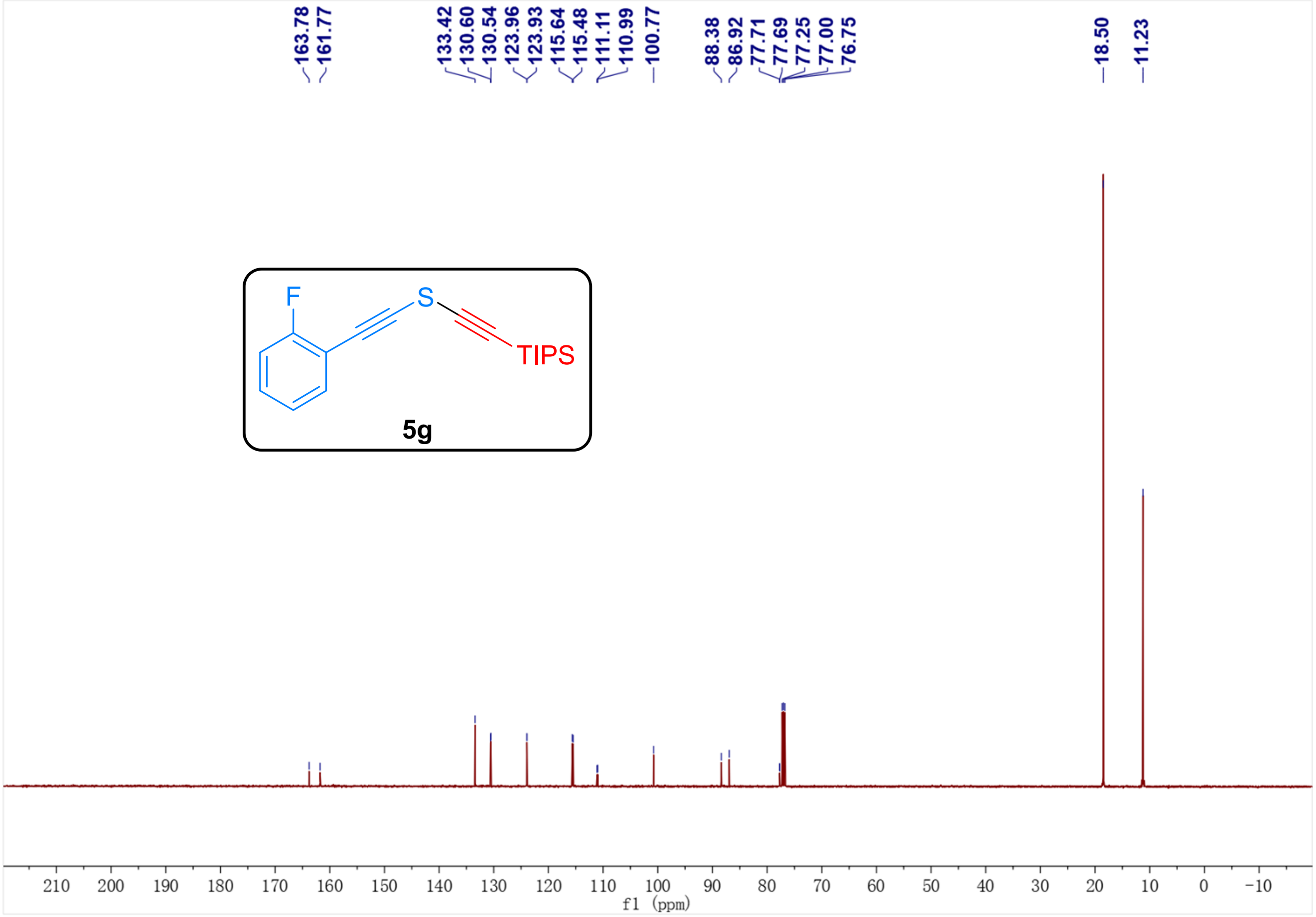
7.10
7.09
7.07
7.05
1.10
F
S
TIPS
5g
1.00
1.01
2.06
21.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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88.38
86.92
77.71
77.69
77.25
77.00
76.75
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F
S
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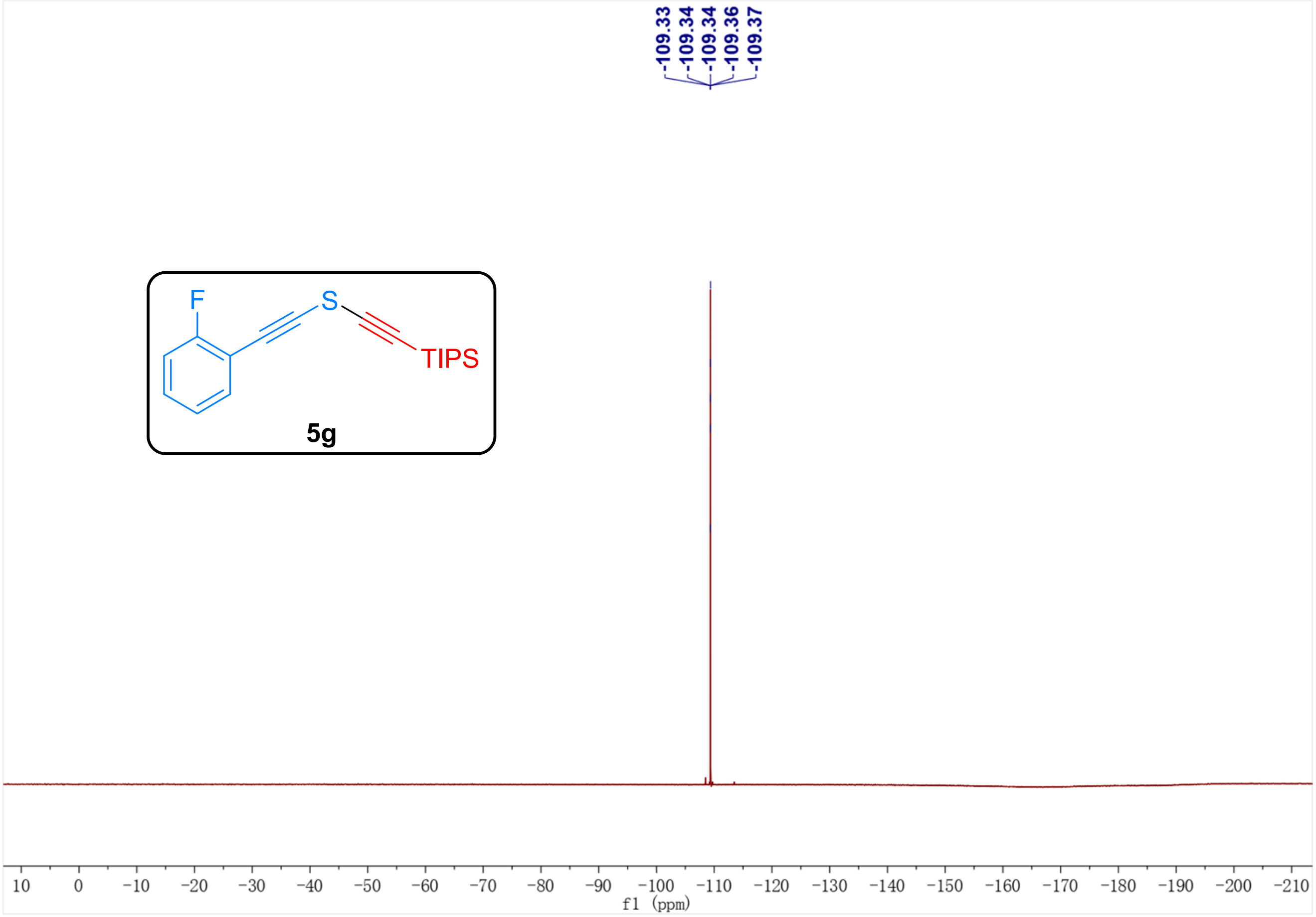
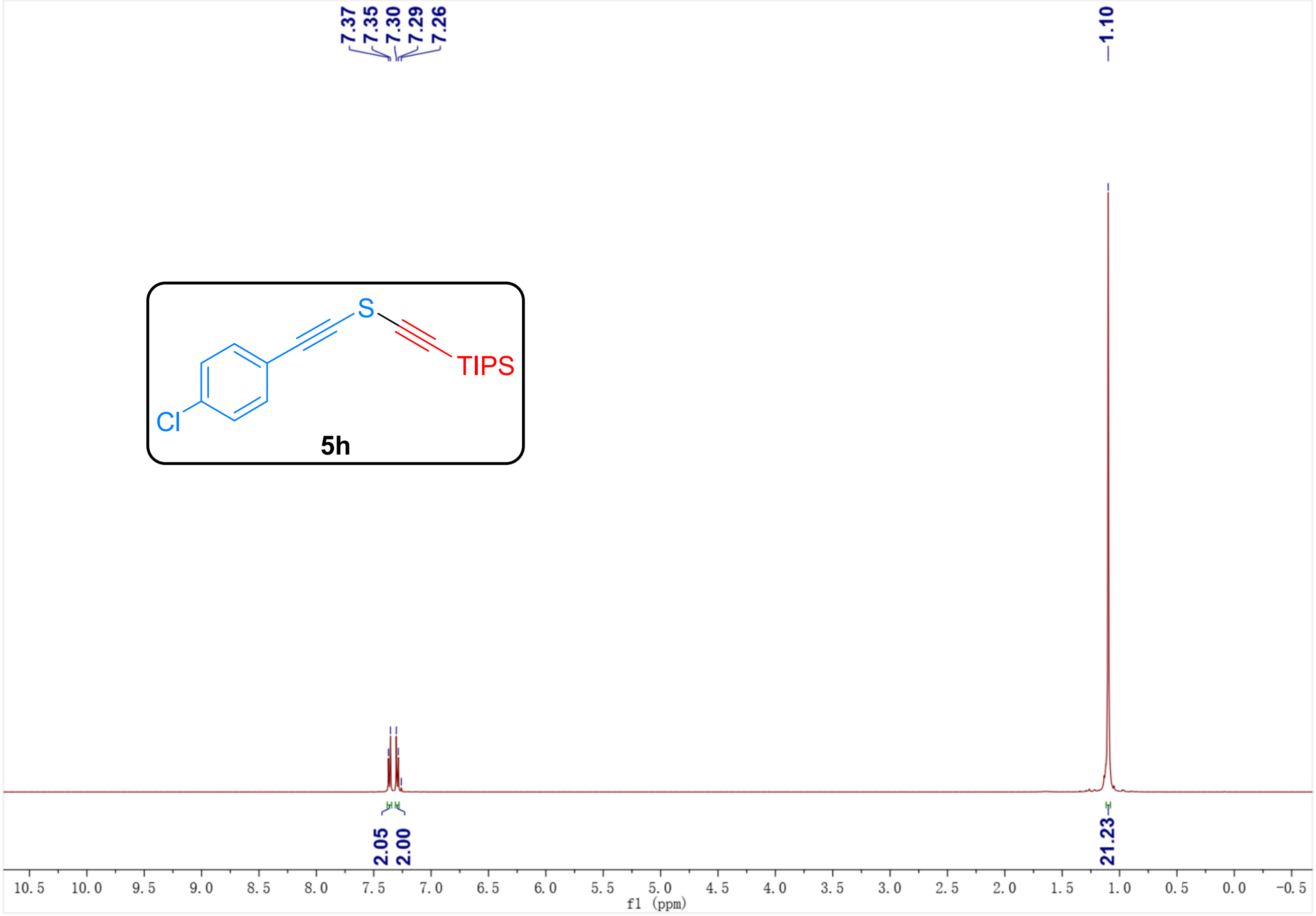
5g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-109.33
-109.34
-109.34
-109.36
-109.37
F
S
TIPS
5g
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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S
TIPS
Cl
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2.00
21.23
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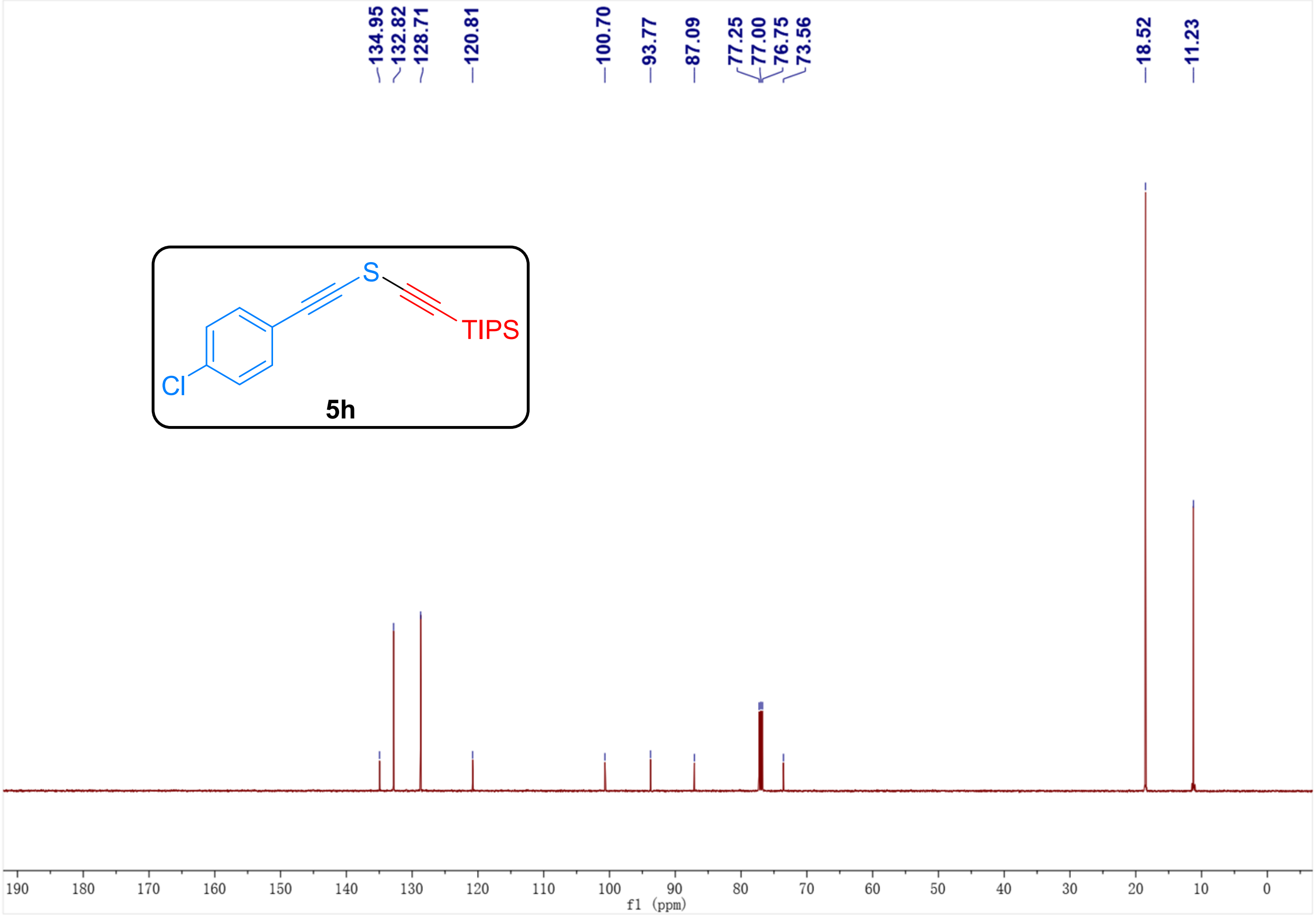
f1 (ppm)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77.00
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11.23
S
TIPS
Cl
5h
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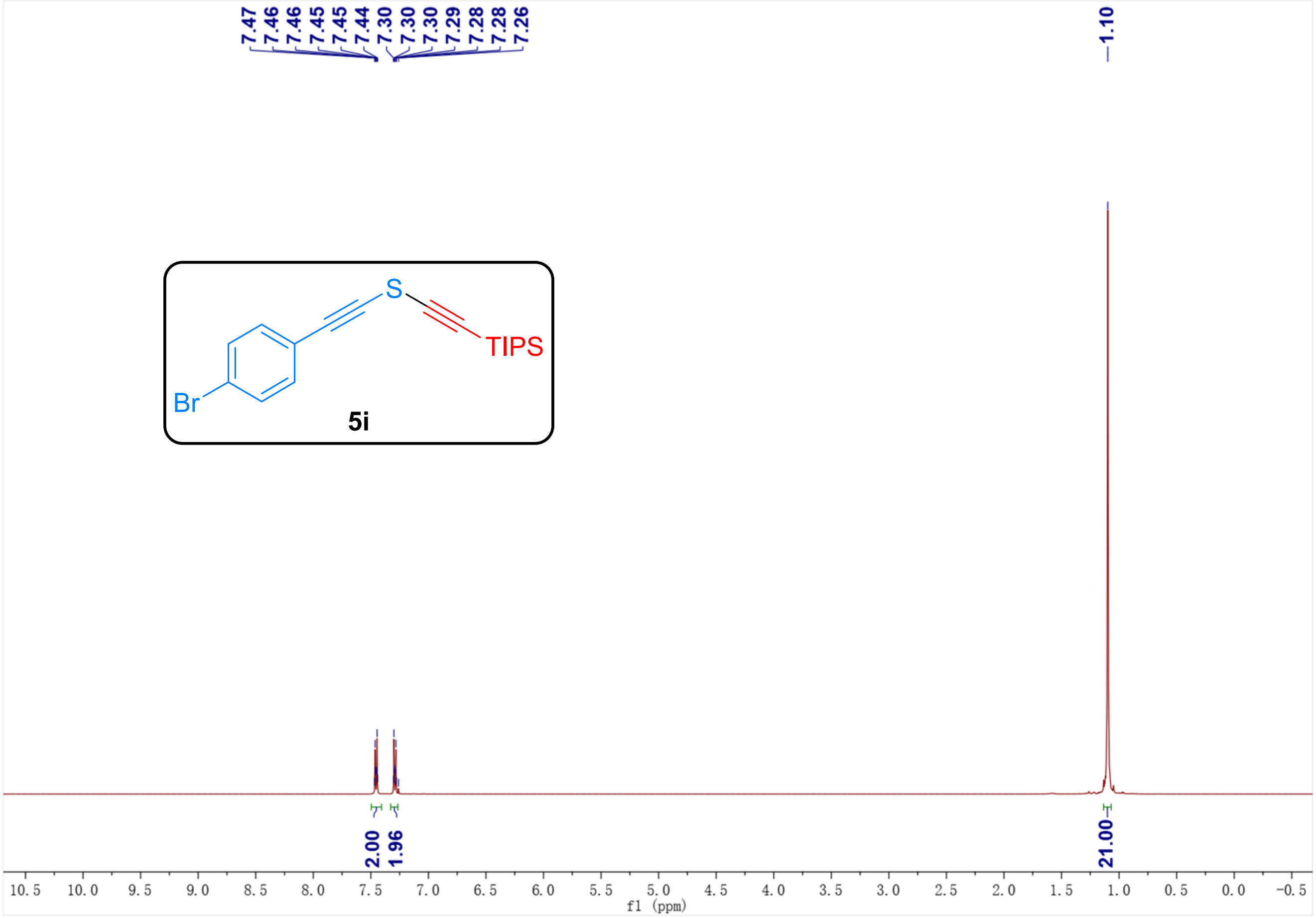
f1 (ppm)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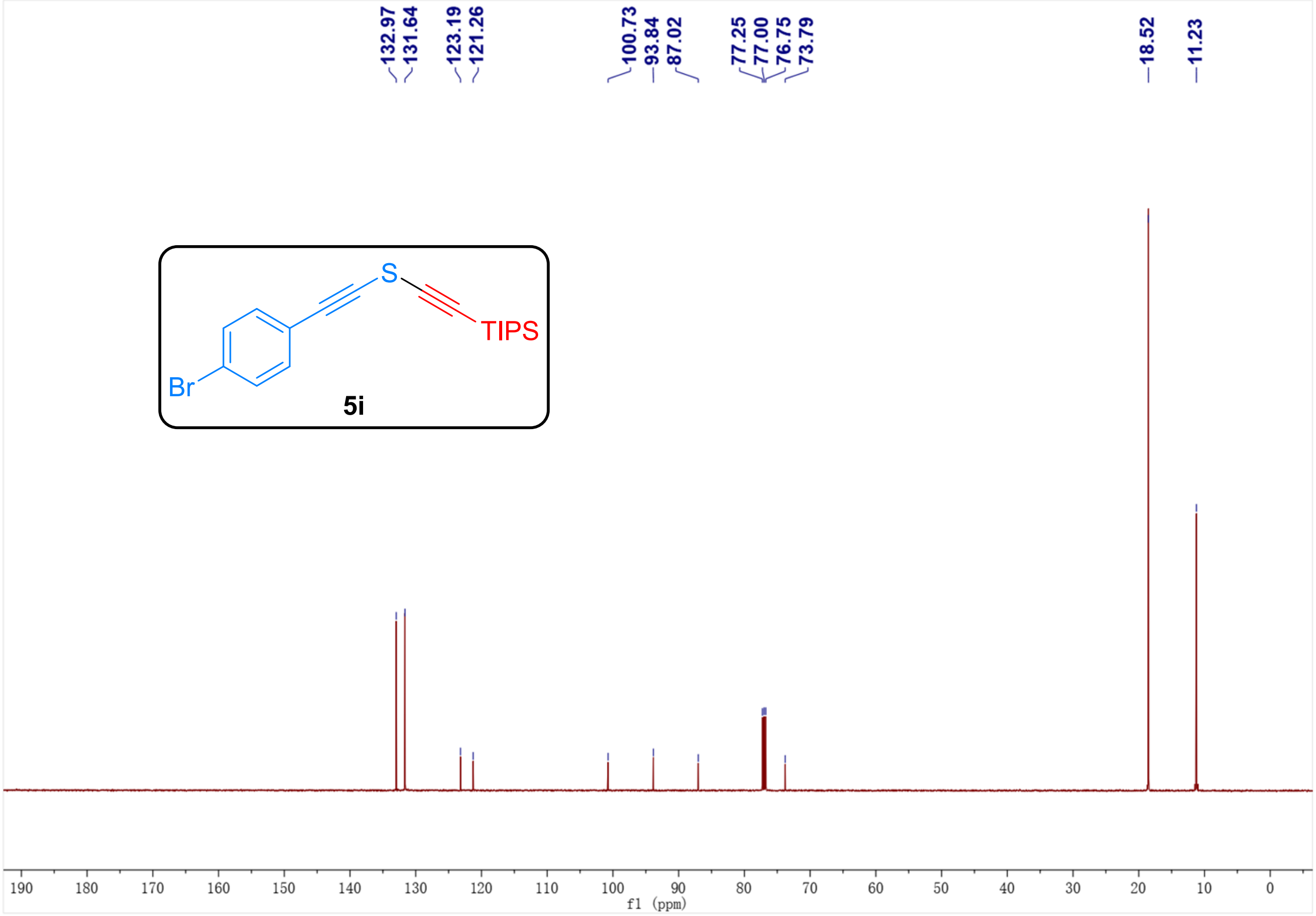
7.26
1.10
S
TIPS
Br
5i
2.00
1.96
21.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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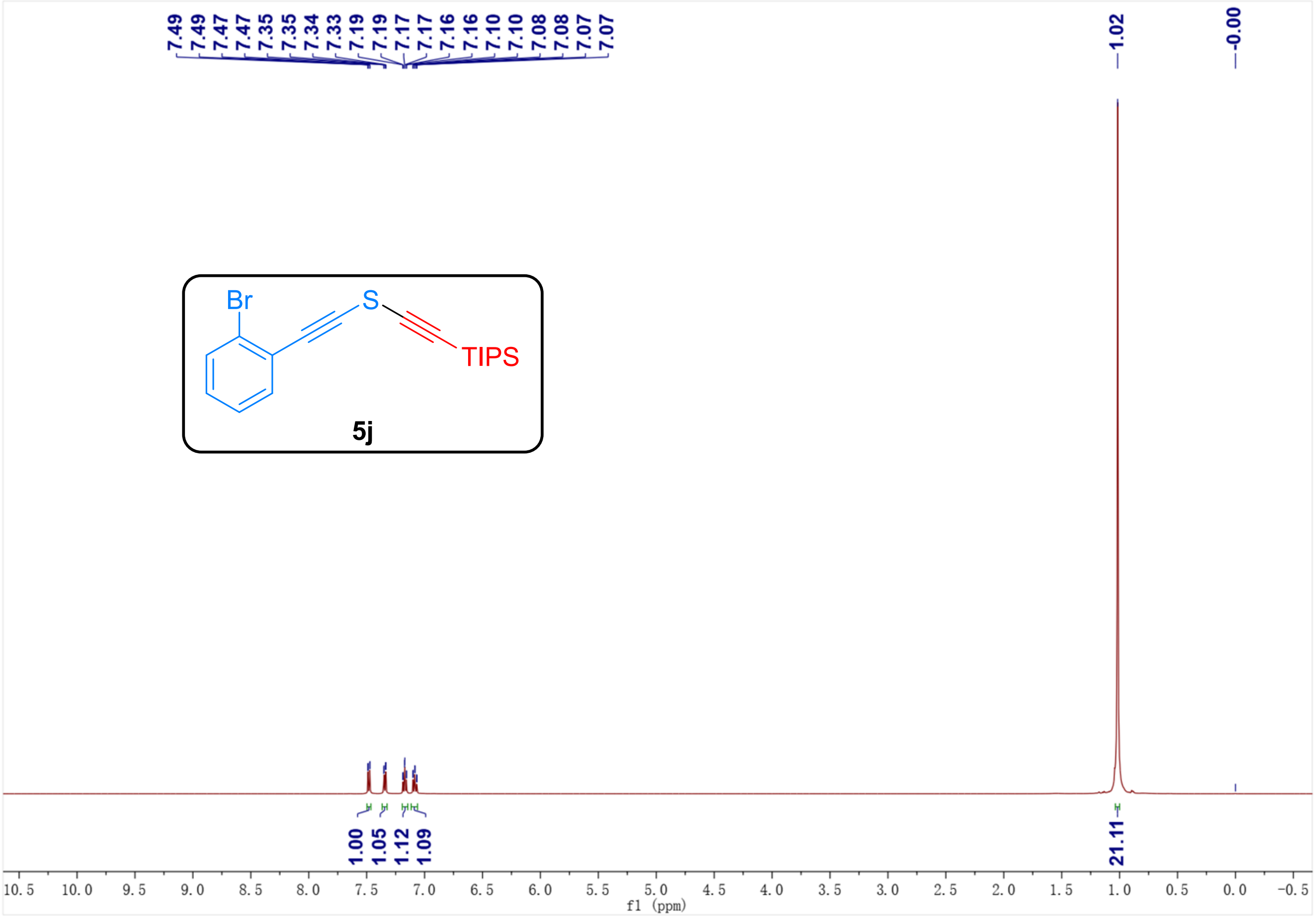
76.75
73.79
18.52
11.23
Br
S
TIPS
5i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.10
7.08
7.08
7.07
7.07
1.02
-0.00
Br
S
TIPS
5j
1.00
1.05
1.12
1.09
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6.5
6.0
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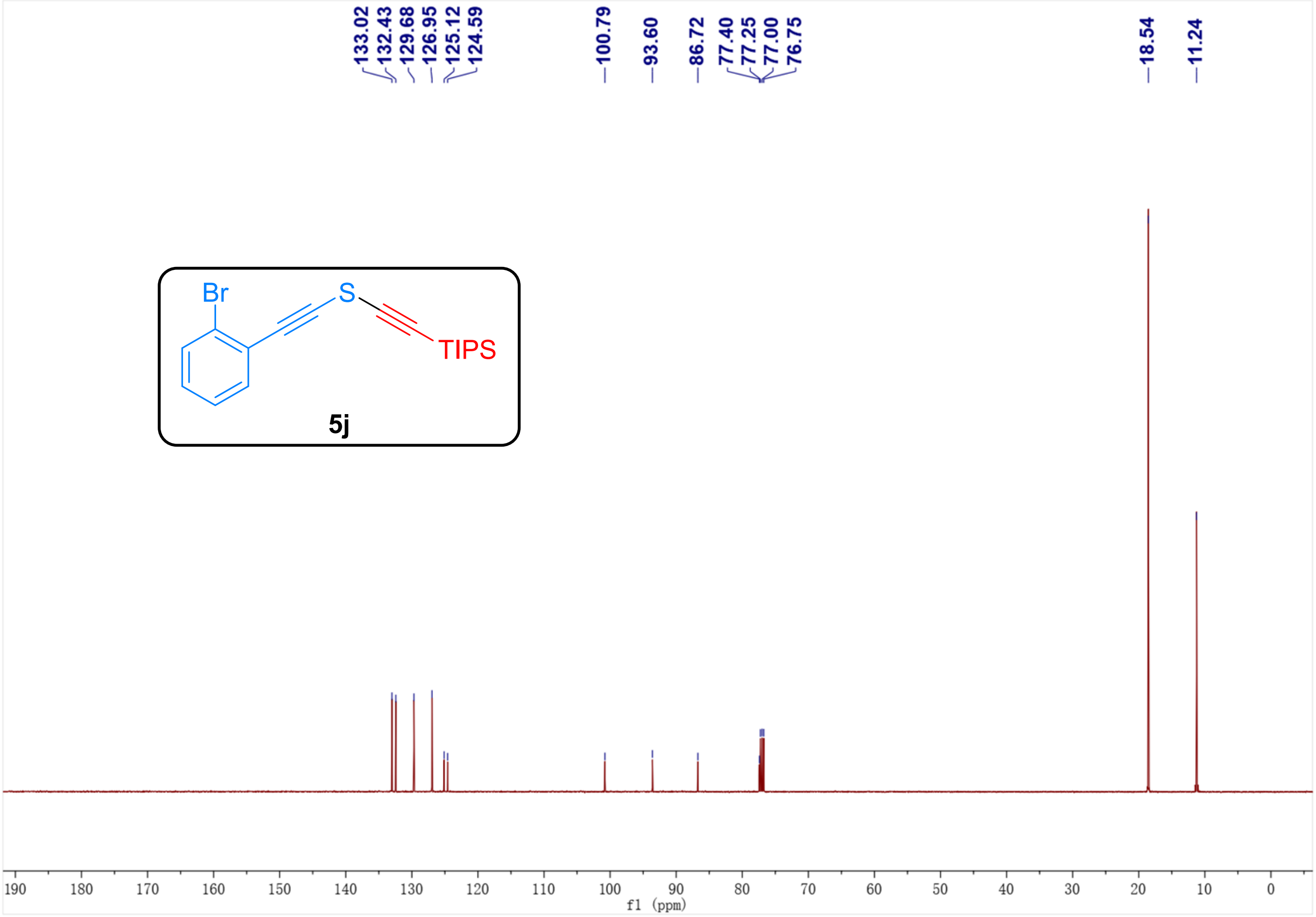
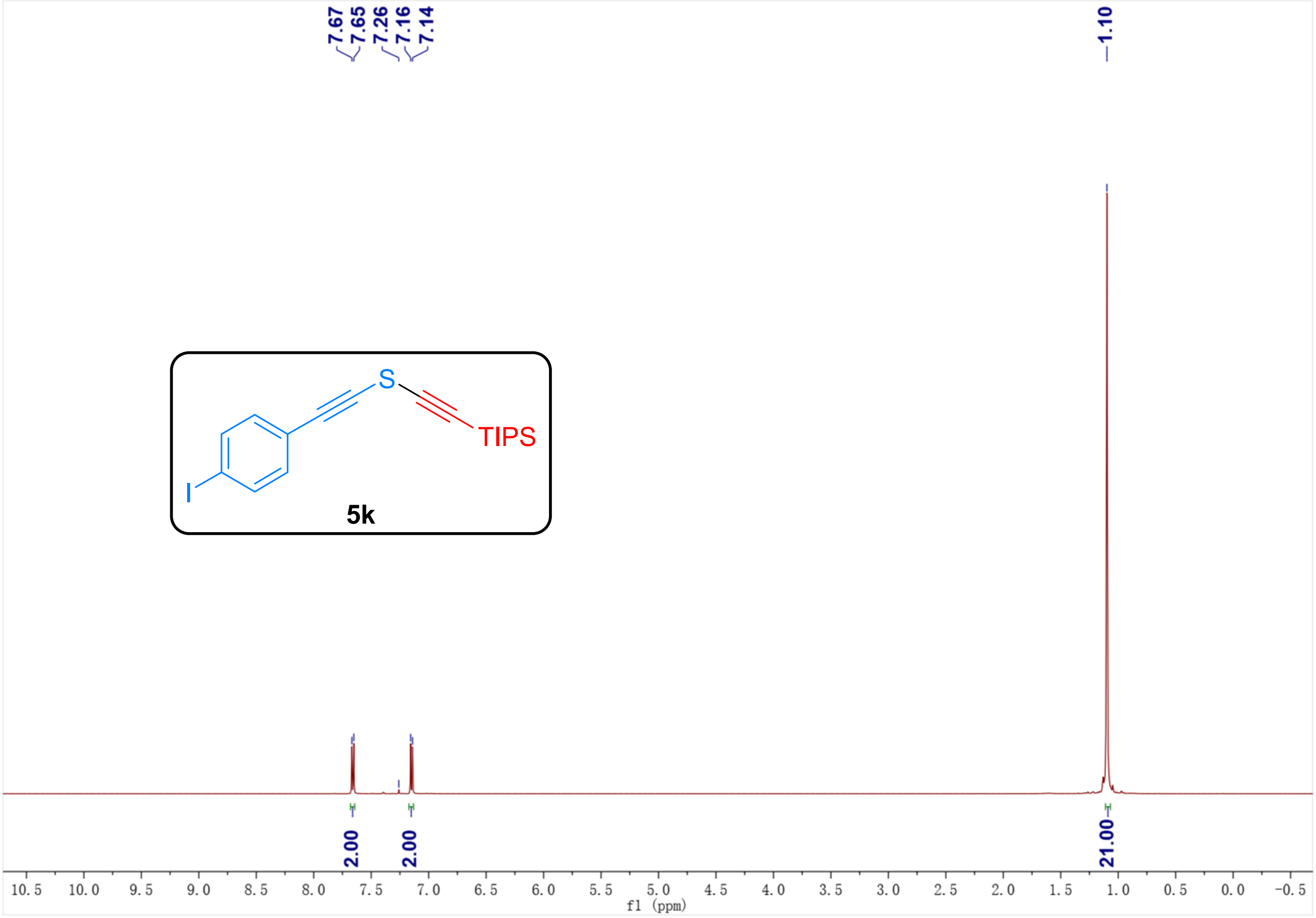
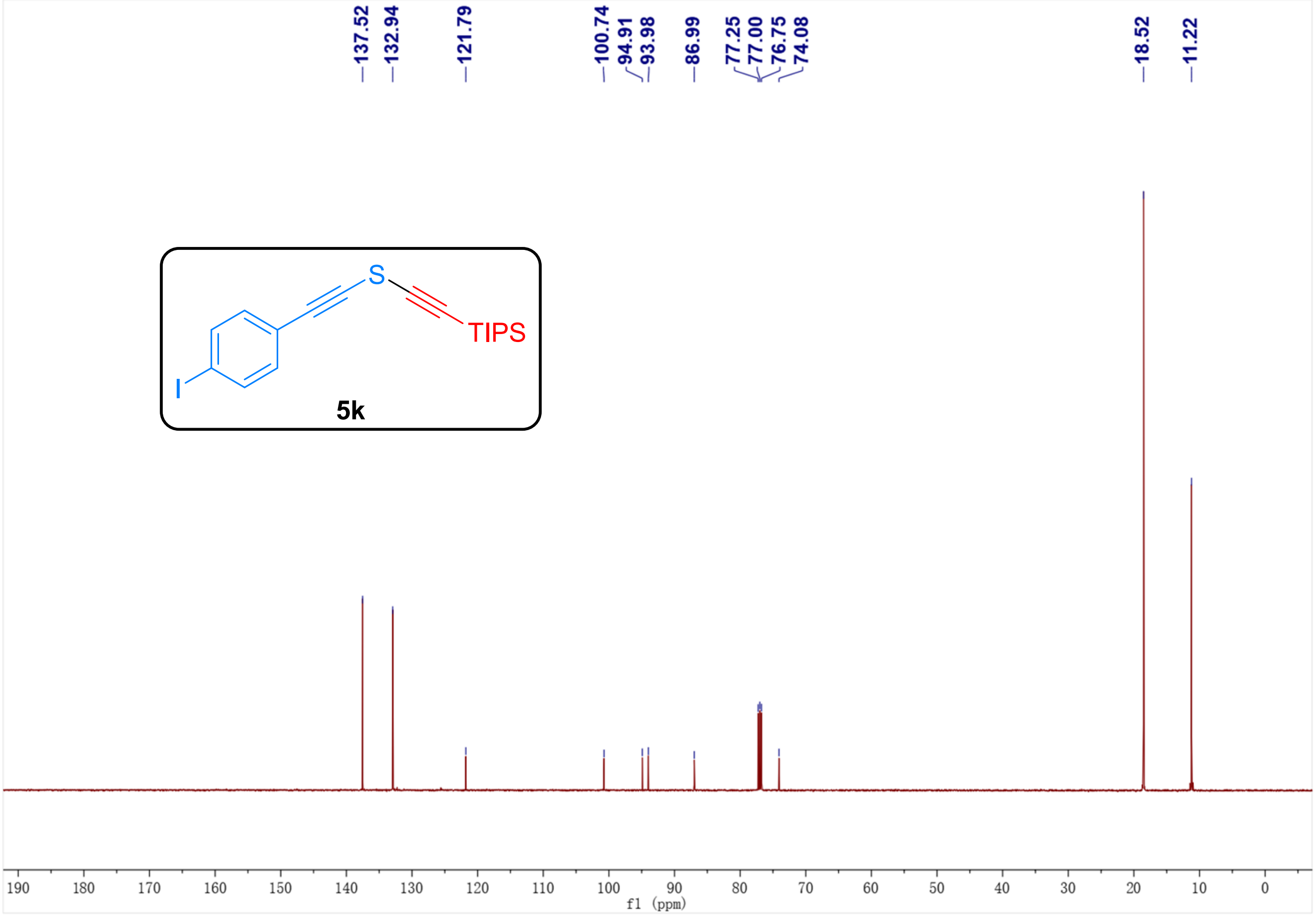
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

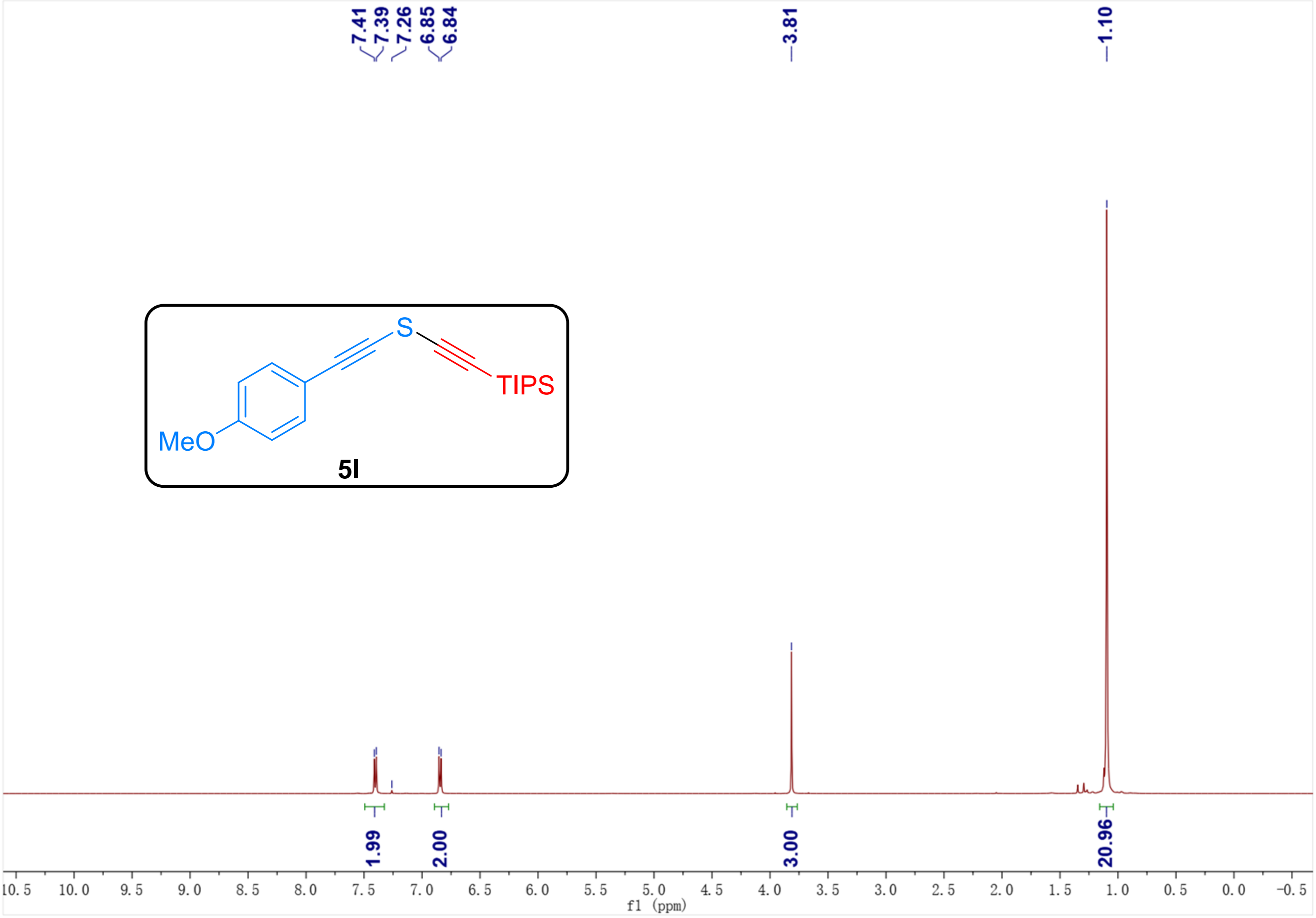

5j
133.02
132.43
129.68
126.95
125.12
124.59
100.79
93.60
86.72
77.40
77.25
77.00
76.75
18.54
11.24
Br
S
TIPS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5k
7.67
7.65
7.26
7.16
7.14
1.10
S
TIPS
I
2.00
2.00
21.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



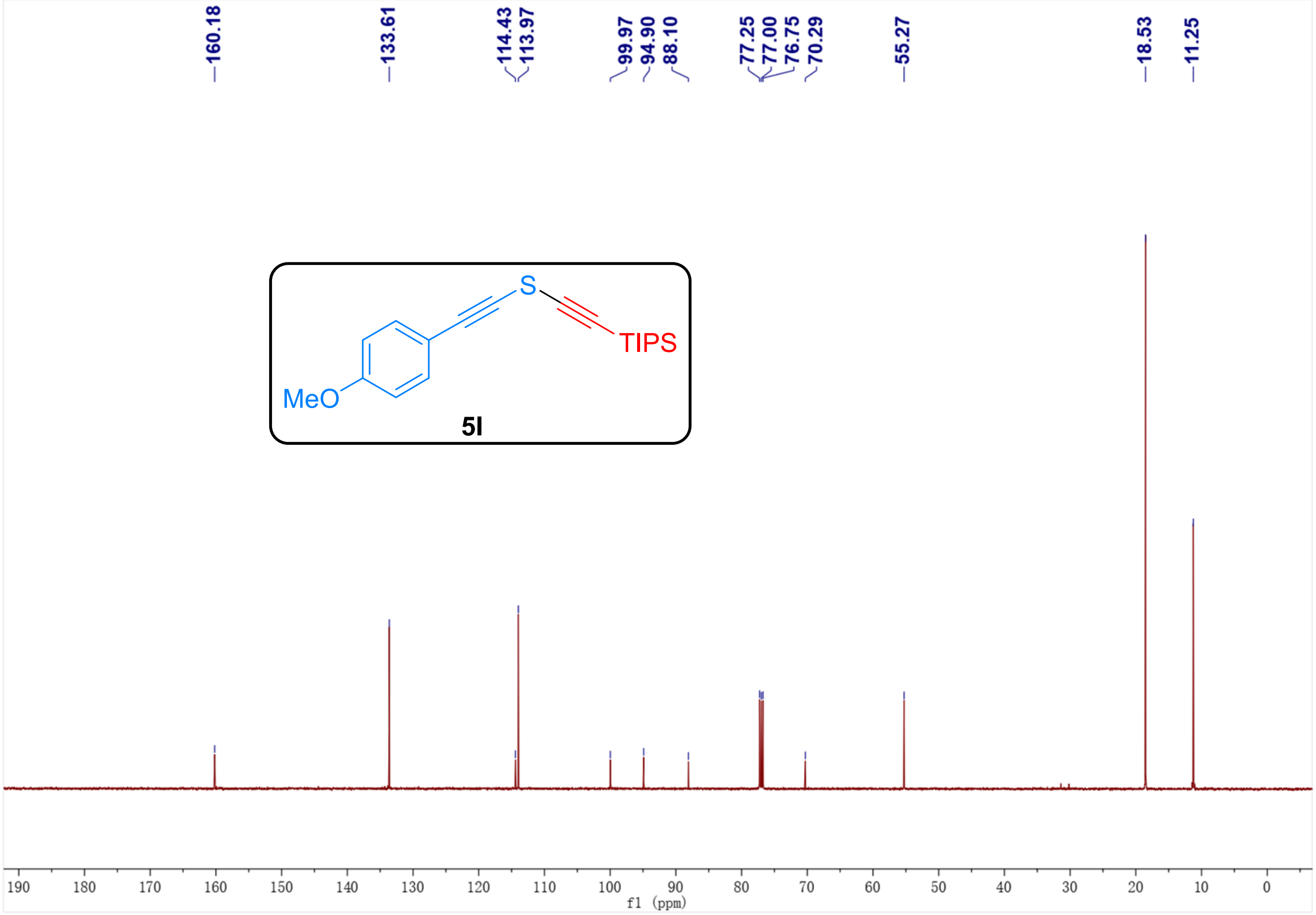
5k

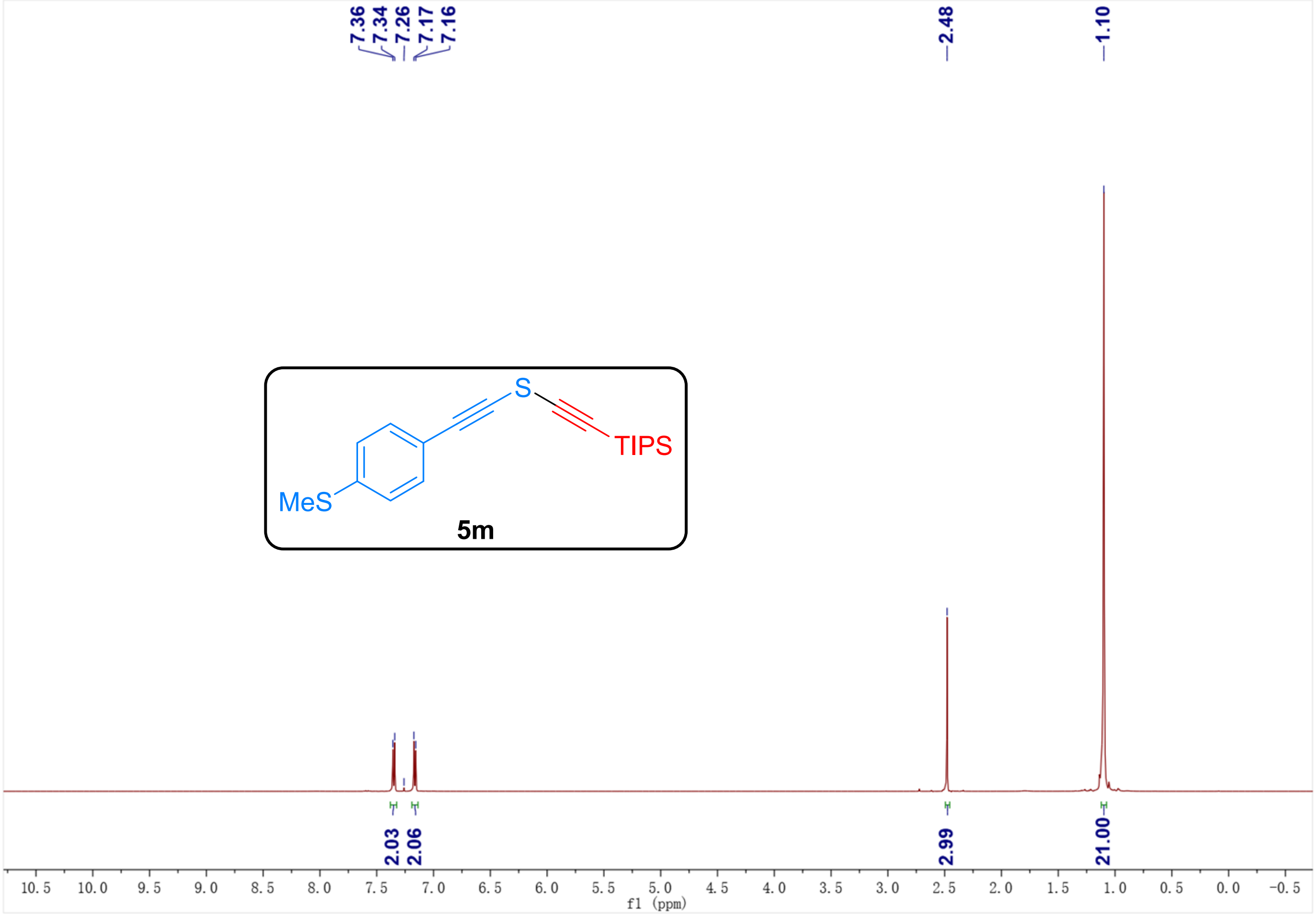
137.52
132.94
121.79
100.74
94.91
93.98
86.99
77.25
77.00
76.75
74.08
18.52
11.22
S
TIPS
I
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

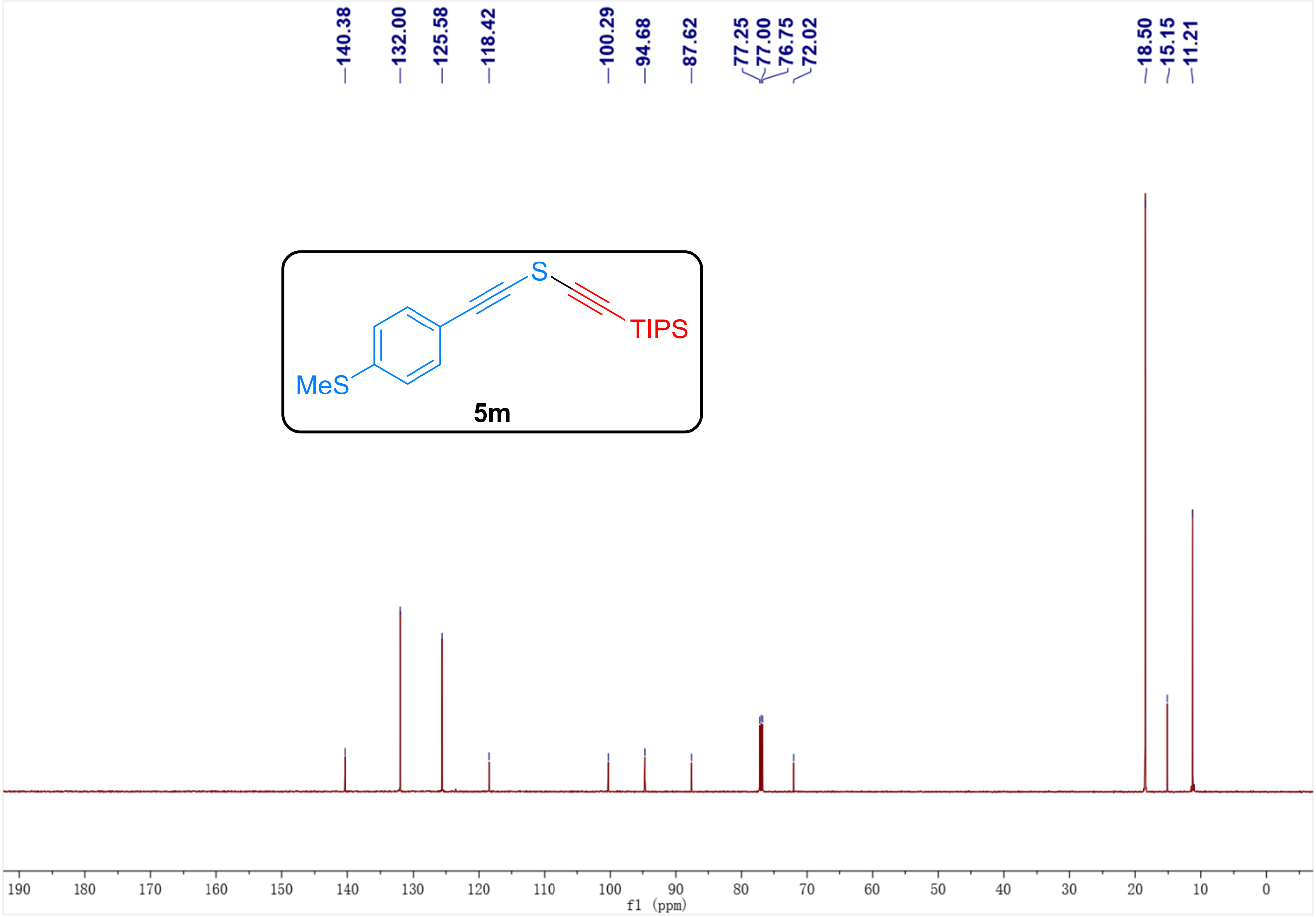


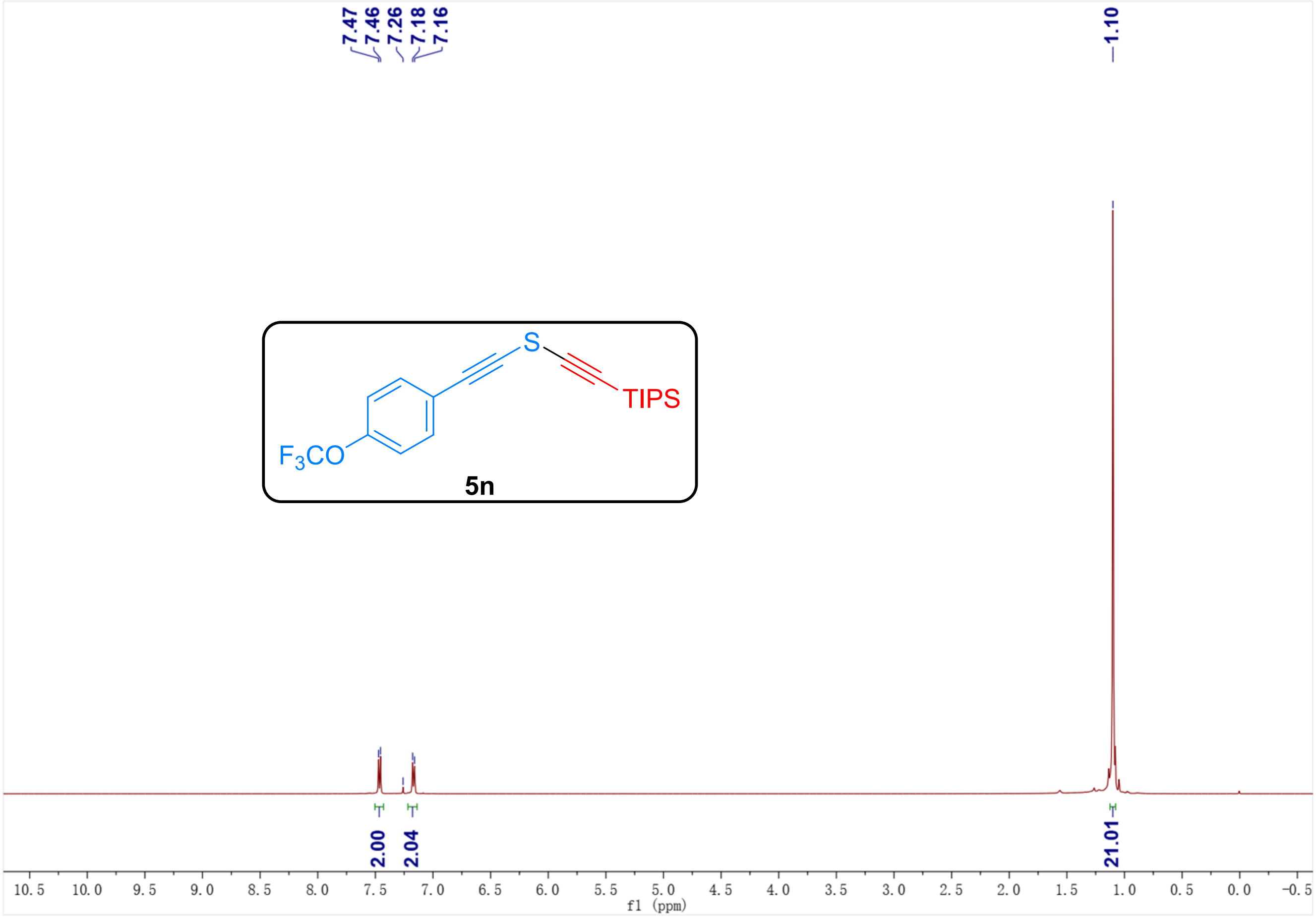
5l

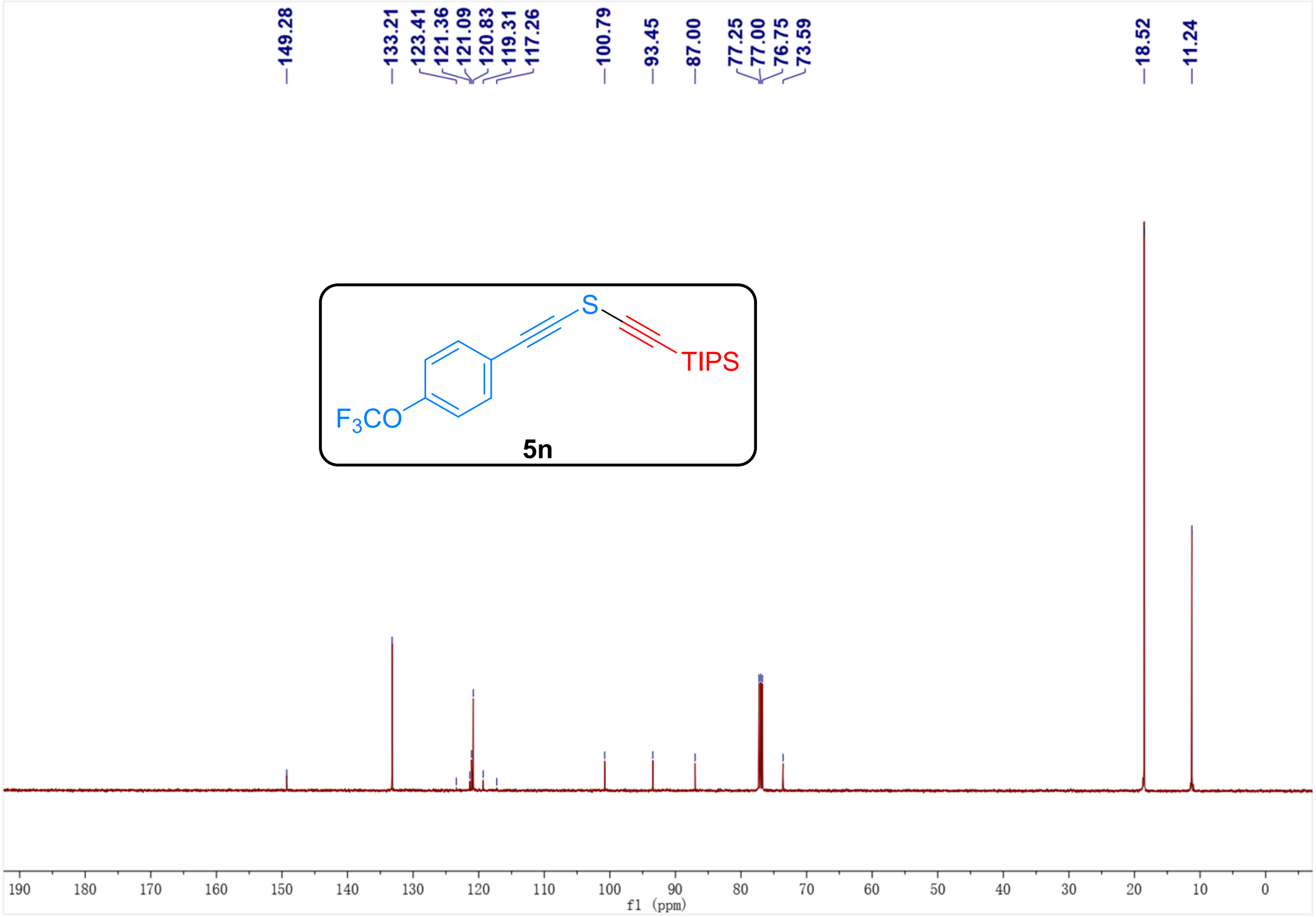
7.41
7.39
7.26
6.85
6.84
3.81
1.10
S
TIPS
MeO
1.99
2.00
3.00
20.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

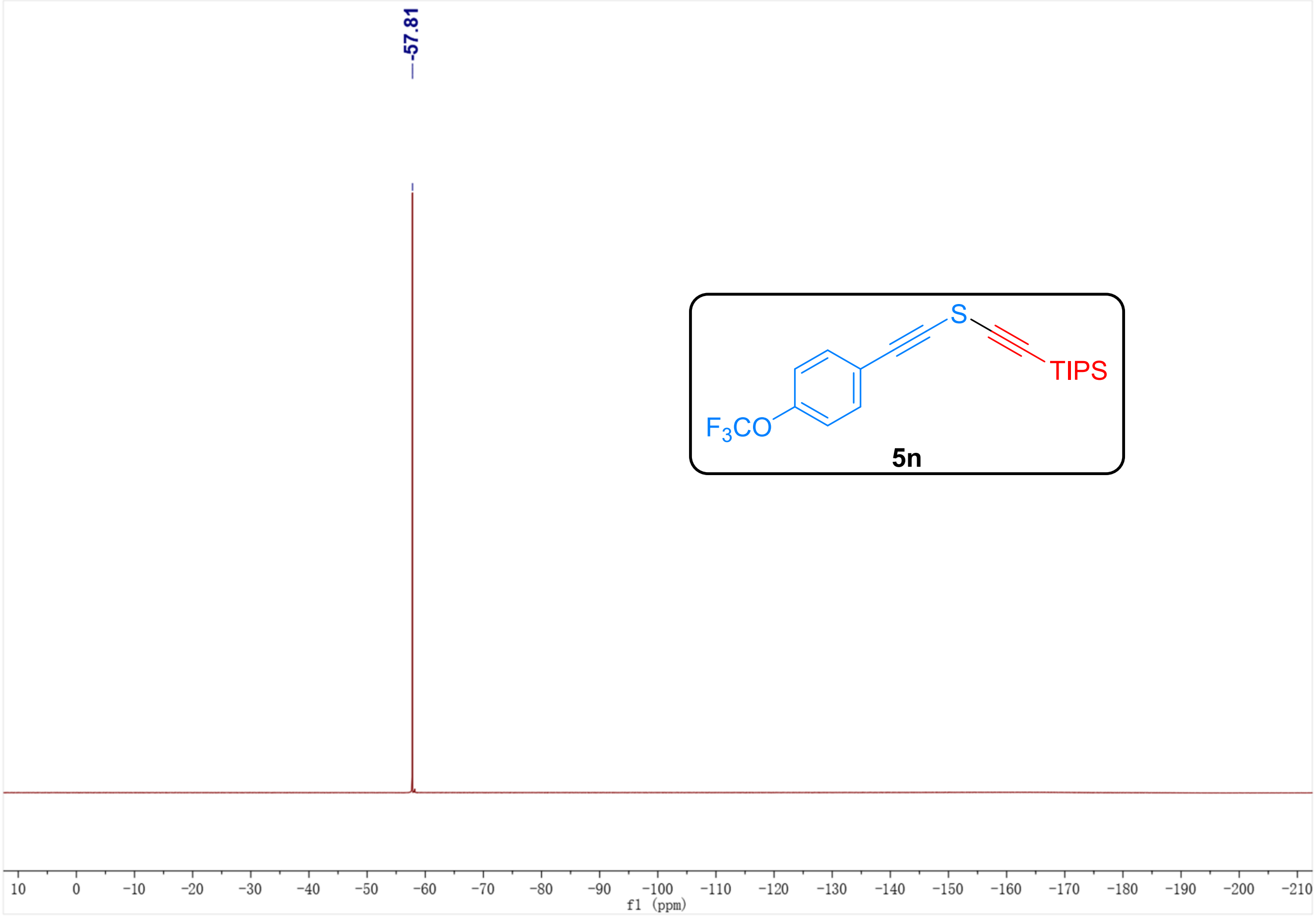

160.18
133.61
114.43
113.97
99.97
94.90
88.10
77.25
77.00
76.75
70.29
55.27
18.53
11.25
MeO
S
TIPS
5l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

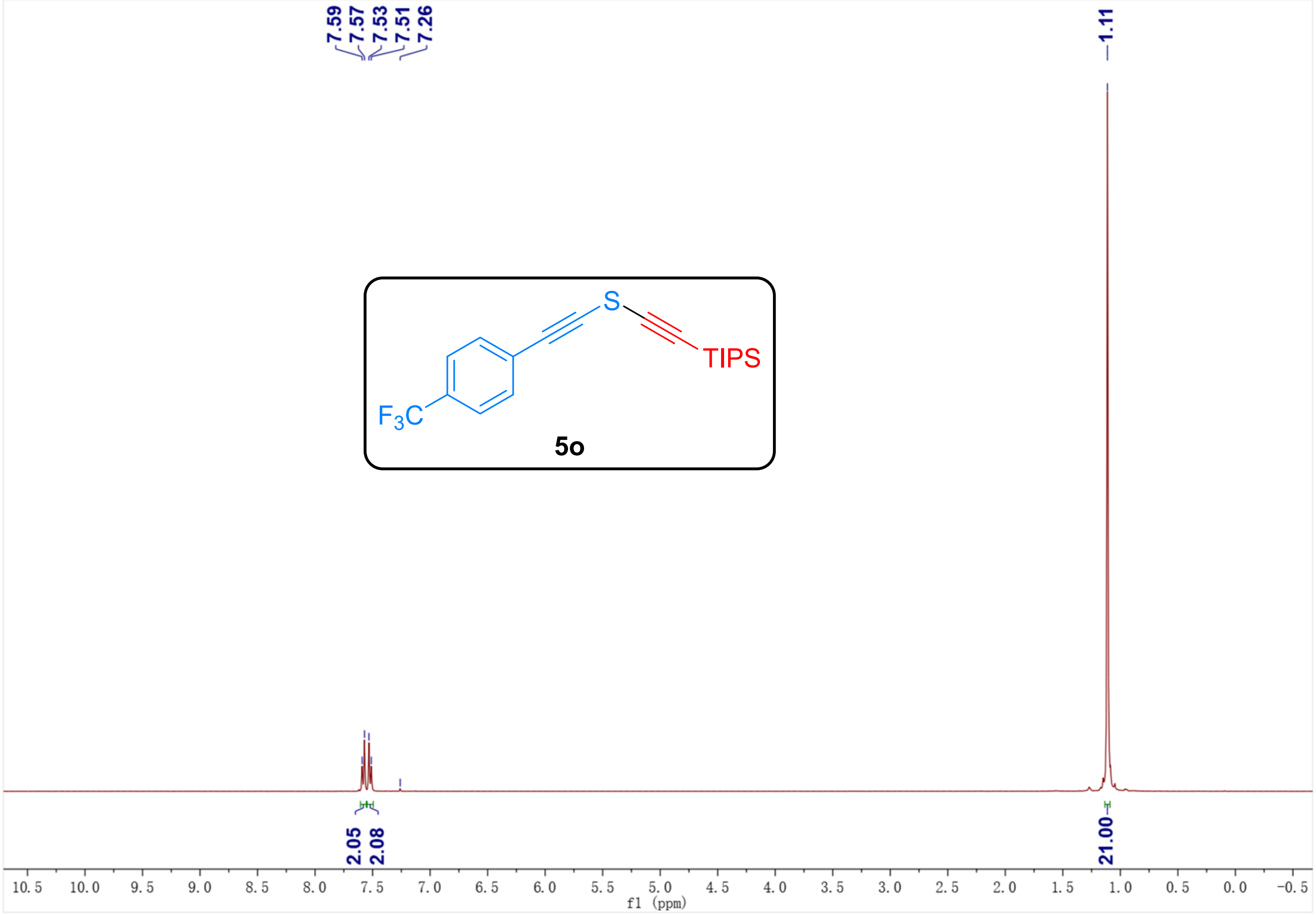

7.36
7.34
7.26
7.17
7.16
2.48
1.10
MeS
S
TIPS
5m
2.03
2.06
2.99
21.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

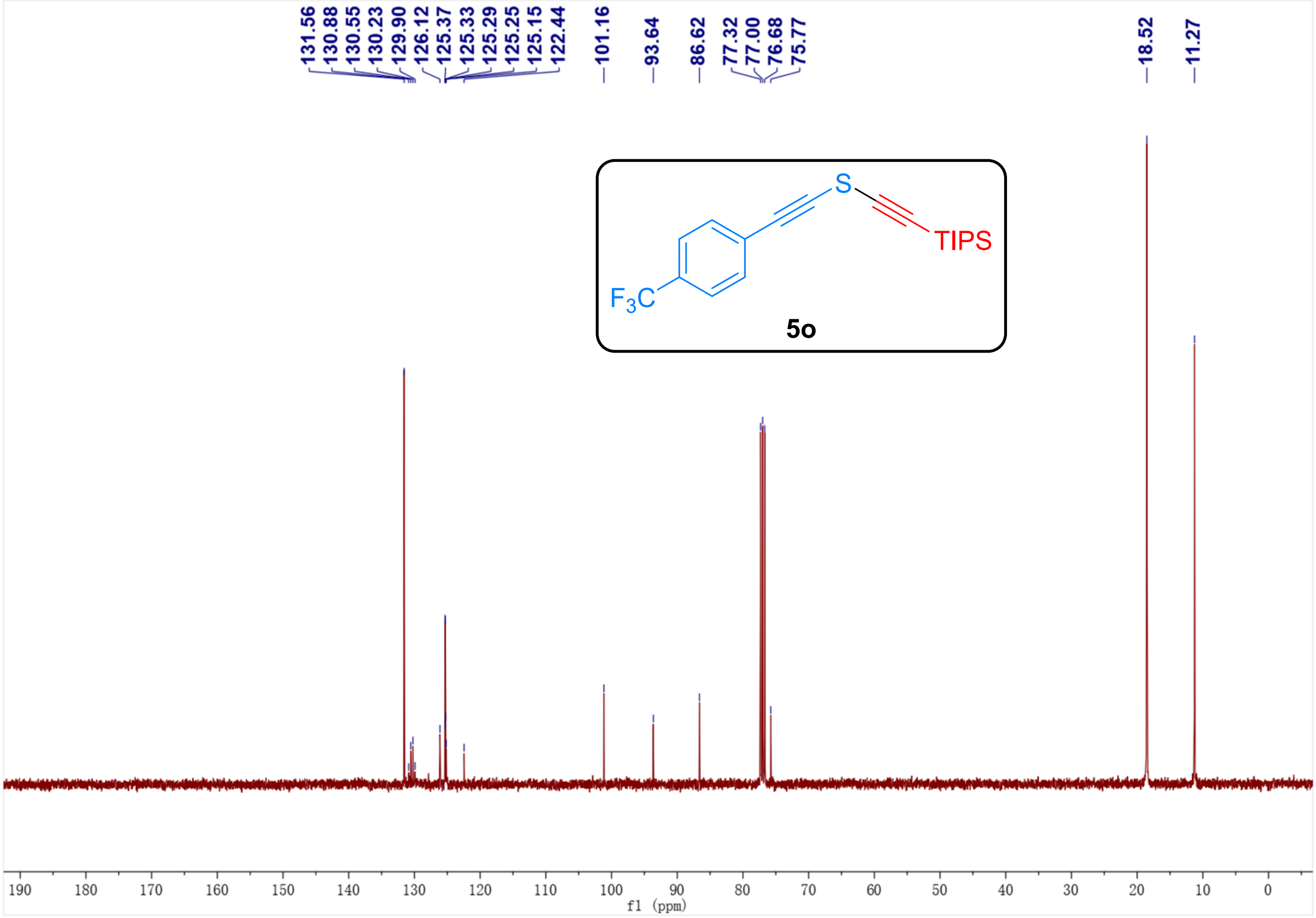

140.38
132.00
125.58
118.42
100.29
94.68
87.62
77.25
77.00
76.75
72.02
18.50
15.15
11.21
S
TIPS
MeS
5m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

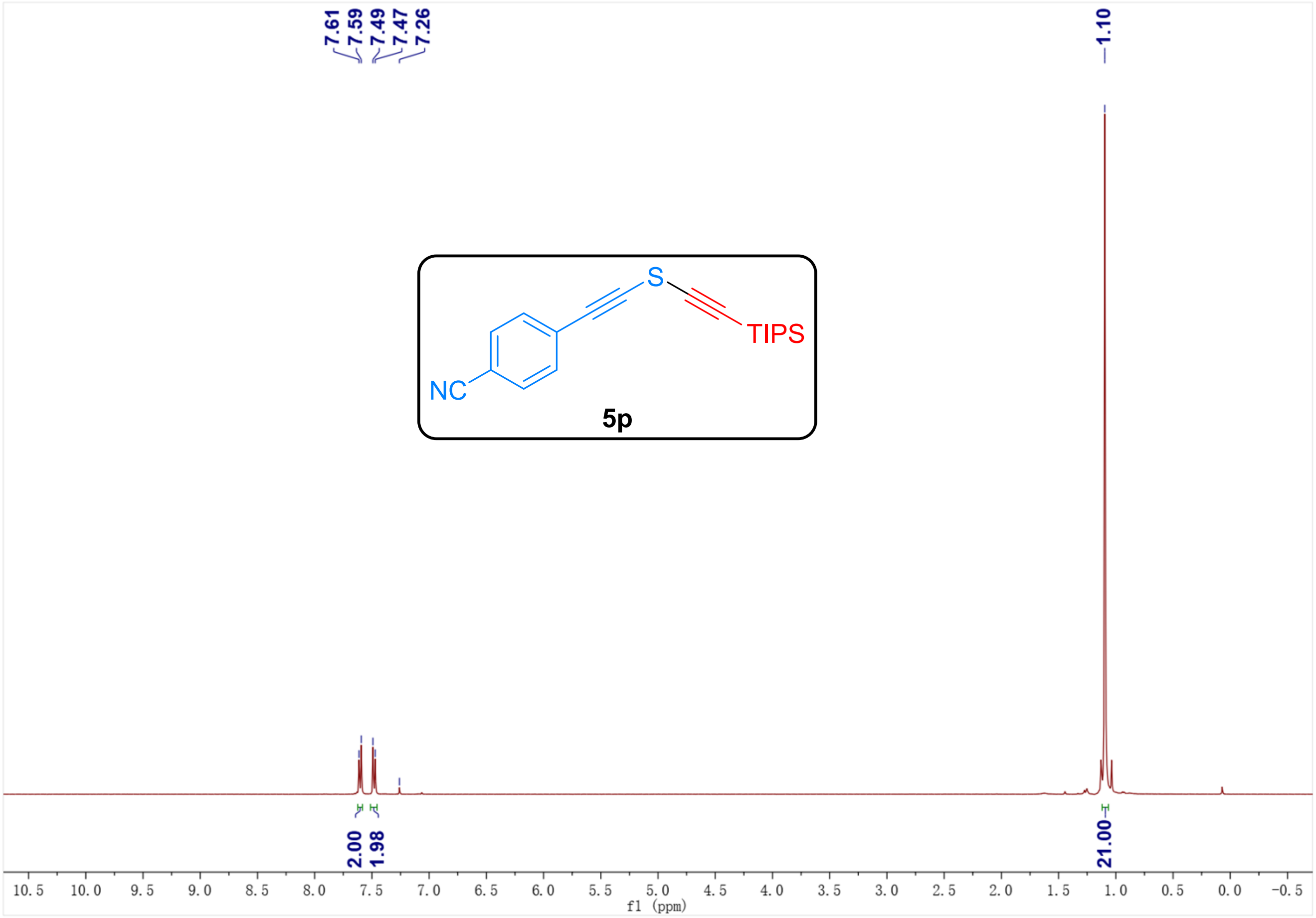

7.47
7.46
7.26
7.18
7.16
1.10
S
TIPS
F3CO
5n
2.00
2.04
21.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

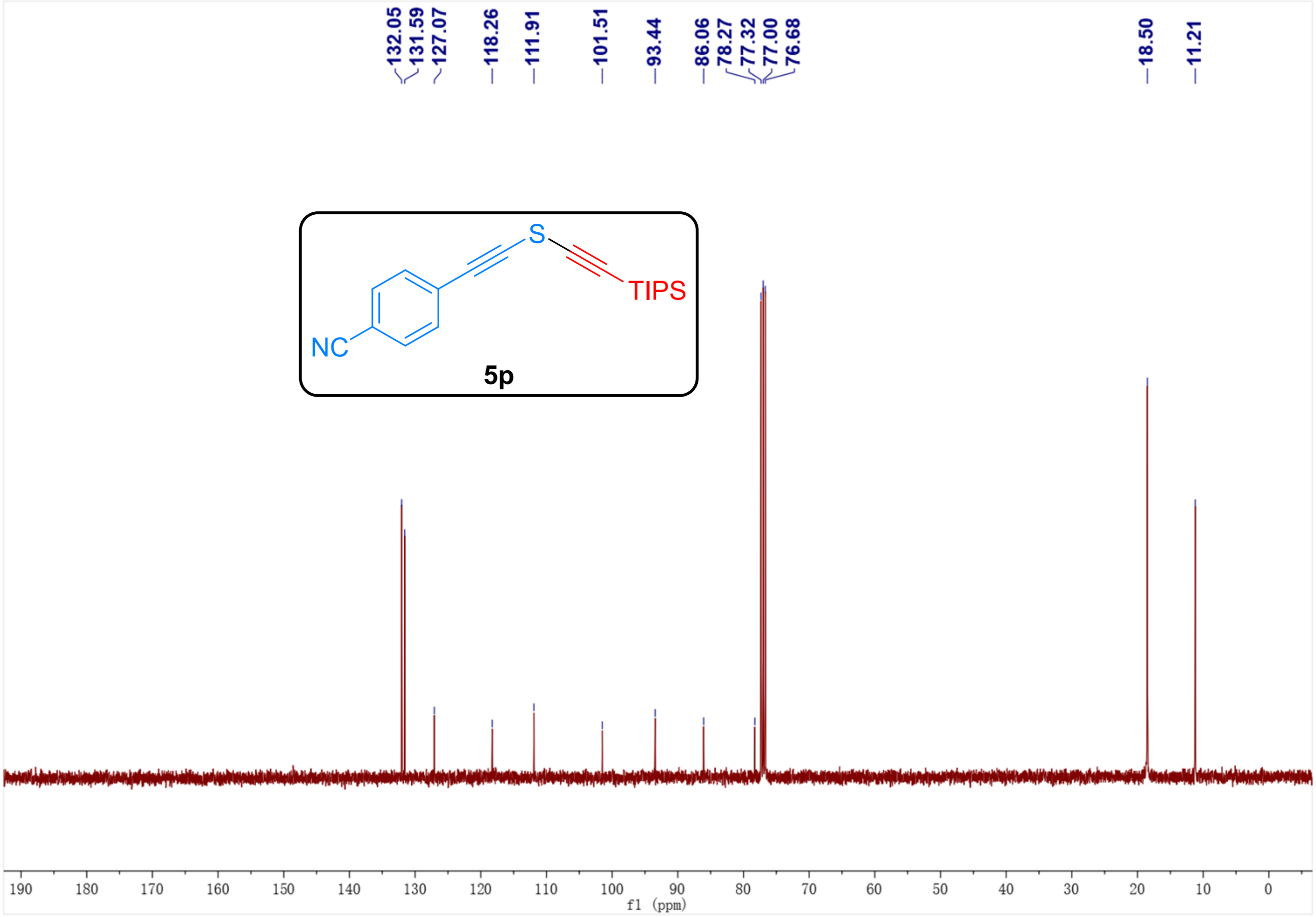

149.28
133.21
123.41
121.36
121.09
120.83
119.31
117.26
100.79
93.45
87.00
77.25
77.00
76.75
73.59
18.52
11.24
S
TIPS
F$_3$CO
5n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

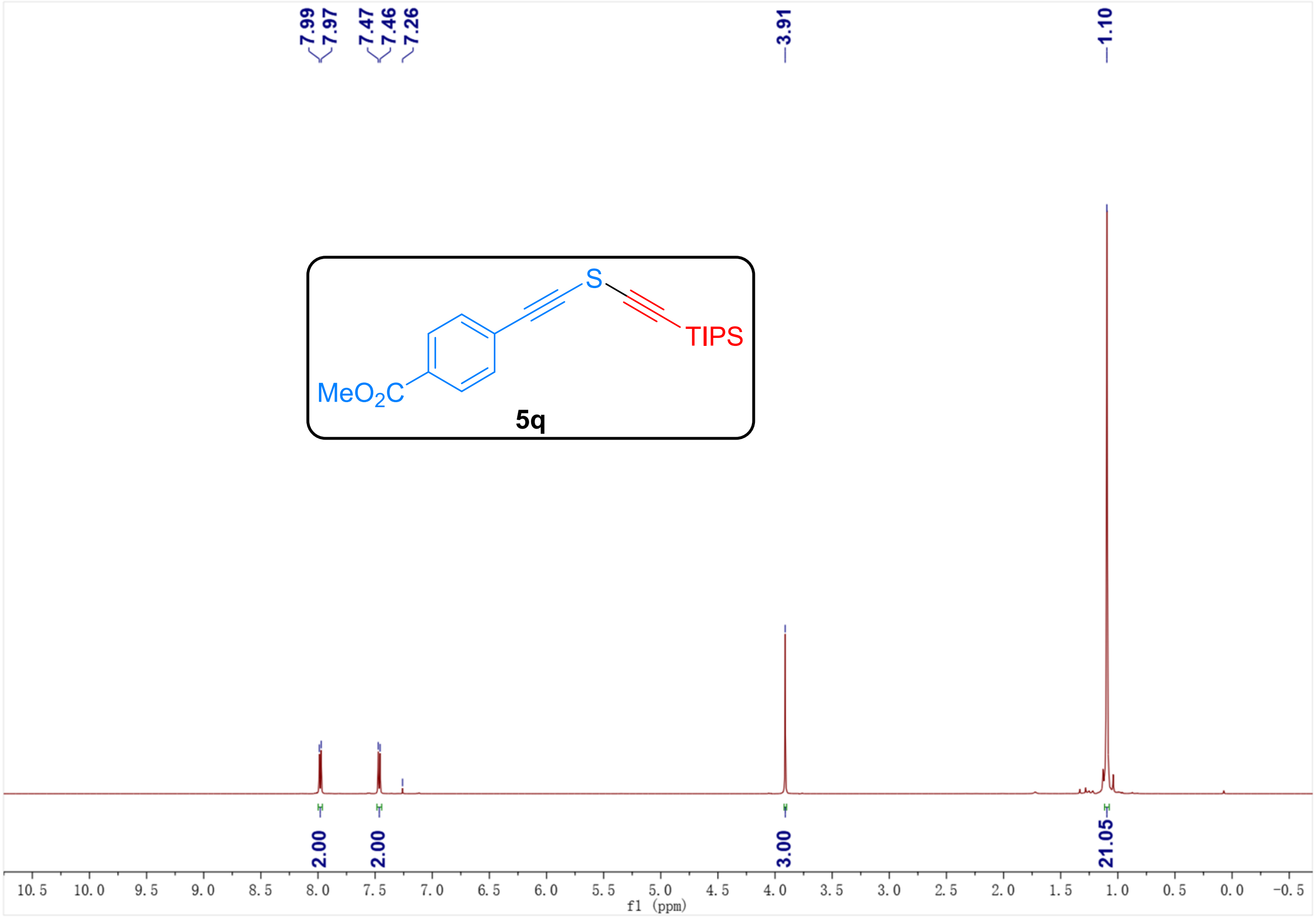

-57.81
S
TIPS
F$_3$CO
5n
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

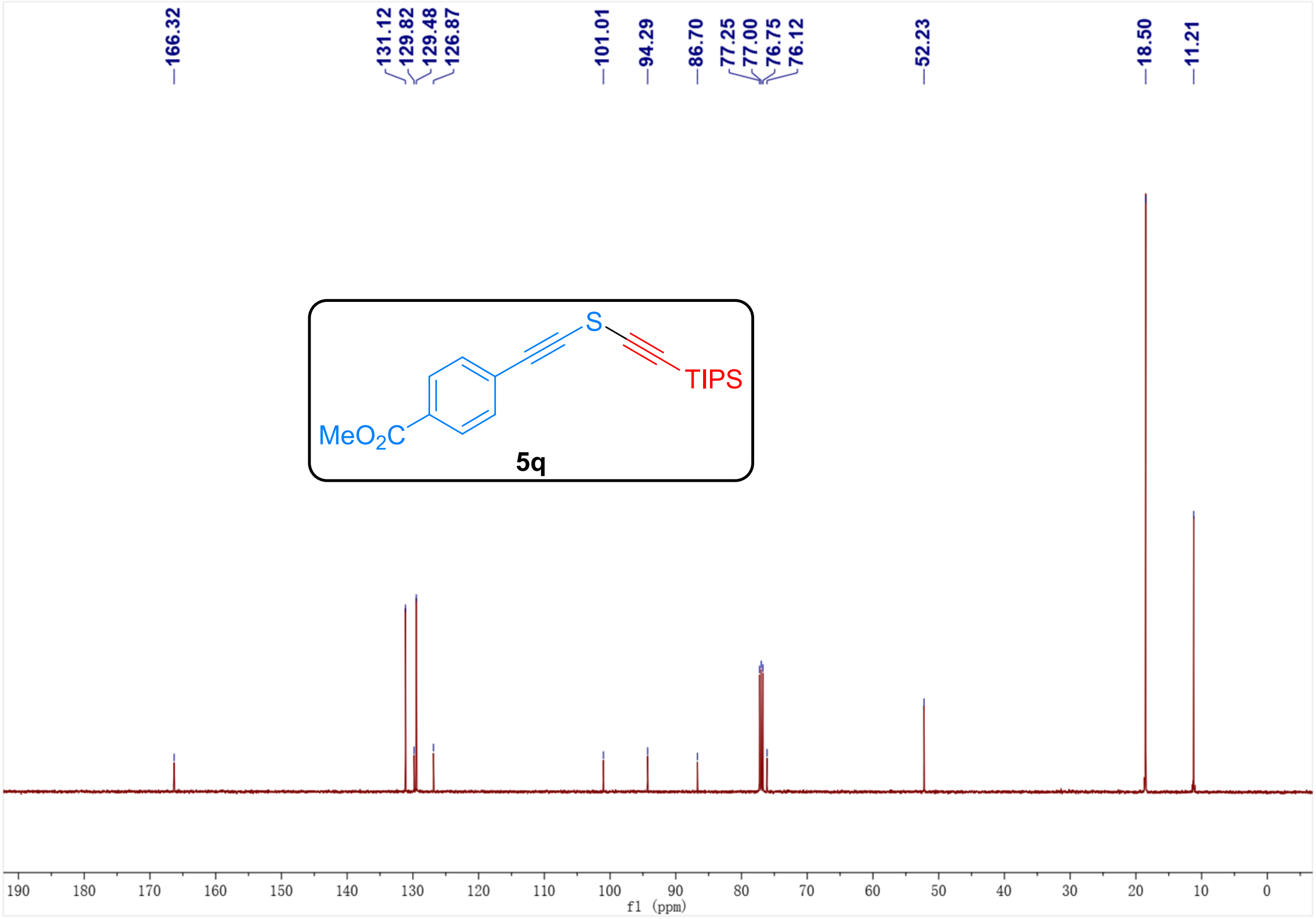

7.59
7.57
7.53
7.51
7.26
1.11
S
TIPS
F3C
5o
2.05
2.08
21.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

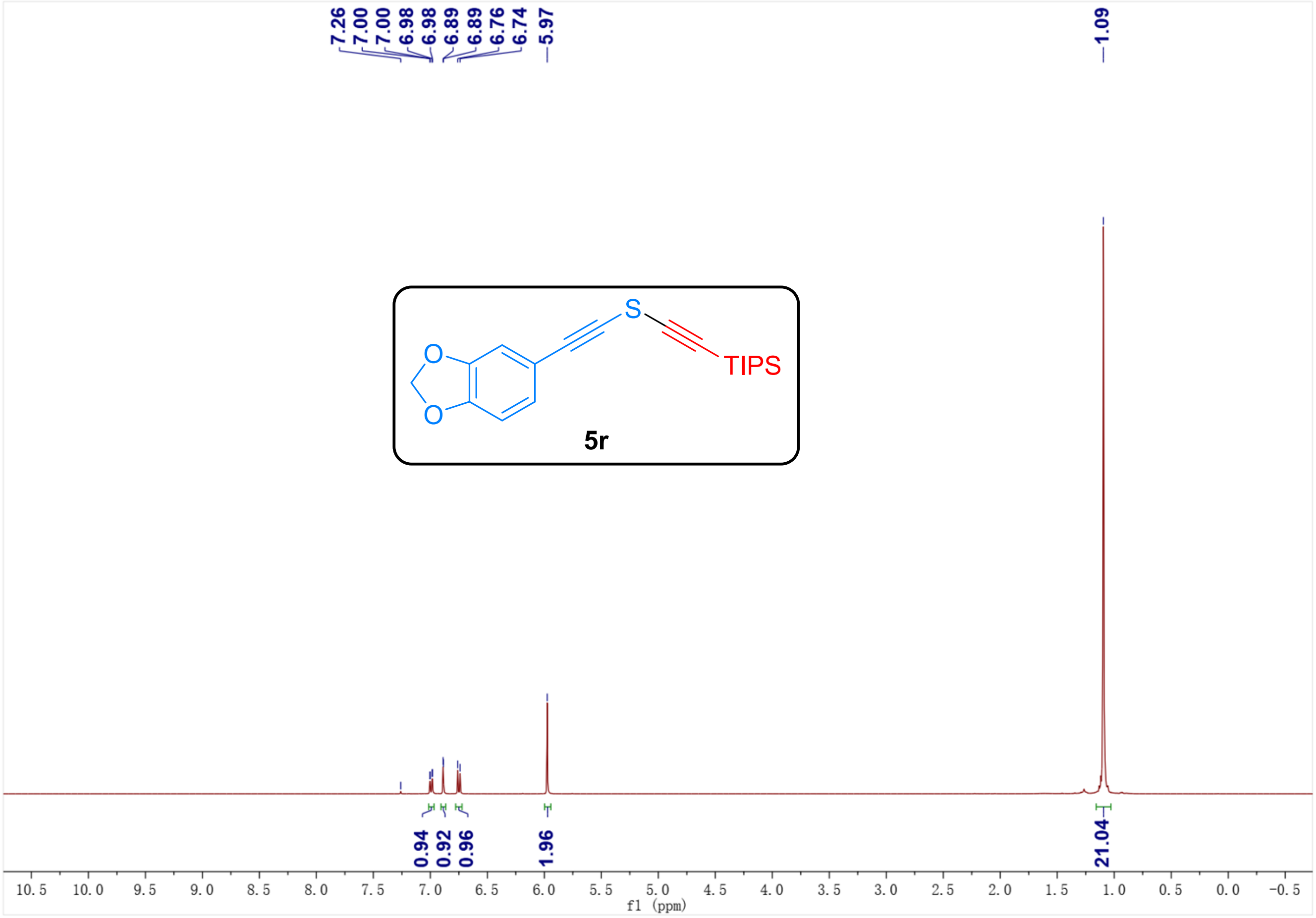

131.56
130.88
130.55
130.23
129.90
126.12
125.37
125.33
125.29
125.25
125.15
122.44
101.16
93.64
86.62
77.32
77.00
76.68
75.77
18.52
11.27
S
TIPS
F3C
5o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

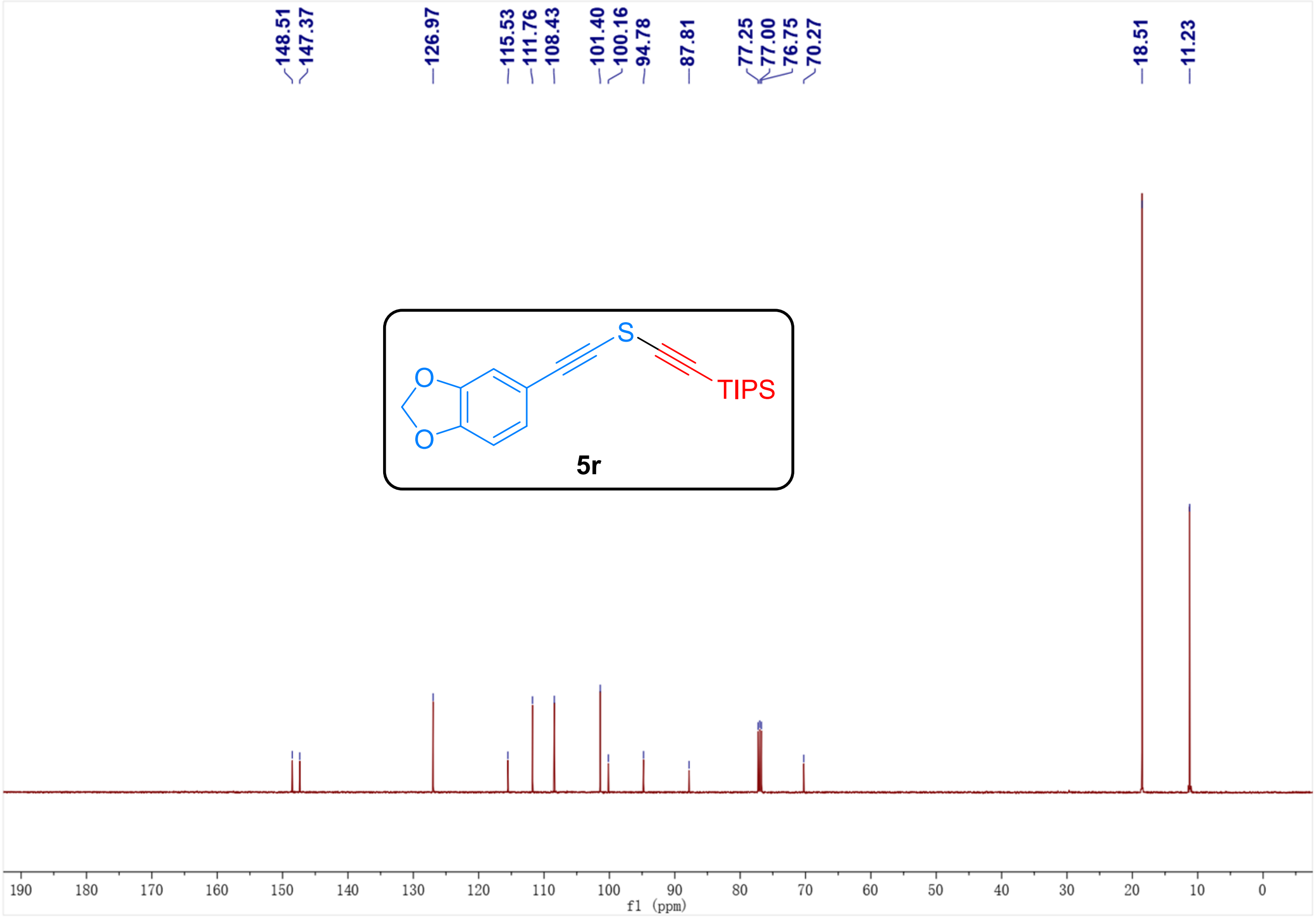

7.61
7.59
7.49
7.47
7.26
1.10
NC
S
TIPS
5p
2.00
1.98
21.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

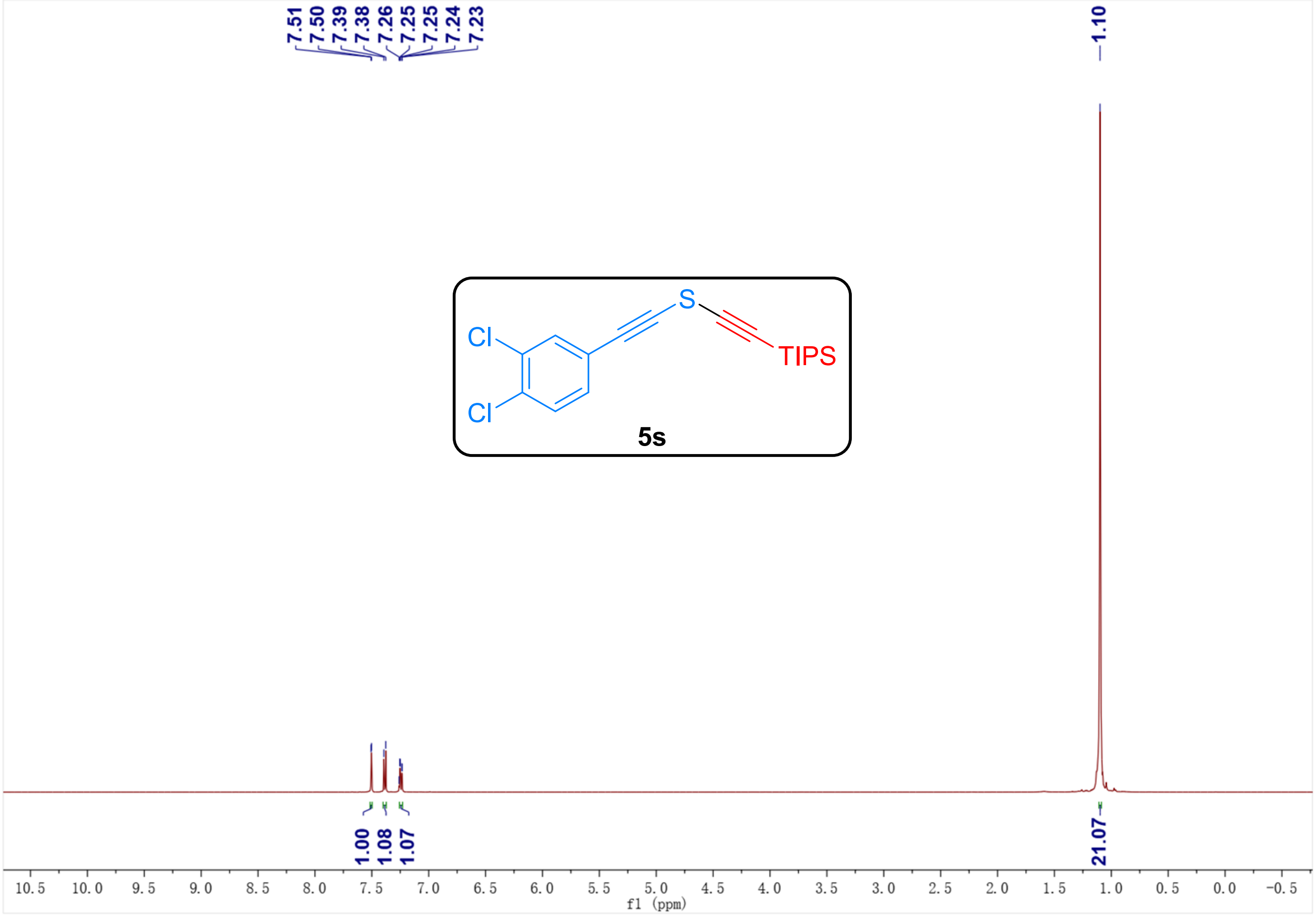

132.05
131.59
127.07
118.26
111.91
101.51
93.44
86.06
78.27
77.32
77.00
76.68
18.50
11.21
NC
S
TIPS
5p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

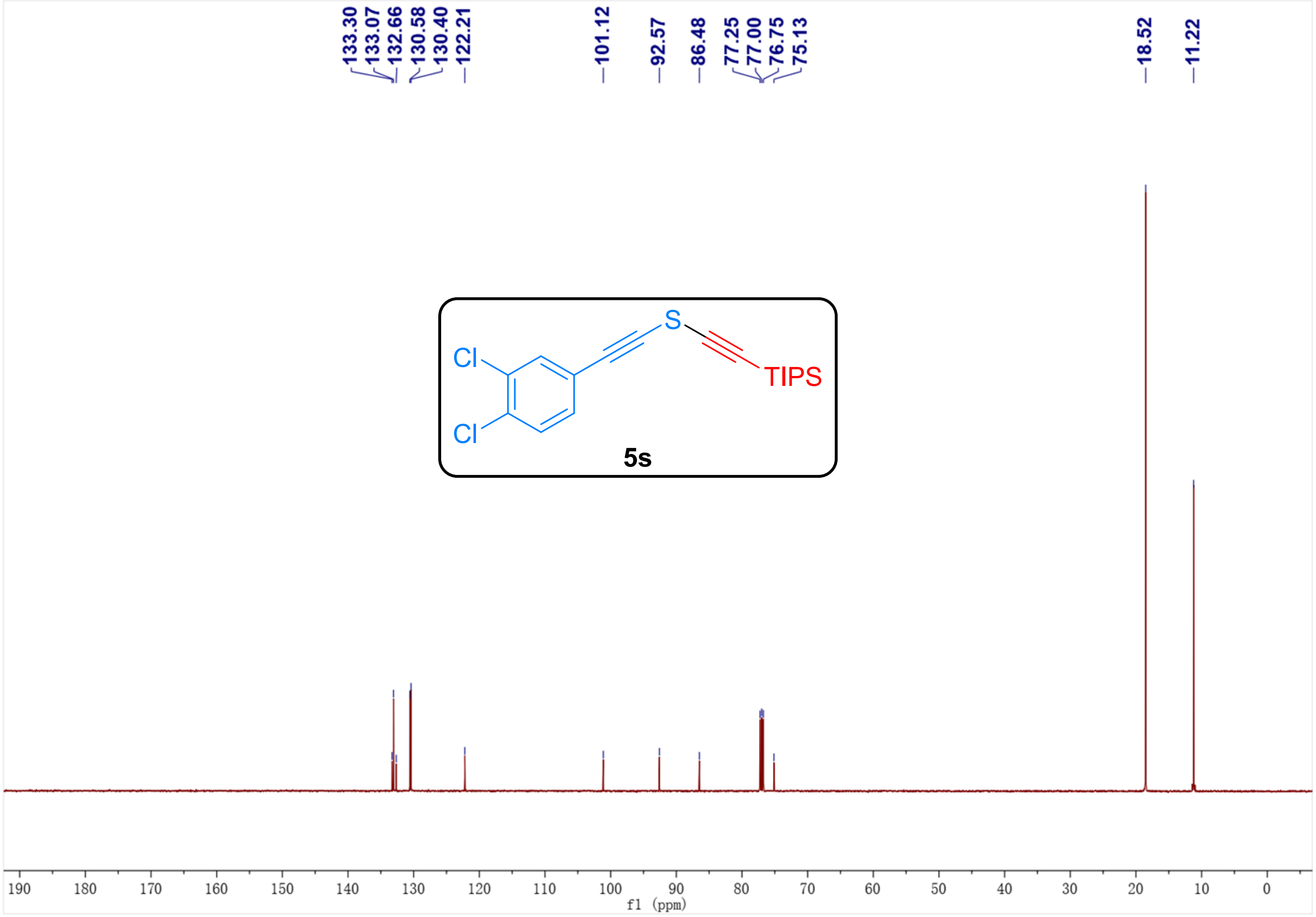

7.99
7.97
7.47
7.46
7.26
3.91
1.10
MeO$_2$C
S
TIPS
5q
2.00
2.00
3.00
21.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

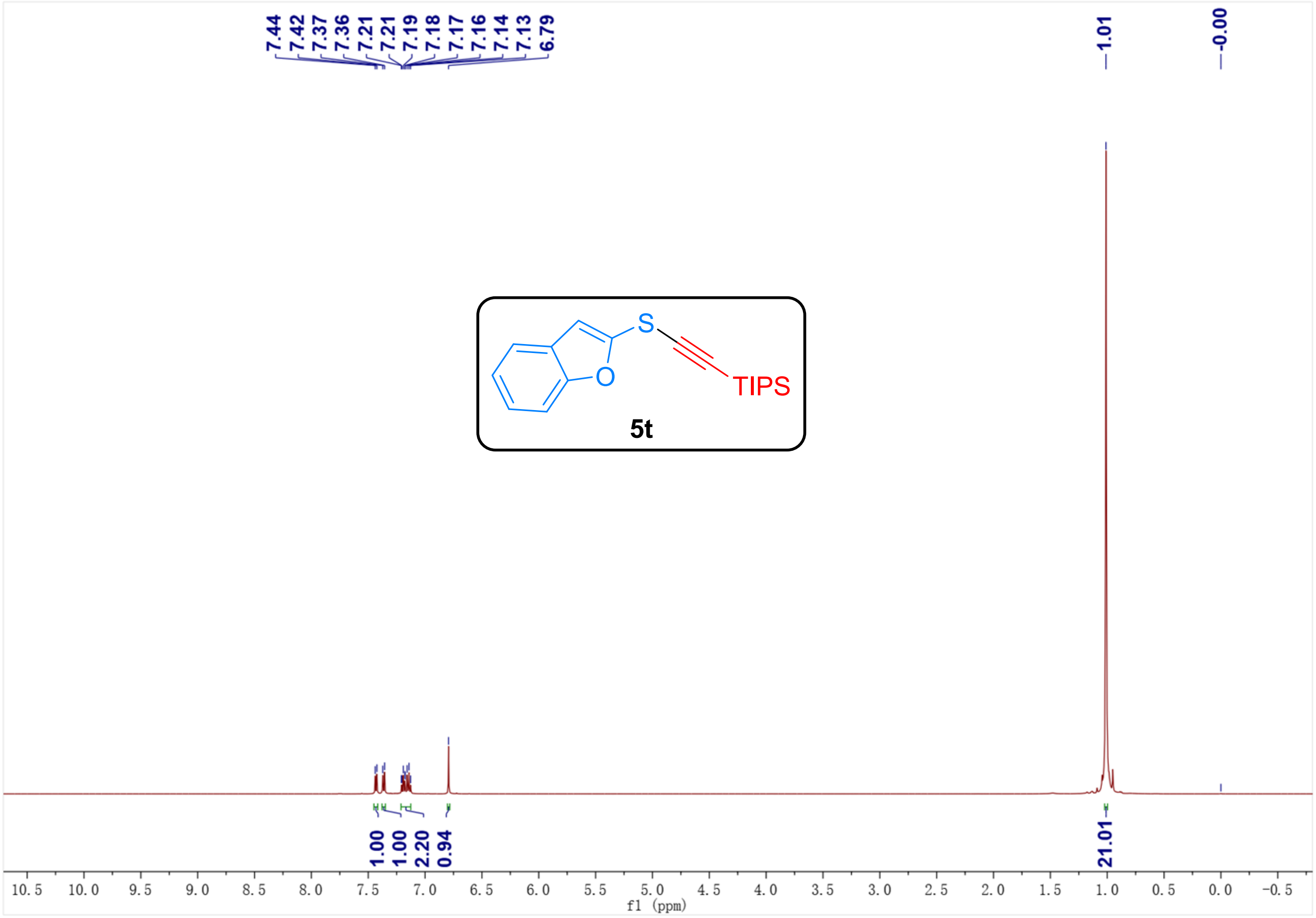

166.32
131.12
129.82
129.48
126.87
101.01
94.29
86.70
77.25
77.00
76.75
76.12
52.23
18.50
11.21
MeO$_2$C
S
TIPS
5q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

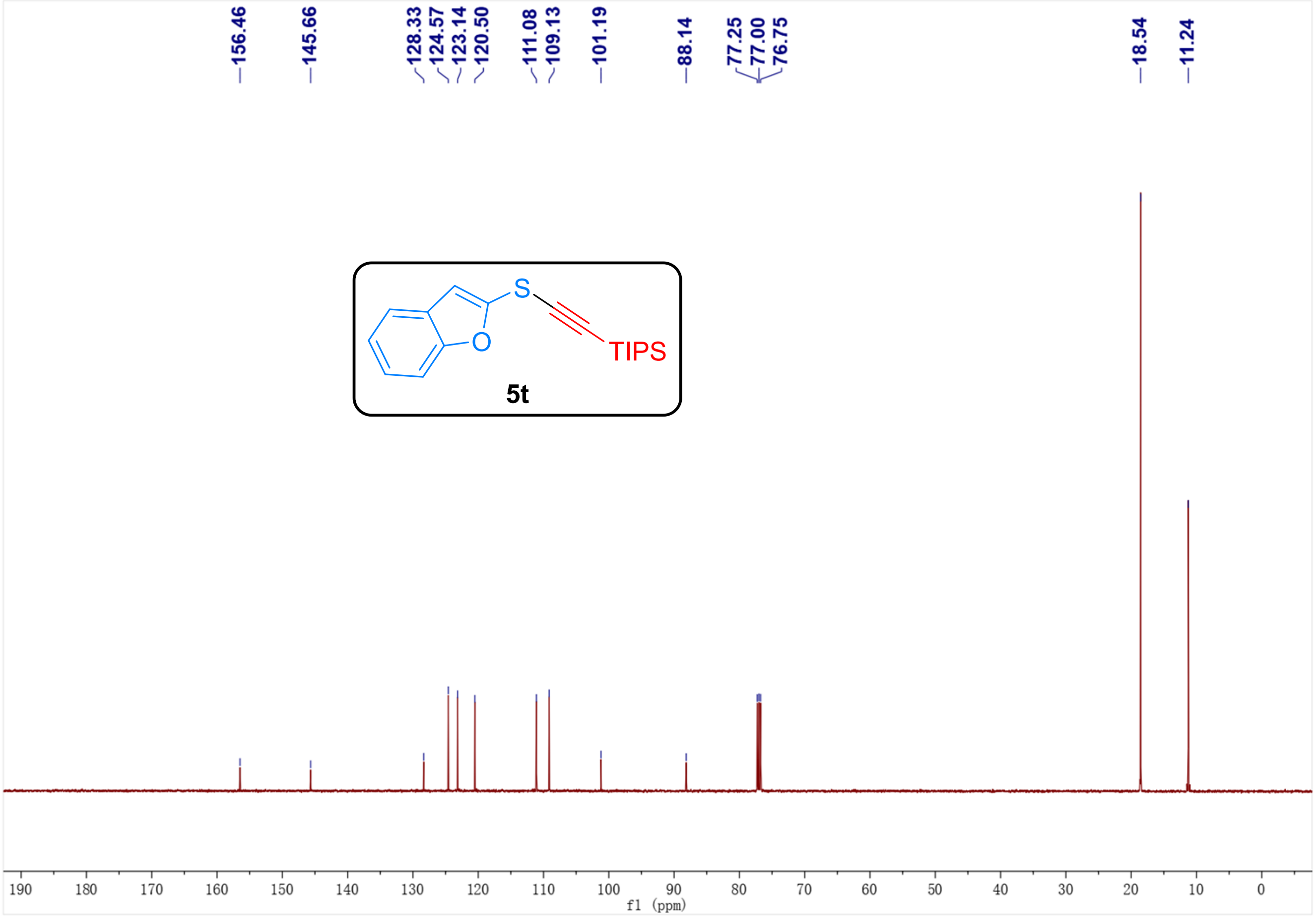

7.26
7.00
7.00
6.98
6.98
6.89
6.89
6.76
6.74
5.97
1.09
O
O
S
TIPS
5r
0.94
0.92
0.96
1.96
21.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


148.51
147.37
126.97
115.53
111.76
108.43
101.40
100.16
94.78
87.81
77.25
77.00
76.75
70.27
18.51
11.23
O
O
S
TIPS
5r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.51
7.50
7.39
7.38
7.26
7.25
7.25
7.24
7.23
1.10
Cl
Cl
S
TIPS
5s
1.00
1.08
1.07
21.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


133.30
133.07
132.66
130.58
130.40
122.21
101.12
92.57
86.48
77.25
77.00
76.75
75.13
18.52
11.22
Cl
Cl
S
TIPS
5s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.44
7.42
7.37
7.36
7.21
7.21
7.19
7.18
7.17
7.16
7.14
7.13
6.79
1.01
-0.00
S
O
TIPS
5t
1.00
1.00
2.20
0.94
21.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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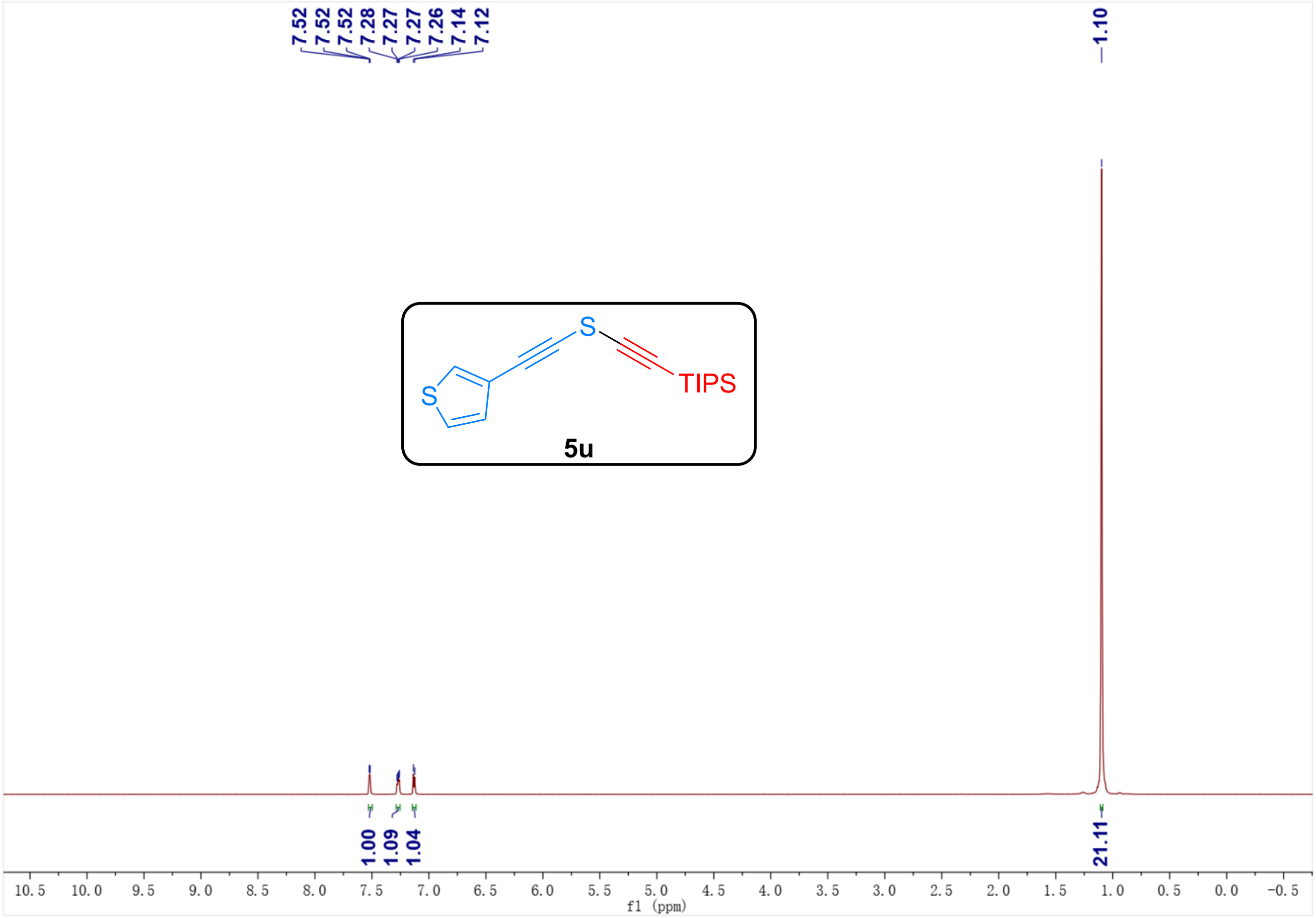
124.57
123.14
120.50
111.08
109.13
101.19
88.14
77.25
77.00
76.75
18.54
11.24
S
O
TIPS
5t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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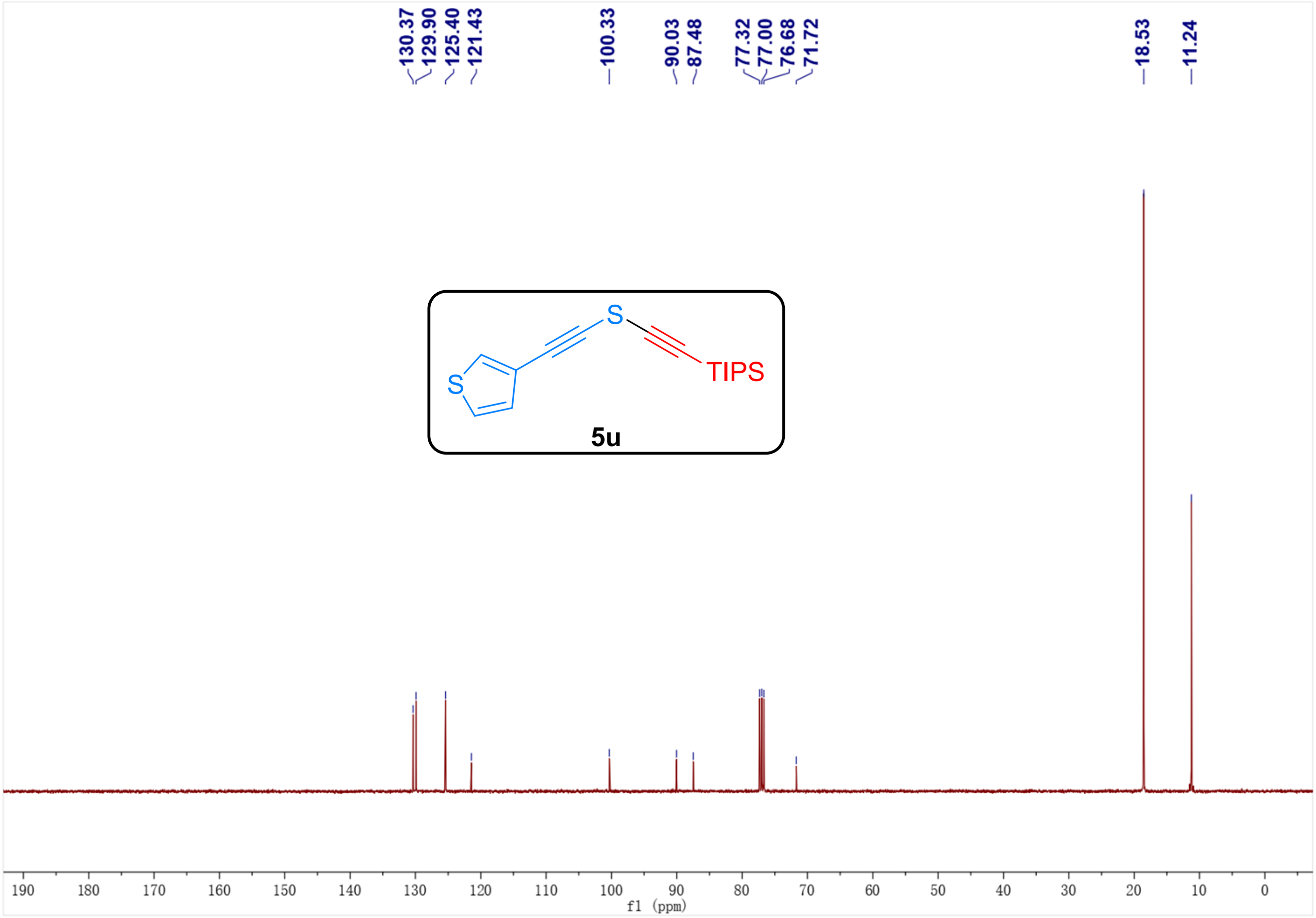
7.52
7.52
7.28
7.27
7.27
7.26
7.14
7.12
1.10
S
S
TIPS
1.00
1.09
1.04
21.11
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

5u


130.37
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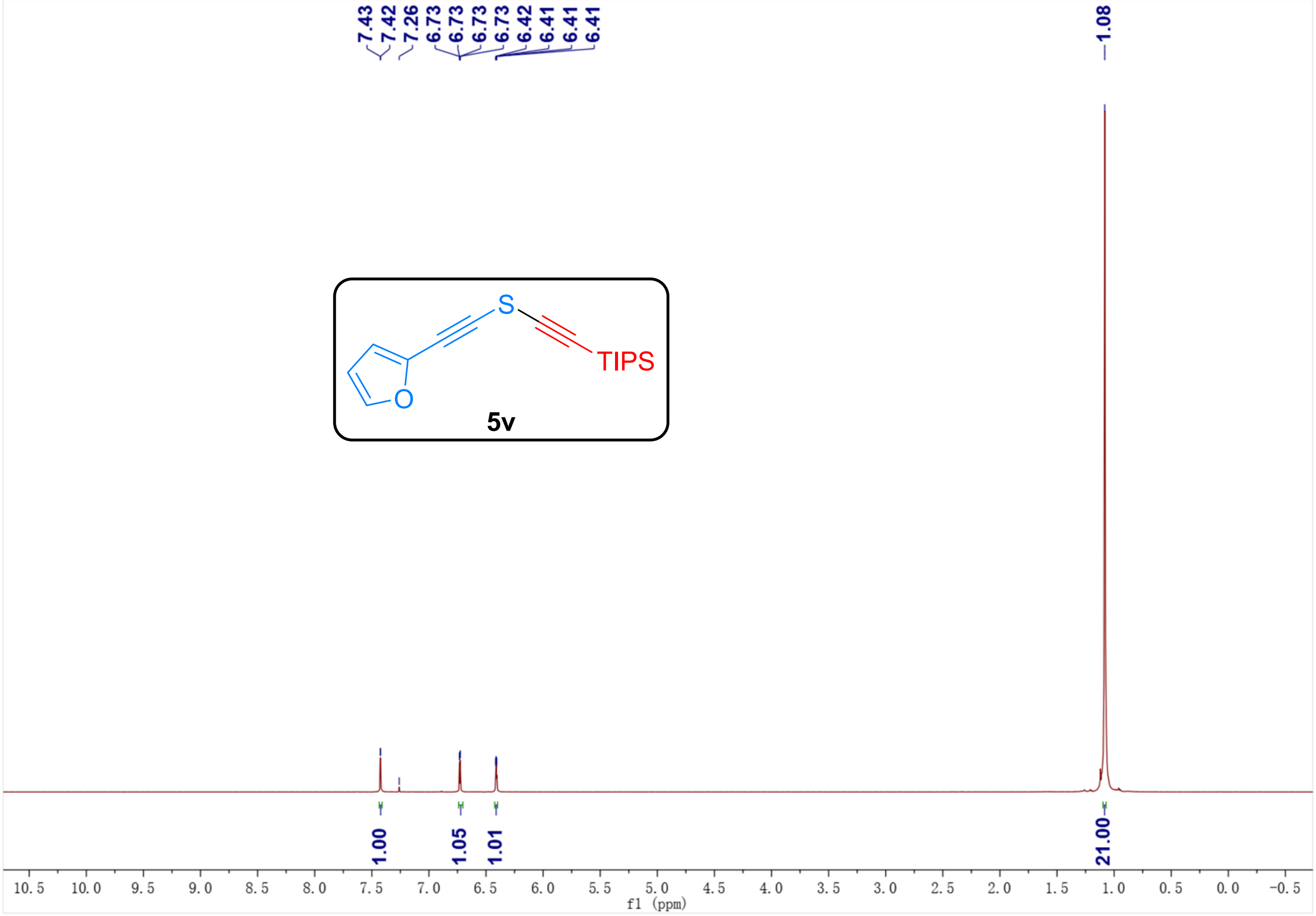
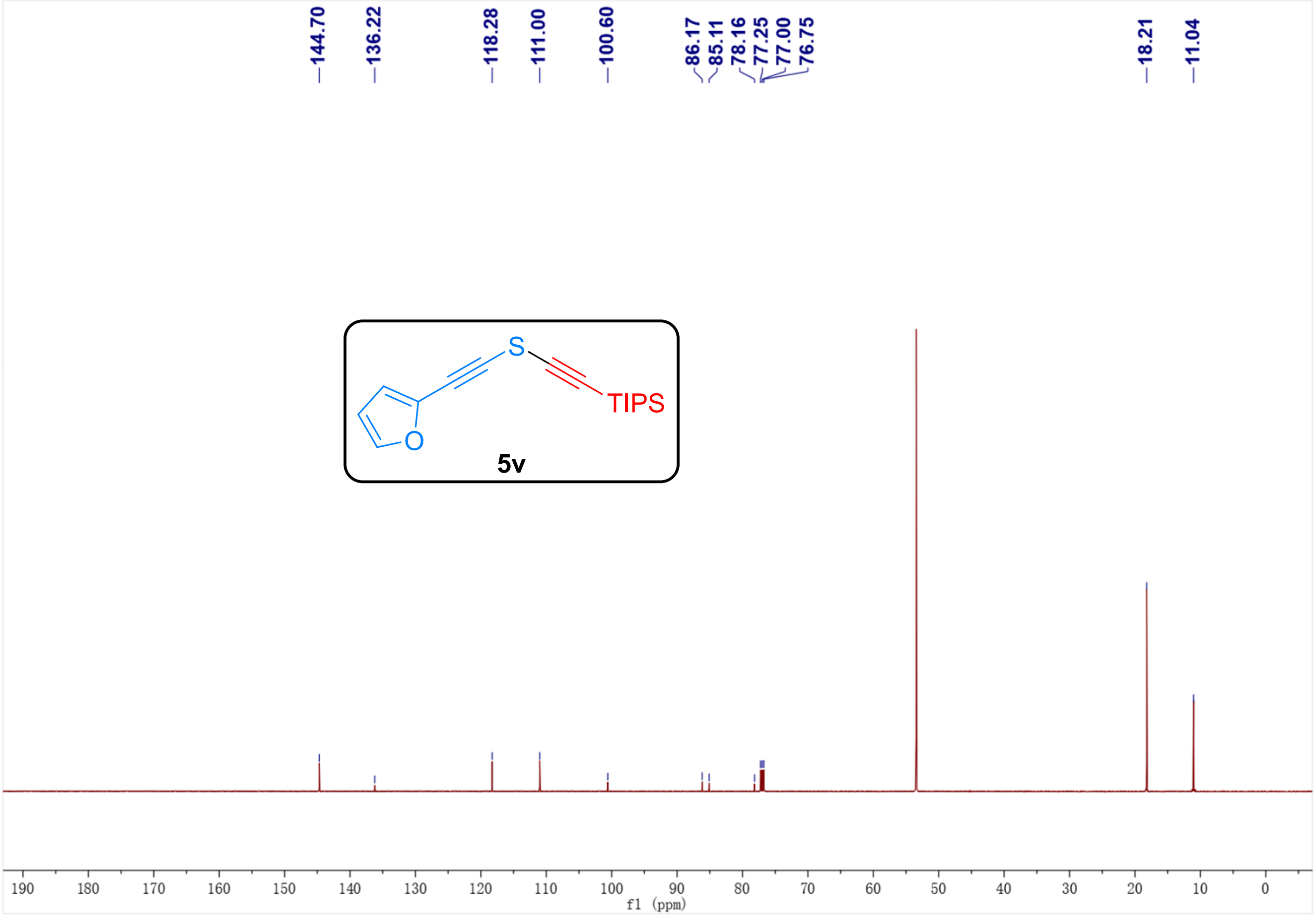
125.40
121.43
100.33
90.03
87.48
77.32
77.00
76.68
71.72
18.53
11.24
S
S
TIPS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5u


7.43
7.42
7.26
6.73
6.73
6.73
6.73
6.42
6.41
6.41
6.41
1.08
S
TIPS
O
5v
1.00
1.05
1.01
21.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


144.70
136.22
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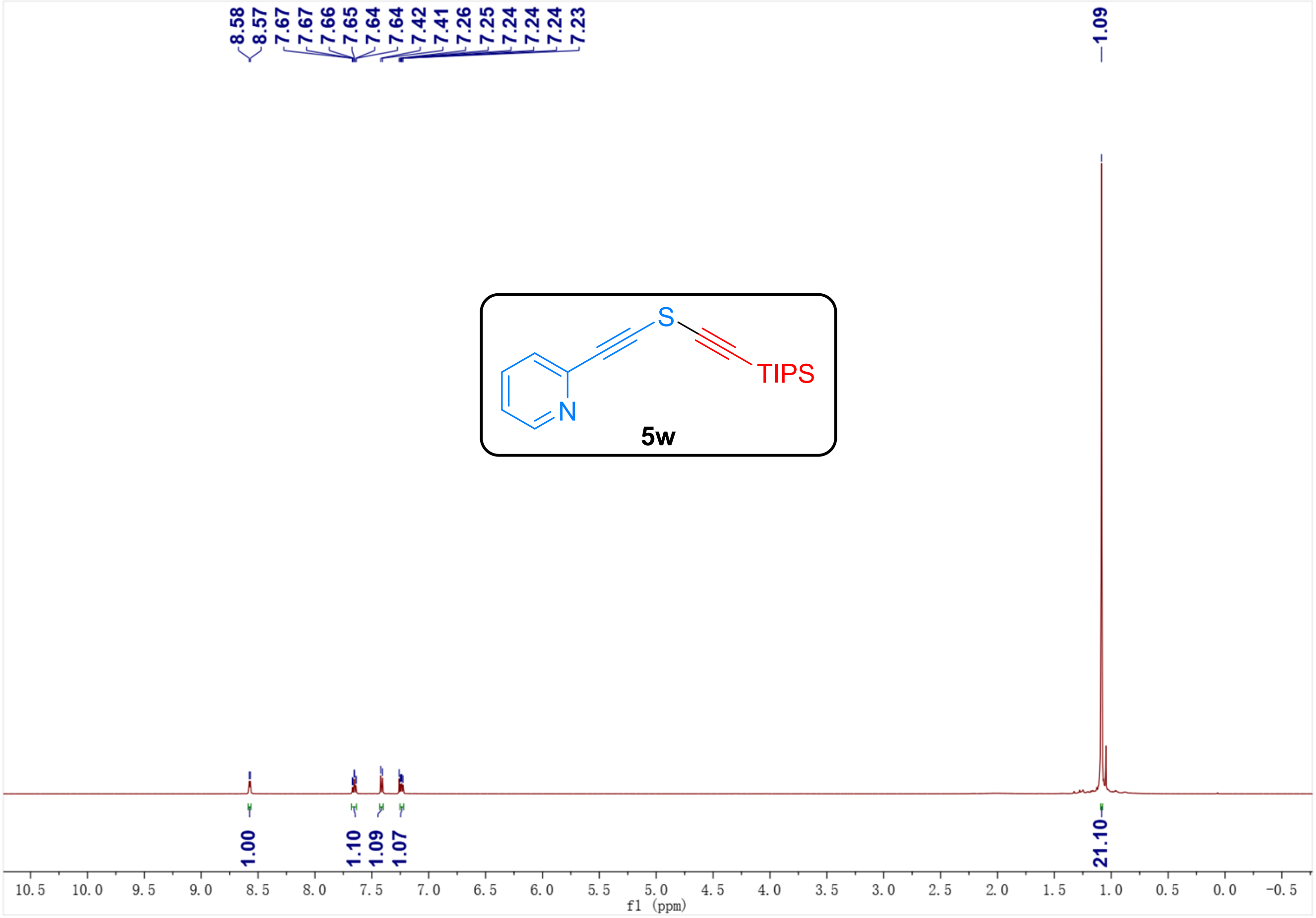
111.00
100.60
86.17
85.11
78.16
77.25
77.00
76.75
18.21
11.04
S
TIPS
O
5v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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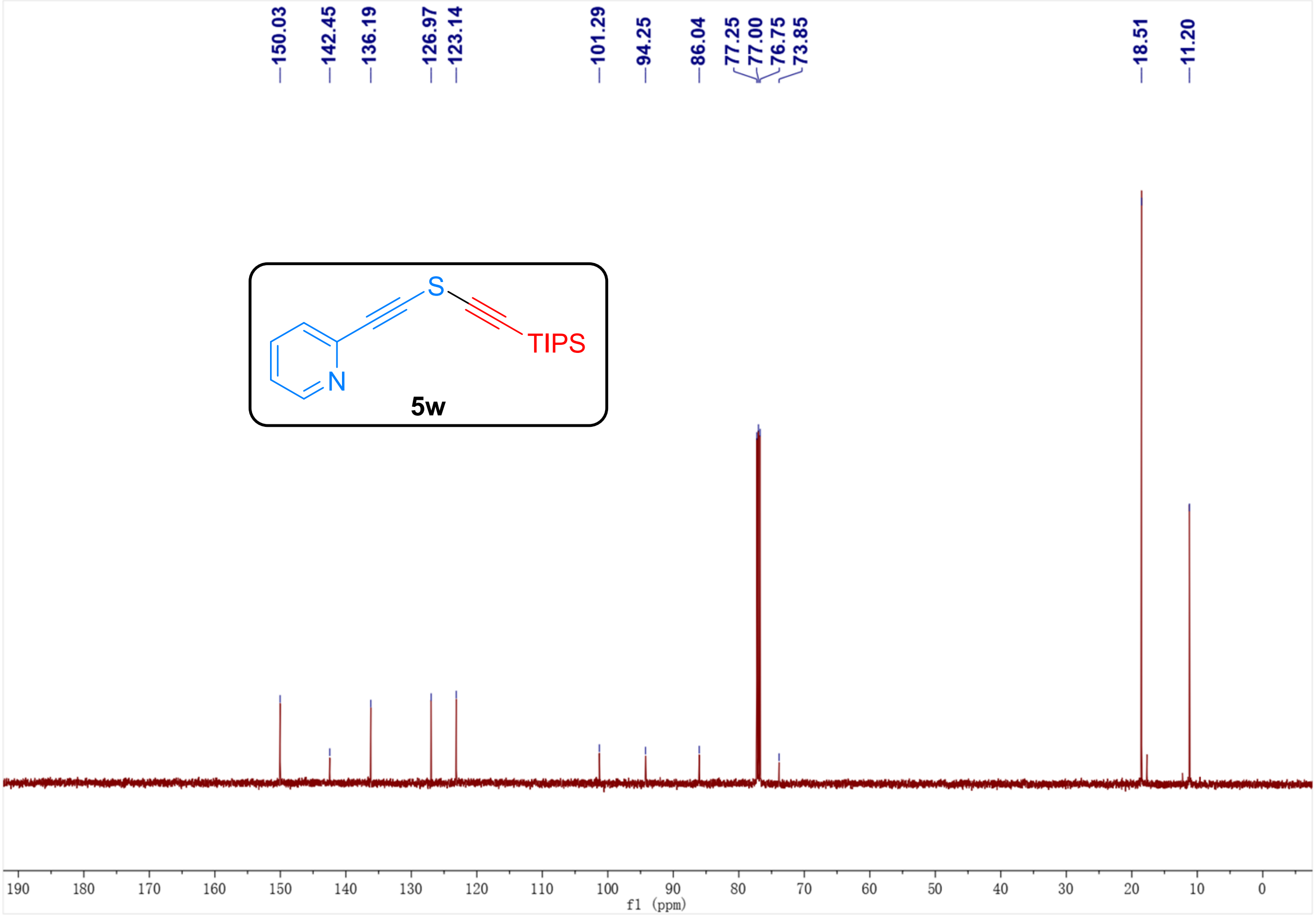
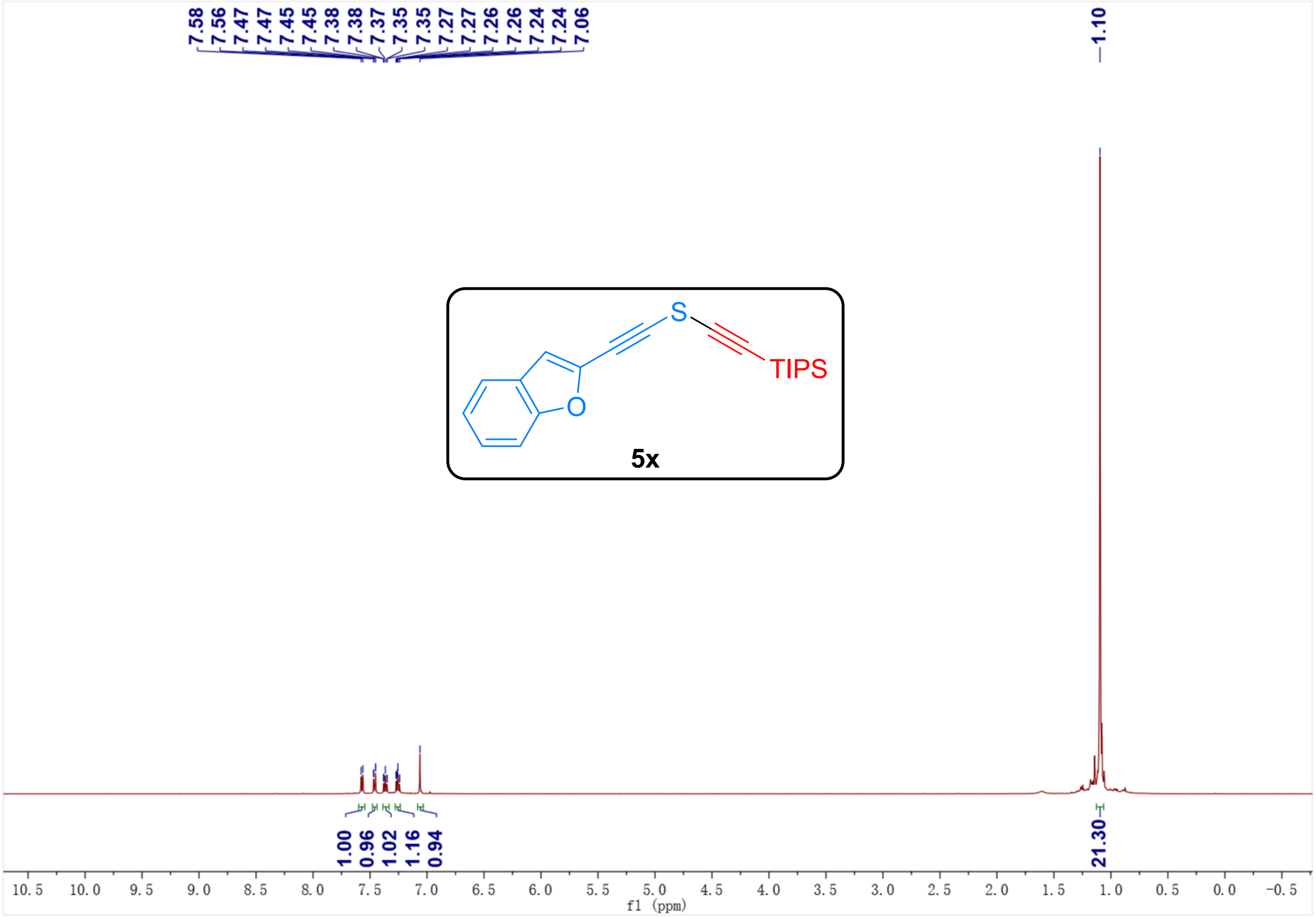
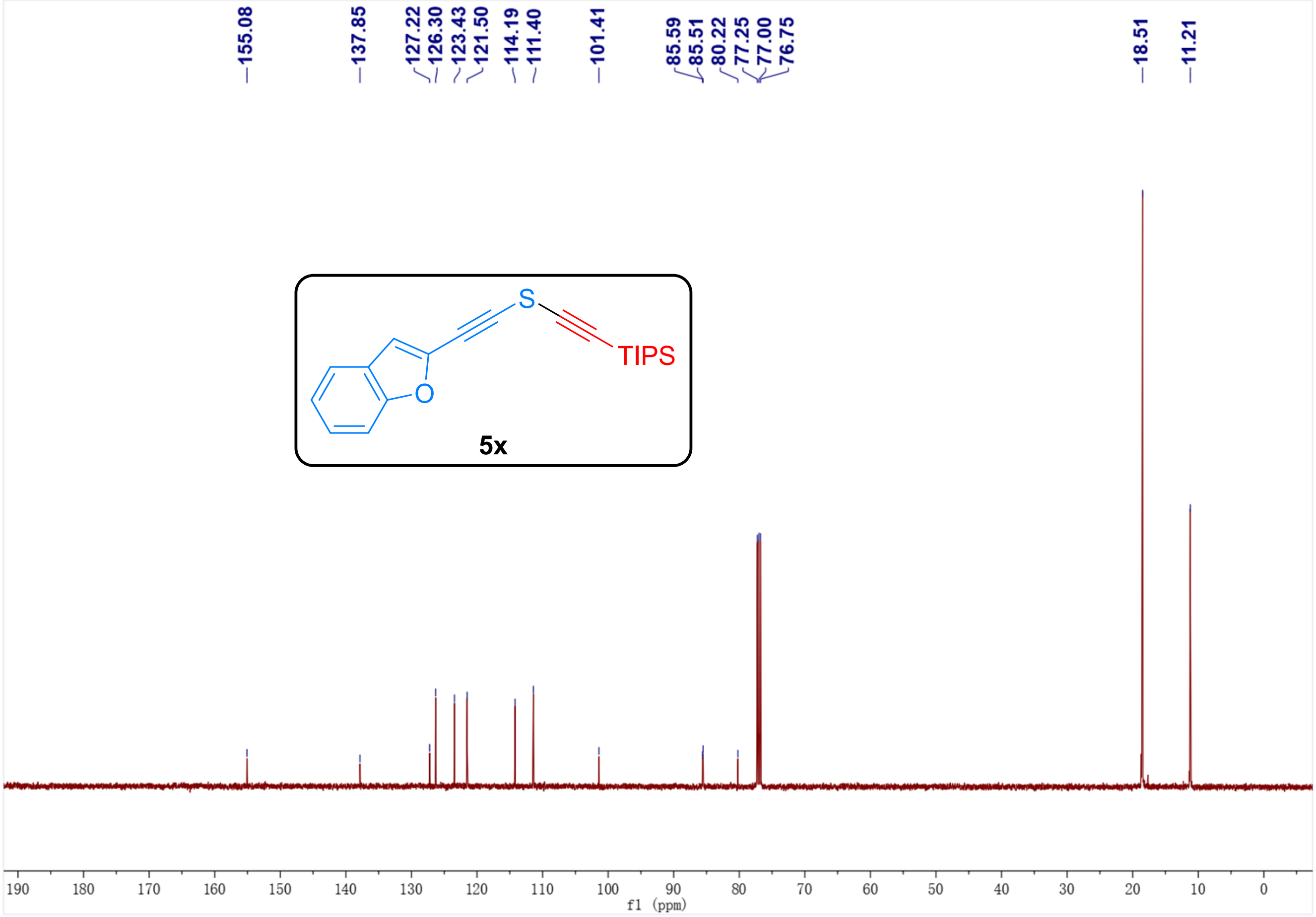
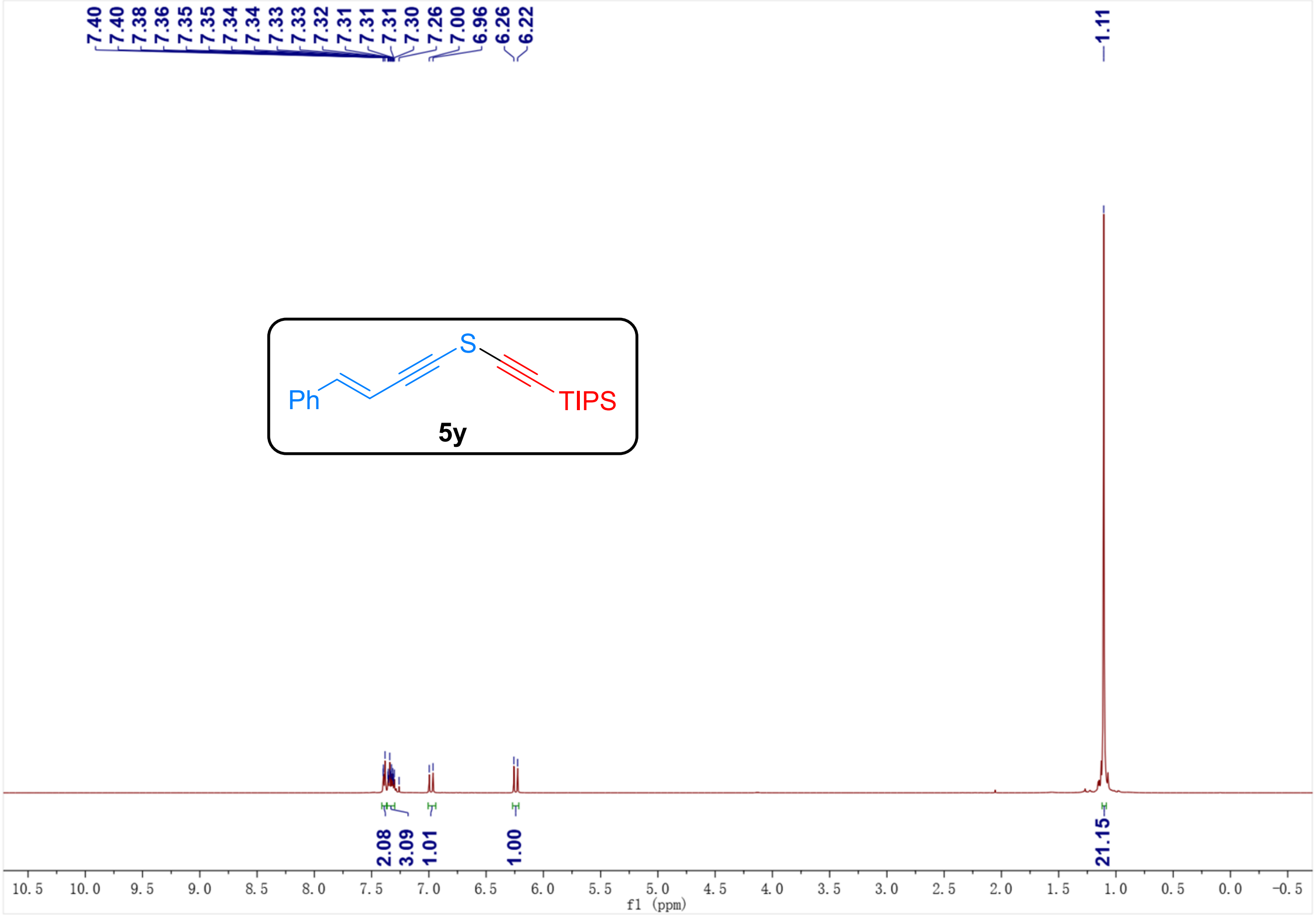
8.57
7.67
7.67
7.66
7.65
7.64
7.64
7.42
7.41
7.26
7.25
7.24
7.24
7.24
7.23
1.09
S
N
TIPS
5w
1.00
1.10
1.09
1.07
21.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


150.03
142.45
136.19
126.97
123.14
101.29
94.25
86.04
77.25
77.00
76.75
73.85
18.51
11.20
S
N
TIPS
5w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.58
7.56
7.47
7.47
7.45
7.45
7.38
7.38
7.37
7.35
7.35
7.27
7.27
7.26
7.26
7.24
7.24
7.06
1.10
S
TIPS
O
5x
1.00
0.96
1.02
1.16
0.94
21.30
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.08
137.85
127.22
126.30
123.43
121.50
114.19
111.40
101.41
85.59
85.51
80.22
77.25
77.00
76.75
18.51
11.21
S
TIPS
O
5x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.40
7.40
7.38
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.26
7.00
6.96
6.26
6.22
1.11
Ph
S
TIPS
5y
2.08
3.09
1.01
1.00
21.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
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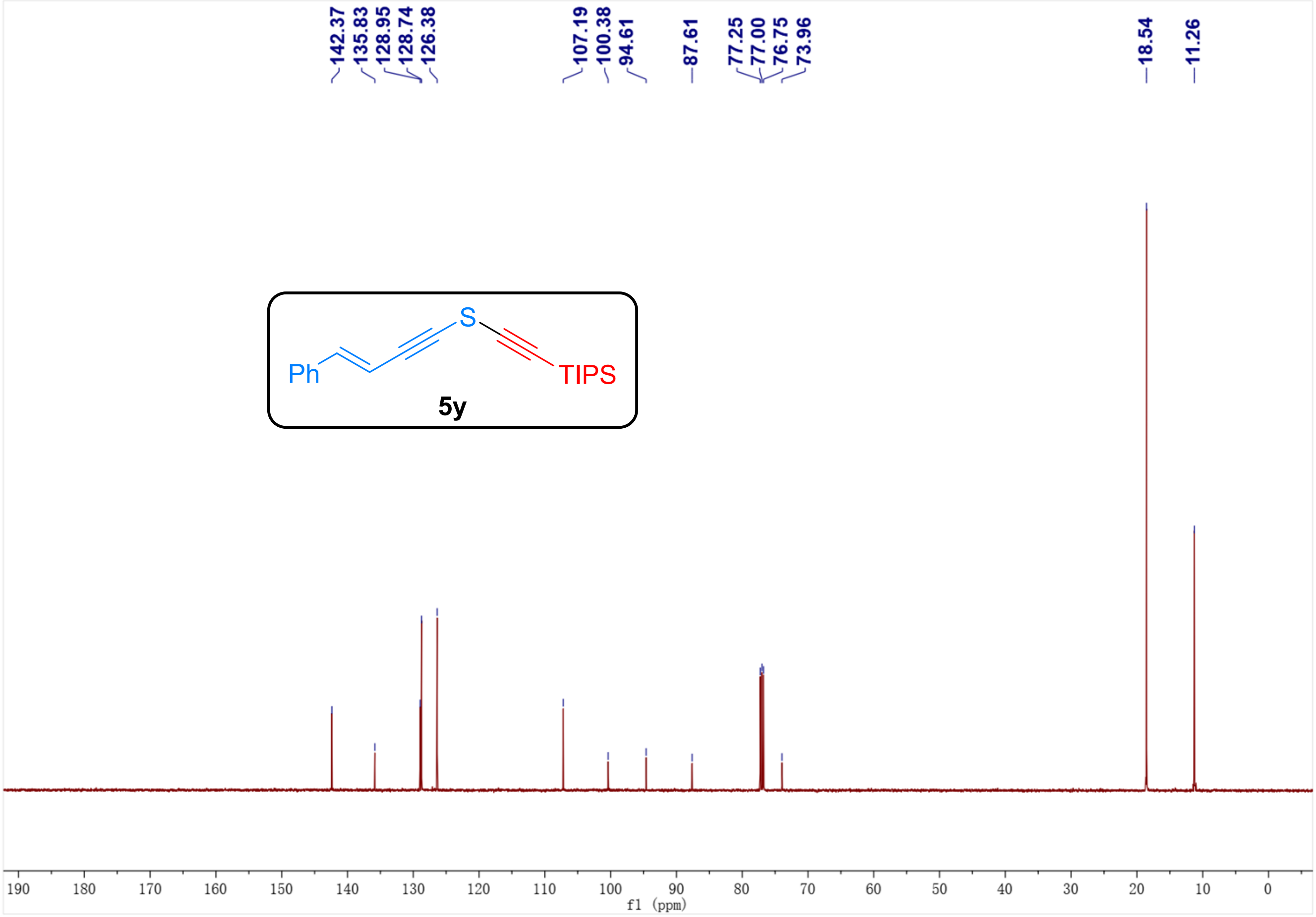
f1 (ppm)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73.96
18.54
11.26
Ph
S
TIPS
5y
190
180
170
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140
130
120
110
100
90
80
70
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50
40
30
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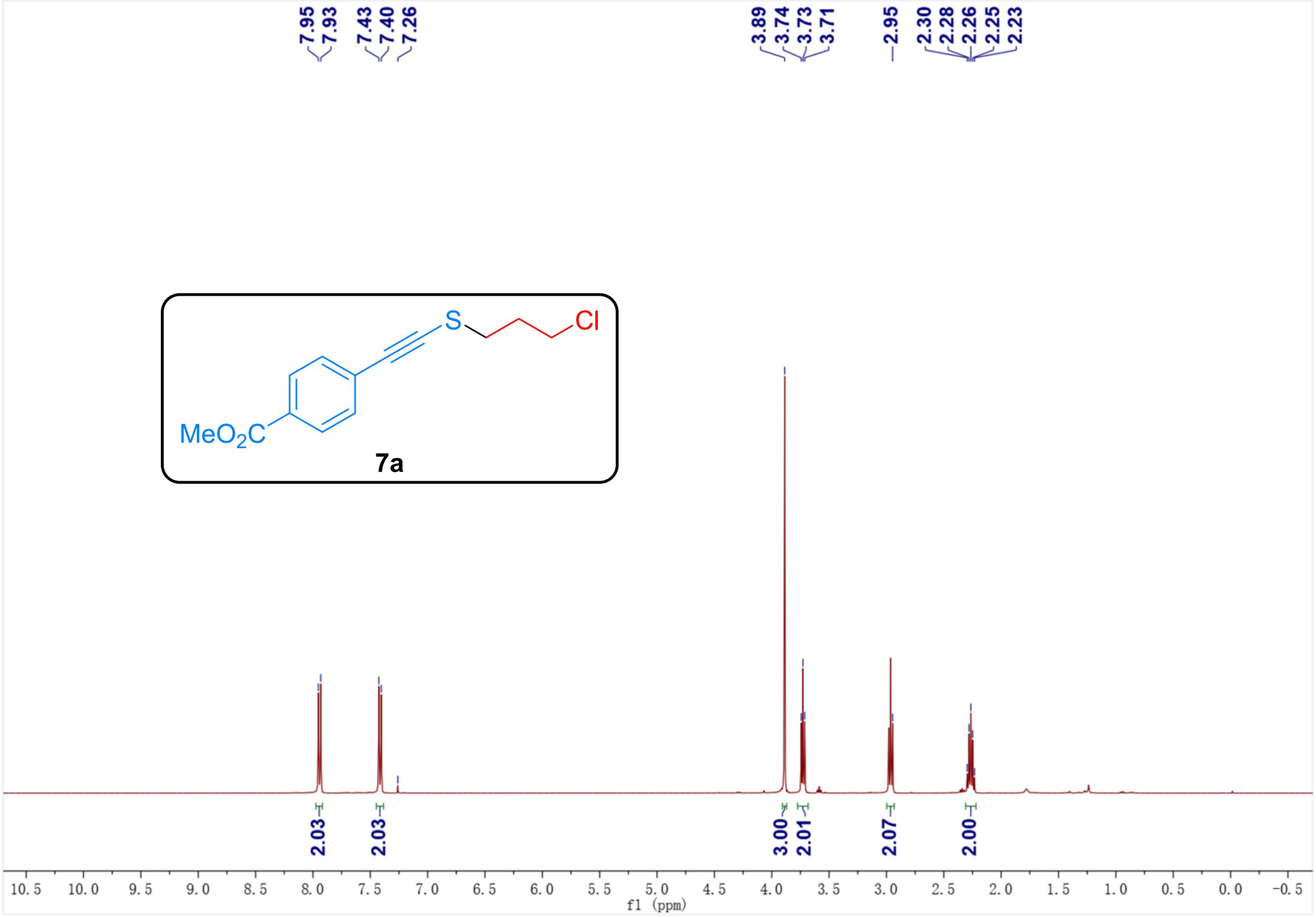
10
0
f1 (ppm)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3.73
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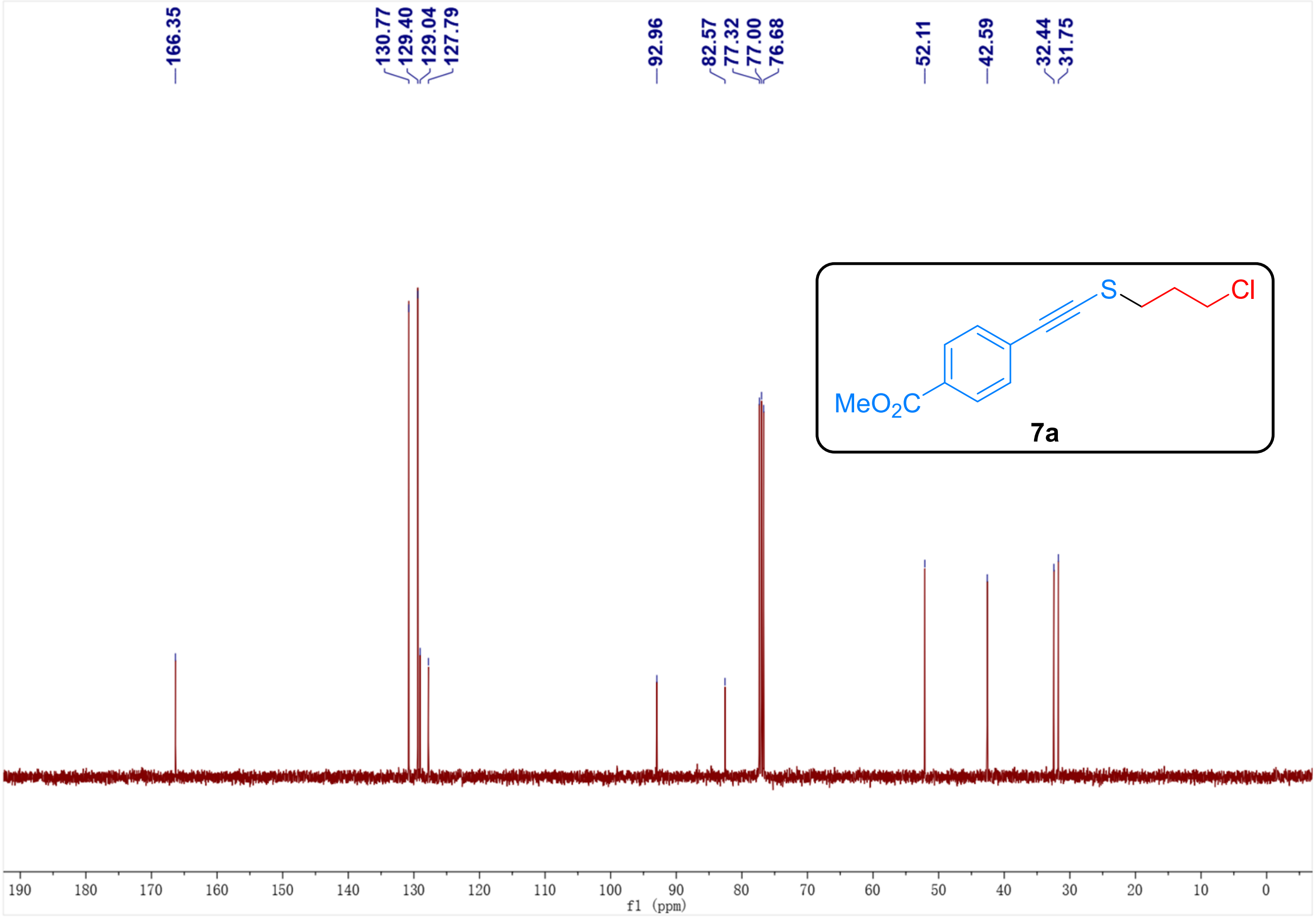
2.95
2.30
2.28
2.26
2.25
2.23
MeO$_2$C
S
Cl
7a
2.03
2.03
3.00
2.01
2.07
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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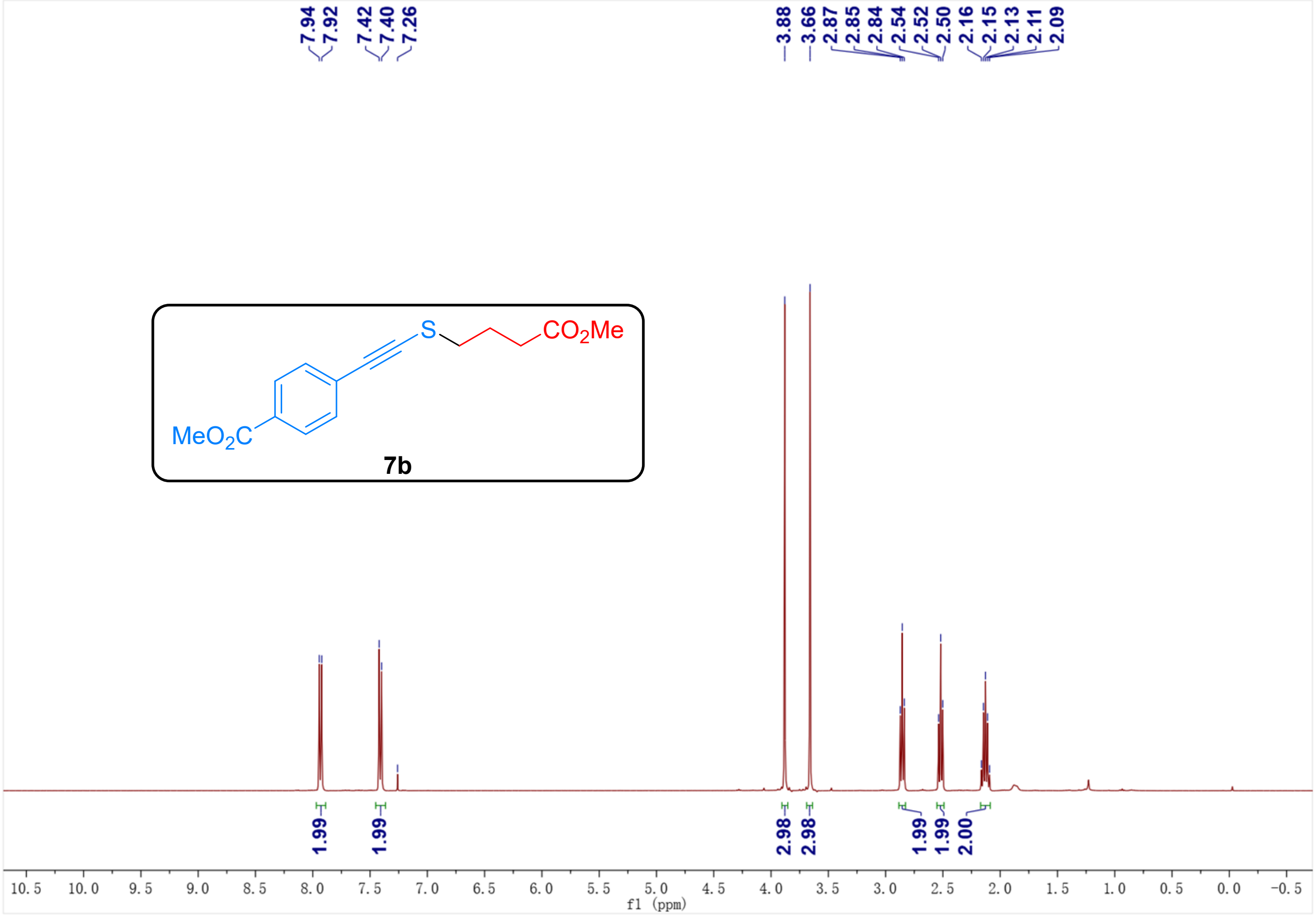
77.32
77.00
76.68
52.11
42.59
32.44
31.75
MeO$_2$C
S
Cl
7a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.92
7.42
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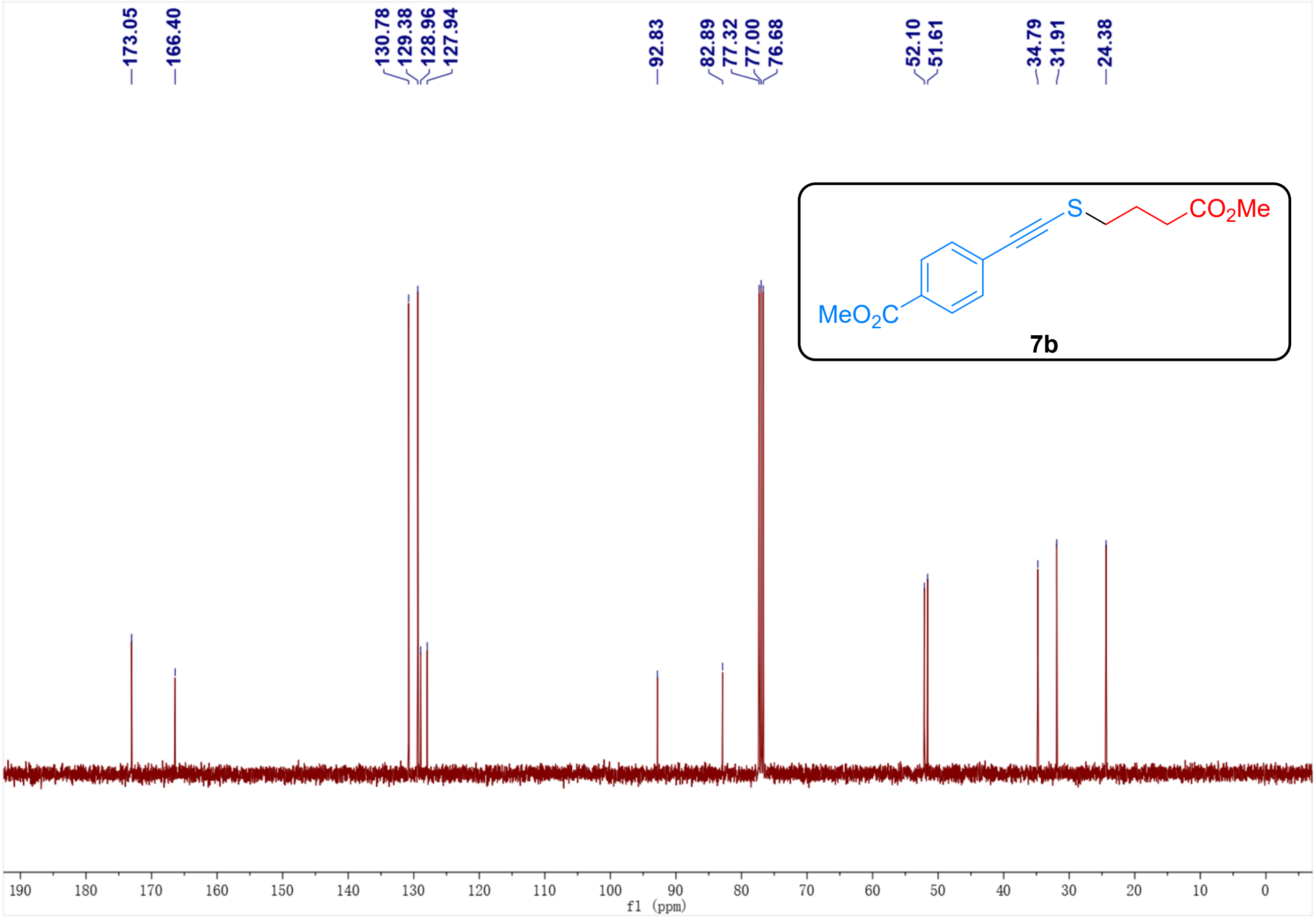
3.66
2.87
2.85
2.84
2.54
2.52
2.50
2.16
2.15
2.13
2.11
2.09
S
CO2Me
MeO2C
7b
1.99
1.99
2.98
2.98
1.99
1.99
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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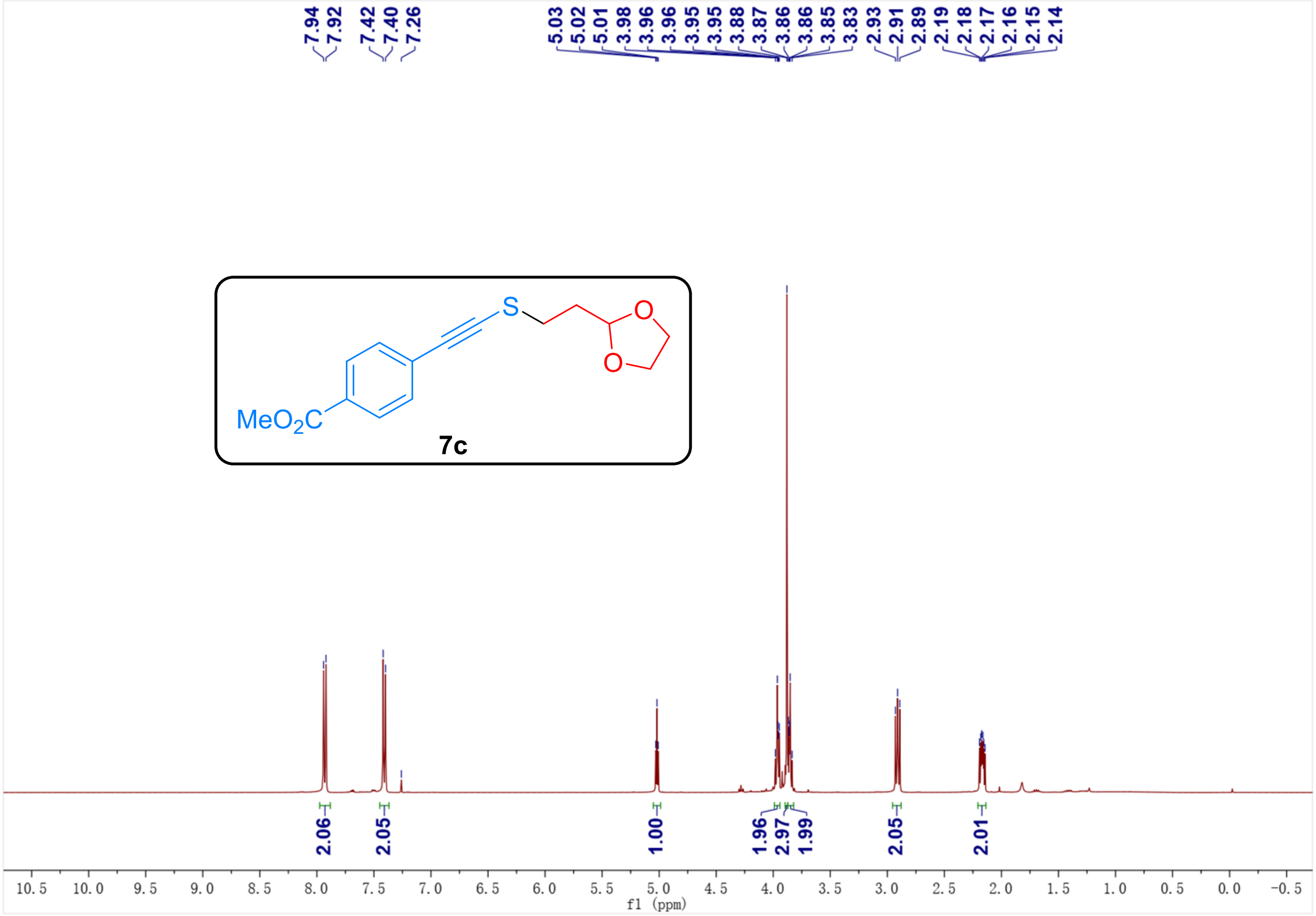
127.94
92.83
82.89
77.32
77.00
76.68
52.10
51.61
34.79
31.91
24.38
S
CO2Me
MeO2C
7b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.26
5.03
5.02
5.01
3.98
3.96
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3.95
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3.88
3.87
3.86
3.86
3.85
3.83
2.93
2.91
2.89
2.19
2.18
2.17
2.16
2.15
2.14
MeO2C
S
O
O
7c
2.06
2.05
1.00
1.96
2.97
1.99
2.05
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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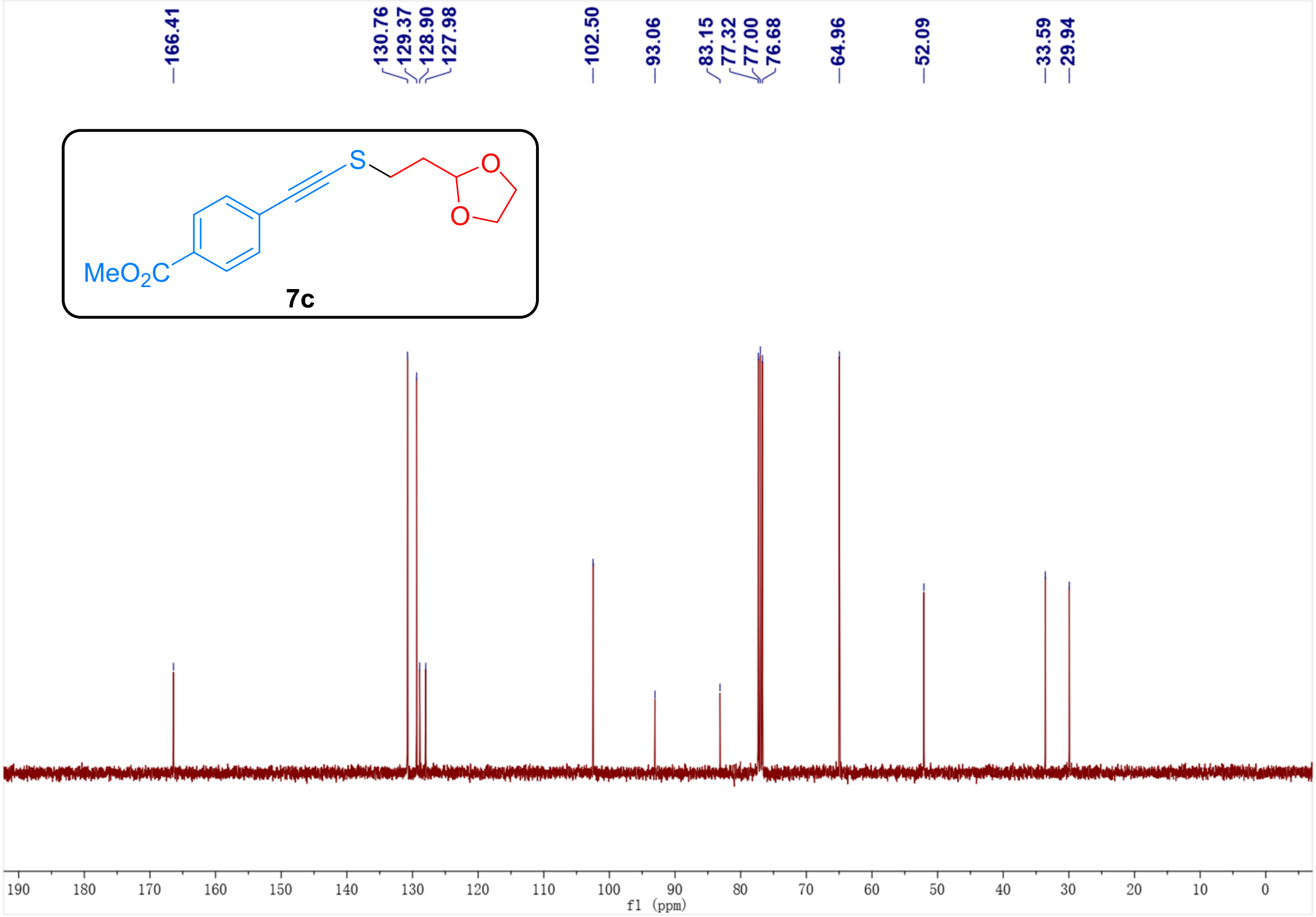
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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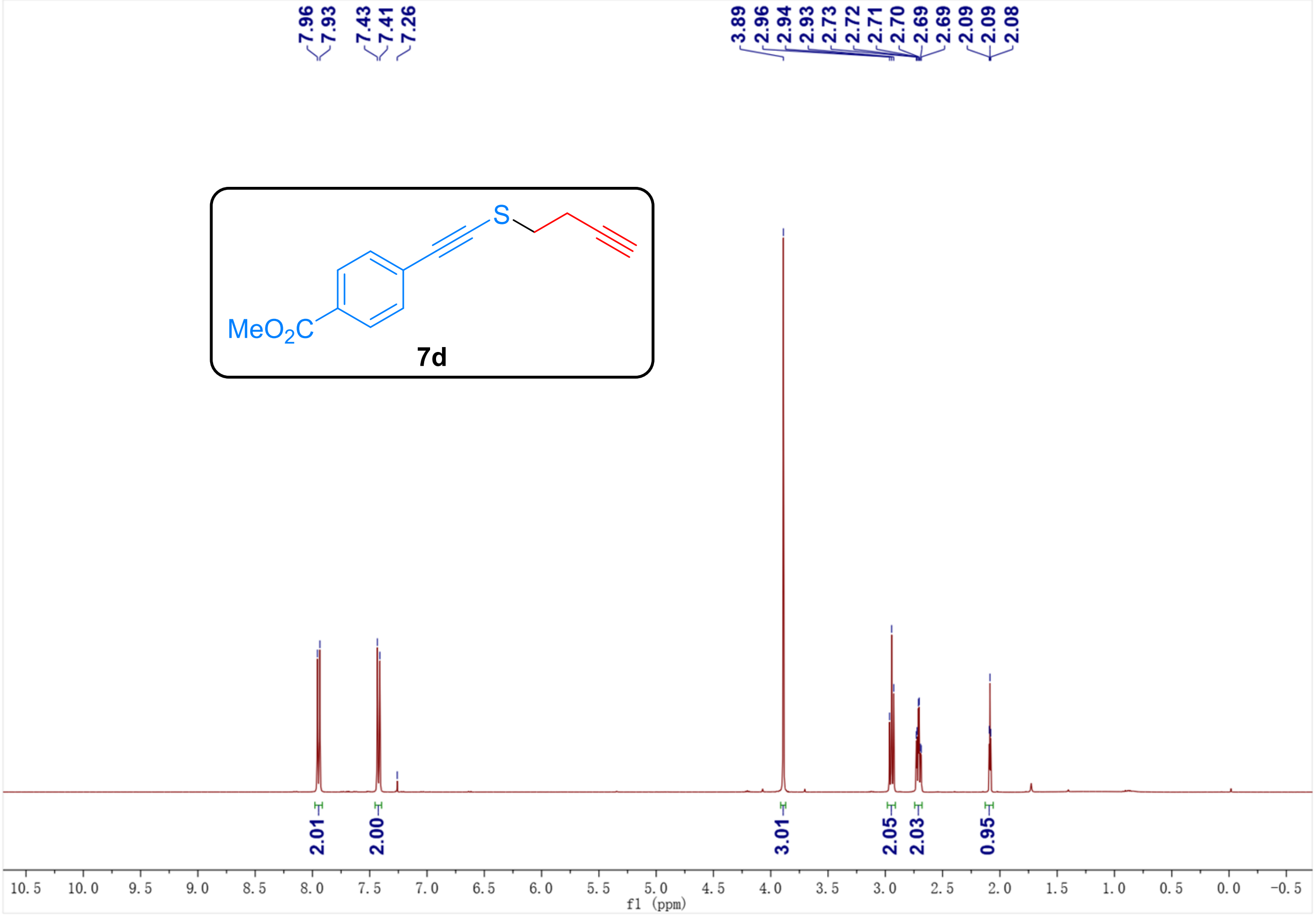
77.00
76.68
64.96
52.09
33.59
29.94
MeO2C
S
O
O
7c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.89
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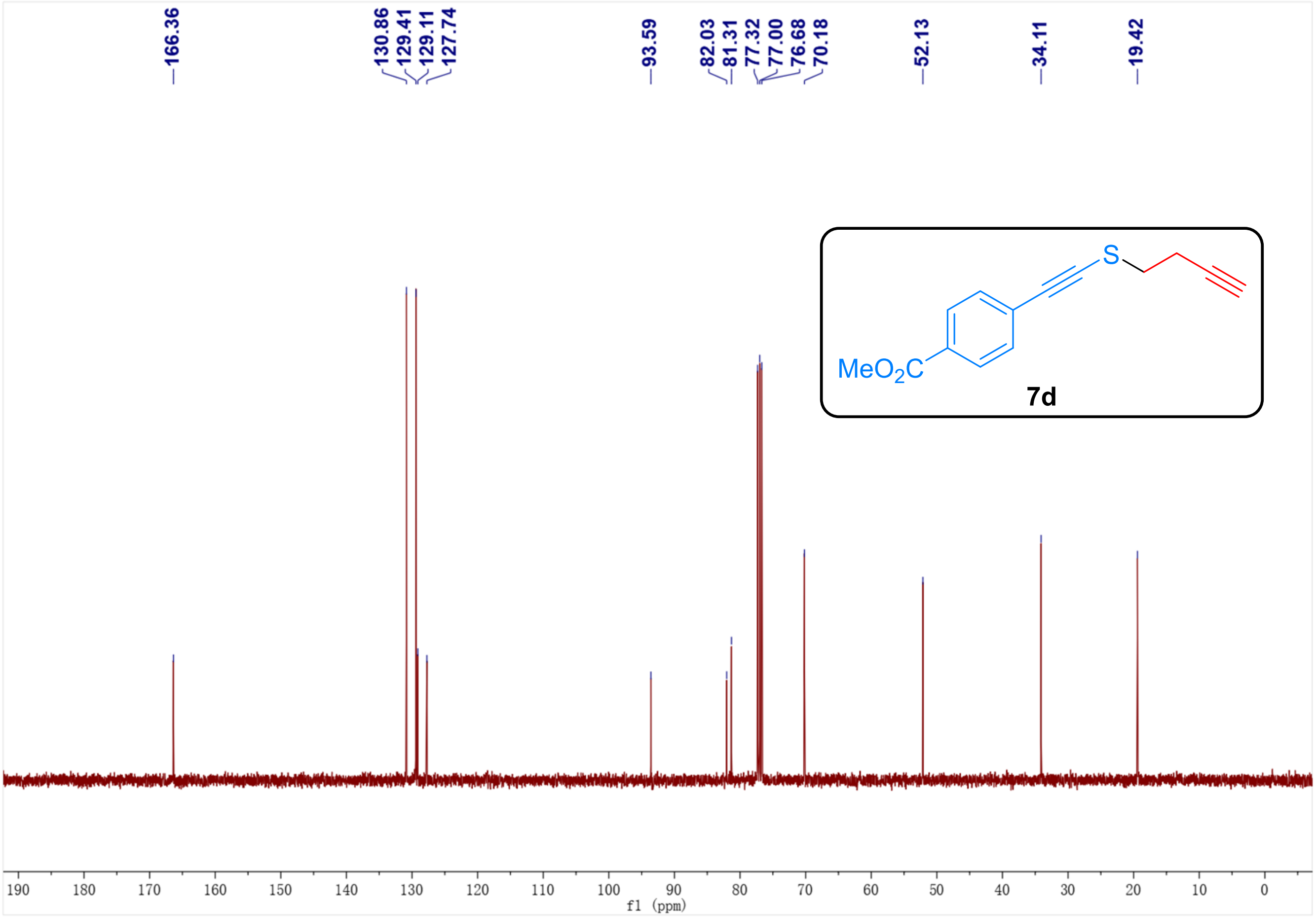
2.94
2.93
2.73
2.72
2.71
2.70
2.69
2.69
2.09
2.09
2.08
MeO$_2$C
S
7d
2.01
2.00
3.01
2.05
2.03
0.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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93.59
82.03
81.31
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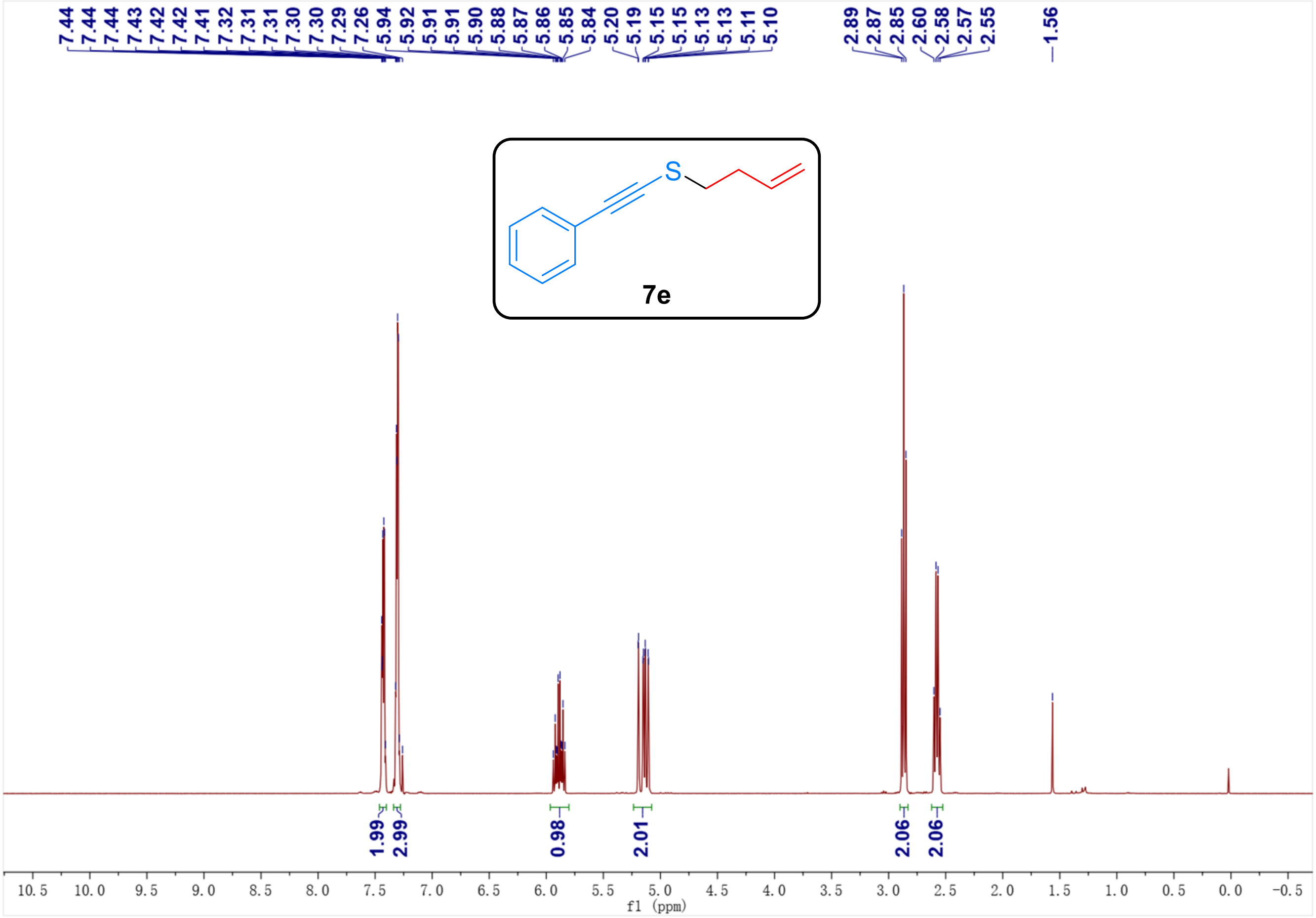
77.00
76.68
70.18
52.13
34.11
19.42
MeO$_2$C
S
7d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.31
7.30
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7.29
7.26
5.94
5.92
5.91
5.91
5.90
5.88
5.87
5.86
5.85
5.84
5.20
5.19
5.15
5.15
5.13
5.13
5.11
5.10
2.89
2.87
2.85
2.60
2.58
2.57
2.55
1.56
S
7e
1.99
2.99
0.98
2.01
2.06
2.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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2.0
1.5
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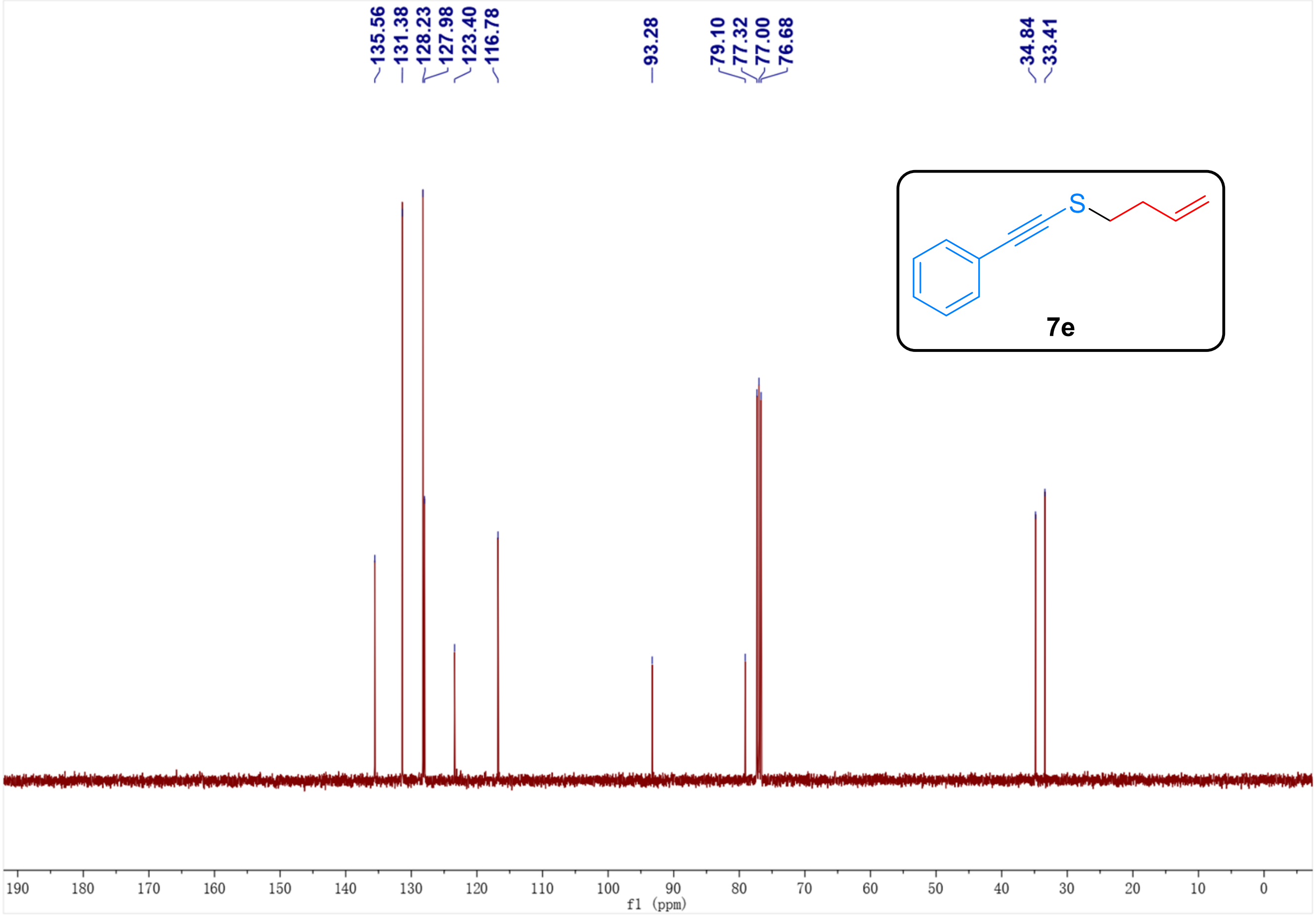
0.0
-0.5
f1 (ppm)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77.00
76.68
34.84
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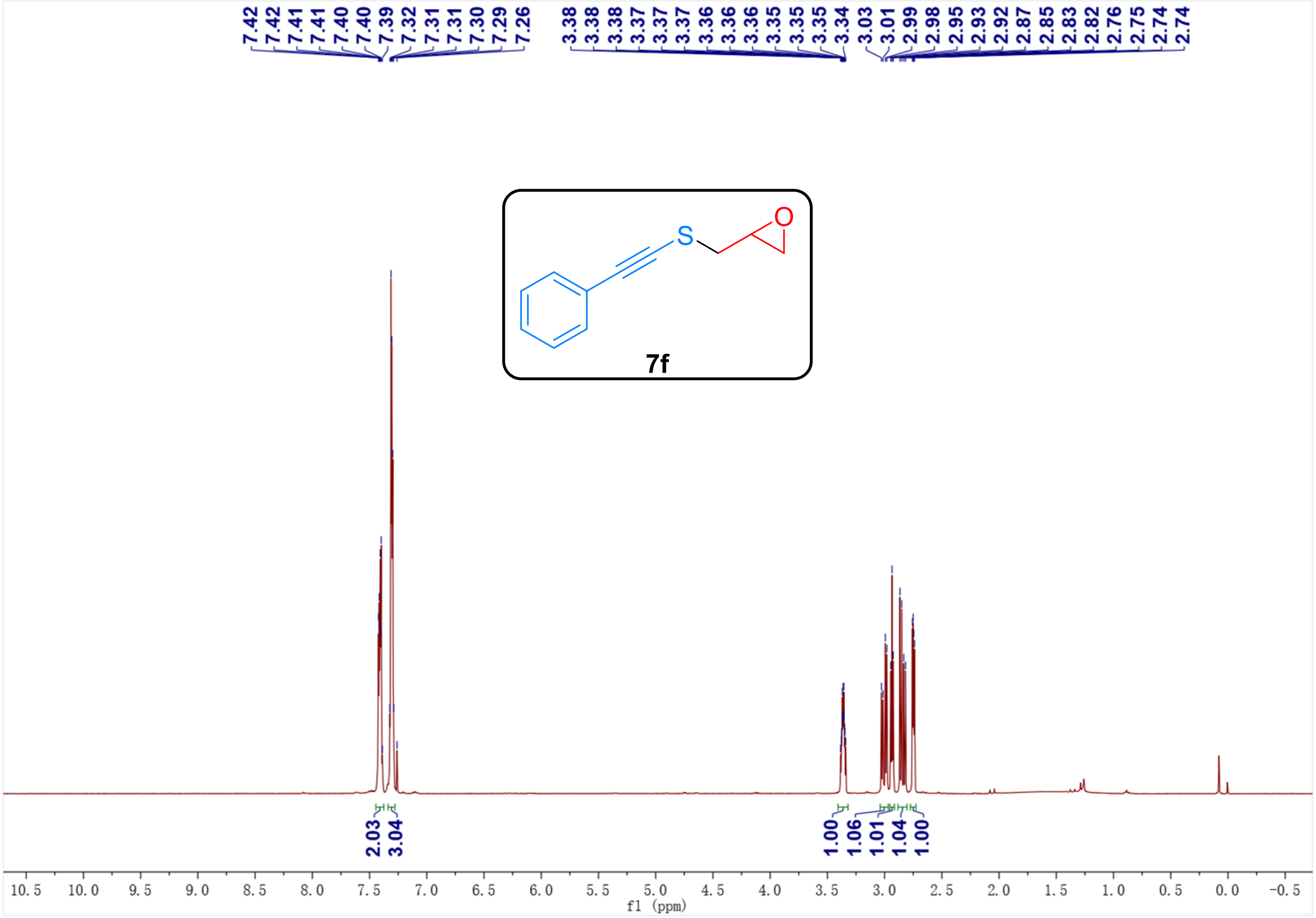
S
7e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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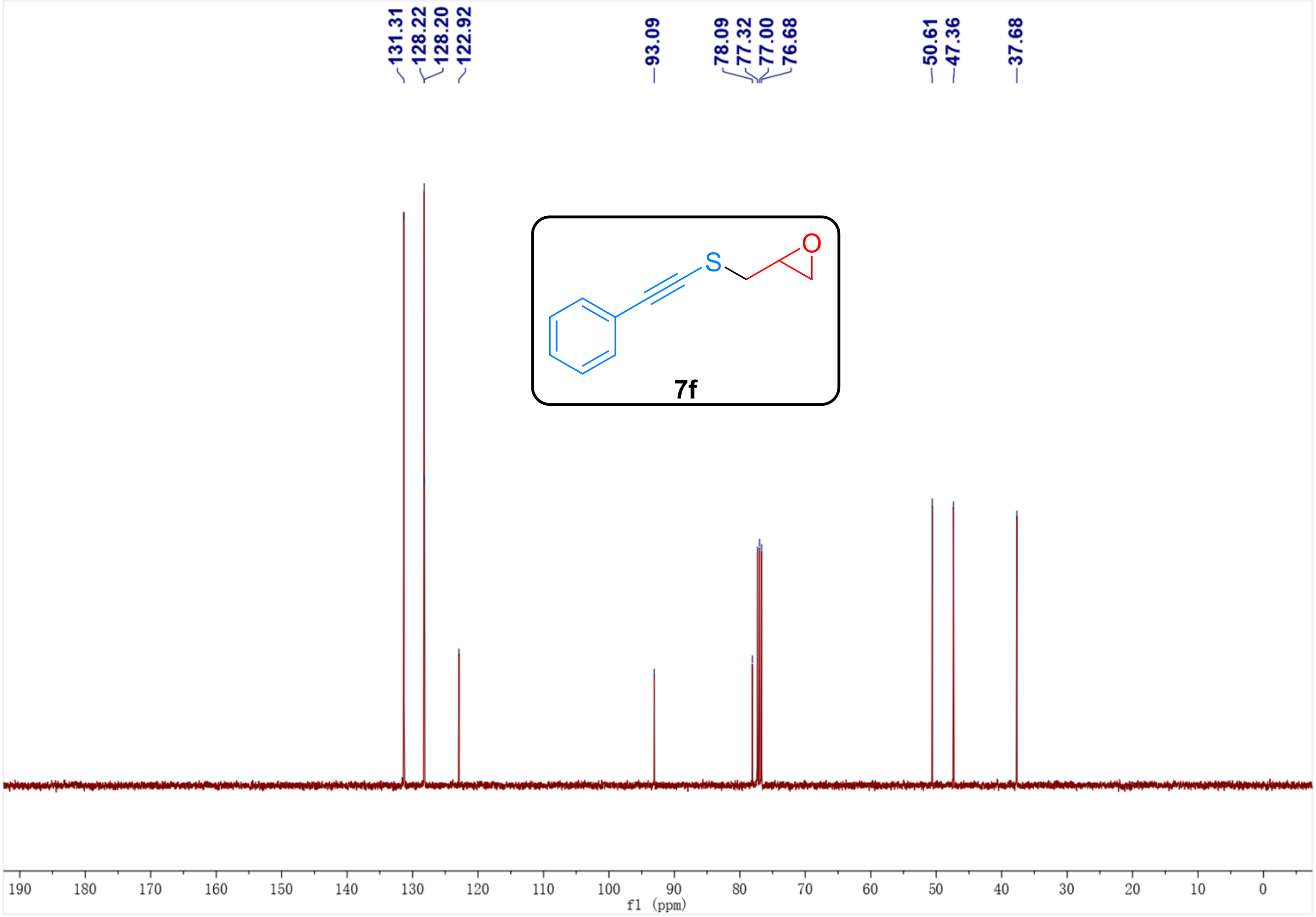
7.31
7.31
7.30
7.29
7.26
3.38
3.38
3.38
3.37
3.37
3.37
3.36
3.36
3.36
3.35
3.35
3.35
3.34
3.03
3.01
2.99
2.98
2.95
2.93
2.92
2.87
2.85
2.83
2.82
2.76
2.75
2.74
2.74
S
O
7f
2.03
3.04
1.00
1.06
1.01
1.04
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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78.09
77.32
77.00
76.68
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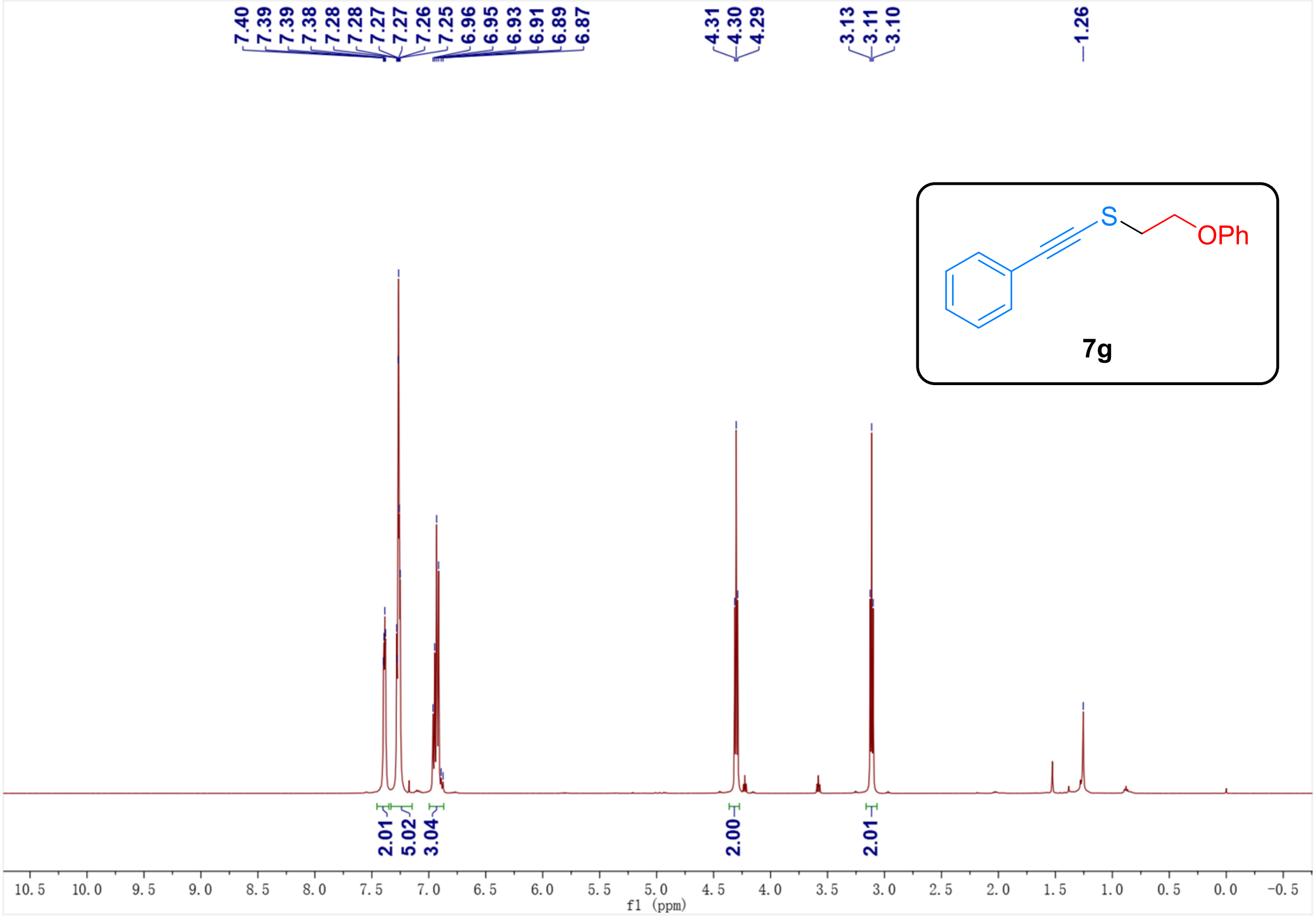
47.36
37.68
S
O
7f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.26
7.25
6.96
6.95
6.93
6.91
6.89
6.87
4.31
4.30
4.29
3.13
3.11
3.10
1.26
S
OPh
7g
2.01
5.02
3.04
2.00
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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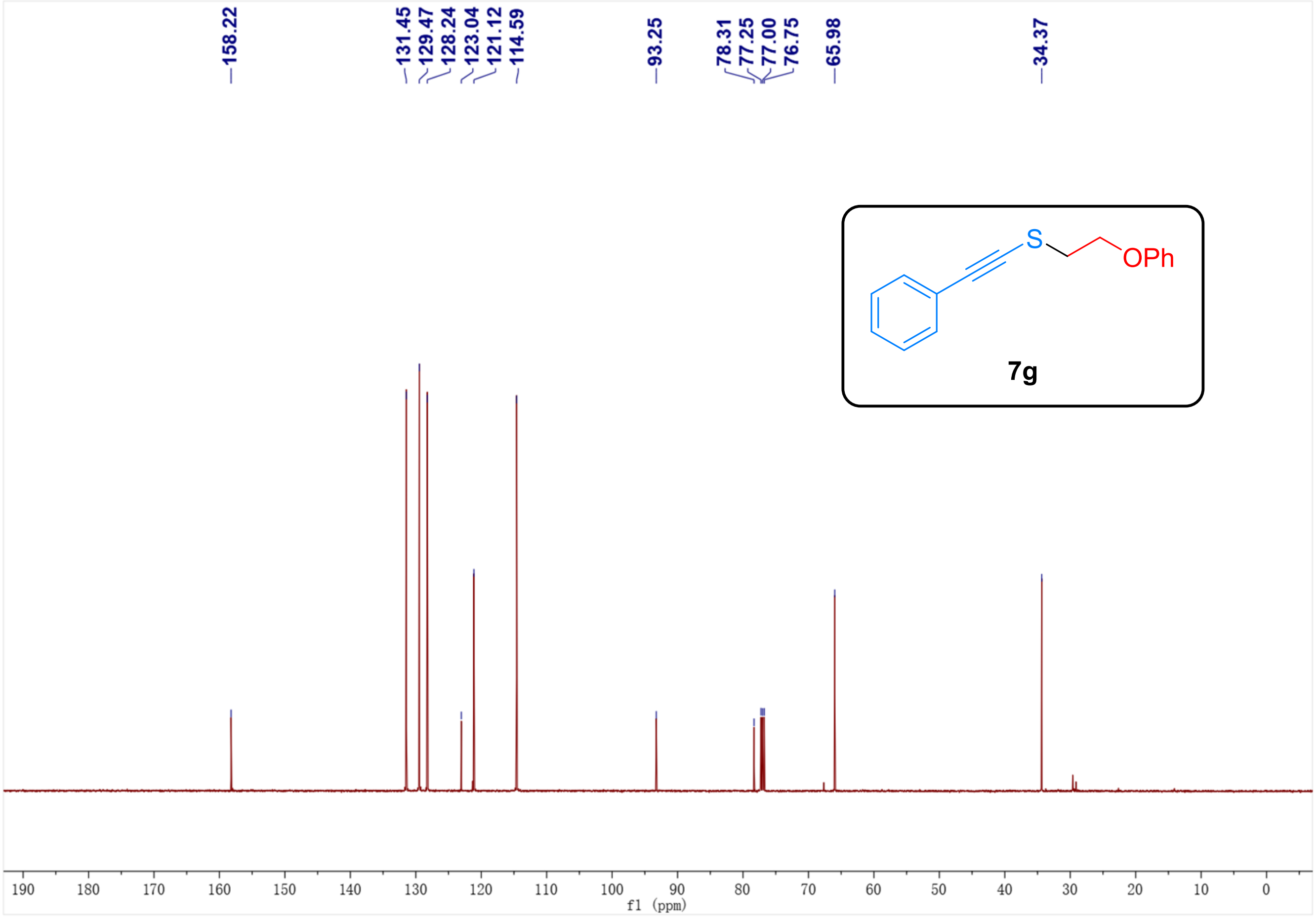
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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121.12
114.59
93.25
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77.25
77.00
76.75
65.98
34.37
S
OPh
7g
190
180
170
160
150
140
130
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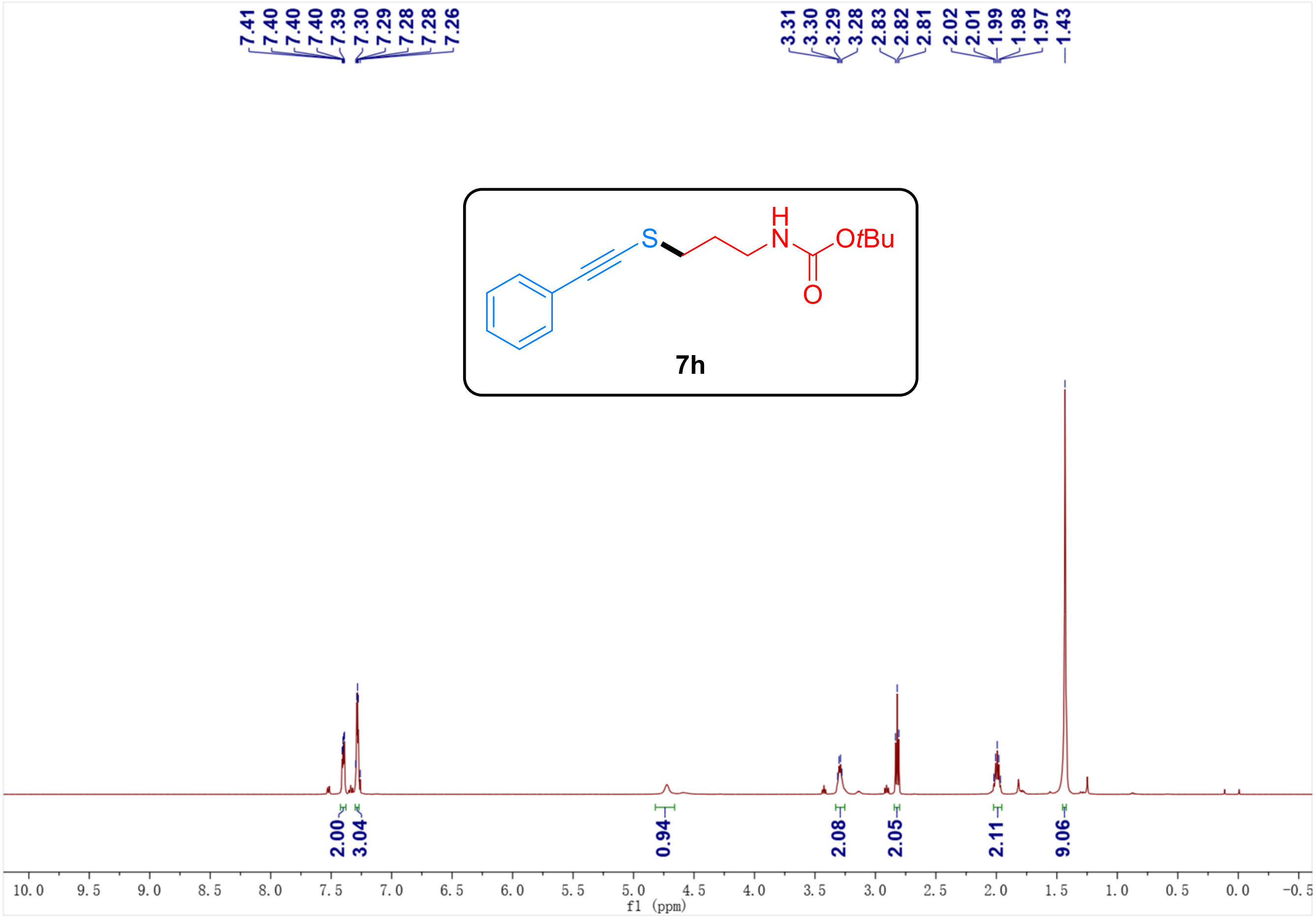
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.28
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7.26
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3.30
3.29
3.28
2.83
2.82
2.81
2.02
2.01
1.99
1.98
1.97
1.43
S
H
N
OtBu
O
7h
2.00
3.04
0.94
2.08
2.05
2.11
9.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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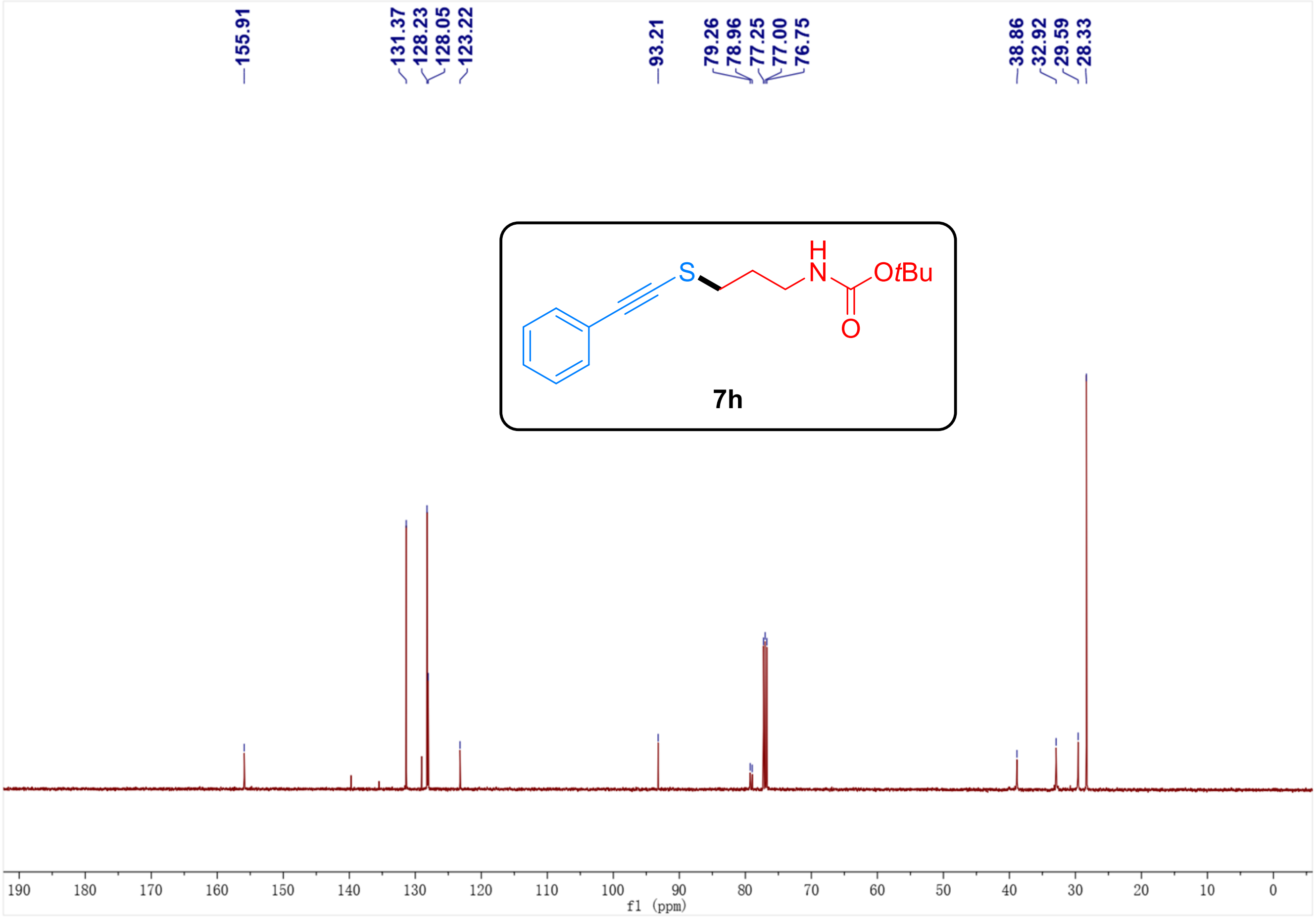
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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77.00
76.75
38.86
32.92
29.59
28.33
S
H
N
OtBu
O
7h
190
180
170
160
150
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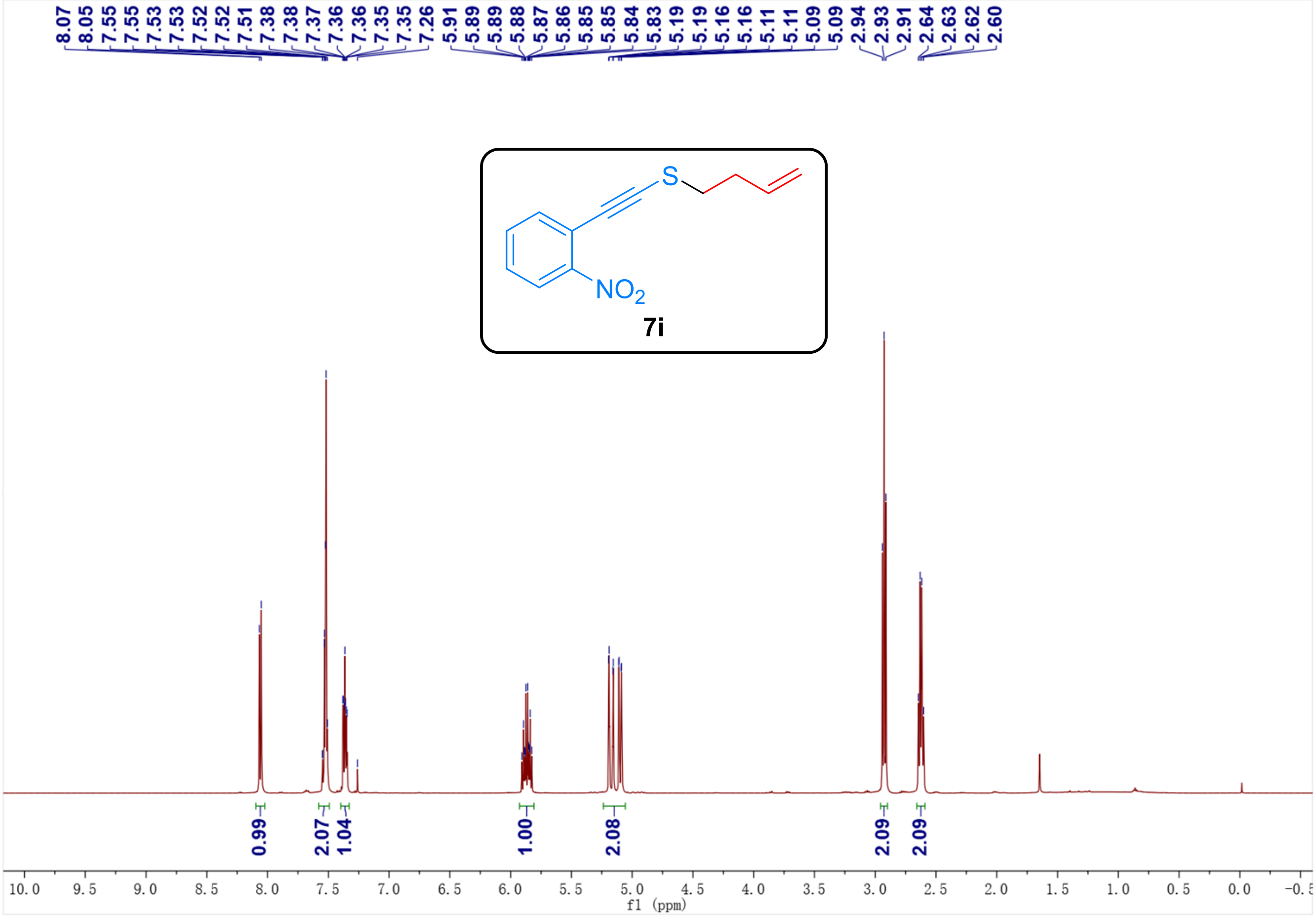
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.36
7.36
7.35
7.26
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5.89
5.89
5.88
5.87
5.86
5.85
5.85
5.84
5.83
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5.11
5.11
5.09
5.09
2.94
2.93
2.91
2.64
2.63
2.62
2.60
S
NO2
7i
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2.07
1.04
1.00
2.08
2.09
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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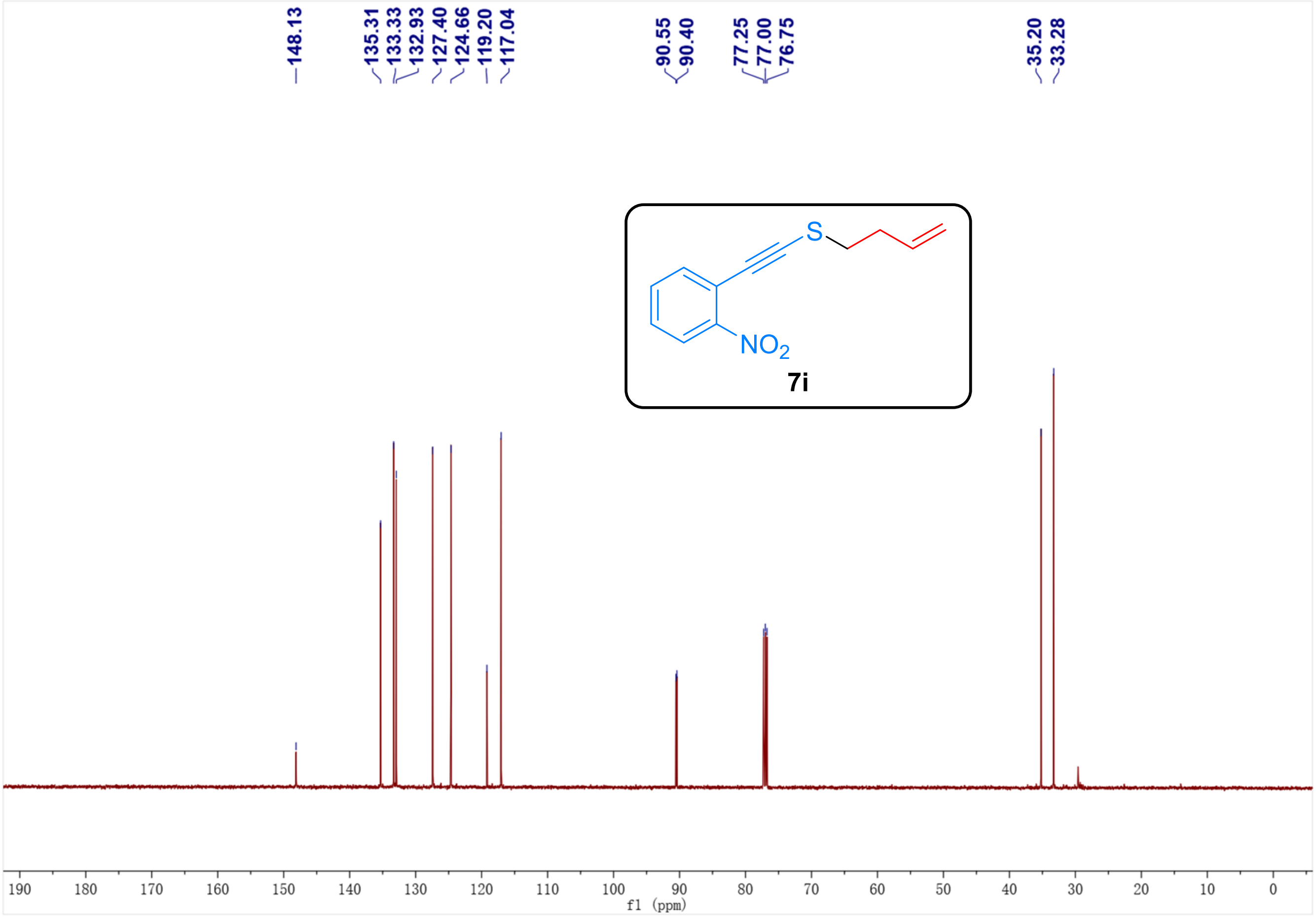
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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90.40
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77.00
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35.20
33.28
S
NO2
7i
190
180
170
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150
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110
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90
80
70
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50
40
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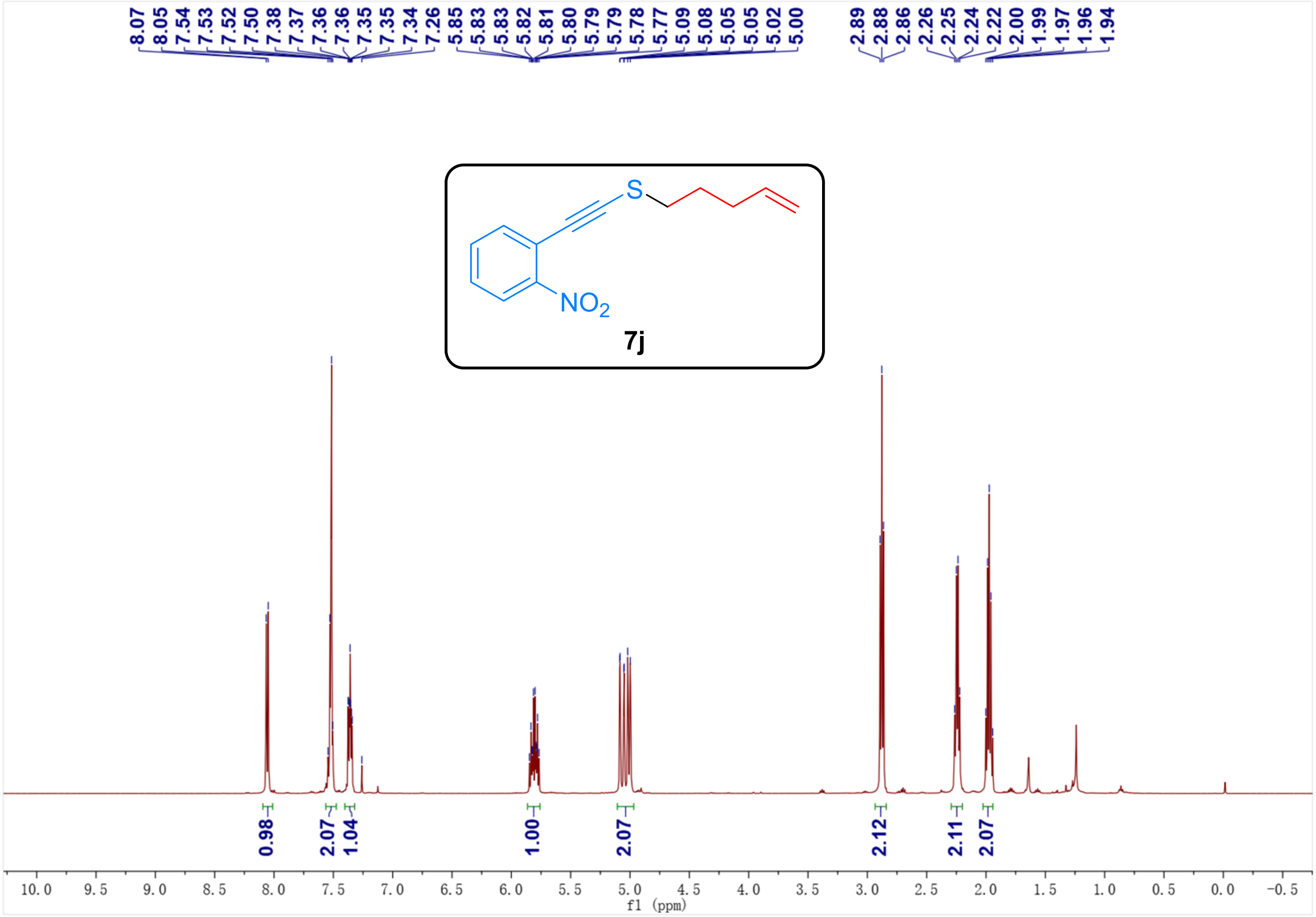
20
10
0
f1 (ppm)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7.34
7.26
5.85
5.83
5.83
5.82
5.81
5.80
5.79
5.79
5.78
5.77
5.09
5.08
5.05
5.05
5.02
5.00
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2.88
2.86
2.26
2.25
2.24
2.22
2.00
1.99
1.97
1.96
1.94
S
NO2
7j
0.98
2.07
1.04
1.00
2.07
2.12
2.11
2.07
10.0
9.5
9.0
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5.0
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2.5
2.0
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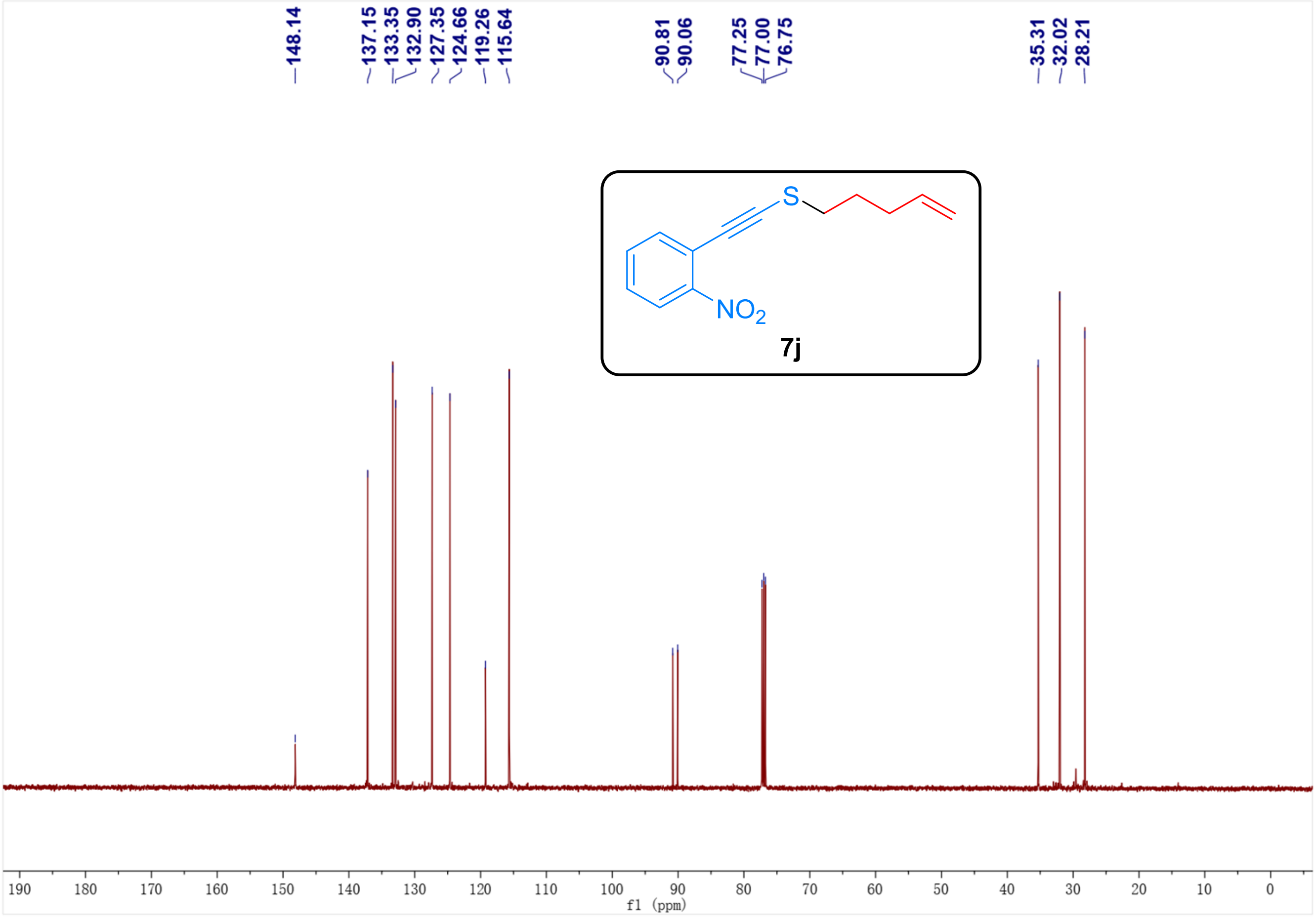
0.5
0.0
-0.5
f1 (ppm)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77.00
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35.31
32.02
28.21
S
NO2
7j
190
180
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110
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90
80
70
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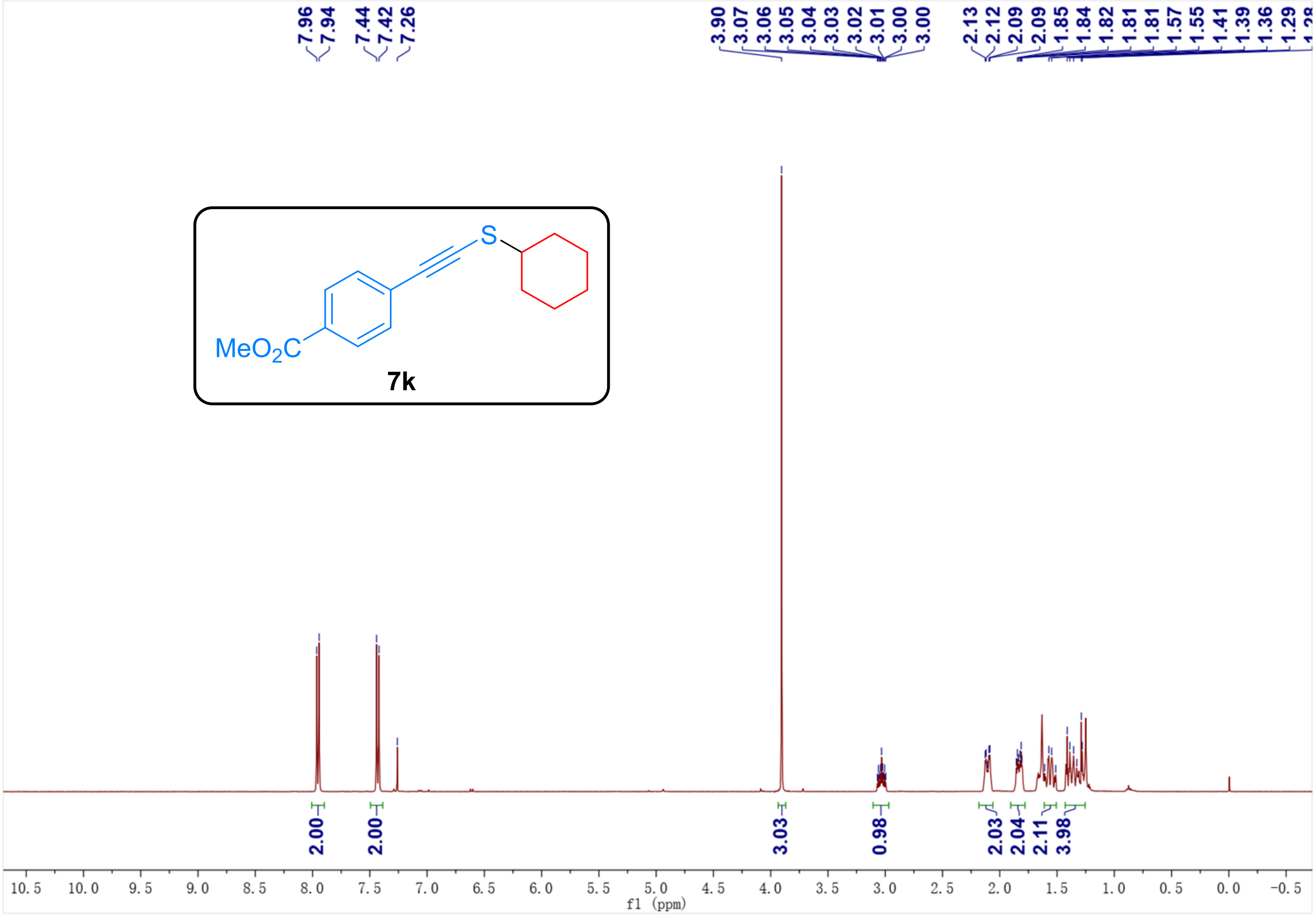
50
40
30
20
10
0
f1 (ppm)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7.42
7.26
3.90
3.07
3.06
3.05
3.04
3.03
3.02
3.01
3.00
3.00
2.13
2.12
2.09
2.09
1.85
1.84
1.82
1.81
1.81
1.57
1.55
1.41
1.39
1.36
1.29
S
MeO$_2$C
7k
2.00
2.00
3.03
0.98
2.03
2.04
2.11
3.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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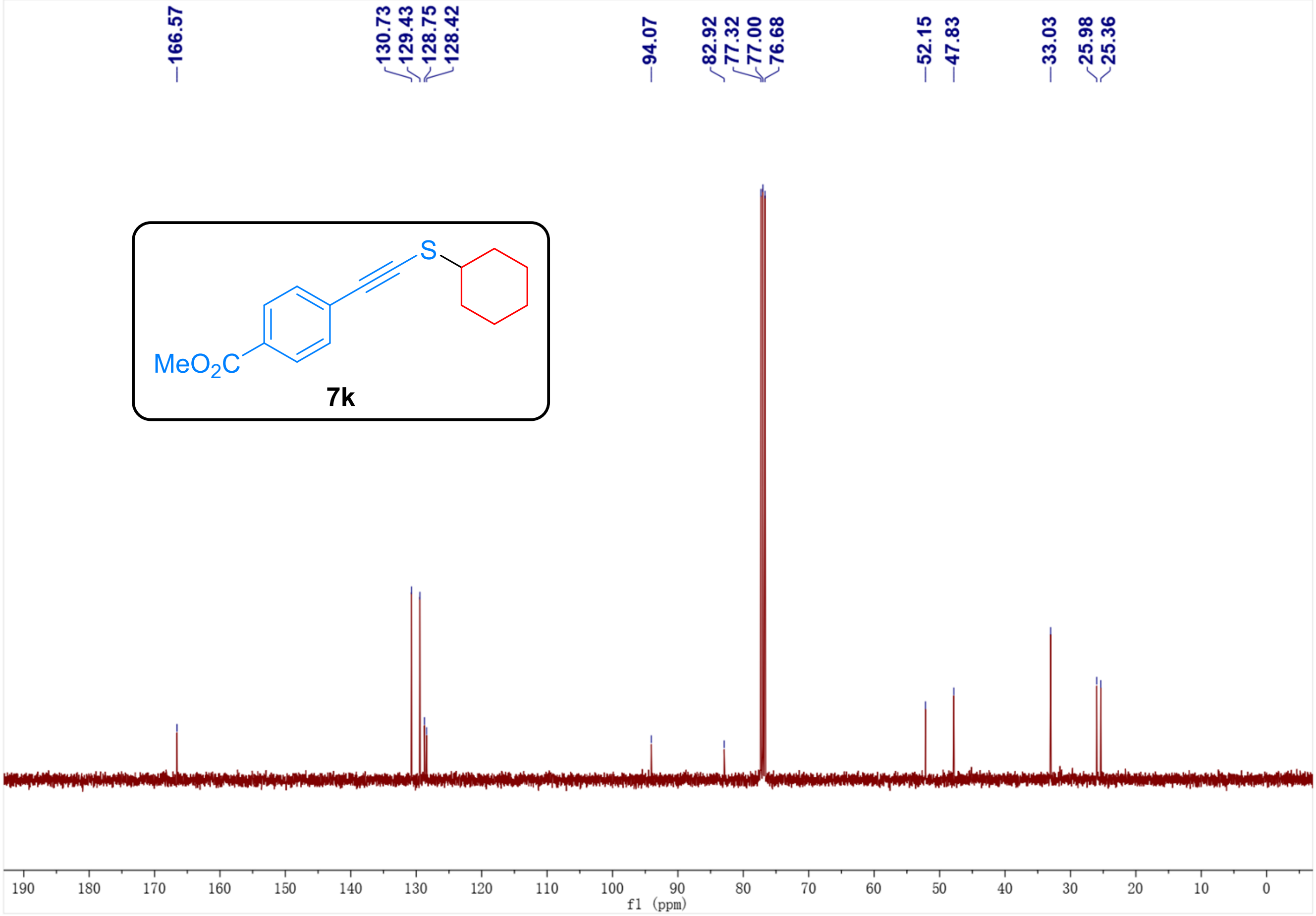
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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94.07
82.92
77.32
77.00
76.68
52.15
47.83
33.03
25.98
25.36
S
MeO$_2$C
7k
190
180
170
160
150
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110
100
90
80
70
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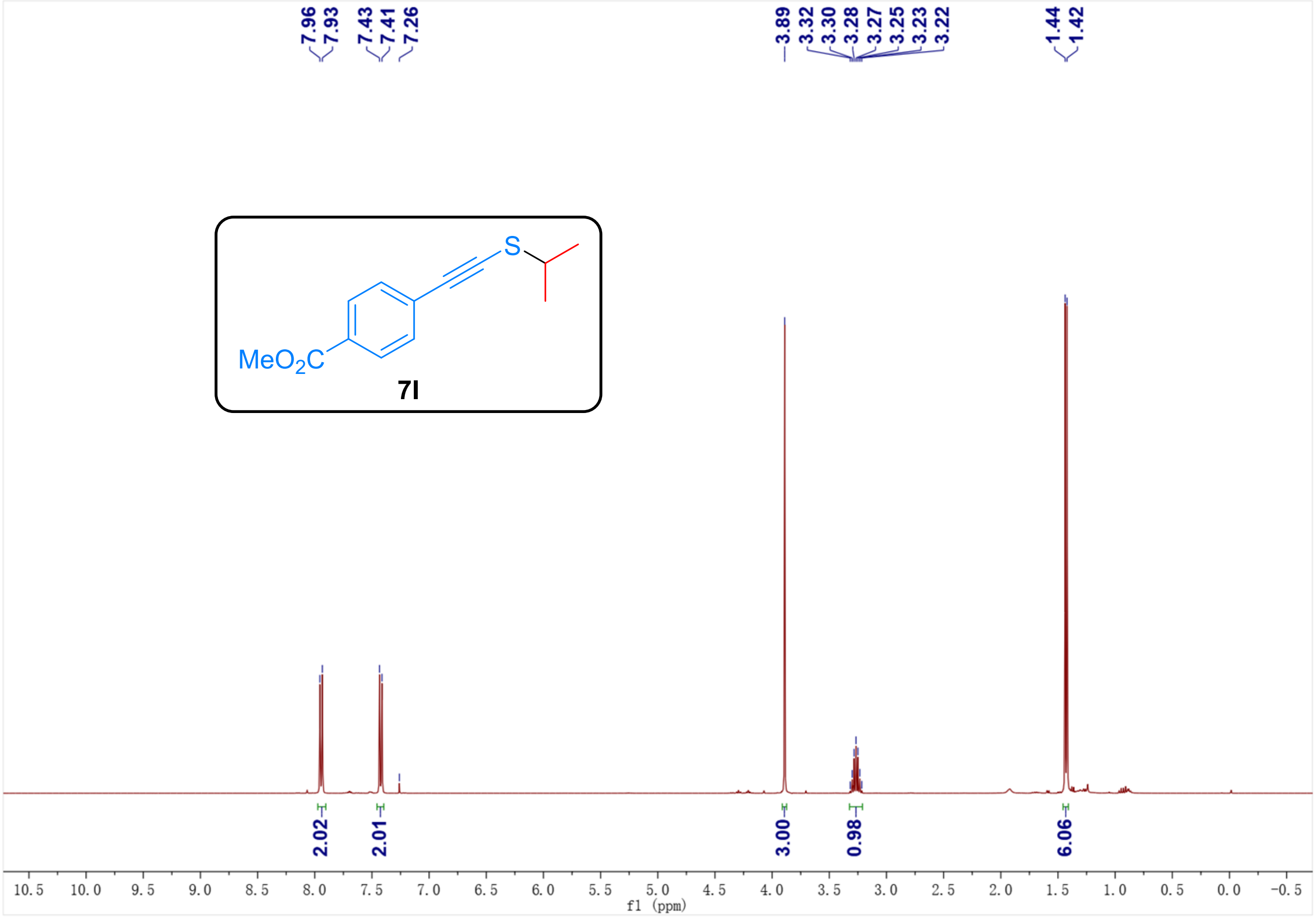
50
40
30
20
10
0
f1 (ppm)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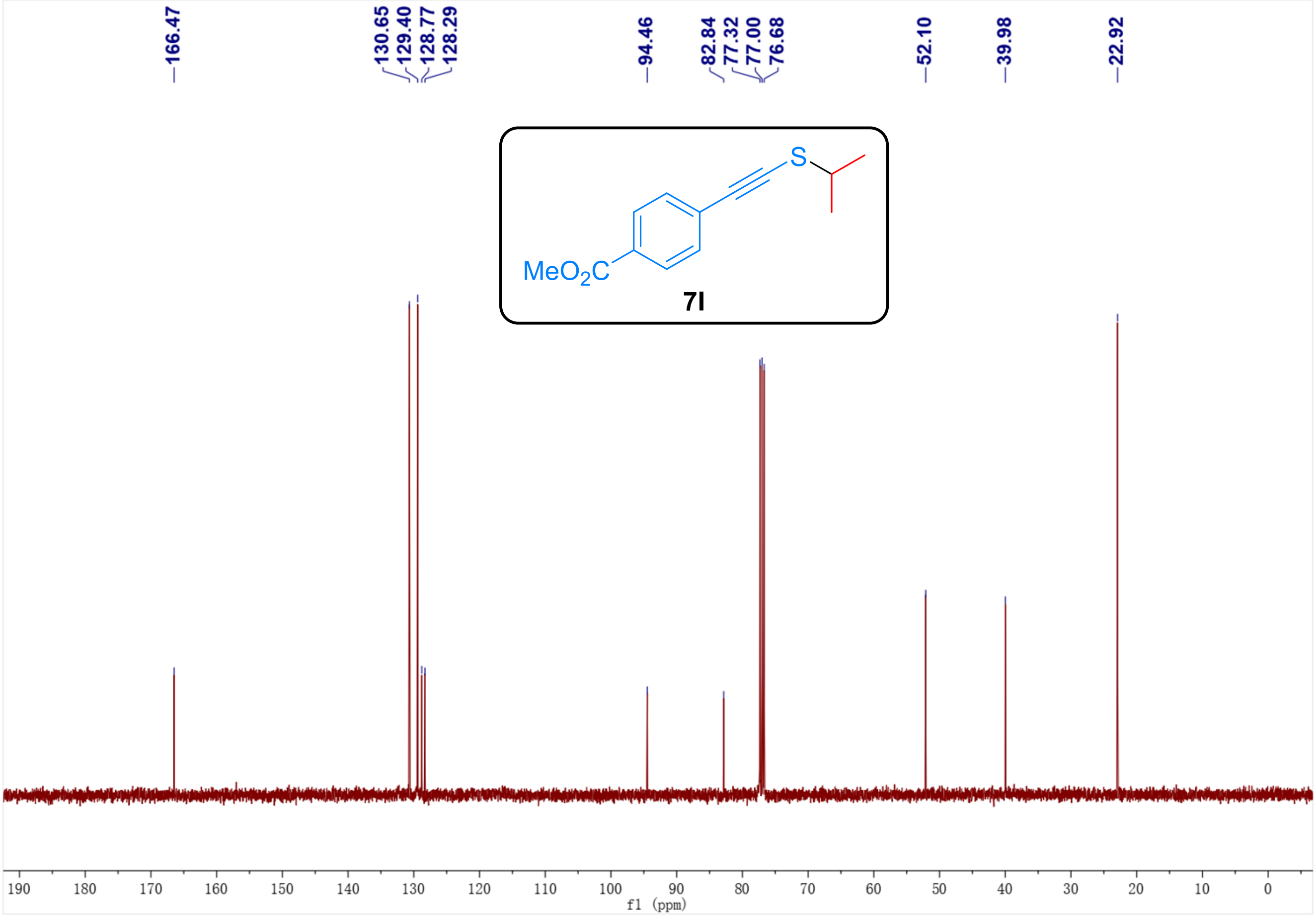
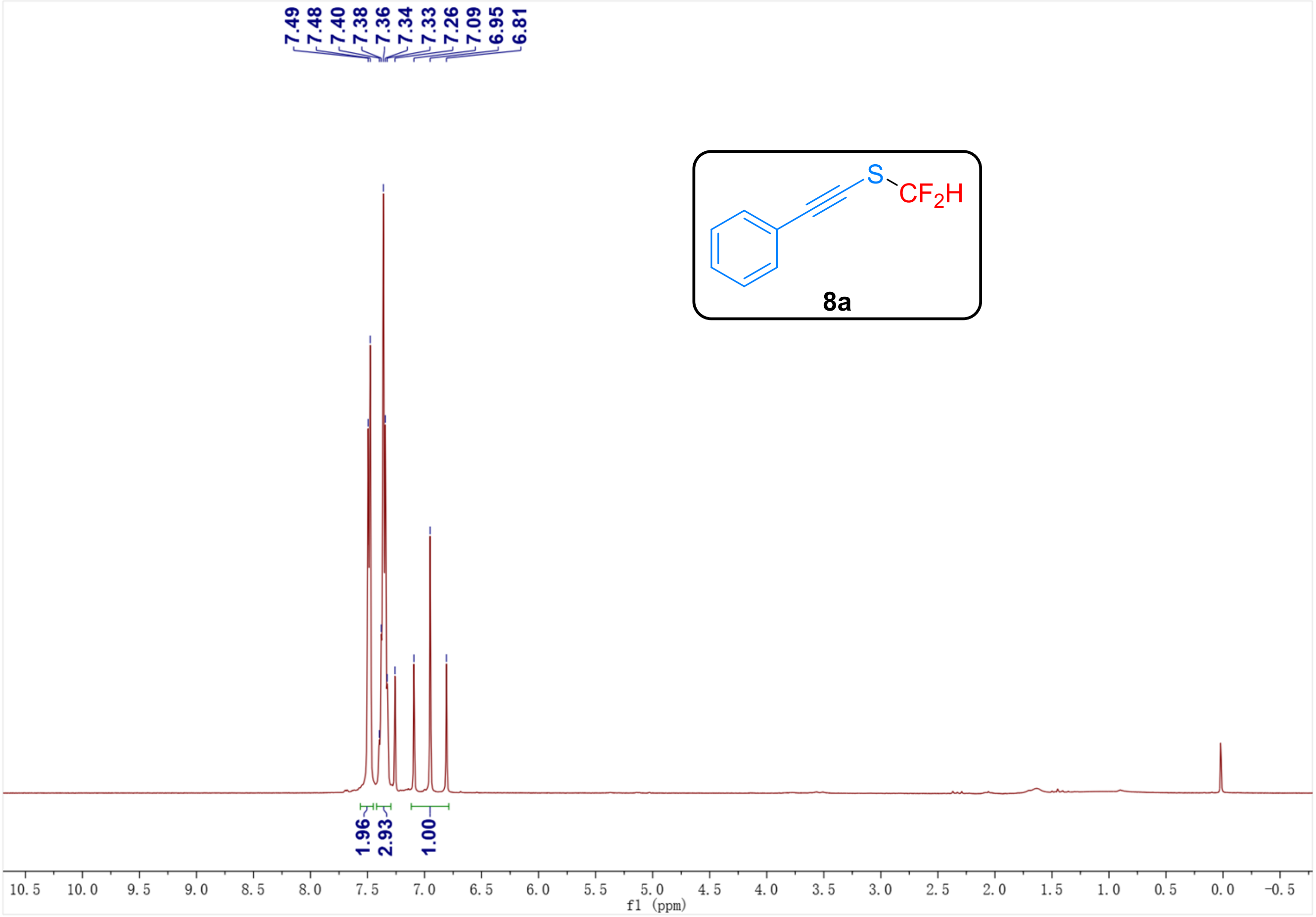
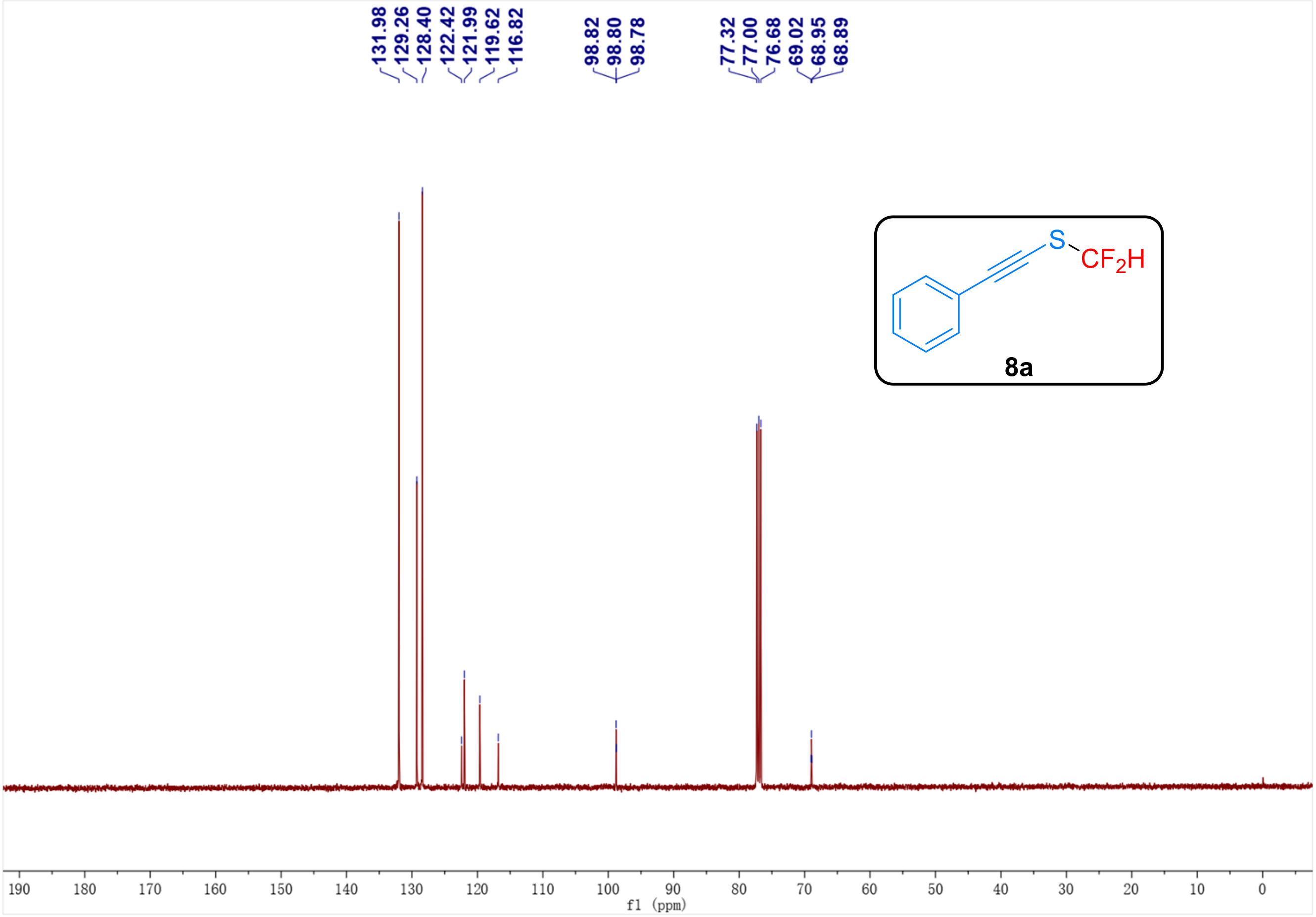
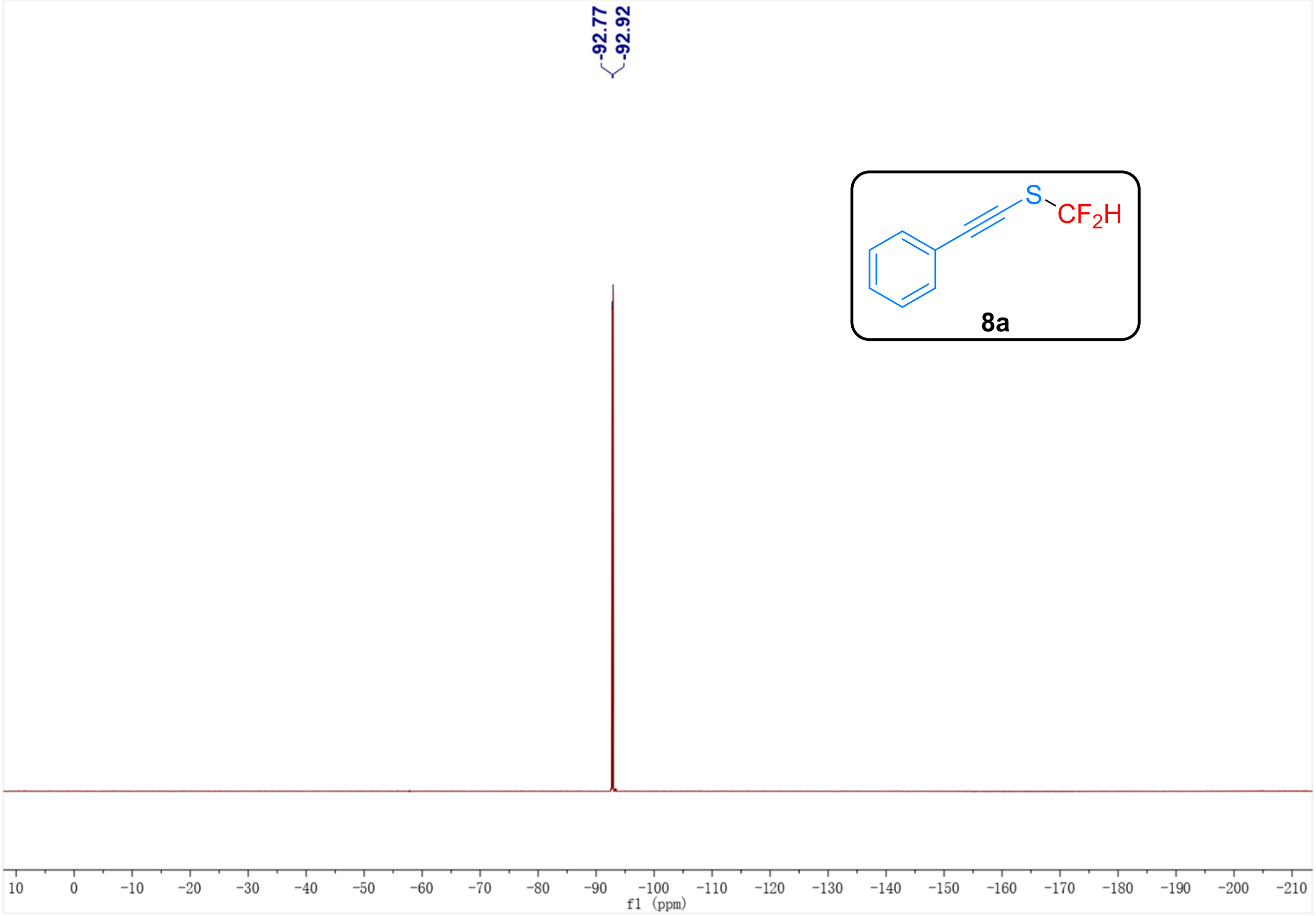
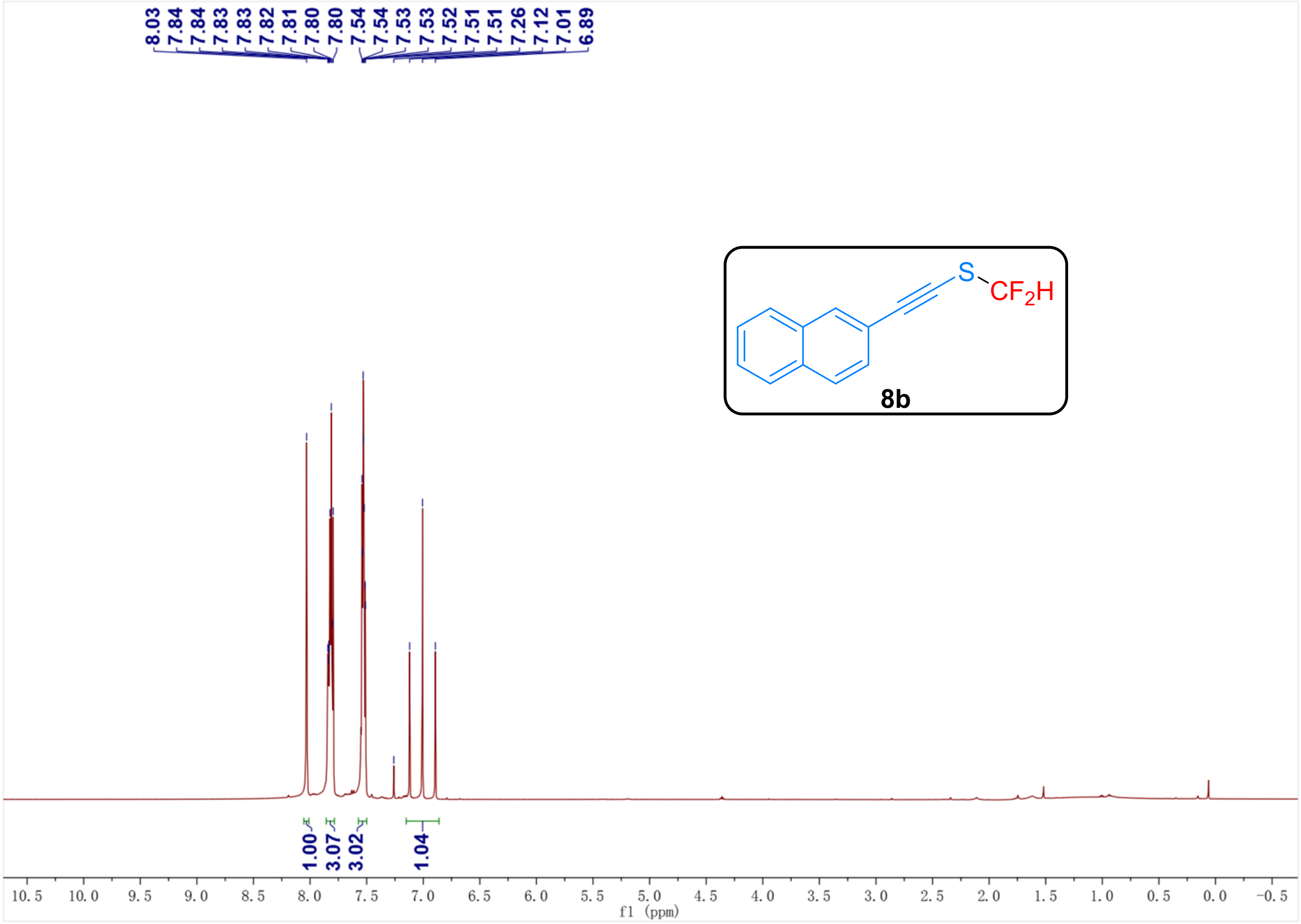
3.30
3.28
3.27
3.25
3.23
3.22
1.44
1.42
MeO$_2$C
S
7l
2.02
2.01
3.00
0.98
6.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

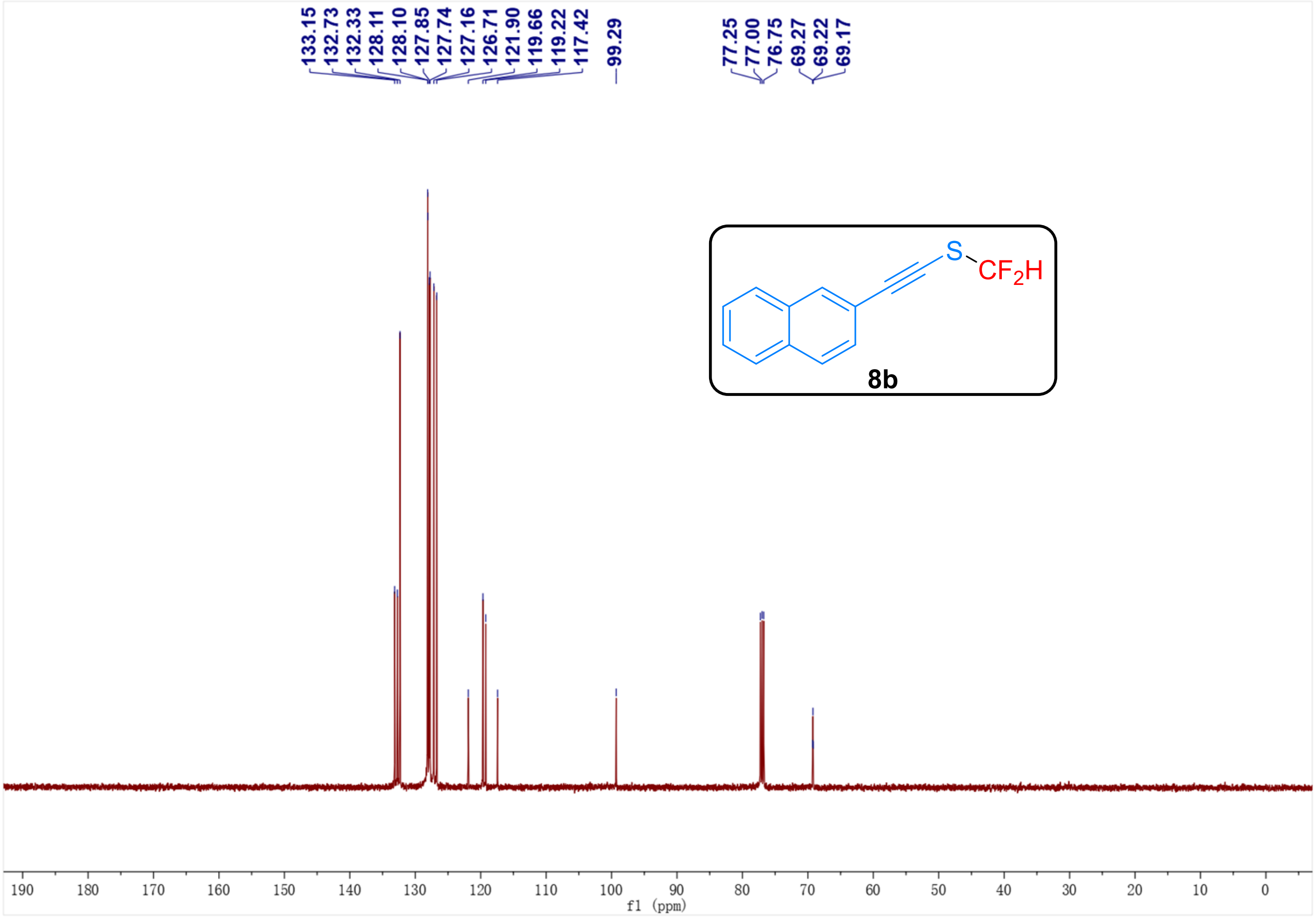

166.47
130.65
129.40
128.77
128.29
94.46
82.84
77.32
77.00
76.68
52.10
39.98
22.92
MeO$_2$C
S
7l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

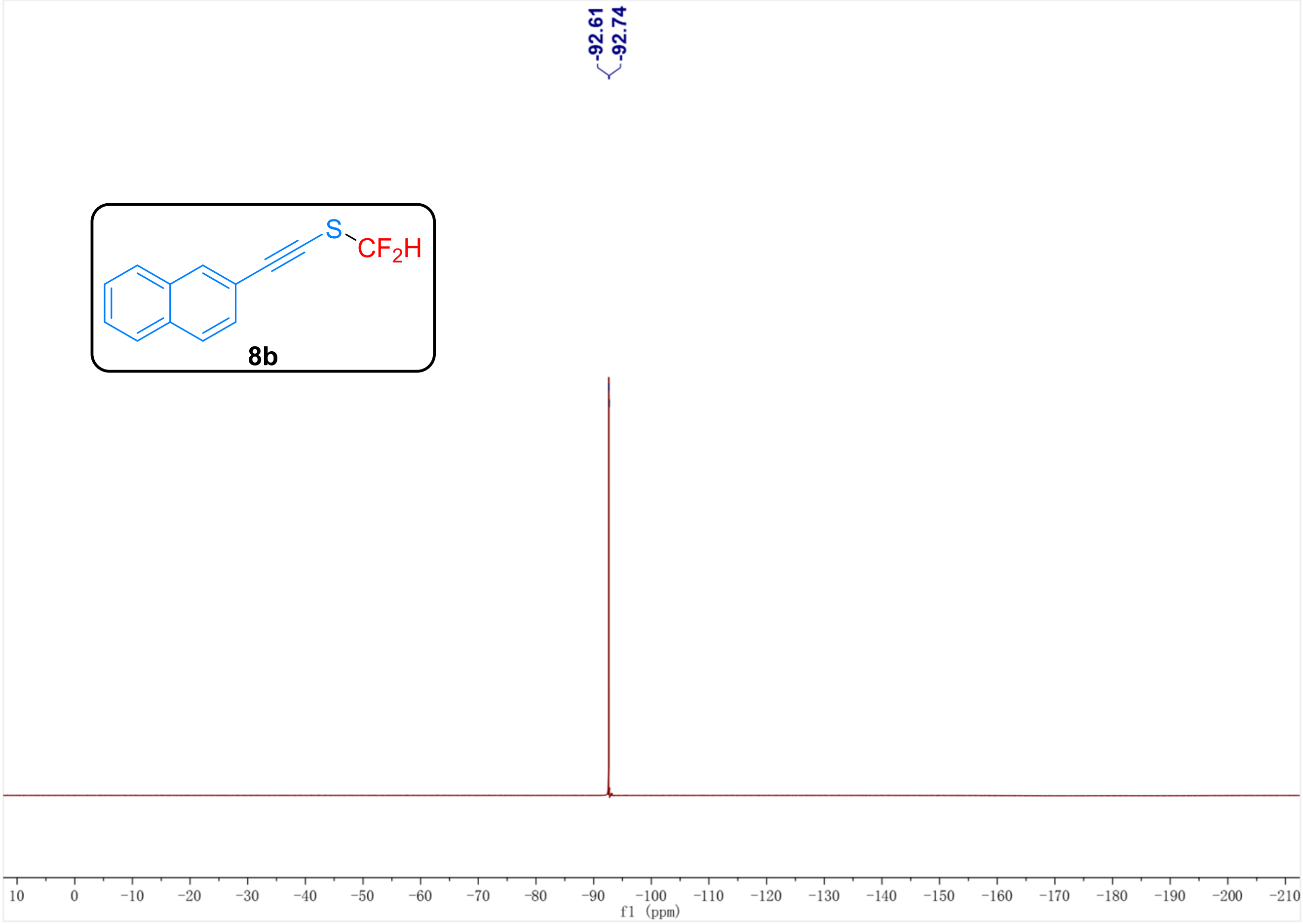

7.49
7.48
7.40
7.38
7.36
7.34
7.33
7.26
7.09
6.95
6.81
S
CF2H
8a
1.96
2.93
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

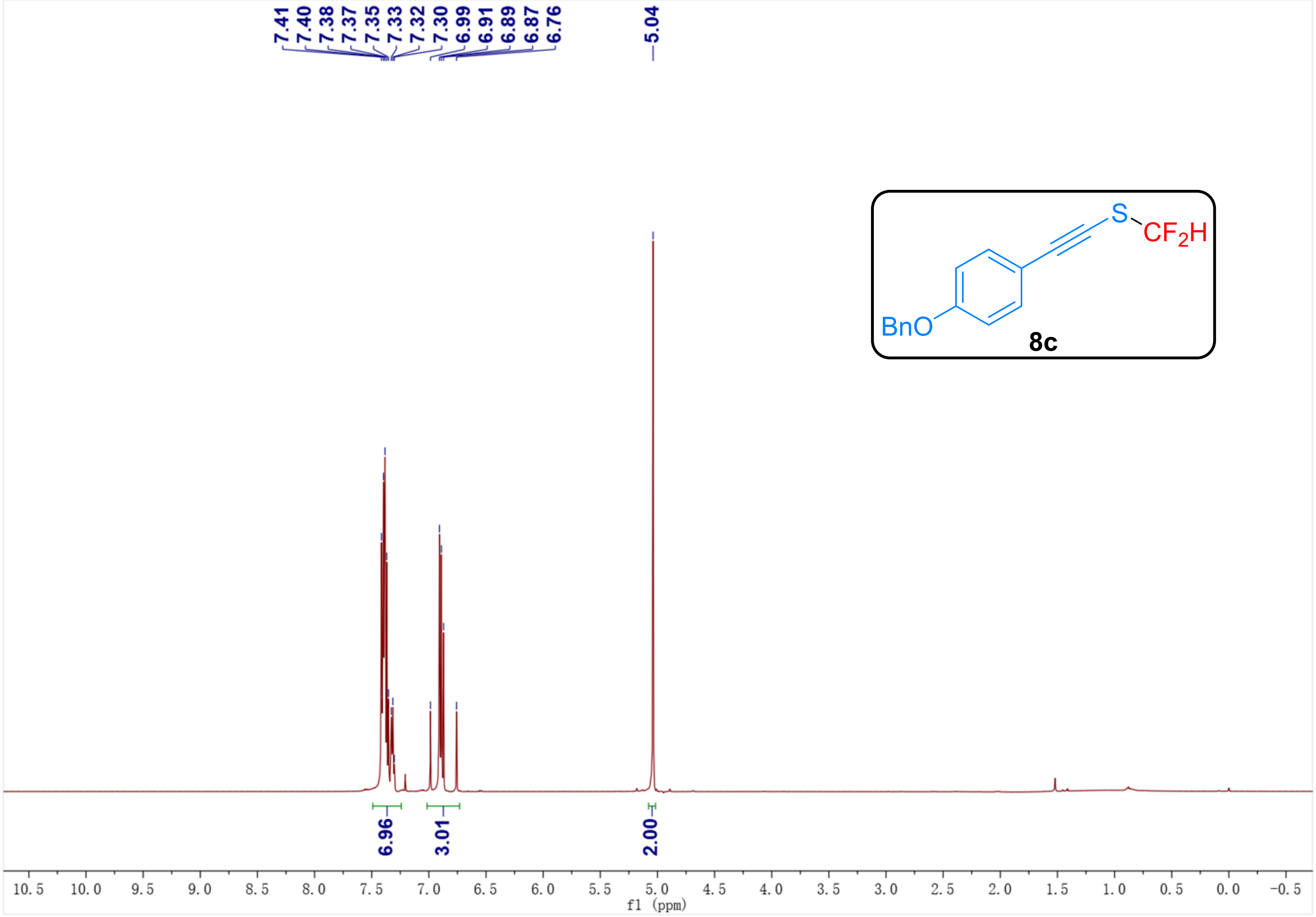

131.98
129.26
128.40
122.42
121.99
119.62
116.82
98.82
98.80
98.78
77.32
77.00
76.68
69.02
68.95
68.89
S
CF2H
8a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

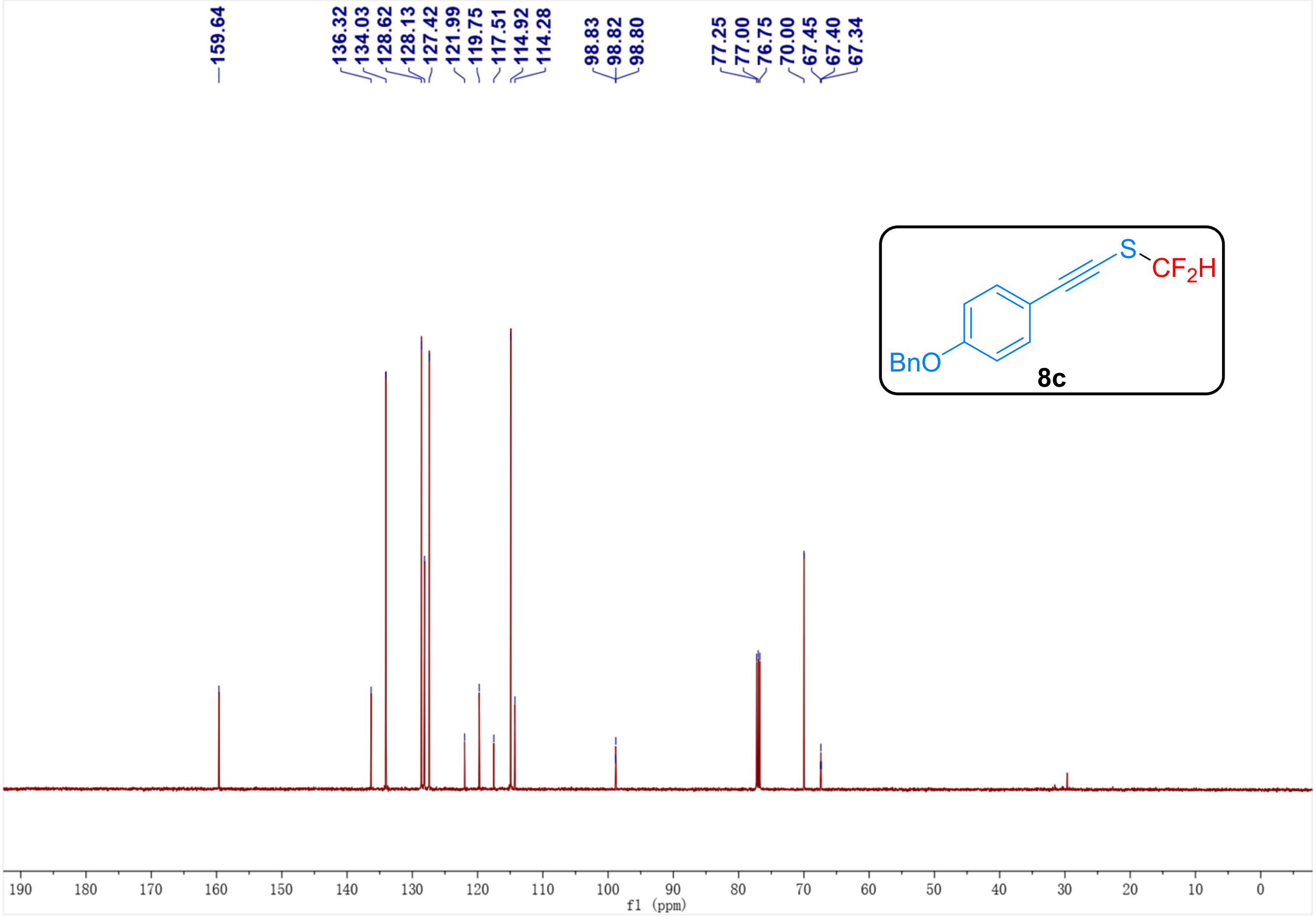

-92.77
-92.92
S
CF$_2$H
8a
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

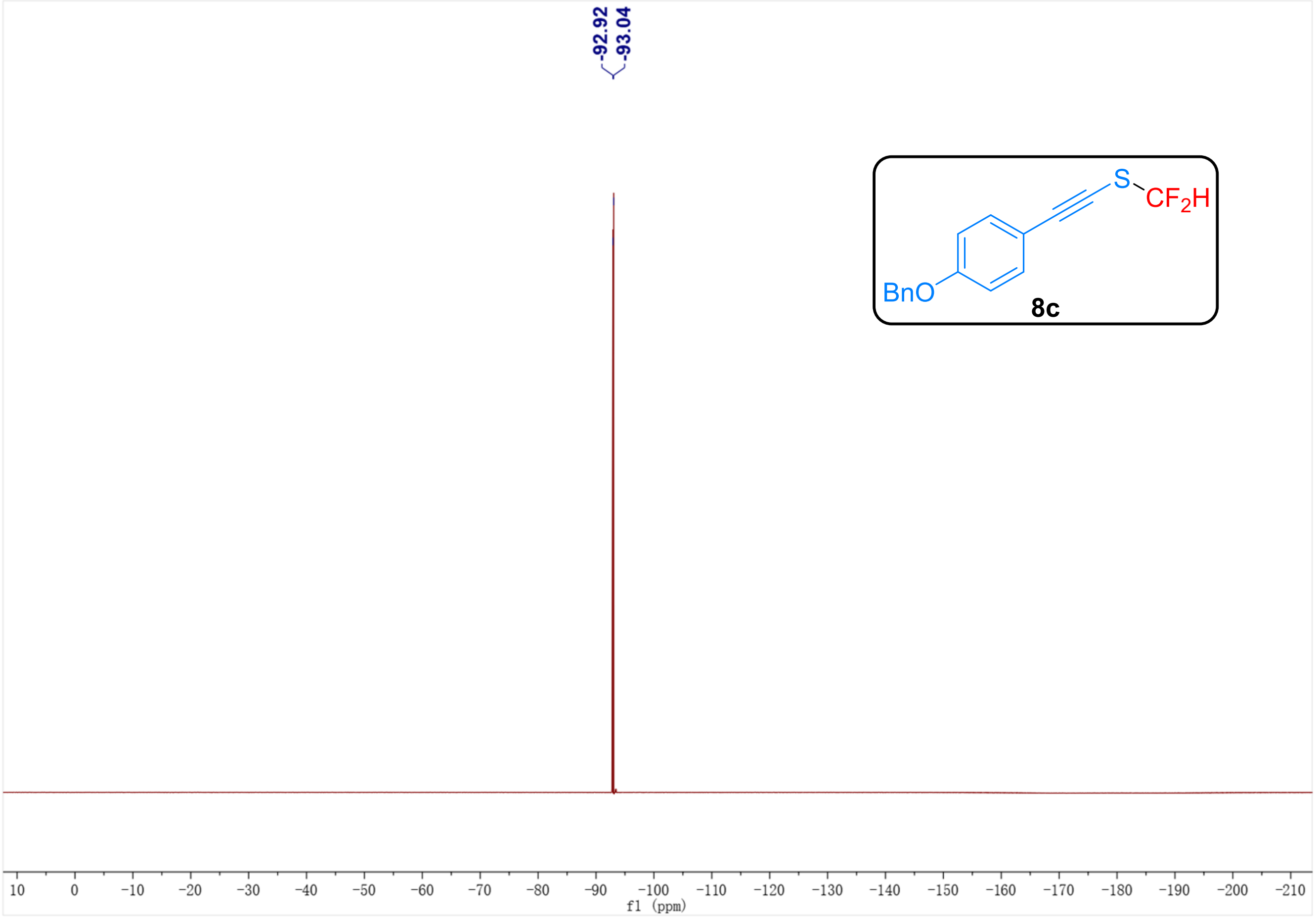

8.03
7.84
7.84
7.83
7.83
7.82
7.81
7.80
7.80
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.26
7.12
7.01
6.89
S
CF$_2$H
8b
1.00
3.07
3.02
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

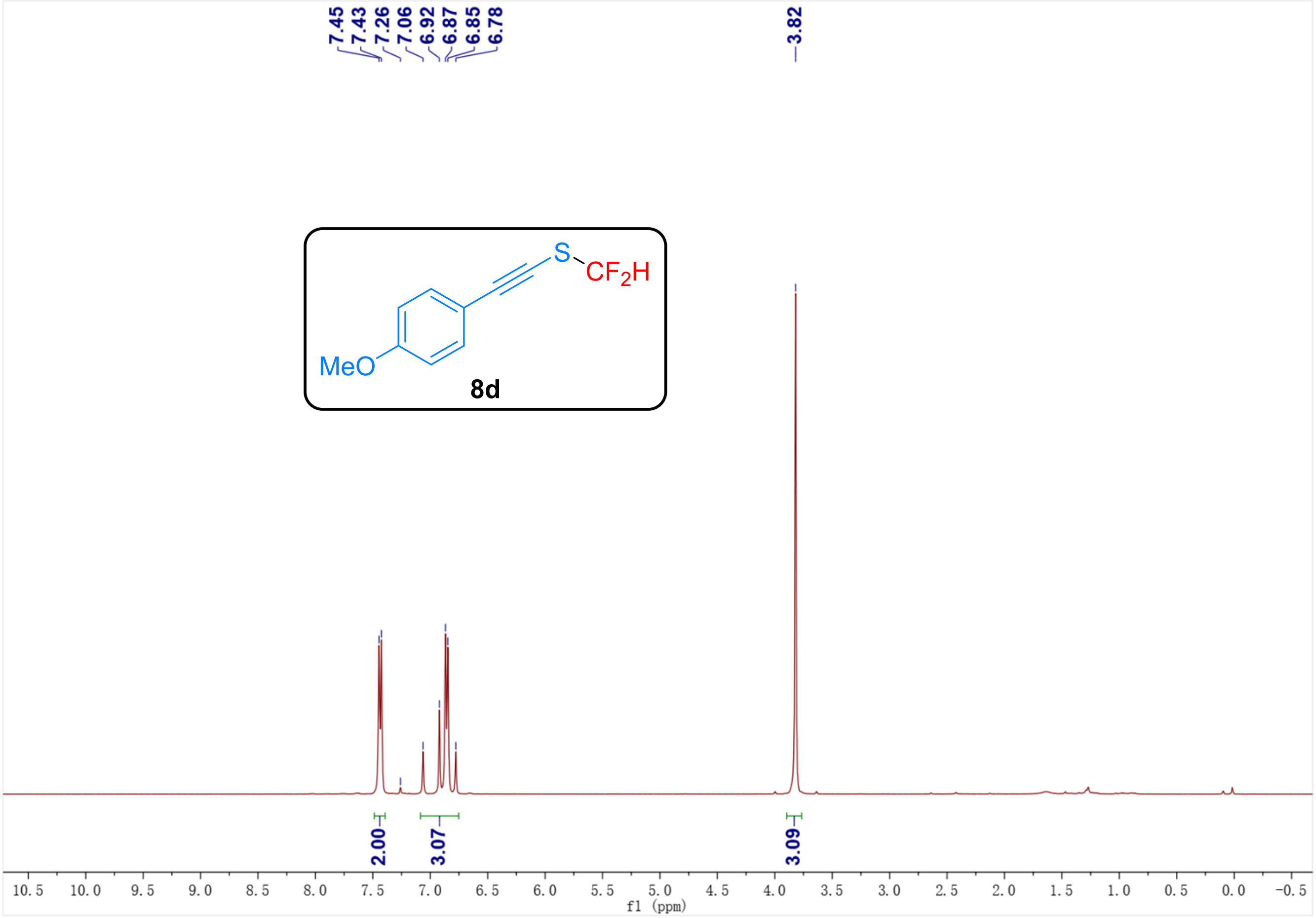

133.15
132.73
132.33
128.11
128.10
127.85
127.74
127.16
126.71
121.90
119.66
119.22
117.42
99.29
77.25
77.00
76.75
69.27
69.22
69.17
S
CF2H
8b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

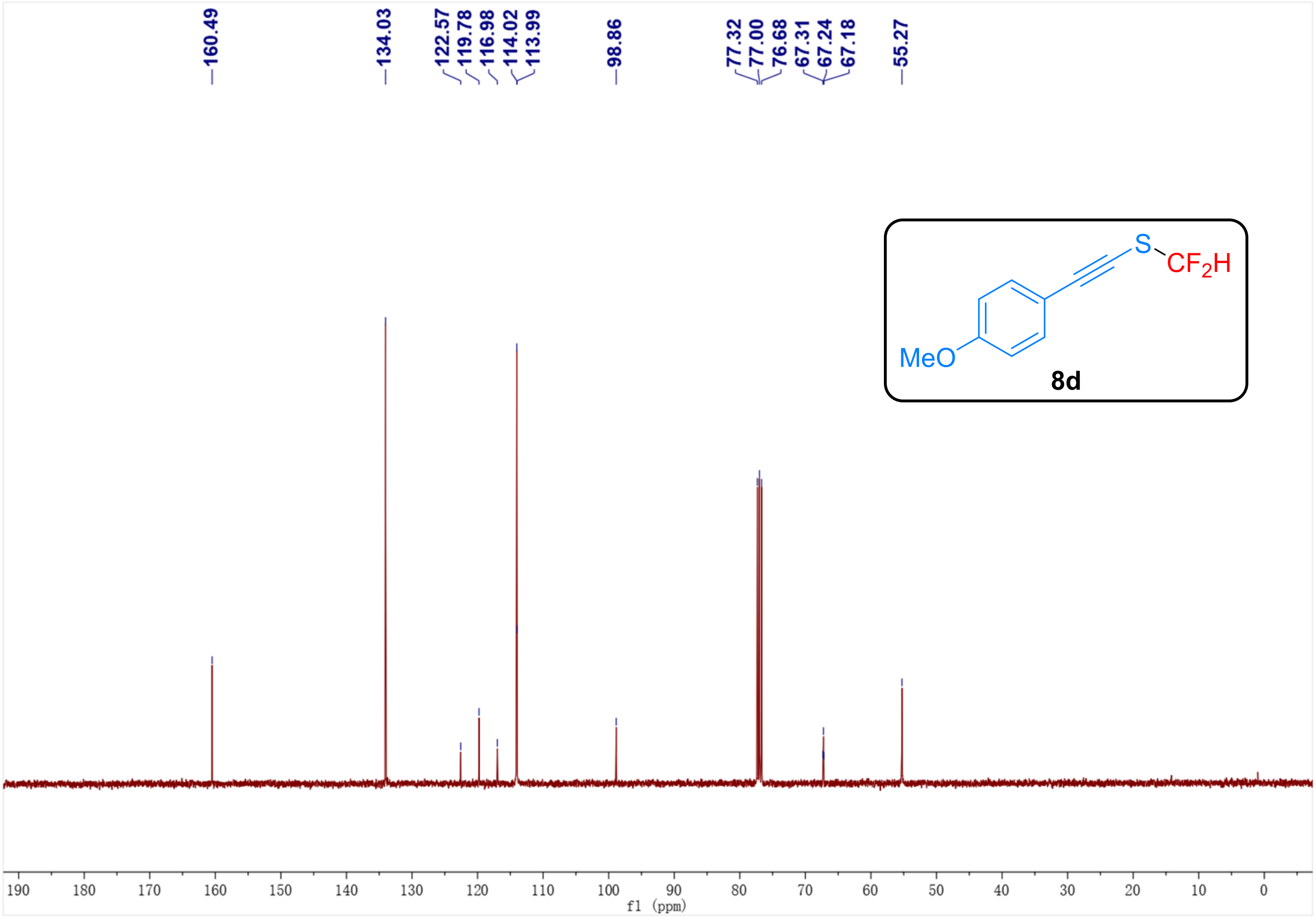

-92.61
-92.74
S
CF2H
8b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

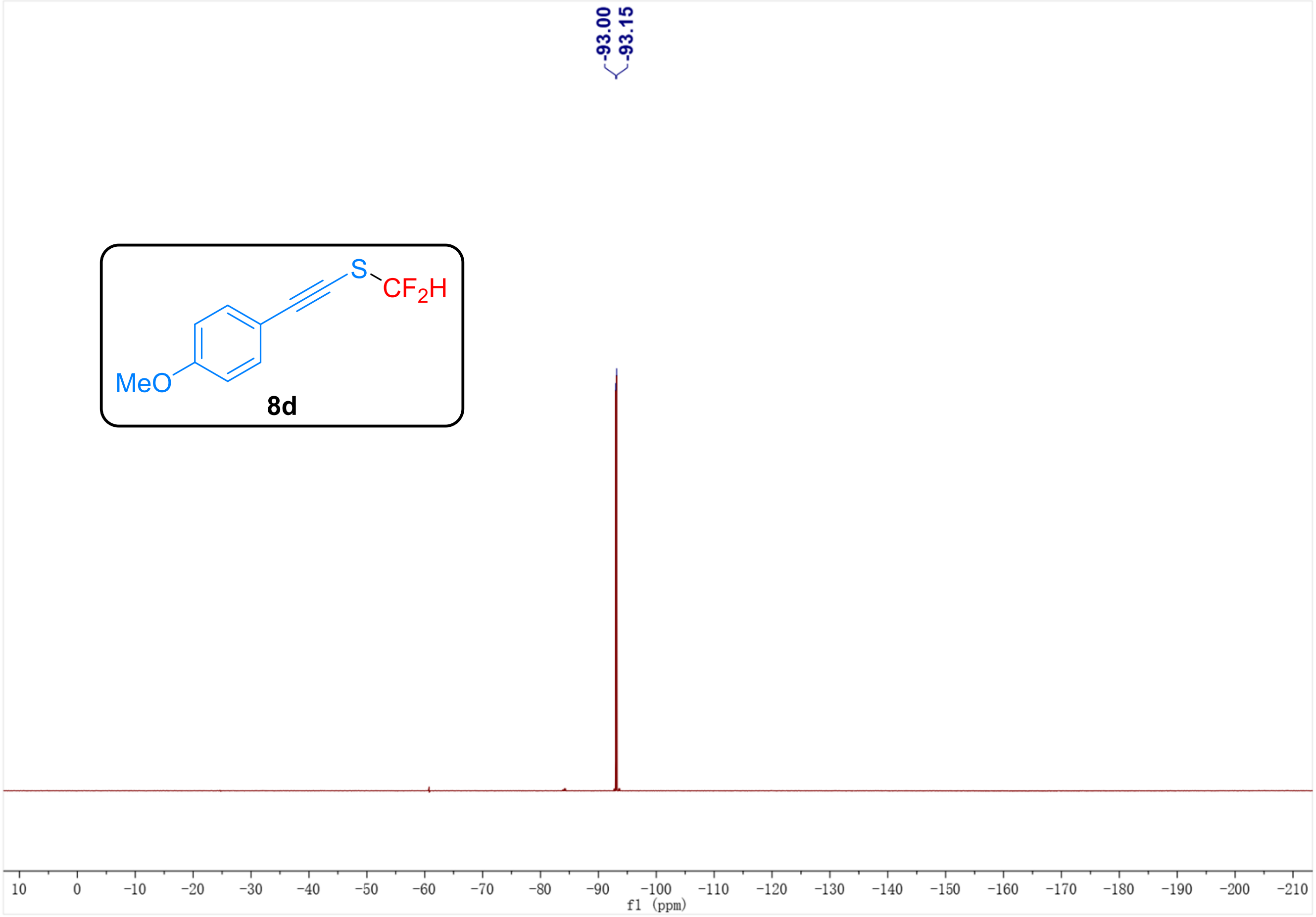

7.41
7.40
7.38
7.37
7.35
7.33
7.32
7.30
6.99
6.91
6.89
6.87
6.76
5.04
S
CF2H
BnO
8c
6.96
3.01
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

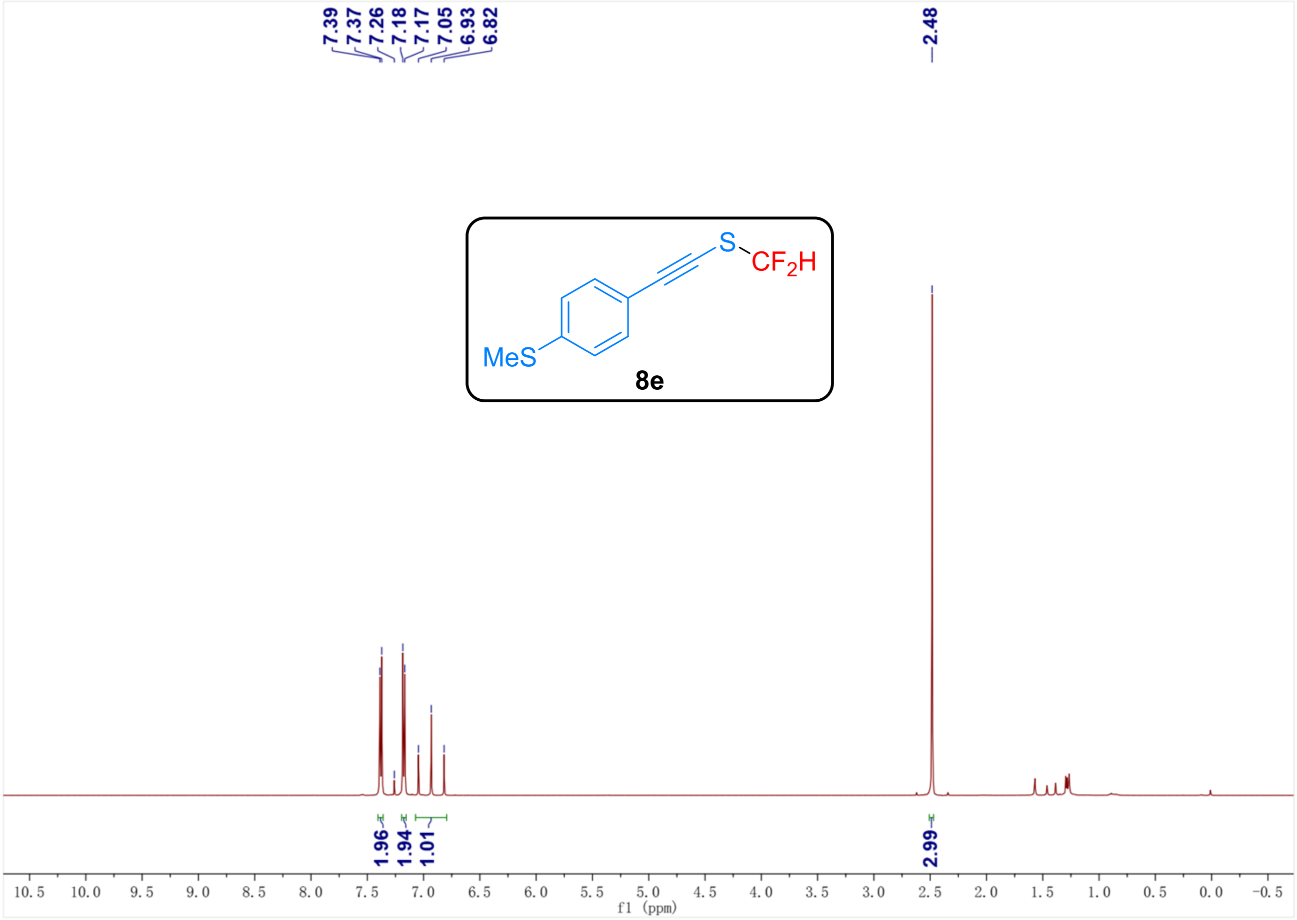

159.64
136.32
134.03
128.62
128.13
127.42
121.99
119.75
117.51
114.92
114.28
98.83
98.82
98.80
77.25
77.00
76.75
70.00
67.45
67.40
67.34
S
CF2H
BnO
8c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

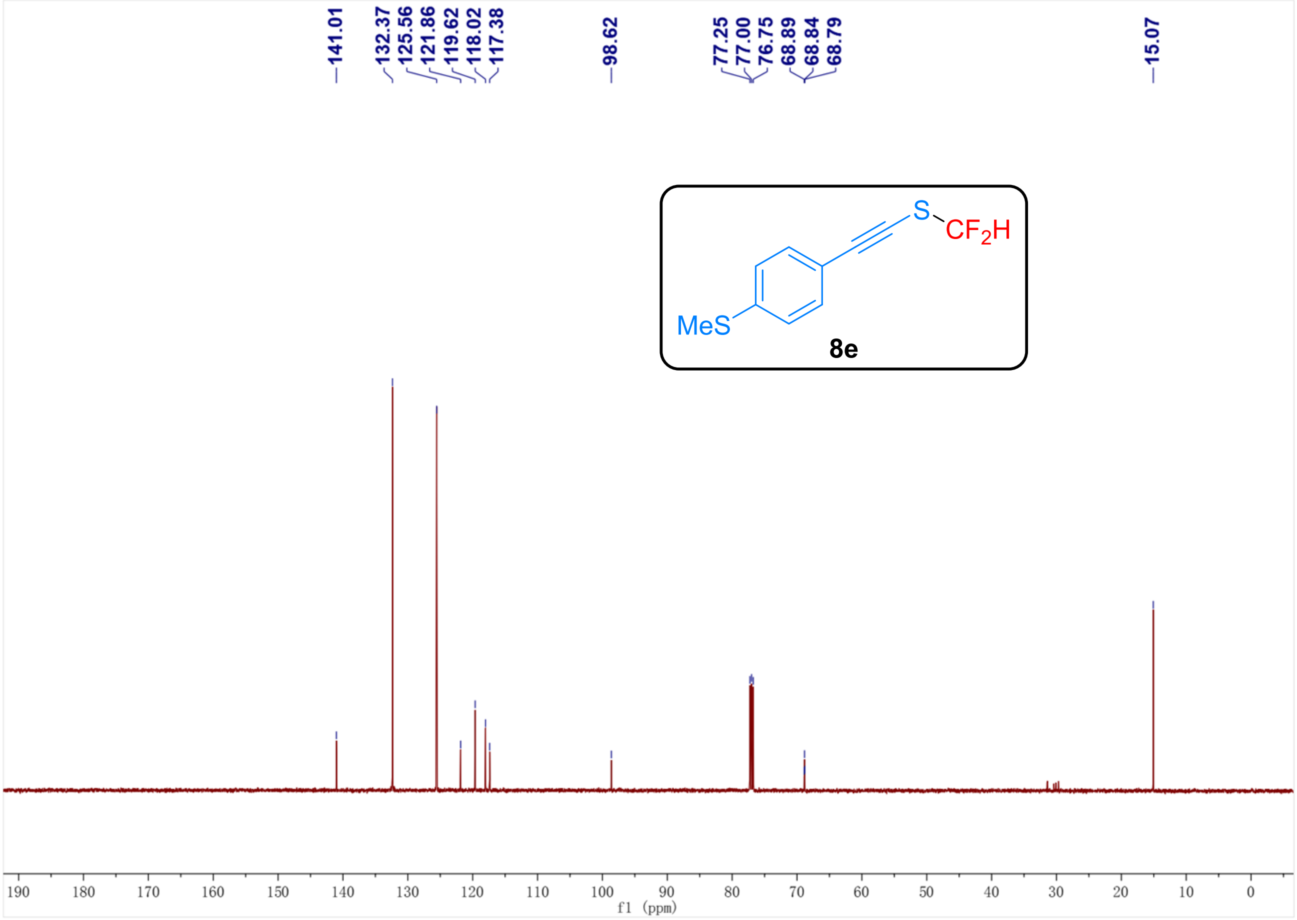

-92.92
-93.04
S
CF2H
BnO
8c
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

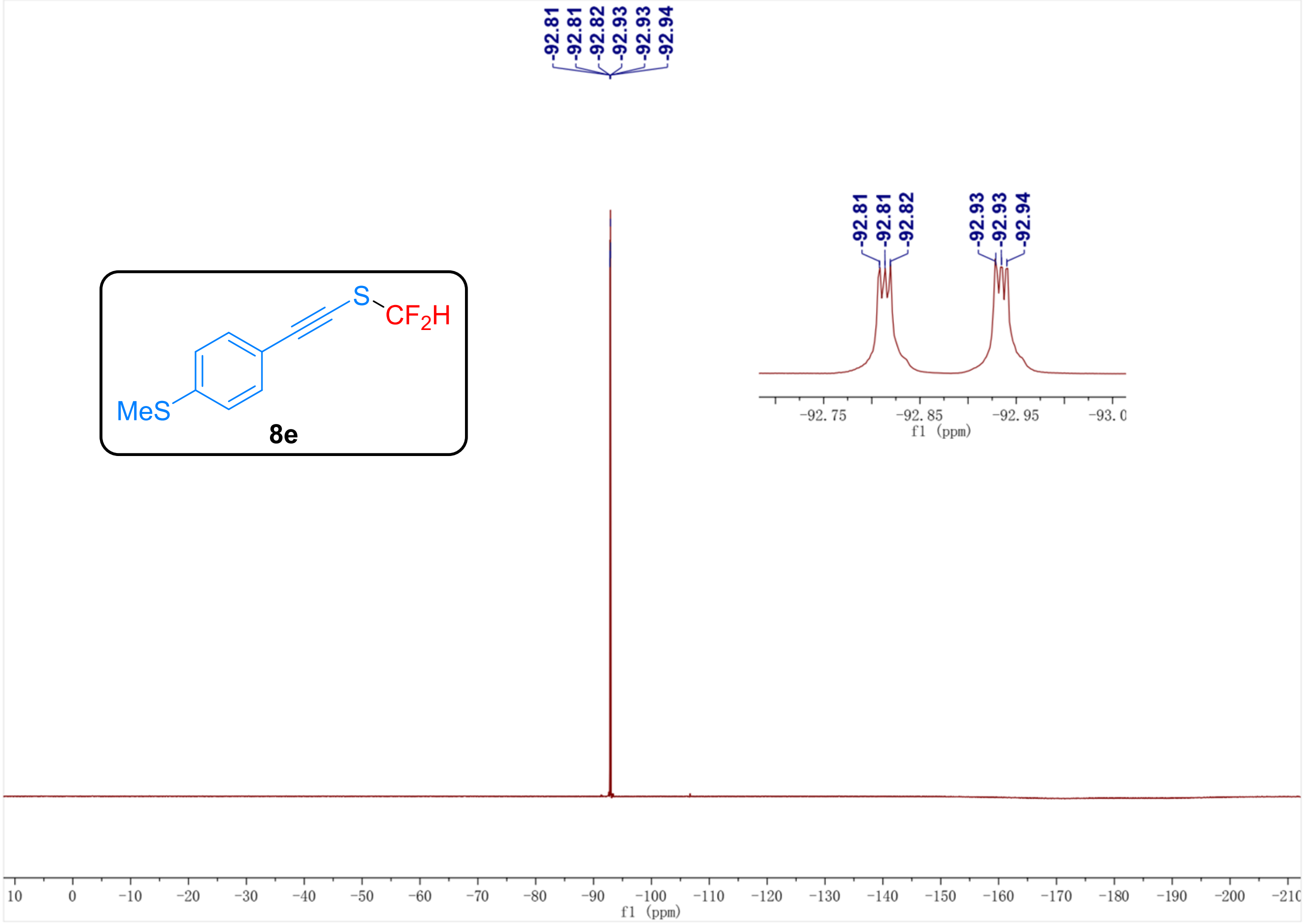

7.45
7.43
7.26
7.06
6.92
6.87
6.85
6.78
3.82
S
CF2H
MeO
8d
2.00
3.07
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

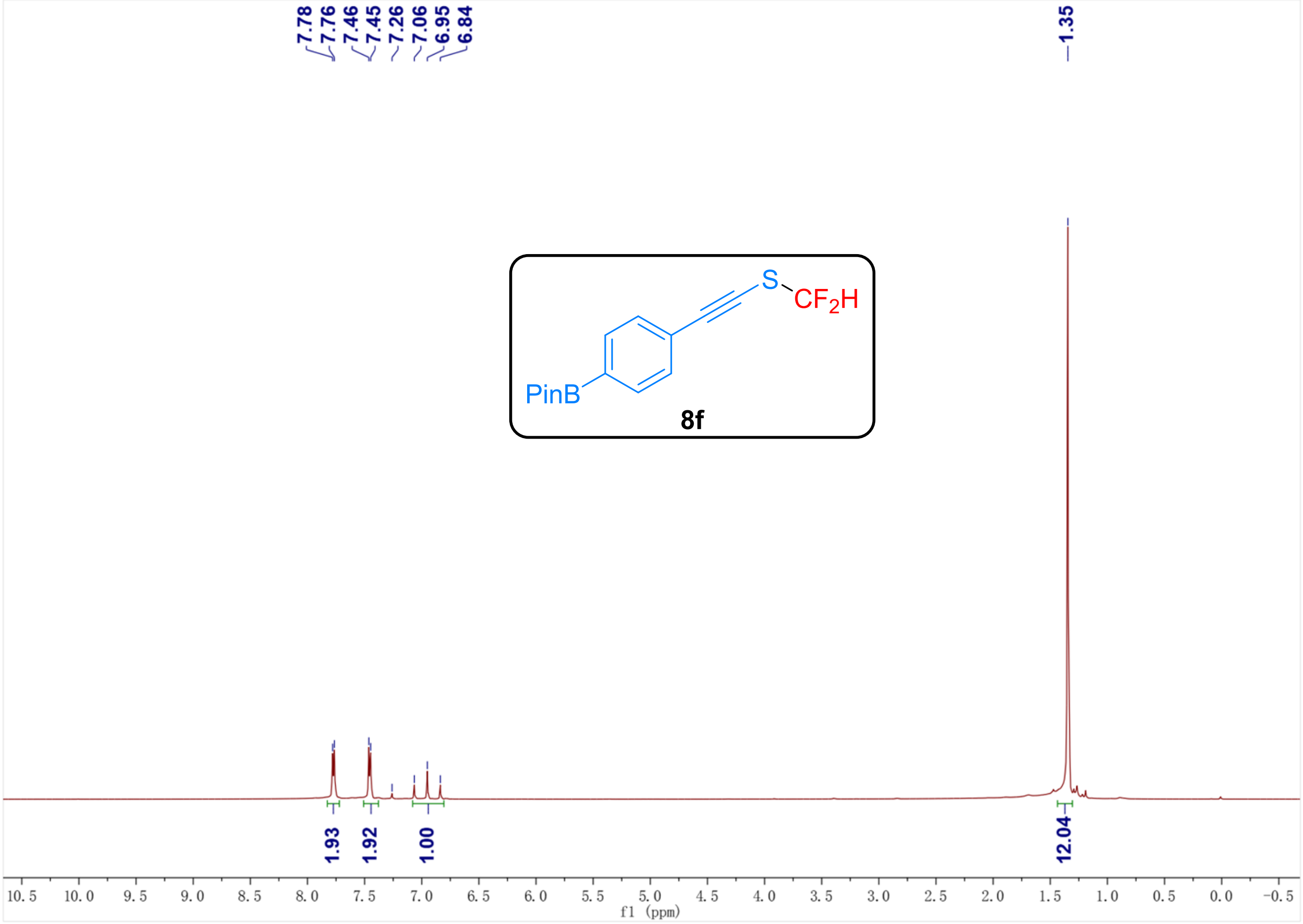

160.49
134.03
122.57
119.78
116.98
114.02
113.99
98.86
77.32
77.00
76.68
67.31
67.24
67.18
55.27
S
CF2H
MeO
8d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

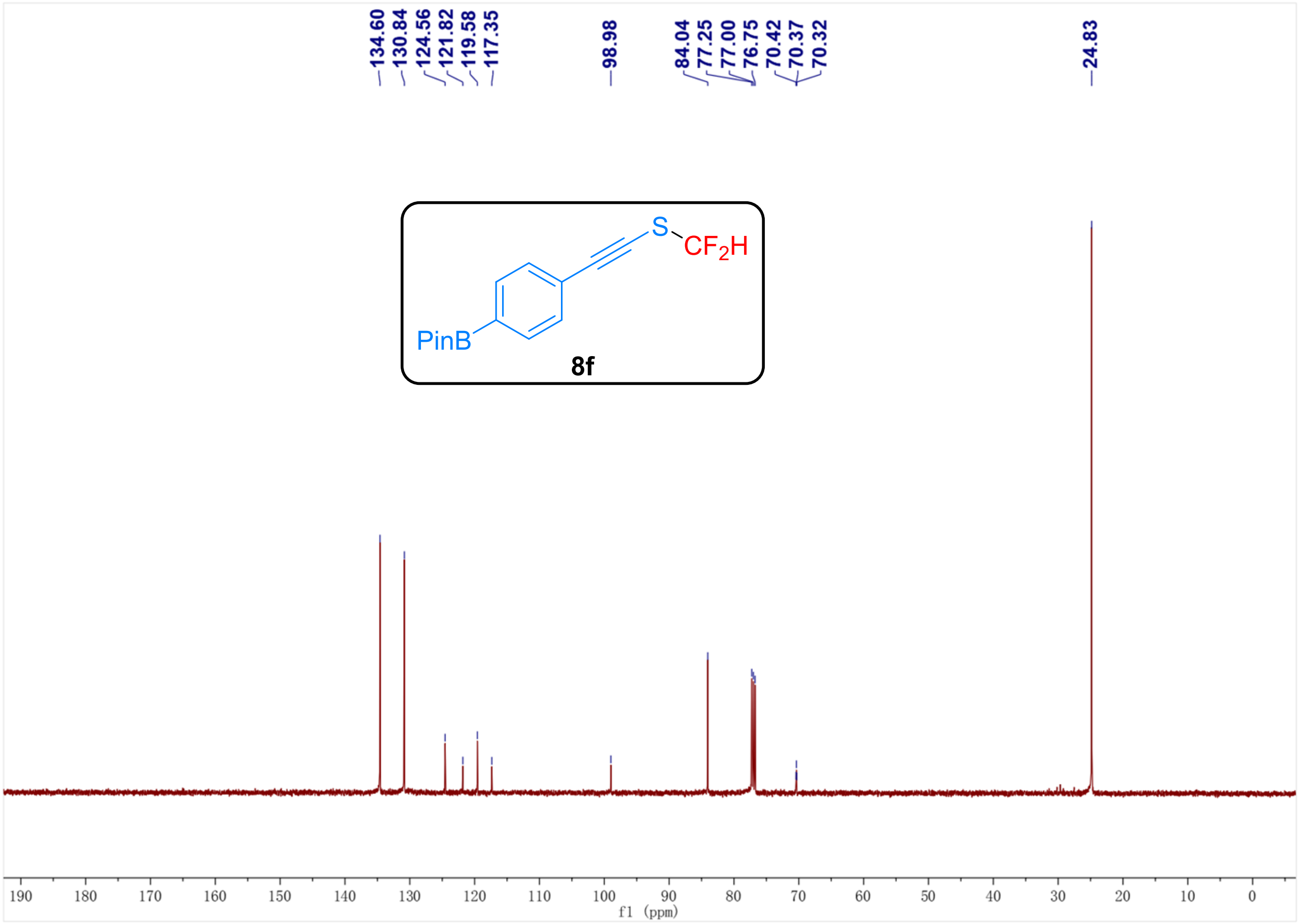

-93.00
-93.15
S
CF2H
MeO
8d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

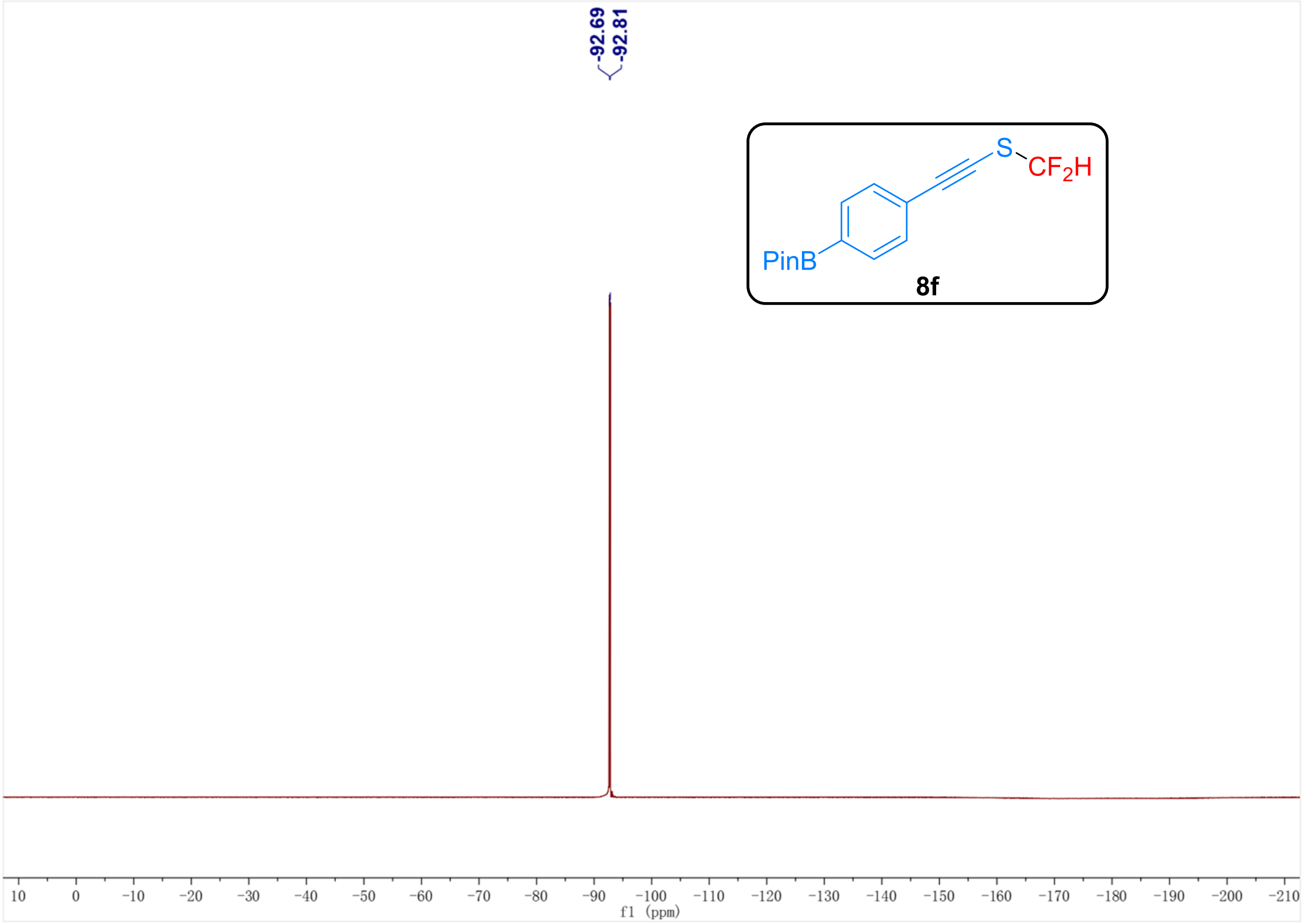

7.39
7.37
7.26
7.18
7.17
7.05
6.93
6.82
2.48
S
CF2H
MeS
8e
1.96
1.94
1.01
2.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

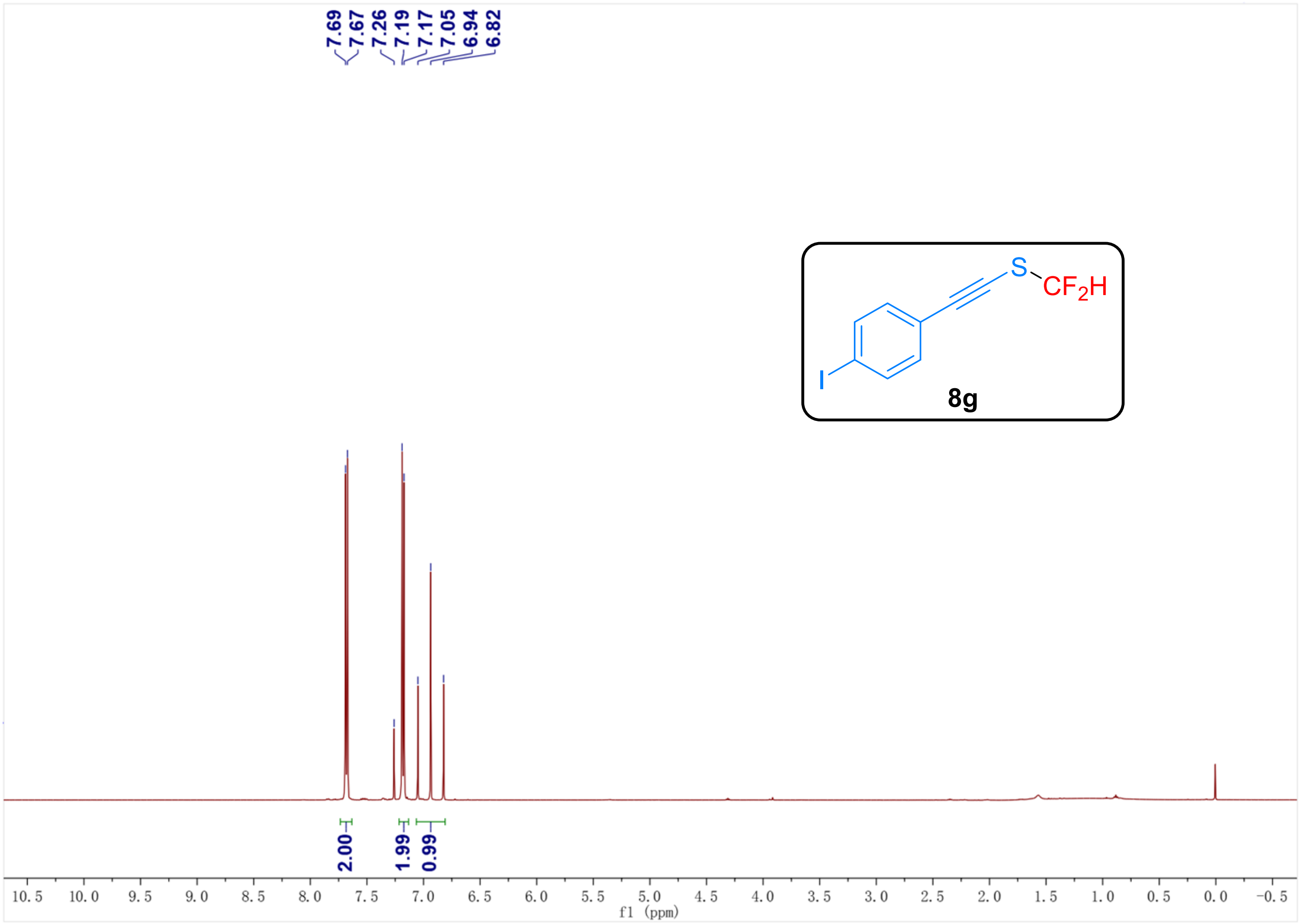

141.01
132.37
125.56
121.86
119.62
118.02
117.38
98.62
77.25
77.00
76.75
68.89
68.84
68.79
15.07
S
CF2H
MeS
8e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

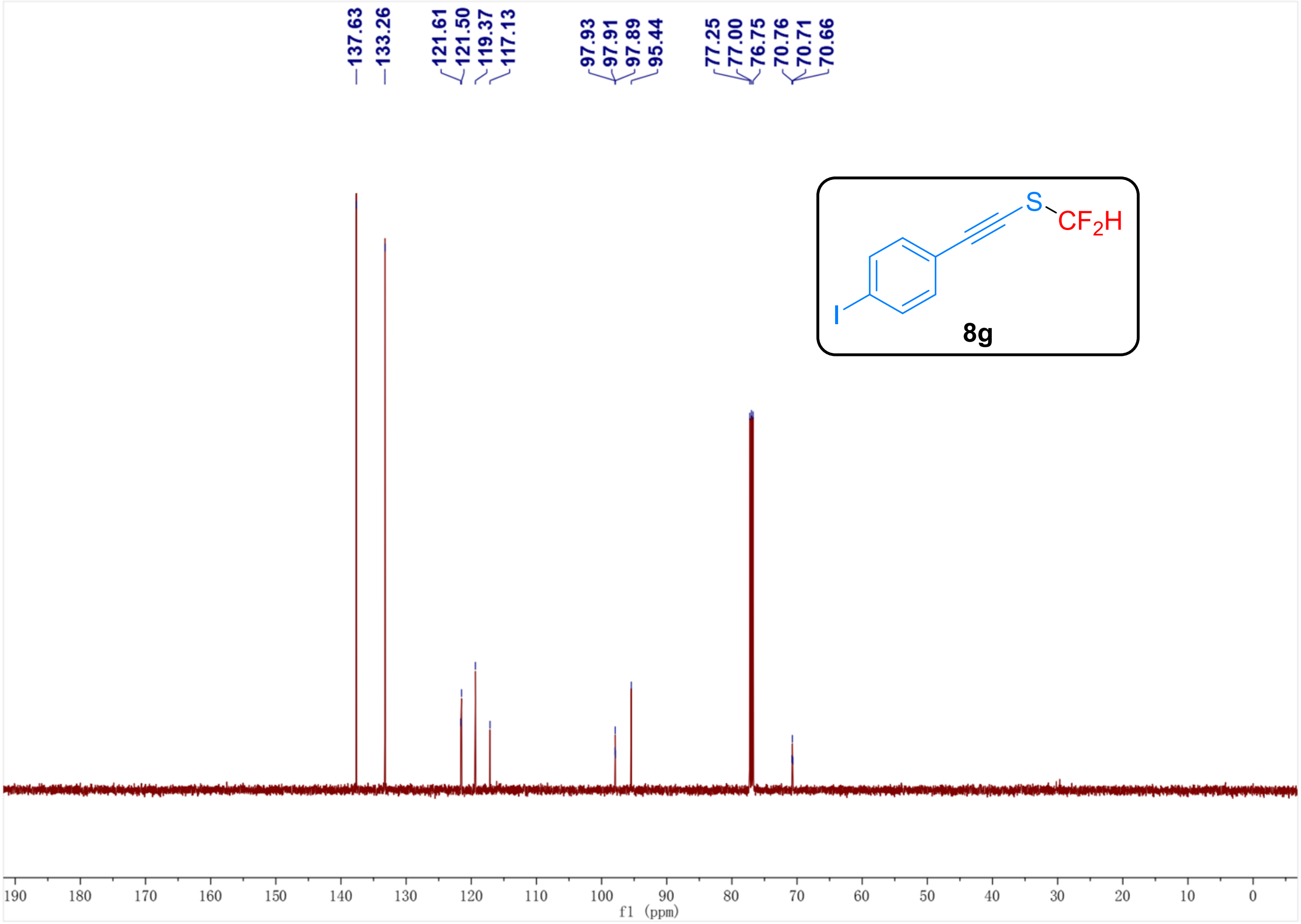

-92.81
-92.81
-92.82
-92.93
-92.93
-92.94
MeS
S
CF2H
8e
-92.75
-92.85
-92.95
-93.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

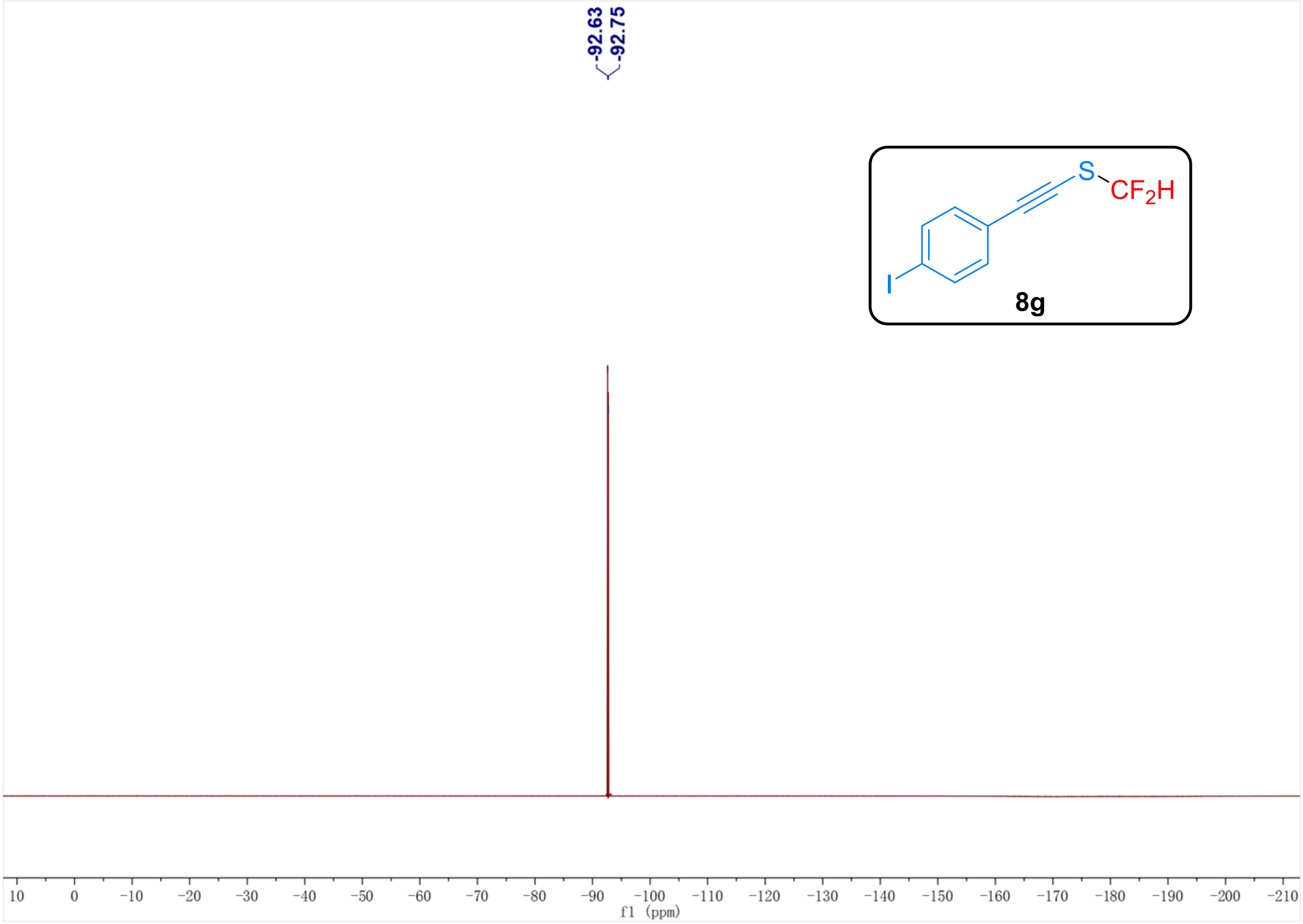

7.78
7.76
7.46
7.45
7.26
7.06
6.95
6.84
1.35
PinB
S
CF2H
8f
1.93
1.92
1.00
12.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

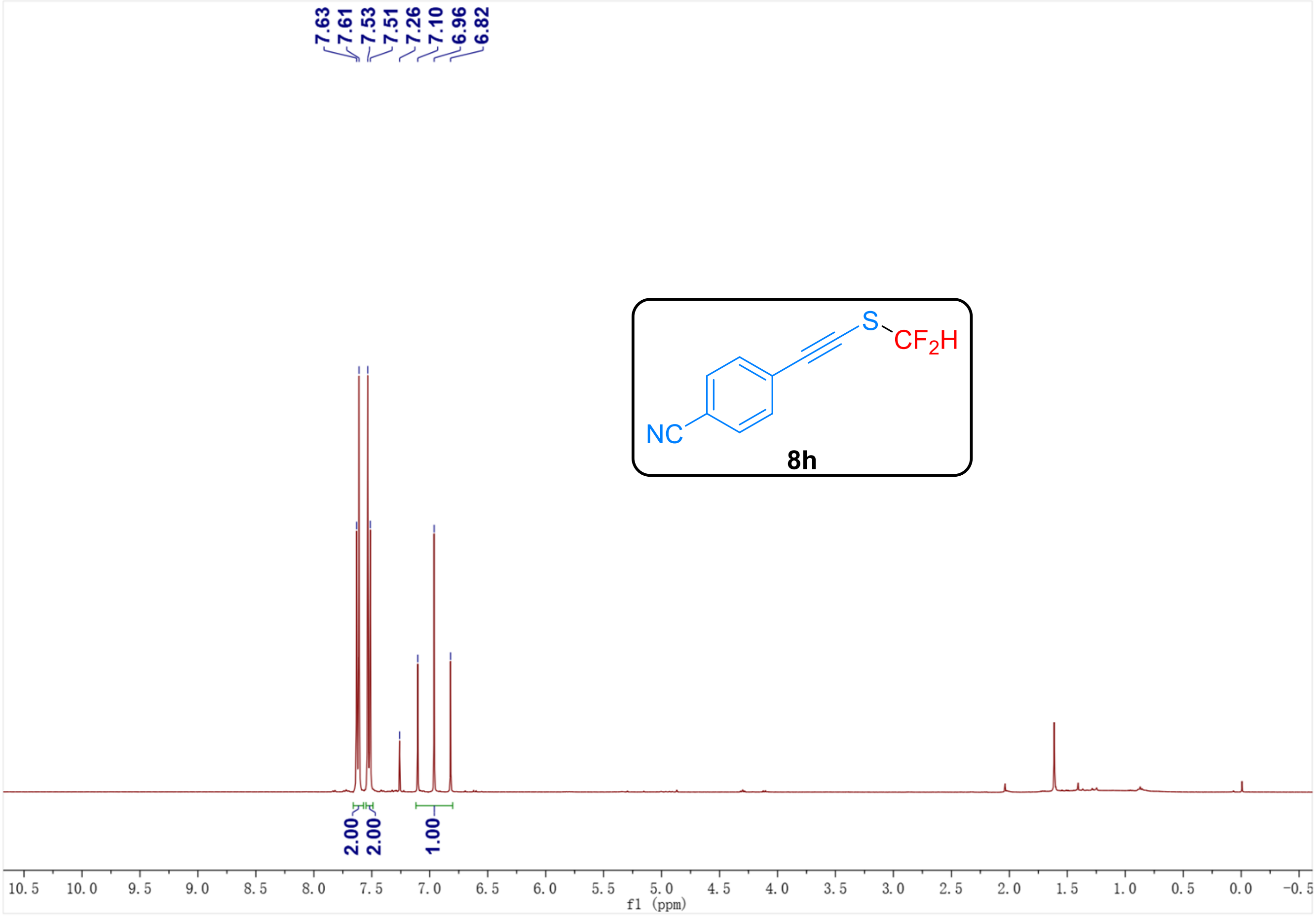

134.60
130.84
124.56
121.82
119.58
117.35
98.98
84.04
77.25
77.00
76.75
70.42
70.37
70.32
24.83
S
CF$_2$H
PinB
8f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

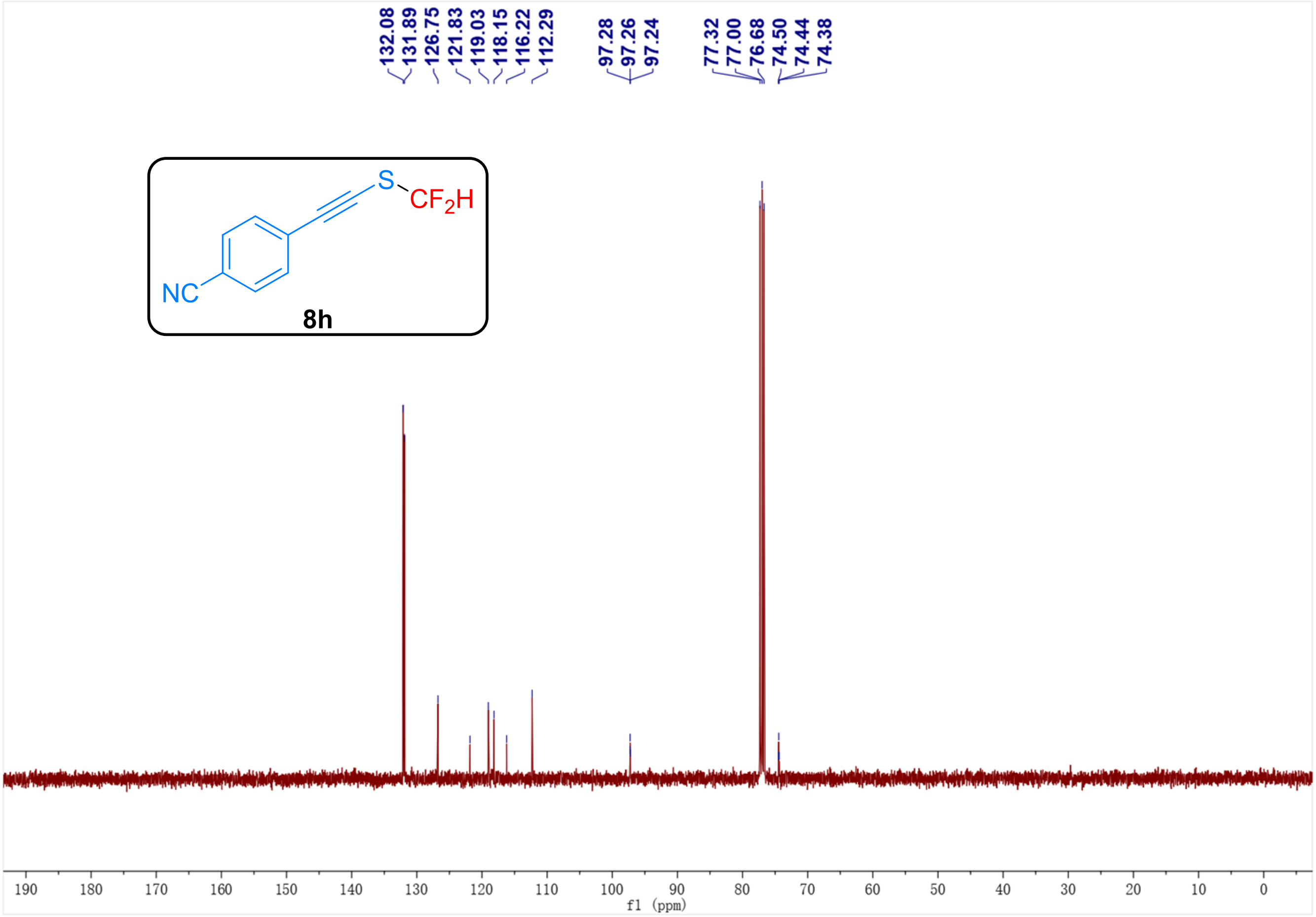

-92.69
-92.81
S
CF$_2$H
PinB
8f
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

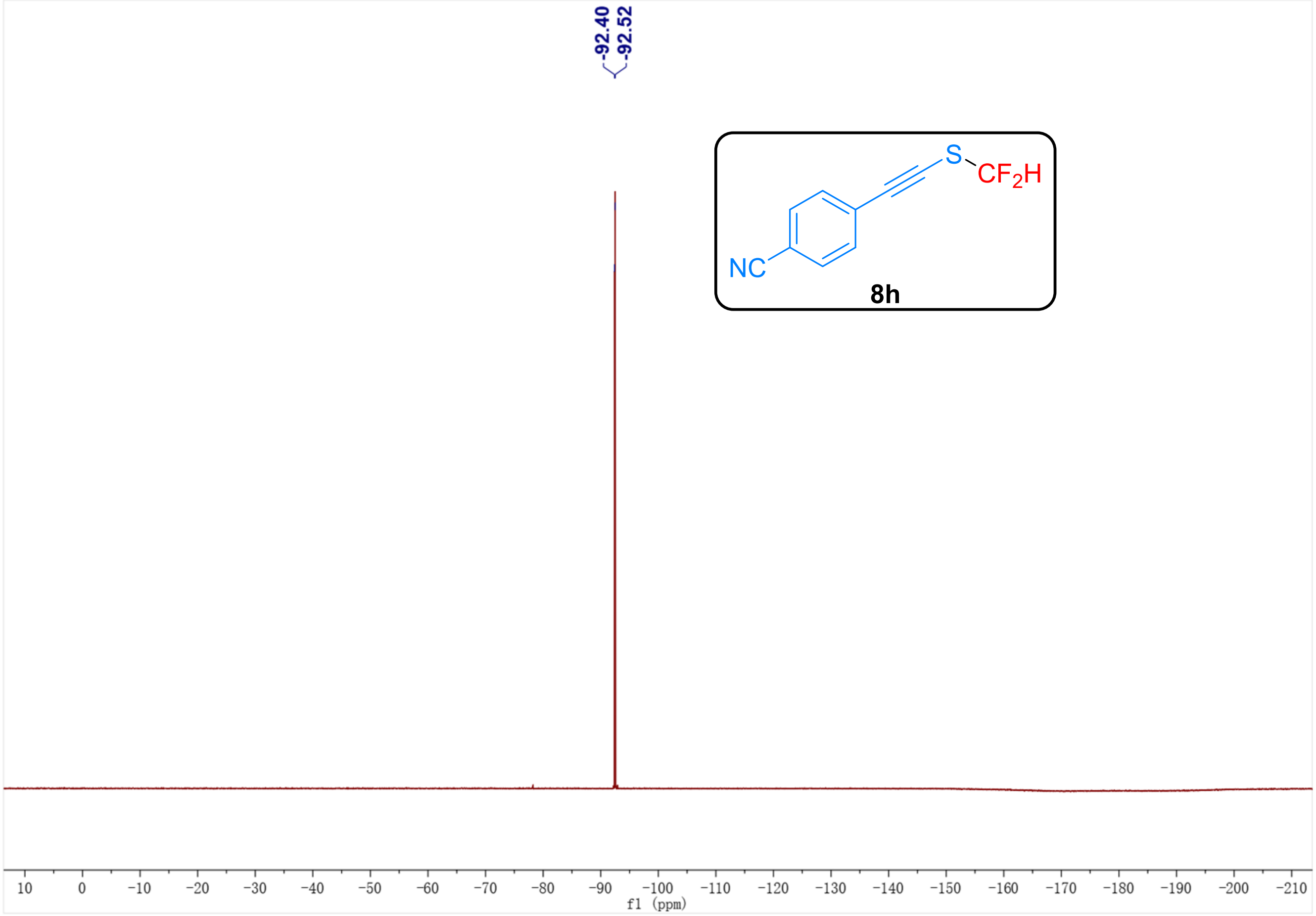

7.69
7.67
7.26
7.19
7.17
7.05
6.94
6.82
2.00
1.99
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
I
S
CF2H
8g

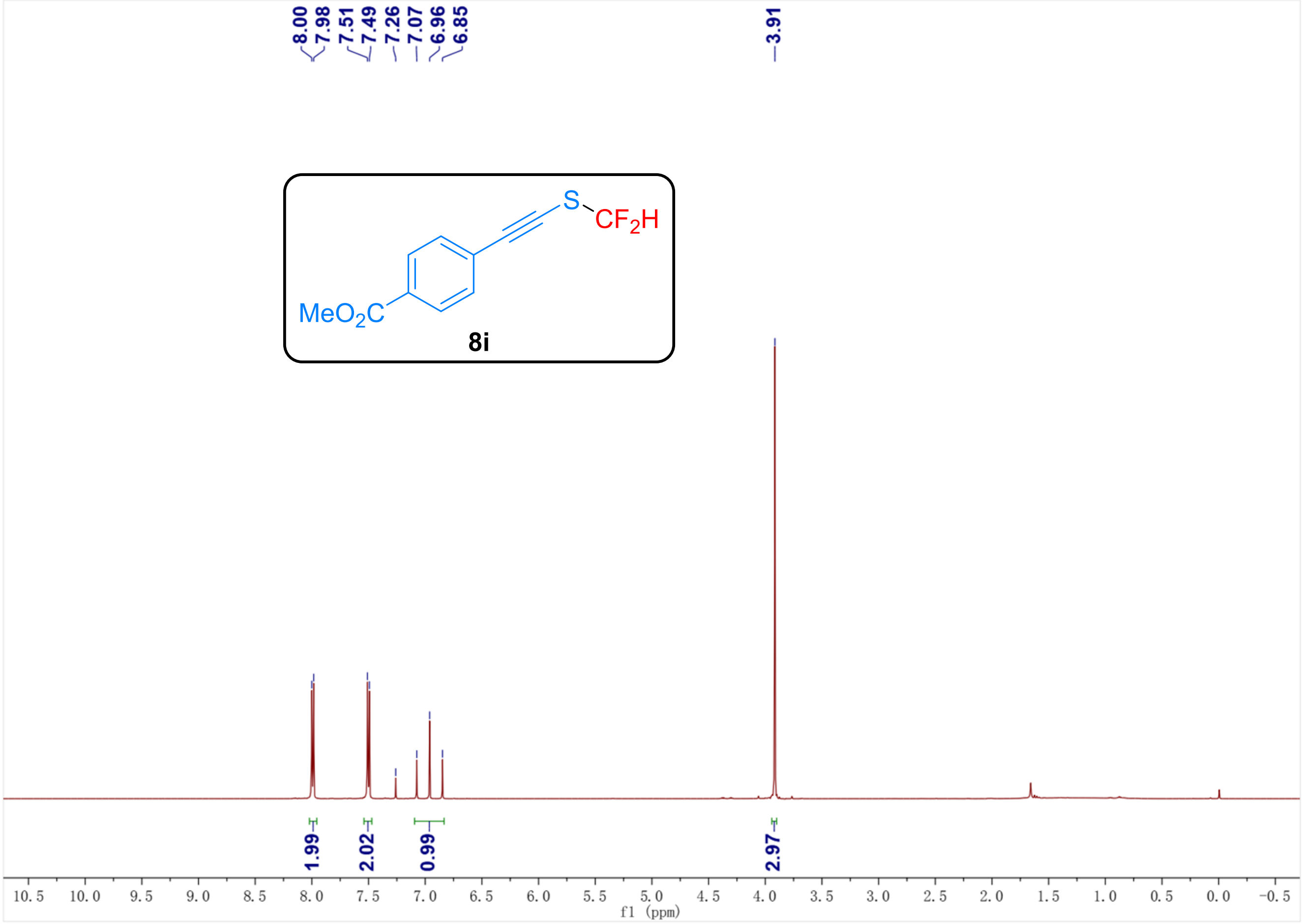

137.63
133.26
121.61
121.50
119.37
117.13
97.93
97.91
97.89
95.44
77.25
77.00
76.75
70.76
70.71
70.66
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
I
S
CF2H
8g

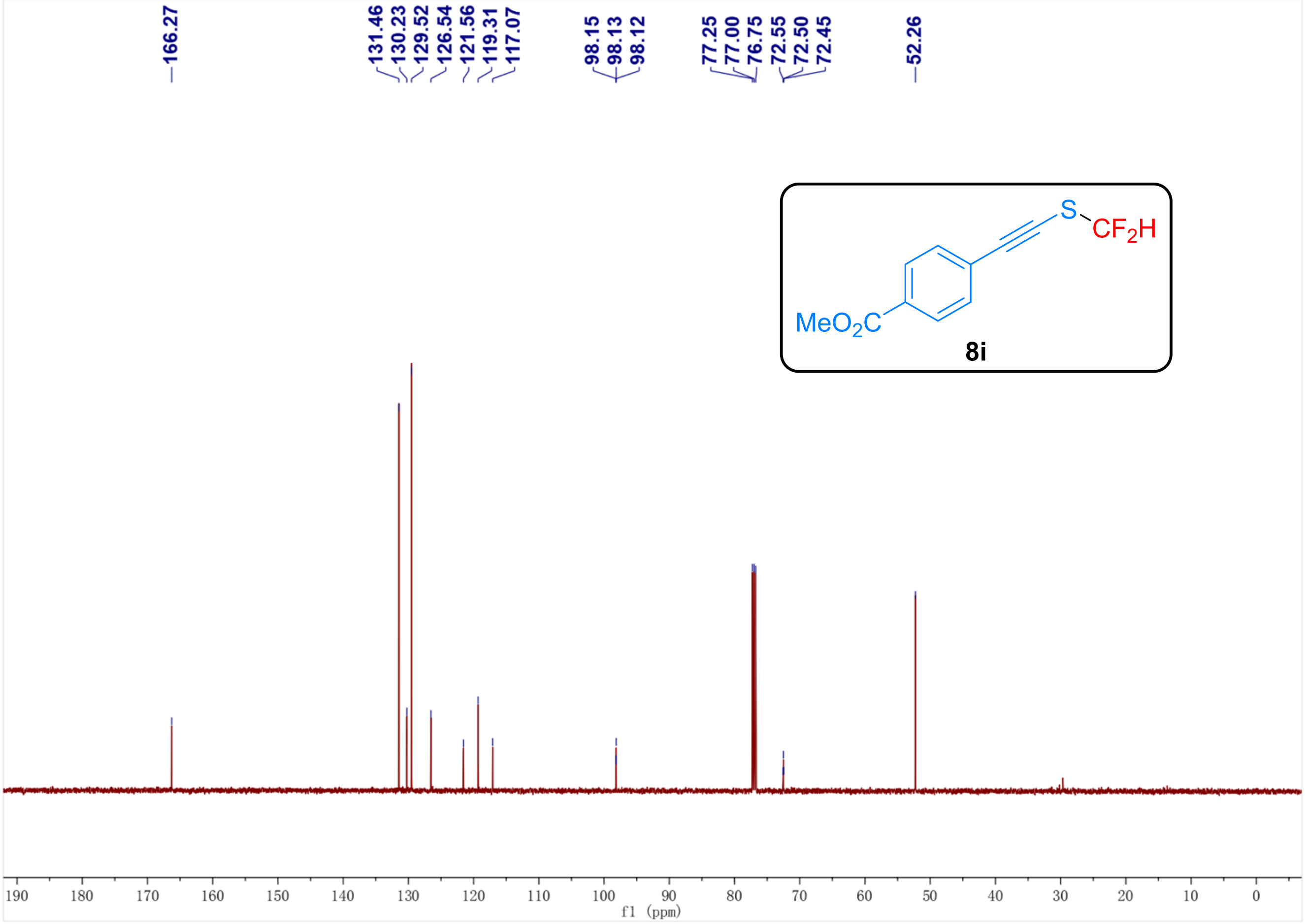

-92.63
-92.75
8g
S
CF$_2$H
I
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

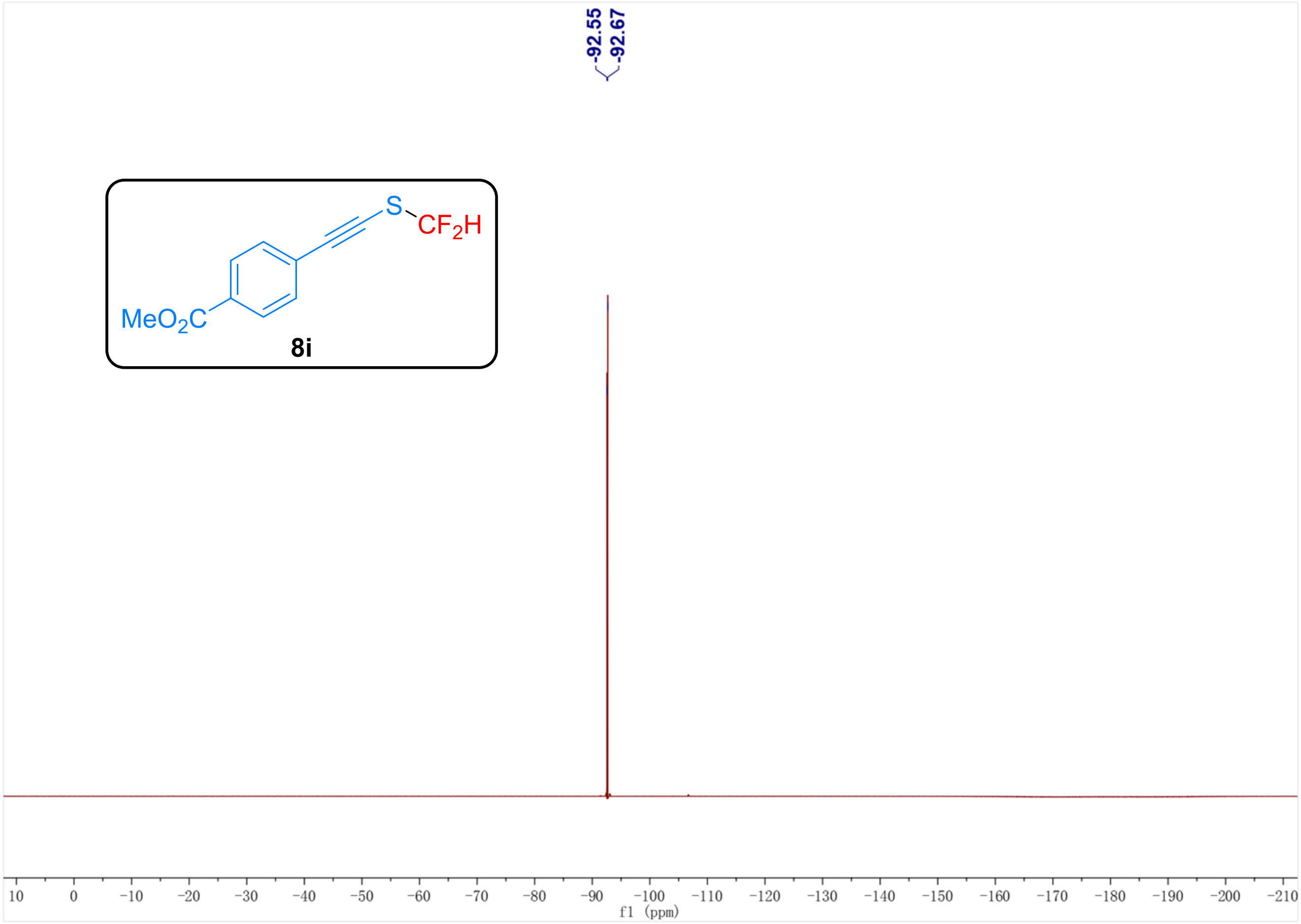

7.63
7.61
7.53
7.51
7.26
7.10
6.96
6.82
8h
S
CF$_2$H
NC
2.00
2.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

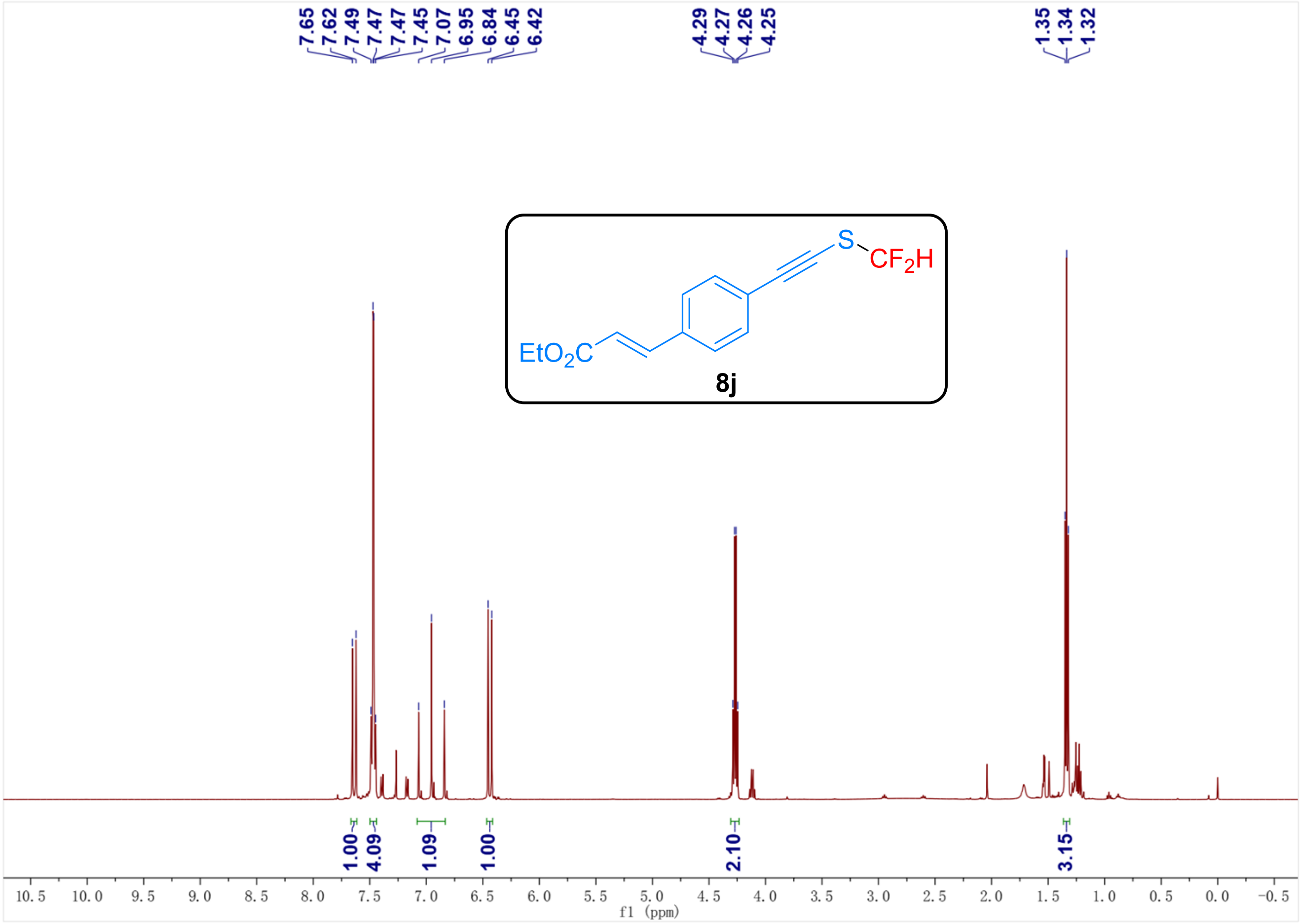

132.08
131.89
126.75
121.83
119.03
118.15
116.22
112.29
97.28
97.26
97.24
77.32
77.00
76.68
74.50
74.44
74.38
NC
S
CF2H
8h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

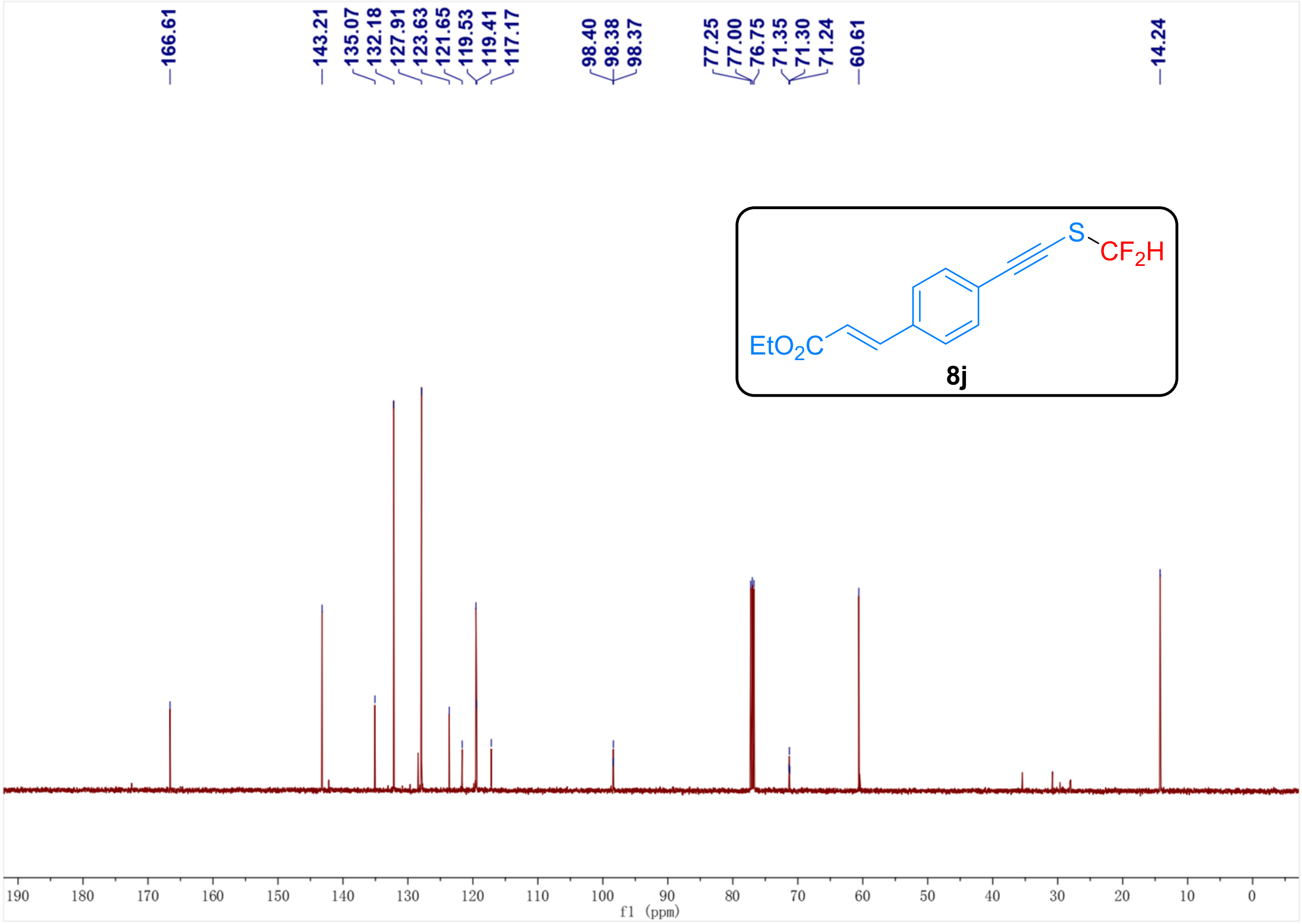

-92.40
-92.52
NC
S
CF2H
8h
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

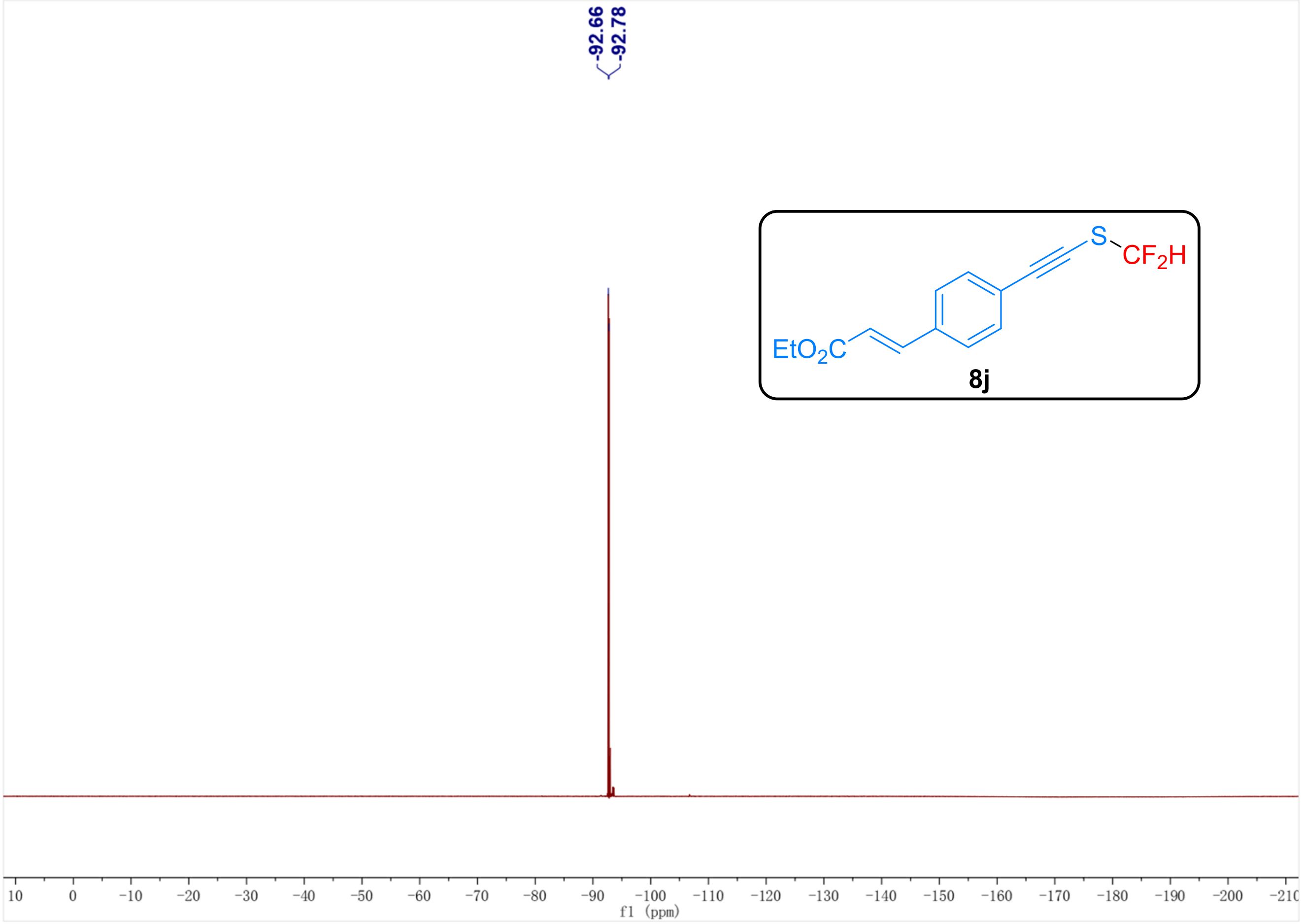

8.00
7.98
7.51
7.49
7.26
7.07
6.96
6.85
3.91
MeO2C
S
CF2H
8i
1.99
2.02
0.99
2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

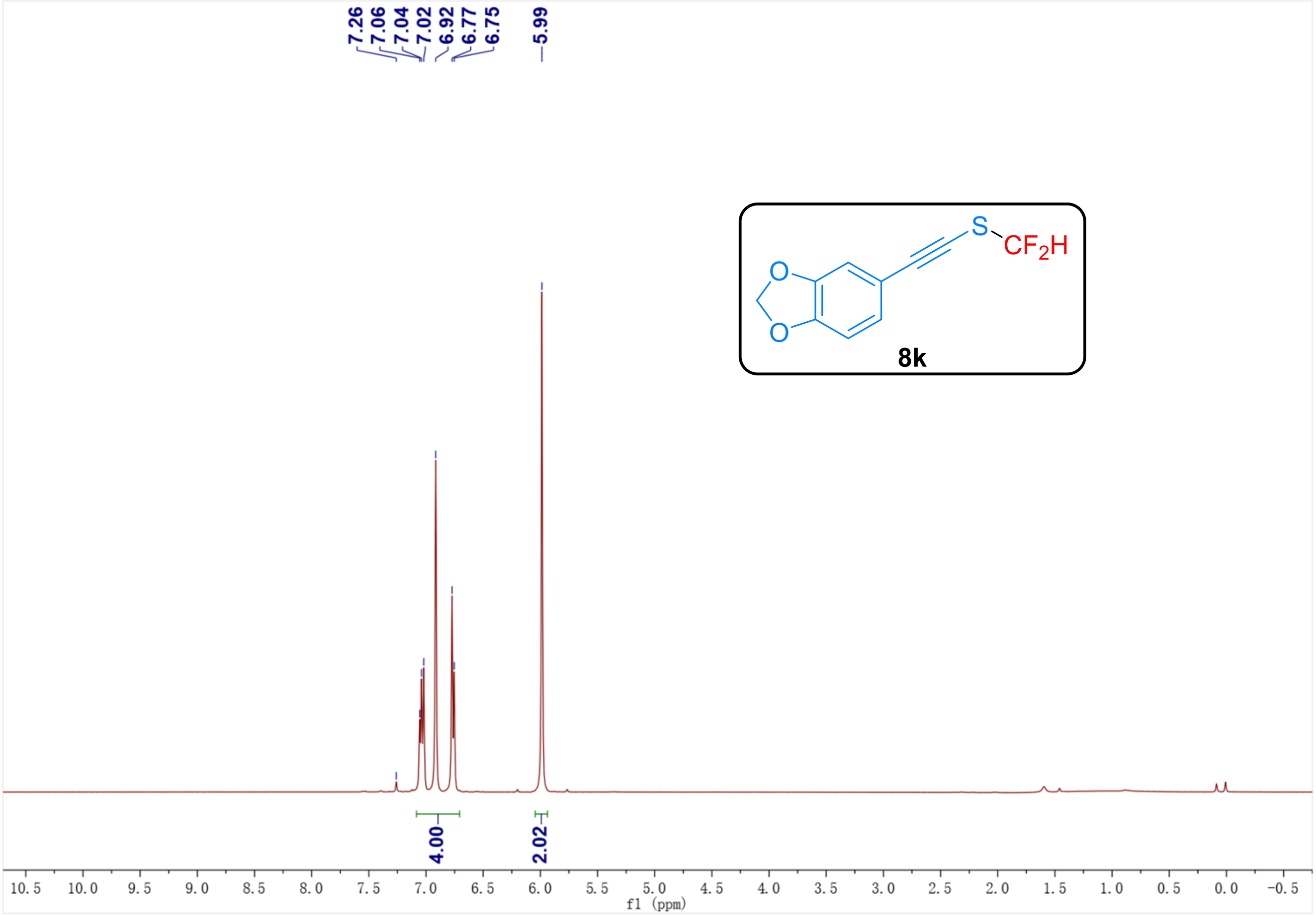

166.27
131.46
130.23
129.52
126.54
121.56
119.31
117.07
98.15
98.13
98.12
77.25
77.00
76.75
72.55
72.50
72.45
52.26
MeO2C
S
CF2H
8i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

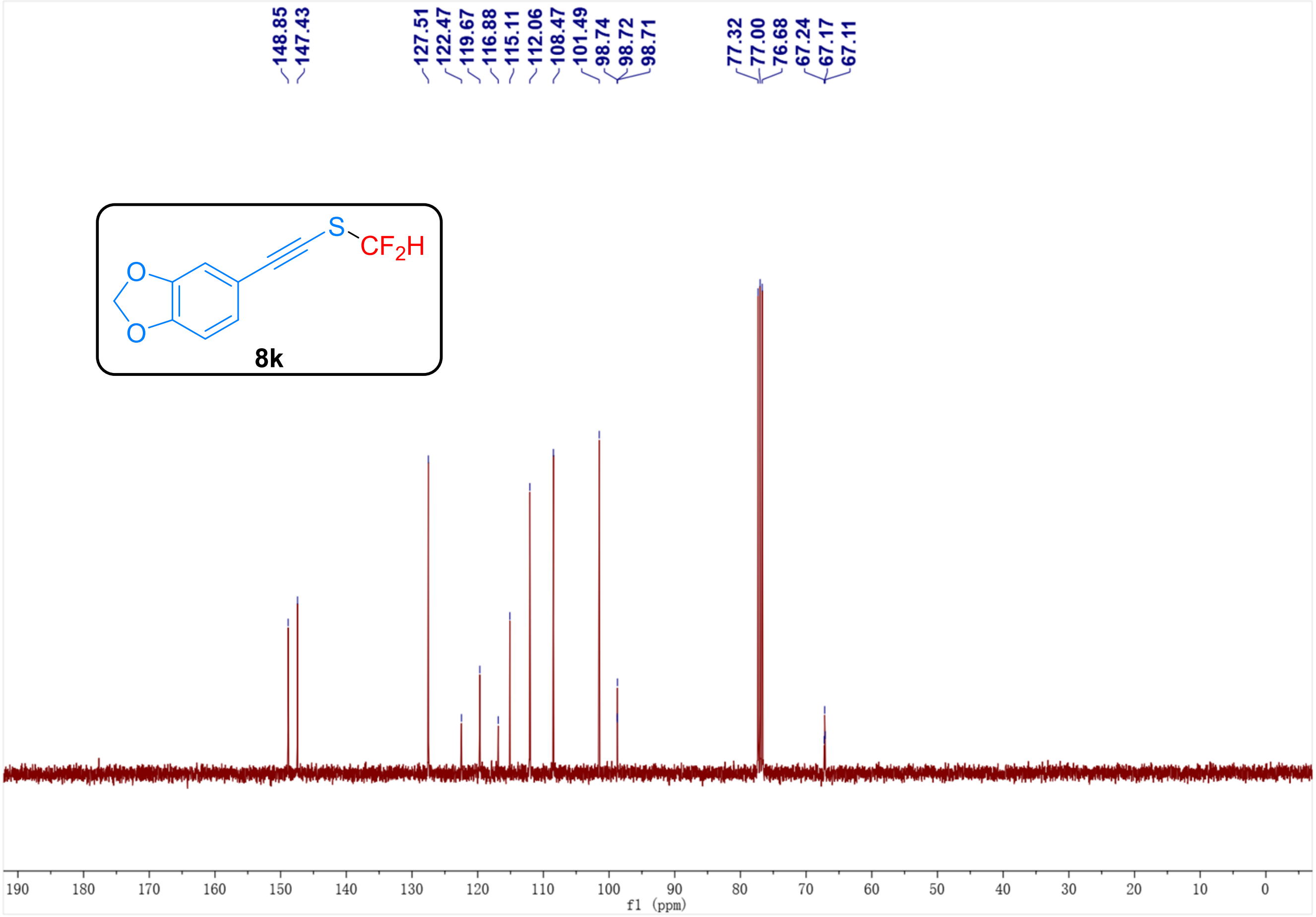

-92.55
-92.67
S
CF2H
MeO2C
8i
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.65
7.62
7.49
7.47
7.47
7.45
7.07
6.95
6.84
6.45
6.42
4.29
4.27
4.26
4.25
1.35
1.34
1.32
S
CF2H
EtO2C
8j
1.00
4.09
1.09
1.00
2.10
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


166.61
143.21
135.07
132.18
127.91
123.63
121.65
119.53
119.41
117.17
98.40
98.38
98.37
77.25
77.00
76.75
71.35
71.30
71.24
60.61
14.24
S
CF2H
EtO2C
8j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-92.66
-92.78
S
CF2H
EtO2C
8j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.26
7.06
7.04
7.02
6.92
6.77
6.75
5.99
S
CF2H
O
O
8k
4.00
2.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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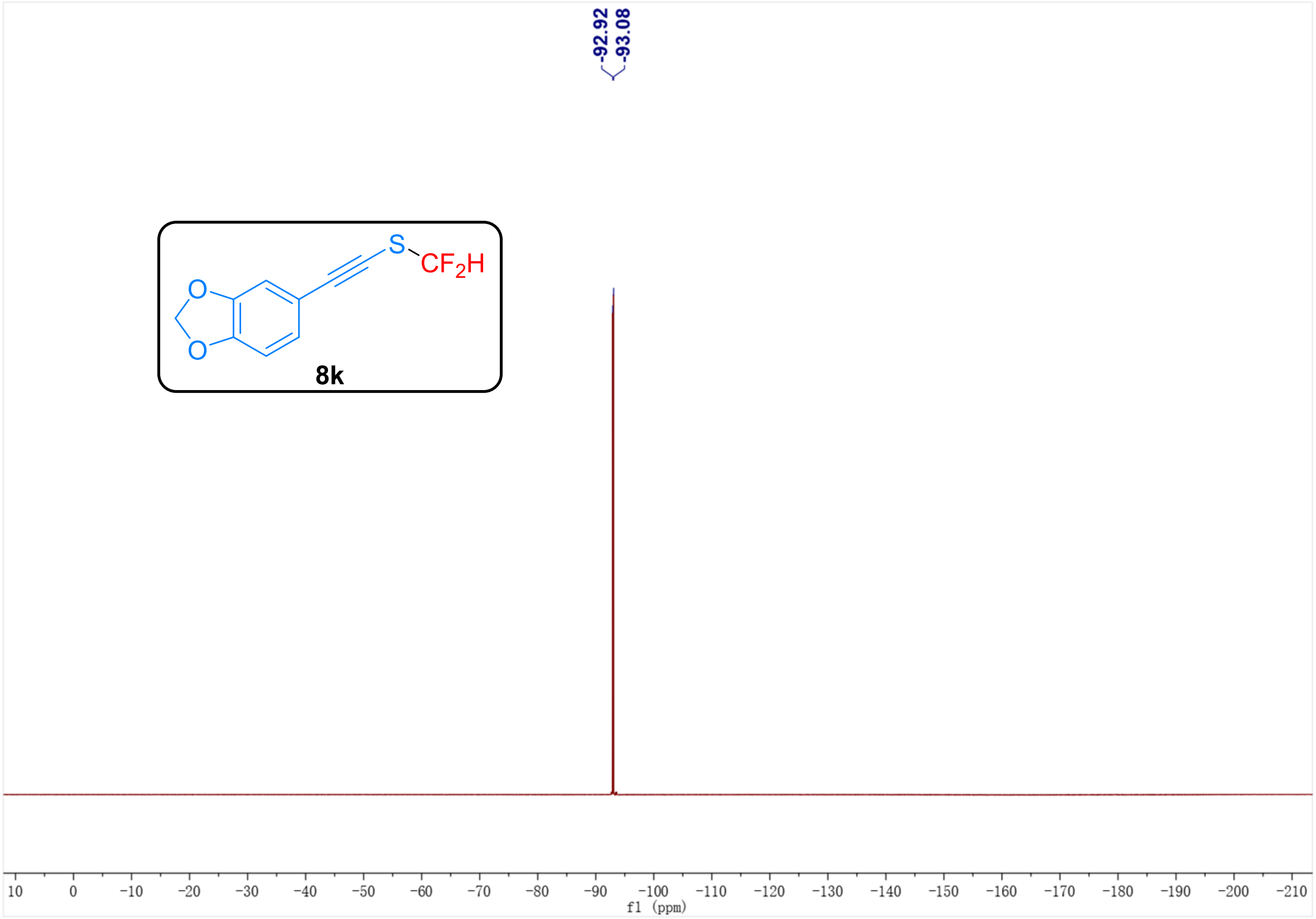
147.43
127.51
122.47
119.67
116.88
115.11
112.06
108.47
101.49
98.74
98.72
98.71
77.32
77.00
76.68
67.24
67.17
67.11
S
CF2H
O
O
8k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-92.92
-93.08
8k
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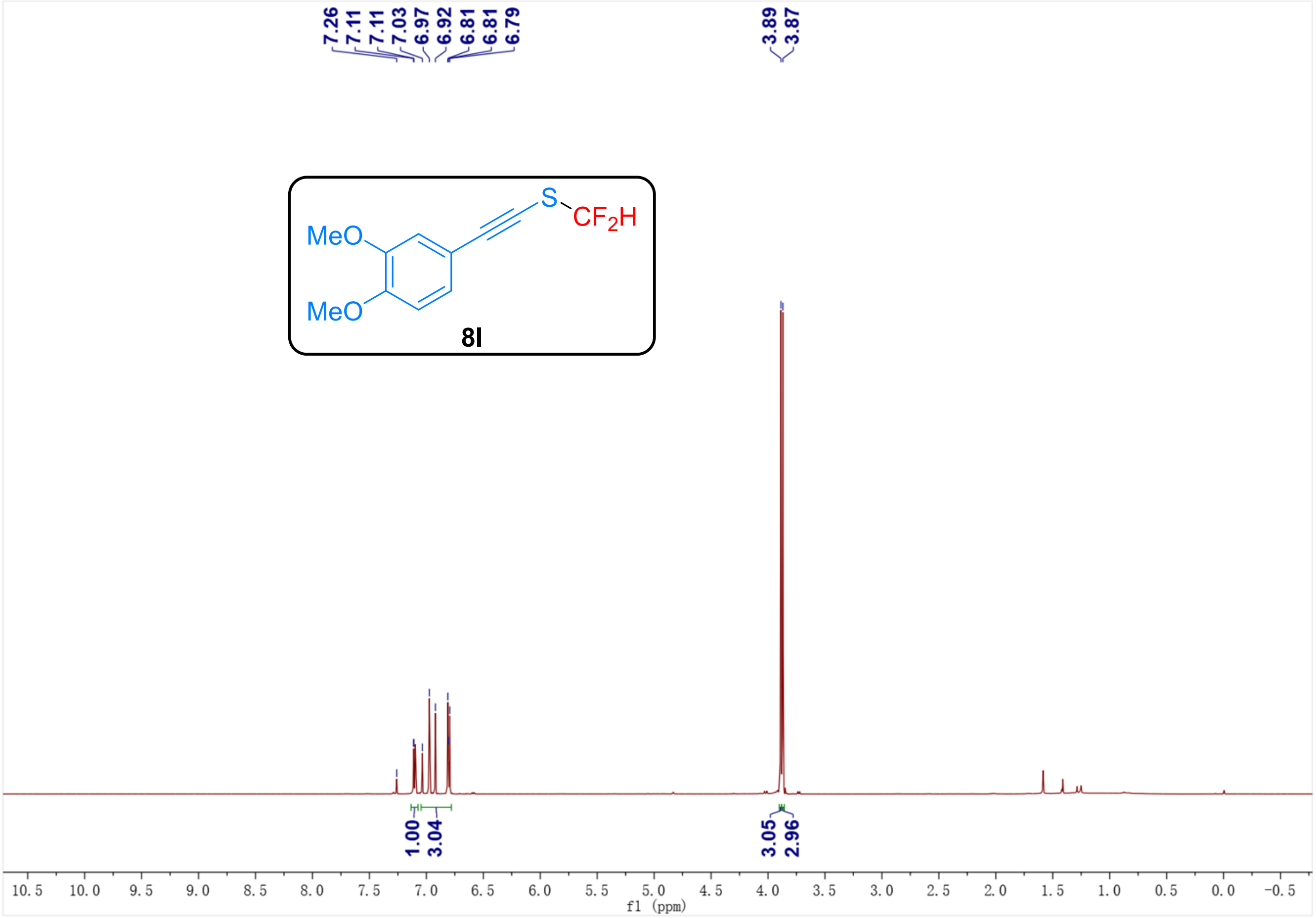
f1 (ppm)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7.11
7.11
7.03
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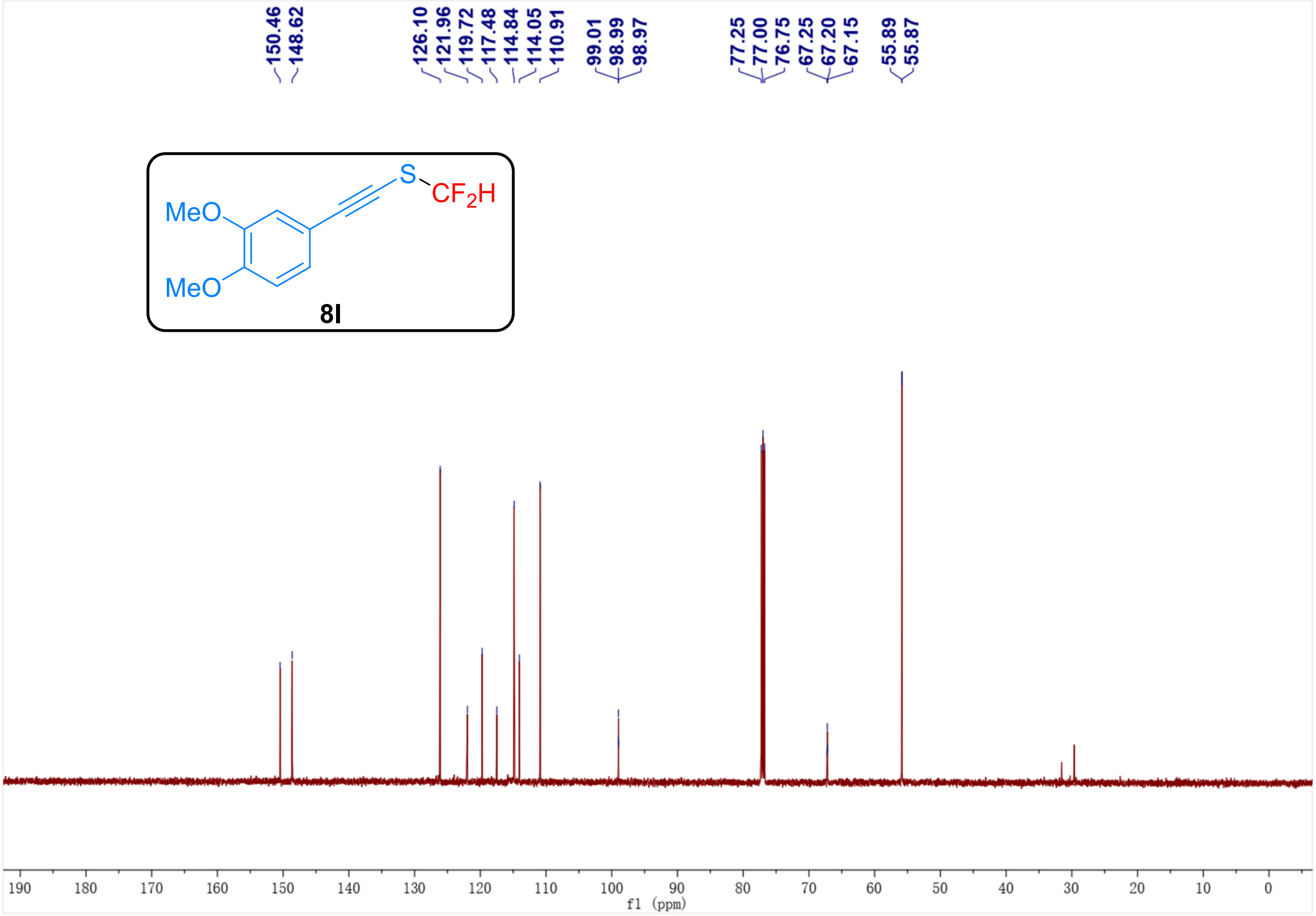
6.92
6.81
6.81
6.79
3.89
3.87
8l
1.00
3.04
3.05
2.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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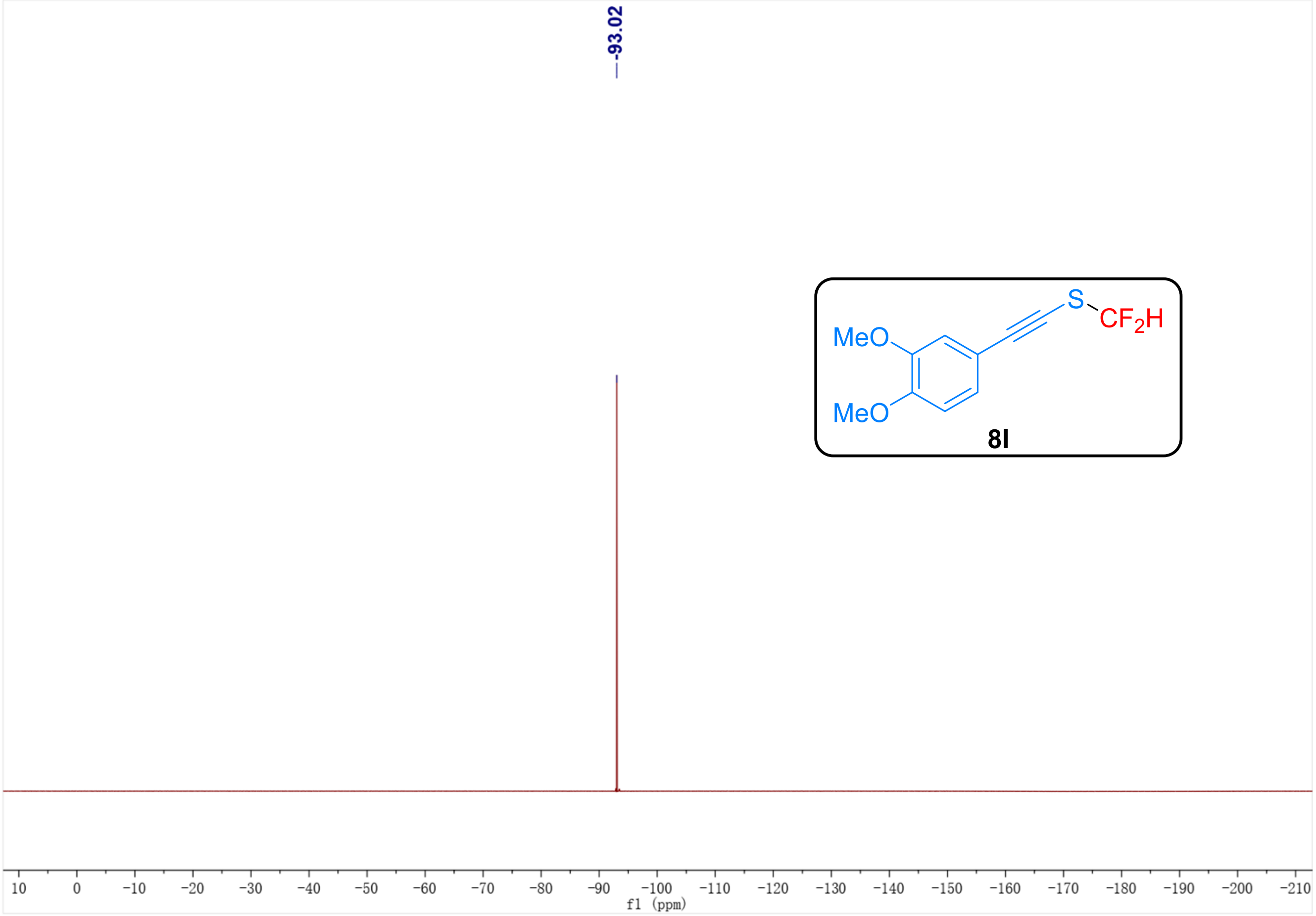
121.96
119.72
117.48
114.84
114.05
110.91
99.01
98.99
98.97
77.25
77.00
76.75
67.25
67.20
67.15
55.89
55.87
MeO
MeO
S
CF$_2$H
8l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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MeO
MeO
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8l
10
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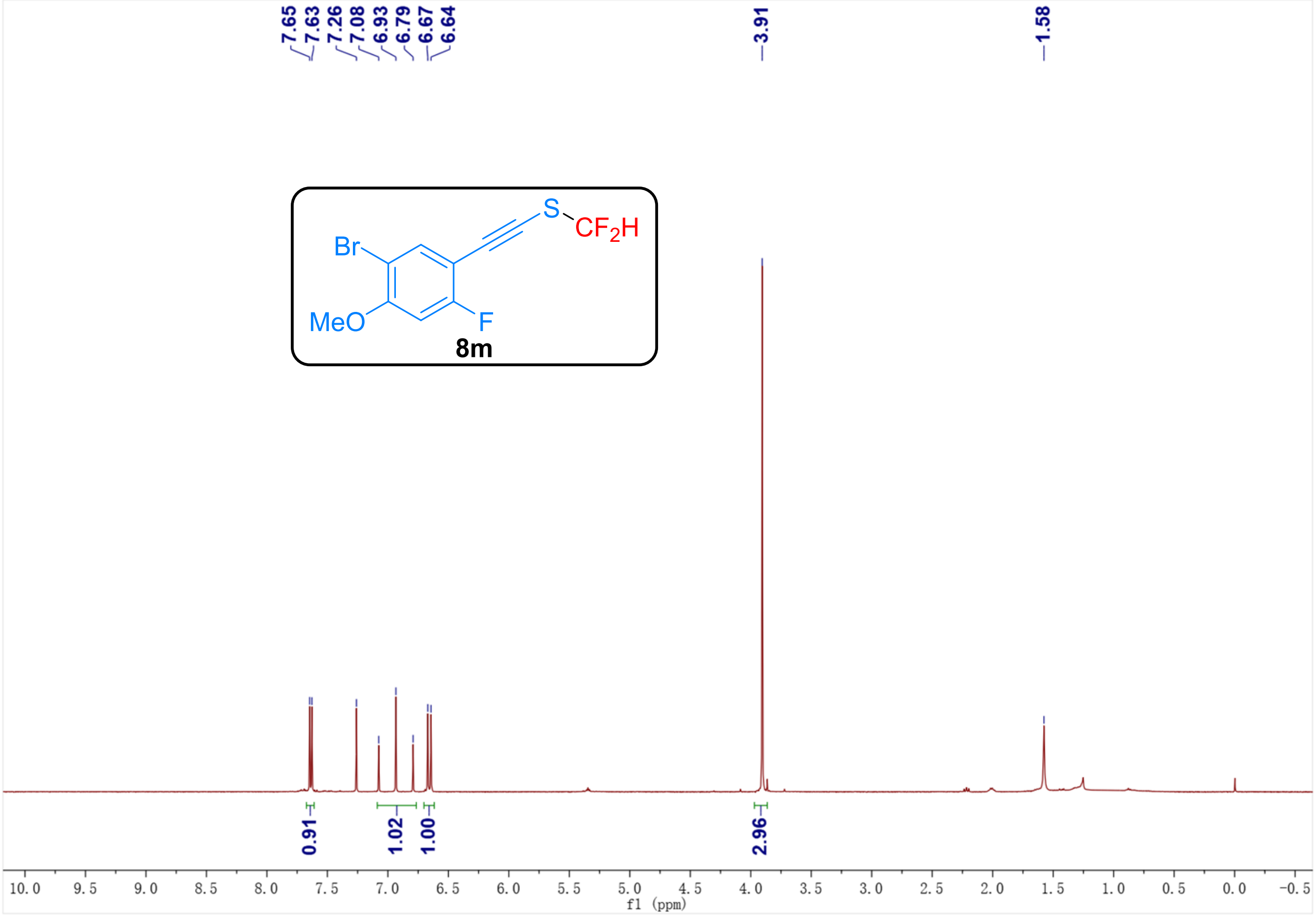
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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7.26
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6.93
6.79
6.67
6.64
3.91
1.58
Br
MeO
S
CF_2H
F
8m
0.91
1.02
1.00
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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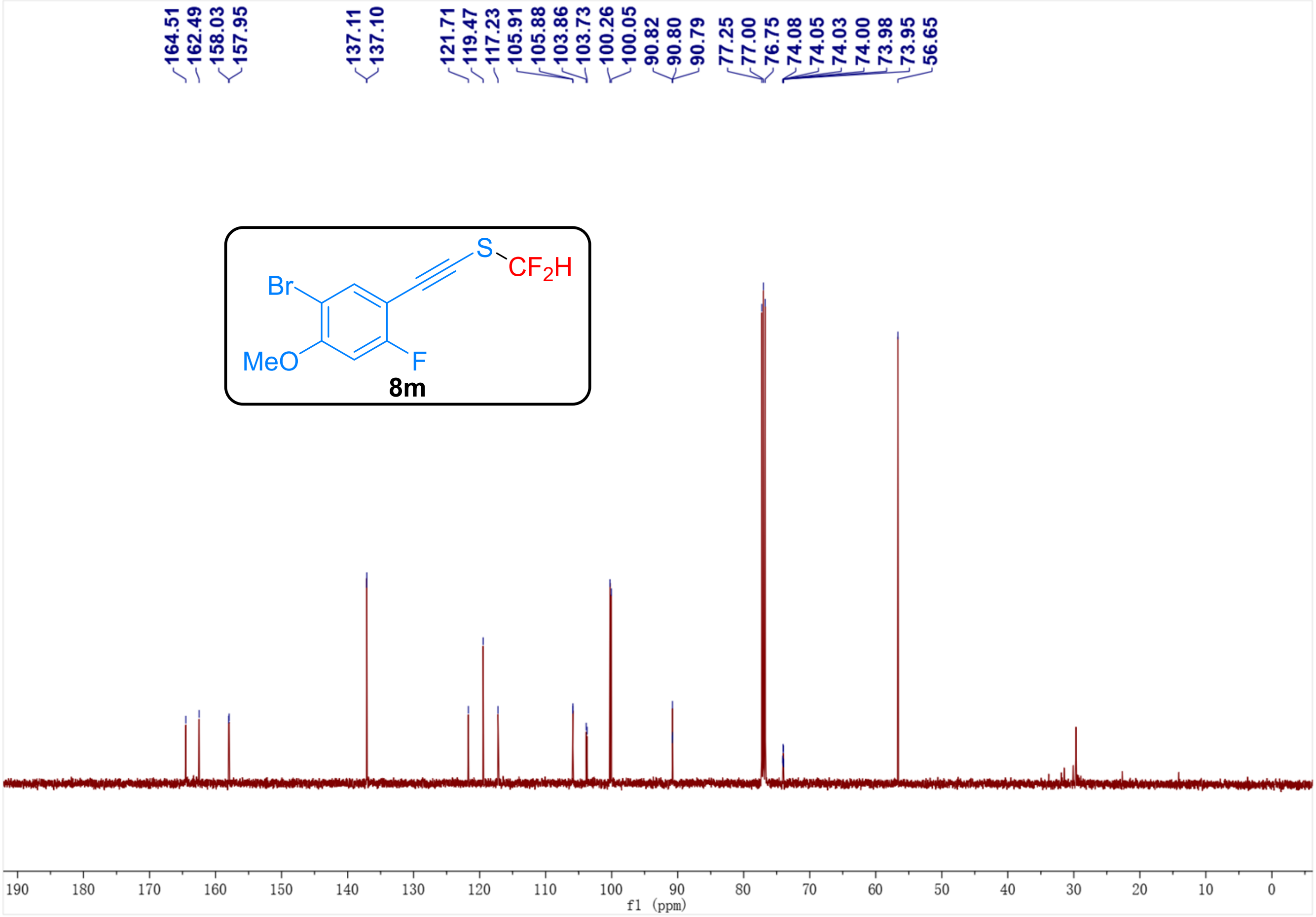
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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119.47
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105.88
103.86
103.73
100.26
100.05
90.82
90.80
90.79
77.25
77.00
76.75
74.08
74.05
74.03
74.00
73.98
73.95
56.65
Br
MeO
S
CF_2H
F
8m
190
180
170
160
150
140
130
120
110
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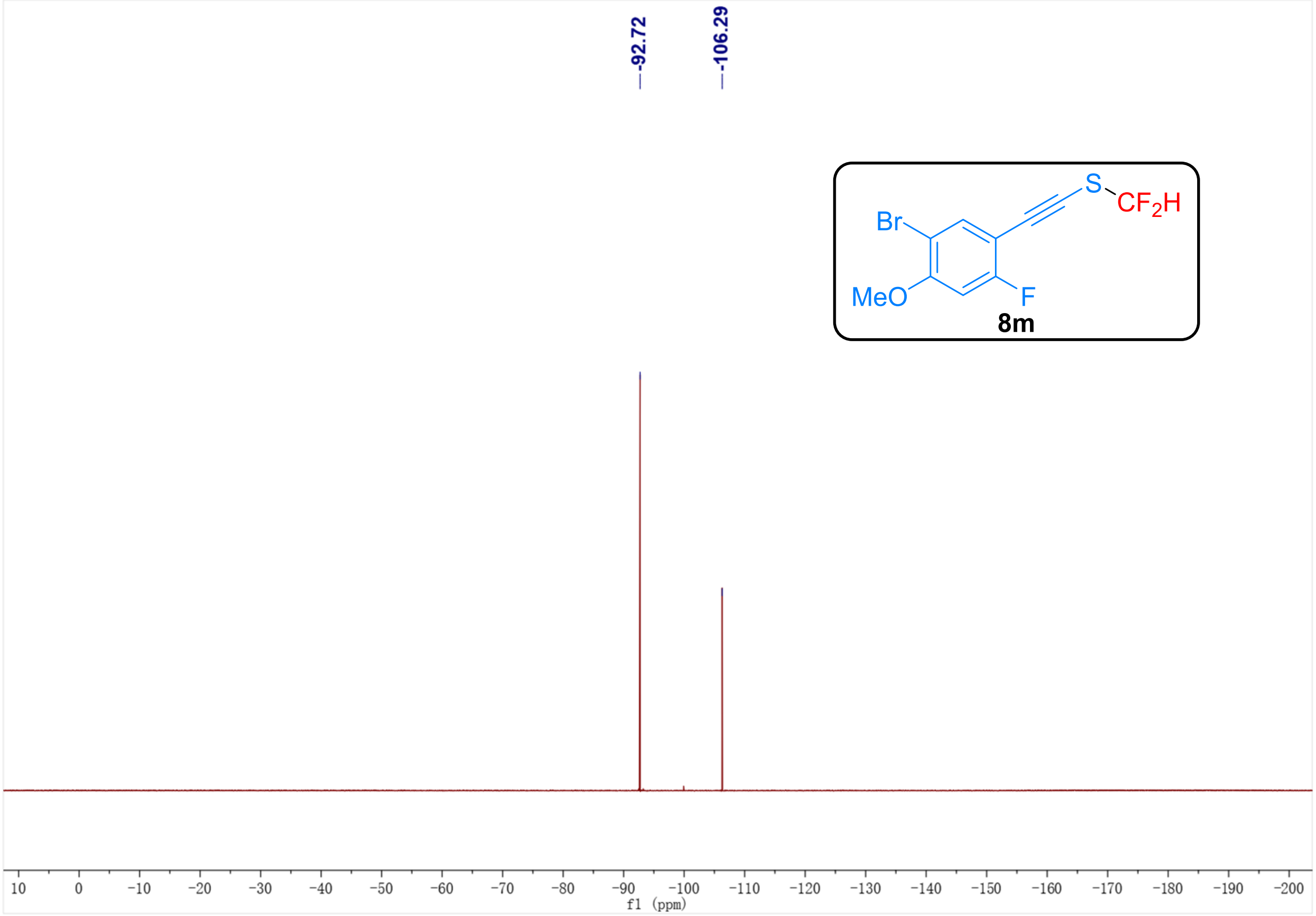
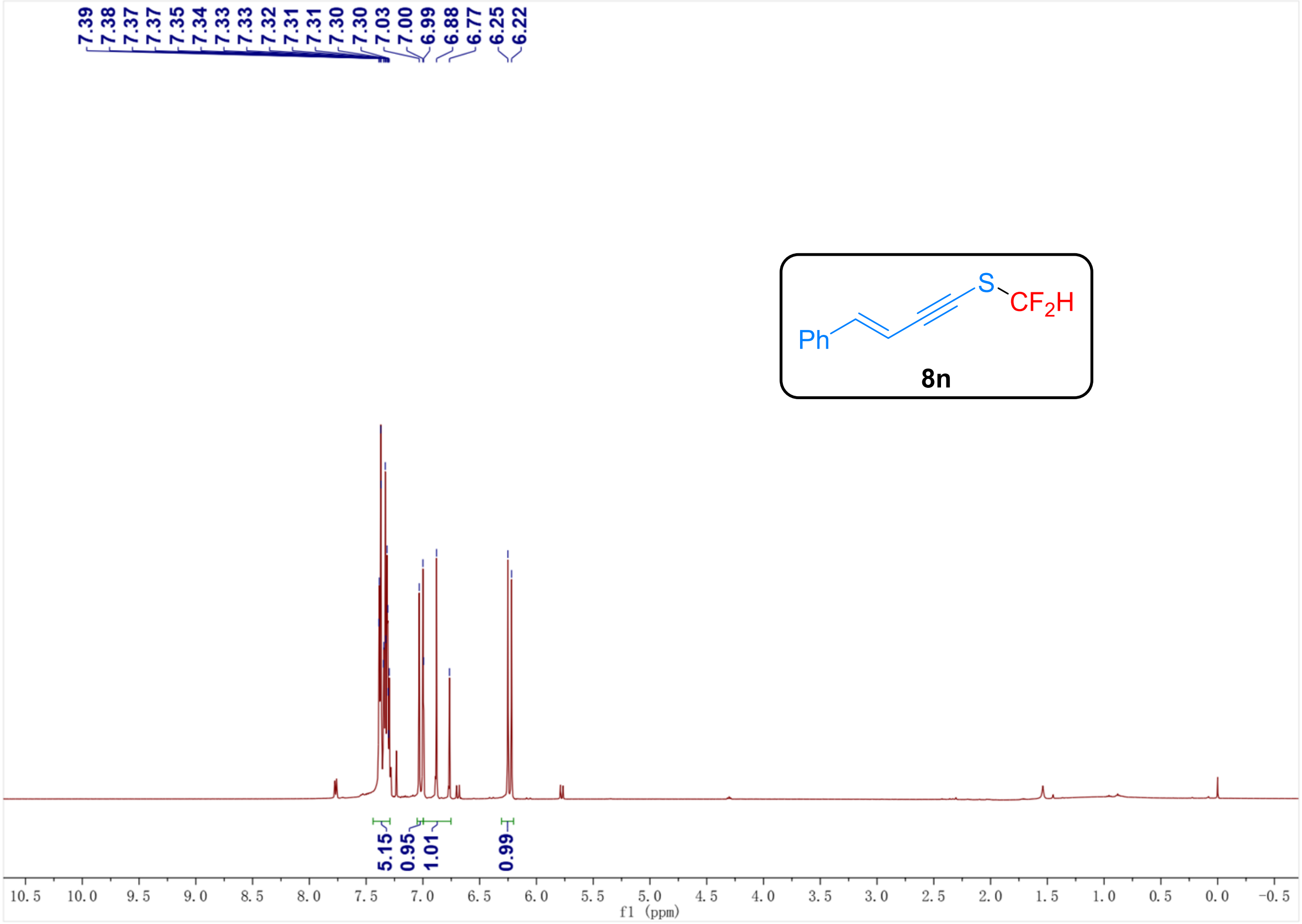
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8m
-92.72
-106.29
Br
MeO
F
S
CF2H
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


8n
7.39
7.38
7.37
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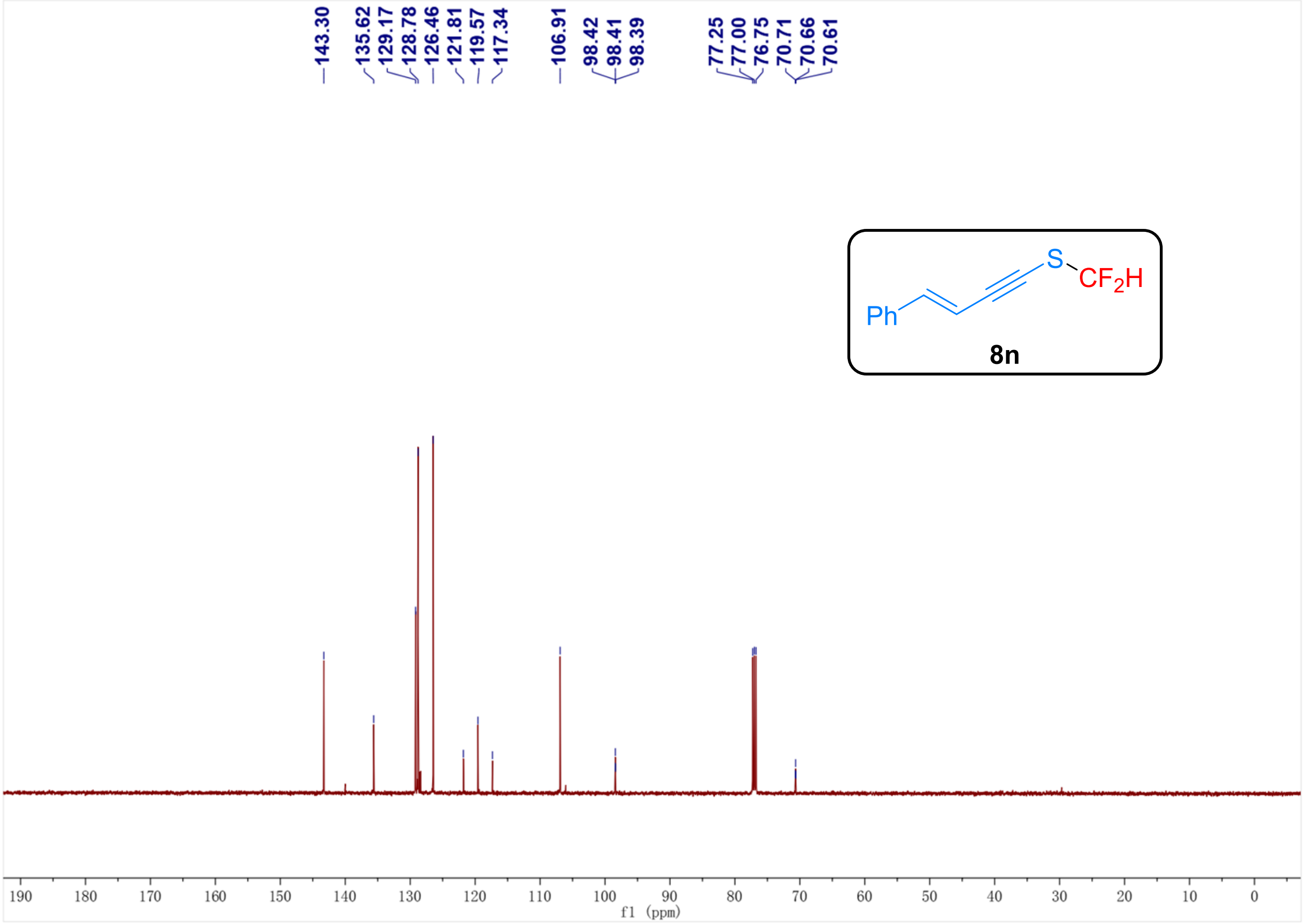
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.03
7.00
6.99
6.88
6.77
6.25
6.22
Ph
S
CF2H
5.15
0.95
1.01
0.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


143.30
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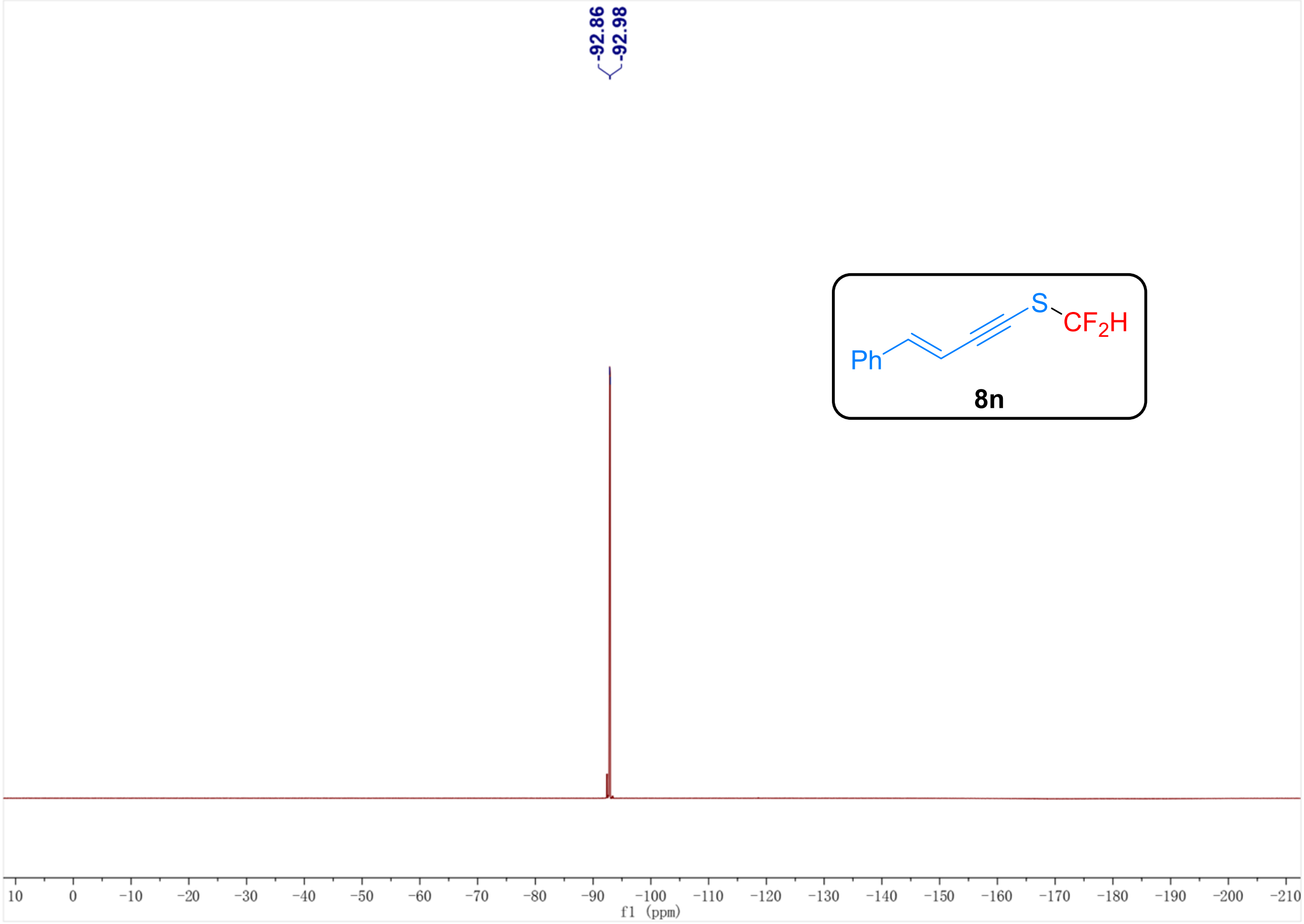
129.17
128.78
126.46
121.81
119.57
117.34
106.91
98.42
98.41
98.39
77.25
77.00
76.75
70.71
70.66
70.61
Ph
S
CF_2H
8n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-92.86
-92.98
Ph
S
CF_2H
8n
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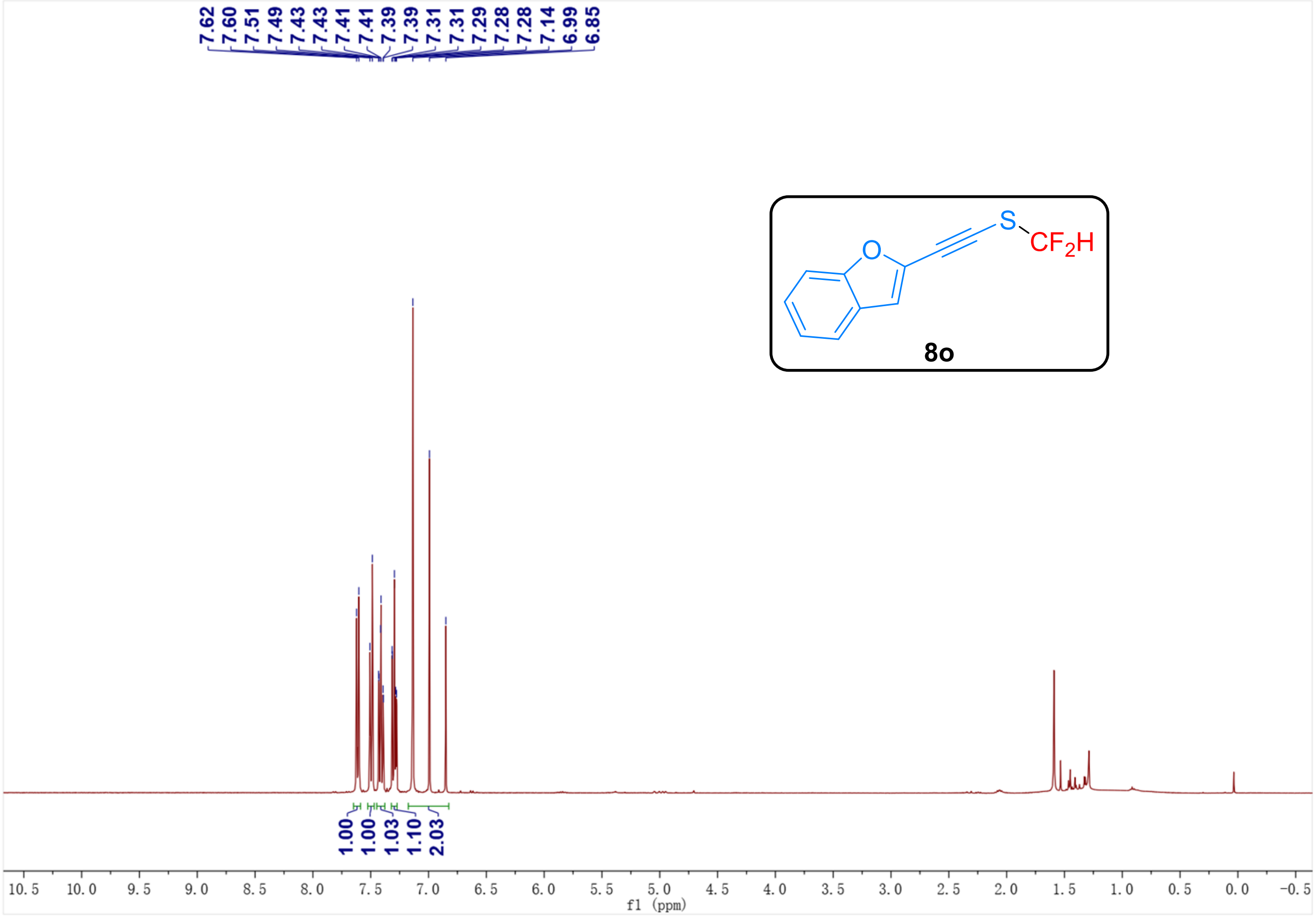
f1 (ppm)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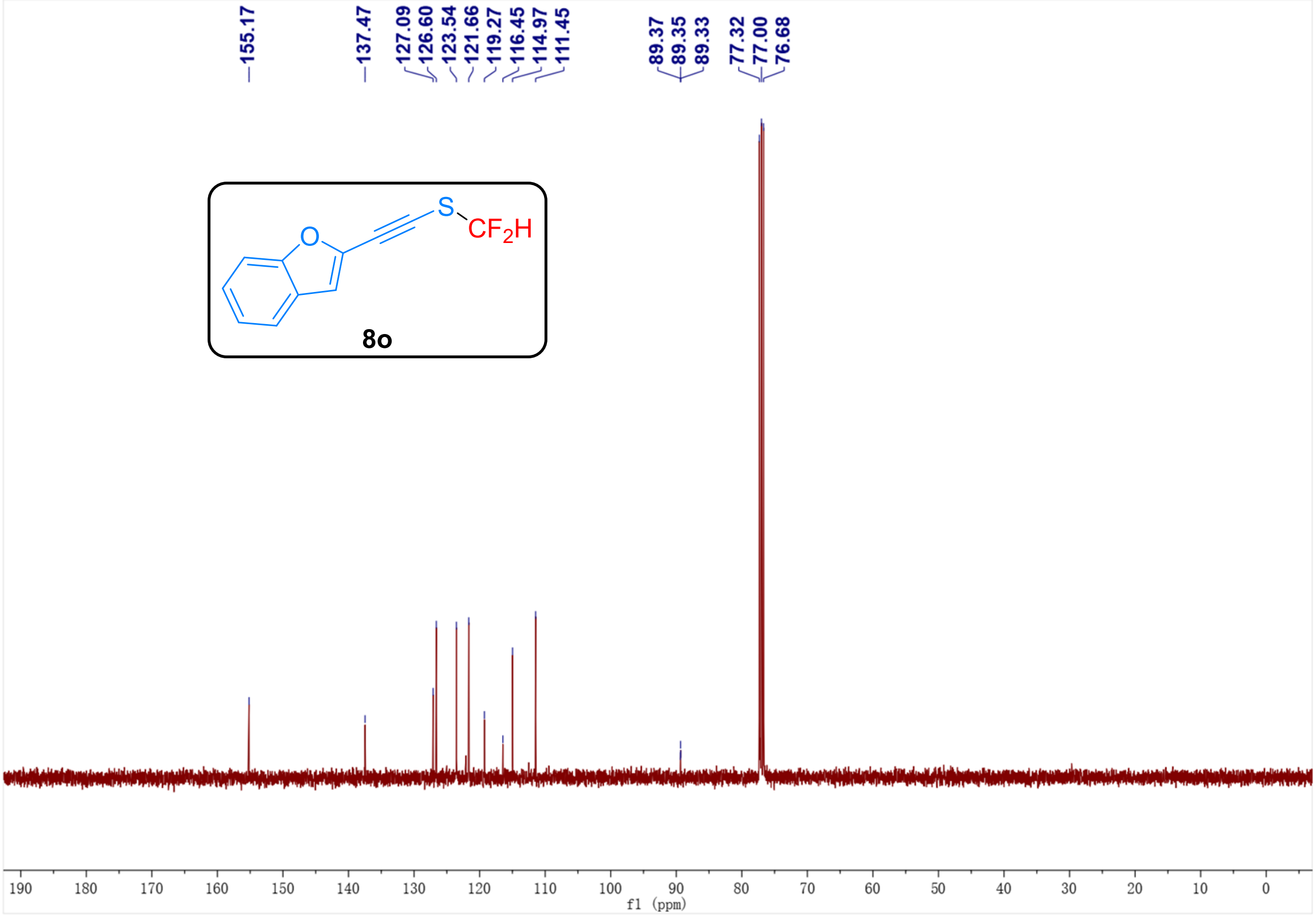
7.51
7.49
7.43
7.43
7.41
7.41
7.39
7.39
7.31
7.31
7.29
7.28
7.28
7.14
6.99
6.85
S
CF$_2$H
O
8o
1.00
1.00
1.03
1.10
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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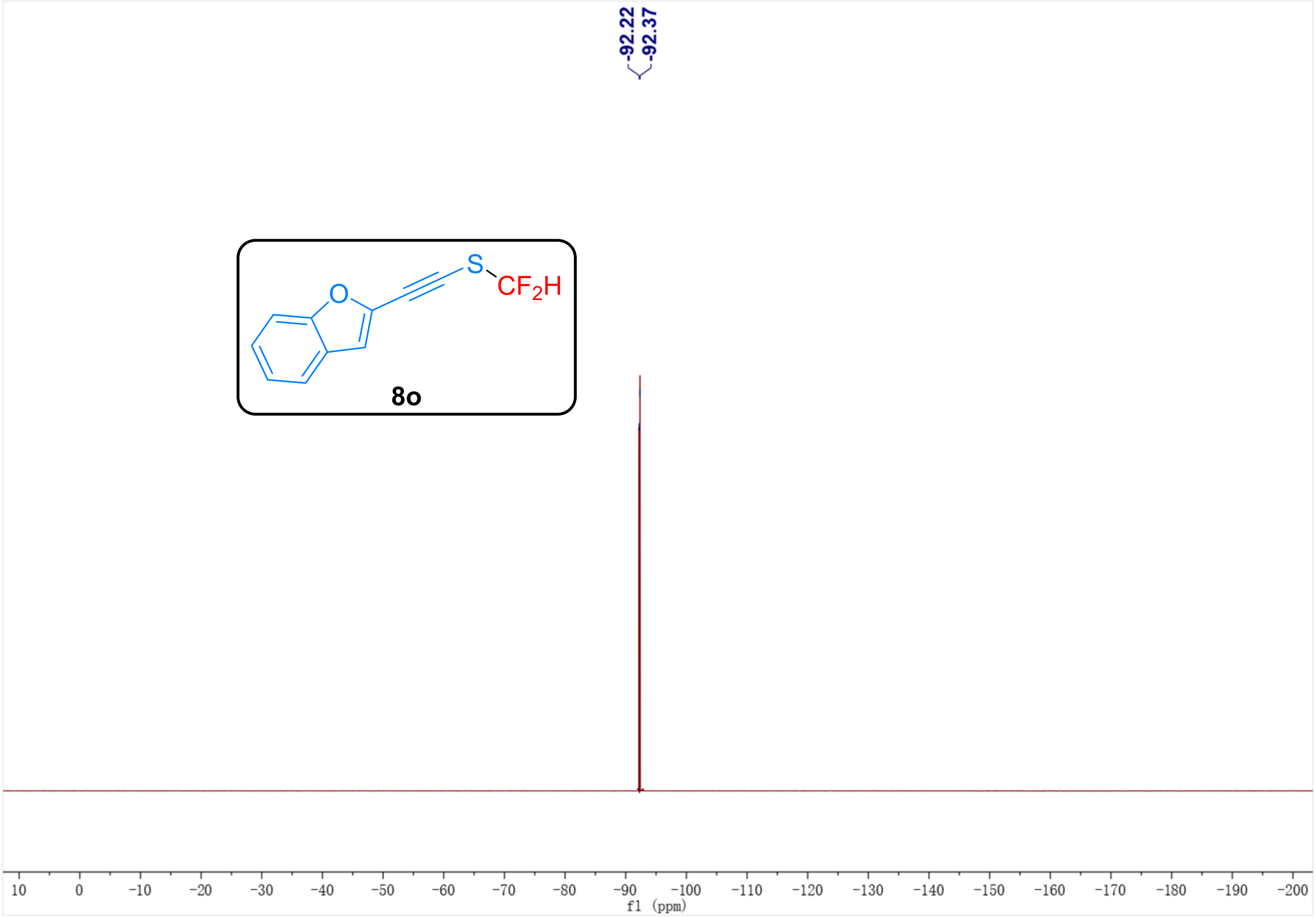
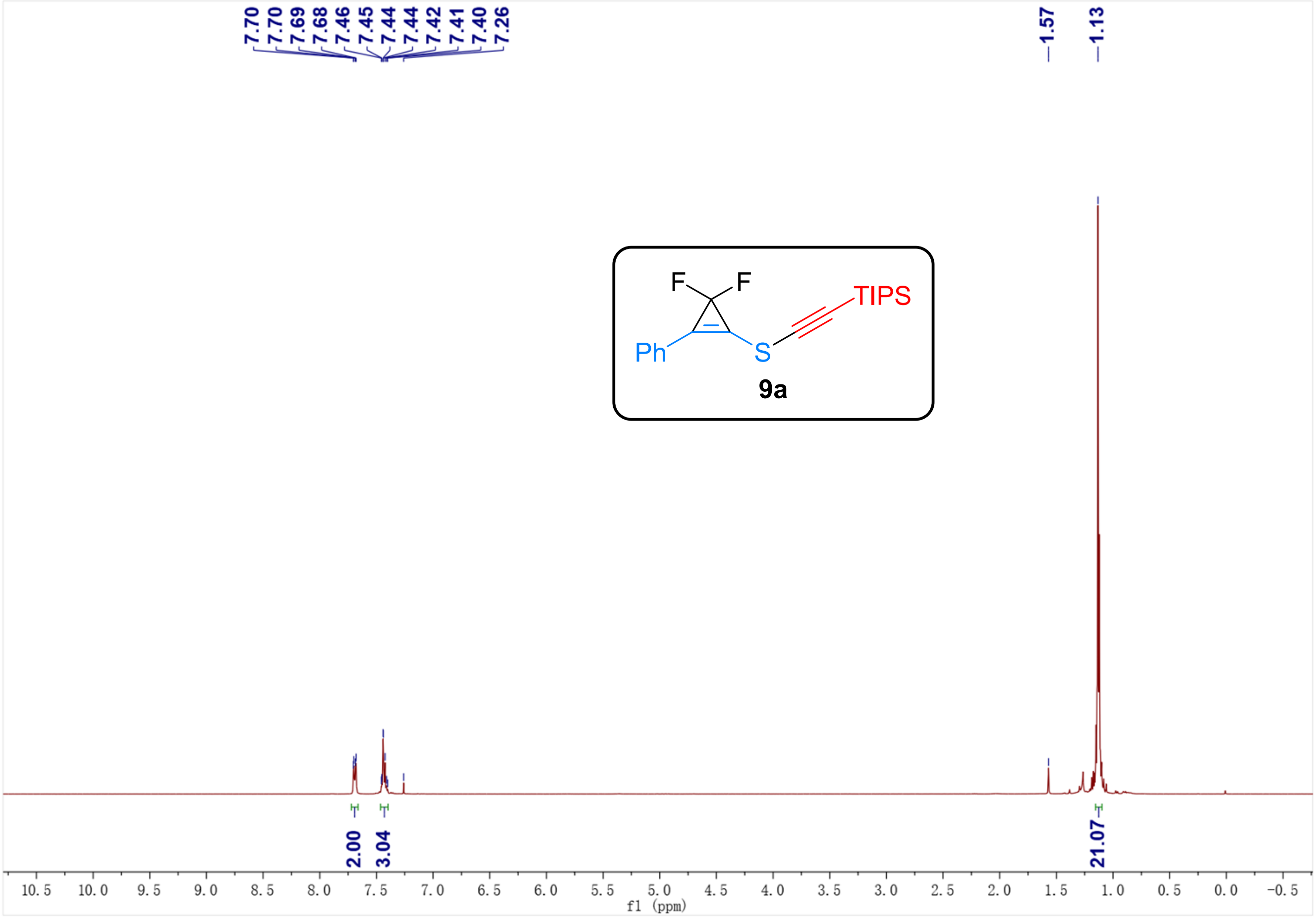
137.47
127.09
126.60
123.54
121.66
119.27
116.45
114.97
111.45
89.37
89.35
89.33
77.32
77.00
76.68
S
CF$_2$H
O
8o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-92.22
-92.37
S
O
CF2H
8o
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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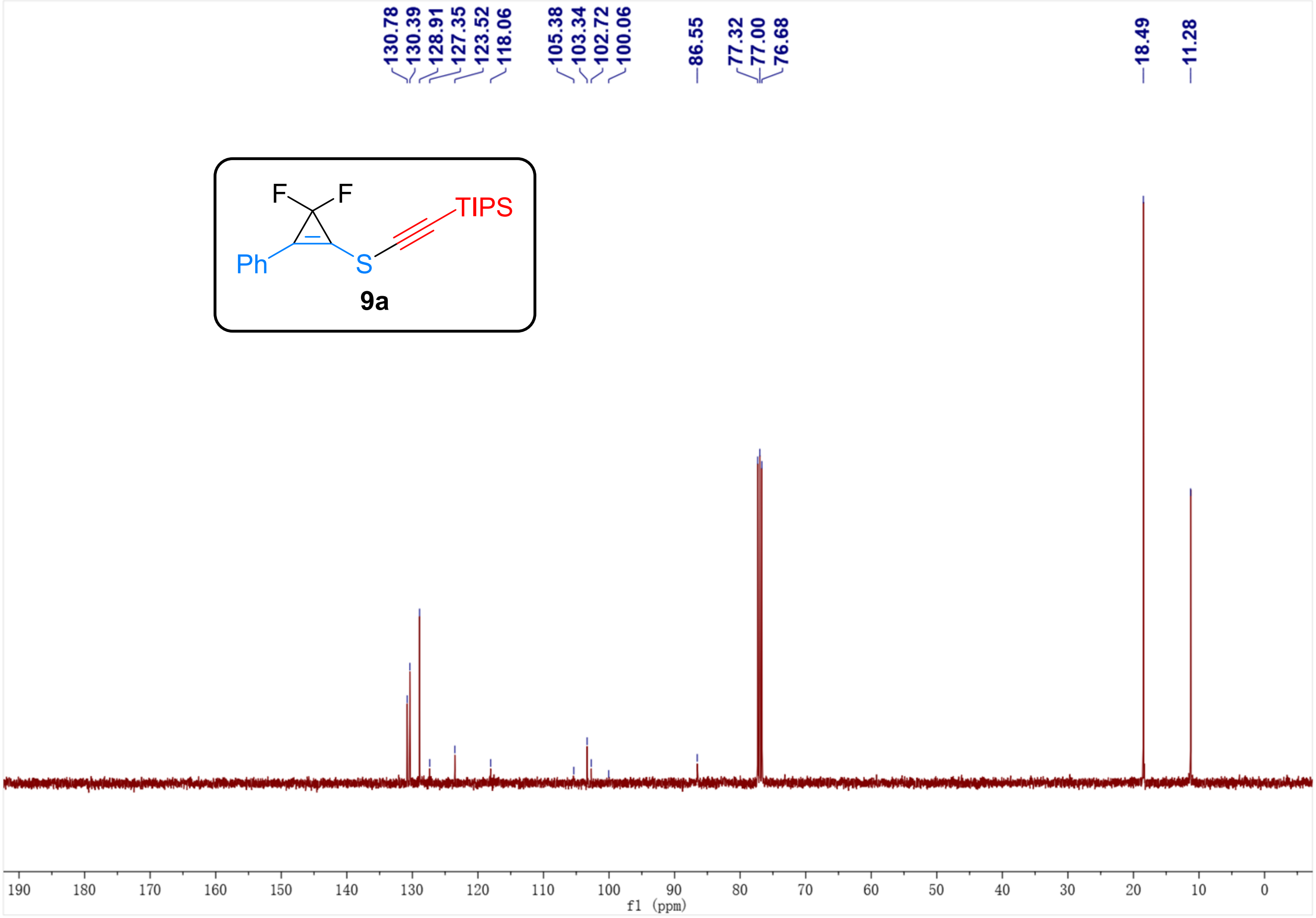
7.70
7.69
7.68
7.46
7.45
7.44
7.44
7.42
7.41
7.40
7.26
1.57
1.13
F
F
TIPS
Ph
S
9a
2.00
3.04
21.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


130.78
130.39
128.91
127.35
123.52
118.06
105.38
103.34
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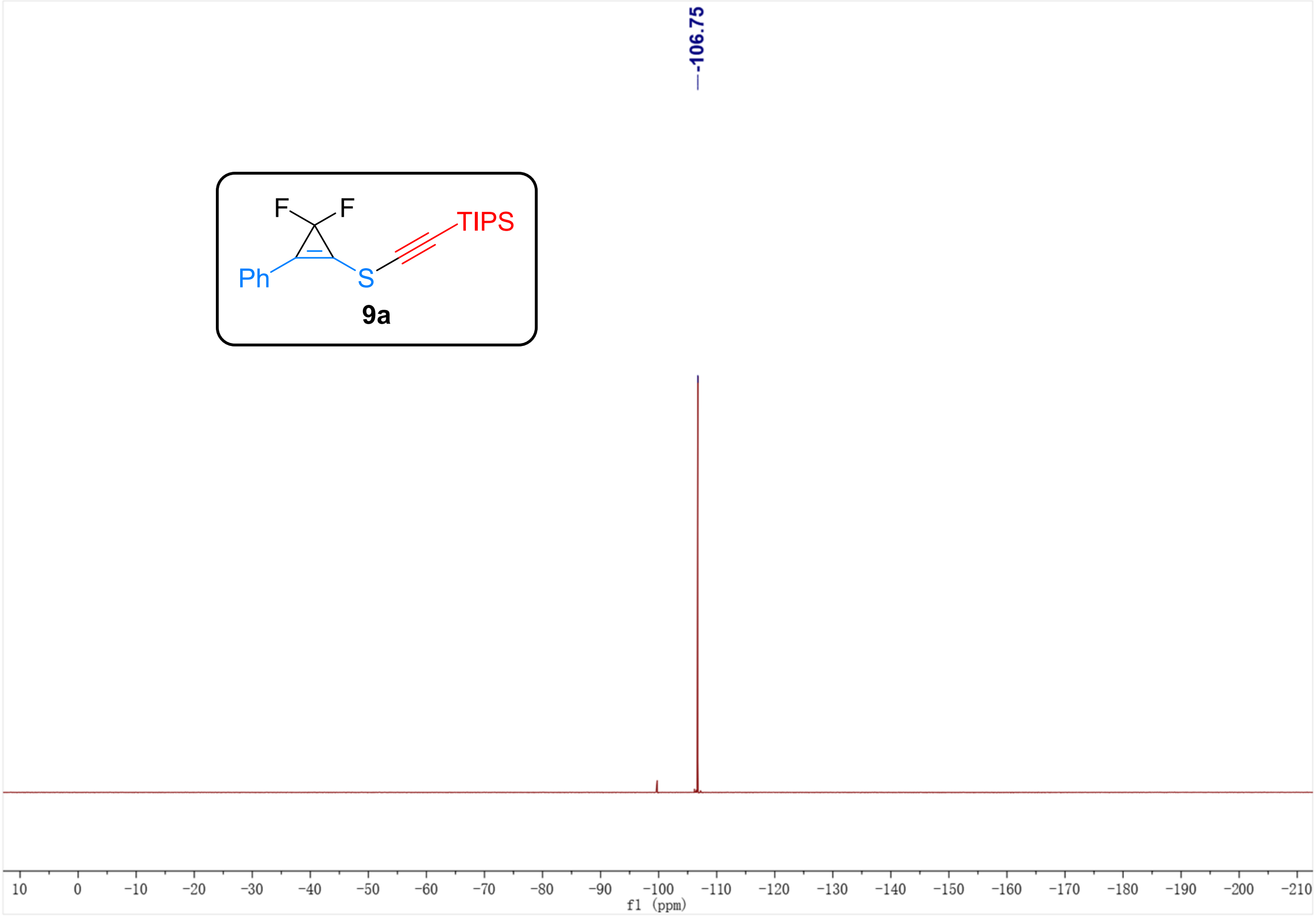
100.06
86.55
77.32
77.00
76.68
18.49
11.28
F
F
TIPS
Ph
S
9a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-106.75
F
F
TIPS
Ph
S
9a
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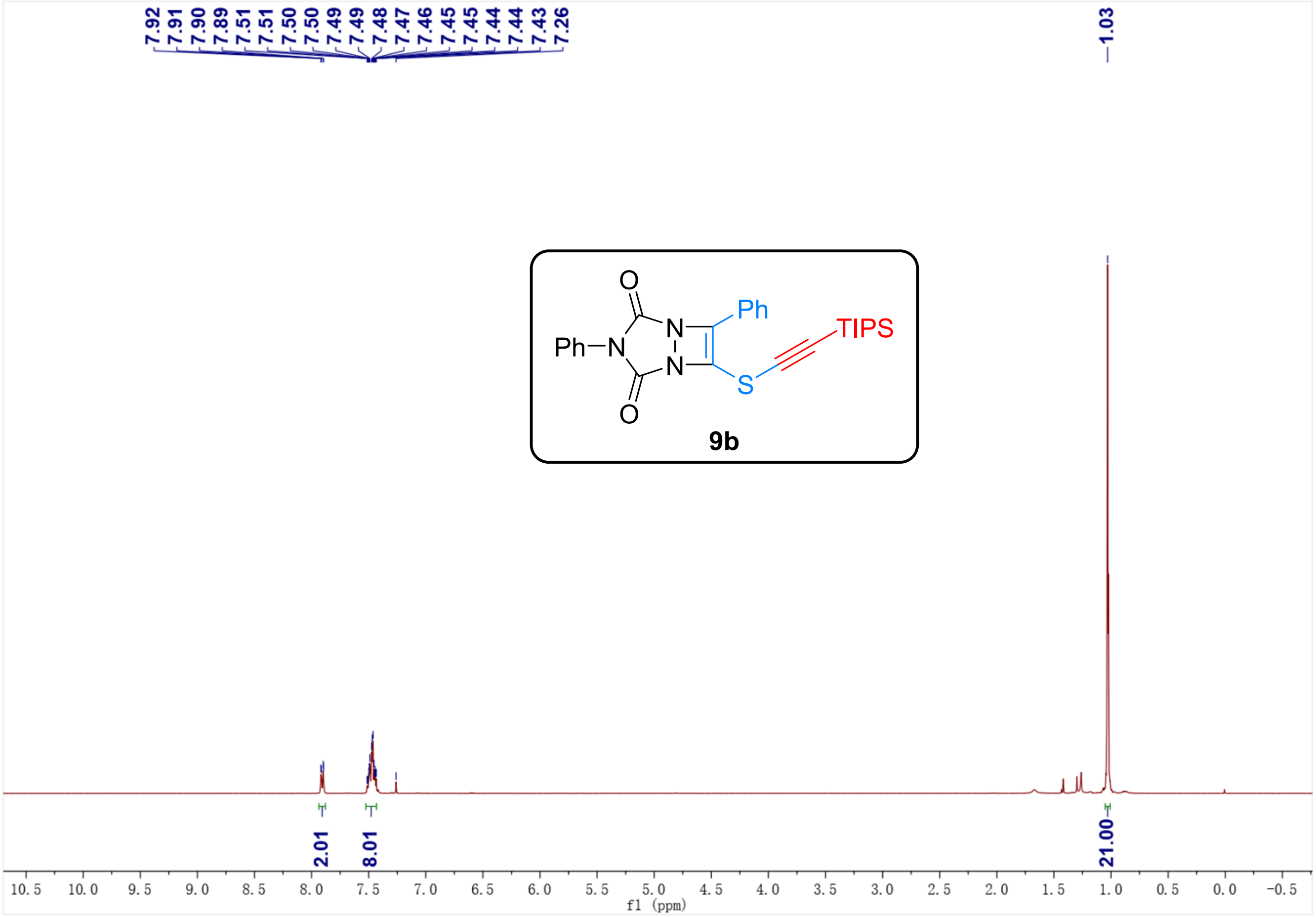
f1 (ppm)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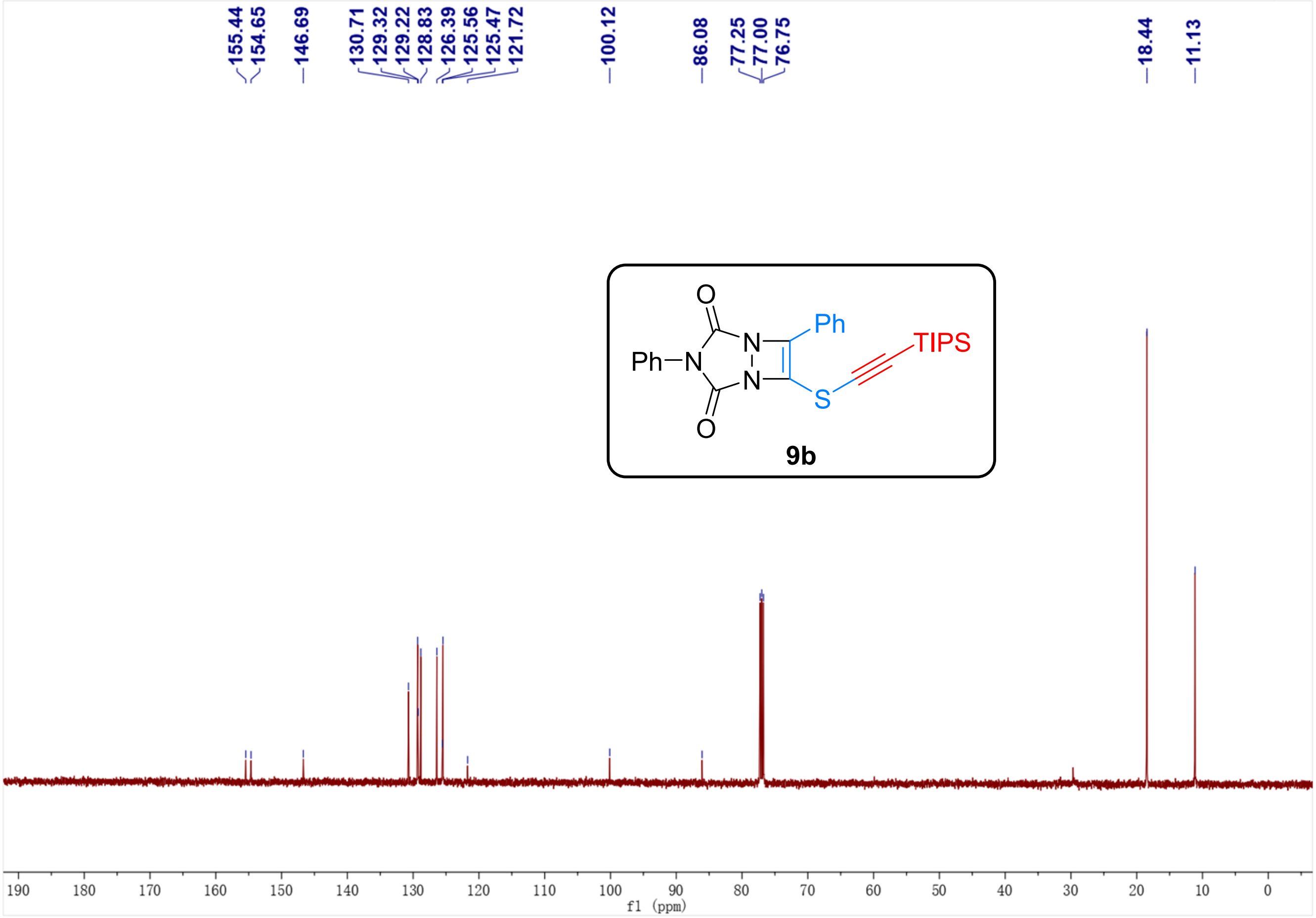
7.91
7.90
7.89
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.26
1.03
Ph
TIPS
O
N
Ph–N
N
S
O
9b
2.01
8.01
21.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.44
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129.22
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126.39
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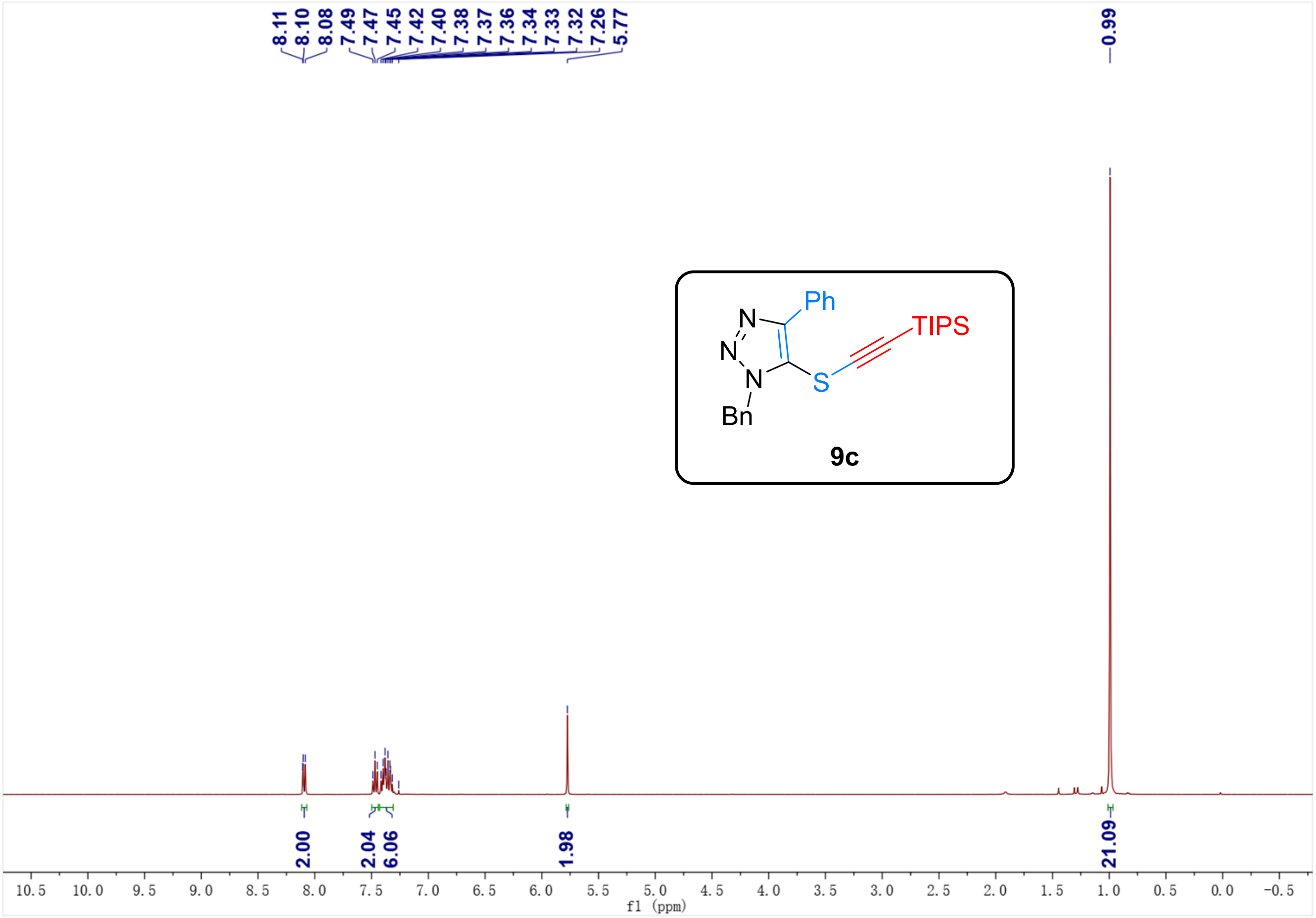
125.47
121.72
100.12
86.08
77.25
77.00
76.75
18.44
11.13
Ph
TIPS
O
N
Ph–N
N
S
O
9b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.40
7.38
7.37
7.36
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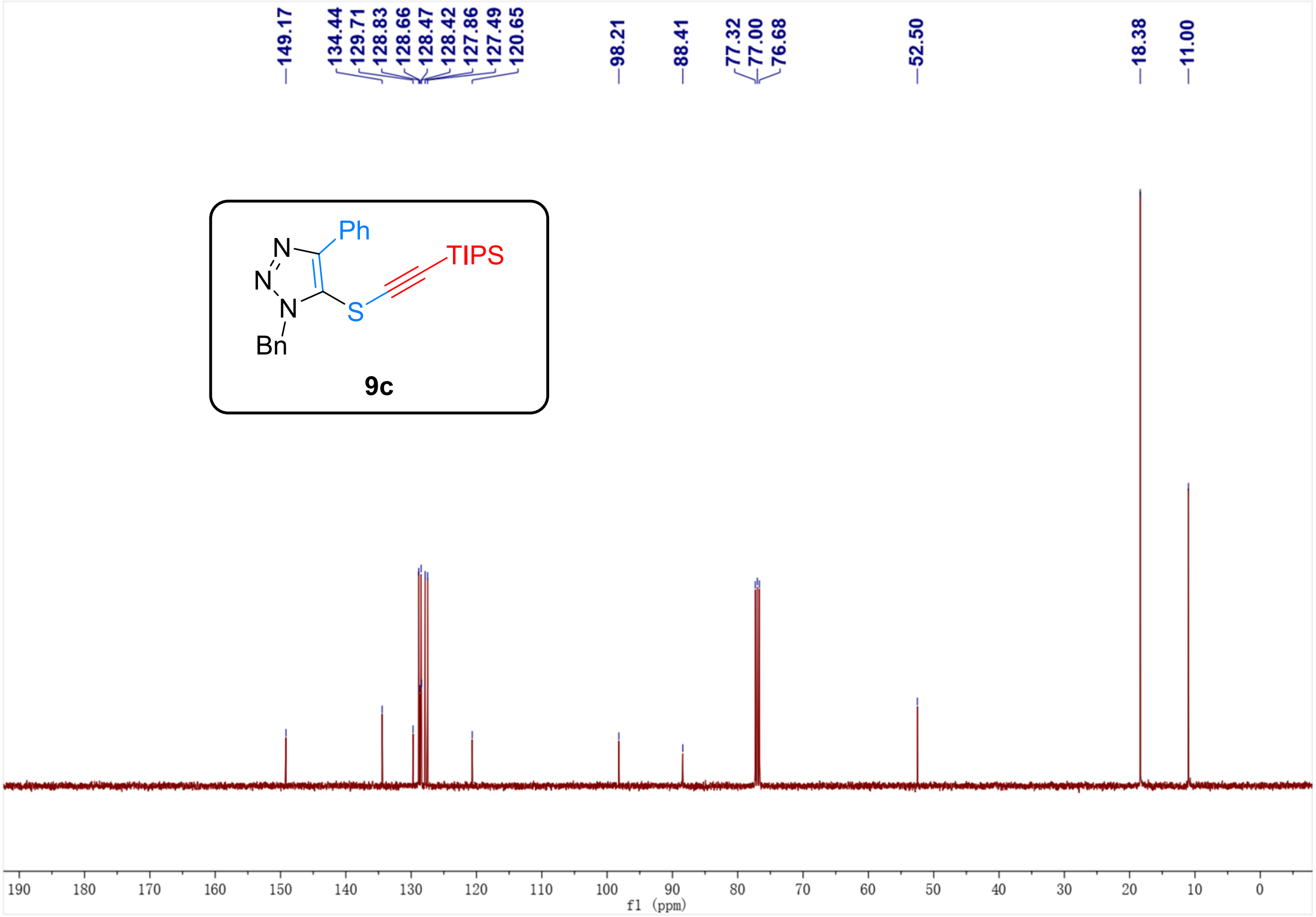
7.33
7.32
7.26
5.77
0.99
N
N
N
Bn
Ph
S
TIPS
9c
2.00
2.04
6.06
1.98
21.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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120.65
98.21
88.41
77.32
77.00
76.68
52.50
18.38
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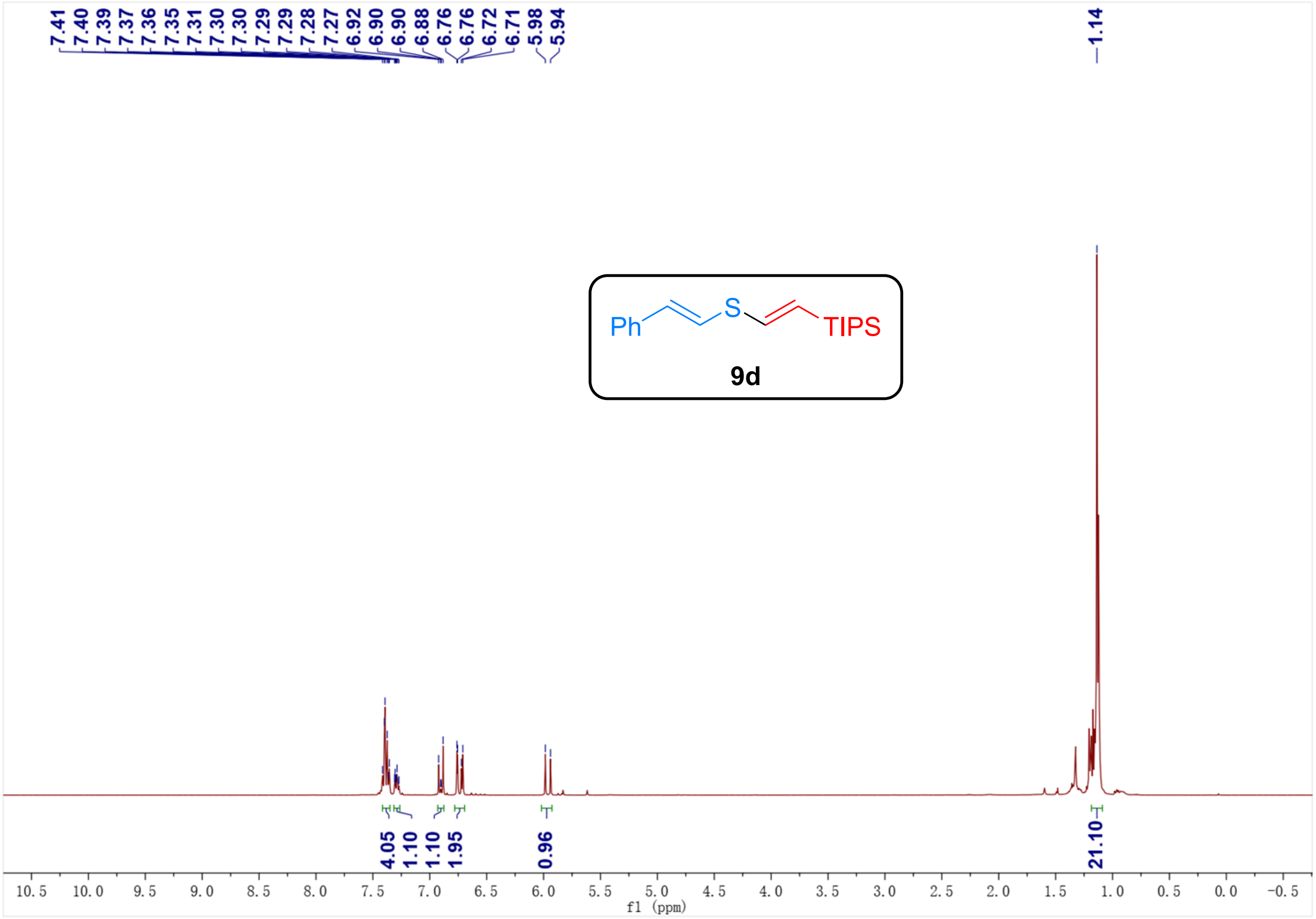
N
Bn
Ph
S
TIPS
9c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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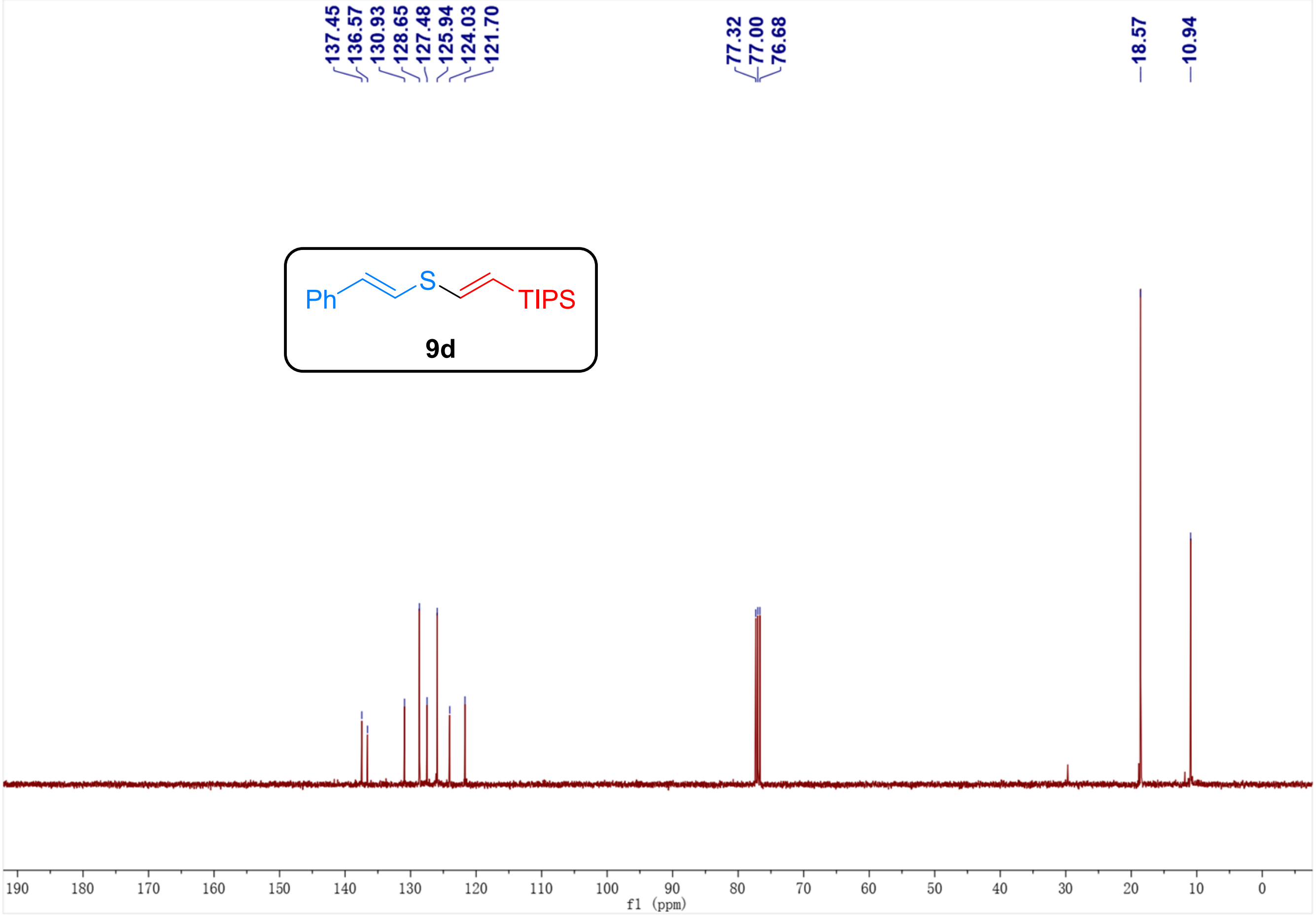
7.29
7.29
7.28
7.27
6.92
6.90
6.90
6.88
6.76
6.76
6.72
6.71
5.98
5.94
1.14
Ph
S
TIPS
9d
4.05
1.10
1.10
1.95
0.96
21.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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125.94
124.03
121.70
77.32
77.00
76.68
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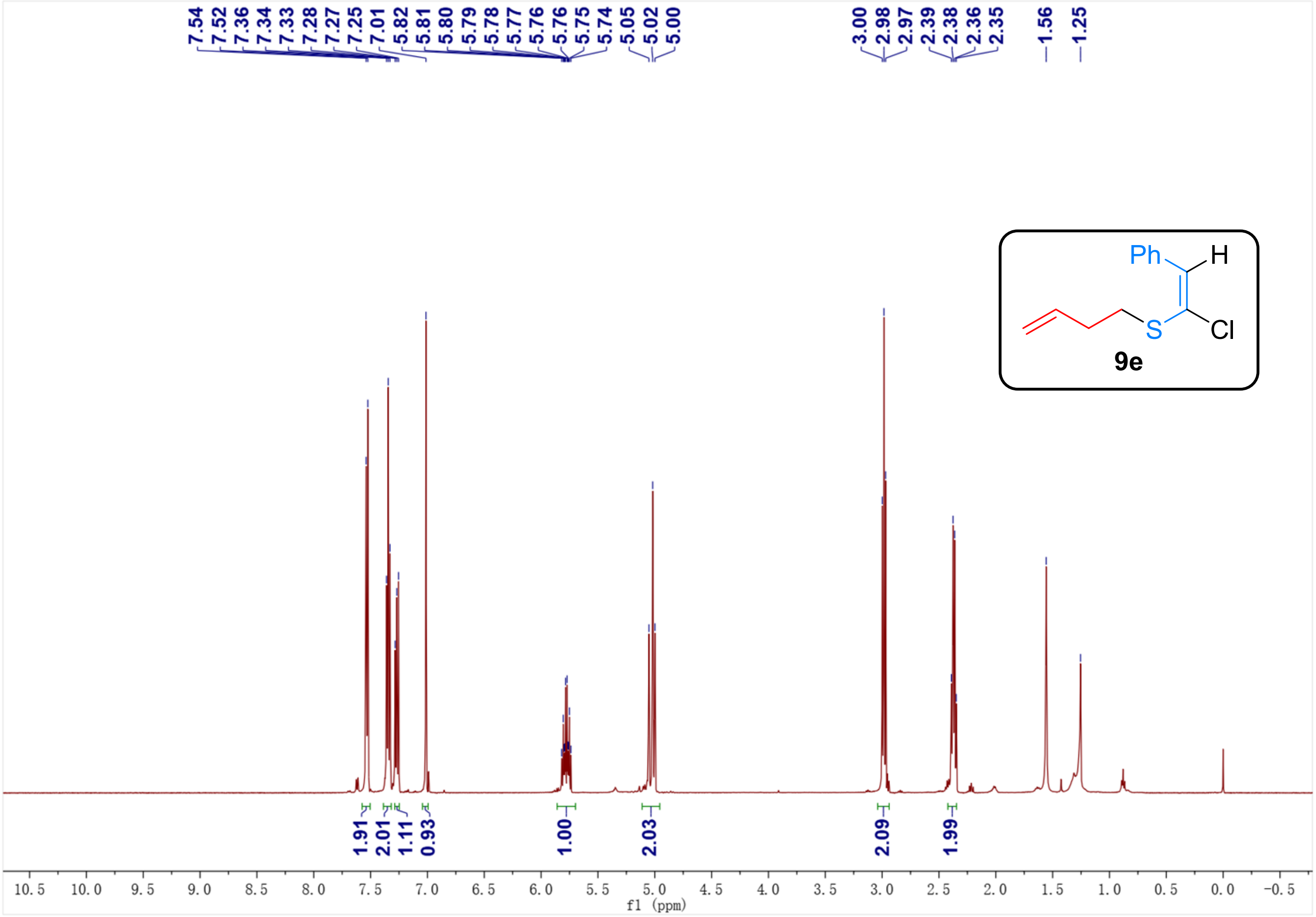
10.94
Ph
S
TIPS
9d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.28
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7.25
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5.81
5.80
5.79
5.78
5.77
5.76
5.76
5.75
5.74
5.05
5.02
5.00
3.00
2.98
2.97
2.39
2.38
2.36
2.35
1.56
1.25
1.91
2.01
1.11
0.93
1.00
2.03
2.09
1.99
Ph
H
S
Cl
9e
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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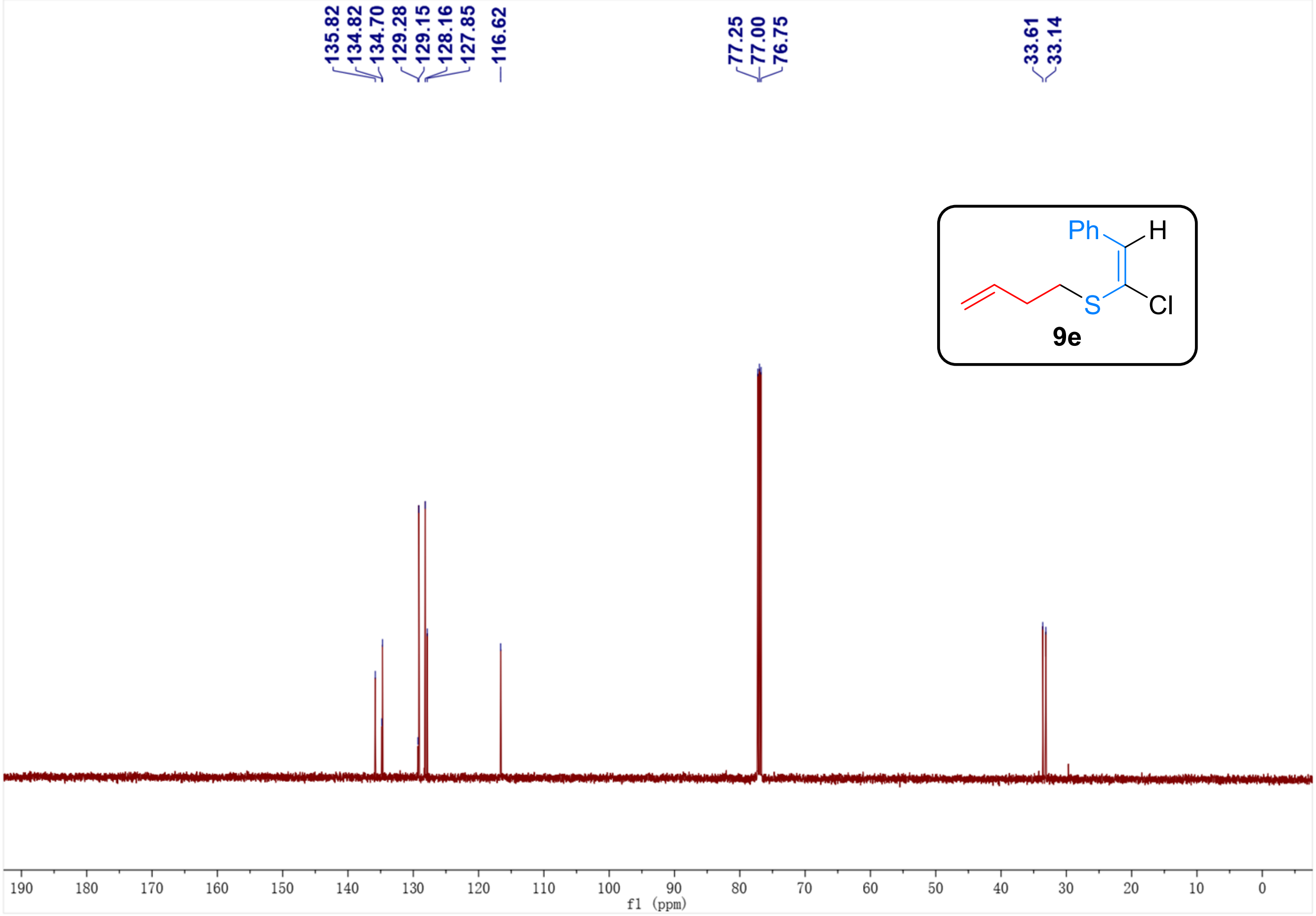
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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33.61
33.14
Ph
H
S
Cl
9e
190
180
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120
110
100
90
80
70
60
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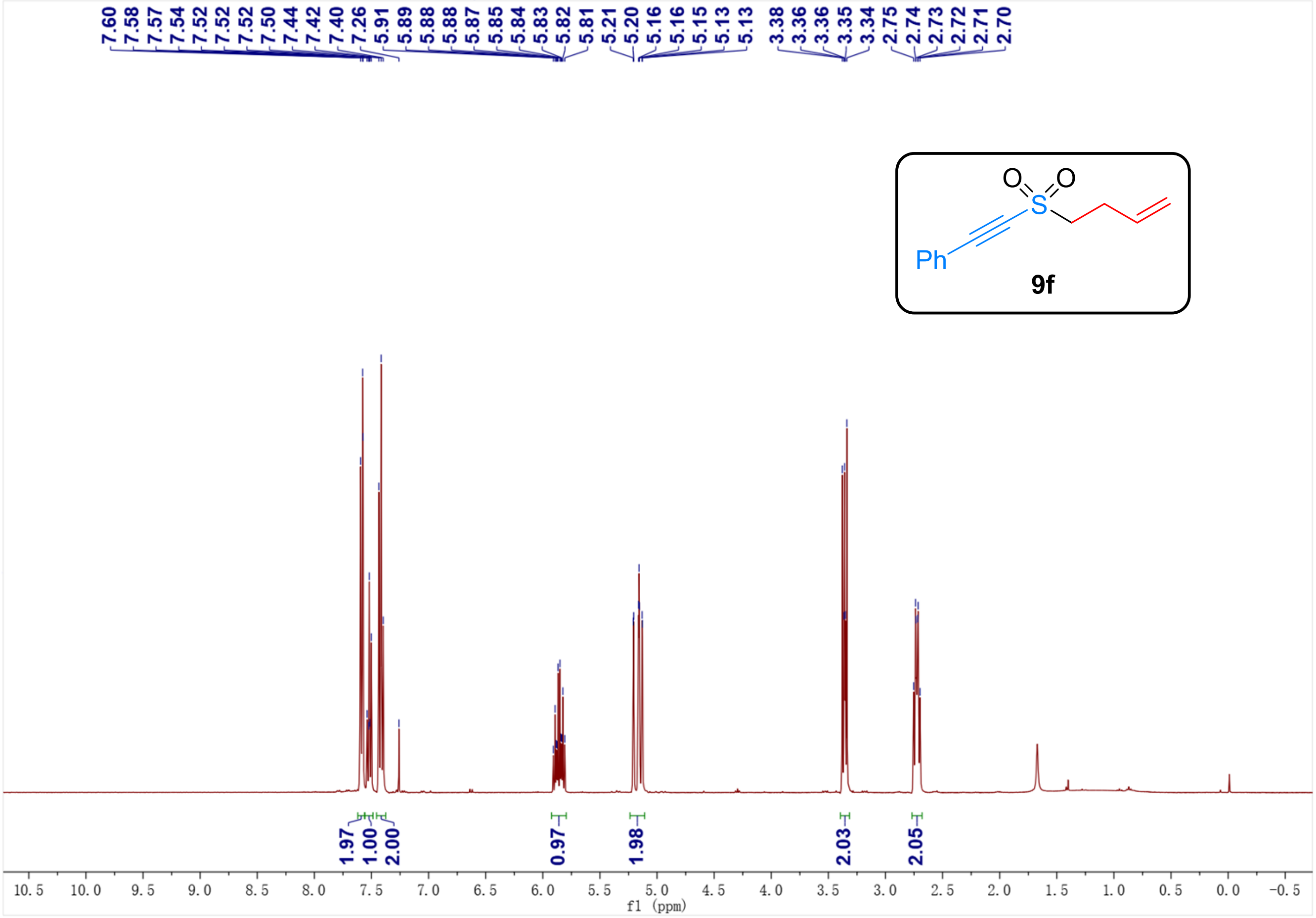
40
30
20
10
0
f1 (ppm)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7.40
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5.89
5.88
5.88
5.87
5.85
5.84
5.83
5.82
5.81
5.21
5.20
5.16
5.16
5.15
5.13
5.13
3.38
3.36
3.36
3.35
3.34
2.75
2.74
2.73
2.72
2.71
2.70
O
O
S
Ph
9f
1.97
1.00
2.00
0.97
1.98
2.03
2.05
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
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5.5
5.0
4.5
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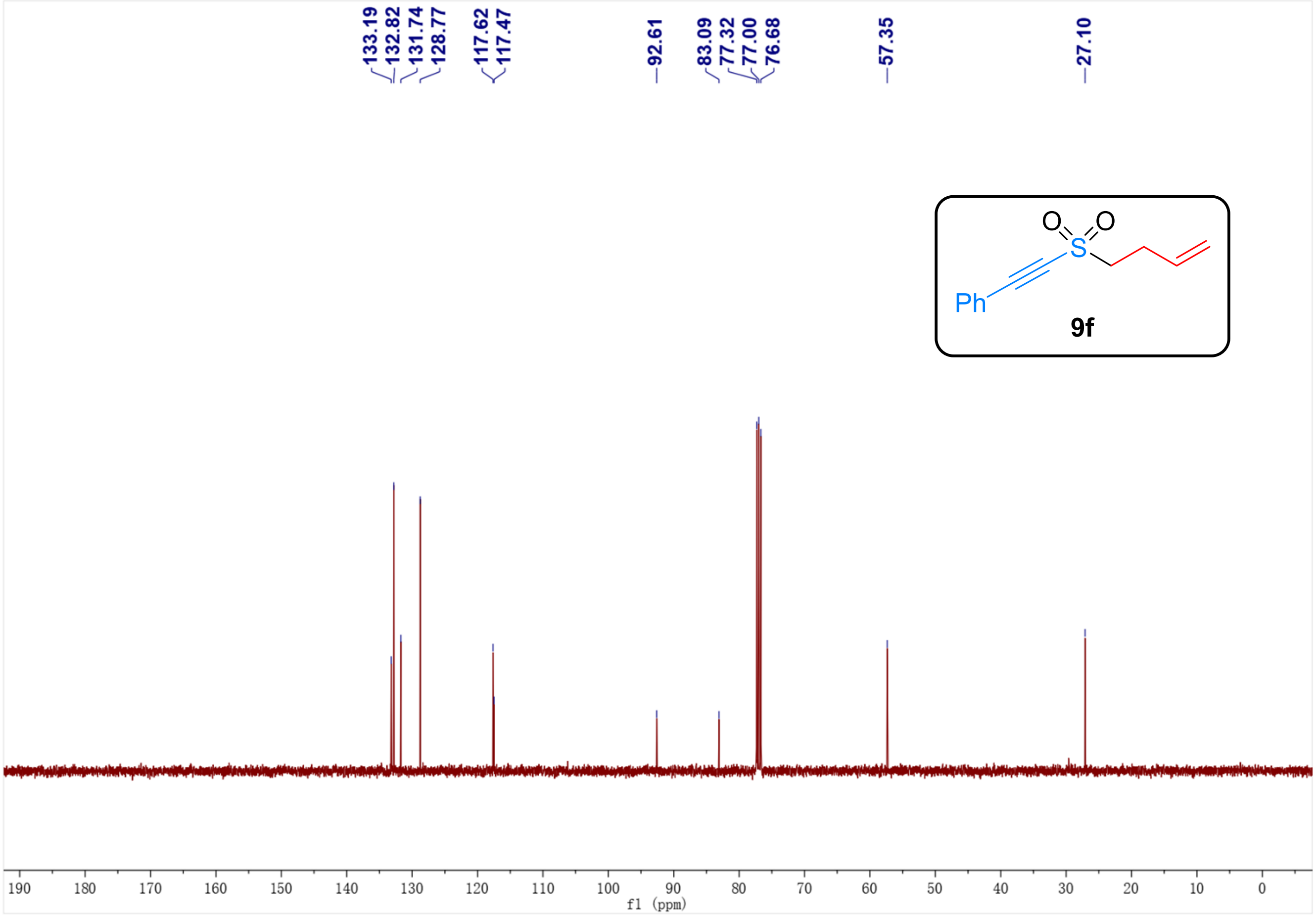
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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117.47
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83.09
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77.00
76.68
57.35
27.10
O
O
S
Ph
9f
190
180
170
160
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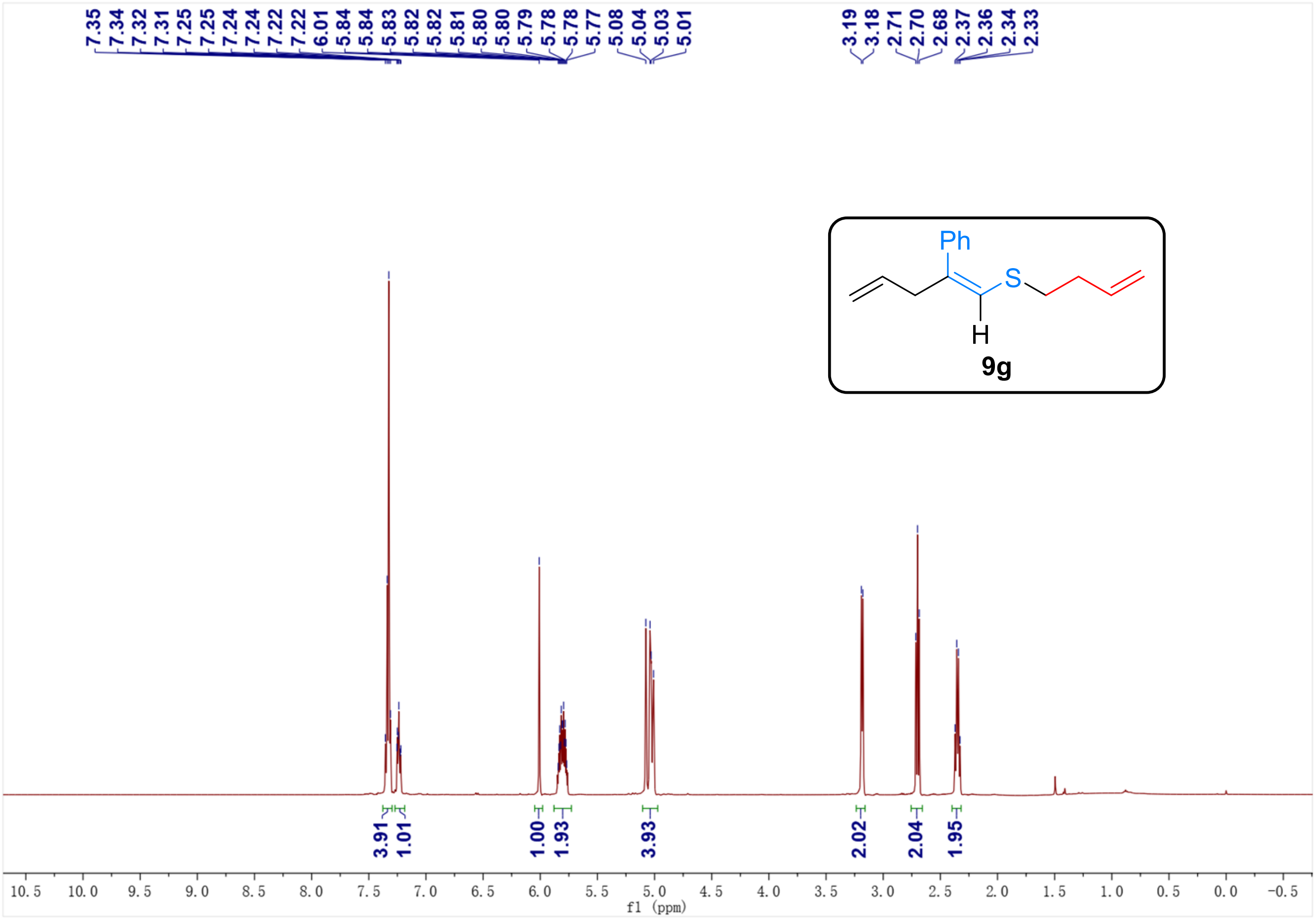
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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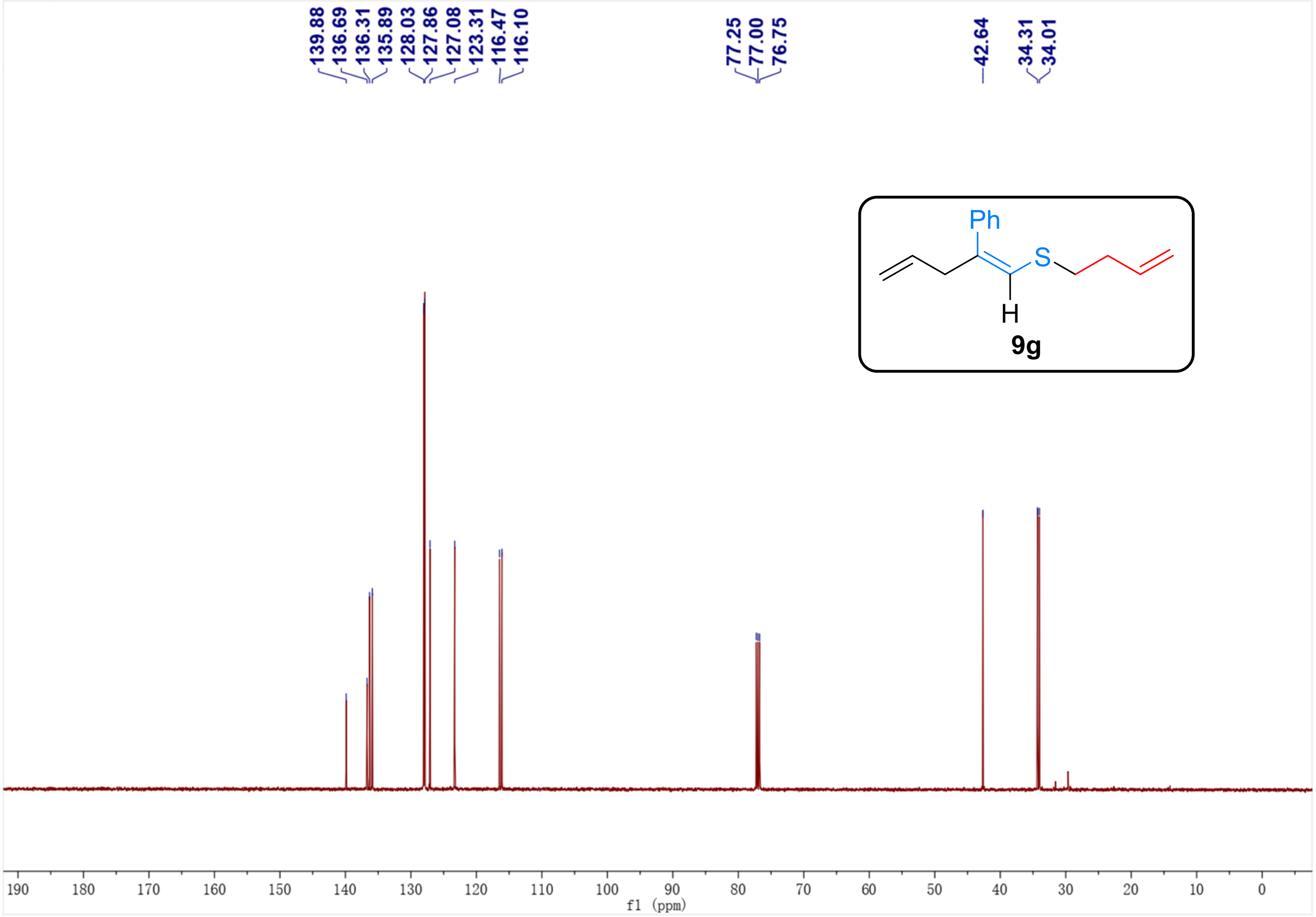
7.22
6.01
5.84
5.84
5.83
5.82
5.82
5.81
5.80
5.80
5.79
5.78
5.78
5.77
5.08
5.04
5.03
5.01
3.19
3.18
2.71
2.70
2.68
2.37
2.36
2.34
2.33
Ph
S
H
9g
3.91
1.01
1.00
1.93
3.93
2.02
2.04
1.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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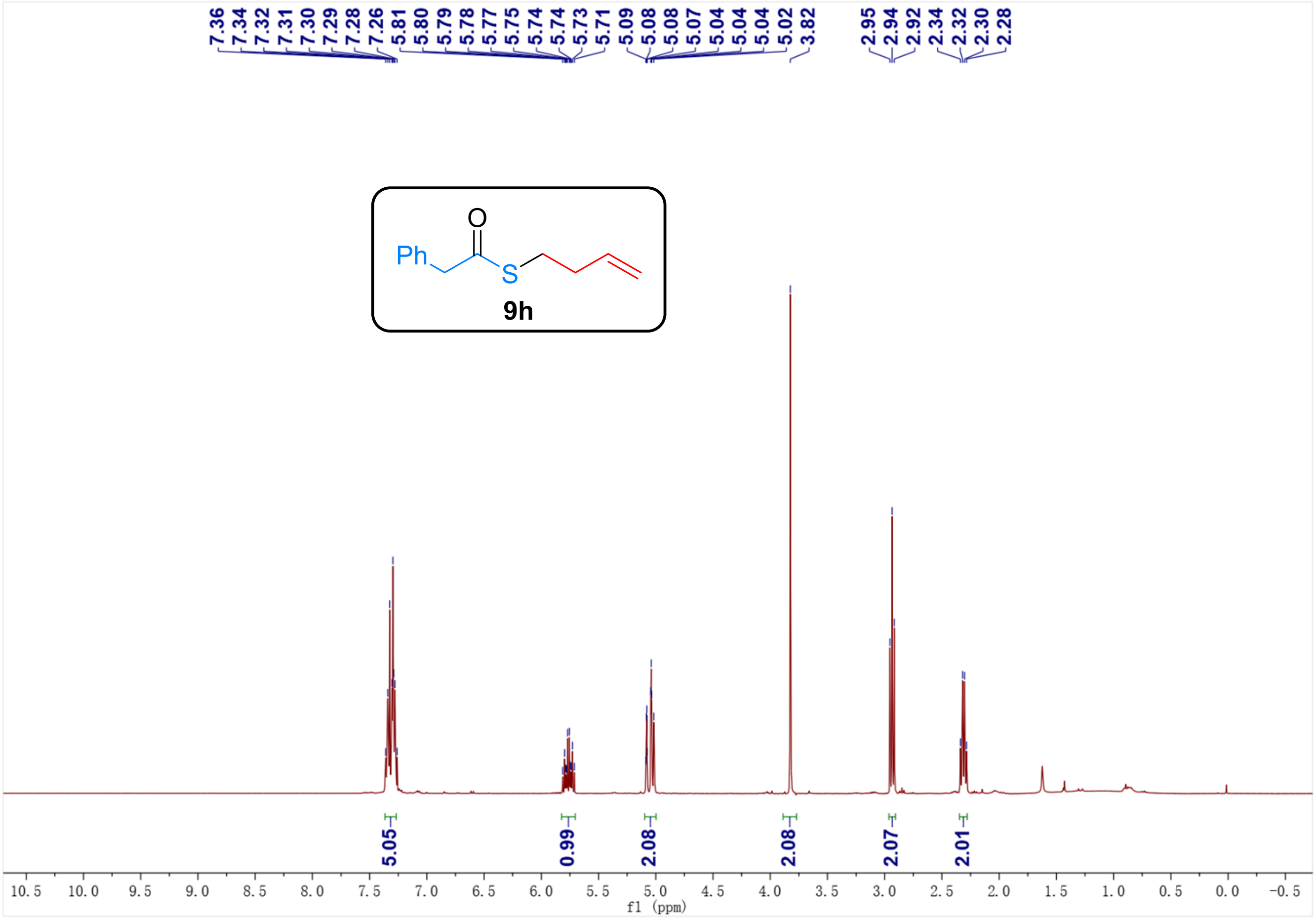
116.10
77.25
77.00
76.75
42.64
34.31
34.01
Ph
S
H
9g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.74
5.73
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5.08
5.08
5.07
5.04
5.04
5.04
5.02
3.82
2.95
2.94
2.92
2.34
2.32
2.30
2.28
Ph
O
S
9h
5.05
0.99
2.08
2.08
2.07
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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0.5
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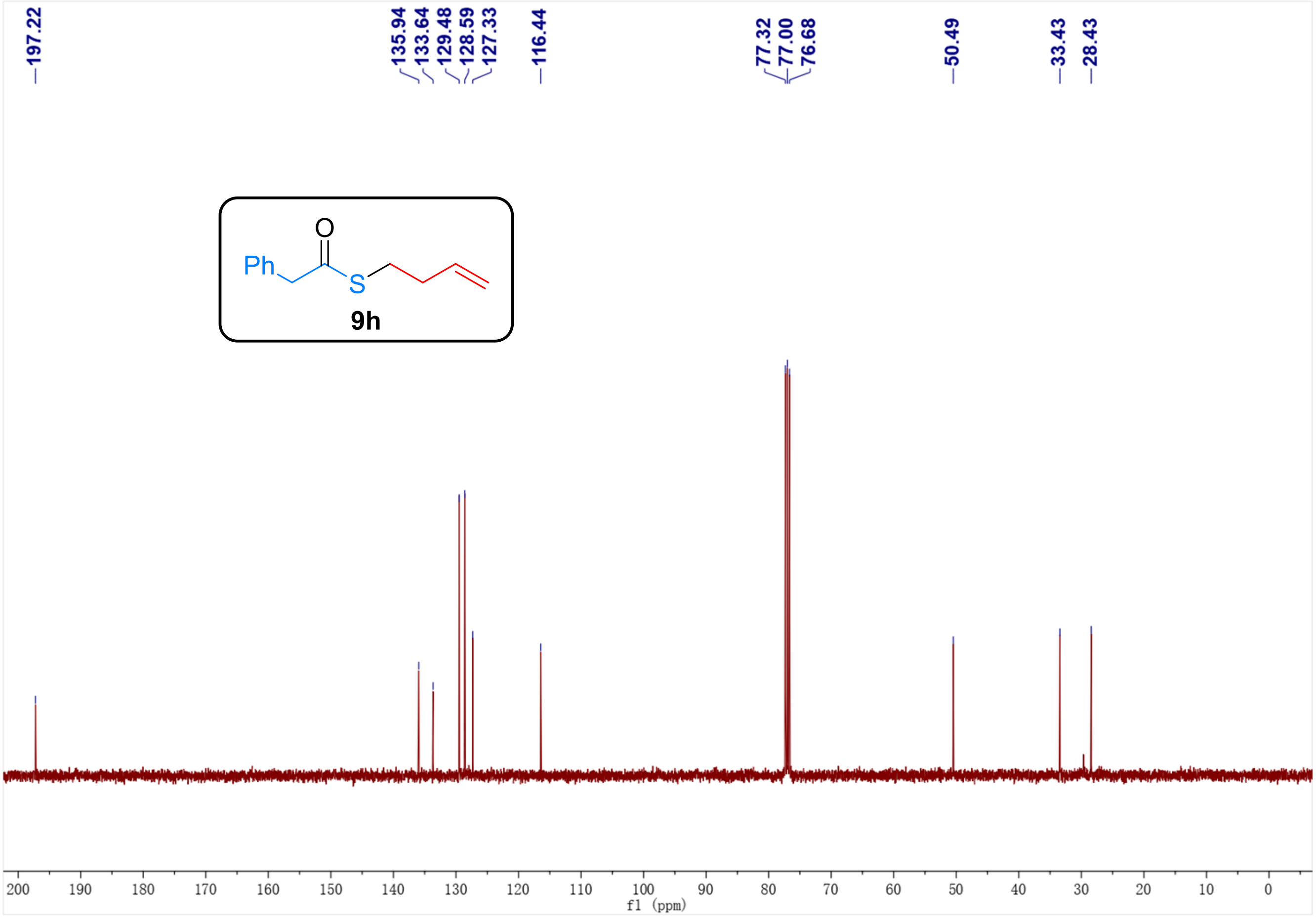
f1 (ppm)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28.43
Ph
O
S
9h
200
190
180
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140
130
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100
90
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50
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30
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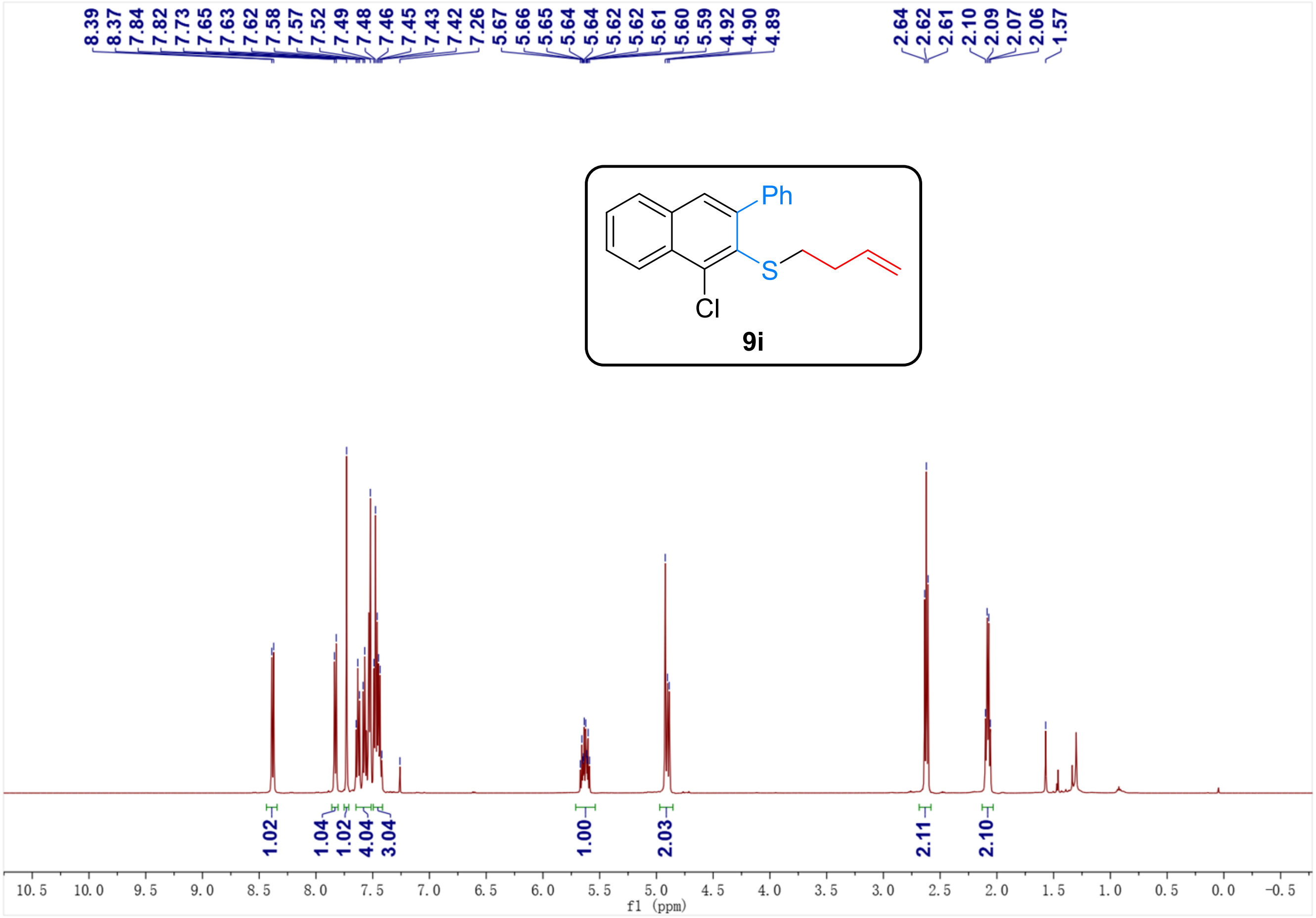
10
0
f1 (ppm)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7.48
7.46
7.45
7.43
7.42
7.26
5.67
5.66
5.65
5.64
5.64
5.62
5.62
5.61
5.60
5.59
4.92
4.90
4.89
2.64
2.62
2.61
2.10
2.09
2.07
2.06
1.57
Ph
S
Cl
9i
1.02
1.04
1.02
4.04
3.04
1.00
2.03
2.11
2.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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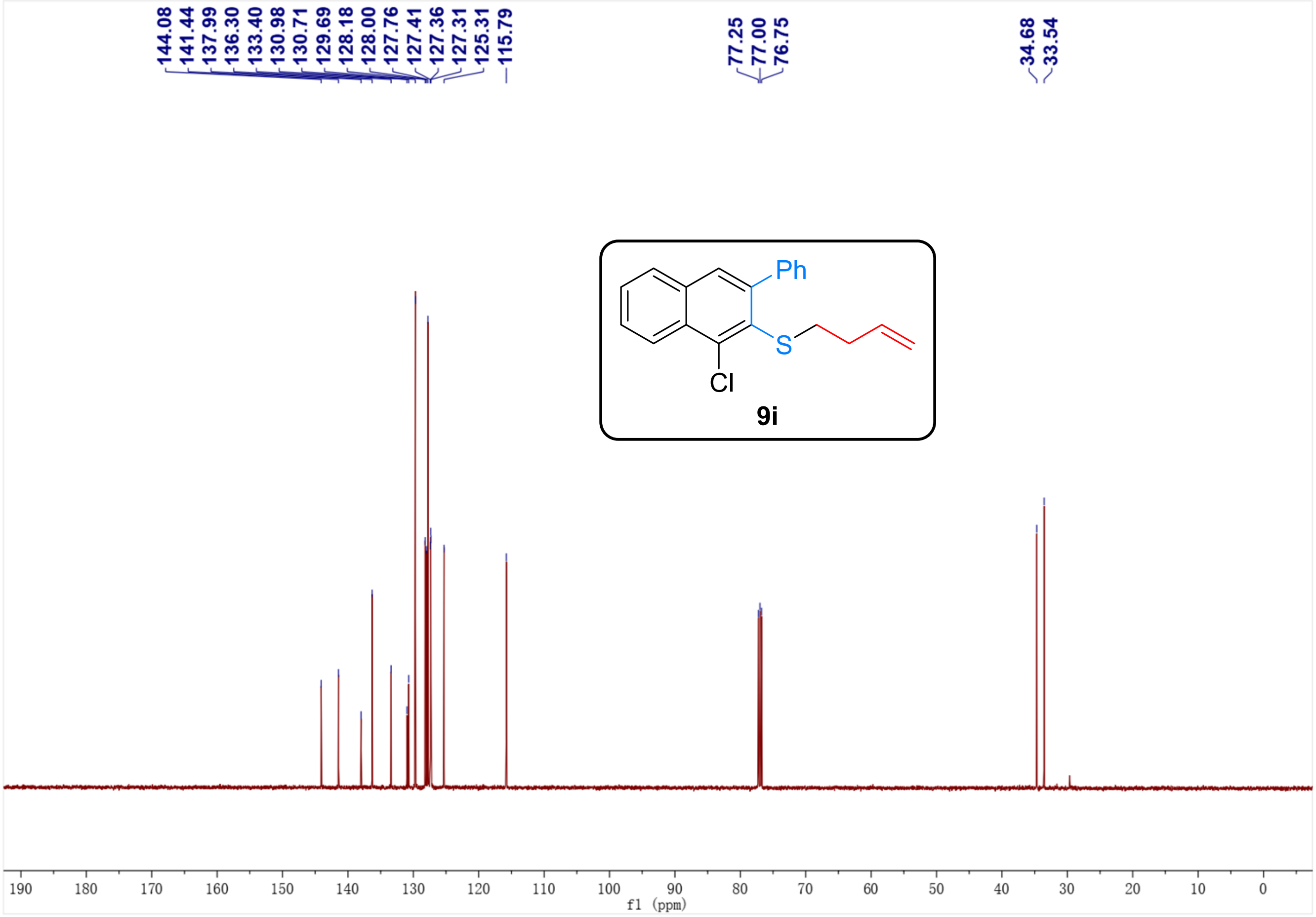
f1 (ppm)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127.36
127.31
125.31
115.79
77.25
77.00
76.75
34.68
33.54
Ph
S
Cl
9i
190
180
170
160
150
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130
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110
100
90
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50
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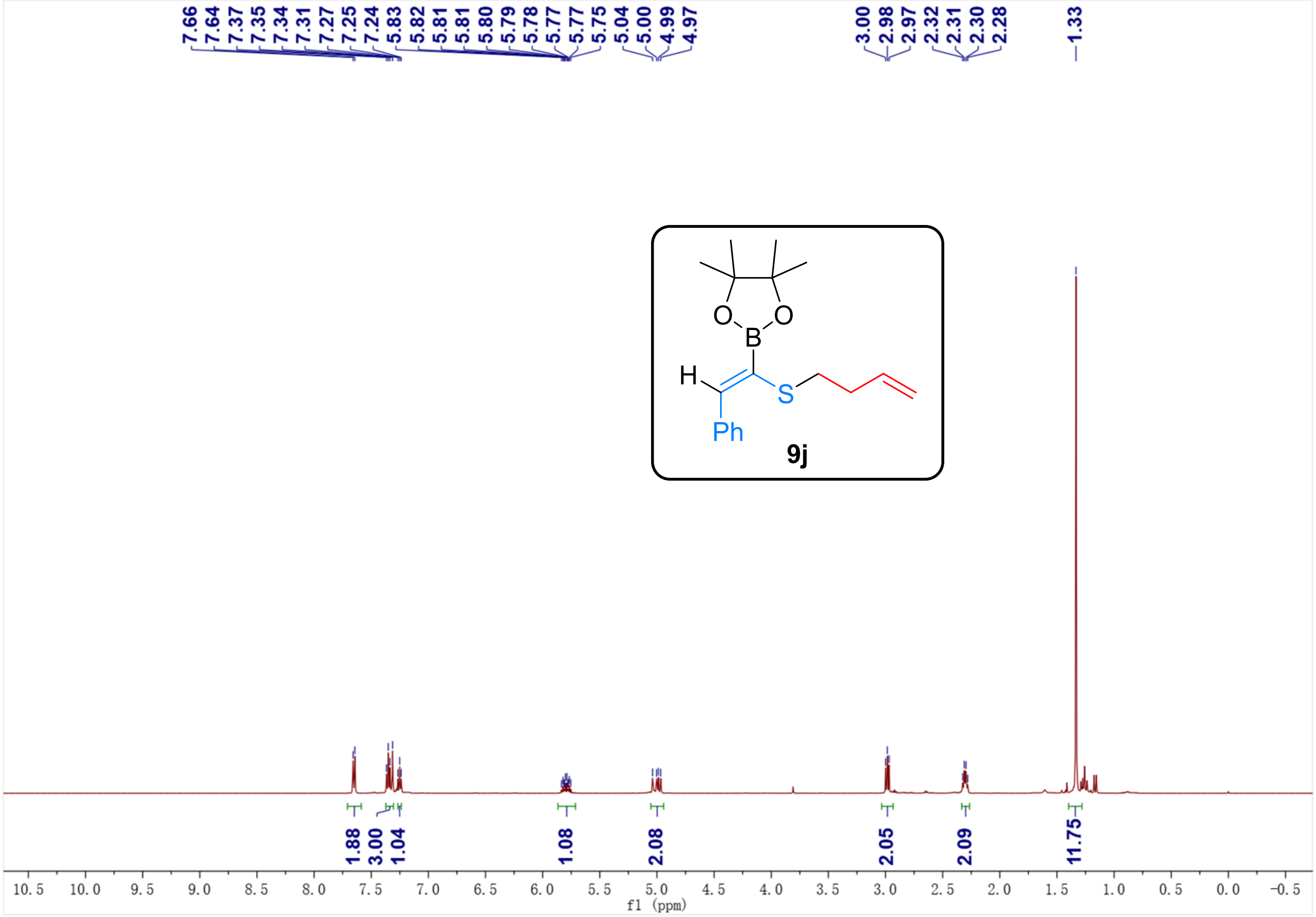
30
20
10
0
f1 (ppm)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5.81
5.80
5.79
5.78
5.77
5.77
5.75
5.04
5.00
4.99
4.97
3.00
2.98
2.97
2.32
2.31
2.30
2.28
1.33
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B
O
H
S
Ph
9j
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1.04
1.08
2.08
2.05
2.09
11.75
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9.5
9.0
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7.0
6.5
6.0
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5.0
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3.0
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2.0
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0.5
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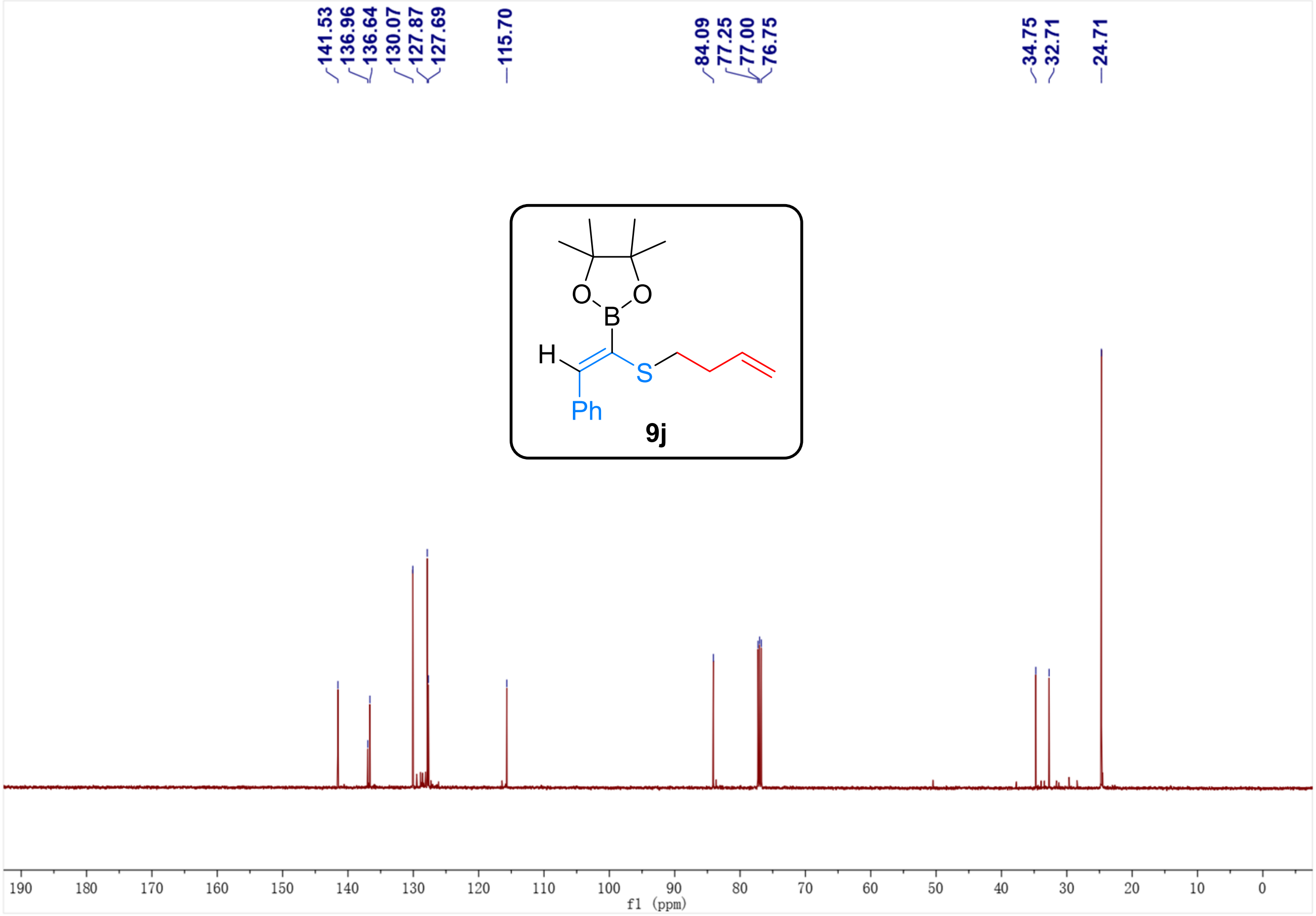
f1 (ppm)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84.09
77.25
77.00
76.75
34.75
32.71
24.71
O
B
O
H
S
Ph
9j
190
180
170
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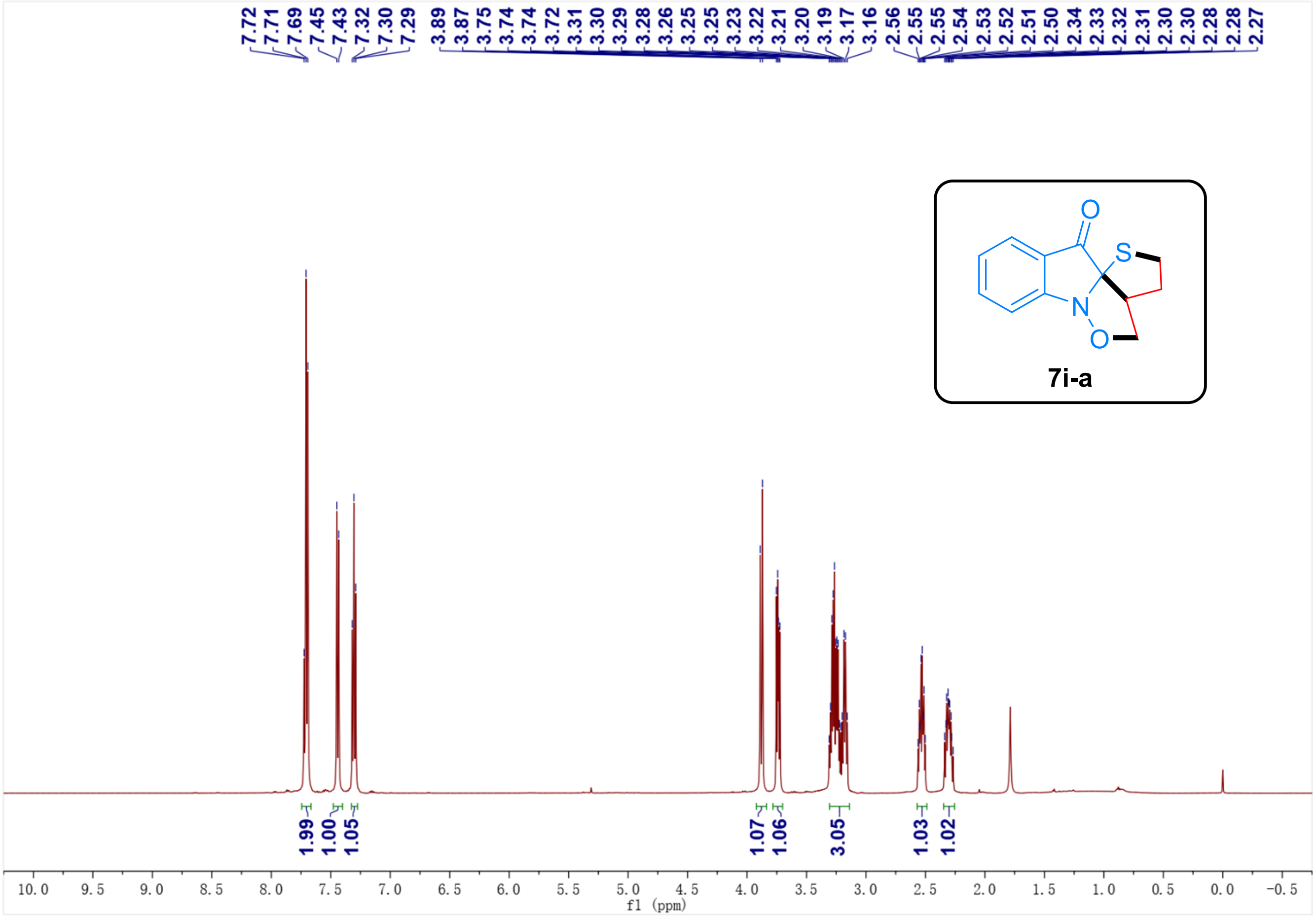
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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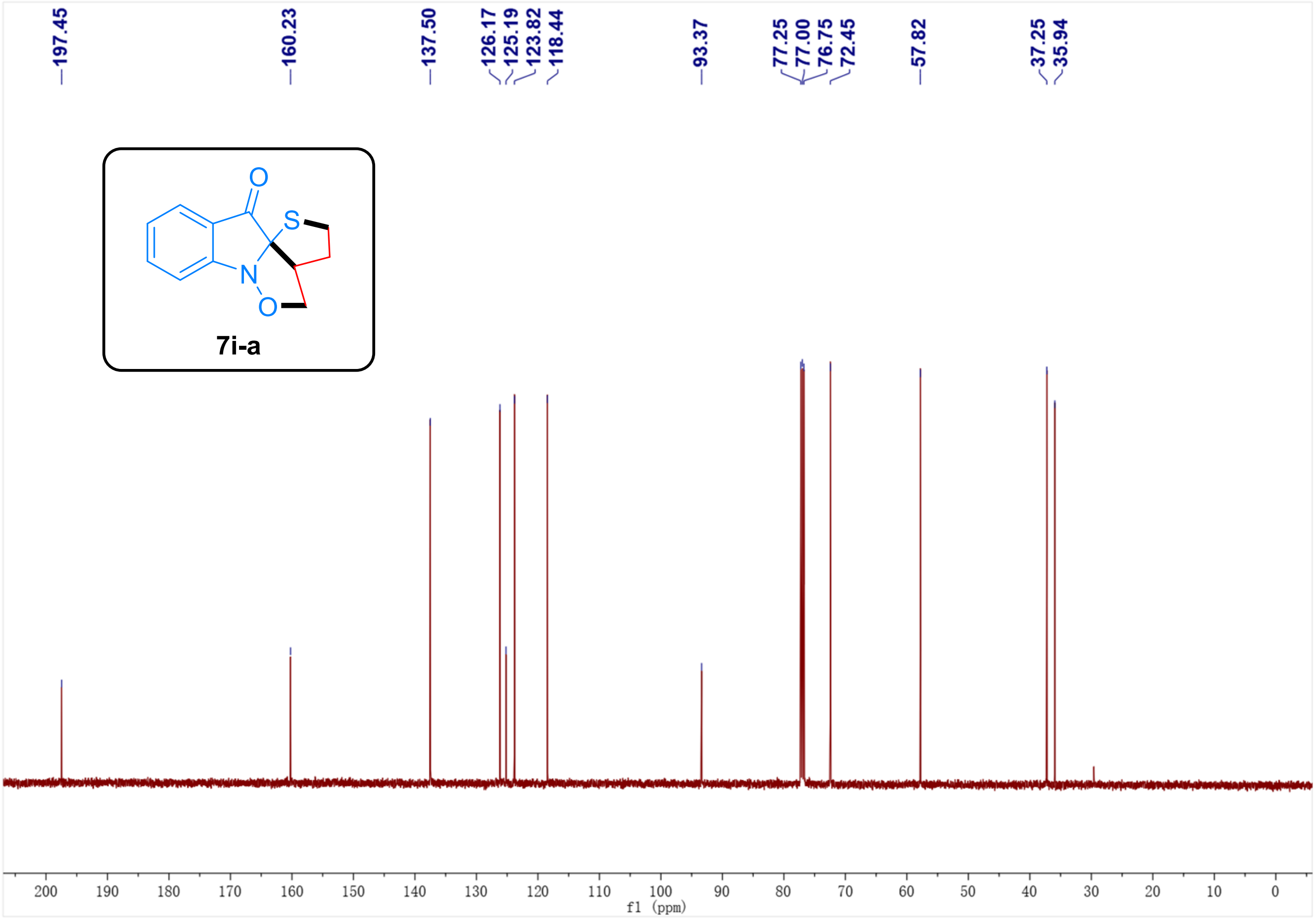
3.74
3.72
3.31
3.30
3.29
3.28
3.26
3.25
3.25
3.23
3.22
3.21
3.20
3.19
3.17
3.16
2.56
2.55
2.55
2.54
2.53
2.52
2.51
2.50
2.34
2.33
2.32
2.31
2.30
2.28
2.28
2.27
O
S
N
O
7i-a
1.99
1.00
1.05
1.07
1.06
3.05
1.03
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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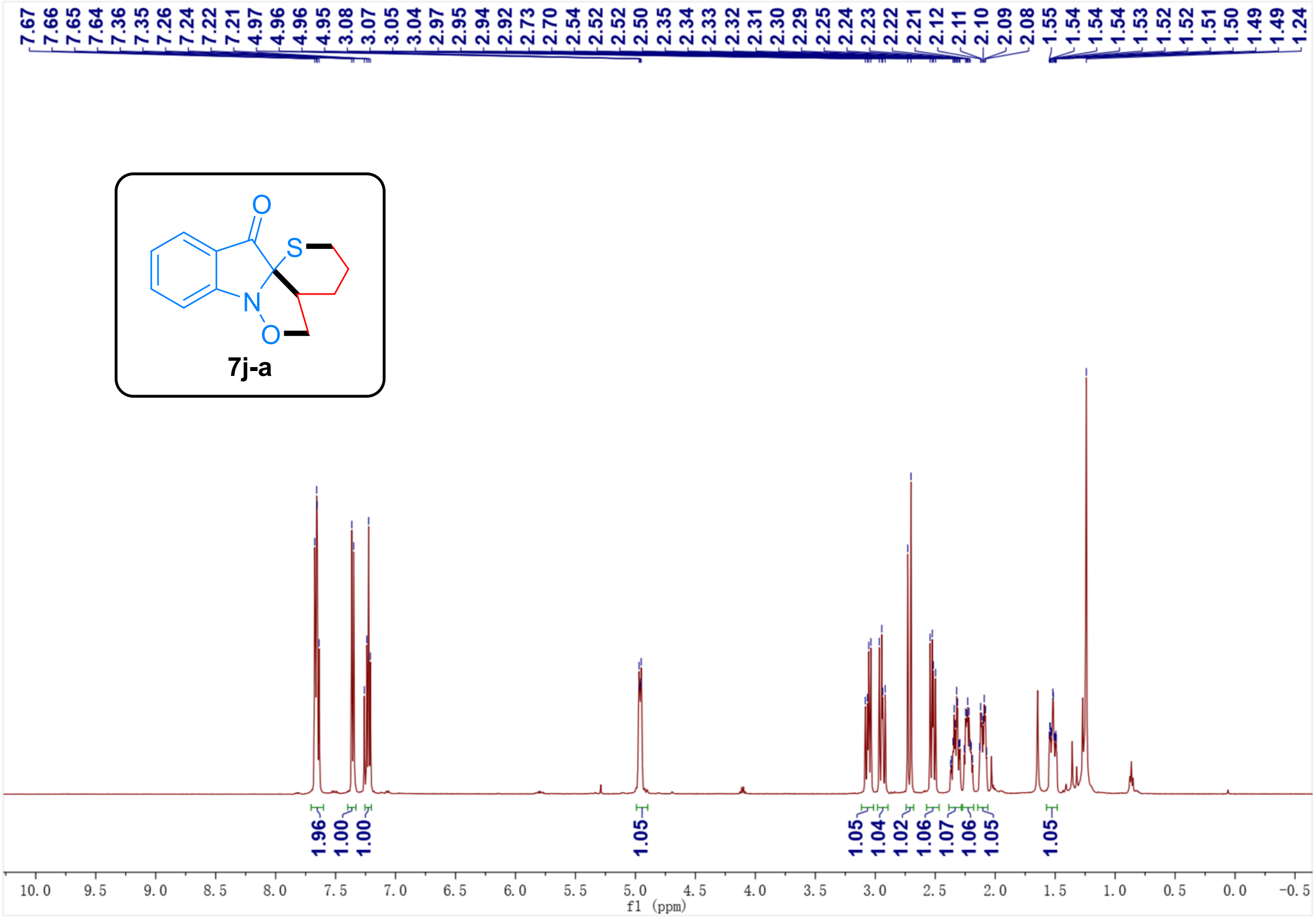
37.25
35.94
O
S
N
O
7i-a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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4.96
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4.95
3.08
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1.54
1.54
1.54
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.24
O
S
N
O
7j-a
1.96
1.00
1.00
1.05
1.05
1.04
1.02
1.06
1.07
1.06
1.05
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
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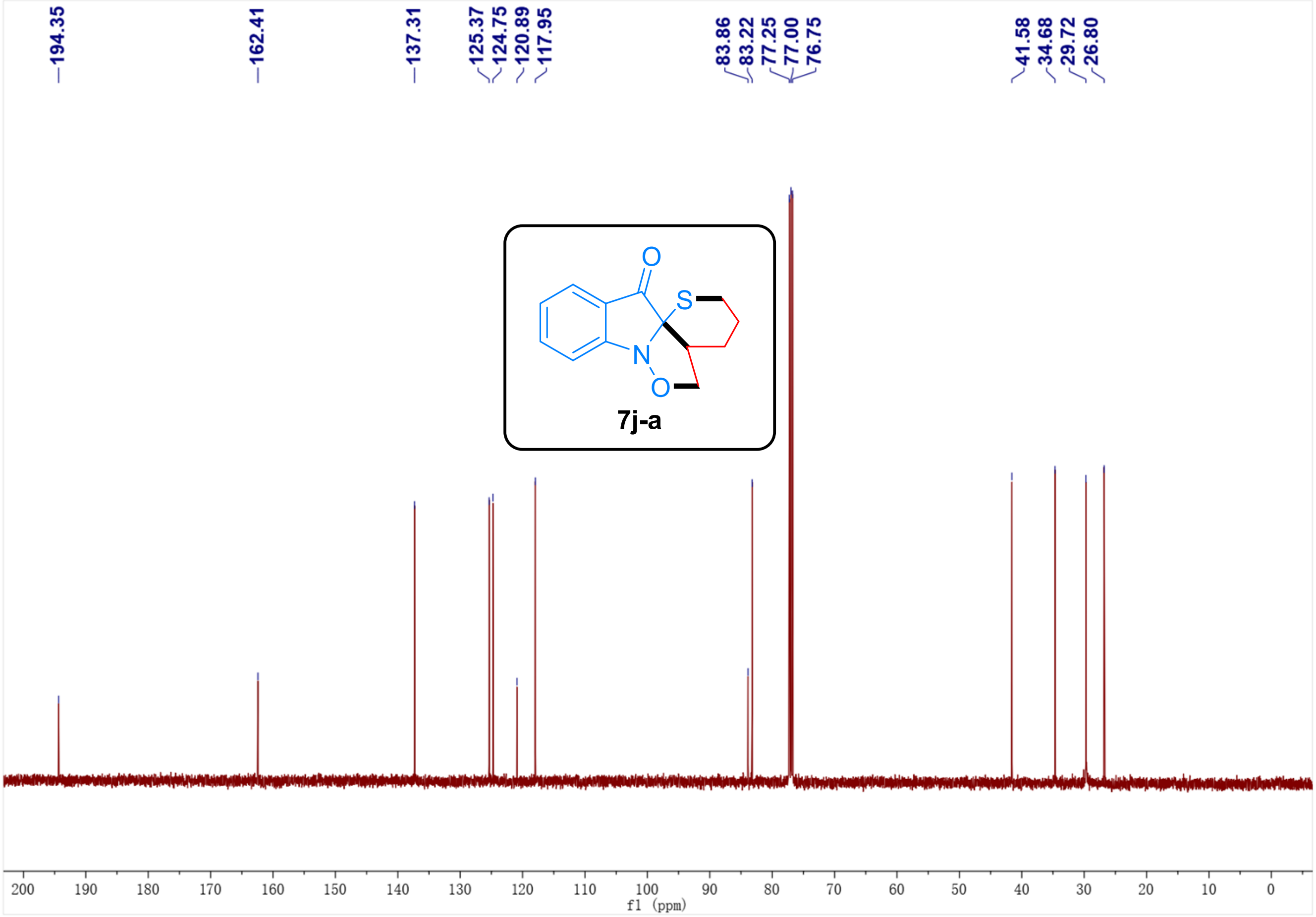
0.5
0.0
-0.5
f1 (ppm)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83.86
83.22
77.25
77.00
76.75
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34.68
29.72
26.80
O
S
N
O
7j-a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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