Supporting Information

Direct methylthiolation of *C*-, *S*-, and *P*- nucleophiles with Sodium *S*-Methyl Thiosulfate

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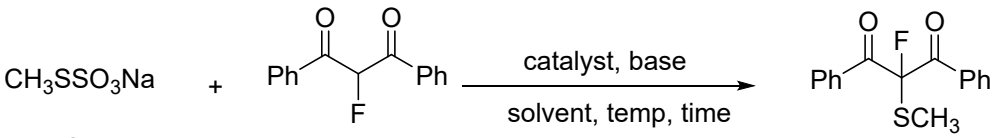
1 General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compoundsare identified by appropriate technique such as ^{1}H NMR, ^{13}C NMR and compared with previously reported data. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR and HRMS. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a 500 MHz Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.26) and chemical shifts are reported in ppm. Some impurity peak in proton spectrum was water δ 1.59 and hexane δ 1.26. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. GC-MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). High resolution mass spectral data were acquired on Waters Micromass GCT Premier Spectrometer (electrospray ionization: EI) and Waters Q-Tof microTM (electrospray ionization: ESI).

2 Screening Reaction

Table S1. Optimization of conditions for reaction of 1,3-diketone with sodium *S*-methyl sulfothioate [a]



1 **4** **5**

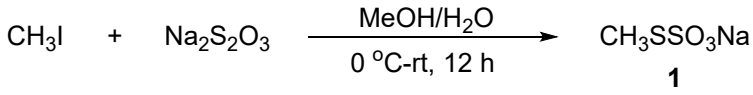
Entry	Catalyse	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	$CuSO_4$ (0.2 equiv)		DMF	80	10	23
2	$CuSO_4$		DMF	80	10	53
4	CuI		DMF	80	10	33
5	$Cu(OAc)_2$		DMF	80	10	14
6	$CuSO_4$	Cs_2CO_3	DMF	80	10	42
7	$CuSO_4$	KF	DMF	80	10	35
8	$CuSO_4$	NaH	DMF	80	10	47
9	$CuSO_4$		DMSO	80	10	51
10	$CuSO_4$		THF	80	10	32
11	$CuSO_4$		DMF	50	10	59
12	$CuSO_4$		DMF	30	10	48
13	$CuSO_4$		DMF	110	10	52
14	$CuSO_4$		DMF	50	12	65
15	**$CuSO_4$**		**DMF**	**50**	24	**74(70[c])**

[a] Unless otherwise specified, the reaction was carried out in the presence of *β*-ketoester (0.4 mmol, 1.0 equiv), sodium *S*-methyl sulfothioate **1** (99 mg, 0.6 mmol, 1.5 equiv), catalyst (0.2 mmol, 0.5 equiv), base (0.4 mmol, 1.0 equiv) and solvent (4 mL), air. [b] GC yield. [c] isolated yield.

3 General procedure

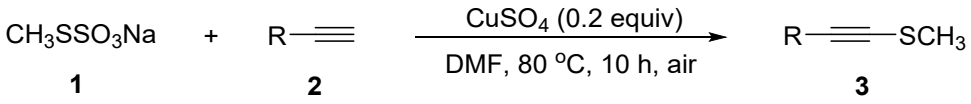
Tabulated ^{1}H and ^{13}C NMR data and copies of ^{1}H and ^{13}C spectra are given for all products. For solid products, melting point ranges are given. For new compounds, HRMS data is provided. The following compounds have previously been reported in the literature: **3a**[1], **3b**[1], **3c**[1], **3e**[1], **3f**[1], **3g**[2], **3h**[3], **3l**[1], **3m**[4], **3n**[5], **6a**[6], **6b**[7], **6d**[7], **6e**[8], **6g**[9], **6h**[10], **6j**[9], **6n**[6], **6o**[11], **7a**[12], **7b**[13].

3.1 General procedures for Sodium *S*-methyl sulfothioate

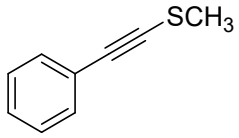


A 250 mL flask was charged with iodomethane (2.5 mL, 40.0 mmol, 1.0 equiv), sodium thiosulfate pentahydrate (11.9 g, 48.0 mmol, 1.2 equiv), water (50.0 mL) and MeOH (10 mL) for 12 h at 0 °C to rt. The reaction mixture then concentrated on a rotovap at a bath temperature of 40-45 °C to remove the MeOH and water. The resultant solid was treated with MeOH (50 mL), heated to 50 °C (most solid dissolves), and filtered through a medium stone frit filter. This removes excess sodium thiosulfate and sodium iodide. The filtrate was concentrated to a white solid. Trituration of this solid with hexanes, filtration, and drying under vacuum at 50 °C gave **1** (5.75 g, 90.8 wt.% purity by assay, 87% yield) as a white solid.

3.2 General procedures for methylthiolation of alkynes

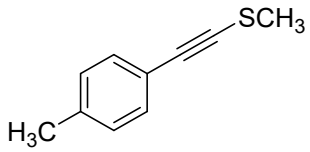


A flask was charged with alkynes (0.4 mmol, 1.0 equiv), sodium *S*-methyl sulfothioate **1** (99 mg, 0.6 mmol, 1.5 equiv), $CuSO_4$ (12.8 mg, 0.08 mmol, 0.2 equiv) and DMF (4 mL). The reaction mixture was stirred at 80 ˚C in air for 10 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into EtOAc (20 mL) and H_2O (20 mL), and extracted several times with EtOAc (3 *15 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, Petroleum ether/ Ethyl acetate) to afford the methylthiolated alkene **3**.



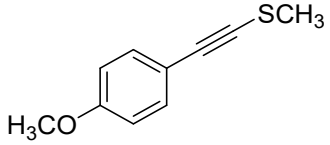
Chemical Formula: C_9H_8S
Exact Mass: 148.0347

Methyl(phenylethynyl)sulfane. **3a**[1], Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (83%, 49.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 – 7.39 (m, 2H), 7.31 – 7.28 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.70 , 128.51 , 128.29 , 123.64 , 92.10 , 81.14 , 19.66 .



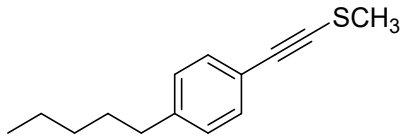
Chemical Formula: $C_{10}H_{10}S$
Exact Mass: 162.0503

Methyl(p-tolylethynyl)sulfane. **3b**[1], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (86%, 55.7 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 2H), 7.10 (d, J = 7.8 Hz, 2H), 2.47 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 138.52 , 131.75 , 129.28 , 120.55 , 92.15 , 80.11 , 21.71 , 19.70.



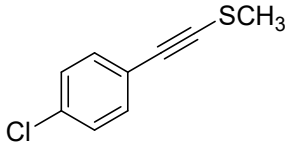
Chemical Formula: $C_{10}H_{10}OS$
Exact Mass: 178.0452

((4-Methoxyphenyl)ethynyl)(methyl)sulfane. **3c**[1], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=20:1) afforded a light yellow oil (88%, 62.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 – 7.33 (m, 2H), 6.85 – 6.79 (m, 2H), 3.81 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 159.85 , 133.63 , 115.74 , 114.16 , 91.86 , 79.19 , 55.53 , 19.76 .



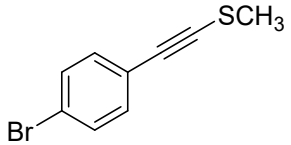
Chemical Formula: $C_{14}H_{18}S$
Exact Mass: 218.1129

Methyl((4-pentylphenyl)ethynyl)sulfane. **3d**, Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (83%, 72.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 2.58 (t, J = 7.8 Hz, 2H), 2.46 (s, 3H), 1.60 (q, J = 7.6 Hz, 2H), 1.30 (dtt, J = 17.9, 8.6, 5.1 Hz, 4H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 143.58 , 131.77 , 128.63 , 120.72 , 92.20 , 80.10 , 36.08 , 31.66 , 31.14 , 22.75 , 19.72 , 14.25 . HRMS (EI) Calcd. for $C_{14}H_{18}S$ 218.1129, found 218.1135.



Chemical Formula: C_9H_7ClS
Exact Mass: 181.9957

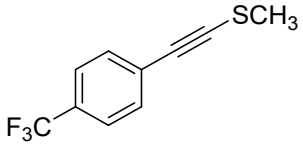
((4-Chlorophenyl)ethynyl)(methyl)sulfane. **3e**[1], Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (75%, 54.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.26 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 134.27 , 132.87 , 128.86 , 122.15 , 91.00 , 82.45 , 19.58 .



Chemical Formula: C_9H_7BrS
Exact Mass: 225.9452

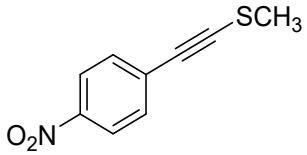
((4-Bromophenyl)ethynyl)(methyl)sulfane. **3f**[1], Purification by column

chromatography on silica gel (pertroleum ether) afforded a yellow oil (74%, 66.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 (d, J = 8.5 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.04 , 131.78 , 122.62 , 122.43 , 91.09 , 82.70 , 19.56 .



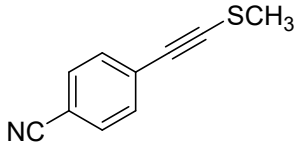
Chemical Formula: $C_{10}H_7F_3S$
Exact Mass: 216.0221

Methyl((4-(trifluoromethyl)phenyl)ethynyl)sulfane. **3g**[2], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (81%, 70.0 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.54 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.47 , 129.87 , 129.61 , 129.35 , 127.45 , 125.46 , 125.27 , 123.09 , 91.08 , 84.70 , 19.54 ; ^{19}F NMR (470 MHz, Chloroform-d) δ -62.72 .



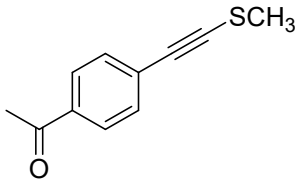
Chemical Formula: $C_9H_7NO_2S$
Exact Mass: 193.0197

Methyl((4-nitrophenyl)ethynyl)sulfane. **3h**[3], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a red solid (63%, 48.6 mg). Mp: 71-75 °C. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.25 (d, J = 8.9 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 2.61 (s, 3H).; ^{13}C NMR (126 MHz, Chloroform-d) δ 150.60 , 141.60 , 129.54 , 124.10 , 93.10 , 79.96 , 27.23 .



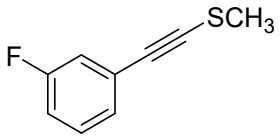
Chemical Formula: $C_{10}H_7NS$
Exact Mass: 173.0299

4-((Methylthio)ethynyl)benzonitrile. **3i**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow solid (70%, 48.5 mg). Mp: 74-79 °C. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.05 (d, J = 8.7 Hz, 2H), 7.82 – 7.73 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 140.17 , 132.77 , 128.95 , 118.17 , 116.69 , 95.38, 81.82, 27.01 . HRMS (EI) Calcd. for $C_{10}H_7NS$ 173.0299, found 173.0303.



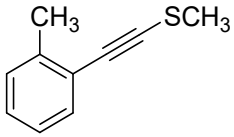
Chemical Formula: $C_{11}H_{10}OS$
Exact Mass: 190.0452

1-(4-((methylthio)ethynyl)phenyl)ethan-1-one. **3j**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=3:1, v/v) afforded a yellow solid (68%, 51.7 mg). Mp: 71-74 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.48 – 7.42 (m, 2H), 2.59 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 197.23 , 135.81 , 131.00 , 128.32 , 128.26 , 91.58 , 85.55 , 26.57 , 19.38 . HRMS (EI) Calcd. for $C_{11}H_{10}OS$ 190.0452, found 190.0457.



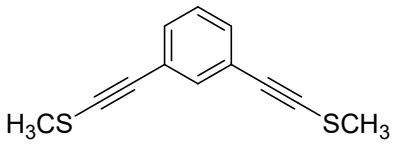
Chemical Formula: C_9H_7FS
Exact Mass: 166.0252

((3-Fluorophenyl)ethynyl)(methyl)sulfane. **3k**, Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (72%, 47.8 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.24 (dd, J = 8.0, 5.8 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.09 (ddd, J = 9.5, 2.6, 1.4 Hz, 1H), 7.03 – 6.96 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 162.58 (d, J = 246.5 Hz), 130.07 , 127.39 , 125.49 , 118.28 (d, J = 22.7 Hz), 115.56 (d, J = 21.0 Hz), 90.97 , 82.68 , 19.55 ; ^{19}F NMR (470 MHz, Chloroform-d) δ -112.99 . HRMS (EI) Calcd. for C_9H_7FS 166.0252, found 166.0247.



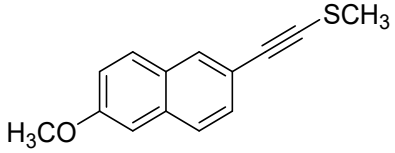
Chemical Formula: $C_{10}H_{10}S$
Exact Mass: 162.0503

Methyl(*o*-tolylethynyl)sulfane. **3l**, Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (74%, 47.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.25 – 7.15 (m, 3H), 7.10 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 138.19 , 132.27 , 129.21 , 128.76 , 128.40 , 123.42 , 92.27 , 80.67 , 21.44 , 19.68 . HRMS (EI) Calcd. for $C_{10}H_{10}S$ 162.0503, found 162.0510.



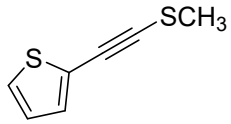
Chemical Formula: $C_{12}H_{10}S_2$
Exact Mass: 218.0224

1,3-Bis((methylthio)ethynyl)benzene. **3m**[4], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow oil (65%, 56.7 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.43 (m, 1H), 7.32 – 7.29 (m, 2H), 7.22 (m, 1H), 2.47 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-d) δ 134.17 , 130.86 , 128.45 , 123.79 , 91.20 , 81.96 , 19.49 .



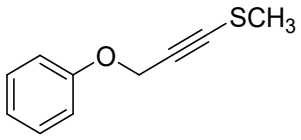
Chemical Formula: $C_{14}H_{12}OS$
Exact Mass: 228.0609

((6-Methoxynaphthalen-2-yl)ethynyl)(methyl)sulfane. **3n**[1], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow solid (70%, 63.8 mg). Mp: 94-97 °C. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (s, 1H), 7.65 (dd, J = 12.5, 8.7 Hz, 2H), 7.43 (dd, J = 8.5, 1.7 Hz, 1H), 7.14 (dd, J = 9.0, 2.5 Hz, 1H), 7.09 (d, J = 2.6 Hz, 1H), 3.91 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 158.52 , 134.26 , 131.51 , 129.51 , 129.25 , 128.66 , 126.98 , 119.62 , 118.51 , 106.02 , 92.58 , 80.52 , 55.59 , 19.77 .



Chemical Formula: $C_7H_6S_2$
Exact Mass: 153.9911

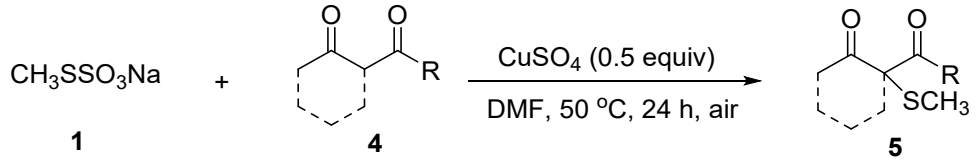
2-((Methylthio)ethynyl)thiophene. **3o**[5], Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (62%, 38.2mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.26 – 7.24 (m, 1H), 7.21 (dd, J = 3.6, 1.2 Hz, 1H), 6.96 (dd, J = 5.2, 3.7 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.18 , 127.99 , 127.16 , 123.82 , 85.60 , 84.84 , 19.76 .



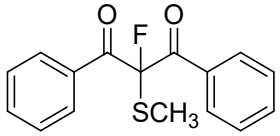
Chemical Formula: $C_{10}H_{10}OS$
Exact Mass: 178.0452

Methyl(3-phenoxyprop-1-yn-1-yl)sulfane. **3p**, Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (87%, 61.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 – 7.27 (m, 2H), 7.01 – 6.92 (m, 3H), 4.78 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 157.90 , 129.68 , 121.63 , 115.16 , 88.30 , 80.30 , 57.05 , 19.21 . HRMS (EI) Calcd. for $C_{10}H_{10}OS$ 178.0452, found 178.0446.

3.3 General procedures for methylthiolation of 1,3-diketones



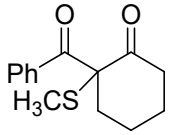
A flask was charged with 1,3-diketones (0.4 mmol, 1.0 equiv), sodium *S*-methyl sulfothioate 1 (99 mg, 0.6 mmol, 1.5 equiv), $CuSO_4$ (32 mg, 0.2 mmol, 0.5 equiv) and DMF (4 mL). The reaction mixture was stirred at 50 ˚C in air for 24 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into EtOAc (20 mL) and H_2O (20 mL), and extracted several times with EtOAc (3 *15 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, Petroleum ether/ Ethyl acetate) to afford the methylthiolated product **5**.



Chemical Formula: $C_{16}H_{13}FO_2S$
Exact Mass: 288.0620

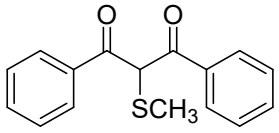
2-Fluoro-2-(methylthio)-1,3-diphenylpropane-1,3-dione. **5a**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=5:1, v/v) afforded a colorless oil (60%, 69.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.05 (d, J = 7.7 Hz, 4H), 7.56 – 7.50 (m, 2H), 7.39 (t, J = 7.9 Hz, 4H), 2.15 (d, J = 1.9 Hz, 3H); ^{13}C

NMR (126 MHz, Chloroform-*d*) δ 189.46, 134.58, 133.41, 130.31, 130.13, 128.92, 29.96; ^{19}F NMR (470 MHz, Chloroform-*d*) δ -130.65 . HRMS (EI) Calcd. for $C_{16}H_{13}FO_2S$ 288.0620, found 288.0627.



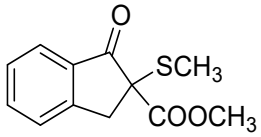
Chemical Formula: $C_{14}H_{16}O_2S$
Exact Mass: 248.0871

2-Benzoyl-2-(methylthio)cyclohexan-1-one. **5b**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=5:1, v/v) afforded a light yellow oil (32%, 31.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.05 – 7.98 (m, 2H), 7.55 – 7.48 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 3.05 (dd, *J* = 13.3, 2.9 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.12 (td, *J* = 12.8, 5.8 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.91 (s, 3H), 1.86 – 1.72 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-d) δ 207.34 , 191.21 , 133.29 , 129.71 , 128.98 , 128.75 , 128.31 , 42.76 , 37.85 , 28.58 , 23.07 , 11.40 . HRMS (EI) Calcd. for $C_{14}H_{16}O_2S$ 248.0871, found 248.0869.



Chemical Formula: $C_{16}H_{14}O_2S$
Exact Mass: 270.07

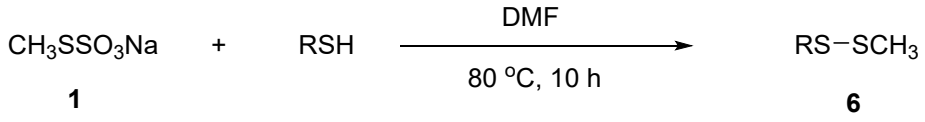
2-(methylthio)-1,3-diphenylpropane-1,3-dione. **5c**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow oil (10%, 10.8 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.99 (d, *J* = 7.7 Hz, 4H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 4H), 5.75 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.67, 135.41, 133.99, 129.33, 129.10, 58.10, 29.96.



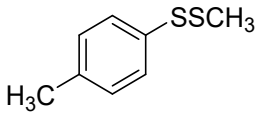
Chemical Formula: $C_{12}H_{12}O_3S$
Exact Mass: 236.0507

Methyl 2-(methylthio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate. **5d**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=3:1, v/v) afforded a yellow oil (75%, 70.8 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.87 – 7.80 (m, 1H), 7.64 (m, 1.2 Hz, 1H), 7.50 – 7.40 (m, 2H), 3.90 (d, J = 17.8 Hz, 1H), 3.81 (s, 3H), 3.16 (d, J = 17.7 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 196.42 , 170.00 , 150.59 , 135.61 , 134.10 , 128.47 , 126.37 , 125.78 , 58.21 , 53.52 , 40.22 , 13.84 . HRMS (EI) Calcd. for $C_{12}H_{12}O_3S$ 236.0507, found 236.0504.

3.4 General procedures for methylthiolation of thiols

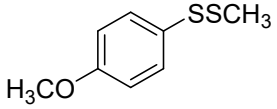


A flask was charged with thiol (0.4 mmol, 1.0 equiv), sodium *S*-methyl sulfothioate (99 mg, 0.6 mmol, 1.5 equiv) and DMF (4 mL). The reaction mixture was stirred at 80 ˚C for 10 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into EtOAc (20 mL) and H_2O (20 mL), and and extracted several times with EtOAc (3 *15 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, Petroleum ether/ Ethyl acetate) to afford the methylthiolated thiol **6**.



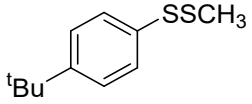
Chemical Formula: $C_8H_{10}S_2$
Exact Mass: 170.0224

1-Methyl-2-(p-tolyl)disulfane . **6a**[11], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (81%, 55.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.52 , 133.74 , 130.05 , 128.93 , 23.15 , 21.28 .



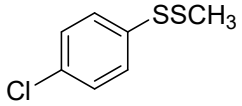
Chemical Formula: $C_8H_{10}OS_2$
Exact Mass: 186.0173

1-(4-Methoxyphenyl)-2-methyldisulfane. **6b**[12], Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (76%, 56.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.51 – 7.45 (m, 2H), 6.90 – 6.84 (m, 2H), 3.81 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 159.99 , 132.34 , 128.11 , 114.96 , 55.65 , 23.12 .



Chemical Formula: $C_{11}H_{16}S_2$
Exact Mass: 212.0693

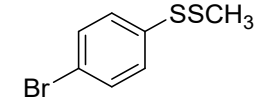
(1-(4-(tert-Butyl)phenyl)-2-methyldisulfane. **6c**, Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (78%, 66.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 2.44 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, Chloroform-d) δ 150.68 , 133.78 , 128.41 , 126.36 , 34.79 , 31.53 , 23.26 . HRMS (EI) Calcd. for $C_{11}H_{16}S_2$ 212.0693, found 212.0694.



Chemical Formula: $C_7H_7ClS_2$
Exact Mass: 189.9678

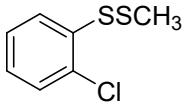
1-(4-Chlorophenyl)-2-methyldisulfane. **6d**[12], Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (82%, 62.3 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 (dd, J = 8.6, 0.9 Hz, 2H), 7.30 (dd, J = 8.7, 1.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 135.78 , 133.16 , 129.39 ,

129.25 , 23.09 .



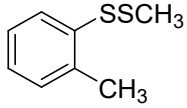
Chemical Formula: $C_7H_7BrS_2$
Exact Mass: 233.9173

1-(4-Bromophenyl)-2-methyldisulfane. **6e**[13], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (79%, 73.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 136.48 , 132.31 , 129.40 , 121.02 , 23.08 .



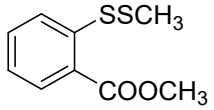
Chemical Formula: $C_7H_7ClS_2$
Exact Mass: 189.9678

1-(2-Clorophenyl)-2-methyldisulfane. **6f**, Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (78%, 59.3 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (dd, J = 8.0, 1.4 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 135.72 , 132.27 , 130.03 , 127.60 , 127.55 , 127.28 , 22.80 . HRMS (EI) Calcd. for $C_7H_7ClS_2$ 189.9678, found 189.9680.



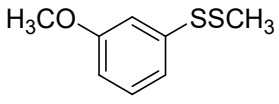
Chemical Formula: $C_8H_{10}S_2$
Exact Mass: 170.0224

1-Methyl-2-(o-tolyl)disulfane. **6g**[14], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (83%, 56.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 – 7.67 (m, 1H), 7.24 – 7.19 (m, 1H), 7.19 – 7.13 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.49 , 135.53 , 130.72 , 128.20 , 127.27 , 126.78 , 22.87 , 20.17 .



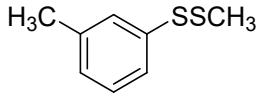
Chemical Formula: $C_9H_{10}O_2S_2$
Exact Mass: 214.0122

Methyl 2-(methyldisulfanyl)benzoate. **6h**[15], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow oil (87%, 74.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.19 – 8.11 (m, 1H), 8.03 (dd, J = 7.7, 1.5 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.24 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 166.99 , 141.49 , 133.09 , 131.75 , 127.19 , 125.35 , 125.29 , 52.45 , 22.22 .



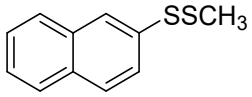
Chemical Formula: $C_8H_{10}OS_2$
Exact Mass: 186.0173

1-(3-Methoxyphenyl)-2-methyldisulfane. **6i**, Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (84%, 62.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.23 (d, J = 7.9 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.77 (ddd, J = 8.2, 2.4, 1.0 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) 160.38 , 138.47 , 130.10 , 119.81 , 112.89 , 112.75 , 55.57 , 23.19 . HRMS (EI) Calcd. for $C_8H_{10}OS_2$ 186.0173, found 186.0179.



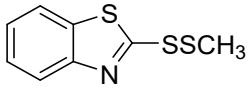
Chemical Formula: $C_8H_{10}S_2$
Exact Mass: 170.0224

1-Methyl-2-(m-tolyl)disulfane. **6j**[14], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (74%, 62.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.34 (d, J = 7.3 Hz, 2H), 7.22 (td, J = 7.3, 1.5 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 139.20 , 136.94 , 129.12 , 128.50 , 128.07 , 125.05 , 23.23 , 21.63 .



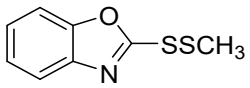
Chemical Formula: $C_{11}H_{10}S_2$
Exact Mass: 206.0224

1-Methyl-2-(naphthalen-2-yl)disulfane. **6k**, Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (77%, 63.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.99 (d, J = 1.8 Hz, 1H), 7.80 (t, J = 9.3 Hz, 3H), 7.61 (dd, J = 8.7, 1.9 Hz, 1H), 7.53 – 7.42 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 134.37 , 133.79 , 132.63 , 129.13 , 128.03 , 127.59 , 126.96 , 126.44 , 126.31 , 126.04 , 23.12 . HRMS (EI) Calcd. for $C_{11}H_{10}S_2$ 206.0224, found 206.0226.



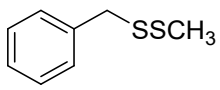
Chemical Formula: $C_8H_7NS_3$
Exact Mass: 212.9741

2-(Methyldisulfanyl)benzo[d]thiazole. **6l**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow oil (80%, 68.2 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.88 (d, J = 8.2 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.47 – 7.40 (m, 1H), 7.37 – 7.31 (m, 1H), 2.68 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 172.54 , 155.43 , 136.11 , 126.50 , 124.84 , 122.44 , 121.41 , 23.77 . HRMS (EI) Calcd. for $C_8H_7NS_3$ 212.9741, found 212.9745.



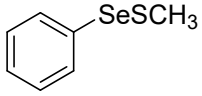
Chemical Formula: $C_8H_7NOS_2$
Exact Mass: 196.9969

2-(Methyldisulfanyl)benzo[d]oxazole. **6m**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a light yellow oil (83%, 65.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 – 7.68 (m, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.29 (m, 2H), 2.72 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 163.65 , 152.74 , 142.14 , 125.00 , 124.87 , 119.63 , 110.53 , 23.85 . HRMS (EI) Calcd. for $C_8H_7NOS_2$ 196.9969, found 196.9973.



Chemical Formula: $C_8H_{10}S_2$
Exact Mass: 170.0224

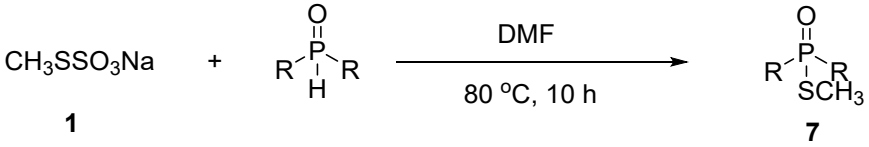
1-Benzyl-2-methyldisulfane. **6n**[11], Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (76%, 51.7 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.28 (d, J = 6.0 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.22 – 7.18 (m, 1H), 3.84 (s, 2H), 2.04 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.78 , 129.55 , 128.76 , 127.63 , 43.26 , 23.25 .



Chemical Formula: C_7H_8SSe
Exact Mass: 203.9512

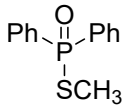
Methyl(phenylselanyl)sulfane. **6o**[10], Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (65%, 53.0 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.70 – 7.64 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 (dd, J = 8.1, 1.9 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.78 , 130.36 , 129.47 , 127.71 , 29.95 .

3.5 General procedures for methylthiolation of *H*-phosphineoxides



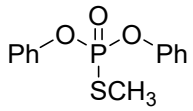
1 **7**

A flask was charged with *H*-phosphineoxides (0.4 mmol, 1.0 equiv), sodium S-methyl sulfothioate 1 (99 mg, 0.6 mmol, 1.5 equiv) and DMF (4 mL). The reaction mixture was stirred at 80 ˚C or 30 ˚C for 10-24 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into EtOAc (20 mL) and H_2O (20 mL), and extracted several times with EtOAc (3 *15 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, Petroleum ether/ Ethyl acetate) to afford the methylthiolated *H*-phosphineoxide **7**.



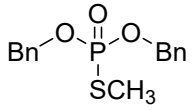
Chemical Formula: $C_{13}H_{13}OPS$
Exact Mass: 248.0425

S-Methyl diphenylphosphinothioate. **7a**[12], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=30:1, v/v) afforded a colorless oil (85%, 84.3 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.93 – 7.82 (m, 4H), 7.61 – 7.41 (m, 6H), 2.24 (d, J = 12.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.38 , 132.57 , 131.73 (d, J = 10.6 Hz), 128.94 (d, J = 13.2 Hz), 10.82 .



Chemical Formula: $C_{13}H_{13}O_3PS$
Exact Mass: 280.0323

S-Methyl *O,O*-diphenyl phosphorothioate. **7b**[13], Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a yellow oil (73%, 81.8 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.38 (dd, J = 8.6, 7.2 Hz, 4H), 7.34 – 7.27 (m, 4H), 7.23 (td, J = 7.3, 1.2 Hz, 2H), 2.38 (d, J = 16.2 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 150.51 , 130.11 , 125.89 , 120.85 , 13.26 .

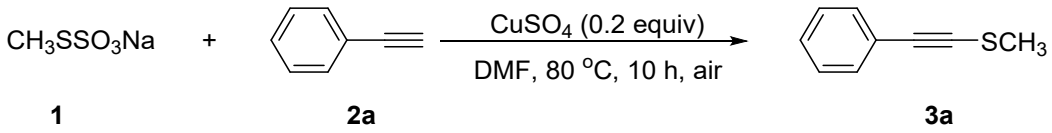


Chemical Formula: $C_{15}H_{17}O_3PS$
Exact Mass: 308.0636

O,O-Dibenzyl *S*-methyl phosphorothioate. **7c**, Purification by column chromatography on silica gel (pertroleum ether/Ethyl acetate=10:1, v/v) afforded a

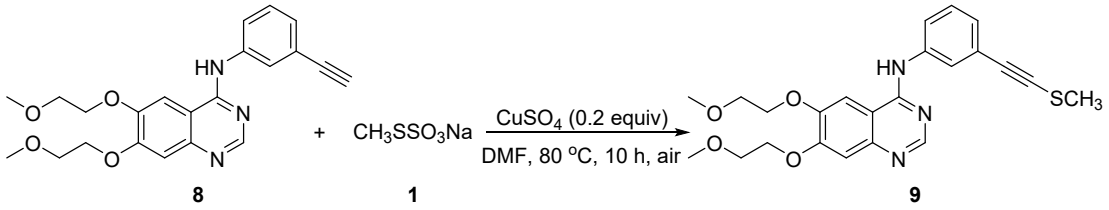
light yellow oil (76%, 93.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 – 7.28 (m, 10H), 5.21 – 5.05 (m, 4H), 2.19 (d, J = 15.3 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 135.73 , 135.67 , 128.82 , 128.29 , 69.11 (d, J = 5.7 Hz), 12.54 . HRMS (EI) Calcd. for $C_{15}H17O_3PS$ 308.0636, found 308.0644.

3.6 General procedures for gram-Scale Synthesis

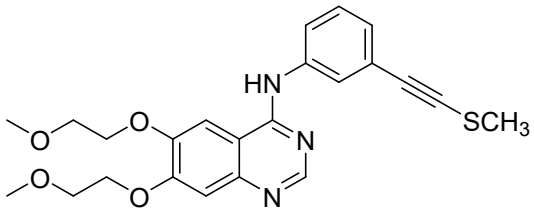


A 50 mL flask was charged with phenyl-acetylene 2a (1.04 g, 10.0 mmol, 1.0 equiv), sodium *S*-methyl sulfothioate **1** (2.3 g, 15.0 mmol, 1.5 equiv), $CuSO_4$ (32 mg, 2.0 mmol, 0.2 equiv) and DMF (20 mL). The reaction mixture was stirred at 80 ˚C in air for 10 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into EtOAc (80 mL) and H_2O (20 mL), and extracted several times with EtOAc (3 *50 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, Petroleum ether) to afford the methylthiolated alkene **3a** as light yellow oil (1.02g, 69%).

3.7 General procedures for methylthiolation of erlotinib



A flask was charged with erlotinib (162.0 mg, 0.4 mmol, 1.0 equiv), sodium *S*-methyl sulfothioate **1** (99 mg, 0.6 mmol, 1.5 equiv), $CuSO_4$ (12.8 mg, 0.08 mmol, 0.2 equiv) and DMF (4 mL). The reaction mixture was stirred at 80 ˚C in air for 10 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into EtOAc (20 mL) and H_2O (20 mL), and extracted several times with EtOAc (3 *15 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, Petroleum ether/ Ethyl acetate =1:50, v/v) to afford the methylthiolated erlotinib **9**.



Chemical Formula: $C_{23}H_{25}N_3O_4S$
Exact Mass: 439.1566

6,7-Bis(2-methoxyethoxy)-*N*-(3-((methylthio)ethynyl)phenyl)quinazolin-4-amine. **9**, a white solid (93%, 163.3 mg). Mp: 113-115 °C. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.63 (s, 1H), 7.77 (s, 1H), 7.73 (s, 1H), 7.67 (dd, J = 8.1, 2.1 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.25 (s, 1H), 7.20 – 7.11 (m, 2H), 4.20 (dt, J = 11.6, 4.5 Hz, 4H), 3.79 (q, J = 5.1 Hz, 4H), 3.43 (s, 6H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 156.58 , 154.61 , 153.79 , 148.91 , 147.64 , 139.04 , 129.13 , 127.30 , 124.60 , 124.27 , 121.85 , 109.41 , 108.79 , 102.71 , 91.86 , 81.54 , 71.11 , 70.60 , 69.21 , 68.42 , 59.48 , 59.41 , 19.59 . HRMS (EI) Calcd. for $C_{23}H_{25}N_3O_4S$ 439.1566, found 439.1561.

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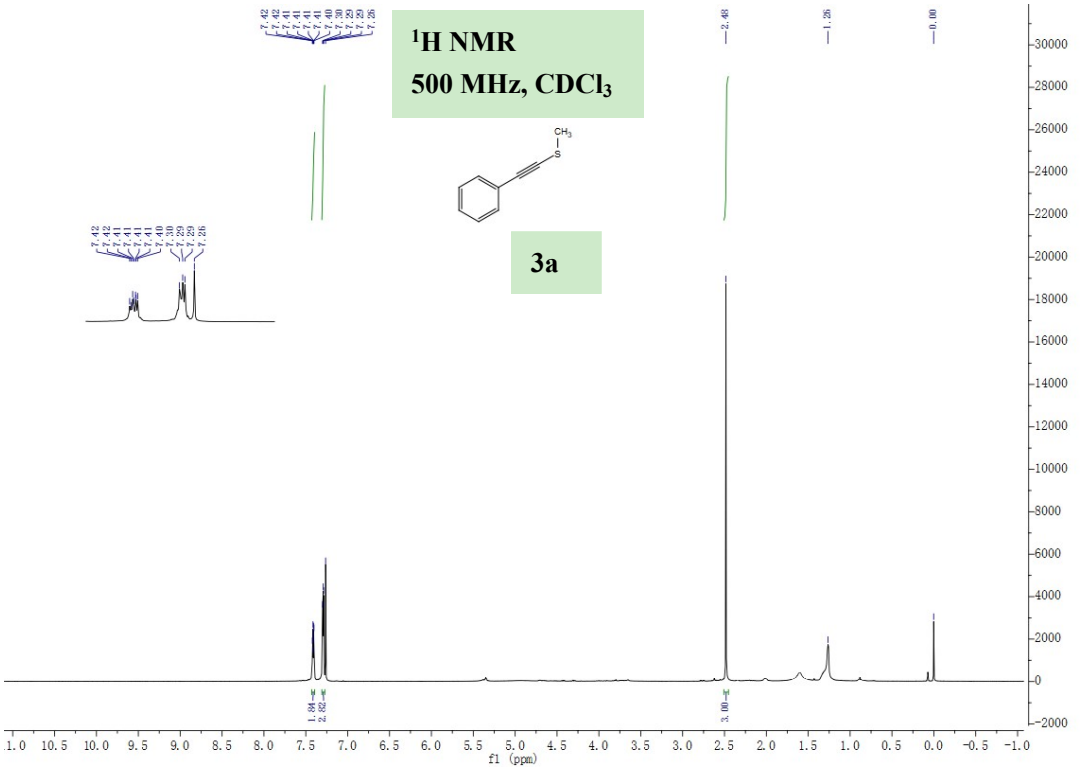
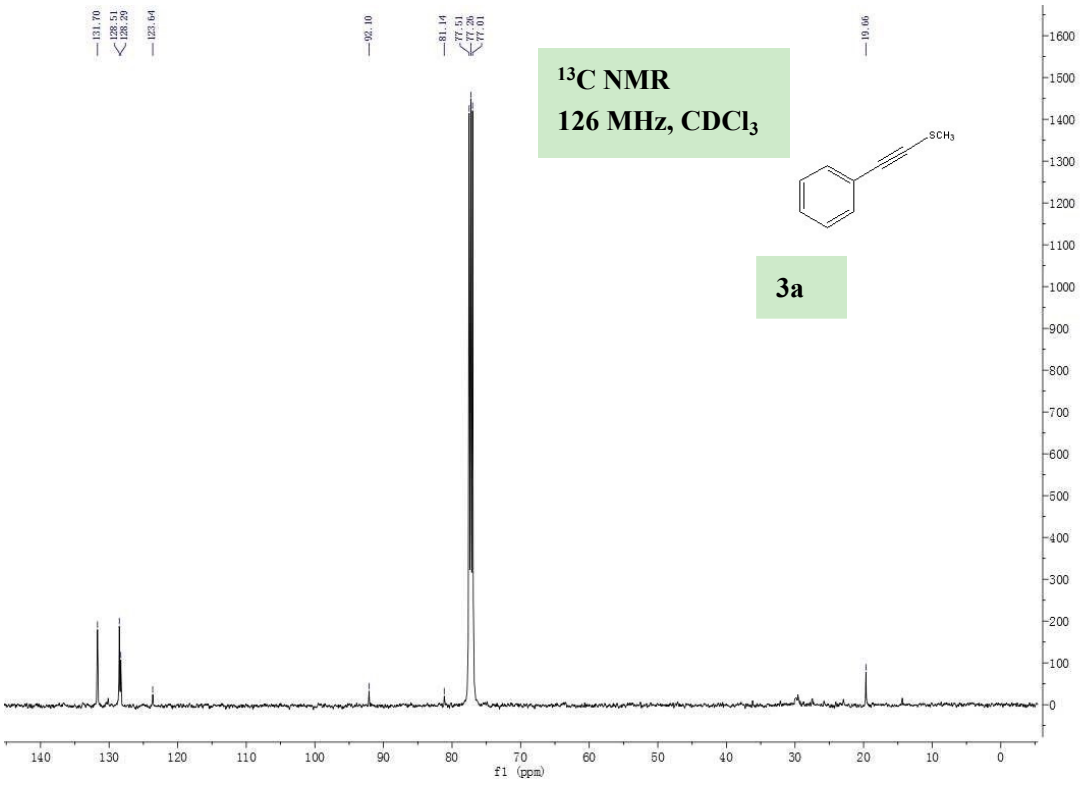
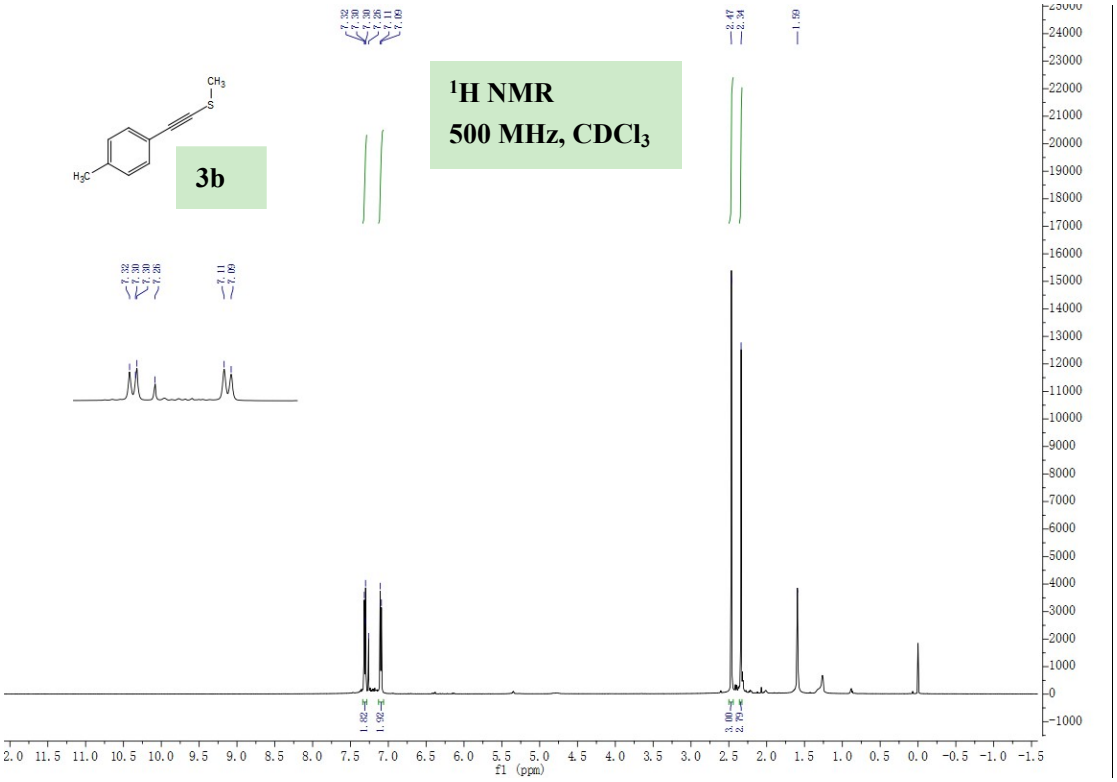
4. NMR Spectra



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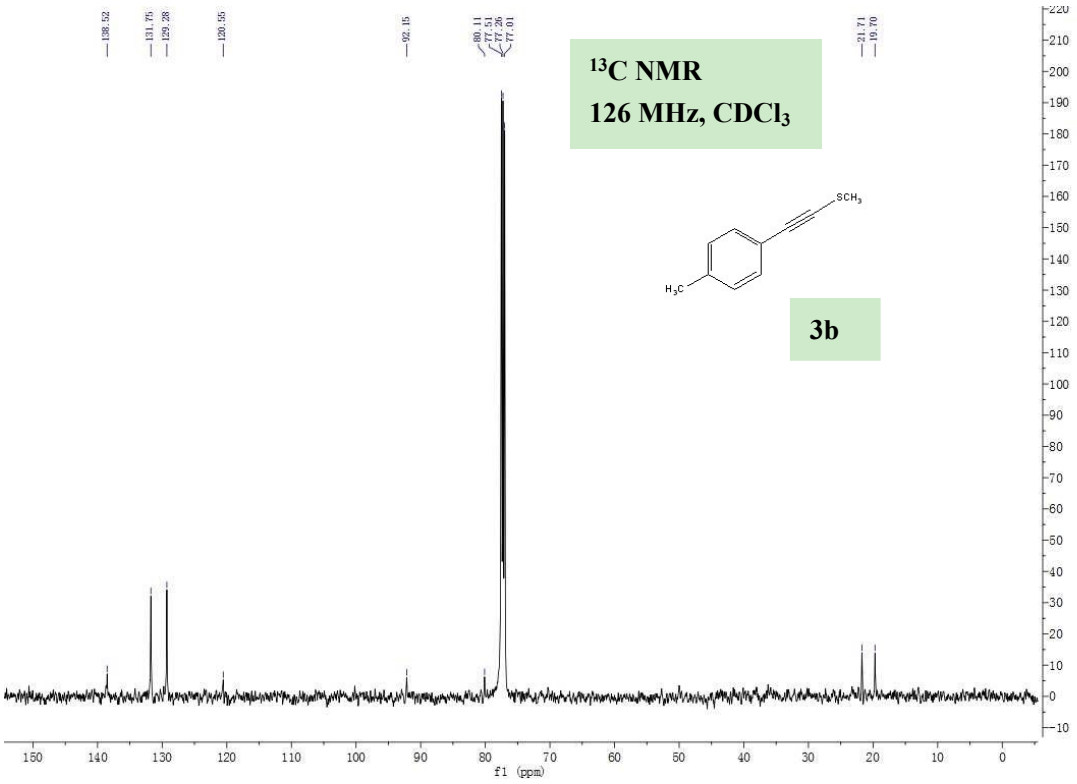
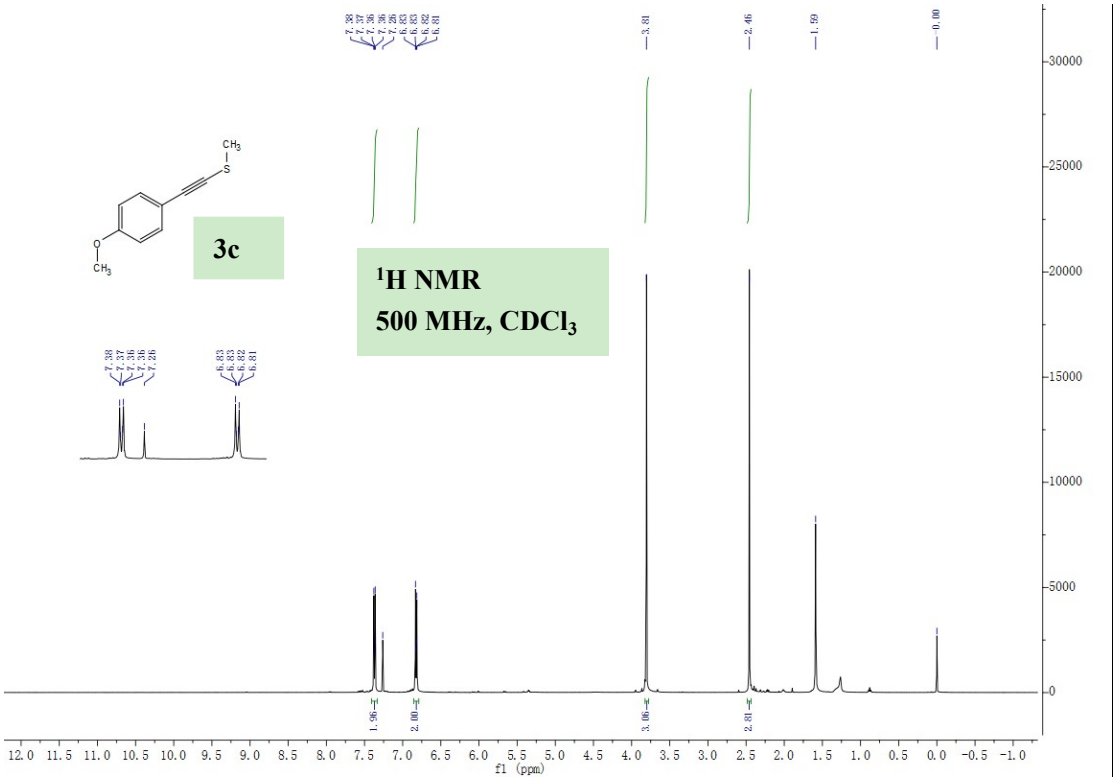
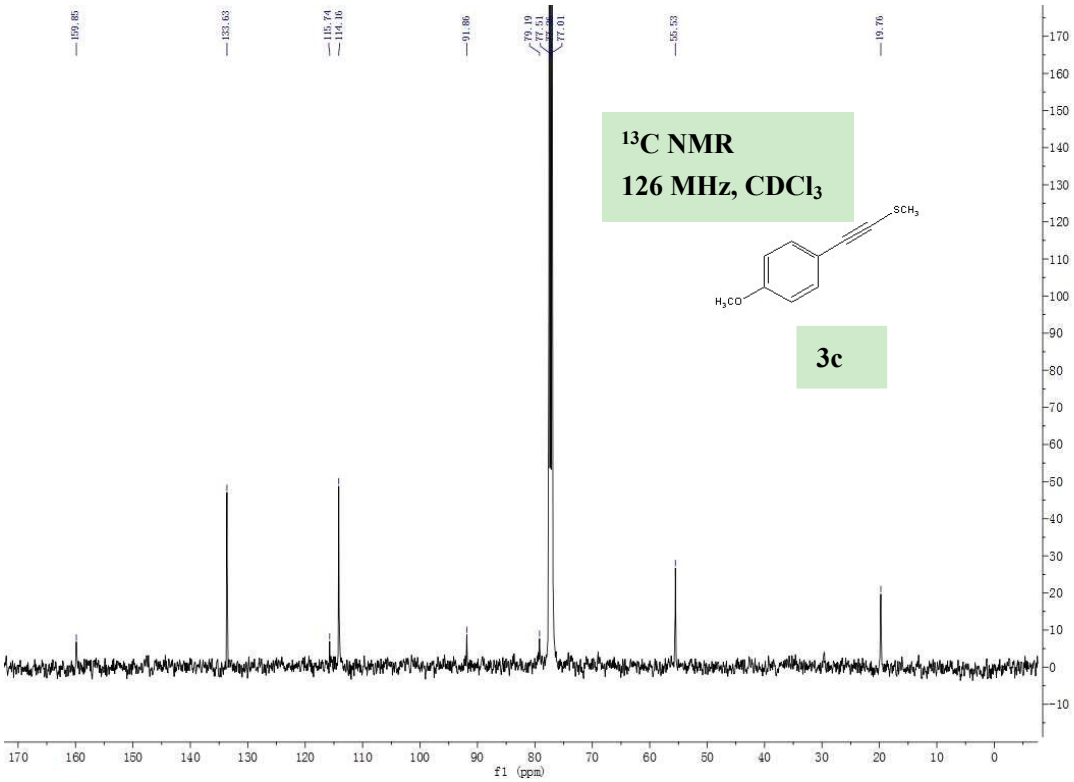
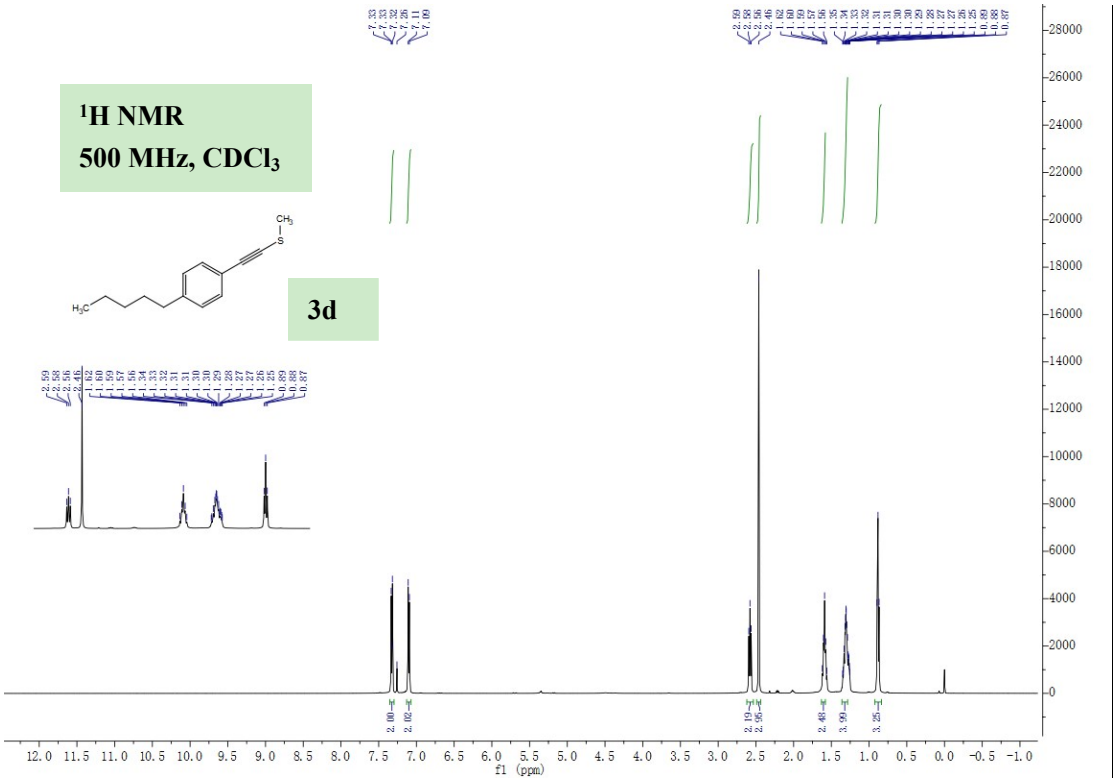
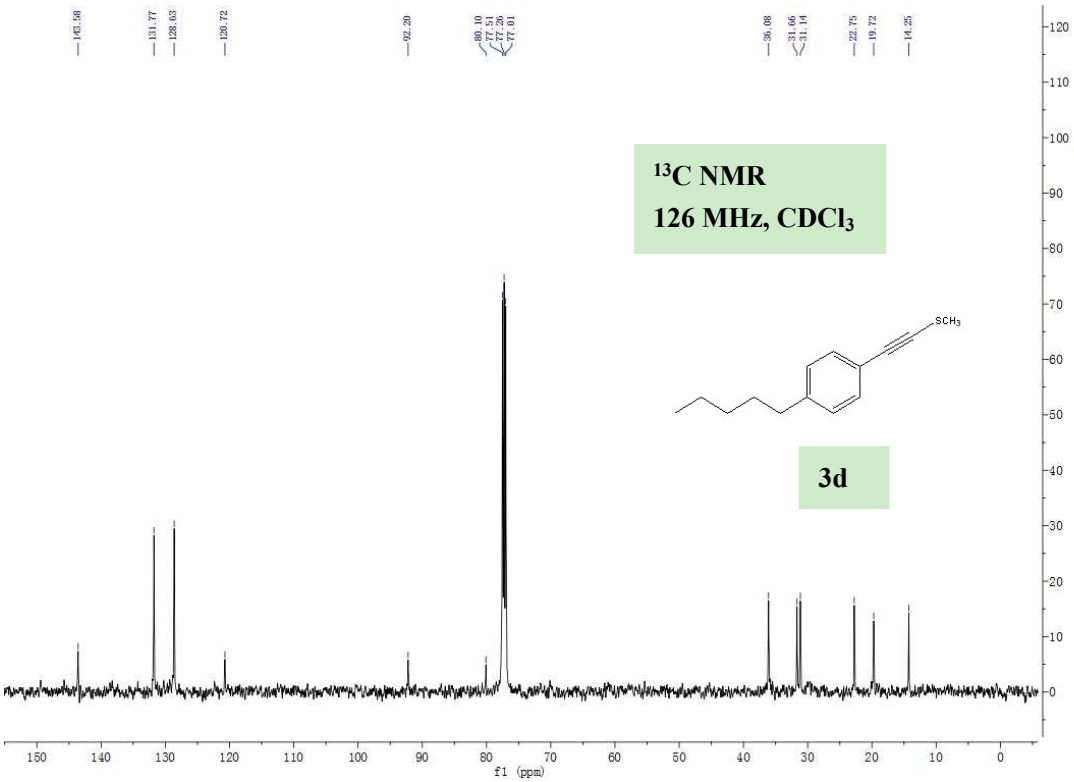
500 MHz, $CDCl_3$
3b
f1 (ppm)

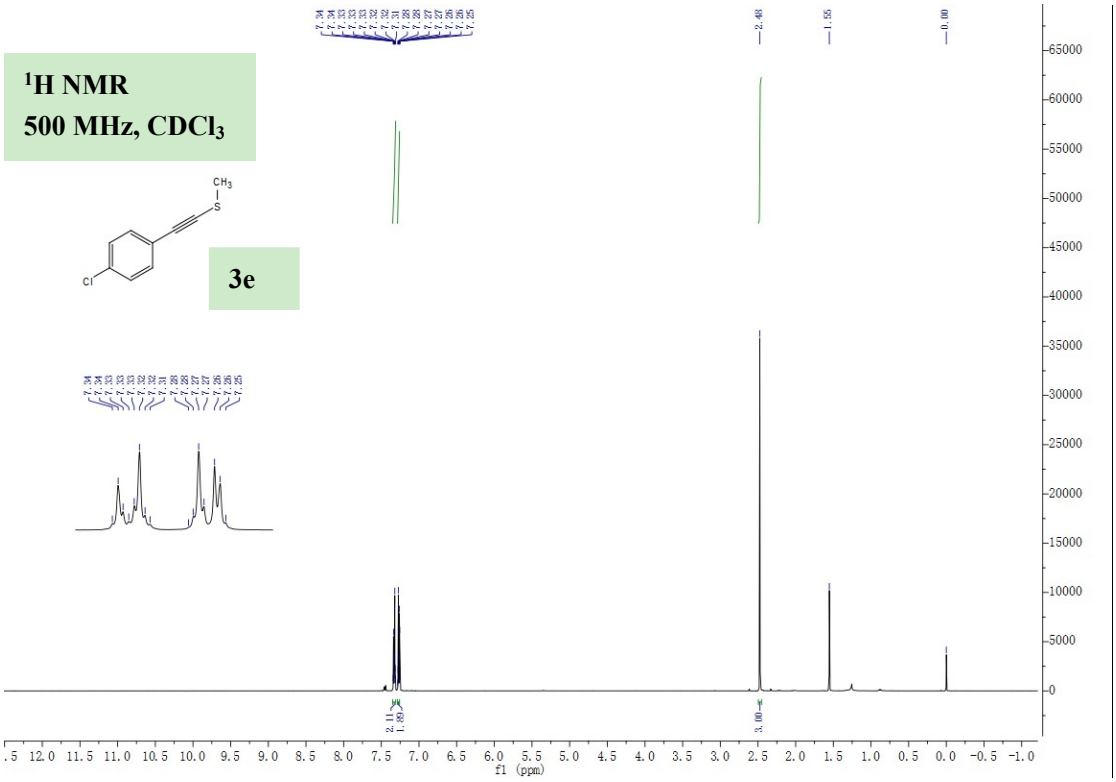

^{13}C NMR
126 MHz, $CDCl_3$
3b
f1 (ppm)

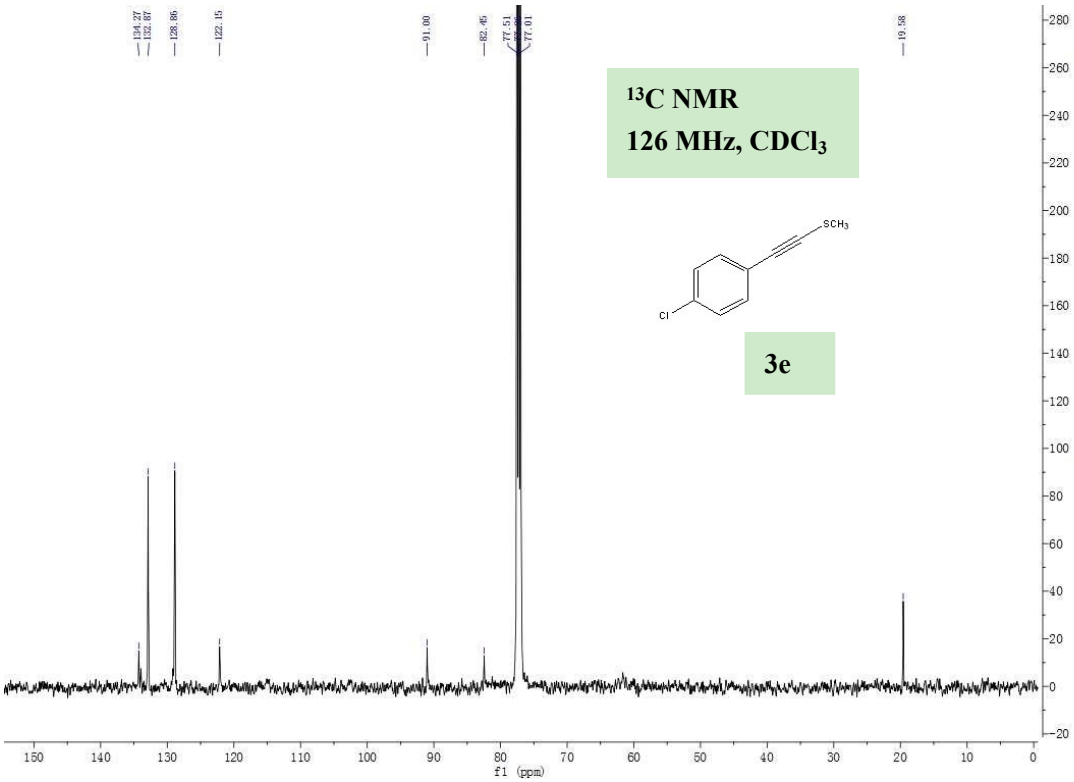

3c
^{1}H NMR
500 MHz, CDCl$_3$
f1 (ppm)


^{13}C NMR
126 MHz, CDCl$_3$
3c
f1 (ppm)

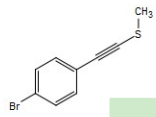

^{1}H NMR
500 MHz, $CDCl_3$
3d
f1 (ppm)


^{13}C NMR
126 MHz, $CDCl_3$
3d
f1 (ppm)


1H NMR
500 MHz, CDCl3
3e
f1 (ppm)

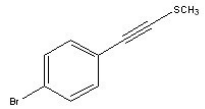

13C NMR
126 MHz, CDCl3
3e
f1 (ppm)

^{1}H NMR
500 MHz, $CDCl_3$



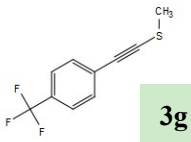
3f

^{13}C NMR
126 MHz, $CDCl_3$



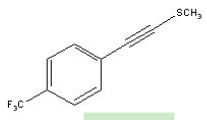
3f

^{1}H NMR
500 MHz, $CDCl_3$

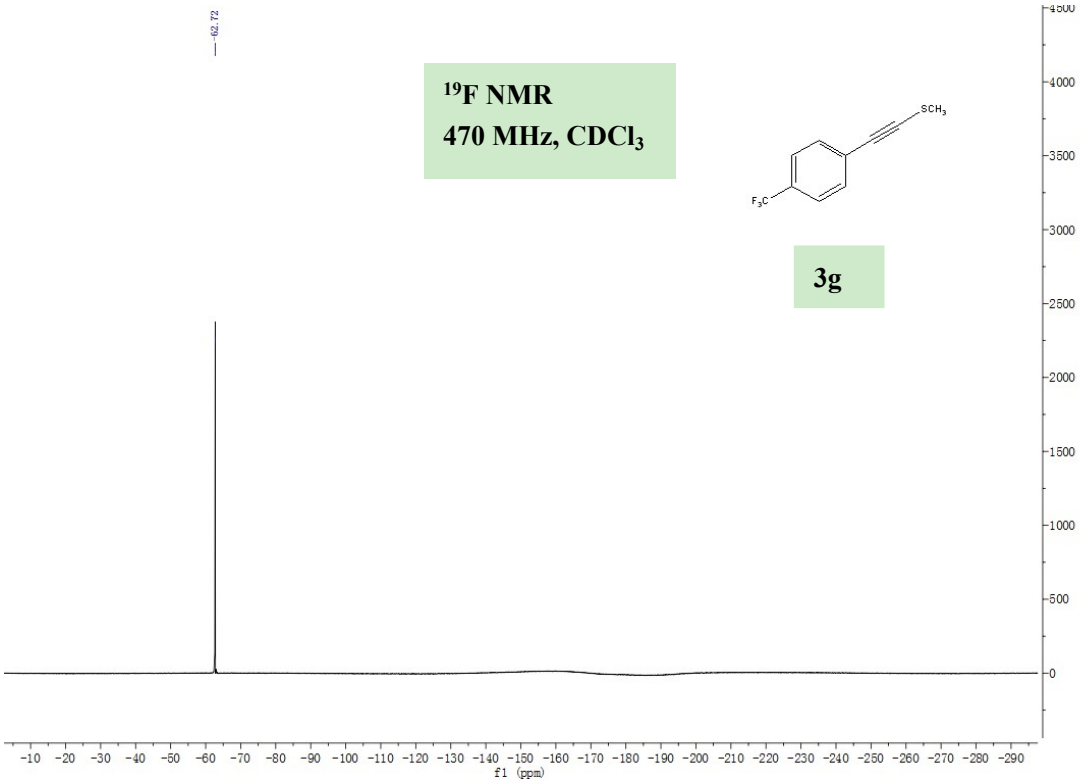


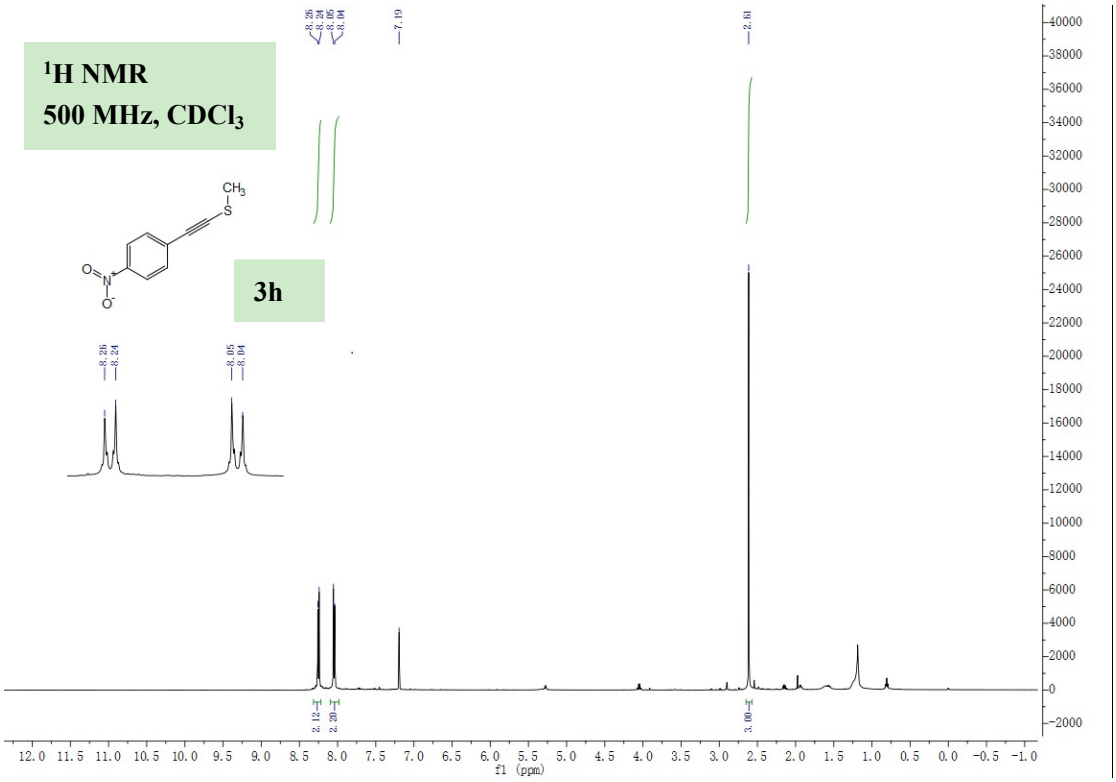
3g

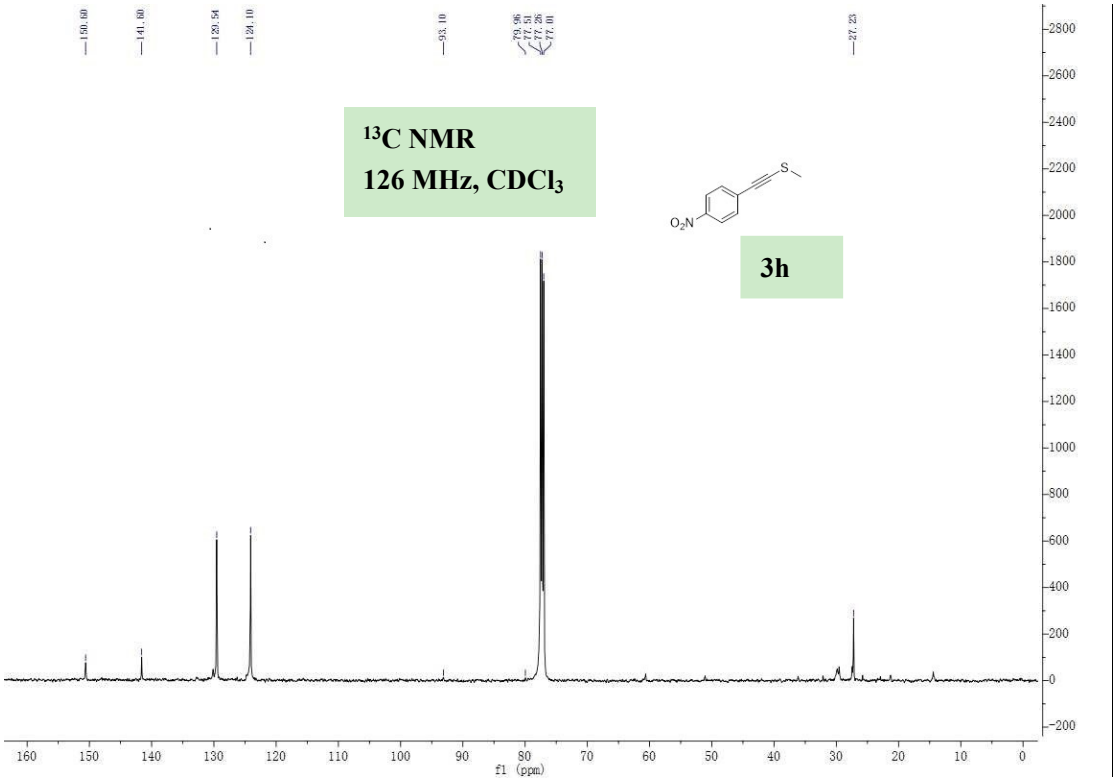
^{13}C NMR
126 MHz, $CDCl_3$

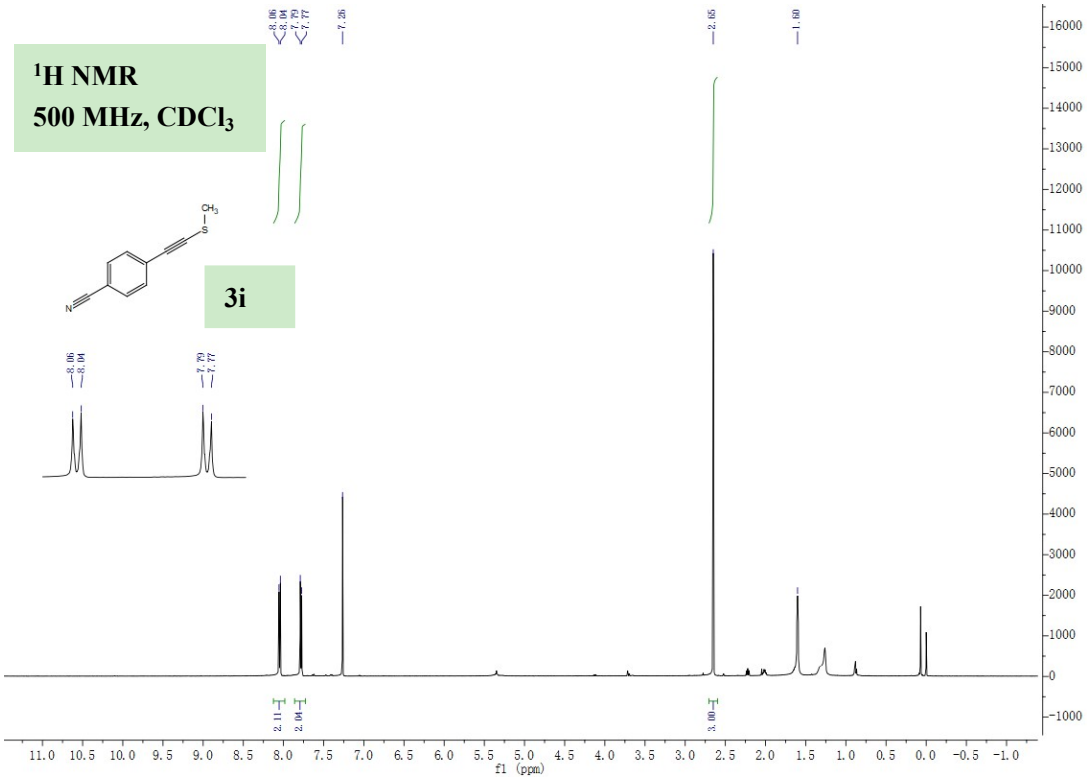


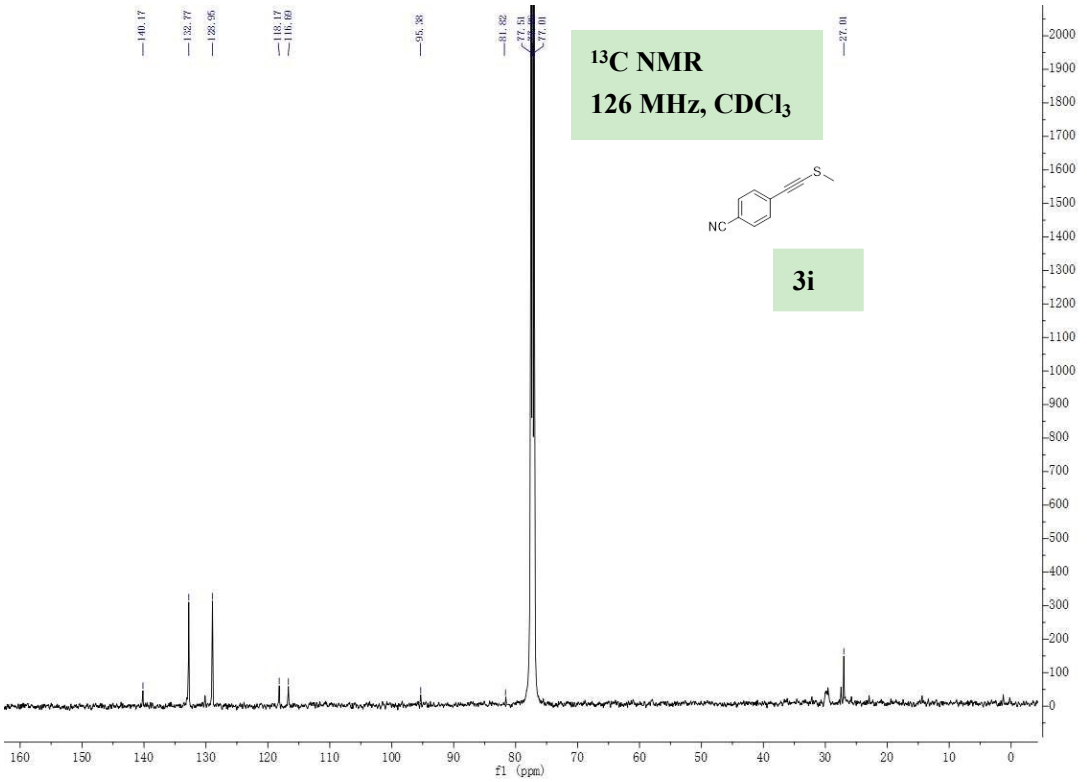
3g

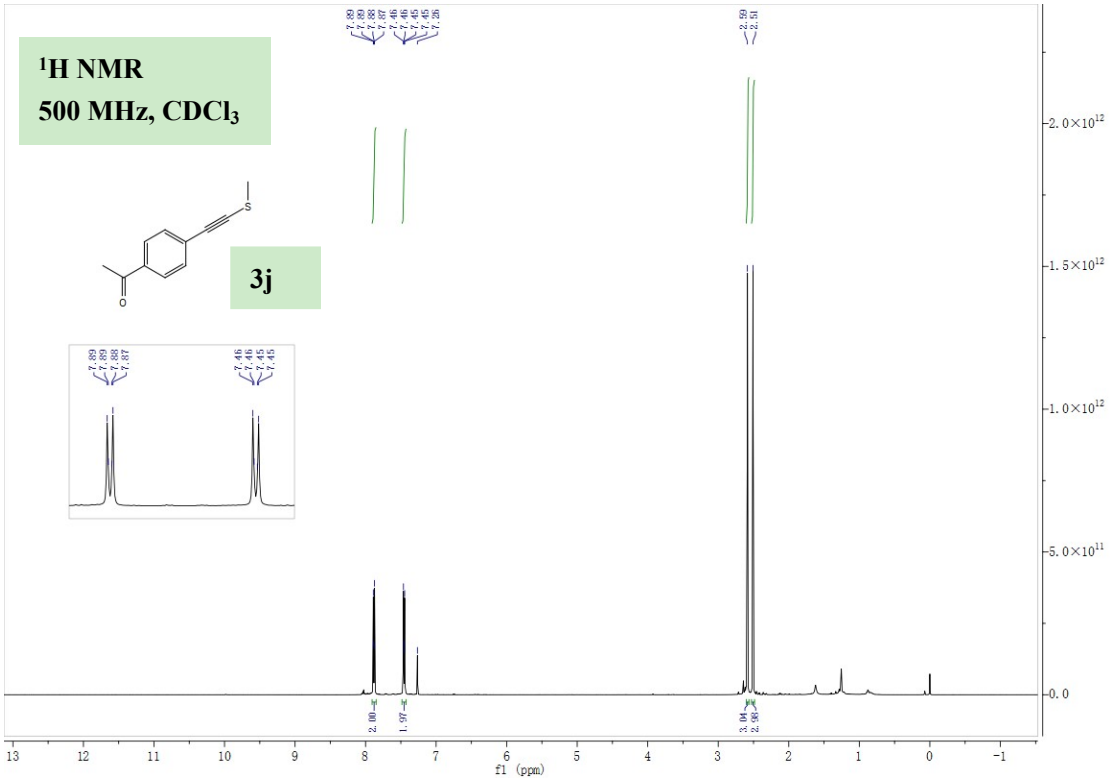

-62.72
19F NMR
470 MHz, CDCl3
SCH3
F3C
3g
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)

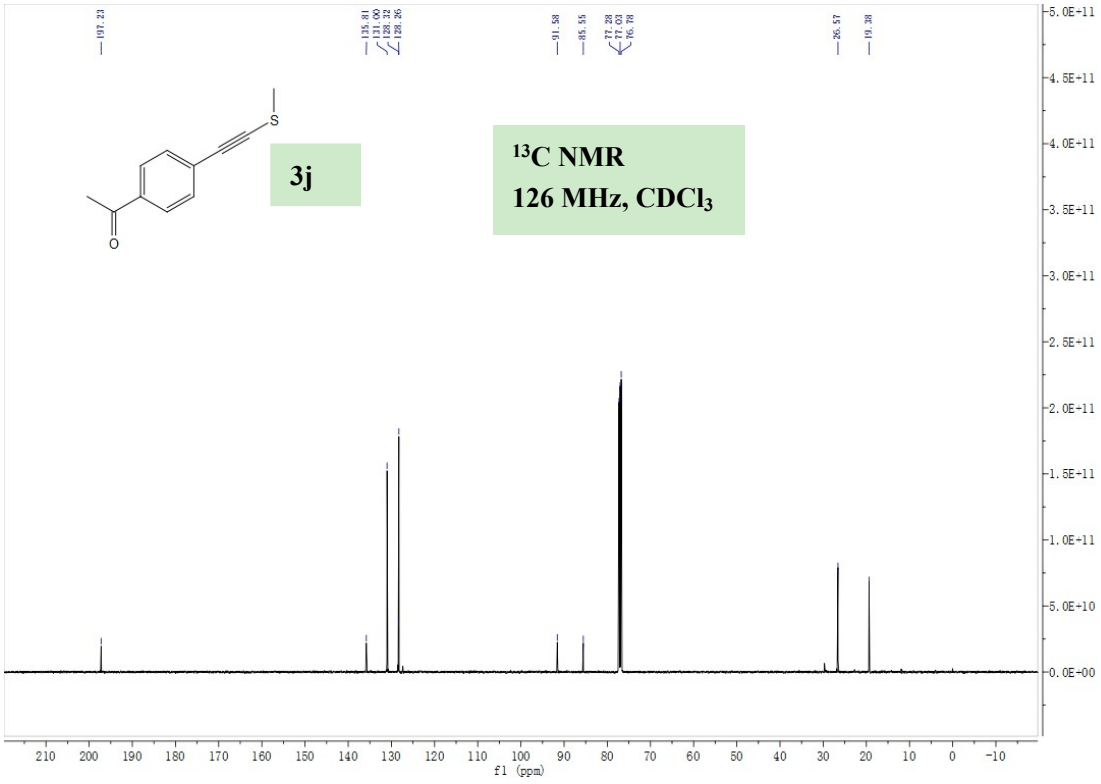

1H NMR
500 MHz, CDCl3
3h
8.26
8.24
8.05
8.04
7.19
2.61
2.12
2.20
3.00
f1 (ppm)


13C NMR
126 MHz, CDCl3
3h
150.69
141.60
129.54
124.10
93.10
79.96
77.51
77.26
77.01
27.23
f1 (ppm)


1H NMR
500 MHz, CDCl3
3i


13C NMR
126 MHz, CDCl3
3i


^{1}H NMR
500 MHz, CDCl$_3$
3j
f1 (ppm)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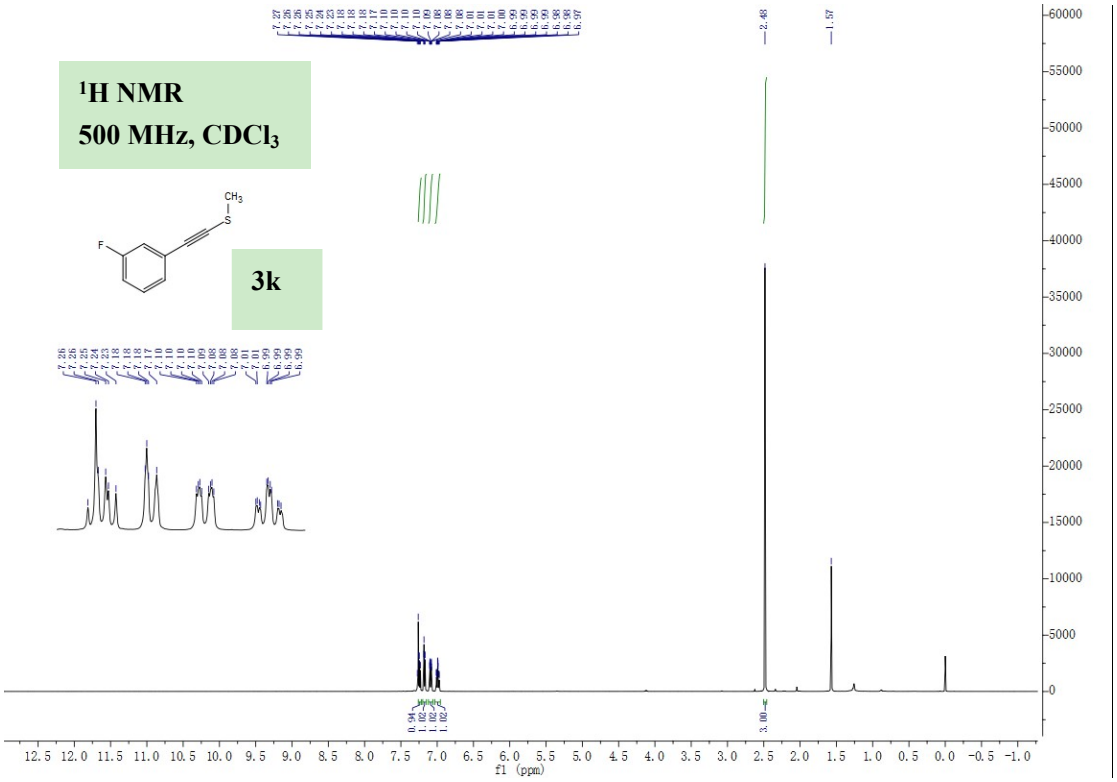
126 MHz, CDCl$_3$
3j
f1 (ppm)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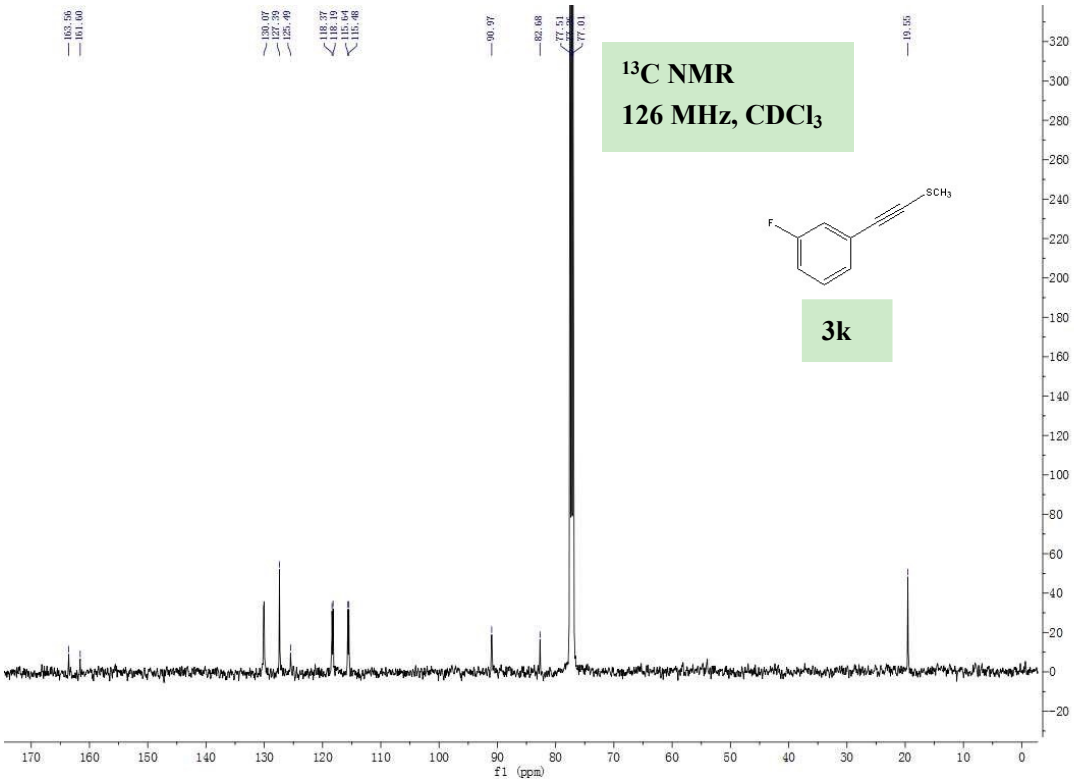
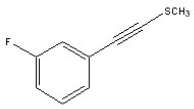
500 MHz, $CDCl_3$
3k
f1 (ppm)

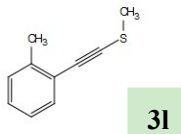

^{13}C NMR
126 MHz, $CDCl_3$
3k
f1 (ppm)

^{19}F NMR
470 MHz, $CDCl_3$



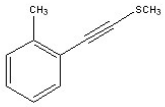
3k

^{1}H NMR
500 MHz, $CDCl_3$

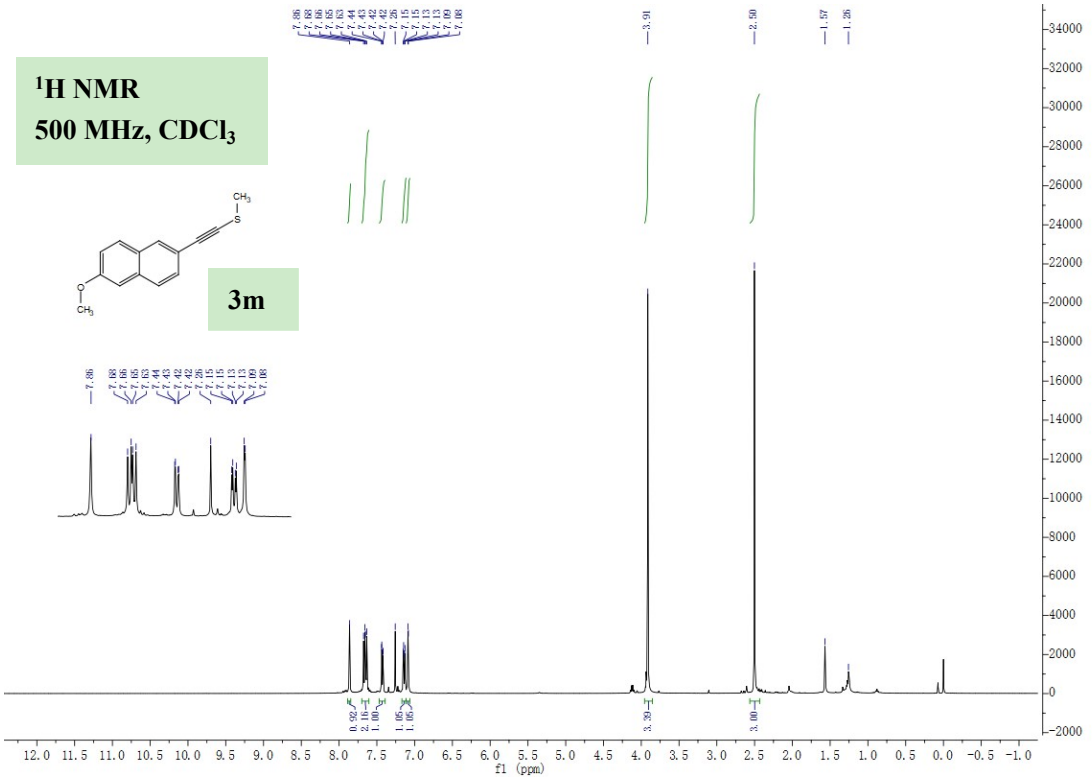


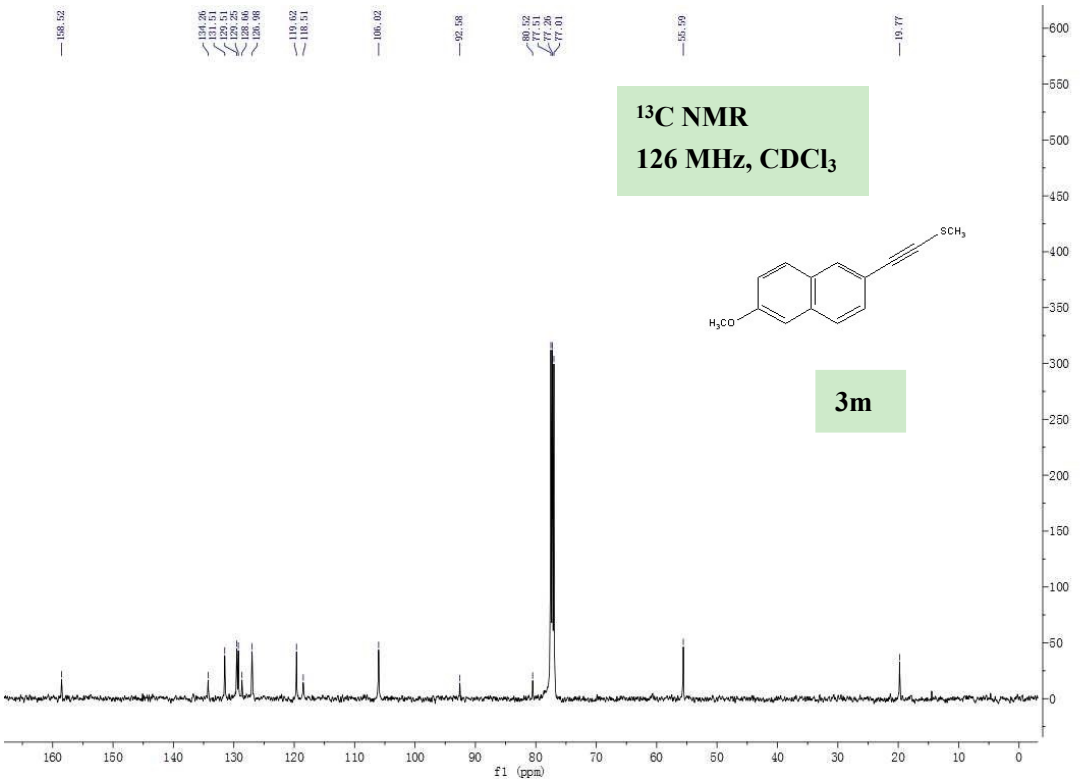
3l

^{13}C NMR
126 MHz, $CDCl_3$



3l


1H NMR
500 MHz, CDCl3
3m
f1 (ppm)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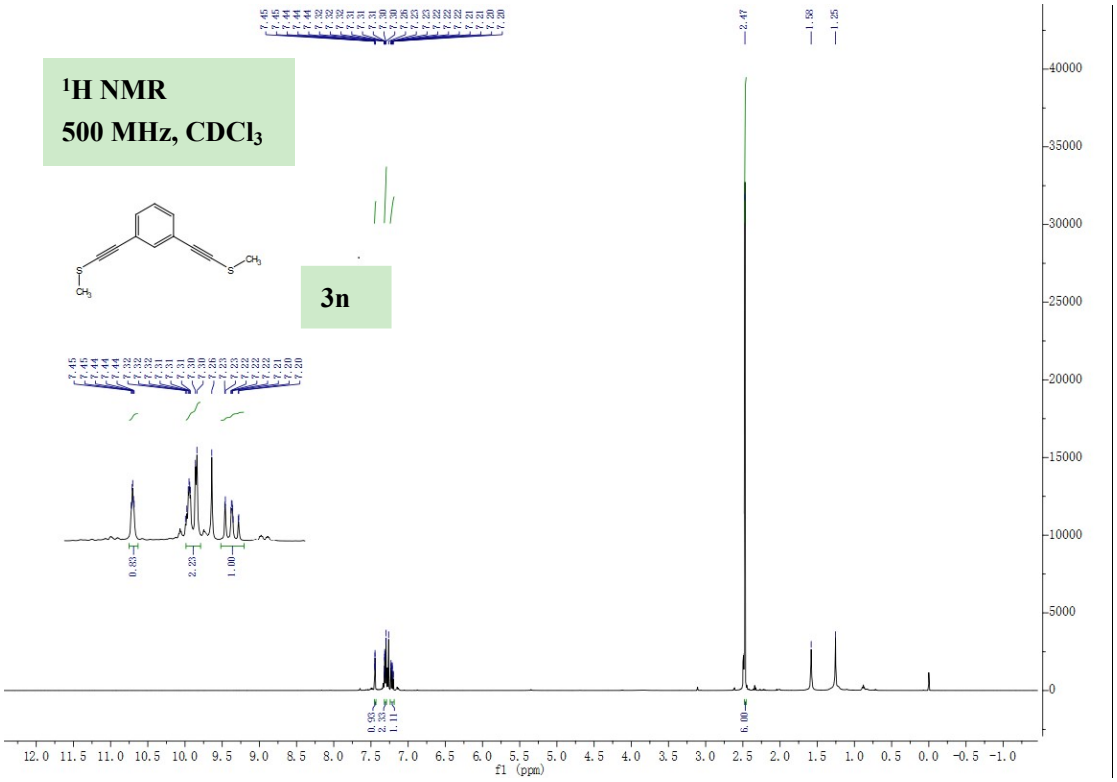
126 MHz, CDCl3
3m
f1 (ppm)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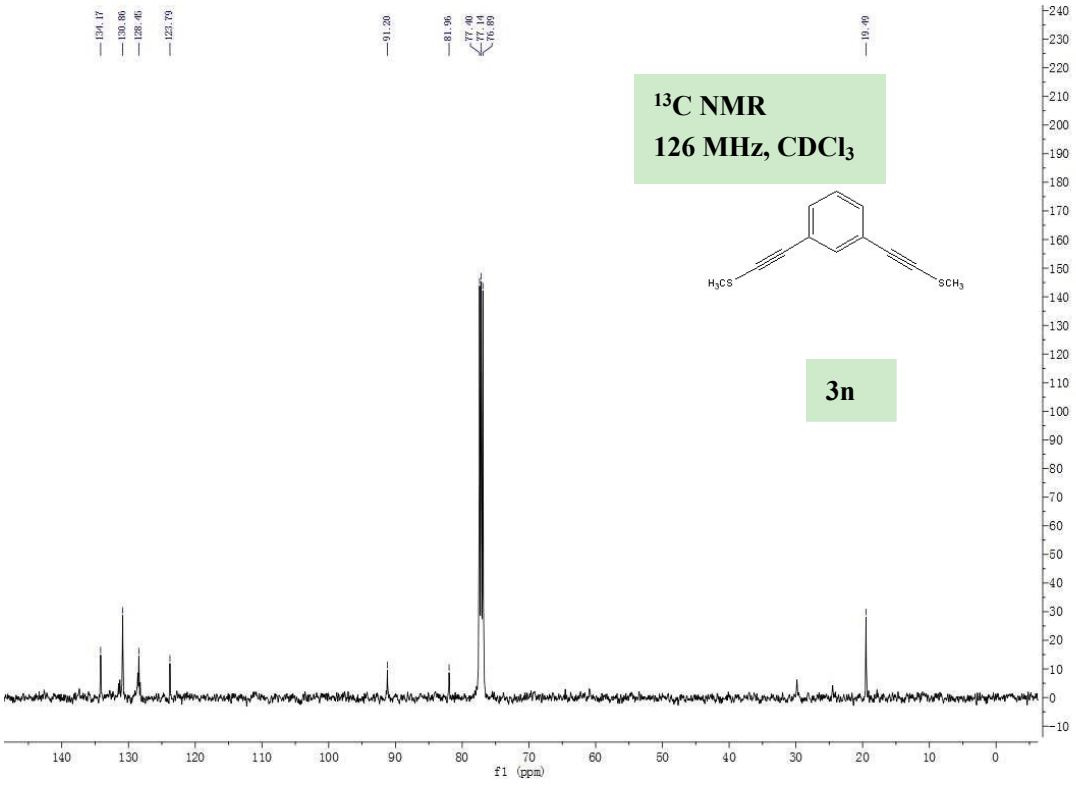
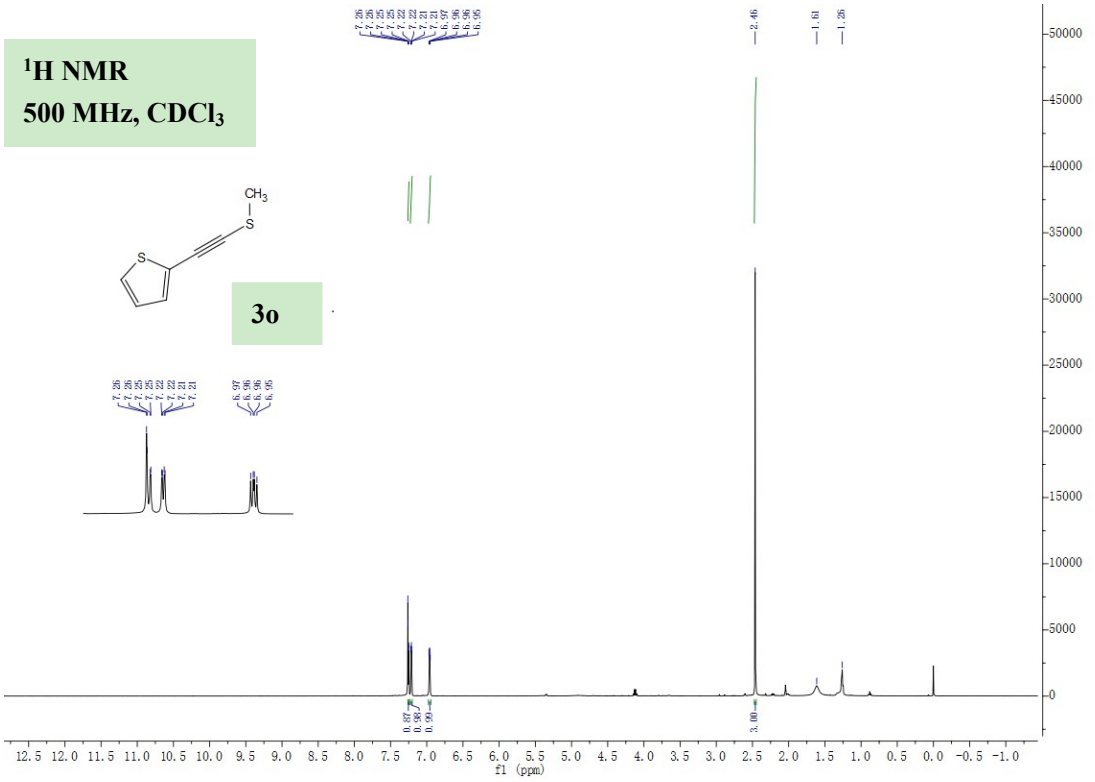
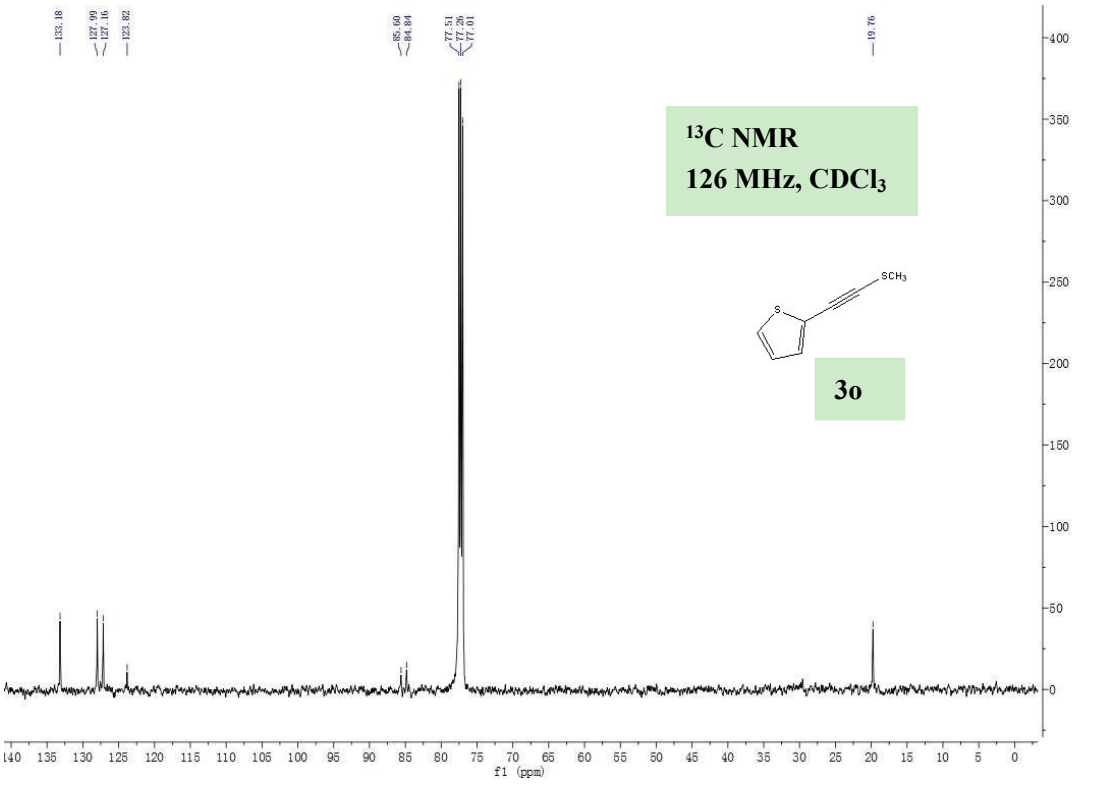
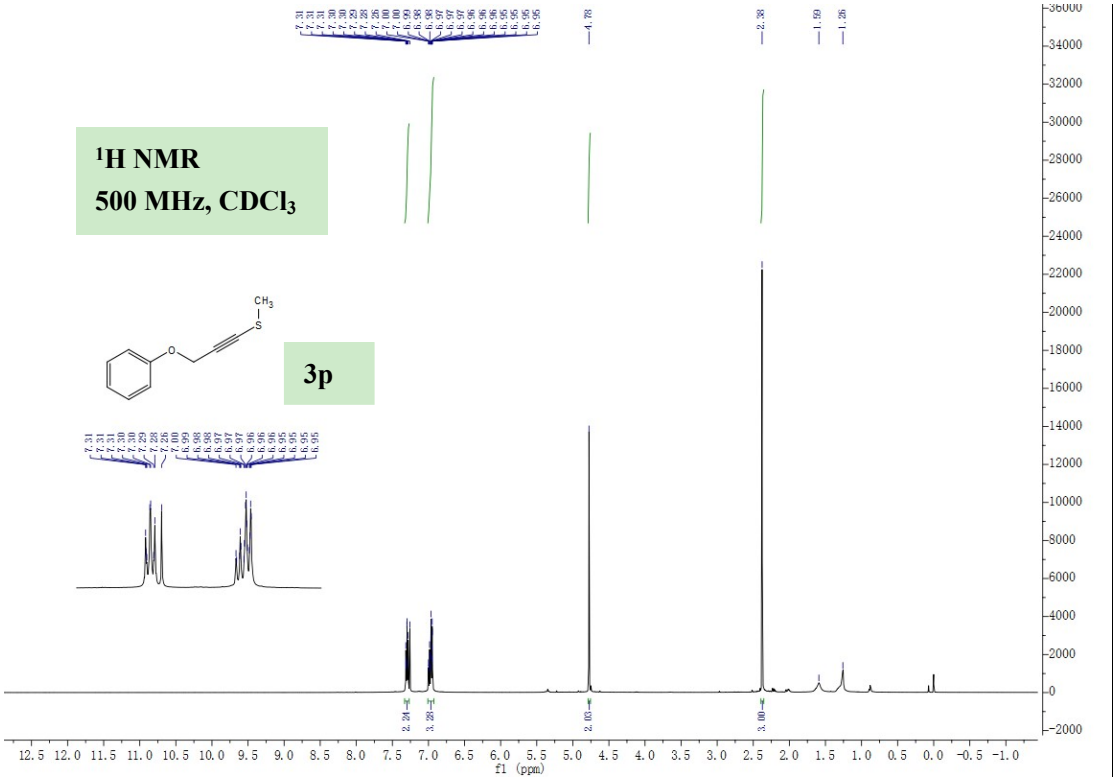
500 MHz, CDCl3
3n
f1 (ppm)


13C NMR
126 MHz, CDCl3
3n
f1 (ppm)


1H NMR
500 MHz, CDCl3
CH3
S
S
3o
7.26
7.25
7.22
7.21
6.97
6.96
6.95
2.46
1.61
1.26
0.87
0.98
0.99
3.00
f1 (ppm)


133.18
127.99
127.16
123.82
85.60
84.04
77.51
77.26
77.01
19.76
13C NMR
126 MHz, CDCl3
SCH3
S
3o
f1 (ppm)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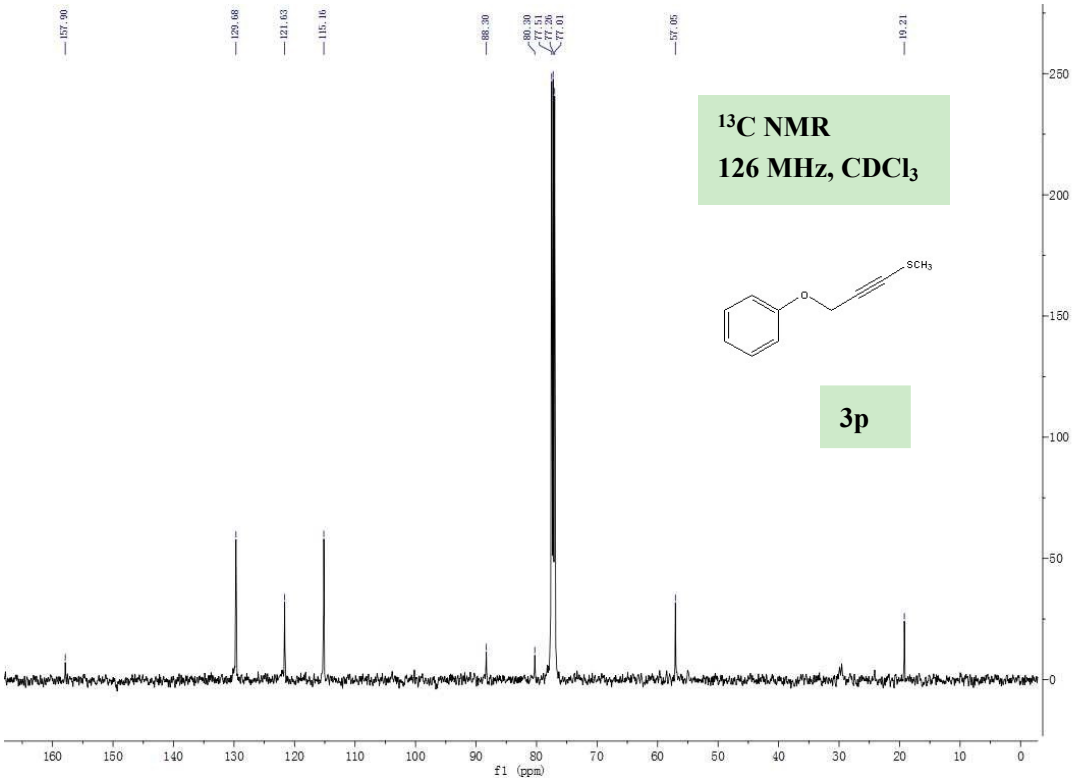
500 MHz, $CDCl_3$
3p
f1 (ppm)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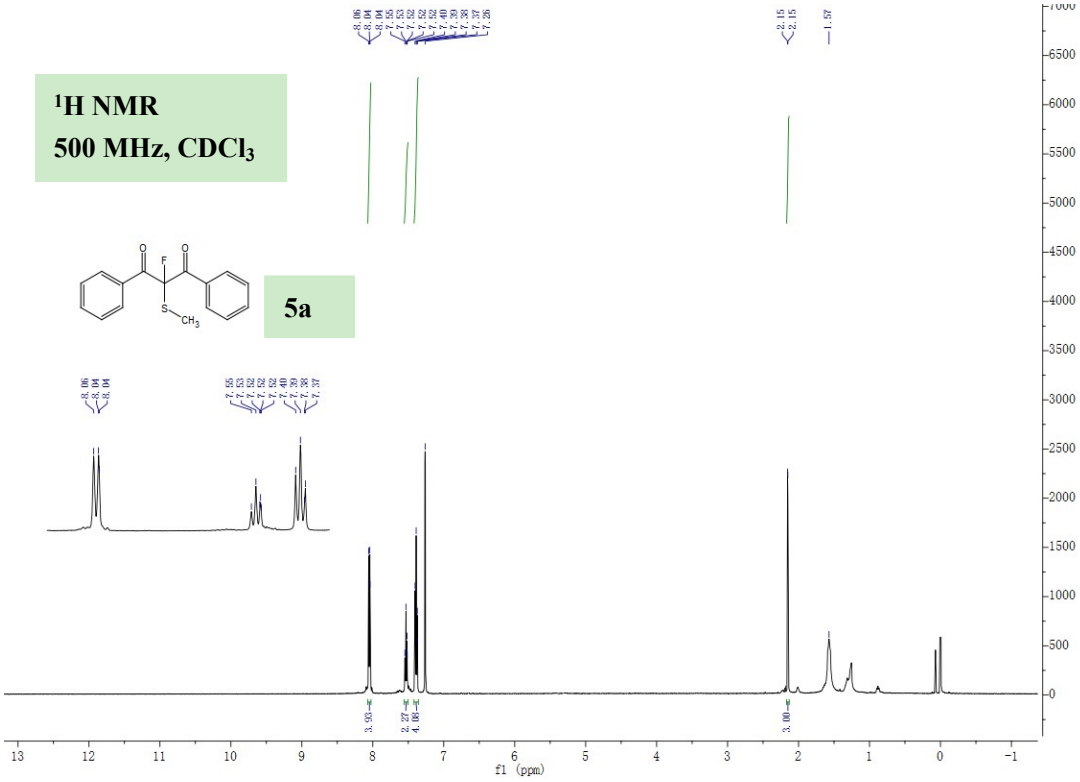
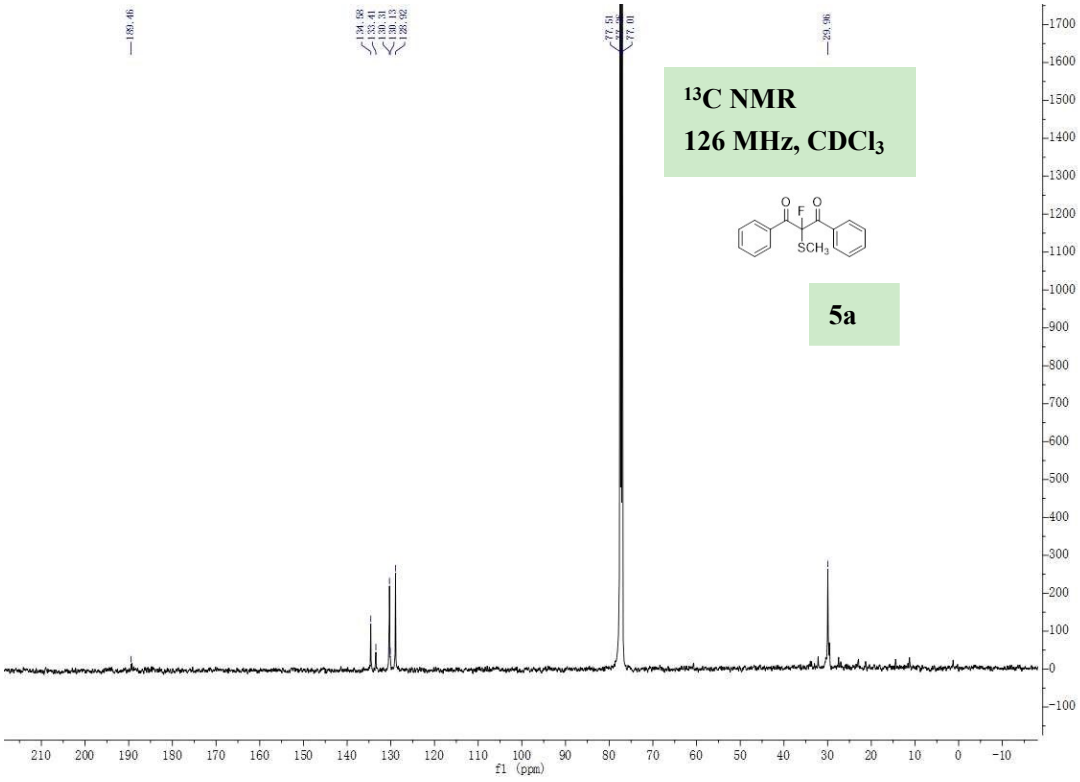
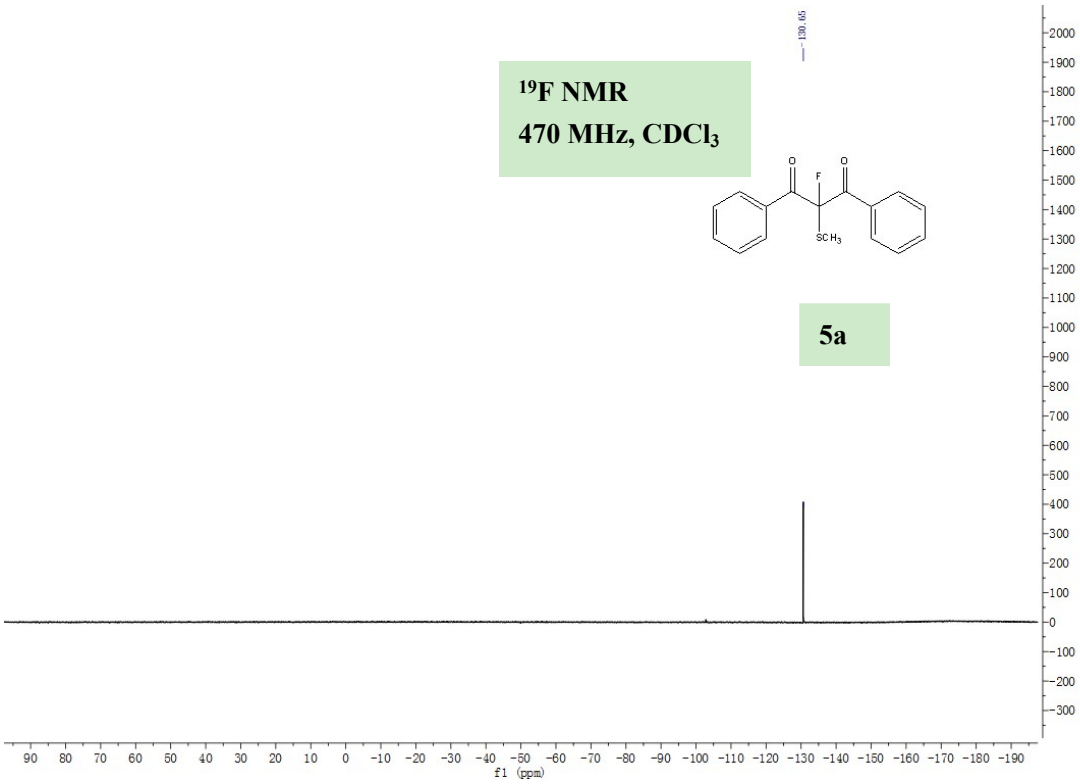
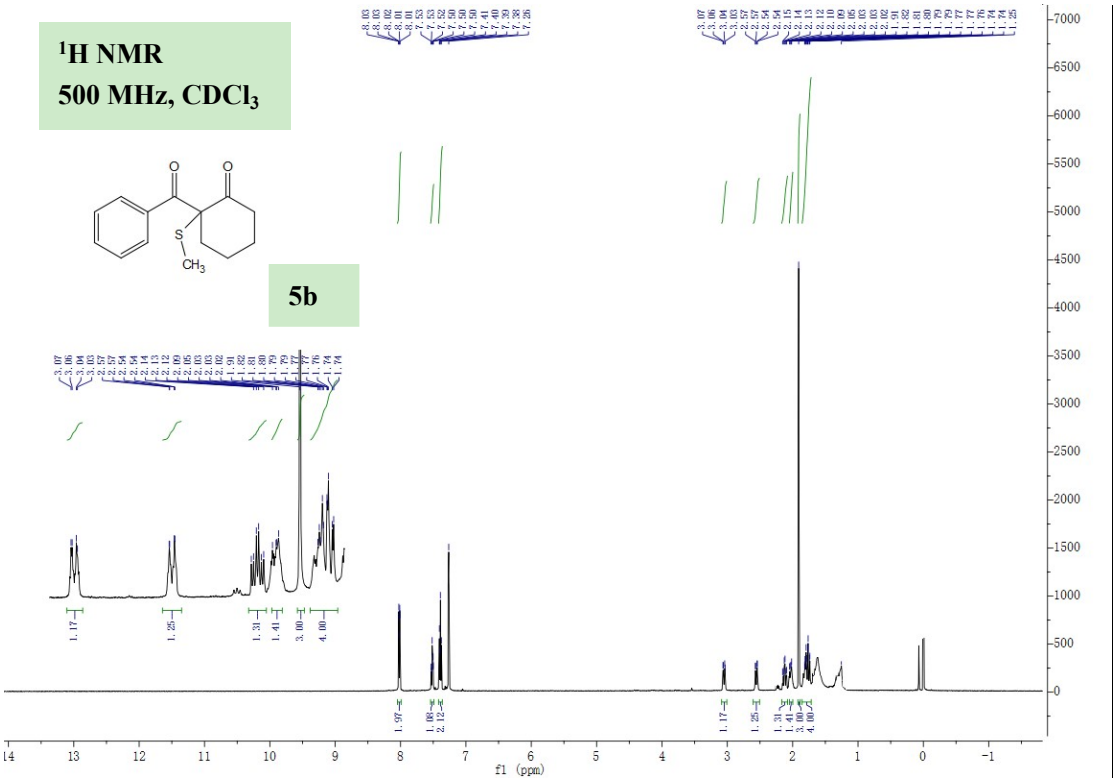
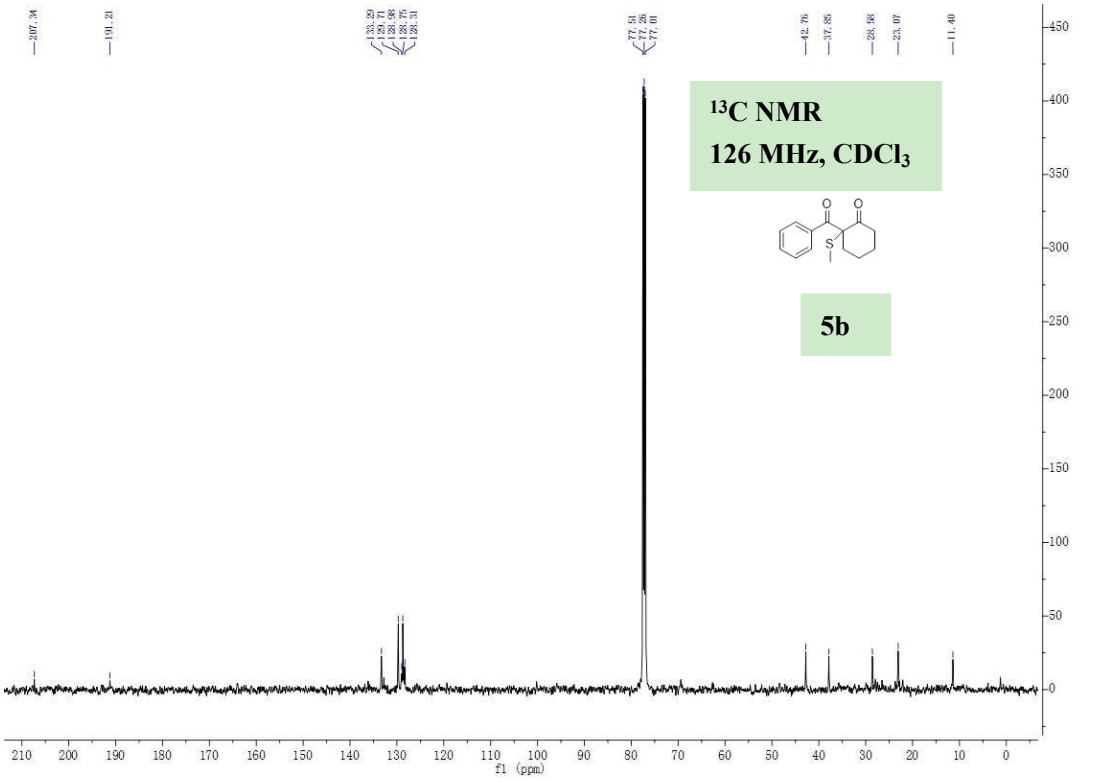
126 MHz, $CDCl_3$
3p
f1 (ppm)

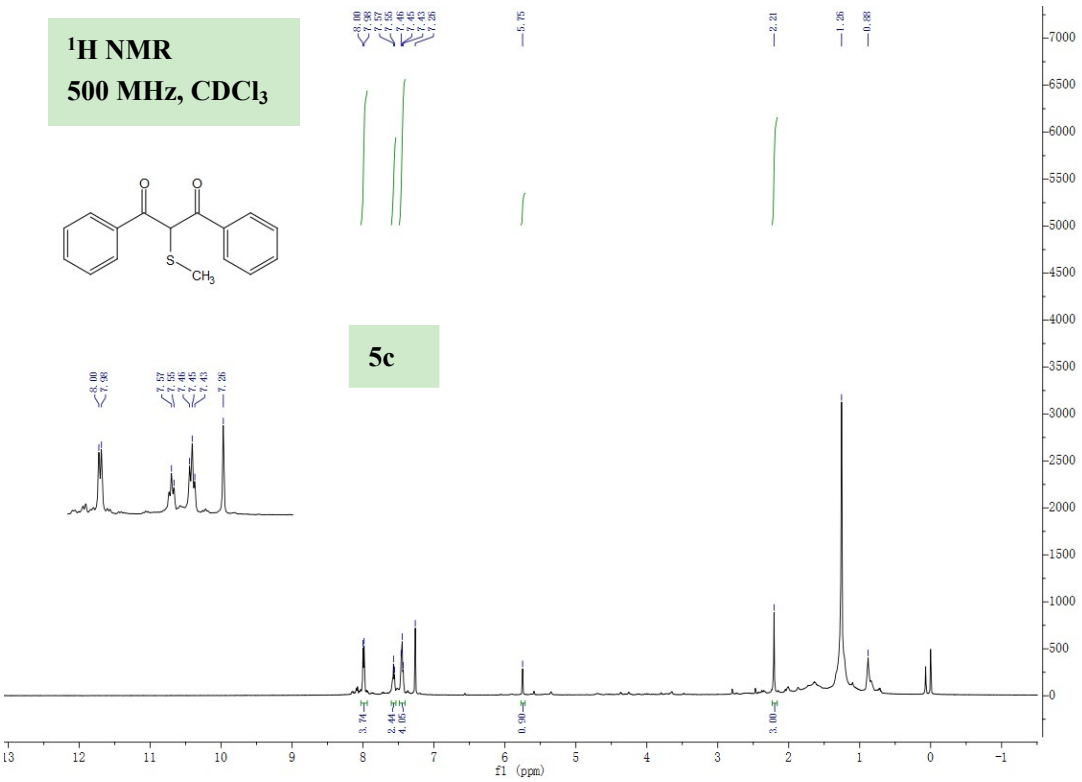

1H NMR
500 MHz, CDCl3
5a
f1 (ppm)


13C NMR
126 MHz, CDCl3
5a
f1 (ppm)


19F NMR
470 MHz, CDCl3
O
F
O
SCH3
5a
f1 (ppm)


^{1}H NMR
500 MHz, $CDCl_3$
5b
f1 (ppm)


^{13}C NMR
126 MHz, $CDCl_3$
5b
f1 (ppm)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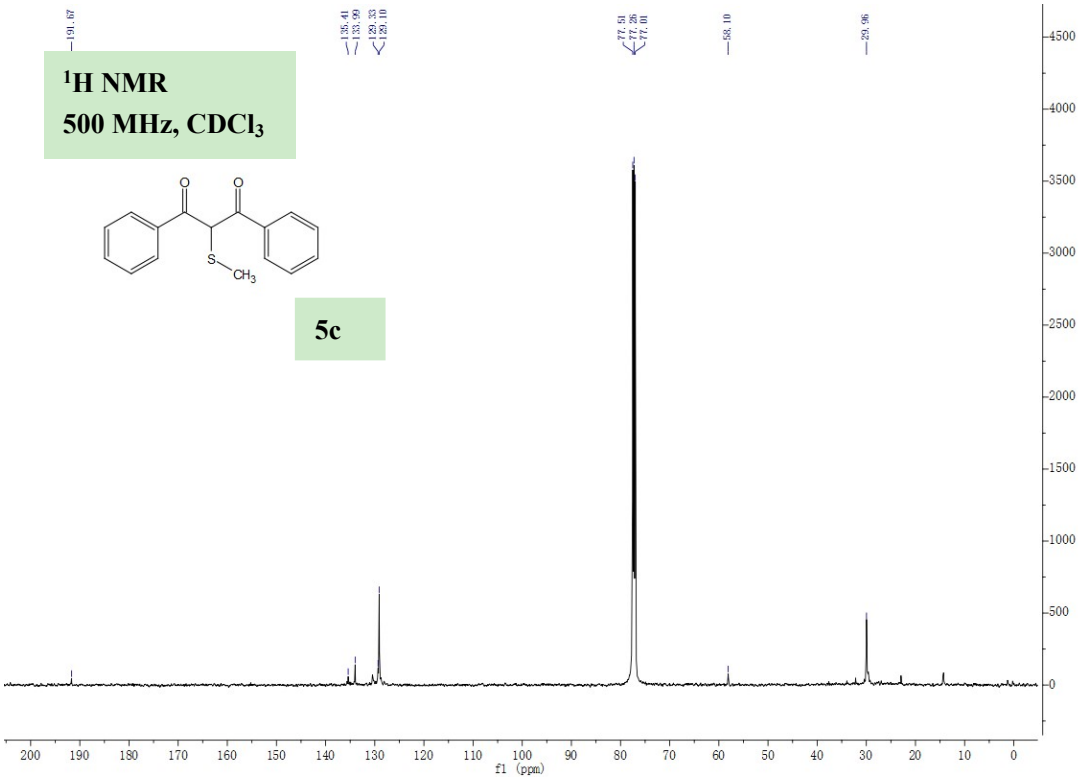
500 MHz, CDCl3
5c
f1 (ppm)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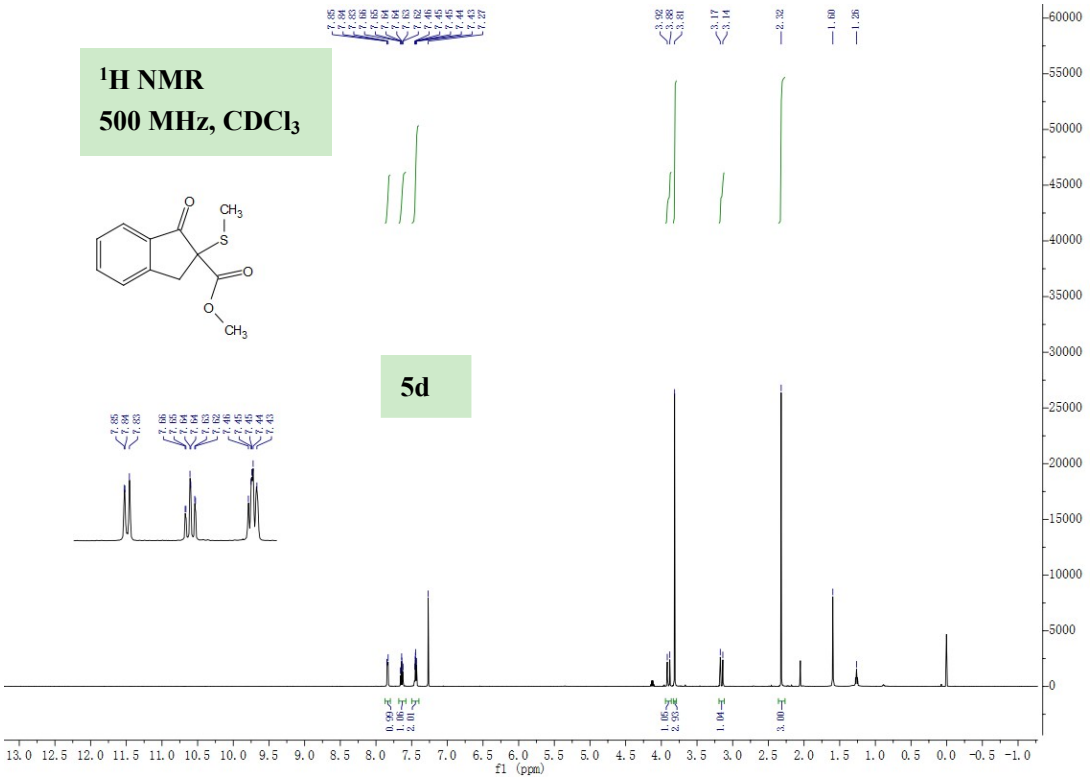
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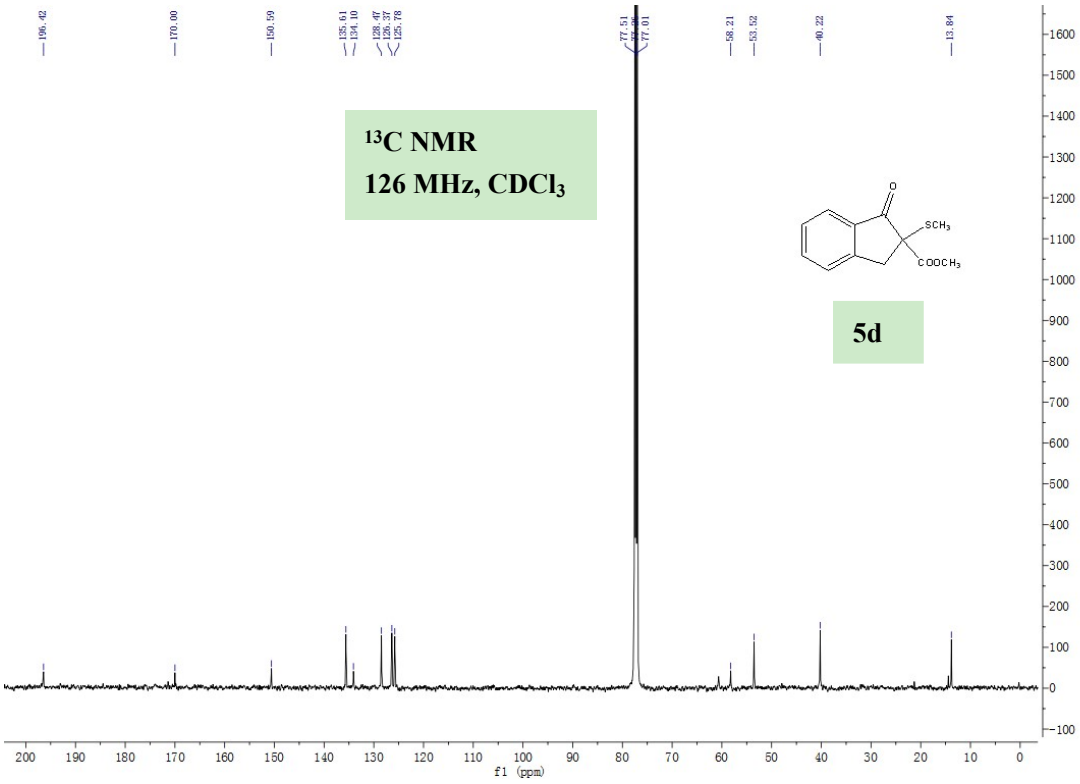
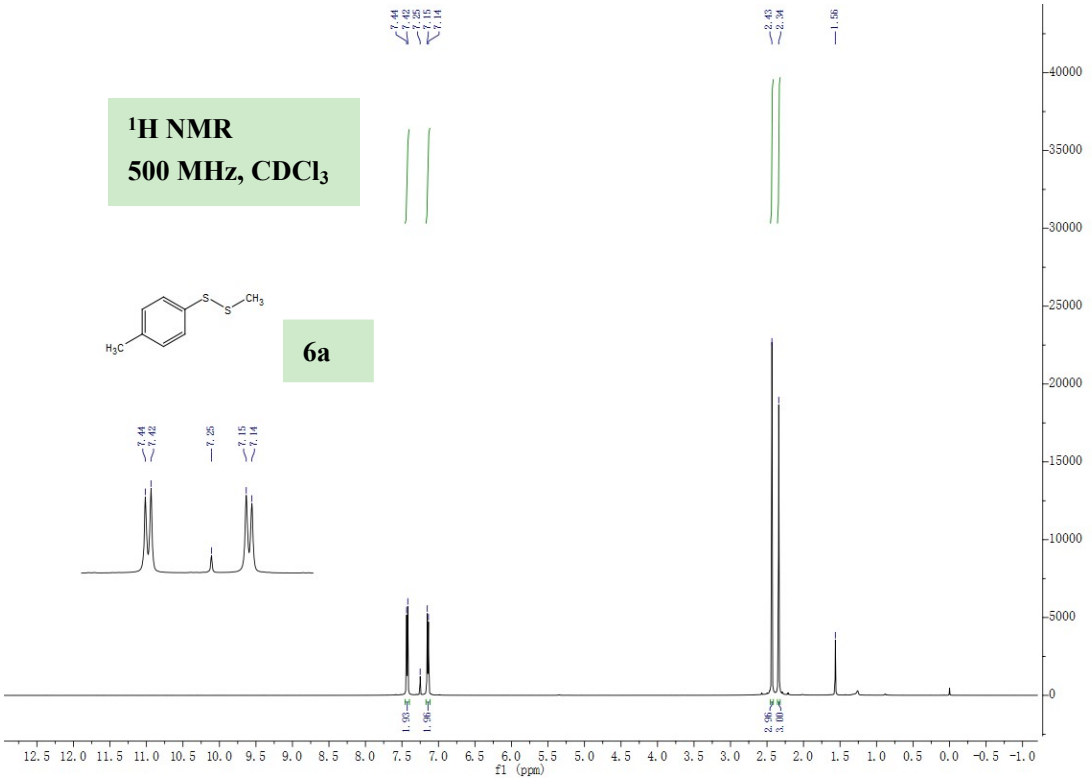
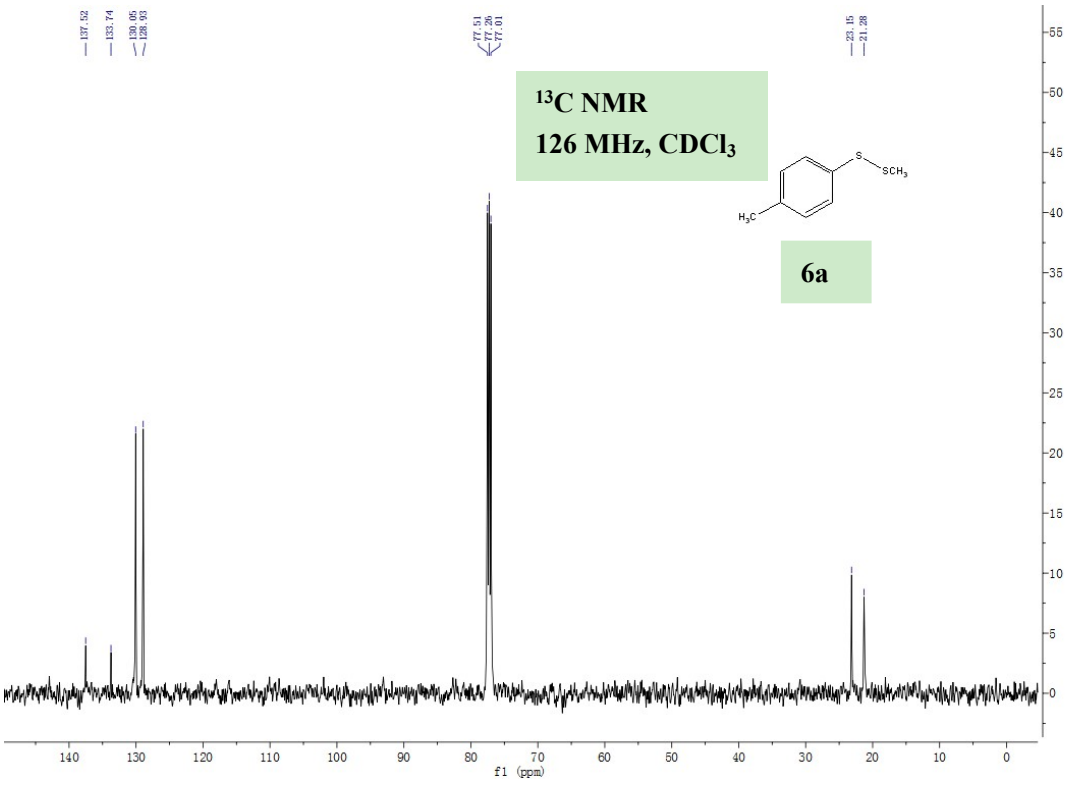
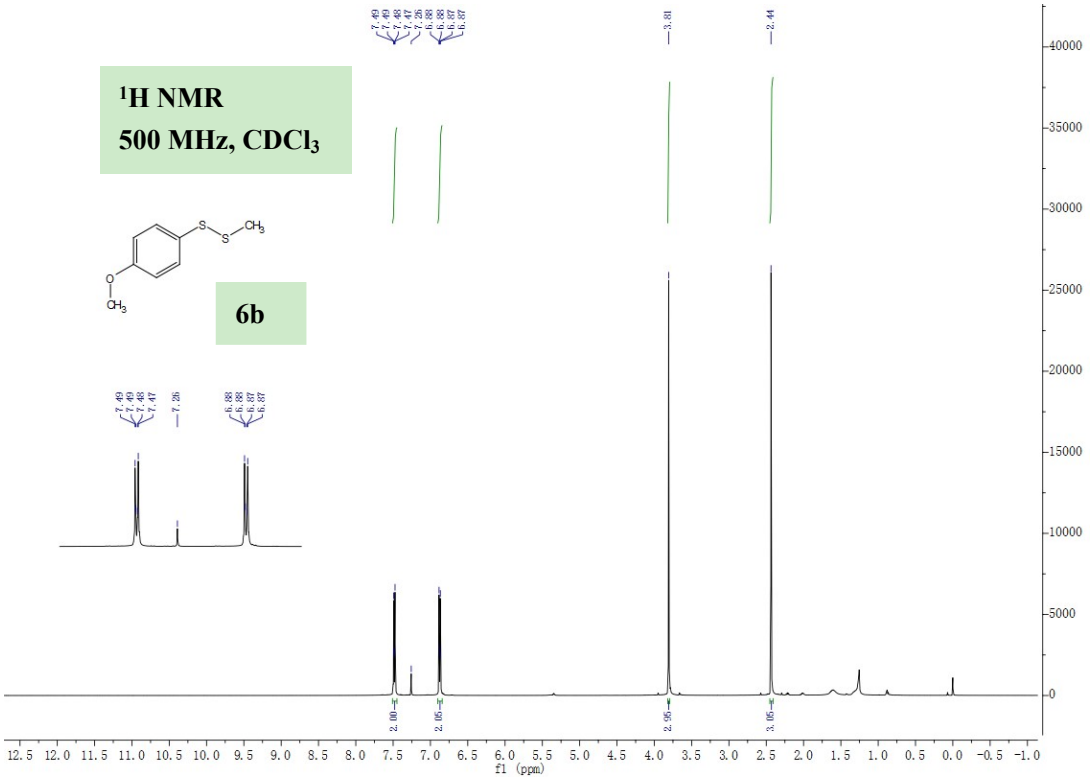
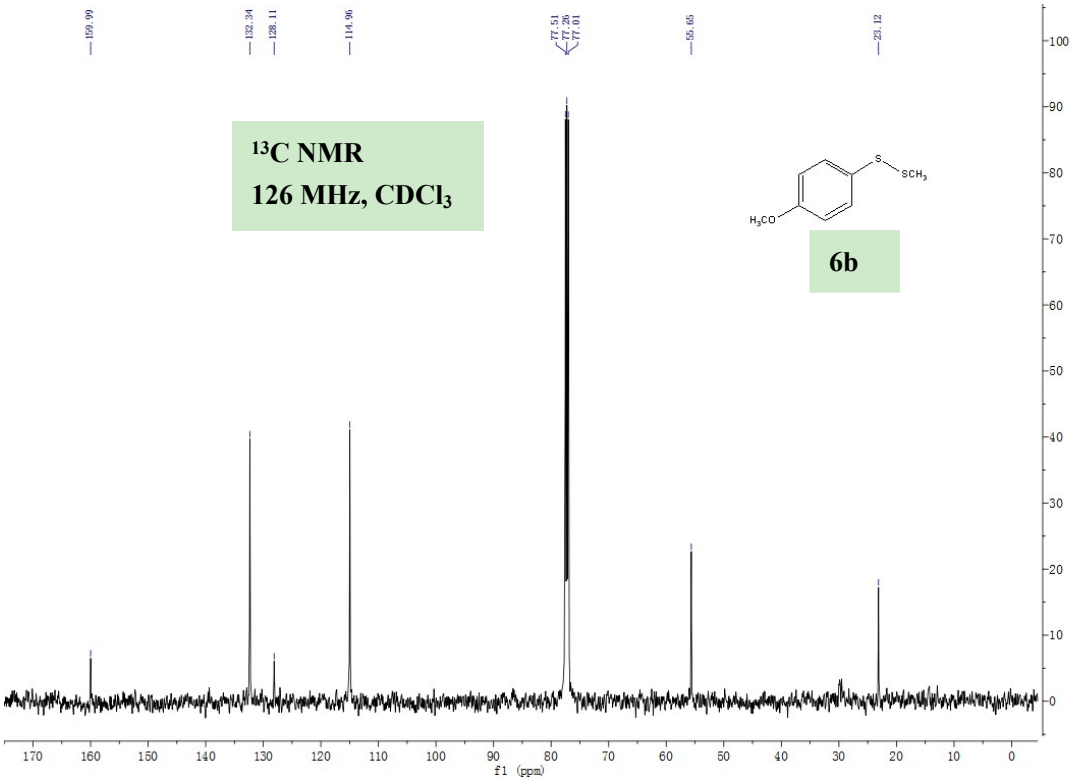
500 MHz, CDCl3
5d
f1 (ppm)

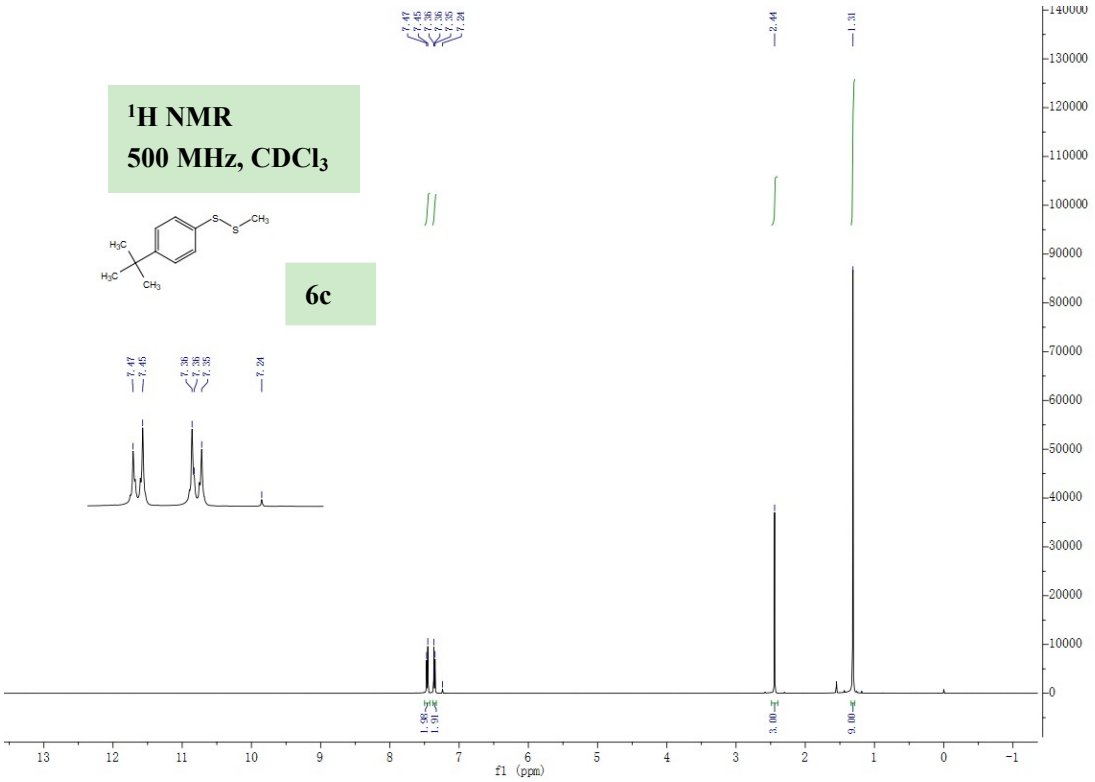

13C NMR
126 MHz, CDCl3
5d
f1 (ppm)


7.44
7.42
7.25
7.15
7.14
2.43
2.34
1.56
1H NMR
500 MHz, CDCl3
6a
1.93
1.96
2.96
3.00
f1 (ppm)


137.52
133.74
130.05
128.93
77.51
77.26
77.01
23.15
21.28
13C NMR
126 MHz, CDCl3
6a
f1 (ppm)


1H NMR
500 MHz, CDCl3
6b
f1 (ppm)


13C NMR
126 MHz, CDCl3
6b
f1 (ppm)


1H NMR
500 MHz, CDCl3
6c
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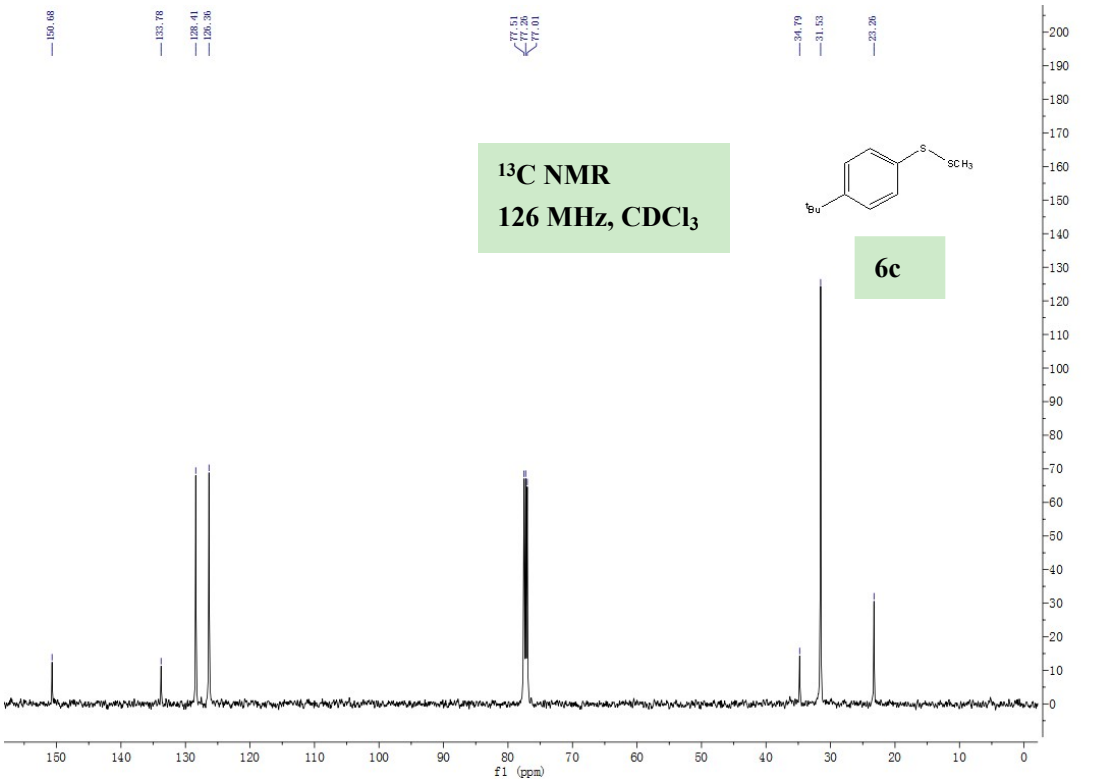
7.45
7.36
7.35
7.24
2.44
1.31
1.98
1.91
3.00
9.00
f1 (ppm)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126 MHz, CDCl3
6c
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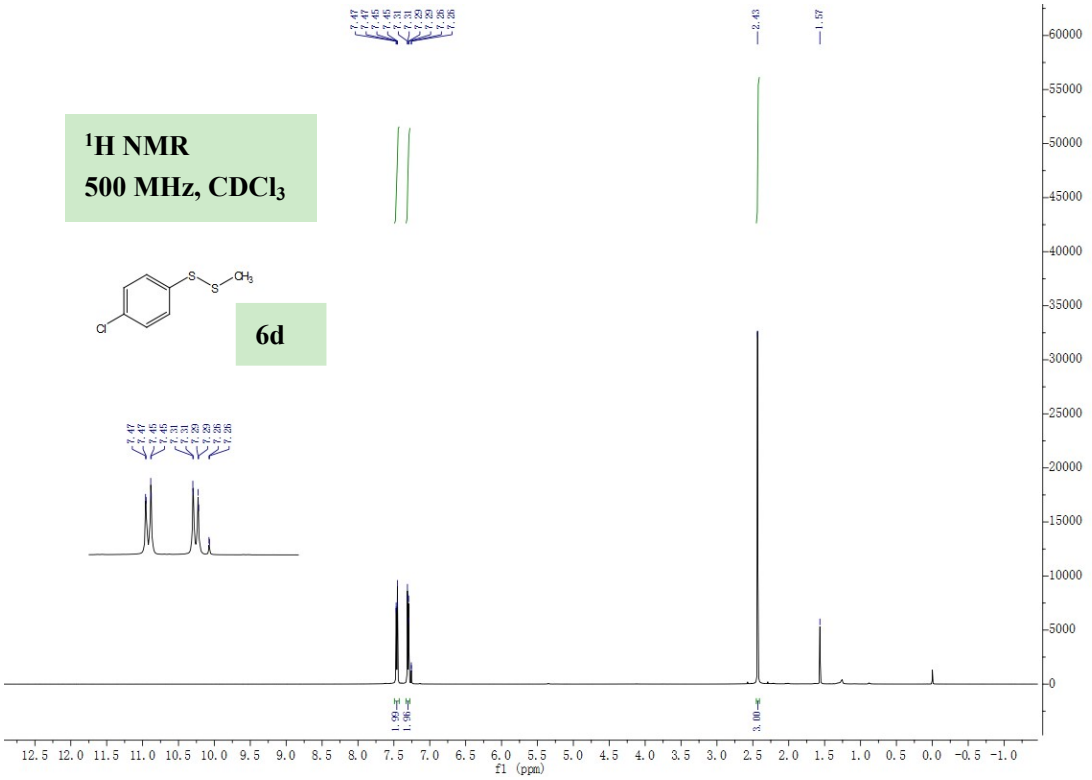
128.41
126.36
77.51
77.26
77.01
34.79
31.53
23.26
f1 (ppm)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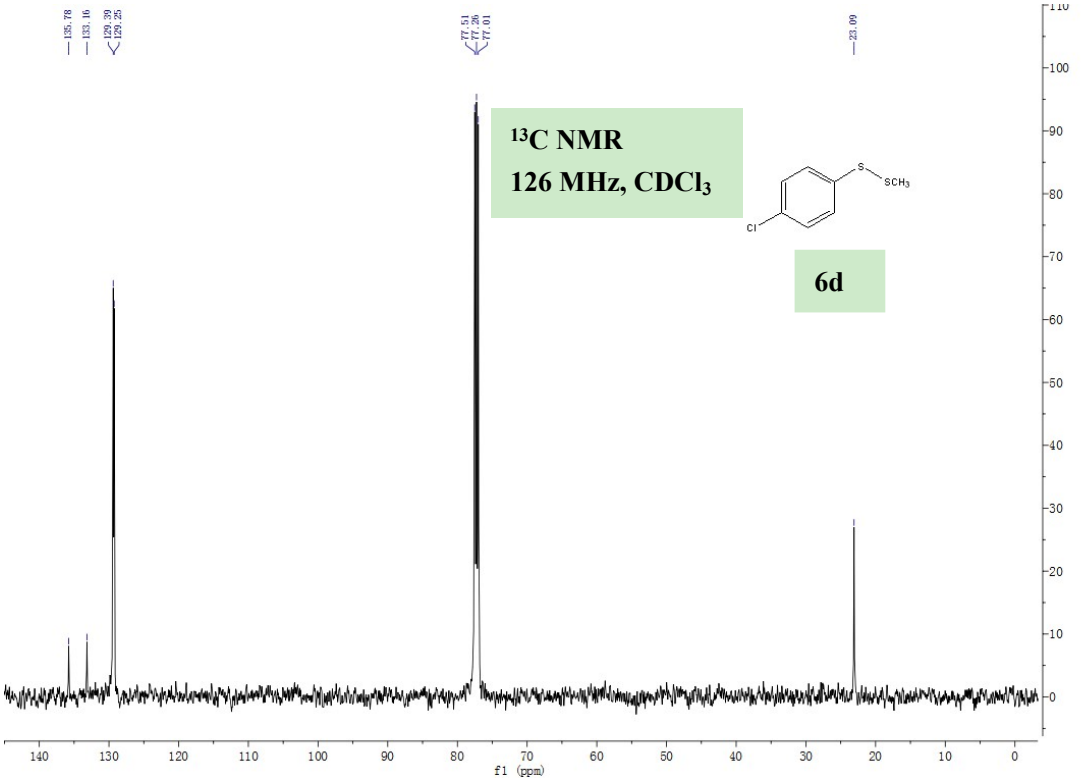
500 MHz, $CDCl_3$
6d
f1 (ppm)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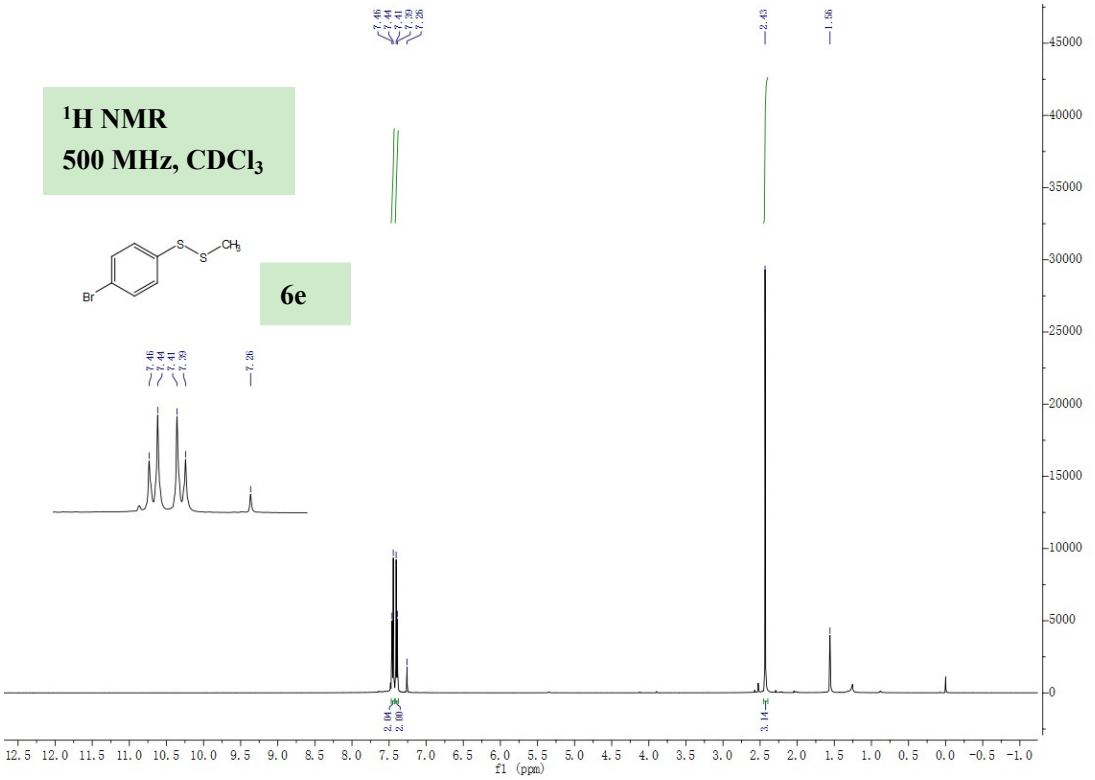
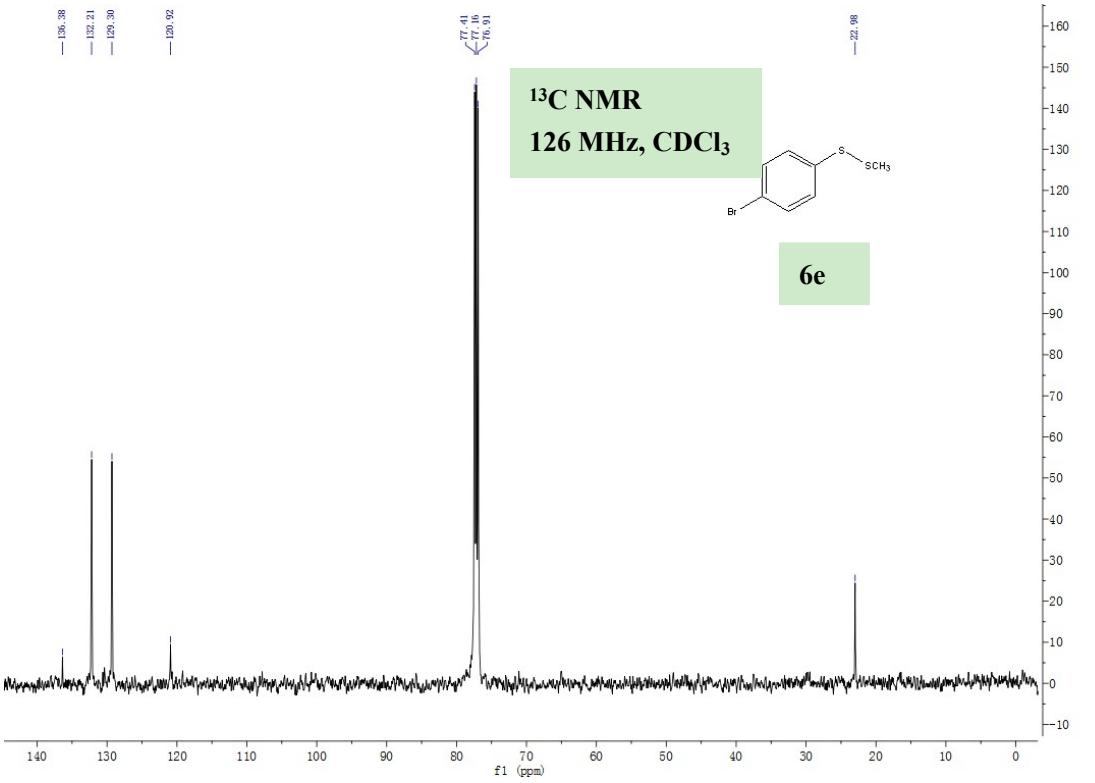
126 MHz, $CDCl_3$
6d
f1 (ppm)



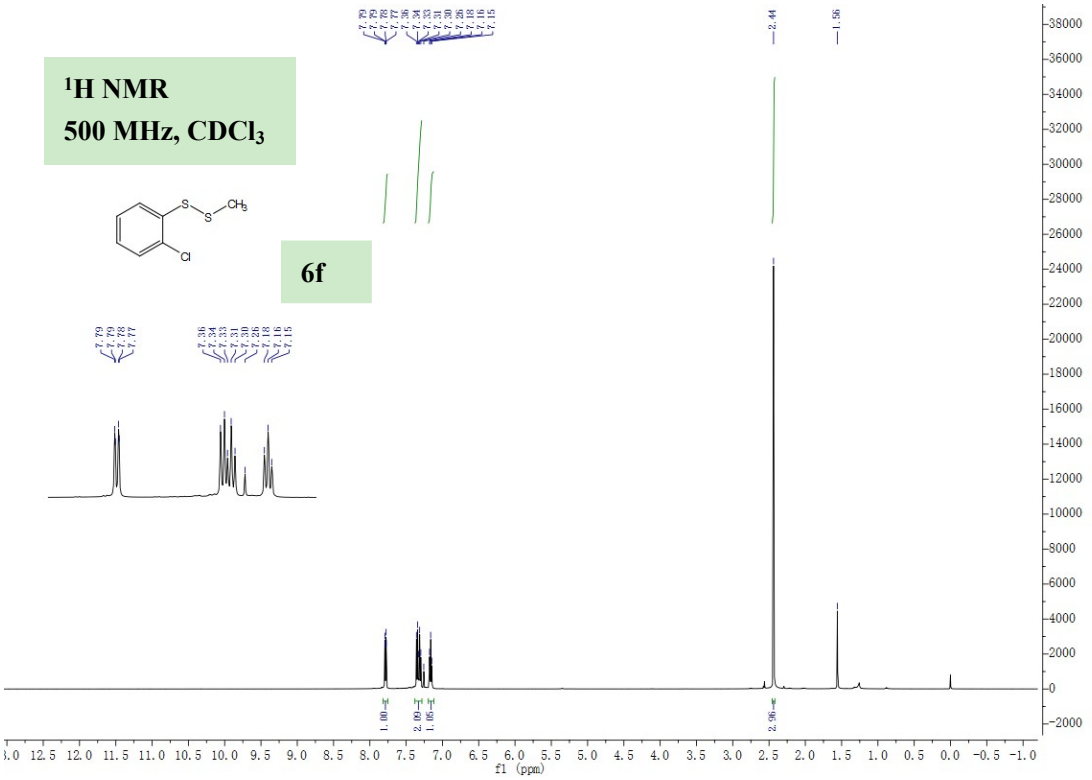
^{1}H NMR
500 MHz, $CDCl_3$

6e



^{13}C NMR
126 MHz, $CDCl_3$

6e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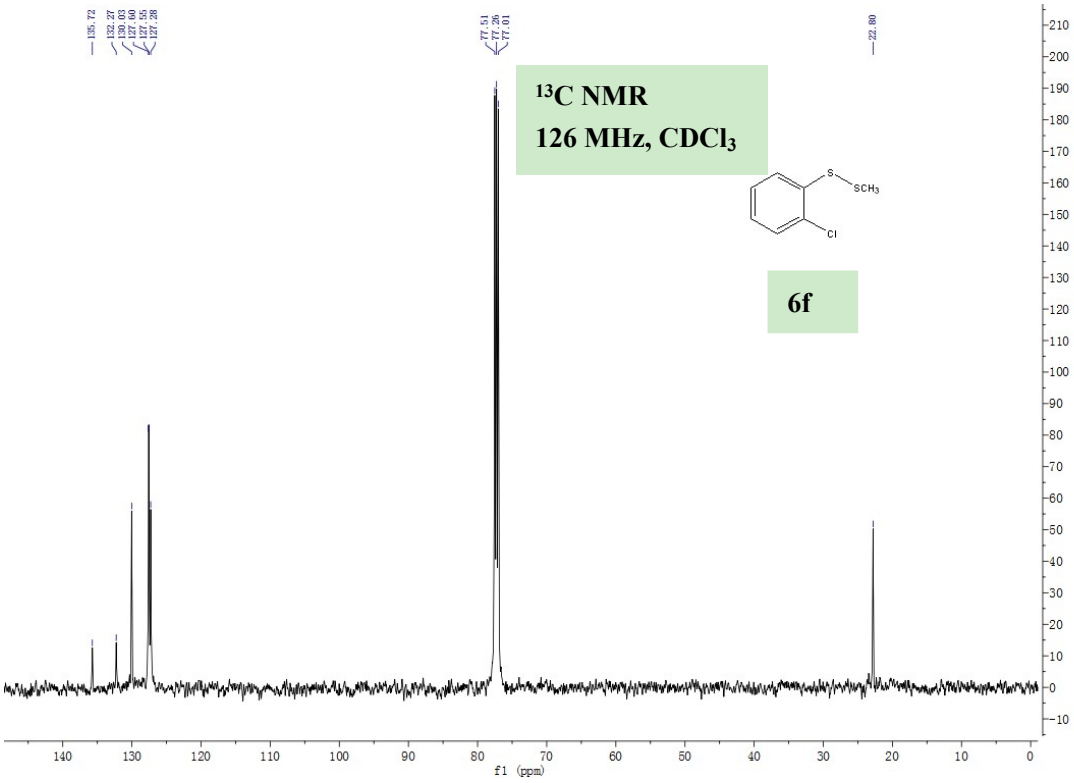
500 MHz, CDCl3
6f
f1 (ppm)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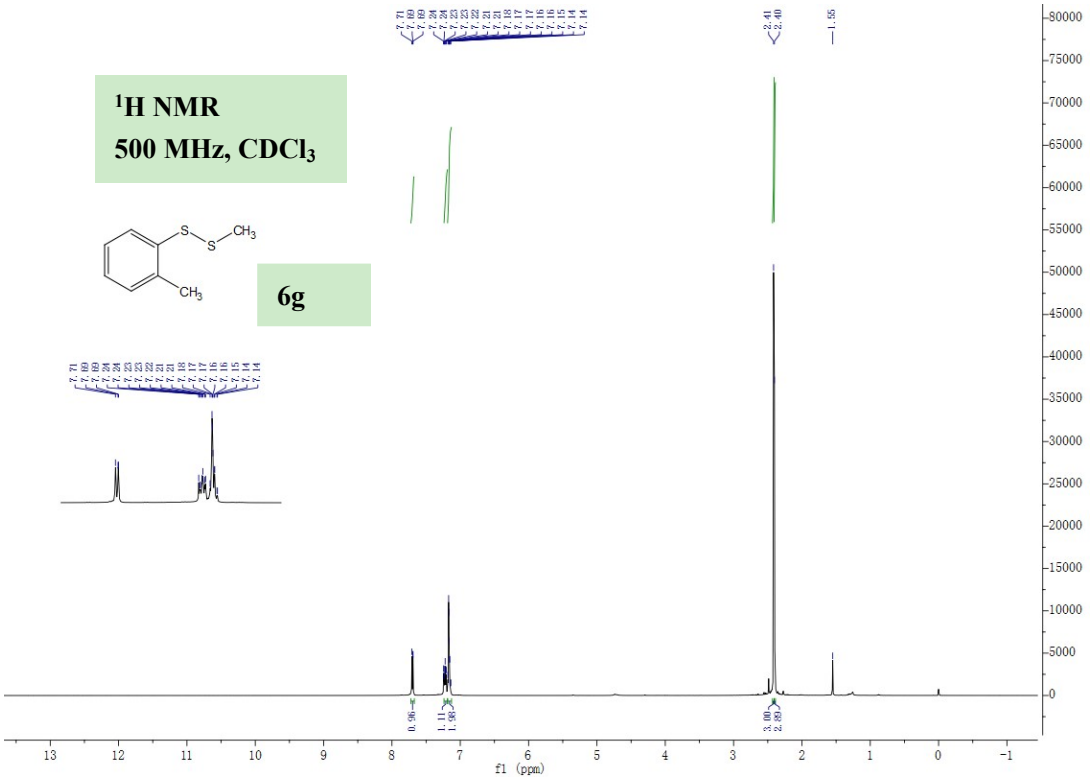
126 MHz, CDCl3
6f
f1 (ppm)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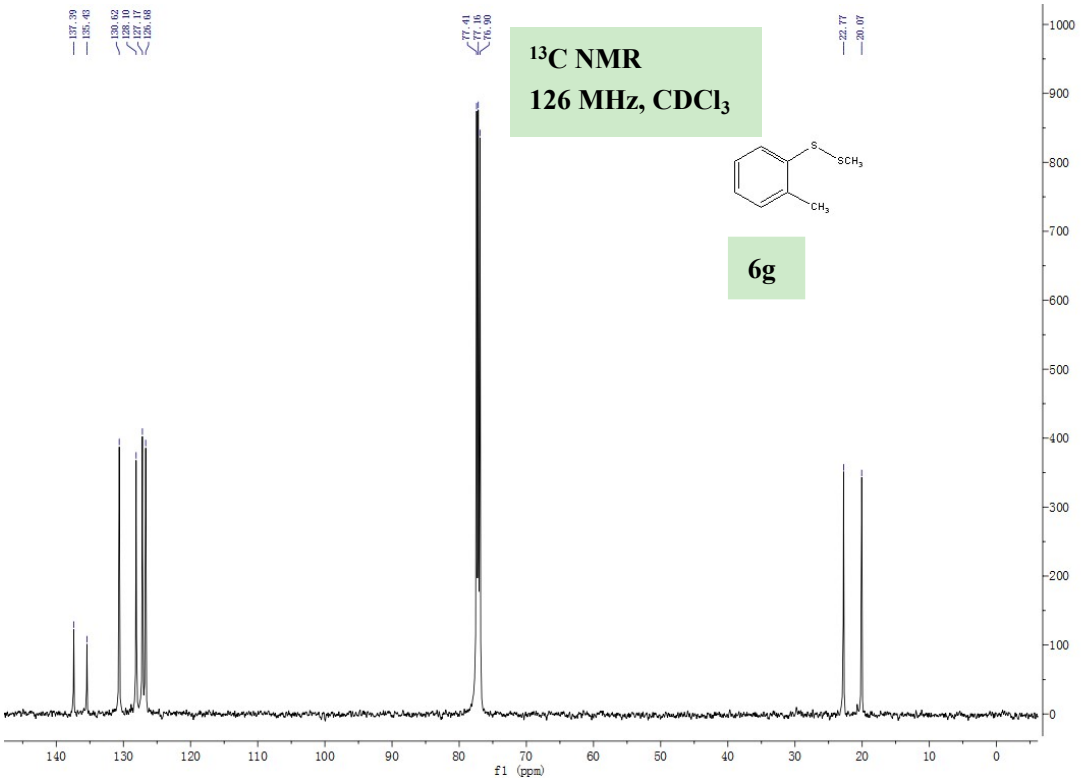
500 MHz, $CDCl_3$
6g
f1 (ppm)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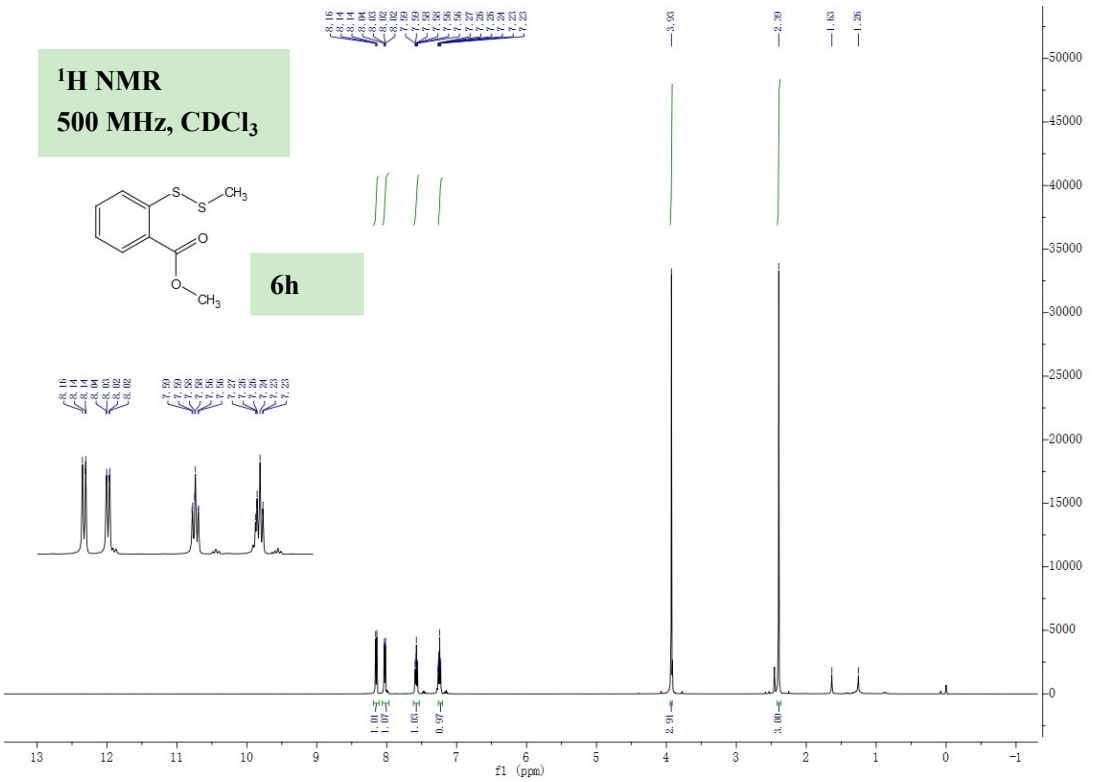
126 MHz, $CDCl_3$
6g
f1 (ppm)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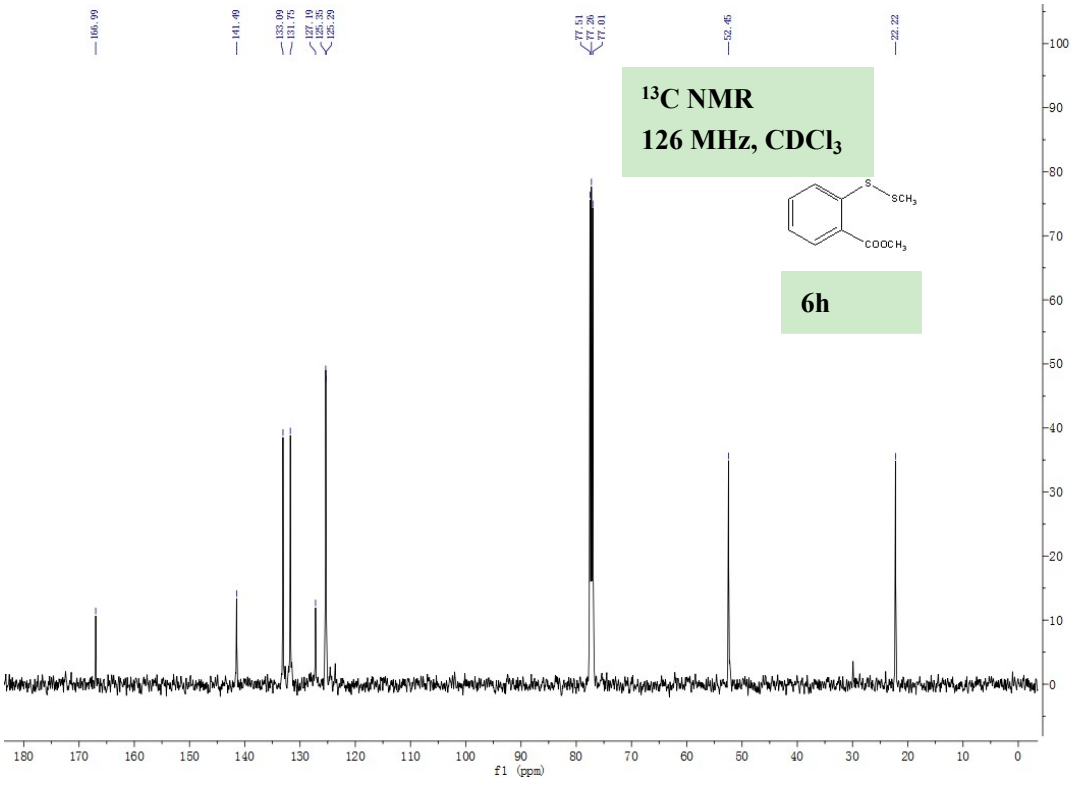
500 MHz, CDCl3
6h
f1 (ppm)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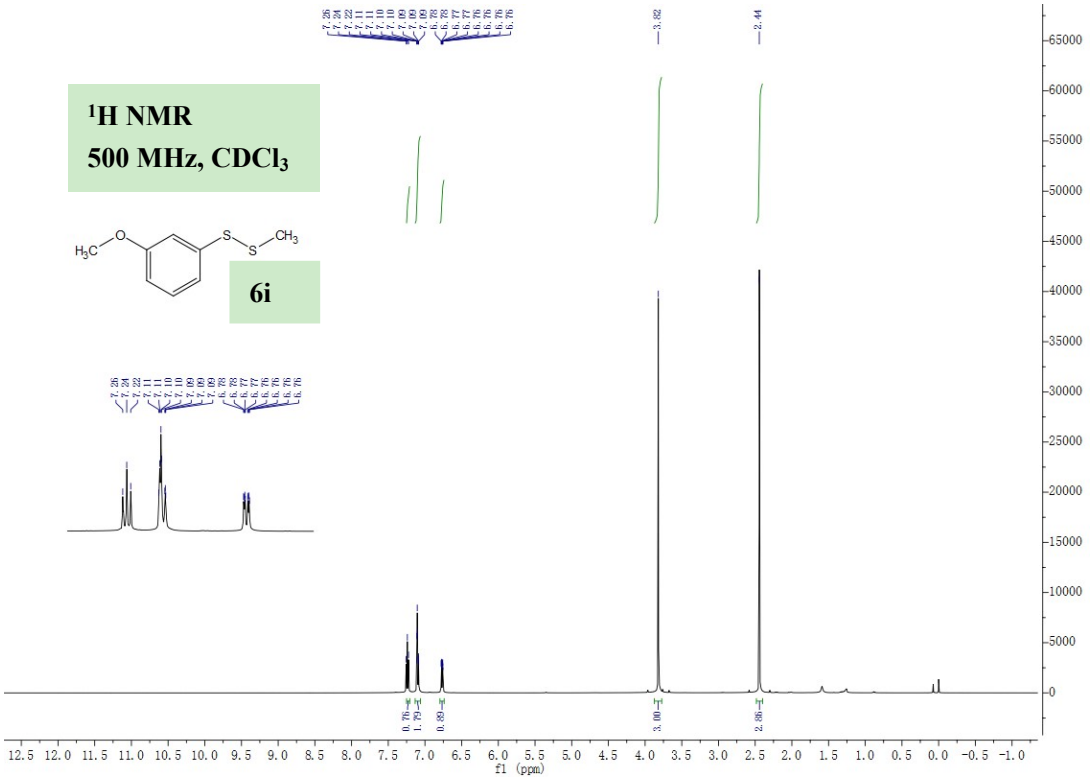
126 MHz, CDCl3
6h
f1 (ppm)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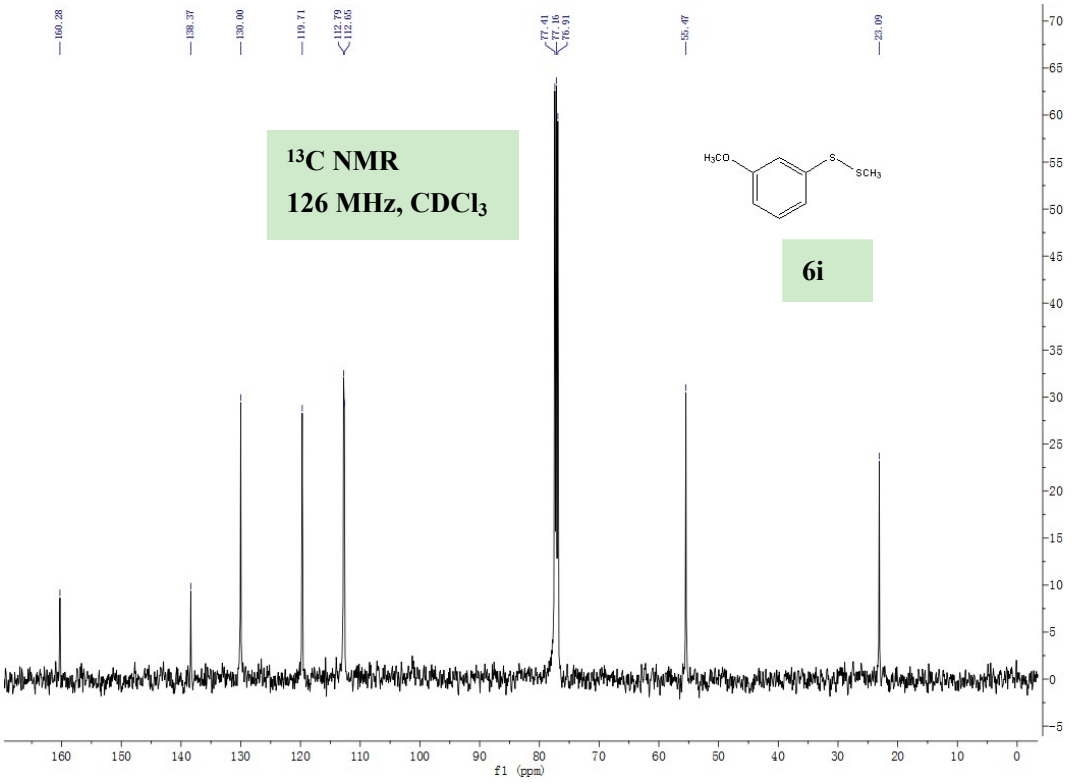
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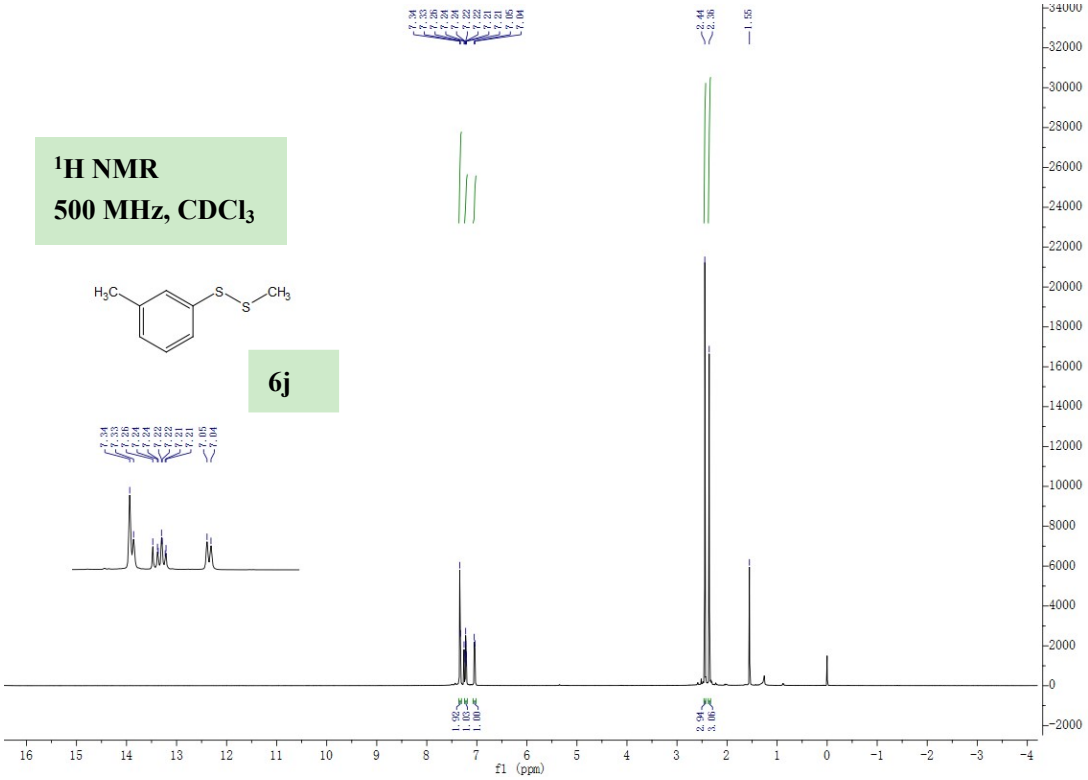
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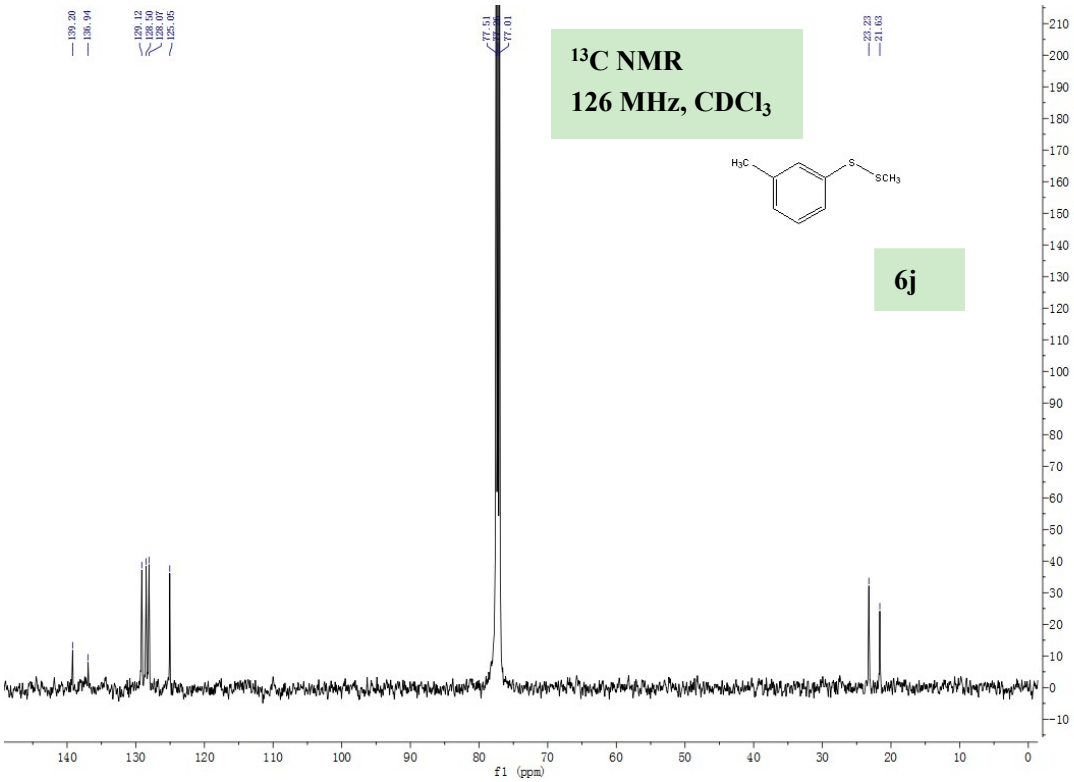
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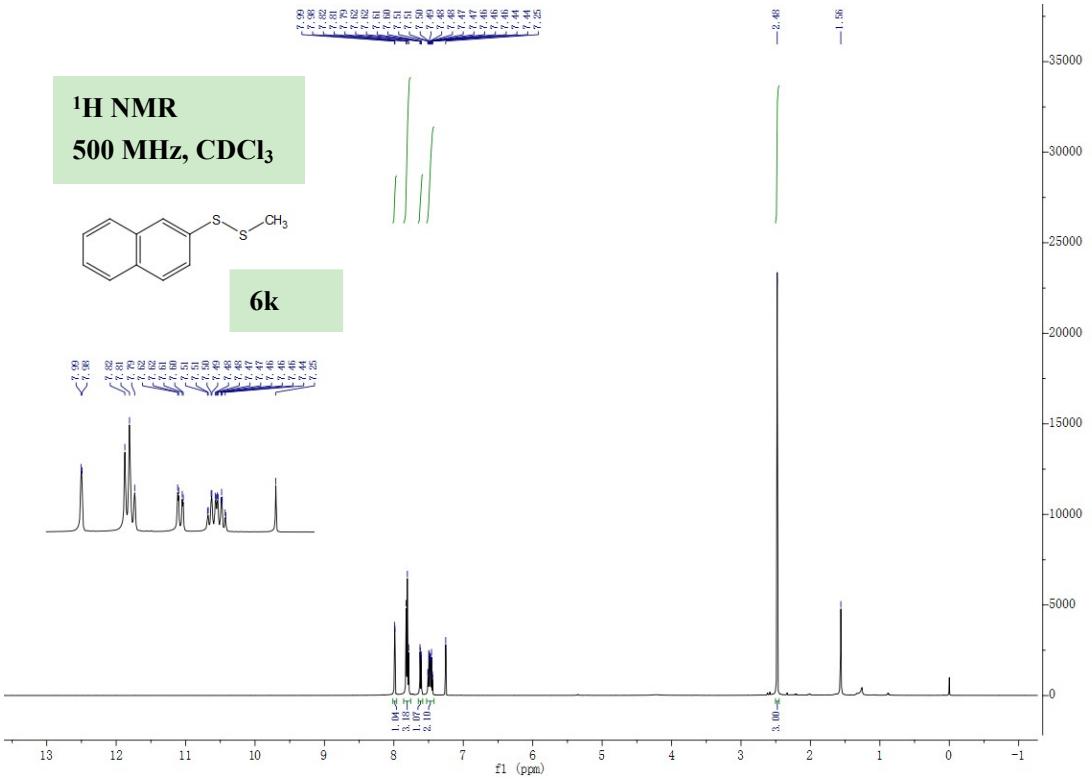
f1 (ppm)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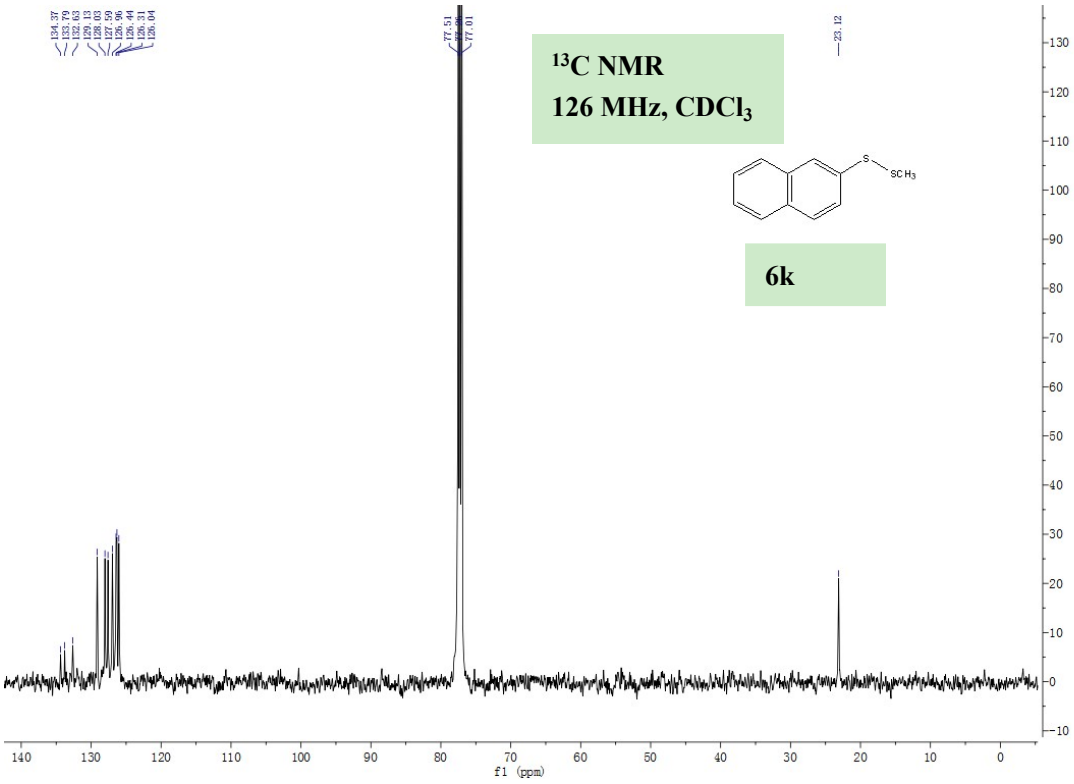
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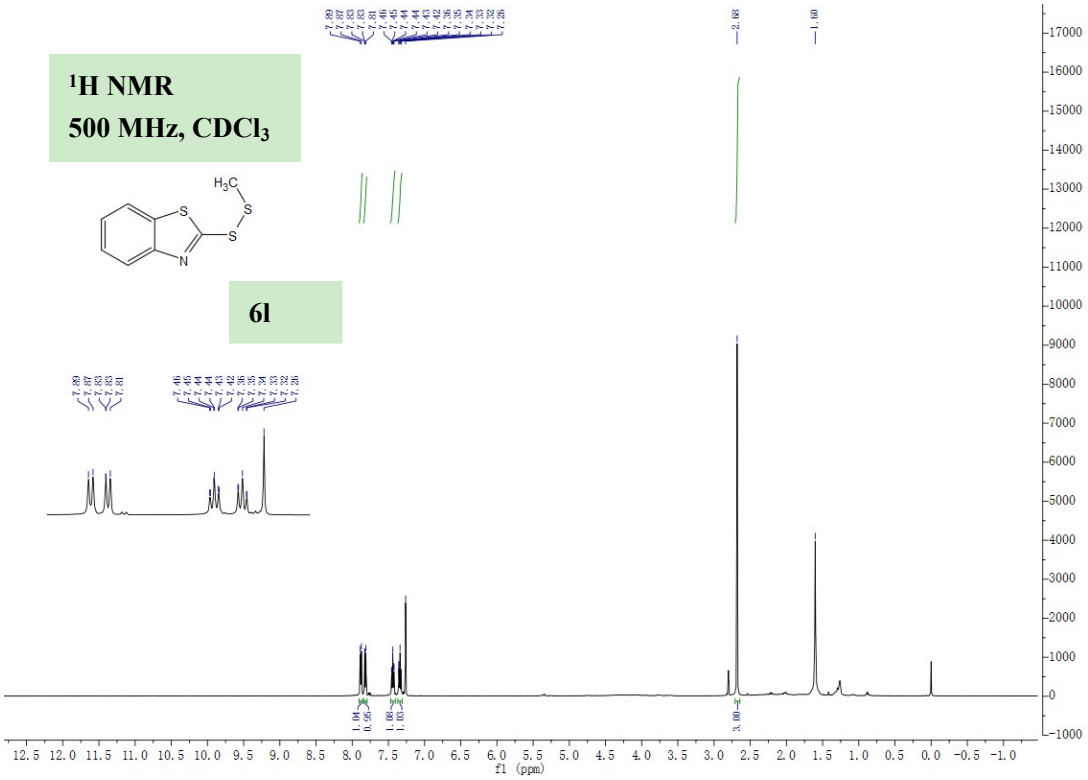
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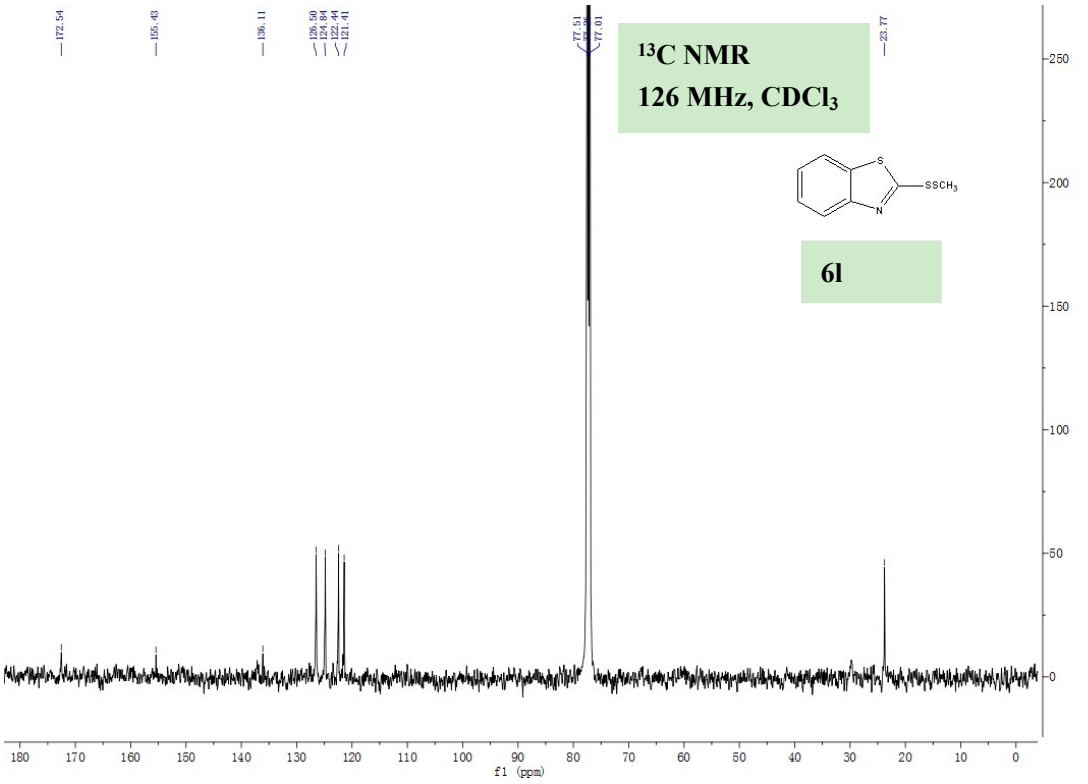
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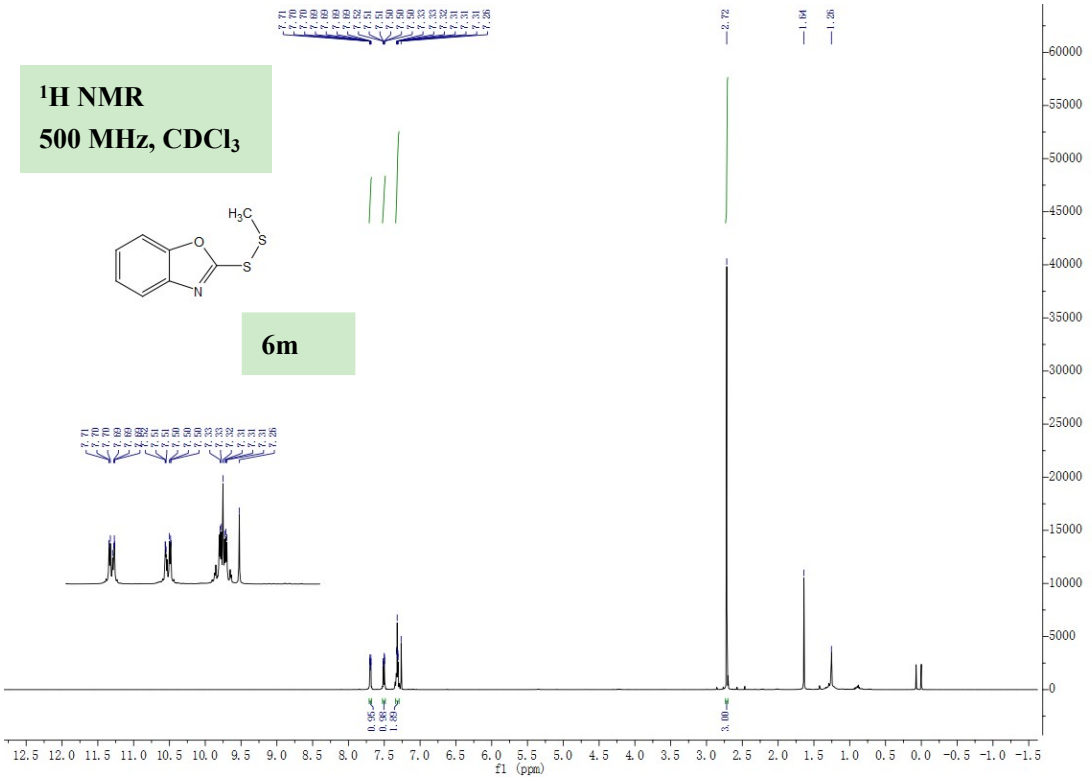
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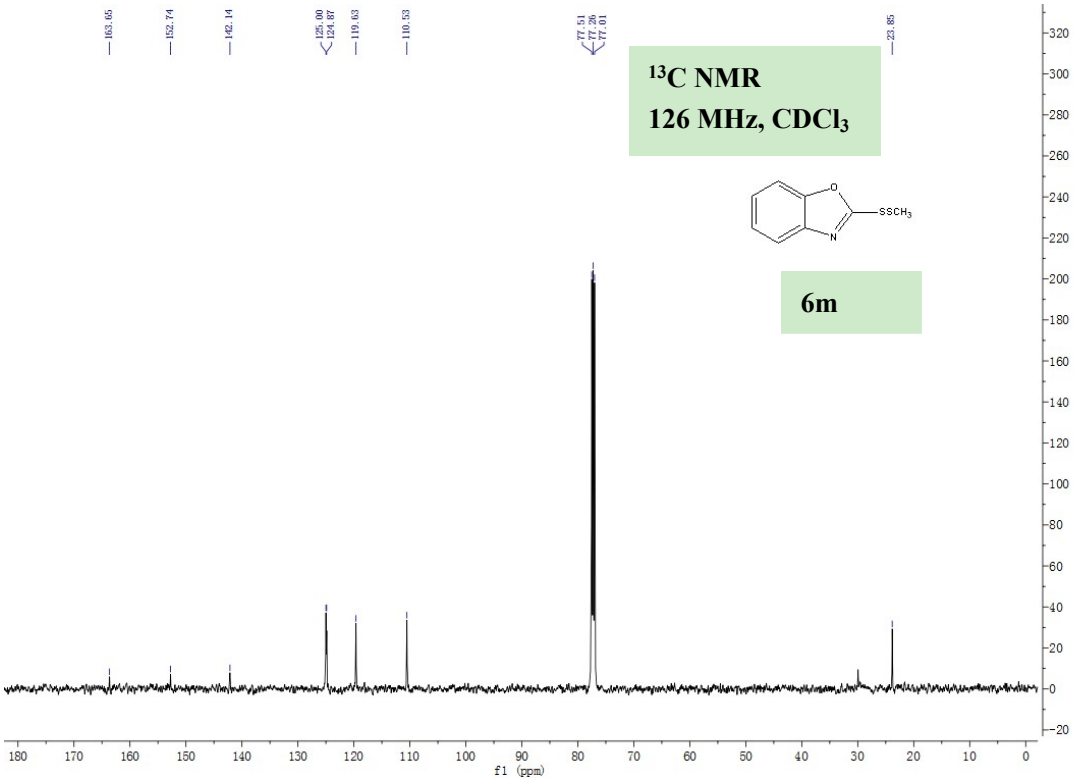
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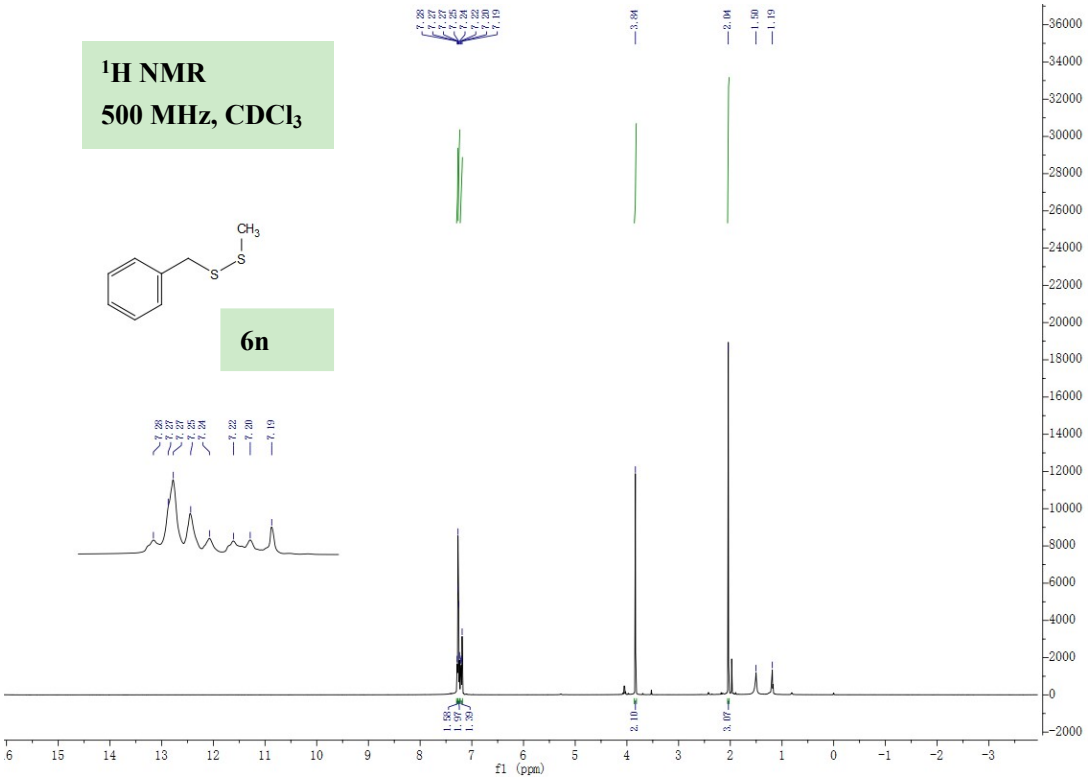
f1 (ppm)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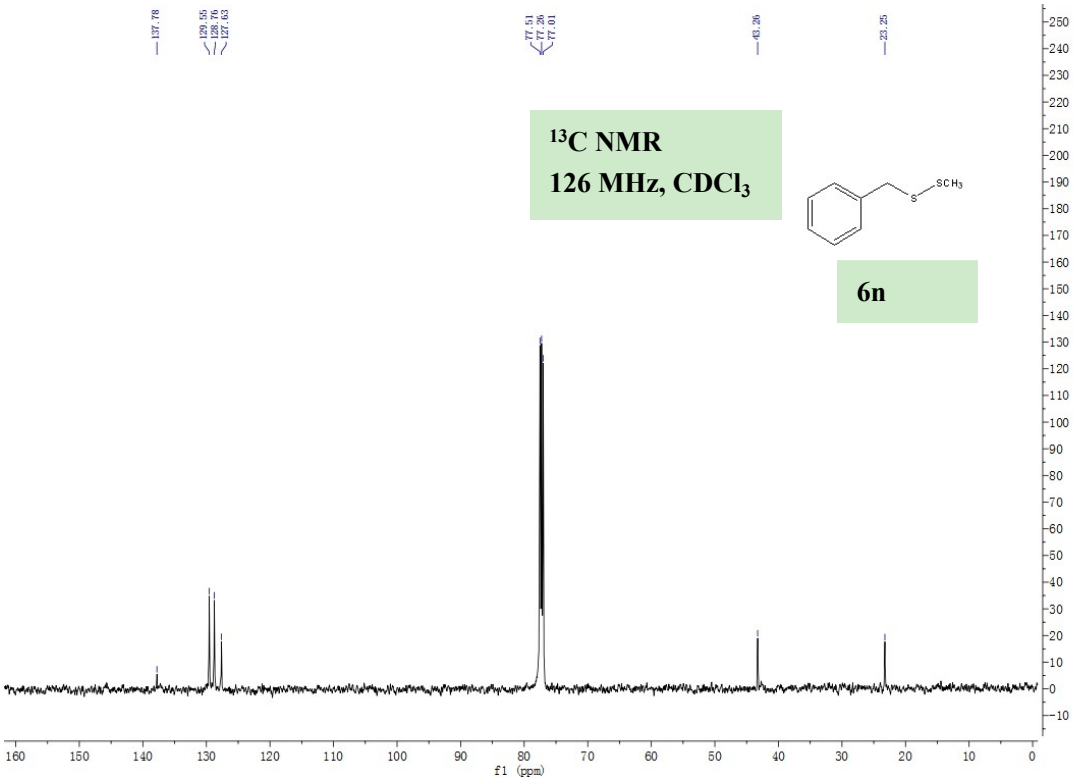
6n
f1 (ppm)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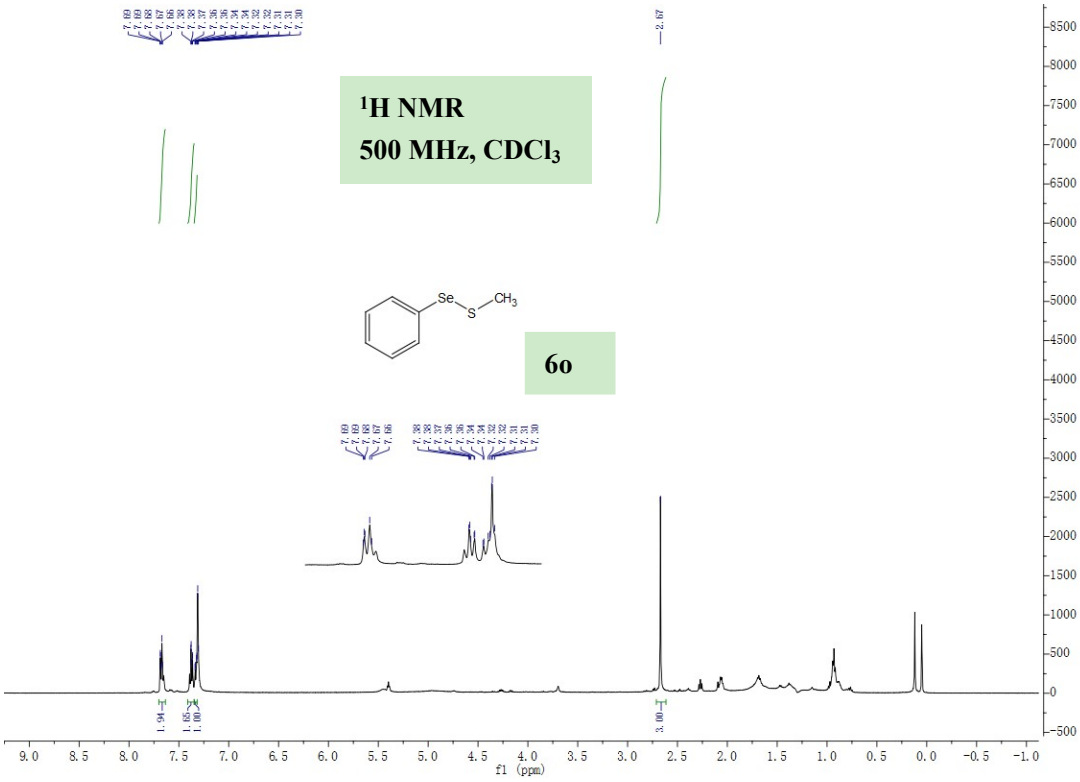
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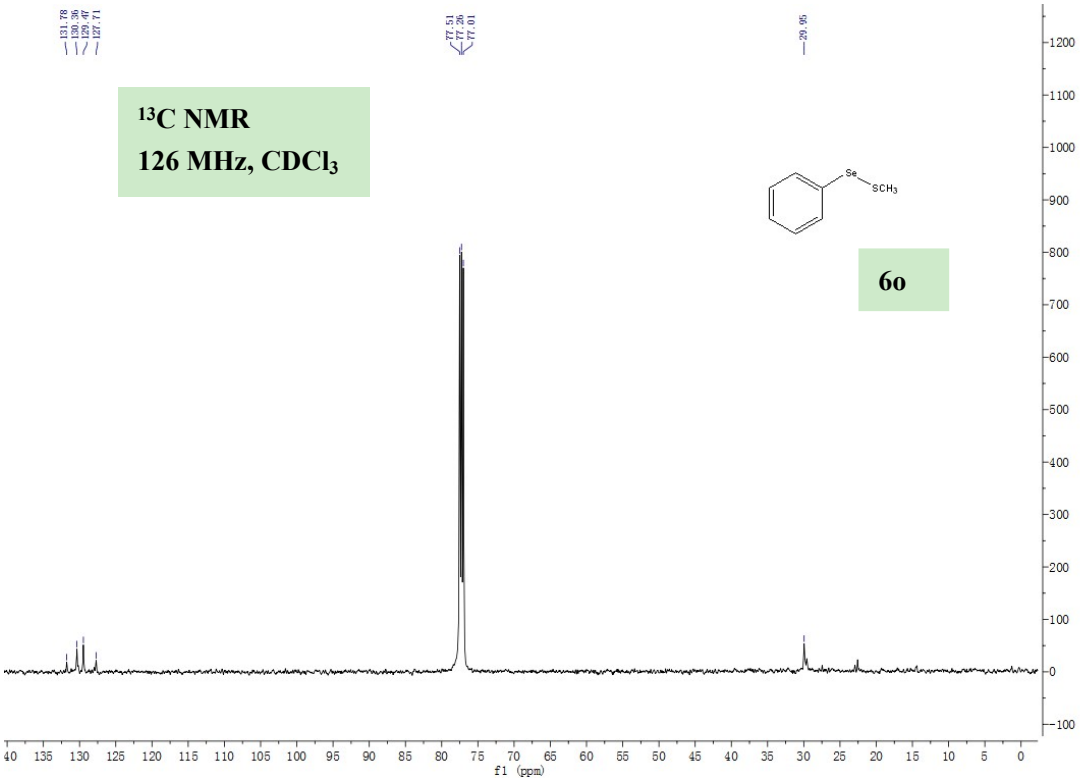
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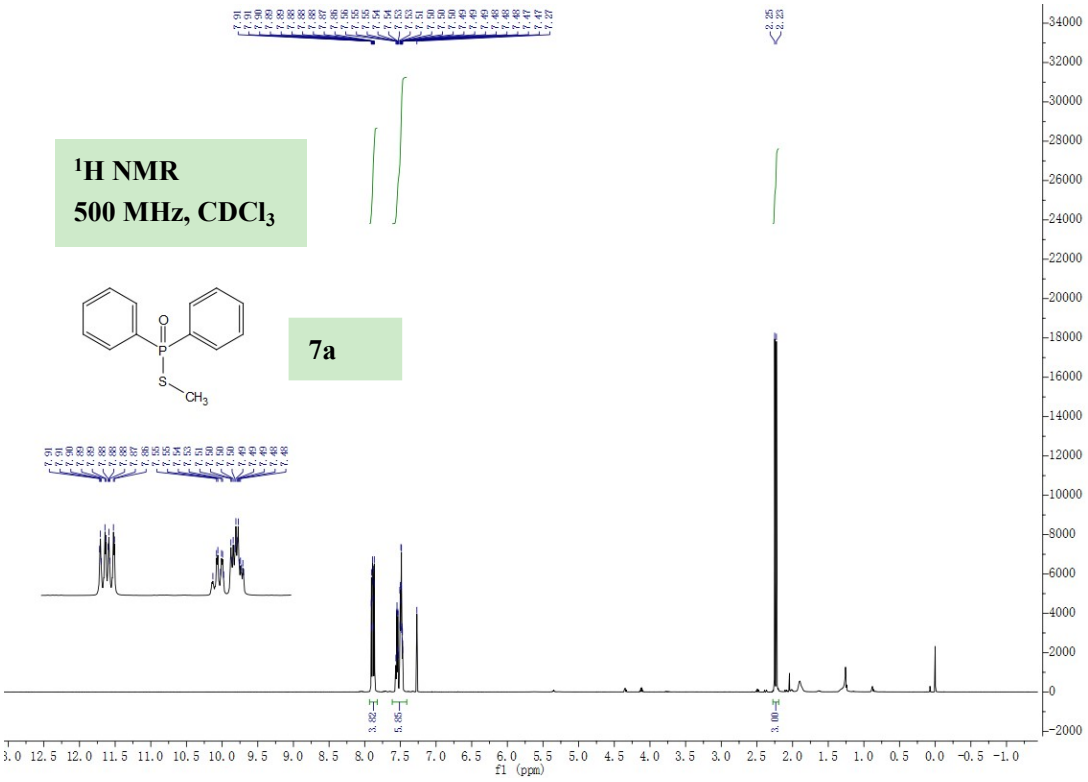
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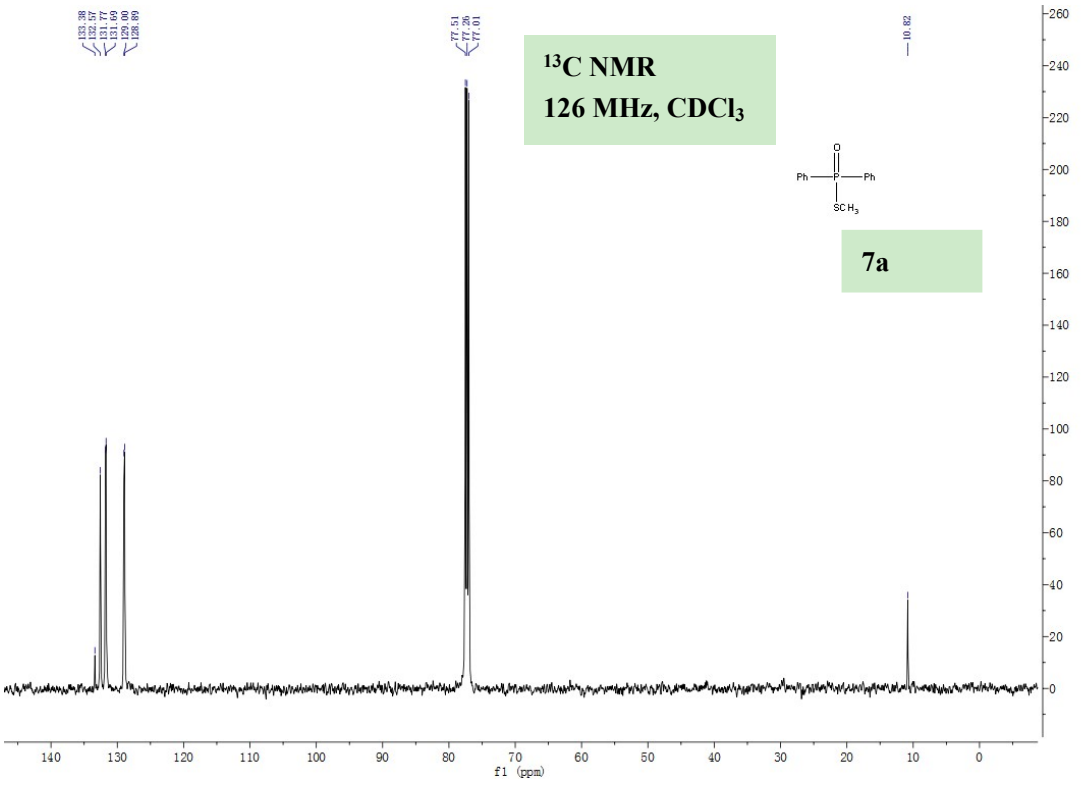
7a
f1 (ppm)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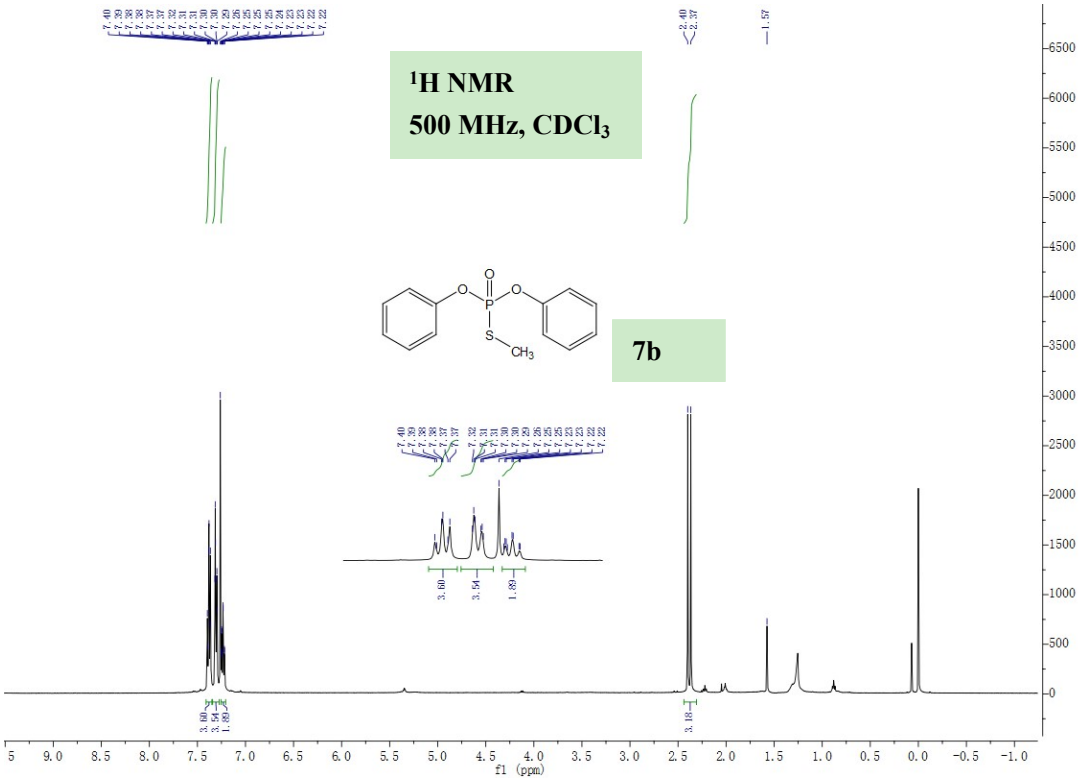
7a
f1 (ppm)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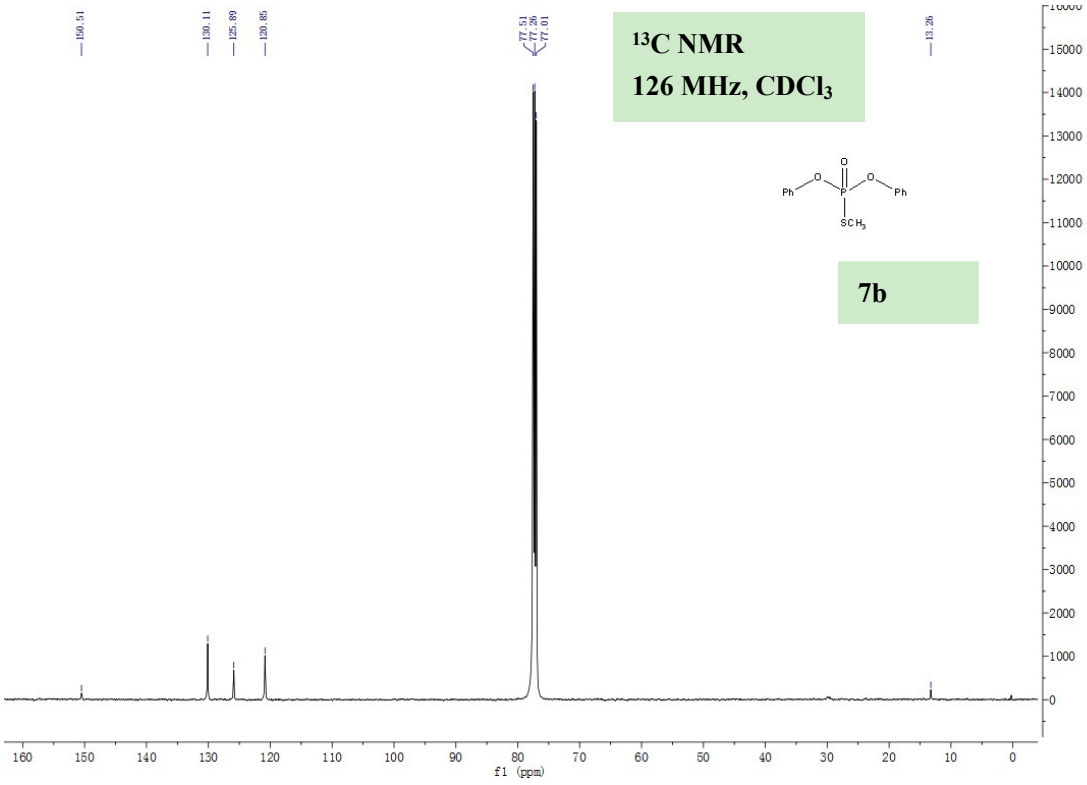
7b
f1 (ppm)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7b
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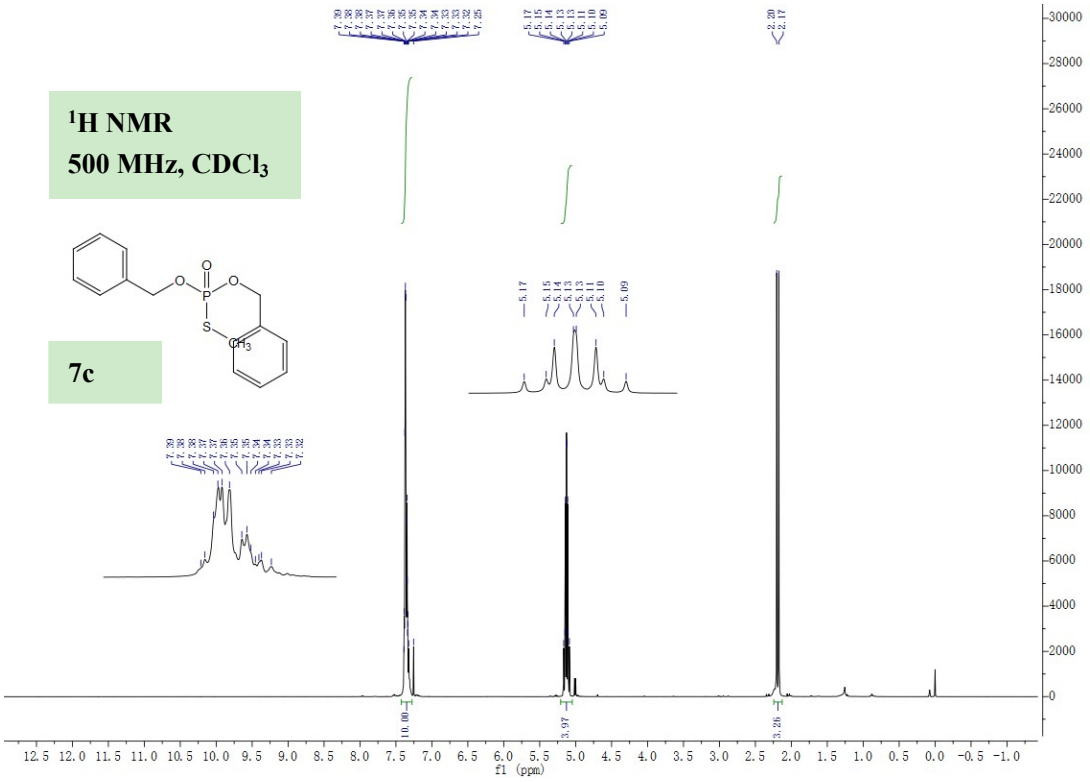
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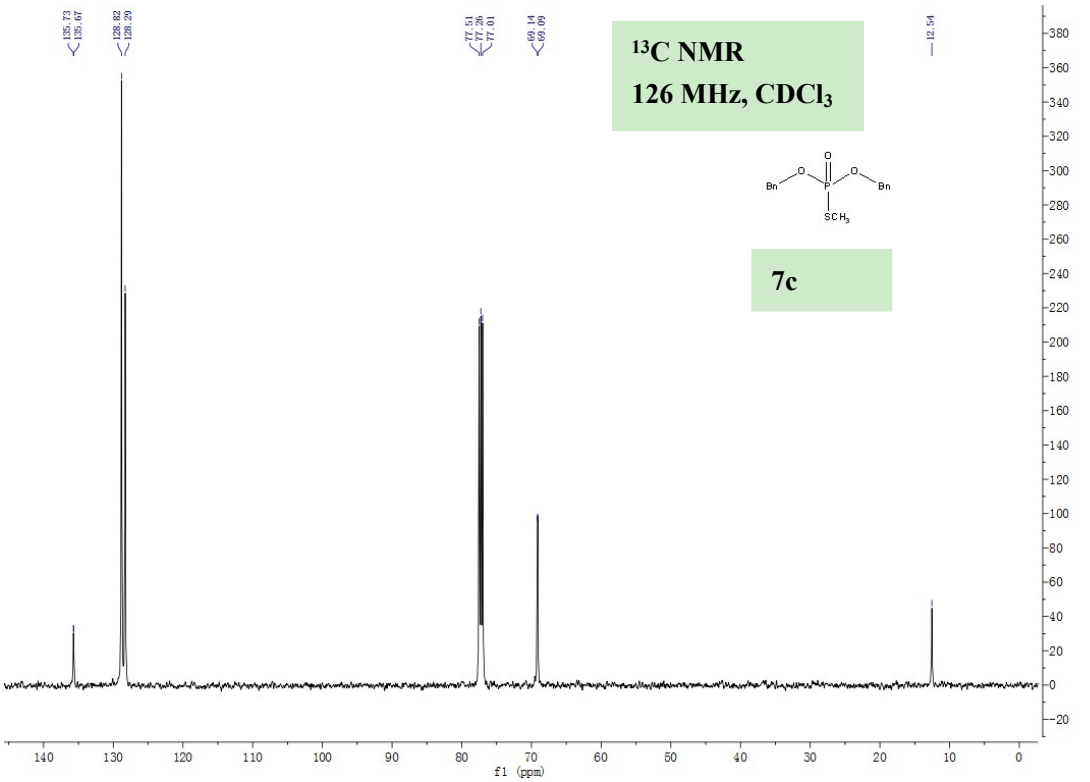
500 MHz, $CDCl_3$
7c
f1 (ppm)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7c
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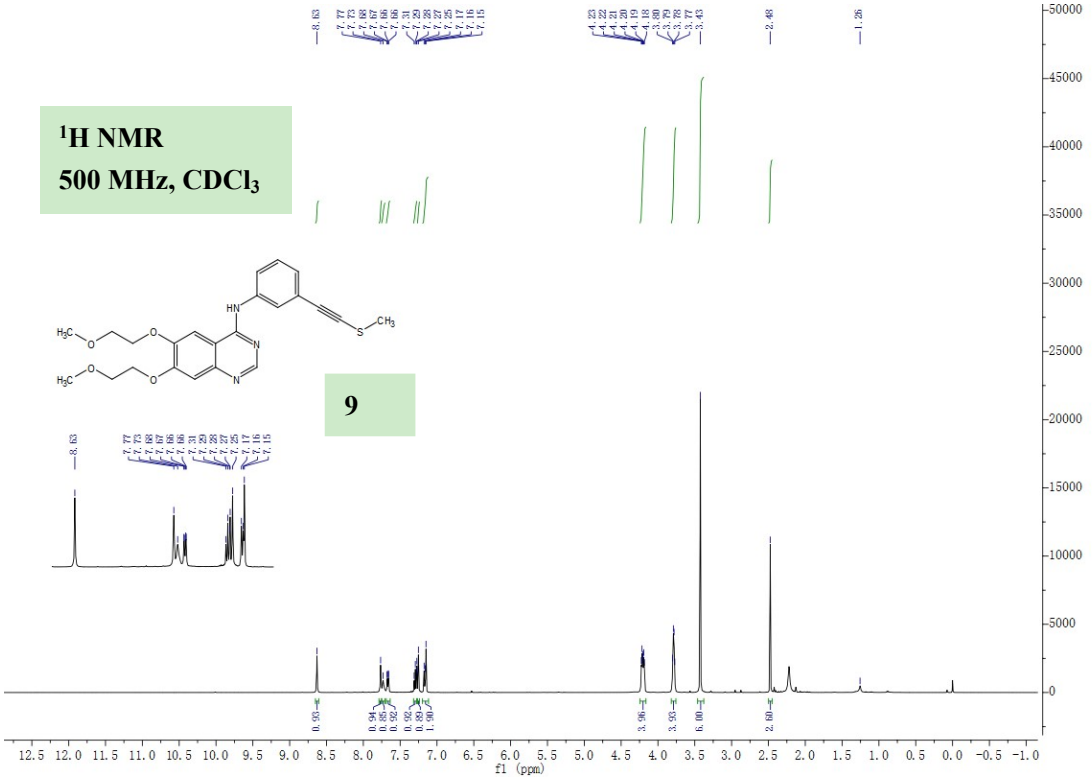
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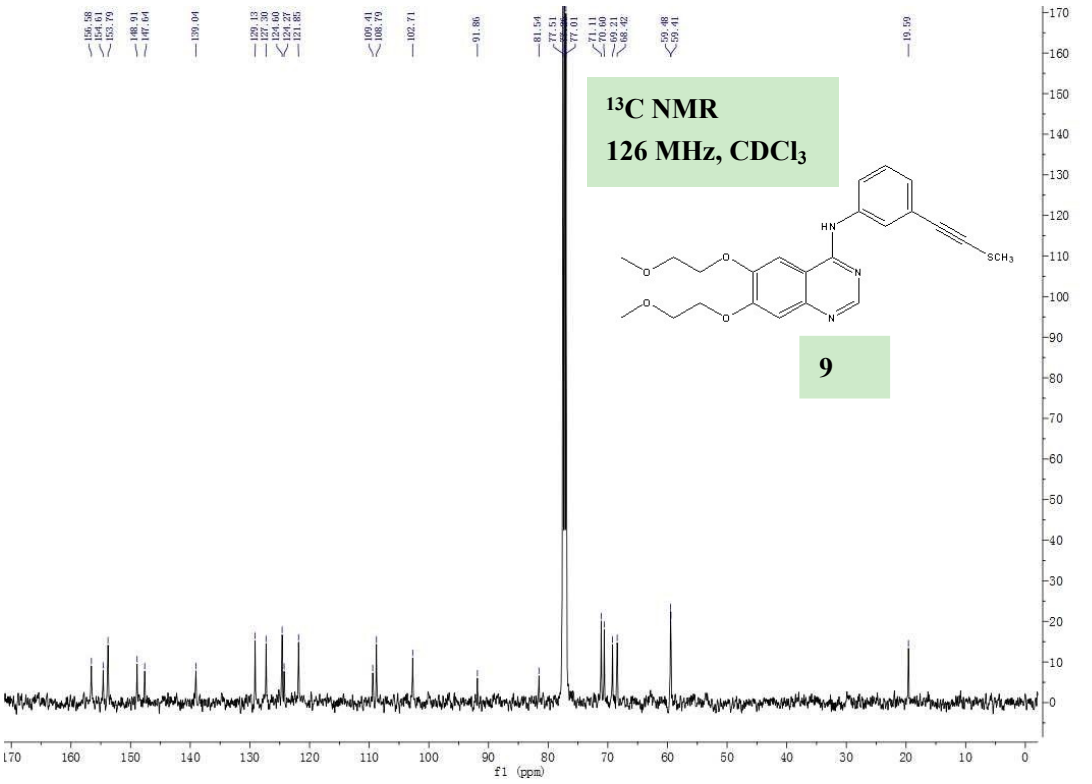
9
f1 (ppm)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126 MHz, CDCl3
9
f1 (ppm)