Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A Thiol-Free Synthesis of Alkynyl Chalcogenides by Copper-Catalyzed C-X (X=S, Se) Cross-Coupling of Alkynyl Carboxylic Acids with Bunte Salts

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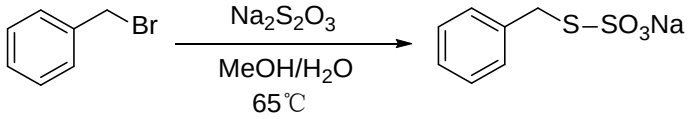
1 Experimental

1.1 General Information

All reactions were run using flame-dried glassware and magnetic stirring. Chemicals and solvents were purchased from commercial suppliers and used as received. ^{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, acetone δ 2.09, DMSO δ 2.50), carbon (chloroform δ 77.0, acetone δ 205.87, 30.60, DMSO δ 40.45). GC-MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). For thin-layer chromatography (TLC), Sorbent silica gel XHL TLC plates (130815) were used, and compounds were visualized with a UV light at 254 nm. High resolution mass spectral data were acquired on Waters Micromass GCT Premier Spectrometer. Bunte salts can't be accurately weighed because it contain sodium thiosulfate pentahydrate and NaX (X=Cl, I).

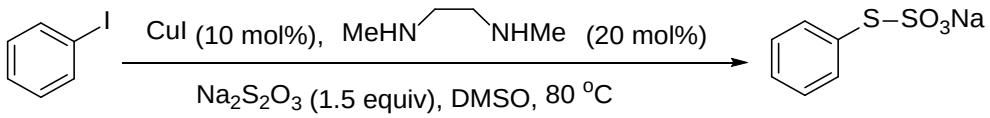
1.2 Experimental Procedure

General procedures for the Synthesis of S-alkyl Bunte salts[1]



A flask was charged with benzyl bromide (1.2 mL, 10 mmol, 1.0 equiv), sodium thiosulfate pentahydrate (2.976 g, 12 mmol, 1.2 equiv), water (10.0 mL) and MeOH (30 mL). The reaction mixture was stirred and heated to 65 ^{o}C. After 10h at 65 ^{o}C, the reaction mixture was cooled to rt, and then concentrated on a rotovap at a bath temperature of 40-45 ^{o}C to remove the MeOH and water. The resultant solid was treated with MeOH (100mL), heated to 50 ^{o}C (most solid dissolves), and filtered through a frit funnel. This removes excess sodium thiosulfate and sodium bromide. The filtrate was concentrated to a white solid. Trituration of this solid with hexanes, filtration, and drying under vacuum at 50 ^{o}C gave crude product (67%, 1.5 g) as a white solid.

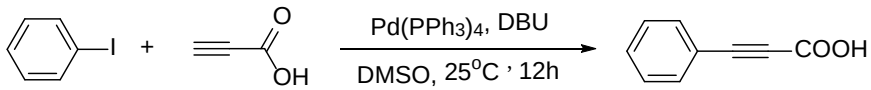
General procedures for the Synthesis of S-aryl Bunte salts[1]



A 100 mL flask equipped with a football shaped magnetic stirbar was charged with iodobenzene (2.04 g, 10 mmol, 1.0 equiv), anhydrous sodium thiosulfate (2.37 g, 15 mmol, 1.5 equiv) and CuI (190 mg, 1mmol, 0.10 equiv). The flask was sealed with a septum, evacuated and filled with nitrogen. DMSO (10 mL) was charged via syringe followed by N,N'- dimethylethylenediamine (DMEDA, 0.22 mL, 2 mmol, 0.20 equiv).

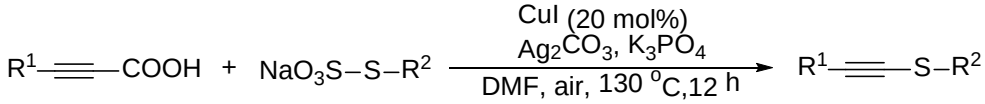
The mixture was stirred for 5 min at rt and then heated at 80 ^{o}C for 24 h, at which time HPLC anaylsis indicated complete consumption of iodobenzene. The reaction mixture was cooled to rt. Saturated aqueous NaCl (10 mL) was added, and the resultant slurry was stirred vigorously at rt for 5h. The mixture was filtered and the solid was washed successively with saturated aqueous NaCl and hexanes. The solid was dried as a solid (60%, 1.27g).

General procedures for the Synthesis of aryl alkynyl carboxylic acids from aryl iodides[2]



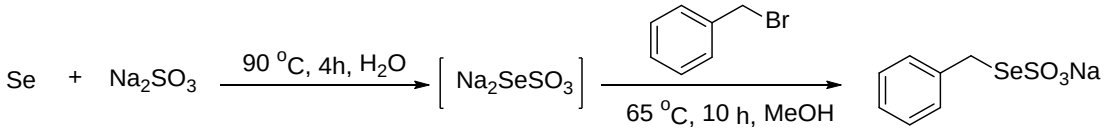
A small round-bottom flask was charged with aryl iodide (10.0 mmol), DBU (3.66 g, 24 mmol, 2.4 equiv.), $Pd(PPh_3)_4$ (288 mg, 0.26 mmol, 2.5 mol%) and DMSO (12 mL). The solution of propiolic acid (840 mg, 12.0 mmol, 1.2 equiv.) in DMSO (12 mL) was poured to the flask. The mixture was stirred at 25 ^{o}C for 12 h. The reaction mixture was diluted with EtOAc (50.0 mL), and extracted with $NaHCO_3$ (sat. aq.). The aqueous layer was separated, acidified to pH 2.0 by adding cold HCl (1 N), and extracted with CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel (100-200 mesh) [ethyl acetate/hexane, 1:4 with HOAc (1 %, v/v)].

General procedure for the synthesis of alkynyl sulfides (3a-3ai)



The reaction mixture of alkynyl propiolic acid (0.3 mmol), Bunte salt (0.45 mmol, 1.5 equiv.), CuI (11.4 mg, 0.06 mmol, 20 mol%), Ag_2CO_3 (82.8 mg, 0.3 mmol, 1.0 equiv.), K_3PO_4 (127.2 mg, 0.6 mmol, 2.0 equiv.) and DMF (4 mL) was stirred at 130 ^{o}C under air for 12 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into a solution of HCl in water (1 N, 15 mL), and extracted several times with 15 mL of ethyl acetate. 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 coupling product.

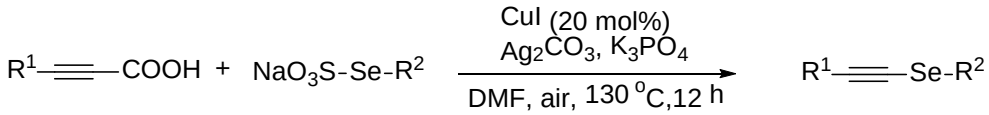
General procedures for the Synthesis of seleno Bunte salts[3]



A flask was charged with finely powdered selenium (0.8 g, 12 mmol), sodium sodium thiosulfate (3.024 g, 24 mmol, 2 equiv) and water (10.0 mL). The reaction mixture was stirred and heated to 90 ^{o}C. After 4h at 90 ^{o}C, the reaction mixture was cooled to rt, and then added the alkyl halides (10 mmol) in 30 mL MeOH. The solution was

stirred for additional 10 h at 65 ^{o}C before the reaction mixture was cooled to rt, and then concentrated on a rotovap at a bath temperature of 40-45 ^{o}C to remove the MeOH and water. The resultant solid was treated with MeOH (100mL), heated to 50 ^{o}C (most solid dissolves), and filtered through a frit funnel. This removes excess sodium thiosulfate and sodium bromide. The filtrate was concentrated to a solid. Trituration of this solid with hexanes, filtration, and drying under vacuum at 50 ^{o}C gave crude Seleno Bunte salt as a solid.

General procedure for the synthesis of alkynyl selenosulfides (5a-5n)



The reaction mixture of alkynyl propiolic acid (0.3 mmol), seleno Bunte salt (0.45 mmol, 1.5 equiv.), CuI (11.4 mg, 0.06 mmol, 20 mol%), Ag_2CO_3 (82.8 mg, 0.3 mmol, 1.0 equiv.), K_3PO_4 (127.2 mg, 0.6 mmol, 2.0 equiv.) and DMF (4 mL) was stirred at 130 ^{o}C under air for 12 h. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature, poured into a solution of HCl in water (1 N, 15 mL), and extracted several times with 15 mL of ethyl acetate. 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 coupling product.

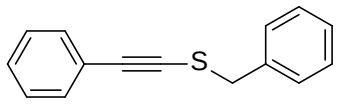
[1] a) J. T. Reeves, K. Camara, Z. S. Han, Y. Xu, H. Lee, C. A. Busacca, C. H. Senanayake, *Org. Lett.* **2014,** *16*, 1196-1199; b) X. Xiao, M. Feng, X. Jiang, *Chem. Commun.* **2015**, *51*, 4208-4211; c) Z. Qiao, N. Ge, X. Jiang, *Chem. Commun.* **2015,** *51*, 10295-10298; c) P. Jansa, L. Cechova, M. Dracinsky, Z. Janeba, *RSC Adv.* **2013**, *3*, 2650-2654.

[2] M. Zhou, M. Chen, Y. Zhou, K. Yang, J. Su, J. Du, Q. Song, *Org. Lett.* **2015**, *17*, 1786-1789.

[3] D. Crich, V. Krishnamurthy, T. K. Hutton, *J. Am. Chem. Soc.* **2006**, *128*, 2544-2545

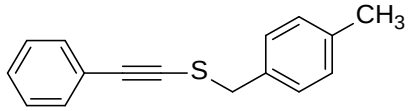
2. Characterization Data

Tabulated ^{1}H and ^{13}C NMR data and copies of ^{1}H and ^{13}C spectra are given for new Bunte salts and all sulfide products. For solid sulfide products, melting point ranges are given. Melting points ranges are not provided for Bunte salts, since the salts contain variable amounts of residual NaCl and also because the salts, even in the absence of residual NaCl, did not display a melting point but rather decomposition. For new compounds, HRMS data is provided. The following compounds have previously been reported in the literature: **3a**[4], **3h**[5], **3i**[4], **3l**[6], **3m**[6], **3n**[7], **3o**[6], **3p**[6], **3q**[7], **3s**[8], **3ai**[9], **5a**[10].



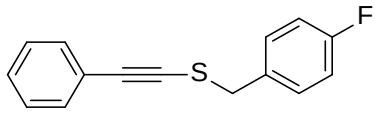
Chemical Formula: $C_{15}H_{12}S$
Exact Mass: 224.0660

Benzyl(phenylethynyl)sulfane (3a[4]**)**, Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (80%, 53.8 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 – 7.35 (m, 3H), 7.35 – 7.29 (m, 4H), 7.29 – 7.25 (m, 3H), 4.01 (s, 2H).; ^{13}C NMR (126 MHz, Chloroform-d) δ 136.72 , 131.47 , 129.27 , 128.72 , 128.39 , 128.19 , 127.92 , 123.51 , 94.75 , 79.33 , 40.61.



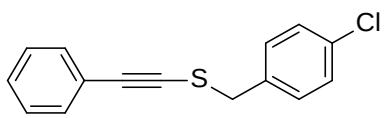
Chemical Formula: $C_{16}H_{14}S$
Exact Mass: 238.0816

(4-Methylbenzyl)(phenylethynyl)sulfane (3b), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (68%, 48.5 mg). 1H NMR (500 MHz, Chloroform-d) δ 7.34 (m, 2H), 7.30 – 7.25 (m, 5H), 7.16 (d, *J* = 7.7 Hz, 2H), 3.99 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.70 , 133.67 , 131.46 , 129.43 , 129.15 , 128.38 , 128.13 , 123.60 , 94.62 , 79.59 , 40.48 , 21.34 . HRMS (EI) Calcd. for $C_{16}H_{14}S$ 238.0816, found 238.0826.



Chemical Formula: $C_{15}H_{11}FS$
Exact Mass: 242.0565

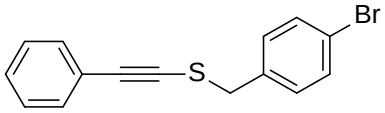
(4-Fluorobenzyl)(phenylethynyl)sulfane (3c), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (65%, 47.2 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.38 – 7.31 (m, 4H), 7.31 – 7.26 (m, 3H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.98 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 162.54 (d, *J* = 247.1 Hz), 132.61 , 132.51 ,130.91 (d, *J* = 8.3 Hz), 128.44 , 128.32 , 123.38 , 115.63 (d, *J* = 21.6 Hz), 95.03 , 78.93 , 39.77; ^{19}F NMR (470 MHz, Chloroform-d) δ -114.46. HRMS (EI) Calcd. for $C_{15}H_{11}SF$ 242.0565, found 242.0558



Chemical Formula: $C_{15}H_{11}ClS$
Exact Mass: 258.0270

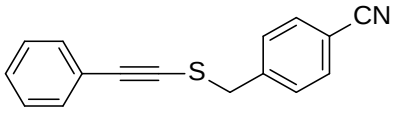
(4-Chlorobenzyl)(phenylethynyl)sulfane (3d), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (73%, 56.5 mg).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 (dd, *J* = 7.9, 2.5 Hz, 5H), 7.31 – 7.26 (m, 4H), 3.96 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 135.38 , 133.85 , 131.54 , 130.58 , 128.90 , 128.45 , 128.37 , 123.34 , 95.16 , 78.76 , 39.82. HRMS (EI) Calcd. for $C_{15}H_{11}SCl$ 258.0270, found 258.0269.



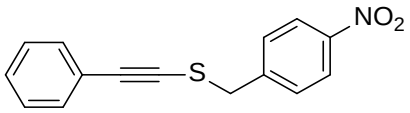
Chemical Formula: $C_{15}H_{11}BrS$
Exact Mass: 301.9765

(4-Bromobenzyl)(phenylethynyl)sulfane (3e), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (75%, 67.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 6.8, 3.1 Hz, 2H), 7.29 (dt, *J* = 4.0, 2.6 Hz, 3H), 7.25 (d, *J* = 6.9 Hz, 2H), 3.94 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 135.89 , 131.85 , 131.53 , 130.91 , 128.45 , 128.37 , 123.29 , 121.95 , 95.18 , 78.70 , 39.84 . HRMS (EI) Calcd. for $C_{15}H_{11}SBr$ 301.9765, found 301.9771.



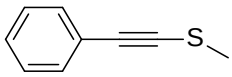
Chemical Formula: $C_{16}H_{11}NS$
Exact Mass: 249.0612

4-(((Phenylethynyl)thio)methyl)benzonitrile (3f), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a yellow oil (81%, 60.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 2.9 Hz, 5H), 3.98 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 142.32 , 132.44 , 131.51 , 129.92 , 128.59 , 128.48 , 122.92 , 118.75 , 111.68 , 95.63 , 77.80 , 39.76 . HRMS (EI) Calcd. for $C_{16}H_{11}NS$ 249.0612, found 249.0610.



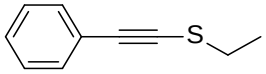
Chemical Formula: $C_{15}H_{11}NO_2S$
Exact Mass: 269.0510

(4-Nitrobenzyl)(phenylethynyl)sulfane (3g), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a brown solid (82%, 66.2 mg). Mp: 62-65 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-d) 1H NMR (500 MHz, Chloroform-d) δ 8.22 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.30 (qd, J = 3.8, 3.2, 1.7 Hz, 5H), 4.02 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ147.60 , 144.42 , 131.59 , 130.07 , 128.68 , 128.53 , 123.96 , 122.91 , 95.82 , 77.64 , 39.48. HRMS (EI) Calcd. for $C_{15}H_{11}NO_2S$ 269.0510, found 269.0508.



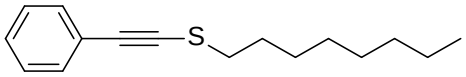
Chemical Formula: C_9H_8S
Exact Mass: 148.0347

Methyl(phenylethynyl)sulfane (3h[5]), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (53%, 23.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.60 , 128.41 , 128.19 , 123.54 , 92.00 , 81.04 , 19.56.



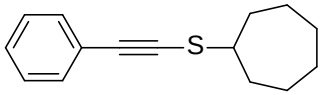
Chemical Formula: $C_{10}H_{10}S$
Exact Mass: 162.0503

Ethyl(phenylethynyl)sulfane (3i[4]), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (56%, 27.2 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.29 (dd, *J* = 5.0, 1.9 Hz, 3H), 2.82 (q, *J* = 7.3 Hz, 2H), 1.46 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.55 , 128.41 , 128.10 , 123.70 , 93.63 , 79.36 , 30.14 , 14.88.



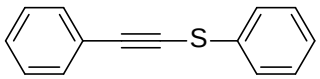
Chemical Formula: $C_{16}H_{22}S$
Exact Mass: 246.1442

Octyl(phenylethynyl)sulfane (3j), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (46%, 33.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.31 – 7.25 (m, 3H), 2.80 (t, *J* = 7.3 Hz, 2H), 1.80 (p, *J* = 7.4 Hz, 2H), 1.44 (q, *J* = 7.0 Hz, 2H), 1.38 – 1.19 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.53 , 128.39 , 128.05 , 123.74 , 92.99 , 79.84 , 36.00 , 31.95 , 29.49 , 29.31 , 29.25 , 28.43 , 22.80 , 14.25. HRMS (EI) Calcd. for $C_{16}H_{22}S$ 246.1442, found 246.1449.



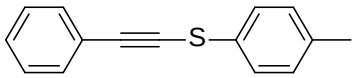
Chemical Formula: $C_{15}H_{18}S$
Exact Mass: 230.1129

Cycloheptyl(phenylethynyl)sulfane (3k), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (40%, 27.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.44 – 7.38 (m, 2H), 7.29 (dd, *J* = 5.1, 2.1 Hz, 3H), 3.25 (tt, *J* = 9.0, 4.4 Hz, 1H), 2.25 – 2.11 (m, 3H), 2.01 (d, *J* = 6.2 Hz, 1H), 1.81 – 1.71 (m, 4H), 1.65 – 1.58 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.55 , 128.40 , 128.00 , 123.86 , 94.01 , 79.96 , 50.15 , 34.86 , 28.34 , 25.85. HRMS (EI) Calcd. for $C_{15}H_{18}S$ 230.1129, found 230.1134.



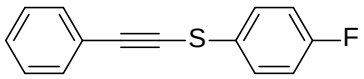
Chemical Formula: $C_{14}H_{10}S$
Exact Mass: 210.0503

Phenyl(phenylethynyl)sulfane (3l[6]), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (82%, 51.7 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.54 – 7.46 (m, 4H), 7.39 – 7.31 (m, 5H), 7.23 (t, J = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.11 , 131.88 , 129.41 , 128.77 , 128.54 , 126.67 , 126.38 , 123.07 , 98.03 , 75.62.



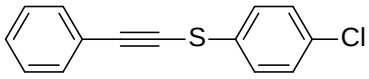
Chemical Formula: $C_{15}H_{12}S$
Exact Mass: 224.0660

(Phenylethynyl)(p-tolyl)sulfane (3m[6]), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (71%, 47.7 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 – 7.47 (m, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.04 , 132.08 , 130.45 , 129.61 , 128.90 , 128.76 , 127.02 , 123.47 , 97.64 , 76.57 , 21.40.



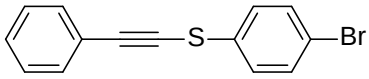
Chemical Formula: $C_{14}H_9FS$
Exact Mass: 228.0409

(4-Fluorophenyl)(phenylethynyl)sulfane (**3n**[7]), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (75%, 51.3 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 – 7.42 (m, 4H), 7.34 (dd, J = 5.0, 2.0 Hz, 3H), 7.06 (t, J = 8.7 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 162.02 (d, *J* = 246.3 Hz), 131.90 , 128.88 , 128.60 , 128.55 , 128.03 , 122.90 , 116.60 (d, *J* = 22.4 Hz), 97.68 , 75.82; ^{19}F NMR (470 MHz, Chloroform-d) δ -115.39.



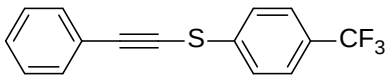
Chemical Formula: $C_{14}H_9ClS$
Exact Mass: 244.0113

(4-Chlorophenyl)(phenylethynyl)sulfane (3o[6]**)**, Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow solid (82%, 60.0 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.55 – 7.47 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.29 (m, 5H); ^{13}C NMR (126 MHz, Chloroform-d) δ 132.67 , 131.94 , 131.73 , 129.52 , 128.99 , 128.57 , 127.64 , 122.78 , 98.52 , 74.96.



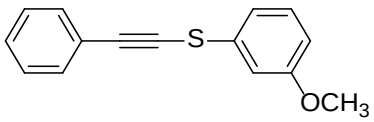
Chemical Formula: $C_{14}H_9BrS$
Exact Mass: 287.9608

(4-Bromophenyl)(phenylethynyl)sulfane (3p[6]**)**, Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (84%, 72.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.54 – 7.49 (m, 2H), 7.49 – 7.44 (m, 2H), 7.38 – 7.31 (m, 5H); ^{13}C NMR (126 MHz, Chloroform-d) δ 132.42 , 131.94 , 129.01 , 128.58 , 127.88 , 122.75 , 120.44 , 98.66 , 74.79.



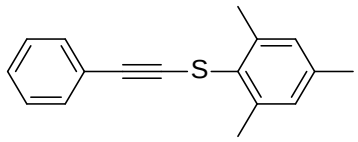
Chemical Formula: $C_{15}H_9F_3S$
Exact Mass: 278.0377

(Phenylethynyl)(4-(trifluoromethyl)phenyl)sulfane (3q[7]**)**, Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (79%, 65.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.61 – 7.56 (m, 4H), 7.54 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.37 (dd, *J* = 6.0, 1.7 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 138.48 , 132.02 , 129.22 , 128.81 , 128.63 , 126.62 , 126.18 , 125.89 , 125.18 , 123.02 , 122.48 , 99.58 , 73.67; ^{19}F NMR (470 MHz, Chloroform-d) δ -62.58.



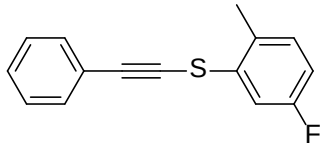
Chemical Formula: $C_{15}H_{12}OS$
Exact Mass: 240.0609

(3-Methoxyphenyl)(phenylethynyl)sulfane (3r), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a light yellow oil (74%, 53.2mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.56 – 7.47 (m, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.23 (m, 1H), 7.08 – 7.02 (m, 2H), 6.80 – 6.73 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 160.39 , 134.34 , 131.81 , 130.21 , 128.78 , 128.54 , 123.02 , 118.60 , 112.56 , 111.75 , 98.43 , 55.47. HRMS (EI) Calcd. for $C_{15}H_{12}OS$ 240.0609, found 240.0615.



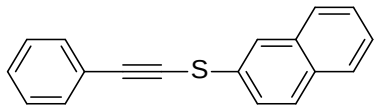
Chemical Formula: $C_{17}H_{16}S$
Exact Mass: 252.0973

Mesityl(phenylethynyl)sulfane (**3s**[8]), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (76%, 57.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.39 – 7.33 (m, 2H), 7.26 – 7.24 (m, 3H), 6.96 (s, 2H), 2.59 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 141.95 , 139.32 , 131.60 , 129.55 , 128.32 , 128.05 , 126.49 , 123.66 , 90.48 , 79.14 , 21.97 , 21.15.



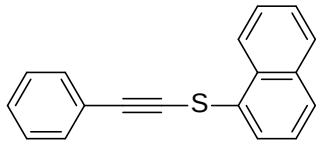
Chemical Formula: $C_{15}H_{11}FS$
Exact Mass: 242.0565

(5-Fluoro-2-methylphenyl)(phenylethynyl)sulfane (3t), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (70%, 50.8 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 – 7.50 (m, 2H), 7.45 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.10 (dd, *J* = 8.3, 5.8 Hz, 1H), 6.84 (td, *J* = 8.3, 2.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 161.86 (d, *J* = 245.9 Hz), 131.98 , 131.40 (d, *J* = 6.4 Hz), 130.30 , 129.04 , 128.60 , 122.73 , 113.32 (d, *J* = 10.6 Hz), 113.20 , 113.08 , 99.10 , 74.51 , 18.68; ^{19}F NMR (470 MHz, Chloroform-d) δ -115.61. HRMS (EI) Calcd. for $C_{15}H_{11}FS$ 242.0565, found 242.0561.



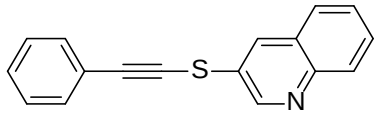
Chemical Formula: $C_{18}H_{12}S$
Exact Mass: 260.0660

Naphthalen-2-yl(phenylethynyl)sulfane (3u), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (66%, 51.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (s, 1H), 7.86 – 7.76 (m, 3H), 7.56 (ddt, *J* = 6.8, 5.4, 2.3 Hz, 3H), 7.52 – 7.43 (m, 2H), 7.41 – 7.34 (m, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.86 , 132.14 , 131.94 , 130.34 , 129.12 , 128.85 , 128.57 , 127.97 , 127.27 , 126.99 , 126.11 , 124.67 , 124.25 , 122.99 , 98.18 , 75.59; HRMS (EI) Calcd. for $C_{18}H_{12}S$ 260.0660, found 260.0655.



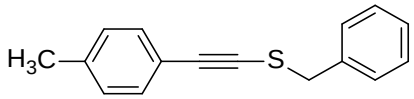
Chemical Formula: $C_{18}H_{12}S$
Exact Mass: 260.0660

Naphthalen-1-yl(phenylethynyl)sulfane (3v), Purification by column chromatography on silica gel (pertroleum ether) afforded a white solid (61%, 47.6 mg). MP: 67-69 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.45 (m, 5H), 7.39 – 7.29 (m, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.95 , 131.93 , 130.81 , 129.81 , 128.80 , 128.53 , 127.66 , 126.75 , 126.61 , 126.07 , 125.64 , 123.58 , 123.07 , 97.95 , 75.70; HRMS (EI) Calcd. for $C_{18}H_{12}S$ 260.0660, found 260.0658.



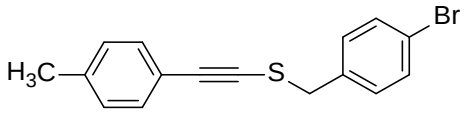
Chemical Formula: $C_{17}H_{11}NS$
Exact Mass: 261.0612

3-((Phenylethynyl)thio)quinoline (3w), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a brown solid (70%, 54.8 mg). MP: 54-56 ^{o}C. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.94 (d, *J* = 2.4 Hz, 1H), 8.26 (d, *J* = 2.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.38 (qd, *J* = 4.8, 1.8 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 148.26 , 146.83 , 132.76 , 132.04 , 129.63 , 129.58 , 129.18 , 128.64 , 128.32 , 127.71 , 127.21 , 122.58 , 98.57 , 73.90; HRMS (EI) Calcd. for $C_{17}H_{11}NS$ 261. 0612, found 261.0608.



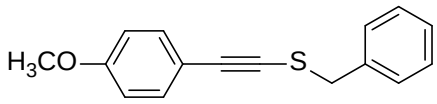
Chemical Formula: $C_{16}H_{14}S$
Exact Mass: 238.0816

Benzyl(p-tolylethynyl)sulfane (3x), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (73%, 52.8mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.01 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 138.44 , 136.81 , 131.56 , 129.27 , 129.16 , 128.71 , 127.88 , 120.45 , 94.81 , 78.32 , 40.68 , 21.63; HRMS (EI) Calcd. for $C_{16}H_{14}S$ 238.0816, found 238.0821.



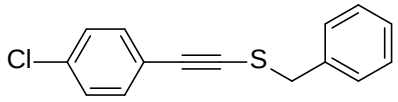
Chemical Formula: $C_{16}H_{13}BrS$
Exact Mass: 315.9921

(4-Bromobenzyl)(p-tolylethynyl)sulfane (3y), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (68%, 64.5mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.24 (dd, *J* = 8.1, 4.5 Hz, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 3.92 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.50 , 134.80 , 130.66 , 130.44 , 129.74 , 128.05 , 120.73 , 119.05 , 94.11 , 76.51 , 38.72 , 20.47; HRMS (EI) Calcd. for $C_{16}H_{13}BrS$ 315.9921, found 315.9926.



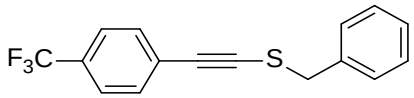
Chemical Formula: $C_{16}H_{14}OS$
Exact Mass: 254.0765

Benzyl((4-methoxyphenyl)ethynyl)sulfane (3z), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (75%, 57.1mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.32 (m, 4H), 7.30 (dt, *J* = 6.9, 1.3 Hz, 3H), 6.84 – 6.78 (m, 2H), 4.00 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 159.79 , 136.86 , 133.43 , 129.27 , 128.70 , 127.84 , 115.63 , 114.05 , 94.52 , 78.87 , 55.44 , 40.76; HRMS (EI) Calcd. for $C_{16}H_{14}OS$ 254.0765, found 254.0767.



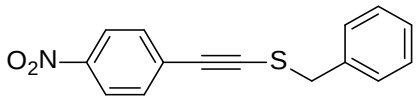
Chemical Formula: $C_{15}H_{11}ClS$
Exact Mass: 258.0270

Benzyl((4-chlorophenyl)ethynyl)sulfane (3aa), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (68%, 52.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 5H), 7.24 (s, 4H), 4.01 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 136.56 , 134.15 , 133.83 , 132.63 , 129.26 , 128.74 , 127.98 , 121.99 , 93.66 , 80.62 , 40.53; HRMS (EI) Calcd. for $C_{15}H_{11}ClS$ 258.0270, found 258.0275.



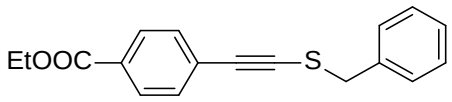
Chemical Formula: $C_{16}H_{11}F_3S$
Exact Mass: 292.0534

Benzyl((4-(trifluoromethyl)phenyl)ethynyl)sulfane (3ab), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (72%, 63.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.29 (m, 7H), 4.04 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 136.41 , 131.26 , 129.77 , 129.51 , 129.30 , 128.79 , 128.09 , 127.29 , 125.35 , 125.16 , 122.99 , 93.75 , 82.83 , 40.49; ^{19}F NMR (470 MHz, Chloroform-d) δ -62.75. HRMS (EI) Calcd. for $C_{16}H_{11}F_3S$ 292.0534, found 292.0544.



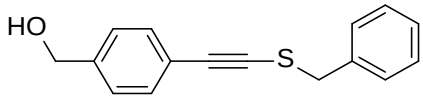
Chemical Formula: $C_{15}H_{11}NO_2S$
Exact Mass: 269.0510

Benzyl((4-nitrophenyl)ethynyl)sulfane (3ac), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a brown oil (67%, 54.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.14 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.45 – 7.30 (m, 7H), 4.07 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 146.63 , 136.14 , 131.33 , 130.40 , 129.32 , 128.85 , 128.23 , 123.78 , 93.81 , 86.92 , 40.51; HRMS (EI) Calcd. for $C_{15}H_{11}NO_2S$ 269.0510, found 269.0544.



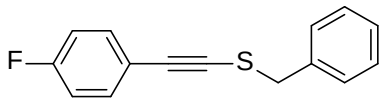
Chemical Formula: $C_{18}H_{16}O_2S$
Exact Mass: 296.0871

Ethyl 4-((benzylthio)ethynyl)benzoate (3ad), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (59%, 52.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.29 (m, 7H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 166.20 , 139.28 , 136.43 , 130.84 , 129.55 , 129.30 , 128.79 , 128.07 , 94.50 , 83.31 , 61.24 , 40.55 , 14.46; HRMS (EI) Calcd. for $C_{18}H_{16}O_2S$ 296.0871, found 296.0873.



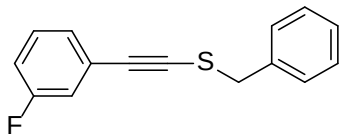
Chemical Formula: $C_{16}H_{14}OS$
Exact Mass: 254.0765

(4-((Benzylthio)ethynyl)phenyl)methanol (3ae), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (61%, 46.5mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.31 (m, 6H), 7.28 (d, *J* = 8.1 Hz, 3H), 4.68 (s, 2H), 4.02 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 140.94 , 136.71 , 131.68 , 129.28 , 128.74 , 127.94 , 126.91 , 122.80 , 94.59 , 79.46 , 65.12 , 40.63; HRMS (EI) Calcd. for $C_{16}H_{14}OS$ 254.0765, found 254.0766.



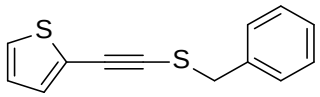
Chemical Formula: $C_{15}H_{11}FS$
Exact Mass: 242.0565

Benzyl((4-fluorophenyl)ethynyl)sulfane (3af), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (65%, 47.2 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 7H), 6.97 (t, J = 8.7 Hz, 2H), 4.01 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 162.52 (d, *J* = 249.2 Hz), 136.66 , 133.52 (d, *J* = 8.4 Hz), 129.26 , 128.73 , 127.94 , 119.58 , 115.69 (d, *J* = 22.1 Hz), 93.60 , 79.01 , 40.55; ^{19}F NMR (470 MHz, Chloroform-d) δ -110.88. HRMS (EI) Calcd. for $C_{15}H_{11}FS$ 242.0565, found 242.0573.



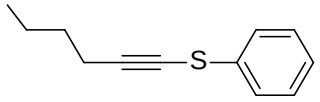
Chemical Formula: $C_{15}H_{11}FS$
Exact Mass: 242.0565

Benzyl((3-fluorophenyl)ethynyl)sulfane (3ag), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow oil (62%, 45,0 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 5H), 7.22 (dd, *J* = 8.2, 6.2 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03 – 6.93 (m, 2H), 4.02 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 162.43 (d, *J* = 246.3 Hz), 136.52 , 129.98 , 129.92 , 129.28 , 128.77 , 128.03 , 127.15 , 118.04 (d, *J* = 22.4 Hz), 115.45 (d, *J* = 21.3 Hz), 93.65 , 80.84 , 40.49; 19F NMR (470 MHz, Chloroform-d) δ -113.00; HRMS (EI) Calcd. for $C_{15}H_{11}FS$ 242.0565, found 242.0571.



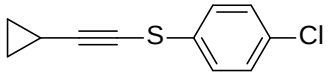
Chemical Formula: $C_{13}H_{10}S_2$
Exact Mass: 230.0224

2-((Benzylthio)ethynyl)thiophene (3ah), Purification by column chromatography on silica gel (pertroleum ether) afforded a brown oil (64%, 44.2 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.33 (m, 4H), 7.31 (dd, J = 5.6, 3.1 Hz, 1H), 7.25 (dd, J = 5.2, 1.2 Hz, 1H), 7.17 (dd, J = 3.6, 1.2 Hz, 1H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 4.01 (s, 2H); ^{13} C NMR (126 MHz, Chloroform-d) δ 136.55 , 133.00 , 129.25 , 128.78 , 127.95 , 127.07 , 123.67 , 87.47 , 83.89 , 40.97; HRMS (EI) Calcd. for $C_{13}H_{10}S_2$ 230.0224, found 230.0223.



Chemical Formula: $C_{12}H_{14}S$
Exact Mass: 190.0816

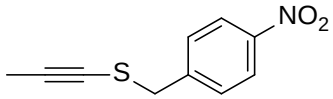
Hex-1-yn-1-yl(phenyl)sulfane (3ai[9]), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (50%, 28.5 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.**32** (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.47 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 133.94 , 129.16 , 126.16 , 125.87 , 100.15 , 64.69 , 30.87 , 22.12 , 20.13 , 13.70 .



Chemical Formula: $C_{11}H_9ClS$
Exact Mass: 208.0113

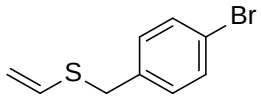
(4-chlorophenyl)(cyclopropylethynyl)sulfane (3aj[10]), Purification by column

chromatography on silica gel (pertroleum ether) afforded a light yellow oil (52%, 32.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 – 7.29 (m, 2H), 7.29 – 7.26 (m, 2H), 1.48 (tt, J = 8.2, 5.0 Hz, 1H), 0.94 – 0.86 (m, 2H), 0.83 (ddd, J = 7.8, 5.4, 3.0 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 132.83 , 132.21 , 129.38 , 127.17 , 104.84 , 60.04 , 9.51 , 1.13 .



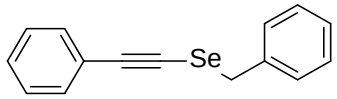
Chemical Formula: $C_{10}H_9NO_2S$
Exact Mass: 207.0354

(4-nitrobenzyl)(prop-1-yn-1-yl)sulfane (3ak), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a colorless oil (42%, 26.1 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.21 (d, J = 8.7 Hz, 2H), 7.51 – 7.46 (m, 2H), 3.90 (s, 2H), 1.91 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 147.64 , 145.00 , 130.02 , 124.00 , 92.89 , 66.16 , 39.26 , 5.21.



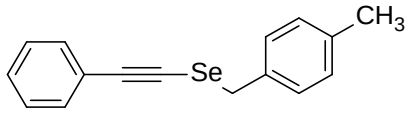
Chemical Formula: C_9H_9BrS
Exact Mass: 227.9608

(4-bromobenzyl)(prop-1-en-1-yl)sulfane (3al[1a]), Purification by column chromatography on silica gel (pertroleum ether) afforded a colorless oil (32%, 14.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.44 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.32 (dd, J = 16.7, 10.1 Hz, 1H), 5.21 (d, J = 10.1 Hz, 1H), 5.15 (d, J = 16.7 Hz, 1H), 3.86 (s, 2H); 13C NMR (126 MHz, Chloroform-d) δ 136.51 , 131.94 , 131.71 , 130.68 , 121.36 , 112.46 , 35.84 .



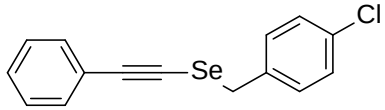
Chemical Formula: $C_{15}H_{12}Se$
Exact Mass: 272.0104

Benzyl(phenylethynyl)selane (5a[11]), Purification by column chromatography on silica gel (pertroleum ether) afforded a yellow solid (74%, 60.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.38 (d, *J* = 7.5 Hz, 4H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.31 – 7.27 (m, 4H), 4.12 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.72 , 131.64 , 129.25 , 128.81 , 128.46 , 128.34 , 127.77 , 123.73 , 101.50 , 71.25 , 33.28 .



Chemical Formula: $C_{16}H_{14}Se$
Exact Mass: 286.0261

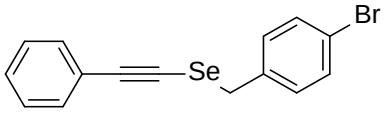
(4-Methylbenzyl)(phenylethynyl)selane (5b), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (64%, 54.9 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.34 (m, 2H), 7.30 – 7.24 (m, 5H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.10 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.57 , 134.64 , 131.65 , 129.54 , 129.13 , 128.47 , 128.30 , 123.82 , 101.38 , 71.52 , 33.25 , 21.43 . HRMS (EI) Calcd. for $C_{16}H_{14}{}^{74}Se$ 280.0320, found 280.0317.



Chemical Formula: $C_{15}H_{11}ClSe$
Exact Mass: 305.9714

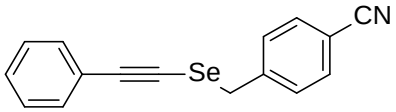
(4-Chlorobenzyl)(phenylethynyl)selane (5c), Purification by column

chromatography on silica gel (pertroleum ether) afforded a light yellow oil (78%, 71.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.37 (dd, *J* = 4.1, 2.2 Hz, 2H), 7.31 (d, *J* = 5.4 Hz, 7H), 4.06 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 136.44 , 133.59 , 131.66 , 130.55 , 128.94 , 128.51 , 123.54 , 101.91 , 70.69 , 32.24 . HRMS (EI) Calcd. for $C_{15}H_{11}Cl^{74}Se$ 299.9774, found 299.9775.



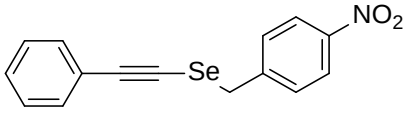
Chemical Formula: $C_{15}H_{11}BrSe$
Exact Mass: 349.9209

(4-Bromobenzyl)(phenylethynyl)selane (5d), Purification by column chromatography on silica gel (pertroleum ether) afforded a light yellow oil (74%, 77.7 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.33 (dq, *J* = 6.9, 2.1 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.02 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 136.98 , 131.92 , 131.70 , 130.90 , 128.83 , 128.54 , 123.54 , 121.74 , 101.96 , 70.62 , 32.29 . HRMS (EI) Calcd. for $C_{15}H_{11}Br^{74}Se$ 343.9269, found 343.9263.



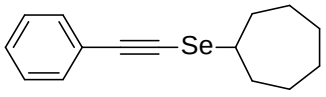
Chemical Formula: $C_{16}H_{11}NSe$
Exact Mass: 297.0057

4-((Benzylselanyl)ethynyl)benzonitrile (5e), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a yellow solid (81%, 72.2 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.24 (dp, *J* = 5.6, 3.2 Hz, 5H), 3.97 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 143.60 , 132.48 , 131.65 , 129.89 , 128.74 , 128.57 , 123.20 , 118.90 , 111.40 , 102.50 , 69.75 , 31.97 . HRMS (EI) Calcd. for $C_{16}H_{11}N^{74}Se$ 291.0116, found 291.0114.



Chemical Formula: $C_{15}H_{11}NO_2Se$
Exact Mass: 316.9955

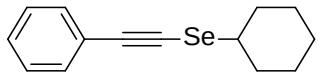
(4-Nitrobenzyl)(phenylethynyl)selane (5f), Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afforded a light yellow solid (81%, 77.0 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.33 (dtd, *J* = 7.3, 5.8, 5.3, 2.1 Hz, 5H), 4.10 (s, 2H); 13C NMR (126 MHz, Chloroform-d) δ 147.45 , 145.78 , 131.73 , 130.02 , 128.83 , 128.63 , 124.05 , 123.19 , 102.73 , 69.58 , 31.60 . HRMS (EI) Calcd. for $C_{15}H_{11}NO_2{}^{74}Se$ 311.0015, found 311.0002.



Chemical Formula: $C_{15}H_{18}Se$
Exact Mass: 278.0574

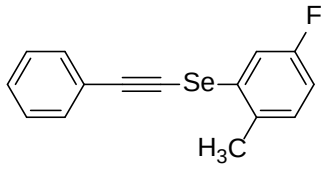
Cycloheptyl(phenylethynyl)selane (5g), Purification by column chromatography on silica gel (petroleum ether) afforded a light yellow oil (64%, 53.4 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 – 7.37 (m, 2H), 7.28 (dd, *J* = 5.1, 2.0 Hz, 3H), 3.51 (tt, *J* = 9.3, 4.4 Hz, 1H), 2.22 (ddd, *J* = 14.5, 7.6, 3.4 Hz, 2H), 1.82 (dtd, *J* = 14.4, 9.6, 3.0 Hz, 2H), 1.74 (ddt, *J* = 14.7, 7.4, 3.6 Hz, 2H), 1.65 – 1.55 (m, 4H), 1.48 (ddd, *J* = 13.0, 8.4, 3.3 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.73 , 128.48 , 128.17 ,

124.08 , 100.82 , 72.04 , 47.08 , 35.76 , 28.35 , 26.73 . HRMS (EI) Calcd. for $C_{15}H_{18}{}^{74}Se$ 272.0633, found 272.0631.



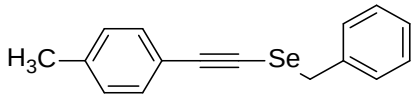
Chemical Formula: $C_{14}H_{16}Se$
Exact Mass: 264.0417

Cyclohexyl(phenylethynyl)selane (5h), Purification by column chromatography on silica gel (petroleum ether) afforded a light yellow oil (67%, 53.1mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 – 7.39 (m, 2H), 7.29 (dd, *J* = 5.2, 2.1 Hz, 3H), 3.29 (ddd, *J* = 11.0, 7.2, 3.8 Hz, 1H), 2.17 (dd, *J* = 13.1, 4.0 Hz, 2H), 1.86 – 1.75 (m, 2H), 1.70 – 1.63 (m, 2H), 1.45 – 1.20 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-d) δ 131.72 , 128.47 , 128.16 , 124.08 , 101.25 , 70.46 , 44.86 , 34.28 , 27.11 , 25.73 . HRMS (EI) Calcd. for $C_{14}H_{16}{}^{74}Se$ 258.0477, found 258.0484.



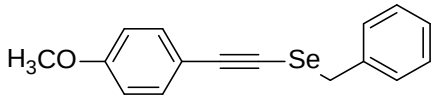
Chemical Formula: $C_{15}H_{11}FSe$
Exact Mass: 290.0010

(5-Fluoro-2-methylphenyl)(phenylethynyl)selane (5i), Purification by column chromatography on silica gel (petroleum ether) afforded a yellowoil (75%, 65.3 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 – 7.52 (m, 3H), 7.44 – 7.35 (m, 3H), 7.11 (dd, *J* = 8.3, 5.6 Hz, 1H), 6.90 (td, *J* = 8.3, 2.7 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 161.97 (d, *J* = 247.3 Hz), 132.01 , 131.71 , 131.31 , 131.25 , 129.04 , 128.63 , 123.05 , 115.82 (d, *J* = 24.8 Hz), 113.93 (d, *J* = 21.4 Hz), 104.56 , 68.46 , 20.02 ; ^{19}F NMR (470 MHz, Chloroform-d) δ -115.55 . HRMS (EI) Calcd. for $C_{15}H_{11}F{}^{74}Se$ 284.0070, found 284.0064.



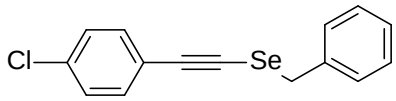
Chemical Formula: $C_{16}H_{14}Se$
Exact Mass: 286.0261

Benzyl(p-tolylethynyl)selane (5j), Purification by column chromatography on silica gel (petroleum ether) afforded a yellow solid (80%, 68.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.36 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 3H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.12 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 138.54 , 137.78 , 131.66 , 129.23 , 128.78 , 127.72 , 120.68 , 101.56 , 70.19 , 33.28 , 21.71 . HRMS (EI) Calcd. for $C_{16}H_{14}{}^{74}Se$ 280.0320, found 280.0315.



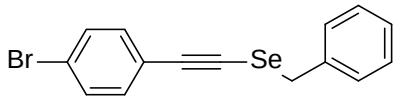
Chemical Formula: $C_{16}H_{14}OSe$
Exact Mass: 302.0210

Benzyl((4-methoxyphenyl)ethynyl)selane (5k), Purification by column chromatography on silica gel (petroleum ether) afforded a yellow solid (78%, 70.1mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.37 – 7.27 (m, 6H), 7.27 – 7.23 (m, 1H), 6.83 – 6.76 (m, 2H), 4.07 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 159.81 , 137.81 , 133.43 , 129.22 , 128.76 , 127.68 , 115.87 , 114.08 , 101.27 , 69.20 , 55.48 , 33.30 . HRMS (EI) Calcd. for $C_{16}H_{14}O{}^{74}Se$ 296.0269, found 296.0272.



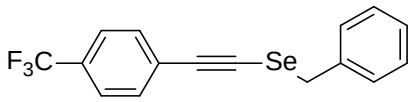
Chemical Formula: $C_{15}H_{11}ClSe$
Exact Mass: 305.9714

Benzyl((4-chlorophenyl)ethynyl)selane (5l), Purification by column chromatography on silica gel (petroleum ether) afforded a yellow solid (87%, 79.9 mg). 1H NMR (500 MHz, Chloroform-d) δ 7.38 – 7.30 (m, 4H), 7.28 – 7.23 (m, 5H), 4.11 (s, 2H); 13C NMR (126 MHz, Chloroform-d) δ 137.56 , 134.28 , 132.80 , 129.25 , 128.80 , 127.82 , 122.18 , 100.39 , 72.63 , 33.26 . HRMS (EI) Calcd. for $C_{15}H_{11}Cl^{74}Se$ 299.9774, found 299.9778.



Chemical Formula: $C_{15}H_{11}BrSe$
Exact Mass: 349.9209

Benzyl((4-bromophenyl)ethynyl)selane (5m), Purification by column chromatography on silica gel (petroleum ether) afforded a yellow solid (86%, 90.3mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.27 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.11 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.52 , 132.96 , 131.70 , 129.24 , 128.79 , 127.81 , 122.62 , 122.48 , 100.45 , 72.90 , 33.25 . HRMS (EI) Calcd. for $C_{15}H_{11}Br^{74}Se$ 343.9269, found 343.9281.



Chemical Formula: $C_{16}H_{11}F_3Se$
Exact Mass: 339.9978

Benzyl((4-(trifluoromethyl)phenyl)ethynyl)selane (5n), Purification by column chromatography on silica gel (petroleum ether) afforded a yellow solid (82%, 83.6 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 4.13 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.45 , 131.54 , 130.19 , 129.93 , 129.66 , 129.30 , 128.85 , 127.93 , 127.45 , 125.42 , 125.24 , 123.07 , 100.45 , 74.99 , 33.31; ^{19}F NMR (470 MHz, Chloroform-d) δ -62.76 . HRMS (EI) Calcd. for $C_{16}H_{11}F_3{}^{74}Se$ 334.0038, found 334.0030.

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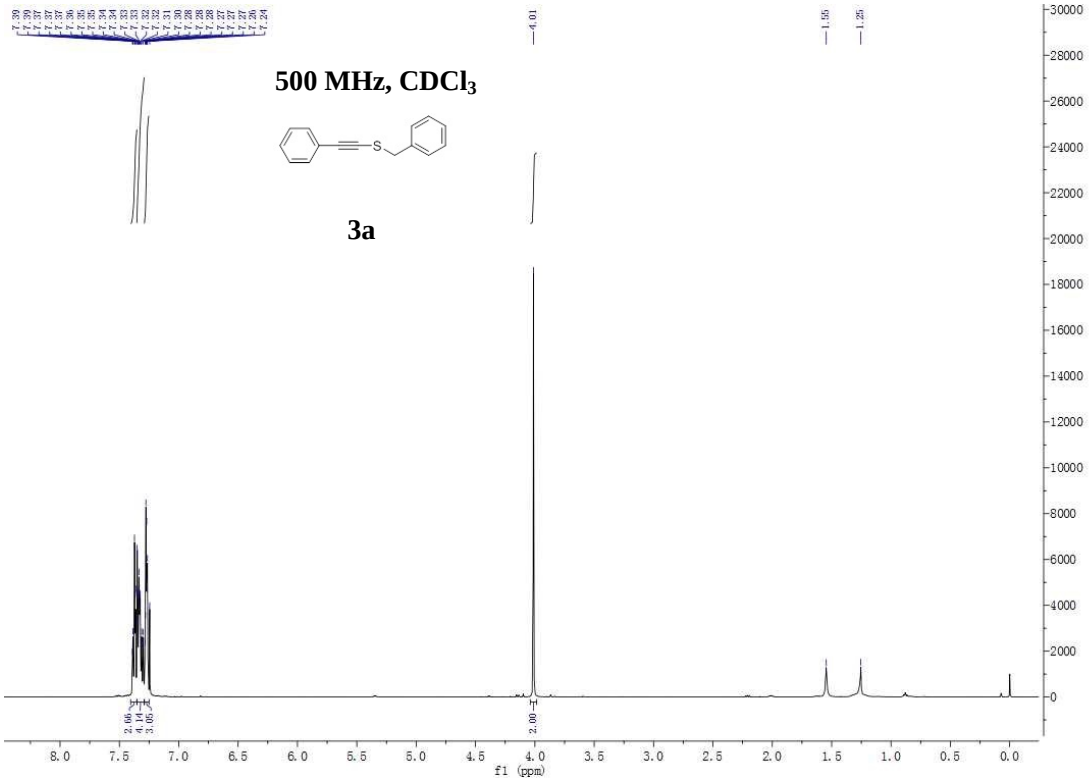
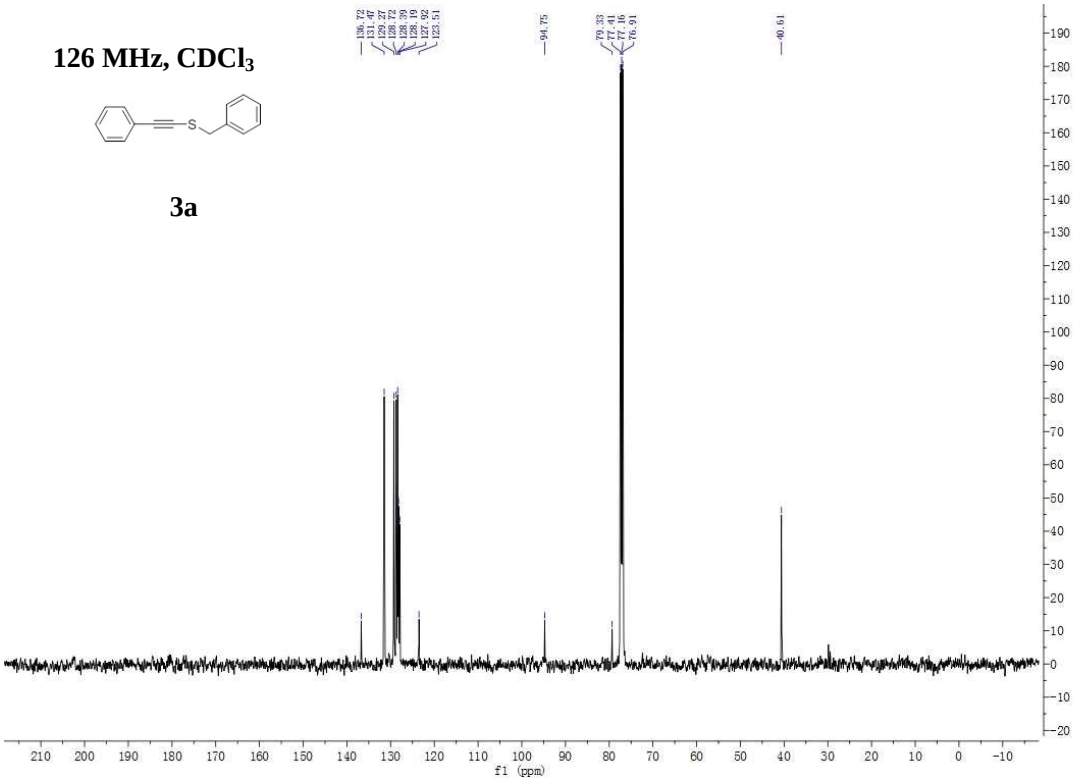
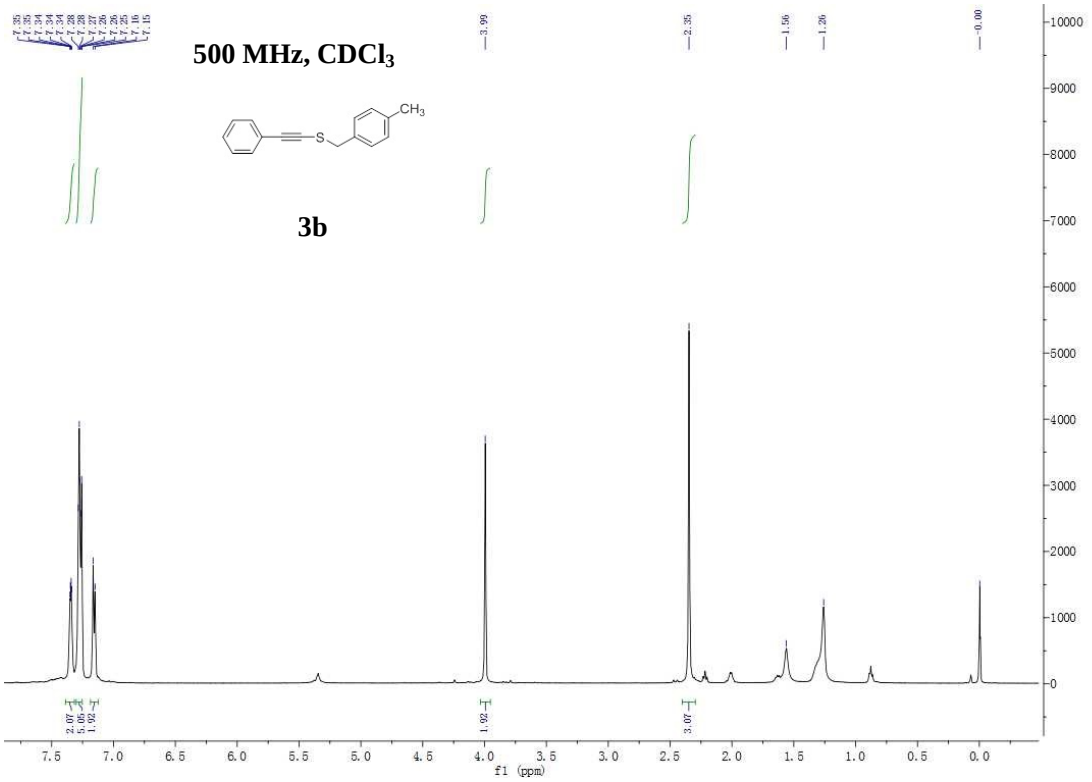
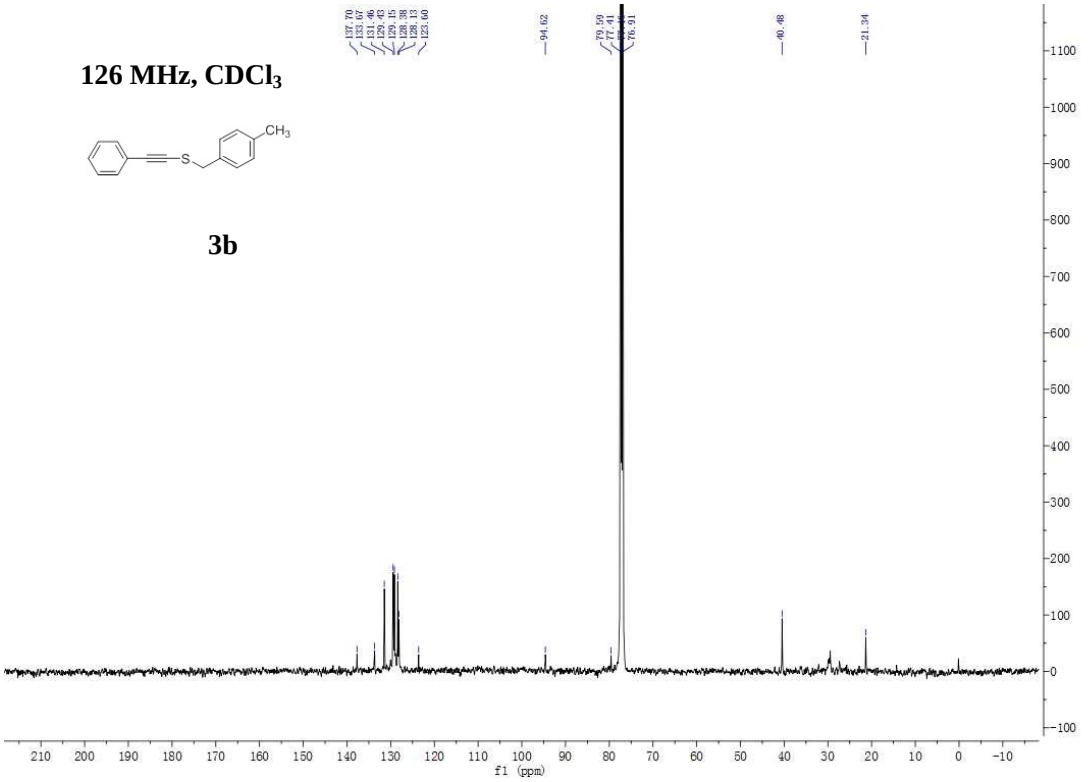
3. NMR Spectra

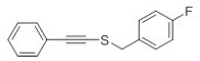





500 MHz, CDCl3
3b
f1 (ppm)

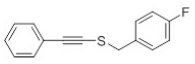

126 MHz, CDCl3
3b
f1 (ppm)

500 MHz, $CDCl_3$



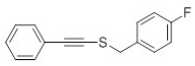
3c

126 MHz, $CDCl_3$

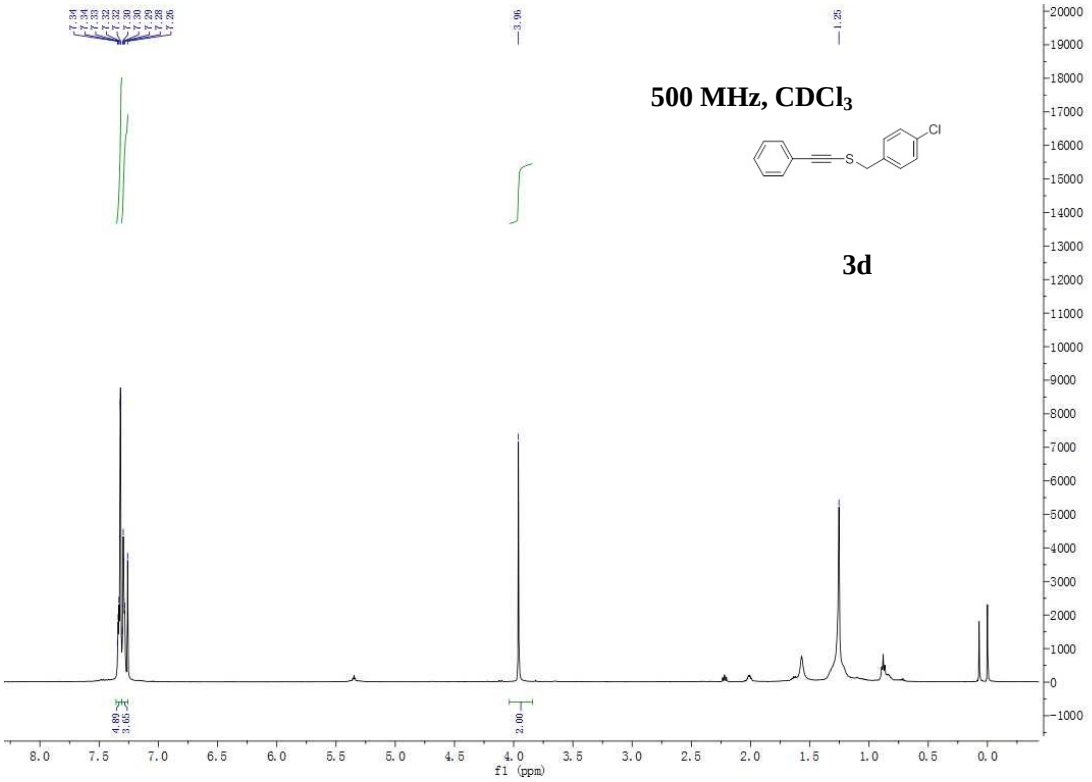


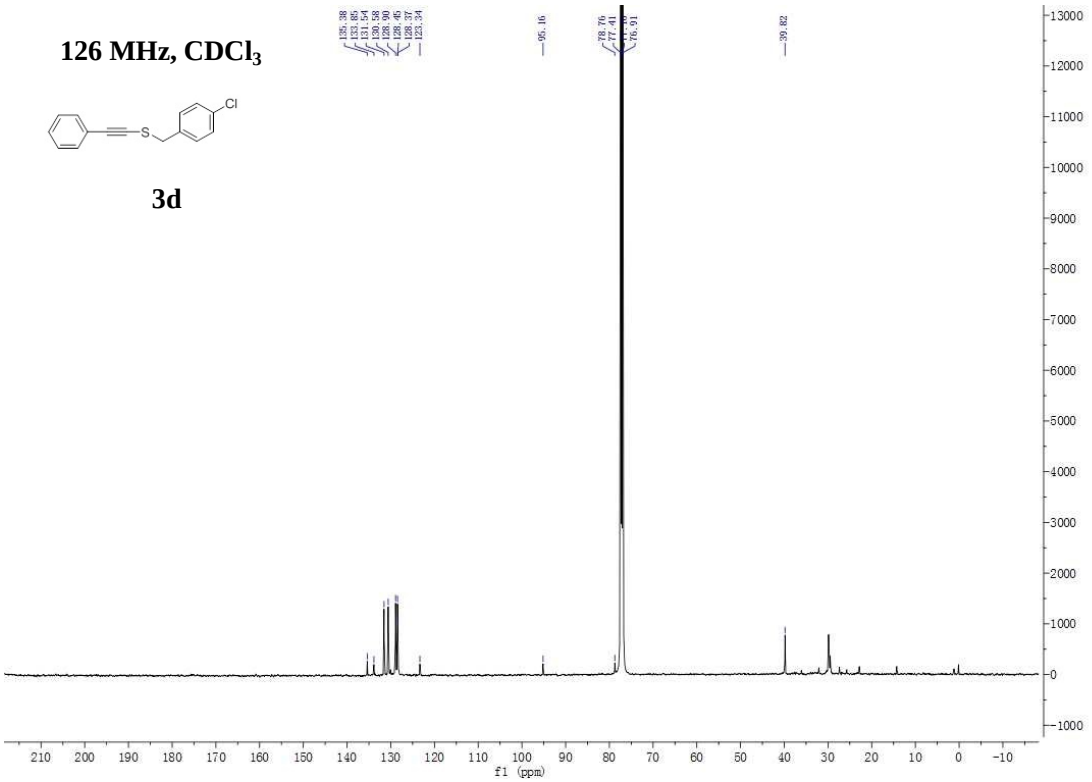
3c

470 MHz, $CDCl_3$

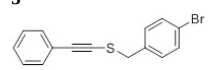


3c


500 MHz, CDCl3
3d
f1 (ppm)

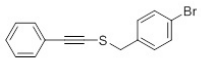

126 MHz, CDCl3
3d
f1 (ppm)

500 MHz, $CDCl_3$

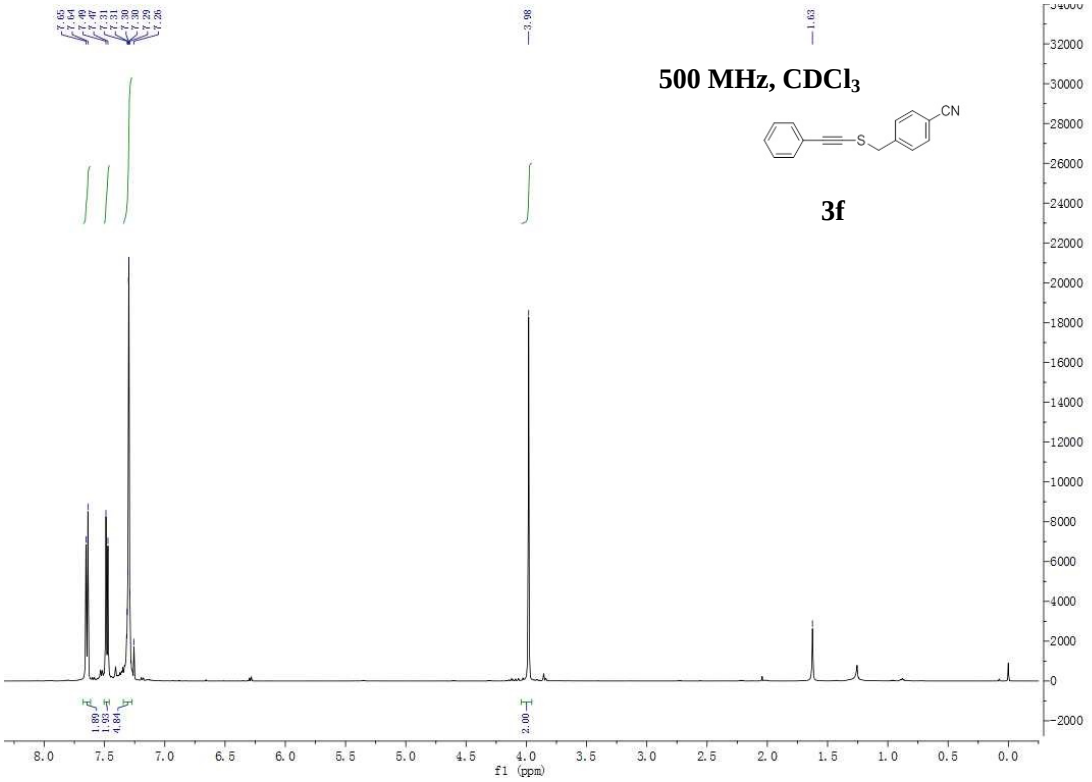


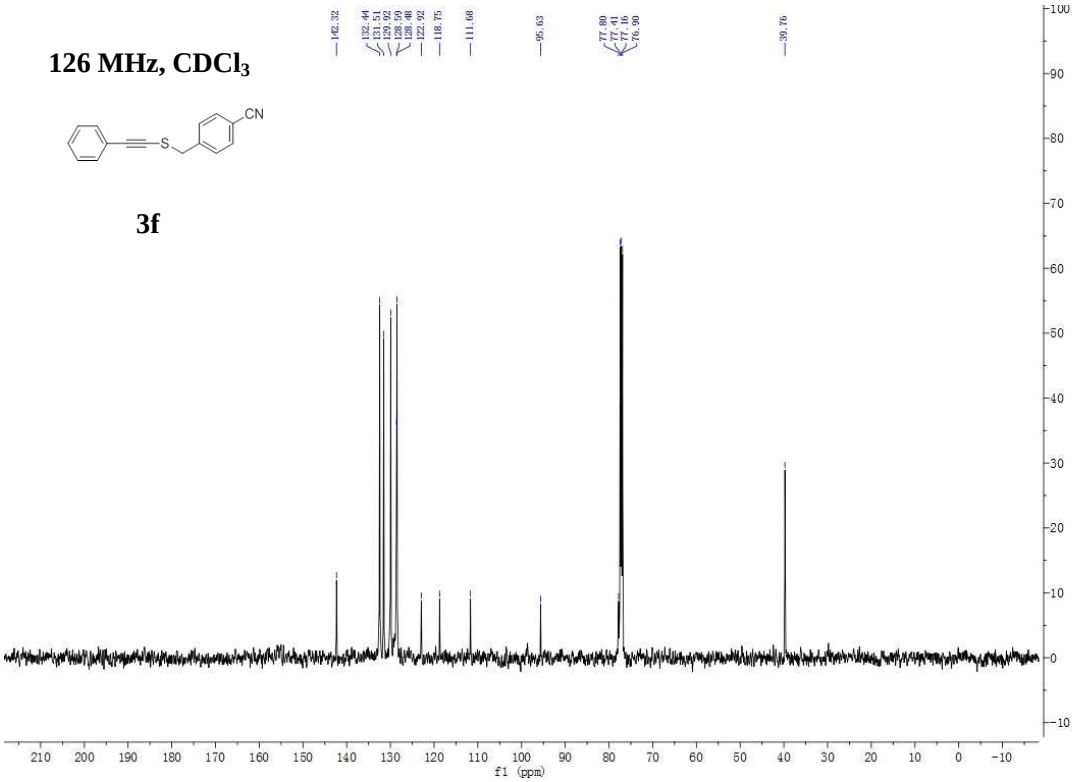
3e

126 MHz, $CDCl_3$

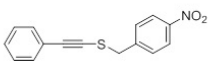


3e


500 MHz, CDCl3
CN
S
3f
f1 (ppm)

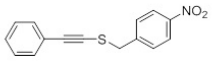

126 MHz, CDCl3
CN
S
3f
f1 (ppm)

500 MHz, $CDCl_3$

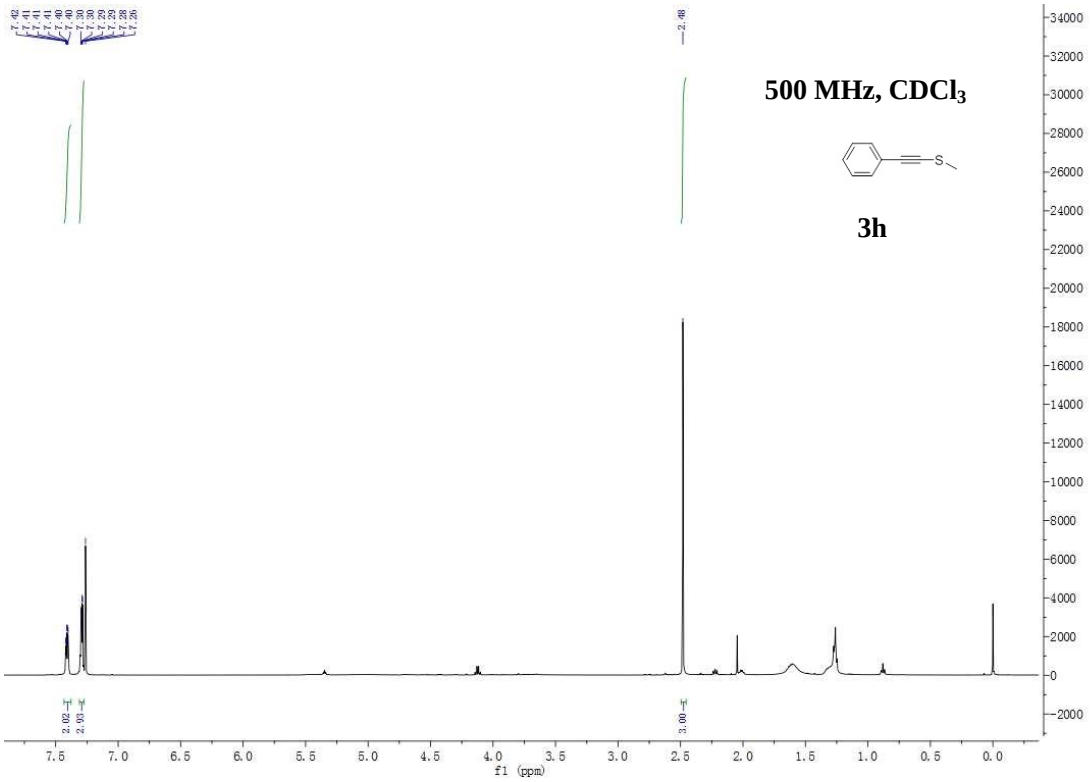


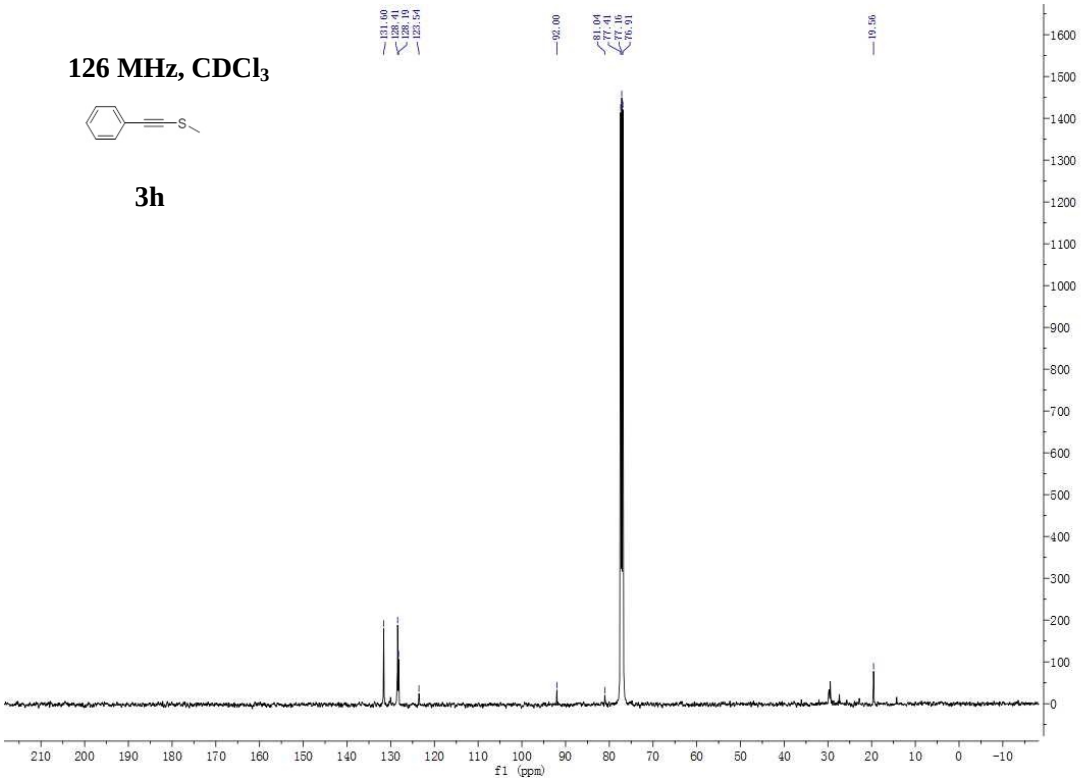
3g

126 MHz, $CDCl_3$



3g


500 MHz, CDCl3
3h
f1 (ppm)


126 MHz, CDCl3
3h
f1 (ppm)

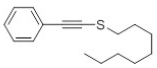
500 MHz, $CDCl_3$

3i

126 MHz, $CDCl_3$

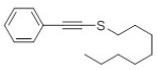
3i

500 MHz, $CDCl_3$



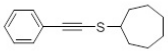
3j

126 MHz, $CDCl_3$



3j

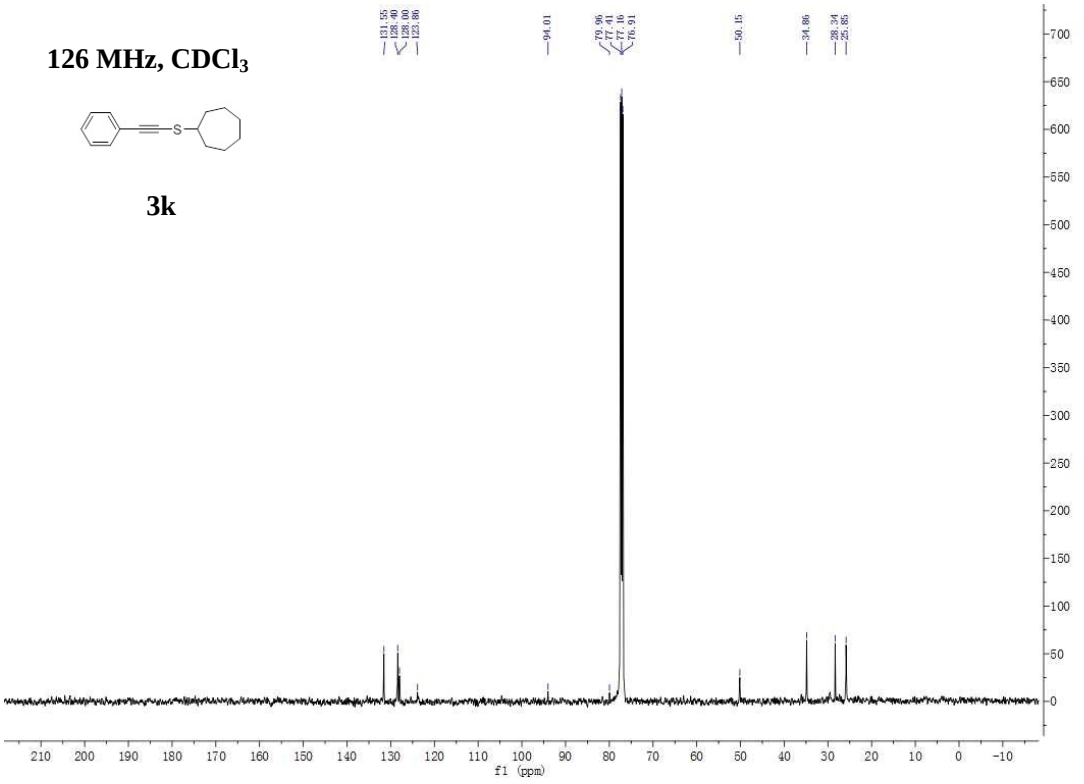
500 MHz, $CDCl_3$



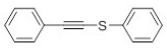
3k

126 MHz, $CDCl_3$

3k

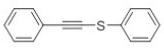


500 MHz, $CDCl_3$



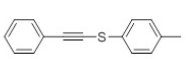
3l

126 MHz, $CDCl_3$



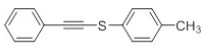
3l

500 MHz, $CDCl_3$



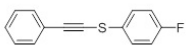
3m

126 MHz, $CDCl_3$



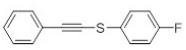
3m

500 MHz, $CDCl_3$



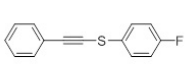
3n

126 MHz, $CDCl_3$



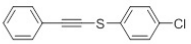
3n

470 MHz, $CDCl_3$



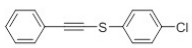
3n

500 MHz, $CDCl_3$



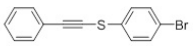
3o

126 MHz, $CDCl_3$



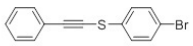
3o

500 MHz, $CDCl_3$



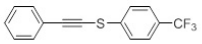
3p

126 MHz, $CDCl_3$



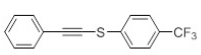
3p

500 MHz, $CDCl_3$



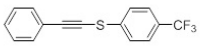
3q

126 MHz, $CDCl_3$

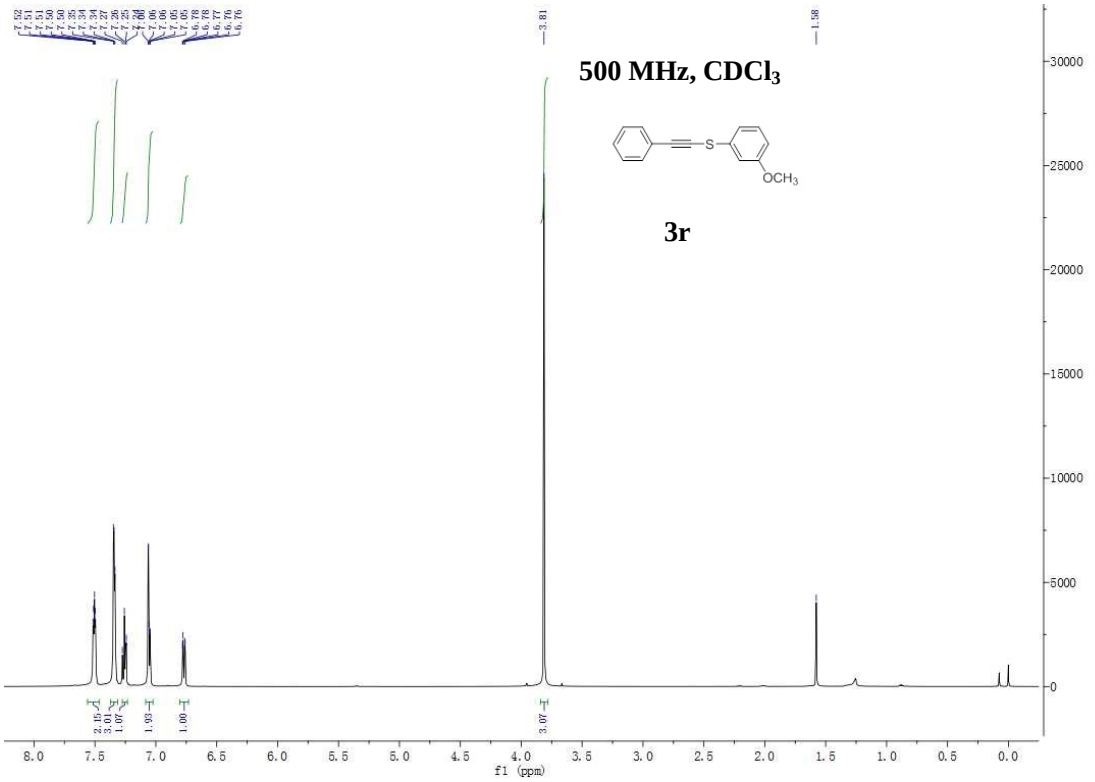


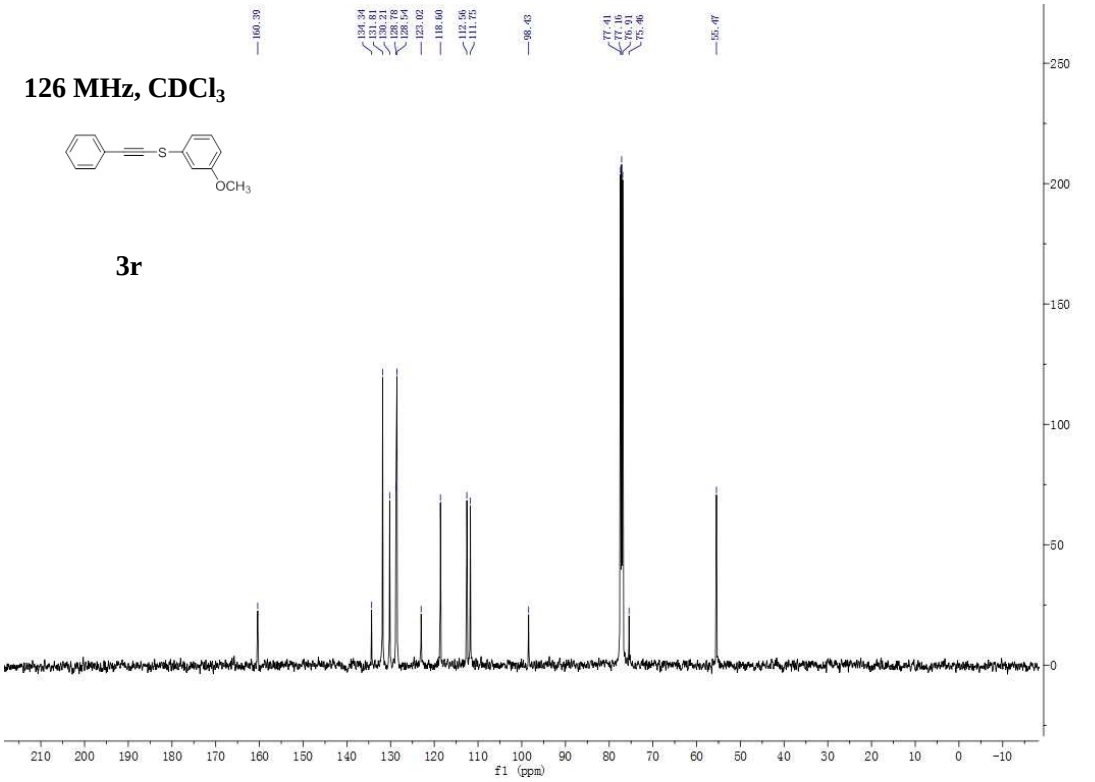
3q

470 MHz, $CDCl_3$

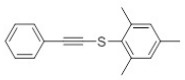


3q


500 MHz, CDCl3
3r
f1 (ppm)

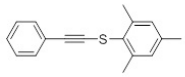

126 MHz, CDCl3
3r
f1 (ppm)

500 MHz, $CDCl_3$



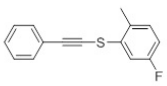
3s

126 MHz, $CDCl_3$



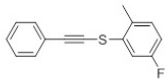
3s

500 MHz, $CDCl_3$



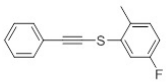
3t

126 MHz, $CDCl_3$



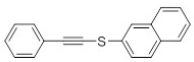
3t

470 MHz, $CDCl_3$



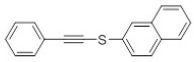
3t

500 MHz, $CDCl_3$



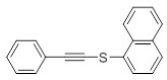
3u

126 MHz, $CDCl_3$



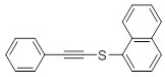
3u

500 MHz, $CDCl_3$



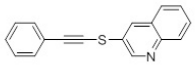
3v

126 MHz, $CDCl_3$



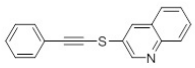
3v

500 MHz, $CDCl_3$



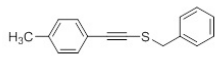
3w

126 MHz, $CDCl_3$



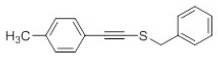
3w

500 MHz, $CDCl_3$



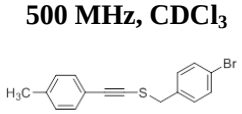
3x

126 MHz, $CDCl_3$



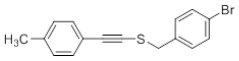
3x

500 MHz, $CDCl_3$



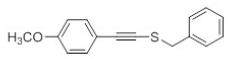
3y

126 MHz, $CDCl_3$



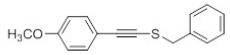
3y

500 MHz, $CDCl_3$



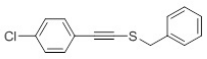
3z

126 MHz, $CDCl_3$



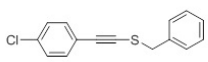
3z

500 MHz, $CDCl_3$



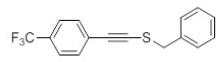
3aa

126 MHz, $CDCl_3$



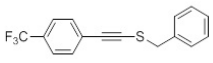
3aa

500 MHz, $CDCl_3$



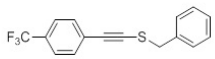
3ab

126 MHz, $CDCl_3$



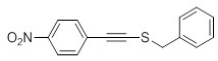
3ab

470 MHz, $CDCl_3$



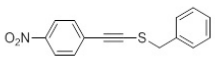
3ab

500 MHz, $CDCl_3$

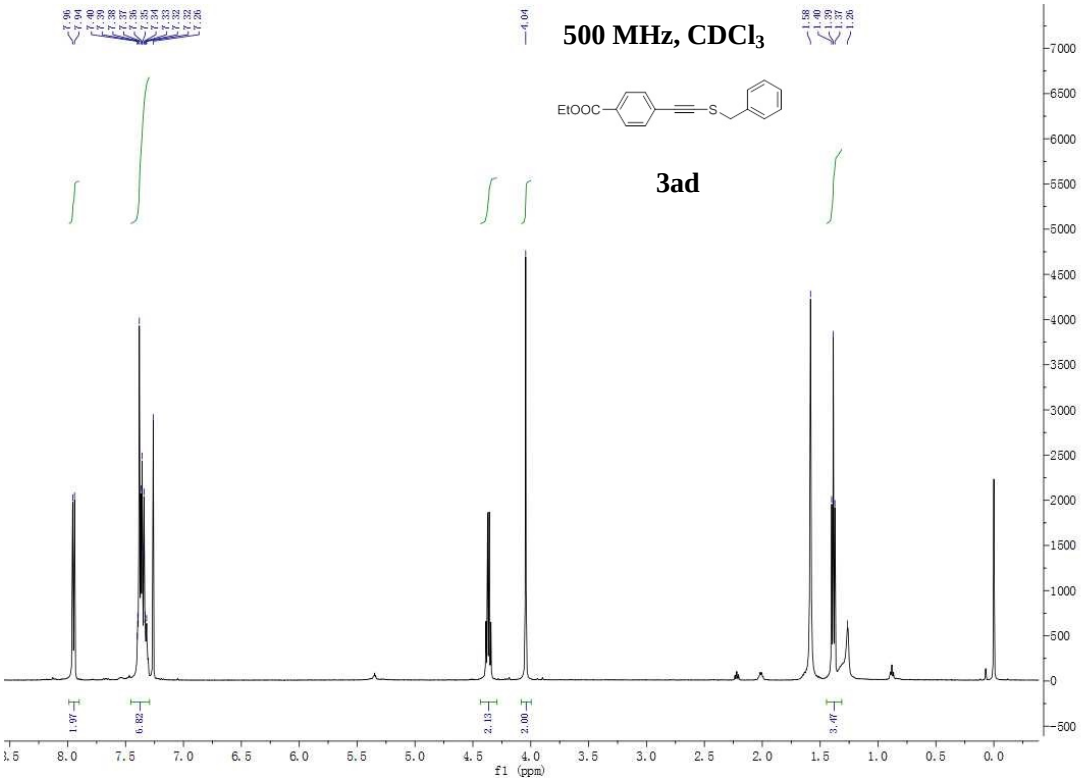


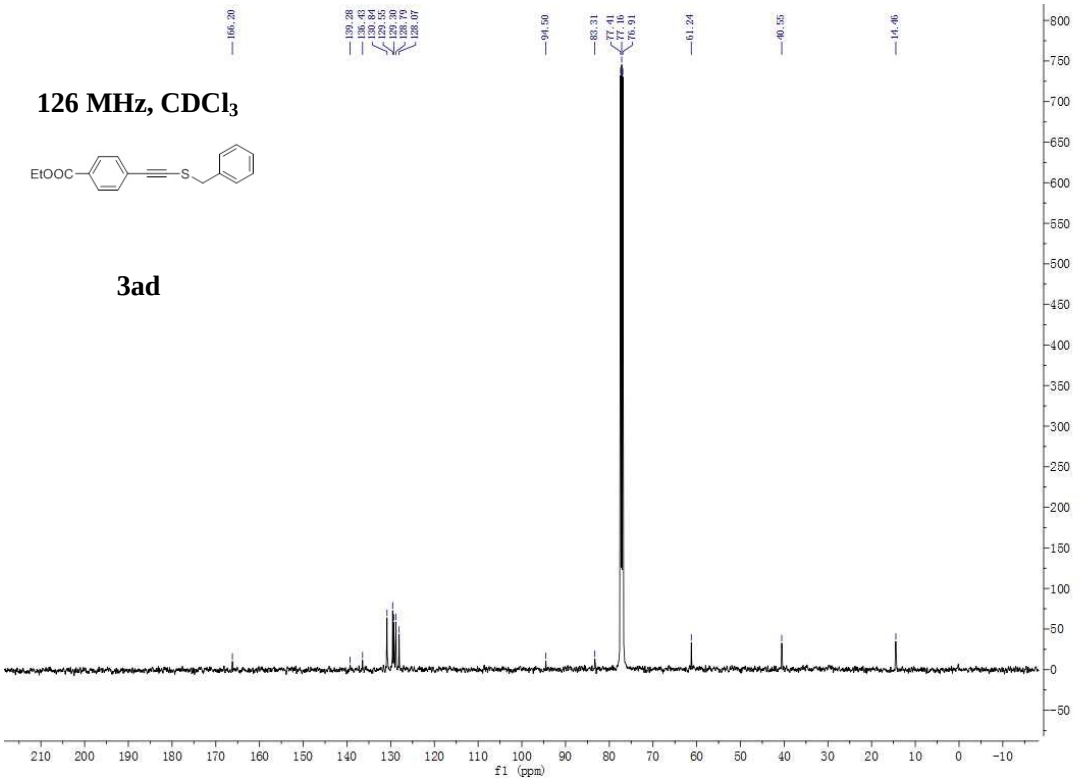
3ac

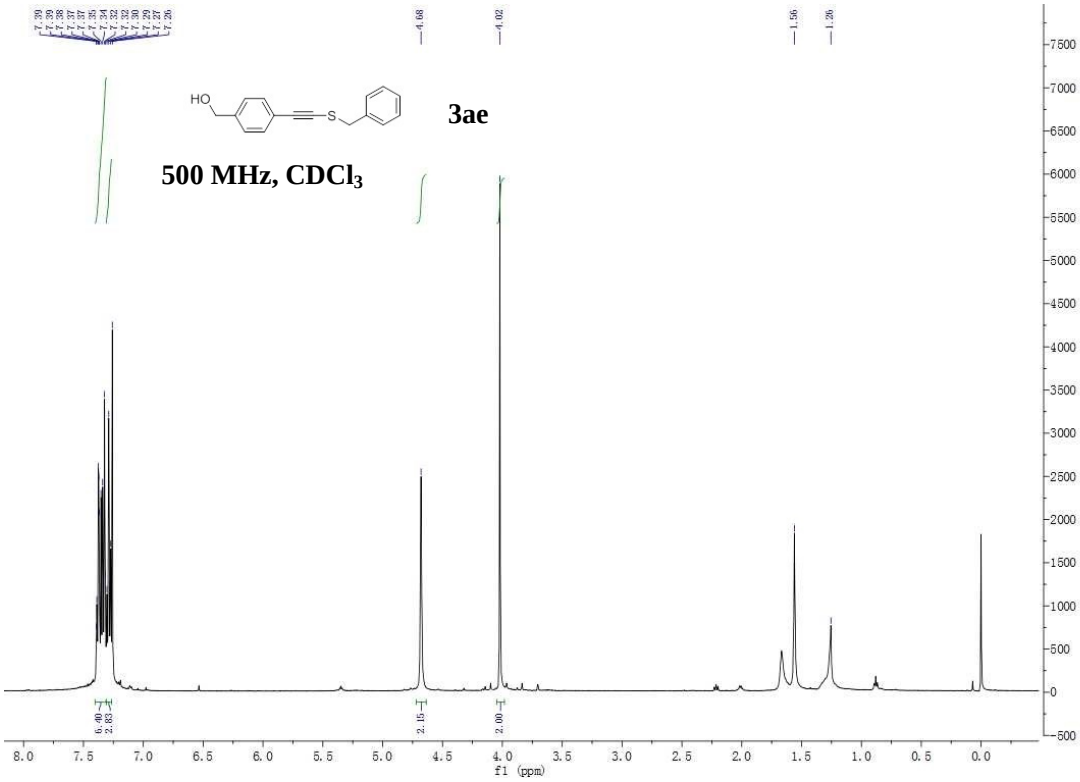
126 MHz, $CDCl_3$

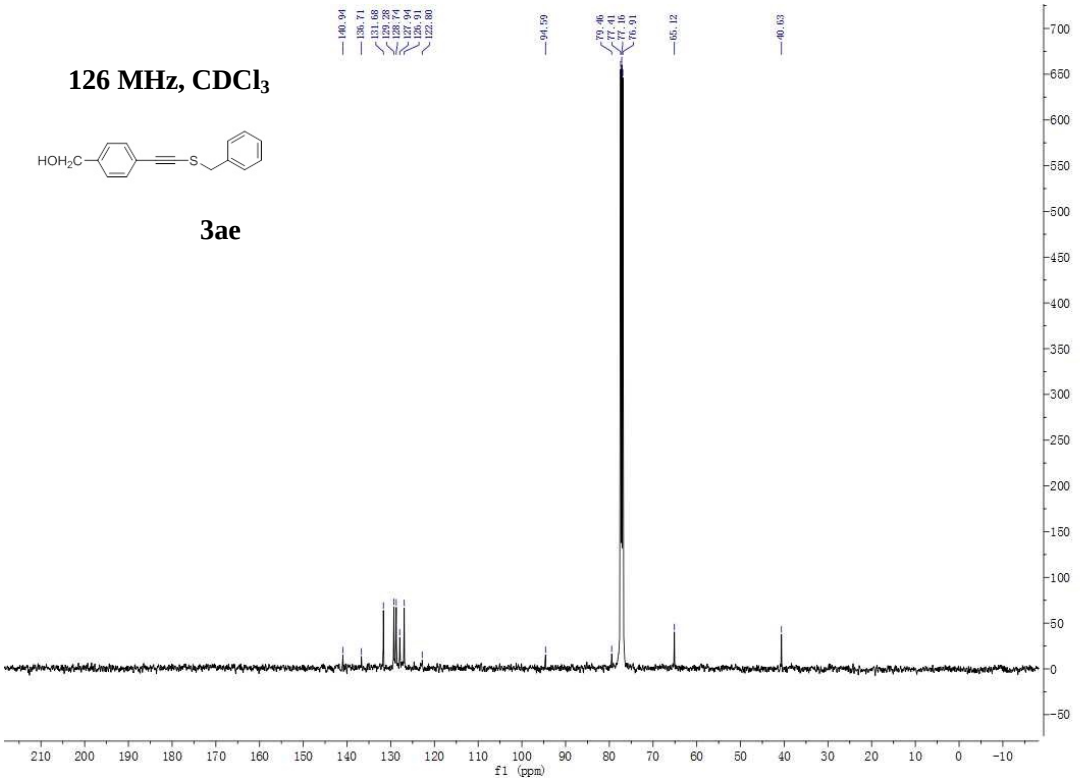


3ac

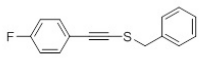

500 MHz, CDCl3
EtOOC
S
3ad
f1 (ppm)


126 MHz, CDCl3
EtOOC
S
3ad
f1 (ppm)


HO
S
3ae
500 MHz, CDCl3
f1 (ppm)

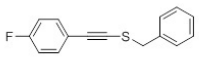

126 MHz, CDCl3
HOH2C
S
3ae
f1 (ppm)

500 MHz, $CDCl_3$



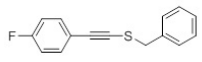
3af

126 MHz, $CDCl_3$

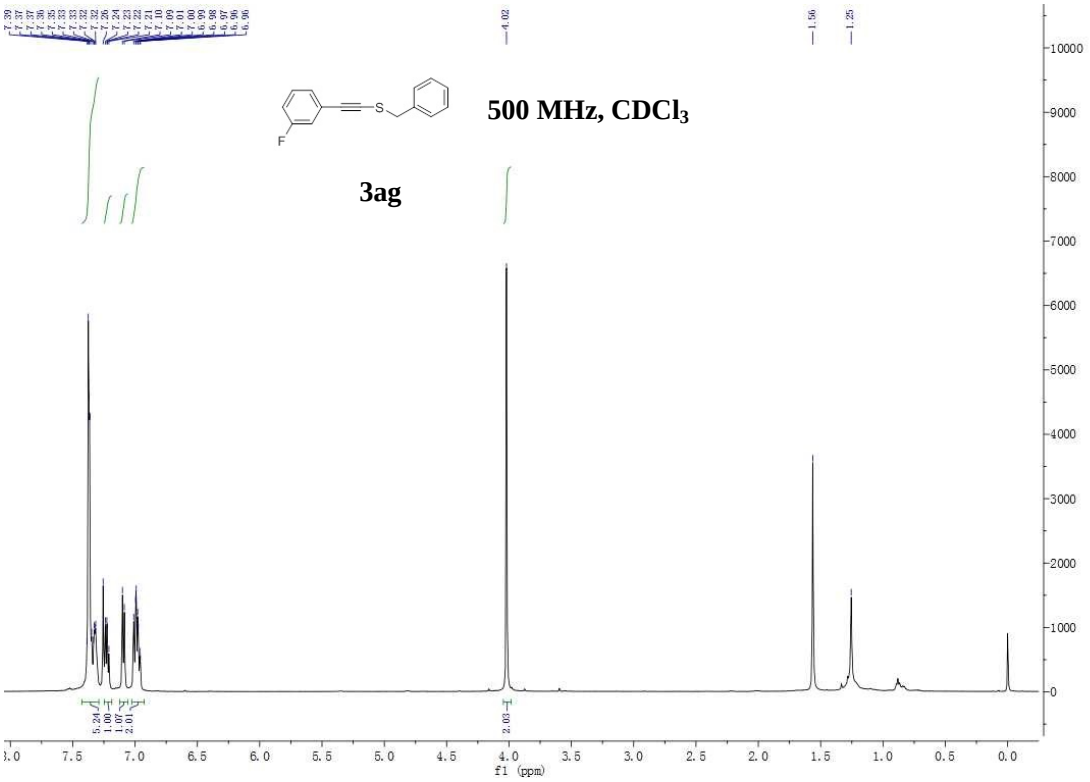


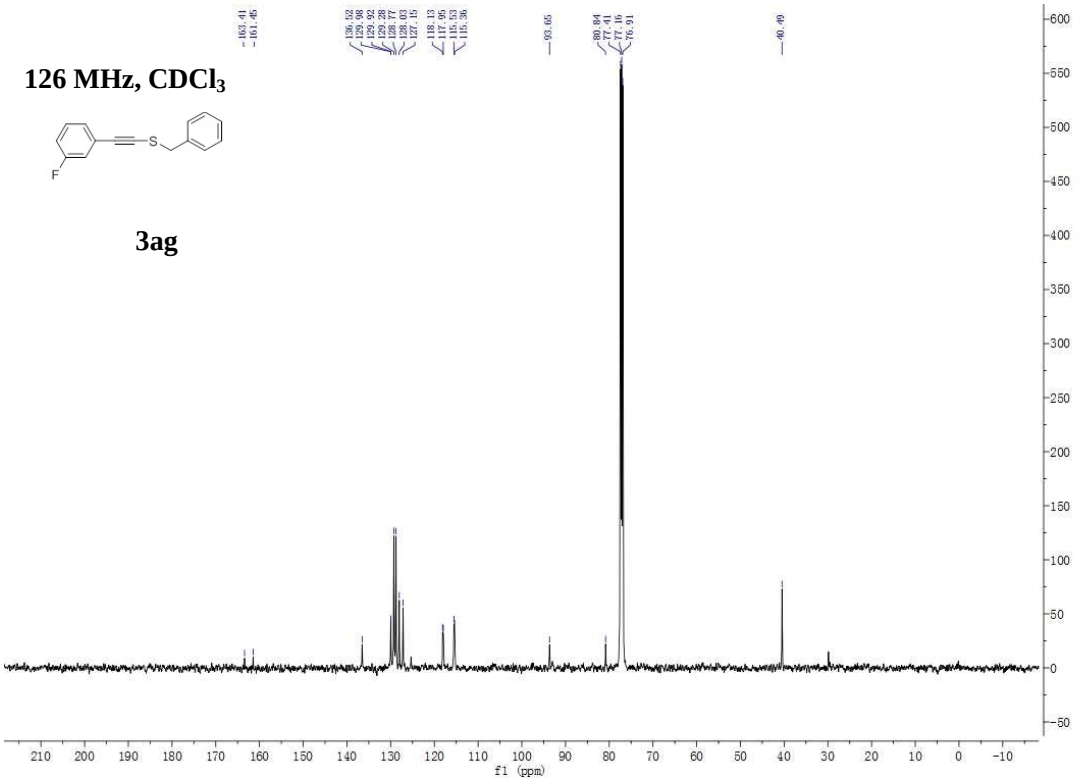
3af

470 MHz, $CDCl_3$

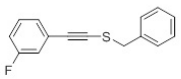


3af


500 MHz, CDCl3
3ag
f1 (ppm)

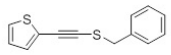

126 MHz, CDCl3
3ag
f1 (ppm)

470 MHz, $CDCl_3$



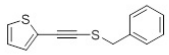
3ag

500 MHz, $CDCl_3$



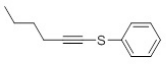
3ah

126 MHz, $CDCl_3$



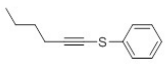
3ah

500 MHz, $CDCl_3$



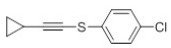
3ai

126 MHz, $CDCl_3$



3ai

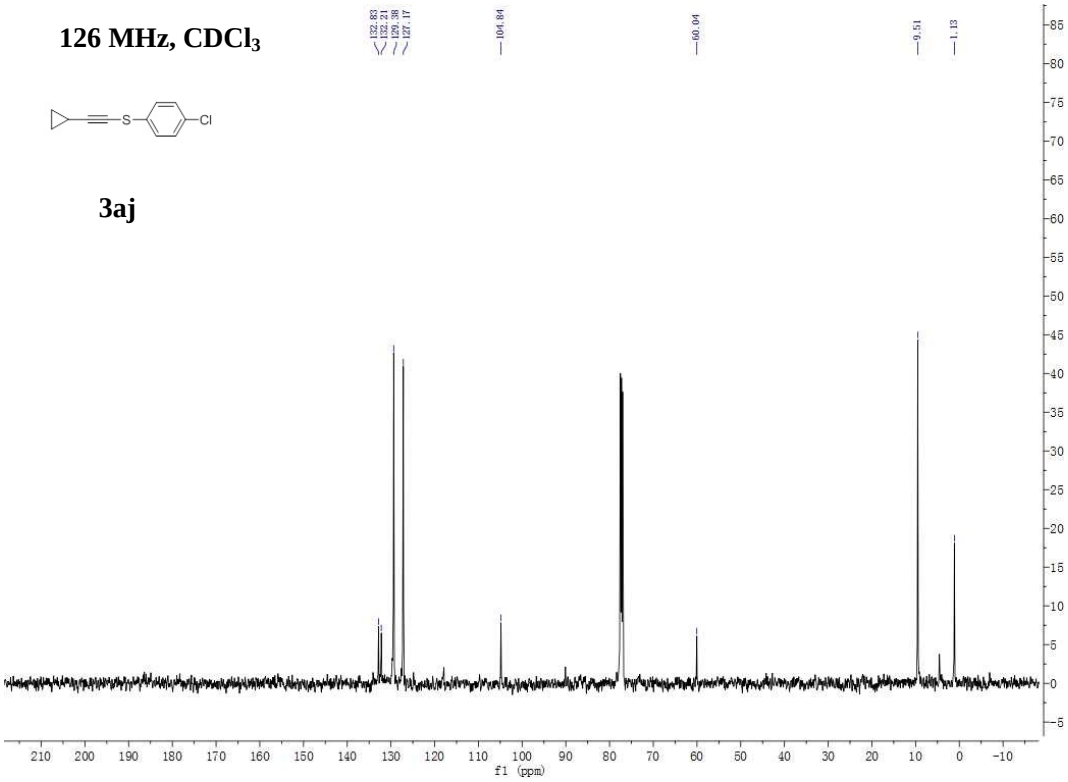
500 MHz, $CDCl_3$



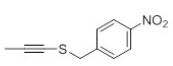
3aj

126 MHz, $CDCl_3$

3aj

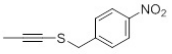


500 MHz, $CDCl_3$



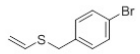
3ak

126 MHz, $CDCl_3$



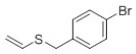
3ak

500 MHz, $CDCl_3$



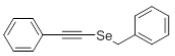
3al

126 MHz, $CDCl_3$



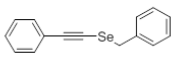
3al

500 MHz, $CDCl_3$



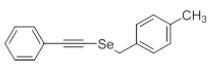
5a

126 MHz, $CDCl_3$



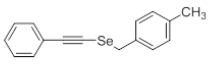
5a

500 MHz, $CDCl_3$



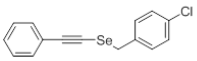
5b

126 MHz, $CDCl_3$



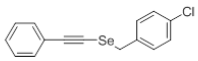
5b

500 MHz, $CDCl_3$



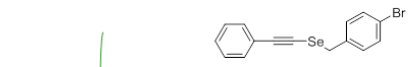
5c

126 MHz, $CDCl_3$



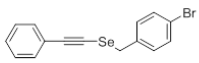
5c

500 MHz, $CDCl_3$



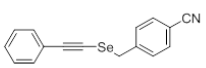
5d

126 MHz, $CDCl_3$



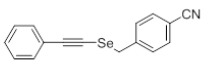
5d

500 MHz, $CDCl_3$

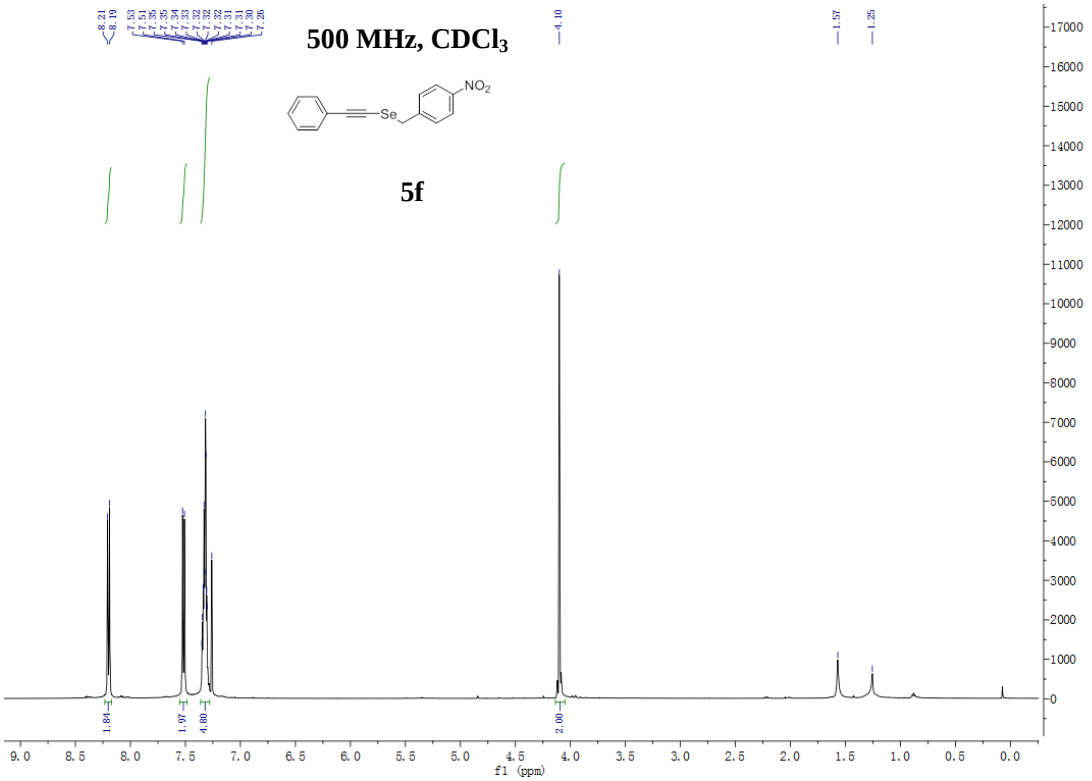


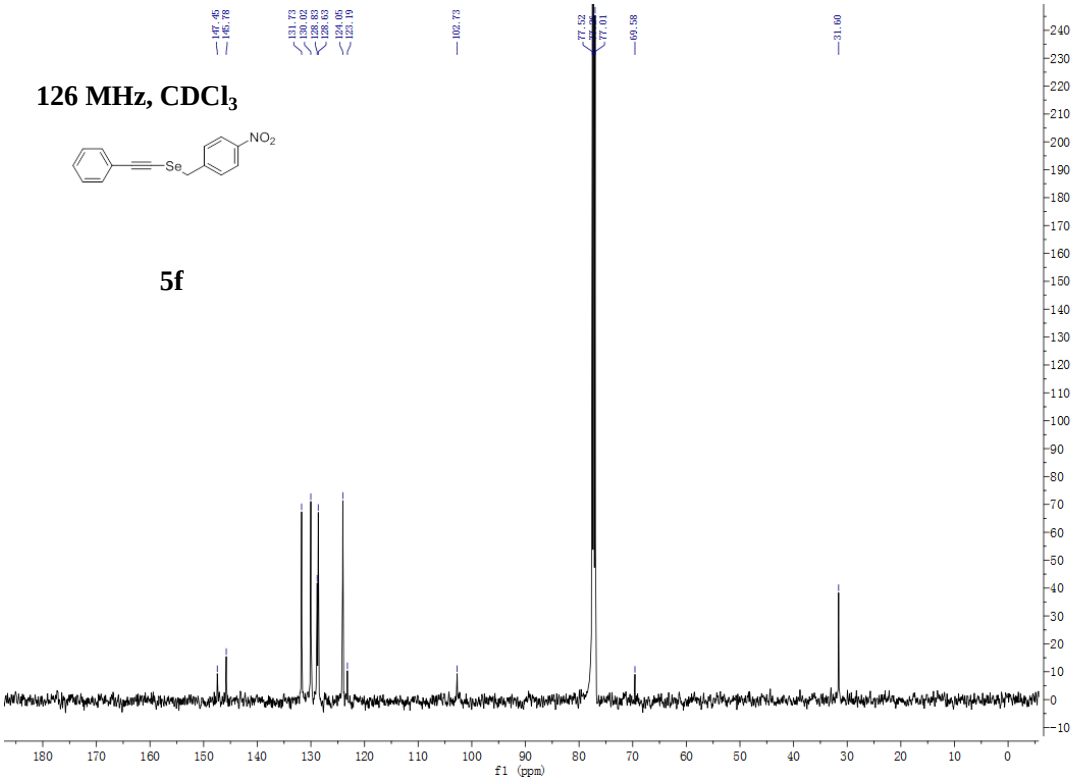
5e

500 MHz, $CDCl_3$

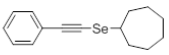


5e


500 MHz, CDCl3
NO2
Se
5f
8.21
8.19
7.53
7.51
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.26
4.10
1.57
1.25
1.84
1.97
4.80
2.00
f1 (ppm)

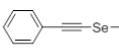

126 MHz, CDCl3
NO2
Se
5f
147.45
145.78
131.73
130.02
128.83
128.63
124.05
123.10
102.73
77.52
77.00
77.01
69.58
31.60
f1 (ppm)

500 MHz, $CDCl_3$



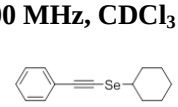
5g

126 MHz, $CDCl_3$



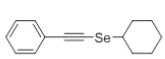
5g

500 MHz, $CDCl_3$



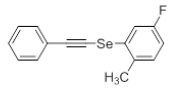
5h

126 MHz, $CDCl_3$



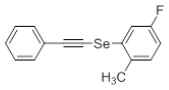
5h

500 MHz, $CDCl_3$



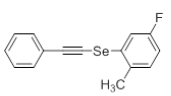
5i

126 MHz, $CDCl_3$



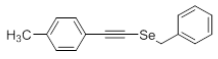
5i

500 MHz, $CDCl_3$



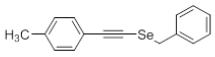
5i

500 MHz, $CDCl_3$



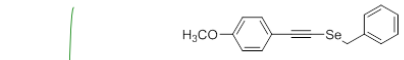
5j

126 MHz, $CDCl_3$



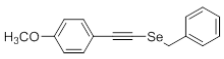
5j

500 MHz, $CDCl_3$



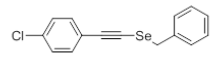
5k

126 MHz, $CDCl_3$



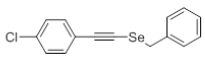
5k

500 MHz, $CDCl_3$



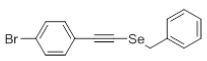
5l

126 MHz, $CDCl_3$



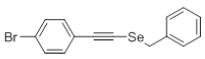
5l

500 MHz, $CDCl_3$



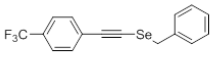
5m

126 MHz, $CDCl_3$



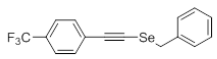
5m

500 MHz, $CDCl_3$



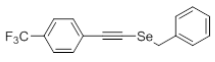
5n

126 MHz, $CDCl_3$



5n

500 MHz, $CDCl_3$



5n