Photoredox Catalytic Deoxygenative Divergent Functionalizations of Alcohols Assisted by N, O-Heterocyclic Carbenes

(Supporting Information)

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1. General Information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. All new compounds were fully characterized. NMR-spectra were recorded on ARX-600 MHz Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26) if collected in $CDCl_3$. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00). ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25-mL schlenk tubes with Teflon screw caps under of N_2, using IKA stirrer with metal heating module as heating source. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Blue LED (45 W, λmax = 440-450 nm) purchased was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.

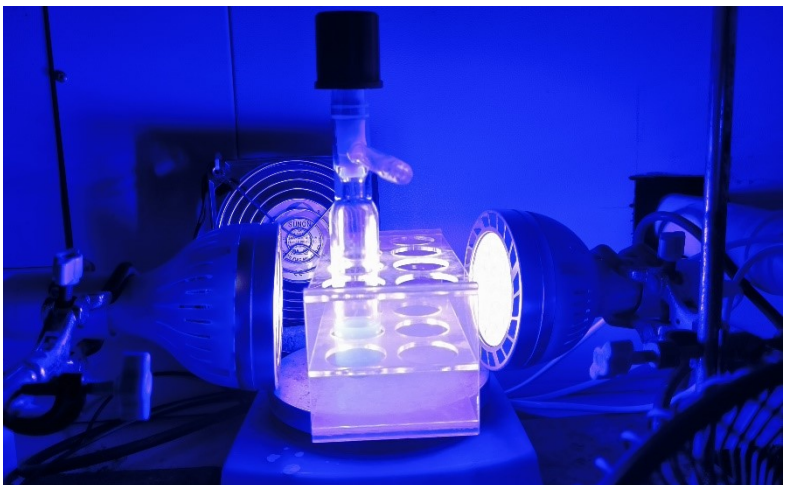
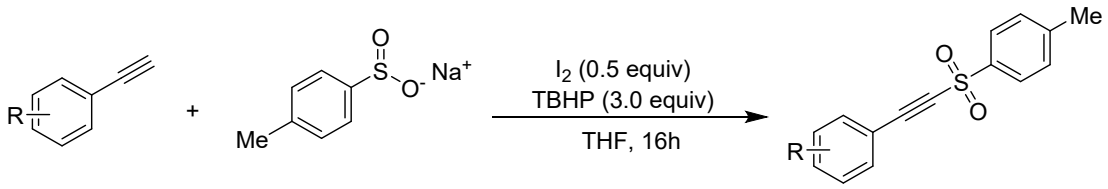


Figure S1. Reaction set up for this project

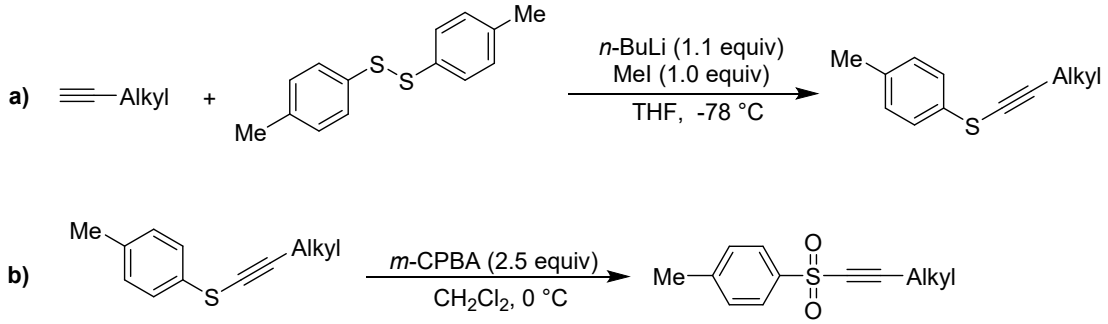
2. General Procedure for Preparation of Radical Receptor

2.1 General Procedure for Preparation of Aromatic Sulfone-type Alkynes.



According to the reported procedure[1]. To a suspension sodium *p*-toluenesulfinate (1.78 g, 10.0 mmol, 2.0 equiv) in THF (25 mL) was added alkynes (5.0 mmol, 1.00 equiv.) followed by iodine (0.20 g, 2.5 mmol, 0.50 equiv), TBHP (15 mmol, 3 equiv). The mixture was stirred for 16 h at room temperature before the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. $NaHCO_3$ was added and the product extracted into DCM. The combined organic phases were washed with H_2O, brine, which were dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography.

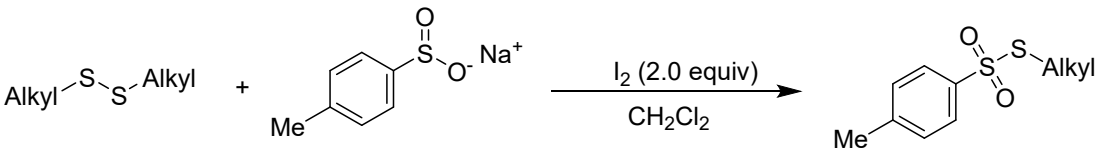
2.2 General Procedure for Preparation of Aliphatic Sulfone-type Alkynes.



According to the reported procedure[2]. To a solution of a terminal alkyne (2.0 mmol 1.0 equiv) in THF (10 mL) cooled to -78 °C was added *n*-BuLi (2.2 mmol, 2.5 M in hexane, 1.1 equiv) dropwise. The resulting solution was stirred for 1 h and then warmed to r.t., to which was added a premixed solution of phenyl disulfide (2.0 mmol 1.0 equiv) with an equivalent of methyl iodide (2.0 mmol 1.0 equiv). The reaction was monitored by TLC. Upon completion, aqueous NH_4Cl was added to quench the reaction. The aqueous layer was extracted with hexanes three times. The combined extracts were washed with brine and dried over $MgSO_4$. After rotary evaporation, the residue was

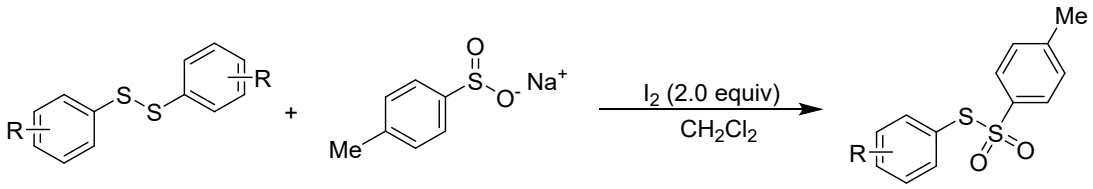
further condensed under high vacuum to remove methyl phenyl sulfide, and then purified by silica gel column chromatograph to afford the corresponding alkynyl sulfide. *m*-CPBA (85%, 5.0 mmol, 2.5 equiv) was added at 0 °C to a solution of the sulfide (2 mmol, 1.0 equiv) in dichloromethane (12 mL). The reaction mixture was stirred for 1 h at 0 °C and then for 12 h at room temperature. After reaction, the reaction mixture was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatograph (eluent: petroleum ether/ethyl acetate) to afford the desired sulfone alkyne.

2.3 General Procedure for Preparation of Aliphatic Sulfone-type Sulfides.



According to the reported procedure[3]. To a mixture of sodium *p*-toluenesulfinate (1.05 g, 6.4 mmol, 3.2 equiv) and 1,2-alkyl disulfide (2.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added I_2 (1.02 g, 4.0 mmol, 2.0 equiv). The mixture was stirred until the disulfide was consumed (2 h), then CH_2Cl_2 was added followed by aqueous $Na_2S_2O_3$. The organic layer was washed with H_2O and dried over $MgSO_4$. The organic layer was concentrated under reduced pressure. The crude product was purified by flash column chromatography to afford the desired **aliphatic** sulfone sulfides.

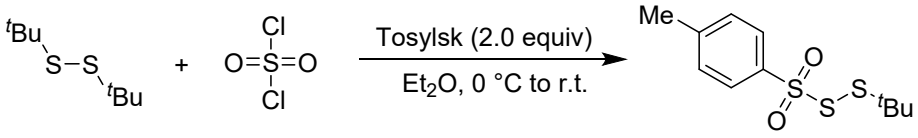
2.4 General Procedure for Preparation of Aromatic Sulfone-type Sulfides



According to the reported procedure[3].To a mixture of sodium *p*-toluenesulfinate (1.05 g, 6.4 mmol, 3.2 equiv) and diphenyldisulfide (0.44 g, 2.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added I_2 (1.02 g, 4.0 mmol, 2.0 equiv) while mixing. The mixture was stirred until the disulfide was consumed (2 h), then CH_2Cl_2 was added followed by aqueous $Na_2S_2O_3$. The organic layer was washed with H_2O and dried over $MgSO_4$. The

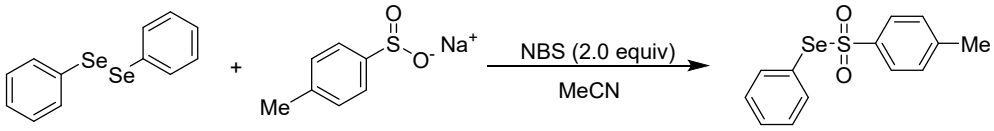
organic layer was concentrated under reduced pressure. The crude product was purified by flash column chromatography omatography to afford the aromatic sulfone-type sulfides.

2.5 General Procedure for Preparation of Sulfone-type Disulfide



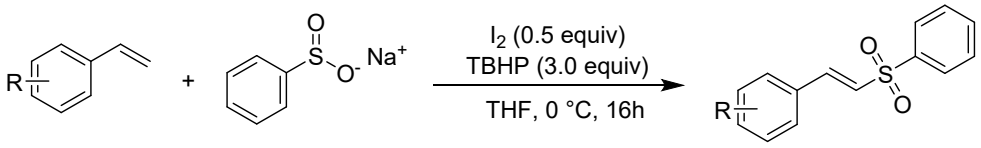
According to the reported procedure[4].To a solution of *t*ert-butyl disulfide (561mg, 3.15 mmol, 1.05 equiv) in 12 mL of Et_2O was added sulfuryl chloride (405 mg, 3 mmol, 1.00 equiv) at 0 °C. 10 min later, a solution of TosylSK (1.36 g, 6 mmol, 2.00 equiv) in 30 mL of acetone was added dropwise at 0 °C. The reaction was then stirred at room temperature for 45 min. The mixture was diluted with EtOAc, washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude residue was purified using silica gel column chromatography (petroleum ester/EtOAc=10:1) to afford product (680 mg, 82%).

2.6 General Procedure for Preparation of Sulfone-type Selenide



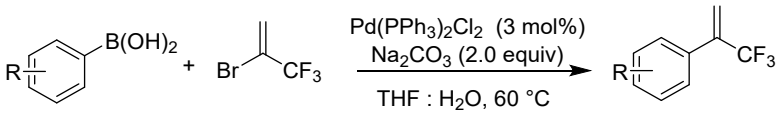
According to the reported procedure[3].Asolution of sodium *p*-toluenesulfinate (1.78 g, 10 mmol, 4.0 equiv), diselenide (785 mg, 2.5mmol, 1.0 equiv), and NBS (890 mg, 5 mmol, 2.0 equiv) in MeCN (20 mL) was stirred atroom temperature. The reaction was monitored by TLC until thesubstrate was completely consumed, the reaction quenched withwater, and the mixture extracted with ethyl acetate. Theorganic layer was dried with anhydrous Na_2SO_4 and concentratedwith a rotary evaporator under reduced pressure. The residue waspurified byflash column chromatography to give product as a yellow solid (1.11 g, 75%).

2.7 General Procedure for Preparation of Aromatic Sulfone-type Alkene



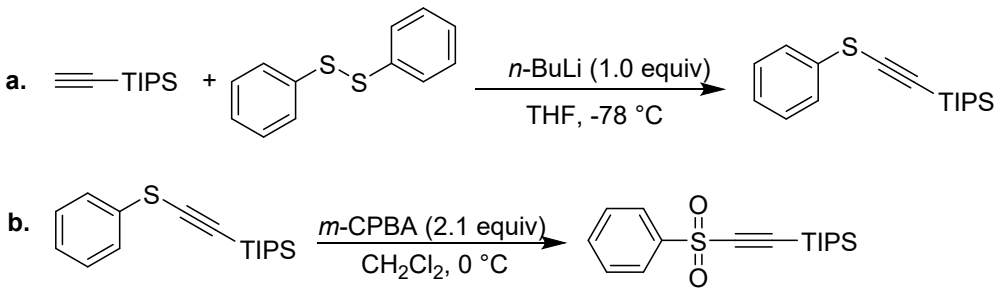
According to the reported procedure[1].To a suspension of benzenesulfinic acid sodium salt (2.46 g, 15.0 mmol, 3.00 equiv.) and NaOAc (0.62 g, 7.5 mmol, 1.50 equiv.) in MeCN (20 mL) was added olefin (5.0 mmol, 1.00 equiv.) followed by iodine (1.9 g, 7.5 mmol, 1.50 equiv.). The mixture was heated to reflux for 1 h before being allowed to cool and the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. $NaHCO_3$ was added and the product extracted into DCM. The combined organic phases were washed with H_2O, brine, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford aromatic sulfone-type alkene.

2.8 General Procedure for Preparation of α-Trifluoromethylstyrene Derivatives



According to the reported procedure[1].To a Schlenk tube equipped with a magnetic stir bar were added aqueous Na_2CO_3 (0.5 M, 8 mL), THF (8 mL), arylboronic acid (2 mmol, 1 equiv), 2-bromo-3,3,3-trifluoropropene (4 mmol, 0.4 mL, 2equiv) and $Pd(PPh_3)_4$ (0.1 mmol, 115.6 mg, 5 mol%) under an N_2 atmosphere. The resulting solution was stirred at 60 °C for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed carefully under reduced pressure. The crude product was purified by flash column chromatography to afford α-trifluoromethylstyrene derivatives.

2.9 General Procedure for Preparation of Triisopropyl((phenylsulfonyl)ethynyl)silane

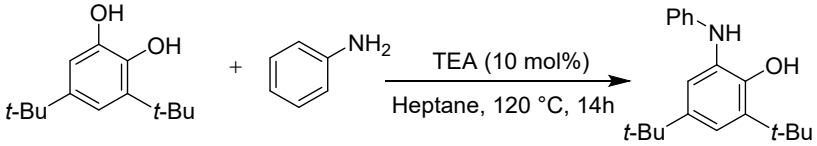


According to the reported procedure[5]. **a.** (Triisopropylsilyl)acetylene (1.18 mL, 5.25 mmol, 1.05 equiv) was dissolved in dry THF (5 mL) and the solution was cooled to -78 °C. *n*-BuLi (2.5 M in hexane, 2.0 mL, 5 mmol, 1.0 equiv) was added dropwise and the mixture was stirred for 30 min at this temperature. Diphenyldisulfide (1.1 g, 5 mmol, 1.0 equiv) in dry THF (2 mL) was slowly added at -78 °C. After being stirred at -78 °C for 30 min, the reaction mixture was allowed to warm up to rt and stirred overnight. The reaction mixture was cooled to 0 °C, stirred for further 10 min and subsequently treated with dist. water. The reaction mixture was diluted with Et_2O. The phases were separated and the aqueous phase was extracted twice with Et_2O. The combined organic phase was washed with aq. NaOH (0.1 M), dist. water and brine. The organic phase was dried over Na_2SO_4, concentrated and the obtained oil was dried under high vacuum. Trimethyl(2-phenylsulfanylethynyl)silane was obtained after FC (heptanes) (1.43 g, 99%).

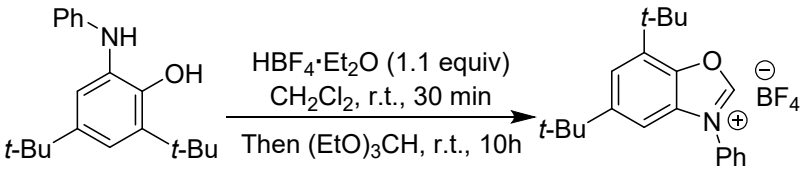
b. To a stirred solution of the crude trimethyl(2- phenylsulfanylethynyl)silane in dry CH_2Cl_2 was added drop wise a solution of *m*-CPBA (85%, 2.38 g,10.5 mmol, 2.1 equiv) in dry CH_2Cl_2 at r.t. over 2 h using a dropping funnel. The white suspension was stirred for 2 h until complete consumption of the thioether. The reaction was cooled to 0 °C and transferred into a beaker flask. Sat. $NaHCO_3$ was added and the mixture was stirred vigorously for 20 min at r.t. to give a white suspension. The organic phase was

separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed with sat. $NaHCO_3$, water and brine, dried over Na_2SO_4 and concentrated. afforded triisopropyl((phenylsulfonyl)ethynyl)silane (1.55 g, 98%).

3. General Procedure for Preparation of N, O-Heterocyclic Carbenes



Step 1: To a suspension of 3,5-di-*t*ert-butylcatechol (2.22 g, 10 mmol, 1.0 equiv) and aniline (1 mL, 10.2 mmol, 1.02 equiv) in *n*-heptane (10 mL), triethylamine (0.1g, 1 mmol, 0,1 equiv) was added in one portion under air. The resulting mixture was heated with dean-stark trap under air for 14 h. (Oil bath temperature was 120 °C. The suspension would form a brown homogenous solution upon heating.) The resulting reaction crude mixture was slowly cooled down to room temperature. The entire reaction mixture was stored at -20 °C for additional 12 h. Then the desired product was collected by filtration, washed with cold hexane, and air dried. The white precipitate (2.46 g, 8.3 mmol, 83% yield) was pure enough for next step, no further purification was required. The ^{1}H-NMR and ^{13}C-NMR data was consistent with literature report.[6]

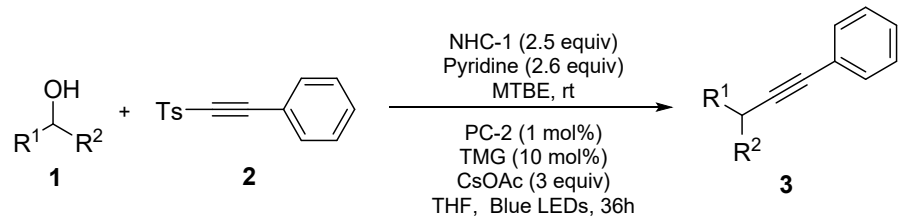


Step 2: Tetrafluoroboric acid diethyl ether complex (1.2 mL; 8.72 mmol; 1.05 equiv) was added dropwise to a suspension of 3,5-di-*t*ert-butyl-2-hydroxy-N-phenylaniline (2.465 g, 8.3 mmol) with 8 mL of dry dichloromethane in 50 ml flask under nitrogen atmosphere. After 5 min finishing the addition, the suspension became a red

homogenous solution. Further stirringat room temperature for additional 25 min, then the solvent was carefully removed by rotavap. The resulting solid was dissolved in triethyl orthoformate (21 mL) at room temperature, white solid cake precipitate out after several minutes. The suspension was stirred at room temperature under nitrogen atmosphere for additional 8 hours. The desired product was collected by filtration as a white powder. The solid was further washed with 100 ml dry diethyl ether to give the pure NHC salts. (2.95 g; 7.5 mmol; 91%). ^{1}H-NMR and ^{13}C-NMR data are consistent with literature report.[6]

4. General Procedure for Deoxygenative Divergent Functionalizations of Alcohols

4.1 General Procedure A



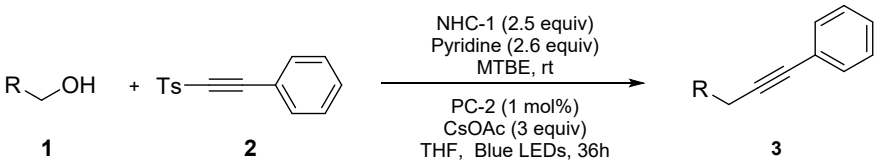
To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **1a** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (2.0 μmol, 1 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **2a** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. TMG (0.02 mmol, 10 mol%) was added upon completion of the sparge. The mixture was then

stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The reaction mixture was then directly purified by column chromatography.

4.2 General Procedure B

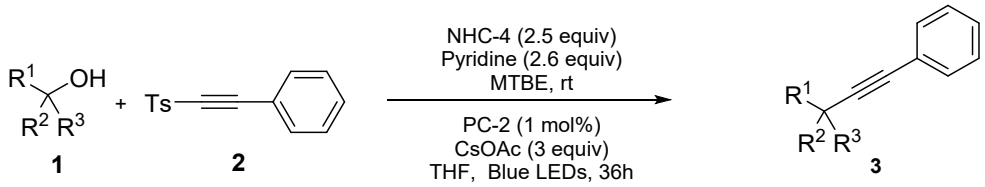


To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **1** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (2.0 μmol, 1 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **2** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl tert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The reaction mixture was then directly purified by column chromatography.

4.3 General Procedure C

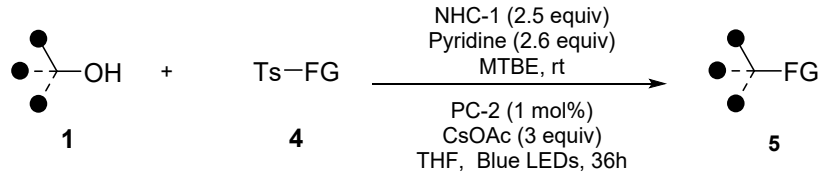


To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-4 (0.5 mmol, 1.00 equiv), **1** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (2.0 μmol, 1 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **2** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The reaction mixture was then directly purified by column chromatography.

4.4 General Procedure D



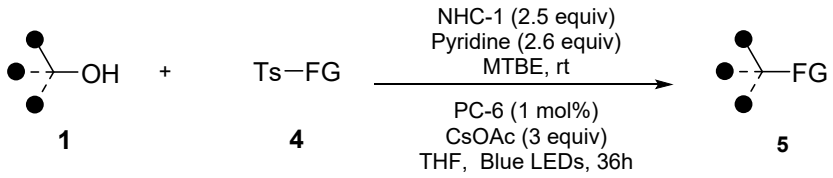
To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **1** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2

(2.0 μmol, 1 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **4** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The reaction mixture was then directly purified by column chromatography.

4.5 General Procedure E



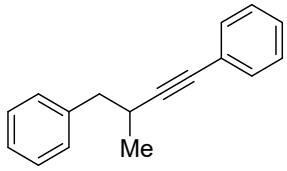
To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **1** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-6 (10 μmol, 5 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **4** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc

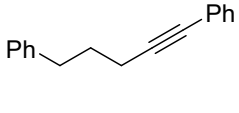
was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The reaction mixture was then directly purified by column chromatography.

5. Experimental data for products



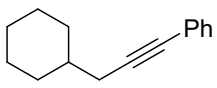
3a

(3-Methylbut-1-yne-1,4-diyl)dibenzene (3a): The desired product was prepared according to General Procedure A. Colorless oil, 38.7 mg (88% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.35 (m, 2H), 7.34 – 7.21 (m, 8H), 2.97 – 2.89 (m, 2H), 2.83 – 2.77 (m, 1H), 1.28 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 152.5, 139.6, 131.5, 129.4, 128.2, 127.6, 126.3, 123.9, 94.1, 81.6, 43.2, 28.6, 20.6; **HRMS m/z (ESI)** calcd for $C_{17}H_{17}$ $(M + H)^+$ 221.1325, found 221.1325.



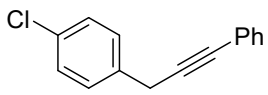
3b

Pent-1-yne-1,5-diyldibenzene (3b): The desired product was prepared according to General Procedure B. Colorless oil, 20.4 mg (46% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 – 7.40 (m, 2H), 7.32 – 7.27 (m, 5H), 7.25 – 7.18 (m, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.94 (p, *J* = 7.1 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.6, 131.6, 128.6, 128.4, 128.2, 127.5, 125.9, 124.0, 89.8, 81.2, 34.8, 30.3, 18.8; **HRMS m/z (ESI)** calcd for $C_{17}H_{17}$ $(M + H)^+$ 221.1325, found 221.1324.



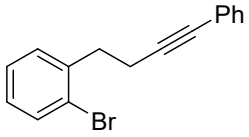
3c

(3-Cyclohexylprop-1-yn-1-yl)benzene (3c): The desired product was prepared according to General Procedure B. Colorless oil, 22.2 mg (56% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 – 7.38 (m, 2H), 7.30 – 7.24 (m, 3H), 2.30 (d, *J* = 6.7 Hz, 2H), 1.91 – 1.84 (m, 2H), 1.75 (dt, *J* = 13.4, 3.5 Hz, 2H), 1.70 – 1.66 (m, 1H), 1.57 (dddd, *J* = 14.7, 11.4, 6.7, 3.3 Hz, 1H), 1.33 – 1.24 (m, 2H), 1.19 (tt, *J* = 12.6, 3.4 Hz, 1H), 1.07 (qd, *J* = 12.2, 3.3 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.5, 128.1, 127.4, 124.1, 89.3, 81.4, 37.5, 32.8, 27.2, 26.3, 26.2; **HRMS m/z (ESI)** calcd for $C_{15}H_{19}$ $(M + H)^+$ 199.1482, found 199.1482.



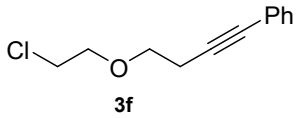
3d

1-Chloro-4-(3-phenylprop-2-yn-1-yl)benzene (3d): The desired product was prepared according to General Procedure B. Yellow oil, 19.5 mg (43% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.43 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.30 (m, 5H), 3.80 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 135.2, 132.4, 131.6, 129.3, 128.6, 128.3, 128.0, 123.4, 86.8, 83.0, 25.2; **HRMS m/z (ESI)** calcd for $C_{15}H_{12}Cl$ $(M + H)^+$ 227.0622, found 227.0634.



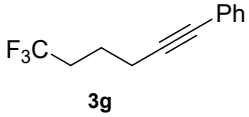
3e

1-Bromo-2-(4-phenylbut-3-yn-1-yl)benzene (3e): The desired product was prepared according to General Procedure B. Colorless oil, 36.7 mg (65% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.30 – 7.26 (m, 4H), 7.10 (td, *J* = 7.7, 1.8 Hz, 1H), 3.06 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.7, 132.8, 131.5, 130.9, 128.2, 128.1, 127.6, 127.3, 124.4, 123.7, 89.0, 81.5, 35.4, 19.8; **HRMS m/z (ESI)** calcd for $C_{16}H_{14}Br$ $(M + H)^+$ 285.0274, found 285.0273.



3f

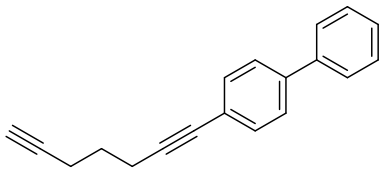
(4-(2-Chloroethoxy)but-1-yn-1-yl)benzene (3f): The desired product was prepared according to General Procedure B. Yellow oil, 39.6 mg (95% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.39 (m, 2H), 7.28 (dd, *J* = 4.9, 1.9 Hz, 3H), 3.79 (t, *J* = 5.9 Hz, 2H), 3.73 (t, *J* = 7.1 Hz, 2H), 3.65 (t, *J* = 5.9 Hz, 2H), 2.72 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.2, 127.8, 123.5, 86.3, 81.7, 71.0, 69.6, 42.7, 20.8; **HRMS m/z (ESI)** calcd for $C_{12}H_{14}ClO$ $(M + H)^+$ 209.0728, found 209.0728.



3g

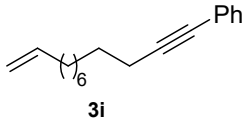
(6,6,6-Frifluorohex-1-yn-1-yl)benzene (3g): The desired product was prepared according to General Procedure B. Colorless oil, 21.0 mg (49% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.38 (m, 2H), 7.30 (dt, *J* = 4.4, 2.8 Hz, 3H), 2.53 (t, *J* = 6.9 Hz, 2H), 2.34 – 2.24 (m, 2H), 1.92 – 1.84 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.3, 127.9,

127.1 (q, *J* = 276.2 Hz) 123.4, 87.9, 81.9, 32.8 (q, *J* = 28.7 Hz), 21.3 (q, *J* = 3.0 Hz), 18.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -66.1; **HRMS m/z (ESI)** calcd for $C_{12}H_{12}F_3$ $(M + H)^+$ 213.0886, found 213.0885.



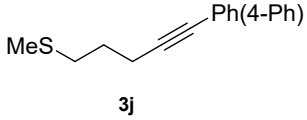
3h

4-(Hepta-1,6-diyn-1-yl)-1,1'-biphenyl (3h): The desired product was prepared according to General Procedure B. Brown oil, 29.5 mg (60% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.60 – 7.57 (m, 2H), 7.54 – 7.51 (m, 2H), 7.48 – 7.42 (m, 4H), 7.37 – 7.33 (m, 1H), 2.58 (t, *J* = 7.0 Hz, 2H), 2.40 (td, *J* = 7.1, 2.7 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.86 (p, *J* = 7.1 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.5, 140.4, 132.0, 128.8, 127.5, 127.0, 126.9, 122.7, 89.6, 83.6, 81.1, 68.9, 27.6, 18.6, 17.6; **HRMS m/z (ESI)** calcd for $C_{14}H_{15}$ $(M + H)^+$ 245.1325, found 245.1324.



3i

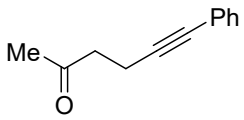
Dodec-11-en-1-yn-1-ylbenzene (3i): The desired product was prepared according to General Procedure B. Light yellow, 25.2 mg (52% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 (dd, *J* = 7.6, 2.2 Hz, 2H), 7.29 – 7.26 (m, 3H), 5.82 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.03 – 4.90 (m, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.05 (q, *J* = 7.0 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.48 – 1.42 (m, 2H), 1.38 (q, *J* = 7.0 Hz, 2H), 1.34 – 1.31 (m, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.2, 131.5, 128.2, 127.4, 124.1, 114.1, 90.4, 80.5, 33.8, 29.4, 29.09, 29.08, 28.91, 28.89, 28.7, 19.4; **HRMS m/z (ESI)** calcd for $C_{18}H_{25}$ $(M + H)^+$ 241.1951, found 241.1949.



3j

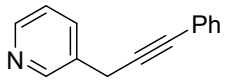
(5-([1,1'-Biphenyl]-4-yl)pent-4-yn-1yl)(methyl) sulfane (3j): The desired product was prepared according to General Procedure B. Yellow oil, 23.4 mg (44% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 – 7.56 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.36 – 7.33 (m, 1H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 1.92 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.45, 140.38, 131.9, 128.8,

127.5, 127.0, 126.9, 122.7, 89.8, 81.1, 33.2, 28.1, 18.5, 15.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{19}S$ $(M + H)^+$ 267.1202, found 267.1200.



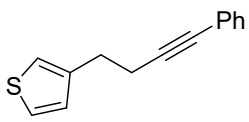
3k

6-Phenylhex-5-yn-2-one (3k): The desired product was prepared according to General Procedure B. Yellow oil, 23.8 mg (69% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.36 (m, 2H), 7.27 (dd, *J* = 5.0, 1.8 Hz, 3H), 2.77 (dd, *J* = 8.2, 6.2 Hz, 2H), 2.67 (dd, *J* = 8.5, 6.4 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 206.6, 131.5, 128.2, 127.7, 123.6, 88.5, 81.0, 42.5, 29.9, 14.0; **HRMS m/z (ESI)** calcd for $C_{12}H_{13}O$ $(M + H)^+$ 173.0961, found 173.0963.



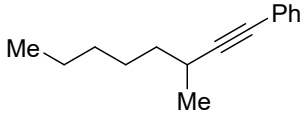
3l

3-(3-Phenylprop-2-yn-1-yl)pyridine (3l): The desired product was prepared according to General Procedure B. Brownish-black solid, 25.5 mg (66% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.65 (d, *J* = 2.5 Hz, 1H), 8.53 – 8.50 (m, 1H), 7.78 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.33 – 7.27 (m, 4H), 3.84 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.4, 148.1, 135.6, 132.5, 131.6, 128.3, 128.1, 123.5, 123.2, 85.9, 83.3, 23.3; **HRMS m/z (ESI)** calcd for $C_{14}H_{12}N$ $(M + H)^+$ 194.0964, found 194.0964.



3m

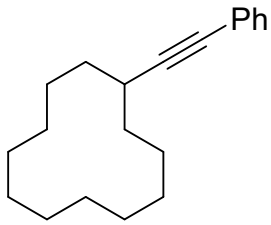
3-(4-Phenylbut-3-yn-1-yl)thiophene (3m): The desired product was prepared according to General Procedure B. Yellow oil, 39.0 mg (92% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.37 (m, 2H), 7.28 (ddd, *J* = 6.0, 3.6, 2.5 Hz, 4H), 7.08 (dq, *J* = 3.1, 1.0 Hz, 1H), 7.04 (dd, *J* = 5.0, 1.4 Hz, 1H), 2.96 (td, *J* = 7.4, 0.8 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.1, 131.5, 128.2, 128.1, 127.6, 125.4, 123.8, 120.9, 89.5, 81.3, 29.6, 20.9; **HRMS m/z (ESI)** calcd for $C_{14}H_{13}S$ $(M + H)^+$ 213.0733, found 213.0733.



3n

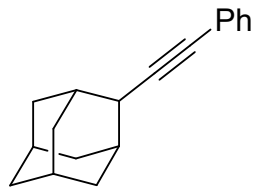
(3-Methyloct-1-yn-1-yl)benzene (3n): The desired product was prepared according to General Procedure A. Yellow oil, 35.2 mg (88% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40

(dd, J = 7.9, 1.7 Hz, 2H), 7.30 – 7.25 (m, 3H), 2.68 – 2.60 (m, 1H), 1.56 – 1.43 (m, 4H), 1.37 – 1.30 (m, 4H), 1.26 (d, J = 6.9 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.1, 127.4, 124.2, 94.9, 80.7, 37.0, 31.7, 27.1, 26.5, 22.6, 21.1, 14.0; **HRMS m/z (ESI)** calcd for $C_{15}H_{21}$ $(M + H)^+$ 201.1638, found 201.1634.



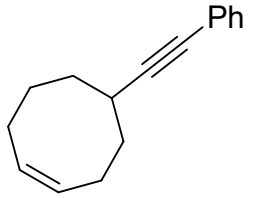
3o

(Phenylethynyl)cyclododecane (3o): The desired product was prepared according to General Procedure A. Yellow oil, 45.6 mg (85% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 (dd, J = 7.8, 2.2 Hz, 2H), 7.27 (q, J = 7.7, 7.0 Hz, 3H), 2.70 (tt, J = 7.5, 5.0 Hz, 1H), 1.71 (dq, J = 15.5, 8.6, 7.8 Hz, 2H), 1.64 – 1.52 (m, 4H), 1.44 – 1.29 (m, 16H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.1, 127.3, 124.2, 94.9, 80.2, 29.9, 27.5, 23.93, 23.86, 23.5, 23.4, 22.2; **HRMS m/z (ESI)** calcd for $C_{20}H_{29}$ $(M + H)^+$ 269.2264, found 269.2261.



3p

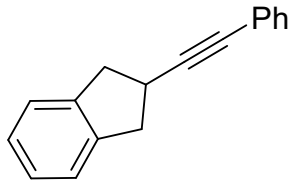
2-(Phenylethynyl)adamantane (3p): The desired product was prepared according to General Procedure A. Colorless oil, 35.8 mg (76% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (dd, J = 8.0, 1.9 Hz, 2H), 7.30 – 7.24 (m, 3H), 2.93 (s, 1H), 2.29 (dd, J = 12.7, 2.9 Hz, 2H), 2.07 – 2.04 (m, 2H), 1.90 – 1.87 (m, 4H), 1.80 – 1.76 (m, 4H), 1.63 (d, J = 12.6 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.5, 128.1, 127.3, 124.3, 94.2, 82.3, 38.2, 37.6, 37.5, 32.9, 32.7, 27.7, 27.3; **HRMS m/z (ESI)** calcd for $C_{18}H_{21}$ $(M + H)^+$ 237.1638, found 237.1636.



3q

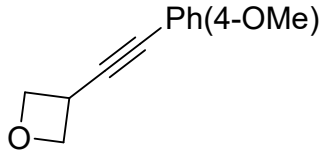
5-(Phenylethynyl)cyclooct-1-ene (3q): The desired product was prepared according to General Procedure A. Colorless oil, 21.5 mg (51% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.37 (m, 2H), 7.28 – 7.25 (m, 3H), 5.74 – 5.61 (m, 2H), 2.84 (dddd, J = 9.1, 7.6, 4.5, 1.5 Hz, 1H), 2.45 (dddd, J = 14.3, 10.5, 8.0, 4.2 Hz, 1H), 2.33 (dddd, J = 13.3, 11.8, 5.9, 3.7 Hz, 1H), 2.17 – 2.04 (m, 2H), 1.95 – 1.89 (m, 1H), 1.87 – 1.74 (m, 4H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.4, 130.1, 130.0, 128.1,

127.4, 124.2, 94.9, 81.4, 35.2, 32.0, 30.0, 27.3, 25.4, 24.2; **HRMS m/z (ESI)** calcd for $C_{16}H_{19}$ $(M + H)^+$ 211.1482, found 211.1480.



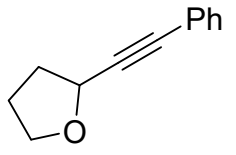
3r

2-(Phenylethynyl)-2,3-dihydro-1H-indene (3r): The desired product was prepared according to General Procedure A. White solid, 38.4 mg (88% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.24 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.20 – 7.17 (m, 2H), 3.46 (p, *J* = 8.5 Hz, 1H), 3.33 (dd, *J* = 15.0, 8.1 Hz, 2H), 3.15 (dd, *J* = 15.1, 8.8 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 142.0, 131.6, 128.2, 127.6, 126.5, 124.3, 123.7, 93.0, 80.6, 40.3, 30.7; **HRMS m/z (ESI)** calcd for $C_{17}H_{15}$ $(M + H)^+$ 219.1169, found 219.1167.



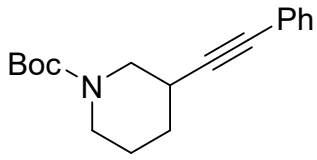
3s

3-((4-Methoxyphenyl)ethynyl)oxetane (3s): The desired product was prepared according to General Procedure A. Yellow oil, 19.1 mg (51% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.86 (dd, *J* = 8.5, 5.5 Hz, 2H), 4.80 (dd, *J* = 7.4, 5.5 Hz, 2H), 4.06 (tt, *J* = 8.5, 7.4 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.5, 133.0, 115.1, 113.9, 86.7, 83.9, 77.3, 55.3, 26.6; **HRMS m/z (ESI)** calcd for $C_{12}H_{13}O_2$ $(M + H)^+$ 189.0910, found 189.0910.



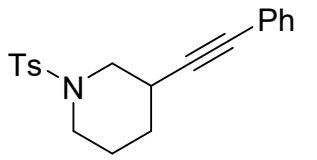
3t

2-(Phenylethynyl)tetrahydrofuran (3t): The desired product was prepared according to General Procedure A. Yellow oil, 30.7 mg (88% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 (dt, *J* = 5.8, 3.6 Hz, 2H), 7.28 (dd, *J* = 5.0, 1.9 Hz, 3H), 4.08 (t, *J* = 7.7 Hz, 1H), 3.96 (td, *J* = 8.2, 6.0 Hz, 1H), 3.88 (dt, *J* = 8.4, 6.7 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.25 – 3.16 (m, 1H), 2.29 (dtd, *J* = 12.2, 8.3, 5.9 Hz, 1H), 2.07 (dq, *J* = 12.2, 6.8 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.2, 127.8, 123.4, 90.0, 81.7, 73.3, 68.0, 33.7, 30.8; **HRMS m/z (ESI)** calcd for $C_{12}H_{12}ONa$ $(M + Na)^+$ 195.0780, found 195.0783.



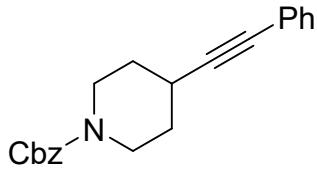
3u

***tert*-Butyl 3-(phenylethynyl)piperidine-1-carboxylate (3u):** The desired product was prepared according to General Procedure A. Yellow oil, 37.1mg (65% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 (q, *J* = 3.0, 2.3 Hz, 2H), 7.27 (dd, *J* = 5.0, 1.9 Hz, 3H), 3.94 (s, 1H), 3.76 (dt, *J* = 13.2, 4.1 Hz, 1H), 3.03 (s, 2H), 2.65 (tt, *J* = 9.4, 3.9 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.75 (s, 1H), 1.69 – 1.61 (m, 1H), 1.48 – 1.45 (m, 10H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.6, 131.6, 128.1, 127.7, 123.4, 90.5, 81.7, 79.5, 49.1, 43.6, 31.0, 29.1, 28.4, 24.0; **HRMS m/z (ESI)** calcd for $C_{18}H_{24}NO_2$ $(M + H)^+$ 286.1802, found 286.1794.



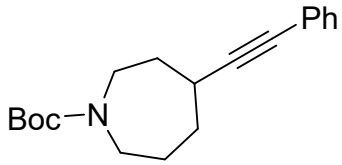
3v

3-(Phenylethynyl)-1-tosylpiperidine (3v): The desired product was prepared according to General Procedure A. Yellow oil, 61.9 mg (91% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.27 (m, 3H), 3.87 – 3.82 (m, 1H), 3.65 – 3.59 (m, 1H), 3.00 – 2.96 (m, 1H), 2.81 (tt, *J* = 10.5, 3.9 Hz, 1H), 2.47 (dd, *J* = 11.6, 9.9 Hz, 1H), 2.43 (s, 3H), 2.06 – 2.00 (m, 1H), 1.80 (dt, *J* = 13.7, 3.4 Hz, 1H), 1.64 (dp, *J* = 9.5, 6.1, 5.1 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.5, 133.5, 131.6, 129.7, 128.2, 128.0, 127.6, 123.1, 89.5, 82.2, 50.7, 46.2, 30.4, 29.0, 24.1, 21.5; **HRMS m/z (ESI)** calcd for $C_{20}H_{22}NO_2S$ $(M + H)^+$ 340.1366, found 340.1363.



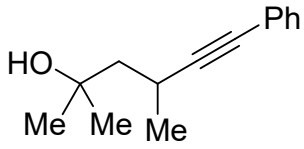
3w

Benzyl 4-(phenylethynyl)piperidine-1-carboxylate (3w): The desired product was prepared according to General Procedure A. Yellow oil, 41.5 mg (65% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.39 (m, 2H), 7.37 (d, *J* = 4.5 Hz, 4H), 7.34 – 7.31 (m, 1H), 7.31 – 7.26 (m, 3H), 5.15 (s, 2H), 3.87 – 3.75 (m, 2H), 3.37 (ddd, *J* = 13.5, 8.2, 3.5 Hz, 2H), 2.84 (tt, *J* = 8.0, 4.0 Hz, 1H), 1.88 (s, 2H), 1.71 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 155.2, 136.8, 131.5, 128.5, 128.2, 127.9, 127.83, 127.80, 123.4, 91.4, 82.1, 67.0, 42.3, 31.3, 27.4; **HRMS m/z (ESI)** calcd for $C_{21}H_{22}NO_2$ $(M + H)^+$ 320.1645, found 320.1646.



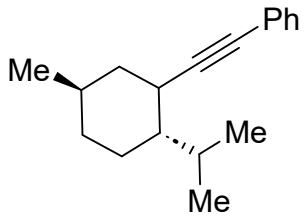
3x

***t*ert-Butyl 4-(phenylethynyl)azepane-1-carboxylate (3x):** The desired product was prepared according to General Procedure A. Yellow oil, 57.5 mg (96% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.37 (m, 2H), 7.27 (dd, *J* = 4.9, 2.9 Hz, 3H), 3.55 (ddt, *J* = 16.5, 13.6, 5.0 Hz, 1H), 3.46 (dq, *J* = 22.6, 6.2, 5.5 Hz, 2H), 3.35 (dddd, *J* = 21.9, 13.6, 7.8, 5.3 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.03 – 1.72 (m, 6H), 1.45 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 155.5, 131.6, 131.5, 128.2, 128.1, 127.62, 127.57, 123.8, 123.7, 92.7, 92.3, 82.1, 81.9, 79.2, 79.1, 46.3, 45.7, 44.3, 43.9, 34.9, 34.5, 32.5, 32.2, 30.8, 30.4, 28.5, 25.5, 25.3; **HRMS m/z (ESI)** calcd for $C_{19}H_{26}NO_2$ $(M + H)^+$ 300.1958, found 300.1958.



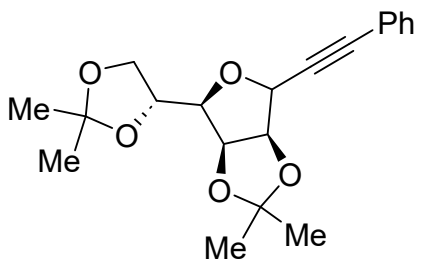
3y

2,4-Dimethyl-6-phenylhex-5-yn-2-ol (3y): light yellow oil, 16.5 mg (40% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.37 (m, 2H), 7.28 – 7.27 (m, 3H), 2.86 (dqd, *J* = 10.8, 6.9, 3.9 Hz, 1H), 1.82 (dd, *J* = 14.0, 10.9 Hz, 1H), 1.65 (dd, *J* = 14.0, 4.0 Hz, 1H), 1.34 (s, 3H), 1.31 – 1.28 (m, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.4, 128.2, 127.9, 123.2, 94.3, 82.6, 71.0, 49.7, 30.2, 29.0, 22.7, 22.3; **HRMS m/z (ESI)** calcd for $C_{14}H_{19}O$ $(M + H)^+$ 203.1431, found 203.1431.



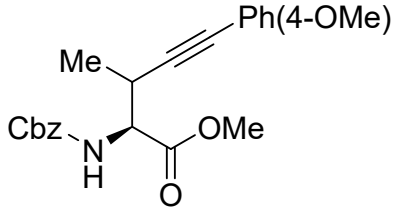
3z, d.r > 20 : 1

((2-Isopropyl-5-methylcyclohexyl)ethynyl)benzene (3z): The desired product was prepared according to General Procedure A. Light yellow oil, 37.9 mg (78% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 – 7.72 (m, 2H), 7.63 – 7.58 (m, 3H), 2.76 – 2.65 (m, 2H), 2.42 (dtd, *J* = 12.9, 3.6, 2.2 Hz, 1H), 2.09 (dt, *J* = 12.7, 2.9 Hz, 1H), 2.01 (dq, *J* = 12.7, 3.2 Hz, 1H), 1.73 (tdq, *J* = 14.8, 6.5, 3.0 Hz, 1H), 1.63 (tt, *J* = 12.0, 3.1 Hz, 1H), 1.54 (dt, *J* = 12.9, 11.9 Hz, 1H), 1.38 – 1.26 (m, 8H), 1.19 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.1, 127.3, 124.3, 93.6, 81.4, 47.5, 42.4, 34.9, 34.1, 32.5, 28.9, 24.4, 22.3, 21.3, 15.9; **HRMS m/z (ESI)** calcd for $C_{18}H_{25}$ $(M + H)^+$ 241.1951, found 241.1949.



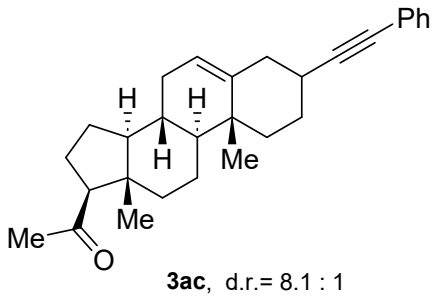
3aa, d.r. > 20 : 1
From D-Mannofuranose

(3aS,4R,6aR)-4-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(phenylethynyl)tetrahydrofuro[3,4-d][1,3]dioxole (3aa): The desired product was prepared according to General Procedure A. Light yellow oil, 30.2 mg (44% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 – 7.40 (m, 2H), 7.32 (q, *J* = 6.9, 6.2 Hz, 3H), 4.95 (s, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 4.88 (dd, *J* = 6.1, 3.4 Hz, 1H), 4.44 (ddd, *J* = 7.8, 6.1, 4.7 Hz, 1H), 4.16 – 4.07 (m, 2H), 4.00 (dd, *J* = 7.8, 3.6 Hz, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.8, 128.8, 128.3, 122.0, 112.9, 109.2, 87.3, 86.4, 84.6, 81.3, 80.4, 74.5, 73.0, 67.0, 26.9, 25.9, 25.2, 24.7; **HRMS m/z (ESI)** calcd for $C_{20}H_{25}O_5$ $(M + H)^+$ 345.1697, found 345.1696.



3ab, d.r. > 20 : 1
From L-Threonine methyl ester

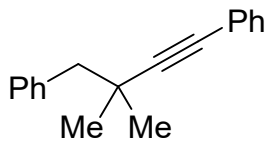
Methyl (2S)-2-(((benzyloxy)carbonyl)amino)-5-(4-methoxyphenyl)-3-methylpent-4-ynoate (3ab): The desired product was prepared according to General Procedure A. Yellow oil, 45.7 mg (60% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.35 (m, 4H), 7.33 (dd, *J* = 6.3, 2.5 Hz, 1H), 7.30 – 7.28 (m, 2H), 6.83 – 6.78 (m, 2H), 5.49 (d, *J* = 9.7 Hz, 1H), 5.14 (s, 2H), 4.48 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.795 (s, 3H), 3.786 (s, 3H), 3.39 (dd, *J* = 7.1, 3.7 Hz, 1H), 1.34 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.1, 159.5, 156.5, 136.1, 133.1, 128.5, 128.22, 128.17, 114.8, 113.8, 86.2, 83.7, 67.2, 57.8, 55.3, 52.6, 30.3, 18.2; **HRMS m/z (ESI)** calcd for $C_{22}H_{24}NO_5$ $(M + H)^+$ 382.1649, found 382.1649.



3ac, d.r.= 8.1 : 1
From Pregnenolone

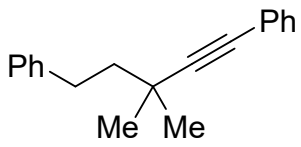
1-((8S,9S,10R,13S,14S,17S)-10,13-Dimethyl-3-(phenylethynyl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-

17-yl)ethan-1-one (3ac): The desired product was prepared according to General Procedure A. Yellow oil, 44.0 mg (55% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.27 (dd, *J* = 6.2, 1.7 Hz, 3H), 5.39 (d, *J* = 5.0 Hz, 1H, minor), 5.37 – 5.36 (m, 1H, major), 2.54 (t, *J* = 9.0 Hz, 1H), 2.46 – 2.40 (m, 2H), 2.34 (dd, *J* = 9.4, 2.2 Hz, 1H, major), 2.32 (d, *J* = 4.3 Hz, 1H, minor), 2.21 – 2.16 (m, 1H), 2.13 (s, 3H), 2.08 – 1.98 (m, 1H), 1.95 – 1.87 (m, 1H), 1.73 – 1.62 (m, 2H), 1.53 – 1.43 (m, 5H), 1.28 – 1.21 (m, 3H), 1.19 – 1.07 (m, 2H), 1.11 (d, *J* = 3.9 Hz, 2H), 1.04 (s, 3H, major), 1.02 (s, 3H, minor), 0.64 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 209.6, 141.4, 131.6, 128.2, 127.5, 123.8, 120.6, 93.9, 80.5, 63.7, 56.9, 50.1, 44.0, 39.0, 38.9, 38.8, 36.8, 31.8, 31.7, 31.5, 29.2, 24.5, 22.8, 20.9, 19.4, 13.2; **HRMS m/z (ESI)** calcd for $C_{29}H_{37}O$ $(M + H)^+$ 401.2839, found 401.2836.



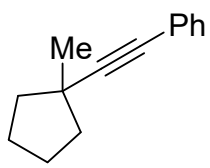
3ad

(3,3-Dimethylbut-1-yne-1,4-diyl)dibenzene (3ad): The desired product was prepared according to General Procedure C. Colorless oil, 26.1 mg (56% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 – 7.35 (m, 2H), 7.34 – 7.26 (m, 8H), 2.80 (s, 2H), 1.30 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.3, 131.4, 130.6, 128.1, 127.7, 127.5, 126.3, 124.0, 96.9, 81.6, 49.1, 32.8, 29.1; **HRMS m/z (ESI)** calcd for $C_{18}H_{19}$ $(M + H)^+$ 235.1482, found 235.1482.



3ae

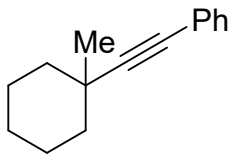
(3,3-Dimethylpent-1-yne-1,5-diyl)dibenzene (3ae): The desired product was prepared according to General Procedure C. Colorless oil, 23.8 mg (48% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 – 7.40 (m, 2H), 7.28 (dddd, *J* = 8.8, 7.0, 4.7, 1.9 Hz, 5H), 7.25 – 7.21 (m, 2H), 7.18 (td, *J* = 7.1, 1.5 Hz, 1H), 2.89 – 2.82 (m, 2H), 1.85 – 1.76 (m, 2H), 1.36 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 142.8, 131.6, 128.41, 128.35, 128.2, 127.5, 125.7, 124.0, 96.9, 80.9, 45.5, 32.1, 31.9, 29.3; **HRMS m/z (ESI)** calcd for $C_{19}H_{21}$ $(M + H)^+$ 249.1638, found 249.1636.



3af

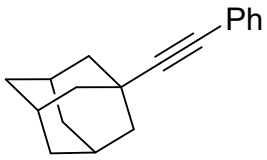
((1-Methylcyclopentyl)ethynyl)benzene (3af): The desired product

was prepared according to General Procedure C. Colorless oil, 25.5 mg (69% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.36 (m, 2H), 7.29 – 7.22 (m, 3H), 2.01 – 1.95 (m, 2H), 1.89 – 1.79 (m, 2H), 1.75 – 1.66 (m, 2H), 1.62 – 1.55 (m, 2H), 1.36 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.5, 128.1, 127.3, 124.2, 98.4, 79.5, 41.6, 38.3, 27.4, 24.4; **HRMS m/z (ESI)** calcd for $C_{14}H_{17}$ $(M + H)^+$ 185.1325, found 185.1325.



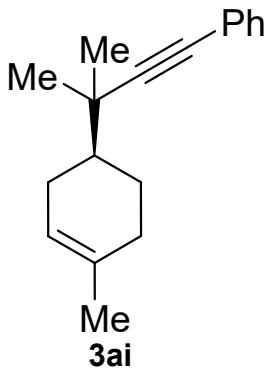
3ag

((1-Methylcyclohexyl)ethynyl)benzene (3ag): The desired product was prepared according to General Procedure C. Light yellow oil, 25.0 mg (63% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 – 7.38 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 3H), 1.81 (dd, *J* = 12.9, 4.2 Hz, 2H), 1.71 (tddt, *J* = 16.5, 11.4, 7.5, 3.7 Hz, 3H), 1.60 (dt, *J* = 13.8, 3.9 Hz, 2H), 1.29 – 1.22 (m, 5H), 1.21 – 1.12 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.1, 127.3, 124.3, 96.8, 81.7, 39.5, 33.1, 30.2, 25.9, 23.4; **HRMS m/z (ESI)** calcd for $C_{15}H_{19}$ $(M + H)^+$ 199.1482, found 199.1484.



3ah

1-(Phenylethynyl)adamantane (3ah): The desired product was prepared according to General Procedure C. Colorless oil, 42.5 mg (90% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.37 (m, 2H), 7.28 – 7.23 (m, 3H), 2.00 (p, *J* = 3.2 Hz, 3H), 1.97 (d, *J* = 3.3 Hz, 6H), 1.73 (t, *J* = 3.3 Hz, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.6, 128.1, 127.3, 124.1, 98.4, 79.4, 42.9, 36.4, 30.1, 28.1; **HRMS m/z (ESI)** calcd for $C_{18}H_{21}$ $(M + H)^+$ 237.1638, found 237.1637.

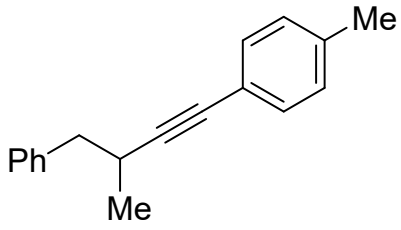


3ai

From (-)-alpha-Terpineol

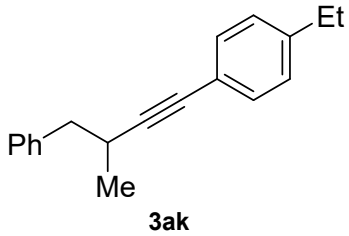
(S)-(3-Methyl-3-(4-methylcyclohex-3-en-1-yl)but-1-yn-1-yl)benzene (3ai): The desired product was prepared according to General Procedure C. White solid, 25.3 mg (53% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.36 (m, 2H), 7.25 (d, *J* = 8.1 Hz, 3H), 5.42 – 5.39 (m, 1H), 2.20 – 2.14 (m, 1H), 2.06 – 1.96 (m, 4H), 1.68 – 1.65 (m, 3H), 1.45 (tdd, *J* = 12.4, 9.5, 6.6 Hz, 2H), 1.30 (s,

3H), 1.27 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 133.8, 131.6, 128.1, 127.3, 124.2, 120.8, 96.6, 81.0, 43.9, 34.7, 31.0, 27.5, 27.3, 27.0, 24.8, 23.3; **HRMS m/z (ESI)** calcd for $C_{18}H_{23}$ $(M + H)^+$ 239.1795, found 239.1791.



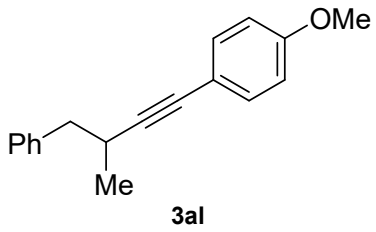
3aj

1-Methyl-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3aj): The desired product was prepared according to General Procedure C. Yellow oil, 39.3 mg (84% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 – 7.26 (m, 5H), 7.26 – 7.21 (m, 2H), 7.11 – 7.07 (m, 2H), 2.95 – 2.87 (m, 2H), 2.81 – 2.75 (m, 1H), 2.34 (s, 3H), 1.27 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** 139.7, 137.5, 131.4, 129.4, 128.9, 128.1, 126.2, 120.9, 93.3, 81.6, 43.2, 28.6, 21.4, 20.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{19}$ $(M + H)^+$ 235.1482, found 235.1481.



3ak

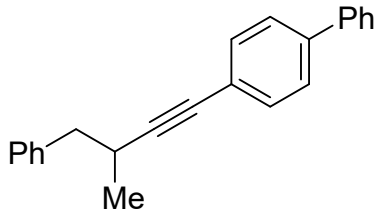
1-Ethyl-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3ak): The desired product was prepared according to General Procedure C. Brown oil, 39.7 mg (80% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 – 7.26 (m, 6H), 7.25 – 7.21 (m, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.94 – 2.87 (m, 2H), 2.81 – 2.75 (m, 1H), 2.63 (q, *J* = 7.7 Hz, 2H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.22 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.8, 139.7, 131.4, 129.4, 128.1, 127.7, 126.2, 121.1, 93.3, 81.6, 43.2, 28.7, 28.6, 20.6, 15.4; **HRMS m/z (ESI)** calcd for $C_{19}H_{21}$ $(M + H)^+$ 249.1638, found 249.1633.



3al

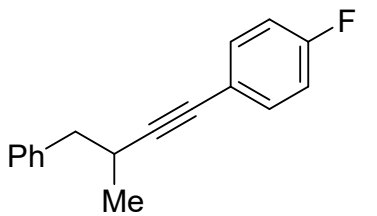
1-Methoxy-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3al): The desired product was prepared according to General Procedure A. Yellow oil, 41.5 mg (83% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36 – 7.26 (m, 6H), 7.25 – 7.22 (m, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 2.94 – 2.87 (m, 2H), 2.80 – 2.75 (m, 1H), 1.26 (d, *J* = 6.7 Hz, 3H); **^{13}C**

NMR (151 MHz, $CDCl_3$) δ 159.0, 139.7, 132.8, 129.3, 128.1, 126.2, 116.1, 113.8, 92.5, 81.2, 55.2, 43.3, 28.6, 20.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{19}O$ $(M + H)^+$ 251.1431, found 251.1428.



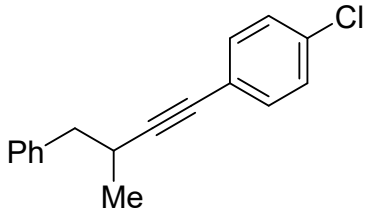
3am

4-(3-Methyl-4-phenylbut-1-yn-1-yl)-1,1'-biphenyl (3am): The desired product was prepared according to General Procedure A. Yellow oil, 37.3 mg (63% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.60 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.43 (m, 4H), 7.38 – 7.30 (m, 5H), 7.28 – 7.24 (m, 1H), 2.99 – 2.92 (m, 2H), 2.85 – 2.80 (m, 1H), 1.31 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.5, 140.3, 139.6, 131.9, 129.4, 128.8, 128.2, 127.4, 127.0, 126.8, 126.3, 122.9, 94.8, 81.4, 43.2, 28.7, 20.6; **HRMS m/z (ESI)** calcd for $C_{23}H_{21}$ $(M + H)^+$ 297.1638, found 297.1643.



3an

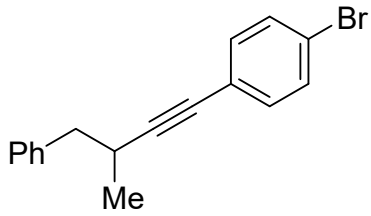
1-Fluoro-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3an): The desired product was prepared according to General Procedure A. Yellow oil, 22.5 mg (47% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.21 (m, 7H), 2.94 – 2.85 (m, 2H), 2.81 – 2.75 (m, 1H), 1.26 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.1 (d, *J* = 248.2 Hz), 139.6, 133.3 (d, *J* = 7.7 Hz), 129.3, 128.2, 126.3, 120.0 (d, *J* = 3.3 Hz), 115.3 (d, *J* = 21.6 Hz), 93.7, 80.5, 43.1, 28.5, 20.5. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -112.31; **HRMS m/z (ESI)** calcd for $C_{17}H_{16}F$ $(M + H)^+$ 239.1231, found 239.1227.



3ao

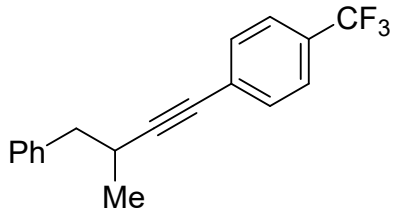
1-Chloro-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3ao): The desired product was prepared according to General Procedure A. Yellow oil, 24.7 mg (49% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 7H), 2.93 – 2.86 (m, 2H), 2.82 – 2.75 (m, 1H), 1.26 (d, *J* = 6.7 Hz, 3H).; **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.5,

133.5, 132.7, 129.3, 128.4, 128.2, 126.3, 122.4, 95.1, 80.6, 43.1, 28.6, 20.5; **HRMS m/z (ESI)** calcd for $C_{17}H_{16}Cl$ $(M + H)^+$ 255.0935, found 255.0934.



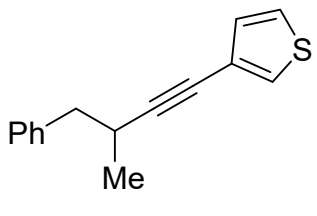
3ap

1-Bromo-4-(3-methyl-4-phenylbut-1-yn-1-yl)benzene (3ap): The desired product was prepared according to General Procedure A. Yellow oil, 31.1 mg (52% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 – 7.38 (m, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.19 (m, 5H), 2.94 – 2.86 (m, 2H), 2.81 – 2.76 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** 139.5, 133.0, 131.4, 129.3, 128.2, 126.3, 122.9, 121.6, 95.3, 80.6, 43.0, 28.6, 20.4; **HRMS m/z (ESI)** calcd for $C_{17}H_{16}Br$ $(M + H)^+$ 299.0430, found 299.0426.



3aq

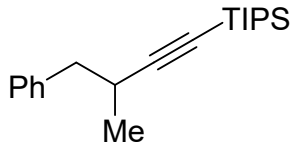
1-(3-Methyl-4-phenylbut-1-yn-1-yl)-4-(trifluoromethyl) benzene (3aq): The desired product was prepared according to General Procedure A. Colorless oil, 27.1 mg (47% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.53 – 7.51 (m, 2H), 7.44 – 7.41 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 (d, *J* = 11.4 Hz, 3H), 2.97 – 2.87 (m, 2H), 2.80 (dd, *J* = 12.9, 6.4 Hz, 1H), 1.28 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.4, 131.7, 129.4, 129.3, 129.2, 128.2, 127.8, 126.4, 125.1 (q, *J* = 3.9 Hz), 96.8, 80.6, 43.0, 28.7, 20.4; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.8; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}F_3$ $(M + H)^+$ 289.1199, found 289.1190.



3ar

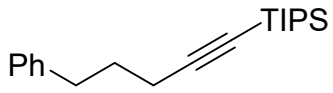
3-(3-Methyl-4-phenylbut-1-yn-1-yl)thiophene (3ar): The desired product was prepared according to General Procedure A. Yellow oil, 26.6 mg (59% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 – 7.20 (m, 7H), 7.03 (dd, *J* = 5.0, 1.2 Hz, 1H), 2.93 – 2.85 (m, 2H), 2.79 – 2.74 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.6, 130.0, 129.3, 128.1, 127.5, 126.3, 124.9, 122.8, 93.5, 76.6, 43.1, 28.6, 20.5; **HRMS m/z (ESI)** calcd for $C_{15}H_{15}S$

$(M + H)^+$ 227.0889, found 227.0889.



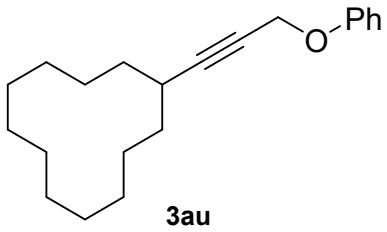
3as

Triisopropyl(3-methyl-4-phenylbut-1-yn-1-yl)silane (3as): The desired product was prepared according to General Procedure A. Colorless oil, 37.8 mg (63% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 – 7.23 (m, 4H), 7.22 – 7.18 (m, 1H), 2.81 (dd, *J* = 12.2, 7.1 Hz, 1H), 2.74 (ddd, *J* = 26.6, 12.7, 6.3 Hz, 2H), 1.20 (d, *J* = 6.5 Hz, 3H), 1.06 – 1.00 (m, 21H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.6, 129.3, 128.1, 126.1, 113.1, 80.7, 43.2, 28.9, 21.0, 18.6, 11.3; **HRMS m/z (ESI)** calcd for $C_{20}H_{33}Si$ $(M + H)^+$ 301.2346, found 301.2343.



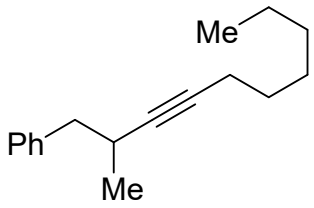
3at

Triisopropyl(5-phenylpent-1-yn-1-yl)silane (3at): The desired product was prepared according to General Procedure A. Colorless oil, 25.2 mg (42% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.22 – 7.17 (m, 3H), 2.79 – 2.74 (m, 2H), 2.28 (t, *J* = 6.9 Hz, 2H), 1.85 (dq, *J* = 9.2, 6.9 Hz, 2H), 1.12 – 1.03 (m, 21H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.8, 128.6, 128.3, 125.8, 108.6, 80.7, 34.7, 30.7, 19.3, 18.6, 11.3; **HRMS m/z (ESI)** calcd for $C_{20}H_{33}Si$ $(M + H)^+$ 301.2346, found 301.2346.



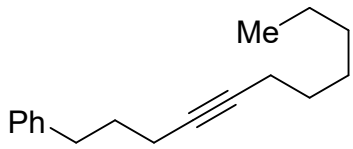
3au

(3-Phenoxyprop-1-yn-1-yl)cyclododecane (3au): The desired product was prepared according to General Procedure B. Yellow oil, 22.1 mg (37% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.01 – 6.95 (m, 3H), 4.68 (d, *J* = 2.0 Hz, 2H), 2.51 (dqd, *J* = 7.3, 5.1, 3.0 Hz, 1H), 1.59 (t, *J* = 7.0 Hz, 2H), 1.50 – 1.43 (m, 4H), 1.32 (q, *J* = 5.3, 4.3 Hz, 16H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.8, 129.3, 121.1, 115.0, 99.1, 92.8, 56.6, 29.7, 26.8, 23.7, 23.7, 23.4, 23.4, 22.1; **HRMS m/z (ESI)** calcd for $C_{21}H_{31}O$ $(M + H)^+$ 299.2370, found 299.2368.



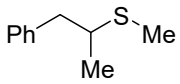
3av

(2-Methyldec-3-yn-1-yl)benzene (3av): The desired product was prepared according to General Procedure A. Yellow oil, 18.3 mg (40% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 (td, *J* = 7.3, 1.5 Hz, 2H), 7.21 (dt, *J* = 8.3, 2.1 Hz, 3H), 2.81 – 2.75 (m, 1H), 2.70 – 2.60 (m, 2H), 2.14 – 2.11 (m, 2H), 1.44 (dq, *J* = 8.8, 7.2, 6.6 Hz, 2H), 1.36 – 1.24 (m, 6H), 1.14 (d, *J* = 6.7 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.0, 129.3, 128.0, 126.1, 84.2, 81.3, 43.6, 31.4, 29.0, 28.5, 27.9, 22.6, 21.0, 18.7, 14.1; **HRMS m/z (ESI)** calcd for $C_{17}H_{25}$ $(M + H)^+$ 229.1951, found 229.1949.



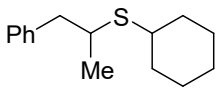
3aw

Undec-4-yn-1-ylbenzene (3aw): The desired product was prepared according to General Procedure B. Colorless oil, 18.4 mg (40% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.19 (dt, *J* = 8.3, 2.1 Hz, 3H), 2.73 – 2.70 (m, 2H), 2.20 – 2.13 (m, 4H), 1.80 (dq, *J* = 9.1, 6.9 Hz, 2H), 1.53 – 1.46 (m, 2H), 1.43 – 1.37 (m, 2H), 1.35 – 1.22 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.9, 128.5, 128.3, 125.8, 80.9, 79.6, 34.8, 31.4, 30.7, 29.1, 28.6, 22.6, 18.8, 18.2, 14.1; **HRMS m/z (ESI)** calcd for $C_{17}H_{25}$ $(M + H)^+$ 229.1951, found 229.1949.



5a

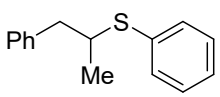
Methyl(1-phenylpropan-2-yl)sulfane (5a): The desired product was prepared according to General Procedure D. Yellow oil, 20.0 mg (60% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.18 (m, 3H), 2.99 (dd, *J* = 13.4, 5.9 Hz, 1H), 2.91 (dt, *J* = 8.4, 6.3 Hz, 1H), 2.67 (dd, *J* = 13.4, 8.4 Hz, 1H), 2.10 (s, 3H), 1.23 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.6, 129.2, 128.3, 126.3, 43.3, 42.8, 20.2, 13.7; **HRMS m/z (ESI)** calcd for $C_{10}H_{14}SNa$ $(M + Na)^+$ 189.0708, found 189.0706.



5b

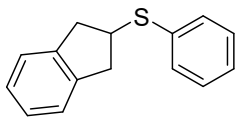
Cyclohexyl(1-phenylpropan-2-yl)sulfane (5b): The desired product was prepared according to General Procedure E. Colorless

oil, 23.9 mg (51% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.16 (m, 3H), 3.08 (dt, *J* = 9.0, 6.1 Hz, 1H), 2.98 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.64 (ddd, *J* = 22.4, 13.8, 9.7 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.76 (tt, *J* = 11.4, 3.4 Hz, 2H), 1.34 – 1.25 (m, 6H), 1.20 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.7, 129.2, 128.2, 126.2, 44.2, 42.4, 39.4, 34.1, 33.9, 25.8, 21.1; **HRMS m/z (ESI)** calcd for $C_{15}H_{23}S$ $(M + H)^+$ 235.1515, found 235.1515.



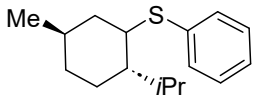
5c

Phenyl(1-phenylpropan-2-yl)sulfane (5c): The desired product was prepared according to General Procedure E. Light yellow oil, 24.7 mg (54% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 – 7.42 (m, 2H), 7.30 (dt, *J* = 10.9, 7.5 Hz, 4H), 7.25 – 7.20 (m, 2H), 7.18 – 7.15 (m, 2H), 3.45 (dqd, *J* = 9.1, 6.7, 5.1 Hz, 1H), 3.04 (dd, *J* = 13.7, 5.2 Hz, 1H), 2.65 (dd, *J* = 13.7, 9.1 Hz, 1H), 1.23 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.3, 135.1, 132.0, 129.2, 128.9, 128.3, 126.9, 126.4, 44.5, 43.1, 20.1; **HRMS m/z (ESI)** calcd for $C_{15}H_{17}S$ $(M + H)^+$ 229.1046, found 229.1054.



5d

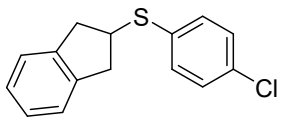
(2,3-Dihydro-1H-inden-2-yl)(phenyl)sulfane (5d): The desired product was prepared according to General Procedure D. Yellow oil, 25.0 mg (55% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 – 7.40 (m, 2H), 7.31 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.24 – 7.22 (m, 1H), 7.21 – 7.19 (m, 2H), 7.17 (dt, *J* = 5.0, 3.6 Hz, 2H), 4.12 (tt, *J* = 7.5, 6.0 Hz, 1H), 3.38 (dd, *J* = 16.0, 7.5 Hz, 2H), 3.01 (dd, *J* = 16.0, 6.0 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.5, 136.1, 130.6, 128.9, 126.7, 126.4, 124.5, 45.3, 40.2; **HRMS m/z (ESI)** calcd for $C_{15}H_{15}S$ $(M + H)^+$ 227.0889, found 227.0889.



5e, d.r > 20 : 1

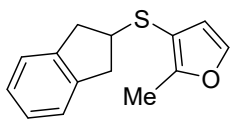
(2-isopropyl-5-Methylcyclohexyl)(phenyl)sulfane (5e): The desired product was prepared according to General Procedure E. Colorless oil, 26.4 mg (53% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.38 (m, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.20 – 7.16 (m, 1H), 3.63 (d, *J* = 4.1 Hz, 1H), 2.02 (tdp, *J* = 13.2, 6.7, 3.3 Hz, 1H), 1.90 (dd, *J* = 13.5, 2.6 Hz, 1H), 1.77

(dddd, *J* = 16.3, 9.6, 5.8, 3.3 Hz, 3H), 1.27 – 1.23 (m, 1H), 1.18 (ddd, *J* = 12.8, 9.1, 3.2 Hz, 2H), 0.94 (dd, *J* = 6.6, 4.0 Hz, 6H), 0.92 – 0.87 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 136.9, 131.1, 128.8, 126.1, 49.7, 48.9, 40.5, 35.4, 30.2, 26.5, 26.2, 22.1, 21.1, 20.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{25}S$ $(M + H)^+$ 249.1672, found 249.1674.



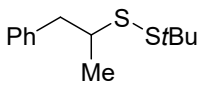
5f

(4-Chlorophenyl)(2,3-dihydro-1H-inden-2-yl)sulfane (5f): The desired product was prepared according to General Procedure E. Colorless oil, 19.8 mg (38% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.22 – 7.16 (m, 4H), 4.08 (tt, *J* = 7.4, 5.8 Hz, 1H), 3.37 (dd, *J* = 16.0, 7.5 Hz, 2H), 2.98 (dd, *J* = 16.0, 5.8 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.3, 134.6, 132.5, 131.9, 129.1, 126.7, 124.5, 45.5, 40.1; **HRMS m/z (ESI)** calcd for $C_{15}H_{14}ClS$ $(M + H)^+$ 261.0499, found 261.0474.



5g

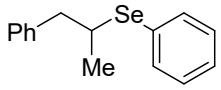
3-((2,3-Dihydro-1H-inden-2-yl)thio)-2-methylfuran (5g): The desired product was prepared according to General Procedure E. Colorless oil, 20.9 mg (45% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 1.9 Hz, 1H), 7.20 – 7.11 (m, 4H), 6.38 (d, *J* = 1.9 Hz, 1H), 3.75 (tt, *J* = 7.4, 6.2 Hz, 1H), 3.22 (dd, *J* = 16.0, 7.4 Hz, 2H), 2.92 (dd, *J* = 15.9, 6.2 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 155.9, 141.7, 140.5, 126.6, 124.4, 115.7, 109.6, 47.0, 39.9, 11.9; **HRMS m/z (ESI)** calcd for $C_{14}H_{15}OS$ $(M + H)^+$ 231.0838, found 231.0839.



5h

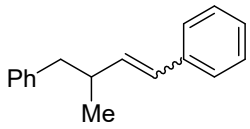
1-(*t*ert-Butyl)-2-(1-phenylpropan-2-yl)disulfane (5h): The desired product was prepared according to General Procedure E. Colorless oil, 22.1 mg (46% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.20 – 7.16 (m, 2H), 3.19 (dd, *J* = 13.5, 5.0 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.57 (dd, *J* = 13.5, 9.3 Hz, 1H), 1.33 (s, 9H), 1.22 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.4, 129.3, 128.3, 126.3, 48.3, 47.7, 42.8, 30.1,

19.5; **HRMS m/z (ESI)** calcd for $C_{13}H_{21}S_2$ $(M + H)^+$ 241.1079, found 241.1079.



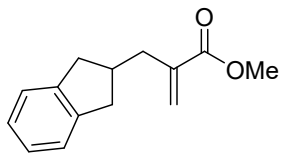
5i

Phenyl(1-phenylpropan-2-yl)selane (5i): The desired product was prepared according to General Procedure E. Yellow oil, 17.2 mg (31% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.58 – 7.55 (m, 2H), 7.30 – 7.27 (m, 5H), 7.23 – 7.20 (m, 1H), 7.17 – 7.13 (m, 2H), 3.57 – 3.48 (m, 1H), 3.09 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.77 (dd, *J* = 13.7, 9.2 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.8, 134.9, 129.3, 129.1, 128.9, 128.3, 127.5, 126.4, 44.1, 40.0, 21.0; **HRMS m/z (ESI)** calcd for $C_{15}H_{17}Se$ $(M + H)^+$ 277.0490, found 277.0487.



5j, *E* : *Z* = 1 : 3

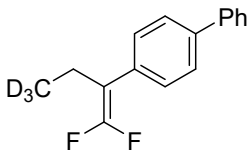
(3-Methylbut-1-ene-1,4-diyl)dibenzene (5j): The desired product was prepared according to General Procedure D. Colorless oil, 34.2 mg (77% yield, E:Z=1:3). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 7.2 Hz, 2H), 7.29 (td, *J* = 7.4, 3.6 Hz, 4H), 7.22 – 7.18 (m, 4H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 15.9, 6.8 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.63 (qd, *J* = 7.5, 6.6, 3.0 Hz, 2H), 1.10 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.5, 137.8, 135.9, 129.3, 128.4, 128.2, 128.1, 126.8, 126.0, 125.8, 43.6, 38.8, 19.8; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.31 – 7.24 (m, 4H), 7.23 – 7.18 (m, 2H), 7.15 – 7.10 (m, 4H), 6.38 (d, *J* = 11.6 Hz, 1H), 5.52 (dd, *J* = 11.6, 10.3 Hz, 1H), 3.06 (dq, *J* = 10.4, 6.6 Hz, 1H), 2.74 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.60 (dd, *J* = 13.5, 7.2 Hz, 1H), 1.04 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.3, 138.3, 137.7, 129.2, 128.5, 128.1, 128.1, 127.8, 126.4, 125.8, 43.6, 34.1, 20.6; **HRMS m/z (ESI)** calcd for $C_{17}H_{19}$ $(M + H)^+$ 223.1482, found 223.1480.



5k

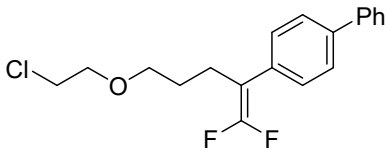
Methyl 2-((2,3-dihydro-1H-inden-2-yl)methyl)acrylate (5k): The desired product was prepared according to General Procedure E. Light yellow oil, 24.5 mg (57% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.18 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.12 (dd, *J* = 5.5, 3.2 Hz, 2H), 6.21 (d, *J* = 1.7 Hz, 1H), 5.58 (d, *J* = 1.4 Hz, 1H), 3.77 (s, 3H),

3.04 (dd, *J* = 15.1, 7.6 Hz, 2H), 2.71 (dt, *J* = 14.6, 7.3 Hz, 1H), 2.62 (dd, *J* = 15.3, 7.2 Hz, 2H), 2.48 (dd, *J* = 7.4, 1.3 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.7, 143.0, 139.5, 126.1, 125.8, 124.5, 51.8, 38.8, 38.2, 37.8; **HRMS m/z (ESI)** calcd for $C_{14}H_{17}O_2$ $(M + H)^+$ 217.1223, found 217.1223.



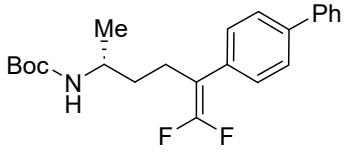
5l

4-(1,1-Difluorobut-1-en-2-yl-4,4,4-d3)-1,1'-biphenyl (5l): The desired product was prepared according to General Procedure D. Light yellow oil, 22.3 mg (45% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 – 7.58 (m, 4H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.37 – 7.34 (m, 1H), 2.45 – 2.44 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.4 (dd, *J* = 290.5, 287.3 Hz), 140.6, 139.9, 132.7, 128.8, 128.5 (t, *J* = 3.3 Hz), 127.4, 127.1, 127.0, 93.5 (dd, *J* = 17.9, 10.3 Hz), 29.7, 20.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -91.54 (d, *J* = 43.7 Hz), -91.72 (d, *J* = 43.7 Hz); **HRMS m/z (ESI)** calcd for $C_{16}H_{12}D_3F_2$ $(M + H)^+$ 248.1325, found 248.1329.



5m

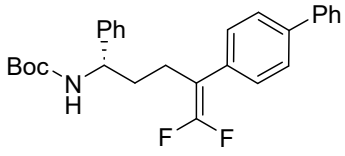
4-(5-(2-Chloroethoxy)-1,1-difluoropent-1-en-2-yl)-1,1'-biphenyl (5m): The desired product was prepared according to General Procedure D. Light yellow oil, 42.4 mg (63% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 – 7.59 (m, 4H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.34 (m, 1H), 3.68 – 3.58 (m, 4H), 3.49 (t, *J* = 6.2 Hz, 2H), 2.59 – 2.52 (m, 2H), 1.75 – 1.67 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.7 (dd, *J* = 291.4, 288.4 Hz), 140.5, 140.1, 132.4, 128.8, 128.5 (t, *J* = 3.3 Hz), 127.4, 127.1, 127.0, 91.6 (dd, *J* = 19.9, 14.9 Hz), 70.8, 70.1, 42.8, 27.8 (t, *J* = 2.5 Hz), 24.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.63 (dd, *J* = 6.9, 2.1 Hz); **HRMS m/z (ESI)** calcd for $C_{19}H_{20}ClF_2O$ $(M + H)^+$ 337.1165, found 337.1155.



5n

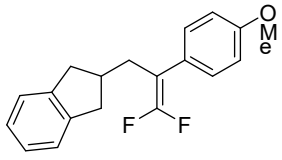
***t*ert-Butyl (R)-(5-([1,1'-biphenyl]-4-yl)-6,6-difluorohex-5-en-2-yl)carbamate (5n):** The desired product was prepared according to General Procedure D.

Yellow oil, 31.0 mg (40% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 (dd, *J* = 8.2, 6.0 Hz, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.34 (m, 3H), 4.34 – 4.27 (m, 1H), 3.74 – 3.65 (m, 1H), 2.50 – 2.47 (m, 2H), 1.55 – 1.47 (m, 2H), 1.45 (s, 9H), 1.11 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.5 (dd, *J* = 292.9 Hz, 282.4 Hz), 140.5, 140.1, 132.3, 128.8, 128.5 (t, *J* = 3.3 Hz), 127.4, 127.2, 127.0, 91.6 (dd, *J* = 21.6, 13.8 Hz), 46.2, 37.0, 35.4, 28.4, 24.4, 21.4; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.68 (d, *J* = 42.3 Hz), -90.89 (d, *J* = 43.0 Hz); **HRMS m/z (ESI)** calcd for $C_{23}H_{28}F_2NO_2$ $(M + H)^+$ 388.2083, found 388.2083.



5o

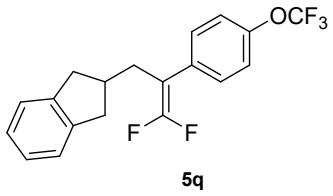
***t*ert-Butyl (S)-(4-([1,1'-biphenyl]-4-yl)-5,5-difluoro-1-phenylpent-4-en-1-yl)carbamate (5o):** The desired product was prepared according to General Procedure D. Yellow oil, 36.8 mg (41% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 – 7.55 (m, 4H), 7.45 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.30 (m, 4H), 7.26 – 7.24 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 4.79 (s, 1H), 4.67 (s, 1H), 2.51 (ddt, *J* = 11.5, 6.3, 2.4 Hz, 1H), 2.44 (dtt, *J* = 14.3, 9.0, 4.4 Hz, 1H), 1.84 (d, *J* = 7.3 Hz, 2H), 1.43 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.4, 153.6 (dd, J = 291.1, 287.2 Hz), 140.5, 140.1, 132.1, 128.8, 128.6, 128.5 (t, J = 3.3 Hz), 127.4, 127.3, 127.2, 127.1, 127.0, 126.3, 91.4 (dd, J = 21.4, 12.9 Hz), 54.4, 47.4, 34.9, 28.3, 24.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.19 (d, *J* = 41.6 Hz), -90.58 (d, *J* = 41.6 Hz); **HRMS m/z (ESI)** calcd for $C_{28}H_{30}F_2NO_2$ $(M + H)^+$ 450.2239, found 450.2239.



5p

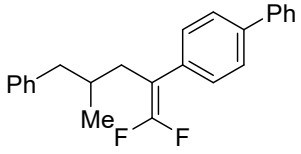
2-(3,3-Difluoro-2-(4-methoxyphenyl)allyl)-2,3-dihydro-1H-indene (5p): The desired product was prepared according to General Procedure D. Colorless oil, 54.1 mg (90% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.30 – 7.27 (m, 2H), 7.17 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.13 – 7.11 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.97 (dd, *J* = 15.3, 7.7 Hz, 2H), 2.64 (dd, *J* = 15.3, 7.4 Hz, 2H), 2.60 – 2.54 (m, 2H), 2.48 (p, *J* = 7.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.7, 153.9 (dd, *J* = 288.6, 285.8 Hz), 142.9, 129.5, 126.1, 125.7 (q, *J* = 2.8 Hz), 124.4, 113.9, 91.2 (dd, *J* = 21.0, 14.4 Hz),

55.2, 38.6, 38.1 (t, J = 2.7 Hz), 33.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -92.36 (d, J = 46.0 Hz), -92.51 (d, J = 47.0 Hz); **HRMS m/z (ESI)** calcd for $C_{19}H_{19}F_2O$ $(M + H)^+$ 301.1399, found 301.1399.



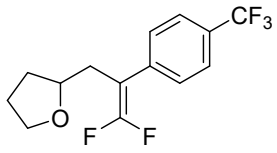
5q

2-(3,3-Difluoro-2-(4-(trifluoromethoxy)phenyl)allyl)-2,3-dihydro-1H-indene (5q): The desired product was prepared according to General Procedure D. Colorless oil, 34.9 mg (49% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 (dd, J = 8.8, 1.1 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.15 (ddd, J = 25.3, 5.5, 3.3 Hz, 4H), 2.97 (dd, J = 15.2, 7.7 Hz, 2H), 2.64 (dd, J = 15.3, 7.4 Hz, 2H), 2.59 (dt, J = 7.6, 2.3 Hz, 2H), 2.46 (pd, J = 7.6, 1.1 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.1 (dd, J = 290.9, 287.4 Hz), 148.3, 142.7, 132.3 (dd, J = 4.6, 3.1 Hz), 129.8 (t, J = 3.3 Hz), 126.2, 124.4, 121.3, 121.0, 90.9 (dd, J = 22.9, 13.0 Hz), 38.6, 38.0 (t, J = 2.6 Hz), 33.2; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -57.82, -90.46 (dd, J = 42.0, 2.4 Hz), -90.86 (dd, J = 41.6, 2.8 Hz); **HRMS m/z (ESI)** calcd for $C_{19}H_{16}F_5O$ $(M + H)^+$ 355.1116, found 355.1125.



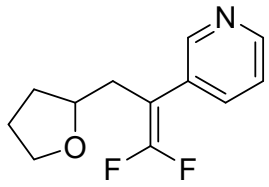
5r

4-(1,1-Difluoro-4-methyl-5-phenylpent-1-en-2-yl)-1,1'-biphenyl (5r): The desired product was prepared according to General Procedure D. Yellow oil, 60.1 mg (86% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 (dd, J = 8.3, 1.2 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.46 (dd, J = 8.6, 6.9 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.31 (dd, J = 8.4, 1.4 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.09 – 7.06 (m, 2H), 2.68 (dd, J = 13.5, 6.3 Hz, 1H), 2.51 – 2.38 (m, 2H), 2.30 (ddd, J = 14.4, 8.5, 2.7 Hz, 1H), 1.80 (hept, J = 7.2, 6.6 Hz, 1H), 0.89 (d, J = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.1 (dd, J = 291.4 Hz, d, J = 286.9 Hz), 140.8, 140.5, 139.9, 132.5 (t, J = 3.9 Hz), 129.1, 128.8, 128.6 (t, J = 3.3 Hz), 128.2, 127.4, 127.1, 127.0, 125.8, 91.1 (dd, J = 22.0, 12.8 Hz), 43.1, 34.3, 33.2, 19.1; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -90.59 (d, J = 42.9 Hz), -90.86 (d, J = 42.9 Hz); **HRMS m/z (ESI)** calcd for $C_{24}H_{23}F_2$ $(M + H)^+$ 349.1763, found 349.1769.



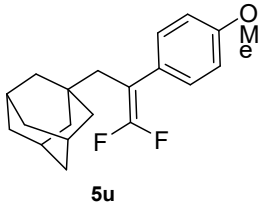
5s

2-(3,3-Difluoro-2-(4-(trifluoromethyl)phenyl)allyl) tetrahydrofuran (5s): The desired product was prepared according to General Procedure D. Yellow oil, 28.3 mg (48% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 3.86 (td, *J* = 8.3, 5.0 Hz, 1H), 3.75 (dd, *J* = 8.5, 6.9 Hz, 1H), 3.70 (dt, *J* = 8.5, 7.4 Hz, 1H), 3.39 (dd, *J* = 8.5, 6.2 Hz, 1H), 2.52 (dd, *J* = 7.7, 2.5 Hz, 2H), 2.18 (p, *J* = 7.3 Hz, 1H), 1.93 (dtd, *J* = 12.7, 7.7, 5.1 Hz, 1H), 1.55 (dq, *J* = 12.2, 7.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.2 (dd, *J* = 292.0, 288.5 Hz), 137.2, 129.6 (dd, *J* = 65.2, 32.6 Hz), 125.5 (q, *J* = 3.6 Hz), 124.8, 123.0, 91.0 (dd, *J* = 23.2, 13.3 Hz), 72.6, 67.7, 37.6 (t, *J* = 2.8 Hz), 31.7, 30.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.70 (d, *J* = 3.5 Hz), -89.06 (dd, *J* = 38.8, 3.5 Hz), -89.60 (dd, *J* = 38.8, 3.5 Hz); **HRMS m/z (ESI)** calcd for $C_{14}H_{14}F_5O$ $(M + H)^+$ 293.0960, found 293.0961.



5t

3-(1,1-Difluoro-3-(tetrahydrofuran-2-yl)prop-1-en-2-yl) pyridinee (5t): The desired product was prepared according to General Procedure D. Yellow oil, 23.1 mg (51% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.57 (s, 1H), 8.53 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.62 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.31 (ddd, *J* = 8.0, 4.9, 0.9 Hz, 1H), 3.86 (td, *J* = 8.3, 5.1 Hz, 1H), 3.76 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.70 (dt, *J* = 8.6, 7.4 Hz, 1H), 3.39 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.50 (dd, *J* = 7.6, 2.6 Hz, 2H), 2.20 (h, *J* = 7.6 Hz, 1H), 1.94 (dtd, *J* = 12.7, 7.7, 5.0 Hz, 1H), 1.55 (dq, *J* = 12.2, 7.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.3 (dd, *J* = 291.9, 288.6 Hz), 149.2 (t, *J* = 3.6 Hz), 148.6, 135.7 (t, *J* = 3.2 Hz), 129.4, 123.4, 88.9 (dd, *J* = 23.2, 13.9 Hz), 72.6, 67.7, 37.5 (t, *J* = 2.6 Hz), 31.6, 30.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.75 (dd, *J* = 38.8, 2.8 Hz), -89.64 (dd, *J* = 38.8, 2.8 Hz); **HRMS m/z (ESI)** calcd for $C_{12}H_{14}F_2NO$ $(M + H)^+$ 226.1038, found 226.1048.



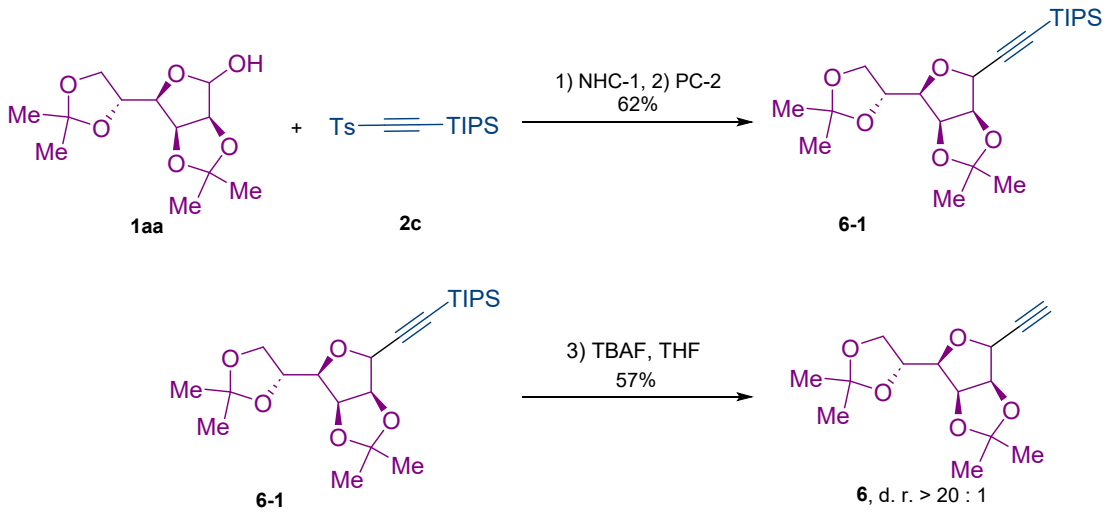
5u

(3r,5r,7r)-1-(3,3-Difluoro-2-(4-methoxyphenyl)allyl) adamantane (5u): The desired product was prepared according to General Procedure D. Light yellow oil, 40.0 mg (63% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.16 (s, 2H), 1.86 (t, *J* = 3.2 Hz, 3H), 1.62 (d, *J* = 12.3 Hz, 3H), 1.55 – 1.51 (m, 3H), 1.37 (d, *J* = 3.2 Hz, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.3, 143.8, 129.4 (t, *J* = 3.0 Hz), 113.7, 93.5, 55.2, 42.7, 42.0, 36.9, 34.6 (d, *J* = 2.8 Hz), 28.6; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.06 (d, *J* = 43.7 Hz), -93.07 (dd, *J* = 43.3, 2.4 Hz); **HRMS m/z (ESI)** calcd for $C_{22}H_{25}F_2O$ $(M + H)^+$ 319.1868, found 319.1870.

6. Late-stage functionalization and synthetic applications.

(3aS,4R,6S,6aR)-4-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-6-ethynyl-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (6)



1) To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **1aa** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

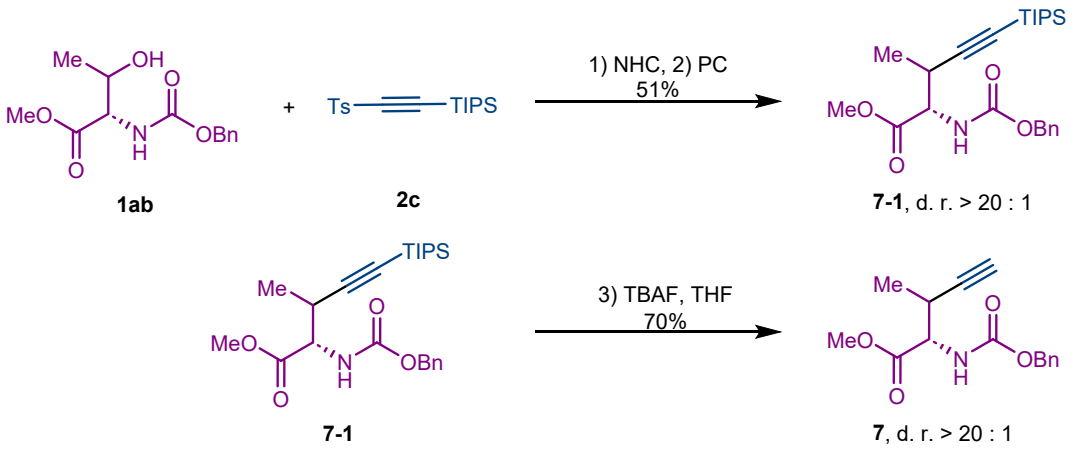
2) Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (2.0 μmol, 1 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **2c** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution.

The reaction solution was degassed by sparging with nitrogen for 15 minutes. TMG (0.02 mmol, 10 mol%) was added upon completion of the sparge. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The residue was purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **6-1** (53.0 mg, 62%) as a colorless oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.82 – 4.77 (m, 2H), 4.70 (s, 1H), 4.45 – 4.38 (m, 1H), 4.13 – 4.09 (m, 1H), 4.05 – 4.00 (m, 1H), 3.94 (dd, *J* = 8.2, 3.5 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H), 1.06 (d, *J* = 1.5 Hz, 21H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 112.9, 109.3, 103.0, 89.3, 86.6, 81.2, 80.3, 74.4, 72.9, 67.2, 26.9, 25.9, 25.3, 24.7, 18.5, 11.0; **HRMS m/z (ESI)** calcd for $C_{23}H_{41}O_5Si$ $(M + H)^+$ 425.2718, found 425.2713.

3) To a solution of **6-1** (0.12 mmol, 53 mg, 1.0 equiv.) in dry THF (1 mL) was added TBAF solution (1 mmol, 1M in THF, 1 mL) dropwiseunder a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 h at roomtemperature. The reaction was quenched by adding H_2O (0.5 mL) and the mixture wasextracted with EtOAc. The combined organic layers were dried overanhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **6** (19.0 mg, 57%) as a light yellow oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.82 (d, *J* = 3.3 Hz, 2H), 4.71 (d, *J* = 2.6 Hz, 1H), 4.41 (ddd, *J* = 7.9, 6.2, 4.4 Hz, 1H), 4.10 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.06 (dd, *J* = 8.8, 4.5 Hz, 1H), 3.92 (dd, *J* = 7.8, 3.0 Hz, 1H), 2.48 (d, *J* = 2.4 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 113.0, 109.3, 86.2, 81.2, 80.3, 75.6, 73.7, 72.9, 67.0, 26.9, 25.9, 25.2, 24.6, 18.4; **HRMS m/z (ESI)** calcd for $C_{14}H_{21}O_5$ $(M + H)^+$ 269.1384, found 269.1382.

Methyl (2S,3S)-2-(((benzyloxy)carbonyl)amino)-3-methylpent-4-ynoate (7)



1) To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **1ab** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

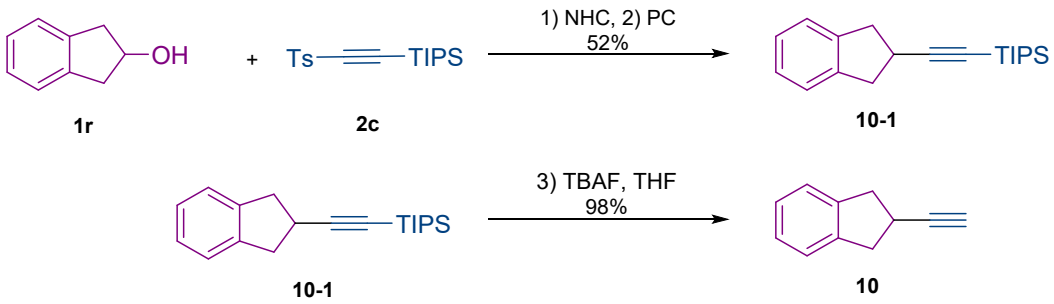
2) Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (2.0 µmol, 1 mol%), cesium acetate (0.60 mmol, 3.00 equiv) and **2c** (0.20 mmol, 1.0 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. TMG (0.02 mmol, 10 mol%) was added upon completion of the sparge. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The residue was purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **7-1** (44 mg, 51%) as a light yellow oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.30 (m, 5H), 5.42 (d, *J* = 9.7 Hz, 1H), 5.14 (s, 2H), 4.40 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.74 (s, 3H), 3.24 (dd, *J* = 7.1, 3.6 Hz, 1H), 1.27 (d, *J* = 7.1 Hz, 3H), 1.04 (d, *J* = 4.6 Hz, 21H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 170.9, 156.4, 136.3, 128.5, 128.1, 127.8, 106.6, 84.3, 67.0, 57.6, 52.5, 30.7, 18.5, 18.3, 11.0;

HRMS m/z (ESI) calcd for $C_{24}H_{38}NO_4S$ $(M + H)^+$ 432.2565, found 432.2565.

3) To a solution of **7-1** (0.10 mmol, 44 mg, 1.0 equiv.) in dry THF (1 mL) was added TBAF solution (1 mmol, 1M in THF, 1 mL) dropwiseunder a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 h at roomtemperature. The reaction was quenched by adding H_2O (0.5 mL) and the mixture wasextracted with EtOAc. The combined organic layers were dried overanhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to give **7** (19.6 mg, 70%) as a colorless oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.32 (m, 5H), 5.45 (d, *J* = 10.0 Hz, 1H), 5.14 (s, 2H), 4.43 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.77 (s, 3H), 3.19 (dt, *J* = 6.8, 3.3 Hz, 1H), 2.12 (d, *J* = 2.5 Hz, 1H), 1.28 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 170.9, 156.4, 136.1, 128.6, 128.3, 128.1, 82.6, 71.9, 67.3, 57.4, 52.7, 29.4, 18.0; **HRMS m/z (ESI)** calcd for $C_{15}H_{18}NO_4$ $(M + H)^+$ 276.1231, found 276.1229.

2-Ethynyl-2,3-dihydro-1H-indene (8)



1) To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (2.0 mmol, 1.00 equiv), **1r** (2.0 mmol, 1.00 equiv), and anhydrous MTBE (10 ml). Pyridine (2.1 mmol, 1.05 equiv) was added drop wise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

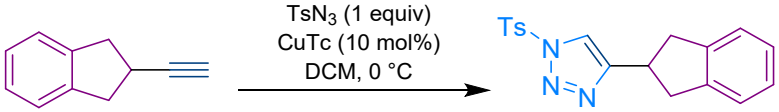
2) Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (8.0 µmol, 1 mol%), cesium acetate (2.4 mmol, 3.00 equiv) and **2c** (0.80 mmol, 1.0 equiv) and THF (10.0 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 10.0 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl

*t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. TMG (0.08 mmol, 10 mol%) was added upon completion of the sparge. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to give **8-1** (122 mg, 52%) as a colorless oil. ^{1}H-NMR and ^{13}C-NMR data are consistent with literature report.[7] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.20 (dd, *J* = 5.5, 3.3 Hz, 2H), 7.17 – 7.13 (m, 2H), 3.30 – 3.22 (m, 3H), 3.10 – 3.03 (m, 2H), 1.09 – 1.03 (m, 21H).

3) To a solution of **8-1** (0.40 mmol, 122 mg, 1.0 equiv.) in dry THF (4 mL) was added TBAF solution (0.48 mmol, 1M in THF, 0.48 mL, 1.2 equiv) dropwiseunder a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 h at roomtemperature. The reaction was quenched by adding H_2O (0.5 mL) and the mixture wasextracted with EtOAc. The combined organic layers were dried overanhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to give **8** (55.7 mg, 98%) as a colorless oil. ^{1}H-NMR and ^{13}C-NMR data are consistent with literature report.[7] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.22 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.19 – 7.15 (m, 2H), 3.26 (d, *J* = 12.2 Hz, 3H), 3.09 – 3.04 (m, 2H), 2.11 (d, *J* = 2.2 Hz, 1H).

4-(2,3-Dihydro-1H-inden-2-yl)-1-tosyl-1H-1,2,3-triazole (9)

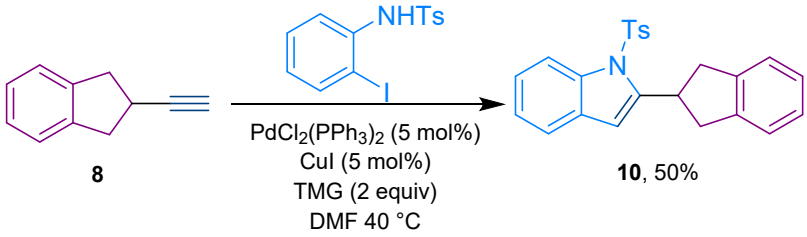


8 **9**, 74%

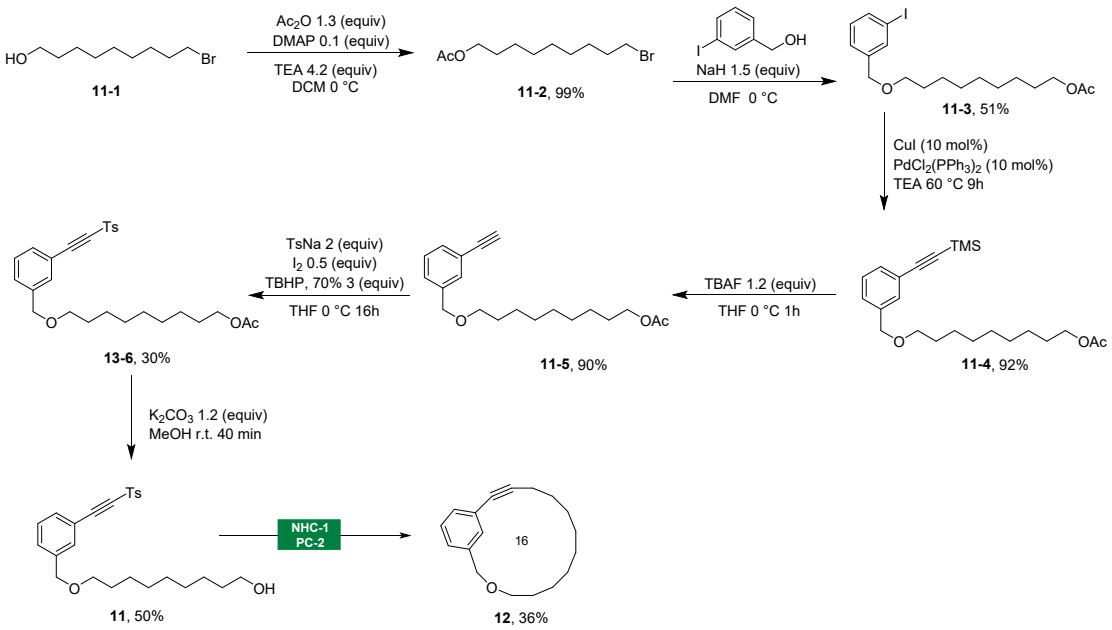
Flame-dried 10 mL schlenk tube filled with N_2. 2-Ethynyl-2,3-dihydro-1H-indene **8** (0.2 mmol, 1.0 equiv), TsN_3 (0.2 mmol), CuTc (0.02 mmol, 10 mol%) were added at 0 °C, and DCM (1.0 mL) was added under N_2. The formed mixture was stirred at r.t. for

12 h as monitored by TLC. The solvent was removed under vacuum directly. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to give **9** as a white solid (50.2 mg, 74%): **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.23 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.17 (dd, *J* = 5.6, 3.2 Hz, 2H), 3.83 (p, *J* = 7.9 Hz, 1H), 3.38 (dd, *J* = 15.4, 8.2 Hz, 2H), 3.10 (dd, *J* = 15.4, 7.7 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 151.5, 147.1, 141.8, 133.2, 130.4, 128.7, 126.7, 124.5, 119.6, 39.3, 36.3, 21.8; **HRMS m/z (ESI)** calcd for $C_{18}H_{18}N_3O_2S$ $(M + H)^+$ 340.1114, found 340.1113.

2-(2,3-Dihydro-1H-inden-2-yl)-1-tosyl-1H-indole (10)



Flame-dried 10 mL schlenk tube filled with N_2. 2-Ethynyl-2,3-dihydro-1H-indene **8** (0.2 mmol, 1.0 equiv), N-(2-iodophenyl)-4-methylbenzenesulfonamide (0.26 mmol, 1.3 equiv), $PdCl_2(PPh_3)_2$ (0.01 mmol, 5 mol%) , CuI (0.01 mmol, 5 mol%), TMG (0.4 mmol, 2.0 equiv) were added in a glovebox, and DMF (1.0 mL) was added under N_2 outside the glovebox. The formed mixture was stirred at 40 °C for 4 h as monitored by TLC. The solvent was removed under vacuum directly. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to give **10** as a white solid (39.2 mg, 50%): **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 8.20 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.37 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.21 – 7.18 (m, 5H), 6.44 (d, *J* = 0.9 Hz, 1H), 4.42 – 4.35 (m, 1H), 3.48 (dd, *J* = 15.4, 8.0 Hz, 2H), 3.13 (dd, *J* = 15.5, 6.8 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 145.8, 144.6, 142.2, 137.5, 136.2, 129.8, 129.7, 126.5, 126.2, 124.4, 124.1, 123.6, 120.3, 115.1, 107.9, 40.4, 38.4, 21.5; **HRMS m/z (ESI)** calcd for $C_{24}H_{22}NO_2S$ $(M + H)^+$ 388.1366, found 388.1366.



11-2: Flame-dried 100 mL tube filled with N_2. 9-Bromo-1-nonanol **11-1** (10 mmol, 1.0 equiv), Ac_2O (13 mmol, 1.3 equiv), DMAP (1 mmol, 10 mol%), TEA (42 mmol, 4.2 equiv), TMG (0.4 mmol, 2.0 equiv) were added, and DCM (20.0 mL) was added under N_2. The formed mixture was stirred at 0 ℃ for 1 h as monitored by TLC. Neutralized by a aqueous HCl (0.1 M), and neutralized by $NaHCO_3$ solution and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. Afford the product **11-2** as a colorless oil (2.64 g, 99%).[1]H-NMR and [13]C-NMR data are consistent with literature report.[8] **^{1}H NMR (600 MHz, $CDCl_3$):** δ 4.04 (t, *J* = 6.8 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.03 (s, 3H), 1.87 – 1.79 (m, 2H), 1.63 – 1.56 (m, 2H), 1.43 – 1.39 (m, 2H), 1.30 (h, *J* = 4.4, 3.7 Hz, 8H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.2, 64.5, 33.9, 32.7, 29.2, 29.1, 28.6, 28.5, 28.1, 25.8, 21.0.

11-3: Flame-dried 100 mL tube filled with N_2. 3-Lodobenzyl alcohol (9 mmol, 1.0 equiv), NaH (10.8 mmol, 1.2 equiv) and DMF (1M) were added, the formed mixture was stirred at 0 ℃ for 0.5 h. Then **11-2** (9.9 mmol, 1.1 equiv) in DMF (1M) was added under N_2 at 0 ℃. The formed mixture was stirred at room tempurature for 2 h as monitored by TLC. Neutralized by a aqueous HCl (0.1 M), and neutralized by NaHCO3 solution and extracted with DCM. The combined organic layers were dried over

anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to give product **11-3** as a light yellow oil (1.90 g, 45%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 1.7 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 4.43 (s, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.04 (s, 4H), 1.61 (dt, *J* = 7.6, 3.9 Hz, 4H), 1.30 (t, *J* = 5.9 Hz, 10H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.2, 141.1, 136.5, 136.4, 130.1, 126.6, 94.3, 71.9, 70.7, 64.6, 29.7, 29.4, 29.3, 29.2, 28.6, 26.1, 25.9, 21.0; **HRMS m/z (ESI)** calcd for $C_{18}H_{27}IO_3Na$ $(M + Na)^+$ 441.0897, found 441.0899.

11-4: Flame-dried 10 mL schlenk tube filled with N_2. 9-((3-Iodobenzyl)oxy)nonyl acetate **11-3** (4.5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (0.18 mmol, 4 mol%), Trimethylsilylacetylene (6.75 mmol, 1.5 equiv), CuI (0.18 mmol, 4 mol%) were added in a glovebox, and TEA (4.5 mL) was added under N_2 outside the glovebox. The formed mixture was stirred at 60 ºC for 9 h as monitored by TLC. The solvent was removed under vaccum directly. The residue was purifiedby flash column chromatography through silica gel using Petroleum ether/ethyl acetate as eluent to giveproduct **11-4** as a light yellow oil (1.61 g, 92%): **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.31 – 7.27 (m, 2H), 4.45 (s, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.04 (s, 3H), 1.63 – 1.57 (m, 4H), 1.35 – 1.28 (m, 10H), 0.24 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.2, 138.8, 134.1, 131.1, 131.0, 128.2, 127.7, 123.1, 105.1, 94.1, 72.3, 70.6, 64.6, 29.7, 29.4, 29.3, 29.2, 28.6, 26.1, 25.9, 21.0; **HRMS m/z (ESI)** calcd for $C_{23}H_{37}O_3Si$ $(M + H)^+$ 389.2507, found 389.2509.

11-5: To a solution of 9-((3-((trimethylsilyl)ethynyl)benzyl)oxy)nonyl acetate **11-4** (4 mmol, 1.0 equiv.) in dry THF (4 mL) was added TBAF solution (4.8 mmol, 1M in THF, 4.8 mL, 1.2 equiv) dropwiseunder a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 h at 0 ºC. The reaction was quenched by adding H_2O (0.5 mL) and the mixture wasextracted with Et_2O. The combined organic layers were dried overanhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was

purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **11-5** (1.14 g, 90%) as a white solid: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.5 (s, 1H), 7.4 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.3 – 7.3 (m, 2H), 4.5 (s, 2H), 4.0 (t, *J* = 6.8 Hz, 2H), 3.4 (t, *J* = 6.6 Hz, 2H), 3.1 (s, 1H), 2.0 (s, 3H), 1.6 – 1.6 (m, 4H), 1.3 (t, *J* = 6.0 Hz, 10H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.2, 139.0, 131.2, 131.2, 128.3, 128.0, 122.1, 83.6, 77.1, 72.3, 70.6, 64.6, 29.7, 29.4, 29.3, 29.2, 28.6, 26.1, 25.9, 21.0; **HRMS m/z (ESI)** calcd for $C_{20}H_{29}O_3$ $(M + H)^+$ 317.2111, found 317.2116.

11-6: To a suspension sodium *p*-toluenesulfinate (7.2 mmol, 2.00 equiv.) in THF (18 mL) was added 9-((3-ethynylbenzyl)oxy)nonyl acetate **11-5** (5.0 mmol, 1.00 equiv.) followed by iodine (1.8 mmol, 0.50 equiv.), TBHP (10.8 mmol, 3 equiv) at 0 ºC. The mixture was stirred for 16 h at room temperature before the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. $NaHCO_3$ was added and the product extracted into DCM. The combined organic phases were washed with H_2O, brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography using petroleum ether/ethyl acetate as eluent to give **11-6** (0.67 g, 40%) as a colorless oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.0 (d, *J* = 8.4 Hz, 2H), 7.5 (d, *J* = 1.8 Hz, 1H), 7.4 (dt, *J* = 8.1, 1.7 Hz, 2H), 7.4 (d, *J* = 8.3 Hz, 2H), 7.3 (t, *J* = 7.7 Hz, 1H), 4.5 (s, 2H), 4.0 (t, *J* = 6.8 Hz, 2H), 3.4 (t, *J* = 6.7 Hz, 2H), 2.5 (s, 3H), 2.0 (s, 3H), 1.6 (t, *J* = 3.3 Hz, 4H), 1.3 – 1.3 (m, 10H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.2, 145.3, 139.7, 138.9, 131.7, 131.5, 130.5, 130.0, 128.7, 127.5, 118.0, 93.0, 85.5, 71.9, 70.9, 64.6, 29.6, 29.4, 29.3, 29.2, 28.6, 26.1, 25.9, 21.7, 21.0; **HRMS m/z (ESI)** calcd for $C_{27}H_{35}O_5S$ $(M + H)^+$ 471.2200, found 471.2201.

11: To a solution of 9-((3-(tosylethynyl)benzyl)oxy)nonyl acetate **11-6** (1.44 mmol, 1.0 equiv.) in dry MeOH (6 mL) was added K_2CO_3 (1.73 mmol, 1.2 equiv) wiseunder a nitrogen atmosphere. The reaction mixture was allowed to stir for 40 min at 0 ºC. The reaction was quenched by adding H_2O (0.5 mL) and the mixture wasextracted with DCM. The combined organic layers were dried overanhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purifiedby flash column chromatography

through silica gel using petroleum ether/ethyl acetate as eluent to give **11** (0.31 g, 50%) as a colorless oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.50 (s, 1H), 7.42 (dd, *J* = 5.6, 3.8 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 4.45 (s, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.47 (s, 3H), 1.59 (dd, *J* = 15.5, 7.6 Hz, 4H), 1.35 – 1.28 (m, 10H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 145.4, 139.6, 138.9, 131.7, 131.5, 130.5, 130.0, 128.7, 127.5, 118.0, 93.0, 85.4, 71.8, 70.9, 63.0, 32.7, 29.7, 29.6, 29.5, 29.3, 26.1, 25.7, 21.7; **HRMS m/z (ESI)** calcd for $C_{25}H_{32}O_4SNa$ $(M + Na)^+$ 451.1913, found 451.1915.

12: To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.3 mmol, 1.00 equiv), **11** (0.30 mmol, 1.00 equiv), and anhydrous MTBE (1.5 ml). Pyridine (0.32 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

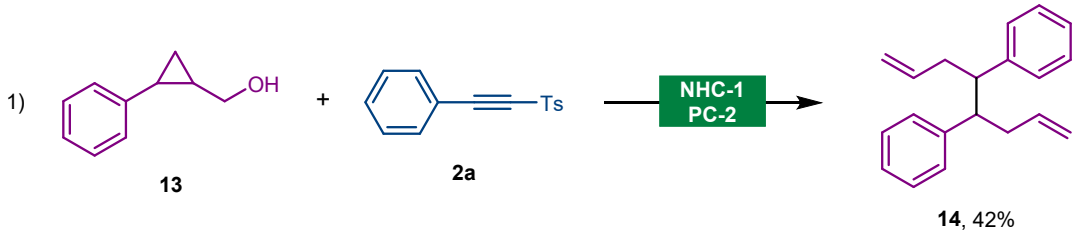
Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.0 μmol, 1 mol%), cesium acetate (0.90 mmol, 3.00 equiv) and THF (21 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The residue was purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **12** (18.6 mg, 36%) as a yellow oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.65 (s, 1H), 7.21 (d, *J* = 4.7 Hz, 2H), 7.03 – 6.99 (m, 1H), 4.58 (s, 2H), 3.47 (t, *J* = 5.2 Hz, 2H), 2.44 – 2.41 (m, 2H), 1.63 (tdd, *J* = 11.2, 7.8, 4.4 Hz, 8H), 1.46 – 1.36 (m, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.4, 130.4, 128.5, 128.0, 125.4, 124.4, 91.9, 81.9, 71.3, 68.6, 30.0, 29.3, 28.8, 28.7, 28.4, 27.2, 26.4, 19.6;

HRMS m/z (ESI) calcd for $C_{18}H_{25}O$ $(M + H)^+$ 257.1900, found 257.1894.

7. Mechanistic experiments.

7.1 The Radical Clock Experiment



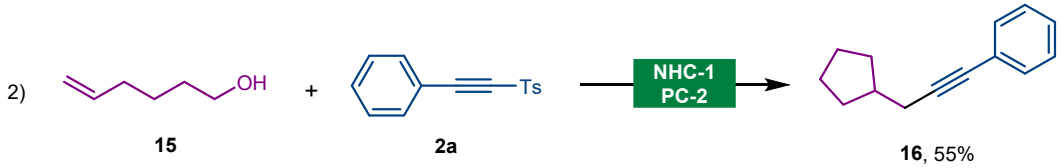
13 **2a** **14**, 42%

To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **13** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.0 μmol, 1 mol%), **2a** (0.2 mmol, 1.0 equiv) cesium acetate (0.90 mmol, 3.00 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The residue was purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **14** (22.0 mg, 42%) as a colorless oil. ^{1}H-NMR and ^{13}C-NMR data are consistent with literature report.[9]: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (t, *J* = 7.6 Hz, 4H), 7.24 – 7.21 (m, 2H), 7.19 – 7.16 (m, 4H), 5.41 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 2H), 4.81 – 4.67 (m, 4H), 2.88 – 2.80 (m, 2H), 2.15 (dddd,

J = 9.4, 7.2, 4.3, 1.3 Hz, 4H).



15 **2a** **16**, 55%

To an oven dried 25 mL schlenk tube equipped with a N_2 was added NHC-1 (0.5 mmol, 1.00 equiv), **15** (0.50 mmol, 1.00 equiv), and anhydrous MTBE (2.5 ml). Pyridine (0.53 mmol, 1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere for 15 minutes.

Another oven-dried 25mL schlenk tube was charged with iridium photocatalyst PC-2 (2.0 µmol, 1 mol%), **2a** (0.2 mmol, 1.0 equiv) cesium acetate (0.90 mmol, 3.00 equiv) and THF (2.5 ml) was added to the mixture.

The methyl *t*ert-butyl ether suspension was transferred to a 2.5 mL syringe under air. Then a syringe filter and new needle were installed on the syringe, before the methyl *t*ert-butyl ether solution was injected through the syringe filter into the THF solution. The reaction solution was degassed by sparging with nitrogen for 15 minutes. The mixture was then stirred irradiated with a 45 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. The crude reaction mixture was directly concentrated to remove both methyl *t*ert-butyl ether and THF solvents. EtOAc was added to the concentrated crude reaction mixture followed by filtration through a silica plug. The residue was purifiedby flash column chromatography through silica gel using petroleum ether/ethyl acetate as eluent to give **16** (20.3 mg, 55%) as a colorless oil: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 (dd, J = 7.8, 1.7 Hz, 2H), 7.30 – 7.25 (m, 3H), 2.42 (d, J = 6.8 Hz, 2H), 2.14 (hept, J = 7.7 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.72 – 1.63 (m, 2H), 1.58 (tddd, J = 9.6, 7.4, 5.0, 2.9 Hz, 2H), 1.42 – 1.32 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 131.5, 128.1, 127.4, 124.1, 89.9, 80.6, 39.1, 32.0, 25.3, 25.2; **HRMS m/z (ESI)** calcd for $C_{14}H_{17}$ $(M + H)^+$ 185.1325, found 185.1325.

7.2. Emission Quenching Experiments (Stern–Volmer Studies)

Fluorescence quenching studies were performed using an EDINBURCH

INSTRUMENTS Spectrofluorometer FS5. In each experiment, the photocatalyst and varying concentrations of quencher were weighed and diluted in the glove box, and combined in a THF in screw top 1.0 cm quartz cuvettes. THF were degassed separately outside of the glove box by sparging with N_2 for 5 minutes, the emission of the sample was collected. For the emission quenching of $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$, the photocatalyst concentration was 2.0×10^{-5} M, the solution was irradiated at 430 nm, and the emission intensity was observed at 480 nm. Plots were constructed according to the Stern–Volmer equation $I_0/I = 1+k_q\tau_0[Q]$.

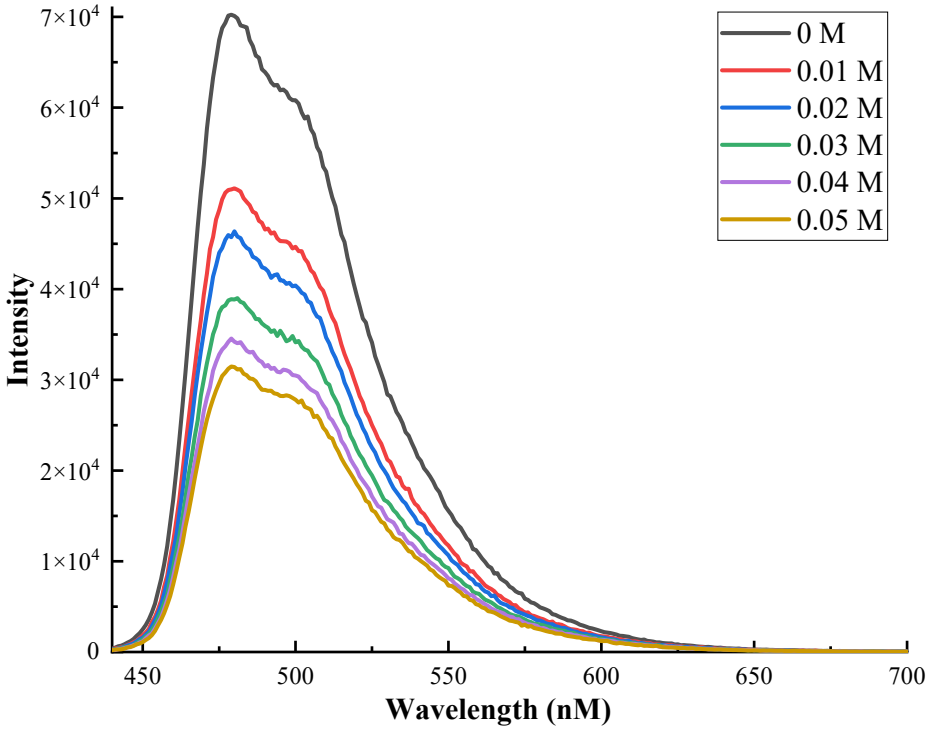


Figure S2. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching with Alkyne.

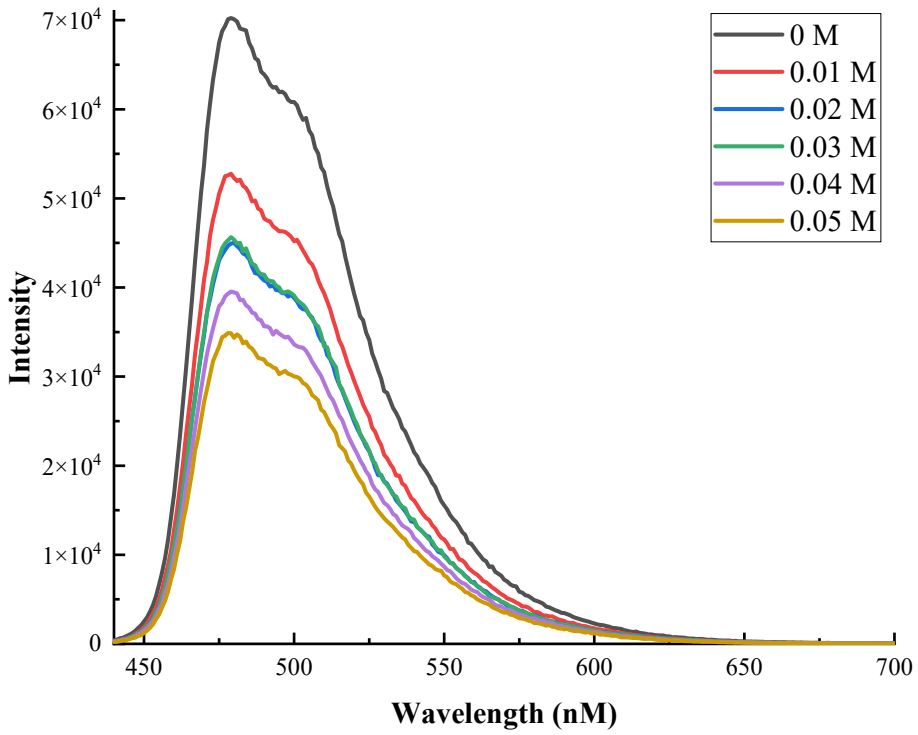


Figure S3. Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 emission quenching with TMG.

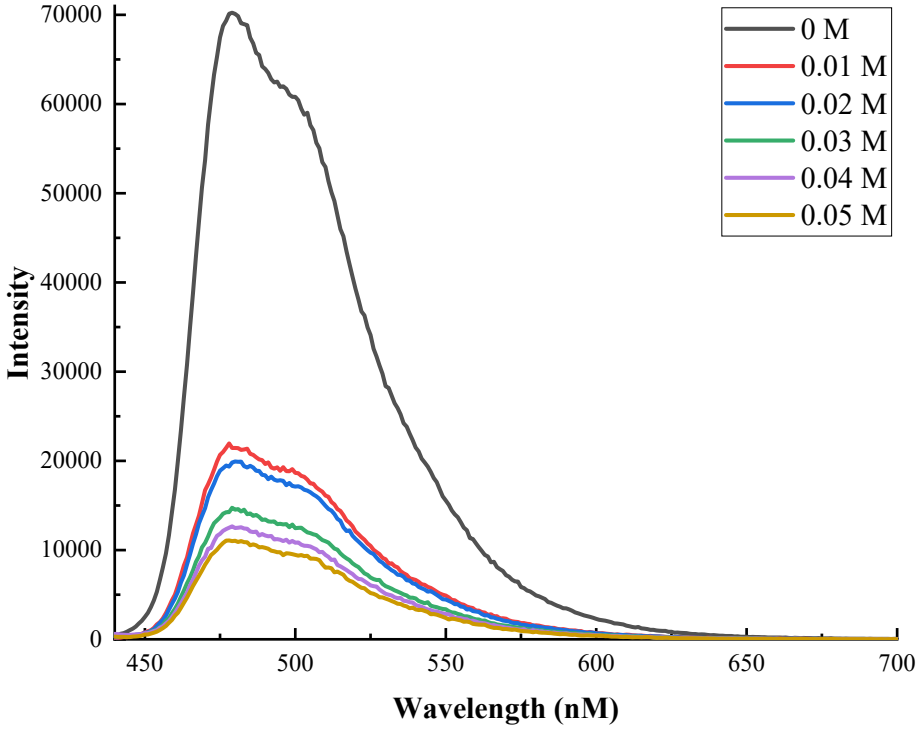


Figure S4. Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 emission quenching with NHC-alcohol .

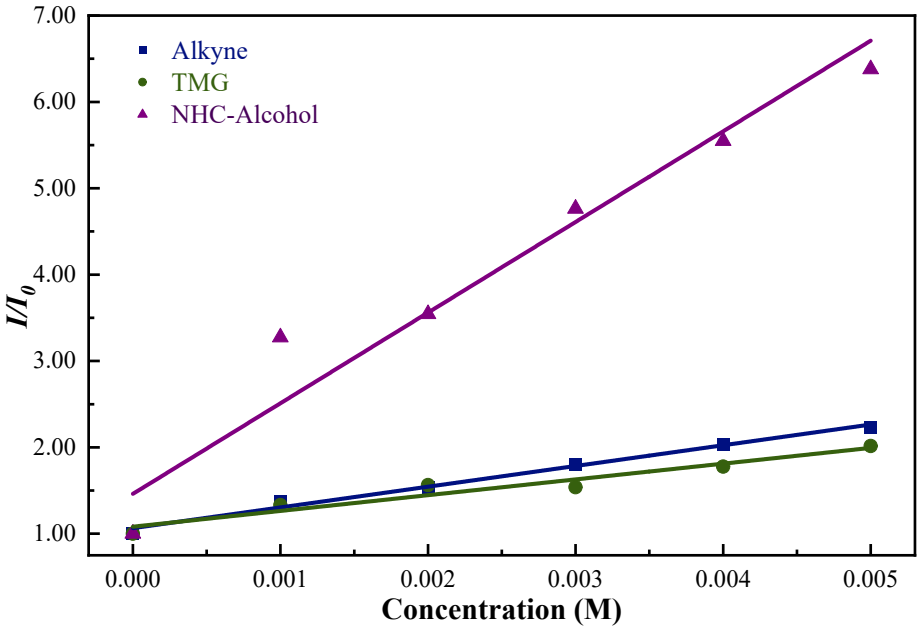


Figure S5. Stern–Volmer fluorescence quenching

8. References

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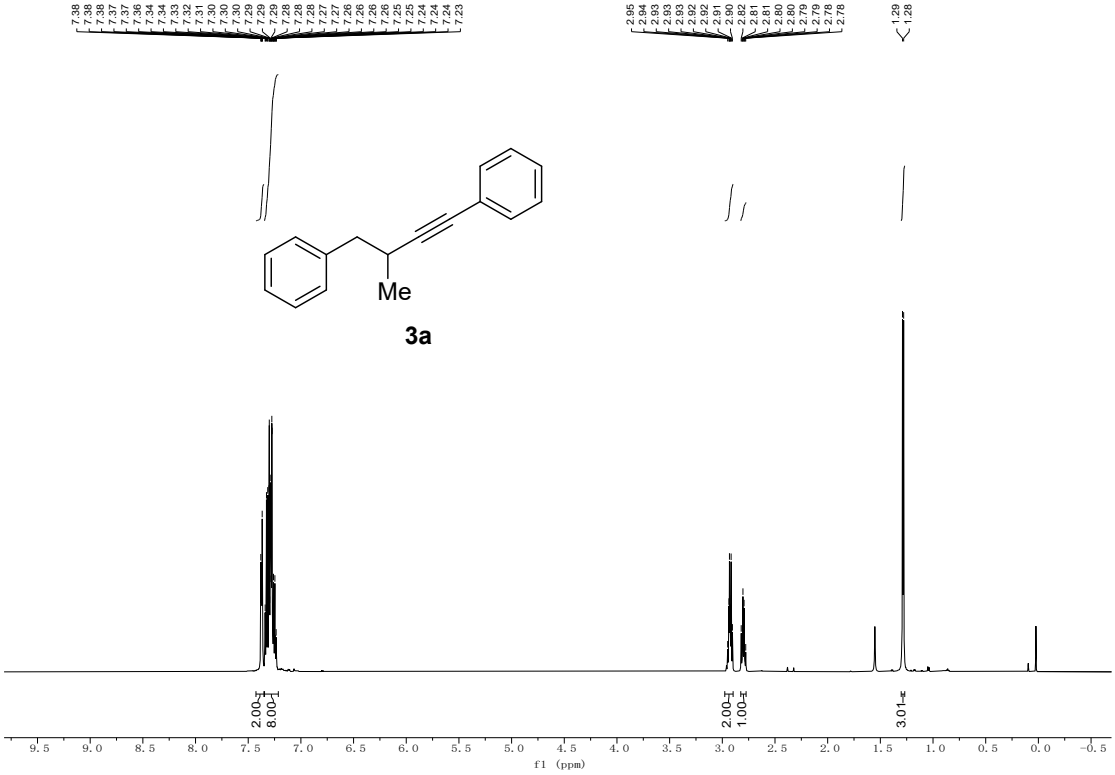
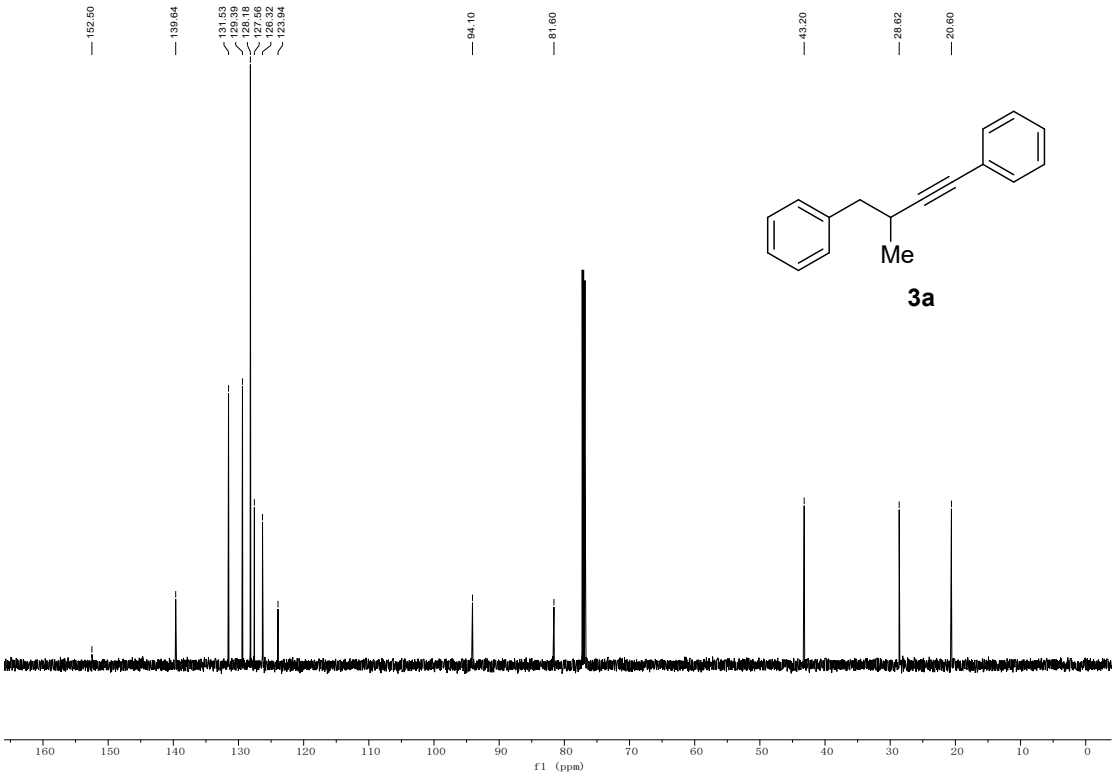
9. Copies of NMR Spectra

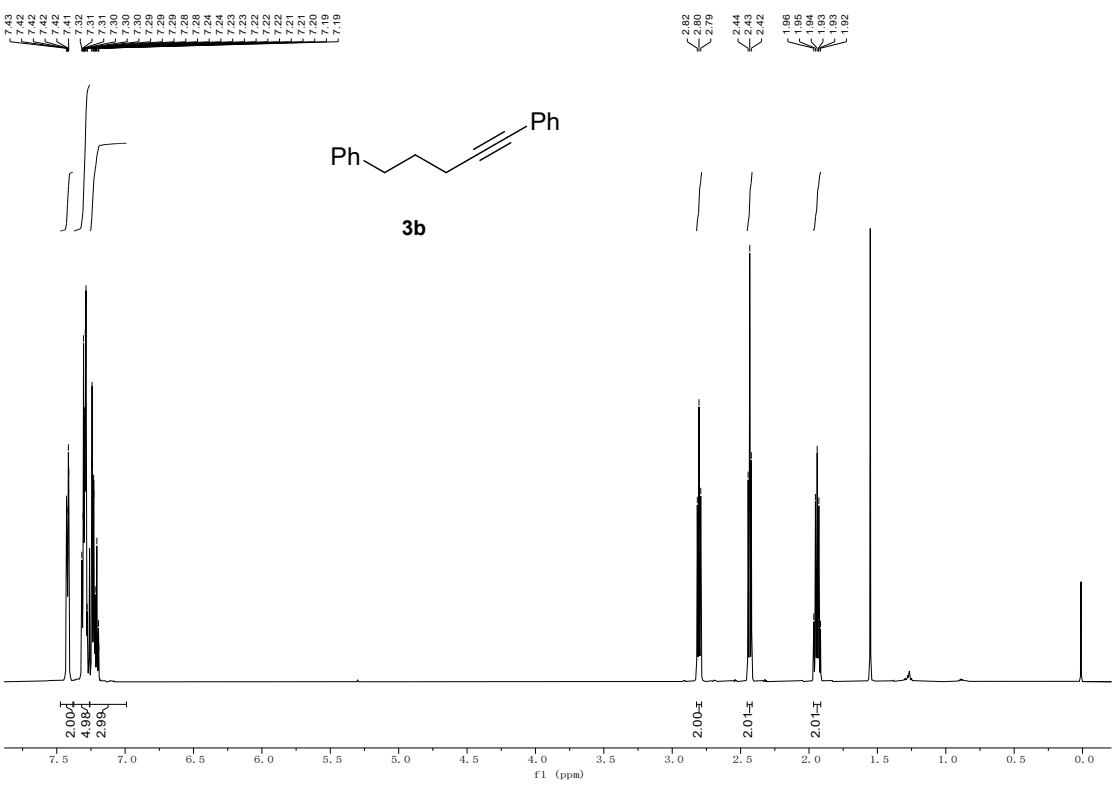
^{1}H NMR Spectrum of 3a



^{13}C NMR Spectrum of 3a



^{1}H NMR Spectrum of 3b



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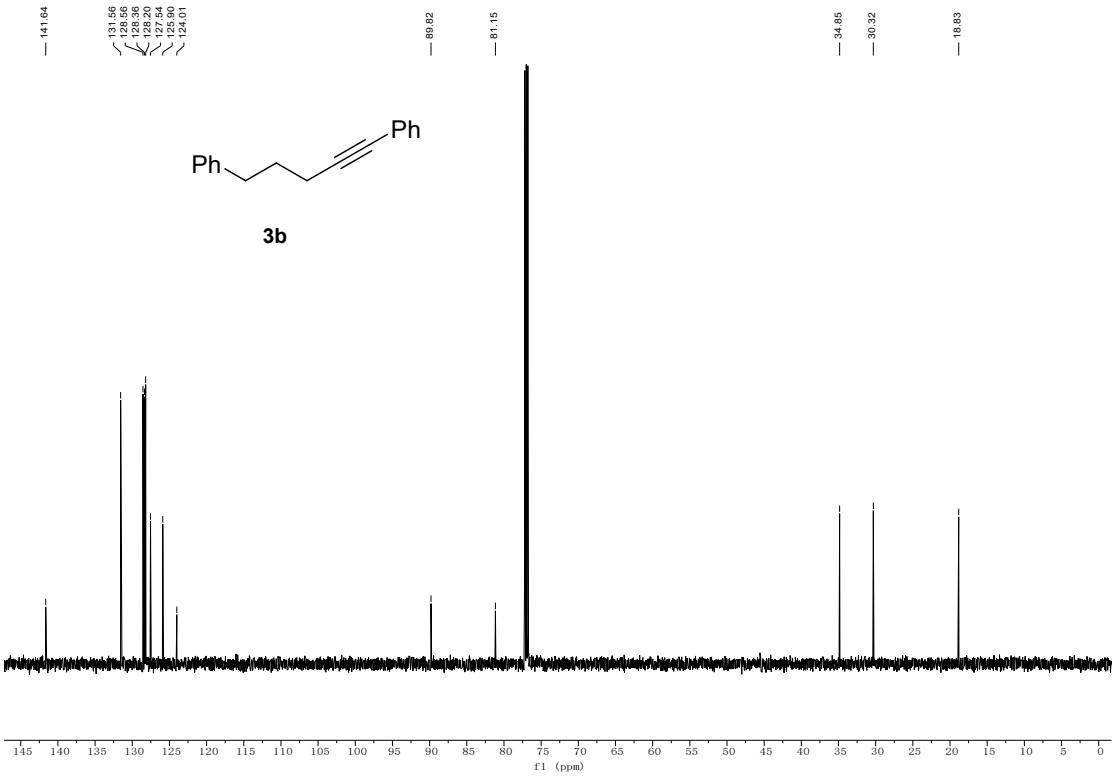

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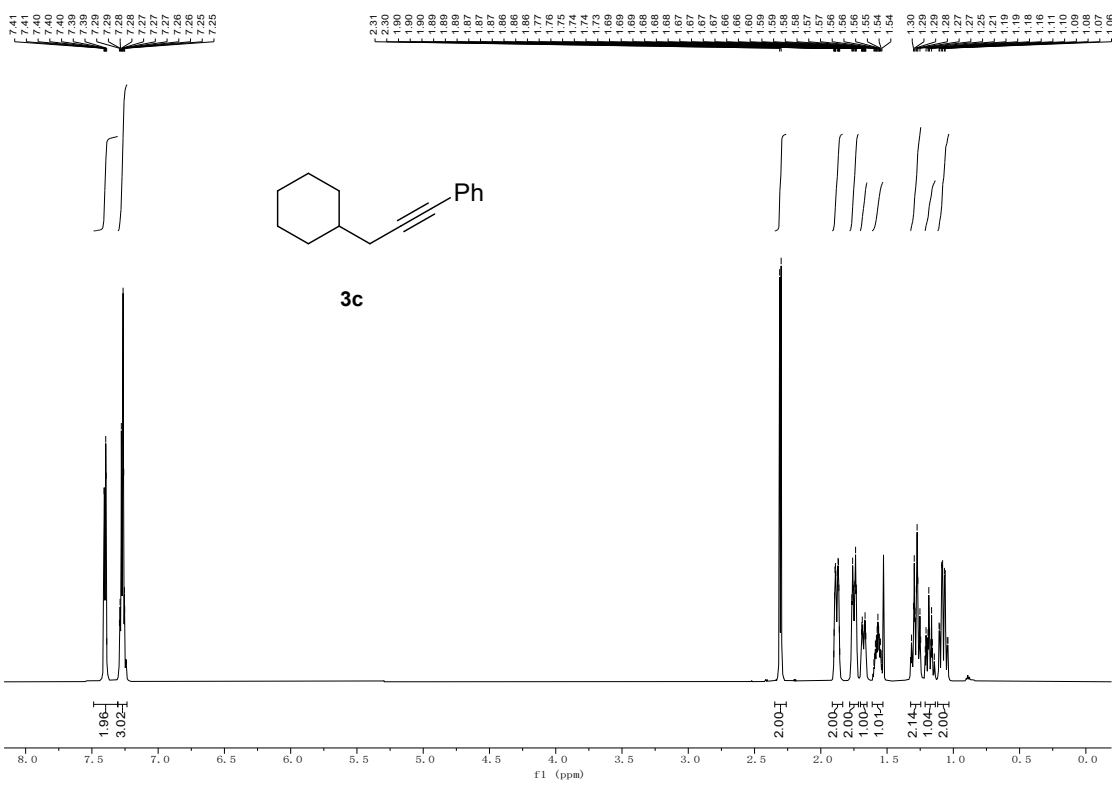
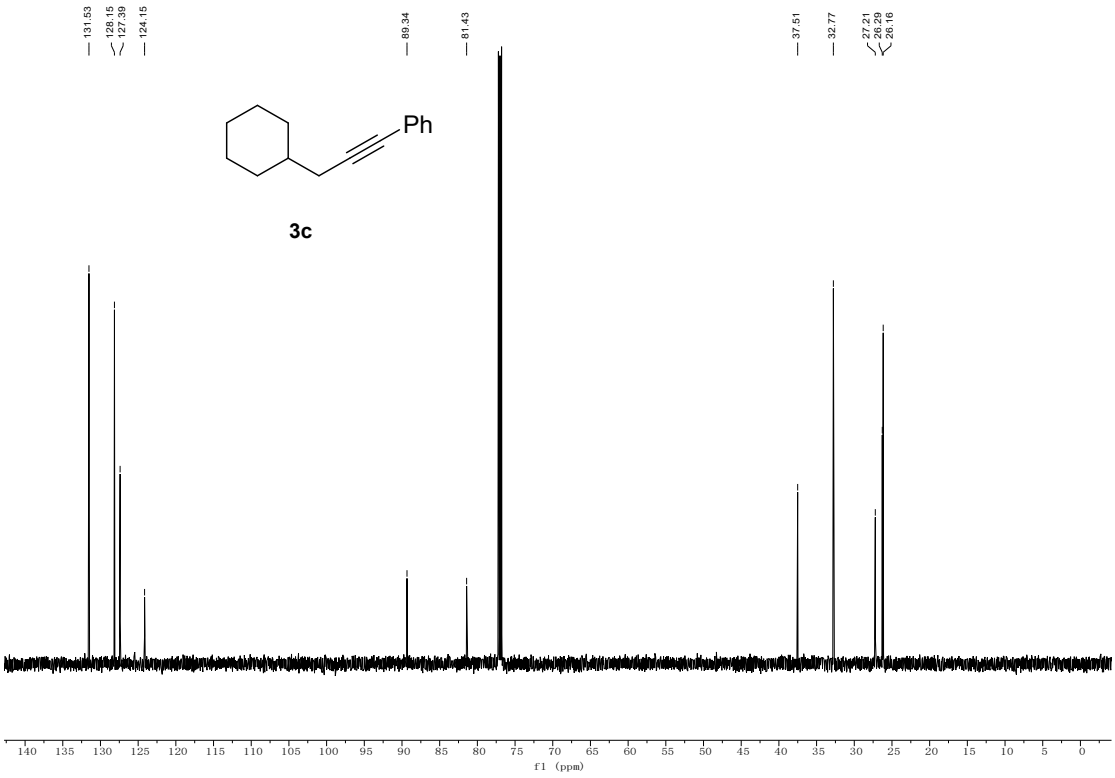


^{13}C NMR Spectrum of 3c



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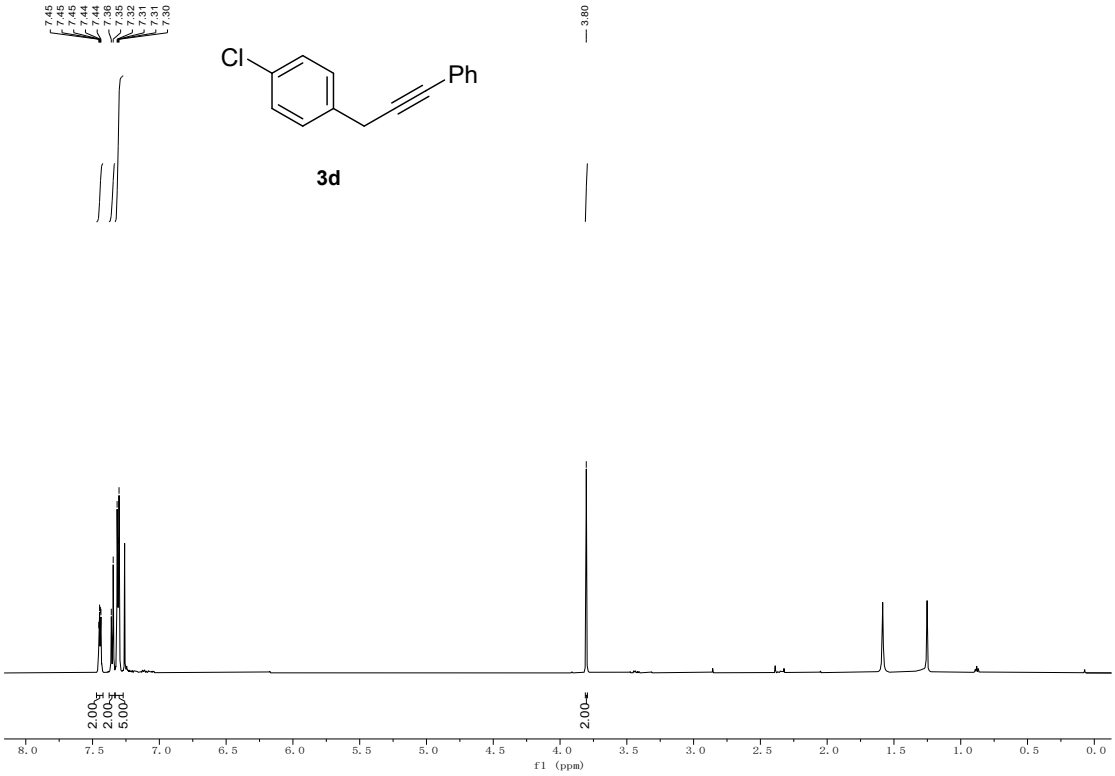
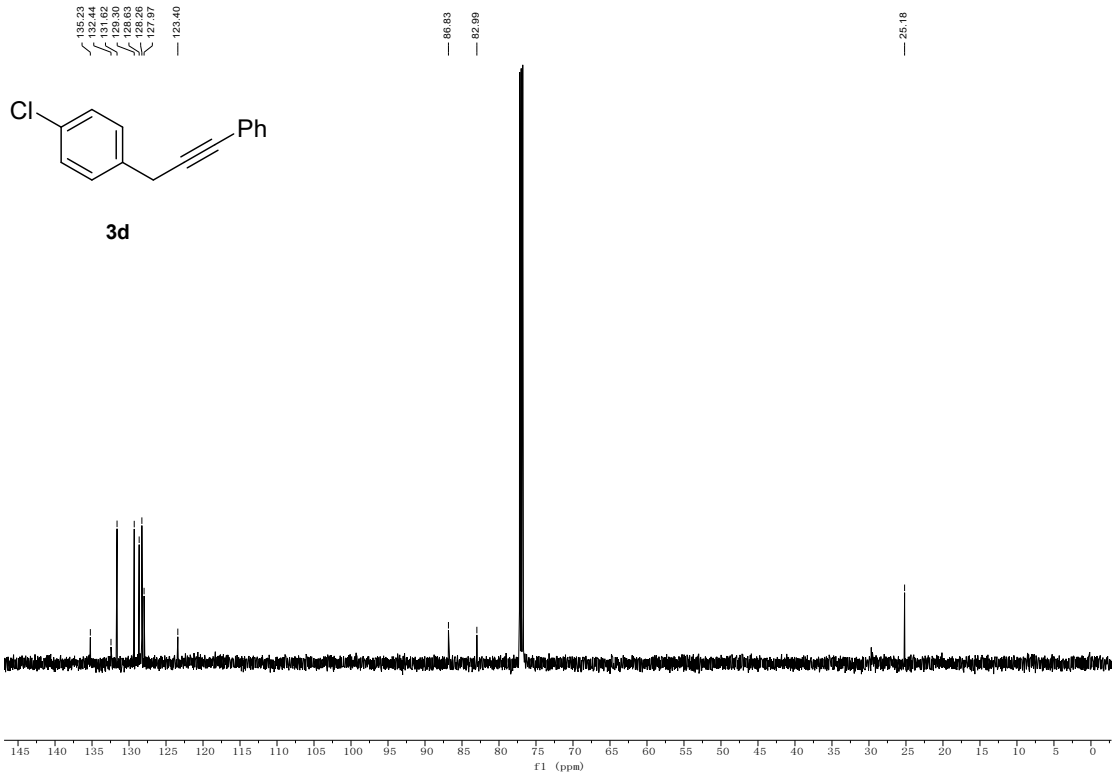
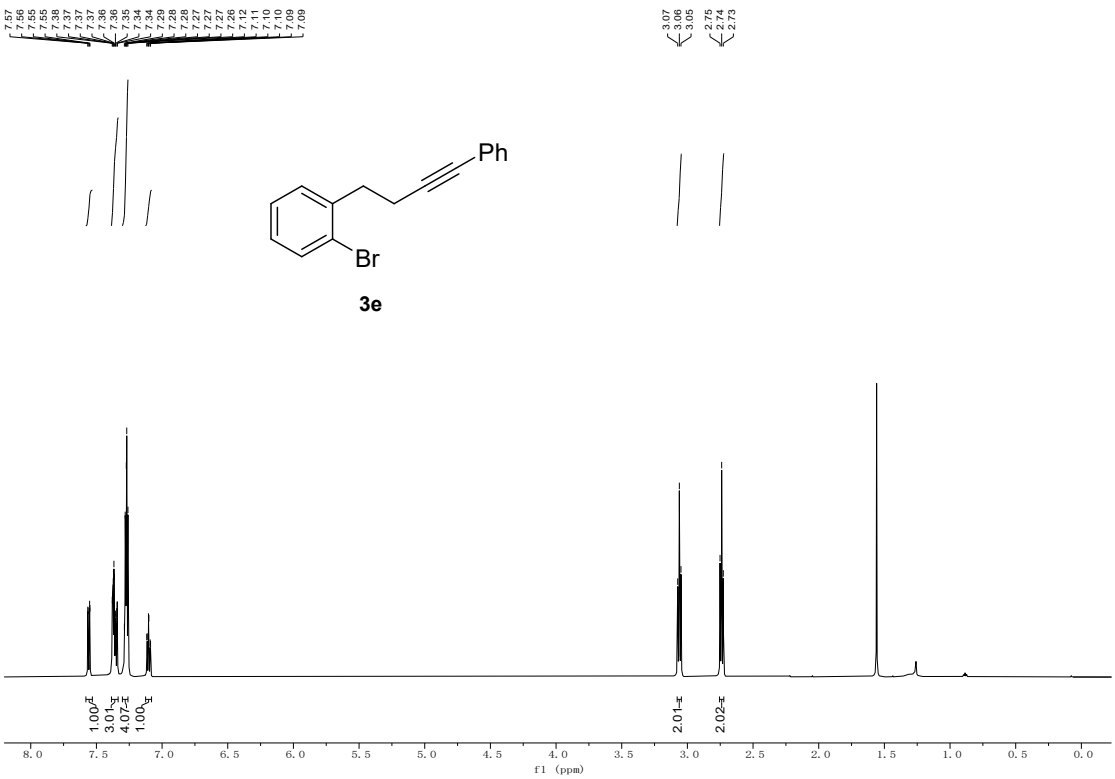


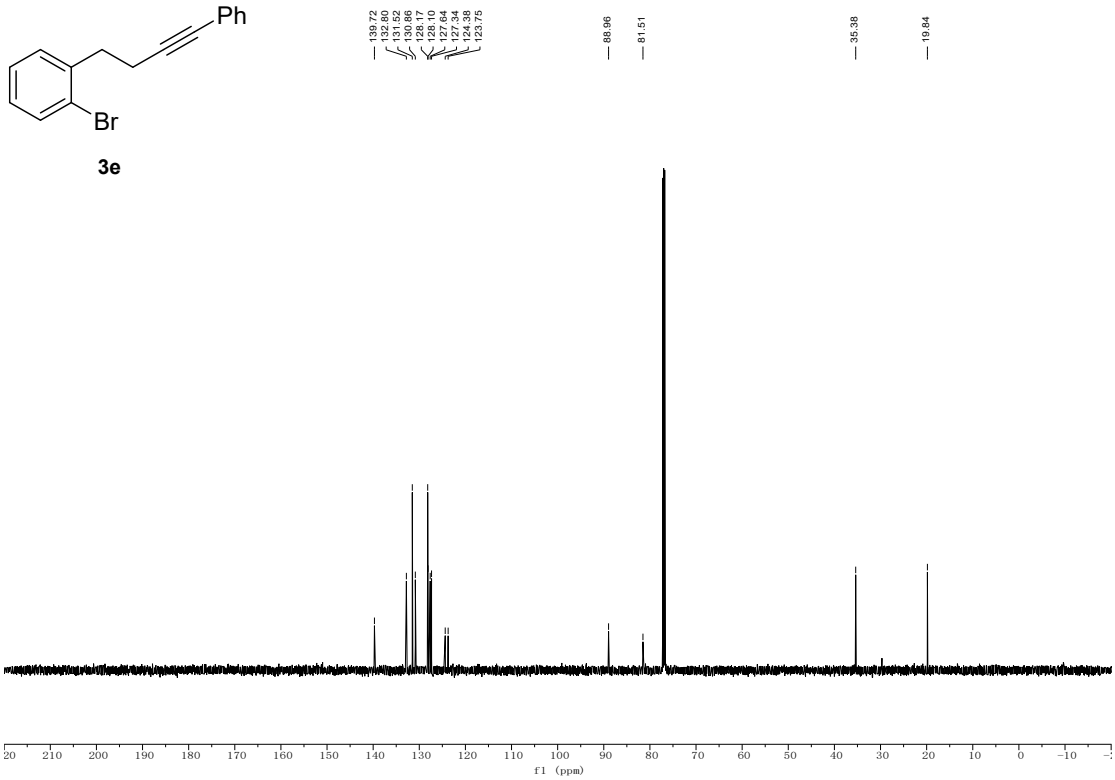
^{13}C NMR Spectrum of 3d



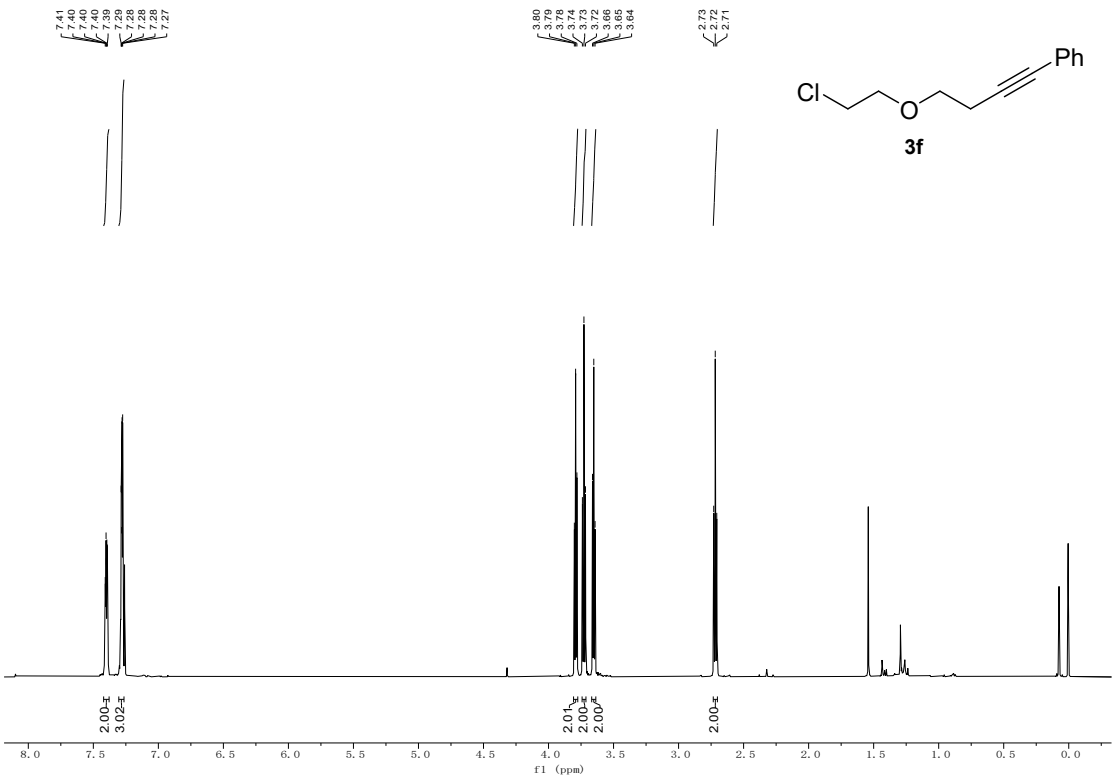
^{1}H NMR Spectrum of 3e



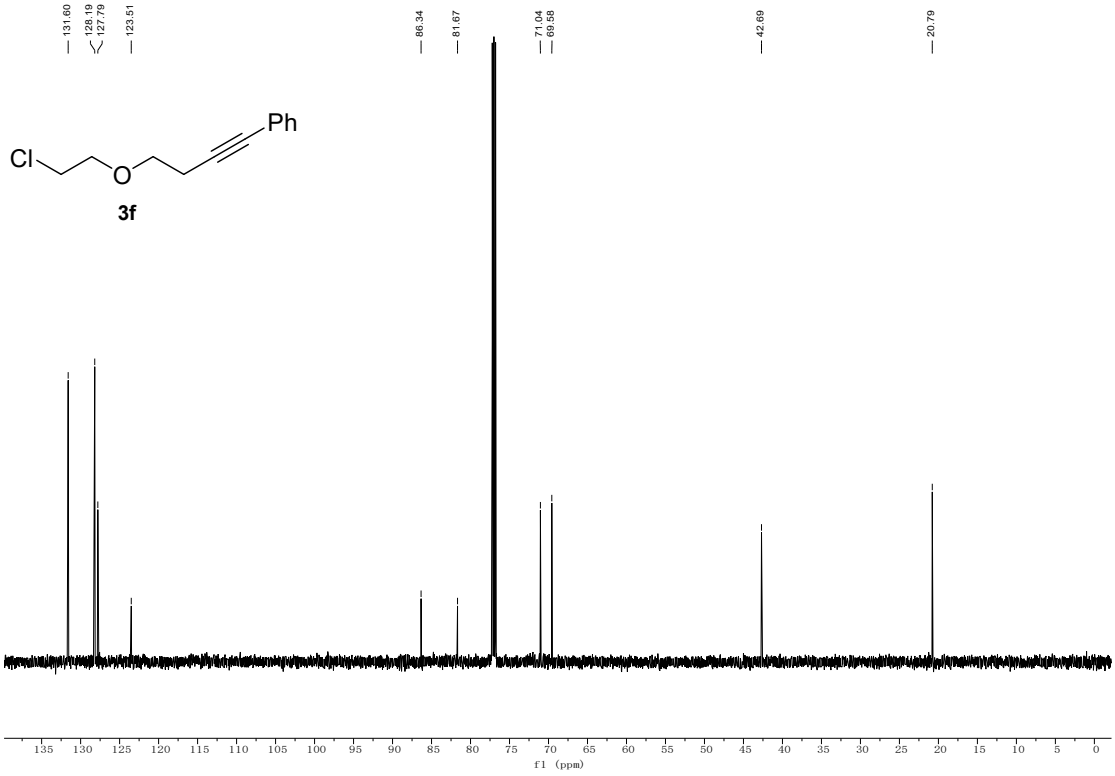
^{13}C NMR Spectrum of 3e



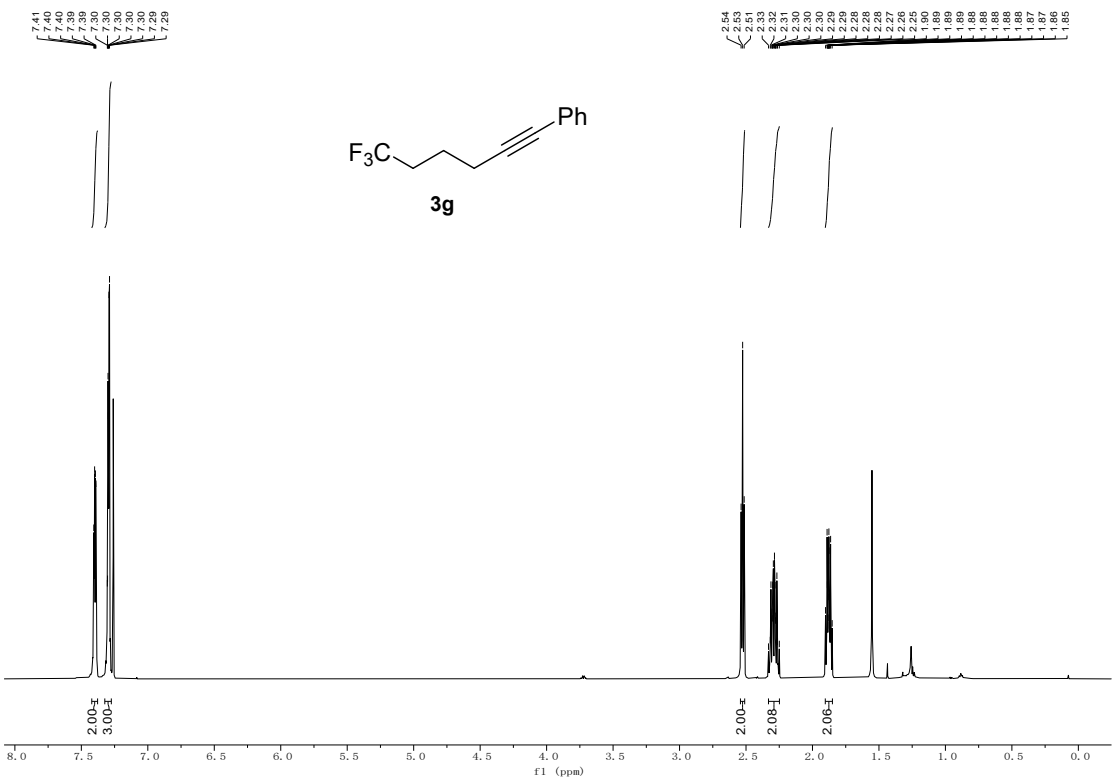
^{1}H NMR Spectrum of 3f



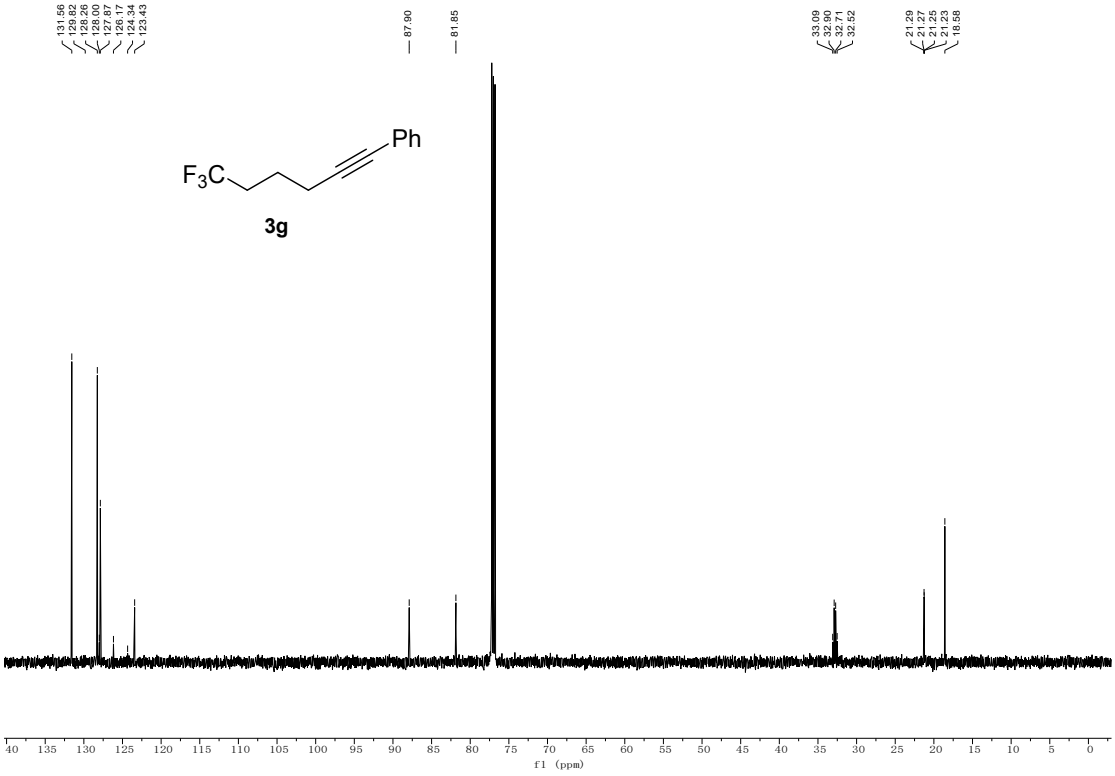
^{13}C NMR Spectrum of 3f



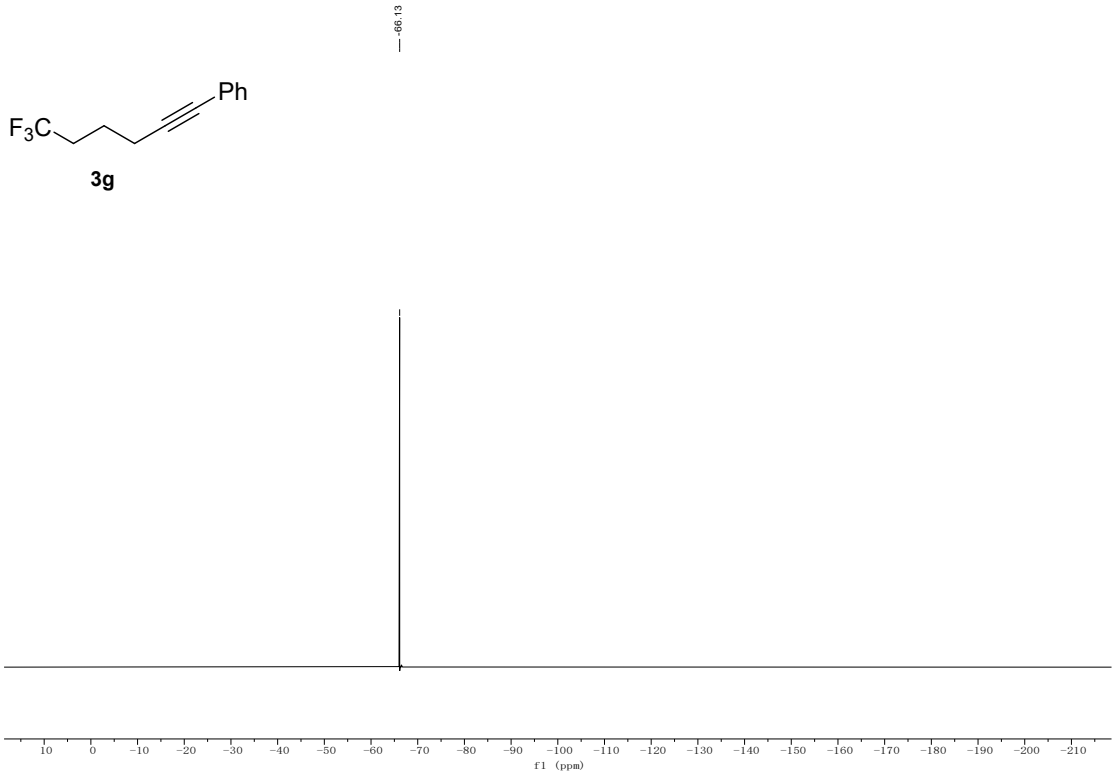
^{1}H NMR Spectrum of 3g



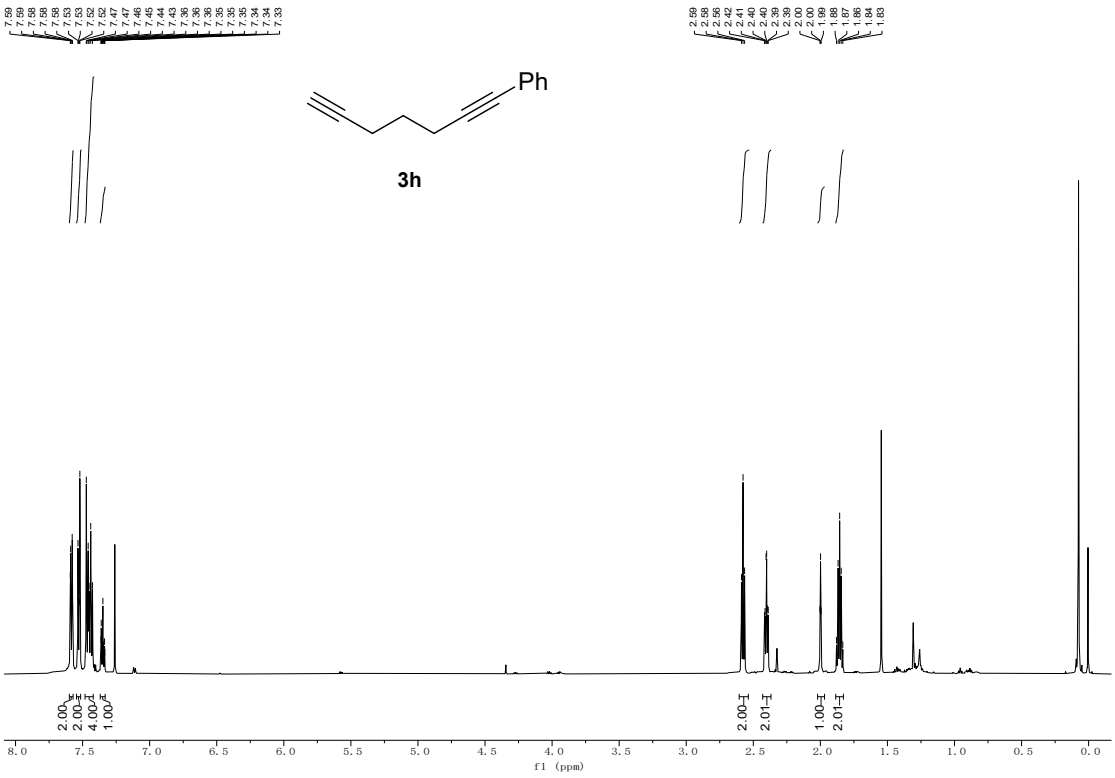
^{13}C NMR Spectrum of 3g



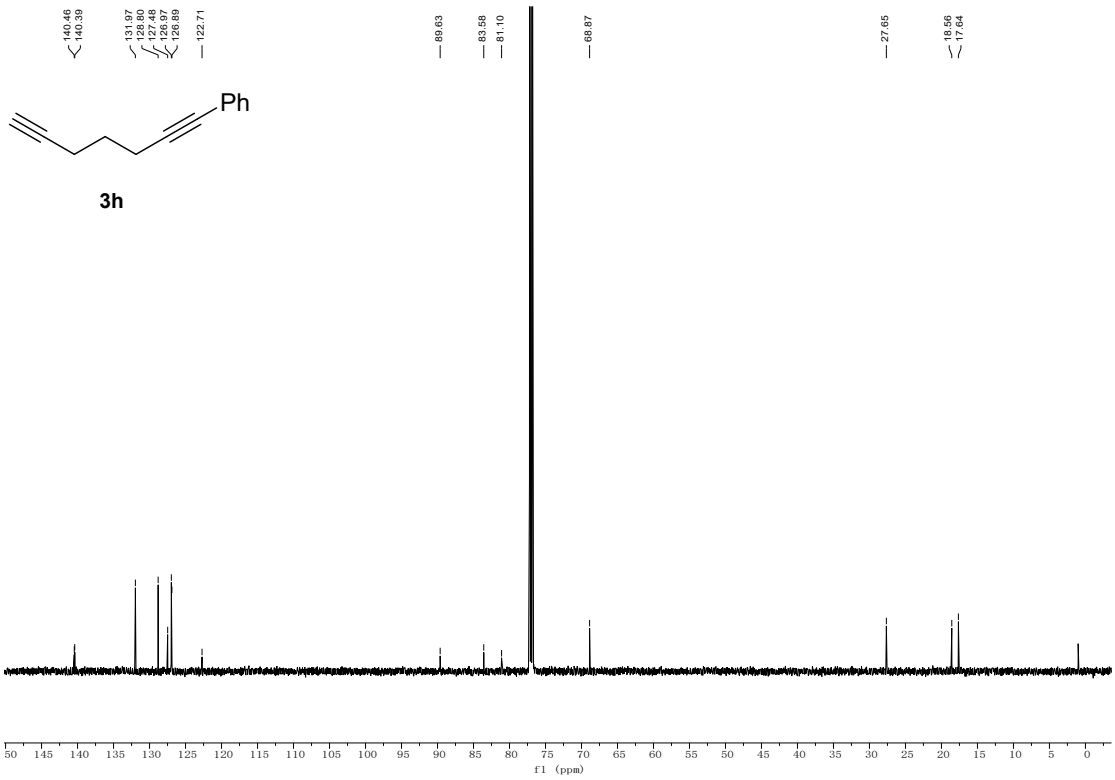
^{19}F NMR Spectrum of 3g



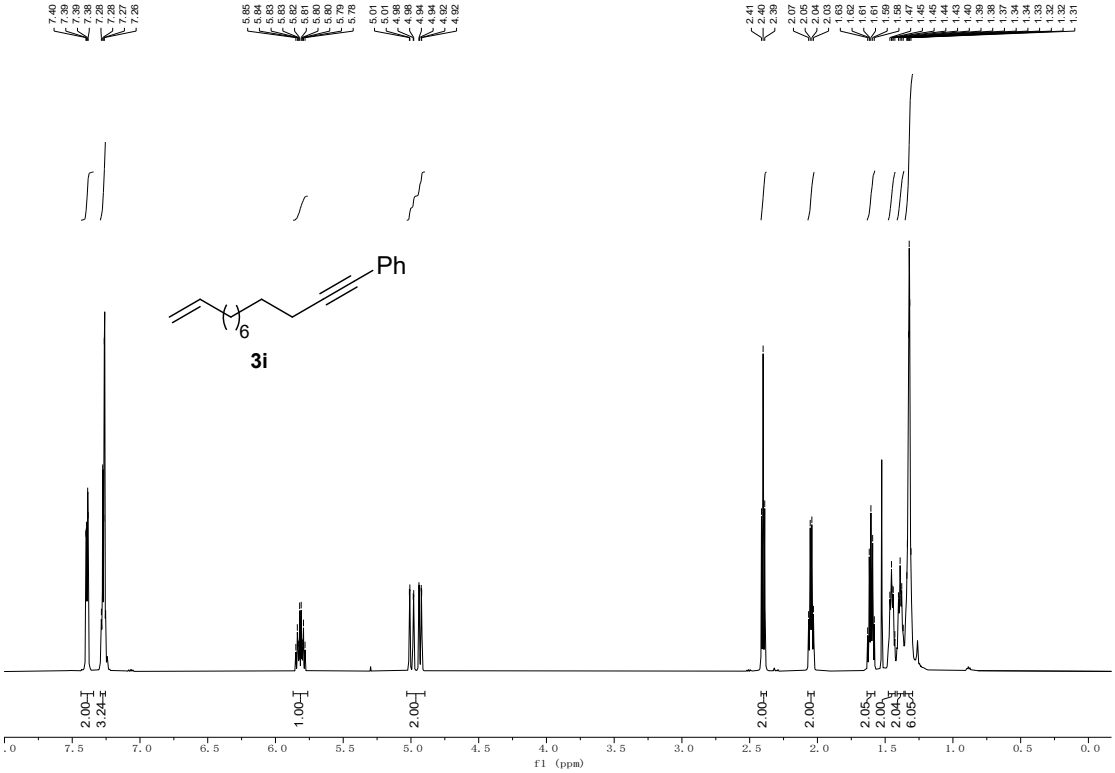
^{1}H NMR Spectrum of 3h



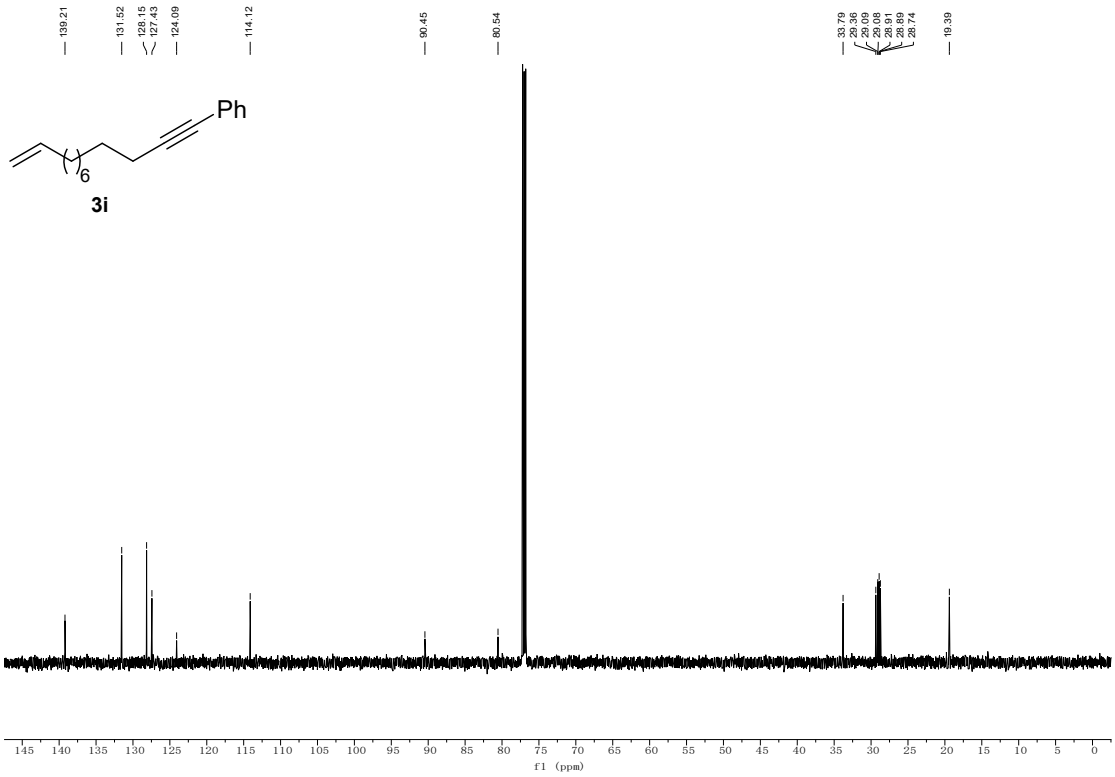
^{13}C NMR Spectrum of 3h



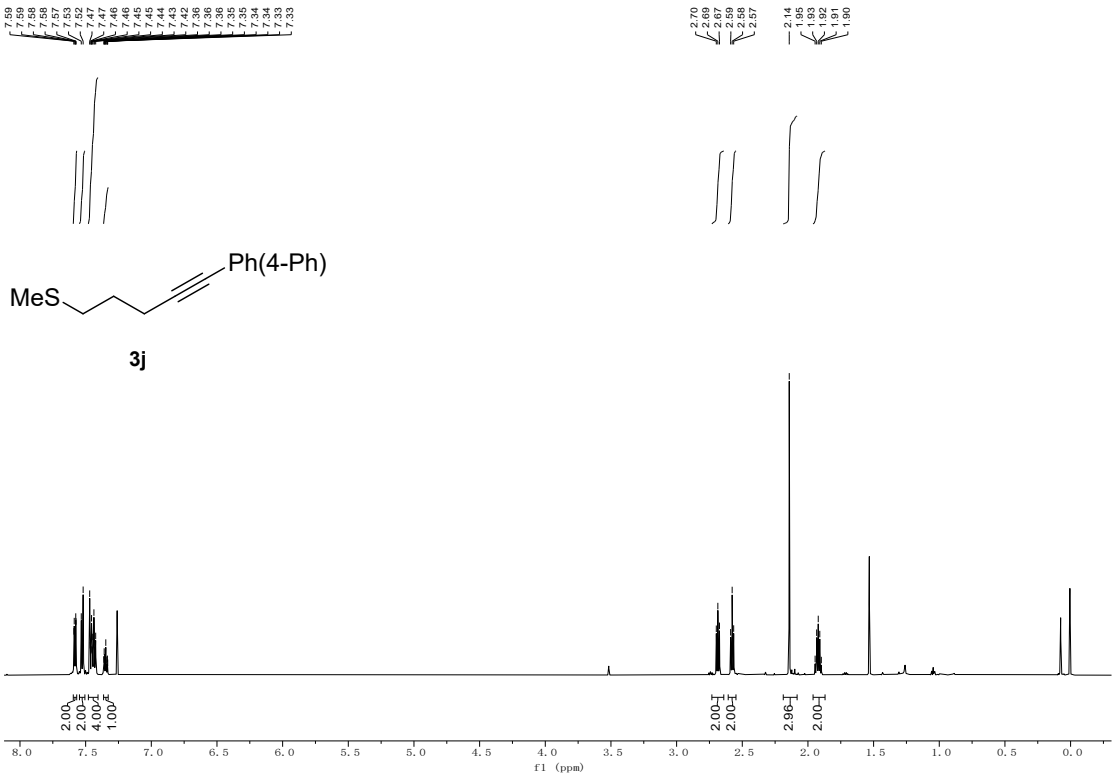
^{1}H NMR Spectrum of 3i



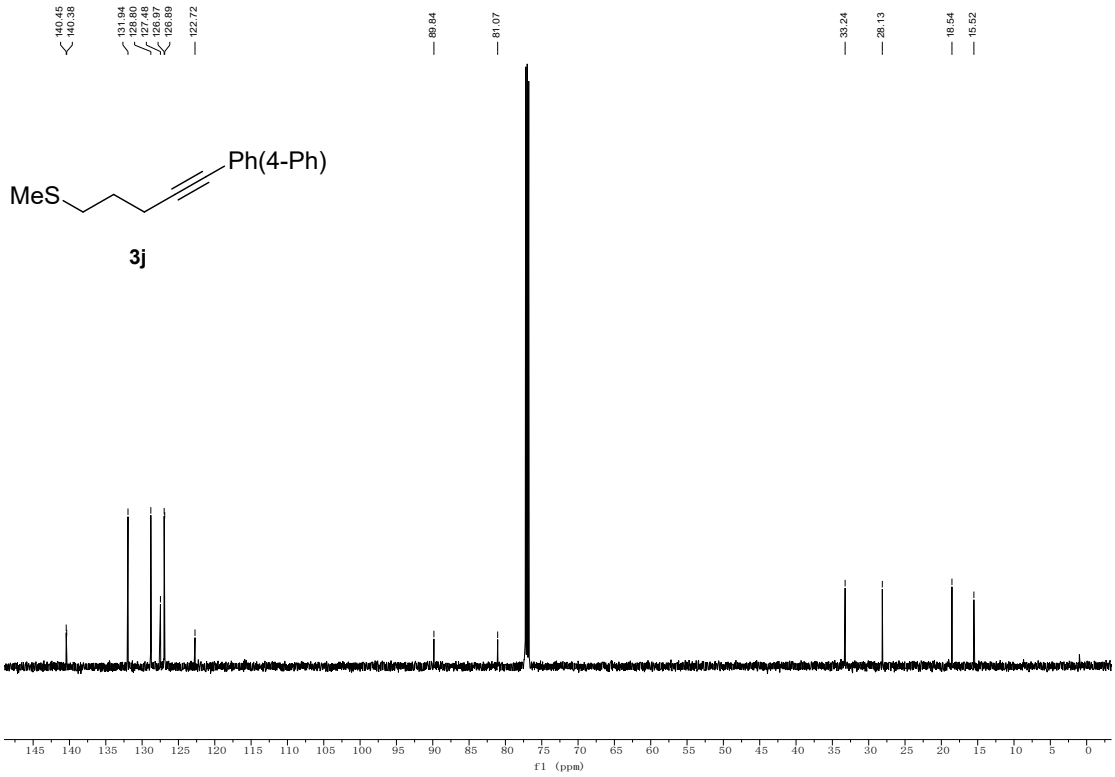
^{13}C NMR Spectrum of 3i



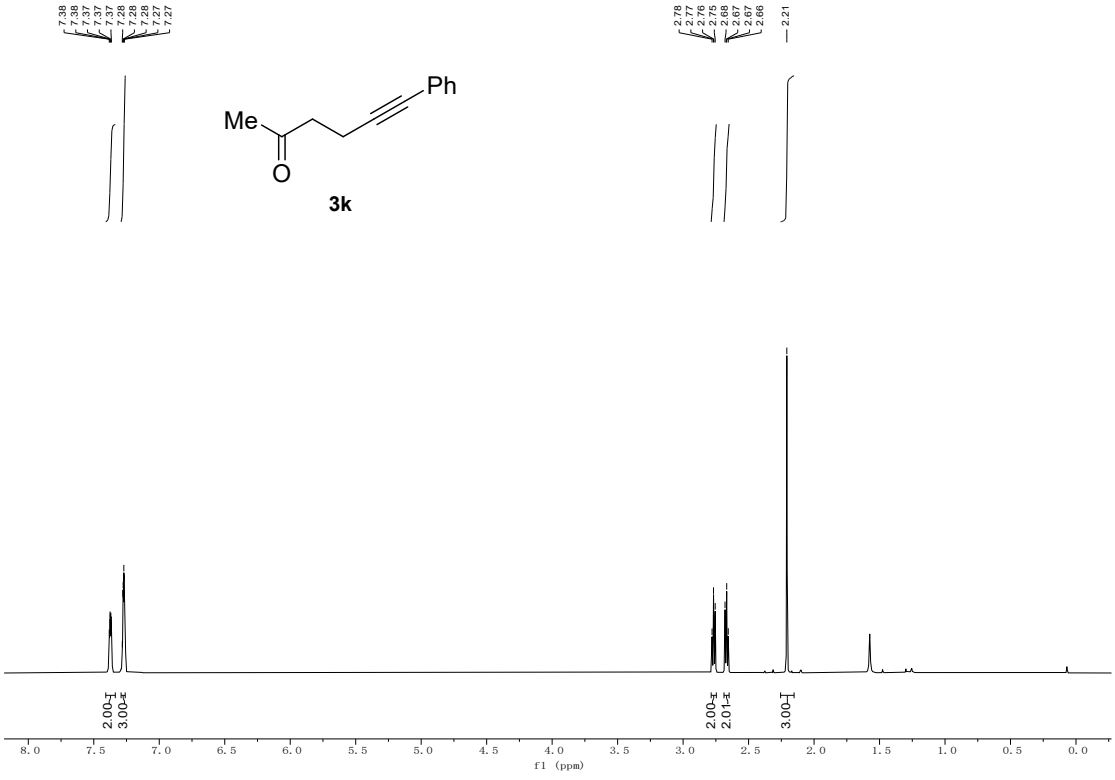
^{1}H NMR Spectrum of 3j



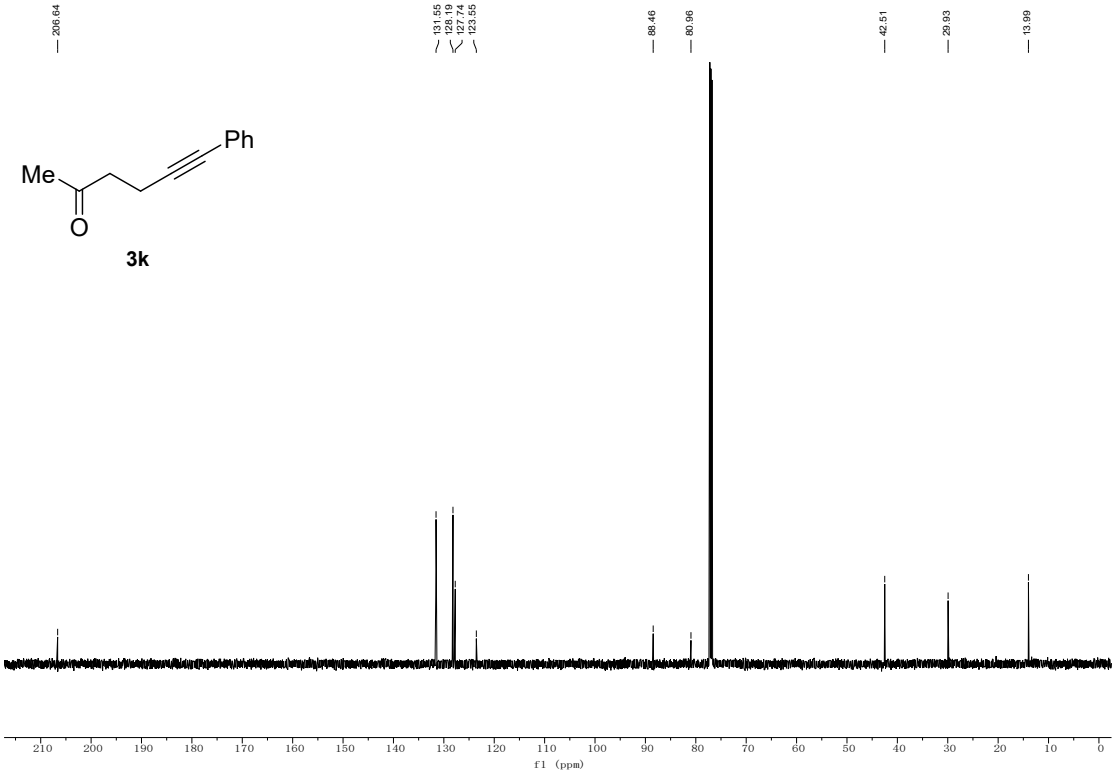
^{13}C NMR Spectrum of 3j



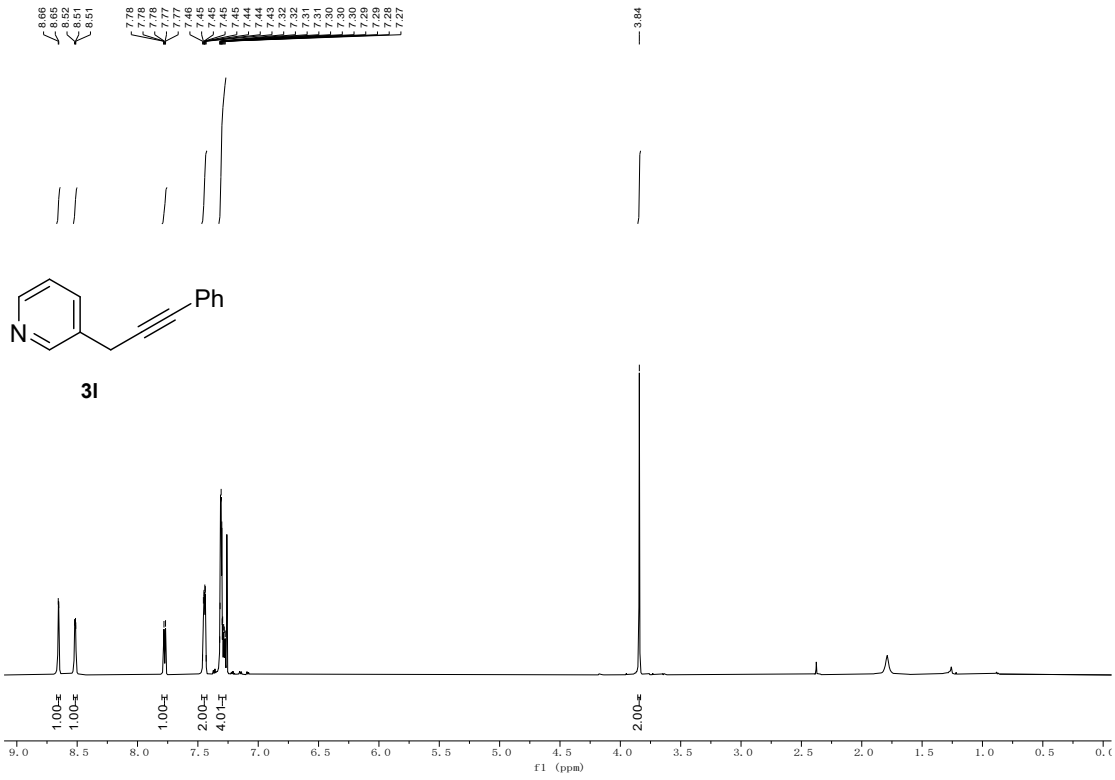
^{1}H NMR Spectrum of 3k



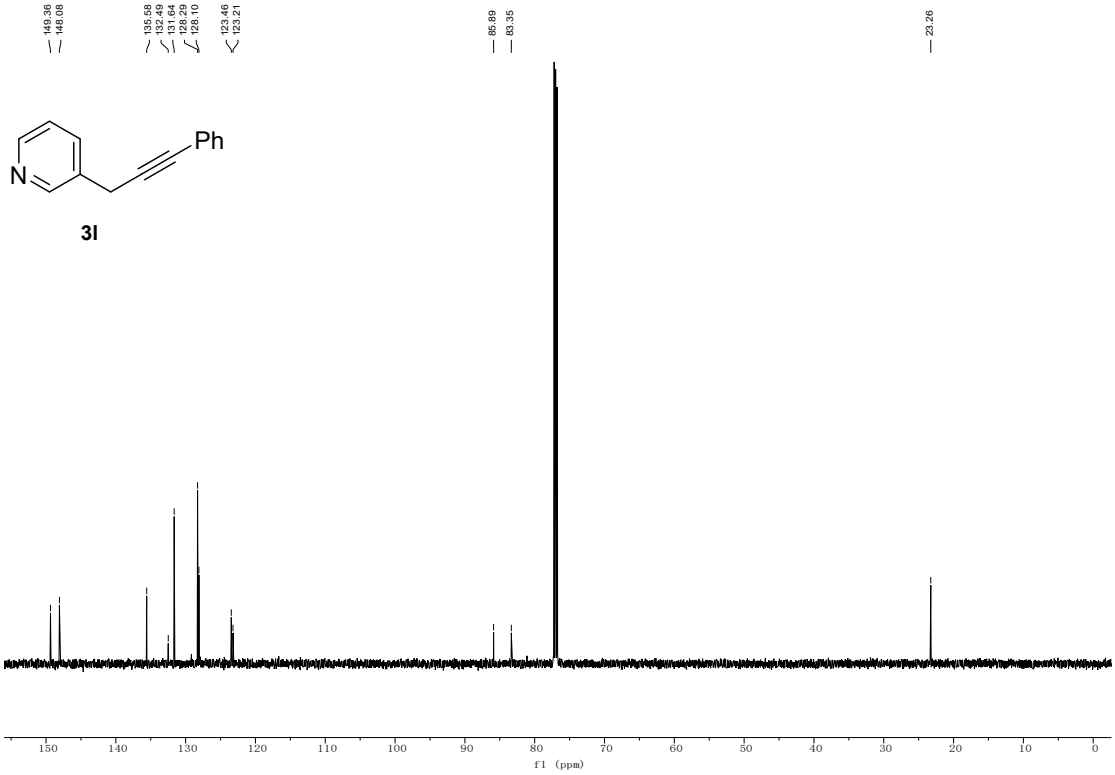
^{13}C NMR Spectrum of 3k



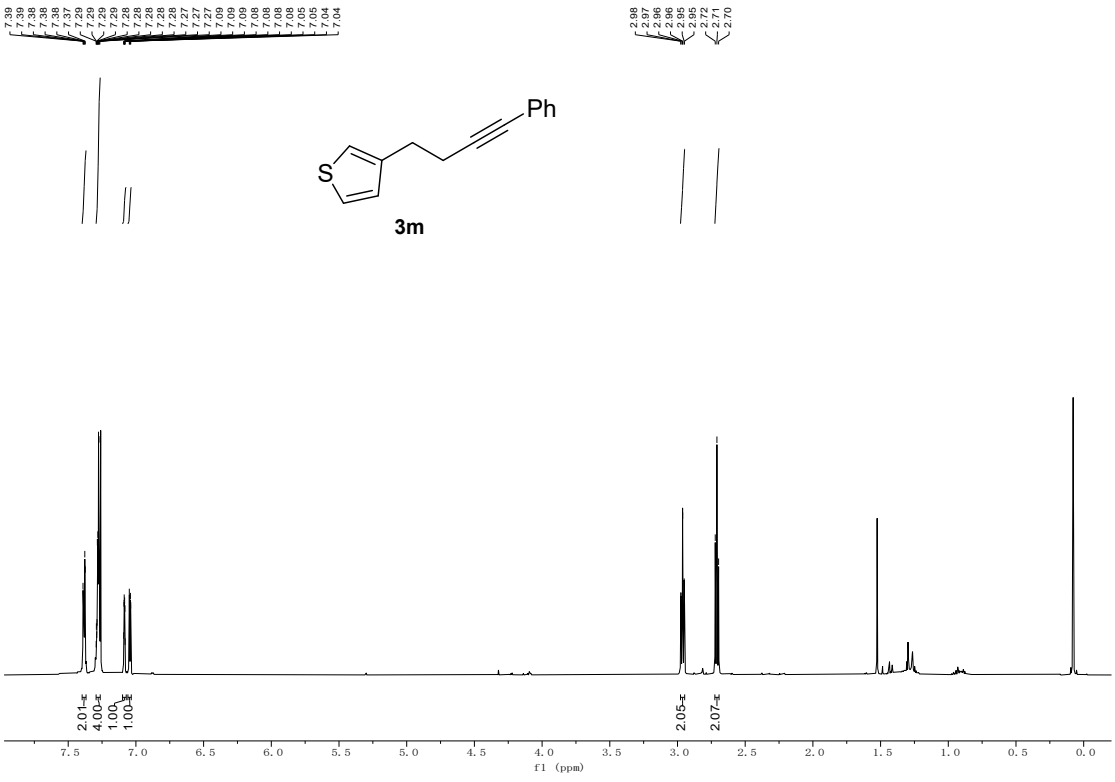
^{1}H NMR Spectrum of 3l



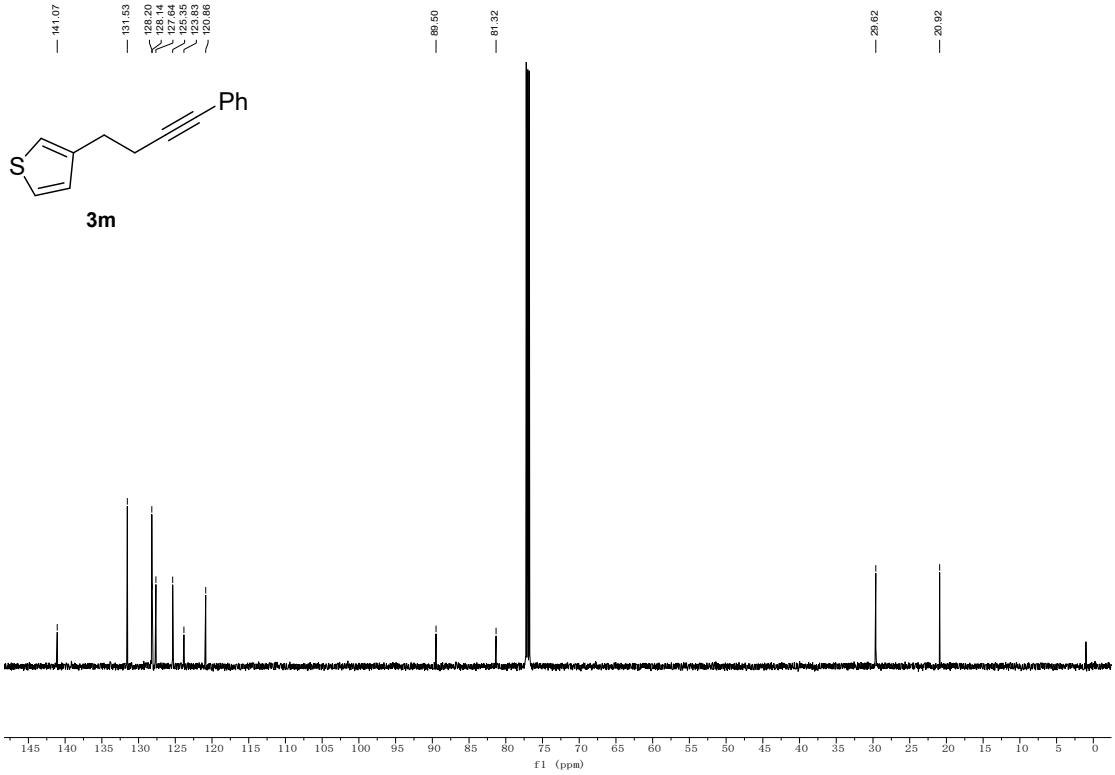
^{13}C NMR Spectrum of 3l



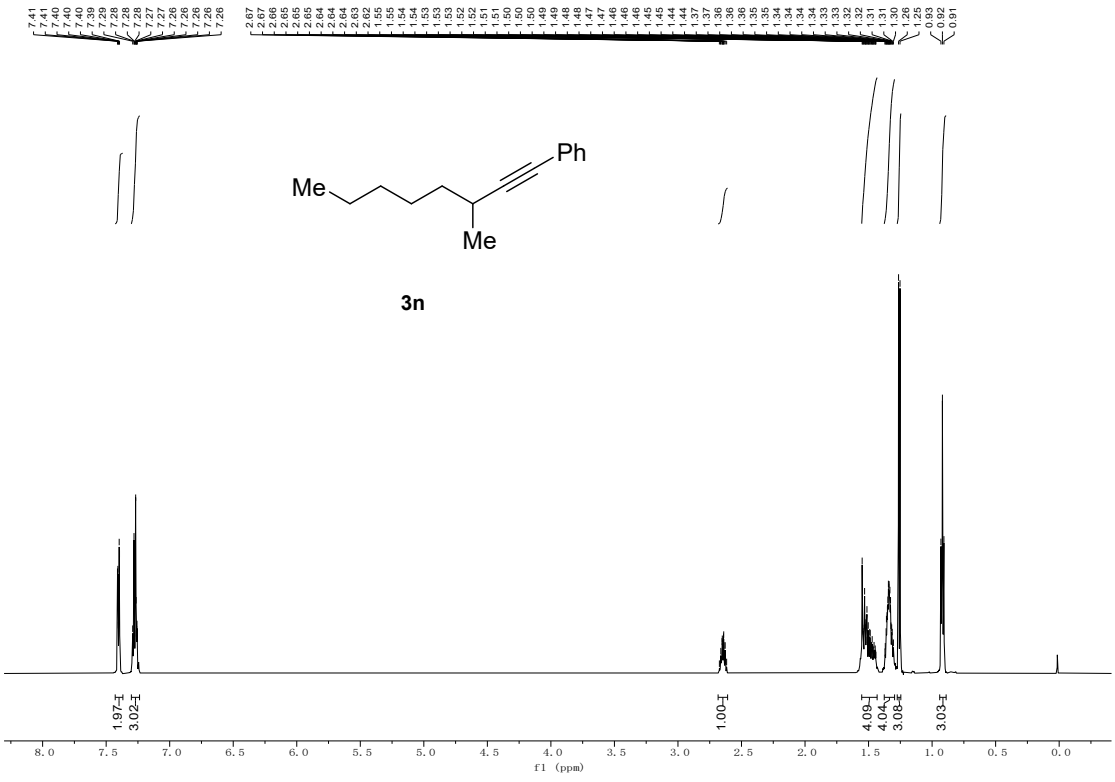
^{1}H NMR Spectrum of 3m



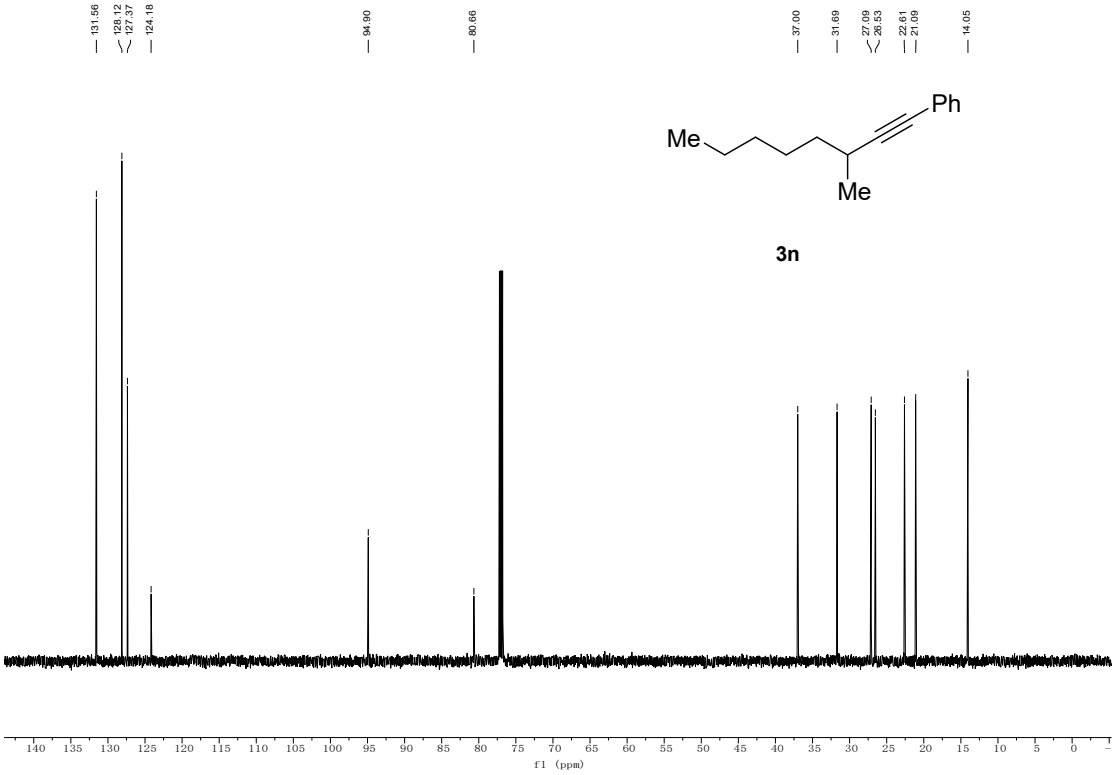
^{13}C NMR Spectrum of 3m



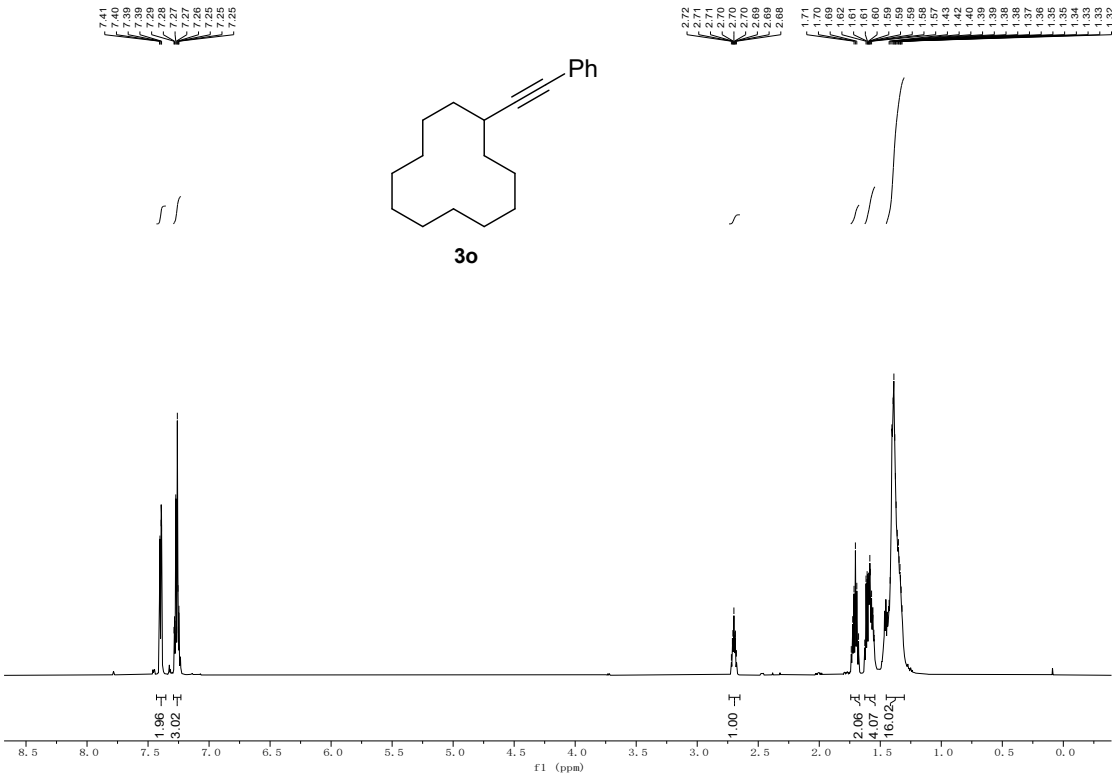
^{1}H NMR Spectrum of 3n



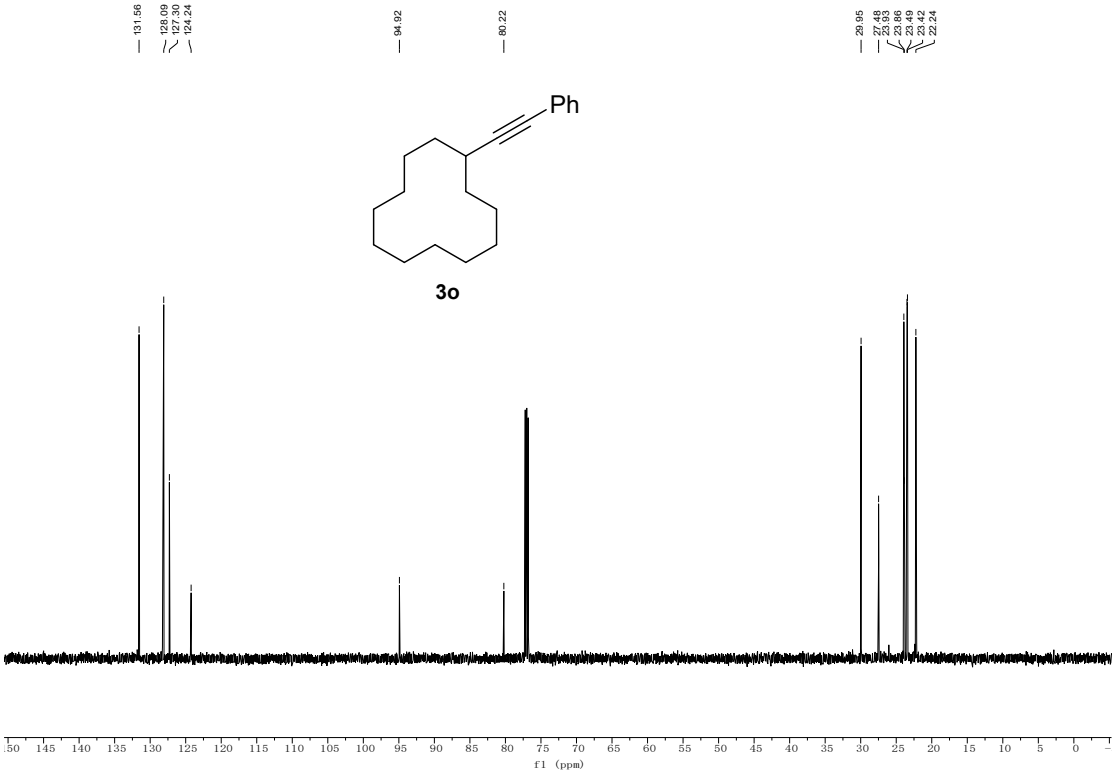
^{13}C NMR Spectrum of 3n



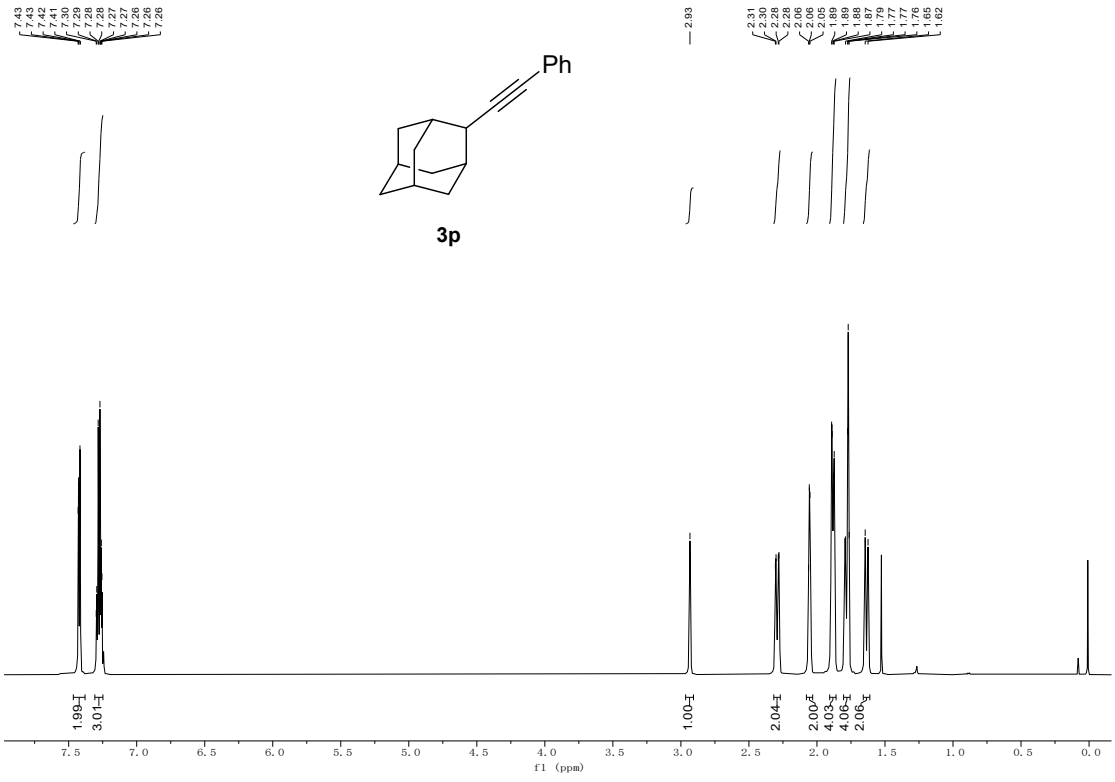
^{1}H NMR Spectrum of 3o



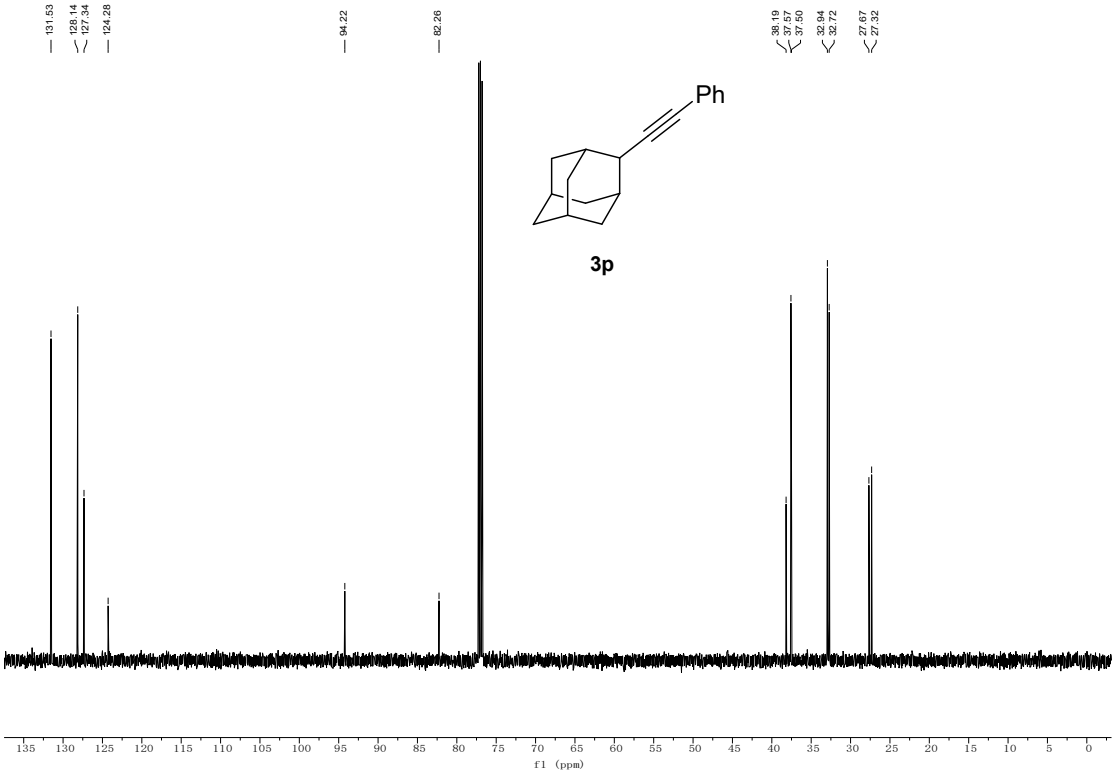
^{13}C NMR Spectrum of 3o



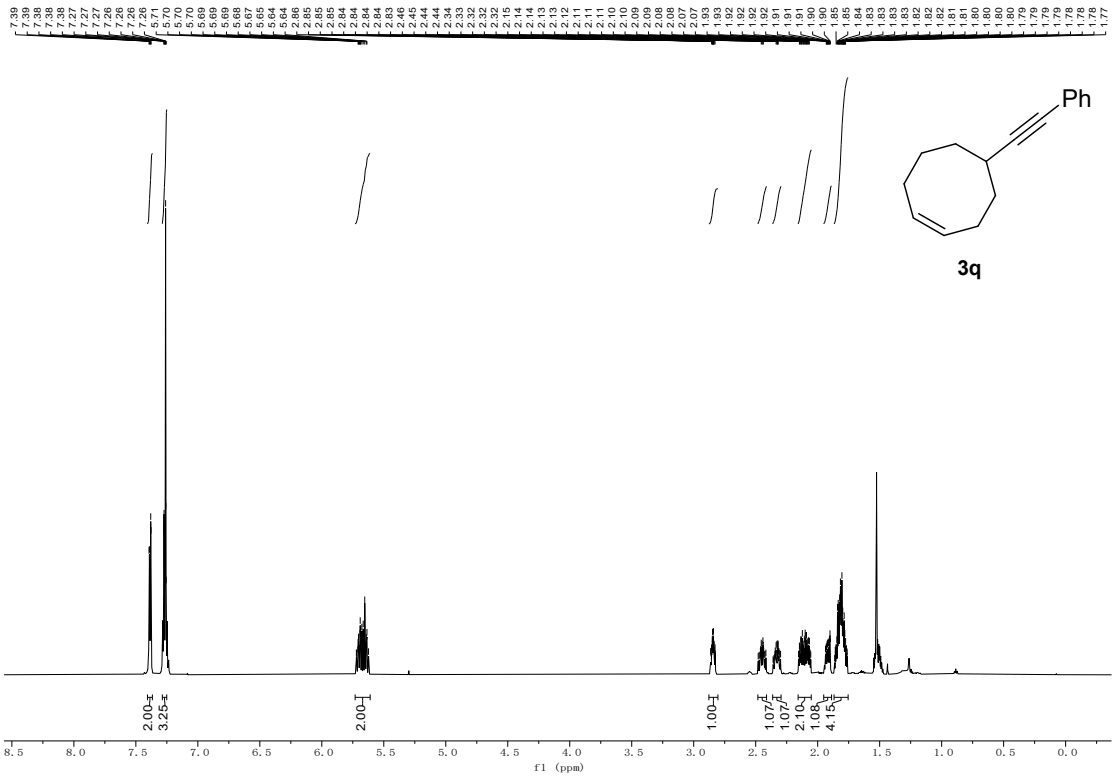
^{1}H NMR Spectrum of 3p



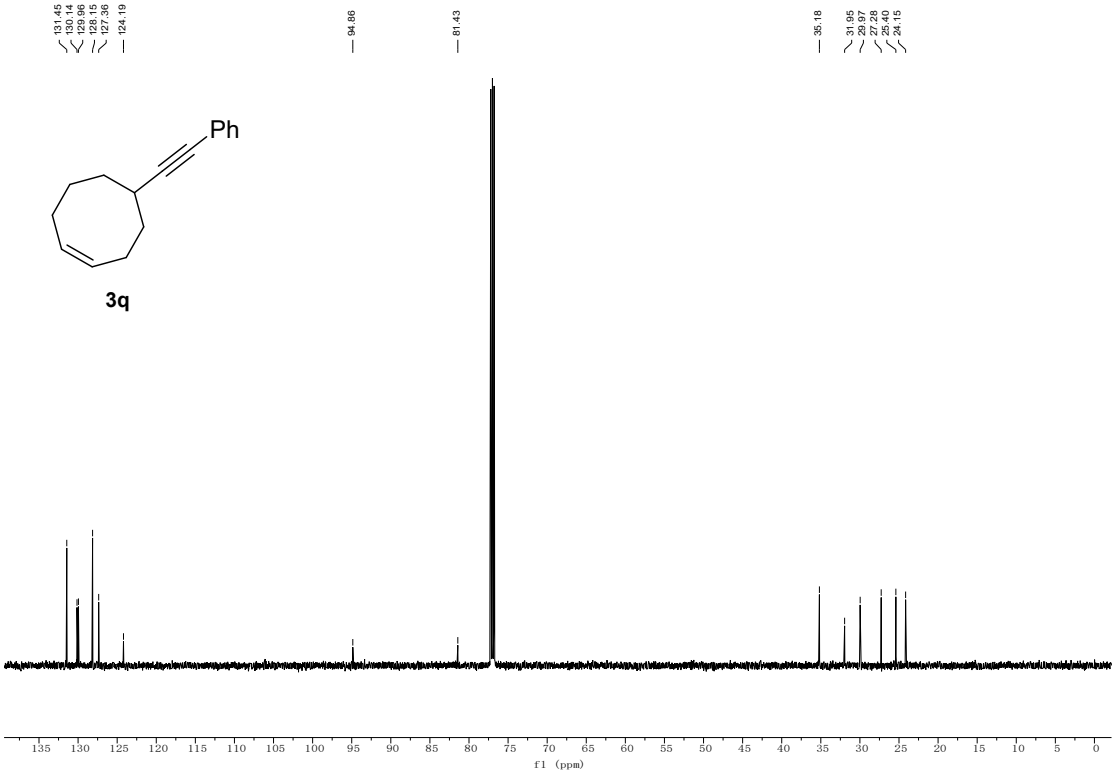
^{13}C NMR Spectrum of 3p



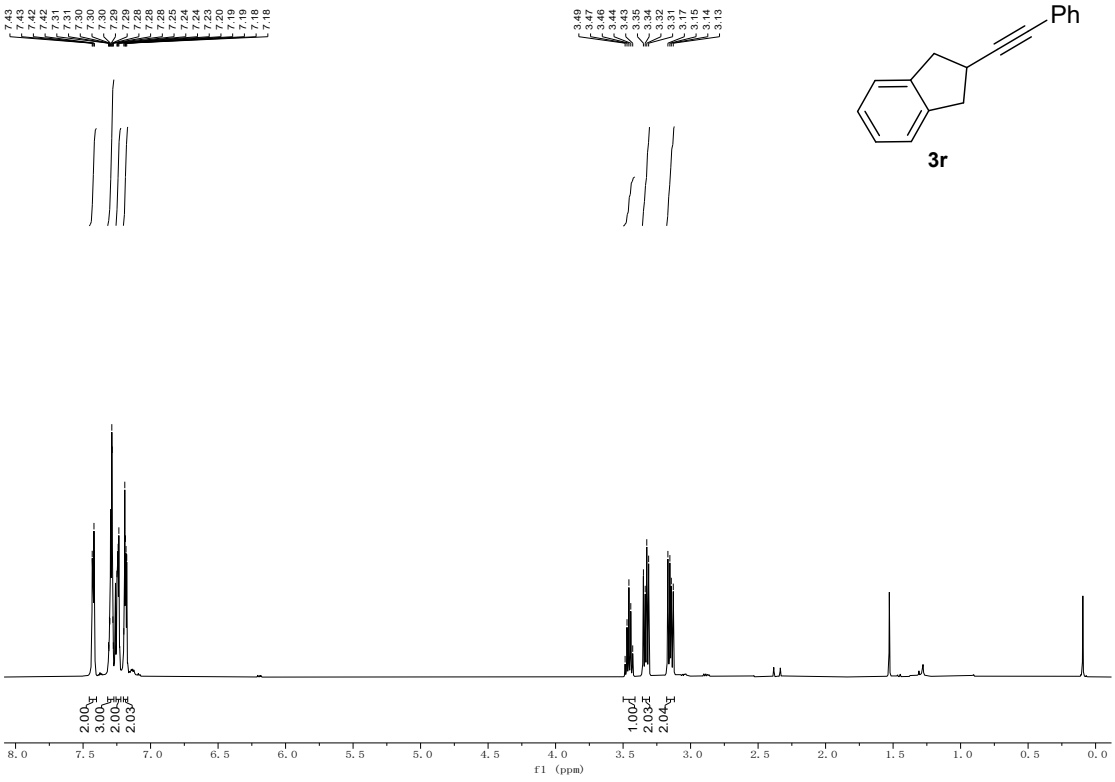
^{1}H NMR Spectrum of 3q



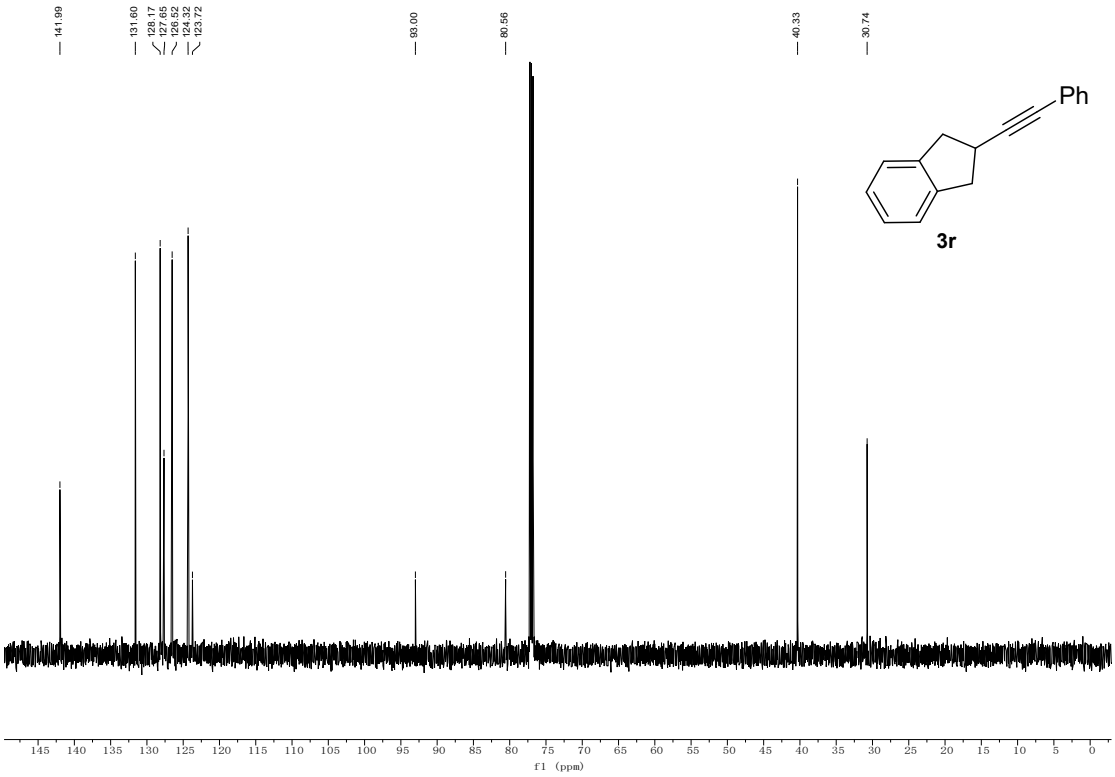
^{13}C NMR Spectrum of 3q



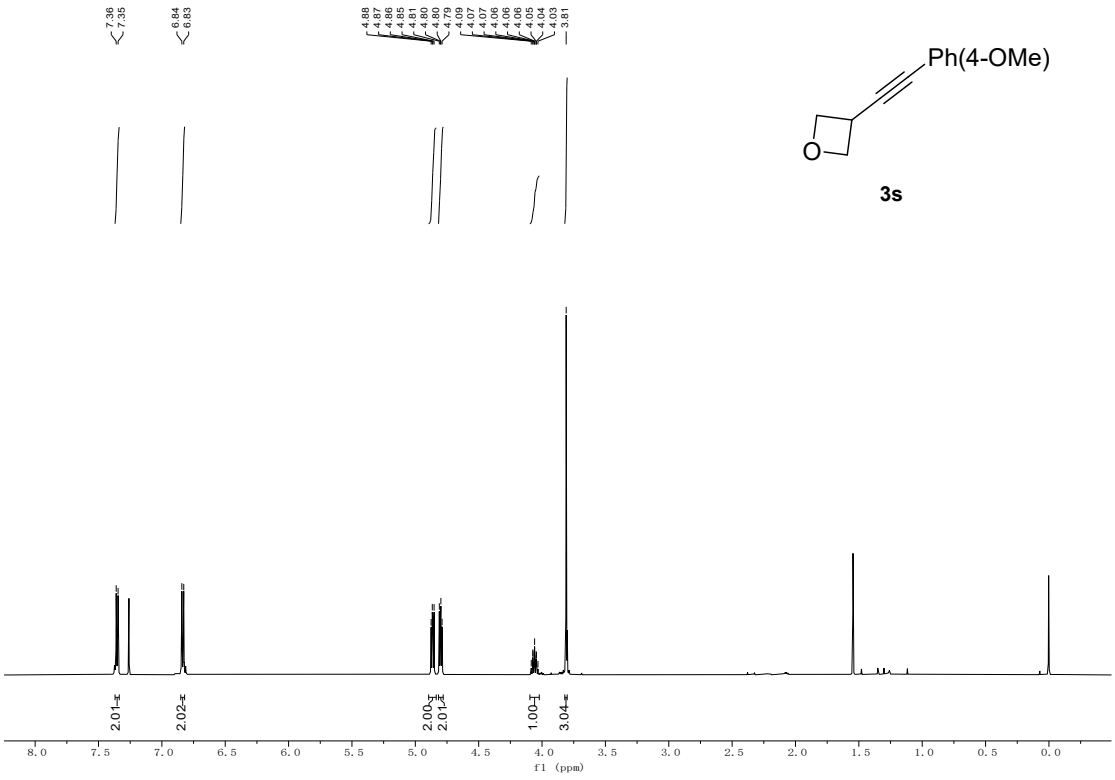
^{1}H NMR Spectrum of 3r



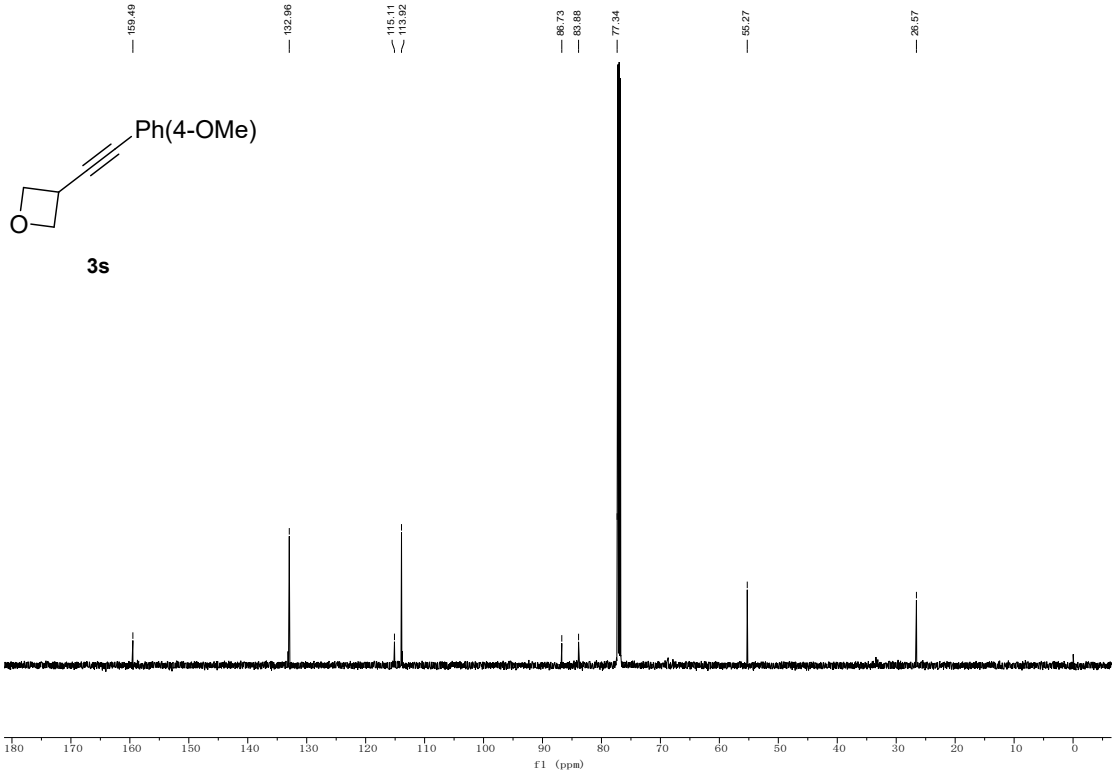
^{13}C NMR Spectrum of 3r



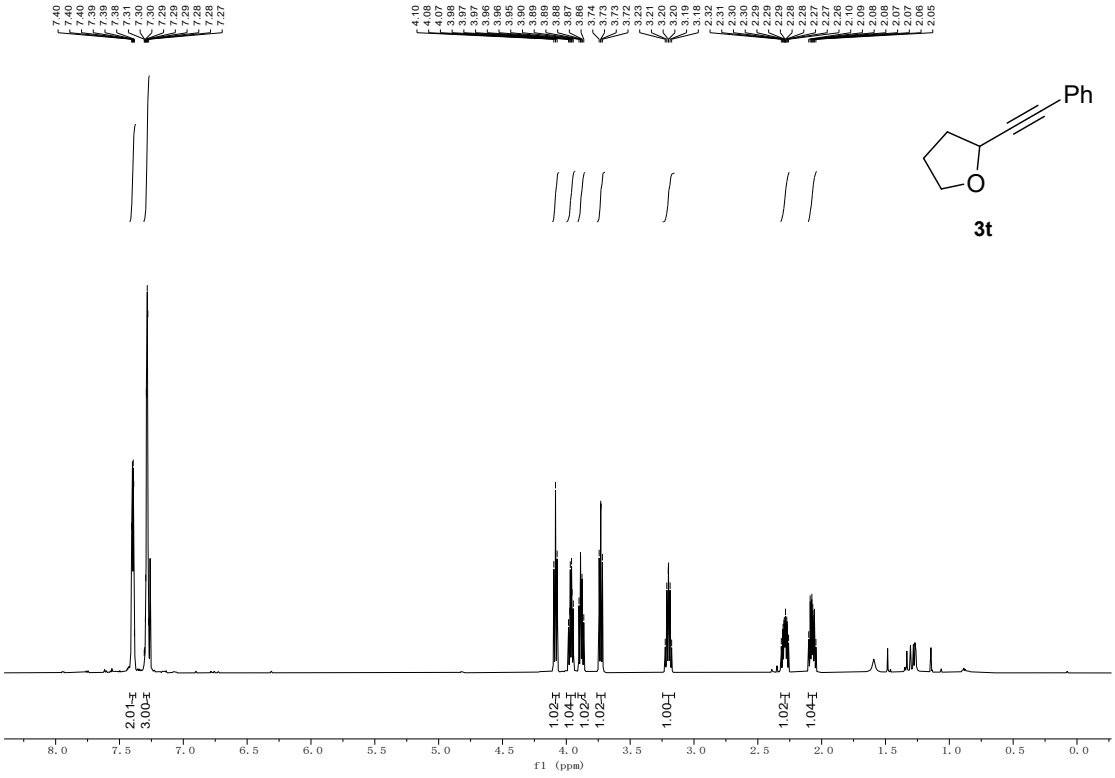
^{1}H NMR Spectrum of 3s



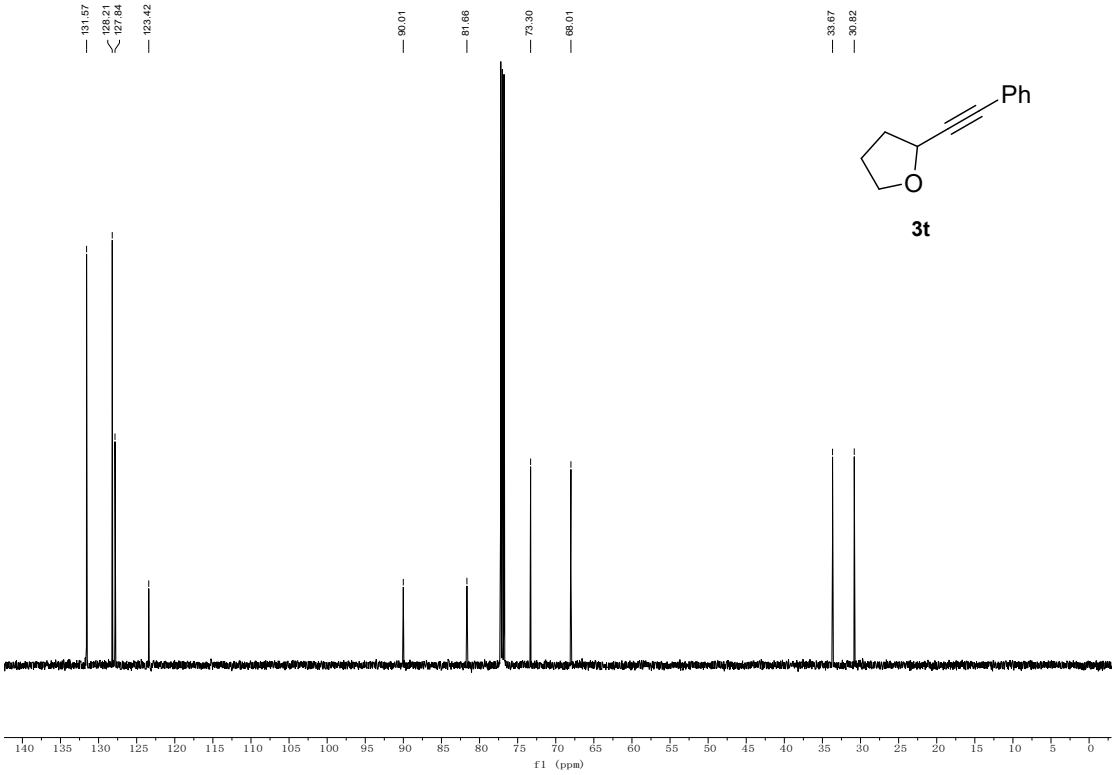
^{13}C NMR Spectrum of 3s



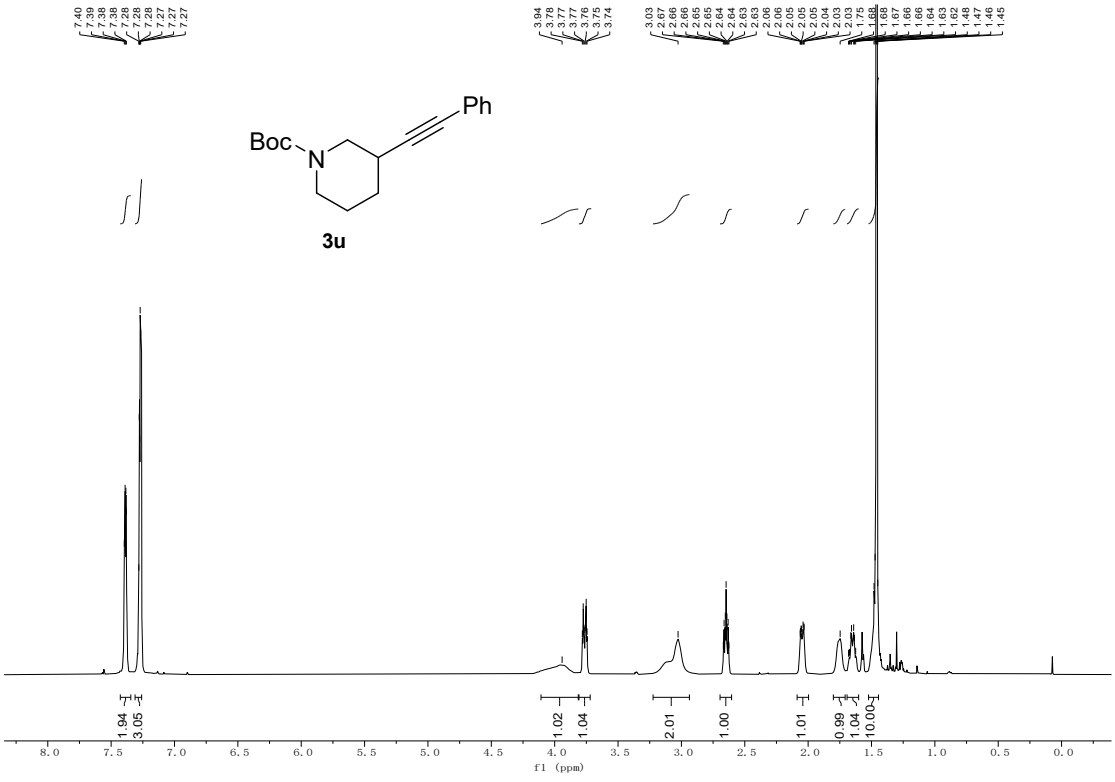
^{1}H NMR Spectrum of 3t



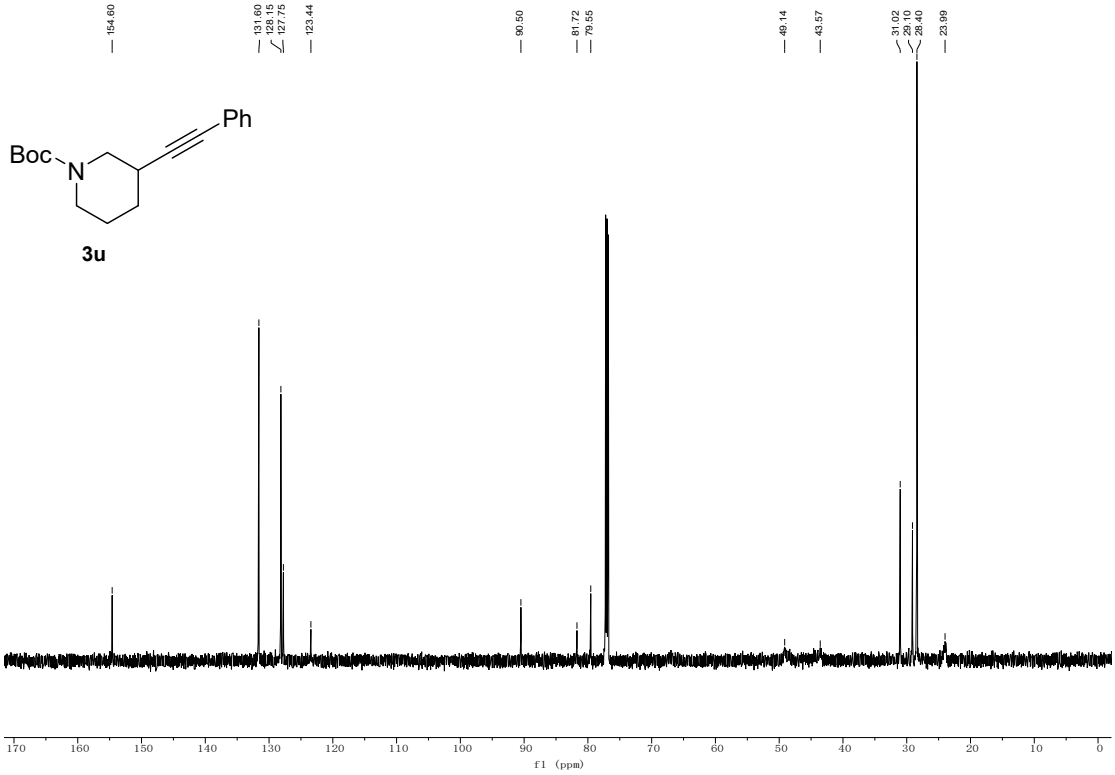
^{13}C NMR Spectrum of 3t



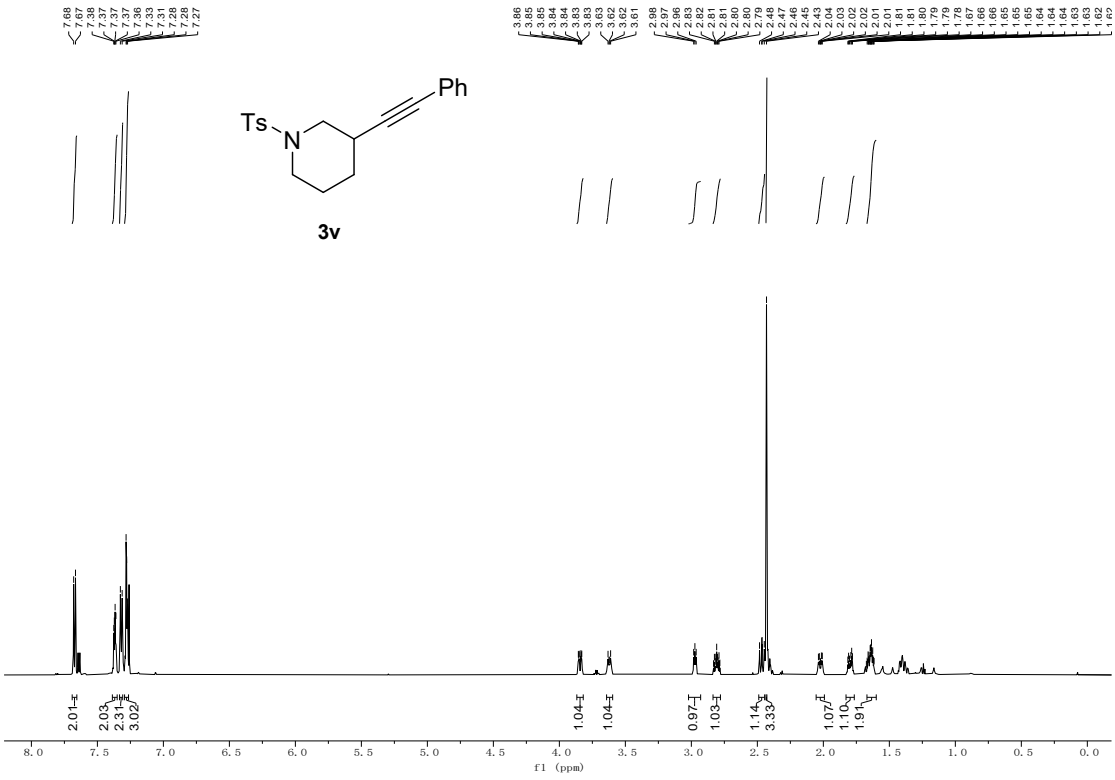
^{1}H NMR Spectrum of 3u



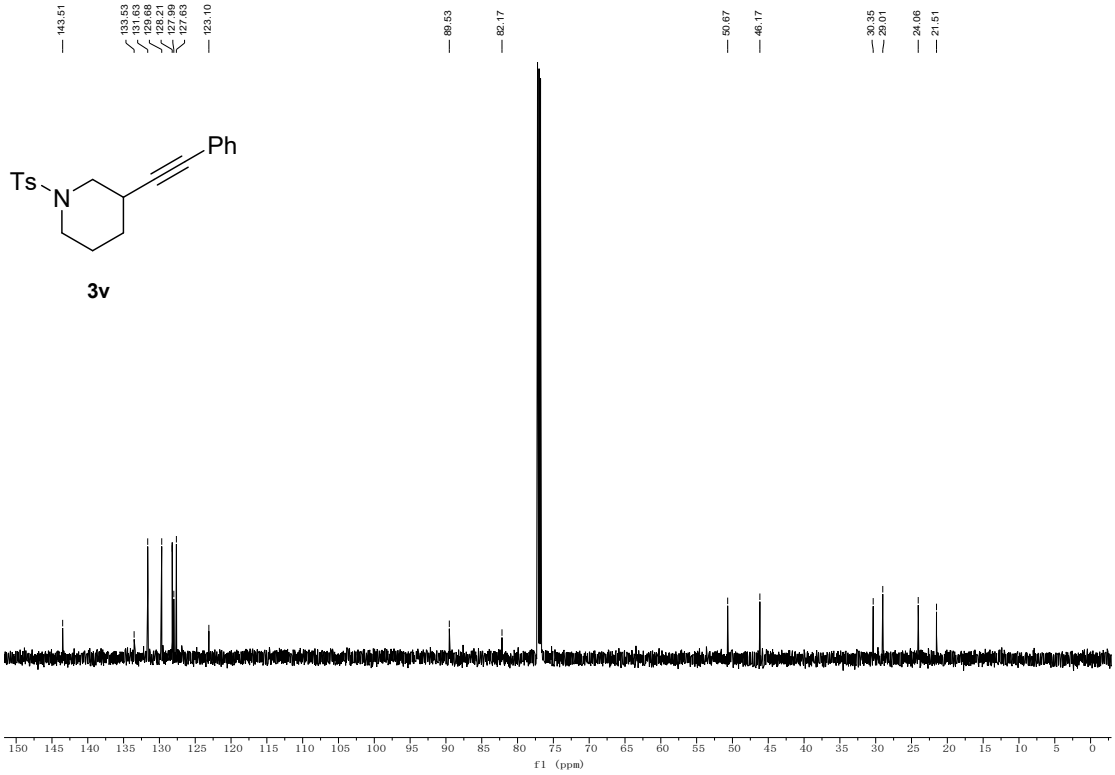
^{13}C NMR Spectrum of 3u



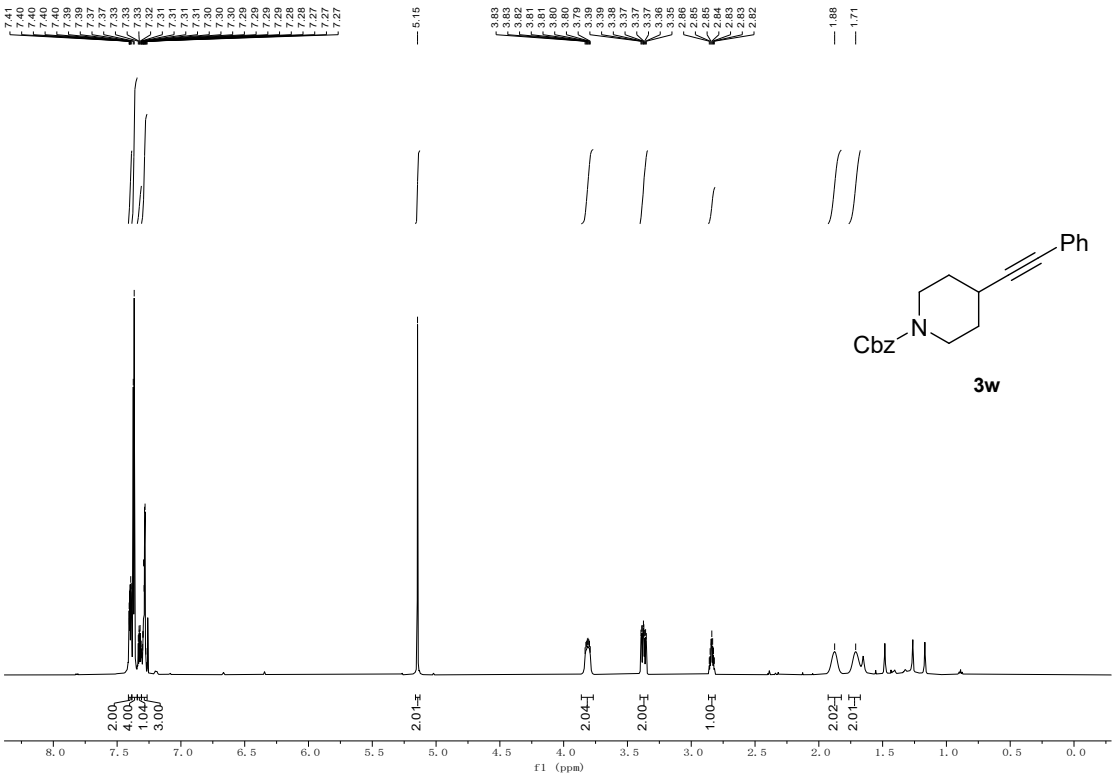
^{1}H NMR Spectrum of 3v



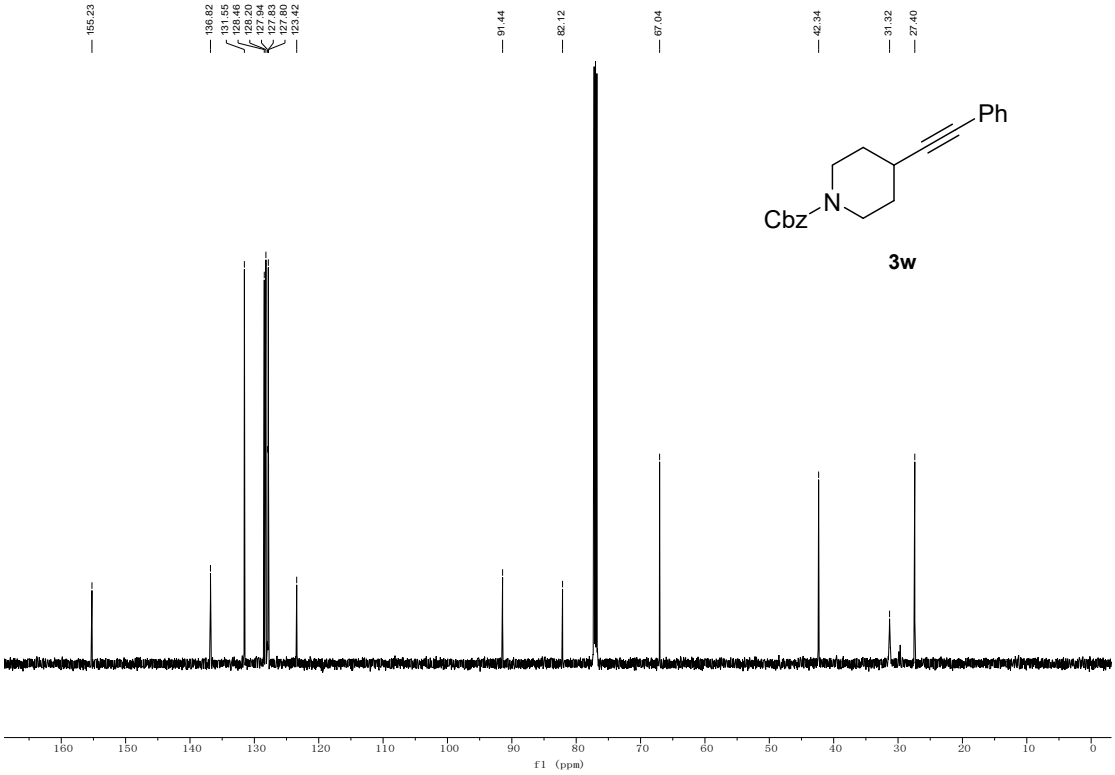
^{13}C NMR Spectrum of 3v



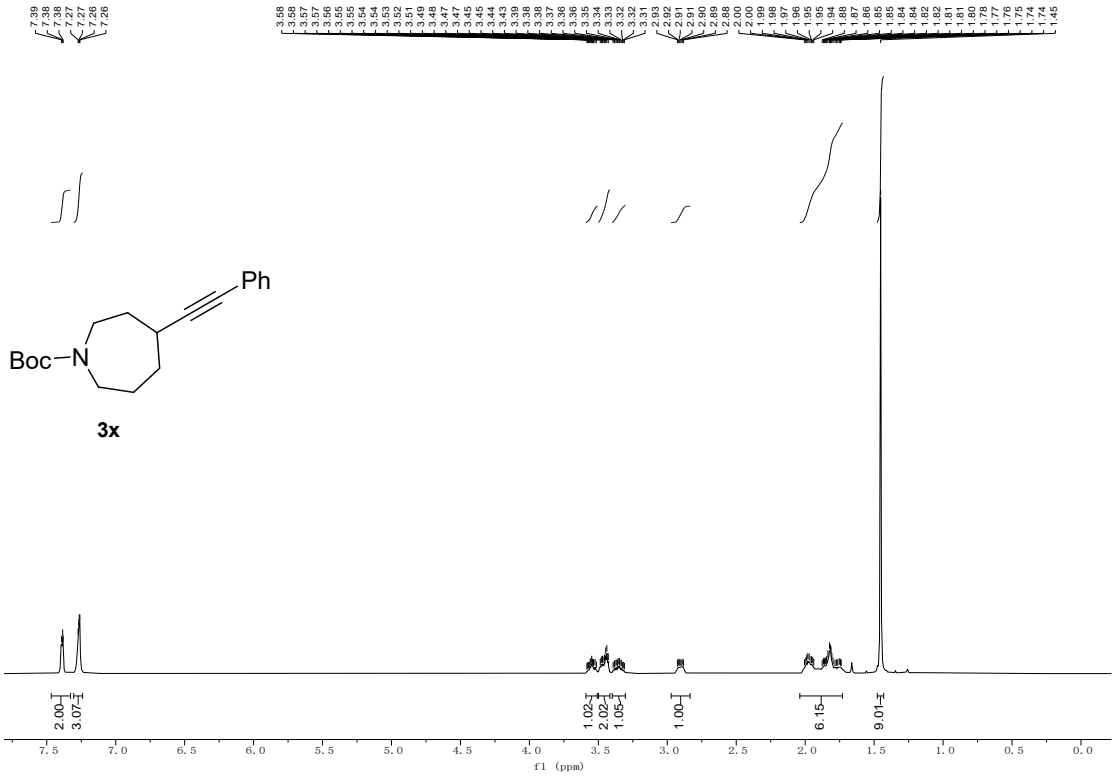
^{1}H NMR Spectrum of 3w



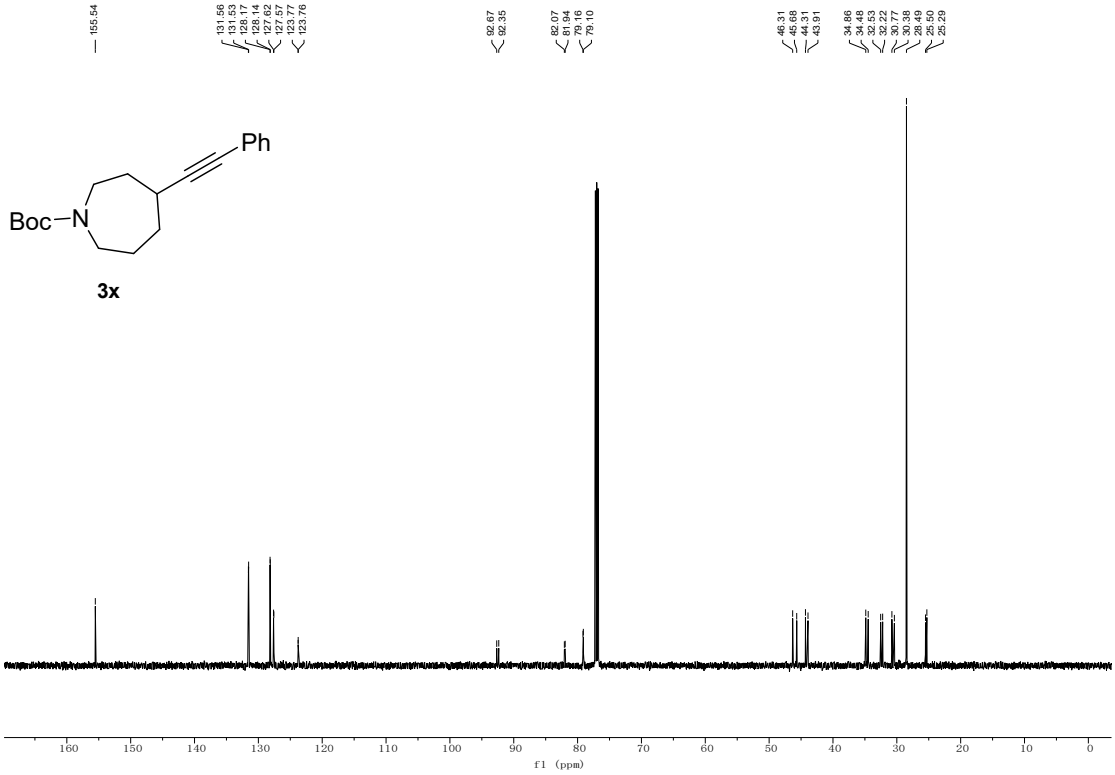
^{13}C NMR Spectrum of 3w



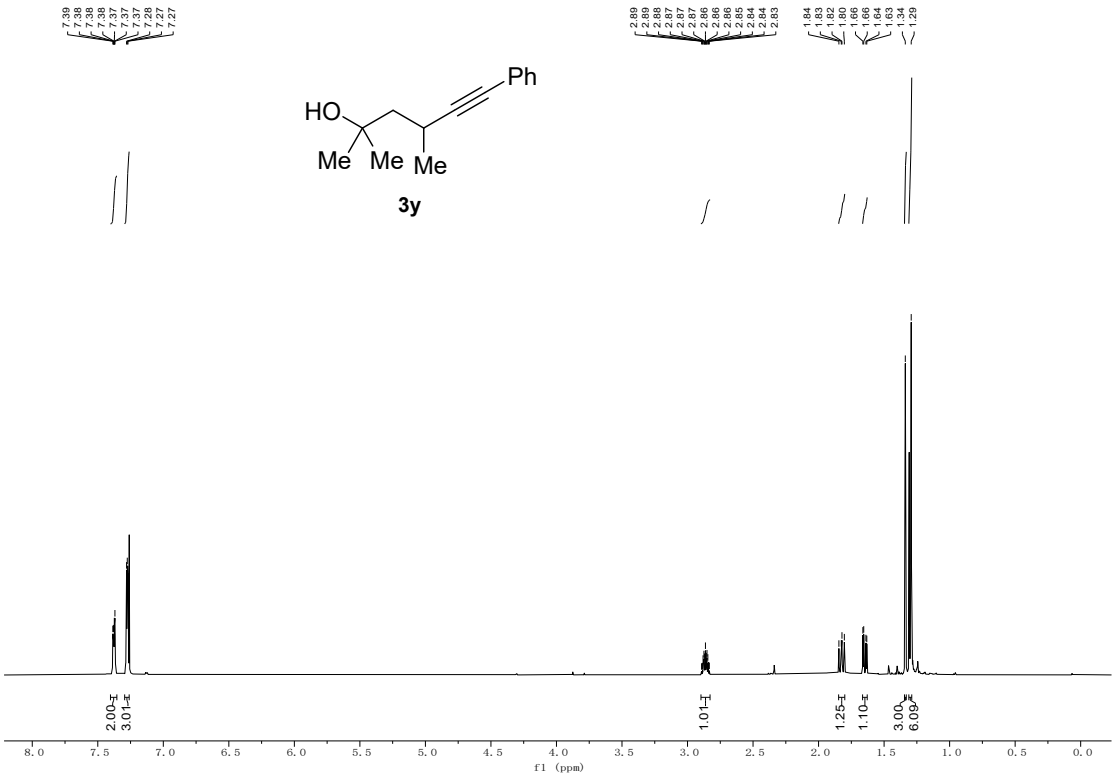
^{1}H NMR Spectrum of 3x



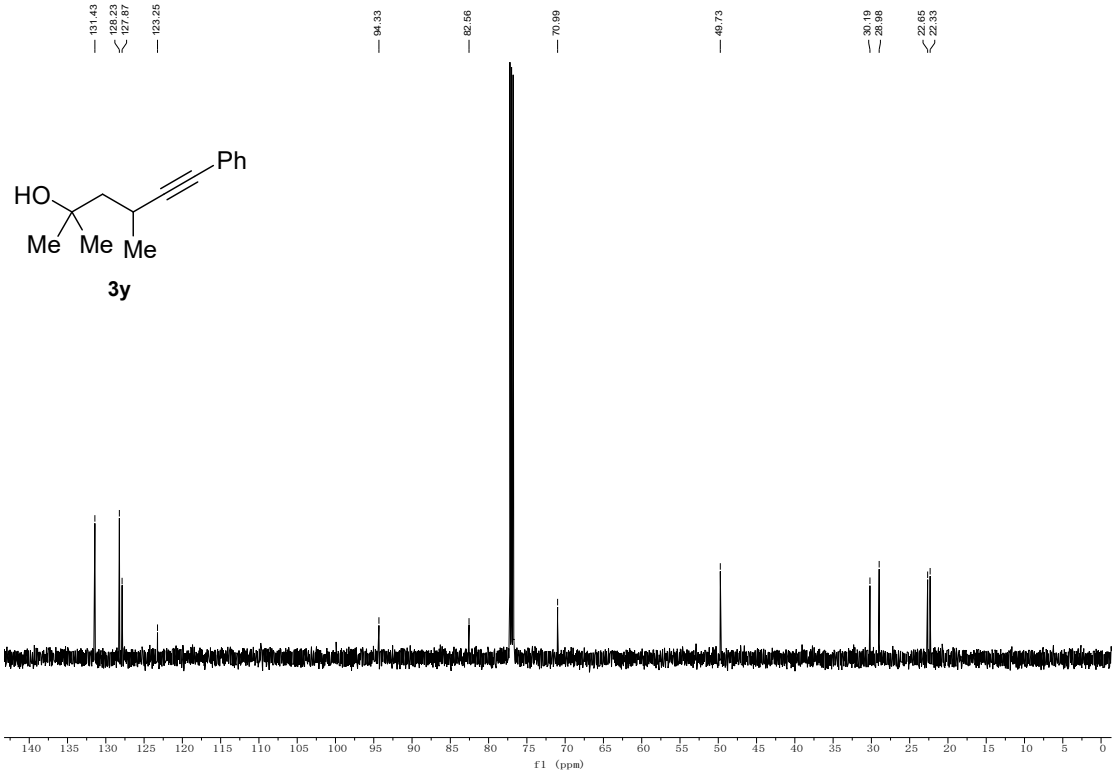
^{13}C NMR Spectrum of 3x



^{1}H NMR Spectrum of 3y

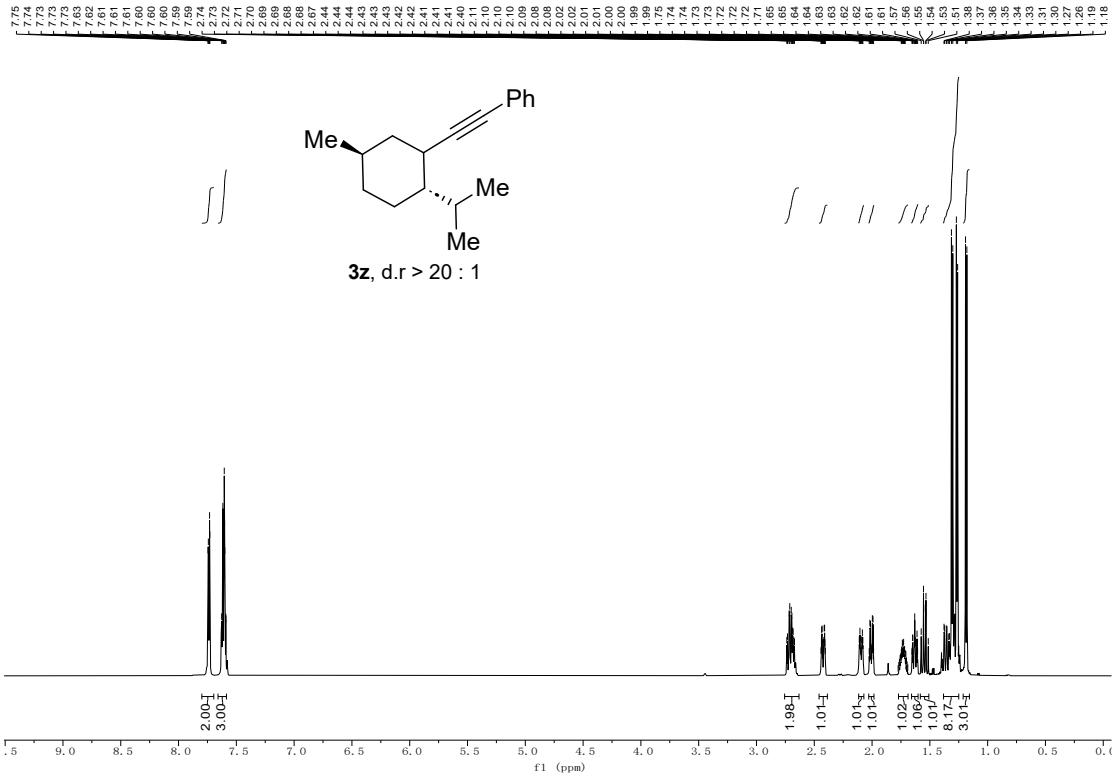


^{13}C NMR Spectrum of 3y



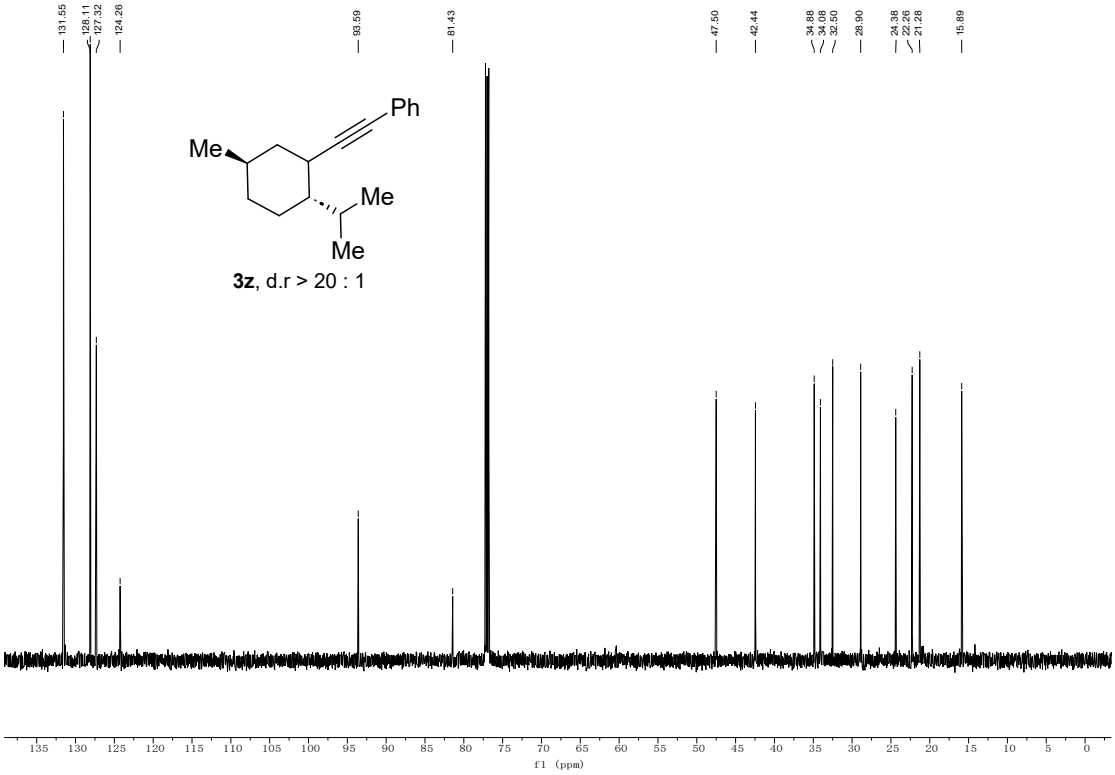
3y

^{1}H NMR Spectrum of 3z



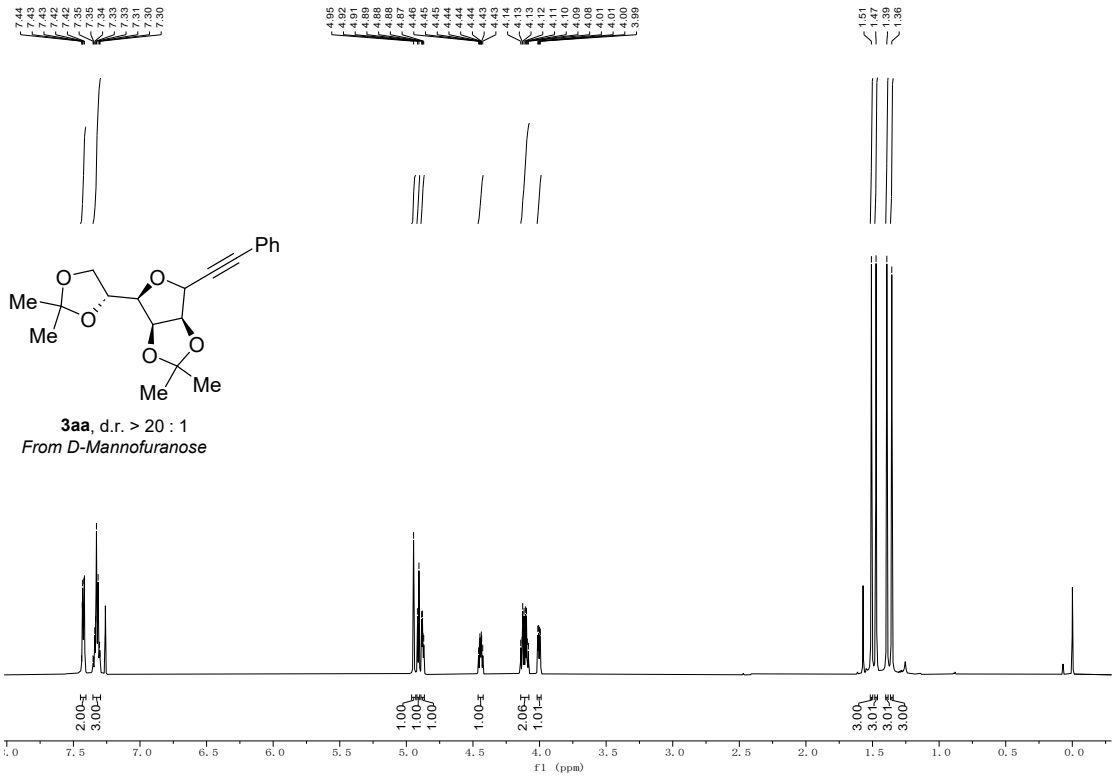
3z, d.r > 20 : 1

^{13}C NMR Spectrum of 3z



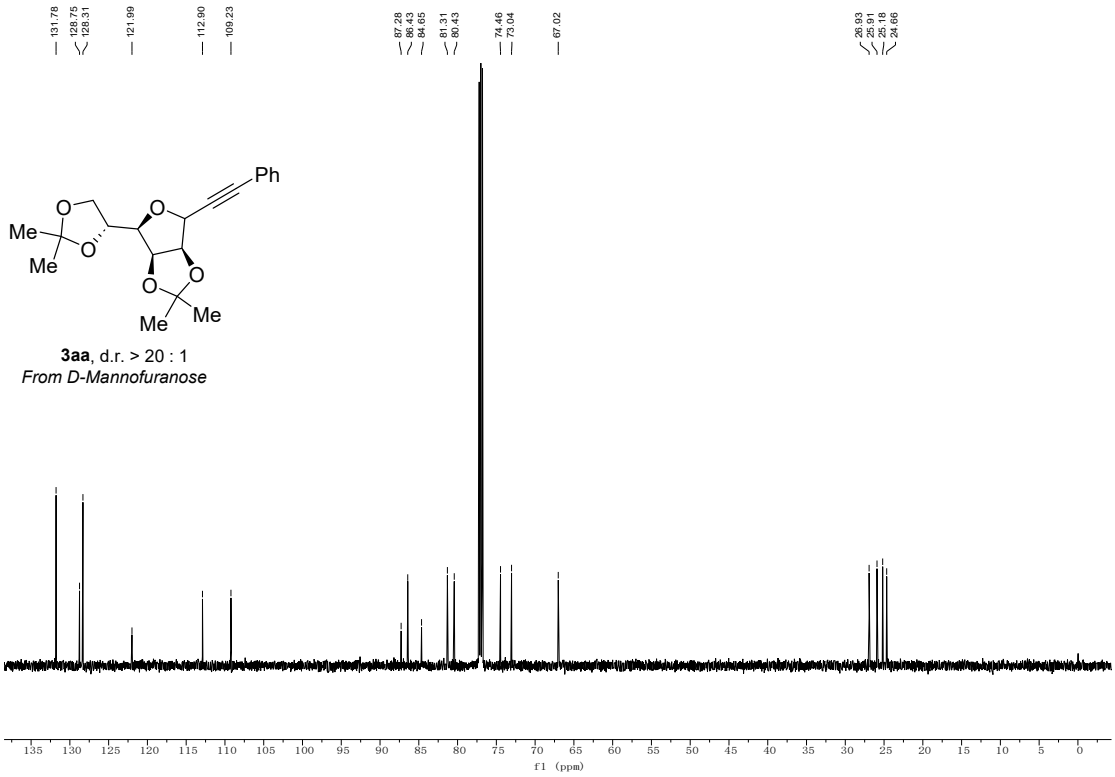
3z, d.r > 20 : 1

^{1}H NMR Spectrum of 3aa



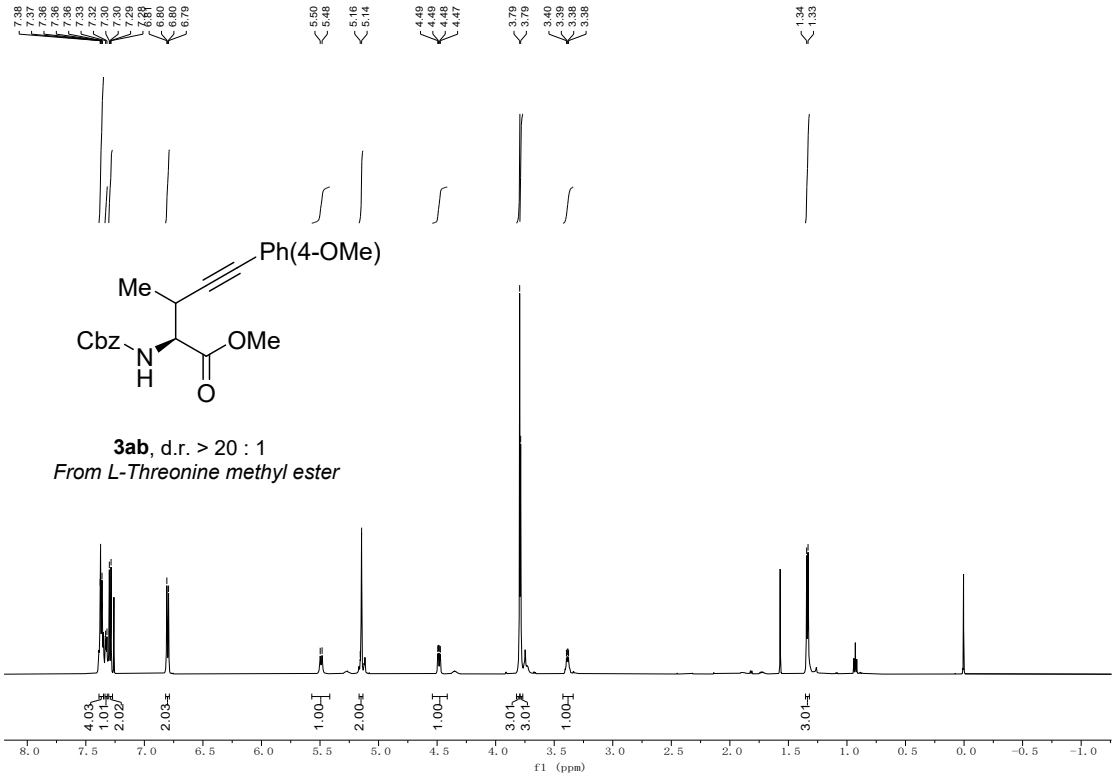
3aa, d.r. > 20 : 1
From D-Mannofuranose

^{13}C NMR Spectrum of 3aa



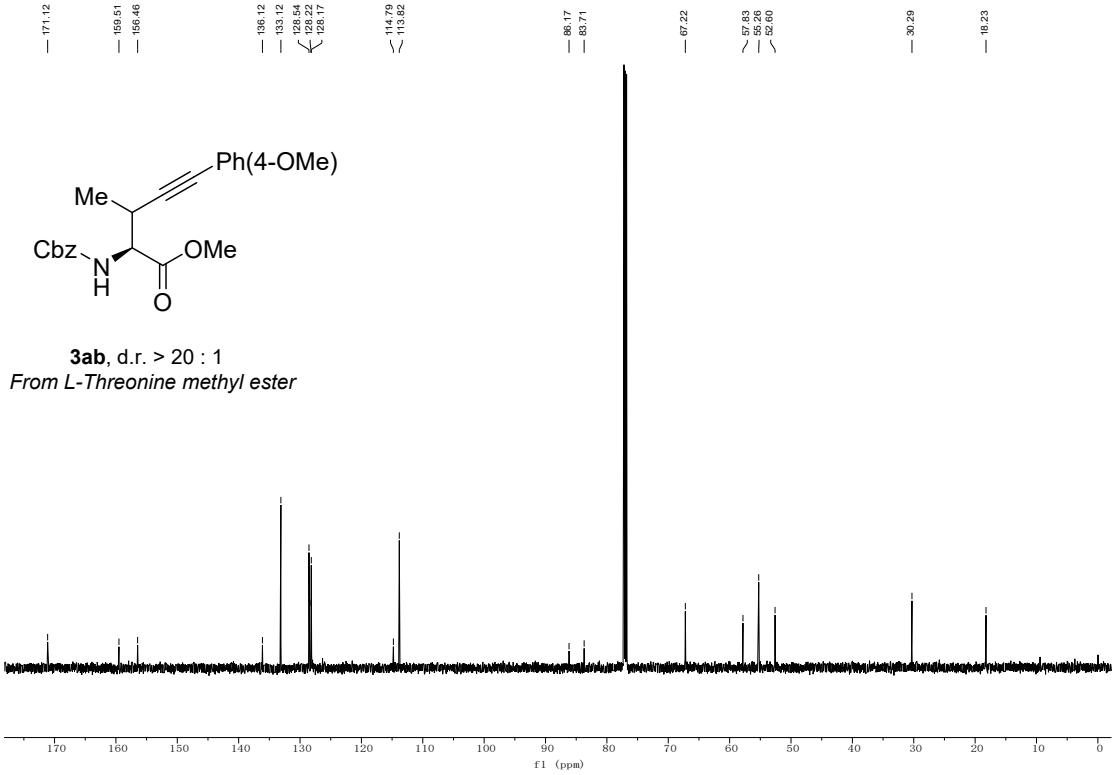
3aa, d.r. > 20 : 1
From D-Mannofuranose

^{1}H NMR Spectrum of 3ab



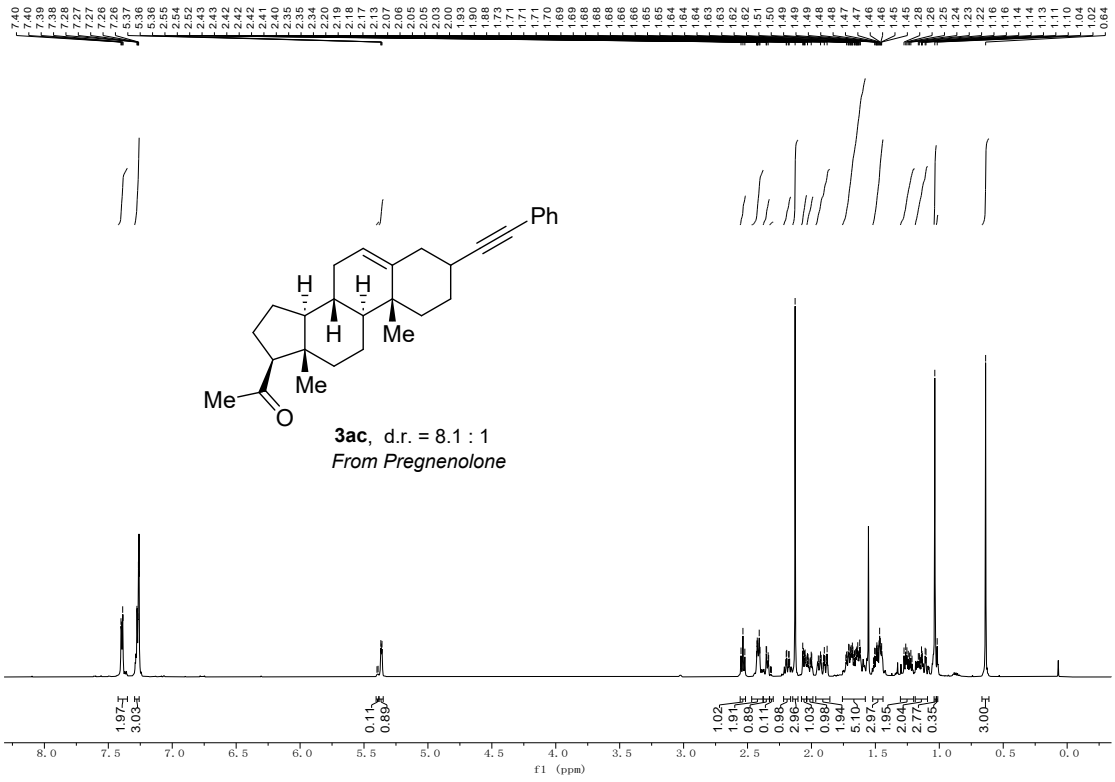
3ab, d.r. > 20 : 1
From L-Threonine methyl ester

^{13}C NMR Spectrum of 3ab



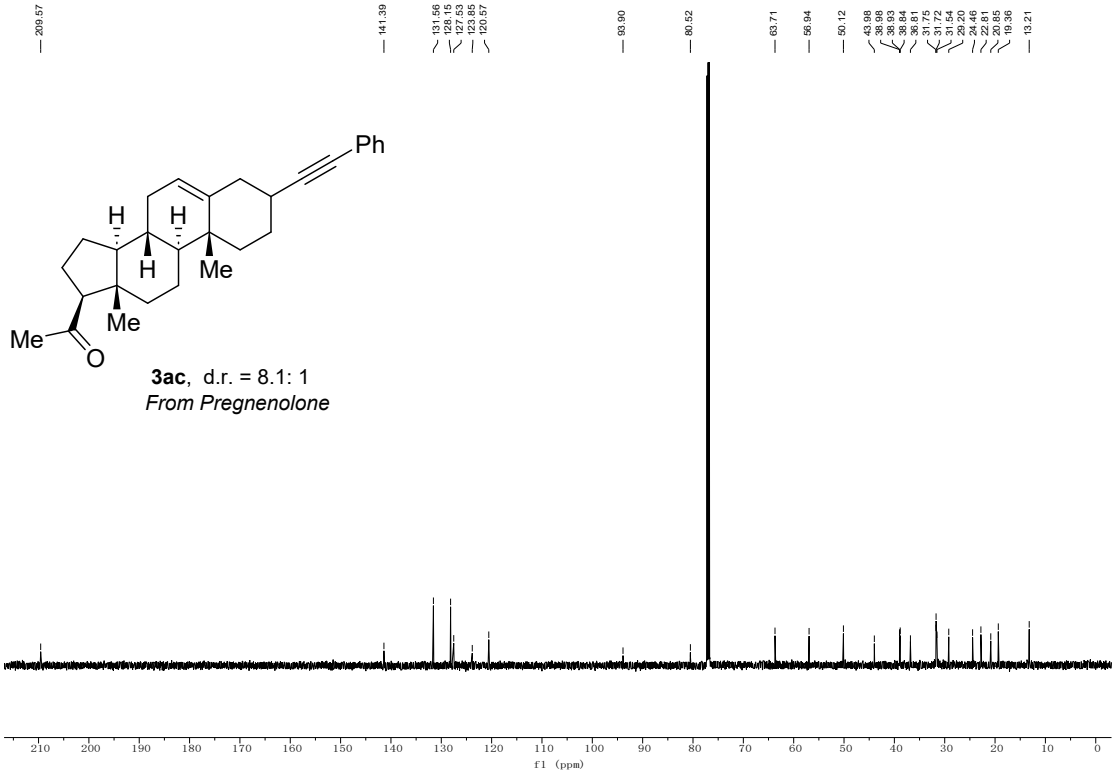
3ab, d.r. > 20 : 1
From L-Threonine methyl ester

^{1}H NMR Spectrum of 3ac



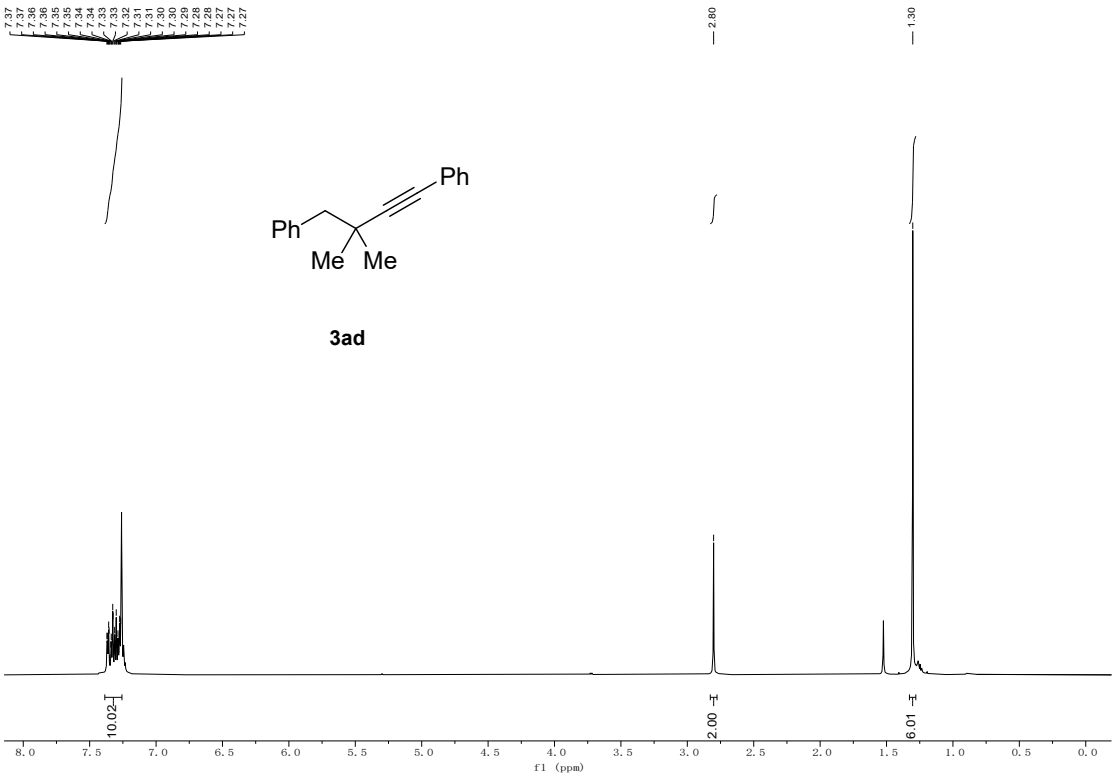
3ac, d.r. = 8.1 : 1
From Pregnenolone

^{13}C NMR Spectrum of 3ac



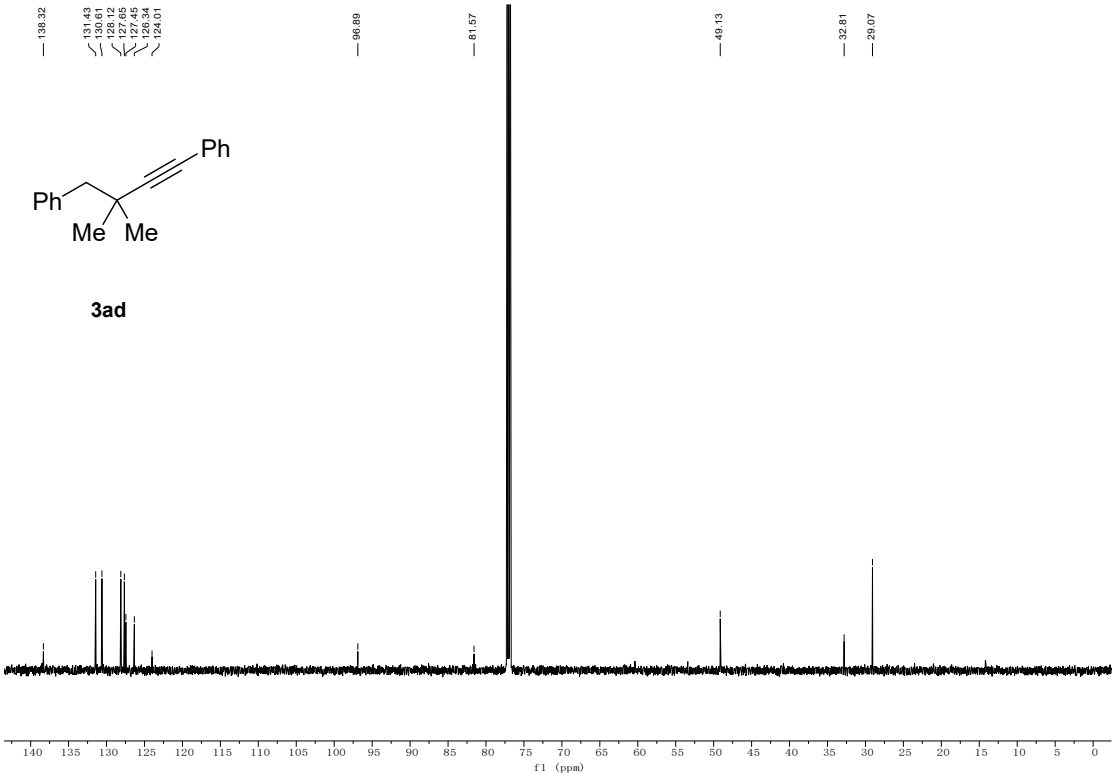
3ac, d.r. = 8.1: 1
From Pregnenolone

^{1}H NMR Spectrum of 3ad

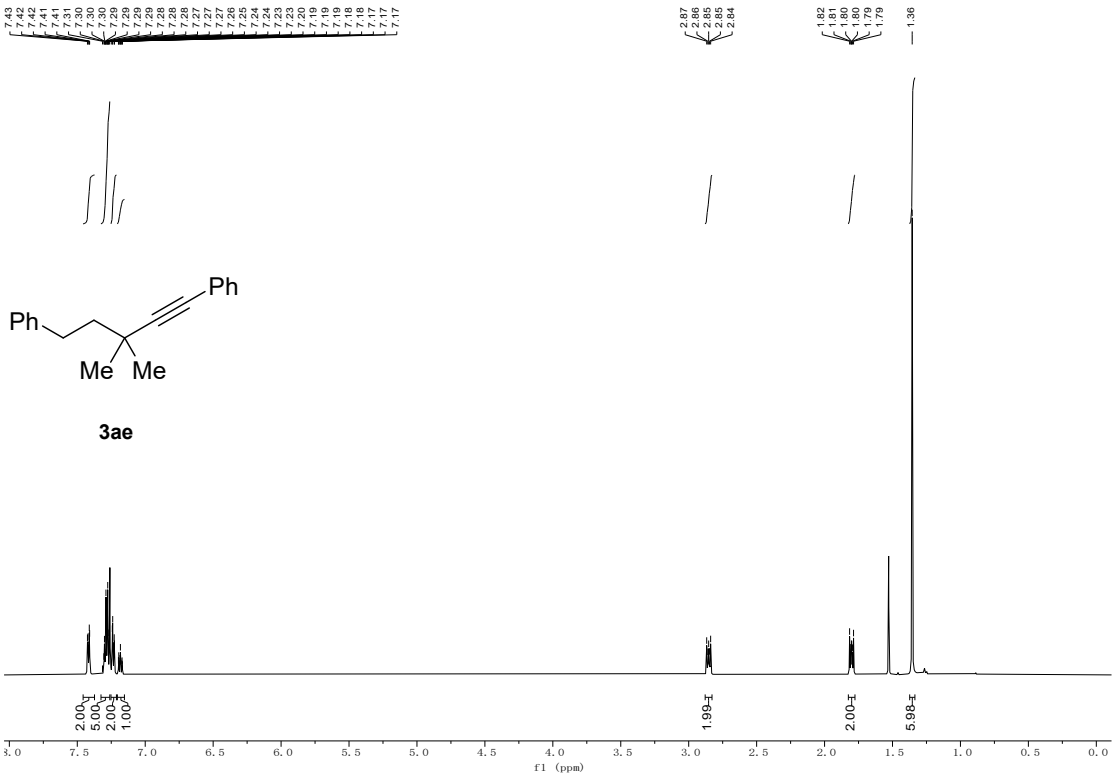


3ad

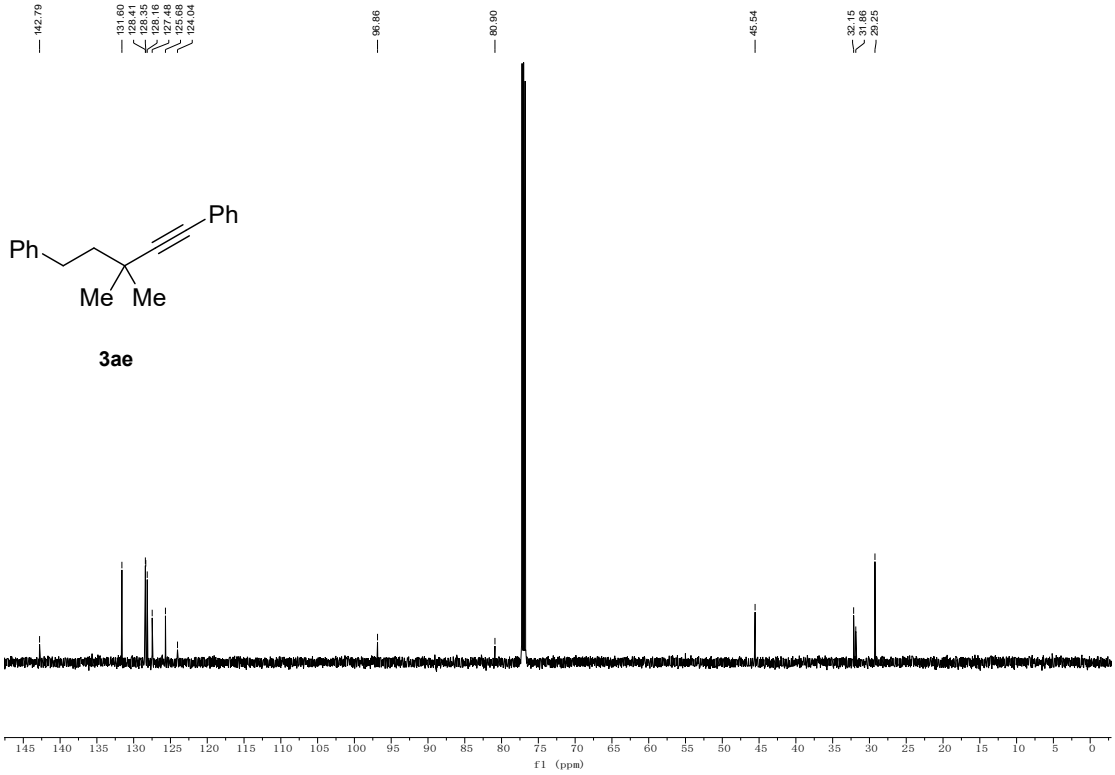
^{13}C NMR Spectrum of 3ad



^{1}H NMR Spectrum of 3ae

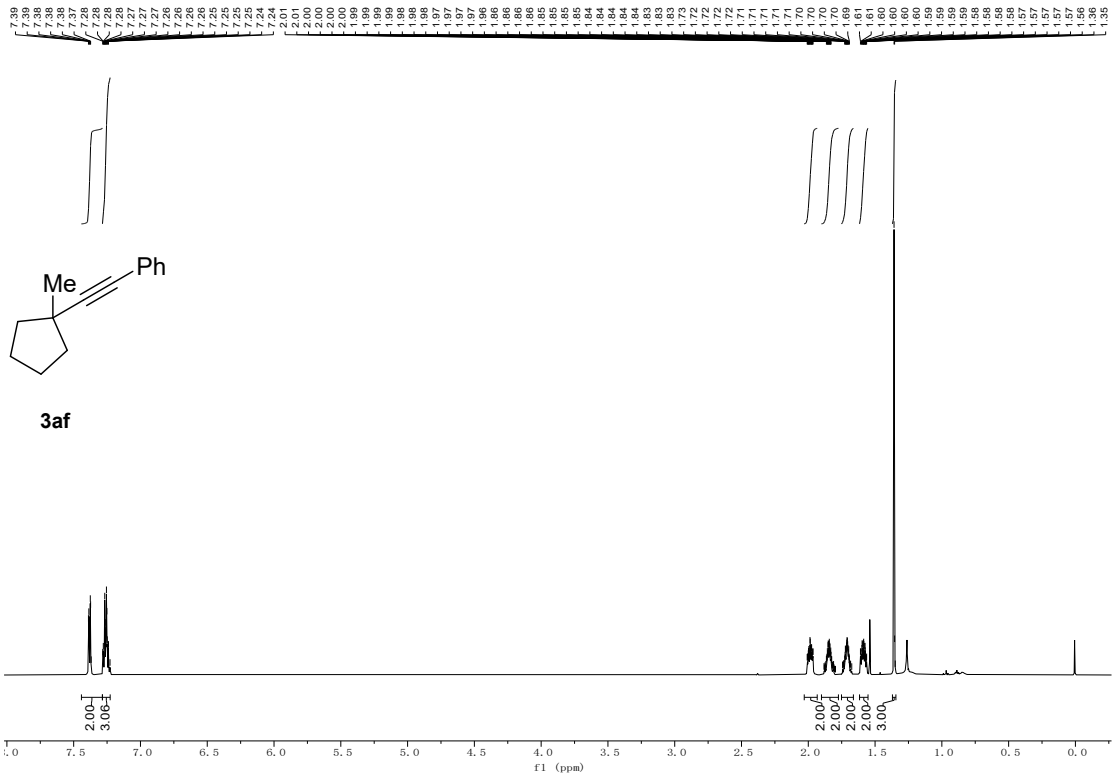


^{13}C NMR Spectrum of 3ae



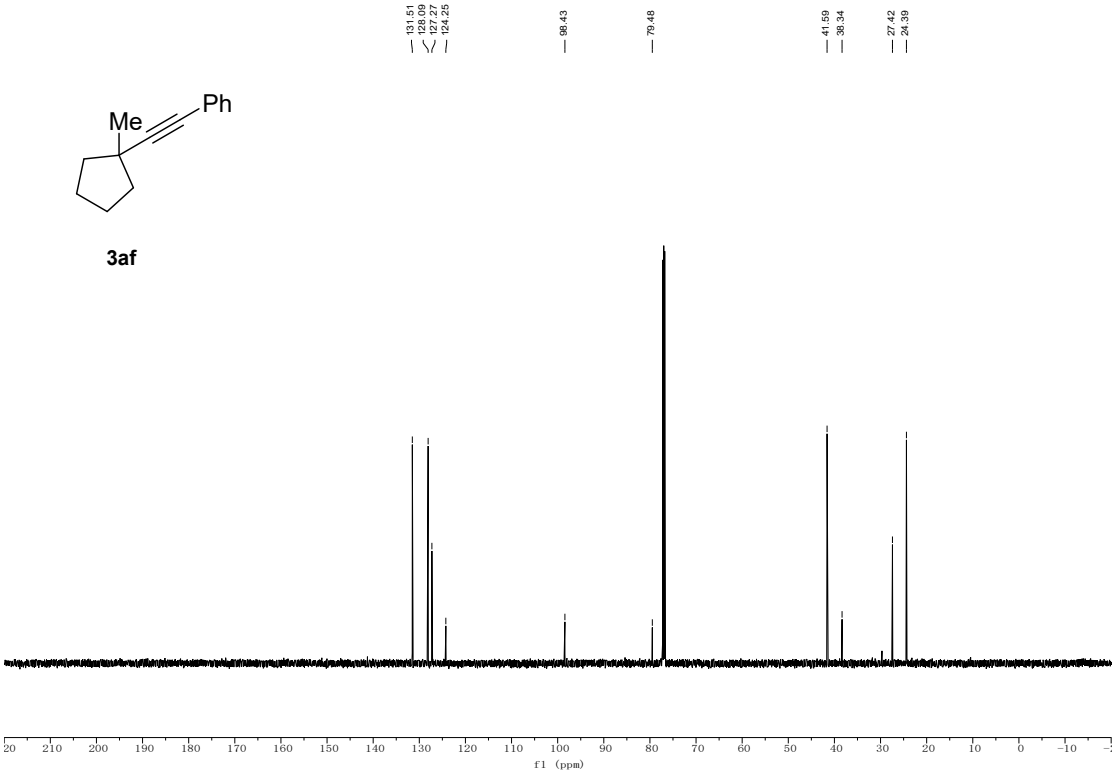
3ae

^{1}H NMR Spectrum of 3af

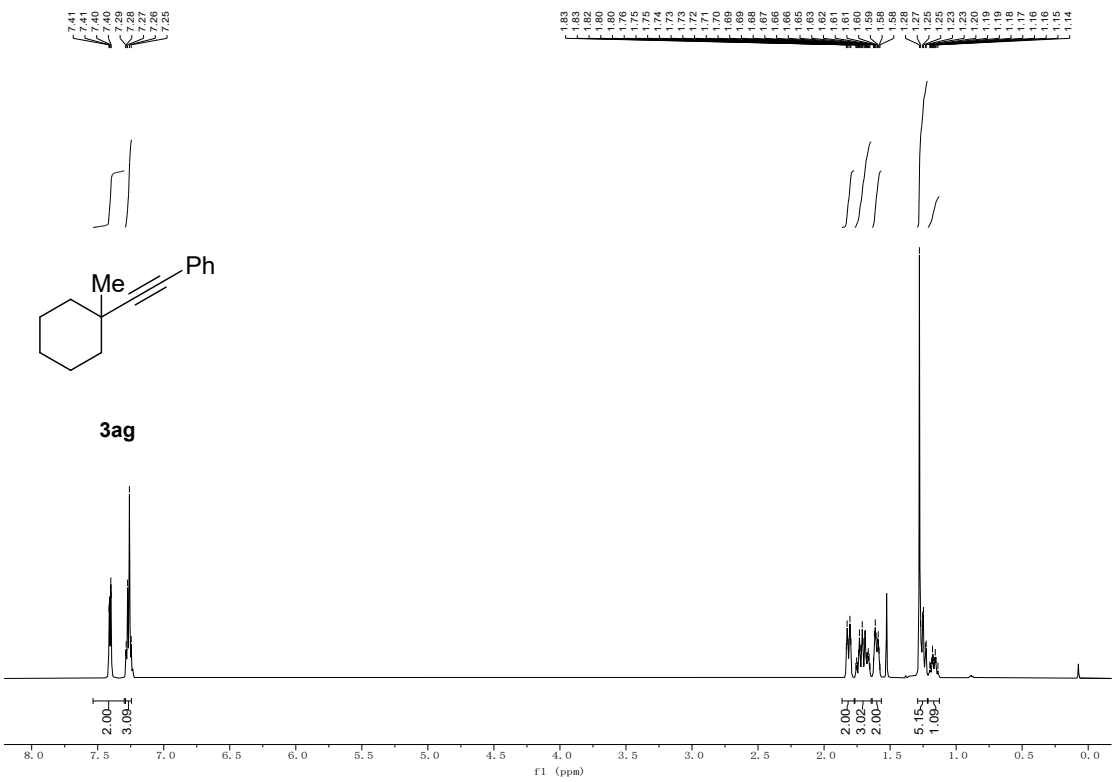


3af

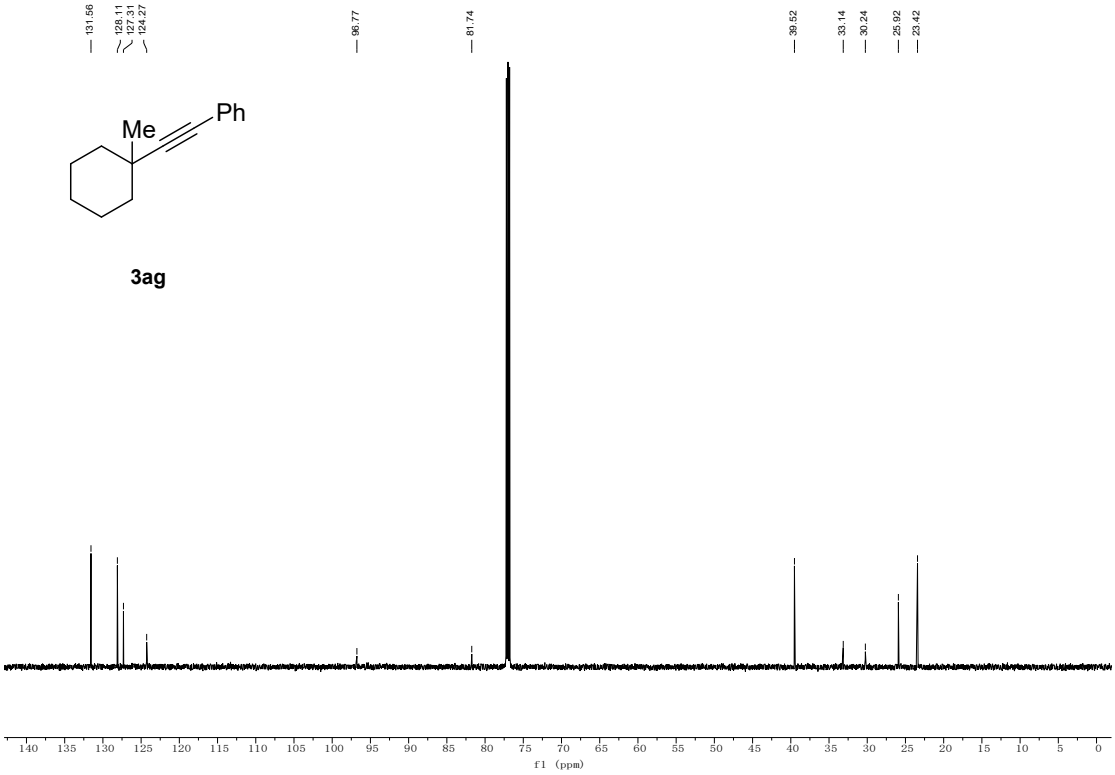
^{13}C NMR Spectrum of 3af



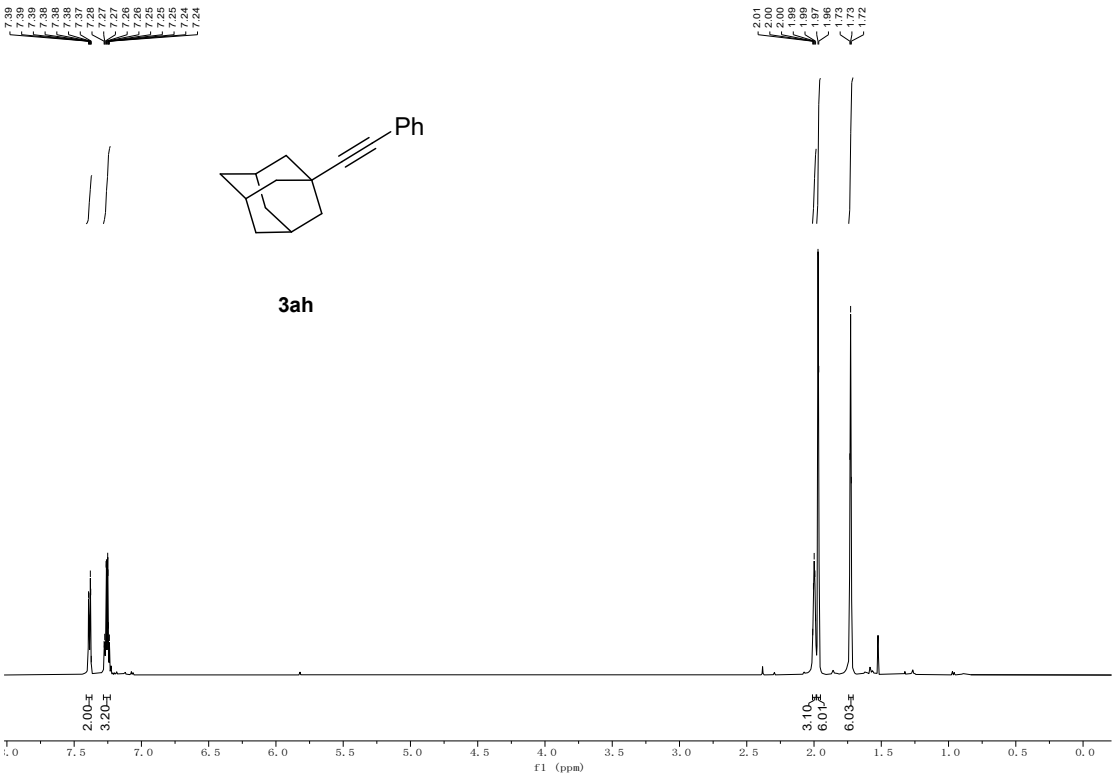
^{1}H NMR Spectrum of 3ag



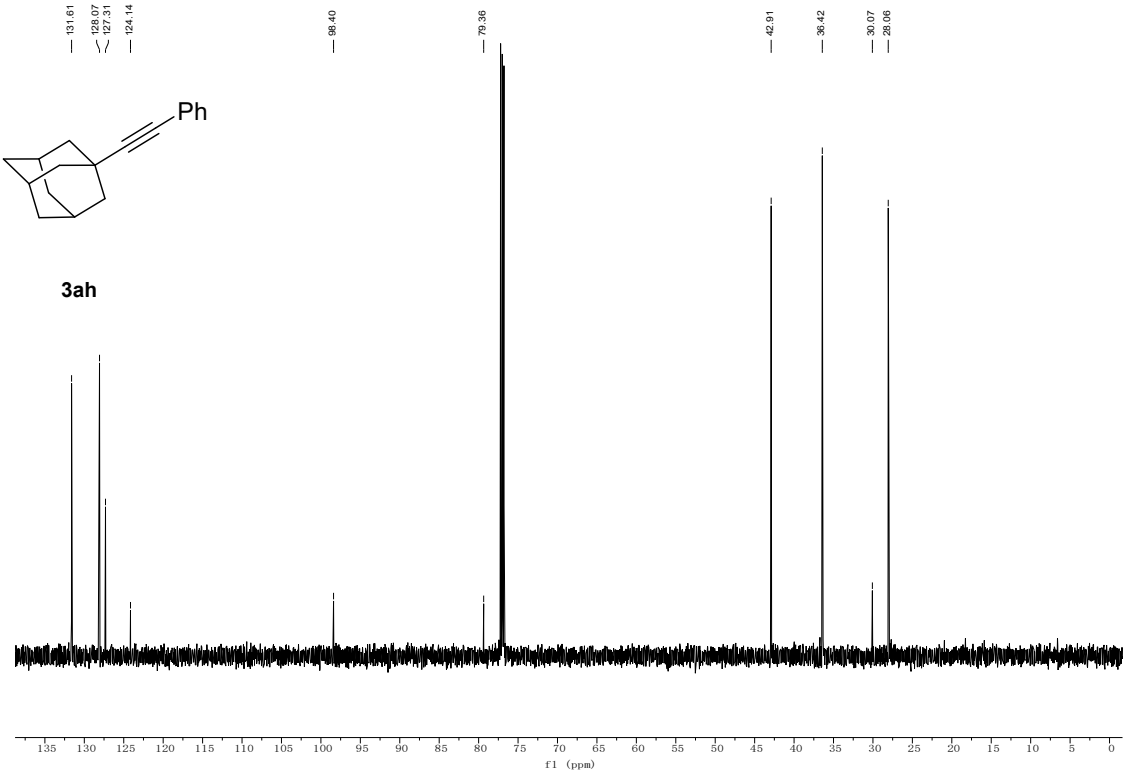
^{13}C NMR Spectrum of 3ag



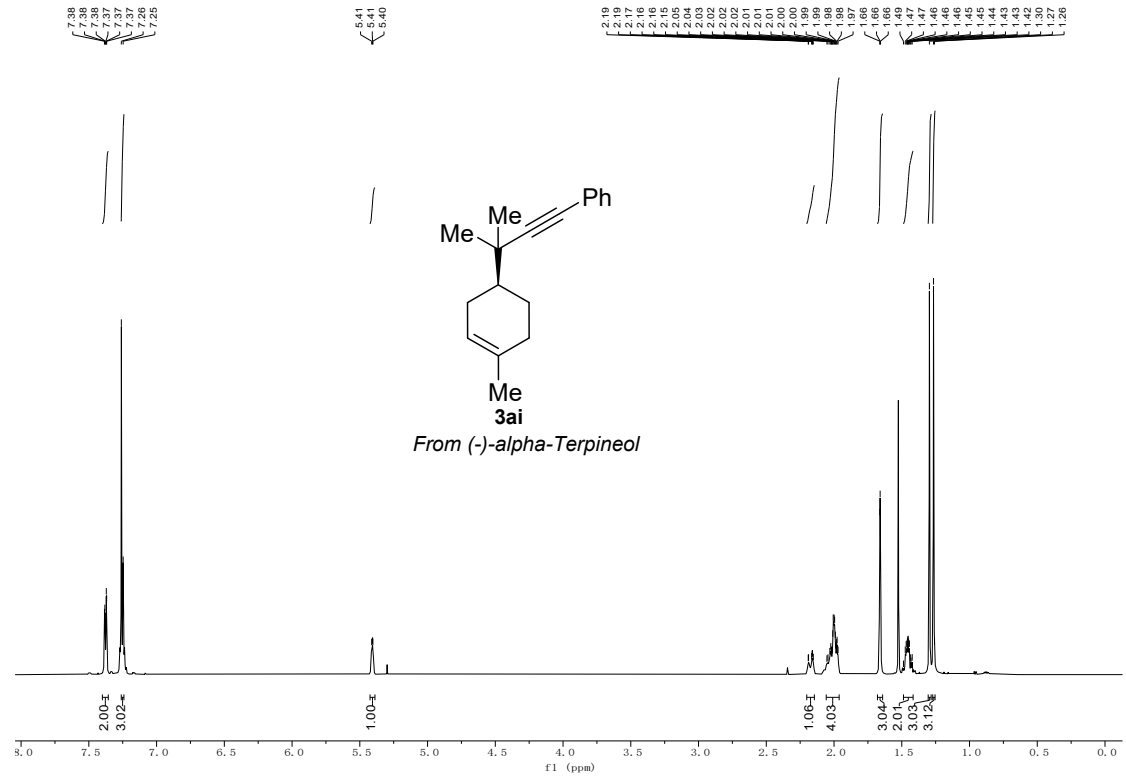
^{1}H NMR Spectrum of 3ah



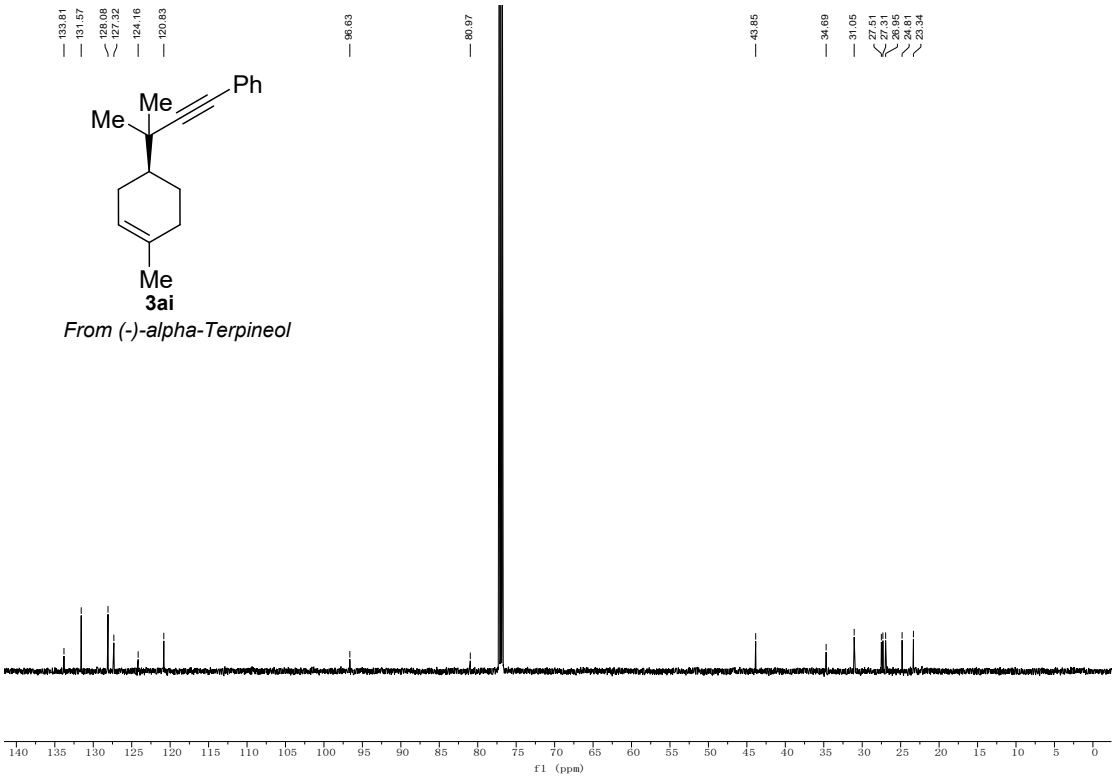
^{13}C NMR Spectrum of 3ah



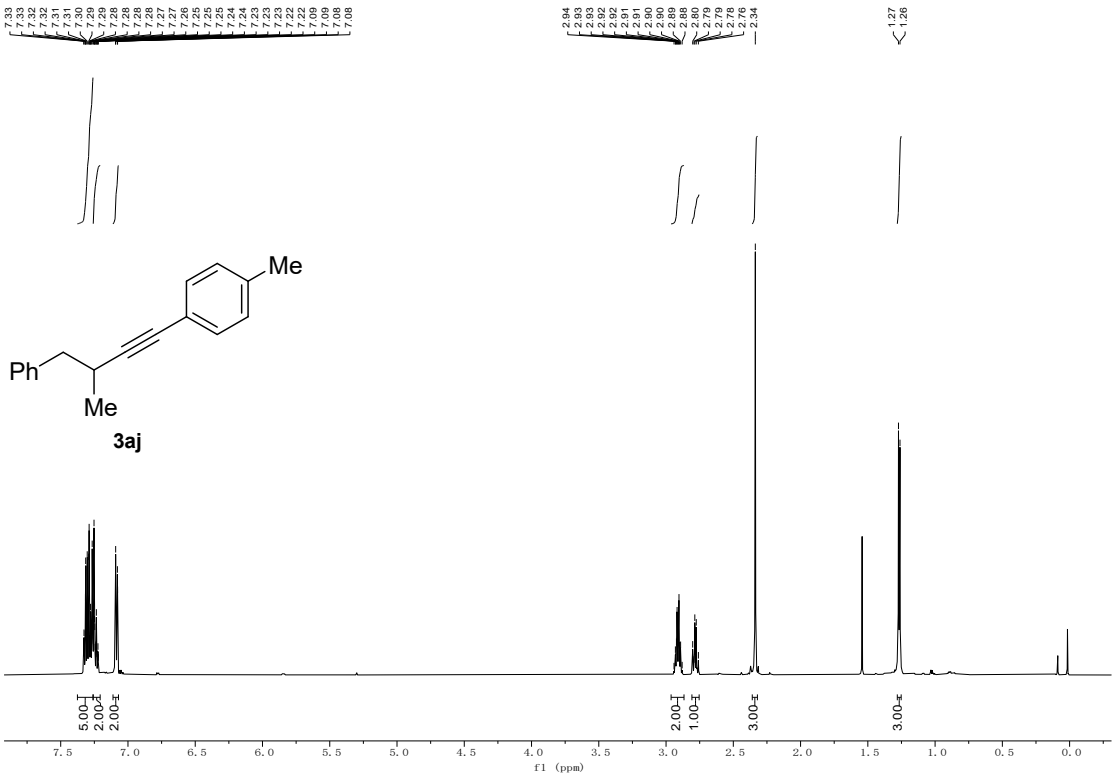
^{1}H NMR Spectrum of 3ai



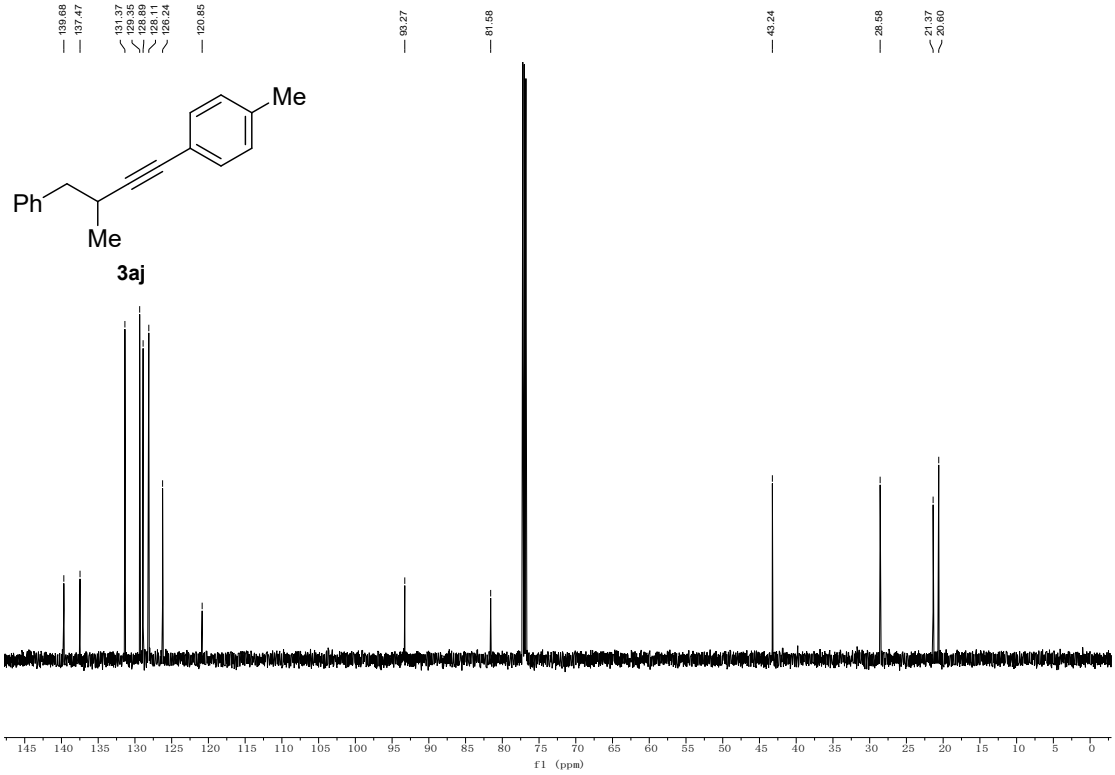
^{13}C NMR Spectrum of 3ai



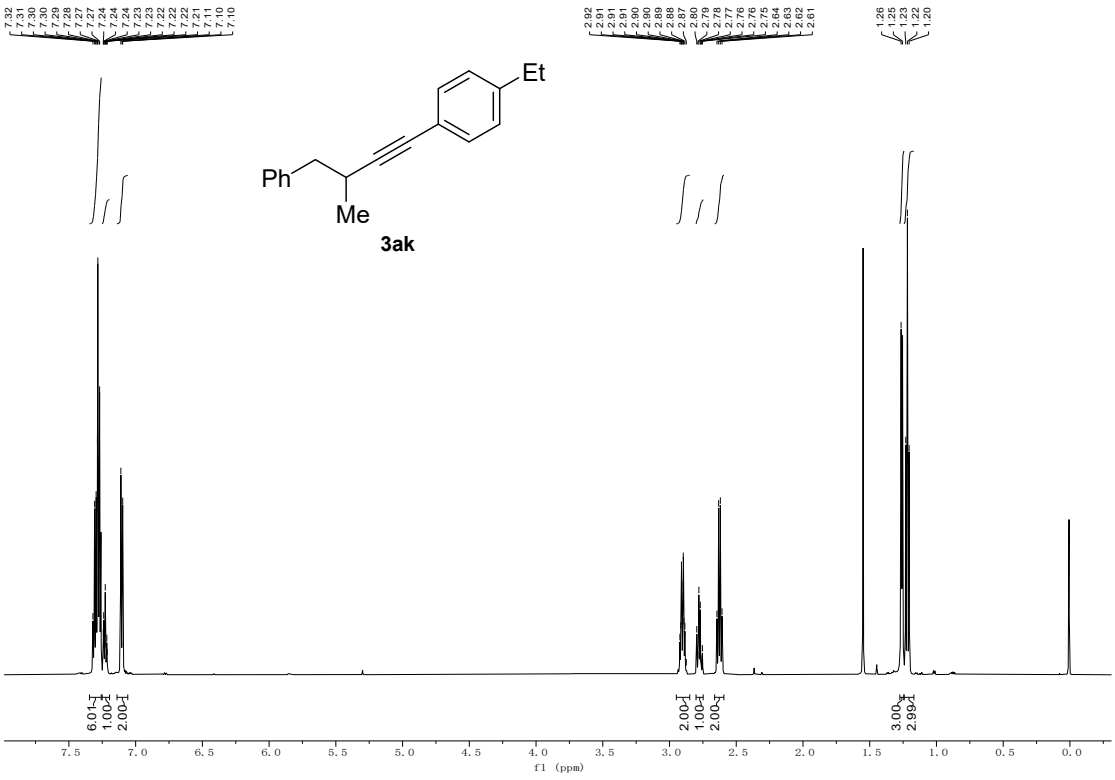
^{1}H NMR Spectrum of 3aj



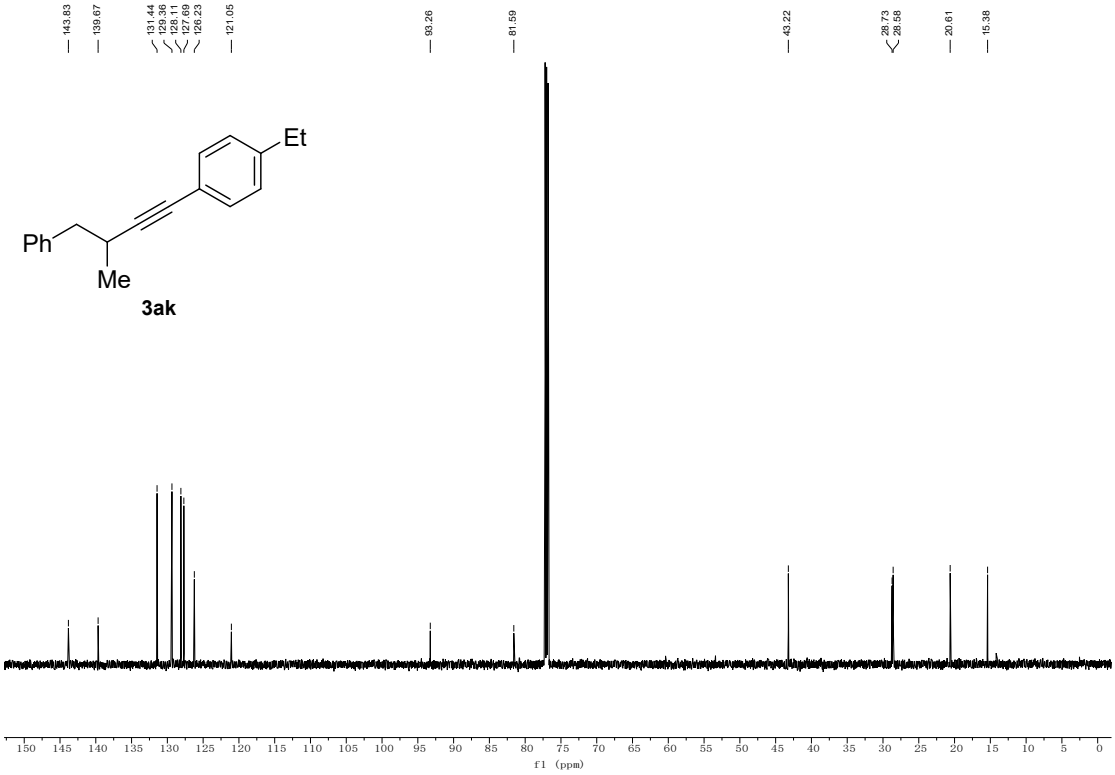
^{13}C NMR Spectrum of 3aj



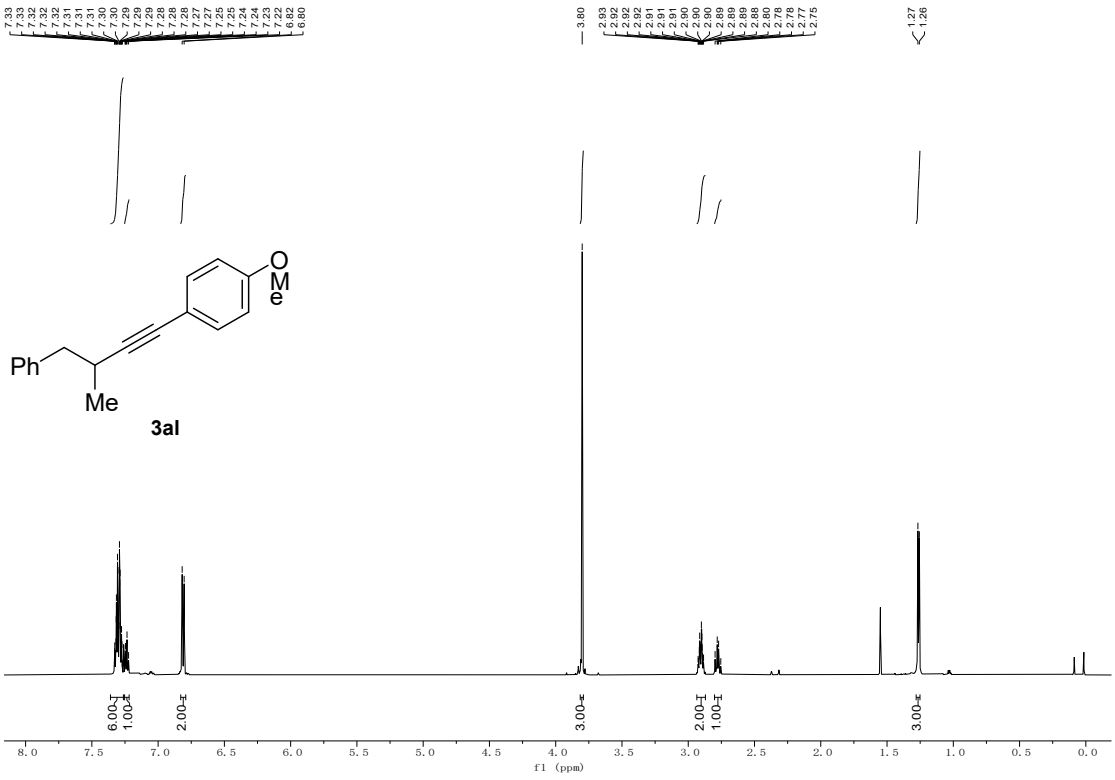
^{1}H NMR Spectrum of 3ak



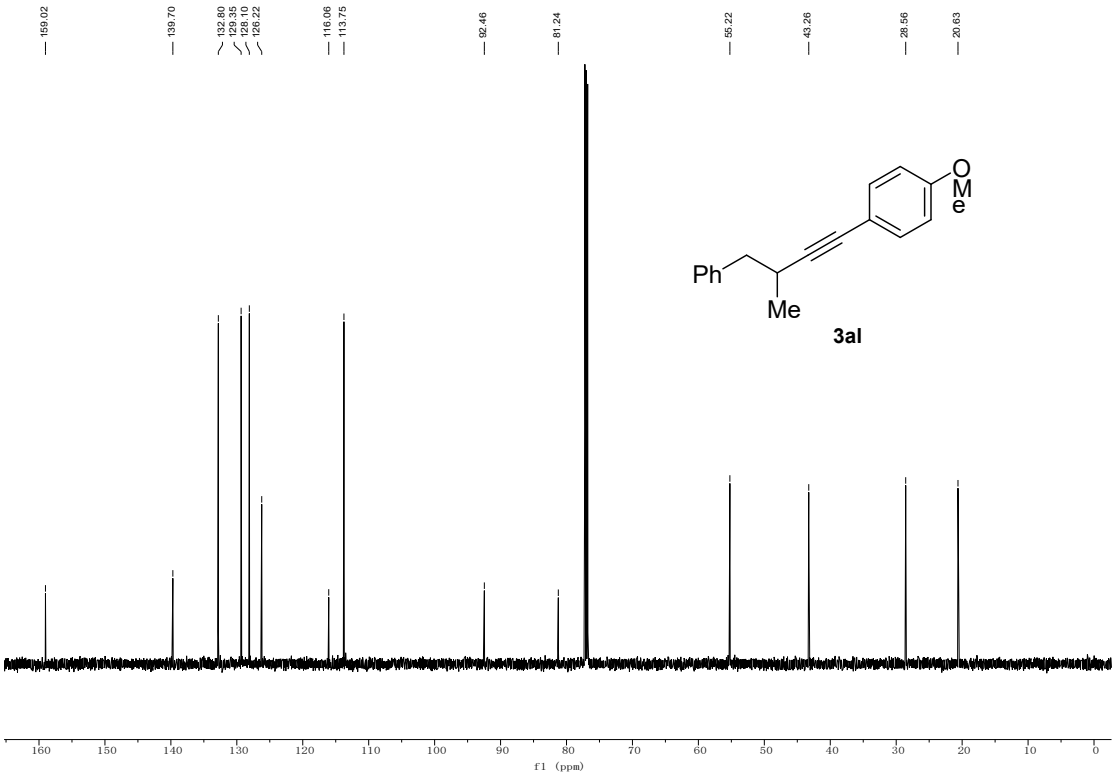
^{13}C NMR Spectrum of 3ak



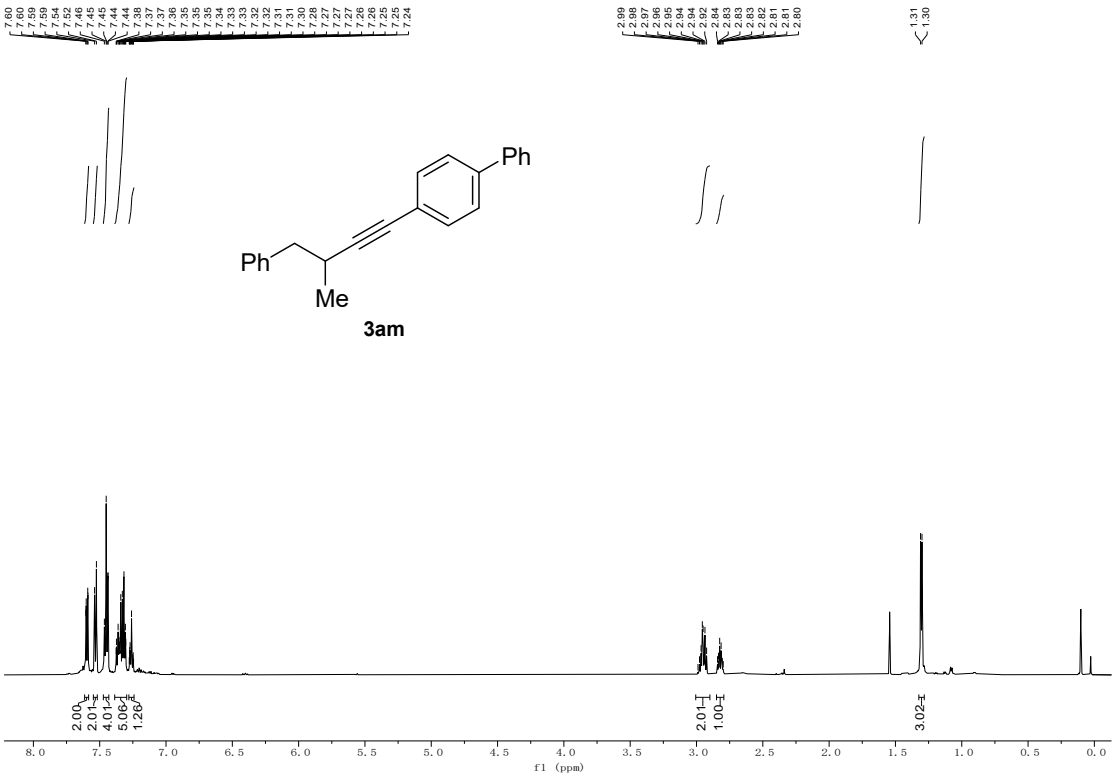
^{1}H NMR Spectrum of 3al



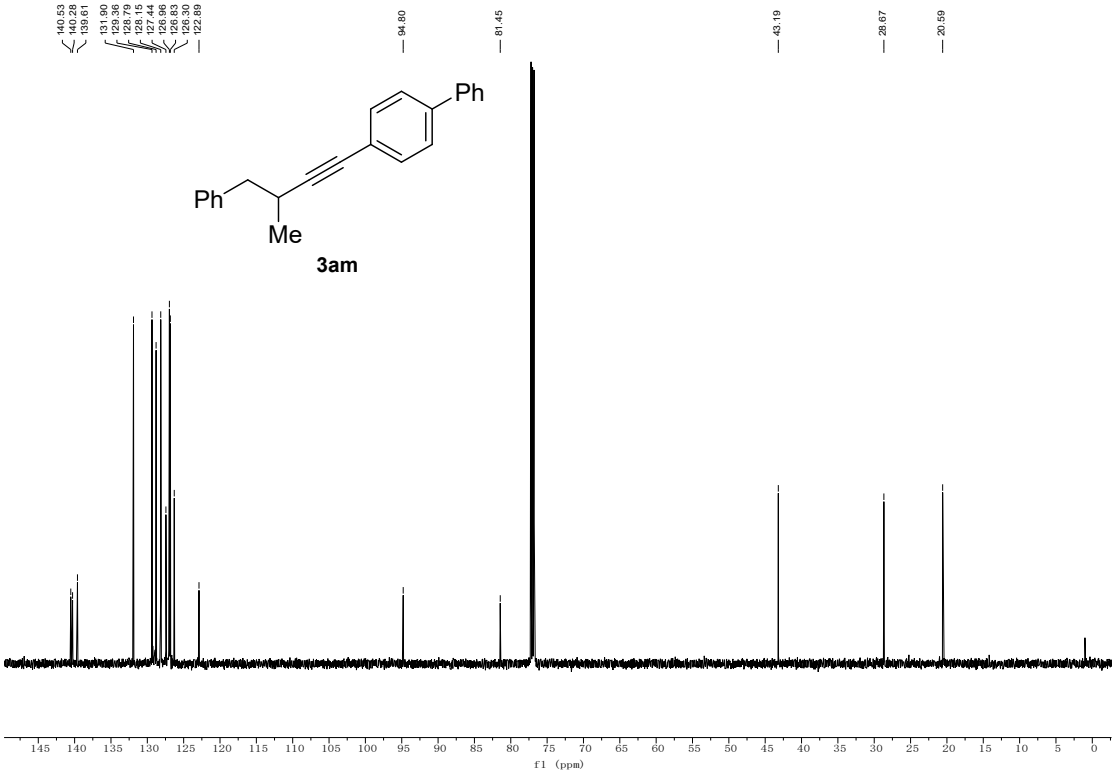
^{13}C NMR Spectrum of 3al



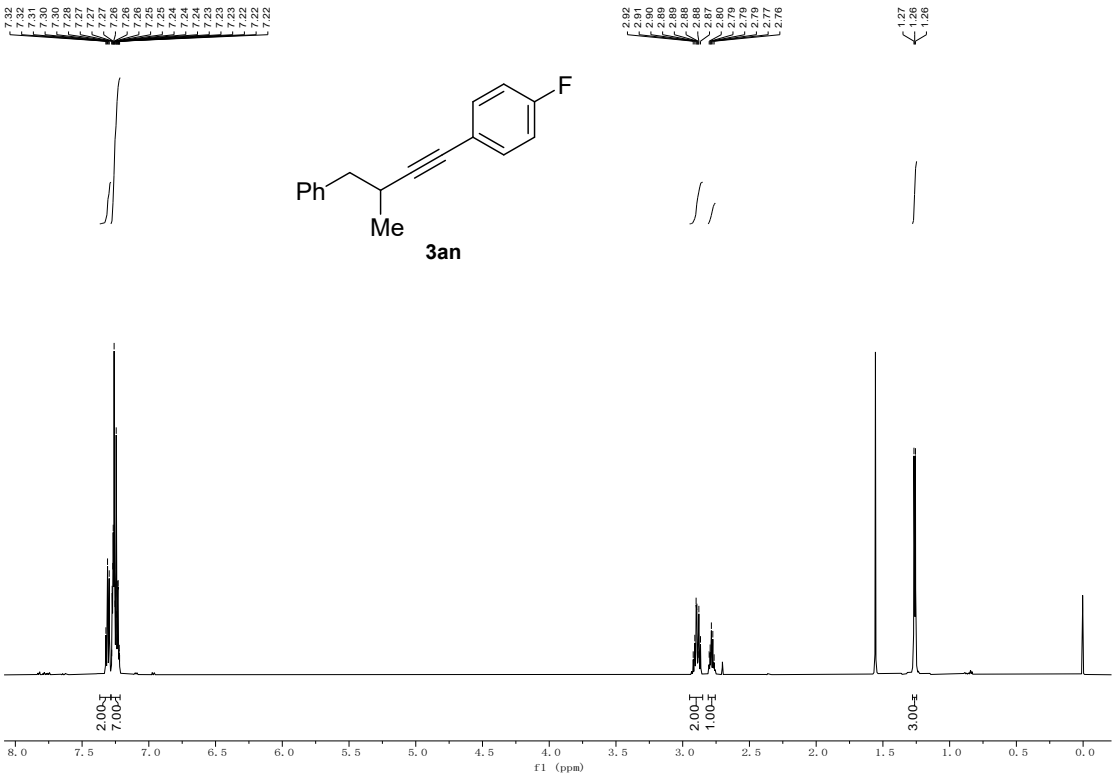
^{1}H NMR Spectrum of 3am



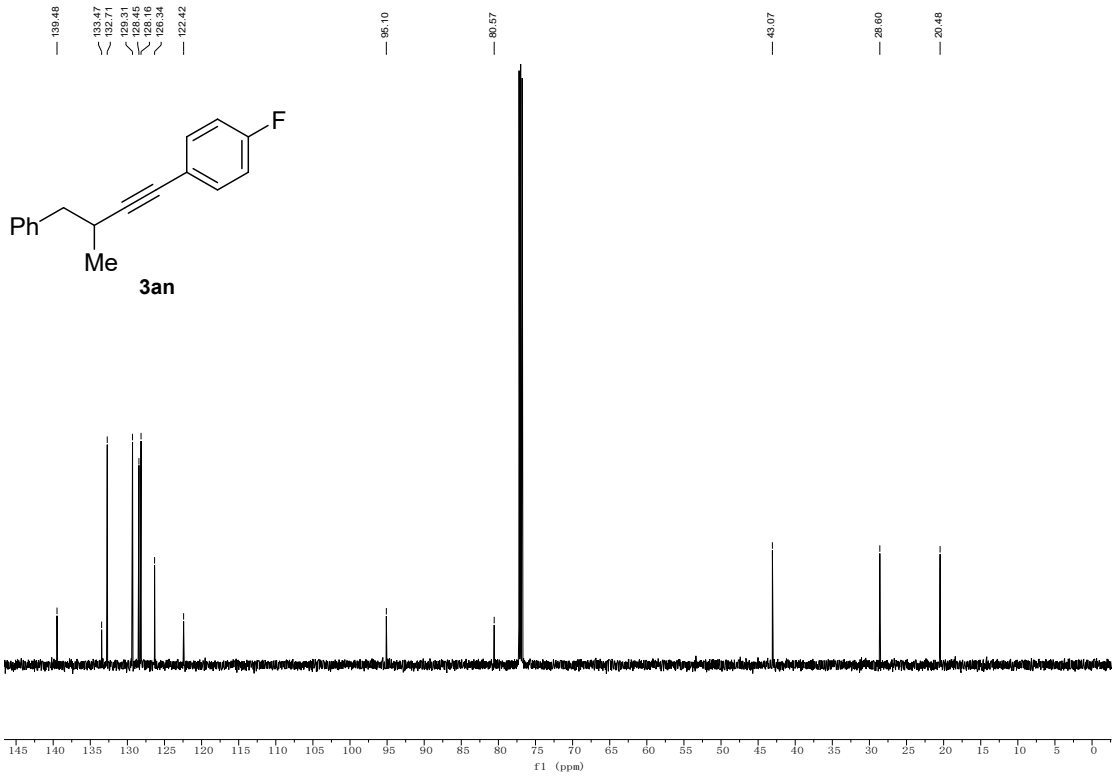
^{13}C NMR Spectrum of 3am



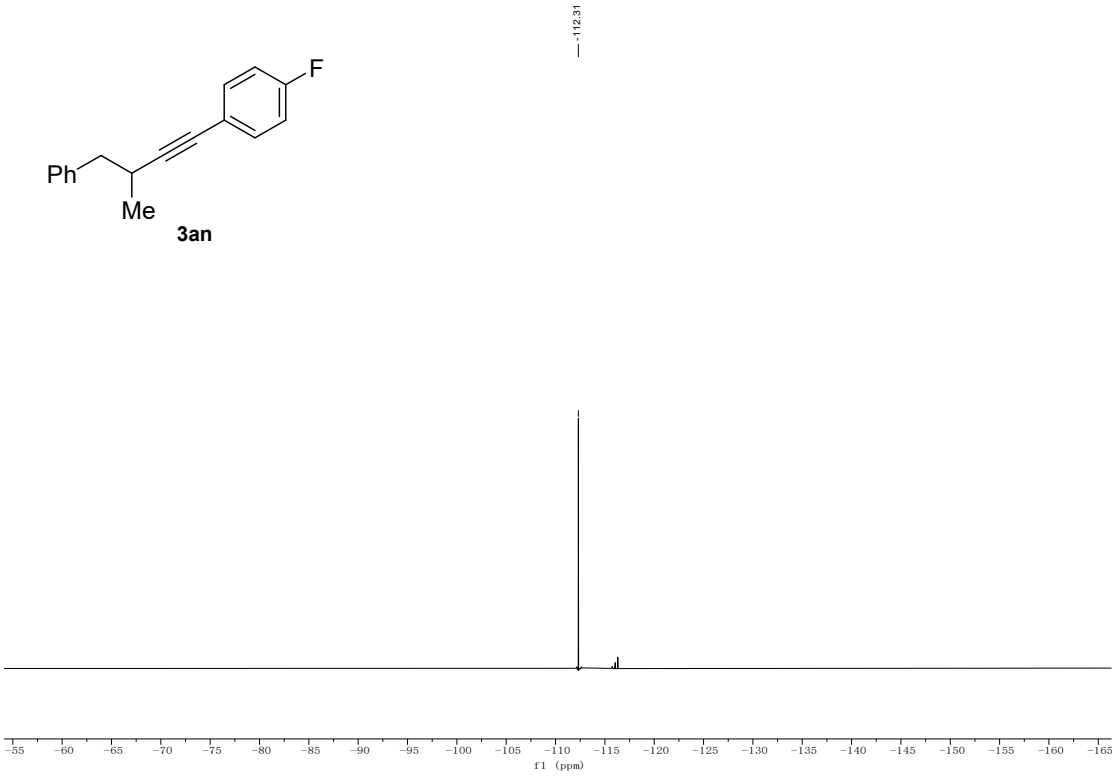
^{1}H NMR Spectrum of 3an



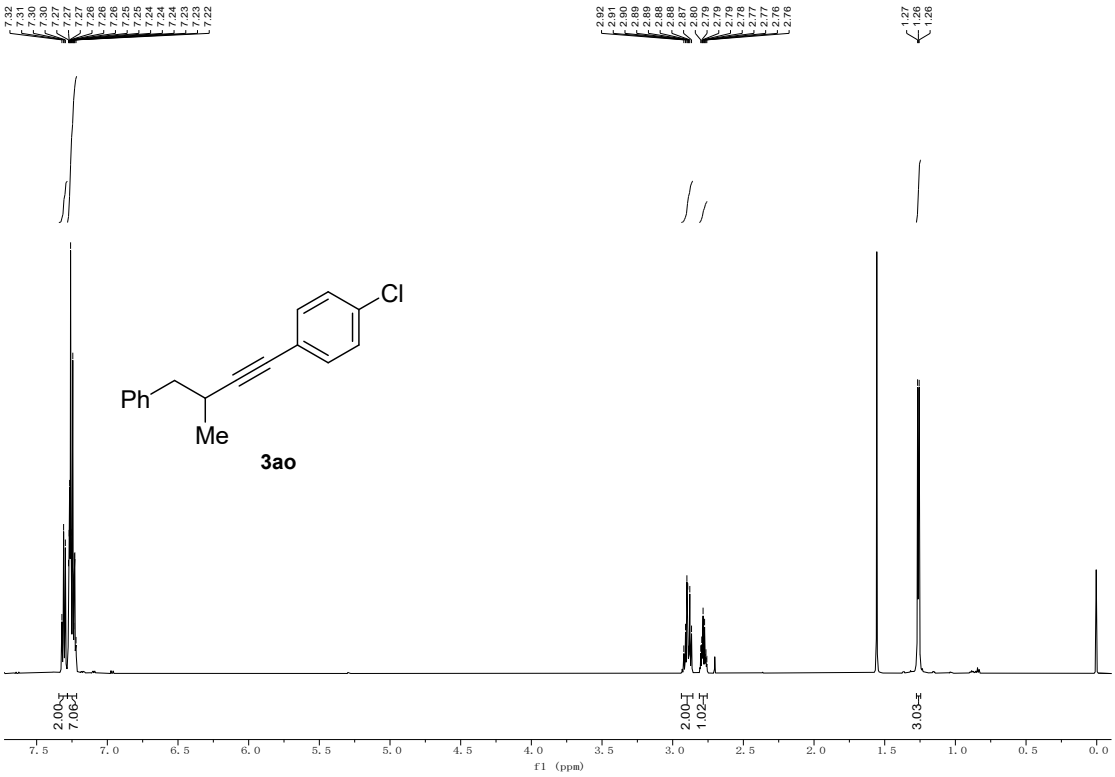
^{13}C NMR Spectrum of 3an



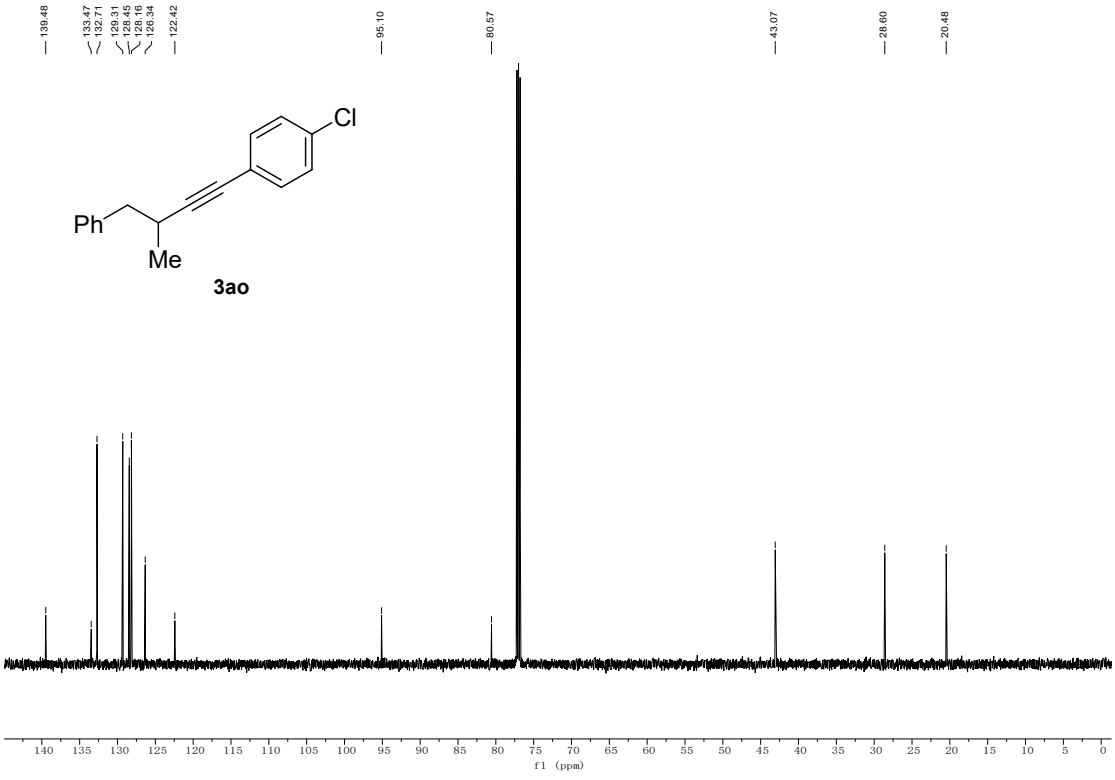
^{19}F NMR Spectrum of 3an



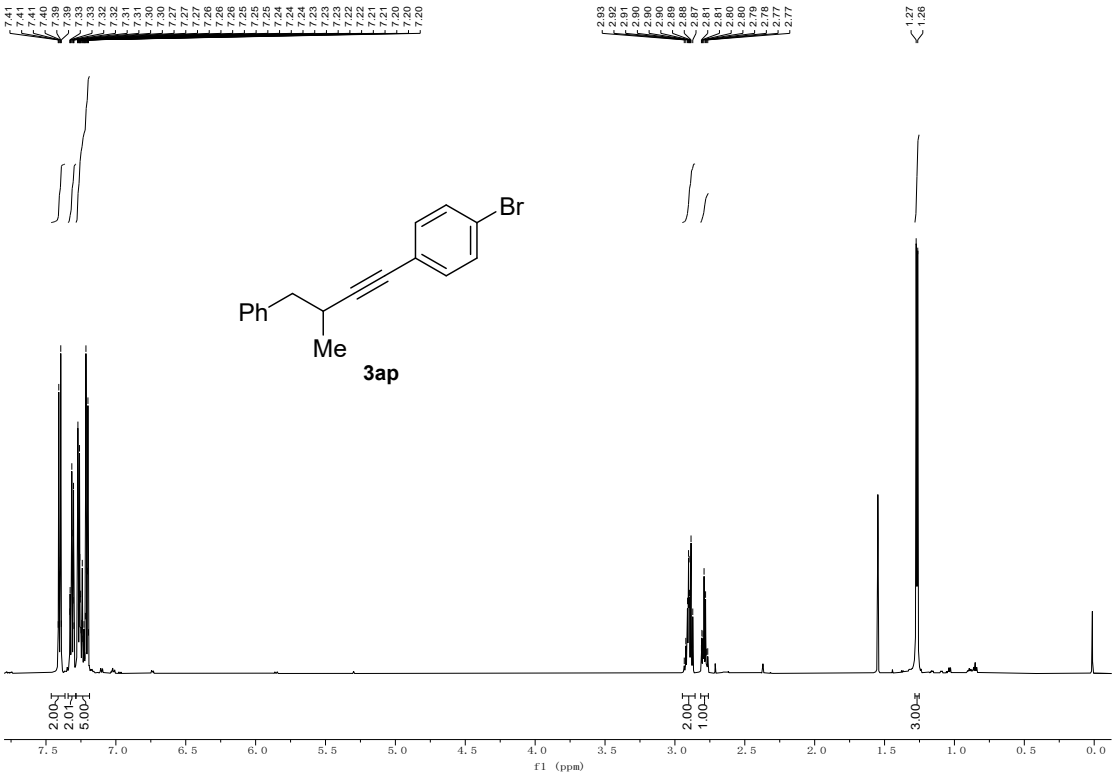
^{1}H NMR Spectrum of 3ao



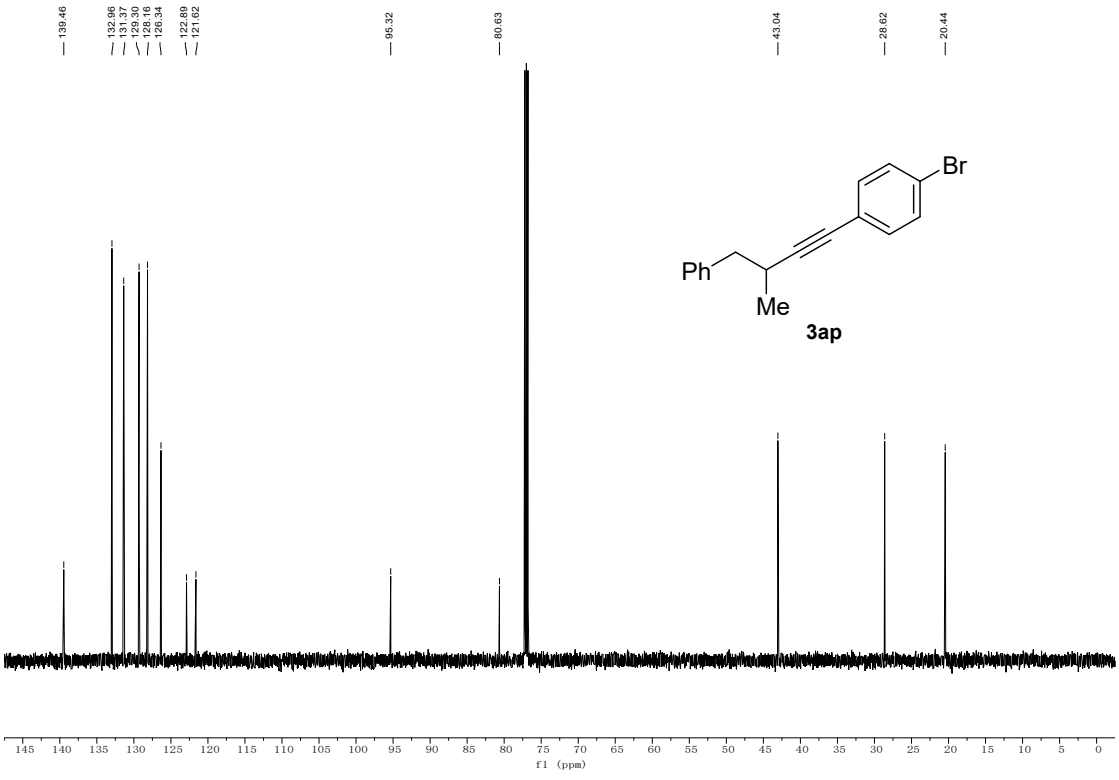
^{13}C NMR Spectrum of 3ao



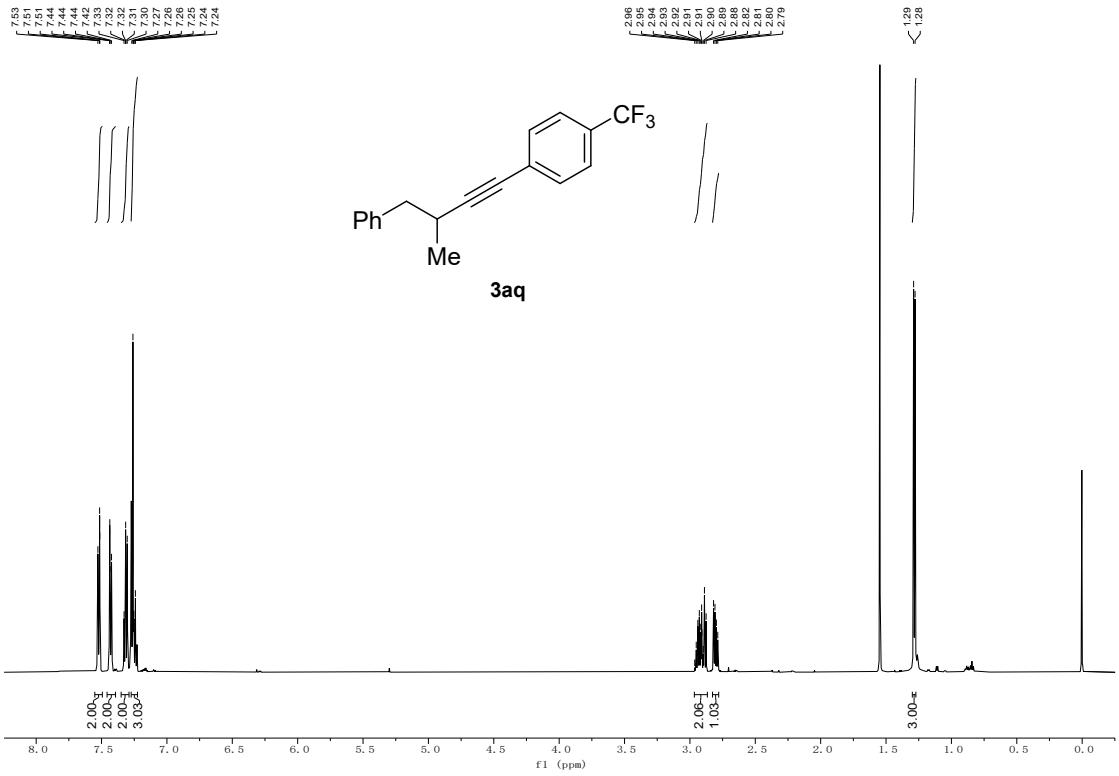
^{1}H NMR Spectrum of 3ap



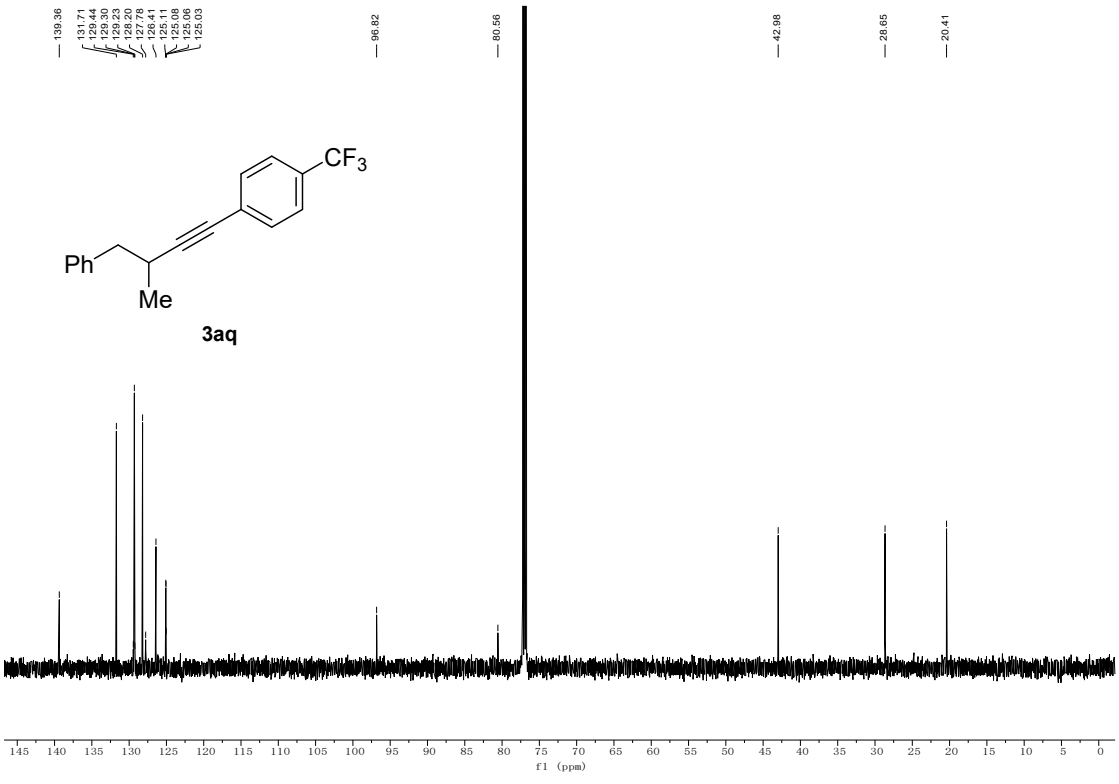
^{13}C NMR Spectrum of 3ap



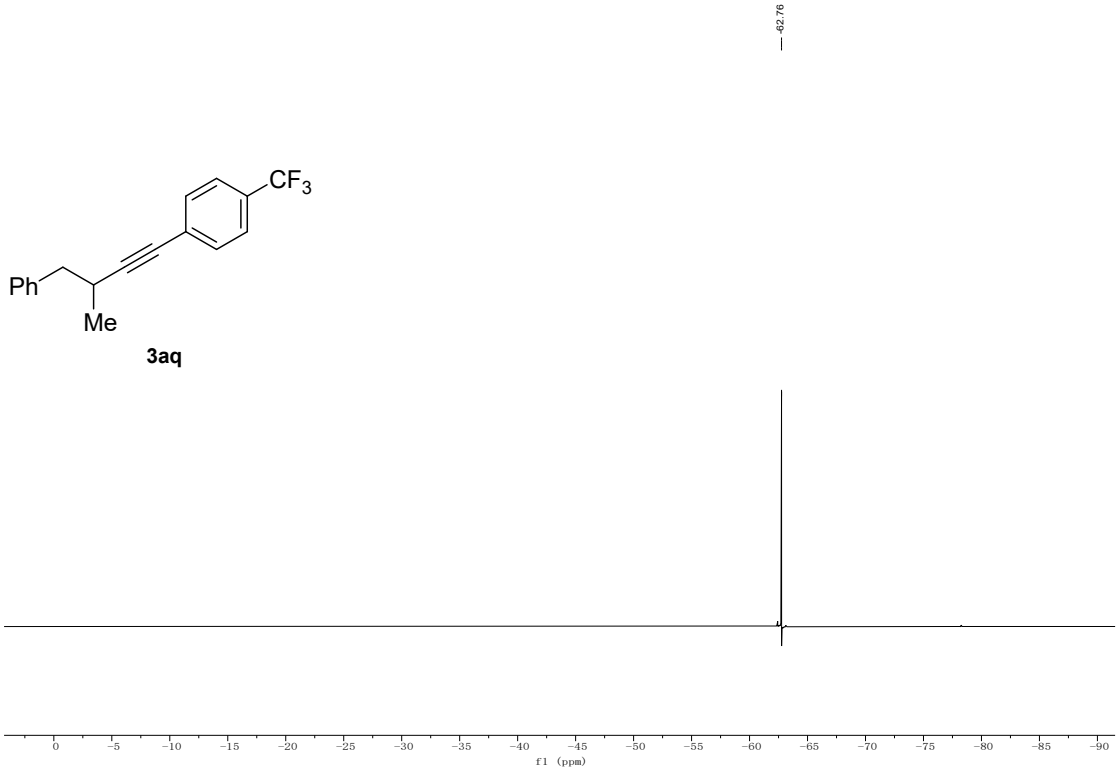
^{1}H NMR Spectrum of 3aq



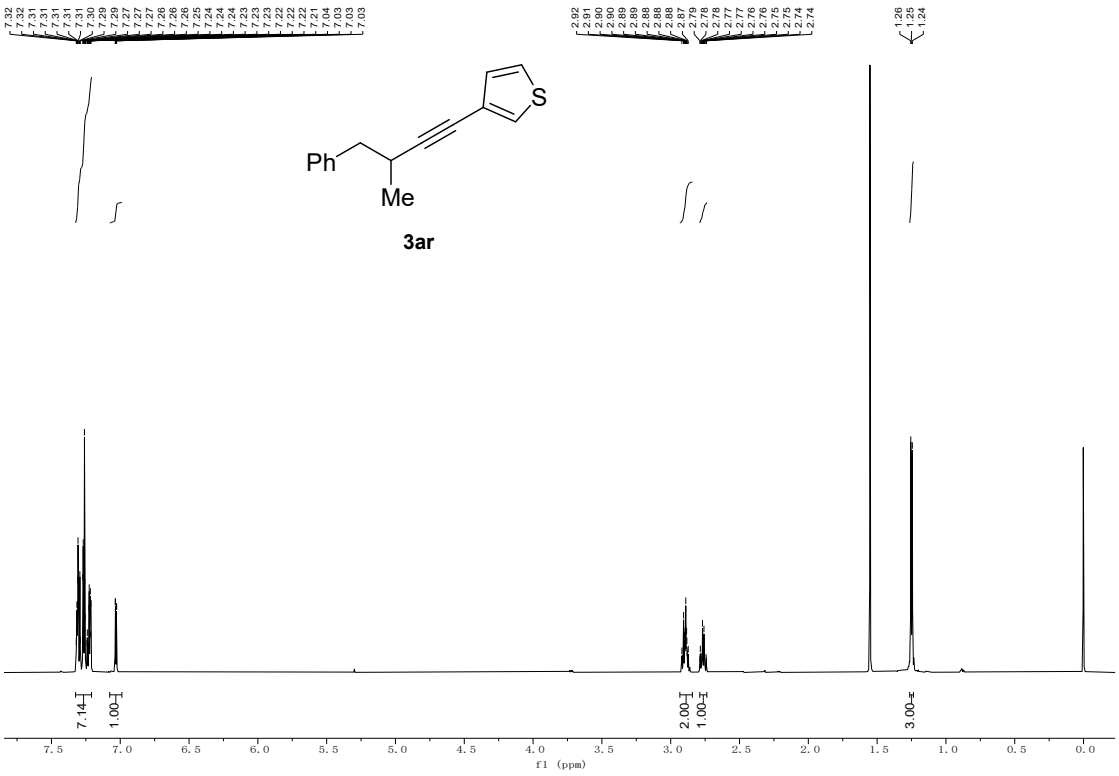
^{13}C NMR Spectrum of 3aq



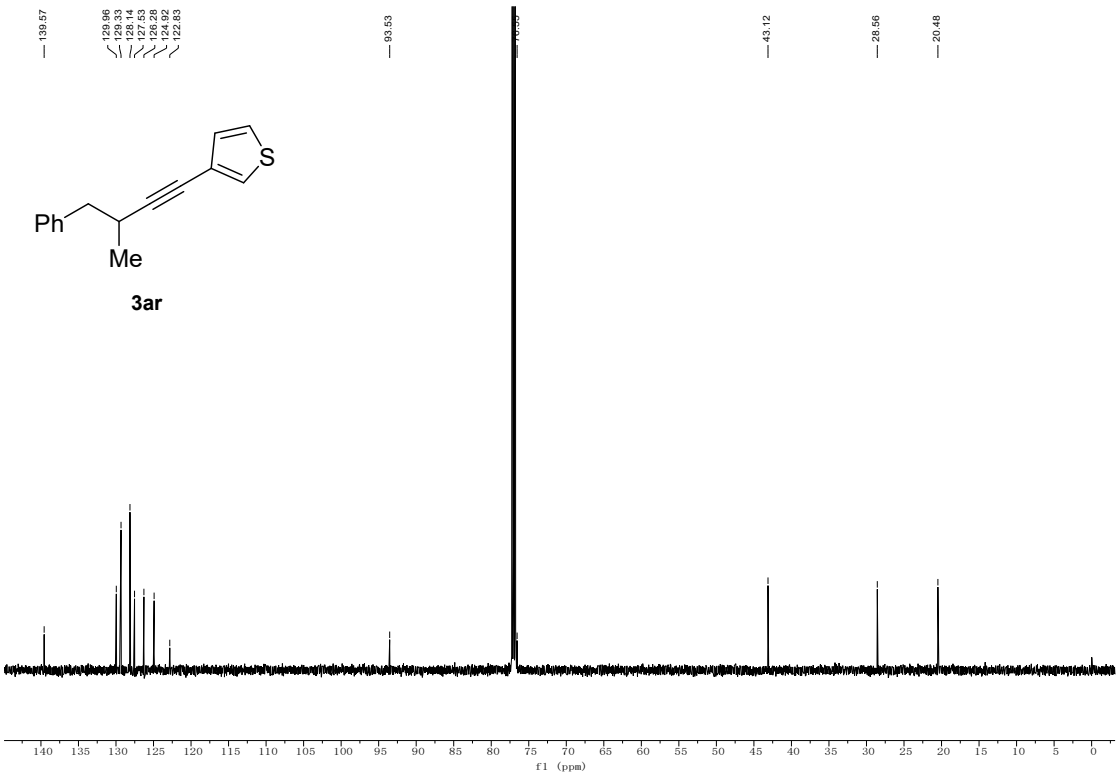
^{19}F NMR Spectrum of 3aq



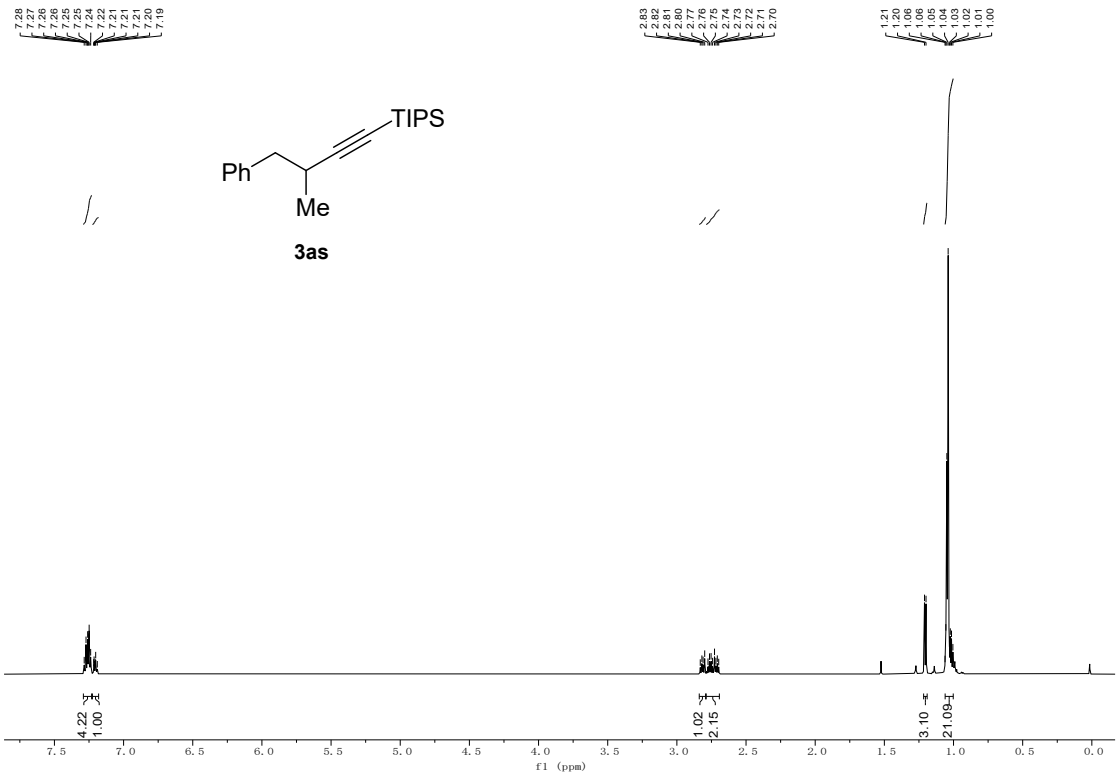
^{1}H NMR Spectrum of 3ar



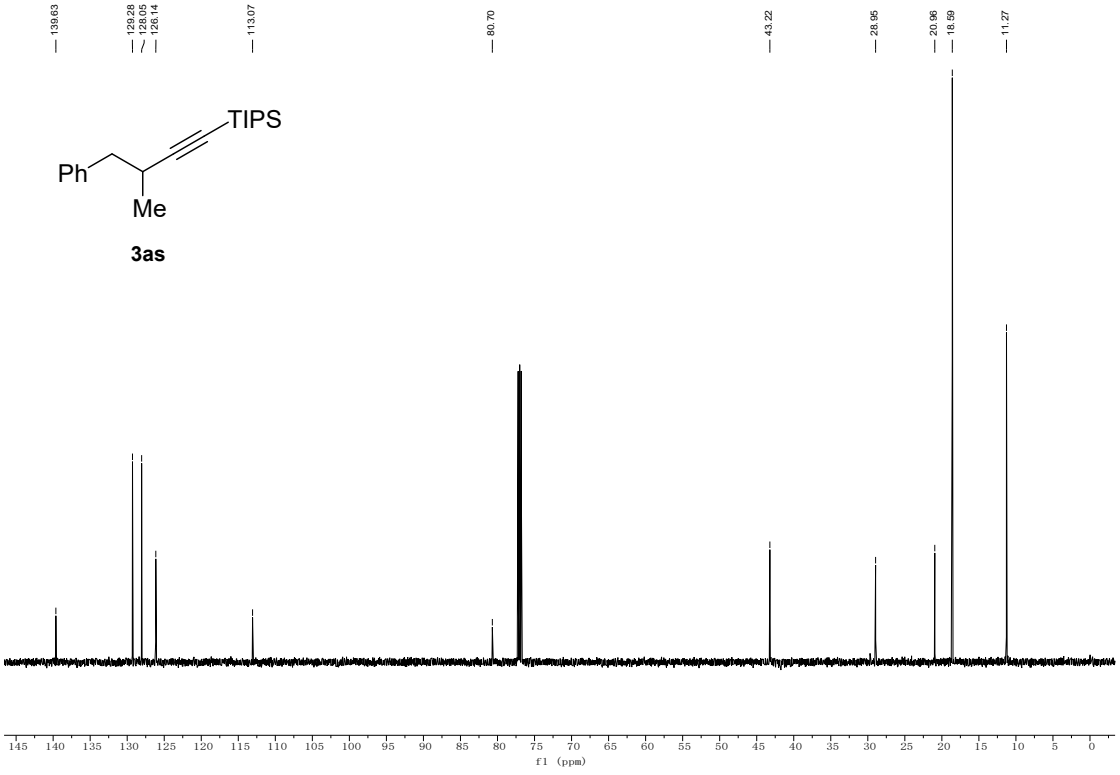
^{13}C NMR Spectrum of 3ar



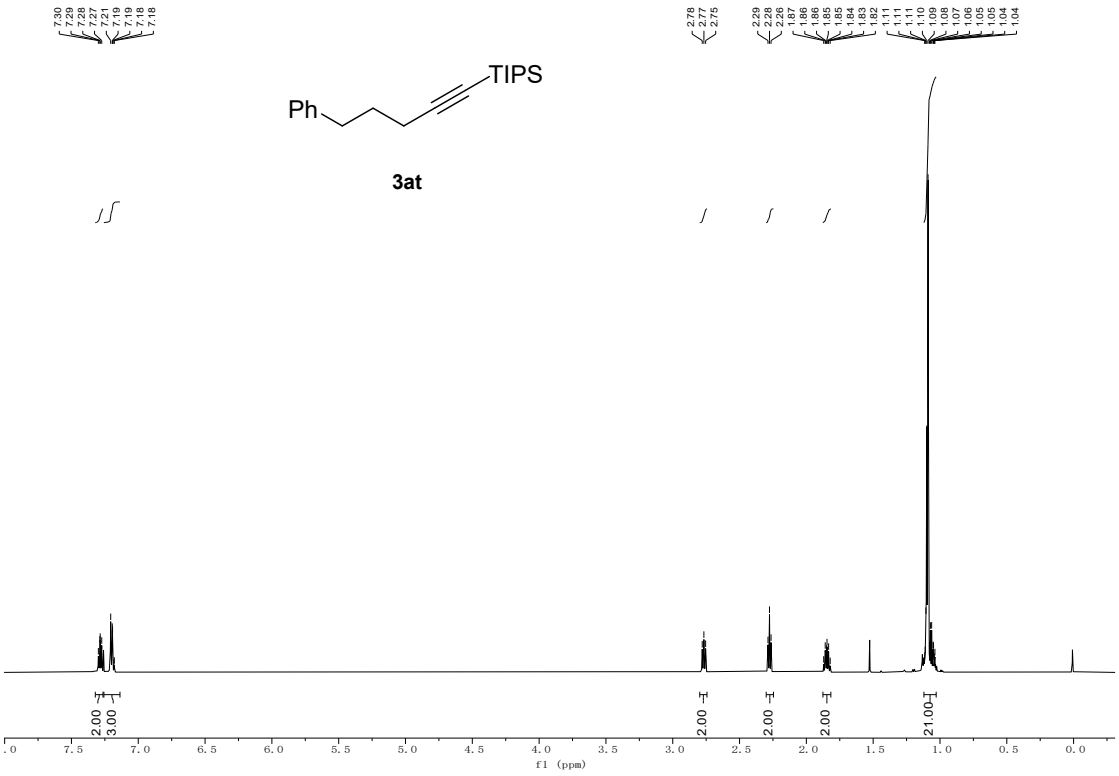
^{1}H NMR Spectrum of 3as



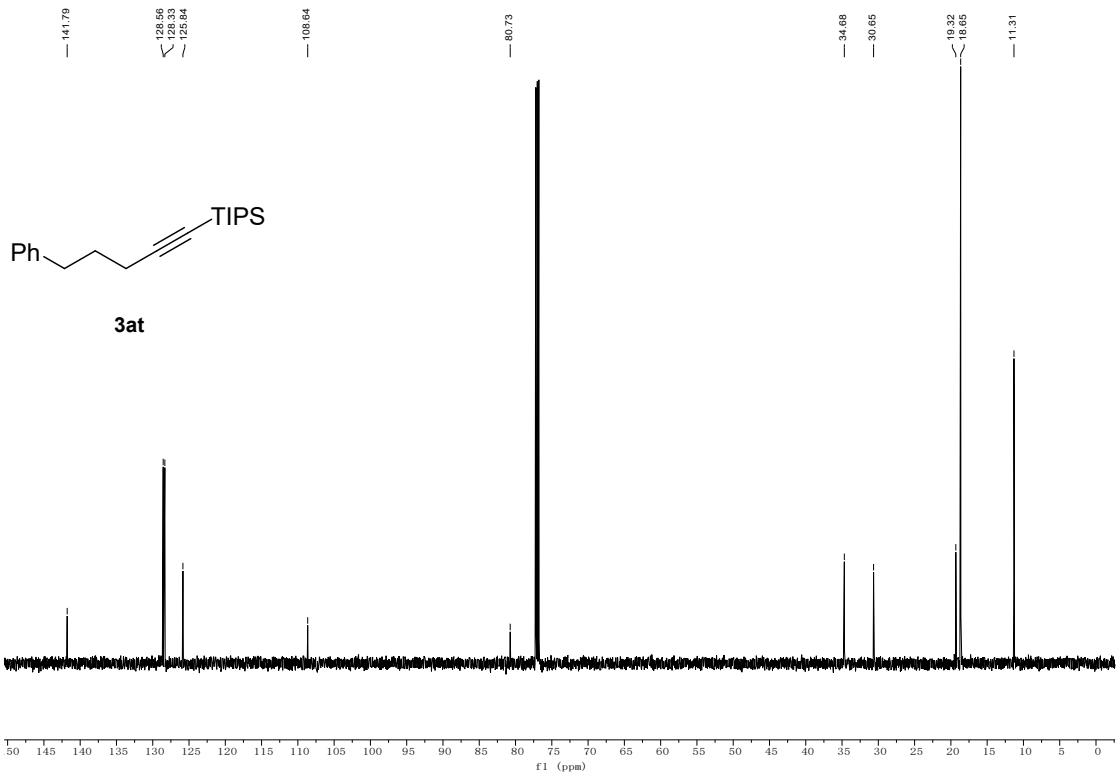
^{13}C NMR Spectrum of 3as



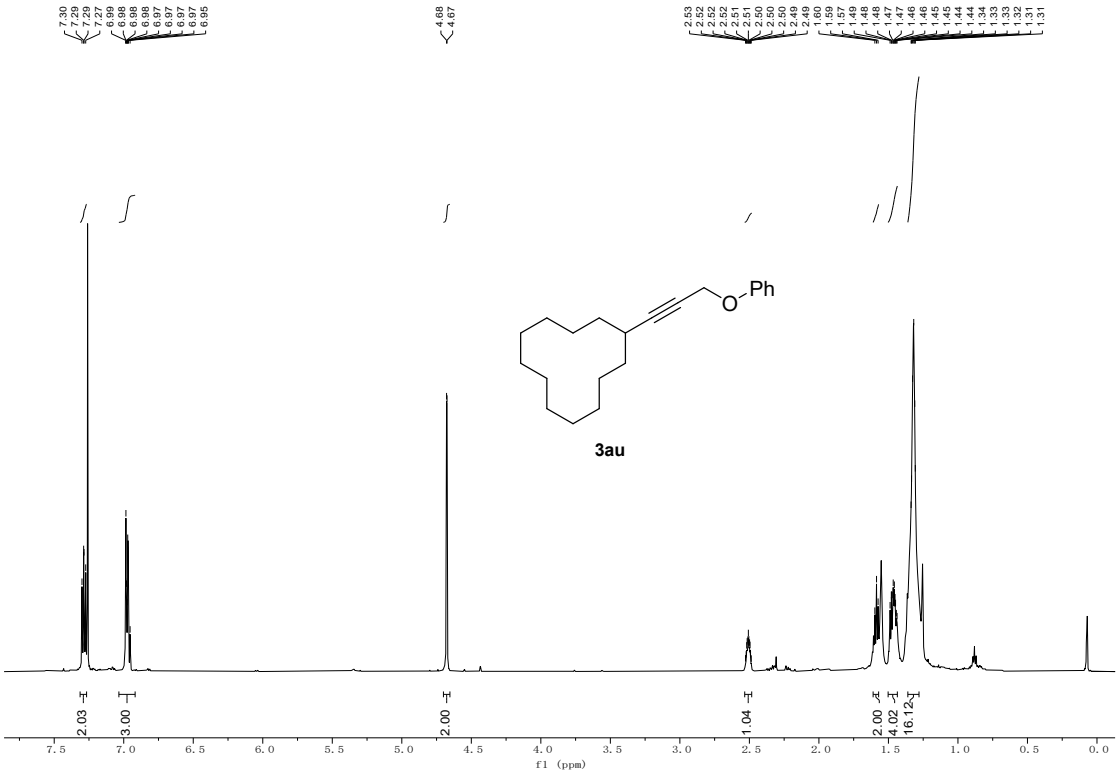
^{1}H NMR Spectrum of 3at



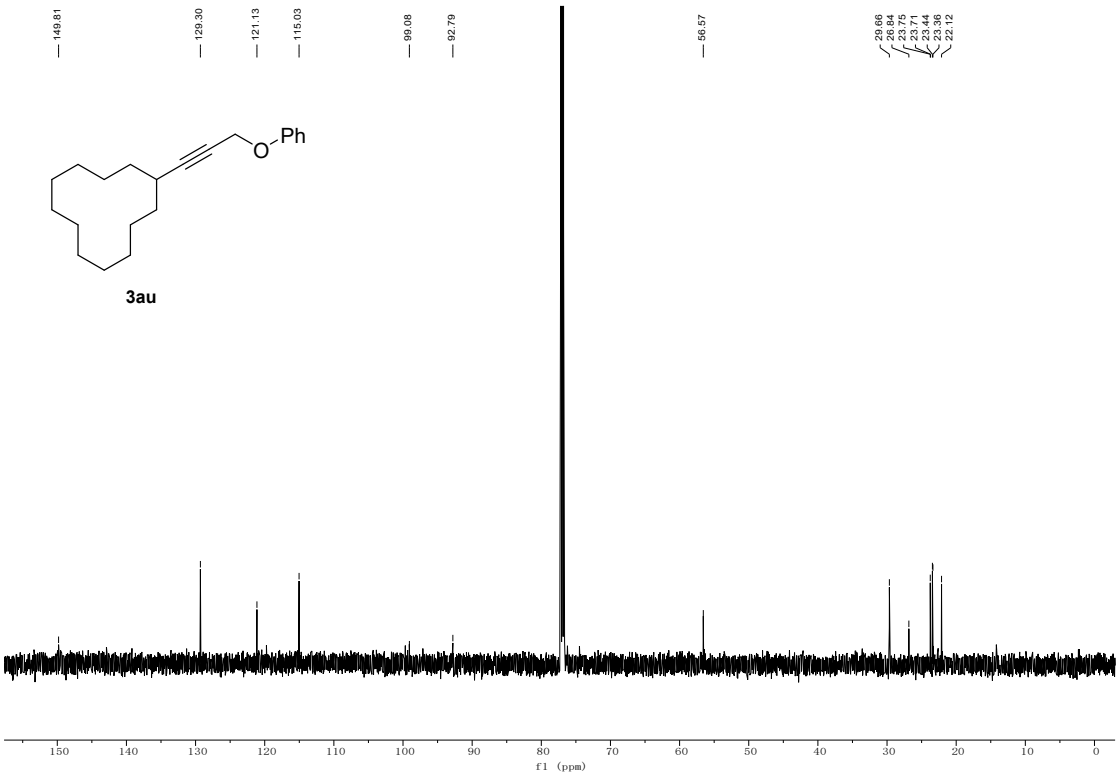
^{13}C NMR Spectrum of 3at



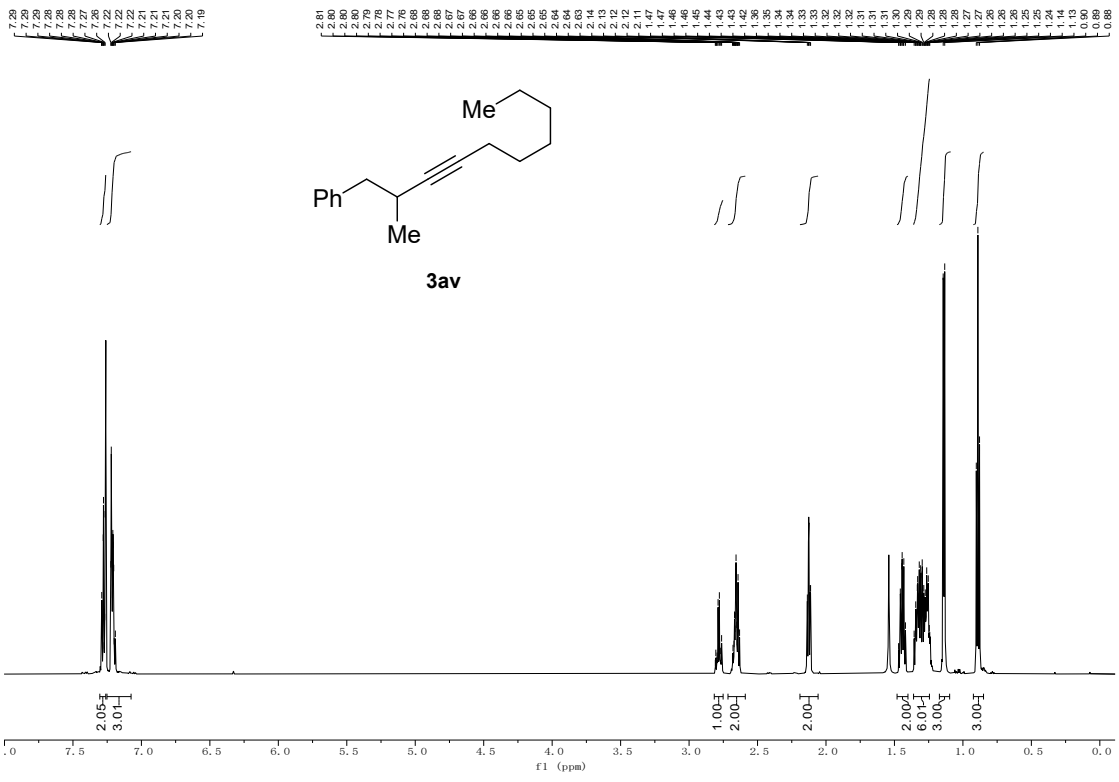
^{1}H NMR Spectrum of 3au



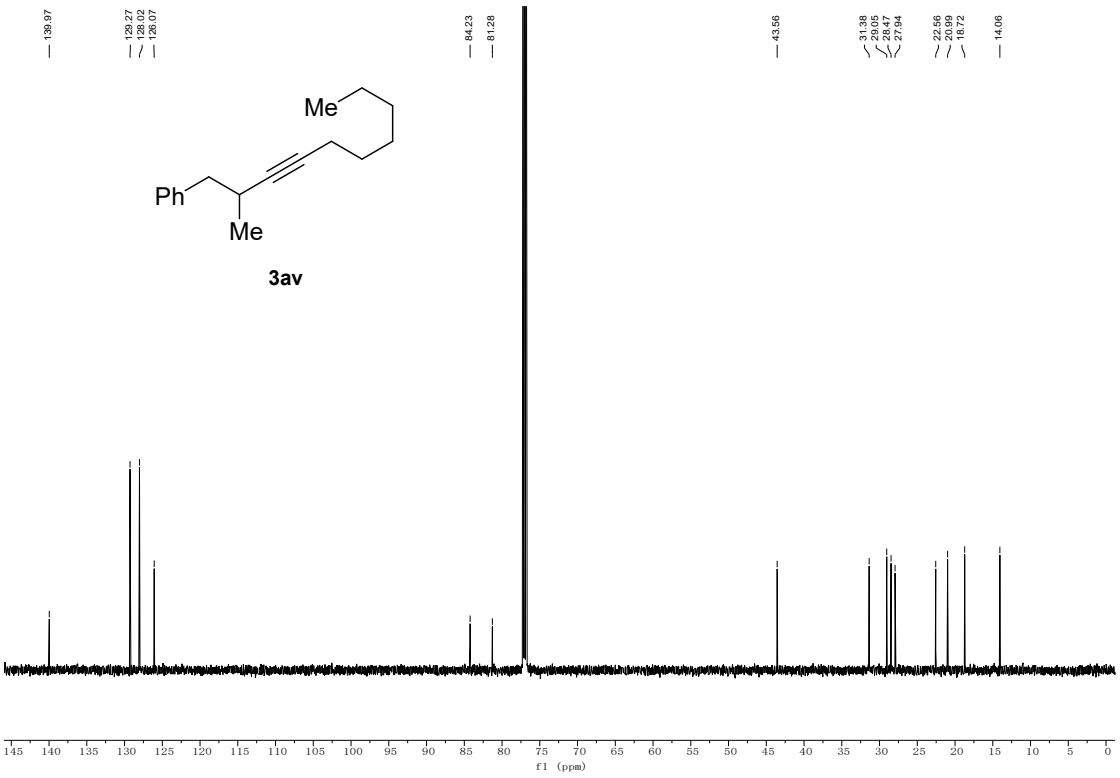
^{13}C NMR Spectrum of 3au



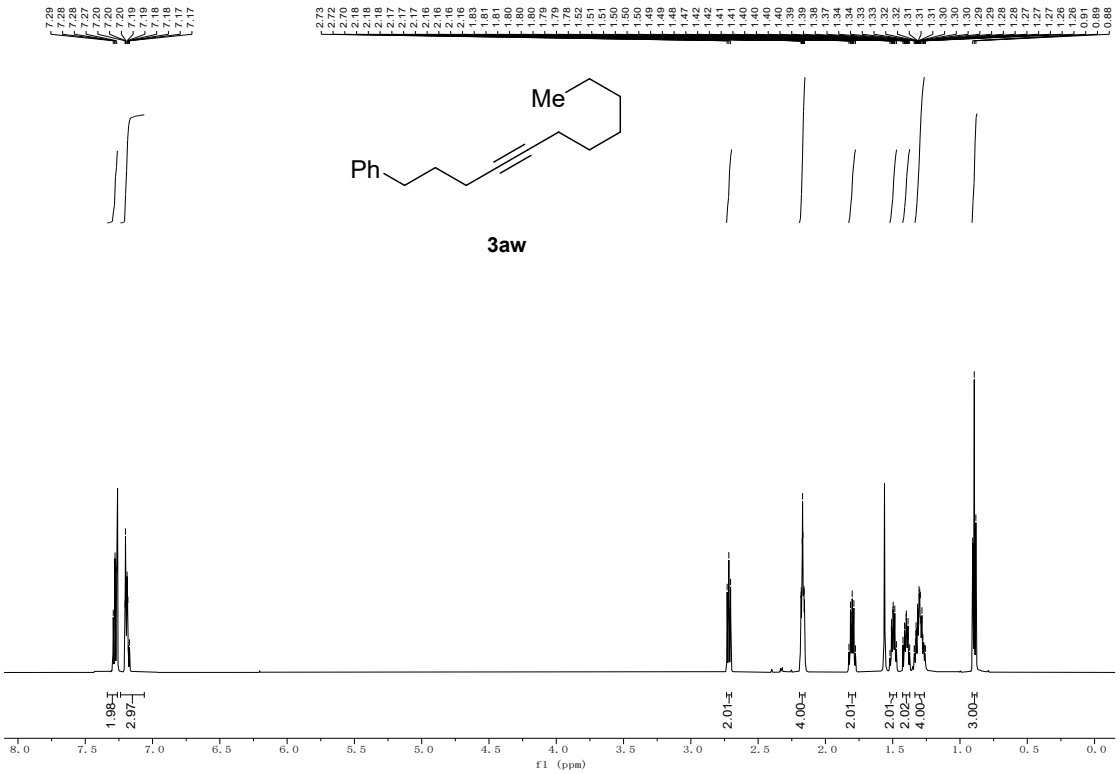
^{1}H NMR Spectrum of 3av



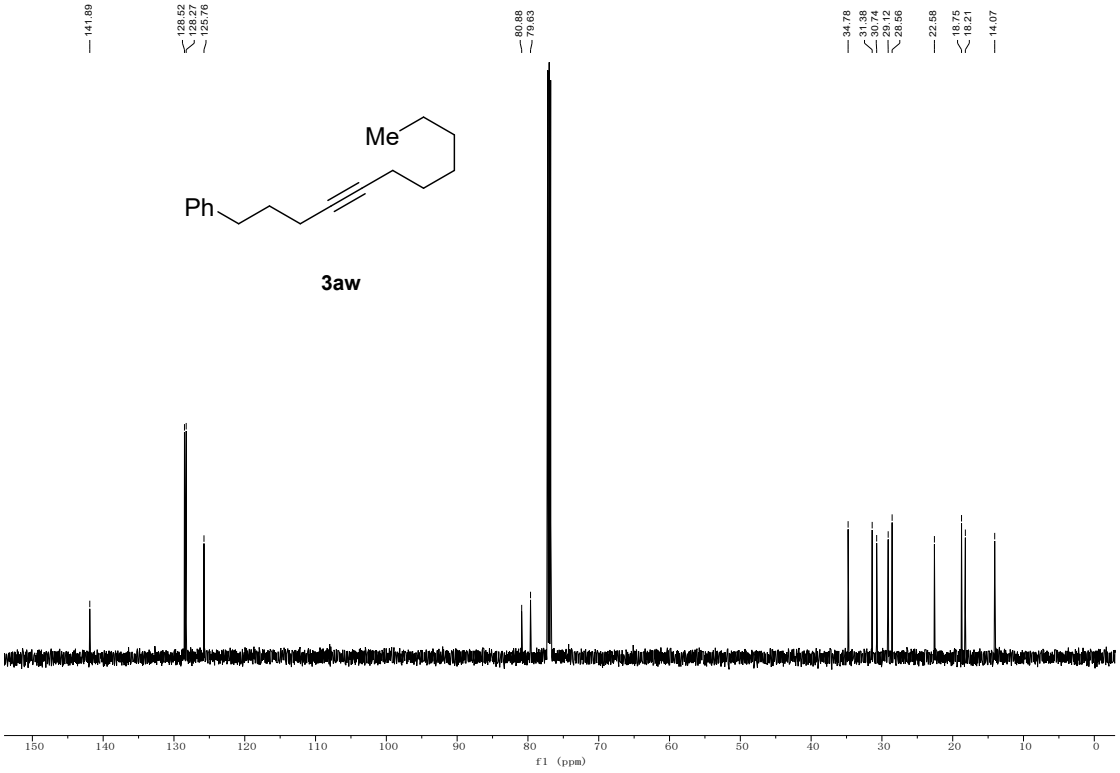
^{13}C NMR Spectrum of 3av



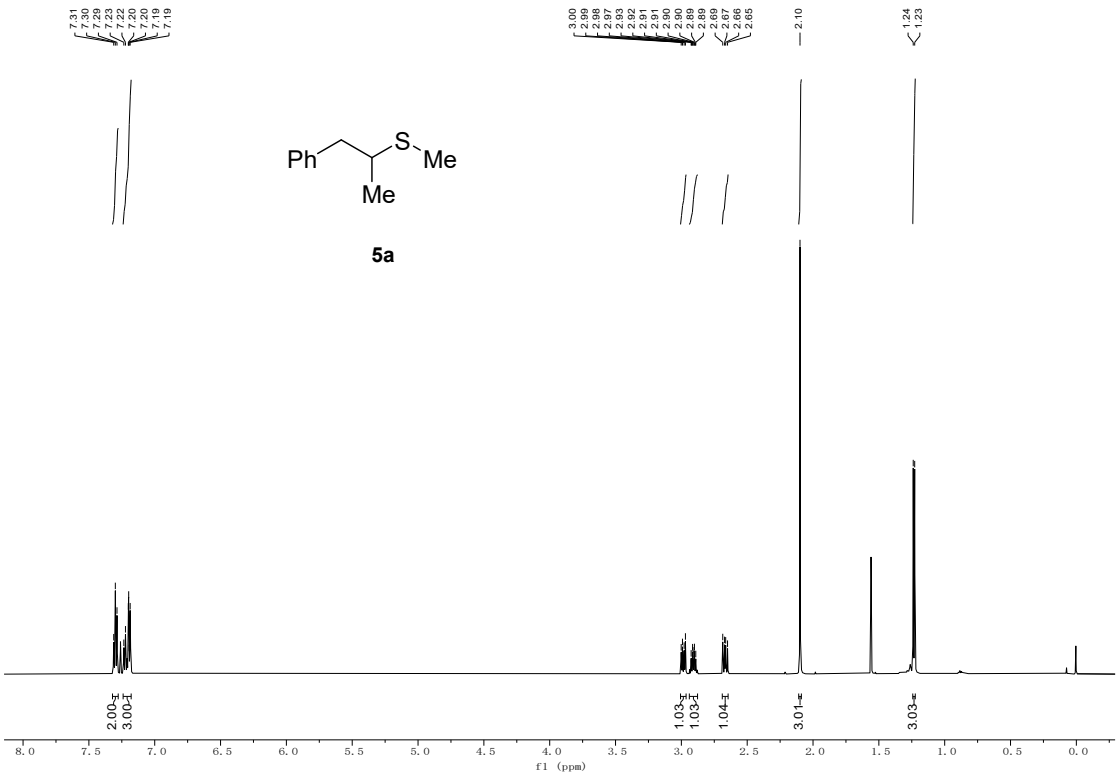
^{1}H NMR Spectrum of 3aw



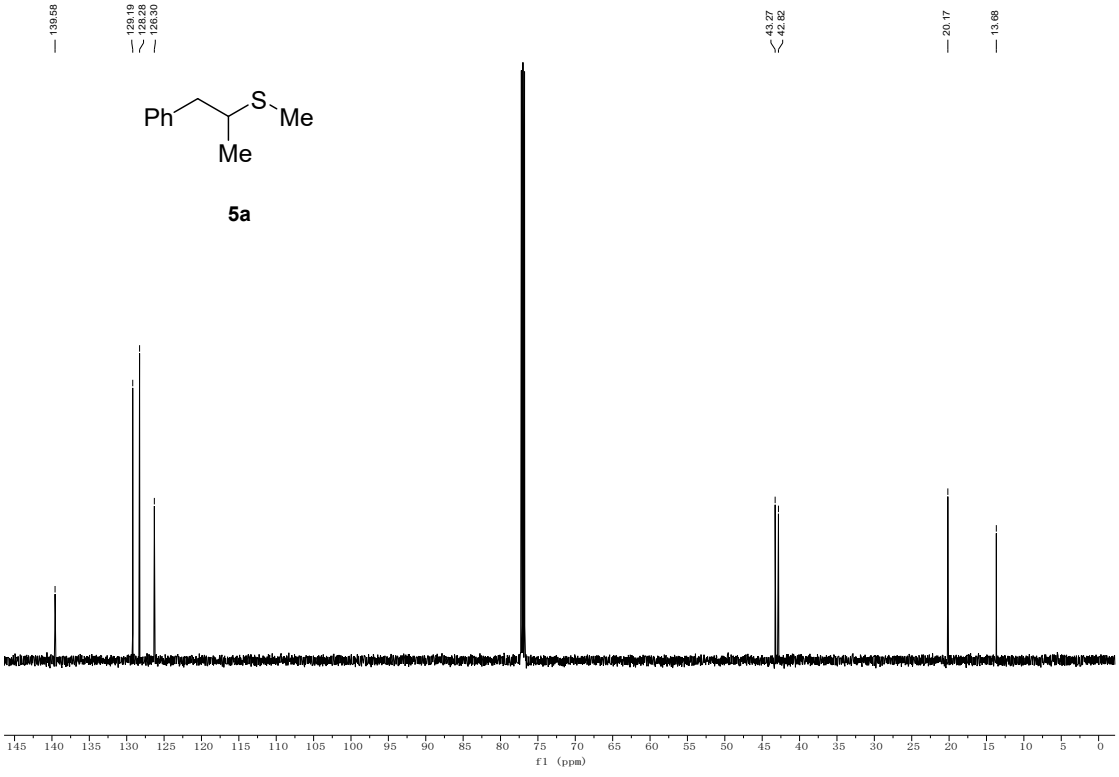
^{13}C NMR Spectrum of 3aw



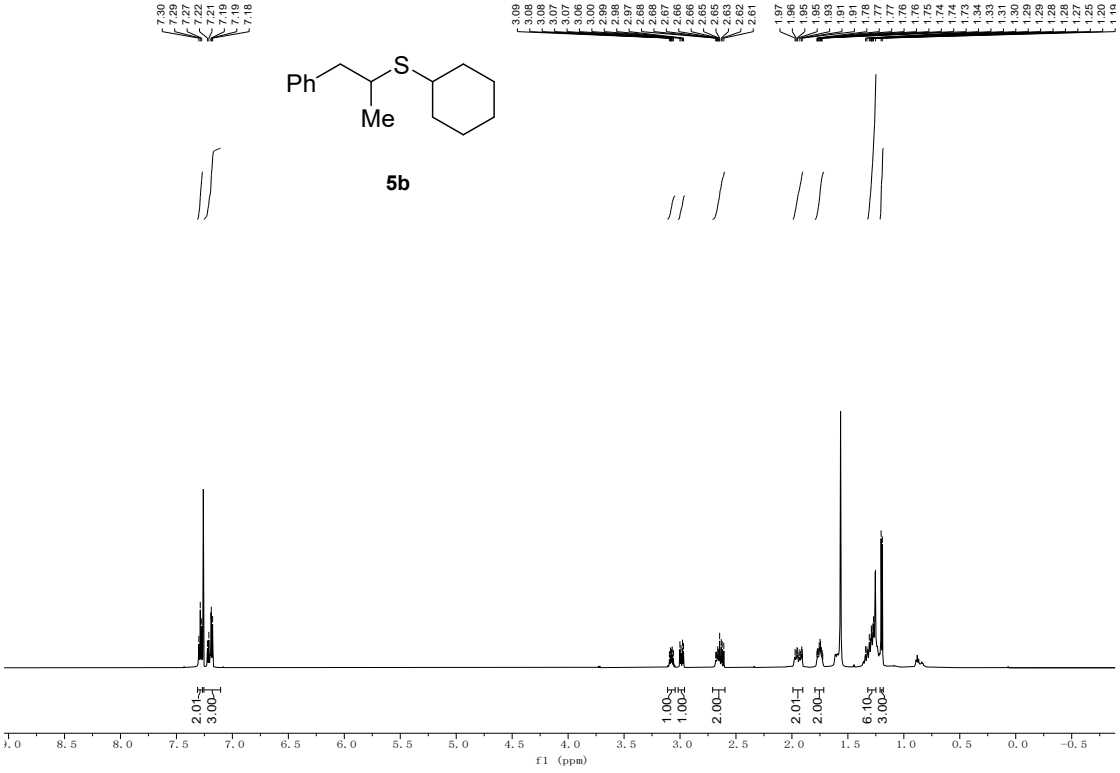
^{1}H NMR Spectrum of 5a



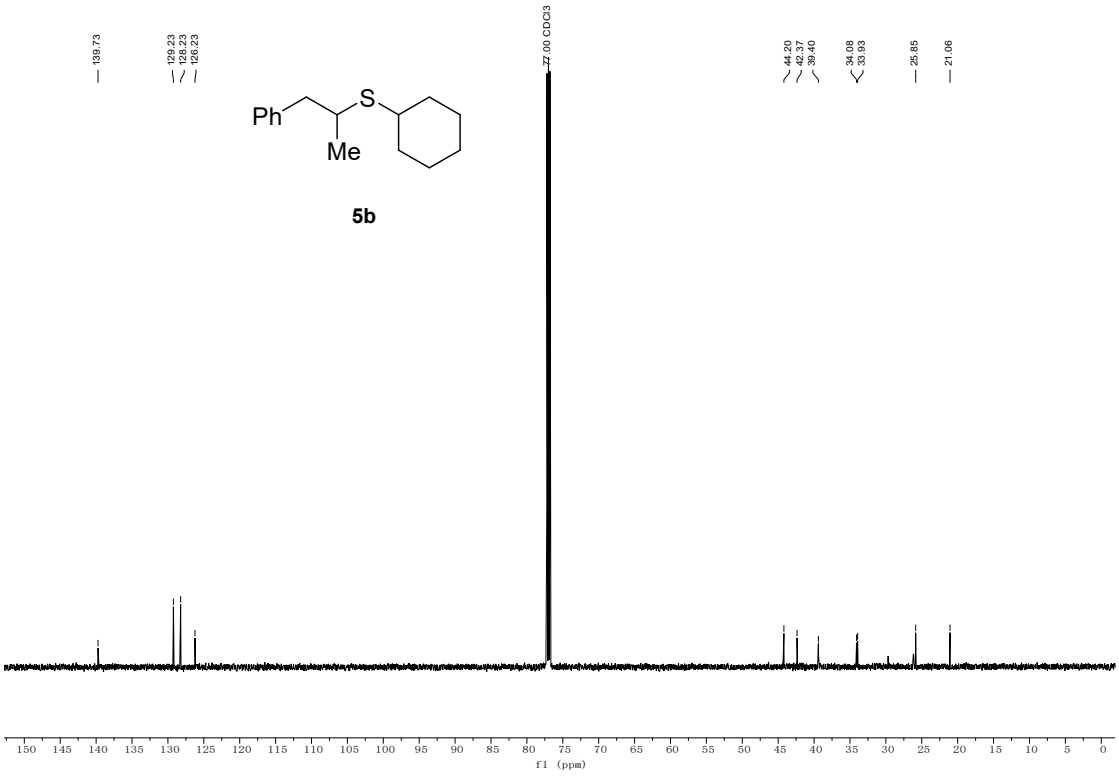
^{13}C NMR Spectrum of 5a



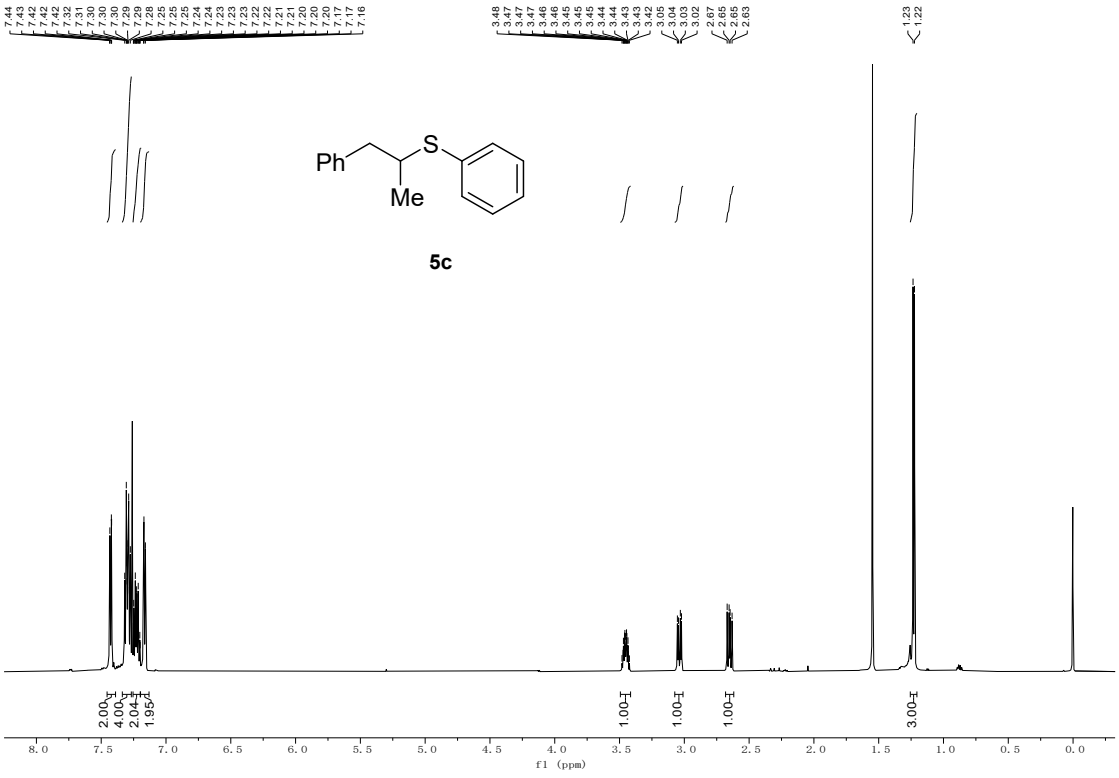
^{1}H NMR Spectrum of 5b



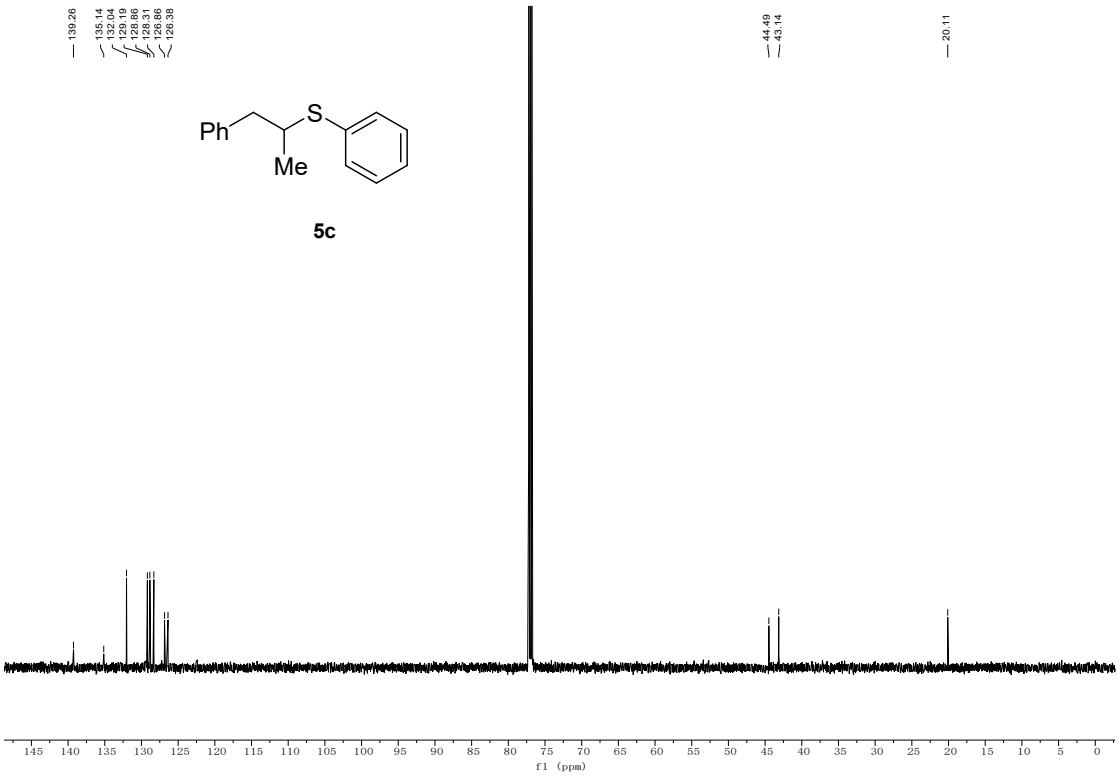
^{13}C NMR Spectrum of 5b



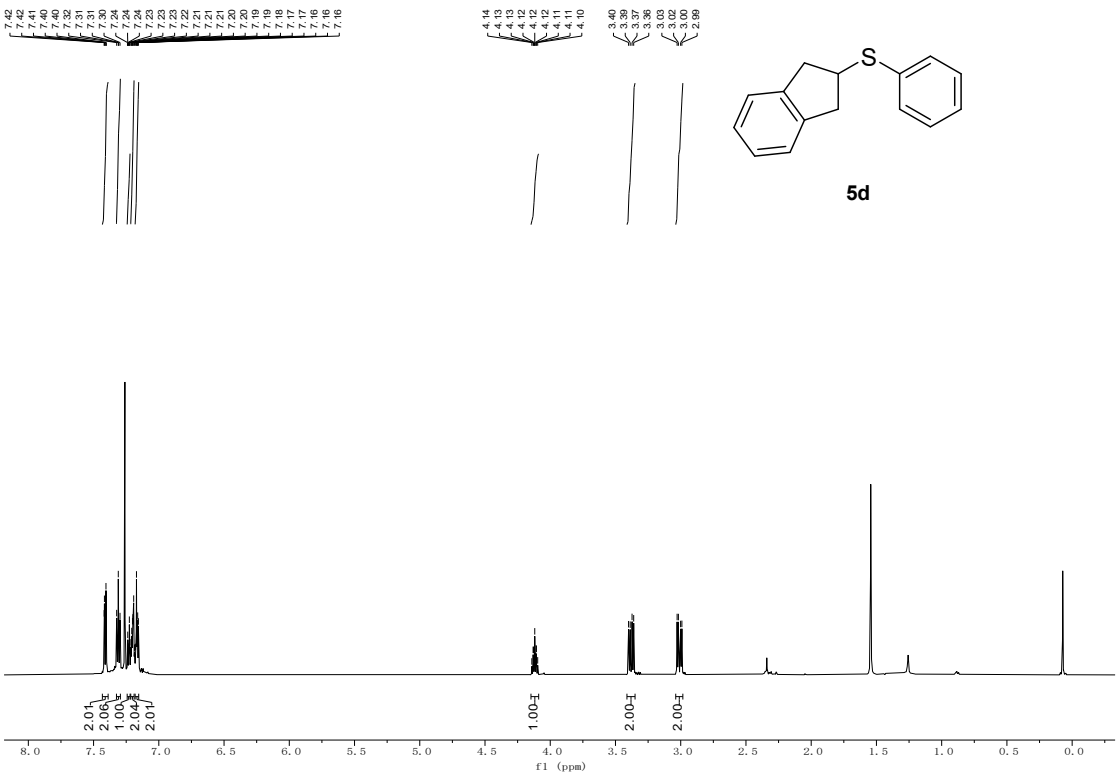
^{1}H NMR Spectrum of 5c



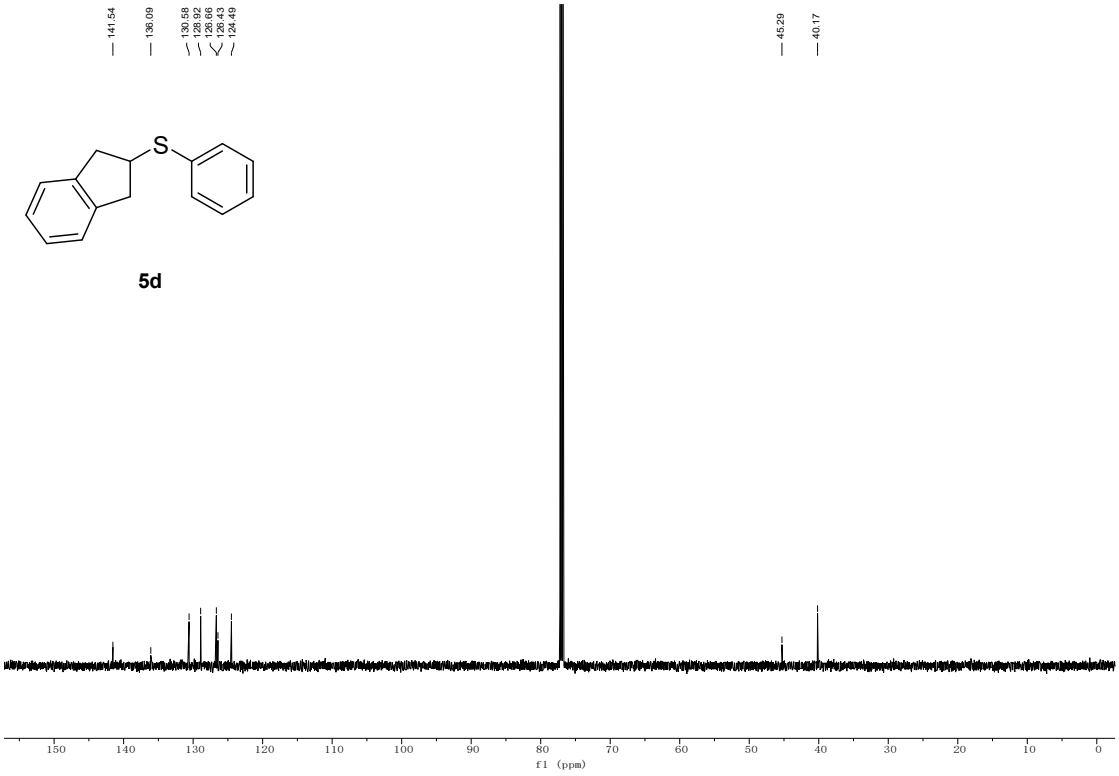
^{13}C NMR Spectrum of 5c



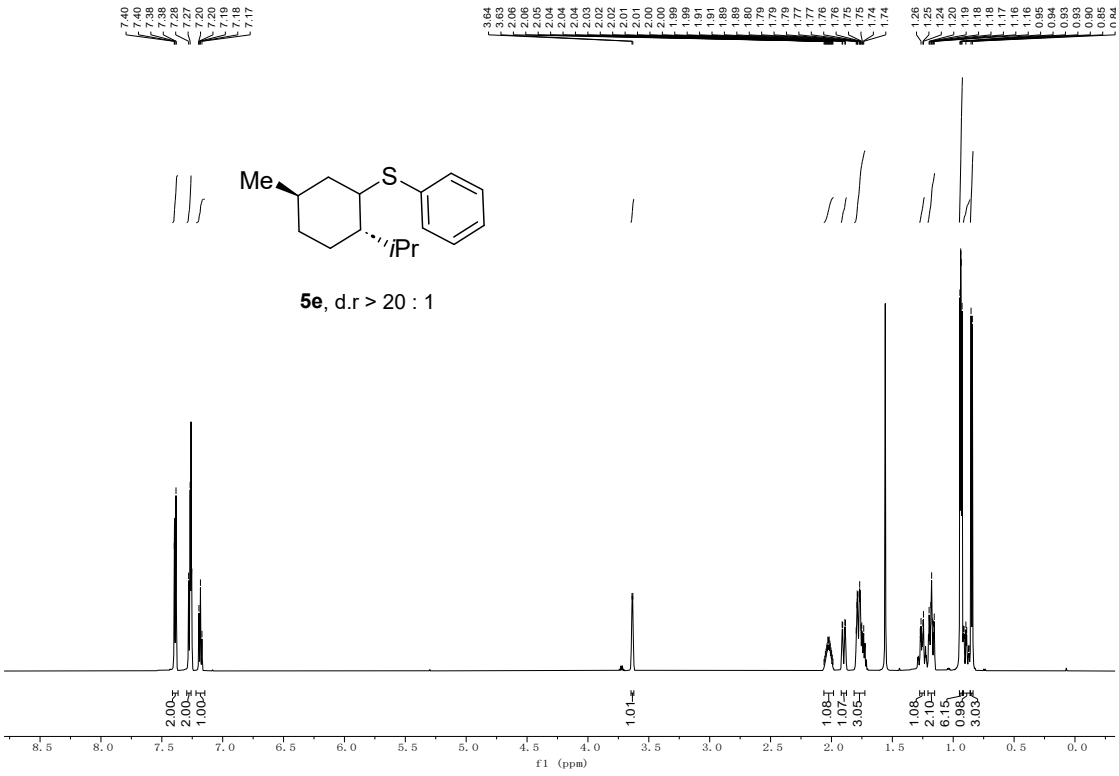
^{1}H NMR Spectrum of 5d



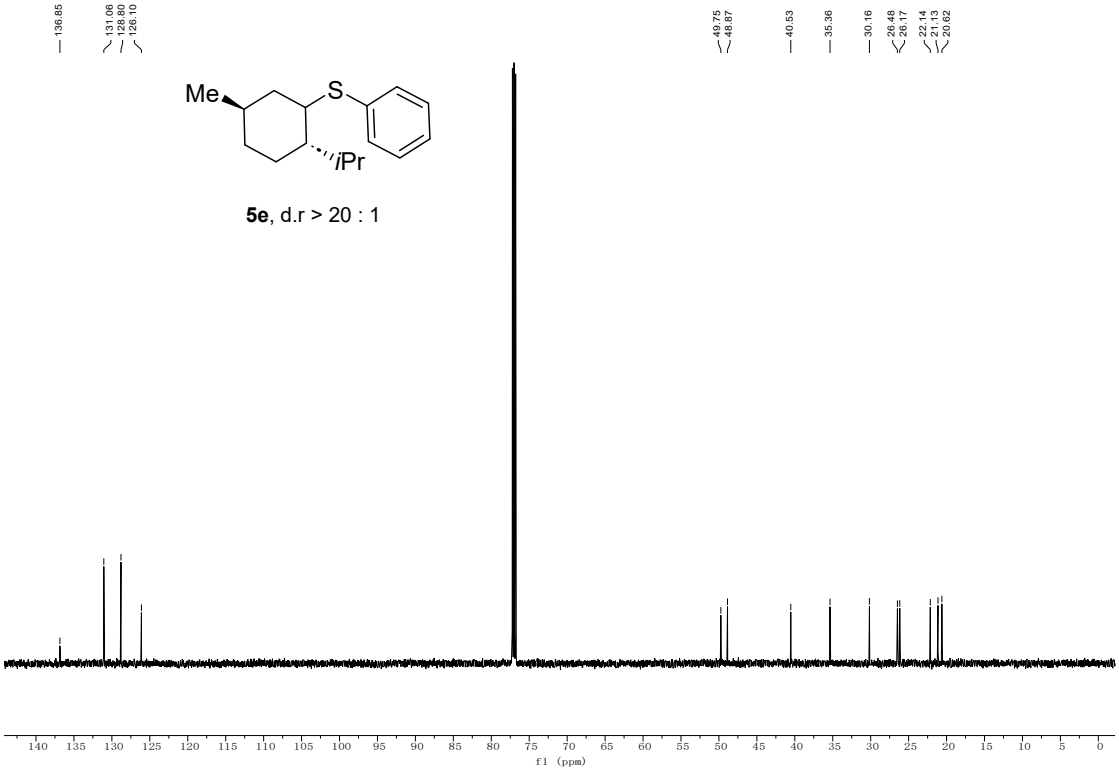
^{13}C NMR Spectrum of 5d



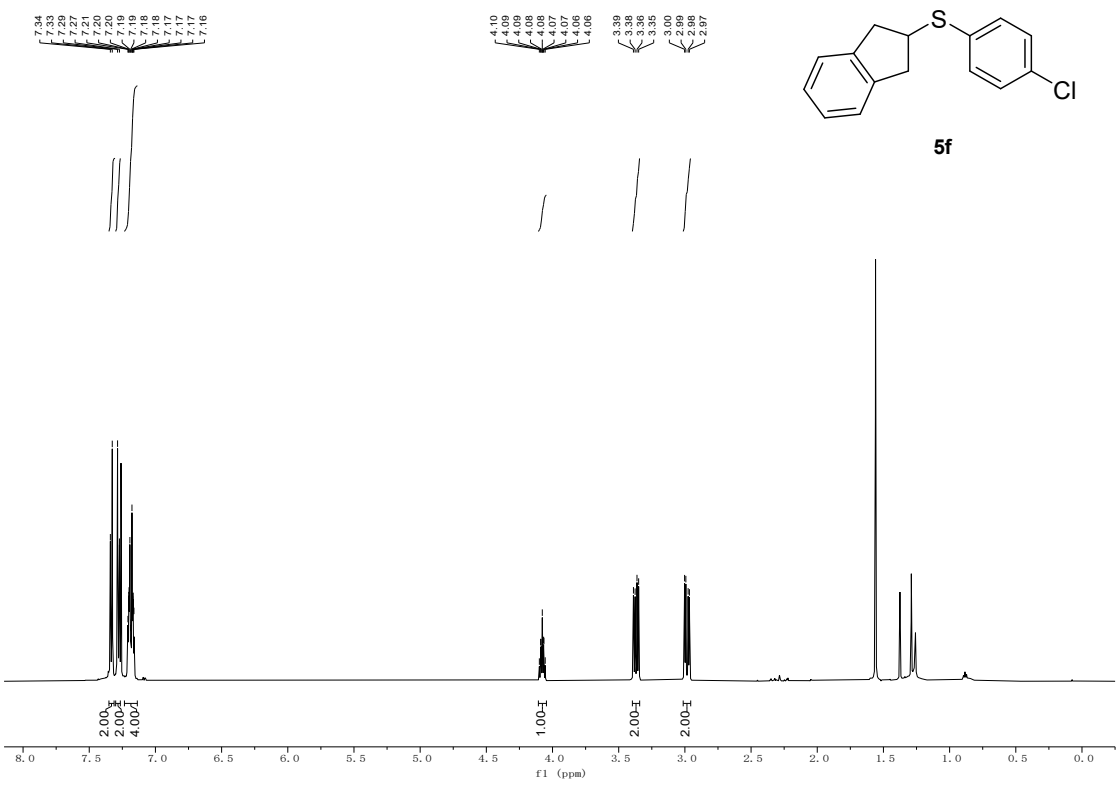
^{1}H NMR Spectrum of 5e



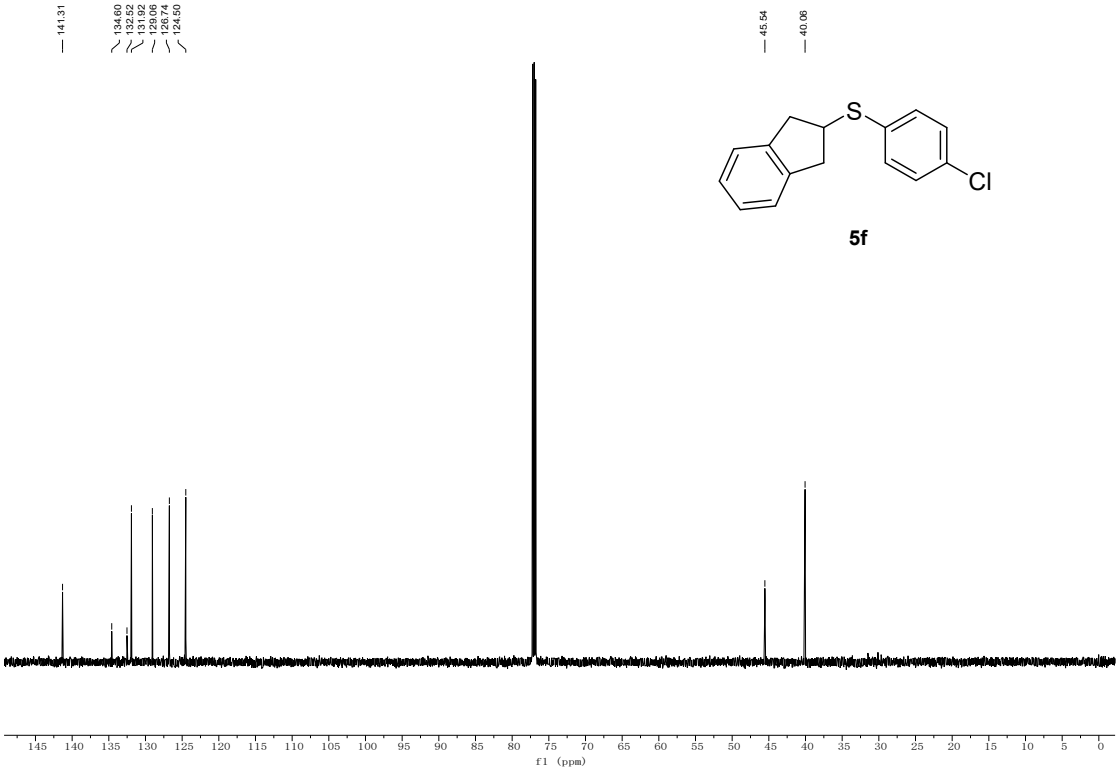
^{13}C NMR Spectrum of 5e



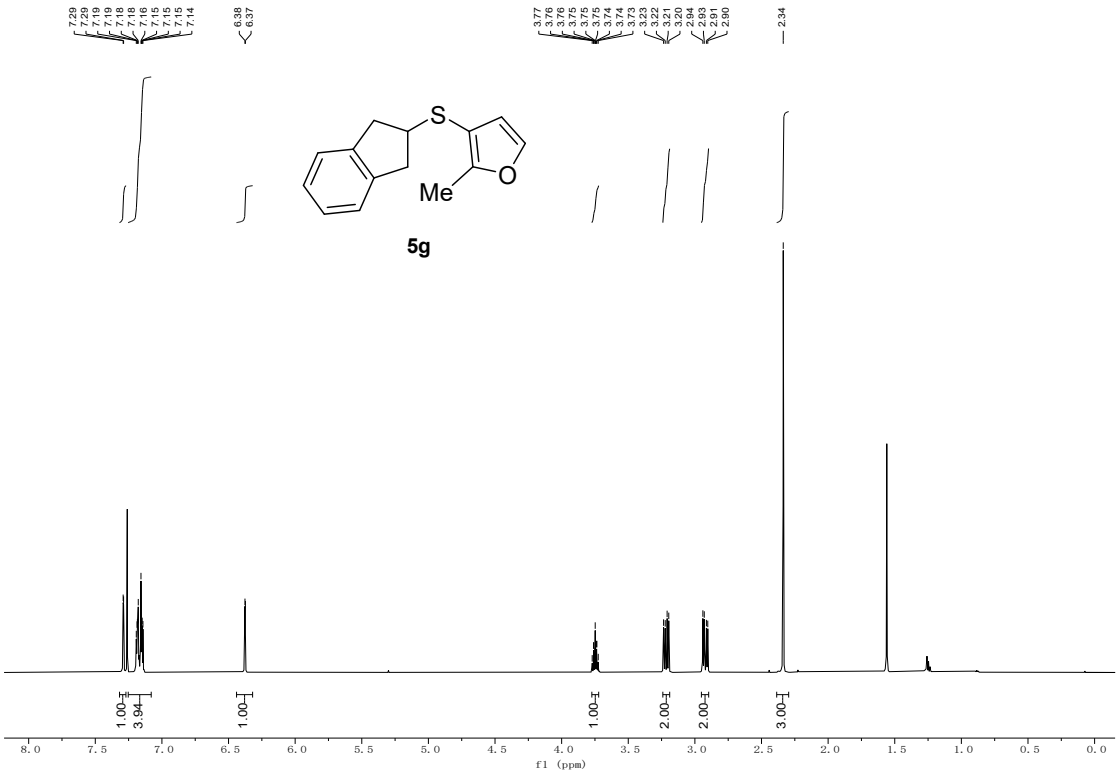
^{1}H NMR Spectrum of 5f



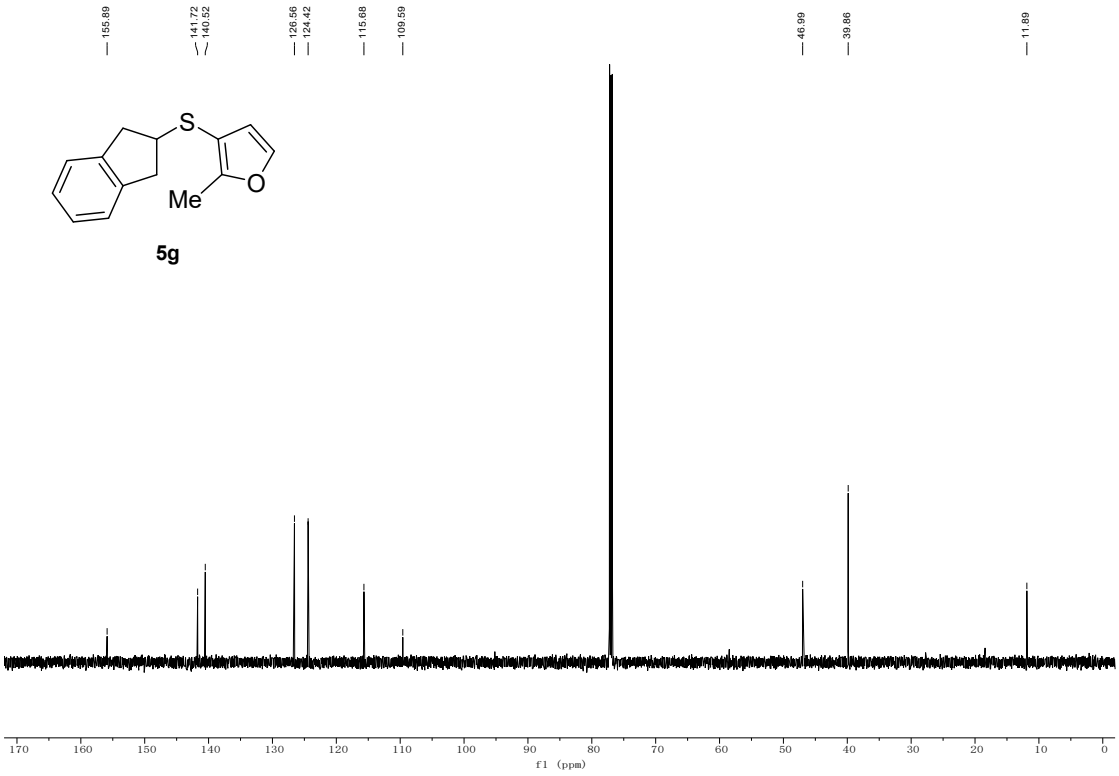
^{13}C NMR Spectrum of 5f



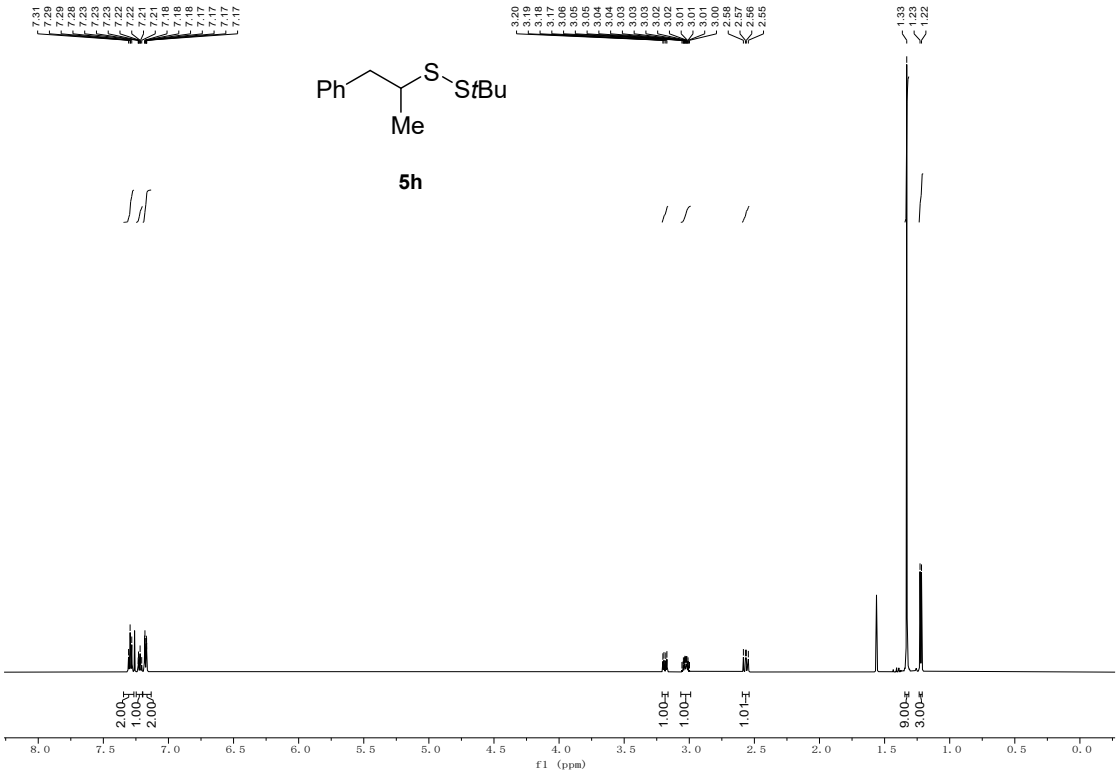
^{1}H NMR Spectrum of 5g



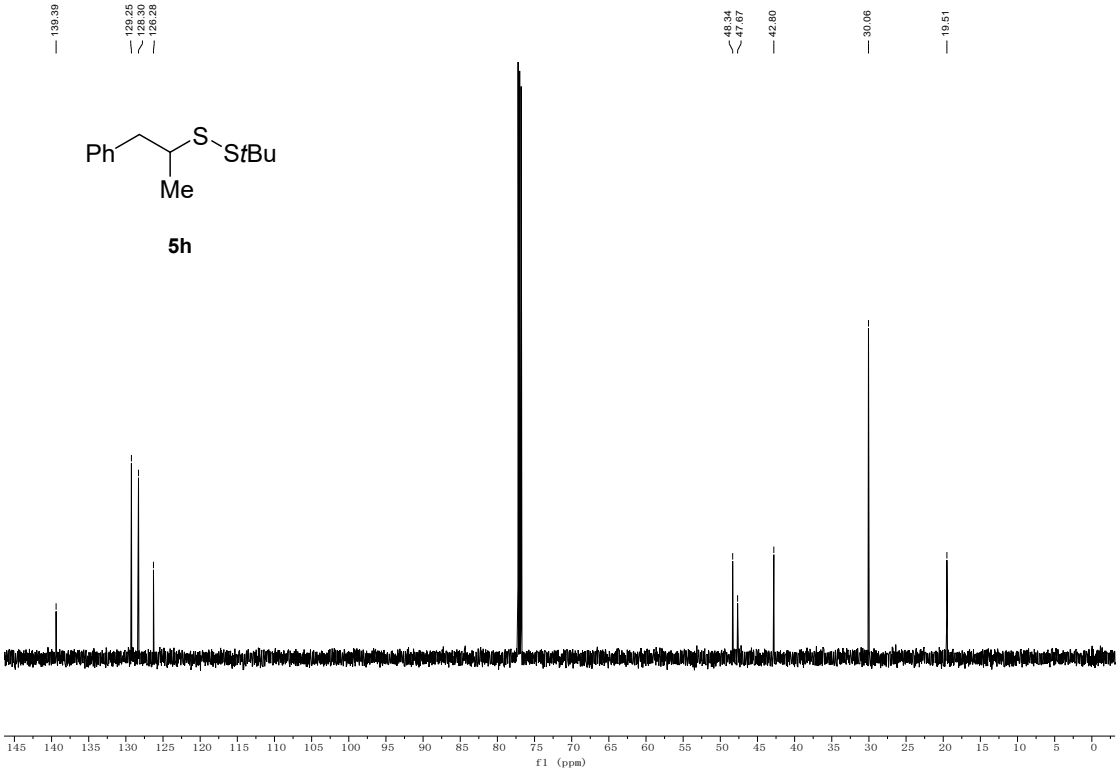
^{13}C NMR Spectrum of 5g



^{1}H NMR Spectrum of 5h

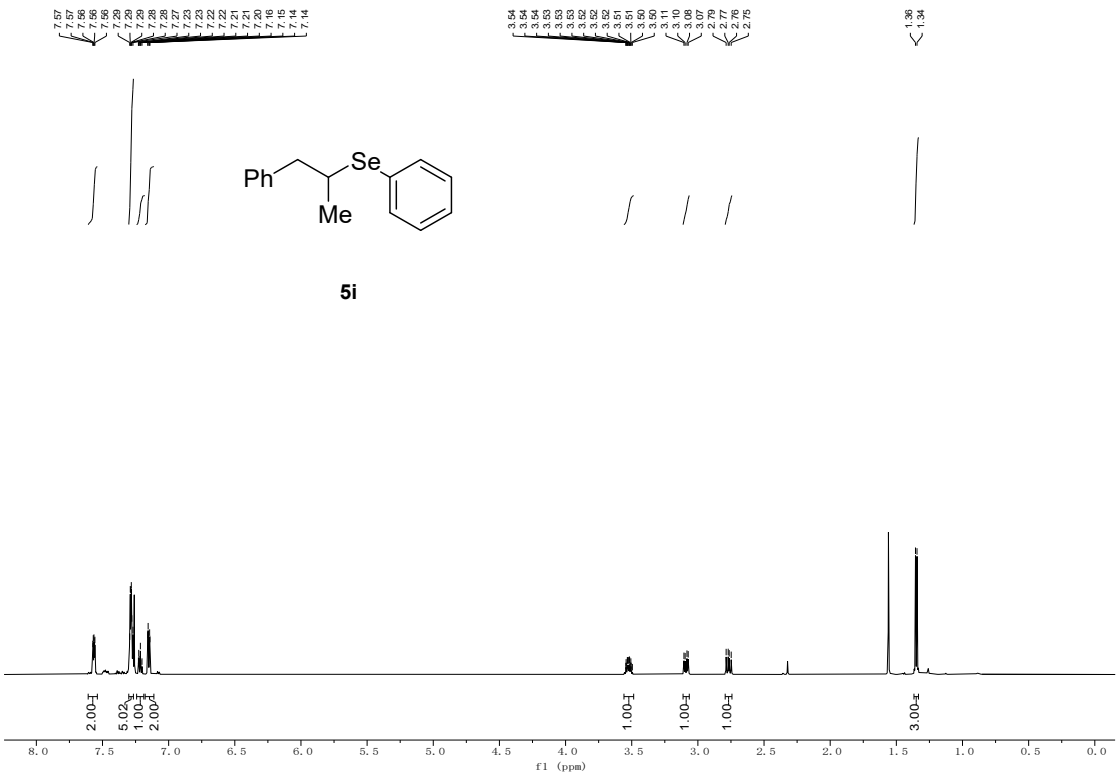


^{13}C NMR Spectrum of 5h



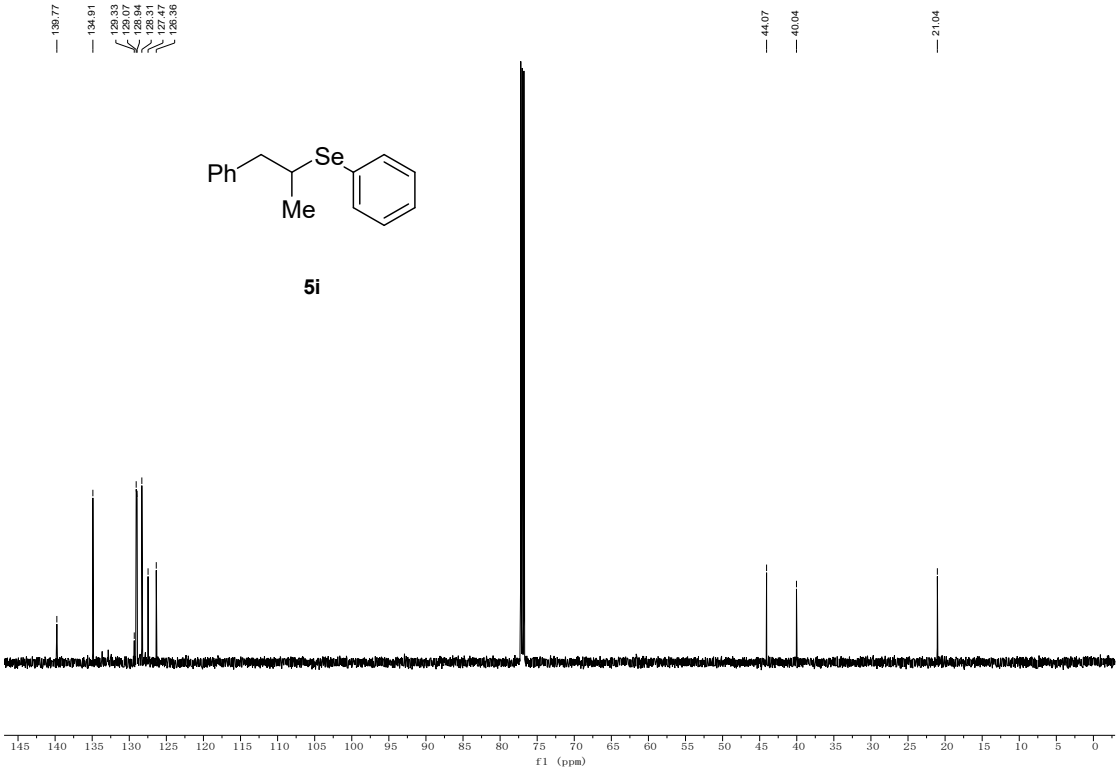
5h

^{1}H NMR Spectrum of 5i

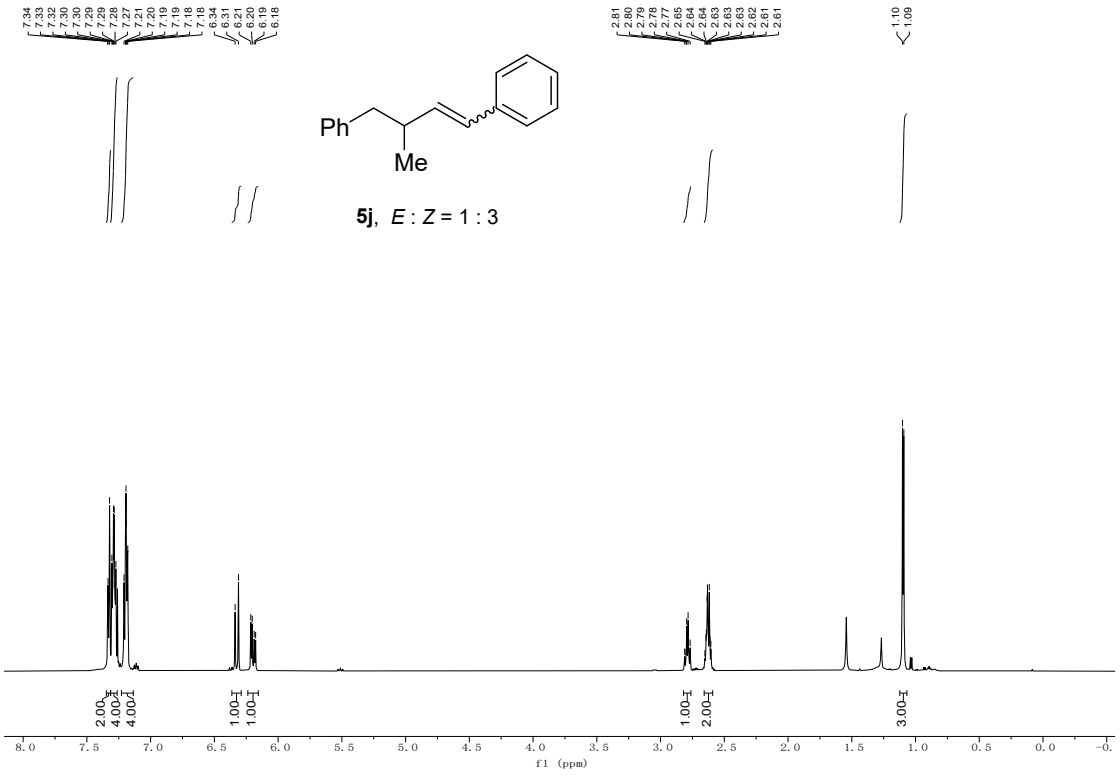


5i

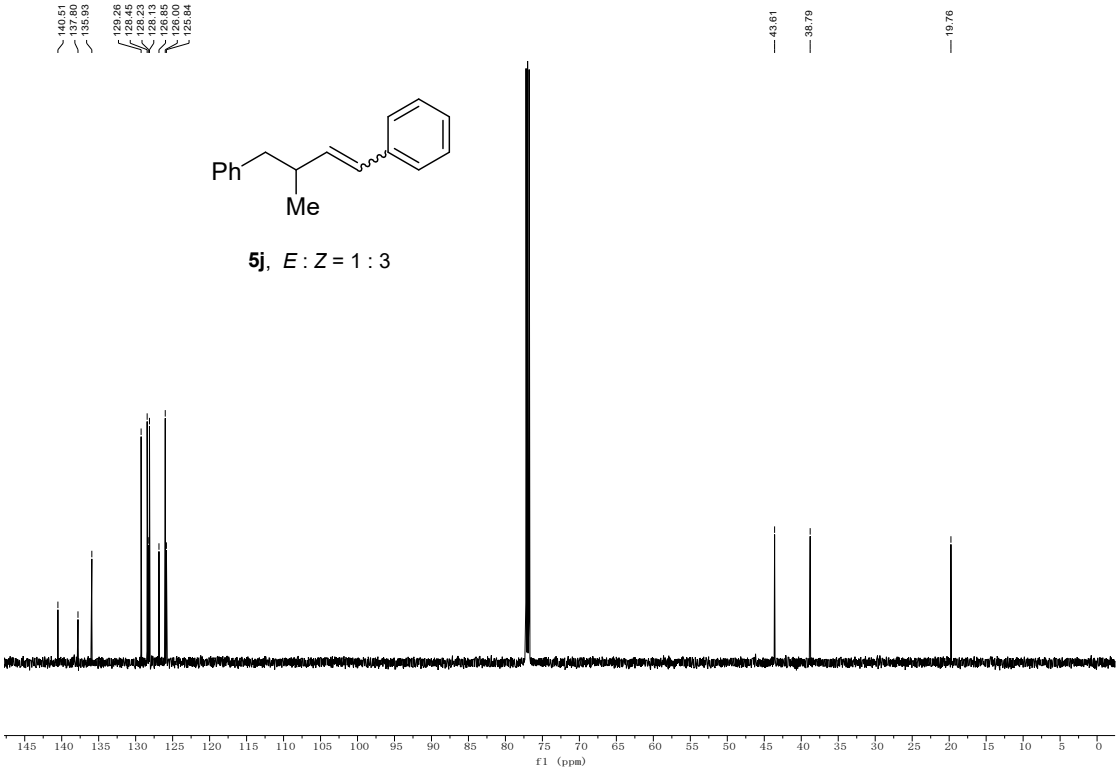
^{13}C NMR Spectrum of 5i



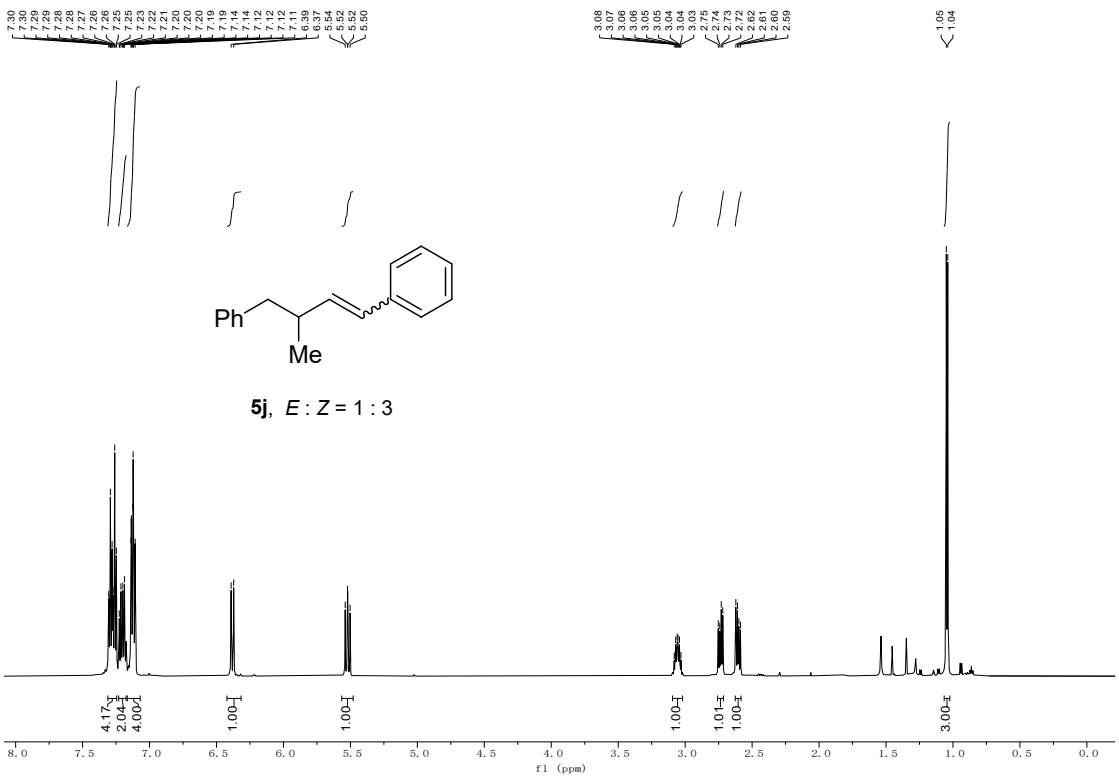
^{1}H NMR Spectrum of 5j(*E*)



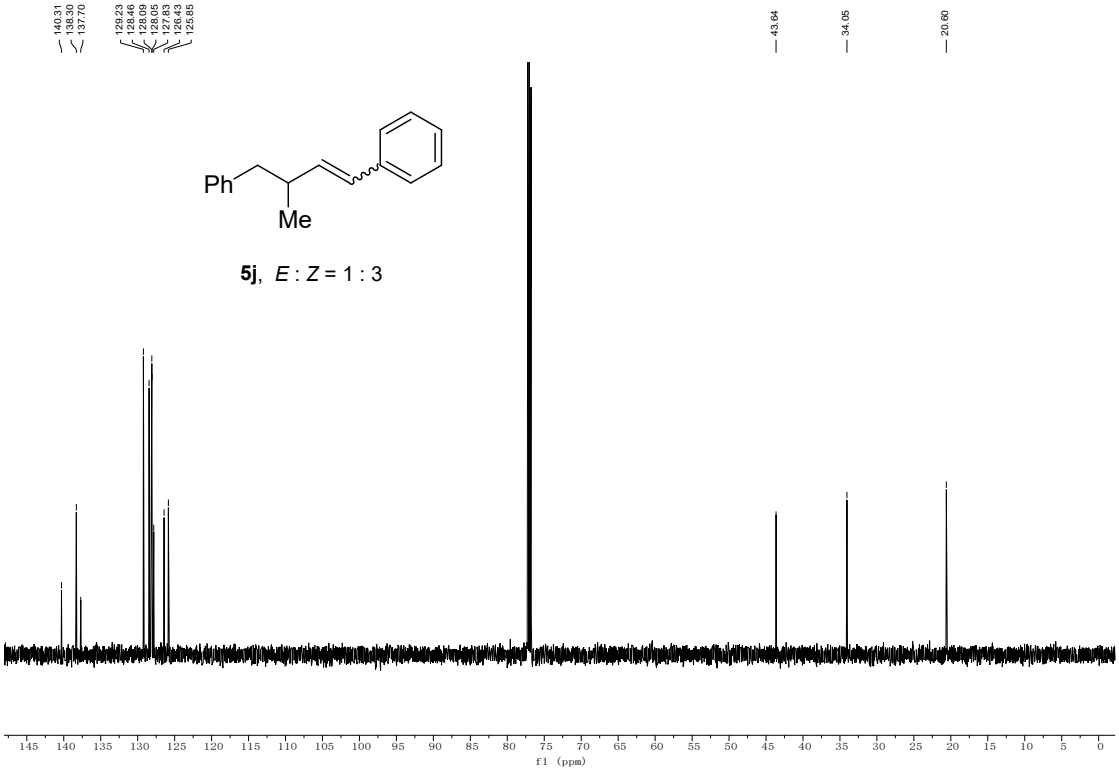
^{13}C NMR Spectrum of 5j*(E)*



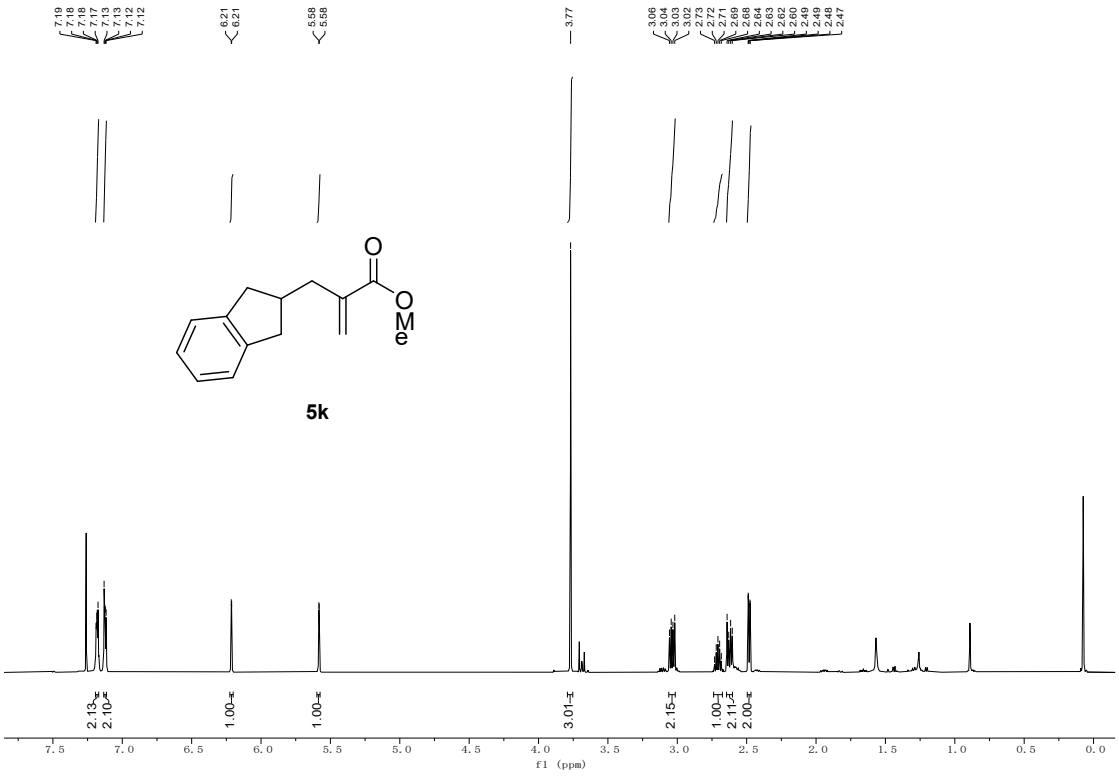
^{1}H NMR Spectrum of 5j(*Z*)



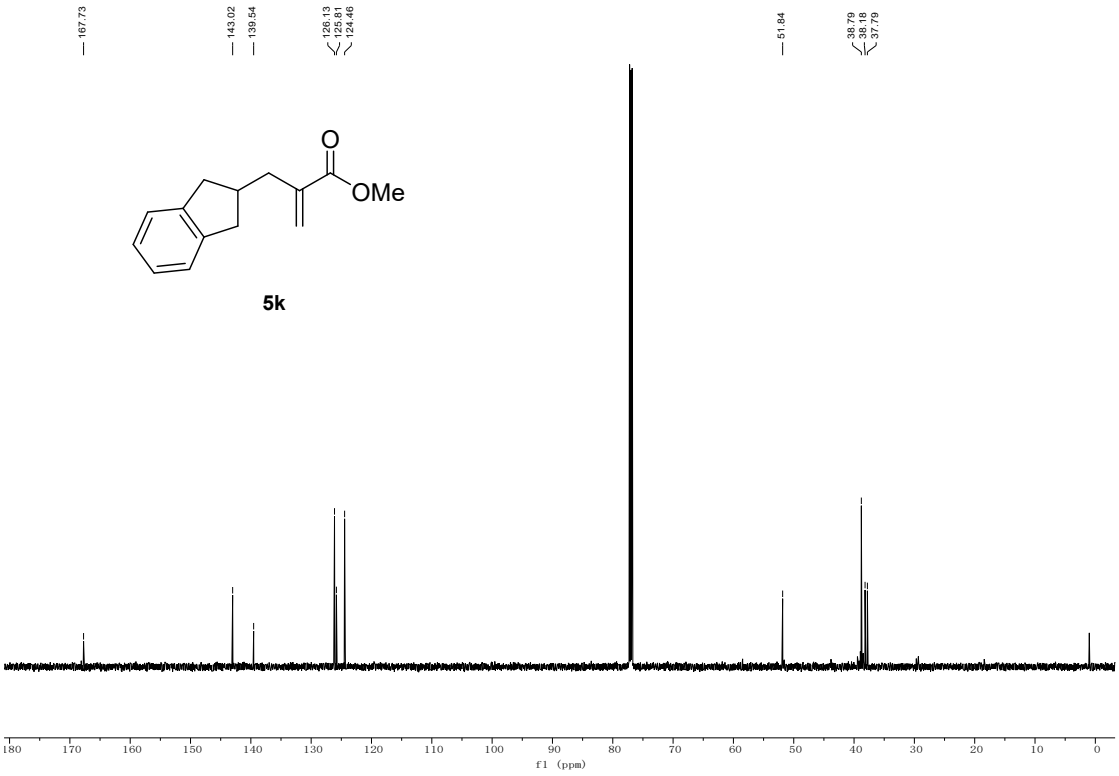
^{13}C NMR Spectrum of 5j(*Z*)



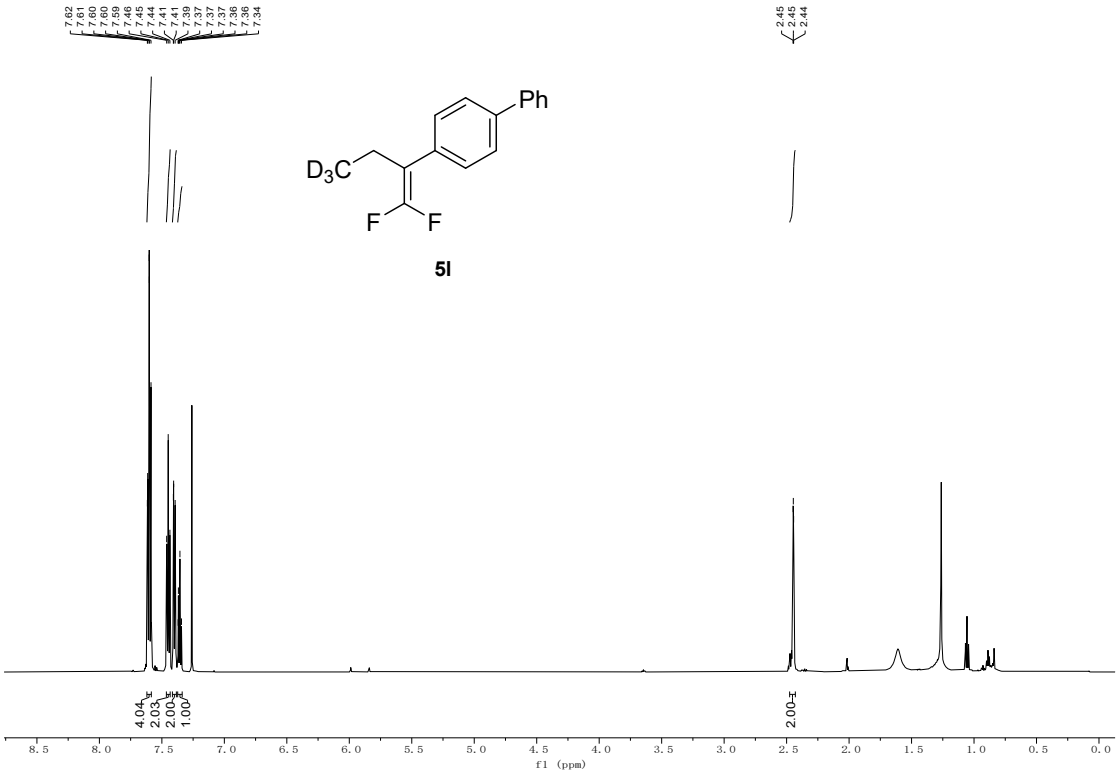
^{1}H NMR Spectrum of 5k



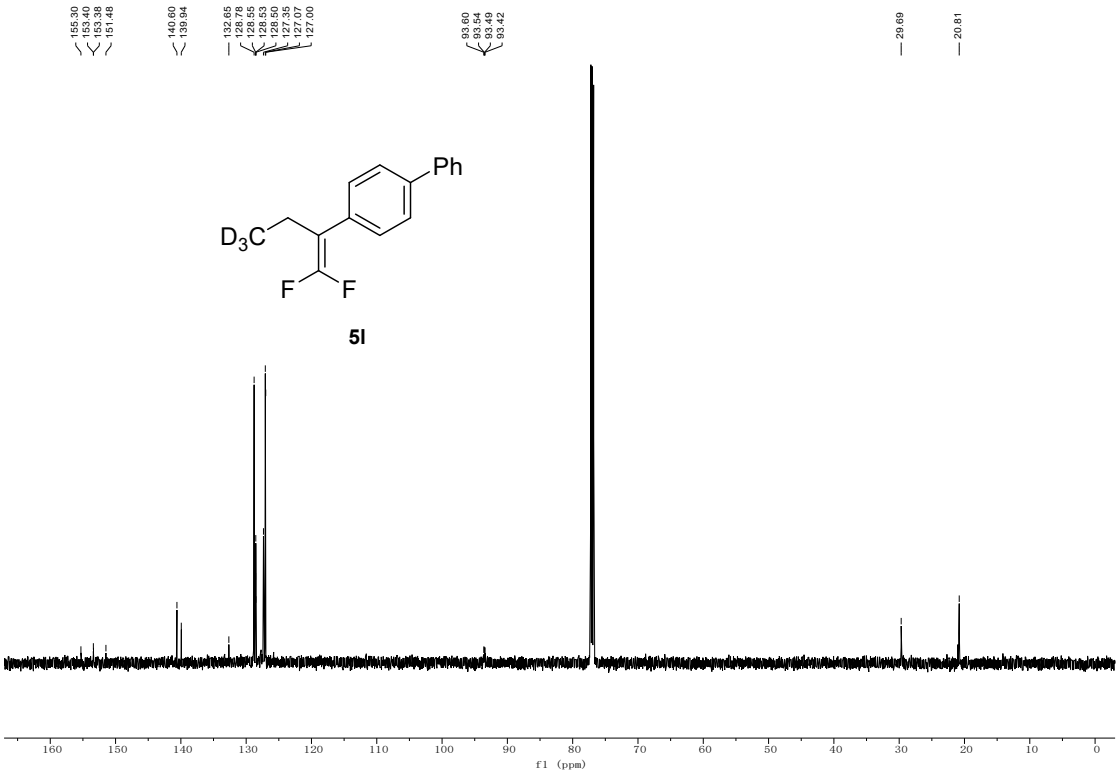
^{13}C NMR Spectrum of 5k



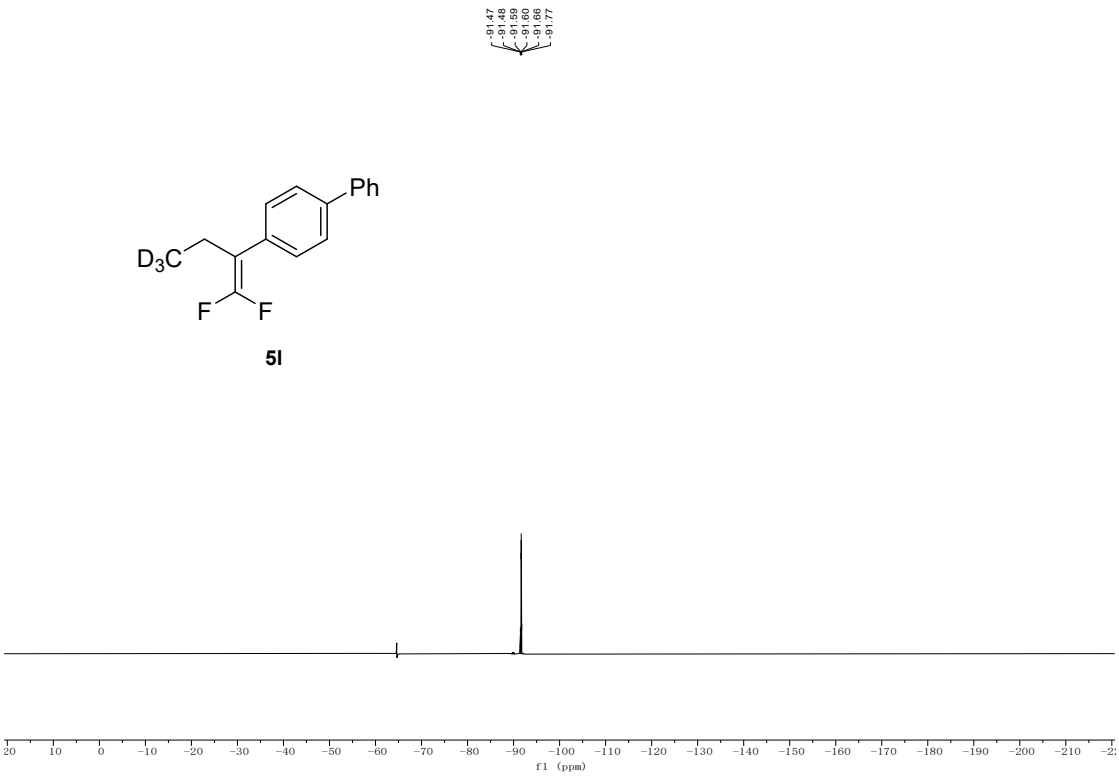
^{1}H NMR Spectrum of 5l



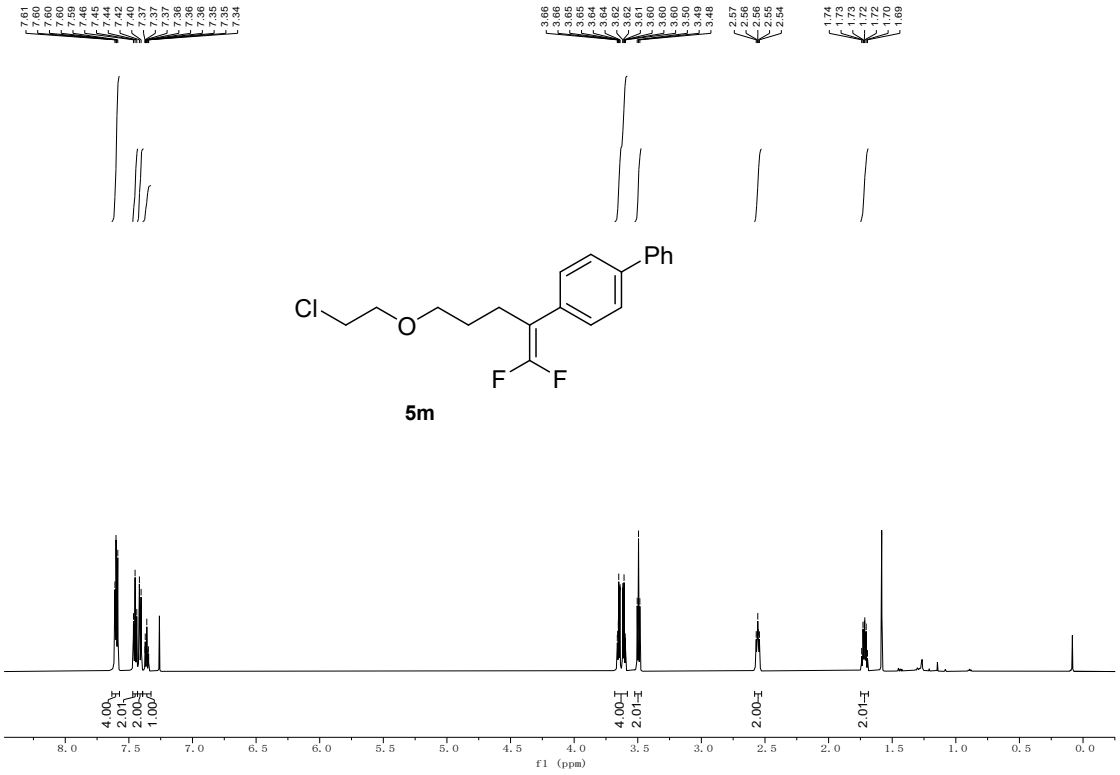
^{13}C NMR Spectrum of 5l



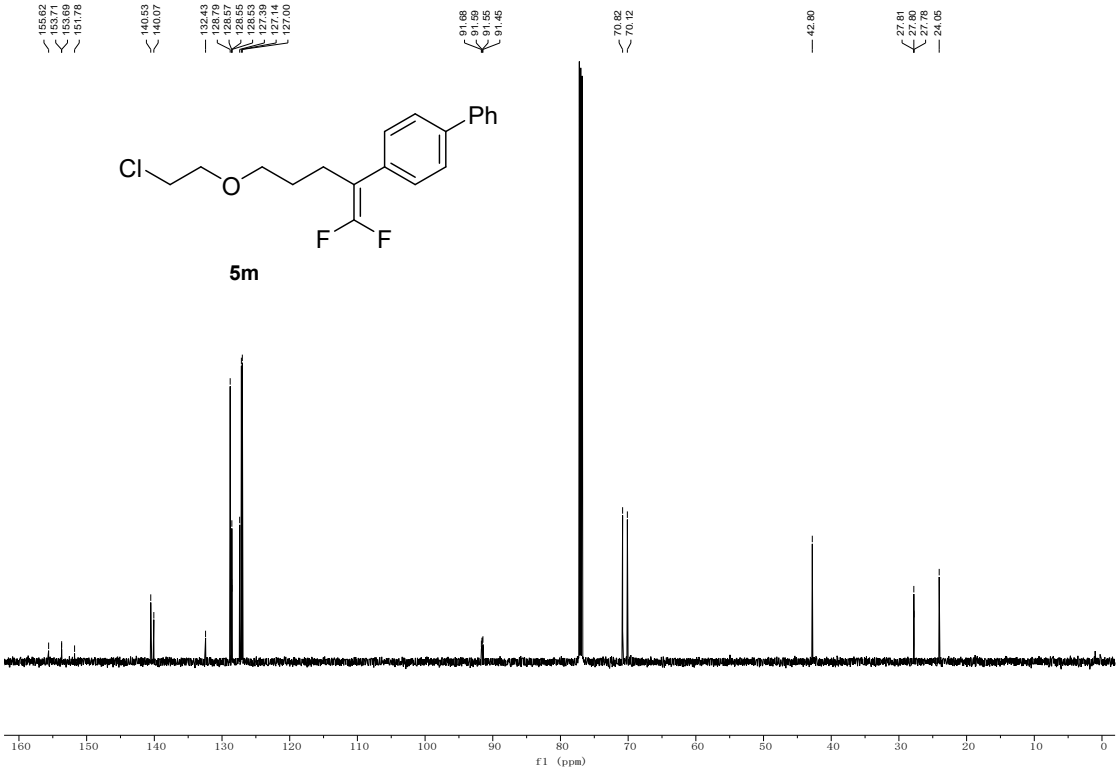
^{19}F NMR Spectrum of 5l



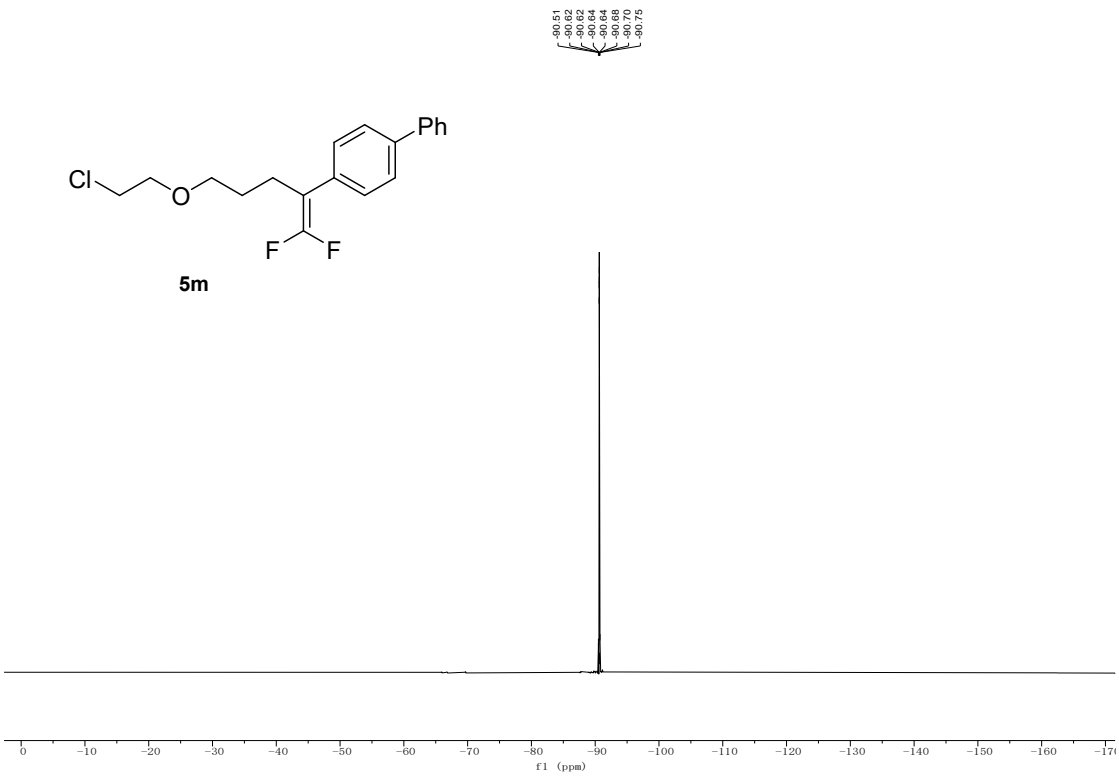
^{1}H NMR Spectrum of 5m



^{13}C NMR Spectrum of 5m

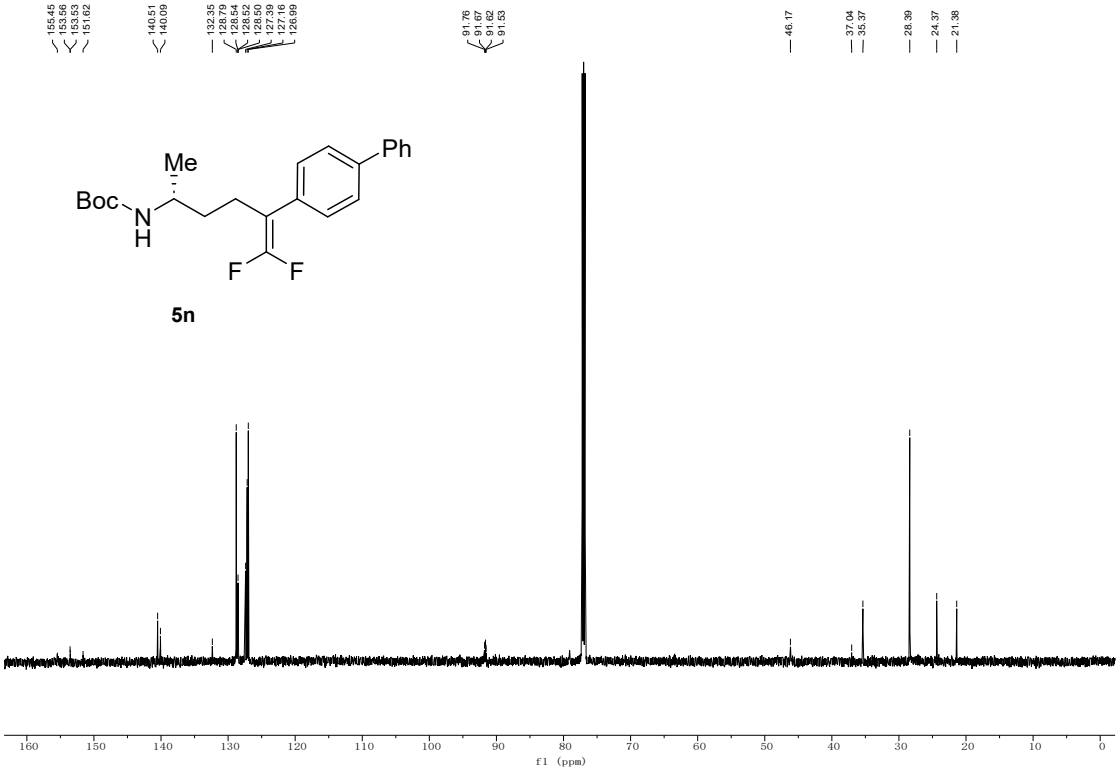


^{19}F NMR Spectrum of 5m

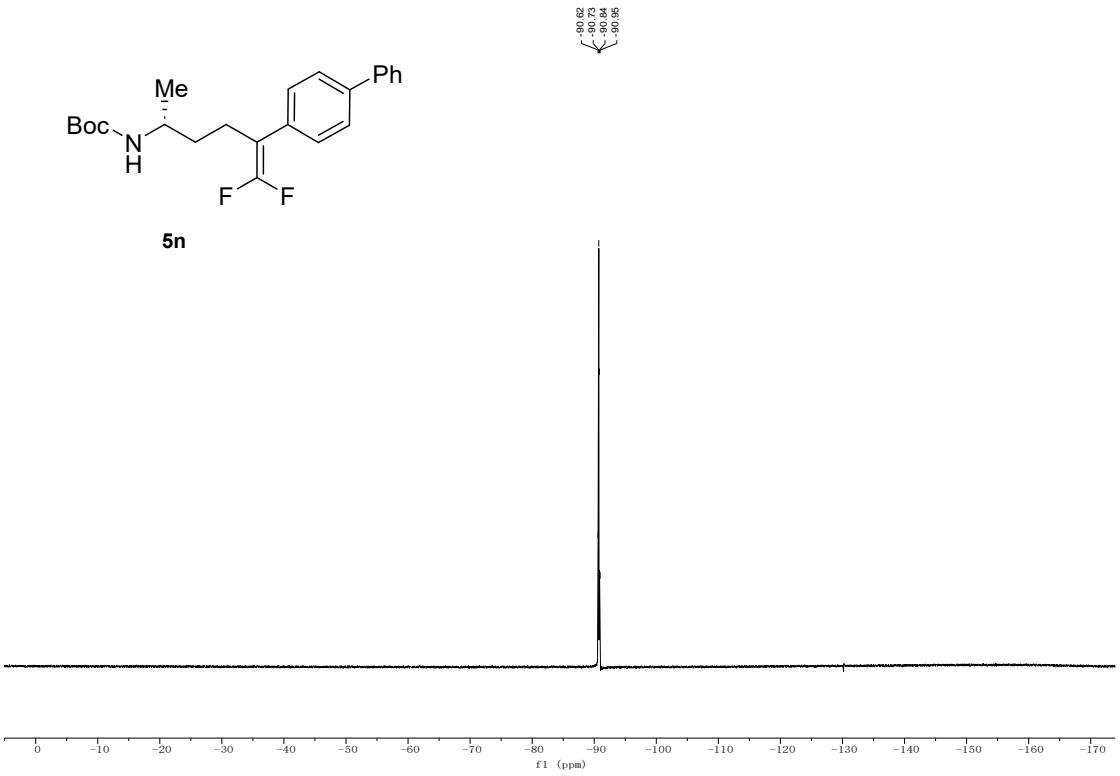


^{1}H NMR Spectrum of 5n

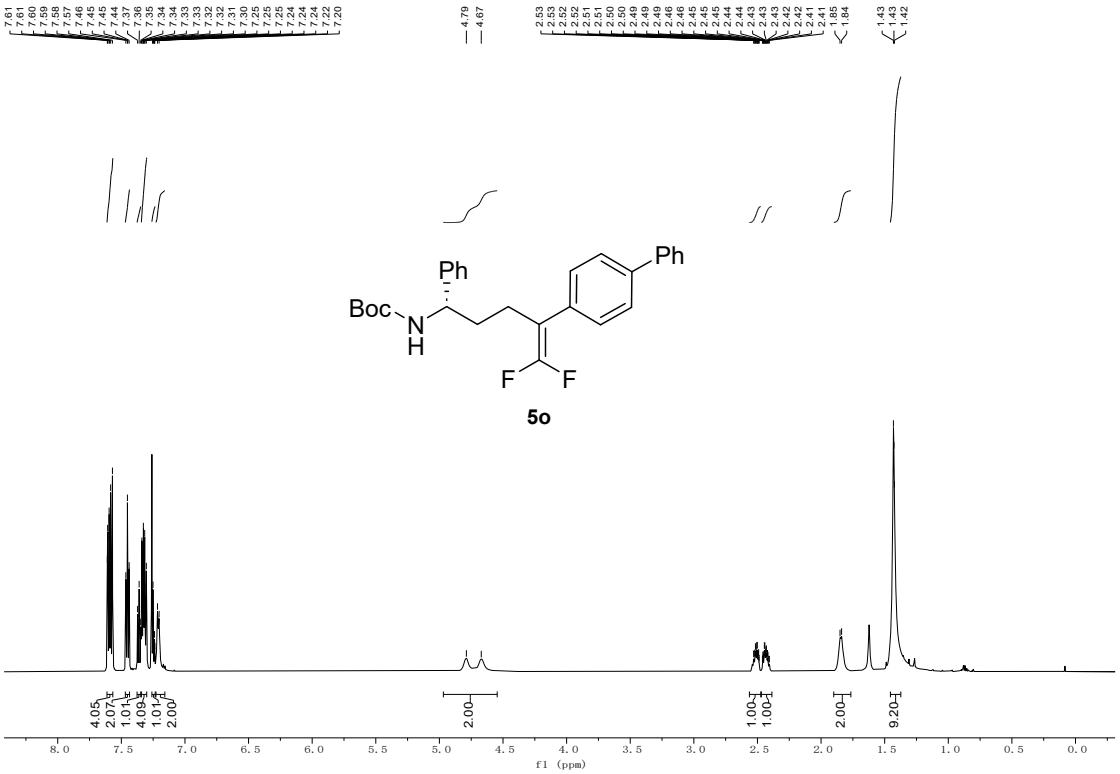
^{13}C NMR Spectrum of 5n



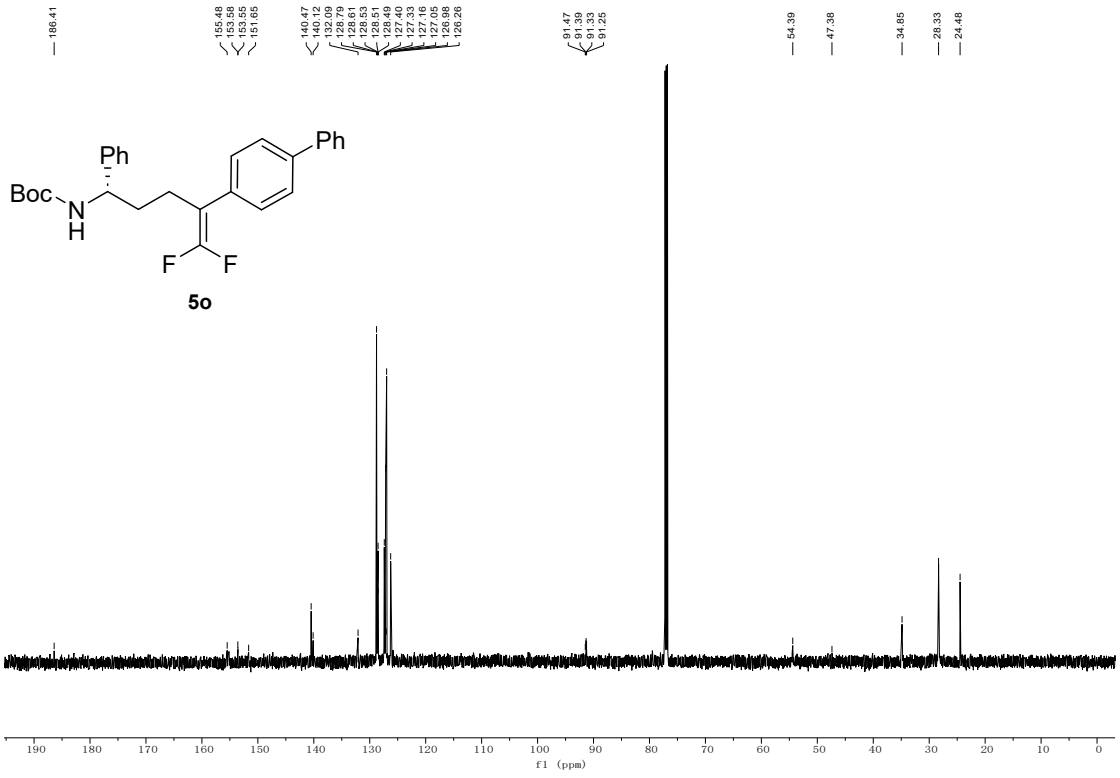
^{19}F NMR Spectrum of 5n



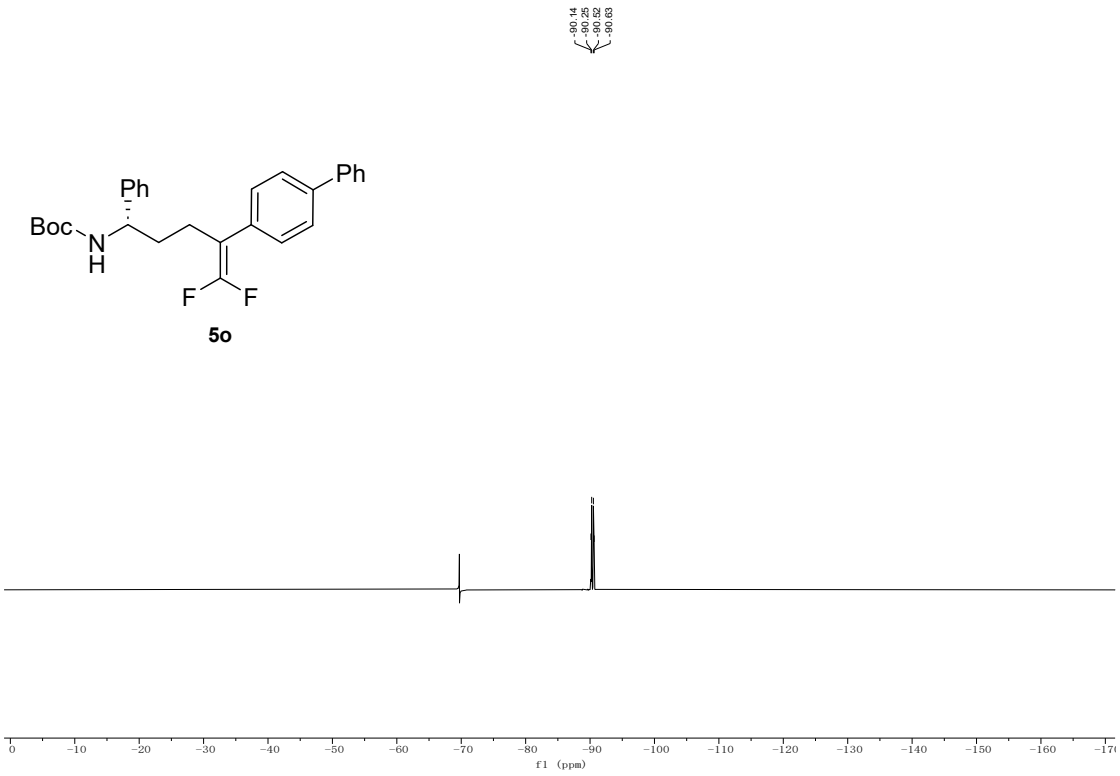
^{1}H NMR Spectrum of 5o



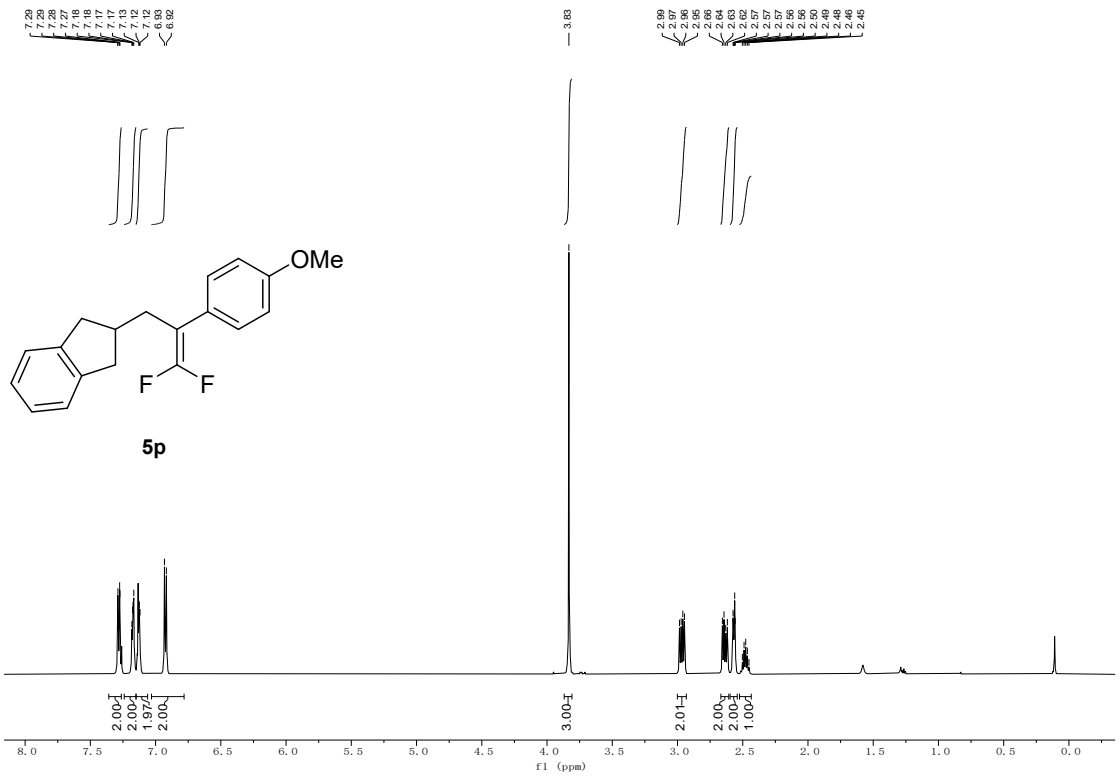
^{13}C NMR Spectrum of 5o



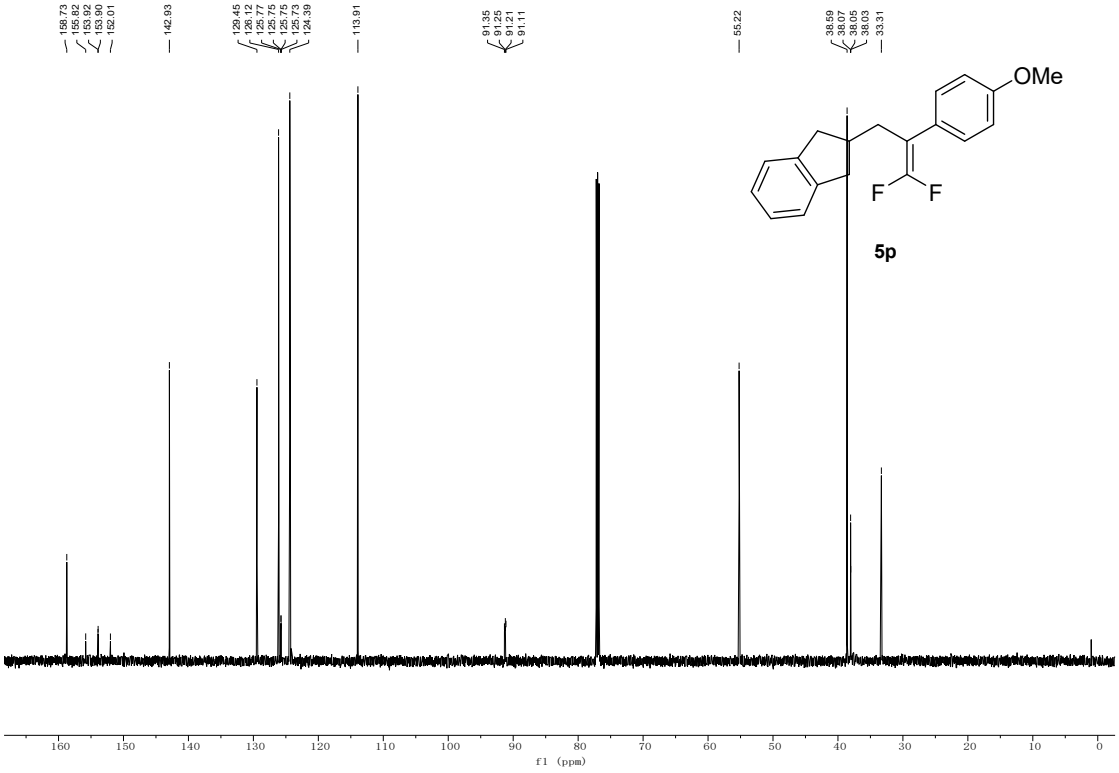
^{19}F NMR Spectrum of 5o



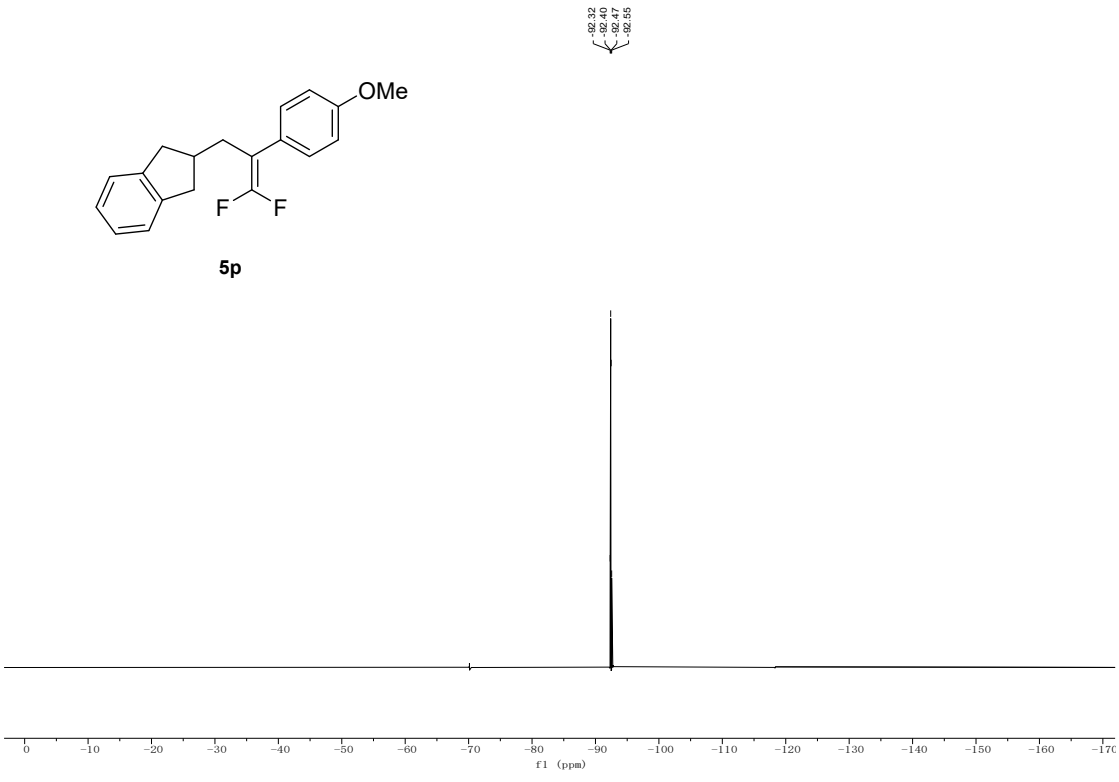
^{1}H NMR Spectrum of 5p



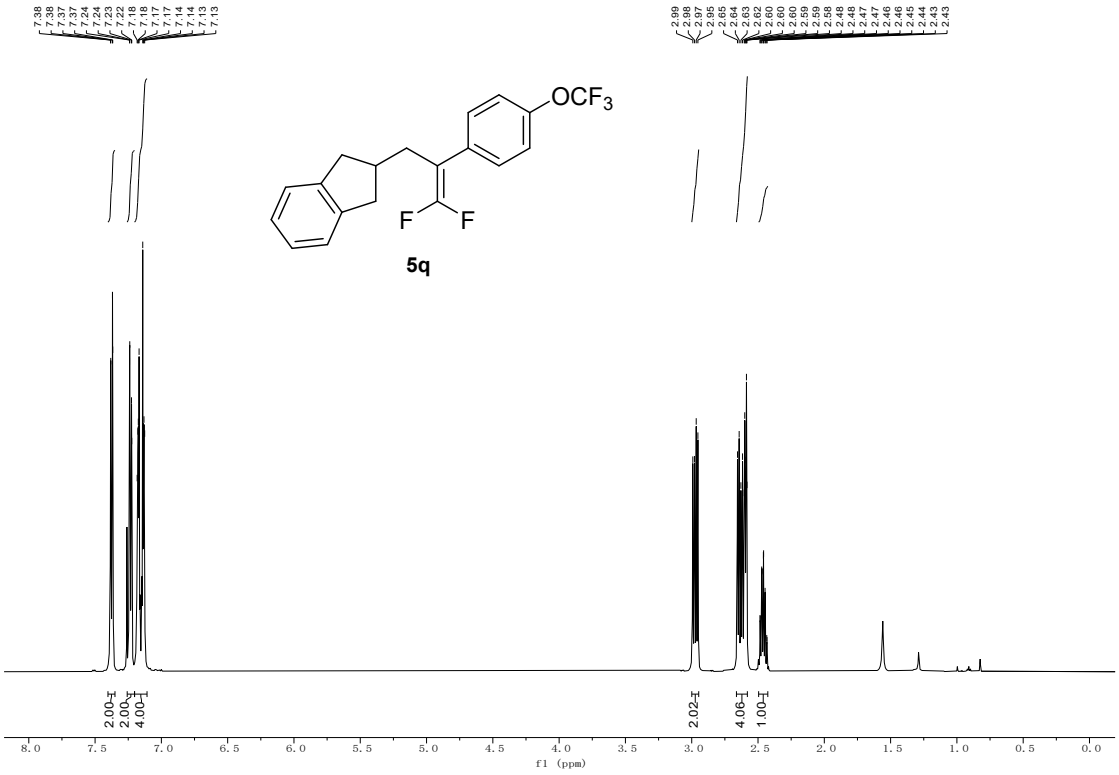
^{13}C NMR Spectrum of 5p



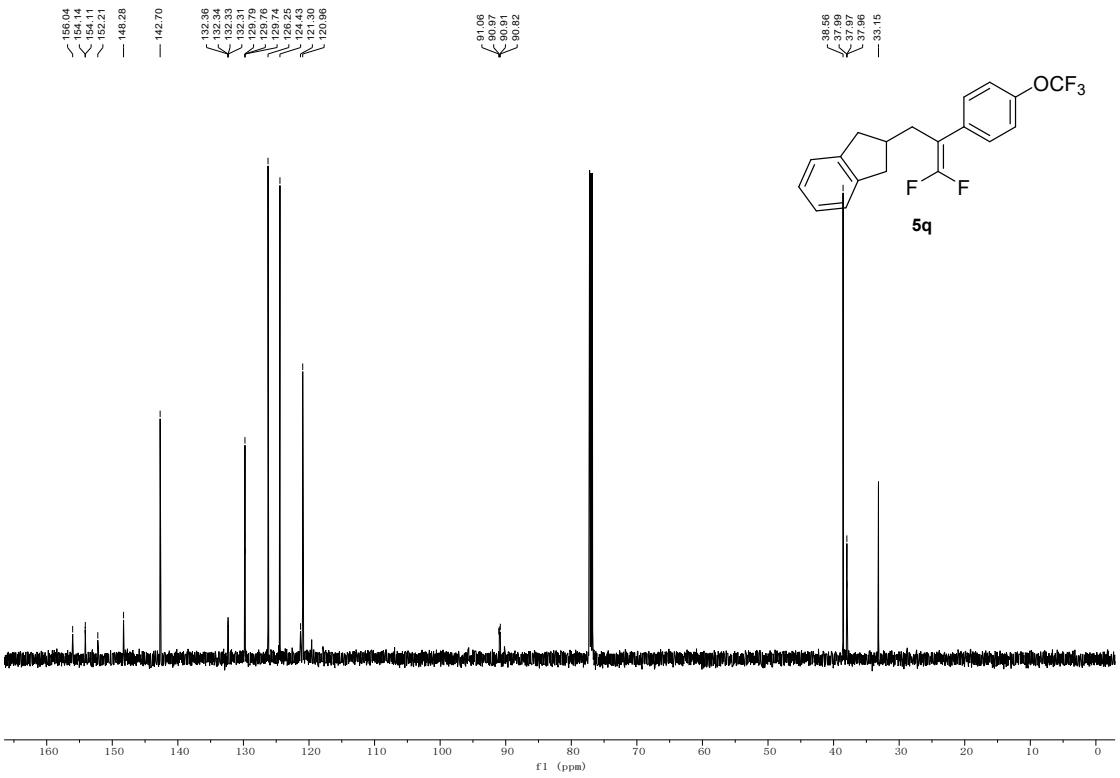
^{19}F NMR Spectrum of 5p



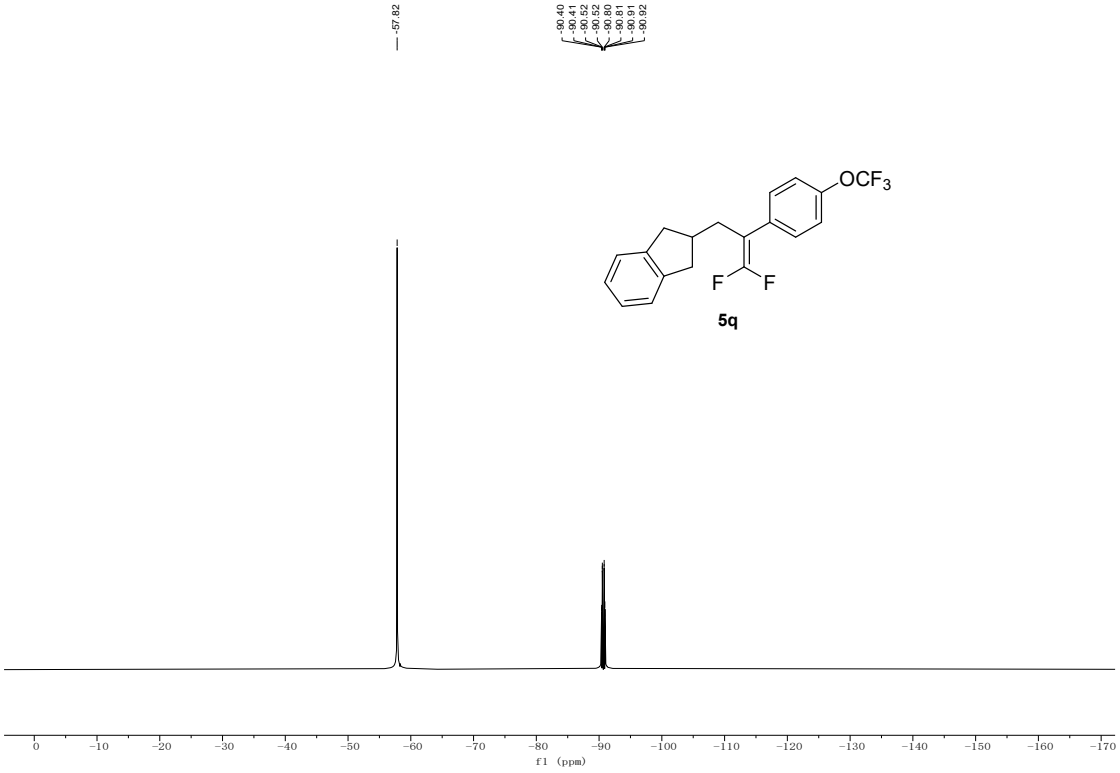
^{1}H NMR Spectrum of 5q



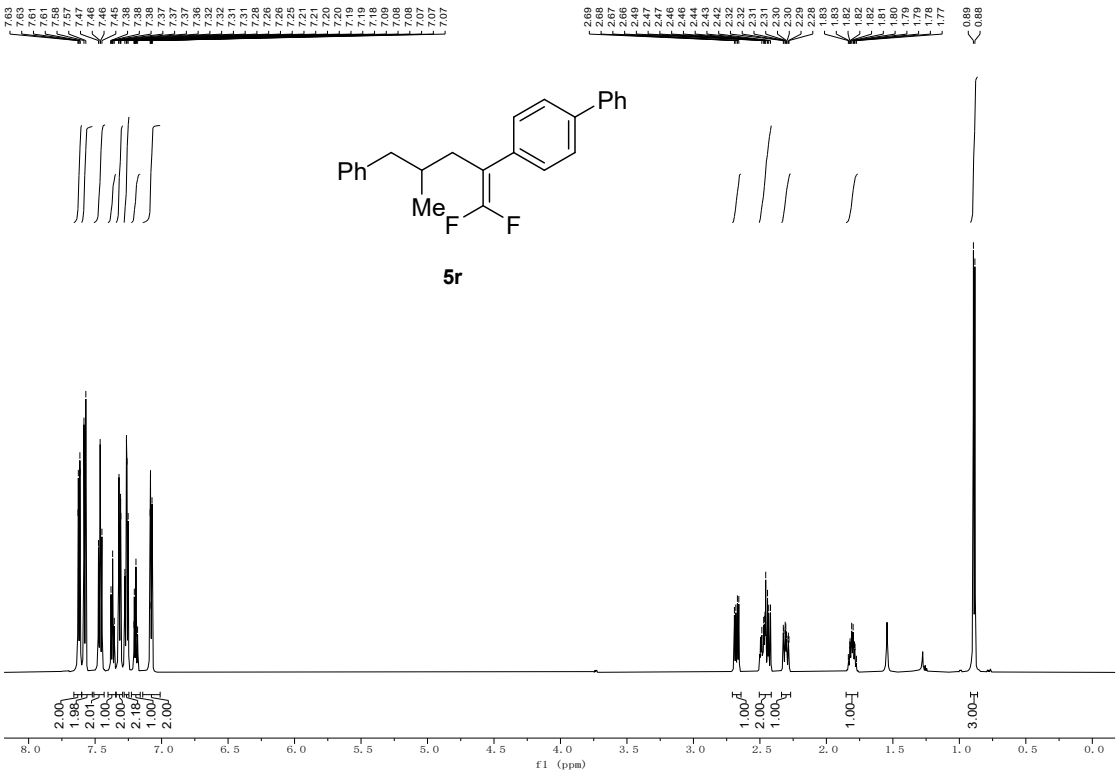
^{13}C NMR Spectrum of 5q



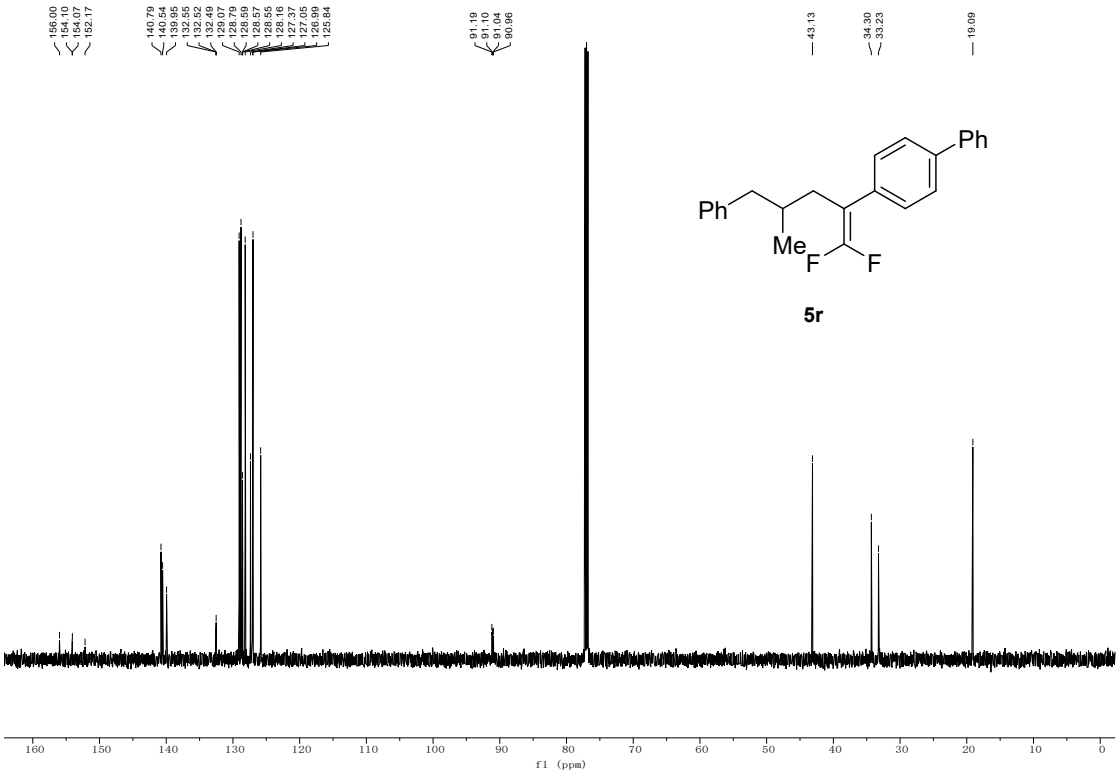
^{19}F NMR Spectrum of 5q



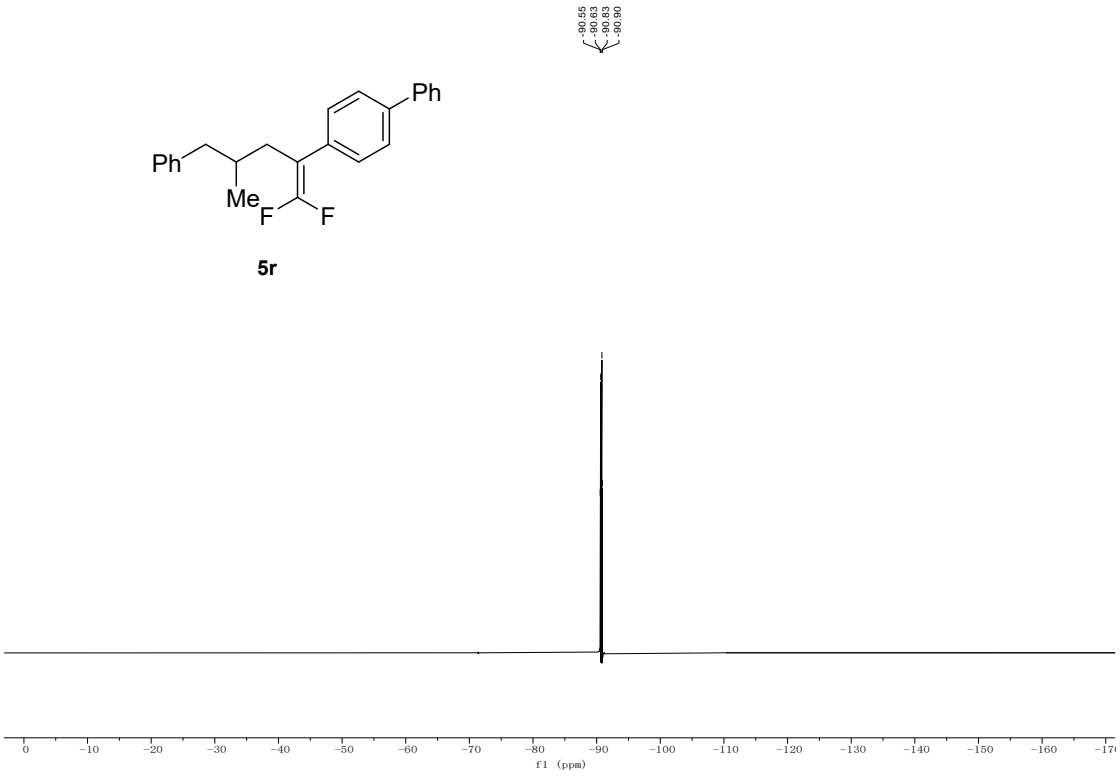
^{1}H NMR Spectrum of 5r



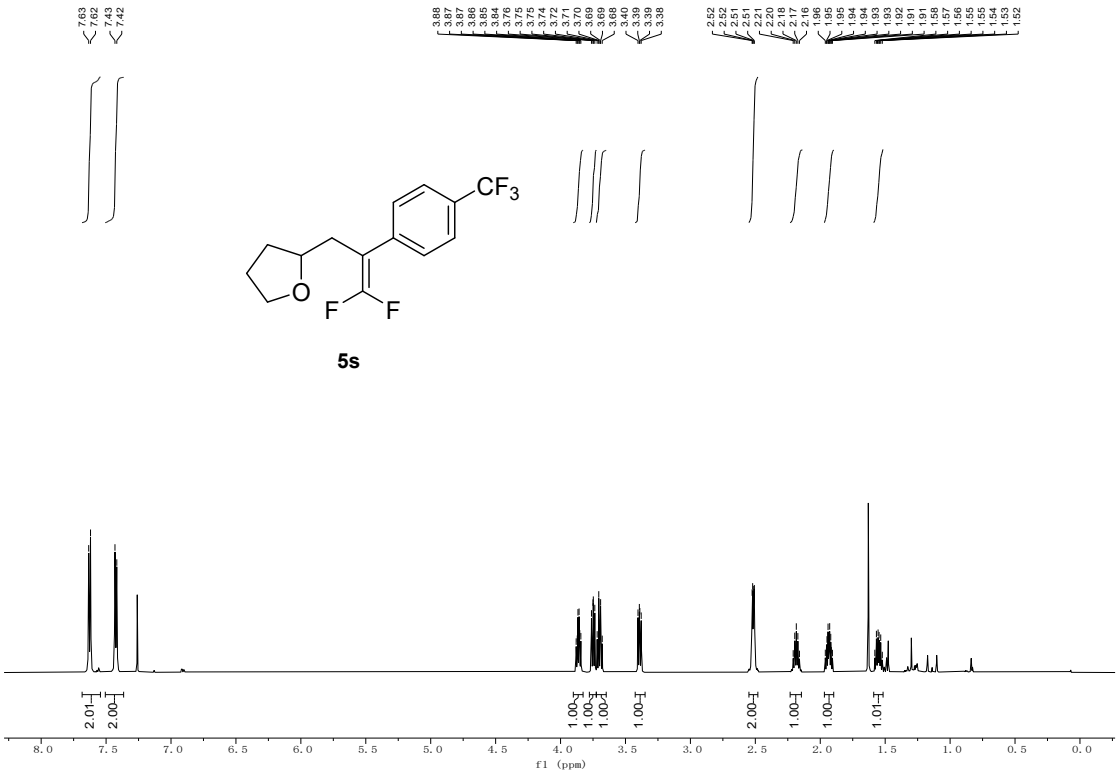
^{13}C NMR Spectrum of 5r



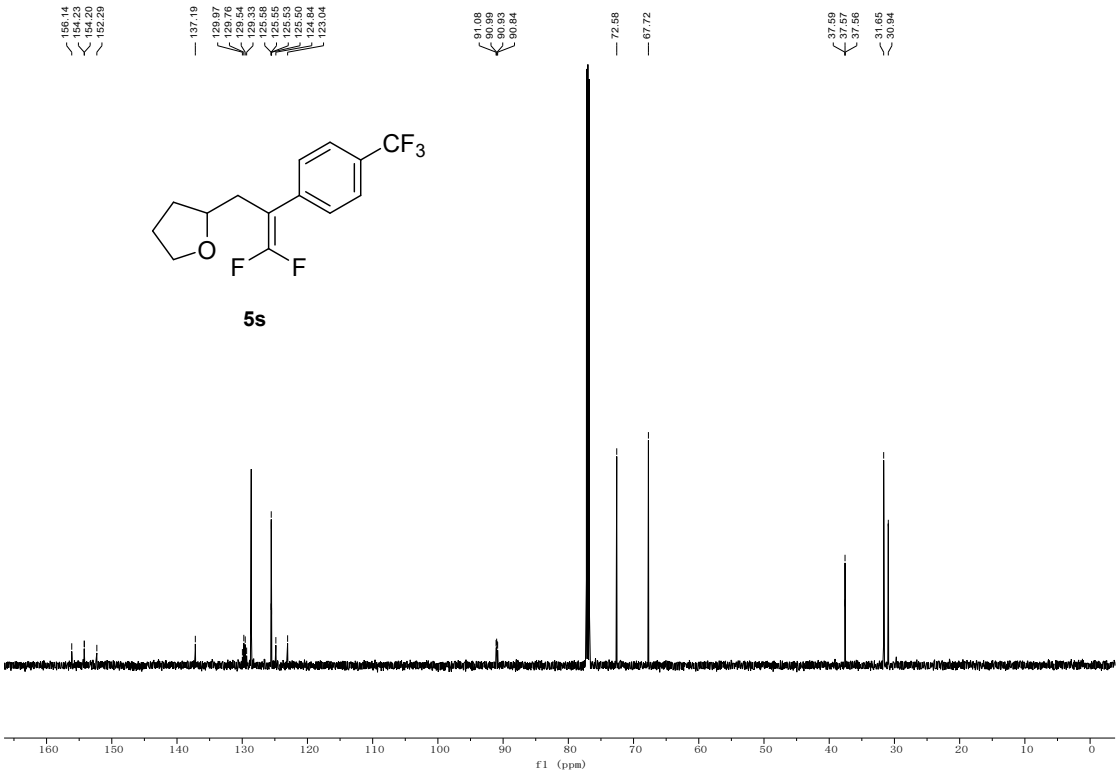
^{19}F NMR Spectrum of 5r



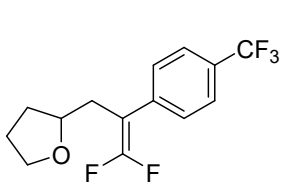
^{1}H NMR Spectrum of 5s



^{13}C NMR Spectrum of 5s

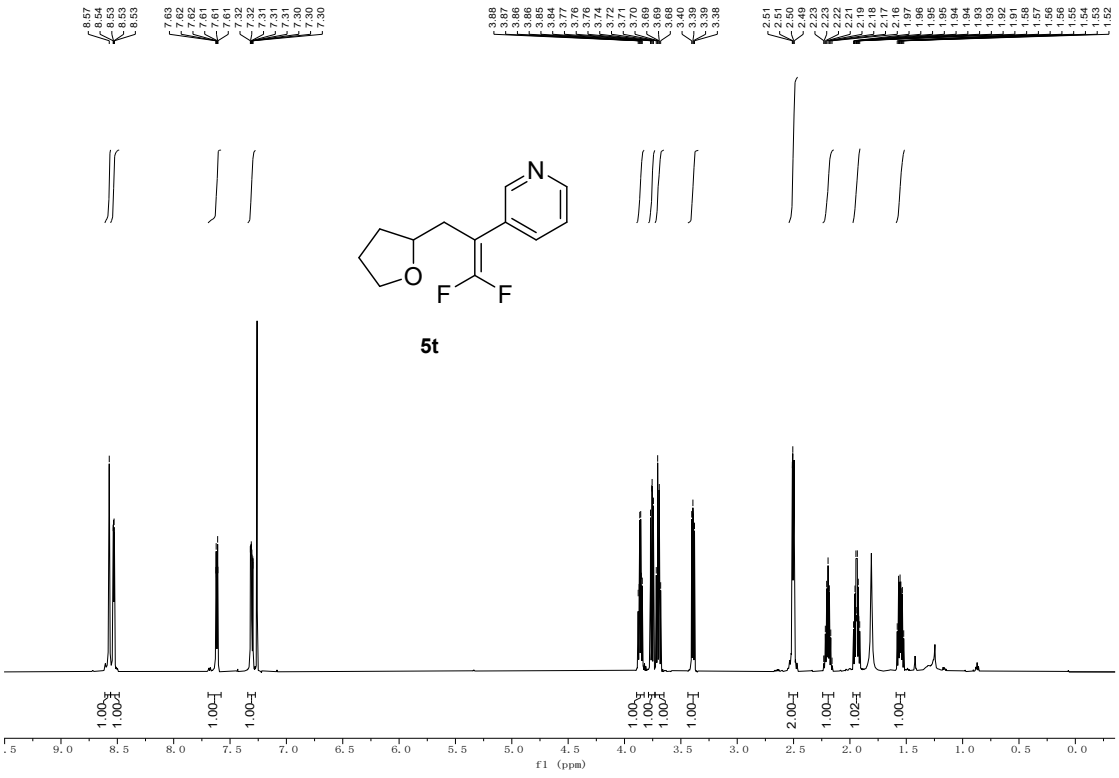


^{19}F NMR Spectrum of 5s



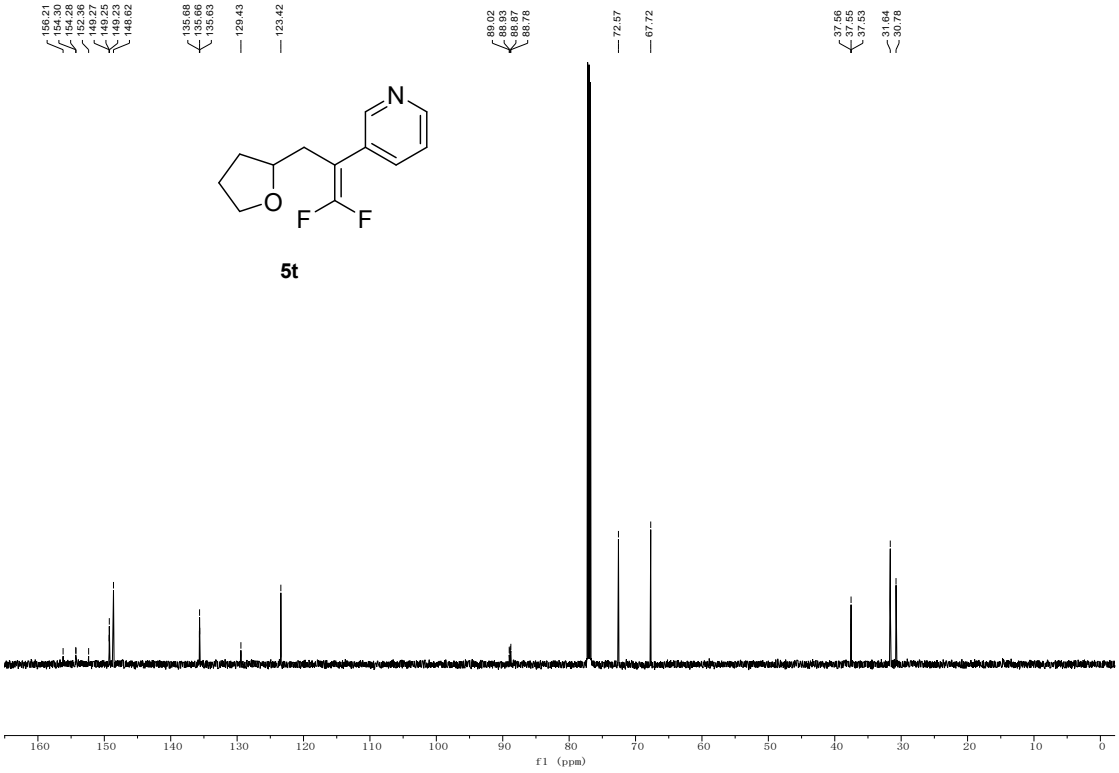
5s

^{1}H NMR Spectrum of 5t

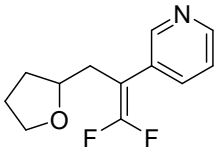


5t

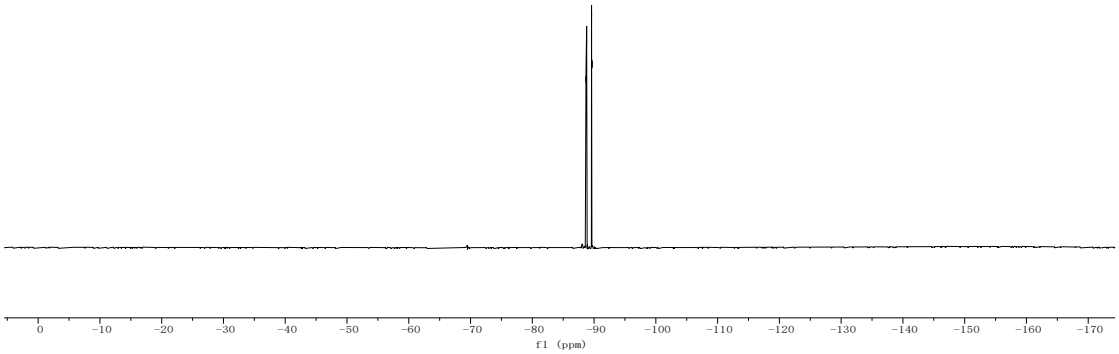
^{13}C NMR Spectrum of 5t



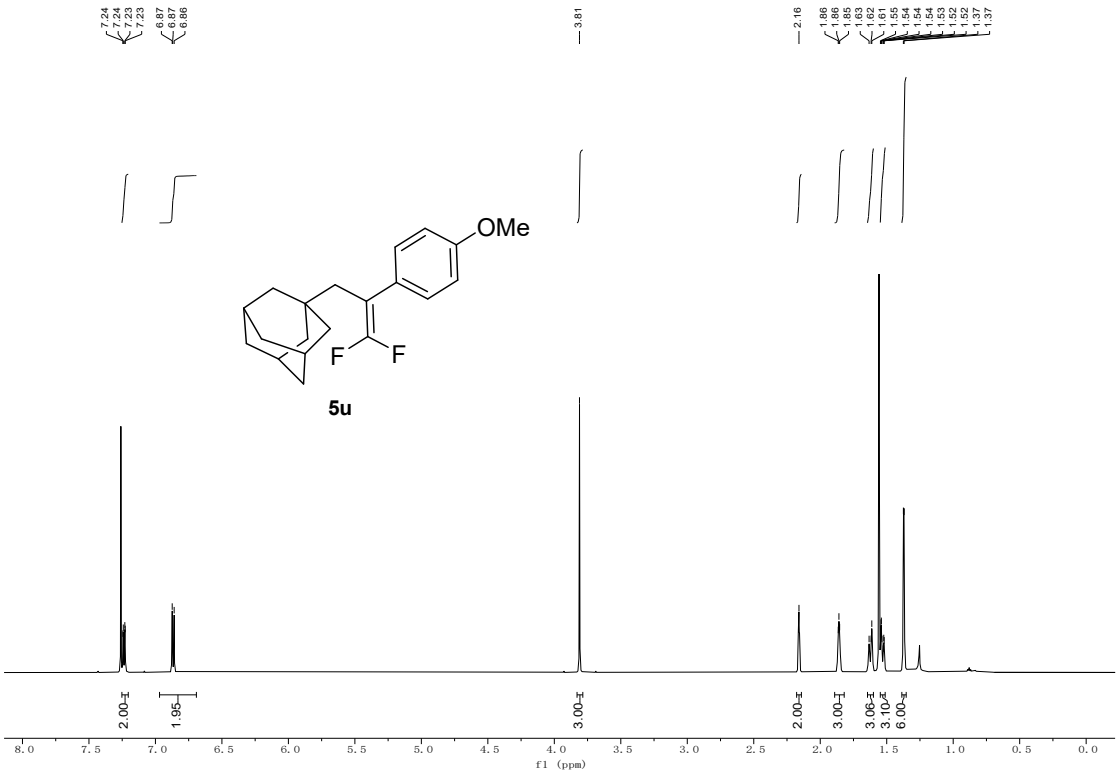
^{19}F NMR Spectrum of 5t



5t

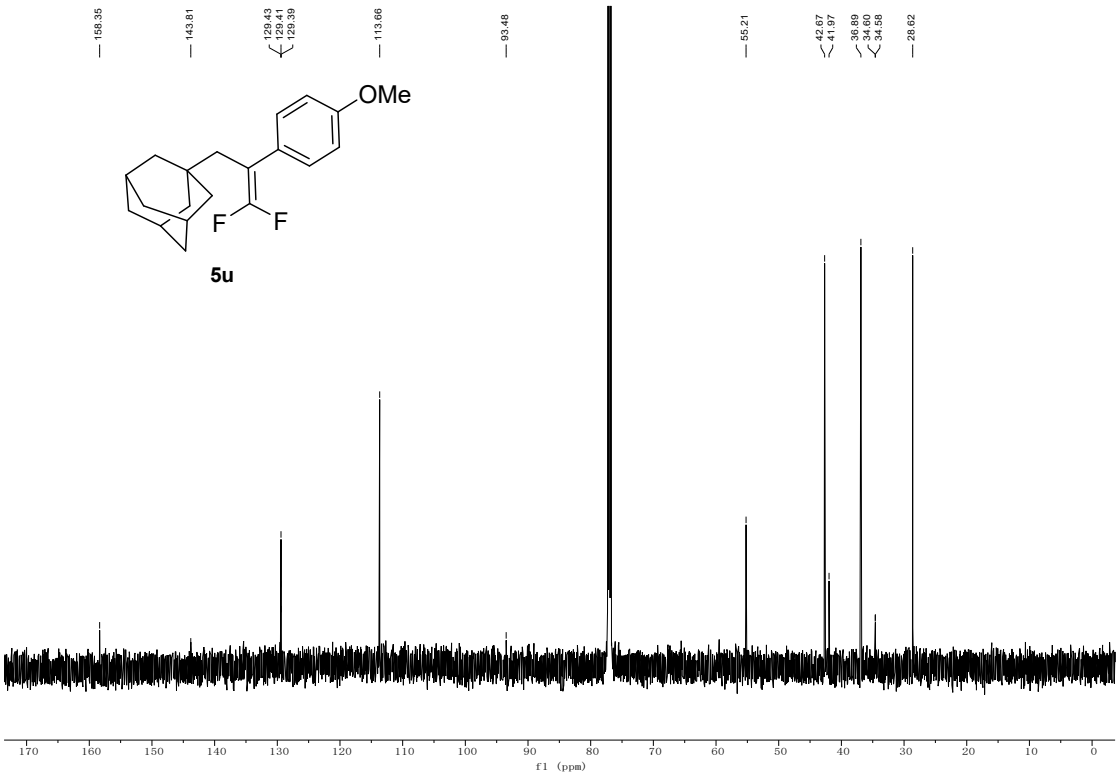


^{1}H NMR Spectrum of 5u

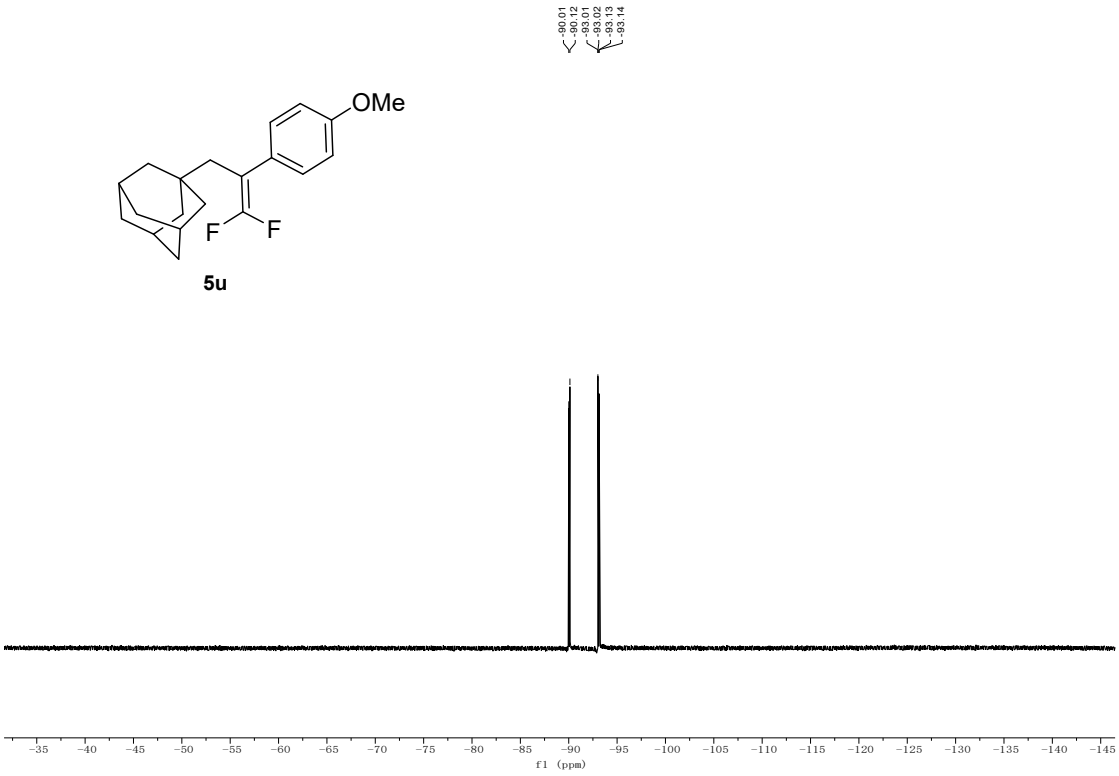


5u

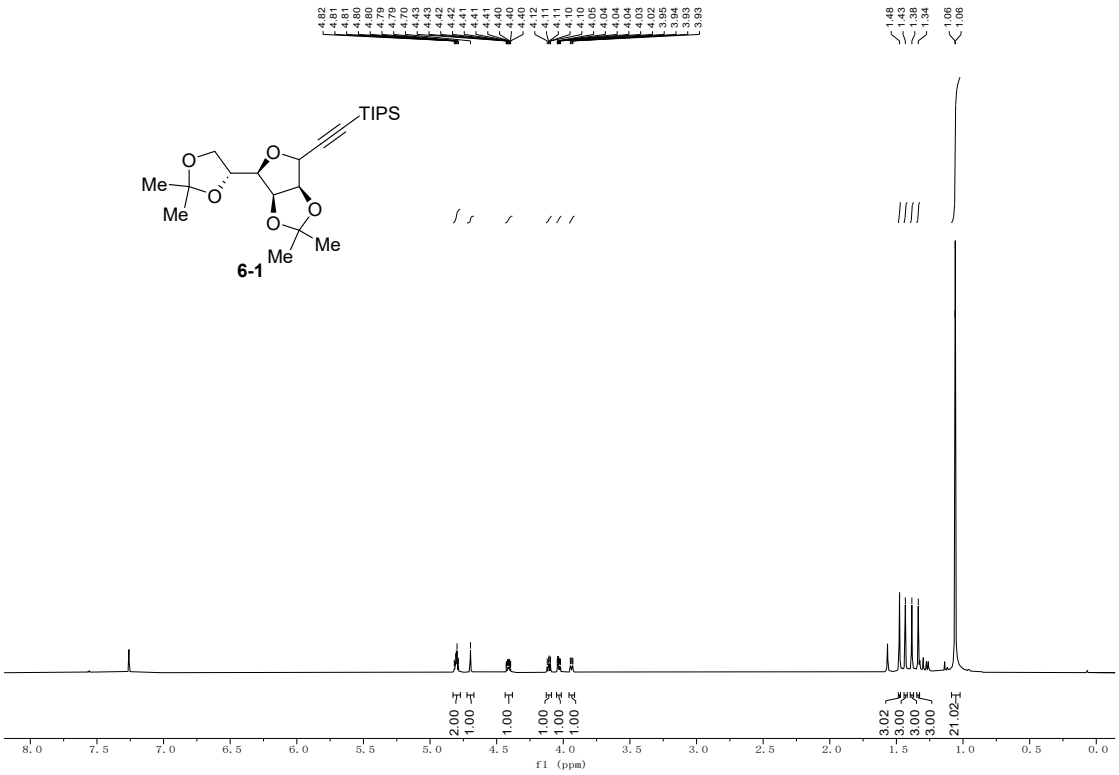
^{13}C NMR Spectrum of 5u



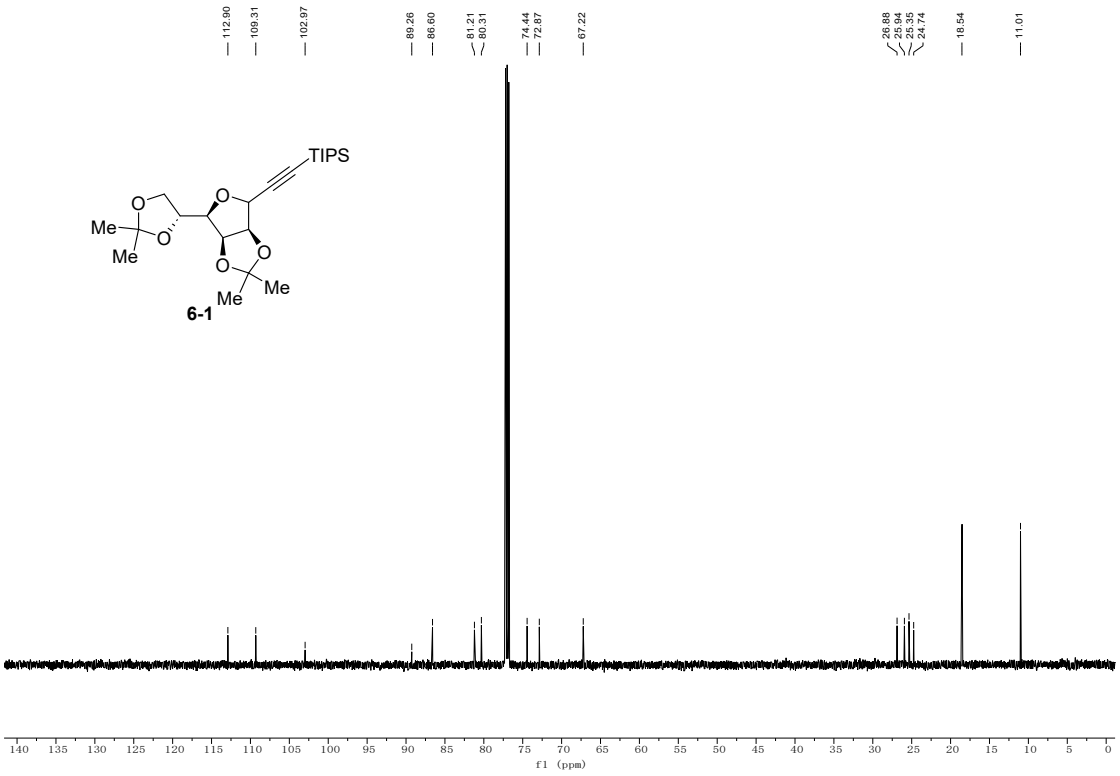
^{19}F NMR Spectrum of 5u



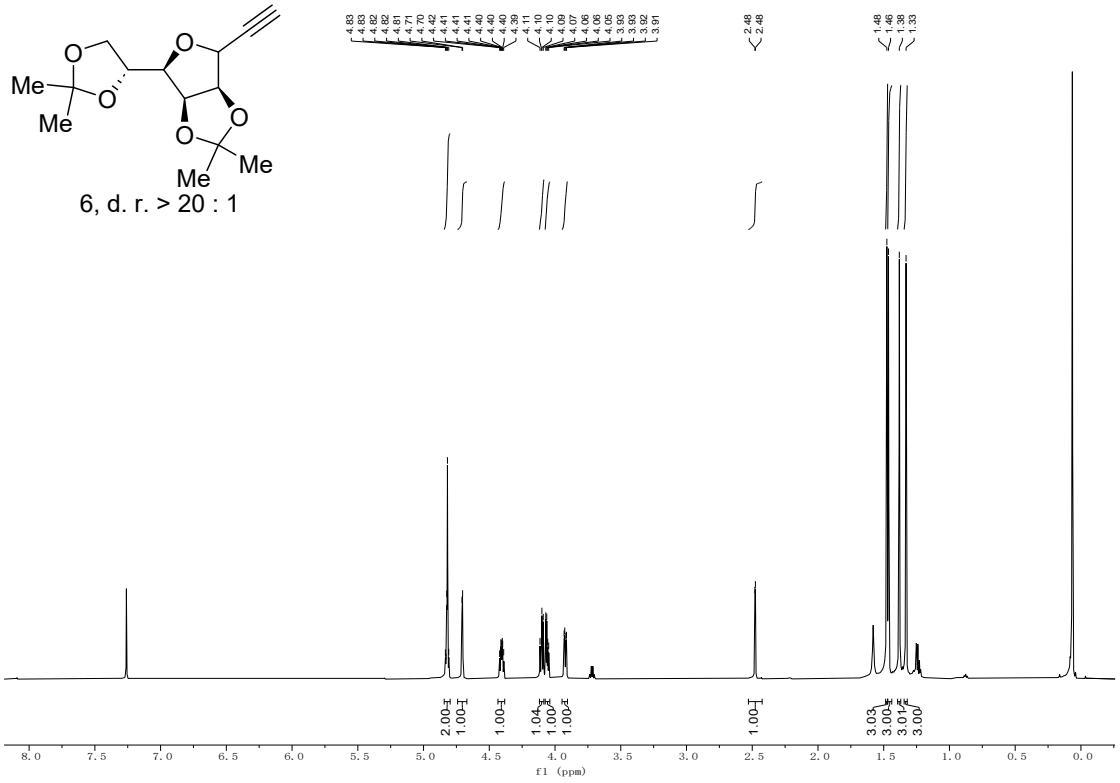
^{1}H NMR Spectrum of 6-1



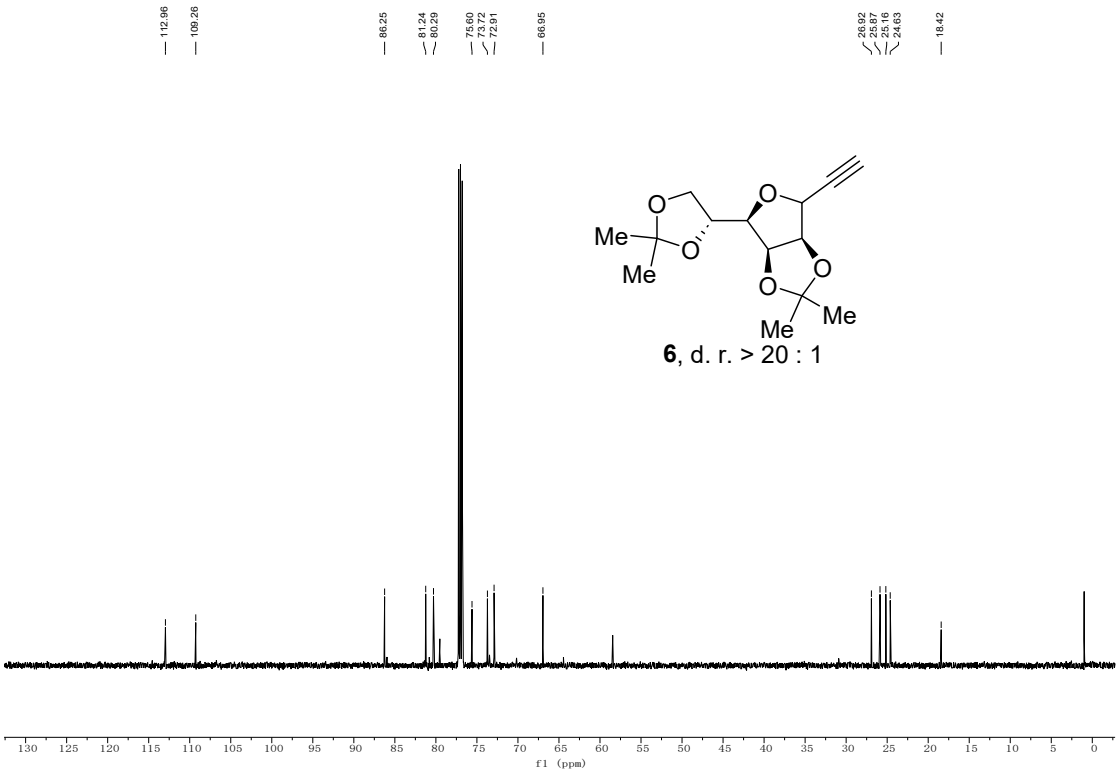
^{13}C NMR Spectrum of 6-1



^{1}H NMR Spectrum of 6

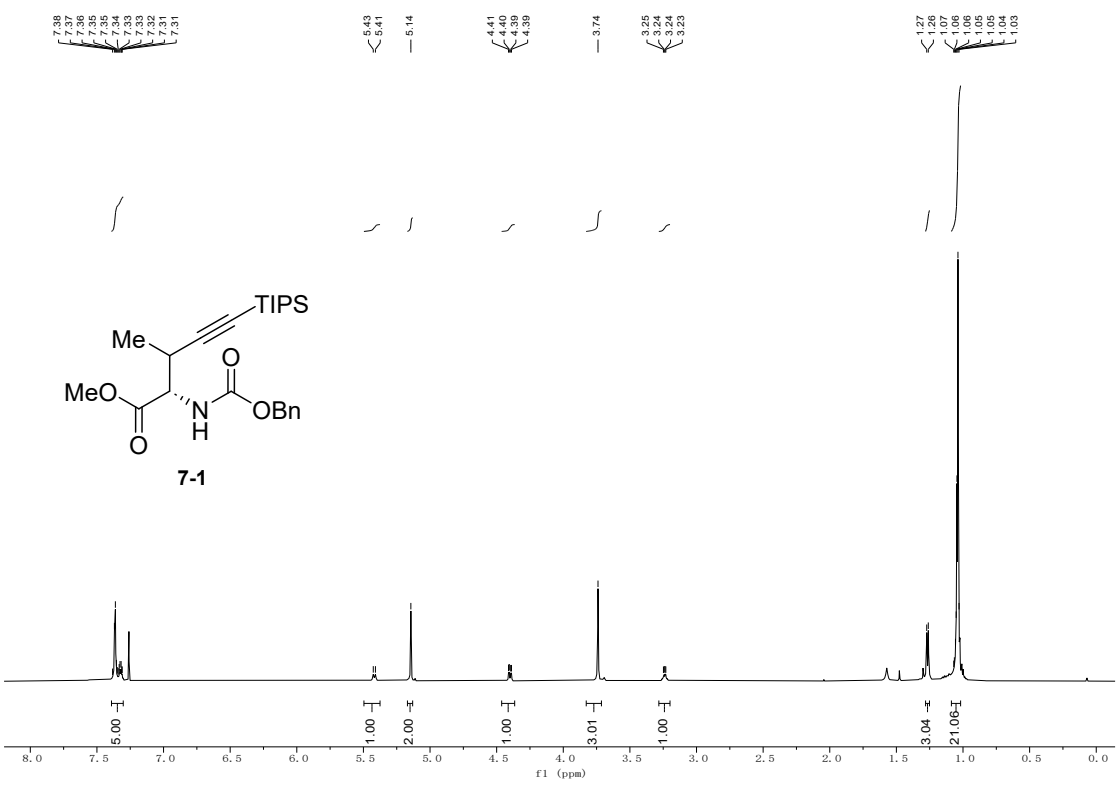


^{13}C NMR Spectrum of 6

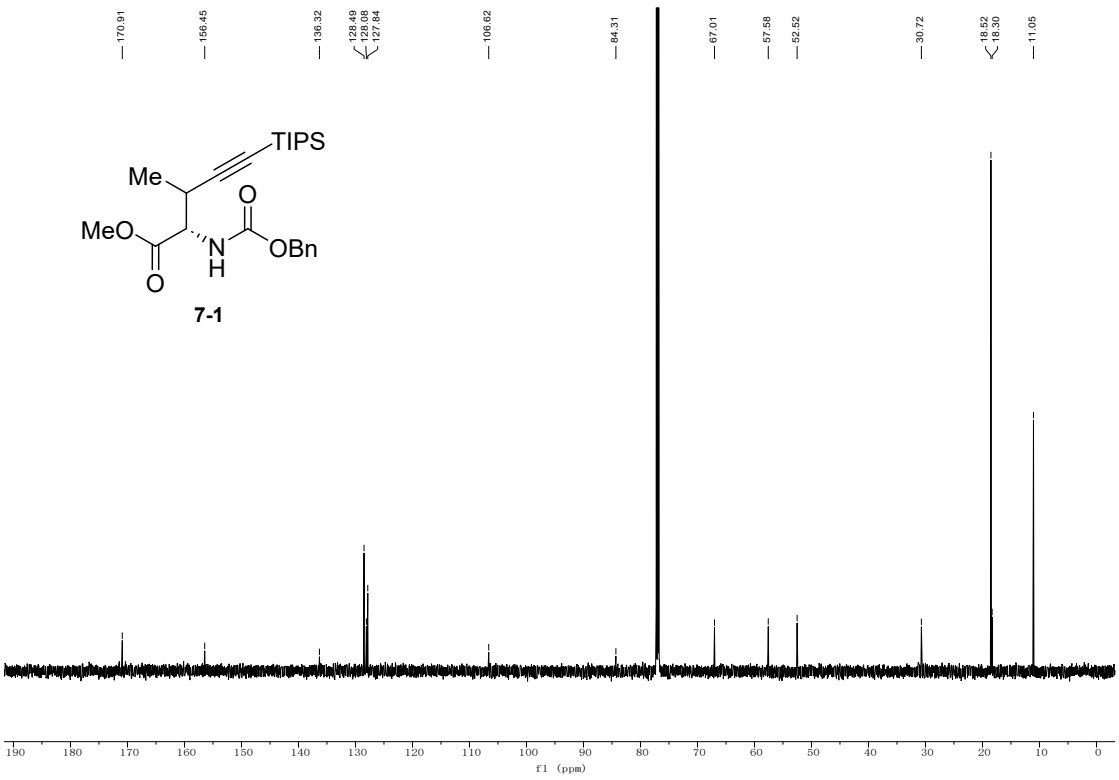


6, d. r. > 20 : 1

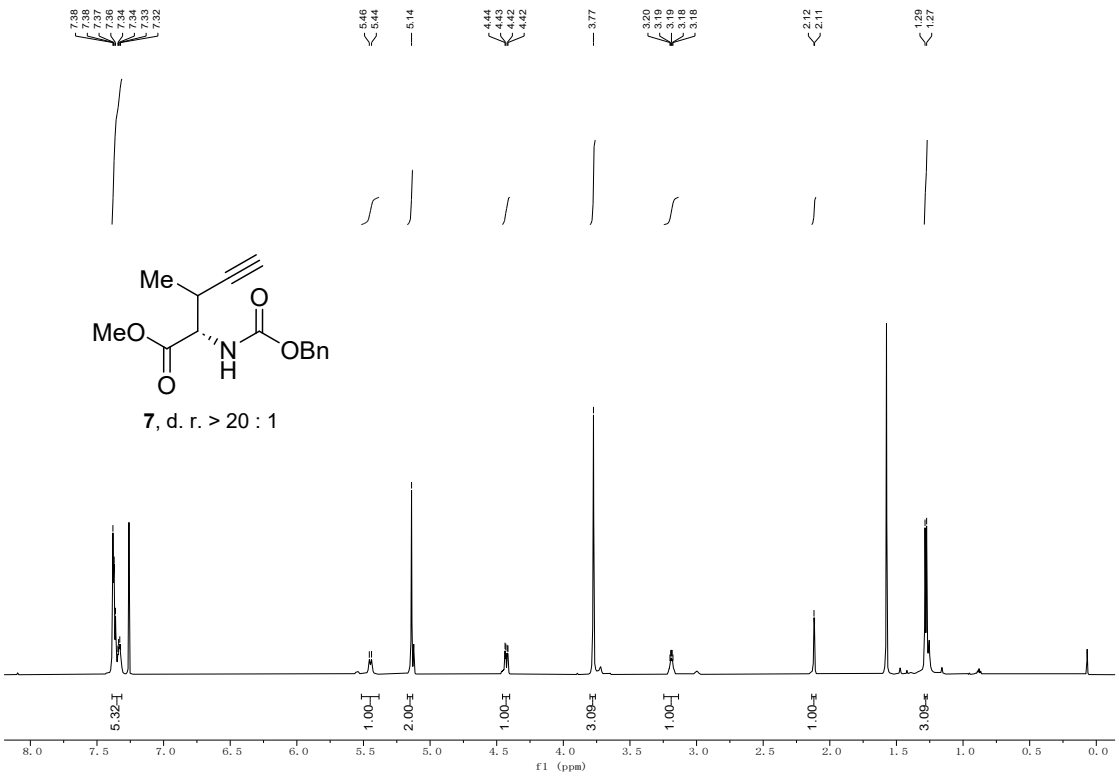
^{1}H NMR Spectrum of 7-1



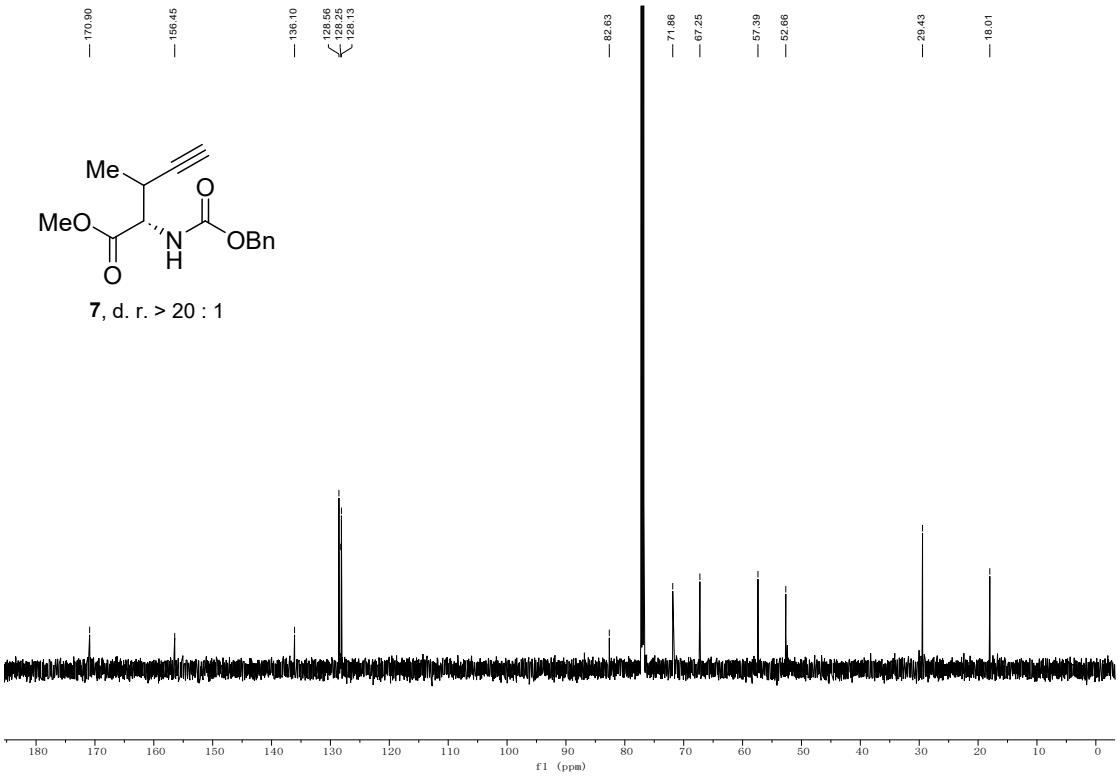
^{13}C NMR Spectrum of 7-1



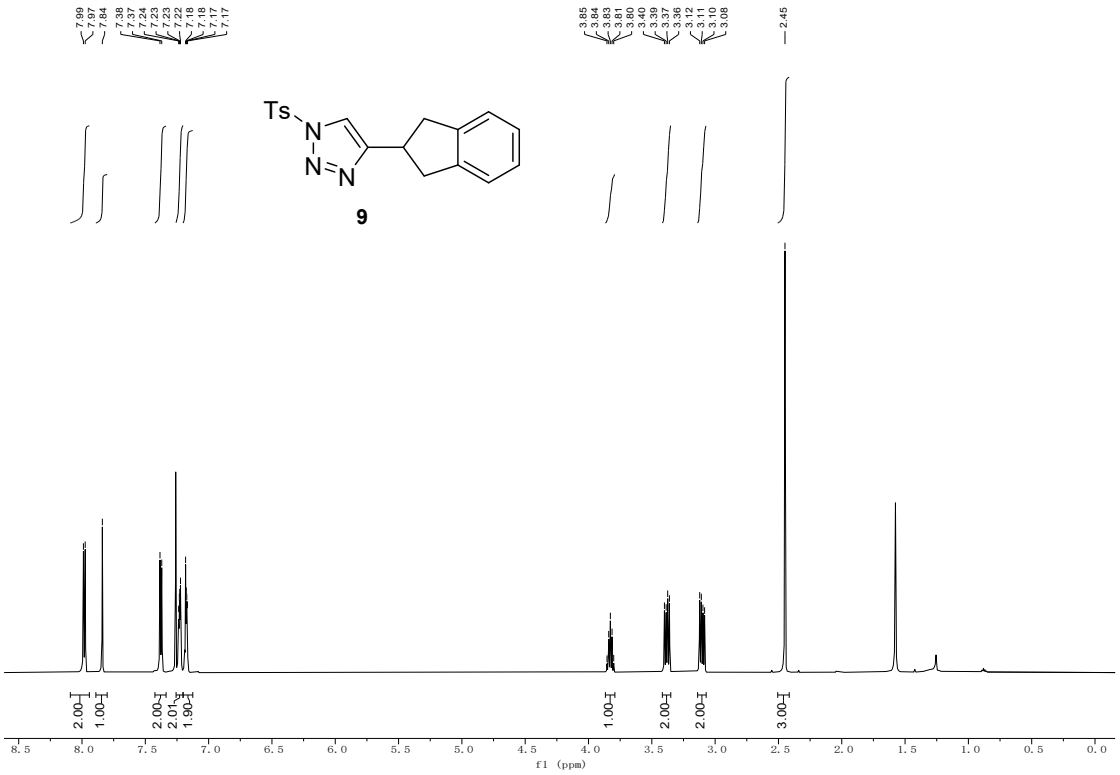
^{1}H NMR Spectrum of 7



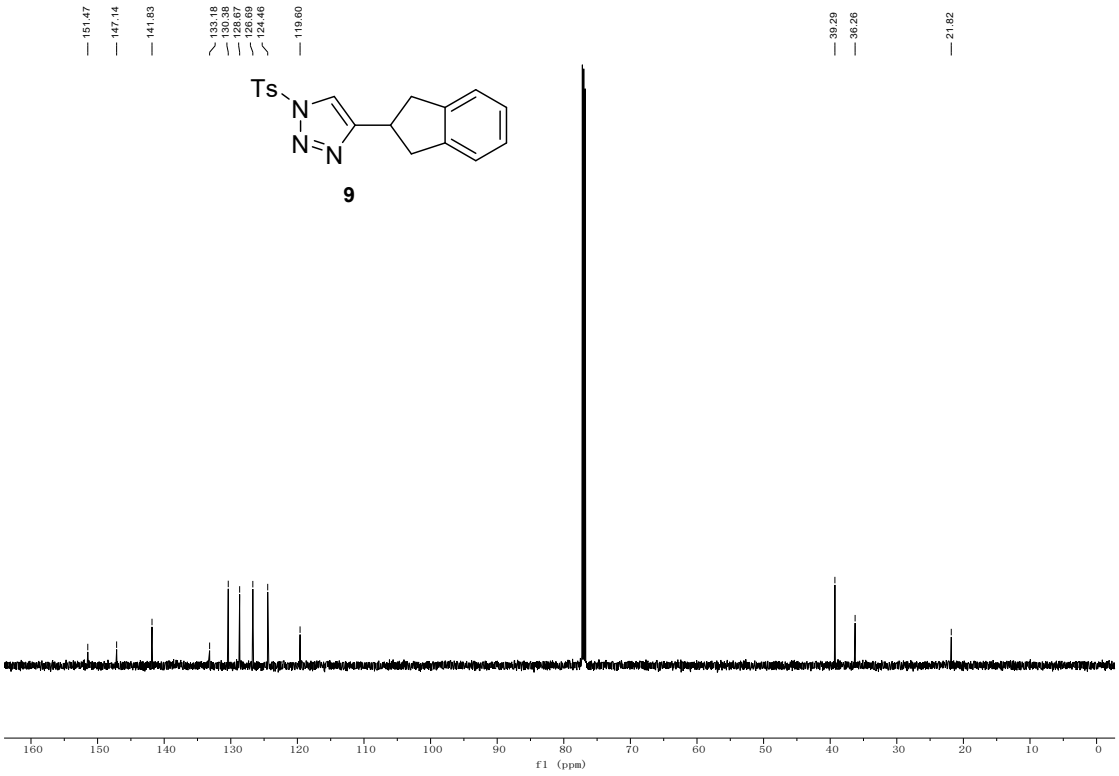
^{13}C NMR Spectrum of 7



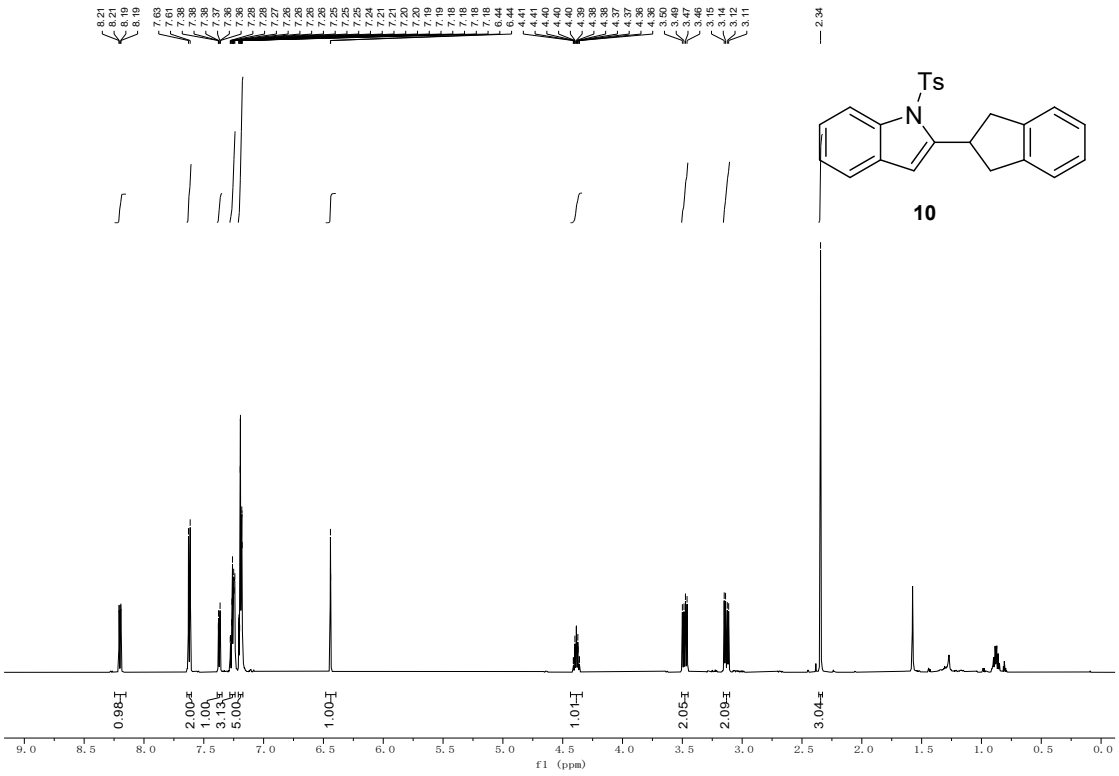
^{1}H NMR Spectrum of 9



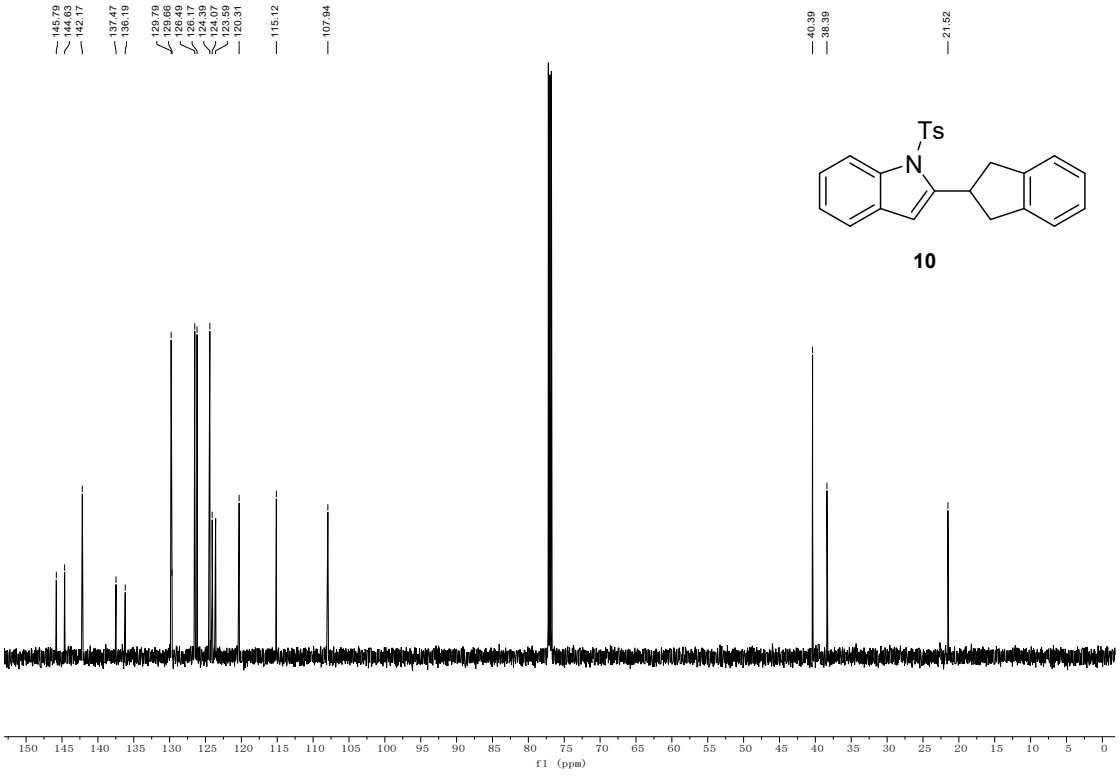
^{13}C NMR Spectrum of 9



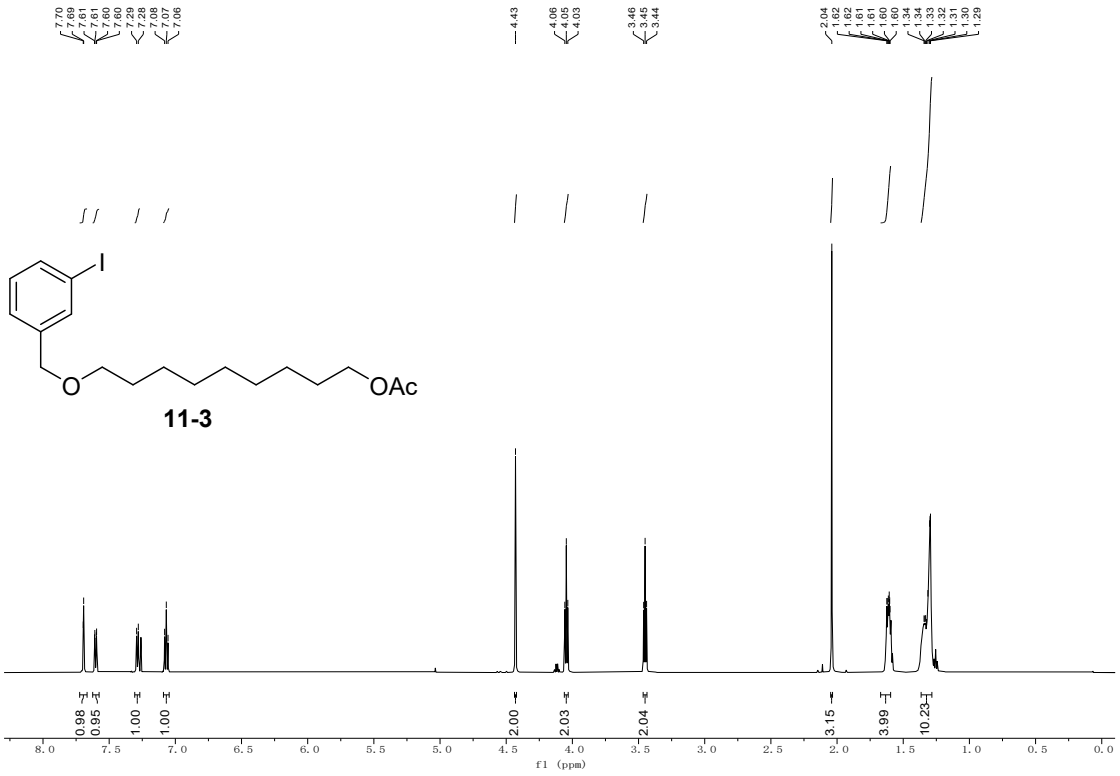
^{1}H NMR Spectrum of 10



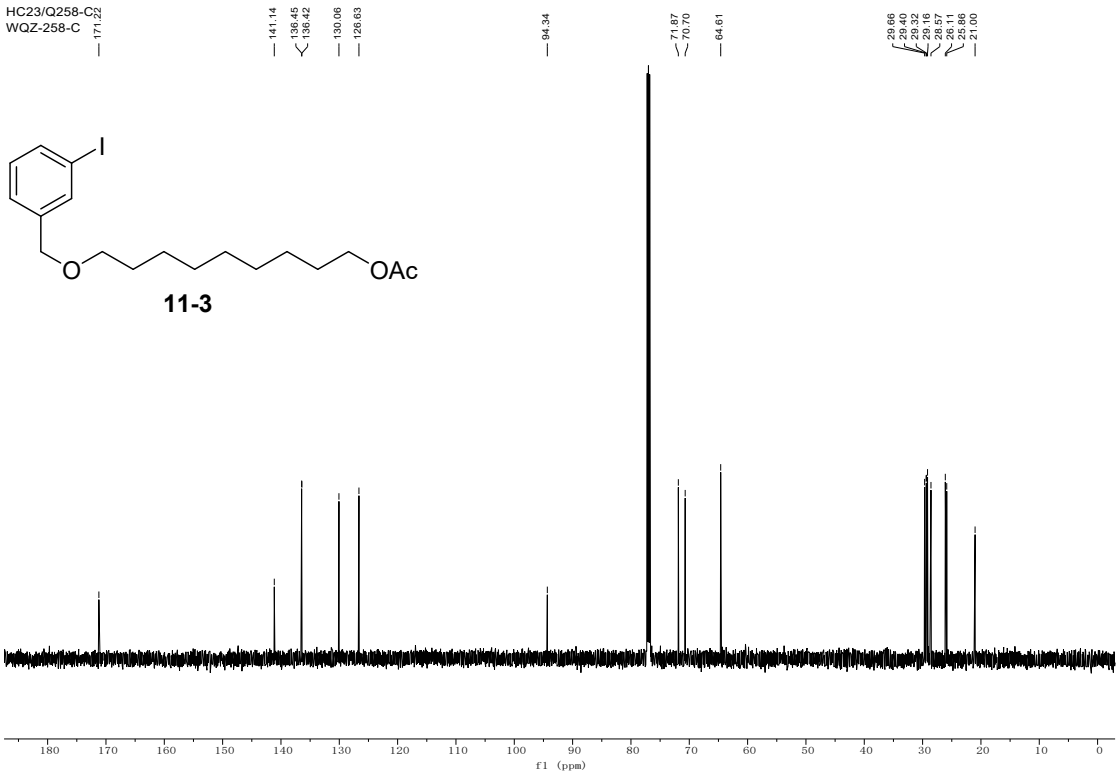
^{13}C NMR Spectrum of 10



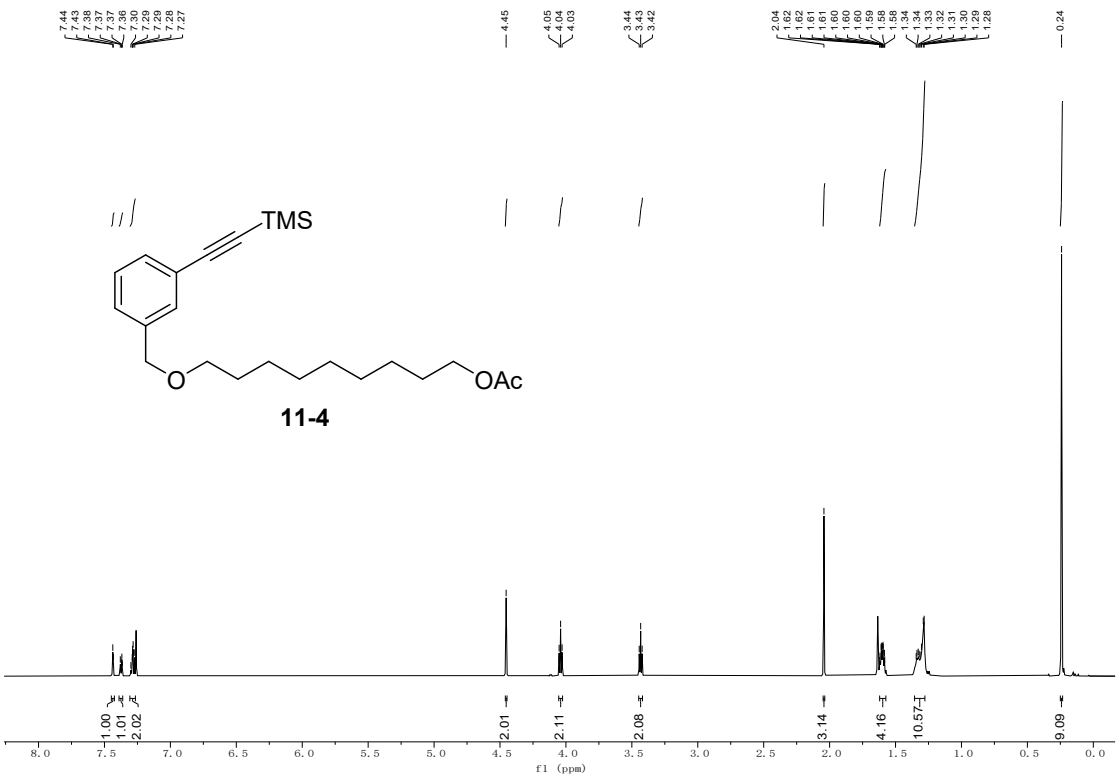
^{1}H NMR Spectrum of 11-3



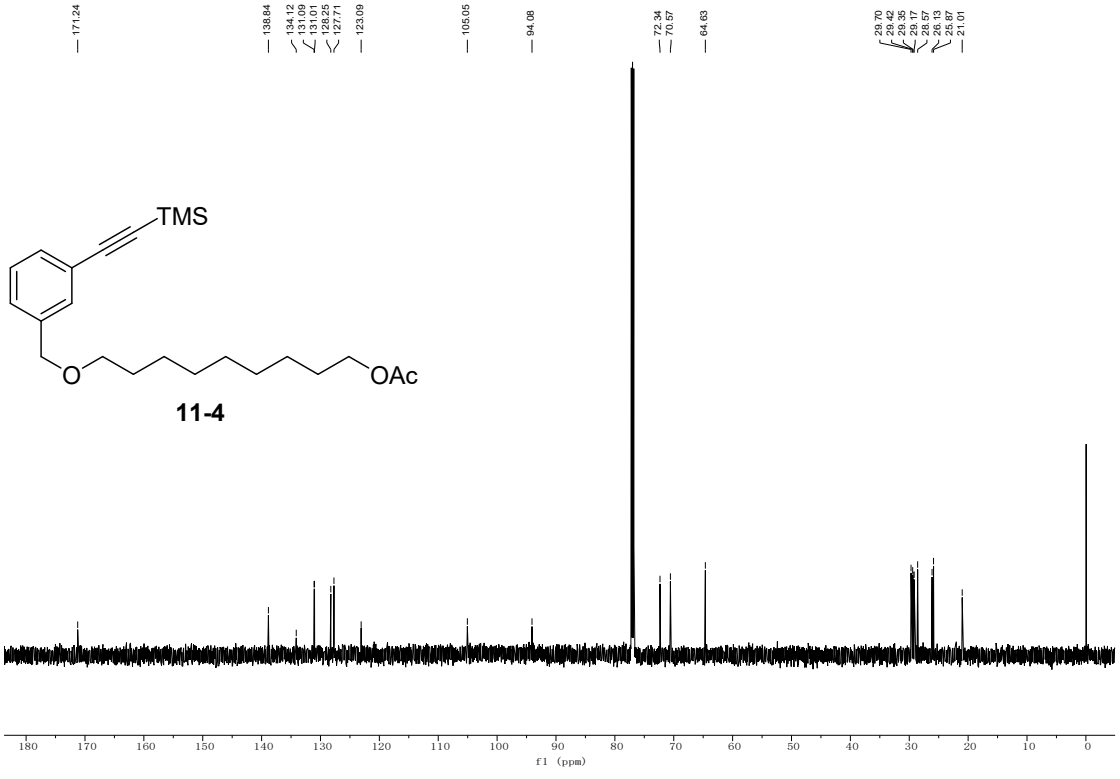
^{13}C NMR Spectrum of 11-3



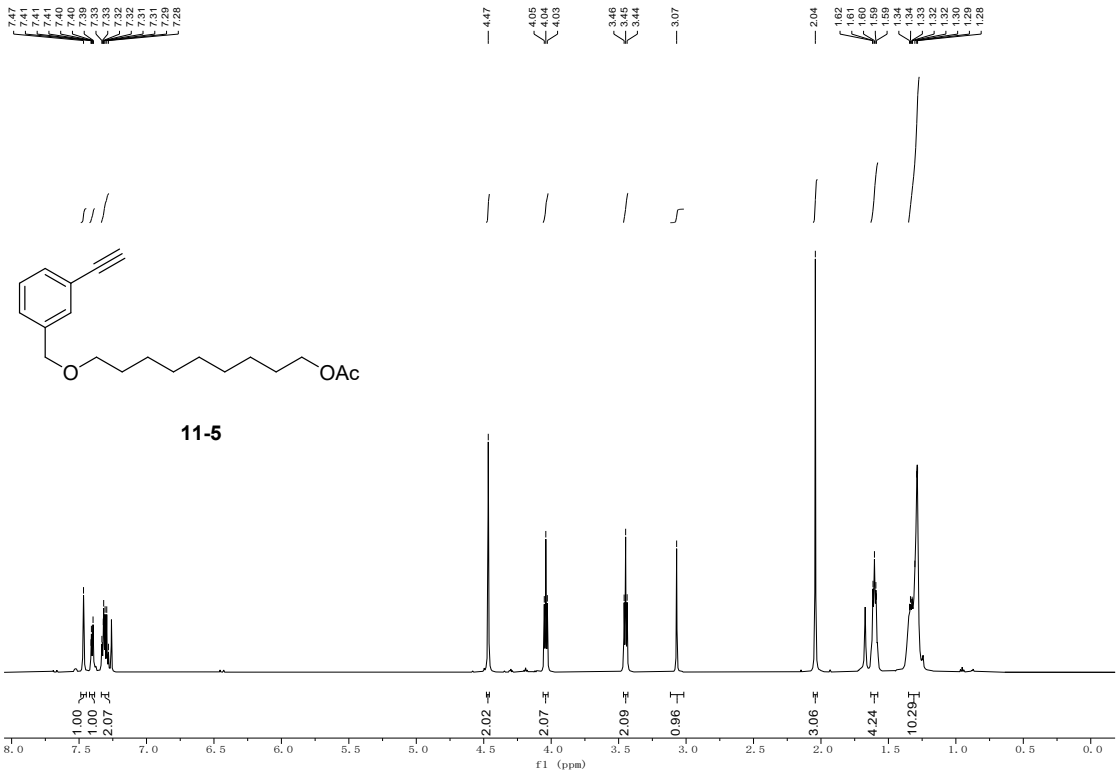
^{1}H NMR Spectrum of 11-4



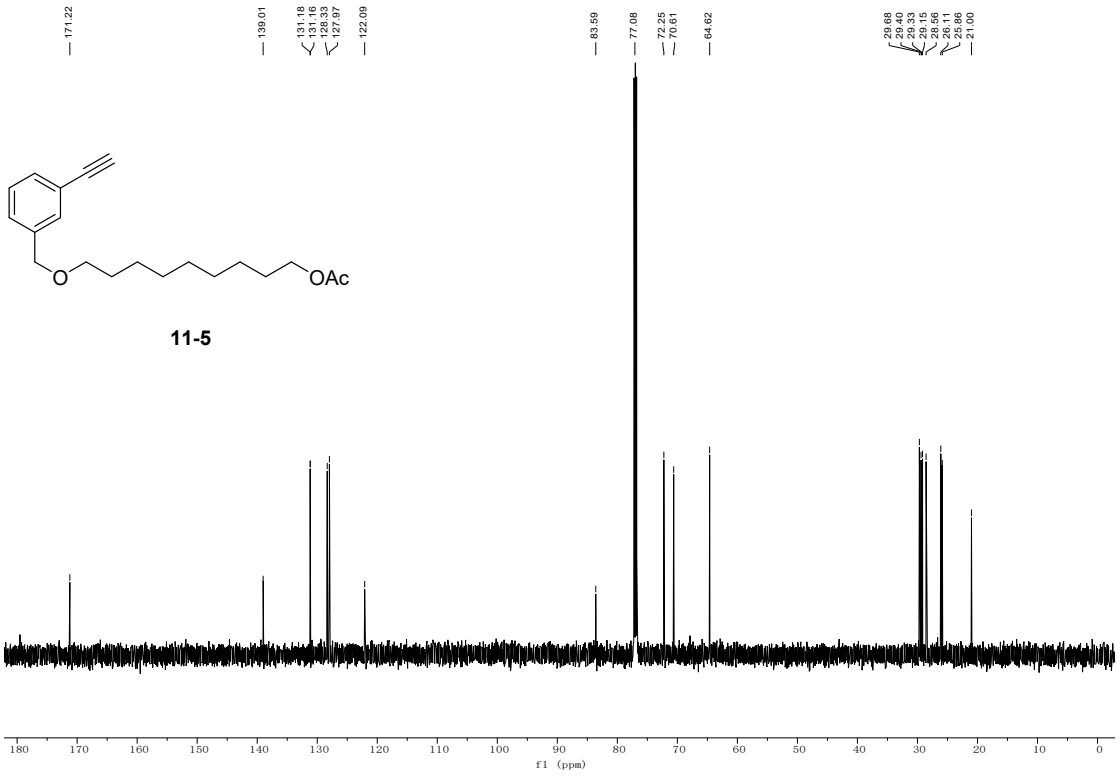
^{13}C NMR Spectrum of 11-4



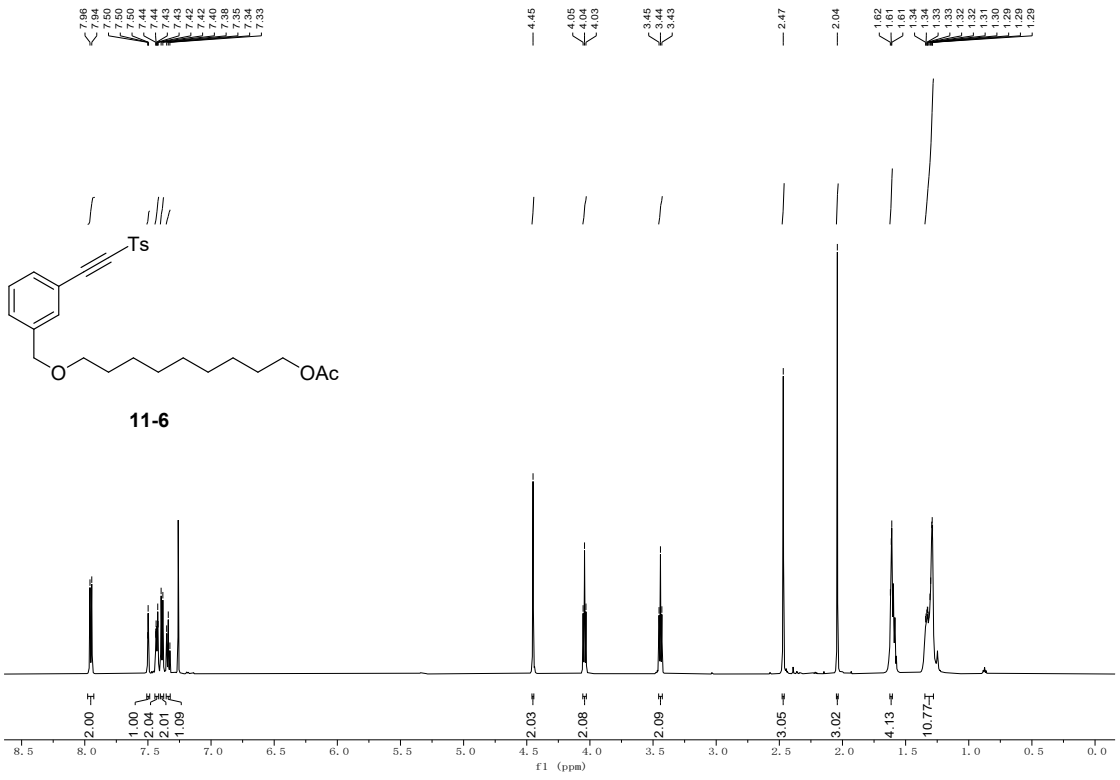
^{1}H NMR Spectrum of 11-5



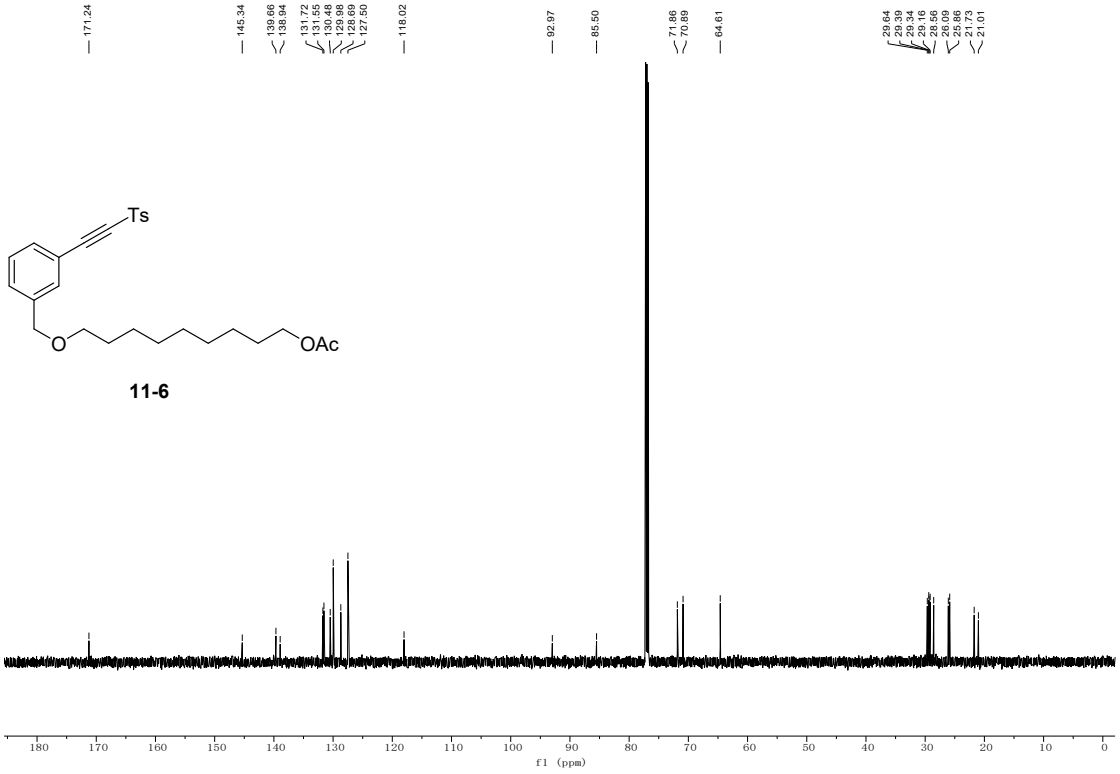
^{13}C NMR Spectrum of 11-5



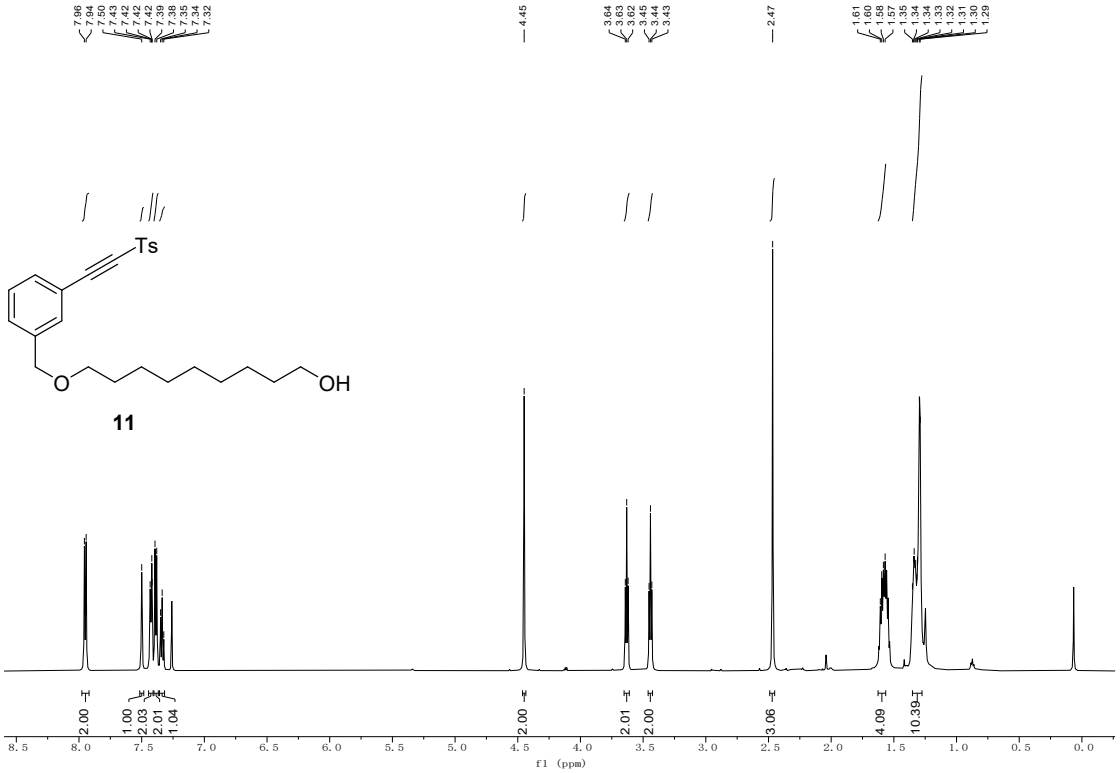
^{1}H NMR Spectrum of 11-6



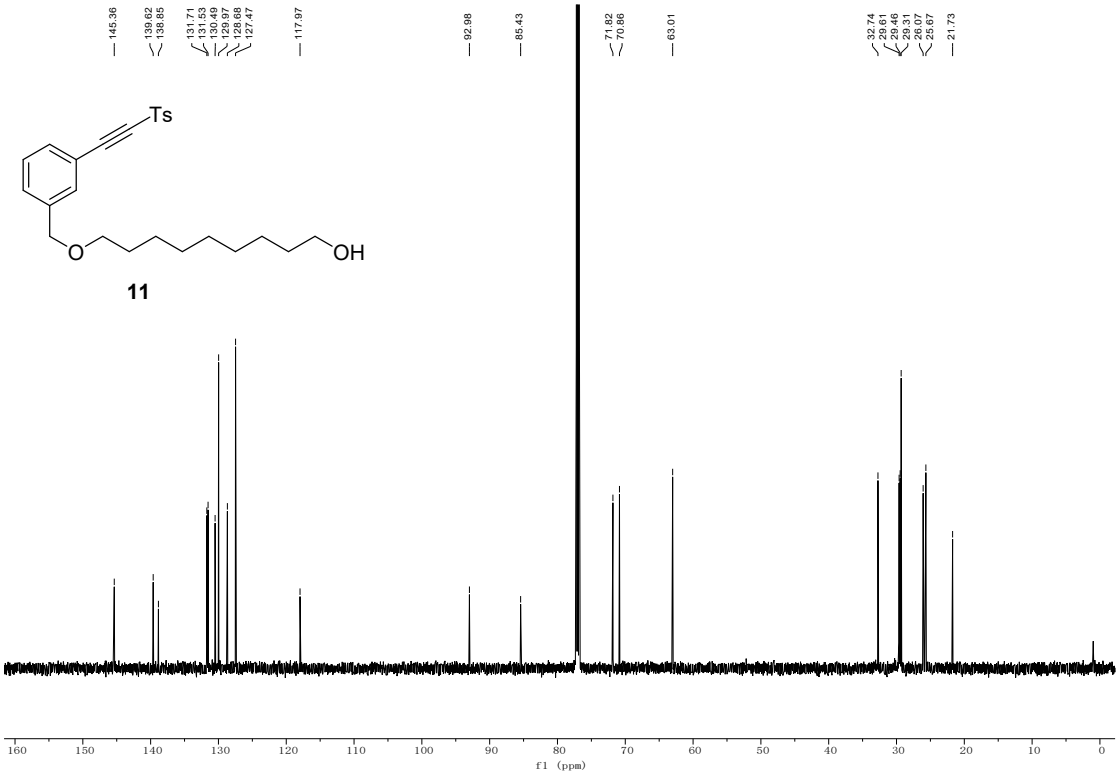
^{13}C NMR Spectrum of 11-6



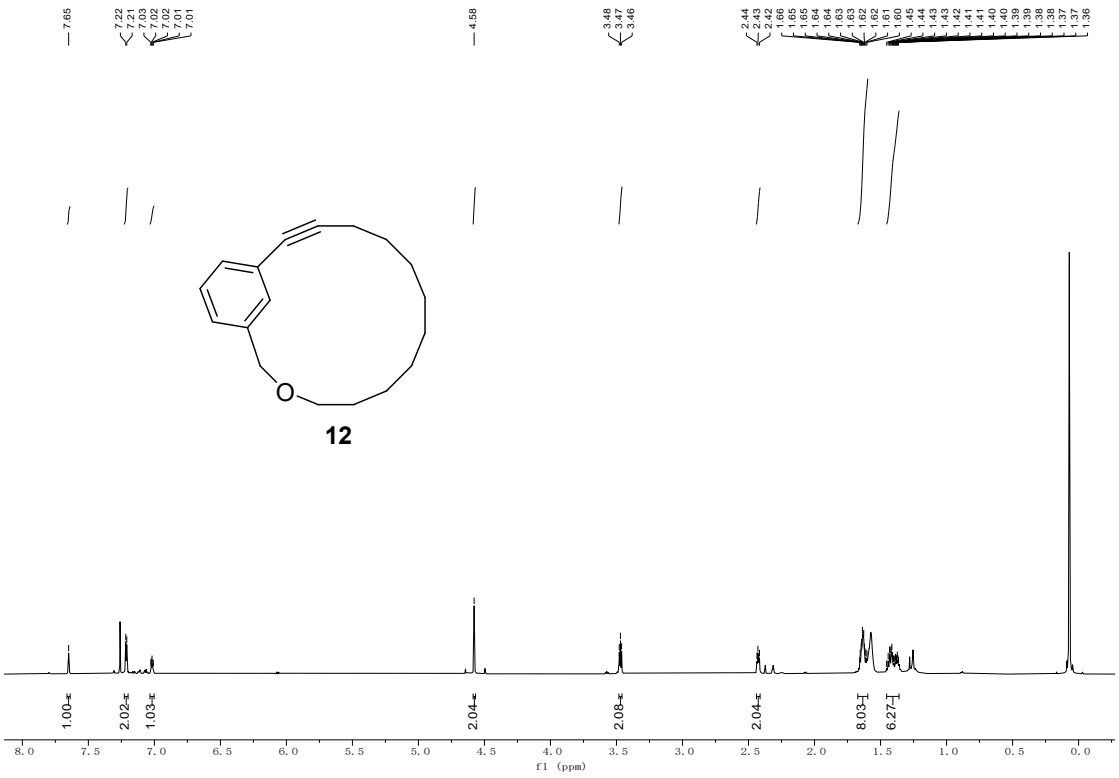
^{1}H NMR Spectrum of 11



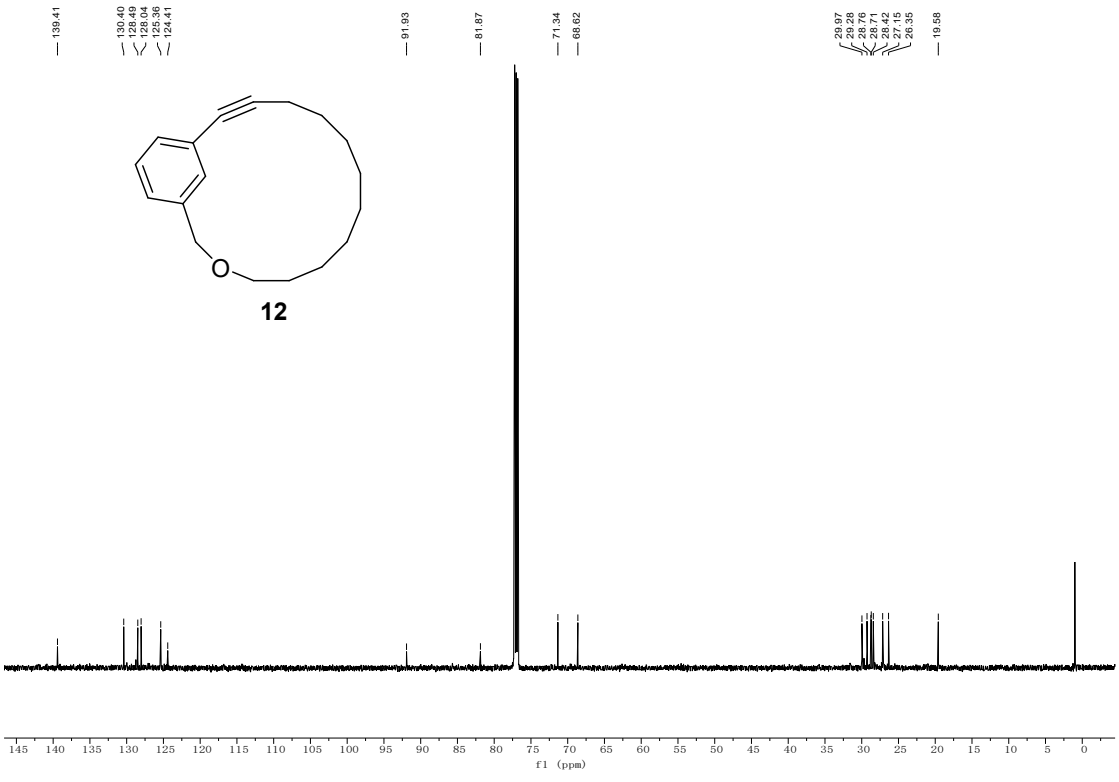
^{13}C NMR Spectrum of 11



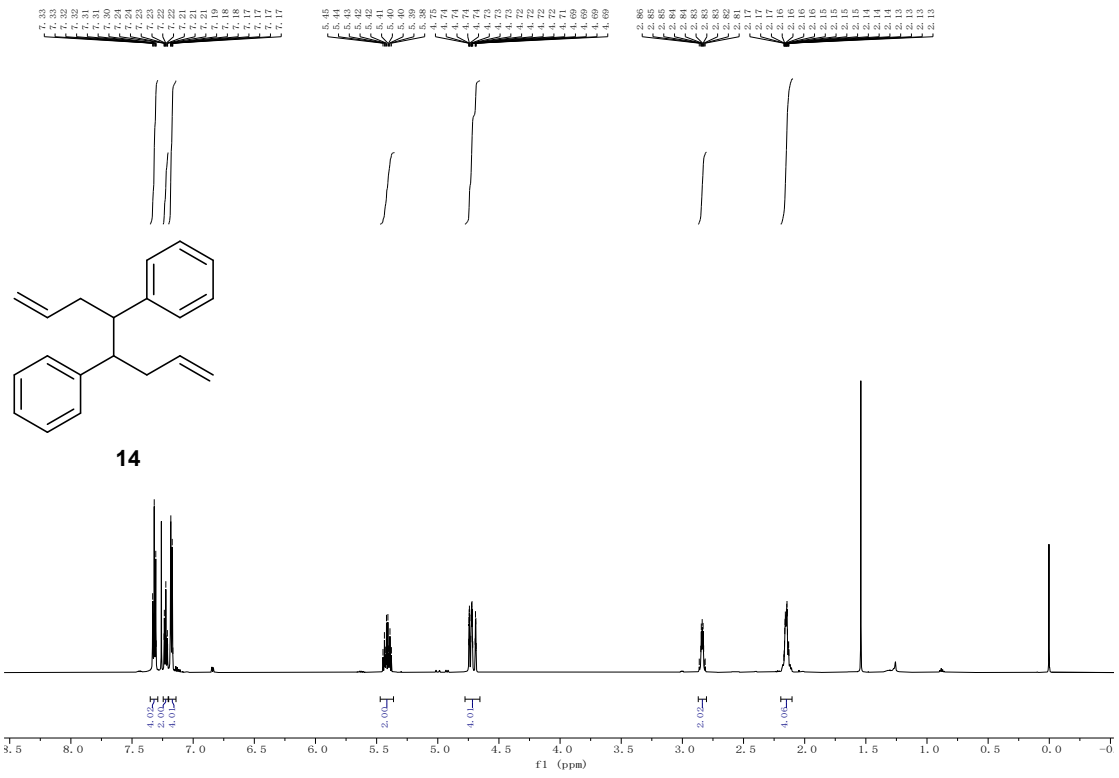
^{1}H NMR Spectrum of 12



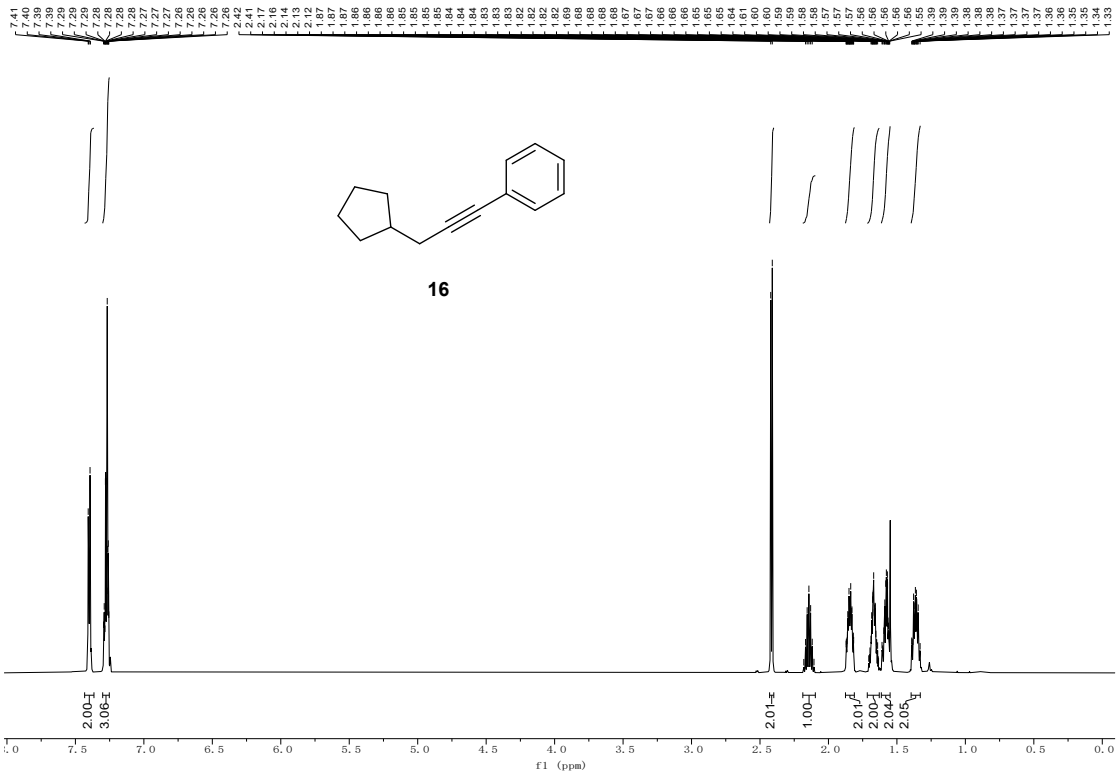
^{13}C NMR Spectrum of 12



^{1}H NMR Spectrum of 14



^{1}H NMR Spectrum of 16



^{13}C NMR Spectrum of 16