Supporting Information

Iron-catalyzed Radical Alkynylation, Alkenylation and Allylation Cascades Enabled by Photoinduced Ligand-to-Metal Charge Transfer

Yining Zhu,[a,b] Han Gao,[b] Jia-Lin Tu,[b] Chao Yang,[b] Lin Guo,[b] Yating Zhao,[a]* and Wujiong Xia[b,c]*

[a] College of Chemical and Material Engineering, Quzhou University, Quzhou 324000, China
[b] State Key Lab of Urban Water Resource and Environment, School of Science, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China
[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China
E-mail: liveagain@126.com; xiawj@hit.edu.cn

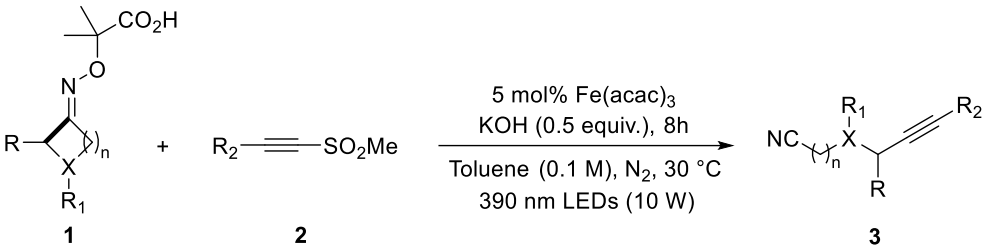
Table Content

1. General Information

Unless otherwise mentioned, all reagents were purchased from commercial sources and used as received. The visible-light mediated reactions were performed on RLH-18 instruments which are purchased from ROGER, China. All yields of products refer to the isolated yields after chromatography. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Quantum-I Plus 400 in $CDCl_3$. For ^{1}H NMR, $CDCl_3$ (δ 7.26 ppm) or tetramethylsilane (TMS, δ 0 ppm) serves as the internal standard; for ^{13}C NMR, $CDCl_3$ (δ 77.16 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration. HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization.

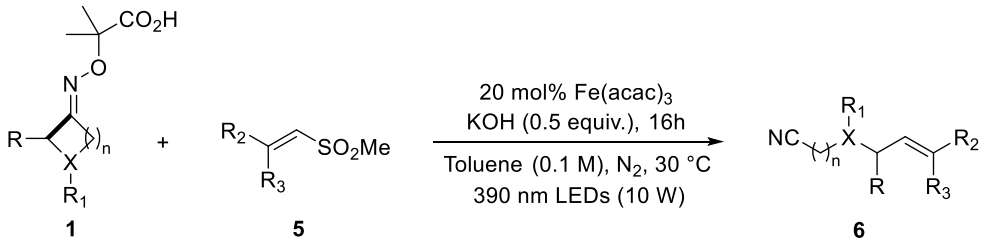
2. General Synthetic Procedures

General procedure 1: cascade ring-opening-alkynylation – GP1:



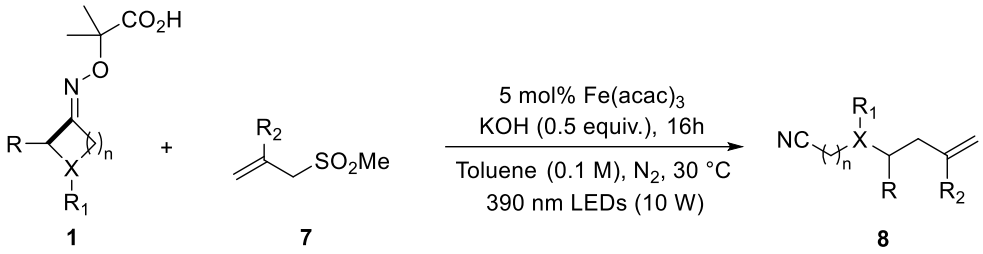
To an oven-dried 25 mL quartz vial equipped with a magnetic stir bar were sequentially added the corresponding $Fe(acac)_3$ (3.5 mg, 5 mol%), oxime acid (0.4 mmol), alkynyl sulfone (0.2 mmol), toluene (2 mL), KOH (5 mg, 0.5 eq.). The vial was degassed, backfilled with nitrogen three times. The vial was then put into the reactor and was irradiated and stirred for 8h under 10 W 390 nm LEDs at 30 ℃. After the reaction was complete, the crude system was filtered, and all volatiles were removed in vacuo and the crude product was purified by column chromatography (1:10 to 1:2 EtOAc:petroleum ether, varied from structures) to obtain corresponding product.

General procedure 2: cascade ring-opening-alkenylation – GP2:



To an oven-dried 25 mL quartz vial equipped with a magnetic stir bar were sequentially added the corresponding $Fe(acac)_3$ (14 mg, 20 mol%), oxime acid (0.4 mmol), alkenyl sulfone (0.2 mmol), toluene (2 mL), KOH (5 mg, 0.5 eq.). The vial was degassed, backfilled with nitrogen three times. The vial was then put into the reactor and was irradiated and stirred for 16 h under 10 W 390 nm LEDs at 30 ℃. After the reaction was complete, the crude system was filtered, and all volatiles were removed in vacuo and the crude product was purified by column chromatography (1:10 to 2:1 EtOAc:petroleum ether, varied from structures) to obtain corresponding product.

General procedure 3: cascade ring-opening-allylation – GP3:



To an oven-dried 25 mL quartz vial equipped with a magnetic stir bar were sequentially added the corresponding $Fe(acac)_3$ (3.5 mg, 5 mol%), oxime acid (0.4 mmol), allyl sulfone (0.2 mmol), toluene (2 mL), KOH (5 mg, 0.5 eq.). The vial was degassed, backfilled with nitrogen three times. The vial was then put into the reactor and was irradiated and stirred for 16 h under 10 W 390 nm LEDs at 30 ℃. After the reaction was complete, the crude system was filtered, and all volatiles were removed in vacuo and the crude product was purified by column chromatography (1:10 EtOAc:petroleum ether) to obtain corresponding product.

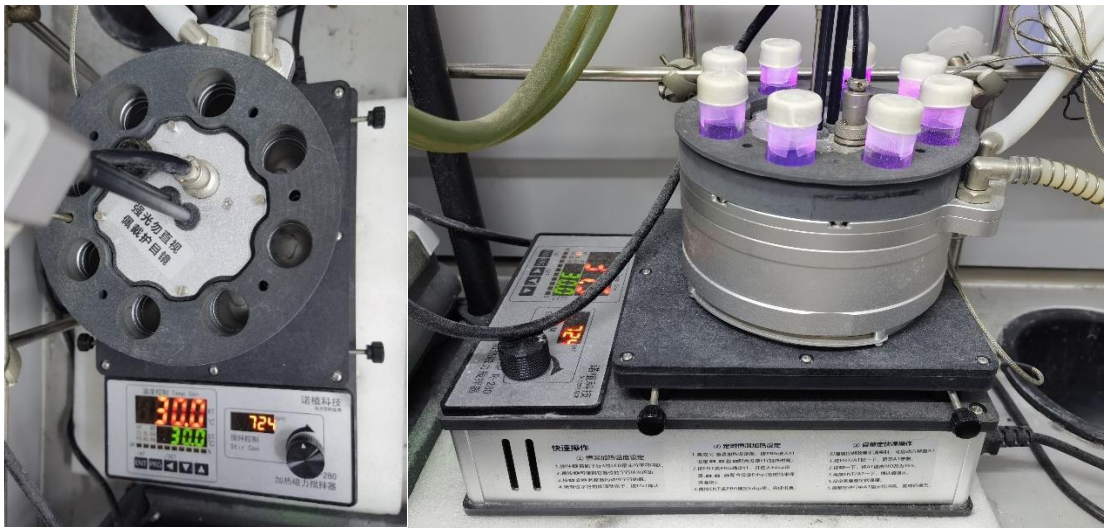
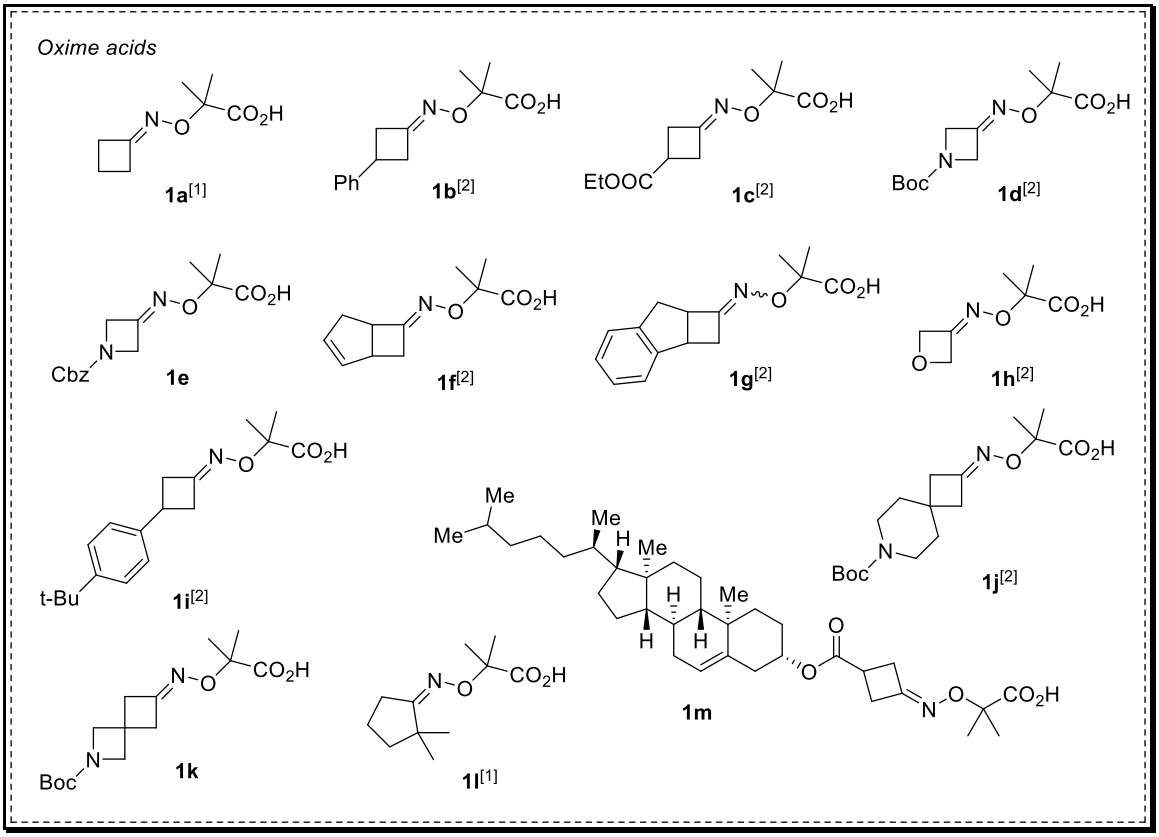


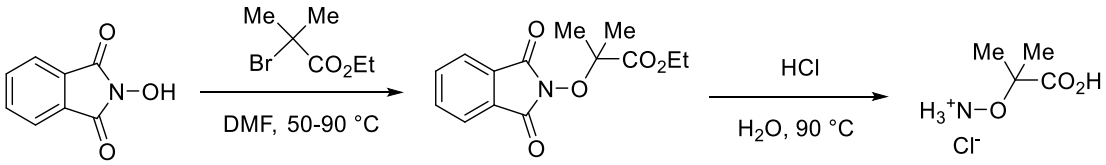
Figure S1. Photoreactor Setup

3. Synthesis of Starting Materials

3.1 Oxime acids used in this work



Synthesis of the oximes:

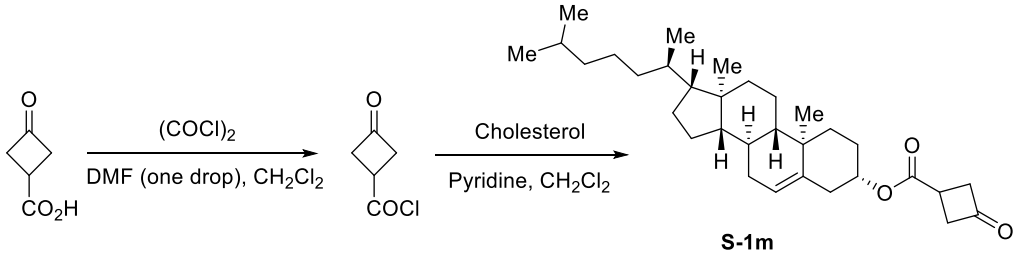


Step1: Following a reported procedure,[1] N-hydroxyphthalimide (9.00 g, 55.2 mmol, 1.0 equiv.) was suspended in DMF (21.6 mL). The suspension was heated to 50 °C, leading to the complete dissolution of the solid to provide a clear bright yellow solution. Ethyl 2-bromo-2-methylpropanoate (9.4 mL, 66 mmol, 1.2 equiv.) was then added, followed by triethylamine (10.9 mL, 78.0 mmol, 1.42 equiv.). The mixture was then stirred at 90 °C. After 5 hours since the beginning of the reaction, heating was stopped and the brown mixture was allowed to cool down to room temperature. The mixture was then cooled in ice for 20 min. The bright red liquid was then filtered off to furnish a solid, the solid was washed with two portions of water (50 mL each) and dried under high vacuum for 5 hours. Ethyl 2-((1,3-dioxoisoindolin-2-yl)oxy)-2-methylpropanoate (13.6 g, 49.1 mmol, 89% yield) was obtained as a pale brown-colored solid.

Step2: The obtained Ethyl 2-((1,3-dioxoisoindolin-2-yl)oxy)-2-methylpropanoate was suspended in aq. HCl (6.0 N; 81.8 mL, 491 mmol, 10.0 equiv.). The pale brown suspension was stirred, while being heated to 90 °C. After 4 hours, heating was stopped and the mixture was allowed to cool down to room temperature. The reaction flask was stored at 4 °C overnight. After 16 hours, the solids were filtered off. The collected pale yellow clear aqueous solution was concentrated under reduced pressure. The resulting pale-yellow solid was further dried at 65 °C under vacuum for 3 hours. It was then suspended in EtOAc (41 mL) and EtOH (1.8 mL) and the mixture was stirred at reflux for 20 minutes. It was then allowed to slowly cool down to room temperature and then stored at -18 °C for 24 hours. The crystalline colorless solid was filtered and washed with EtOAc/Pentane (30/10 mL) and pentane (20 mL). (Aminooxy)-2-methylpropanoic acid hydrochloride (6.50 g, 41.7 mmol, 85%) was obtained as a white solid.

Spectroscopic datas were consistent with those previously reported.[1]

Synthesis of cholesterol ketone:



S-1m

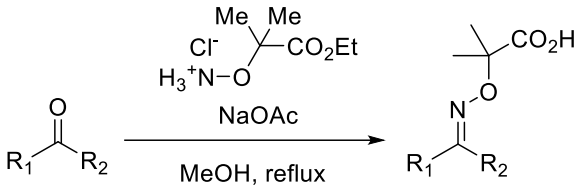
Step1: 3-oxocyclobutane-1-carboxylic acid (570 mg, 5 mmol, 1.0 equiv.) was dissolved in 20 mL CH_2Cl_2 in a 100 mL round-bottom flask with a stir bar, one drop of DMF was added, then oxalyl chloride (847 μL, 10 mmol, 2.0 equiv.) was slowly added into the mixture at room temperature, the obtained solution was stirred for 2 h at room temperature. The solvent was evaporated and the crude acyl chloride was used without further purification.

Step2: Cholesterol (1.93 g, 5 mmol, 1.0 equiv.) was dissolved in 40 mL CH_2Cl_2 in a 100 mL round-bottom flask with a stir bar, then pyridine (404 μL, 5 mmol, 1.0 equiv.) was added, to the stirring mixture, a solution of the crude acyl chloride in 20 mL CH_2Cl_2 was slowly added at room temperature. After the addition was finished, the reaction mixture was stirred for further 1 h at room temperature, then the solution was concentrated. The crude residue was purified via column chromatography (silica gel, petroleum ether/ethyl acetate mixtures as the eluant) to afford the product ketone as an white solid (1.54 g, 3.75 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (d, *J* = 5.0 Hz, 1H), 4.74 – 4.60 (m, 1H), 3.47 – 3.35 (m, 2H), 3.33 – 3.13 (m, 3H), 2.34 (d, *J* = 8.2 Hz, 2H), 2.06 – 1.94 (m, 2H), 1.92 – 1.76 (m, 3H), 1.70 – 1.42 (m, 8H), 1.41 – 1.26 (m, 4H), 1.23 – 1.07 (m, 7H), 1.03 (s, 5H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.68 (s, 3H).

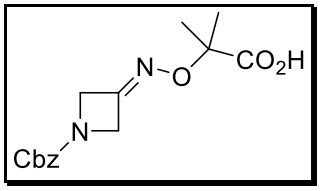
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.1, 173.5, 139.4, 123.1, 75.0, 56.8, 56.2, 51.7, 50.1, 42.4, 39.8, 39.6, 38.1, 37.0, 36.7, 36.3, 35.9, 32.0, 31.9, 28.3, 28.1, 27.8, 27.7, 24.4, 23.9, 22.9, 22.7, 21.1, 19.4, 18.8, 12.0.
HRMS (ESI): calcd for $[M+Na]^+$ 505.3652, found 505.3663.

General procedure for the synthesis of oxime acids – GP4:



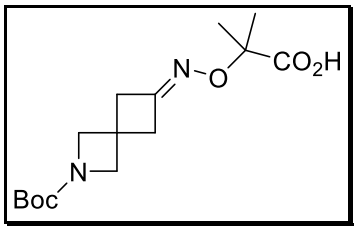
Following a reported procedure,[1] a solution of ketone (5.0 mmol, 1.0 equiv.) in MeOH (15 mL) was treated with 2-(aminooxy)-2-methylpropanoic acid hydrochloride (778 mg, 6.0 mmol, 1.2 equiv.), sodium acetate (984 mg, 12 mmol, 2.4 equiv.) and heated to reflux for 6.0 hours. The mixture was then allowed to cool to room temperature, concentrated under reduced pressure, and aq. Na_2CO_3 (2.0 M; 20 mL) was added to dissolve product in the aqueous solution. The resulting solution was extracted once with ethyl acetate and the organic layer was washed with aq. Na_2CO_3 (2.0 M; 2×15 mL). The combined aqueous extracts were then acidified by careful addition of aq. HCl solution (6.0 N) until pH < 2, and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum to provide the corresponding product (yield varied from 64% to 86%).

Characterization data of new oxime acids:



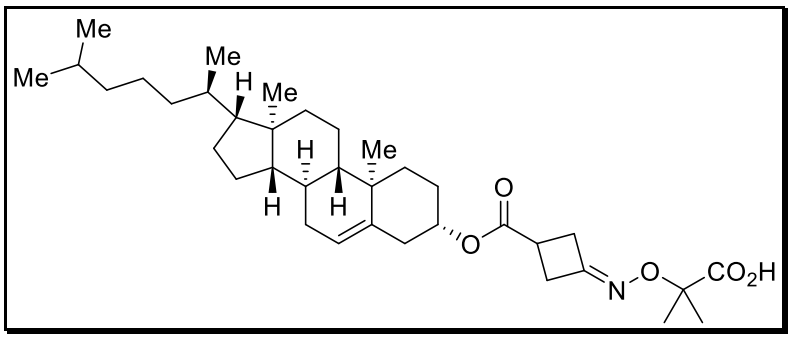
2-(((1-((benzyloxy)carbonyl)azetidin-3-ylidene)amino)oxy)-2-methylpropanoic acid (1e)

Following **GP4**, **1e** was given as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 5.13 (s, 2H), 4.71 (dq, *J* = 5.2, 2.5 Hz, 4H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 156.6, 148.6, 136.1, 128.6, 128.4, 128.2, 81.7, 67.5, 58.6, 24.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 329.1108, found 329.1105.



2-(((2-(tert-butoxycarbonyl)-2-azaspiro[3.3]heptan-6-ylidene)amino)oxy)-2-methylpropanoic acid (1k)

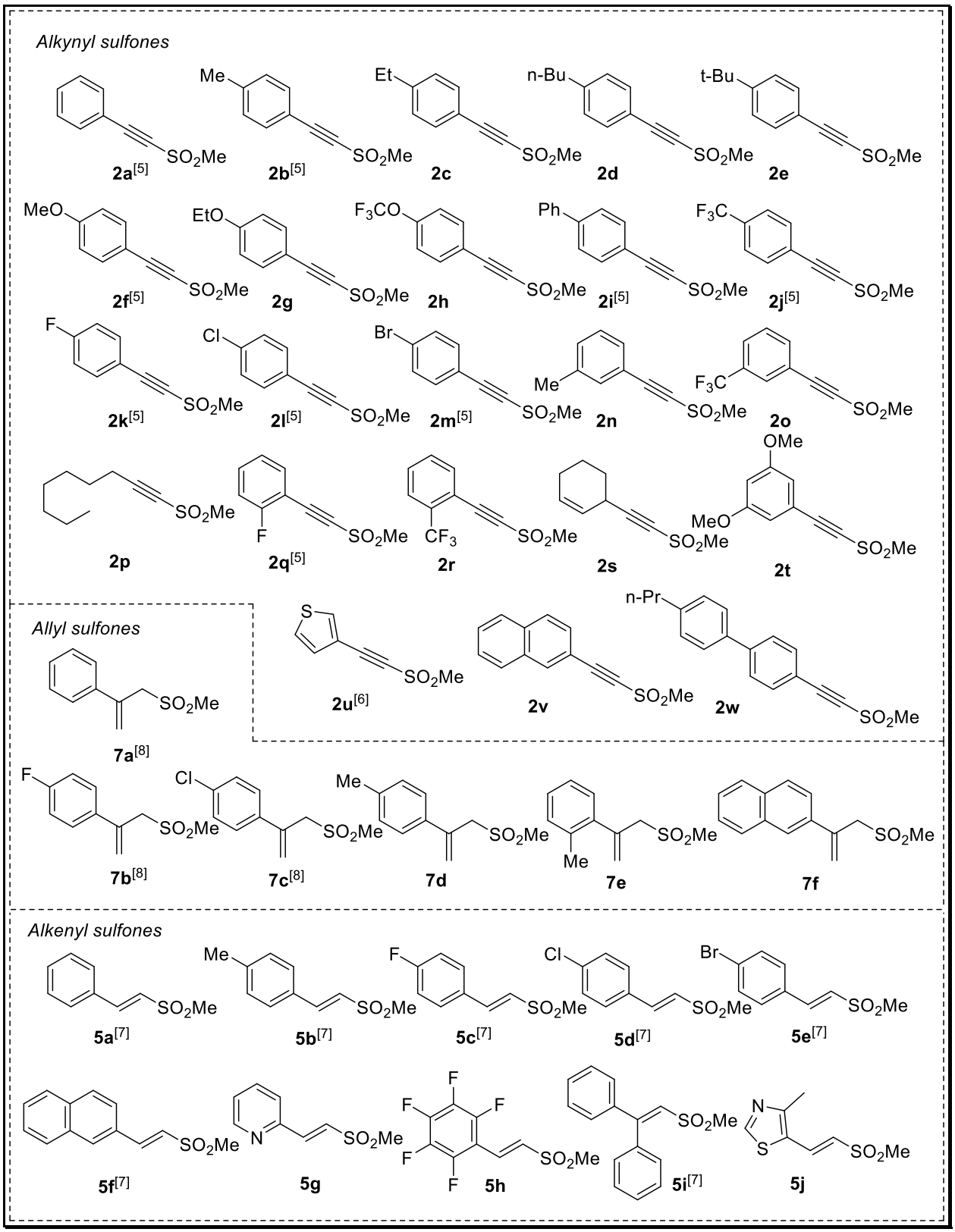
Following **GP4**, **1k** was given as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (m, 4H), 3.13 (m, 4H), 1.50 (s, 6H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): 178.6, 156.3, 154.7, 81.1, 80.0, 61.0, 43.1, 42.3, 32.0, 28.5, 24.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 335.1577, found 335.1593.



2-(((3-((((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)cyclobutylidene)amino)oxy)-2-methylpropanoic acid (1m)

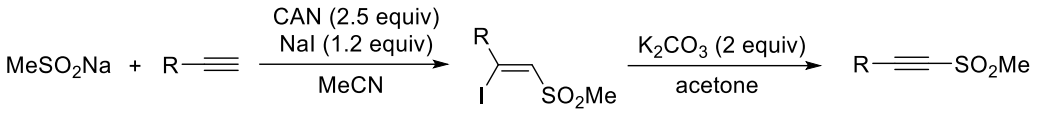
Following **GP4**, **1m** was given as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 1H), 5.39 (s, 1H), 4.65 (m, 1H), 3.18 (m, 5H), 2.33 (d, *J* = 8.2 Hz, 2H), 2.07 – 1.92 (m, 2H), 1.86 (m, 3H), 1.64 – 1.41 (m, 14H), 1.40 – 1.26 (m, 4H), 1.20 – 1.08 (m, 6H), 1.03 (s, 4H), 0.97 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.1 Hz, 3H), 0.86 (d, *J* = 2.2 Hz, 3H), 0.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.0, 173.4, 156.0, 139.5, 122.9, 81.0, 74.8, 56.7, 56.2, 50.0, 42.4, 39.8, 39.6, 38.1, 37.0, 36.6, 36.2, 35.8, 35.6, 35.2, 32.0, 31.9, 31.6, 28.3, 28.1, 27.7, 24.3, 24.2, 24.0, 23.9, 22.9, 22.6, 21.1, 19.4, 18.8, 11.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 606.4129, found 606.4116.

Sulfone substrates used in this work



3.2 Sulfone substrates

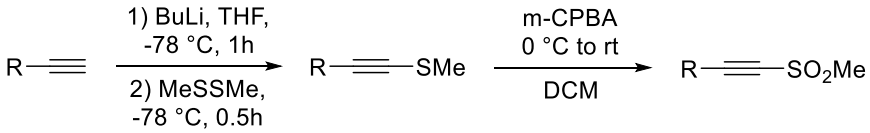
General procedure for the synthesis of alkynyl sulfones – GP5



Step1: Following a reported procedure,[3] An oven-dried 3-neck 100 mL round-bottom flask was charged with sodium methanesulfinate (354 mg, 3.0 mmol, 1.2 equiv.) and NaI (449 mg, 3.0 mmol, 1.2 equiv.) under nitrogen atmosphere. Dry MeCN (15 mL) and the alkyne (2.5 mmol, 1.0 equiv.) was added and the flask was degassed and refilled with nitrogen 3 times. Then CAN (3.4 g, 6.25 mmol, 2.5 equiv.) in dry MeCN (25 mL) was added dropwise by pressure-equalizing dropping funnel. The reaction was checked via TLC, and when completed, quenched with brine (50 mL). Then, the crude mixture was extracted with ethyl acetate. The organic phase was washed again with brine (3×30 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure to get crude iodosulfones. These products were directly used in the next step.

Step2: The crude iodosulfones were dissolved in acetone (25 mL) and refluxed with K_2CO_3 (2 equiv.) to completion. The reaction was checked via TLC, and once completed carbonate was filtered away, acetone was removed via rotary evaporation and the crude was purified via column chromatography (1:5 EtOAc:petroleum ether) to obtain the sulfone product (yield varied from 42% to 81%).

General procedure for the synthesis of alkynyl sulfones – GP6

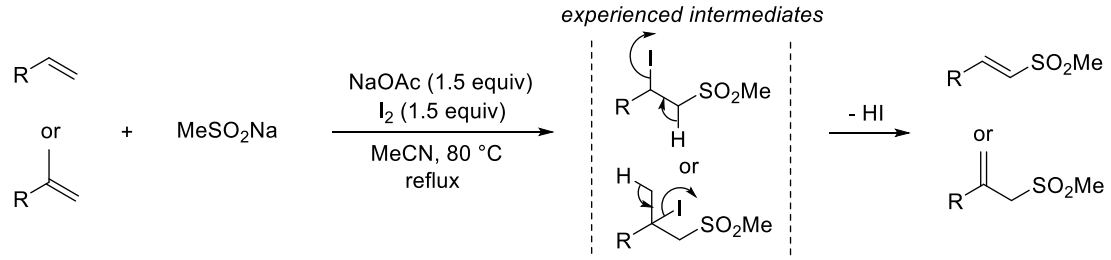


Step1: To a dry and degassed 3-necked round bottom flask was charged with terminalalkyne (5.0 mmol) and anhydrous THF (50 mL). The solution was cooled to –78 °C under dry nitrogen atmosphere, and n-butyllithium (2.5 M in hexanes, 2.20 mL, 1.1 equiv.) was added dropwise. The reaction mixture was stirred for 1 h at –78 °C, and dimethyl disulfide (532 µL, 6.0 mmol, 1.2 equiv.) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 0.5 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (30 mL) and extracted with DCM (3×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude alkynylsulfide.

Step2: The crude alkynylsulfide was immediately oxidized to the corresponding alkynylsulfones. m-Chloroperoxybenzoic acid (85%, 3.045 g, 15.0 mmol, 3.0 equiv.) was added portion-wise to a stirred solution of the crude alkynylsulfide in dichloromethane (50 mL) at 0 °C. Then, the reaction was stirred at room

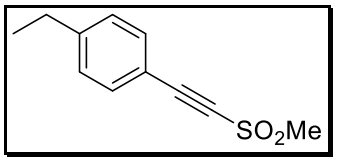
temperature overnight. Next, aqueous K_2CO_3 (10%, 50 mL) was added, and the emulsion was extracted by DCM (3×50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, the solvent was removed via rotary evaporation, and the product was purified by column chromatography (1:5 EtOAc:petroleum ether) to obtain the sulfone product (yields varied from 62% to 92%).

General procedure for the synthesis of alkenyl sulfones and allyl sulfones – GP7



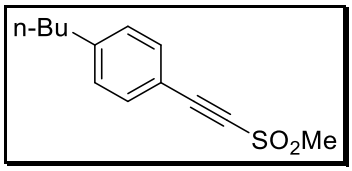
Following a reported procedure,[4] I_2 (1.14 g, 4.5 mmol, 1.5 equiv.) was added to a suspension mixture of styrene derivative (3.0 mmol, 1.0 equiv.), sodium methanesulfinate (918 mg, 9.0 mmol, 3.0 equiv.), and NaOAc (612 mg, 4.5 mmol, 1.5 equiv.) in MeCN (30 mL), and the reaction mixture was vigorously stirred at refluxing temperature for 2 hours. Upon completion of the reaction, the reaction mixture was quenched by the addition of saturated aqueous sodium thiosulfate ($Na_2S_2O_3$) (10 mL) and basified with saturated aqueous sodium hydrogen carbonate ($NaHCO_3$) (10 mL). Further stirring was followed by extraction with ethyl acetate (3×20 mL). The combined organic extracts were washed with water (20 mL), and brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (1:3 EtOAc:petroleum ether) to furnish the product (yield varied from 61% to 84%).

Characterization data of new sulfone substrates



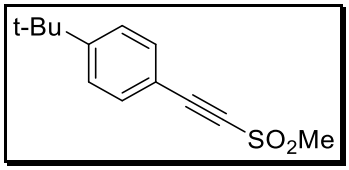
1-Ethyl-4-[2-(methylsulfonyl)ethynyl]benzene (2c)

Following **GP5**, **2c** was given as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.30 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 133.1, 128.6, 114.7, 92.4, 84.1, 47.0, 29.2, 15.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 231.0450, found 231.0462.



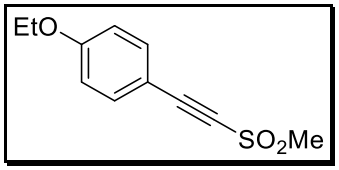
1-Butyl-4-[2-(methylsulfonyl)ethynyl]benzene (2d)

Following **GP2**, **2d** was given as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.30 (s, 3H), 2.69 – 2.62 (m, 2H), 1.62 – 1.57 (m, 2H), 1.35 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 133.0, 129.1, 114.6, 92.5, 84.1, 47.0, 35.9, 33.2, 22.4, 14.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 259.0763, found 259.0782.



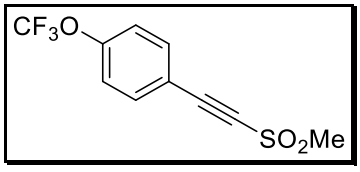
1-(1,1-Dimethylethyl) -4-[2-(methylsulfonyl)ethynyl]benzene (2e)

Following **GP5**, **2e** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 3.30 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 132.9, 126.0, 114.4, 92.4, 84.1, 47.0, 35.3, 31.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 259.0763, found 259.0758.



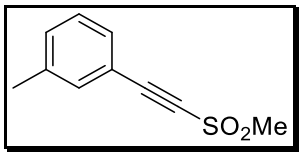
1-Ethoxy-4-[2-(methylsulfonyl)ethynyl]benzene (2g)

Following **GP5**, **2g** was given as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.29 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 134.9, 115.1, 108.9, 93.0, 83.8, 64.0, 47.0, 14.7. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 247.0399, found 247.0395.



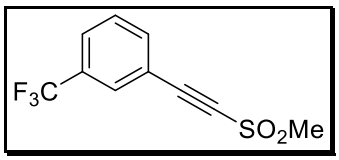
1-(Trifluoromethoxy)-4-[2-(methylsulfonyl)ethynyl]benzene (2h)

Following **GP5**, **2h** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 134.9, 121.6, 120.3 (q, *J* = 259.1 Hz), 116.1, 89.8, 85.2, 46.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.7. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 286.9960, found 286.9982.



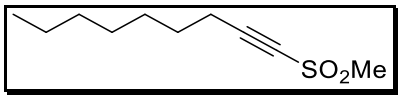
1-Methyl-3-[2-(methylsulfonyl)ethynyl]benzene (2n)

Following **GP5**, **2n** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 3.31 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 133.4, 132.8, 130.1, 128.8, 117.4, 92.1, 84.2, 46.9, 21.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 217.0294, found 217.283.



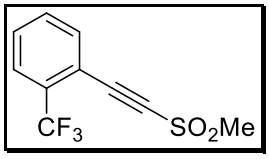
1-[2-(Methylsulfonyl)ethynyl]-3-(trifluoromethyl)benzene (2o)

Following **GP5**, **2o** was given as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.84 – 7.74 (m, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, δ 131.7 (q, *J* = 33.4 Hz), 129.8 (q, *J* = 4.1 Hz), 129.7, 128.4 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.6 Hz), 118.7, 89.1, 85.6, 46.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 271.0011, found 271.0014.



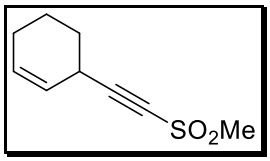
1-(methylsulfonyl)non-1-yne (2p)

Following **GP6**, **2c** was given as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.61 (p, *J* = 7.5, 6.6 Hz, 2H), 1.39 (d, *J* = 8.1 Hz, 2H), 1.30 (d, *J* = 8.9 Hz, 6H), 0.89 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 95.9, 77.4, 46.8, 31.6, 28.9, 28.7, 27.1, 22.7, 18.8, 14.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 225.0920, found 225.0919.



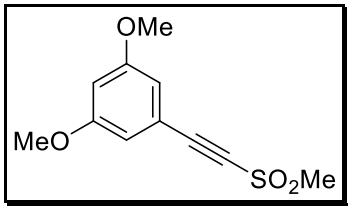
1-[2-(Methylsulfonyl)ethynyl]-2-(trifluoromethyl)benzene (2r)

Following **GP5**, **2r** was given as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 2H), 7.64 (dd, *J* = 5.9, 3.0 Hz, 2H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, δ 133.1 (q, *J* = 31.6 Hz), 132.1, 131.7, 126.6 (q, *J* = 4.7 Hz), 123.0 (q, *J* = 273.4 Hz). 115.8, 88.9, 86.9, 46.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 271.0011, found 271.0000.



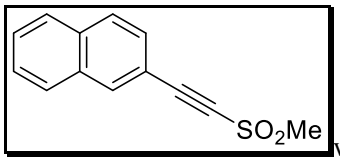
1-((methylsulfonyl)ethynyl)cyclohex-1-ene (2s)

Following **GP6**, **2s** was given as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (dq, *J* = 4.0, 2.0 Hz, 1H), 3.22 (s, 3H), 2.18 (tdd, *J* = 6.1, 4.7, 2.6 Hz, 4H), 1.69 – 1.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 117.0, 93.8, 82.3, 46.9, 27.4, 26.1, 21.6, 20.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 207.0450, found 207.0436.



1,3-Dimethoxy-5-[2-(methylsulfonyl)ethynyl]benzene (2t)

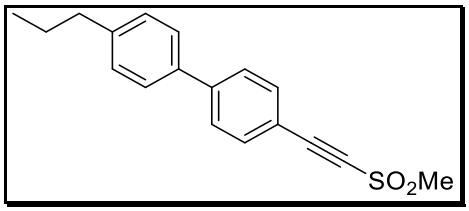
Following **GP5**, **2t** was given as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 2.3 Hz, 2H), 6.60 (t, *J* = 2.3 Hz, 1H), 3.80 (s, 6H), 3.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 118.7, 110.6, 105.3, 91.7, 83.8, 55.7, 46.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 263.0349, found 263.0349.



w’hi

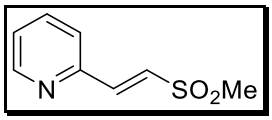
2-[2-(Methylsulfonyl)ethynyl]naphthalene (2v)

Following **GP5**, **2v** was given as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.89 – 7.80 (m, 3H), 7.62 – 7.51 (m, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 134.3, 132.5, 128.8, 128.7, 128.4, 128.1, 127.6, 127.5, 114.6, 92.2, 84.6, 47.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 253.0294, found 253.0294.



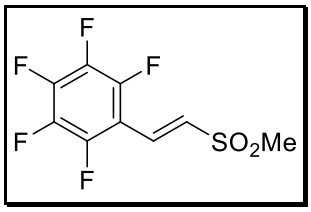
4-Propyl-4′-[2-(Methylsulfonyl)ethynyl]-1,1′-biphenyl (2w)

Following **GP5**, **2w** was given as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 3.31 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.67 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 143.4, 136.7, 133.4, 129.3, 127.2, 127.0, 115.7, 92.0, 84.9, 46.9, 37.7, 24.6, 13.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 321.0920, found 321.0925.



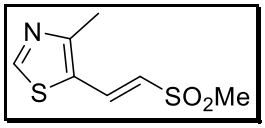
(E)-2-(2-(methylsulfonyl)vinyl)pyridine (5g)

Following **GP7**, **5g** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.9 Hz, 0H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.67 – 7.50 (m, 2H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 7.7, 4.8 Hz, 1H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 150.4, 142.2, 137.2, 130.6, 125.7, 125.3, 43.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 206.0246, found 206.0233.



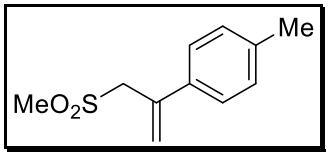
1,2,3,4,5-Pentafluoro-6-[(1E)-2-(methylsulfonyl)ethenyl]benzene (5h)

Following **GP7**, **5h** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.9 Hz, 1H), 7.31 (d, *J* = 15.9 Hz, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 144.6, 144.0, 141.4, 139.2, 136.7, 134.1, 134.1, 134.0, 127.7, 107.9, 42.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.1, -138.1, -138.1, -138.1, -138.1, -138.1, -138.2, -138.2, -148.2, -148.2, -148.2, -148.2, -148.3, -148.3, -160.4, -160.4, -160.4, -160.4, -160.5, -160.5, -160.5, -160.5. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 294.9823, found 294.9828.



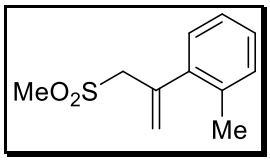
4-Methyl-5-[(1E)-2-(methylsulfonyl)ethenyl]thiazole (5j)

Following **GP7**, **5j** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.77 (d, *J* = 15.0 Hz, 1H), 6.66 (d, *J* = 15.0 Hz, 1H), 3.05 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 154.2, 133.4, 126.9, 125.8, 43.4, 15.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 225.9967, found 225.9969.



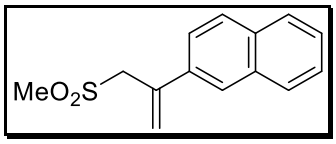
1-methyl-4-(3-(methylsulfonyl)prop-1-en-2-yl)benzene (7d)

Following **GP7**, **7d** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.73 (s, 1H), 5.51 (s, 1H), 4.18 (s, 2H), 2.71 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.6, 135.8, 129.7, 126.3, 121.4, 60.9, 40.3, 21.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 233.0607, found 233.0620.



1-methyl-2-(3-(methylsulfonyl)prop-1-en-2-yl)benzene (7e)

Following **GP7**, **7f** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 5.72 (s, 1H), 5.43 (s, 1H), 4.06 (s, 2H), 2.64 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.1, 135.0, 130.9, 128.8, 128.3, 126.2, 124.8, 62.7, 40.9, 20.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 233.0607, found 233.0617.



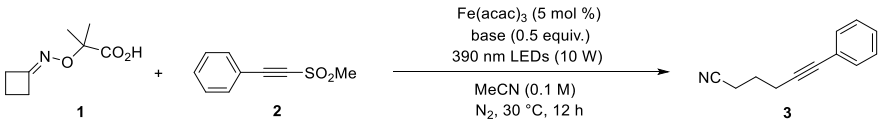
2-(3-(methylsulfonyl)prop-1-en-2-yl)naphthalene (7f)

Following **GP7**, **7e** was given as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.82 – 7.76 (m, 3H), 7.54 (d, *J* = 8.6, 1.9 Hz, 1H), 7.47 – 7.43 (m, 2H), 5.84 (s, 1H), 5.58 (s, 1H), 4.24 (s, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.9, 133.3, 133.2, 128.8, 128.4, 127.7, 126.8, 126.8, 125.6, 124.1, 122.7, 60.9, 40.4. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 269.0607, found 269.0601.

4. Optimization of Reaction Conditions

Optimization of cascade ring-opening-alkynylation:

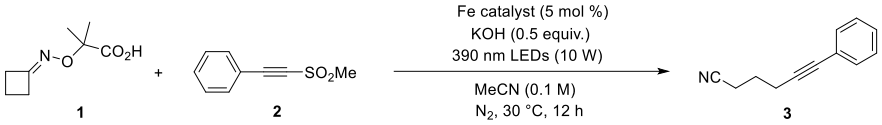
Table S1. Optimization of bases



Entry	Base	Yield%[a]
1	$NaHCO_3$	33
2	K_3PO_4	N.R.
3	Na_2CO_3	< 5%
4	K_2CO_3	31
5	Cs_2CO_3	N.R.
6	KOH	45
7	DABCO	< 5%
8	Et_3N	35
9	TMG	23

[a] conditions: **1** (0.4 mmol), **2** (0.2 mmol), $Fe(acac)_3$ (5 mol%), base (0.5 eq.) in MeCN under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram. N.R.: no reaction.

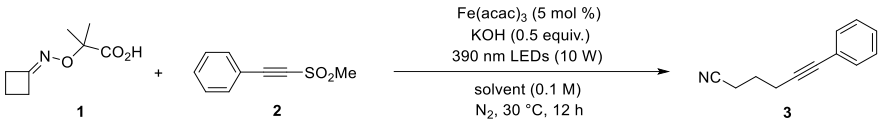
Table S2. Optimization of Fe catalyst



Entry	Solvent	Yield%[a]
1	$Fe(acac)_3$	45
2	$FeCl_3$	38
3	$Fe_2(SO_4)_3$	N.R.
4	$Fe(NO_3)_3$	23
5	$Fe(OTF)_3$	N.R.

[a] conditions: **1** (0.4 mmol), **2** (0.2 mmol), Fe catalyst (5 mol%), KOH (0.5 eq.) in MeCN under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram. N.R.: no reaction.

Table S3. Optimization of solvents

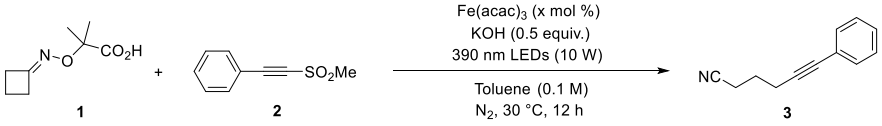


1 2 3

Entry	Solvent	Yield%[a]
2	Dry MeCN	45
3	Dry DCE	48
6	Dry DCM	23
7	Toluene	65
9	Dry THF	N.R.

[a] conditions: **1** (0.4 mmol), **2** (0.2 mmol), $Fe(acac)_3$ (5 mol%), KOH (0.5 eq.) under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram. N.R.: no reaction.

Table S4. Optimization on loadings of Fe catalyst

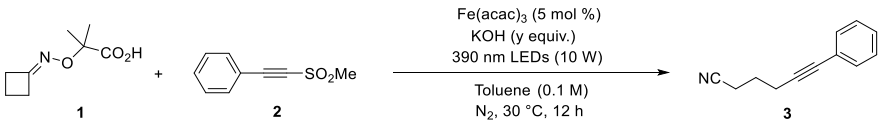


1 2 3

Entry	x	Yield%[a]
1	5	65
2	10	32
3	20	< 5%

[a] conditions: **1** (0.4 mmol), **2** (0.2 mmol), KOH (0.5 eq.) in toluene under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram.

Table S5. Optimization on loadings of base

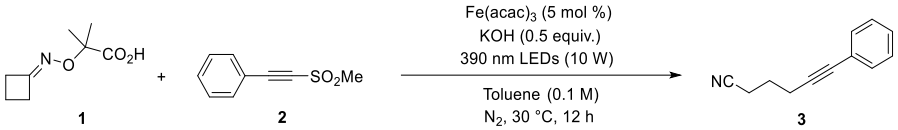


1 2 3

Entry	y	Yield%[a]
1	0	N.R.
2	0.2	25
3	0.5	65
4	1.0	45

[a] conditions: **1** (0.4 mmol), **2** (0.2 mmol), $Fe(acac)_3$ (5 mol%) in toluene, under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram.

Table S6. Optimization on loadings of oxime acid

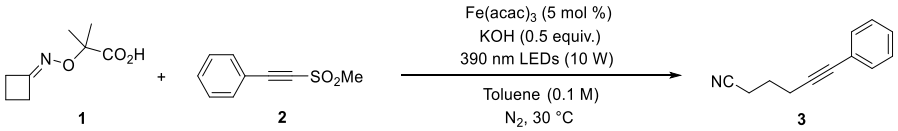


1 2 3

Entry	Equiv. of oximic acid	Yield%[a]
1	1	31
2	1.5	45
3	2	65
4	3	53

[a] conditions: **2** (0.2 mmol), $Fe(acac)_3$ (5 mol%), KOH (0.5 eq.) in toluene under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram.

Table S7. Optimization of reaction time



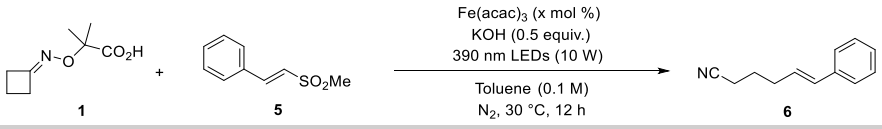
1 2 3

Entry	Reaction time	Yield%[a]
1	4	71
2	8	88
3	12	67
4	24	62

[a] conditions: **1** (0.4 mmol), **2** (0.2 mmol), $Fe(acac)_3$ (5 mol%), KOH (0.5 eq.) in toluene under 10 W 390 nm LEDs, 30 ℃. The isolated yield was calculated after chromatogram.

Optimization of cascade ring-opening-alkenylation:

Table S8. Optimization on loadings of Fe catalyst

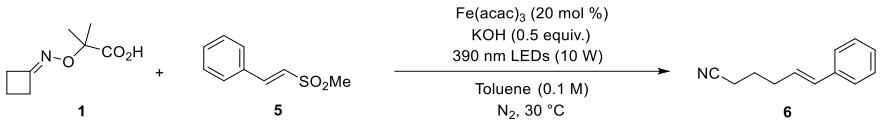


1 5 6

Entry	x	Yield%[a]
1	5	42
2	10	49
3	15	53
4	20	65

[a] conditions: **1** (0.4 mmol), **5** (0.2 mmol), KOH (0.5 eq.) in toluene under 10 W 390 nm LEDs for 12 h, 30 ℃. The isolated yield was calculated after chromatogram.

Table S9. Optimization on reaction time



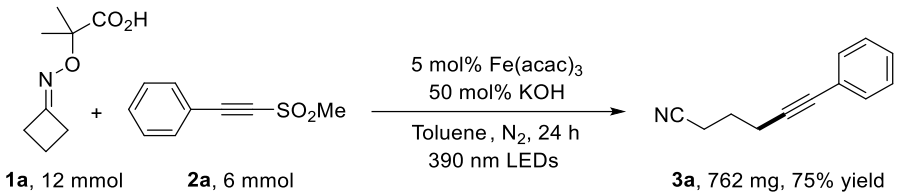
1 5 6

Entry	Reaction time	Yield%[a]
1	8	39
2	12	65
3	16	72
4	24	69

[a] conditions: **1** (0.4 mmol), **5** (0.2 mmol), $Fe(acac)_3$ (5 mol%), KOH (0.5 eq.) in toluene under 10 W 390 nm LEDs, 30 ℃. The isolated yield was calculated after chromatogram.

5. Gram Scale Reaction

General procedure: To an oven-dried 250 mL flask equipped with a magnetic stir bar were sequentially added the corresponding KOH (168 mg, 50 mol%), $Fe(acac)_3$ (106 mg, 5 mol%), oxime acid (12 mmol), sulfone (6 mmol), toluene (60 mL). The flask was degassed, backfilled with nitrogen three times and equipped with a N_2 balloon. The flask was then put under the 390 nm LED light strips and was irradiated and stirred for 24 h at around 30 ℃ by TLC monitoring. After the reaction was complete, the crude system was filtered, and all volatiles were removed in vacuo and the crude product was purified by column chromatography (1:10 EtOAc:petroleum ether) to obtain the corresponding product.



According to the general procedure, the purified internal alkyne product was obtained in 762 mg, 75% yield.

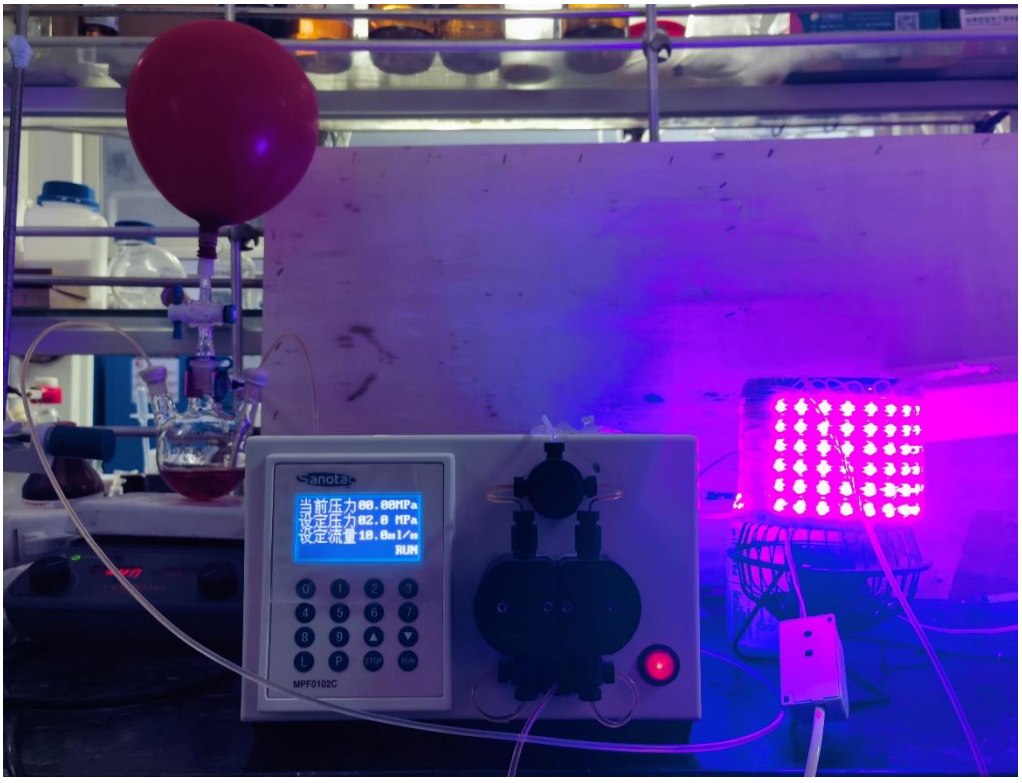


Figure S2. Gram-scale synthesis in continuous flow

6. Mechanistic studies

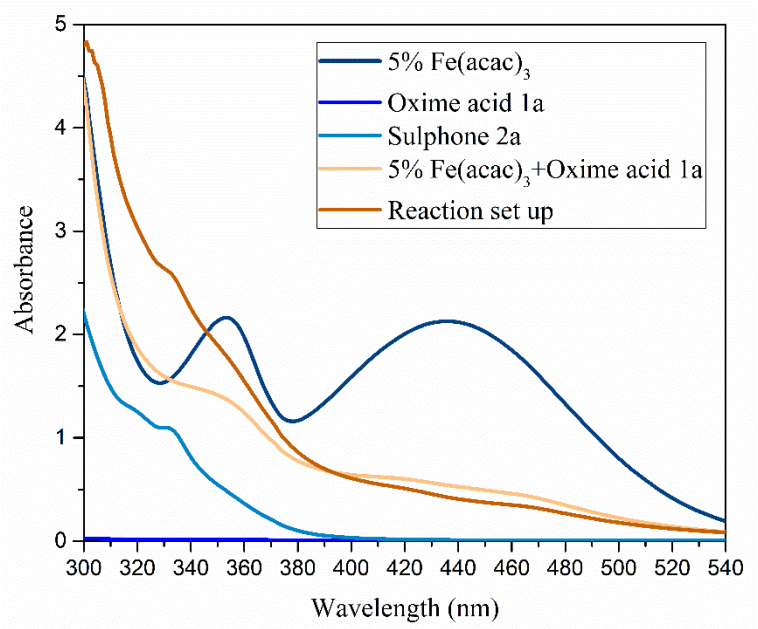
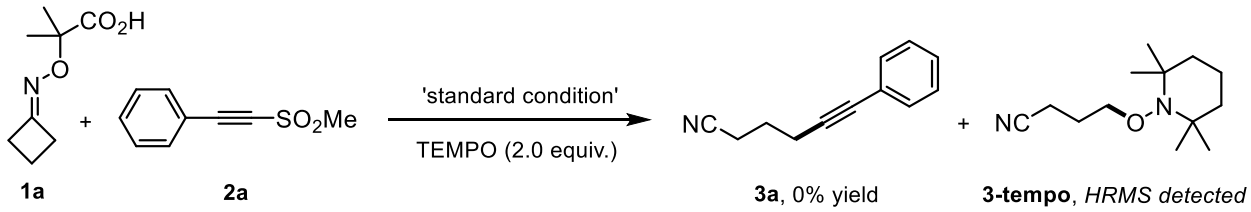
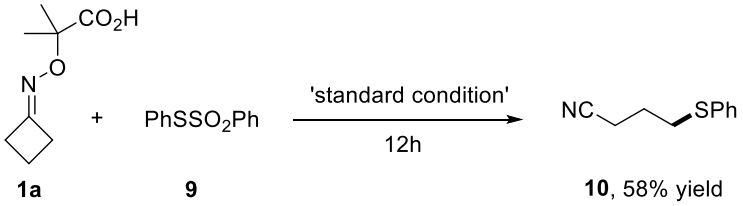


Figure S3. UV-vis absorption spectra showing different compounds in a solution of toluene



General procedure: To an oven-dried 25 mL quartz vial equipped with a magnetic stir bar were sequentially added the corresponding $Fe(acac)_3$ (3.5 mg, 5 mol%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.4 mg, 2.0 equiv.), oxime acid **1a** (0.4 mmol), sulfone **2a** (0.2 mmol), KOH (5 mg, 50 mol%), toluene (2 mL). The vial was degassed, backfilled with nitrogen three times. The vial was then put into the reactor and was irradiated and stirred under 10 W 390 nm LEDs for 8 h at 30℃, TLC and GC-MS monitored. After 8 h, the crude system was diluted, filtered, and then tested under HRMS. The radical-capture product **3-tempo** was detected by HRMS (ESI) m/z $[M+Na]^+$; calcd for $C_{13}H_{24}N_2ONa$ 247.1781; found 247.1778.



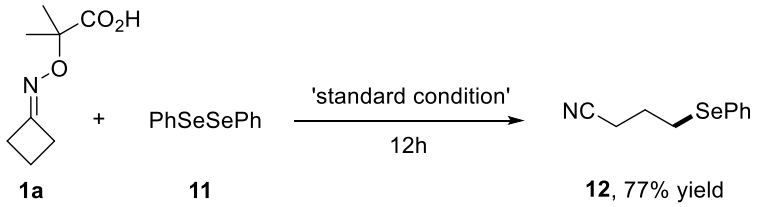
General procedure: To an oven-dried 25 mL quartz vial equipped with a magnetic stir bar were sequentially added the corresponding $Fe(acac)_3$ (3.5 mg, 5 mol%), oxime acid **1a** (0.4 mmol), o-phenyl benzenesulfonothioate **9** (0.2 mmol), KOH (5 mg, 50 mol%), toluene (2 mL). The vial was degassed, backfilled with nitrogen three times. The vial was then put into the reactor and was irradiated and stirred under 10 W 390 nm LEDs for 12 h at 30℃, TLC and GC-MS monitored. After 12h, the crude system was filtered, and all volatiles were removed in vacuo and the crude product was purified by column chromatography (1:10 EtOAc:petroleum ether) to obtain corresponding product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.95 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.8, 130.2, 129.3, 126.9, 119.2, 32.6, 24.9, 16.0.

HRMS (ESI, m/z): calcd for $[M+Na]^+$ 200.0504, found 200.0498.

Characterization data matched that reported in the literature. [9]



General procedure: To an oven-dried 25 mL quartz vial equipped with a magnetic stir bar were sequentially added the corresponding $Fe(acac)_3$ (3.5 mg, 5 mol%), oxime acid **1a** (0.4 mmol), seleninoselenoyldibenzene **11** (0.2 mmol), KOH (5 mg, 50 mol%), toluene (2 mL). The vial was degassed, backfilled with nitrogen three times. The vial was then put into the reactor and was irradiated and stirred under 10 W 390 nm LEDs for 12 h at 30℃, TLC and GC-MS monitored. After 12h, the crude system was filtered, and all volatiles were removed in vacuo and the crude product was purified by column chromatography (1:10 EtOAc:petroleum ether) to obtain corresponding product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 2H), 7.34 – 7.23 (m, 3H), 2.99 (t, *J* = 6.9 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 1.99 (p, *J* = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 133.3, 133.3, 129.4, 128.8, 127.6, 119.1, 26.1, 25.8, 17.1.

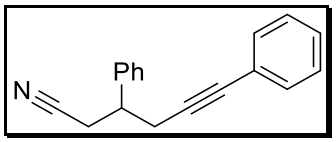
HRMS (ESI, m/z): calcd for $[M+Na]^+$ 247.9949, found 247.9947.

Characterization data matched that reported in the literature. [9]

7. Product Characterization

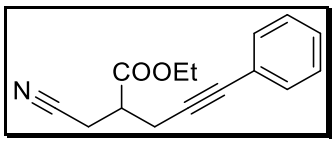
6-Phenyl-5-hexynenitrile (3a)

Colorless oil, 29.8 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.27 (m, 3H), 2.58 (dt, *J* = 17.8, 7.0 Hz, 4H), 1.96 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5, 128.2, 127.9, 123.1, 119.1, 86.8, 82.3, 24.5, 18.4, 16.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 192.0784, found 192.0783.



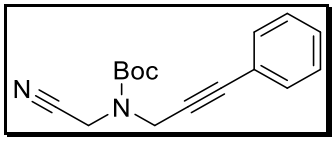
β-(3-Phenyl-2-propyn-1-yl)benzenepropanenitrile (3b)

Colorless oil, 29.9 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.34 – 7.27 (m, 6H), 3.30 (p, *J* = 7.0 Hz, 1H), 2.99 – 2.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 131.6, 129.0, 128.4, 128.2, 127.9, 127.1, 123.1, 118.3, 86.0, 83.6, 41.2, 25.9, 23.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 268.1097, found 268.1098.



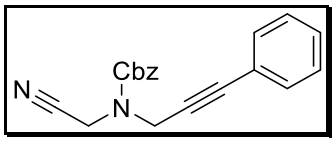
Ethyl 2-(cyanomethyl)-5-phenyl-4-pentynoate (3c)

Colorless oil, 30.9 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.30 (dd, *J* = 5.2, 2.0 Hz, 3H), 4.26 (qd, *J* = 7.2, 2.3 Hz, 2H), 3.02 – 2.96 (m, 1H), 2.95 – 2.84 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 131.8, 128.4, 122.8, 117.7, 84.1, 62.0, 40.9, 21.7, 18.5, 14.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 264.0995, found 264.0998.



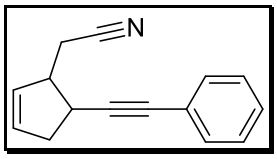
1,1-Dimethylethyl N-(cyanomethyl)-N-(3-phenyl-2-propyn-1-yl)carbamate (3d)

Yellow oil, 30.8 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.32 (d, *J* = 6.4 Hz, 3H), 4.36 (d, *J* = 42.6 Hz, 4H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 128.9, 128.5, 122.2, 115.9, 82.7, 82.5, 37.2, 34.5, 28.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 293.1261, found 293.1257.



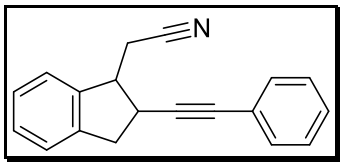
benzyl (cyanomethyl)(3-phenylprop-2-yn-1-yl)carbamate (3e)

Yellowish oil, 39.0 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.28 (m, 10H), 5.23 (s, 2H), 4.44 (dd, *J* = 34.8, 19.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 135.5, 131.9, 129.0, 128.8, 128.6, 128.5, 128.3, 122.0, 115.5, 86.0, 81.9, 68.8, 37.7, 34.8, 34.4. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 327.1104, found 327.1115.



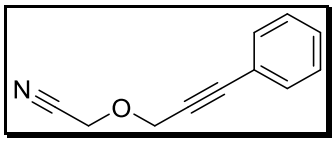
2-(2-(phenylethynyl)cyclopent-3-en-1-yl)acetonitrile (3f)

Brown-yellow solid, 22.0 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.32 – 7.27 (m, 3H), 5.91 (dq, *J* = 4.2, 2.3 Hz, 1H), 5.71 (dq, *J* = 5.9, 1.9 Hz, 1H), 3.17 (tdt, *J* = 7.7, 5.0, 2.6 Hz, 1H), 2.96 – 2.82 (m, 2H), 2.69 (dd, *J* = 16.9, 5.2 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.52 (dd, *J* = 16.8, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 131.7, 130.6, 128.4, 128.4, 128.1, 123.3, 118.2, 90.8, 82.0, 49.7, 40.2, 35.4, 22.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 230.0941, found 230.0945.



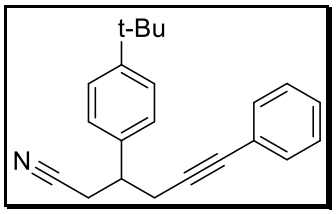
2-(2-(phenylethynyl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (3g)

Colorless oil, 47.3 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.36 – 7.26 (m, 6H), 3.57 (q, *J* = 5.2, 3.7 Hz, 1H), 3.40 – 3.31 (m, 1H), 3.22 – 3.07 (m, 2H), 3.02 – 2.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.3, 131.8, 128.4, 128.3, 128.1, 127.4, 124.9, 123.2, 118.1, 89.7, 82.7, 48.1, 38.7, 37.6, 20.7. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 280.1097, found 280.1100.



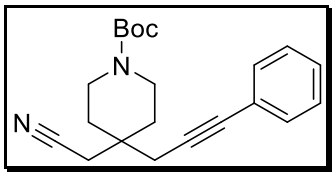
2-[(3-Phenyl-2-propyn-1-yl)oxy]acetonitrile (3h)

Colorless oil, 14.0 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.40 – 7.31 (m, 3H), 4.55 (s, 2H), 4.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 129.1, 128.5, 121.8, 115.6, 88.7, 82.1, 59.0, 54.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 194.0577, found 194.0573.



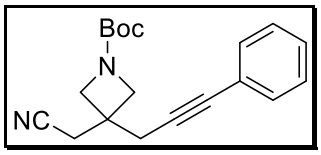
4-(1,1-Dimethylethyl)-β-[3-phenyl-2-propyn-1-yl]benzenepropanenitrile (3i)

Colorless oil, 36.2 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.32 – 7.27 (m, 3H), 7.24 (d, *J* = 3.2 Hz, 2H), 3.27 (p, *J* = 6.9 Hz, 1H), 2.98 – 2.77 (m, 4H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 137.5, 131.6, 128.4, 128.2, 126.7, 125.8, 123.2, 118.5, 86.3, 83.5, 40.7, 34.6, 31.4, 25.8, 23.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 324.1723, found 324.1727.



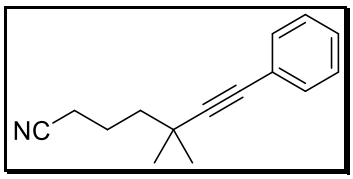
1-Piperidinecarboxylic acid, 4-(cyanomethyl)-4-(3-phenyl-2-propyn-1-yl)-, 1,1-dimethylethyl ester (3j)

Yellowish oil, 61.0 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.30 (dd, *J* = 4.6, 2.0 Hz, 3H), 3.53 (dt, *J* = 13.9, 5.4 Hz, 2H), 3.37 (ddd, *J* = 13.8, 8.2, 4.1 Hz, 2H), 2.63 (s, 2H), 2.58 (s, 2H), 1.68 (dqd, *J* = 17.8, 9.5, 3.2 Hz, 4H), 1.46 (s, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 131.7, 128.5, 128.3, 123.0, 117.4, 84.5, 84.4, 80.1, 35.2, 33.7, 28.5, 27.6, 26.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 361.1886, found 361.1890.



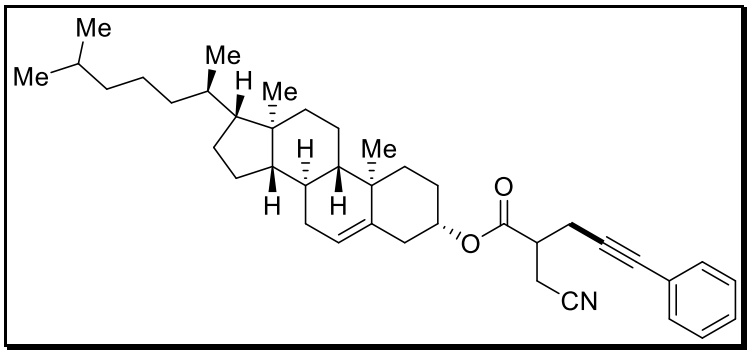
tert-butyl 3-(cyanomethyl)-3-(3-phenylprop-2-yn-1-yl)azetidine-1-carboxylate (3k)

White solid, 43.5 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.30 (m, 3H), 3.91 (d, *J* = 8.7 Hz, 2H), 3.82 (d, *J* = 9.0 Hz, 2H), 2.83 (d, *J* = 5.6 Hz, 4H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 131.8, 128.5, 128.4, 122.6, 116.9, 84.0, 83.7, 80.2, 35.3, 28.4, 28.1, 25.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 333.1573, found 333.1564.



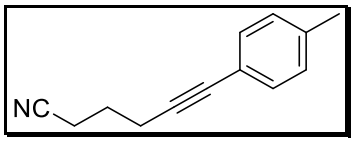
5,5-dimethyl-7-phenylhept-6-ynenitrile (3l)

Colorless oil, 22.0 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.28 (m, 3H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.96 – 1.85 (m, 2H), 1.66 – 1.57 (m, 2H), 1.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.3, 127.8, 123.7, 119.8, 96.0, 81.2, 42.3, 31.5, 29.3, 21.9, 17.7. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 234.1253, found 234.1260.



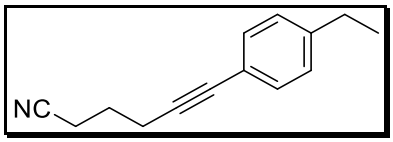
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(cyanomethyl)-5-phenylpent-4-ynoate (3m)

White solid, 72.2 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.29 (m, 3H), 5.37 (dd, *J* = 11.0, 4.8 Hz, 1H), 4.70 (m, 1H), 3.46 – 3.13 (m, 1H), 2.96 (m, 1H), 2.90 (t, *J* = 5.5 Hz, 2H), 2.84 (t, *J* = 5.9 Hz, 2H), 2.36 (d, *J* = 7.8 Hz, 2H), 2.06 – 1.77 (m, 6H), 1.68 – 1.41 (m, 9H), 1.41 – 1.23 (m, 6H), 1.12 (m, 8H), 1.02 (d, *J* = 5.4 Hz, 6H), 0.91 (d, *J* = 6.5 Hz, 4H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 9H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 170.3, 170.3, 139.3, 131.8, 128.4, 128.4, 123.2, 123.2, 123.1, 122.9, 117.8, 84.2, 84.0, 75.8, 56.8, 56.2, 51.7, 50.1, 42.4, 41.0, 39.8, 39.6, 38.1, 38.0, 37.0, 37.0, 36.7, 36.3, 35.9, 32.0, 31.9, 28.3, 28.1, 27.8, 27.8, 27.7, 24.4, 23.9, 22.9, 22.7, 21.7, 21.1, 19.4, 18.8, 18.5, 12.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 604.4125, found 604.4125.



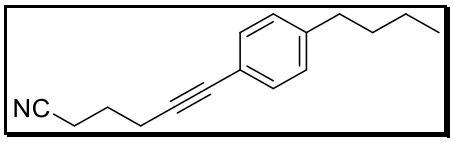
6-(4-Methylphenyl)-5-hexynenitrile (4a)

Yellowish oil, 25.7 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 2.57 (dt, *J* = 14.4, 7.0 Hz, 4H), 2.34 (s, 3H), 1.95 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 131.3, 128.9, 120.0, 119.2, 86.0, 82.4, 24.6, 21.3, 18.5, 16.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 206.0940, found 206.0939.



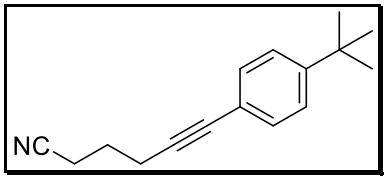
6-[4-(1,1-Dimethylethyl)phenyl]-5-hexynenitrile (4b)

Yellowish oil, 28.0 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 2.72 – 2.56 (m, 6H), 1.99 (p, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 131.6, 127.9, 120.4, 119.3, 86.2, 82.5, 28.8, 24.7, 18.6, 16.2, 15.47. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 220.1097, found 220.1101.



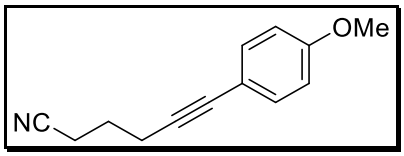
6-(4-Butylphenyl)-5-hexynenitrile (4c)

Yellowish oil, 30.6 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 2.57 (dt, *J* = 14.5, 6.8 Hz, 3H), 1.94 (p, *J* = 7.0 Hz, 1H), 1.63 – 1.52 (m, 1H), 1.32 (dt, *J* = 14.6, 7.4 Hz, 1H), 0.91 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 131.6, 128.5, 120.4, 119.4, 86.2, 82.6, 35.6, 33.5, 24.8, 22.4, 18.7, 16.3, 14.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 248.1410, found 248.1410.



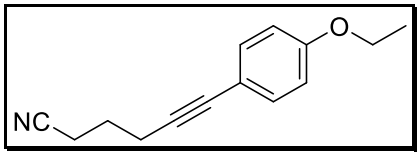
6-[4-(1,1-Dimethylethyl)phenyl]-5-hexynenitrile (4d)

White solid, 31.1 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4H), 2.57 (dt, *J* = 15.9, 7.0 Hz, 4H), 1.95 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 131.3, 125.3, 120.2, 119.3, 86.2, 82.5, 34.7, 31.2, 24.7, 18.6, 16.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 248.1410, found 248.1414.



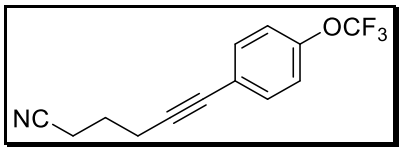
6-(4-Methoxyphenyl)-5-hexynenitrile (4e)

Yellowish oil, 23.1 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 6.85 – 6.79 (m, 2H), 3.80 (s, 3H), 2.57 (dt, *J* = 11.1, 7.0 Hz, 4H), 1.95 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 133.0, 119.3, 115.3, 113.9, 85.4, 82.2, 55.3, 24.8, 18.6, 16.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 222.0890, found 222.0894.



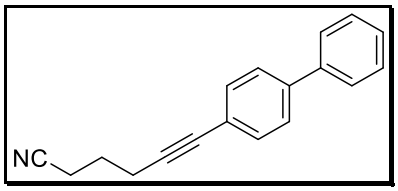
6-(4-Ethoxyphenyl)-5-hexynenitrile (4f)

Colorless oil, 27.3 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 2.56 (dt, *J* = 11.0, 6.9 Hz, 4H), 1.94 (p, *J* = 6.9 Hz, 2H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 133.0, 119.4, 115.2, 114.5, 85.4, 82.4, 63.6, 24.9, 18.7, 16.3, 14.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 236.1046, found 236.1047.



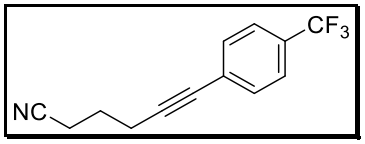
6-[4-(Trifluoromethoxy)phenyl]-5-hexynenitrile (4g)

Colorless oil, 33.9 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.18 – 7.12 (m, 2H), 2.58 (dt, *J* = 20.1, 6.9 Hz, 4H), 1.97 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 133.1, 121.7, 120.9, 120.5 (q, *J* = 257.6 Hz), 119.1, 87.9, 81.1, 24.5, 18.5, 16.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.82. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 276.0607, found 276.0594.



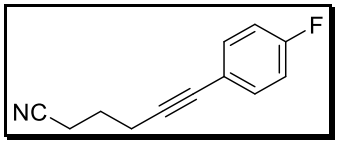
6-[1,1′-Biphenyl]-4-yl-5-hexynenitrile (4h)

Colorless oil, 25.0 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 16.8, 7.9 Hz, 4H), 7.44 (dd, *J* = 13.9, 8.1 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 2.62 (t, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.97 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.4, 132.1, 128.9, 127.7, 127.0, 122.1, 119.3, 87.7, 82.3, 24.7, 18.7, 16.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 268.1097, found 268.1099.



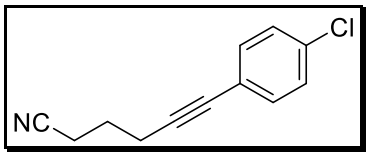
6-[4-(Trifluoromethyl)phenyl]-5-hexynenitrile (4i)

Yellowish oil, 33.7 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 2.63 (t, *J* = 6.8 Hz, 1H), 2.56 (t, *J* = 7.1 Hz, 1H), 1.98 (p, *J* = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 130.0 (q, *J* = 32.7 Hz), 127.1, 125.3 (q, *J* = 4.1 Hz), 123.3 (q, *J* = 272.2 Hz). 120.0, 89.8, 81.3, 24.5, 18.6, 16.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 260.0658, found 260.0657.



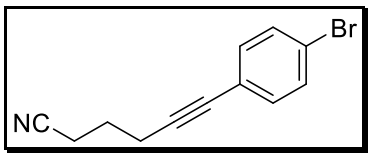
6-(4-Fluorophenyl)-5-hexynenitrile (4j)

Colorless oil, 27.0 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 6.99 (m, 2H), 2.57 (dt, *J* = 14.2, 6.9 Hz, 4H), 1.95 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 248.8 Hz), 133.5 (d, *J* = 8.3 Hz), 119.4 (d, *J* = 3.5 Hz), 119.3, 115.6 (d, *J* = 22.0 Hz) 86.7, 81.4, 24.7, 18.6, 16.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.39. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 210.0690, found 210.0691.



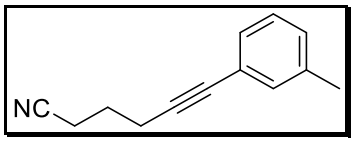
6-(4-Chlorophenyl)-5-hexynenitrile (4k)

Yellow oil, 31.8 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.57 (dt, *J* = 18.2, 6.9 Hz, 4H), 1.96 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 132.9, 128.6, 121.7, 119.2, 88.0, 81.4, 24.5, 18.6, 16.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 226.0394, found 226.0397.



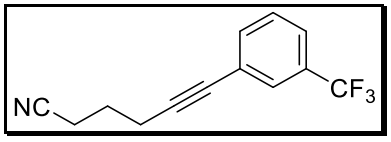
6-(4-Chlorophenyl)-5-hexynenitrile (4l)

Yellowish oil, 24.3 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 2.57 (dt, *J* = 16.1, 6.9 Hz, 4H), 1.96 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 131.7, 131.6, 122.3, 122.2, 119.2, 88.3, 24.6, 18.7, 16.4. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 269.9889, found 269.9899.



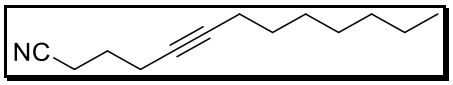
6-(3-Methylphenyl)-5-hexynenitrile (4m)

Yellowish oil, 28.6 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.21 – 7.16 (m, 2H), 7.14 – 7.08 (m, 1H), 2.57 (dt, *J* = 14.5, 6.9 Hz, 4H), 2.32 (s, 3H), 1.95 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 132.2, 128.9, 128.7, 128.2, 123.0, 119.3, 86.6, 82.6, 24.7, 21.2, 18.6, 16.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 206.0941, found 206.0945.



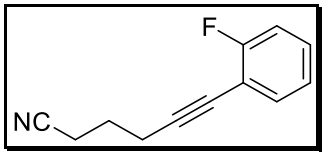
6-[3-(Trifluoromethyl)phenyl]-5-hexynenitrile (4n)

Colorless oil, 28.9 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 1.98 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 131.0 (q, *J* = 32.7 Hz), 129.0, 128.5 (q, *J* = 4.0 Hz), 124.7 (q, *J* = 3.8 Hz), 124.2, 123.8 (q, *J* = 272.6 Hz), 119.2, 88.9, 81.1, 24.6, 18.6, 16.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 260.0658, found 260.0648.



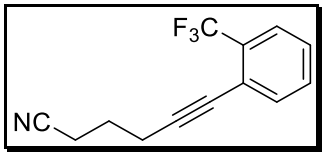
5-tridecynenitrile (4o)

Colorless oil, 28.3 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (t, *J* = 7.2 Hz, 2H), 2.33 (tt, *J* = 6.7, 2.4 Hz, 2H), 2.14 (tt, *J* = 7.2, 2.4 Hz, 2H), 1.83 (p, *J* = 7.0 Hz, 2H), 1.48 (p, *J* = 6.9 Hz, 2H), 1.41 – 1.19 (m, 9H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.4, 82.6, 31.8, 29.0, 28.9, 28.8, 25.0, 22.6, 18.7, 18.0, 16.1, 14.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 214.1567, found 214.1571.



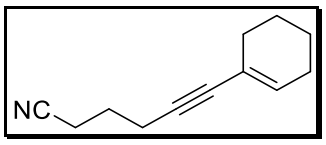
6-(2-Fluorophenyl)-5-hexynenitrile (4p)

Colorless oil, 24.3 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (td, *J* = 7.5, 1.8 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.07 (q, *J* = 9.2, 8.3 Hz, 2H), 2.65 (t, *J* = 6.7 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.98 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 250.7 Hz), 133.5, 129.8 (d, *J* = 7.9 Hz), 124.0 (d, *J* = 3.7 Hz), 119.3, 115.5 (d, *J* = 20.9 Hz), 111.8 (d, *J* = 15.8 Hz), 92.5 (d, *J* = 3.3 Hz), 75.9, 24.6, 18.8, 16.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 210.0690, found 210.0686.



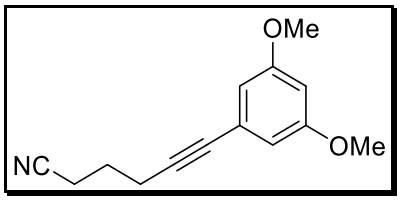
6-[2-(Trifluoromethyl)phenyl]-5-hexynenitrile (4q)

Yellowish oil, 31.3 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 2.65 (t, *J* = 6.6 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.98 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 131.6 (q, *J* = 30.2 Hz), 131.6, 127.9, 125.7 (q, *J* = 5.2 Hz), 123.7 (d, *J* = 273.2 Hz), 121.6, 119.3, 93.2, 78.6, 24.5, 18.7, 16.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 260.0658, found 260.0656.



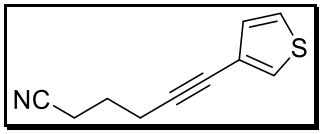
6-(1-Cyclohexen-1-yl)-5-hexynenitrile (4r)

Yellow oil, 21.8 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 – 5.98 (m, 1H), 2.49 (dt, *J* = 8.2, 6.9 Hz, 4H), 2.13 – 2.02 (m, 4H), 1.88 (p, *J* = 7.0 Hz, 2H), 1.65 – 1.55 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 120.6, 119.4, 84.3, 84.1, 29.5, 25.6, 24.9, 22.4, 21.6, 18.5, 16.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 196.1097, found 196.1100.



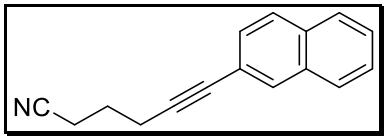
6-(3,5-Dimethoxyphenyl)-5-hexynenitrile (4s)

White solid, 33.0 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, *J* = 2.2 Hz, 2H), 6.42 (t, *J* = 2.2 Hz, 1H), 3.77 (s, 6H), 2.57 (dt, *J* = 14.5, 6.9 Hz, 4H), 1.96 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 124.5, 119.3, 109.4, 101.4, 86.6, 82.4, 55.4, 24.6, 18.5, 16.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 252.0995, found 252.1011.



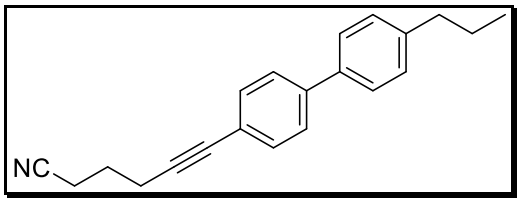
6-(3-Thienyl)-5-hexynenitrile (4t)

Colorless oil, 28.4 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.07 (d, *J* = 4.9 Hz, 1H), 2.56 (dt, *J* = 13.8, 6.9 Hz, 4H), 1.94 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.9, 128.3, 125.3, 122.2, 119.3, 86.6, 77.5, 24.6, 18.6, 16.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 198.0348, found 198.0351.



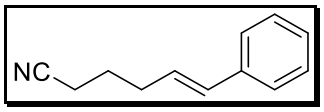
6-(2-Naphthalenyl)-5-hexynenitrile (4u)

Yellowish solid, 21.5 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.78 (m, 3H), 7.51 – 7.41 (m, 3H), 2.61 (dt, *J* = 23.9, 6.9 Hz, 4H), 1.98 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 132.7, 131.4, 128.5, 128.0, 127.8, 127.7, 126.6, 126.6, 120.5, 119.3, 87.3, 82.8, 24.7, 18.7, 16.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 242.0940, found 242.0941.



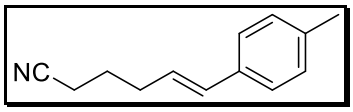
6-(4'-propyl-[1,1'-biphenyl]-4-yl)-5-hexynenitrile (4v)

Colorless solid, 32.8 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 11.1, 8.1 Hz, 4H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 2.61 (td, *J* = 7.1, 6.7, 3.7 Hz, 4H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.96 (p, *J* = 7.0 Hz, 2H), 1.67 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 140.8, 137.7, 132.0, 129.0, 126.8, 126.8, 121.8, 119.3, 87.5, 82.4, 37.7, 24.7, 24.6, 18.7, 16.3, 13.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 310.1567, found 310.1567.



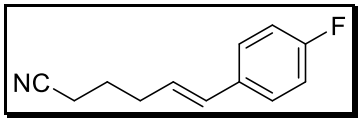
(E)-6-Phenyl-5-hexenenitrile (6a)

Colorless oil, 24.7 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.18 – 6.07 (m, 1H), 2.45 – 2.35 (m, 4H), 1.85 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 132.1, 128.7, 127.7, 127.4, 126.2, 119.7, 31.7, 25.1, 16.5. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 194.0940, found 194.0950.



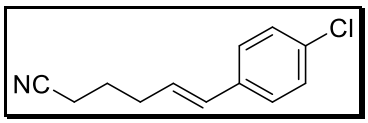
(E)-6-(p-tolyl)hex-5-enenitrile (6b)

White solid, 25.9 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.06 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.40 – 2.30 (m, 7H), 1.82 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 134.4, 132.0, 129.4, 126.6, 126.1, 119.7, 31.7, 25.1, 21.3, 16.5. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 208.1097, found 208.1107.



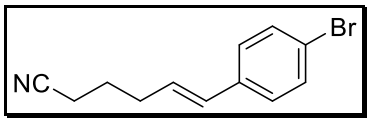
(E)-6-(4-fluorophenyl)hex-5-enenitrile (6c)

Colorless oil, 25.7 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.05 – 6.94 (m, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.04 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.42 – 2.33 (m, 4H), 1.84 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.3 Hz), 133.4 (d, *J* = 3.3 Hz), 130.9, 127.6 (d, *J* = 7.9 Hz), 127.5 (d, *J* = 2.4 Hz), 119.6, 115.6 (d, *J* = 21.5 Hz). 31.7, 25.1, 16.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.8, -114.8, -114.8, -114.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 212.0846, found 212.0850.



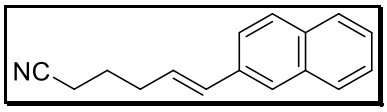
(E)-6-(4-chlorophenyl)hex-5-enenitrile (6d)

Colorless oil, 27.1 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 4H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.8, 7.0 Hz, 1H), 2.38 (q, *J* = 8.5, 7.8 Hz, 4H), 1.84 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 133.0, 130.9, 128.8, 128.5, 127.4, 119.6, 31.7, 25.0, 16.6. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 228.0550, found 228.0545.



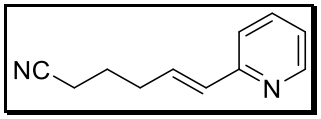
(E)-6-(4-bromophenyl)hex-5-enenitrile (6e)

White solid, 30.0 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.6, 7.0 Hz, 1H), 2.38 (dt, *J* = 9.1, 7.1 Hz, 4H), 1.84 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 131.7, 131.0, 128.6, 127.7, 121.1, 119.6, 31.8, 24.9, 16.6. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 272.0045, found 272.0032.



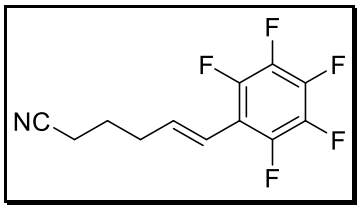
(E)-6-(naphthalen-2-yl)hex-5-enenitrile (6f)

White solid, 18.6 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 7.4 Hz, 3H), 7.69 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.44 (dt, *J* = 13.1, 6.4 Hz, 2H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.6, 7.0 Hz, 1H), 2.43 (dt, *J* = 13.9, 6.9 Hz, 4H), 1.87 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 133.7, 133.0, 132.3, 128.3, 128.1, 128.0, 127.8, 126.4, 125.9, 125.9, 123.5, 119.7, 31.9, 25.1, 16.6. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 244.1097, found 244.1097.



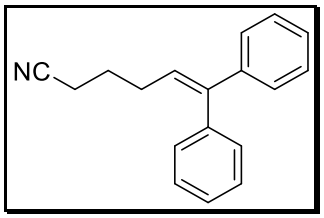
(E)-6-(pyridin-2-yl)hex-5-enenitrile (6g)

Yellow oil, 28.9 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.4 Hz, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.69 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 2.44 (dd, *J* = 14.8, 7.2 Hz, 4H), 1.89 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 149.5, 136.7, 132.5, 131.8, 122.2, 121.6, 119.6, 31.5, 24.7, 16.6. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 195.0893, found 195.0840.



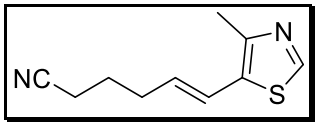
(E)-6-(perfluorophenyl)hex-5-enenitrile (6h)

Colorless oil, 36.6 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (dt, *J* = 16.3, 6.8 Hz, 1H), 6.37 (d, *J* = 16.3 Hz, 1H), 2.50 – 2.39 (m, 4H), 1.89 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 143.5, 141.1, 139.0, 138.5, 137.9, 137.8, 137.8, 137.8, 137.7, 136.5, 119.3, 116.4, 112.1, 112.0, 33.0, 24.7, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.4, -143.4, -143.4, -143.5, -156.7, -156.7, -156.8, -162.9, -162.9, -163.0, -163.0, -163.0, -163.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 284.0469, found 284.0472.



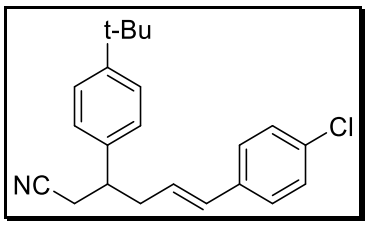
6,6-diphenylhex-5-enenitrile (6i)

Colorless oil, 35.1 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.3 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.29 – 7.19 (m, 5H), 7.17 – 7.13 (m, 2H), 6.01 (t, *J* = 7.4 Hz, 1H), 2.27 (dt, *J* = 17.6, 7.4 Hz, 4H), 1.79 (p, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.2, 139.7, 129.8, 128.5, 128.3, 127.4, 127.3, 127.3, 126.7, 119.7, 28.8, 25.8, 16.8. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 270.1253, found 270.1245.



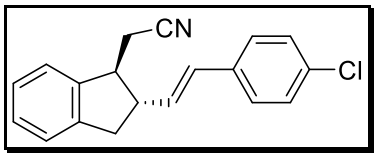
(E)-6-(4-methylthiazol-5-yl)hex-5-enenitrile (6j)

Yellowish oil, 19.6 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 5.90 (dt, *J* = 15.5, 7.1 Hz, 1H), 2.50 – 2.38 (m, 7H), 1.87 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 130.6, 121.9, 120.4, 119.4, 31.9, 24.9, 16.6, 15.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 215.0613, found 215.0643.



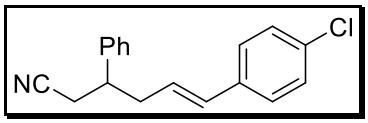
(E)-3-(4-(tert-butyl)phenyl)-6-(4-chlorophenyl)hex-5-enenitrile (6k)

Colorless oil, 48.0 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.27 – 7.15 (m, 6H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.03 (dt, *J* = 15.5, 7.2 Hz, 1H), 3.09 (p, *J* = 6.9 Hz, 1H), 2.72 – 2.56 (m, 4H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 138.2, 135.6, 133.1, 131.9, 128.8, 127.4, 127.2, 126.8, 125.9, 118.7 , 41.5, 38.4, 34.6, 31.4, 24.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 360.1489, found 360.1479.



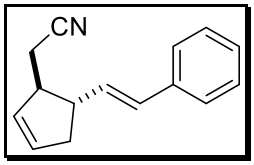
(E)-2-(2-(4-chlorostyryl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (6l)

Colorless oil, 49.9 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 8H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.7, 8.3 Hz, 1H), 3.33 (q, *J* = 6.4 Hz, 1H), 3.24 (dd, *J* = 14.6, 6.7 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.90 – 2.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 142.1, 135.3, 133.3, 131.6, 130.8, 128.9, 127.9, 127.6, 127.1, 124.8, 123.4, 118.5, 50.7, 46.9, 38.3, 20.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 316.0863, found 316.0859.



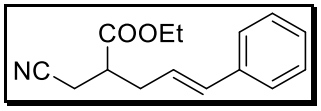
(E)-6-(4-chlorophenyl)-3-phenylhex-5-enenitrile (6m)

Colorless oil, 40.6 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.19 (m, 7H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.00 (dt, *J* = 15.3, 7.2 Hz, 1H), 3.12 (p, *J* = 7.0 Hz, 1H), 2.73 – 2.63 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 135.6, 133.1, 132.1, 129.1, 128.8, 127.7, 127.5, 127.3, 127.0, 118.5, 42.1, 38.5, 24.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 304.0863, found 304.0870.



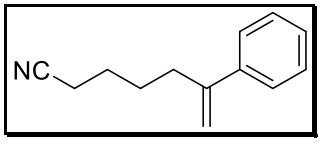
(E)-2-(2-styrylcyclopent-3-en-1-yl)acetonitrile (6n)

Colorless oil, 27.2 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.21 (dd, *J* = 15.8, 7.9 Hz, 1H), 5.91 (dq, *J* = 4.8, 2.2 Hz, 1H), 5.71 (dq, *J* = 6.0, 2.0 Hz, 1H), 2.85 (dtq, *J* = 7.3, 5.0, 2.4 Hz, 1H), 2.76 – 2.66 (m, 2H), 2.55 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.42 – 2.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 132.8, 132.0, 130.9, 130.8, 128.7, 127.5, 126.2, 118.7, 48.7, 48.3, 39.5, 21.7. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 232.1097, found 232.1104.



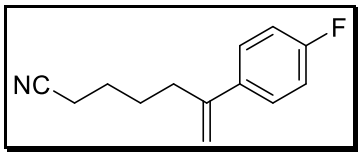
Ethyl (E)-2-(cyanomethyl)-5-phenylpent-4-enoate (6o)

Yellowish oil, 33.6 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 6.52 (d, *J* = 15.4 Hz, 1H), 6.06 (dt, *J* = 15.3, 7.4 Hz, 1H), 4.22 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.89 (p, *J* = 6.8 Hz, 1H), 2.75 – 2.56 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 136.7, 134.3, 128.7, 127.8, 126.3, 124.2, 117.9, 77.5, 77.2, 76.8, 61.6, 41.5, 34.5, 18.7, 14.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 266.1151, found 266.1153.



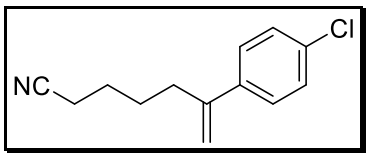
6-phenylhept-6-enenitrile (8a)

Colorless oil, 19.2 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.29 (s, 1H), 5.07 (s, 1H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 6.9 Hz, 2H), 1.70 – 1.57 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 140.8, 128.5, 127.7, 126.2, 119.8, 113.1, 34.5, 27.2, 25.0, 17.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 208.1097, found 208.1104.



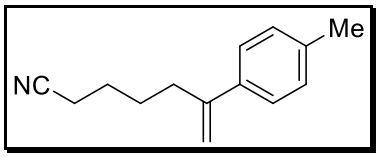
6-(4-fluorophenyl)hept-6-enenitrile (8b)

Colorless oil, 27.2 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 2H), 7.07 – 6.96 (m, 2H), 5.24 (d, *J* = 1.2 Hz, 1H), 5.06 (d, *J* = 1.4 Hz, 1H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.70 – 1.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.5 Hz), 146.5, 136.9 (d, *J* = 3.3 Hz), 127.8 (d, *J* = 7.9 Hz), 119.7, 115.3 (d, *J* = 21.3 Hz), 113.1, 34.6, 27.1, 24.9, 17.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9, -115.0, -115.0, -115.0, -115.0, -115.0. HRMS (ESI, m/z): calcd for [M+Na]+ 226.1002, found 226.0995.



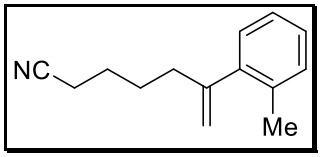
6-(4-chlorophenyl)hept-6-enenitrile (8c)

Colorless oil, 22.0 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 4H), 5.28 (s, 1H), 5.08 (s, 1H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.69 – 1.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 139.3, 133.5, 128.7, 127.5, 119.7, 113.7, 34.4, 27.1, 24.9, 17.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 242.0707, found 242.0716.



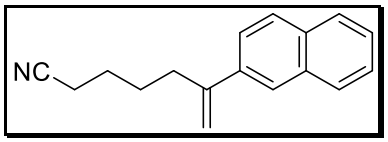
6-(p-tolyl)hept-6-enenitrile (8d)

Colorless oil, 19.1 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 5.26 (s, 1H), 5.02 (s, 1H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.31 (t, *J* = 6.9 Hz, 2H), 1.71 – 1.55 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 137.9, 137.5, 129.2, 126.1, 119.8, 112.4, 34.5, 27.2, 25.0, 21.2, 17.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 222.1253, found 222.1262.



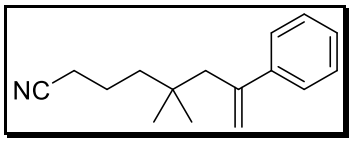
6-(o-tolyl)hept-6-enenitrile (8e)

Colorless oil, 17.5 mg, 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 3H), 7.05 (d, *J* = 6.6 Hz, 1H), 5.19 (d, *J* = 1.6 Hz, 1H), 4.90 (d, *J* = 1.8 Hz, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.68 (p, *J* = 7.4, 7.1 Hz, 2H), 1.54 (p, *J* = 7.5, 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 142.6, 134.9, 130.3, 128.4, 127.1, 125.6, 119.8, 114.6, 36.9, 26.9, 25.2, 20.0, 17.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 222.1253, found 222.1248.



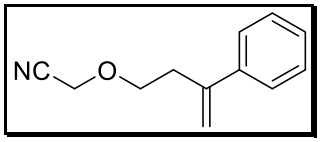
6-(naphthalen-2-yl)hept-6-enenitrile (8f)

Colorless oil, 15.1 mg, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 4H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.47 (m, 2H), 5.44 (s, 1H), 5.17 (s, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H), 1.76 – 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 138.1, 133.5, 133.0, 128.3, 128.1, 127.7, 126.4, 126.1, 124.8, 124.7, 119.8, 113.7, 34.5, 27.3, 25.0, 17.1. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 258.1253, found 258.1261.



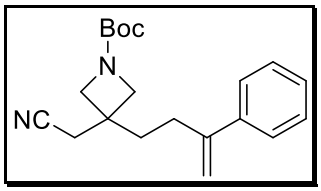
5,5-dimethyl-7-phenyloct-7-enenitrile (8g)

Colorless oil, 15.9 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 (s, 1H), 5.24 (d, *J* = 2.0 Hz, 1H), 5.03 (s, 1H), 2.46 (s, 2H), 2.05 (t, *J* = 7.2 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.25 – 1.15 (m, 2H), 0.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 143.8, 128.3, 127.3, 126.7, 119.9, 117.2, 46.8, 41.1, 34.3, 27.7, 20.7, 17.7. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 250.1566, found 250.1556.



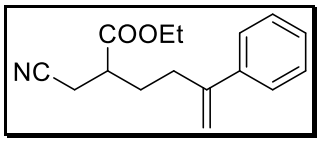
2-((3-phenylbut-3-en-1-yl)oxy)acetonitrile (8h)

Colorless oil, 9.4 mg, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 5.38 (s, 1H), 5.15 (s, 1H), 4.21 (s, 2H), 3.75 – 3.65 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 140.5, 128.6, 127.9, 126.2, 116.1, 114.62, 70.5, 56.4, 35.2. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 210.0889, found 210.0905.



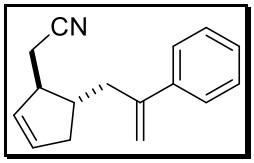
tert-butyl 3-(cyanomethyl)-3-(3-phenylbut-3-en-1-yl)azetidine-1-carboxylate (8i)

Colorless oil, 30.0 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 3H), 7.35 – 7.27 (m, 2H), 5.32 (s, 1H), 5.12 (s, 1H), 3.72 (q, *J* = 8.9 Hz, 4H), 2.68 (s, 2H), 2.56 – 2.48 (m, 2H), 1.93 – 1.85 (m, 2H), 1.43 (s, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 147.1, 140.4, 128.7, 128.0, 126.2, 117.1, 113.6, 80.2, 35.6, 35.3, 30.2, 28.4, 25.9. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 349.1886, found 349.1875.



ethyl 2-(cyanomethyl)-5-phenylhex-5-enoate (8j)

Colorless oil, 21.1 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.33 (s, 1H), 5.10 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.77 (p, *J* = 6.9 Hz, 1H), 2.66 – 2.51 (m, 4H), 2.02 – 1.88 (m, 1H), 1.80 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 146.8, 140.4, 128.6, 127.8, 126.2, 117.8, 113.7, 61.6, 41.1, 32.4, 30.0, 19.6, 14.3. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 280.1308, found 280.1319.



(E)-2-(2-(2-phenylallyl)cyclopent-3-en-1-yl)acetonitrile (8k)

Colorless oil, 13.8 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.9 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 5.84 – 5.76 (m, 1H), 5.64 – 5.57 (m, 1H), 5.32 (s, 1H), 5.10 (s, 1H), 2.77 – 2.65 (m, 2H), 2.65 – 2.51 (m, 2H), 2.31 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.18 (dd, *J* = 16.6, 7.3 Hz, 1H), 2.14 – 2.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 140.7, 132.7, 130.7, 128.6, 127.8, 126.3, 119.0, 114.4, 47.9, 41.6, 41.4, 38.8, 23.0. HRMS (ESI, m/z): calcd for $[M+Na]^+$ 246.1253, found 246.1267.

8. References

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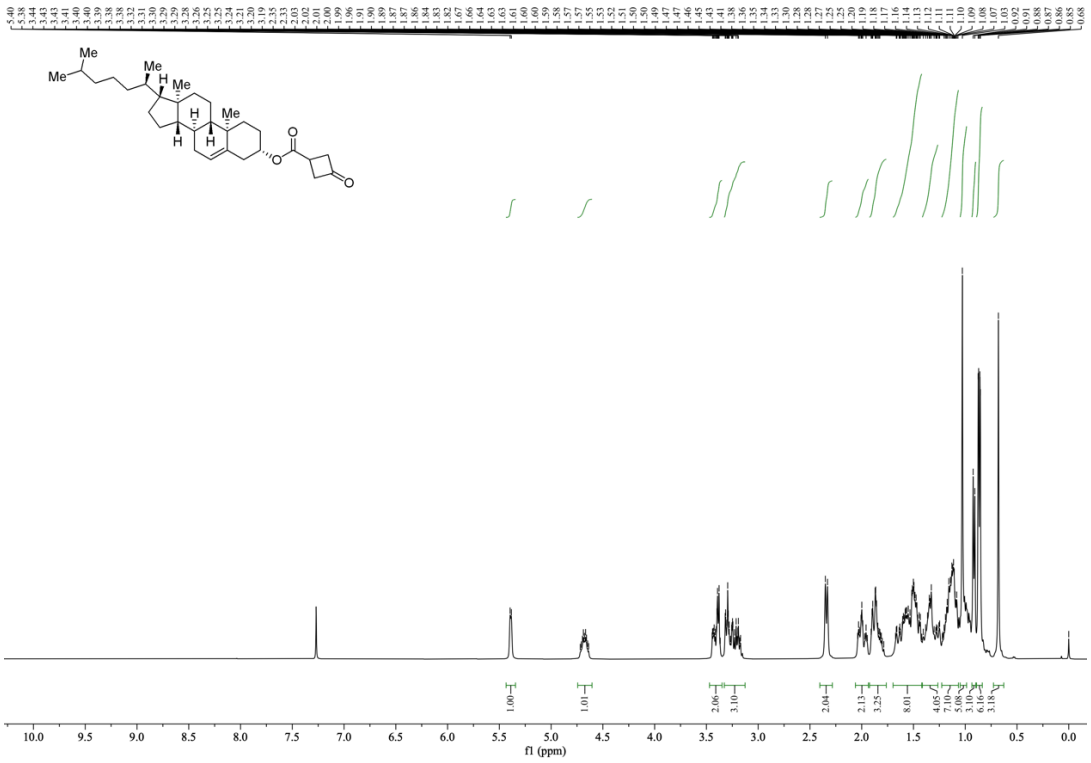
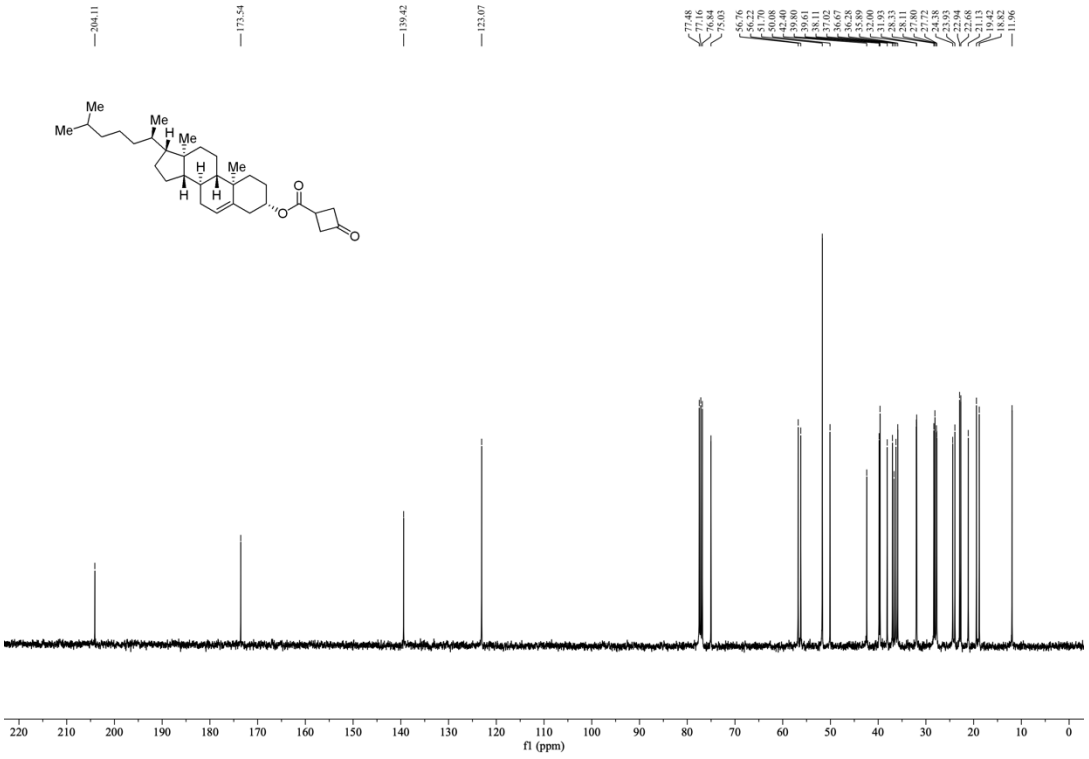
9. NMR Spectra



^{1}H NMR Spectrum of Compound S-1m (400 MHz, $CDCl_3$)



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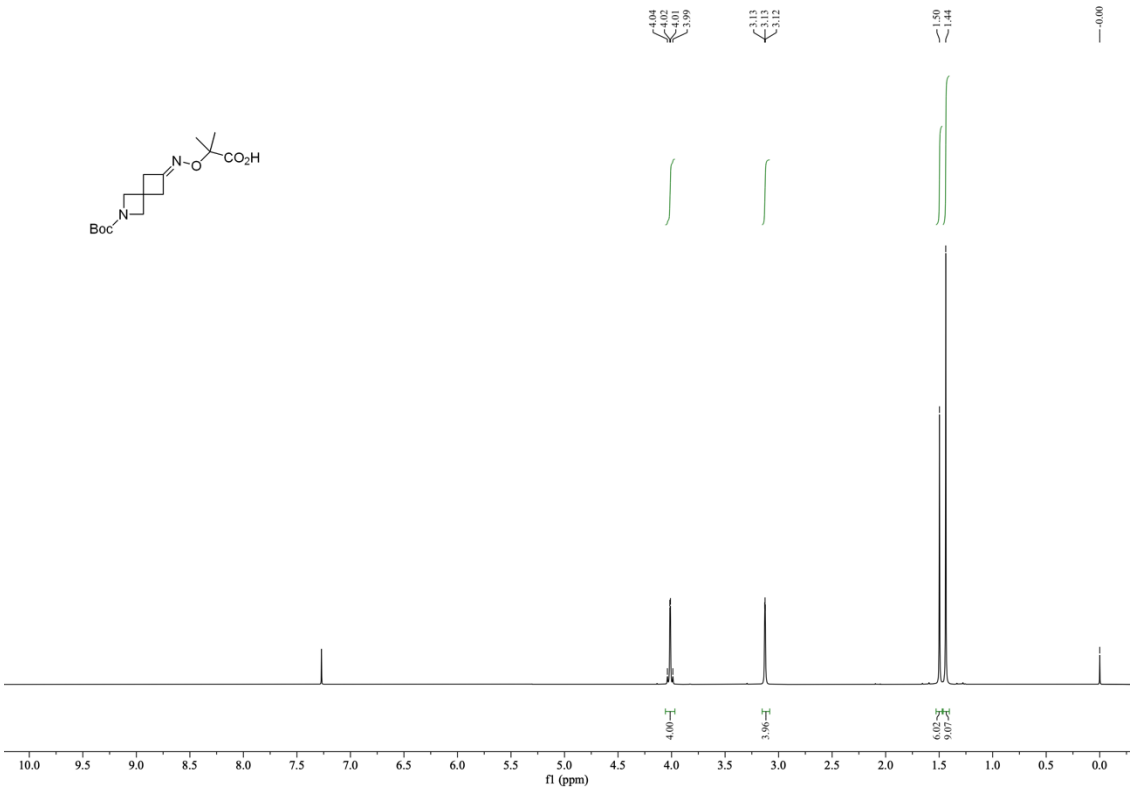
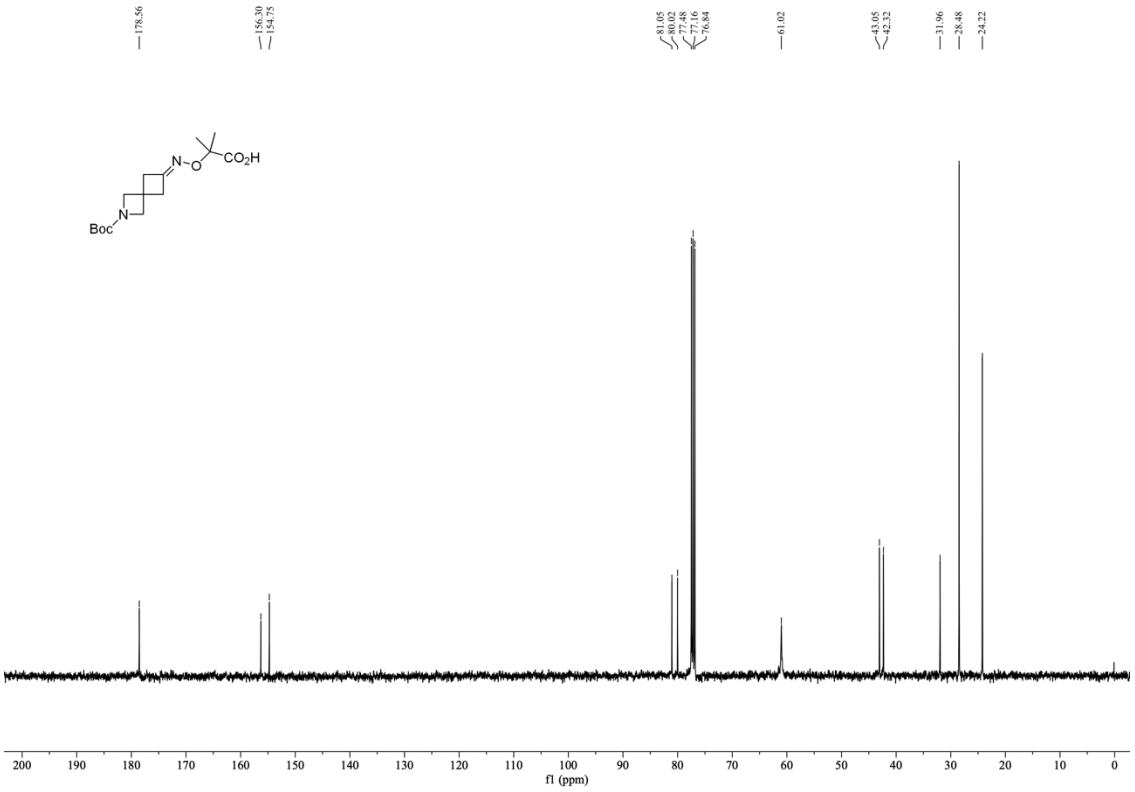


^{1}H NMR Spectrum of Compound 1k (400 MHz, $CDCl_3$)



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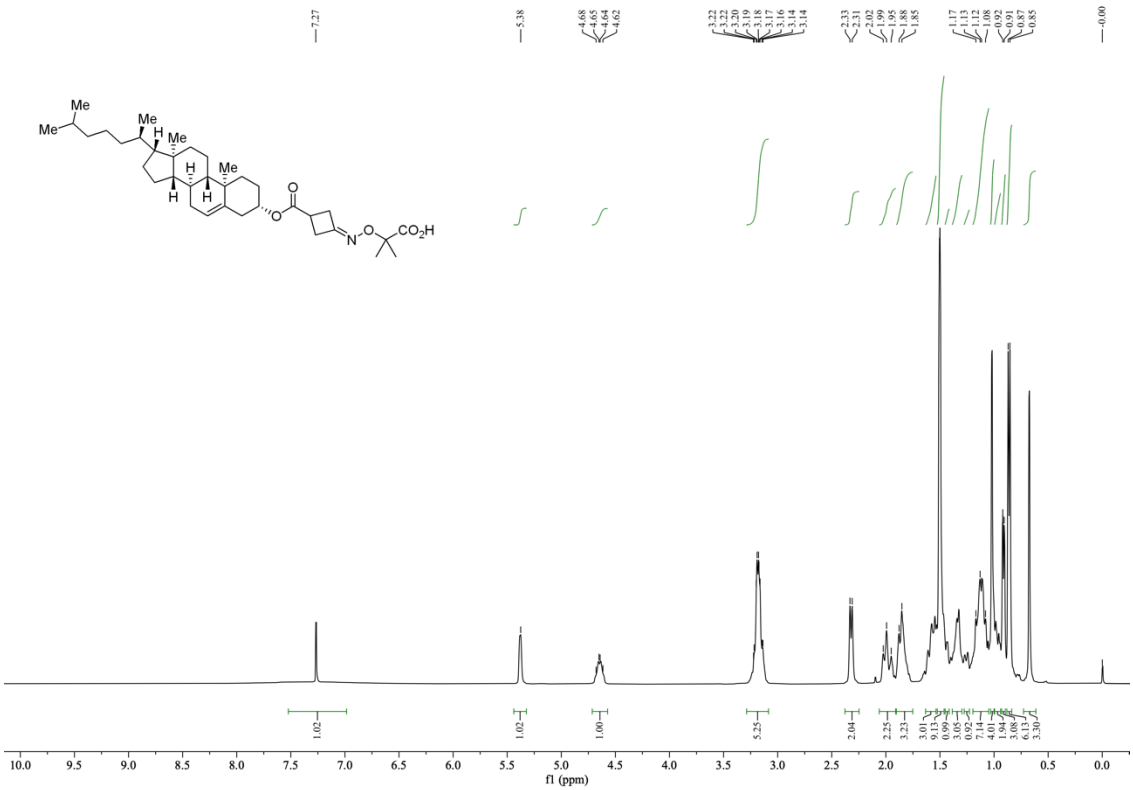

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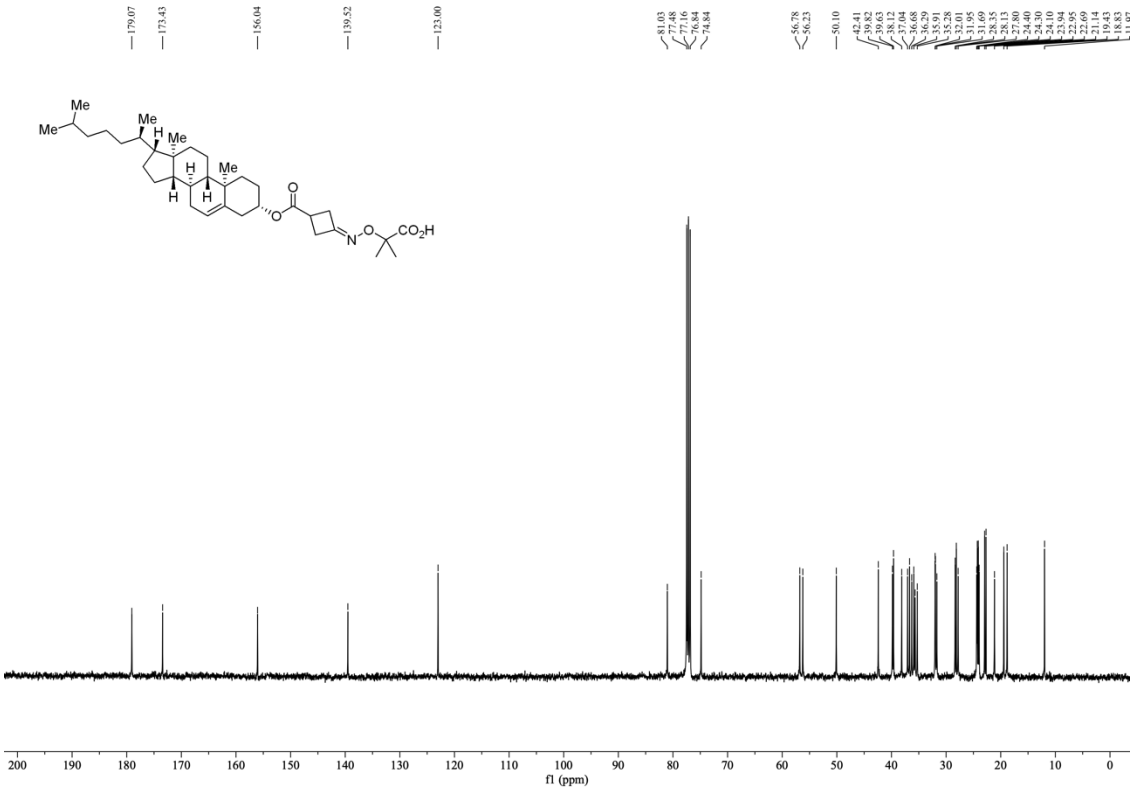

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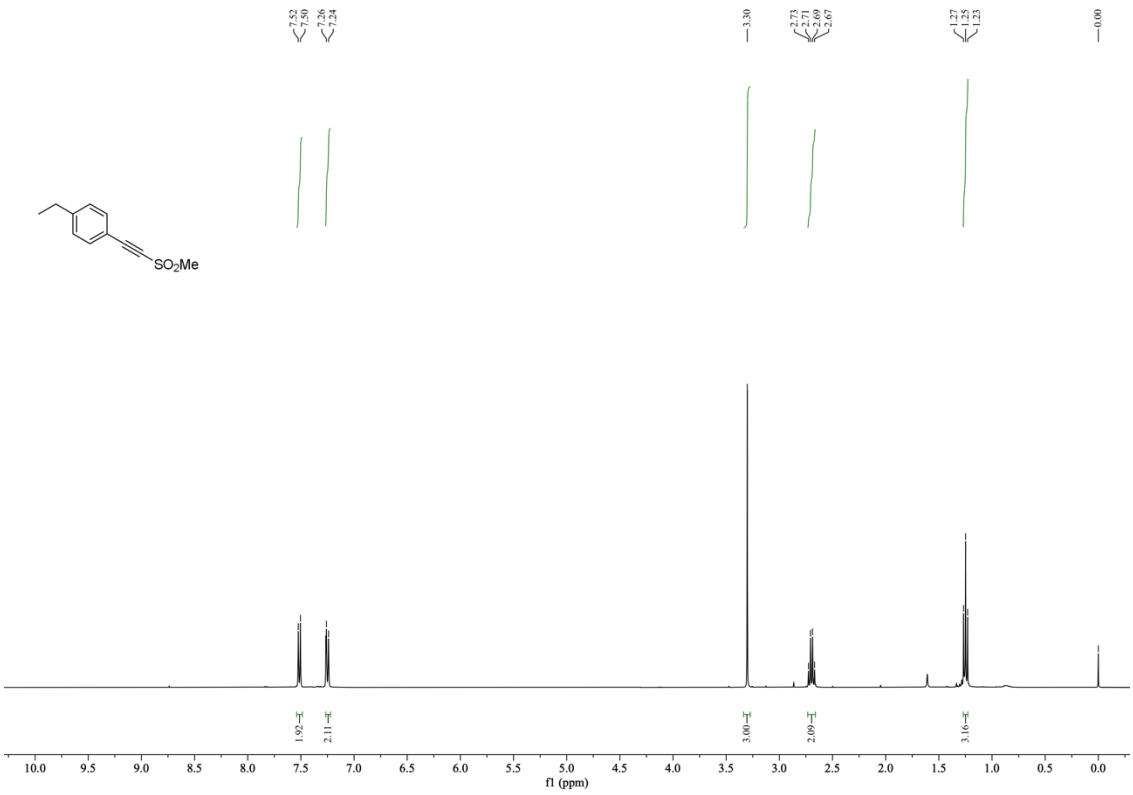

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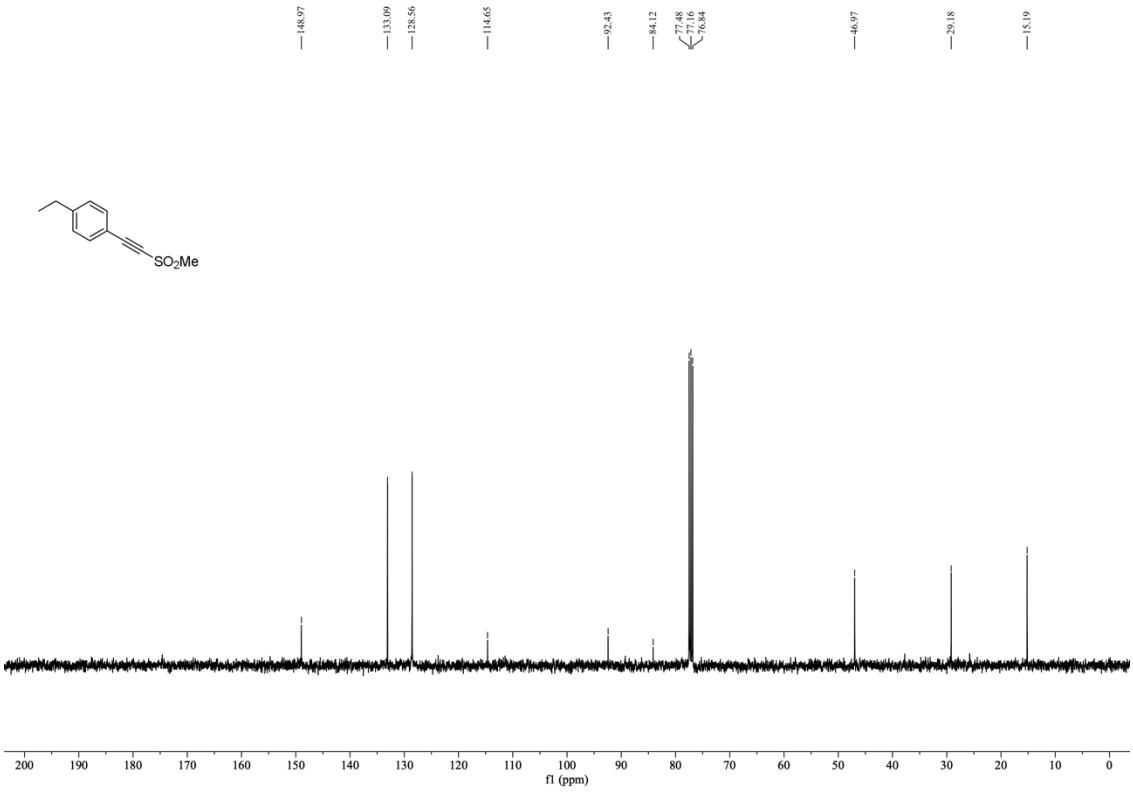

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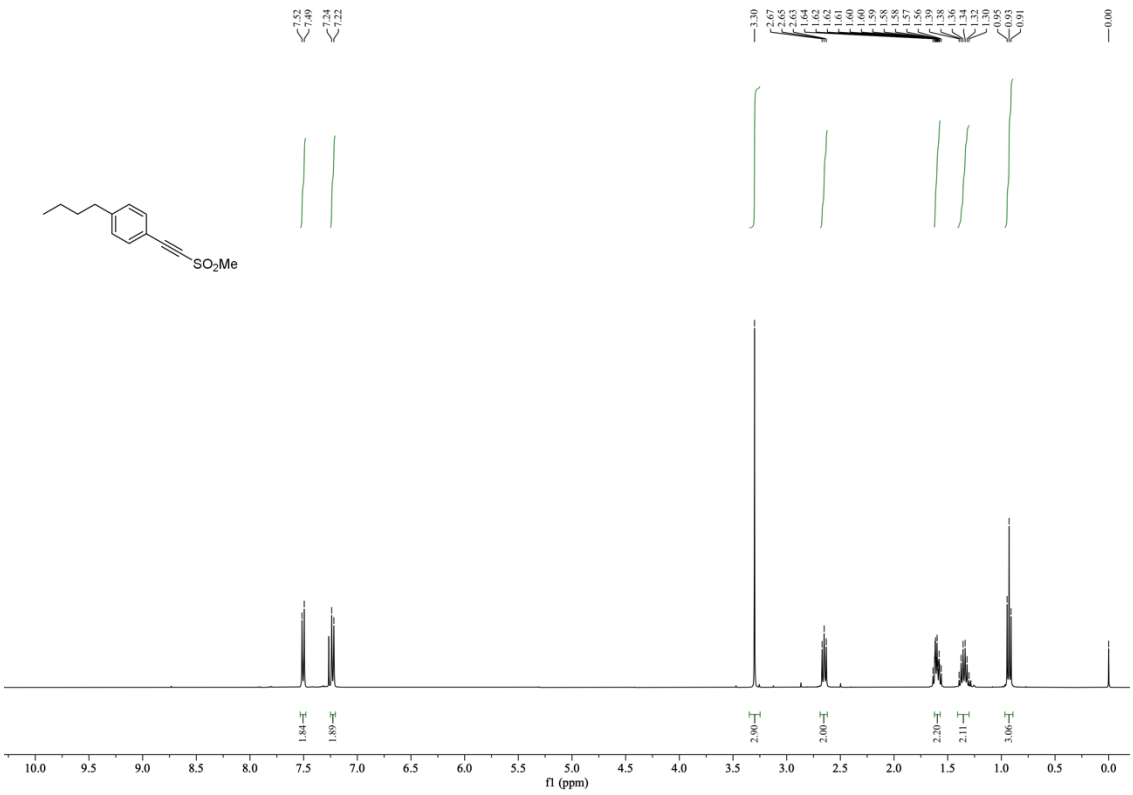
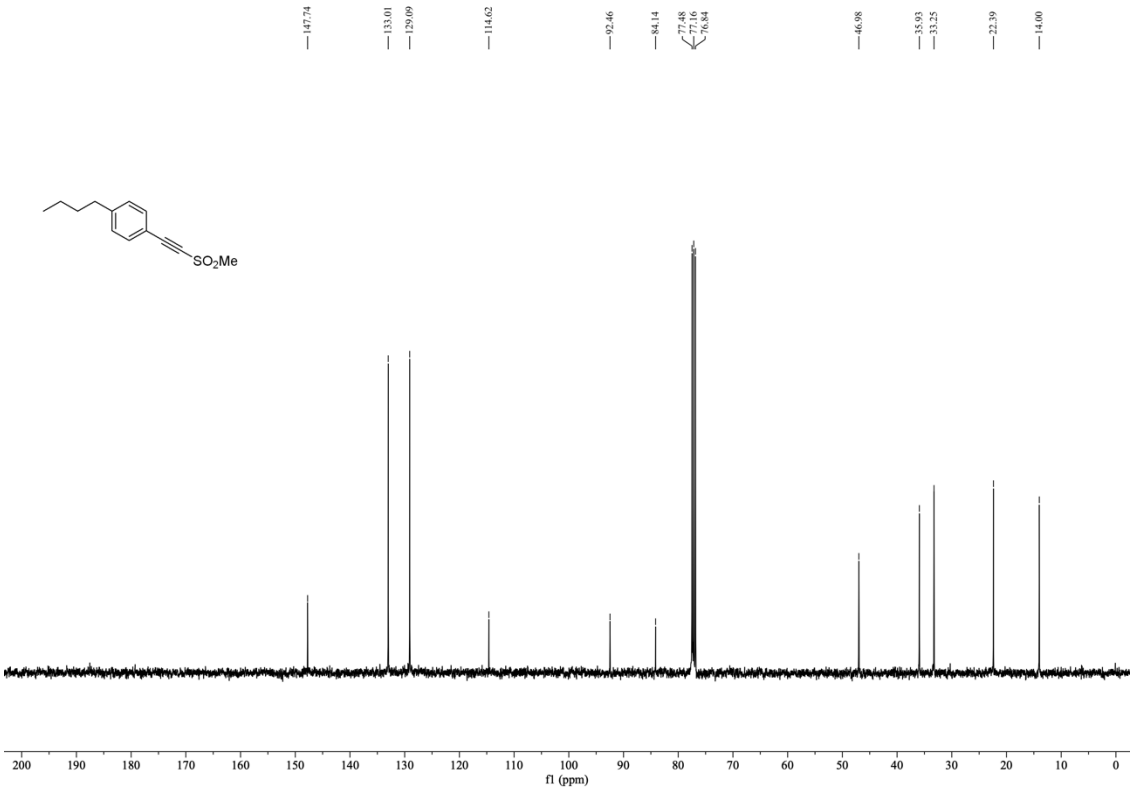


^{1}H NMR Spectrum of Compound 2d (400 MHz, $CDCl_3$)



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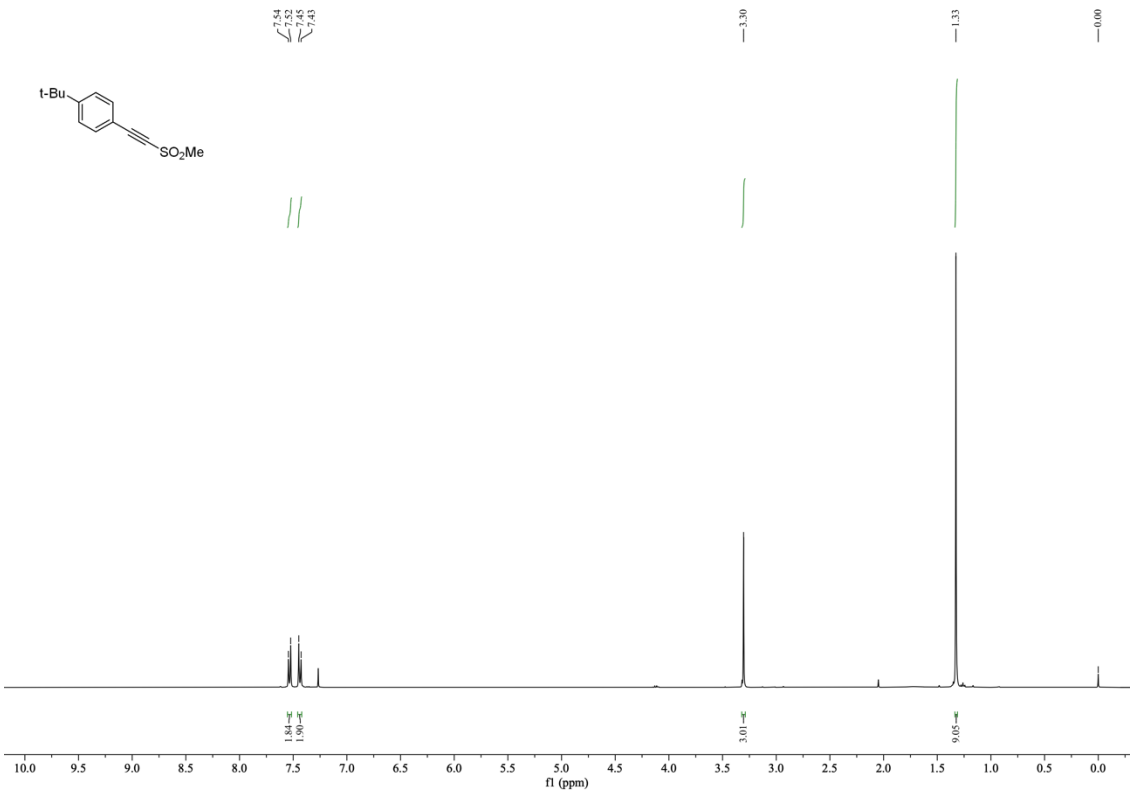
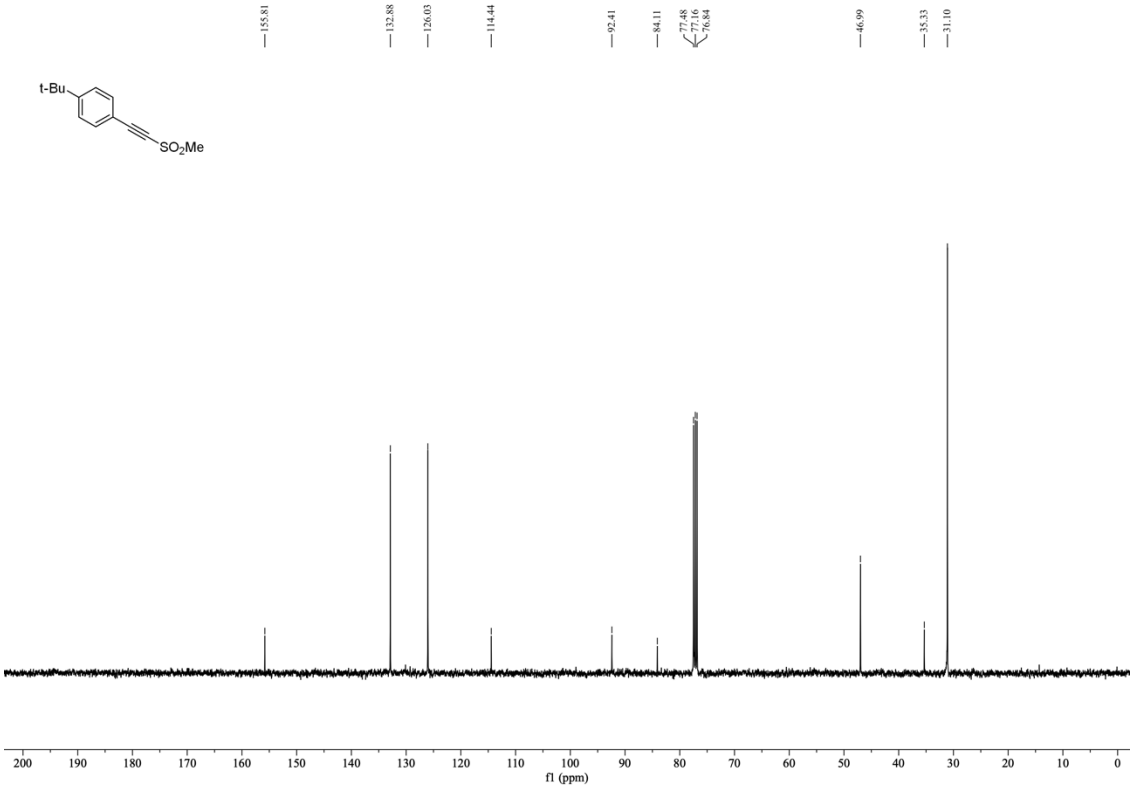


^{1}H NMR Spectrum of Compound 2e (400 MHz, $CDCl_3$)



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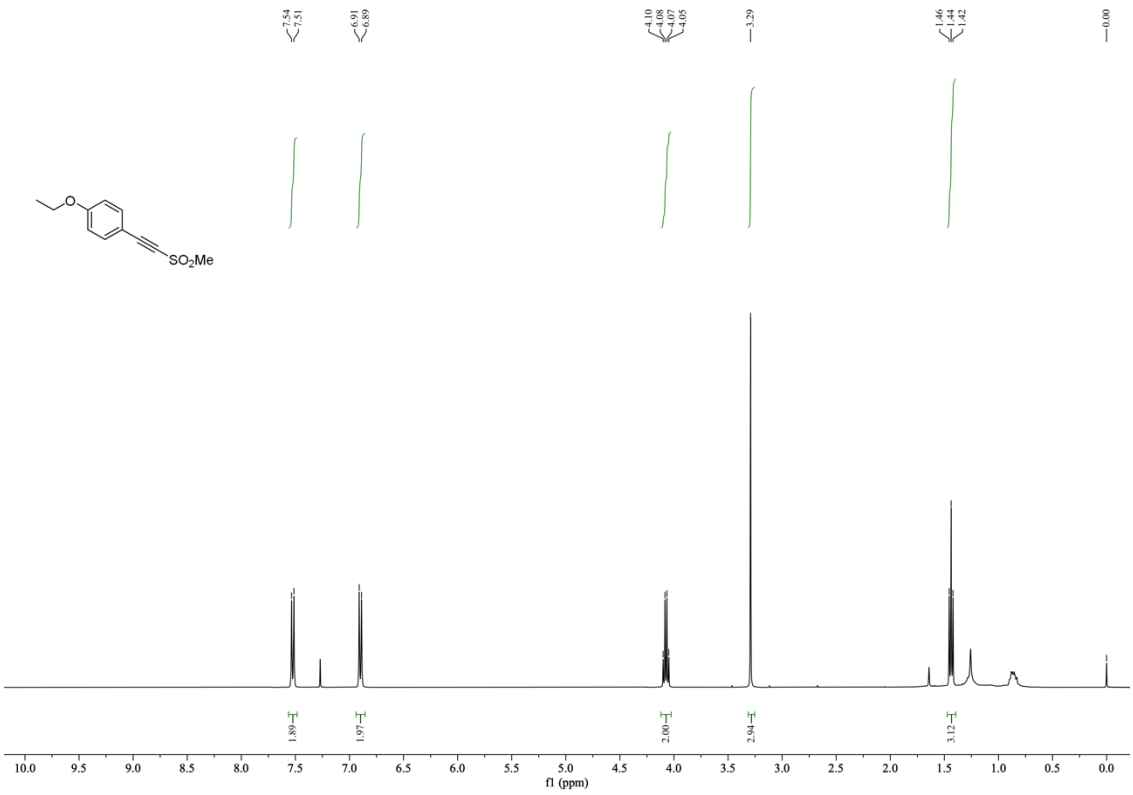
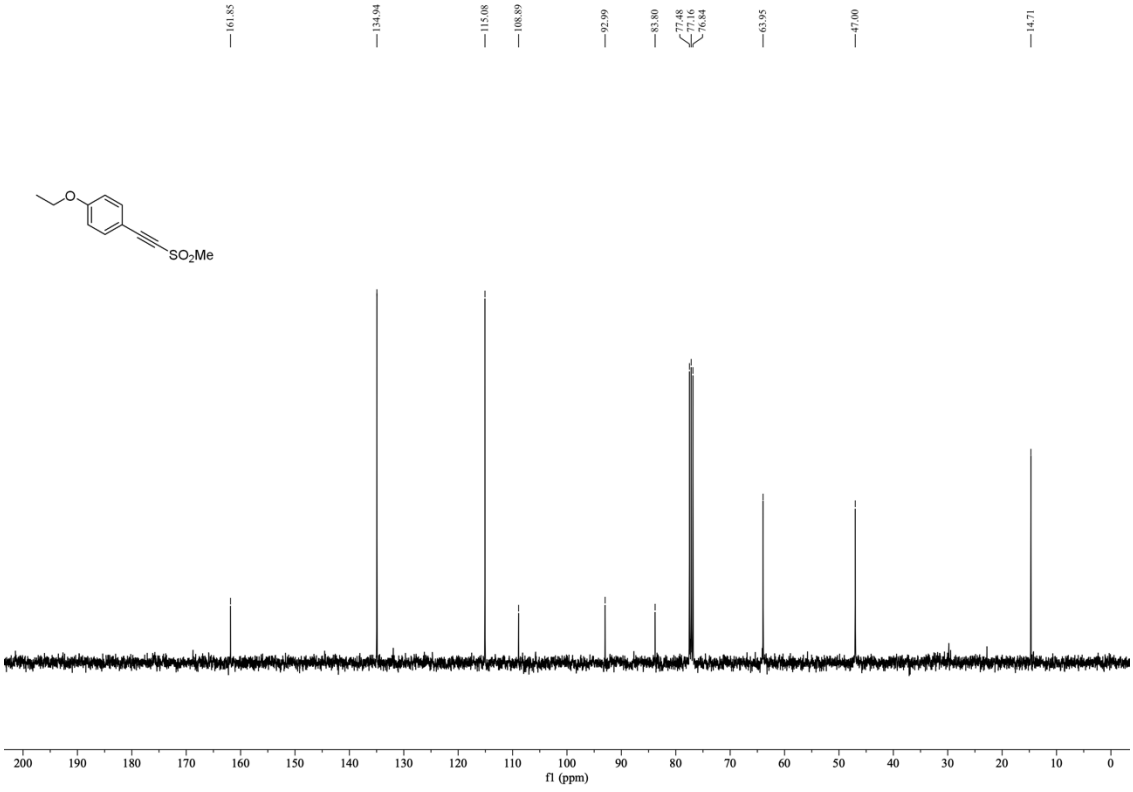
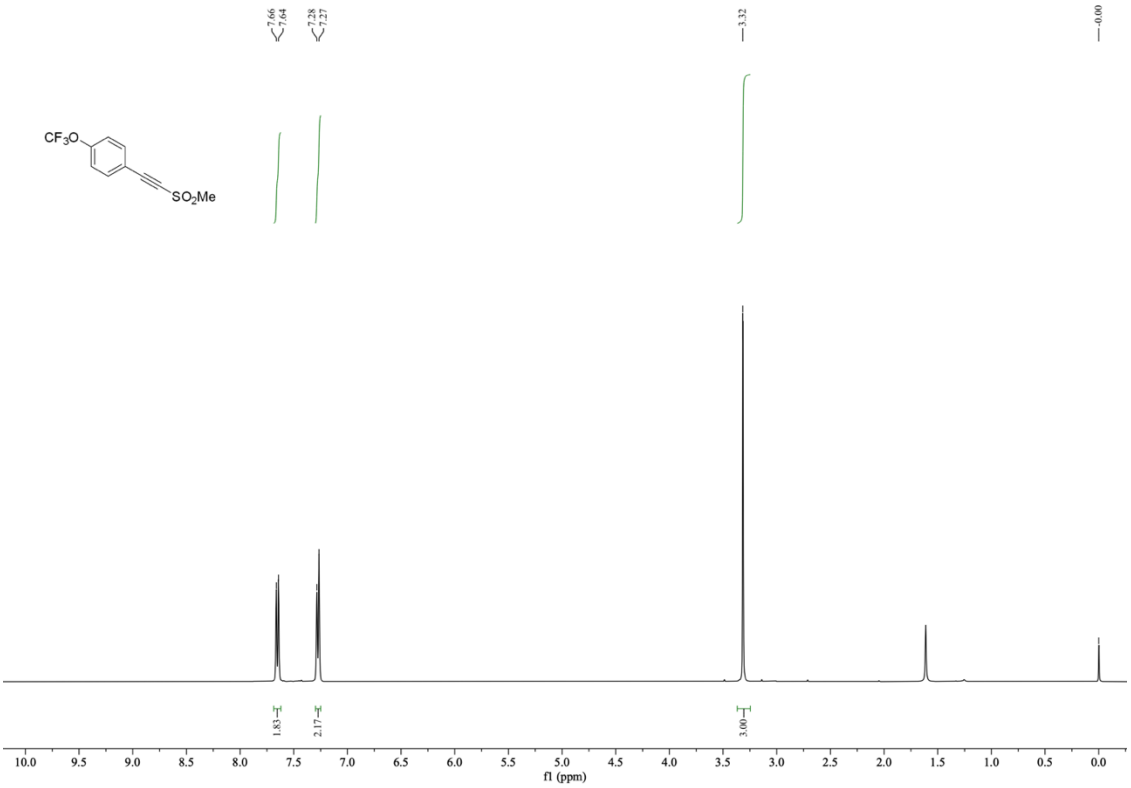


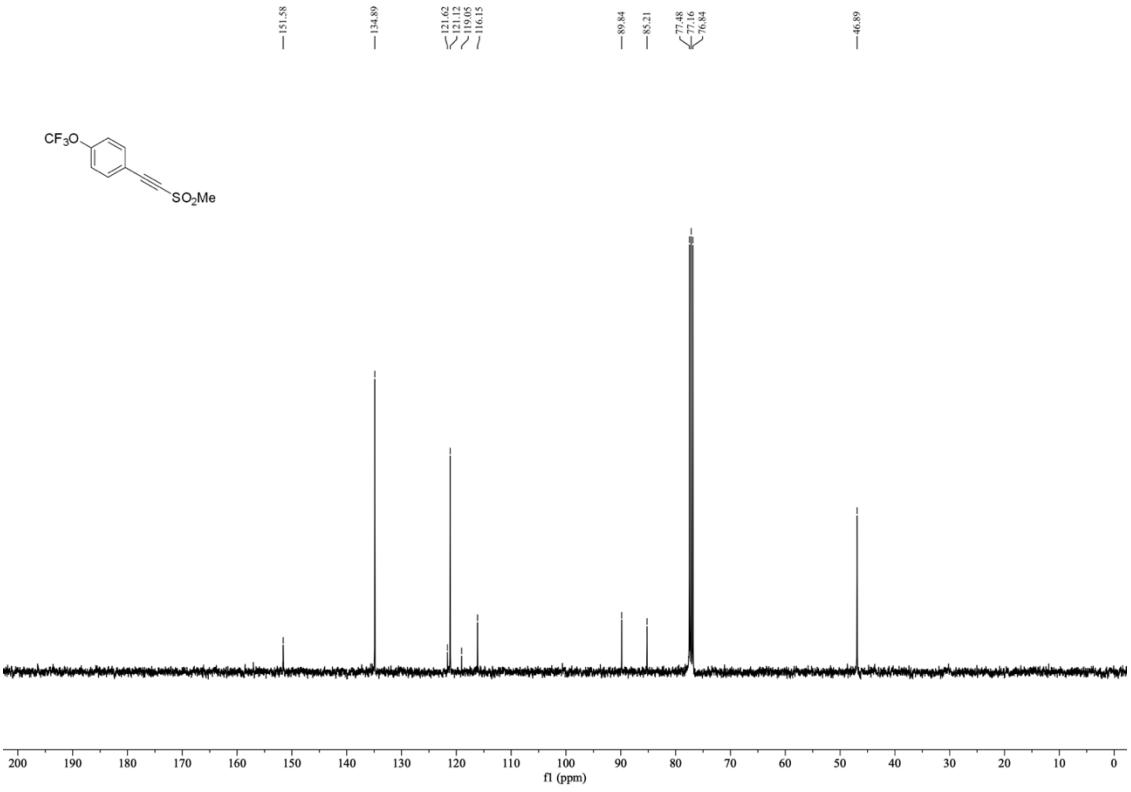
^{1}H NMR Spectrum of Compound 2g (400 MHz, $CDCl_3$)



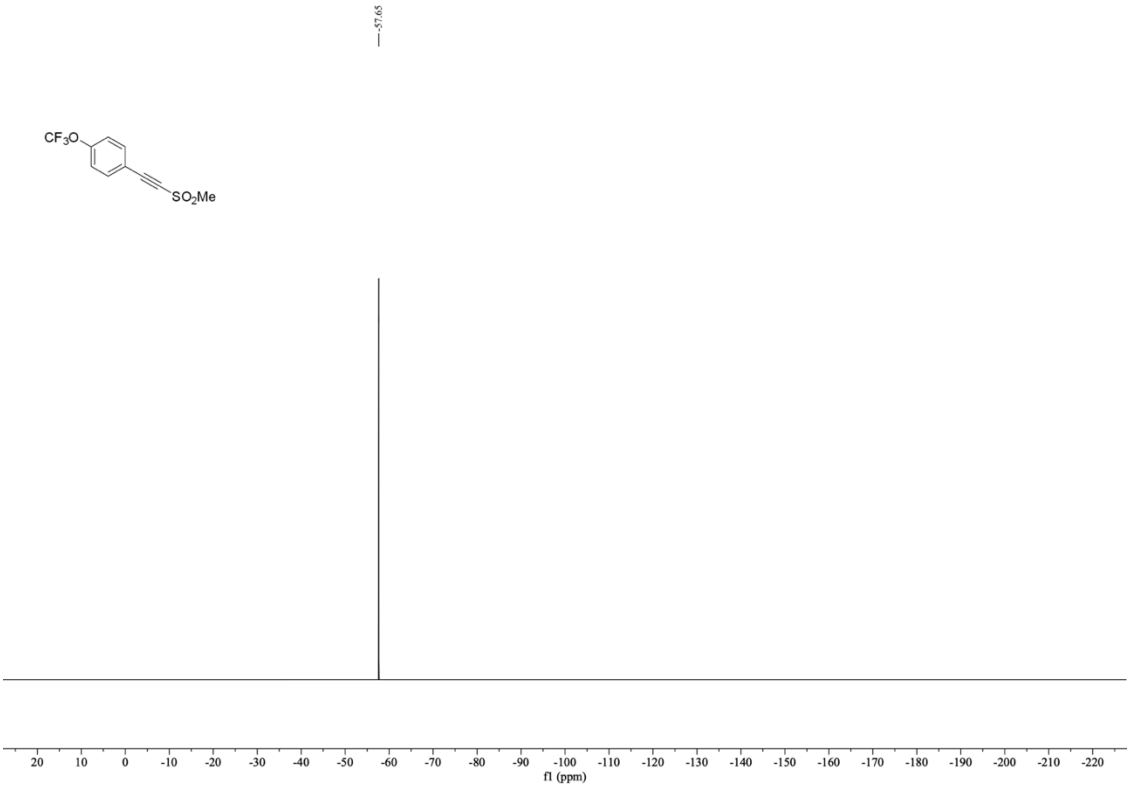
^{13}C NMR Spectrum of Compound 2g (101 MHz, $CDCl_3$)



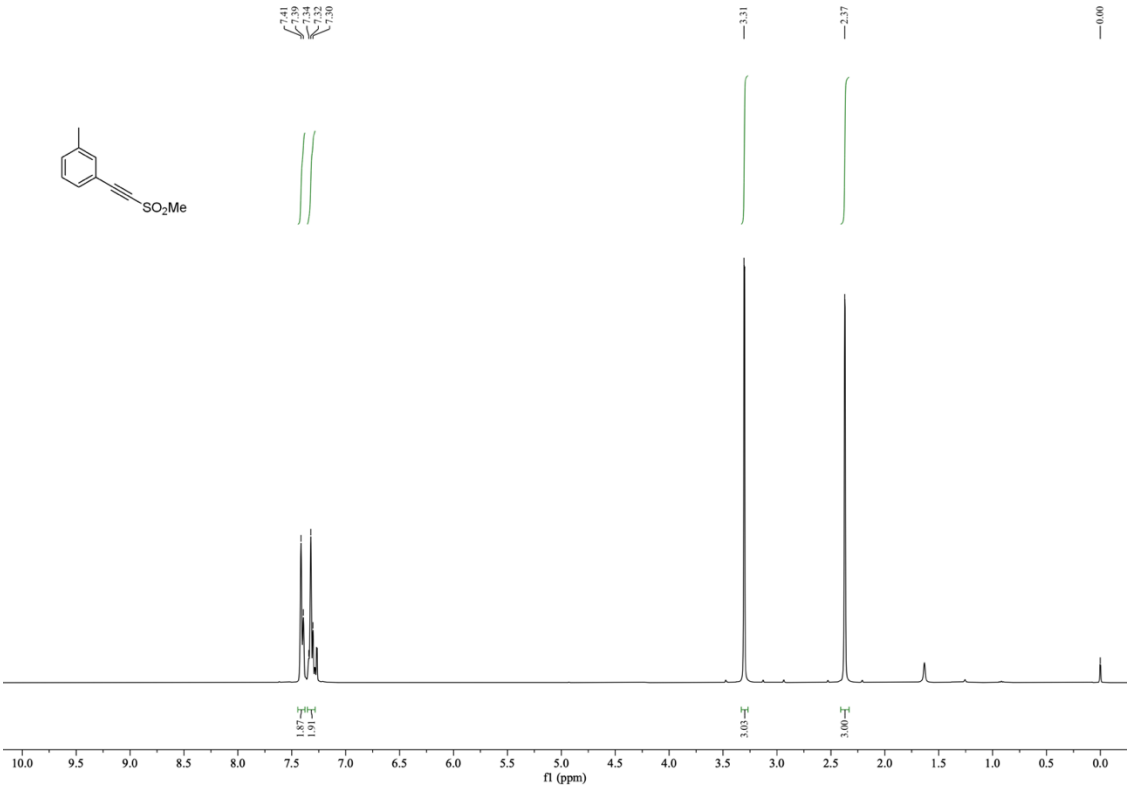
^{1}H NMR Spectrum of Compound 2h (400 MHz, $CDCl_3$)



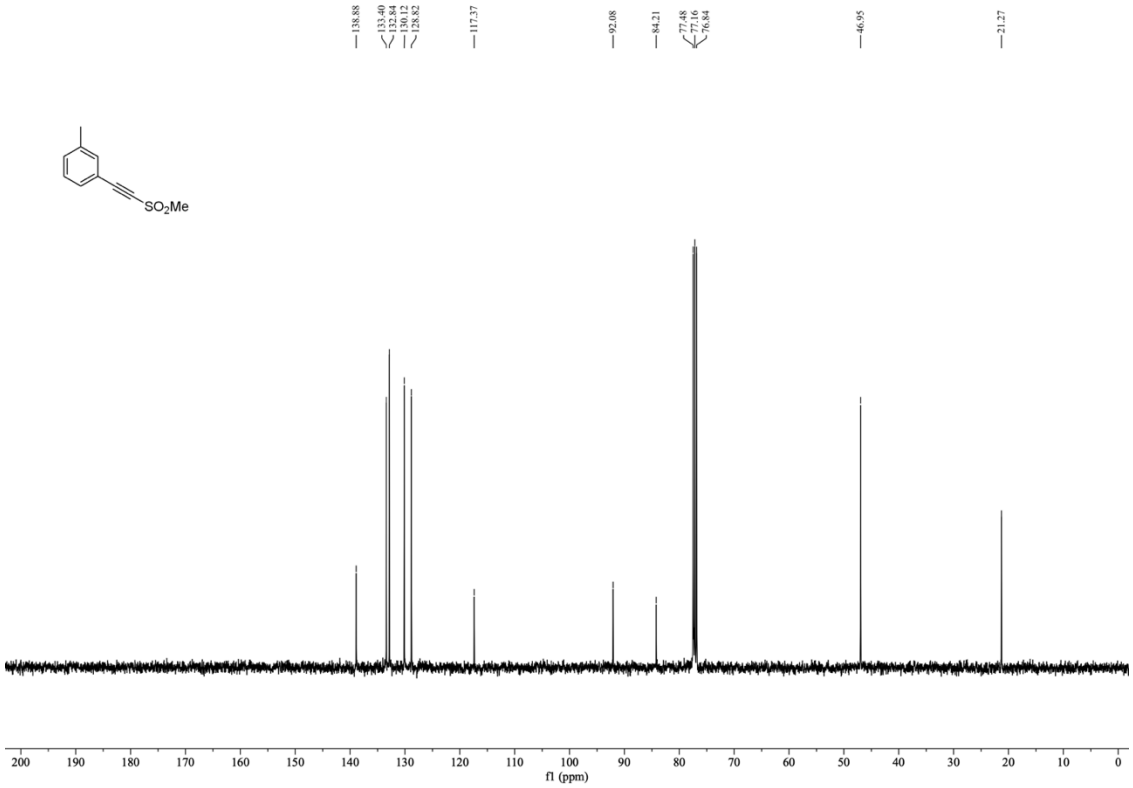
^{13}C NMR Spectrum of Compound 2h (101 MHz, $CDCl_3$)



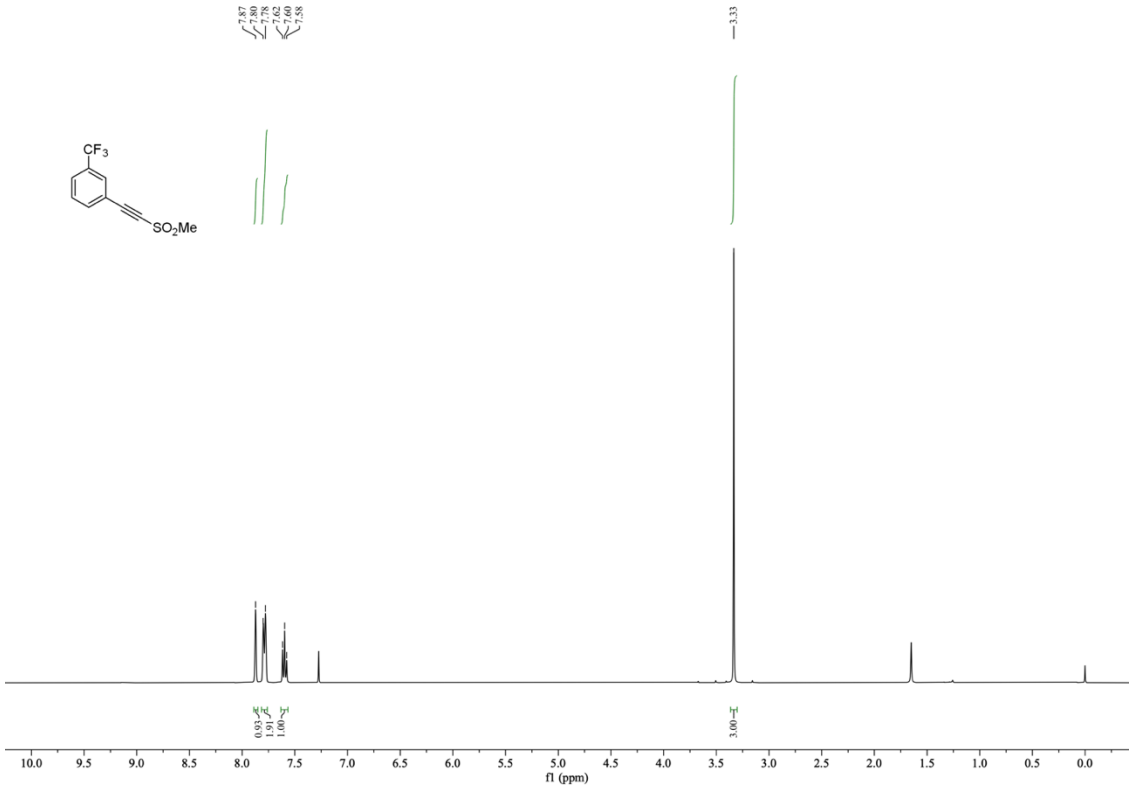
^{19}F NMR Spectrum of Compound 2h (376 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound 2n (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound 2n (101 MHz, $CDCl_3$)



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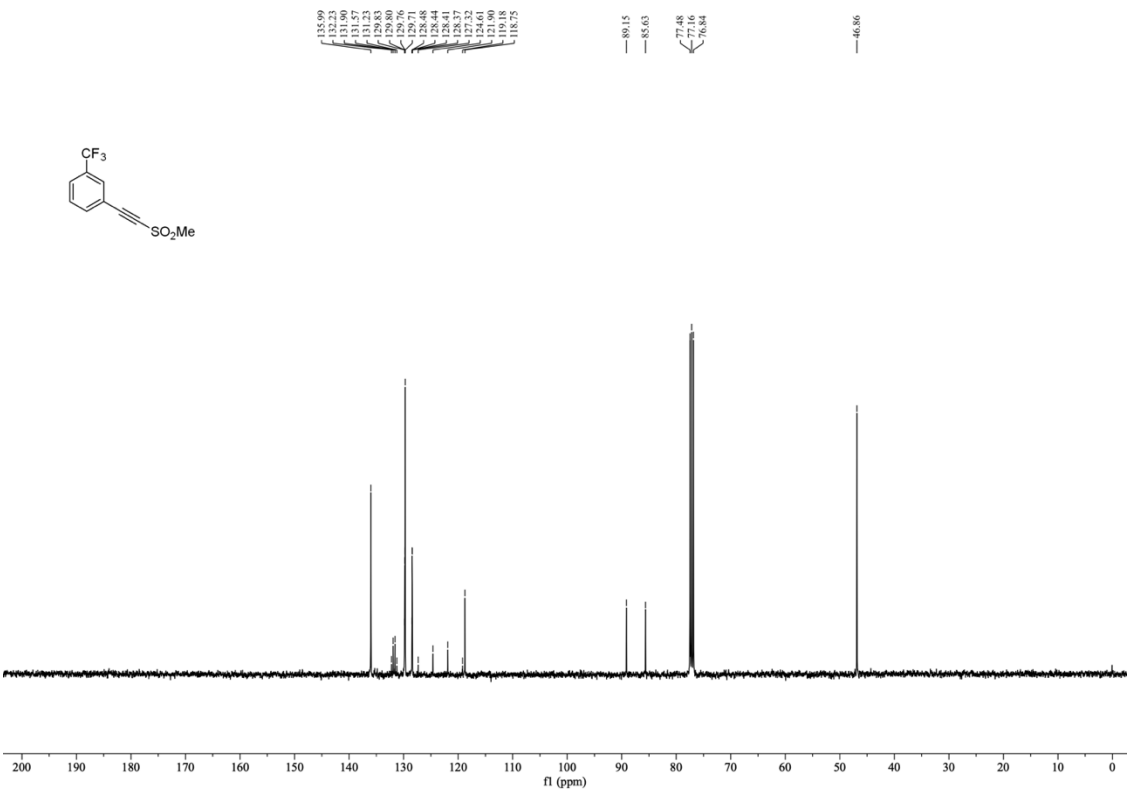
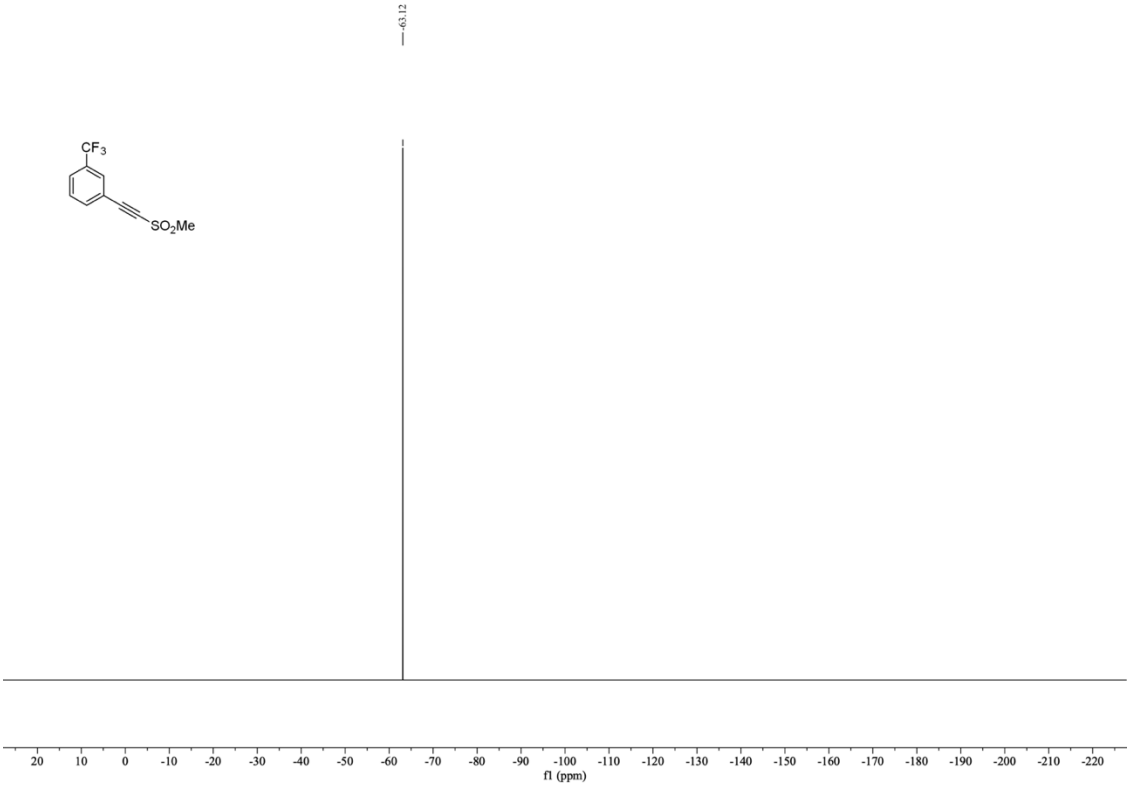
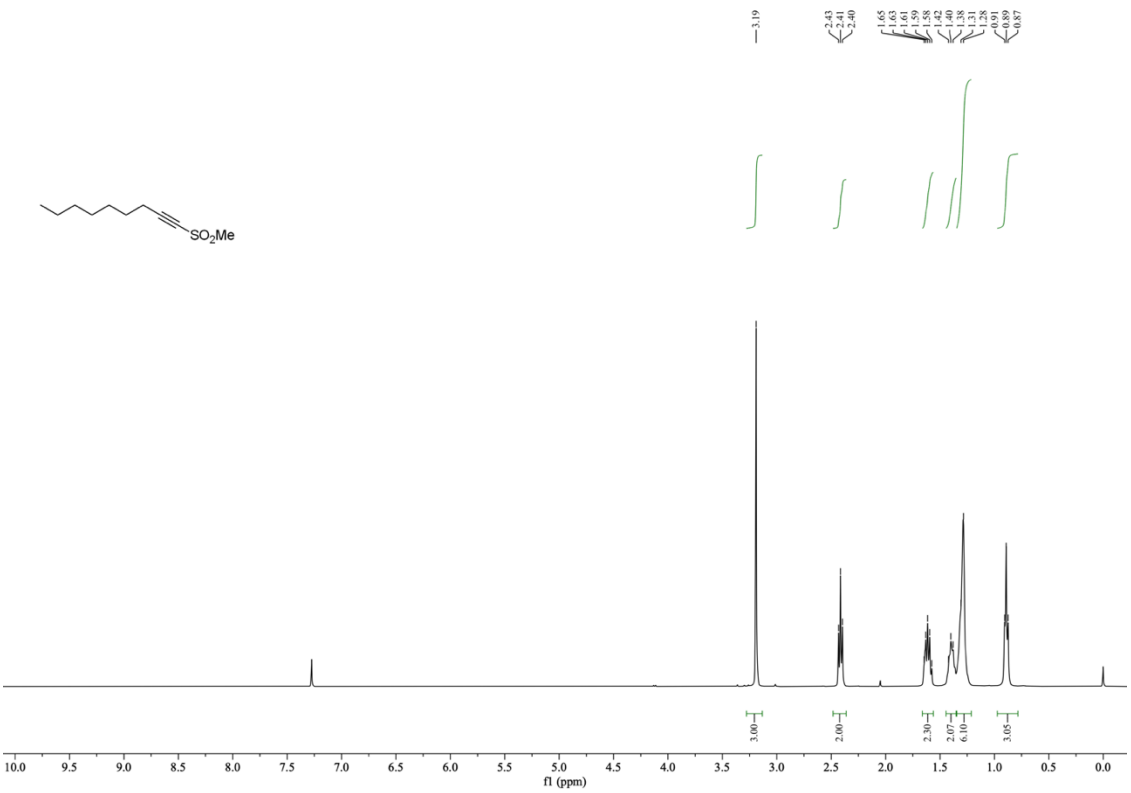


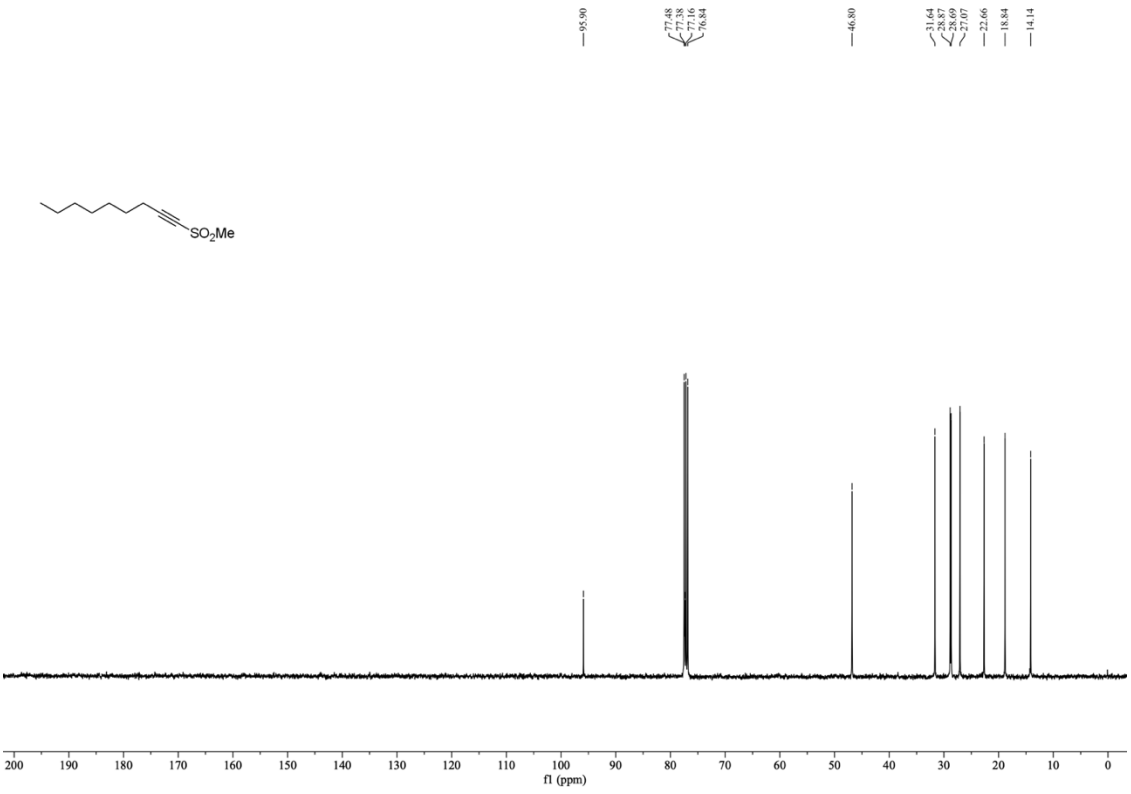
^{13}C NMR Spectrum of Compound 2o (101 MHz, $CDCl_3$)



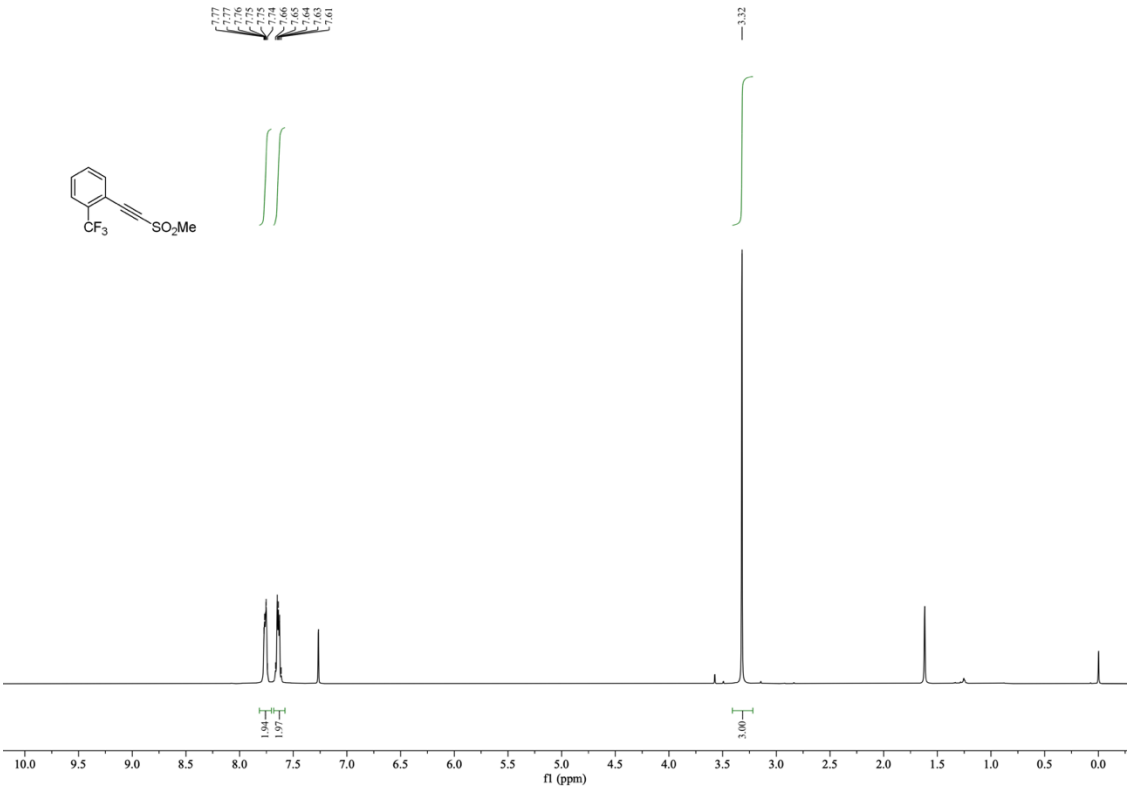
^{19}F NMR Spectrum of Compound 2o (376 MHz, $CDCl_3$)



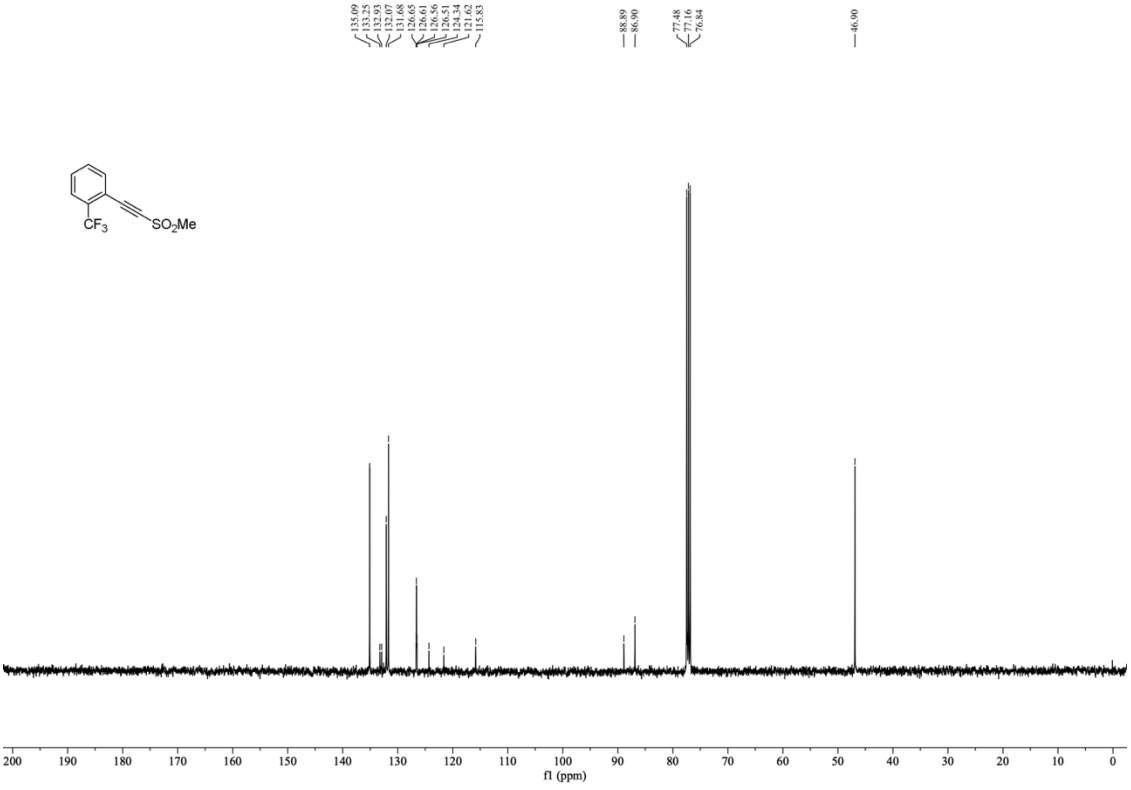
^{1}H NMR Spectrum of Compound 2p (400 MHz, $CDCl_3$)



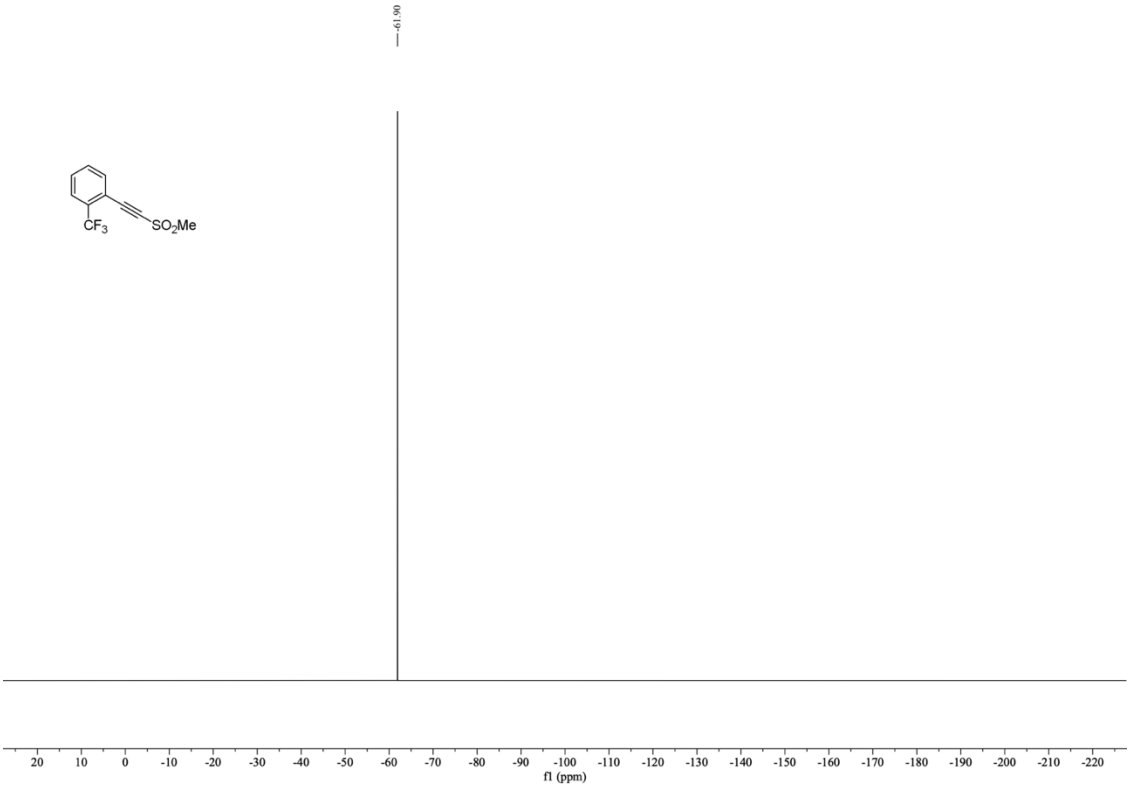
^{13}C NMR Spectrum of Compound 2p (101 MHz, $CDCl_3$)



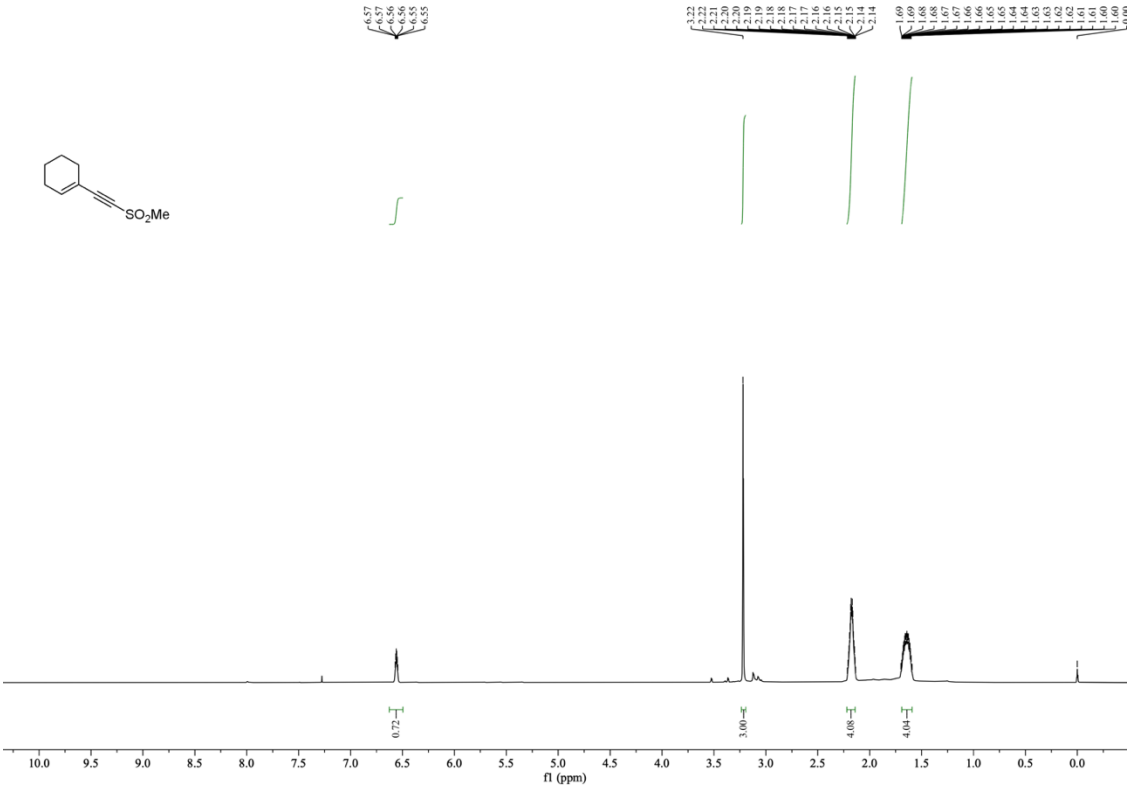
^{1}H NMR Spectrum of Compound 2r (400 MHz, $CDCl_3$)



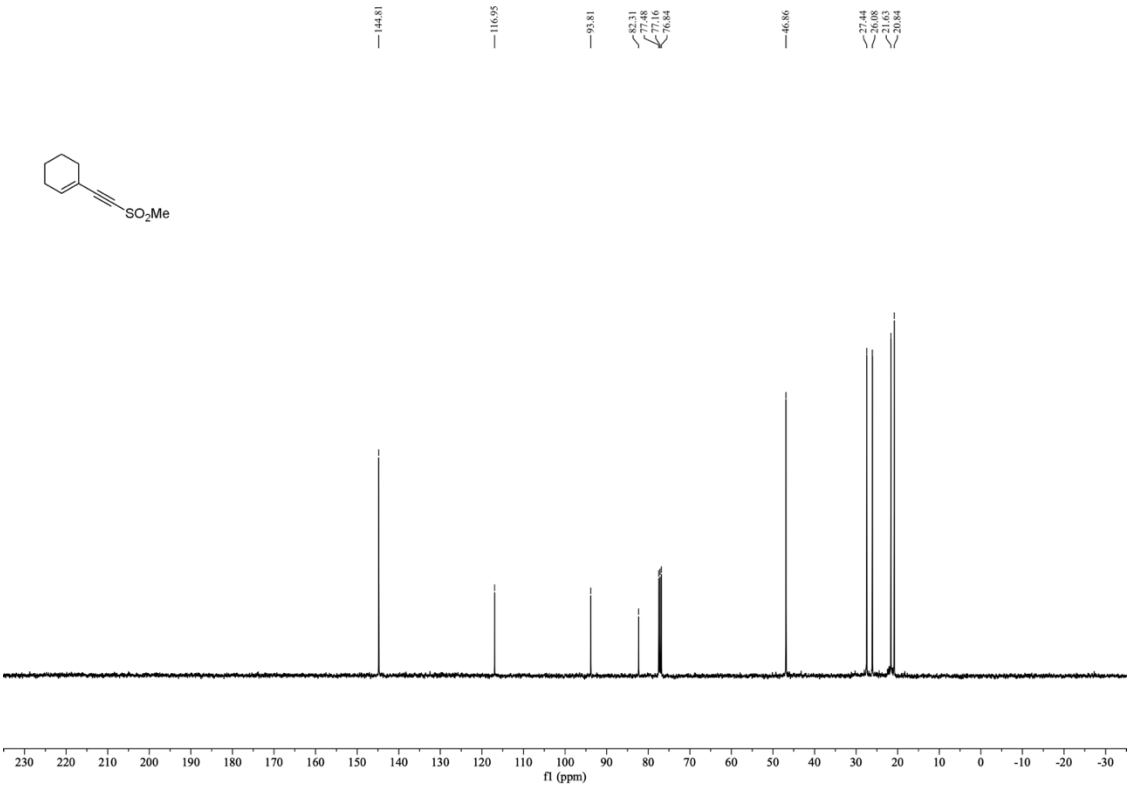
^{13}C NMR Spectrum of Compound 2r (101 MHz, $CDCl_3$)



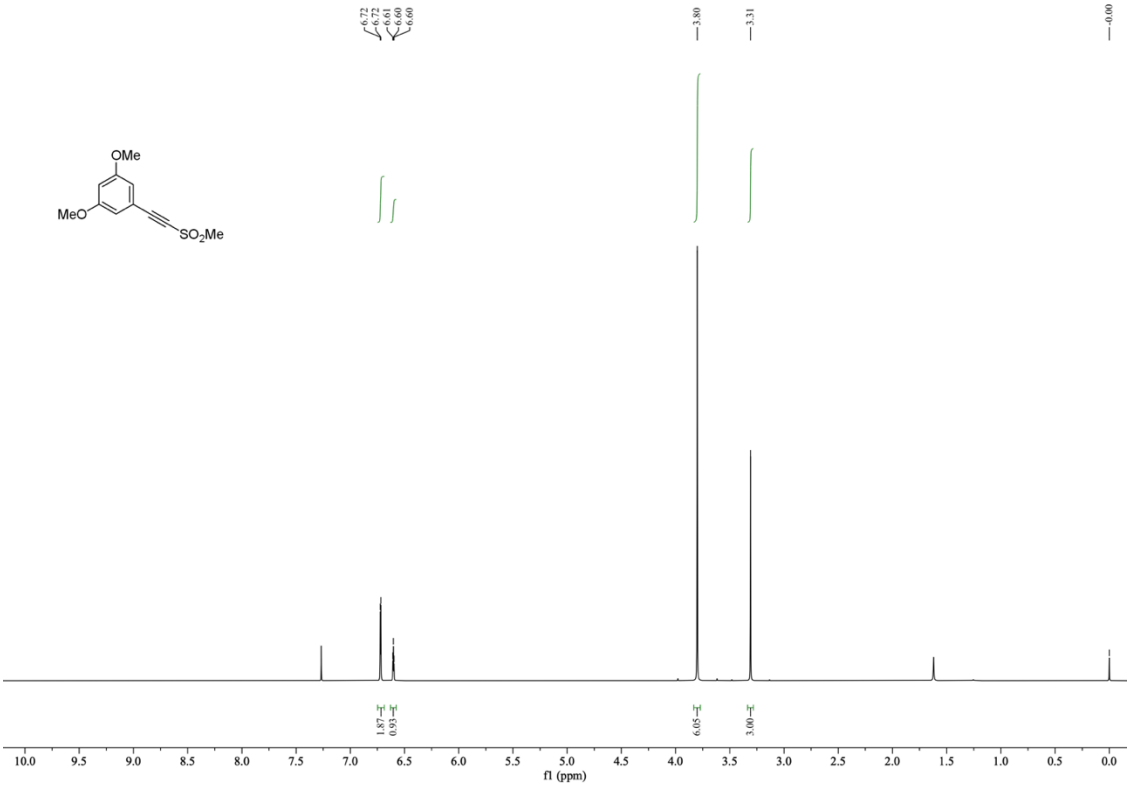
^{19}F NMR Spectrum of Compound 2r (376 MHz, $CDCl_3$)



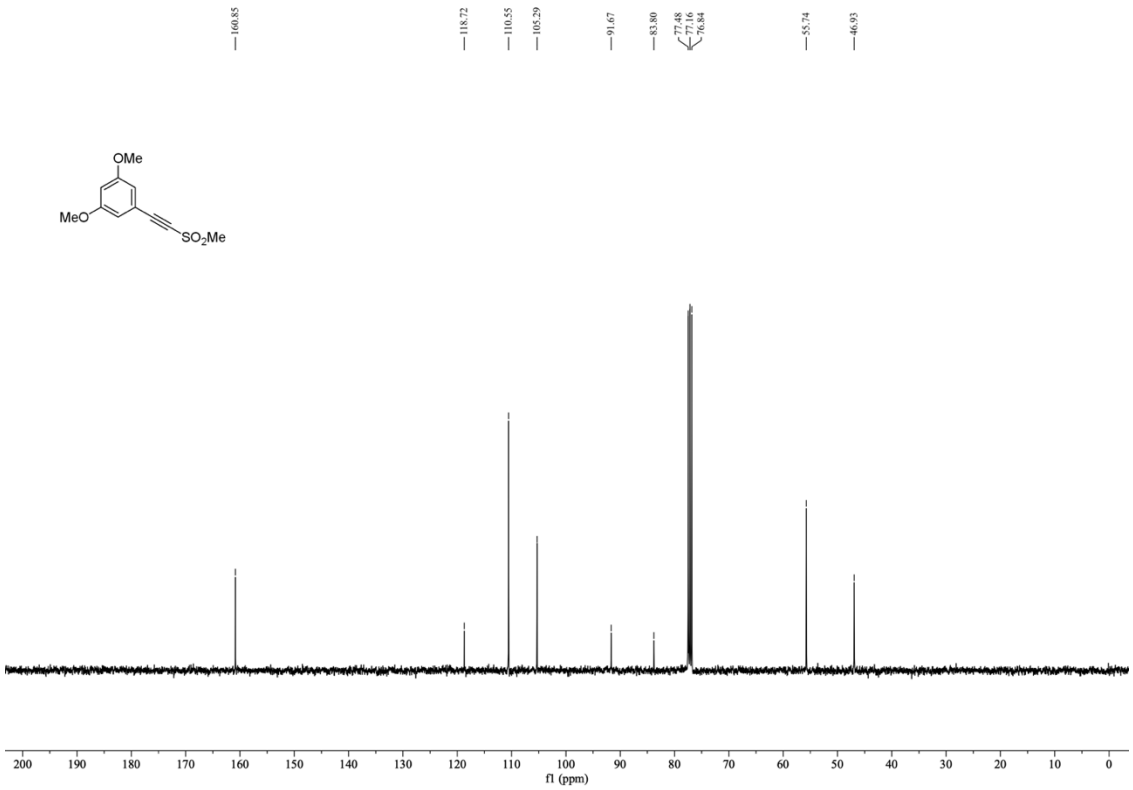
^{1}H NMR Spectrum of Compound 2s (400 MHz, $CDCl_3$)



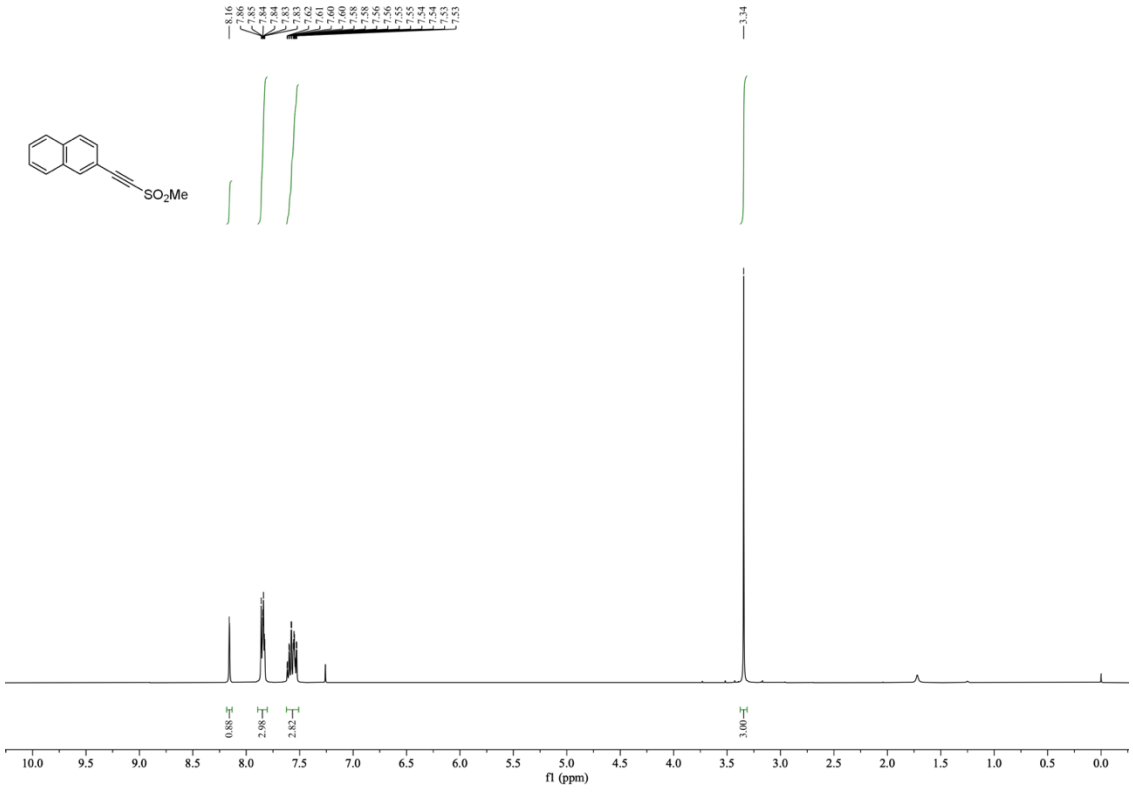
^{13}C NMR Spectrum of Compound 2s (101 MHz, $CDCl_3$)



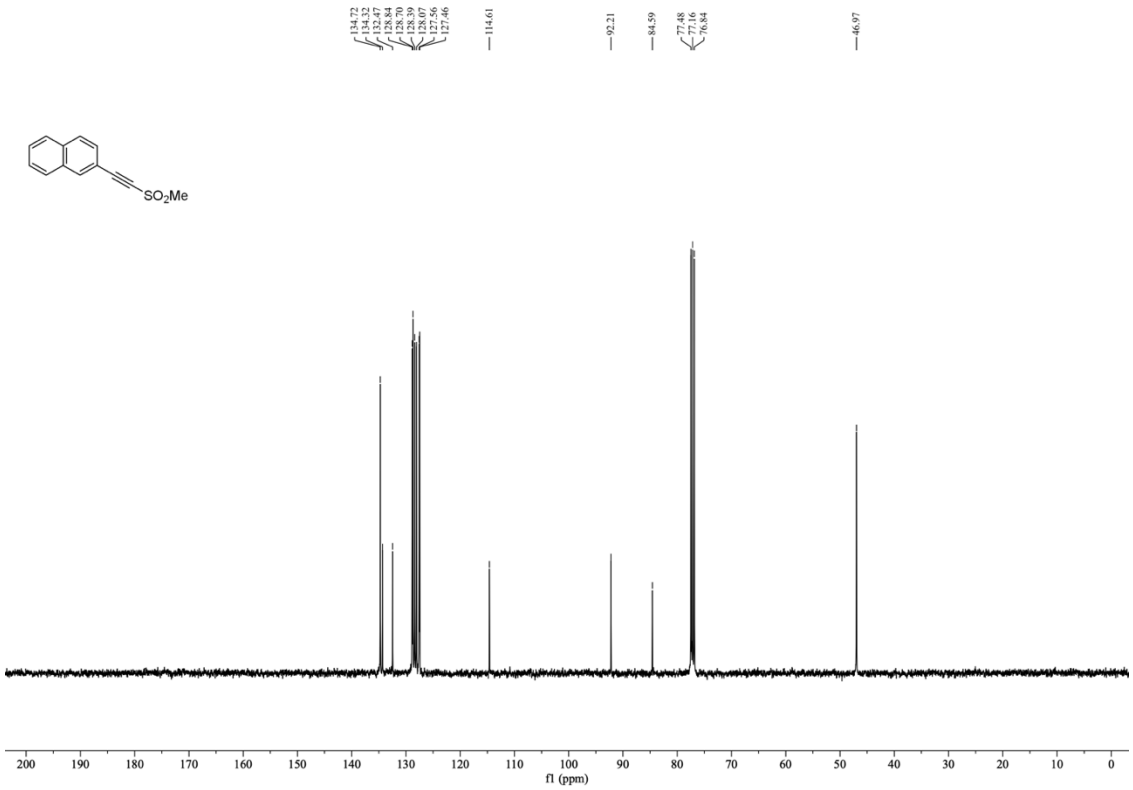
^{1}H NMR Spectrum of Compound 2t (400 MHz, $CDCl_3$)



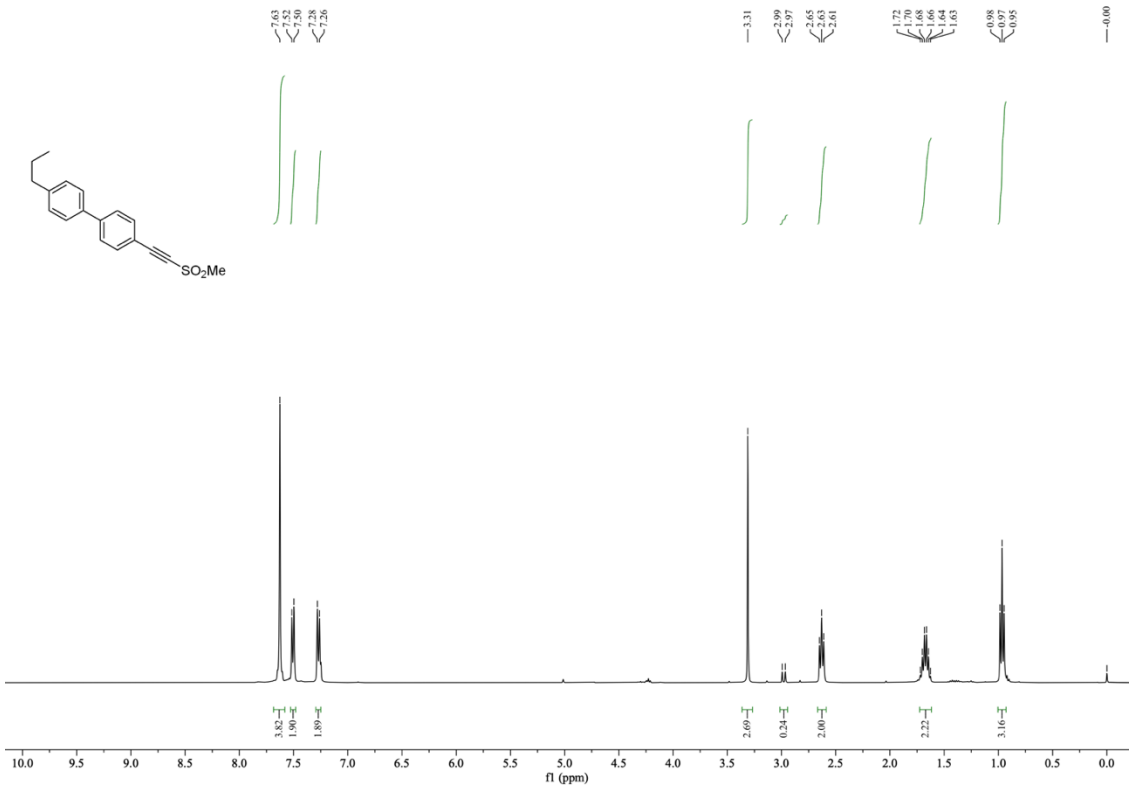
^{13}C NMR Spectrum of Compound 2t (101 MHz, $CDCl_3$)



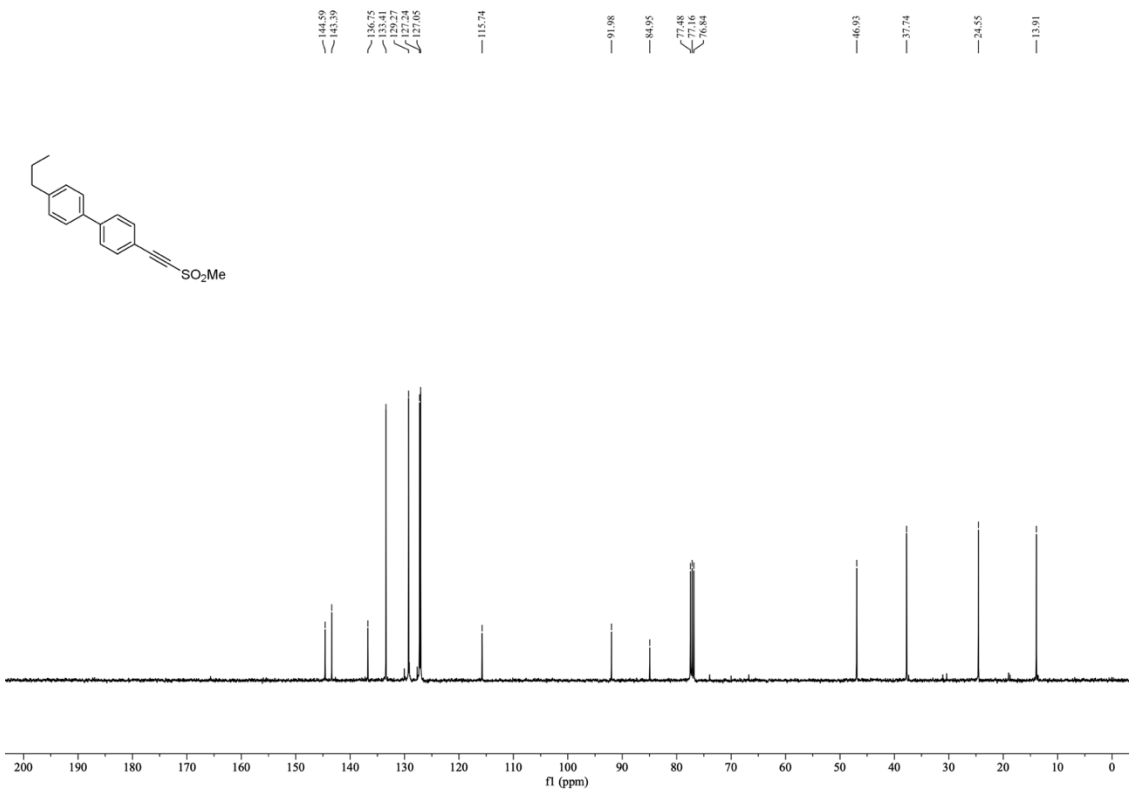
^{1}H NMR Spectrum of Compound 2v (400 MHz, $CDCl_3$)



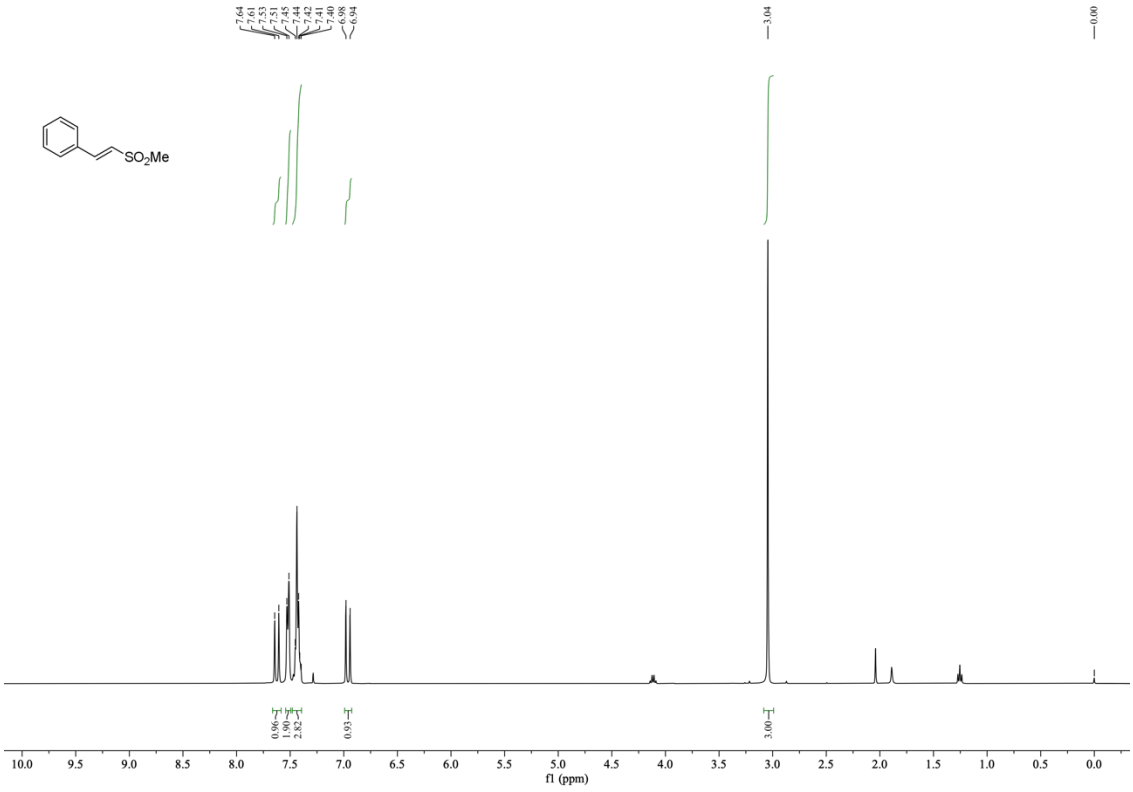
^{13}C NMR Spectrum of Compound 2v (101 MHz, $CDCl_3$)



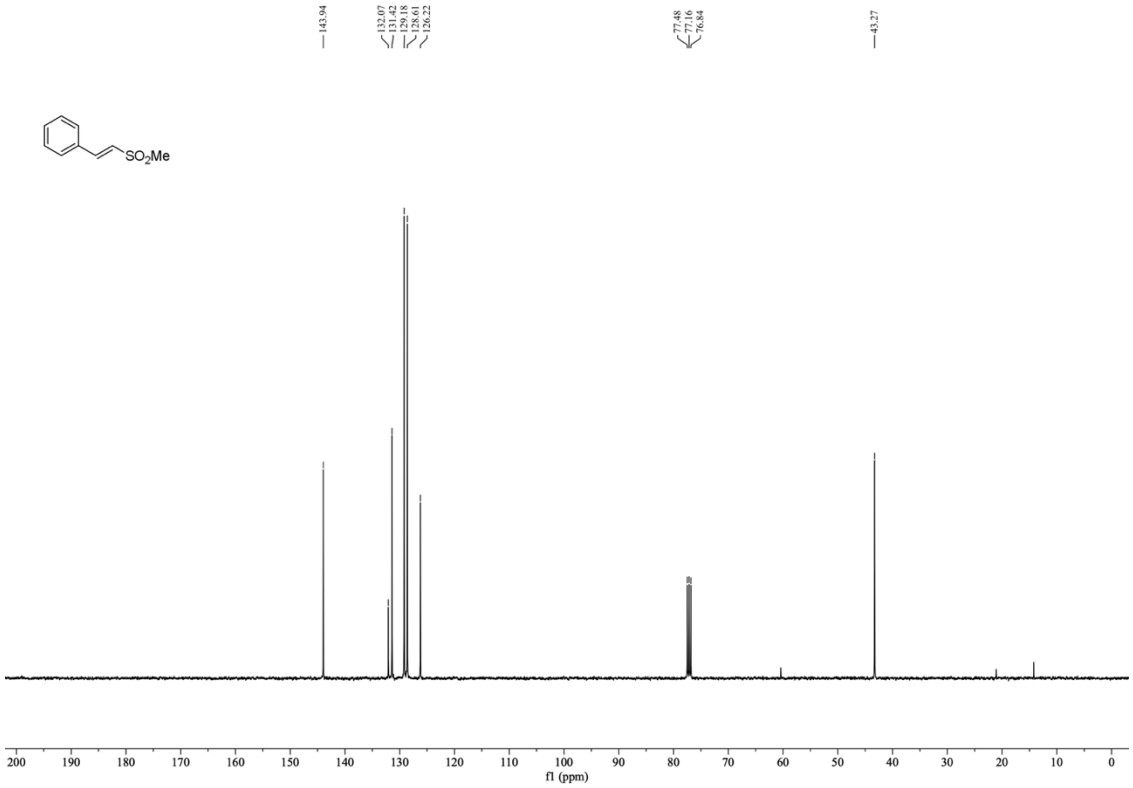
^{1}H NMR Spectrum of Compound 2w (400 MHz, $CDCl_3$)



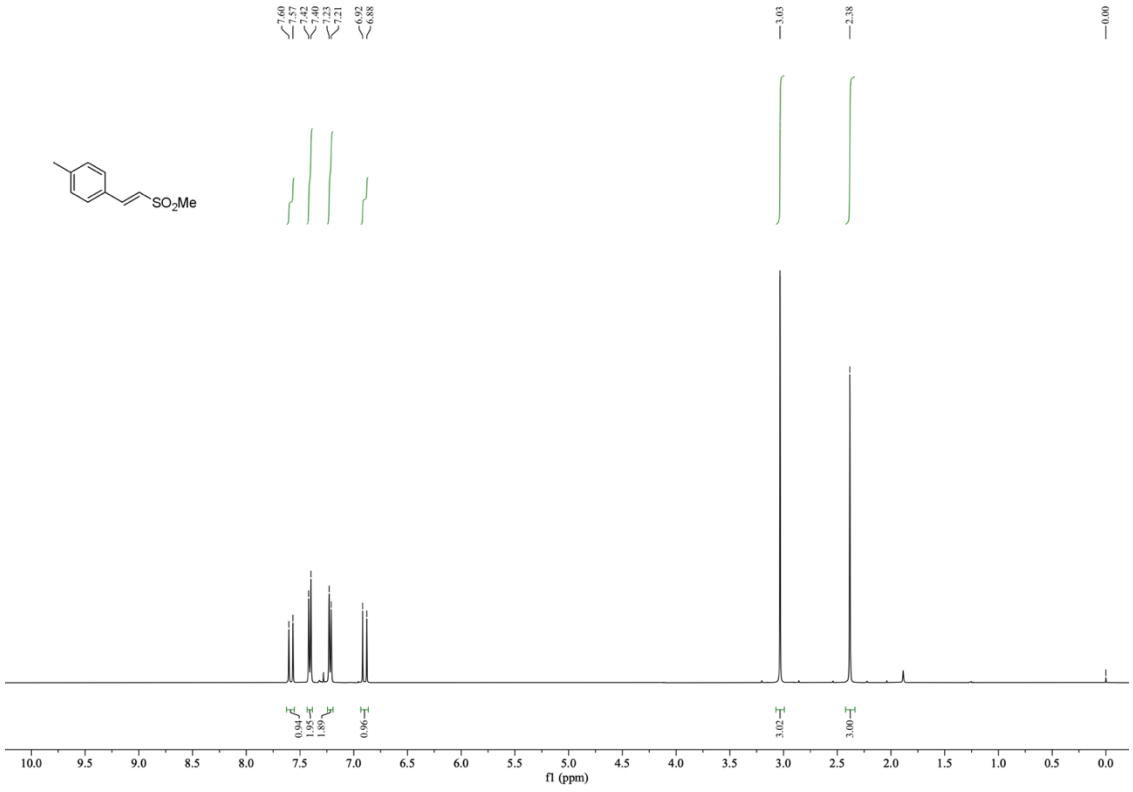
^{13}C NMR Spectrum of Compound 2w (101 MHz, $CDCl_3$)



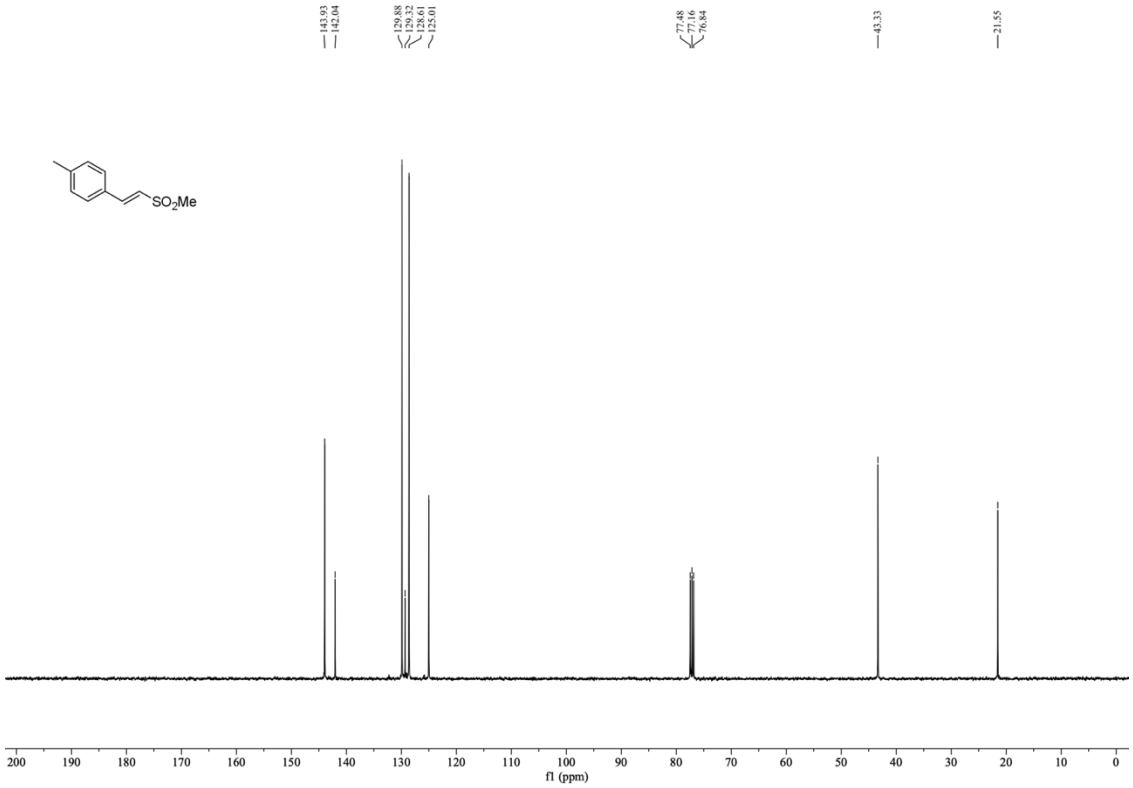
^{1}H NMR Spectrum of Compound 5a (400 MHz, $CDCl_3$)



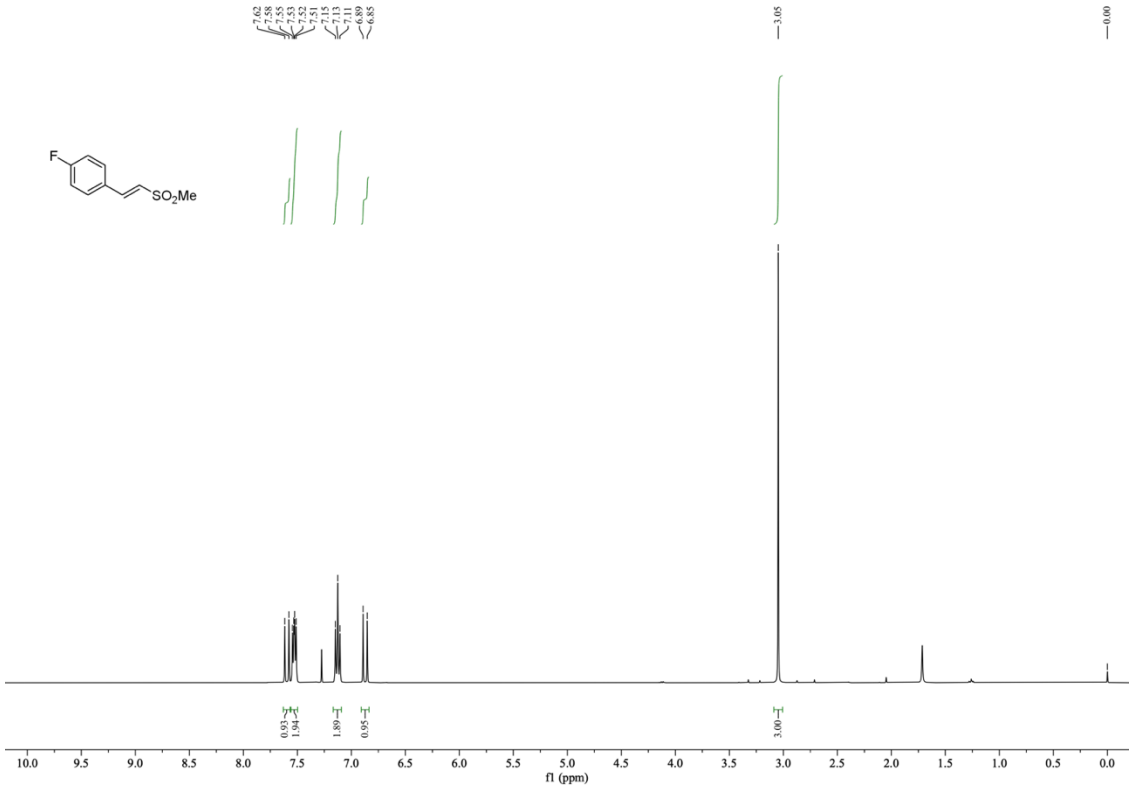
^{13}C NMR Spectrum of Compound 5a (101 MHz, $CDCl_3$)



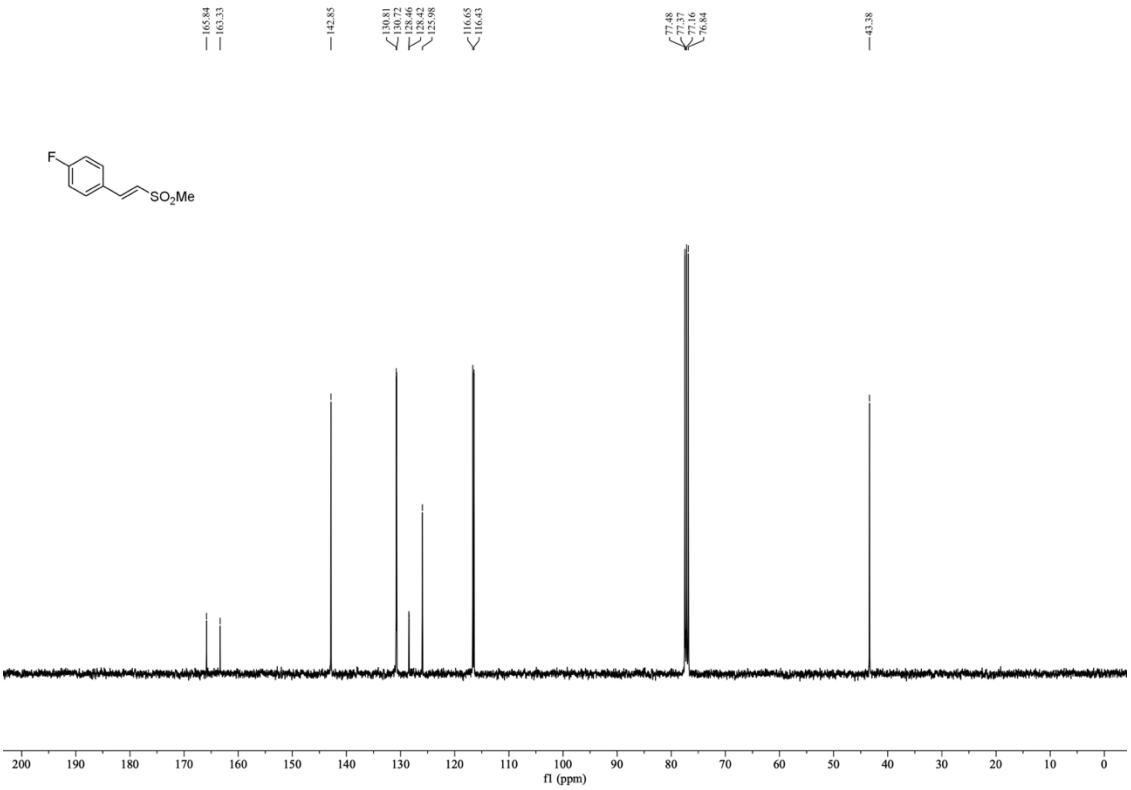
^{1}H NMR Spectrum of Compound 5b (400 MHz, $CDCl_3$)



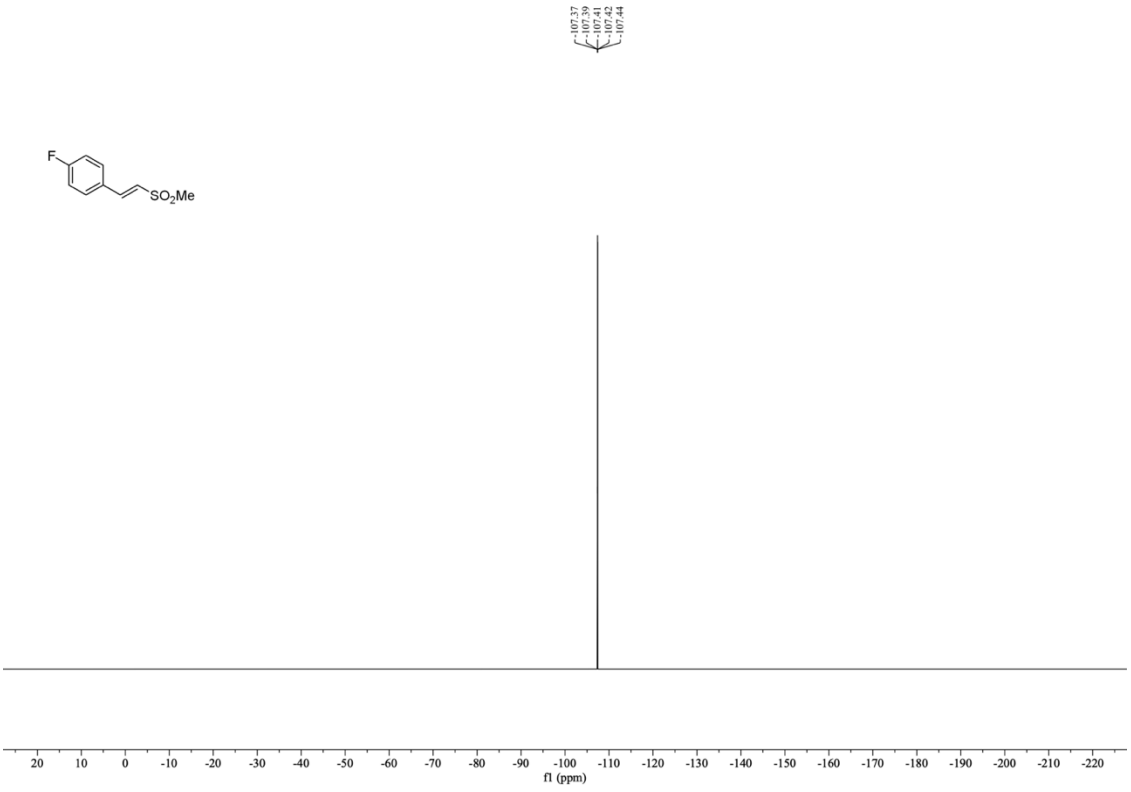
^{13}C NMR Spectrum of Compound 5b (101 MHz, $CDCl_3$)



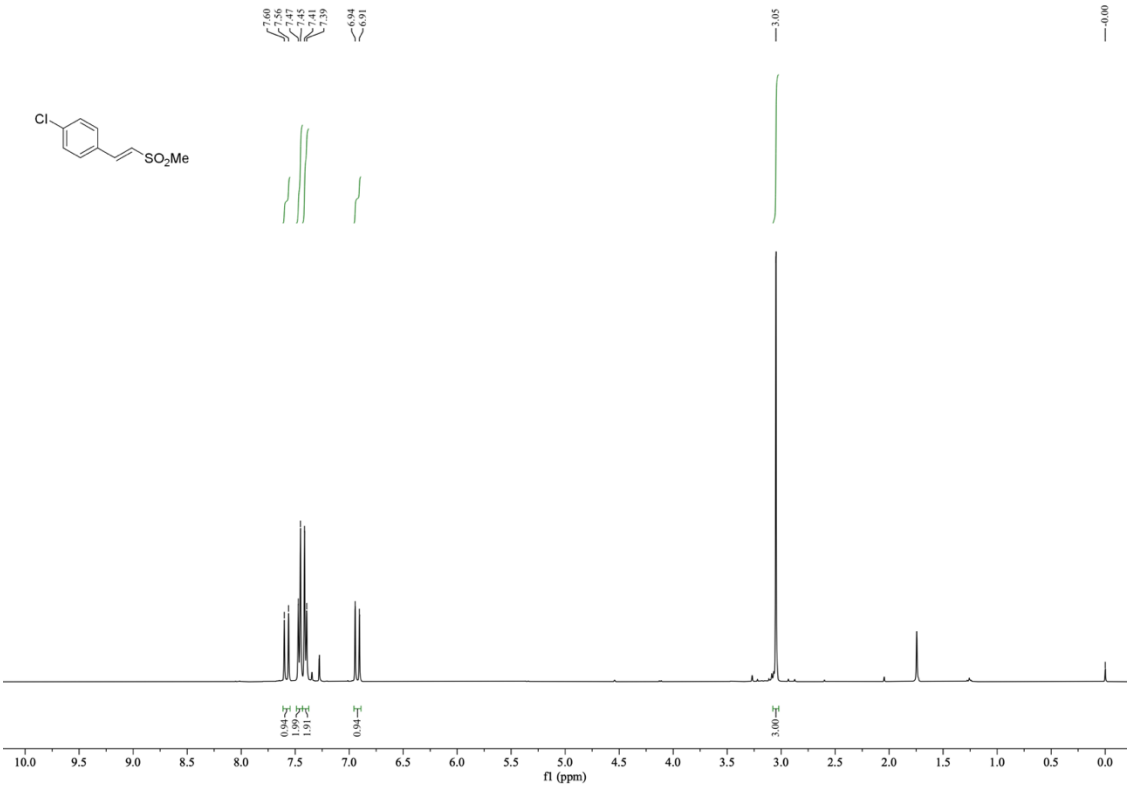
^{1}H NMR Spectrum of Compound 5c (400 MHz, $CDCl_3$)



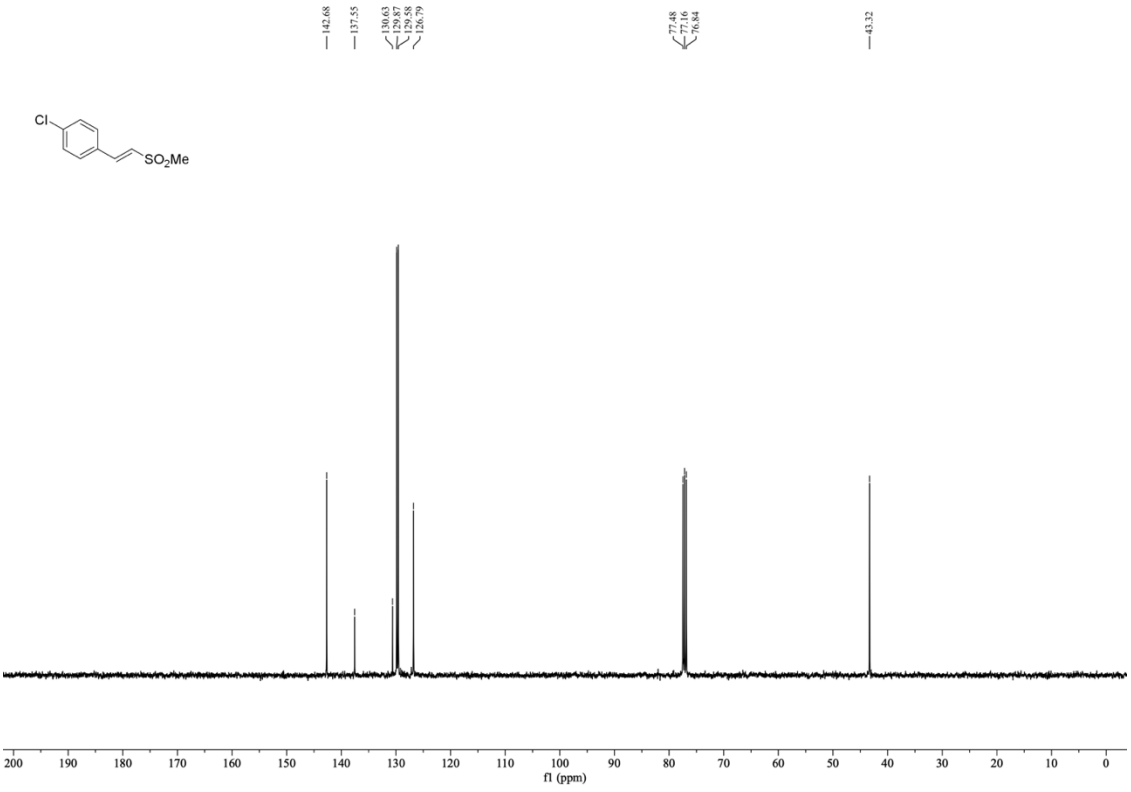
^{13}C NMR Spectrum of Compound 5c (101 MHz, $CDCl_3$)



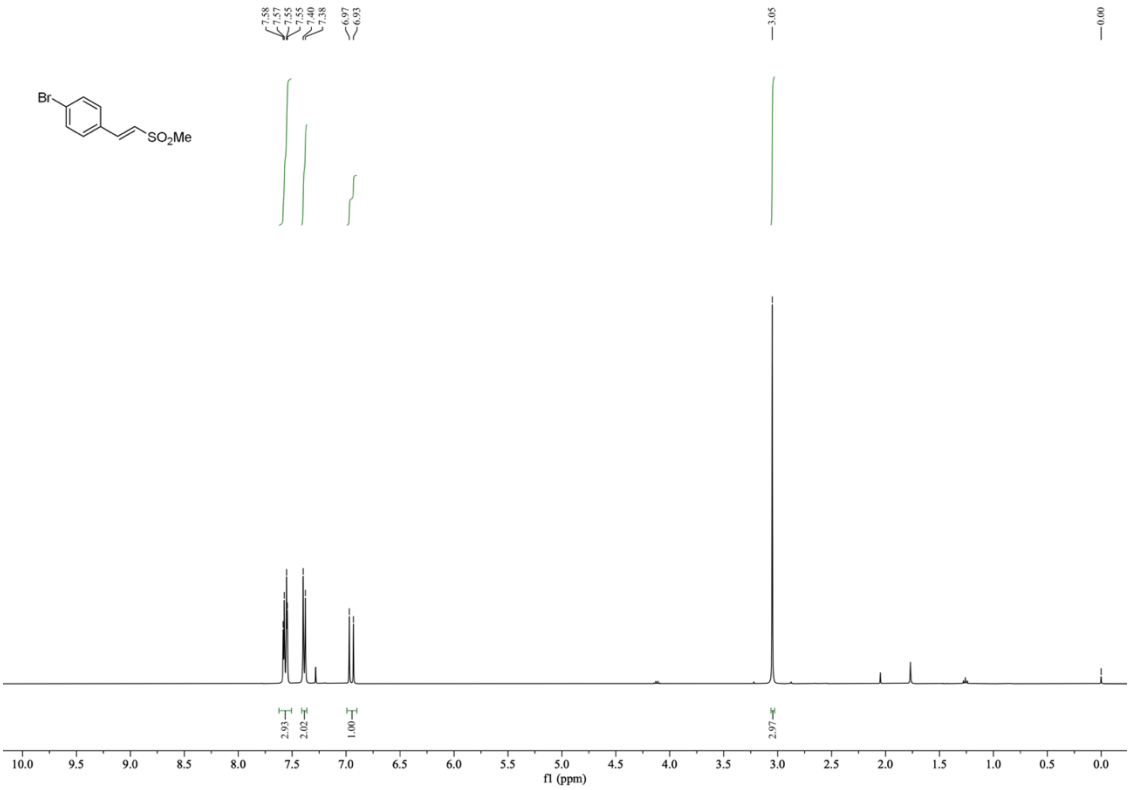
^{19}F NMR Spectrum of Compound 5c (376 MHz, $CDCl_3$)



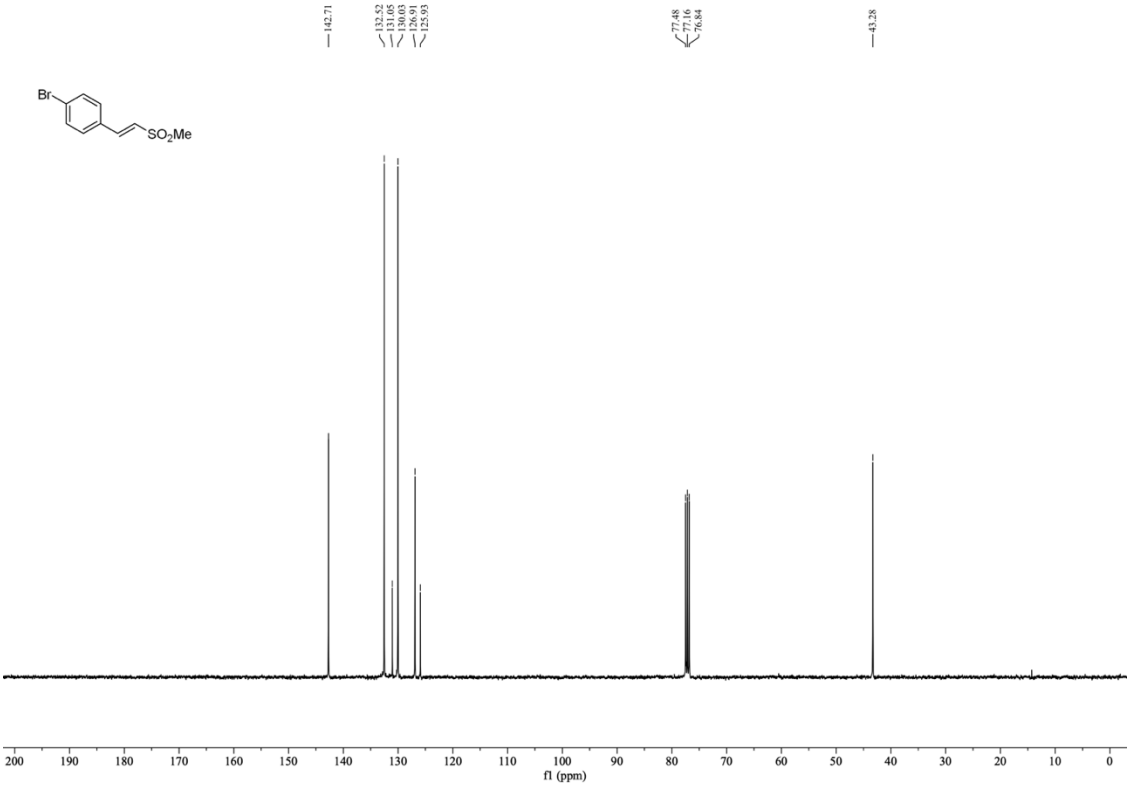
^{1}H NMR Spectrum of Compound 5d (400 MHz, $CDCl_3$)



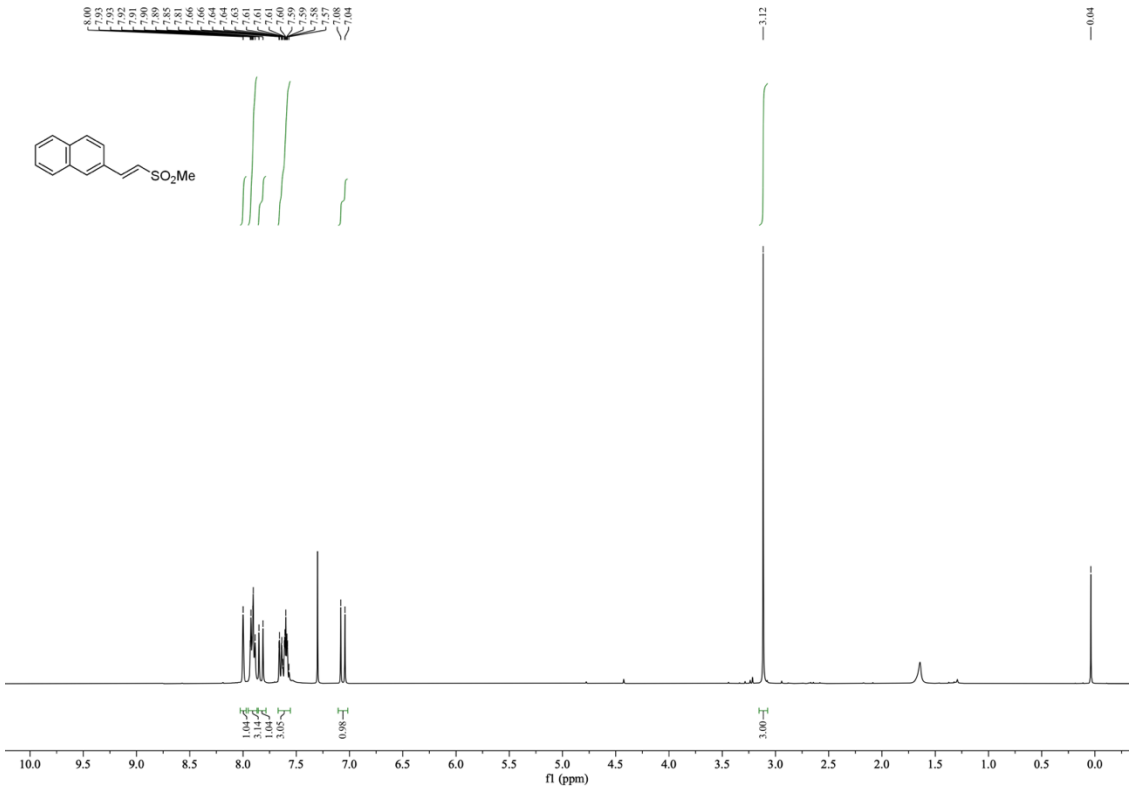
^{13}C NMR Spectrum of Compound 5d (101 MHz, $CDCl_3$)



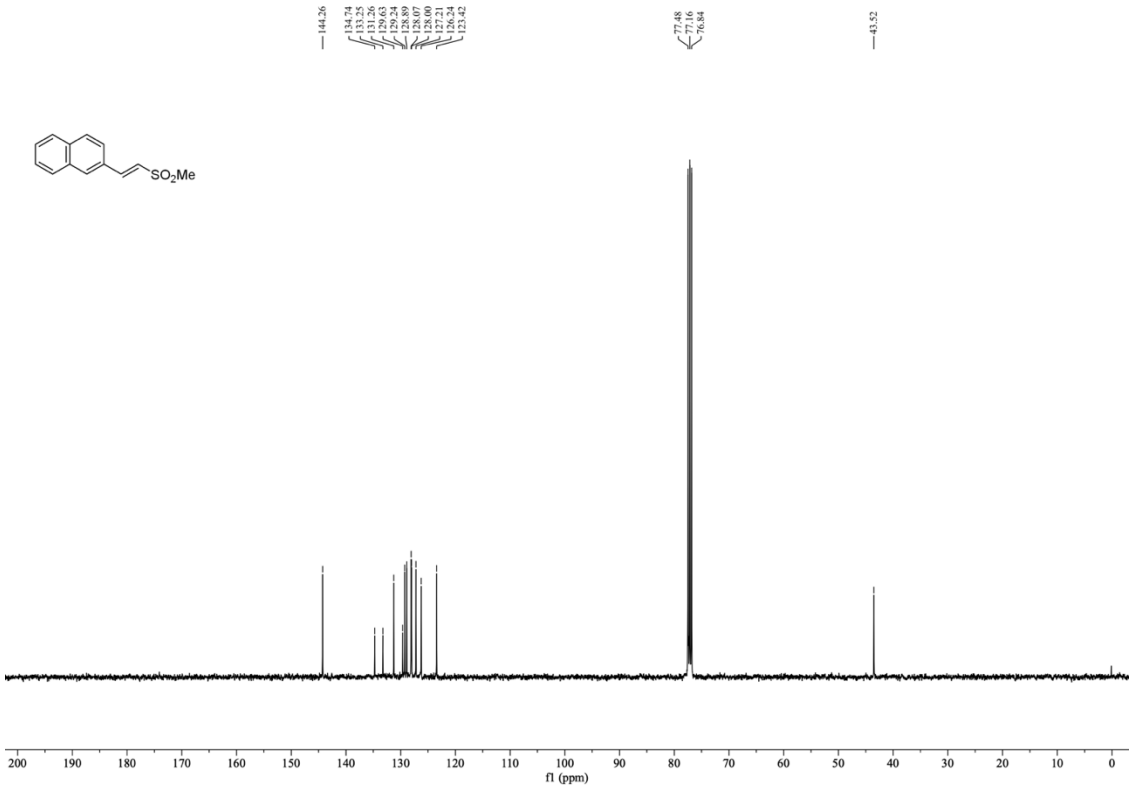
^{1}H NMR Spectrum of Compound 5e (400 MHz, $CDCl_3$)



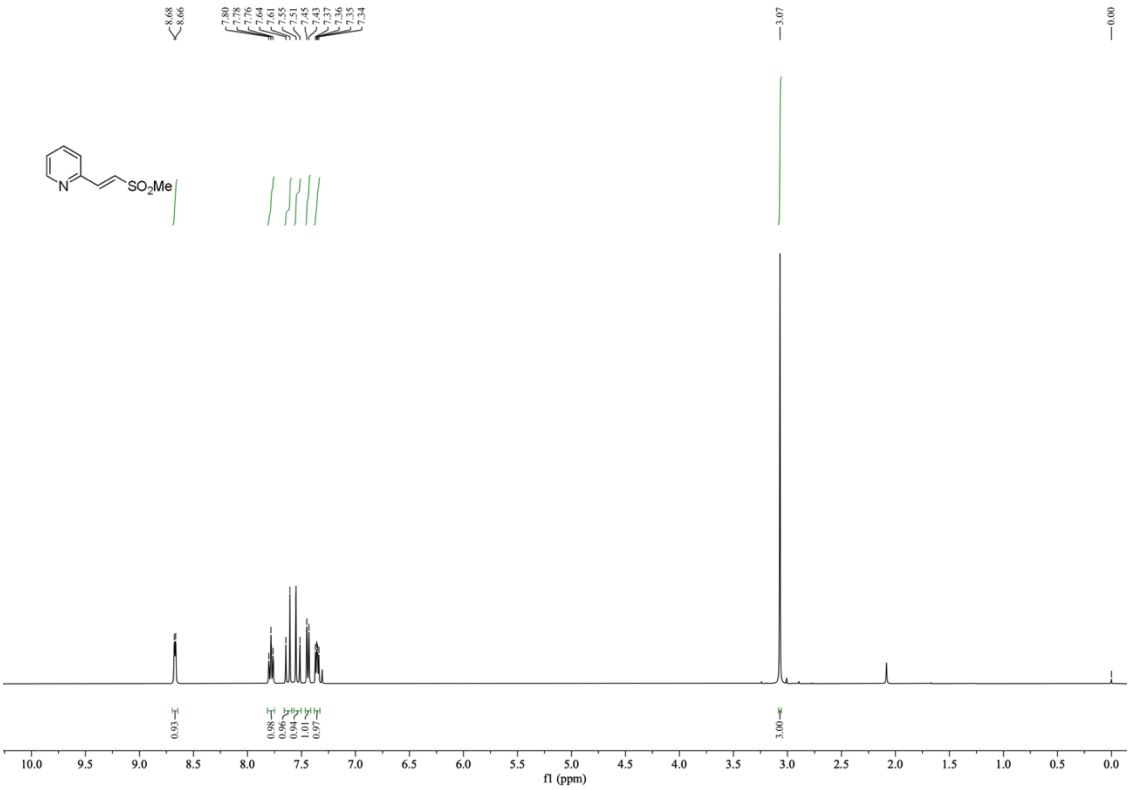
^{13}C NMR Spectrum of Compound 5e (101 MHz, $CDCl_3$)



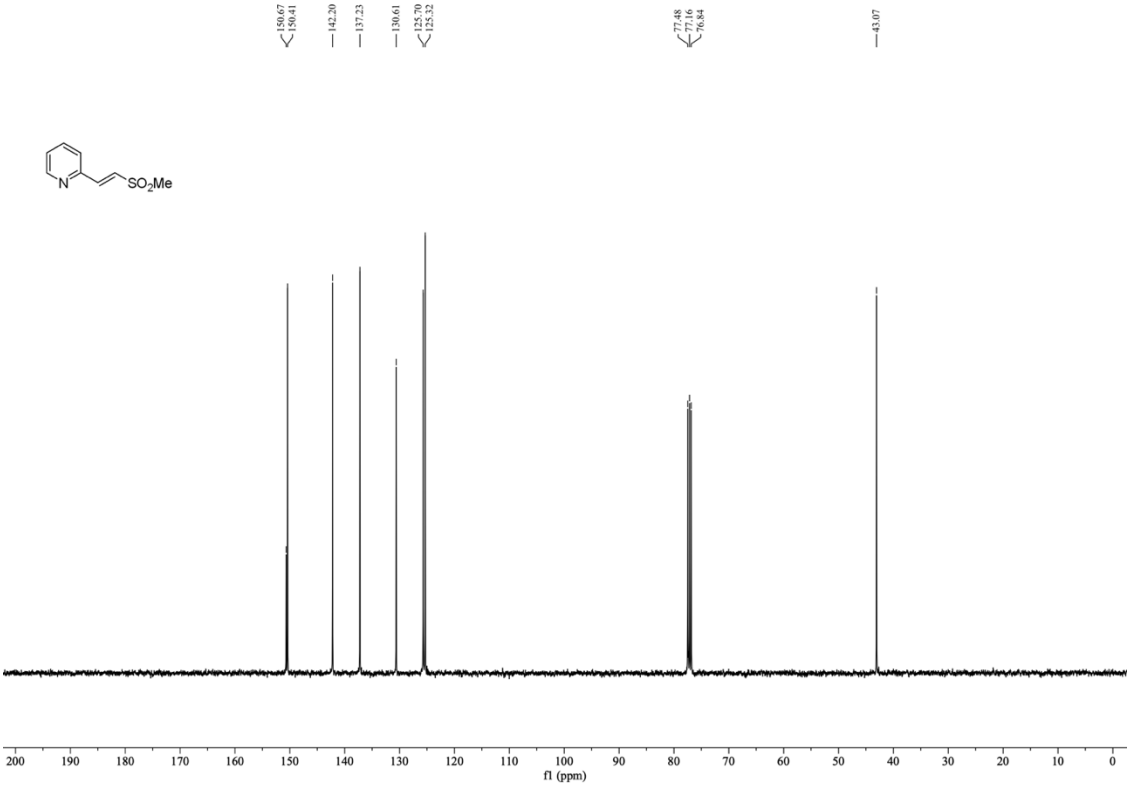
^{1}H NMR Spectrum of Compound 5f (400 MHz, $CDCl_3$)



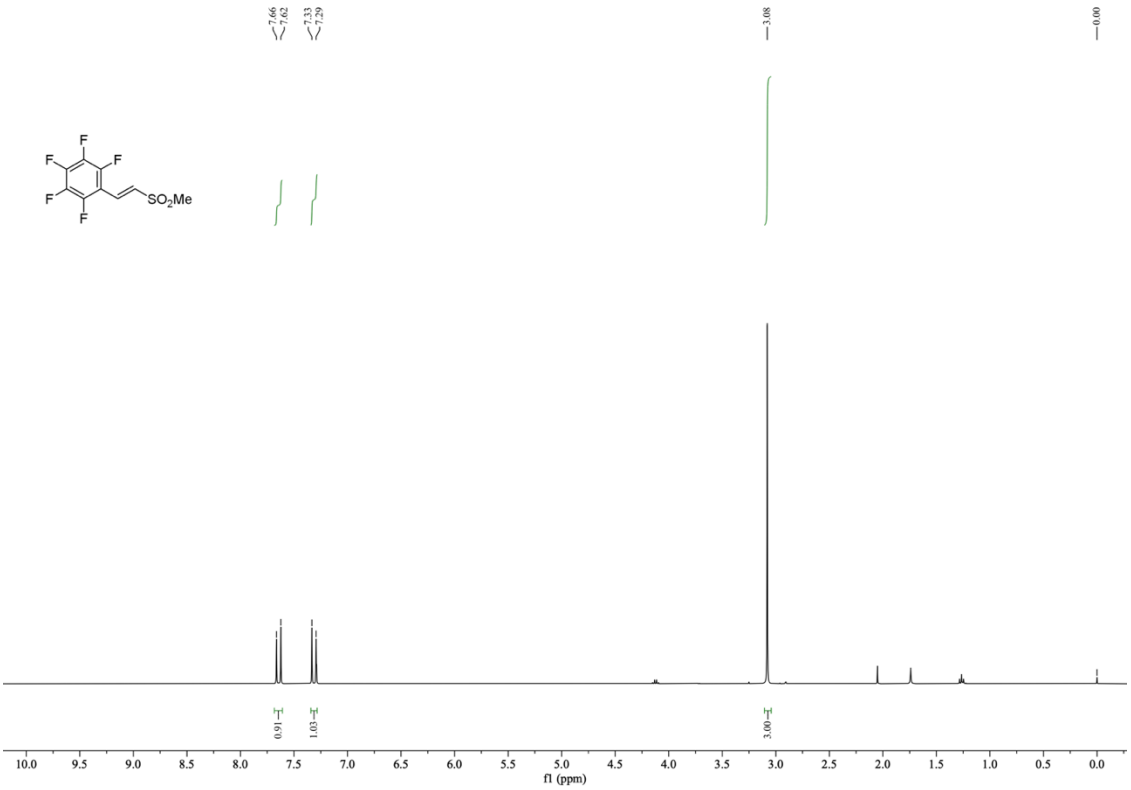
^{13}C NMR Spectrum of Compound 5f (101 MHz, $CDCl_3$)



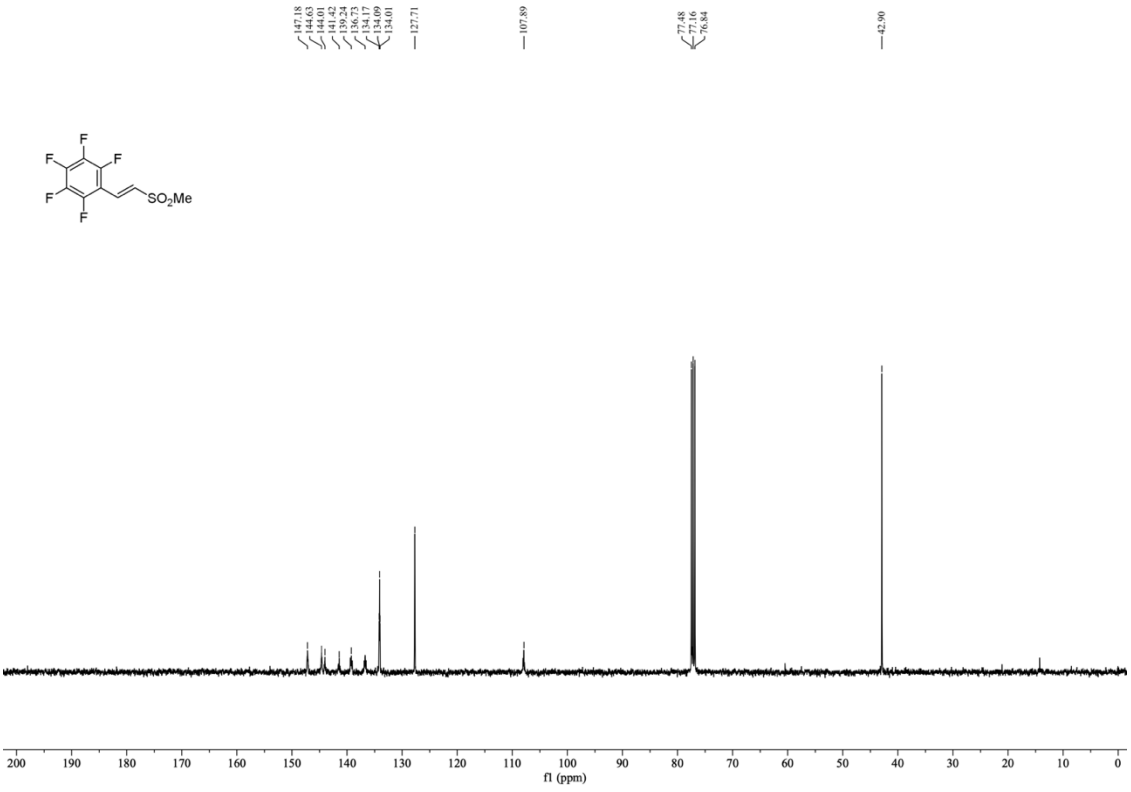
^{1}H NMR Spectrum of Compound 5g (400 MHz, $CDCl_3$)



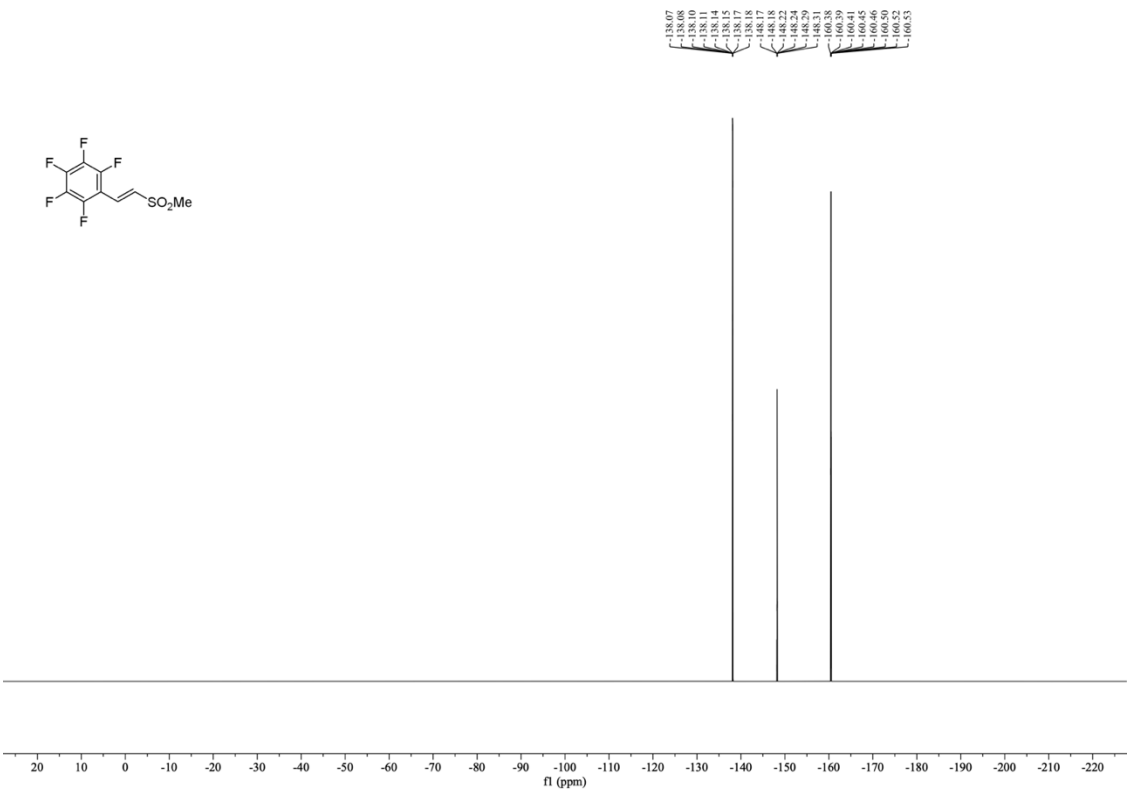
^{13}C NMR Spectrum of Compound 5g (101 MHz, $CDCl_3$)



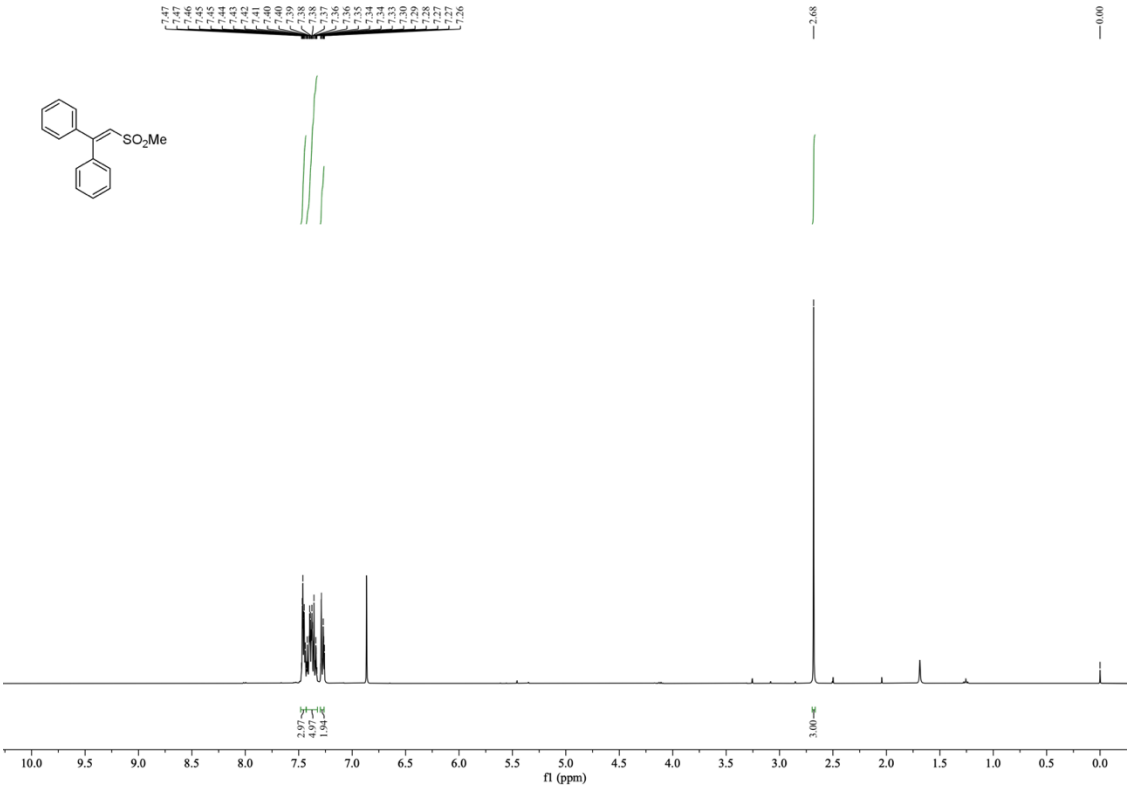
^{1}H NMR Spectrum of Compound 5h (400 MHz, $CDCl_3$)



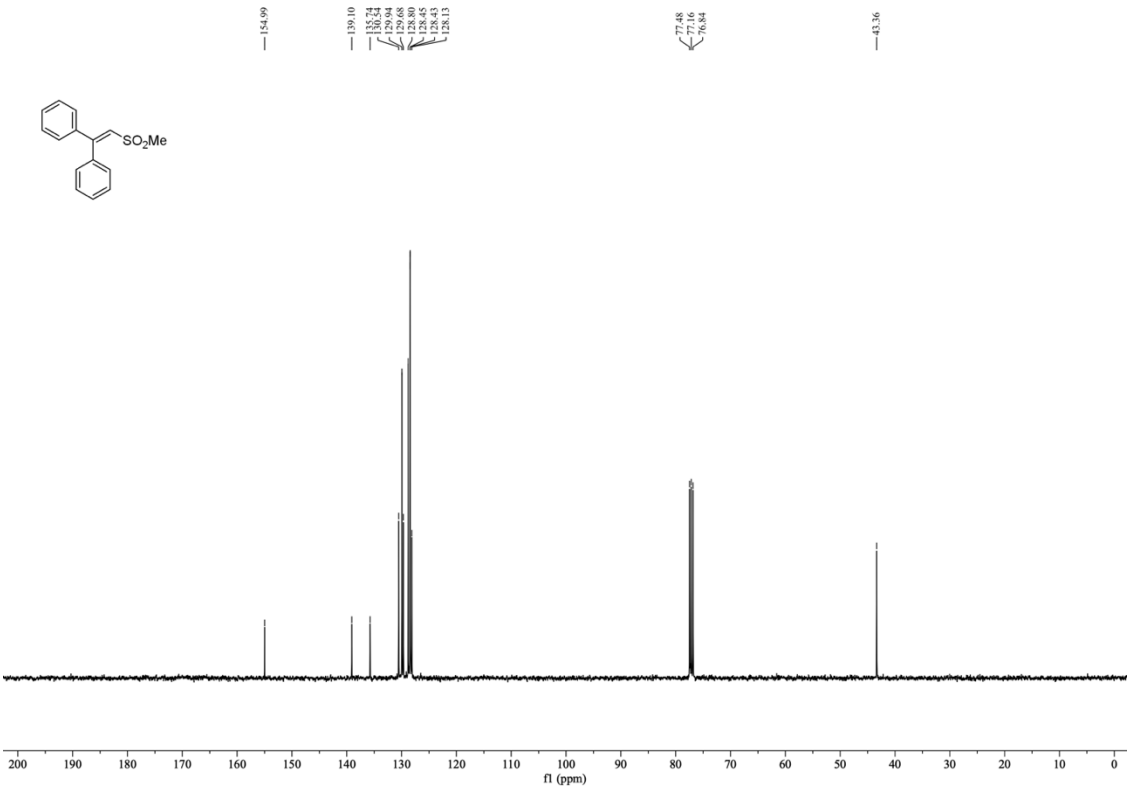
^{13}C NMR Spectrum of Compound 5h (101 MHz, $CDCl_3$)



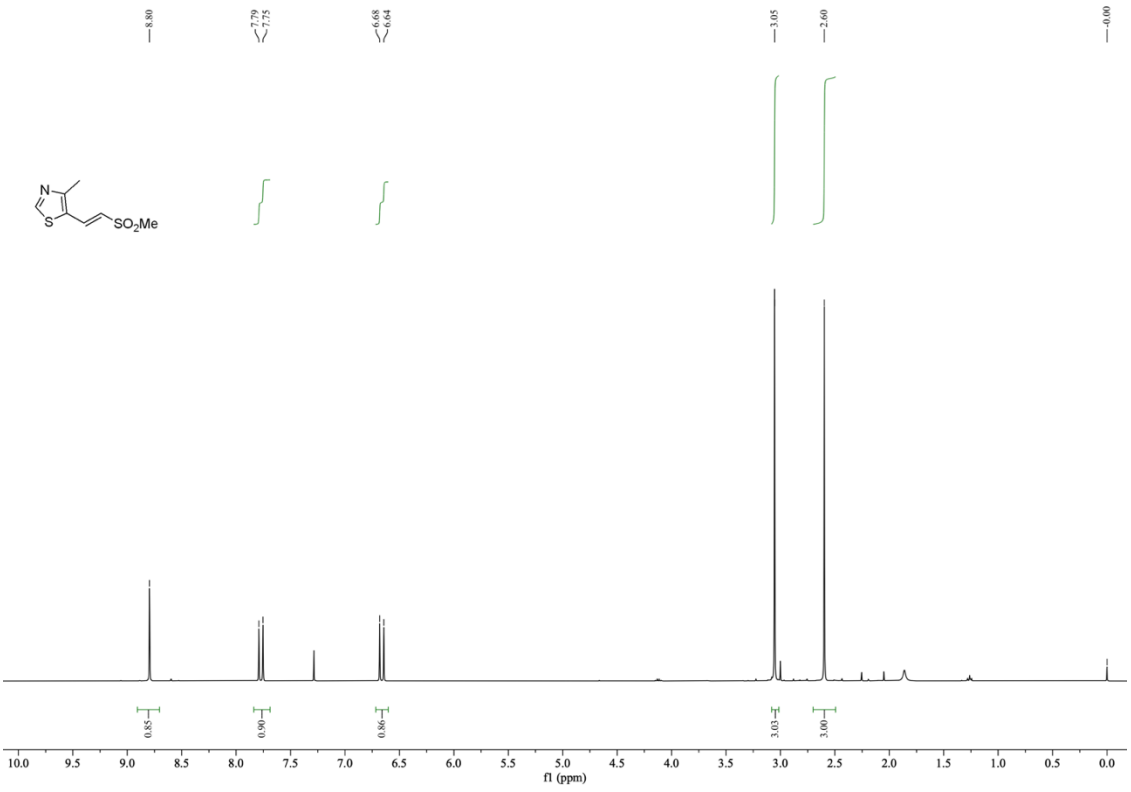
^{19}F NMR Spectrum of Compound 5h (376 MHz, $CDCl_3$)



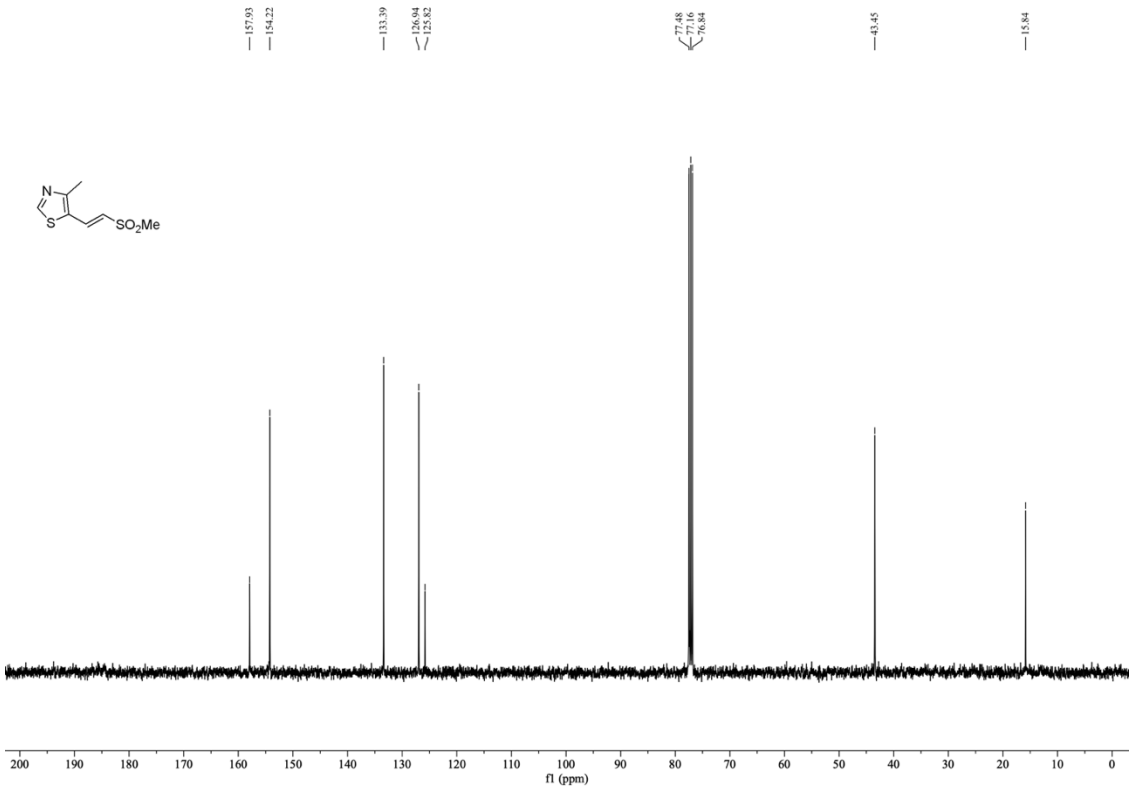
^{1}H NMR Spectrum of Compound 5i (400 MHz, $CDCl_3$)



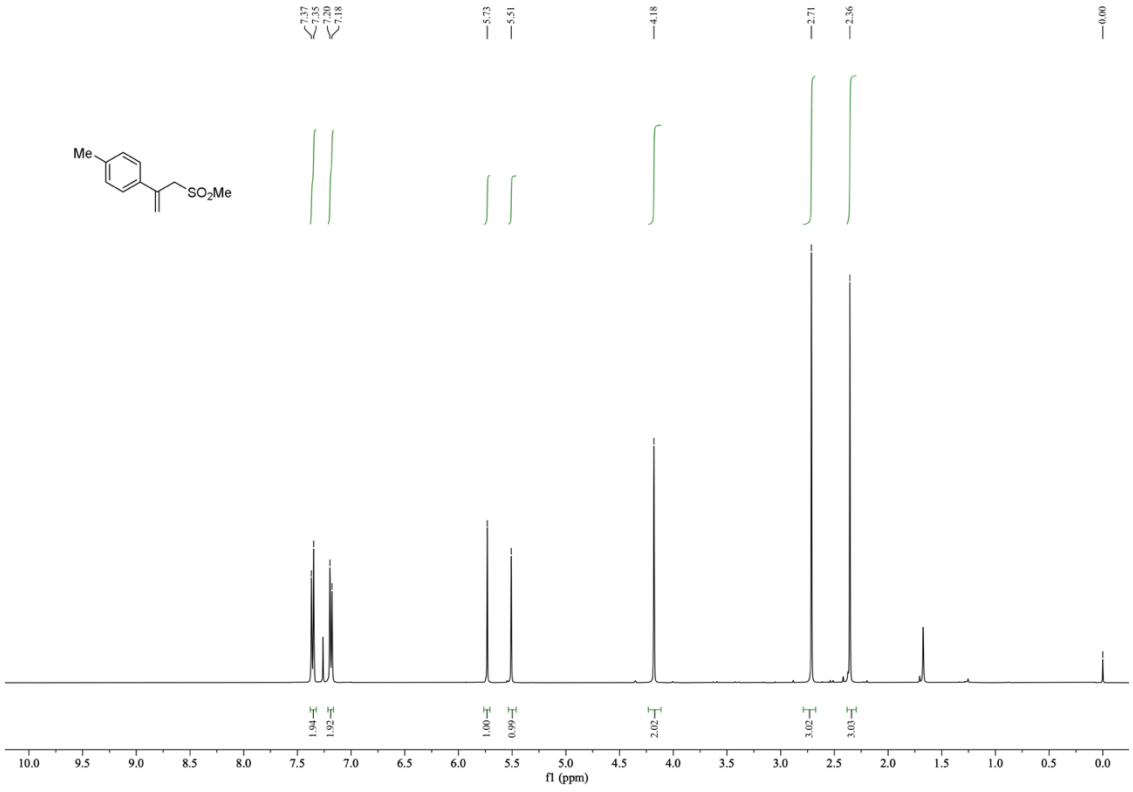
^{13}C NMR Spectrum of Compound 5i (101 MHz, $CDCl_3$)



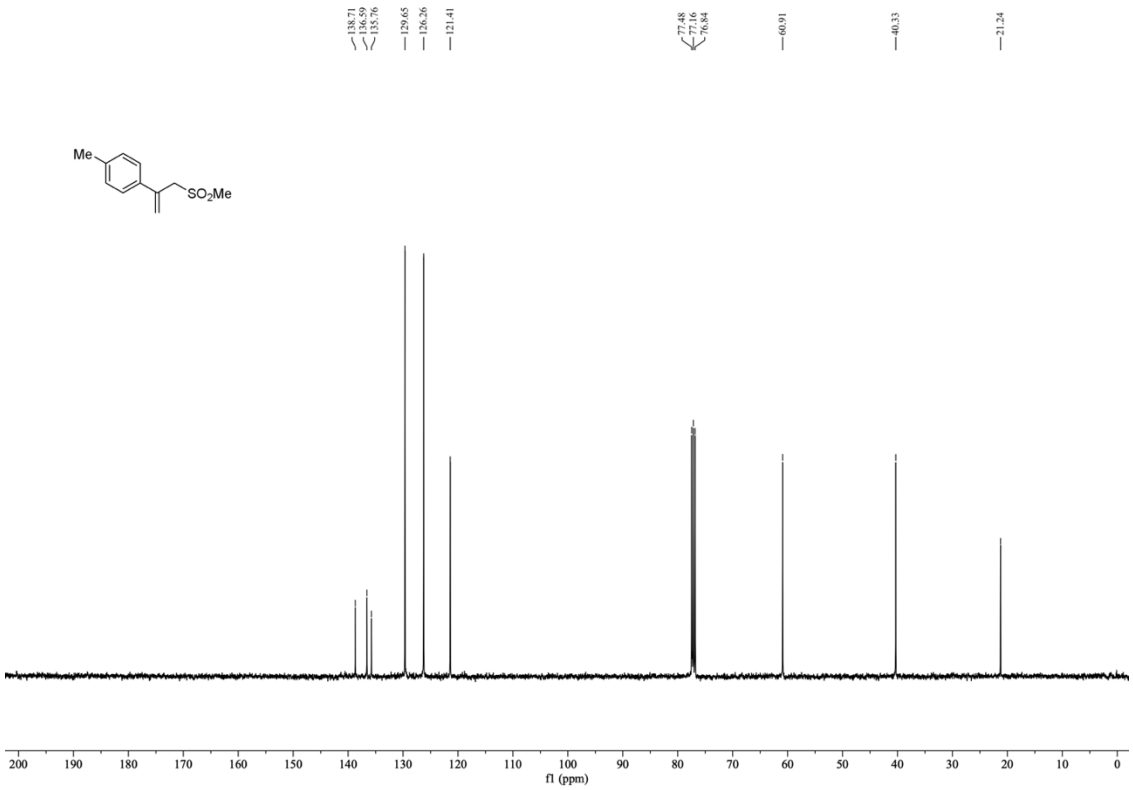
^{1}H NMR Spectrum of Compound 5j (400 MHz, $CDCl_3$)



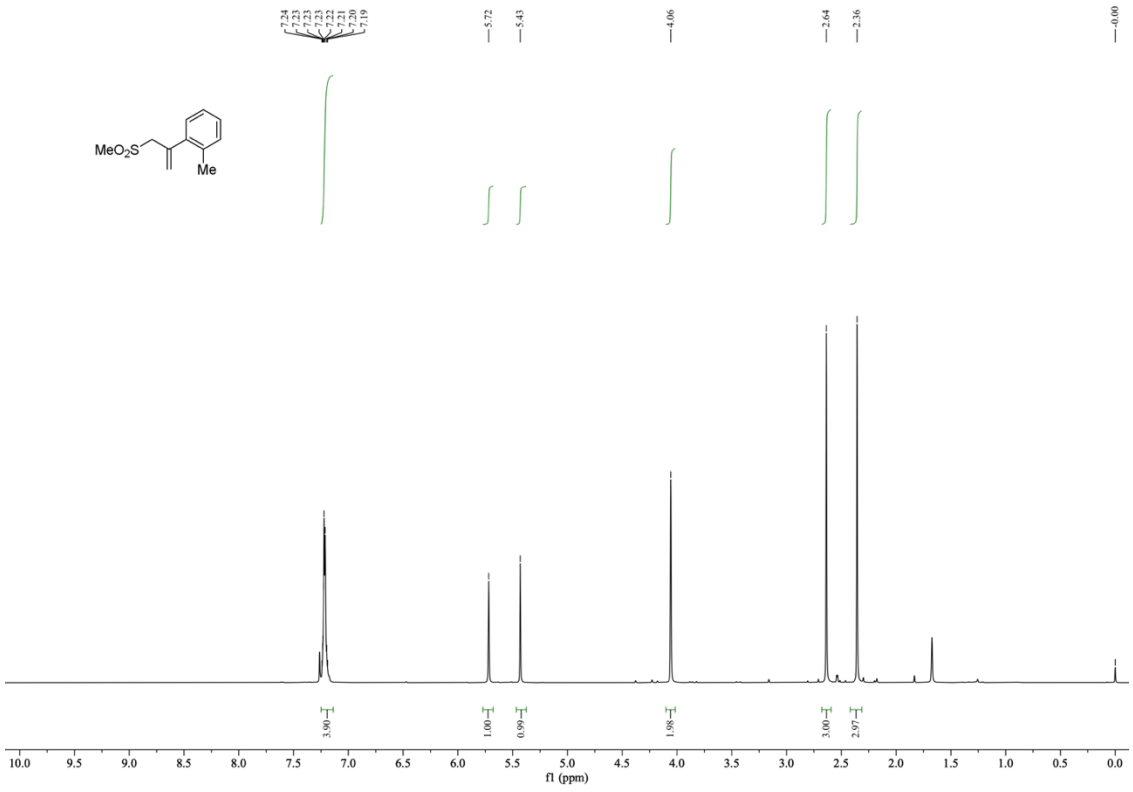
^{13}C NMR Spectrum of Compound 5j (101 MHz, $CDCl_3$)



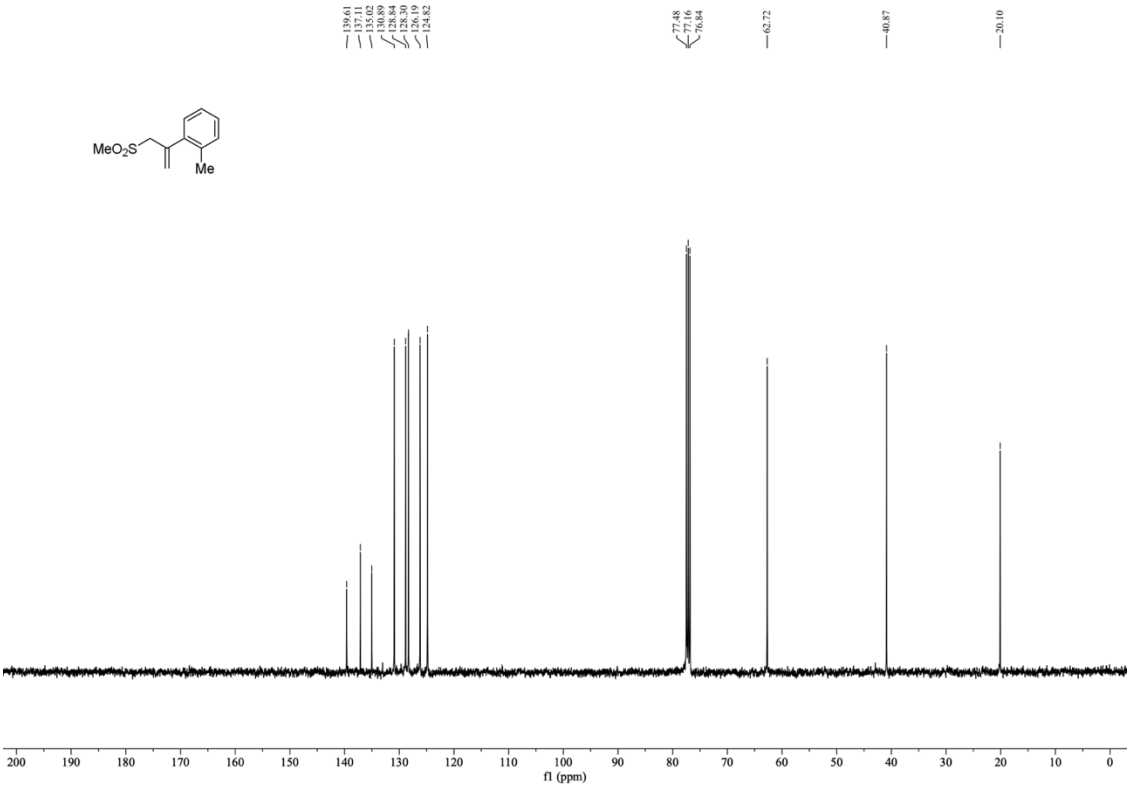
^{1}H NMR Spectrum of Compound 7d (400 MHz, $CDCl_3$)



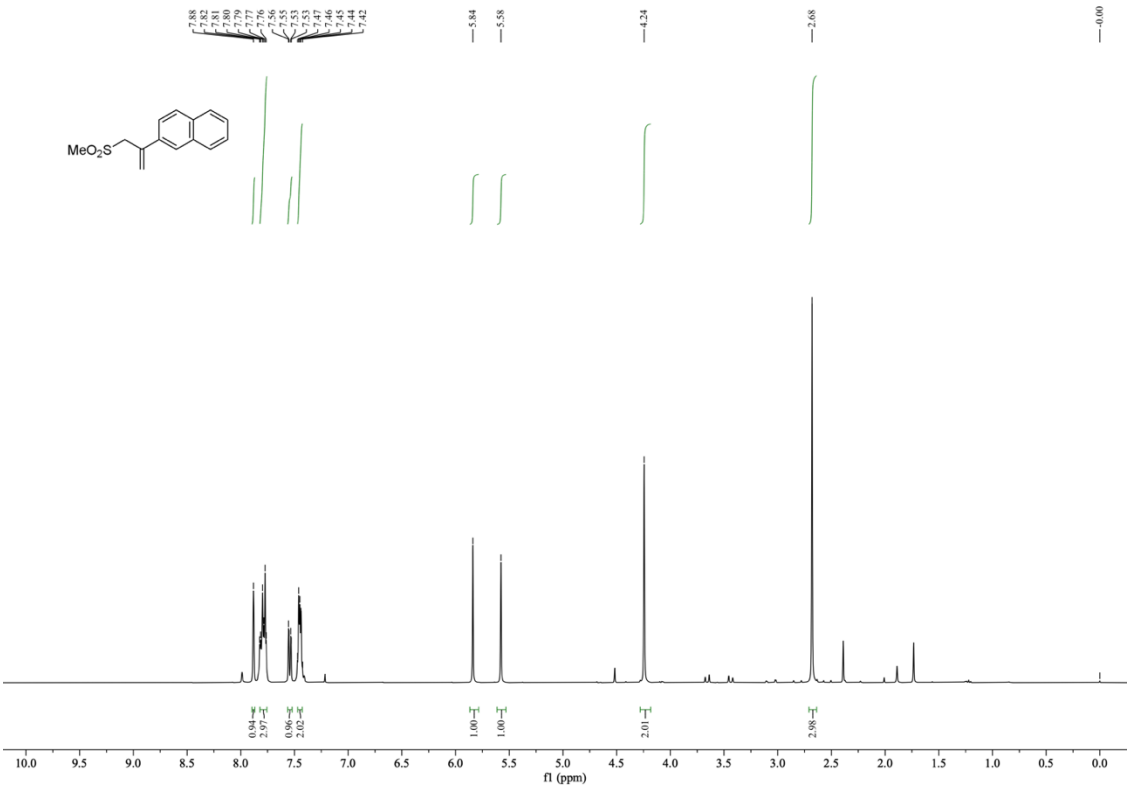
^{13}C NMR Spectrum of Compound 7d (101 MHz, $CDCl_3$)



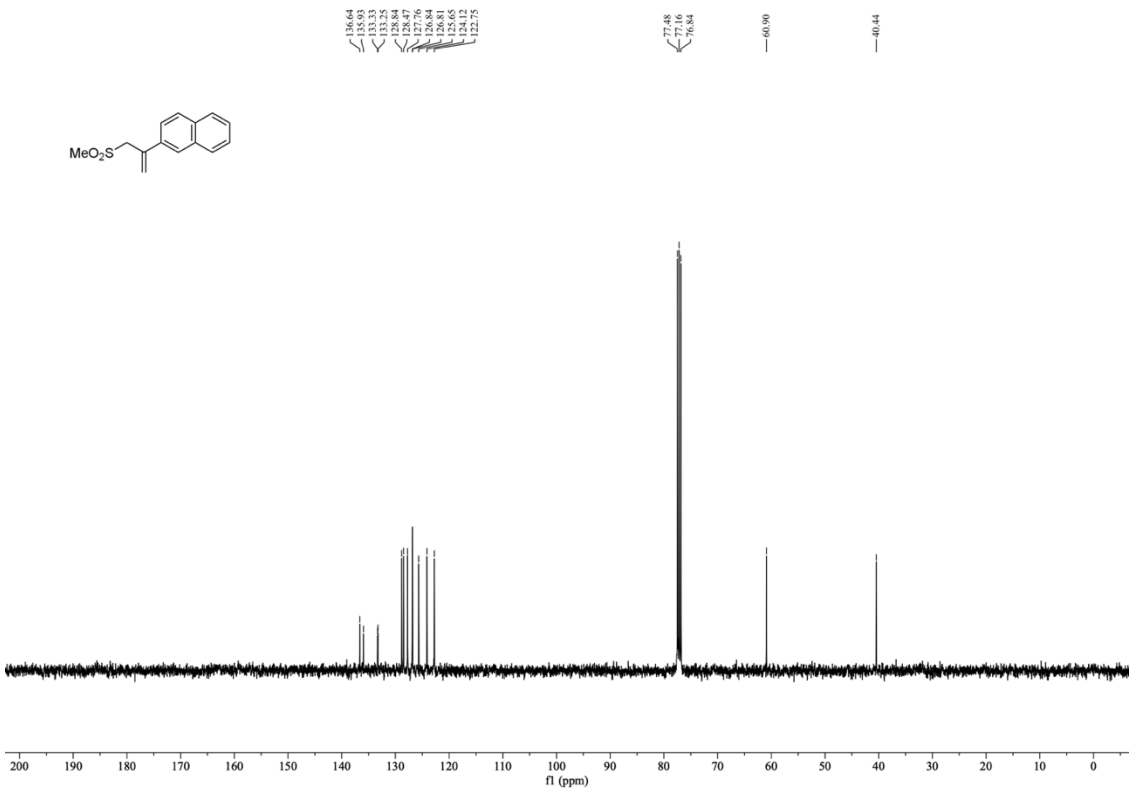
^{1}H NMR Spectrum of Compound 7e (400 MHz, $CDCl_3$)



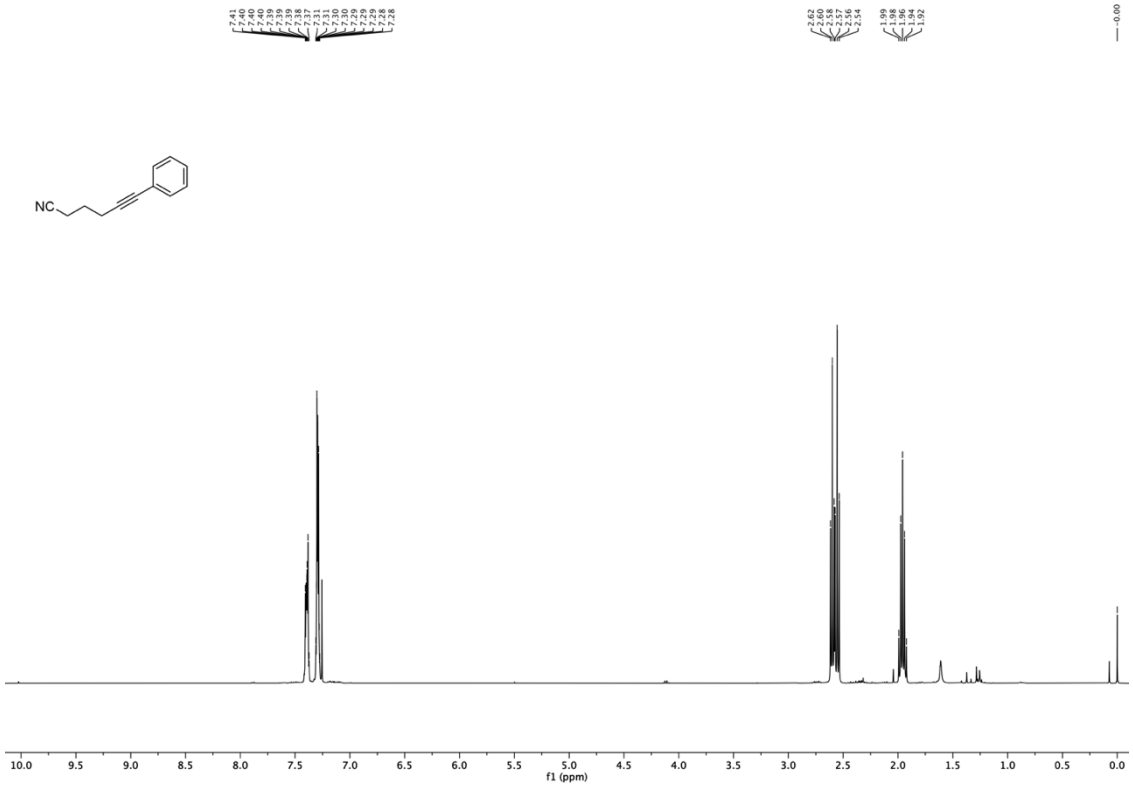
^{13}C NMR Spectrum of Compound 7e (101 MHz, $CDCl_3$)



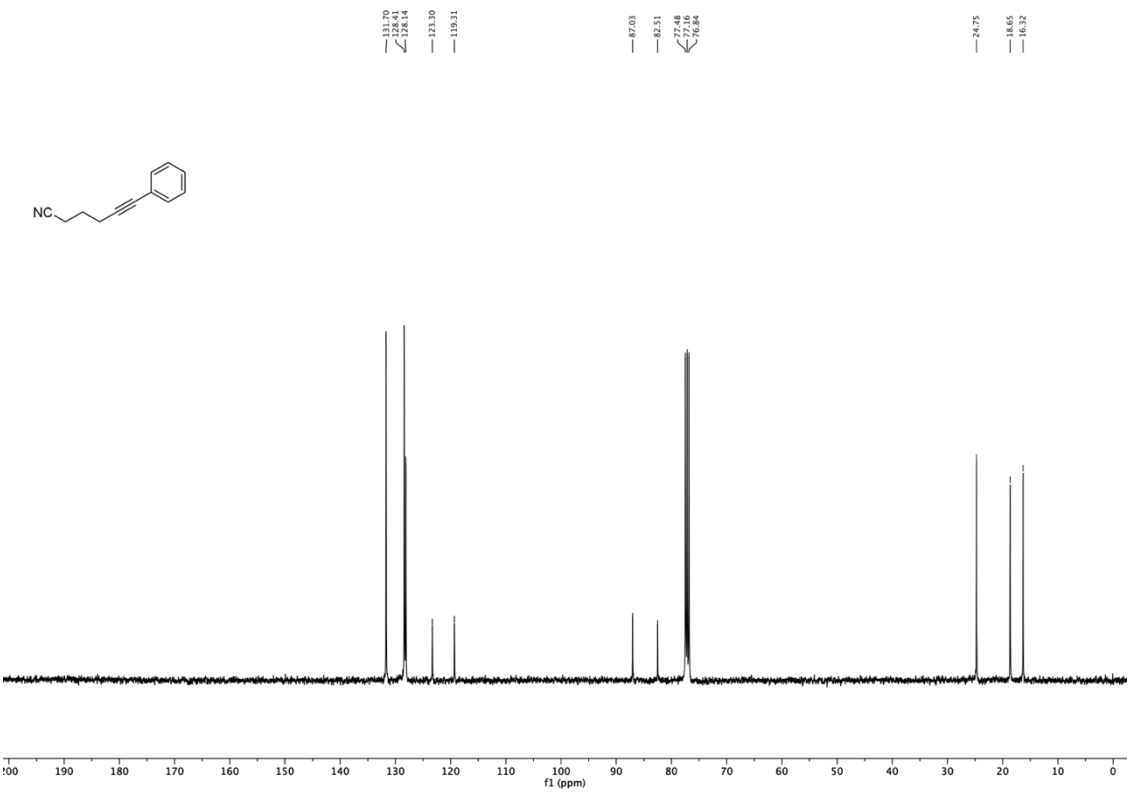
^{1}H NMR Spectrum of Compound 7f (400 MHz, $CDCl_3$)



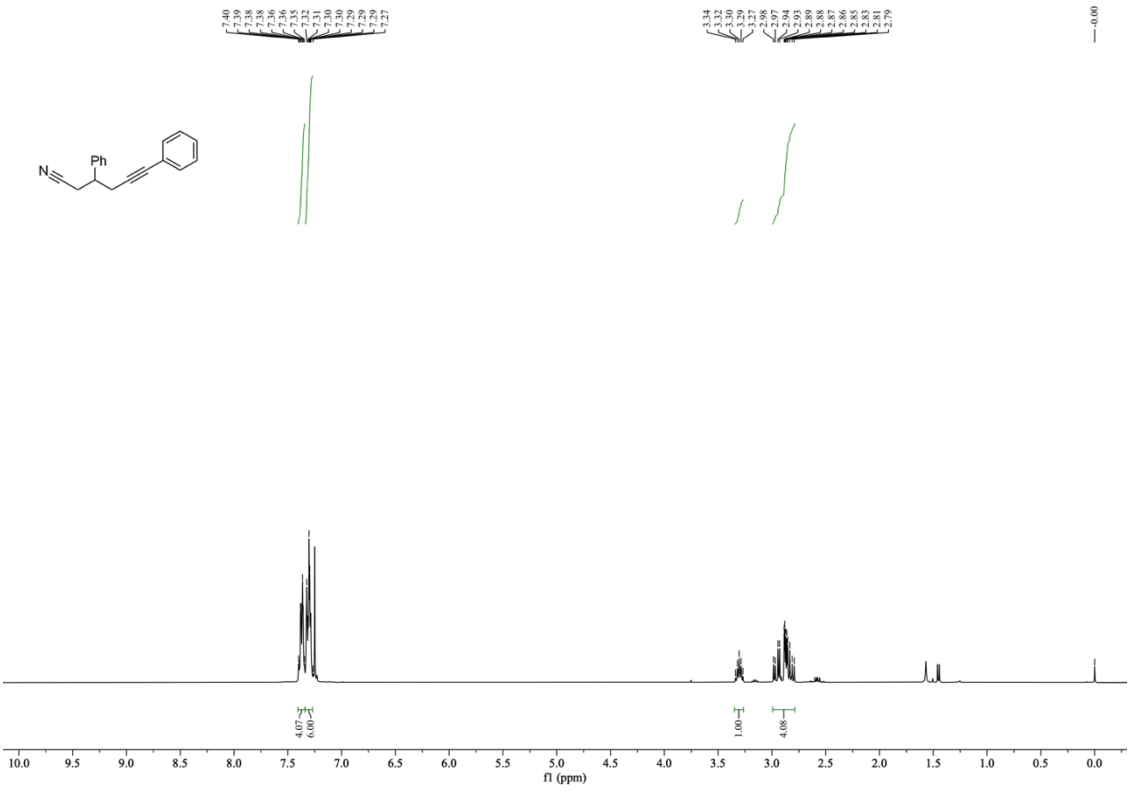
^{13}C NMR Spectrum of Compound 7f (101 MHz, $CDCl_3$)



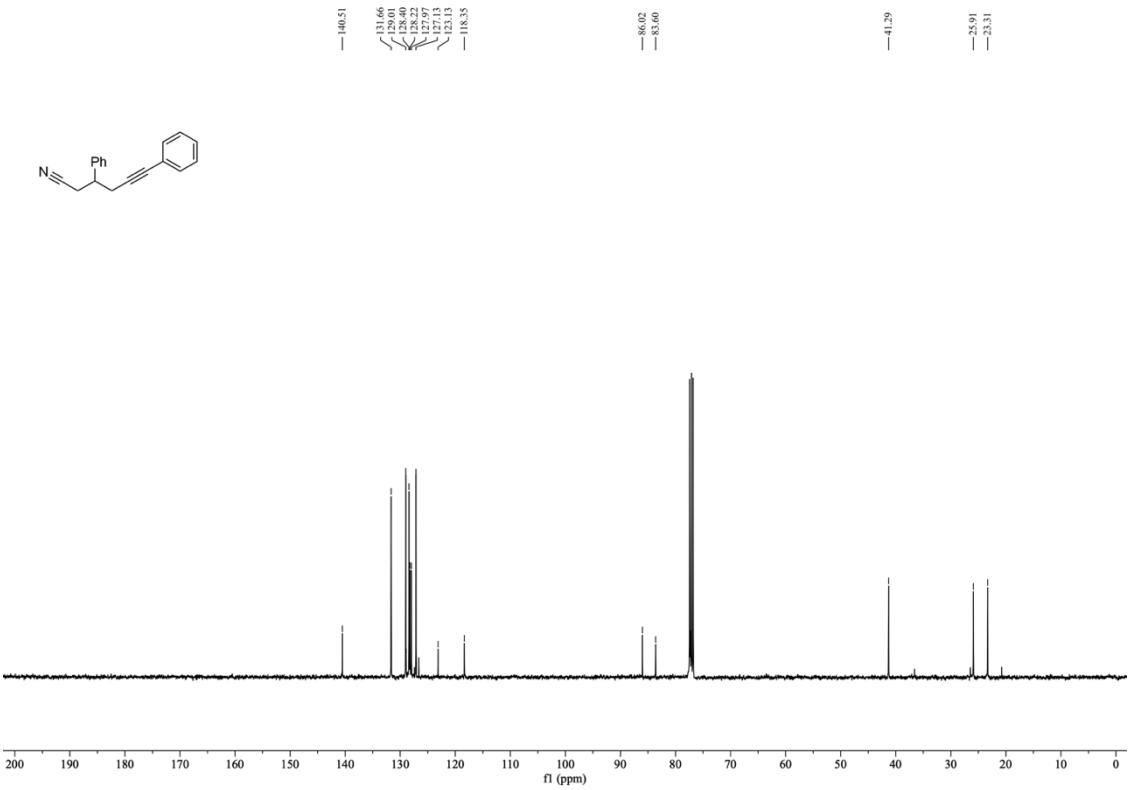
^{1}H NMR Spectrum of Compound 3a (400 MHz, $CDCl_3$)



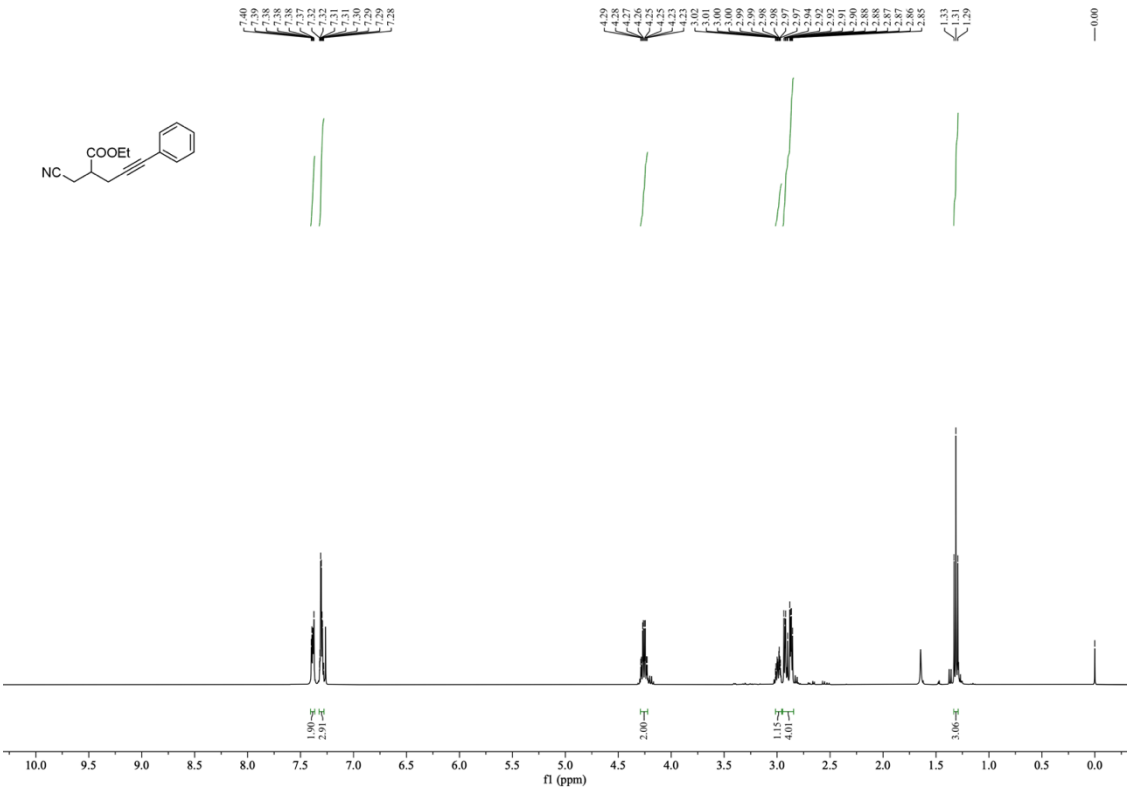
^{13}C NMR Spectrum of Compound 3a (101 MHz, $CDCl_3$)



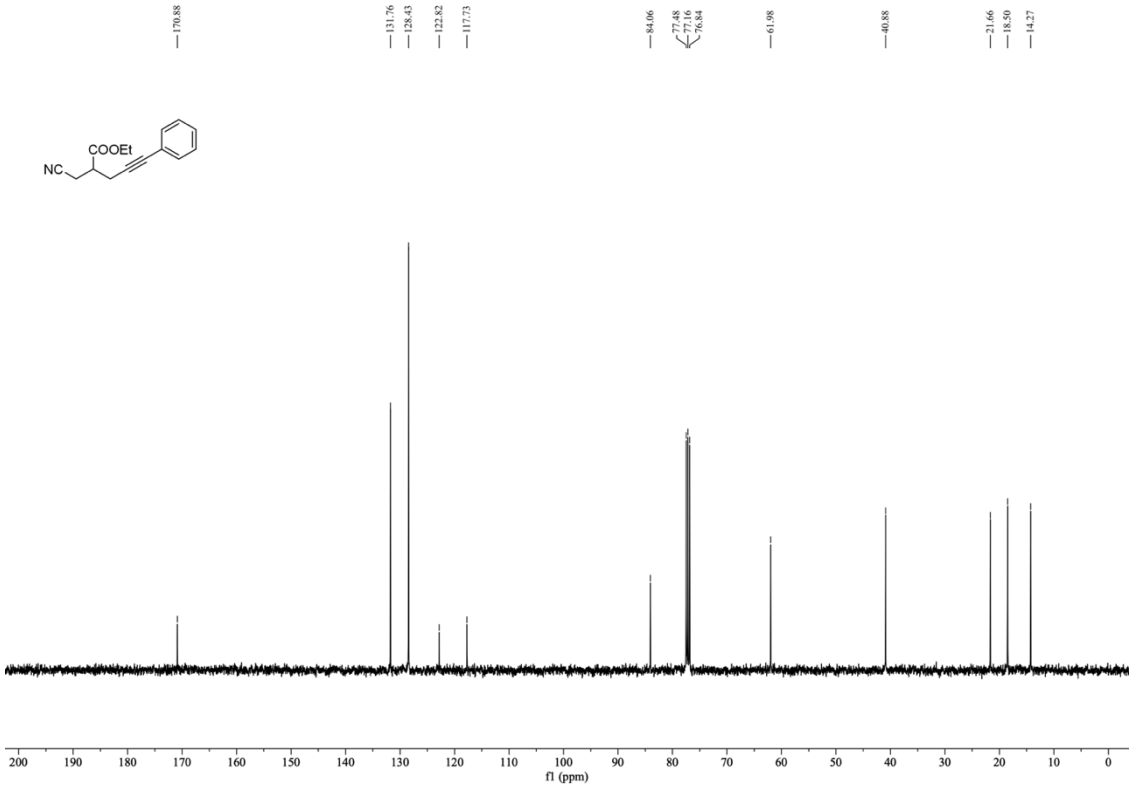
^{1}H NMR Spectrum of Compound 3b (400 MHz, $CDCl_3$)



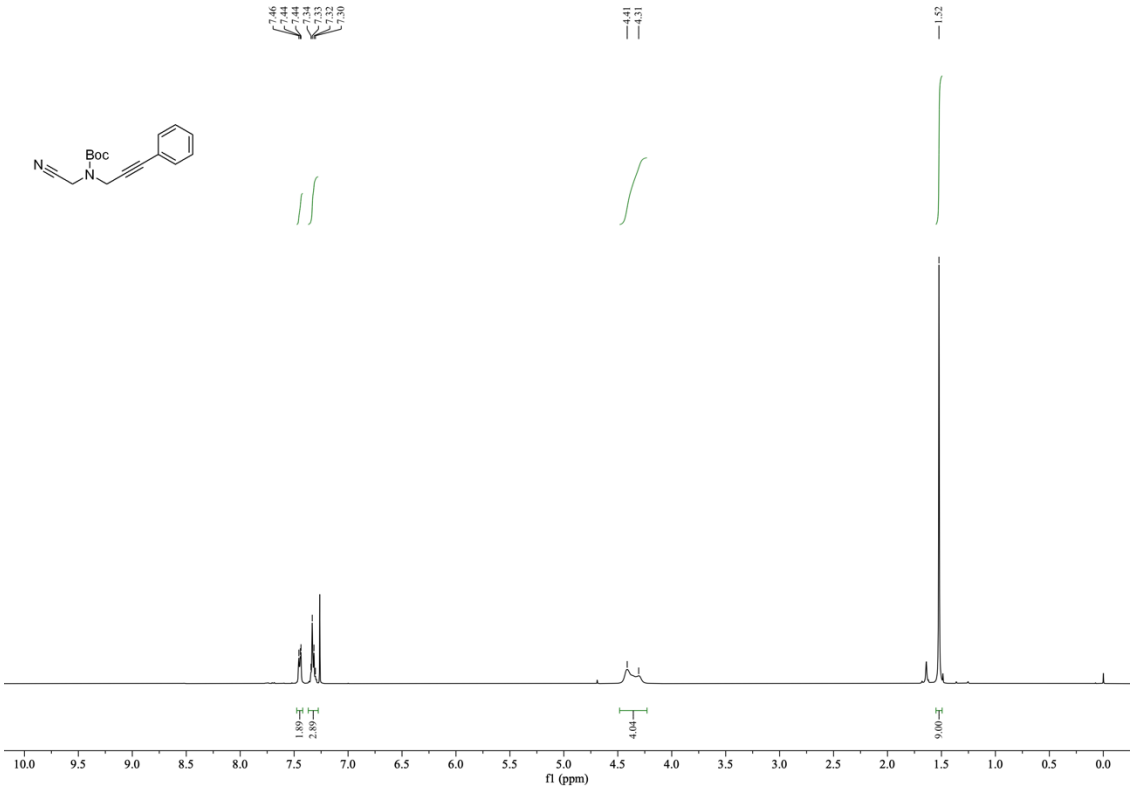
^{13}C NMR Spectrum of Compound 3b (101 MHz, $CDCl_3$)



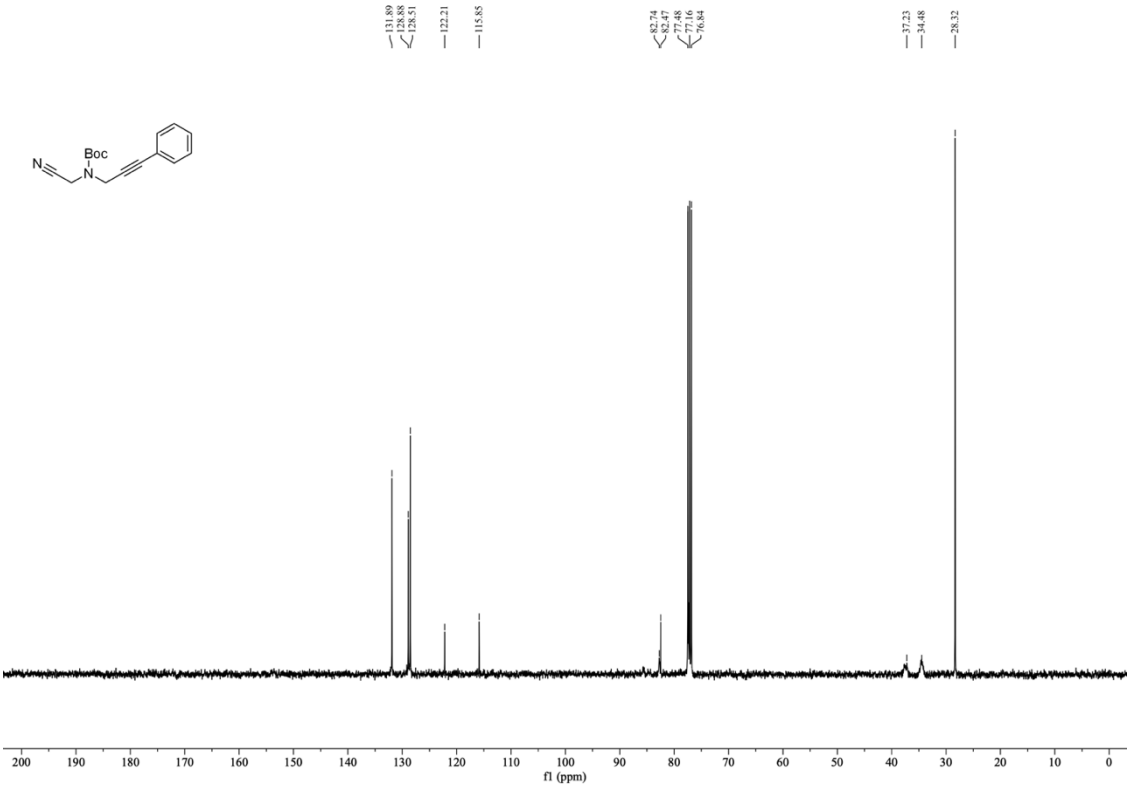
^{1}H NMR Spectrum of Compound 3c (400 MHz, $CDCl_3$)



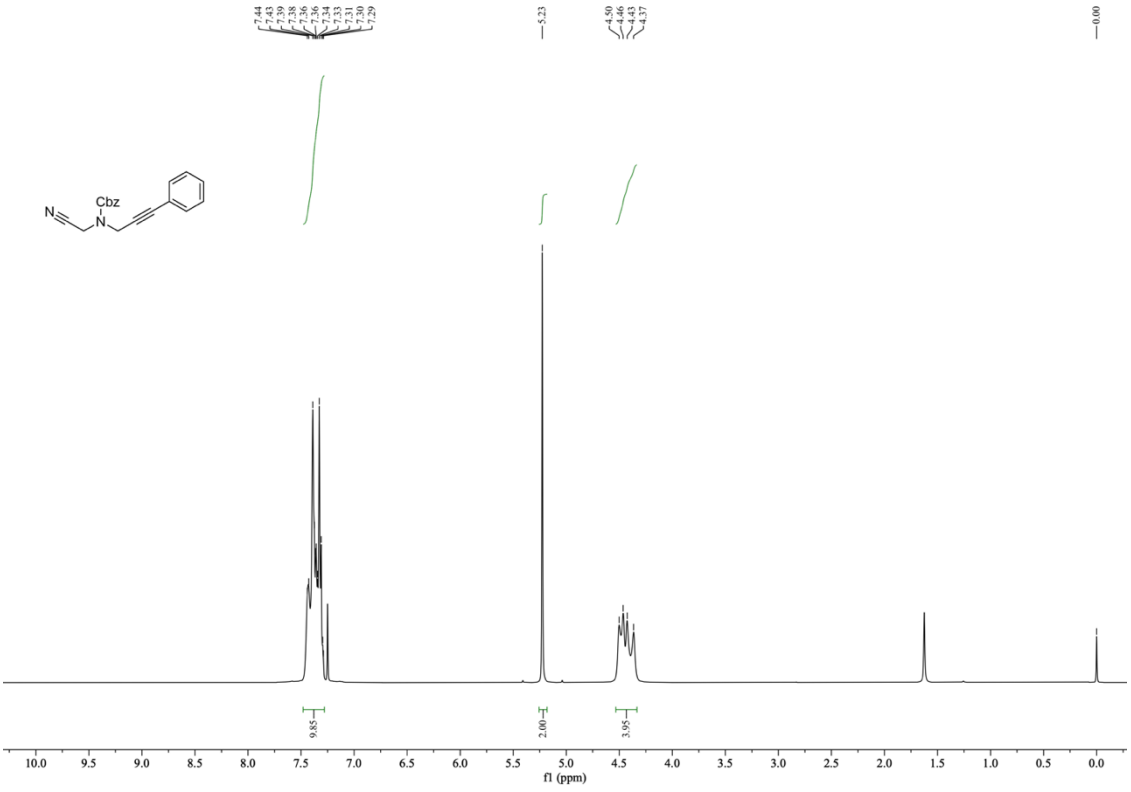
^{13}C NMR Spectrum of Compound 3c (101 MHz, $CDCl_3$)



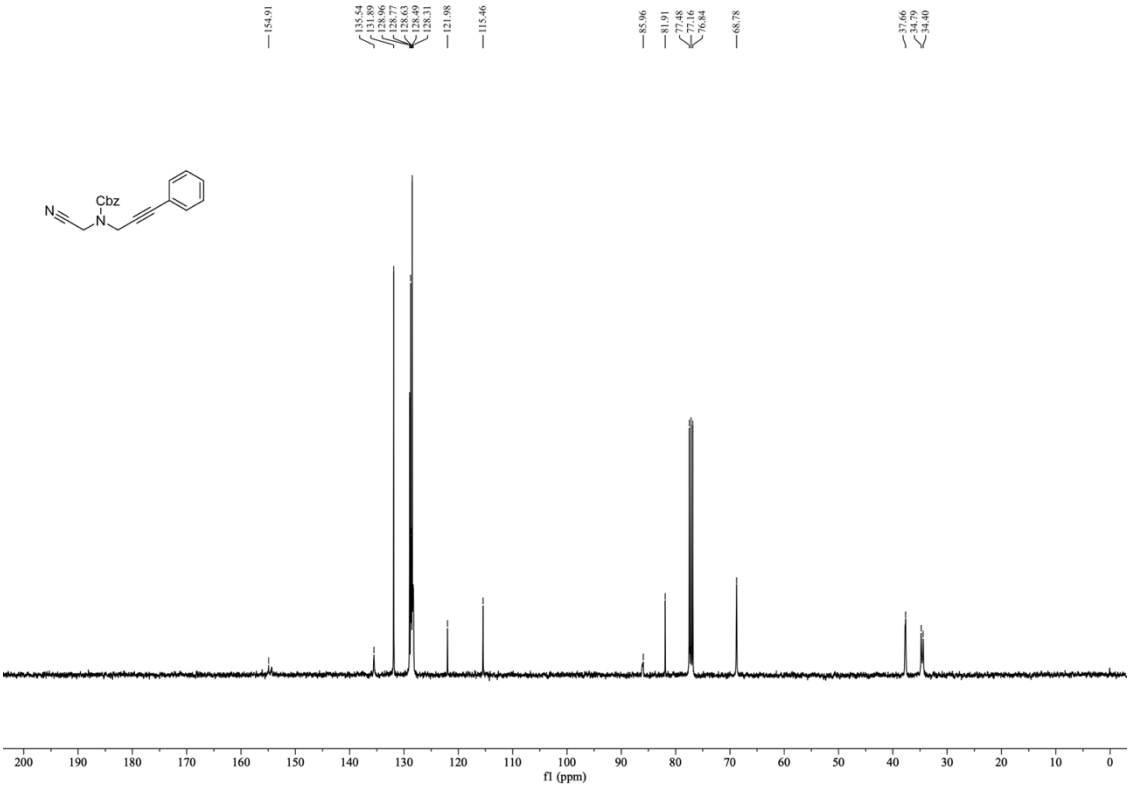
^{1}H NMR Spectrum of Compound 3d (400 MHz, $CDCl_3$)



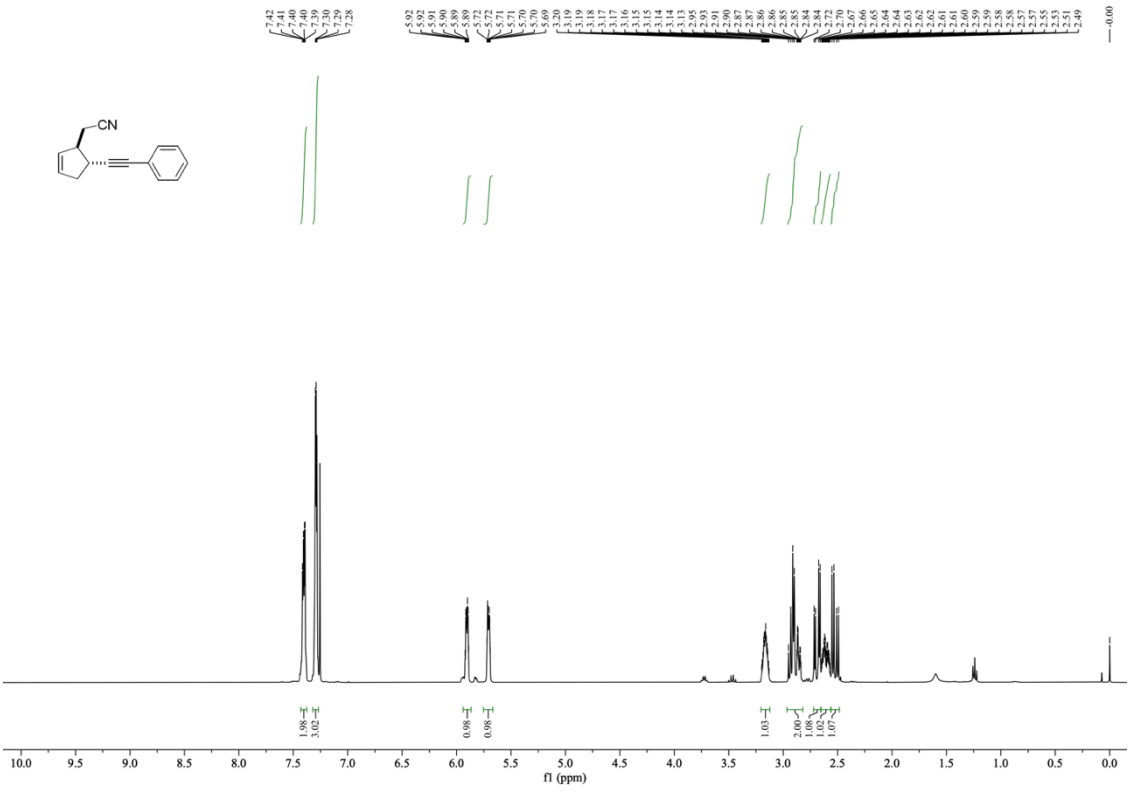
^{13}C NMR Spectrum of Compound 3d (101 MHz, $CDCl_3$)



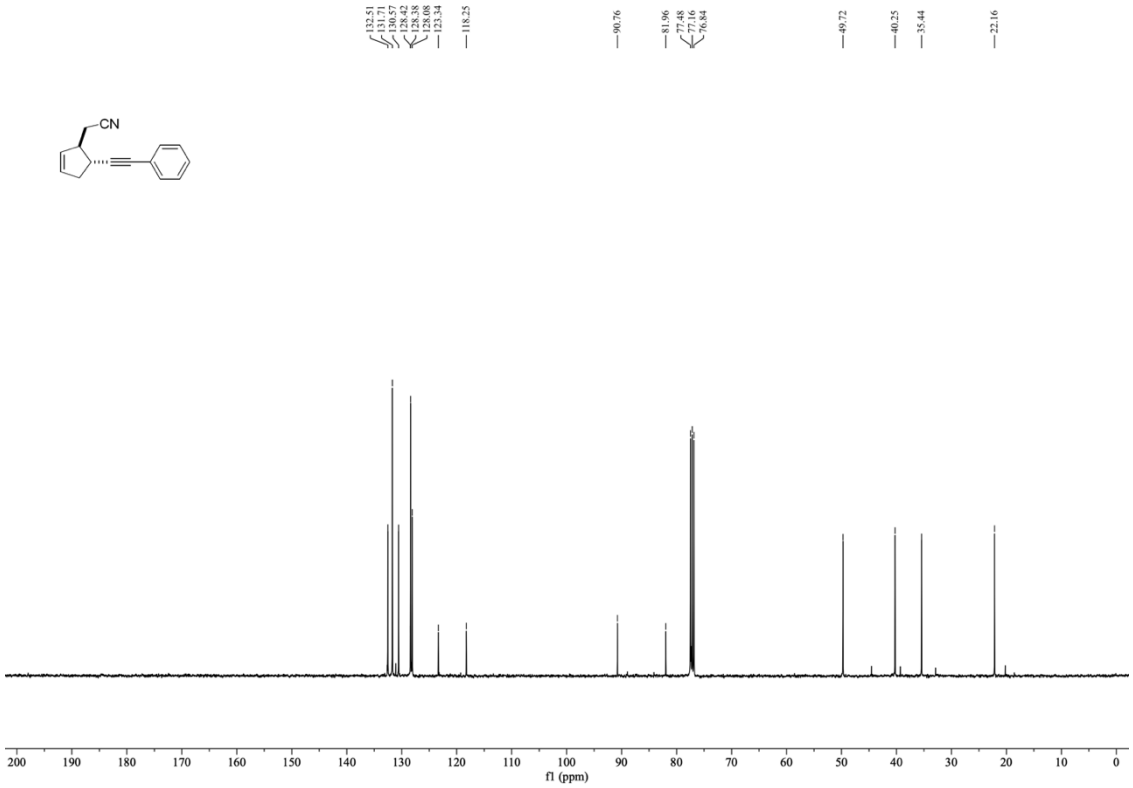
^{1}H NMR Spectrum of Compound 3e (400 MHz, $CDCl_3$)



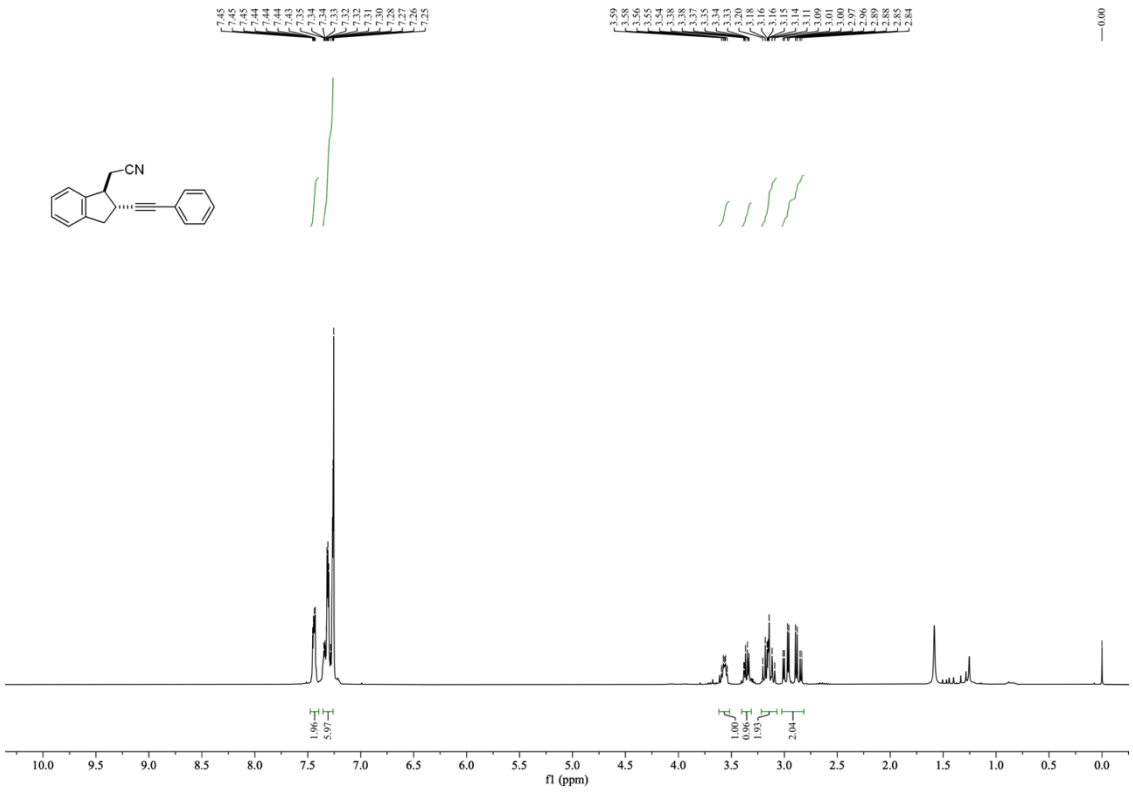
^{13}C NMR Spectrum of Compound 3e (101 MHz, $CDCl_3$)



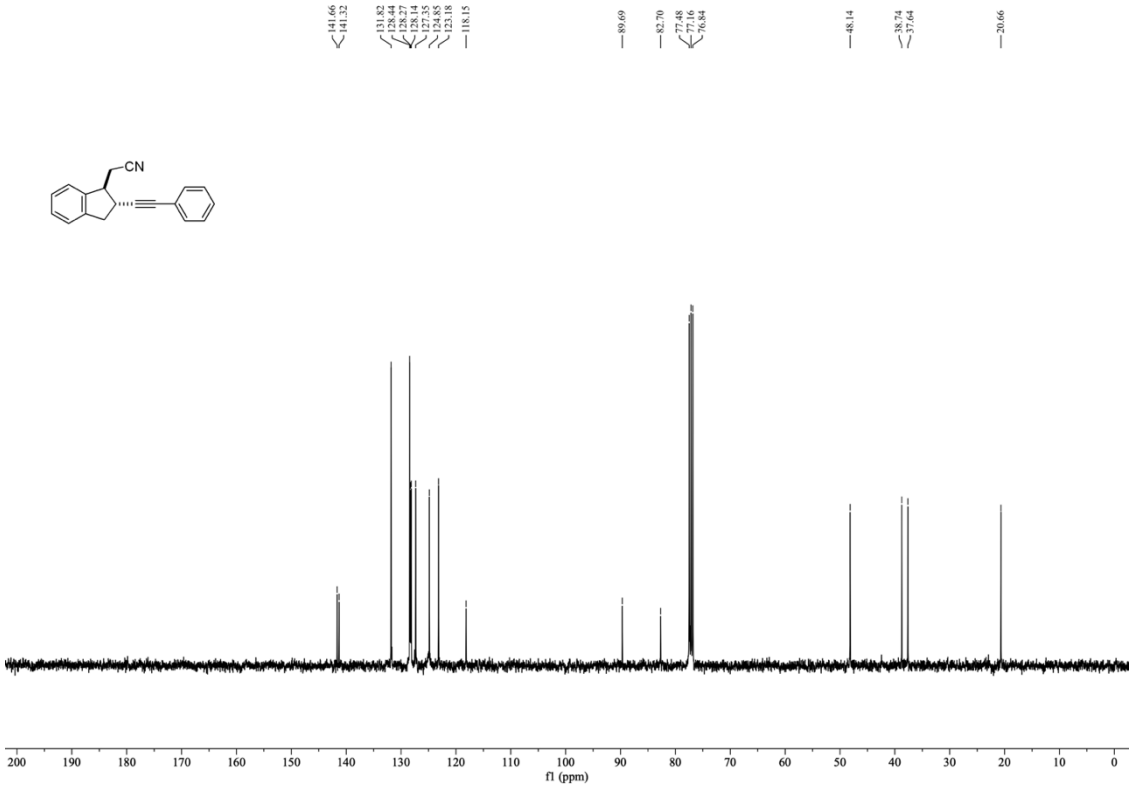
^{1}H NMR Spectrum of Compound 3f (400 MHz, $CDCl_3$)



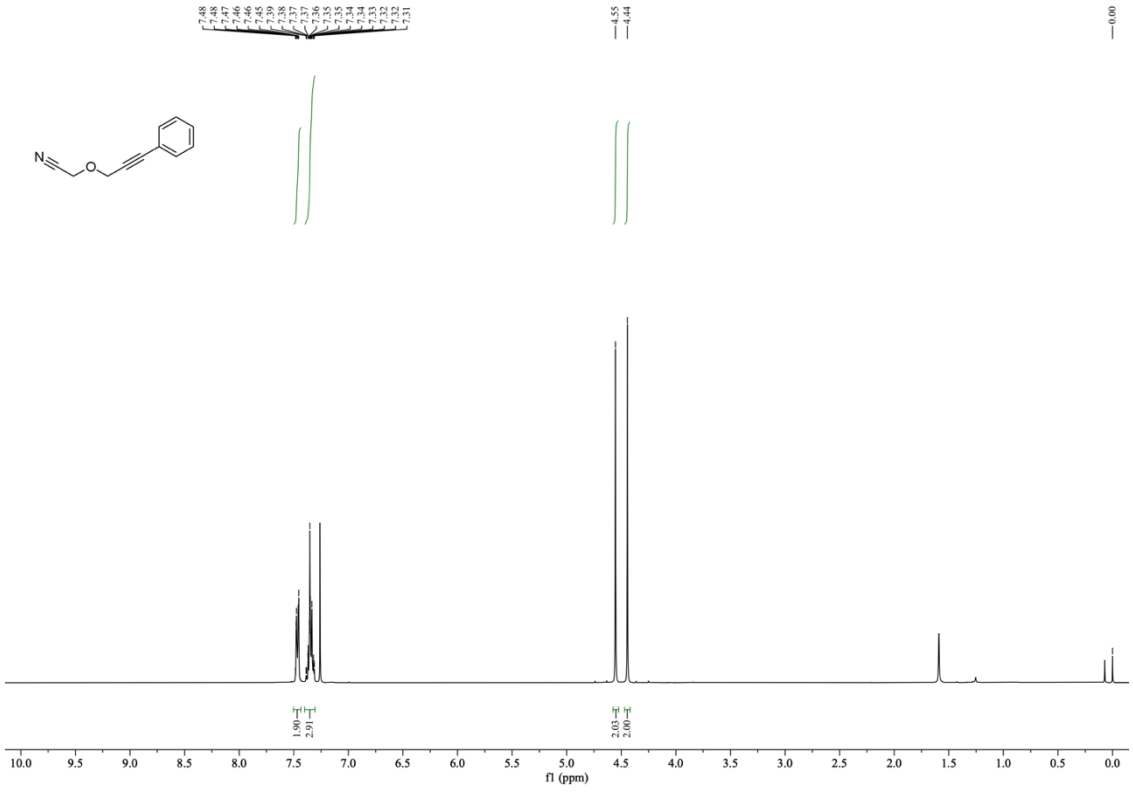
^{13}C NMR Spectrum of Compound 3f (101 MHz, $CDCl_3$)



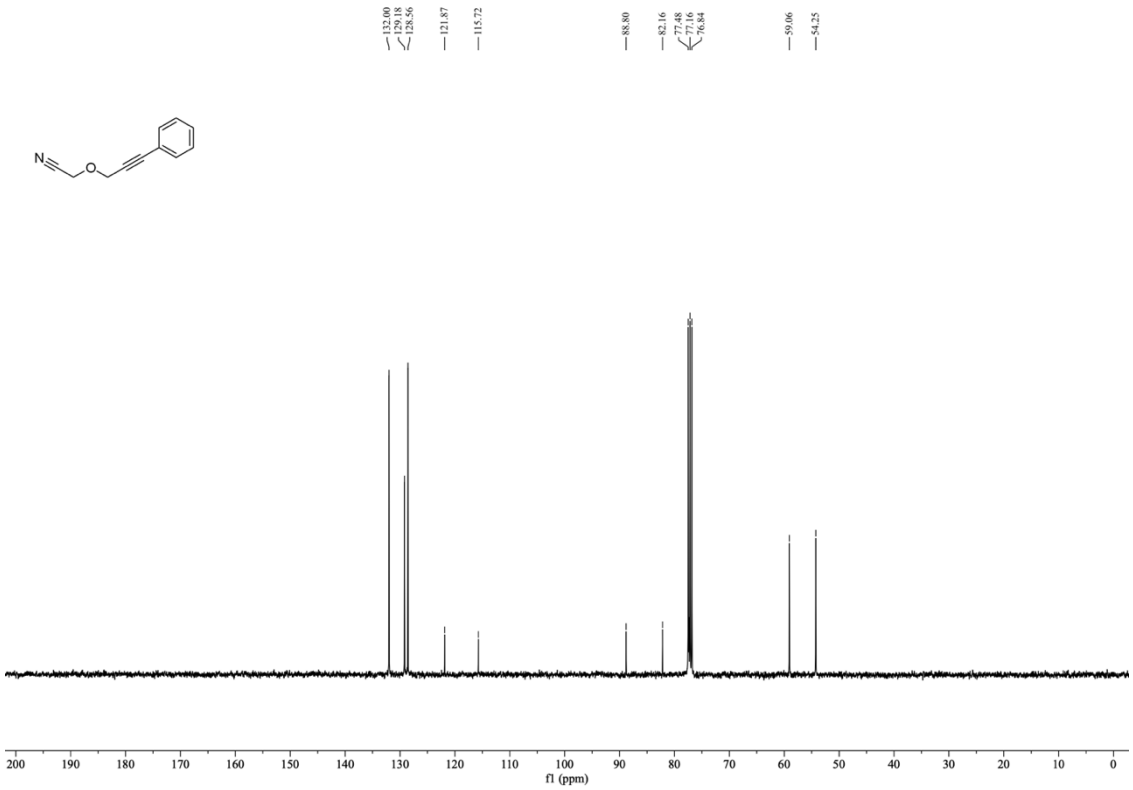
^{1}H NMR Spectrum of Compound 3g (400 MHz, $CDCl_3$)



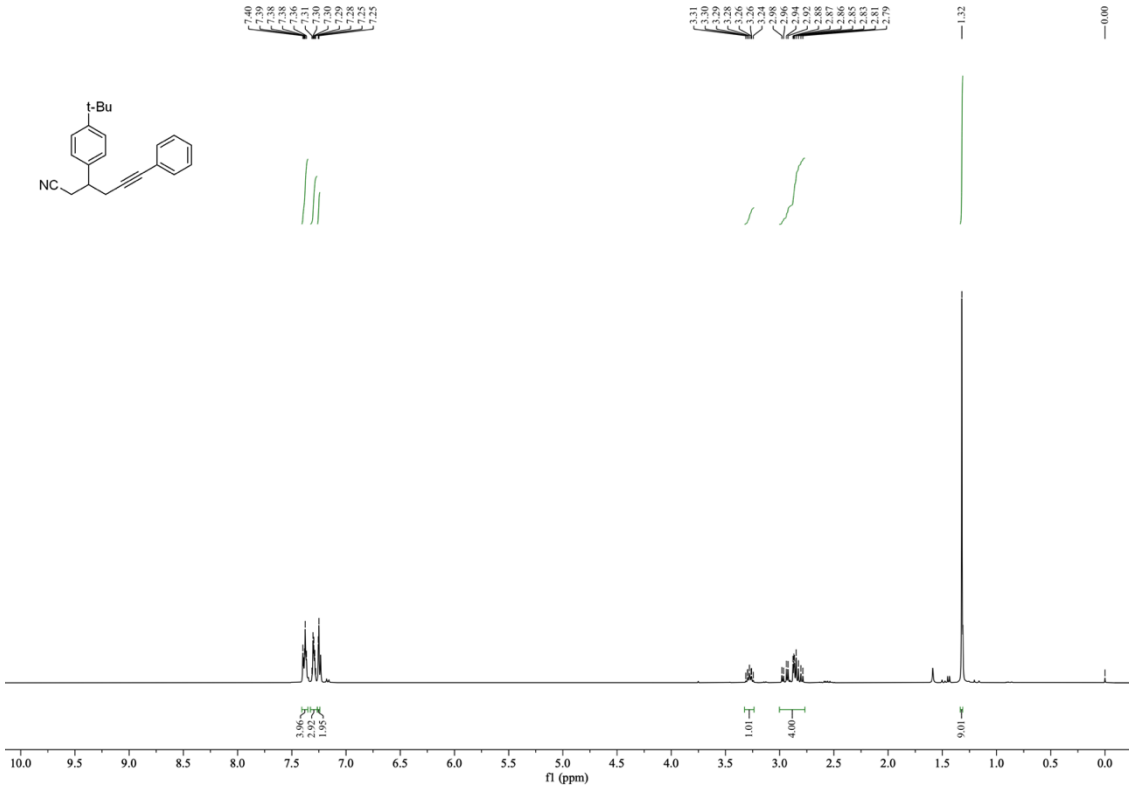
^{13}C NMR Spectrum of Compound 3g (101 MHz, $CDCl_3$)



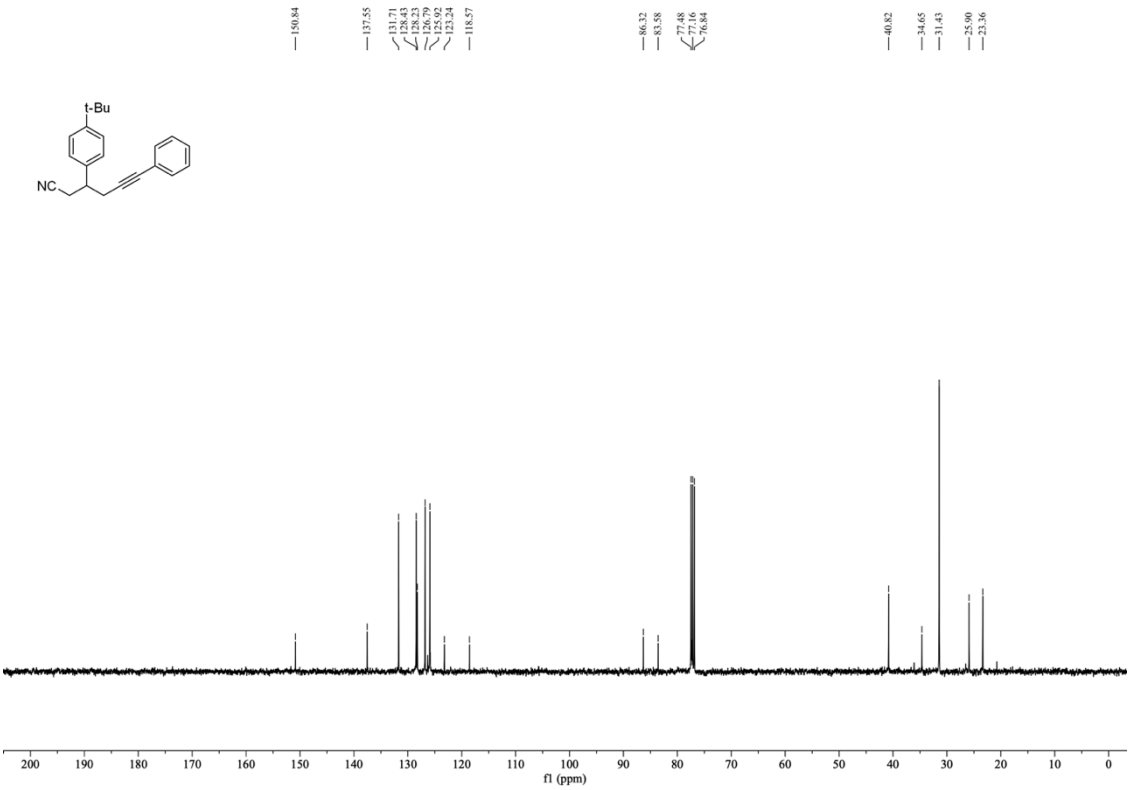
^{1}H NMR Spectrum of Compound 3h (400 MHz, $CDCl_3$)



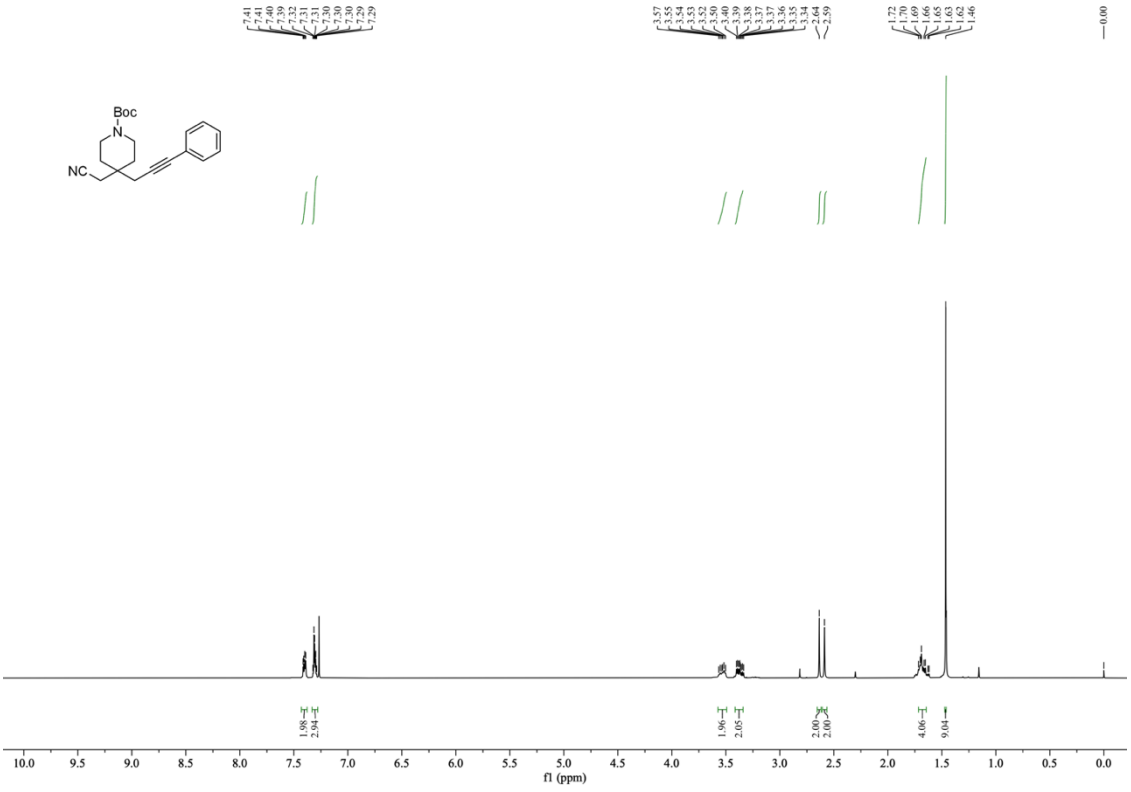
^{13}C NMR Spectrum of Compound 3h (101 MHz, $CDCl_3$)



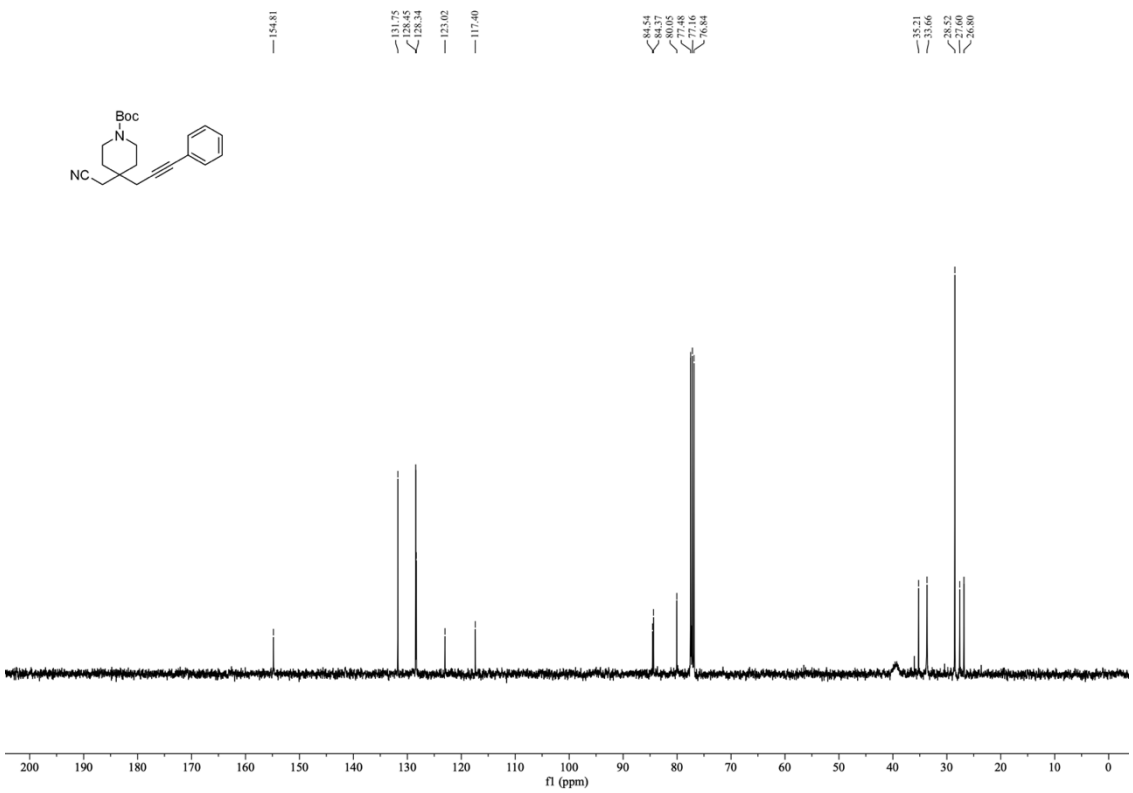
^{1}H NMR Spectrum of Compound 3i (400 MHz, $CDCl_3$)



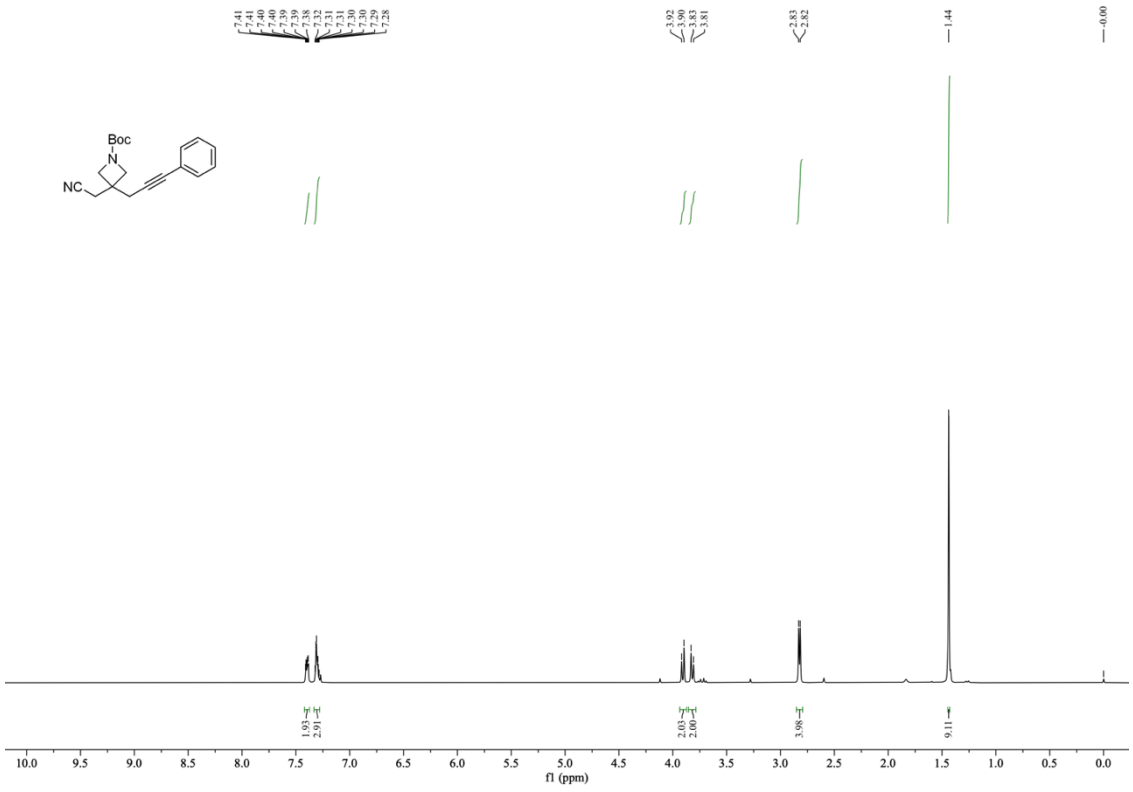
^{13}C NMR Spectrum of Compound 3i (101 MHz, $CDCl_3$)



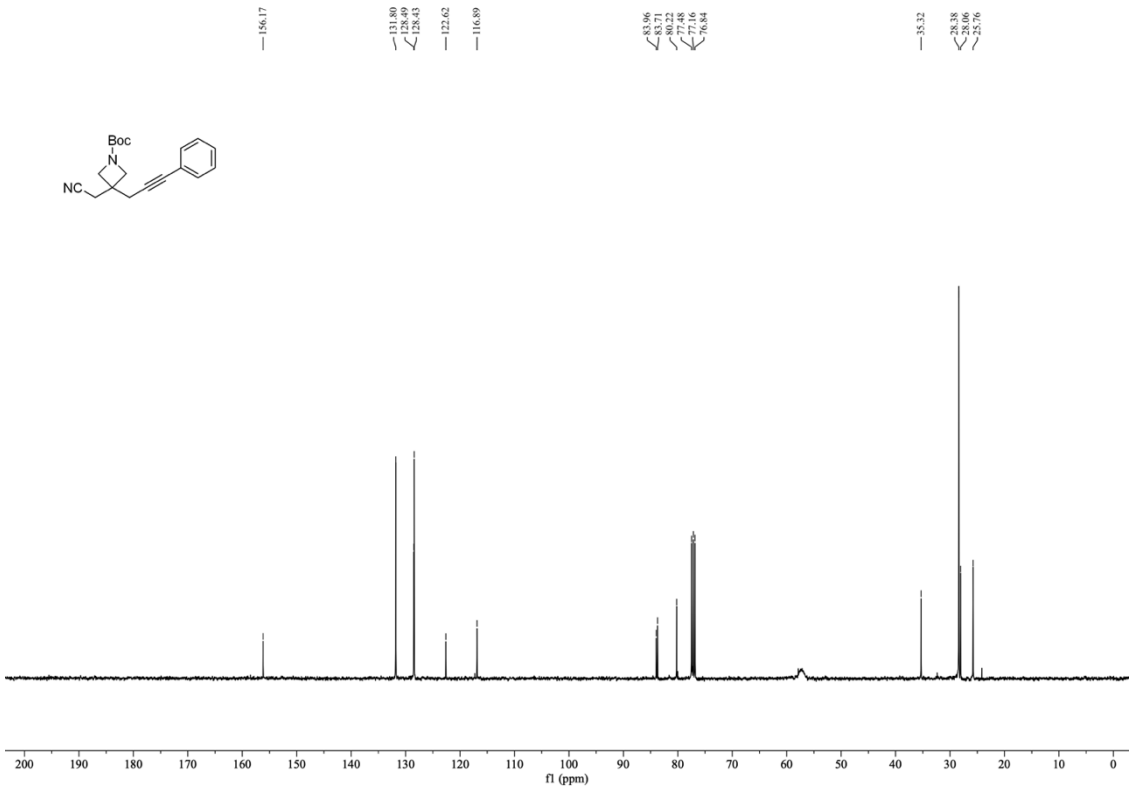
^{1}H NMR Spectrum of Compound 3j (400 MHz, $CDCl_3$)



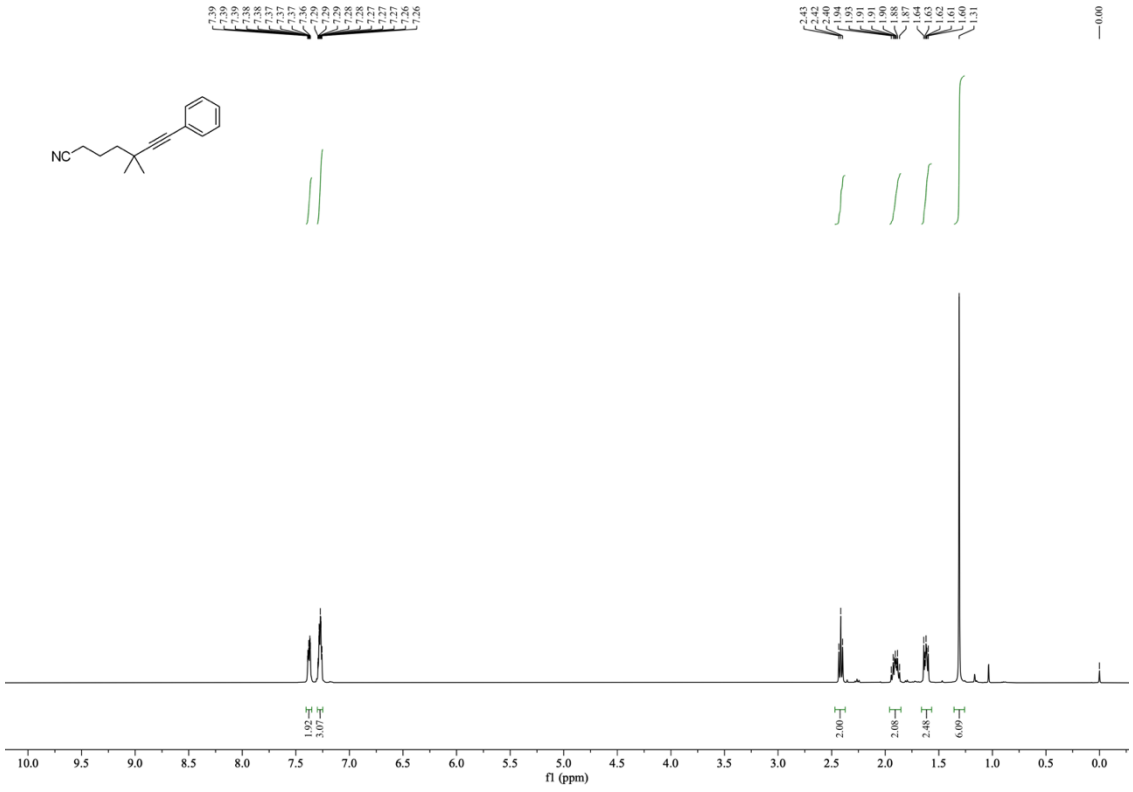
^{13}C NMR Spectrum of Compound 3j (101 MHz, $CDCl_3$)



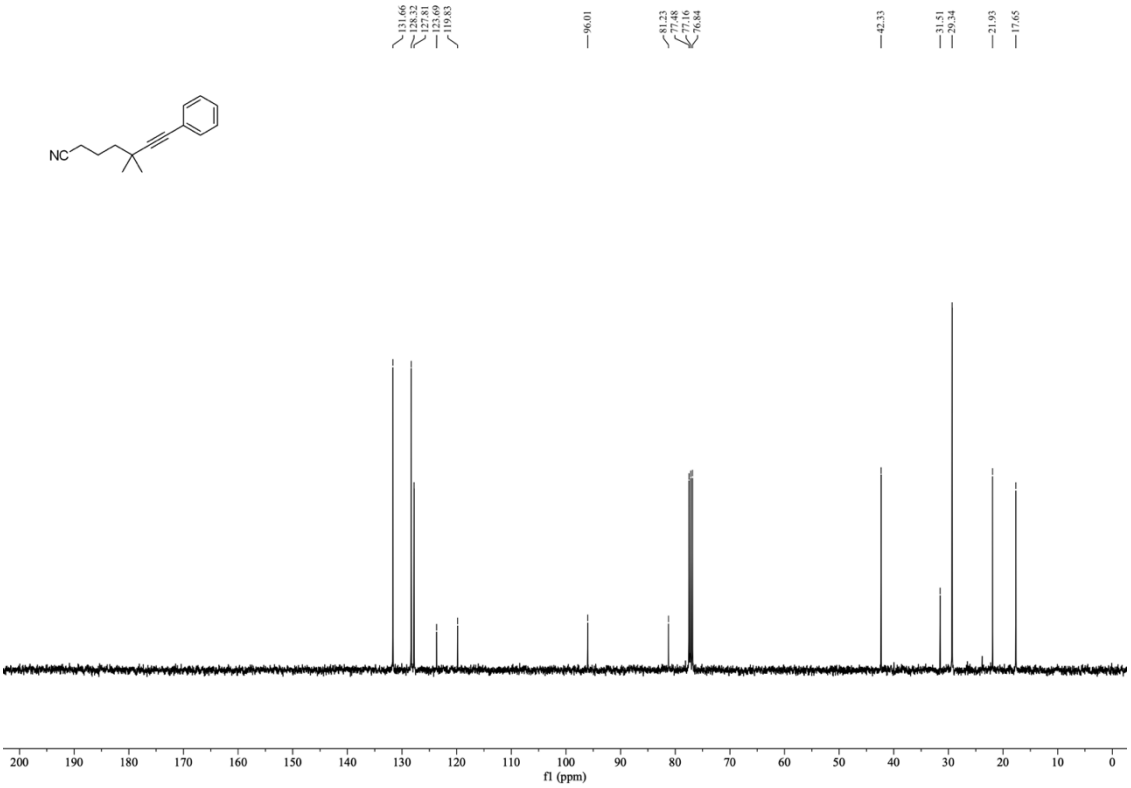
^{1}H NMR Spectrum of Compound 3k (400 MHz, $CDCl_3$)



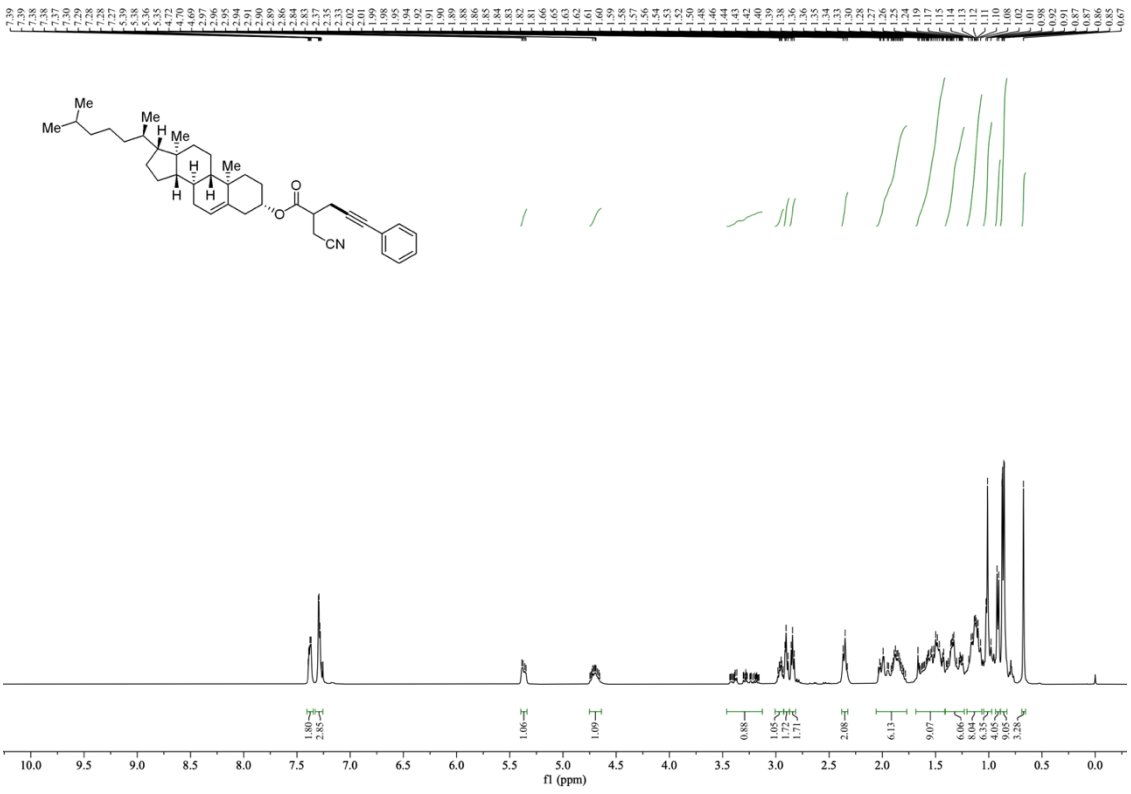
^{13}C NMR Spectrum of Compound 3k (101 MHz, $CDCl_3$)



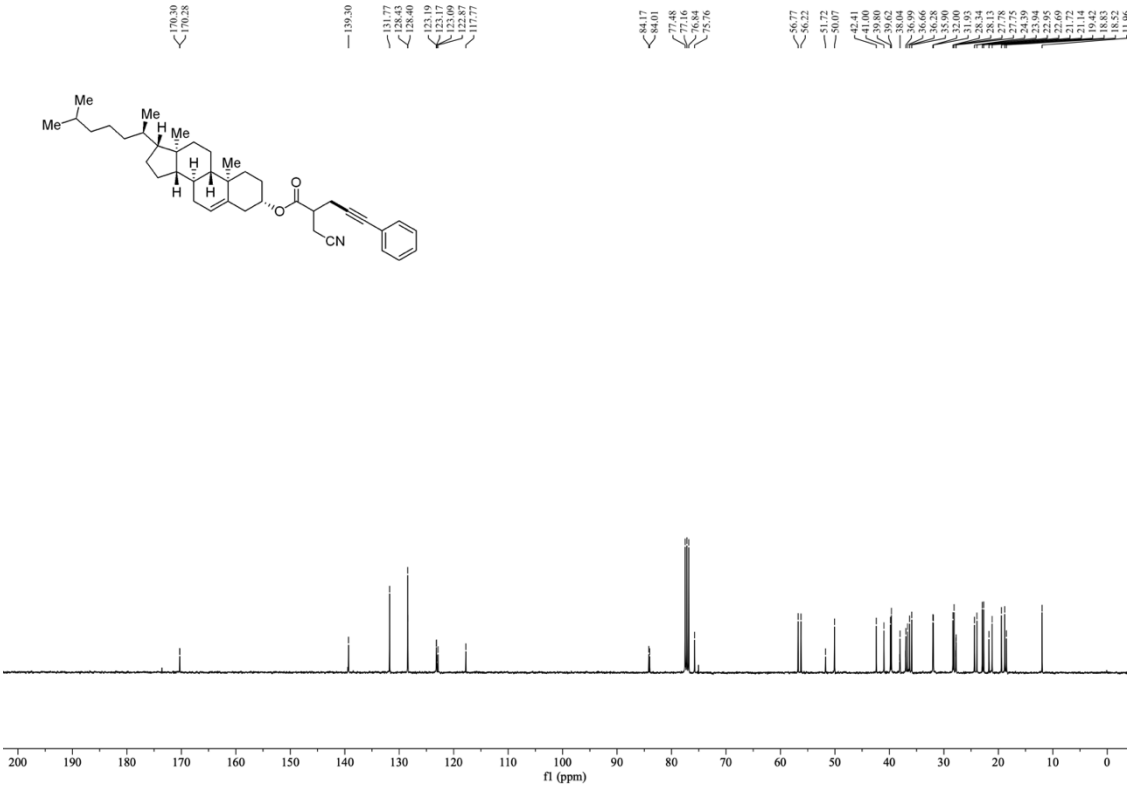
^{1}H NMR Spectrum of Compound 3l (400 MHz, $CDCl_3$)



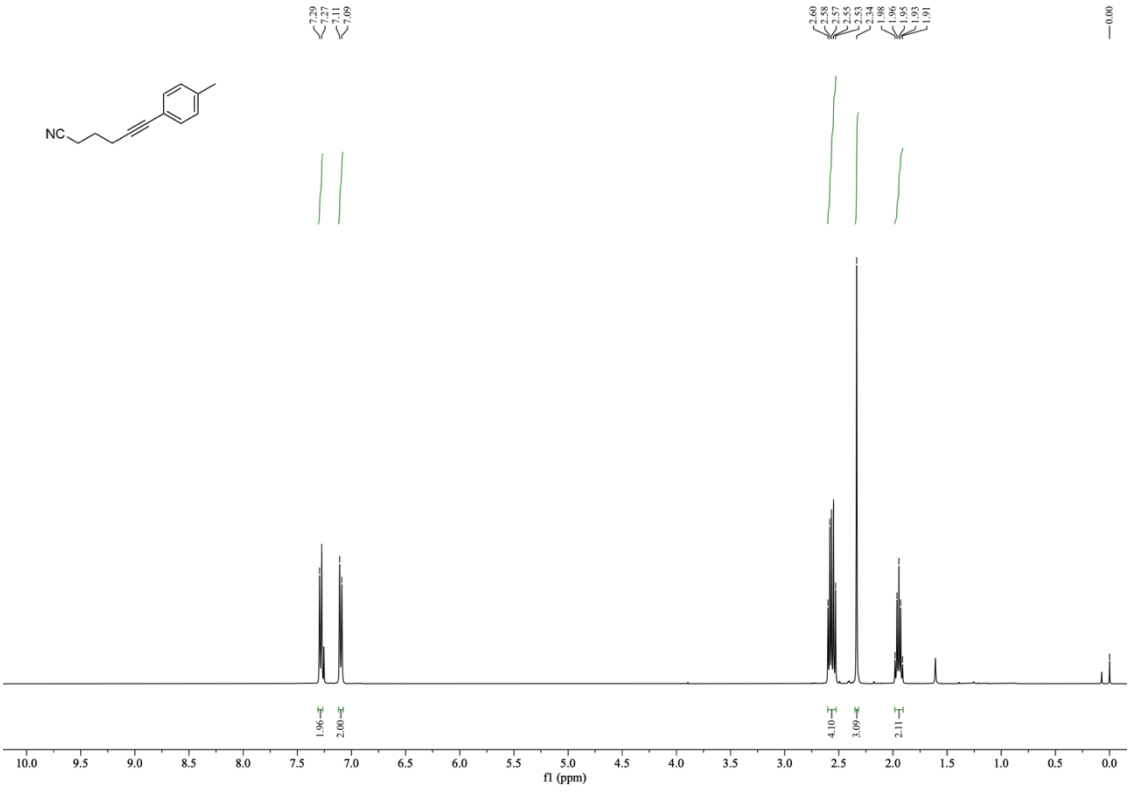
^{13}C NMR Spectrum of Compound 3l (101 MHz, $CDCl_3$)



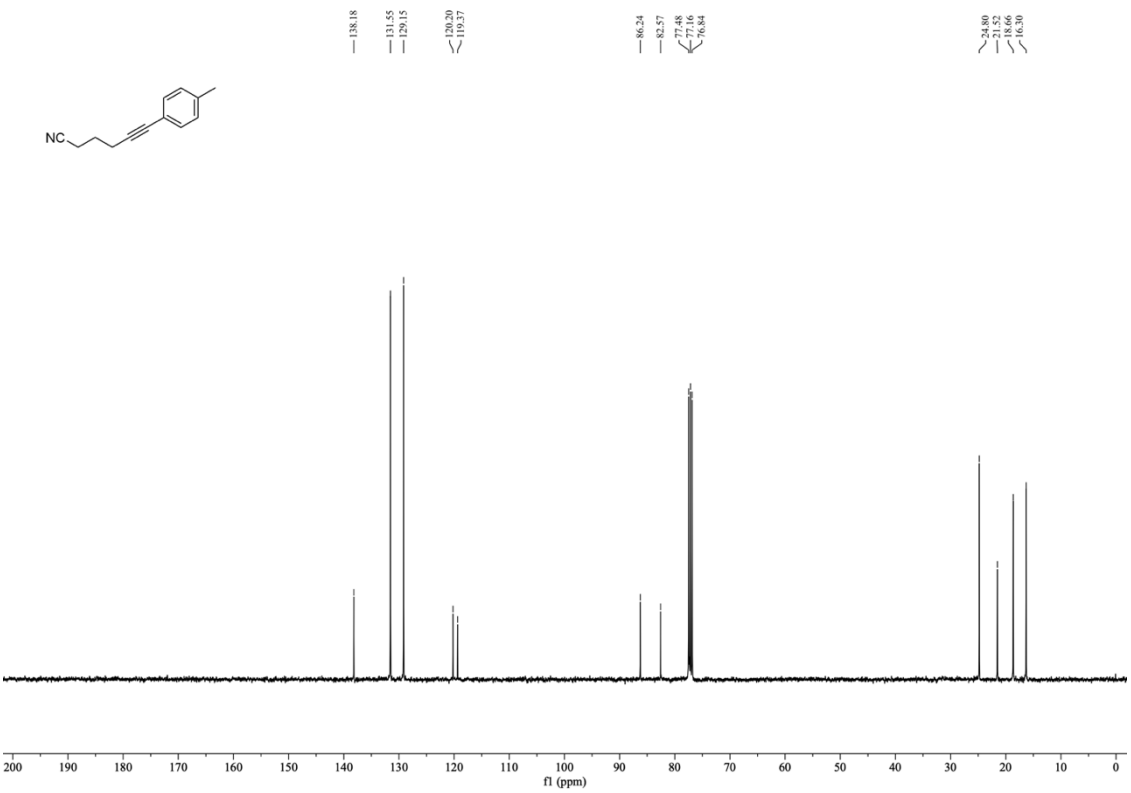
^{1}H NMR Spectrum of Compound 3m (400 MHz, $CDCl_3$)



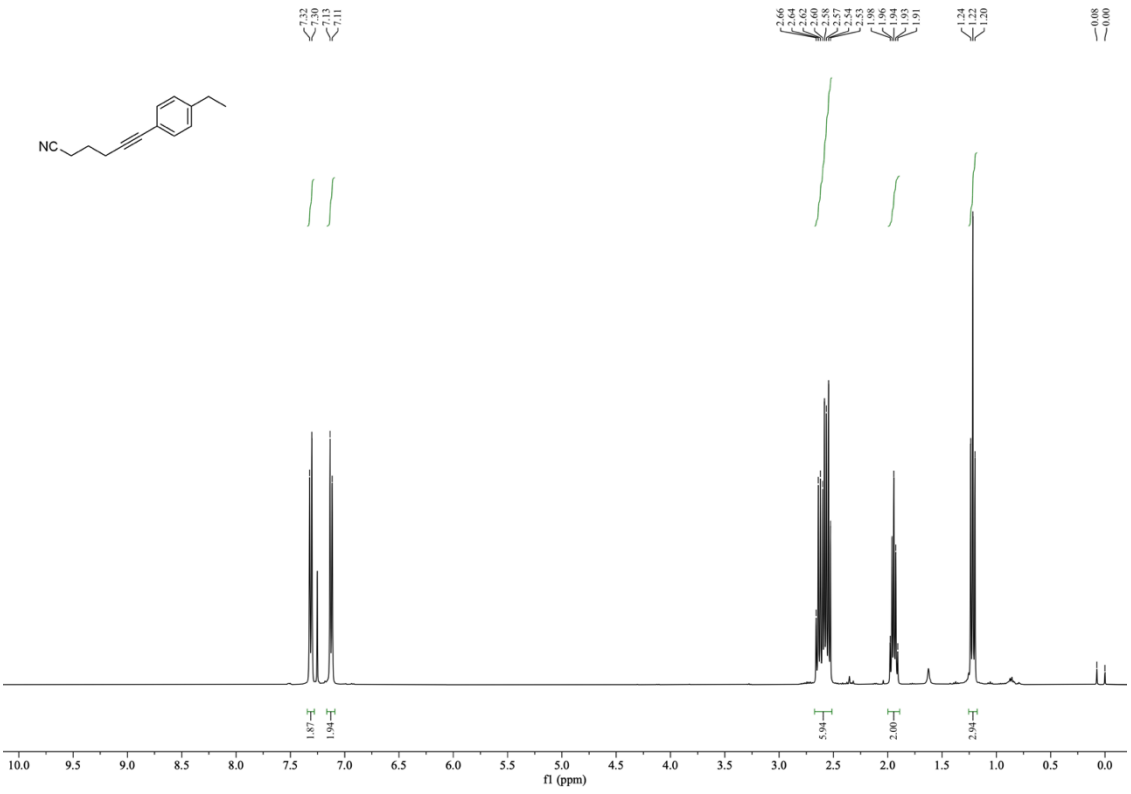
^{13}C NMR Spectrum of Compound 3m (101 MHz, $CDCl_3$)



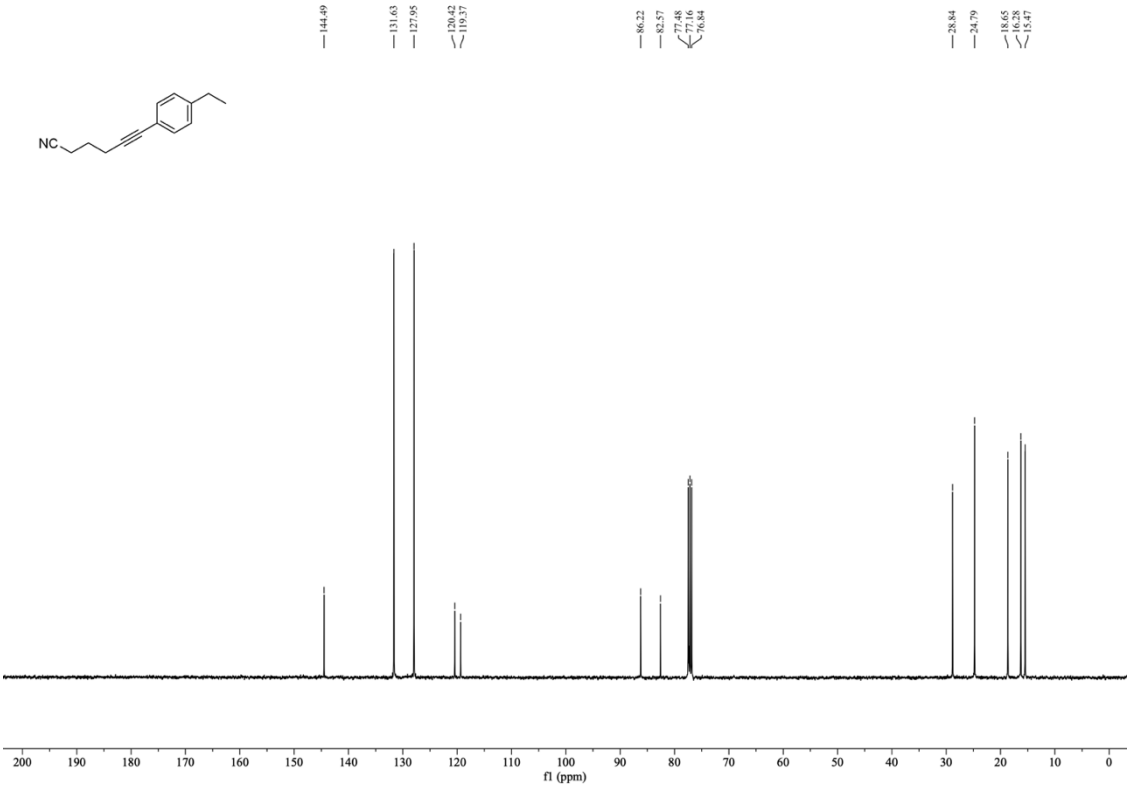
^{1}H NMR Spectrum of Compound 4a (400 MHz, $CDCl_3$)



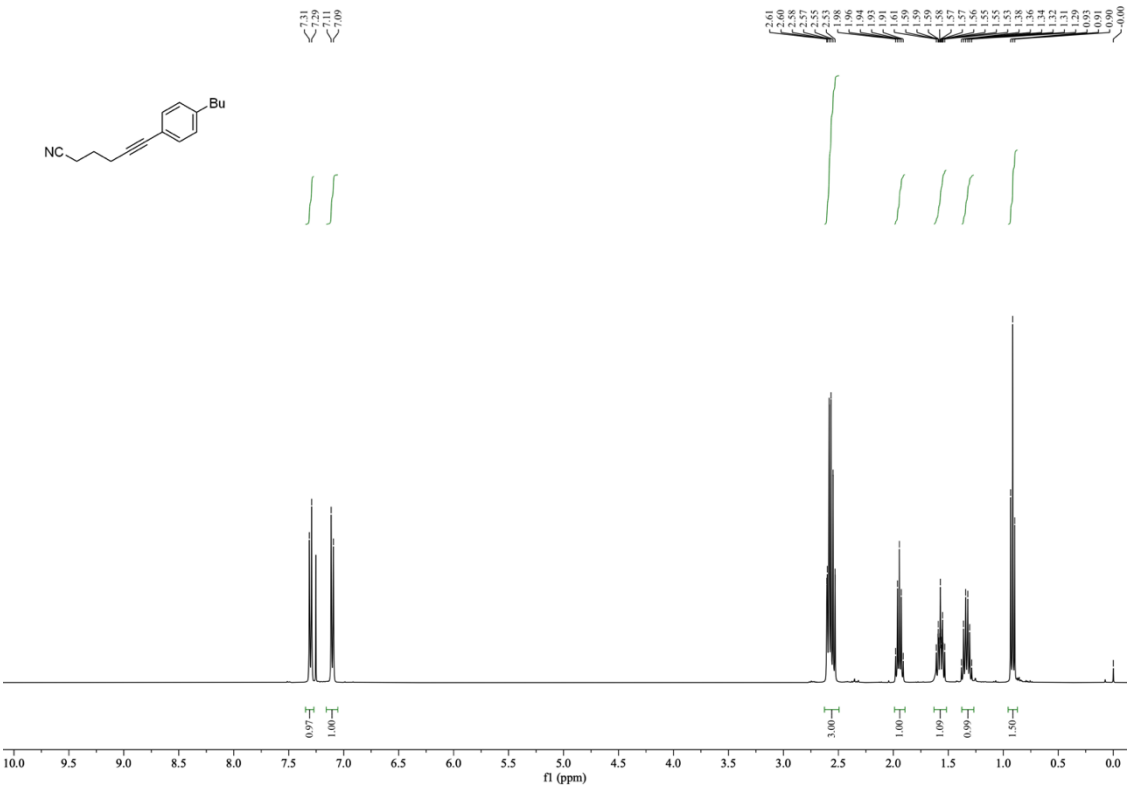
^{13}C NMR Spectrum of Compound 4a (101 MHz, $CDCl_3$)



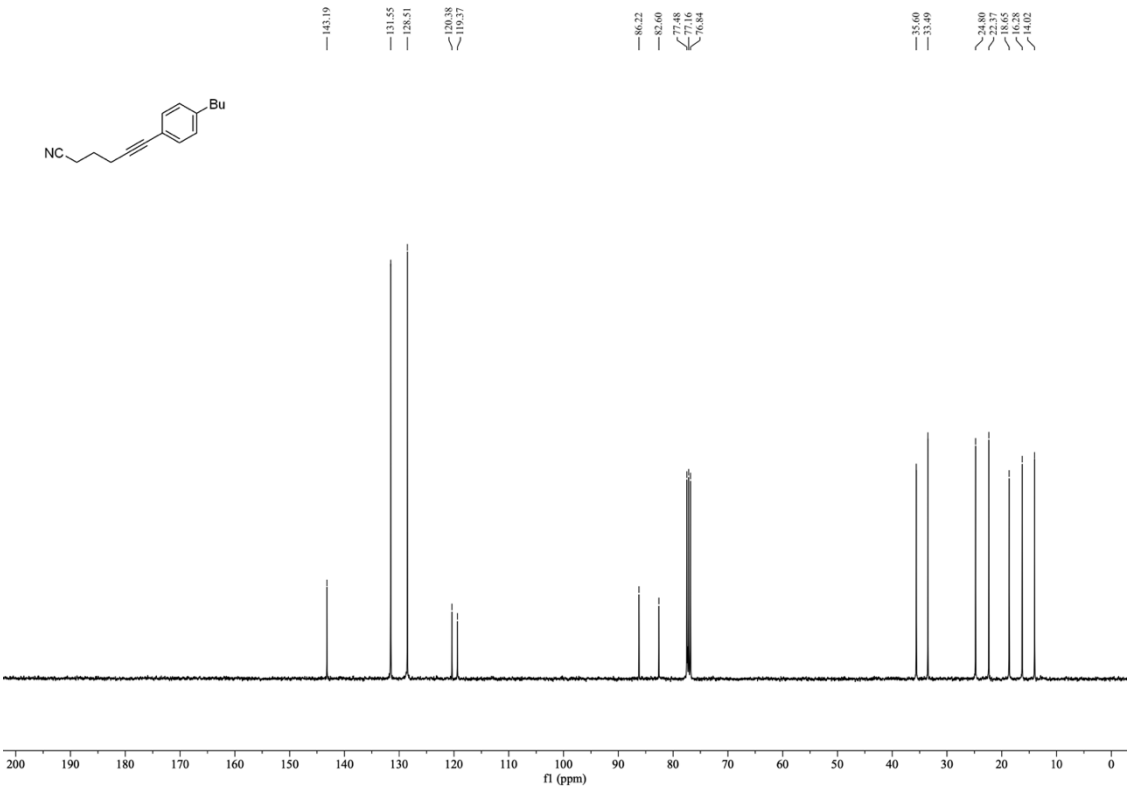
^{1}H NMR Spectrum of Compound 4b (400 MHz, $CDCl_3$)



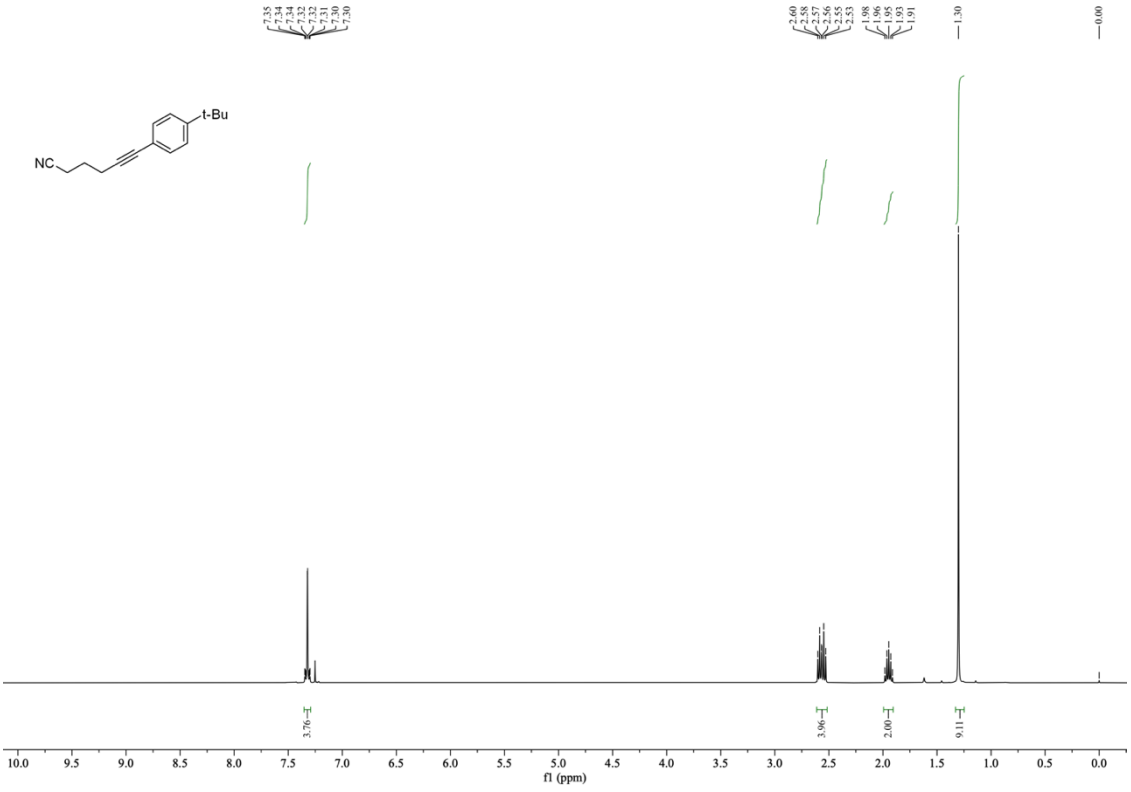
^{13}C NMR Spectrum of Compound 4b (101 MHz, $CDCl_3$)



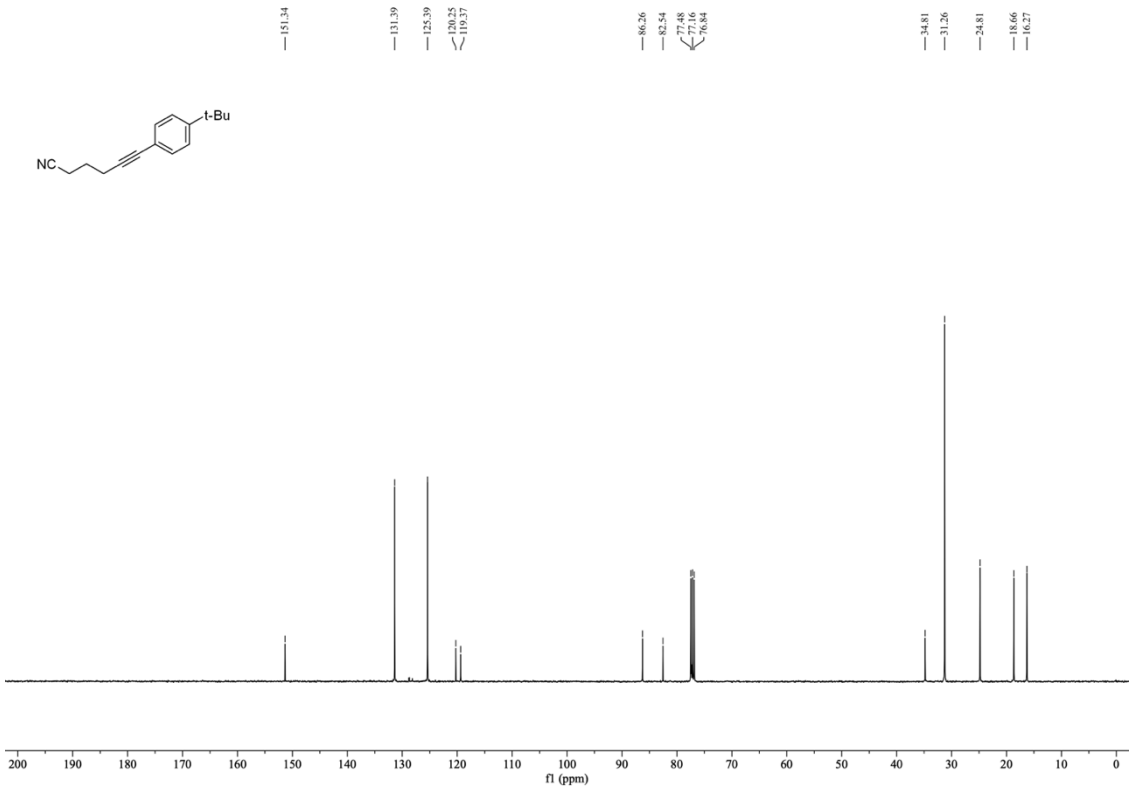
^{1}H NMR Spectrum of Compound 4c (400 MHz, $CDCl_3$)



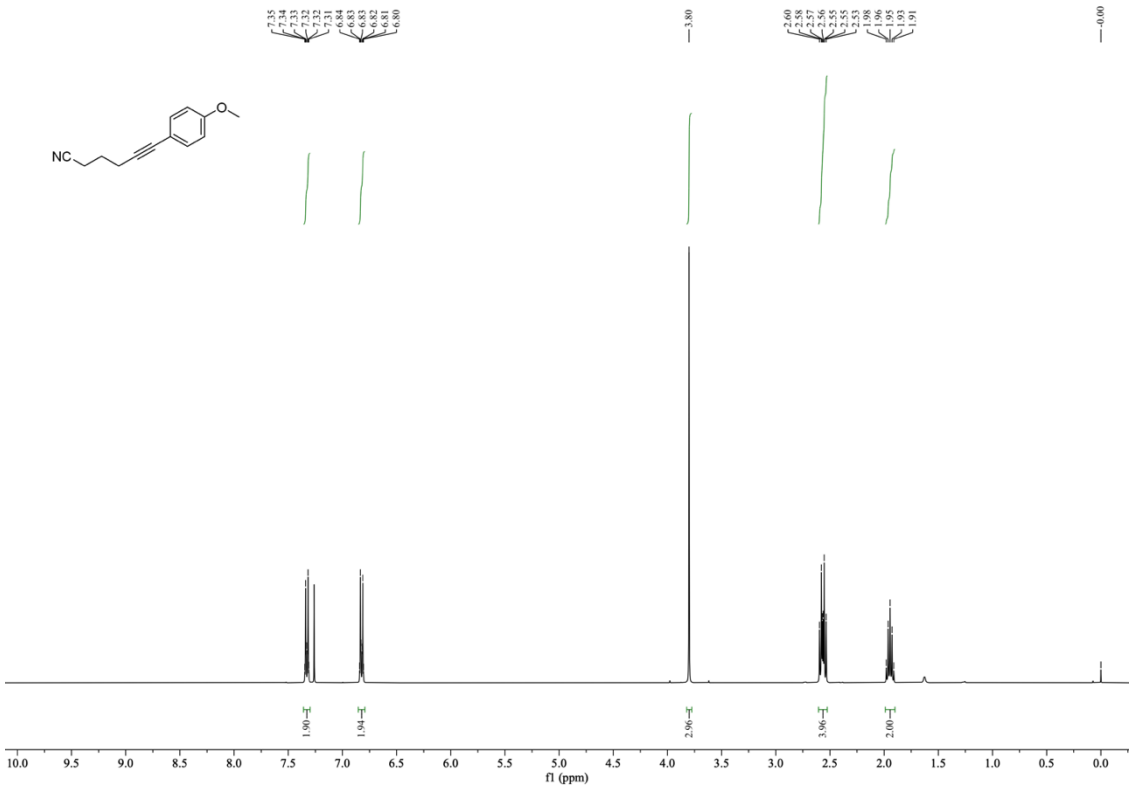
^{13}C NMR Spectrum of Compound 4c (101 MHz, $CDCl_3$)



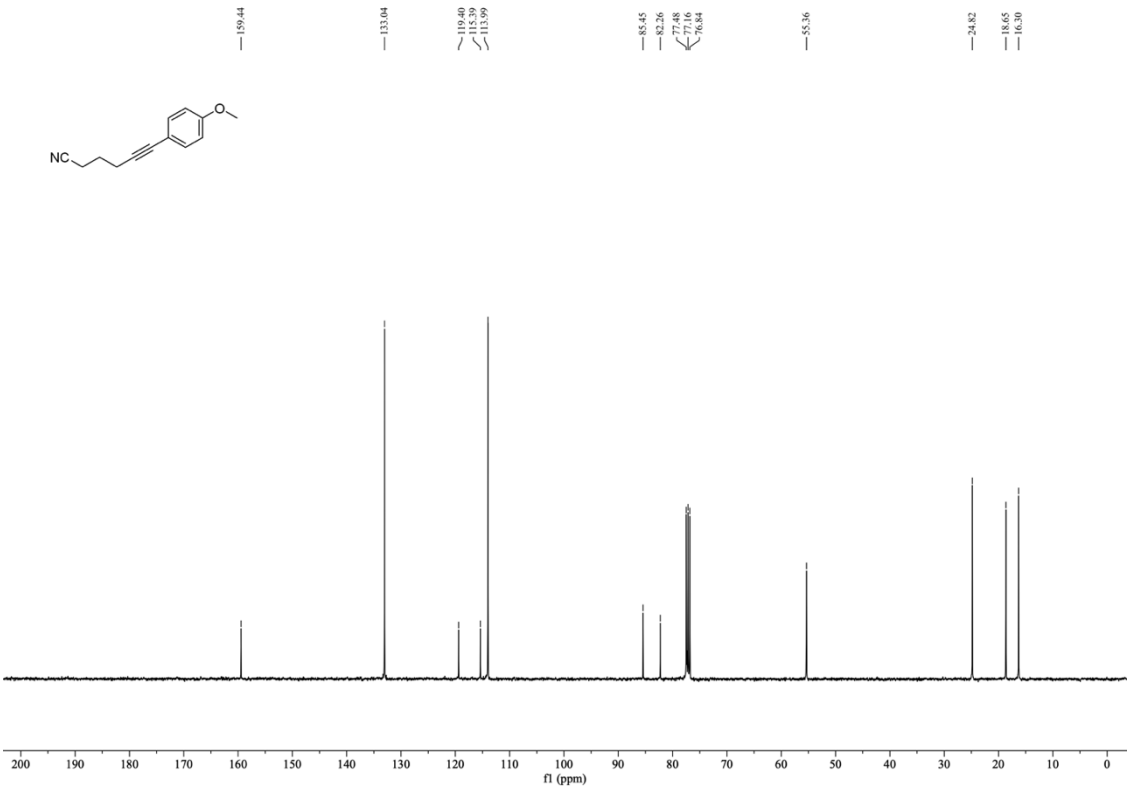
^{1}H NMR Spectrum of Compound 4d (400 MHz, $CDCl_3$)



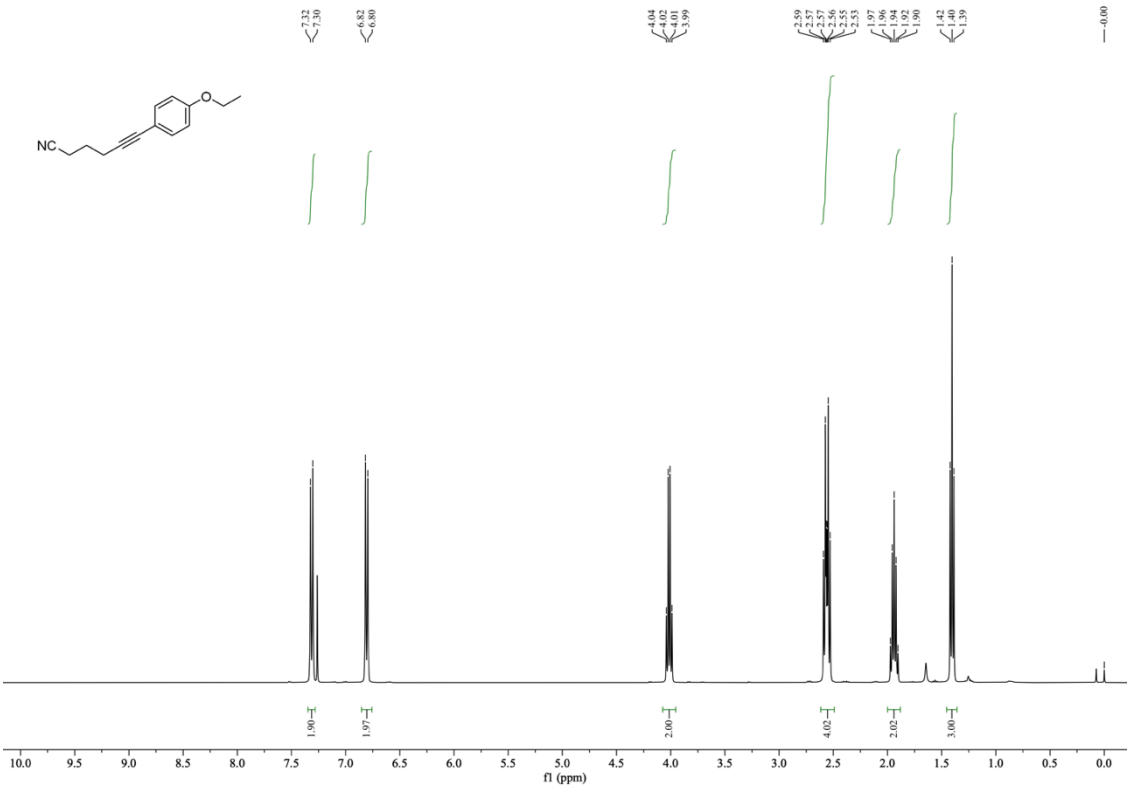
^{13}C NMR Spectrum of Compound 4d (101 MHz, $CDCl_3$)



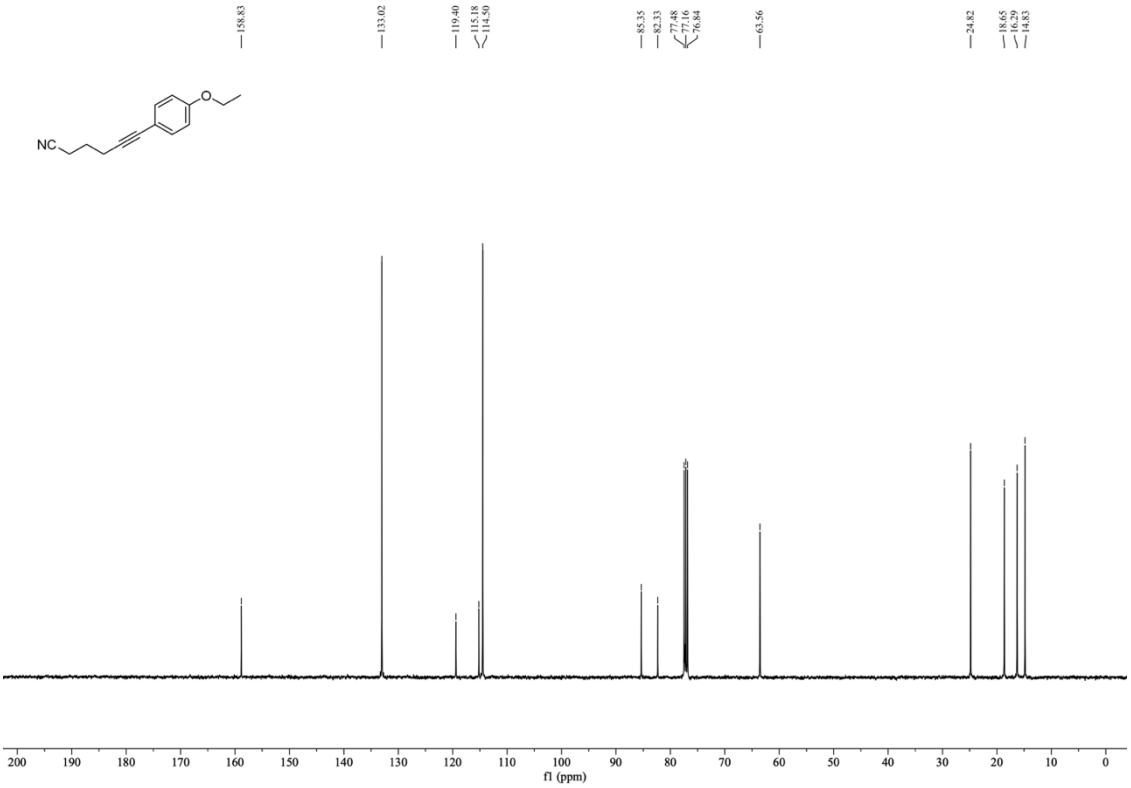
^{1}H NMR Spectrum of Compound 4e (400 MHz, $CDCl_3$)



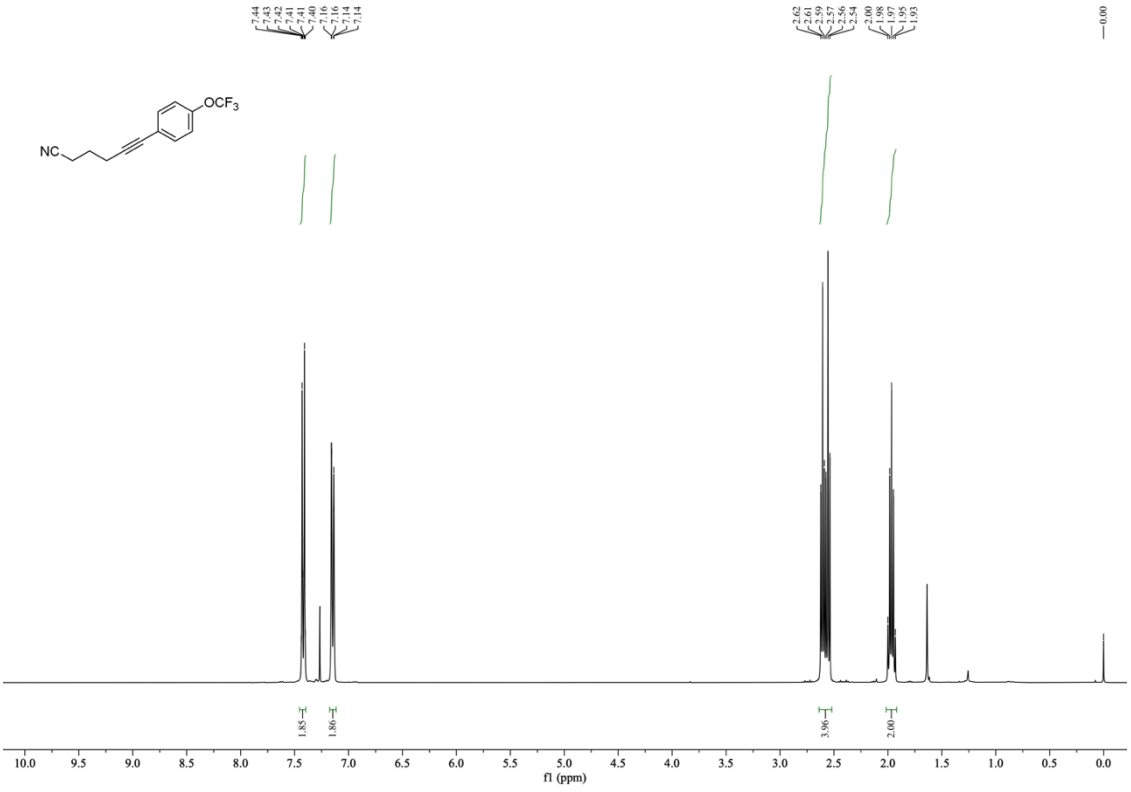
^{13}C NMR Spectrum of Compound 4e (101 MHz, $CDCl_3$)



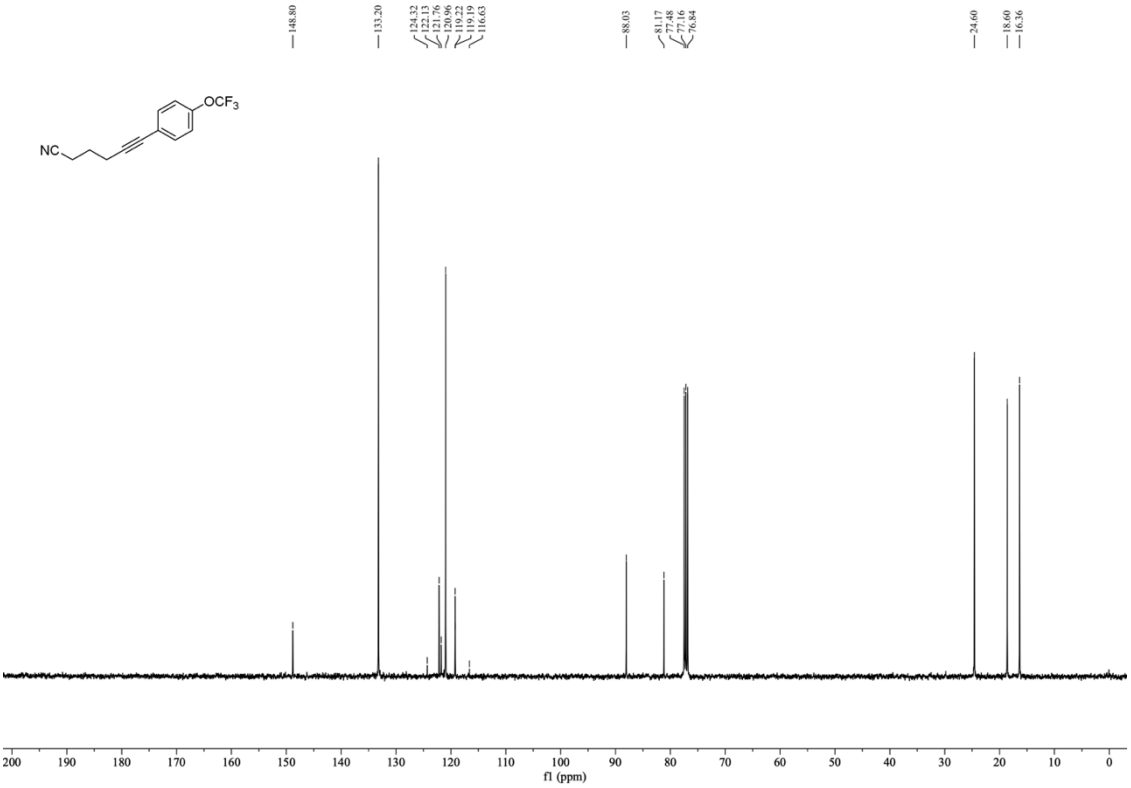
^{1}H NMR Spectrum of Compound 4f (400 MHz, $CDCl_3$)



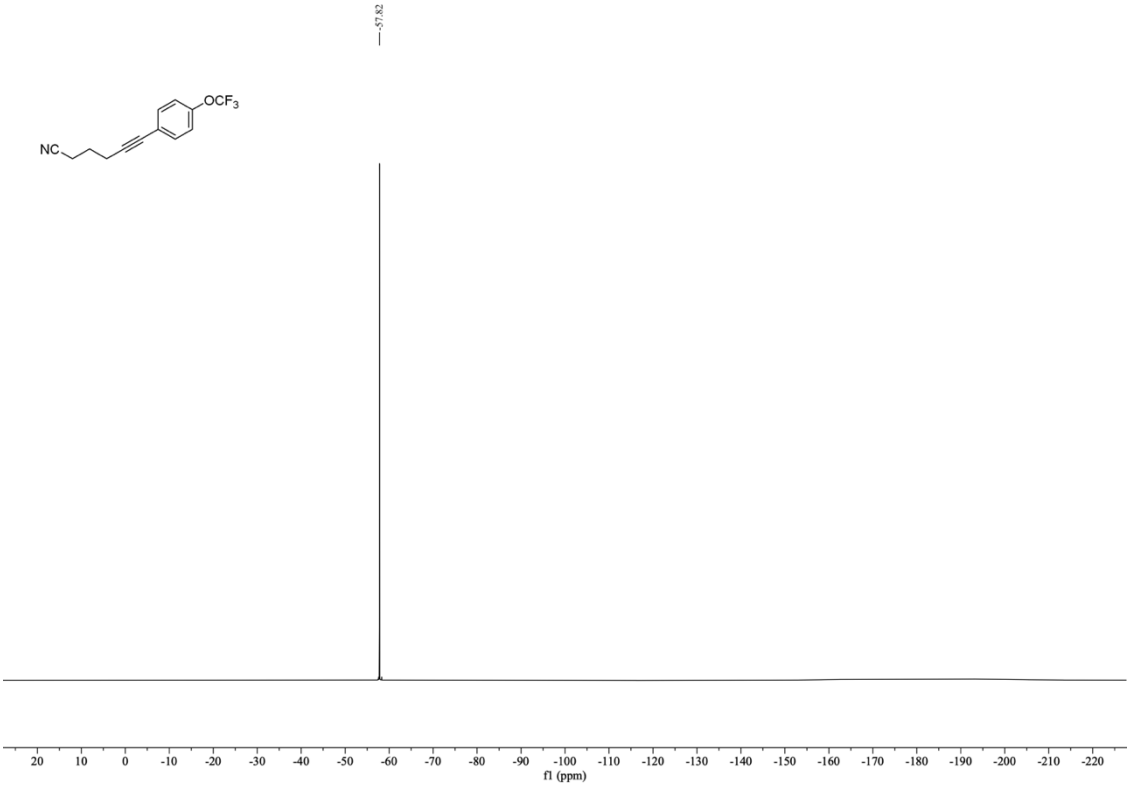
^{13}C NMR Spectrum of Compound 4f (101 MHz, $CDCl_3$)



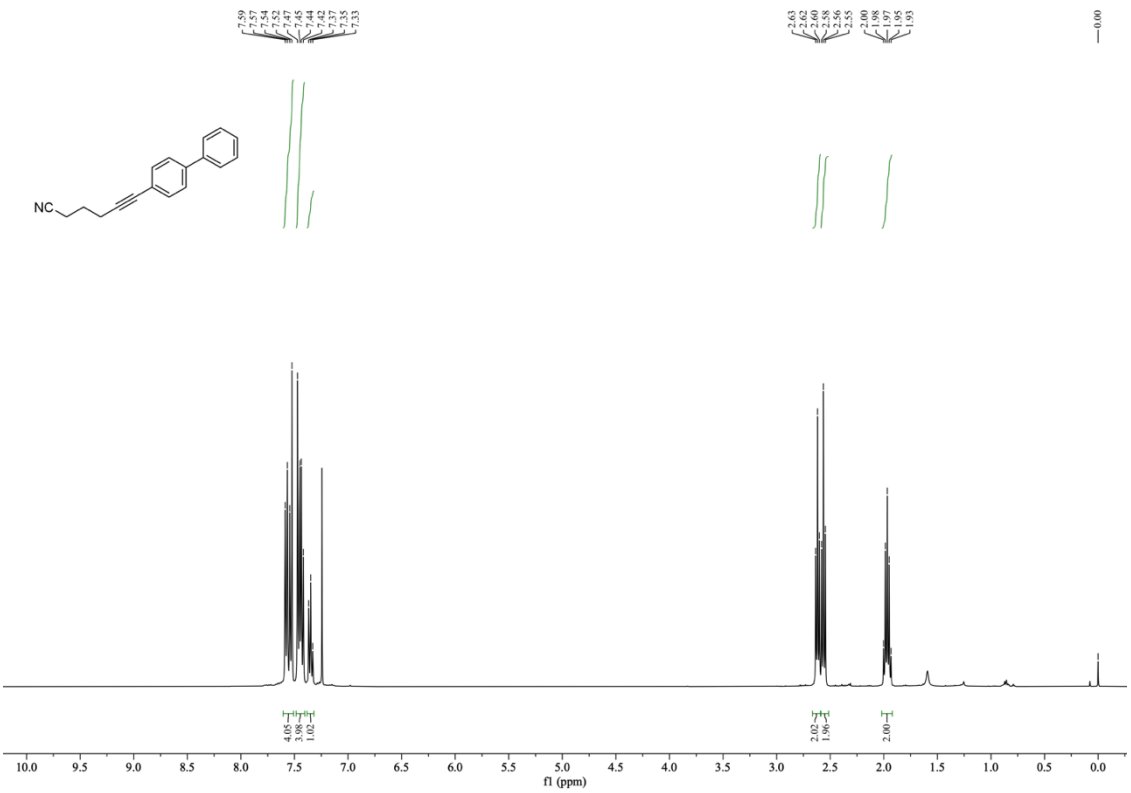
^{1}H NMR Spectrum of Compound 4g (400 MHz, $CDCl_3$)



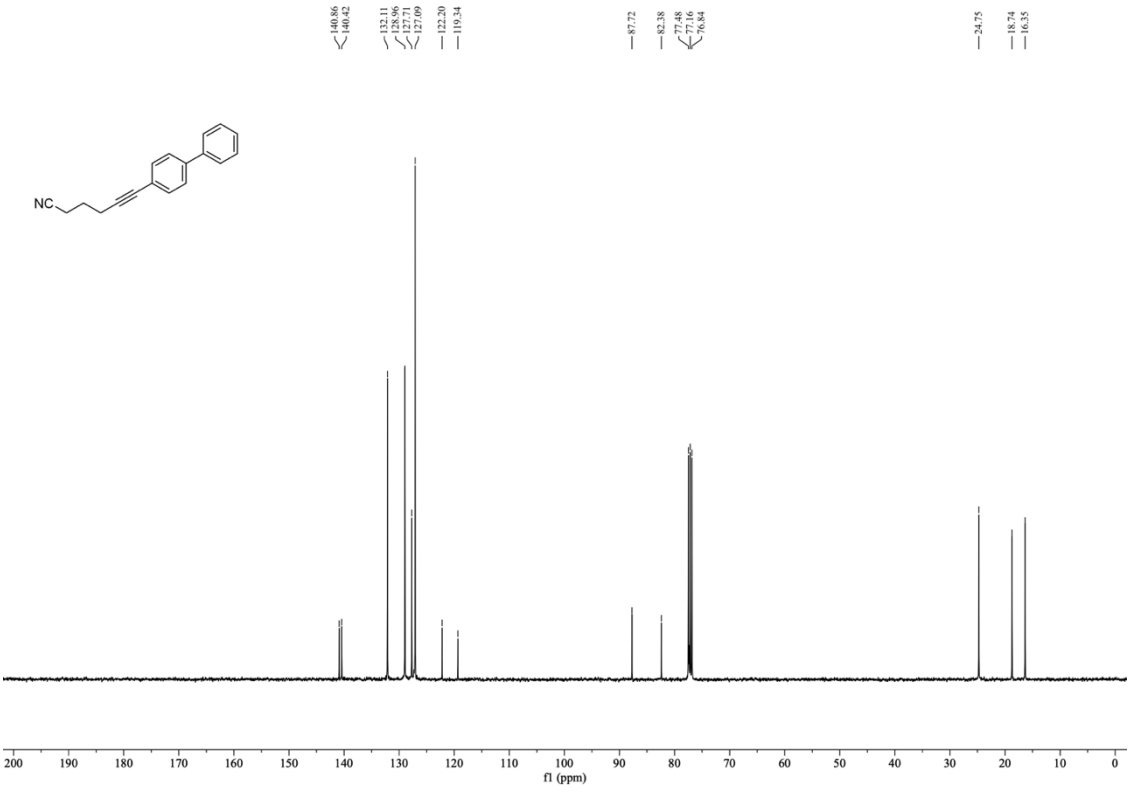
^{13}C NMR Spectrum of Compound 4g (101 MHz, $CDCl_3$)



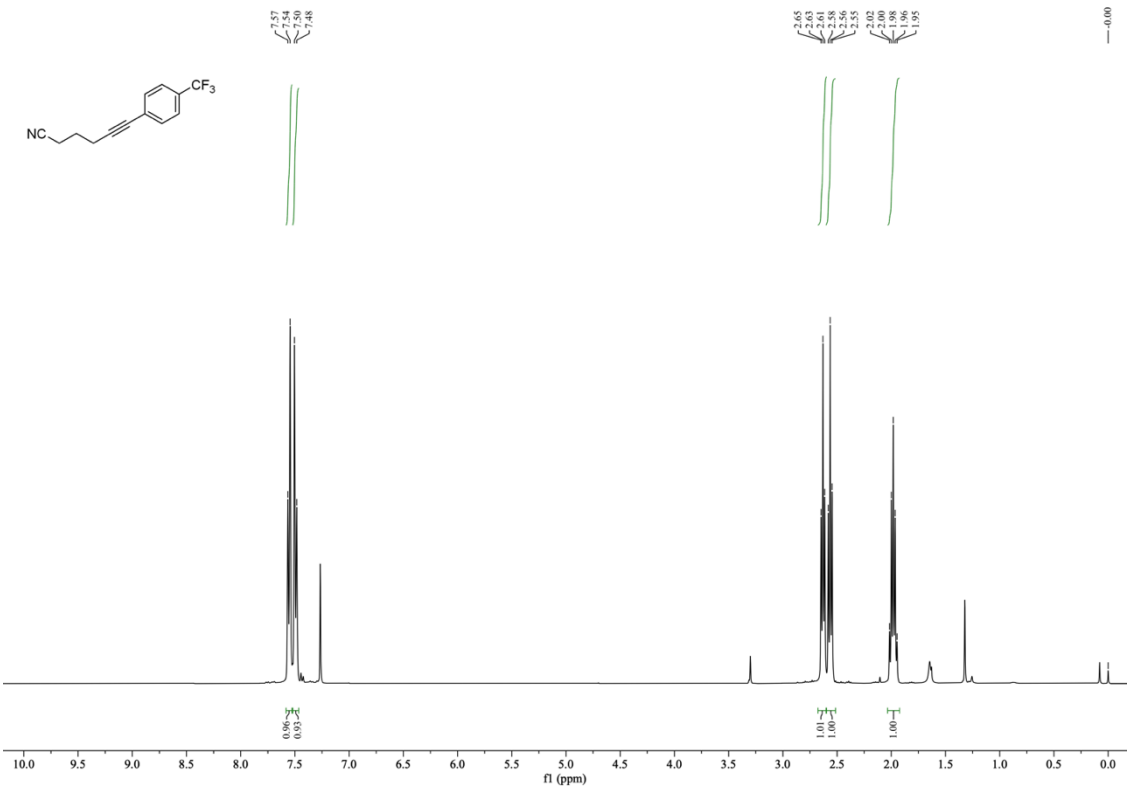
^{19}F NMR Spectrum of Compound 4g (376 MHz, $CDCl_3$)



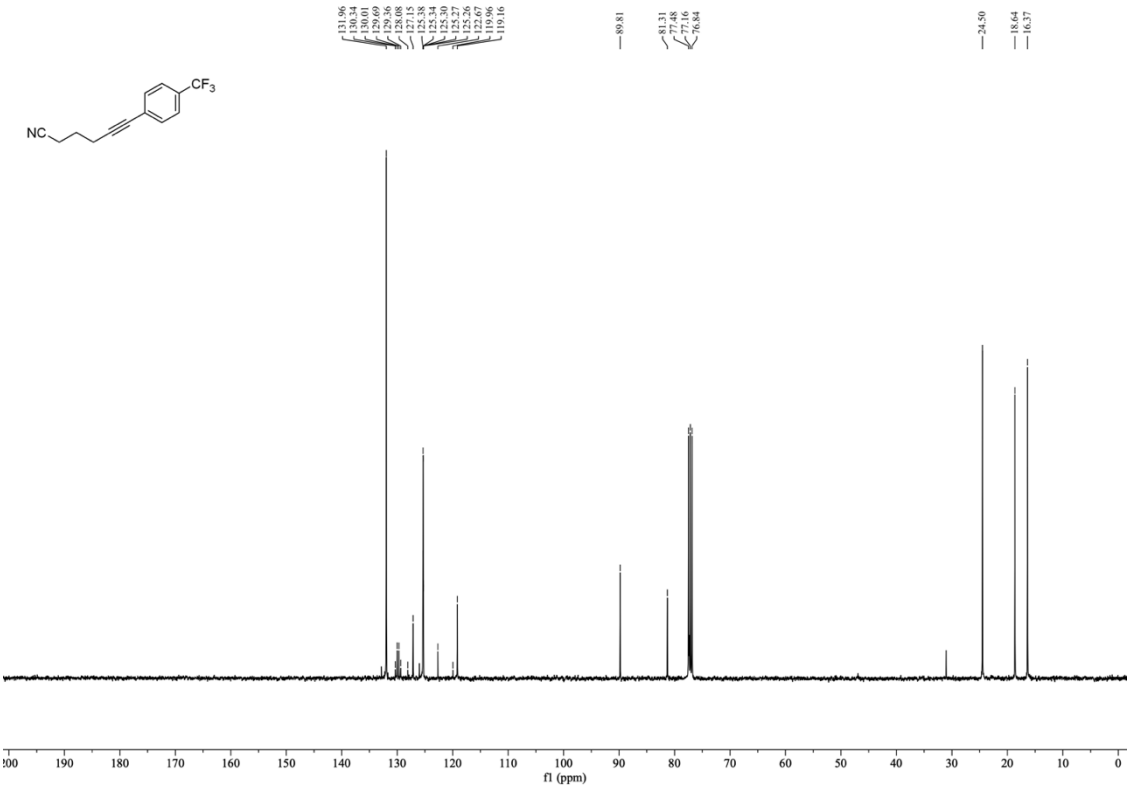
^{1}H NMR Spectrum of Compound 4h (400 MHz, $CDCl_3$)



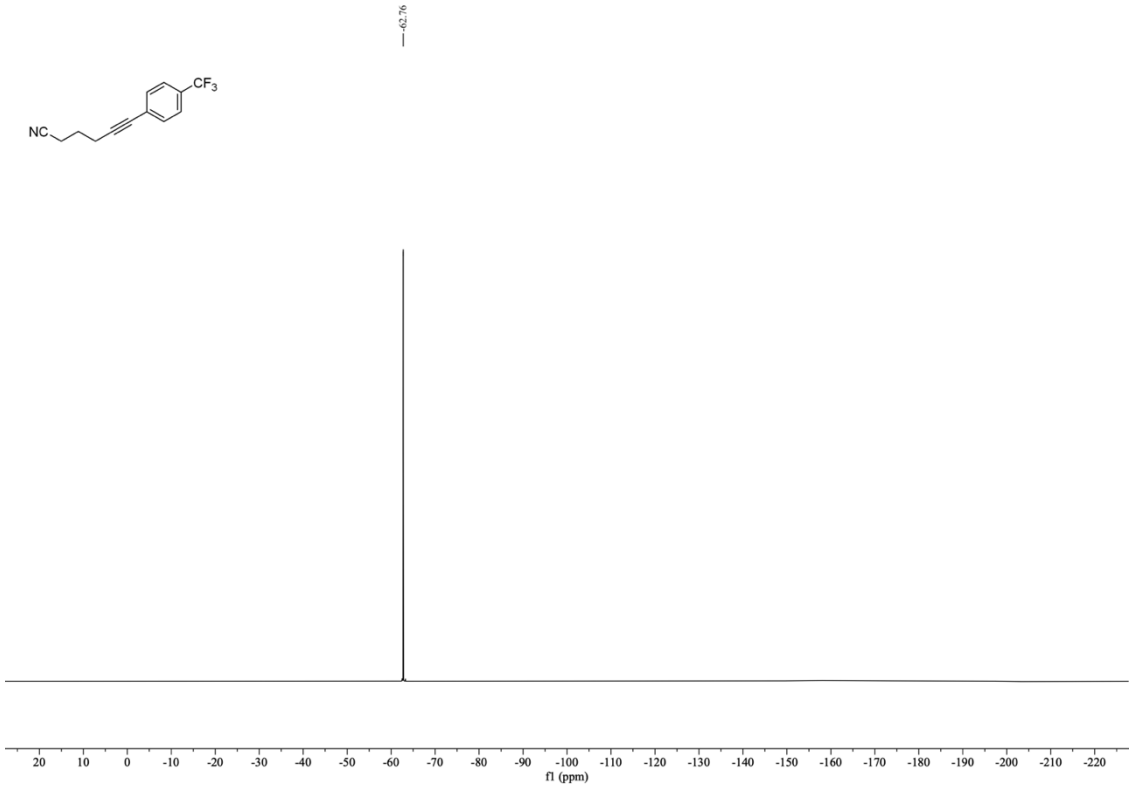
^{13}C NMR Spectrum of Compound 4h (101 MHz, $CDCl_3$)



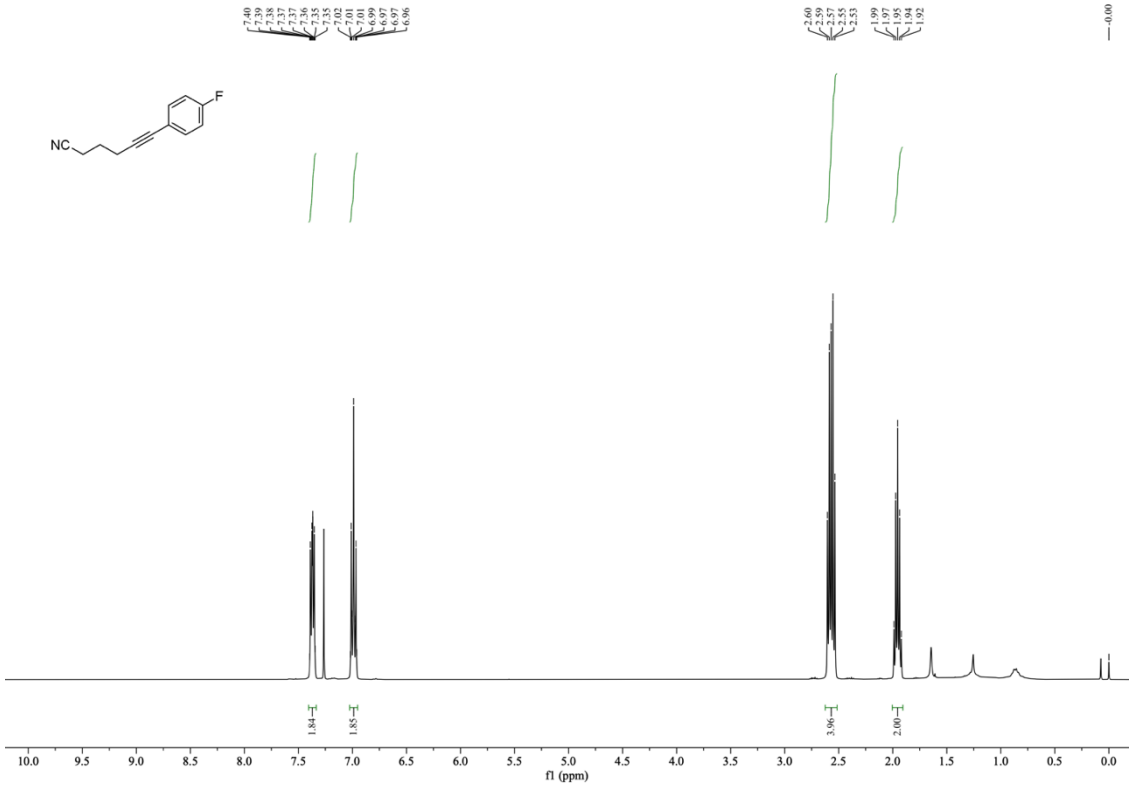
^{1}H NMR Spectrum of Compound 4i (400 MHz, $CDCl_3$)



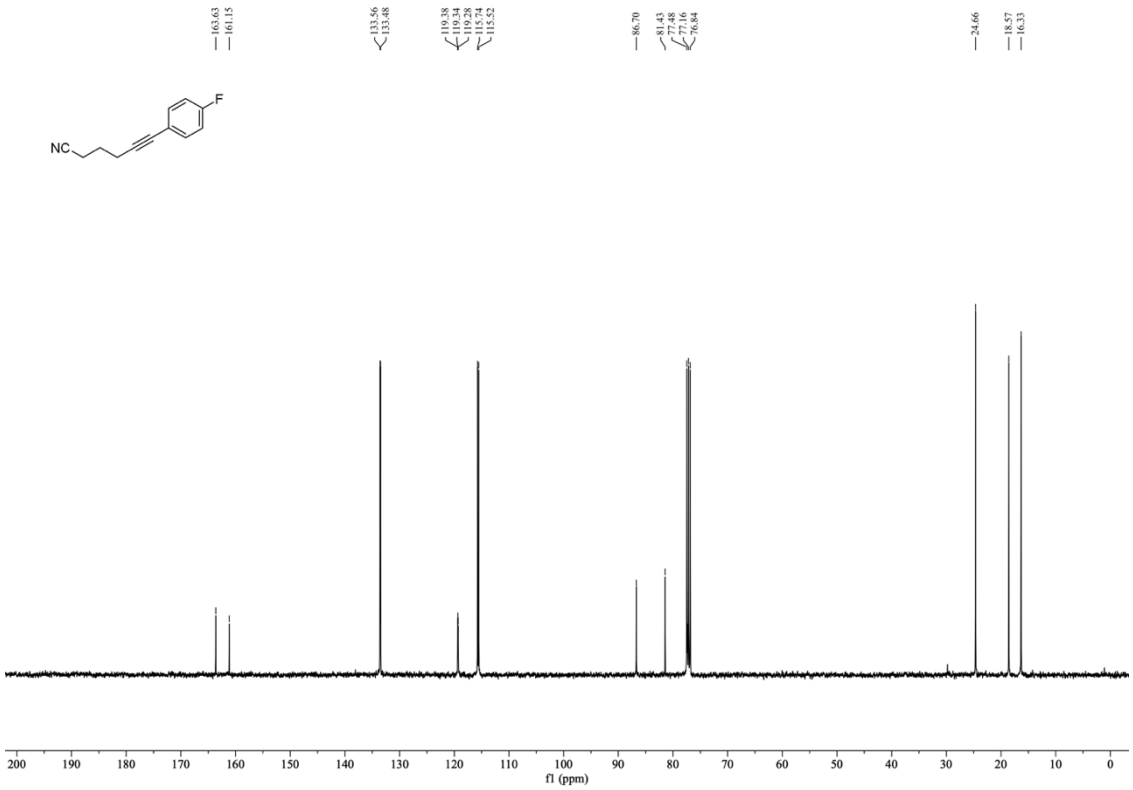
^{13}C NMR Spectrum of Compound 4i (101 MHz, $CDCl_3$)



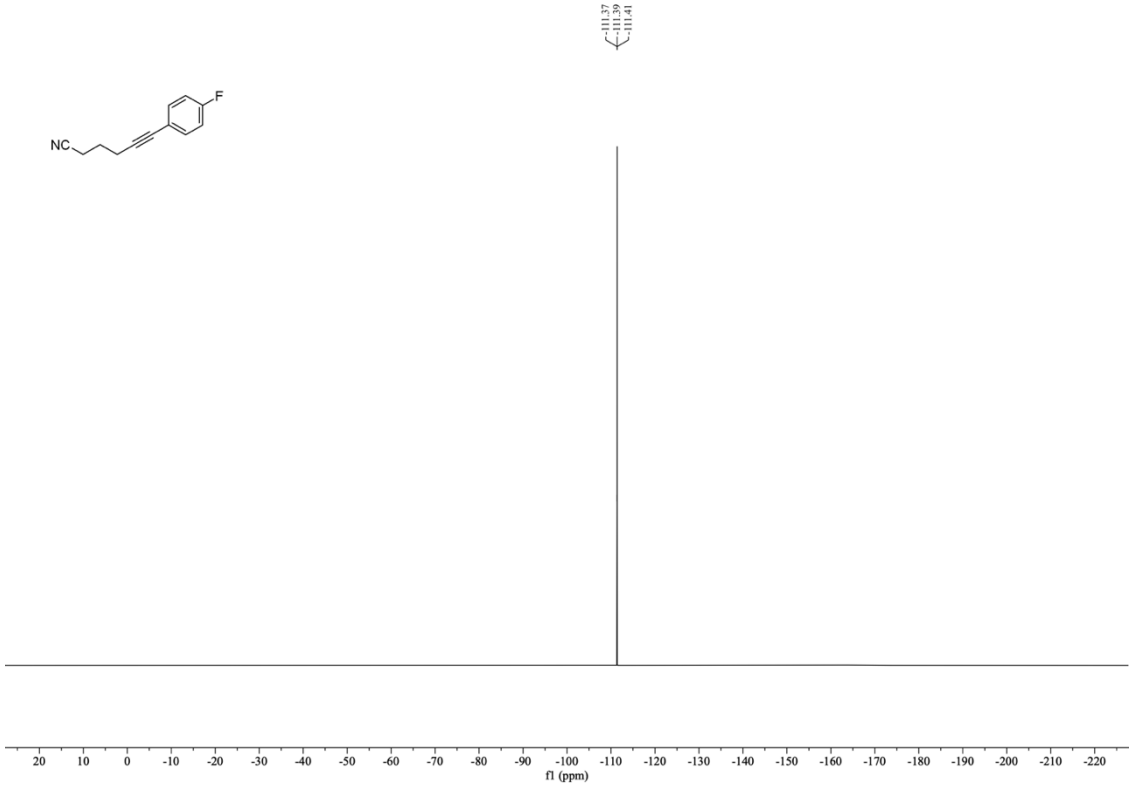
^{19}F NMR Spectrum of Compound 4i (376 MHz, $CDCl_3$)



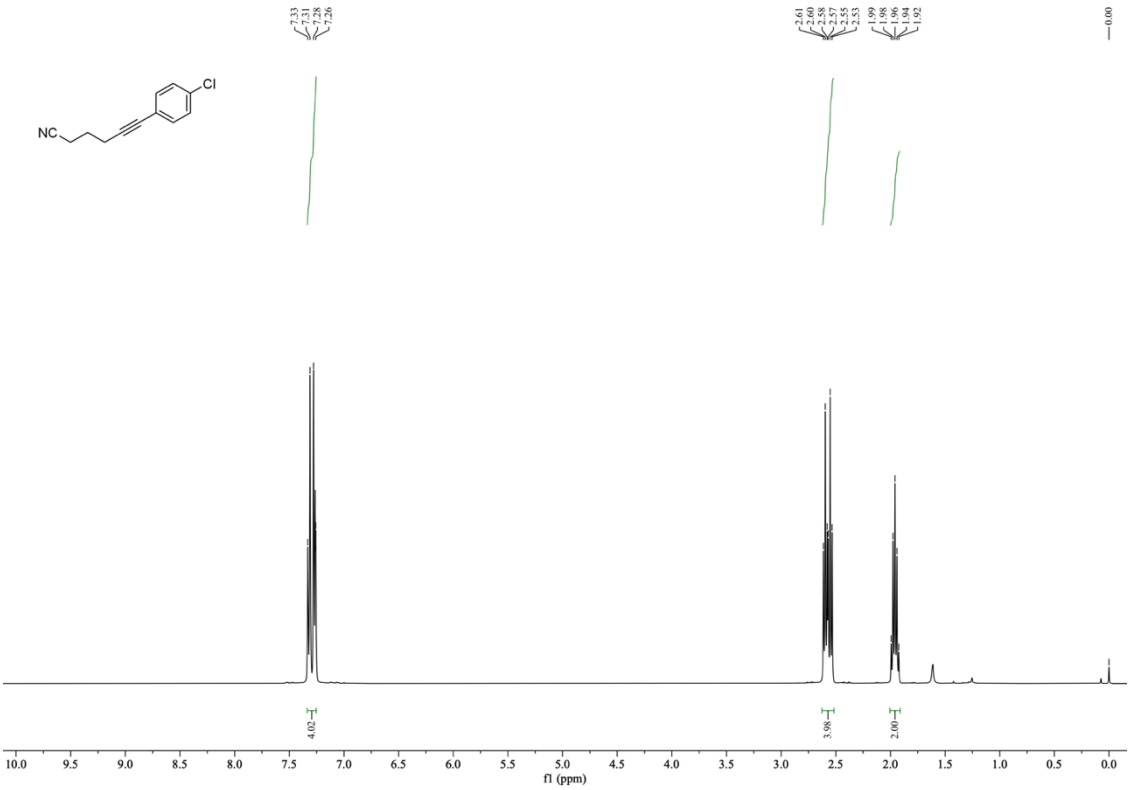
^{1}H NMR Spectrum of Compound 4j (400 MHz, $CDCl_3$)



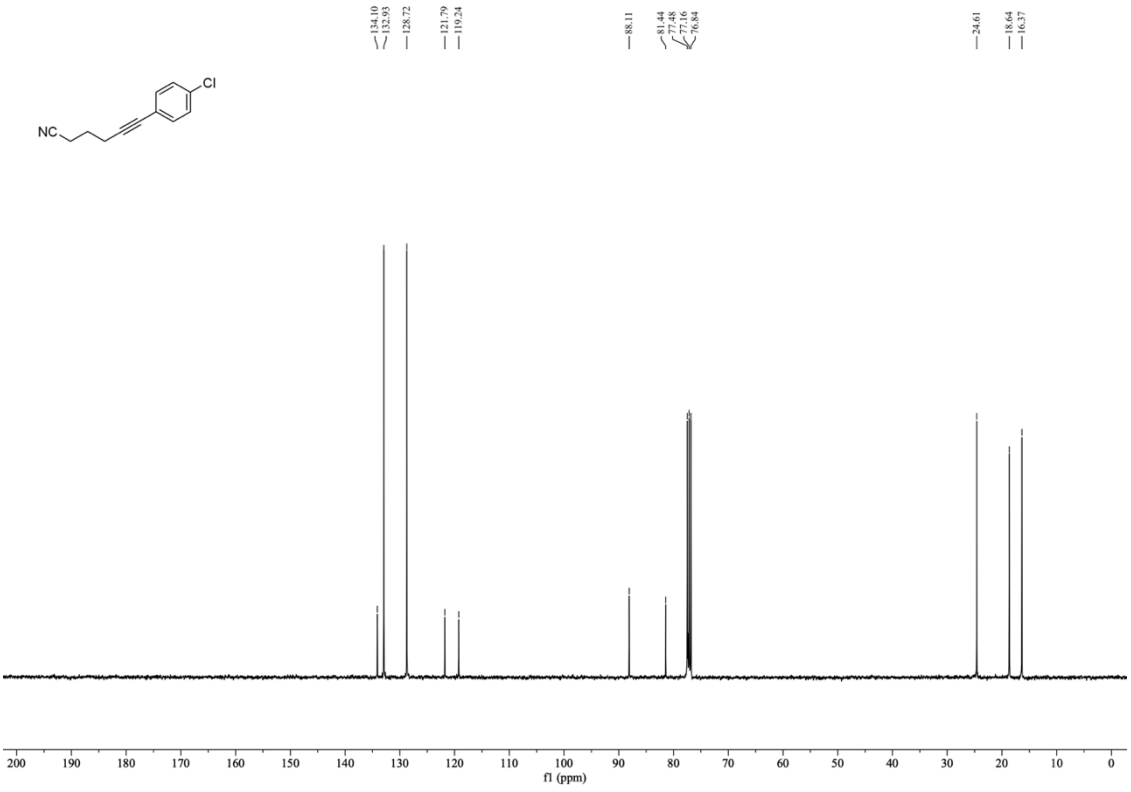
^{13}C NMR Spectrum of Compound 4j (101 MHz, $CDCl_3$)



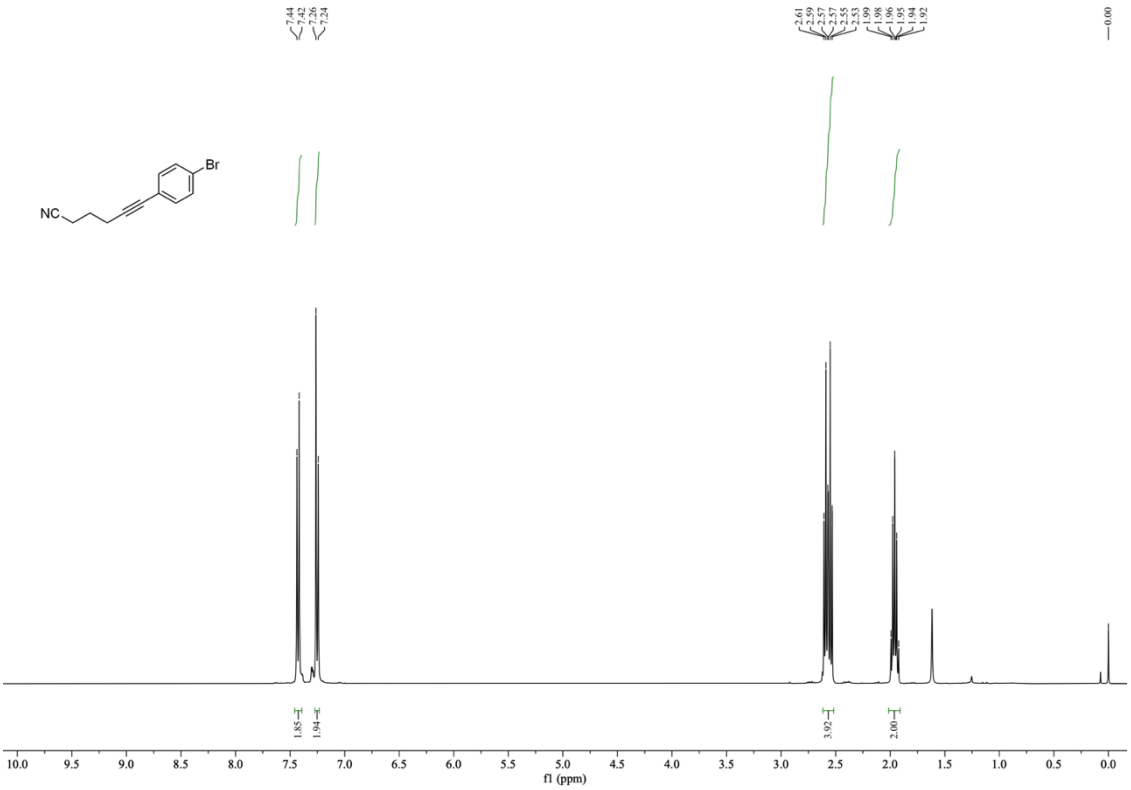
^{19}F NMR Spectrum of Compound 4j (376 MHz, $CDCl_3$)



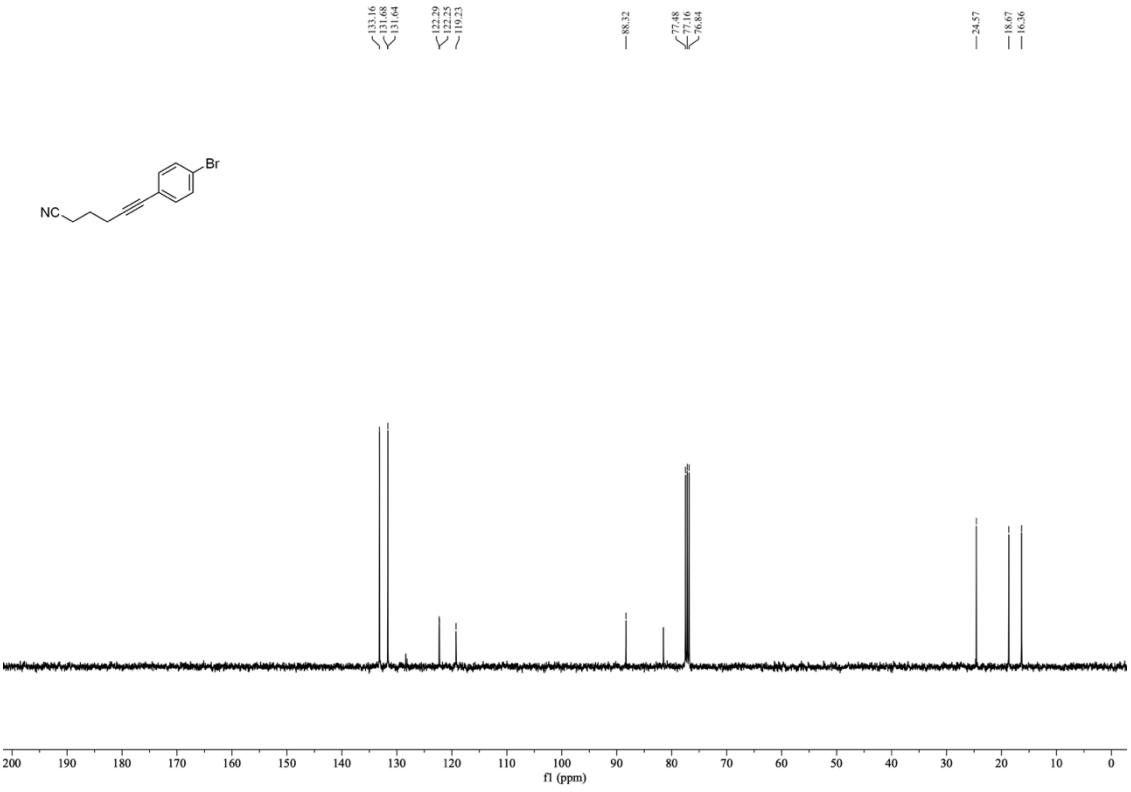
^{1}H NMR Spectrum of Compound 4k (400 MHz, $CDCl_3$)



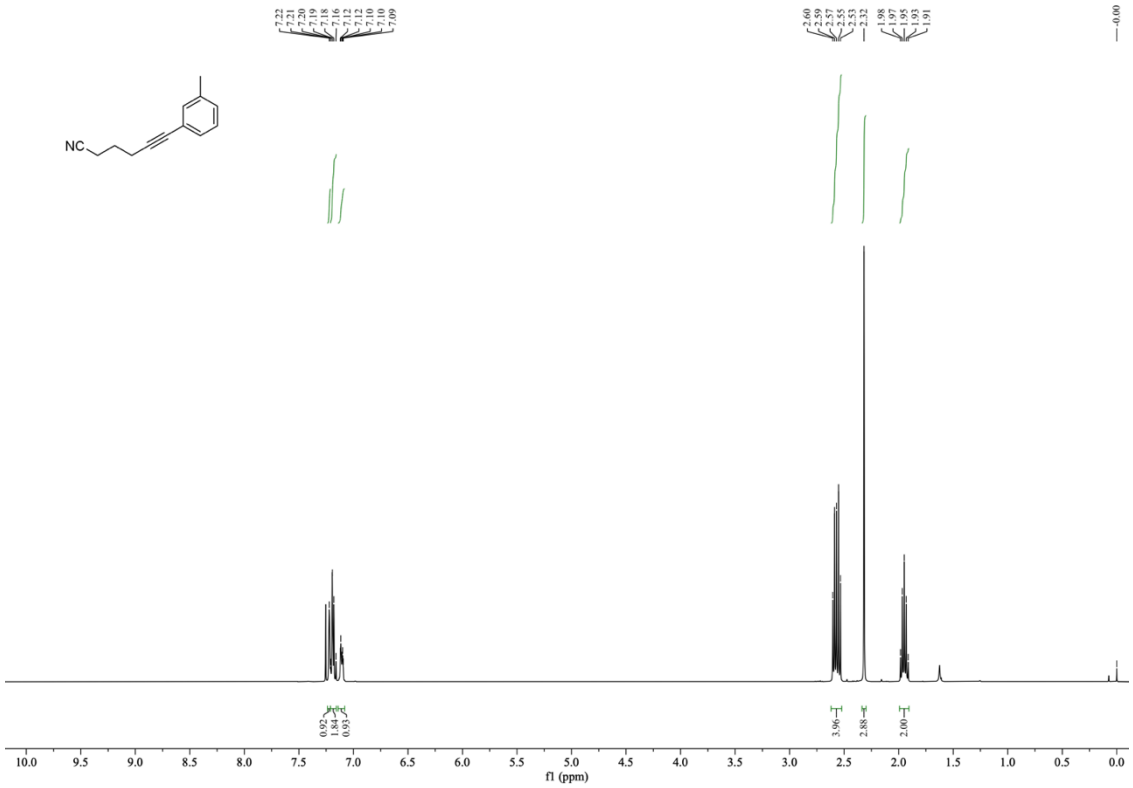
^{13}C NMR Spectrum of Compound 4k (101 MHz, $CDCl_3$)



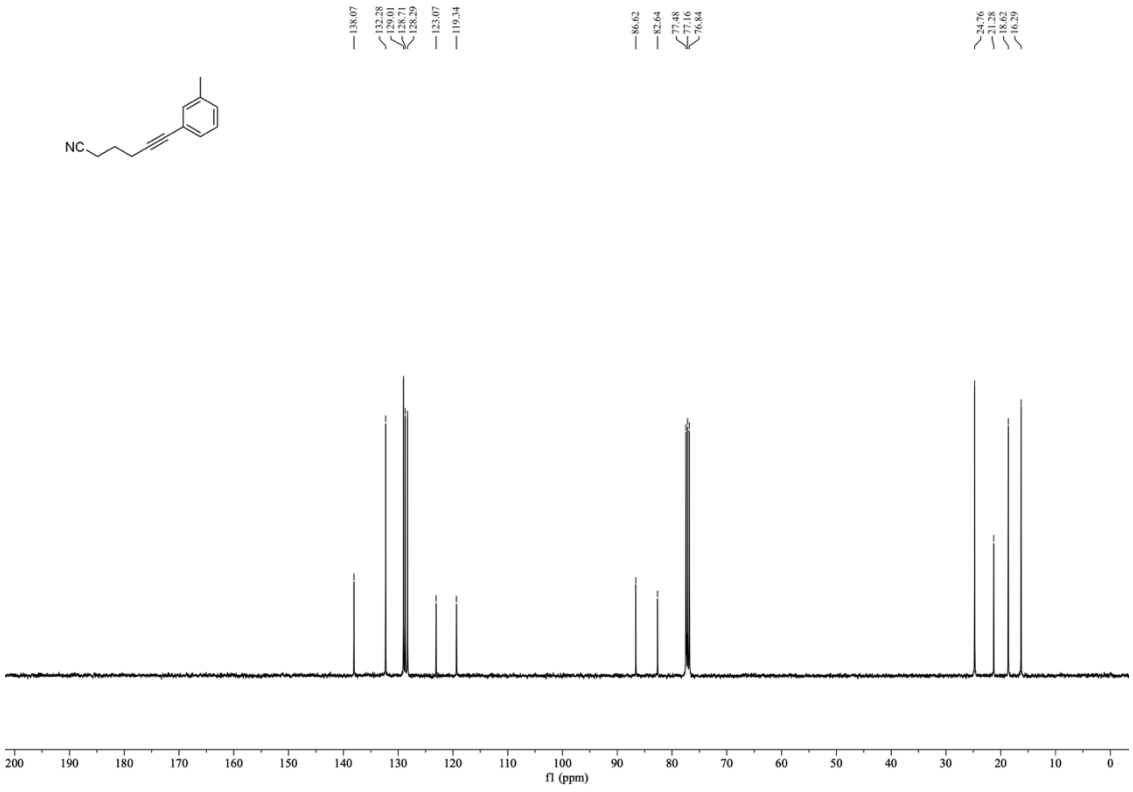
^{1}H NMR Spectrum of Compound 4l (400 MHz, $CDCl_3$)



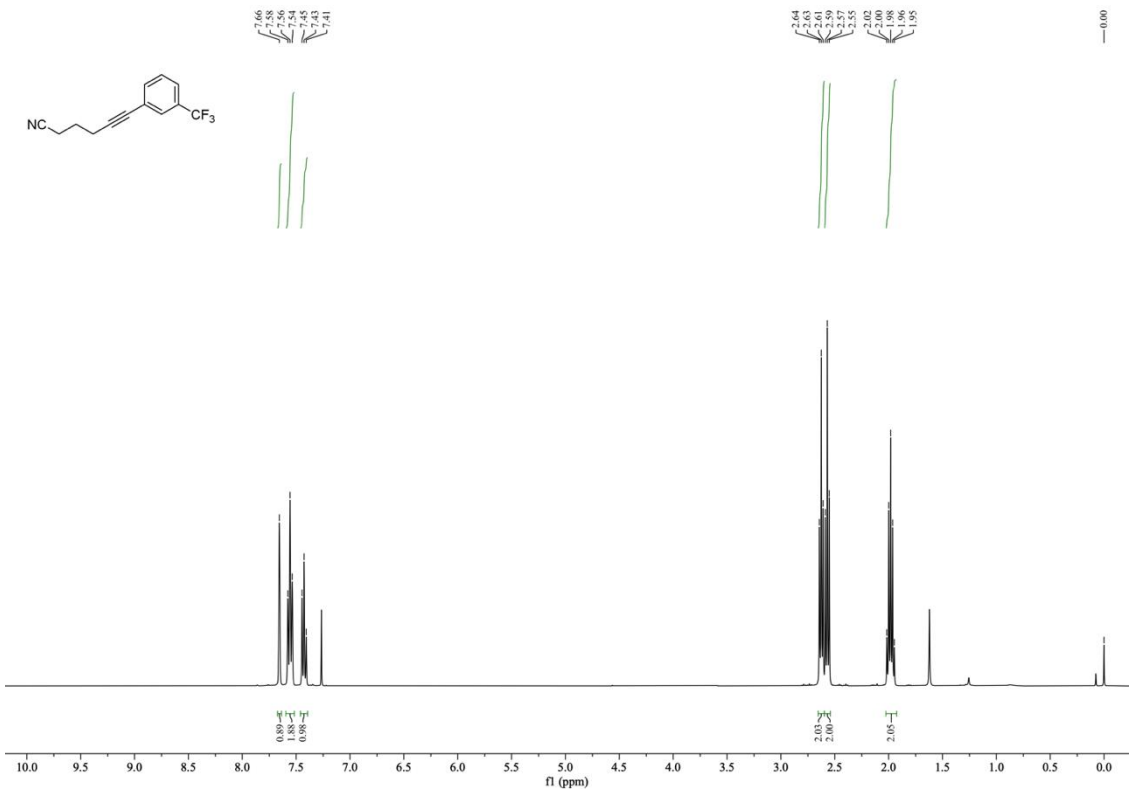
^{13}C NMR Spectrum of Compound 4l (101 MHz, $CDCl_3$)



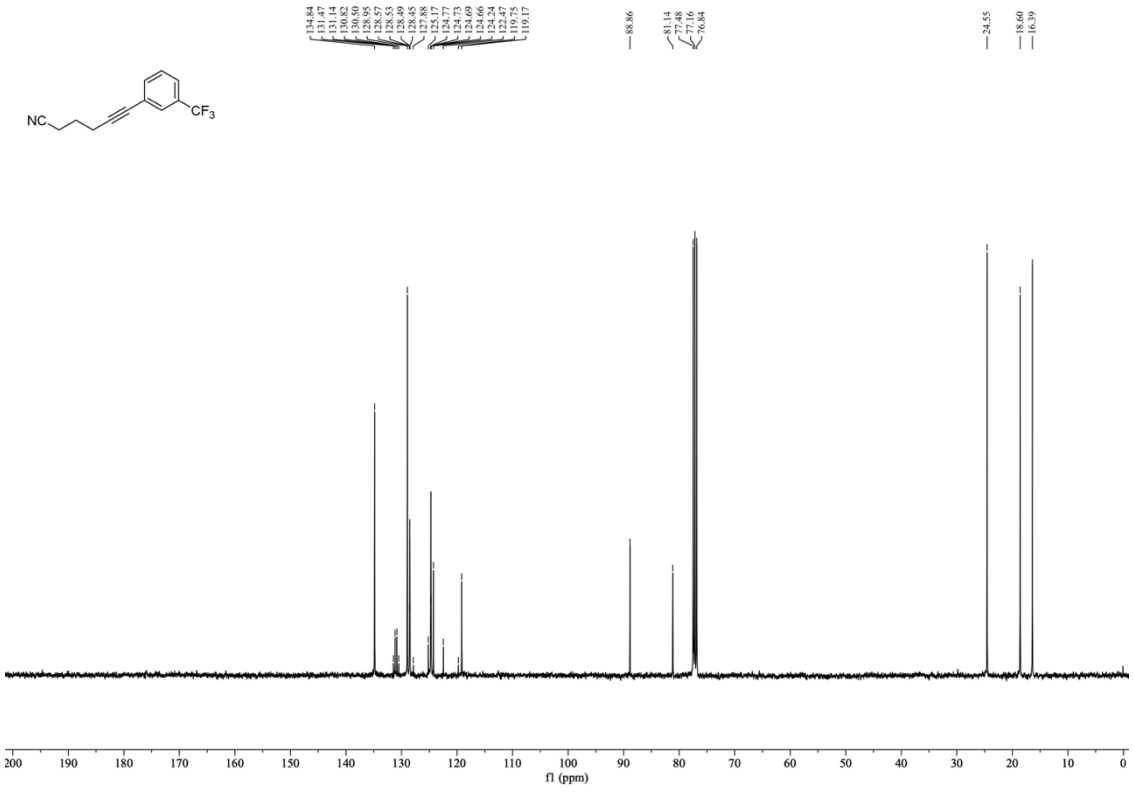
^{1}H NMR Spectrum of Compound 4m (400 MHz, $CDCl_3$)



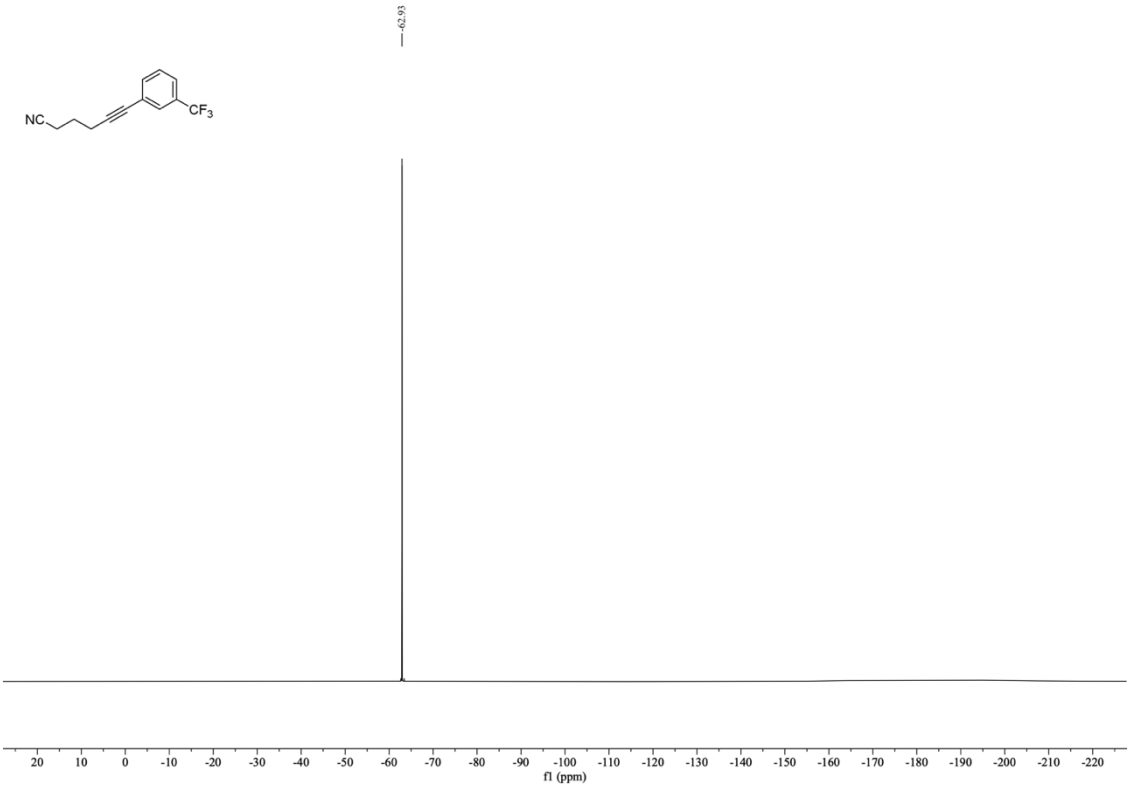
^{13}C NMR Spectrum of Compound 4m (101 MHz, $CDCl_3$)



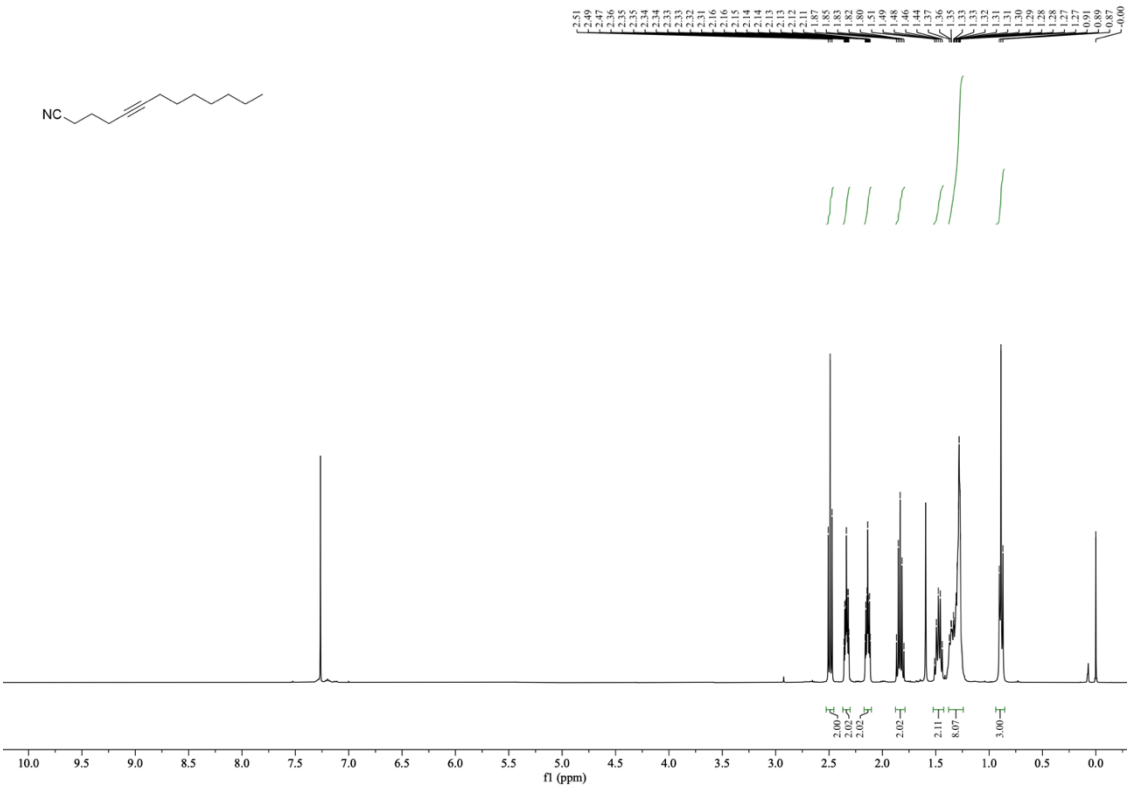
^{1}H NMR Spectrum of Compound 4n (400 MHz, $CDCl_3$)



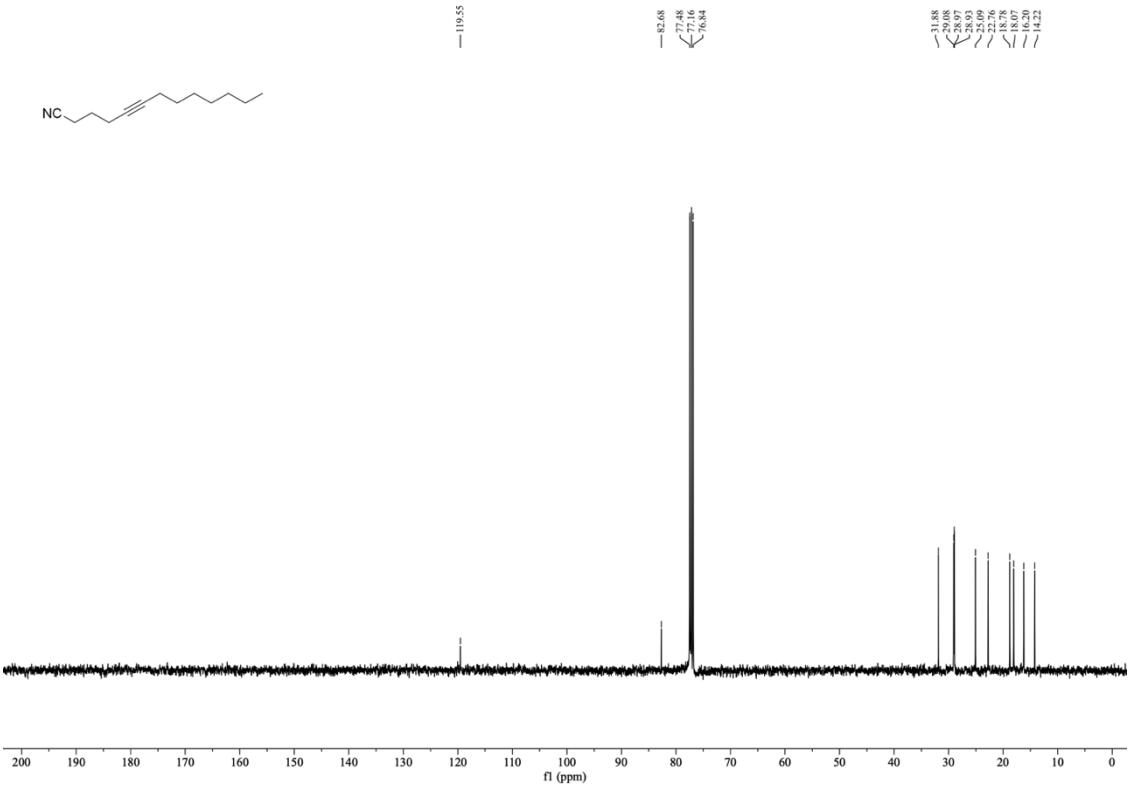
^{13}C NMR Spectrum of Compound 4n (101 MHz, $CDCl_3$)



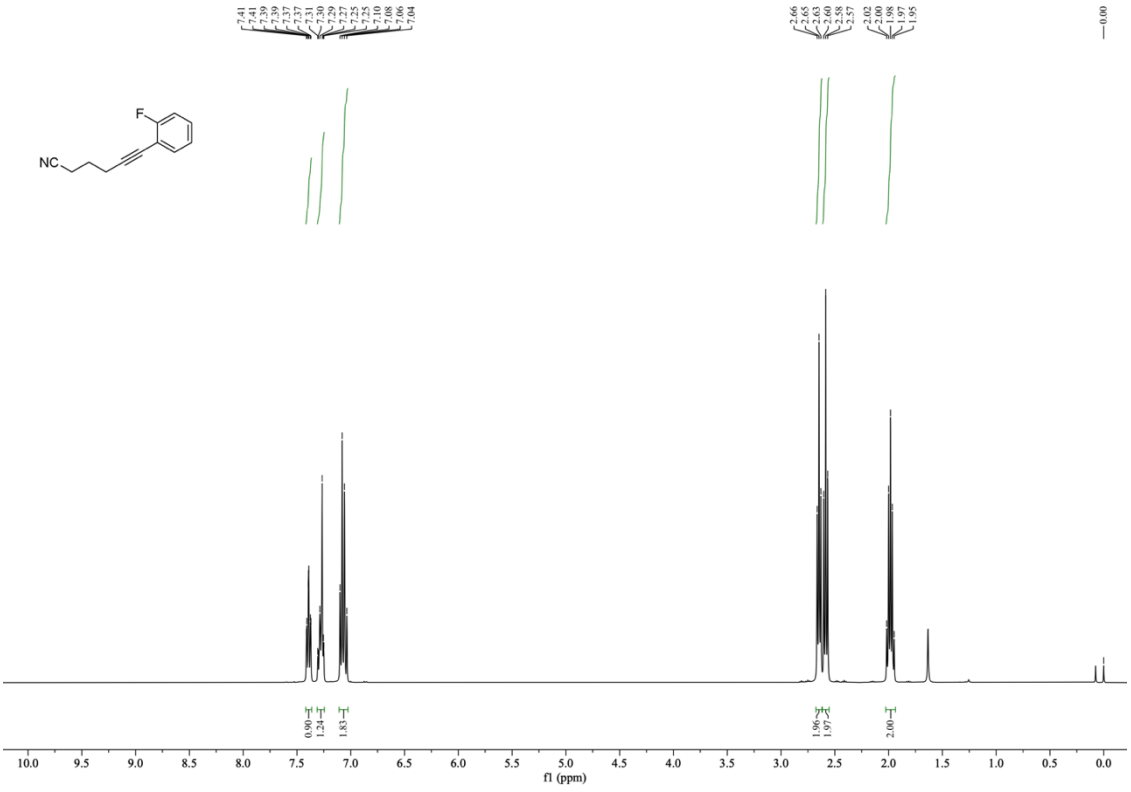
^{19}F NMR Spectrum of Compound 4n (376 MHz, $CDCl_3$)



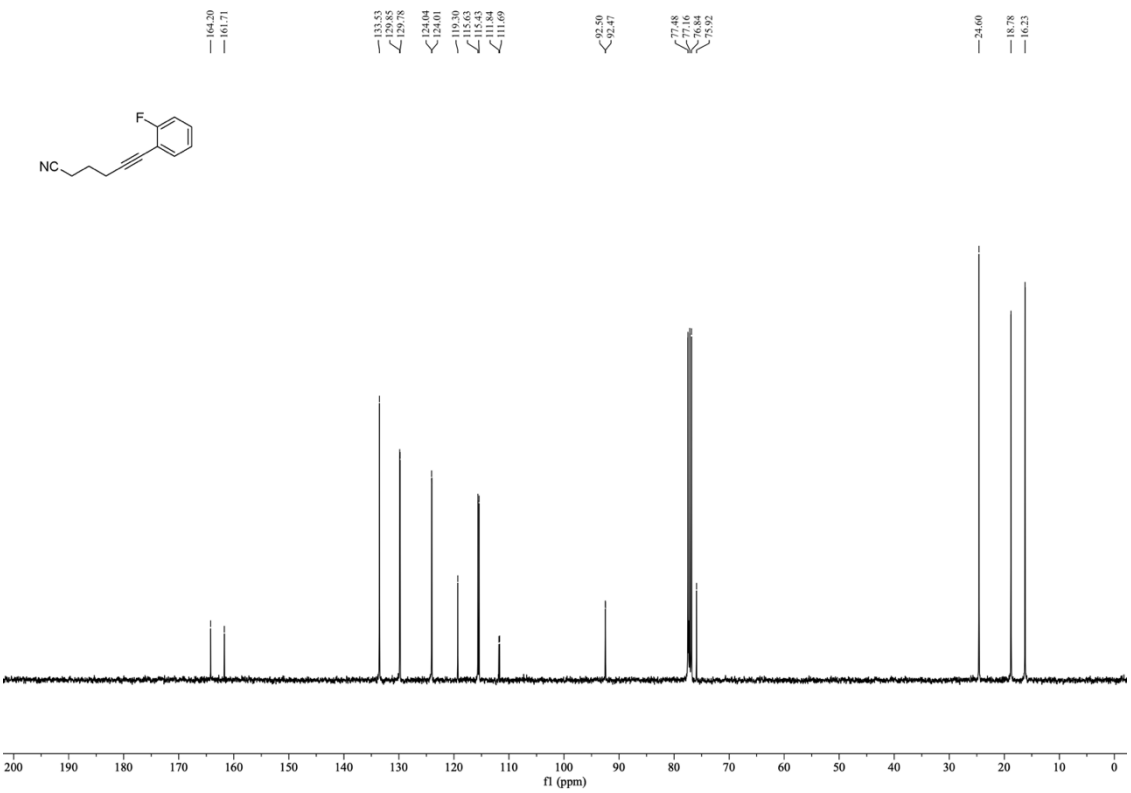
^{1}H NMR Spectrum of Compound 4o (400 MHz, $CDCl_3$)



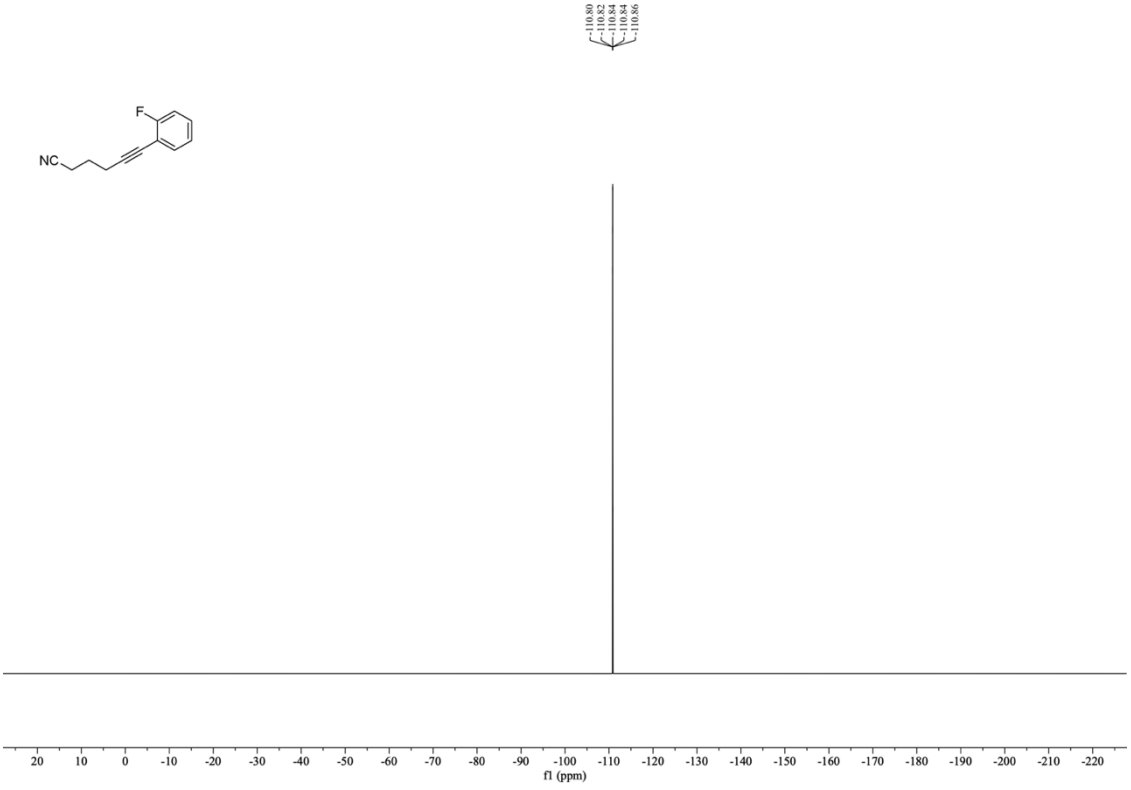
^{13}C NMR Spectrum of Compound 4o (101 MHz, $CDCl_3$)



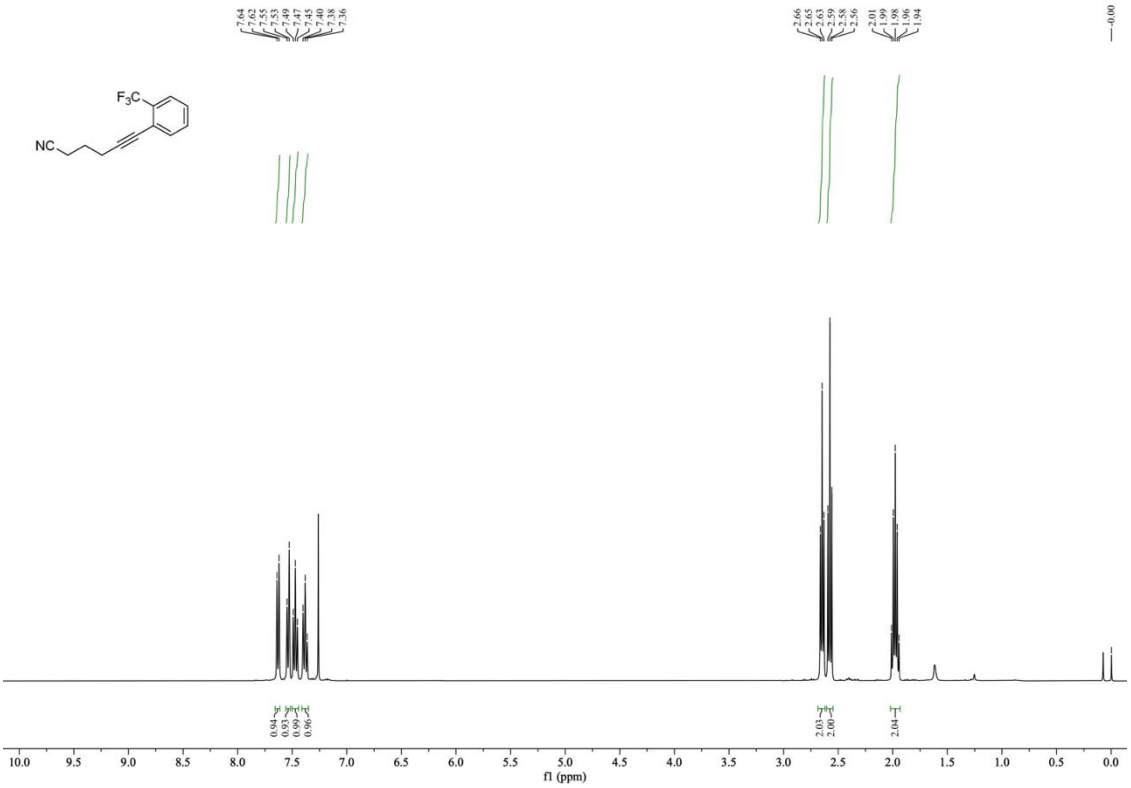
^{1}H NMR Spectrum of Compound 4p (400 MHz, $CDCl_3$)



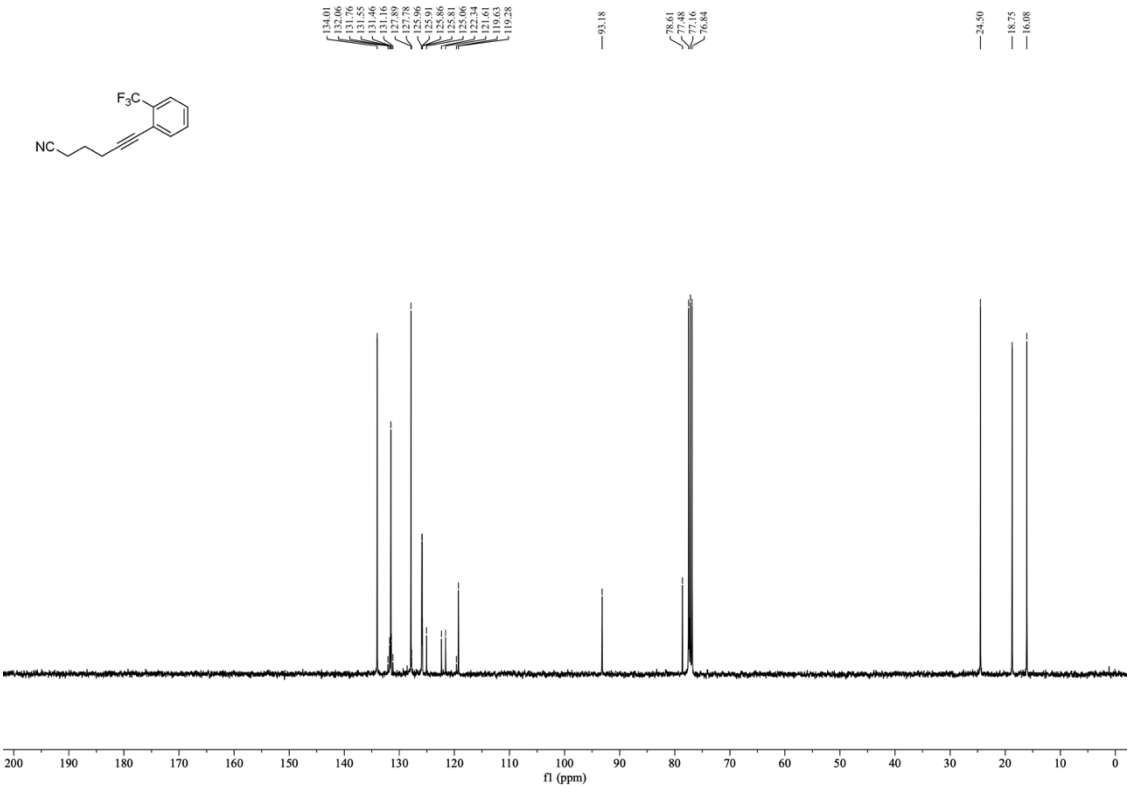
^{13}C NMR Spectrum of Compound 4p (101 MHz, $CDCl_3$)



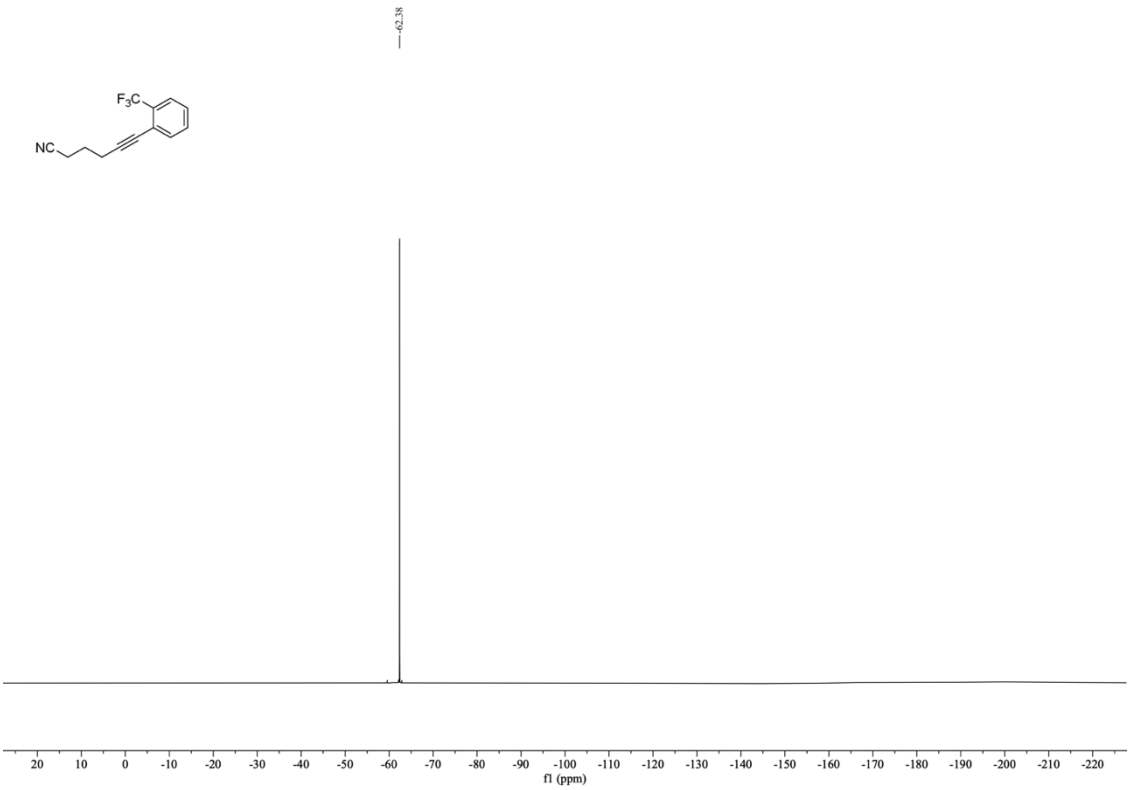
^{19}F NMR Spectrum of Compound 4p (376 MHz, $CDCl_3$)



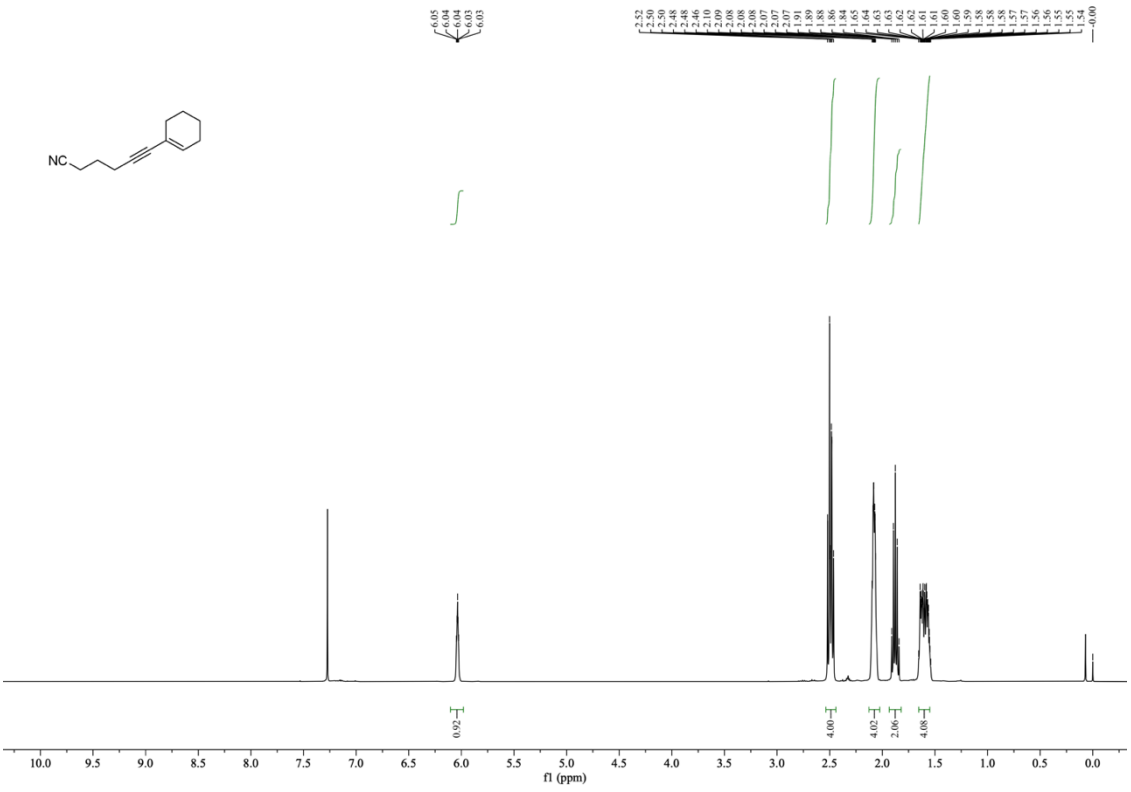
^{1}H NMR Spectrum of Compound 4q (400 MHz, $CDCl_3$)



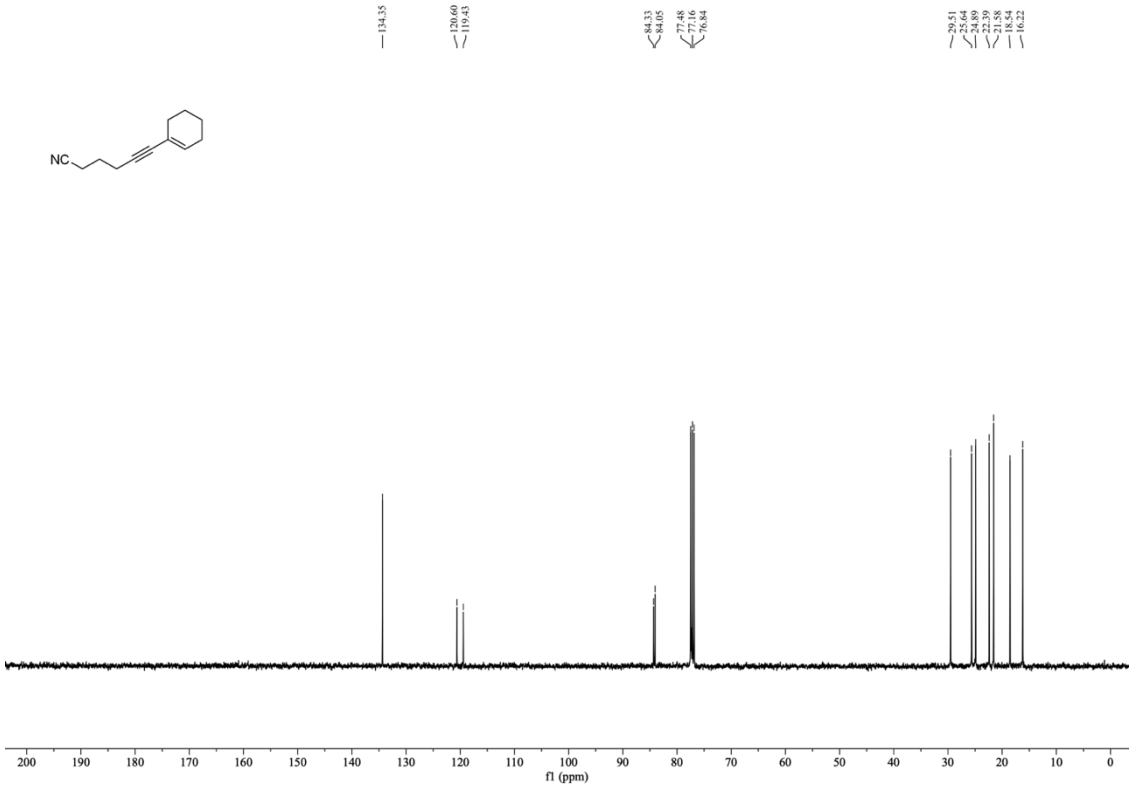
^{13}C NMR Spectrum of Compound 4q (101 MHz, $CDCl_3$)



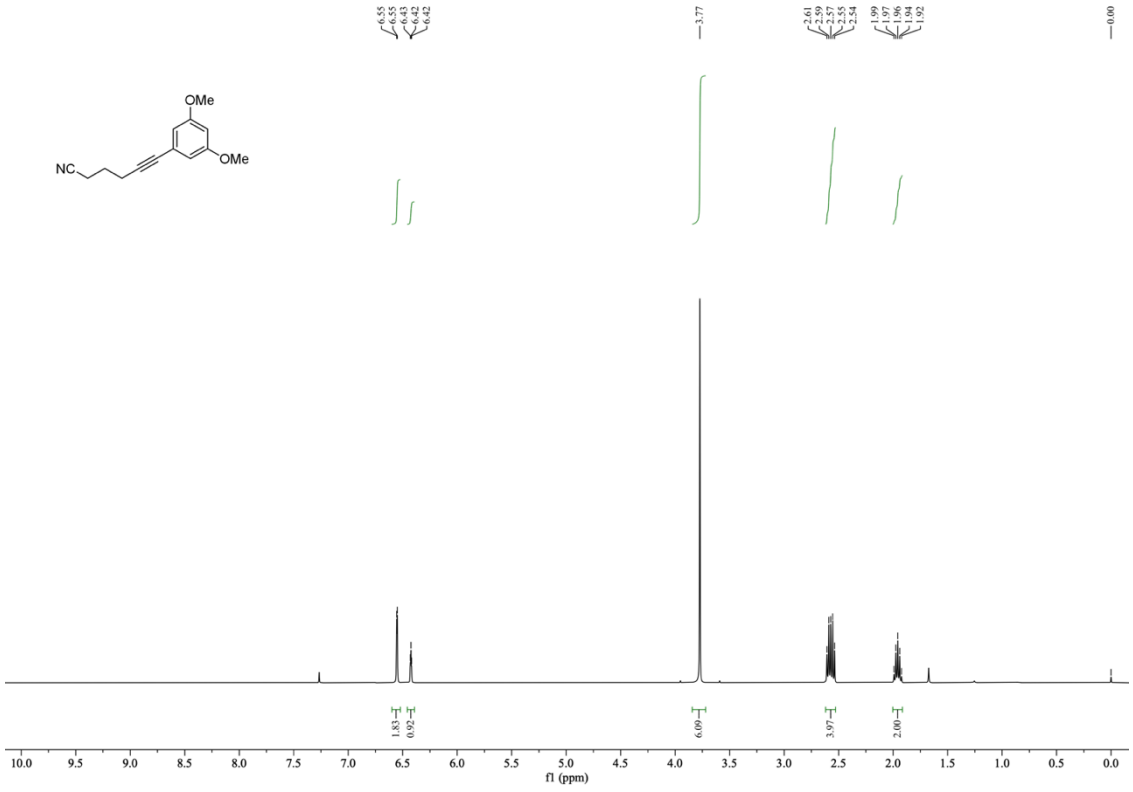
^{19}F NMR Spectrum of Compound 4q (376 MHz, $CDCl_3$)



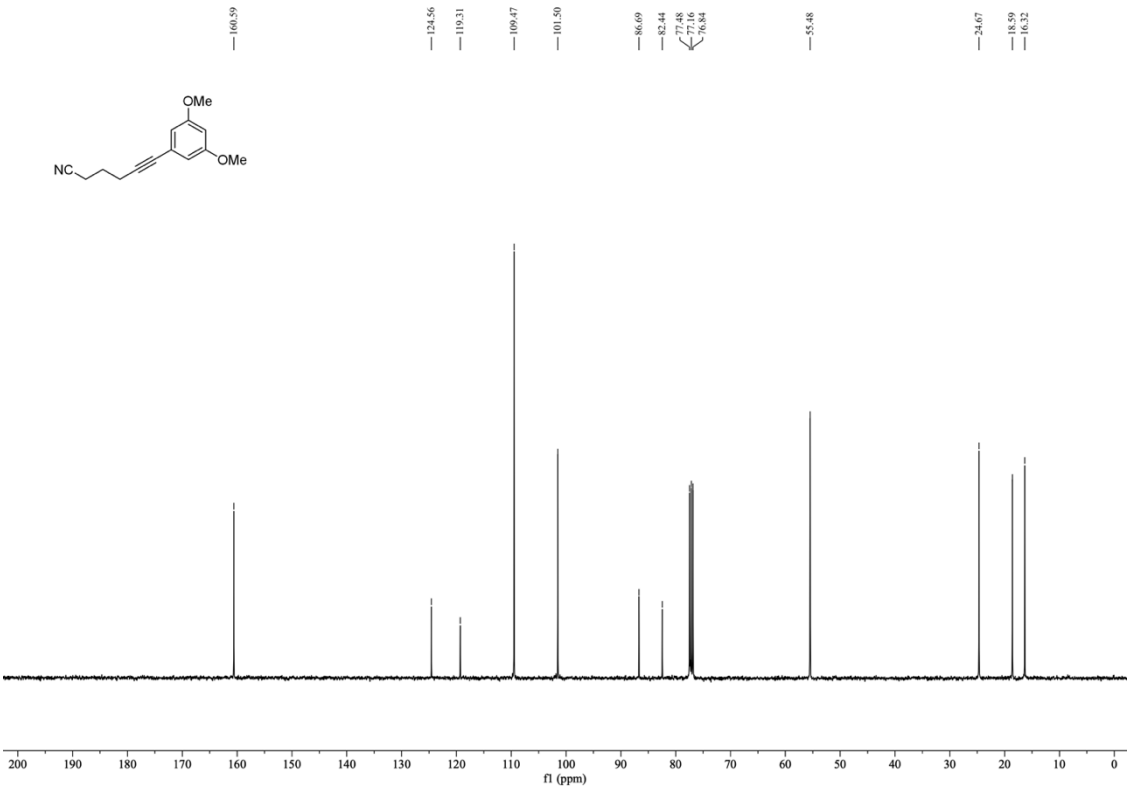
^{1}H NMR Spectrum of Compound 4r (400 MHz, $CDCl_3$)



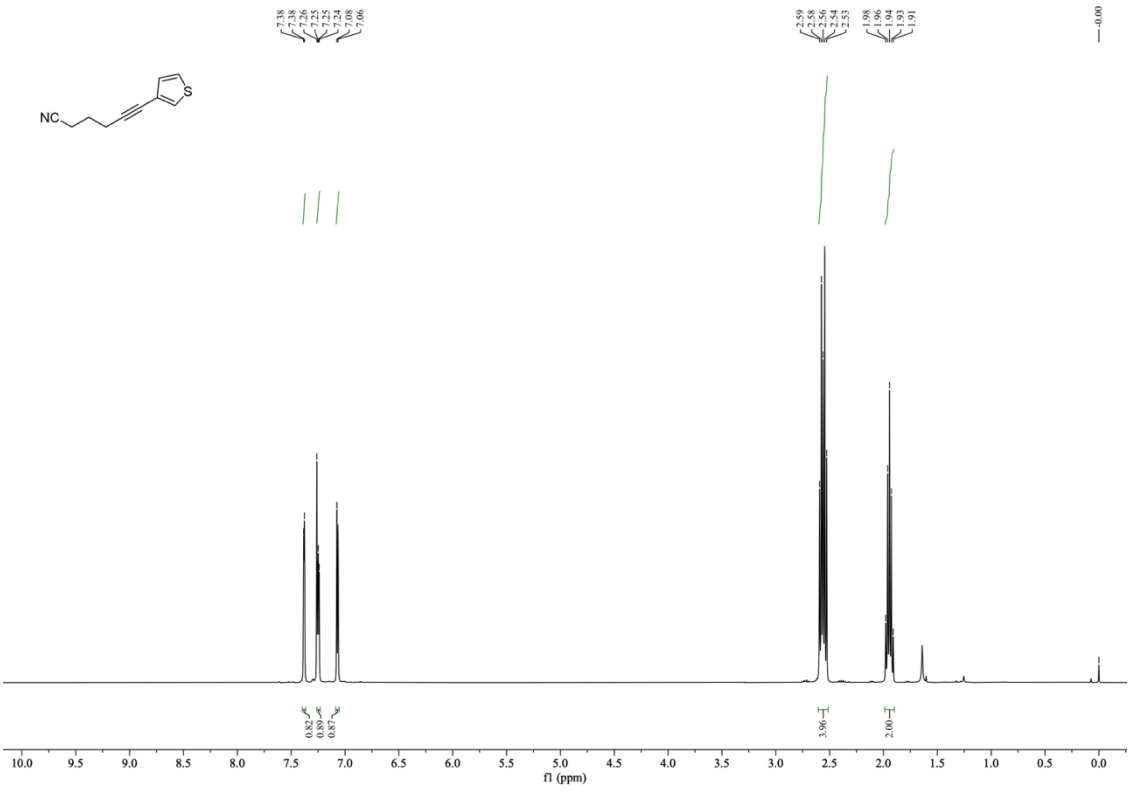
^{13}C NMR Spectrum of Compound 4r (101 MHz, $CDCl_3$)



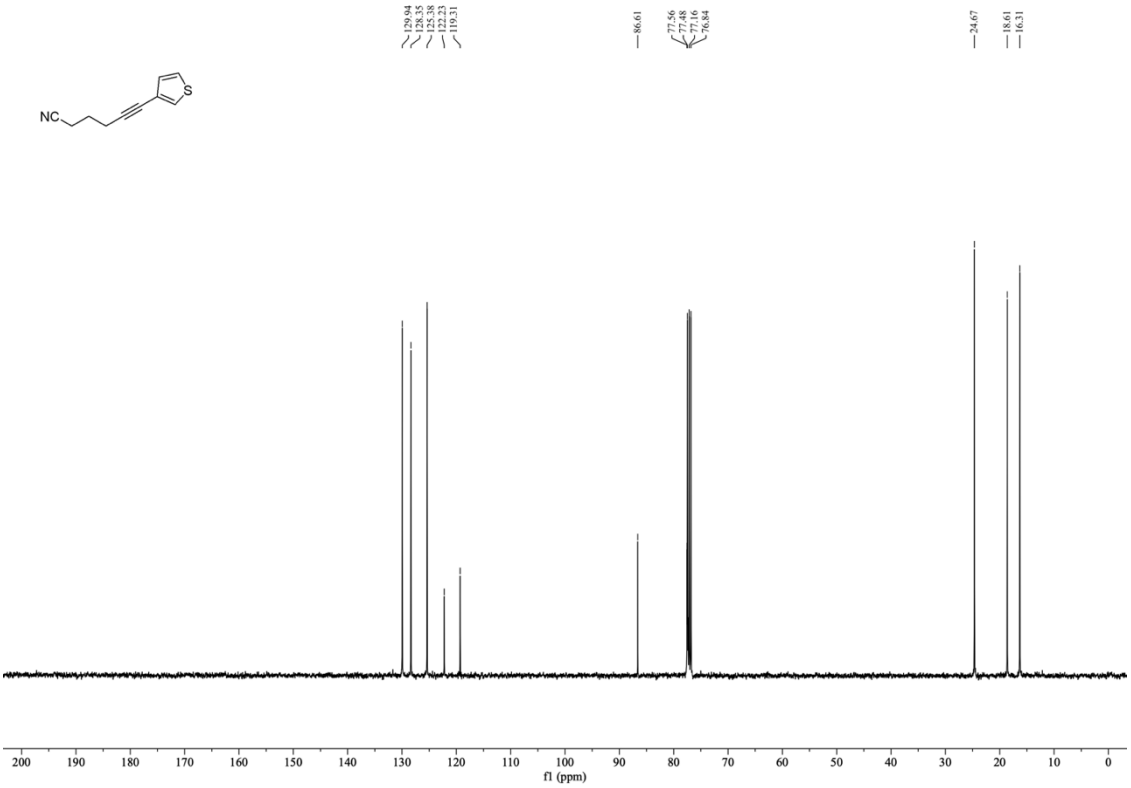
^{1}H NMR Spectrum of Compound 4s (400 MHz, $CDCl_3$)



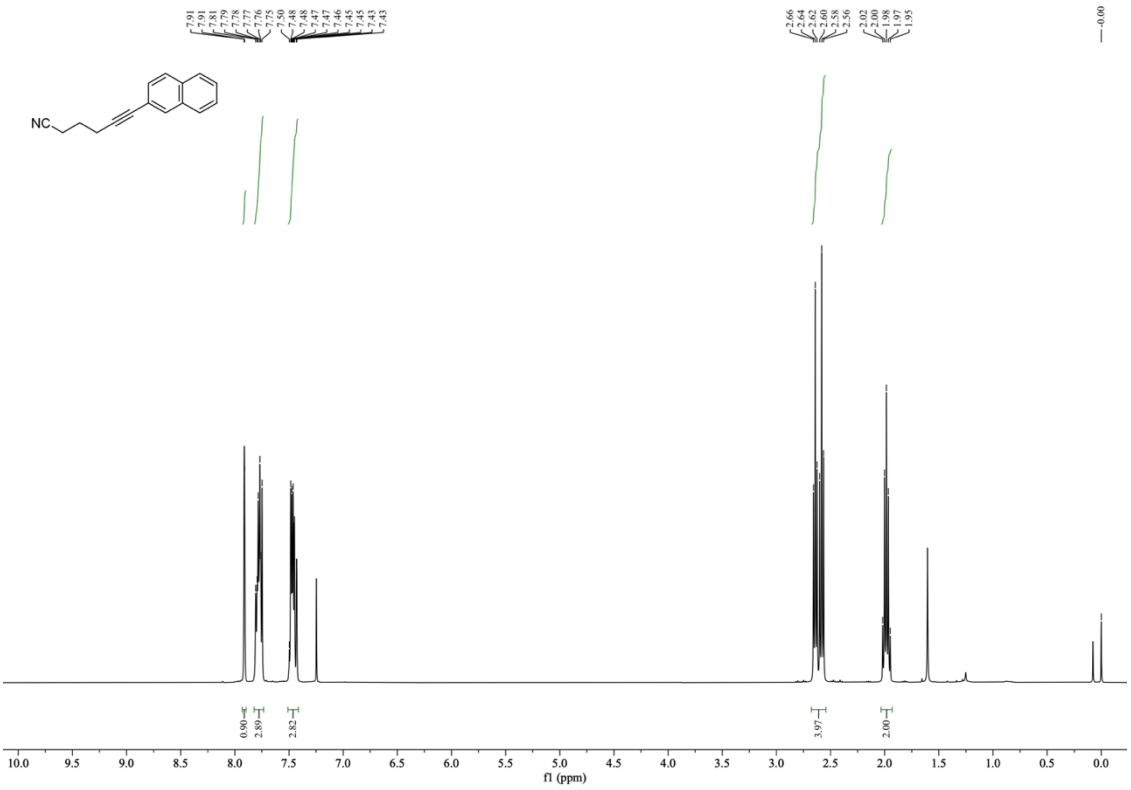
^{13}C NMR Spectrum of Compound 4s (101 MHz, $CDCl_3$)



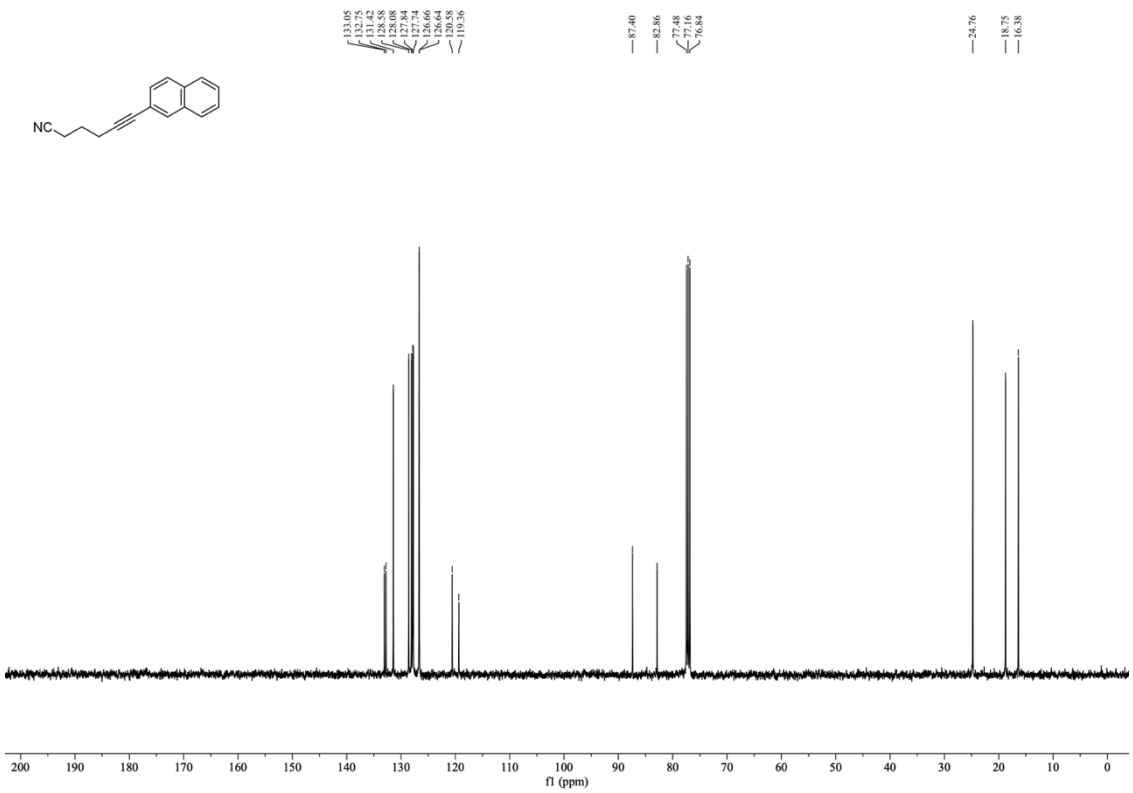
^{1}H NMR Spectrum of Compound 4t (400 MHz, $CDCl_3$)



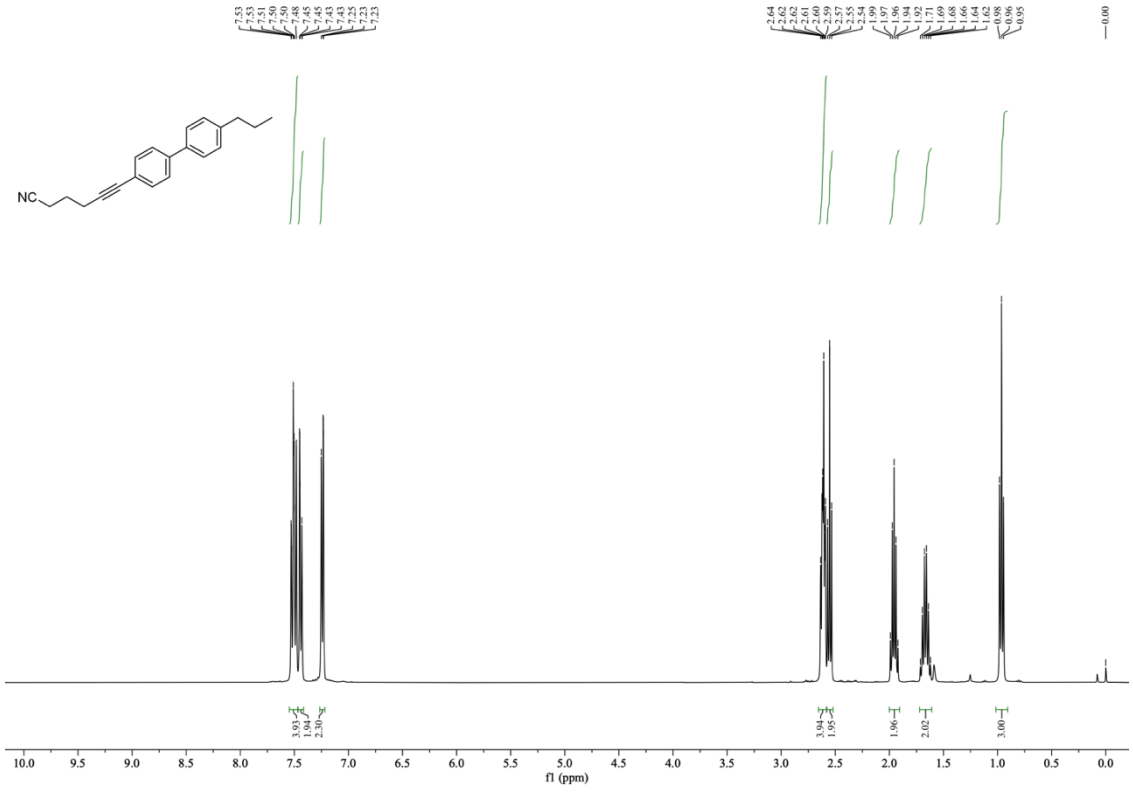
^{13}C NMR Spectrum of Compound 4t (101 MHz, $CDCl_3$)



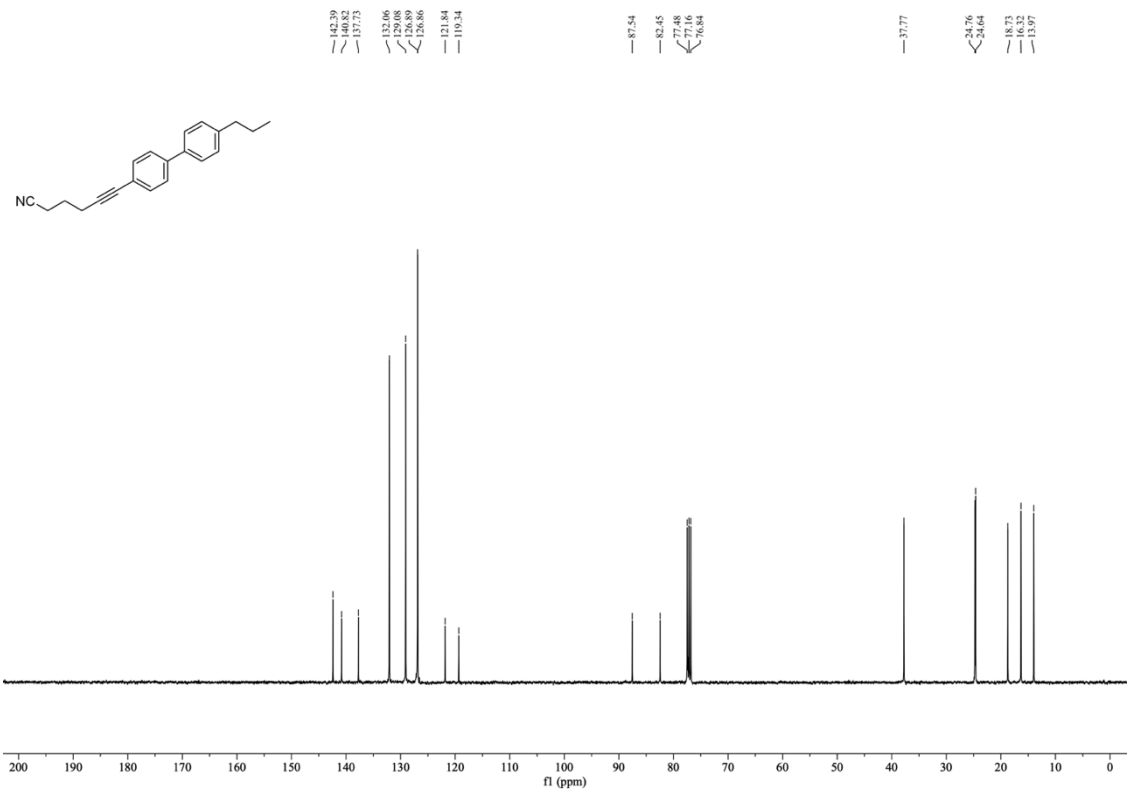
^{1}H NMR Spectrum of Compound 4u (400 MHz, $CDCl_3$)



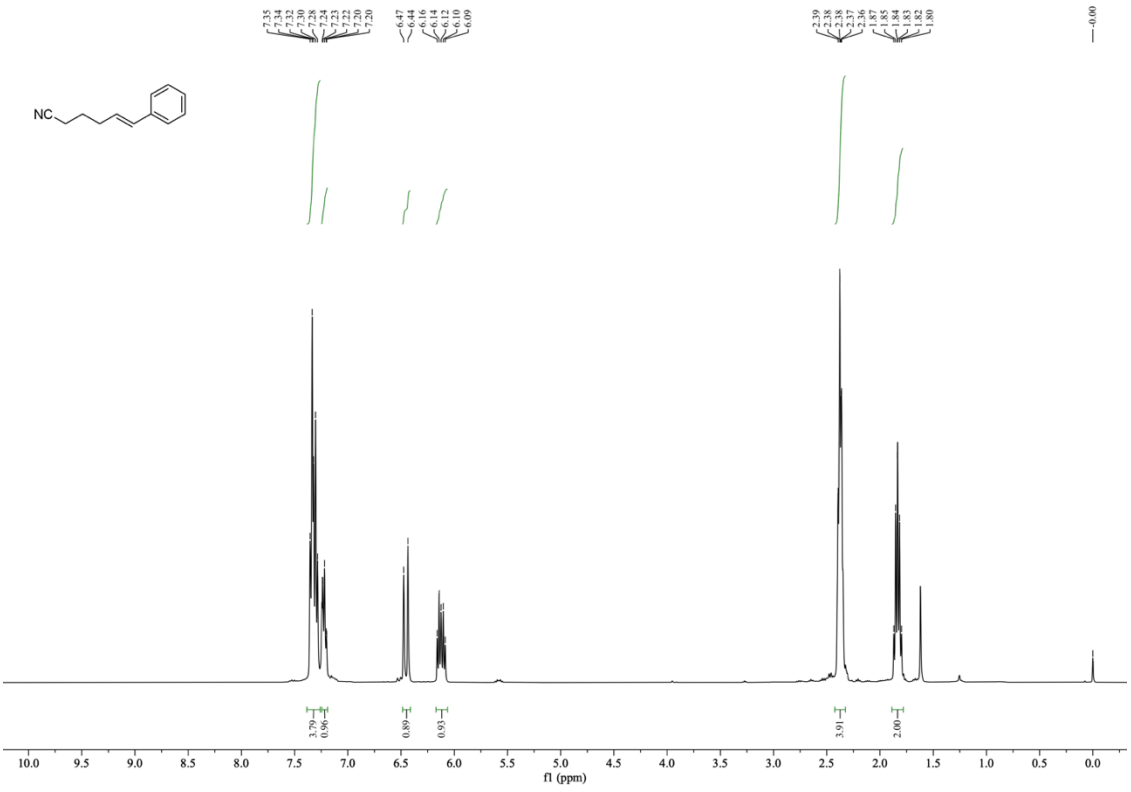
^{13}C NMR Spectrum of Compound 4u (101 MHz, $CDCl_3$)



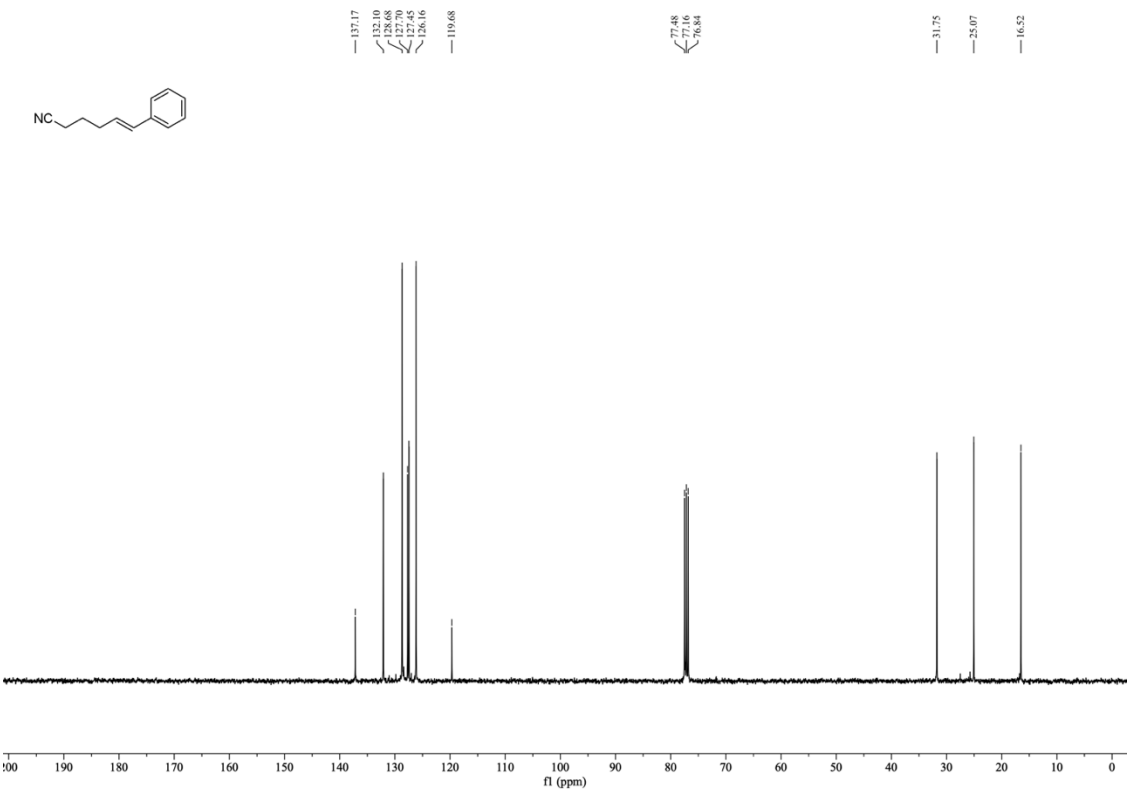
^{1}H NMR Spectrum of Compound 4v (400 MHz, $CDCl_3$)



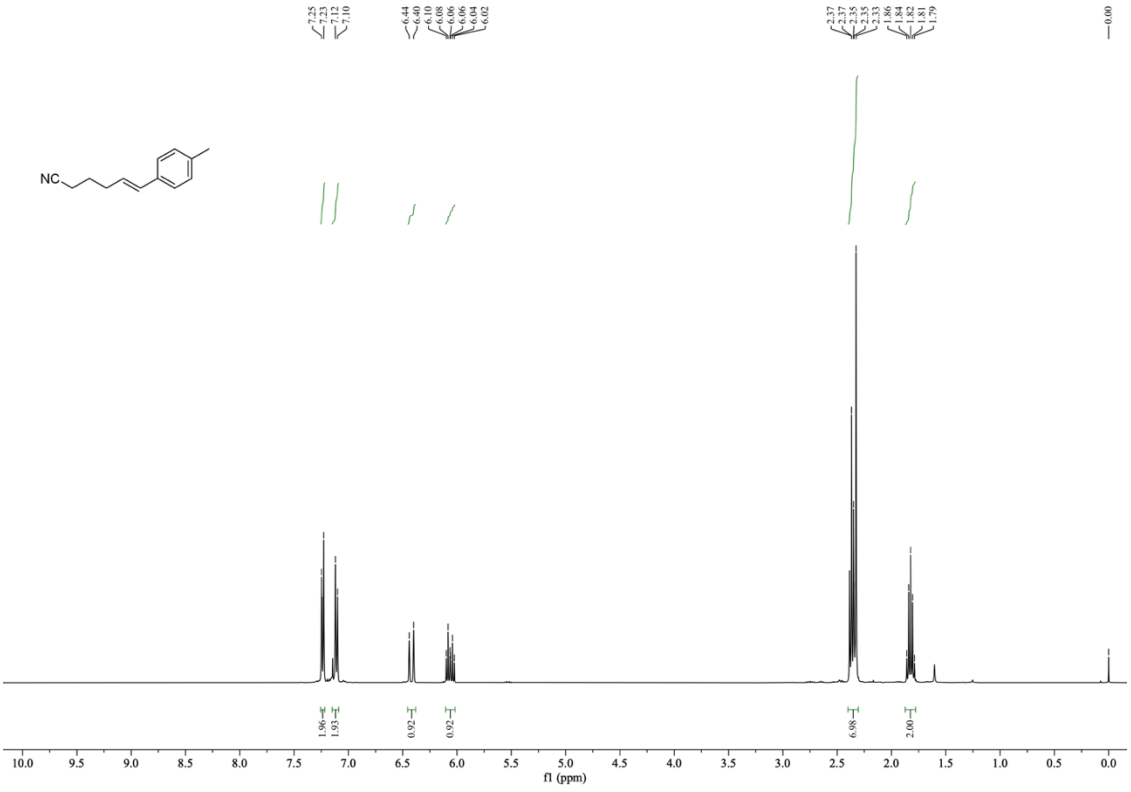
^{13}C NMR Spectrum of Compound 4v (101 MHz, $CDCl_3$)



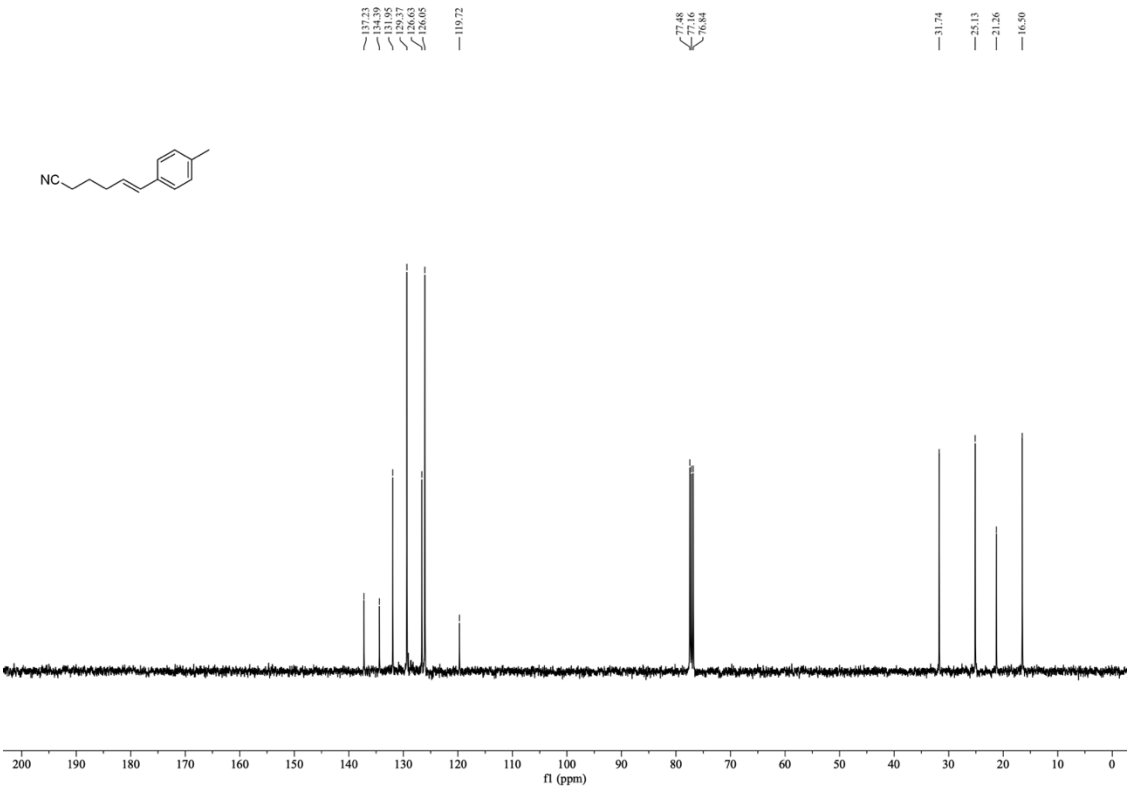
^{1}H NMR Spectrum of Compound 6a (400 MHz, $CDCl_3$)



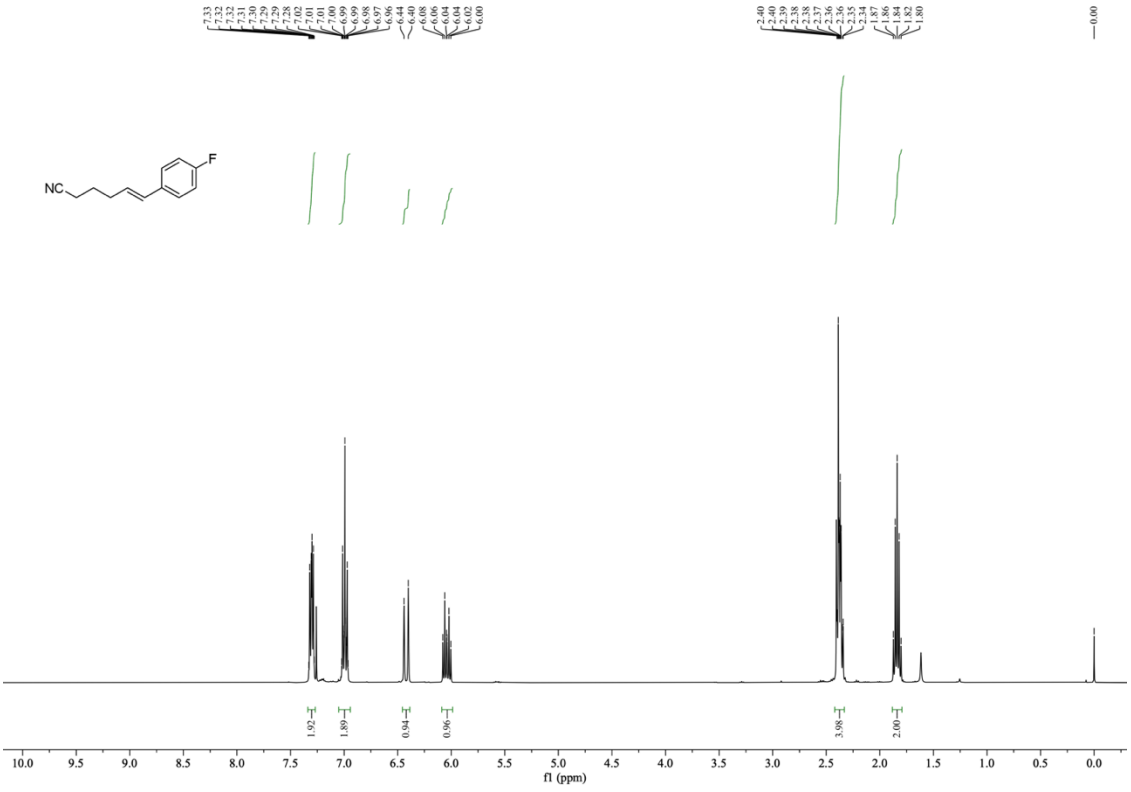
^{13}C NMR Spectrum of Compound 6a (101 MHz, $CDCl_3$)



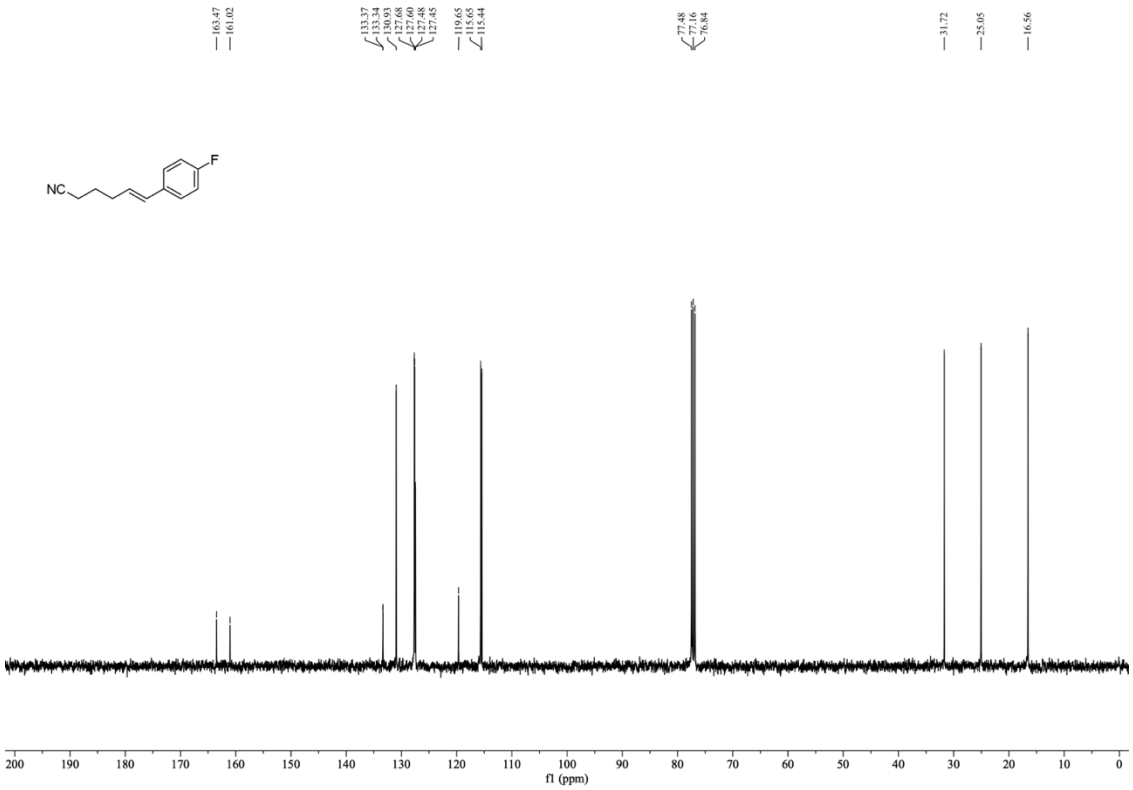
^{1}H NMR Spectrum of Compound 6b (400 MHz, $CDCl_3$)



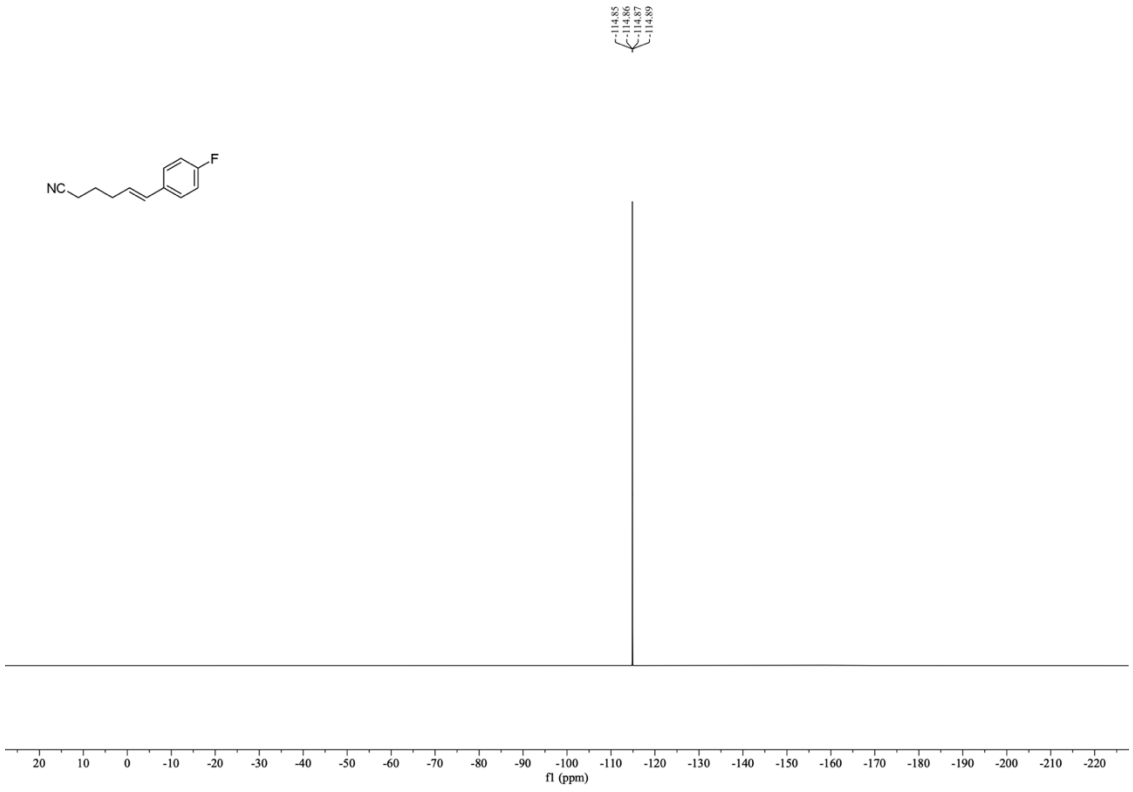
^{13}C NMR Spectrum of Compound 6b (101 MHz, $CDCl_3$)



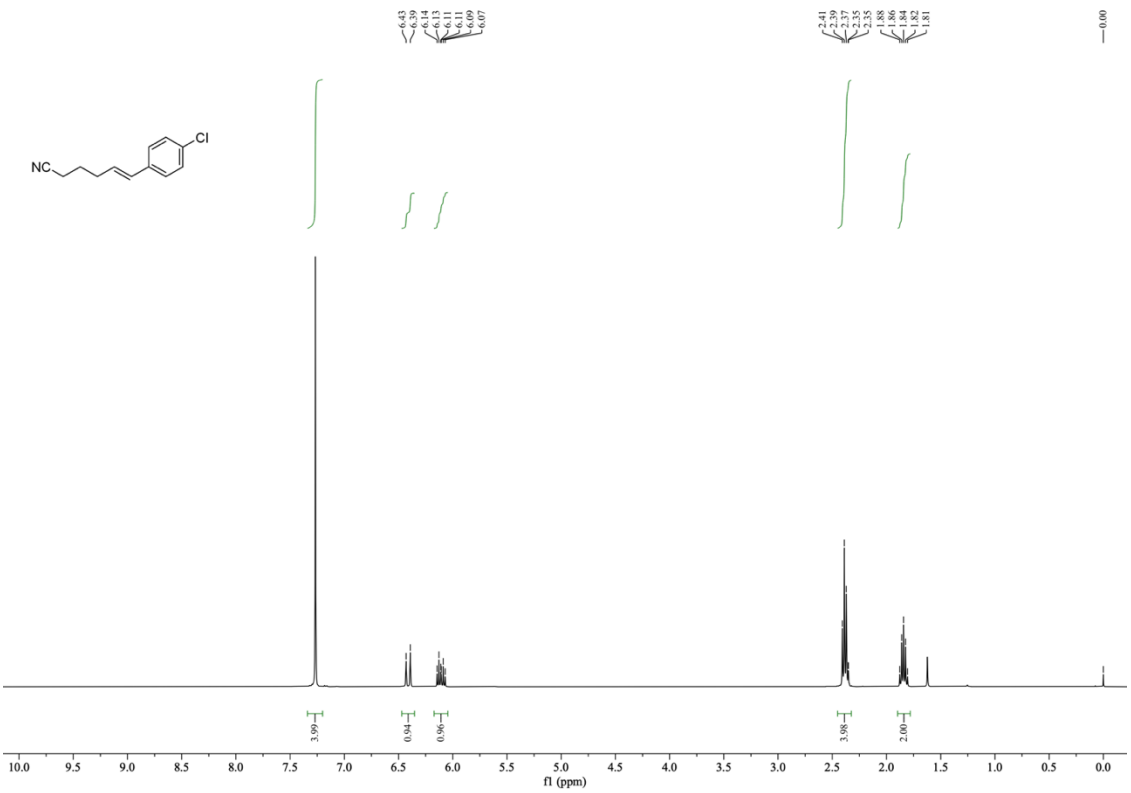
^{1}H NMR Spectrum of Compound 6c (400 MHz, $CDCl_3$)



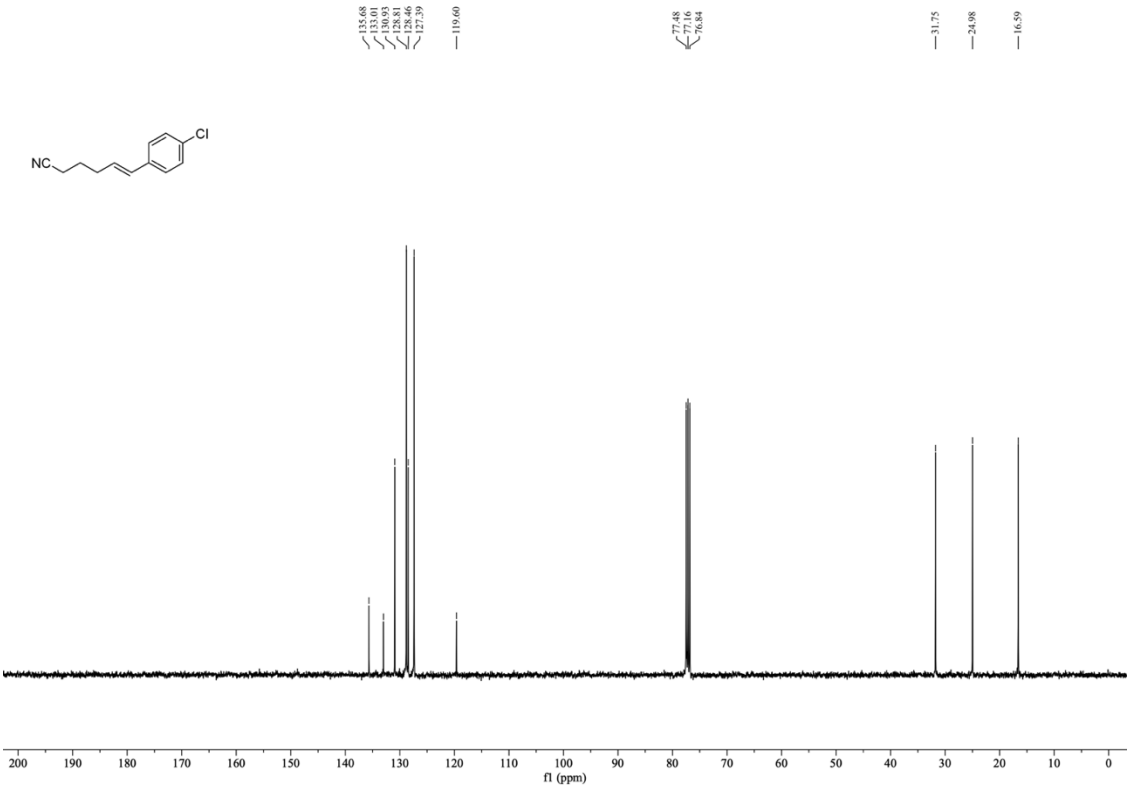
^{13}C NMR Spectrum of Compound 6c (101 MHz, $CDCl_3$)



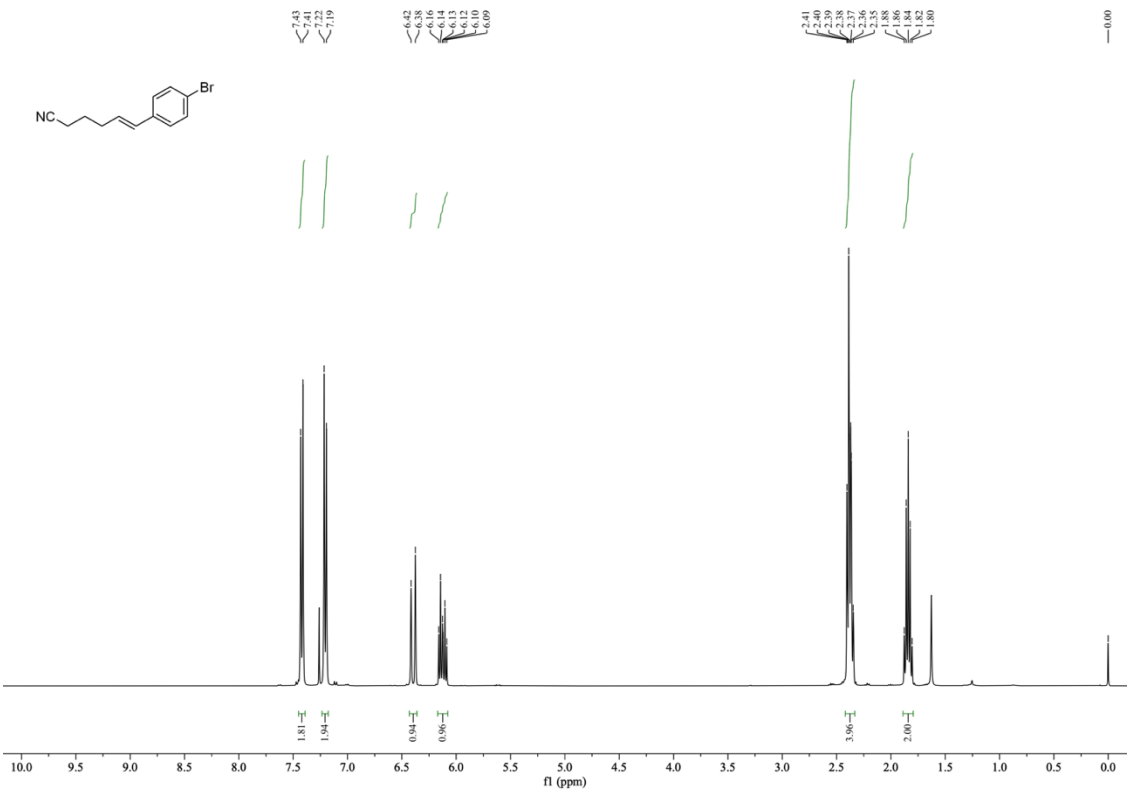
^{19}F NMR Spectrum of Compound 6c (376 MHz, $CDCl_3$)



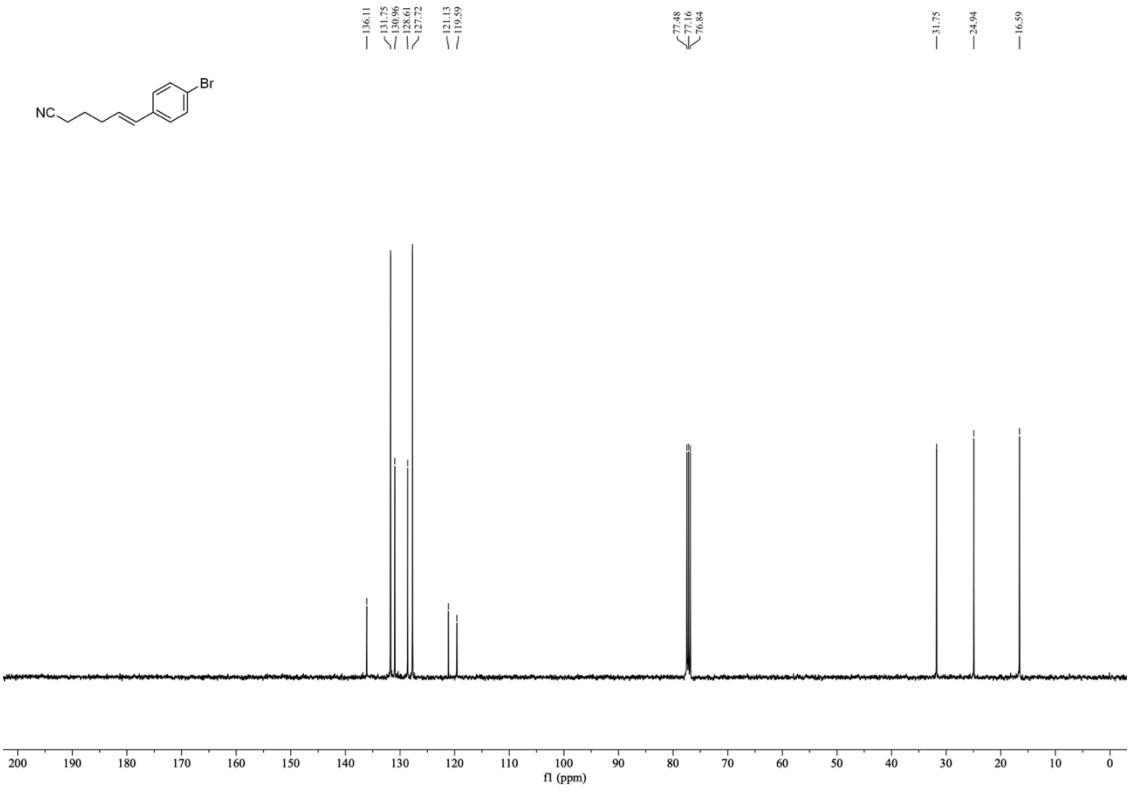
^{1}H NMR Spectrum of Compound 6d (400 MHz, $CDCl_3$)



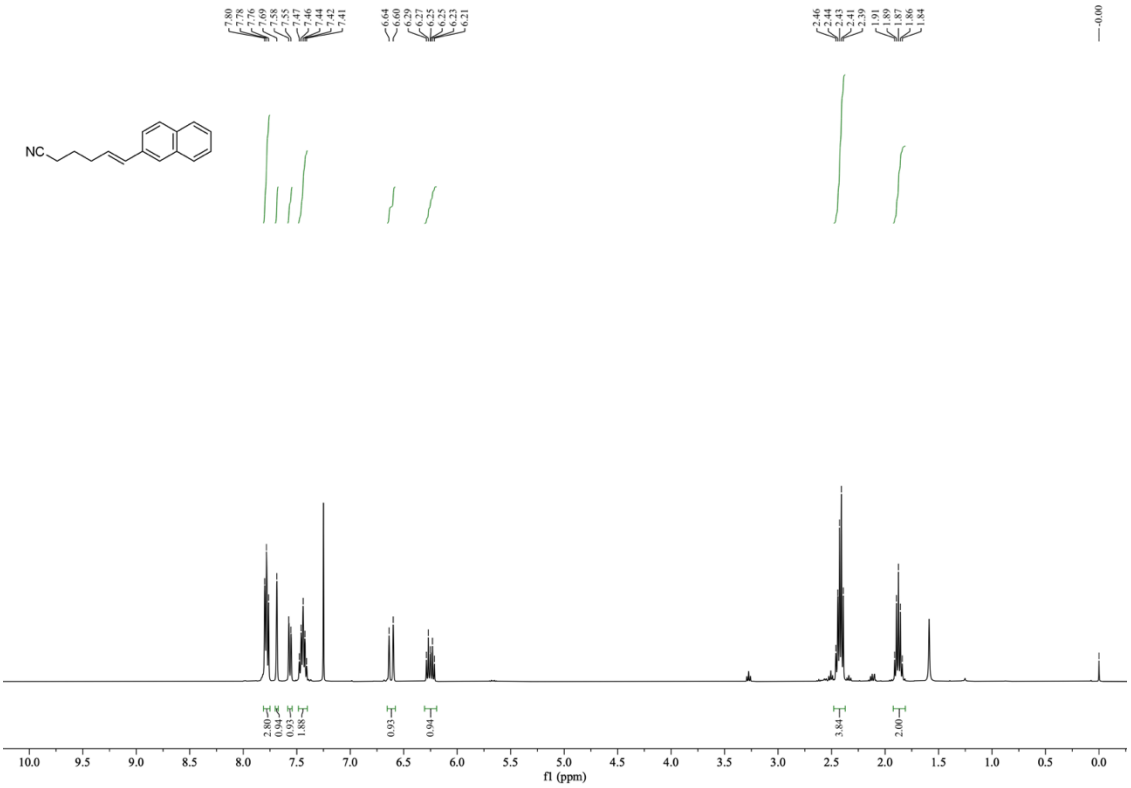
^{13}C NMR Spectrum of Compound 6d (101 MHz, $CDCl_3$)



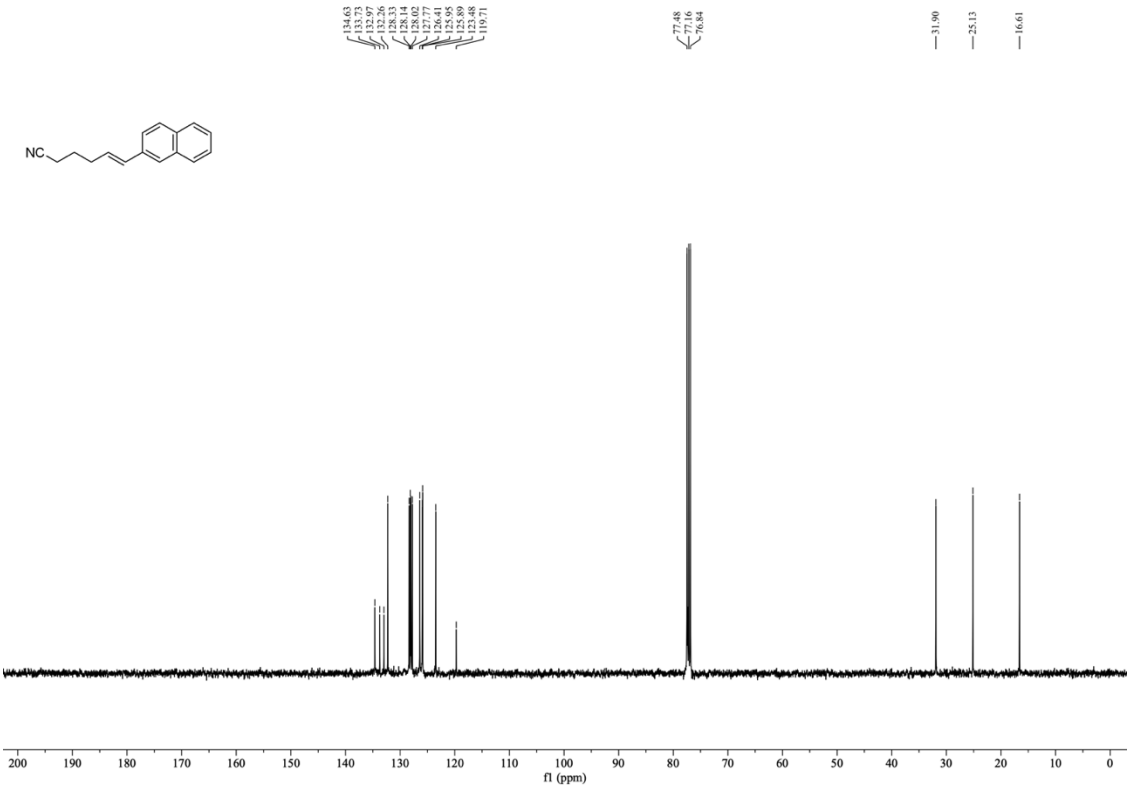
^{1}H NMR Spectrum of Compound 6e (400 MHz, $CDCl_3$)



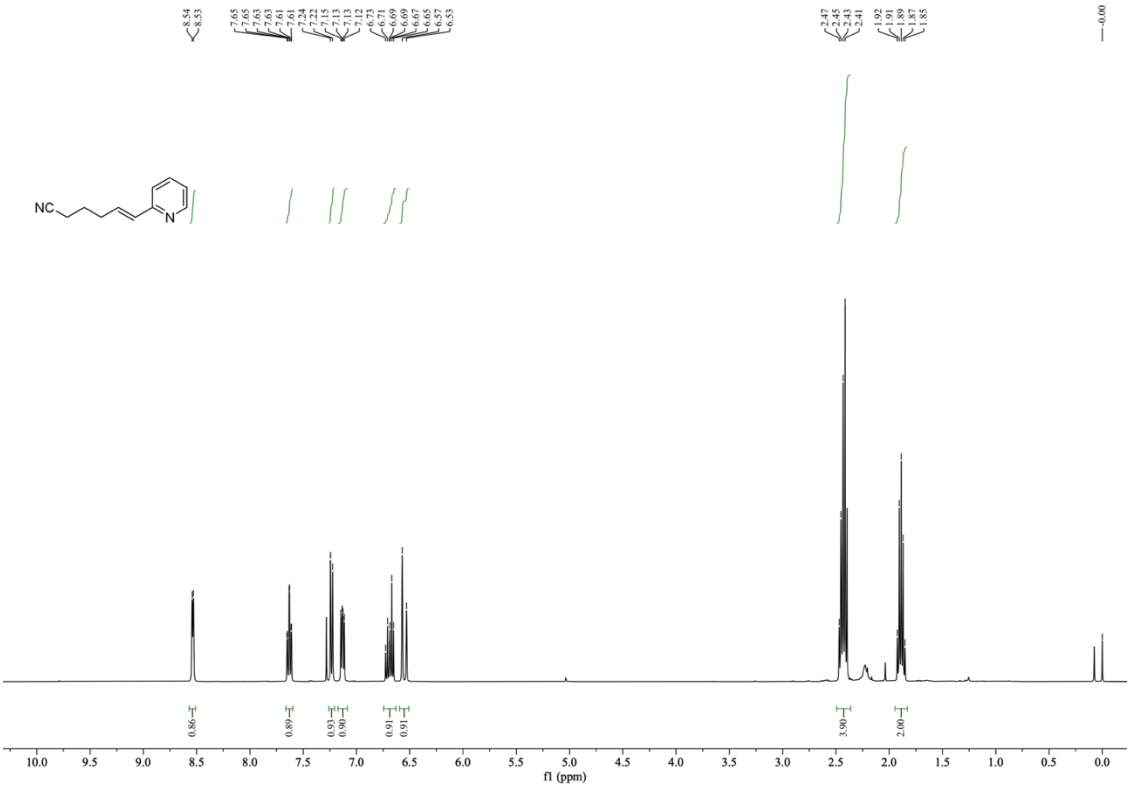
^{13}C NMR Spectrum of Compound 6e (101 MHz, $CDCl_3$)



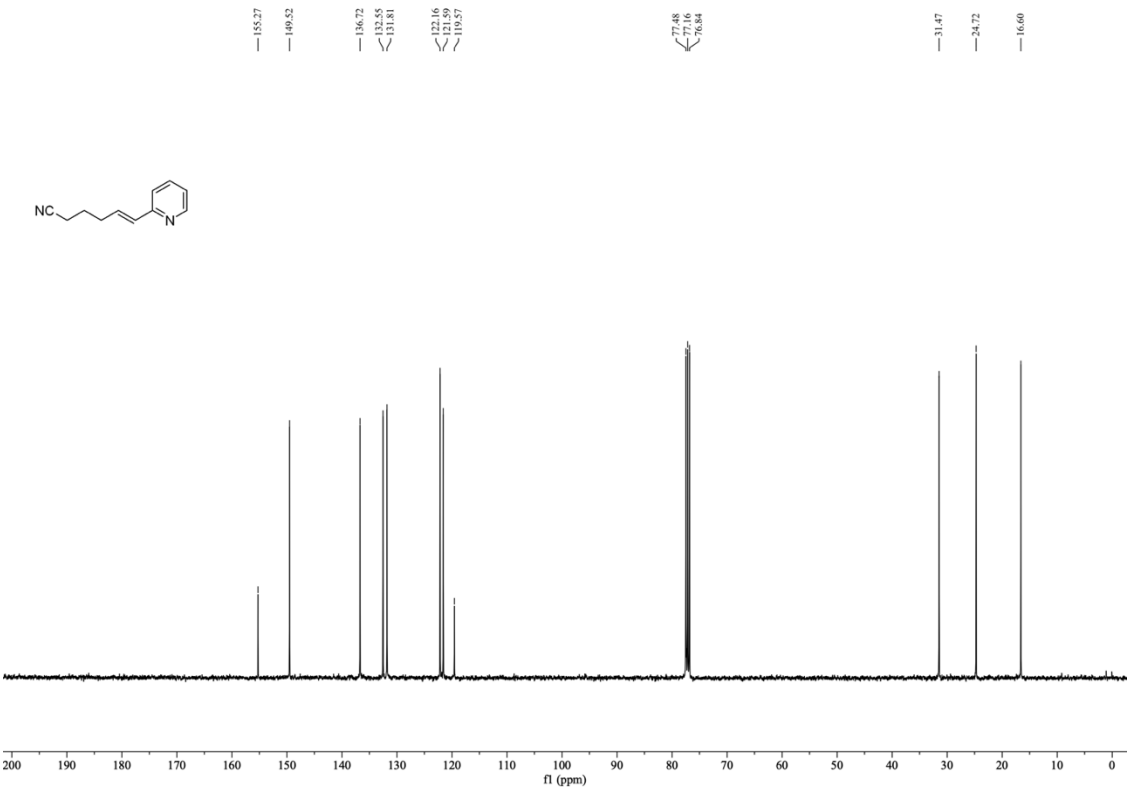
^{1}H NMR Spectrum of Compound 6f (400 MHz, $CDCl_3$)



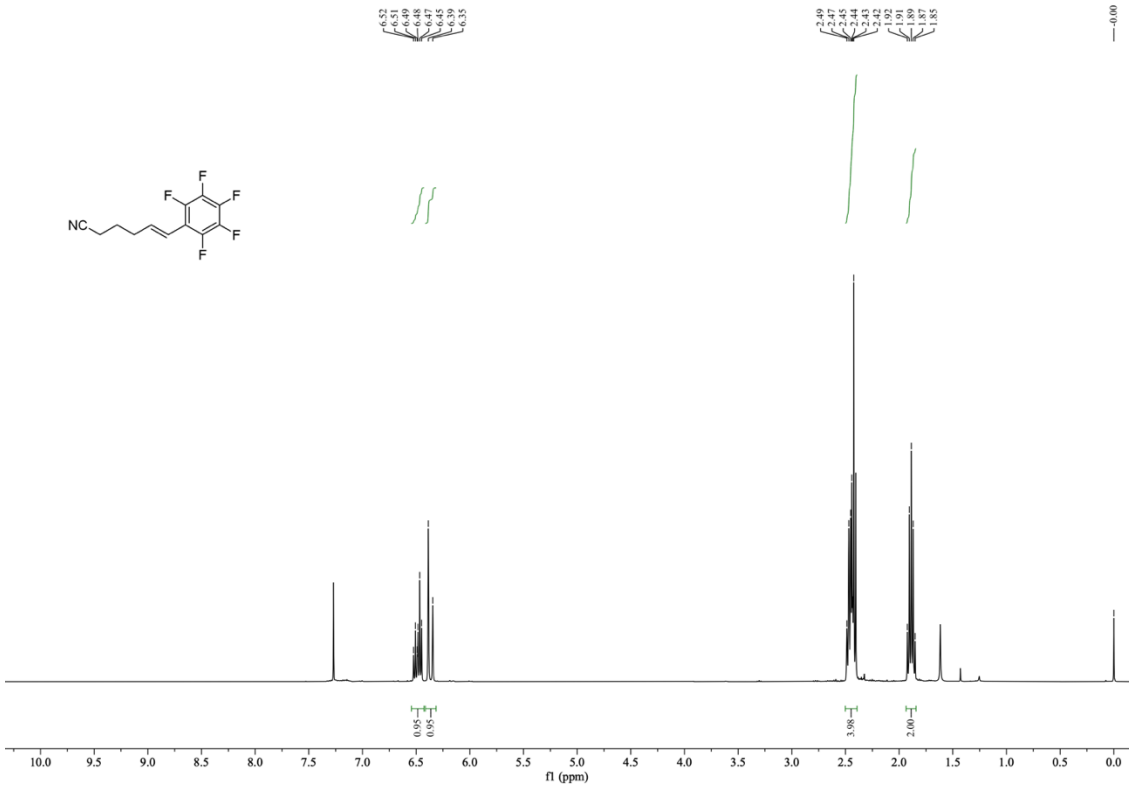
^{13}C NMR Spectrum of Compound 6f (101 MHz, $CDCl_3$)



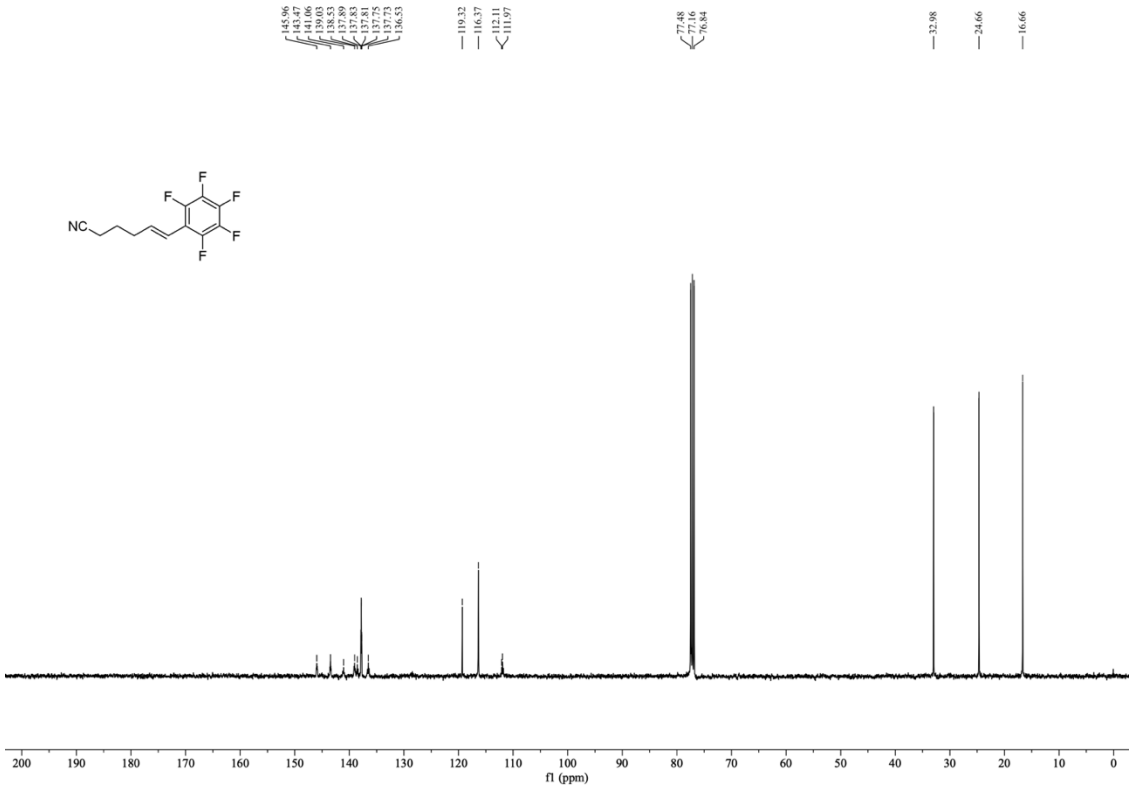
^{1}H NMR Spectrum of Compound 6g (400 MHz, $CDCl_3$)



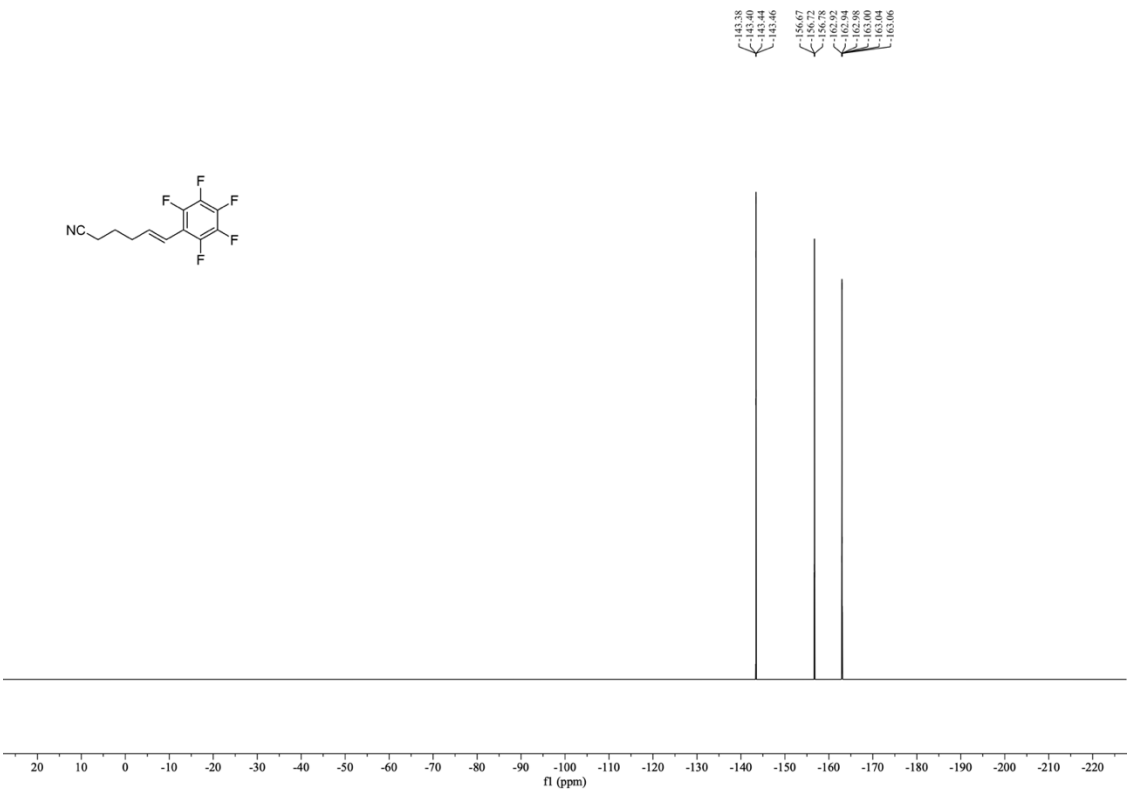
^{13}C NMR Spectrum of Compound 6g (101 MHz, $CDCl_3$)



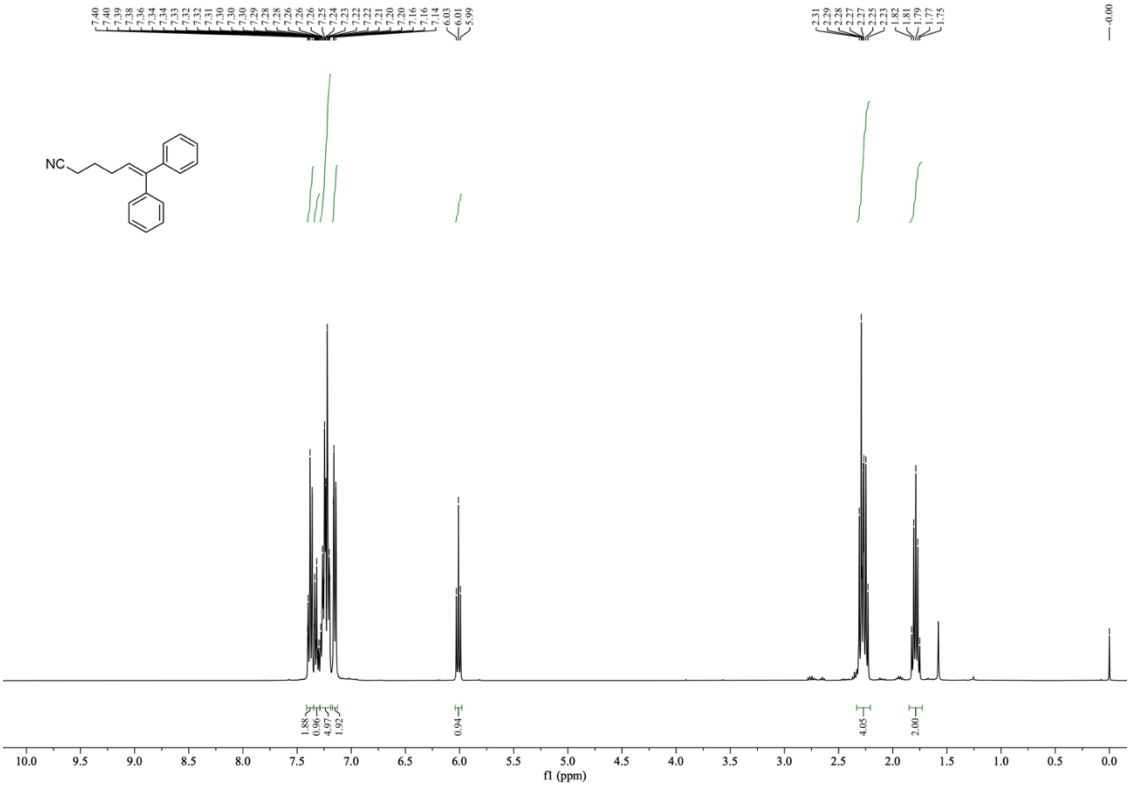
^{1}H NMR Spectrum of Compound 6h (400 MHz, $CDCl_3$)



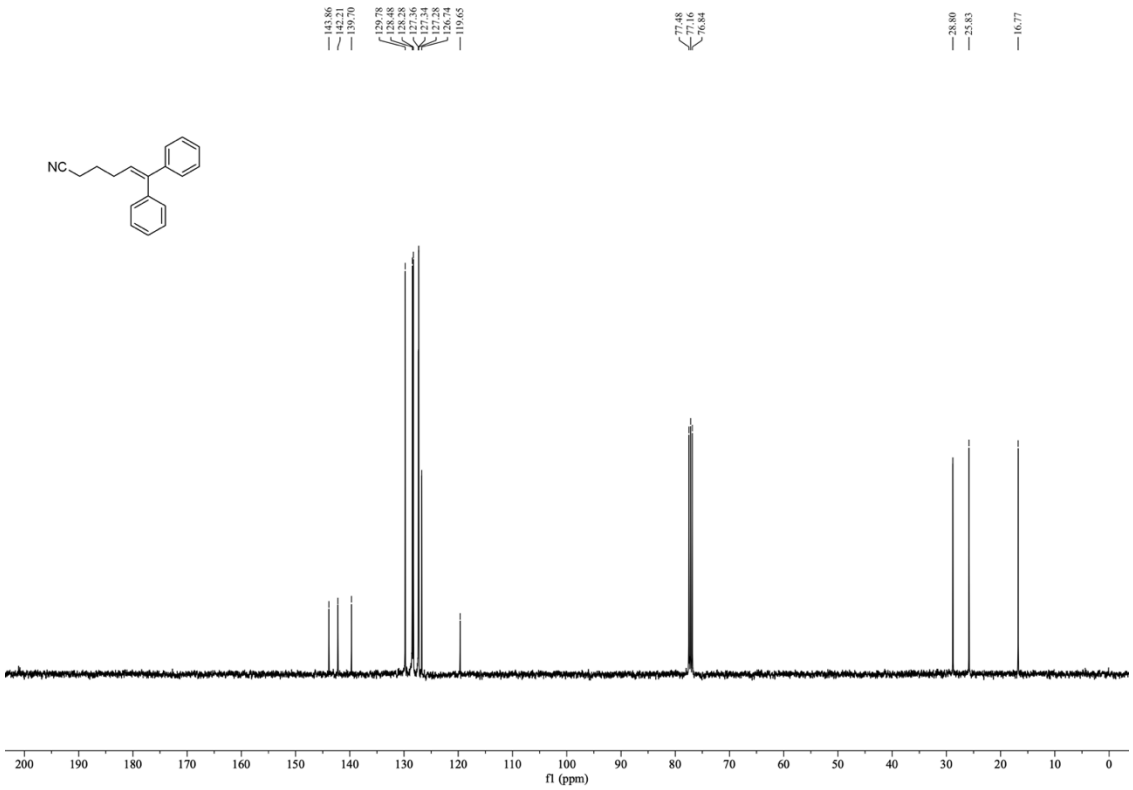
^{13}C NMR Spectrum of Compound 6h (101 MHz, $CDCl_3$)



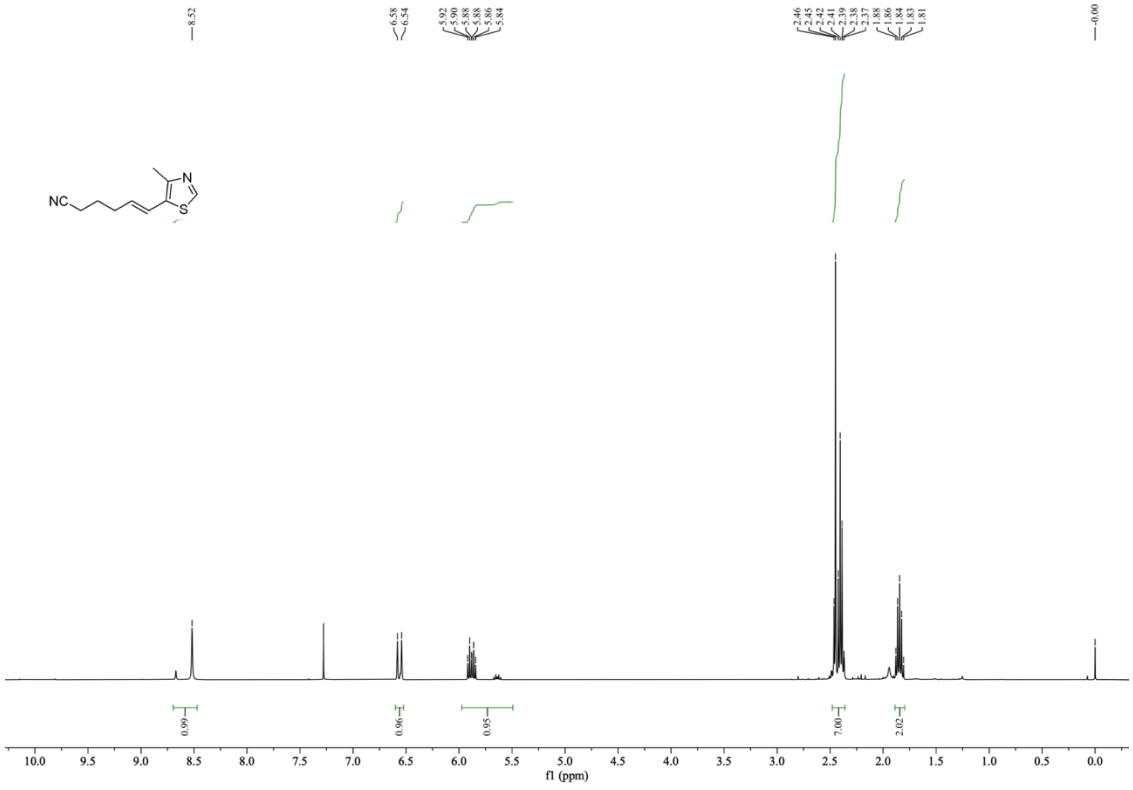
^{19}F NMR Spectrum of Compound 6h (376 MHz, $CDCl_3$)



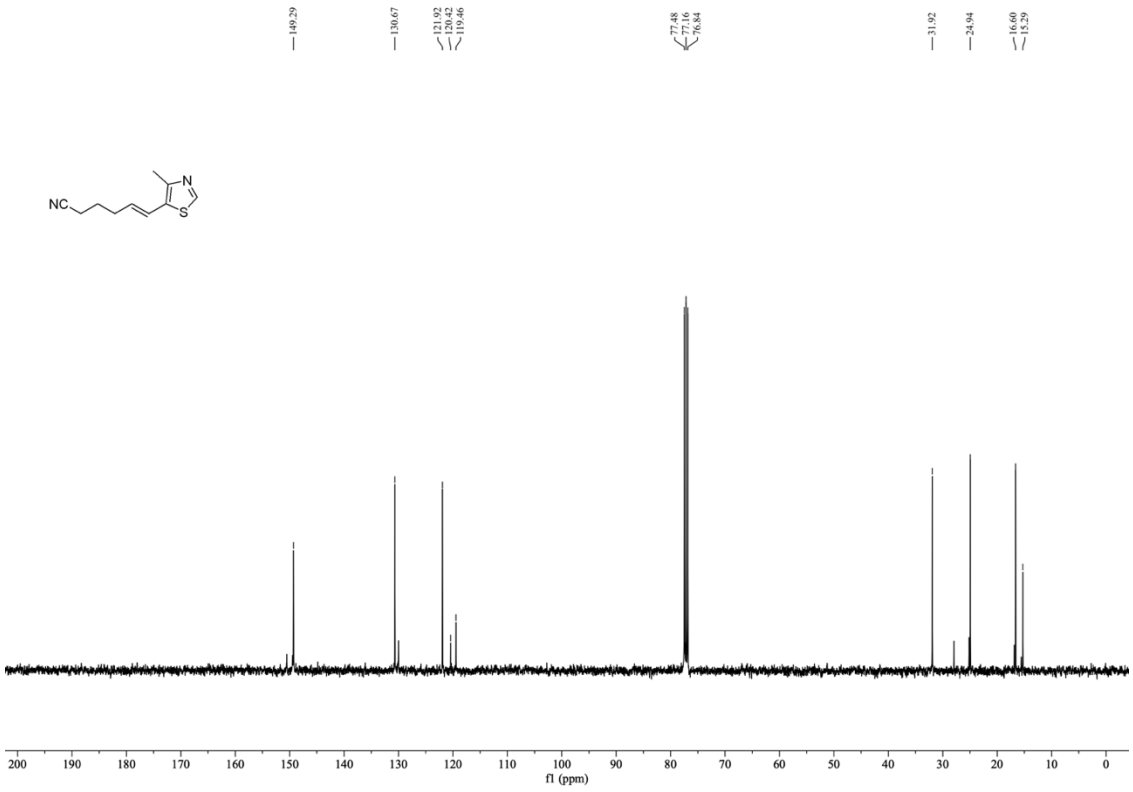
^{1}H NMR Spectrum of Compound 6i (400 MHz, $CDCl_3$)



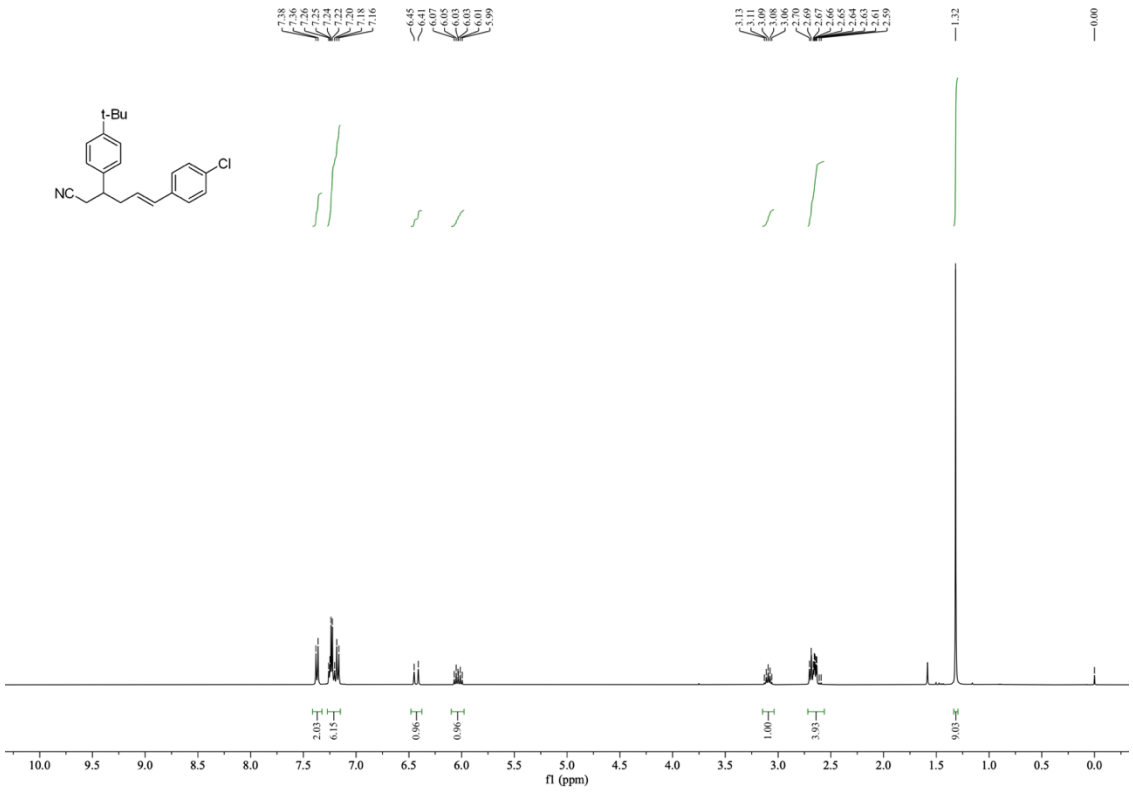
^{13}C NMR Spectrum of Compound 6i (101 MHz, $CDCl_3$)



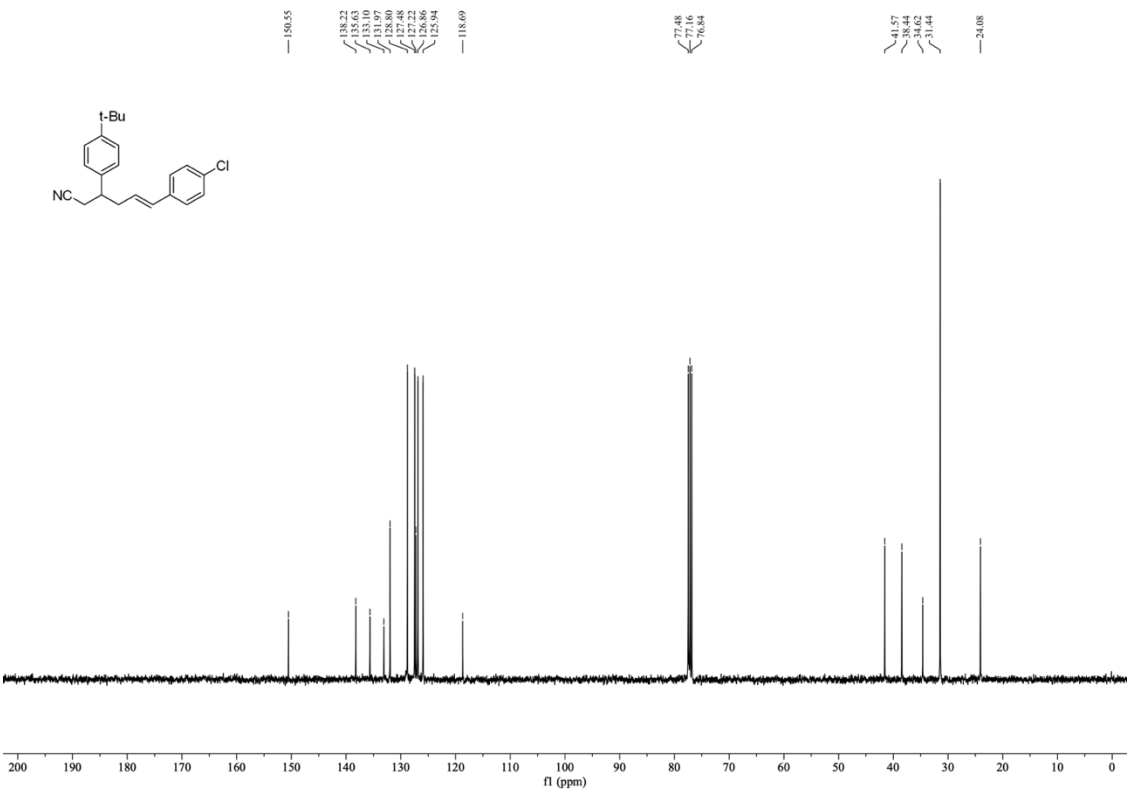
^{1}H NMR Spectrum of Compound 6j (400 MHz, $CDCl_3$)



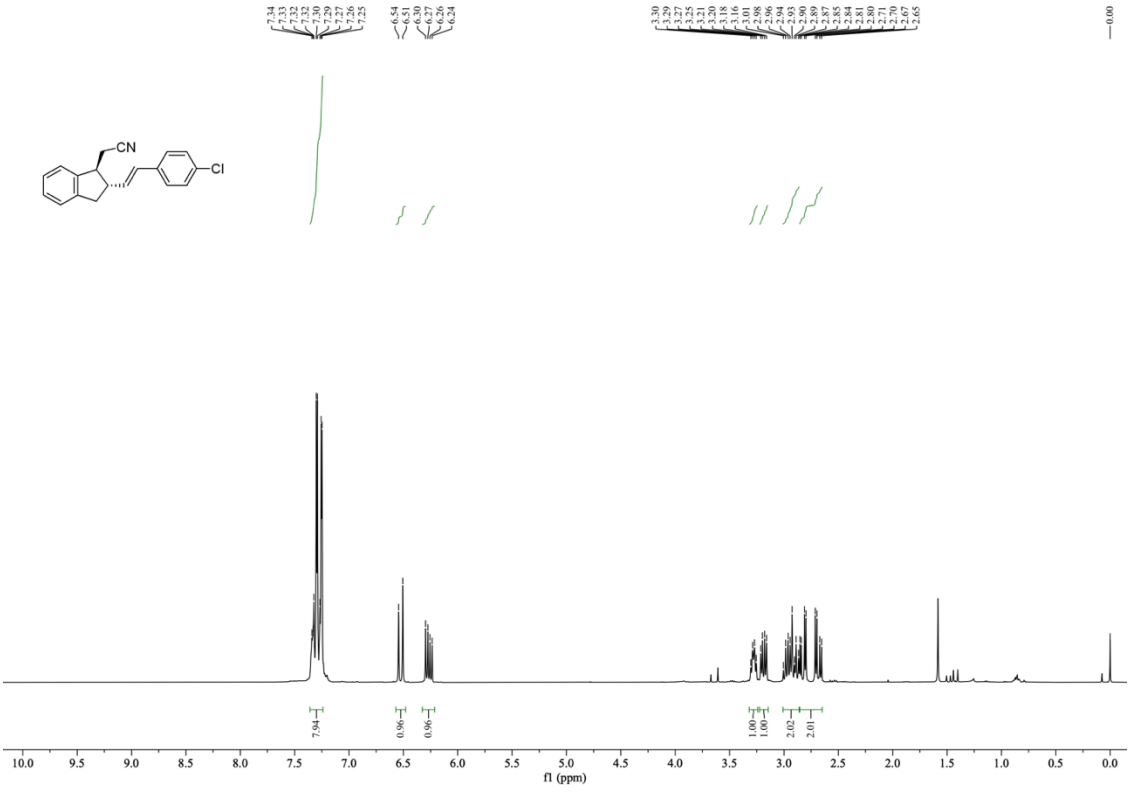
^{13}C NMR Spectrum of Compound 6j (101 MHz, $CDCl_3$)



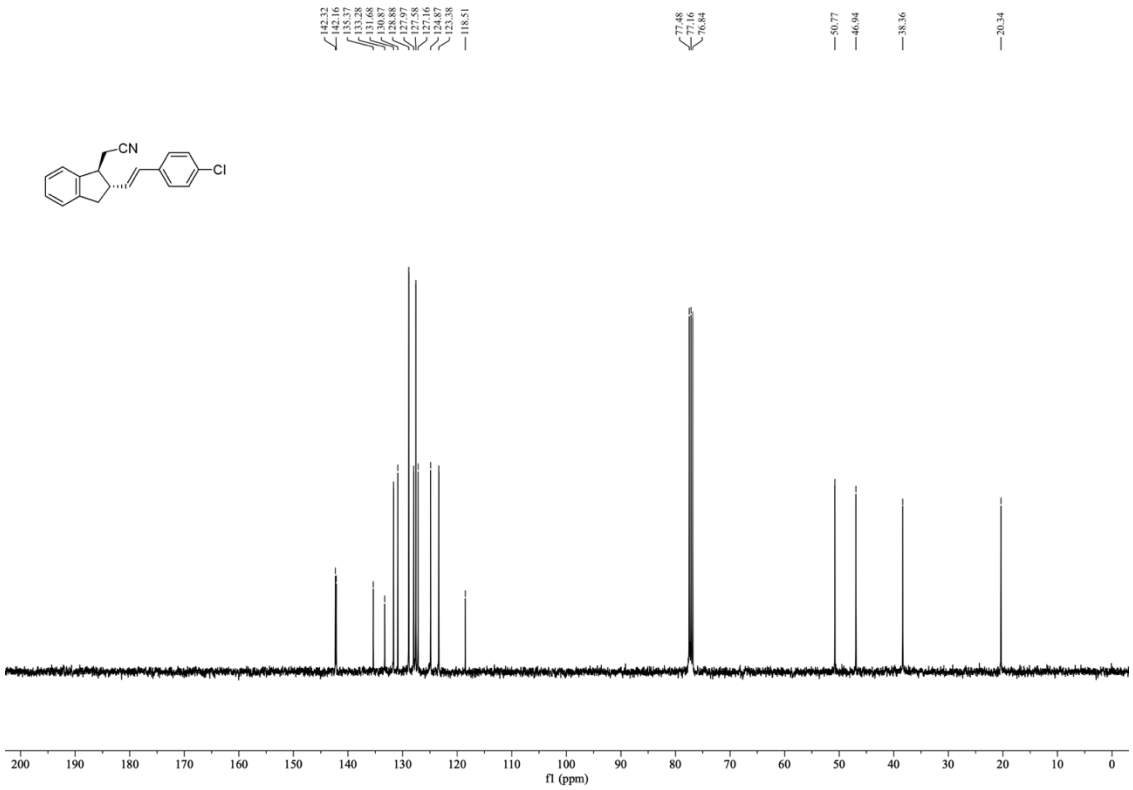
^{1}H NMR Spectrum of Compound 6k (400 MHz, $CDCl_3$)



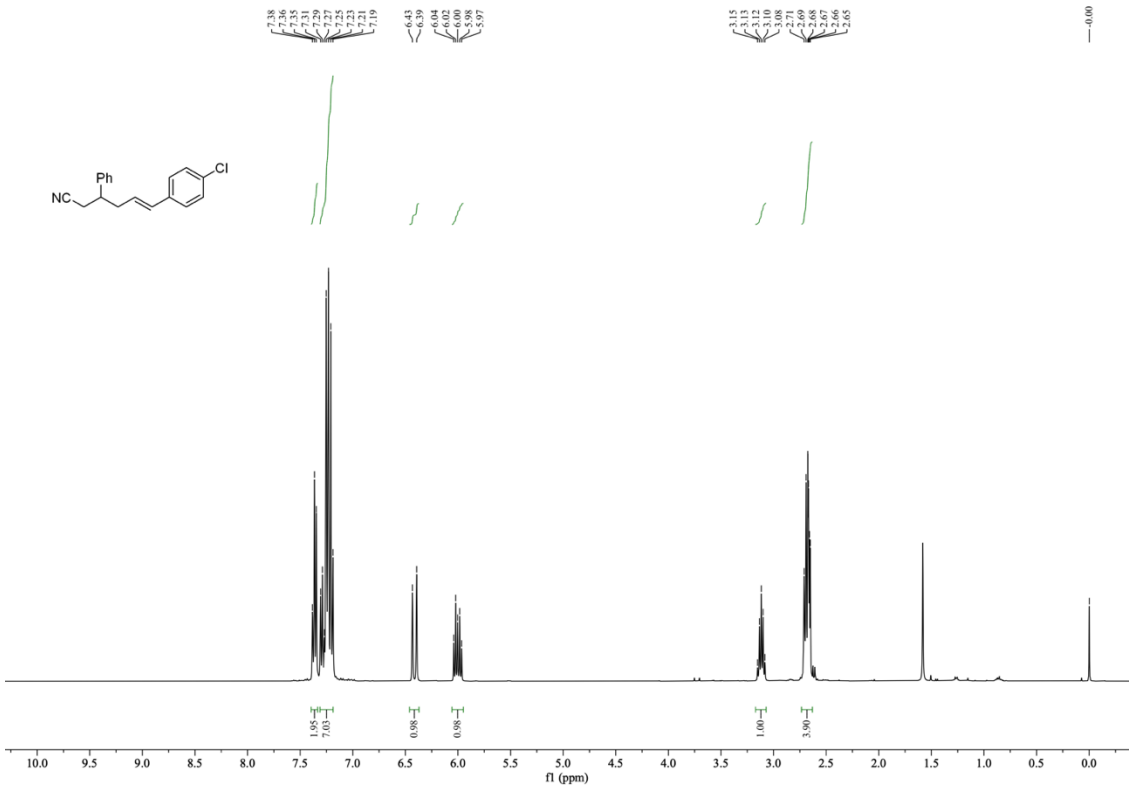
^{13}C NMR Spectrum of Compound 6k (101 MHz, $CDCl_3$)



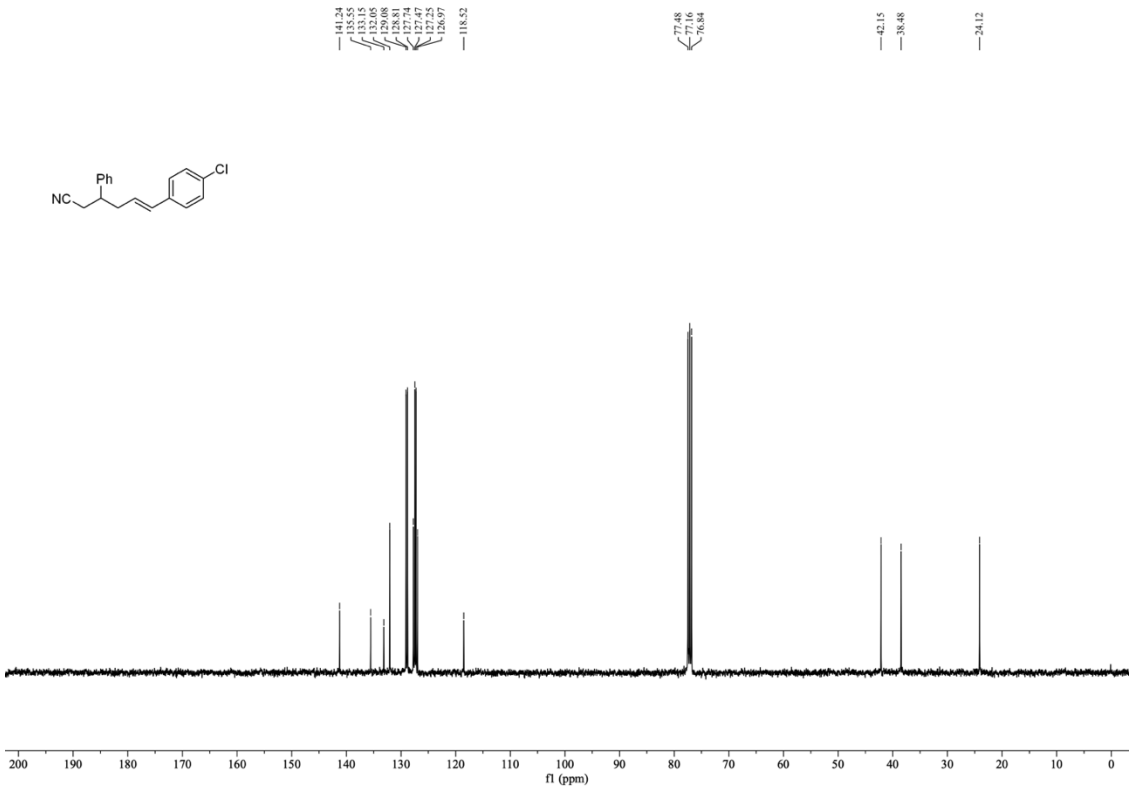
^{1}H NMR Spectrum of Compound 6l (400 MHz, $CDCl_3$)



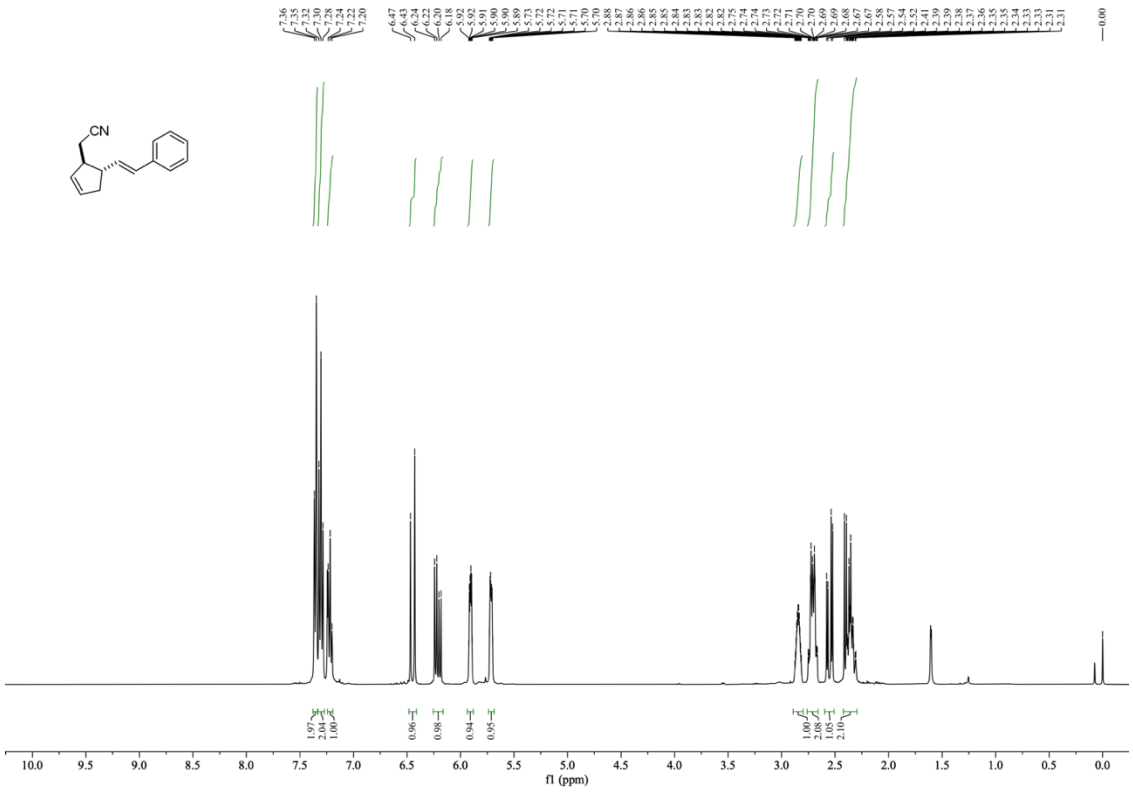
^{13}C NMR Spectrum of Compound 6l (101 MHz, $CDCl_3$)



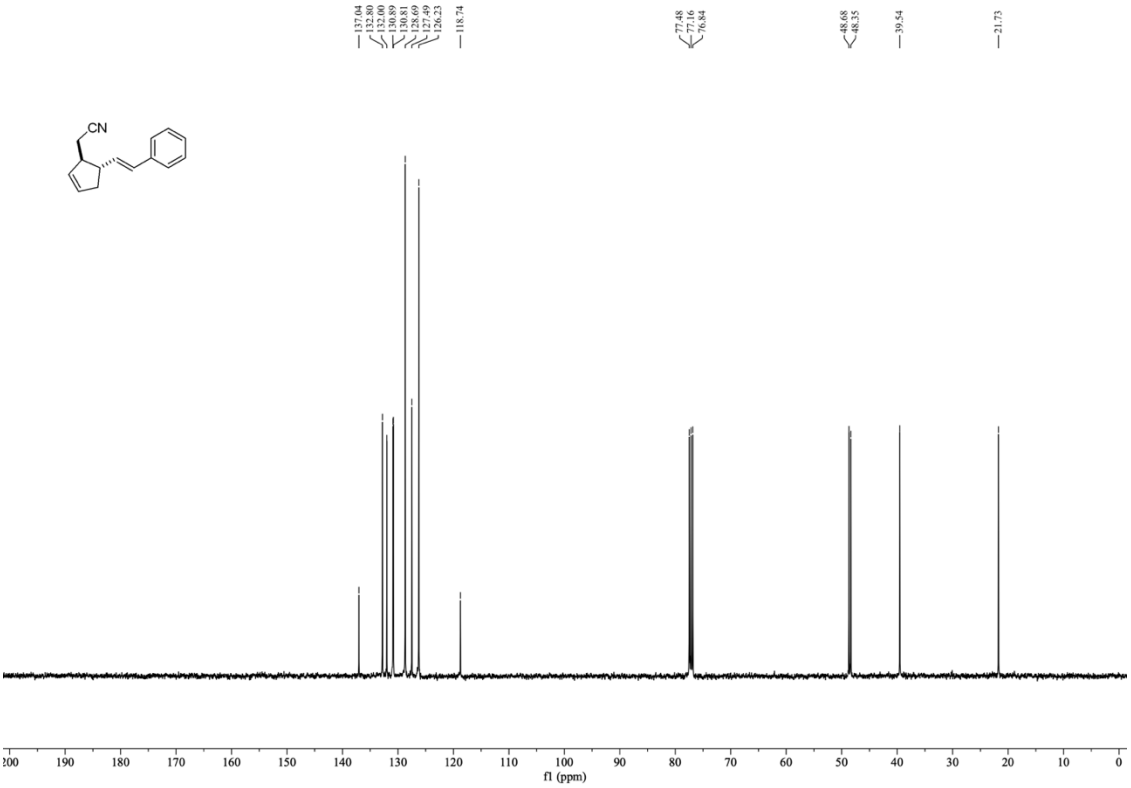
^{1}H NMR Spectrum of Compound 6m (400 MHz, $CDCl_3$)



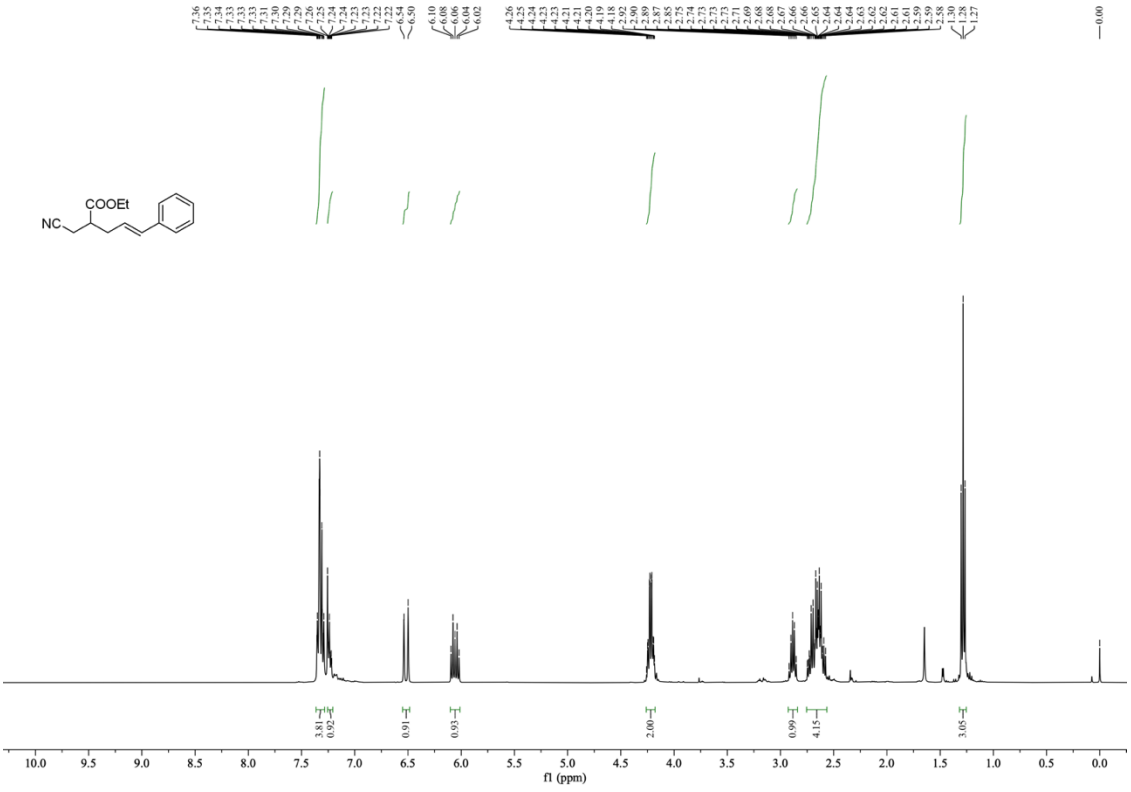
^{13}C NMR Spectrum of Compound 6m (101 MHz, $CDCl_3$)



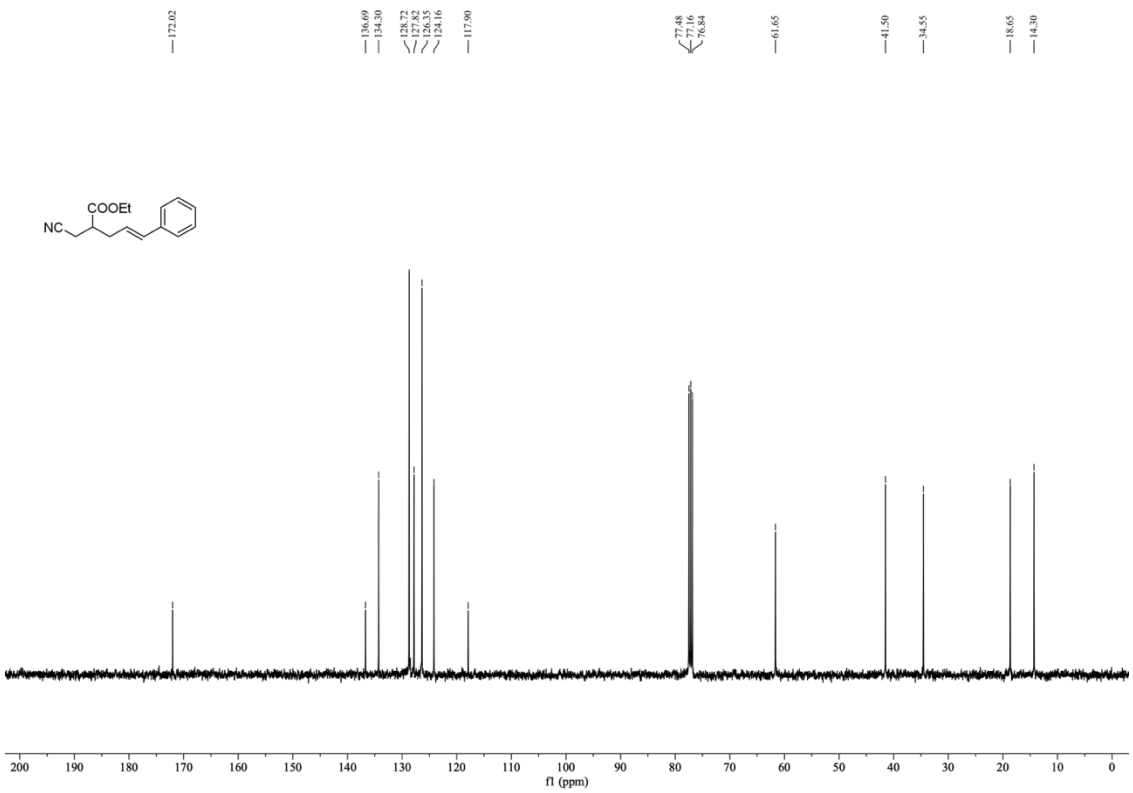
^{1}H NMR Spectrum of Compound 6n (400 MHz, $CDCl_3$)



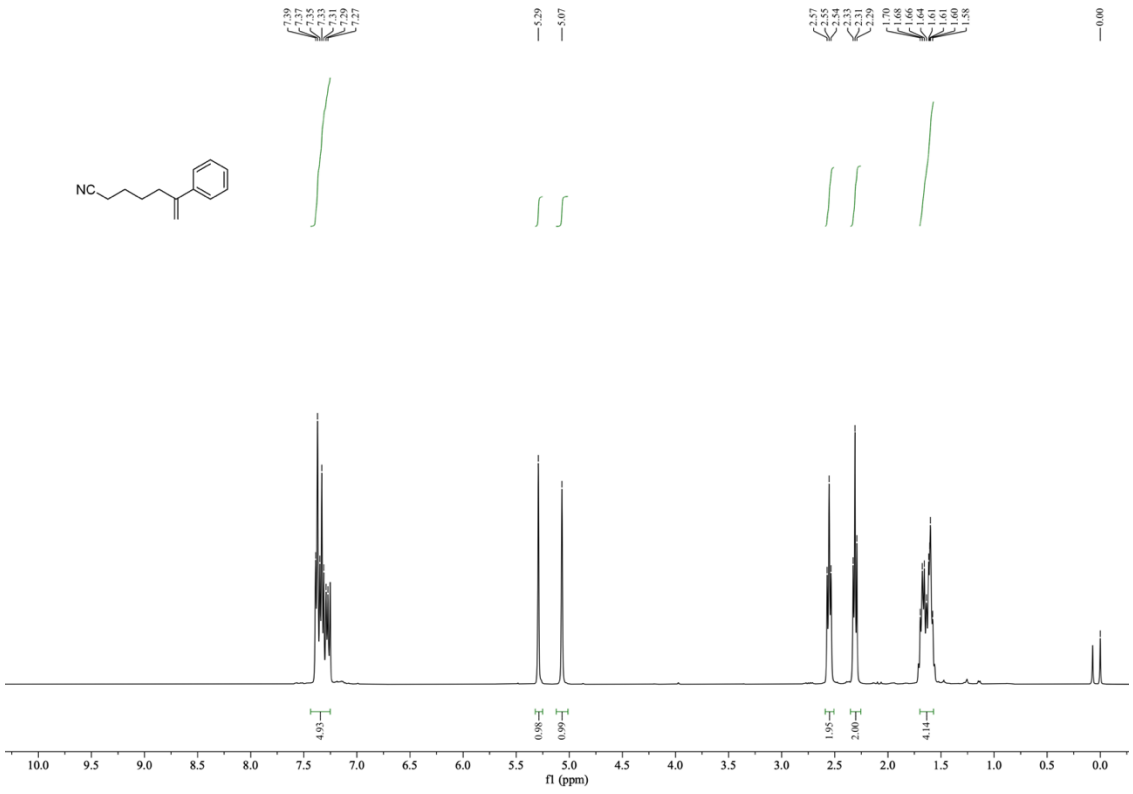
^{13}C NMR Spectrum of Compound 6n (101 MHz, $CDCl_3$)



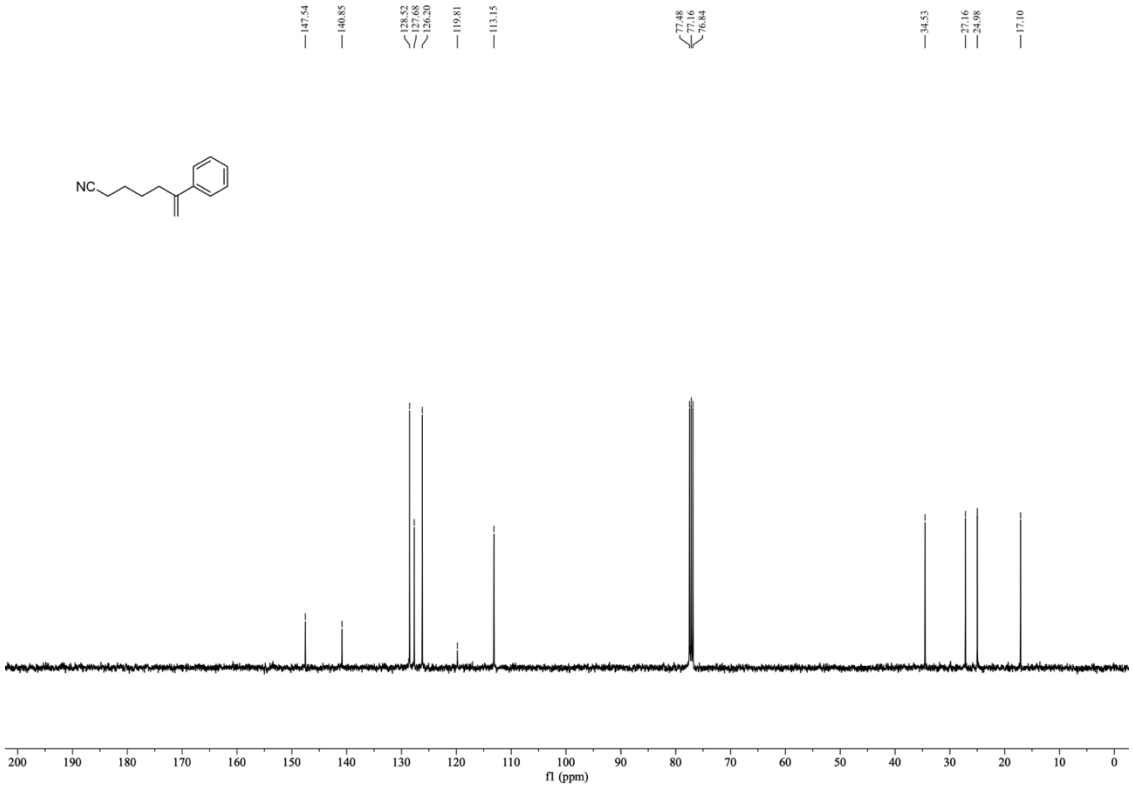
^{1}H NMR Spectrum of Compound 6o (400 MHz, $CDCl_3$)



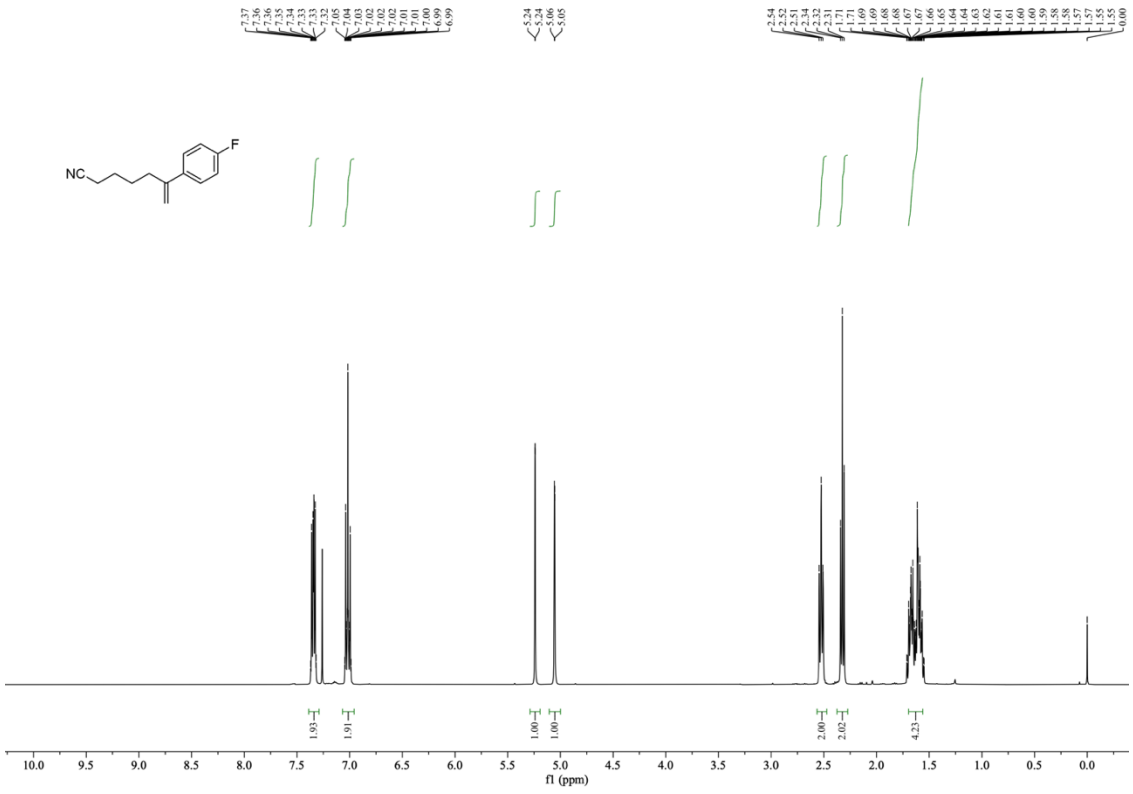
^{13}C NMR Spectrum of Compound 6o (101 MHz, $CDCl_3$)



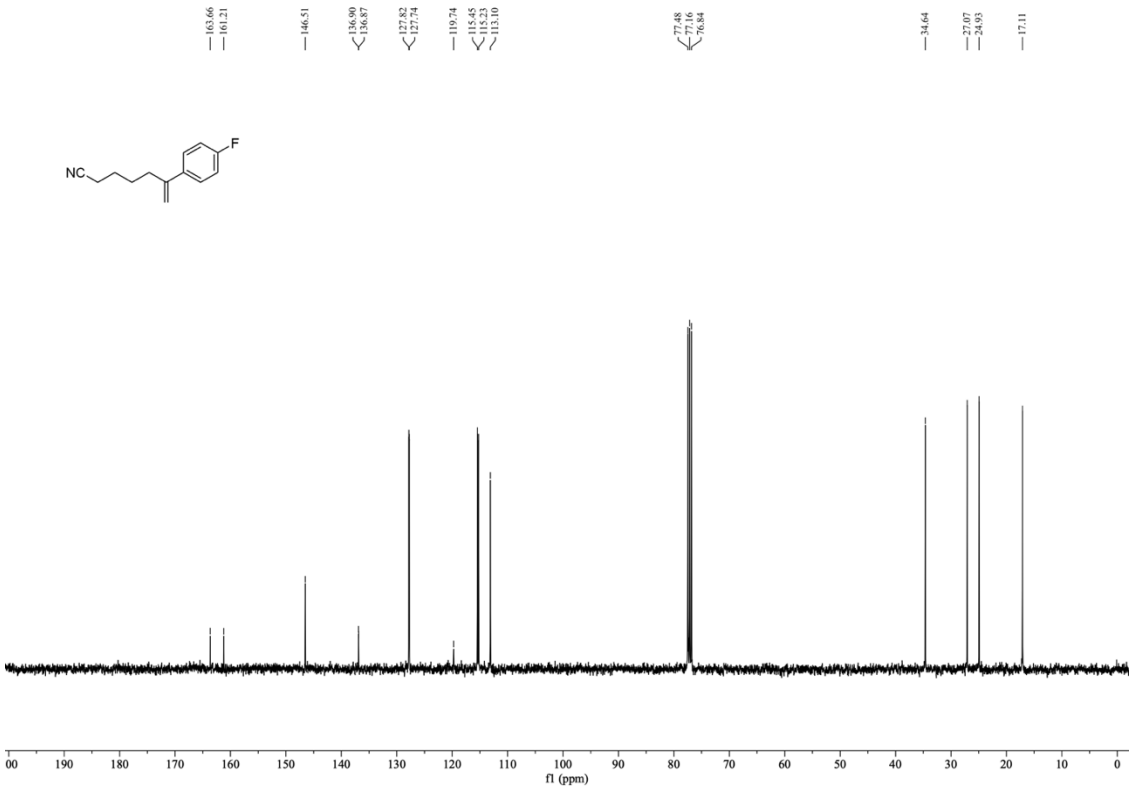
^{1}H NMR Spectrum of Compound 8a (400 MHz, $CDCl_3$)



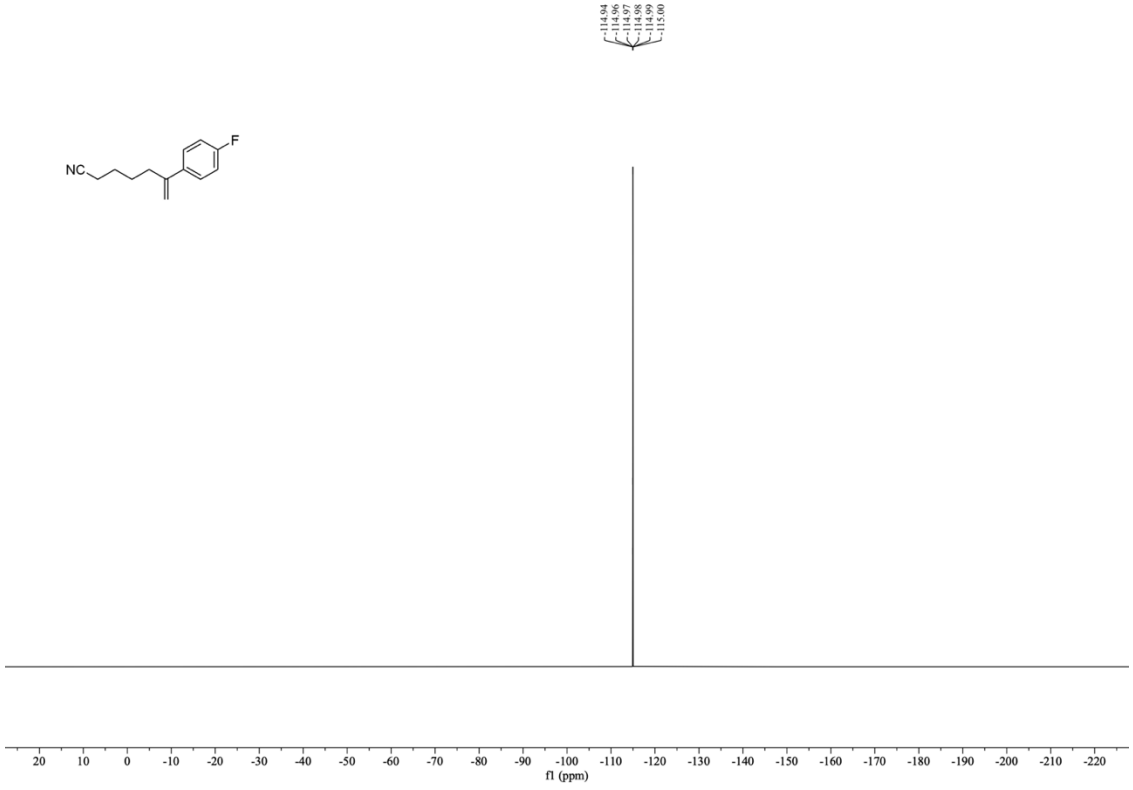
^{13}C NMR Spectrum of Compound 8a (101 MHz, $CDCl_3$)



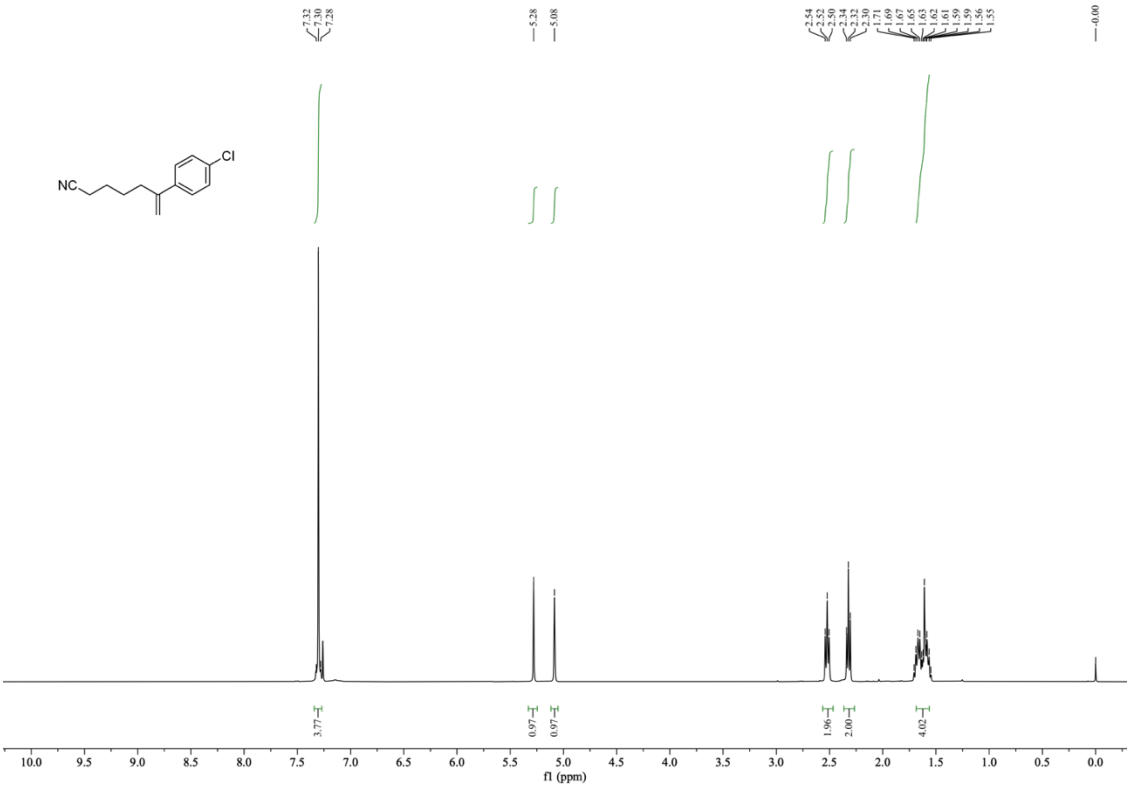
^{1}H NMR Spectrum of Compound 8b (400 MHz, $CDCl_3$)



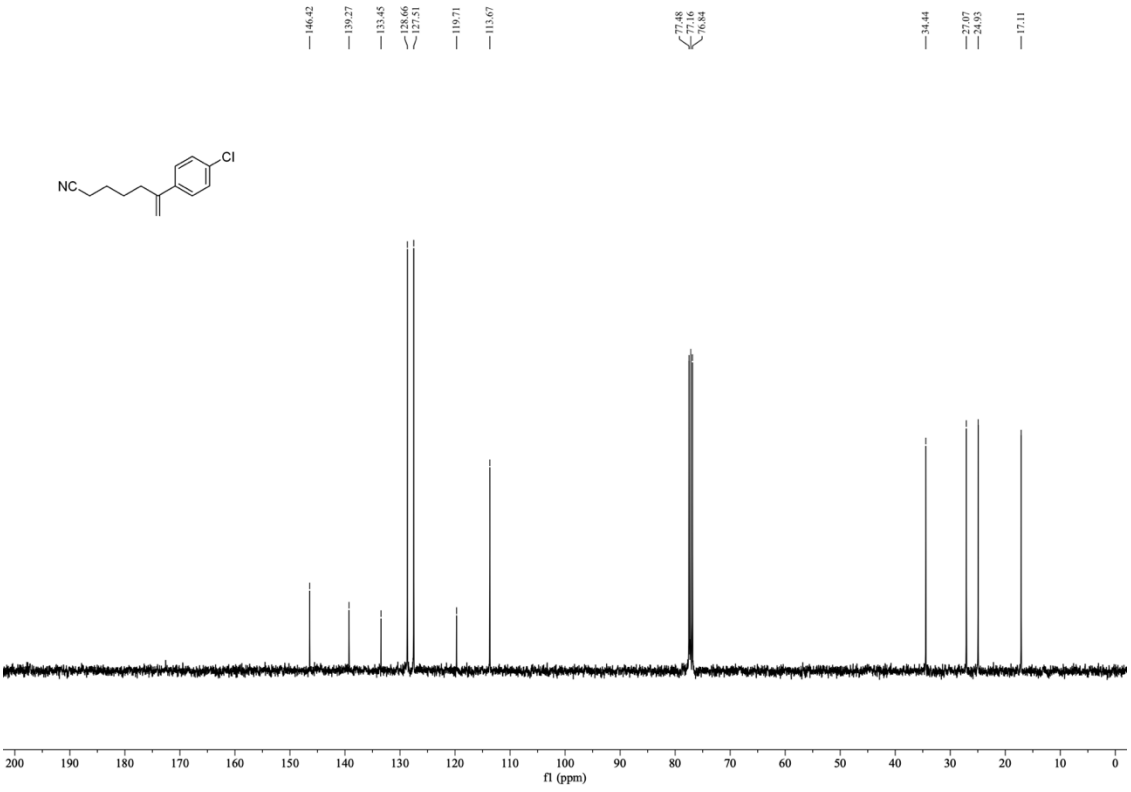
^{13}C NMR Spectrum of Compound 8b (101 MHz, $CDCl_3$)



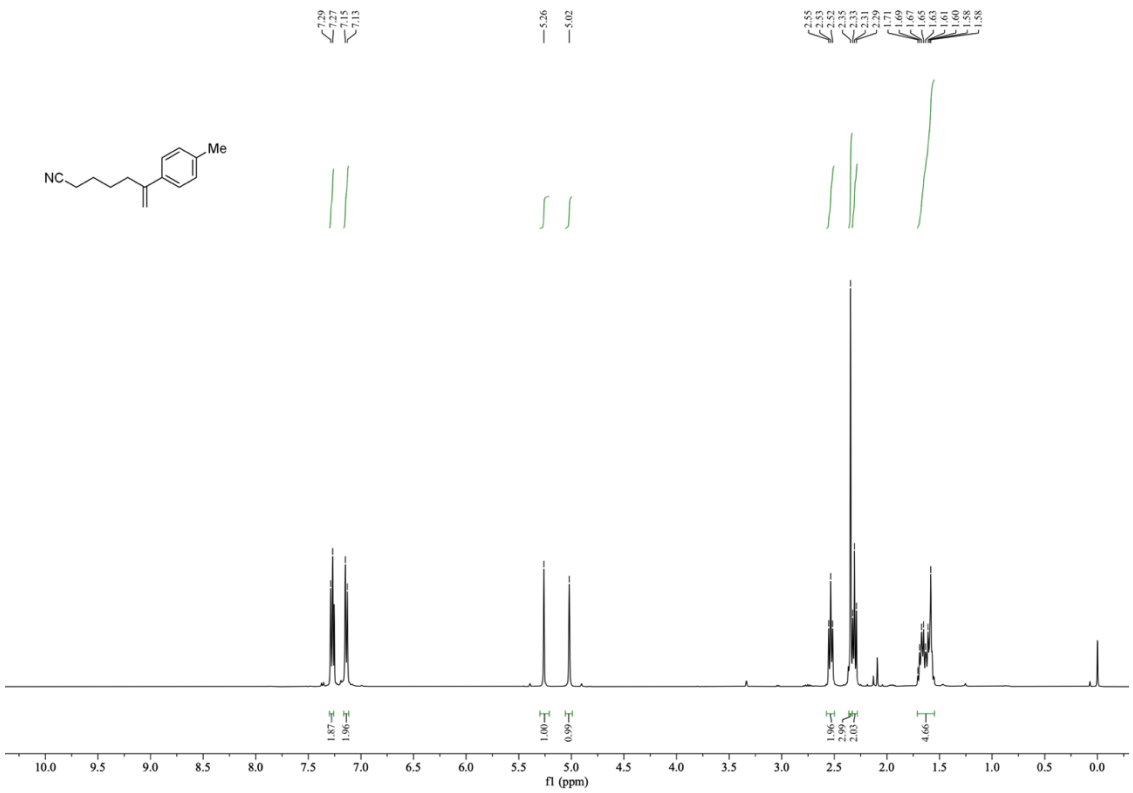
^{19}F NMR Spectrum of Compound 8b (376 MHz, $CDCl_3$)



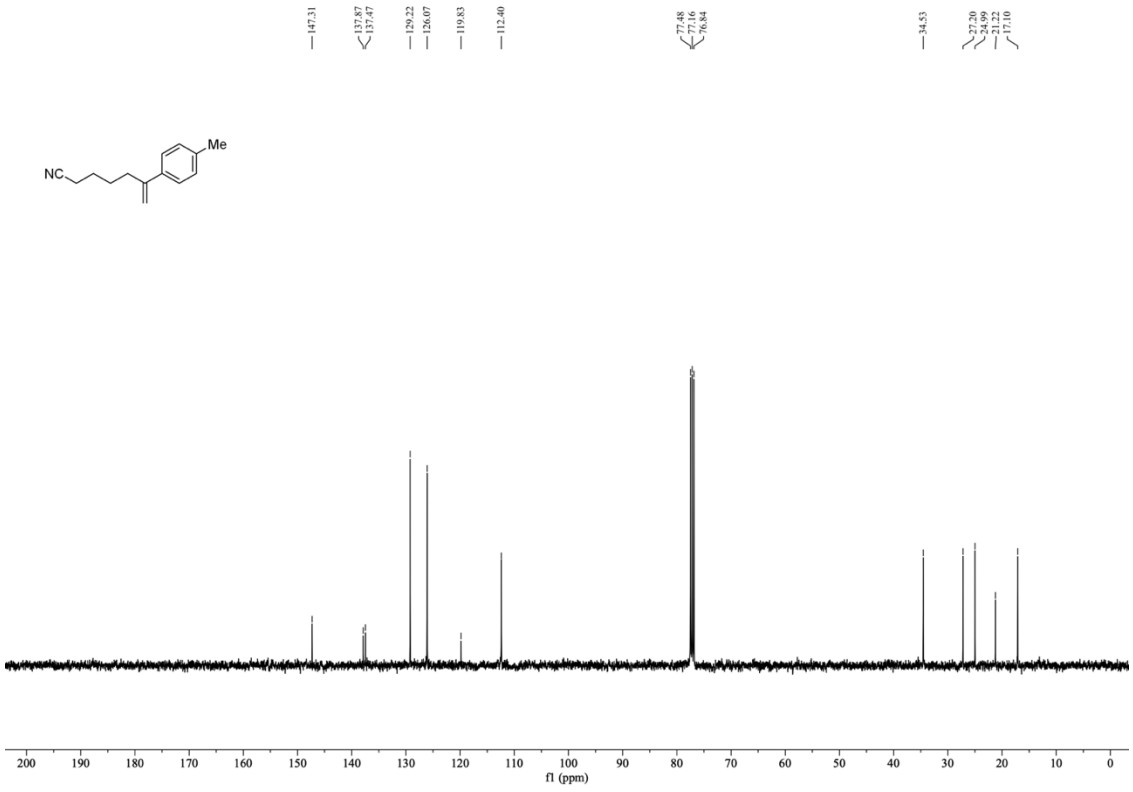
^{1}H NMR Spectrum of Compound 8c (400 MHz, $CDCl_3$)



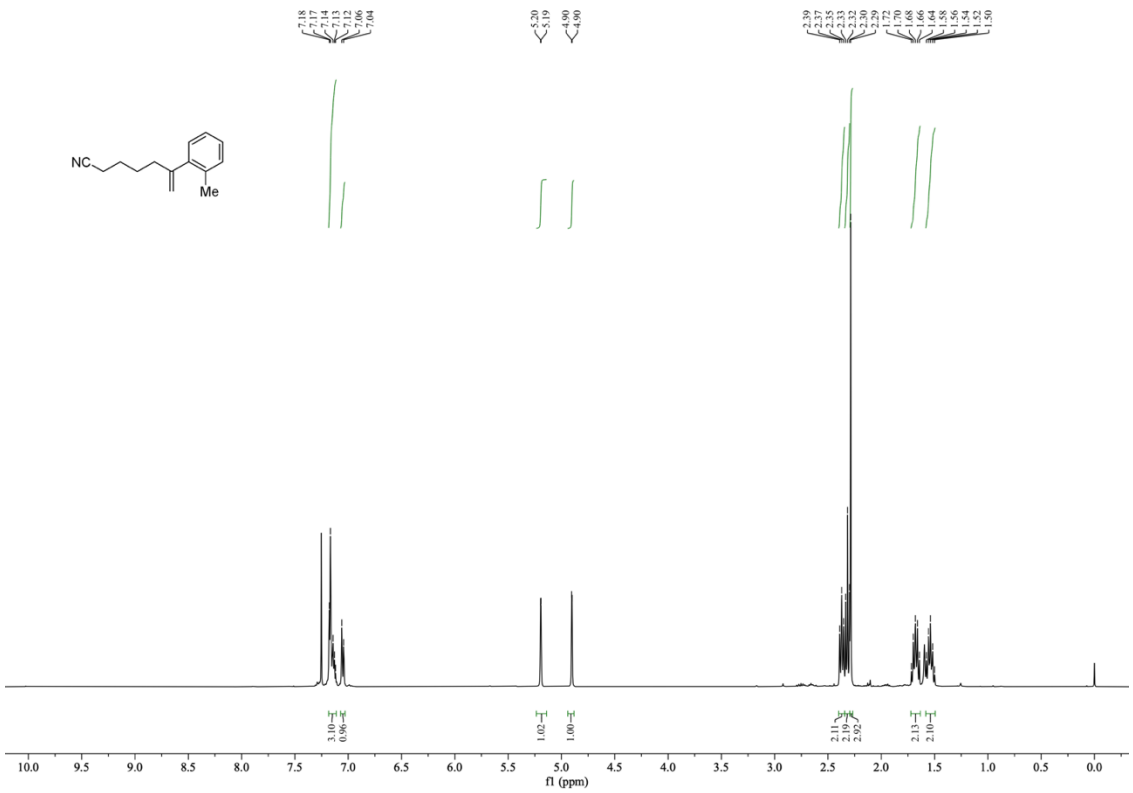
^{13}C NMR Spectrum of Compound 8c (101 MHz, $CDCl_3$)



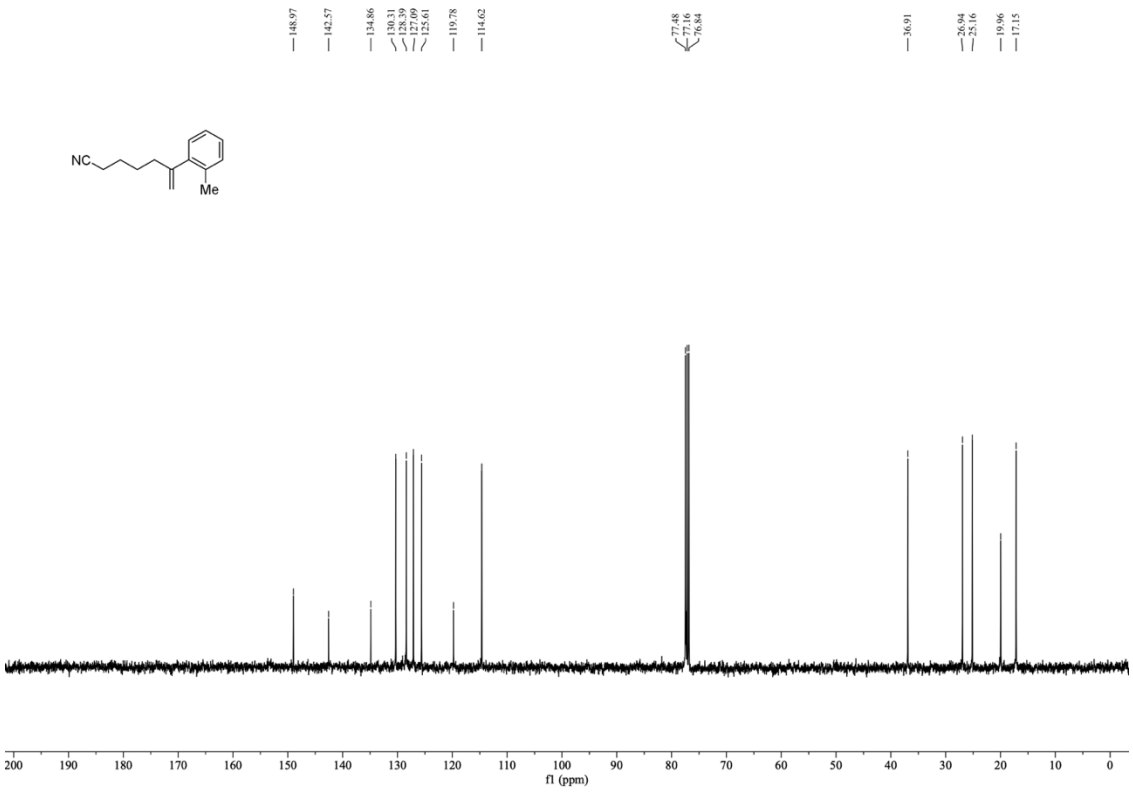
^{1}H NMR Spectrum of Compound 8d (400 MHz, $CDCl_3$)



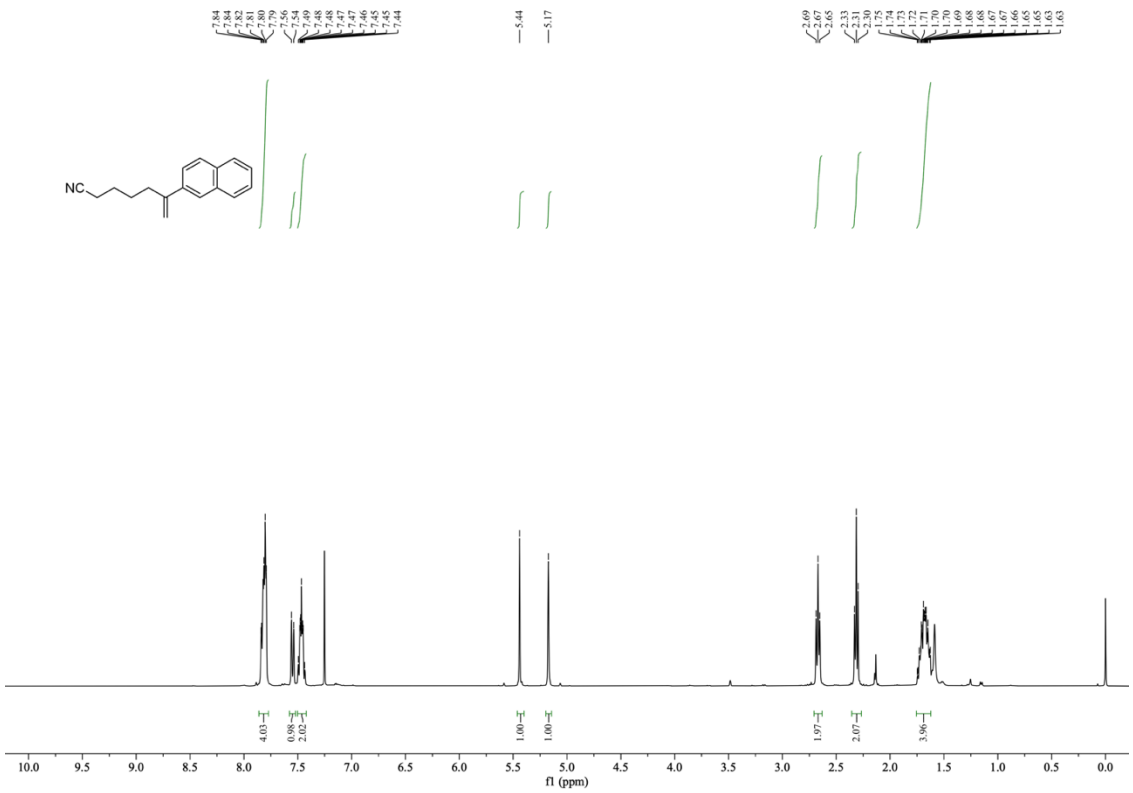
^{13}C NMR Spectrum of Compound 8d (101 MHz, $CDCl_3$)



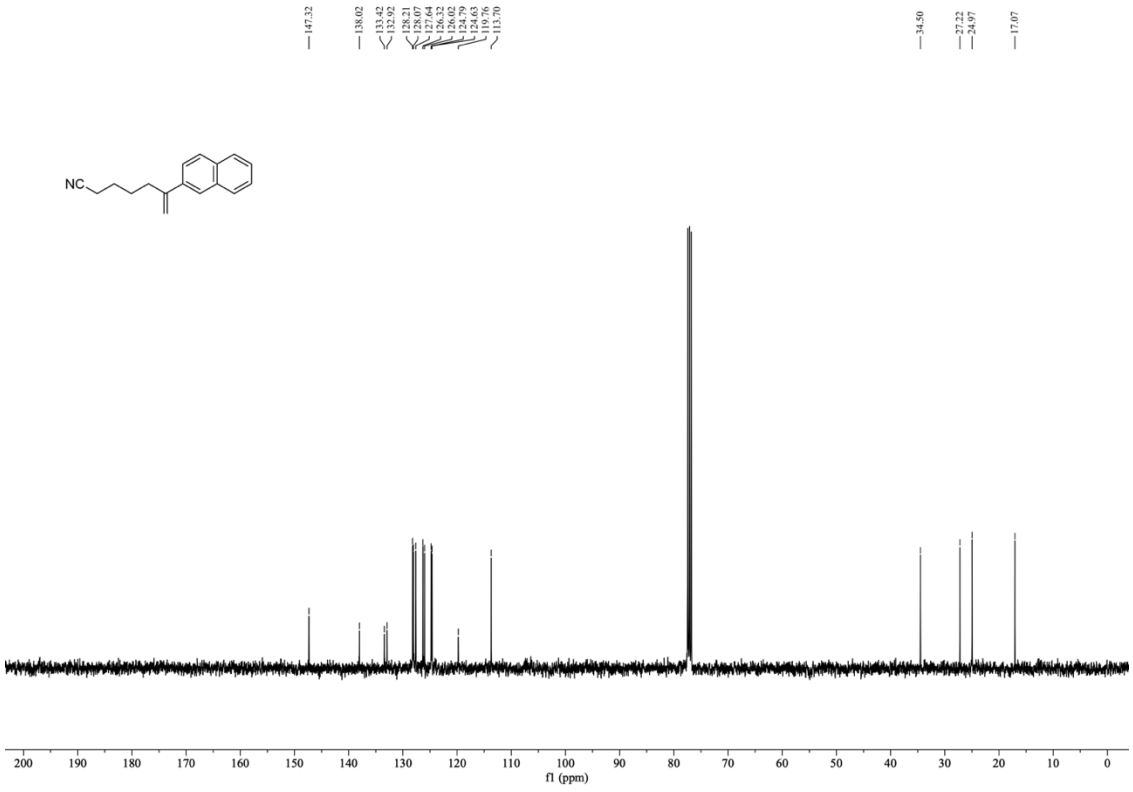
^{1}H NMR Spectrum of Compound 8e (400 MHz, $CDCl_3$)



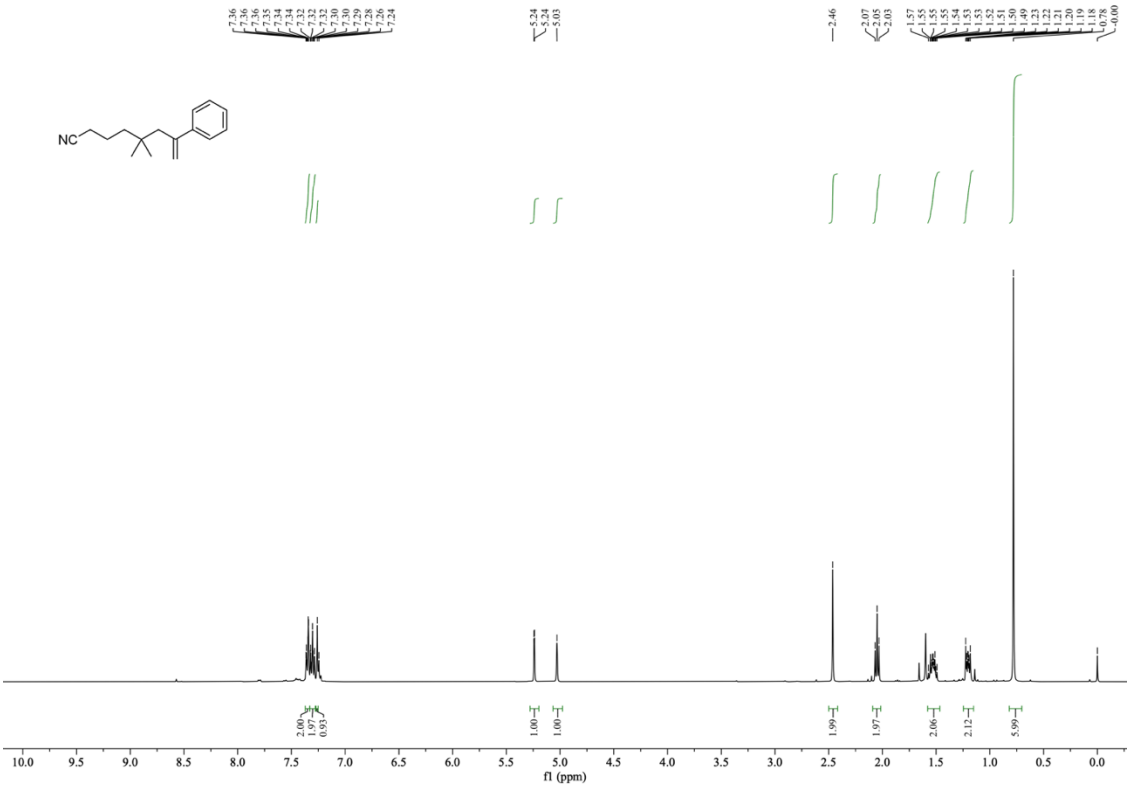
^{13}C NMR Spectrum of Compound 8e (101 MHz, $CDCl_3$)



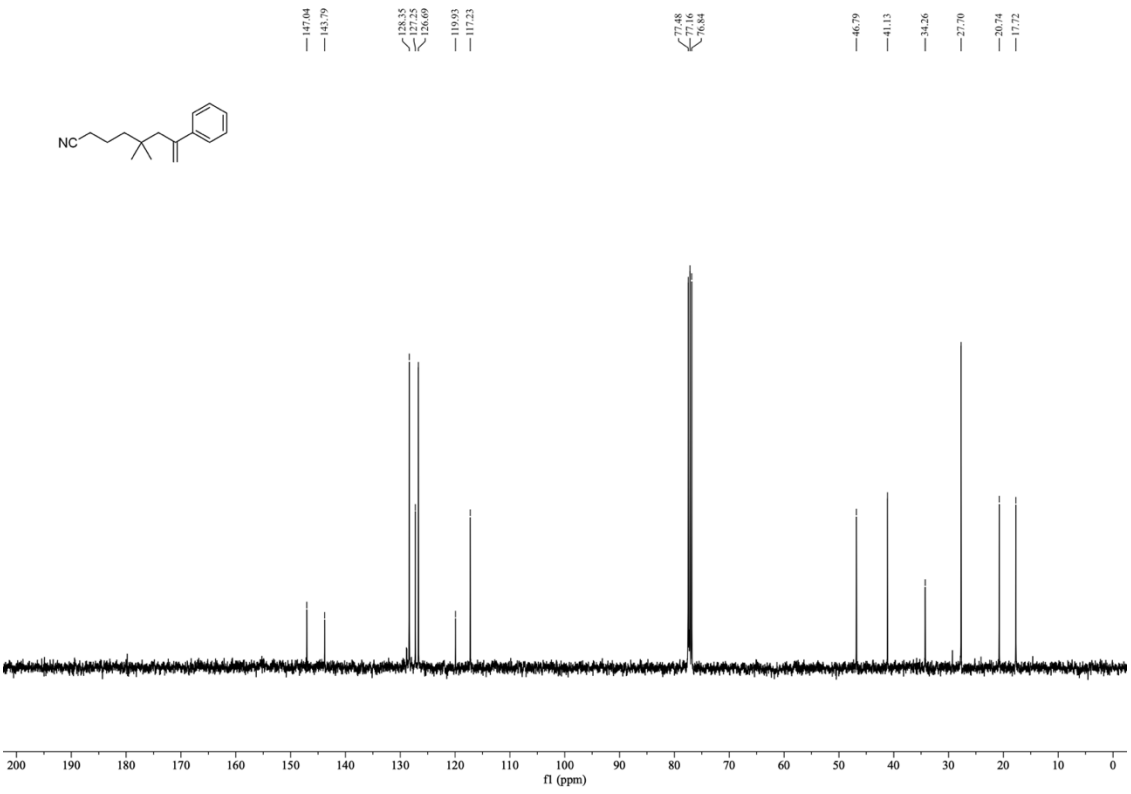
^{1}H NMR Spectrum of Compound 8f (400 MHz, $CDCl_3$)



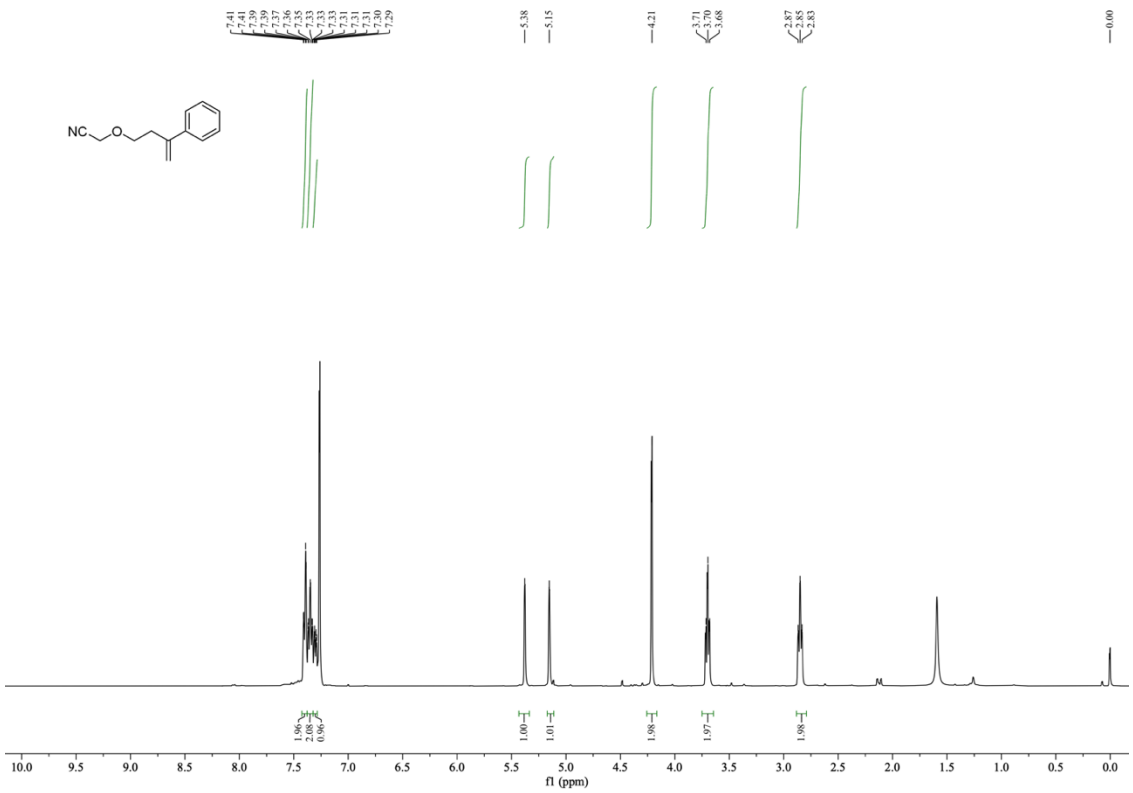
^{13}C NMR Spectrum of Compound 8f (101 MHz, $CDCl_3$)



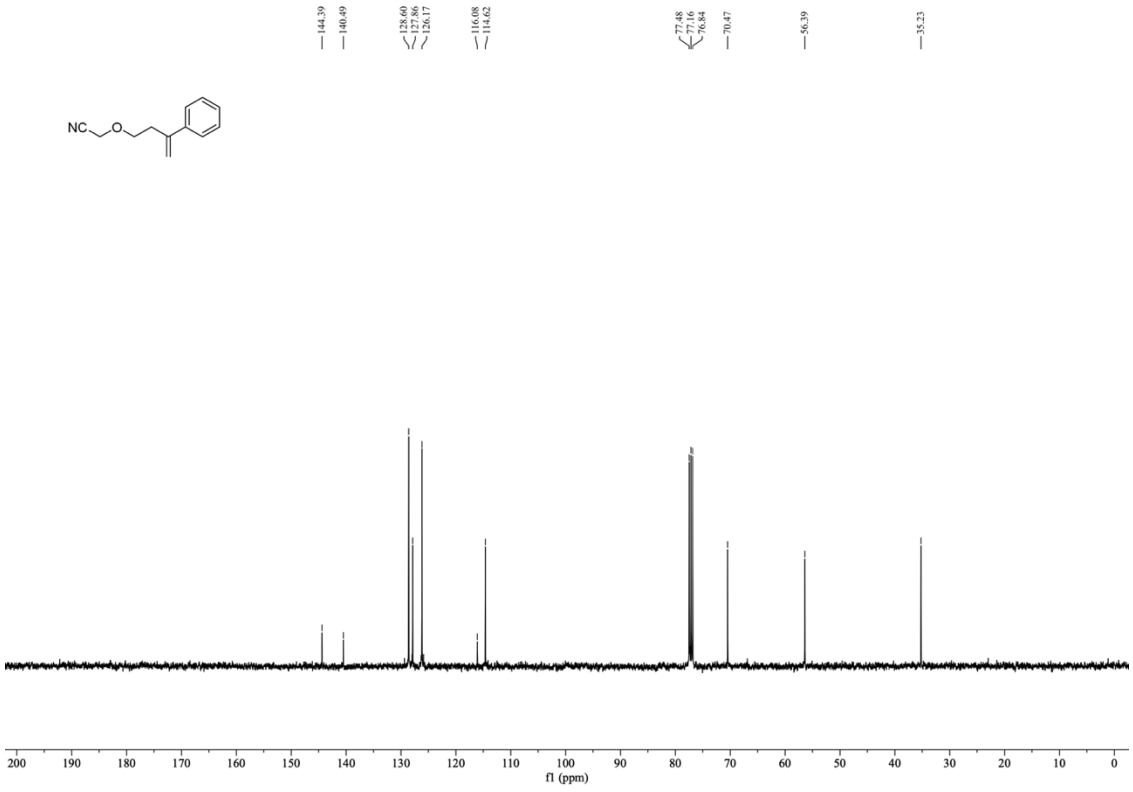
^{1}H NMR Spectrum of Compound 8g (400 MHz, $CDCl_3$)



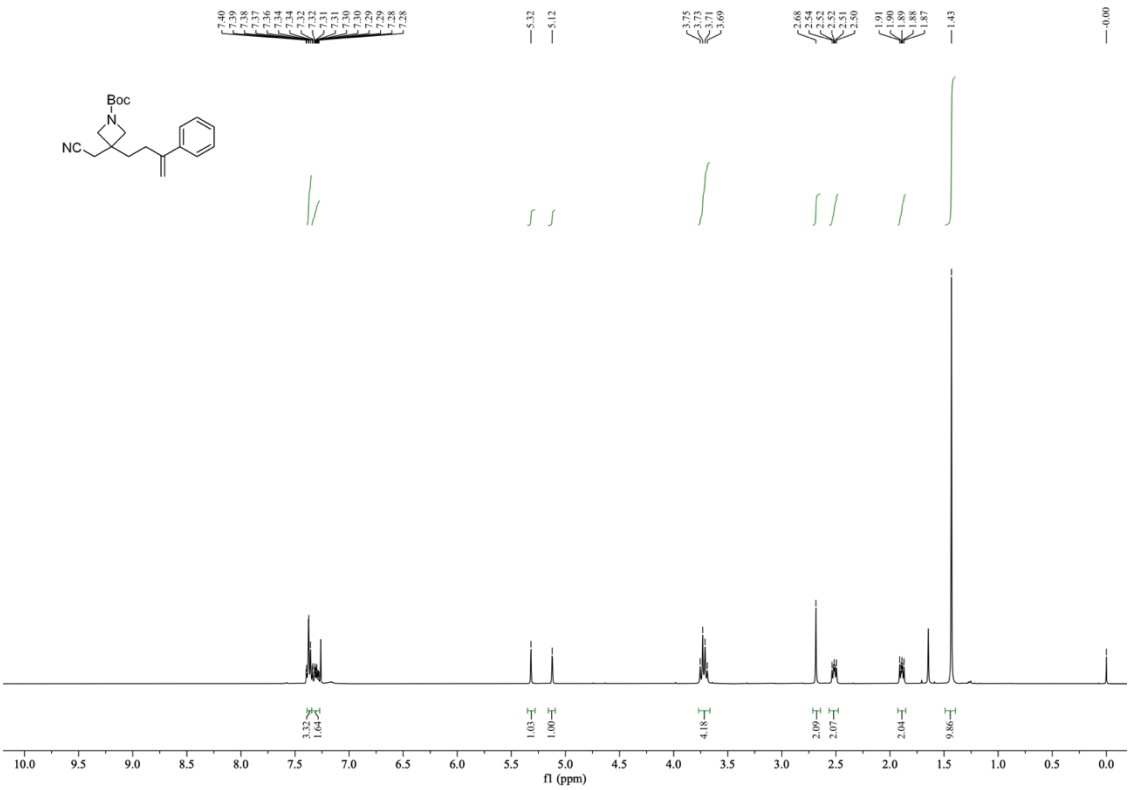
^{13}C NMR Spectrum of Compound 8g (101 MHz, $CDCl_3$)



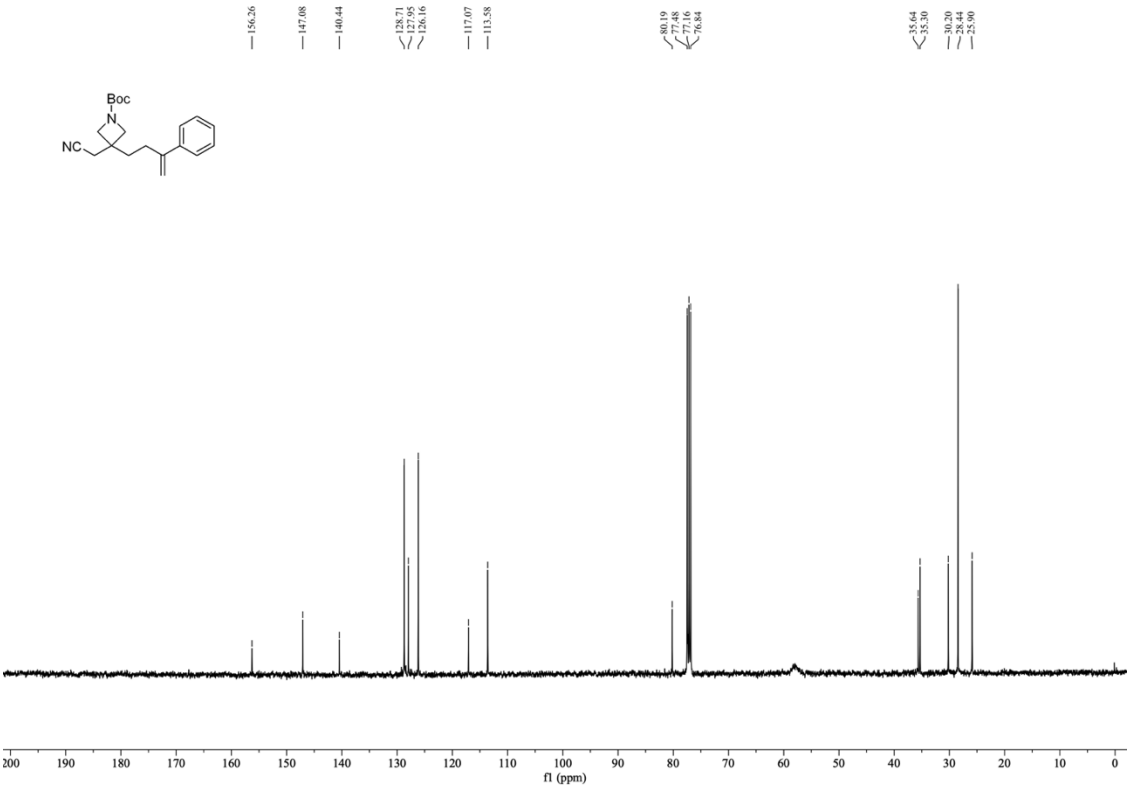
^{1}H NMR Spectrum of Compound 8h (400 MHz, $CDCl_3$)



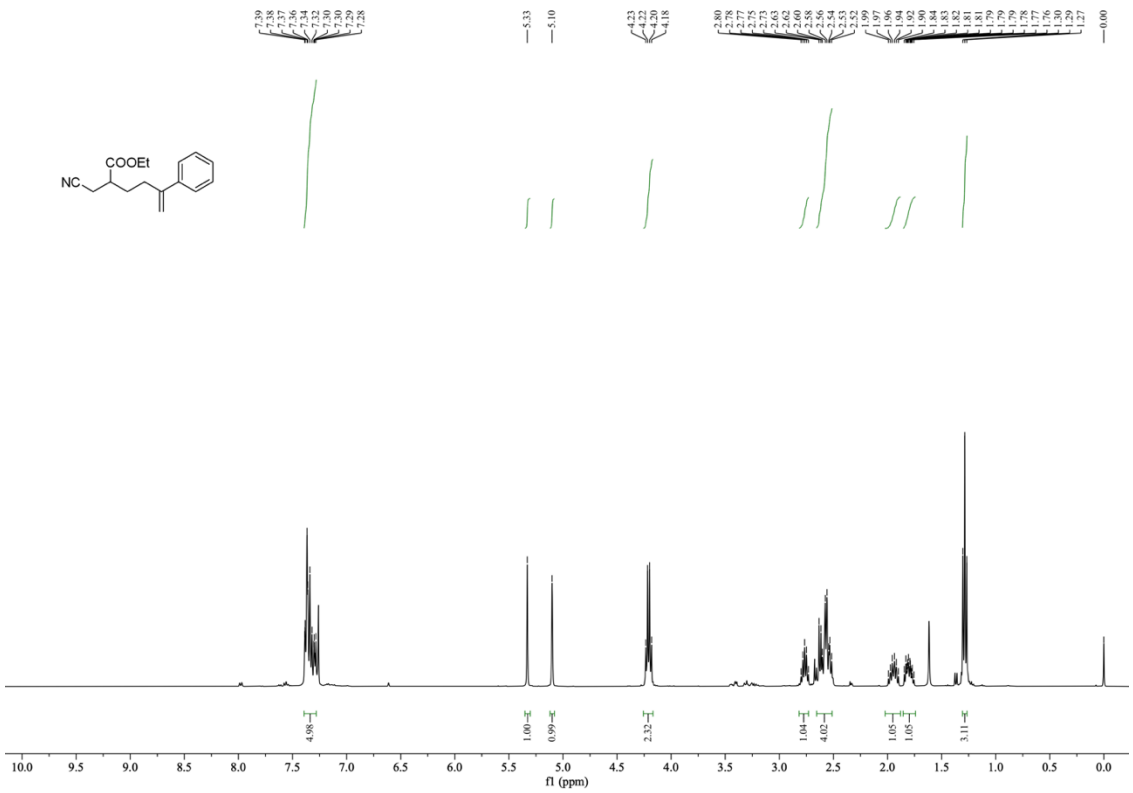
^{13}C NMR Spectrum of Compound 8h (101 MHz, $CDCl_3$)



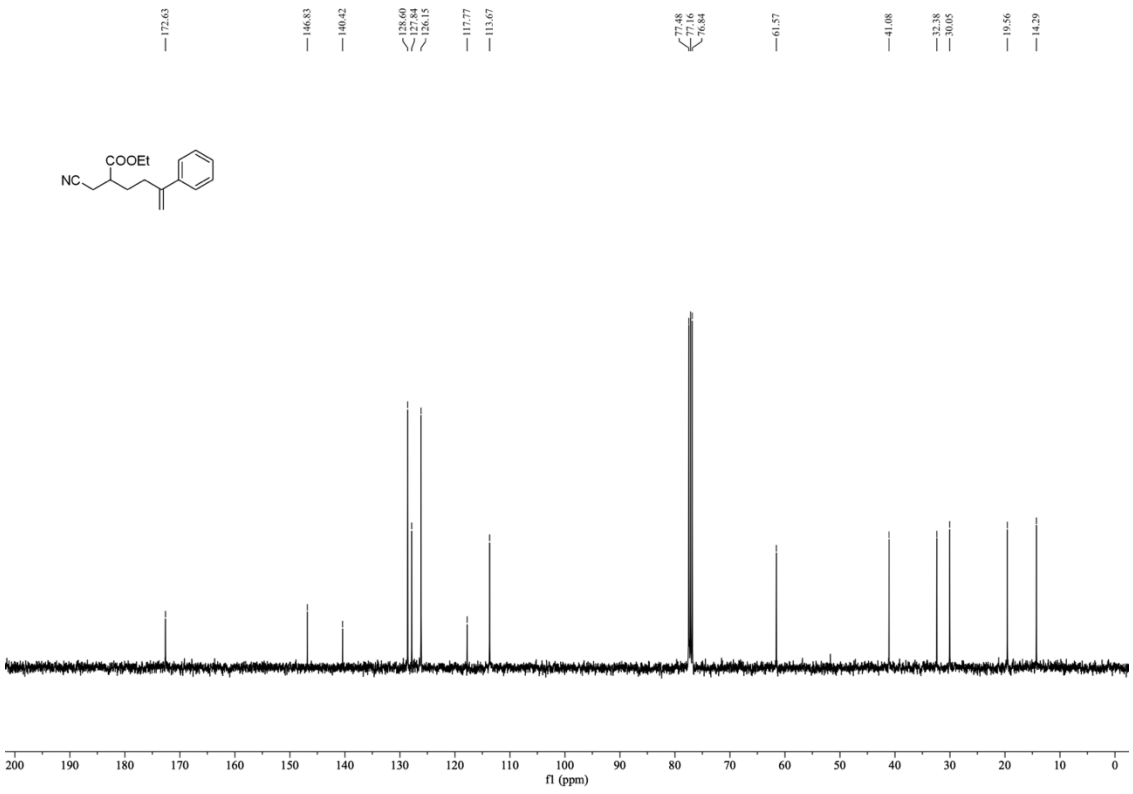
^{1}H NMR Spectrum of Compound 8i (400 MHz, $CDCl_3$)



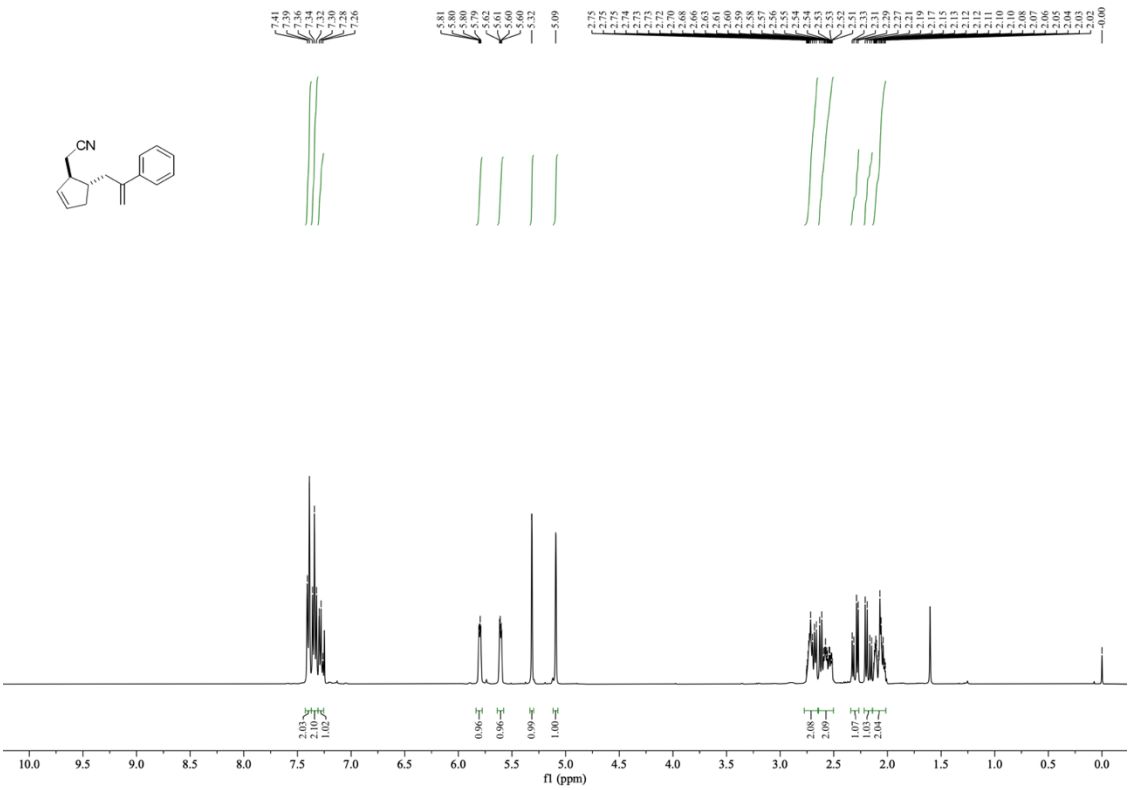
^{13}C NMR Spectrum of Compound 8i (101 MHz, $CDCl_3$)



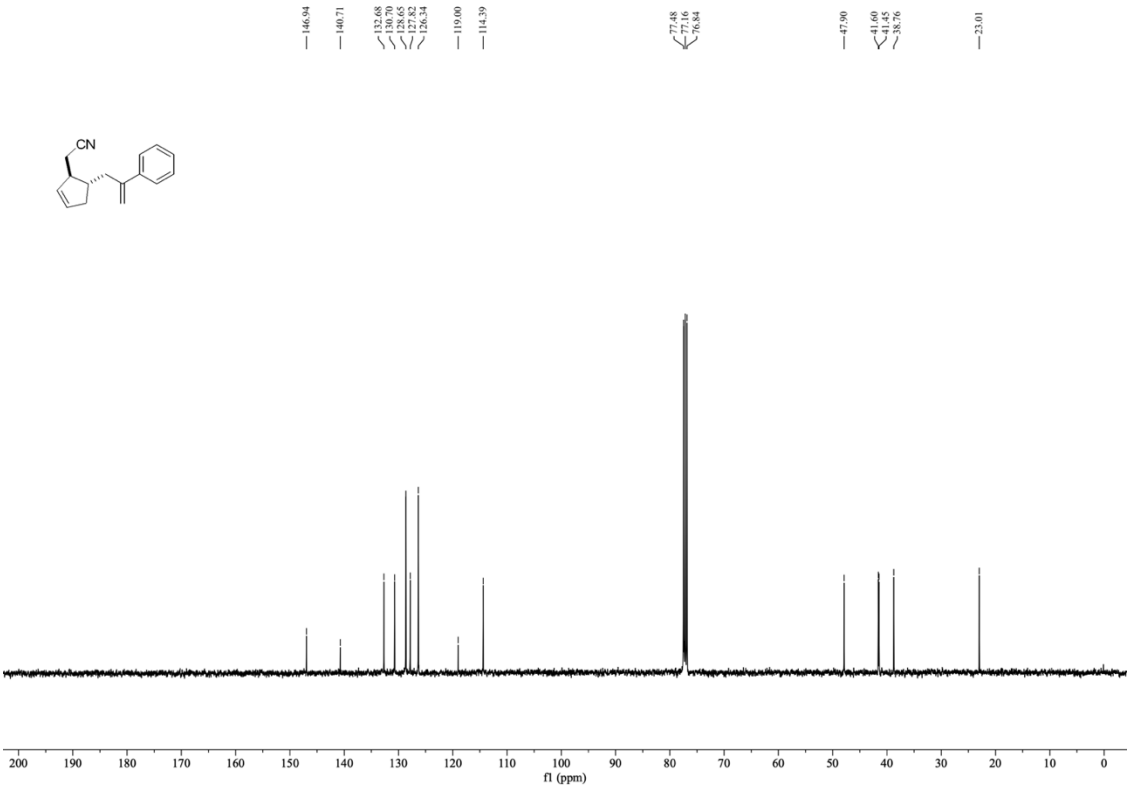
^{1}H NMR Spectrum of Compound 8j (400 MHz, $CDCl_3$)



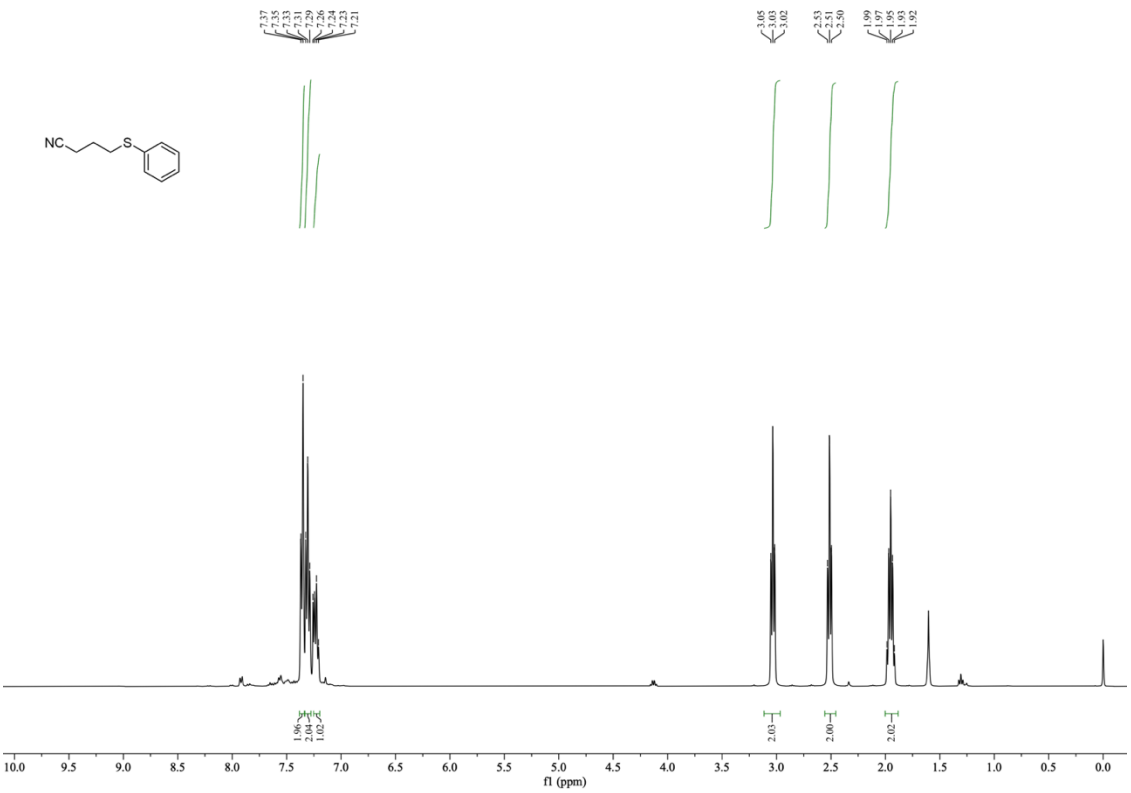
^{13}C NMR Spectrum of Compound 8j (101 MHz, $CDCl_3$)



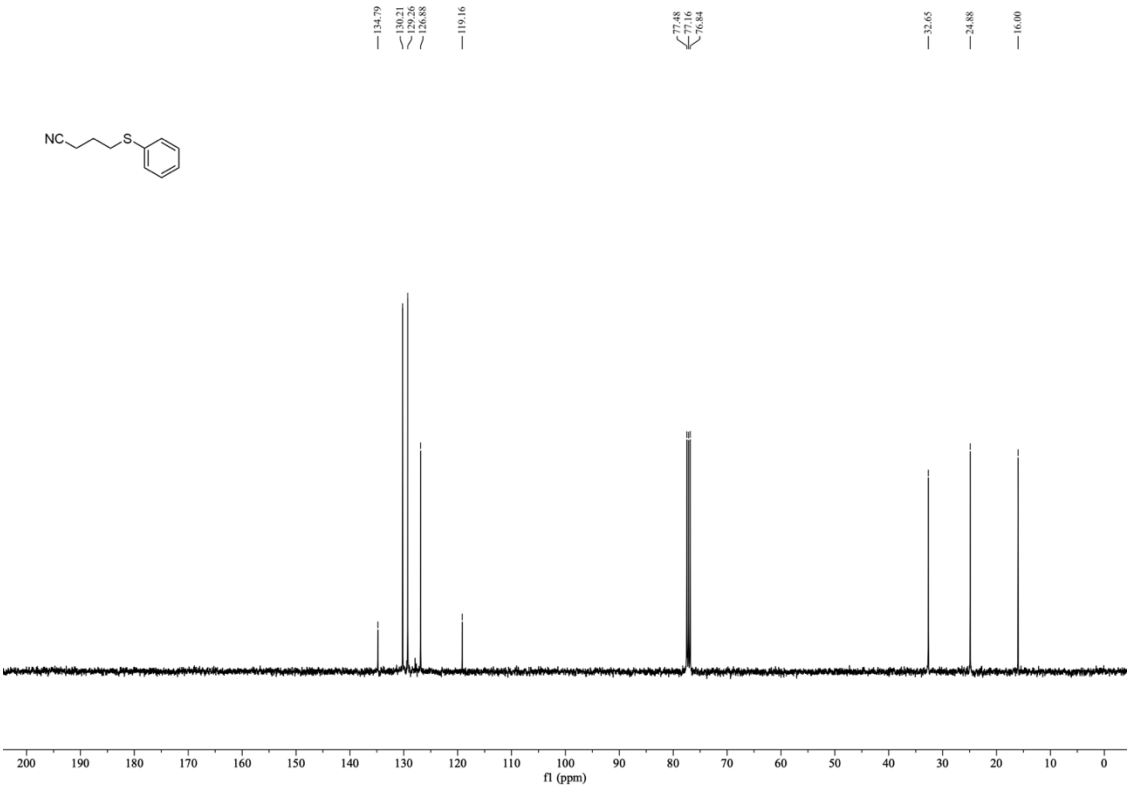
^{1}H NMR Spectrum of Compound 8k (400 MHz, $CDCl_3$)



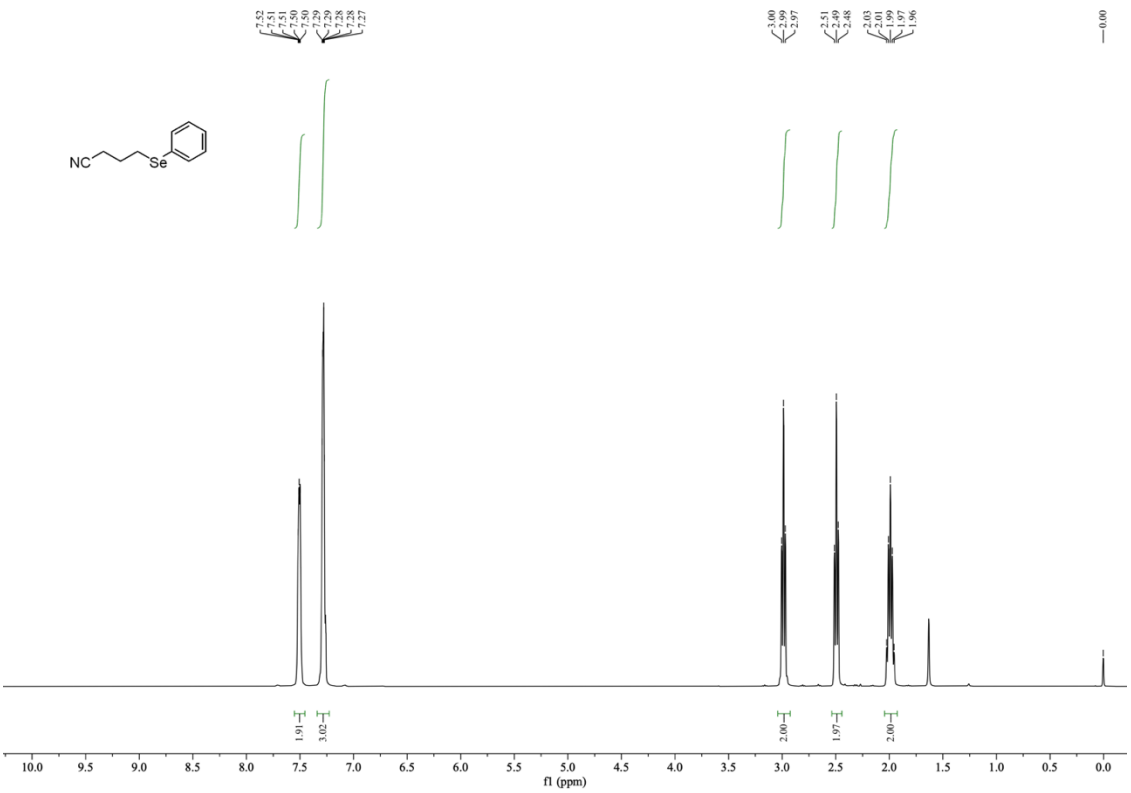
^{13}C NMR Spectrum of Compound 8k (101 MHz, $CDCl_3$)



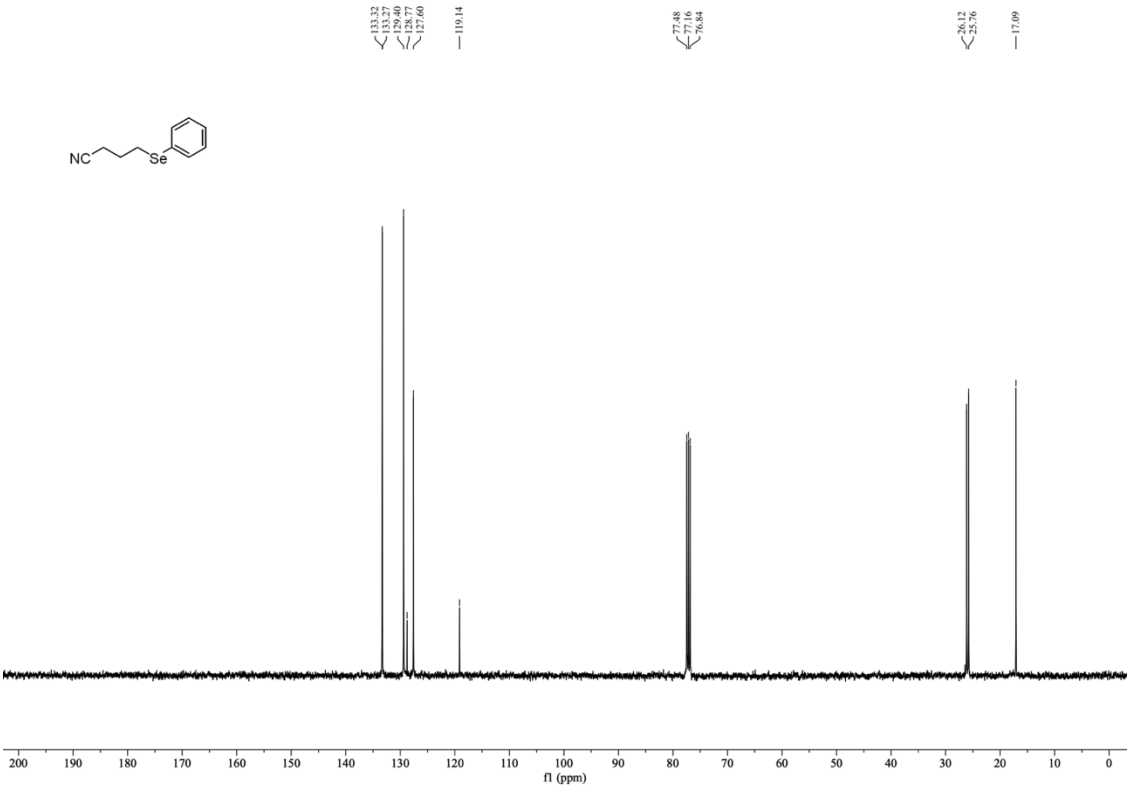
^{1}H NMR Spectrum of Compound 10 (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound 10 (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound 12 (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound 12 (101 MHz, $CDCl_3$)