Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoinduced C-O bond cleavage for copper-catalyzed allenyl radical cyanation

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1. General Information

NMR spectra: ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.0 ppm, t). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants J in Hz, assignment. ^{19}F NMR spectra were recorded on the same Spectrometer. All air- and moisture-sensitive reactions were performed under an atmosphere of Ar in fire dried glassware.

High Resolution Mass Spectrometry (HRMS): All were recorded on Bruker micrOTOF II ESI-TOF using a positive electrospray ionization (EI) or atmospheric pressure chemical ionization (APCI). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualisation was by ultraviolet fluorescence (λ = 254 nm) and/or staining with Phosphomolybdic acid or potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

UV/Vis: Measurements were made on a Shimadzu RF-6000 Spectro Fluorophotometer.

Photoreactor: The photoreactors used in this research were bought from GeAo Chem (Figure S1 and Figure S2: purple LEDs, light intensity = 37.4 mw/cm^2, 1 W for every light bulb; every Schlenk tube was irradiated by 6 light bulbs from the side).

Figure S1. Photoreactor used in this research (2 x 3 W purple LEDs, λ_{max} = 398 nm)

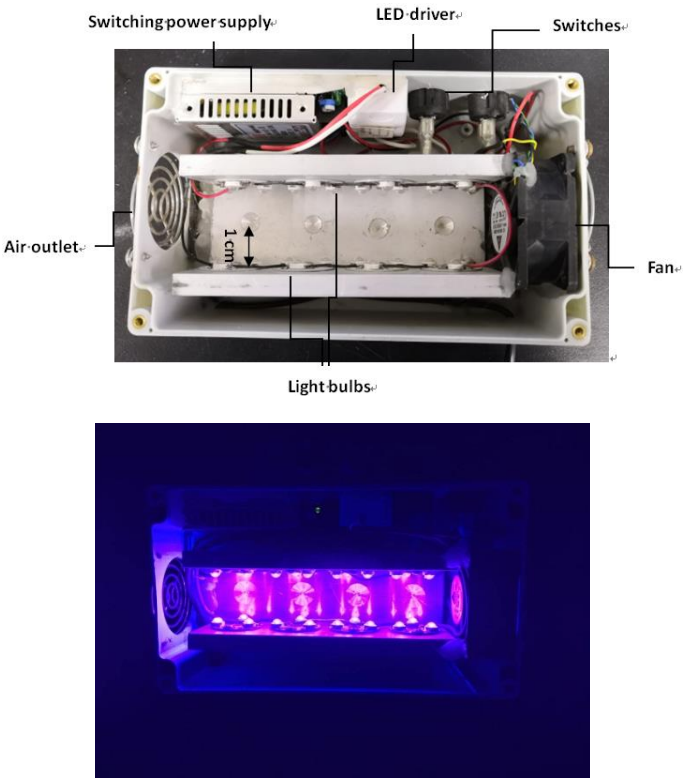
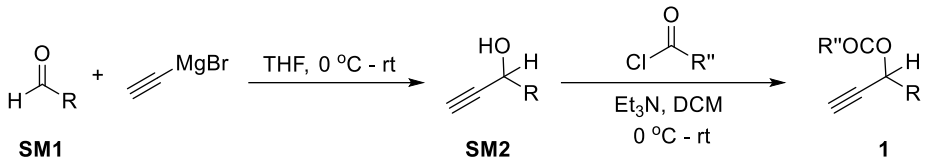


Figure S2. The inside structure of photoreactor

2. Preparation and Characterization of Materials

Materials: Reagents, unless otherwise stated, were used as supplied from commercial sources without further purification. Anhydrous solvent was taken from JC-Meyer solvent purification system. Ligands **L2**, **L3** were purchased from Daicel Chiral Technologies (China) Co., LTD. Ligands **L1**[1], **L4** and photocatalysts[2] were prepared according to literature methods.

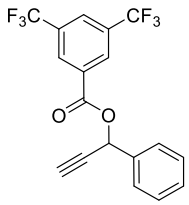
General Procedure A:



Ethynylmagnesium bromide (0.5 M in THF, 60 mL, 30 mmol, 1.5 equiv) was added to a stirred solution of aldehyde (20 mmol) in THF (20 mL) at 0 °C, and the mixture was stirred at 0 °C for 30 min, and the mixture was gradually warmed to rt. The reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash silica gel column chromatography using (pet. ether/ethyl acetate) as eluent to afford secondary propargylic alcohol as a colorless oil.[3]

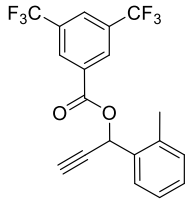
To a solution of propargyl alcohol (20 mmol) in anhydrous CH_2Cl_2 (40 mL) was added Et_3N (40 mmol, 5.58 mL, 2.0 equiv), followed by addition of 3,5-Bis(trifluoromethyl)benzoyl chloride (30 mmol, 5.44 mL, 1.5 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After completion of the reaction (TLC), the reaction was quenched with a saturated $NaHCO_3$ solution. The mixture was diluted with CH_2Cl_2 (25 mL) and sequentially extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash silica gel column chromatography using (pet. ether/ethyl acetate) as eluent to afford propargyl esters.[4]

1-Phenylprop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate(1a)



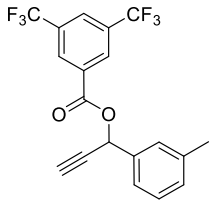
Colourless oil, 65% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.07 (s, 1H), 7.66 – 7.62 (m, 2H), 7.47 – 7.40 (m, 3H), 6.75 (d, *J* = 2.3 Hz, 1H), 2.77 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.8, 135.6, 132.3 (q, *J* = 34.0 Hz), 131.8, 130.0 (m), 129.0, 128.4, 127.7, 127.0, 126.7 (m), 122.8 (q, *J* = 271.0 Hz), 79.3, 76.9, 67.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.95. HRMS (EI) for $C_{18}H_{10}F_6NaO_2$ $[M + Na]^+$: calcd 395.0477, found 395.0461.

1-(*o*-Tolyl)prop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate (**1b**)



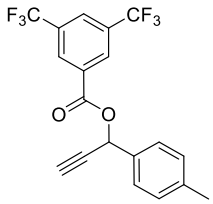
Colorless oil, 70% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.08 (s, 1H), 7.76 – 7.69 (m, 1H), 7.35 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 2.74 (d, *J* = 2.3 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.8, 136.4 (m), 133.6, 132.3 (q, *J* = 33.9 Hz), 131.7, 131.03, 130.0 (m), 129.6, 128.3, 126.7 (m), 126.5, 122.8 (q, *J* = 271.2 Hz), 79.2, 76.5, 65.3, 19.1. **^{19}F NMR** ((376 MHz, $CDCl_3$) δ = -62.95. HRMS (EI) for $C_{19}H_{12}F_6NaO_2$ $[M + Na]^+$: calcd 409.0634, found 409.0637.

1-(m-Tolyl)prop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate (**1c**)



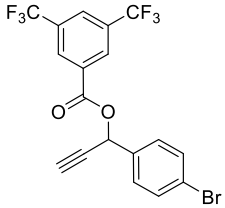
Colorless oil, 77% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.07 (s, 1H), 7.44 – 7.43 (M, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 2.76 (d, *J* = 2.2 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.8, 138.8, 135.5, 132.3 (q, *J* = 34.0 Hz), 131.9, 130.4, 130.0 (m), 128.8, 128.6, 126.7 (m), 125.0, 122.8 (q, *J* = 271.0 Hz), 79.5, 76.5, 67.3, 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.94. HRMS (EI) for $C_{19}H_{12}F_6NaO_2$ $[M + Na]^+$: calcd 409.0634, found 409.0633.

1-(p-Tolyl)prop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate (**1d**)



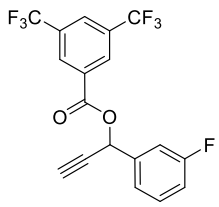
Yellow oil, 78% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.49 (s, 2H), 8.06 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 2H), 6.71 (d, *J* = 2.2 Hz, 1H), 2.75 (d, *J* = 2.2 Hz 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.9, 139.7, 132.7, 132.2 (q, *J* = 34.1 Hz), 131.9, 130.0 (m), 129.6, 128.0, 126.7 (m), 122.8 (q, *J* = 271.3 Hz), 79.5, 76.38, 67.2, 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.94. HRMS (EI) for $C_{19}H_{12}F_6NaO_2$ $[M + Na]^+$: calcd 409.0634, found 409.0643.

1-(4-Bromophenyl)prop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate (**1e**)



Colorless oil, 80% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.48 (s, 2H), 8.08 (s, 1H), 7.58 – 7.51 (m, 4H), 6.70 (d, *J* = 2.3 Hz, 1H), 2.79 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.8, 134.6, 132.4 (q, *J* = 34.0 Hz), 132.1, 131.6, 130.0 (m), 129.7, 126.9 (m), 123.9, 122.8 (q, *J* = 271.0 Hz), 78.8, 77.0, 66.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.98. HRMS (EI) for $C_{18}H_9BrF_6NaO_2$ $[M + Na]^+$: calcd 472.9582, found 472.9588.

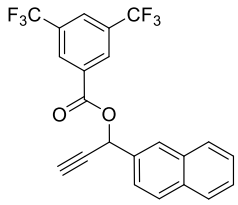
1-(3-Fluorophenyl)prop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate (**1f**)



Colorless oil, 66% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.09 (s, 1H), 7.45 – 7.35 (m, 3H), 7.15 – 7.10 (m, 1H), 6.73 (d, *J* = 2.3 Hz, 1H), 2.79 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.9 (d, *J* = 246.2 Hz), 162.7, 137.9 (d, J = 7.0 Hz), 132.4 (q, *J* = 34.0 Hz), 131.6, 130.5 (d, *J* = 8.0 Hz), 130.0 (m),

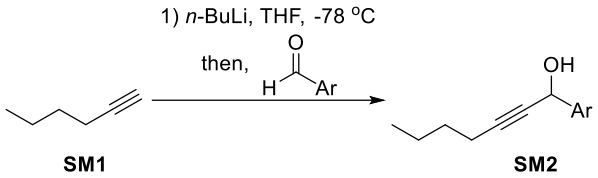
126.8 (m), 124.1, 123.6 (m), 121.4, 116.6 (d, *J* = 21.2 Hz), 115.1 (d, *J* = 23.0 Hz), 78.8, 77.0, 66.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.96, -111.65. HRMS (EI) for $C_{18}H_9F_7NaO_2$ $[M + Na]^+$: calcd 413.0383, found 413.0387.

1-(Naphthalen-2-yl)prop-2-yn-1-yl 3,5-bis(trifluoromethyl)benzoate (**1g**)



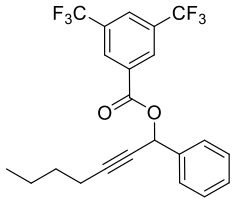
White solid, 81% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.12 (s, 1H), 8.07 (s, 1H), 7.94 – 7.86 (m, 3H), 7.73 – 7.70 (m, 1H), 7.56 – 5.53 (m, 2H), 6.91 (d, *J* = 2.2 Hz, 1H), 2.83 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.9, 133.7, 133.0, 132.8, 132.3 (q, *J* = 34.3 Hz), 131.8, 130.0 (m), 129.0, 128.4, 127.8, 127.1, 126.7 (m), 124.9, 122.8 (q, *J* = 271.1 Hz), 79.3, 76.9, 67.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.94. HRMS (EI) for $C_{22}H_{12}F_6NaO_2$ $[M + Na]^+$: calcd 445.0634, found 445.0642. M.p. 79 - 82 ℃.

General Procedure B:



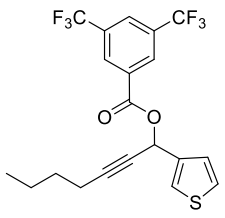
n-BuLi (2.4 M in hexane, 9.2 mL, 22 mmol, 1.1 equiv) was added to a stirred solution of hex-1-yne (1.64 g, 20 mmol) in THF (20 mL) at -78 °C, and the mixture was stirred at -78 °C for 30 min. To the resulting solution was added aldehyde (20 mmol) at -78 °C, and the mixture was gradually warmed to rt. After 12 h, the reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash silica gel column chromatography using (pet. ether/ethyl acetate) as eluent to afford propargylic alcohol. Then, the corresponding propargyl ester could be obtained through the second step of General Procedure A.

1-Phenylhept-2-yn-1-yl-3,5-bis(trifluoromethyl)benzoate (**1i**)



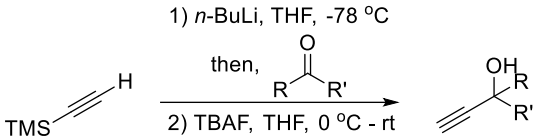
Colorless oil, 81% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.06 (s, 1H), 7.65 – 7.62 (m, 2H), 7.46 – 7.37 (m, 3H), 6.76 (s, 1H), 2.34 – 2.30 (m, 2H), 1.60 – 1.52 (m, 2H), 1.48 – 1.38 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.0, 136.8, 132.6, 132.1 (q, *J* = 34.2 Hz), 132.0, 131.6, 130.0 (m), 129.2, 128.7, 128.0, 126.5 (m), 122.8 (q, *J* = 271.1 Hz), 89.7, 75.85, 68.1, 30.4, 22.0, 18.6, 13.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.94. HRMS (EI) for $C_{22}H_{18}F_6NaO_2$ $[M + Na]^+$: calcd 451.1103, found 451.1098.

1-(Thiophen-3-yl)hept-2-yn-1-yl-3,5-bis(trifluoromethyl)benzoate (**1j**)



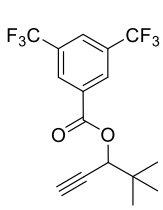
Colorless oil, 73% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.50 (s, 2H), 8.06 (s, 1H), 7.57 (s, 1H), 7.36 – 7.34 (m, 1H), 7.28 – 7.26 (m, 1H), 6.80 (s, 1H), 2.34 – 2.29 (m, 2H), 1.60 – 1.52 (m, 2H), 1.50 – 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.0, 137.8, 132.2 (q, *J* = 34.2 Hz), 132.1, 130.0, 126.9, 126.6, 126.5 (m), 125.3, 122.8 (q, *J* = 271.0 Hz), 88.8, 75.7, 63.4, 30.4, 22.0, 18.5, 13.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.94. HRMS (EI) for $C_{20}H_{16}F_6NaO_2S$ $[M + Na]^+$: calcd 457.0667, found 457.0667.

General Procedure C:



n-BuLi (2.4 M in hexane, 9.2 mL, 22 mmol, 1.1 equiv) was added to a stirred solution of trimethylsilylacetylene (2.04 g, 20 mmol) in THF (20 mL) at -78 °C, and the mixture was stirred at -78 °C for 30 min. To the resulting solution was added aldehyde/ketone (20 mmol) at -78 °C, and the mixture was gradually warmed to rt. The reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under vacuum. Then the crude product obtained above was dissolved in THF (50 mL) and cooled to 0 °C. The resulted mixture was added TBAF (1.0 M in THF, 24.0 mL, 24 mmol, 1.2 equiv) slowly and stirred for 15 min. The reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash silica gel column chromatography using (pet. ether/ethyl acetate) as eluent to afford alcohol. Then, the corresponding propargyl ester could be obtained through the second step of General Procedure A.

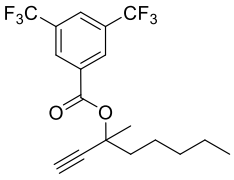
4,4-Dimethylpent-1-yn-3-yl-3,5-bis(trifluoromethyl)benzoate (**1h**)



Colorless oil, 85% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.54 (s, 2H), 8.14 (s, 1H), 5.44 (d, *J* = 2.1 Hz, 1H), 2.56 (d, *J* = 2.2 Hz, 1H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.0, 132.4 (q, *J* = 34.0 Hz), 132.2, 129.8 (m), 126.6 (m), 122.8 (q, *J* = 271.3 Hz), 79.0, 75.0, 73.6, 35.3, 25.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.04. HRMS (EI) for $C_{16}H_{14}F_6NaO_2$ $[M + Na]^+$: calcd 375.0790, found 375.0782.

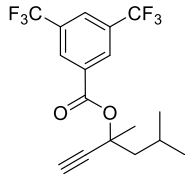
3-Methyloct-1-yn-3-yl 3,5-bis(trifluoromethyl)benzoate (**1k**)

Colorless oil, 71% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.44 (s, 2H), 8.06 (s, 1H), 2.65 (s, 1H), 2.18 – 2.10 (m, 1H), 2.02 – 1.95 (m, 1H), 1.85 (s, 3H), 1.64 – 1.52



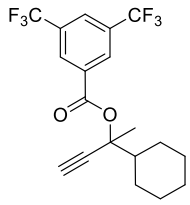
(m, 3H), 1.41 – 1.35 (m, 4H), 0.94 – 0.91 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.1, 133.1, 132.1 (q, *J* = 33.8 Hz), 130.0 (m), 126.2 (m), 122.9 (q, *J* = 271.9 Hz), 83.0, 77.4, 74.3, 41.3, 31.6, 26.4, 23.8, 22.5, 13.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.01. HRMS (EI) for $C_{18}H_{18}F_6NaO_2$ $[M + Na]^+$: calcd 403.1103, found 403.1114.

3,5-Dimethylhex-1-yn-3-yl 3,5-bis(trifluoromethyl)benzoate (**1l**)



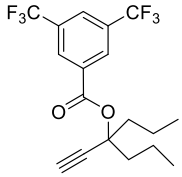
Colorless oil, 76% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.46 (s, 2H), 8.06 (s, 1H), 2.67 (s, 1H), 2.12 – 2.02 (m, 2H), 1.96 – 1.90 (m, 1H), 1.87 (s, 3H), 1.09 – 1.04 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.1, 133.2, 132.2 (q, *J* = 34.0 Hz), 129.7 (m), 126.2 (m), 122.9 (q, *J* = 271.2 Hz), 83.1, 77.5, 74.6, 49.6, 27.1, 25.0, 24.1, 23.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.05. $C_{17}H_{16}F_6NaO_2$ $[M + Na]^+$: calcd 389.0947, found 389.0952.

2-Cyclohexylbut-3-yn-2-yl 3,5-bis(trifluoromethyl)benzoate (**1m**)



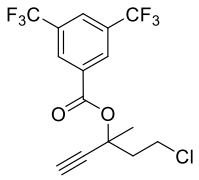
Colorless oil, 65% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.44 (s, 2H), 8.06 (s, 1H), 2.65 (s, 1H), 2.12 – 2.04 (m, 2H), 1.90 – 1.85 (m, 3H), 1.82 (s, 3H), 1.74 (d, *J* = 12.8 Hz, 1H), 1.36 – 1.17 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 133.3, 132.1 (q, *J* = 34.0 Hz), 129.6 (m), 126.2 (m), 122.9 (q, *J* = 271.3 Hz), 82.3, 80.8, 75.0, 46.8, 27.6, 27.1, 26.2, 26.1, 23.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.00. $C_{19}H_{18}F_6NaO_2$ $[M + Na]^+$: calcd 415.1103, found 415.1100.

4-Ethynylheptan-4-yl 3,5-bis(trifluoromethyl)benzoate (**1n**)



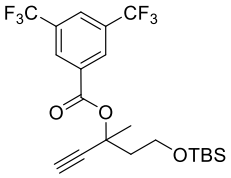
Colorless oil, 67% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.43 (s, 2H), 8.06 (s, 1H), 2.66 (s, 1H), 2.21 – 2.13 (m, 2H), 2.08 – 2.00 (m, 2H), 1.61 – 1.46 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 133.1, 132.2 (q, *J* = 34.0 Hz), 129.6 (m), 126.3 (m), 122.9 (q, *J* = 271.9 Hz), 82.4, 81.0, 75.0, 40.4, 17.4, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.99. HRMS (EI) for $C_{18}H_{18}F_6NaO_2$ $[M + Na]^+$: calcd 403.1103, found, 403.1102.

5-Chloro-3-methylpent-1-yn-3-yl 3,5-bis(trifluoromethyl)benzoate (**1o**)



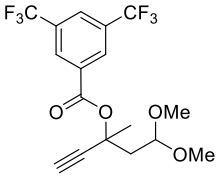
White solid, 74% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.49 (s, 2H), 8.12 (s, 1H), 3.84 (t, *J* = 7.9 Hz, 2H), 2.77 (d, *J* = 2.1 Hz, 1H), 2.73 (2, 1H), 2.72 – 2.55 (m, 1H), 1.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 132.6, 132.3 (q, *J* = 34.1 Hz), 129.7 (m), 126.5 (m), 122.8 (q, *J* = 271.3 Hz), 81.4, 75.7, 75.7, 44.0, 39.1, 26.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.02. HRMS (EI) for $C_{15}H_{11}ClF_6NaO_2$ $[M + Na]^+$: calcd 395.0244, found 395.0261. M.p. 37 - 39 ℃.

5-((*tert*-Butyldimethylsilyl)oxy)-3-methylpent-1-yn-3-yl 3,5-bis(trifluoromethyl) benzoate (**1p**)



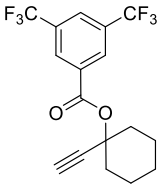
Yellow oil, 68% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.44 (s, 2H), 8.06 (s, 1H), 3.99 – 3.91 (m, 2H), 2.68 (s, 1H), 2.44 – 2.37 (m, 1H), 2.32 – 2.25 (m, 1H), 1.90 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 133.0, 132.3 (q, *J* = 34.0 Hz), 129.7(m), 126.3 (m), 122.8 (q, *J* = 271.0 Hz), 82.5, 76.1, 74.8, 59.1, 43.5, 27.2, 25.8, 18.3, -5.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.98. HRMS (EI) for $C_{21}H_{26}F_6O_3NaSi$ $[M + Na]^+$: calcd 491.1448, found 491.1438.

5,5-Dimethoxy-3-methylpent-1-yn-3-yl 3,5-bis(trifluoromethyl)benzoate (**1q**)



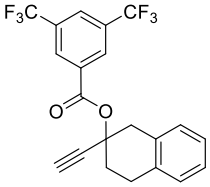
light yellow crystal, 79% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.49 (s, 2H), 8.07 (s, 1H), 4.82 (t, *J* = 4.9 Hz, 1H), 3.36 (s, 6H), 2.74 (s, 1H), 2.54 – 2.49 (m, 1H), 2.37 – 2.32 (m, 1H), 1.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 133.0, 132.3 (q, *J* = 34.2 Hz), 129.7 (m), 126.2 (m), 122.8 (q, *J* = 271.0 Hz), 101.74, 82.39, 74.93, 74.87, 52.91, 52.75, 43.72, 27.12. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.00. HRMS (EI) for $C_{17}H_{16}F_6NaO_4$ $[M + Na]^+$: calcd 421.0845, found 421.0848. M.p. 40 - 43 ℃.

1-Ethynylcyclohexyl 3,5-bis(trifluoromethyl)benzoate (**1r**)



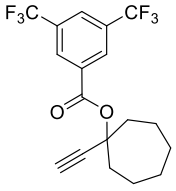
Yellow oil, 80% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.47 (s, 2H), 8.06 (s, 1H), 2.70 (s, 1H), 2.35 – 2.29 (m, 2H), 2.09 – 2.03 (m, 2H), 1.76 – 1.70 (m, 4H), 1.63 – 1.58 (m, 1 H), 1.46 – 1.38 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.9, 133.1, 132.3 (q, *J* = 34.0 Hz,) 129.7 (m), 126.2 (m), 122.8 (q, *J* = 271.1 Hz), 82.7, 77.6, 75.3, 37.0, 25.0, 22.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.98. HRMS (EI) for $C_{17}H_{14}F_6NaO_2$ $[M + Na]^+$: calcd 387.0790, found 387.0790.

2-Ethynyl-1,2,3,4-tetrahydronaphthalen-2-yl 3,5-bis(trifluoromethyl)benzoate (**1s**)



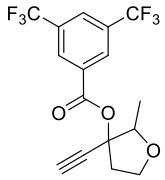
Pink solid, 71% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.40 (s, 2H), 8.04 (s, 1H), 7.21 – 7.09 (m, 4H), 3.69 – 3.48 (m, 2H), 3.18 – 3.10 (m, 1H), 3.03 – 2.96 (m, 1H), 2.65 (s, 1H), 2.60 – 2.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.2, 134.2, 132.1 (q, *J* = 34.1 Hz), 131.9, 129.7 (m), 129.2, 128.5, 126.60, 126.4 (m), 126.3, 122.8 (q, *J* = 271.3 Hz), 82.0, 75.4, 75.0, 41.0, 33.5, 26.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.01. HRMS (EI) for $C_{21}H_{14}F_6NaO_4$ $[M + Na]^+$: calcd 435.0790, found 435.0788. M.p. 81 - 86 ℃.

1-Ethynylcycloheptyl 3,5-bis(trifluoromethyl)benzoate (**1t**)



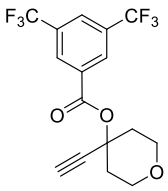
Yellow oil, 83% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.46 (s, 2H), 8.06 (s, 1H), 2.69 (s, 1H), 2.48 – 2.41 (m, 2H), 2.36 – 2.25 (m, 2H), 1.77 – 1.60 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 133.2, 132.1 (q, *J* = 34.0 Hz), 129.7 (m), 126.2 (m), 122.8 (q, *J* = 271.3 Hz), 83.9, 81.0, 74.5, 40.2, 28.2, 22.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.99. HRMS (EI) for $C_{18}H_{16}F_6NaO_4$ $[M + Na]^+$: calcd 401.0947, found 401.0948.

3-Ethynyl-2-methyltetrahydrofuran-3-yl 3,5-bis(trifluoromethyl)benzoate (**1u**)



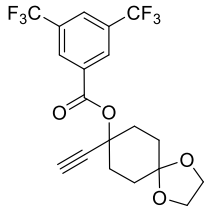
White solid, 62% isolated yield, d.r. = 6:1, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.47 (s, 2H, major), 8.46 (s, 2H, minor),8.09 (s, 1H, major+minor), 4.31 (q, *J* = 8.0 Hz, 1 H, minor), 4.15 – 3.90 (m, 3H, major+minor), 2.86 – 2.68 (m, 3H, major+minor), 1.54 (d, *J* = 8.0 Hz, 3H, major), 1.50 (d, *J* = 8.0 Hz, 3H, minor). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.4, 162.3, 132.5 (m), 132.2 (q, *J* = 34.1 Hz), 129.7 (m), 126.7(m), 122.8 (q, *J* = 272.0 Hz), 83.8, 83.4, 82.1, 80.4, 79.6, 79.1, 77.4, 77.2, 76.8, 75.7, 65.9, 65.7, 40.4, 39.7, 17.8, 13.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.06. HRMS (EI) for $C_{16}H_{12}F_6NaO_3$ $[M + Na]^+$: calcd 389.0583, found 389.0608. M.p. 78 - 83 ℃.

4-Ethynyltetrahydro-2H-pyran-4-yl 3,5-bis(trifluoromethyl)benzoate (**1v**)



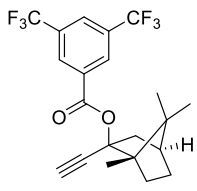
Colorless oil, 74% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.46 (d, J = 1.6 Hz, 2H), 8.08 (s, 1H), 3.95 (dt, *J* = 12.2, 4.3 Hz, 2H), 3.82 (m, 2H), 2.78 (s, 1H), 2.44 (m, 2H), 2.21 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.9, 132.6, 132.2 (q, *J* = 34.0 Hz), 129.7 (m), 126.5 (m), 122.8 (q, *J* = 272.1 Hz), 81.3, 76.4, 74.7, 64.4, 37.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.99. HRMS (EI) for $C_{16}H_{12}F_6NaO_3$ $[M + Na]^+$: calcd 389.0583, found 389.0571.

8-Ethynyl-1,4-dioxaspiro[4.5]decan-8-yl 3,5-bis(trifluoromethyl)benzoate (**1w**)



Colorless oil, 75% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.45 (d, *J* = 1.7 Hz, 2H), 8.07 (s, 1H), 3.98 (m, 4H), 2.70 (s, 1H), 2.39 (m, 4H), 1.87 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.0, 132.8, 132.2 (q, *J* = 34.1 Hz), 129.7 (m), 126.4 (m), 122.8 (q, *J* = 271.9 Hz), 107.2, 81.8, 76.0, 75.4, 64.5, 64.4, 34.4, 31.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.00. HRMS (EI) for $C_{19}H_{16}F_6NaO_4$ $[M + Na]^+$: calcd 445.0845, found 445.0855.

(1S,2R,4S)-2-Ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3,5-bis (trifluoromethyl) benzoate (**1x**)



Colorless oil, 60% isolated yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.43 (s, 2H), 8.06 (s, 1H), 2.60 – 2.55 (m, 2H), 2.27 (d, *J* = 14.7 Hz, 1H), 2.19 – 2.13 (m, 1H), 1.86 (t, *J* = 4.4 Hz, 1H), 1.81 – 1.73 (m, 1H), 1.63 – 1.57 (m, 1H), 1.30 – 1.24 (m, 1H), 1.18 (s, 3H), 1.03 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.6, 133.3, 132.2 (q,

J = 34.2 Hz), 129.5 (m), 126.30 (m), 122.8 (q, *J* = 271.9 Hz), 85.5, 82.6, 73.7, 54.7, 48.4, 46.8, 45.4, 32.0, 26.3, 21.2, 20.7, 11.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.97. HRMS (EI) for $C_{21}H_{20}F_6NaO_2$ $[M + Na]^+$: calcd 441.1260, found 441.1244.

References

[1] (a) C. Liu, J.-C. Yi, Z.-B. Zheng, Y. Tang, L.-X. Dai, S.-L. You, *Angew. Chem. Int. Ed*. 2016, **55**, 751 – 754. (b) N. V. Hanhan, N. R. Ball-Jones, N. T. Tran, A. K. Franz, *Angew. Chem. Int. Ed.* 2012, **51**, 989 – 992.

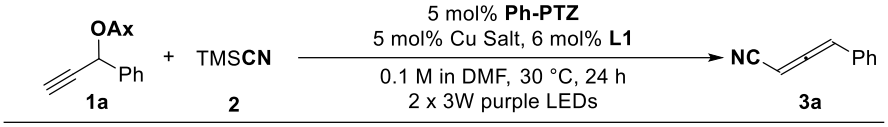
[2] X.-C. Pan, C. Fang, M. Fantin, N. Malhotra, W. Y. So, L. A. Peteanu, A. A. Isse, A. Gennaro, P. Liu, K. Matyjaszewski, *J. Am. Chem. Soc.* 2016, **138**, 2411 – 2425.

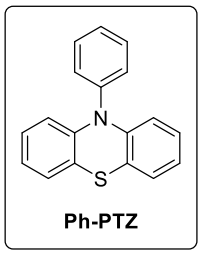
[3] F. Schömberg, Y. Zi, I. Vilotijevic, *Chem. Commun.* 2018, **54**, 3266 – 3269.

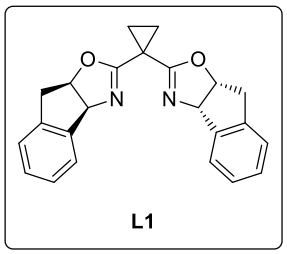
[4] D. Rackl, V. Kais, Peter. Kreitmeier, O. Reiser, *Beilstein J. Org. Chem.* 2014, **10**, 2157 – 2165.

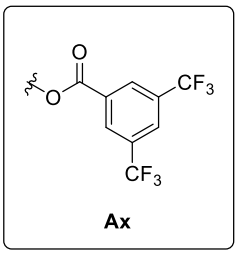
3. Details for Condition Optimization

Table S1. The effect of copper salts[a]





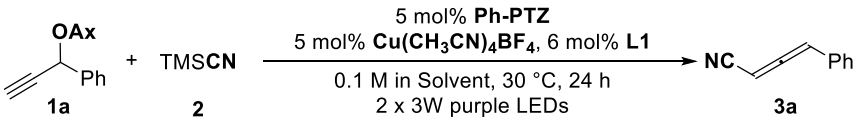




Entry	Cu Salt	Yield/%[b]
1	CuBr	65
2	$Cu(MeCN)_4BF_4$	83
3	$Cu(MeCN)_4PF_6$	70
4	Cu(OAc)	Trace
5	$Cu(OTf)_2$	73

[a]**1a** (0.2 mmol), **2** (0.6 mmol, 3 equiv), Cu salt (0.01 mmol, 5 mol%), chiral ligand **L1** (0.012 mmol, 6 mol%) and organic photocatalyst **Ph-PTZ** (0.01 mmol, 5 mol%) in 2.0 mL of DMF for 24 h under the irradiation of 2 x 3 W purple LEDs. [b]^{1}HNMR yield using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. The effect of solvents[a]

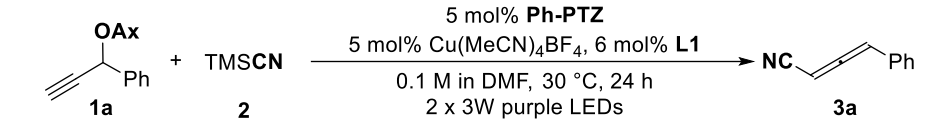


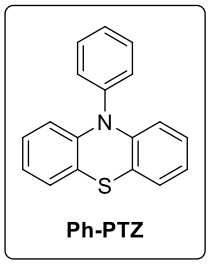
Entry	Solvent	Yield/%[b]
1	THF	42
2[e]	DCM	36
3	MeCN	42
4	DMF	83
5	MeOH	18

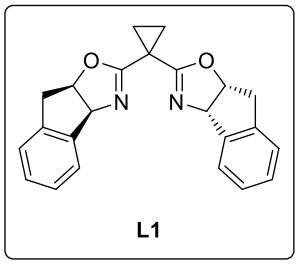
[a]**1a** (0.2 mmol), **2** (0.6 mmol, 3 equiv), Cu salt (0.01 mmol, 5 mol%), chiral ligand **L1** (0.012 mmol, 6 mol%) and organic photocatalyst **Ph-PTZ** (0.01 mmol, 5 mol%) in 2.0 mL of solvent for 24 h under the irradiation of 2 x 3 W purple LEDs. [b]^{1}HNMR yield using 1,3,5-trimethoxybenzene as an internal standard.

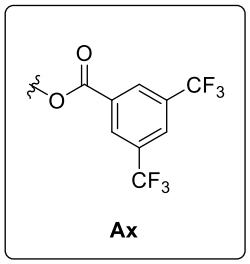
4. General Procedures and Characterization Data of Products

4.1 General Procedures





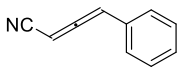




General procedure D: In an argon-filled glove box, a flame-dried 10 ml Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with **$Cu(CH_3CN)_4BF_4$** (3.15 mg, 0.01 mmol) and **L1** (4.28 mg, 0.012 mmol), followed by the addition of DMF (0.5 mL). Then the mixture was stirred at room temperature for 30 min. The vial was closed and the Schlenk tube was removed from the glove box, to the resulting mixture were added propargyl ester **1** (0.20 mmol), DMF (1.5 mL) and organic photocatalyst **Ph-PTZ** (0.01 mmol). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, **TMSCN** (0.6mmol) was added into the mixture. At last, the mixture was stirred at a distance of ~1 cm from a 2 x 3 W purple LEDs at 30 ºC about 24 h until the reaction was completed, as monitored by TLC analysis. Then the reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 100/1) to afford the desired product. Note: Products 3a to 3h are extremely unstable at room temperature and the temperature should not exceed 20 ℃ when the solvent is removed under vacuum.

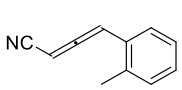
4.2 Characterization Data of Products

4-Phenylbuta-2,3-dienenitrile (**3a**)



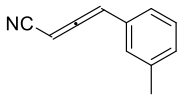
83% (23.4 mg) isolated yield, light yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.29 (m, 5H), 6.72 (d, *J* = 6.7 Hz, 1H), 5.67 (d, *J* = 6.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 217.8, 129.3, 129.1, 128.2, 127.9, 112.5,100.0, 71.3. HRMS (EI) for $C_{10}H_{11}N_2$ $[M+NH_4]^+$: calcd 159.0917, found 159.0919. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3006; 2923; 2360; 2226; 1949; 1733; 1495; 1459; 1280; 1241; 1140; 913; 869; 773; 692.

4-(*o*-Tolyl)buta-2,3-dienenitrile (**3b**)



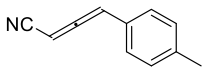
82% (25.5 mg) isolated yield, light yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30 – 7.28 (m, 1H), 7.24 – 7.18 (m, 3H), 6.91 (d, *J* = 6.8 Hz, 1H), 5.63 (d, *J* = 6.7 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 218.3, 136.3, 130.9, 129.0, 128.6, 127.9, 126.6, 112.8, 97.5, 70.4, 20.0. HRMS (EI) for $C_{11}H_{13}N_2$ $[M+NH_4]^+$: calcd 173.1073, found 173.1069. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3006; 2981; 2872; 2226; 1945; 1736; 1460; 1282; 1240; 1142; 1045; 931; 769; 741.

4-(*m*-Tolyl)buta-2,3-dienenitrilee (**3c**)



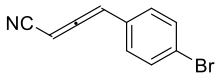
88% (27.3 mg) isolated yield, light yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 – 7.25 (m, 1H), 7.15 – 7.08 (m, 3H), 6.68 (d, *J* = 6.7 Hz, 1H), 5.67 (d, *J* = 6.7 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 217.9, 138.9, 129.9, 129.2, 129.0, 128.5, 125.1, 112.6, 100.0, 71.2, 21.3. HRMS (EI) for $C_{11}H_{13}N_2$ $[M+NH_4]^+$: calcd 173.1073, found 173.1080. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2998; 2360; 2229; 1949; 1742; 1588; 1487; 1280; 1238; 1070; 1009; 871; 827; 749.

4-(*p*-Tolyl)buta-2,3-dienenitrile (**3d**)



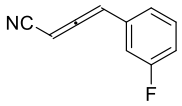
95% (29.5 mg) isolated yield, light yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 (s, 4H), 6.69 (d, *J* = 6.7 Hz, 1H), 5.65 (d, *J* = 6.7 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 218.0, 139.2, 129.8, 127.8, 126.2, 112.7, 99.8, 71.1, 21.3. HRMS (EI) for $C_{11}H_{13}N_2$ $[M+NH_4]^+$: calcd 173.1073, found 173.1070. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3006; 2923; 2850; 2363; 2231; 1949; 1730; 1591; 1490; 1448; 1283; 1140; 877; 787; 745; 681.

4-(4-Bromophenyl)buta-2,3-dienenitrile (**3e**)



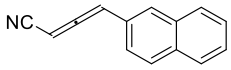
78% (34.3 mg) isolated yield, light yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50 (d, J = 8.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 6.6 Hz, 1H), 5.69 (d, *J* = 6.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 217.7, 132.3, 129.3, 128.3, 123.1, 112.1, 99.2, 71.8. HRMS (EI) for $C_{10}H_{10}BrN_2$ $[M+NH_4]^+$: calcd 237.0022, found 237.0031. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2925, 2219, 1947, 1586, 1486, 1438, 1069, 1009, 878, 818, 670, 496.

4-(3-Fluorophenyl)buta-2,3-dienenitrile (**3f**)



71% (22.6 mg) isolated yield, light yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39 – 7.32 (m, 1H), 7.10 – 6.99 (m, 3H), 6.63 (d, *J* = 6.7 Hz, 1H), 5.64 (d, *J* = 6.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 217.7, 163.0 (d, *J* = 246.0 Hz), 131.6 (d, *J* = 7.8 Hz), 130.7 (d, *J* = 7.7 Hz), 123.7 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 21.2 Hz), 114.6 (d, *J* = 20.0 Hz), 112.1, 99.3 (d, *J* = 2.9 Hz), 71.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -111.98. HRMS (EI) for $C_{10}H_{10}FN_2$ $[M+NH_4]^+$: calcd 177.0823, found 177.0819. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2959, 2929, 2867, 2219, 1970, 1601, 1508, 1227, 1157, 833, 516

4-(Naphthalen-2-yl)buta-2,3-dienenitrile (**3g**)

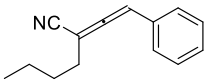


71% (27.2 mg) isolated yield, white solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.84 – 7.80 (m, 3H), 7.72 (s, 1H), 7.53 – 7.48 (m, 2H), 7.41 – 7.38 (m, 1H), 6.80 (d, *J* = 6.7 Hz, 1H), 5.67 (d, *J* = 6.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 218.4, 133.4, 129.0, 128.0, 127.8, 127.7, 126.9, 126.8, 126.7, 124.6, 112.6, 100.3, 71.6. HRMS (EI) for $C_{14}H_{13}N_2$ $[M+NH_4]^+$: calcd 209.1073, found 209.1066. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3055; 2924; 2368; 2215; 1600; 1508; 1367; 1271; 816; 743. We cannot provide the melting point for **3g** because this compound was not stable under heating condition.

5,5-Dimethylhexa-2,3-dienenitrile (**3h**)

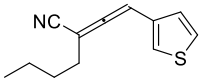
92% (22.3 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.70 (d, *J* = 6.5 Hz, 1H), 5.26 (d, *J* = 6.4 Hz, 1H), 1.12 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.2, 113.9, 108.0, 68.5, 32.8, 29.6. HRMS (EI) for $C_8H_{15}N_2$ $[M+NH_4]^+$: calcd 139.1230, found 139.1235. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2968; 2228; 1958; 1473; 1398; 1368; 1249; 1180; 1189; 913; 872; 717.

2-(2-Phenylvinylidene)hexanenitrile (**3i**)



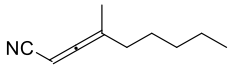
68% (26.8 mg) isolated yield, light yellow oil, 6 mol% dtbpy instead of L1 as ligand. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39 – 7.25 (m, 5H), 6.59 (t, *J* = 2.9 Hz, 1H), 2.36 – 2.31 (m, 2H), 1.65 – 1.53 (m, 2H), 1.48 – 1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.2, 130.7, 129.0, 128.7, 127.7, 114.9, 99.6, 86.2, 31.3, 29.6, 21.8, 13.6. HRMS (APCI) for $C_{14}H_{15}N$ $[M]^+$: calcd 197.1199, found 197.1196. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2958; 2924; 2219; 1944;1600; 1495; 1367; 829; 750; 692.

2-(2-(Thiophen-3-yl)vinylidene)hexanenitrile (**3j**)



70% (28.5 mg) isolated yield, light yellow oil, 6 mol% dtbpy instead of L1 as ligand. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 – 7.33 (m, 1H), 7.25 – 7.21 (m, 1H), 7.03 (d, *J* = 4.0, 1H), 6.66 (t, *J* = 2.9 Hz, 1H), 2.33 – 2.29 (m, 2H), 1.63 – 1.52 (m, 2H), 1.47 – 1.35 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.7, 131.4, 126.8, 126.1, 124.0, 114.9, 94.0, 85.4, 31.4, 29.6, 21.8, 13.7. HRMS (APCI) for $C_{12}H_{13}NS$ $[M]^+$: calcd 203.0763, found 203.0760. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2958; 2928; 2855; 2215; 1944; 1600; 1462; 1379; 1238; 1146; 1081; 864; 831; 772; 620.

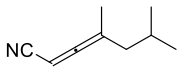
4-Methylnona-2,3-dienenitrile (**3k**)



92% (27.5 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.14 – 5.10 (m, 1H), 2.08 – 2.03 (m, 2H), 1.79 (d, *J* = 2.9 Hz, 3H), 1.49 – 1.41 (m, 2H), 1.36 – 1.25 (m, 4H), 0.92 – 0.88 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.4, 114.4, 106.6, 66.1, 32.9, 31.2, 26.5, 22.3, 17.7, 14.0. HRMS (EI) for $C_{10}H_{19}N_2$ $[M+NH_4]^+$: calcd 167.1543, found 167.1531. IR ν_{max}/cm^{-1} (in

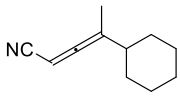
$CHCl_3$): 2956; 2929; 2872; 2860; 2223; 1962; 1739; 1653; 1458; 1394; 1378; 1281; 1259; 767.

4,6-Dimethylhepta-2,3-dienenitrile (**3l**)



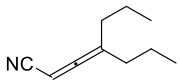
87% (23.5 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.12 -5.09 (m, 1H), 1.96 -1.93 (m, 2H), 1.82 – 1.74 (m, 4H), 0.94 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.8, 114.4, 105.2, 65.6, 42.4, 26.2, 22.3, 17.7. HRMS (EI) for $C_9H_{17}N_2$ $[M+NH_4]^+$: calcd 153.1386, found 153.1387. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2959; 2927; 2872; 2856; 2361; 2340; 2326; 2211; 1738; 1465; 1386; 1280.523; 1259; 1047; 739.

4-Cyclohexylpenta-2,3-dienenitrile (**3m**)



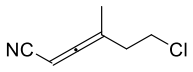
87% (28.1 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.15 – 5.12 (m, 1H), 1.93 – 1.76 (m, 8H), 1.70 – 1.65 (m, 1H), 1.34 – 1.06 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.2, 114.7, 111.4, 66.7, 41.1, 31.2, 26.1, 26.0, 16.1. HRMS (EI) for $C_{11}H_{15}KN$ $[M+K]^+$: calcd 200.0836, found 200.0832. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2925; 2856; 2223; 1956; 1449; 1393; 1368; 889; 778; 733.

4-Propylhepta-2,3-dienenitrile (**3n**)



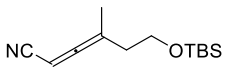
88% (26.3 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.19 – 5.15 (m, 1H), 2.05 – 2.01 (m, 4H), 1.52 – 1.43 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.3, 114.5, 111.0, 67.4, 33.7, 20.36, 13.6. HRMS (EI) for $C_{10}H_{15}NNa$ $[M+Na]^+$: calcd 172.1097, found 172.1115. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2926; 2854; 1957; 1449; 1390; 1371; 890; 776; 733.

6-Chloro-4-methylhexa-2,3-dienenitrile (**3o**)



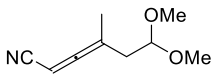
92% (26.1 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.27 – 5.23 (m, 1H), 3.64 – 3.58 (m, 2H), 2.62 – 2.48 (m, 2H), 1.85 (d, *J* = 2.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.2, 113.7, 103.3, 67.7, 41.0, 35.7, 17.6. HRMS (EI) for C_7H_8ClKN $[M+K]^+$: calcd 179.9977, found 179.9999. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3014; 2992; 2963; 2922; 2898; 2224; 1966; 1762; 1656; 1444; 1395; 1329; 1296; 1253; 912; 773;732; 659.

6-((*tert*-Butyldimethylsilyl)oxy)-4-methylhexa-2,3-dienenitrile (**3p**)



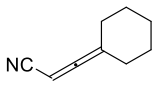
65% (30.9 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.13 – 5.11 (m, 1H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.33 – 2.25 (m, 2H), 1.83 (d, *J* = 3.0 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.6, 114.2, 103.8, 66.0, 60.5, 36.2, 25.8, 18.2, 17.9, -5.4. HRMS (EI) for $C_{13}H_{23}NNaOSi$ $[M+Na]^+$: calcd 260.1441, found 150.1431. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2991; 2929; 2224; 1965; 1445; 1375; 1192; 1120; 1080; 957; 913; 800; 770; 712.

6,6-Dimethoxy-4-methylhexa-2,3-dienenitrile (**3q**)



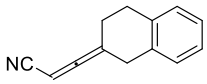
69% (23.1 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.18 – 5.16 (m, 1H), 4.49 (t, *J* = 5.7 Hz, 1H), 3.35 (d, *J* = 3.0 Hz, 6H), 2.39 – 2.37 (m, 2H), 1.84 (d, *J* = 3.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 214.0, 114.0, 102.3, 66.3, 53.2, 53.1, 36.3, 18.2. HRMS (EI) for $C_9H_{14}NO_2$ $[M+H]^+$: calcd 168.1019, found 168.1015. IR ν_{max}/cm^{-1}: 2991; 2933; 2224; 1965; 1445; 1364; 1192; 1120; 1065; 966; 913; 770; 728.

3-Cyclohexylideneacrylonitrile (**3r**)



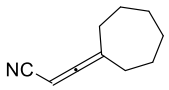
71% (18.9 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.07 – 5.05 (m, 1H), 2.27 – 2.16 (m, 4H), 1.73 – 1.62 (m, 4H), 1.58 – 1.52 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 210.5, 114.7, 108.3, 64.6, 29.8, 26.4, 25.4. HRMS (EI) for $C_9H_{11}KN$ $[M+K]^+$: calcd 172.0523, found 172.0520. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2934; 2855; 2363; 2223; 1960; 1655; 1621; 1448; 975; 913; 799; 734.

3-(3,4-Dihydronaphthalen-2(1H)-ylidene)acrylonitrile (**3s**)



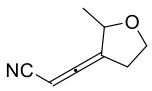
69% (25.7 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.20 – 7.11 (m, 4H), 5.22 – 5.19 (m, 1H), 3.68 – 3.55 (m, 2H), 2.99 – 2.86 (m, 2H), 2.65 – 2.62 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 211.0, 135.9, 133.2, 128.5, 128.2, 126.5, 126.4, 114.1, 105.0, 66.4, 31.5, 29.1, 26.7. HRMS (APCI) for $C_{13}H_{11}N$ $[M]^+$: calcd 181.0886, found 181.0877. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3023; 2925; 2847; 2212; 1966; 1730; 1652; 1495; 1453; 1353; 1258; 1154; 1106; 1036; 953; 916; 759; 743.

3-Cycloheptylideneacrylonitrile (**3t**)



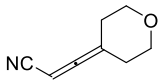
68% (20.0 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.06 – 5.04 (m, 1H), 2.42 – 2.30 (m, 4H), 1.73 – 1.61 (m, 5H), 1.58 – 1.53 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 213.4, 114.6, 110.8, 64.5, 31.0, 29.2, 27.7. HRMS (EI) for $C_{10}H_{13}KN$ $[M+K]^+$: calcd 186.0680, found 186.0682. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2925; 2853; 2209; 1952; 1635; 1459; 1353; 1283; 1022; 958; 911; 796; 734.

3-(2-Methyldihydrofuran-3(2H)-ylidene)acrylonitrile (**3u**)



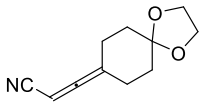
85% (23.0 mg) isolated yield, d.r. = 3:1, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.38 – 5.31 (m, 1H, major+minor), 4.63 – 4.59 (m, 1H, major+minor), 4.14 – 4.08 (m, 1H, major+minor), 3.84 – 3.77 (m, 1H, major+minor), 2.96 – 2.79 (m, 2H, major+minor), 1.40 (d, *J* = 8.0 Hz, 3H, minor) 1.36 (d, *J* = 4.0 Hz, 3H, major). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 206.6, 113.6, 112.0, 77.2, 76.4, 76.2, 70.2, 70.2, 67.7, 32.0, 31.9, 19.3, 19.1. HRMS (EI) for $C_8H_{10}NO$ $[M+H]^+$: calcd 136.0757, found 136.0754. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2980; 2932; 2868; 2224; 1970; 1435; 1378; 1350; 1293; 1229; 1106; 1086; 993; 863.

3-(Tetrahydro-4H-pyran-4-ylidene)acrylonitrile (**3v**)



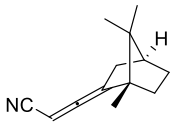
74% (20.0 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.20 – 5.19 (m, 1H), 3.82 – 3.75 (m, 4H), 2.40 – 2.29 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 210.4, 114.0, 104.2, 67.5, 66.3, 29.6. HRMS (EI) for $C_8H_{10}NO$ $[M+H]^+$: calcd 136.0757, found 136.0754. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3011; 2961; 2223; 1964; 1466; 1435; 1376; 1324; 1237; 1167; 1098; 1020; 990; 908; 842; 773; 727; 652; 552.

3-(1,4-Dioxaspiro[4.5]decan-8-ylidene)acrylonitrile (**3w**)



73% (27.9 mg) isolated yield, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.14 – 5.11 (m, 1H), 3.97 (s, 4H), 2.47 – 2.35 (m, 4H), 1.84 – 1.73 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 210.1, 114.3, 107.3, 106.1, 65.3, 64.5, 34.4, 27.1. HRMS (EI) for $C_{11}H_{14}NO_2$ $[M+H]^+$: calcd 192.1019, found 192.1010. IR ν_{max}/cm^{-1} (in $CHCl_3$): 3003; 2956; 2875; 2223; 1965; 1446; 1360; 1335; 1279; 1248; 1118; 1076; 1034; 953; 942; 903; 805; 778; 730, 674.

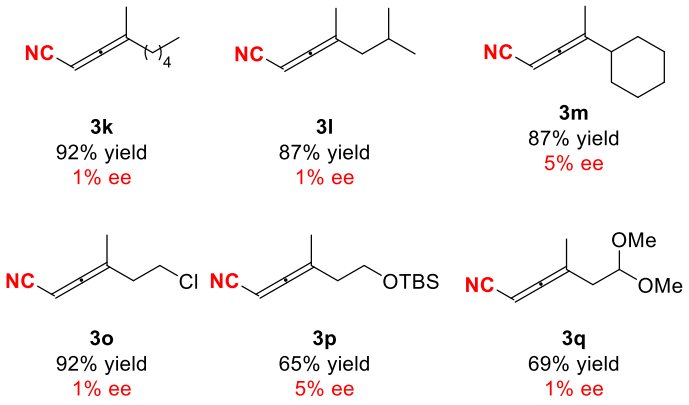
3-((1S,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene)acrylonitrile (**3x**)



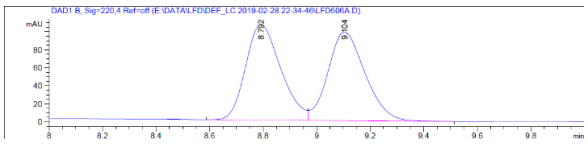
67% (25.1 mg) isolated yield, d.r = 1.6:1, colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.23 (t, *J* = 4.0 Hz, 1H, major), 5.16 (t, *J* = 4.0 Hz, 1H, minor), 2.78 – 2.59 (m, 1H, major+minor), 2.21 – 2.09(m, 1H, major+minor), 1.90 – 1.66 (m, 3H, major+minor), 1.59 – 1.21 (m, 2H, major+minor), 1.00 – 0.82 (m, 9H, major+minor).**^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.7, 117.6, 117.2, 115.1, 114.9, 68.6, 68.3, 53.8, 53.7, 48.9, 48.8, 44.7, 34.8, 34.6, 34.5, 27.5, 27.4, 19.6, 18.5, 13.0. HRMS (EI) for $C_{13}H_{17}NNa$ $[M+Na]^+$: calcd 210.1253, found 210.1246. IR ν_{max}/cm^{-1} (in $CHCl_3$): 2956; 2875; 2363; 2220; 1958; 1656; 1613; 1471; 1450; 1390; 1376; 1307; 1280; 1145; 777; 734.

4.3 Determination of ee value of representative trisubstituted allenes

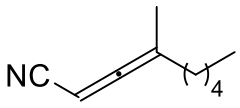
We checked the optical purity of some representative trisubstituted allenyl nitriles (3k-3m, 3o-3q)and found that the ee values of the products were all less than 5%.



Chiral HPLC spectrum of 3k



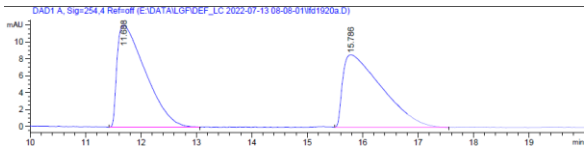
Determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 99:1 v/v, flow rate 0.5 mL/min, λ = 220 nm, 25 °C)



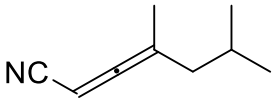
ee = 1%

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.792	BV	0.1400	964.62238	106.18817	50.5315
2	9.104	VB	0.1461	944.33014	98.24298	49.4685

Chiral HPLC spectrum of 3l



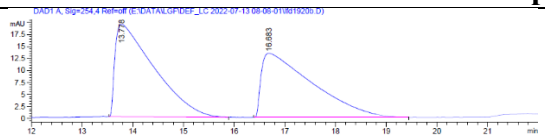
Determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 99:1 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C)



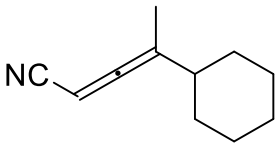
ee = 1%

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.688	BB	0.4961	429.55692	12.10072	50.5739
2	15.786	BB	0.6487	419.80847	8.58226	49.4261

Chiral HPLC spectrum of 3m



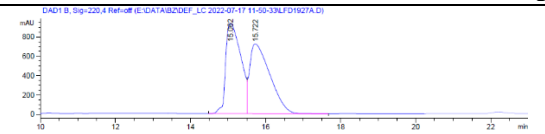
Determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 99:1 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C)



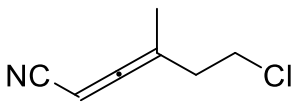
ee = 5%

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.778	BB	0.7054	1031.38733	19.30197	52.4616
2	16.683	BB	0.8964	934.59851	13.35639	47.5384

Chiral HPLC spectrum of 3o



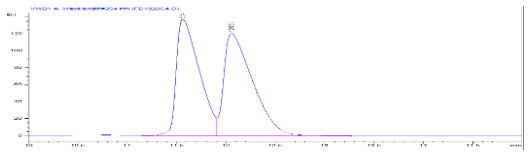
Determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1.0 mL/min, λ = 220 nm, 25 °C)



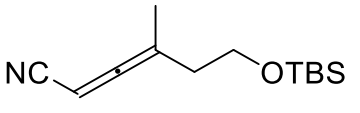
ee = 1%

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.062	BV	0.4509	2.62269e4	936.04742	49.2884
2	15.722	VB	0.5813	2.69842e4	723.16901	50.7116

Chiral HPLC spectrum of 3p



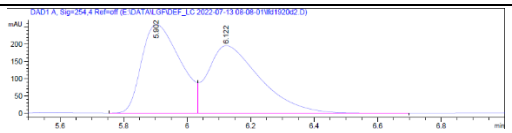
Determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC)



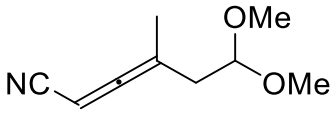
ee = 5%

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.564	VV	0.2496	2228.09619	137.92882	47.4785
2	12.059	VV	0.3075	2464.75317	121.03867	52.5215

Chiral HPLC spectrum of 3q



Determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 ºC)

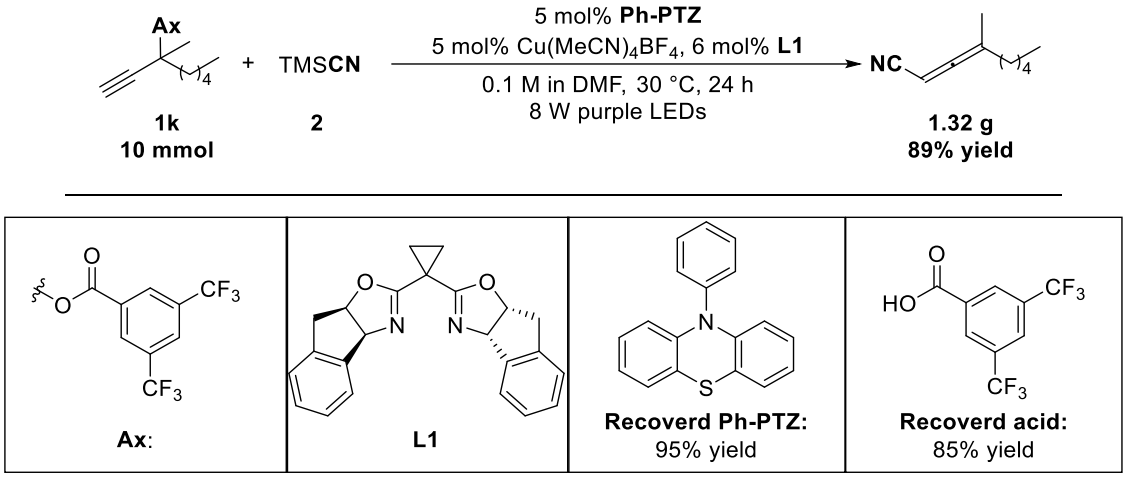


ee = 1%

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.902	BV	0.1325	2168.95313	256.81137	49.4944
2	6.122	VB	0.1682	2213.26685	195.25340	50.5056

5. Scaled-Up Reaction

This reaction was conducted according to the general procedure C: In an argon-filled glove box, a flame-dried 250 ml Schlenk flask equipped with a magnetic stirrer bar was charged sequentially with **$Cu(CH_3CN)_4BF_4$** (78.64 mg, 0.25 mmol) and **L1** (106.9 mg, 0.30 mmol), followed by the addition of DMF (20 mL). Then the mixture was stirred at room temperature for 30 min. The vial was closed and the Schlenk flask was removed from the glove box, to the resulting mixture were added propargyl ester **1k** (10 mmol), DMF (80 mL) and organic photocatalyst **Ph-PTZ** (0.50 mmol). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, **TMSCN** (30 mmol) was added into the mixture. At last, the mixture was stirred at a distance of ~1 cm from 8 W purple LEDs at 30 ºC about 24 h until the reaction was completed, as monitored by TLC analysis. In the separation process, the Ph-PTZ needed to be separated with petroleum ether and dichloromethane (200/1) first, and then the product was separated with petroleum ether and ethyl acetate (100/1). Finally, 3,5-di-CF_3-benzoic acid was separated with petroleum ether, ethyl acetate and acetic acid (100/40/0.1).



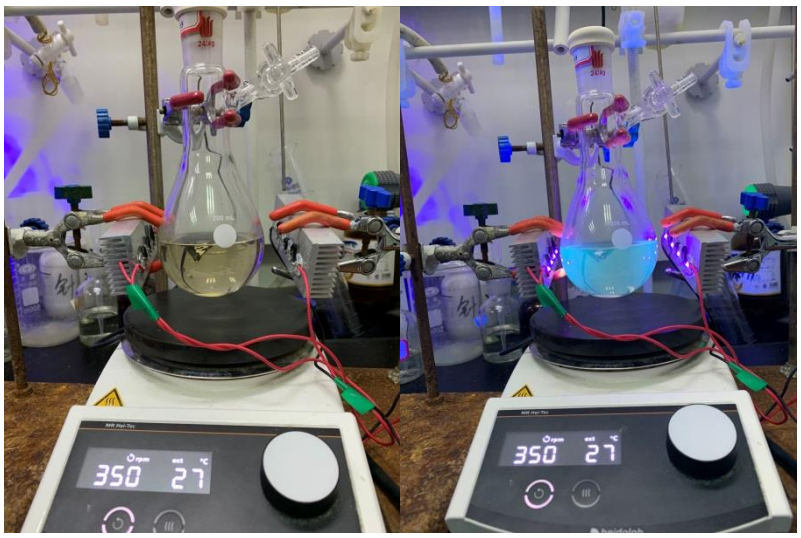
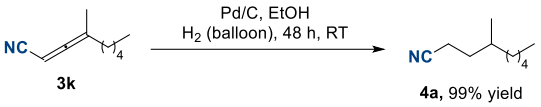
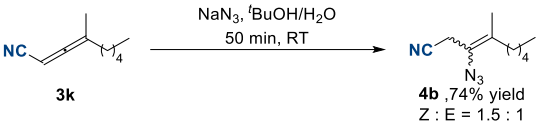


Figure S3. Scaled-up reaction

6. Synthetic Transformation



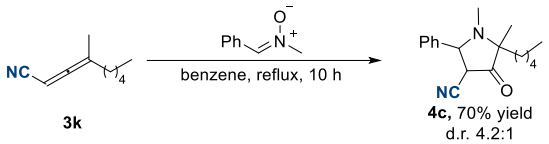
Procedure for hydrogenation: This reaction was conducted according to Sajiki's work. A flame-dried 50 mL Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with 3k (29.9 mg, 0.2 mmol), MeOH (20 mL) and Pd/C (18mg, 20 wt %). The reaction mixture was stirred at room temperature for 48 h after pumped by H_2 ballon. Then the reaction was filtered by the diatomite and washed by ethyl acetate. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1) to afford the desired product in quantative yield (32.3 mg) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.41 – 2.29 (m, 2H), 1.74 – 1.67 (m, 1H), 1.51 – 1.42 (m, 1H), 1.34 – 1.22 (m, 8H), 1.18 – 1.09 (m, 1H), 0.91 – 0.87 (m, 6H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ = 120.0, 36.1, 32.2, 32.0, 26.4, 22.6, 18.8, 14.9, 14.0. HRMS (EI) for $C_{10}H_{23}N_2$ $[M+NH_4]^+$: calcd 171.1856, found 171.1857. IR ν_{max}/cm^{-1}: 2957; 2927; 2872; 2227; 1742; 1464; 1428; 1380; 1280; 917; 791; 734.



Procedure for hydroazidation: This reaction was conducted according to Liu's work. A 10 mL tube equipped with a magnetic stirrer bar was charged sequentially with NaN_3 (52 mg, 0.8 mmol), H_2O (0.4 mL), and ^{t}BuOH solution (1.6 mL) of 3k (29.9 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 50 min. Then the reaction was quenched by NH_4Cl solution and extracted by ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4.The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 100/1) to afford the desired product in 74% yield (32.3 mg, Z/E=1.5:1) as colorless oil.

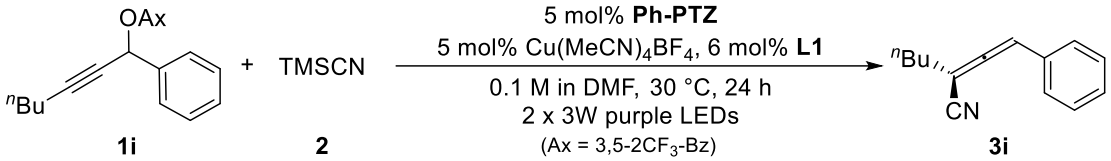
Z-4b: **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.36 (s, 2H), 2.06 – 2.02 (m, 2H), 1.74 (s, 3H), 1.47 – 1.24 (m, 6H), 0.90 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 130.0, 118.5, 115.8, 34.0, 31.5, 27.5, 22.5, 17.4, 17.2, 13.9. HRMS (EI) for $C_{10}H_{20}N_5$ $[M+NH_4]^+$: calcd 210.1713, found 210.1706. IR ν_{max}/cm^{-1}: 2957; 2931; 2871; 2860; 2103; 1753; 1660; 1467; 1459; 1418; 1378; 1262; 735.

E-4b: **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.36 (s, 2H), 2.14 – 2.10 (m, 2H), 1.75 (s, 3H), 1.41 – 1.23 (m, 6H), 0.91 – 0.87 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 130.1, 118.0, 115.7, 32.9, 31.5, 27.1, 22.5, 17.9, 17.5, 14.0. HRMS (EI) for $C_{10}H_{20}N_5$ $[M+NH_4]^+$: calcd 210.1713, found 210.1706. IR ν_{max}/cm^{-1}: 2959; 2931; 2861; 2215; 2105; 1758; 1655; 1456; 1378; 1291; 1098; 911; 734.



Procedure for cyclolization: This reaction was conducted according to Sajiki's work. A flame-dried 10 ml Sealing tube equipped with a magnetic stirrer bar was charged sequentially with (Z)-N-methyl-1-phenylmethanimine oxide (0.2 mmol, 27.03 mg), 3k (29.9 mg, 0.2 mmol) and benzene (2.4 mL). The reaction mixture was stirred at 82 ℃ for 10 h . The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 100/1) to afford the desired product in 70% yield (32.3 mg, dr = 4.2:1) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.48 – 7.37 (m, 6H, major+minor), 4.21 (d, J = 9.7 Hz, 1H, minor), 3.97 (d, J = 10.3 Hz, 1H, major), 3.24 (d, J = 9.7 Hz, 1H, minor), 3.19 (d, J = 10.3 Hz, 1H, major), 2.23 (s, 1H, major+minor), 2.13 (s, 3H, major+minor), 1.81 – 1.72 (m, 1H, major+minor), 1.68 – 1.54 (m, 3H, major+minor), 1.37 (d, J = 9.9 Hz, 2H, major+minor), 1.31 – 1.22 (m, 5H, major+minor), 1.13 (s, 3H, major+minor), 1.10 – 1.00 (m, 1H, major+minor), 0.90 (t, J = 7.0 Hz, 5H, major+minor). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 206.1, 205.3, 138.3, 137.9, 129.2, 129.2, 129.0, 128.9, 128.8, 128.7, 128.3, 127.2, 127.0, 114.6, 114.5, 77.2, 69.1, 69.0, 68.2, 67.4, 66.8, 64.5, 48.5, 47.1, 44.9, 36.4, 36.1, 32.4, 31.9, 31.8, 31.6, 31.4, 31.2, 31.0, 24.4, 24.0, 23.8, 22.6, 22.5, 22.4, 22.3, 15.7, 15.0, 14.0. HRMS (EI) for $C_{18}H_{24}N_2NaO$ $[M+Na]^+$: calcd 307.1781, found 307.1799. IR ν_{max}/cm^{-1}: 2954; 2930; 2970; 2958; 2251; 2206; 1766; 1604; 1495; 1455; 1368; 1147; 759.

7. Preliminary Result of Asymmetric Version

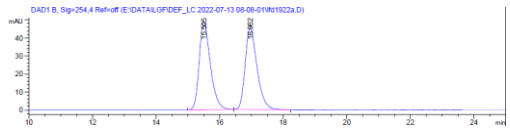


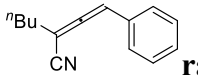
1i **2** **3i**

66% yield, 36% ee

Chiral allenyl nitrile **3i** was obtained according to General Procedure D. Light yellow oil, 29.6 mg, 66% isolated yield, 36% ee, $[\alpha]_D^{25}$ = -21.52 (c = 0.51 in $CHCl_3$); the ee value was determined by HPLC analysis (Chiralpak OJ-H column, hexane/*i*-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 16.83 min, tR (minor) = 15.40 min.

Chiral HPLC spectrum of racemic 3i

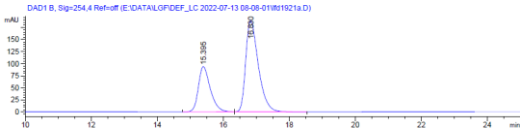


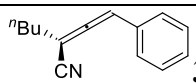


rac-3i

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.791	BB	0.3262	1.78922e4	868.97534	49.2580
2	15.033	BV R	0.4119	1.84313e4	723.64014	50.7420

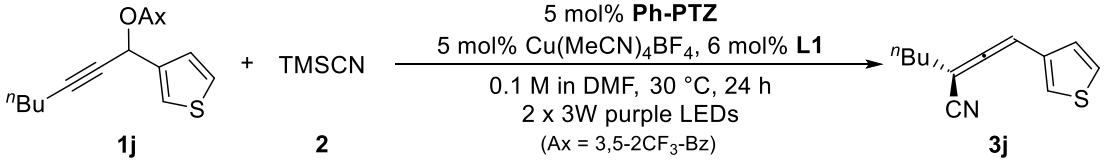
Chiral HPLC spectrum of 3i





3i

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.395	BB	0.3752	2335.31274	93.55769	31.8957
2	16.830	BB	0.4025	4986.40723	188.57965	68.1043

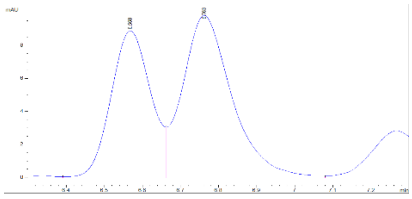


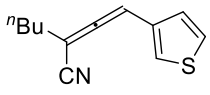
1j **2** **3j**

70% yield, 45% ee

Chiral allenyl nitrile **3j** was obtained according to General Procedure D. Light yellow oil, 28.5 mg, 70% isolated yield, 45% ee, $[\alpha]_D^{25}$ = -14.13 (c = 0.60 in $CHCl_3$); the ee value was determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), tR (major) = 6.93 min, tR (minor) = 6.71 min.

Chiral HPLC spectrum of racemic 3j

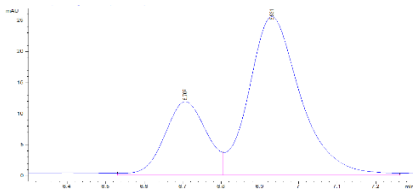


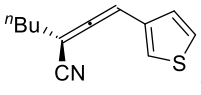


rac-3j

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.568	VV	0.1150	1392.45715	189.08821	48.5515
2	6.763	VV	0.1202	1475.54480	189.08769	51.4485

Chiral HPLC spectrum of 3j





3j

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.707	VV	0.1176	89.63736	11.81416	27.4112
2	6.931	VV	0.1406	237.37280	25.49876	72.5888

8. Mechanistic Investigation

8.1 Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on a GU Instruments Electrochemical Workstation model GU/07078C. CV measurement of starting material was carried out in 0.1 M of Bu_4NPF_6/MeCN at a scan rate of 100 mV/s with the protection of Ar. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is Ag/AgCl.

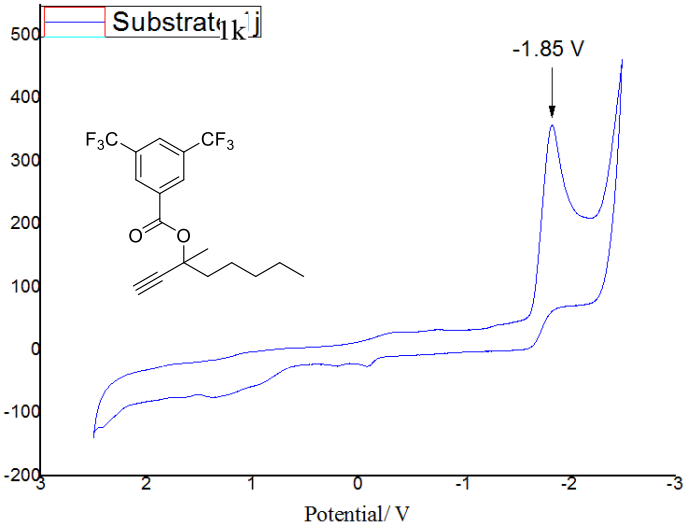


Figure S4. Cyclic voltammogram of 1k

8.2 Luminescence Quenching Experiments

Fluorescence spectra was collected on Agilent Fluorescence Spectrophotometer G9800A for all experiments. Ph-PTZ solutions were excited at 355 nm and the emission intensity was collected at 447 nm. In a typical experiment, the emission spectrum of a 1×10^{-4} M solution of Ph-PTZ in DMF was collected. The significant decrease of Ph-PTZ luminescence could be observed in the presence of substrate **1k**.

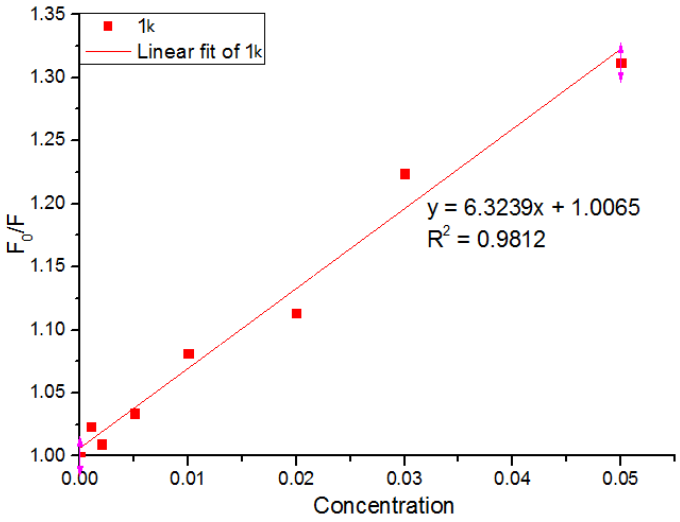


Figure S5. Ph-PTZ emission quenching by **1k**

8.3 Light On-Off Experiments

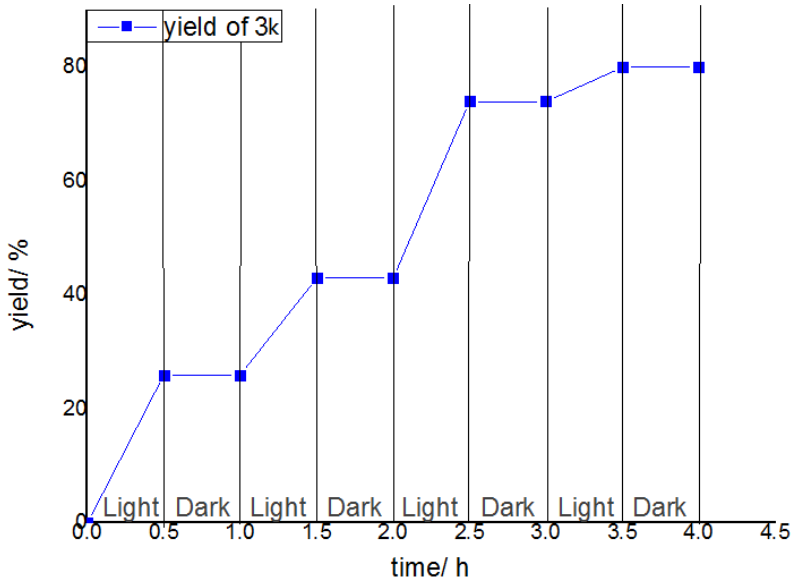
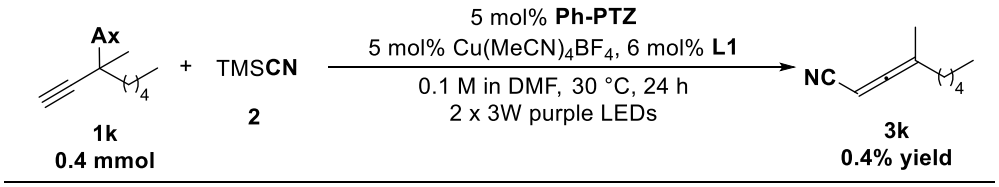
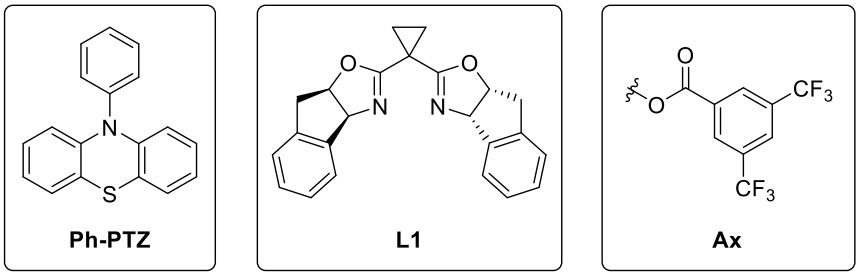


Figure S6. Light on-off experiments

The yield of 3k was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The results revealed that a radical chain process was not the major reaction pathway, while it could not be completely ruled out at the current stage.

8.4 Determination of quantum yield





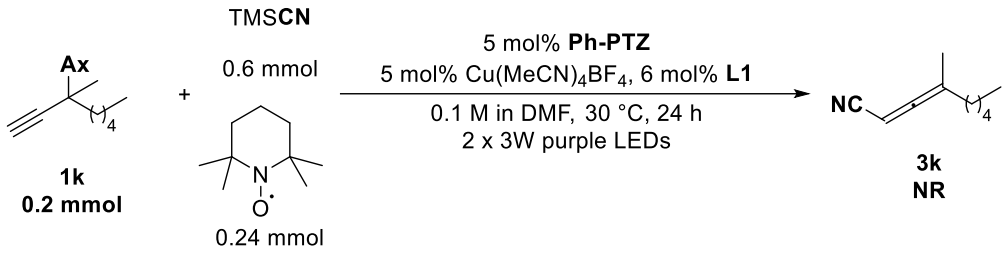
ϕ = Mole number for product/Mole number for absorption of photons = 0.776

$$\phi = \frac{nN_A/t}{fP\lambda/hc}$$

n: the mole number of the product **3k**; t: reaction time (14400 s, 4 h); N_A: 6.02×10^{23} /mol; f: $1\text{-}10^{-A}$(400 nm, A= 0.7); P: P=E*S (E: illumination intensity, E= 0.3 mW/cm^2;

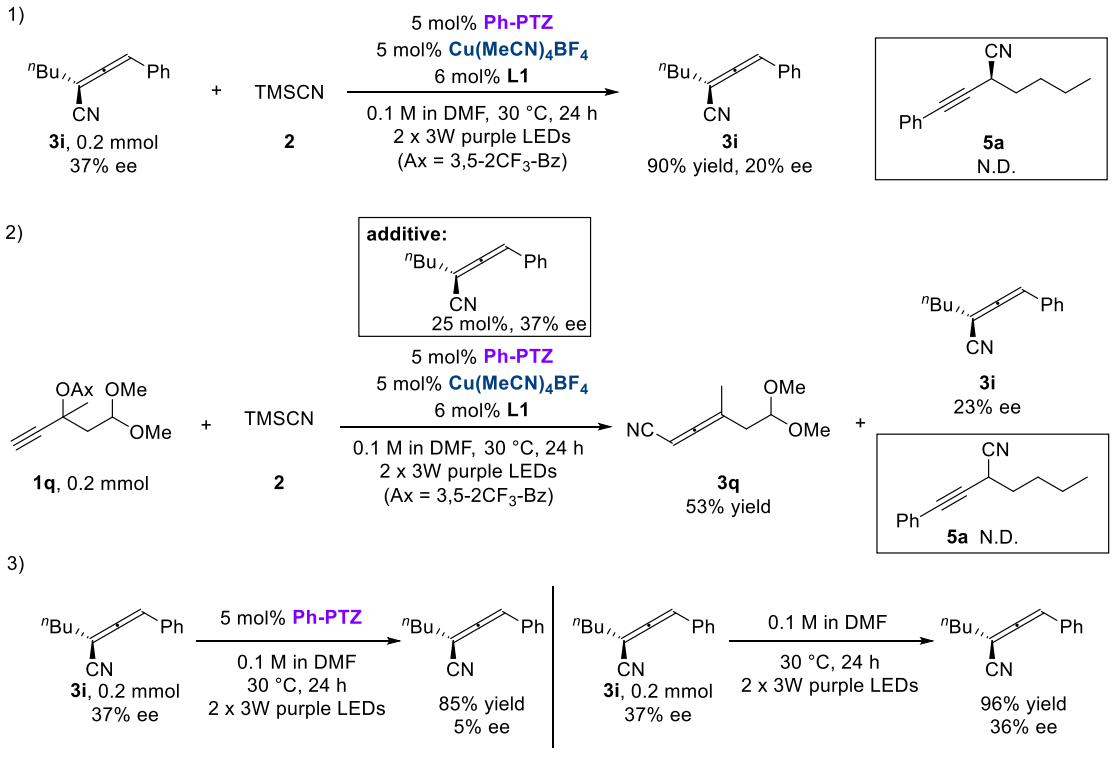
S: the area that irradiated S= 0.15 cm^2); λ: wavelength (λ= 4.0×10^{-7} m); h: planck constant (h=6.626×10^{-34} J*s); c: velocity of light (c=3×10^8 m/s).

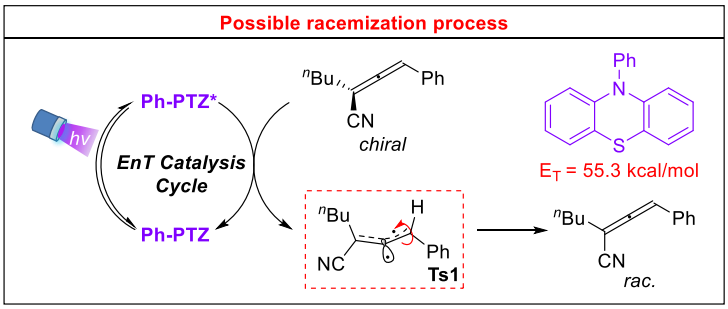
8.5 Radical Trapping Experiments



In an argon-filled glove box, a flame-dried 10 ml Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with $Cu(CH_3CN)_4BF_4$ (3.15 mg, 0.01 mmol) and L1 (4.28 mg, 0.012 mmol), followed by the addition of DMF (0.5 mL). Then the mixture was stirred at room temperature for 30 min. The vial was closed and the Schlenk tube was removed from the glove box, to the resulting mixture were added propargyl ester 1k (0.20 mmol), 2,2,6,6-Tetramethylpiperidinooxy (0.24 mmol), DMF (1.5 mL) and Ph-PTZ (0.01 mmol). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, TMSCN (0.6 mmol) was added into the mixture. At last, the mixture was stirred at a distance of ~1 cm from a 2 x 3 W purple LEDs at 30 °C for 24 h.

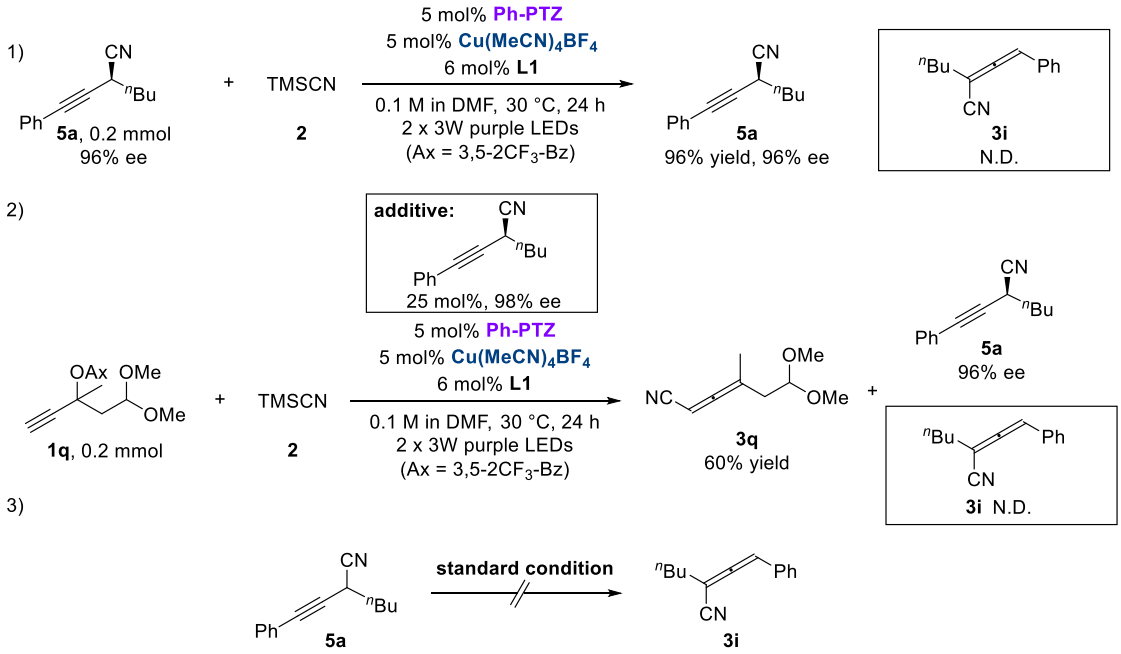
8.6 Product racemization experiments



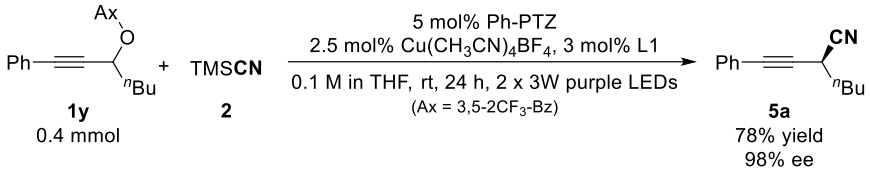


When chiral allenyl nitriles **3i** was subjected to the photocatalysis condition with Ph-PTZ as the photocatalyst and 2x3 W purple LEDs as the light source, we observed different degrees of racemization of **3i**. Thus, we believe that the allene racemization process does exist in the reaction system. Furthermore, through further experimental exploration, we found that the racemization of **3i** requires the participation of both photocatalyst and light. Therefore, we reasoned that the allenyl nitriles in the reaction system would undergo energy transfer with the excited-state photocatalyst to generate the di-radical intermediate **Ts1** leading to racemization.

8.7 Intermediate verification experiments

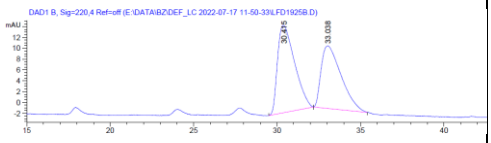


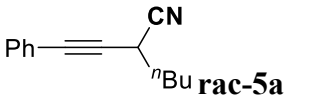
When chiral propargyl nitrile was used as a substrate or an additive under the standard reaction conditions, we observed that the propargyl nitrile would not be converted to allenyl nitrile and no racemization process was observed. Therefore, we reasoned that the propargyl nitrile intermediate was not the intermediate during the reaction, and the allenyl nitrile product is generated by the capture of the allenyl radical by copper.



Chiral propargyl nitrile **5a** was prepared according to our previous work (*J. Am. Chem. Soc.*, **2019**, *141*, 6167-6172). In an argon-filled glove box, a flame-dried 10 ml Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with $Cu(CH_3CN)_4BF_4$ (3.15 mg, 0.01 mmol) and L1 (4.28 mg, 0.012 mmol), followed by the addition of THF (1.0 mL). Then the mixture was stirred at room temperature for 30 min. The vial was closed and removed the Schlenk tube from the glove box, to the resulting mixture were added propargyl ester 1y (171.3 mg, 0.40 mmol), THF (3.0 mL) and Ph-PTZ (5.5 mg, 0.02 mmol). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, TMSCN (118.9 mg, 1.2 mmol) was added into the mixture. At last, the mixture was stirred at a distance of ~1 cm from a 2 x 3 W purple LEDs at room temperature about 24 h until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 100/1) to afford the desired product in 78% (61.5 mg) isolated yield. light yellow oil, $[\alpha]_D^{25}$ = -1.6 (c = 0.50 in $CHCl_3$); 96% ee, determined by HPLC analysis (Chiralpak AS-H column, hexane/*i*-PrOH, 99:2 v/v, flow rate 0.5 mL/min, λ = 200 nm, 25 °C), tR (major) = 30.70 min, tR (minor) = 26.74 min.**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46 – 7.40 (m, 2H), 7.37 – 7.27 (m, 3H), 3.73 (t, *J* = 6.9 Hz, 1H), 1.97 – 1.91 (m, 2H), 1.64 – 1.55 (m, 2H), 1.45 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 131.7, 128.8, 128.3, 121.7, 117.7, 83.8, 81.2, 33.0, 28.7, 23.7, 21.8, 13.7. HRMS (EI) for $C_{14}H_{15}N$ $[M]^+$: calcd 197.1199, found 197.1207. IR ν_{max}/cm^{-1}: 2930, 2252, 1490, 1455, 1260, 1075, 1040, 803, 760, 690, 528.

Chiral HPLC spectrum of racemic 5a

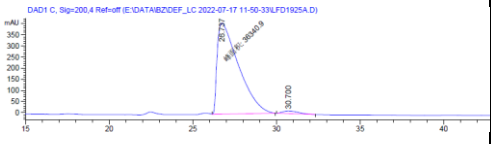


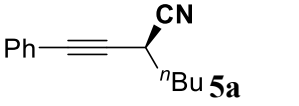


rac-5a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.415	BB	0.8502	640.18890	9.06224	53.6398
2	33.038	BB	0.9948	553.30774	6.55521	46.3602

Chiral HPLC spectrum of 5a



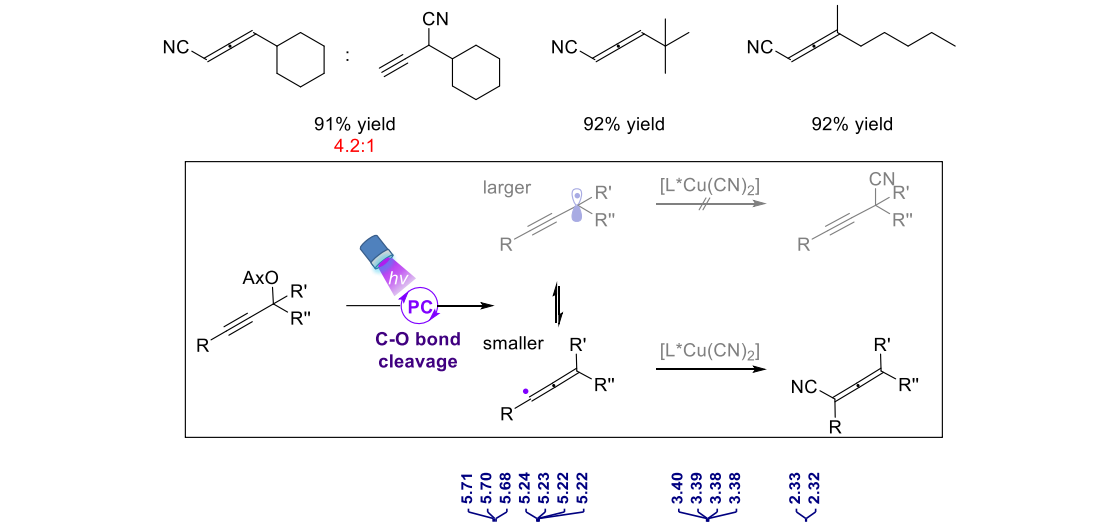


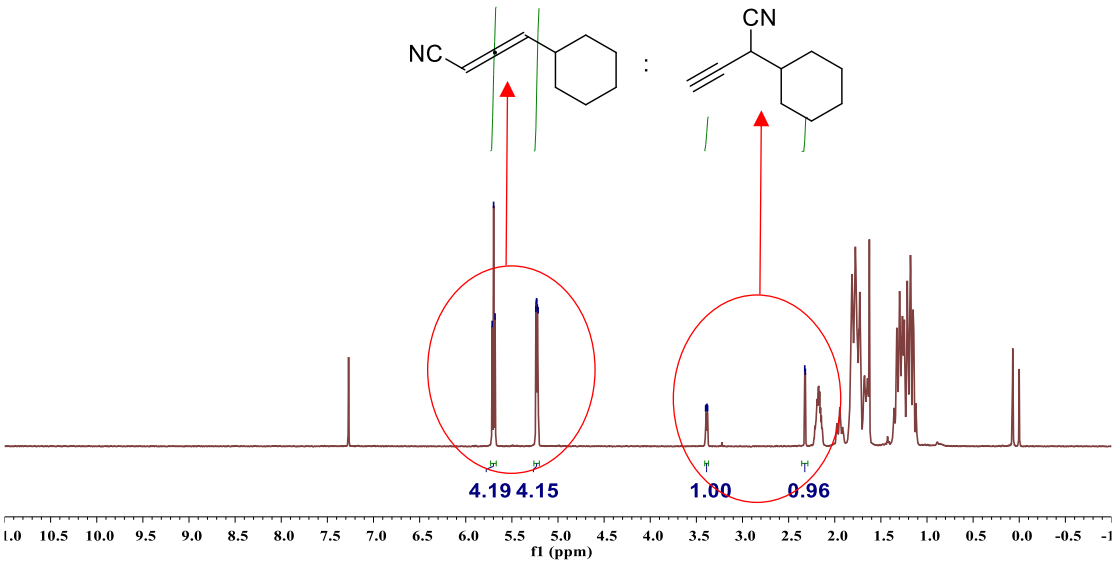
5a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %

	1	26.737	MM	1.4814	3.63409e4	408.86542	97.9993
	2	30.700	BB	0.7690	741.92841	11.43475	2.0007

8.8 Explanation for the chemoselectivity of reaction

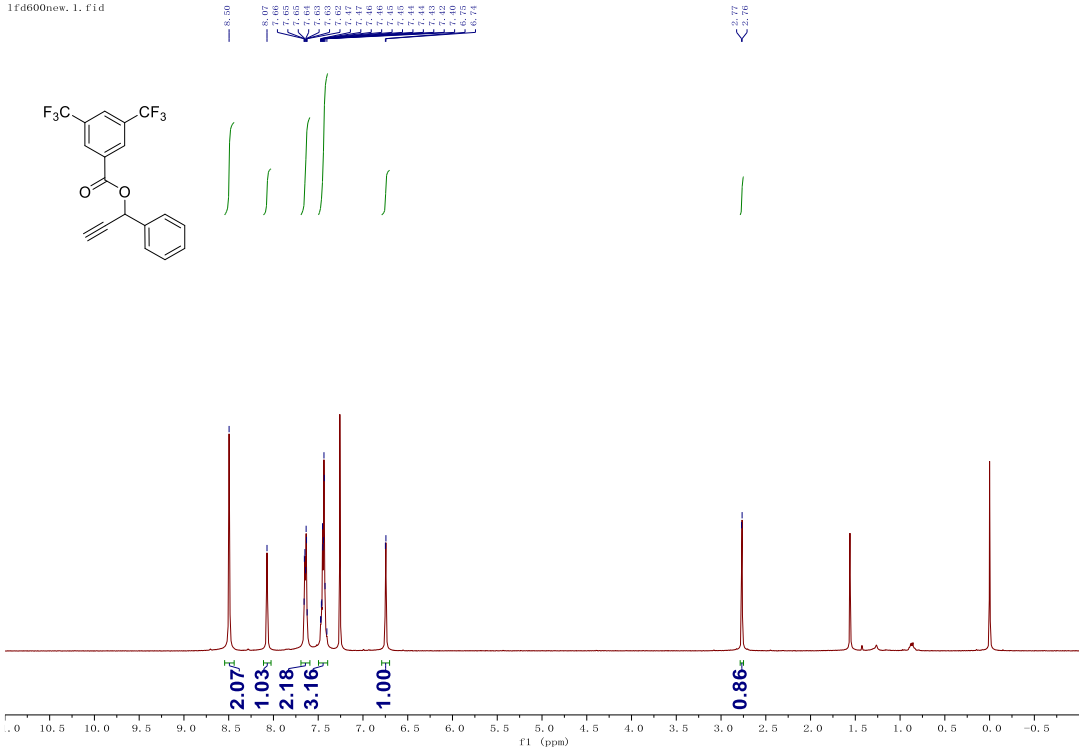




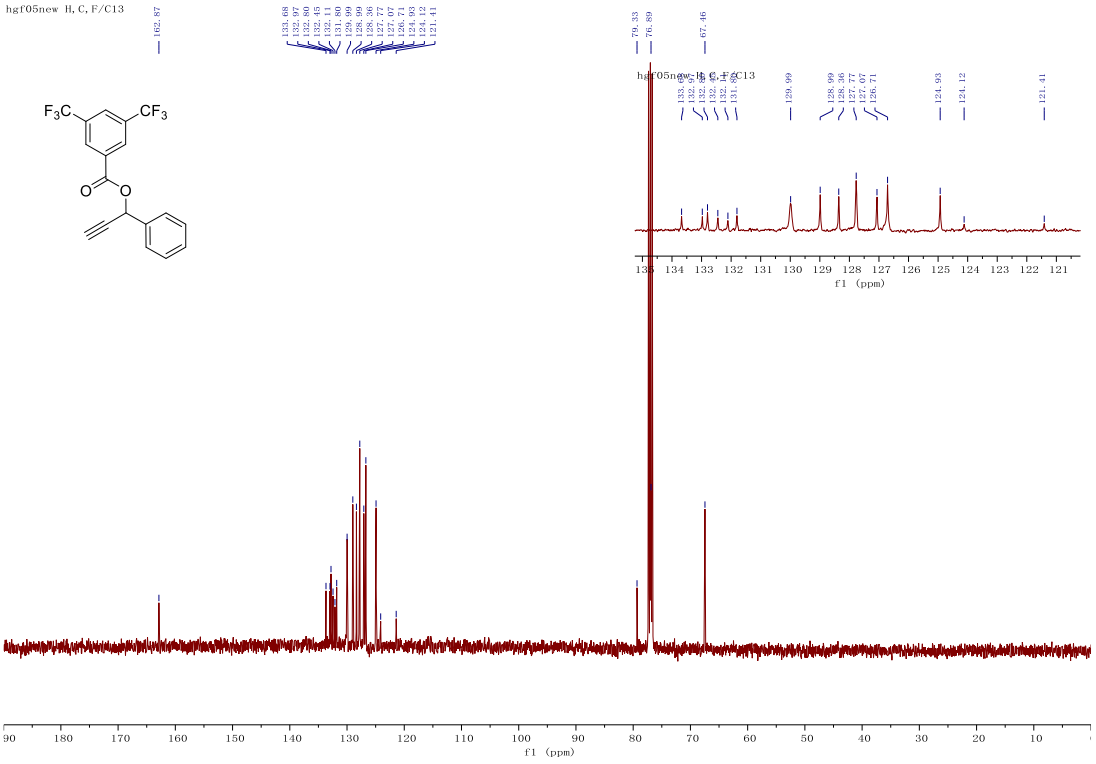
By analyzing the above results, we found that when the steric hindrance of the propargyl radical is relatively small, the propargyl radical can either directly participate in the reaction, or can be isomerized into an allenyl radical to participate in the reaction. When the steric hindrance increases, propargyl radicals tend to isomerize to allenyl radicals with less steric hindrance to participate in the reaction. Therefore, we reasoned that the chemoselectivity of the reaction might be attributed to the steric hindrance of the radical intermediates generated in the reaction.

9. Copies of NMR Spectra

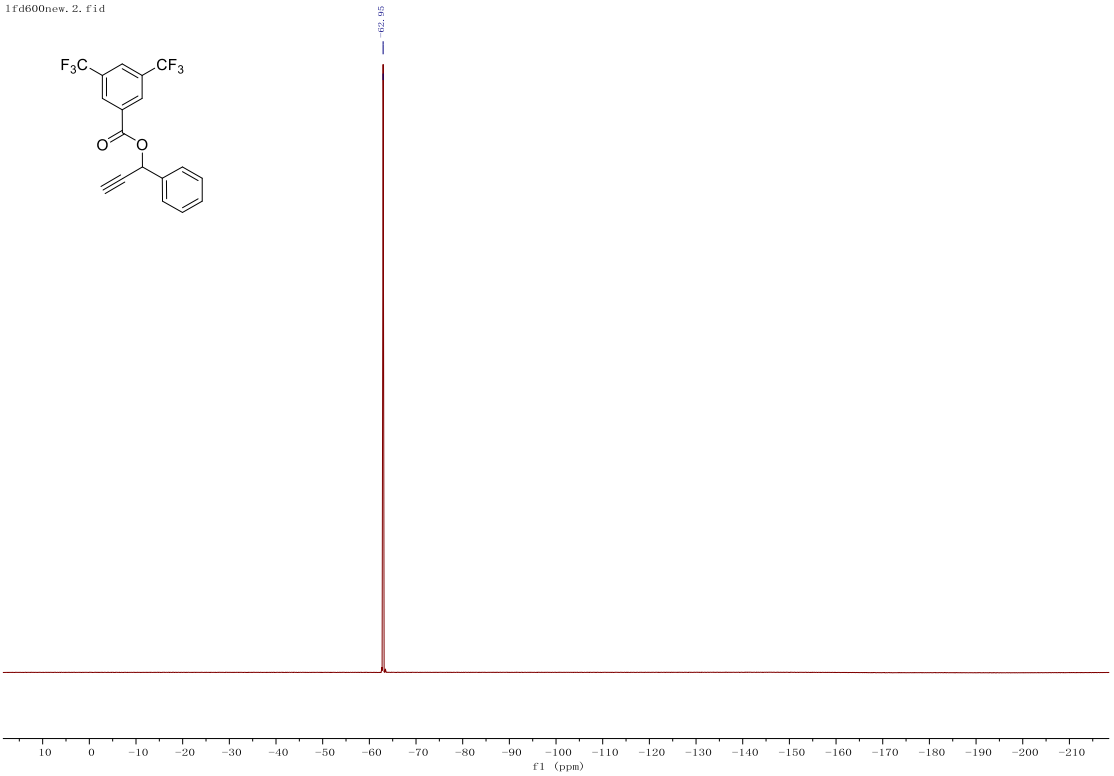
^{1}H NMR spectrum of compound 1a



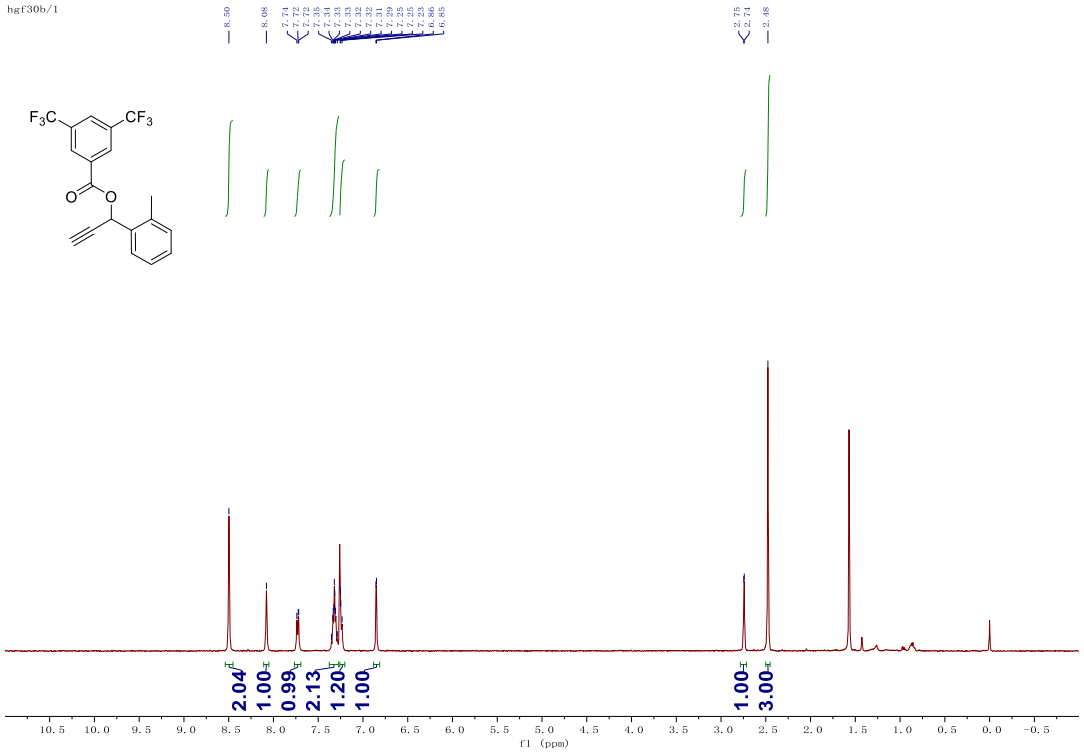
^{13}C NMR spectrum of compound 1a



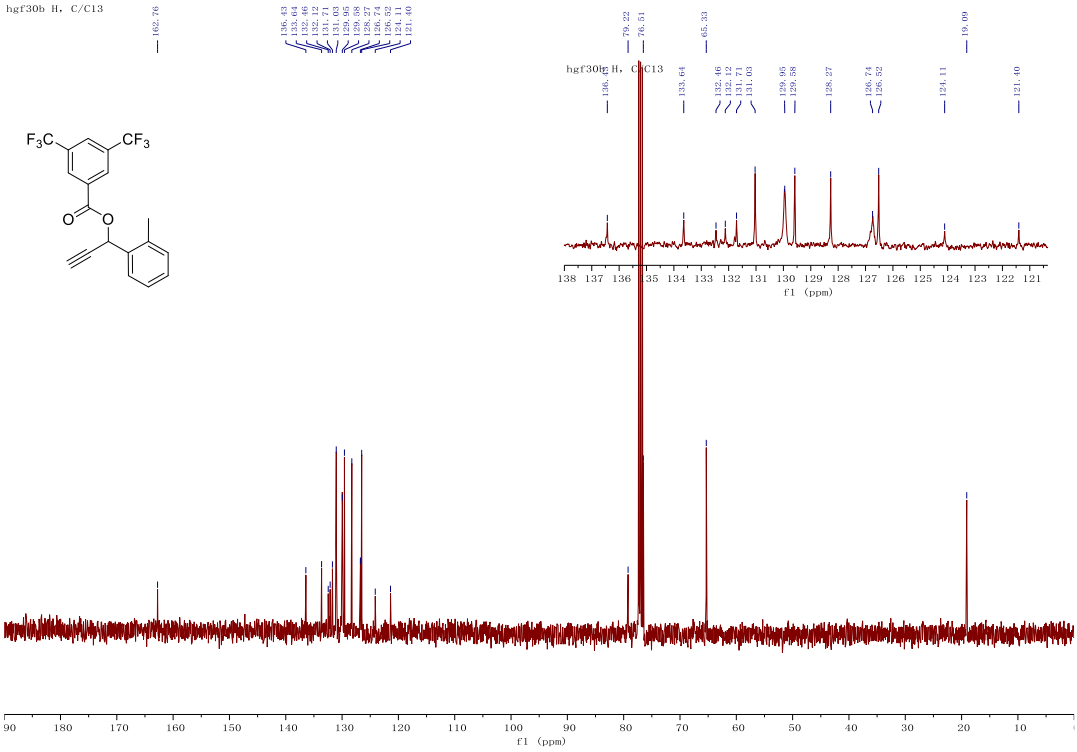
^{19}F NMR spectrum of compound1a



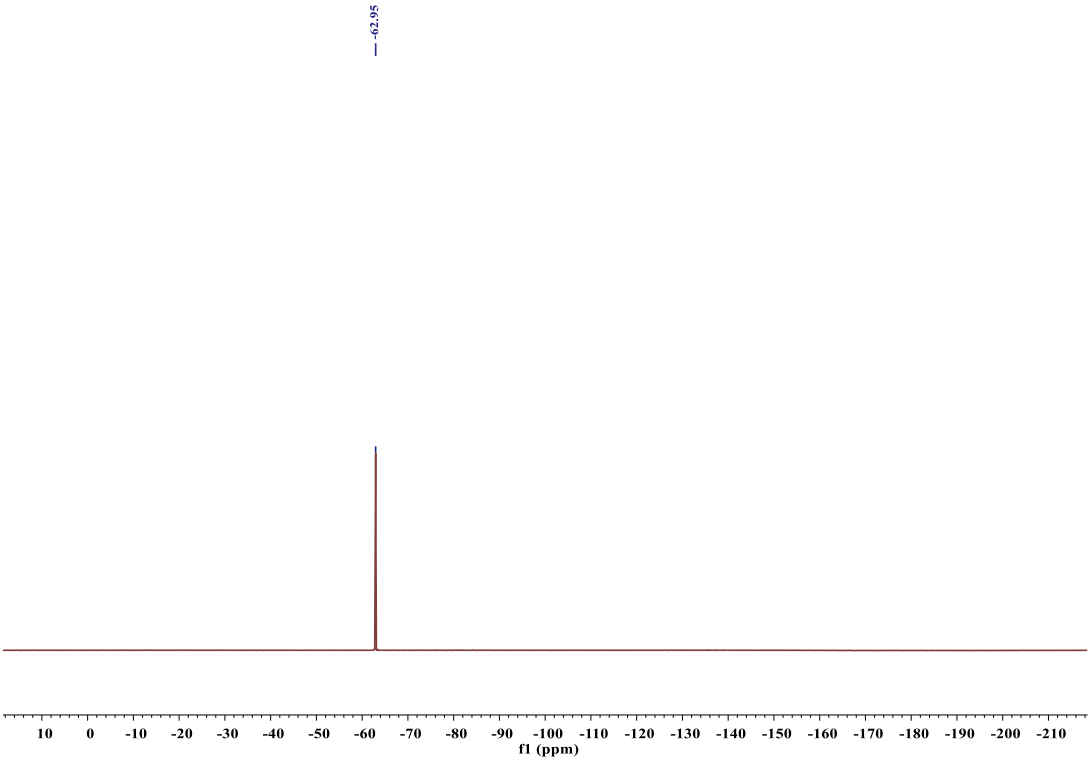
^{1}H NMR spectrum of compound 1b



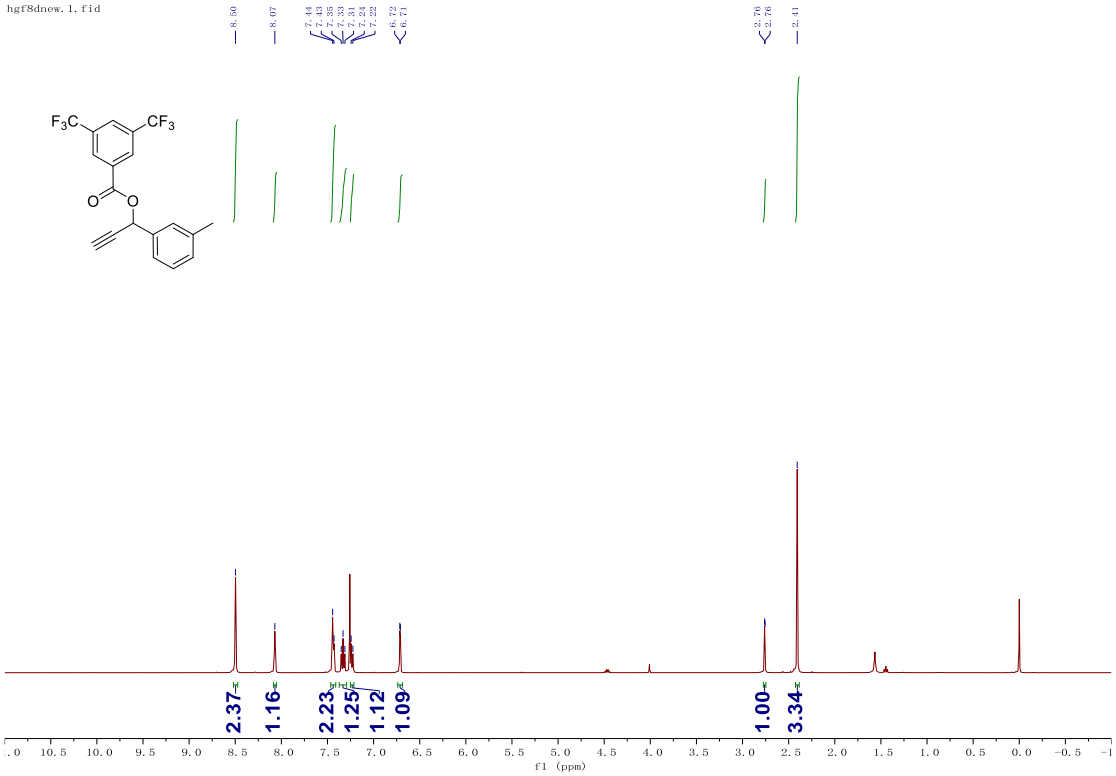
^{13}C NMR spectrum of compound 1b



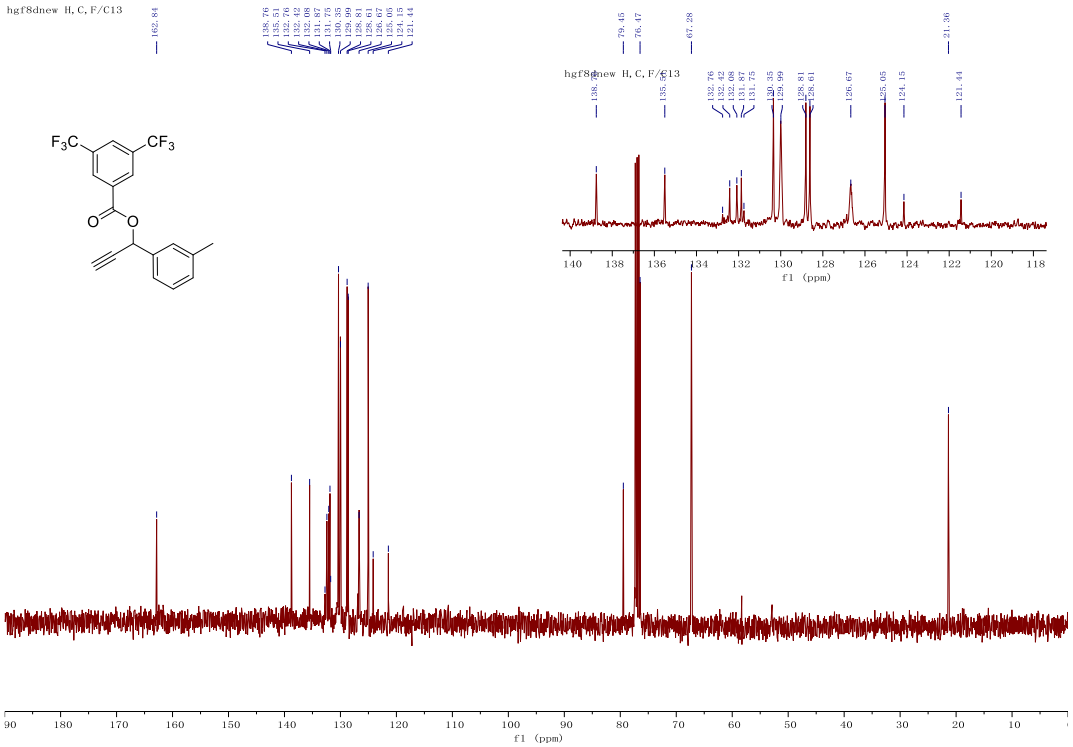
^{19}F NMR spectrum of compound 1b



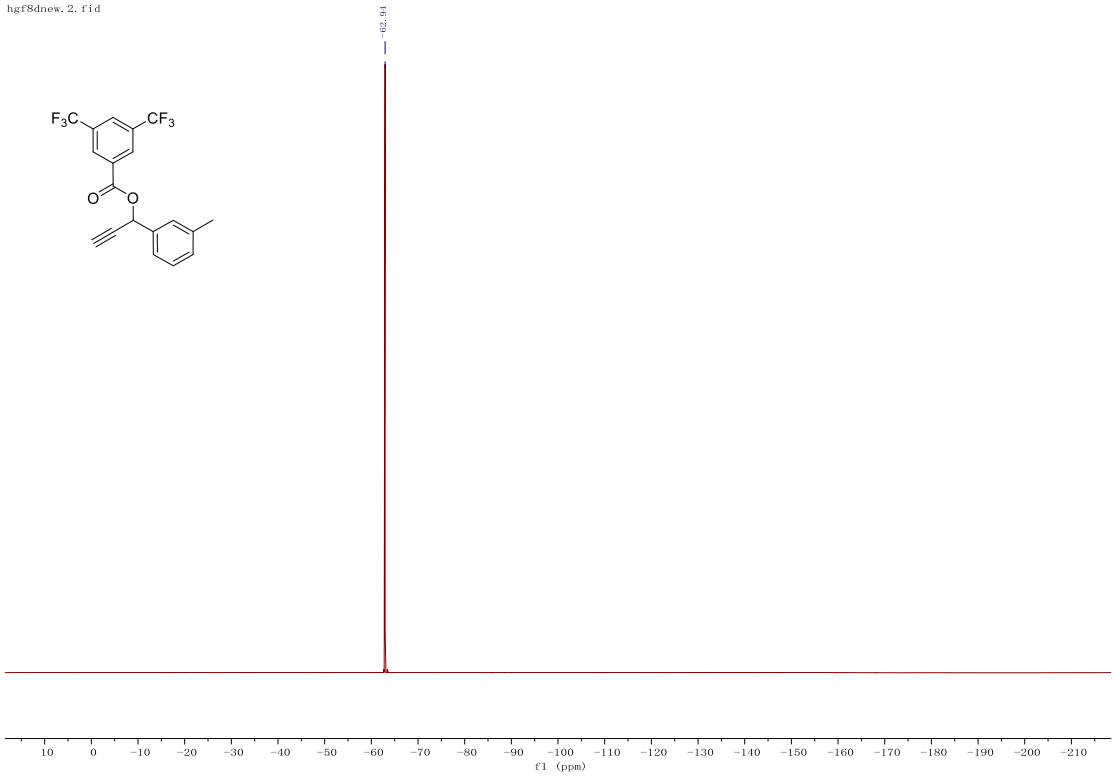
^{1}H NMR spectrum of compound 1c



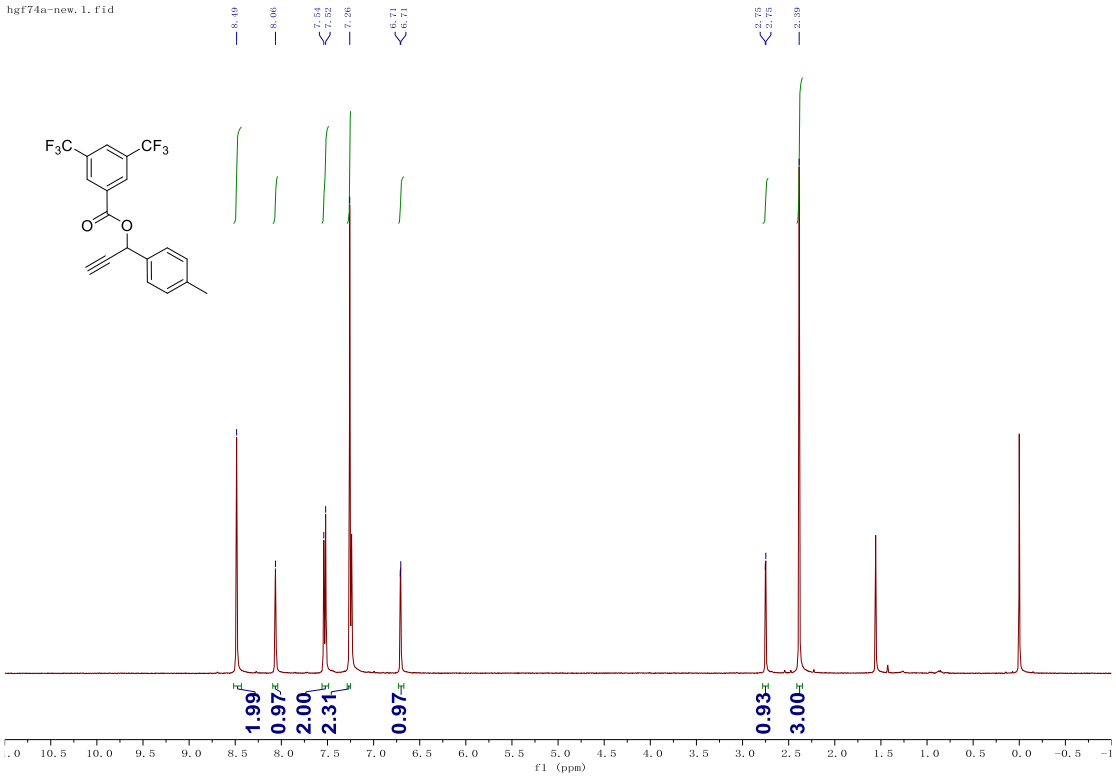
^{13}C NMR spectrum of compound 1c



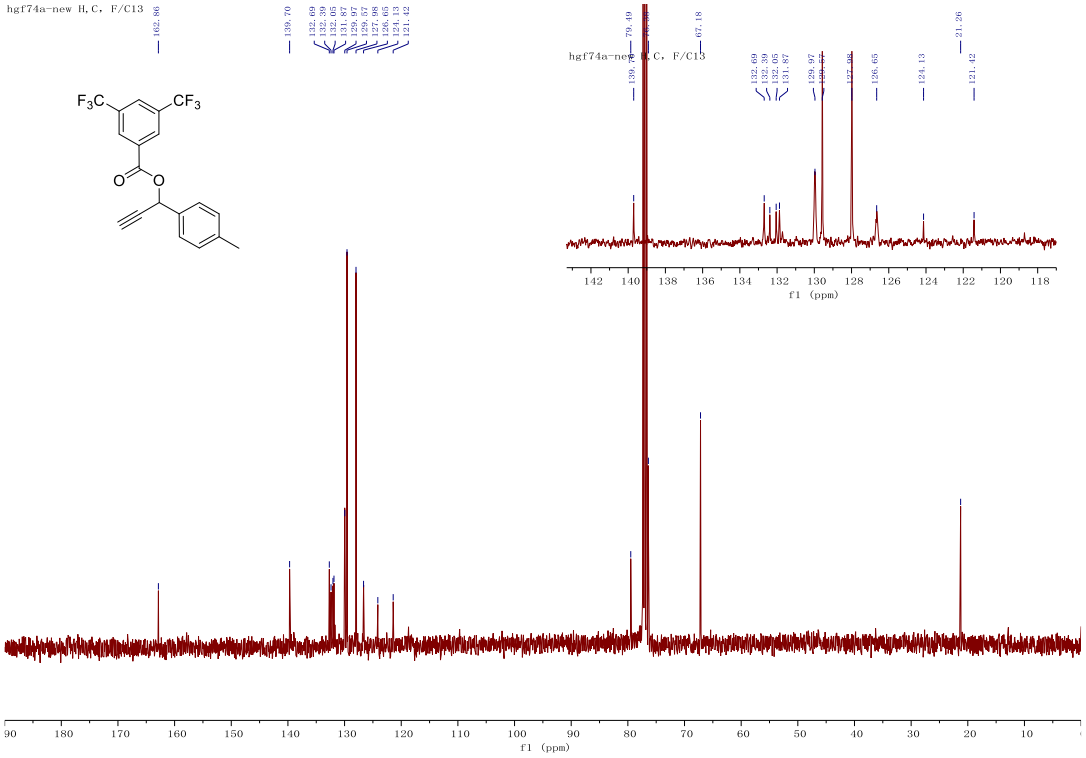
^{19}F NMR spectrum of compound 1c



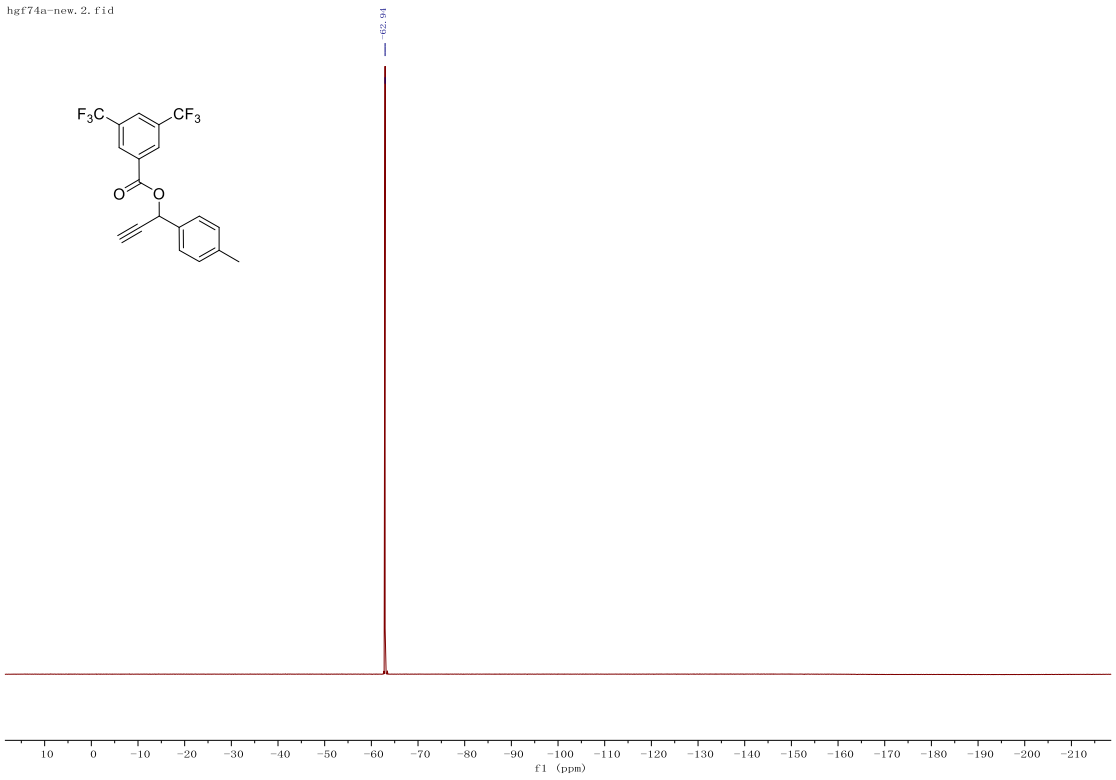
^{1}H NMR spectrum of compound 1d



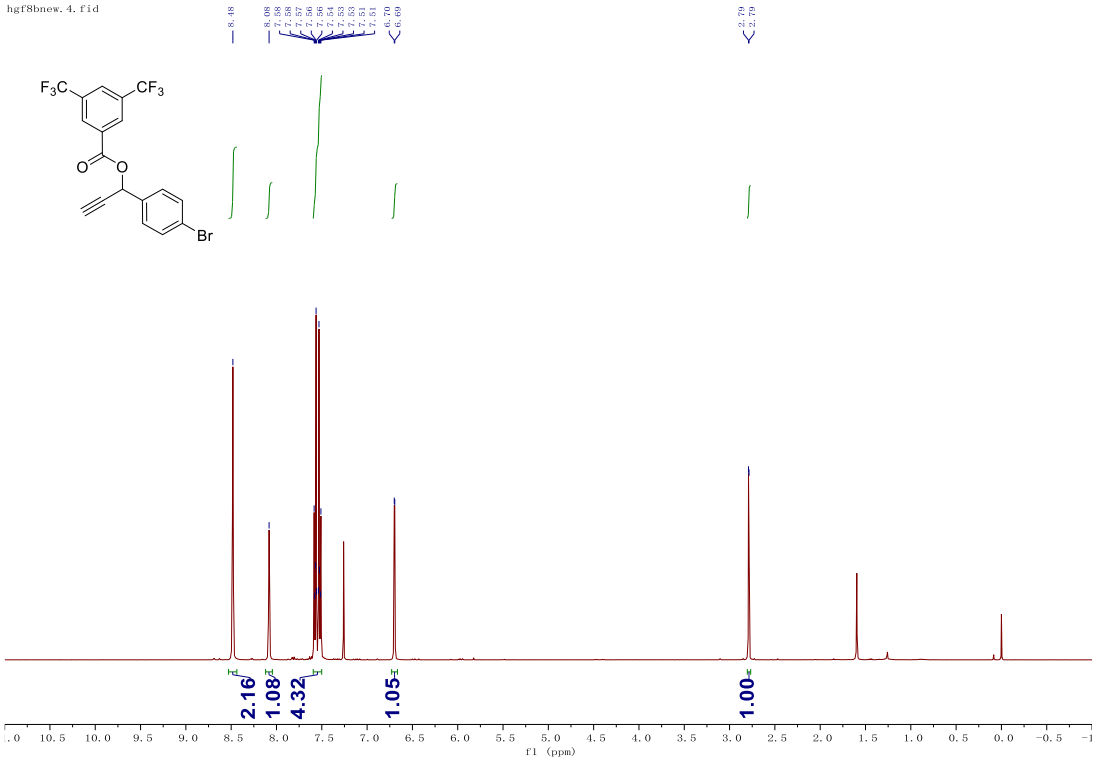
^{13}C NMR spectrum of compound 1d



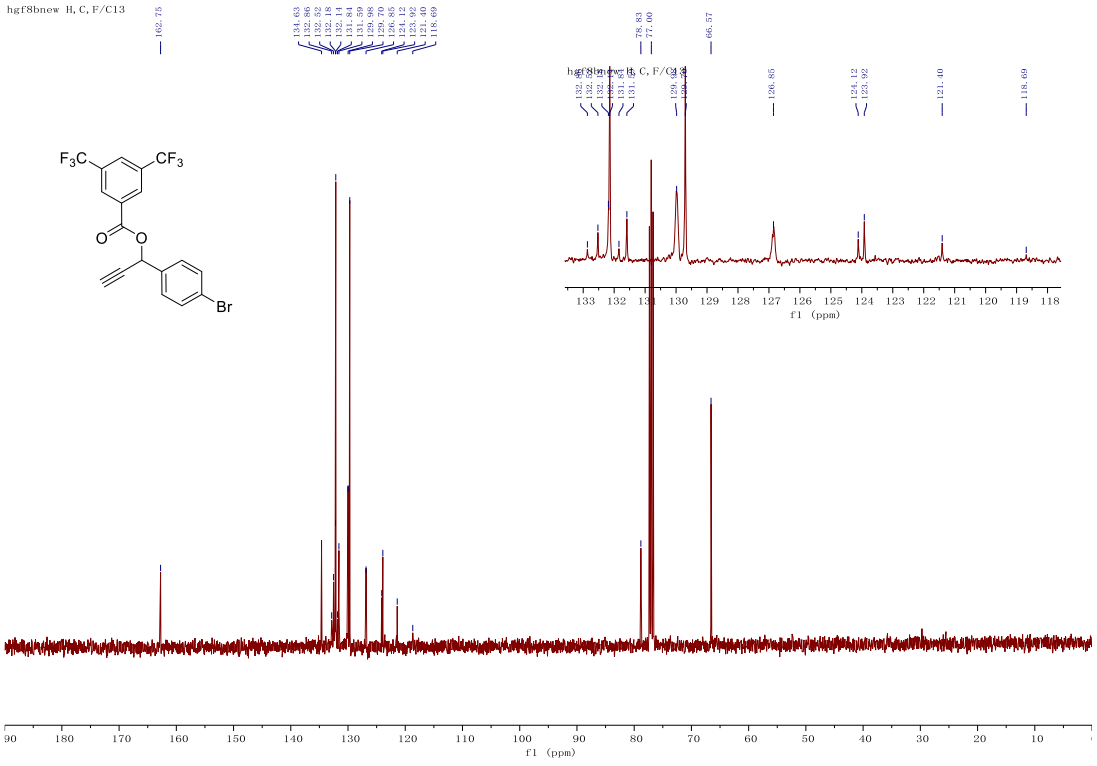
^{19}F NMR spectrum of compound 1d



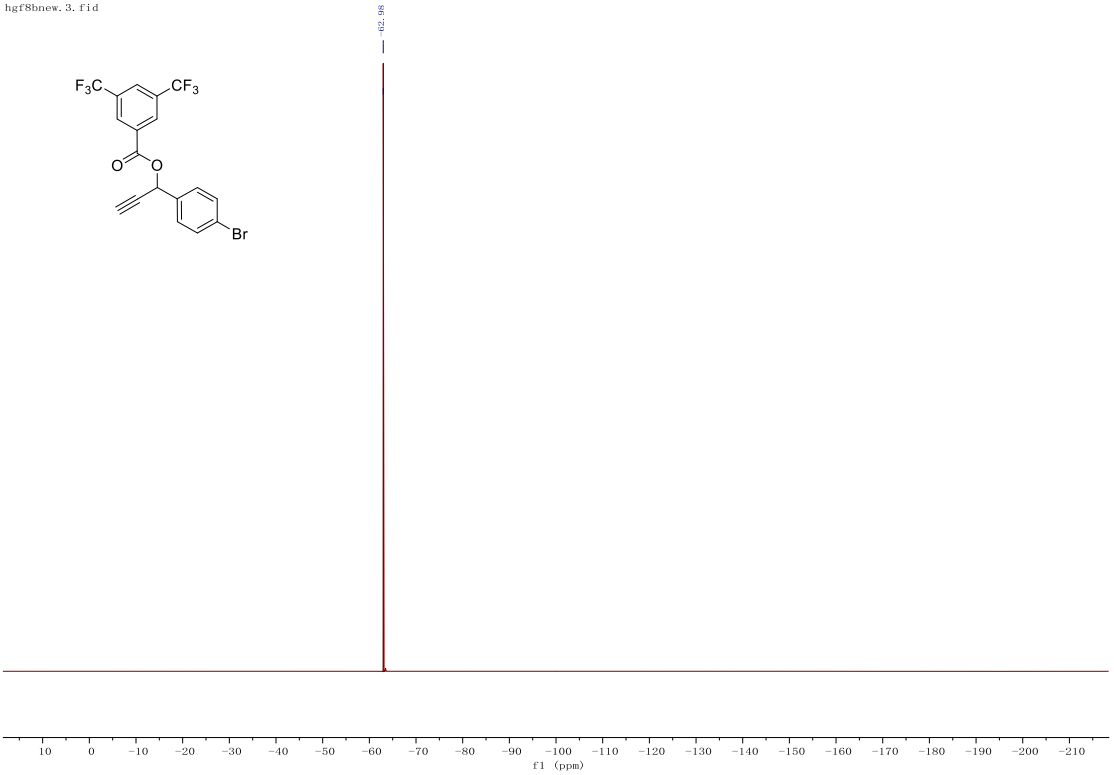
^{1}H NMR spectrum of compound 1e



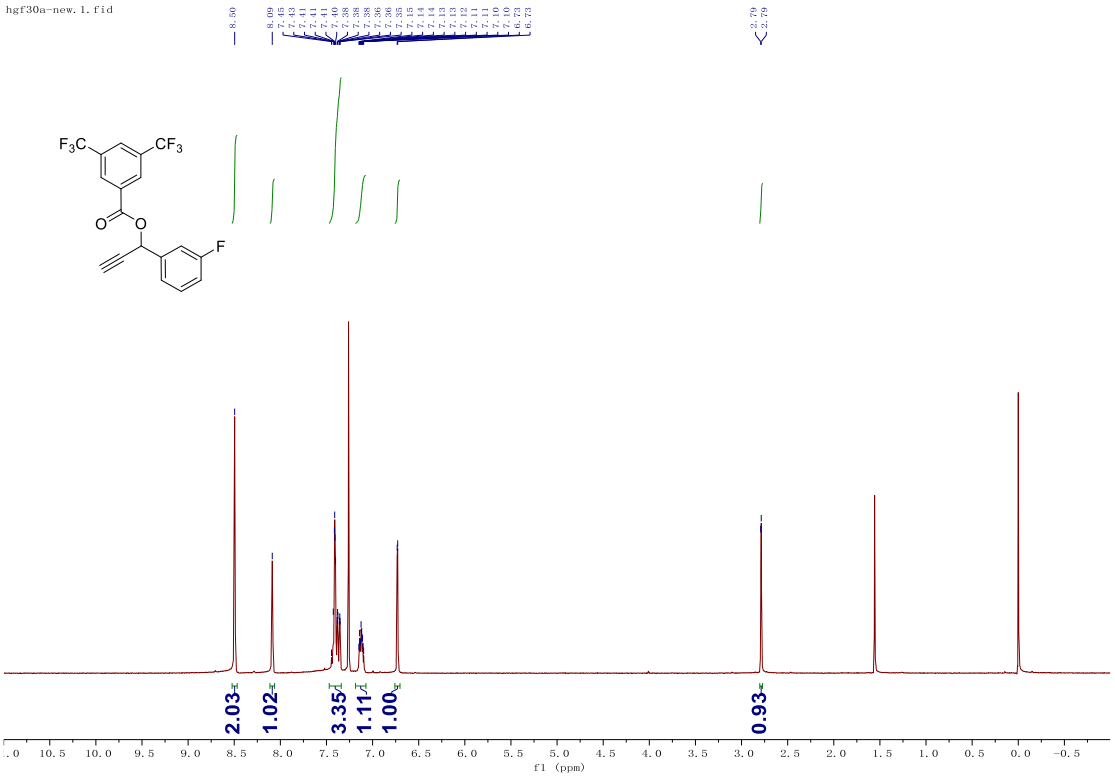
^{13}C NMR spectrum of compound 1e



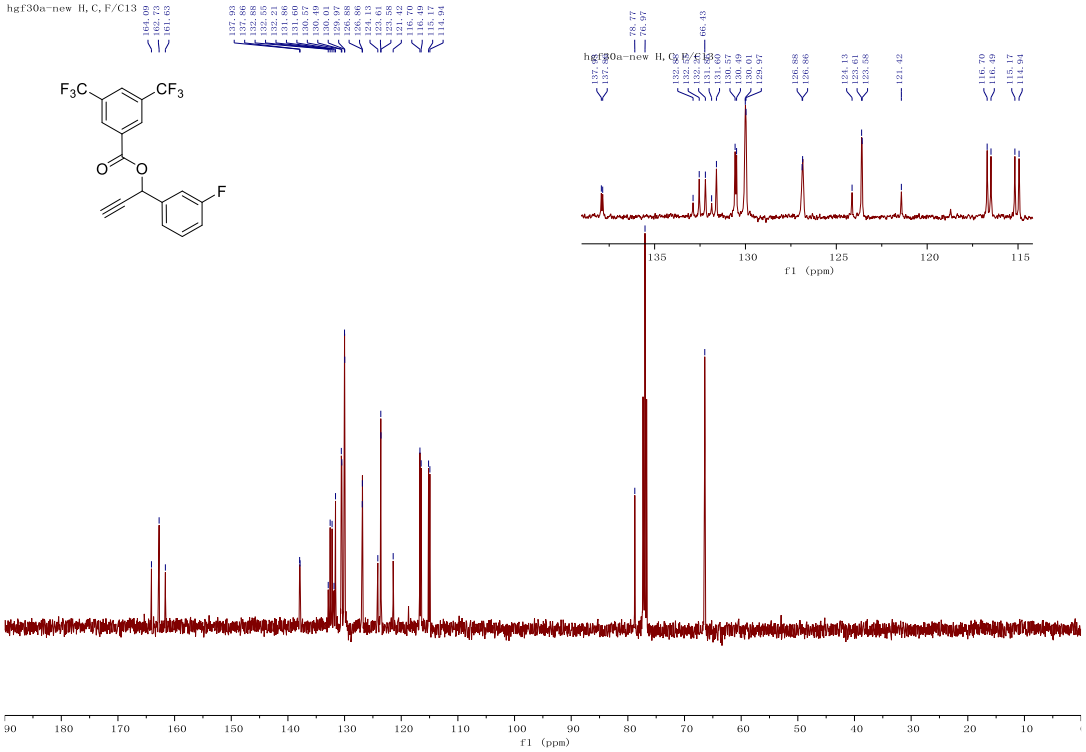
^{19}F NMR spectrum of compound 1e



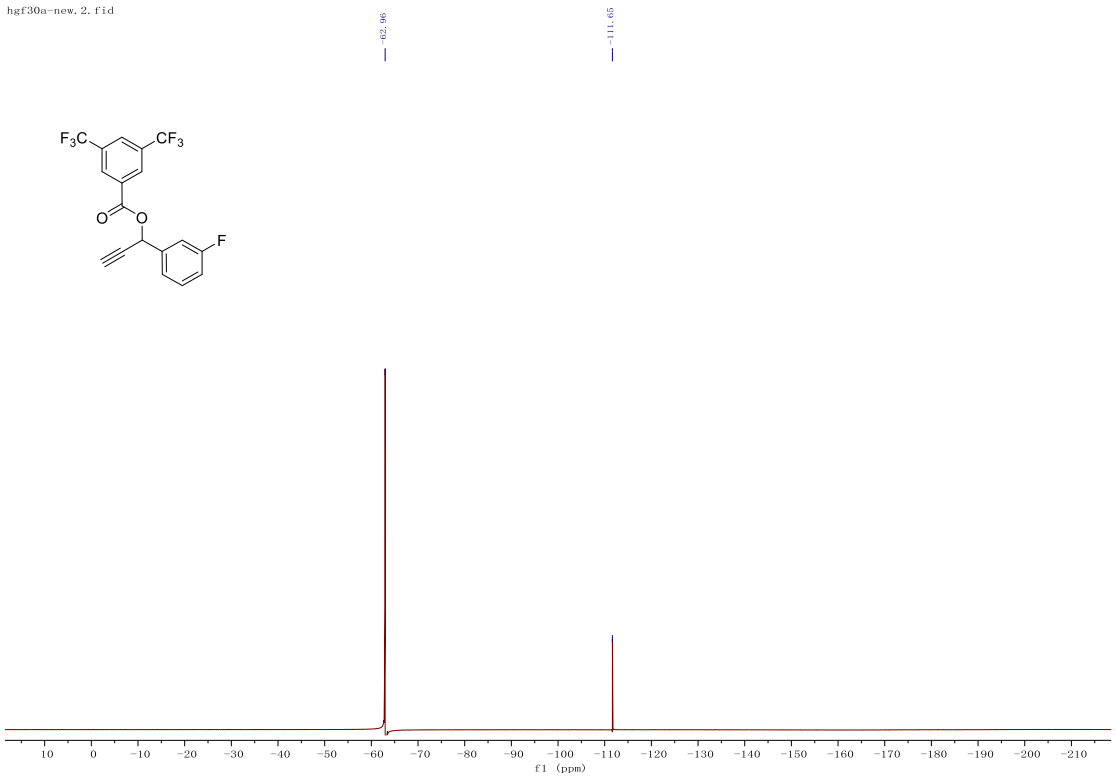
^{1}H NMR spectrum of compound 1f



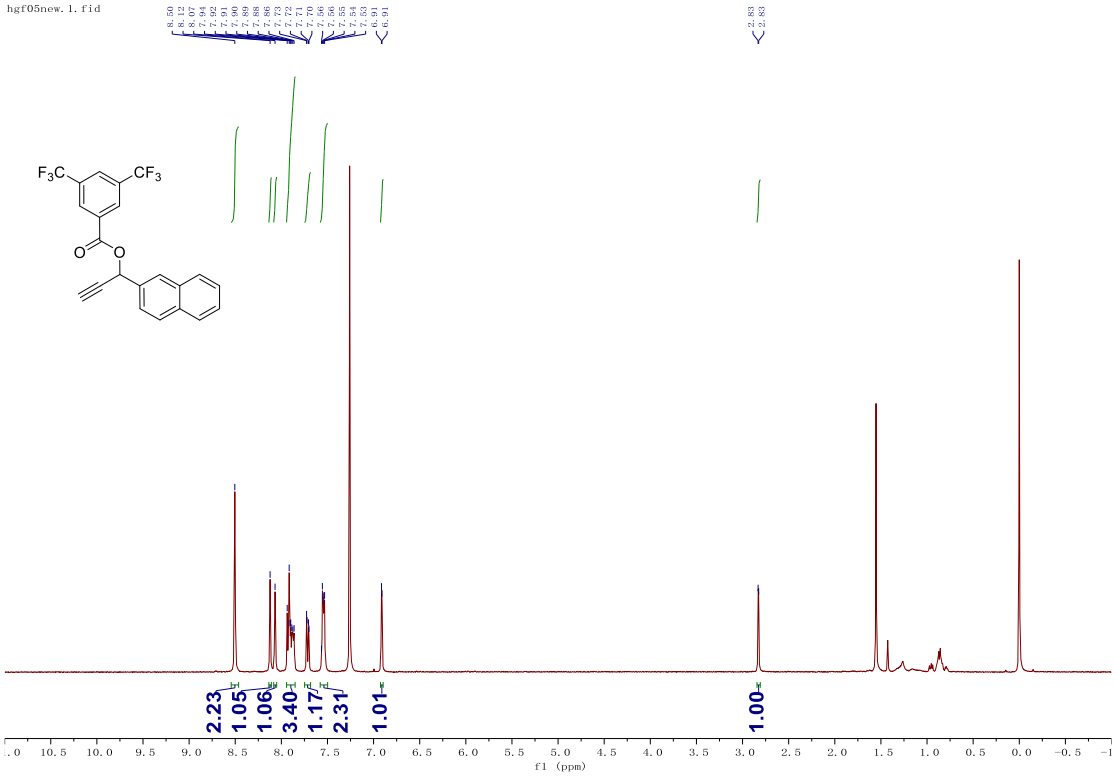
^{13}C NMR spectrum of compound 1f



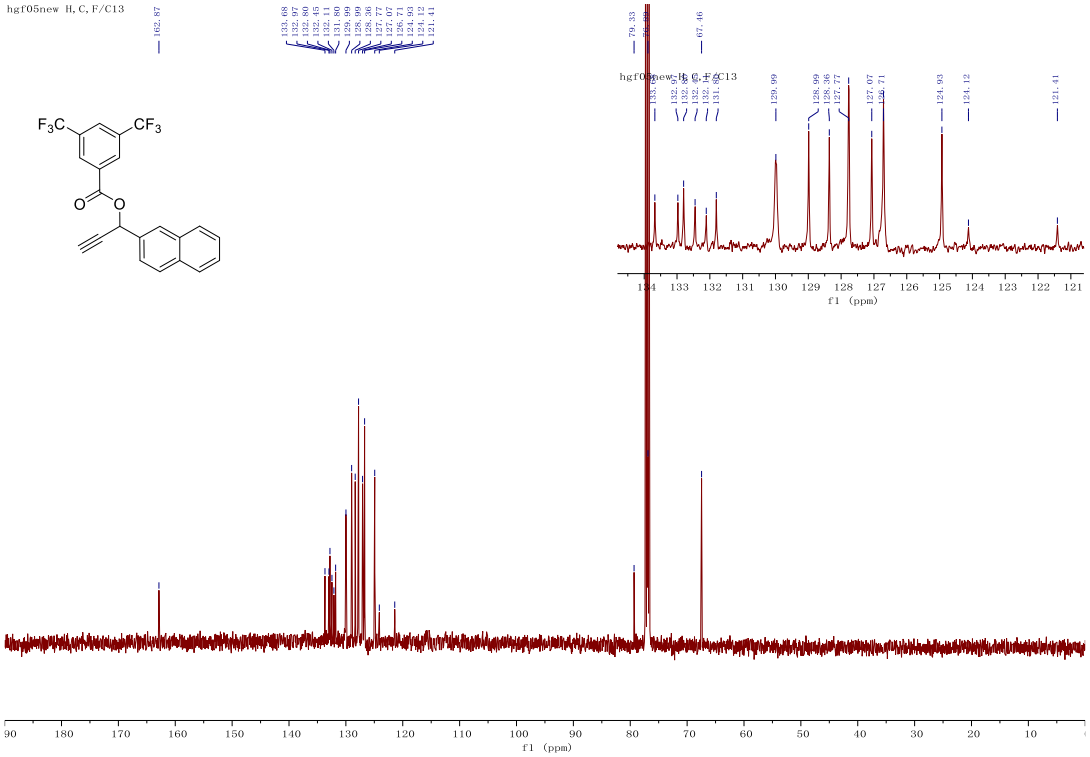
^{19}F NMR spectrum of compound 1f



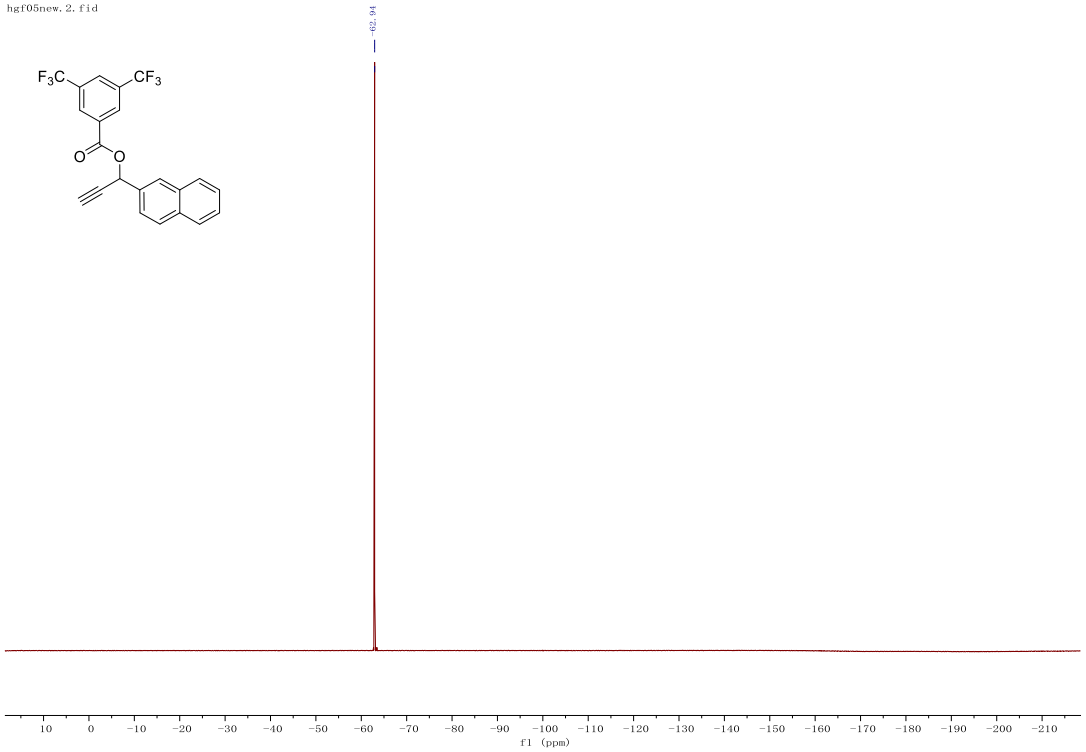
^{1}H NMR spectrum of compound 1g



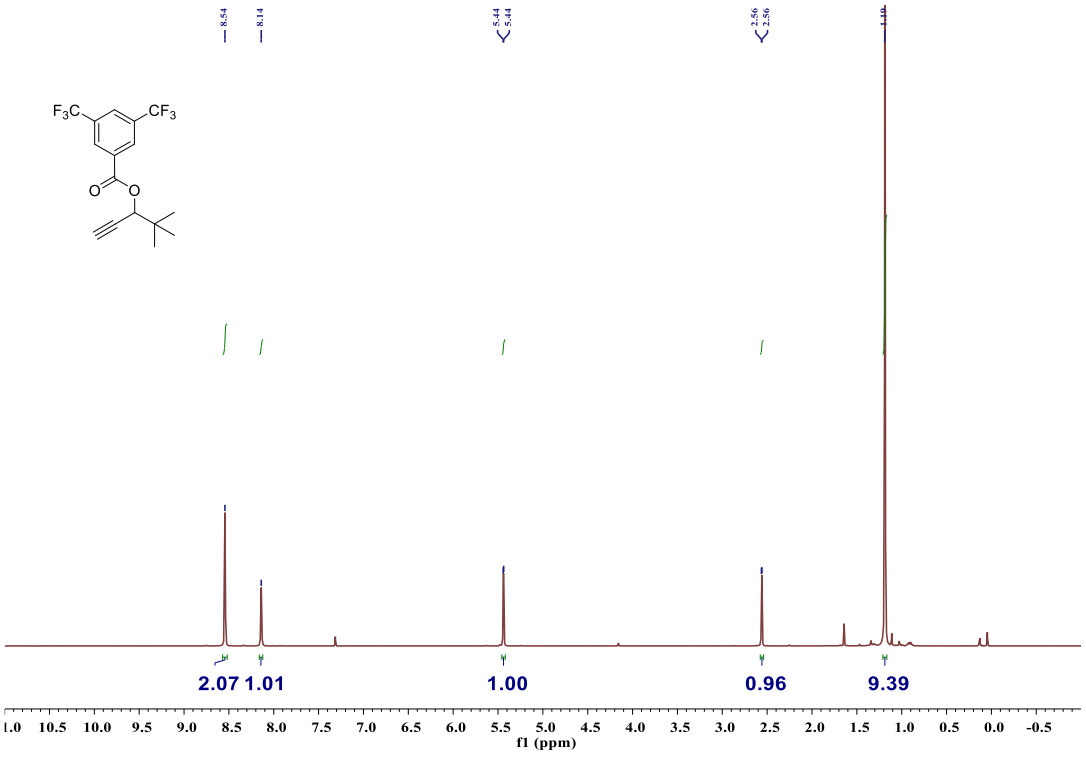
^{13}C NMR spectrum of compound 1g



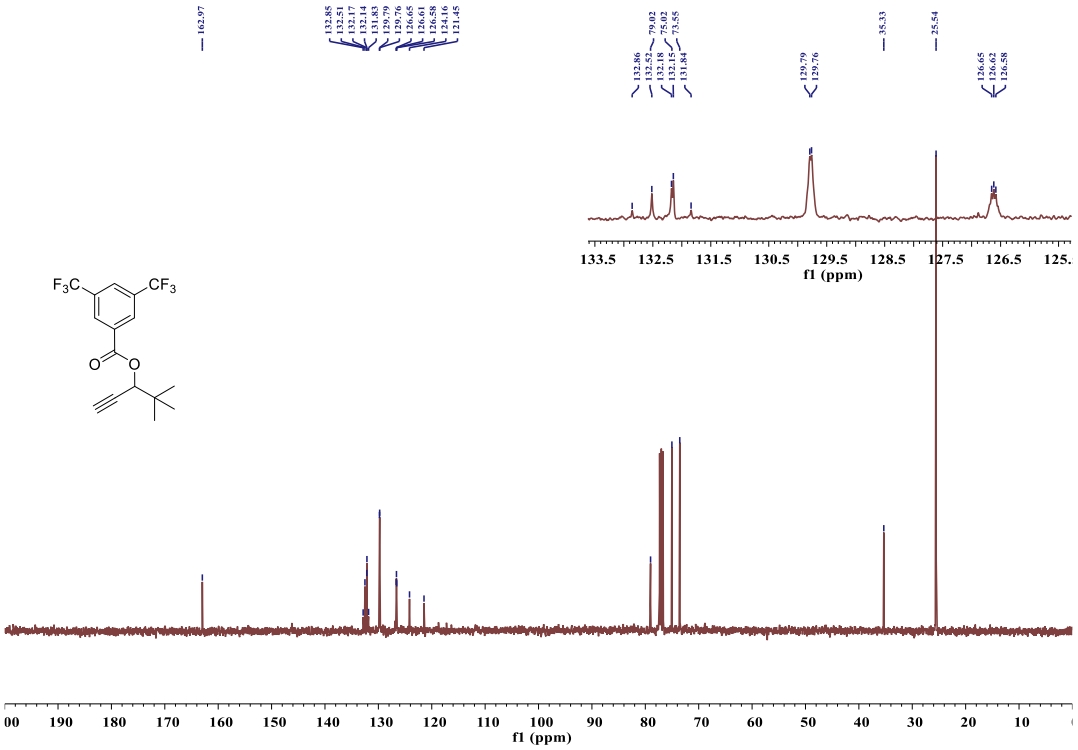
^{19}F NMR spectrum of compound 1g



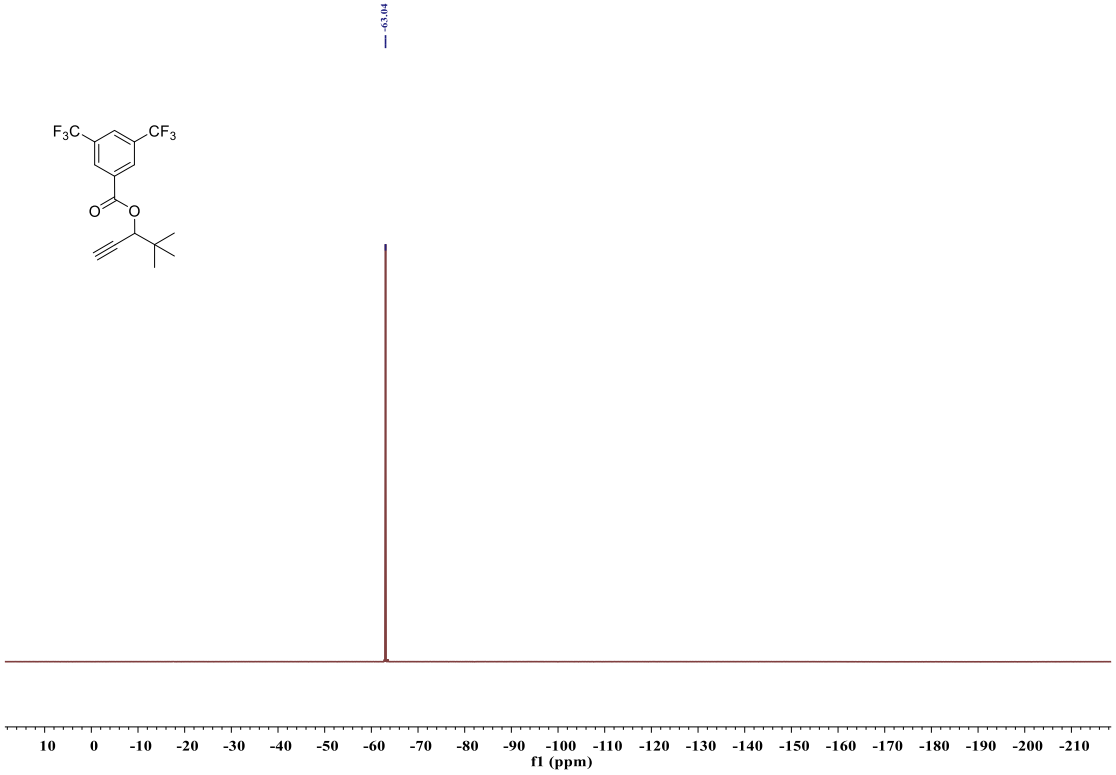
^{1}H NMR spectrum of compound 1h



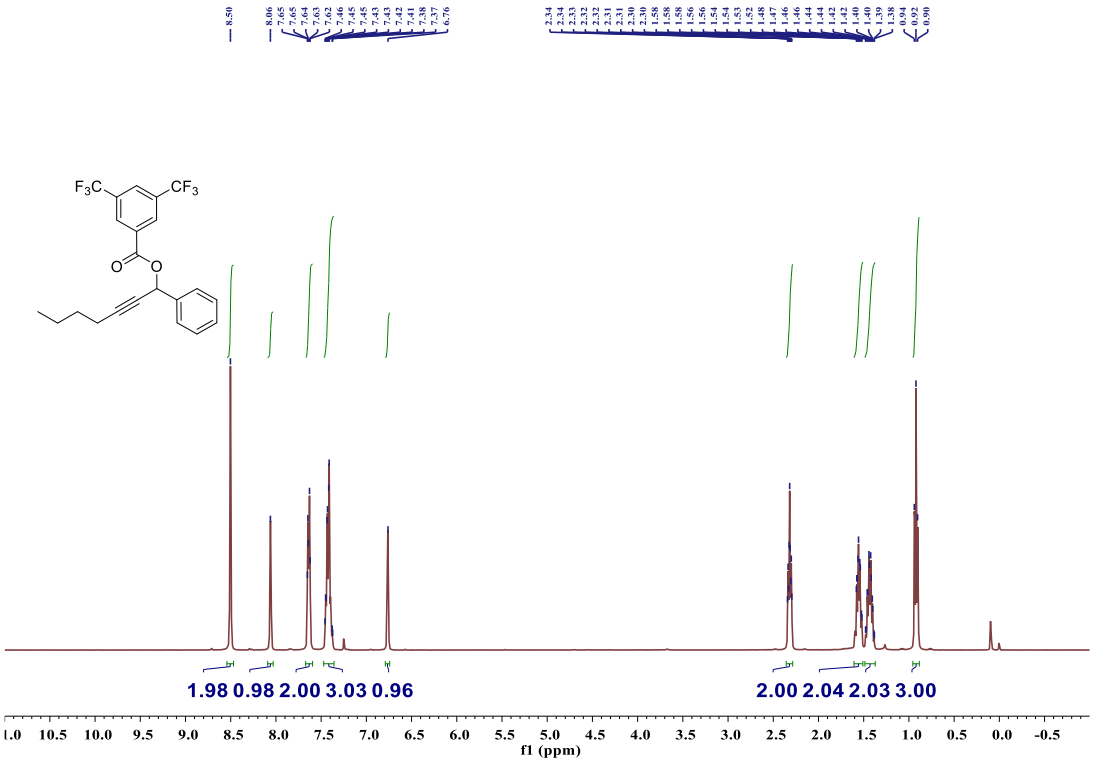
^{13}C NMR spectrum of compound 1h



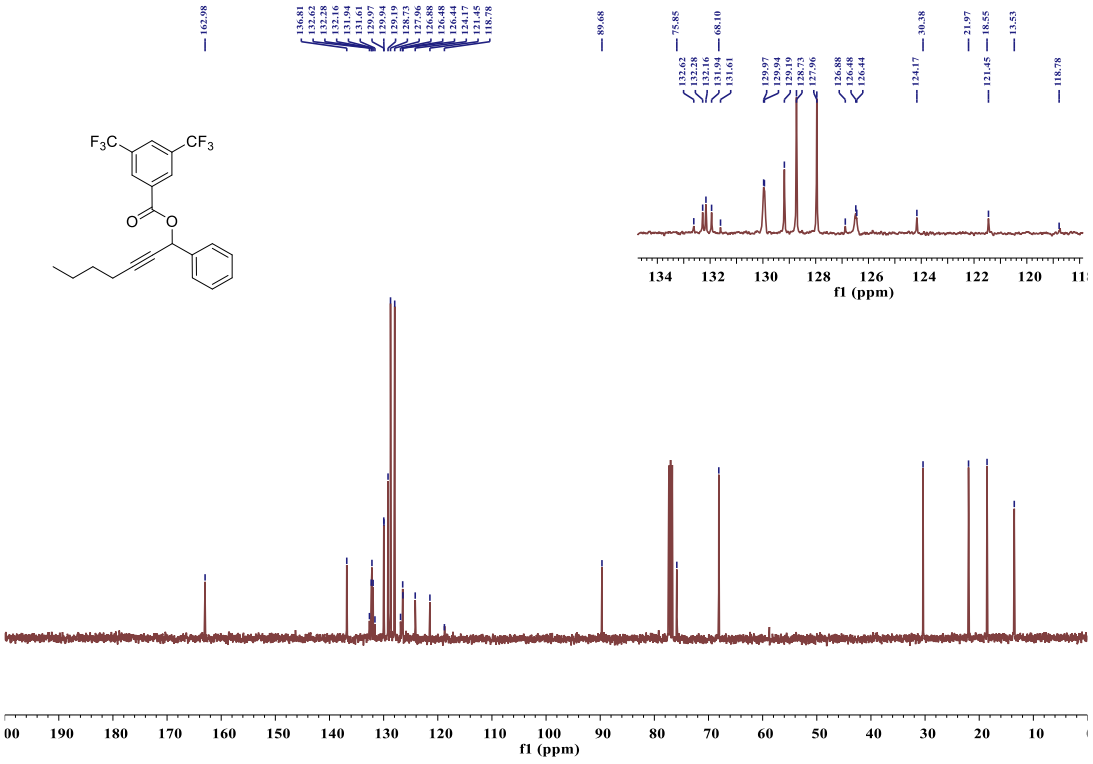
^{19}F NMR spectrum of compound 1h



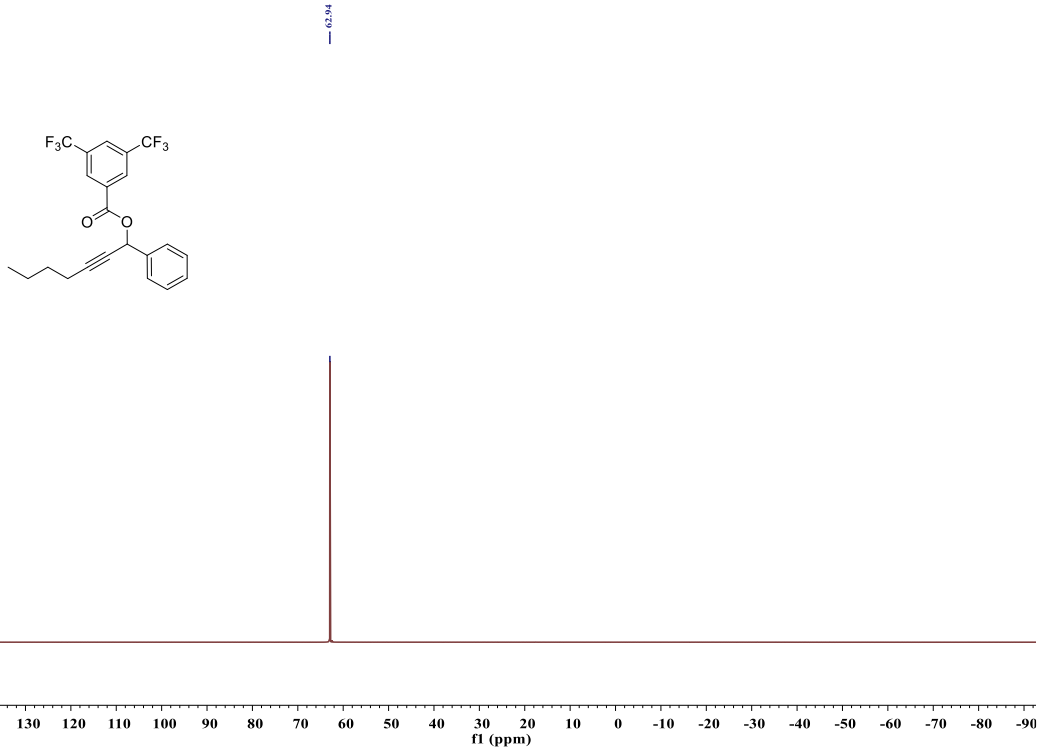
^{1}H NMR spectrum of compound 1i



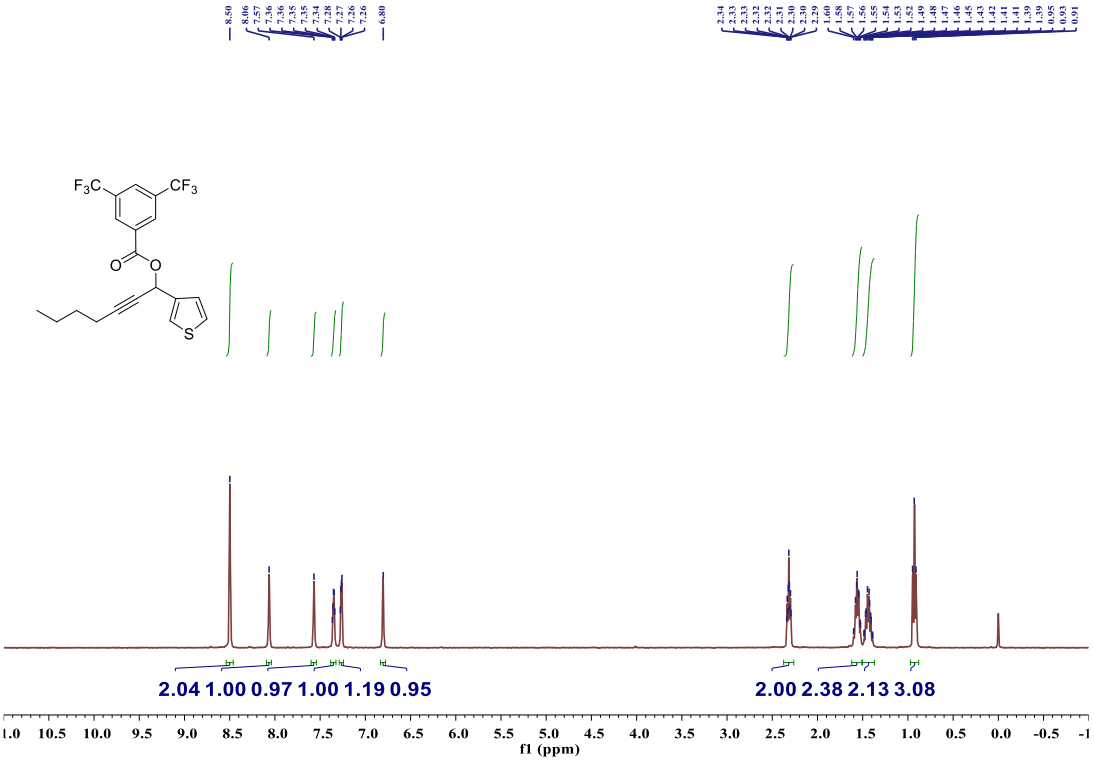
^{13}C NMR spectrum of compound 1i



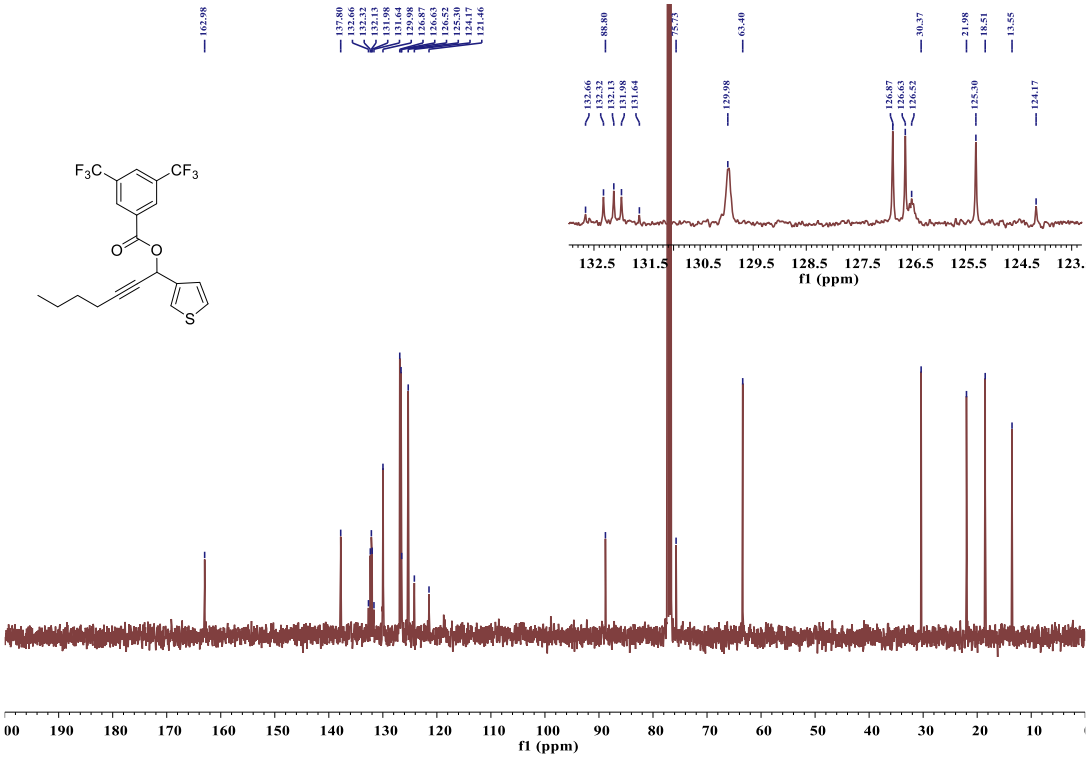
^{19}F NMR spectrum of compound 1i



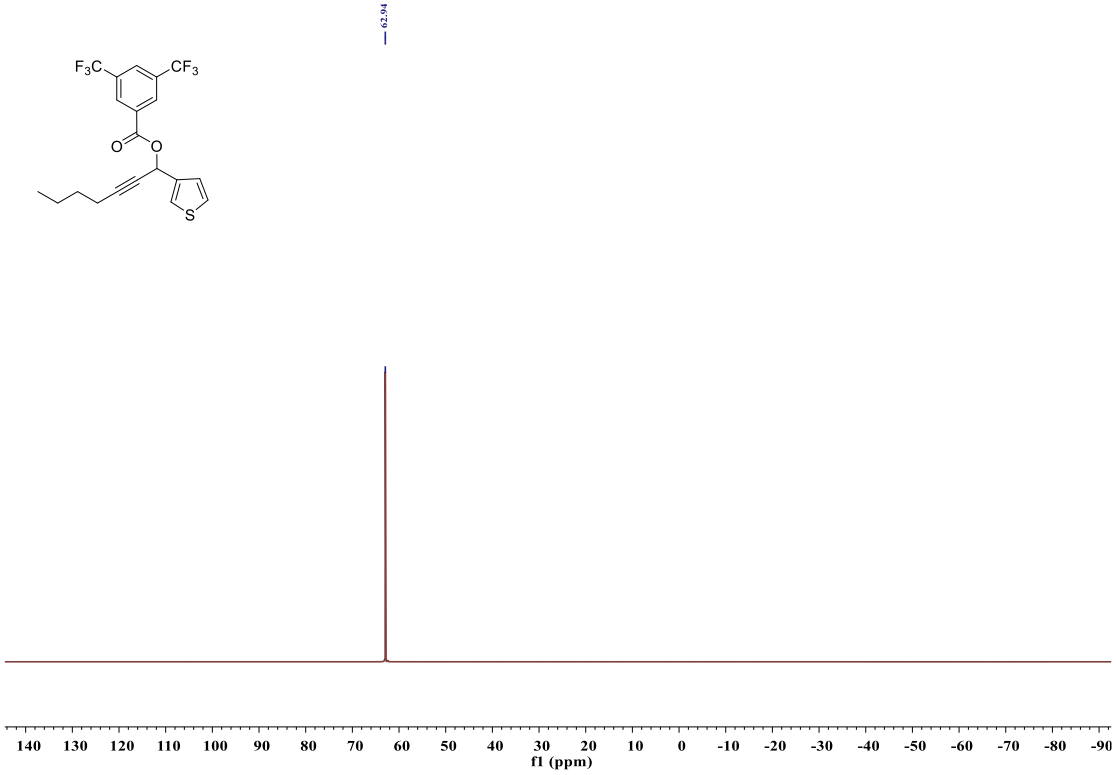
^{1}H NMR spectrum of compound 1j



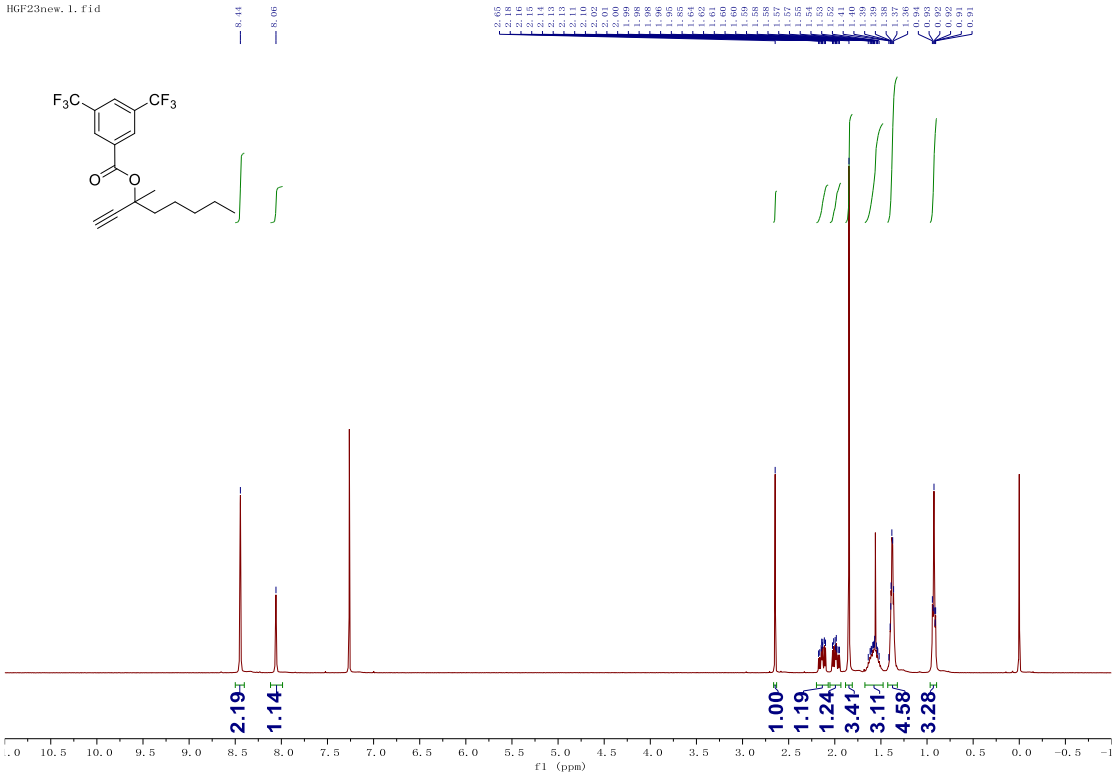
^{13}C NMR spectrum of compound 1j



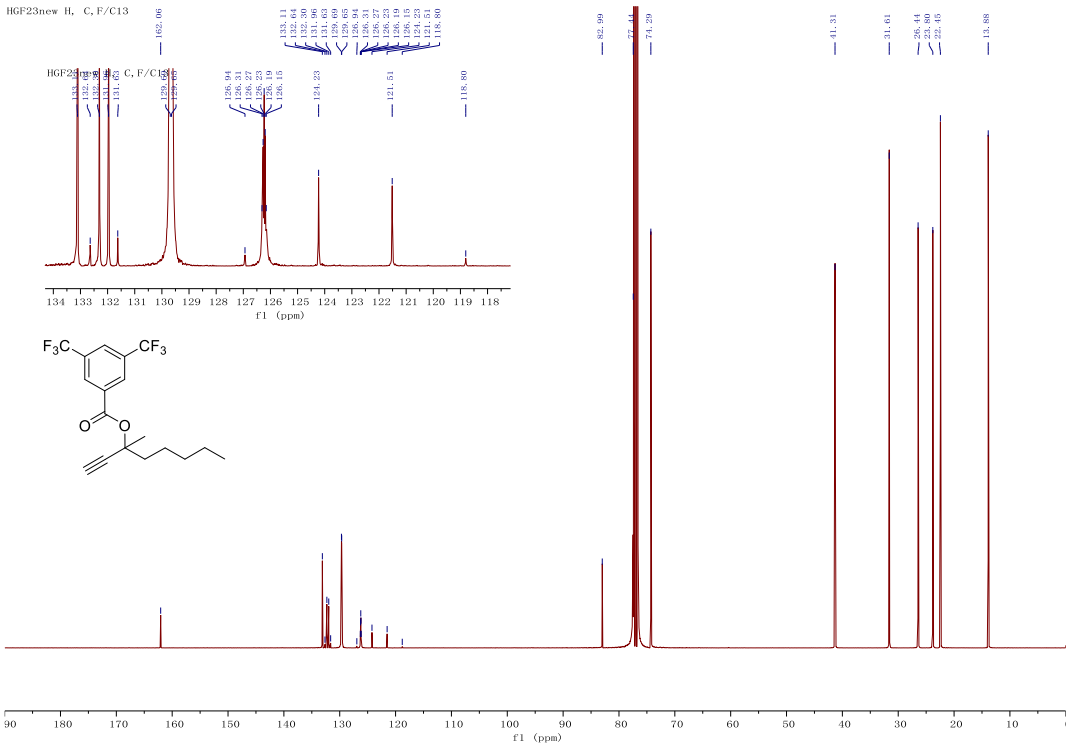
^{19}F NMR spectrum of compound 1j



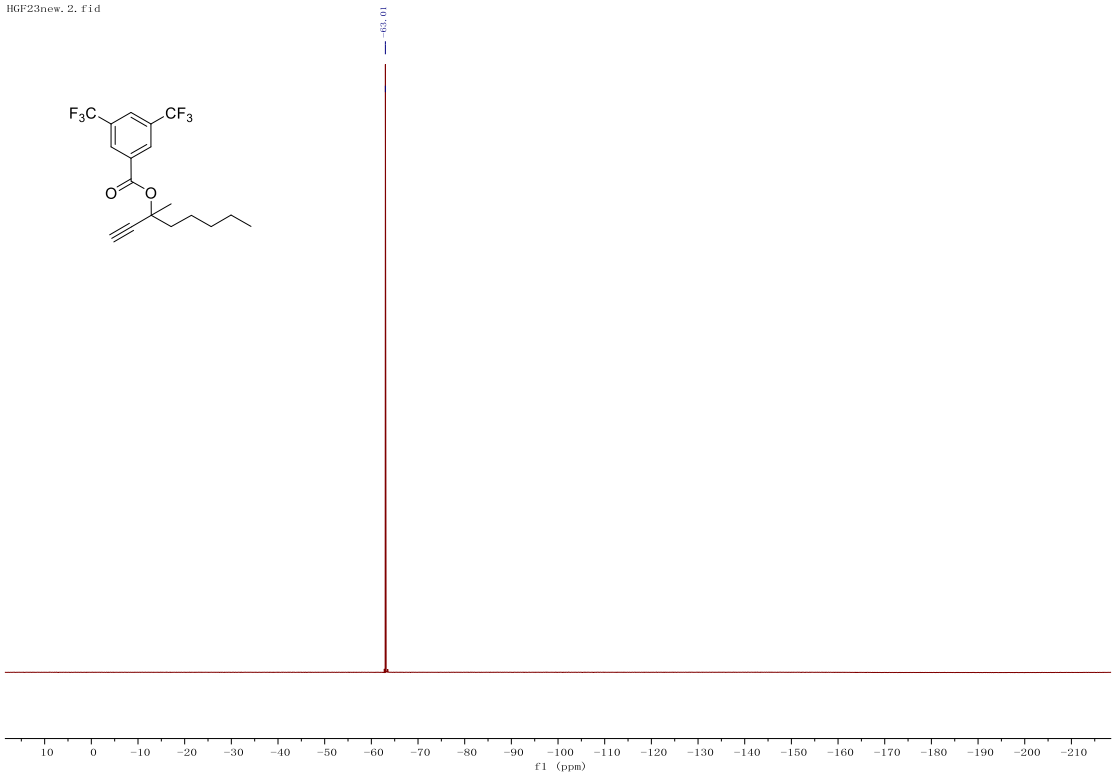
^{1}H NMR spectrum of compound 1k



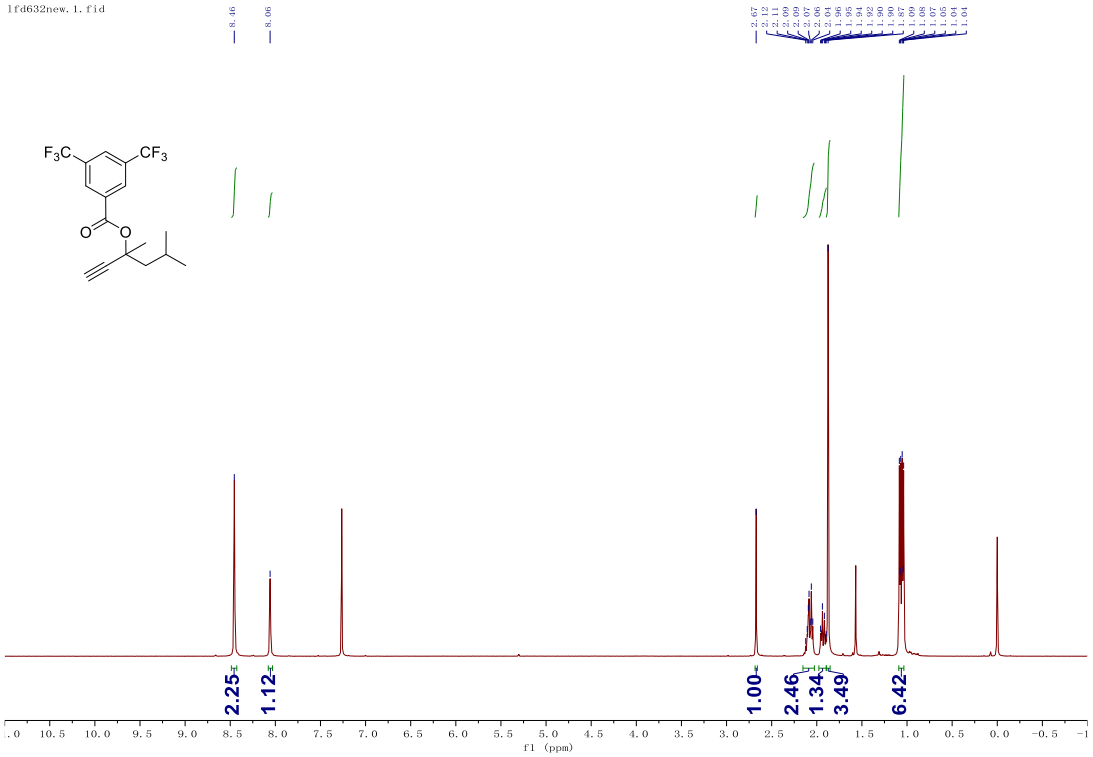
^{13}C NMR spectrum of compound 1k



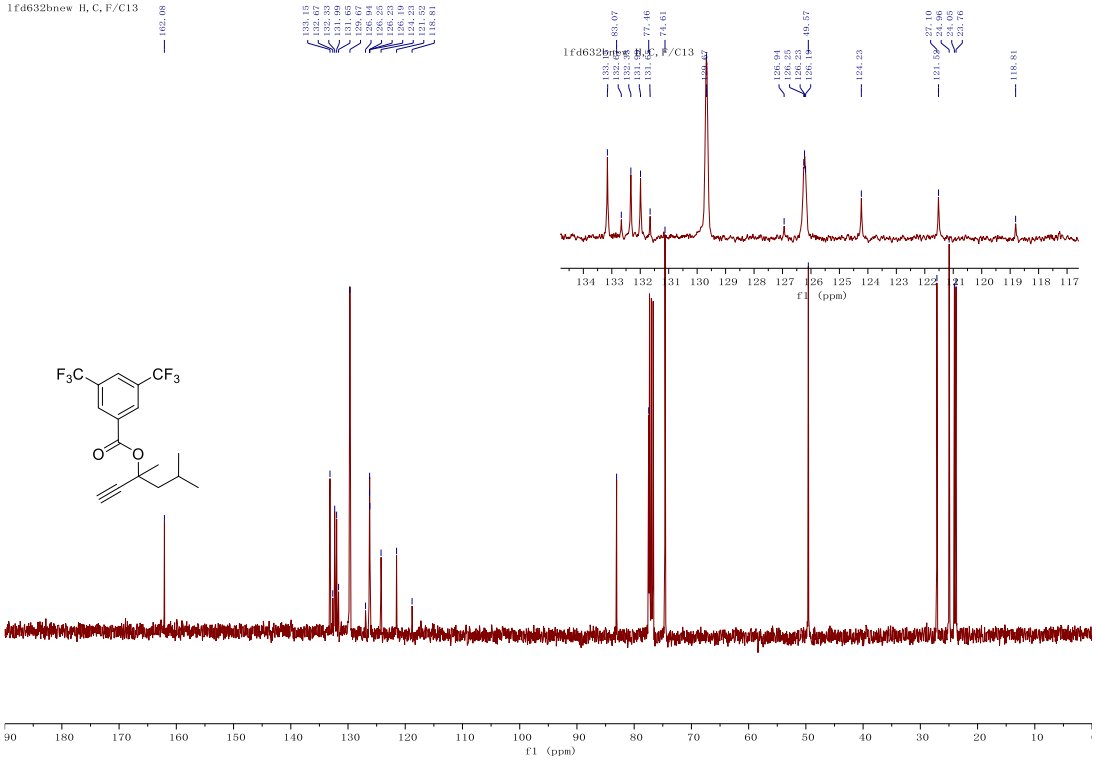
^{19}F NMR spectrum of compound 1k



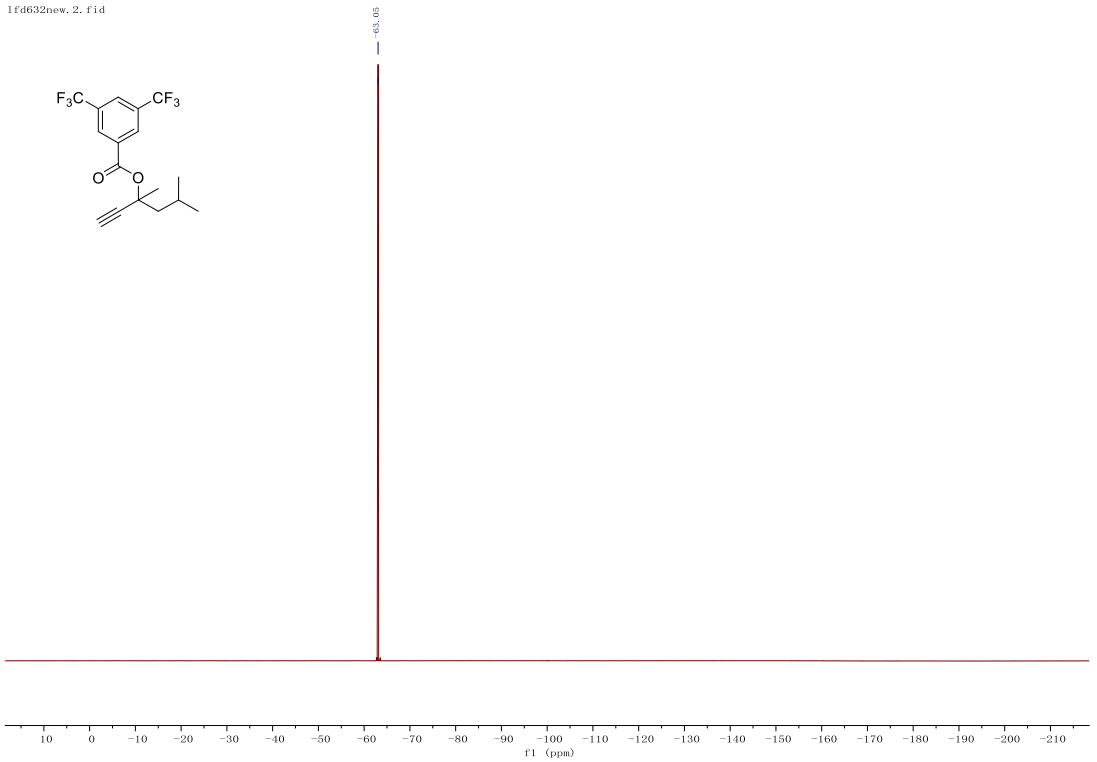
^{1}H NMR spectrum of compound 1l



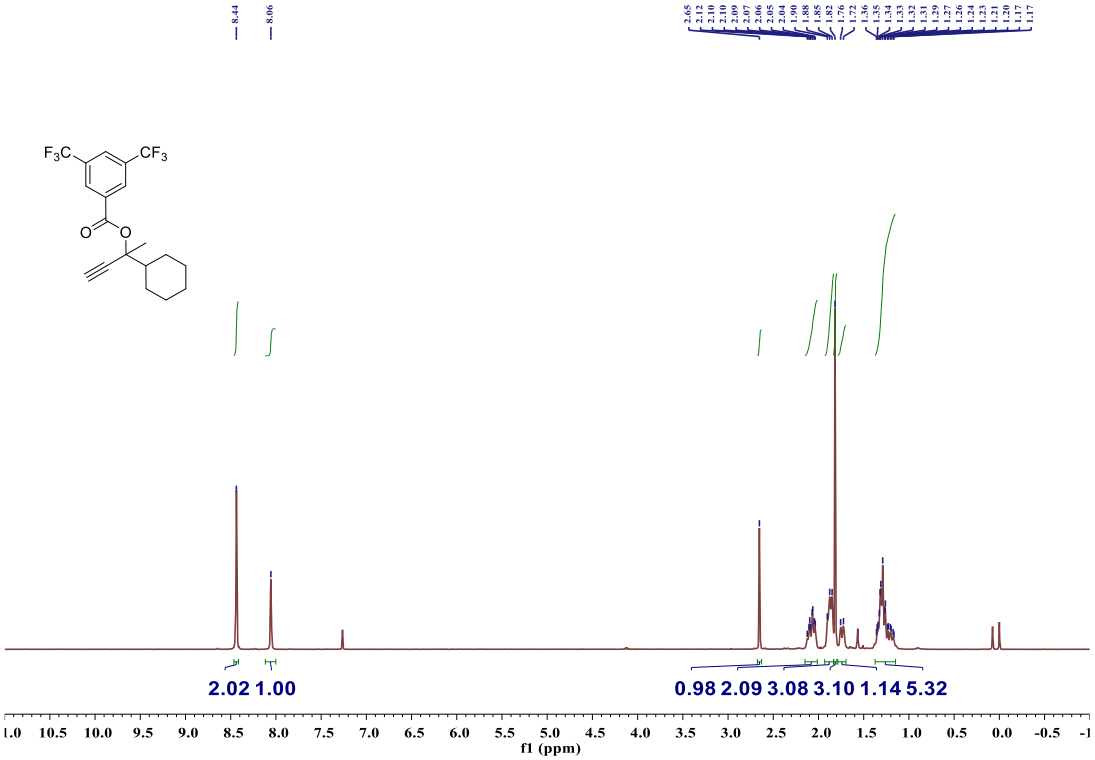
^{13}C NMR spectrum of compound 1l



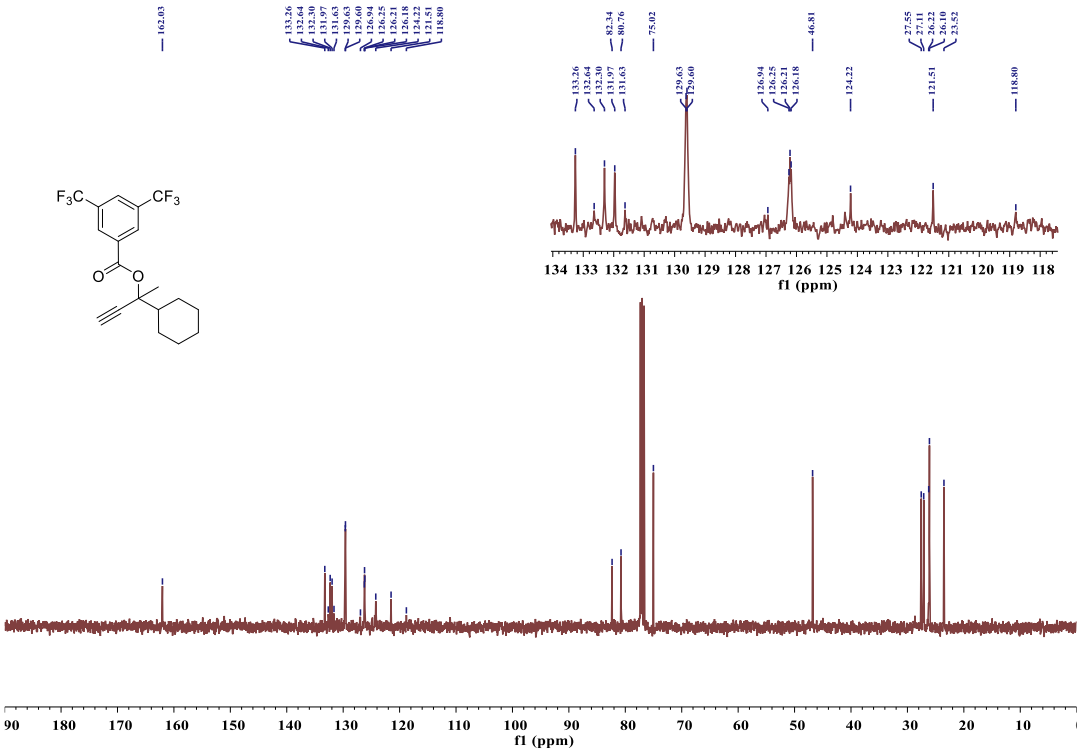
^{19}F NMR spectrum of compound 1l



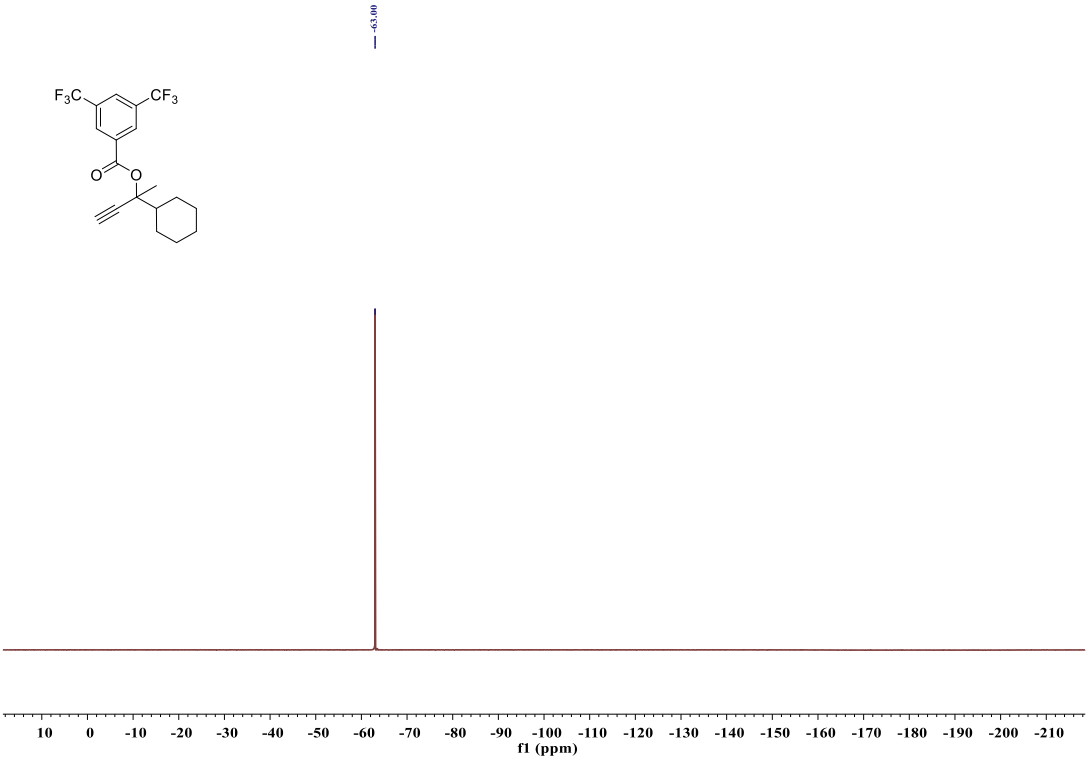
^{1}H NMR spectrum of compound 1m



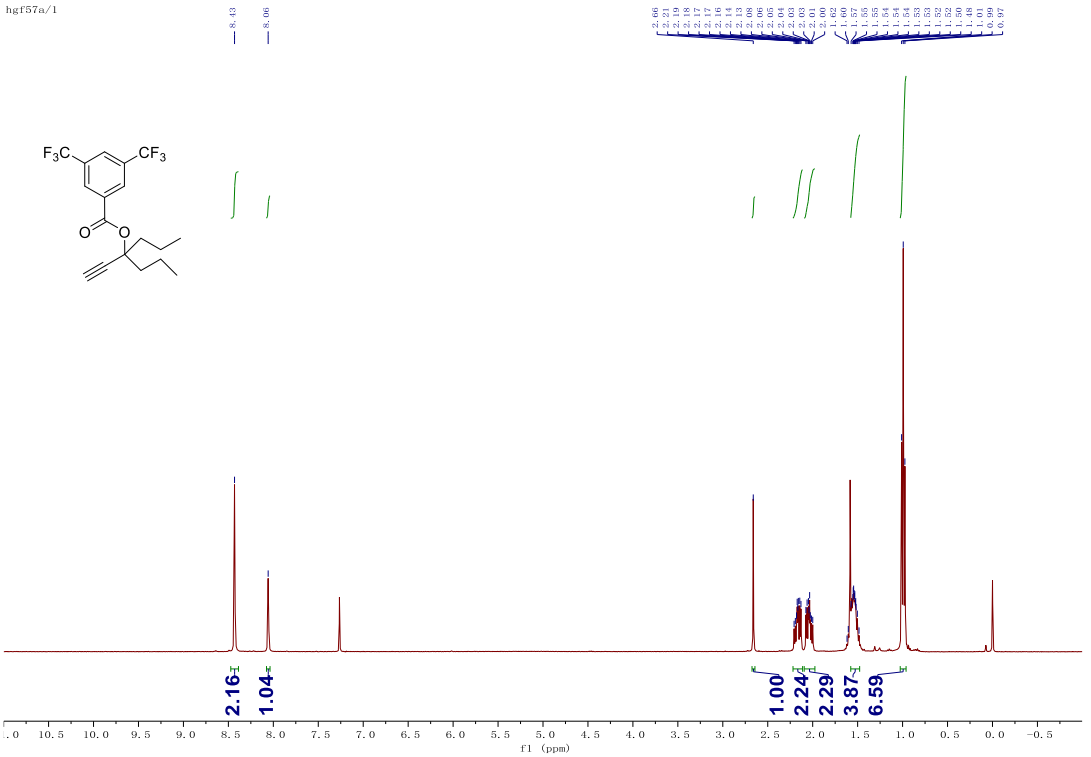
^{13}C NMR spectrum of compound 1m



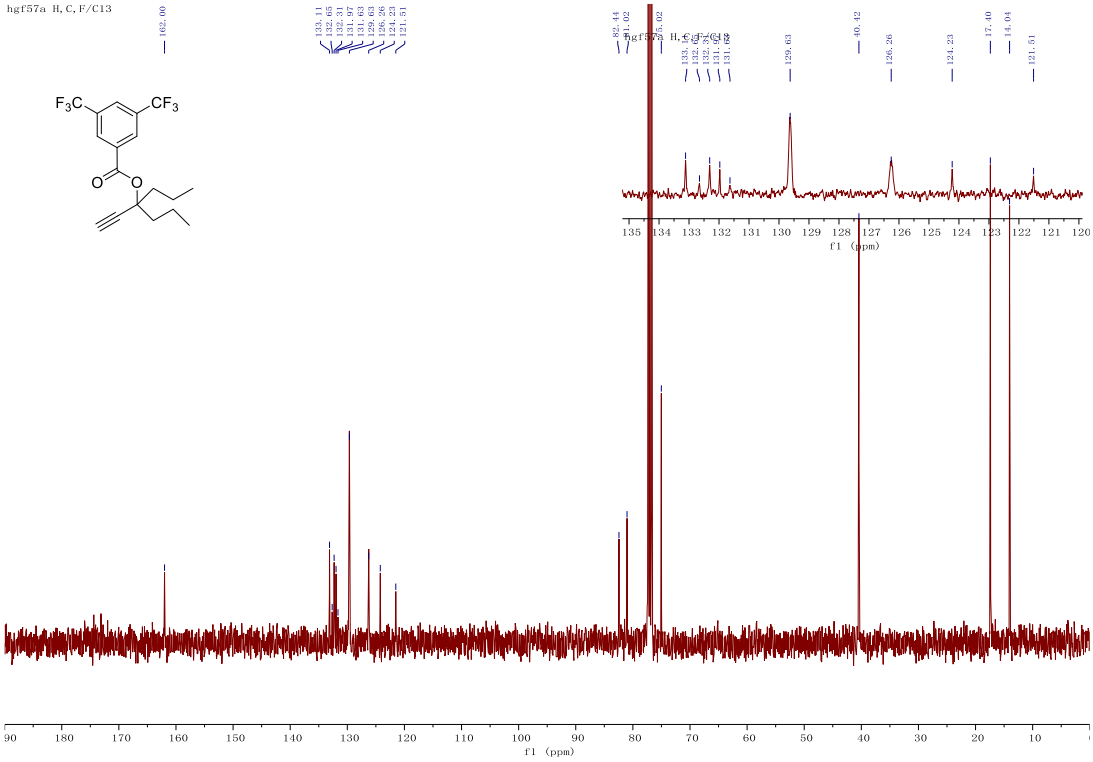
^{19}F NMR spectrum of compound 1m



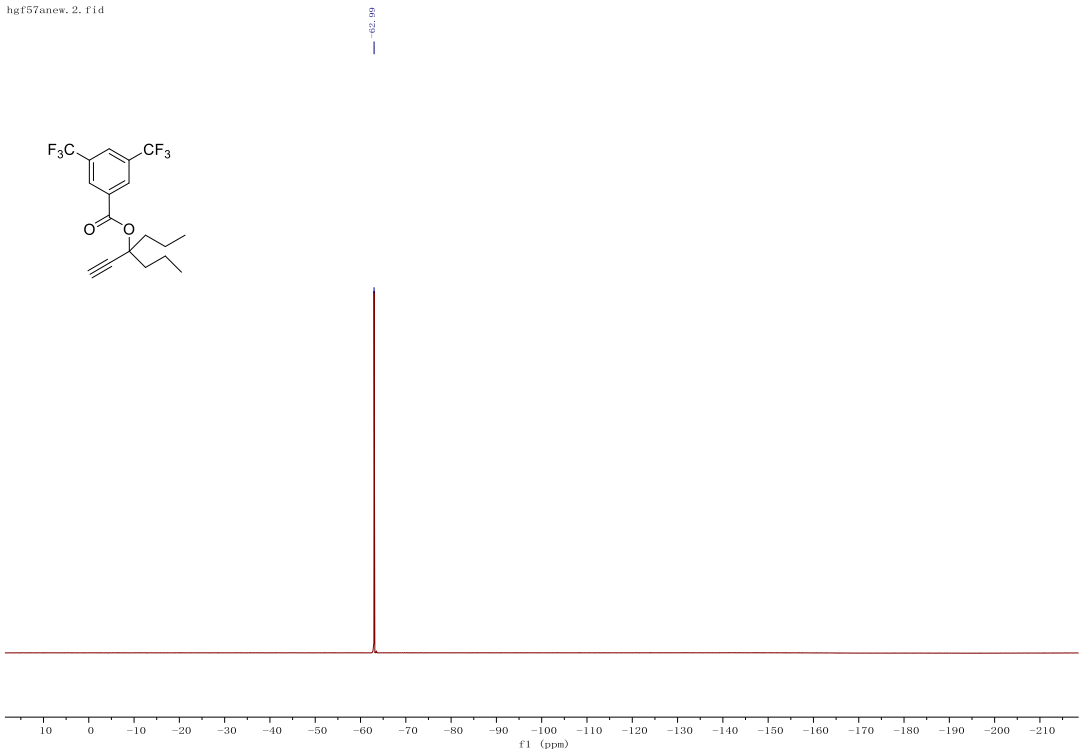
^{1}H NMR spectrum of compound 1n



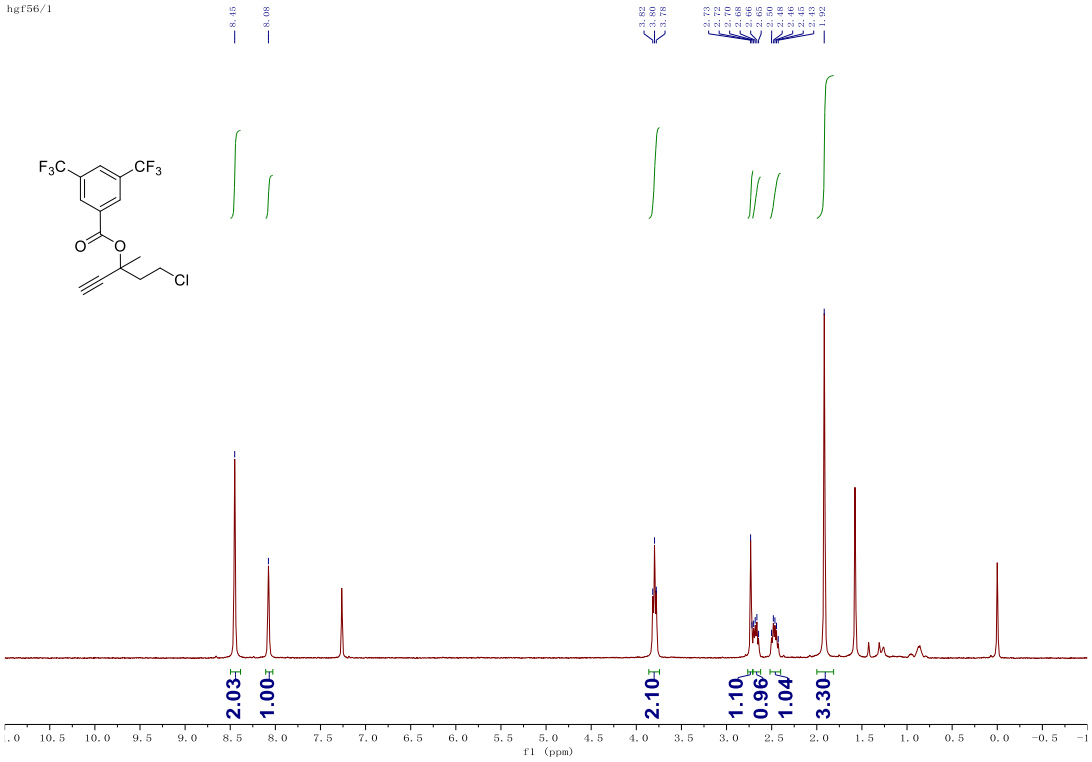
^{13}C NMR spectrum of compound 1n



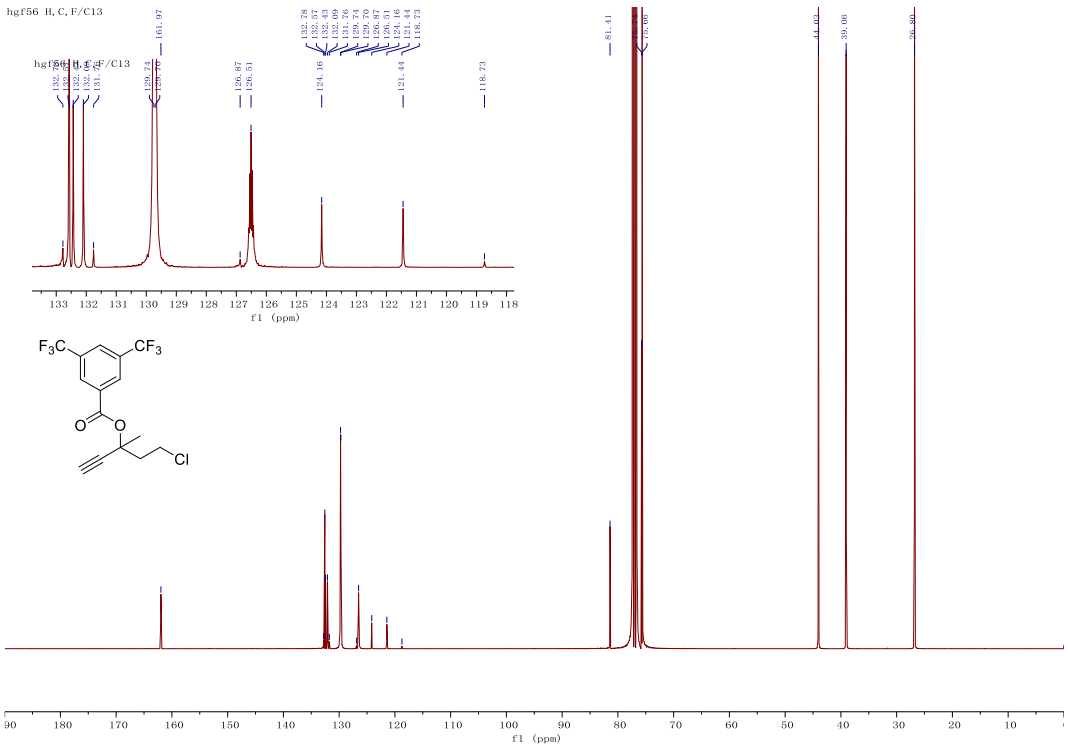
^{19}F NMR spectrum of compound 1n



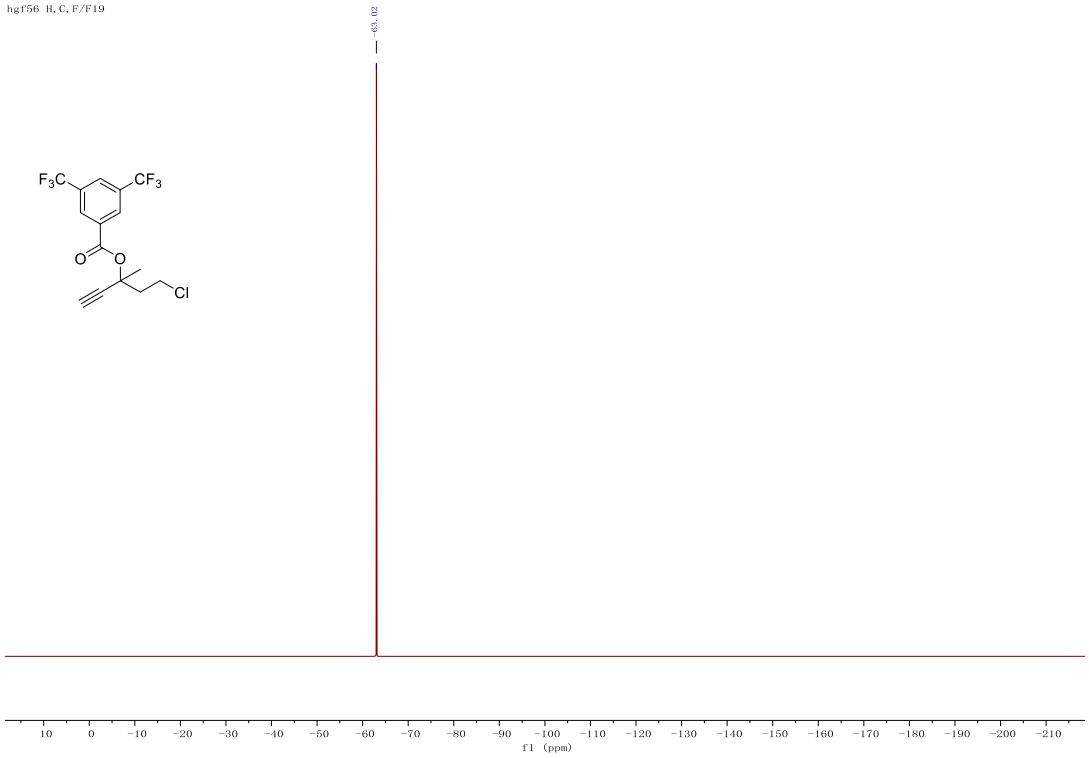
^{1}H NMR spectrum of compound 1o



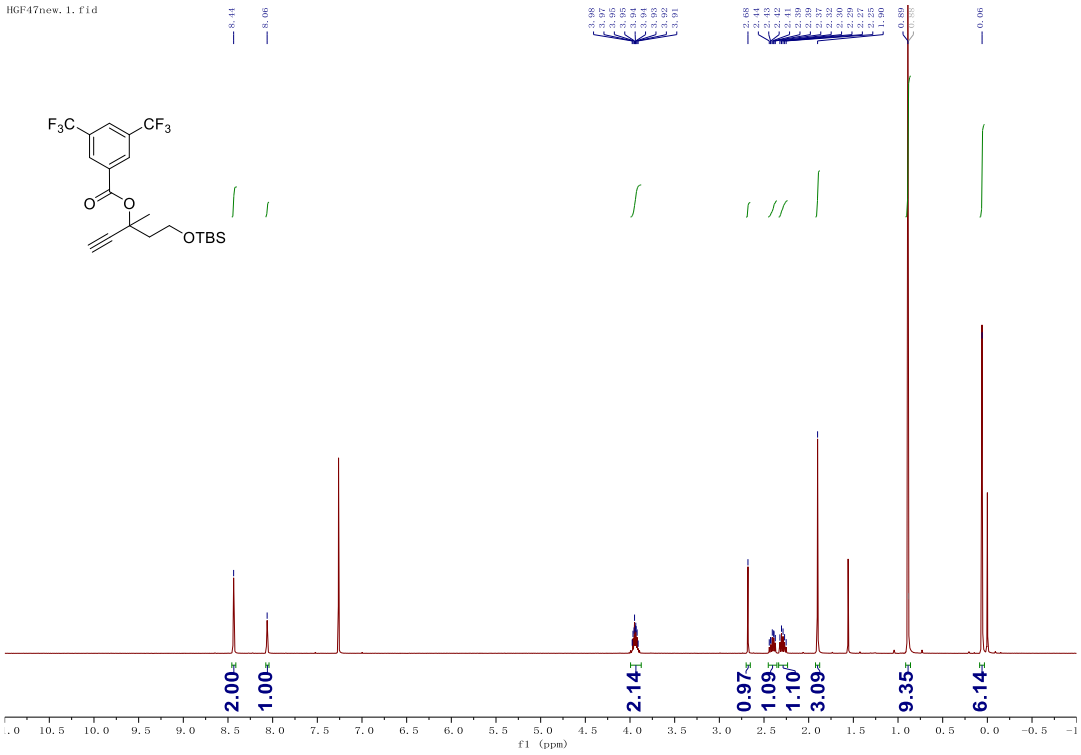
^{13}C NMR spectrum of compound 1o



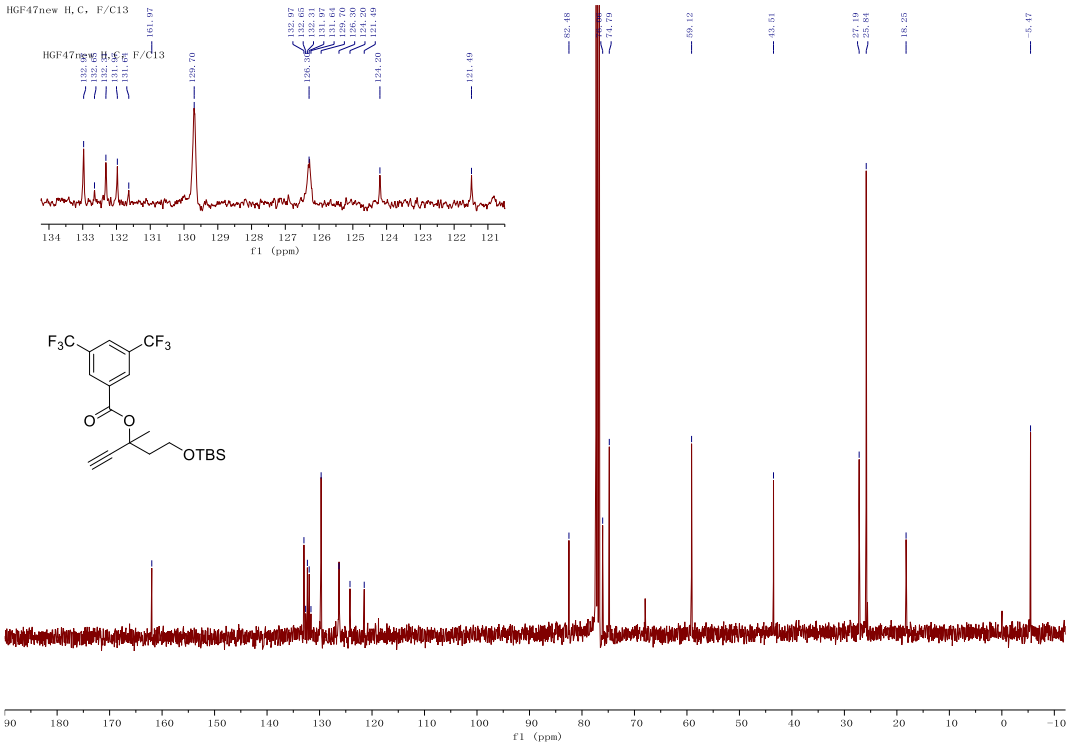
^{19}F NMR spectrum of compound 1o



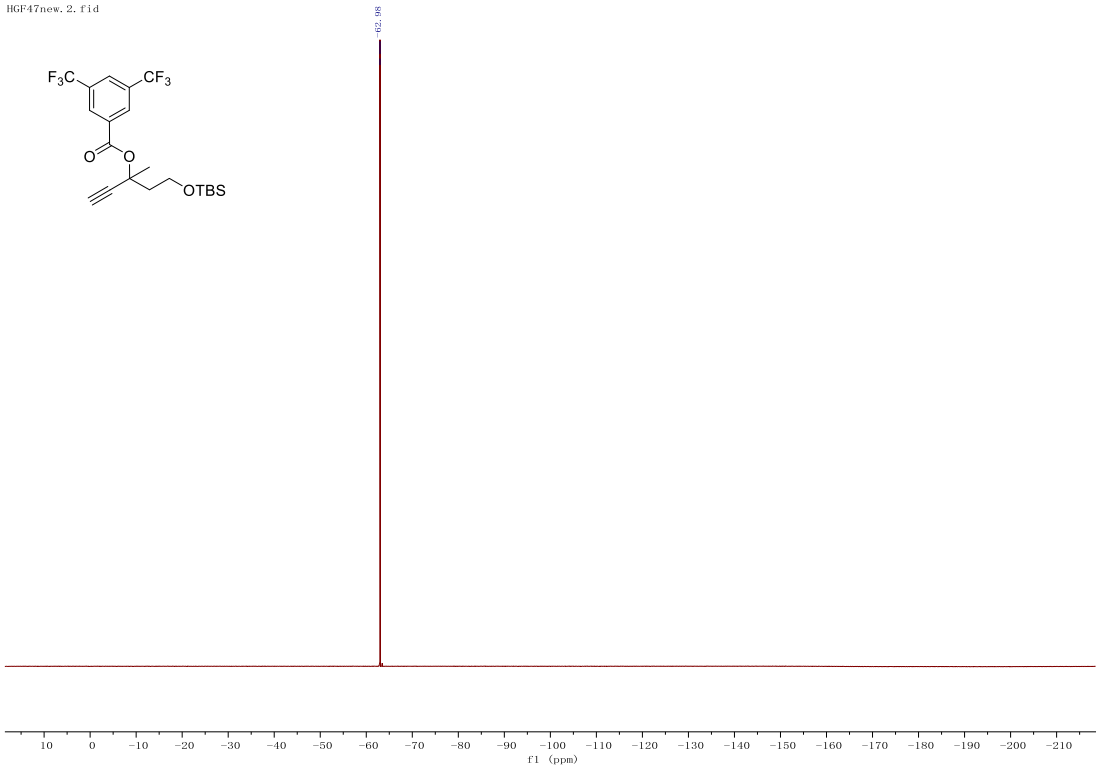
^{1}H NMR spectrum of compound 1p



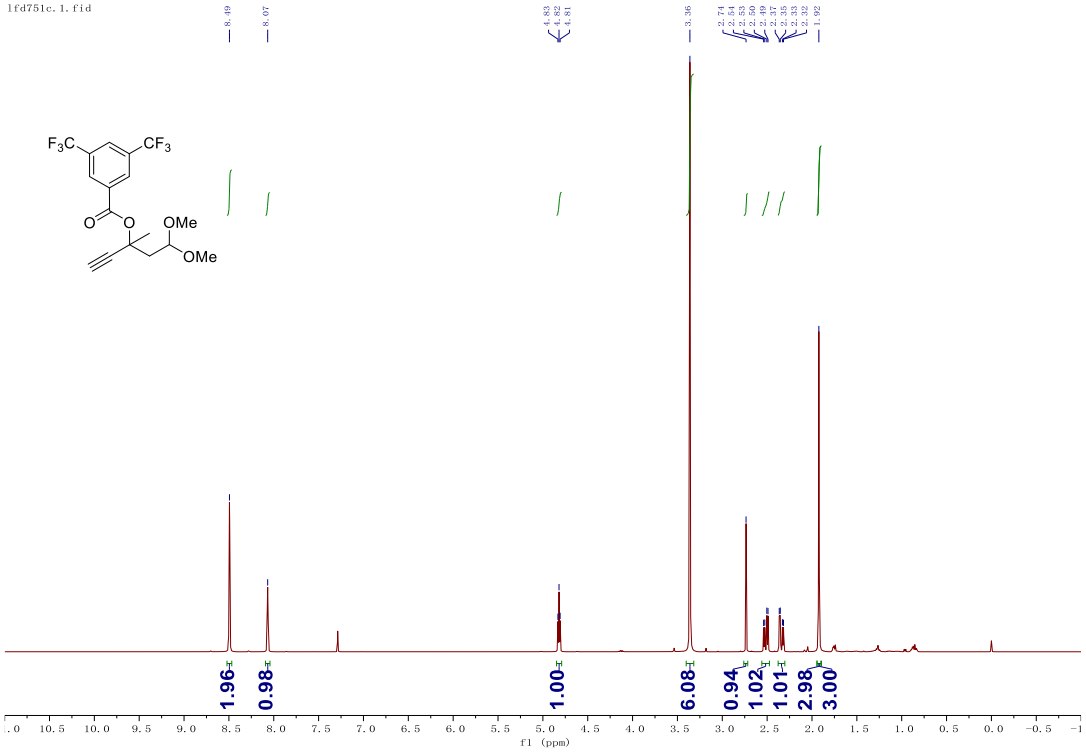
^{13}C NMR spectrum of compound 1p



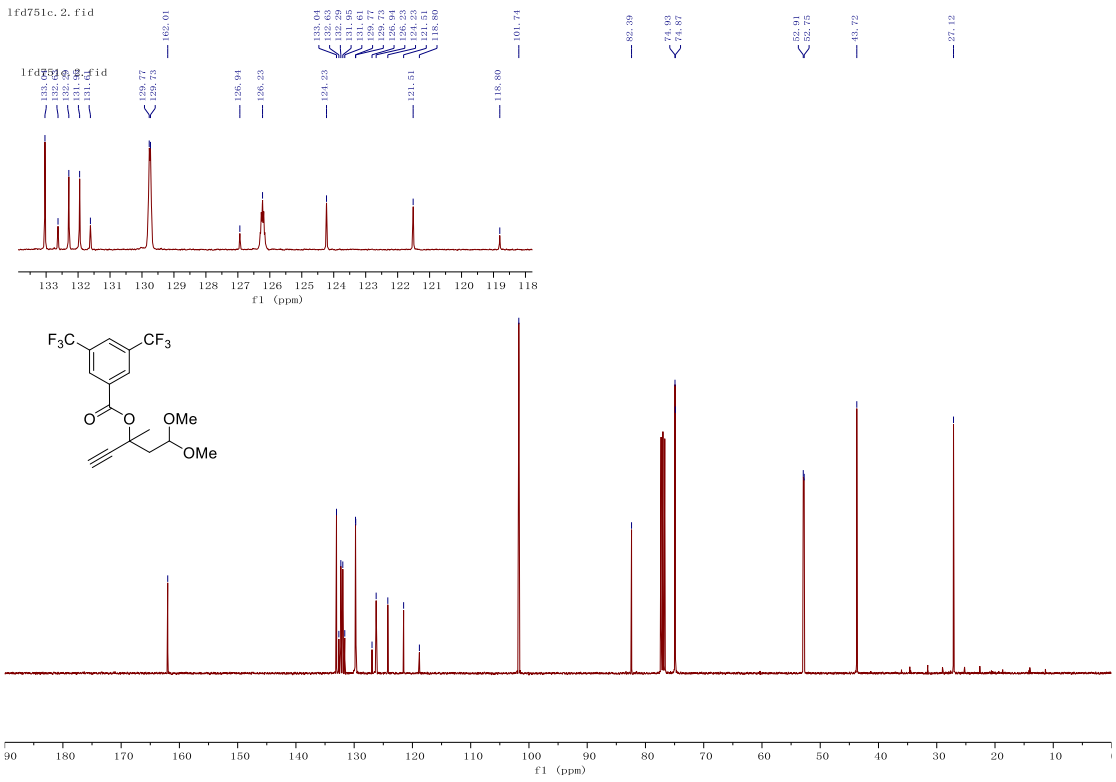
^{19}F NMR spectrum of compound 1p



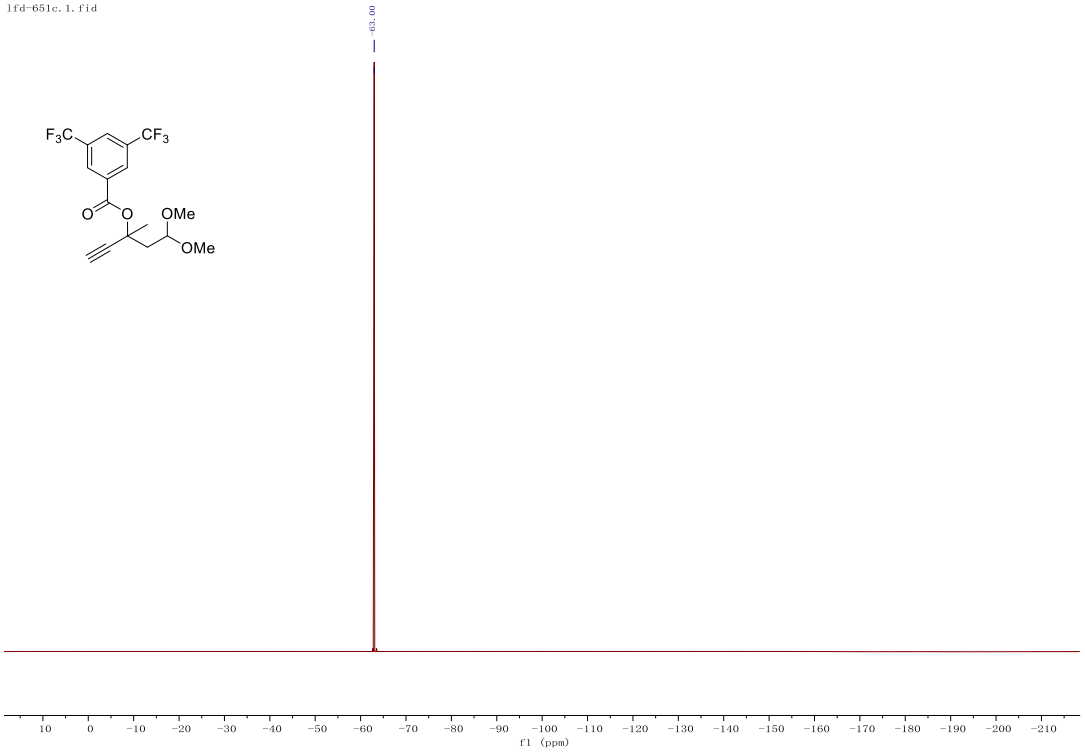
^{1}H NMR spectrum of compound 1q



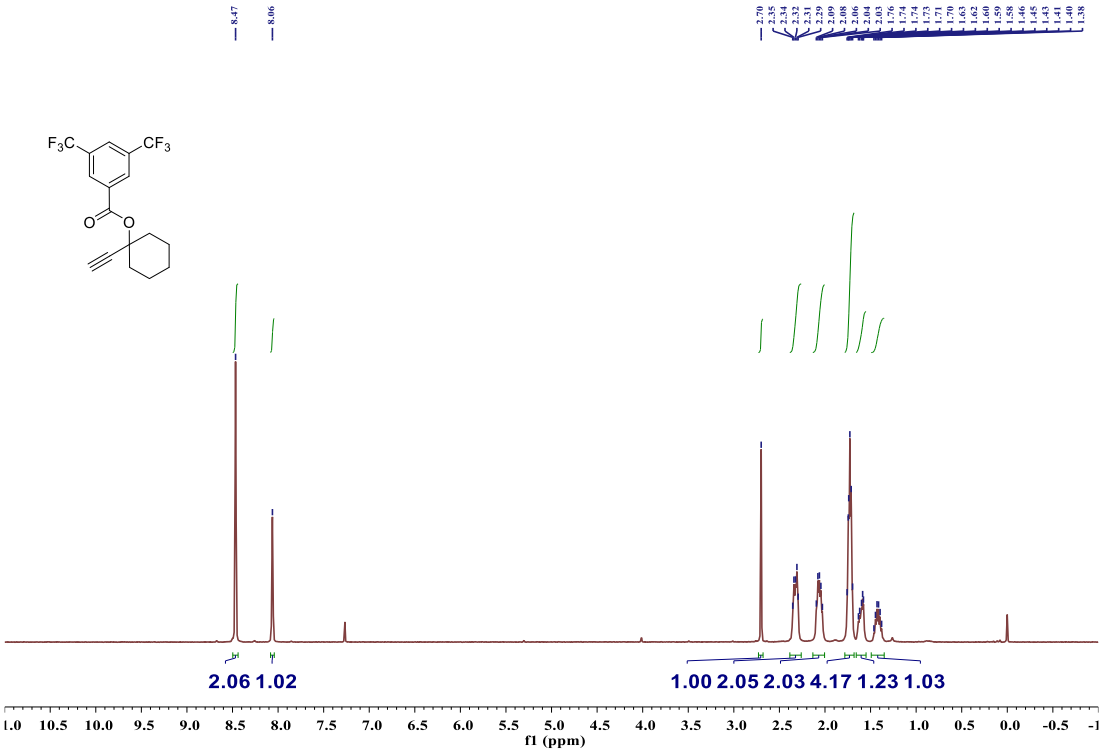
^{13}C NMR spectrum of compound 1q



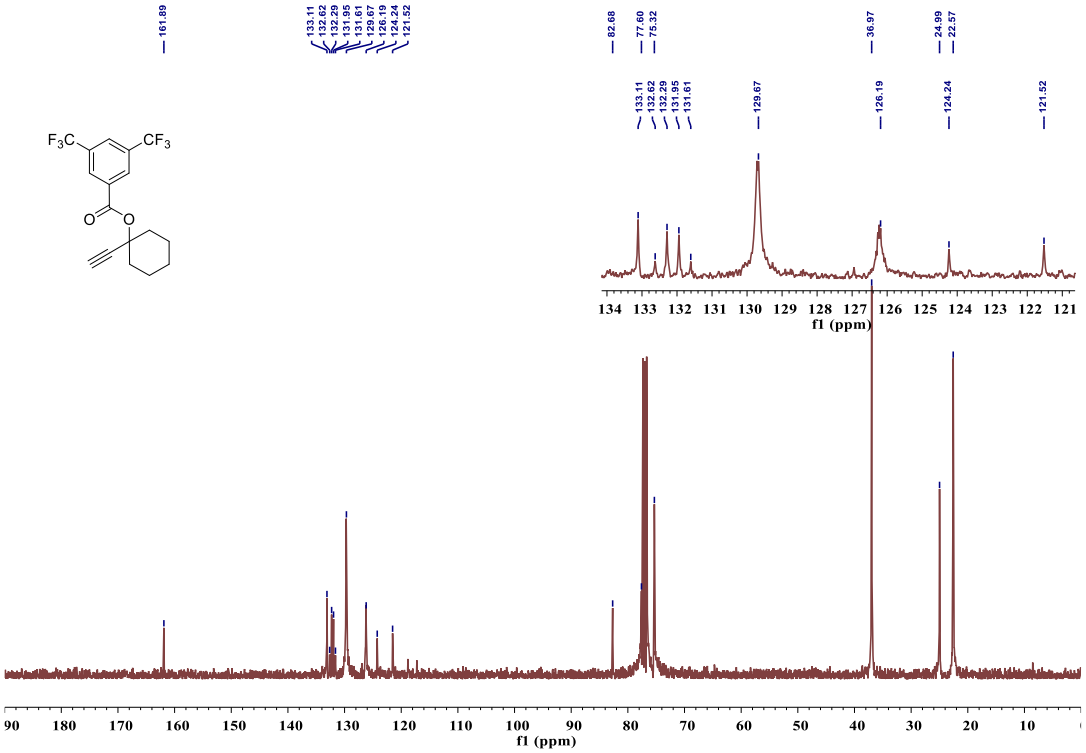
^{19}F NMR spectrum of compound 1q



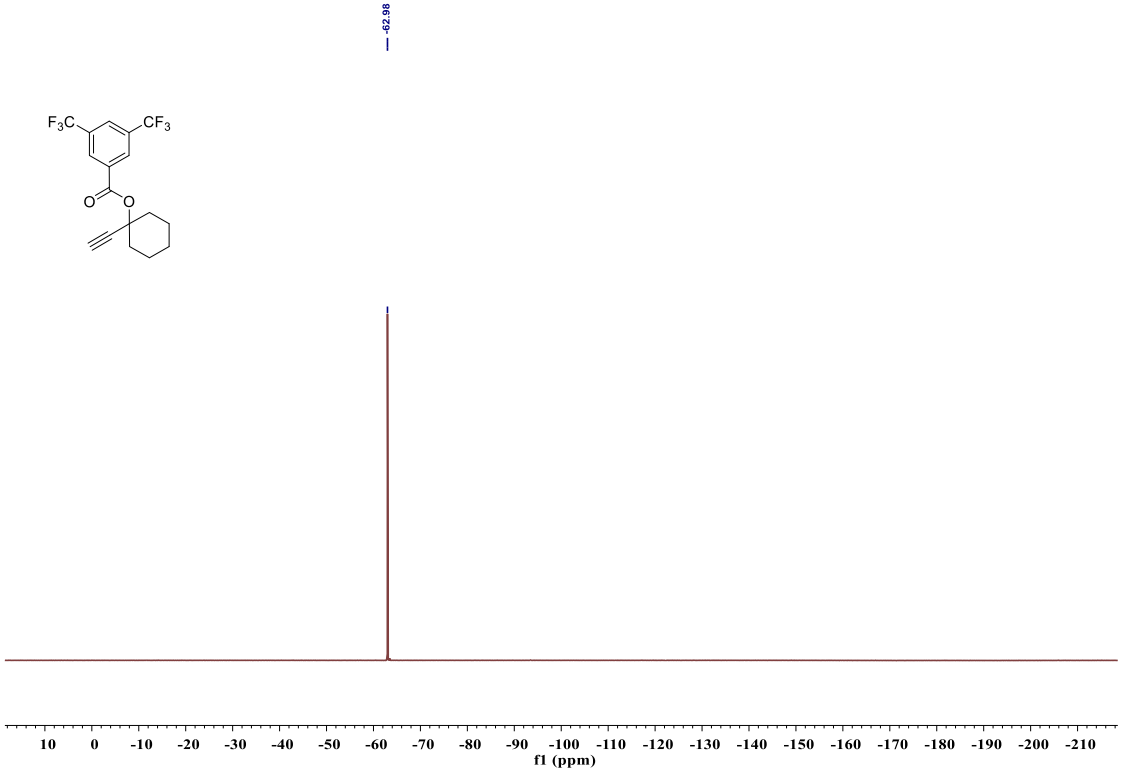
^{1}H NMR spectrum of compound 1r



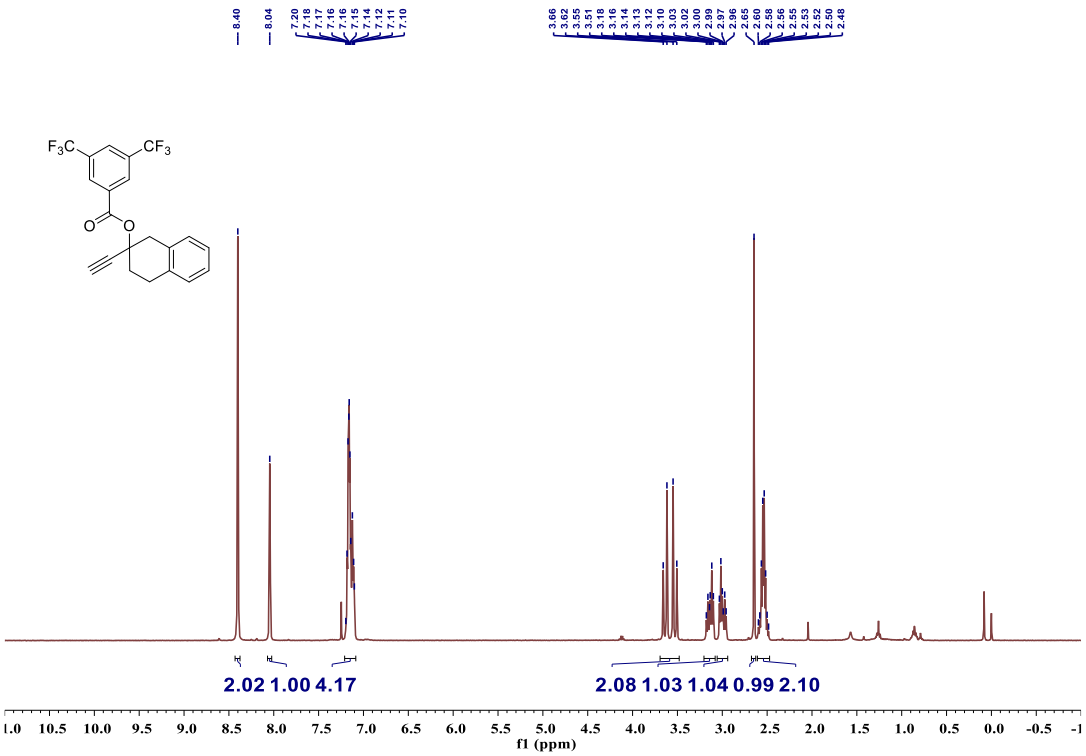
^{13}C NMR spectrum of compound 1r



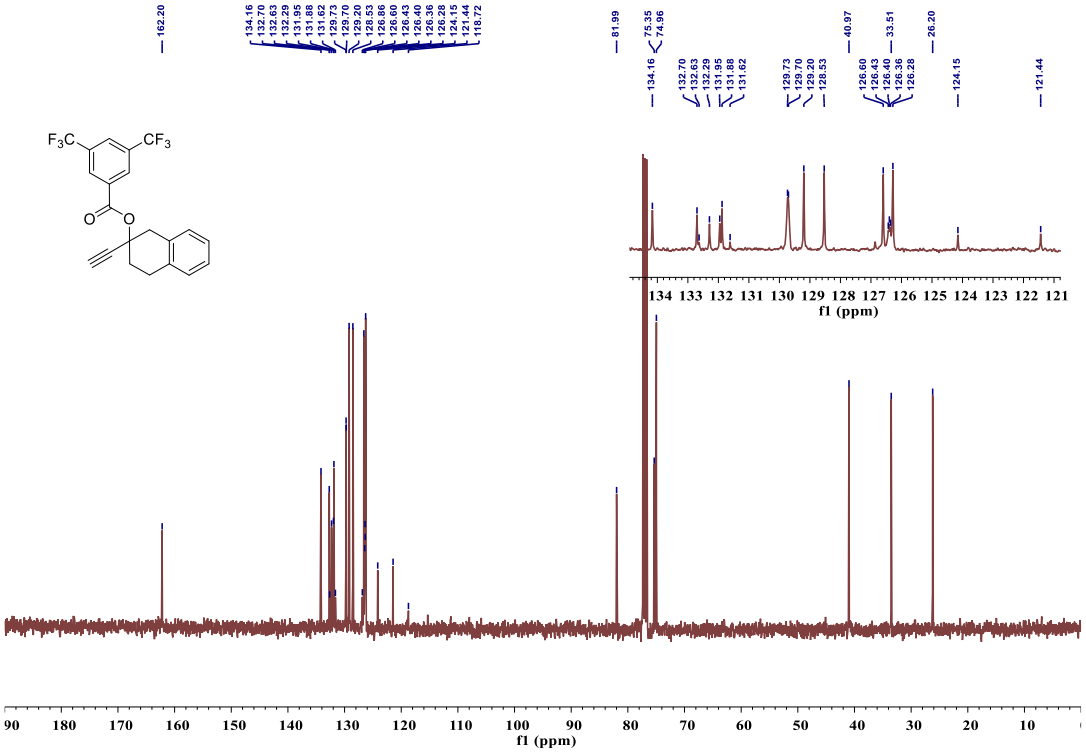
^{19}F NMR spectrum of compound 1r



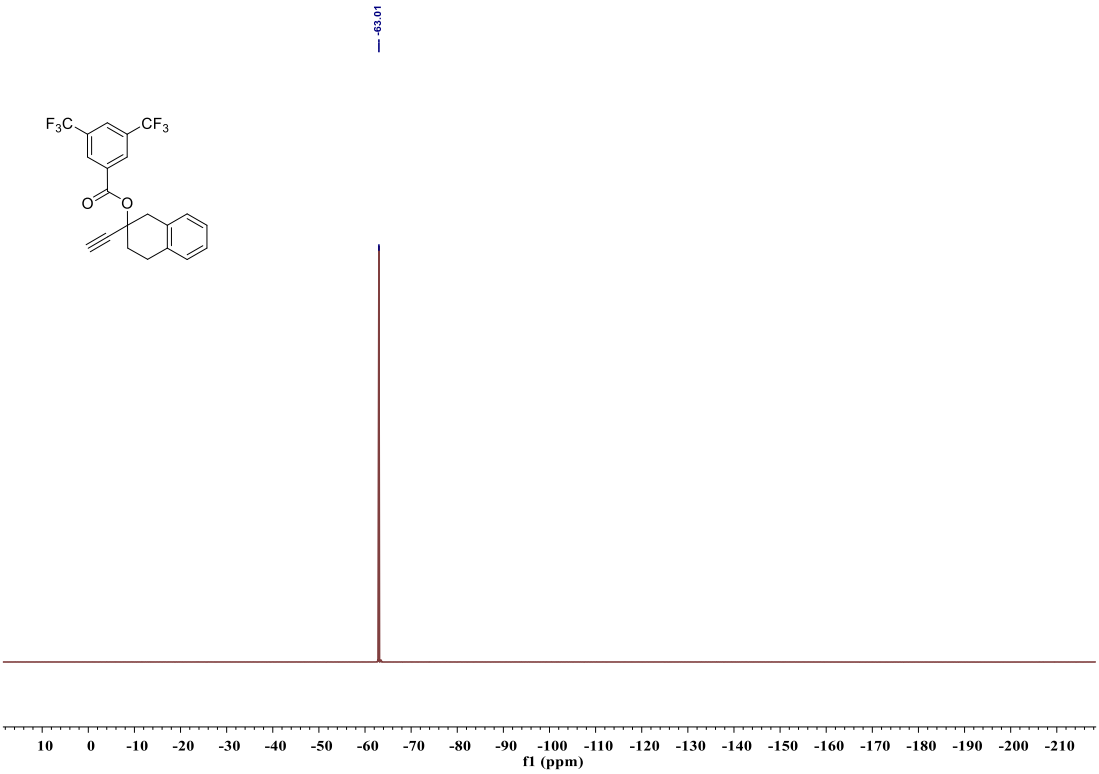
^{1}H NMR spectrum of compound 1s



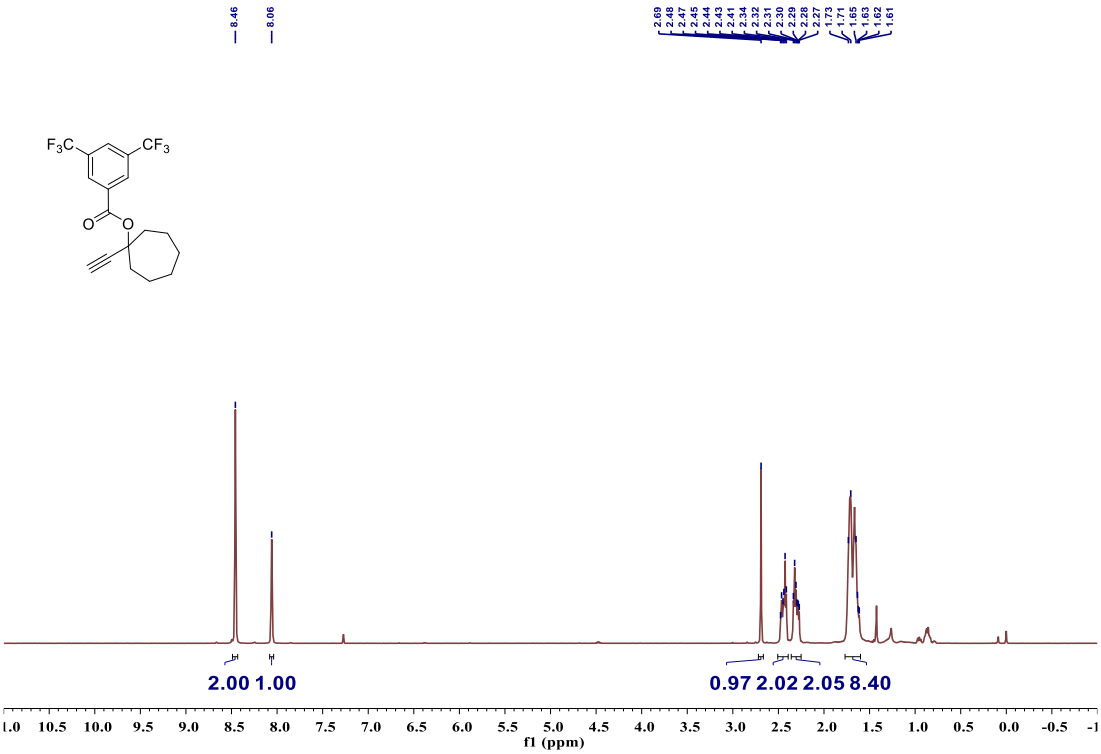
^{13}C NMR spectrum of compound 1s



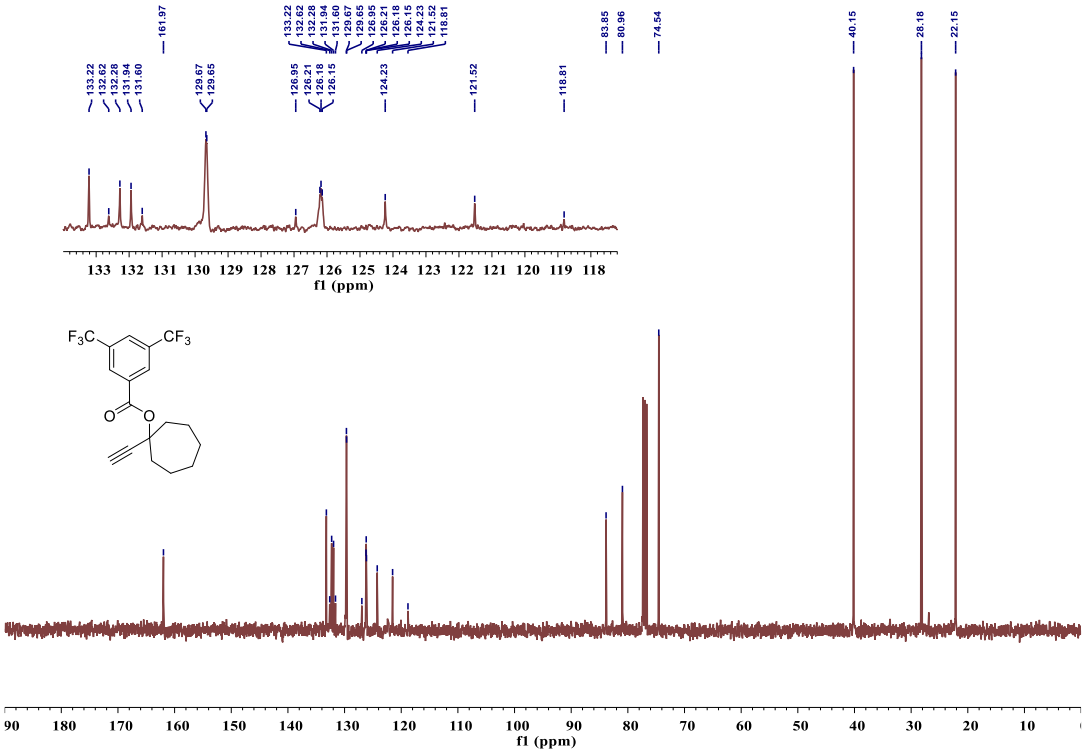
^{19}F NMR spectrum of compound 1s



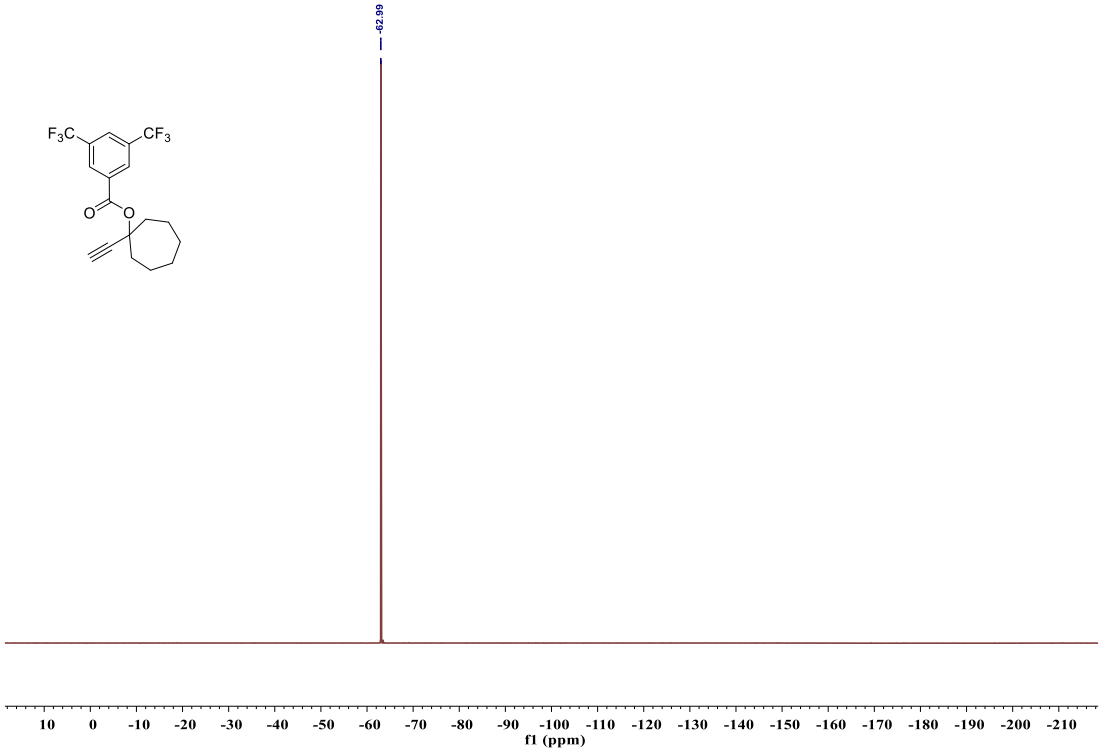
^{1}H NMR spectrum of compound 1t



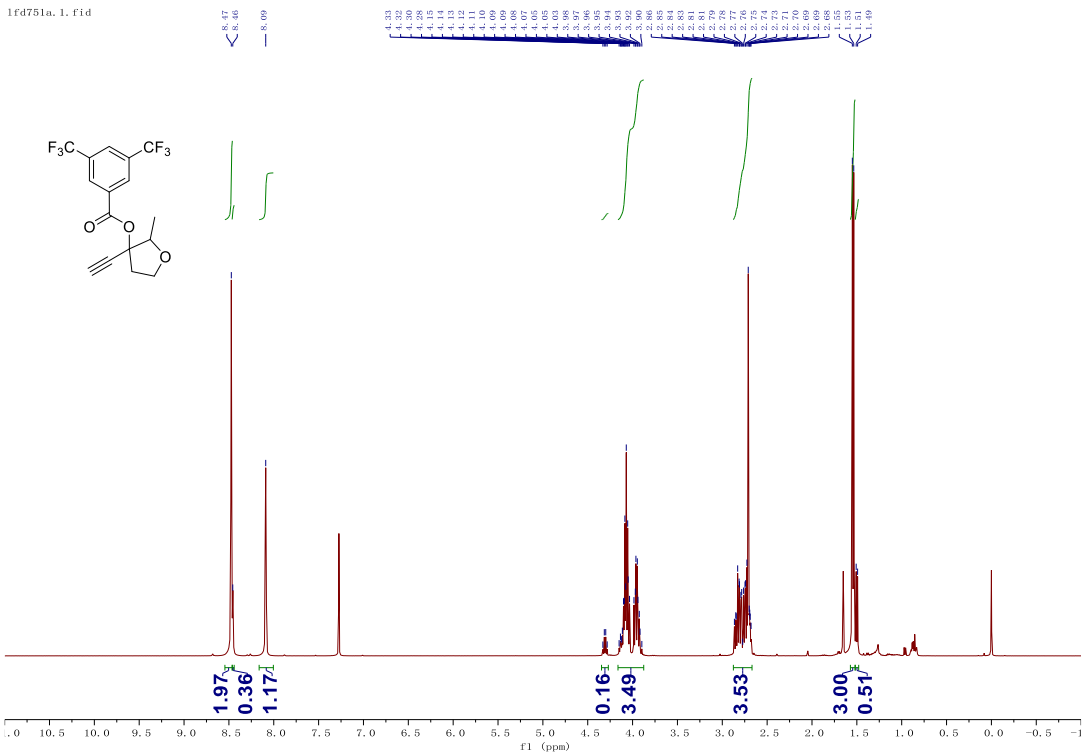
^{13}C NMR spectrum of compound 1t



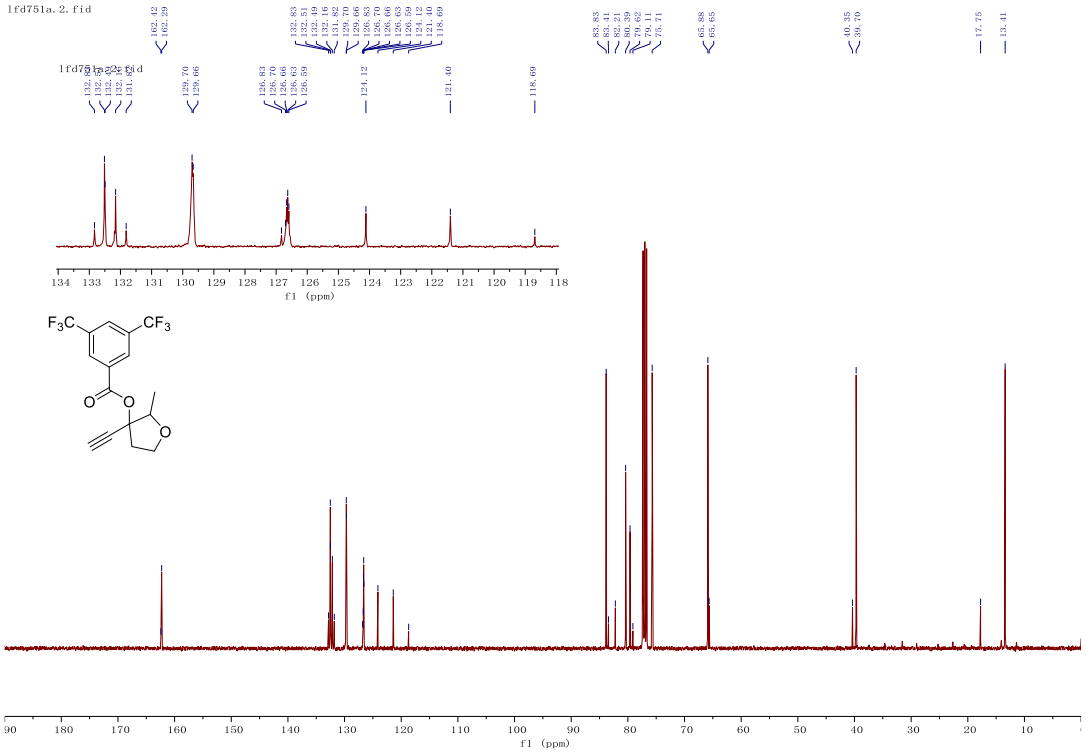
^{19}F NMR spectrum of compound 1t



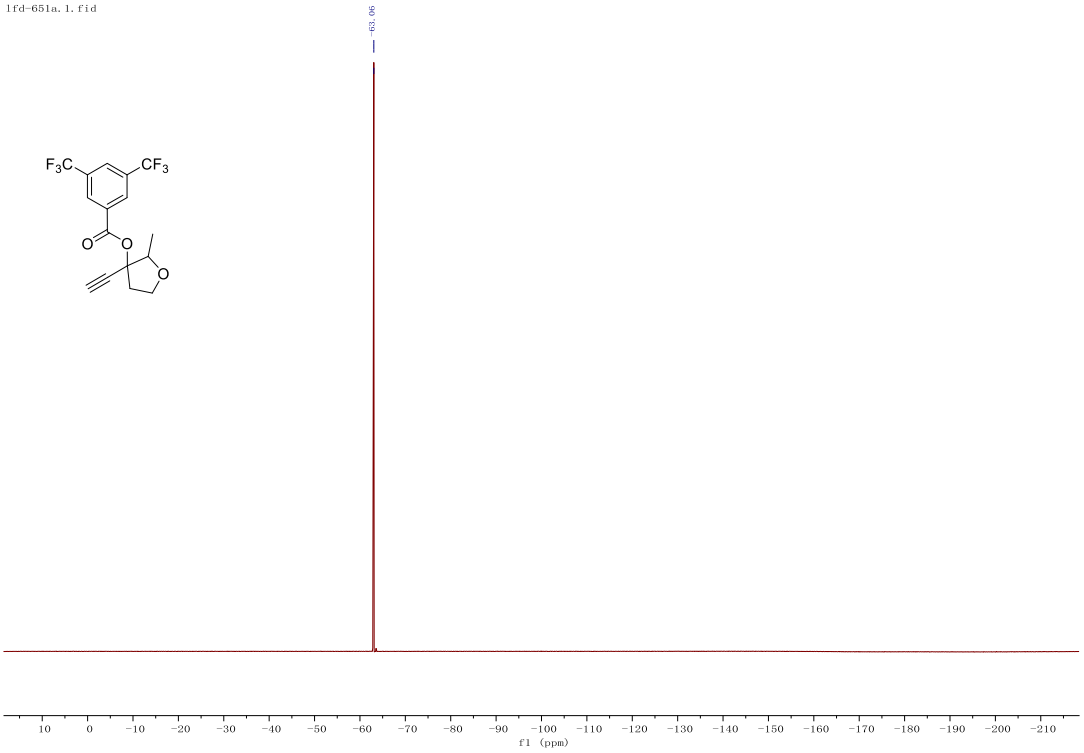
^{1}H NMR spectrum of compound 1u



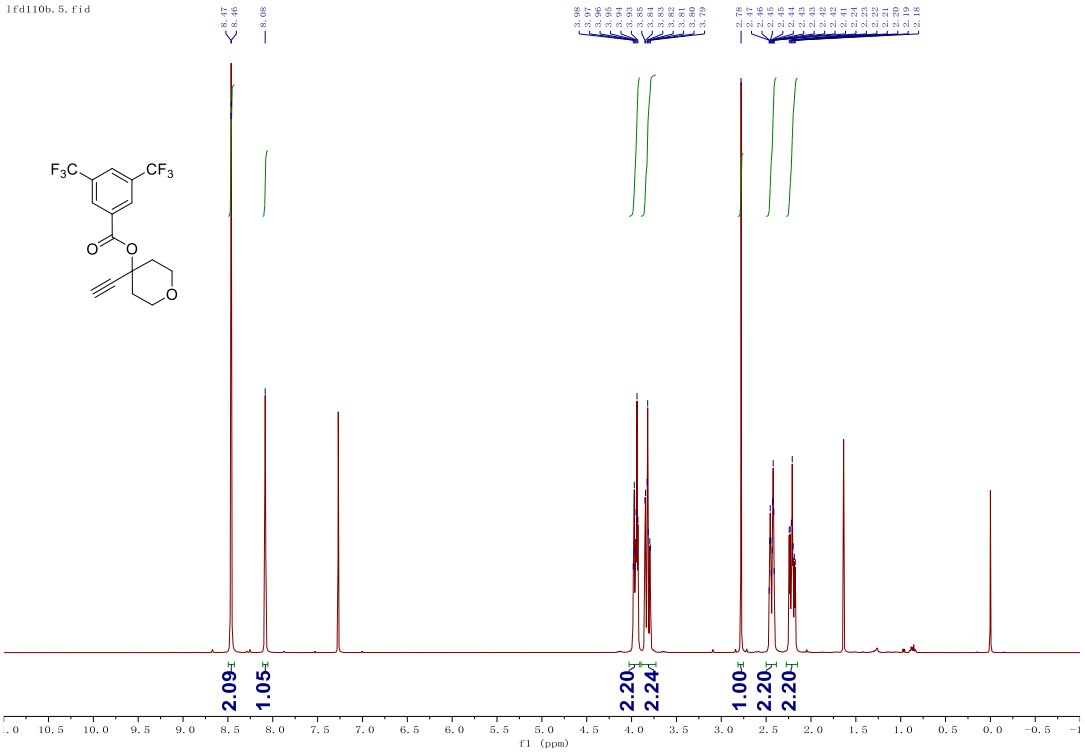
^{13}C NMR spectrum of compound 1u



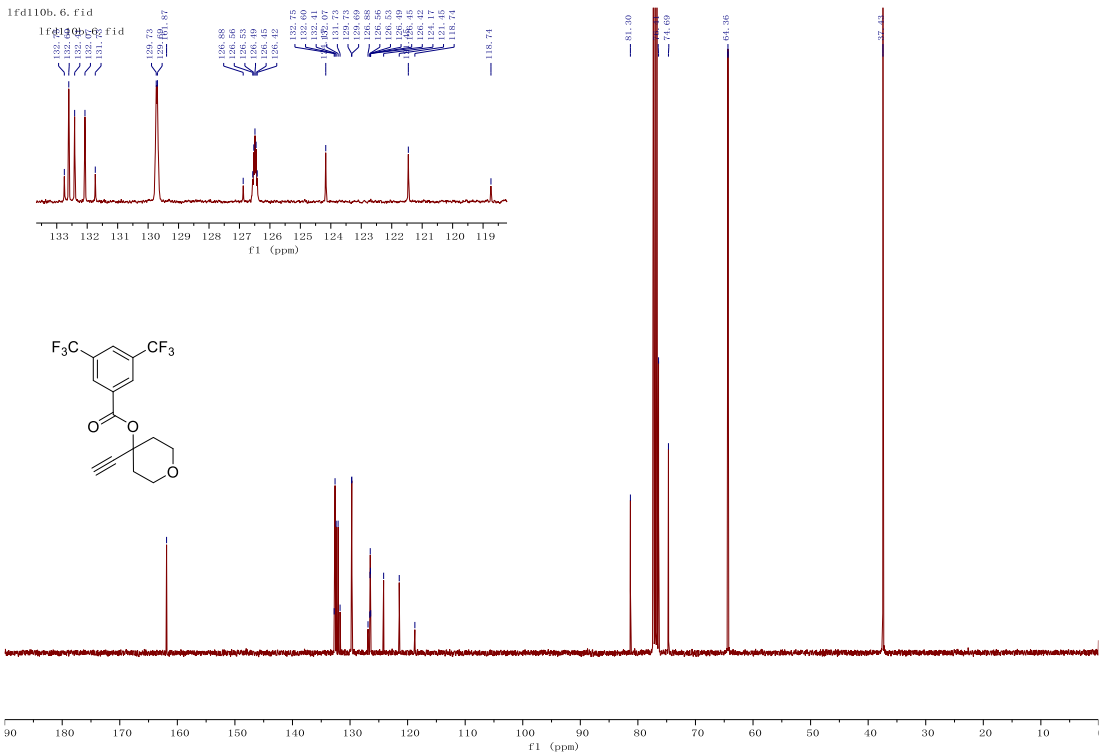
^{19}F NMR spectrum of compound 1u



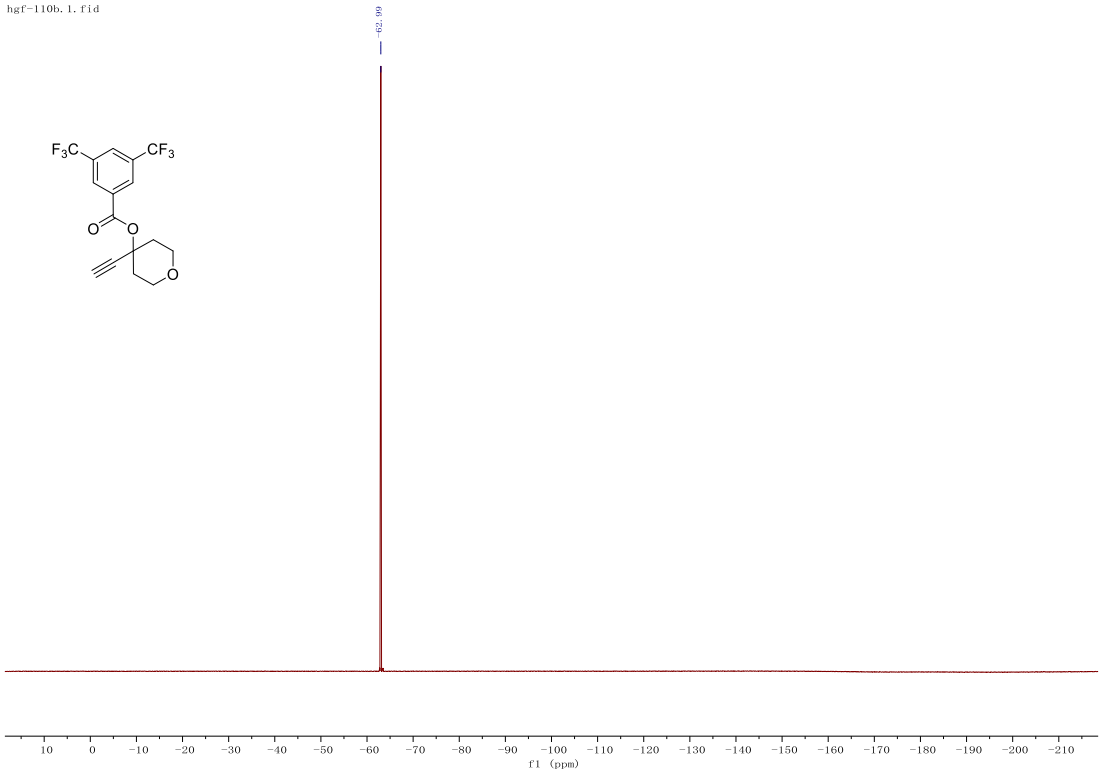
^{1}H NMR spectrum of compound 1v



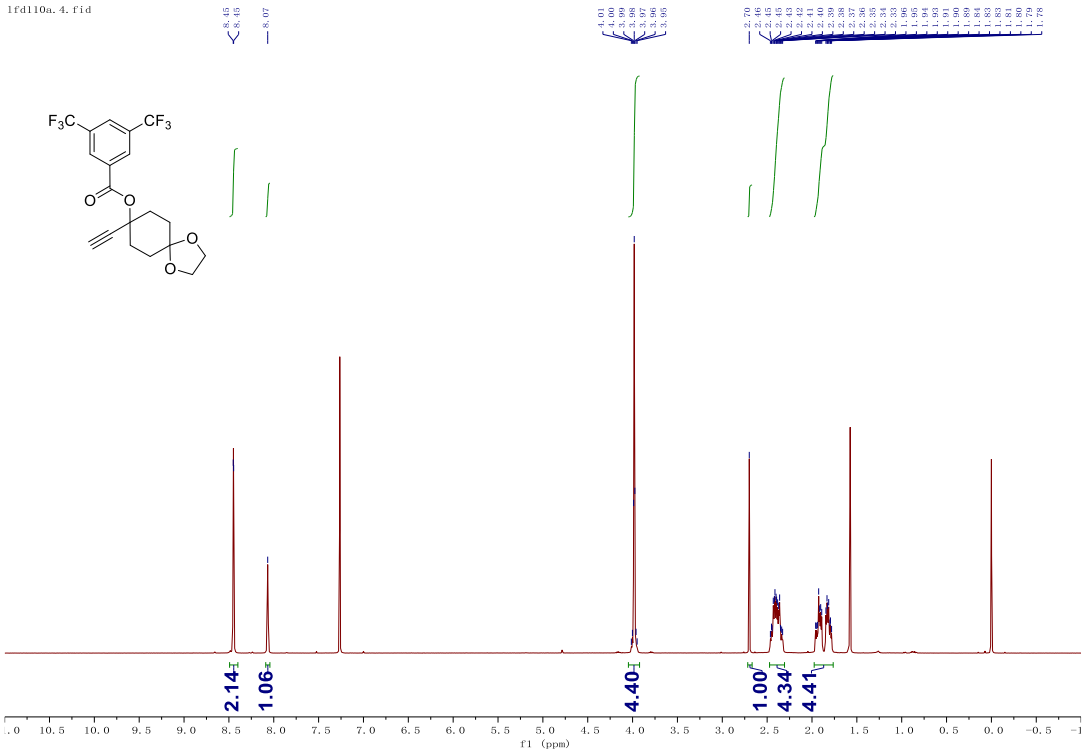
^{13}C NMR spectrum of compound 1v



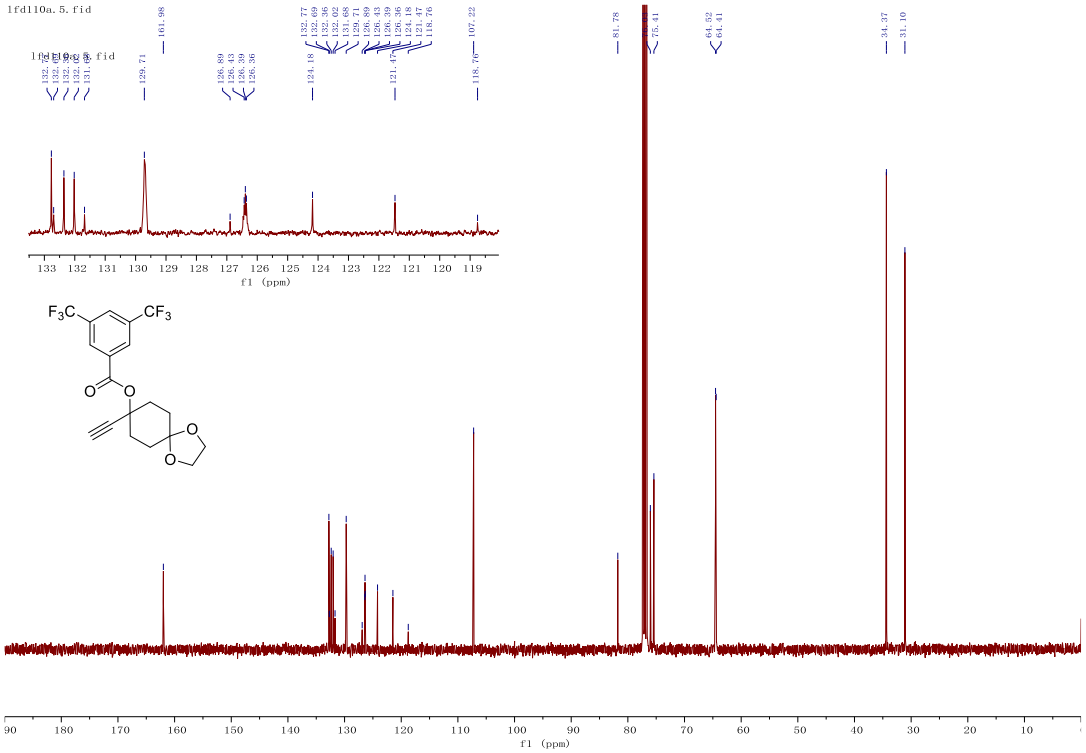
^{19}F NMR spectrum of compound 1v



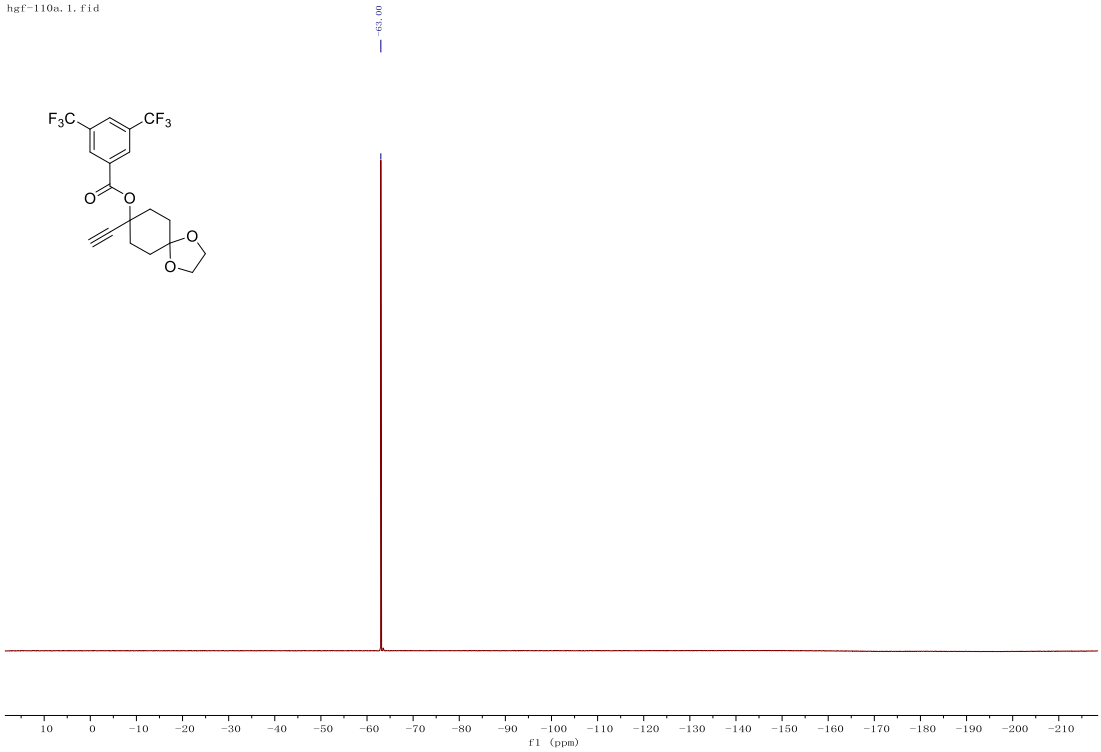
^{1}H NMR spectrum of compound 1w



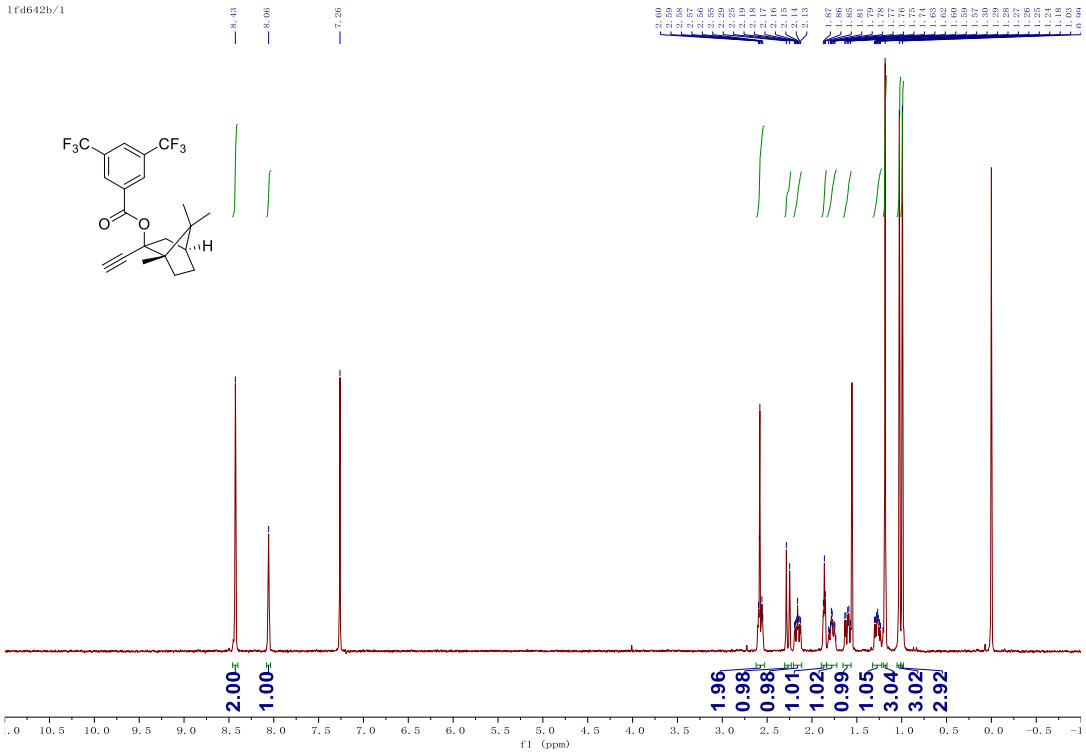
^{13}C NMR spectrum of compound 1w



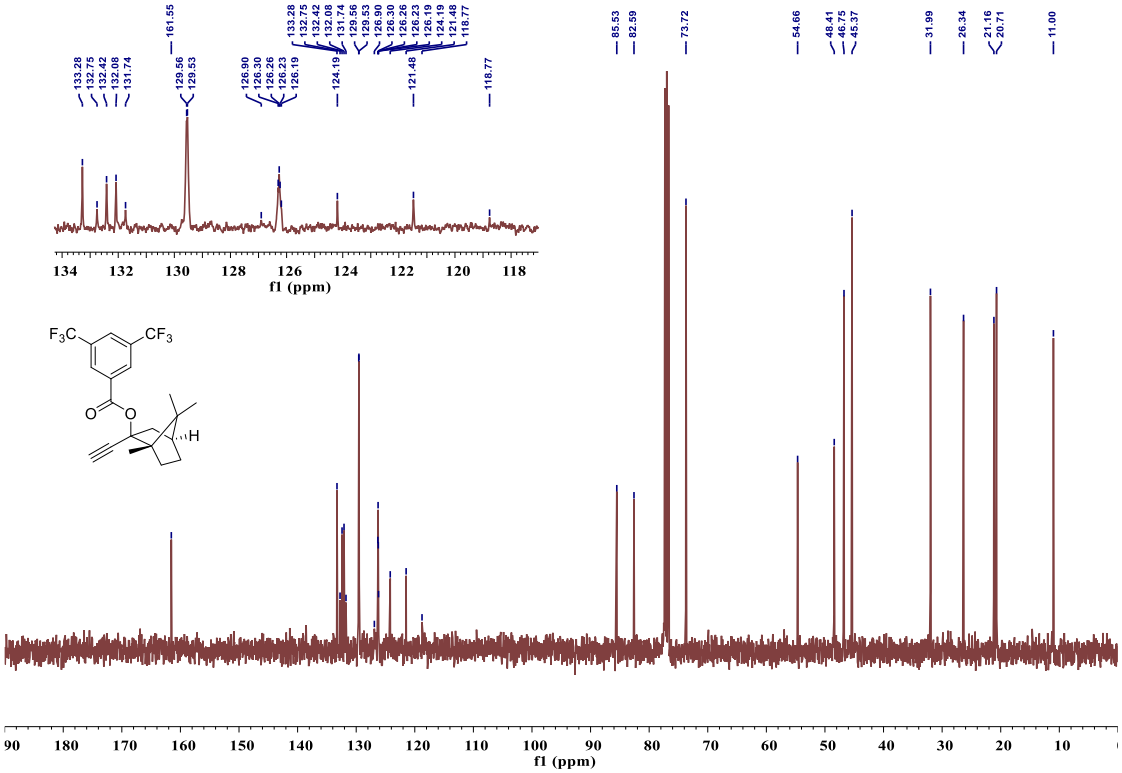
^{19}F NMR spectrum of compound 1w



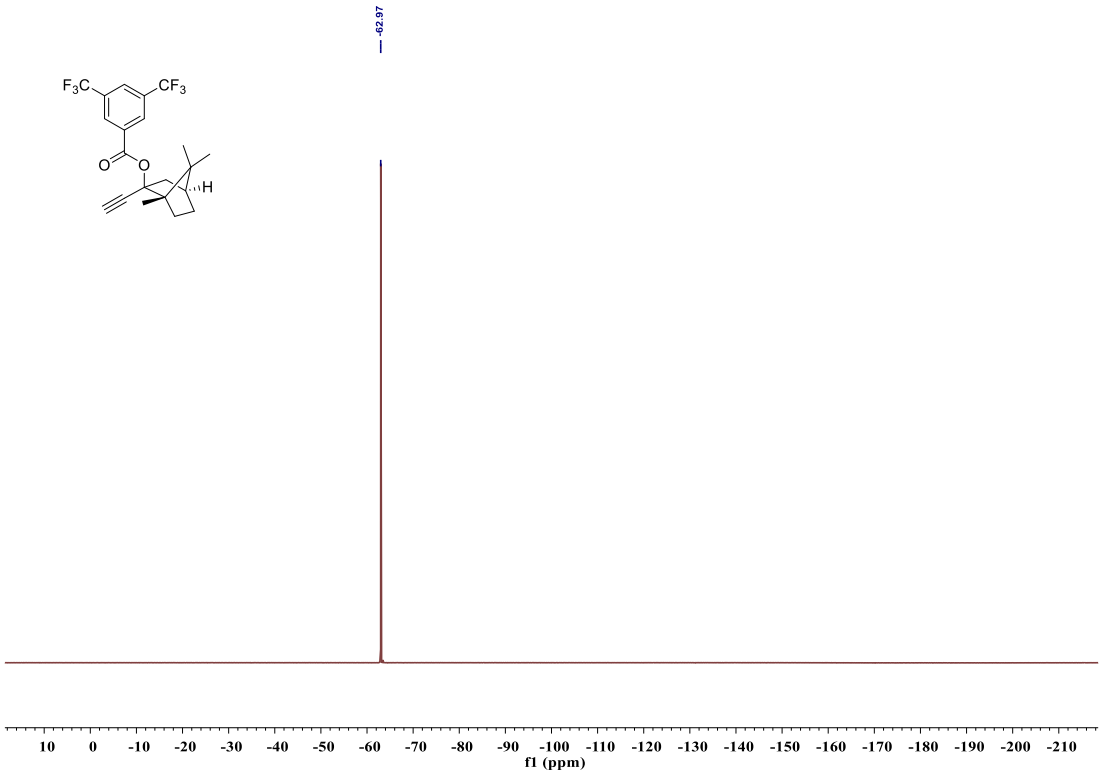
^{1}H NMR spectrum of compound 1x



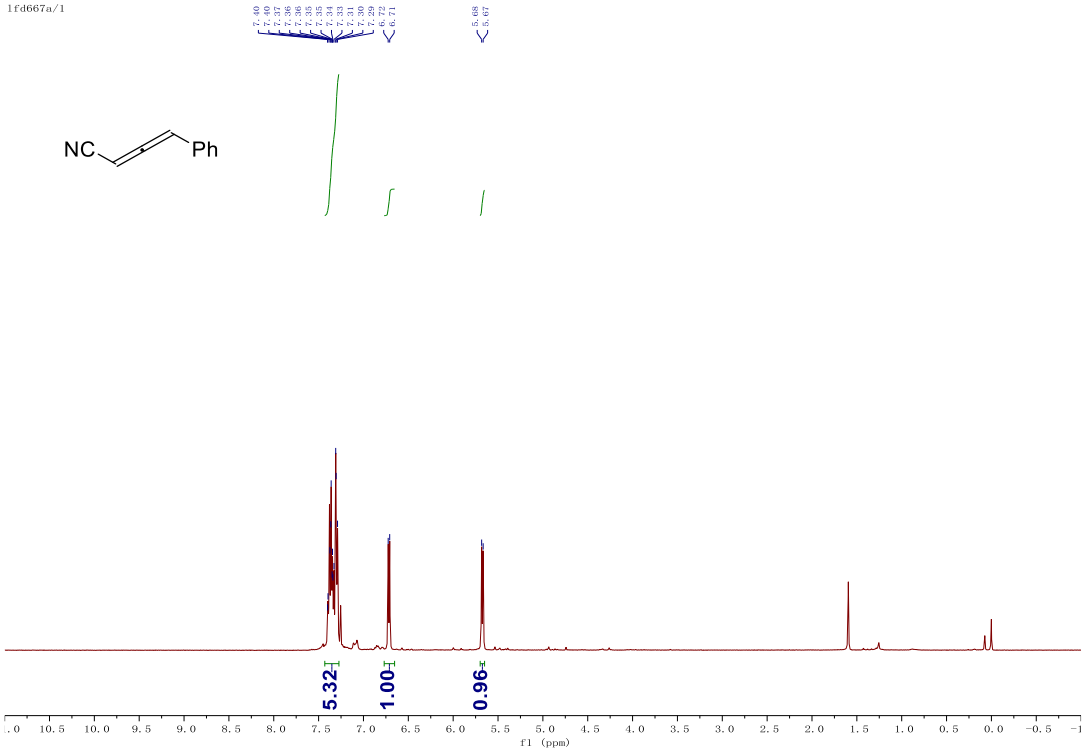
^{13}C NMR spectrum of compound 1x



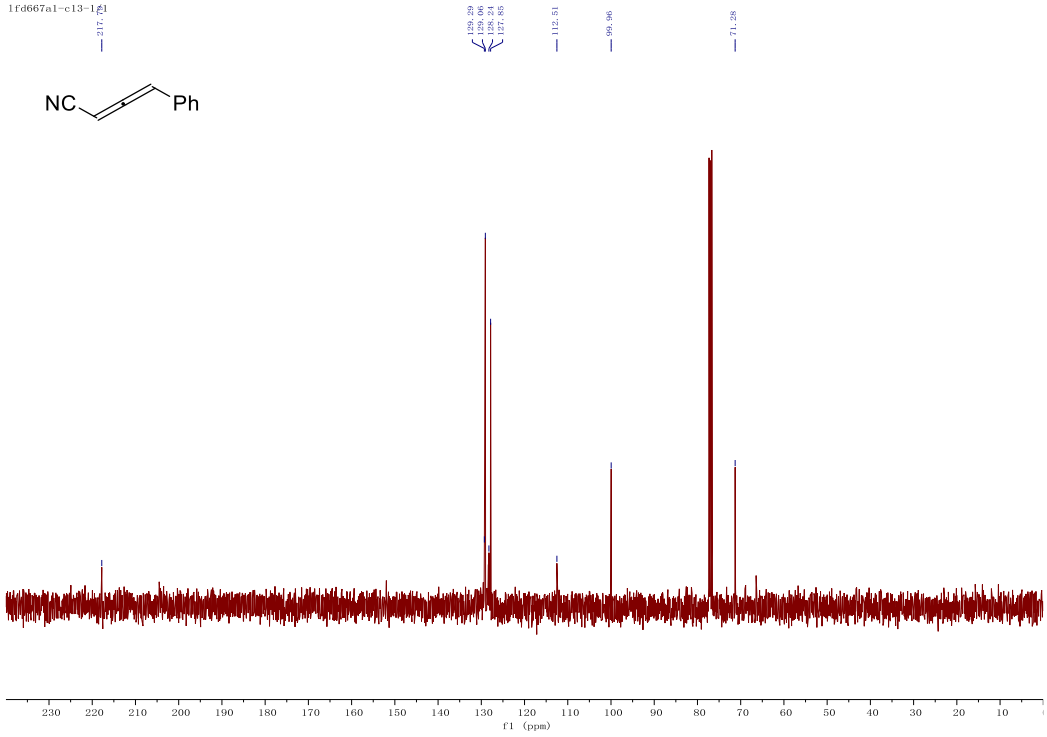
^{19}F NMR spectrum of compound 1x



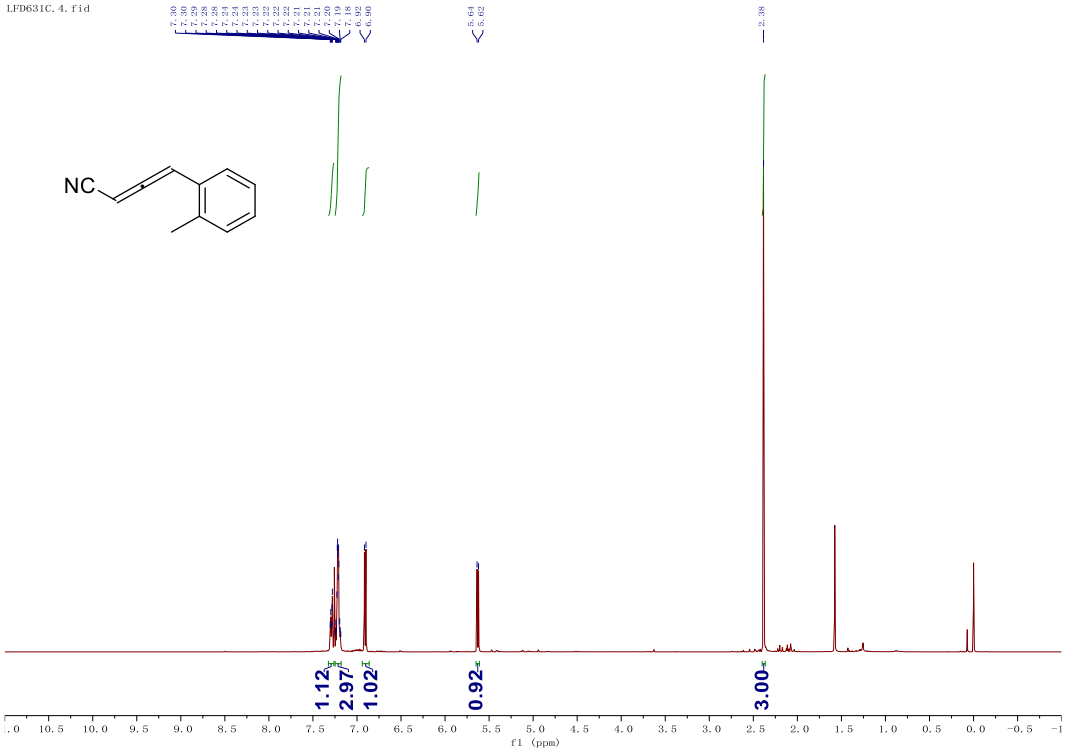
^{1}H NMR spectrum of compound 3a



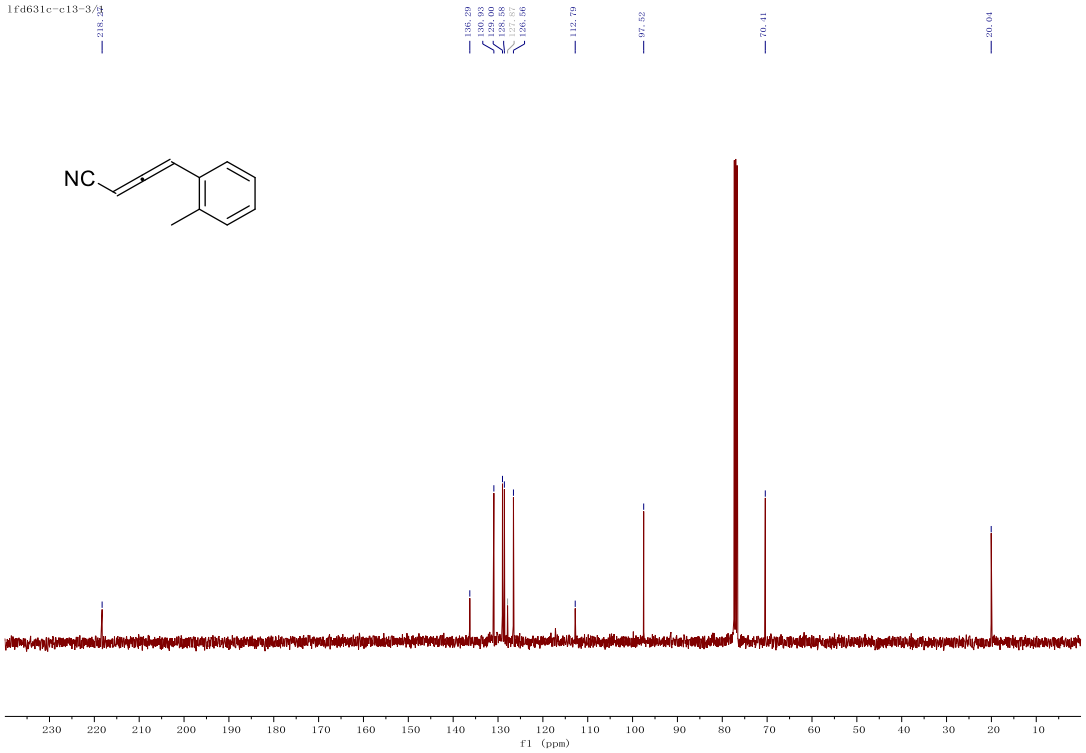
^{13}C NMR spectrum of compound 3a



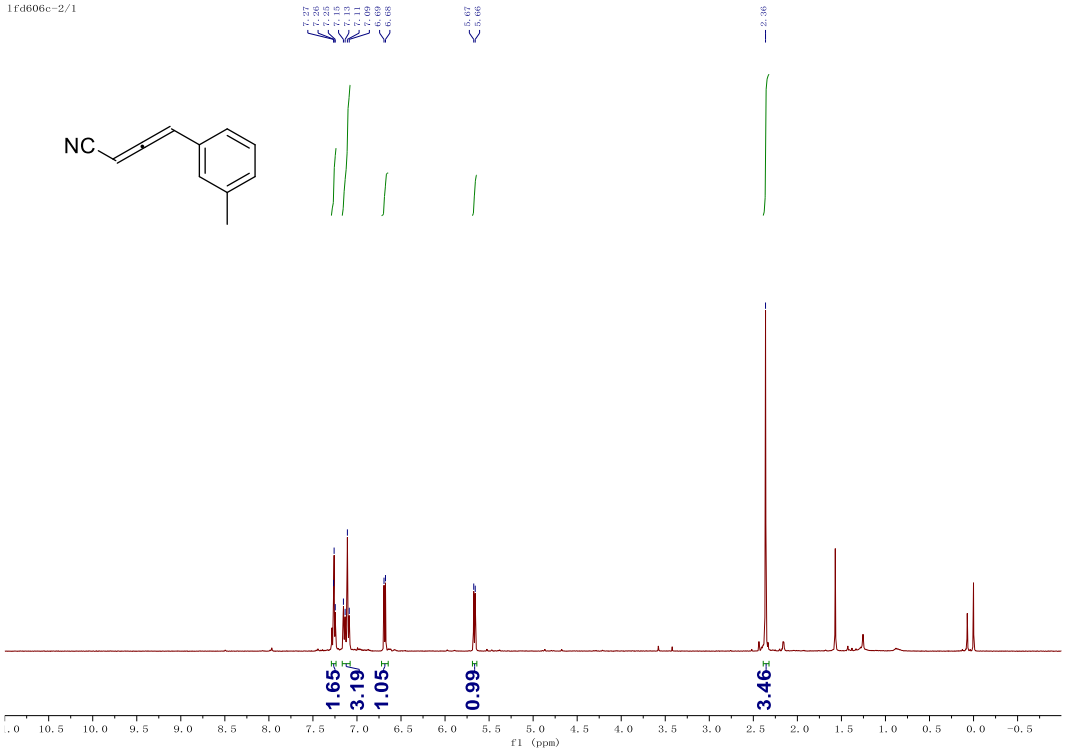
^{1}H NMR spectrum of compound 3b



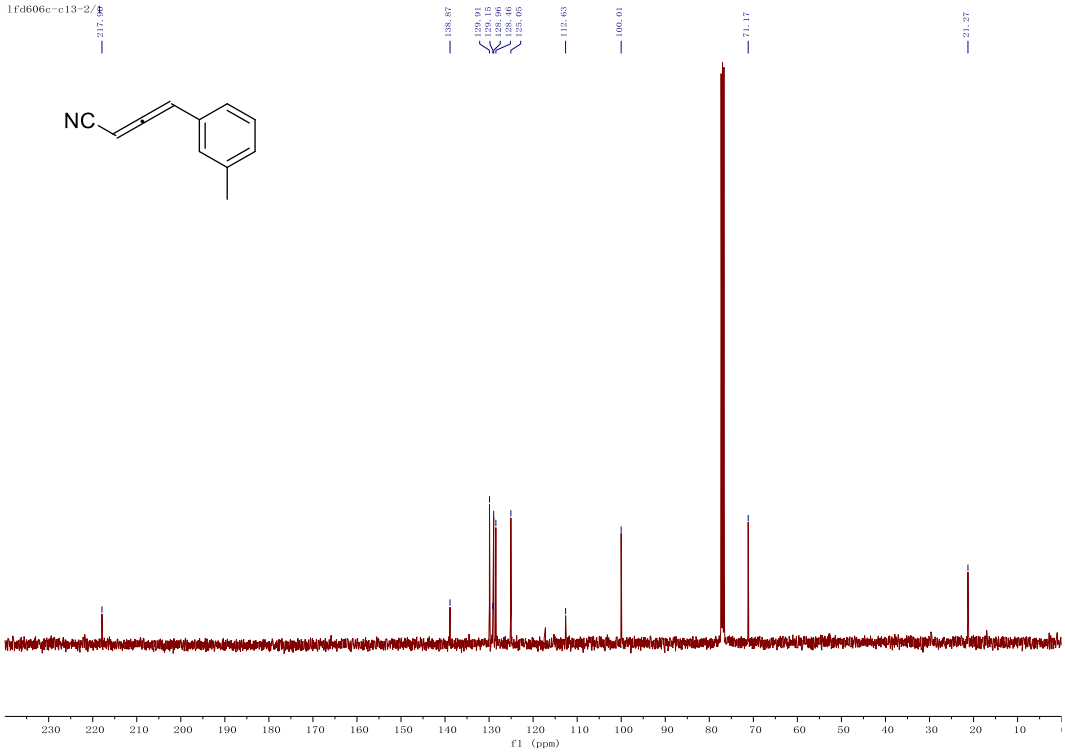
^{13}C NMR spectrum of compound 3b



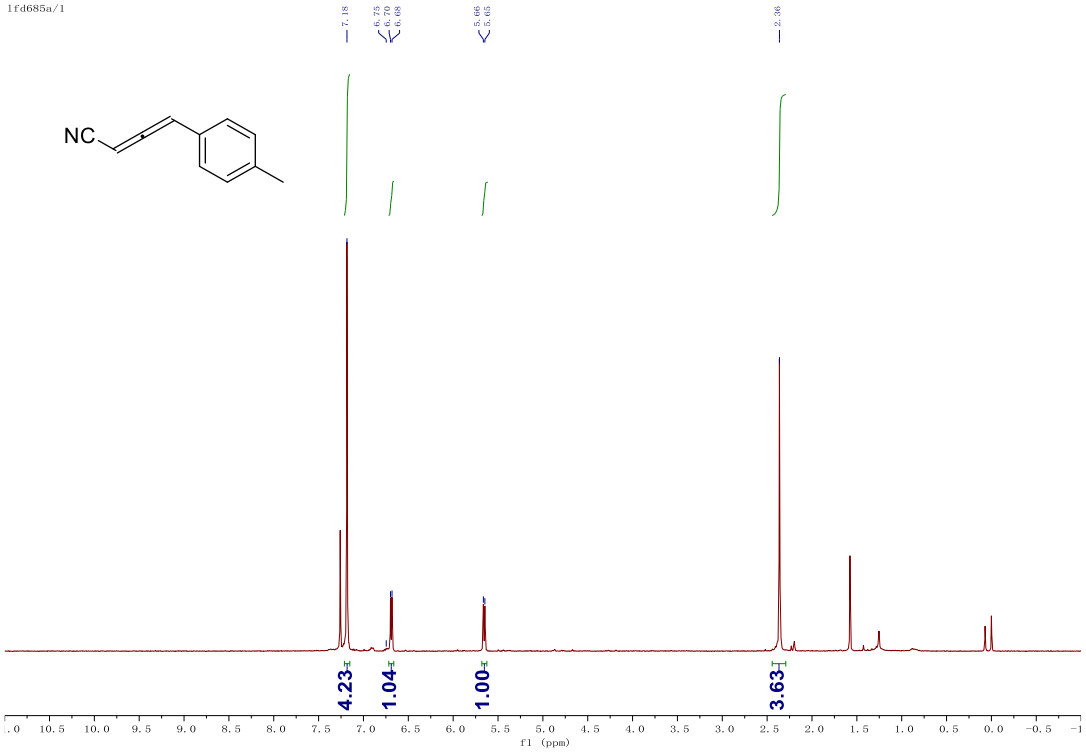
^{1}H NMR spectrum of compound 3c



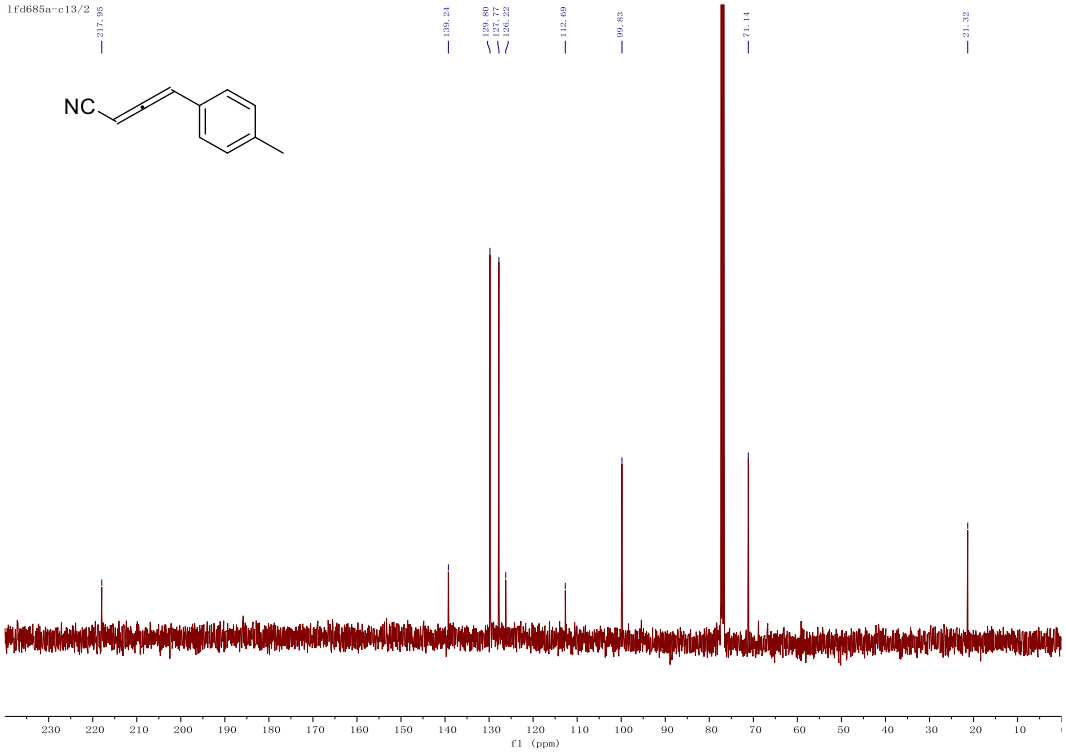
^{13}C NMR spectrum of compound 3c



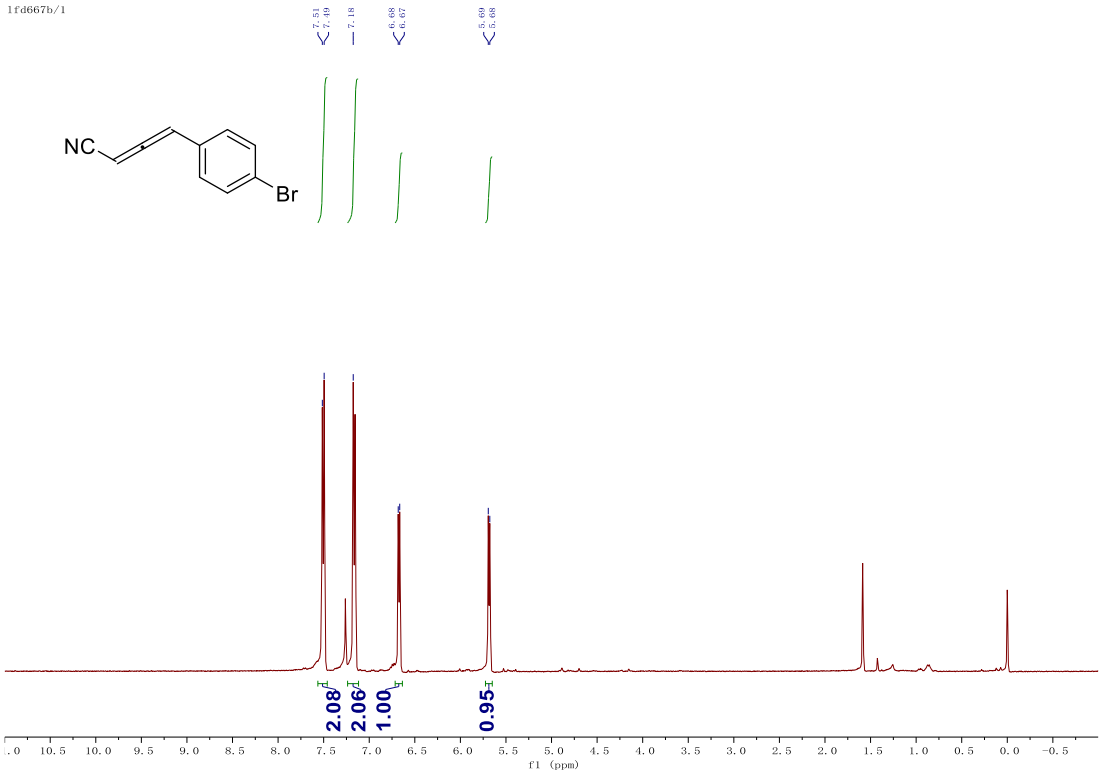
^{1}H NMR spectrum of compound 3d



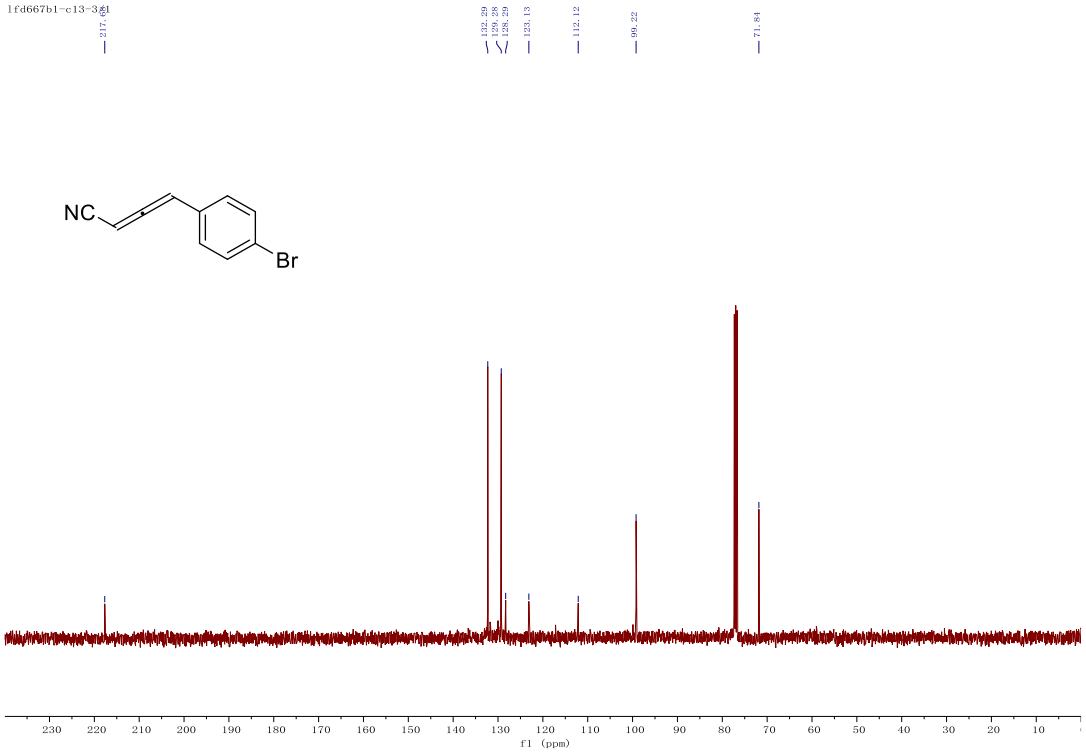
^{13}C NMR spectrum of compound 3d



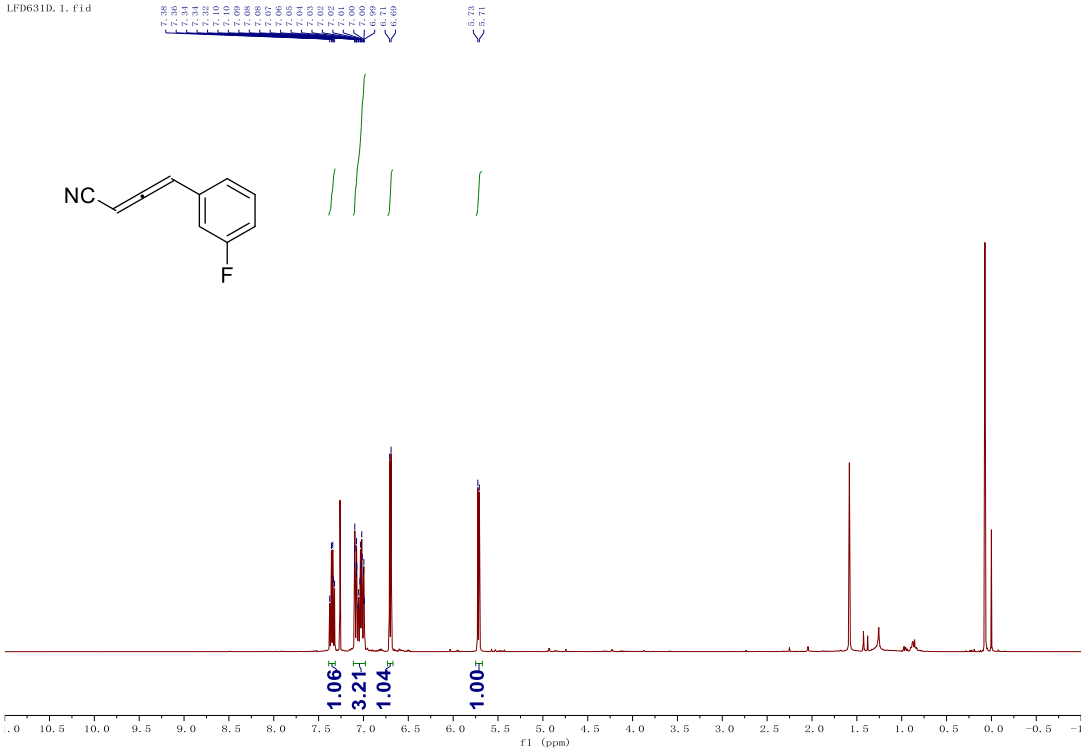
^{1}H NMR spectrum of compound 3e



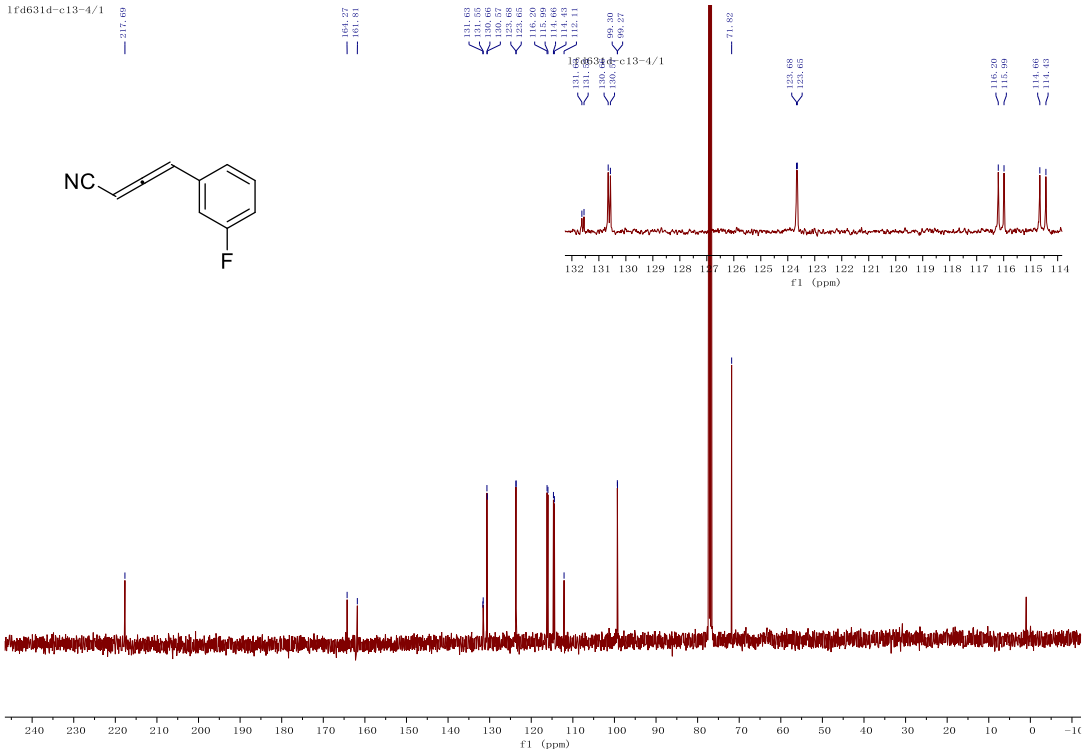
^{13}C NMR spectrum of compound 3e



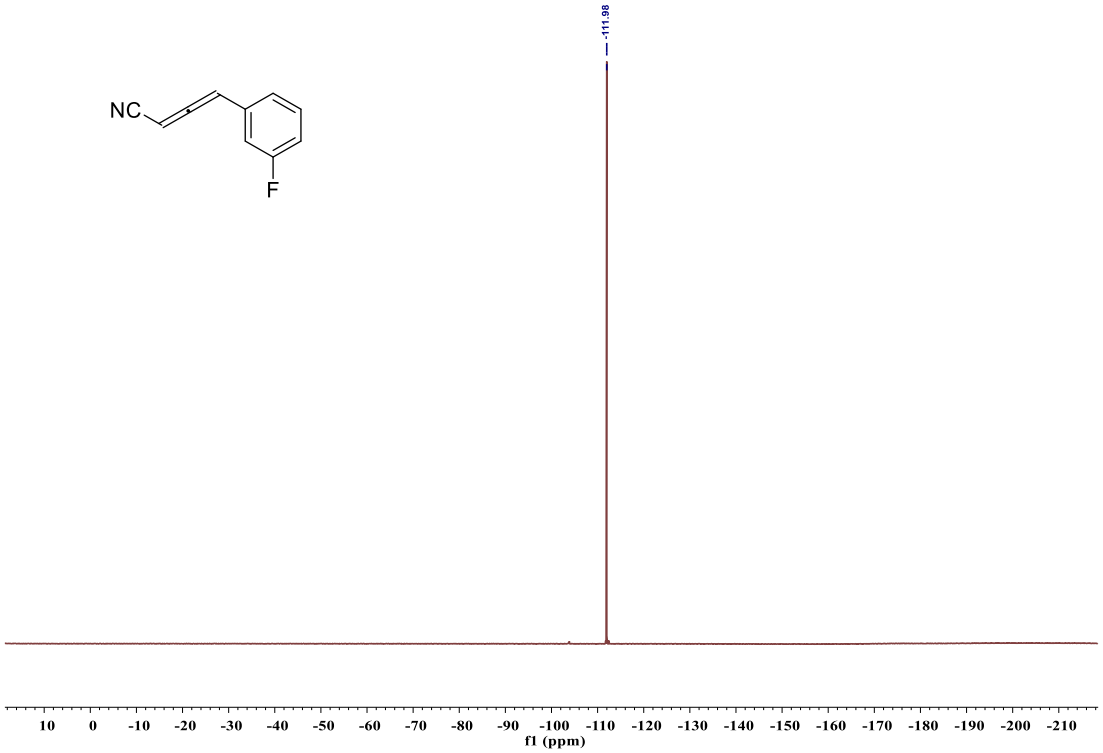
^{1}H NMR spectrum of compound 3f



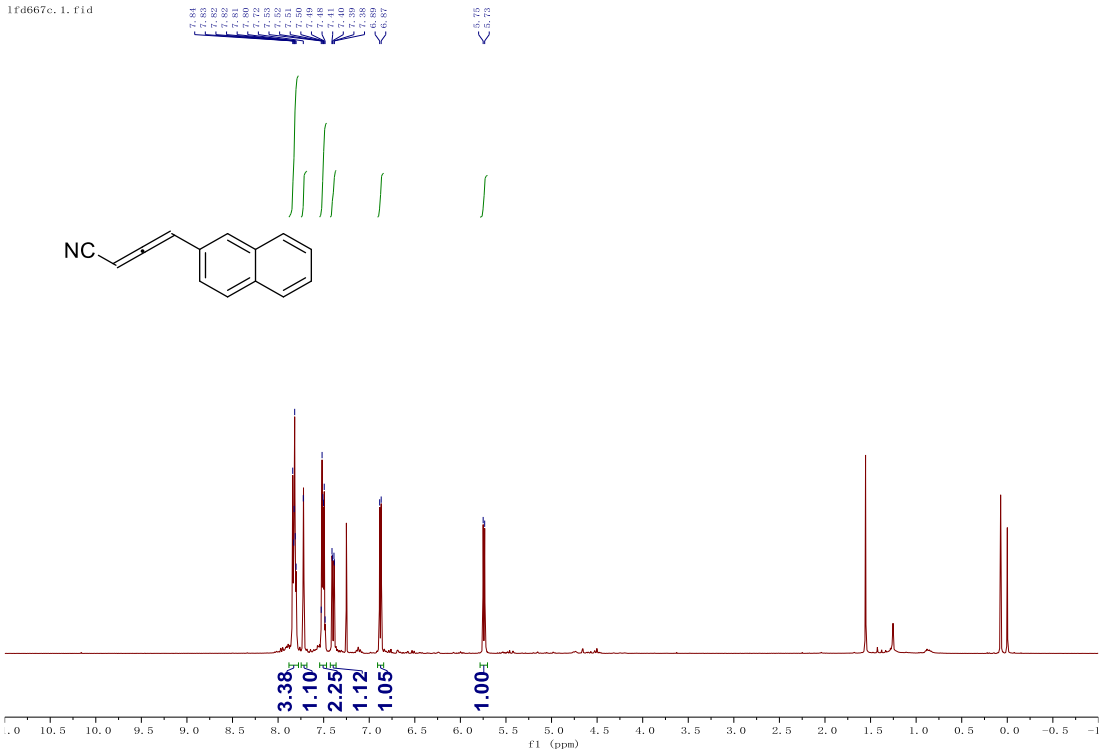
^{13}C NMR spectrum of compound 3f



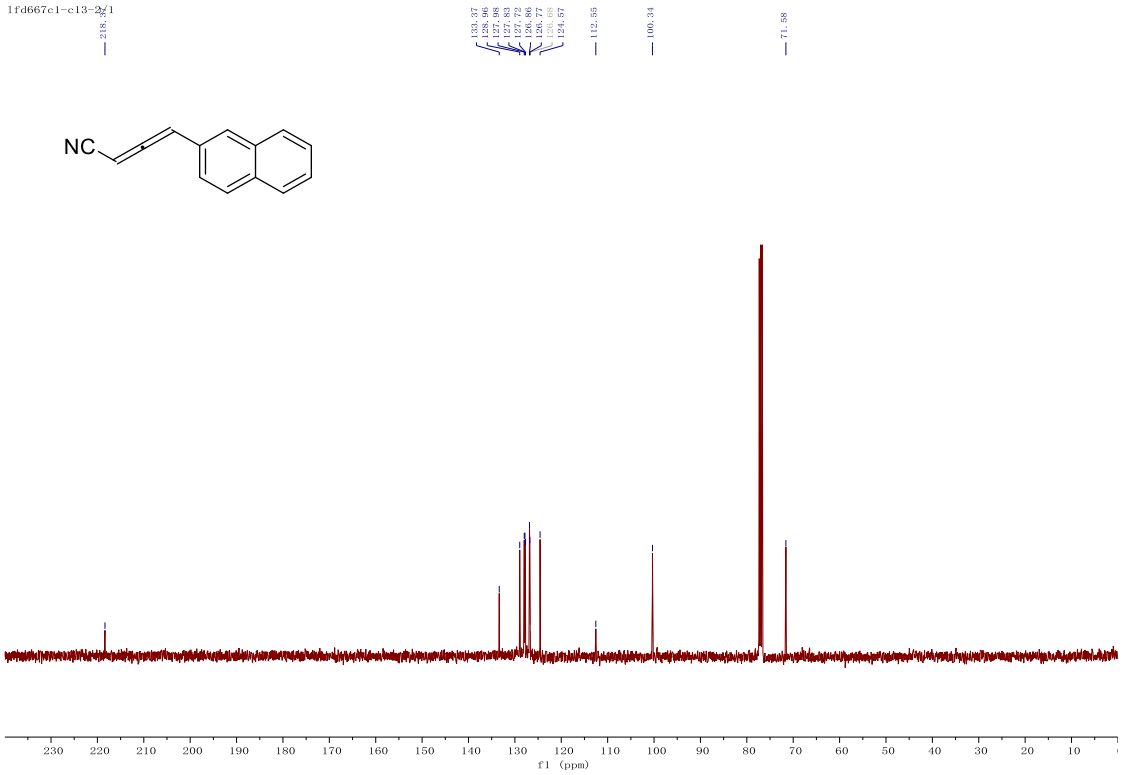
^{19}F NMR spectrum of compound 3f



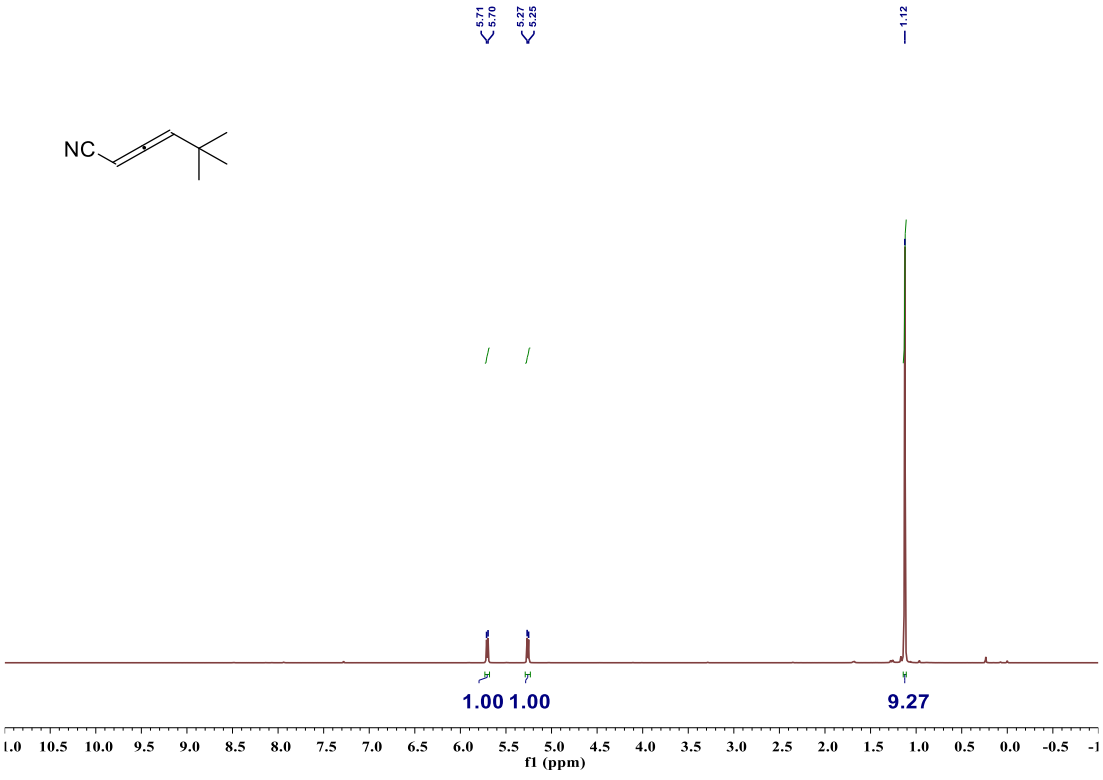
^{1}H NMR spectrum of compound 3g



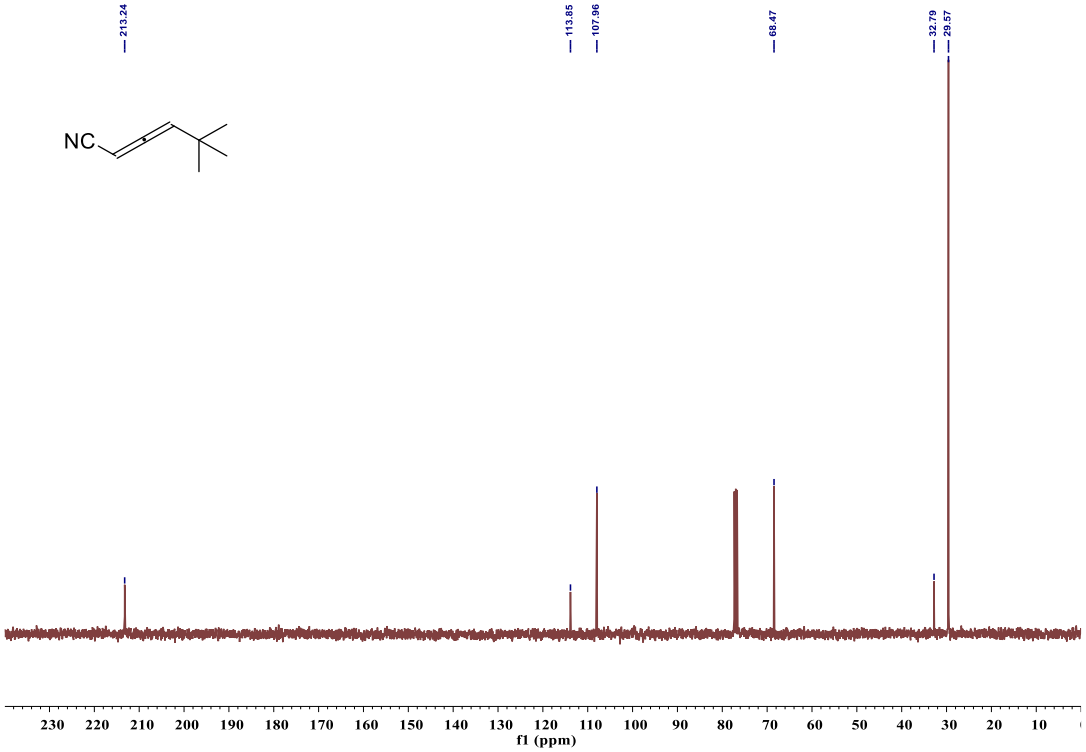
^{13}C NMR spectrum of compound 3g



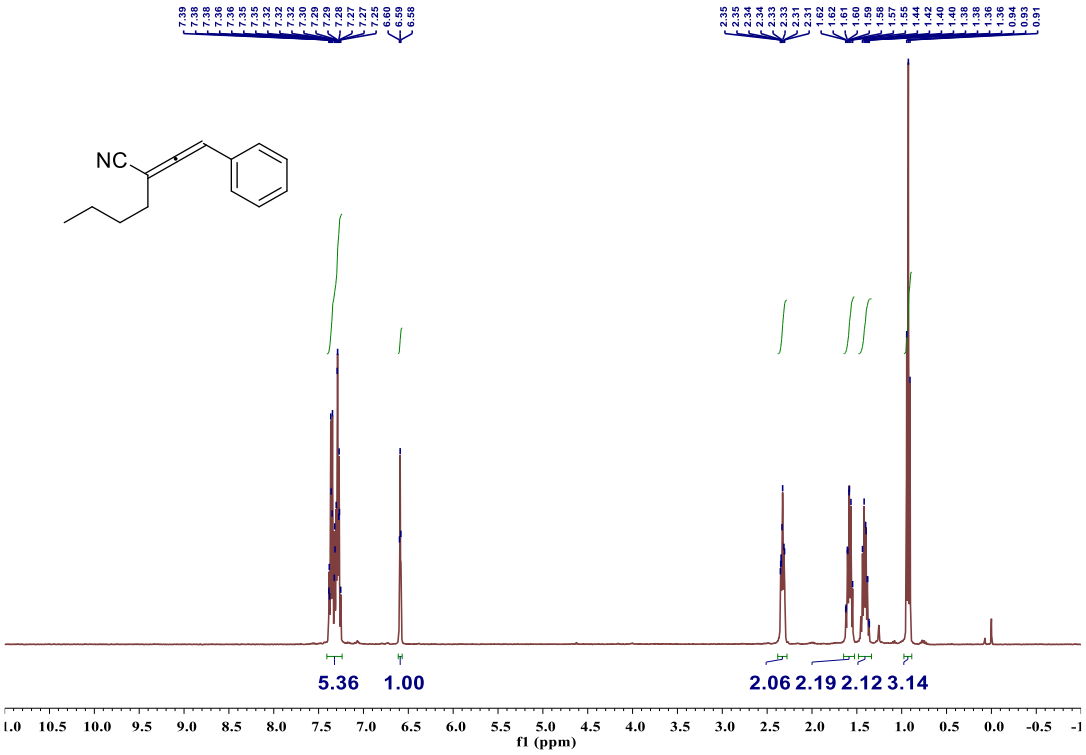
^{1}H NMR spectrum of compound 3h



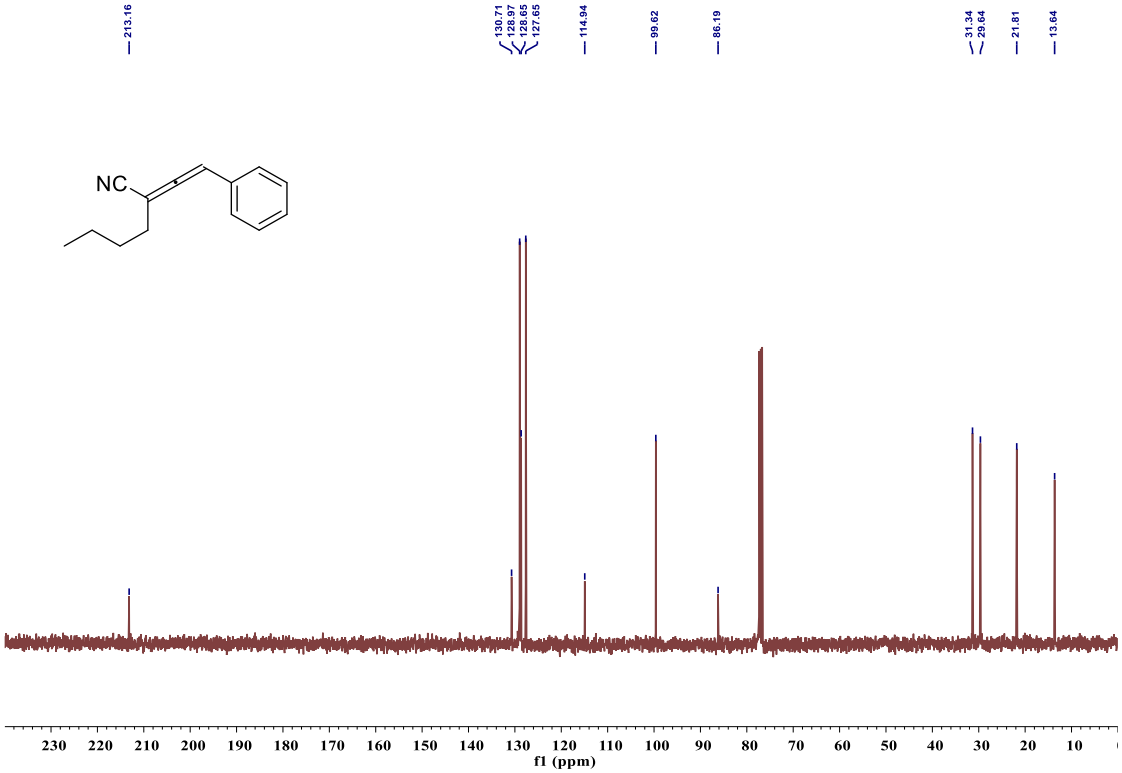
^{13}C NMR spectrum of compound 3h



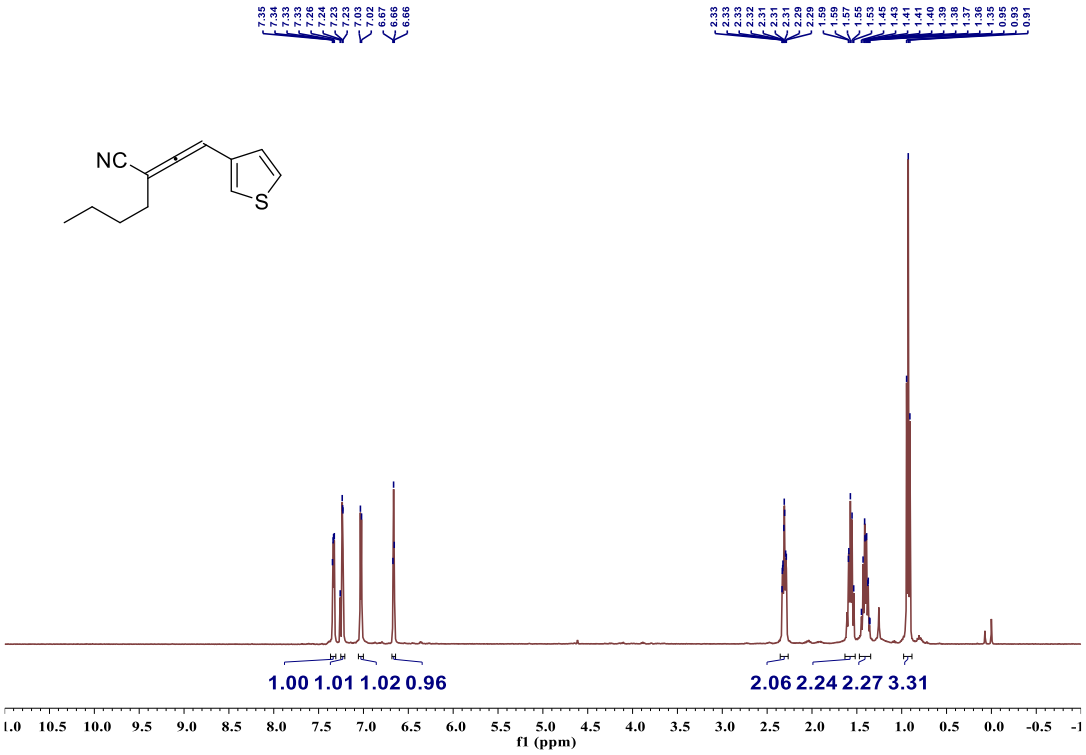
^{1}H NMR spectrum of compound 3i



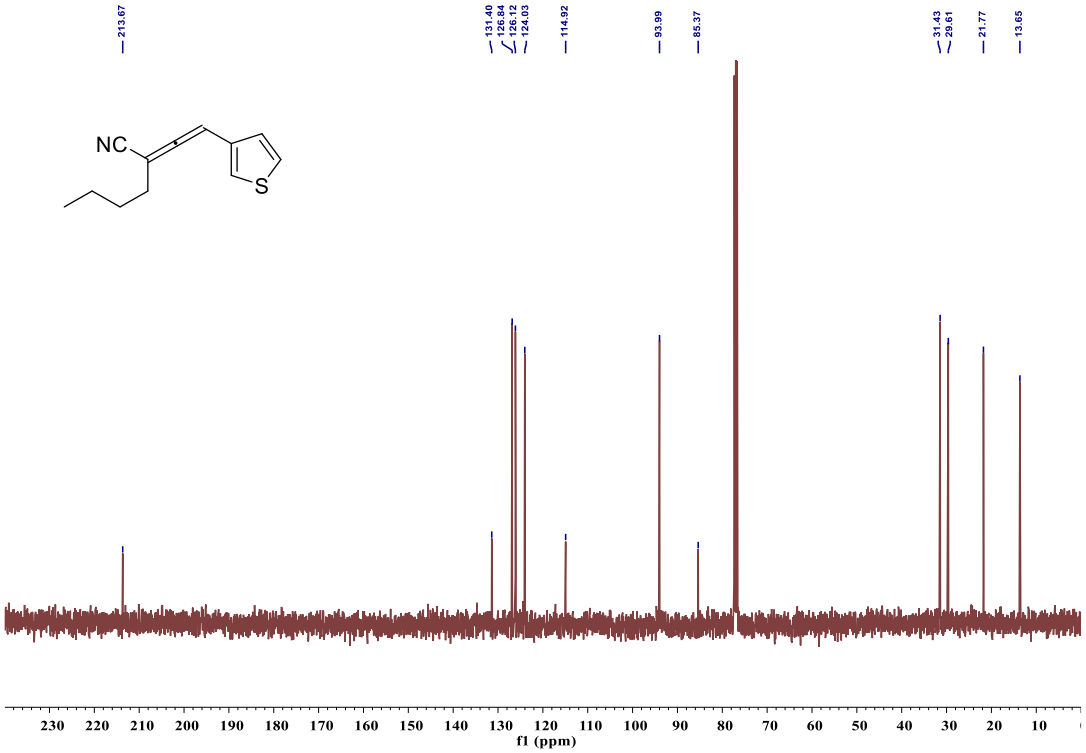
^{13}C NMR spectrum of compound 3i



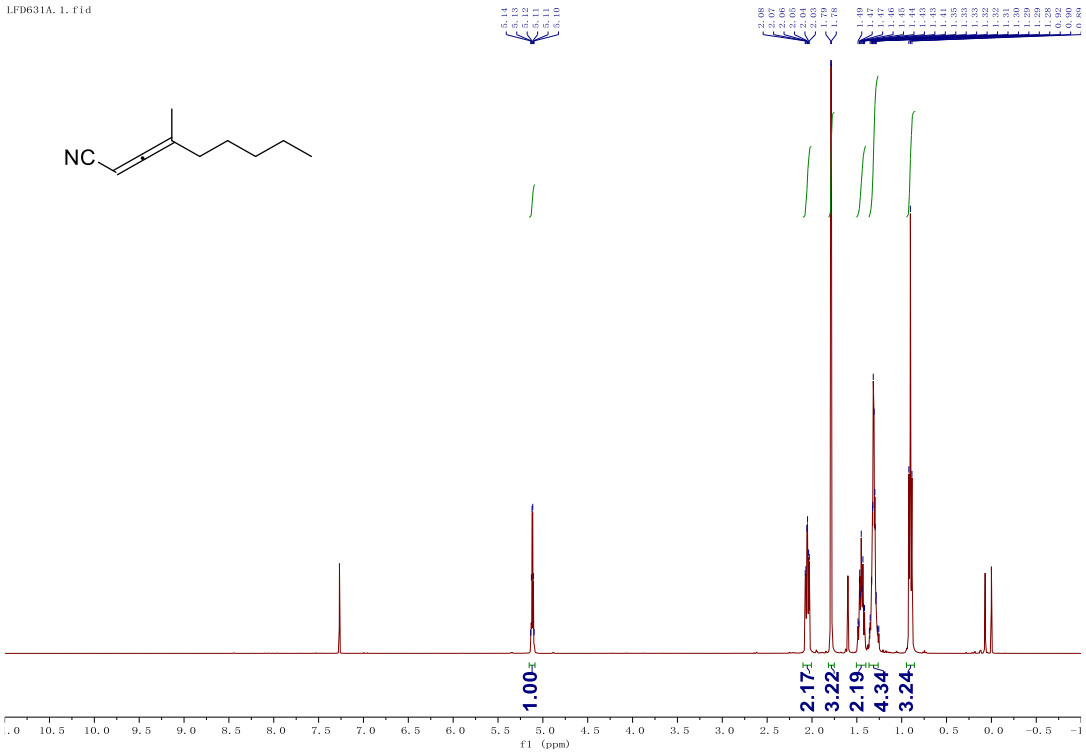
^{1}H NMR spectrum of compound 3j



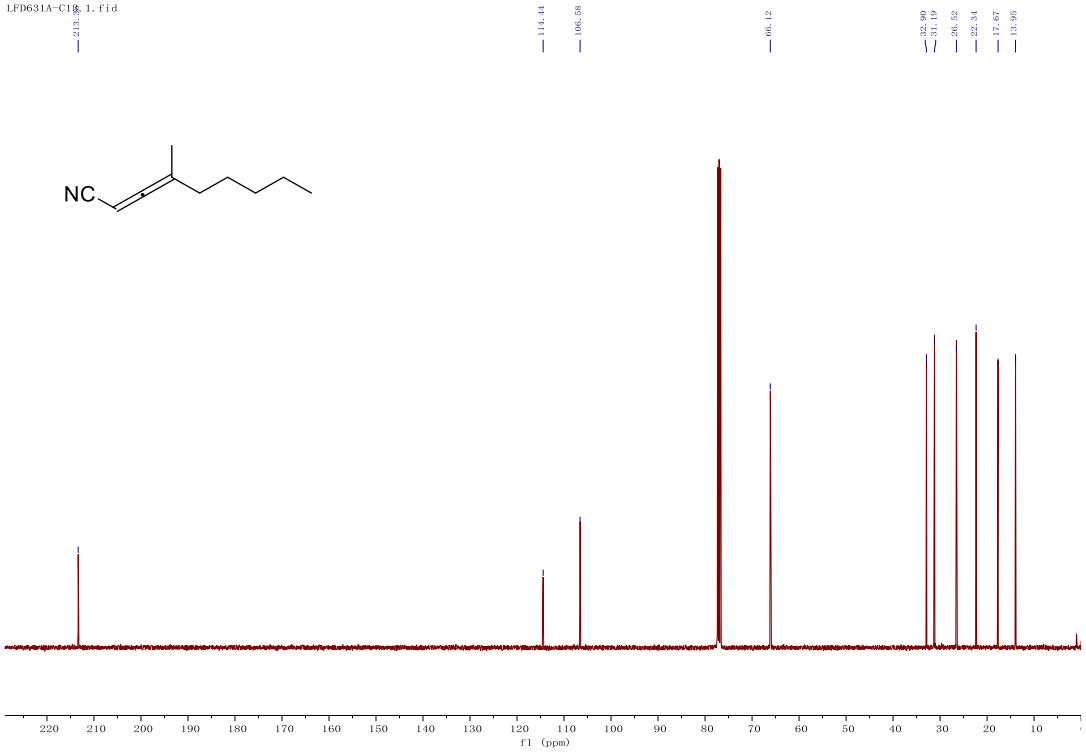
^{13}C NMR spectrum of compound 3j



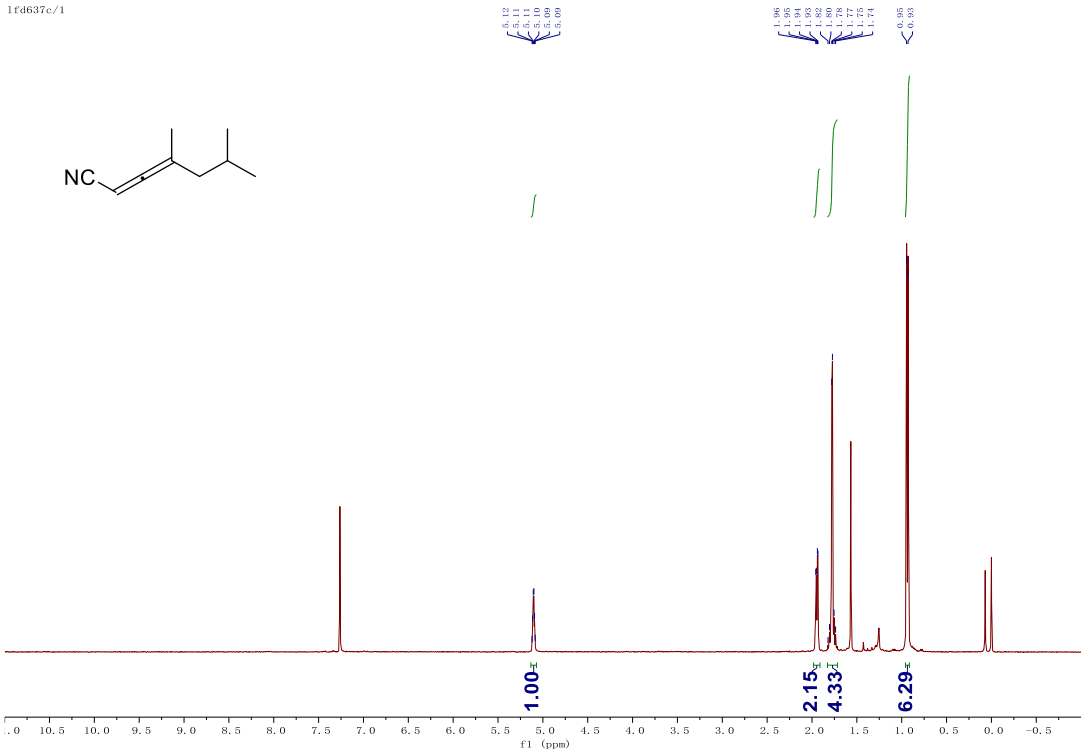
^{1}H NMR spectrum of compound 3k



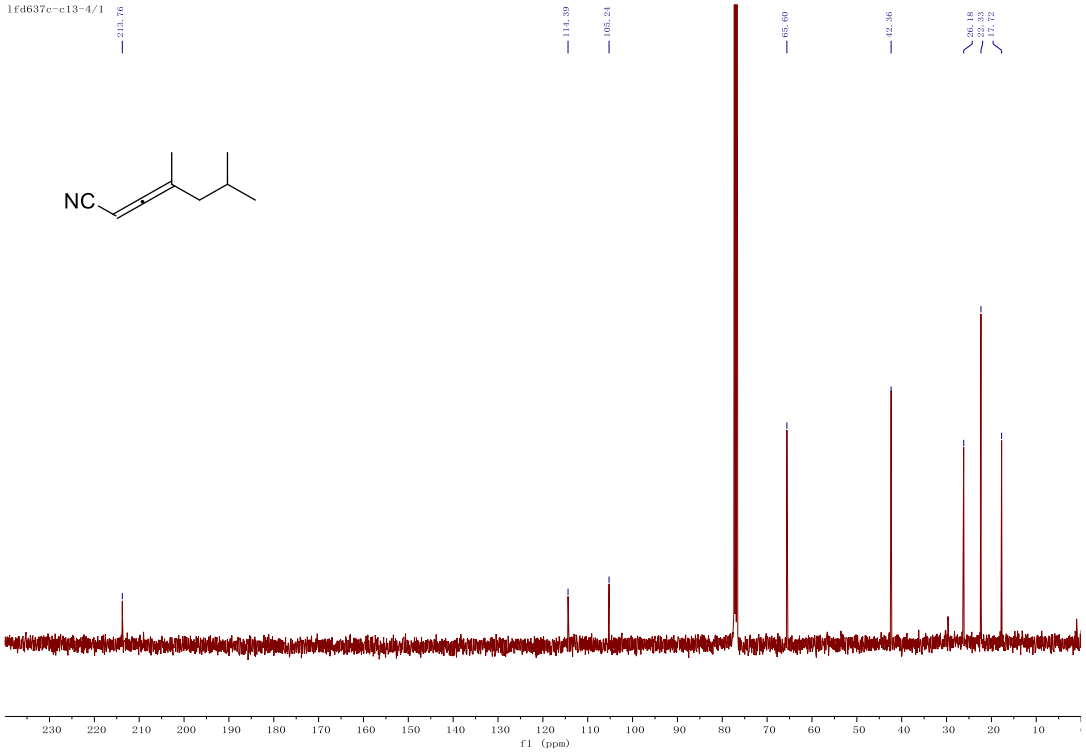
^{13}C NMR spectrum of compound 3k



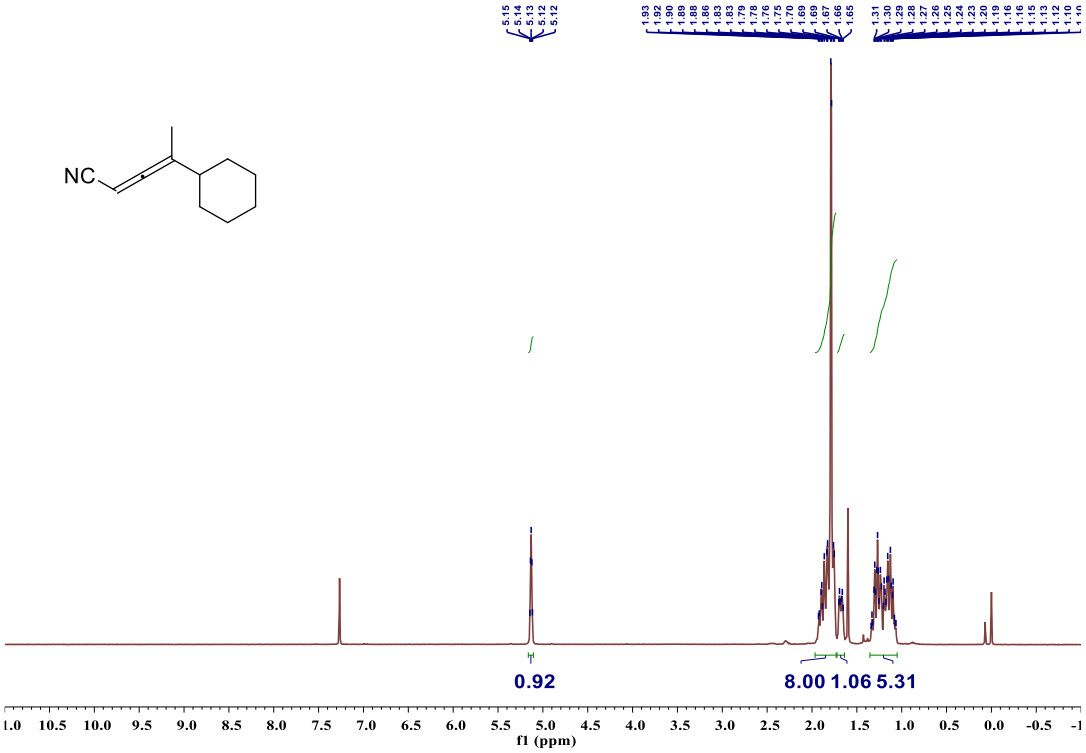
^{1}H NMR spectrum of compound 3l



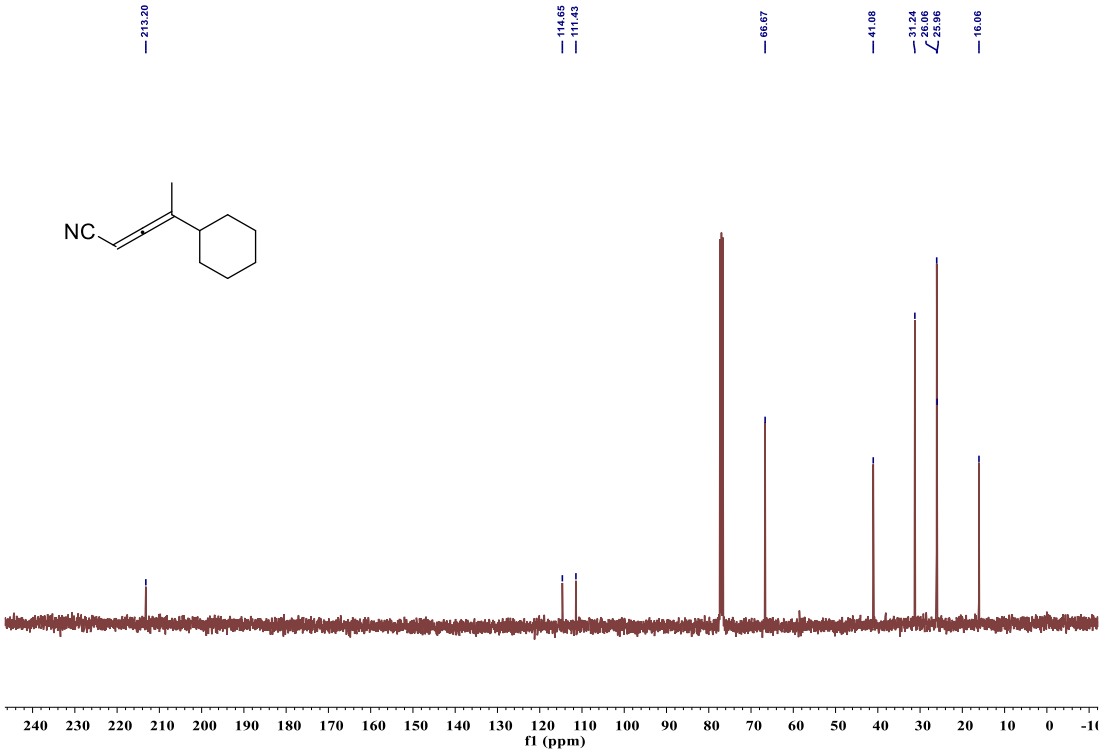
^{13}C NMR spectrum of compound 3l



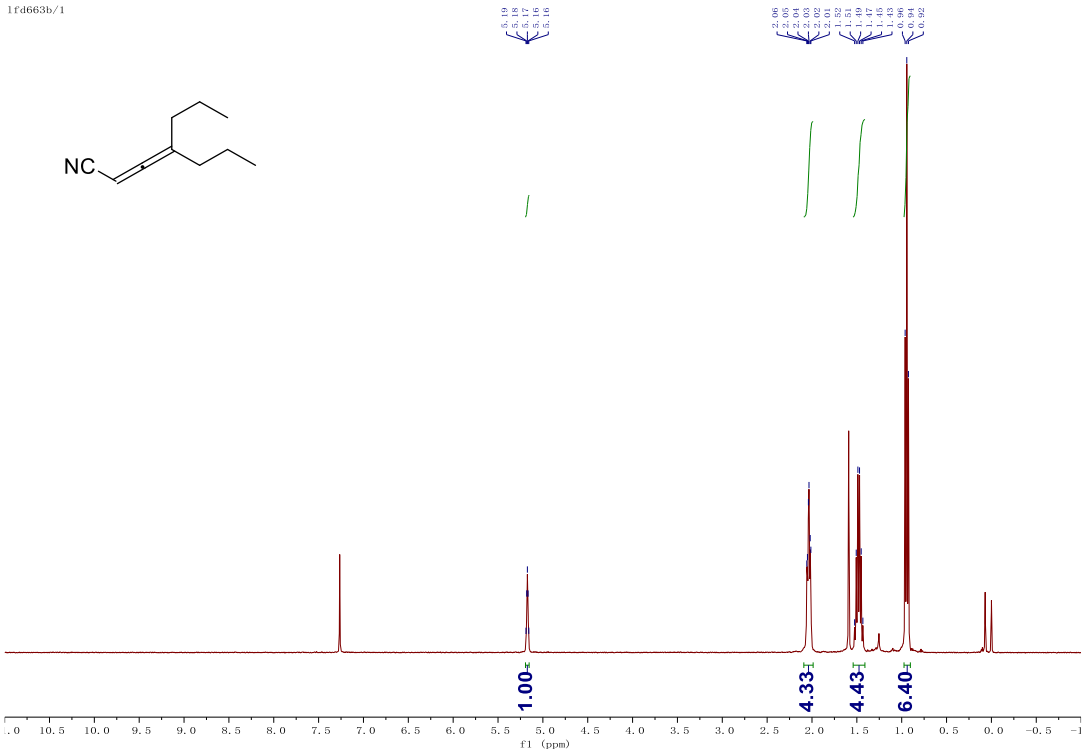
^{1}H NMR spectrum of compound 3m



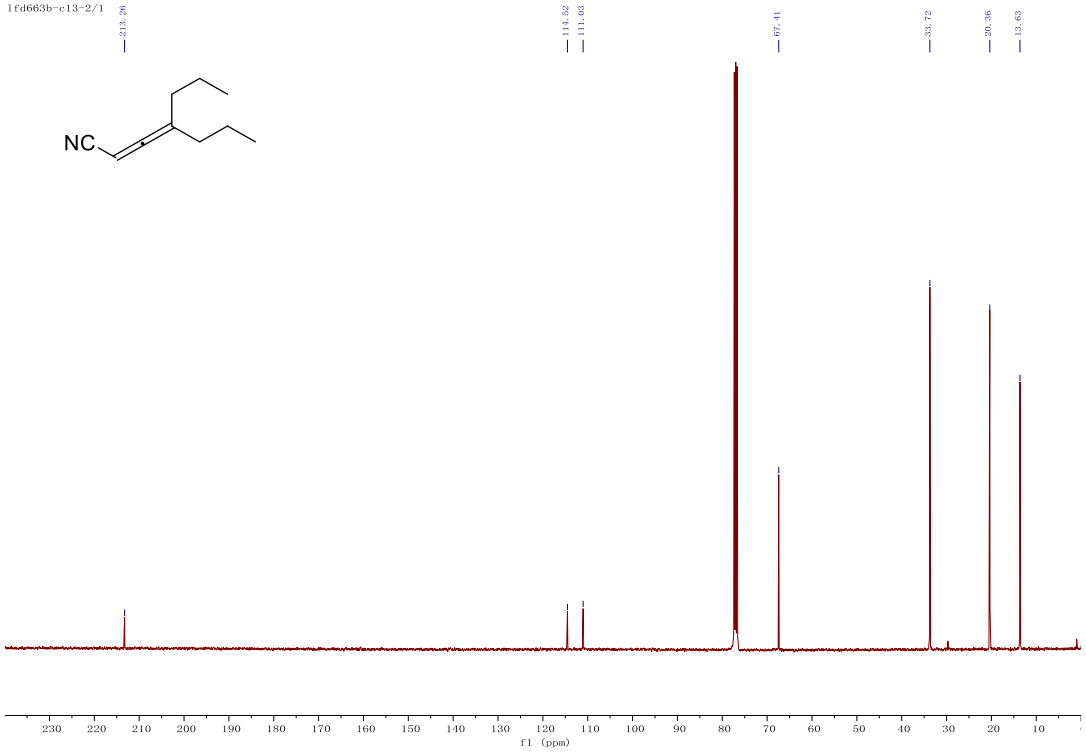
^{13}C NMR spectrum of compound 3m



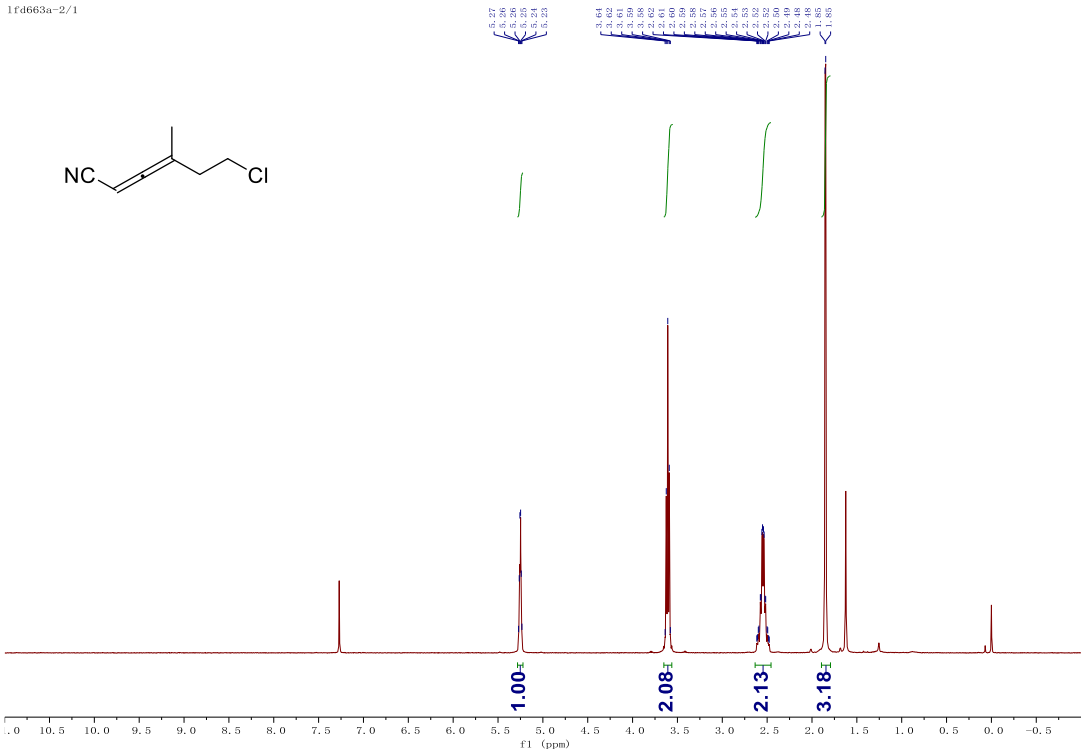
^{1}H NMR spectrum of compound 3n



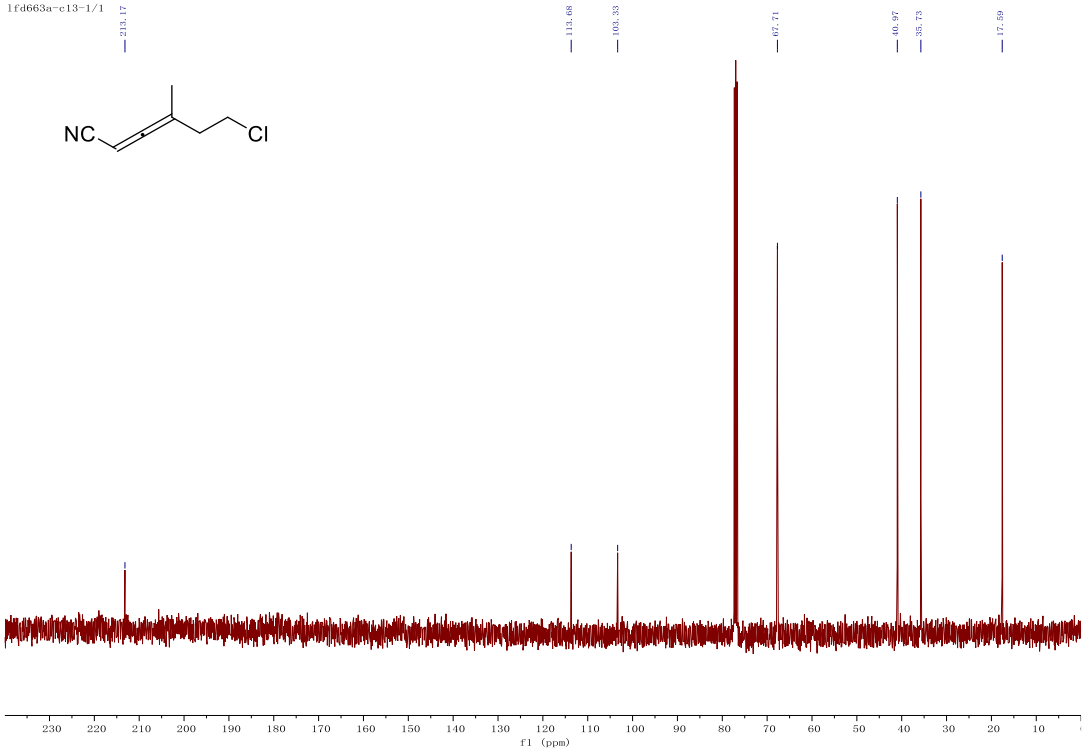
^{13}C NMR spectrum of compound 3n



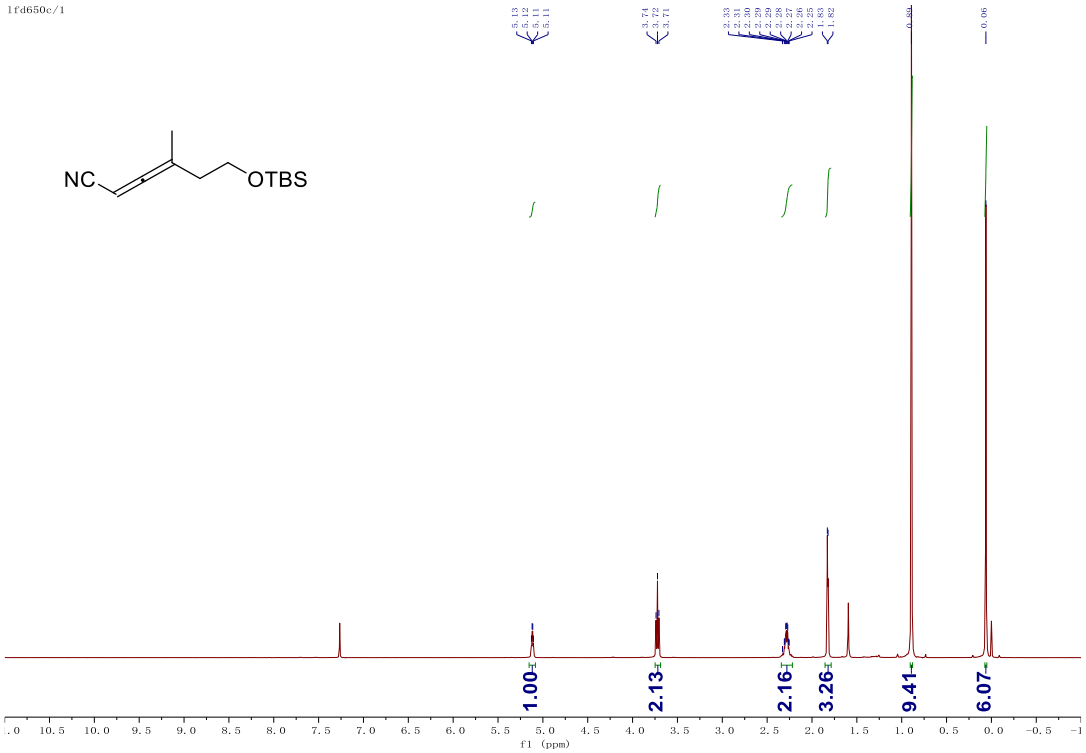
^{1}H NMR spectrum of compound 3o



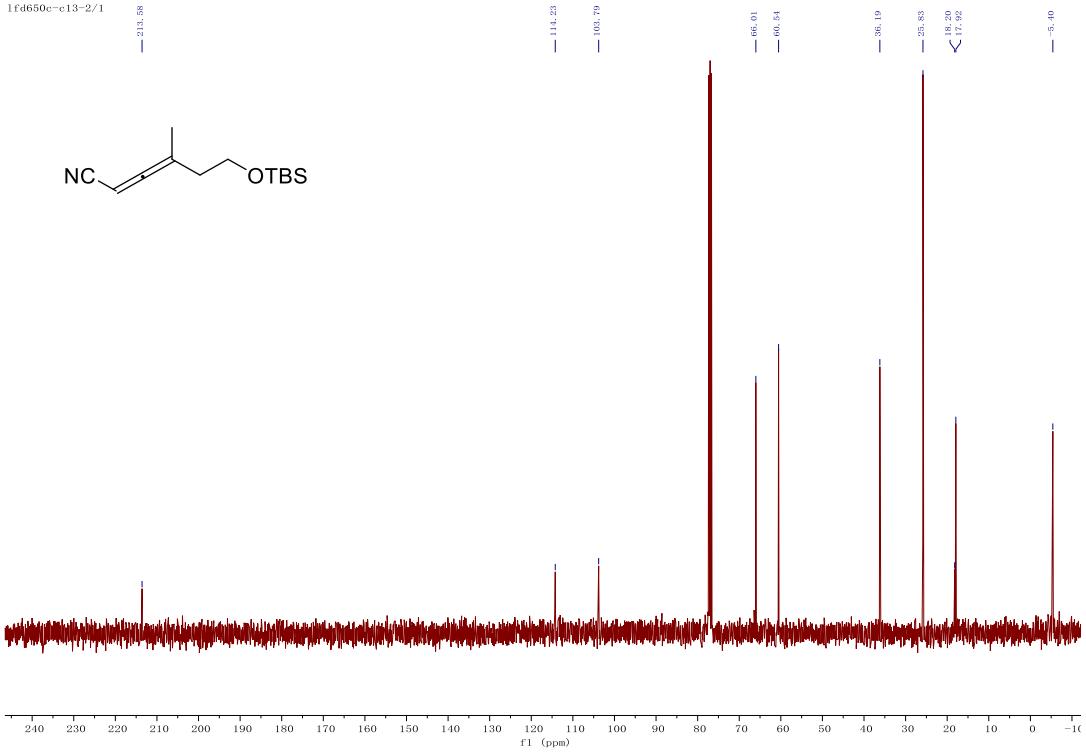
^{13}C NMR spectrum of compound 3o



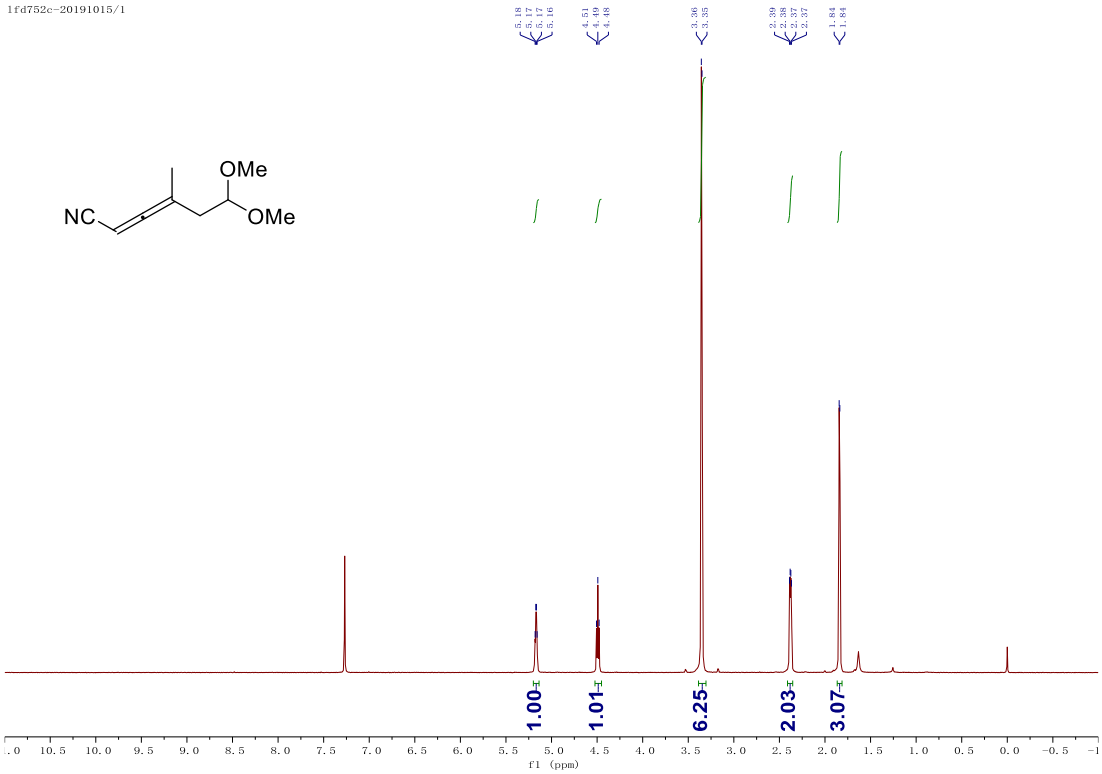
^{1}H NMR spectrum of compound 3p



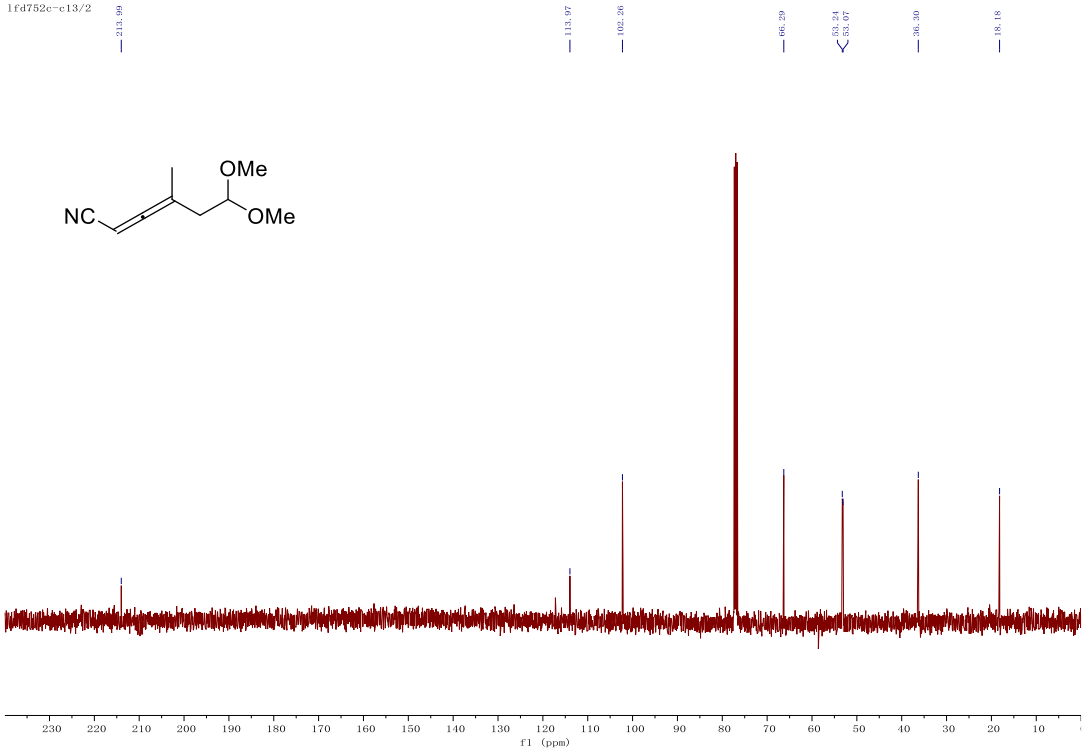
^{13}C NMR spectrum of compound 3p



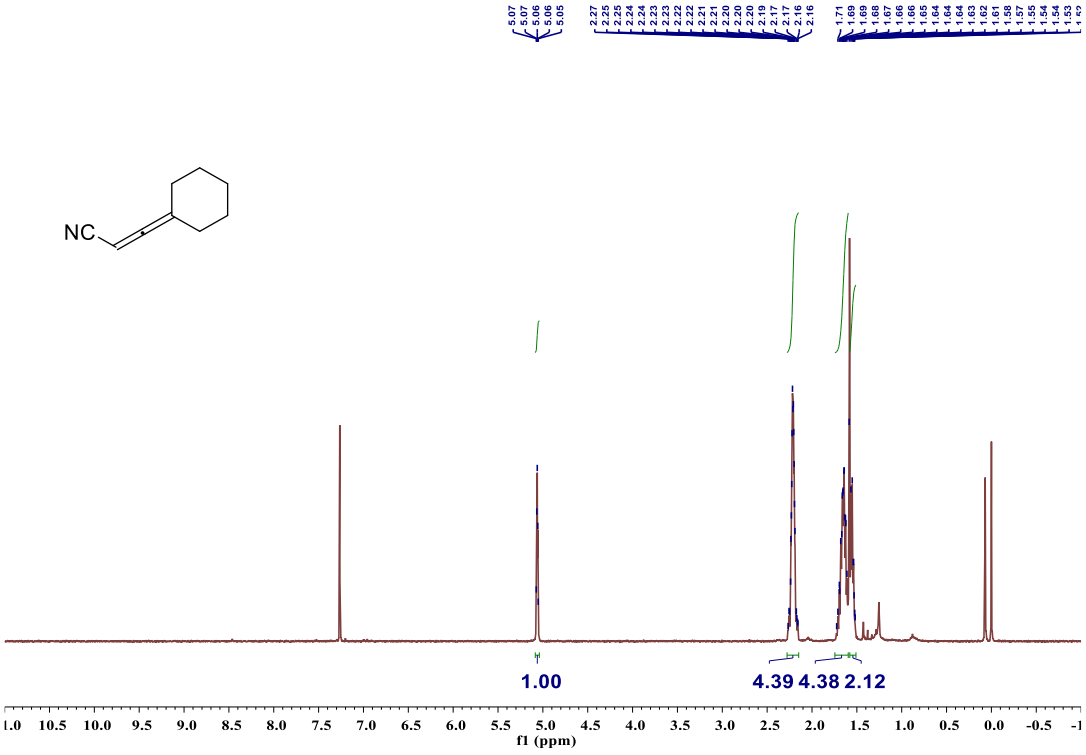
^{1}H NMR spectrum of compound 3q



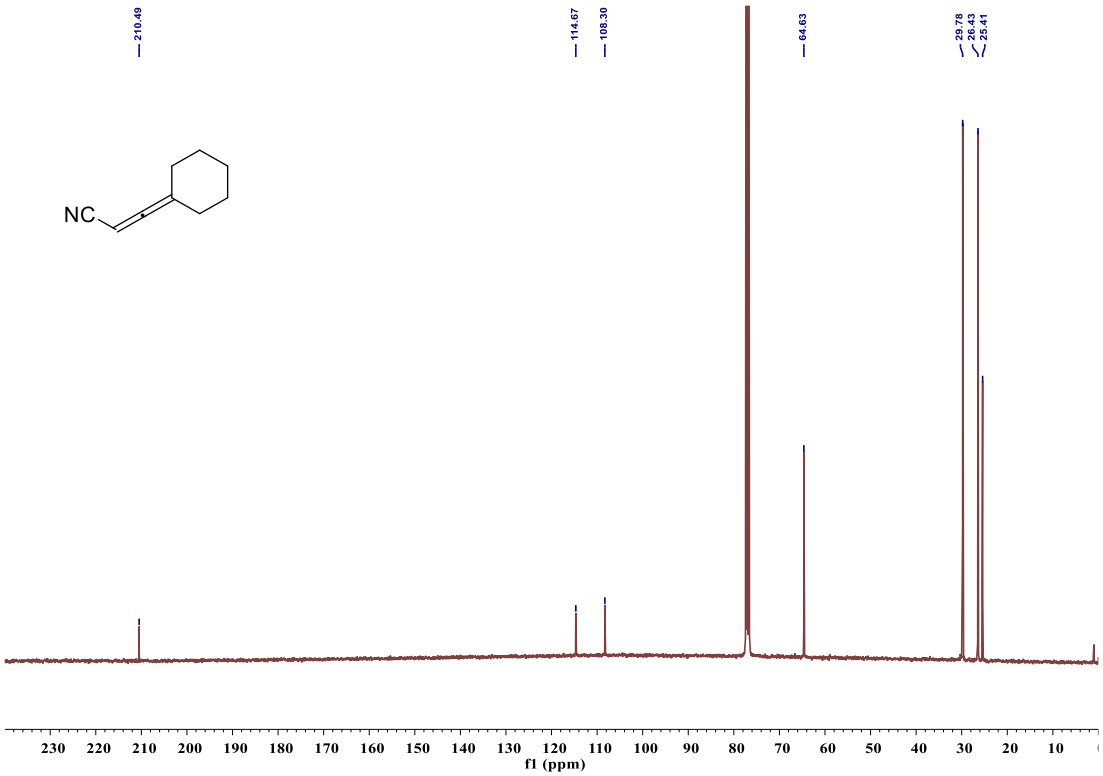
^{13}C NMR spectrum of compound 3q



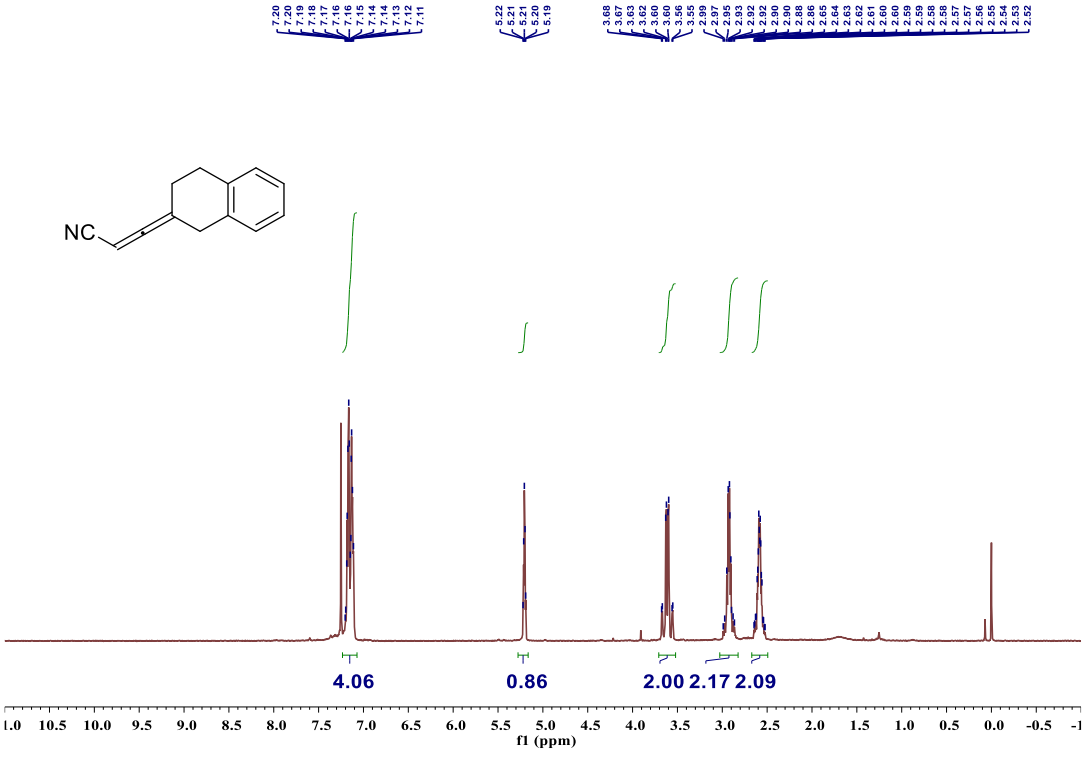
^{1}H NMR spectrum of compound 3r



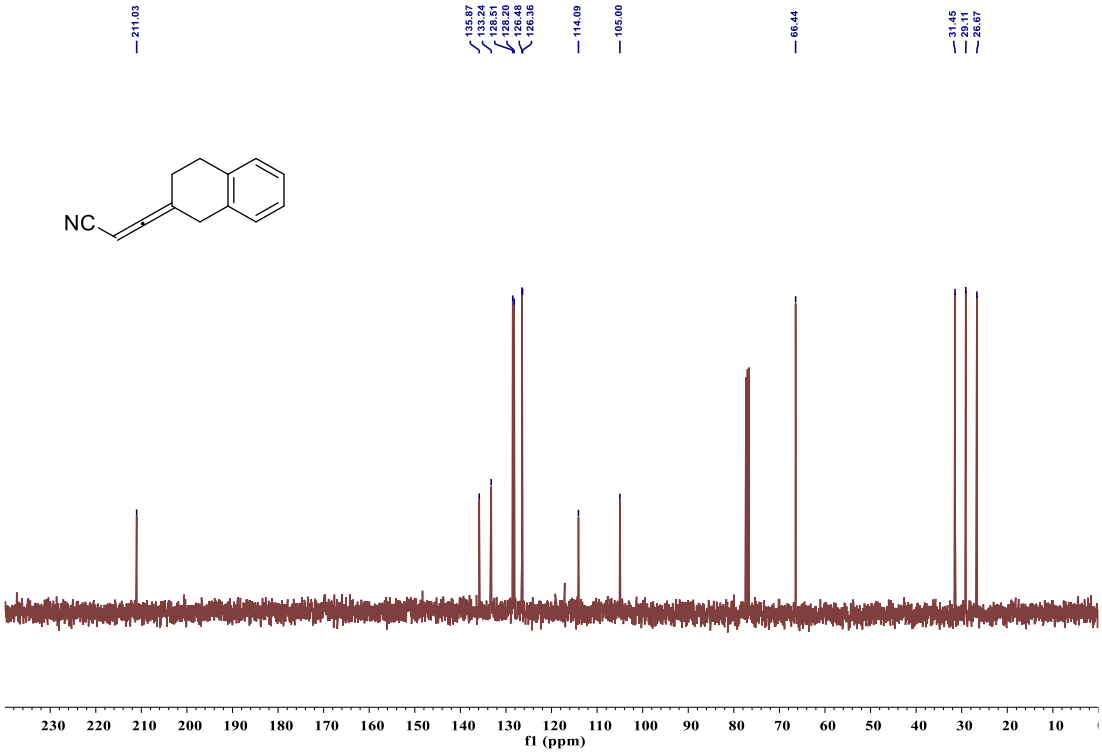
^{13}C NMR spectrum of compound 3r



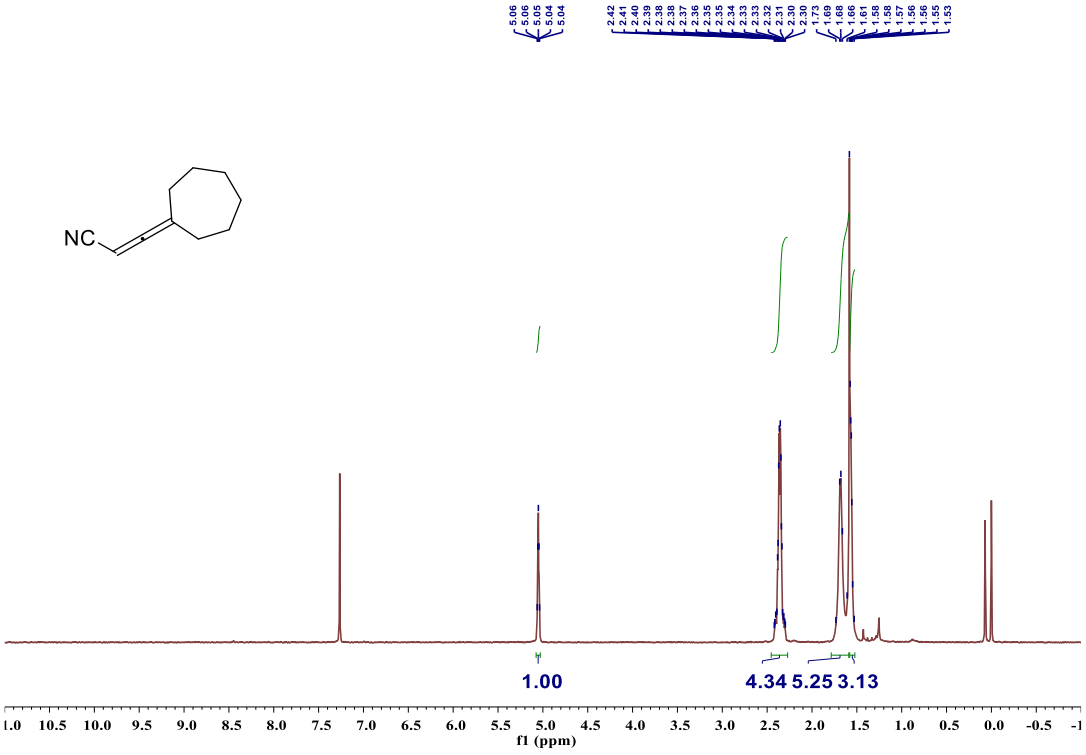
^{1}H NMR spectrum of compound 3s



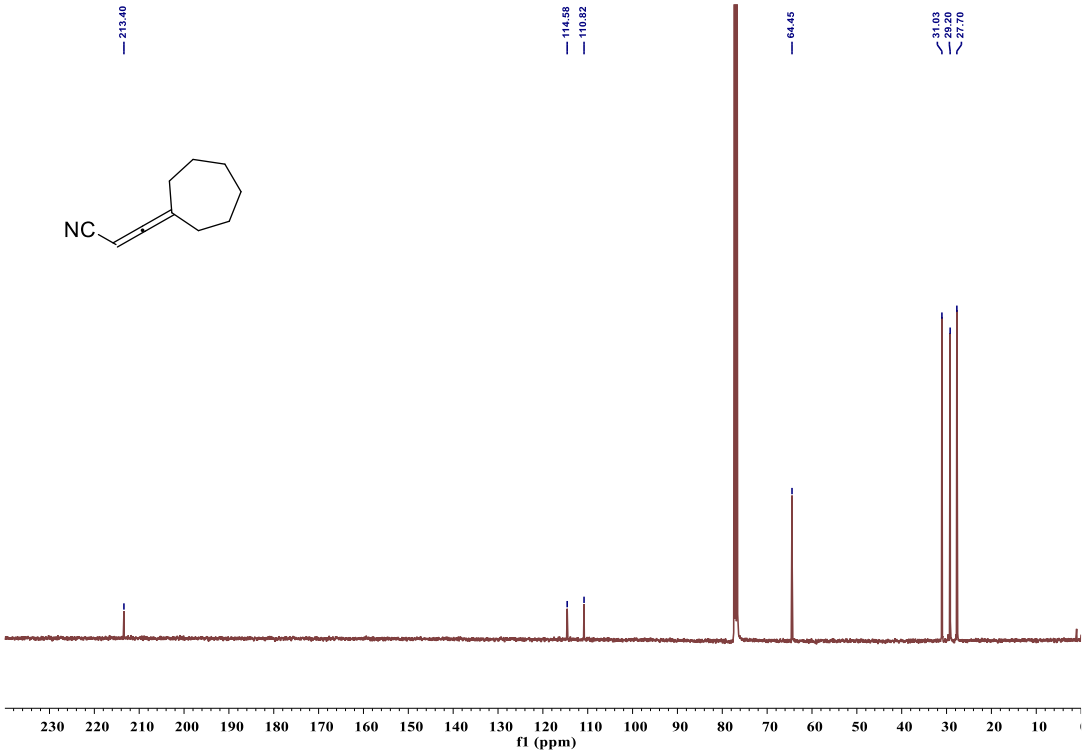
^{13}C NMR spectrum of compound 3s



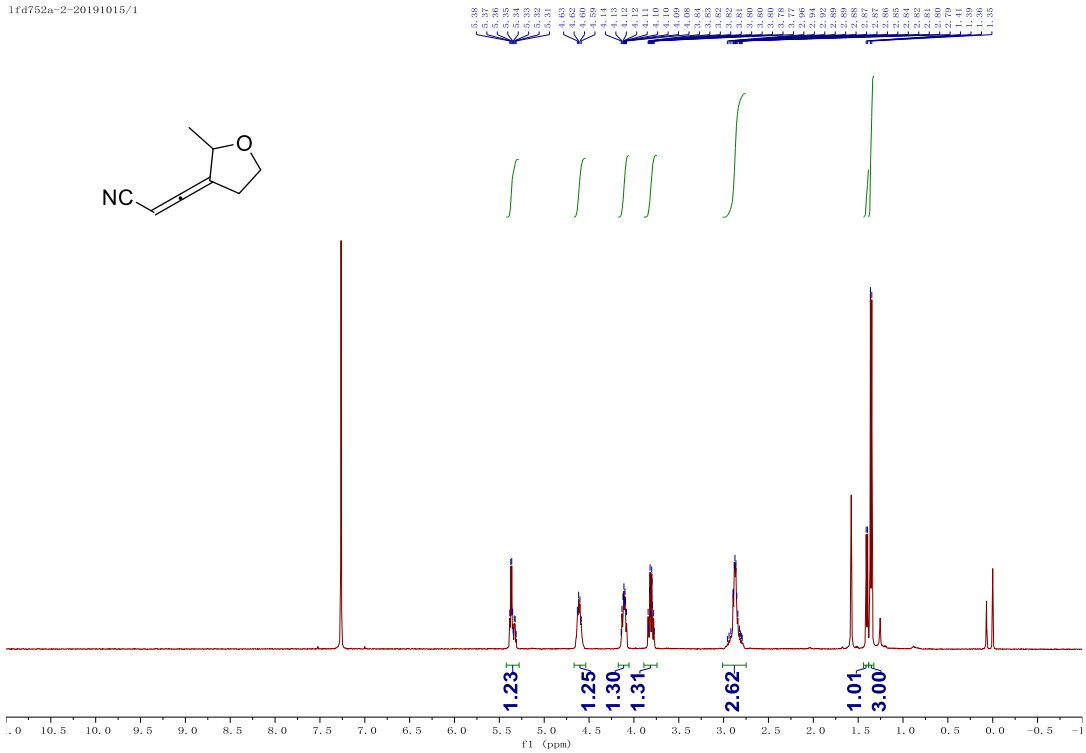
^{1}H NMR spectrum of compound 3t



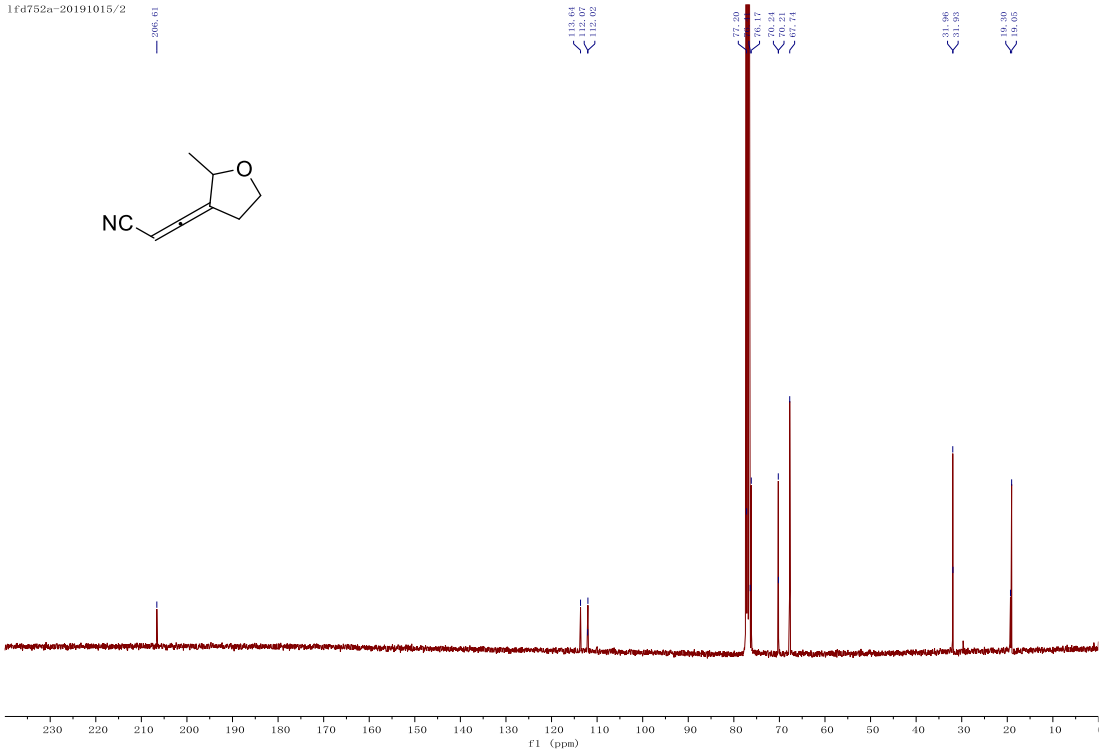
^{13}C NMR spectrum of compound 3t



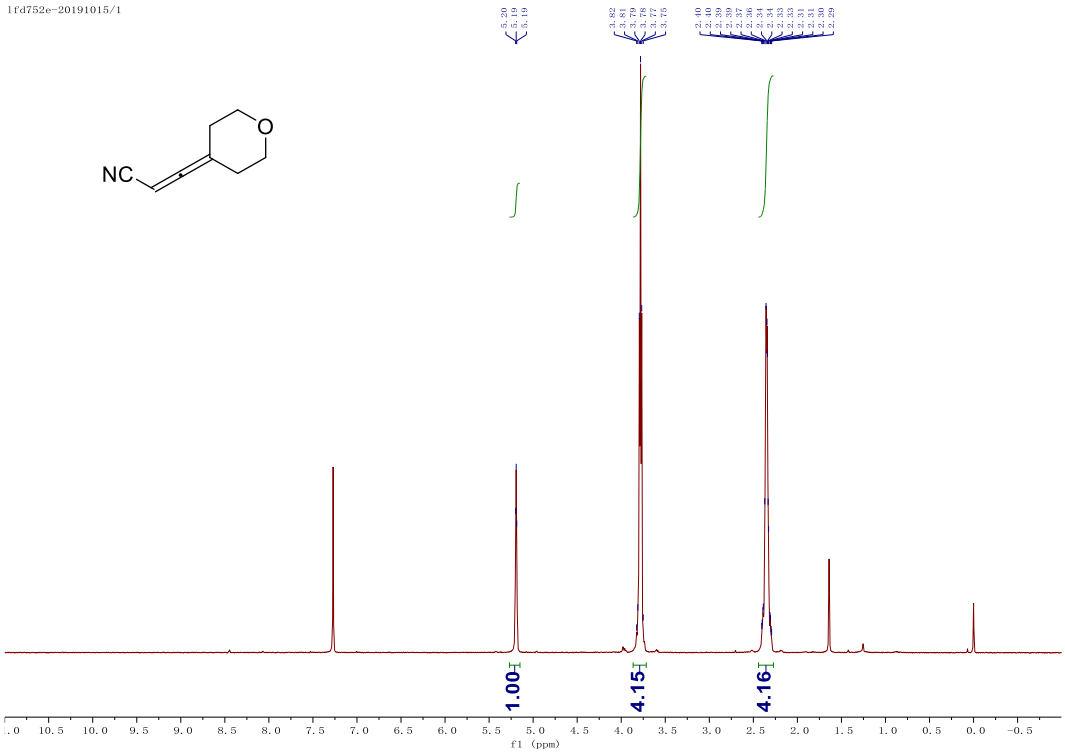
^{1}H NMR spectrum of compound 3u



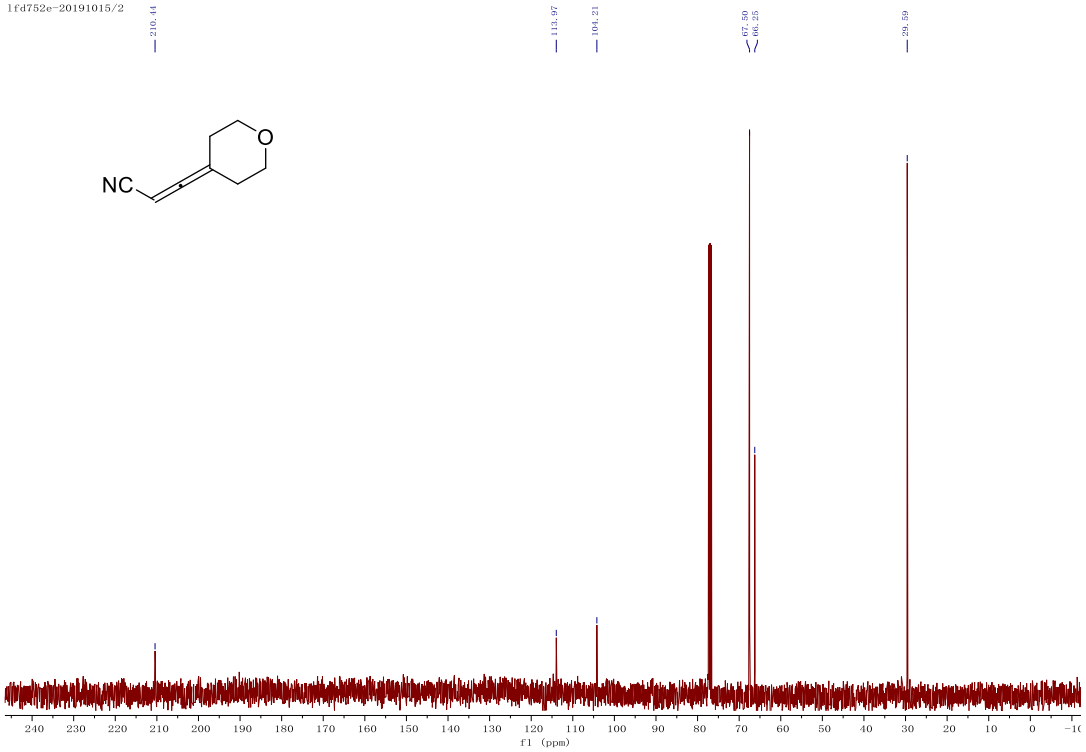
^{13}C NMR spectrum of compound 3u



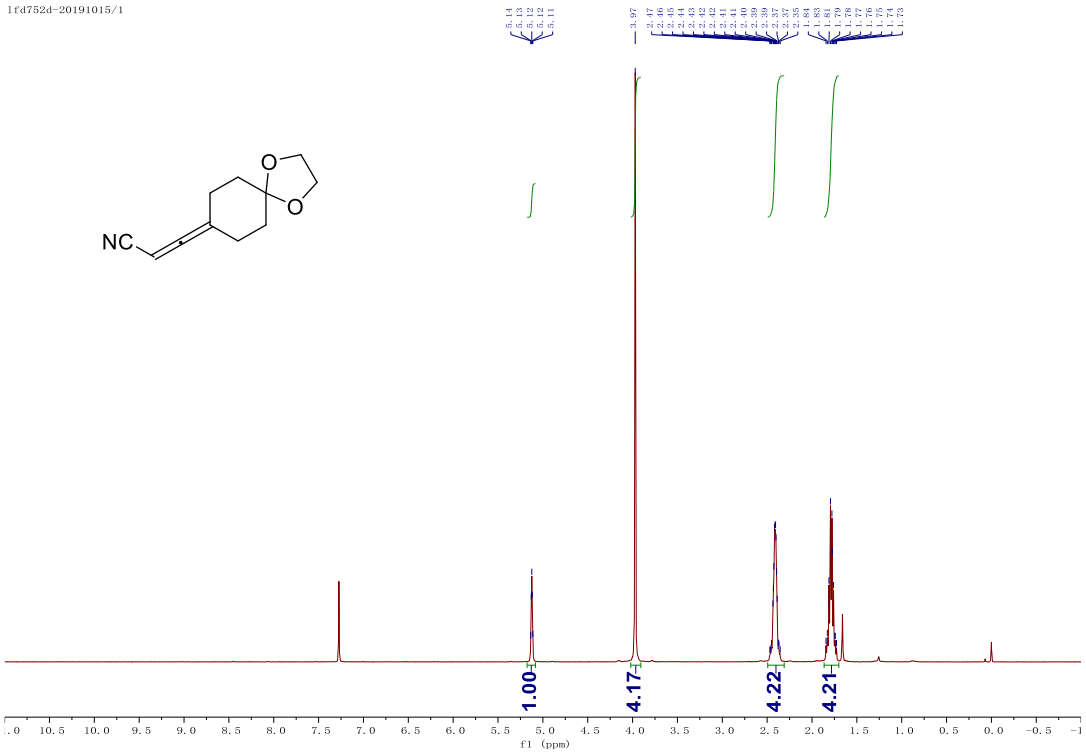
^{1}H NMR spectrum of compound 3v



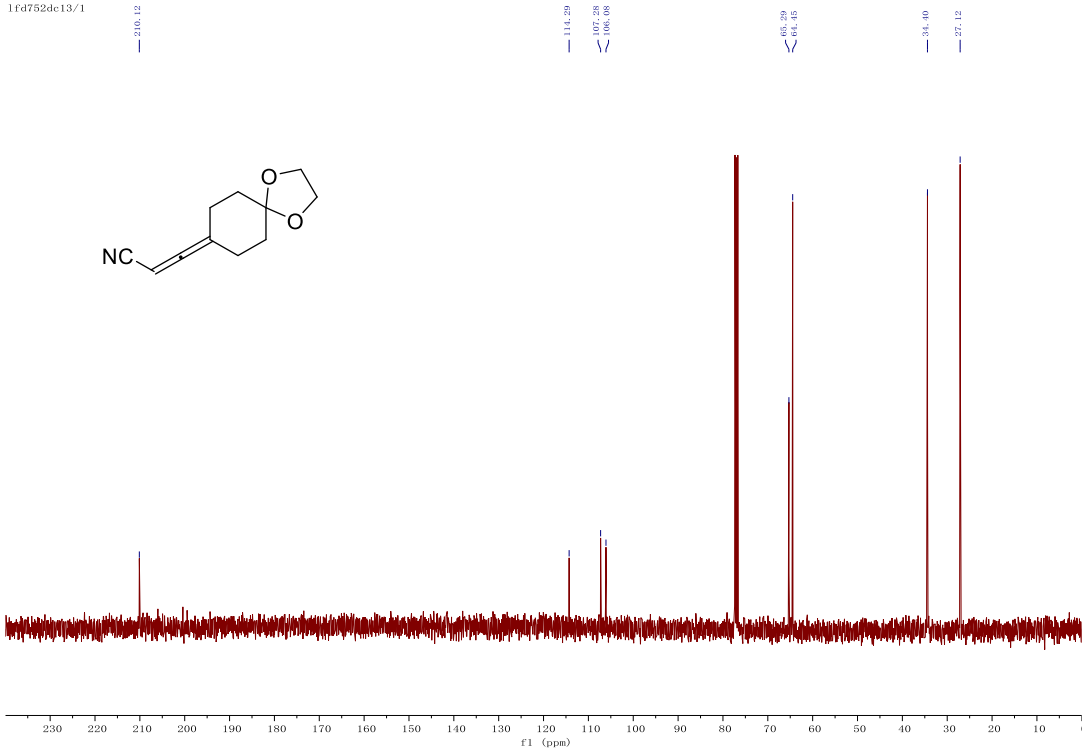
^{13}C NMR spectrum of compound 3v



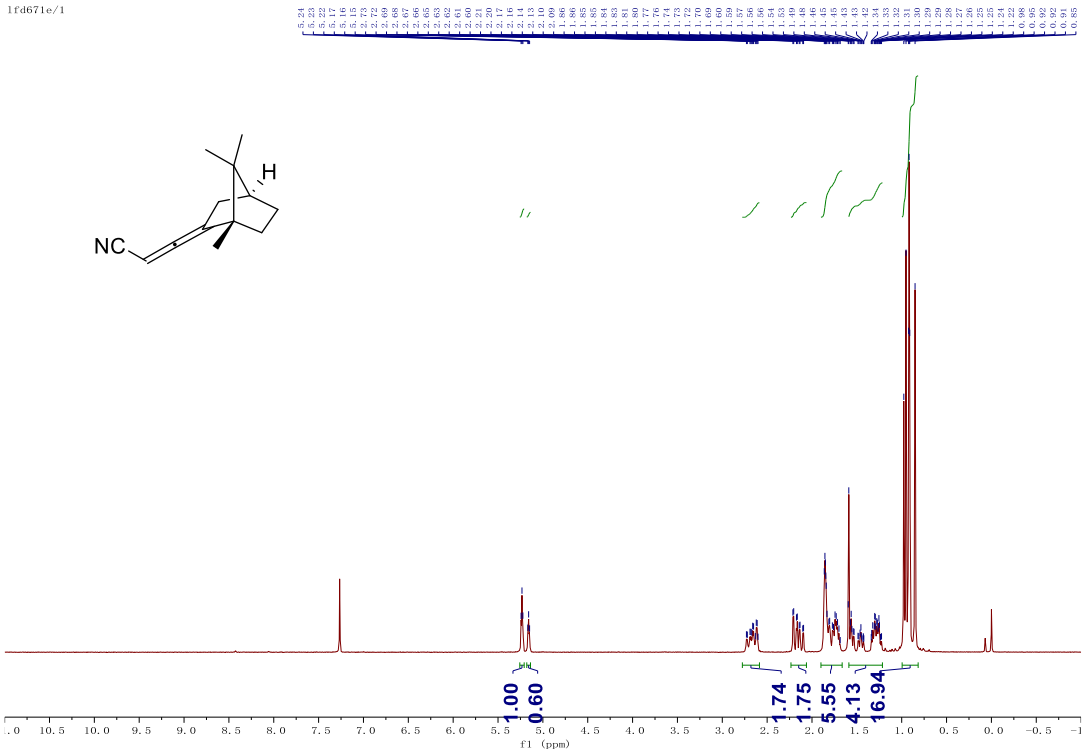
^{1}H NMR spectrum of compound 3w



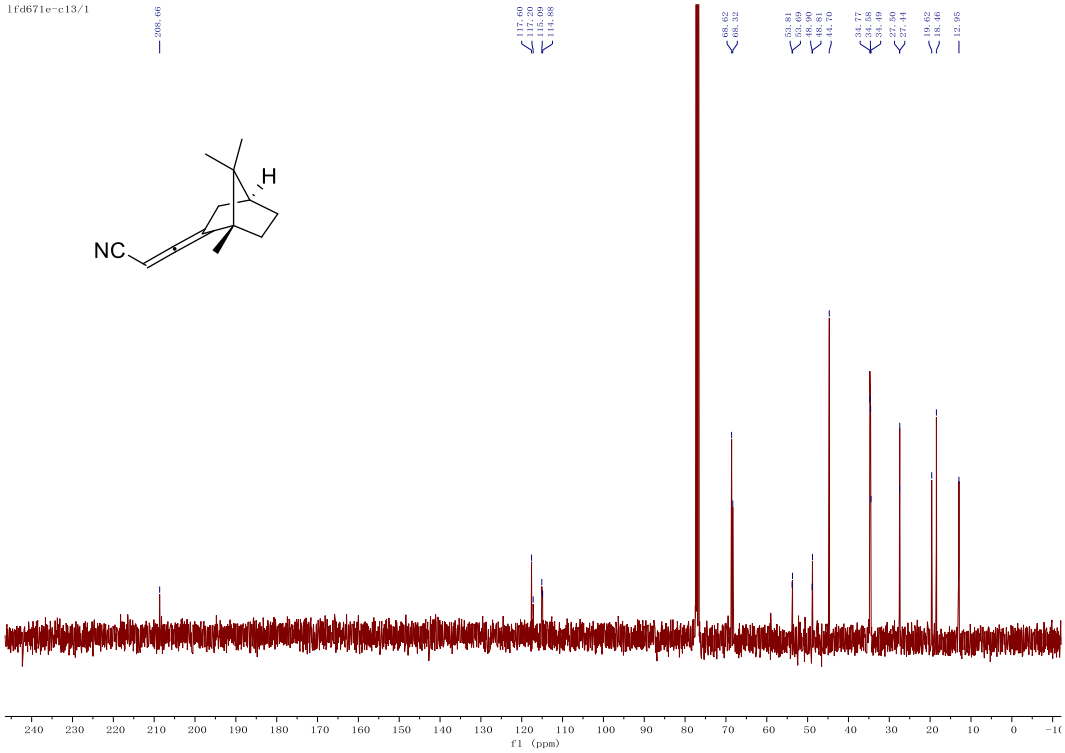
^{13}C NMR spectrum of compound 3w



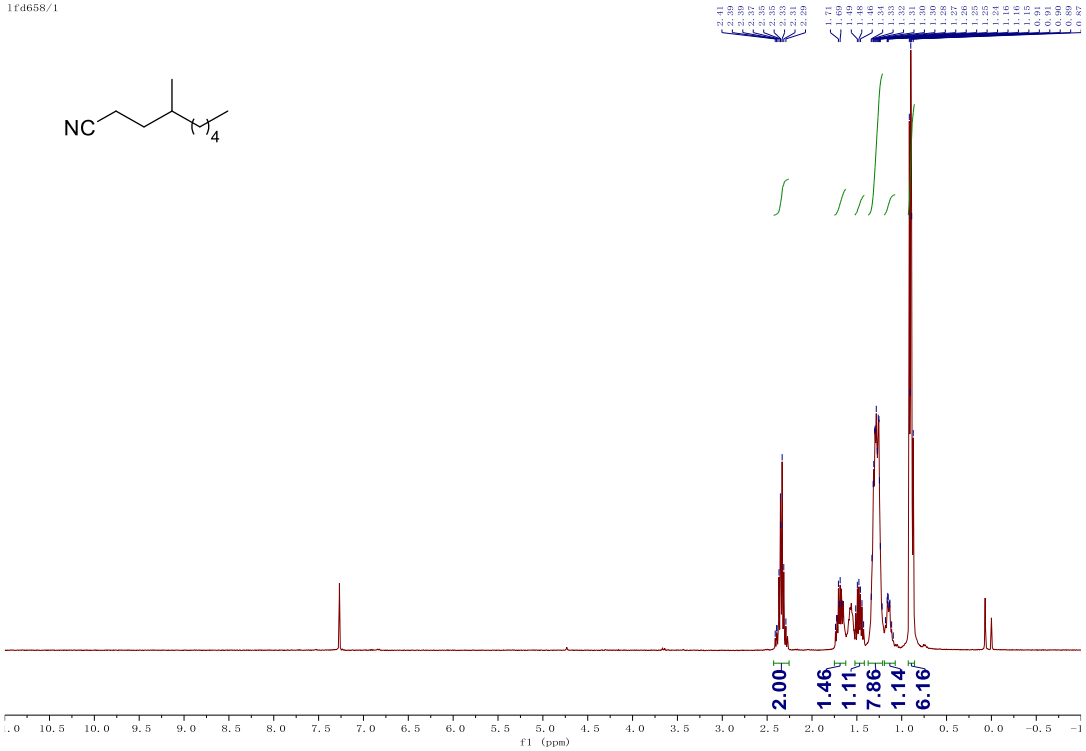
^{1}H NMR spectrum of compound 3x



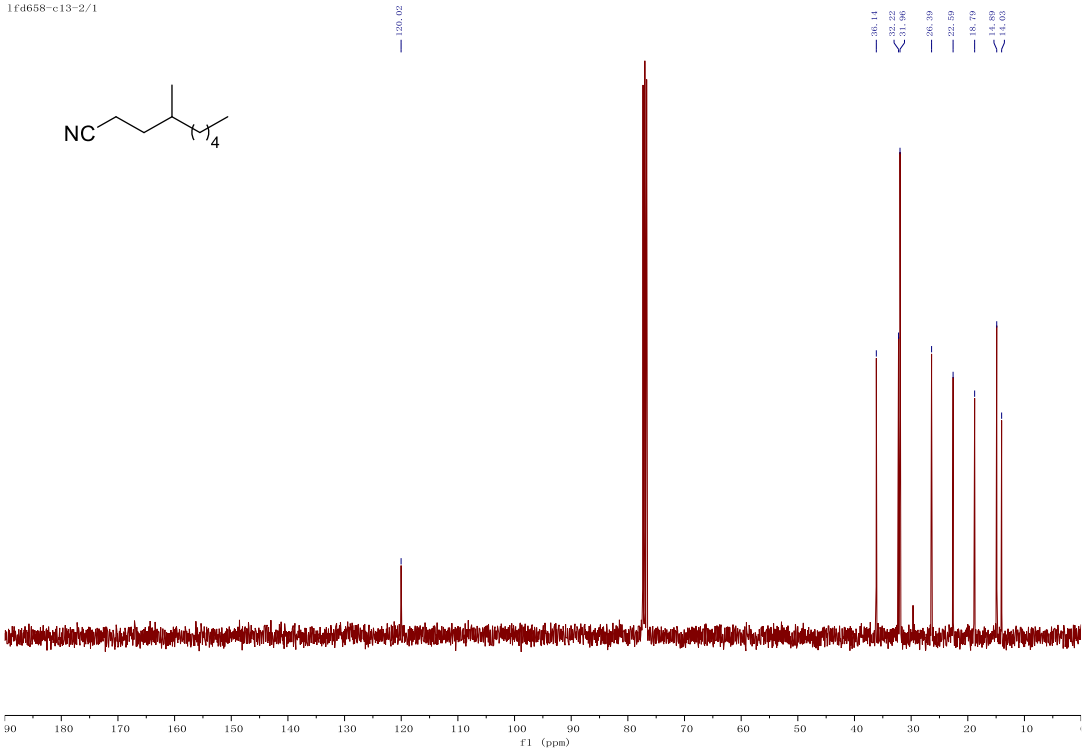
^{13}C NMR spectrum of compound 3x



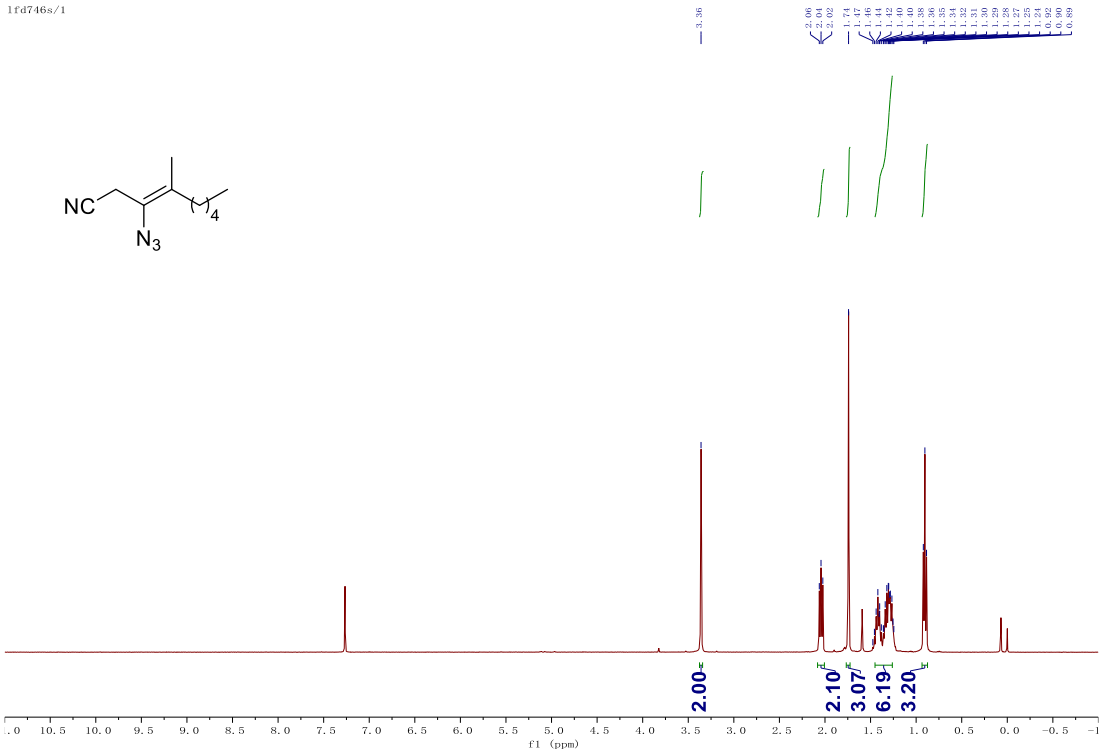
^{1}H NMR spectrum of compound 4a



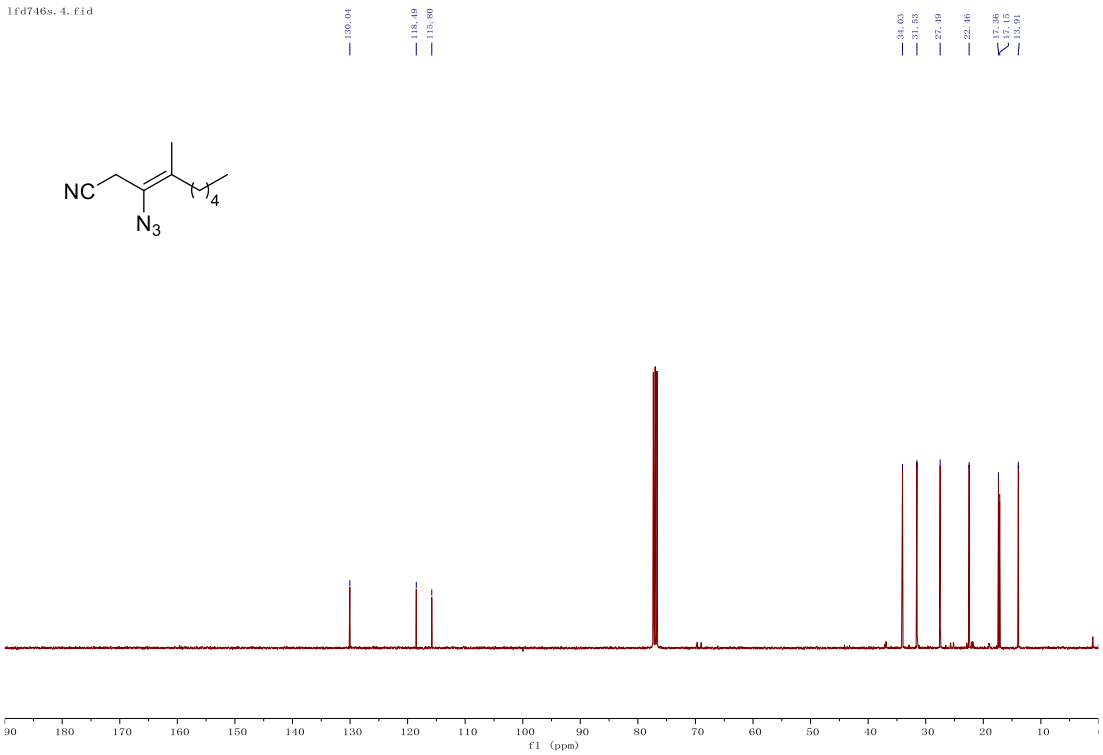
^{13}C NMR spectrum of compound 4a



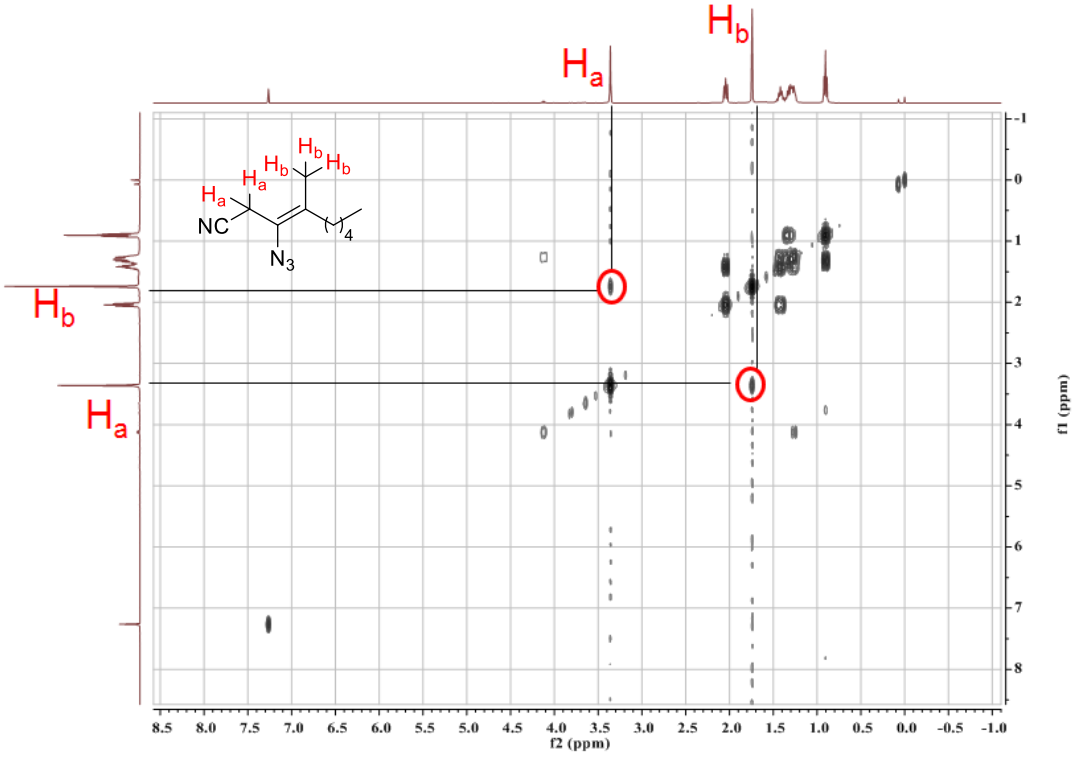
^{1}H NMR spectrum of compound Z-4b



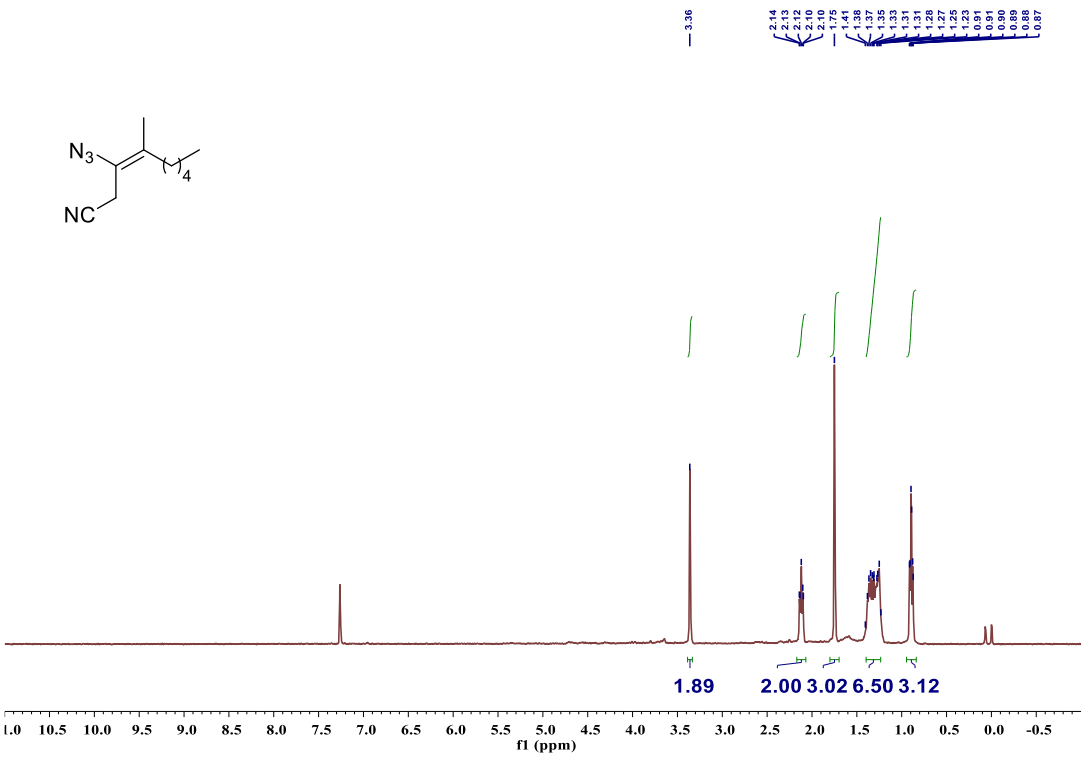
^{13}C NMR spectrum of compound Z-4b



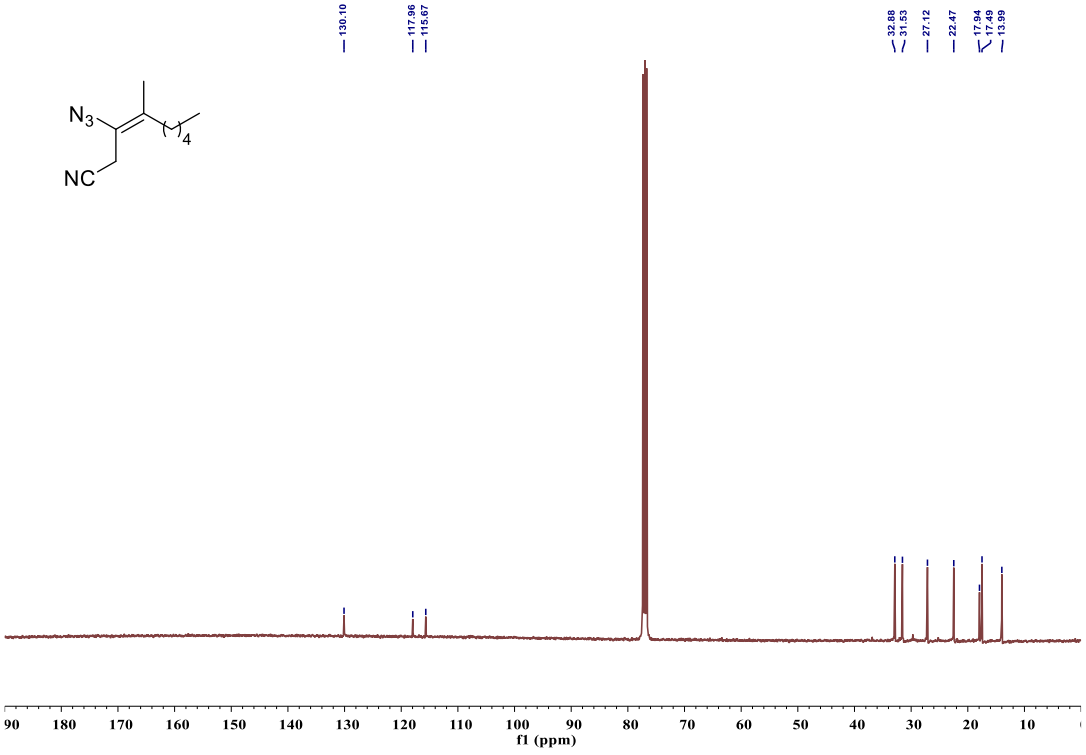
2D-Cosy spectrum of compound Z-4b



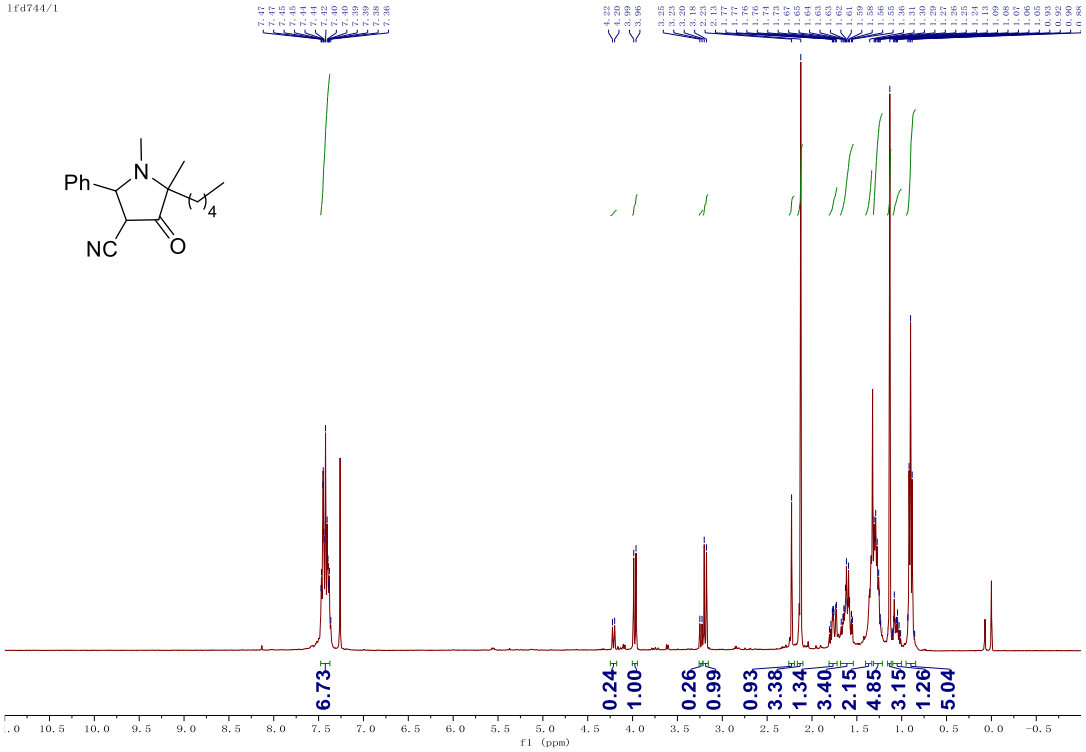
^{1}H NMR spectrum of compound E-4b



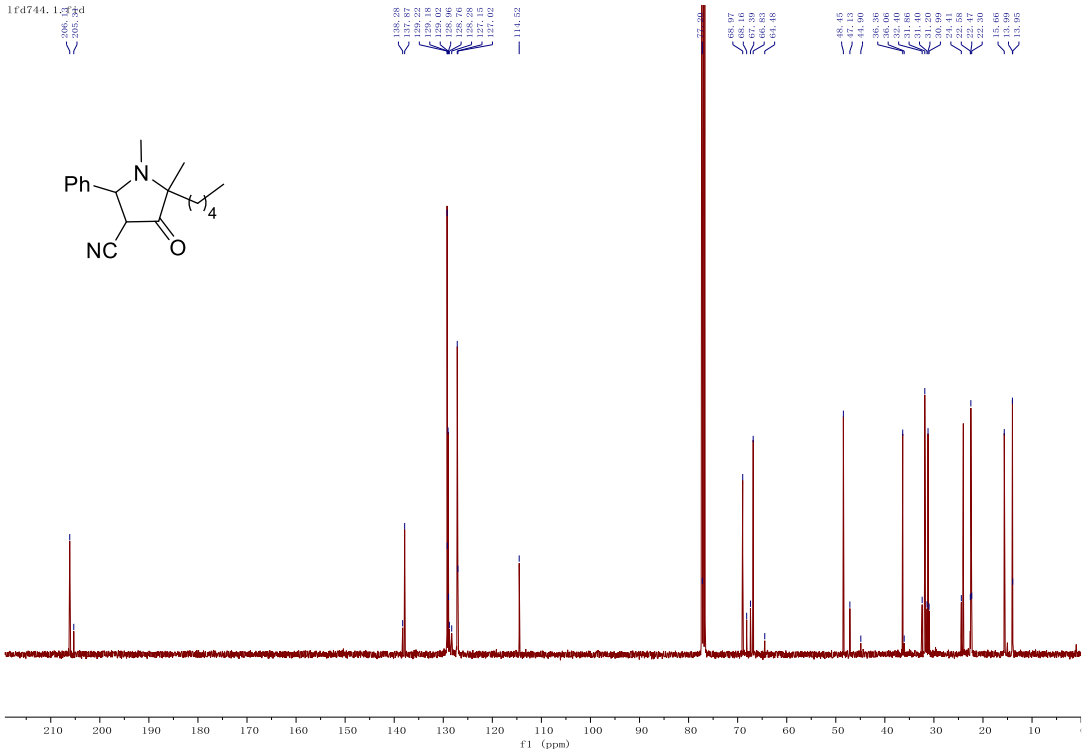
^{13}C NMR spectrum of compound E-4b



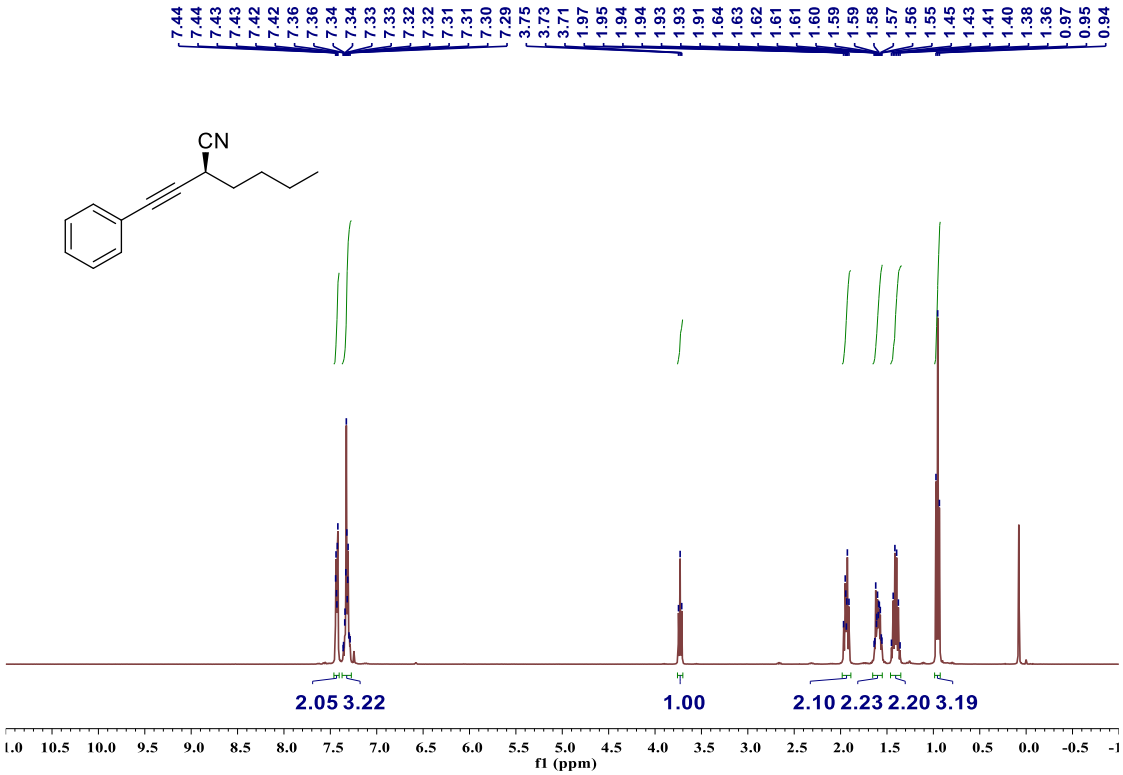
^{1}H NMR spectrum of compound 4c



^{13}C NMR spectrum of compound 4c



^{1}H NMR spectrum of compound 5a



^{13}C NMR spectrum of compound 5a