Supporting Information

Ir-Catalyzed Chemo- and Enantioselective Hydrogenation of Enyne-Conjugated Ketones

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I. General remarks

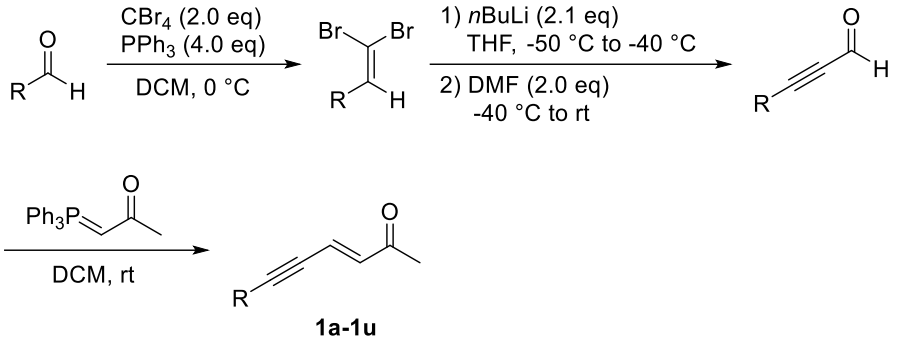
All the reactions dealing with air- or moisture- sensitive compounds were carried out under an atmosphere of argon in a glovebox or using standard Schlenk techniques in a reaction vessel which was dried by a heating gun. Unless otherwise noted, all the reagents were purchased from commercial suppliers without further purification. Solvents for the synthesis of substrates were distilled from sodium/benzophenone (THF, toluene) or calcium hydride (dichloromethane) under a N_2 atmosphere prior to use. Solvents for reaction condition screening were purchased from J&K Chemical and degassed though bubbling argon for 2 hours.

^{1}H NMR, ^{13}C NMR spectra were obtained at room temperature on a Bruker AV400 MHz or Bruker AV600 MHz spectrometer with chemical shifts (d) referred to the residual solvent signal. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^{1}H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. Data were reported as: multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet), coupling constant in herz (Hz) and signal area integration in natural numbers. Enantiomeric excess values were determined by Agilent 1290 Series HPLC instrument on a chiral stationary phase. Optical rotations were measured using 1 mL cell with a 1dm path length on a Rudolph Autopol I polarimeter at 589 nm. High resolution mass spectra (HRMS) were obtained on Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer. A positive ion mass spectrum of sample was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source. Crystal structure was measured with BRUKER APEX III diffractometer.[1]

II. Synthesis of substrates

General procedure:

Procedure A: [1]



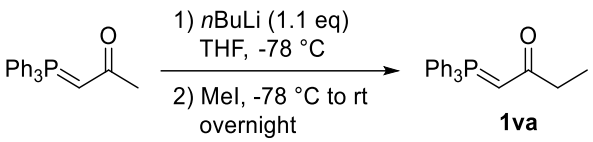
Step 1: A solution of triphenylphosphine (4.0 eq) and tetrabromomethane (2.0 eq) in DCM (0.15 M) was stirred at 0 °C for 30 minutes. The aldehyde was added and the mixture was stirred at 0 °C for another hour. After petroleum ether was added to the solution, the mixture was loaded on silica and subjected to flash chromatography (silica, petroleum ether), the *gem*-dibromoolefines were given after removing solvent under reduced pressure.

Step 2: Under an atmosphere of argon, *n*BuLi (2.1 eq., 2.5 M in *n*-hexane) was added over a period of 30 minutes *via* syringe pump to a solution of *gem*-dibromoolefine (1 eq.) in dry THF (0.4 M) at -50 °C, and the mixture was stirred at -40 °C for 15 minutes. After addition of DMF (2.0 eq.) at once, the mixture was allowed to warm to room temperature and stirred for one hour. The mixture was added to a stirring solution of NaH_2PO_4 (aq.)/MTBE (1:1). After five minutes, the layers were separated and the aqueous layer was extracted with MTBE. The combined organic layers were dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was subjected to flash chromatography (silica, PE/EA = 90:10). The alkynyl aldehydes were given after removing the solvent under reduced pressure.

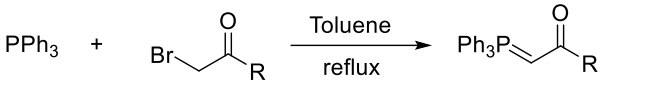
Step 3: A solution of aldehyde (1.0 eq.) and phosphine ylide (1.1 eq.) in dichloromethane (0.1 M) was stirred at room temperature for one hour. The solvent was removed under reduced pressure, the crude product was dry-loaded on silica and subjected to flash chromatography (silica, PE/EA = 90:10). The ketones were given after removing the solvent under reduced pressure.

Procedure B:[2, 3]

Synthesis of the α'-alkylation of 1-triphenylphosphoranylidenepropan-2-one

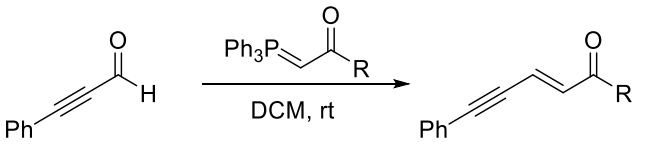


To a solution of 1-triphenylphosphoranylidenepropan-2-one (1.0 eq) in THF (0.125 M) was added at -78 °C *n*BuLi (1.1 eq., 2.5 M in *n*-hexane). The mixture was stirred at -78 °C for one hour. After iodomethane (1.4 eq) was added, the mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo, the residue was taken up in DCM and the mixture was washed three times with H_2O, dried with Na_2SO_4, filtered and concentrated in vacuo. The off-white solid residue was washed with three portions of ice-cold ether and dried in vacuo to give product as slightly brown solid, which was used immediately in the next reaction without further purification.



1wa, R = isopropyl
1xa, R= cyclohexyl
1ya, R = cyclopropyl

A solution of the 1-bromo-3-methylbutan-2-one (2.0 g, 12.1 mmol) and triphenylphosphine (3.2 g, 12.1 mmol) were refluxed in dry toluene (20 mL) for 4 h. After completion, the reaction mixture was allowed to cool to room temperature and the phosphonium salt was filtered and washed with Et_2O (3×100 mL). The phosphonium salt was then dissolved in H_2O: DCM (3:2) and 2 M NaOH aq. (100 mL) was added. The mixture was stirred for 2 h and then extracted with DCM (3×100 mL). The combined organic phases were washed with brine, dried with Na_2SO_4 and concentrated in vacuo to afford **1wa** as a white solid. Compound **1xa** and **1ya** were prepared according to the same procedure for the synthesis of **1wa**.

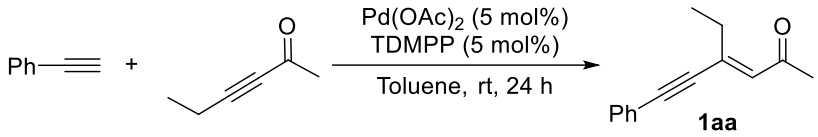


1v, R = Et
1w, R = isopropyl
1x, R= cyclohexyl
1y, R = cyclopropyl
1z, R = Ph

A solution of 3-phenylpropioaldehyde (1.0 eq.) and phosphine ylide (1.1 eq.) in dichloromethane (0.1 M) was stirred at room temperature for one hour. The solvent was removed under reduced pressure, the crude product was dry-loaded on silica and subjected to flash chromatography (silica, PE/EA =

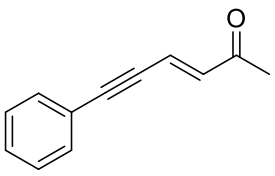
90:10). The ketones (**1v-1z**) were given after removing the solvent under reduced pressure.

Procedure C:[4]



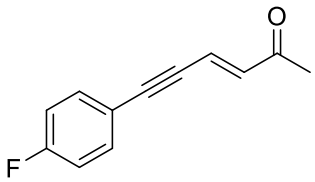
A 2-dram, screw-cap vial equipped with a stir bar was charged with $Pd(OAc)_2$ (22.4 mg, 0.10 mmol, 5 mol %) and tris(2,6-dimethoxyphenyl)phosphine (TDMPP, 44.2 mg, 0.10 mmol, 5 mol %). PhMe (2.0 mL) was added. The mixture was stirred for 15 minutes, generating a homogeneous, orange-red solution. To the solution was added 3-hexyn-2-one (328 µL, 3.0 mmol, 1.5 equivalents) followed by phenylacetylene (220 µL, 2.0 mmol, 1.0 equivalent). Upon addition of the donor alkyne, the reaction quickly changes in appearance to homogeneous and black. The reaction mixture was stirred for 14 h, at which point it was filtered through a pipette plug of Florisil® (3 cm), which was rinsed with Et_2O (10 mL). The solution was concentrated, and the residue was purified via column chromatography (10:1 hexanes: EtOAc) to afford **1aa** (300.0 mg, 76%) as a clear, orange oil.

(*E*)-6-Phenylhex-3-en-5-yn-2-one (1a) [1]



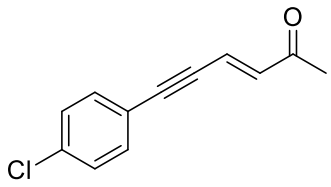
Light yellow solid, 89% yield, 3.8 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.47 (m, 2H), 7.38-7.33 (m, 3H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.08, 137.79, 132.00, 129.45, 128.52, 123.83, 122.16, 99.69, 86.71, 27.69. HRMS (EI) m/z calcd. for $C_{12}H_{11}O$ ($[M+H]^+$): 171.0805. Found: 171.0805.

(*E*)-6-(4-Fluorophenyl)hex-3-en-5-yn-2-one (1b) [1]



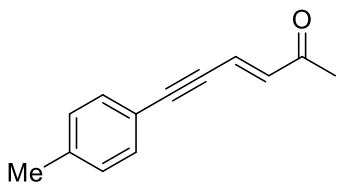
Light yellow solid, 60% yield, 1.1 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.99, 163.16 (d, *J* = 250.6 Hz), 137.78, 134.04 (d, *J* = 8.5 Hz, 2C), 123.58, 118.28 (d, *J* = 3.3 Hz), 115.93 (d, *J* = 22.8 Hz, 2C), 98.51, 86.50, 27.72. ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.63- -108.73 (m). HRMS (EI) m/z Calcd. for $C_{12}H_{10}FO$ ($[M+H]^+$): 189.0710. Found: 189.0710.

(*E*)-6-(4-Chlorophenyl)hex-3-en-5-yn-2-one (1c) [5]



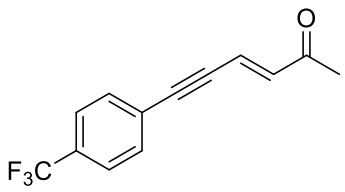
Light brown solid, 36% yield, 0.74 g.^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.35-7.32 (m, 2H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.94, 138.03, 135.63, 133.18, 128.93, 123.39, 120.63, 98.25, 87.56, 27.77. HRMS (EI) m/z Calcd. for $C_{12}H_{10}ClO$ ($[M+H]^+$): 205.0416. Found: 205.0416.

(*E*)-6-(*p*-Tolyl)hex-3-en-5-yn-2-one (1d) [5]



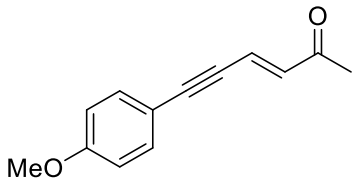
Light yellow solid, 60% yield, 1.1 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.83 (dd, *J* = 16.1, 2.0 Hz, 1H), 6.54 (dd, *J* = 16.0, 2.0 Hz, 1H), 2.36 (s, 3H), 2.29 (d, *J* = 1.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.13, 139.90, 137.42, 131.95, 129.31, 124.08, 119.09, 100.22, 86.33, 27.64, 21.62. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O$ ($[M+H]^+$): 185.0962. Found: 185.0961.

(*E*)-6-(4-(Trifluoromethyl)phenyl)hex-3-en-5-yn-2-one (1e) [1]



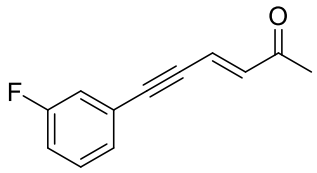
Dark brown solid, 33% yield, 0.8 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 16.1 Hz, 1H), 6.61 (d, *J* = 16.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.80, 138.67, 132.18 (s, 2C), 130.96 (dd, *J* = 32.7 Hz, 32.7 Hz), 125.90, 125.45 (dd, *J* = 4.3, 3.3 Hz, 2C), 124.64, 122.90, 97.36, 88.57, 27.84. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.98 (s). HRMS (EI) m/z Calcd. for $C_{13}H_{10}F_3O$ ($[M+H]^+$): 239.0684. Found: 239.0684.

(*E*)-6-(4-Methoxylphenyl)hex-3-en-5-yn-2-one (1f) [5]



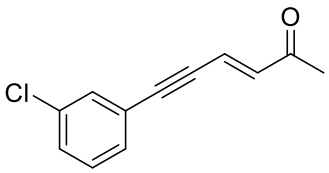
Light yellow solid, 61% yield, 1.2 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44-7.40 (m, 2H), 6.88-6.85 (m, 2H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.16, 160.61, 136.93, 133.72, 124.25, 114.22, 114.20, 100.42, 86.02, 55.37, 27.61. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O_2$ ($[M+H]^+$): 201.0910. Found: 201.0910.

(*E*)-6-(3-Fluorophenyl)hex-3-en-5-yn-2-one (1g) [6]



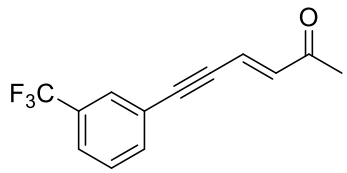
Brown oil, 53% yield, 3.8 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (td, *J* = 7.9, 5.8 Hz, 1H), 7.28-7.24 (m, 1H), 7.17 (ddd, *J* = 9.3, 2.6, 1.4 Hz, 1H), 7.08 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.58 (d, *J* = 16.1 Hz, 1H), 2.31 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.90, 162.34 (d, *J* = 247.4 Hz), 138.32, 130.15 (d, *J* = .8 Hz), 127.8 (d, *J* = 2.8 Hz), 123.94 (d, *J* = 9.5 Hz), 123.21, 118.68 (d, *J* = 22.3 Hz), 116.79 (d, *J* = 21.7 Hz), 97.85 (d, *J* = 3.3 Hz), 87.32, 27.78. ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.36 (td, *J* = 8.9, 5.8 Hz). HRMS (EI) m/z Calcd. for $C_{12}H_{10}FO$ ($[M+H]^+$): 189.0710. Found: 189.0710.

(*E*)-6-(3-Chlorophenyl)hex-3-en-5-yn-2-one (1h)



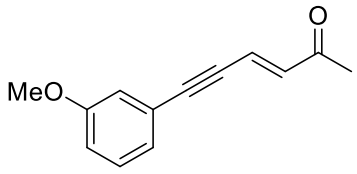
Light yellow solid, 37% yield, 0.8 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (t, *J* = 1.9 Hz, 1H), 7.32 (ddt, *J* = 7.8, 6.3, 1.4 Hz, 2H), 7.27-7.23 (m, 1H), 6.77 (d, *J* = 16.1 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 2.27 (d, *J* = 2.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.87, 138.34, 134.39, 131.73, 130.07, 129.75, 129.65, 123.84, 123.16, 119.85, 97.66, 87.59, 27.78. HRMS (EI) m/z Calcd. for $C_{12}H_{10}ClO$ ($[M+H]^+$): 205.0416. Found: 205.0416.

(*E*)-6-(3-(Trifluoromethyl)phenyl)hex-3-en-5-yn-2-one (1i)



Light yellow solid, 15% yield, 0.4 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 1.8 Hz, 1H), 7.67-7.61 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 16.1 Hz, 1H), 6.61 (d, *J* = 16.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.83, 138.54, 134.97, 131.20 (q, *J* = 32.8 Hz), 129.09, 128.72 (q, *J* = 3.9 Hz), 125.89 (q, *J* = 3.7 Hz), 123.56 (d, *J* = 273.5 Hz), 123.11, 122.95, 97.31, 87.86, 27.84. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.04. HRMS (EI) m/z Calcd. for $C_{13}H_{10}F_3O$ ($[M+H]^+$): 239.0684. Found: 239.0684.

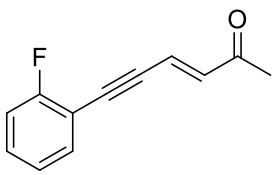
(*E*)-6-(3-Methoxylphenyl)hex-3-en-5-yn-2-one (1j) [1]



Light yellow solid, 53% yield, 1.0 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.24 (m, 1H), 7.08 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.00 (dd, *J* = 2.7, 1.4 Hz, 1H), 6.93 (ddt, *J* = 8.3, 2.5, 1.2 Hz, 1H), 6.82 (dd, *J* = 16.0, 1.4 Hz, 1H), 6.57 (dd, *J* = 16.1, 1.4 Hz, 1H), 3.81 (d, *J* = 1.6 Hz, 3H), 2.30 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.05, 159.40, 137.87, 129.60, 124.56,

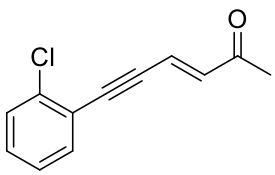
123.74, 123.10, 116.66, 116.10, 99.57, 86.48, 55.33, 27.70. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O_2$ ($[M+H]^+$): 201.0910. Found: 201.0910.

(E)-6-(2-Fluorophenyl)hex-3-en-5-yn-2-one (1k)



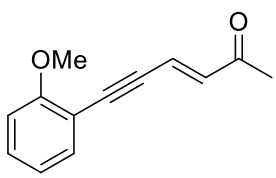
Light yellow solid, 36% yield, 0.7 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 (td, *J* = 7.4, 1.8 Hz, 1H), 7.36 (dddd, *J* = 8.4, 7.2, 5.3, 1.8 Hz, 1H), 7.15-7.07 (m, 2H), 6.84 (d, *J* = 16.1 Hz, 1H), 6.60 (d, *J* = 16.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.94, 162.77 (d, *J* = 253.4 Hz), 138.27, 133.70, 131.29 (d, *J* = 7.9 Hz), 124.17 (d, *J* = 3.8 Hz), 123.27, 115.71 (d, *J* = 20.7 Hz), 110.91 (d, *J* = 15.6 Hz), 92.57, 91.42 (d, *J* = 3.3 Hz), 27.75. ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.81 (dt, *J* = 9.4, 6.0 Hz). HRMS (EI) m/z Calcd. for $C_{12}H_{10}FO$ ($[M+H]^+$): 189.0710. Found: 189.0710.

(*E*)-6-(2-Chlorophenyl)hex-3-en-5-yn-2-one (1l) [1]



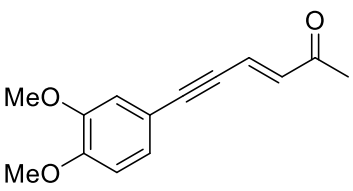
Light yellow oil, 39% yield, 0.8 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.45-7.41 (m, 1H), 7.31 (td, *J* = 7.8, 1.7 Hz, 1H), 7.27-7.23 (m, 1H), 6.87 (d, *J* = 16.1 Hz, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.91, 137.42, 135.31, 132.64, 129.41, 128.46, 125.59, 122.26, 121.15, 94.77, 90.34, 26.70. HRMS (EI) m/z Calcd. for $C_{12}H_{10}ClO$ ($[M+H]^+$): 205.0416. Found: 205.0416.

(*E*)-6-(2-Methoxylphenyl)hex-3-en-5-yn-2-one (1m)



Light yellow oil, 45% yield, 0.9 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.38-7.32 (m, 1H), 6.94 (td, *J* = 7.5, 1.1 Hz, 1H), 6.89 (td, *J* = 7.5, 1.1 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 3.90 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.21, 160.32, 137.52, 133.95, 131.13, 124.24, 120.61, 111.37, 110.76, 96.48, 90.76, 55.84, 27.57. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O_2$ ($[M+H]^+$): 201.0910. Found: 201.0910.

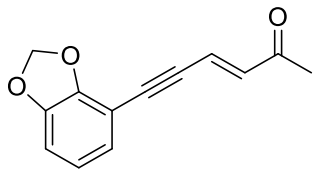
(*E*)-6-(2,3-Dimethoxylphenyl)hex-3-en-5-yn-2-one (1n)



Light yellow solid, 29% yield, 0.7 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (dt, *J* = 8.3, 1.3 Hz, 1H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.84 (d, *J* = 1.9 Hz, 1H), 6.82 (dd, *J* = 16.0, 0.9 Hz, 1H), 6.53 (dd, *J* = 16.0, 0.9 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.12, 150.54, 148.77, 137.04, 125.85, 124.07, 114.46, 114.25, 111.07, 100.45, 85.87,

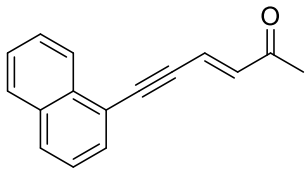
55.95 (s, 2C), 27.66. HRMS (EI) m/z Calcd. for $C_{14}H_{15}O_3$ ([M+H]$^+$): 231.1016. Found: 231.1015.

(*E*)-6-(Benzo[*d*][1,3]dioxol-5-yl)hex-3-en-5-yn-2-one (1o)



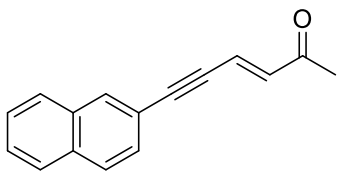
Light yellow solid, 54% yield, 1.2 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.90 (ddt, *J* = 7.8, 3.0, 1.4 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.79 (tdd, *J* = 7.8, 3.4, 1.3 Hz, 1H), 6.58 (ddd, *J* = 16.1, 3.5, 1.4 Hz, 1H), 6.03 (dd, *J* = 3.5, 1.4 Hz, 2H), 2.29 (dd, *J* = 3.3, 1.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.93, 148.95, 147.62, 138.01, 124.88, 123.36, 121.79, 109.80, 103.90, 101.56, 93.39, 90.56, 27.72. HRMS (EI) m/z Calcd. for $C_{13}H_{11}O_3$ ([M+H]$^+$): 215.0702. Found: 215.0703.

(*E*)-6-(Naphthalen-1-yl)hex-3-en-5-yn-2-one (1p) [1]



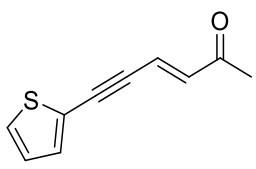
Bronw oil, 55% yield, 1.2 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.29 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.91-7.85 (m, 2H), 7.73 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.61 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.3, 7.1 Hz, 1H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.08, 137.81, 133.16, 131.44, 130.13, 128.47, 127.23, 126.73, 126.72, 125.88, 125.27, 123.84, 119.77, 97.90, 91.55, 27.75. HRMS (EI) m/z Calcd. for $C_{16}H_{12}O$ ([M+H]$^+$): 221.0960. Found: 221.0960.

(*E*)-6-(Naphthalen-2-yl)hex-3-en-5-yn-2-one (1q) [1]



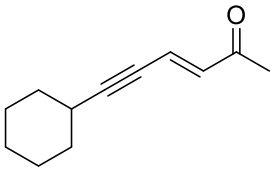
Light yellow solid, 57% yield, 1.3 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 1.6 Hz, 1H), 7.86 – 7.79 (m, 3H), 7.52 (tdd, *J* = 8.4, 6.6, 1.8 Hz, 3H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.09, 137.81, 133.32, 132.86, 132.49, 128.27, 128.17, 128.02, 127.84, 127.36, 126.83, 123.86, 119.41, 100.19, 87.08, 27.73. HRMS (EI) m/z Calcd. for $C_{16}H_{12}O$ ([M+H]$^+$): 221.0960. Found: 221.0960.

(*E*)-6-(Thiophen-2-yl)hex-3-en-5-yn-2-one (1r) [1]



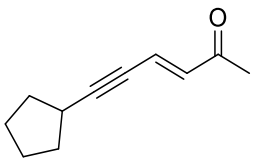
Yellow oil, 2% yield, 0.3 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (dt, *J* = 5.1, 0.9 Hz, 1H), 7.31 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.87, 137.06, 133.74, 129.38, 127.49, 123.31, 122.11, 93.04, 91.01, 27.80. HRMS (EI) m/z Calcd. for $C_{10}H_9OS$ ([M+H]$^+$): 177.0368. Found: 177.0368.

(*E*)-6-Cyclohexylhex-3-en-5-yn-2-one (1s) [7]



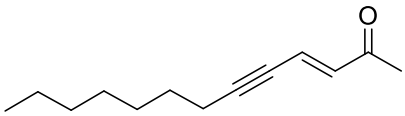
Yellow oil, 61% yield, 1.0 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.62 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.40 (dd, *J* = 16.1, 1.2 Hz, 1H), 2.55 (d, *J* = 10.0 Hz, 1H), 2.24 (d, *J* = 1.1 Hz, 3H), 1.86-1.79 (m, 2H), 1.72-1.67 (m, 2H), 1.55-1.43 (m, 3H), 1.32 (tt, *J* = 9.9, 4.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.45, 137.38, 125.11, 106.38, 78.22, 32.21, 30.09, 27.39, 25.75, 24.78. HRMS (EI) m/z Calcd. for $C_{12}H_{17}O$ ($[M+H]^+$): 177.1274. Found: 177.1274.

(*E*)-6-Cyclopentylhex-3-en-5-yn-2-one (1t) [1]



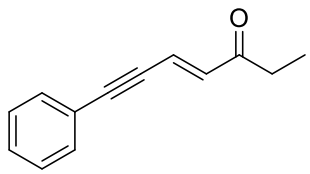
Yellow oil, 25% yield, 0.4 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.61 (dd, *J* = 16.1, 2.2 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 2.79 (pd, *J* = 7.6, 2.3 Hz, 1H), 2.24 (s, 3H), 1.96 (dqd, *J* = 10.9, 5.7, 2.3 Hz, 2H), 1.78-1.70 (m, 2H), 1.67-1.62 (m, 2H), 1.58 (ddt, *J* = 10.0, 7.4, 3.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.45, 137.27, 125.15, 106.70, 77.82, 33.61, 31.11, 27.40, 25.07. HRMS (EI) m/z Calcd. for $C_{11}H_{15}O$ ($[M+H]^+$): 163.1118. Found: 163.1118.

(*E*)-Tridec-3-en-5-yn-2-one (1u)



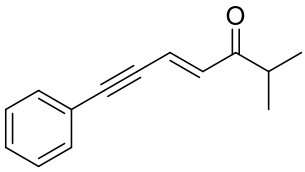
Yellow oil, 52% yield, 1.0 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.60 (dt, *J* = 16.0, 2.3 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 2.38 (td, *J* = 7.1, 2.3 Hz, 2H), 2.24 (s, 3H), 1.55 (p, *J* = 7.2 Hz, 2H), 1.39 (dd, *J* = 10.9, 5.0 Hz, 2H), 1.32-1.25 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.45, 137.47, 125.04, 102.57, 78.26, 31.69, 28.84, 28.75, 28.31, 27.40, 22.61, 19.88, 14.07. HRMS (EI) m/z Calcd. for $C_{13}H_{21}O$ ($[M+H]^+$): 193.1588. Found: 193.1589.

(*E*)-7-Phenylhept-4-en-6-yn-3-one (1v)



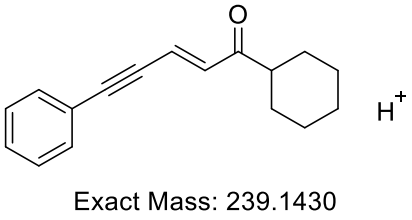
Yellow oil, 89% yield, 1.6 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 2H), 7.42-7.31 (m, 3H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 2.60 (q, *J* = 7.3 Hz, 2H), 1.14 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 199.62, 136.73, 131.99, 129.36, 128.50, 122.75, 122.24, 98.90, 86.99, 34.39, 7.97. HRMS (EI) m/z Calcd. for $C_{13}H_{12}O$ ($[M+H]^+$): 185.0961. Found: 185.0961.

(*E*)-2-Methyl-7-phenylhept-4-en-6-yn-3-one (1w)



Yellow oil, 45% yield, 0.5 g. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.33-7.23 (m, 3H), 6.85 (d, *J* = 15.8 Hz, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 2.71 (p, *J* = 6.9 Hz, 1H), 1.08 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.33, 135.31, 132.00, 129.33, 128.50, 123.00, 122.29, 98.59, 87.28, 39.60, 18.14. HRMS (EI) m/z Calcd. for $C_{14}H_{15}O$ ($[M+H]^+$): 199.1118. Found: 199.1118.

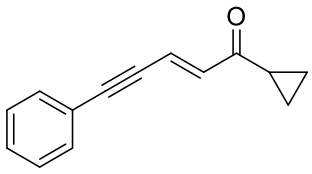
(*E*)-1-cyclohexyl-5-phenylpent-2-en-4-yn-1-one (1x)



Exact Mass: 239.1430

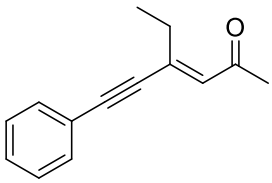
Light yellow solid, 60% yield, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 5.6 Hz, 2H), 7.35 (q, *J* = 6.9, 6.4 Hz, 3H), 6.90 (d, *J* = 15.8 Hz, 1H), 6.70 (d, *J* = 15.8 Hz, 1H), 2.52 (tt, *J* = 11.3, 3.4 Hz, 1H), 1.88 (d, *J* = 17.1 Hz, 2H), 1.81 (d, *J* = 12.8 Hz, 2H), 1.69 (d, *J* = 12.6 Hz, 1H), 1.45 – 1.17 (m, 5H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.71, 135.62, 131.99, 129.30, 128.49, 122.82, 122.32, 98.51, 87.34, 49.52, 28.40, 25.85, 25.66. HRMS (EI) m/z Calcd. for $C_{17}H_{19}O$ ($[M+H]^+$): 239.1430. Found: 239.1431.

(*E*)-1-cyclopropyl-5-phenylpent-2-en-4-yn-1-one (1z)



White solid, 52% yield, 1.0 g. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.37-7.35 (m, 2H), 6.90 (d, *J* = 15.9 Hz, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 2.10 (tt, *J* = 7.8, 4.5 Hz, 1H), 1.15 (dt, *J* = 4.5, 3.4 Hz, 2H), 0.98 (dq, *J* = 7.3, 3.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.92, 137.00, 132.01, 129.34, 128.50, 122.48, 122.30, 98.81, 87.19, 20.02, 11.64. HRMS (EI) m/z Calcd. for $C_{14}H_{13}O$ ($[M+H]^+$): 197.0962. Found: 197.0961.

(*E*)-4-ethyl-6-phenylhex-3-en-5-yn-2-one (1aa) [4]

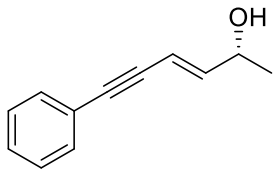


Orange oil, 76% yield, 0.3 g. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.35 (q, *J* = 3.9 Hz, 3H), 6.50 (s, 1H), 2.81 (q, *J* = 7.5 Hz, 2H), 2.24 (s, 3H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.71, 142.90, 131.96, 130.06, 129.07, 128.45, 122.43, 94.81, 90.56, 31.93, 25.83, 12.90. HRMS (EI) m/z Calcd. for $C_{14}H_{15}O$ ($[M+H]^+$): 199.1117. Found: 199.1117.

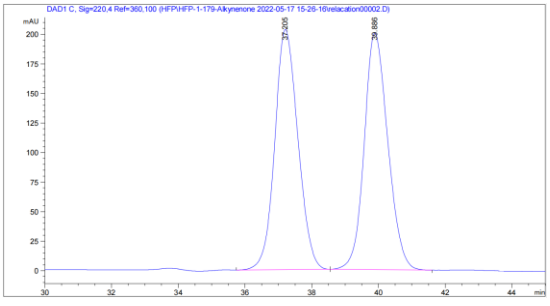
III. General procedure for iridium catalyzed hydrogenation

General procedure for the asymmetric hydrogenation at S/C = 1 000: To a 2.5 mL vial was added the catalyst precursor $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol), ligands (**L1**-**L5**, 0.011 mmol) and anhydrous *i*PrOH (1.0 mL) under argon atmosphere. The mixture was stirred for 3 h at 25 °C giving orange red solution in the argon-filled glovebox. The resulting solution (10 μL) transferred by syringe into a 3.0 mL vial charged with fresh distilled substrate (0.1 mmol) and Cs_2CO_3 (0.001 mmol, 0.33 mg) in 1.0 mL *i*PrOH. The vials were transferred to an autoclave, which was then charged with 50 atm of H_2 and stirred at room temperature for 16 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was concentrated and passed through a short column of silica gel to get the product. The yield was determined by ^1H NMR analysis. The product was analyzed by chiral HPLC for ee values.

(*E*)-6-(3-Methoxylphenyl)hex-3-en-5-yn-2-ol (2a) [8]

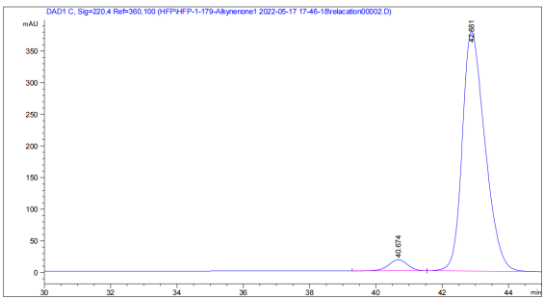


Brown oil, 99% yield, 93% ee; $[\alpha]_D^{25}$ = +13.50 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.9 mL/min; UV detection at 220 nm; t_R = 40.67 min (minor), 42.88 min (major). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.31 (dd, *J* = 5.2, 2.0 Hz, 3H), 6.27 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.93 (dd, *J* = 15.9, 1.6 Hz, 1H), 4.49-4.36 (m, 1H), 1.60 (br, 1H), 1.33 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.62, 131.52, 128.32, 128.22, 123.24, 109.24, 90.14, 87.26, 68.35, 23.08. HRMS (EI) m/z Calcd. for $C_{12}H_{11}$ ($[M+H-H_2O]^+$): 155.0855. Found: 155.0855.



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

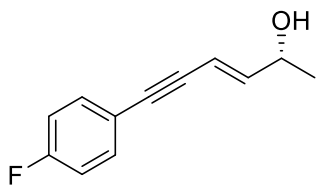
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.205	BB	0.7420	9790.67480	203.23193	49.8759
2	39.886	BB	0.7563	9839.38672	200.59166	50.1241



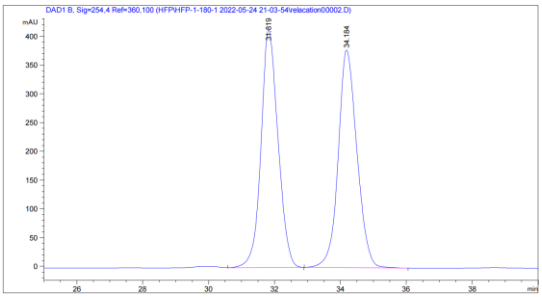
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

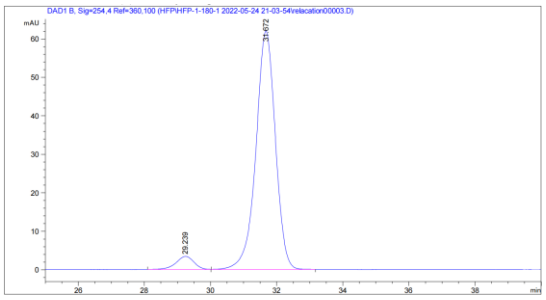
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.674	BB	0.6102	696.12860	17.49568	3.7198
2	42.881	BB	0.7274	1.80180e4	378.47845	96.2802

(*E*)-6-(4-Fluorophenyl)hex-3-en-5-yn-2-ol (2b) [9]



Brown oil, 90% yield, 91% ee; $[\alpha]_D^{25}$ = +3.00 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.9 mL/min; UV detection at 254 nm; t_R = 29.24 min (minor), 32.17 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43-7.39 (m, 2H), 7.03-6.98 (m, 2H), 6.27 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.91 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.42 (t, *J* = 6.6 Hz, 1H), 1.80 (br, 1H), 1.33 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.46 (*J* = 249.2 Hz), 146.71, 133.37 (*J* = 8.0 Hz), 119.35 (*J* = 3.7 Hz), 115.61 (*J* = 22.0 Hz), 109.04, 89.04, 86.96, 68.30, 23.08. ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.01 (dd, *J* = 9.8, 4.9 Hz). HRMS (EI) m/z Calcd. for $C_{12}H_{10}F$ ($[M+H-H_2O]^+$): 173.0761. Found: 173.0761.





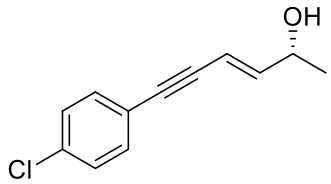
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.819	BB	0.5433	1.48398e4	412.93991	49.8630
2	34.184	BB	0.5982	1.49213e4	378.25098	50.1370

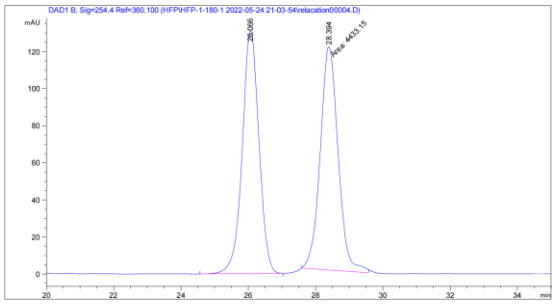
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

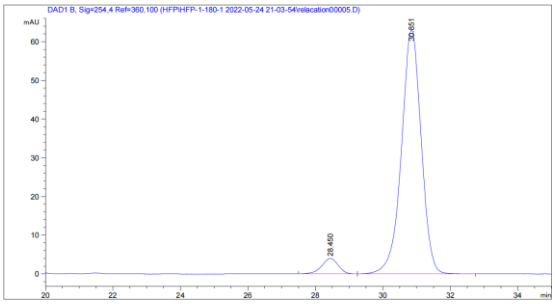
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.239	BB	0.5506	126.26639	3.37378	4.7576
2	31.672	BB	0.6240	2527.74023	61.95370	95.2424

(*E*)-6-(4-Chlorophenyl)hex-3-en-5-yn-2-ol (2c)



Light yellow solid, 95% yield, 90% ee; $[\alpha]_D^{25}$ = +6.40 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.9 mL/min; UV detection at 254 nm; t_R = 28.45 min (minor), 30.85 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.33 (m, 2H), 7.30-7.26 (m, 2H), 6.27 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.91 (dd, *J* = 15.9, 1.4 Hz, 1H), 4.41 (pd, *J* = 6.4, 1.5 Hz, 1H), 1.68 (br, 1H), 1.33 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.08, 134.22, 132.71, 128.74, 128.67, 121.75, 108.92, 88.97, 88.25, 68.27, 23.08. HRMS (EI) m/z Calcd. for $C_{12}H_{10}Cl$ ($[M+H-H_2O]^+$): 189.0466. Found: 189.0466.





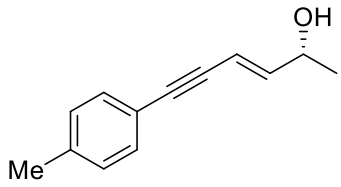
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.066	BB	0.5276	4511.02100	131.03139	50.4353
2	28.394	MM	0.6133	4433.14697	120.46500	49.5647

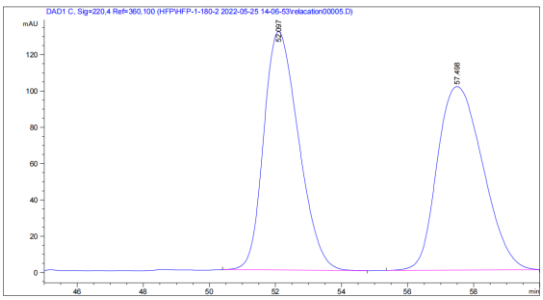
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

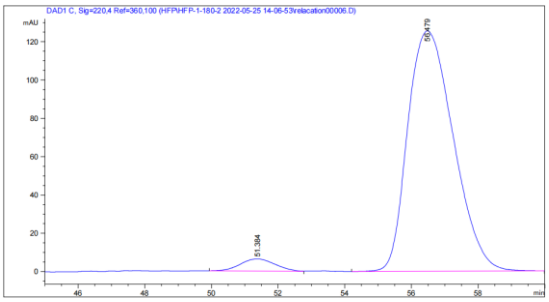
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.450	BB	0.5063	134.82475	3.98901	4.9893
2	30.851	BB	0.6277	2567.45679	62.96851	95.0107

(*E*)-6-(*p*-Tolyl)hex-3-en-5-yn-2-ol (2d)



Light yellow oil, 99% yield, 93% ee; $[\alpha]_D^{25}$ = +13.10 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 51.38 min (minor), 56.48 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 3H), 7.12 (dd, *J* = 7.9, 5.8 Hz, 3H), 6.25 (dd, *J* = 15.9, 5.9 Hz, 1H), 5.91 (dd, *J* = 15.8, 1.4 Hz, 1H), 4.41 (pd, *J* = 6.4, 1.5 Hz, 1H), 2.35 (s, 3H), 1.75 (br, 1H), 1.32 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.12, 138.27, 131.31, 128.99, 120.04, 109.30, 90.24, 86.53, 68.26, 22.96, 21.39. HRMS (EI) m/z Calcd. for $C_{13}H_{13}$ ([M+H-H_2O]$^+$): 169.1012. Found: 169.1011.





Signal 1: DAD1 C, Sig=220,4 Ref=360,100

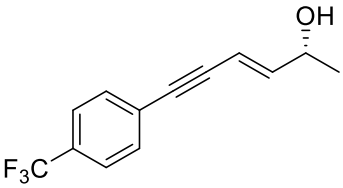
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.097	BB	1.1529	9623.35938	131.32373	49.7889
2	57.498	BBA	1.4544	9704.97266	101.05866	50.2111

Signal 1: DAD1 C, Sig=220,4 Ref=360,100

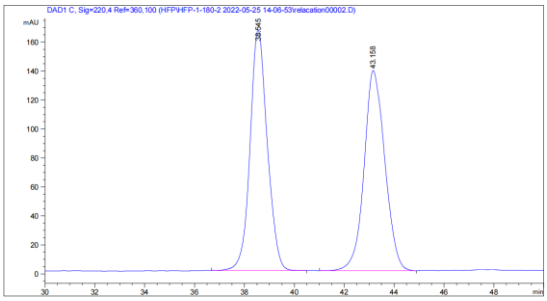
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.384	BB	0.8819	452.05243	6.32434	3.6475
2	56.479	BBA	1.4816	1.19416e4	125.55444	96.3525

(*E*)-6-(4-(Trifluoromethyl)phenyl)hex-3-en-5-yn-2-ol (2e)

Brown oil, 89% yield, 90% ee; $[\alpha]_D^{25}$ = +14.70 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 97:3; flow rate = 0.9 mL/min; UV detection at 220 nm; t_R = 34.11 min (minor), 38.19 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4

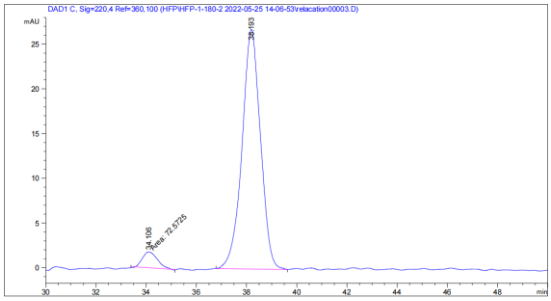


Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.33 (dd, *J* = 15.9, 5.6 Hz, 1H), 5.94 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.44 (pd, *J* = 6.4, 1.5 Hz, 1H), 1.83 (br, 1H), 1.34 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.87, 131.70, 129.84 (q, *J* = 34.2 Hz), 127.10, 125.24 (q, *J* = 3.6 Hz), 122.72, 108.62, 89.69, 88.65, 68.20, 23.05. ^{19}F NMR (377 MHz, $CDCl_3$): δ -62.82. HRMS (EI) m/z Calcd. for $C_{13}H_{10}F_3$ ($[M+H-H_2O]^+$): 223.0729. Found: 223.0728.



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

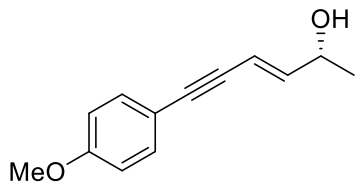
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.545	BB	0.7180	7960.38721	165.83539	49.8509
2	43.158	BB	0.8881	8008.00635	138.18913	50.1491



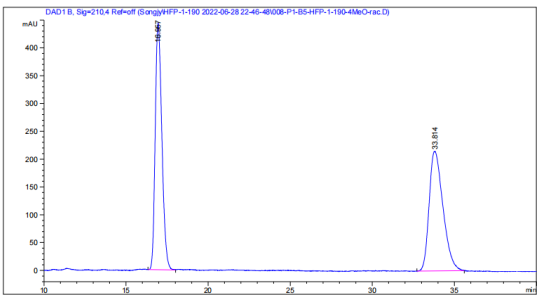
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

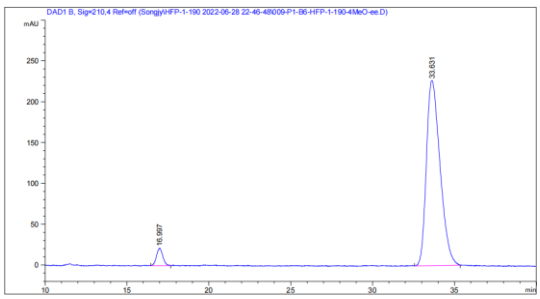
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.106	MM	0.6776	72.57250	1.78516	5.0377
2	38.193	BB	0.7495	1368.01831	26.80314	94.9623

(*E*)-6-(4-Methoxylphenyl)hex-3-en-5-yn-2-ol (2f) [9]



Light yellow oil, 99% yield, 92% ee; $[\alpha]_D^{25}$ = +53.30 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 17.00 min (minor), 33.63 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.23 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.97-5.87 (m, 1H), 4.41 (p, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 1.70 (br, 1H), 1.33 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.58, 145.82, 132.97, 115.35, 113.99, 109.49, 90.17, 85.99, 68.39, 55.29, 23.08. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O$ ($[M+H-H_2O]^+$): 185.0961. Found: 185.0958.





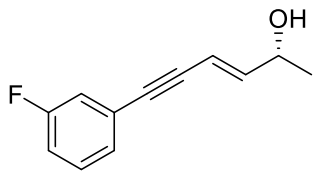
Signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.957	BV R	0.4341	1.24732e4	443.46393	49.8112
2	33.814	VV R	0.6900	1.25677e4	215.00420	50.1888

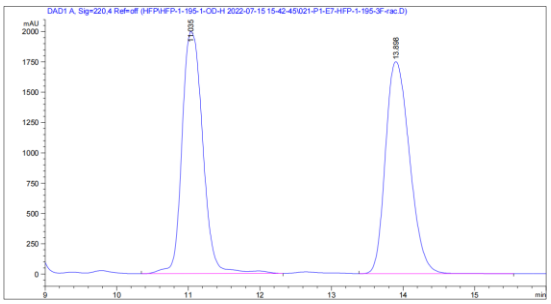
Signal 1: DAD1 B, Sig=210,4 Ref=off

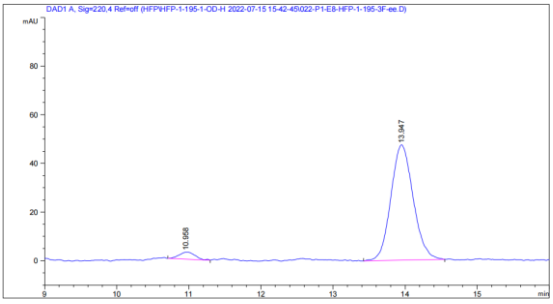
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.997	VV R	0.3250	566.77216	21.40012	4.1412
2	33.631	VB R	0.6797	1.31196e4	226.53383	95.8588

(*E*)-6-(3-Fluorophenyl)hex-3-en-5-yn-2-ol (2g)



Brown oil, 89% yield, 90% ee; $[\alpha]_D^{25}$ = +23.20 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 10.96 min (minor), 13.95 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (q, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.13-7.10 (m, 1H), 7.01 (td, *J* = 8.5, 2.7 Hz, 1H), 6.29 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.91 (dd, *J* = 16.0, 1.5 Hz, 1H), 4.55-4.35 (m, 1H), 1.89 (br, 1H), 1.33 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.36 (d, *J* = 246.3 Hz), 147.36, 129.87 (d, *J* = 8.7 Hz), 127.39 (d, *J* = 2.8 Hz), 125.10 (d, *J* = 9.4 Hz), 118.26 (d, *J* = 22.6 Hz), 115.54 (d, *J* = 21.2 Hz), 108.80, 88.81 (d, *J* = 3.6 Hz), 88.19, 68.25, 23.05. ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.03 (td, *J* = 9.2, 5.9 Hz). HRMS (EI) m/z Calcd. for $C_{14}H_{15}O$ ($[M+H-H_2O]^+$): 173.0761. Found: 173.0761.





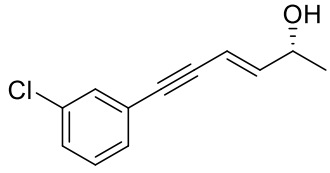
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.035	BV R	0.3164	4.03538e4	1998.46814	49.6305
2	13.898	BV R	0.3691	4.09546e4	1748.41650	50.3695

Signal 1: DAD1 A, Sig=220,4 Ref=off

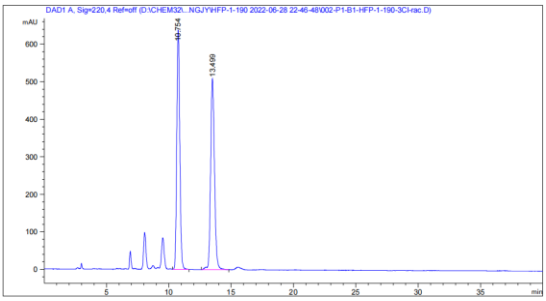
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.958	BV R	0.1984	44.01674	2.91097	4.1507
2	13.947	BB	0.3361	1016.44257	47.41914	95.8493

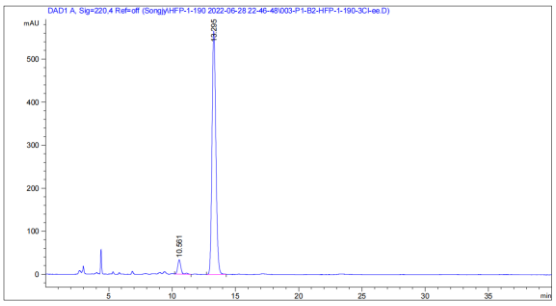
(*E*)-6-(3-Chlorophenyl)hex-3-en-5-yn-2-ol (2h)



Light yellow oil, 97% yield, 90% ee; $[\alpha]_D^{25}$ = +6.40 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.56 min (minor), 13.29 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.31-7.26 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.29 (dd, *J* =

15.9, 5.7 Hz, 1H), 5.91 (dd, *J* = 15.9, 1.6 Hz, 1H), 4.42 (p, *J* = 6.2 Hz, 1H), 1.80 (br, 1H), 1.33 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.42, 134.14, 131.34, 129.75, 129.62, 129.54, 128.45, 124.98, 108.78, 88.63, 88.49, 68.24, 23.06. HRMS (EI) m/z Calcd. for $C_{12}H_{10}Cl$ ($[M+H-H_2O]^+$): 189.0466. Found: 189.0466.





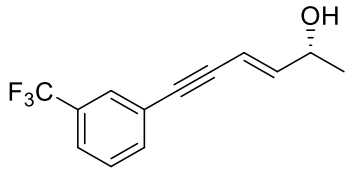
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.754	BB	0.2633	1.07716e4	637.05548	49.5469
2	13.499	VB R	0.3323	1.09687e4	508.67017	50.4531

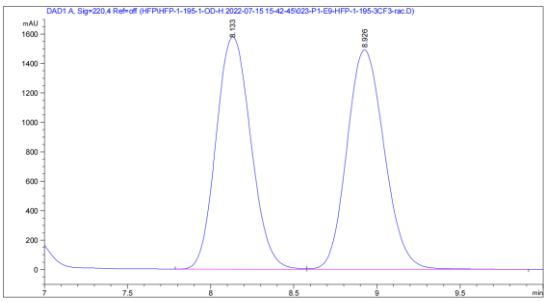
Signal 1: DAD1 A, Sig=220,4 Ref=off

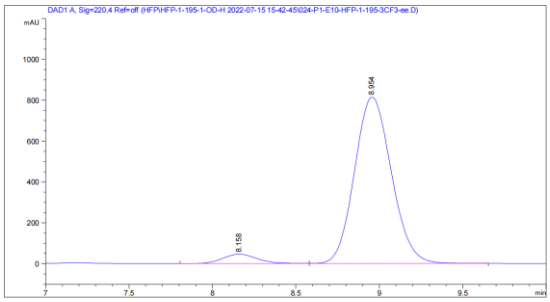
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.561	BV R	0.2532	591.30859	33.16810	4.7316
2	13.295	BB	0.3259	1.19056e4	564.82953	95.2684

(*E*)-6-(3-(Trifluoromethyl)phenyl)hex-3-en-5-yn-2-ol (2i)



Brown oil, 87% yield, 90% ee; $[\alpha]_D^{25}$ = +14.70 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 8.16 min (minor), 8.95 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 6.32 (dd, *J* = 16.0, 5.6 Hz, 1H), 5.93 (dd, *J* = 16.0, 1.5 Hz, 1H), 4.51-4.32 (m, 1H), 1.84 (br, 1H), 1.34 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.70, 134.53, 130.94 (d, *J* = 32.5 Hz), 128.84, 128.29 (q, *J* = 3.9 Hz), 124.71 (q, *J* = 3.7 Hz), 124.22, 122.80, 108.62, 88.83, 88.47, 68.22, 23.06. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.00. HRMS (EI) m/z Calcd. for $C_{13}H_{10}F_3$ ($[M+H-H_2O]^+$): 223.0729. Found: 223.0728.





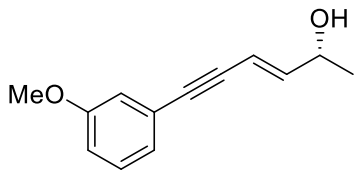
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.133	BV	0.2314	2.29455e4	1580.34155	49.6816
2	8.926	VB	0.2437	2.32396e4	1492.36121	50.3184

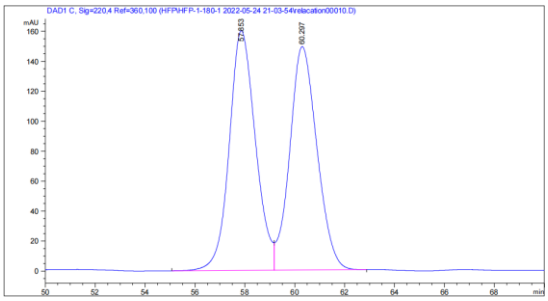
Signal 1: DAD1 A, Sig=220,4 Ref=off

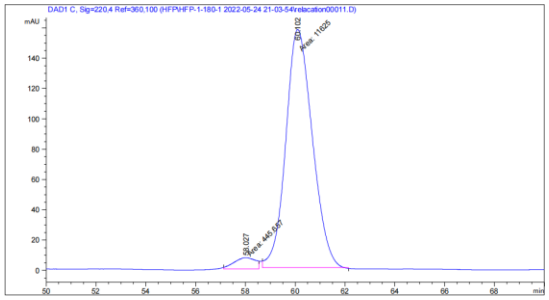
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.158	BV	0.2217	645.11975	45.42713	4.9148
2	8.954	VB	0.2389	1.24808e4	814.13019	95.0852

(*E*)-6-(3-Methoxylphenyl)hex-3-en-5-yn-2-ol (2j)



Light yellow oil, 98% yield, 93% ee; $[\alpha]_D^{25}$ = +12.30 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.56 min (minor), 13.29 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.95 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.89 (dd, *J* = 2.7, 1.4 Hz, 1H), 6.79 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.20 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.84 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.33 (pd, *J* = 6.4, 1.5 Hz, 1H), 3.73 (s, 1H), 3.72 (s, 3H), 1.71 (br, 1H), 1.25 (zd, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.31, 146.80, 129.39, 124.23, 124.10, 116.28, 114.89, 109.13, 90.05, 87.14, 68.30, 55.27, 23.06. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O$ ($[M+H-H_2O]^+$): 185.0961. Found: 185.0958.





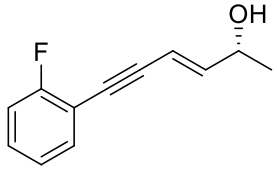
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.853	BV	1.1138	1.16540e4	159.99001	50.6981
2	60.297	VB	1.1487	1.13331e4	149.11703	49.3019

Signal 1: DAD1 C, Sig=220,4 Ref=360,100

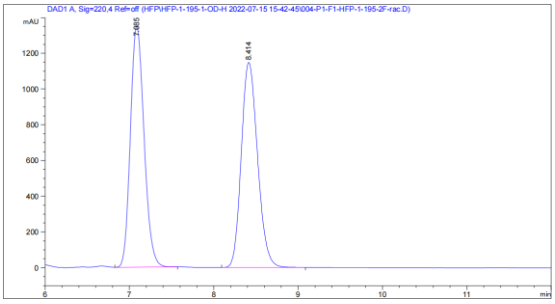
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.027	MM	1.0009	445.65683	7.42070	3.6921
2	60.102	MM	1.2340	1.16250e4	157.00688	96.3079

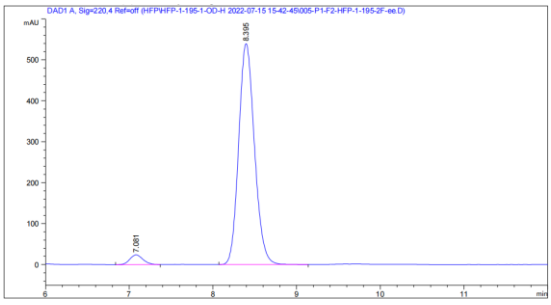
(E)-6-(2-Fluorophenyl)hex-3-en-5-yn-2-ol (2k)



Brown oil, 89% yield, 93% ee; $[\alpha]_D^{25}$ = +18.20 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 7.08 min (minor), 8.39 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (td, *J* = 7.4, 1.8 Hz, 1H), 7.28 (dddd, *J* = 8.4, 7.3, 5.3, 1.8 Hz, 1H), 7.11-7.05 (m, 2H), 6.32 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.96 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.58-4.20 (m, 1H), 1.89 (br, 1H), 1.33 (d, *J* = 6.5

Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.56 (d, *J* = 251.5 Hz), 147.36, 133.38, 129.92 (d, *J* = 8.1 Hz), 123.94 (d, *J* = 3.8 Hz), 115.49 (d, *J* = 21.0 Hz), 111.87 (d, *J* = 15.4 Hz), 108.93, 92.32 (d, *J* = 3.2 Hz), 83.32, 68.29, 23.02. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.13 (m). HRMS (EI) m/z Calcd. for $C_{14}H_{15}O$ ($[M+H-H_2O]^+$): 173.0761. Found: 173.0761.





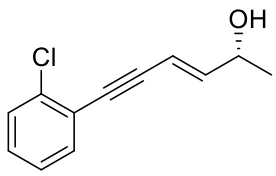
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.085	BB	0.1773	1.51677e4	1347.83350	49.6104
2	8.414	BB	0.2085	1.54059e4	1148.38062	50.3896

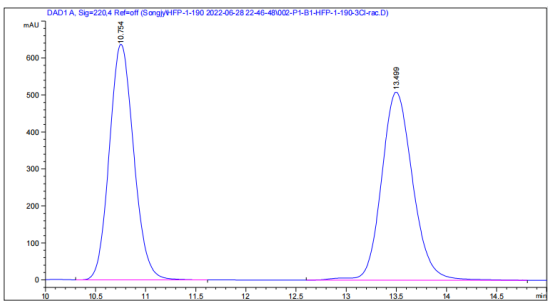
Signal 1: DAD1 A, Sig=220,4 Ref=off

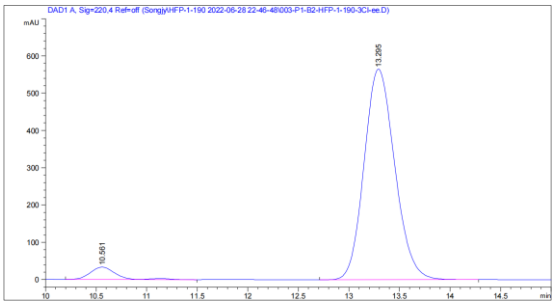
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.081	BB	0.1744	266.20370	24.19430	3.6318
2	8.395	BB	0.2027	7063.61182	539.78387	96.3682

(*E*)-6-(2-Chlorophenyl)hex-3-en-5-yn-2-ol (2l)



Light yellow oil, 93% yield, 92% ee; $[\alpha]_D^{25}$ = +13.80 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 10.56 min (minor), 13.29 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47-7.44 (m, 1H), 7.40-7.37 (m, 1H), 7.24-7.18 (m, 2H), 6.34 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.98 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.51-4.27 (m, 1H), 1.75 (s, 1H), 1.33 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.55, 135.75, 133.24, 129.26, 129.21, 126.44, 123.18, 108.92, 92.44, 86.77, 68.27, 23.01. HRMS (EI) m/z Calcd. for $C_{12}H_{10}Cl$ ($[M+H-H_2O]^+$): 189.0466. Found: 189.0466.





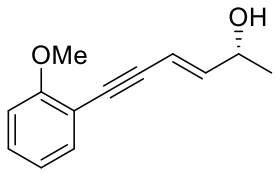
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.754	BB	0.2633	1.07716e4	637.05548	49.5469
2	13.499	VB R	0.3323	1.09687e4	508.67017	50.4531

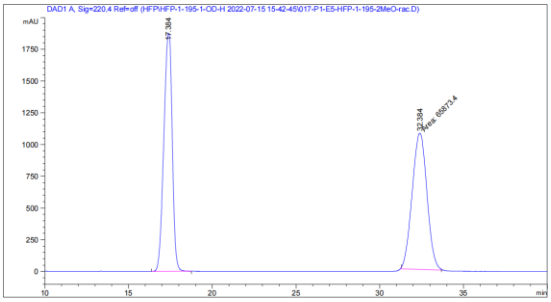
Signal 1: DAD1 A, Sig=220,4 Ref=off

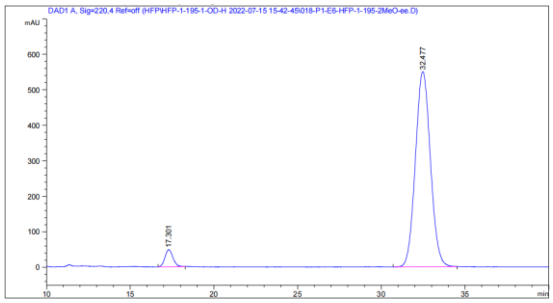
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.561	BV R	0.2532	591.30859	33.16810	4.7316
2	13.295	BB	0.3259	1.19056e4	564.82953	95.2684

(*E*)-6-(2-Methoxylphenyl)hex-3-en-5-yn-2-ol (2m)



Light yellow oil, 99% yield, 91% ee; $[\alpha]_D^{25}$ = +12.10 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 17.30 min (minor), 32.48 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.30-7.26 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.29 (dd, *J* = 15.9, 5.9 Hz, 1H), 5.98 (dd, *J* = 15.9, 1.4 Hz, 1H), 4.41 (pd, *J* = 6.4, 1.4 Hz, 1H), 3.89 (s, 3H), 1.60 (br, 1H), 1.32 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.82, 146.35, 133.52, 129.74, 120.49, 112.37, 110.60, 109.59, 91.30, 86.44, 68.44, 55.82, 23.03. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O$ ($[M+H-H_2O]^+$): 185.0961. Found: 185.0958.





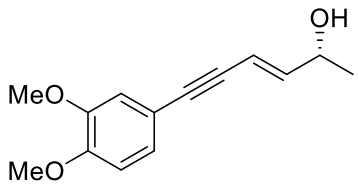
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.384	BB	0.4200	6.53026e4	1876.32715	49.7824
2	32.384	MM	1.0235	6.58734e4	1072.66650	50.2176

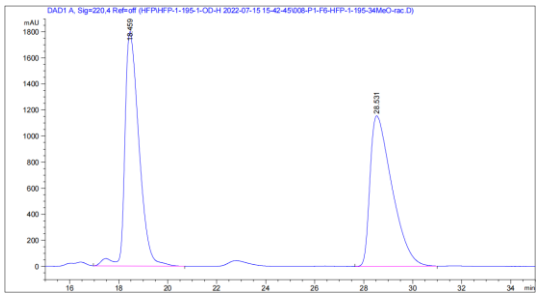
Signal 1: DAD1 A, Sig=220,4 Ref=off

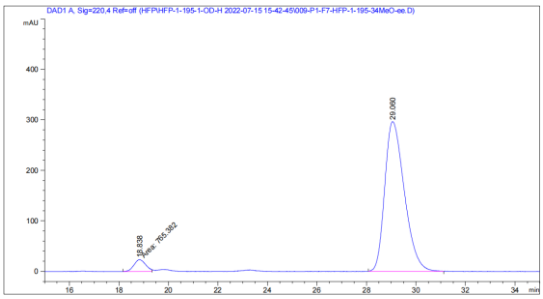
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.301	BV R	0.4464	1568.95361	47.86911	4.3821
2	32.477	VV R	0.8507	3.42348e4	549.63275	95.6179

(*E*)-6-(2,3-Dimethoxylphenyl)hex-3-en-5-yn-2-ol (2n)



Light yellow oil, 96% yield, 91% ee; $[\alpha]_D^{25}$ = +21.70 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 18.84 min (minor), 29.06 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.04 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.24 (dd, *J* = 15.9, 5.9 Hz, 1H), 5.91 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.57-4.33 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 1.59 (br, 1H), 1.33 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.48, 148.62, 146.03, 124.82, 115.41, 114.19, 111.01, 109.35, 90.28, 85.88, 68.39, 55.89, 23.11. HRMS (EI) m/z Calcd. for $C_{14}H_{15}O_2$ ($[M+H-H_2O]^+$): 215.1067. Found: 215.1067.





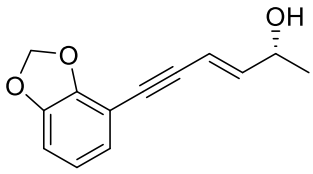
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.459	VB R	0.4641	7.21558e4	1798.49377	50.1878
2	28.531	BB	0.7614	7.16157e4	1154.96924	49.8122

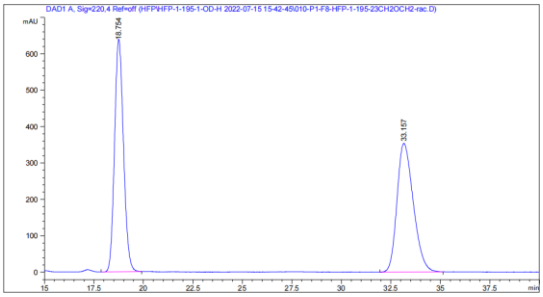
Signal 1: DAD1 A, Sig=220,4 Ref=off

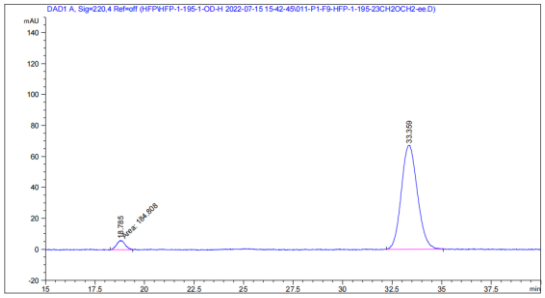
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.838	MF	0.5463	765.38196	23.35213	4.4905
2	29.060	BV R	0.7788	1.62793e4	296.40308	95.5095

(*E*)-6-(Benzo[*d*][1,3]dioxol-5-yl)hex-3-en-5-yn-2-ol (2o)



Light yellow oil, 98% yield, 91% ee; $[\alpha]_D^{25}$ = +21.00 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 17.30 min (minor), 32.48 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.87 (dd, *J* = 6.1, 3.1 Hz, 1H), 6.77 (q, *J* = 3.9, 3.1 Hz, 2H), 6.30 (dd, *J* = 15.9, 5.7 Hz, 1H), 6.01 (s, 2H), 5.95 (dd, *J* = 15.9, 1.6 Hz, 1H), 4.41 (pd, *J* = 6.5, 1.5 Hz, 1H), 1.66 (br, 1H), 1.32 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.30, 147.41, 147.21, 124.77, 121.60, 108.90, 108.74, 105.02, 101.29, 91.36, 83.85, 68.29, 23.02. HRMS (EI) m/z Calcd. for $C_{13}H_{11}O_2$ ($[M+H-H_2O]^+$): 199.0754. Found: 199.0753.





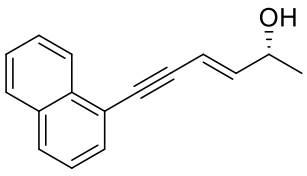
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.754	BB	0.4828	2.00676e4	638.23840	49.8402
2	33.157	BB	0.7904	2.01963e4	353.56485	50.1598

Signal 1: DAD1 A, Sig=220,4 Ref=off

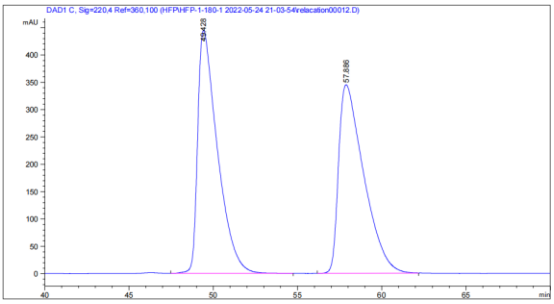
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.785	MM	0.5123	184.80820	6.01290	4.6504
2	33.359	BV R	0.7119	3789.23486	67.19691	95.3496

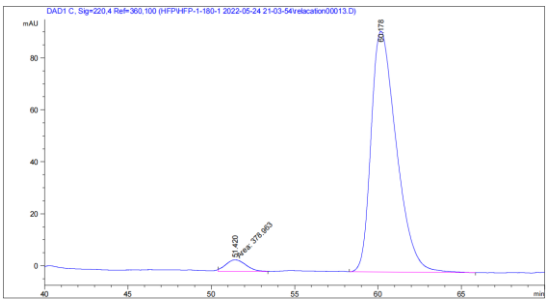
(*E*)-6-(Naphthalen-1-yl)hex-3-en-5-yn-2-ol (2p)



Light yellow oil, 96% yield, 92% ee; $[\alpha]_D^{25}$ = +11.60 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.9 mL/min; UV detection at

220 nm; t_R = 51.42 min (minor), 60.18 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36-8.28 (m, 1H), 7.83 (ddt, *J* = 12.9, 8.3, 1.0 Hz, 2H), 7.70-7.64 (m, 1H), 7.55 (dddd, *J* = 22.2, 8.1, 6.8, 1.4 Hz, 3H), 7.43 (dt, *J* = 8.3, 6.2 Hz, 1H), 6.39 (dd, *J* = 15.9, 5.8 Hz, 1H), 6.15-5.99 (m, 1H), 4.47 (pd, *J* = 6.5, 1.5 Hz, 1H), 1.72 (br, 1H), 1.38 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.75, 133.22, 133.19, 130.33, 128.73, 128.29, 126.75, 126.43, 126.18, 125.27, 120.92, 109.40, 92.22, 88.26, 68.40, 23.12. HRMS (EI) m/z Calcd. for $C_{16}H_{13}$ ([M+H-H_2O]$^+$): 205.1012. Found: 205.1012.





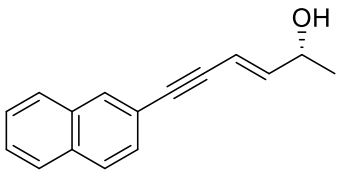
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.428	BB	1.2038	3.61690e4	444.25500	50.3582
2	57.886	BB	1.4825	3.56545e4	344.76144	49.6418

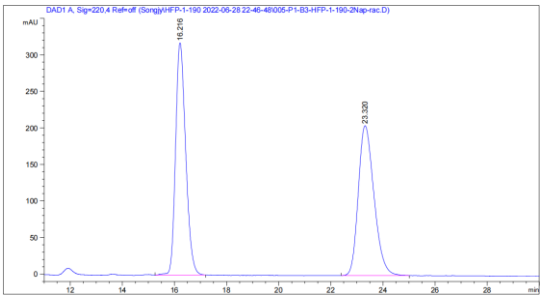
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

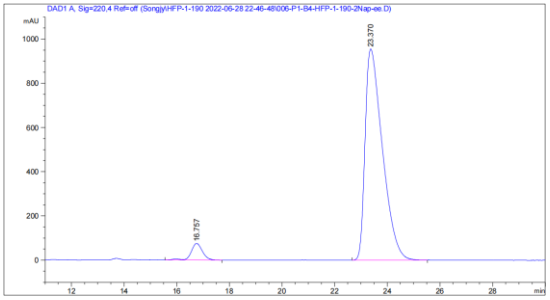
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.420	MM	1.4060	378.96301	4.49229	3.7349
2	60.178	BB	1.5551	9767.70703	92.56463	96.2651

(*E*)-6-(Naphthalen-2-yl)hex-3-en-5-yn-2-ol (2q)



Light yellow oil, 94% yield, 90% ee; $[\alpha]_D^{25}$ = +27.10 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 92:8; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 16.75 min (minor), 23.37 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.82-7.76 (m, 3H), 7.49 (ddd, *J* = 7.2, 3.4, 2.0 Hz, 3H), 6.33 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 1.5 Hz, 1H), 4.44 (pd, *J* = 6.5, 1.5 Hz, 1H), 1.73 (br, 1H), 1.35 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.80, 133.01, 132.79, 131.37, 128.34, 128.00, 127.77 (d, 2 C), 126.68, 126.56, 120.56, 109.27, 90.57, 87.69, 68.36, 23.10. HRMS (EI) m/z Calcd. for $C_{16}H_{13}$ ([M+H-H_2O]$^+$): 205.1012. Found: 205.1012.





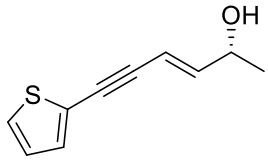
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.216	BB	0.4100	8552.31934	317.76370	49.9427
2	23.320	BB	0.6359	8571.95703	204.97488	50.0573

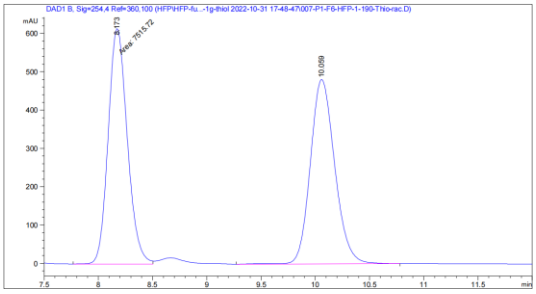
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.757	VB R	0.4192	2259.26221	75.34460	4.9310
2	23.370	BB	0.6340	4.35587e4	955.30060	95.0690

(*E*)-6-(Thiophen-2-yl)hex-3-en-5-yn-2-ol (2r)

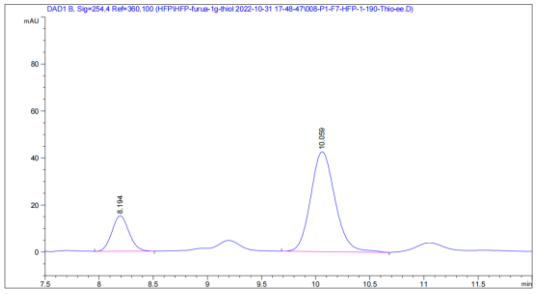


Brown oil, 78% yield, 60% ee; $[\alpha]_D^{25}$ = +2.00 (c = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:110; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R = 8.19 min (minor), 10.06 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (d, *J* = 3.7 Hz, 1H), 7.19 (d, *J* = 3.7 Hz, 1H), 6.97 (dd, *J* = 5.2, 3.7 Hz, 1H), 6.26 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.93 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.42 (pd, *J* = 6.3, 1.5 Hz, 1H), 1.57 (br, 1H), 1.33 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.68, 131.79, 127.22, 127.07, 123.30, 108.90, 91.10, 83.30, 68.30, 23.08. HRMS (EI) m/z Calcd. for $C_{10}H_9S$ ($[M+H-H_2O]^+$): 161.0420. Found: 161.0420.



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

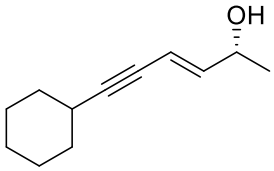
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.173	MF	0.2039	7515.72217	614.23846	49.9730
2	10.059	BB	0.2404	7523.84619	481.22772	50.0270



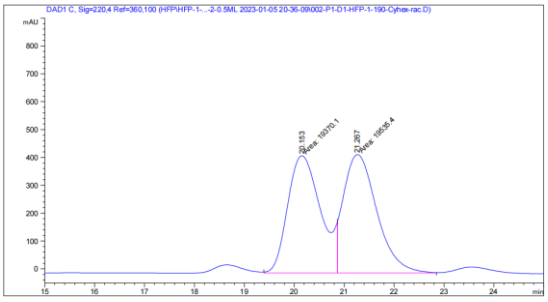
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

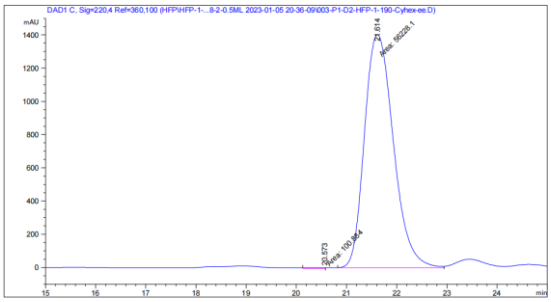
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.194	BB	0.1695	165.49106	15.14762	19.9449
2	10.059	BB	0.2401	664.25189	42.55073	80.0551

(*E*)-6-Cyclohexylhex-3-en-5-yn-2-ol (2s)



Light yellow oil, 99% yield, 99% ee; $[\alpha]_D^{25}$ = +13.90 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 98:2; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 20.57 min (minor), 21.61 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.07 (ddd, *J* = 15.8, 6.2, 0.6 Hz, 1H), 5.69 (ddd, *J* = 15.8, 2.1, 1.4 Hz, 1H), 4.37-4.26 (m, 1H), 2.61-2.37 (m, 1H), 1.83-1.78 (m, 2H), 1.73-1.67 (m, 2H), 1.55-1.49 (m, 1H), 1.43 (dtd, *J* = 15.3, 8.6, 7.7, 3.3 Hz, 2H), 1.35-1.26 (m, 4H). 1.27 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.96, 109.96, 96.21, 78.13, 68.43, 32.66, 29.69, 25.86, 24.92, 23.00. HRMS (EI) m/z Calcd. for $C_{12}H_{17}$ ($[M+H-H_2O]^+$): 161.1325. Found: 161.1326.





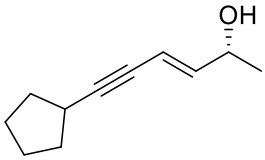
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.153	MF	0.7679	1.93701e4	420.43927	49.7875
2	21.267	FM	0.7667	1.95354e4	424.66470	50.2125

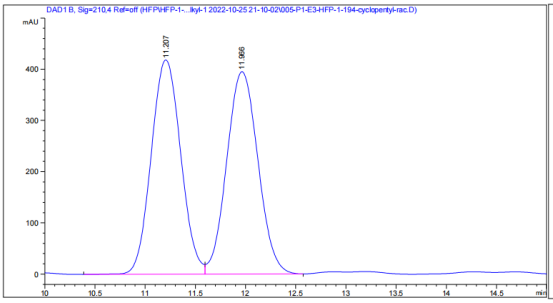
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

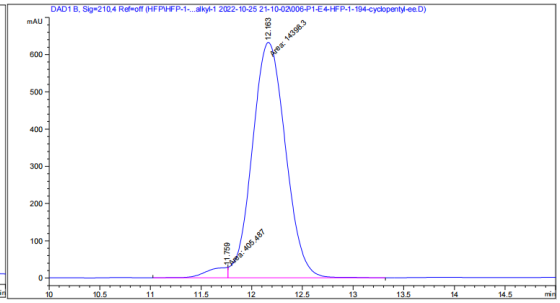
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.573	MM	0.4428	100.88435	3.79688	0.1791
2	21.614	FM	0.6677	5.62281e4	1403.56348	99.8209

(*E*)-6-Cyclopentylhex-3-en-5-yn-2-ol (2t)



Light yellow oil, 97% yield, 95% ee; $[\alpha]_D^{25}$ = +10.40 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 98:2; flow rate = 0.8 mL/min; UV detection at 220 nm; t_R = 11.21 min (minor), 11.97 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.08 (ddd, *J* = 15.8, 6.4, 0.6 Hz, 1H), 5.70 (ddd, *J* = 15.8, 2.1, 1.4 Hz, 1H), 4.34 (pd, *J* = 6.4, 1.4 Hz, 1H), 2.73 (pd, *J* = 7.6, 2.1 Hz, 1H), 2.00-1.90 (m, 2H), 1.80-1.70 (m, 2H), 1.69-1.50 (m, 6H), 1.29 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.91, 109.98, 95.57, 77.76, 68.43, 33.82, 30.76, 24.99, 23.01. HRMS (EI) m/z Calcd. for $C_{11}H_{15}$ ($[M+H-H_2O]^+$): 147.1168. Found: 147.1169.





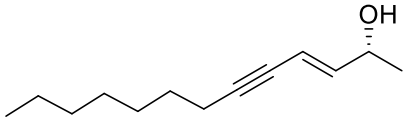
Signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.207	BV	0.3228	8564.08301	418.37183	50.0252
2	11.966	VB	0.3424	8555.45996	395.38840	49.9748

Signal 1: DAD1 B, Sig=210,4 Ref=off

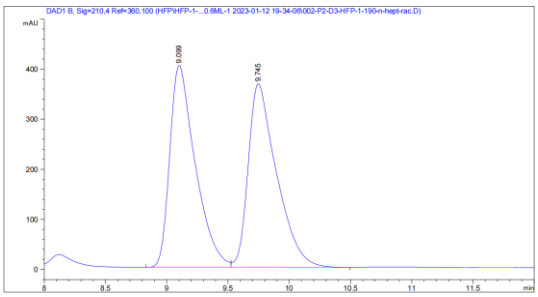
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.759	MF	0.2414	405.48688	27.98990	2.7391
2	12.163	FM	0.3797	1.43983e4	631.99536	97.2609

(*E*)-Tridec-3-en-5-yn-2-ol (2u)



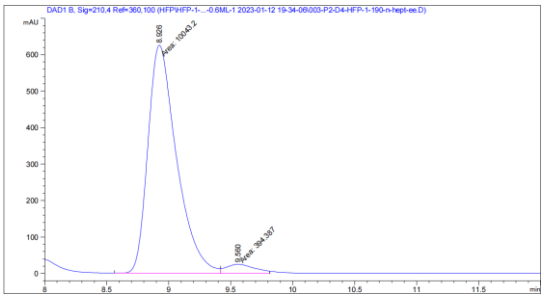
Light yellow oil, 99% yield, 93% ee; $[\alpha]_D^{25}$ = +8.10 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on AS-H column, hexane: isopropanol = 97:3; flow rate = 0.6

mL/min; UV detection at 210 nm; t_R = 8.92 min (major), 9.56 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.07 (dd, *J* = 15.8, 6.1 Hz, 1H), 5.68 (dq, *J* = 15.8, 1.9 Hz, 1H), 4.33 (pd, *J* = 6.1, 1.3 Hz, 1H), 2.29 (td, *J* = 7.2, 2.1 Hz, 2H), 1.52 (p, *J* = 7.2 Hz, 3H), 1.33-1.24 (m, 11H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.04, 109.92, 91.48, 78.23, 68.42, 31.74, 28.87, 28.82, 28.72, 23.03, 22.63, 19.39, 14.09. HRMS (EI) m/z Calcd. for $C_{13}H_{21}$ ([M+H-H_2O]$^+$): 177.1638. Found: 177.1639.



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

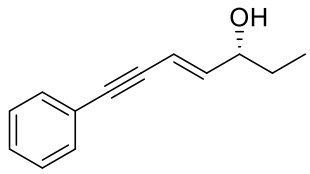
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.099	BV	0.2128	5831.32959	403.10901	49.7374
2	9.745	VB	0.2316	5892.91650	366.57050	50.2626



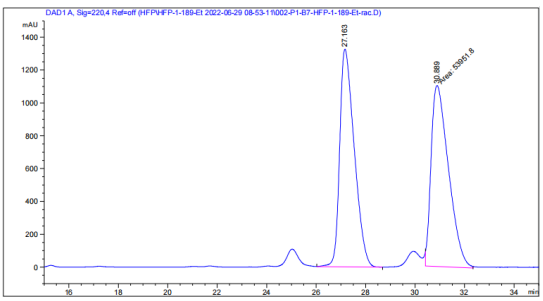
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

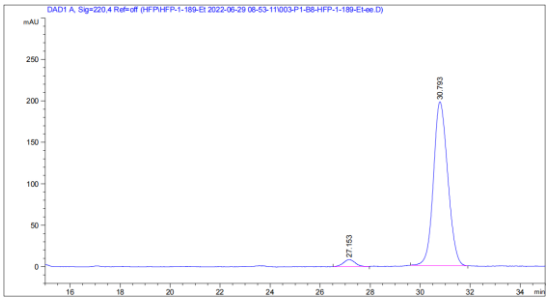
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.926	MF	0.2677	1.00432e4	625.20978	96.2215
2	9.560	MF	0.2668	394.38736	24.64115	3.7785

(*E*)-7-Phenylhept-4-en-6-yn-3-ol (2v)



Light yellow oil, 98% yield, 93% ee; $[\alpha]_D^{25}$ = +15.60 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.9 mL/min; UV detection at 220 nm; t_R = 27.15 min (minor), 30.79 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.31 (m, 3H), 6.24 (dd, *J* = 15.9, 6.1 Hz, 1H), 5.94 (dd, *J* = 15.9, 1.4 Hz, 1H), 4.15 (qd, *J* = 6.3, 1.4 Hz, 1H), 1.71 (br, 1H), 1.61 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.47, 131.52, 128.32, 128.21, 123.26, 110.07, 90.04, 87.40, 73.68, 29.91, 9.58. HRMS (EI) m/z Calcd. for $C_{13}H_{13}O$ ([M+H-H_2O]$^+$): 169.1012. Found: 169.1013.





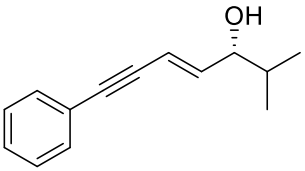
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.163	VB	0.5847	5.41548e4	1325.30591	50.0939
2	30.889	MM	0.8160	5.39518e4	1101.90552	49.9061

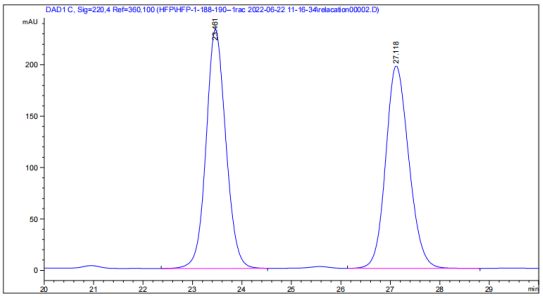
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.153	BV R	0.3895	278.92084	8.52983	3.4318
2	30.793	BB	0.6014	7848.70605	197.59824	96.5682

(*E*)-2-Methyl-7-phenylhept-4-en-6-yn-3-ol (2w)

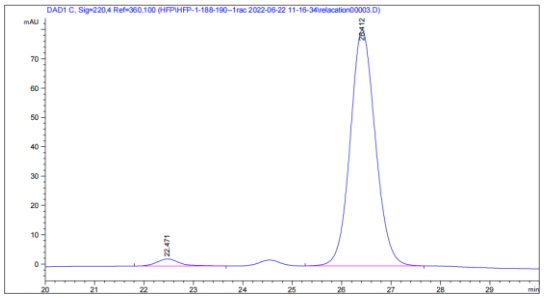


Light yellow oil, 98% yield, 93% ee; $[\alpha]_D^{25}$ = +5.80 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.9 mL/min; UV detection at 220 nm; t_R = 22.47 min (minor), 26.41 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46-7.41 (m, 2H), 7.30 (dd, *J* = 5.1, 2.0 Hz, 3H), 6.24 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.93 (dd, *J* = 15.9, 1.4 Hz, 1H), 3.98 (td, *J* = 6.3, 1.4 Hz, 1H), 1.86-1.73 (m, 1H), 1.60 (s, 1H), 0.95 (dd, *J* = 10.7, 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.19, 131.52, 128.32, 128.20, 123.27, 110.81, 89.93, 87.49, 77.38, 33.88, 18.20, 17.78. HRMS (EI) m/z Calcd. for $C_{14}H_{15}$ ($[M+H-H_2O]^+$): 183.1168. Found: 183.1169.



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

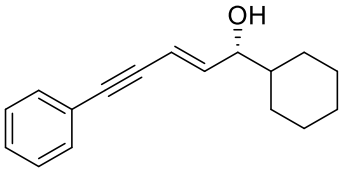
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.461	BB	0.4251	6433.05566	232.27856	50.0693
2	27.118	BB	0.5018	6415.26074	197.05025	49.9307



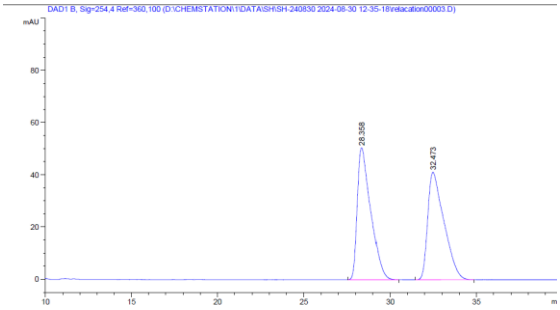
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

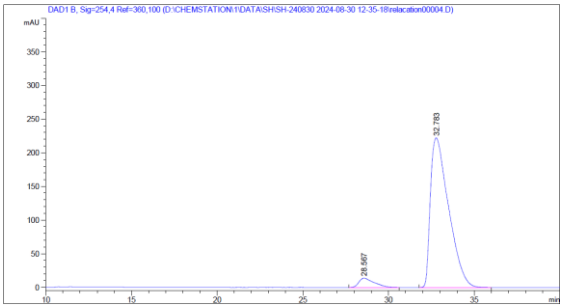
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.471	BB	0.4504	77.36378	2.42352	2.6569
2	26.412	BB	0.5451	2834.46240	80.44243	97.3431

(*R*,*E*)-1-cyclohexyl-5-phenylpent-2-en-4-yn-1-ol (2x)



95% yield, 90% ee. $[\alpha]_D^{26}$ = -16.10 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiral OJ-3 column, 254 nm, 25 °C, ^{n}Hexane: ^{i}PrOH = 95: 5; flow 1.0 mL/min; t_R (major) = 32.8 min; t_R (minor) = 28.6 min. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.18 – 7.00 (m, 3H), 6.29 (dd, *J* = 15.9, 6.1 Hz, 1H), 6.01 (dd, *J* = 15.9, 1.5 Hz, 1H), 3.73 – 3.59 (m, 1H), 1.87 – 1.59 (m, 5H), 1.34 – 0.93 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.33, 131.55, 128.40, 123.92, 110.15, 90.14, 88.34, 43.68, 28.74, 28.07, 26.49, 26.19, 26.15.





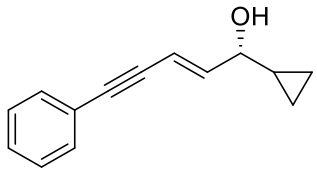
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.567	BB	0.8482	851.78851	13.83654	4.9395
2	32.783	BB	1.0941	1.63928e4	222.35150	95.0605

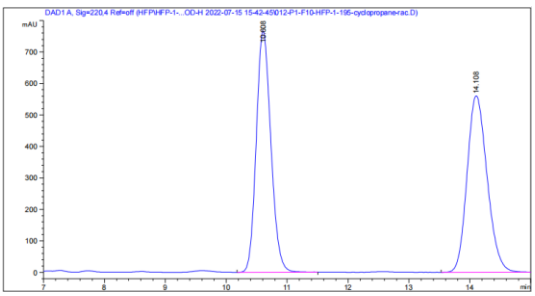
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

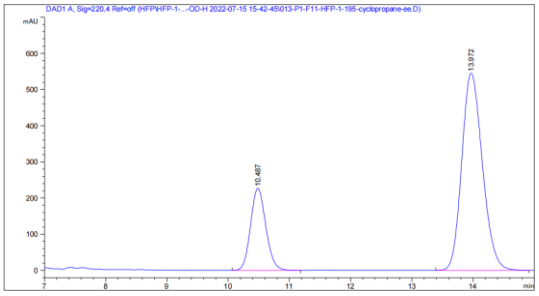
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.567	BB	0.8482	851.78851	13.83654	4.9395
2	32.783	BB	1.0941	1.63928e4	222.35150	95.0605

(*E*)-1-cyclopropyl-5-phenylpent-2-en-4-yn-1-ol (2y)



Light yellow oil, 97% yield, 53% ee; $[\alpha]_D^{25}$ = +9.80 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 10.79 min (minor), 13.97 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46-7.41 (m, 2H), 7.31 (qd, *J* = 4.1, 1.3 Hz, 3H), 6.32 (dd, *J* = 15.9, 5.6 Hz, 1H), 5.98 (dd, *J* = 15.9, 1.5 Hz, 1H), 3.58 (ddd, *J* = 8.2, 5.6, 1.5 Hz, 1H), 1.61 (br, 1H), 1.03 (qt, *J* = 8.2, 4.9 Hz, 1H), 0.64-0.54 (m, 2H), 0.43-0.38 (m, 1H), 0.34-0.29 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.90, 129.33, 126.12, 126.00, 121.09, 107.63, 87.91, 85.25, 74.18, 15.18, 1.02. HRMS (EI) m/z Calcd. for $C_{14}H_{13}$ ($[M+H-H_2O]^+$): 181.1012. Found: 181.1011.





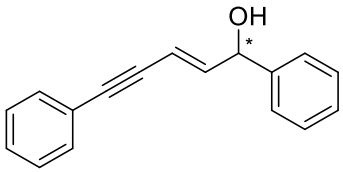
Signal 1: DAD1 A, Sig=220,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.608	BV R	0.2603	1.27569e4	765.91907	49.8791
2	14.108	BV R	0.3508	1.28188e4	560.59119	50.1209

Signal 1: DAD1 A, Sig=220,4 Ref=off

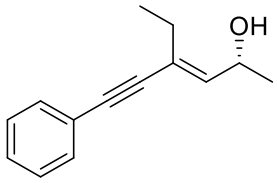
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.487	BV R	0.2697	3917.98242	226.57425	23.4870
2	13.972	BV R	0.3650	1.27635e4	545.41449	76.5130

(*E*)-1,5-diphenyl-1λ^3-pent-2-en-4-yn-1-ol (2z)[10]

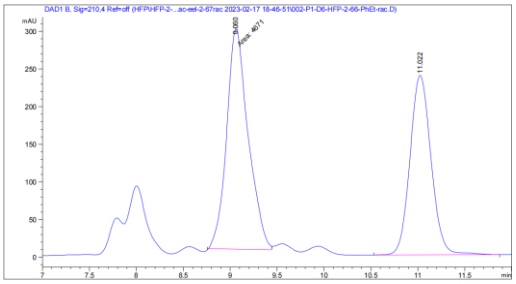


55% yield, 63% ee，$[\alpha]_D^{26}$ = 17.50 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiral IF column, 254 nm, 25 °C, ^{n}Hexane: ^{i}PrOH = 95: 5; flow 1.0 mL/min; t_R (major) = 14.1 min; t_R (minor) = 16.4 min. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.25 – 7.13 (m, 4H), 7.07 (q, *J* = 5.3 Hz, 3H), 6.38 (dd, *J* = 15.8, 5.7 Hz, 1H), 6.12 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.90 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 94.40, 91.63, 80.84, 77.73, 76.90, 75.71, 73.05, 58.95, 40.07, 37.31, 23.32.

(*E*)-4-ethyl-6-phenylhex-3-en-5-yn-2-ol (2aa)

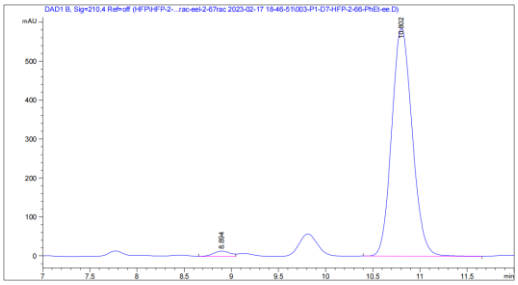


Light yellow oil, 90% yield, 96% ee; $[\alpha]_D^{25}$ = +40.00 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 8.89 min (minor), 10.80 min (major). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48-7.41 (m, 2H), 7.30 (qd, *J* z= 4.8, 1.7 Hz, 3H), 5.91 (d, *J* = 8.9 Hz, 1H), 4.68 (dq, *J* = 8.9, 6.3 Hz, 1H), 2.29 (q, *J* = 7.6 Hz, 2H), 1.57 (br, 1H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.18 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.80, 131.56, 128.29, 128.09, 126.17, 123.36, 90.35, 88.54, 64.32, 24.52, 23.44, 13.54. HRMS (EI) m/z Calcd. for $C_{14}H_{15}$ ($[M+H-H_2O]^+$): 183.1168. Found: 183.1168.



Signal 1: DAD1 B, Sig=210,4 Ref=off

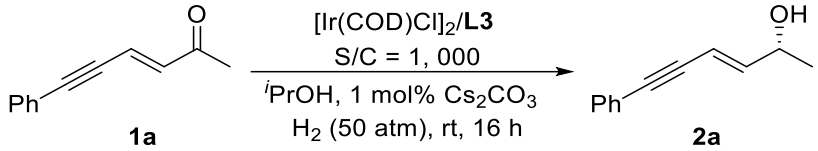
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.060	MM	0.2655	4671.00391	293.24487	55.6950
2	11.022	BB	0.2420	3715.75684	238.25311	44.3050



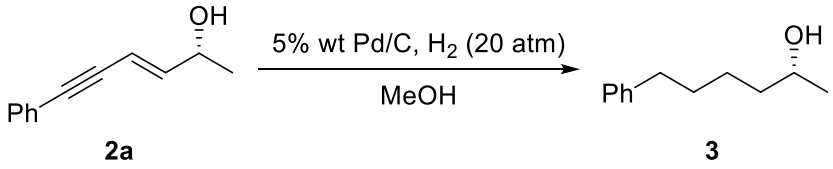
Signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.894	BV	0.1831	164.63252	13.42265	1.8242
2	10.802	BB	0.2367	8860.26074	584.98914	98.1758

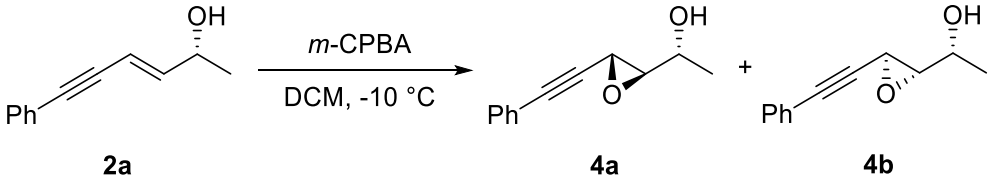
IV. Gram-scale reaction and transformation of products



Asymmetric hydrogenation of (*E*)-6-phenylhex-3-en-5-yn-2-one at S/C = 1000: To a 2.5 mL vial was added the catalyst precursor $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol), ligands (**L3**, 0.011 mmol) and anhydrous *i*PrOH (1.0 mL) under argon atmosphere. The mixture was stirred for 3 h at 25 °C giving orange red solution in the argon-filled glovebox. An aliquot of the catalyst solution (580 μL, 0.0058mmol) was transferred into a 50 mL hydrogenation vessel, then Cs_2CO_3 (1.9 mg, 0.06 mmol), ketone (5.8 mmol, 1.0 g) and anhydrous *i*PrOH (10 mL) was added. The vessel was placed in an autoclave which was then charged with 50 atm of H_2 and stirred at 25-30 °C for 16 h. The work-up was identical to that described for the asymmetric hydrogenation at S/C = 1 000. (*R*)-(*E*)-6-phenylhex-3-en-5-yn-2-ol (**2a**): 95% yield, 90% ee.



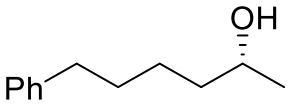
Hydrogenation of (*R*)-(*E*)-6-phenylhex-3-en-5-yn-2-ol (2a): In a 2.5 mL vial was added the (*R*)-(*E*)-6-phenylhex-3-en-5-yn-2-ol (**2a**) (17.0 mg, 0.1 mmol) and 5% wt Pd/C (1 mg) and 1mL MeOH, Then the vial was placed in an autoclave which was then charged with 20 atm of H_2 and stirred at 25-30 °C for 12 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was concentrated and passed through a short column of silica gel to get the product in almost quantitative yield (16.9 mg, 99% yield).[11] The yield was determined by ^1H NMR analysis. The product was analyzed by chiral HPLC for determination of ee values (85% ee).



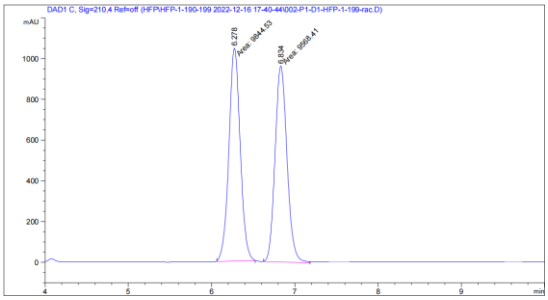
Oxidation of (*R*)-(*E*)-6-phenylhex-3-en-5-yn-2-ol (2a): To a solution of **2a** (0.10 mmol, 1.00 eq.) in DCM (2 mL) at 0 °C was added mchloroperbenzoic acid (0.20 mmol, 2.00 eq.). After 0.5 h, the resulting solution was stirred at room temperature for 24 h until complete consumption of starting

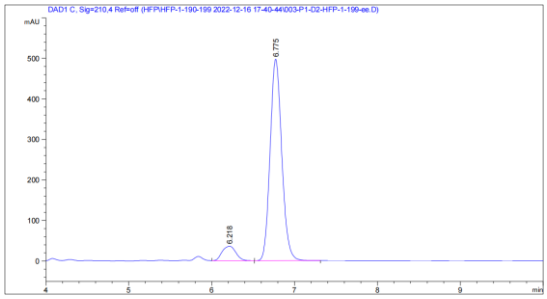
material (verified by TLC). The mixture was washed with 10% solution of Na_2CO_3 (2 mL) and then extracted with DCM (2 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica to afford product **4** as mixtures of two diastereomers (**4a**, 57% yield, 90% ee; **4b**, 38% yield, 90% ee).[6,7] Mixture of two diastereoisomers that could not be separated by flash cromatography.

(*R*)-6-phenylhexan-2-ol (3) [11]



Colorless oil, 16.9 mg, 99% yield, 85% ee; $[\alpha]_D^{25}$ = -5.50 (c = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 90:10; flow rate = 0.9 mL/min; UV detection at 210 nm; t_R = 6.22 min (minor), 6.77 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.29-7.26 (m, 2H), 7.20-7.15 (m, 3H), 3.82-3.74 (m, 1H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.71-1.58 (m, 2H), 1.52-1.42 (m, 3H), 1.35 (m, 2H), 1.18 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.59, 128.39, 128.28, 125.66, 68.09, 39.18, 35.92, 31.48, 25.44, 23.53.





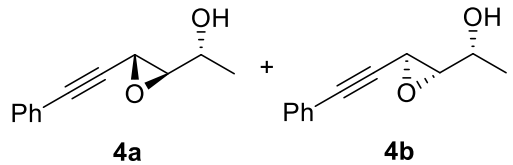
Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.278	MM	0.1569	9844.52539	1045.52209	50.7112
2	6.834	MM	0.1656	9568.40625	962.74890	49.2888

Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.218	BB	0.1863	409.39331	35.56622	7.7782
2	6.775	BB	0.1519	4853.94238	497.38000	92.2218

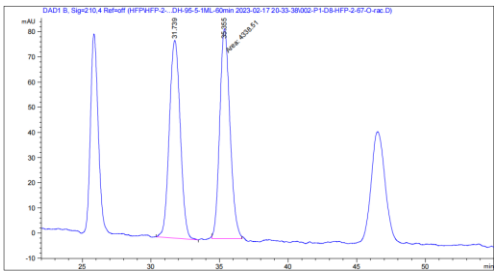
1-(3-(phenylethynyl)oxiran-2-yl)ethan-1-ol (4) [12, 13]



4a **4b**

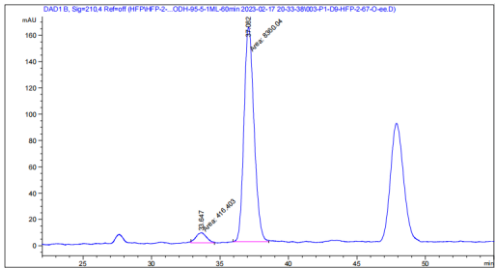
Light yellow oil (17.0 mg, 95% total yield), 57% yield, 90% ee for the major diastereoisomer (**4a**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.32 (m, 3H), 3.81 (m, 1H), 3.61 (d, *J* = 2.2 Hz, 1H), 3.26 (dd, *J* = 2.2 Hz, 1H), 1.88 (s, 1H), 1.36 (d, *J* = 6.5 Hz, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.91, 128.89, 128.35, 121.85, 84.90, 84.22, 66.42, 64.03, 44.03, 20.04. The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection

at 210 nm; t_R = 33.65 min (minor), 37.08 min (major).



Signal 1: DAD1 B, Sig=210,4 Ref=off

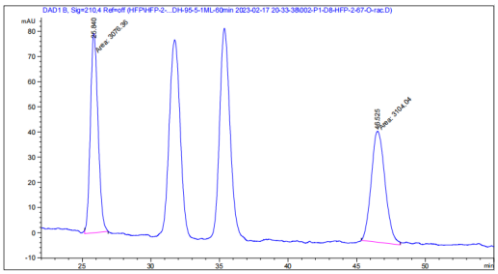
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.739	BB	0.8203	4368.71826	78.62385	50.1735
2	35.355	MM	0.8670	4338.51221	83.40285	49.8265



Signal 1: DAD1 B, Sig=210,4 Ref=off

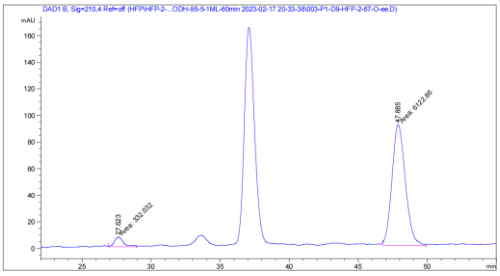
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.647	MM	0.9111	416.40338	7.61730	4.7446
2	37.082	MM	0.8552	8360.03613	162.93330	95.2554

38% yield and 90% ee for the minor diastereoisomer (**4b**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.32 (m, 3H), 4.06 (m, 1H), 3.68 (d, *J* = 2.5 Hz, 1H), 3.30 (t, *J* = 2.5 Hz, 1H), 1.94 (s, 1H), 1.33 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.89, 128.87, 128.41, 121.89, 85.17, 84.20, 64.17, 63.52, 42.30, 18.56. The enantiomeric excess was determined by HPLC on OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 27.62 min (minor), 47.89 min (major).



Signal 1: DAD1 B, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.840	MM	0.6469	3076.36108	79.26109	49.7761
2	46.525	MM	1.1725	3104.03516	44.12152	50.2239

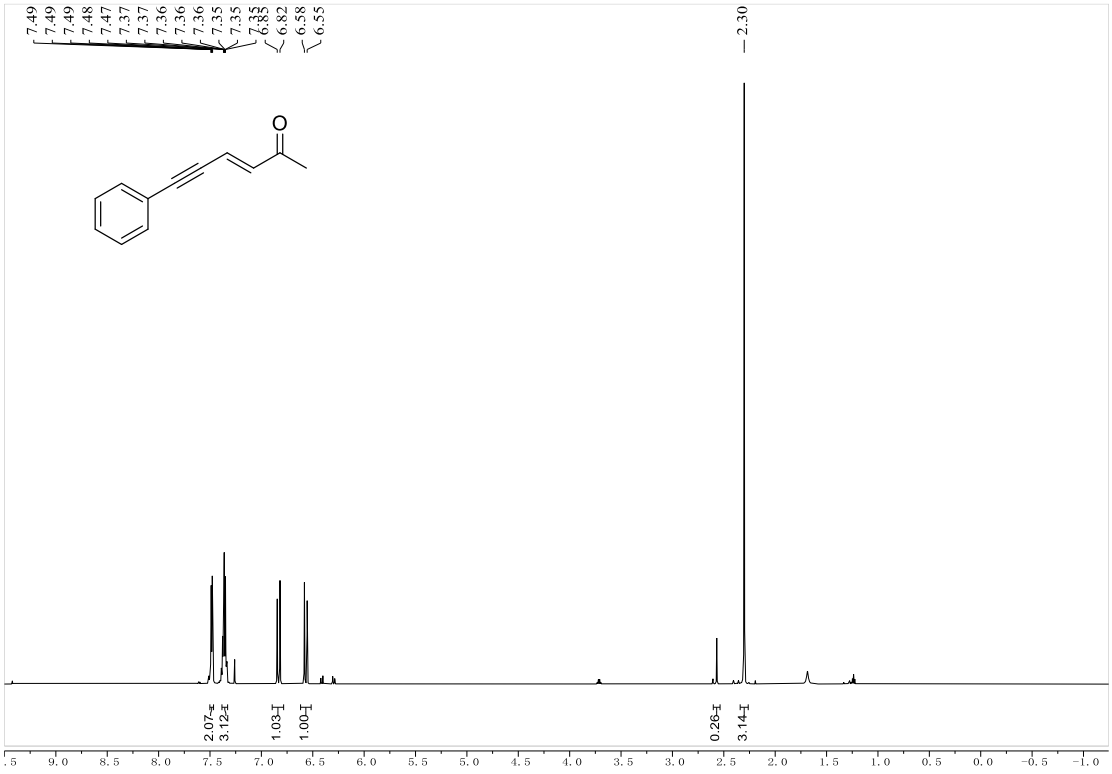


Signal 1: DAD1 B, Sig=210,4 Ref=off

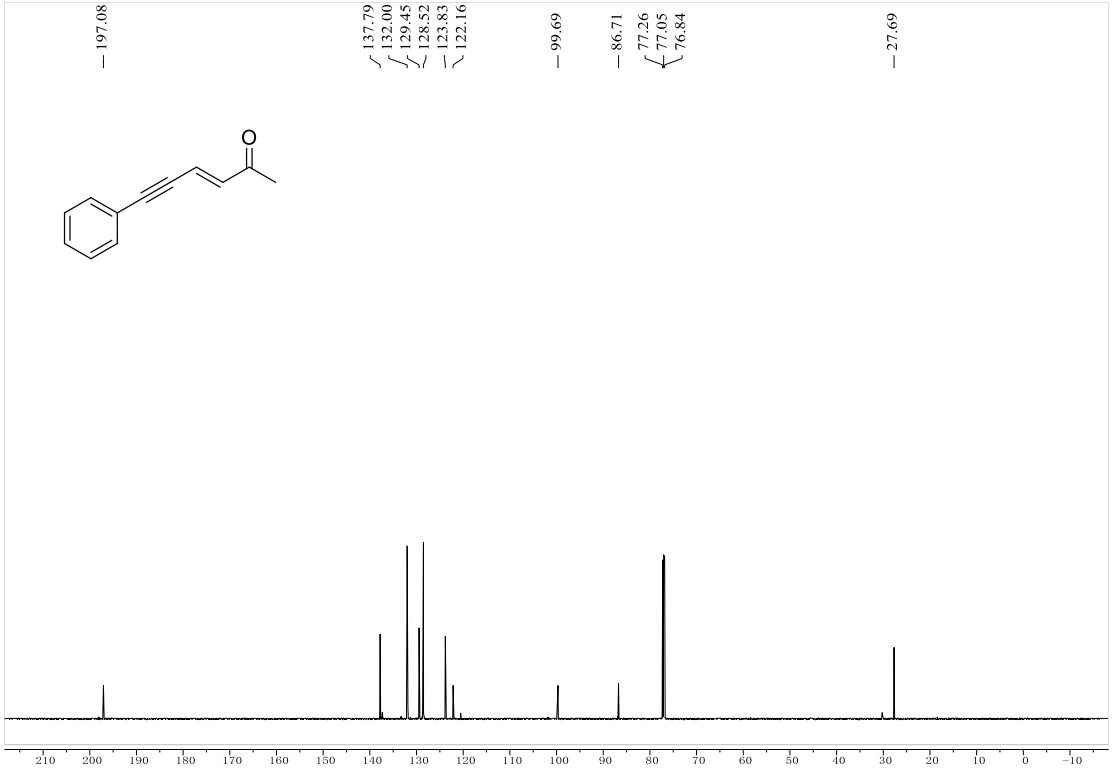
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.623	MM	0.7632	332.03229	7.25124	5.1439
2	47.885	MM	1.1230	6122.85742	90.86827	94.8561

V. NMR spectra of all the compounds

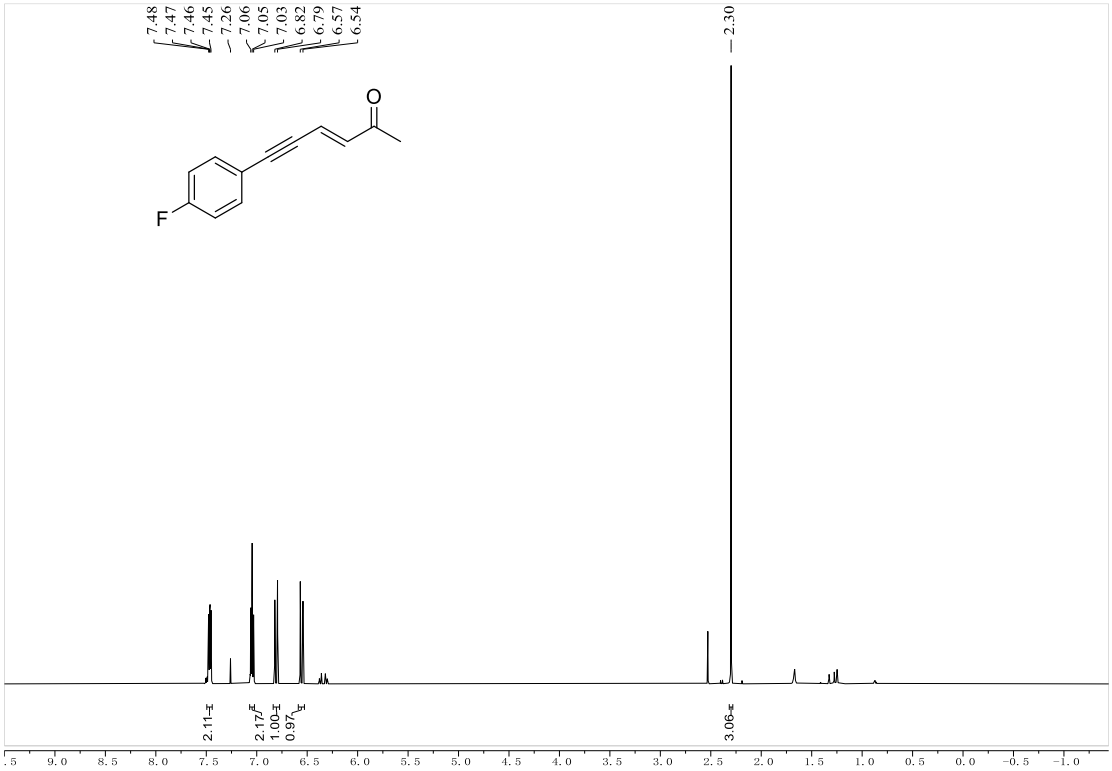
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1a**



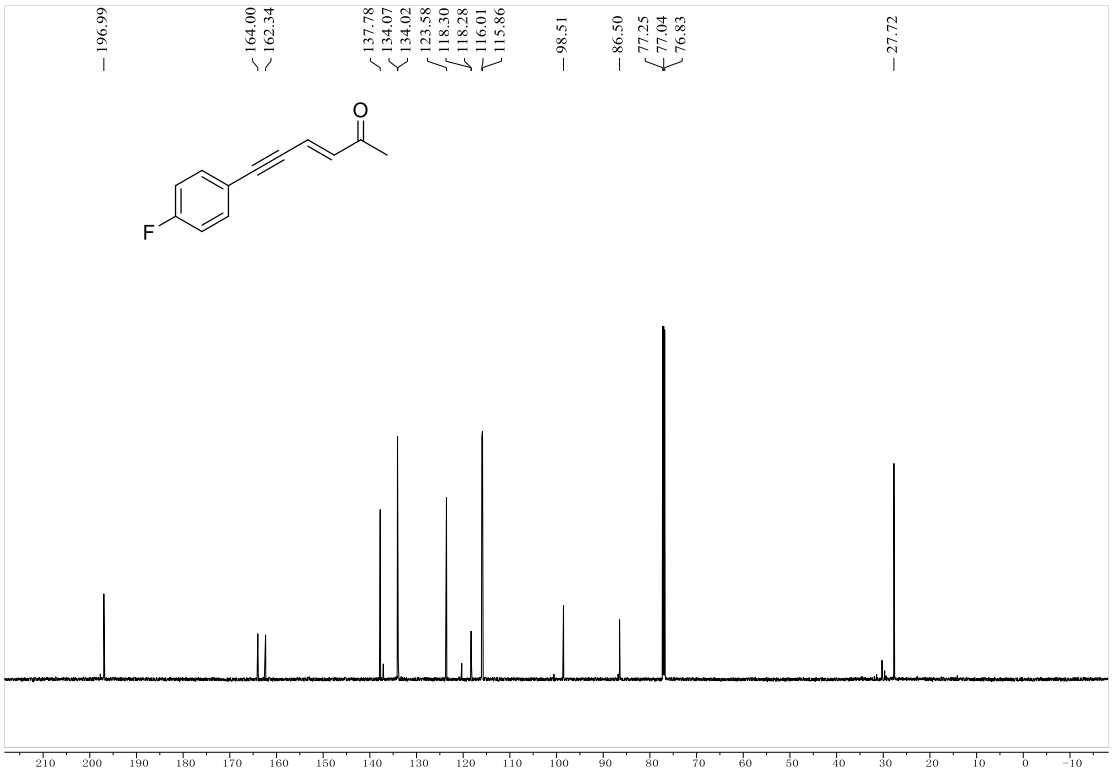
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1a**



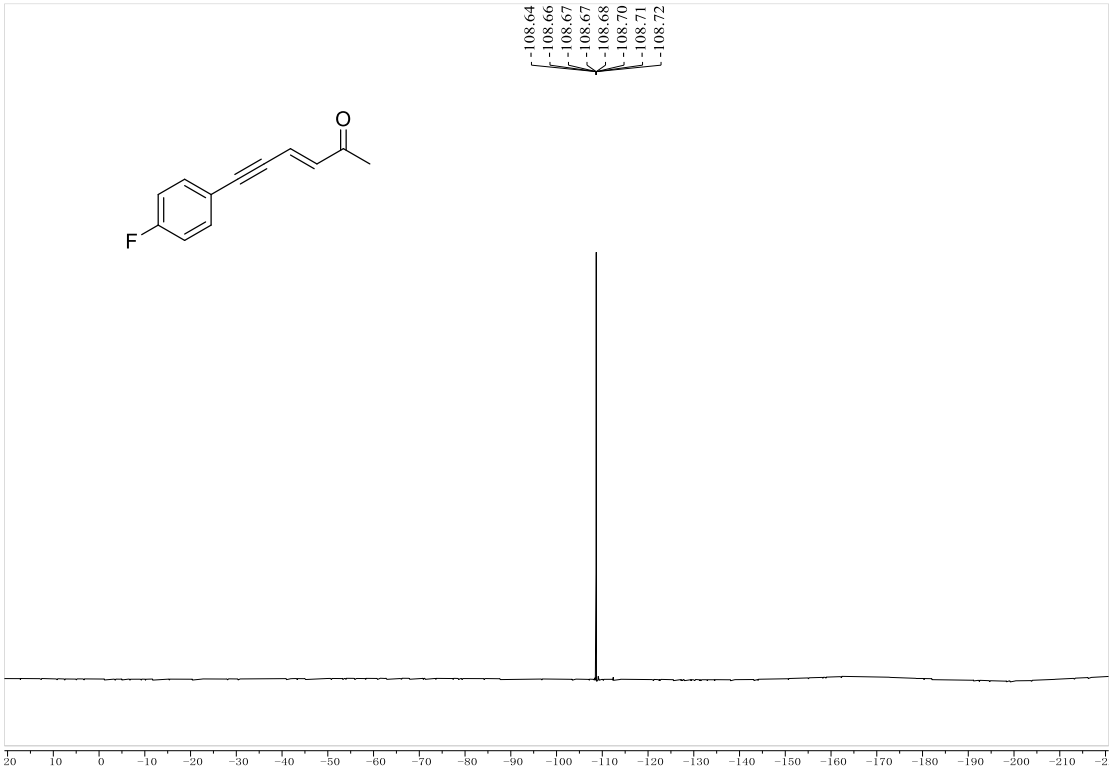
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1b**



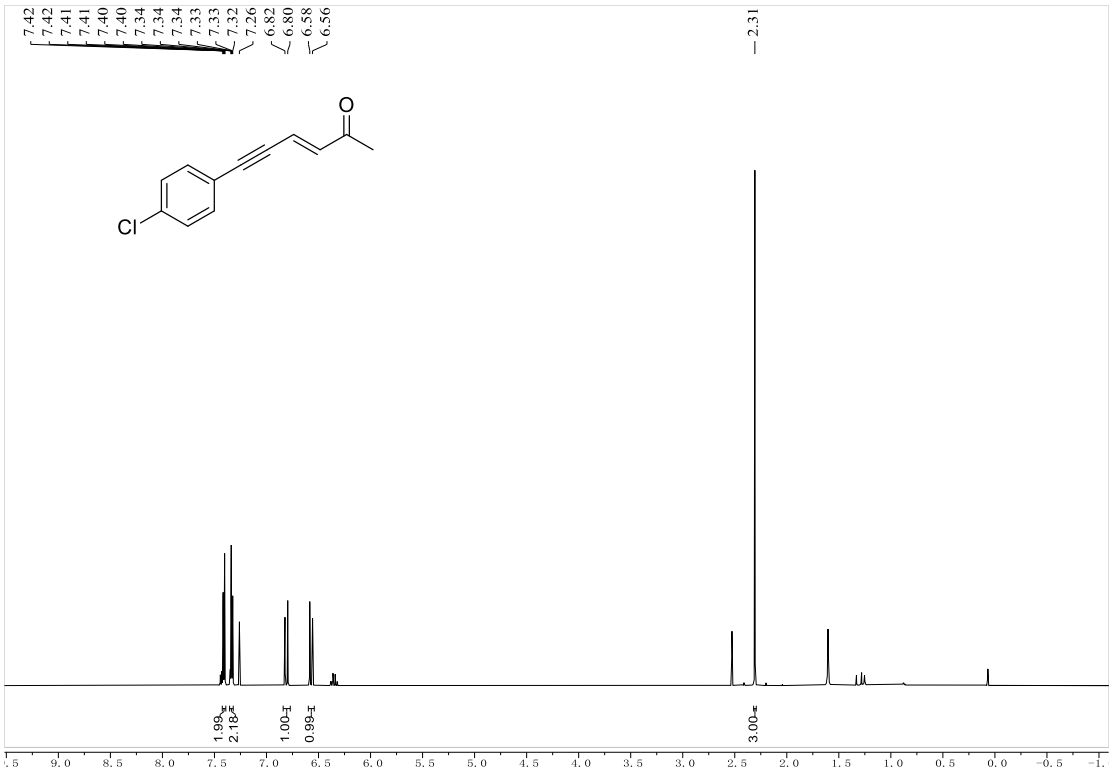
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1b**



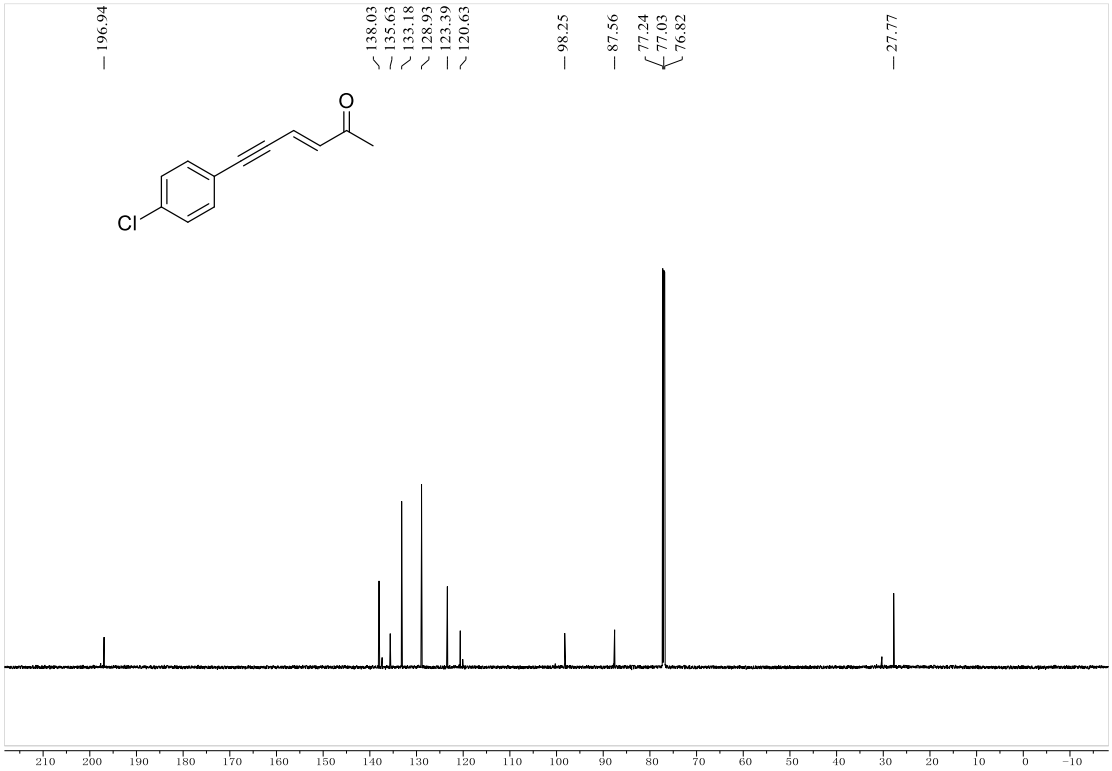
^{13}F NMR spectra (376 MHz, $CDCl_3$) of **1b**



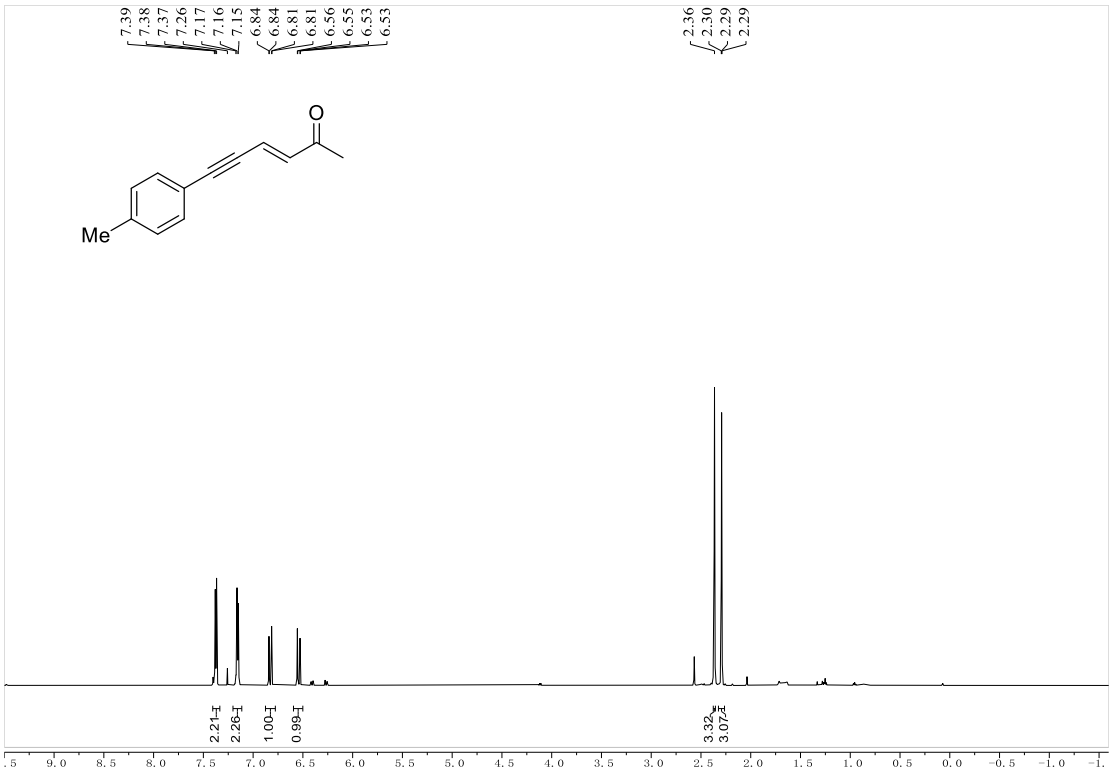
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1c**



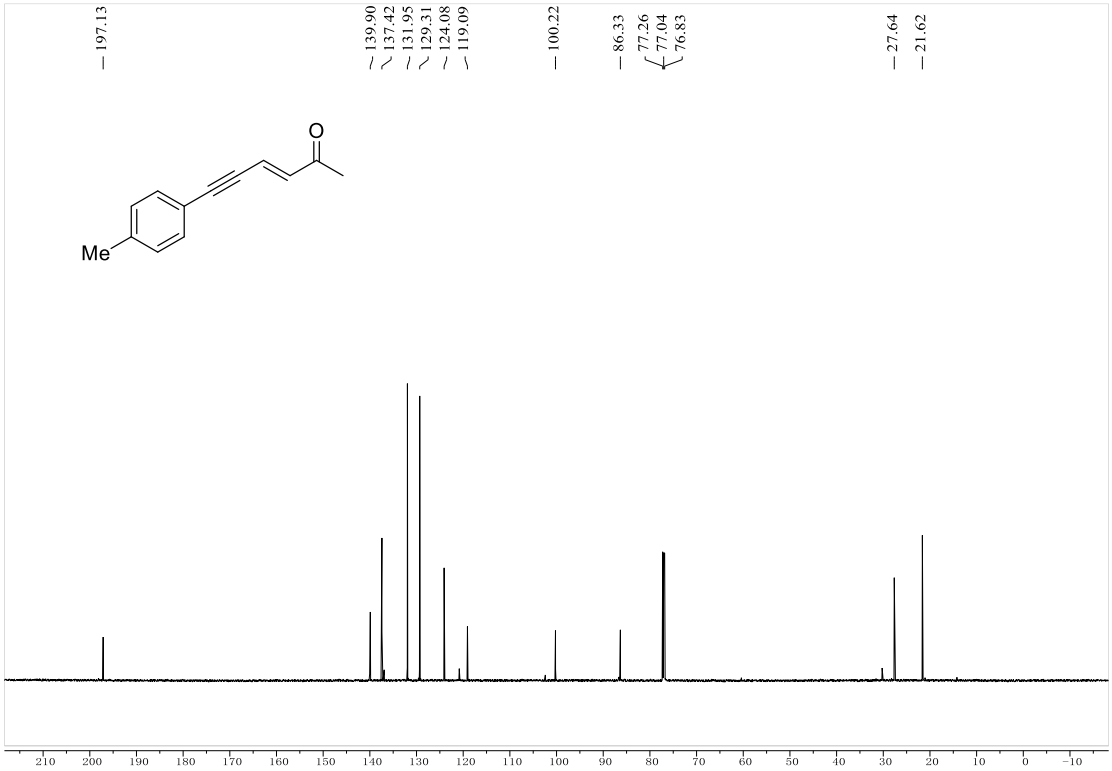
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1c**



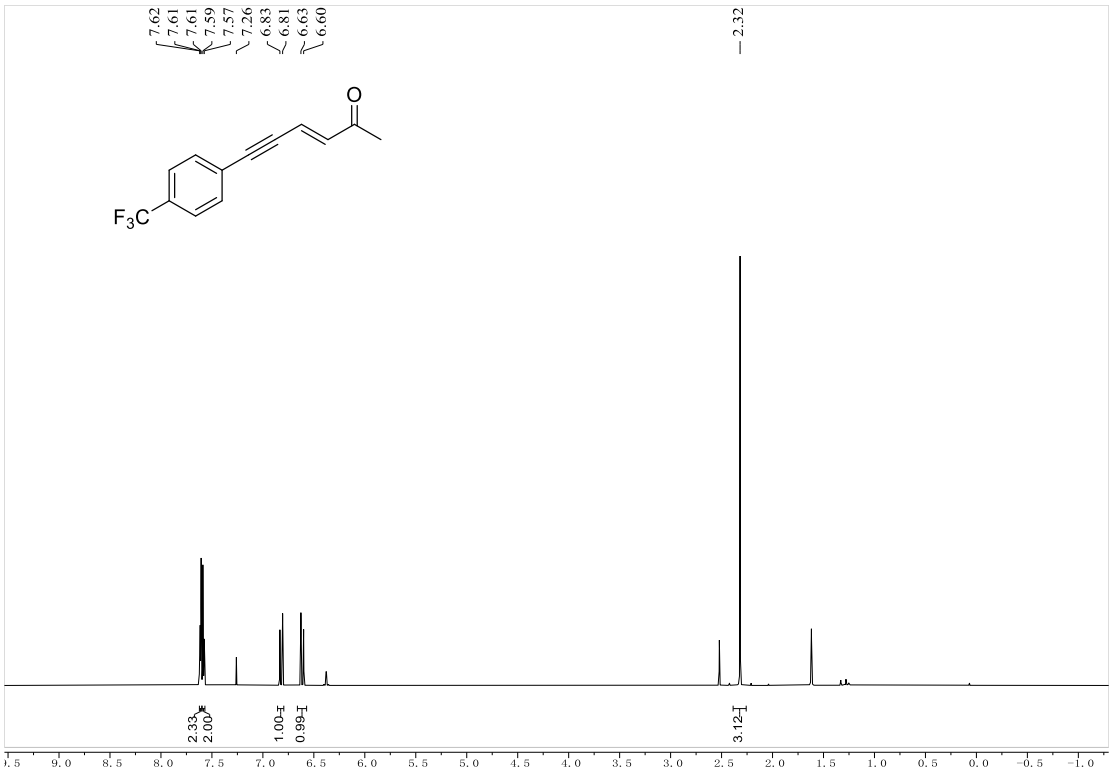
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1d**



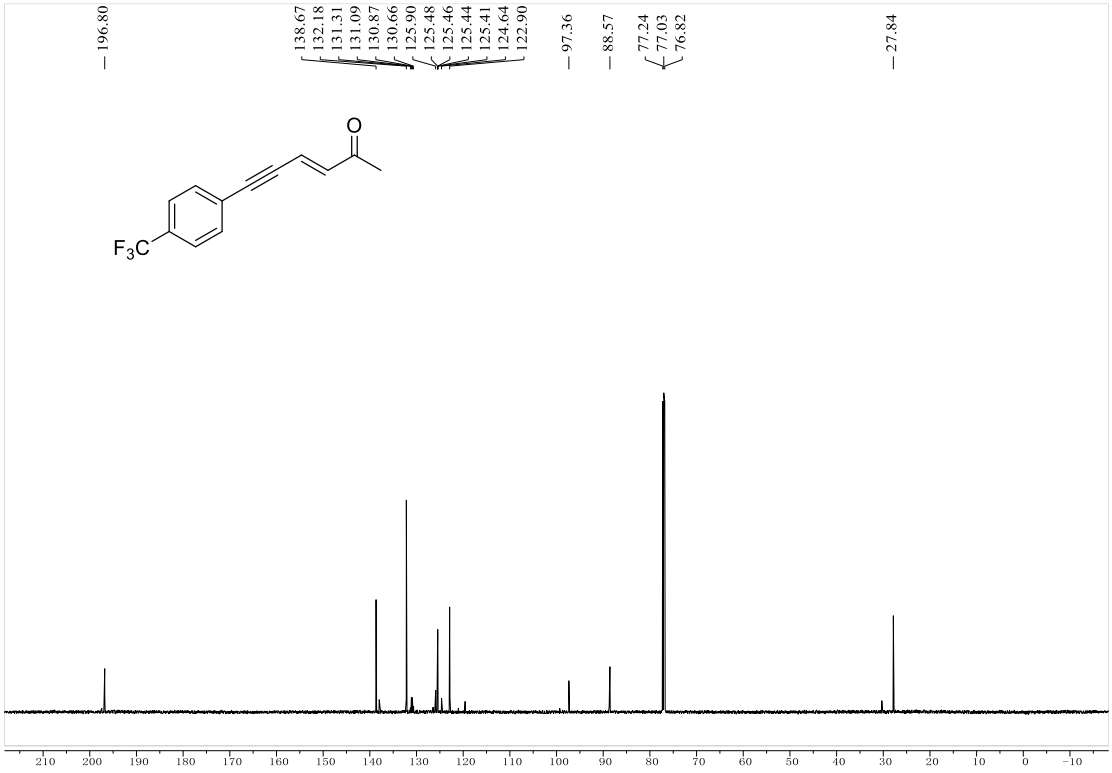
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1d**



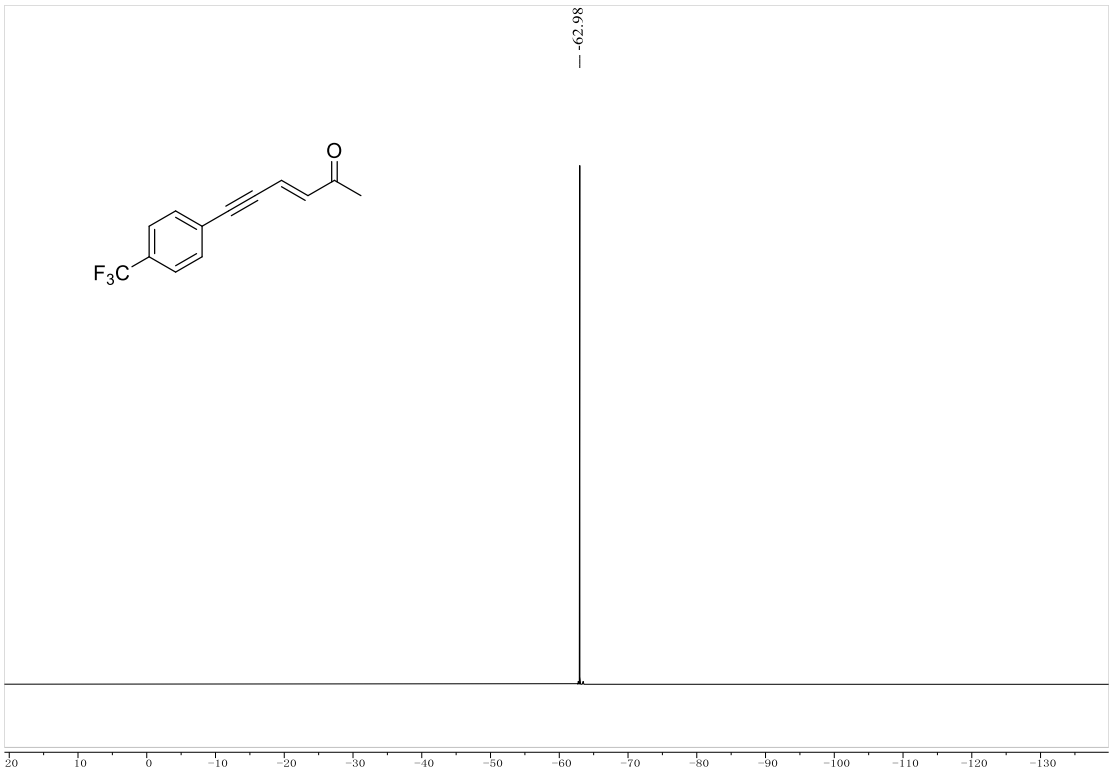
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1e**



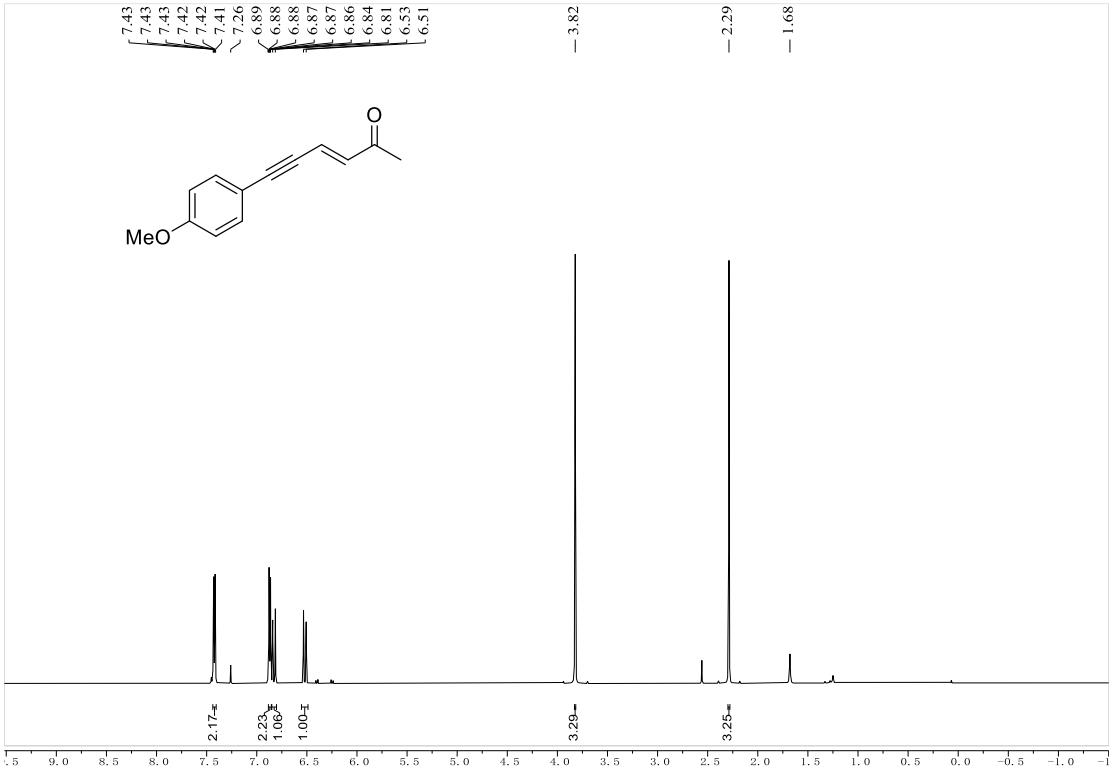
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1e**



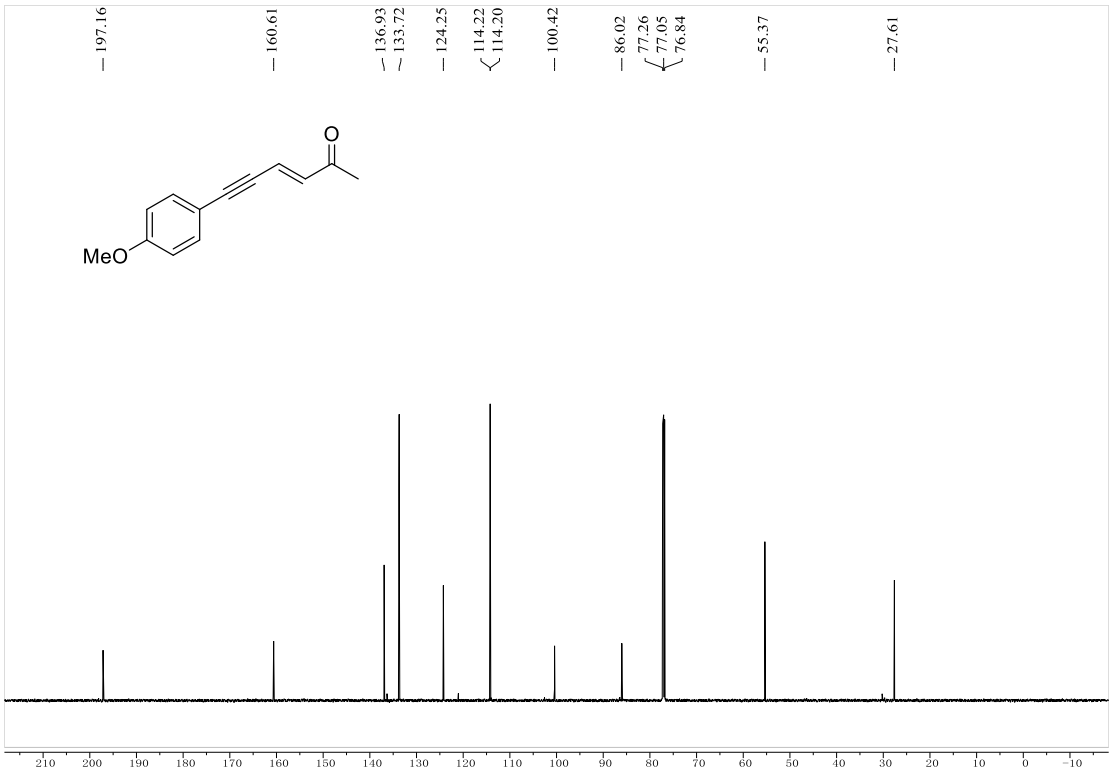
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1e**



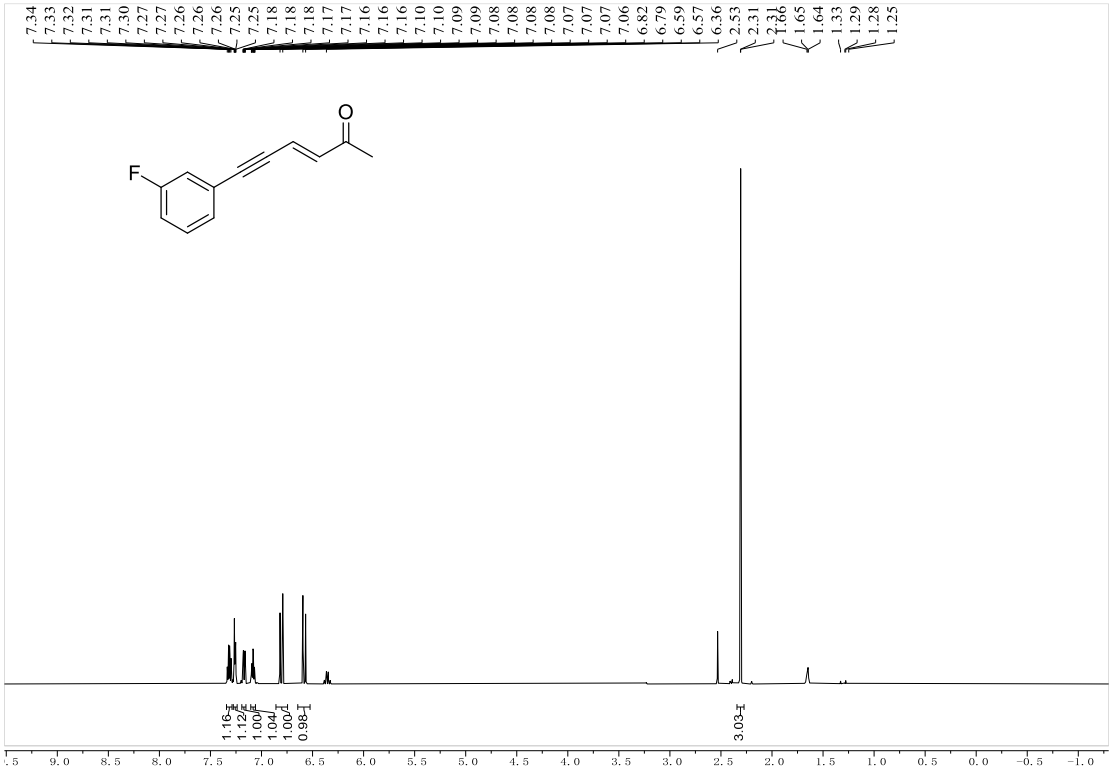
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1f**



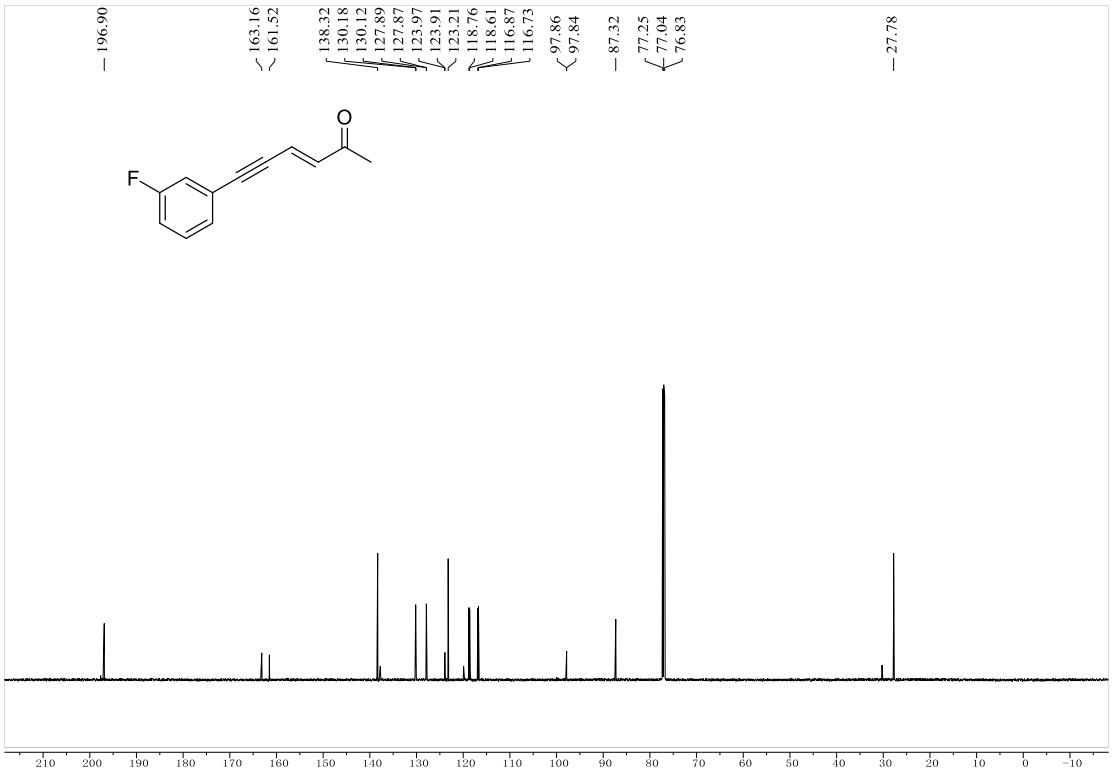
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1f**



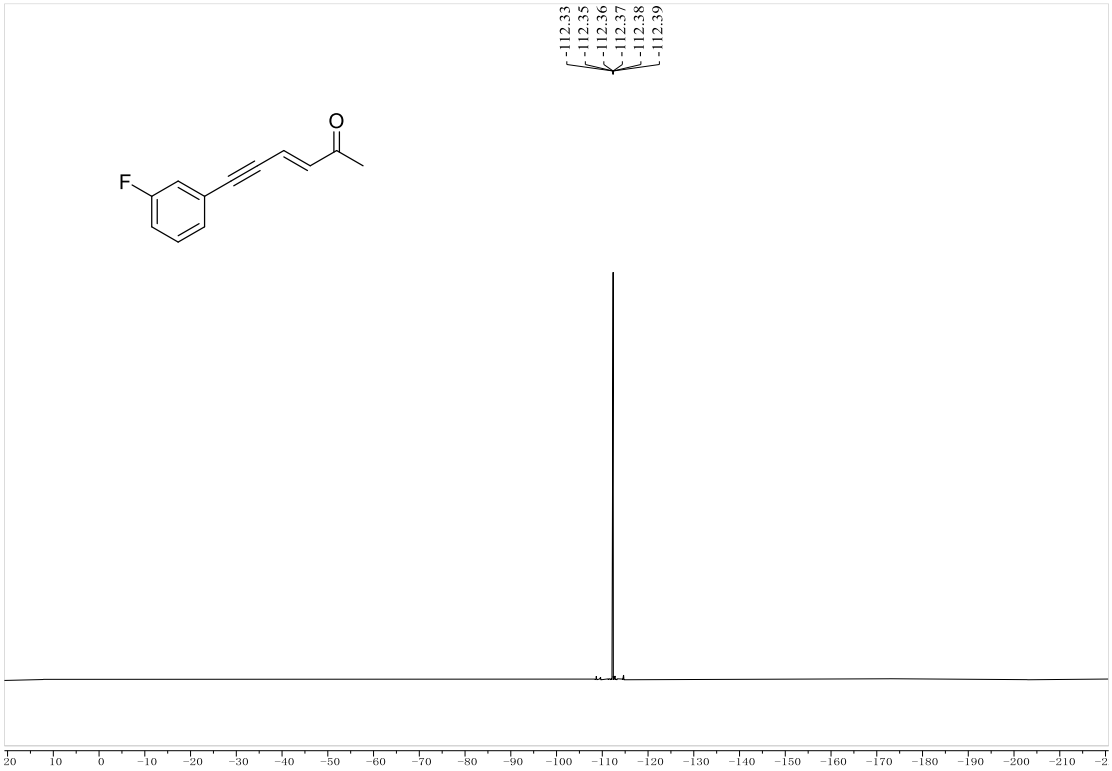
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1g**



^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1g**

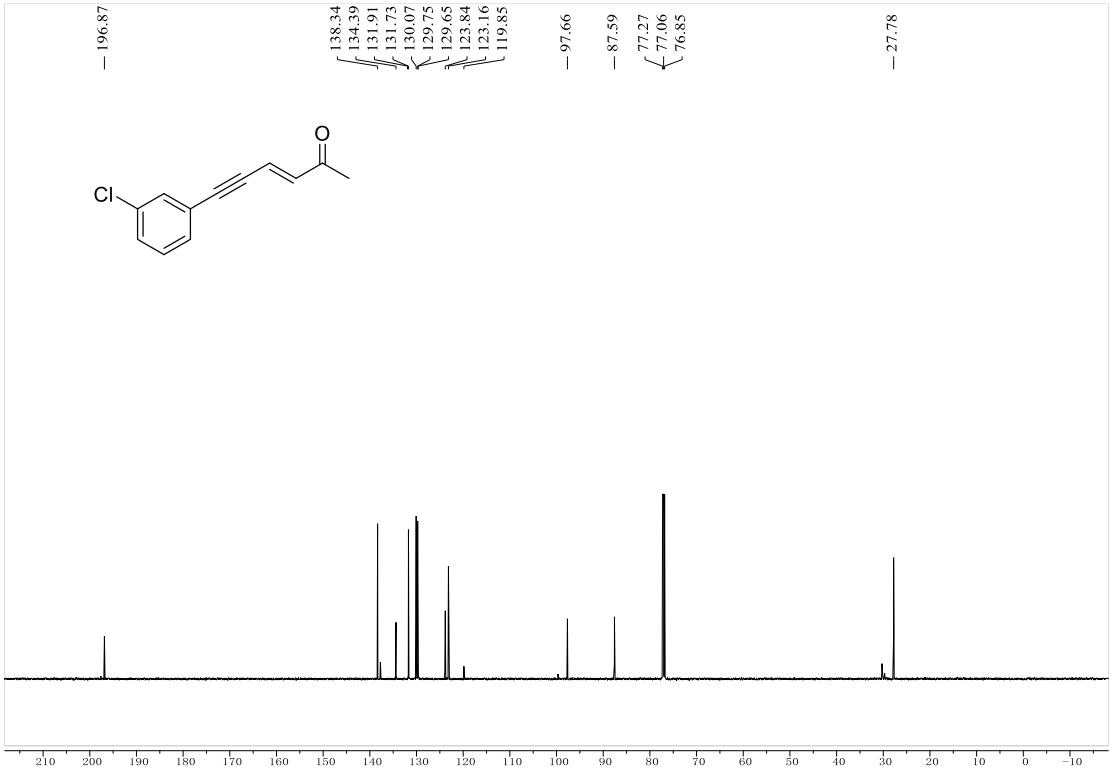


^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1g**

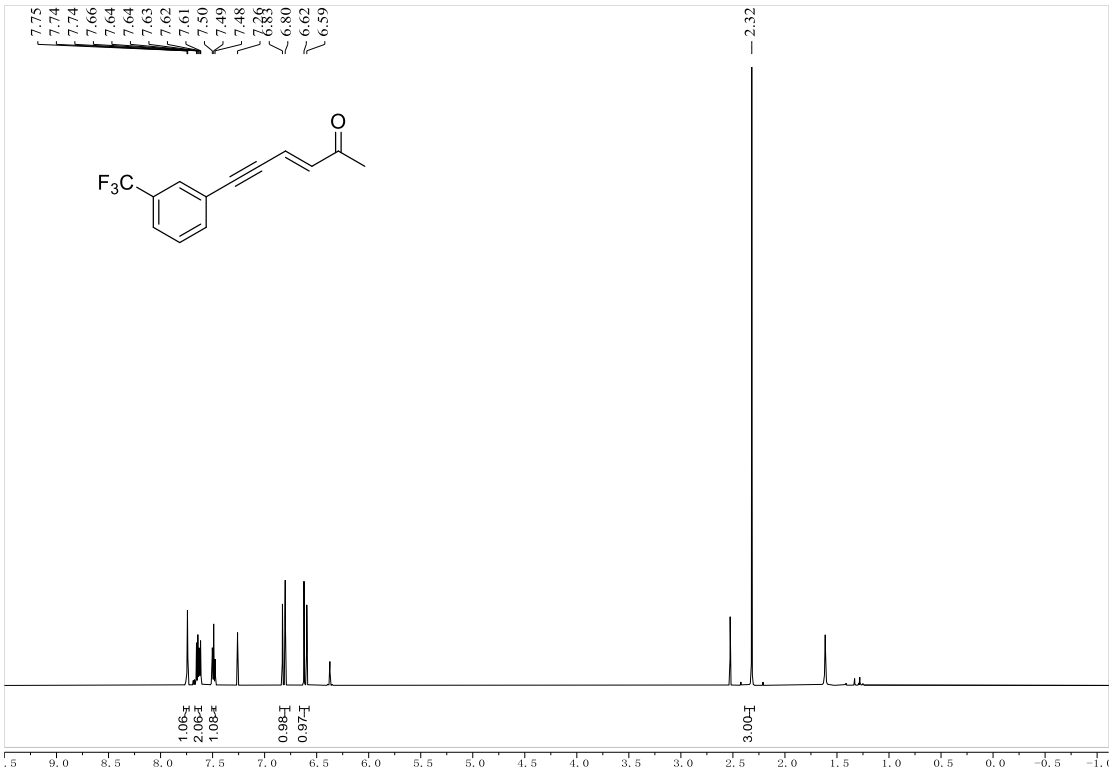


^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1h**

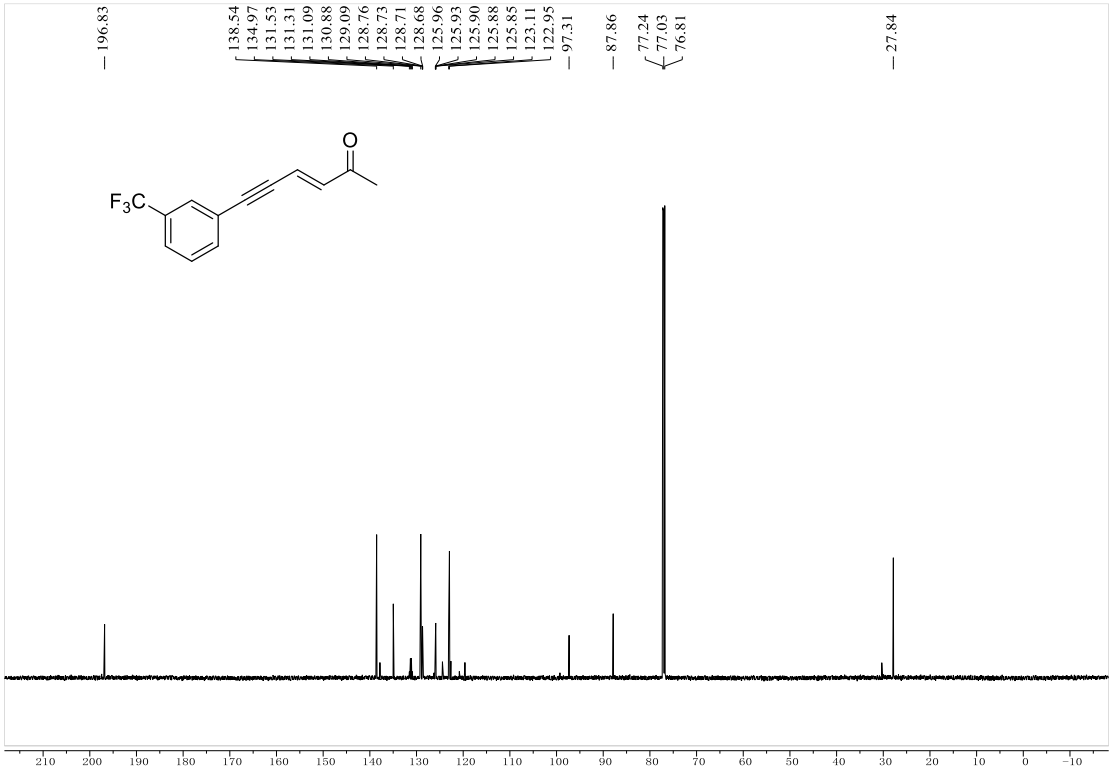
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1h**



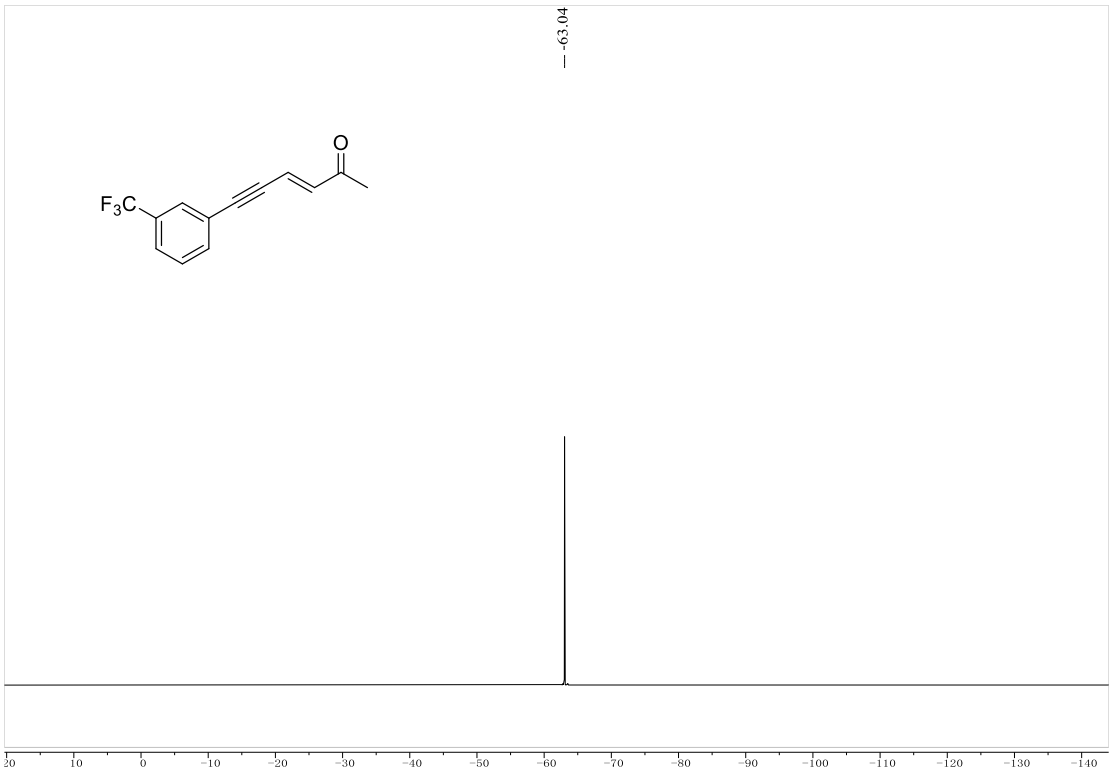
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1i**



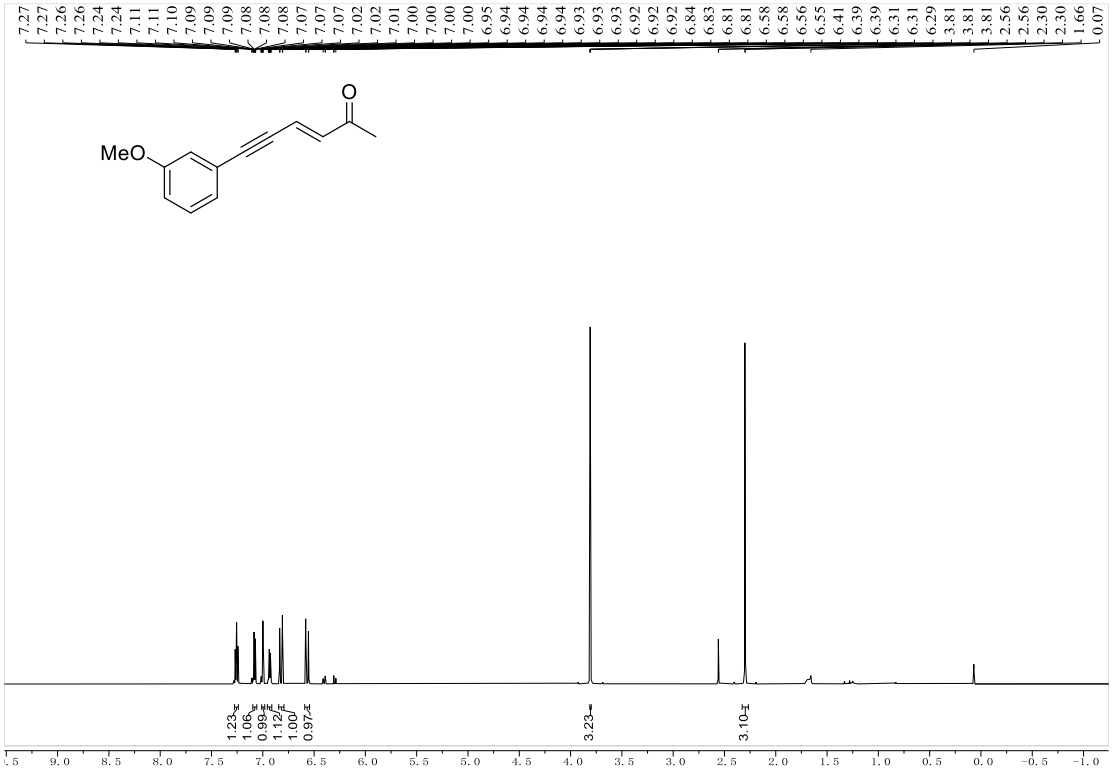
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1i**



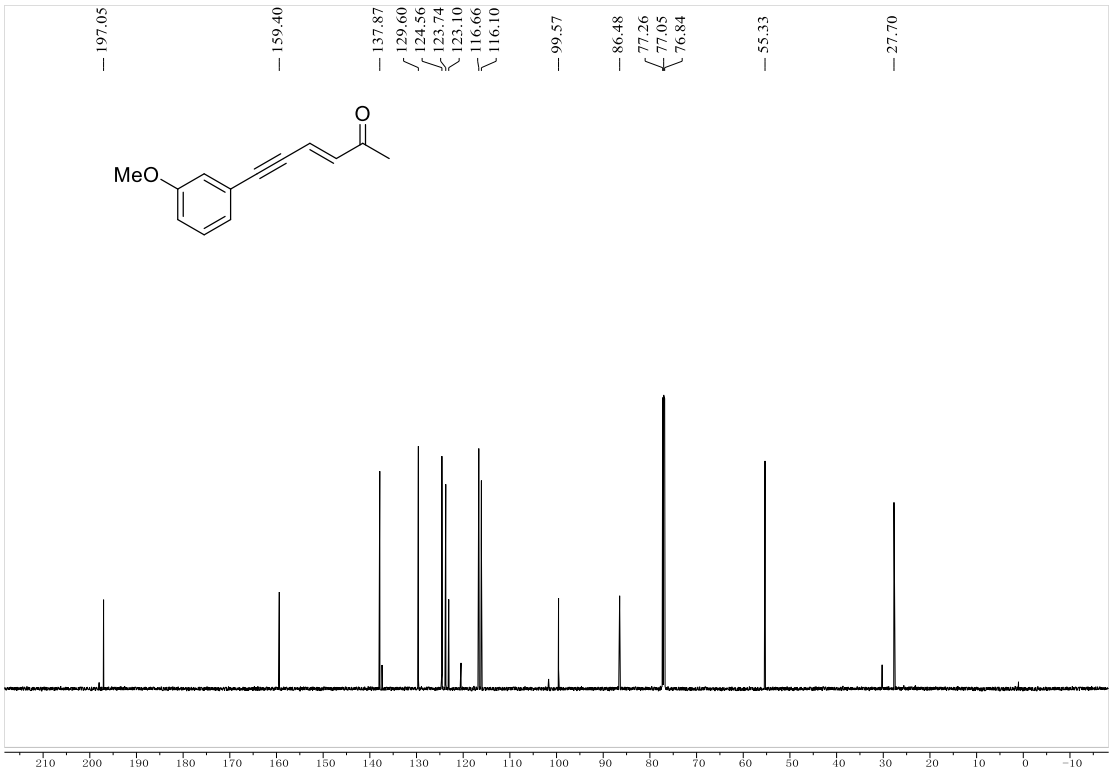
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1i**



^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1j**



^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1j**



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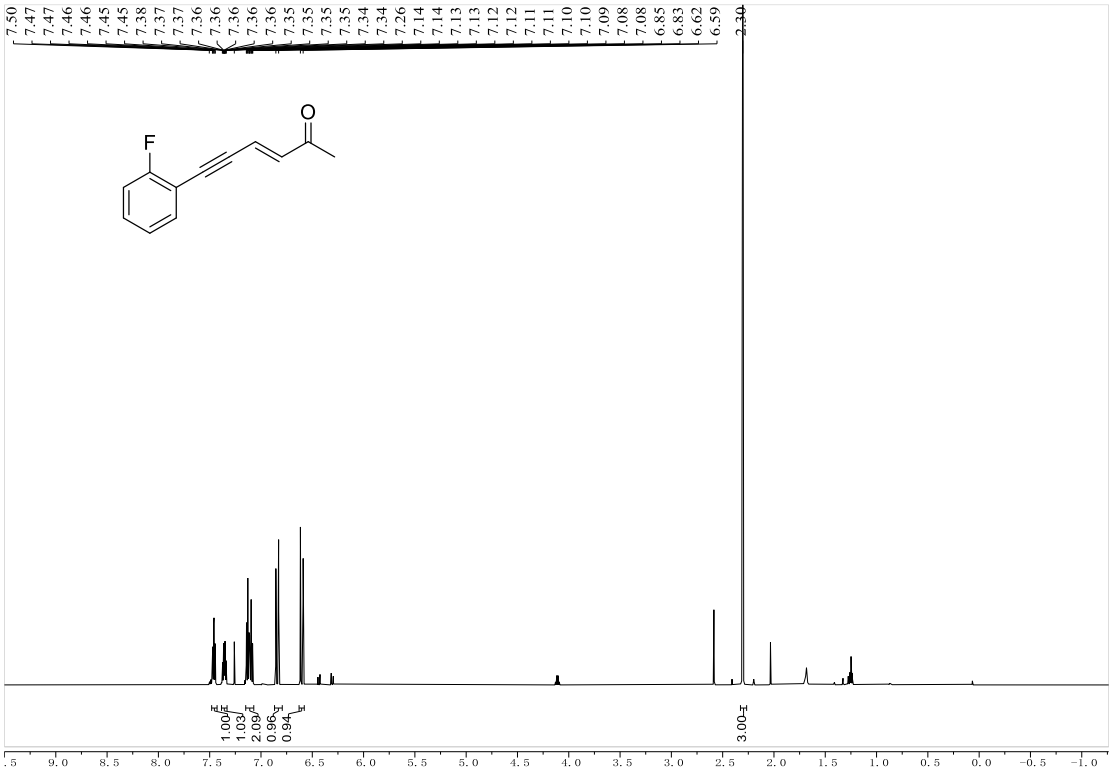
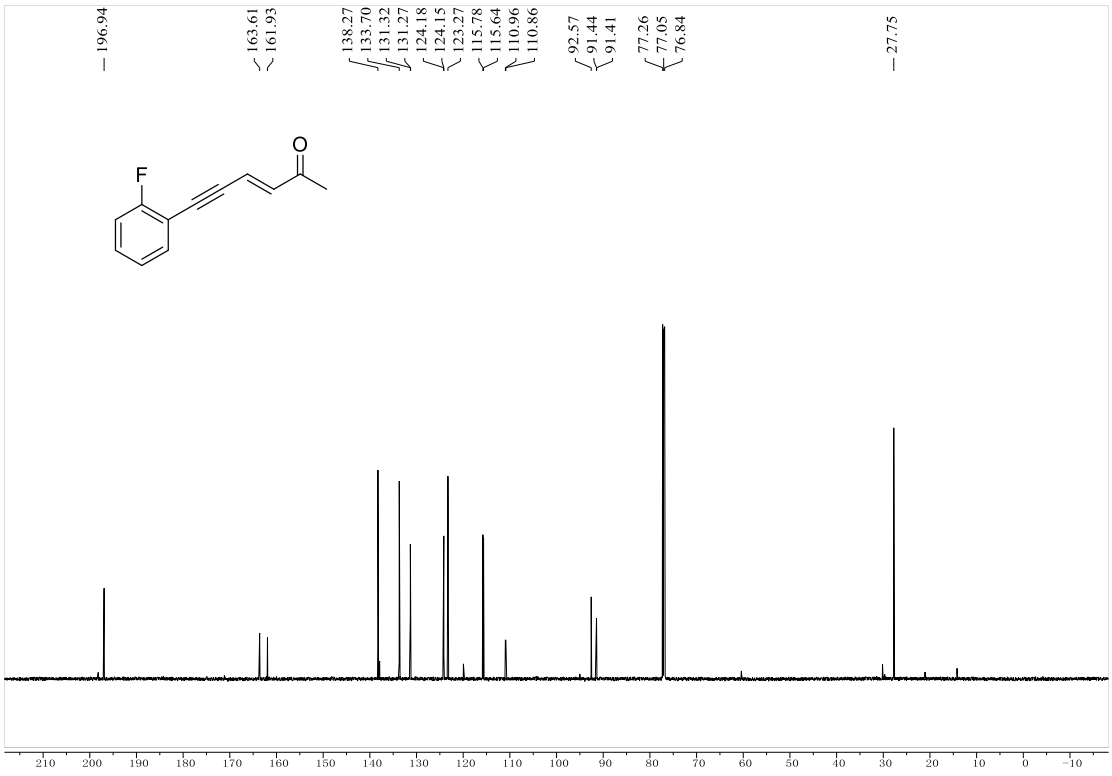
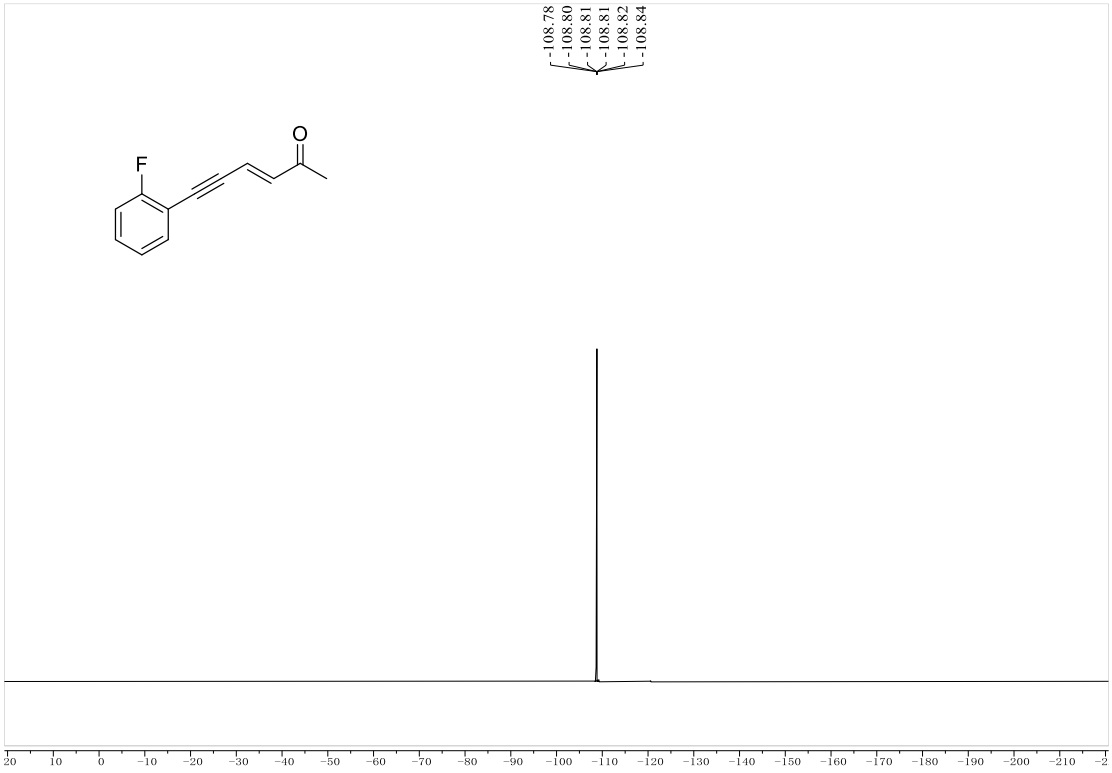


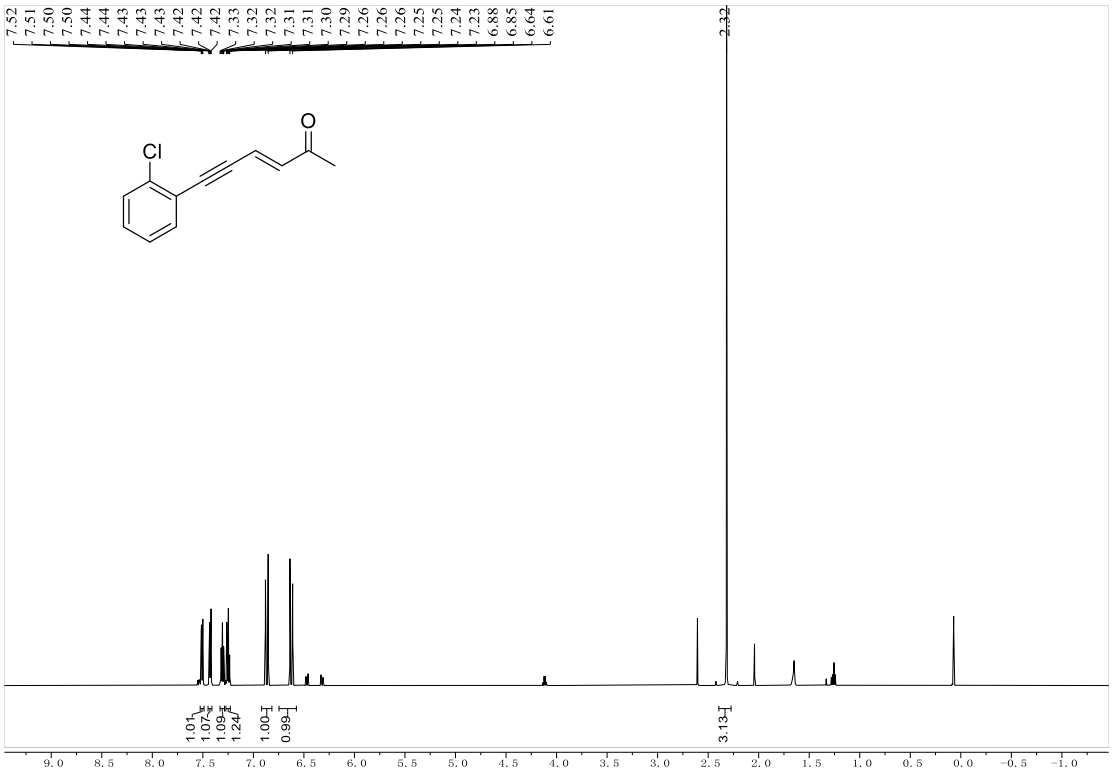
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1k**



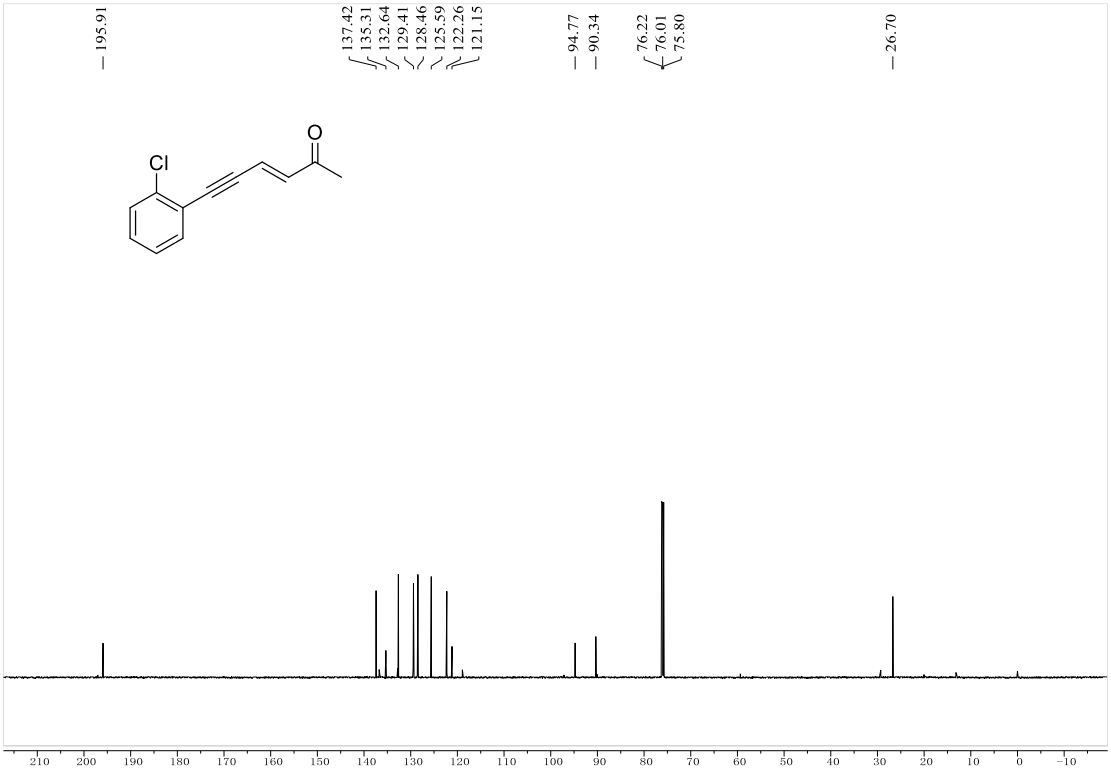
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **1k**



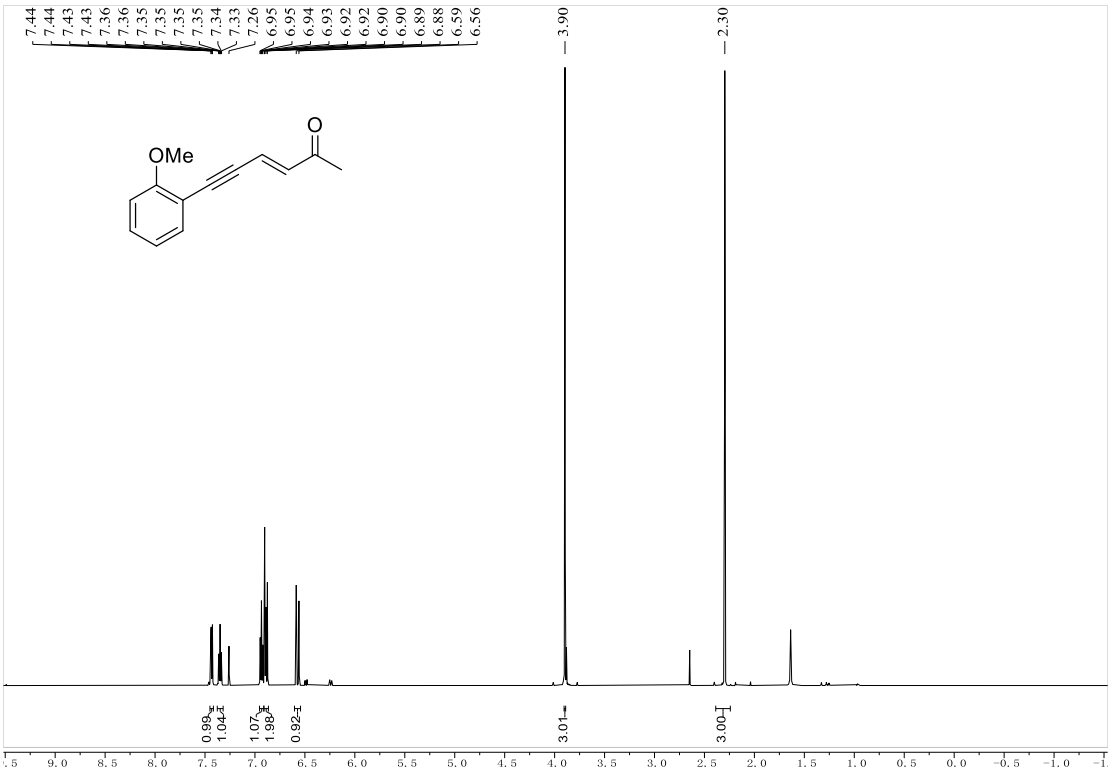
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1l**



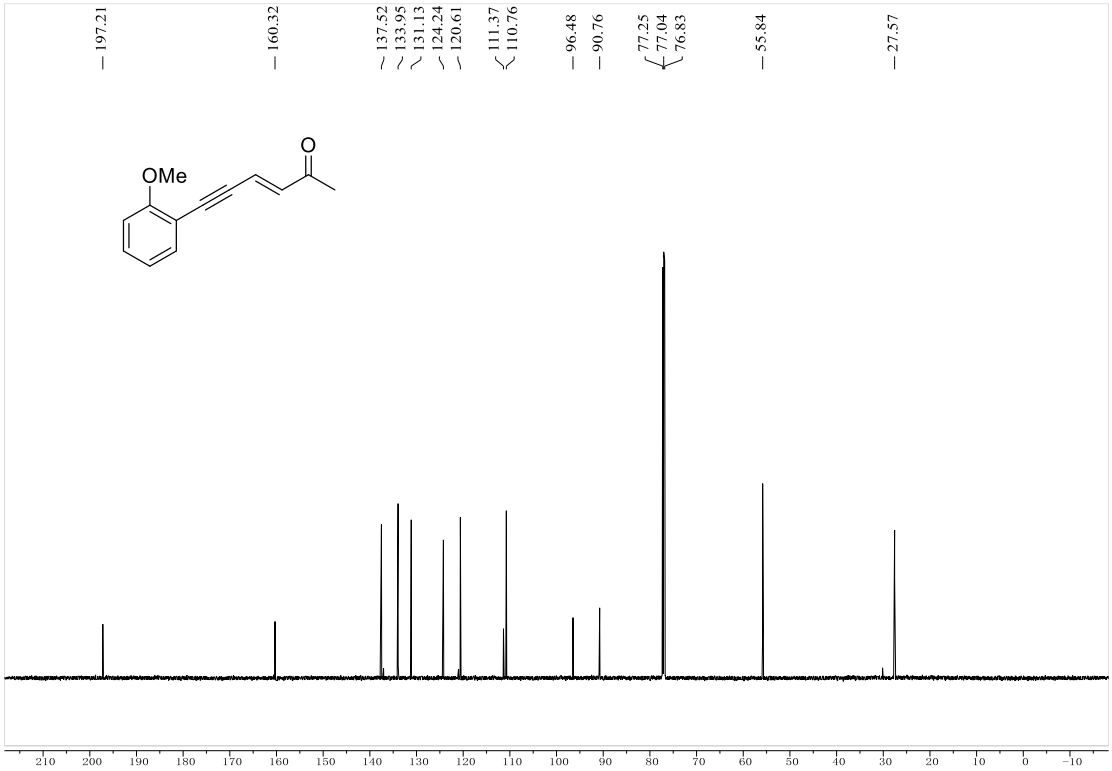
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1l**



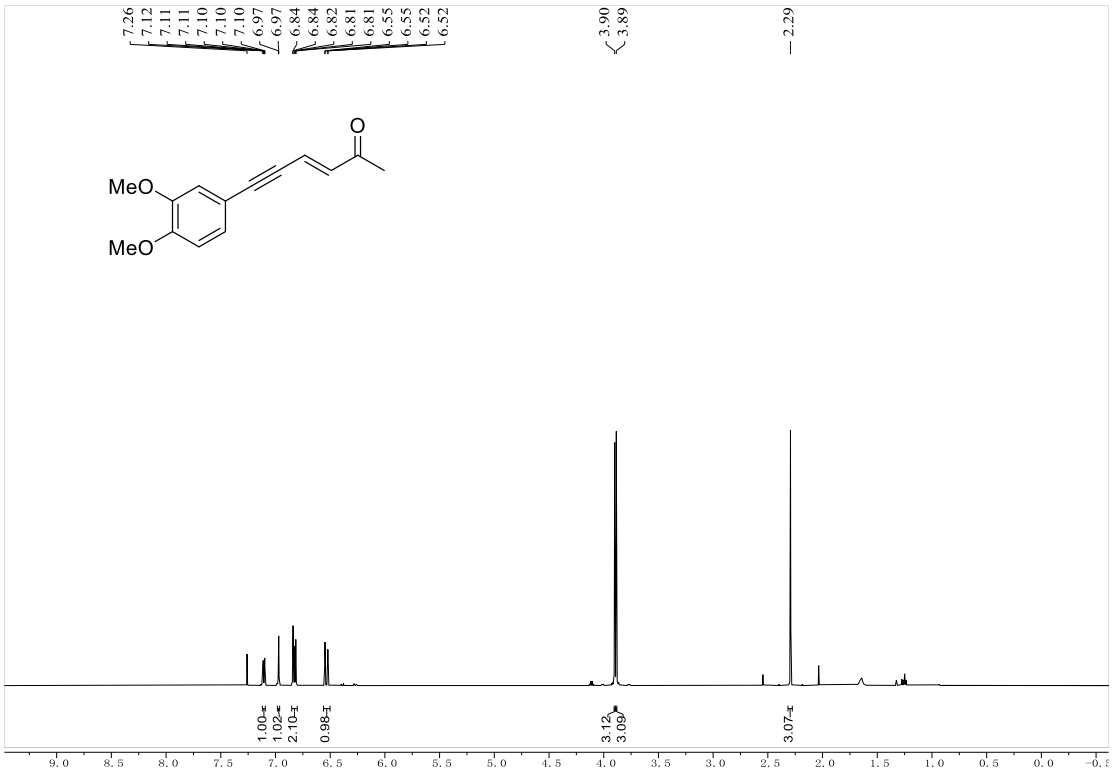
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1m**



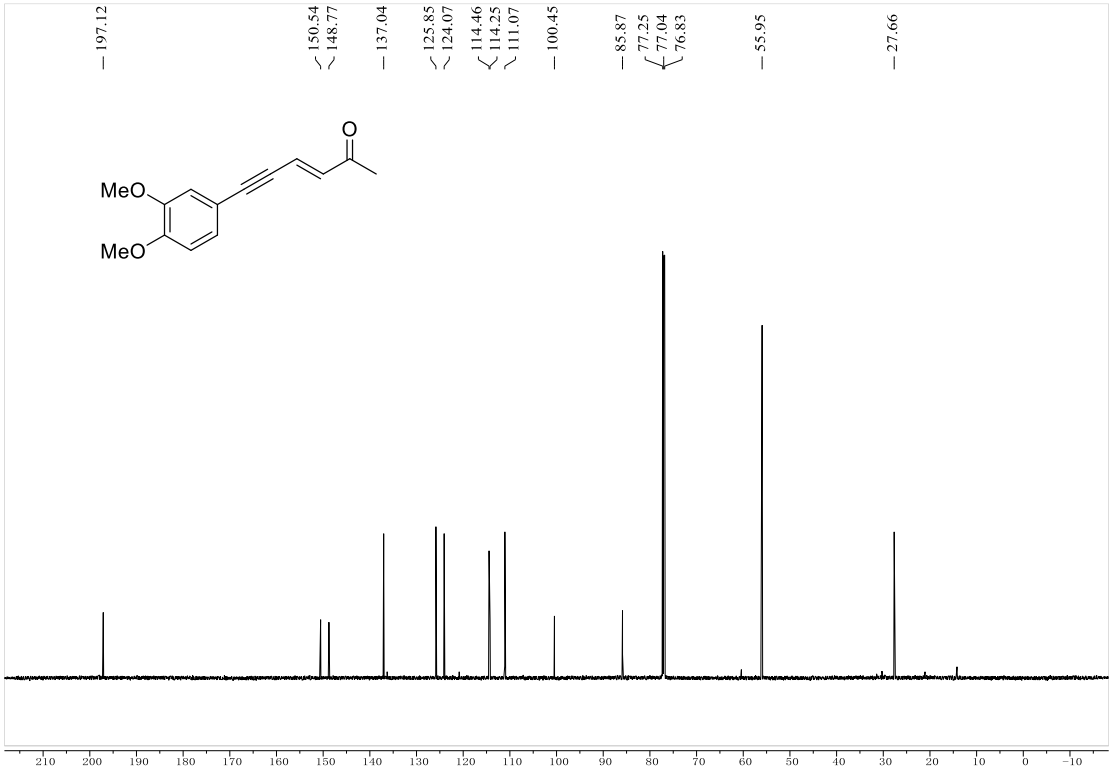
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1m**



^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1n**



^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1n**



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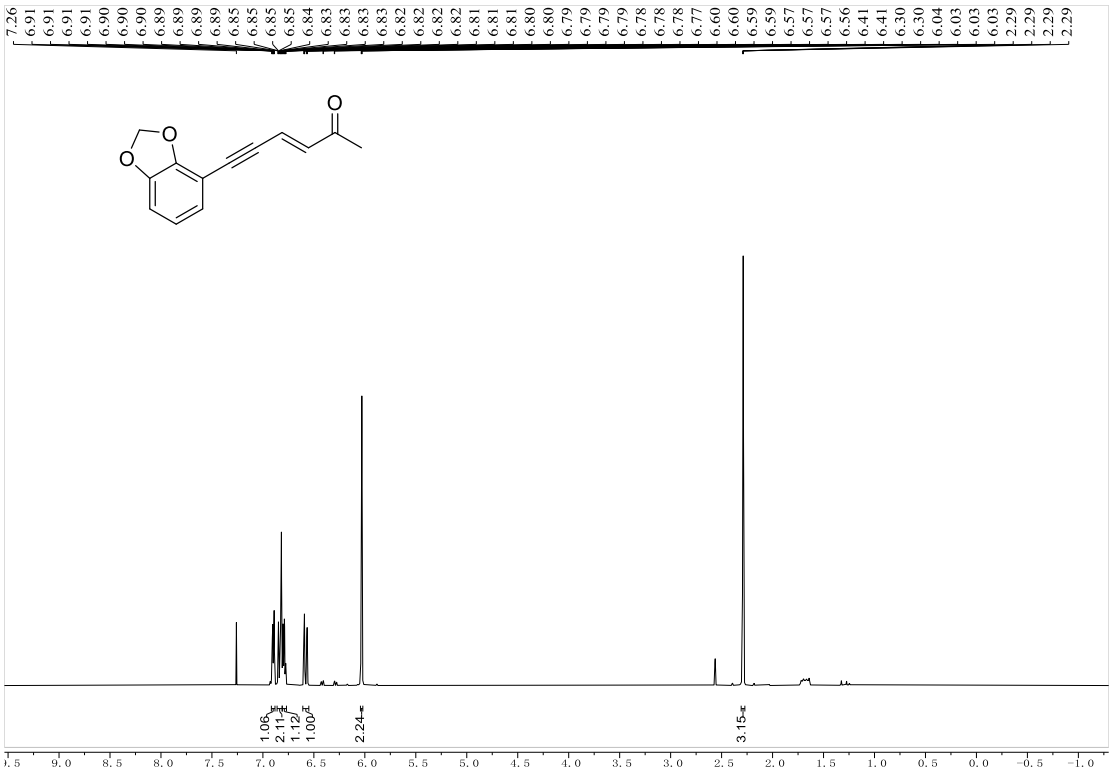
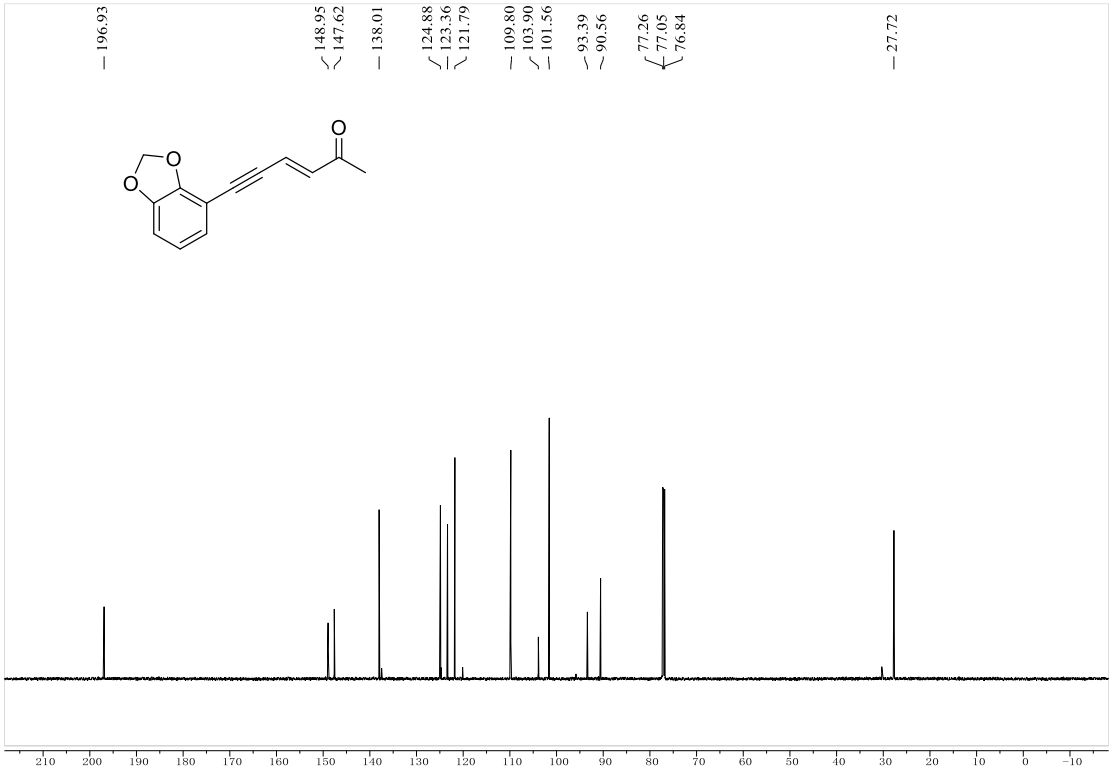


^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1o**



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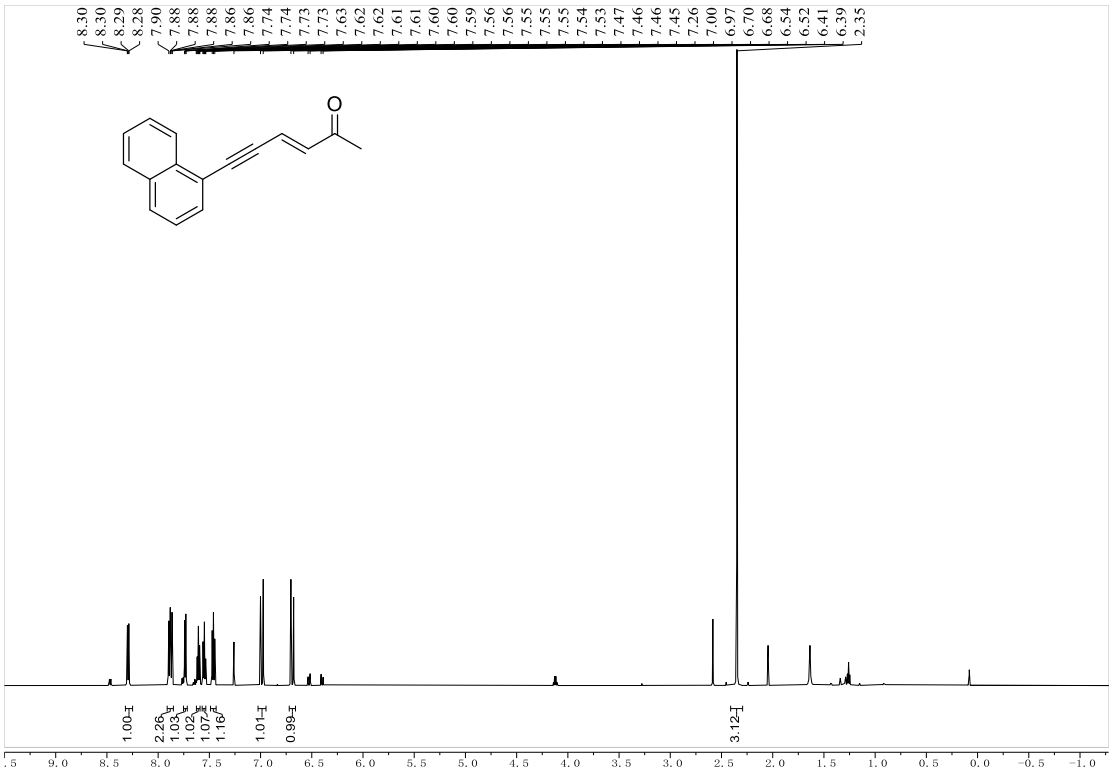
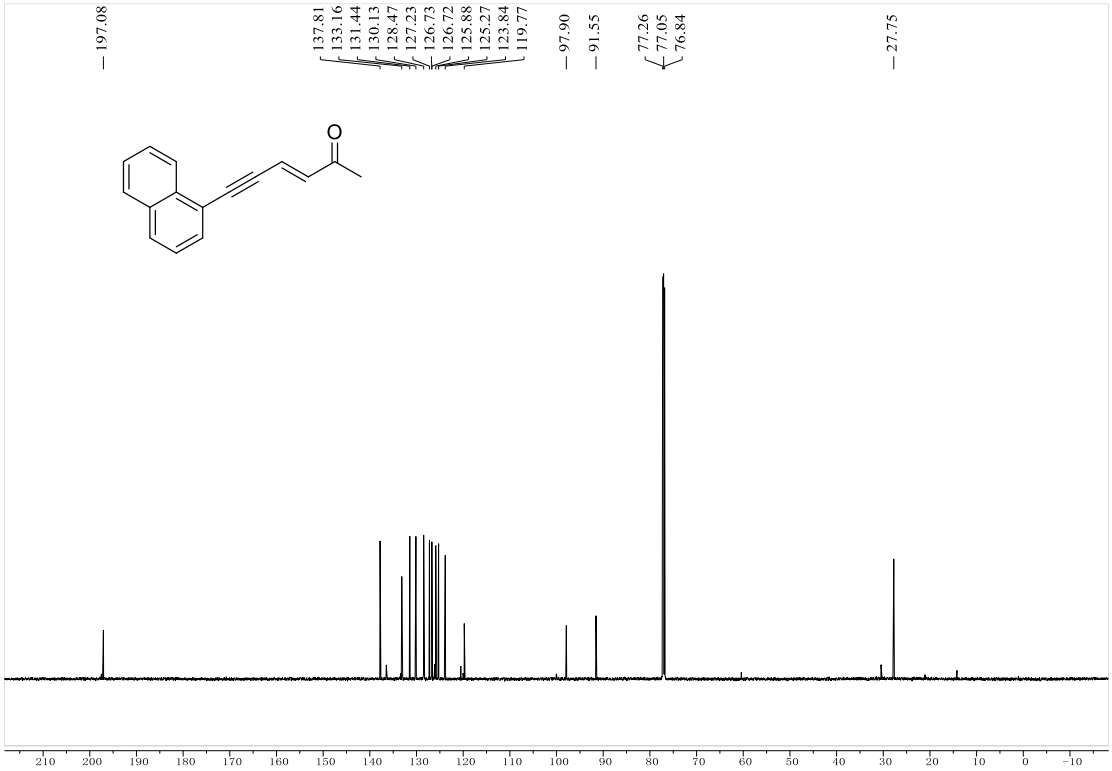


^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1p**



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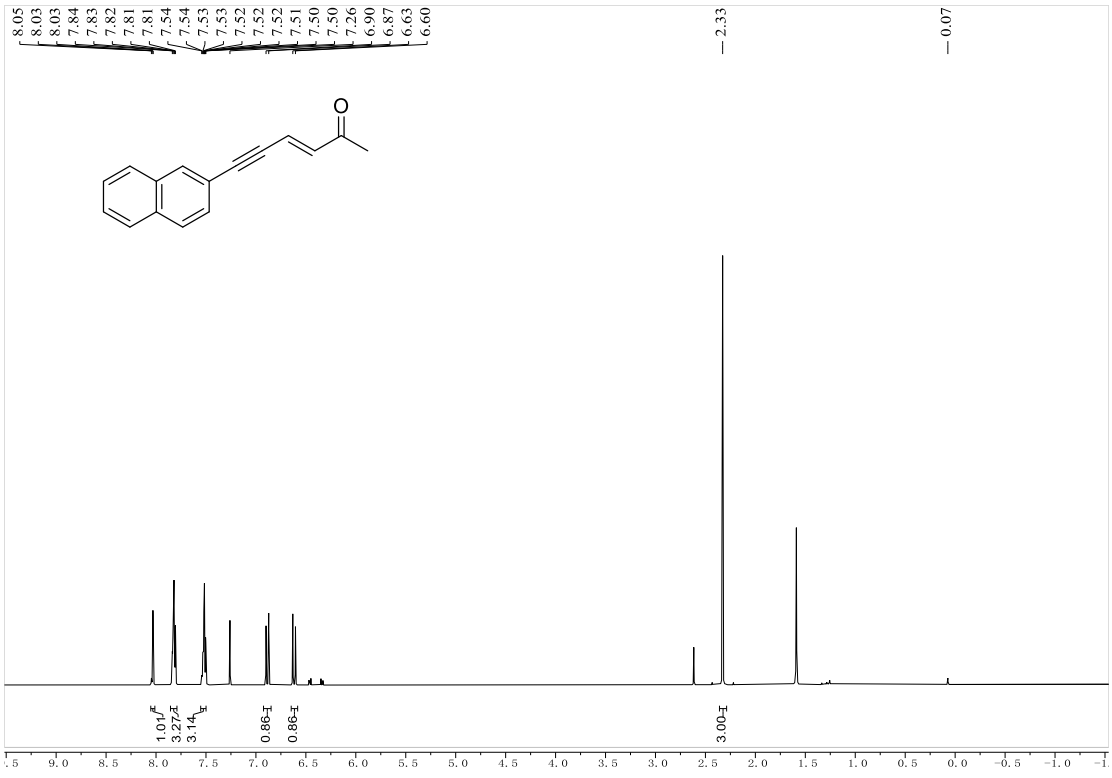
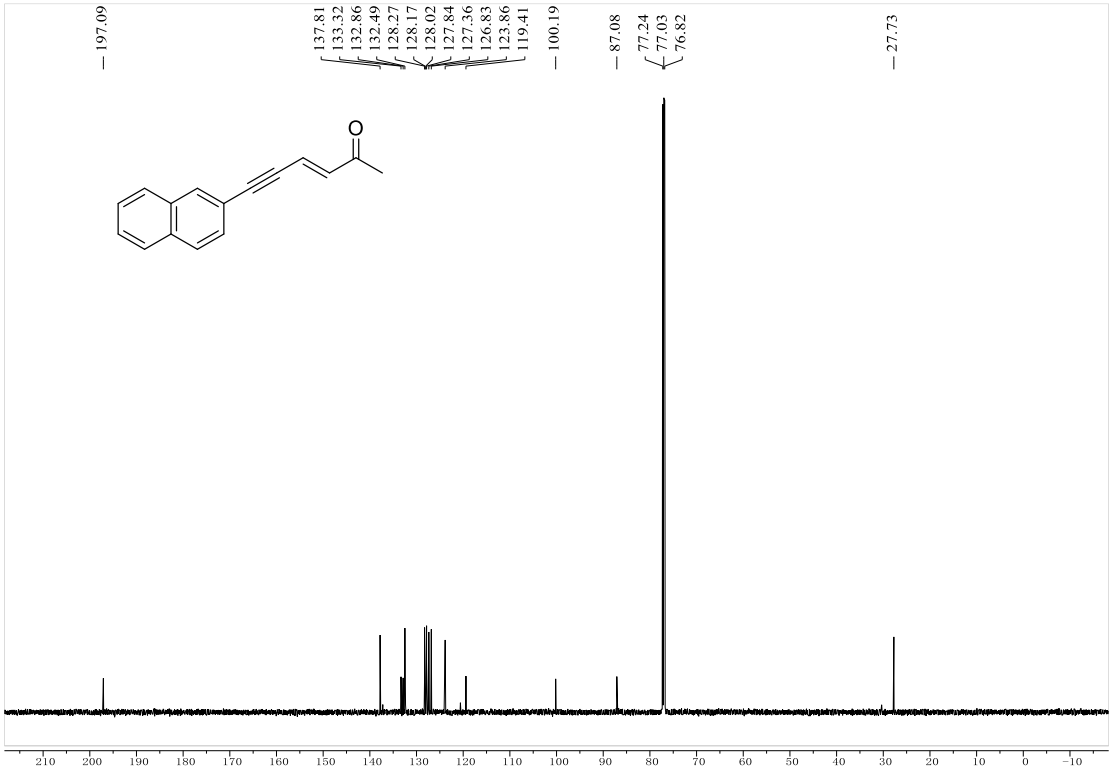


^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1q**



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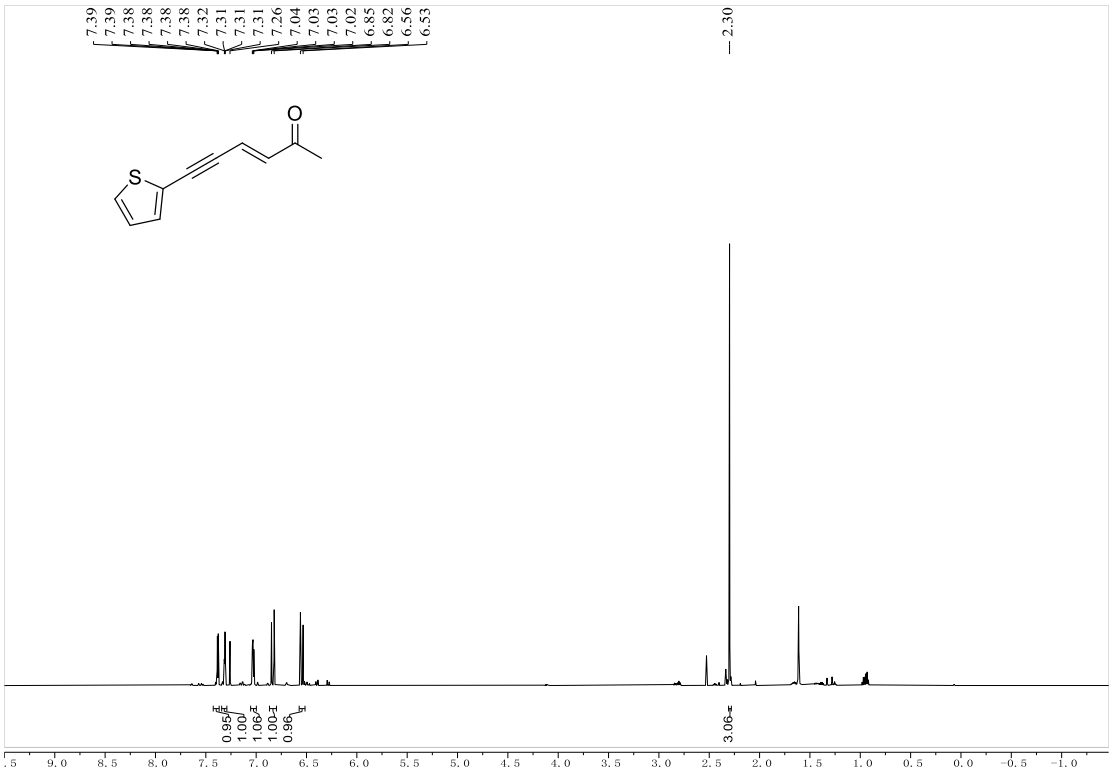
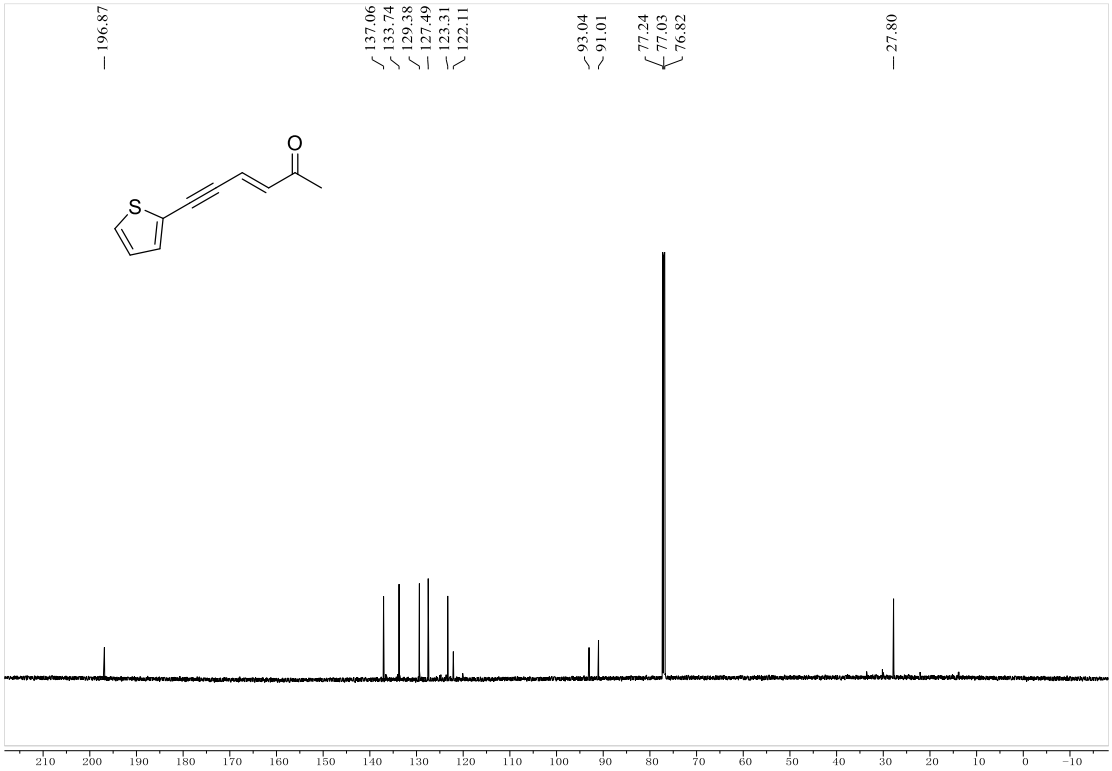


^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1r**



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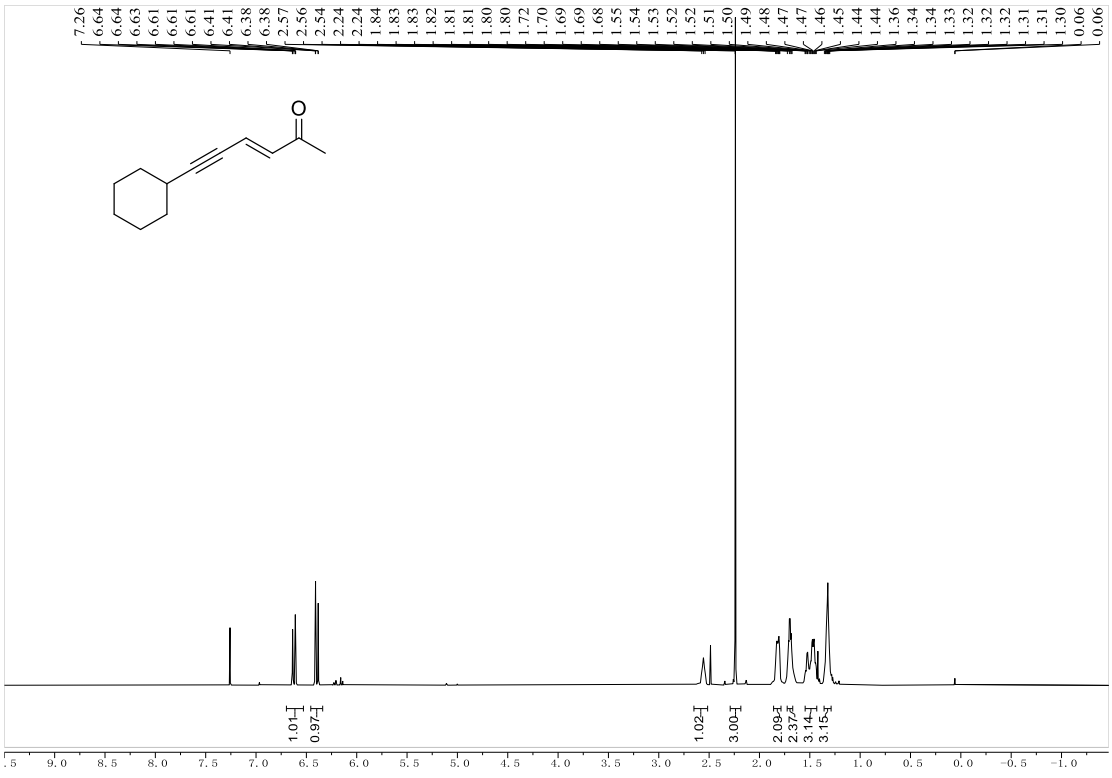
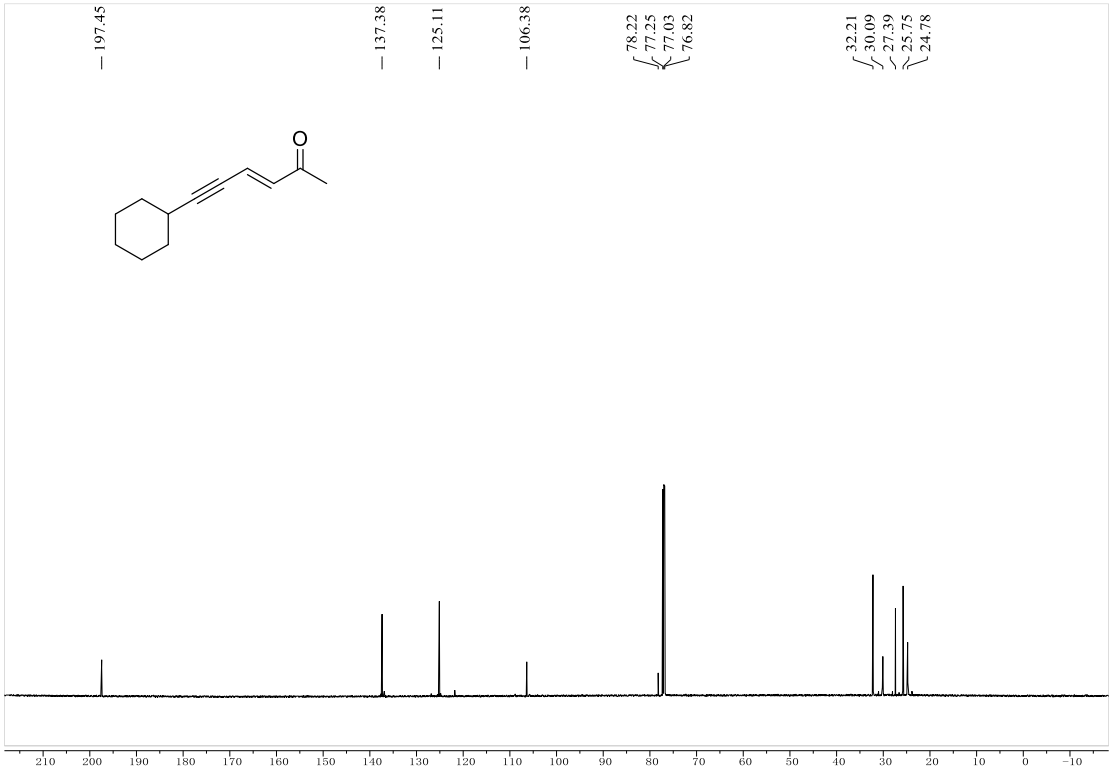


^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1s**



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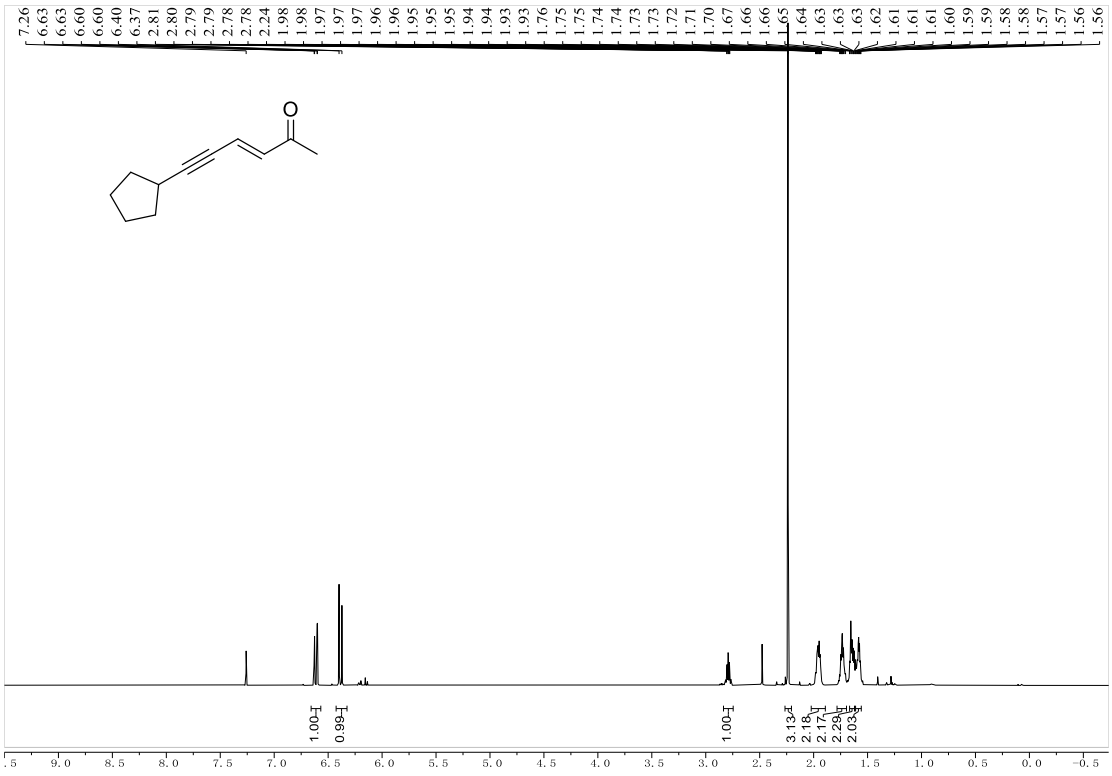

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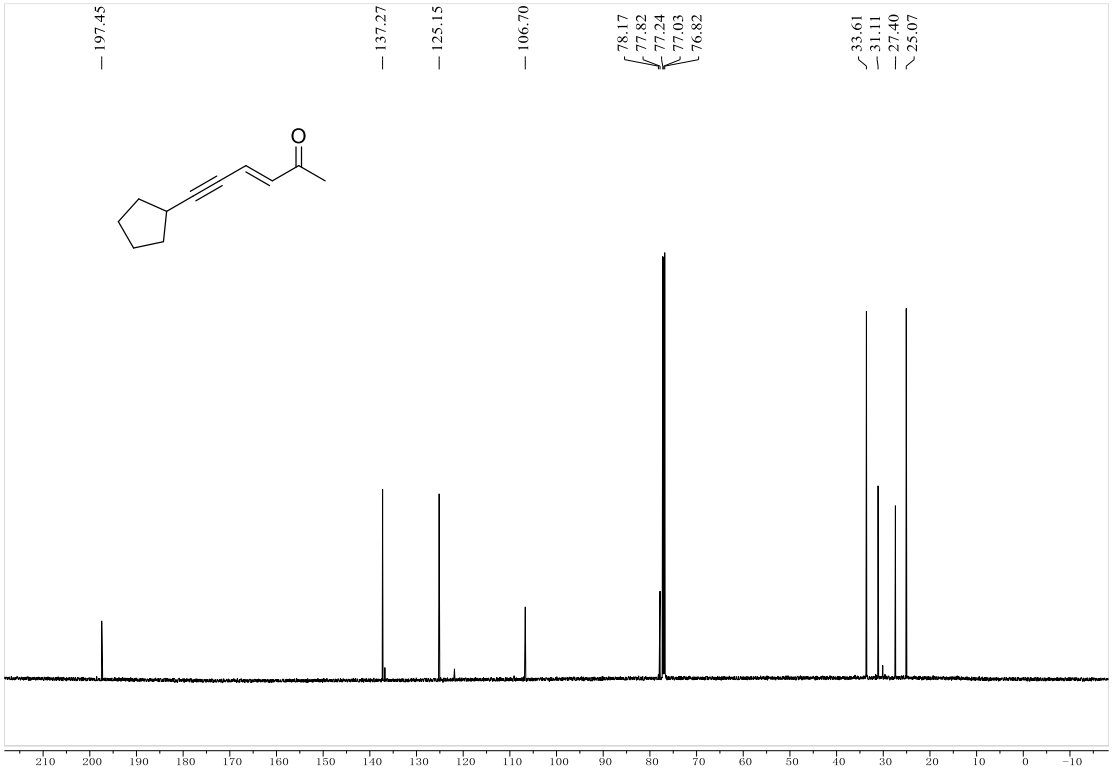
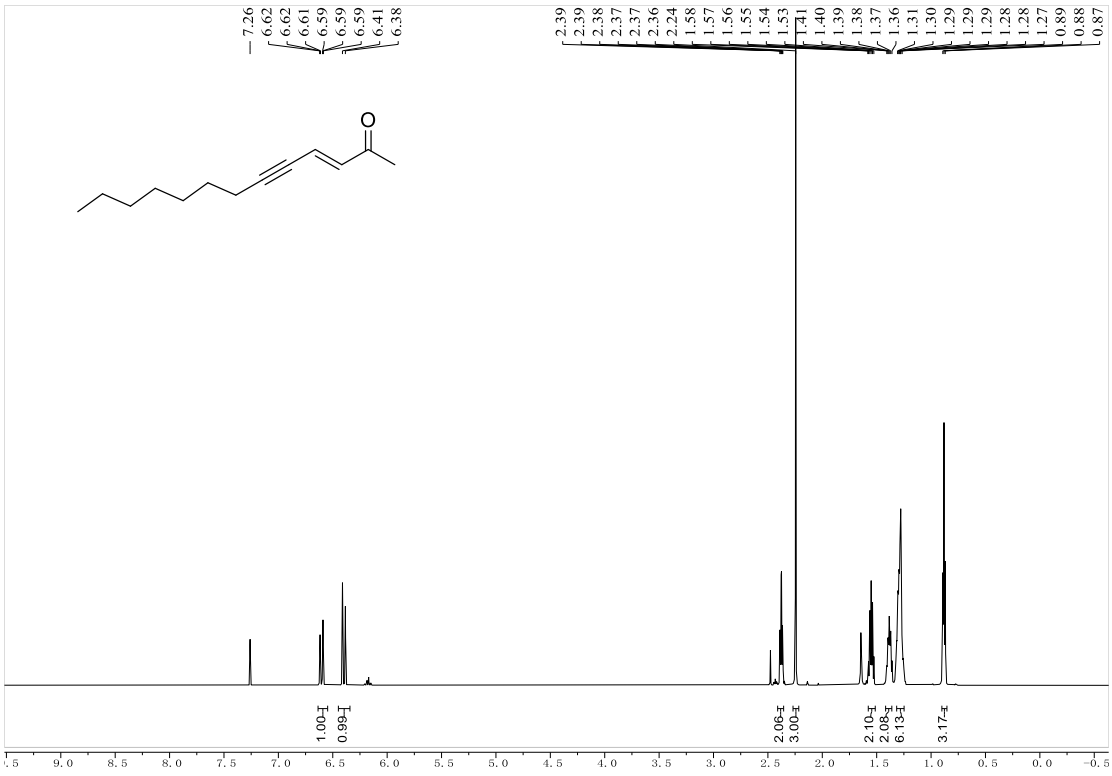
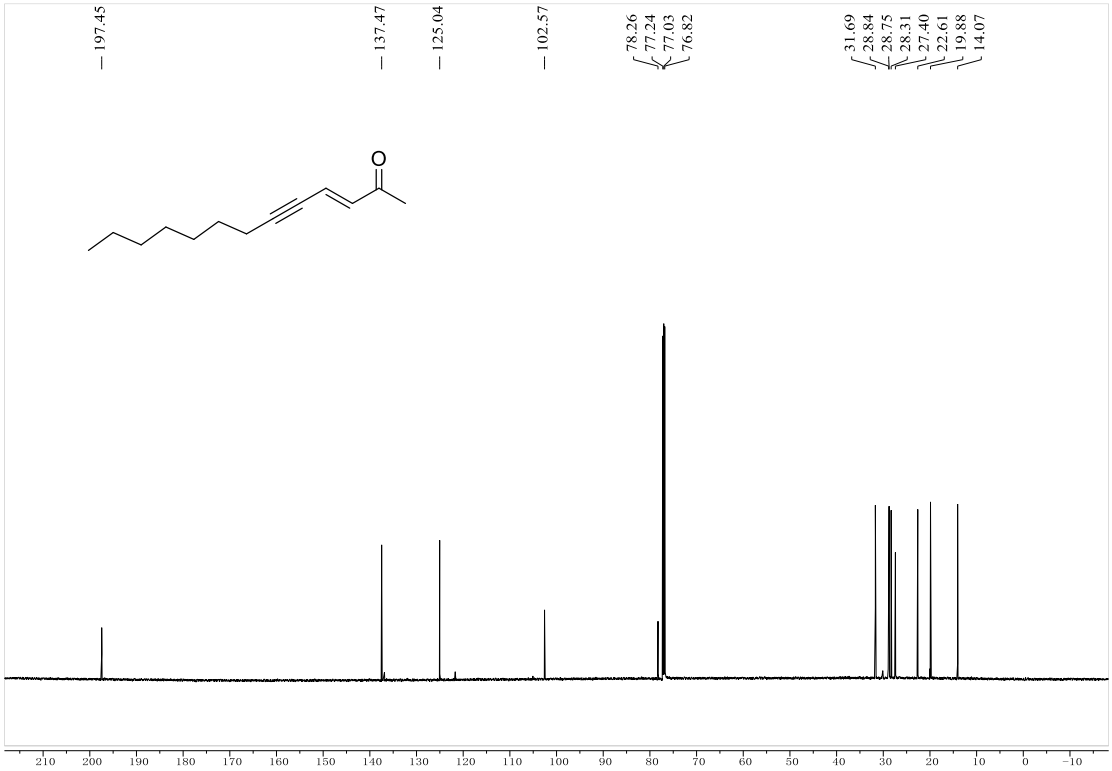


^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1u**



^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1u**



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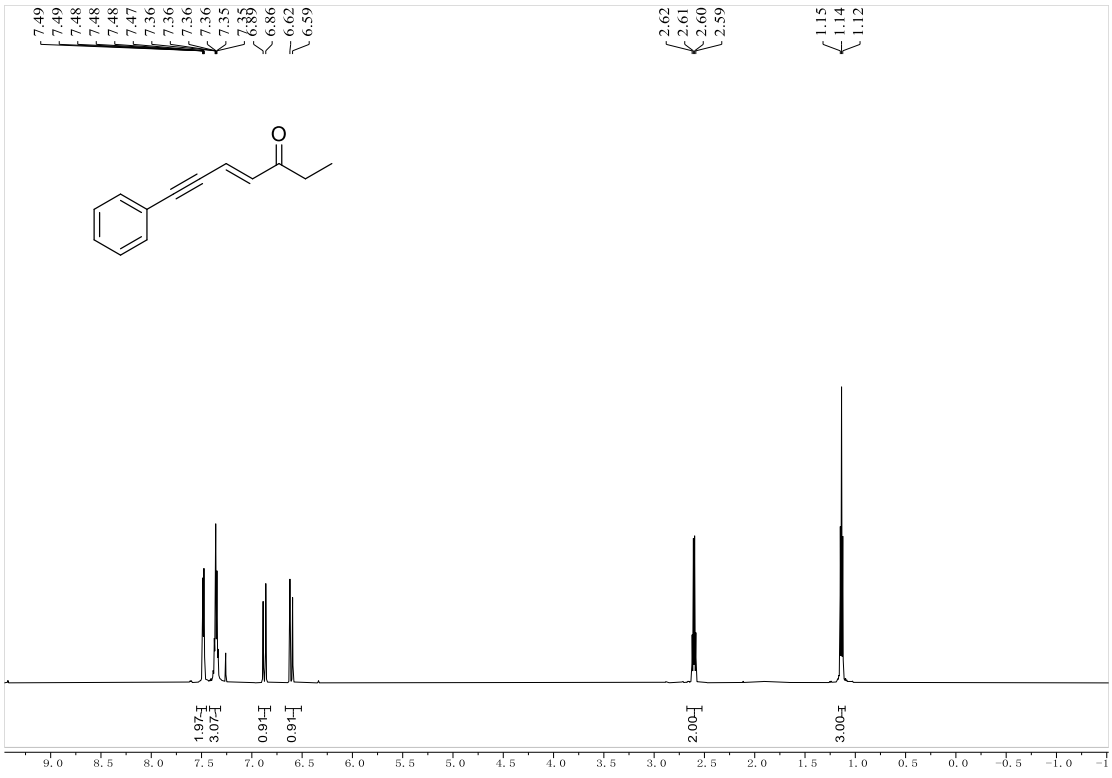
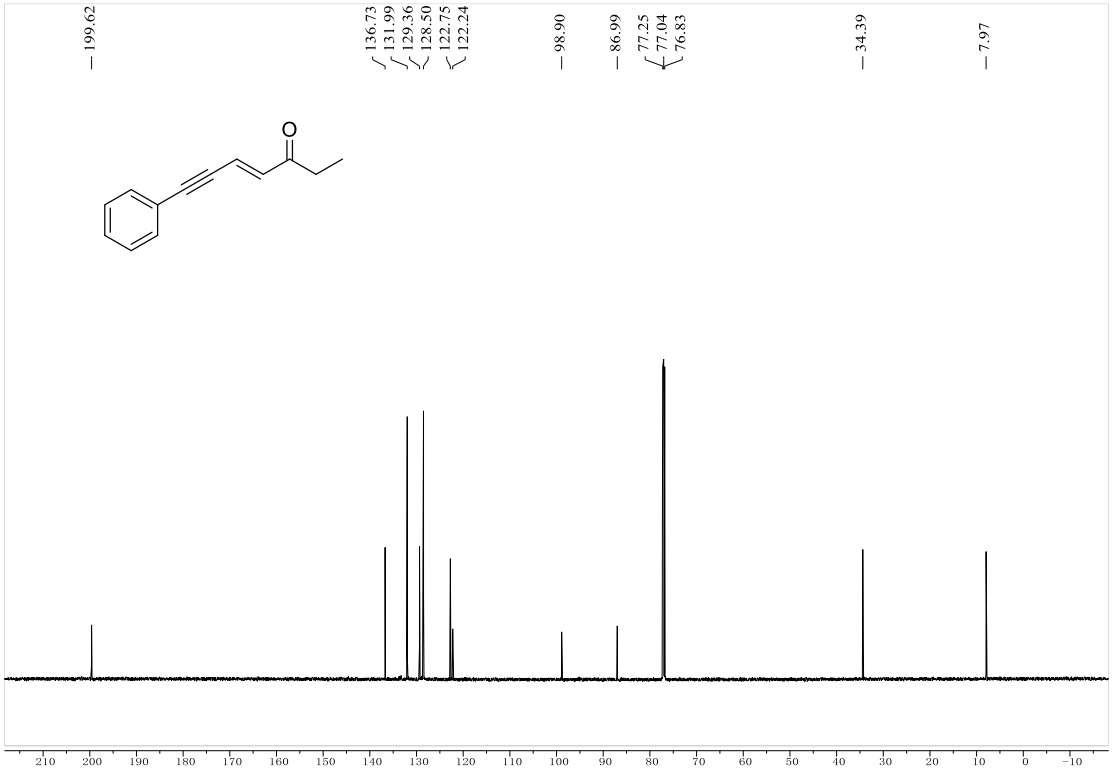
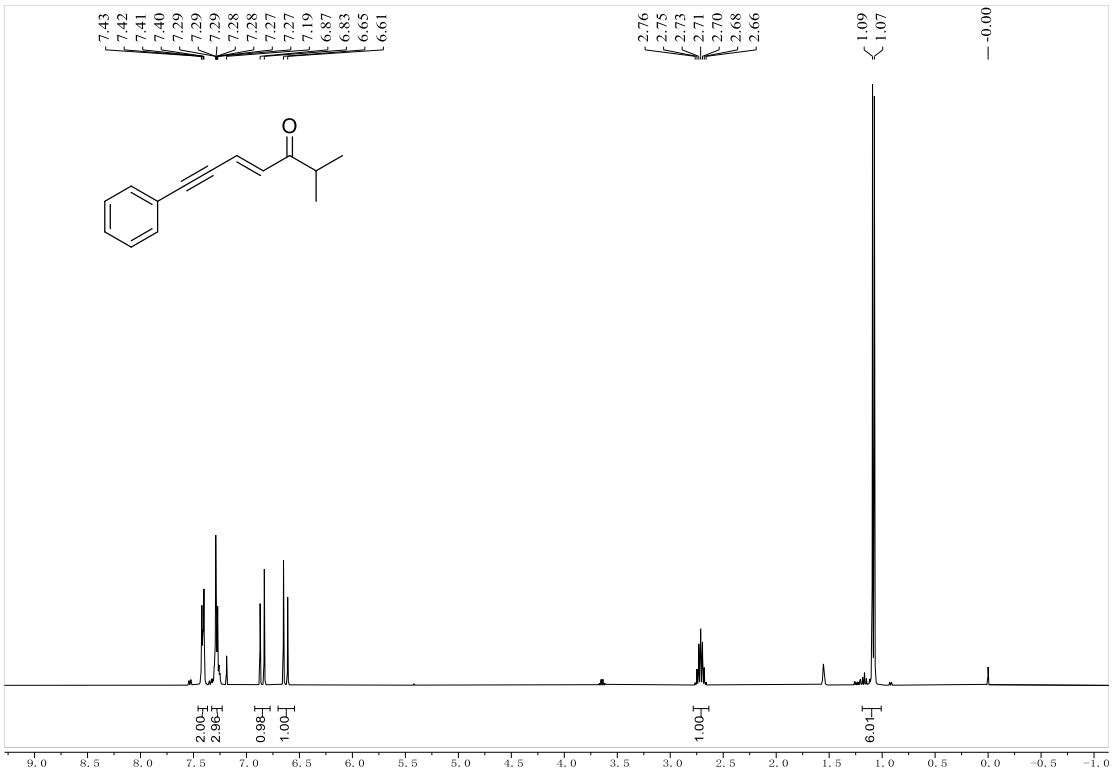


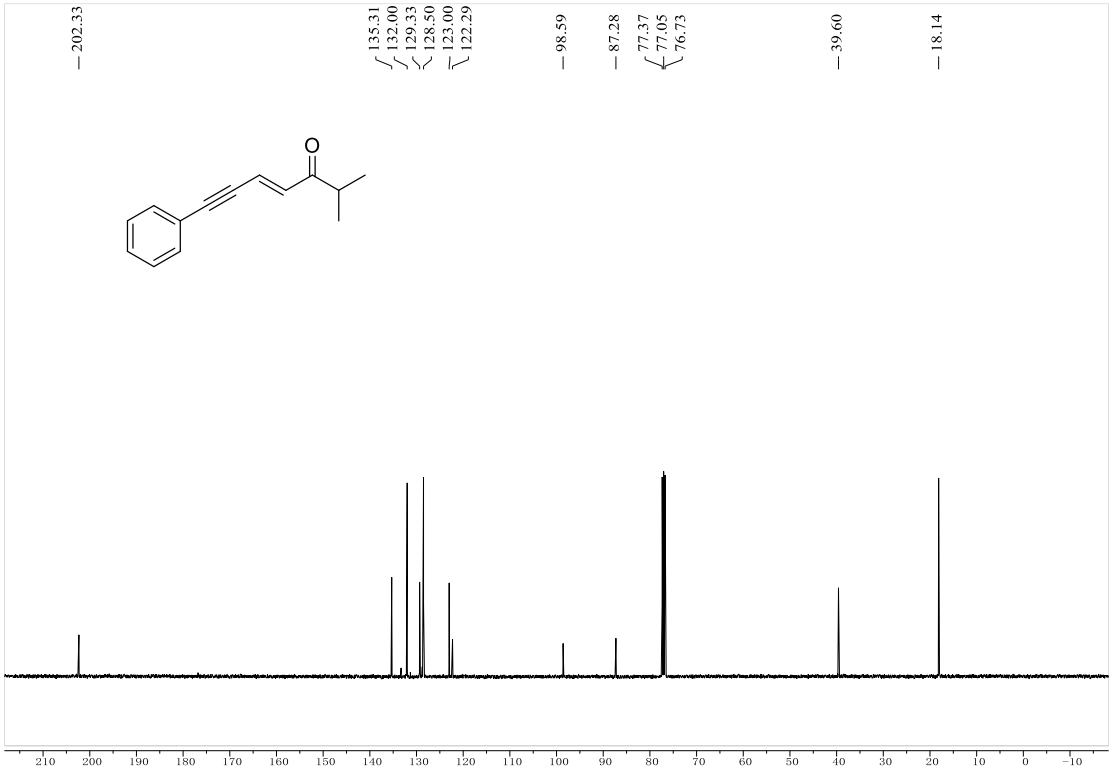
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1v**



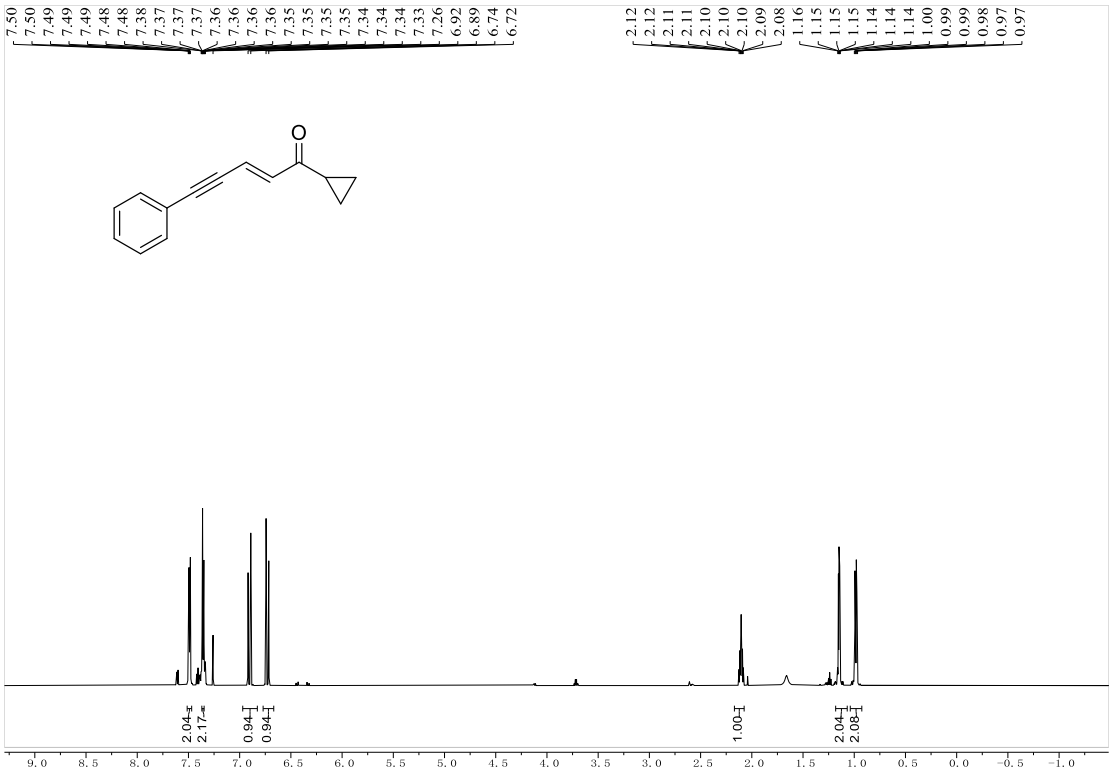
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1w**



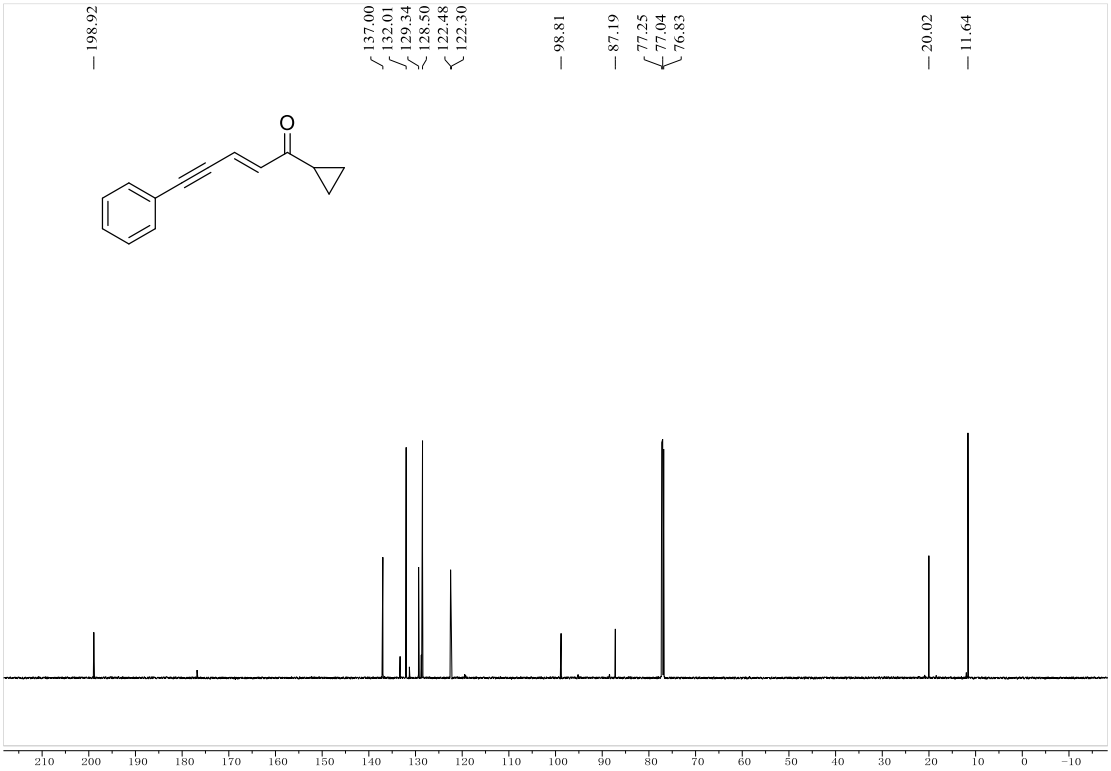
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **1w**



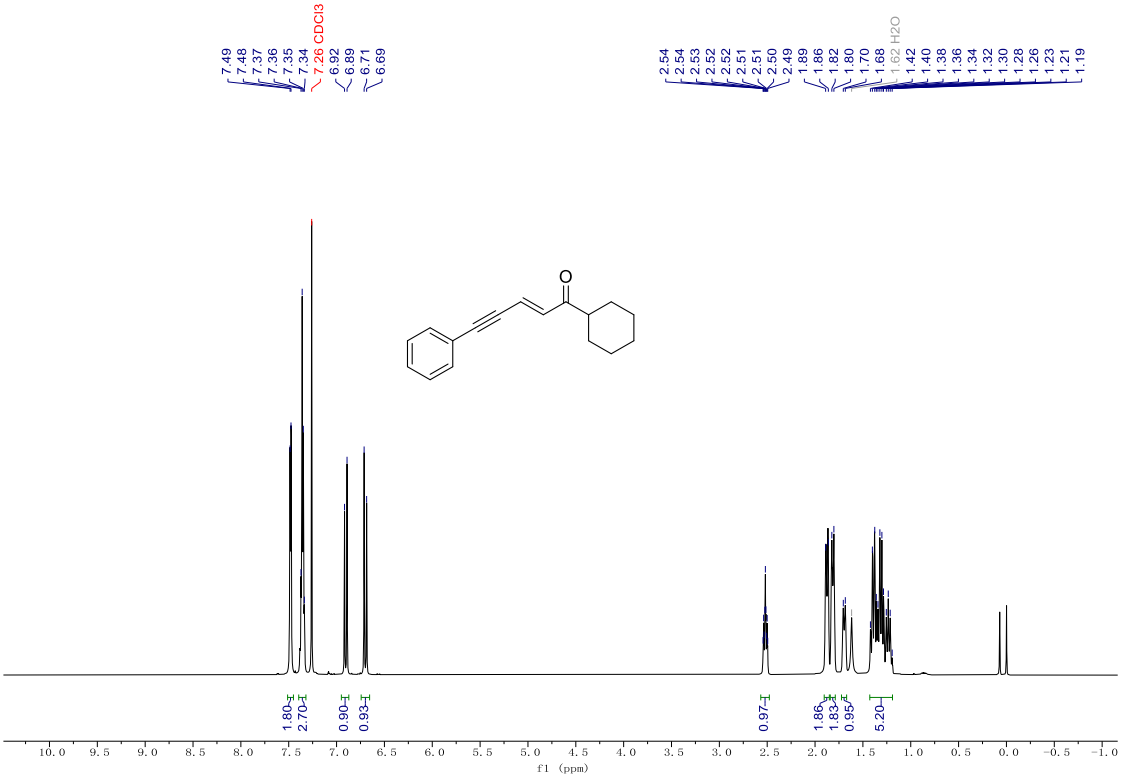
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1x**



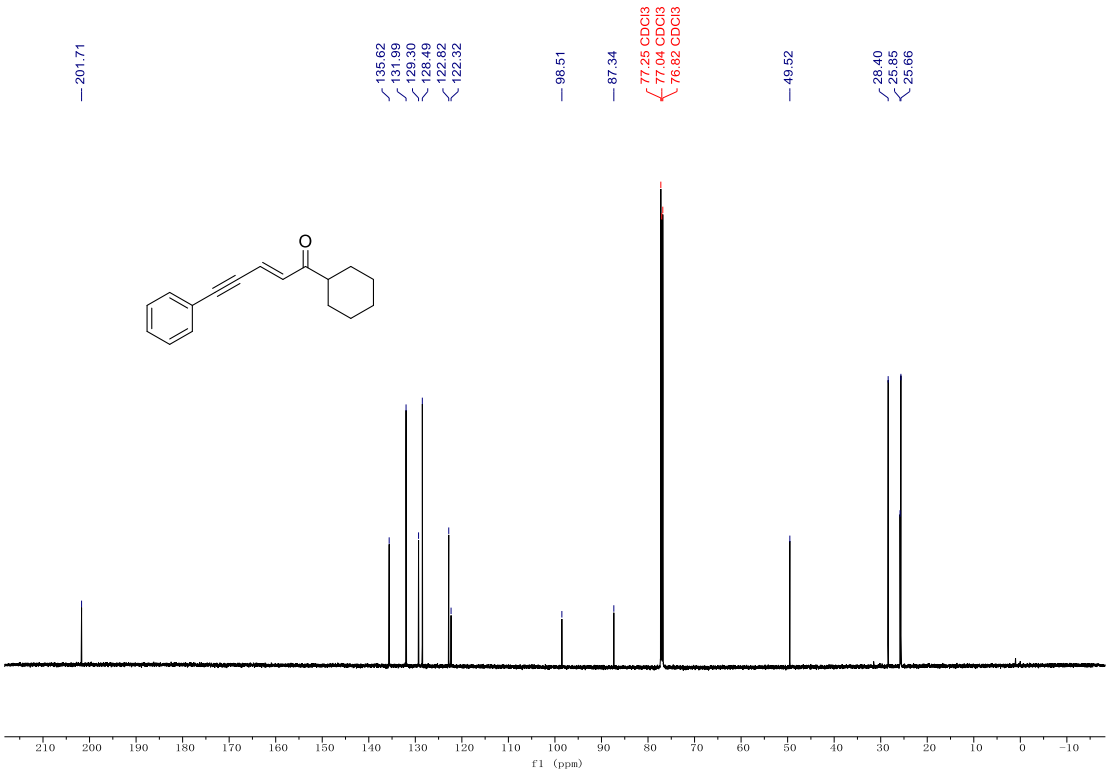
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1x**



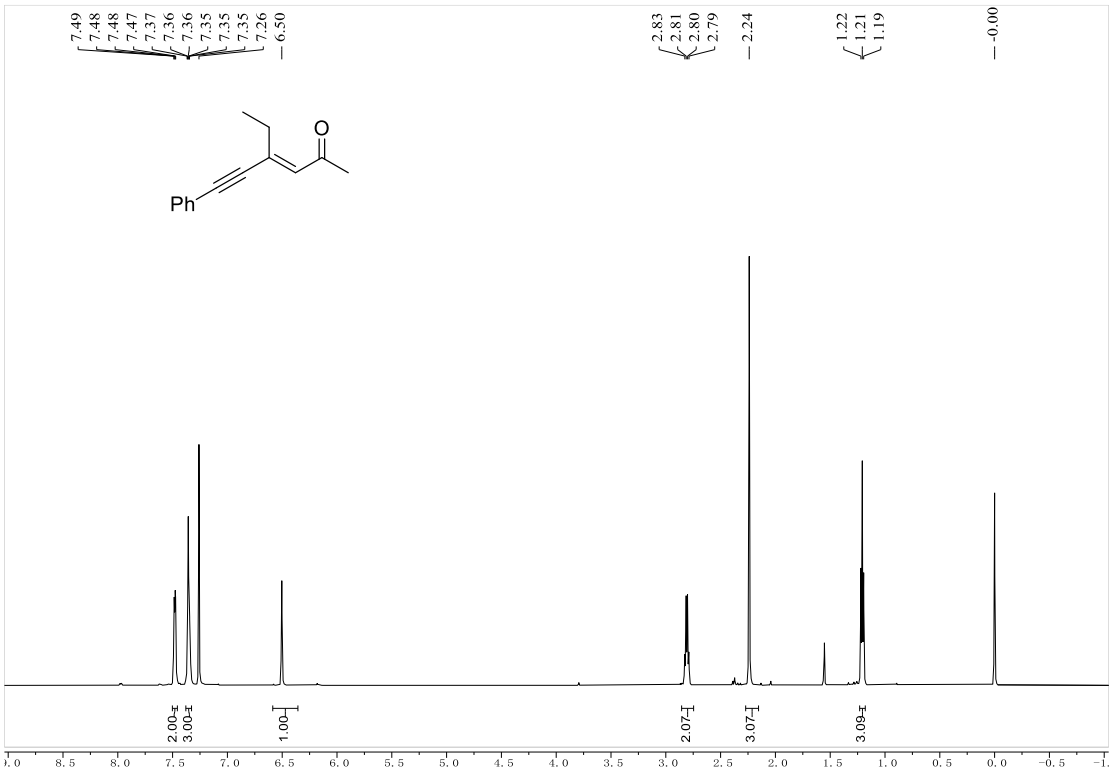
^{1}H NMR (600 MHz, $CDCl_3$) of **1y**



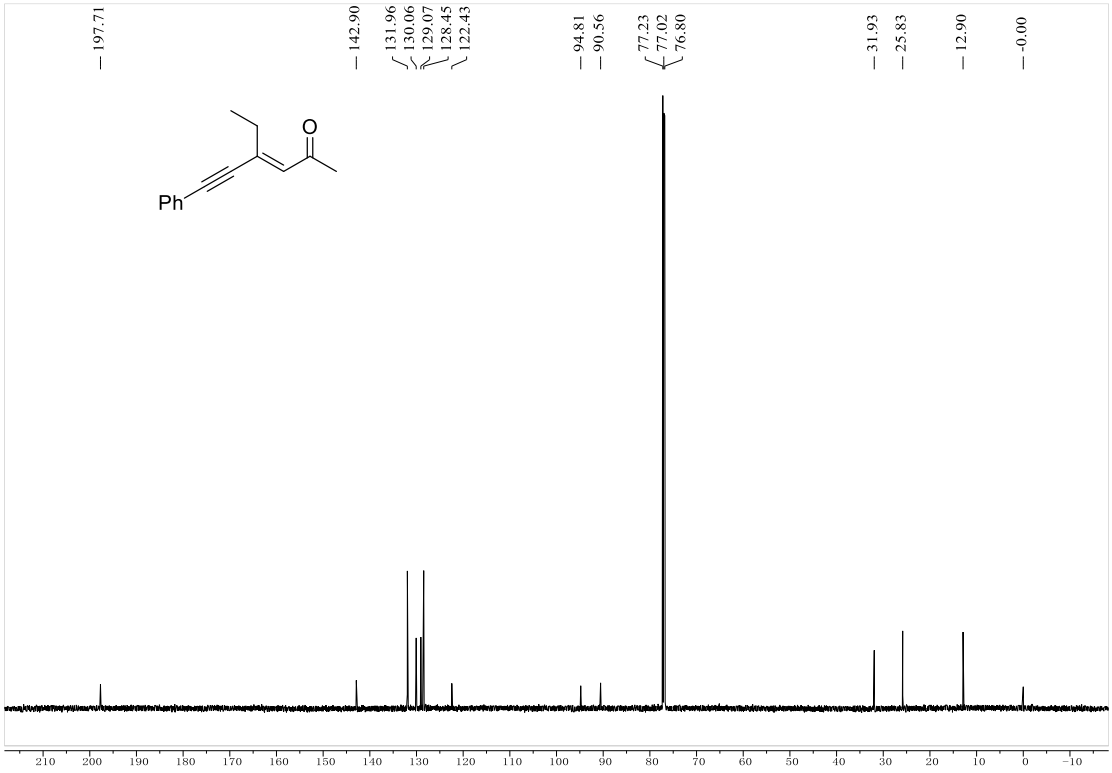
^{13}C NMR (151 MHz, $CDCl_3$) of **1y**



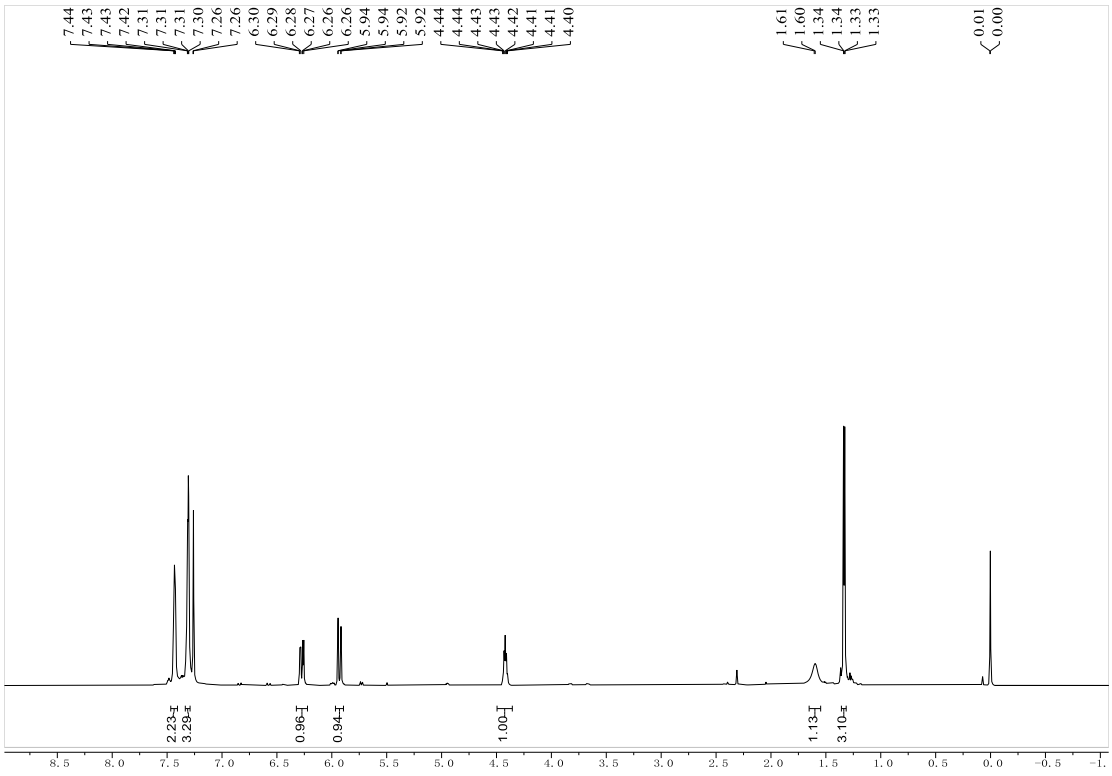
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1aa**



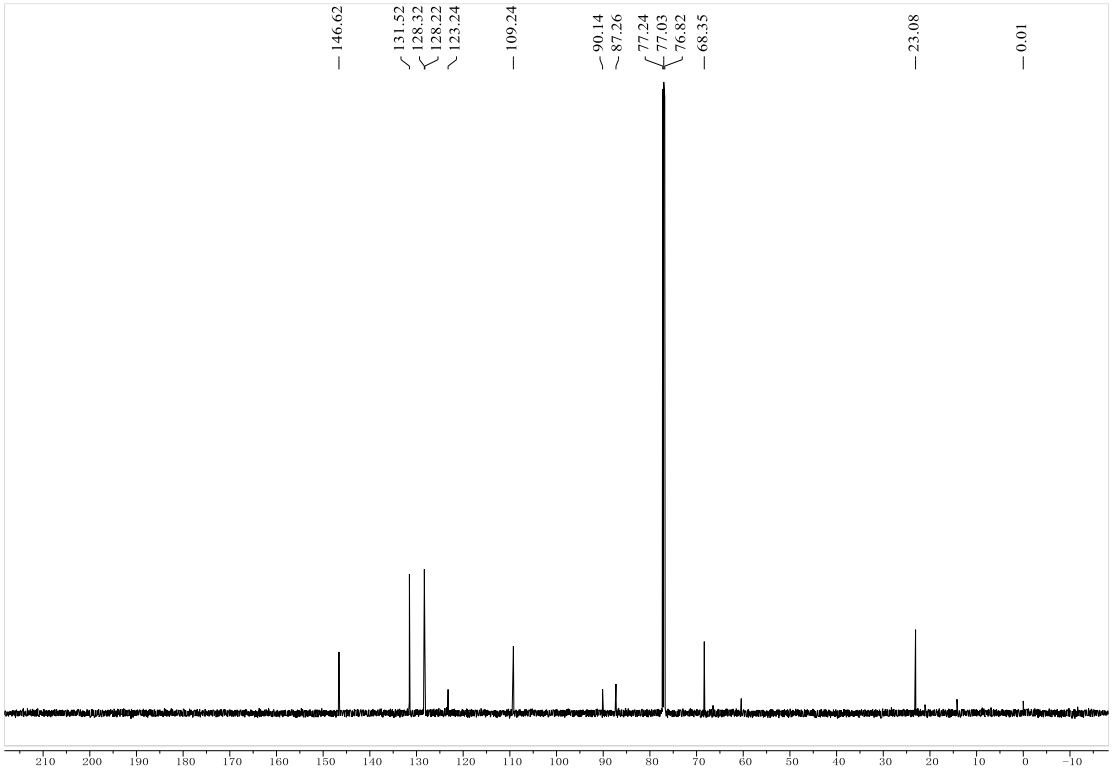
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **1aa**



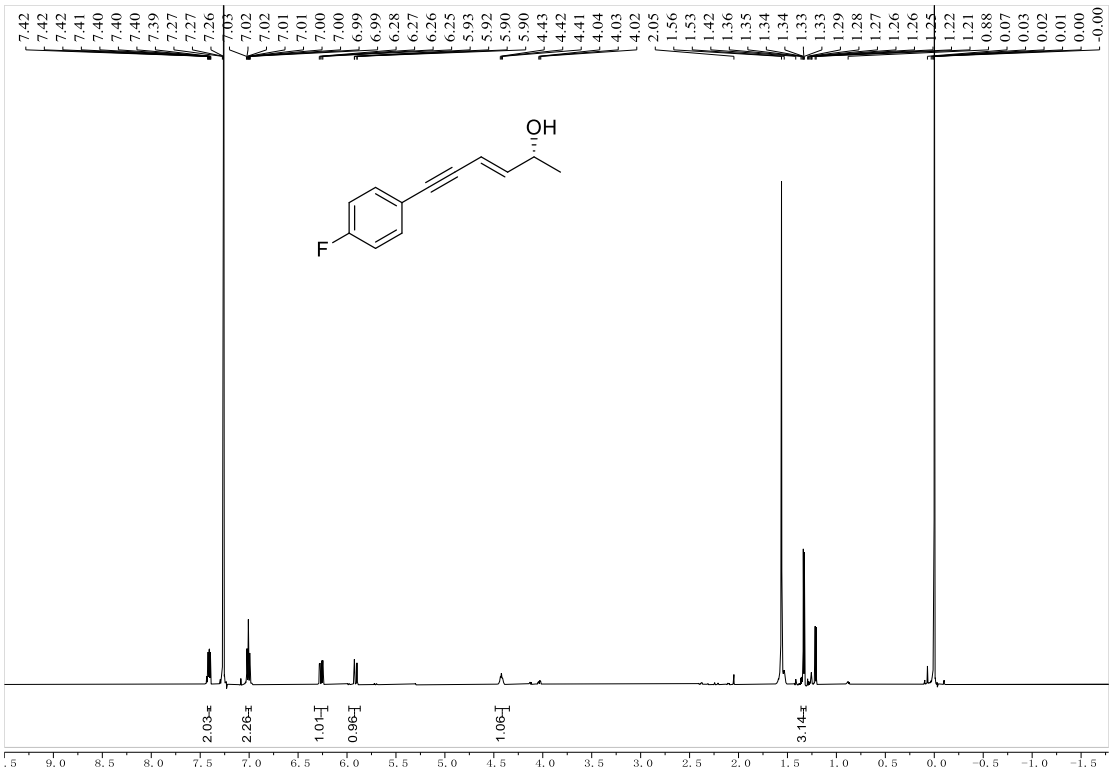
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2a**



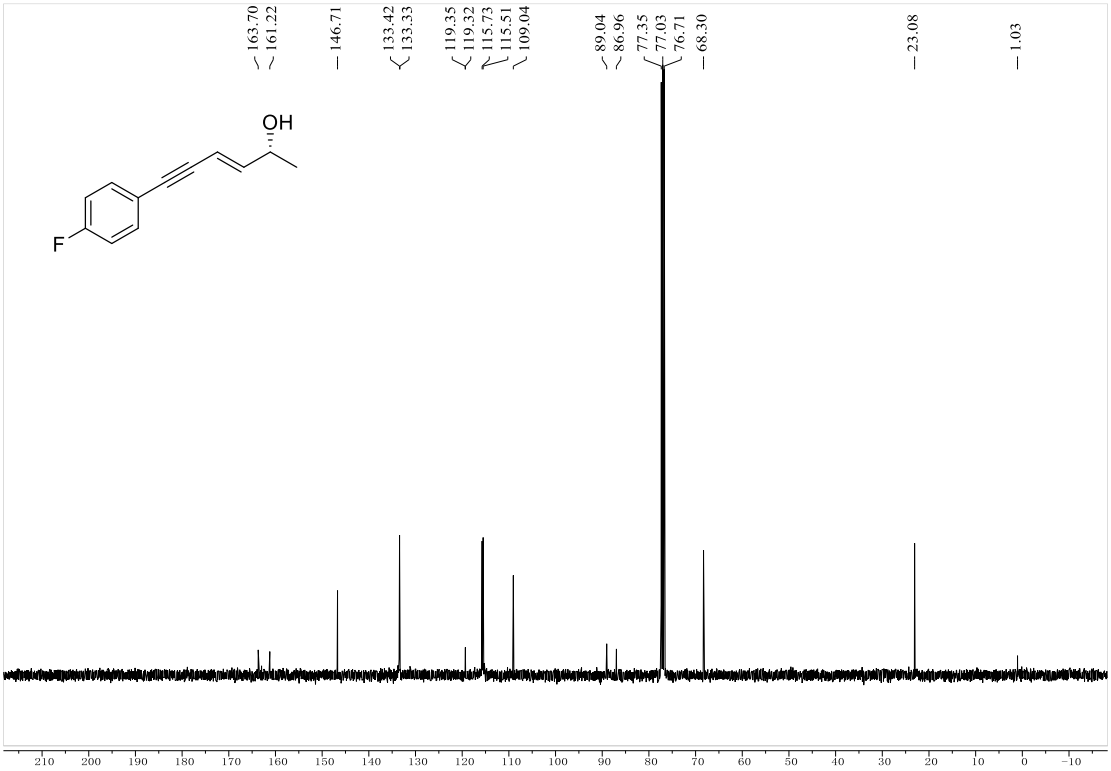
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2a**



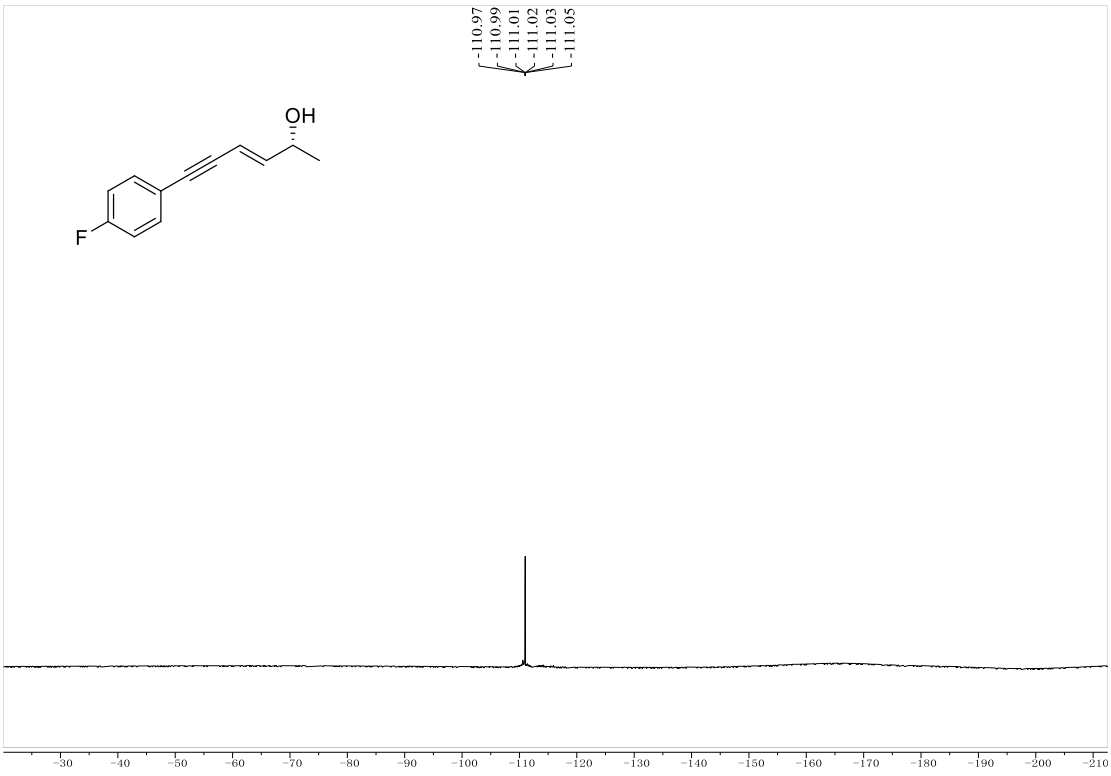
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2b**



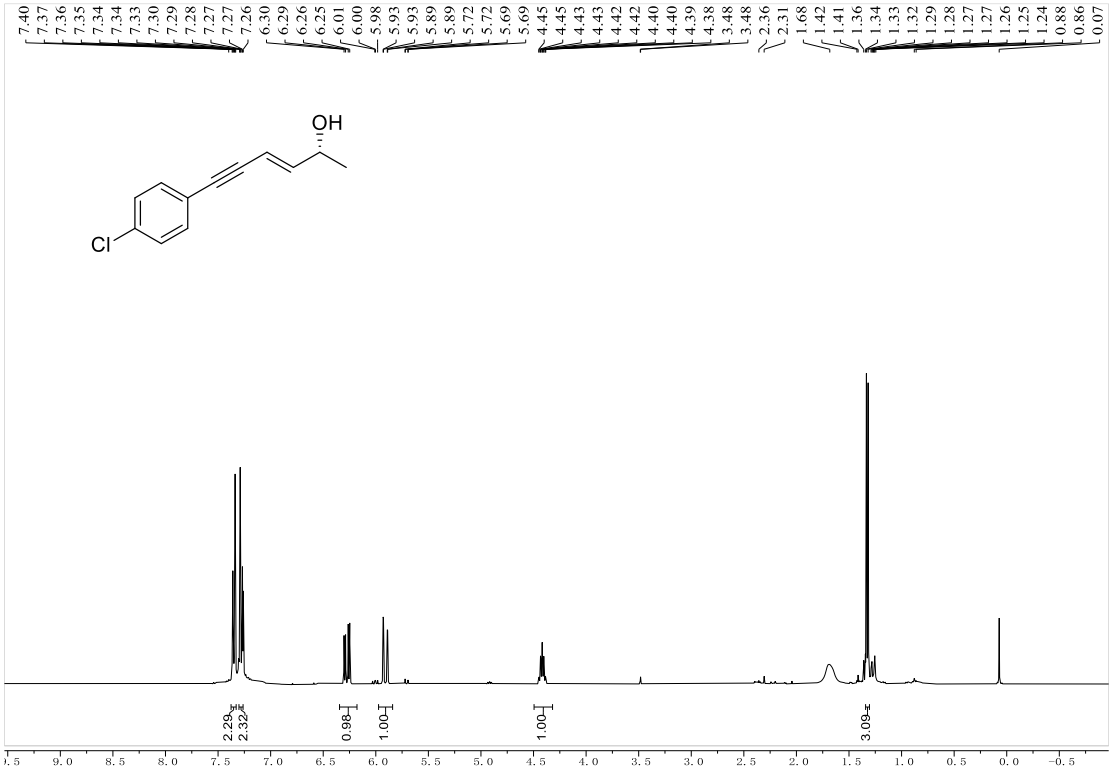
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2b**



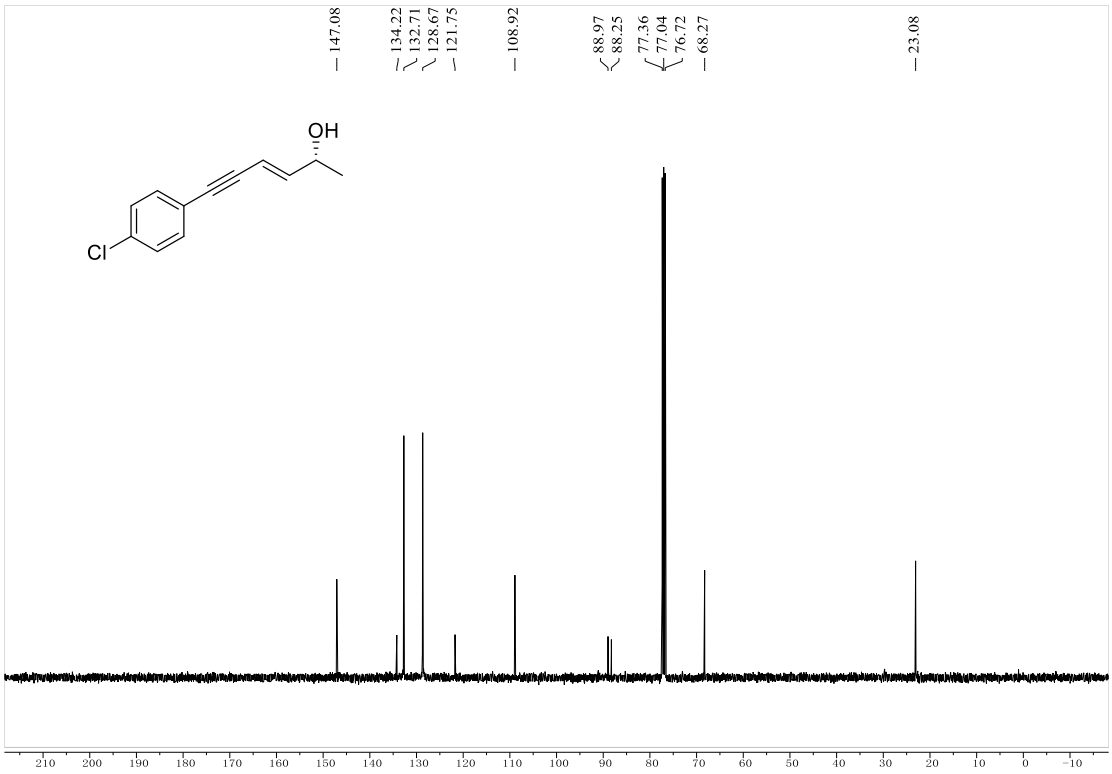
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **2b**



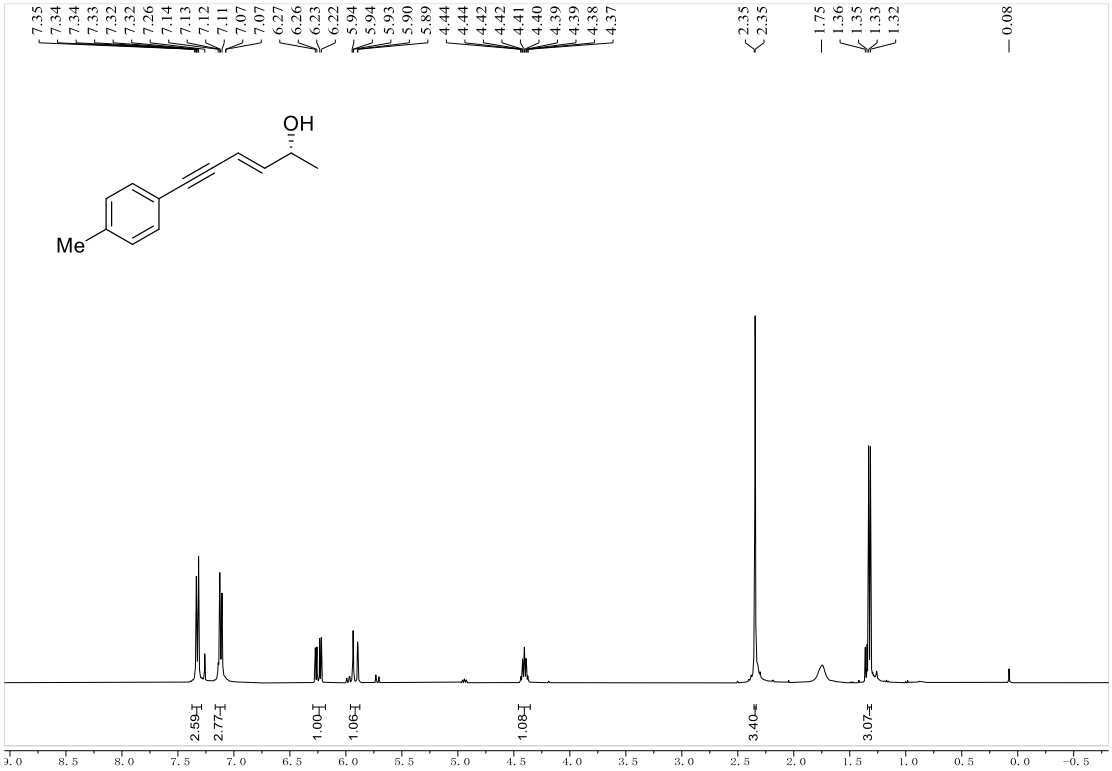
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2c**



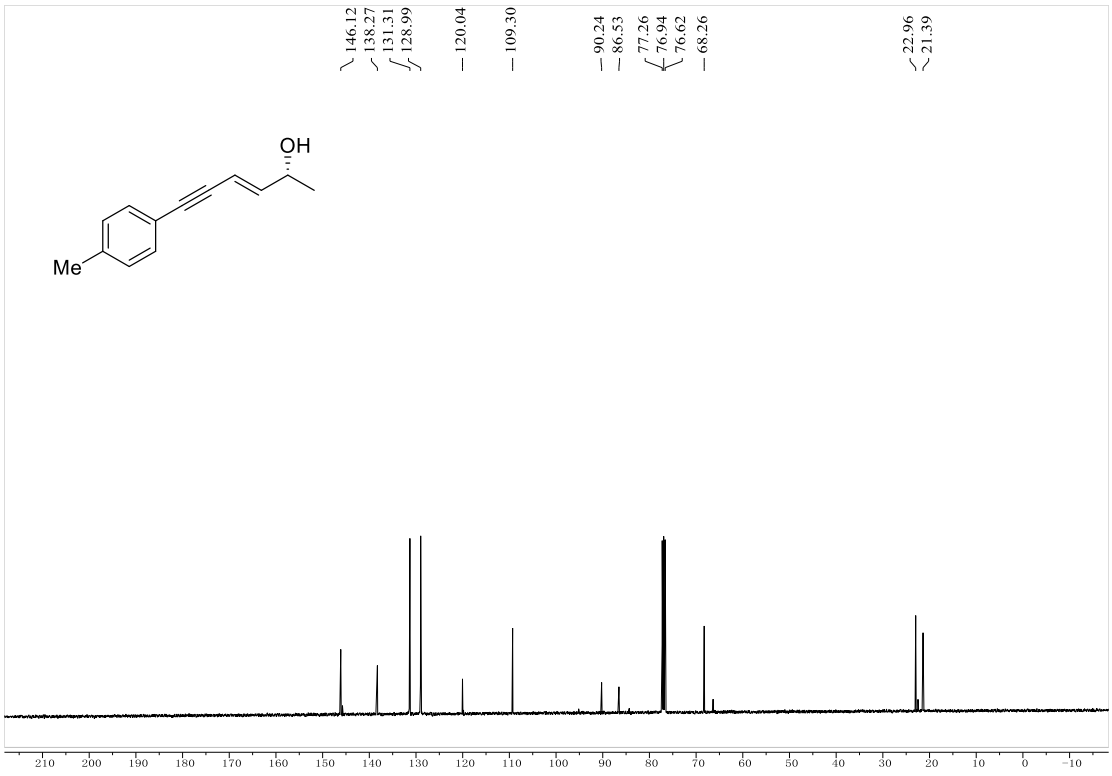
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **2c**



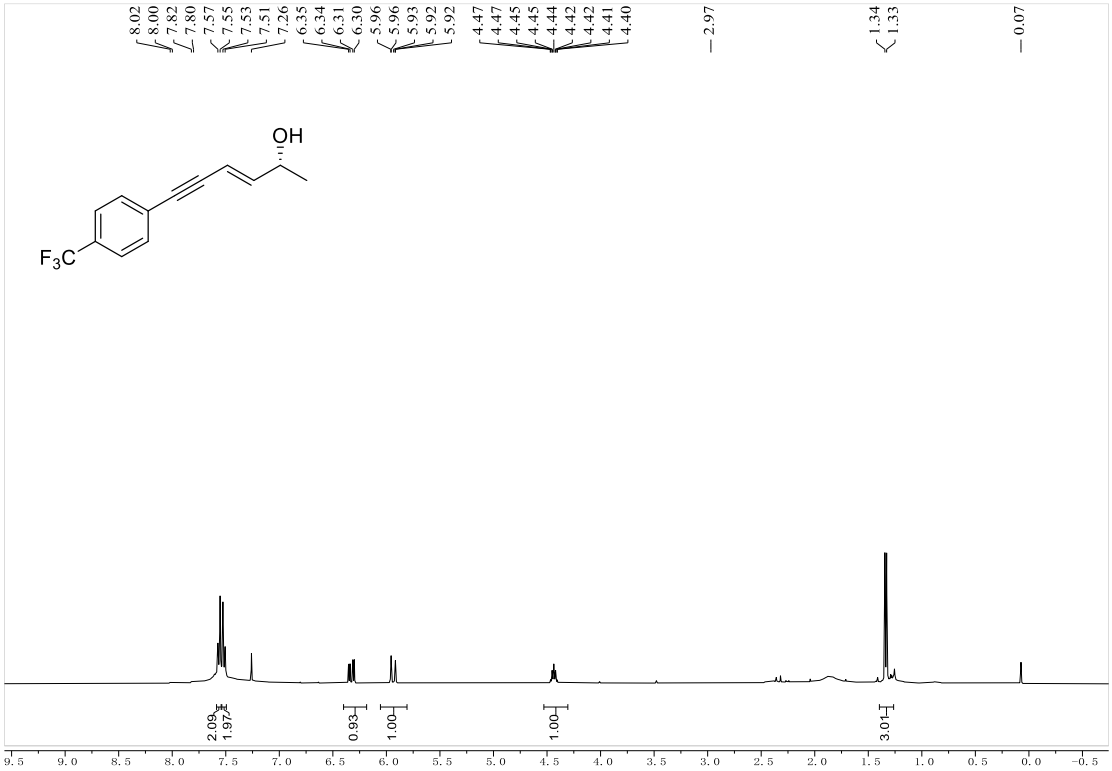
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2d**



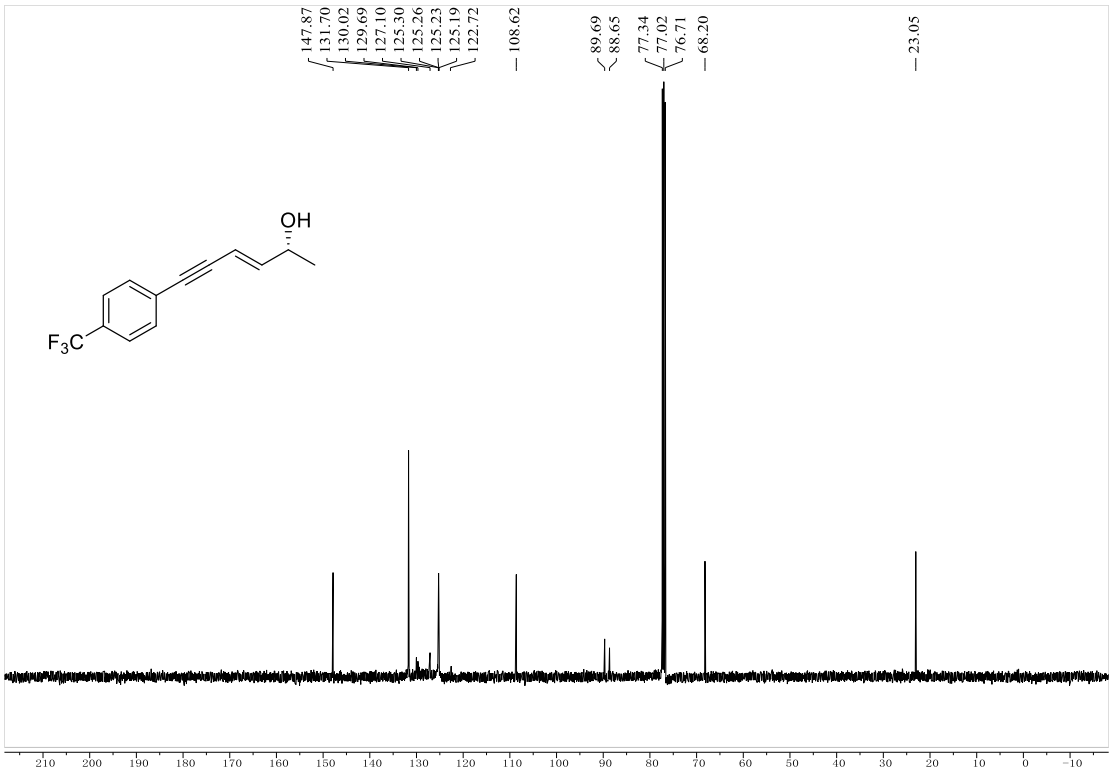
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **2d**



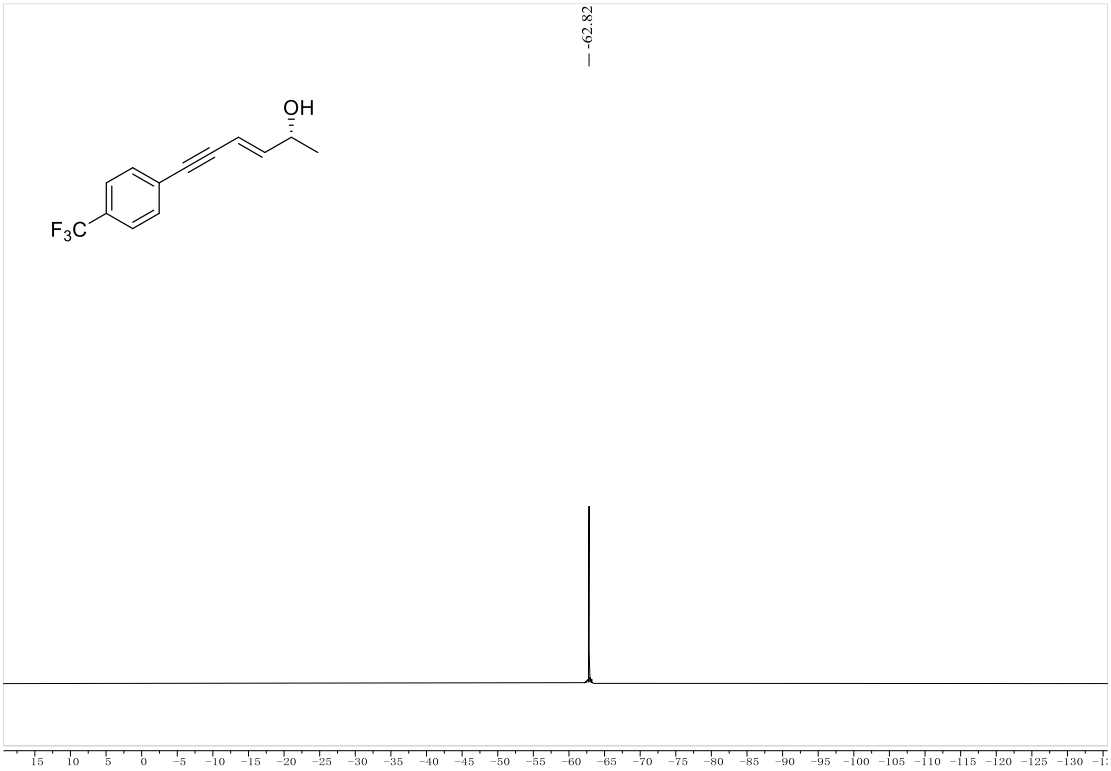
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2e**



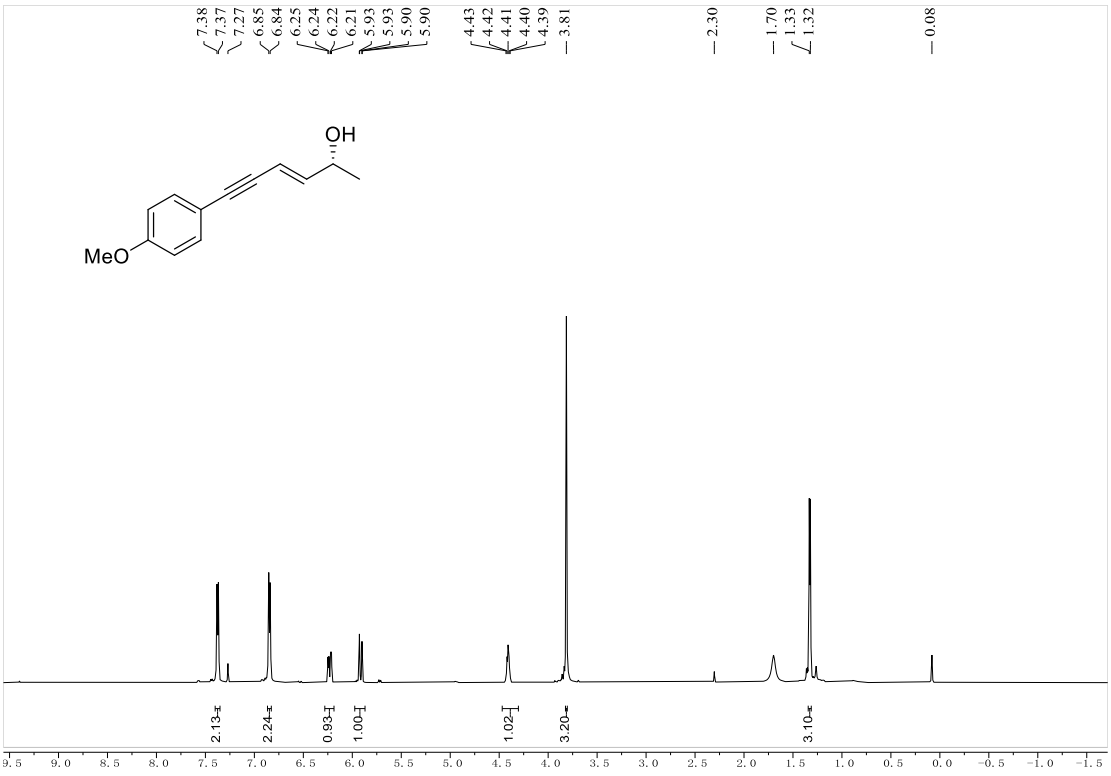
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **2e**



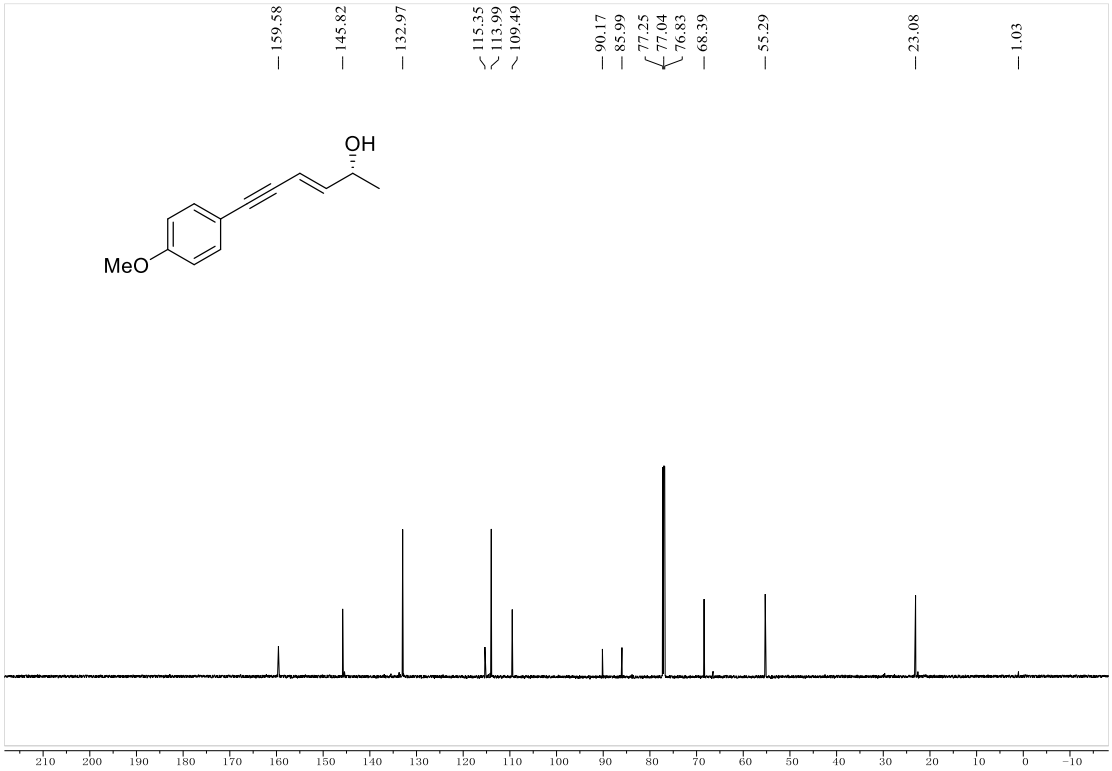
^{19}F NMR spectra (377 MHz, $CDCl_3$) of **2e**



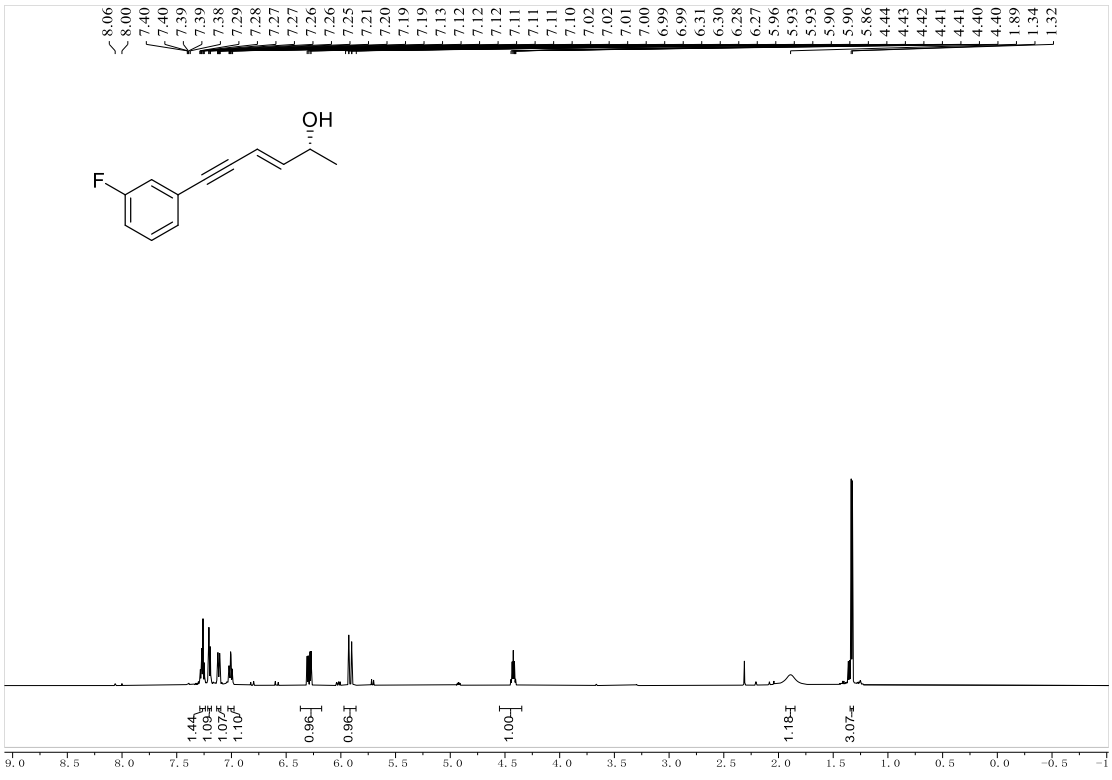
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2f**



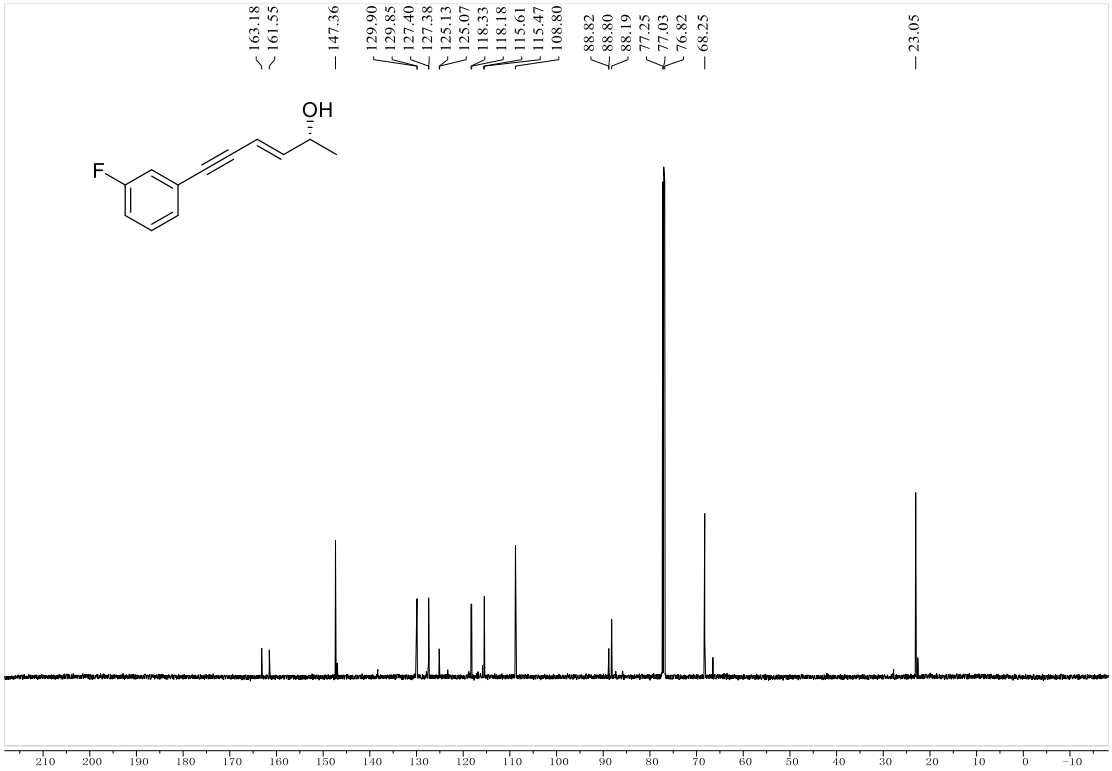
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2f**



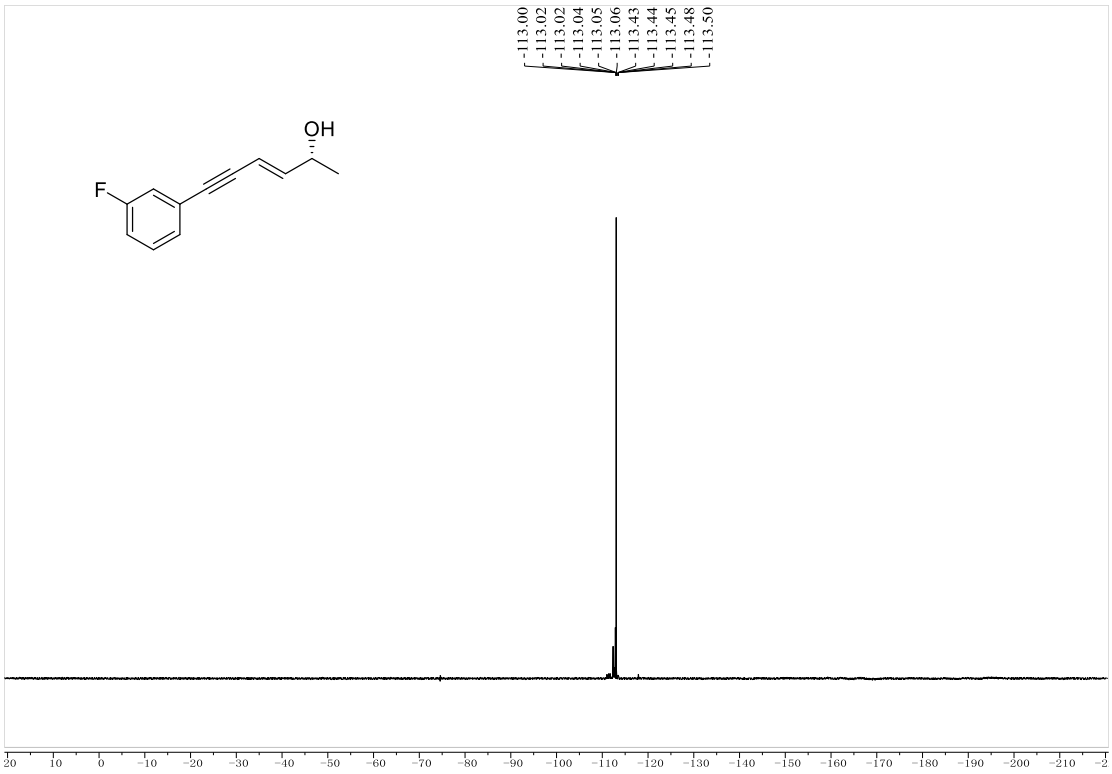
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2g**



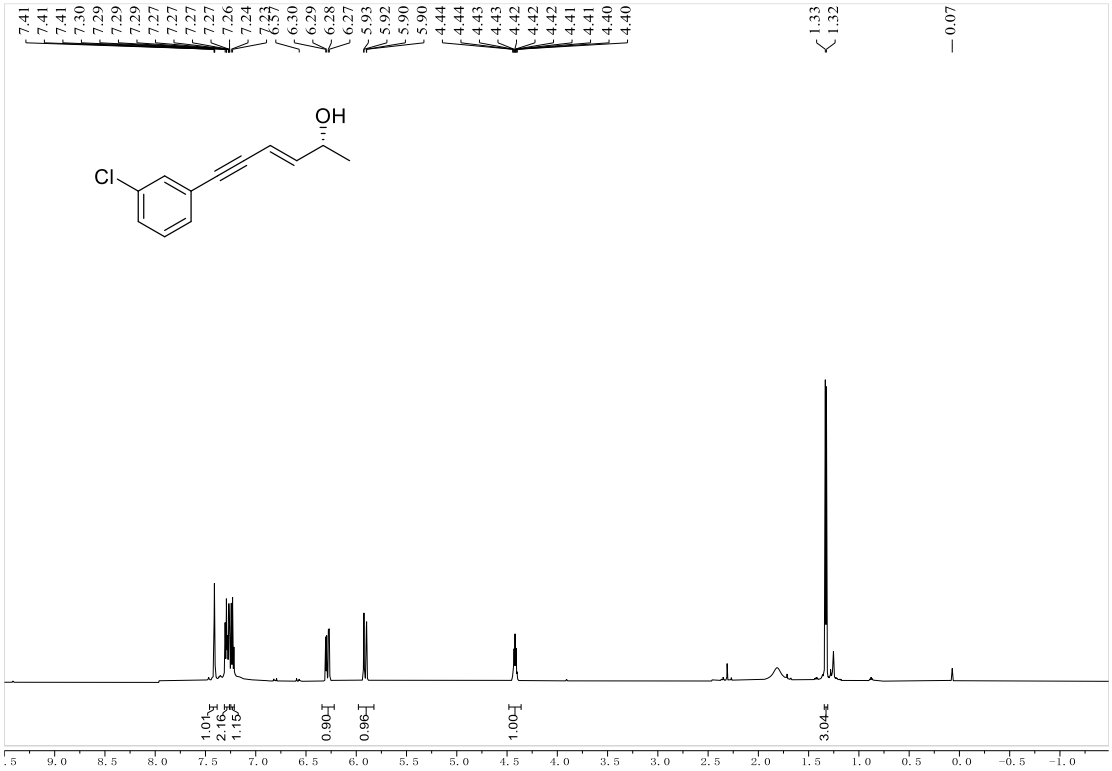
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2g**



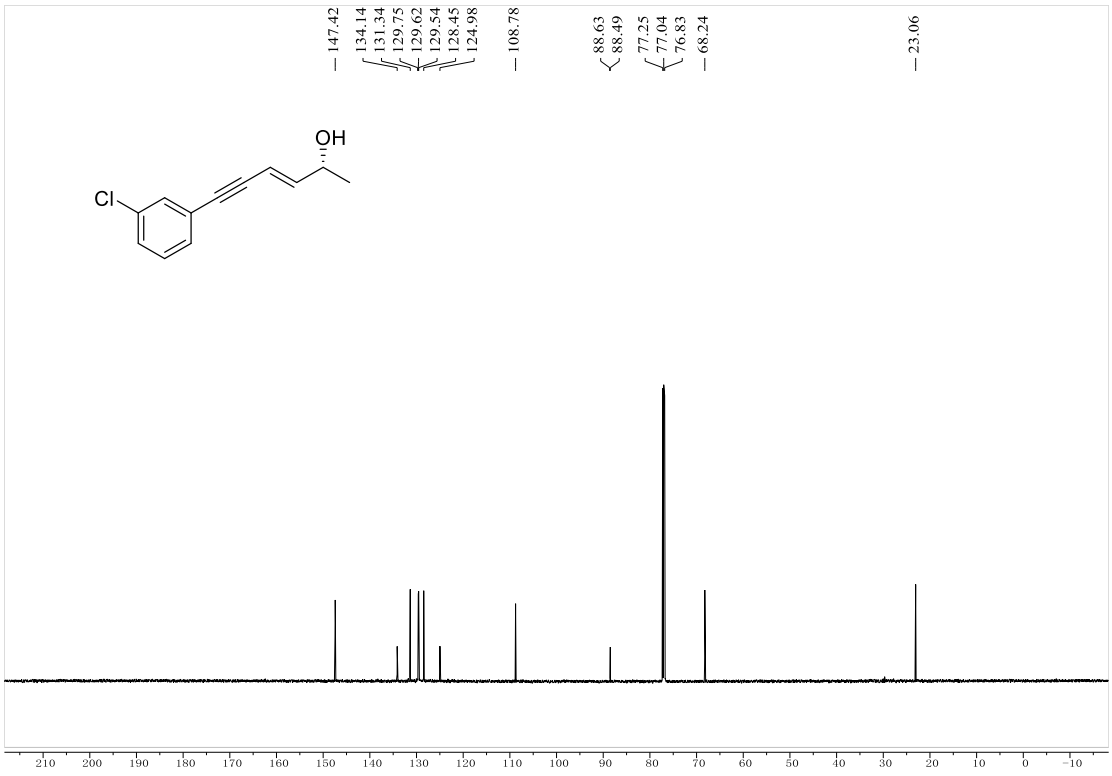
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **2g**



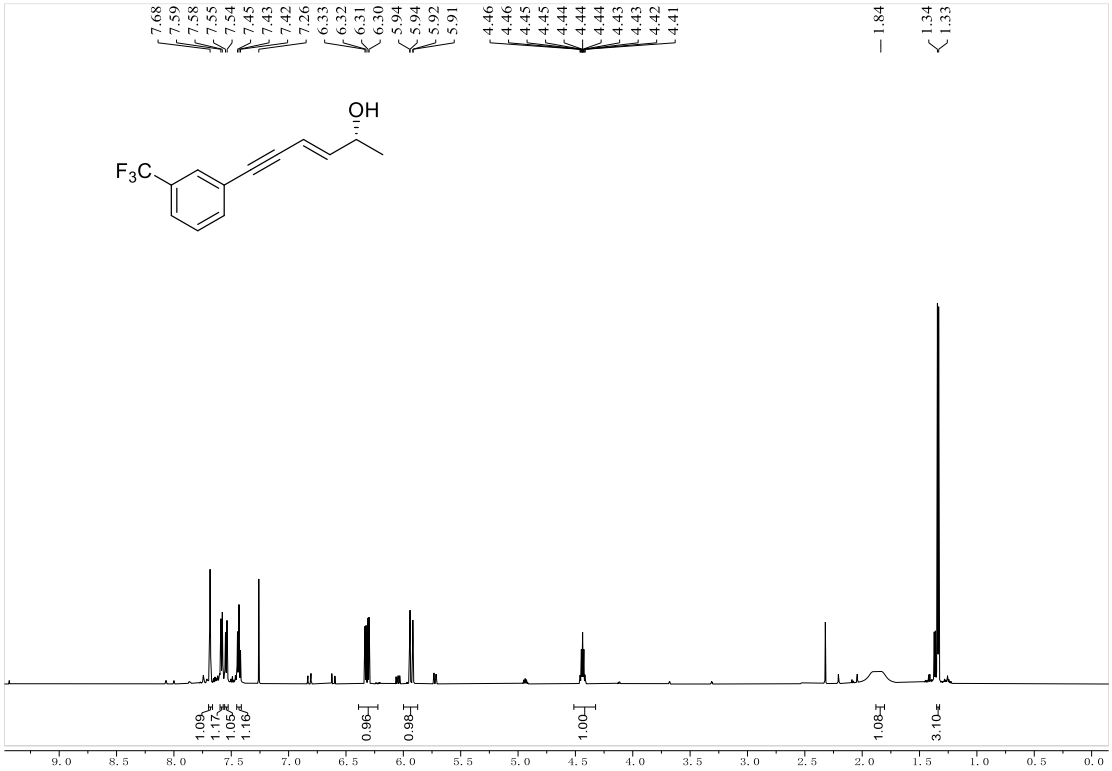
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2h**



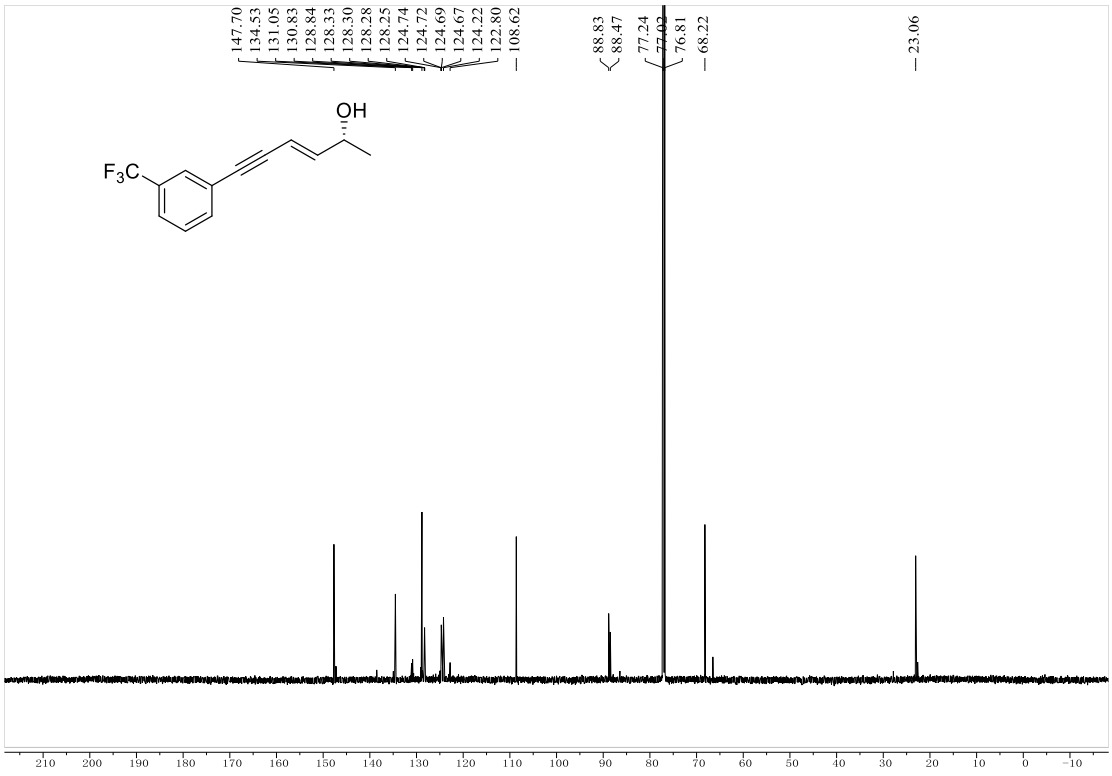
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2h**



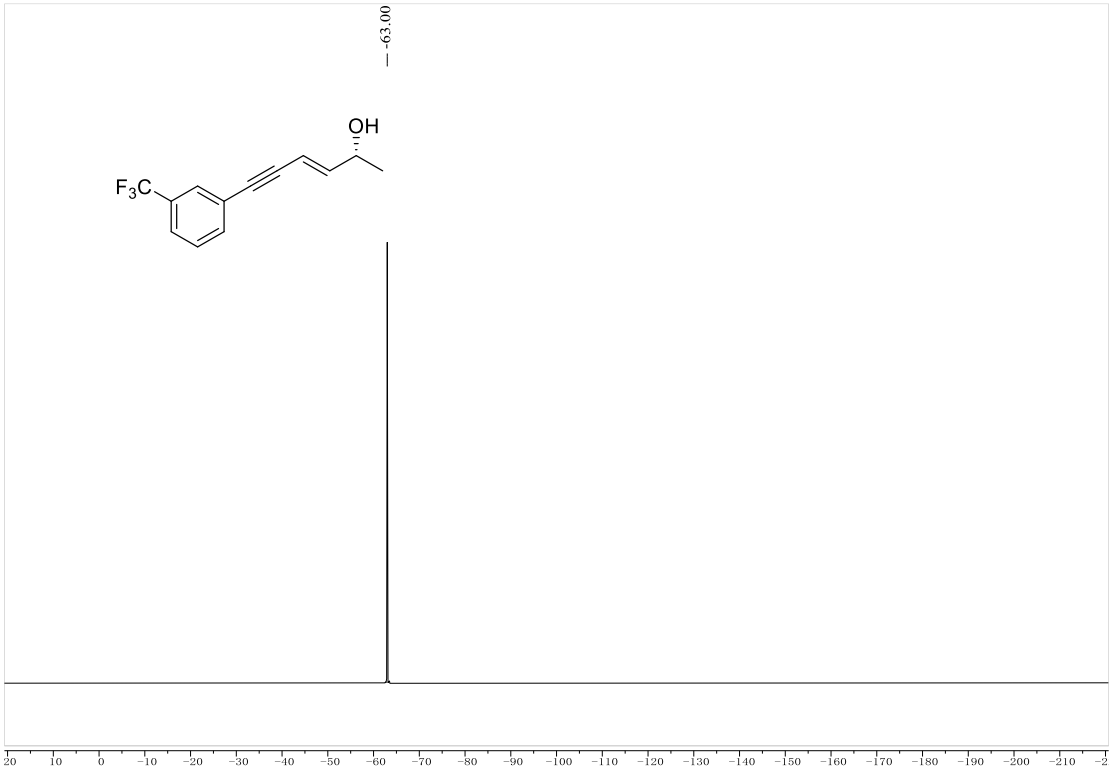
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2i**



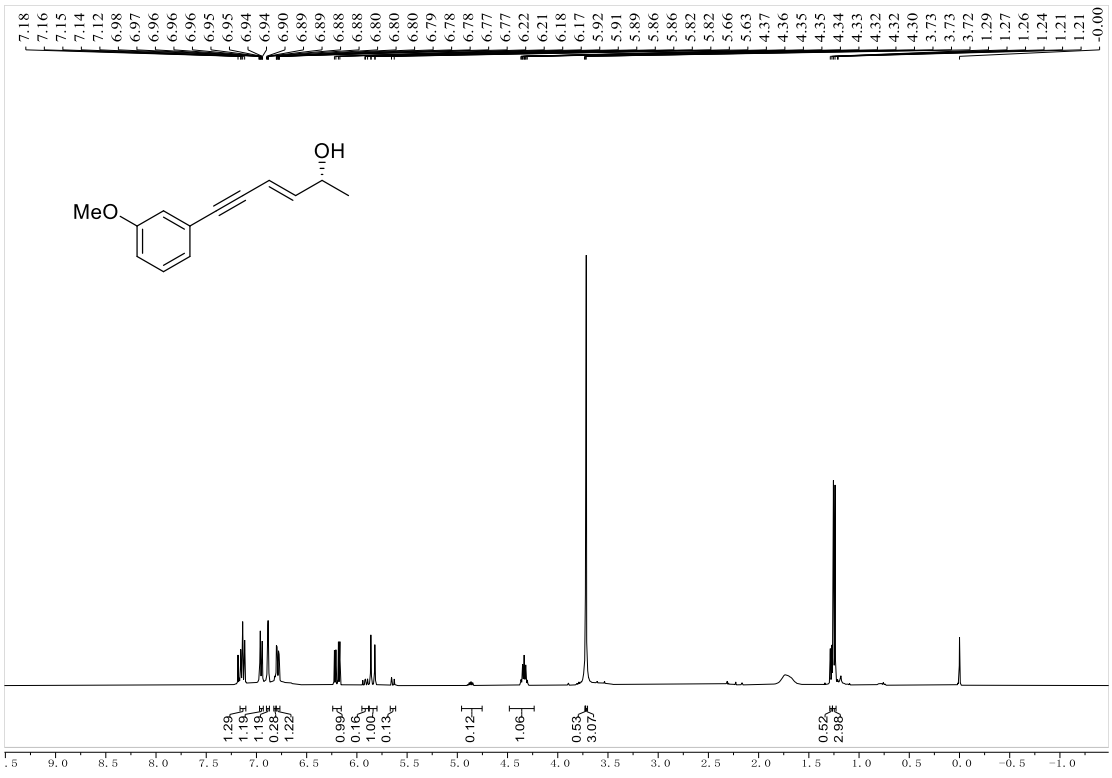
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2i**



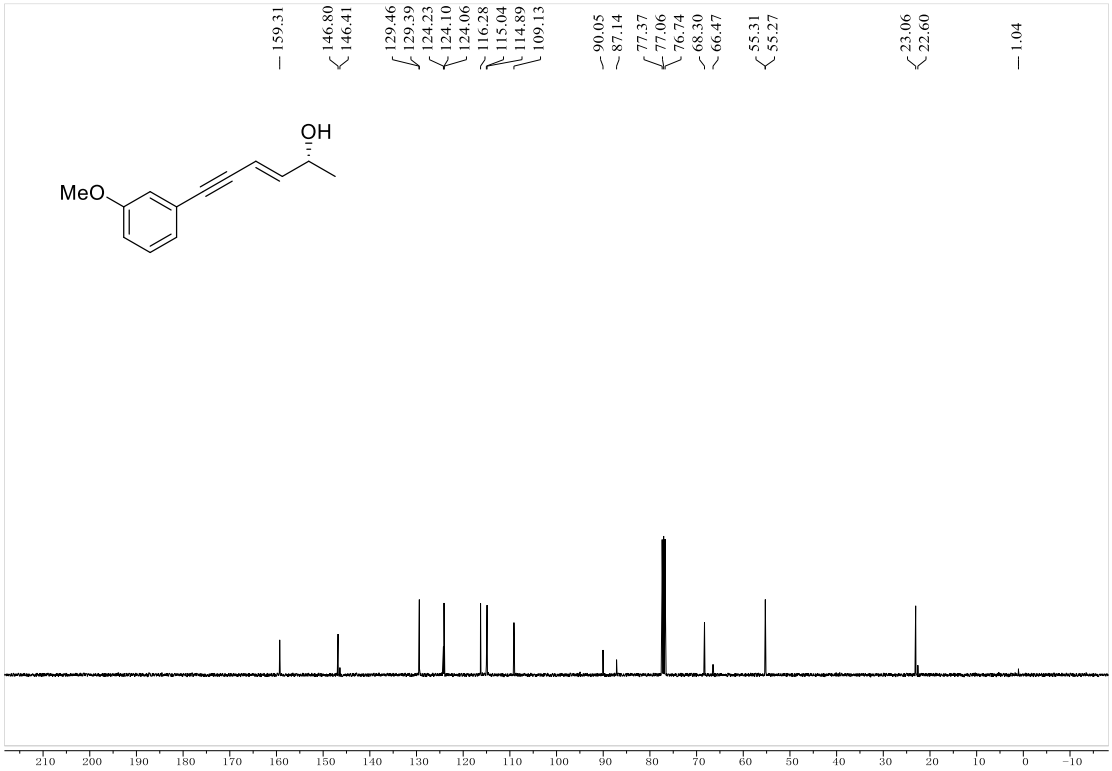
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **2i**



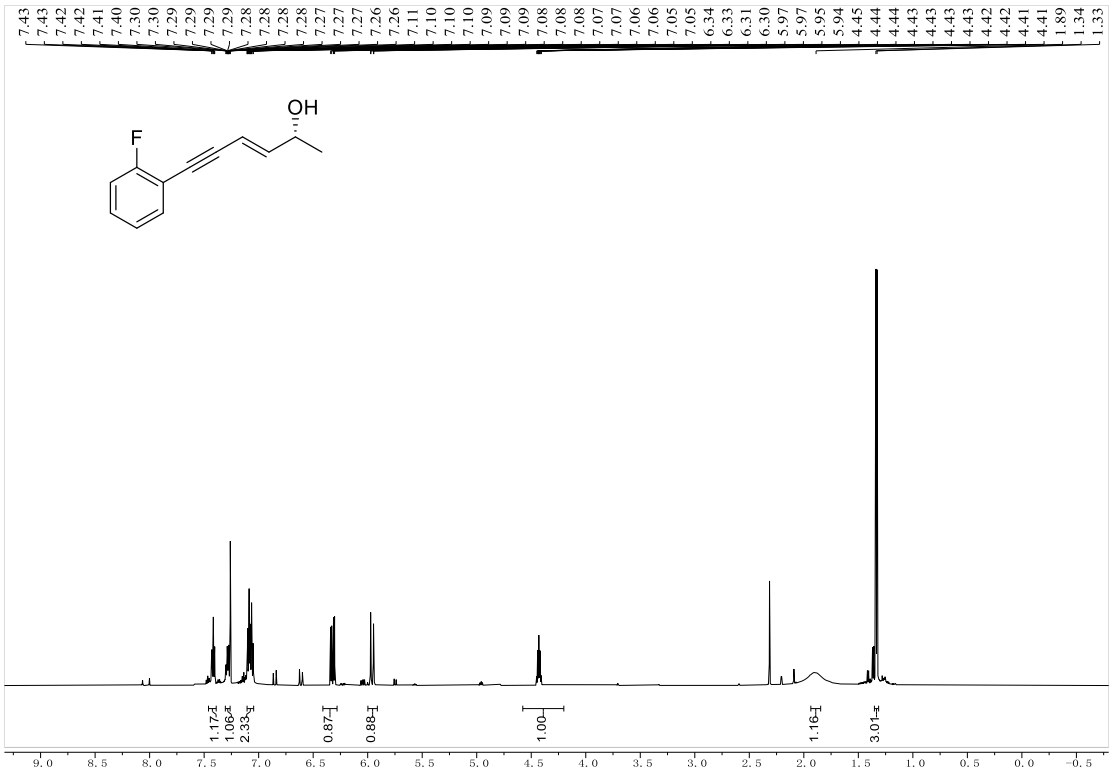
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2j**



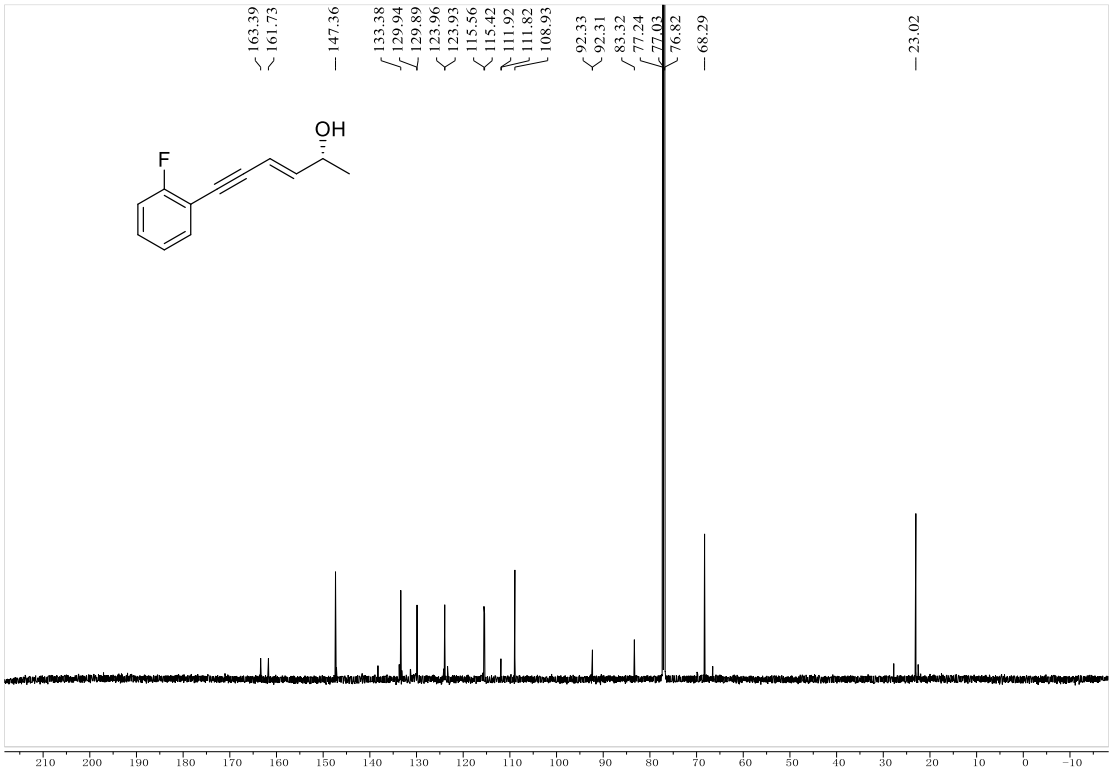
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **2j**



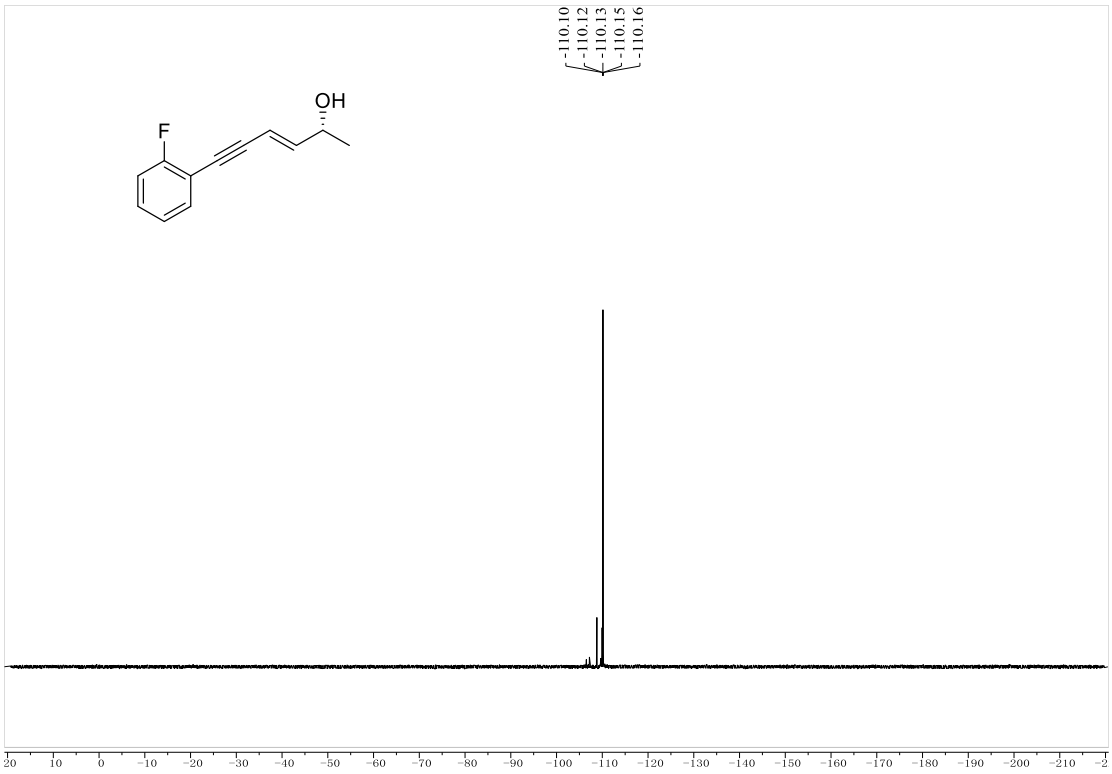
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2k**



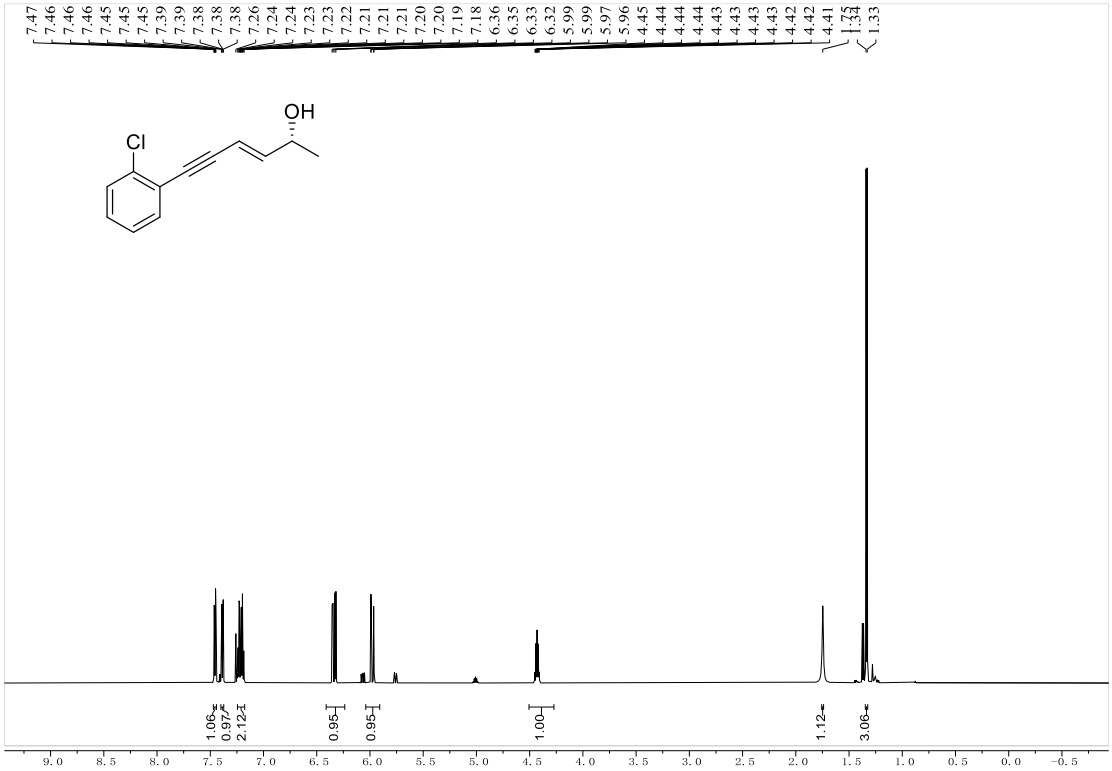
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2k**



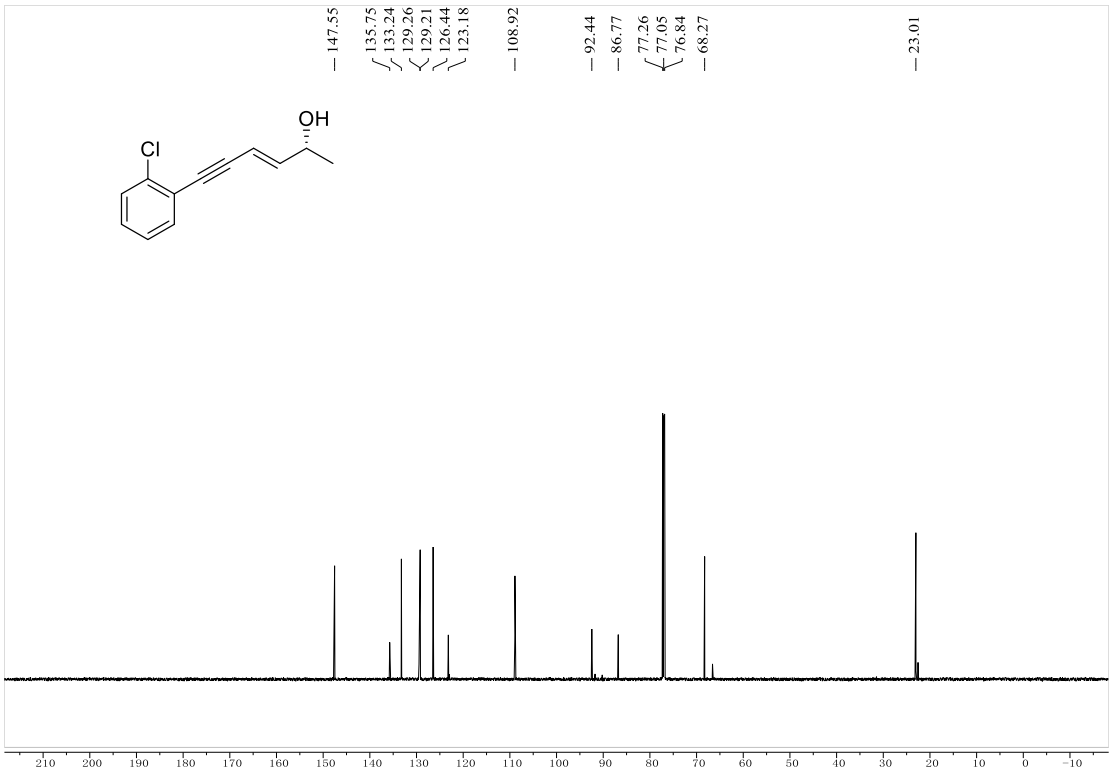
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **2k**



^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2l**



^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2l**



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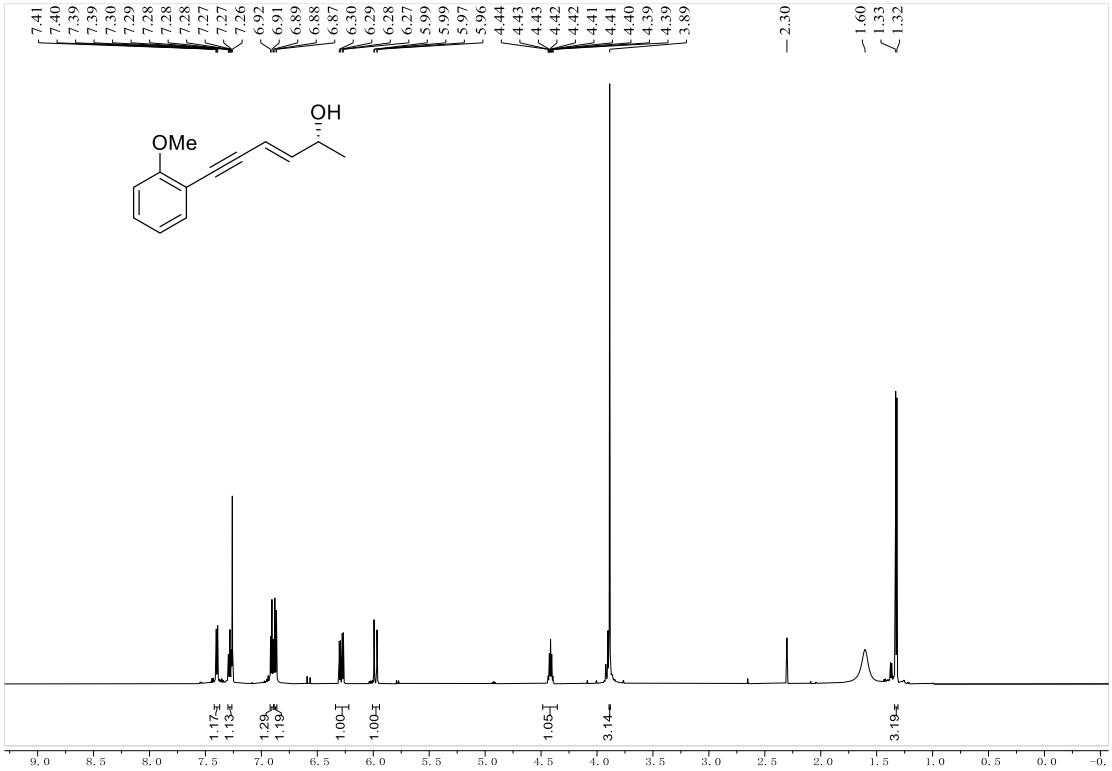
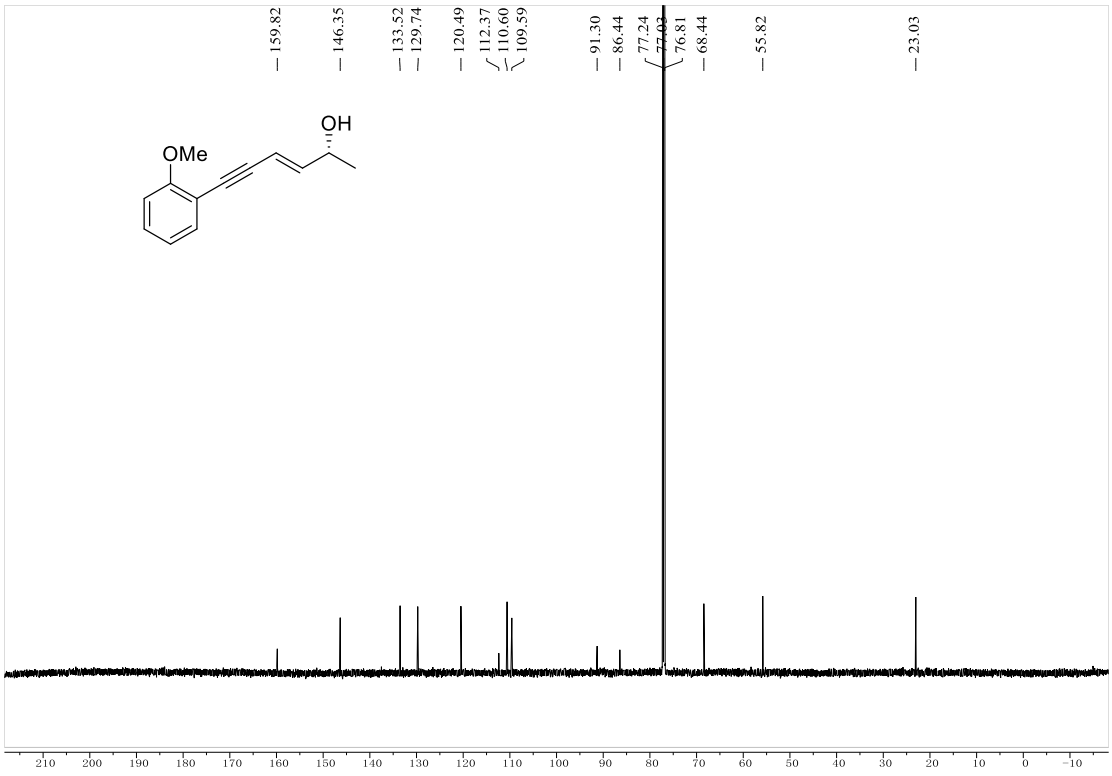
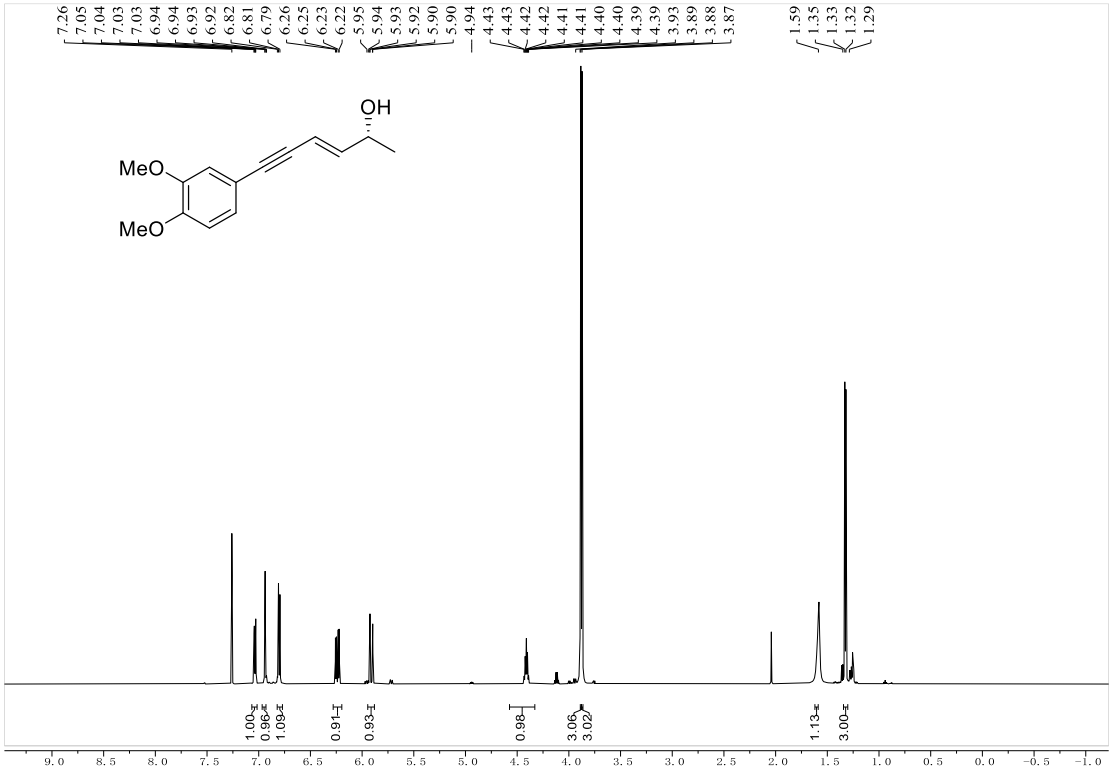


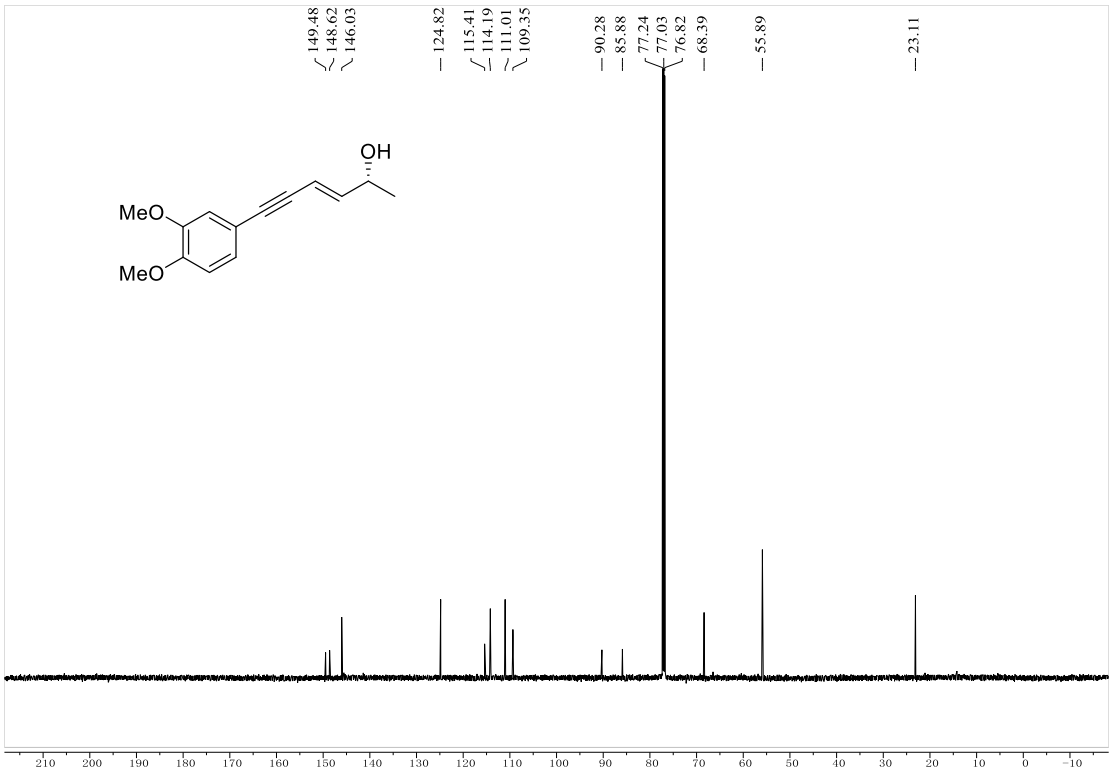
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2m**



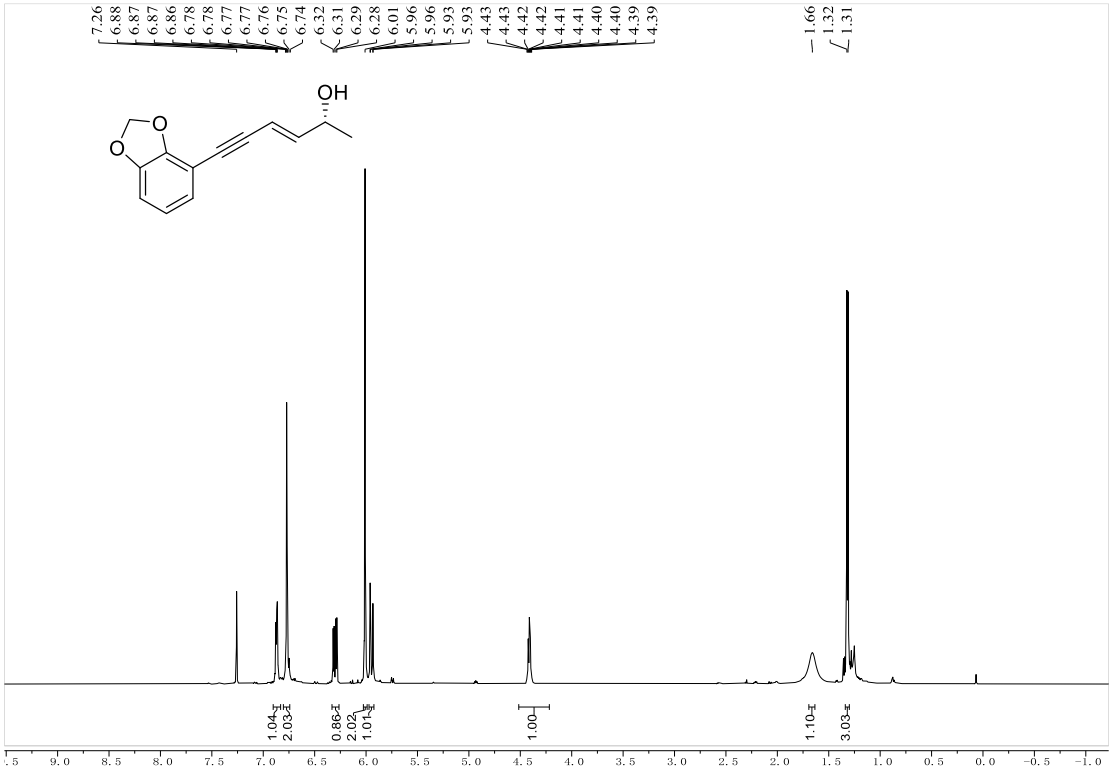
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2n**



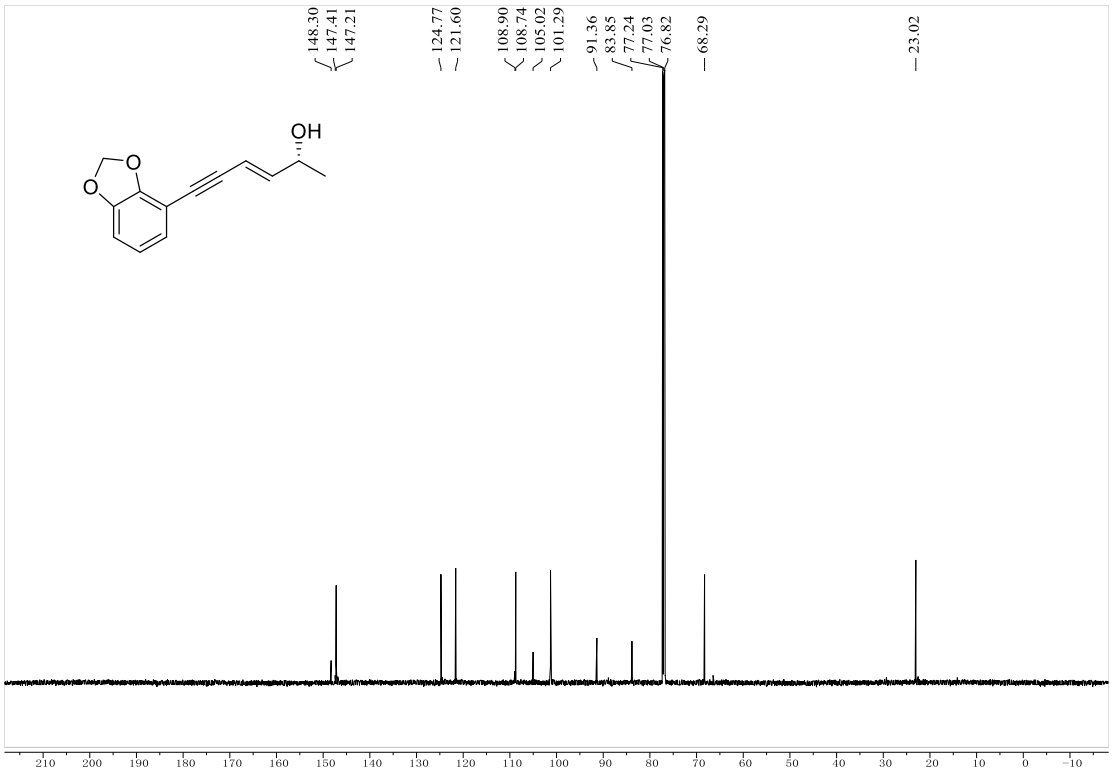
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2n**



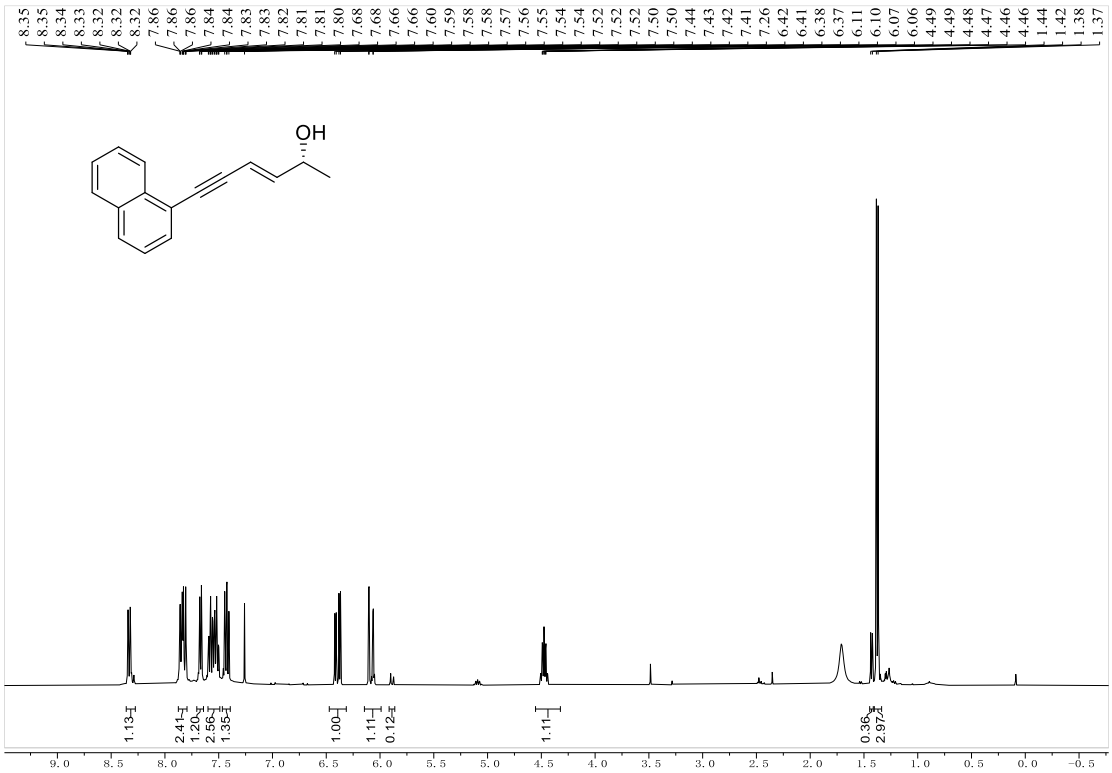
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2o**



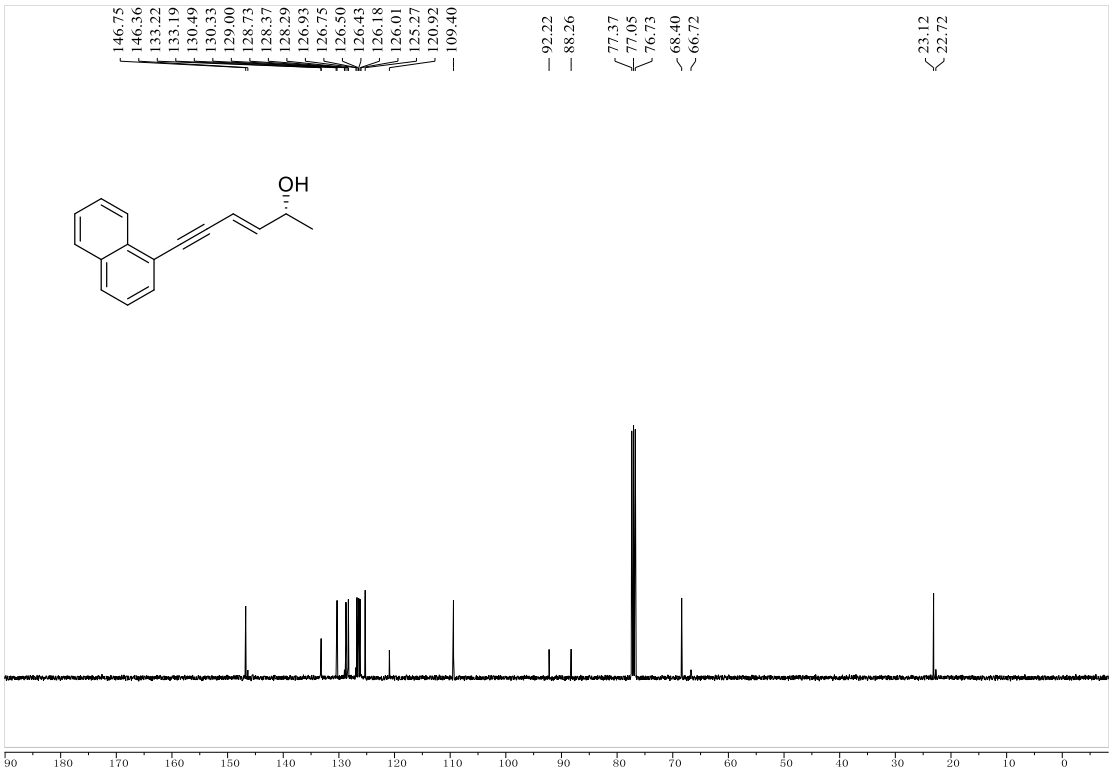
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2o**



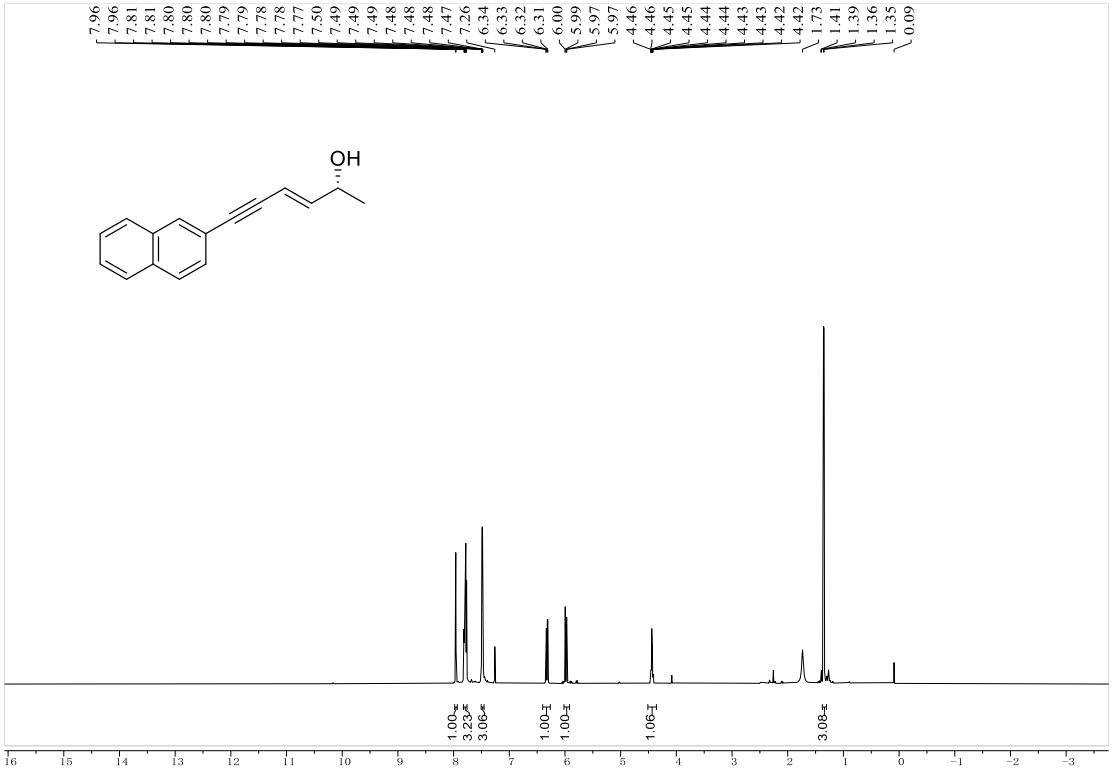
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2p**



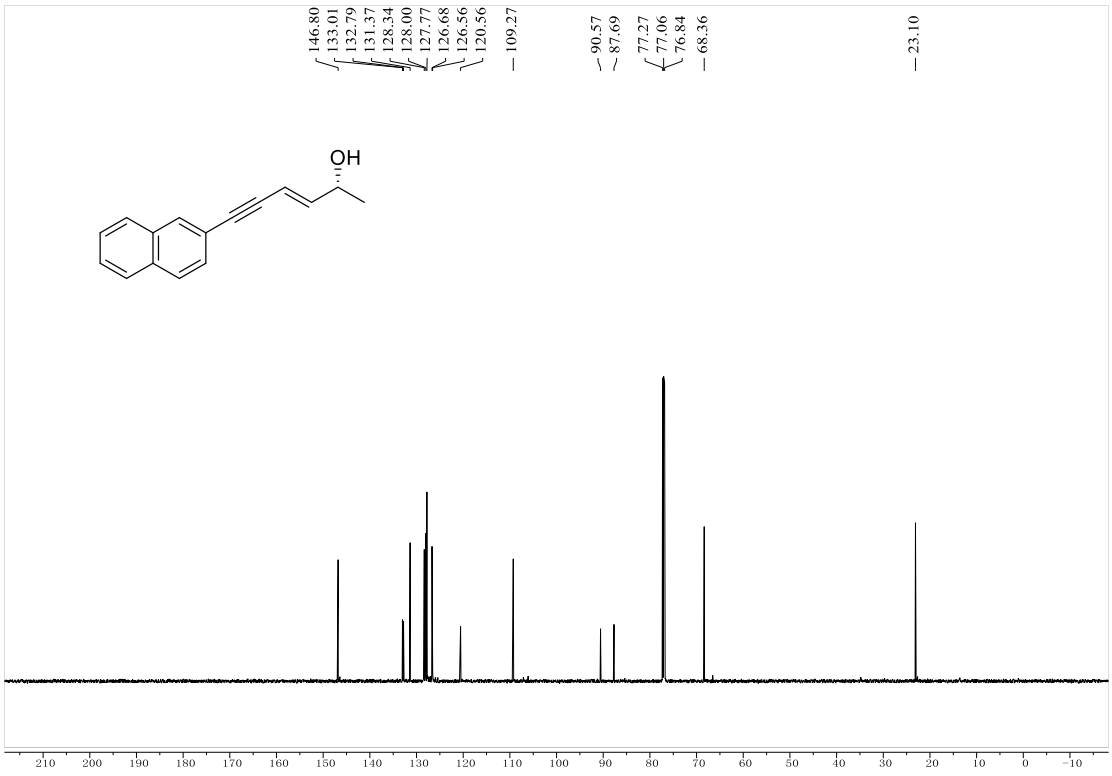
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **2p**



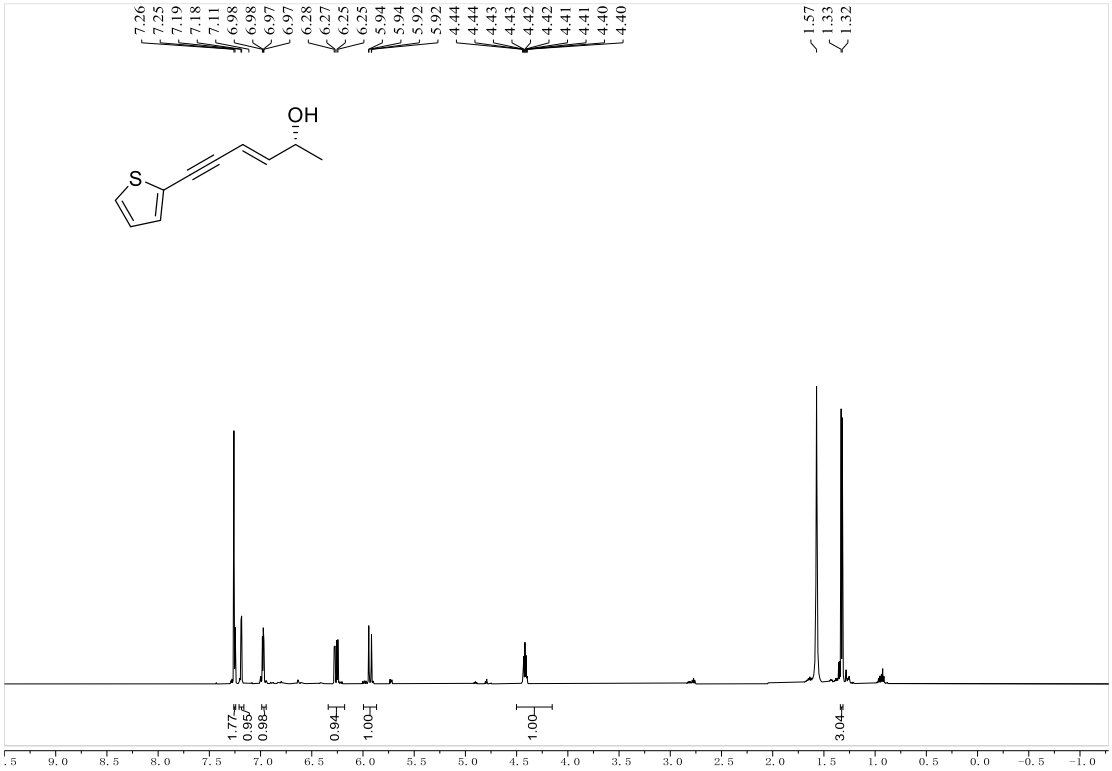
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2q**



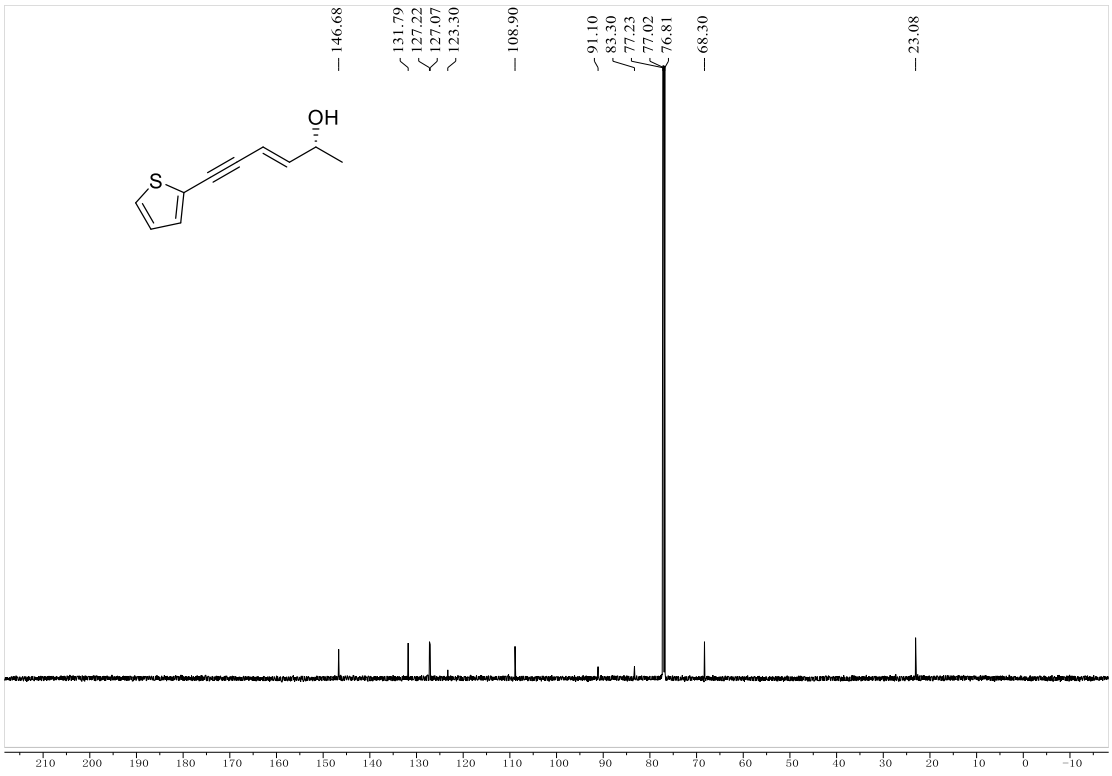
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2q**



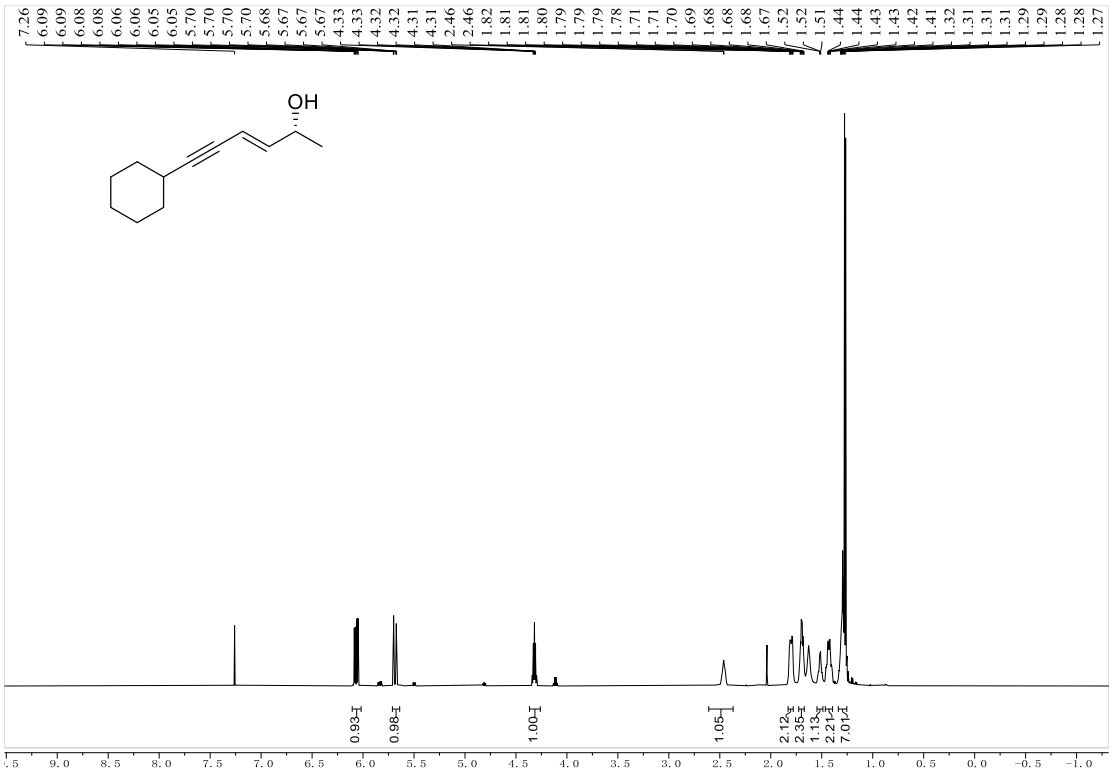
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2r**



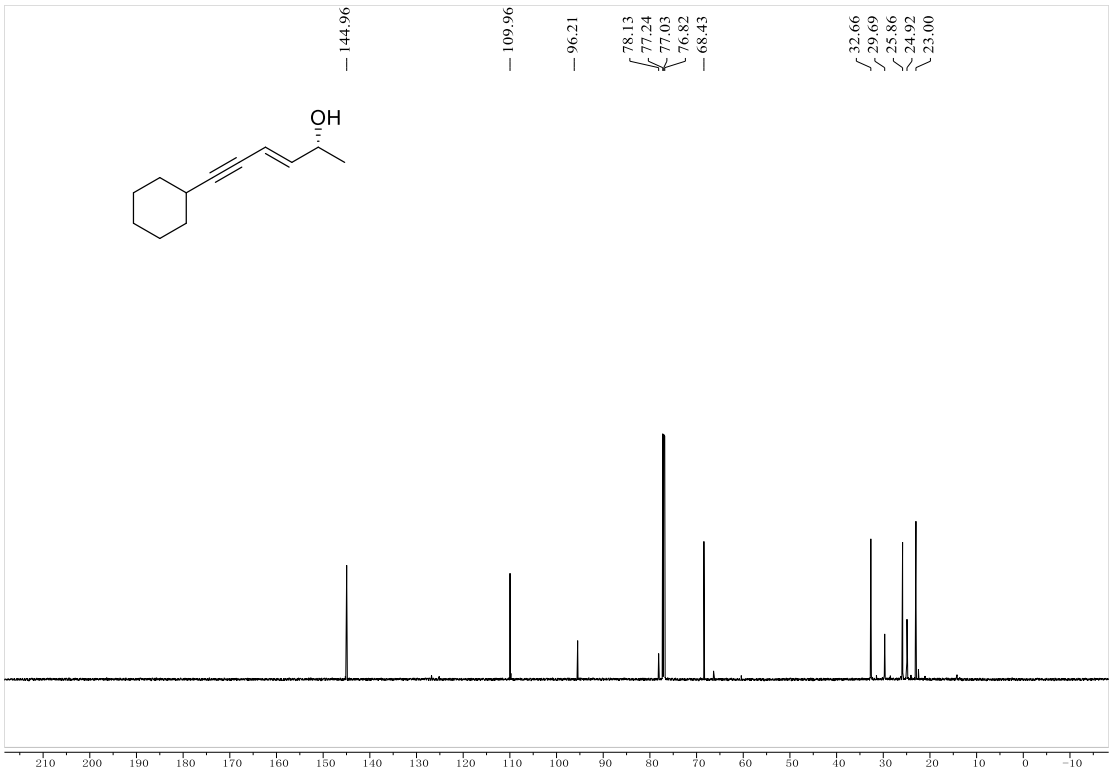
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2r**



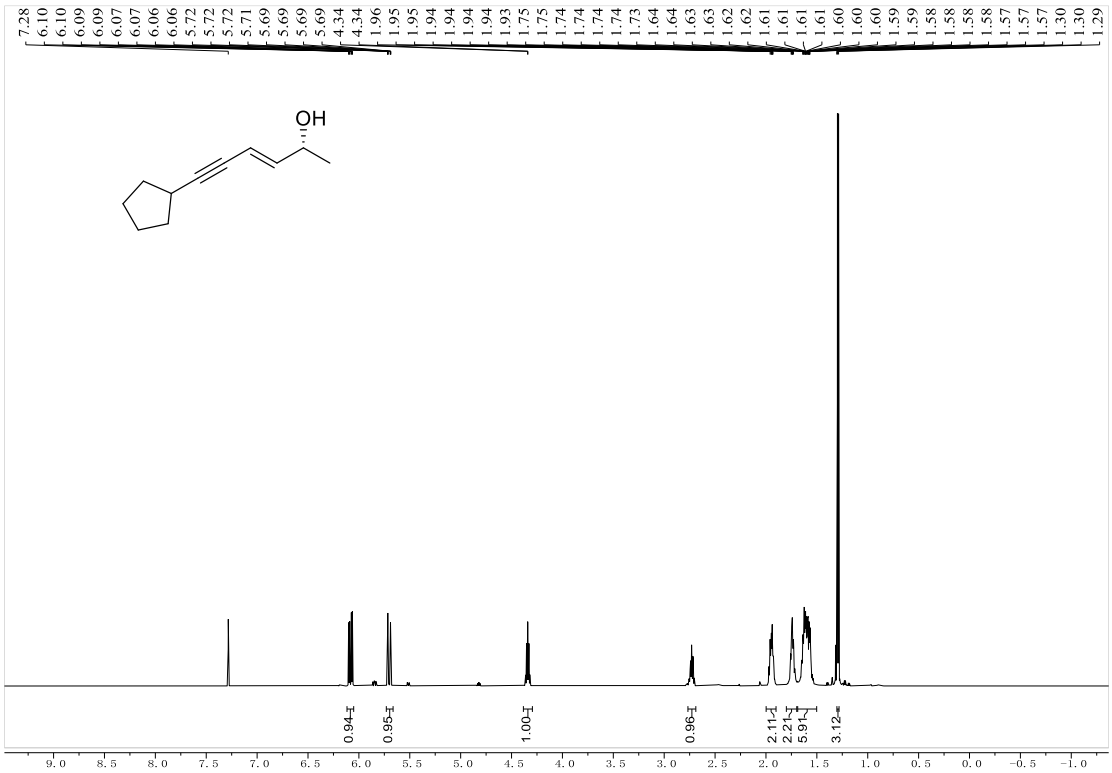
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2s**



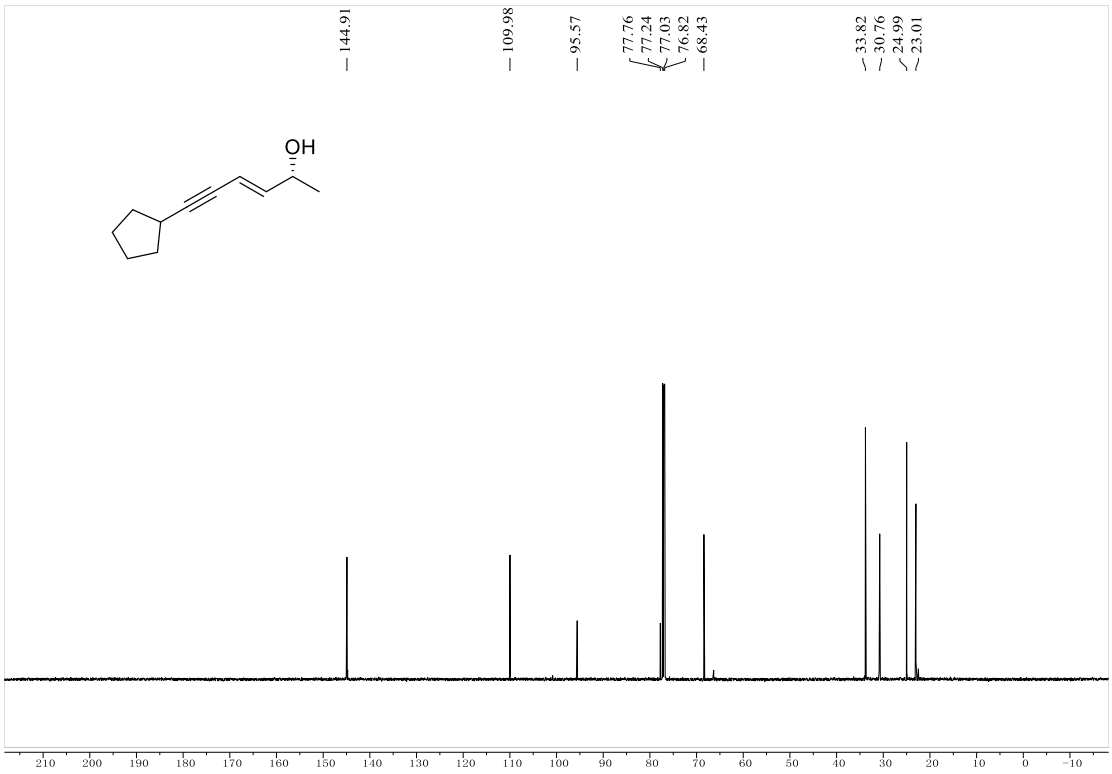
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2s**



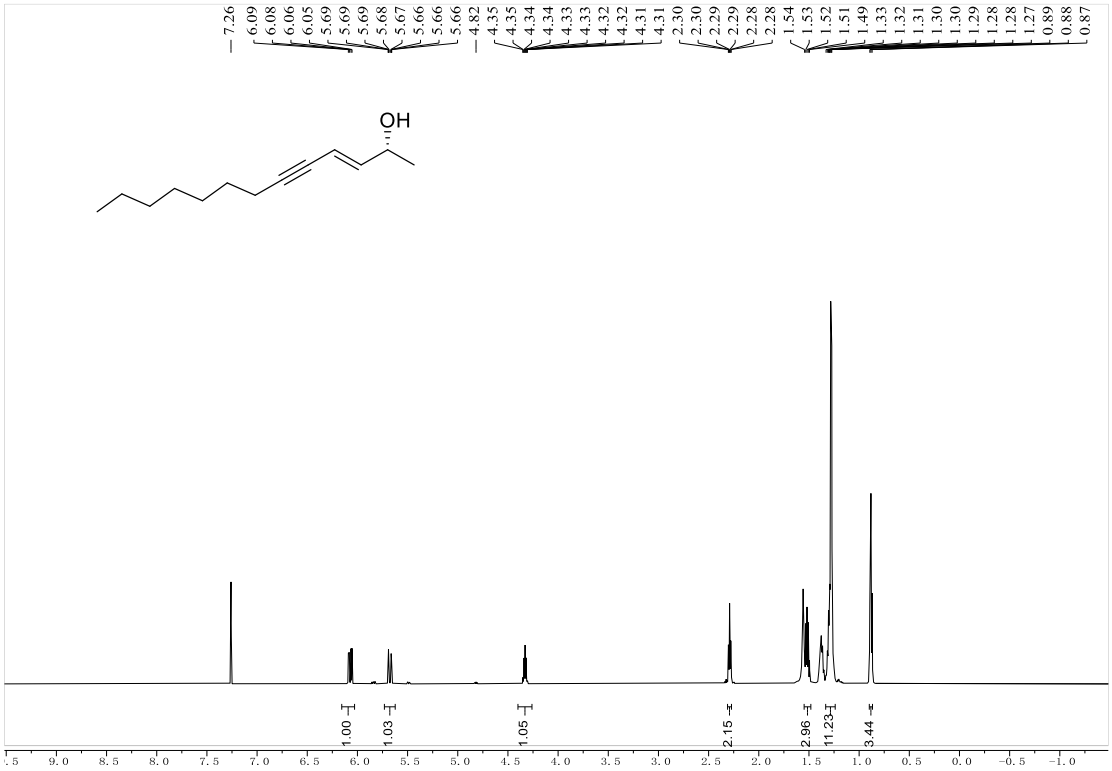
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2t**



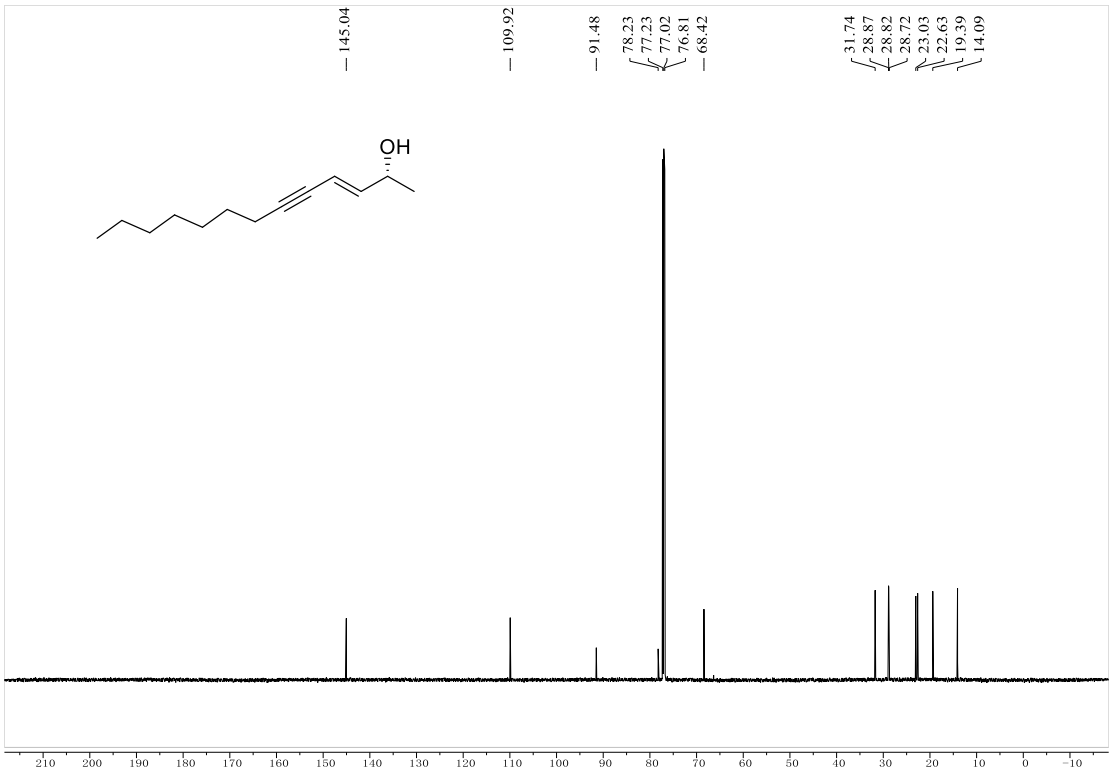
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2t**



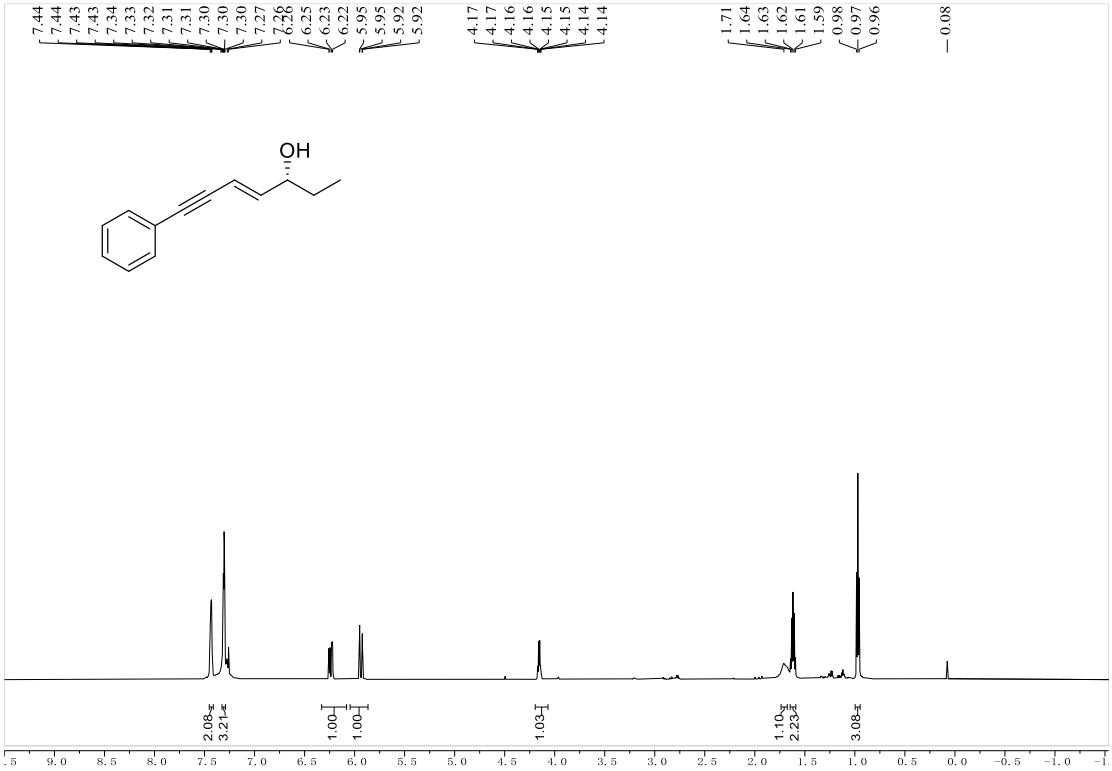
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2u**



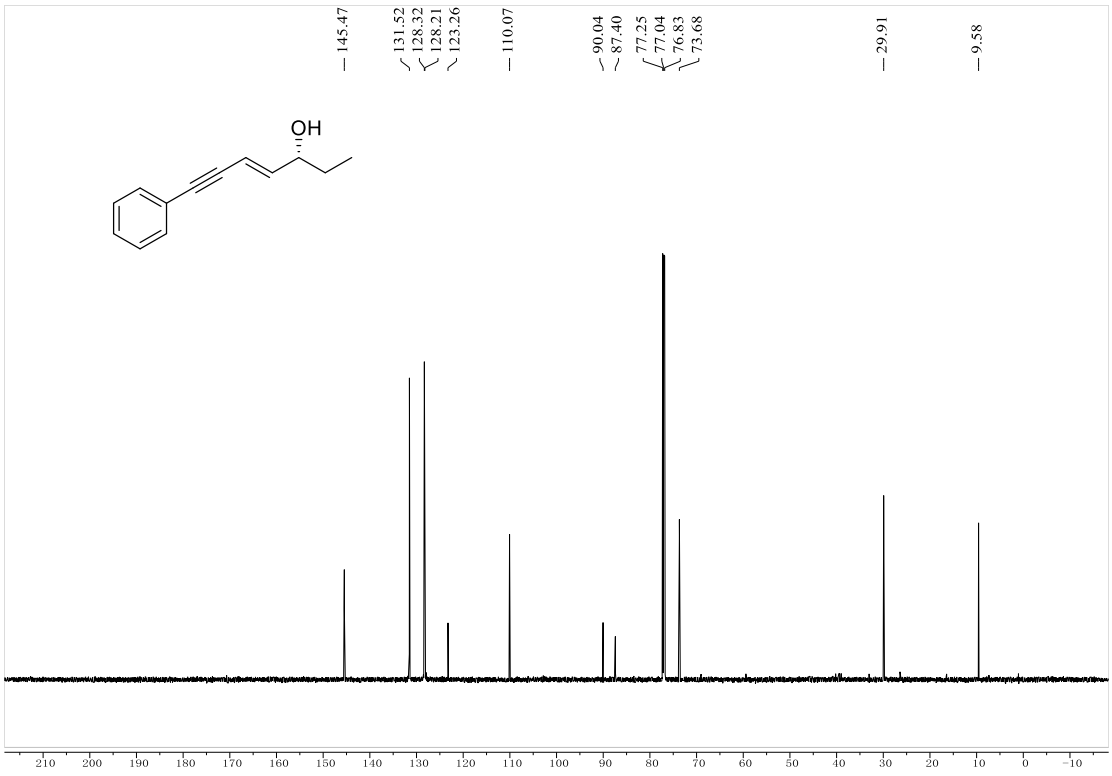
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2u**



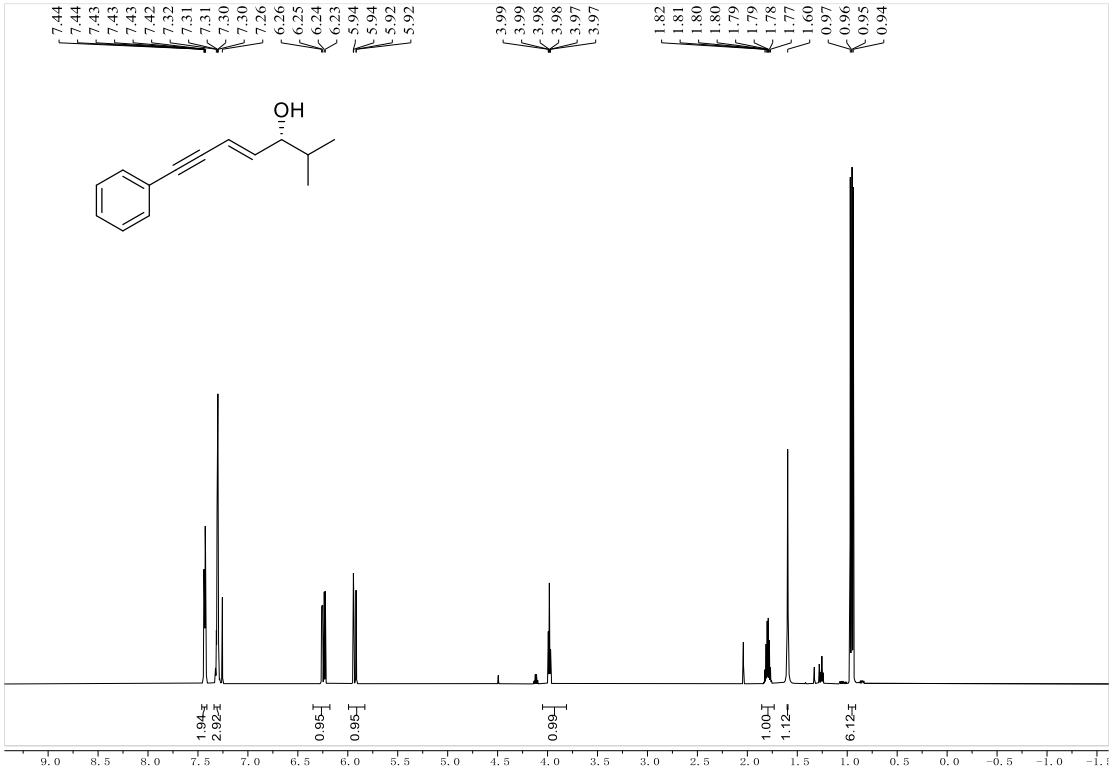
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2v**



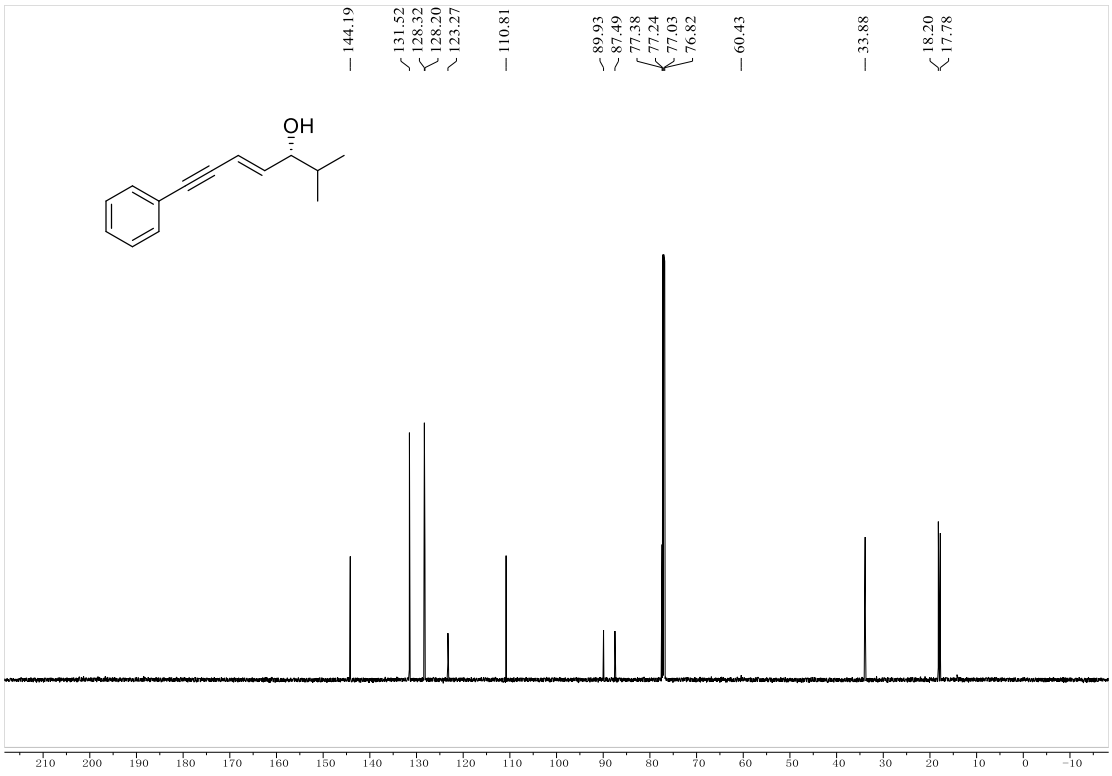
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2v**



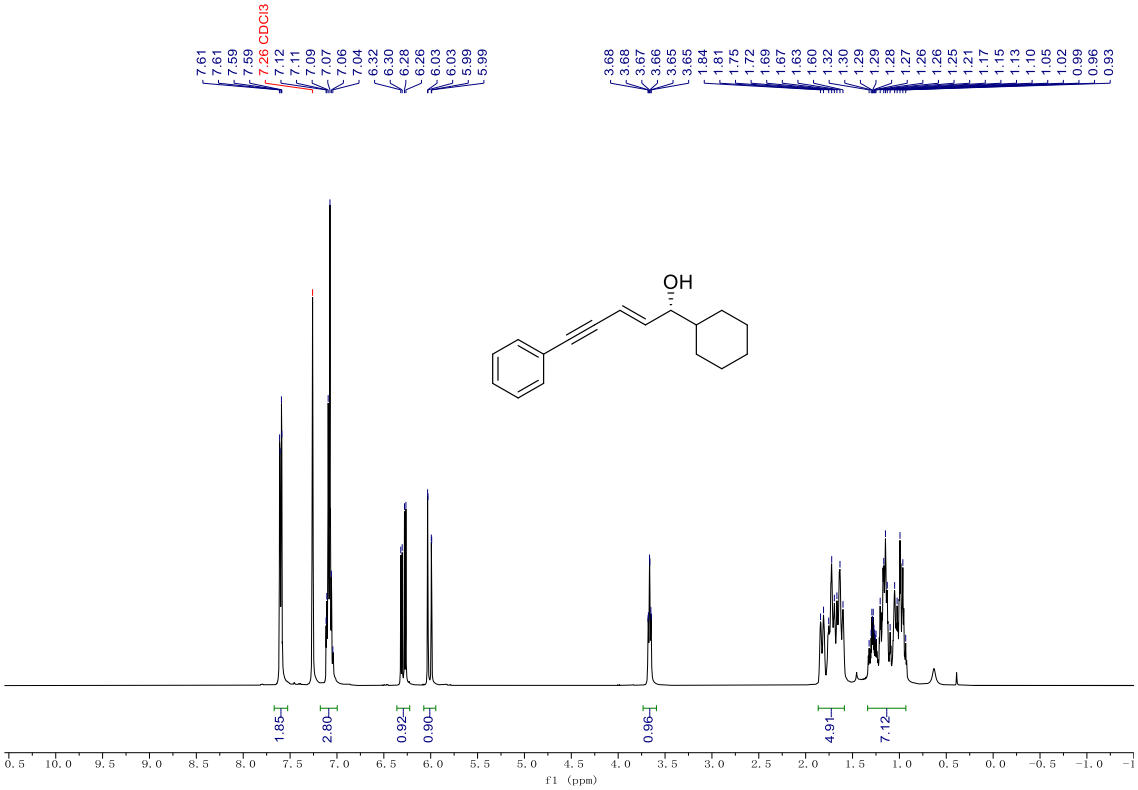
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2w**



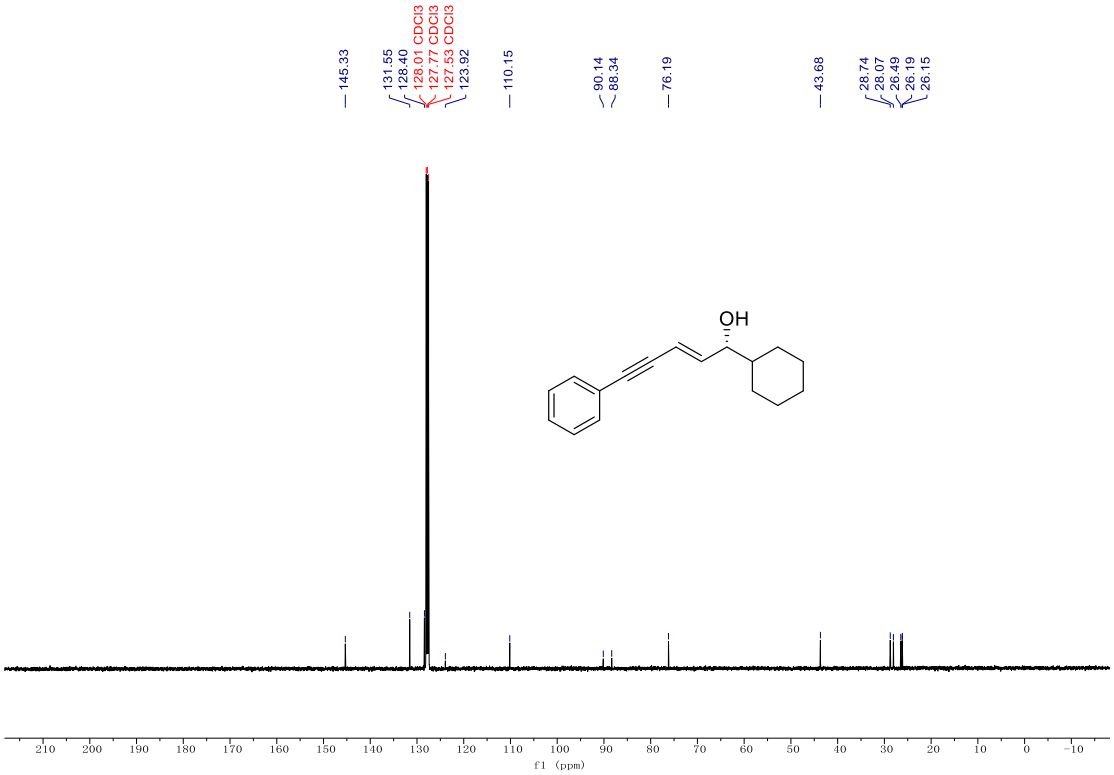
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2w**



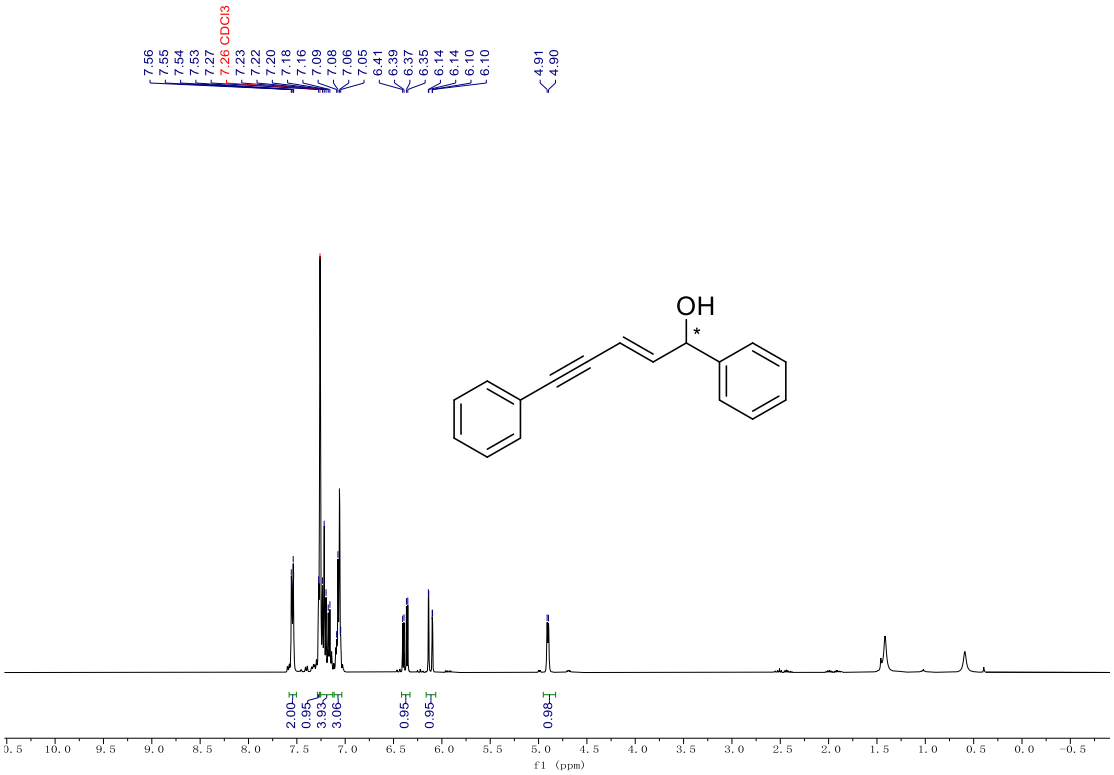
^{1}H NMR (400 MHz, $CDCl_3$) of **2x**



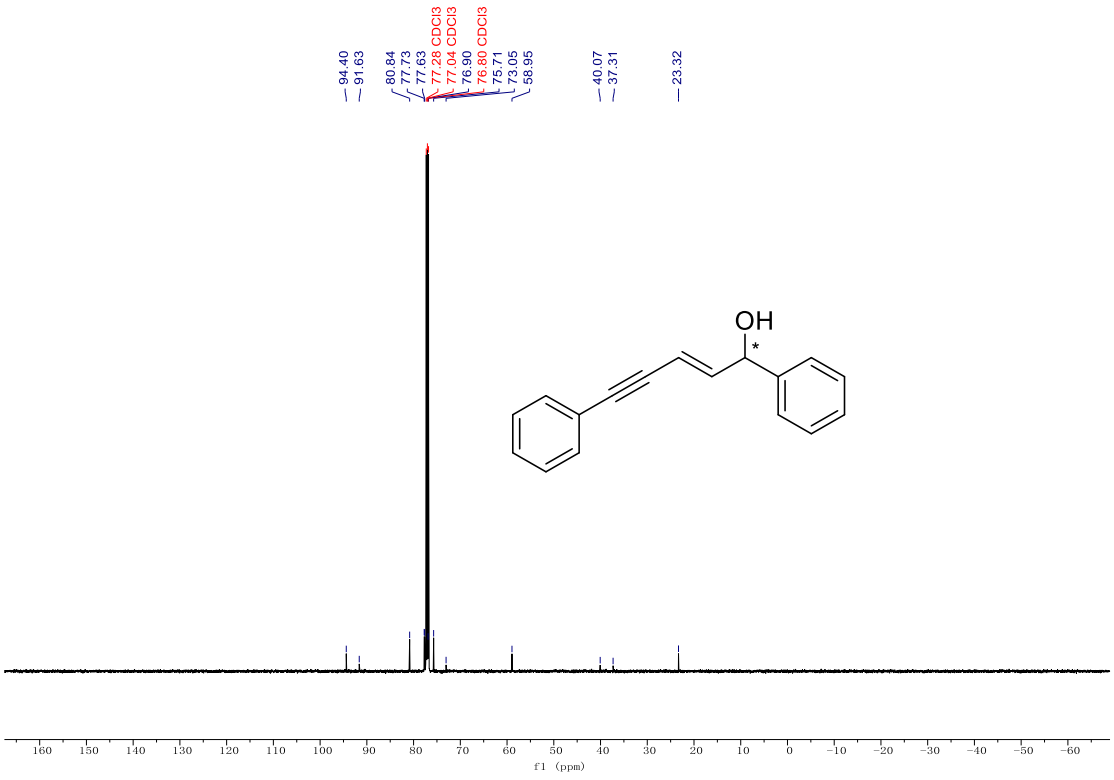
^{13}C NMR (101 MHz, $CDCl_3$) of **2x**



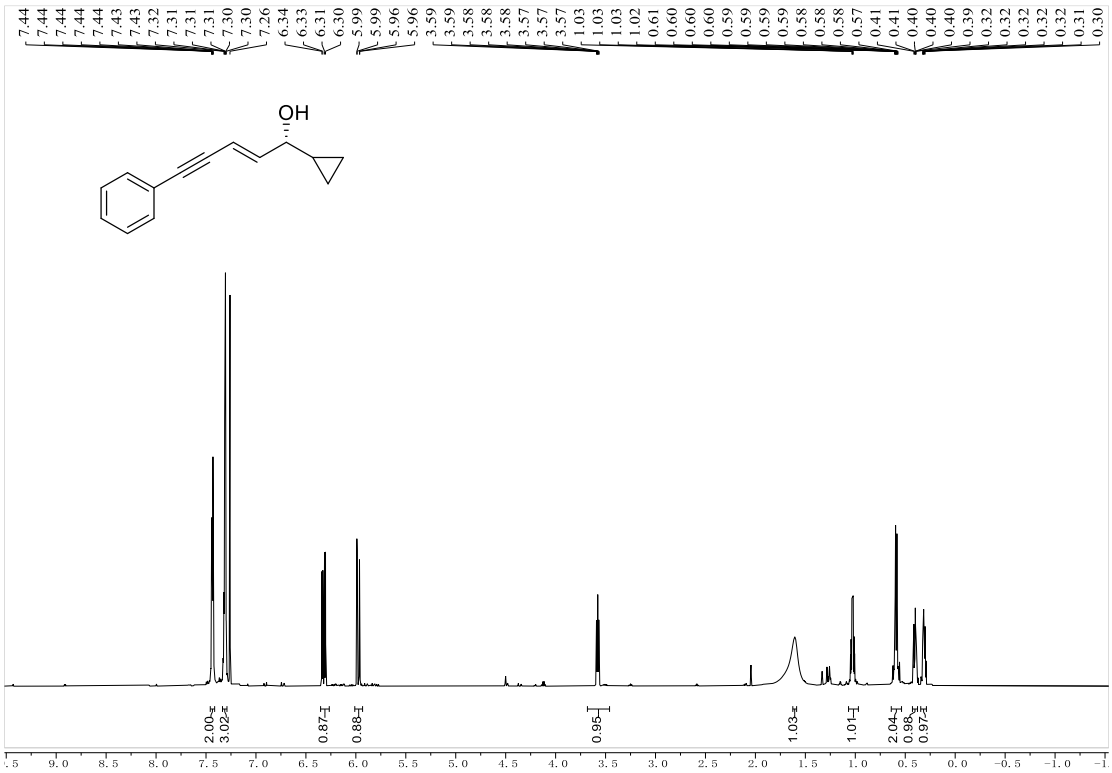
^{1}H NMR (400 MHz, $CDCl_3$) of **2y**



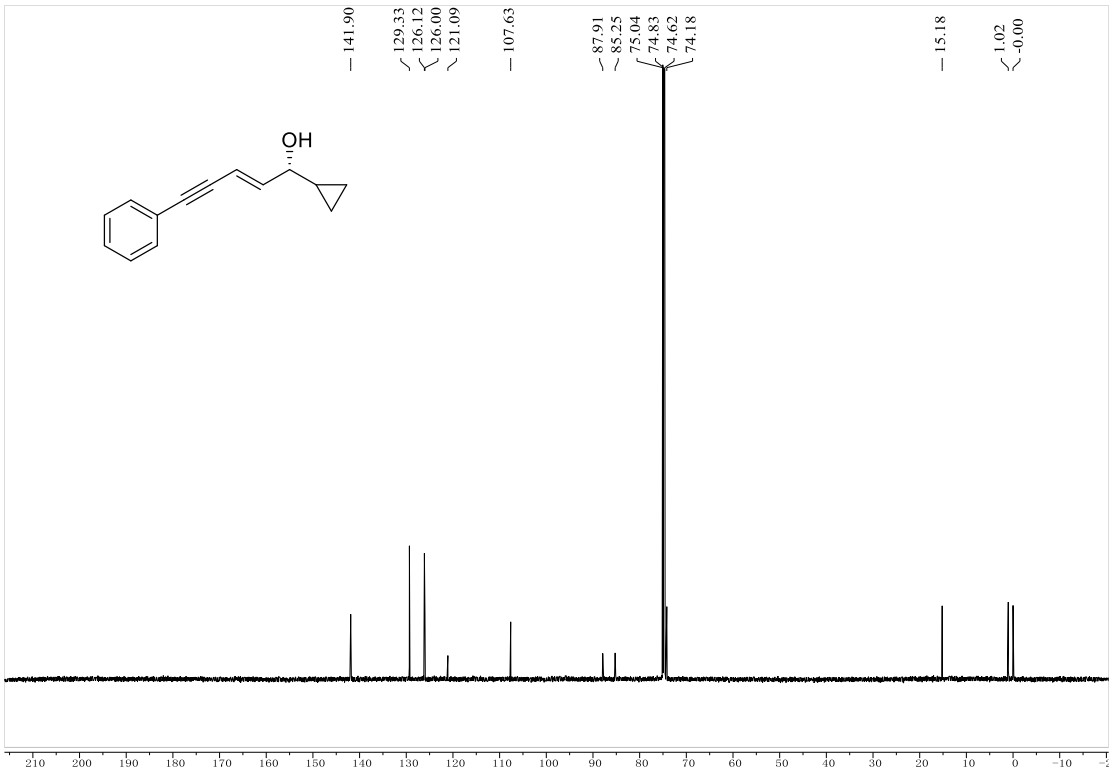
^{13}C NMR (101 MHz, $CDCl_3$) of **2y**



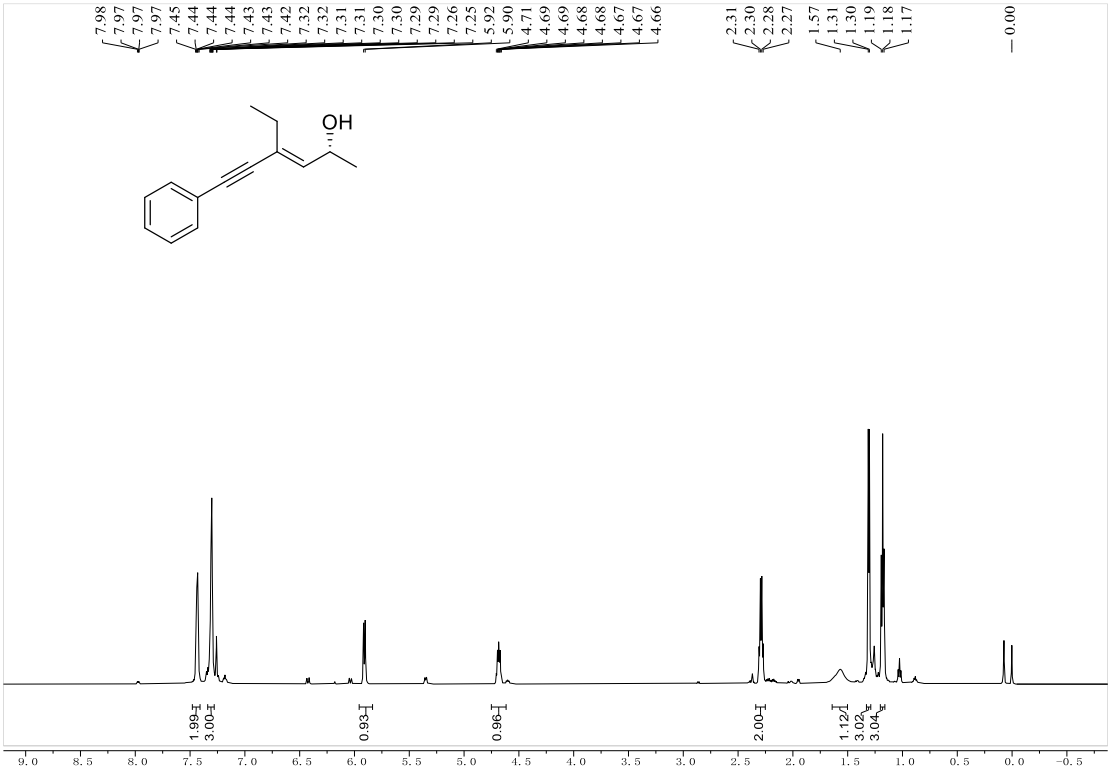
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2z**



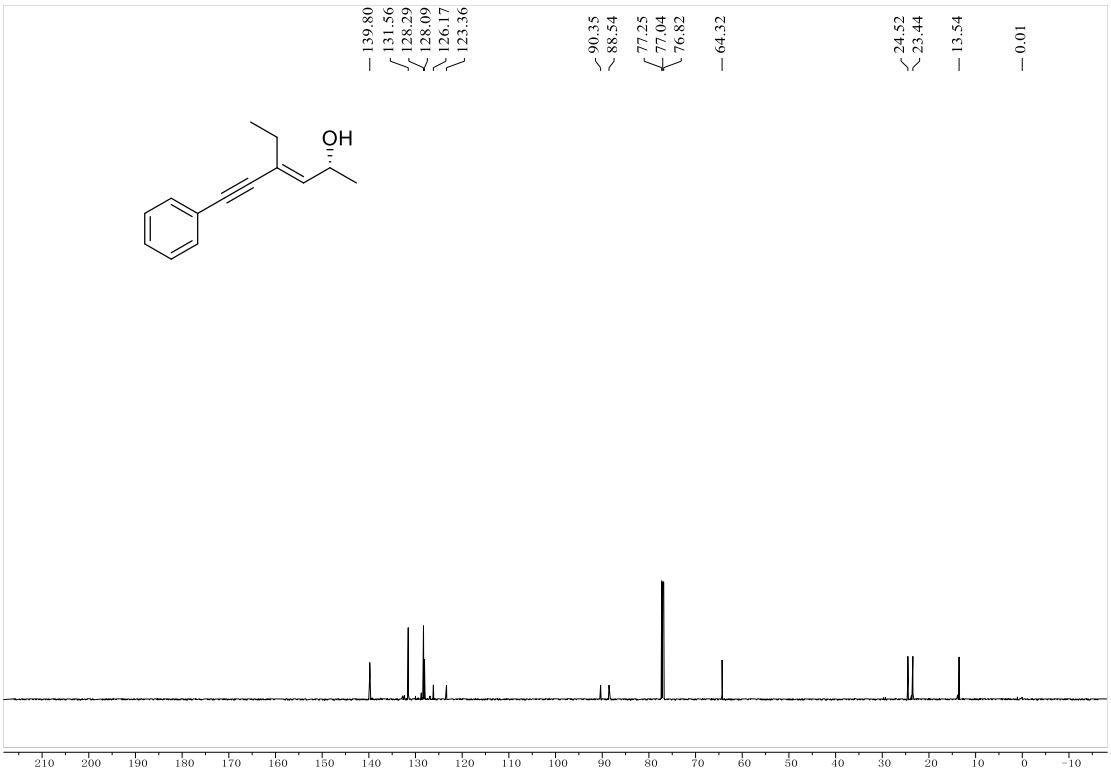
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2z**



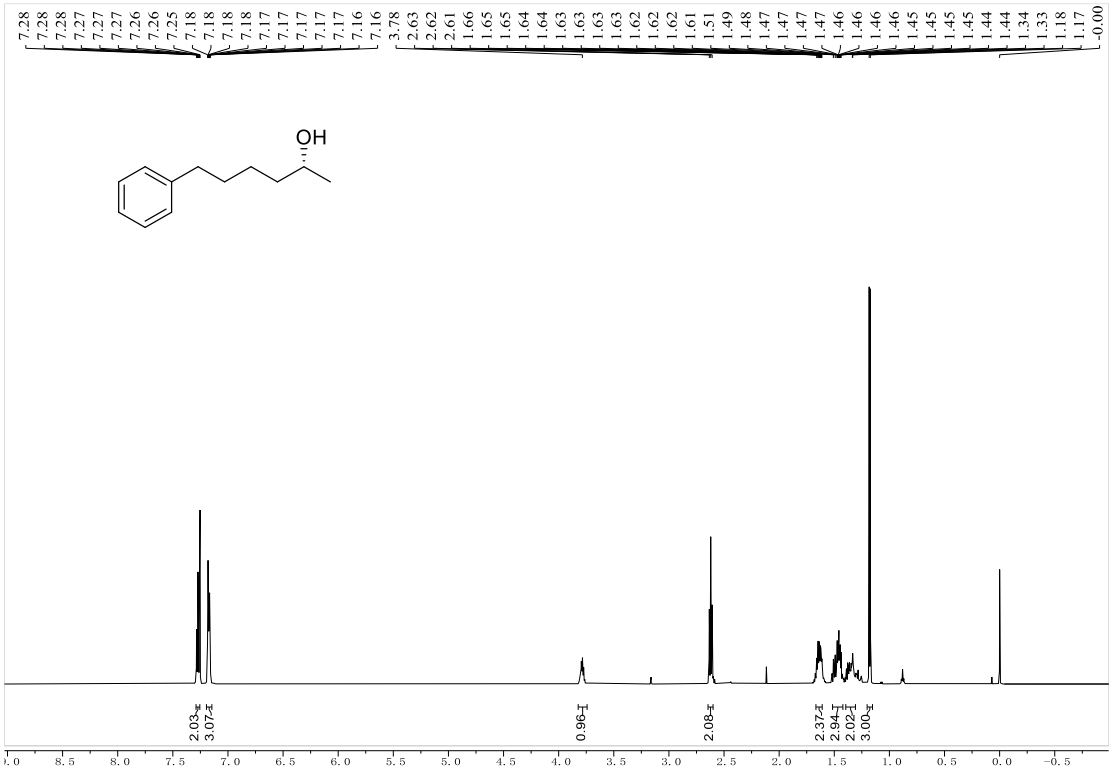
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **2aa**



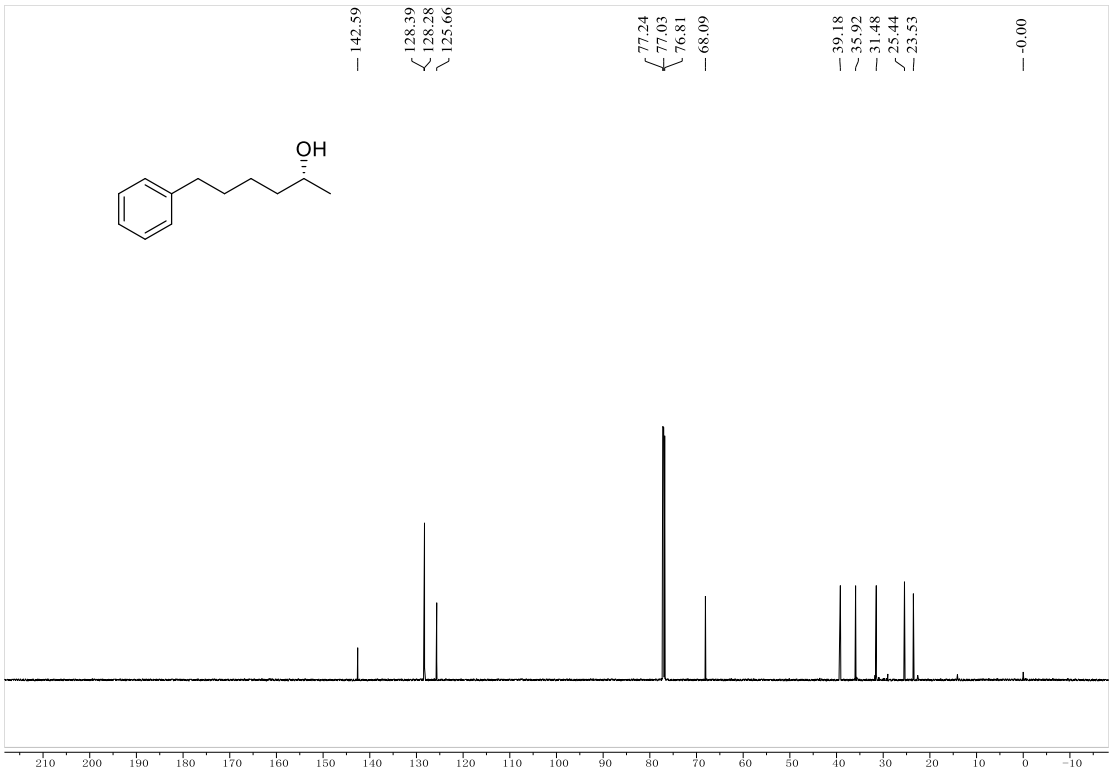
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **2aa**



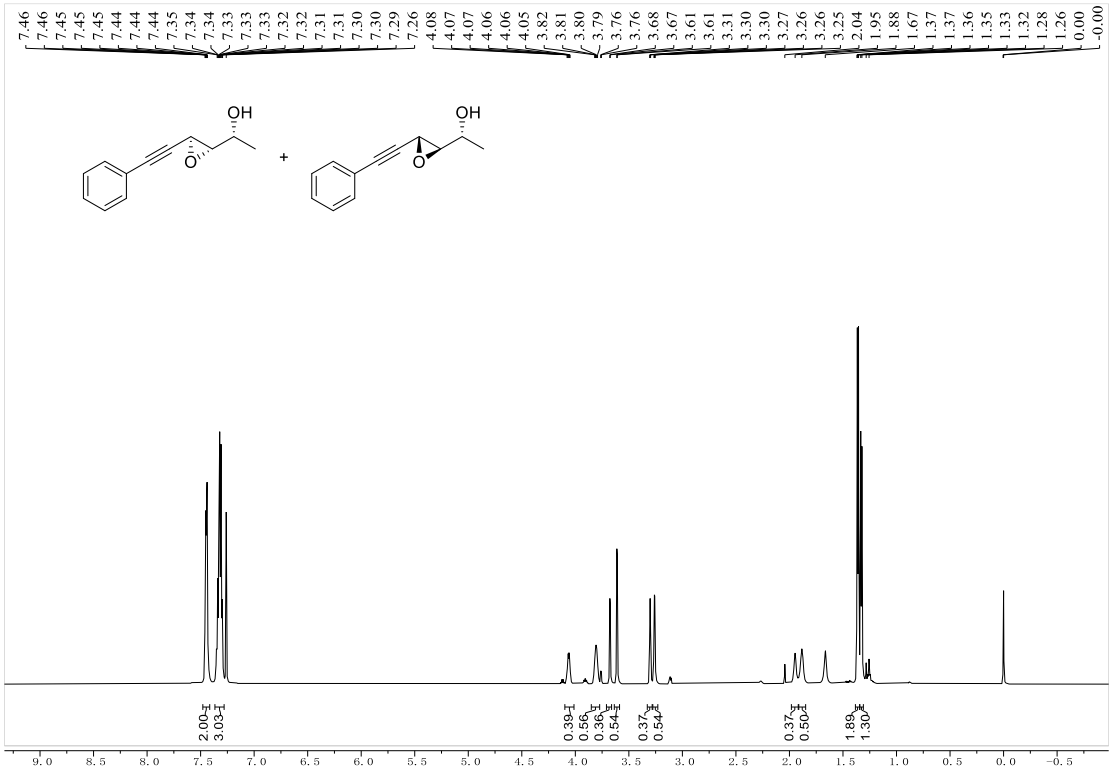
^{1}H NMR spectra (600 MHz, $CDCl_3$) of **3**



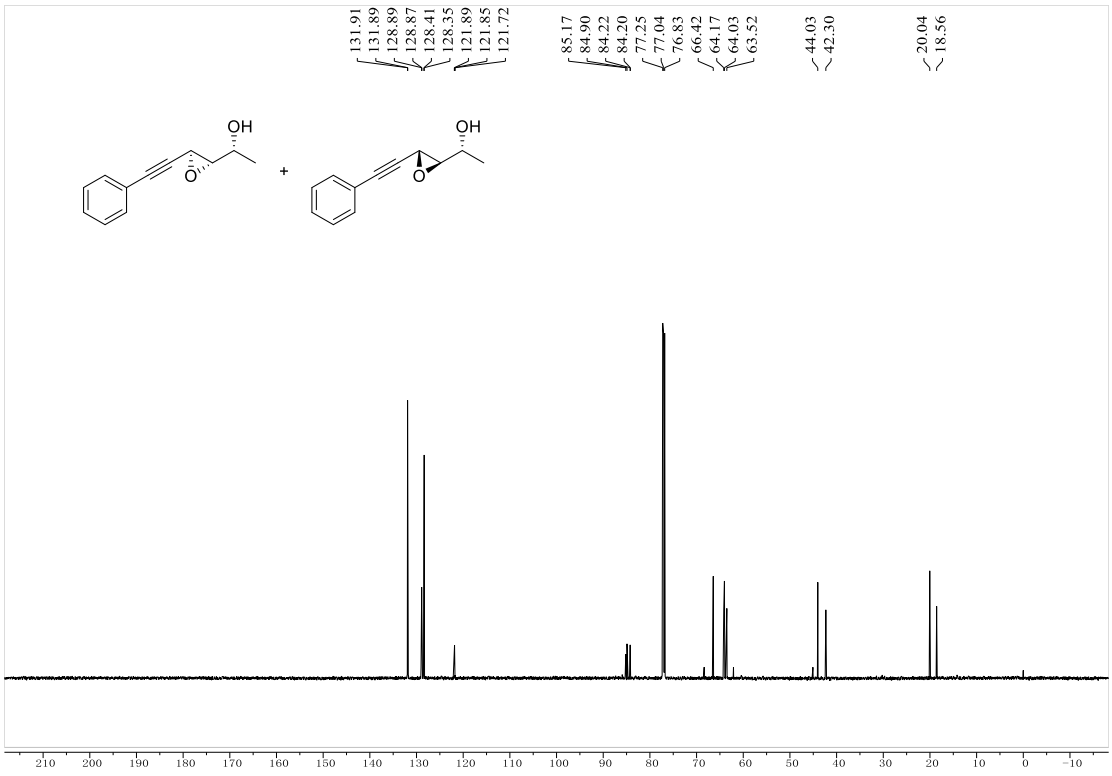
^{13}C NMR spectra (151 MHz, $CDCl_3$) of **3**



^{1}H NMR spectra (600 MHz, $CDCl_3$) of **4**



^{13}C NMR spectra (151 MHz, $CDCl_3$) of **4**



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