Supporting Information

Iridium-Catalyzed Regioselective Hydroalkynylation of Internal Alkenes Directed by an Oxime

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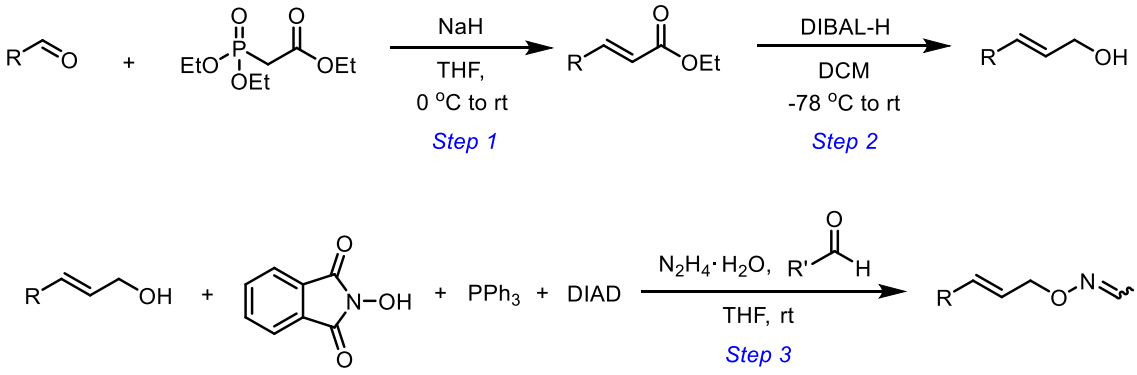
Materials and methods

Unless otherwise noted, all reactions were assembled on a Schlenk vacuum line or in an Ar filled glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. All ligands were purchased from Strem Chemicals and were used as received. [$Ir(COD)_2OTf$] was prepared according to literature methods.[1] Triisopropylsilylacetylene was purchased from Alfa Aesar and was used as received. All solvents and reagents were used as received. All work-up and purification procedures were carried out with reagent grade solvents with Schlenk techniques unless otherwise specified. Reaction temperatures above 23 °C refer to temperatures of a silicon oil bath, which were controlled by an electronic temperature modulator from IKA. NMR spectra were acquired on NMR spectrometer with 400 MHz for ^1H NMR and 101 MHz for ^{13}C NMR at the NMR facility at Center of Basic Molecular Science (CBMS). Chemical shifts (δ) are reported in ppm relative to the residual solvent signal. Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The HRMS analysis was carried out on UHPLC-Q-Exactive mass spectrometry system (Thermo Fisher, USA) consisting of an U3000 series ultra-high performance liquid chromatography system connected to an ion trap detector with an electrospray ionization interface in the positive ion mode. Enantiomeric excess (ee) values were determined by analytical liquid chromatography (HPLC) analysis on a Shimadzu chromatograph (Daicel chiral columns Chiralpak OD-H (4.6 x 250 mm)).

Synthesis and characterization of starting materials

General procedure



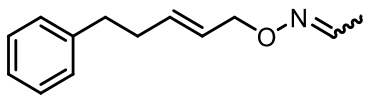
Step 1: To a solution of THF (0.40 M) and NaH (60% dispersion in mineral oil, 1.1 equiv.), triethyl phosphonoacetate (1.1 equiv.) was added dropwise at 0 °C. The reaction was stirred for 30 min, corresponding aldehyde (1.0 equiv.) was added slowly in THF. The reaction was stirred for another 5 minutes before quenched with saturated NH_4Cl. The mixture was extracted with ethyl acetate. The organic phase was collected and dried with Na_2SO_4. The solvent was evaporated, and the residue was purified by silica gel column chromatography with EtOAc/Hexane as eluent to give the α,β-unsaturated ester. *All the yields are not optimized*.

Step 2: To a solution of α,β-unsaturated ester (1.0 equiv.) in dry DCM (0.50 M) was added DIBAL-H (2.1 equiv.) dropwise at -78 °C. The cooling bath was removed and the reaction temperature was slowly warmed to room temperature. The mixture was stirred for 2 h and quenched with water (4.7 equiv.), 15% NaOH (9.4 equiv.) and water (4.7 equiv.) sequentially at 0 °C. The mixture was stirred for another 15 min and filtered through Celite. The solvent was evaporated and the residue was purified by silica gel column chromatography with EtOAc/Hexane as eluent to give the allylic alcohol. *All the yields are not optimized*.

Step 3: A Schlenk flask was charged with THF (0.20 M), 2-hydroxyisoindoline-1,3-dione (1.1 equiv.) and PPh_3 (1.1 equiv.) were added under Ar. Allylic alcohol (1.0 equiv.) was added, followed by DIAD (1.1 equiv.). The reaction was stirred for 30 min and hydrazine hydrate (2.0 equiv.) was added. The mixture was stirred for 15 min and the corresponding

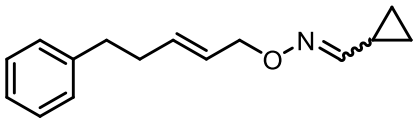
aldehyde (2.0 equiv.) was added. The mixture was stirred overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography with EtOAc/Hexane as eluent to give the desired oxime product. *All the yields are not optimized*.

Characterization of starting materials



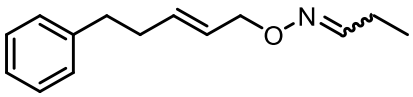
1a

The titled compound was prepared according to **General Procedure** in 6.2 mmol scale. Colorless oil. 819 mg, 65% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (q, *J* = 5.9 Hz, 0.5H), 7.30 (m, 2H), 7.19 (m, 3H), 6.77 (q, *J* = 5.5 Hz, 0.5H), 5.77 (m, 1H), 5.70 (m, 1H), 4.50 (m, 2H), 2.72 (m, 2H), 2.40 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ147.0, 141.9, 141.9, 134.6, 134.1, 128.6, 128.6, 128.4, 126.7, 126.3, 126.0, 74.5, 74.2, 35.6, 35.6, 34.3, 34.3, 15.4, 12.1. **IR** ν (cm^{-1}) 2921, 2361, 2341, 1020, 970, 669. **HRMS** (ESI-ion trap) calcd for $C_{13}H_{18}NO^+$ ($[M+H]^+$) 204.1383, found 204.1378



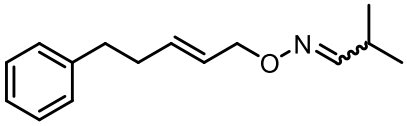
1b

The titled compound was prepared according to **General Procedure** in 2.0 mmol scale. Colorless oil. 252 mg, 55% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (m, 2H), 7.20 (m, 3H), 6.90 (d, *J* = 8.5 Hz, 0.5H), 5.95 (d, *J* = 8.9 Hz, 0.5H), 5.81 (m, 1H), 5.71 (m, 1H), 4.50 (m, 2H), 2.72 (m, 2H), 2.40 (m, 2H), 2.23 (m, 0.5H), 1.63 (m, 0.6H), 0.90 (m, 2H), 0.61 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ154.9, 154.4, 141.9, 141.9, 134.6, 134.1, 128.5, 128.5, 128.4, 126.7, 126.3, 126.0, 125.9, 74.6, 74.3, 35.6, 35.6, 34.3, 11.1, 8.0, 6.3, 5.7 **IR** ν (cm^{-1}) 2923, 2857, 1732, 1671, 970, 699. **HRMS** (ESI-ion trap) calcd for $C_{15}H_{20}NO^+$ ($[M+H]^+$) 230.1539, found 230.1532



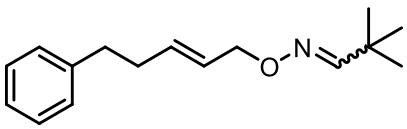
1c

The titled compound was prepared according to **General Procedure** in 2.4 mmol scale. Colorless oil. 328 mg, 63% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1.2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (t, *J* = 5.9 Hz, 0.4H), 7.27 (m, 2H), 7.19 (m, 3H), 6.63 (t, *J* = 5.3 Hz, 1H), 5.78 (m, 1H), 5.70 (m, 1H), 4.49 (m, 2H), 2.72 (m, 2H), 2.36 (m, 3H), 2.22 (m, 1H), 1.08 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.4, 152.2, 141.9, 134.7, 134.0, 128.6, 128.6, 128.5, 128.4, 126.7, 126.2, 126.0, 126.0, 74.6, 74.3, 35.6, 35.6, 34.3, 34.3, 23.2, 19.3, 11.3, 10.8. **IR** ν (cm^{-1}) 3027, 2971, 2922, 1496, 1454, 970, 699. **HRMS** (ESI-ion trap) calcd for $C_{14}H_{20}NO^{+}$ ($[M+H]^{+}$) 218.1539, found 218.1532



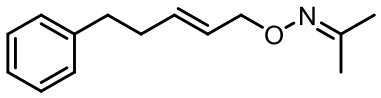
1d

The titled compound was prepared according to **General Procedure** in 1.2 mmol scale. Colorless oil. 203 mg, 72% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (m, 2H), 7.19 (m, 3H), 6.48 (d, *J* = 7.2 Hz, 0.2H), 5.79 (m, 1H), 5.68 (m, 1H), 4.48 (m, 2H), 3.13 (m, 0.2H), 2.72 (m, 2H), 2.50 (m, 0.8H), 2.39 (m, 2H), 1.06 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ157.5, 156.1, 141.9, 134.7, 133.8, 128.6, 128.5, 128.5, 128.4, 126.8, 126.2, 126.0, 126.0, 74.5, 74.2, 35.6, 35.6, 34.3, 34.3, 29.5, 25.2, 20.3, 19.9. **IR** ν (cm^{-1}) 2959, 2865, 2361, 2341, 2164, 1496, 1060, 699. **HRMS** (ESI-ion trap) calcd for $C_{15}H_{22}NO^{+}$ ($[M+H]^{+}$) 232.1696, found 232.1689



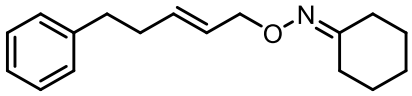
1e

The titled compound was prepared according to **General Procedure** in 2.0 mmol scale. Colorless oil. 289 mg, 59% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (m, 3H), 7.20 (dd, *J* = 6.5, 3.5 Hz, 3H), 5.79 (m, 1H), 5.71 (m, 1H), 4.47 (m, 2H), 2.72 (dd, *J* = 9.3, 6.5 Hz, 2H), 2.39 (d, *J* = 7.8 Hz, 2H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.5, 141.9, 134.7, 128.5, 128.5, 128.5, 126.2, 126.0, 74.3, 35.6, 34.3, 33.7, 27.8. **IR** ν (cm^{-1}) 2962, 2929, 2865, 2360, 2341, 1365, 1023, 669. **HRMS** (ESI-ion trap) calcd for $C_{16}H_{24}NO^+$ ($[M+H]^+$) 246.1852, found 246.1845



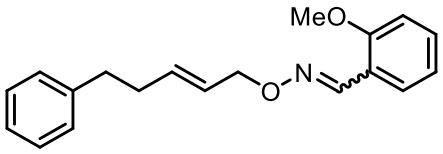
1f

The titled compound was prepared according to **General Procedure** in 10 mmol scale. Colorless oil. 1.4 g, 64% Yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (m, 2H), 7.19 (m, 3H), 5.77 (m, 1H), 5.70 (m, 1H), 4.48 (d, *J* = 5.9 Hz, 2H), 2.72 (m, 2H), 2.39 (m, 2H), 1.87 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 154.9, 142.0, 133.7, 128.6, 128.4, 126.8, 125.9, 74.1, 35.6, 34.3, 22.0, 15.8. **IR** ν (cm^{-1}) 3062, 3026, 2919, 2855, 1724, 1672, 911, 658. **HRMS** (ESI-ion trap) calcd for $C_{14}H_{20}NO^+$ ($[M+H]^+$) 218.1539, found 218.1533



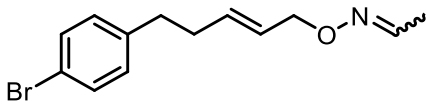
1g

The titled compound was prepared according to **General Procedure** in 0.9 mmol scale. Colorless oil. 159 mg, 69% Yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (m, 2H), 7.19 (m, 3H), 5.77 (m, 1H), 5.70 (m, 1H), 4.47 (d, *J* = 5.9 Hz, 2H), 2.72 (m, 2H), 2.47 (m, 2H), 2.39 (m, 2H), 2.21 (m, 2H), 1.61 (m, 6H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.5, 142.0, 133.8, 128.6, 128.4, 126.7, 125.9, 74.0, 35.6, 34.3, 32.4, 27.2, 26.0, 25.9, 25.5. **IR** ν (cm^{-1}) 2929, 2856, 2360, 2341, 1274, 970, 934. **HRMS** (ESI-ion trap) calcd for $C_{17}H_{24}NO^+$ ($[M+H]^+$) 258.1852, found 258.1842



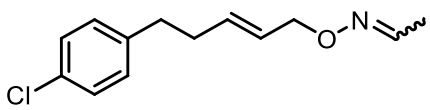
1h

The titled compound was prepared according to **General Procedure** in 3.0 mmol scale. Colorless oil. 514 mg, 58% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (6:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.51 (s, 0.86H), 7.80 (m, 1H), 7.34 (m, 1H), 7.28 (m, 2H), 7.20 (m, 3H), 6.95 (m, 1H), 6.89 m, 1H), 5.85 (m, 1H), 5.78 (m, 1H), 4.63 (d, J = 6.1 Hz, 2H), 3.84 (s, 3H), 2.74 (m, 2H), 2.42 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.7, 145.0, 141.9, 134.8, 131.2, 128.6, 128.5, 128.4, 126.6, 126.3, 126.0, 121.1, 120.9, 111.2, 75.0, 55.7, 35.6, 34.4. **IR** ν (cm^{-1}) 2921, 2838, 2361, 2341, 1605, 1196, 1023, 779**. HRMS** (ESI-ion trap) calcd for $C_{19}H_{22}NO_2^+$ ($[M+H]^+$) 296.1645, found 296.1635



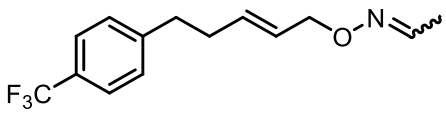
1i

The titled compound was prepared according to **General Procedure** in 5.5 mmol scale. Colorless oil. 857 mg, 61% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (m, 0.5H), 7.39 (m, 2H), 7.05 (m, 2H), 6.76 (q, J = 5.5 Hz, 0.5H), 5.79 (m, 1H), 5.65 (m, 1H), 4.48 (m, 2H), 2.67 (m, 2H), 2.35 (m 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 140.8, 140.8, 133.9, 133.4, 131.5, 131.5, 130.4, 130.3, 127.1, 126.7, 119.7, 74.4, 74.1, 34.9, 34.0, 34.0, 15.4, 12.1. **IR** ν (cm^{-1}) 2920, 2857, 2361, 2341, 1488, 1010, 814. **HRMS** (ESI-ion trap) calcd for $C_{13}H_{17}BrNO^+$ ($[M+H]^+$) 282.0488, found 282.0482



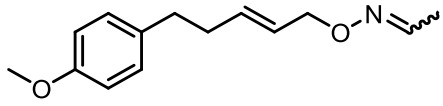
1j

The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 830 mg, 70% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.9 Hz, 0.5H), 7.24 (m, 2H), 7.10 (m, 2H), 6.77 (q, *J* = 5.6 Hz, 0.5H), 5.74 (m, 1H), 5.67 (m, 1H), 4.48 (m, 2H), 2.68 (m, 2H), 2.36 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ147.1, 140.3, 140.3, 134.0, 133.5, 131.7, 129.9, 129.9, 128.5, 128.5, 127.1, 126.7, 74.4, 74.1, 72.8, 72.5, 34.9, 34.1, 34.1, 31.7, 31.6, 30.8, 30.7, 15.4, 12.1. **IR** ν (cm^{-1}) 2920, 2858, 2361, 2341, 1492, 1091, 1014, 818. **HRMS** (ESI-ion trap) calcd for $C_{13}H_{17}ClNO^+$ ($[M+H]^+$) 238.0993, found 238.0984



1k

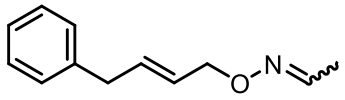
The titled compound was prepared according to **General Procedure** in 4.0 mmol scale. Colorless oil. 846 mg, 78% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (m, 2.5H), 7.28 (m, 2H), 6.76 (q, *J* = 5.3 Hz, 0.5H), 5.75 (m, 1H), 5.69 (m, 1H), 4.49 (m, 2H), 2.77 (m, 2H), 2.40 (m, 2H), 1.84 (t, *J* = 5.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.1, 145.9, 133.7, 133.5, 133.2, 128.9, 128.9, 127.3, 127.1, 127.0, 125.7, 125.4, 125.3, 125.3, 74.3, 74.1, 35.4, 35.3, 33.9, 33.9, 15.4, 12.1. **IR** ν (cm^{-1}) 2923, 2859, 2360, 2342, 1619, 1324, 1119, 1067, 1018, 827. **HRMS** (ESI-ion trap) calcd for $C_{14}H_{17}F_3NO^+$ ($[M+H]^+$) 272.1257, found 272.1253



1l

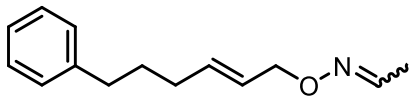
The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 944 mg, 81% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.9 Hz, 0.5H), 7.09 (m, 2H), 6.83 (m, 2H), 6.77 (m, 0.5H), 5.77 (m, 1H), 5.69 (m, 1H), 4.52 (m, 2H), 3.79 (s, 3H), 2.66 (m, 2H), 2.35 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ

157.9, 147.0, 134.7, 134.2, 134.0, 129.4, 126.6, 126.2, 113.9, 74.6, 74.3, 55.4, 34.7, 34.6, 34.6, 15.4, 12.1. **IR** ν (cm^{-1}) 2919, 2361, 2341, 1511, 1243, 1020, 824. **HRMS** (ESI-ion trap) calcd for $C_{14}H_{20}NO_2^+$ ([M+H]$^+$) 234.1489, found 234.1479



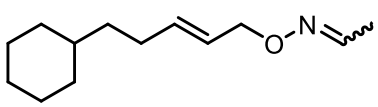
1m

The titled compound was prepared according to **General Procedure** in 6.0 mmol scale. Colorless oil. 760 mg, 67% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (q, *J* = 5.8 Hz, 0.5H), 7.30 (m, 2H), 7.20 (m, 3H), 6.78 (m, 0.5H), 5.90 (m, 1H), 5.74 (m, 1H), 4.54 (m, 2H), 3.42 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 140.1, 140.0, 133.7, 133.2, 131.9, 128.7, 128.6, 128.5, 128.3, 127.6, 127.2, 127.2, 126.7, 126.2, 126.2, 74.3, 74.0, 73.1, 72.8, 38.9, 33.1, 33.0, 15.3, 12.1. **IR** ν (cm^{-1}) 3027, 2921, 2360, 1495, 1020, 699 **HRMS** (ESI-ion trap) calcd for $C_{12}H_{16}NO^+$ ([M+H]$^+$) 190.1226, found 190.1221



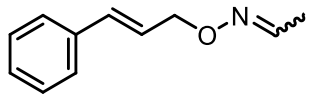
1n

The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 771 mg, 71% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (q, *J* = 5.9 Hz, 0.5H), 7.29 (m, 2H), 7.19 (m, 3H), 6.77 (q, *J* = 5.6 Hz, 0.5H), 5.79 (m, 1H), 5.68 (m, 1H), 4.51 (m, 2H), 2.63 (m, 2H), 2.12 (m, 2H), 1.85 (m, 3H), 1.74 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 147.0, 142.5, 135.2, 134.7, 128.6, 128.5, 128.4, 126.5, 126.1, 125.8, 74.6, 74.3, 35.5, 32.0, 30.8, 30.8, 15.4, 12.1. **IR** ν (cm^{-1}) 2922, 2857, 2361, 2341, 1454, 1016, 968, 670. **HRMS** (ESI-ion trap) calcd for $C_{14}H_{20}NO^+$ ([M+H]$^+$) 218.1539, found 218.1534



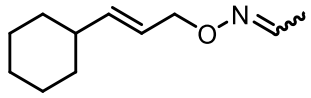
1o

The titled compound was prepared according to **General Procedure** in 6.0 mmol scale. Colorless oil. 891 mg, 71% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (q, *J* = 5.7 Hz, 0.5H), 6.76 (q, *J* = 5.5 Hz, 0.5H), 5.73 (m, 1H), 5.62 (m, 1H), 4.50 (m, 2H), 2.06 (m, 2H), 1.84 (m, 3H), 1.65 (m, 6H), 1.22 (m, 7H), 0.87 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ146.9, 136.3, 135.7, 125.7, 125.3, 74.8, 74.5, 74.4, 74.1, 37.6, 37.3, 37.3, 36.8, 36.8, 33.7, 33.7, 33.5, 33.5, 33.4, 29.8, 26.8, 26.6, 26.5, 26.5, 15.4, 12.1, 12.0. **IR** ν (cm^{-1}) 2920, 2850, 2361, 2341, 1448, 1022, 971. **HRMS** (ESI-ion trap) calcd for $C_{13}H_{24}NO^+$ ($[M+H]^+$) 210.1852, found 210.1849



1p

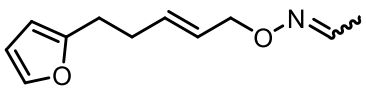
The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 657 mg, 75% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (q, *J* = 5.8 Hz, 0.5H), 7.40 (m, 2H), 7.32 (m, 2H), 7.23 (m, 1H), 6.81 (q, *J* = 5.5 Hz, 0.5H), 6.64 (m, 1H), 6.37 (m, 1H), 4.72 (m, 2H), 1.88 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.3, 136.8, 133.3, 133.0, 128.7, 127.9, 127.9, 126.7, 125.8, 125.5, 74.5, 74.2, 15.4, 12.1. **IR** ν (cm^{-1}) 2919, 2855, 2361, 2341, 1436, 1017, 747, 692. **HRMS** (ESI-ion trap) calcd for $C_{11}H_{14}NO^+$ ($[M+H]^+$) 176.1070, found 176.1068



1q

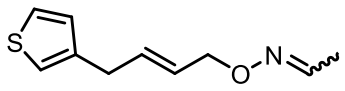
The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 661 mg, 73% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.9 Hz, 0.5H), 6.78 (q, *J* = 5.5 Hz, 0.5H), 5.70 (m, 1H), 5.62 (m, 1H), 4.51 (m, 2H), 2.01 (m, 1H), 1.87 (m, 3H), 1.65 (m, 6H), 1.21 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.9, 141.5, 140.9, 123.4, 122.9, 75.0, 74.7, 40.5, 32.8, 32.8, 26.3, 26.2, 15.4, 12.1. **IR** ν (cm^{-1})

2922, 2851, 2360, 2341, 1448, 1022, 970. **HRMS** (ESI-ion trap) calcd for $C_{11}H_{20}NO^+$ ($[M+H]^+$) 182.1539, found 182.1537



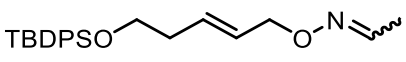
1r

The titled compound was prepared according to **General Procedure** in 6.0 mmol scale. Colorless oil. 869 mg, 75% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.9 Hz, 0.5H), 7.30 (m, 1H), 6.77 (q, *J* = 5.5 Hz, 0.5H), 6.27 (m, 1H), 5.99 (m, 1H), 5.76 (m, 1H), 5.71 (m, 1H), 4.50 (m, 2H), 2.73 (m, 2H), 2.42 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.6, 155.6, 147.1, 141.0, 134.0, 133.4, 127.0, 126.6, 110.2, 105.1, 74.4, 74.2, 30.9, 27.7, 27.7, 15.4, 12.1. **IR** ν (cm^{-1}) 2919, 2854, 2360, 2341, 1508, 1012, 731. **HRMS** (ESI-ion trap) calcd for $C_{11}H_{16}NO_2^+$ ($[M+H]^+$) 194.1176, found 194.1173



1s

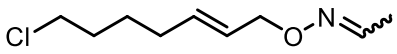
The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Yellow oil. 683 mg, 70% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (q, *J* = 5.9 Hz, 0.5H), 7.14 (m, 1H), 6.93 (m, 1H), 6.81 (m, 1H), 6.79 (m, 0.5H), 5.92 (m, 1H), 5.78 (m, 1H), 4.59 (m, 1H), 4.50 (m, 1H), 3.59 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.1, 143.0, 142.9, 132.6, 132.1, 128.0, 127.7, 127.3, 127.0, 126.7, 125.1, 124.8, 123.8, 123.5, 74.0, 73.7, 32.9, 15.3, 12.1. **IR** ν (cm^{-1}) 2919, 2865, 2360, 2341, 1436, 1368, 1012, 968, 695. **HRMS** (ESI-ion trap) calcd for $C_{10}H_{14}NOS^+$ ($[M+H]^+$) 196.0791, found 196.0790



1t

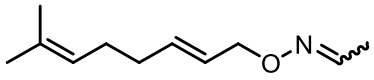
The titled compound was prepared according to **General Procedure** in 1.9 mmol scale. Colorless oil. 572 mg, 77% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (m, 4H), 7.38 (m, 6H), 6.76

(q, *J* = 5.5 Hz, 0.5H), 5.71 (m, 2H), 4.49 (m, 2H), 3.71 (m, 2H), 2.33 (m, 2H), 1.84 (m, 3H), 1.05 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 135.7, 134.1, 131.8, 131.3, 129.7, 128.1, 127.7, 74.6, 74.3, 63.5, 35.9, 27.0, 19.4, 15.4, 12.1. **IR** ν (cm^{-1}) 2930, 2858, 2360, 2341, 1428, 1109, 688. **HRMS** (ESI-ion trap) calcd for $C_{23}H_{32}NO_2Si^+$ ($[M+H]^+$) 382.2197, found 382.2184



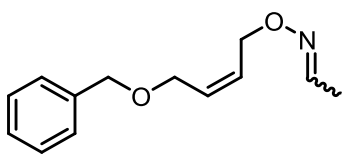
1u

The titled compound was prepared according to **General Procedure** in 2.0 mmol scale. Colorless oil. 250 mg, 60% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.8 Hz, 0.5H) 6.77 (q, *J* = 5.5 Hz, 0.5H), 5.68 (m, 2H), 4.52 (d, *J* = 5.7 Hz, 1H), 4.46 (d, *J* = 6.0 Hz, 1H), 3.53 (m, 2H), 2.10 (m, 2H), 1.85 (m, 3H), 1.80 (m, 2H), 1.55 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 134.7, 134.2, 126.7, 126.4, 74.5, 74.2, 45.0, 32.2, 31.7, 26.3, 26.3, 15.4, 12.1. **IR** ν (cm^{-1}) 2923, 2861, 2360, 2341, 1672, 1637, 1021, 971. **HRMS** (ESI-ion trap) calcd for $C_9H_{17}ClNO^+$ ($[M+H]^+$) 190.0993, found 190.0986



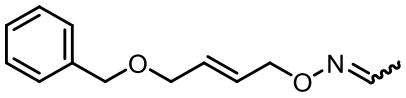
1v

The titled compound was prepared according to **General Procedure** in 2.1 mmol scale. Colorless oil. 276 mg, 65% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.9 Hz, 0.5H), 6.76 (q, *J* = 5.5 Hz, 0.5H), 5.74 (m, 1H), 5.65 (m, 1H), 5.11 (m, 1H), 4.49 (m, 2H), 2.08 (m, 4H), 1.84 (m, 3H), 1.68 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ146.9, 135.4, 134.9, 132.0, 132.0, 126.1, 125.7, 123.9, 123.9, 74.7, 74.4, 32.7, 32.7, 27.7, 27.7, 25.8, 17.9, 15.4, 12.1. **IR** ν (cm^{-1}) 2918, 2360, 2341, 1438, 1376, 1019, 969. **HRMS** (ESI-ion trap) calcd for $C_{11}H_{20}NO^+$ ($[M+H]^+$) 182.1539, found 182.1534



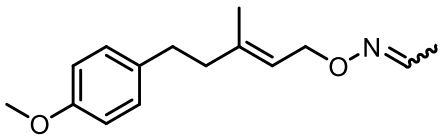
(*Z*)-1w

The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 646 mg, 59% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1.2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (q, *J* = 5.9 Hz, 0.6H), 7.34 (m, 5H), 6.77 (q, *J* = 5.5 Hz, 0.4H), 5.81 (m, 2H), 4.61 (m, 2H), 4.52 (m, 2H), 4.14 (m, 2H), 1.84 (t, *J* = 5.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ147.3, 138.3, 130.1, 129.8, 129.0, 128.7, 128.5, 127.9, 127.8, 72.4, 72.4, 69.5, 69.1, 66.0, 66.0, 15.4, 12.0. **IR** ν (cm^{-1}) 2921, 2856, 2360, 2341, 1739, 1454, 1027. **HRMS** (ESI-ion trap) calcd for $C_{13}H_{18}NO_2^+$ ($[M+H]^+$) 220.1332, found 220.1326



(*E*)-1w

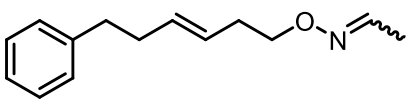
The titled compound was prepared according to **General Procedure** in 5.0 mmol scale. Colorless oil. 762 mg, 70% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1.2:1) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (m, 0.4H), 7.32 (m, 5H), 6.78 (q, *J* = 5.5 Hz, 0.6H), 5.90 (m, 2H), 4.61 (d, *J* = 5.3 Hz, 1H), 4.54 (m, 3H), 4.06 (m, 2H), 1.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.2, 147.2, 138.4, 130.2, 129.7, 129.3, 129.0, 128.5, 127.9, 127.9, 127.7, 73.7, 73.4, 72.3, 72.3, 70.2, 70.2, 15.3, 12.0. **IR** ν (cm^{-1}). 2852, 1737, 1364, 736, 679. **HRMS** (ESI-ion trap) calcd for $C_{13}H_{18}NO_2^+$ ($[M+H]^+$) 220.1332, found 220.1326



1x

The titled compound was prepared according to **General Procedure** in 10 mmol scale. Colorless oil. 1.6 g, 66% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1.2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (q, *J* = 5.9 Hz, 0.4H), 7.10 (m, 2H), 6.82 (m, 2H), 6.77 (q, *J* = 5.6 Hz, 0.6H), 5.44 (m, 1H), 4.56 (m, 2H), 3.79 (s, 3H), 2.69 (m, 2H), 2.32 (m, 2H), 1.85 (m, 3H), 1.75 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-

d) δ 157.9, 146.9, 146.9, 146.8, 141.0, 140.2, 134.3, 134.1, 129.4, 129.4, 129.3, 121.7, 121.2, 120.7, 120.1, 113.9, 113.9, 70.5, 70.1, 70.1, 69.7, 55.4, 41.9, 41.9, 34.8, 34.7, 33.8, 33.8, 33.6, 23.8, 16.9, 16.9, 15.4, 12.1. **IR** ν (cm^{-1}) 2921, 2361, 2341, 1511, 1244, 1035, 823. **HRMS** (ESI-ion trap) calcd for $C_{15}H_{22}NO_2^+$ ($[M+H]^+$) 248.1645, found 248.1637



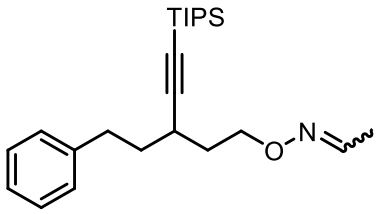
1y

The titled compound was prepared according to **General Procedure** in 2.8 mmol scale. Colorless oil. 456 mg, 74% Yield. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (q, *J* = 5.8 Hz, 0.5H), 7.29 (m, 2H), 7.17 (m, 3H), 6.75 (q, *J* = 5.5 Hz, 1H), 5.55 (m, 1H), 5.46 (m, 1H), 4.03 (m, 2H), 2.68 (m, 2H), 2.33 (m, 4H), 1.84 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ147.0, 147.0, 142.5, 135.2, 134.7, 128.6, 128.5, 128.4, 126.5, 126.1, 125.8, 74.6, 74.3, 35.5, 32.0, 30.8, 30.8, 15.4, 12.1. **IR** ν (cm^{-1}) 2923, 2361, 2341, 1474, 1044, 669. **HRMS** (ESI-ion trap) calcd for $C_{14}H_{20}NO^+$ ($[M+H]^+$) 218.1539, found 218.1534

General procedure for Ir-catalyzed hydroalkynylation

In an Ar-filled glovebox, $Ir(COD)_2OTf$ (5.6 mg, 10 mol%), Ph-BPE (6.1 mg, 12 mol%) and unsaturated oxime (0.10 mmol) were weighed into a Schlenk tube. Then 0.40 mL DCE and triisopropylsilylacetylene (55 mg, 0.30 mmol) were added via syringes. The vial was capped with a Teflon-lined screw cap and removed from the glovebox. Subsequently the vial was put in a preheated oil bath (60 °C). After 24h, the vial was cool to room temperature, and the reaction mixture was purified by column chromatography with ethyl acetate/hexanes as eluent.

Characterization of products

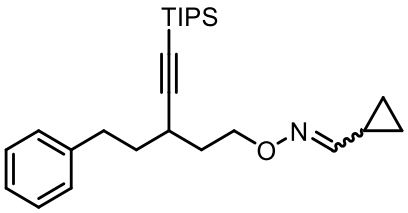


3a

Following the **general procedure**, oxime **1a** (20.3 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3a** (31.6 mg, 82% yield) as a light-yellow oil.

Following the **general procedure**, oxime **1a** (203 mg, 1.00 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3a** (346 mg, 90% yield) as a light-yellow oil.

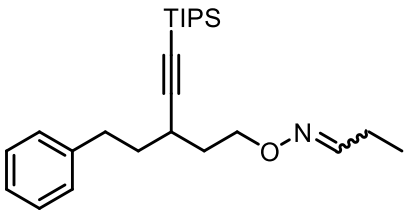
Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (q, *J* = 5.8 Hz, 0.5H), 7.29 (m, 2H), 7.21 (m, 3H), 6.74 (q, *J* = 5.5 Hz, 0.5H), 4.22 (m, 2H), 2.90 (m, 1H), 2.78 (m, 1H), 2.56 (m, 1H), 1.82 (m, 7H), 1.11 (m, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 146.7, 142.3, 142.2, 128.7, 128.5, 128.5, 125.9, 111.3, 111.3, 82.2, 82.2, 71.7, 71.5, 37.5, 37.4, 34.7, 33.8, 33.7, 29.3, 29.2, 18.8, 15.3, 11.9, 11.4. **IR** ν (cm^{-1}) 2941, 2864, 2360, 2341, 2164, 1461, 862, 675. **HRMS** (ESI-ion trap) calcd for $C_{24}H_{40}NOSi^+$ ($[M+H]^+$) 386.2874, found 386.2861



3b

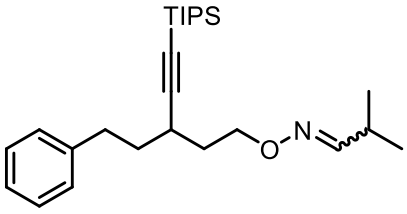
Following the **general procedure**, oxime with **1b** (22.9 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3b** (15.6 mg, 38% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (m, 2H), 7.20 (m, 3H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.17 (m, 2H), 2.88 (m, 1H), 2.76

(m, 1H), 2.54 (m, 1H), 1.86 (m, 1H), 1.76 (m, 3H), 1.59 (m, 1H), 1.07 (m, 21H), 0.85 (m, 2H), 0.59 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.1, 142.3, 128.7, 128.5, 125.9, 111.3, 82.2, 71.5, 37.5, 34.7, 33.8, 29.3, 18.9, 11.4, 11.1, 5.7, 5.7. **IR** ν (cm^{-1}) 2941, 2864, 2360, 2341, 1382, 1058, 883. **HRMS** (ESI-ion trap) calcd for $C_{26}H_{42}NOSi^+$ ($[M+H]^+$) 412.3030, found 412.3013



3c

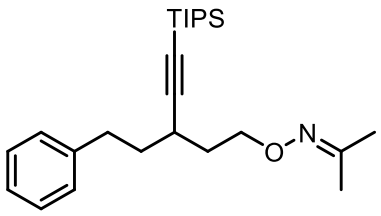
Following the **general procedure**, oxime **1c** (21.7 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3c** (23.5 mg, 59% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1.2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 6.0 Hz, 0.6H), 7.28 (m, 2H), 7.20 (m, 3H), 6.60 (t, *J* = 5.3 Hz, 0.4H), 4.20 (m, 2H), 2.89 (m, 1H), 2.77 (m, 1H), 2.55 (m, 1H), 2.29 (m, 2H), 1.87 (m, 1H), 1.78 (m, 2H), 1.08 (m, 24H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.2, 151.9, 142.3, 142.3, 128.7, 128.6, 128.5, 128.5, 125.9, 111.3, 111.3, 82.2, 71.8, 71.5, 37.5, 37.4, 34.7, 33.8, 33.8, 29.3, 29.2, 23.2, 19.3, 18.8, 11.4, 11.3, 10.8. **IR** ν (cm^{-1}) 2941, 2865, 2361, 2341, 2164, 1459, 1059, 883. **HRMS** (ESI-ion trap) calcd for $C_{25}H_{42}NOSi^+$ ($[M+H]^+$) 400.3030, found 400.3017



3d

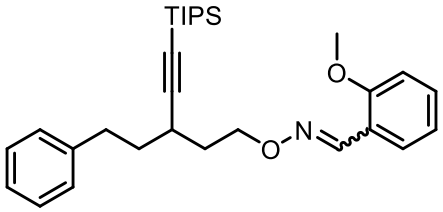
Following the **general procedure**, oxime **1d** (23.1 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3d** (19.8 mg, 48% yield) as a colorless oil. Spectroscopic data are

given as a mixture of *cis* and *trans* isomers (4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (m, 2H), 7.20 (m, 3H), 6.43 (d, *J* = 7.2 Hz, 0.2H), 4.18 (m, 2H), 2.91 (m, 0.2H), 2.89 (m, 1H), 2.76 (m, 1H), 2.49 (m, 2H), 1.80 (m, 4H), 1.08 (m, 28H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.4, 155.8, 142.3, 128.7, 128.5, 125.9, 111.3, 82.2, 71.7, 71.4, 37.5, 37.4, 34.7, 33.8, 33.8, 29.5, 29.3, 29.2, 25.2, 20.3, 20.2, 19.9, 18.8, 11.5. **IR** ν (cm^{-1}) 2959, 2865, 2361, 2341, 2164, 1496, 1060, 883, 676. **HRMS** (ESI-ion trap) calcd for $C_{26}H_{44}NOSi^+$ ($[M+H]^+$) 414.3187, found 414.3176



3f

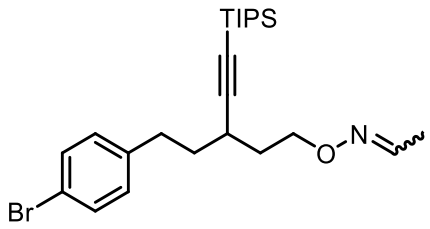
Following the **general procedure**, oxime **1f** (43.4 mg, 0.200 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3f** (8.40 mg, 10% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.5 Hz, 2H), 7.25 (m, 3H), 4.17 (m, 2H), 2.88 (m, 1H), 2.76 (m, 1H), 2.54 (m, 1H), 1.82 (m, 10H), 1.09 (m, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.7, 142.3, 128.7, 128.5, 125.9, 111.5, 82.1, 71.2, 37.4, 34.8, 33.8, 29.3, 22.0, 18.8, 15.7, 11.5. **IR** ν (cm^{-1}) 2942, 2864, 2360, 2341, 1558, 1070, 919. **HRMS** (ESI-ion trap) calcd for $C_{25}H_{42}NOSi^+$ ($[M+H]^+$) 400.3030, found 400.3014



3h

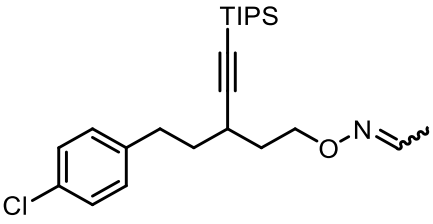
Following the **general procedure**, oxime **1h** (29.5 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3h** (14.8 mg, 31% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ

7.28 (m, 2H), 7.20 (m, 3H), 6.85 (m, 2H), 4.17 (m, 2H), 3.84 (m, 3H), 2.91 (m, 1H), 2.75 (m, 1H), 2.54 (m, 1H), 1.85 (m, 4H), 1.76 (m, 1H), 1.11 (m, 21H), 0.84 (m, 2H), 0.59 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ157.6, 144.7, 142.3, 131.1, 128.7, 128.5, 126.5, 125.9, 121.2, 120.9, 111.4, 111.2, 82.3, 72.2, 55.7, 37.5, 34.9, 33.8, 29.4, 19.0, 18.9, 11.5. **IR** ν (cm^{-1}) 2940, 2863, 2361, 2341, 2164, 1464, 1251, 752. **HRMS** (ESI-ion trap) calcd for $C_{30}H_{44}NO_2Si^+$ ($[M+H]^+$) 478.3136, found 478.3120



3i

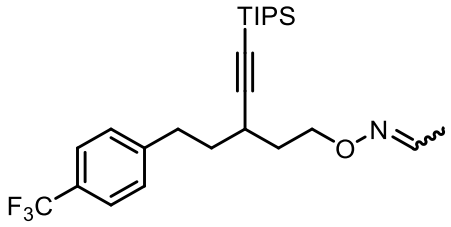
Following the **general procedure**, oxime **1i** (28.1 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3i** (39.4 mg, 85% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (m, 2.5H), 7.07 (m, 2H), 6.73 (q, *J* = 5.5 Hz, 0.5H), 4.17 (m, 2H), 2.85 (m, 1H), 2.73 (m, 1H), 2.51 (m, 1H), 1.81 (m, 6H), 1.09 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 141.2, 141.1, 131.5, 130.4, 119.7, 111.1, 111.0, 82.5, 82.5, 71.6, 71.4, 37.2, 37.1, 34.7, 33.1, 33.1, 29.2, 29.1, 18.8, 15.4, 11.9, 11.4. **IR** ν (cm^{-1}) 2942, 2864, 2360, 2341, 2164, 1489, 1462, 996, 863. **HRMS** (ESI-ion trap) calcd for $C_{24}H_{39}BrNOSi^+$ ($[M+H]^+$) 464.1979, found 464.1962



3j

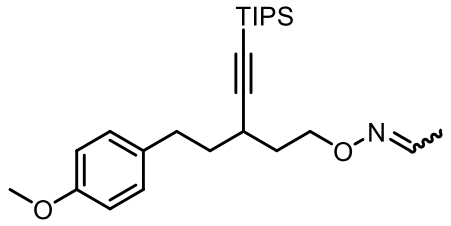
Following the **general procedure**, oxime **1j** (23.7 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3j** (28.9 mg, 69% yield) as a colorless oil. Spectroscopic data are given

as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.8 Hz, 0.5 H), 7.26 (m, 2H), 7.15 (m, 2H), 6.75 (q, *J* = 5.5 Hz, 1H), 4.24 (m, 2H), 2.87 (m, 1H), 2.76 (m, 1H), 2.54 (m, 1H), 1.83 (m, 7H), 1.11 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 140.6, 140.6, 131.7, 130.0, 128.6, 111.1, 111.0, 82.5, 82.4, 71.6, 71.4, 37.2, 37.1, 34.7, 33.1, 33.1, 29.2, 29.1, 18.8, 15.4, 11.9, 11.4. **IR** ν (cm^{-1}) 2941, 2890, 2864, 2361, 2341, 2164, 1492, 863. **HRMS** (ESI-ion trap) calcd for $C_{24}H_{39}ClNOSi^+$ ($[M+H]^+$) 420.2484, found 420.2472



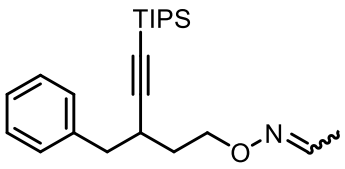
3k

Following the **general procedure**, oxime **1k** (27.1 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3k** (38.1 mg, 84% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (m, 2H), 7.37 (q, *J* = 5.9 Hz, 0.5H), 7.31 (m, 2H), 6.73 (m, 0.5H), 4.20 (m, 2H), 2.94 (m, 1H), 2.83 (m, 1H), 2.52 (m, 1H), 1.80 (m, 7H), 1.09 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 146.8, 146.3, 129.0, 128.5, 128.2, 125.9, 125.5, 125.4, 125.4, 123.2, 110.9, 110.9, 82.6, 71.6, 71.3, 37.0, 36.9, 34.7, 33.6, 33.6, 29.2, 29.1, 18.8, 15.3, 11.9, 11.4. **IR** ν (cm^{-1}) 2943, 2866, 2361, 2341, 1772, 1733, 883, 750. **HRMS** (ESI-ion trap) calcd for $C_{25}H_{39}F_3NOSi^+$ ($[M+H]^+$) 454.2748, found 454.2728



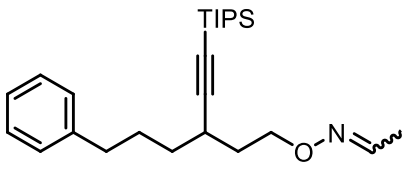
3l

Following the **general procedure**, oxime **1l** (23.3 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3l** (36.5 mg, 88% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.8 Hz, 0.5H), 7.14 (m, 2H), 6.85 (m, 2H), 6.75 (q, *J* = 5.5 Hz, 0.5H), 4.23 (m, 2H), 3.81 (s, 3H), 2.84 (m, 1H), 2.74 (m, 1H), 2.55 (m, 1H), 1.81 (m, 7H), 1.12 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.9, 146.9, 146.7, 134.4, 134.3, 129.5, 113.9, 111.4, 111.4, 82.2, 82.1, 71.8, 71.5, 55.4, 37.7, 37.6, 34.7, 32.8, 32.8, 29.2, 29.2, 18.8, 15.4, 12.0, 11.4, 11.4. **IR** ν (cm^{-1}) 2941, 2864, 2361, 2341, 1513, 1246, 750. **HRMS** (ESI-ion trap) calcd for $C_{25}H_{42}NO_2Si^+$ ($[M+H]^+$) 416.2979, found 416.2965



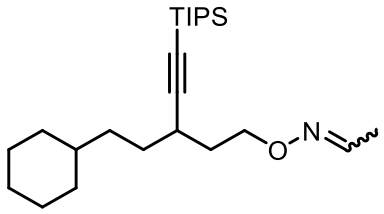
3m

Following the **general procedure**, oxime **1m** (18.9 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3m** (33.4 mg, 90% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.9 Hz, 0.5H), 7.27 (m, 4H), 7.20 (m, 1H), 6.75 (m, 0.5H), 4.22 (m, 2H), 2.81 (m, 3H), 1.93 (m, 1H), 1.84 (m, 3H), 1.74 (m, 1H), 1.03 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 139.5, 129.5, 128.2, 128.2, 126.3, 110.8, 82.7, 71.8, 71.4, 41.7, 34.3, 34.3, 31.7, 31.7, 18.7, 15.4, 12.0, 11.4. **IR** ν (cm^{-1}) 2941, 2864, 2360, 2342, 2165, 1462, 863, 676. **HRMS** (ESI-ion trap) calcd for $C_{23}H_{38}NOSi^+$ ($[M+H]^+$) 372.2717, found 372.2705



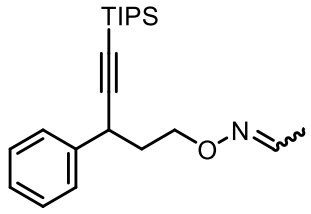
3n

Following the **general procedure**, oxime **1n** (21.7 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3n** (30.3 mg, 76% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (m, 2H), 7.17 (m, 3H), 6.74 (q, *J* = 5.5 Hz, 1H), 4.23 (m, 2H), 2.62 (m, 3H), 1.81 (m, 7H), 1.51 (m, 2H), 1.06 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 142.6, 128.5, 128.4, 125.8, 111.6, 81.7, 71.8, 35.8, 34.9, 34.8, 29.5, 29.1, 18.8, 12.0, 11.4. **IR** ν (cm^{-1}) 2943, 2865, 2360, 2253, 1636, 1375, 1039, 919. **HRMS** (ESI-ion trap) calcd for $C_{25}H_{42}NOSi^+$ ($[M+H]^+$) 400.3030, found 400.3016



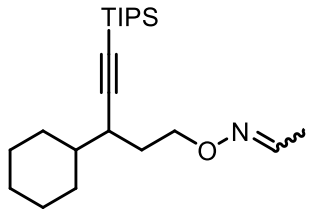
3o

Following the **general procedure**, oxime **1o** (20.9 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3o** (25.4 mg, 65% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.9 Hz, 0.5H), 6.74 (q, *J* = 5.5 Hz, 0.5H), 4.22 (m, 2H), 2.48 (m, 1H), 1.84 (m, 3H), 1.68 (m, 4H), 1.44 (m, 3H), 1.20 (m, 7H), 1.06 (s, 21H), 0.89 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 146.6, 112.0, 112.0, 81.4, 71.9, 71.6, 37.6, 35.0, 34.7, 33.8, 33.3, 32.8, 32.7, 29.8, 29.8, 26.9, 26.5, 26.5, 18.8, 15.4, 12.0, 11.4. **IR** ν (cm^{-1}) 2921, 2863, 2361, 2341, 2165, 2030, 1462, 861, 661. **HRMS** (ESI-ion trap) calcd for $C_{24}H_{46}NOSi^+$ ($[M+H]^+$) 392.3343, found 392.3326



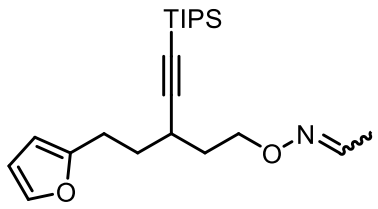
3p

Following **the general procedure**, oxime **1p** (17.5 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3p** (9.60 mg, 27% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (m, 2.5H), 7.32 (m, 2H), 7.22 (m, 1H), 6.76 (q, *J* = 5.5 Hz, 1H), 4.19 (m, 2H), 3.86 (m, 1H), 2.10 (m, 2H), 1.84 (m, 3H), 1.09 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 138.5, 128.5, 127.9, 127.6, 109.0, 82.5, 73.4, 73.3, 73.2, 73.2, 71.5, 71.2, 31.5, 31.5, 30.7, 30.6, 18.8, 15.4, 12.0, 11.4, 11.4. **IR** ν (cm^{-1}) 2941, 2864, 2360, 2341, 1541, 750, 669. **HRMS** (ESI-ion trap) calcd for $C_{22}H_{36}NOSi^+$ ($[M+H]^+$) 358.2561, found 358.2550



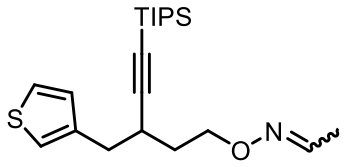
3q

Following the **general procedure**, oxime **1q** (18.1 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3q** (19.6 mg, 54% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.8 Hz, 0.5H), 6.74 (q, *J* = 5.5 Hz, 0.5H), 4.19 (m, 2H), 2.42 (m, 1H), 1.75 (m, 10H), 1.21 (m, 6H), 1.06 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 146.6, 110.5, 110.5, 82.4, 72.3, 72.0, 41.6, 41.5, 35.8, 35.7, 32.2, 31.7, 28.9, 28.8, 26.7, 26.7, 26.5, 18.8, 15.4, 12.0, 11.5. **IR** ν (cm^{-1}) 2925, 2863, 2360, 2341, 2164, 2030, 1463, 883, 676. **HRMS** (ESI-ion trap) calcd for $C_{22}H_{42}NOSi^+$ ($[M+H]^+$) 364.3030, found 364.3015



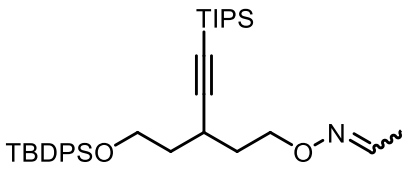
3r

Following the **general procedure**, oxime **1r** (19.3 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3r** (29.6 mg, 79% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (q, *J* = 5.8 Hz, 0.5H), 7.32 (d, *J* = 1.8 Hz, 1H), 6.76 (q, *J* = 5.5 Hz, 0.5H), 6.30 (s, 1H), 6.02 (s, 1H), 4.26 (m, 2H), 2.90 (m, 1H), 2.82 (m, 1H), 2.60 (m, 1H), 1.85 (m, 7H), 1.10 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 155.9, 155.8, 146.9, 146.7, 141.0, 110.9, 110.9, 110.2, 105.1, 105.1, 82.4, 82.3, 71.7, 71.4, 34.6, 33.8, 33.7, 29.2, 26.0, 18.8, 15.4, 12.0, 11.4. **IR** ν (cm^{-1}) 2942, 2864, 2360, 2341, 2165, 1463, 863, 661. **HRMS** (ESI-ion trap) calcd for $C_{22}H_{38}NO_2Si^+$ ($[M+H]^+$) 376.2666, found 376.2647



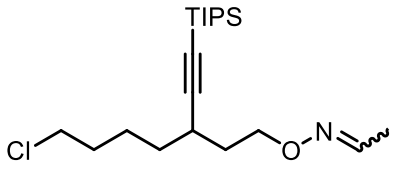
3s

Following the **general procedure**, oxime **1s** (19.5 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3s** (28.3 mg, 75% yield) as a yellow oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.8 Hz, 0.5H), 7.13 (m, 1H), 6.90 (m, 2H), 6.74 (q, *J* = 5.5 Hz, 0.5H), 4.21 (m, 2H), 3.03 (m, 2H), 2.86 (m, 1H), 1.94 (m, 1H), 1.84 (m, 3H), 1.75 (m, 1H), 1.08 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.8, 141.7, 141.7, 126.6, 126.6, 125.9, 125.9, 123.8, 123.8, 110.4, 110.4, 83.0, 83.0, 71.6, 71.3, 35.9, 34.0, 34.0, 32.1, 32.0, 18.8, 18.7, 15.3, 12.0, 11.4. **IR** ν (cm^{-1}) 2941, 2890, 2864, 2360, 2341, 2166, 1462, 1017, 852. **HRMS** (ESI-ion trap) calcd for $C_{21}H_{36}NOSSi^+$ ($[M+H]^+$) 378.2281, found 378.2268



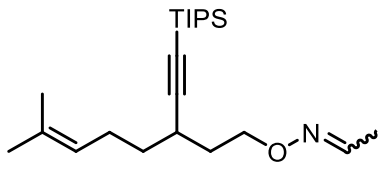
3t

Following the **general procedure**, oxime **1t** (38.1 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3t** (41.7 mg, 74% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (m, 4H), 7.41 (m, 6.5H), 6.78 (q, *J* = 5.5 Hz, 0.5H), 4.28 (m, 2H), 3.90 (m, 2H), 2.88 (m, 1H), 1.84 (m, 7H), 1.07 (m, 30H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 146.6, 135.7, 135.6, 134.2, 134.1, 129.6, 127.7, 111.2, 81.7, 81.7, 71.7, 71.4, 62.0, 62.0, 38.3, 38.3, 34.8, 34.8, 27.0, 26.2, 26.2, 19.4, 18.8, 15.4, 12.0, 11.4. **IR** ν (cm^{-1}) 2941, 2863, 2360, 2341, 2165, 1463, 1428, 1110, 701. **HRMS** (ESI-ion trap) calcd for $C_{34}H_{54}NO_2Si_2^+$ ($[M+H]^+$) 564.3688, found 564.3672



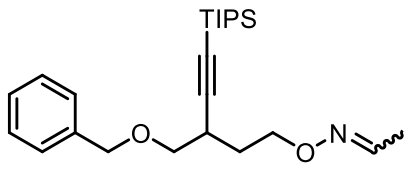
3u

Following the **general procedure**, oxime **1u** (18.9 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3u** (30.8 mg, 83% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 5.9 Hz, 0.5H), 6.75 (q, *J* = 5.5 Hz, 0.5H), 4.23 (m, 1H), 4.17 (m, 1H), 3.53 (m, 2H), 2.54 (m, 1H), 1.83 (m, 8H), 1.50 (m, 3H), 1.06 (m, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 111.3, 111.2, 82.0, 71.8, 71.5, 45.1, 34.8, 34.6, 32.6, 32.6, 29.6, 29.5, 24.8, 24.8, 18.8, 15.4, 12.0, 11.4. **IR** ν (cm^{-1}) 2943, 2866, 2360, 2341, 1717, 1699, 882, 669. **HRMS** (ESI-ion trap) calcd for $C_{20}H_{39}ClNOSi^+$ ($[M+H]^+$) 372.2484, found 372.2468



3v

Following the **general procedure**, oxime **1v** (18.1 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3v** (26.9 mg, 74% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (q, *J* = 5.8 Hz, 0.5H), 6.76 (q, *J* = 5.5 Hz, 0.5H), 5.13 (m, 1H), 4.25 (m, 2H), 2.55 (m, 1H), 2.22 (m, 2H), 1.85 (m, 5H), 1.71 (m, 3H), 1.64 (m, 3H), 1.50 (m, 2H), 1.09 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 146.6, 132.2, 132.2, 124.1, 111.8, 111.7, 81.6, 81.6, 71.9, 71.6, 35.7, 35.6, 34.8, 29.3, 29.3, 26.0, 25.9, 18.8, 17.8, 15.4, 12.0, 11.4. **IR** ν (cm^{-1}) 2941, 2864, 2360, 2341, 2164, 1462, 862, 660. **HRMS** (ESI-ion trap) calcd for $C_{22}H_{42}NOSi^+$ ($[M+H]^+$) 364.3030, found 364.3015

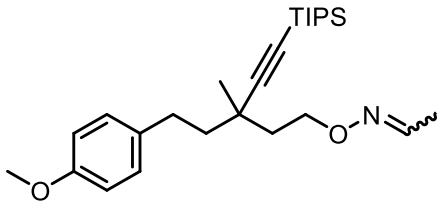


3w

Following the **general procedure**, oxime (*Z*)-**1w** (21.9 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3w** (9.20 mg, 23% yield) as a colorless oil.

Following the **general procedure**, oxime (*E*)-**1w** (21.9 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3w** (27.7 mg, 69% yield) as a colorless oil.

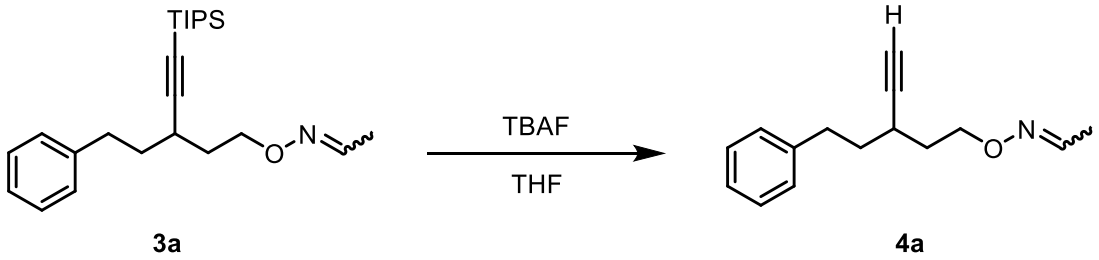
Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 (m, 5.5H), 6.74 (m, 0.5H), 4.57 (m, 2H), 4.27 (m, 2H), 3.61 (m, 1H), 3.50 (m, 1H), 2.89 (m, 1H), 2.07 (m, 1H), 1.84 (m, 3H), 1.75 (m, 1H), 1.03 (m, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 138.5, 128.5, 127.9, 127.6, 109.0, 82.5, 73.4, 73.3, 73.2, 73.2, 72.4, 71.5, 71.2, 31.5, 31.5, 30.7, 30.6, 18.8, 15.4, 12.0, 11.4, 11.4. **IR** ν (cm^{-1}) 2941, 2864, 2360, 2341, 2167, 1463, 860. **HRMS** (ESI-ion trap) calcd for $C_{24}H_{40}NO_2Si^+$ ($[M+H]^+$) 402.2823, found 402.2805



3x

Following the **general procedure**, oxime **1x** (24.7 mg, 0.100 mmol) was converted to the alkynylation product. Purification by column chromatography with EtOAc/Hexane as eluent gave the product **3x** (16.3 mg, 38% yield) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (q, *J* = 5.8 Hz, 0.5H), 7.10 (m, 2H), 6.83 (m, 2H), 6.74 (q, *J* = 5.5 Hz, 0.5H), 4.29 (m, 2H), 3.79 (s, 3H), 2.75 (m, 2H), 1.90 (m, 1H), 1.83 (m, 5H), 1.65 (m, 1H), 1.28 (m, 3H), 1.08 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 146.7, 138.5, 128.5, 127.9, 127.6, 109.0, 82.5, 73.4, 73.3, 73.2, 73.2, 72.4, 71.5, 71.2, 31.5, 31.5, 30.7, 30.6, 18.8, 15.4, 12.0, 11.4, 11.4. **IR** ν (cm^{-1}) 2931, 2858, 2361, 2341, 1511, 1245, 1035, 824. **HRMS** (ESI-ion trap) calcd for $C_{26}H_{44}NO_2Si^+$ ($[M+H]^+$) 430.3136, found 430.3118

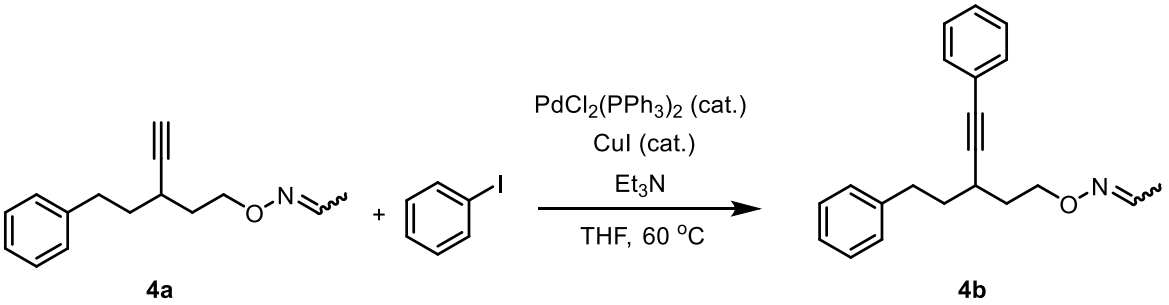
Synthetic transformation of product



3a **4a**

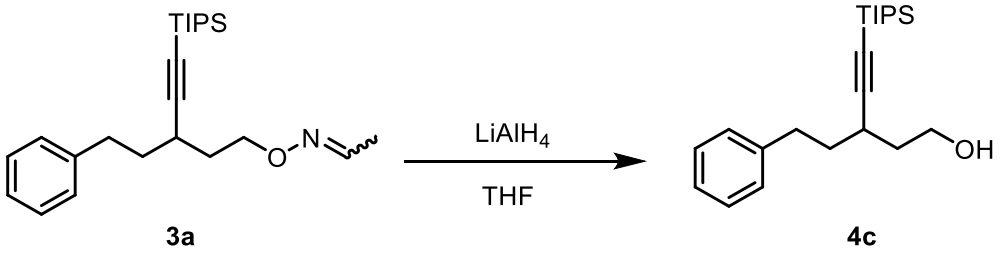
To a solution of **3a** (20 mg, 0.050 mmol) and 0.50 mL THF was added TBAF (1.0 M in THF, 0.50 mL). The reaction was stirred at room temperature for 5 min. Then the crude mixture was purified by column chromatography with EtOAc/Hexane as eluent to give **4a** (20 mg, 86%) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (q, *J* = 5.8 Hz, 0.5H), 7.28 (m, 2H), 7.22 (m, 3H), 6.73 (q, *J* = 5.5 Hz, 0.5H), 4.23 (m, 2H), 2.75 (m, 1H), 2.73 (m, 1H),

2.51 (m, 1H), 2.14 (s, 1H), 1.81 (m, 7H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 146.9, 142.0, 142.0, 128.6, 128.5, 128.5, 126.0, 86.9, 86.8, 71.5, 71.2, 70.4, 70.3, 36.9, 36.8, 34.4, 34.3, 33.6, 33.5, 27.9, 27.9, 15.4, 12.0. **IR** ν (cm^{-1}) 3294, 2925, 2361, 2341, 1053, 700. **HRMS** (ESI-ion trap) calcd for $C_{15}H_{20}NO^+$ ($[M+H]^+$) 230.1539, found 230.1532



4a **4b**

To a Schlenk flask was added **4a** (10 mg, 0.044 mmol), $PdCl_2(PPh_3)_2$ (1.5 mg, 5.0 mol%), CuI (0.50 mg, 5.0 mol%), Et_3N (13 mg, 3.0 equiv) and 2.0 mL THF. The reaction was stirred at 60 °C for 2h. The mixture was purified by column chromatography with EtOAc/Hexane as eluent to give **4b** (9.8 mg, 73%) as a colorless oil. Spectroscopic data are given as a mixture of *cis* and *trans* isomers (1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (m, 2.5H), 7.27 (m, 8H), 6.74 (q, *J* = 5.5 Hz, 1H), 4.28 (m, 2H), 2.93 (m, 1H), 2.72 (m, 2H), 1.82 (m, 7H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.0, 146.9, 142.1, 142.1, 131.8, 128.7, 128.5, 128.3, 127.8, 126.0, 124.0, 92.4, 92.3, 82.9, 82.8, 71.8, 71.5, 37.1, 37.1, 34.6, 34.6, 33.8, 33.8, 29.9, 28.8, 28.8, 15.4, 12.0. **IR** ν (cm^{-1}) 3027, 2923, 2857, 1727, 756, 693. **HRMS** (ESI-ion trap) calcd for $C_{21}H_{24}NO^+$ ($[M+H]^+$) 306.1852, found 306.1842

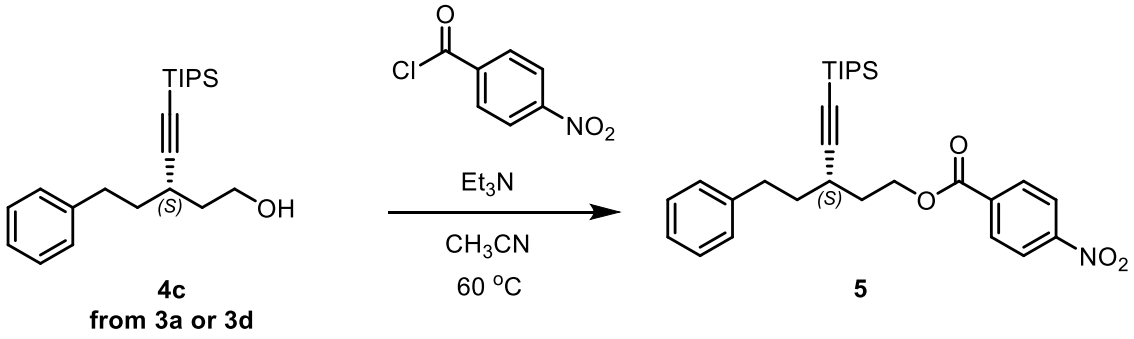


3a **4c**

To a solution of $LiAlH_4$ (7.8 mg, 0.20 mmol) and 1.0 mL THF was added **3a** (20 mg, 0.050 mmol). The reaction was stirred at room temperature for 1 h. The mixture was purified by

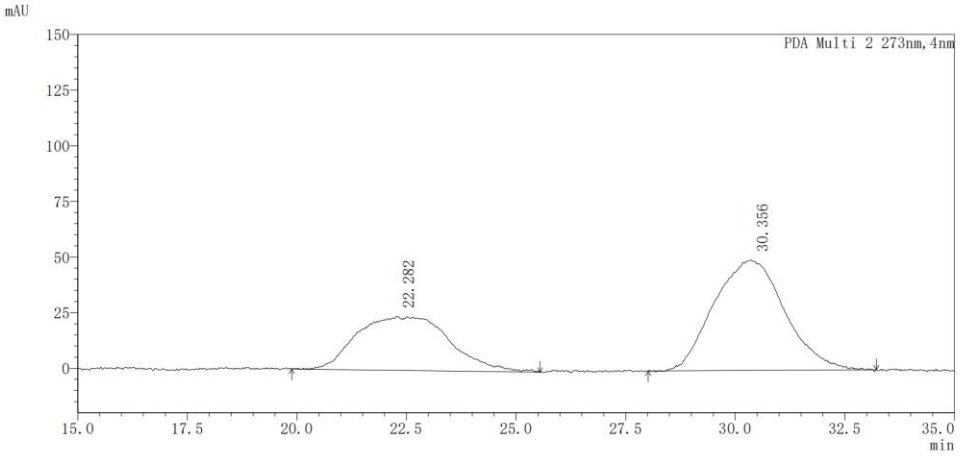
column chromatography with EtOAc/Hexane as eluent to give **4c** (15 mg, 81%) as a colorless yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 (m, 2H), 7.20 (m, 3H), 3.84 (t, *J* = 5.5 Hz, 2H), 2.89 (m, 1H), 2.75 (m, 1H), 2.57 (m, 1H), 1.77 (m, 5H), 1.10 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ142.1, 128.7, 128.5, 126.0, 111.5, 83.1, 61.6, 38.1, 37.6, 33.7, 29.6, 18.8, 11.4. **HRMS** (ESI-ion trap) calcd for $C_{22}H_{37}OSi^+$ ($[M+H]^+$) 345.2608, found 345.2598

Ee determination of 3a and 3d



The ee value of **3a** and **3d** were determined by chiral HPLC analysis of the *p*-nitrobenzoate derivative following a literature procedure.[2]

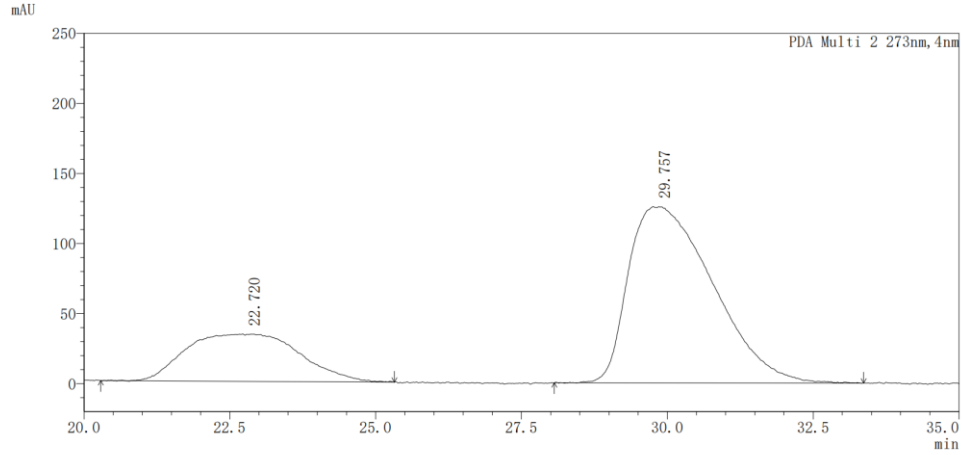
Ee of **3a** (22%) was determined by CHIRALCEL® OD-H, 4.6 mm × 250 mm, hexane/2-propanol = 99:1, 0.5 mL/min, 40 ˚C, retention time = 22.3 min for *R* isomer and 30.4 min for *S* isomer.



PDA Ch2 273nm

Peak	Ret.Time	Height	Area	Area%
1	22.282	24364	3571922	39.023
2	30.356	49659	5581557	60.977

Ee of **3d** (47%) was determined by CHIRALCEL® OD-H, 4.6 mm × 250 mm, hexane/2-propanol = 99:1, 0.5 mL/min, 40 ˚C, retention time = 22.7 min for *R* isomer and 29.8 min for *S* isomer.



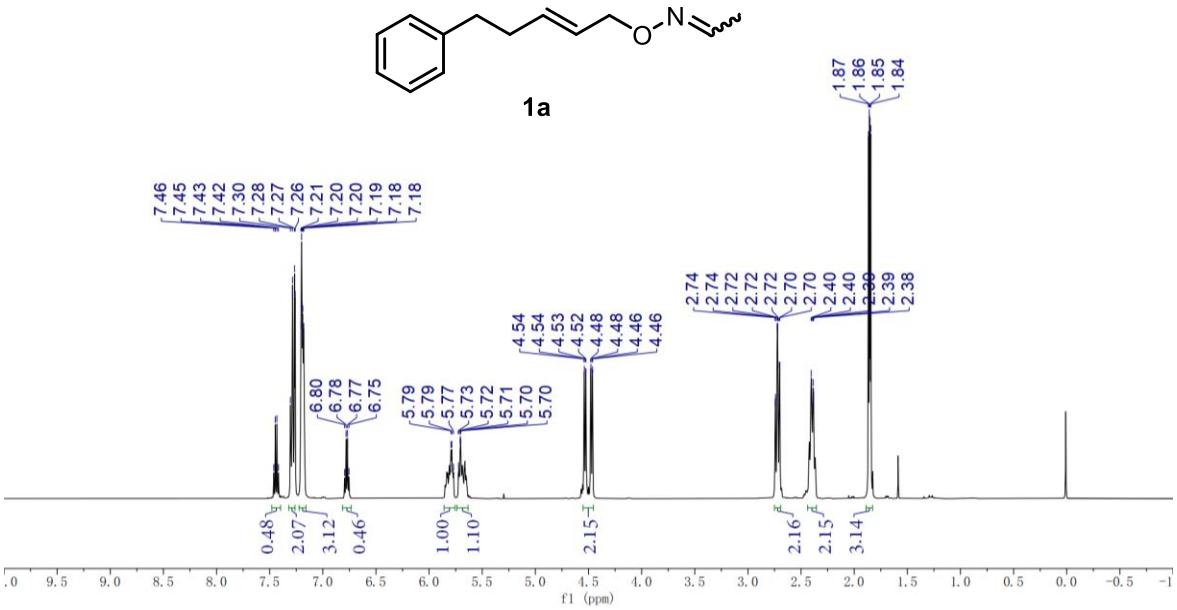
PDA Ch2 273nm

Peak	Ret.Time	Height	Area	Area%
1	22.720	33932	4600181	26.636
2	29.757	125804	12670217	73.364

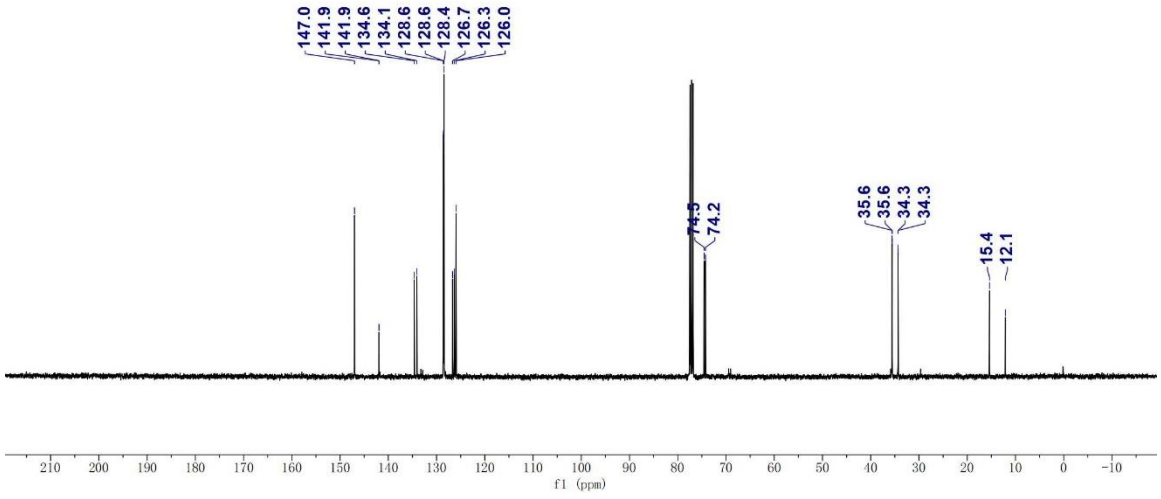
References

1. Tsuchikama, K.; Kasagawa, M.; Endo, K.; Shibata, T. Cationic Ir(I)-Catalyzed sp^3 C−H Bond Alkenylation of Amides with Alkynes. *Org. Lett.* **2009**, *11*, 1821-1823.
2. Harada, A.; Makida, Y.; Sato, T.; Ohmiya, H.; Sawamura, M. Copper-Catalyzed Enantioselective Allylic Alkylation of Terminal Alkyne Pronucleophiles. *J. Am. Chem. Soc.* **2014**, *136*, 13932-13939.

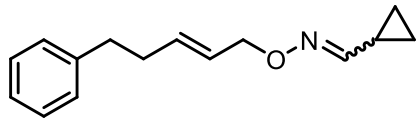
Copy of NMR spectra



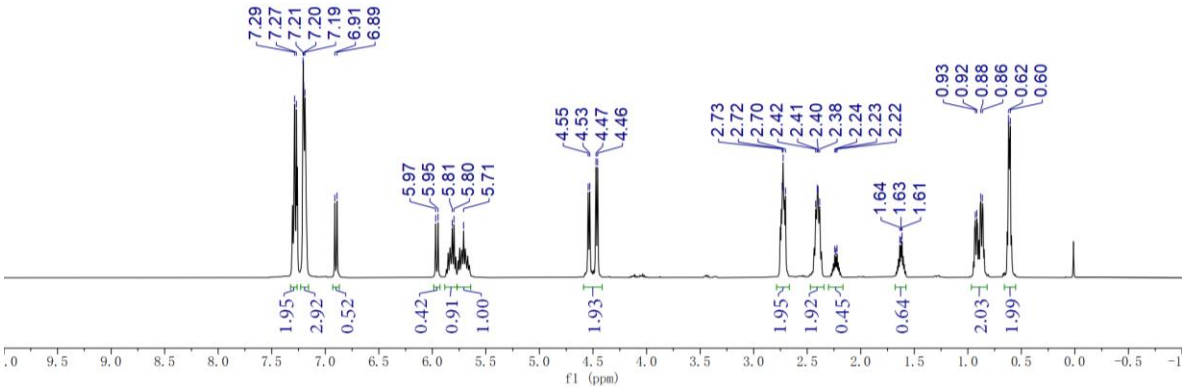
^{1}H NMR spectrum of **1a** was measured in $CDCl_3$ at 400 MHz



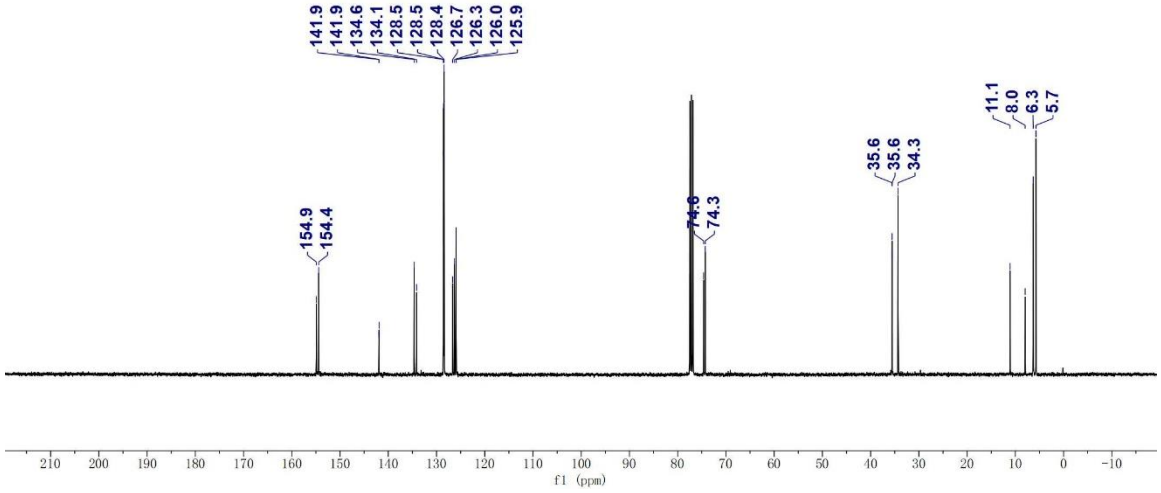
^{13}C NMR spectrum of **1a** was measured in $CDCl_3$ at 101 MHz



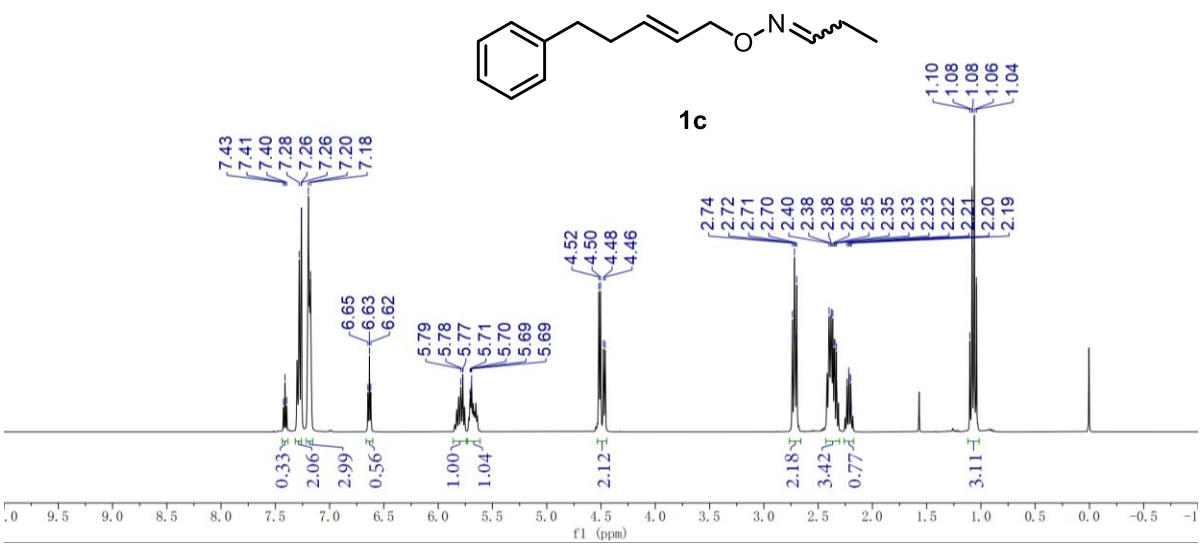
1b



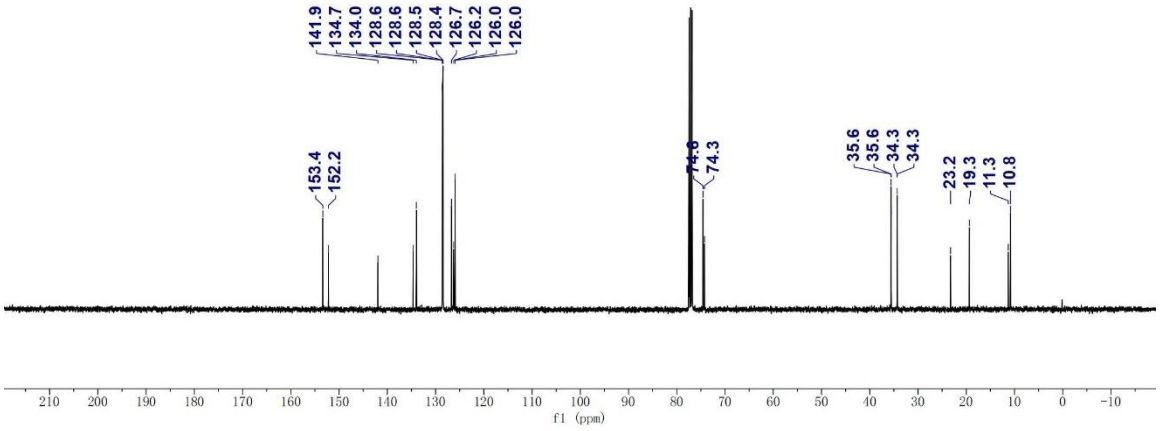
^{1}H NMR spectrum of **1b** was measured in $CDCl_3$ at 400 MHz



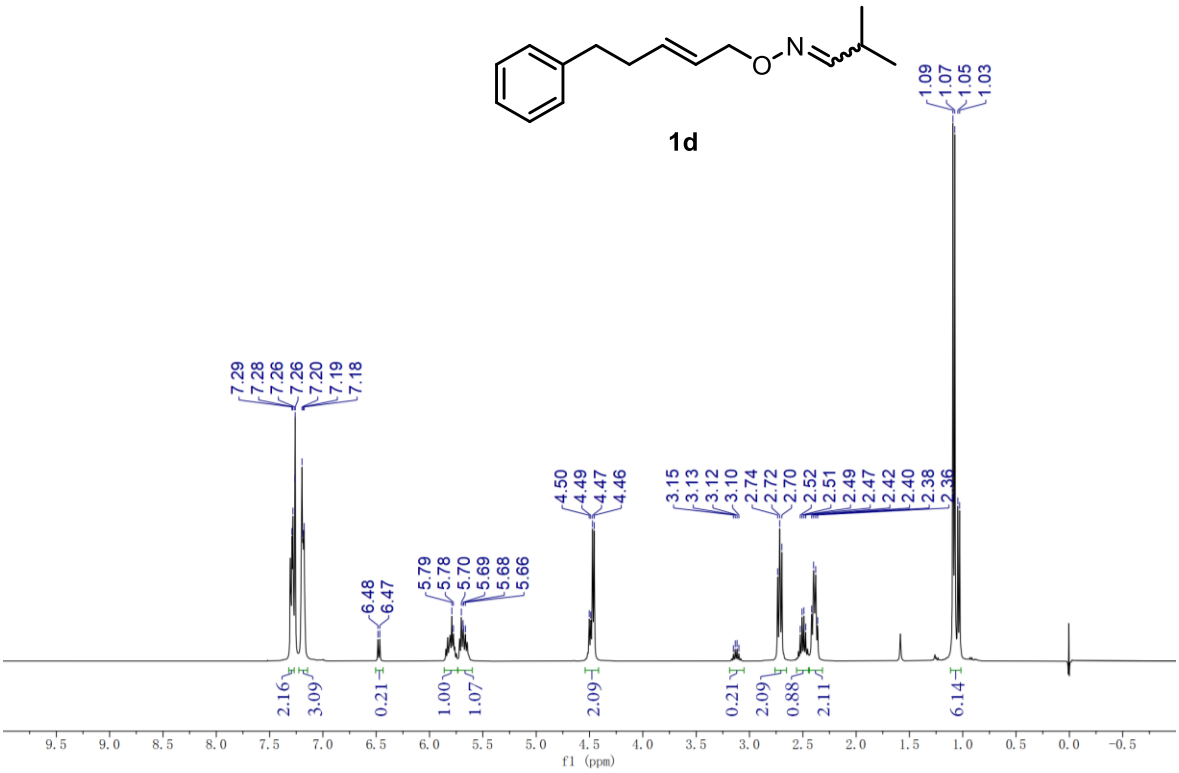
^{13}C NMR spectrum of **1b** was measured in $CDCl_3$ at 101 MHz



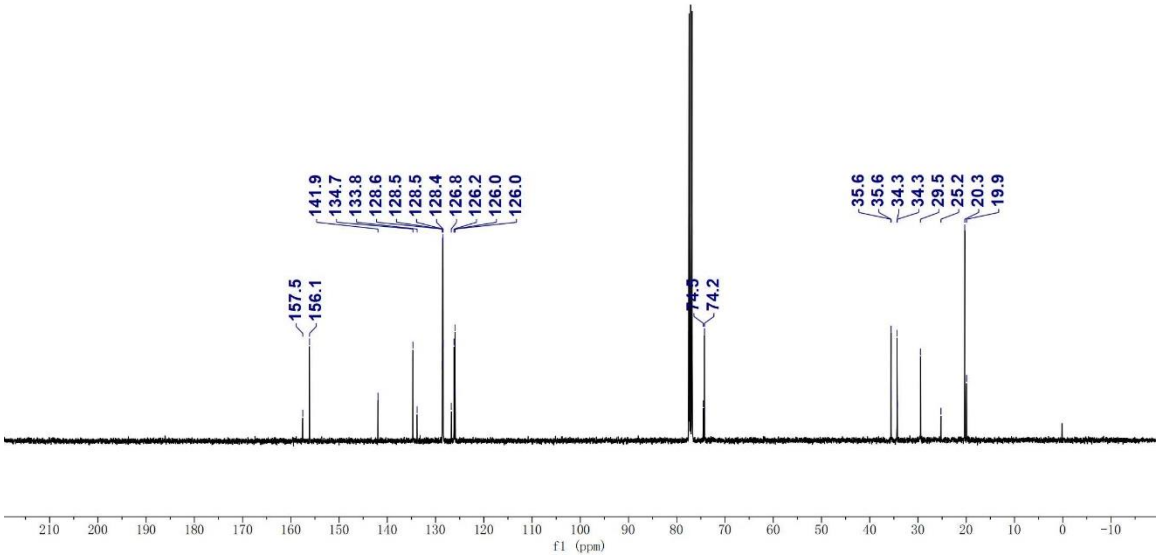
^{1}H NMR spectrum of **1c** was measured in $CDCl_3$ at 400 MHz



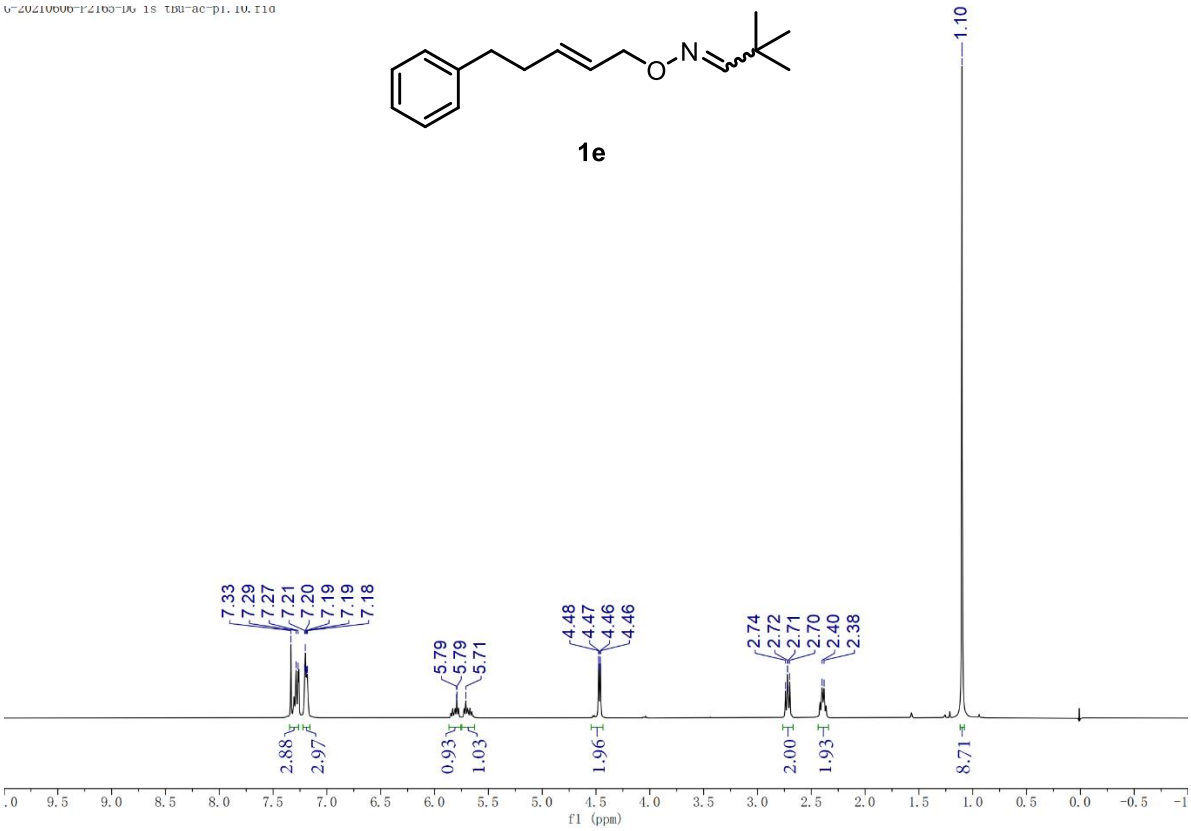
^{13}C NMR spectrum of **1c** was measured in $CDCl_3$ at 101 MHz



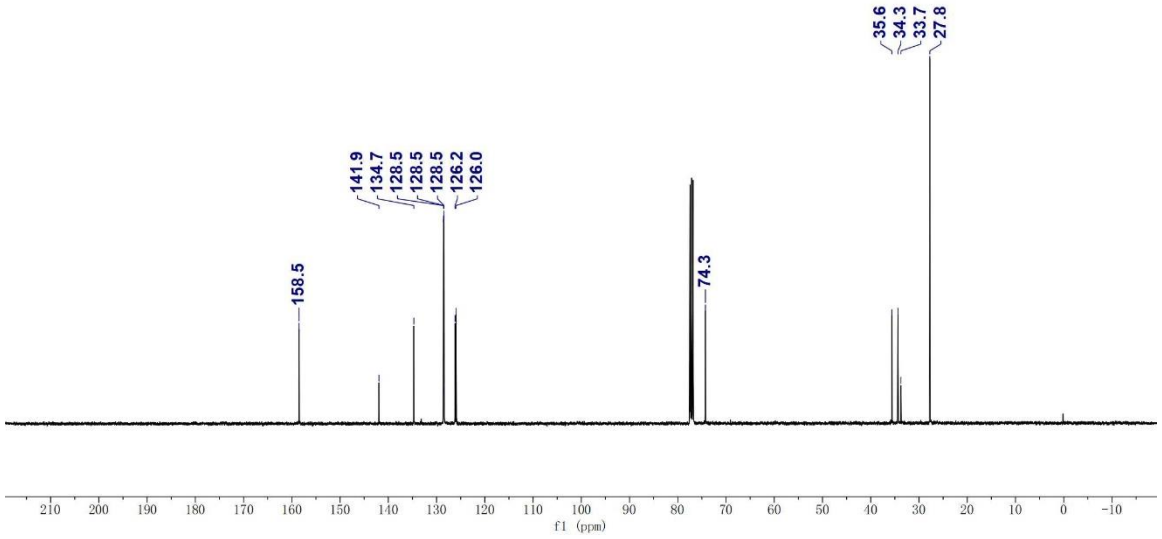
^{1}H NMR spectrum of **1d** was measured in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **1d** was measured in $CDCl_3$ at 101 MHz

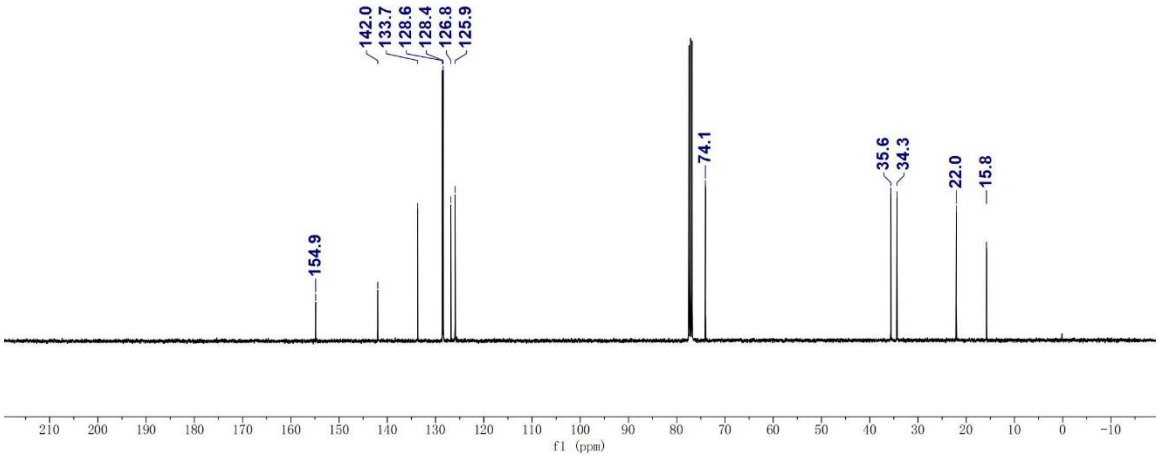


^{1}H NMR spectrum of **1e** was measured in $CDCl_3$ at 400 MHz

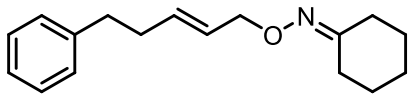


^{13}C NMR spectrum of **1e** was measured in $CDCl_3$ at 101 MHz

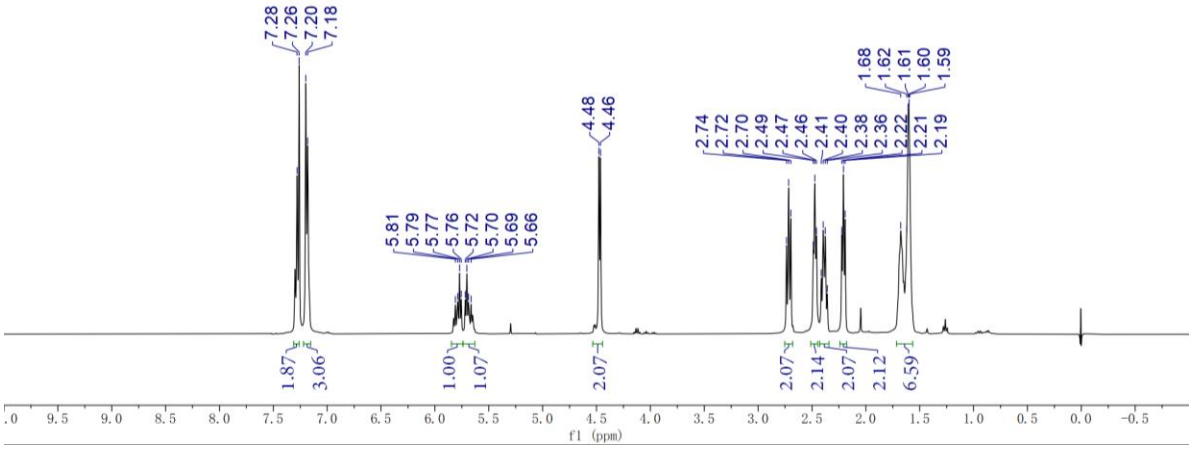
^{1}H NMR spectrum of **1f** was measured in $CDCl_3$ at 400 MHz



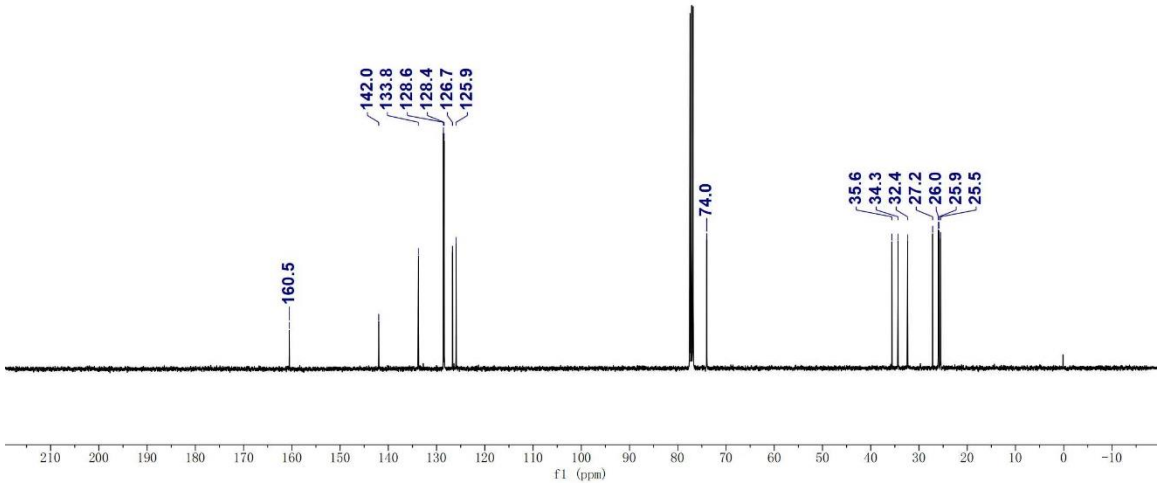
^{13}C NMR spectrum of **1f** was measured in $CDCl_3$ at 101 MHz



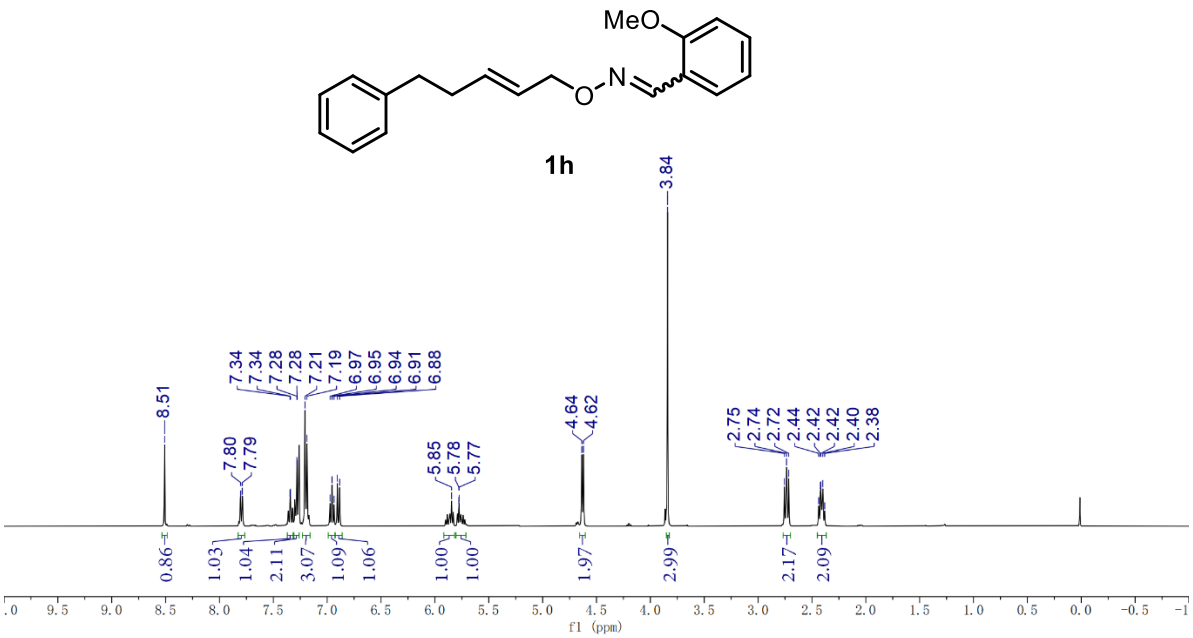
1g



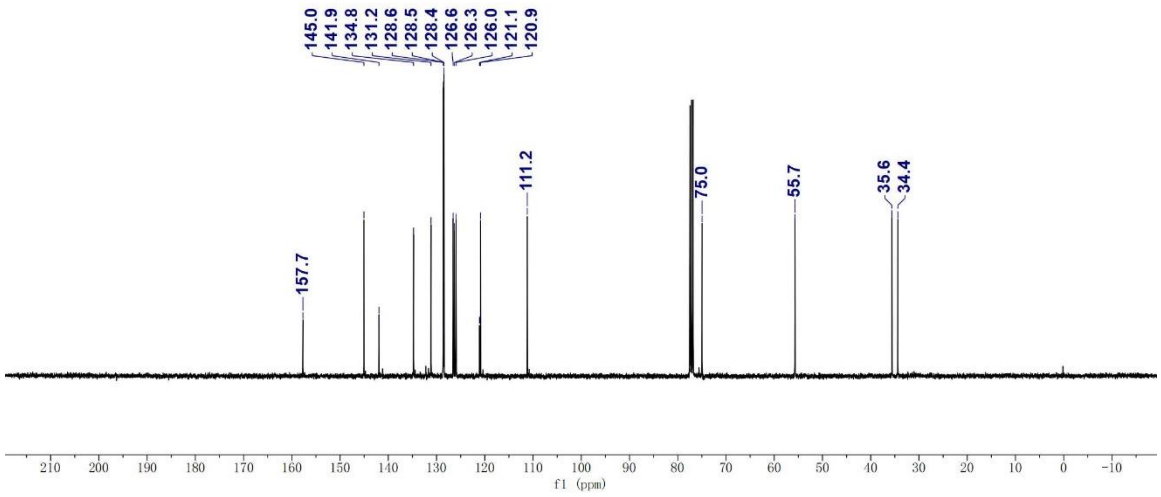
^{1}H NMR spectrum of **1g** was measured in $CDCl_3$ at 400 MHz



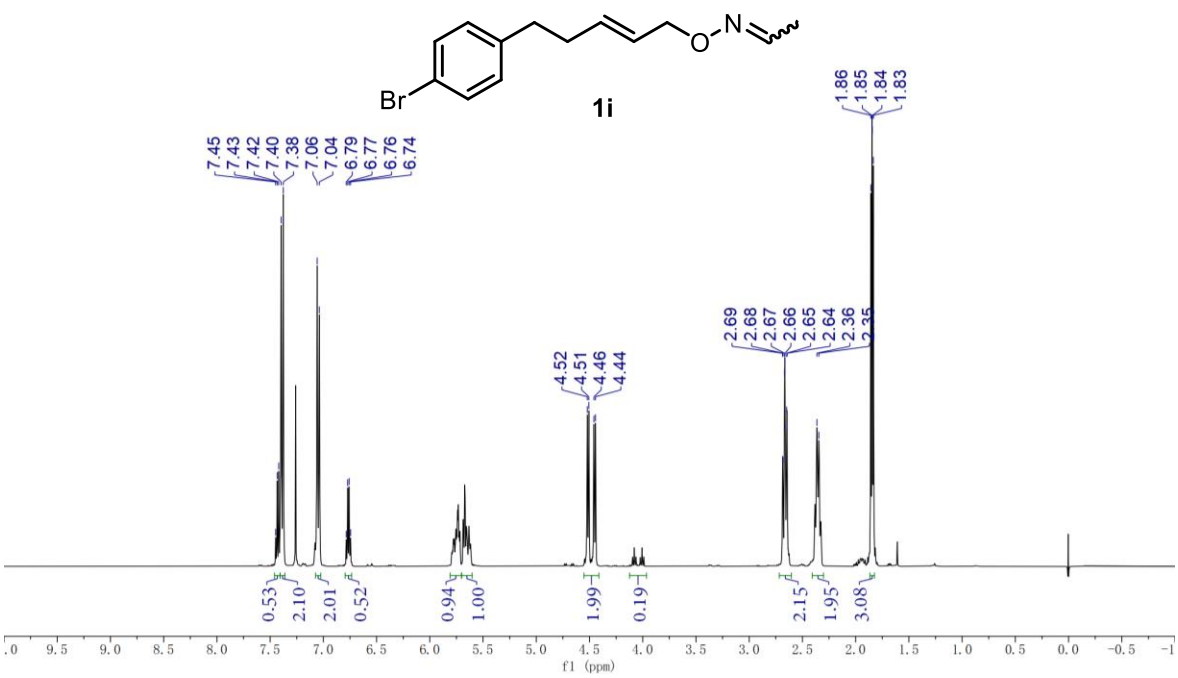
^{13}C NMR spectrum of **1g** was measured in $CDCl_3$ at 101 MHz



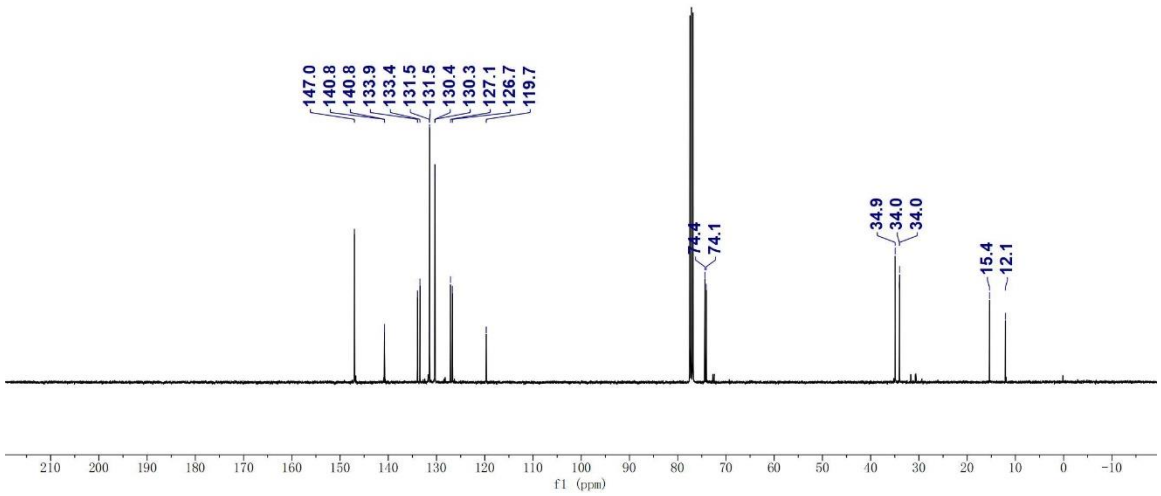
^{1}H NMR spectrum of **1h** was measured in $CDCl_3$ at 400 MHz



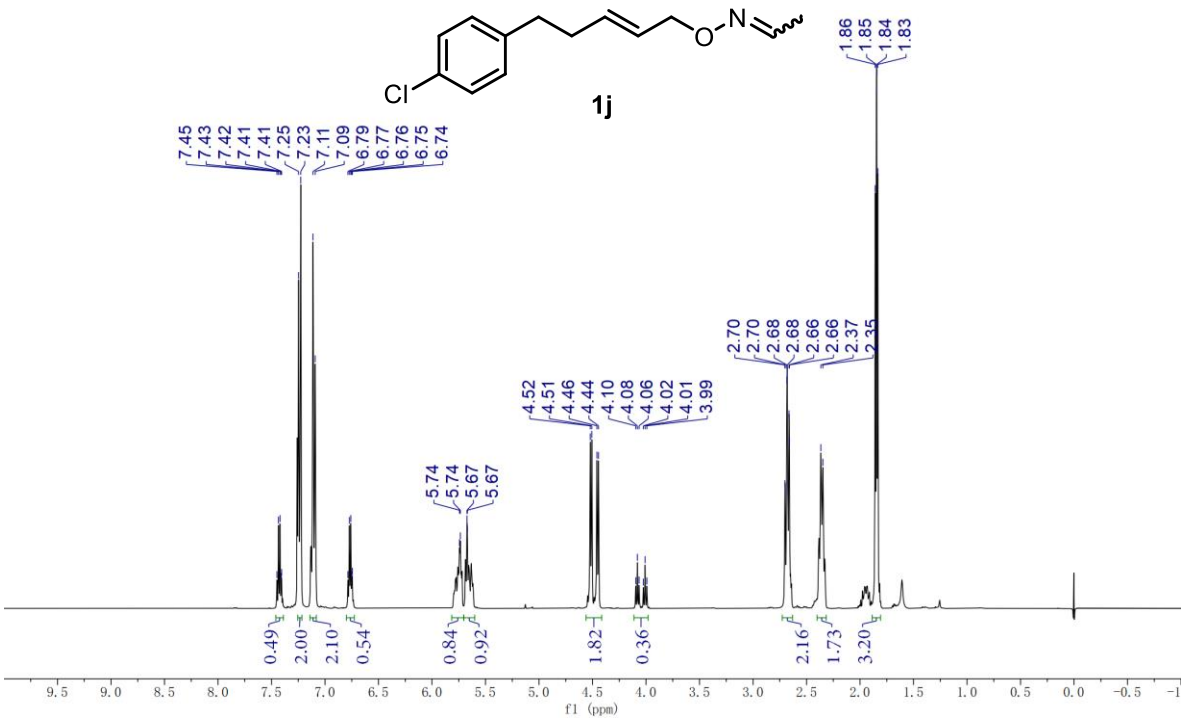
^{13}C NMR spectrum of **1h** was measured in $CDCl_3$ at 101 MHz



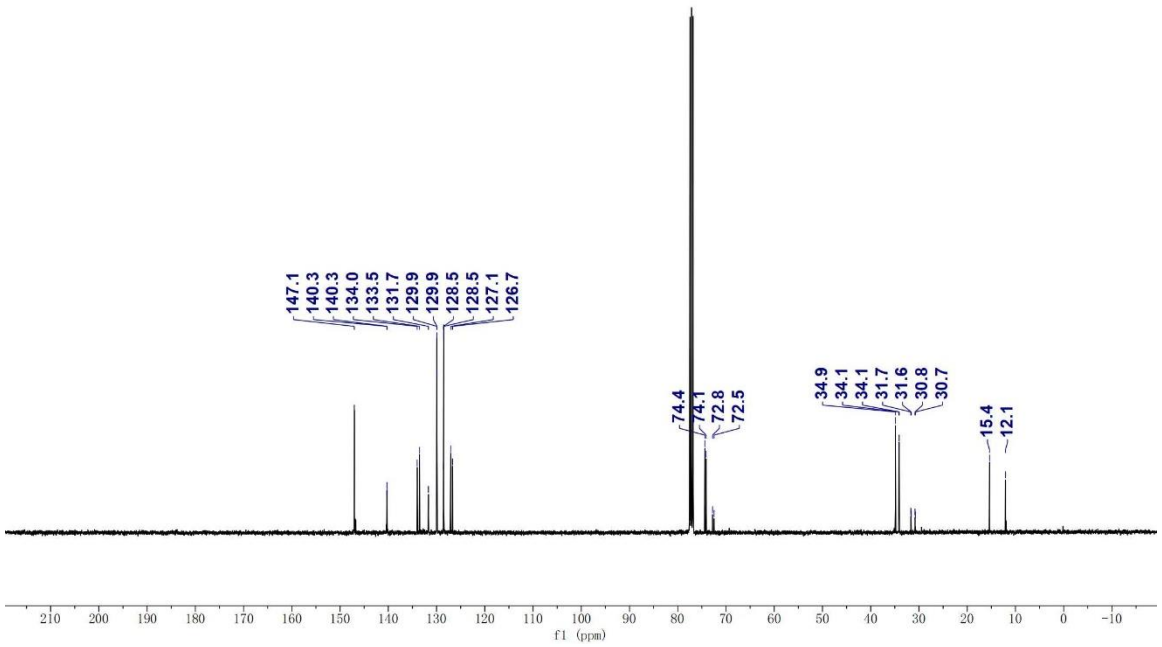
^{1}H NMR spectrum of **1i** was measured in $CDCl_3$ at 400 MH



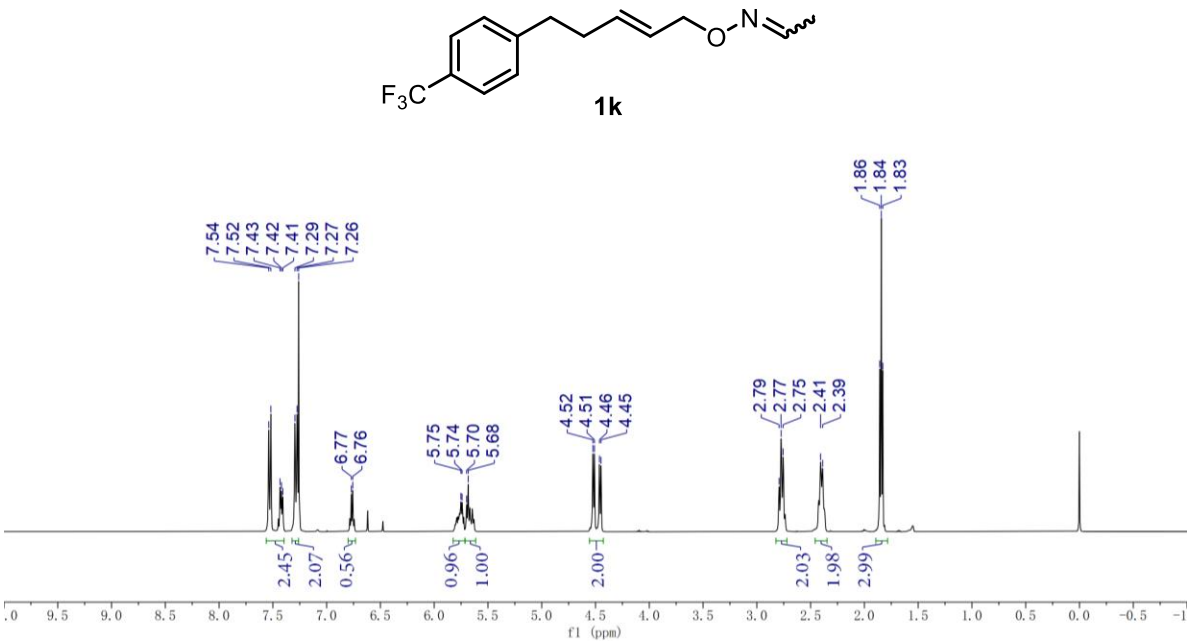
^{13}C NMR spectrum of **1i** was measured in $CDCl_3$ at 101 MHz



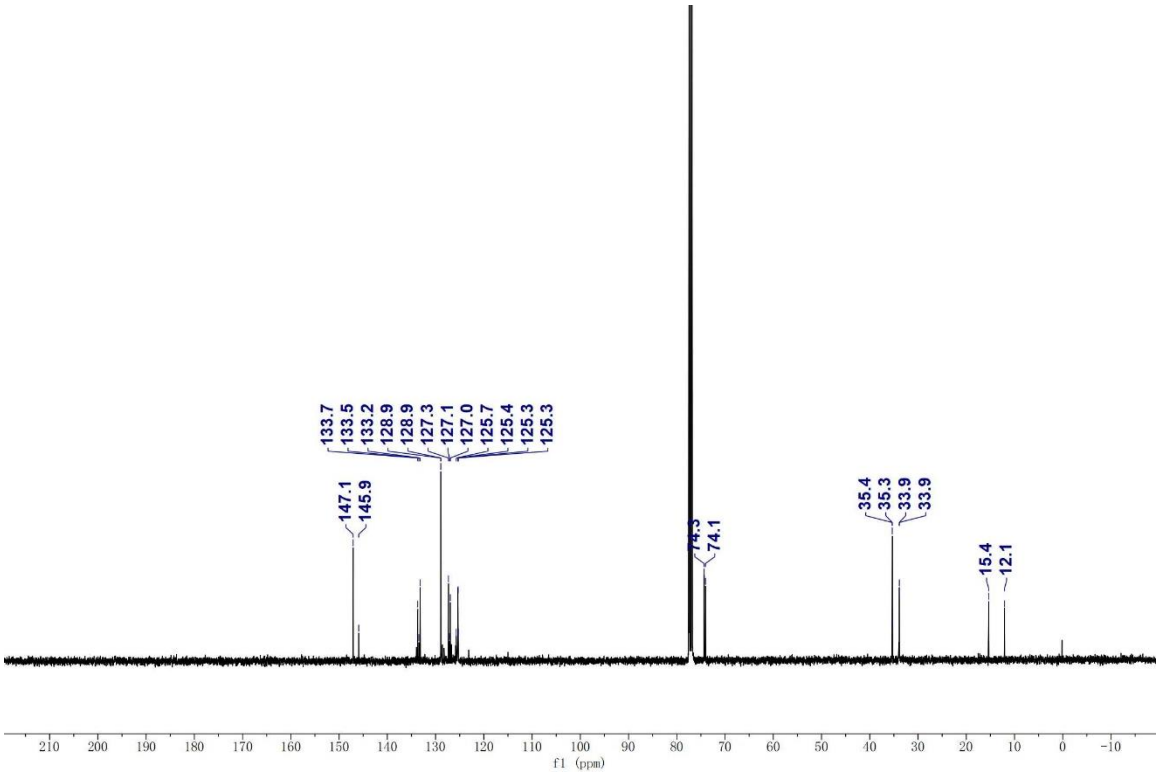
^{1}H NMR spectrum of **1j** was measured in $CDCl_3$ at 400 MH



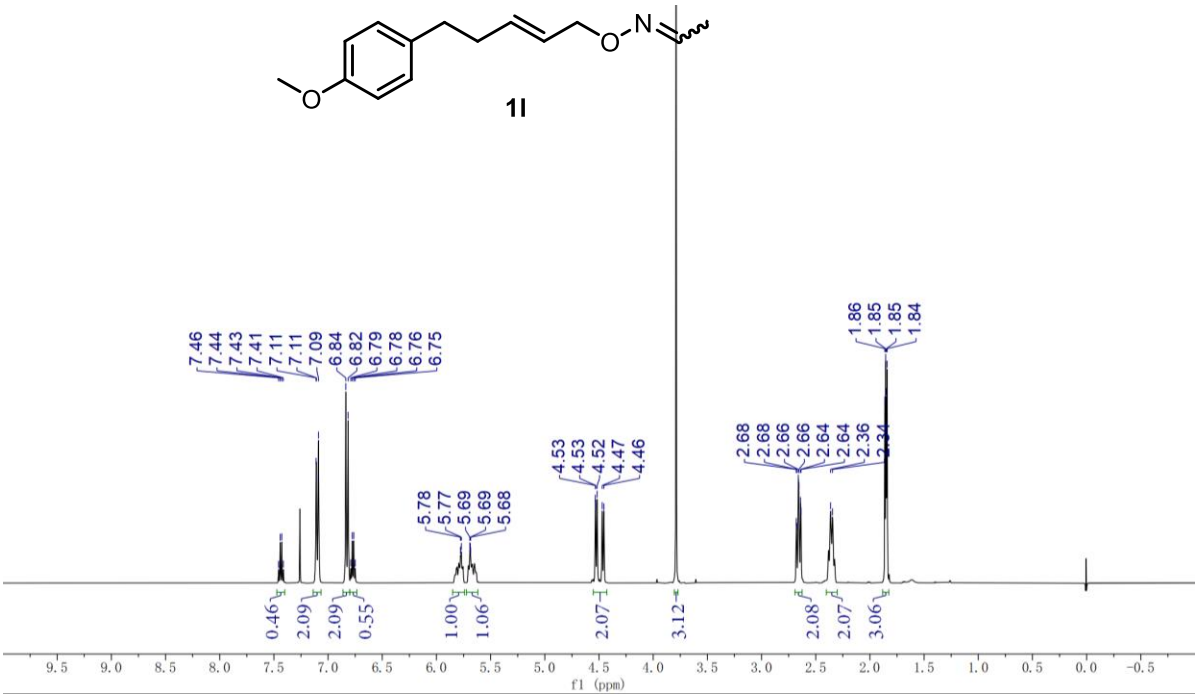
^{13}C NMR spectrum of **1j** was measured in $CDCl_3$ at 101 MHz



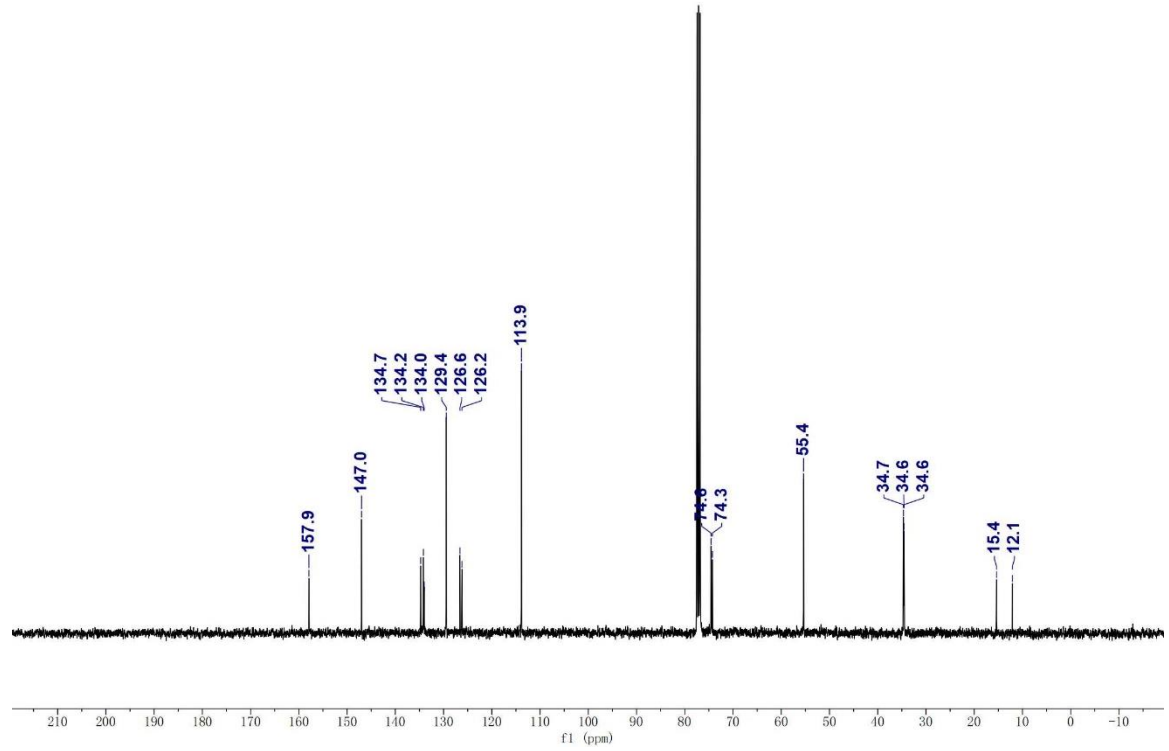
^{1}H NMR spectrum of **1k** was measured in $CDCl_3$ at 400 MH



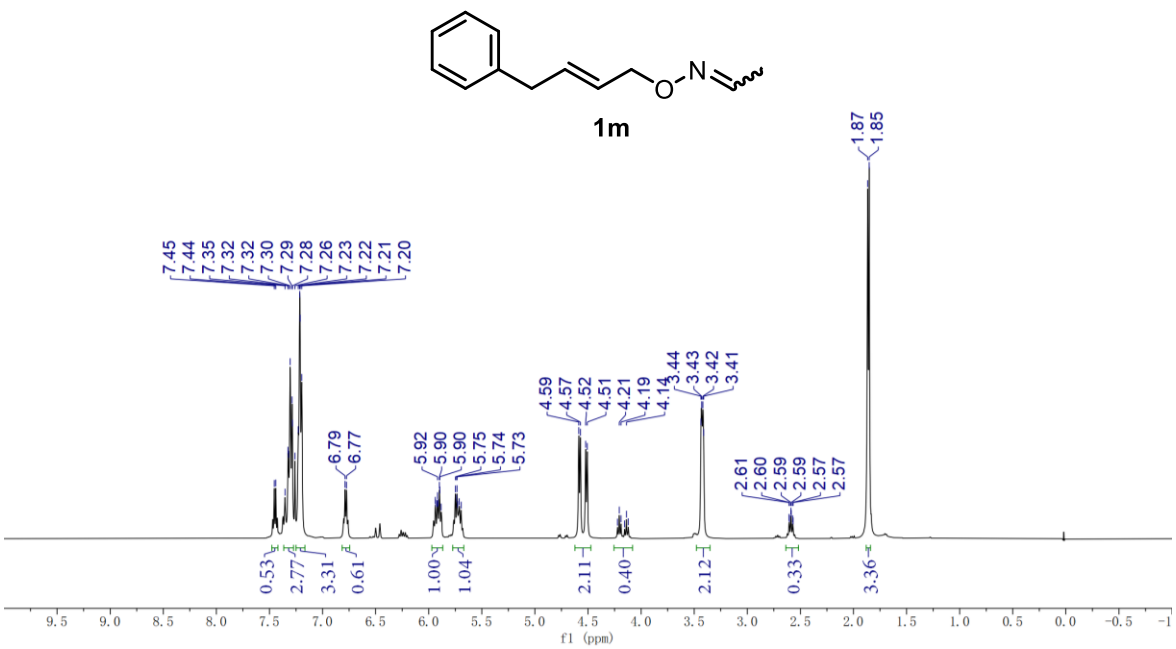
^{13}C NMR spectrum of **1k** was measured in $CDCl_3$ at 101 MHz



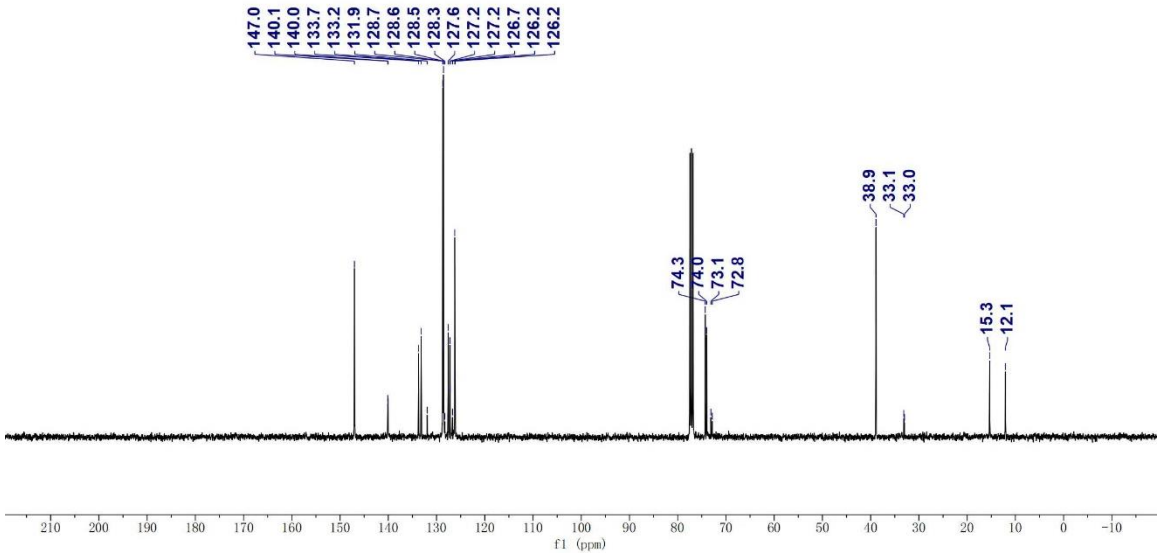
^{1}H NMR spectrum of **1l** was measured in $CDCl_3$ at 400 MH



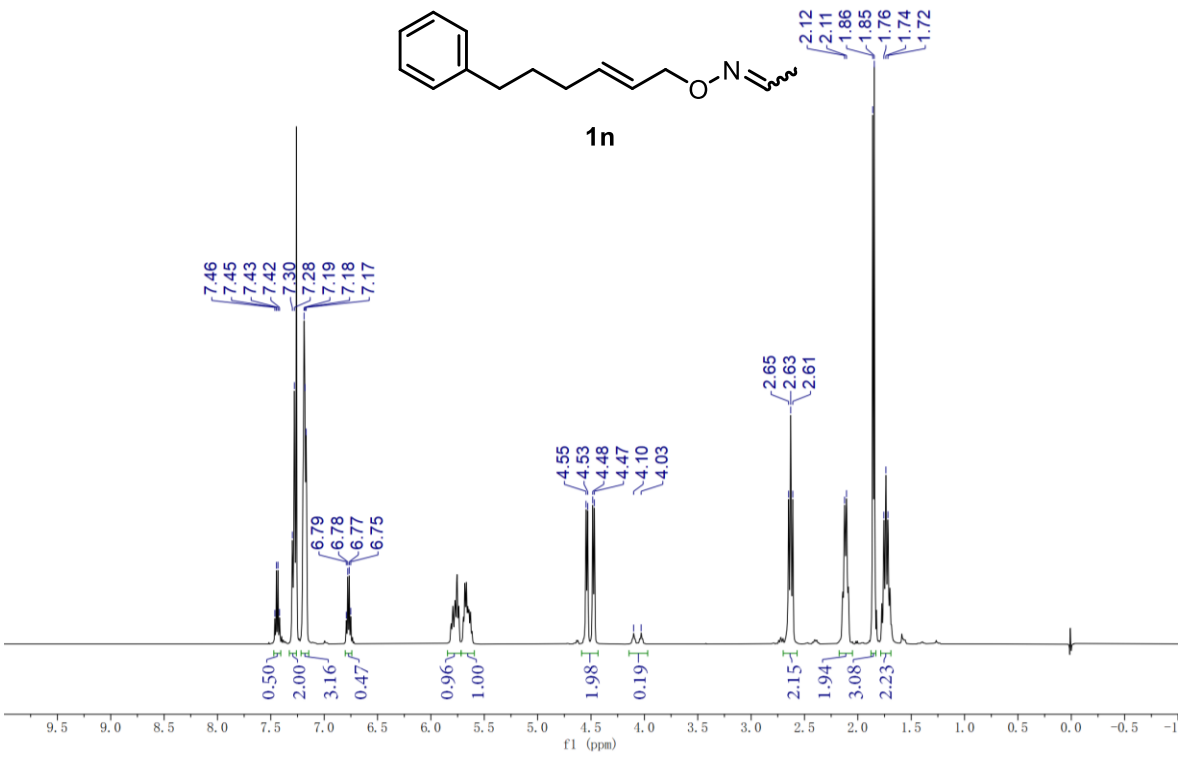
^{13}C NMR spectrum of **1l** was measured in $CDCl_3$ at 101 MHz



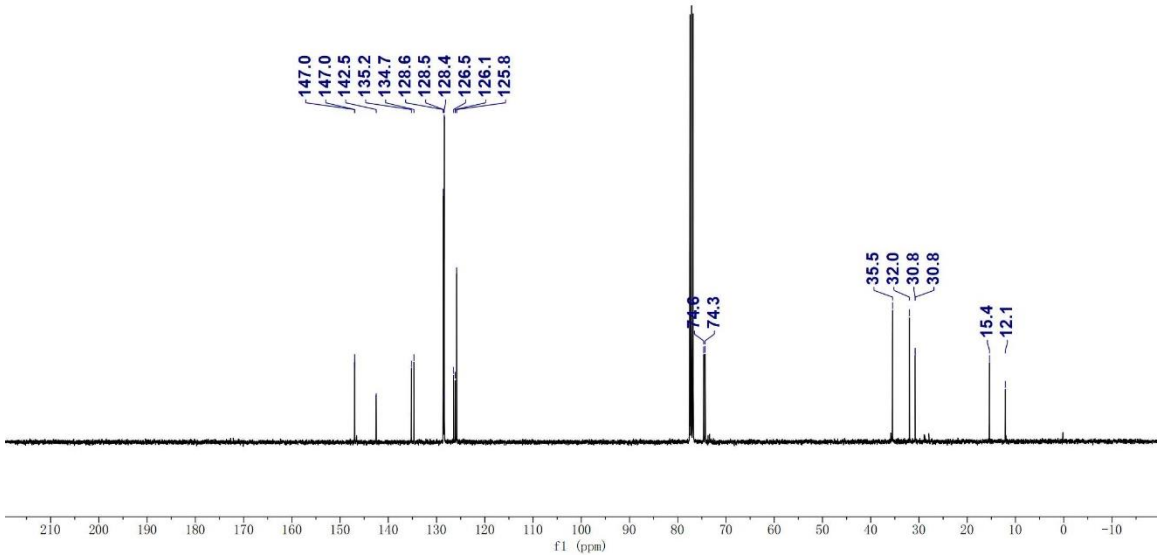
^{1}H NMR spectrum of **1m** was measured in $CDCl_3$ at 400 MH



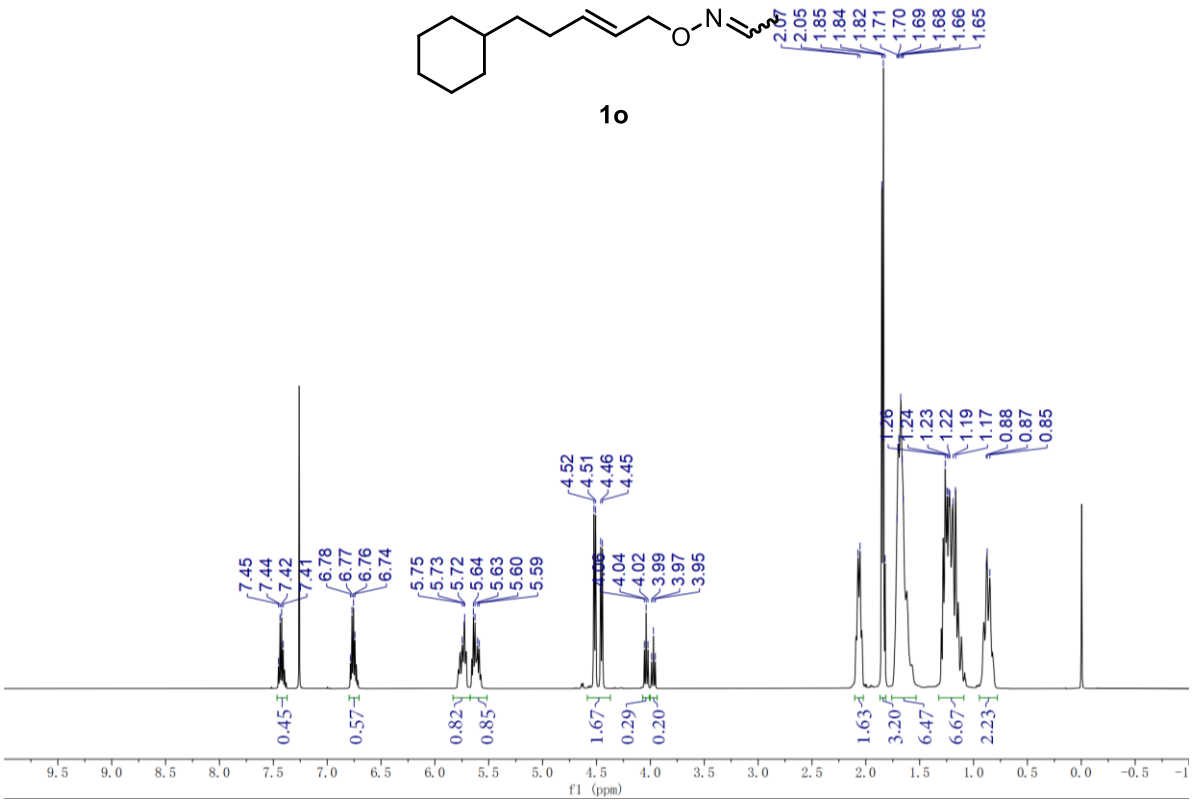
^{13}C NMR spectrum of **1m** was measured in $CDCl_3$ at 101 MHz



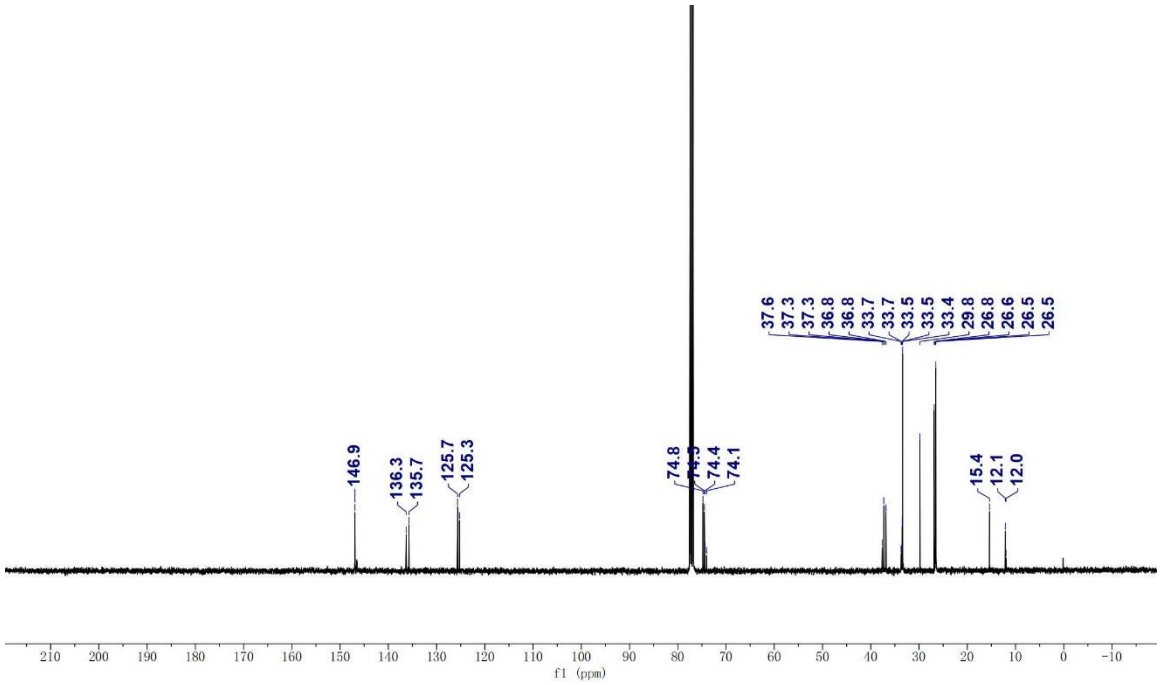
^{1}H NMR spectrum of **1n** was measured in $CDCl_3$ at 400 MH



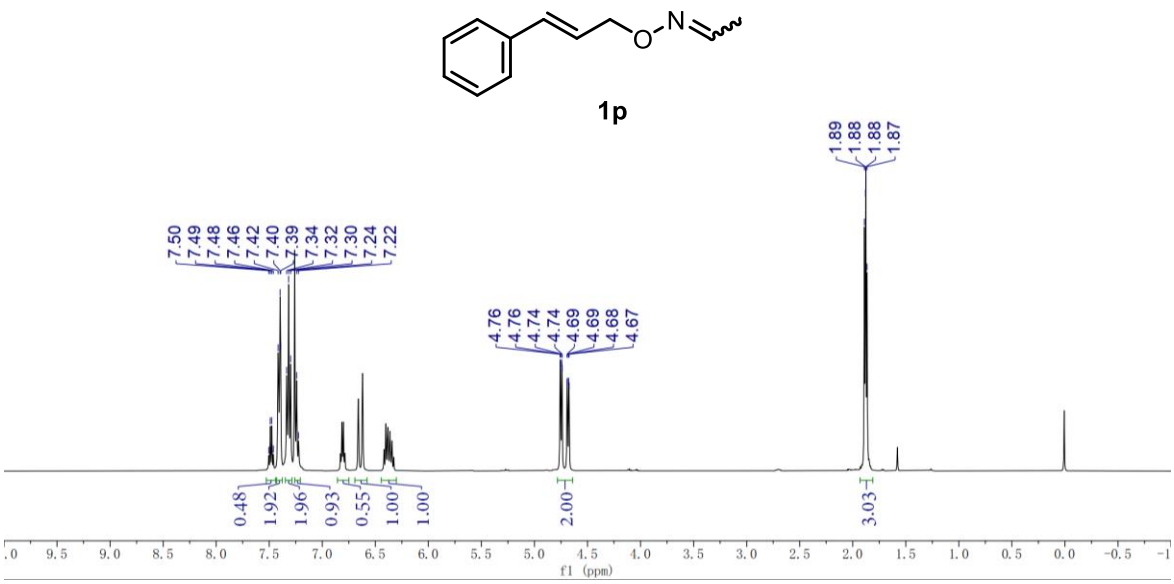
^{13}C NMR spectrum of **1n** was measured in $CDCl_3$ at 101 MHz



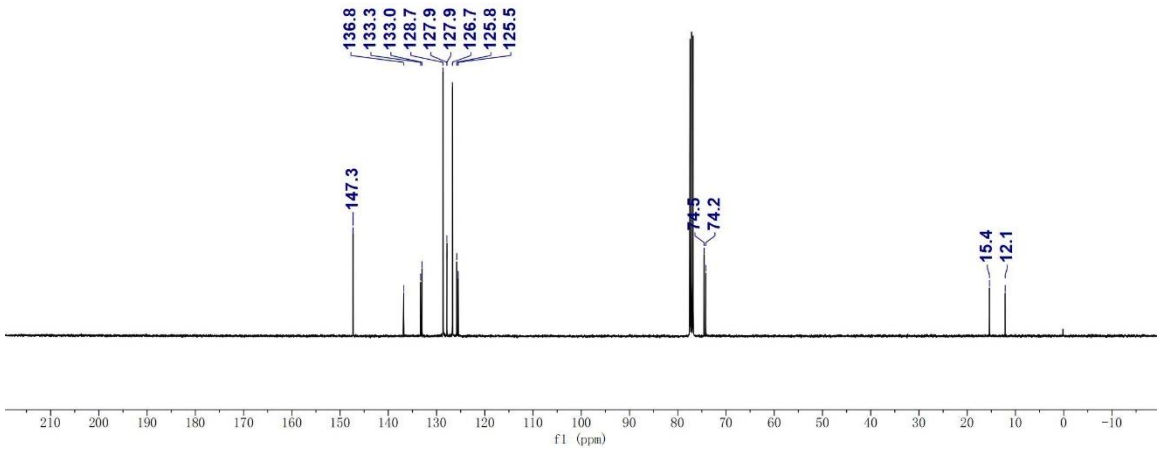
^{1}H NMR spectrum of **1o** was measured in $CDCl_3$ at 400 MH



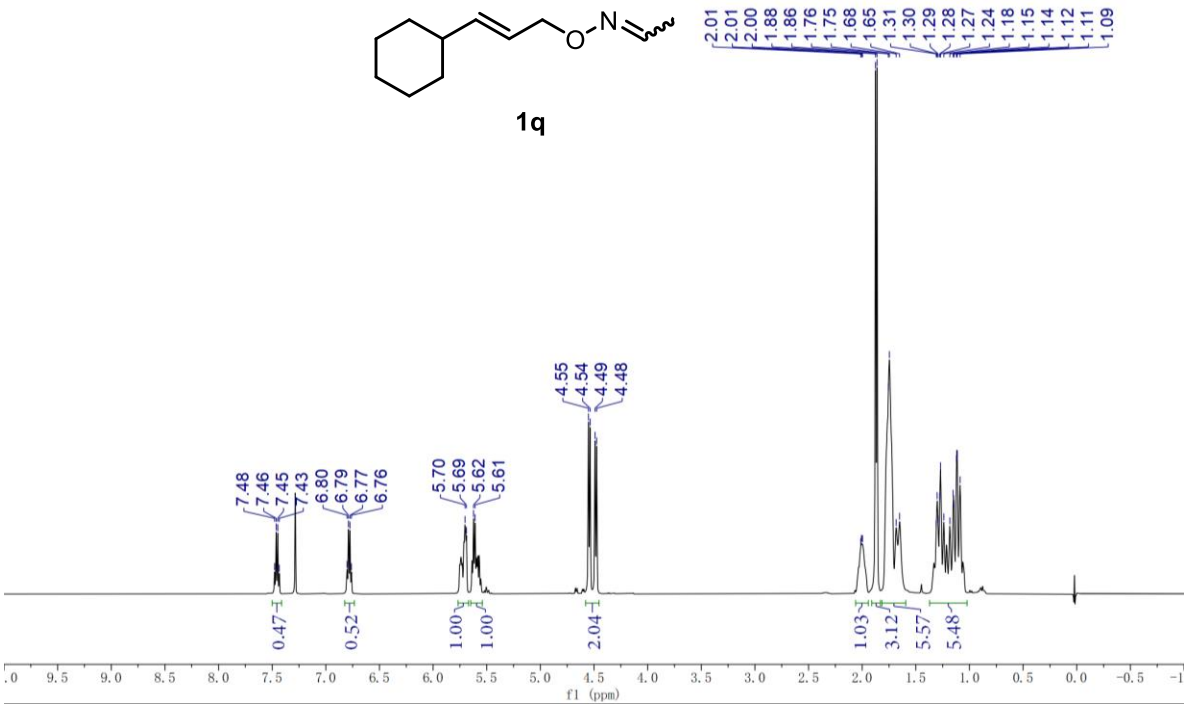
^{13}C NMR spectrum of **1o** was measured in $CDCl_3$ at 101 MHz



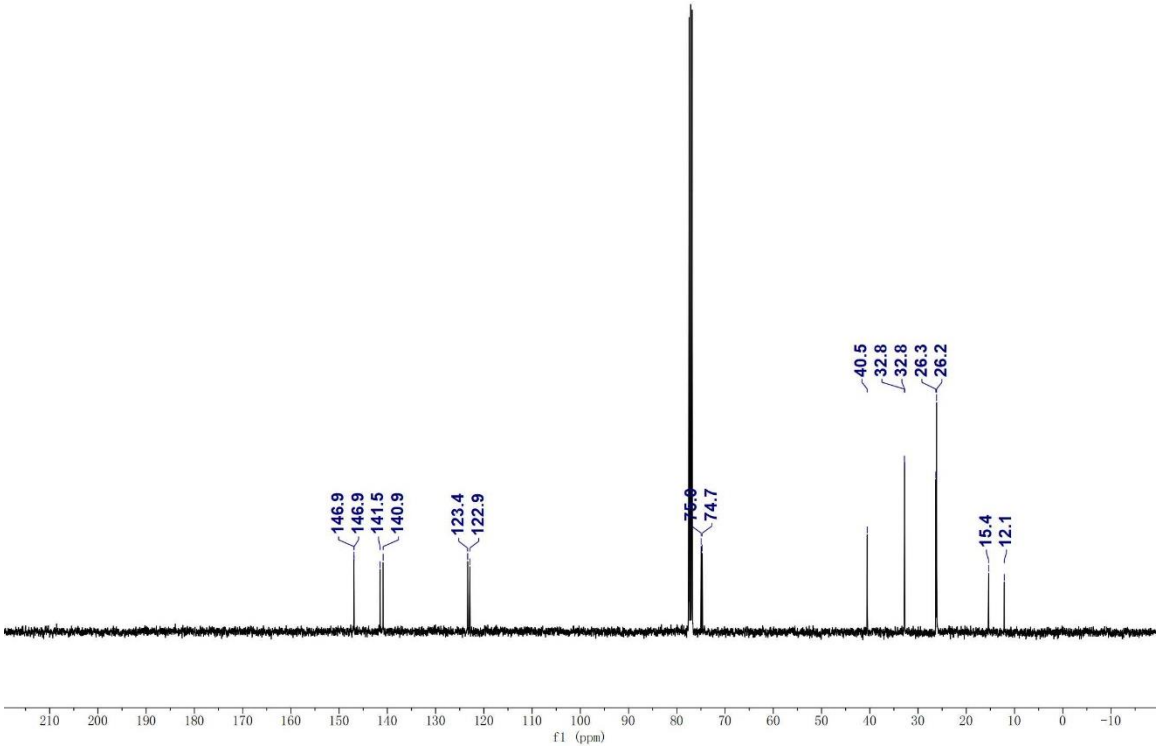
^{1}H NMR spectrum of **1p** was measured in $CDCl_3$ at 400 MH



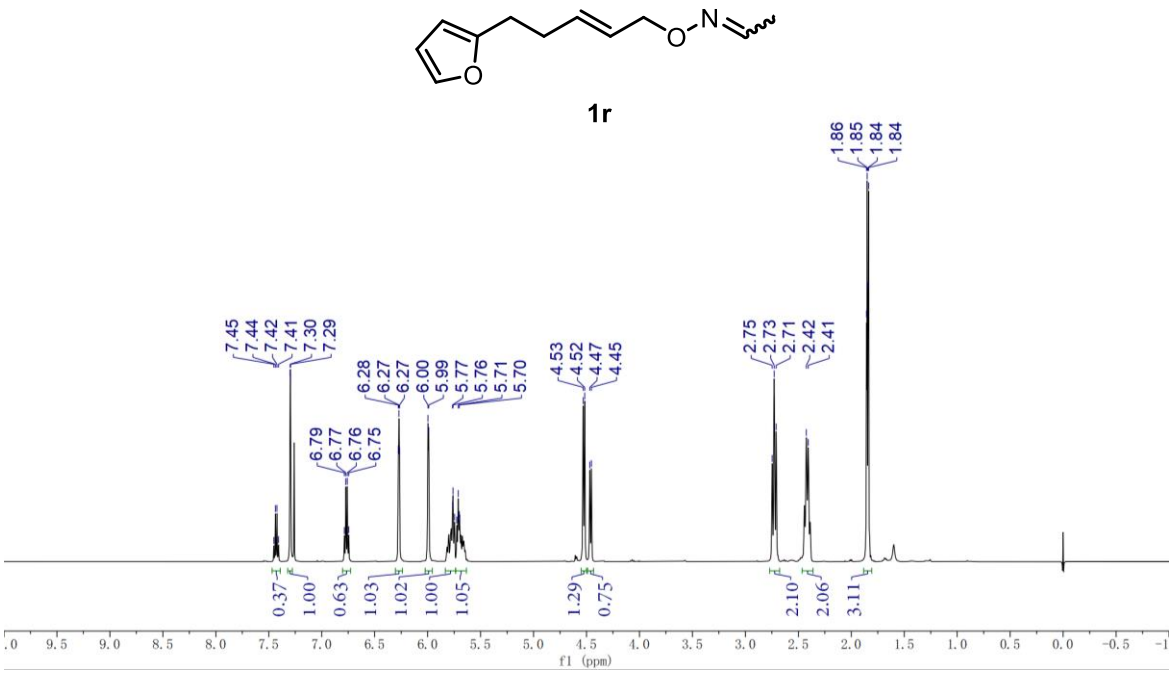
^{13}C NMR spectrum of **1p** was measured in $CDCl_3$ at 101 MHz



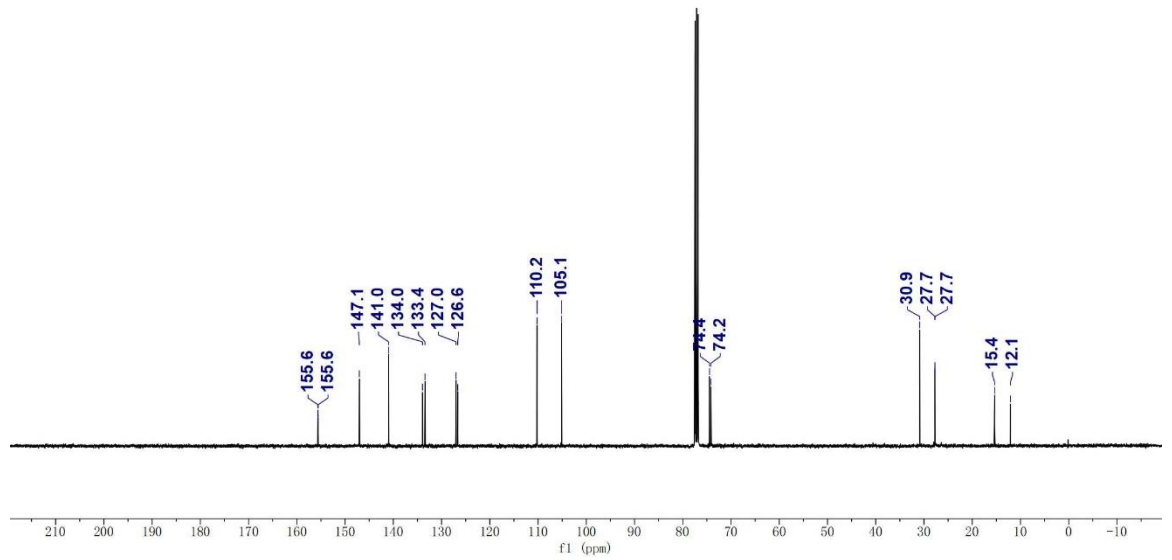
^{1}H NMR spectrum of **1q** was measured in $CDCl_3$ at 400 MH



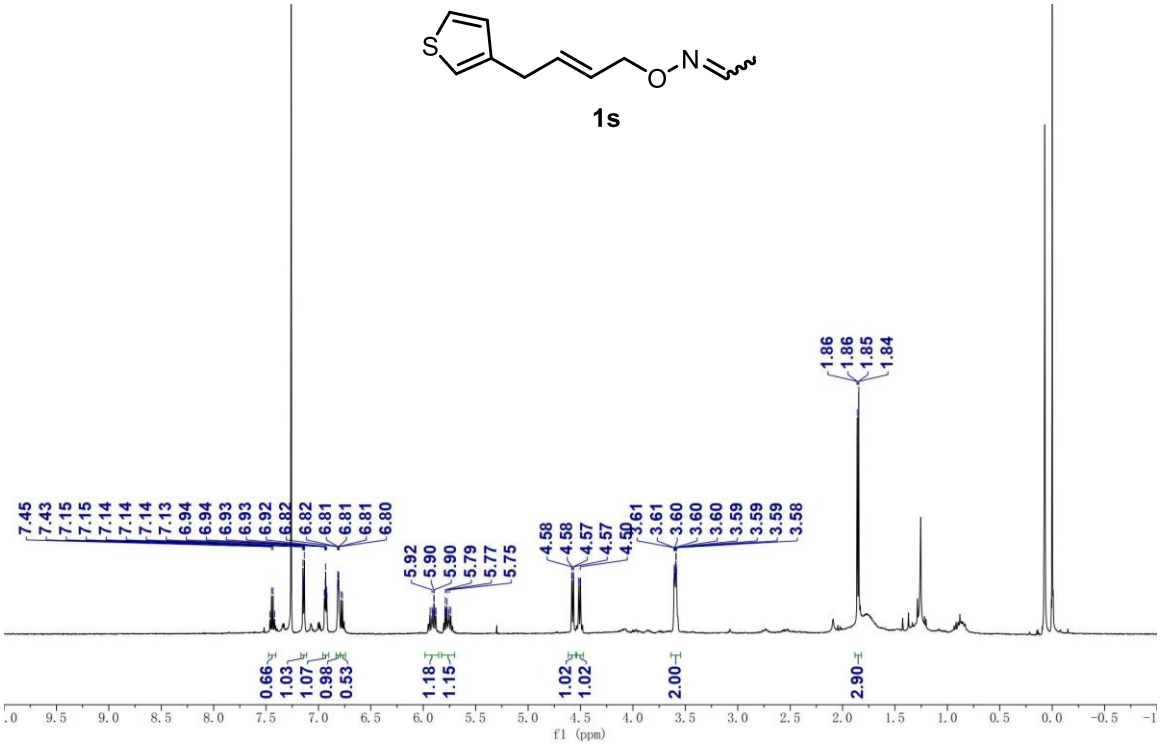
^{13}C NMR spectrum of **1q** was measured in $CDCl_3$ at 101 MHz



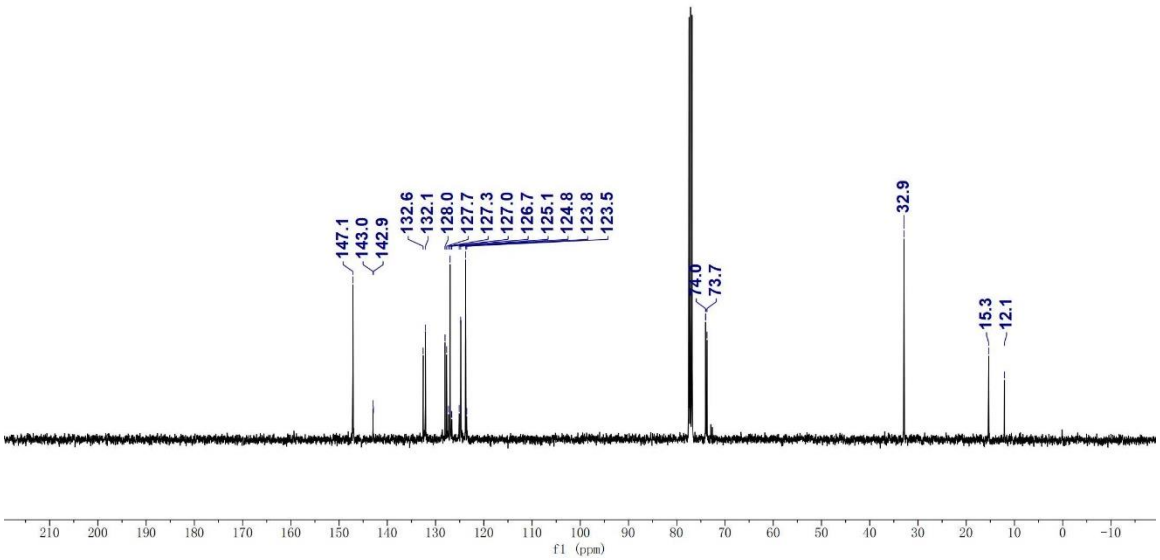
^{1}H NMR spectrum of **1r** was measured in $CDCl_3$ at 400 MH



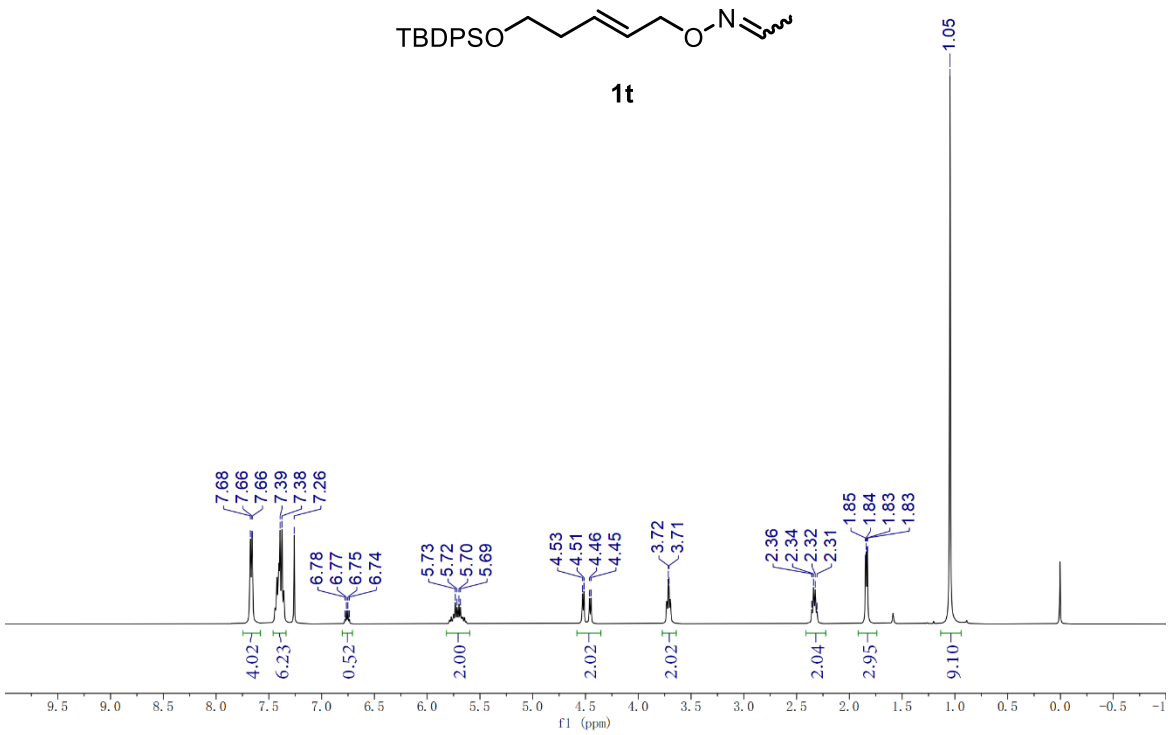
^{13}C NMR spectrum of **1r** was measured in $CDCl_3$ at 101 MHz



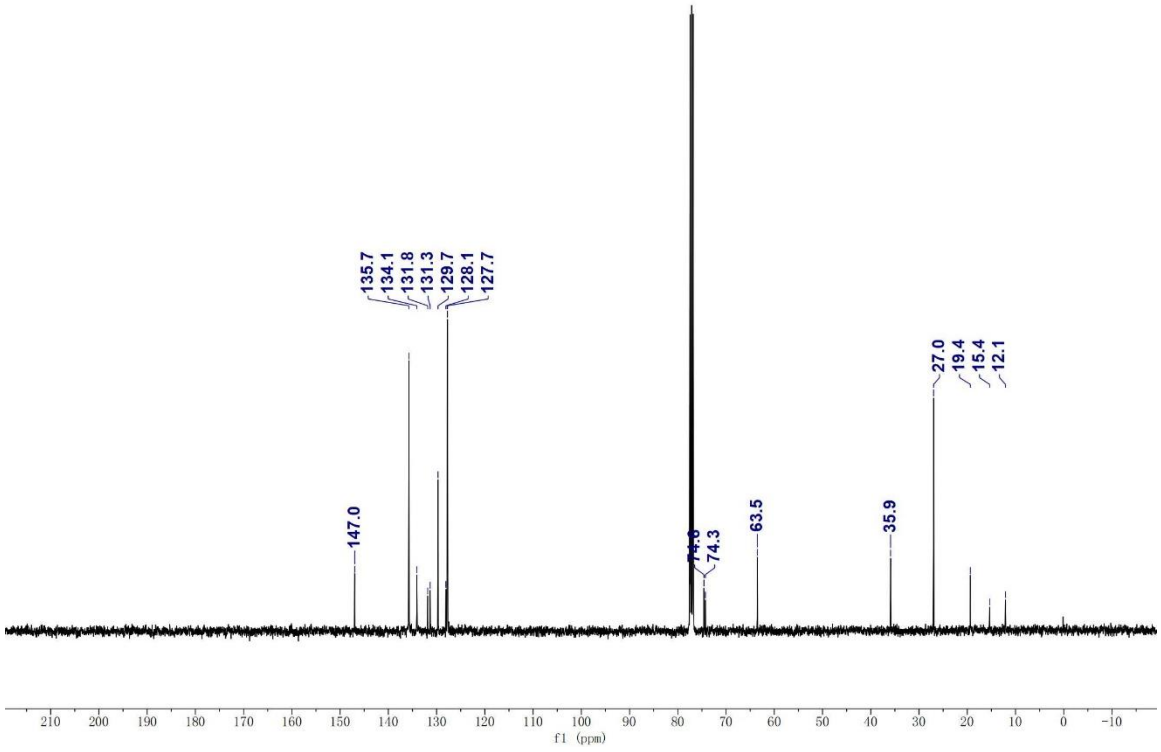
^{1}H NMR spectrum of **1s** was measured in $CDCl_3$ at 400 MH



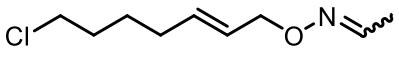
^{13}C NMR spectrum of **1s** was measured in $CDCl_3$ at 101 MHz



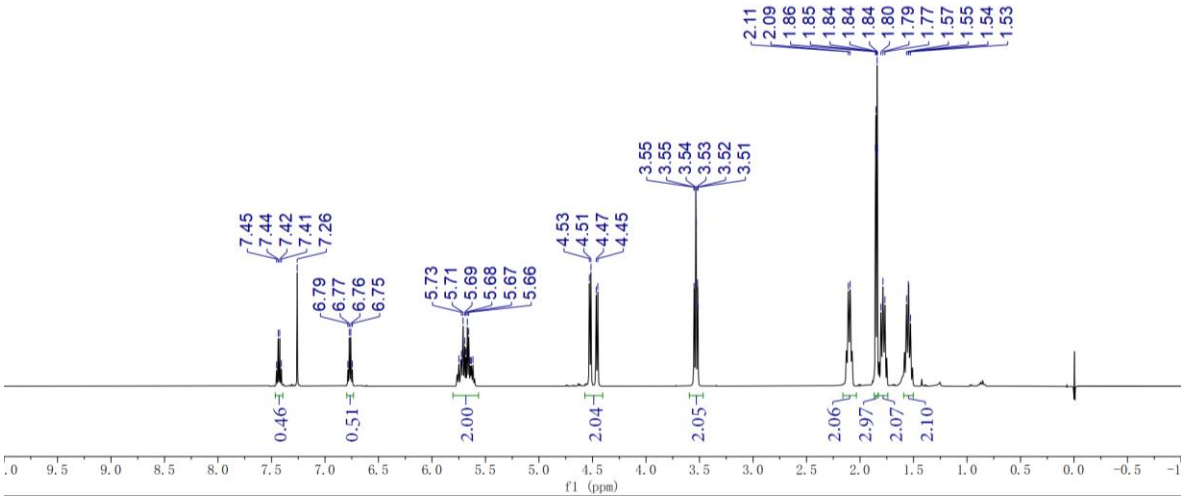
^{1}H NMR spectrum of **1t** was measured in $CDCl_3$ at 400 MH



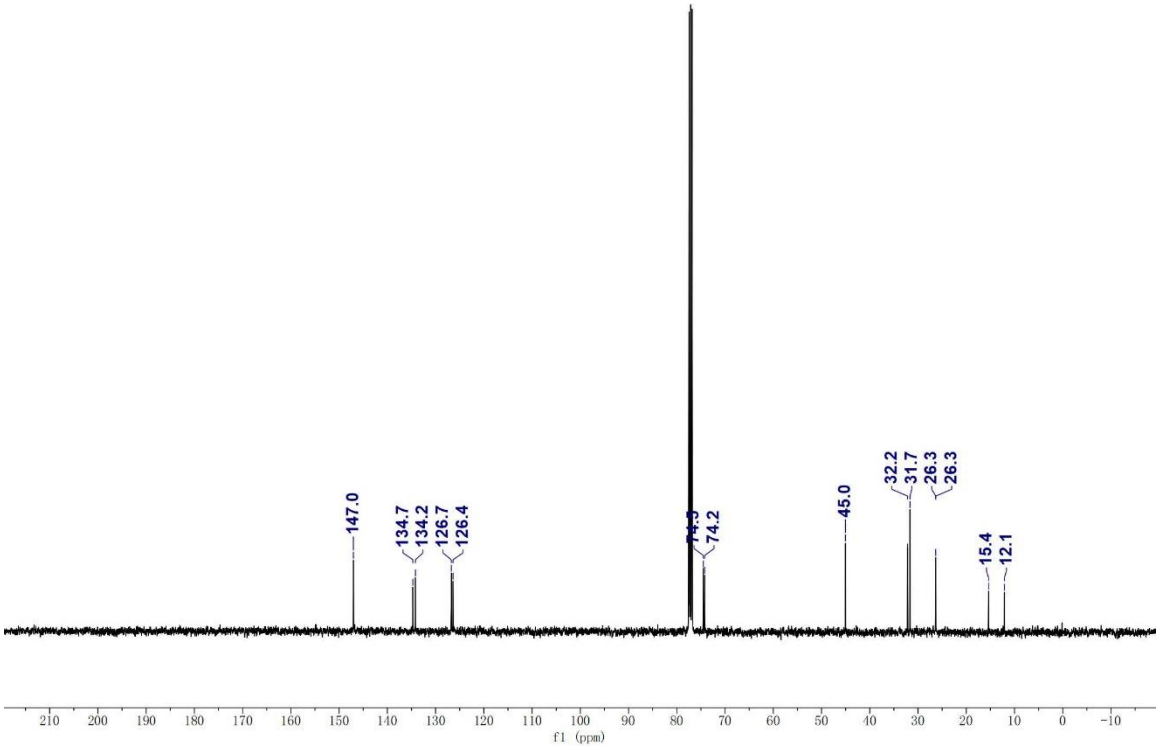
^{13}C NMR spectrum of **1t** was measured in $CDCl_3$ at 101 MHz



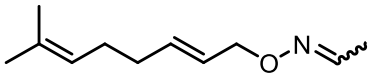
1u



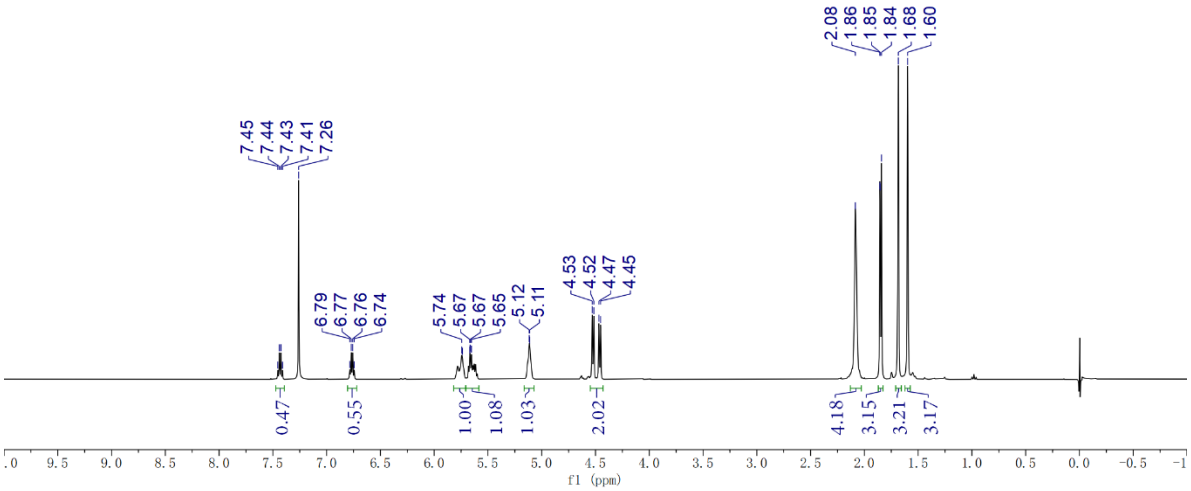
^{1}H NMR spectrum of **1u** was measured in $CDCl_3$ at 400 MH



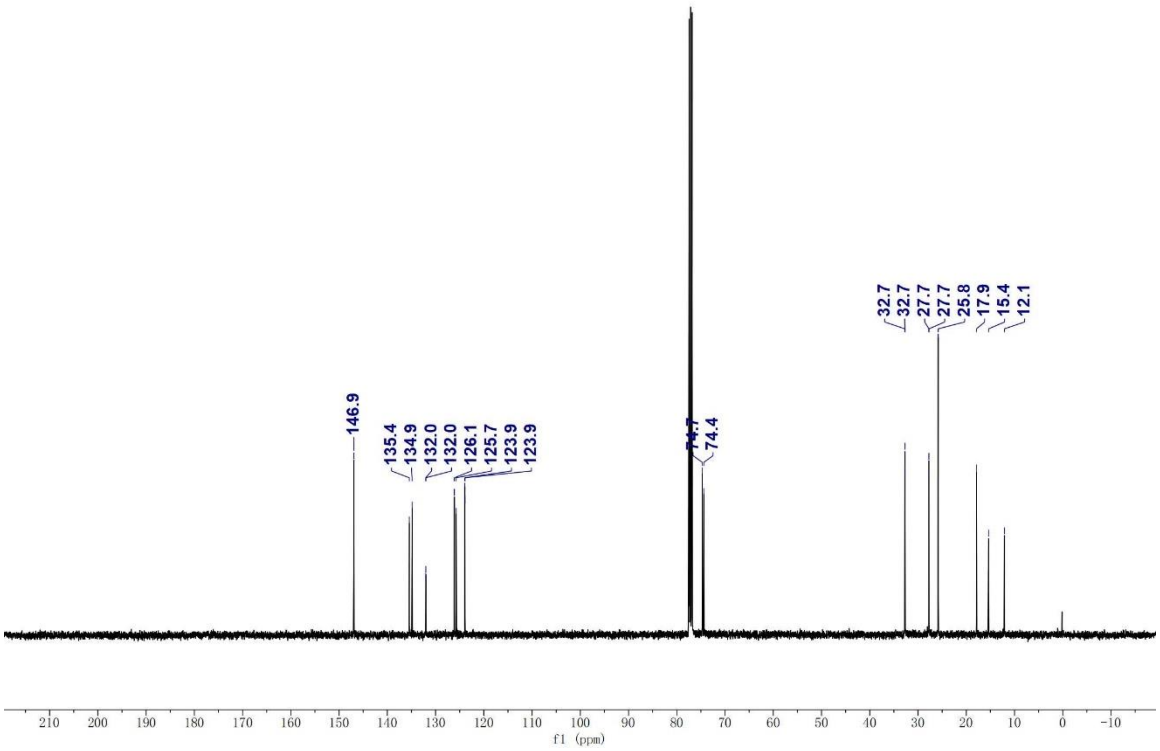
^{13}C NMR spectrum of **1u** was measured in $CDCl_3$ at 101 MHz



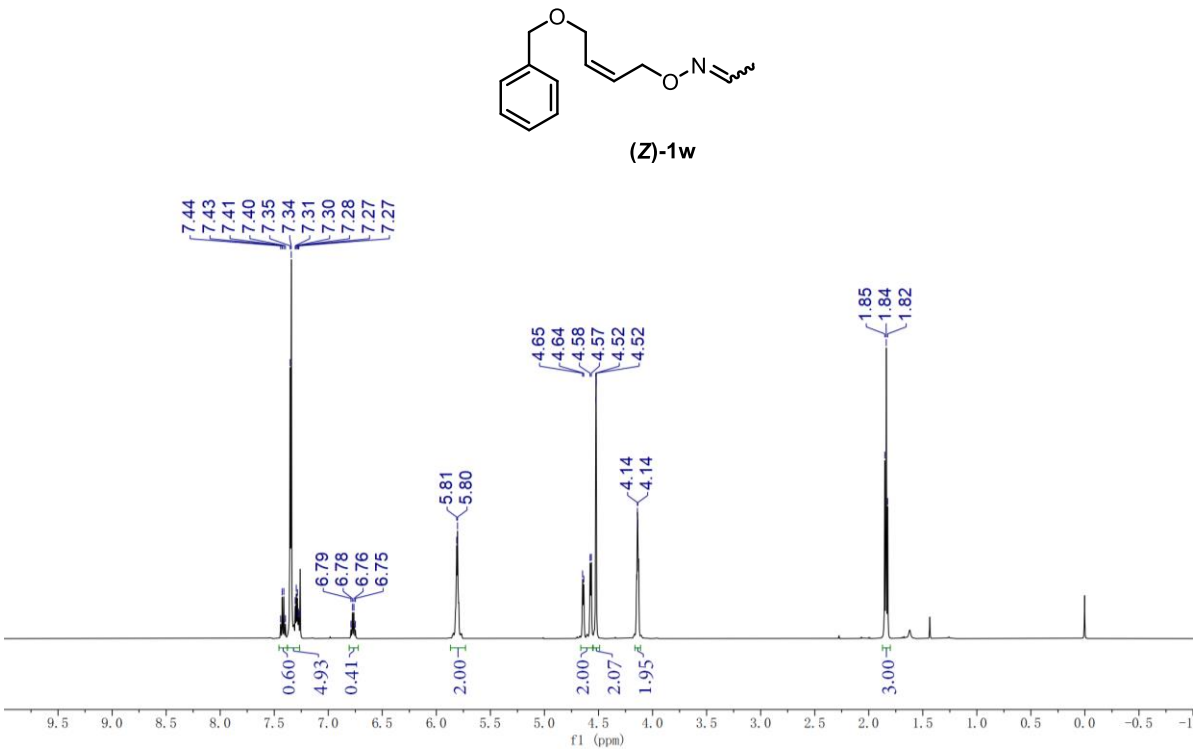
1v



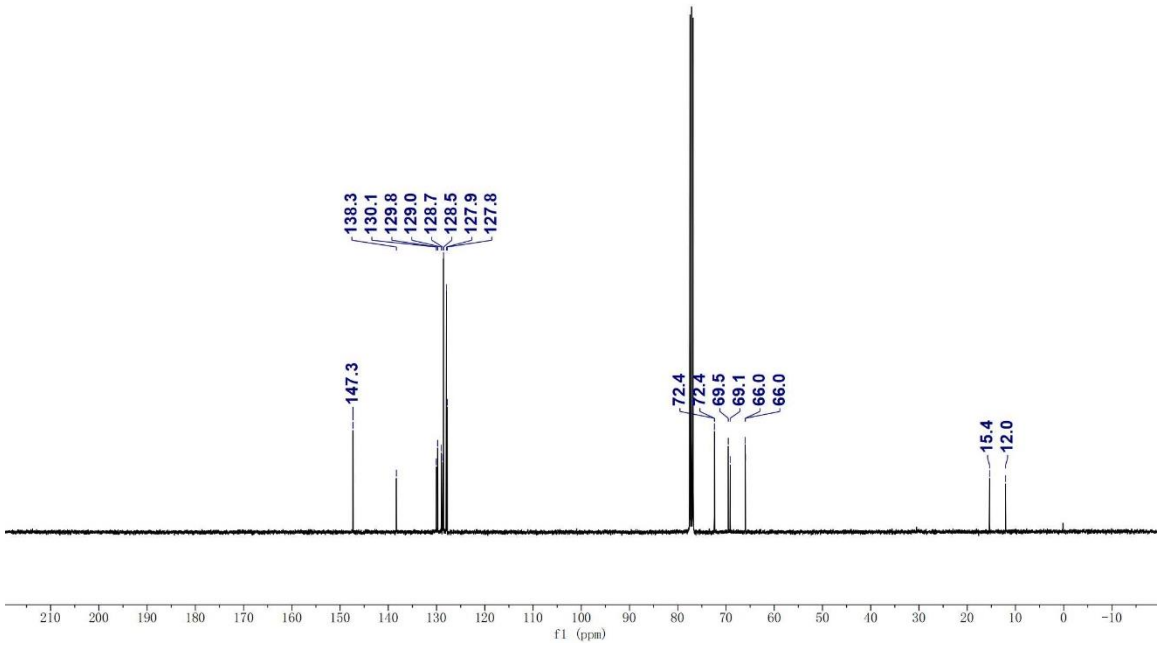
^{1}H NMR spectrum of **1v** was measured in $CDCl_3$ at 400 MH



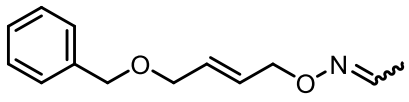
^{13}C NMR spectrum of **1v** was measured in $CDCl_3$ at 101 MHz



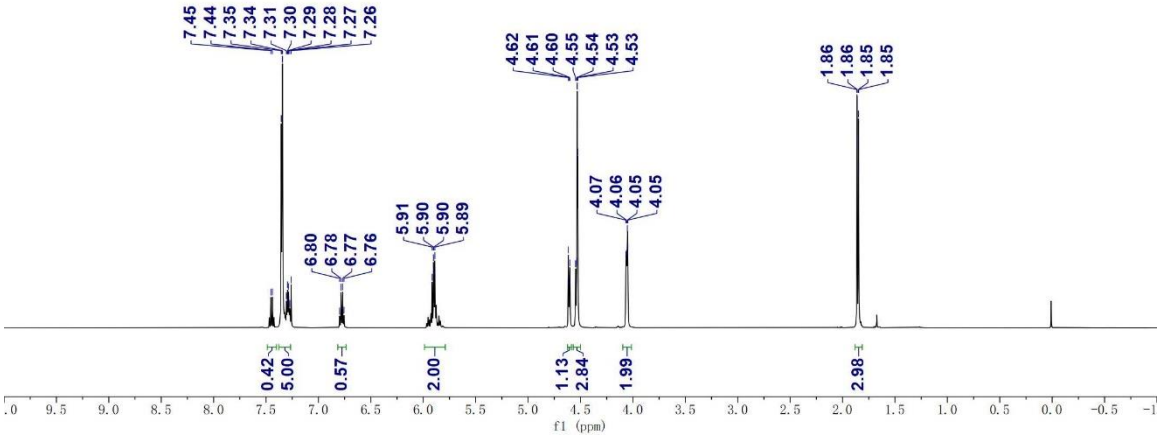
^{1}H NMR spectrum of **(*Z*)-1w** was measured in $CDCl_3$ at 400 MH



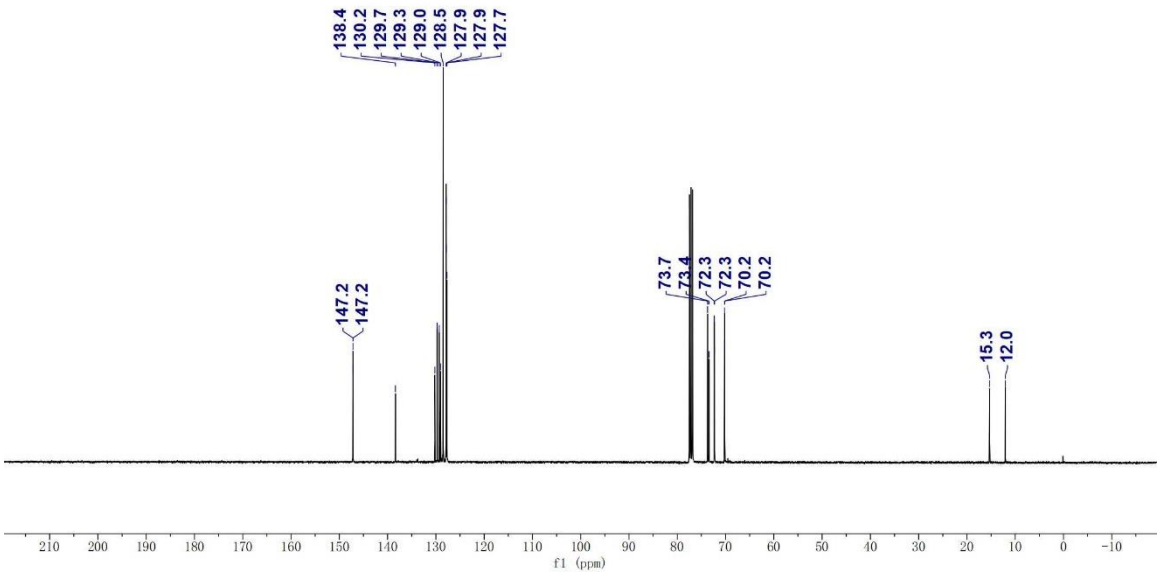
^{13}C NMR spectrum of **(*Z*)-1w** was measured in $CDCl_3$ at 101 MHz



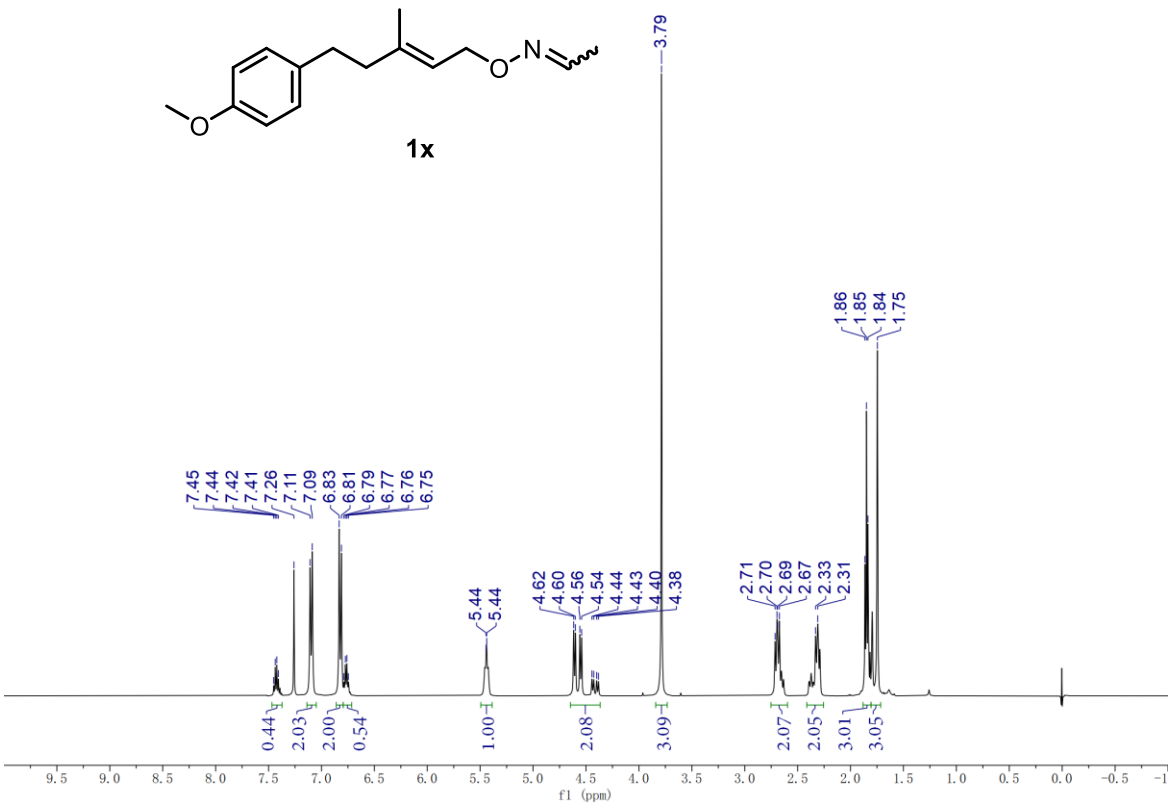
(***E***)-1W



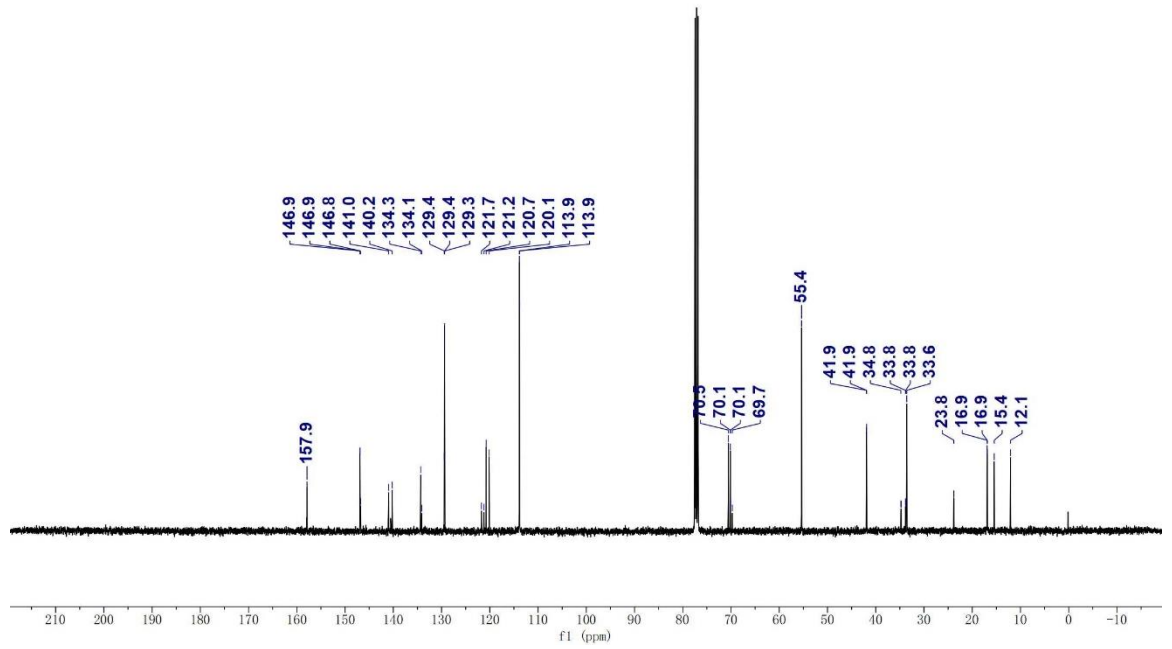
^{1}H NMR spectrum of **(*E*)-1w** was measured in $CDCl_3$ at 400 MH



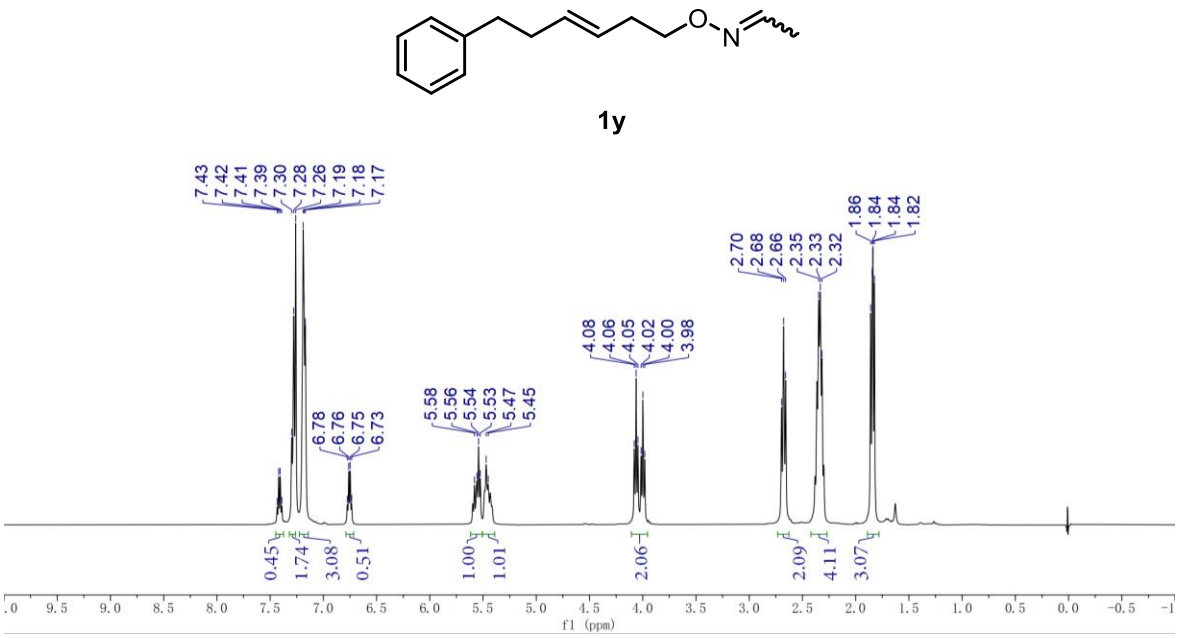
^{13}C NMR spectrum of **(*E*)-1w** was measured in $CDCl_3$ at 101 MHz



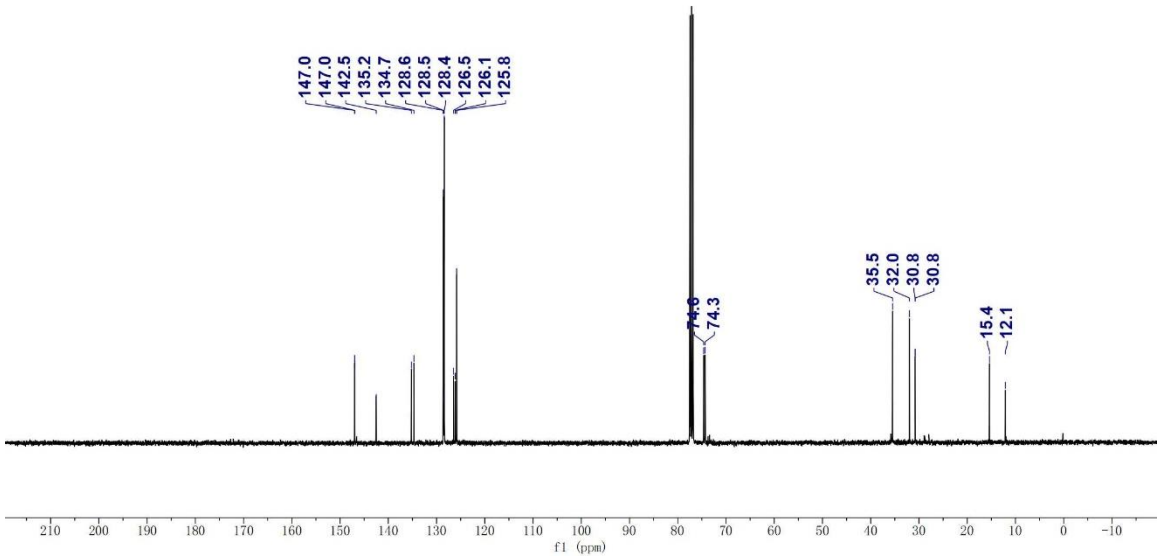
^{1}H NMR spectrum of **1x** was measured in $CDCl_3$ at 400 MH



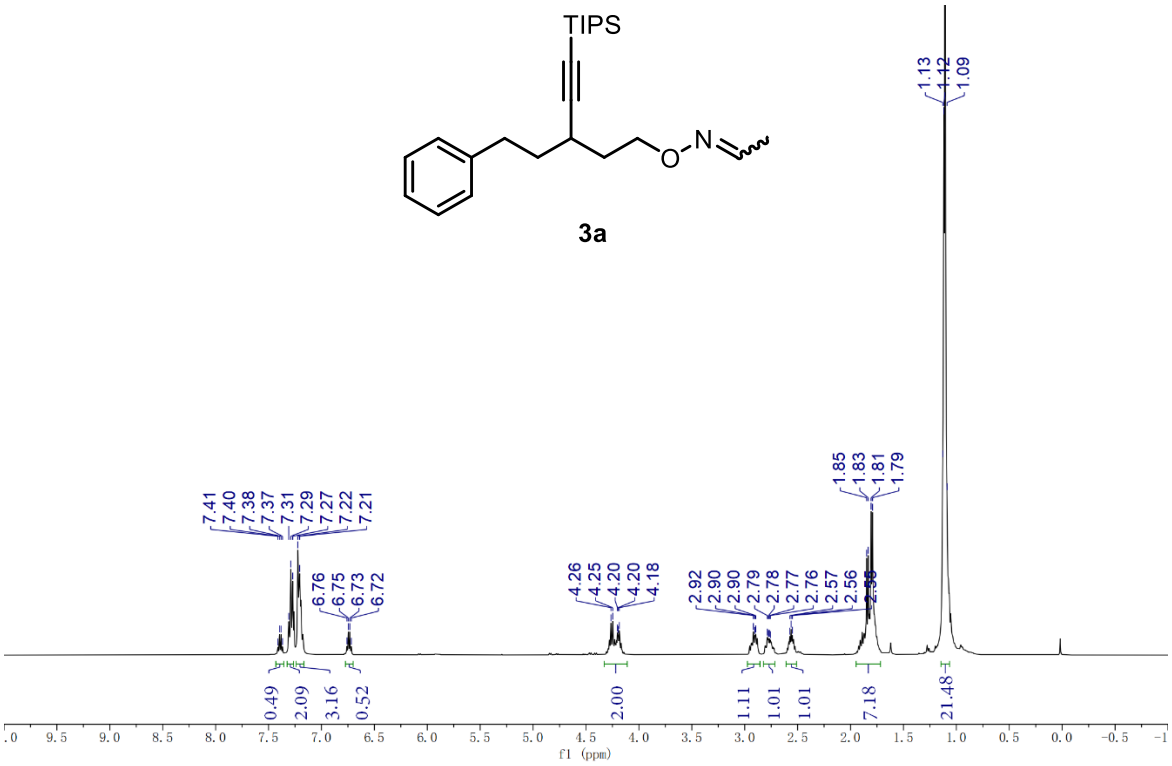
^{13}C NMR spectrum of **1x** was measured in $CDCl_3$ at 101 MHz



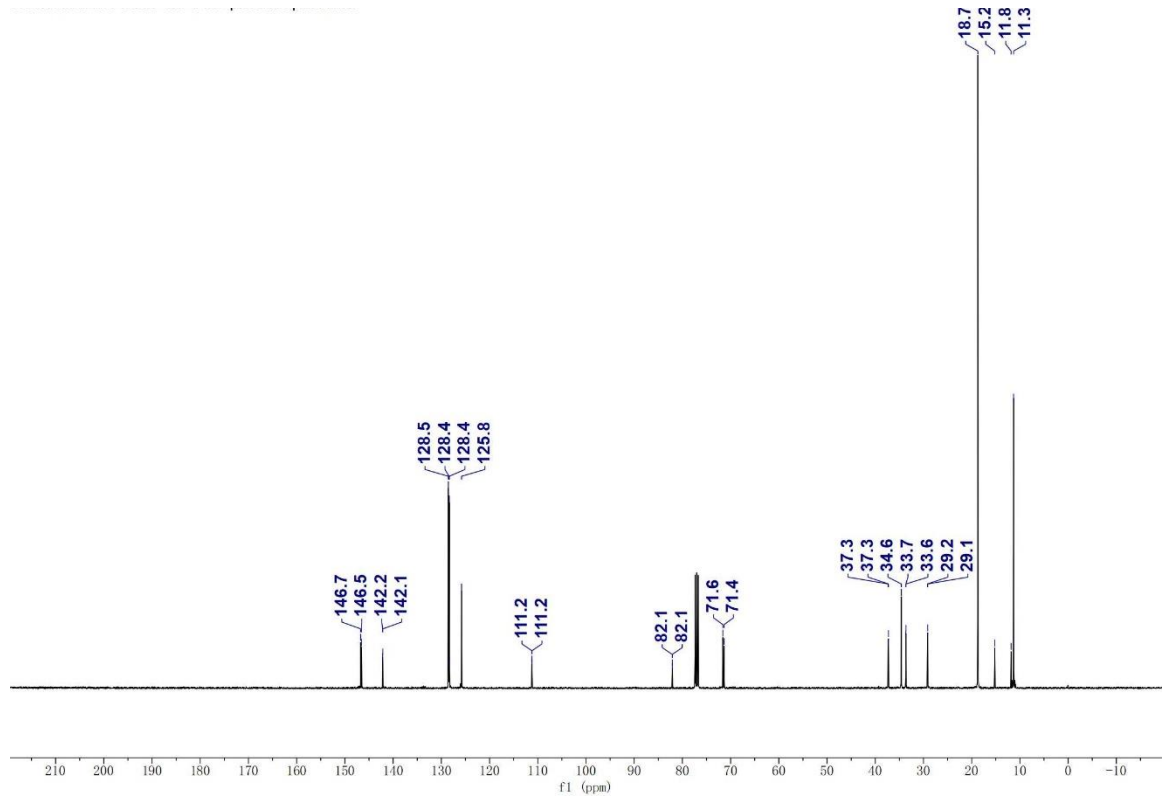
^{1}H NMR spectrum of **1y** was measured in $CDCl_3$ at 400 MH



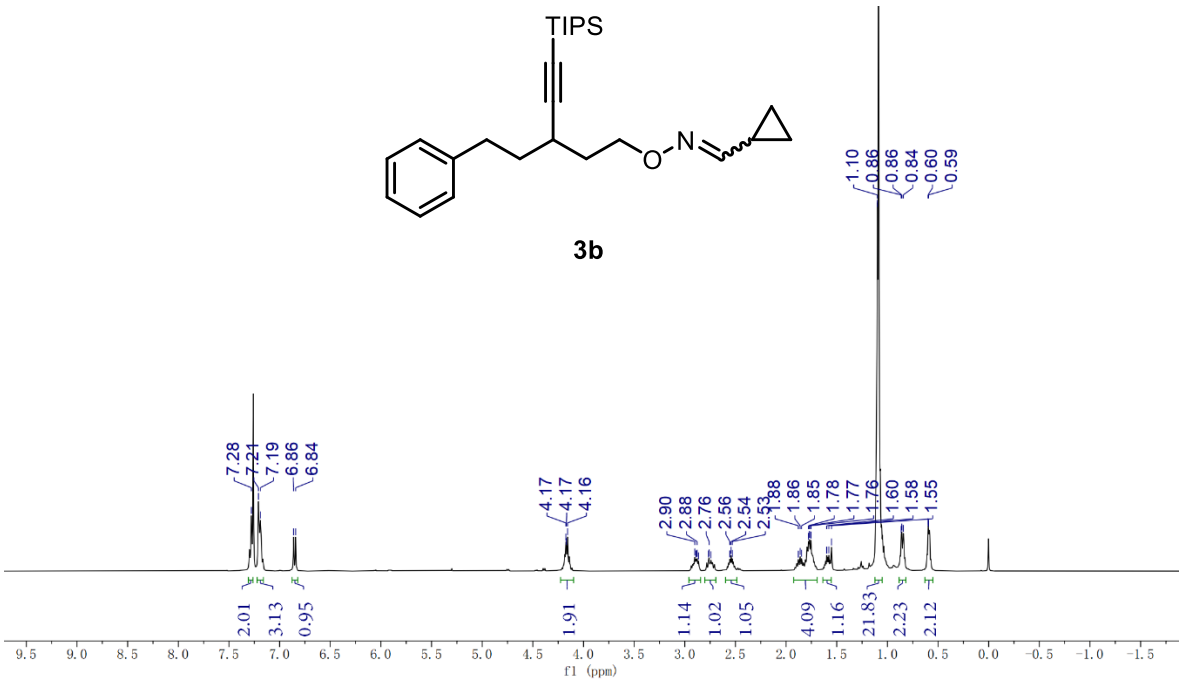
^{13}C NMR spectrum of **1y** was measured in $CDCl_3$ at 101 MHz



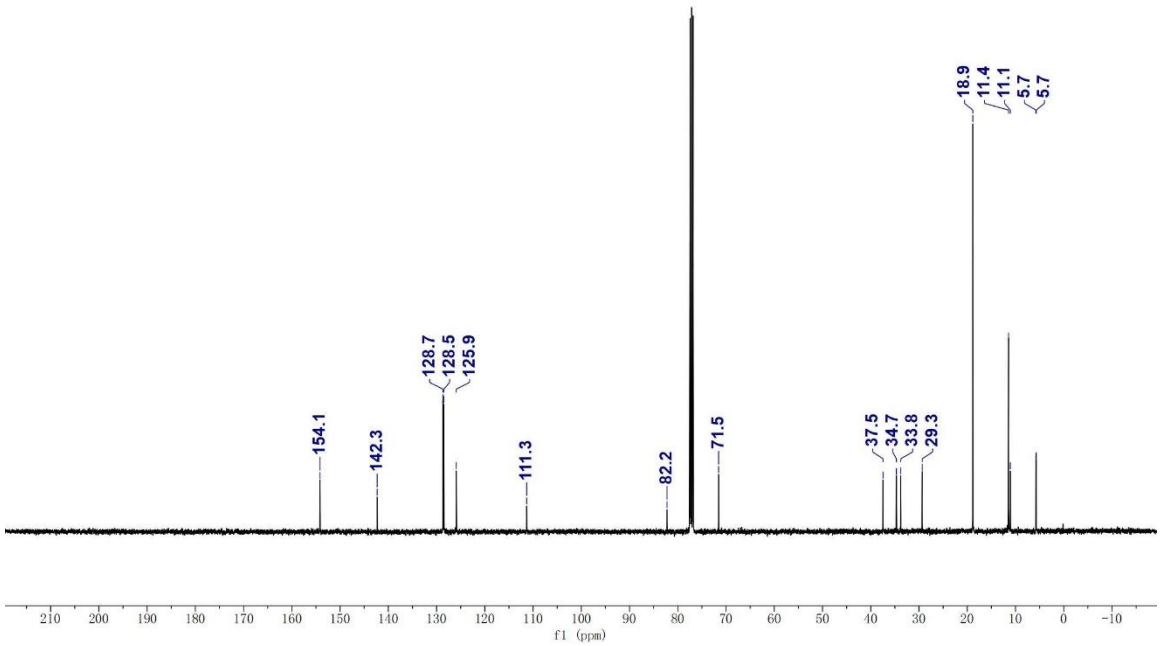
^{1}H NMR spectrum of **3a** was measured in $CDCl_3$ at 400 MH



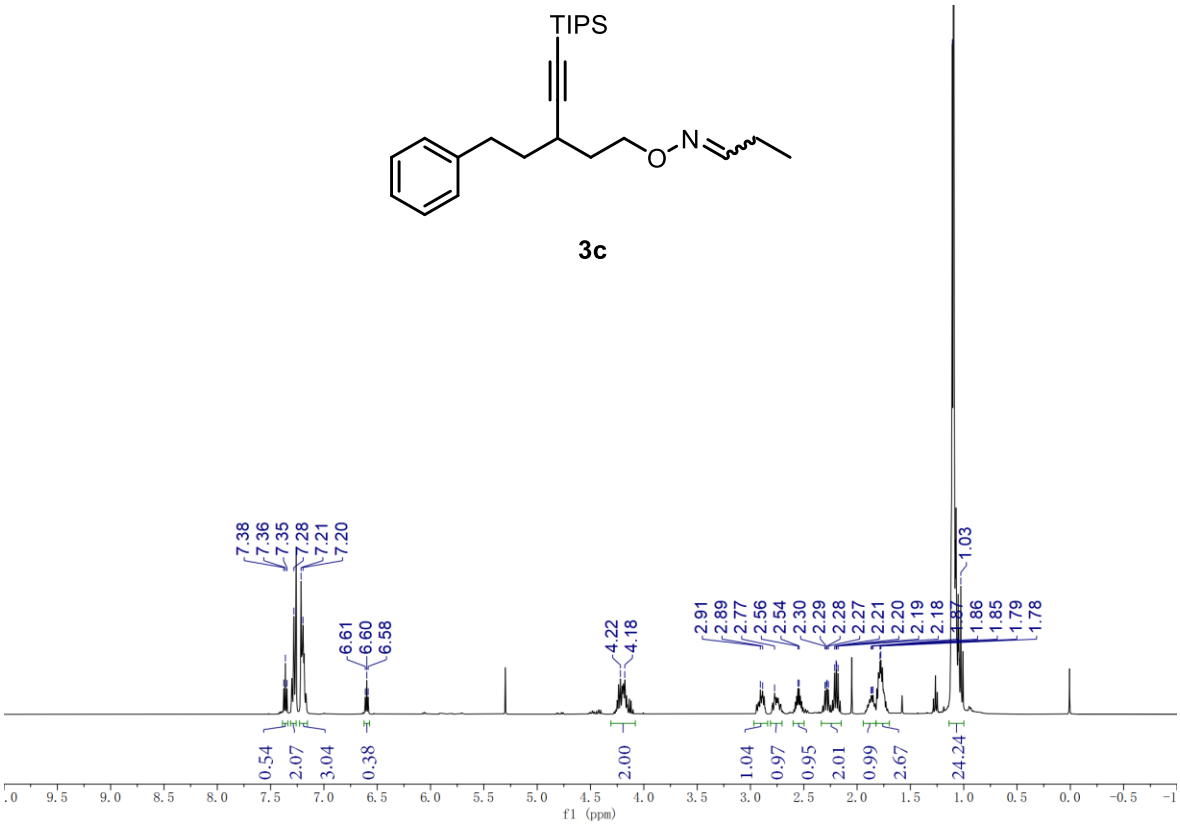
^{13}C NMR spectrum of **3a** was measured in $CDCl_3$ at 101 MHz



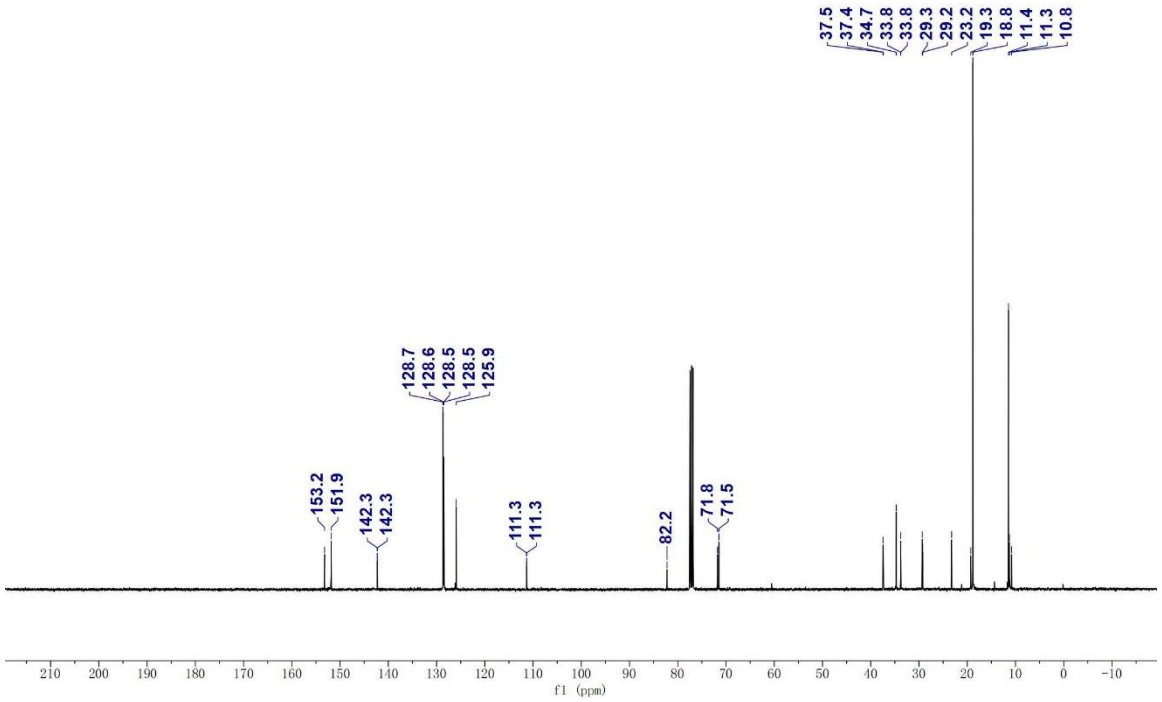
^{1}H NMR spectrum of **3b** was measured in $CDCl_3$ at 400 MH



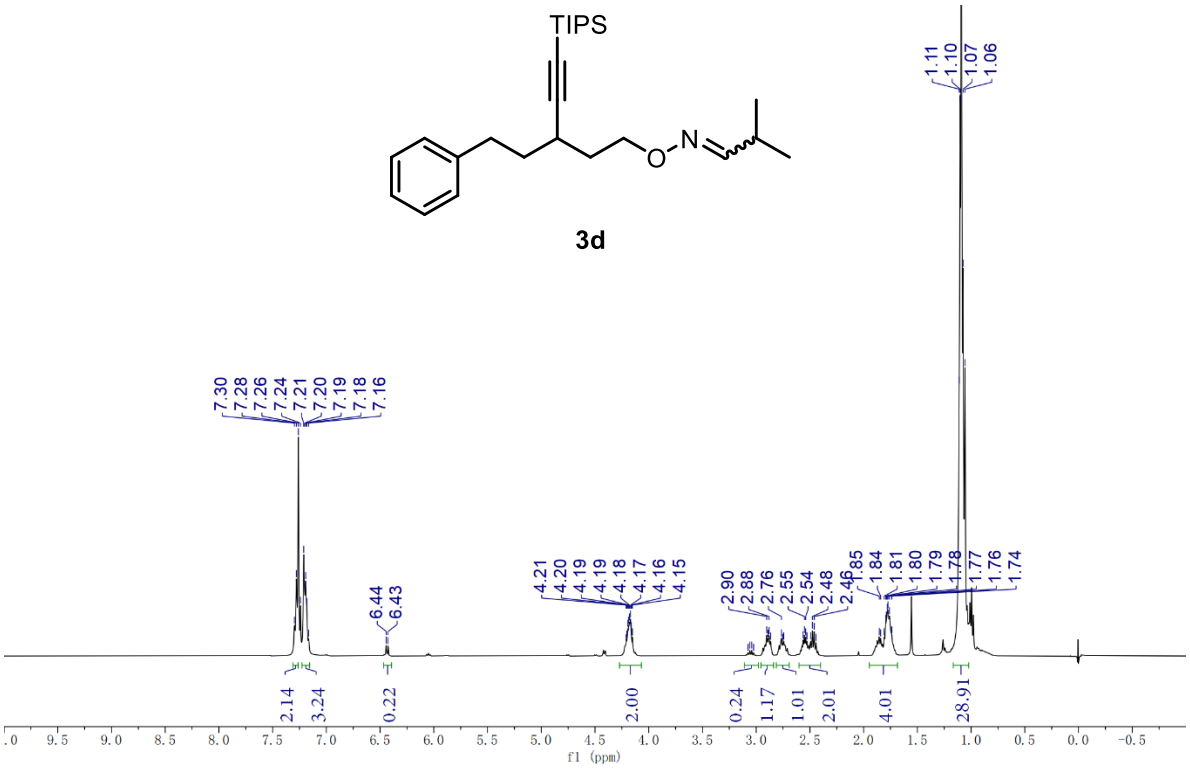
^{13}C NMR spectrum of **3b** was measured in $CDCl_3$ at 101 MHz



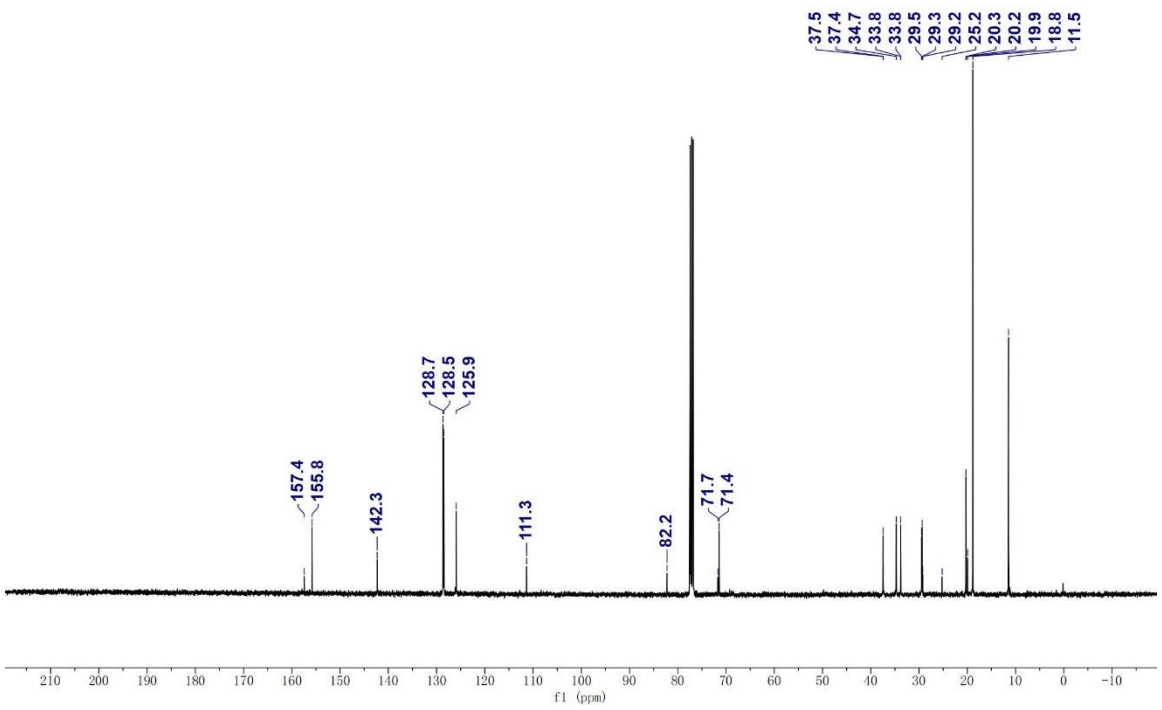
^{1}H NMR spectrum of **3c** was measured in $CDCl_3$ at 400 MH



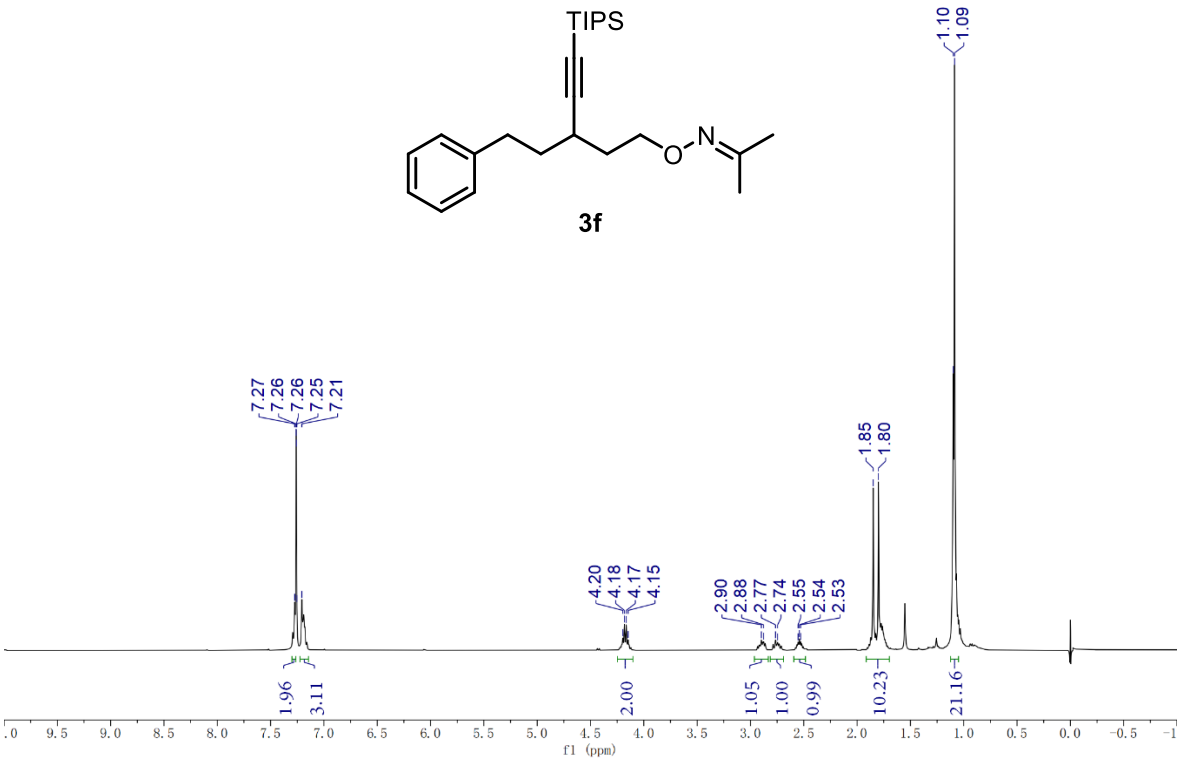
^{13}C NMR spectrum of **3c** was measured in $CDCl_3$ at 101 MHz



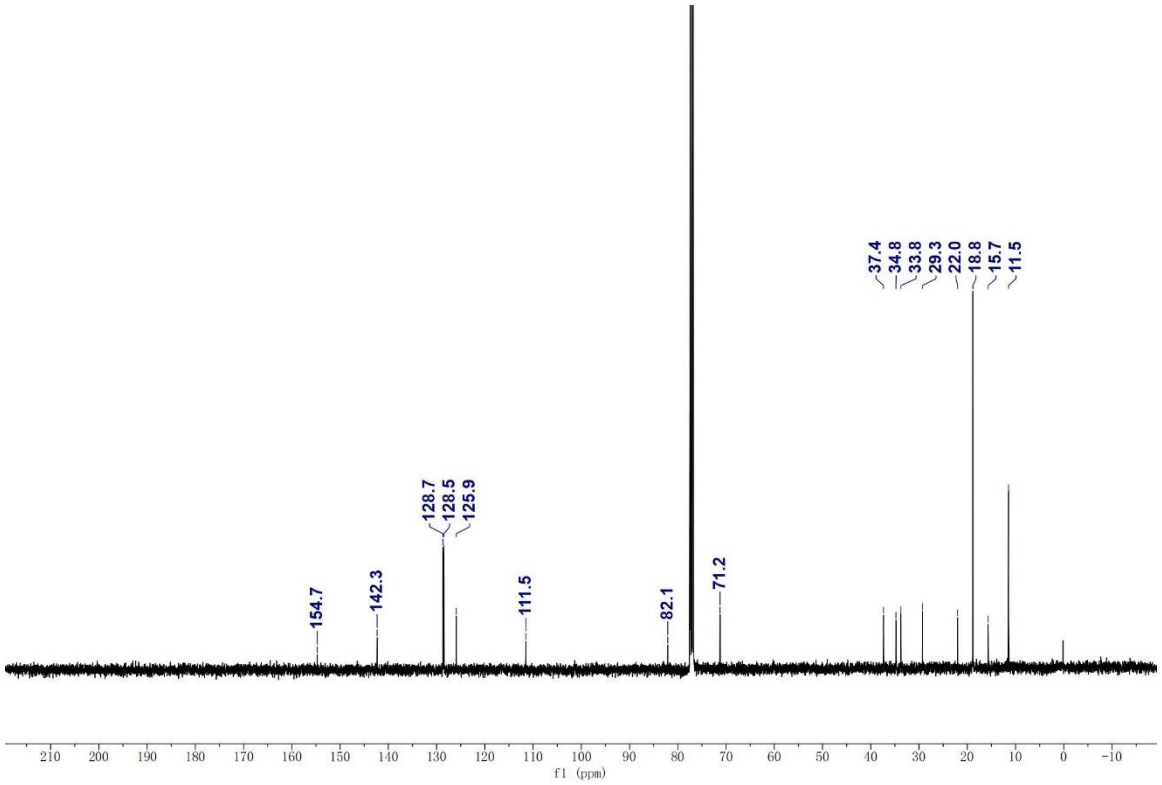
^{1}H NMR spectrum of **3d** was measured in $CDCl_3$ at 400 MH



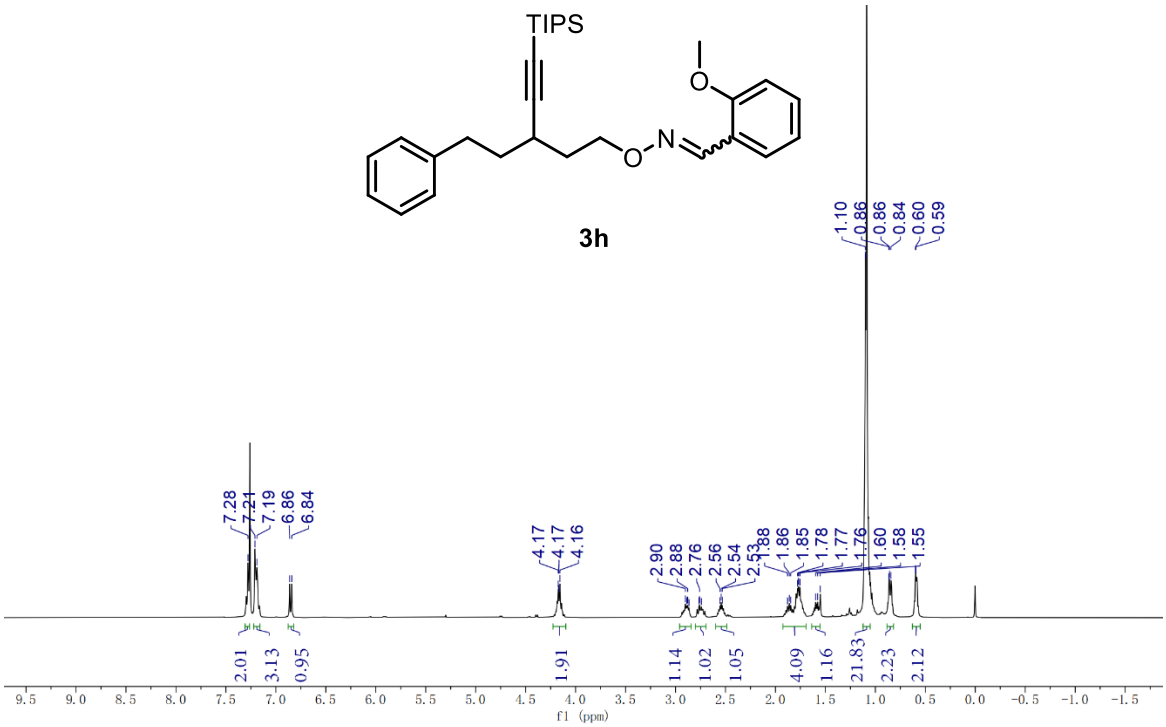
^{13}C NMR spectrum of **3d** was measured in $CDCl_3$ at 101 MHz



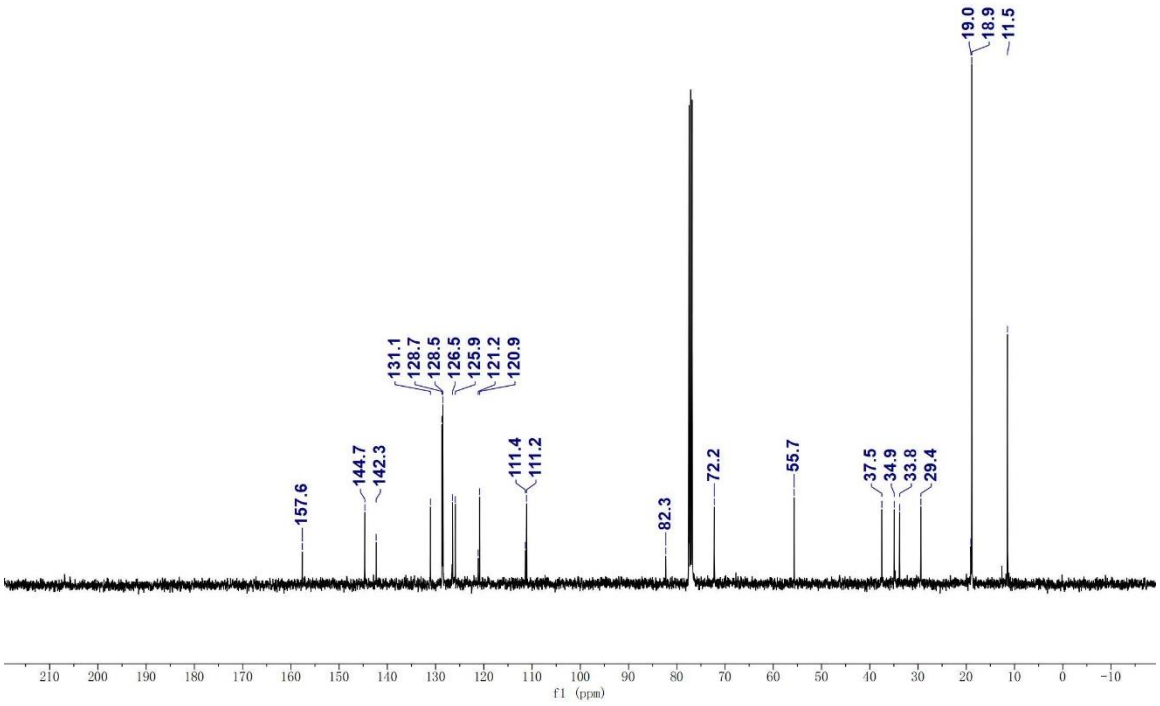
^{1}H NMR spectrum of **3f** was measured in $CDCl_3$ at 400 MH



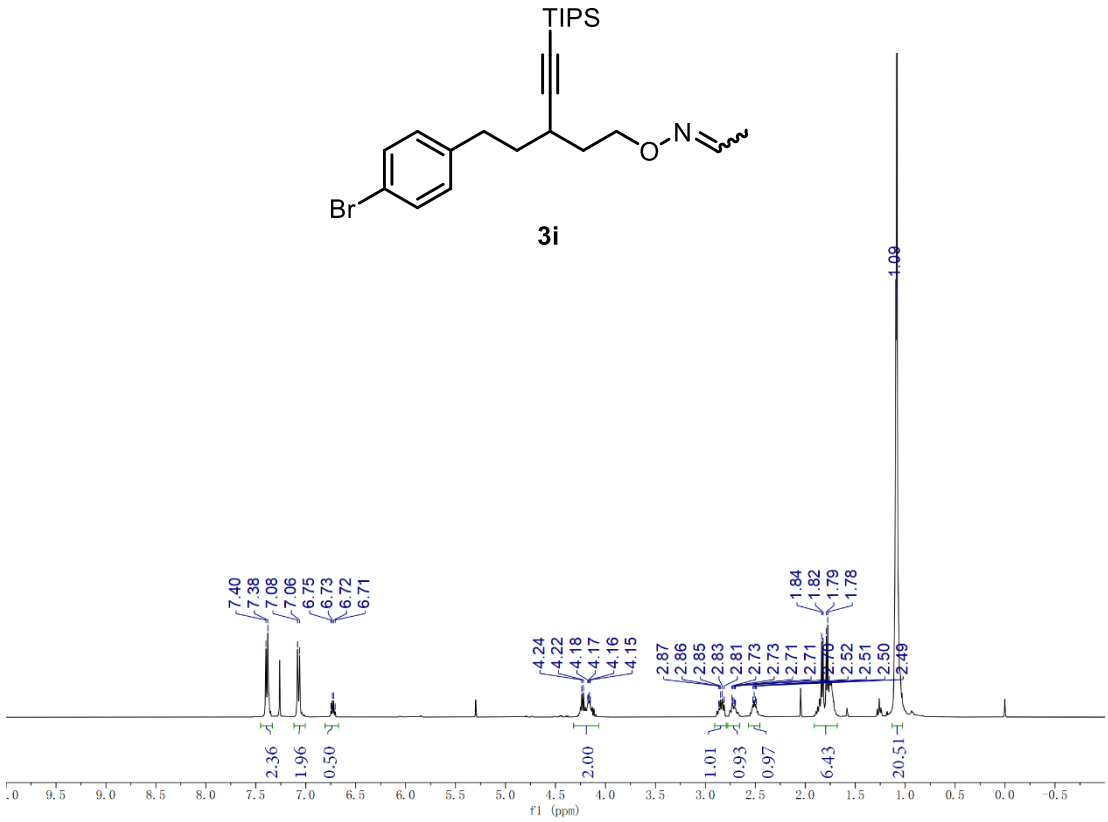
^{13}C NMR spectrum of **3f** was measured in $CDCl_3$ at 101 MHz



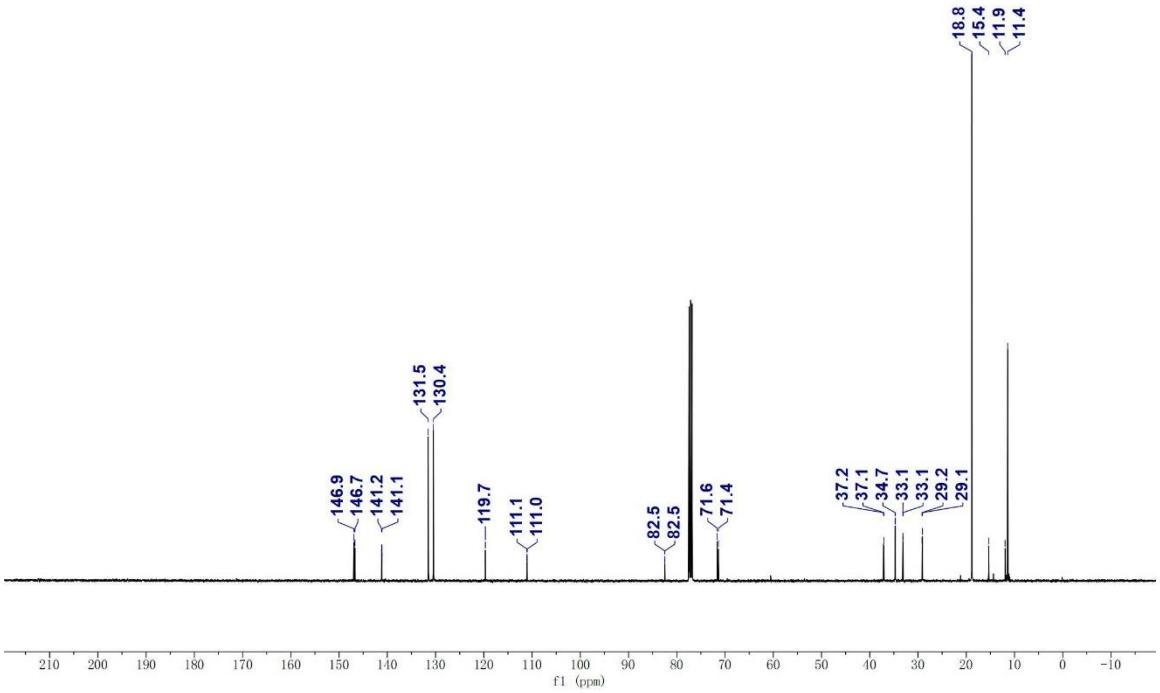
^{1}H NMR spectrum of **3h** was measured in $CDCl_3$ at 400 MH



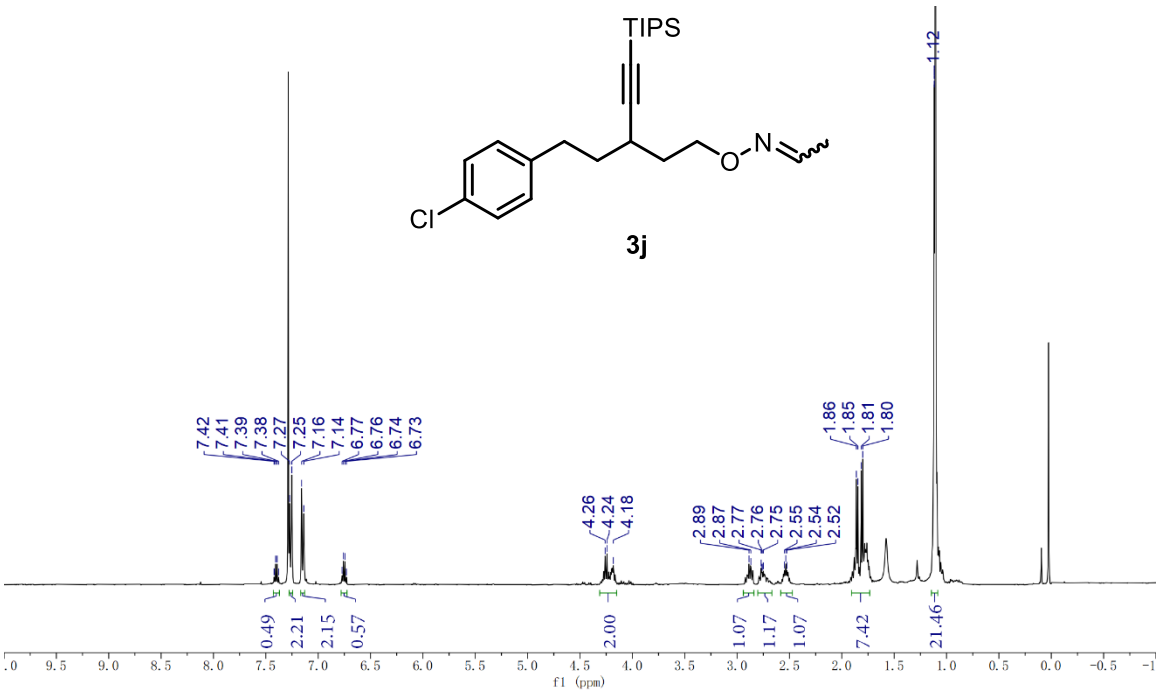
^{13}C NMR spectrum of **3h** was measured in $CDCl_3$ at 101 MHz



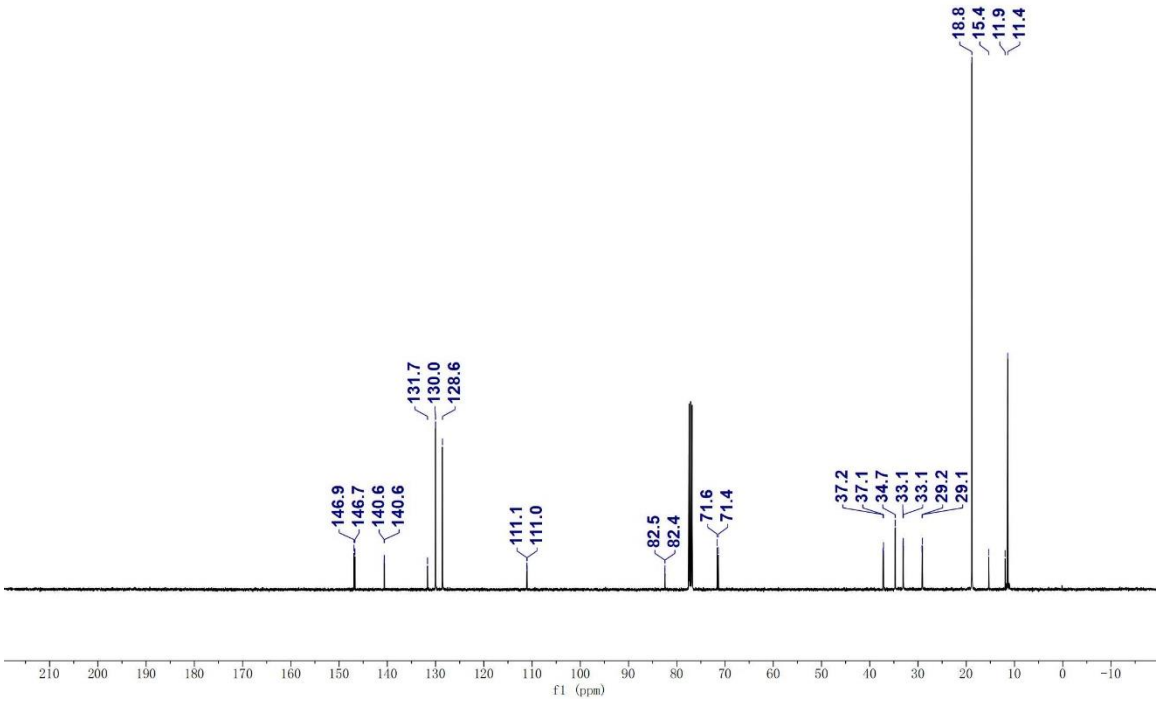
^{1}H NMR spectrum of **3i** was measured in $CDCl_3$ at 400 MH



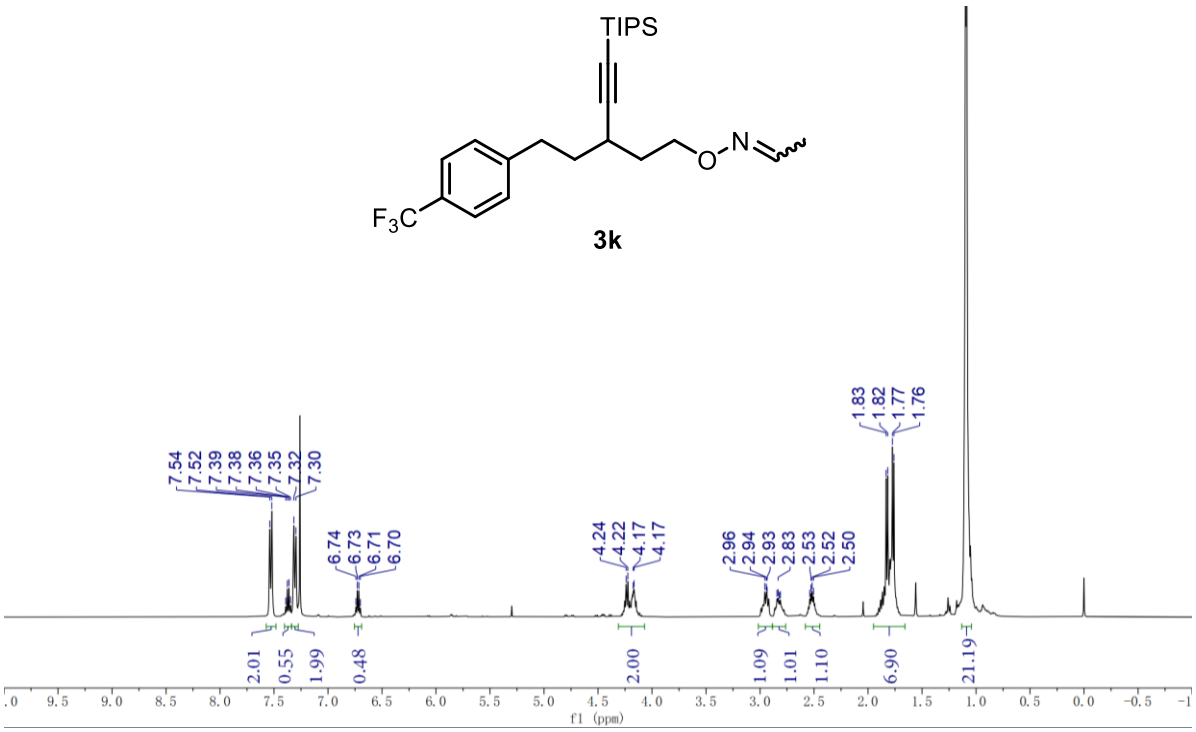
^{13}C NMR spectrum of **3i** was measured in $CDCl_3$ at 101 MHz



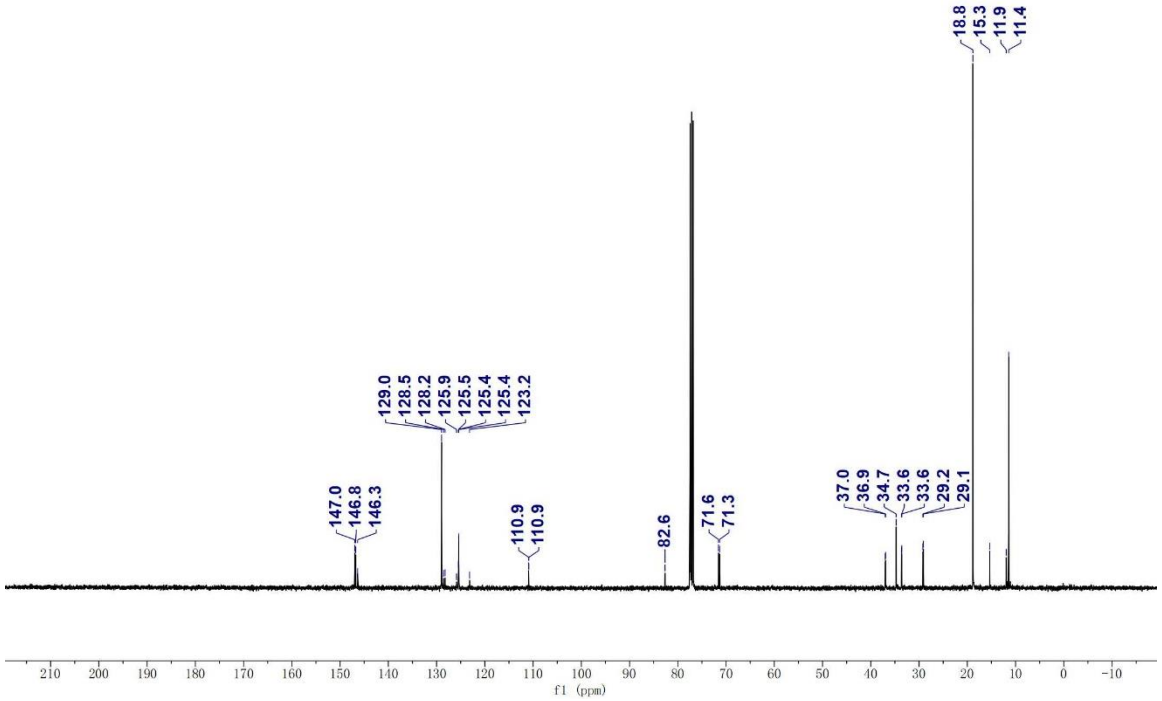
^{1}H NMR spectrum of **3j** was measured in $CDCl_3$ at 400 MH



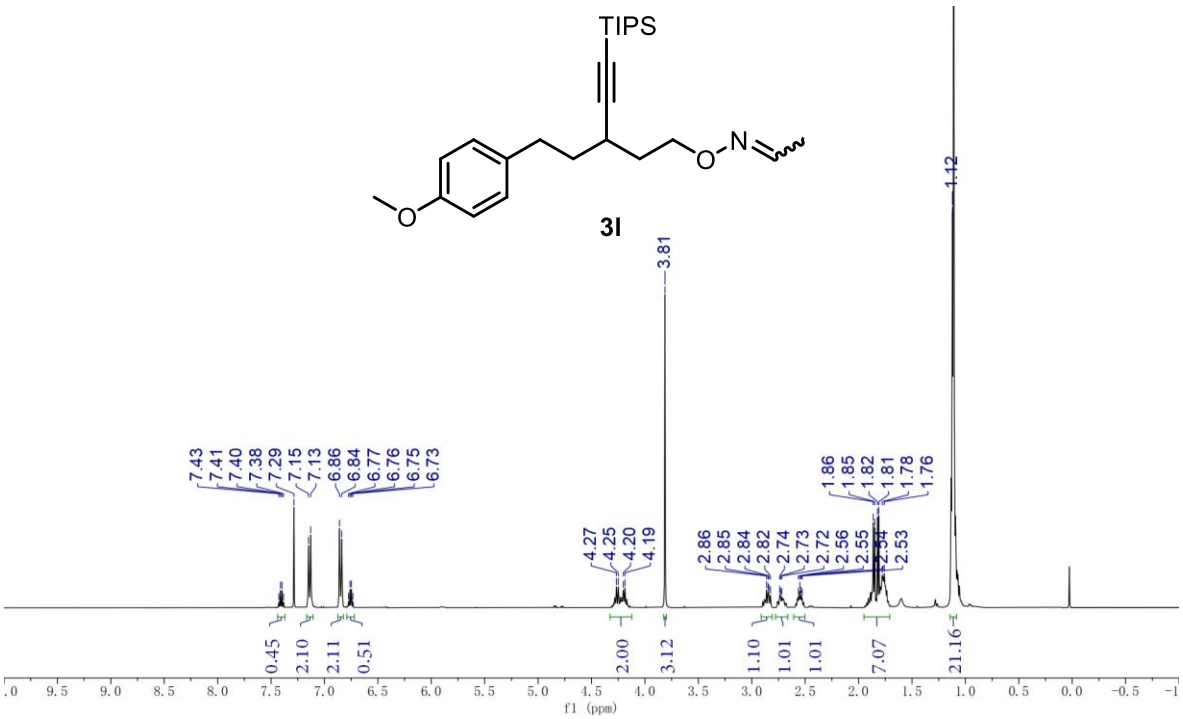
^{13}C NMR spectrum of **3j** was measured in $CDCl_3$ at 101 MHz



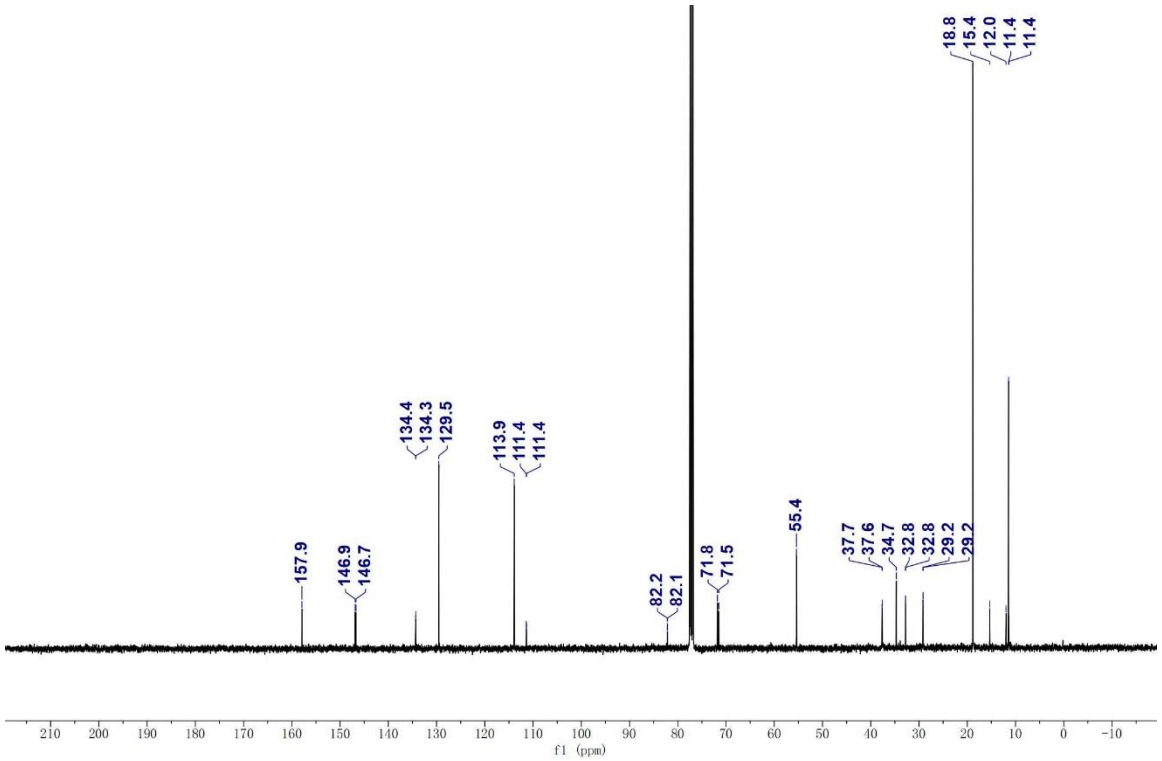
^{1}H NMR spectrum of **3k** was measured in $CDCl_3$ at 400 MH



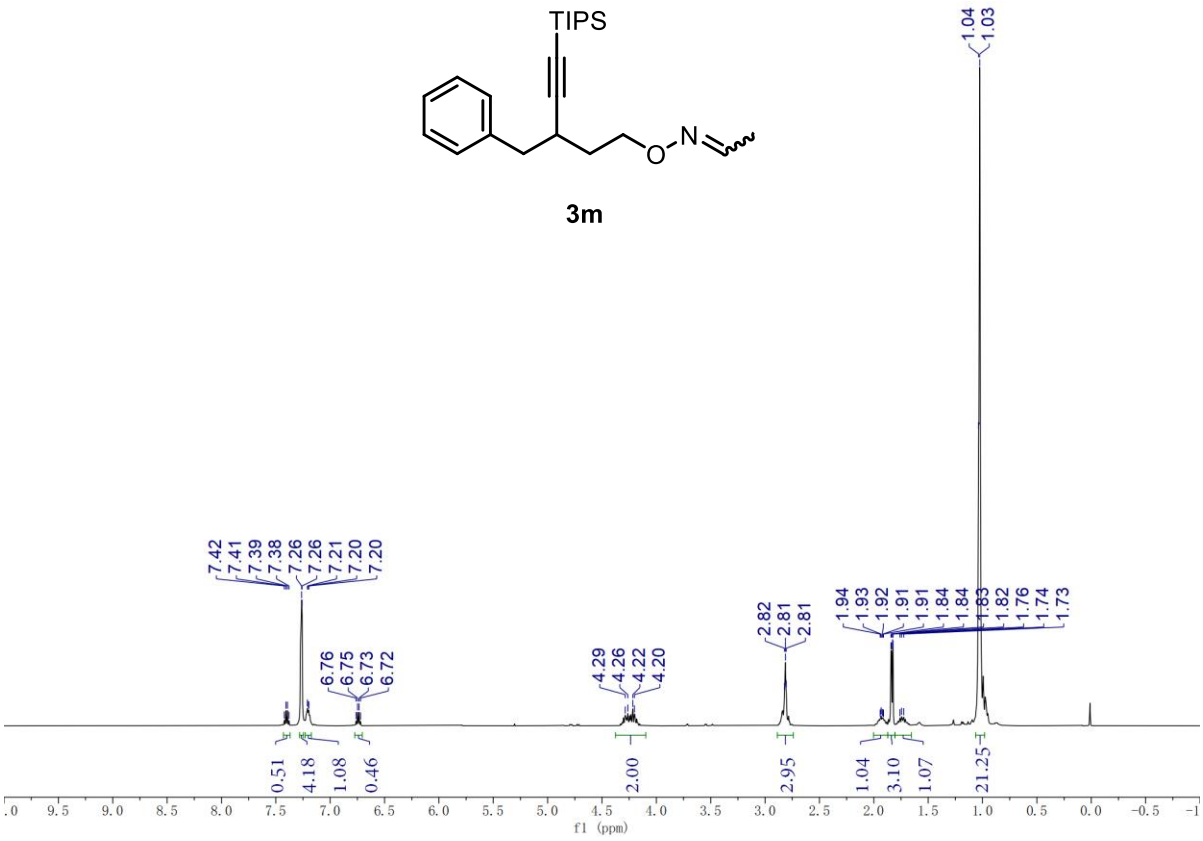
^{13}C NMR spectrum of **3k** was measured in $CDCl_3$ at 101 MHz



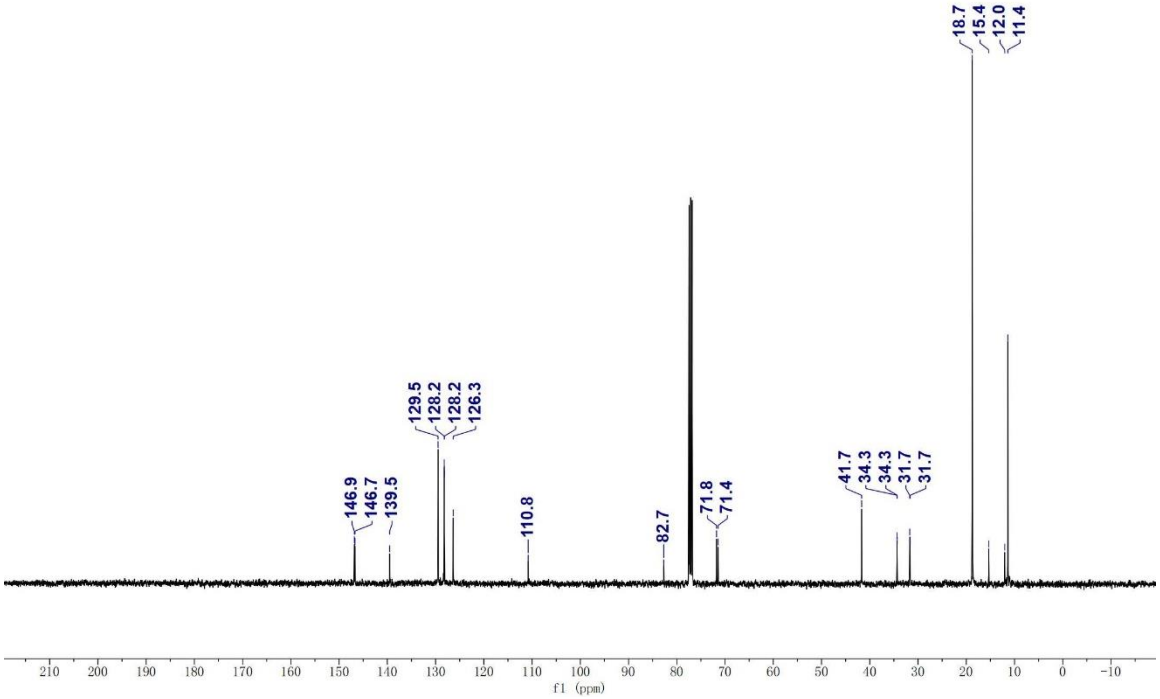
^{1}H NMR spectrum of **3l** was measured in $CDCl_3$ at 400 MH



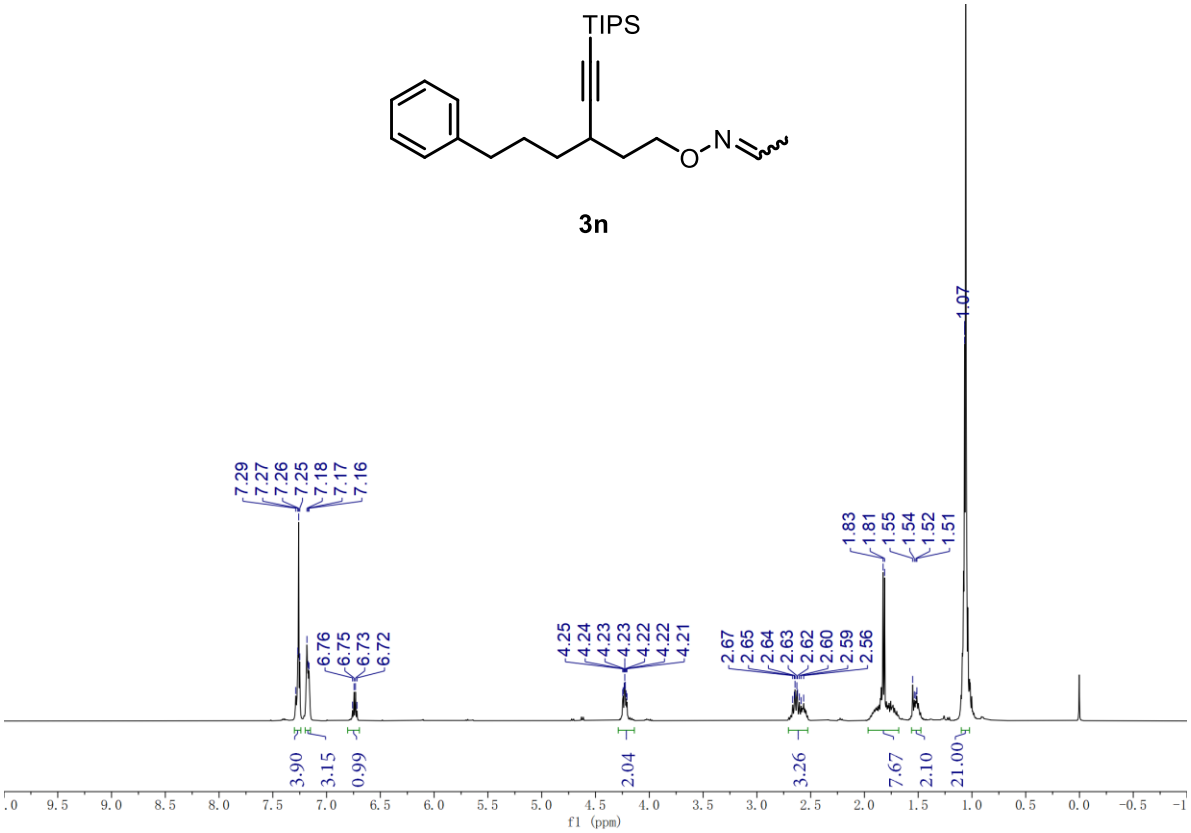
^{13}C NMR spectrum of **3l** was measured in $CDCl_3$ at 101 MHz



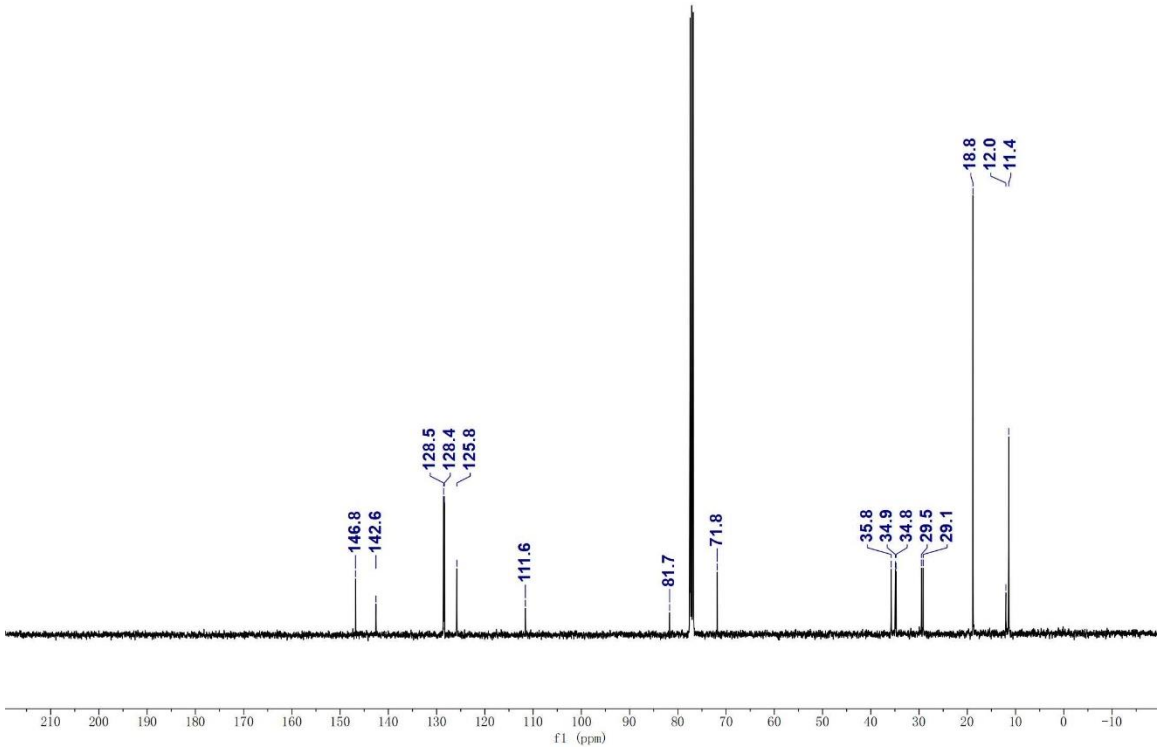
^{1}H NMR spectrum of **3m** was measured in $CDCl_3$ at 400 MH



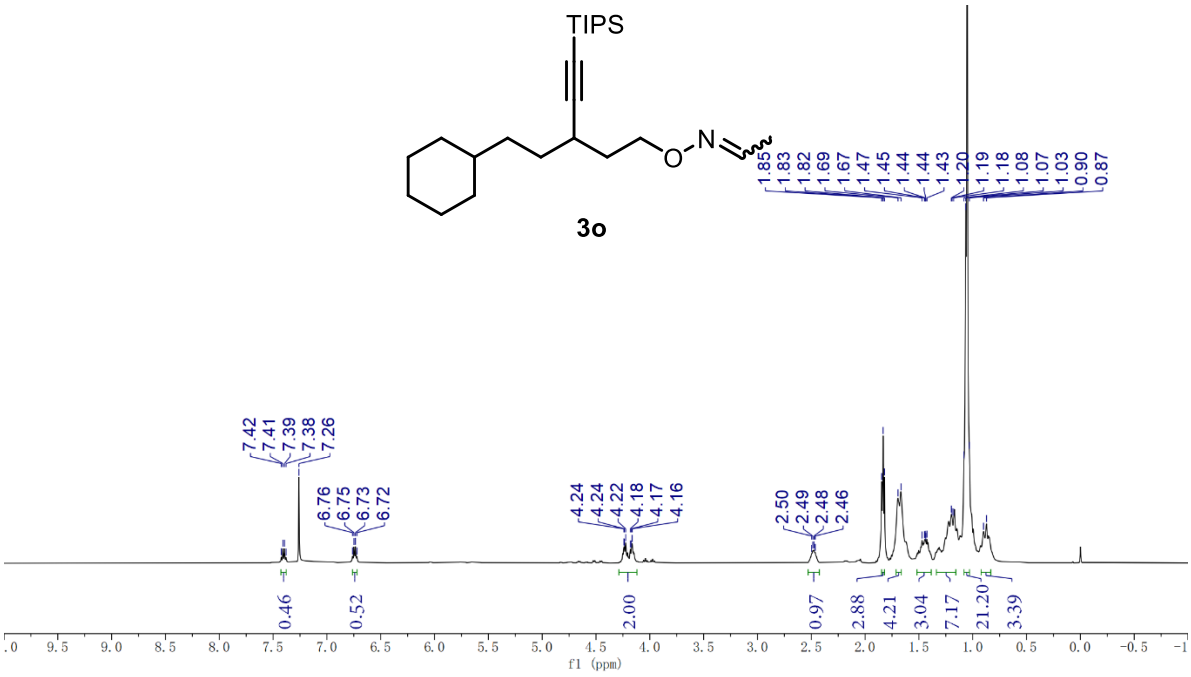
^{13}C NMR spectrum of **3m** was measured in $CDCl_3$ at 101 MHz



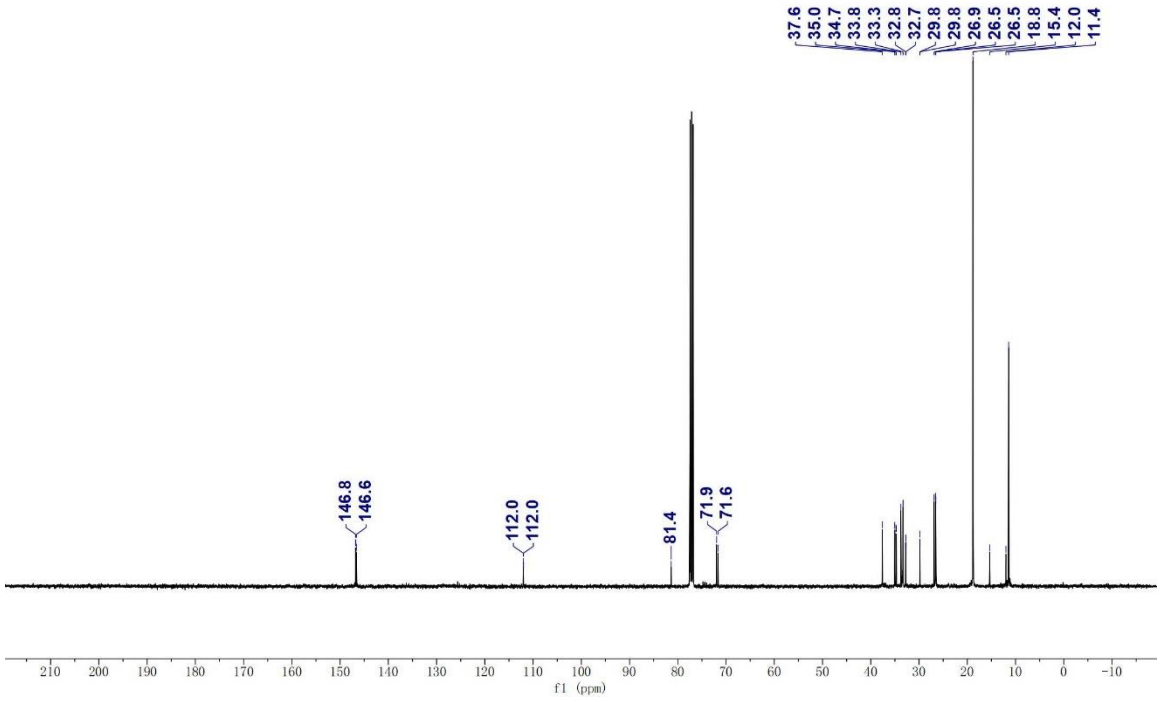
^{1}H NMR spectrum of **3n** was measured in $CDCl_3$ at 400 MH



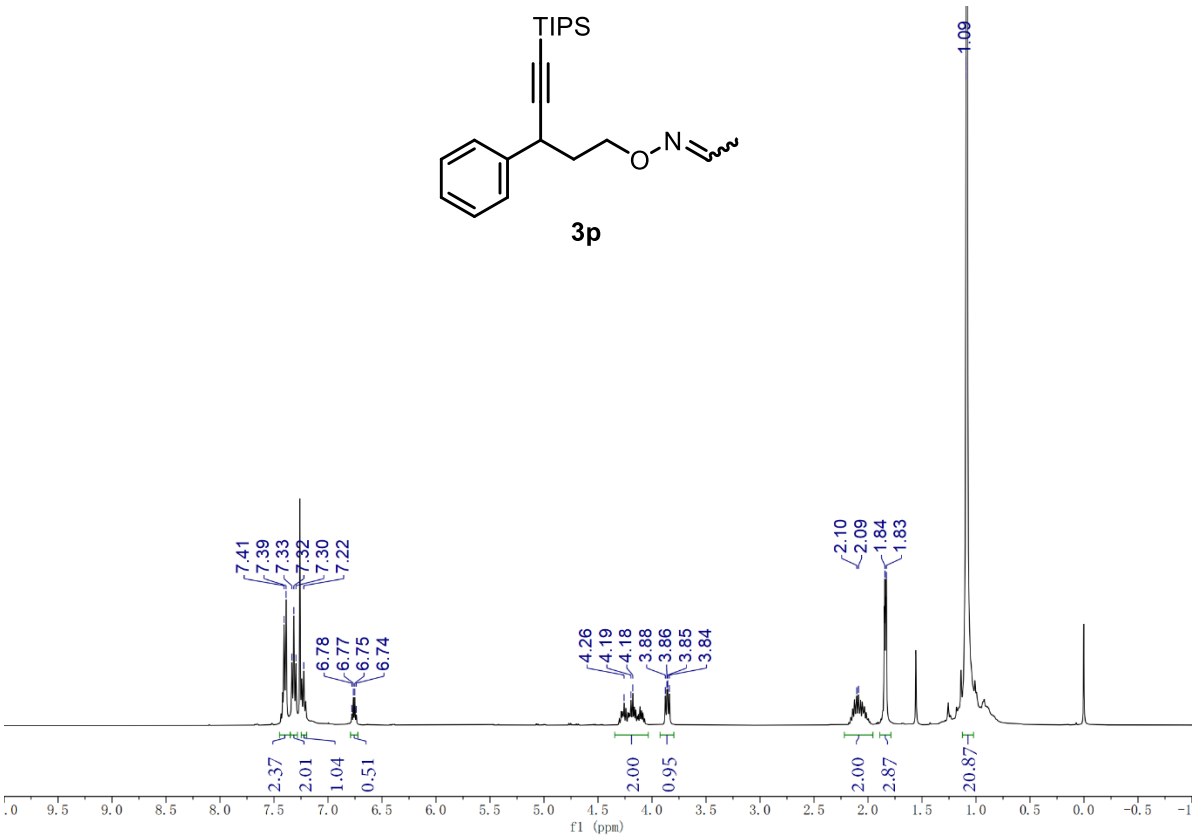
^{13}C NMR spectrum of **3n** was measured in $CDCl_3$ at 101 MHz



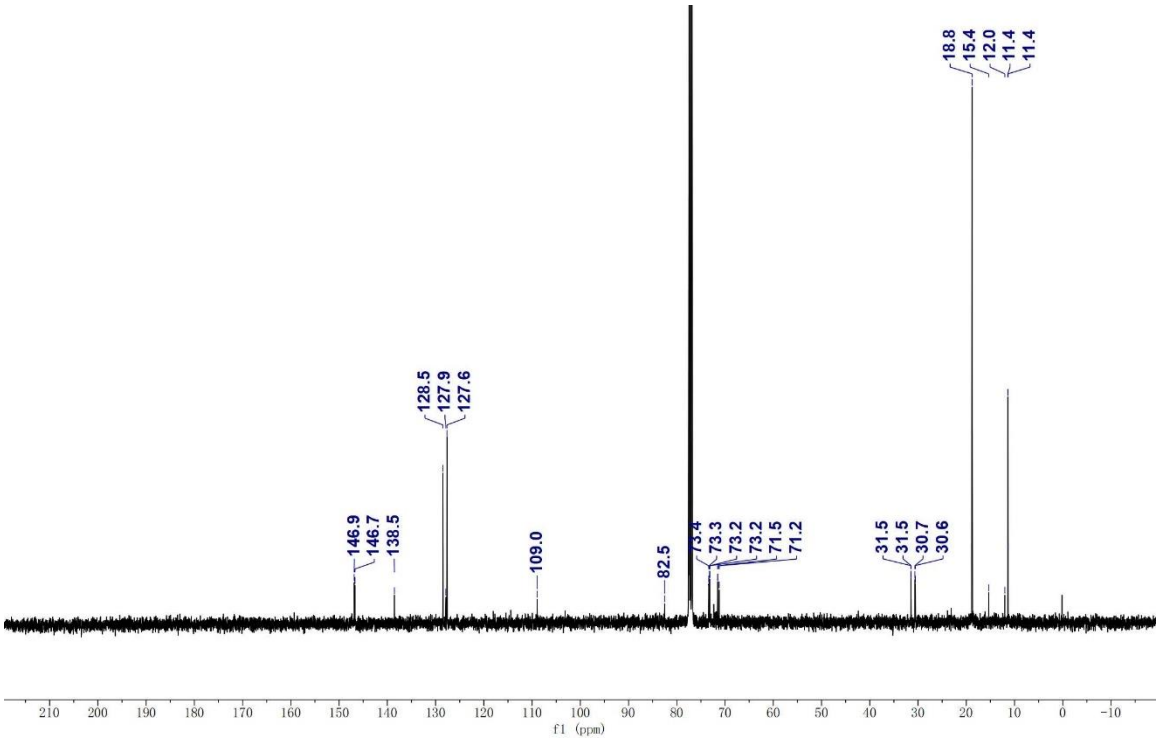
^{1}H NMR spectrum of **3o** was measured in $CDCl_3$ at 400 MH



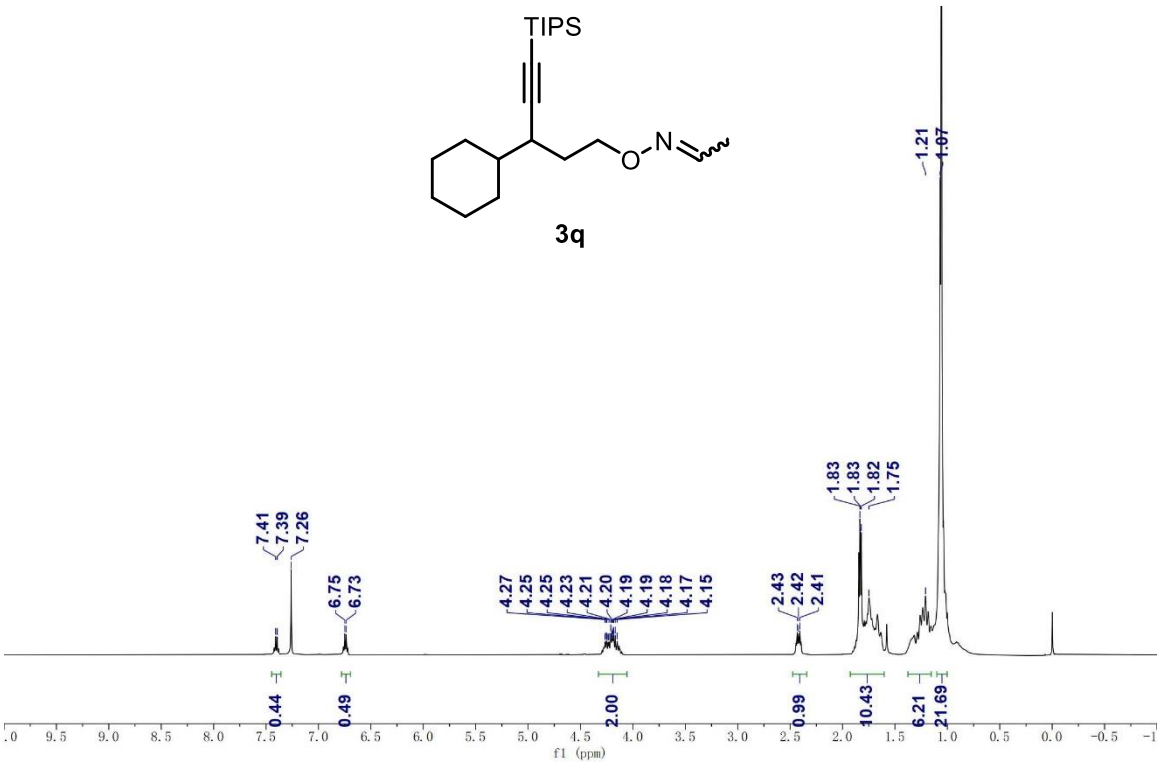
^{13}C NMR spectrum of **3o** was measured in $CDCl_3$ at 101 MHz



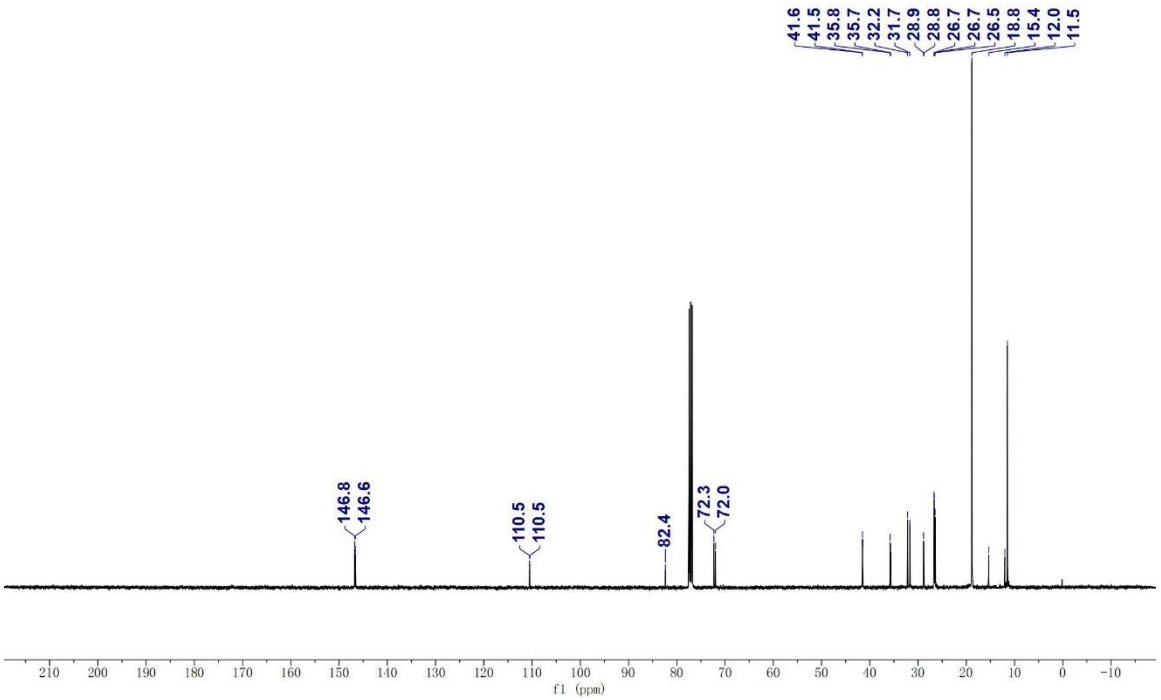
^{1}H NMR spectrum of **3p** was measured in $CDCl_3$ at 400 MH



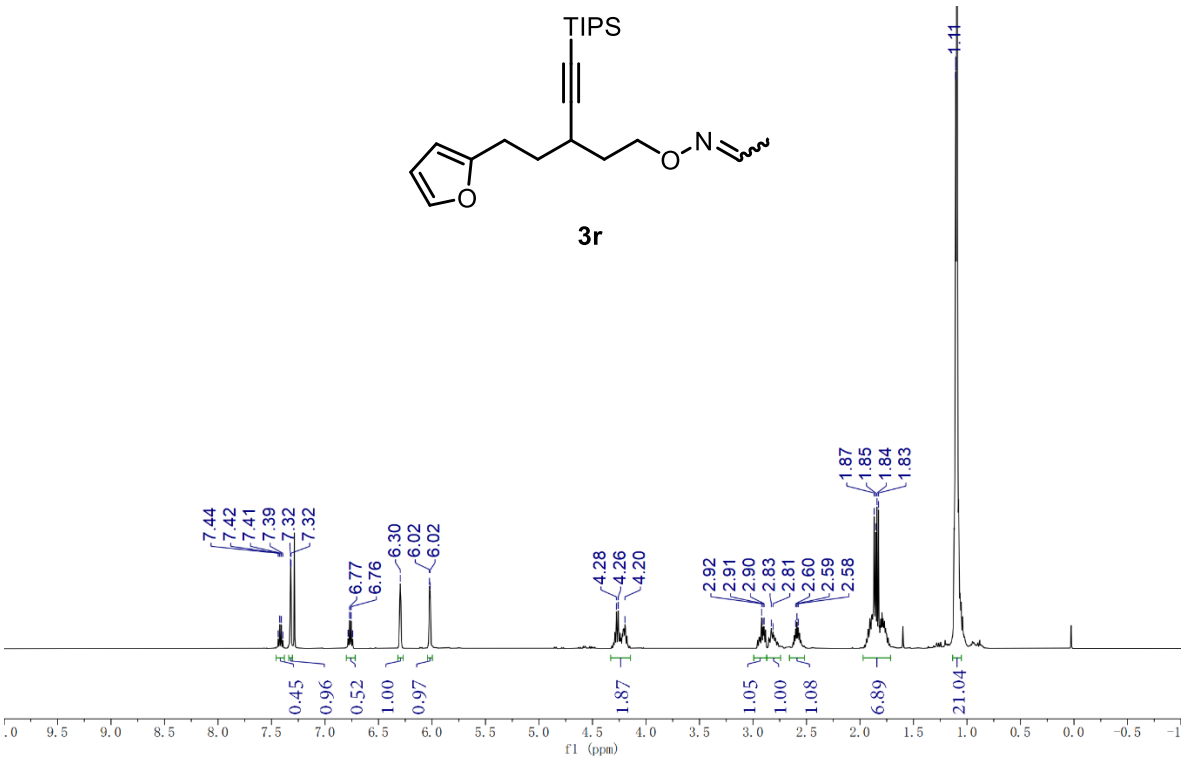
^{13}C NMR spectrum of **3p** was measured in $CDCl_3$ at 101 MHz



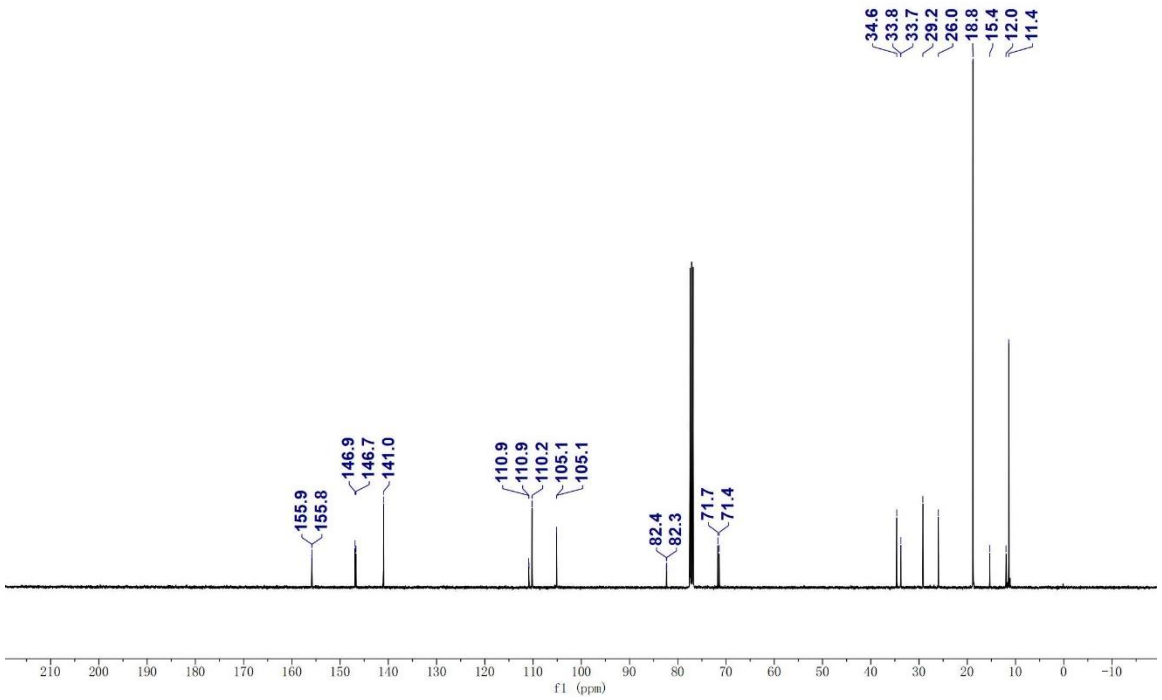
^{1}H NMR spectrum of **3q** was measured in $CDCl_3$ at 400 MH



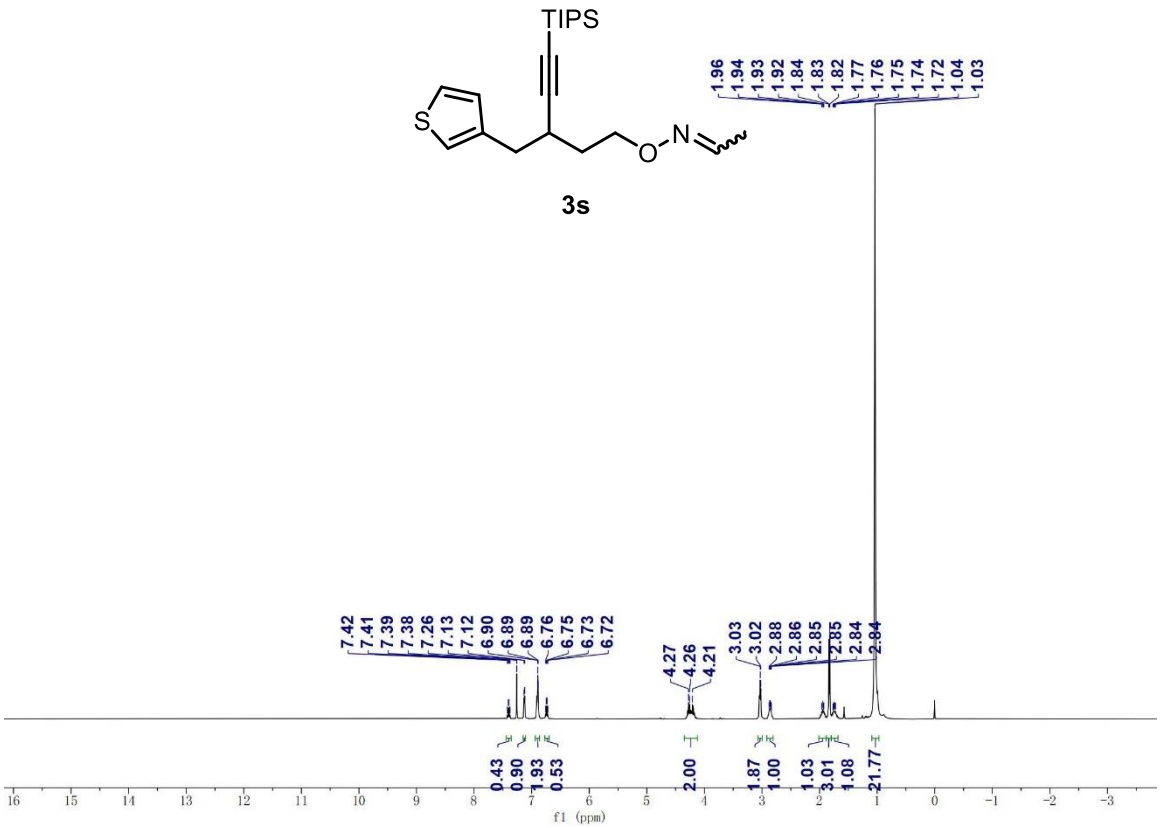
^{13}C NMR spectrum of **3q** was measured in $CDCl_3$ at 101 MHz



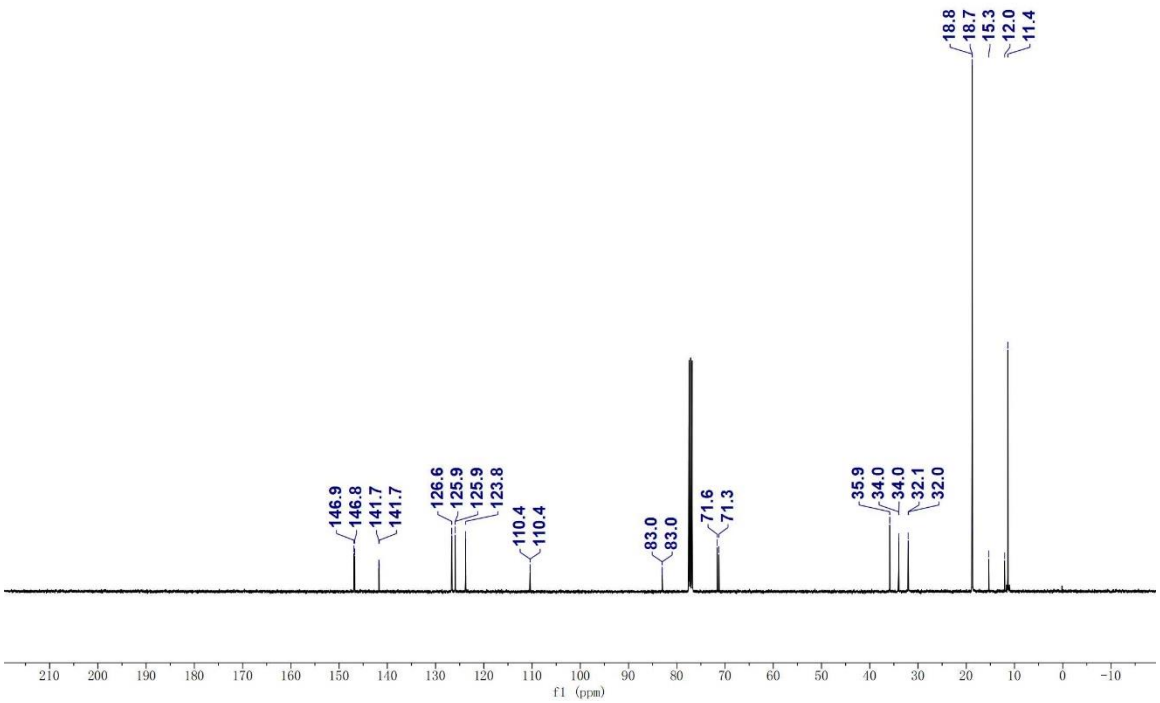
^{1}H NMR spectrum of **3r** was measured in $CDCl_3$ at 400 MH



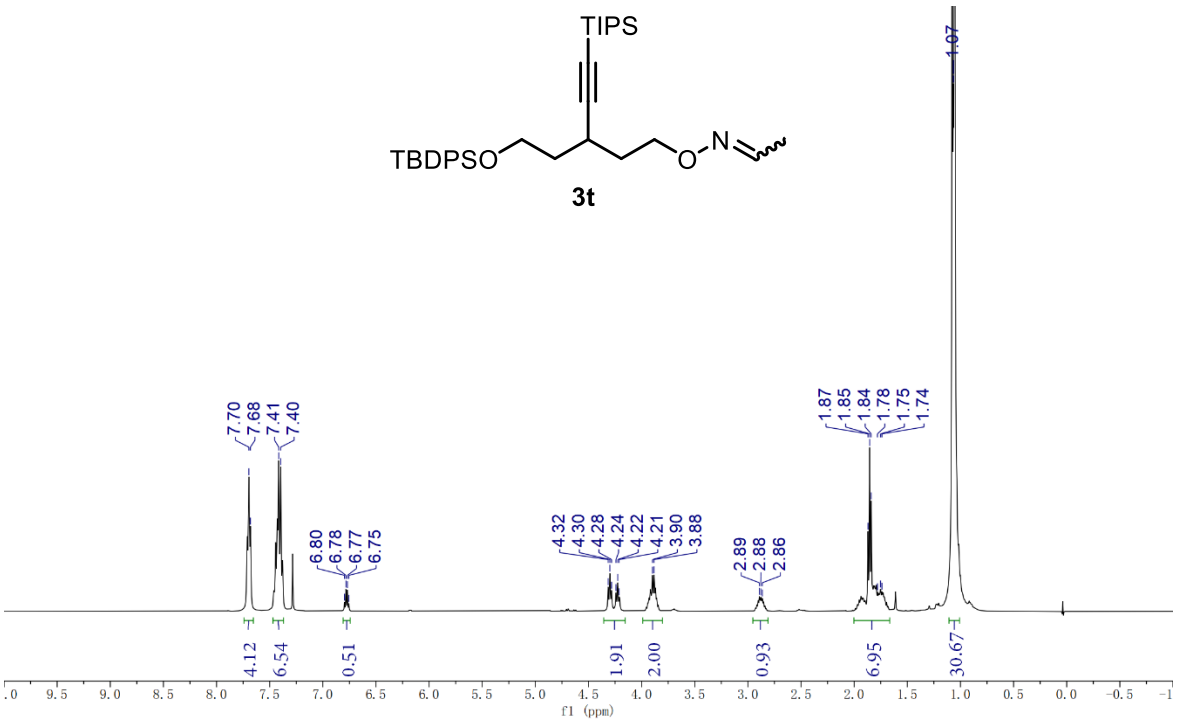
^{13}C NMR spectrum of **3r** was measured in $CDCl_3$ at 101 MHz



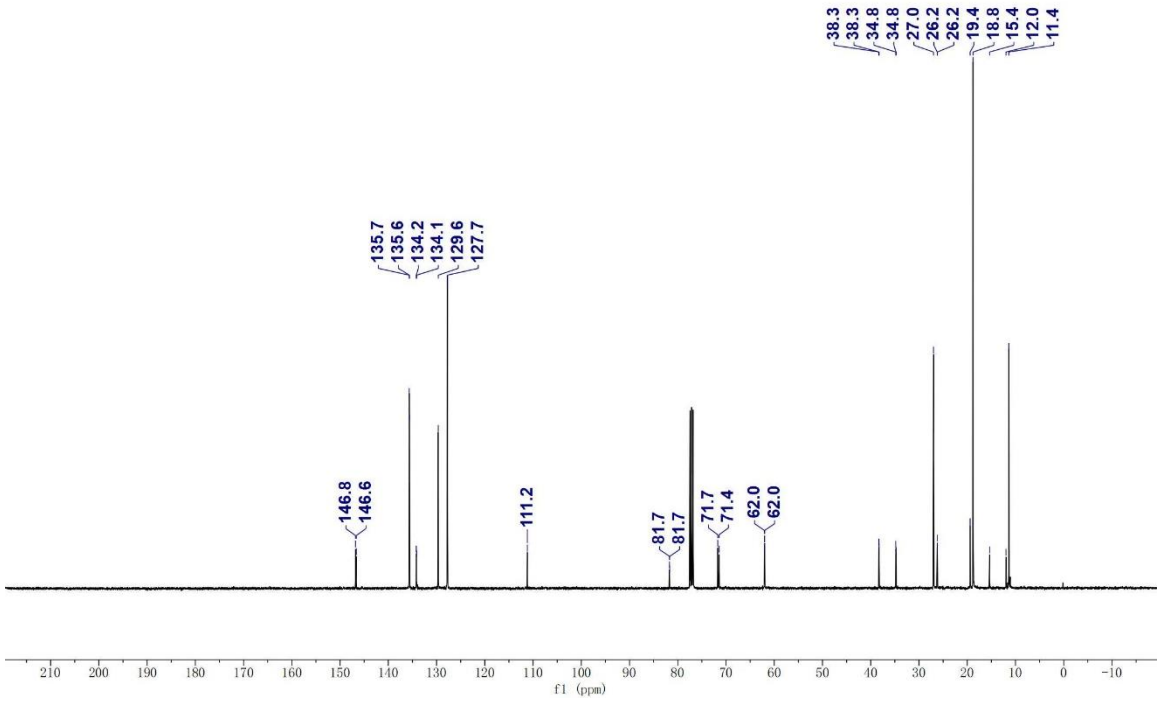
^{1}H NMR spectrum of **3s** was measured in $CDCl_3$ at 400 MH



^{13}C NMR spectrum of **3s** was measured in $CDCl_3$ at 101 MHz

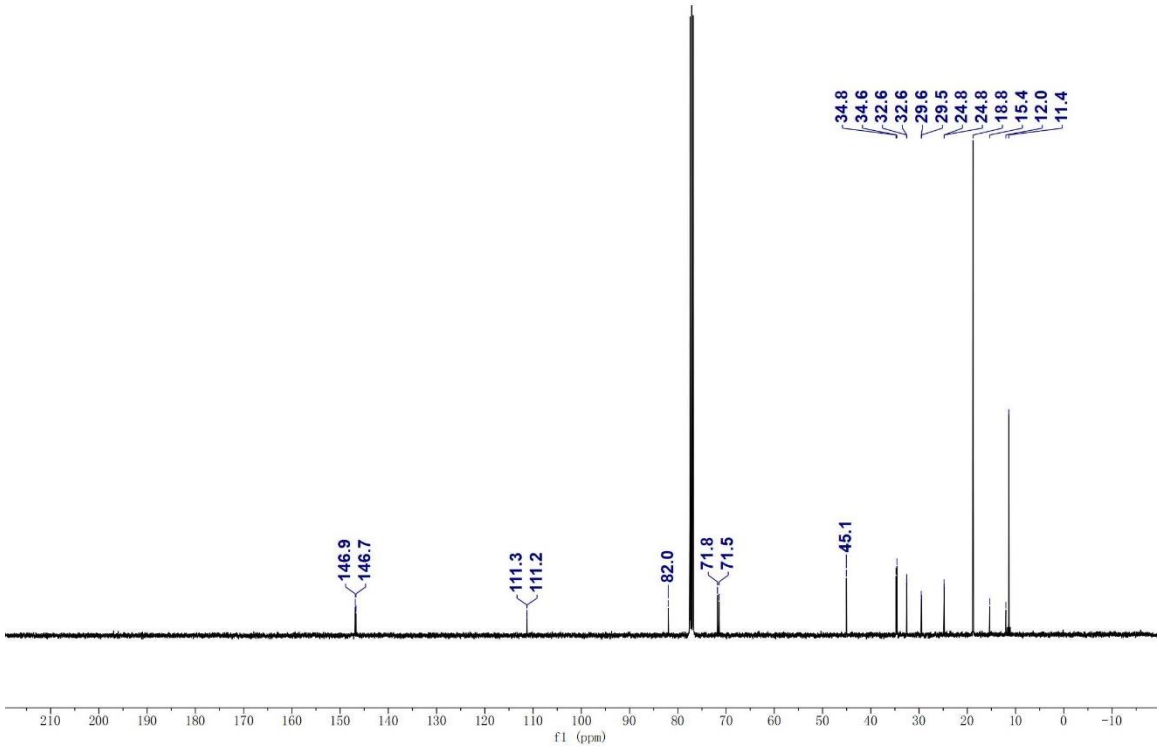


^{1}H NMR spectrum of **3t** was measured in $CDCl_3$ at 400 MH

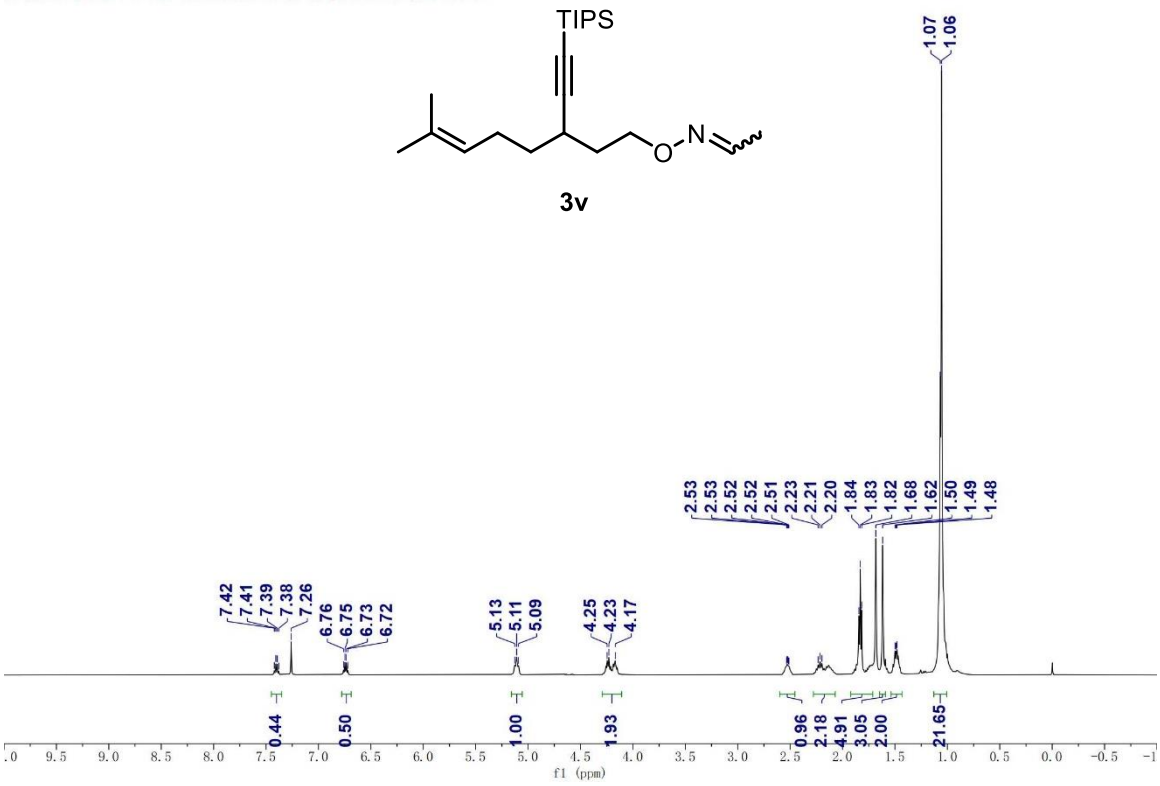


^{13}C NMR spectrum of **3t** was measured in $CDCl_3$ at 101 MHz

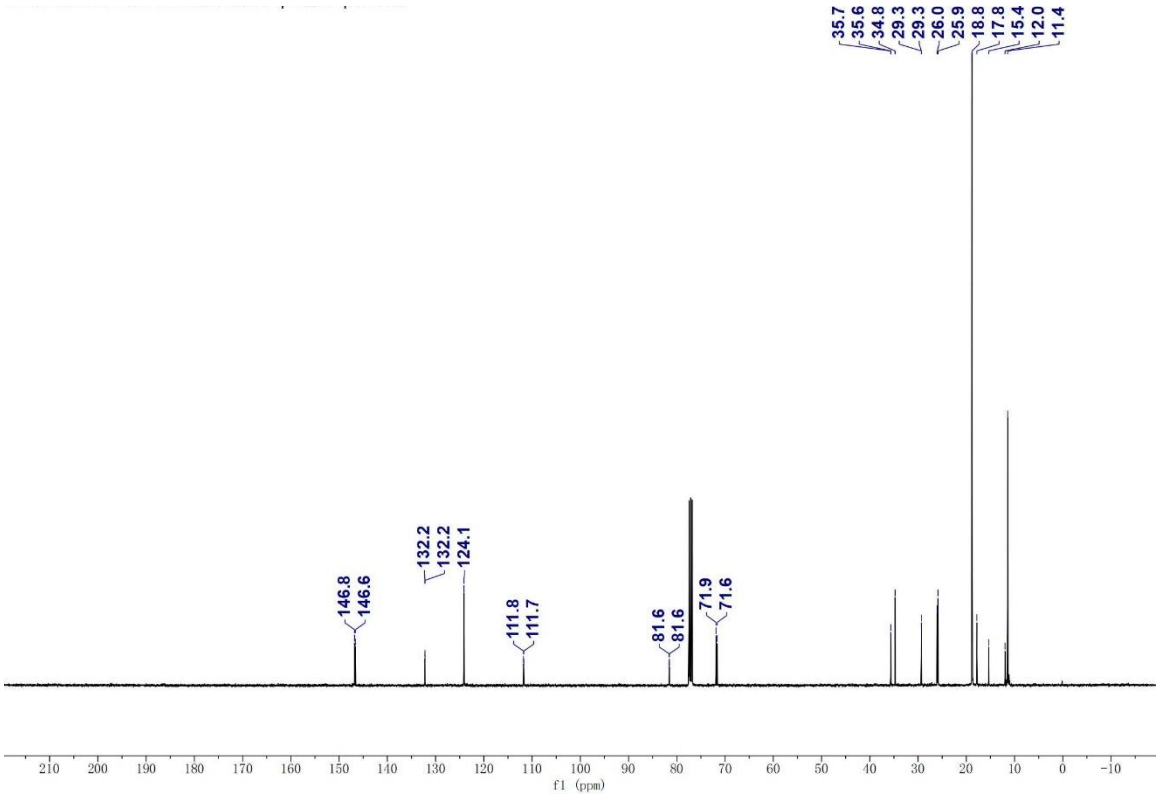
^{1}H NMR spectrum of **3u** was measured in $CDCl_3$ at 400 MH



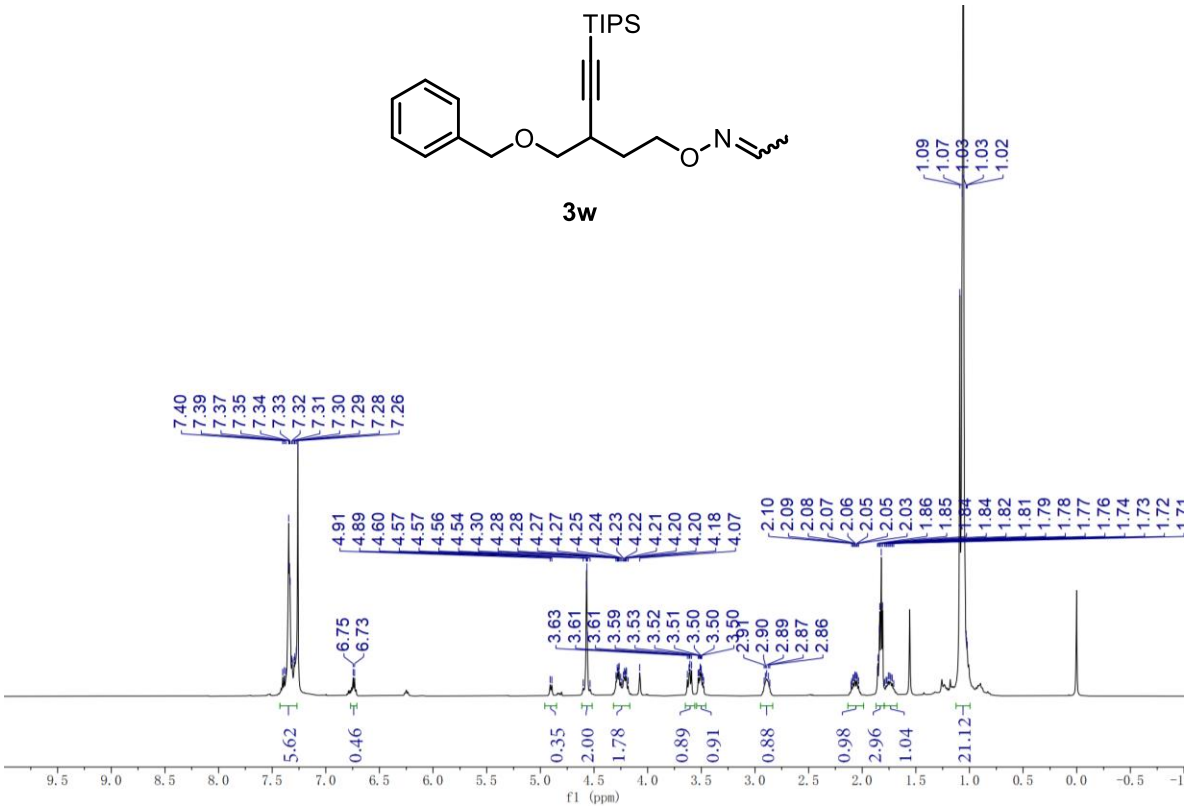
^{13}C NMR spectrum of **3u** was measured in $CDCl_3$ at 101 MHz



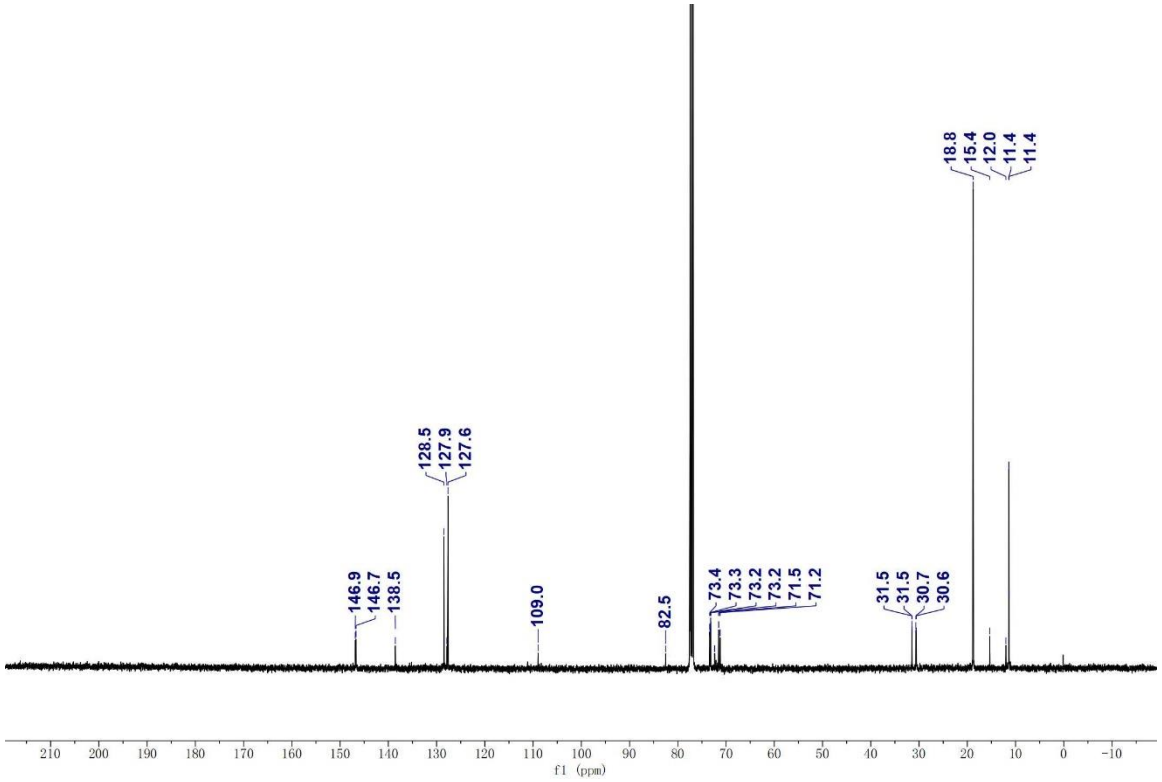
^{1}H NMR spectrum of **3v** was measured in $CDCl_3$ at 400 MH



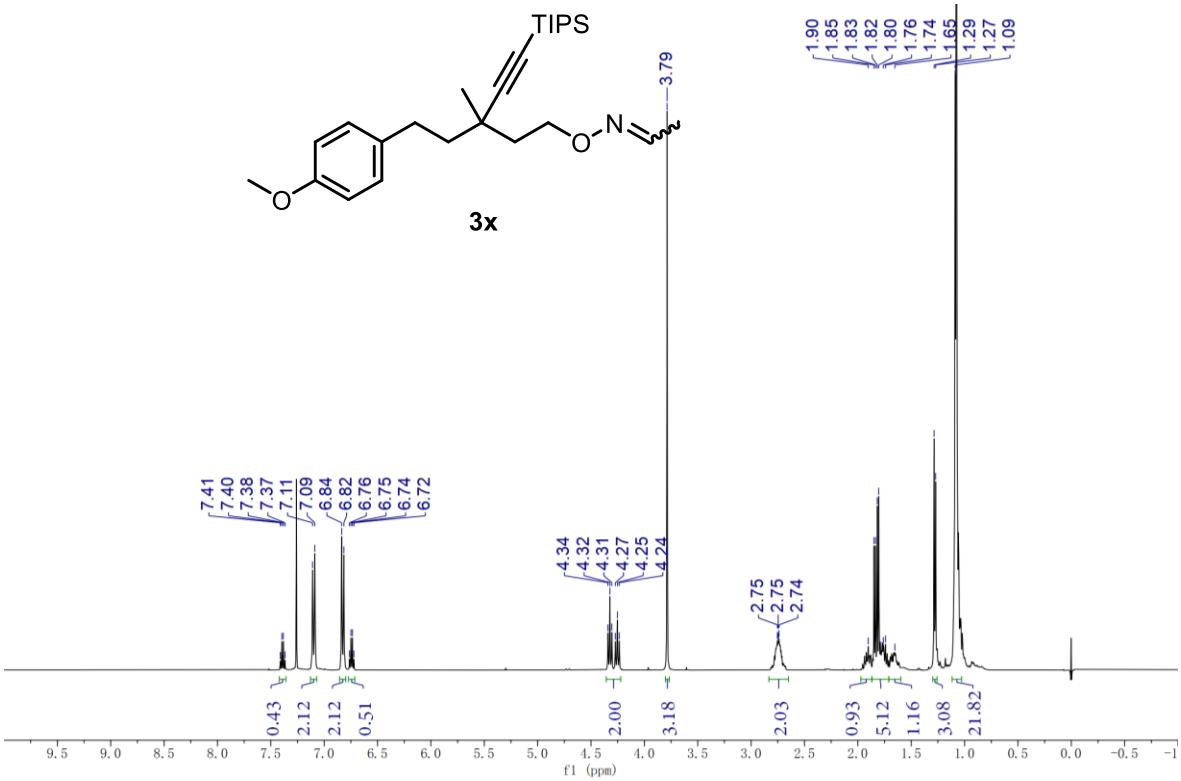
^{13}C NMR spectrum of **3v** was measured in $CDCl_3$ at 101 MHz



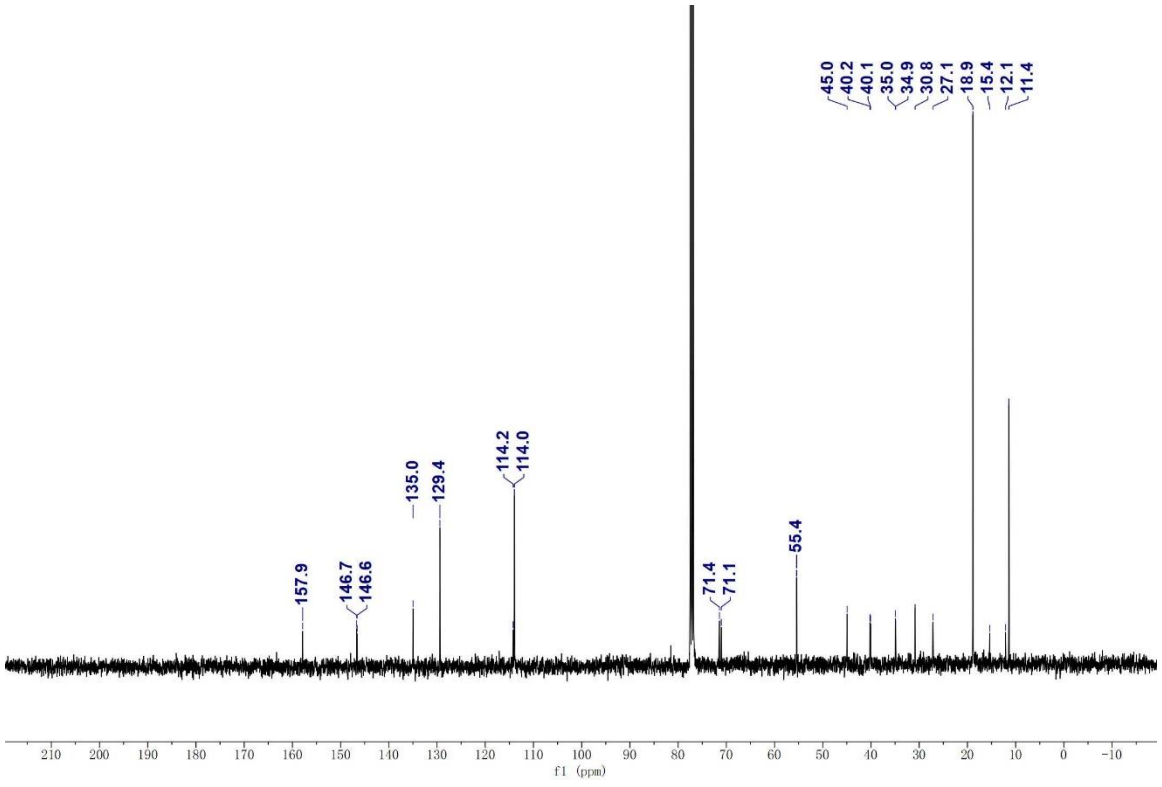
^{1}H NMR spectrum of **3w** was measured in $CDCl_3$ at 400 MH



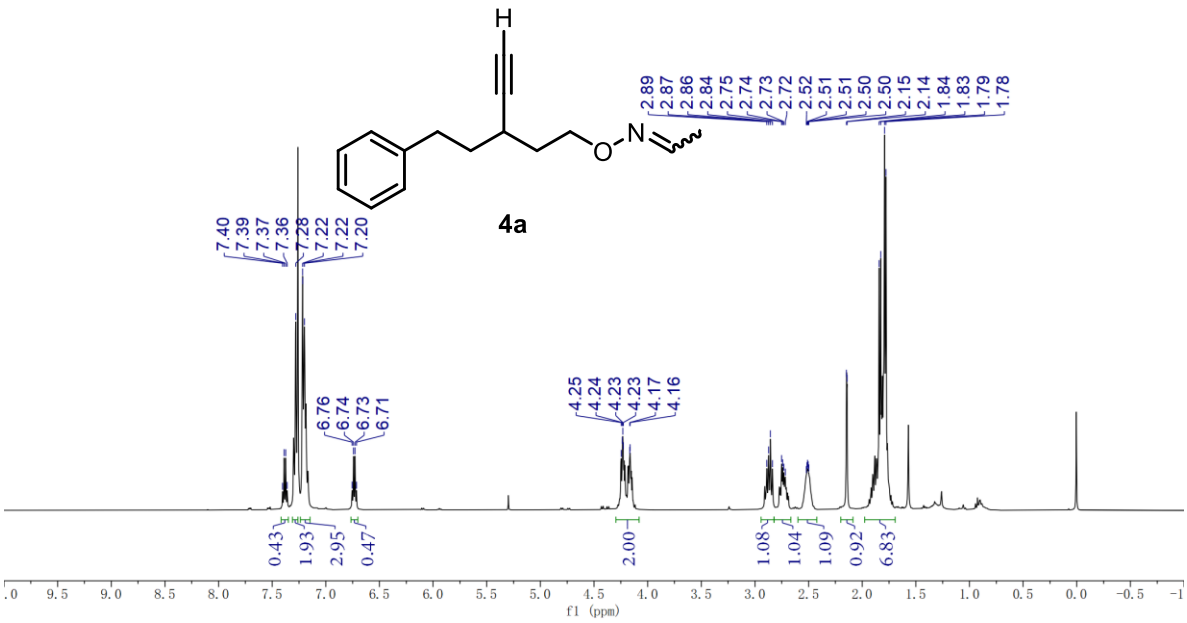
^{13}C NMR spectrum of **3w** was measured in $CDCl_3$ at 101 MHz



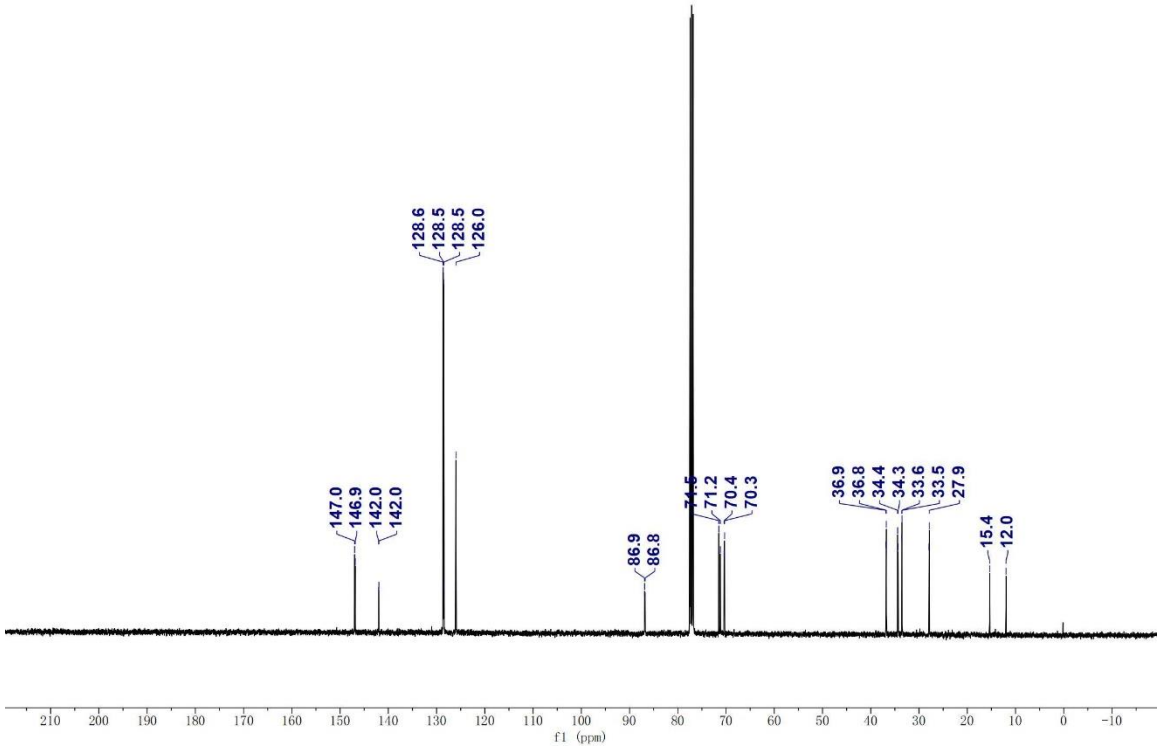
^{1}H NMR spectrum of **3x** was measured in $CDCl_3$ at 400 MH



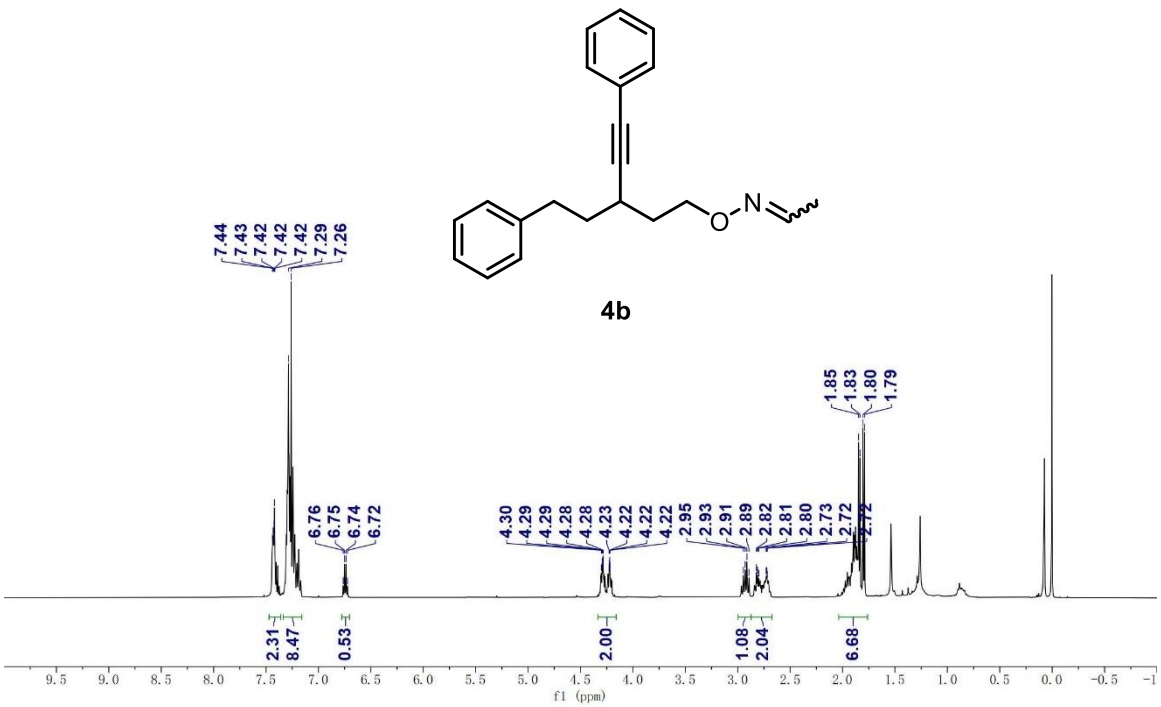
^{13}C NMR spectrum of **3x** was measured in $CDCl_3$ at 101 MHz



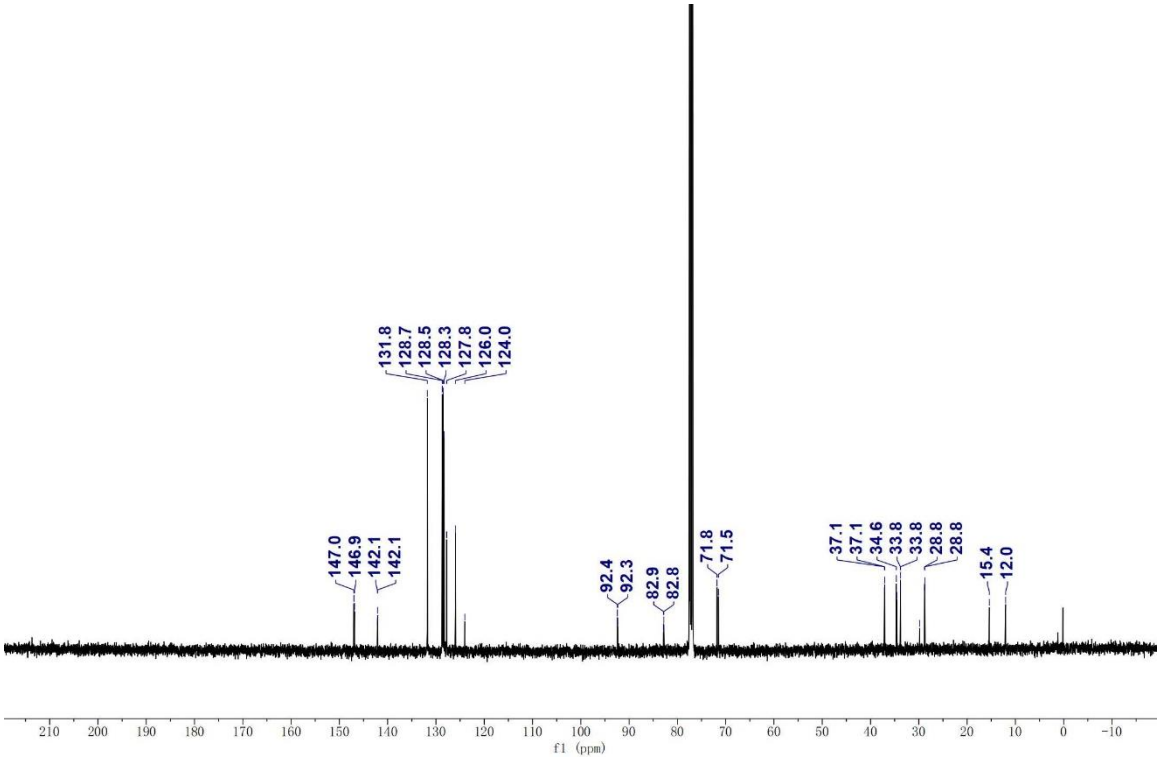
^{1}H NMR spectrum of **4a** was measured in $CDCl_3$ at 400 MH



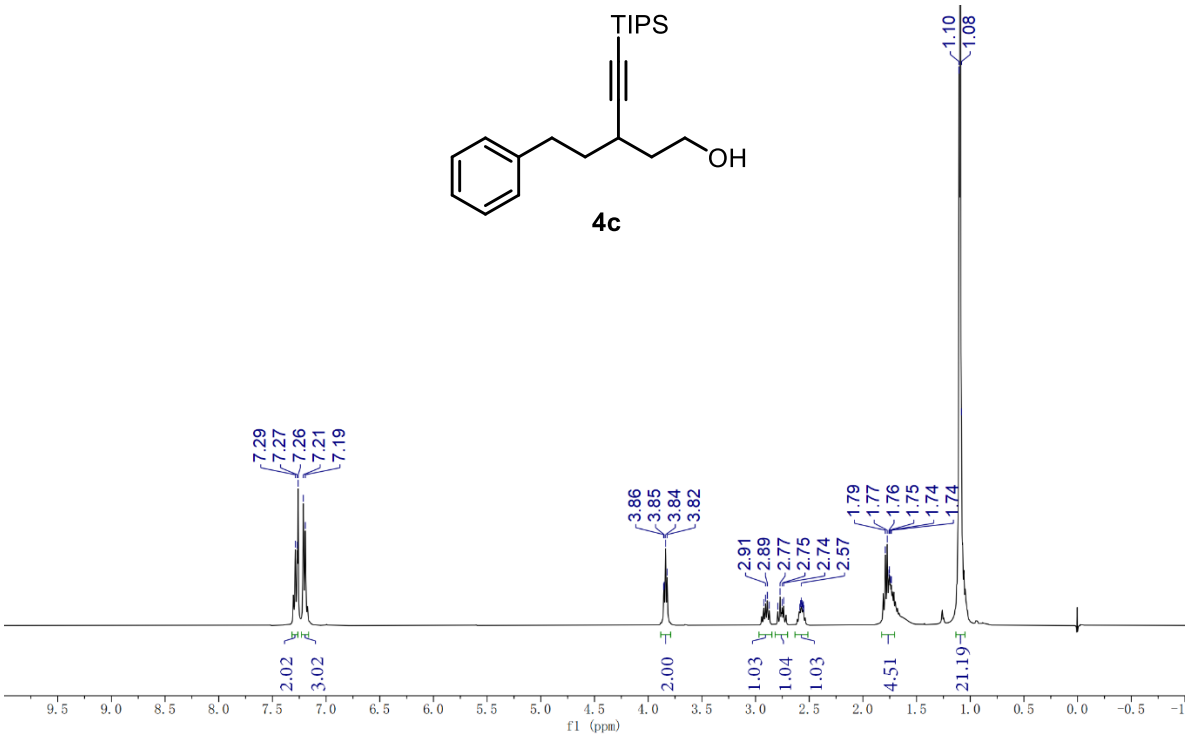
^{13}C NMR spectrum of **4a** was measured in $CDCl_3$ at 101 MHz



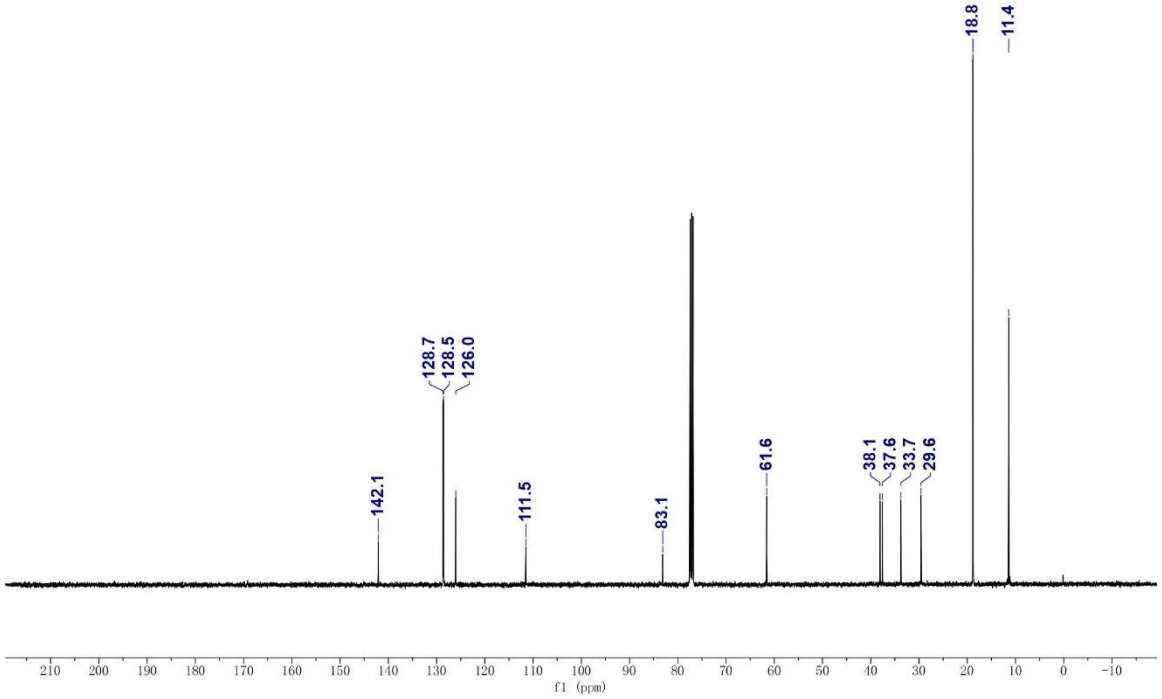
^{1}H NMR spectrum of **4b** was measured in $CDCl_3$ at 400 MH



^{13}C NMR spectrum of **4b** was measured in $CDCl_3$ at 101 MHz



^{1}H NMR spectrum of **4c** was measured in $CDCl_3$ at 400 MH



^{13}C NMR spectrum of **4c** was measured in $CDCl_3$ at 101 MHz