Supplementary Information

The synthesis of isoxazolines and dihydrooxazines by Pd-catalyzed oxyalkynylation alkenyl oximes with alkynyl bromides

Cangzhu Hu‡ Shiji Xu‡ Qiang Wang, Jing Sun, Ying Han, Chao-Guo Yan, Lei Wang*

School of Chemistry and Chemical Engineering, Yangzhou University, 225002, Yangzhou, P. R. China; E-mail: lei.wang@yzu.edu.cn

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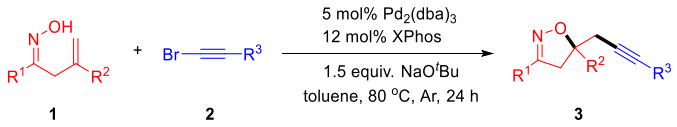
1. General information

Unless otherwise noted, all reactions were carried out under argon atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on an Agilent 400 or on a Bruker 500 MHz spectrometer in $CDCl_3$. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (*d* 7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant (s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Copies of NMR were processed with MestReNova Software. All melting points were uncorrected.

2. Synthesis and reaction

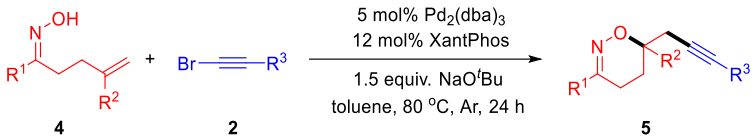
2.1 General procedure for the synthesis of isoxazolines



1 2 3

A sealed tube equipped with a magnetic stir bar was charged with *β*,*γ*-unsaturated ketoximes (0.30 mmol, 1.0 equiv.), bromoalkynes (0.60 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (13.7 mg, 0.015 mmol, 0.05 equiv.), XPhos (17.2 mg, 0.036 mmol, 0.12 equiv.), NaO^tBu (43.2 mg, 0.45 mmol, 1.5 equiv.) and toluene (3.0 mL). The tube was sealed with a Teflon lined cap. Degassed solvent and backfilled with argon for 3 times at -78 °C. The reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

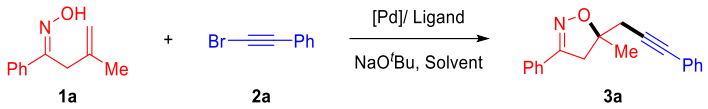
2.2 General procedure for the synthesis of dihydrooxazines



4 2 5

A sealed tube equipped with a magnetic stir bar was charged with *γ*,*δ*- unsaturated oximes (0.30 mmol, 1.0 equiv.), bromoalkynes (0.60 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (13.7 mg, 0.015 mmol, 0.05 equiv.), XantPhos (20.8 mg, 0.036 mmol, 0.12 equiv.), NaO^tBu (43.2 mg, 0.45 mmol, 1.5 equiv.) and toluene (3.0 mL). The tube was sealed with a Teflon lined cap. Degassed solvent and backfilled with argon for 3 times at -78 °C. The reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

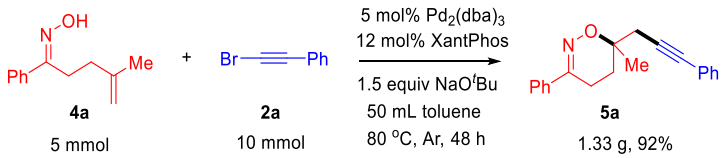
2.3 Table S1. optimization of reaction conditions[a]



Entry	Pd sources	ligand	Solvent	Yield[b] %
1	$Pd_2(dba)_3$	PPh_3	toluene	33
2	$Pd_2(dba)_3$	Dppb	toluene	37
3	$Pd_2(dba)_3$	DpePhos	toluene	81
4	$Pd_2(dba)_3$	RuPhos	toluene	73
5	$Pd_2(dba)_3$	XPhos	toluene	85(77)[c]
6	$Pd_2(dba)_3$	--	toluene	trace
7[d]	$Pd(OAc)_2$	XPhos	toluene	trace
8[d]	$Pd(TFA)_2$	XPhos	toluene	trace
9[d]	$Pd(acac)_2$	XPhos	toluene	9
10[d]	$PdCl_2$	XPhos	toluene	trace
11	$[Pd(allyl)Cl]_2$	XPhos	toluene	trace
12	$Pd_2(dba)_3$	XPhos	THF	16
13	$Pd_2(dba)_3$	XPhos	1,4-Dioxane	23
14	$Pd_2(dba)_3$	XPhos	MeCN	trace
15	$Pd_2(dba)_3$	XPhos	DCE	40

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), NaO^{t}Bu (1.5 equiv.), 5 mol% $Pd_2(dba)_3$ and 12 mol% Ligand in the Solvent (2.0 mL) at 80 °C under Ar for 12 h. [b] Isolated yield. [c] **1a** (0.3 mmol), **2a** (0.6 mmol), NaO^{t}Bu (1.5 equiv.), 5 mol% $Pd_2(dba)_3$ and 12 mol% XPhos in the toluene (3.0 mL) at 80 °C under Ar for 24 h. [d] 10 mol% Pd catalyst.

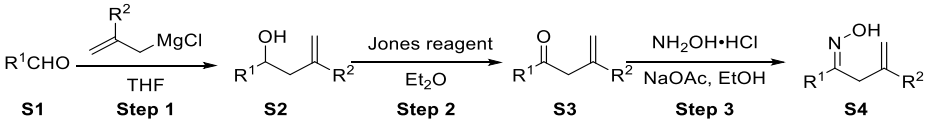
2.4 Gram-scale synthesis of 5a



An oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (228.9 mg, 0.25 mmol, 0.05 equiv.), Xantphos (347.2 mg, 0.60 mmol, 0.12 equiv.), NaO^{t}Bu (720.8 mg, 7.5 mmol, 1.5 equiv.), **4a** (946.3 mg, 5 mmol), **2a**

(1.8103 g, 10 mmol) and toluene (50 mL) were added sequentially. Degassed solvent and backfilled with argon for 3 times at -78 ºC. The reaction mixture was stirred at 80 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **5a** 1.33 g in 92% yield.

2.5.1 General procedure for preparation of substrates 1a-1n.

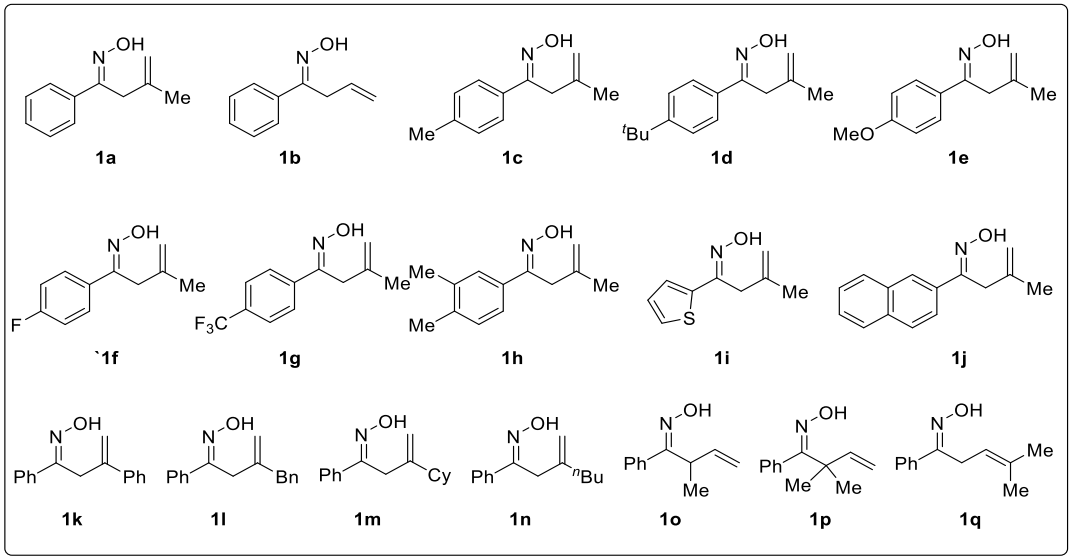


Step 1 A dried round bottle flask equipped with a magnetic stir bar was charged with a solution of **S1** (1.0 equiv.) in dry THF under argon. A solution of Allylmagnesium Chloride (1.3 equiv.) was added slowly at 0 ℃. The reaction mixture was stirred at room temperature overnight. After completion, the reaction was quenched with water, extracted with EtOAc for three times. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue **S2** was used directly in the next step without purification.

Step 2 The residue **S2** was dissolved in Et_2O, a solution of Jones reagent (2.0 equiv.) was added slowly at 0 ℃. The reaction mixture was stirred at room temperature for 1 h. After completion, it was diluted with water, extracted with EtOAc for three times, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product **S3**.

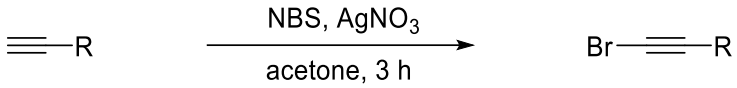
Step 3 A solution of product **S3** (1.0 equiv.) in ethanol and water was added hydroxylamine hydrochloride (5.0 equiv.) and sodium acetate (7.0 equiv.). The reaction mixture was stirred at room temperature overnight. After completion, it was diluted with water, extracted with EtOAc for three times, and then washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford target product **S4**.

2.5.2 Synthesis of β,γ-unsaturated ketoximes



Unless otherwise noted, all the spectra data of β,γ-unsaturated ketoximes **1** were prepared according to the following general procedure, and all the spectra data are in agreement with the reports. [1-4]

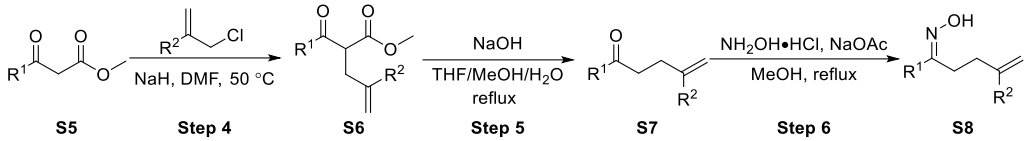
2.6 General procedure for preparation of substrates 2a-2s.



A solution of terminal alkyne (1.0 equiv.) in acetone was added $AgNO_3$ (0.1 equiv.) and *N*-bromosuccinimide (NBS, 1.1 equiv.). The reaction mixture was stirred at room temperature for 3 h. After completion, concentrated under reduced pressure and extracted with petroleum ether for three times, and then dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford target product bromoalkyne.

Unless otherwise noted, all the spectra data of allene substrates **2** were in agreement with the known literatures. [5-9]

2.7 General procedure for preparation of substrates 4a-4h，4p.



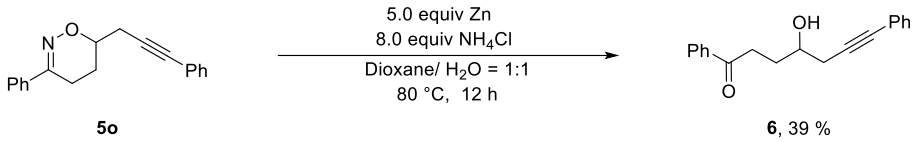
Step 4 A dried round bottle flask equipped with a magnetic stir bar was charged with NaH (1.0 equiv., 60% dispersion in mineral oil) in dry DMF under argon and was kept in ice bath. A solution of β-keto ester **S5** (1.0 equiv.) was added slowly and the reaction mixture was stirred at room temperature for 1 h. A solution of vinyl chlorides (1.1 equiv.) was added at 0 ℃ and the mixture was heated at 70 ℃ overnight. After completion, the reaction was quenched with water, extracted with EtOAc for three times and then washed with water and brine. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue **S6** was used directly in the next step without purification.

Step 5 The residue **S6** was dissolved in THF (2.0 mL/mmol), MeOH (1.0 mL/mmol) and water (1.0 mL/mmol),.and KOH (5.0 equiv.) was added slowly at 0 ℃. The reaction mixture was stirred at 75 ℃ for 6 h. After completion, the reaction was quenched with water and acidified with HCl (1.0 M, 8.0 mL/mmol), extracted with EtOAc for three times and then washed with water and brine. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford target product **S7**.

Step 6 A solution of product **S7** (1.0 equiv.) in methanol and water was added hydroxylamine hydrochloride (1.2 equiv.) and sodium acetate (1.2 equiv.). The reaction mixture was stirred at 75 ℃ for 5 h. After completion, it was diluted with water, extracted with EtOAc for three times, and then washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford target product **S8**.

Unless otherwise noted, all the spectra data of γ,δ- unsaturated oximes substrates **4** were in agreement with the known literatures. [10-11]

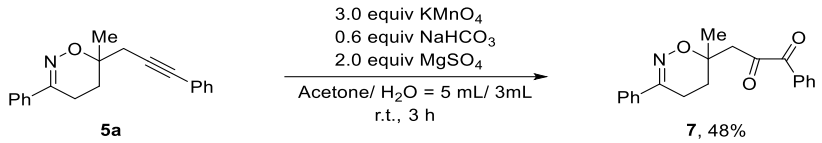
2.8 Experimental procedure for synthesis of 6.[12]



5o **6**, 39 %

A sealed tube equipped with a magnetic stir bar was charged with product **5o** (0.2 mmol, 1.0 equiv.), activated zinc powder (5.0 equiv.), NH_4Cl (8.0 equiv.) and Dioxane/ H_2O (4 mL, 1:1 v/v). The reaction mixture was stirred at 80 ℃ for 12 h. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **6** (21.7 mg, 39%) as a colorless oil.

2.9 Experimental procedure for synthesis of 7.[13]

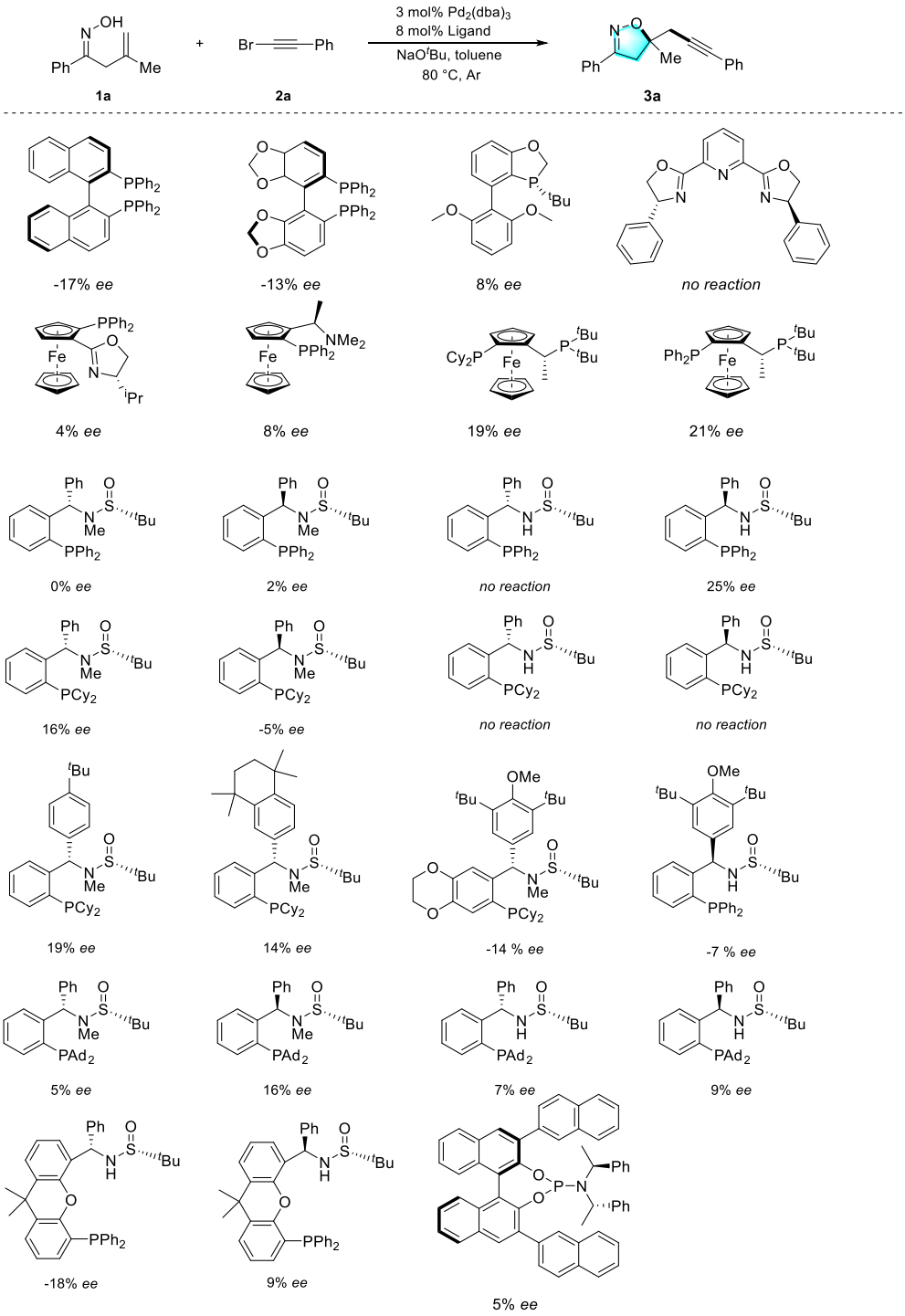


5a **7**, 48%

A sealed tube equipped with a magnetic stir bar was charged with product **5a** (0.2 mmol, 1.0 equiv.), $KMnO_4$ (3.0 equiv.), $NaHCO_3$ (0.6 equiv.), $MgSO_4$ (2.0 equiv.) and Acetone/ H_2O (8 mL, 5:3 v/v). The reaction mixture was stirred at room temperature for 3 h. After completion, it was extracted with EtOAc for three times, and then washed with water and brine, dried over anhydrous Na_2SO_4. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **7** (31.0 mg, 48%) as a yellow oil.

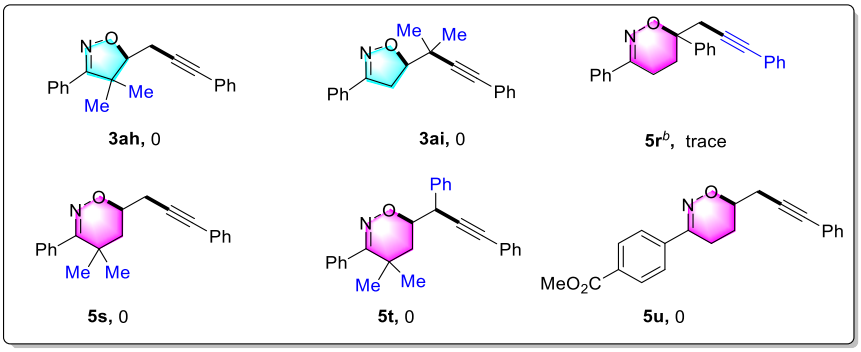
3. Preliminary result of chiral ligands screening

We have tested a series of commercially available chiral ligands in palladium-catalyzed oxyalkynylation alkenyl oximes with alkynyl bromide. Unfortunately, the chiral ligands were found to be inefficient in this reaction, which provided **3a** in poor yield with low enantioselectivity.



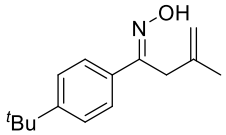
3. The examples of unsuccessful reactions

β,γ-unsaturated oximes containing methyl substitution on the α- or γ-carbon, γ,δ-unsaturated oximes containing substituents on the α- or δ- carbon and others unsaturated oximes substrates were tested, and the corresponding products could not be obtained.



4. Characterization Data

(*E*)-1-(4-(tert-butyl)phenyl)-3-methylbut-3-en-1-one oxime (1d)



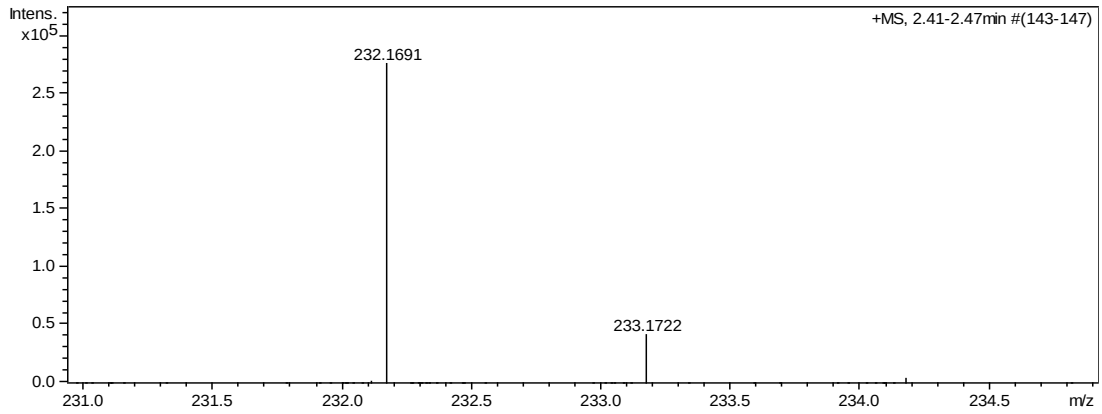
1d

The general synthetic route to give the product **1d** (2.3 g, 50% yield) as white solid by the use of 4-tert butylbenzaldehyde (20 mmol); m.p.: 101-103 °C.

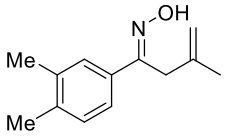
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.16 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 4.86 (s, 1H), 4.79 (s, 1H), 3.58 (s, 2H), 1.85 (s, 3H), 1.35 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6, 152.4, 140.4, 132.9, 126.0, 125.4, 112.1, 34.6, 34.3, 31.2, 23.1;

HRMS Calcd (ESI) m/z for $C_{15}H_{22}NO$ $[M + H]^+$: 232.1696, found: 232.1691.



(*E*)-1-(3,4-dimethylphenyl)-3-methylbut-3-en-1-one oxime (1h)



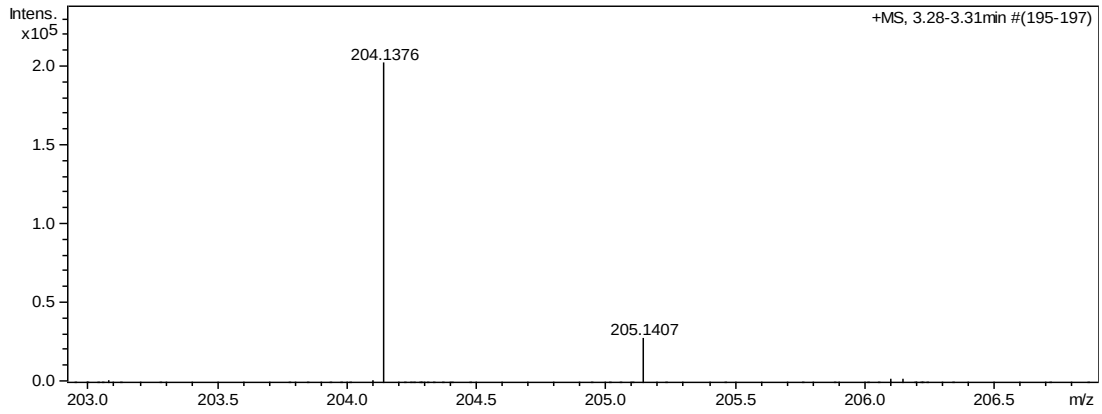
1h

The general synthetic route to give the product **1h** (2.1 g, 51% yield) as white solid by the use of 3,5-dimethylbenzaldehyde (20 mmol); m.p.: 64-66 ºC.

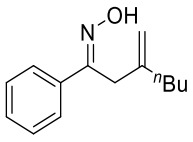
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.58 (s, 1H), 7.44 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.85 (s, 1H), 4.78 (s, 1H), 3.57 (s, 2H), 2.30 (d, *J* = 5.6 Hz, 6H), 1.84 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.9, 140.4, 137.9, 136.6, 133.3, 129.7, 127.4, 123.8, 112.0, 34.3, 23.0, 19.9, 19.6;

HRMS Calcd (ESI) m/z for $C_{13}H_{18}NO$ $[M + H]^+$: 204.1383, found: 204.1376.



(*E*)-3-methylene-1-phenylheptan-1-one oxime (1n)



1n

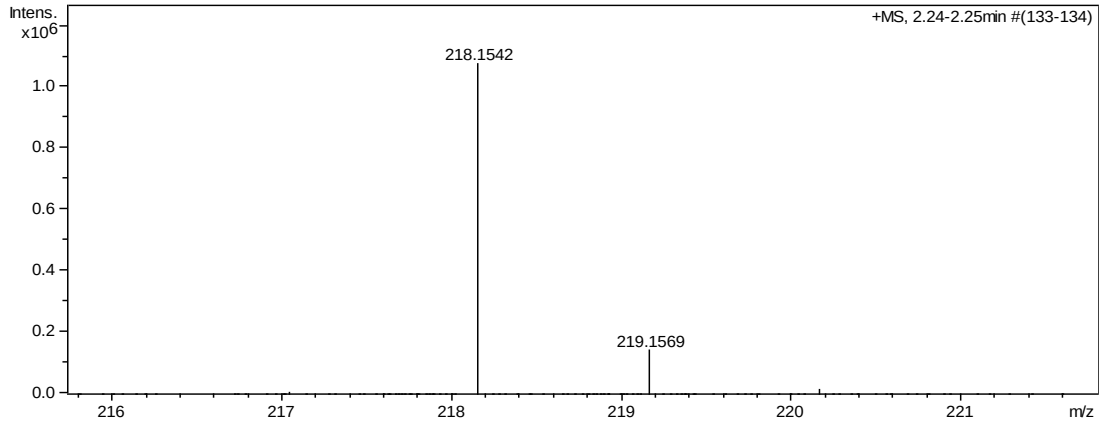
The general synthetic route to give the product **1n** (0.7 g, 40% yield) as a colorless oil by the corresponding ketone (8 mmol).

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) gave the product **1n** (0.7 g, 58% yield) as a colorless oil.

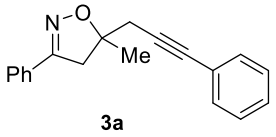
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.36 (s, 1H), 7.64-7.62 (m, 2H), 7.38-7.37 (m, 3H), 4.83 (s, 1H), 4.75 (s, 1H), 3.55 (s, 2H), 2.13-2.10 (m, 2H), 1.52-1.45 (m, 2H), 1.39-1.31 (m, 2H), 0.95-0.90 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.2, 144.1, 135.8, 129.2, 128.4, 126.3, 110.8, 36.5, 33.0, 29.8, 22.4, 14.0;

HRMS Calcd (ESI) m/z for $C_{14}H_{20}NO$ $[M + H]^+$: 218.1539, found: 218.1542.



5-Methyl-3-phenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3a)



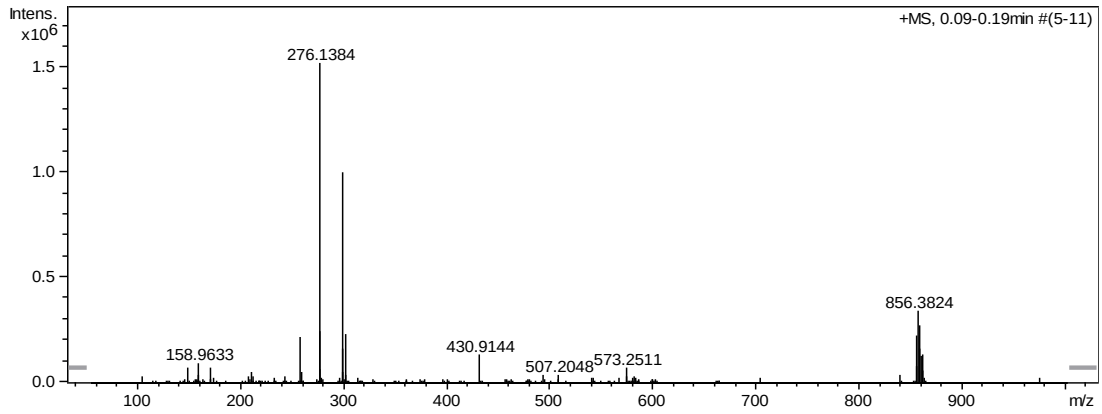
3a

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3a** (63.3 mg, 77% yield) as a brown oil.

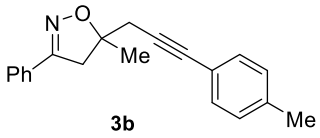
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.59 (m, 2H), 7.33-7.28 (m, 5H), 7.20-7.17 (m, 3H), 3.44 (d, *J* = 16.4 Hz, 1H), 3.07 (d, *J* = 16.4 Hz, 1H), 2.77 (d, *J* = 16.8 Hz, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 1.59 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 131.6, 129.9 (2C), 128.6, 128.2, 128.0, 126.6, 123.2, 86.3, 85.4, 82.6, 45.0, 31.2, 25.1;

HRMS Calcd (ESI) m/z for $C_{19}H_{18}NO$ $[M + H]^+$: 276.1383, found: 276.1384.



5-Methyl-3-phenyl-5-(3-(p-tolyl)prop-2-yn-1-yl)-4,5-dihydroisoxazole (3b)



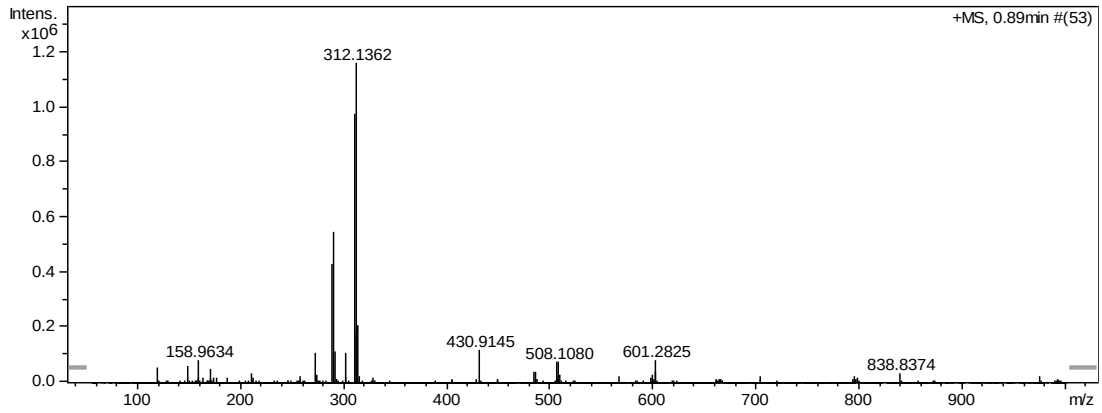
3b

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3b** (61.4 mg, 71% yield) as a brown oil.

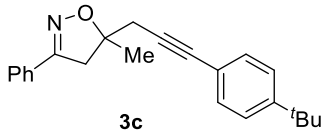
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.58 (m, 2H), 7.31-7.30 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.43 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 16.8 Hz, 1H), 2.75 (d, *J* = 16.8 Hz, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.23 (s, 3H) , 1.57 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 138.0, 131.5, 129.9 (2C), 128.9, 128.6, 126.5, 120.1, 86.4, 84.6, 82.6, 44.9, 31.2, 25.1, 21.4;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO$ $[M + Na]^+$: 312.1359, found: 312.1362.



5-(3-(4-(*tert*-Butyl)phenyl)prop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3c)



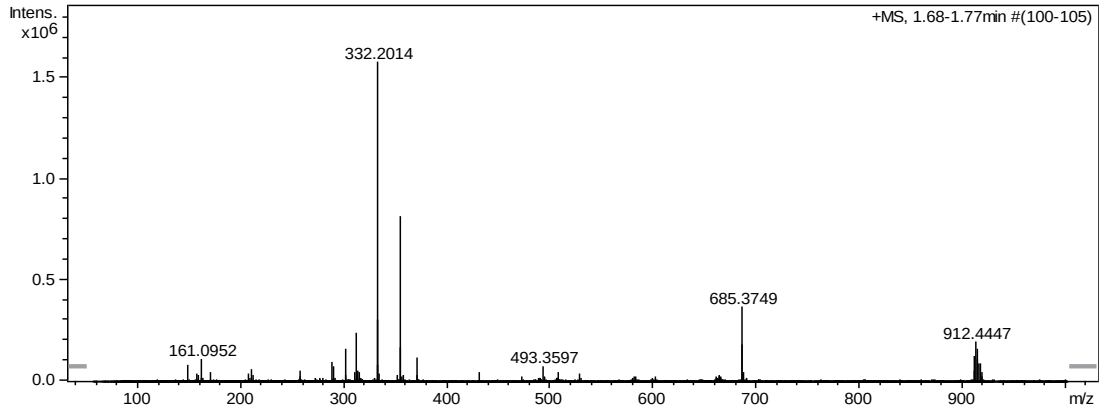
3c

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3c** (79.4 mg, 80% yield) as a brown oil.

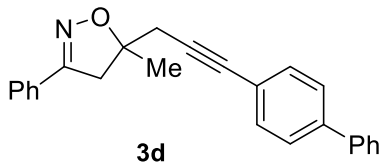
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71-7.69 (m, 2H), 7.42-7.41 (m, 3H), 7.36-7.30 (m, 4H), 3.55 (d, *J* = 16.8 Hz, 1H), 3.15 (d, *J* = 16.8 Hz, 1H), 2.87 (d, *J* = 16.8 Hz, 1H), 2.80 (d, *J* = 16.8 Hz, 1H), 1.68 (s, 3H), 1.32 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 151.1, 131.3, 129.9, 128.6 (2C), 126.5, 125.1, 120.1, 86.4, 84.6, 82.6, 44.9, 34.6, 31.2, 31.1, 25.1;

HRMS Calcd (ESI) m/z for $C_{23}H_{26}NO$ $[M + H]^+$: 332.2009, found: 332.2014.



5-(3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3d)



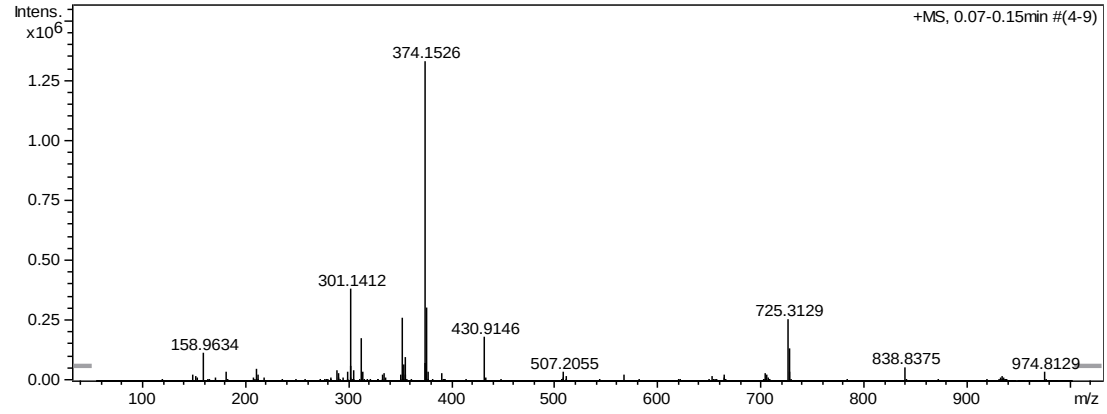
3d

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3d** (67.4 mg, 64% yield) as a yellow solid; m.p.: 96-98 °C.

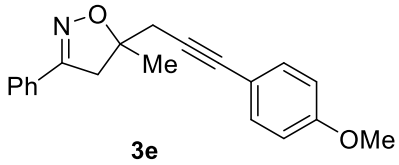
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72-7.70 (m, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.47-7.34 (m, 8H), 3.56 (d, *J* = 16.4 Hz, 1H), 3.18 (d, *J* = 16.8 Hz, 1H), 2.90 (d, *J* = 16.8 Hz, 1H), 2.83 (d, *J* = 16.8 Hz, 1H), 1.70 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 140.7, 140.3, 132.0, 130.0, 129.9, 128.8, 128.7, 127.5, 126.9 (2C), 126.6, 122.1, 86.3, 86.1, 82.5, 45.0, 31.3, 25.2;

HRMS Calcd (ESI) m/z for $C_{25}H_{21}NNaO$ $[M + Na]^+$: 374.1515, found: 374.1526.



5-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3e)



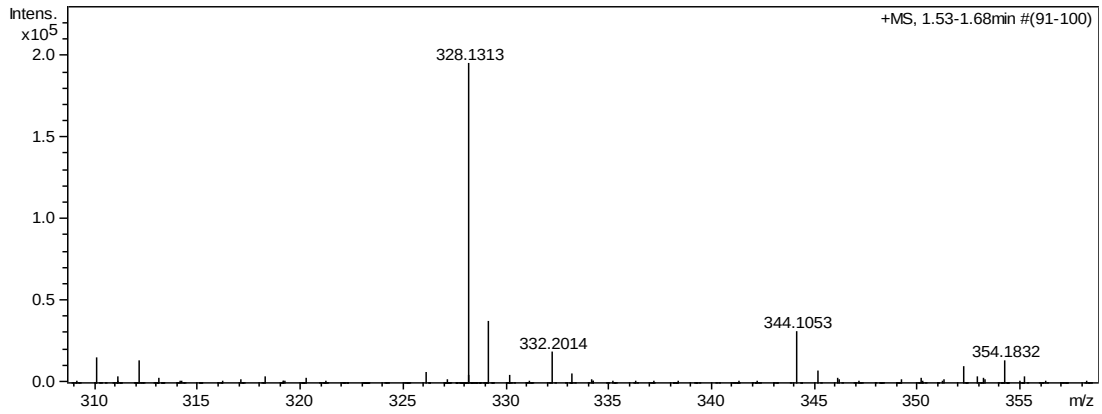
3e

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3e** (53.6 mg, 58% yield) as a yellow oil.

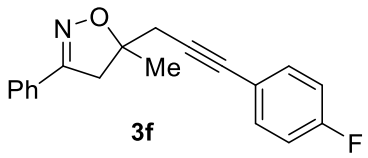
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.67 (m, 2H), 7.41-7.39 (m, 3H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.52 (d, *J* = 16.8 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.78 (d, *J* = 16.8 Hz, 1H), 1.66 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.3, 156.5, 133.0, 129.9 (2C), 128.6, 126.5, 115.3, 113.8, 86.4, 83.8, 82.3, 55.2, 44.9, 31.2, 25.1;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO_2$ $[M + Na]^+$: 328.1308, found: 328.1313.



5-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3f)



3f

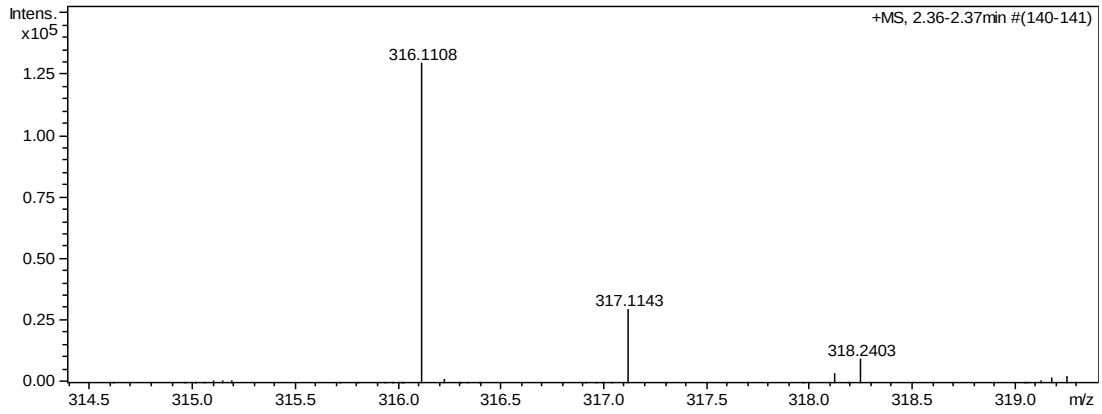
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3f** (47.0 mg, 53% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69-7.67 (m, 2H), 7.41-7.39 (m, 3H), 7.35-7.31 (m, 2H), 6.98-6.93 (m, 2H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.77 (d, *J* = 16.8 Hz, 1H), 1.66 (s, 3H);

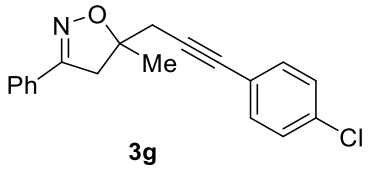
^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2 (d, *J* = 247.6 Hz), 156.5, 133.5 (d, *J* = 8.0 Hz), 130.0, 129.8, 128.7, 126.5, 119.3 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 22.0 Hz), 86.2, 85.0, 81.5, 45.0, 31.2, 25.2;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -111.4;

HRMS Calcd (ESI) m/z for $C_{19}H_{16}FNNaO$ $[M + Na]^+$: 316.1108, found: 316.1108.



5-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole(3g)



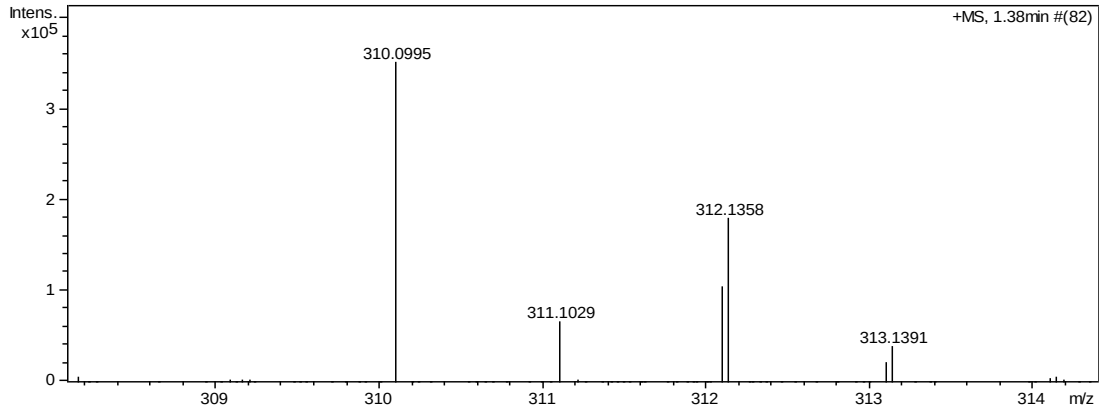
3g

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3g** (51.2 mg, 55% yield) as a brown solid; m.p.: 83-86 ºC.

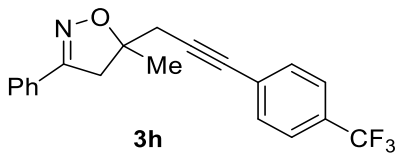
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.58 (m, 2H), 7.32-7.31 (m, 3H), 7.20-7.13 (m, 4H), 3.40 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.76 (d, *J* = 16.8 Hz, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 1.57 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 133.9, 132.8, 130.0, 129.8, 128.6, 128.5, 126.5, 121.7, 86.4, 86.1, 81.5, 45.0, 31.3, 25.2;

HRMS Calcd (ESI) m/z for $C_{19}H_{17}ClNO$ $[M + H]^+$: 310.0993, found: 310.0995.



5-Methyl-3-phenyl-5-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)-4,5-dihydroisoxazole (3h)



3h

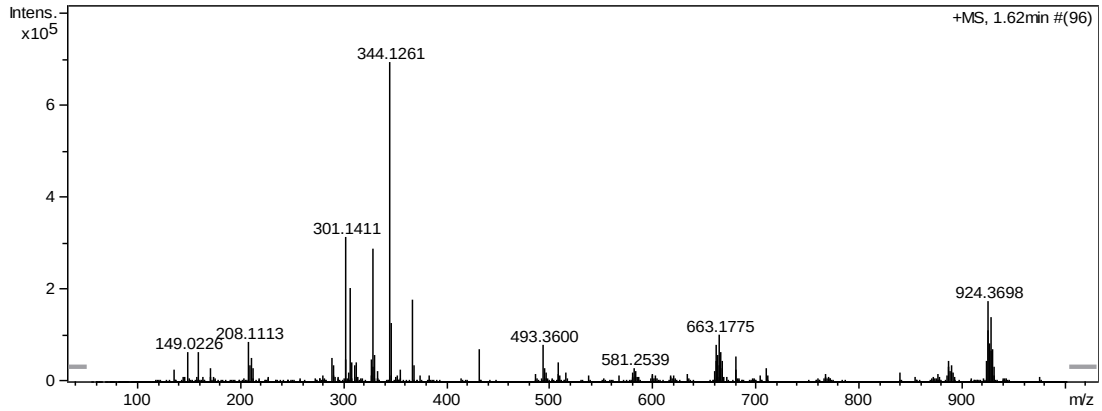
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3h** (74.4 mg, 72% yield) as a brown solid; m.p.: 57-59 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.68 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.45-7.40 (m, 5H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.18 (d, *J* = 16.8 Hz, 1H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.81 (d, *J* = 17.2 Hz, 1H), 1.68 (s, 3H);

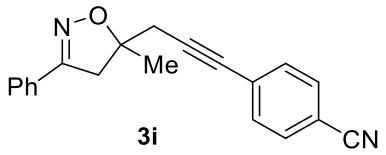
^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 131.9, 130.2, 129.8, 129.8 (q, *J* = 32.4 Hz), 128.7, 127.0, 126.5, 125.1 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 270.8 Hz), 88.1, 86.1, 81.4, 45.0, 31.3, 25.2;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.8;

HRMS Calcd (ESI) m/z for $C_{20}H_{17}F_3NO$ $[M + H]^+$: 344.1257, found: 344.1261.



4-(3-(5-Methyl-3-phenyl-4,5-dihydroisoxazol-5-yl)prop-1-yn-1-yl)benzonitrile (3i)



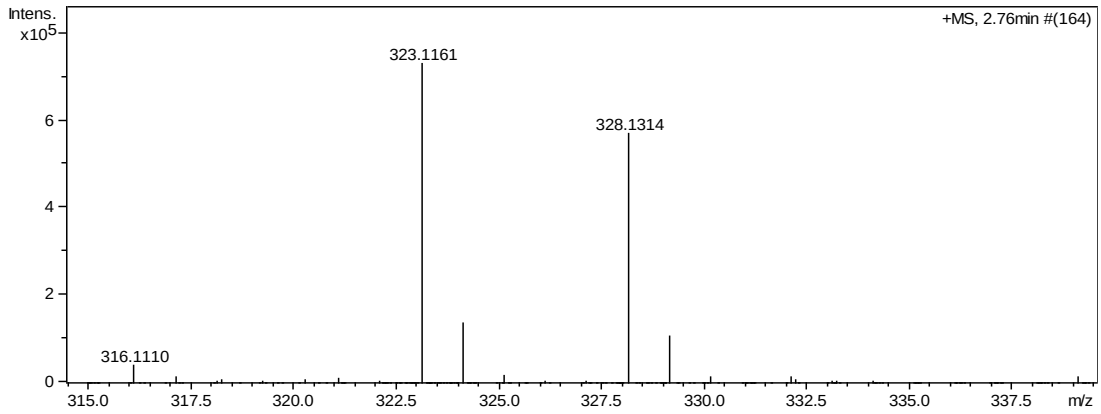
3i

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3i** (61.3 mg, 68% yield) as a yellow solid; m.p.: 82-85 ºC.

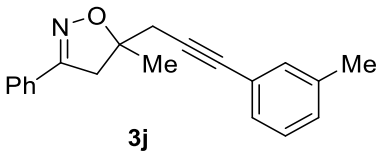
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.66 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41-7.39 (m, 5H), 3.47 (d, *J* = 16.8 Hz, 1H), 3.18 (d, *J* = 16.8 Hz, 1H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.81 (d, *J* = 17.2 Hz, 1H), 1.66 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 132.1, 131.8, 130.0, 129.6, 128.7, 128.1, 126.5, 118.4, 111.2, 90.3, 85.9, 81.2, 45.0, 31.4, 25.2;

HRMS Calcd (ESI) m/z for $C_{20}H_{16}N_2NaO$ $[M + Na]^+$: 323.1155, found: 323.1161.



5-Methyl-3-phenyl-5-(3-(*m*-tolyl)prop-2-yn-1-yl)-4,5-dihydroisoxazole (3j)



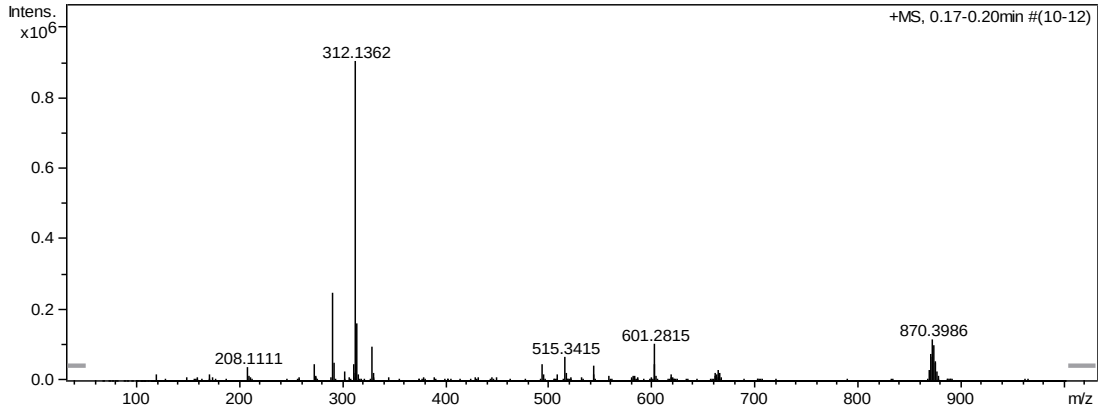
3j

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3j** (62.5 mg, 72% yield) as a brown oil.

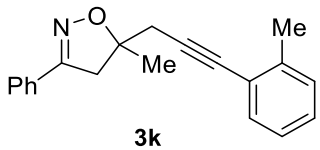
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71-7.69 (m, 2H), 7.42-7.40 (m, 3H), 7.18-7.15 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 1H), 3.53 (d, *J* = 16.8 Hz, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.79 (d, *J* = 16.8 Hz, 1H), 2.30 (s, 3H) , 1.68 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 137.8, 132.2, 129.9 (2C), 128.8, 128.6 (2C), 128.0, 126.5, 122.9, 86.3, 84.9, 82.7, 44.9, 31.2, 25.1, 21.1;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO$ $[M + Na]^+$: 312.1359, found: 312.1362.



5-Methyl-3-phenyl-5-(3-(*o*-tolyl)prop-2-yn-1-yl)-4,5-dihydroisoxazole (3k)



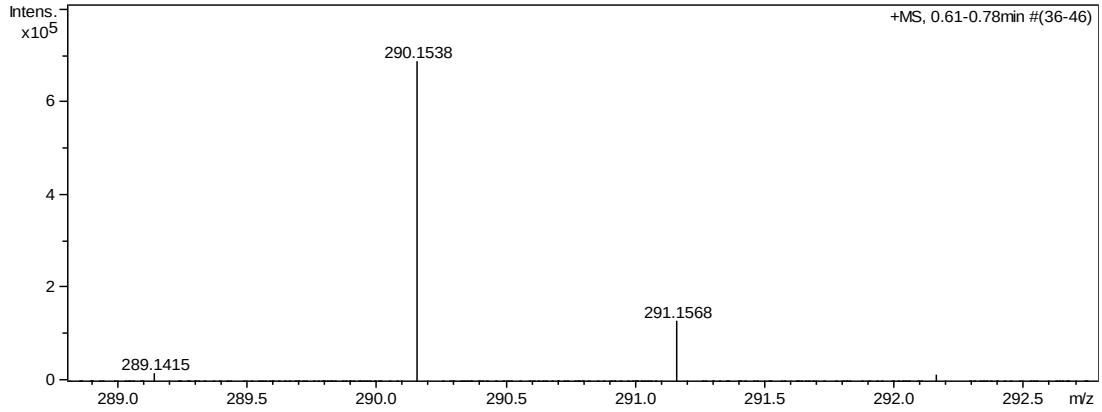
3k

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3k** (63.2 mg, 73% yield) as a yellow oil.

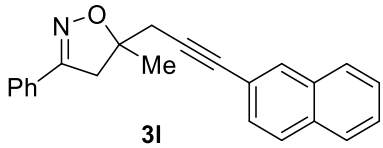
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.68 (m, 2H), 7.42-7.40 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.22-7.17 (m, 2H), 7.13-7.09 (m, 1H), 3.57 (d, *J* = 16.4 Hz, 1H), 3.17 (d, *J* = 16.8 Hz, 1H), 2.92 (d, *J* = 16.8 Hz, 1H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.41 (s, 3H), 1.69 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 140.0, 131.9, 129.9, 129.8, 129.3, 128.6, 127.9, 126.5, 125.4, 122.9, 89.2, 86.3, 81.4, 44.9, 31.3, 25.2, 20.7;

HRMS Calcd (ESI) m/z for $C_{20}H_{20}NO$ $[M + H]^+$: 290.1539, found: 290.1538.



5-Methyl-5-(3-(naphthalen-2-yl)prop-2-yn-1-yl)-3-phenyl-4,5-dihydroisoxazole (3l)



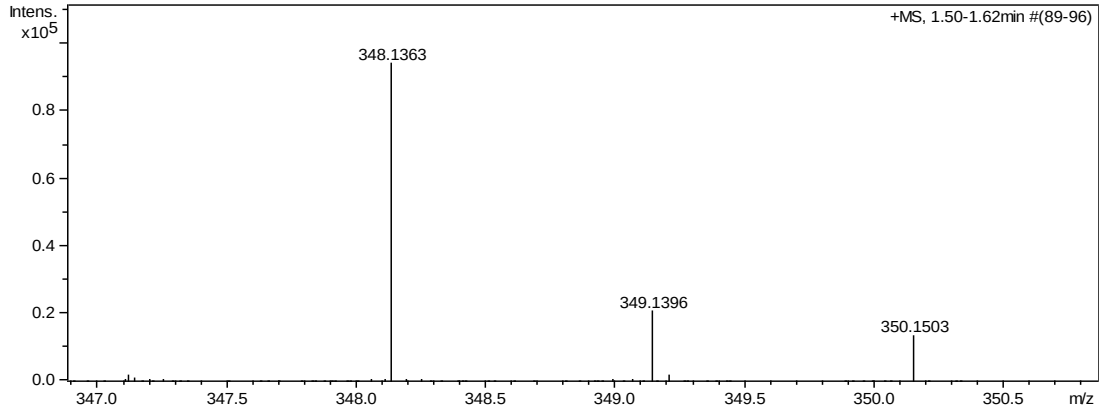
3l

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3l** (51.9 mg, 53% yield) as a brown solid; m.p.: 105-107 °C.

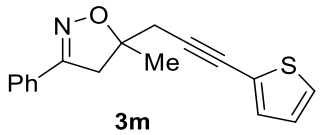
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (s, 1H), 7.79-7.73 (m, 5H), 7.48-7.43 (m, 6H), 3.57 (d, *J* = 16.8 Hz, 1H), 3.19 (d, *J* = 16.8 Hz, 1H), 2.95-2.84 (m, 2H), 1.72 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 132.8, 132.5, 131.3, 129.9, 129.8, 128.6, 128.4, 127.8, 127.6, 127.5, 126.5, 126.4 (2C), 120.4, 86.3, 85.7, 82.9, 44.9, 31.3, 25.2;

HRMS Calcd (ESI) m/z for $C_{23}H_{19}NNaO$ $[M + Na]^+$: 348.1359, found: 348.1363.



5-Methyl-3-phenyl-5-(3-(thiophen-2-yl)prop-2-yn-1-yl)-4,5-dihydroisoxazole (3m)



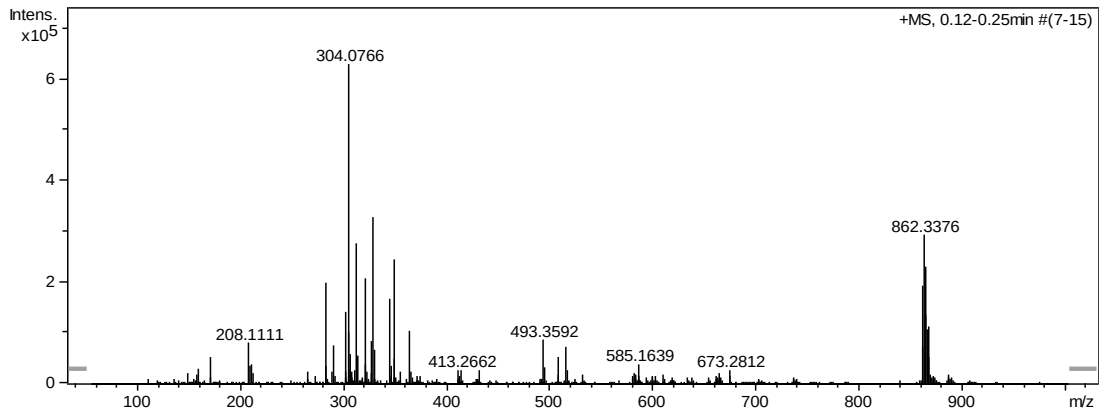
3m

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3m** (56.5 mg, 67% yield) as a brown oil.

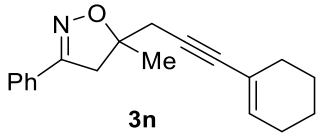
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.68 (m, 2H), 7.42-7.40 (m, 3H), 7.19 (d, J = 5.2 Hz, 1H), 7.13 (d, J = 3.6 Hz, 1H), 6.94-6.92 (m, 1H), 3.49 (d, J = 16.8 Hz, 1H), 3.15 (d, J = 16.4 Hz, 1H), 2.88 (d, J = 16.8 Hz, 1H), 2.82 (d, J = 16.8 Hz, 1H), 1.66 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 131.6, 129.9, 129.7, 128.6, 126.7, 126.5 (2C), 123.1, 89.4, 86.1, 75.7, 44.9, 31.4, 25.1;

HRMS Calcd (ESI) m/z for $C_{17}H_{15}NNaOS$ $[M + Na]^+$: 304.0767, found: 304.0766.



5-(3-(Cyclohex-1-en-1-yl)prop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3n)



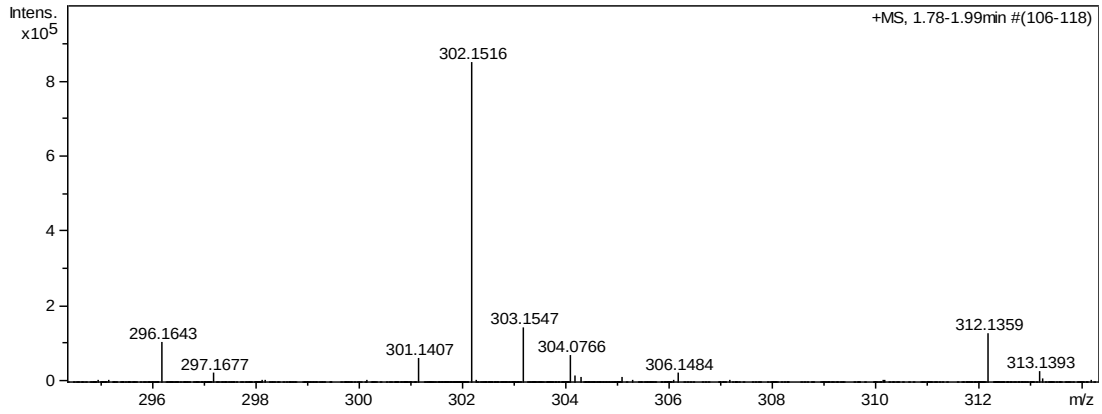
3n

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3n** (63.7 mg, 76% yield) as a brown oil.

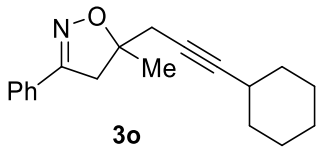
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.65 (m, 2H), 7.41-7.38 (m, 3H), 6.01 (s, 1H), 3.45 (d, *J* = 16.8 Hz, 1H), 3.09 (d, *J* = 16.4 Hz, 1H), 2.73 (d, *J* = 16.8 Hz, 1H), 2.66 (d, *J* = 16.8 Hz, 1H), 2.06-2.04 (m, 4H), 1.61-1.55 (m, 7H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 134.2, 129.9, 129.8, 128.6, 126.5, 120.5, 86.4, 84.4, 82.3, 44.8, 31.1, 29.3, 25.5, 25.0, 22.2, 21.4;

HRMS Calcd (ESI) m/z for $C_{19}H_{21}NNaO$ $[M + Na]^+$: 302.1515, found: 302.1516.



5-(3-Cyclohexylprop-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3o)



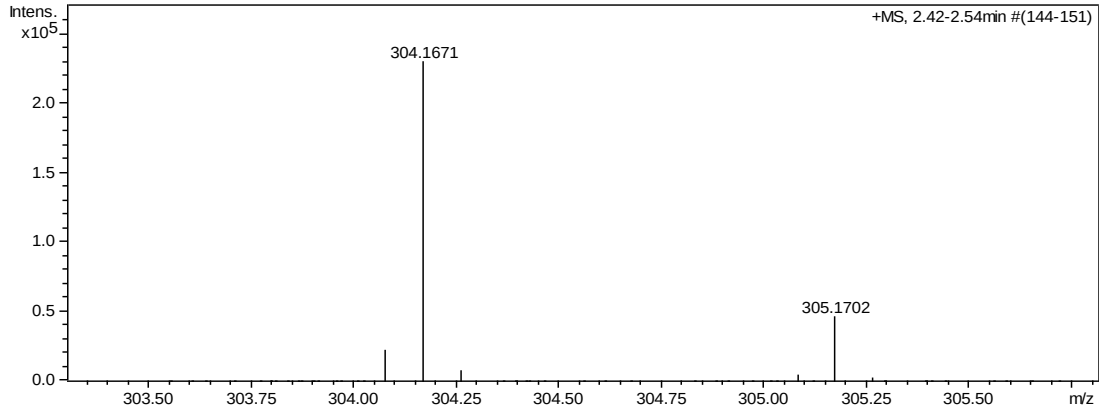
3o

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3o** (53.3 mg, 63% yield) as a yellow solid; m.p.: 35-37 ºC..

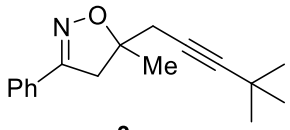
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.65 (m, 2H), 7.39-7.38 (m, 3H), 3.46 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.60 (d, *J* = 16.4 Hz, 1H), 2.53 (d, *J* = 16.8 Hz, 1H), 2.33 (s, 1H), 1.72-1.65 (m, 4H), 1.58 (s, 3H), 1.46-1.35 (m, 3H), 1.26 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 130.0, 129.8, 128.6, 126.5, 86.9, 86.5, 75.5, 44.7, 32.8, 30.7, 29.0, 25.8, 25.1, 24.7;

HRMS Calcd (ESI) m/z for $C_{19}H_{23}NNaO$ $[M + Na]^+$: 304.1672, found: 304.1671.



5-(4,4-Dimethylpent-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3p)



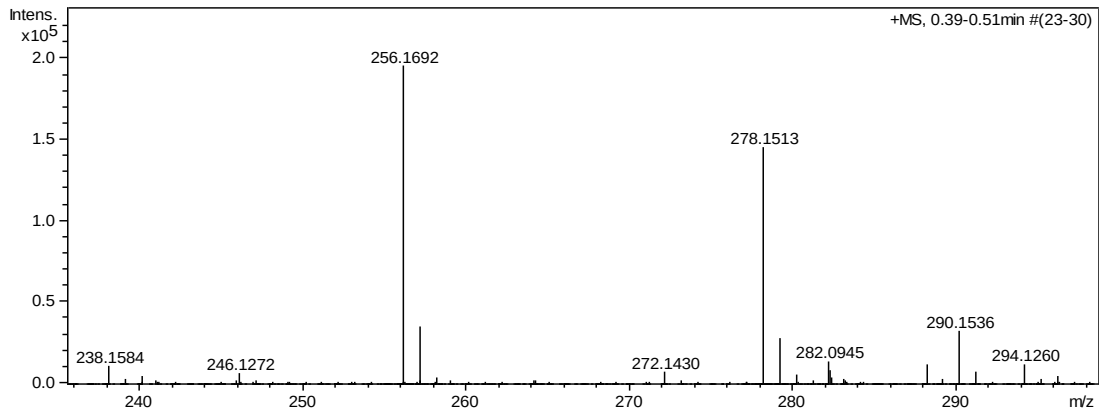
3p

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3p** (55.9 mg, 73% yield) as a yellow solid; m.p.: 54-56 °C.

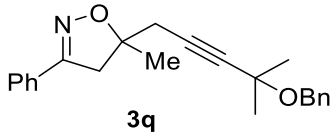
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.65 (m, 2H), 7.41-7.39 (m, 3H), 3.44 (d, J = 16.8 Hz, 1H), 3.06 (d, J = 16.4 Hz, 1H), 2.57 (d, J = 16.8 Hz, 1H), 2.49 (d, J = 16.8 Hz, 1H), 1.57 (s, 3H), 1.15 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 130.0, 129.8, 128.6, 126.5, 91.1, 86.5, 74.0, 44.6, 31.1, 30.6, 27.3, 25.1;

HRMS Calcd (ESI) m/z for $C_{17}H_{22}NO$ $[M + H]^+$: 256.1696, found: 256.1692.



5-(4-(Benzyloxy)-4-methylpent-2-yn-1-yl)-5-methyl-3-phenyl-4,5-dihydroisoxazole (3q)



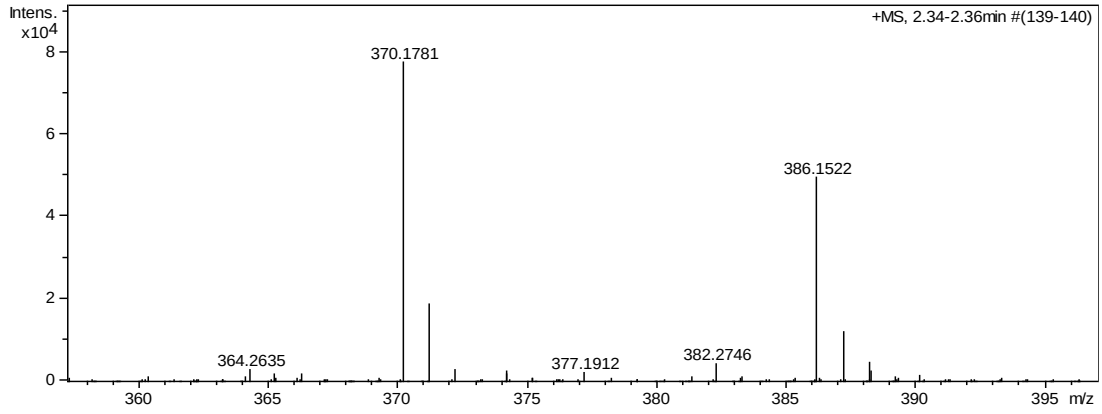
3q

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3q** (85.5 mg, 82% yield) as a yellow solid; m.p.: 73-75 ºC.

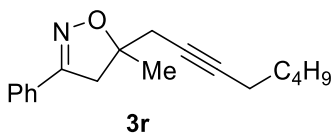
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64-7.62 (m, 2H), 7.40-7.37 (m, 3H), 7.33-7.28 (m, 4H), 7.26-7.23 (m, 1H), 4.58 (s, 2H), 3.42 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.60 (d, *J* = 16.8 Hz, 1H), 1.60 (s, 3H) , 1.49 (d, *J* = 3.6 Hz, 6H) ;

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 139.1, 129.9, 129.8, 128.6, 128.2, 127.5, 127.2, 126.4, 86.0, 84.7, 80.0, 70.7, 66.3, 44.7, 30.6, 29.0, 29.0, 25.3;

HRMS Calcd (ESI) m/z for $C_{23}H_{25}NNaO_2$ $[M + Na]^+$: 370.1778, found: 370.1781.



5-Methyl-5-(oct-2-yn-1-yl)-3-phenyl-4,5-dihydroisoxazole (3r)



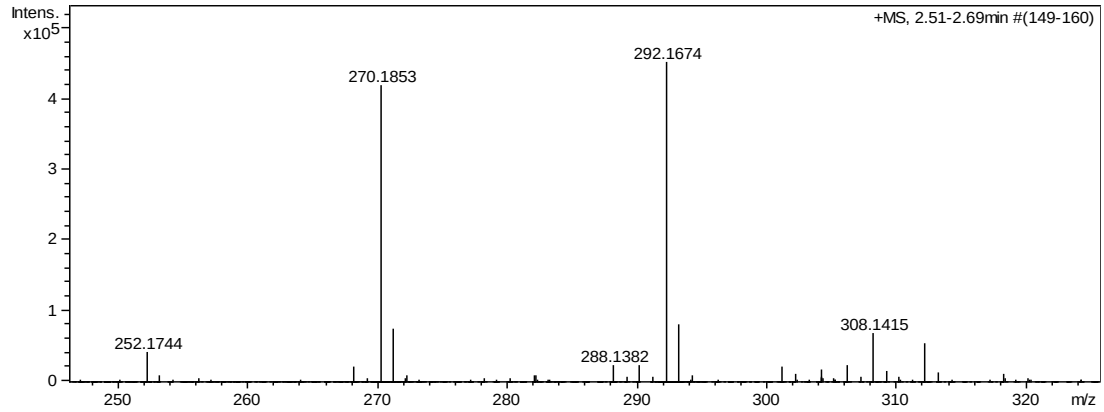
3r

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) gave the product **3r** (57.2 mg, 71% yield) as a yellow oil.

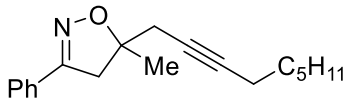
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.65 (m, 2H), 7.40-7.38 (m, 3H), 3.45 (d, *J* = 16.8 Hz, 1H), 2.59 (d, *J* = 16.8 Hz, 1H), 2.52 (d, *J* = 16.4 Hz, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 2.15-2.10 (m, 2H), 1.57 (s, 3H), 1.46-1.41 (m, 2H), 1.34-1.24 (m, 4H), 0.89-0.85 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 130.0, 129.8, 128.6, 126.5, 86.4, 82.7, 75.4, 44.7, 31.0, 30.6, 28.5, 25.1, 22.1, 18.6, 13.9;

HRMS Calcd (ESI) m/z for $C_{18}H_{23}NNaO$ $[M + Na]^+$: 292.1672, found: 292.1674.



5-Methyl-5-(non-2-yn-1-yl)-3-phenyl-4,5-dihydroisoxazole (3s)



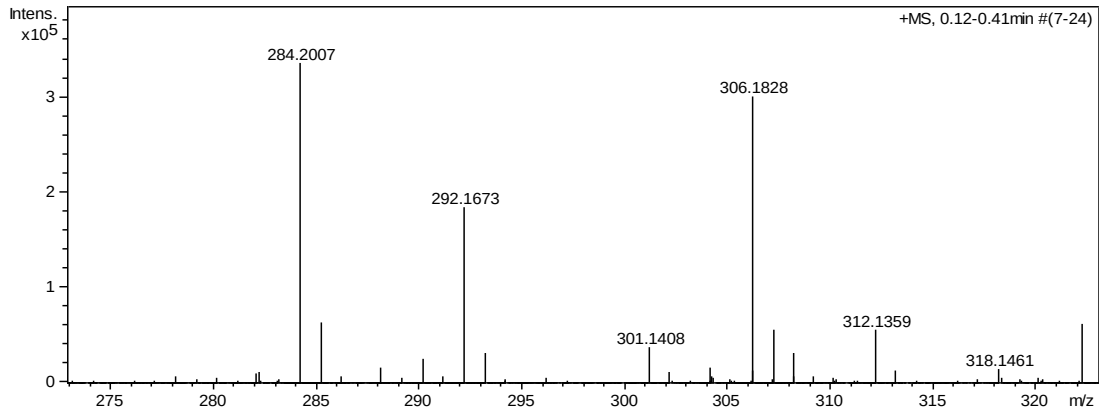
3s

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) gave the product **3s** (62.2 mg, 73% yield) as a yellow oil.

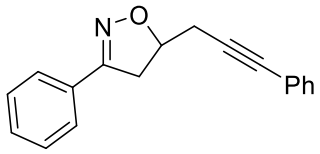
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.65 (m, 2H), 7.40-7.39 (m, 3H), 3.45 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.59 (d, *J* = 16.4 Hz, 1H), 2.52 (d, *J* = 16.4 Hz, 1H), 2.15-2.11 (m, 2H), 1.58 (s, 3H), 1.46-1.41 (m, 2H), 1.36-1.22 (m, 6H), 0.89-0.86 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 130.0, 129.8, 128.6, 126.5, 86.5, 82.7, 75.5, 44.7, 31.3, 30.6, 28.8, 28.5, 25.1, 22.5, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{19}H_{26}NO$ $[M + H]^+$: 284.2009, found: 284.2007.



3-Phenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3t)



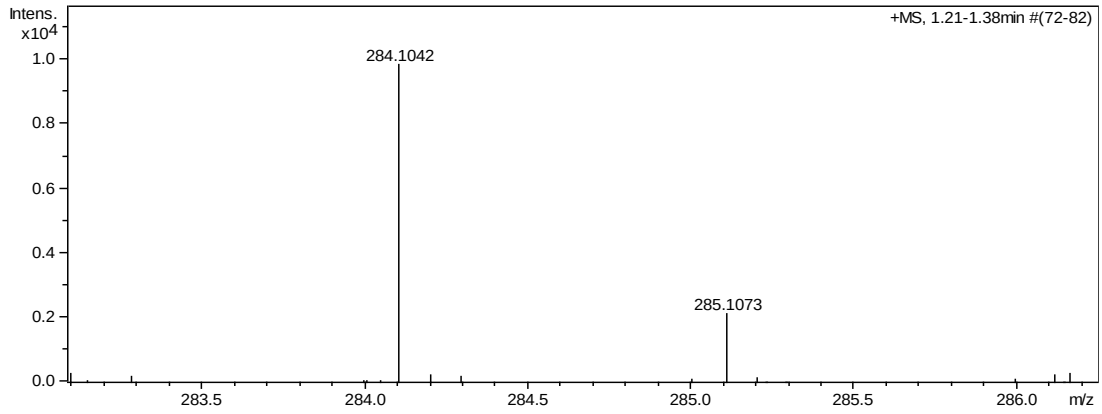
3t

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3t** (30.0 mg, 38% yield) as a brown oil.

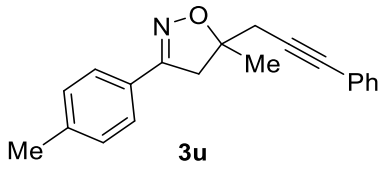
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63-7.61 (m, 2H), 7.33-7.31 (m, 3H), 7.29-7.27 (m, 2H), 7.19-7.17 (m, 3H), 4.94-4.87 (m, 1H), 3.44 (dd, J_1 = 10.4 Hz, J_2 = 16.8 Hz, 1H), 3.27 (dd, J_1 = 6.4 Hz, J_2 = 16.8 Hz, 1H), 2.80 (dd, J_1 = 4.8 Hz, J_2 = 16.8 Hz, 1H), 2.67 (dd, J_1 = 7.6 Hz, J_2 = 16.8 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 131.6, 130.1, 129.4, 128.7, 128.2, 128.0, 126.7, 123.1, 84.5, 82.7, 79.0, 39.6, 25.8;

HRMS Calcd (ESI) m/z for $C_{18}H_{15}NNaO$ $[M + Na]^+$: 284.1046, found: 284.1042.



5-Methyl-5-(3-phenylprop-2-yn-1-yl)-3-(p-tolyl)-4,5-dihydroisoxazole (3u)



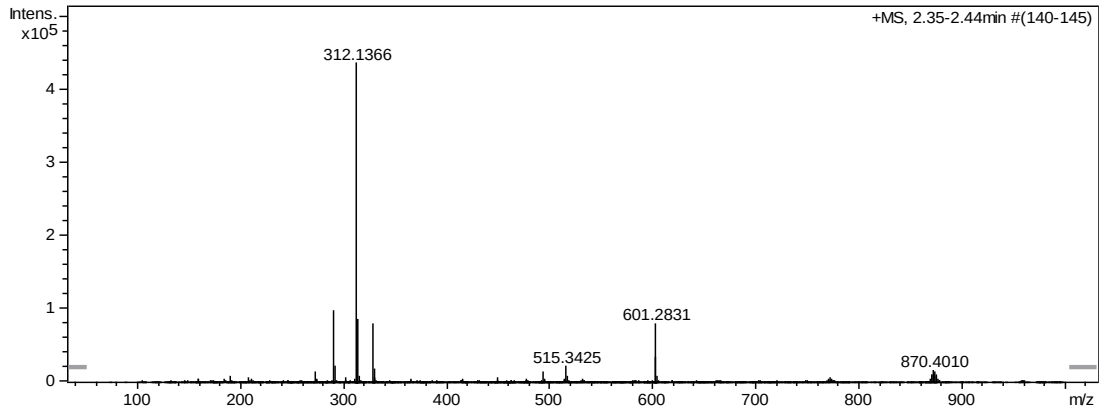
3u

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3u** (69.8 mg, 80% yield) as a brown oil.

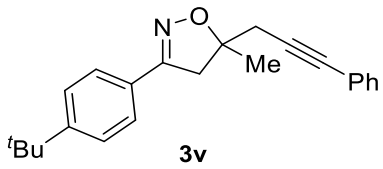
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.28-7.27 (m, 2H), 7.18-7.14 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 2H), 3.39 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.8 Hz, 1H), 2.74 (d, *J* = 16.8 Hz, 1H), 2.68 (d, *J* = 16.4 Hz, 1H), 2.27 (s, 3H), 1.56 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 140.1, 131.6, 129.3, 128.1, 127.9, 127.0, 126.4, 123.2, 86.0, 85.4, 82.5, 45.0, 31.1, 25.0, 21.4;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO$ $[M + Na]^+$: 312.1359, found: 312.1366.



3-(4-(*tert*-Butyl)phenyl)-5-methyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3v)



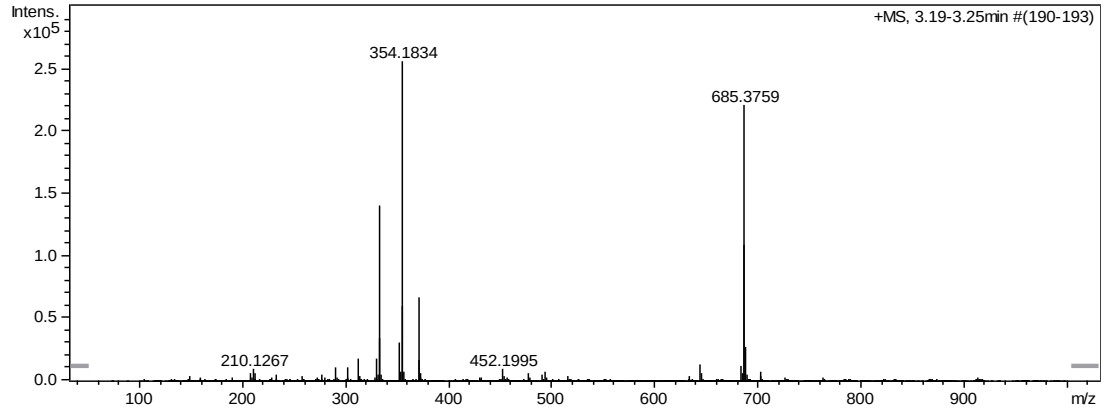
3v

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3v** (67.6 mg, 68% yield) as a brown solid; m.p.: 80-82 ºC.

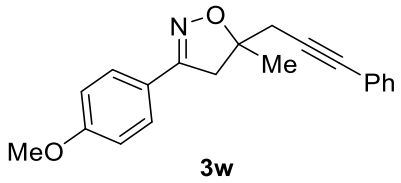
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.51 (m, 2H), 7.35-7.26 (m, 4H), 7.18-7.17 (m, 3H), 3.42 (d, *J* = 16.8 Hz, 1H), 3.05 (d, *J* = 16.8 Hz, 1H), 2.77-2.65 (m, 2H), 1.57 (s, 3H), 1.24 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 153.3, 131.6, 128.1, 127.9, 127.0, 126.4, 125.6, 123.2, 86.1, 85.4, 82.5, 45.0, 34.8, 31.1 (2C), 25.0;

HRMS Calcd (ESI) m/z for $C_{23}H_{25}NNaO$ $[M + Na]^+$: 354.1828, found: 354.1834.



3-(4-Methoxyphenyl)-5-methyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3w)



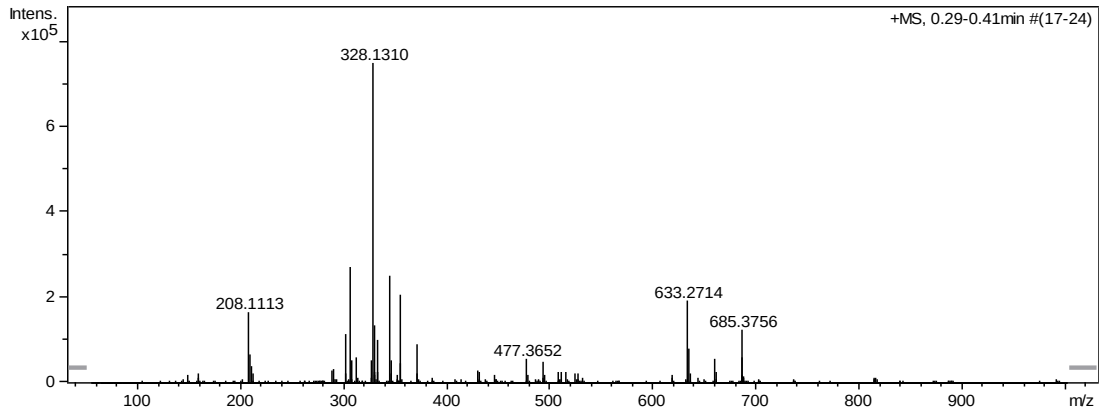
3w

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3w** (52.5 mg, 57% yield) as a brown oil.

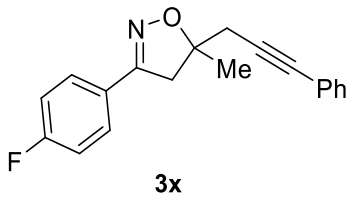
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62 (d, *J* = 9.0 Hz, 2H), 7.38-7.37 (m, 2H), 7.28-7.26 (m, 3H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 3.49 (d, *J* = 16.5 Hz, 1H), 3.13 (d, *J* = 17.0 Hz, 1H), 2.84 (d, *J* = 16.5 Hz, 1H), 2.78 (d, *J* = 17.0 Hz, 1H), 1.66 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.0, 156.2, 131.6, 128.2, 128.1, 127.9, 123.2, 122.5, 114.1, 86.0, 85.5, 82.5, 55.3, 45.2, 31.2, 25.1;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO_2$ $[M + Na]^+$: 328.1308, found: 328.1310.



3-(4-Fluorophenyl)-5-methyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole(3x)



3x

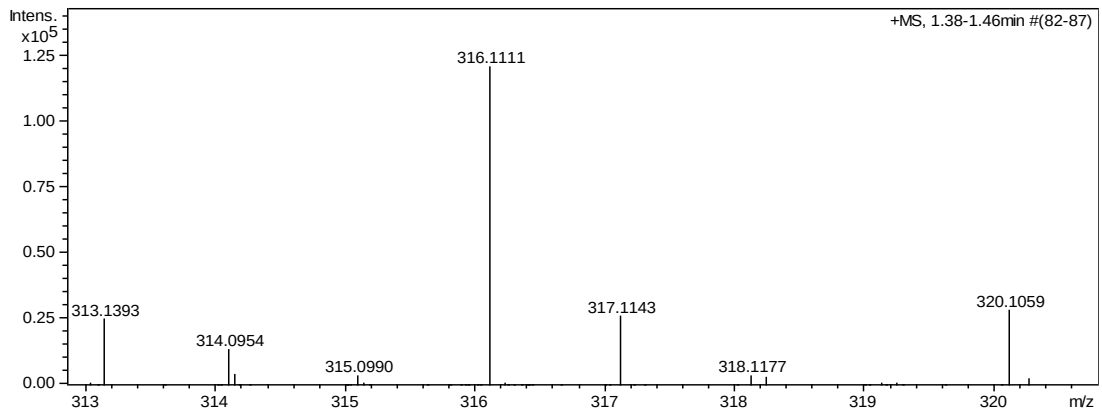
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3x** (61.6 mg, 70% yield) as a brown solid; m.p.: 81-83 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.56 (m, 2H), 7.29-7.26 (m, 2H), 7.19-7.17 (m, 3H), 7.02-6.98 (m, 2H), 3.41 (d, *J* = 16.8 Hz, 1H), 3.04 (d, *J* = 16.8 Hz, 1H), 2.76 (d, *J* = 16.8 Hz, 1H), 2.70 (d, *J* = 16.8 Hz, 1H), 1.58 (s, 3H);

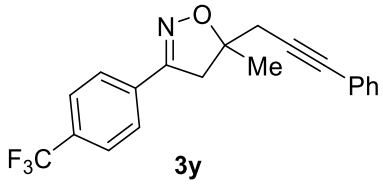
^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.6 (d, *J* = 249.3 Hz), 155.5, 131.6, 128.5 (d, *J* = 8.4 Hz), 128.2, 128.0, 126.1 (d, *J* = 3.4 Hz), 123.1, 115.8 (d, *J* = 21.8 Hz), 86.5, 85.3, 82.6, 45.0, 31.2, 25.1;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -110.1;

HRMS Calcd (ESI) m/z for $C_{19}H_{16}FNNaO$ $[M + Na]^+$: 316.1108, found: 316.1111.



5-Methyl-5-(3-phenylprop-2-yn-1-yl)-3-(4-(trifluoromethyl)phenyl)-4,5-dihydroisoxazole (3y)



3y

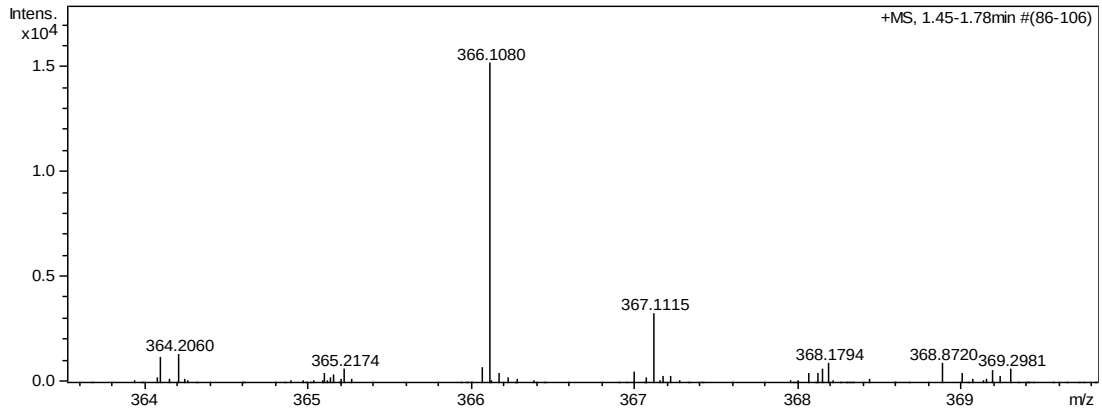
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3y** (61.8 mg, 60% yield) as a yellow solid; m.p.: 100-102 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.27-7.25 (m, 2H), 7.19-7.17 (m, 3H), 3.44 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.78 (d, *J* = 16.8 Hz, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 1.59 (s, 3H);

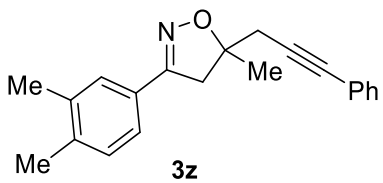
^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 133.3, 131.6, 131.6 (q, *J* = 32.2 Hz), 128.2, 128.0, 126.8, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.9 Hz), 123.0, 87.1, 85.0, 82.8, 44.6, 31.3, 25.2;

^{19}F NMR ($CDCl_3$, 376 MHz) -62.9;

HRMS Calcd (ESI) m/z for $C_{20}H_{16}F_3NNaO$ $[M + Na]^+$: 366.1076, found: 366.1080.



3-(3,4-Dimethylphenyl)-5-methyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3z)



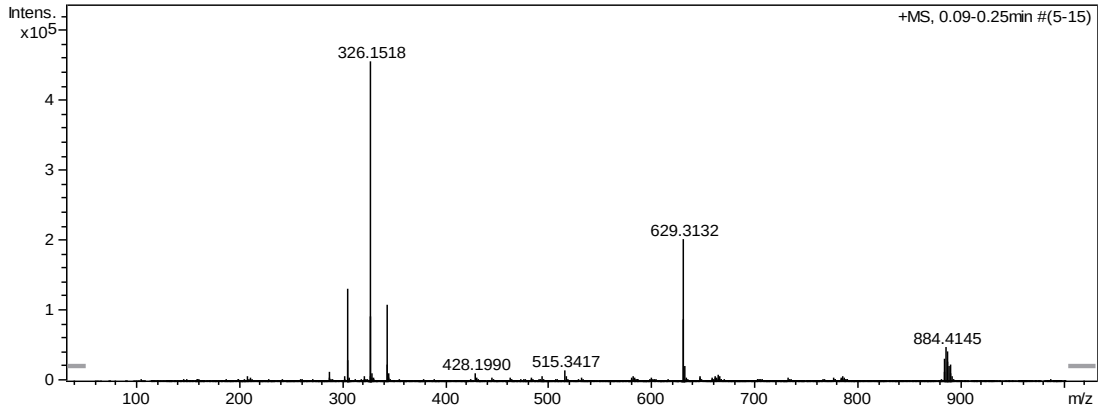
3z

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3z** (71.5 mg, 78% yield) as a brown oil.

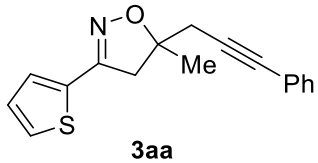
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (s, 1H), 7.39-7.37 (m, 3H), 7.28-7.25 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 1H), 3.49 (d, *J* = 16.8 Hz, 1H), 3.12 (d, *J* = 16.4 Hz, 1H), 2.85-2.75 (m, 2H), 2.27 (s, 6H), 1.65 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6, 138.8, 136.9, 131.6, 129.8, 128.2, 127.9, 127.6, 127.4, 124.1, 123.2, 86.0, 85.5, 82.5, 45.1, 31.1, 25.1, 19.7 (2C);

HRMS Calcd (ESI) m/z for $C_{21}H_{21}NNaO$ $[M + Na]^+$: 326.1515, found: 326.1518.



5-Methyl-5-(3-phenylprop-2-yn-1-yl)-3-(thiophen-2-yl)-4,5-dihydroisoxazole (3aa)



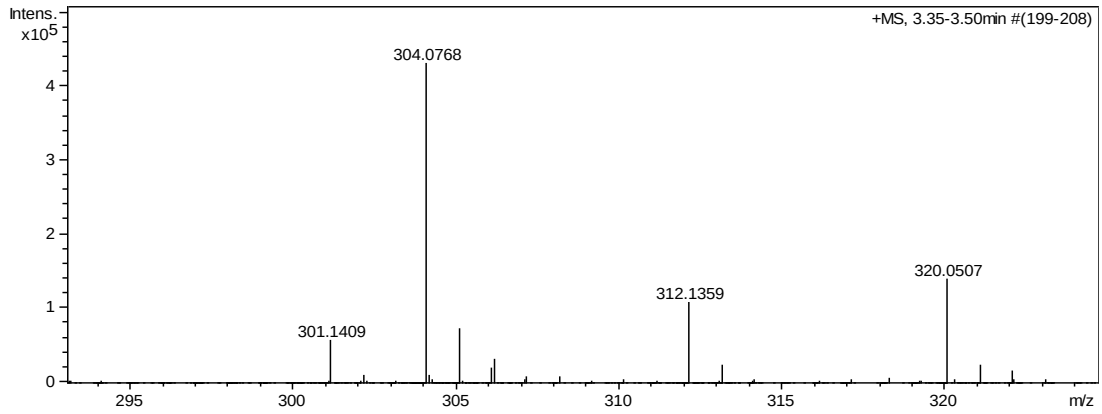
3aa

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3aa** (66.5 mg, 79% yield) as a yellow oil.

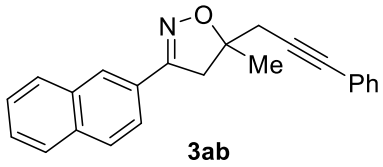
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.36 (m, 3H), 7.29-7.27 (m, 3H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.07-7.05 (m, 1H), 3.53 (d, *J* = 16.4 Hz, 1H), 3.16 (d, *J* = 16.4 Hz, 1H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.79 (d, *J* = 16.8 Hz, 1H), 1.67 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 132.4, 131.6, 128.2 (2C), 128.1, 128.0, 127.2, 123.1, 86.7, 85.2, 82.7, 45.7, 31.1, 25.0;

HRMS Calcd (ESI) m/z for $C_{17}H_{15}NNaOS$ $[M + Na]^+$: 304.0767, found: 304.0768.



5-Methyl-3-(naphthalen-2-yl)-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3ab)



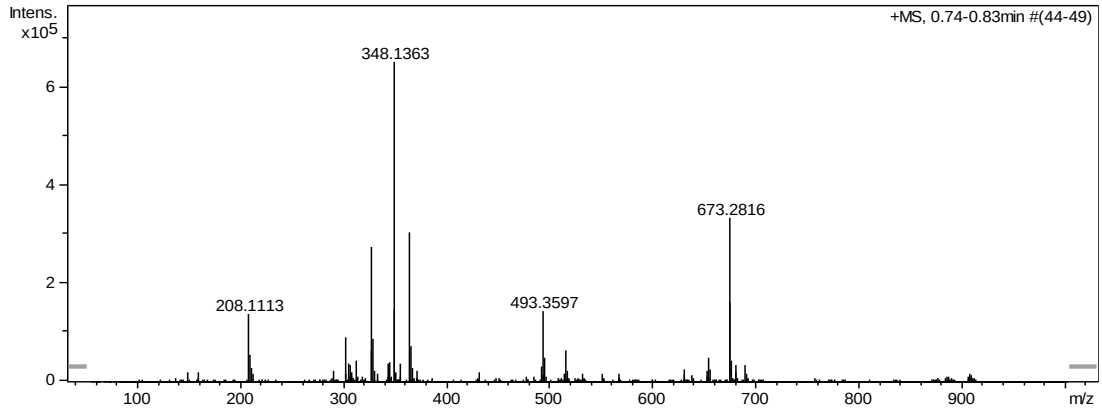
3ab

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3ab** (86.5 mg, 88% yield) as a yellow solid; m.p.: 75-77 ºC.

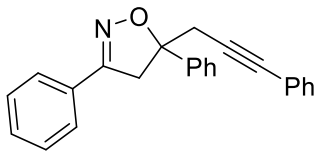
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.79-7.72 (m, 4H), 7.41-7.39 (m, 2H), 7.29-7.28 (m, 2H), 7.16-7.13 (m, 3H), 3.53 (d, *J* = 16.4 Hz, 1H), 3.15 (d, *J* = 16.8 Hz, 1H), 2.81-2.70 (m, 2H), 1.60 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6, 133.9, 132.9, 131.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.5, 127.0, 126.8, 126.6, 123.4, 123.2, 86.5, 85.4, 82.6, 44.9, 31.3, 25.2;

HRMS Calcd (ESI) m/z for $C_{23}H_{19}NNaO$ $[M + Na]^+$: 348.1359, found: 348.1363.



3,5-Diphenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3ac)



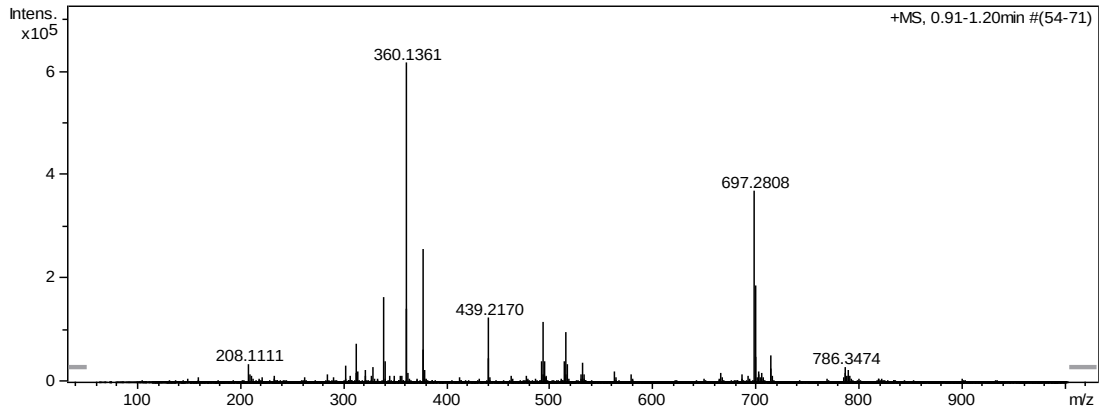
3ac

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3ac** (44.5 mg, 44% yield) as a yellow oil.

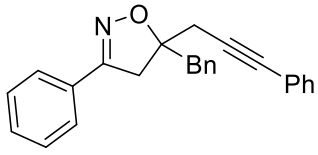
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.59 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.32-7.28 (m, 5H), 7.24-7.19 (m, 3H), 7.15-7.12 (m, 3H), 3.84 (d, *J* = 16.4 Hz, 1H), 3.51 (d, *J* = 16.8 Hz, 1H), 3.07-2.97 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 143.3, 131.5, 130.1, 129.5, 128.6, 128.4, 128.1, 127.9, 127.8, 126.6, 125.3, 123.1, 89.2, 84.9, 83.3, 45.7, 32.8;

HRMS Calcd (ESI) m/z for $C_{24}H_{19}NNaO$ $[M + Na]^+$: 360.1359, found: 360.1361.



5-Benzyl-3-phenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3ad)



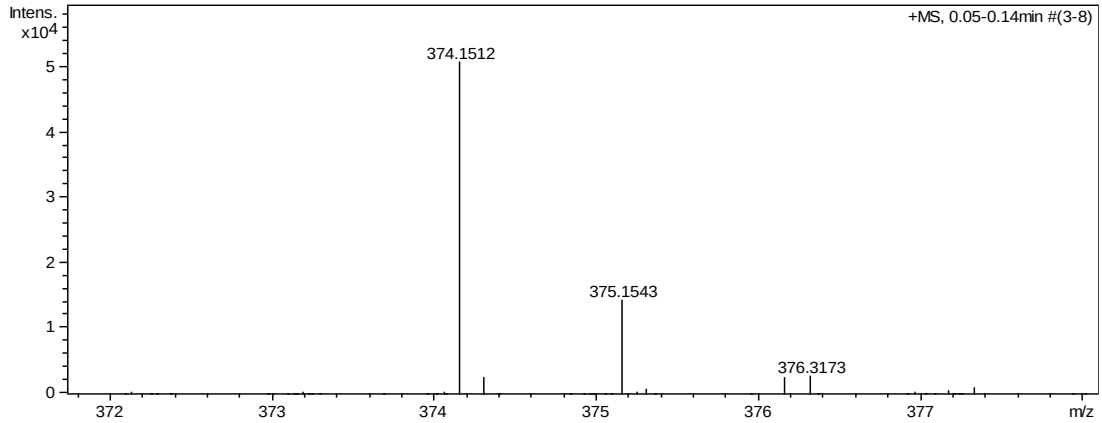
3ad

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3ad** (72.3 mg, 69% yield) as a yellow solid; m.p.: 94-96 °C.

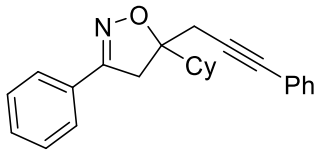
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.53 (m, 2H), 7.33-7.26 (m, 7H), 7.24-7.14 (m, 6H), 3.3 (d, *J* = 16.8 Hz, 1H), 3.21-3.11 (m, 3H), 2.68 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6, 136.0, 131.6, 130.5, 129.9, 129.6, 128.6, 128.3, 128.2, 128.0, 126.9, 126.5, 123.2, 88.7, 85.3, 83.1, 43.1, 43.0, 29.3;

HRMS Calcd (ESI) m/z for $C_{25}H_{21}NNaO$ $[M + Na]^+$: 374.1515, found: 374.1512.



5-Cyclohexyl-3-phenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3ae)



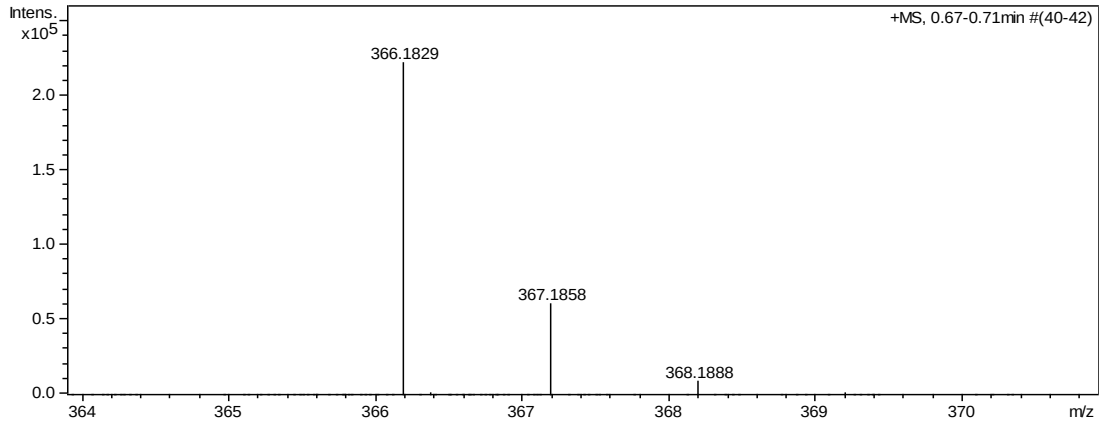
3ae

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) gave the product **3ae** (88.2 mg, 85% yield) as a yellow solid; m.p.: 66-67 ºC.

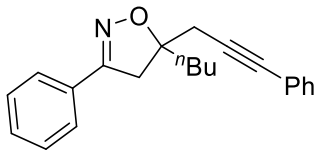
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.59 (m, 2H), 7.31-7.29 (m, 3H), 7.23-7.21 (m, 3H), 3.28-3.18 (m, 2H), 2.80 (d, *J* = 16.8 Hz, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 1.85-1.73 (m, 5H), 1.22-1.04 (m, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 131.6, 129.9, 129.8, 128.6, 128.1, 127.7, 126.5, 123.3, 90.9, 85.4, 82.5, 44.7, 41.3, 28.2, 27.3, 27.1, 26.3 (2C), 26.2;

HRMS Calcd (ESI) m/z for $C_{24}H_{25}NNaO$ $[M + Na]^+$: 366.1828, found: 366.1829.



5-Butyl-3-phenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3af)



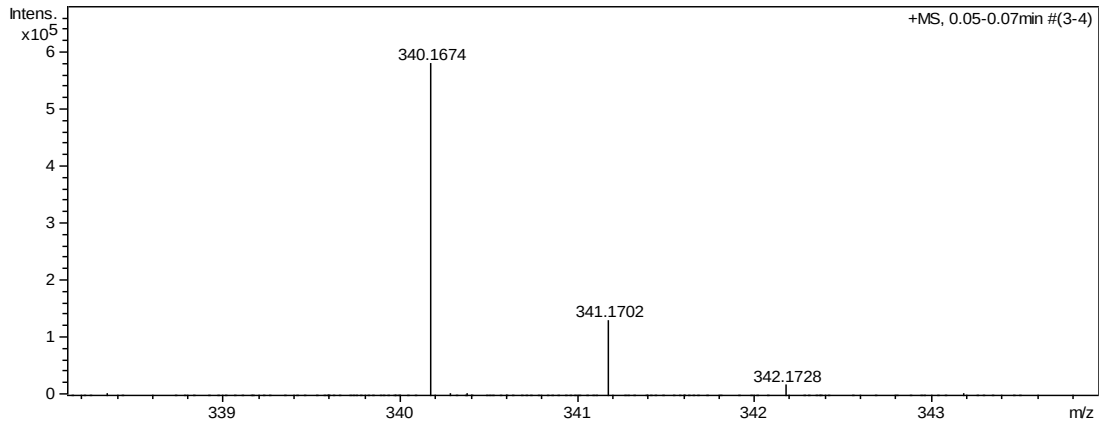
3af

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) gave the product **3af** (65.3 mg, 68% yield) as a brown oil.

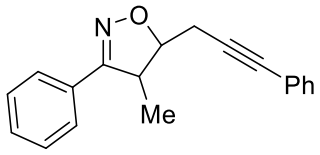
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.59 (m, 2H), 7.32-7.26 (m, 5H), 7.18-7.17 (m, 3H), 3.36 (d, *J* = 17.2 Hz, 1H), 3.12 (d, *J* = 17.2 Hz, 1H), 2.73 (s, 2H), 1.87-1.83 (m, 2H), 1.41-1.28 (m, 4H), 0.87-0.84 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 131.6, 129.9, 128.6, 128.1, 127.9, 126.5, 123.2, 88.6, 85.3, 82.5, 43.1, 37.6, 29.8, 25.9, 22.9, 14.0;

HRMS Calcd (ESI) m/z for $C_{22}H_{23}NNaO$ $[M + Na]^+$: 340.1672, found: 340.1674.



4-Methyl-3-phenyl-5-(3-phenylprop-2-yn-1-yl)-4,5-dihydroisoxazole (3ag)



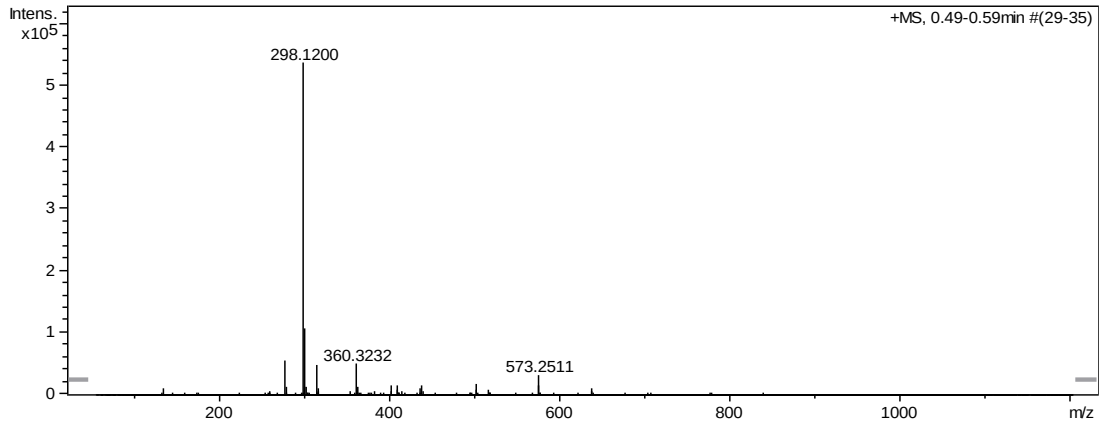
3ag

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **3ag** (29.1 mg, 35% yield) as a yellow oil. The reported peaks are for both diastereomers of title Compound.

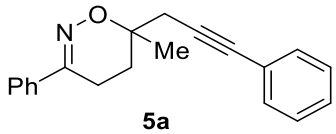
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66-7.63 (m, 2H), 7.35-7.18 (m, 8H), 4.75-4.69 (m, 0.2H), 4.51-4.47 (m, 0.8H), 3.68-3.62 (m, 1H), 2.97 (dd, J_1 = 16.8 Hz, J_2 = 5.6 Hz, 0.2H), 2.82-2.74 (m, 1H), 2.60 (dd, J_1 = 16.4 Hz, J_2 = 8.4 Hz, 0.8H), 1.31 (d, J = 7.2 Hz, 2.4H), 1.22 (d, J = 7.2 Hz, 0.6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.8, 160.5, 131.6, 130.1, 130.0, 129.2, 128.77 (2C), 128.6 (2C), 128.2 (2C), 128 (2C), 127.0 (2C), 123.1 (2C), 86.2, 84.9, 84.5, 82.7, 82.5, 82.0, 47.0, 43.5, 25.1, 19.3, 18.2, 11.3;

HRMS Calcd (ESI) m/z for $C_{19}H_{17}NNaO$ $[M + Na]^+$: 298.1202, found: 298.1200.



6-Methyl-3-phenyl-6-(3-phenylprop-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5a)



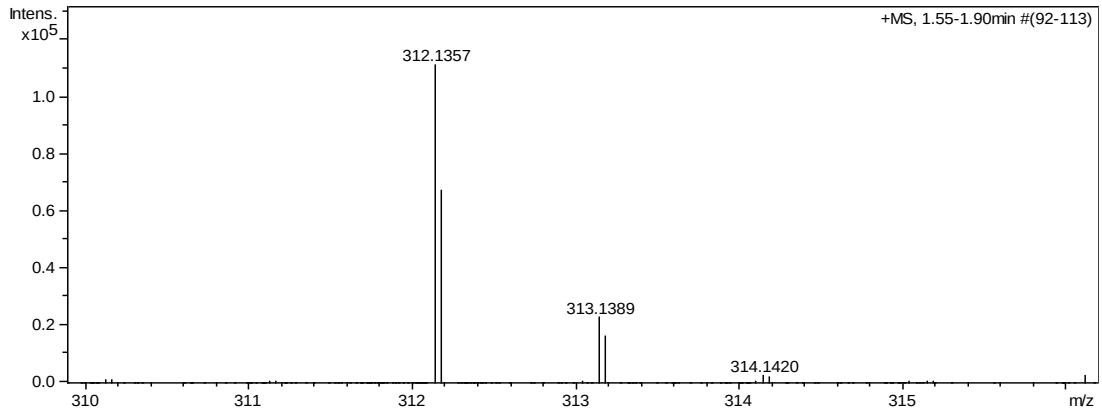
5a

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5a** (81.7 mg, 94% yield) as a yellow solid; m.p.: 79-82 ºC.

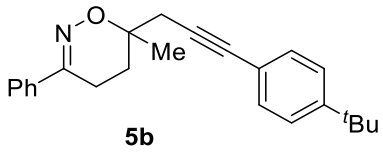
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76-7.74 (m, 2H), 7.45-7.39 (m, 5H), 7.32-7.30 (m, 3H), 2.80 (d, J = 16.8 Hz, 1H), 2.73-2.63 (m, 3H), 2.29-2.23 (m, 1H), 2.01-1.94 (m, 1H), 1.51 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 135.6, 131.5, 129.4, 128.4, 128.2, 127.9, 125.1, 123.3, 85.1, 82.9, 74.8, 28.9, 26.7, 23.8, 19.2;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO$ $[M + Na]^+$: 312.1359, found: 312.1357.



6-(3-(4-(*tert*-Butyl)phenyl)prop-2-yn-1-yl)-6-methyl-3-phenyl-5,6-dihydro-4H-1,2-oxazine (5b)



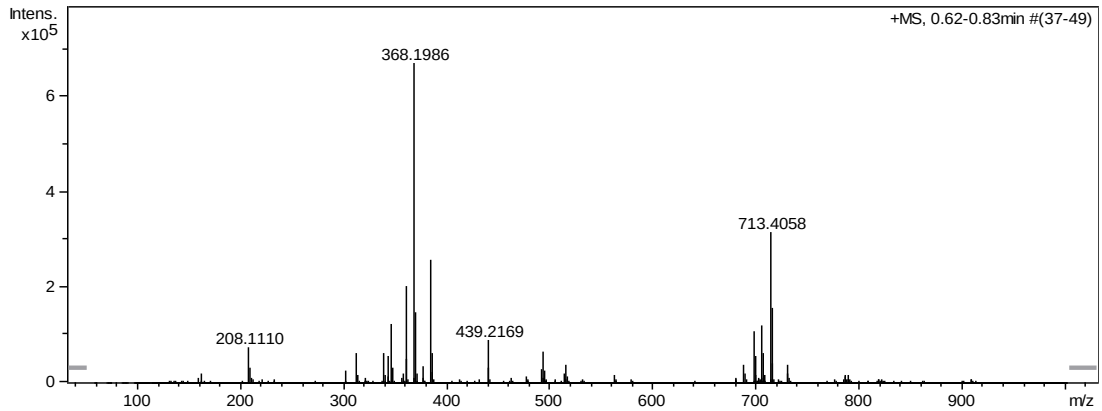
5b

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5b** (95.9 mg, 93% yield) as a yellow solid; m.p.: 69-72 ºC.

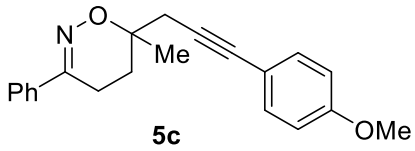
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76-7.74 (m, 2H), 7.41-7.33 (m, 7H), 2.79 (d, J = 16.8 Hz, 1H), 2.72-2.63 (m, 3H), 2.30-2.23 (m, 1H), 2.00-1.93 (m, 1H), 1.51 (s, 3H), 1.33 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 151.1, 135.7, 131.3, 129.4, 128.4, 125.2 (2C), 120.3, 84.3, 82.9, 74.9, 34.6, 31.1, 28.9, 26.7, 23.8, 19.2;

HRMS Calcd (ESI) m/z for $C_{24}H_{27}NNaO$ $[M + Na]^+$: 368.1985, found: 368.1986.



6-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-6-methyl-3-phenyl-5,6-dihydro-4H-1,2-oxazine (5c)



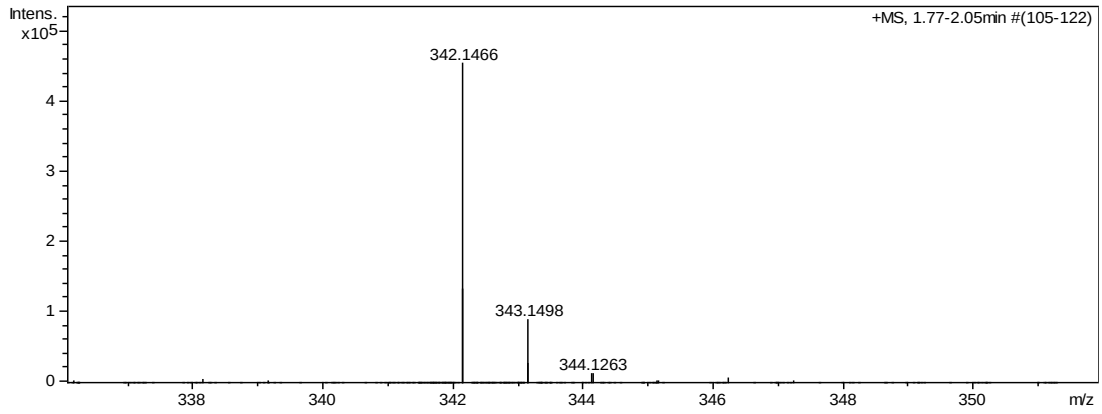
5c

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5c** (84.1 mg, 88% yield) as a white solid; m.p.: 76-78 ºC.

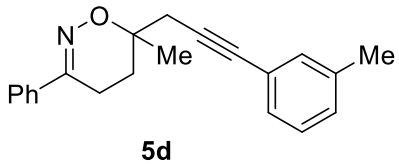
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75-7.73 (m, 2H), 7.40-7.35 (m, 5H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.77 (d, *J* = 16.8 Hz, 1H), 2.70-2.61 (m, 3H), 2.29-2.21 (m, 1H), 1.99-1.92 (m, 1H), 1.49 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.3, 153.7, 135.7, 132.9, 129.4, 128.4, 125.2, 115.5, 113.8, 83.5, 82.7, 74.9, 55.2, 28.9, 26.7, 23.8, 19.3;

HRMS Calcd (ESI) m/z for $C_{21}H_{21}NNaO_2$ $[M + Na]^+$: 342.1465, found: 342.1466.



6-Methyl-3-phenyl-6-(3-(m-tolyl)prop-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5d)



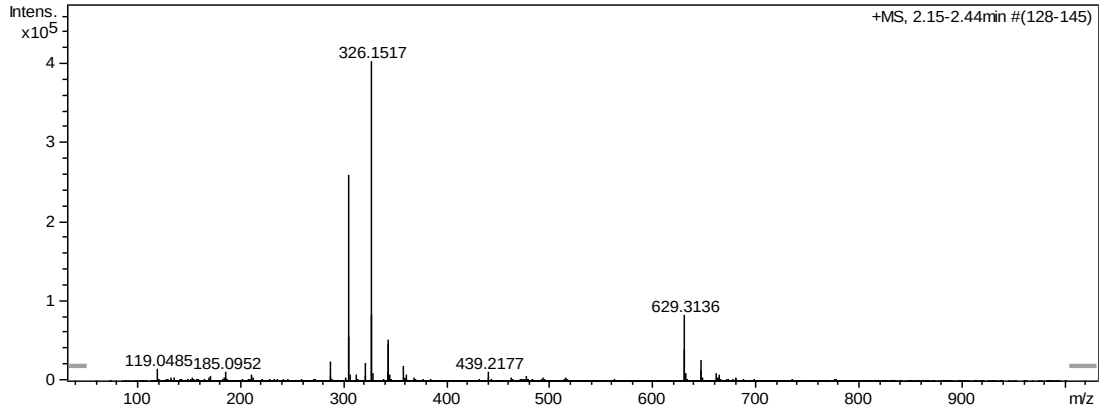
5d

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5d** (78.5 mg, 86% yield) as a yellow oil.

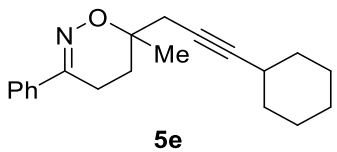
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.63 (m, 2H), 7.30-7.28 (m, 3H), 7.15-7.07 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 2.68 (d, *J* = 16.8 Hz, 1H), 2.61-2.51 (m, 3H), 2.23 (s, 3H), 2.18-2.12 (m, 1H), 1.90-1.82 (m, 1H), 1.40 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 137.8, 135.6, 132.1, 129.4, 128.8, 128.6, 128.4, 128.1, 125.2, 123.1, 84.7, 83.0, 74.8, 28.9, 26.7, 23.8, 21.1, 19.2;

HRMS Calcd (ESI) m/z for $C_{21}H_{21}NNaO$ $[M + Na]^+$: 326.1515, found: 326.1517.



6-(3-Cyclohexylprop-2-yn-1-yl)-6-methyl-3-phenyl-5,6-dihydro-4H-1,2-oxazine (5e)



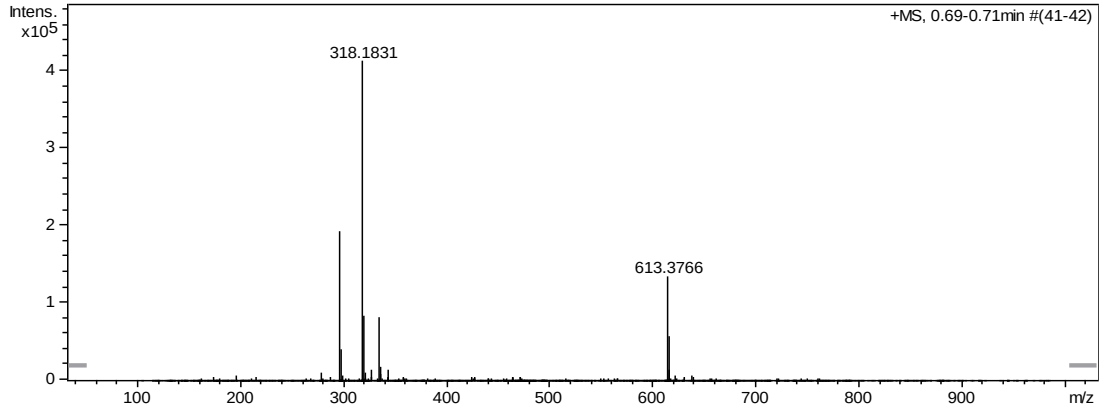
5e

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5e** (68.9 mg, 78% yield) as a yellow oil.

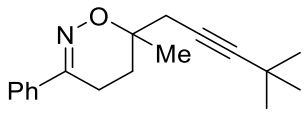
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73-7.70 (m, 2H), 7.38-7.36 (m, 3H), 2.61-2.57 (m, 2H), 2.55-2.40 (m, 2H), 2.37 (s, 1H), 2.21-2.14 (m, 1H), 1.92-1.84 (m, 1H), 1.79-1.75 (m, 2H), 1.70-1.66 (m, 2H), 1.50-1.39 (m, 6H), 1.33-1.29 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 135.8, 129.3, 128.4, 125.2, 87.1, 75.1, 75.0, 32.9, 29.0, 28.1, 26.5, 25.9, 24.8, 23.7, 19.2;

HRMS Calcd (ESI) m/z for $C_{20}H_{25}NNaO$ $[M + Na]^+$: 318.1828, found: 318.1831.



6-(4,4-Dimethylpent-2-yn-1-yl)-6-methyl-3-phenyl-5,6-dihydro-4H-1,2-oxazine (5f)



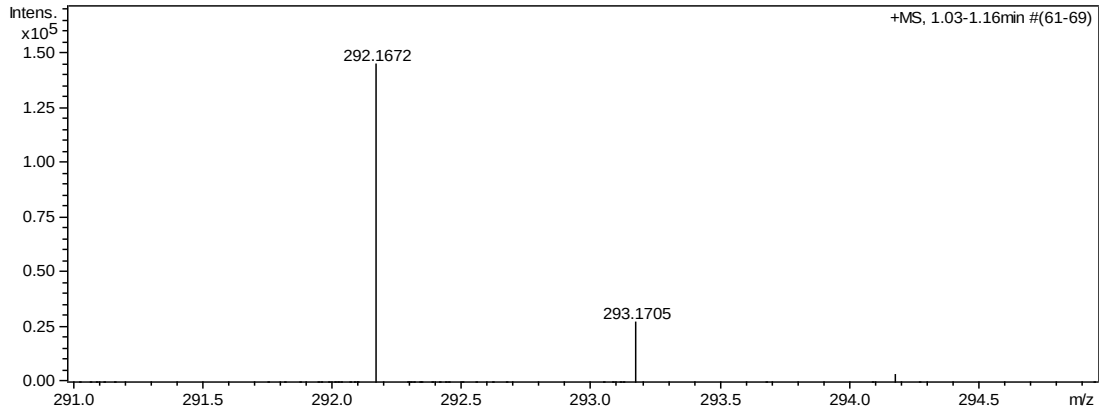
5f

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5f** (52.0 mg, 64% yield) as a white solid; m.p.: 79-81 ºC.

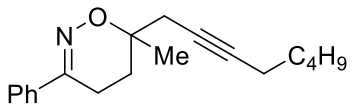
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73-7.70 (m, 2H), 7.38-7.37 (m, 3H), 2.61-2.57 (m, 2H), 2.50 (d, *J* = 16.4 Hz, 1H), 2.40 (d, *J* = 16.4 Hz, 1H), 2.19-2.12 (m, 1H), 1.91-1.84 (m, 1H), 1.40 (s, 3H), 1.22 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 135.8, 129.3, 128.4, 125.2, 91.4, 75.0, 73.6, 31.2, 28.1, 27.4, 26.5, 23.6, 19.3;

HRMS Calcd (ESI) m/z for $C_{18}H_{23}NNaO$ $[M + Na]^+$: 292.1672, found: 292.1672.



6-Methyl-6-(oct-2-yn-1-yl)-3-phenyl-5,6-dihydro-4H-1,2-oxazine (5g)



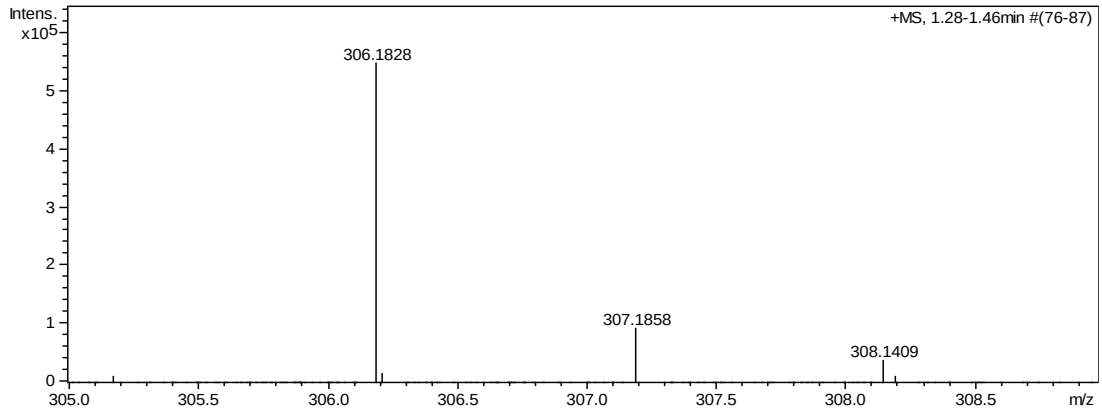
5g

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5g** (71.2 mg, 84% yield) as a brown oil.

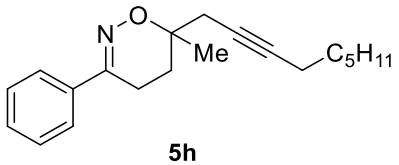
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73-7.70 (m, 2H), 7.38-7.36 (m, 3H), 2.61-2.57 (m, 2H), 2.51 (d, *J* = 16.8 Hz, 1H), 2.42 (d, *J* = 16.8 Hz, 1H), 2.20-2.13 (m, 3H), 1.91-1.84 (m, 1H), 1.54-1.47 (m, 2H), 1.41 (s, 3H), 1.38-1.30 (m, 4H), 0.92-0.89 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 135.8, 129.3, 128.4, 125.1, 82.9, 75.0, 74.9, 31.0, 28.6, 28.2, 26.6, 23.6, 22.1, 19.2, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{19}H_{25}NNaO$ $[M + Na]^+$: 306.1828, found: 306.1828.



6-Methyl-6-(non-2-yn-1-yl)-3-phenyl-5,6-dihydro-4H-1,2-oxazine (5h)



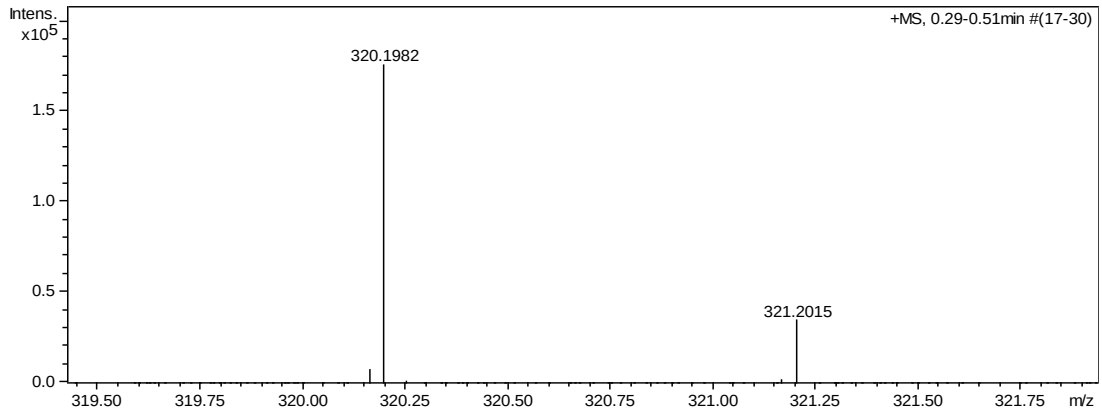
5h

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5h** (85.2 mg, 95% yield) as a brown oil.

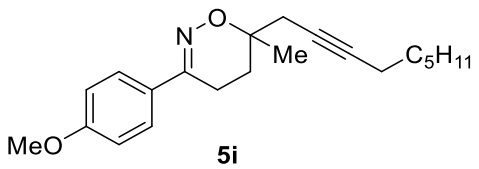
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72-7.70 (m, 2H), 7.38-7.37 (m, 3H), 2.61-2.53 (m, 2H), 2.51(d, *J* = 15.6 Hz, 1H), 2.42 (d, *J* = 16.4 Hz, 1H), 2.18-2.14 (m, 3H), 1.91-1.84 (m, 1H), 1.51-1.46 (m, 2H), 1.41 (s, 3H), 1.37-1.26 (m, 6H), 0.91-0.88 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 135.8, 129.3, 128.4, 125.2, 82.9, 75.1, 74.9, 31.3, 28.9, 28.5, 28.2, 26.6, 23.7, 22.5, 19.2, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{20}H_{27}NNaO$ $[M + Na]^+$: 320.1985, found: 320.1982.



3-(4-Methoxyphenyl)-6-methyl-6-(non-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5i)



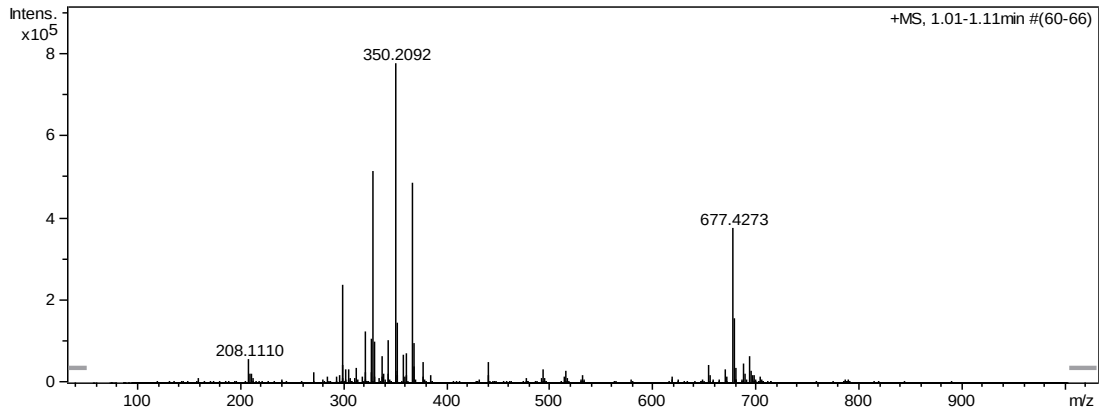
5i

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5i** (84.7 mg, 86% yield) as a yellow solid; m.p.: 45-48 ºC.

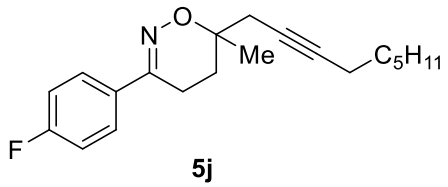
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.57-2.48 (m, 3H), 2.40 (d, *J* = 16.8 Hz, 1H), 2.17-2.11 (m, 3H), 1.89-1.82 (m, 1H), 1.52-1.45 (m, 2H), 1.39-1.26 (m, 9H), 0.91-0.87 (m, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.6, 153.3, 128.4, 126.5, 113.7, 82.9, 75.2, 74.7, 55.3, 31.3, 28.9, 28.5, 28.2, 26.7, 23.7, 22.5, 19.2, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{21}H_{29}NNaO_2$ $[M + Na]^+$: 350.2091, found: 350.2092.



3-(4-Fluorophenyl)-6-methyl-6-(non-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5j)



5j

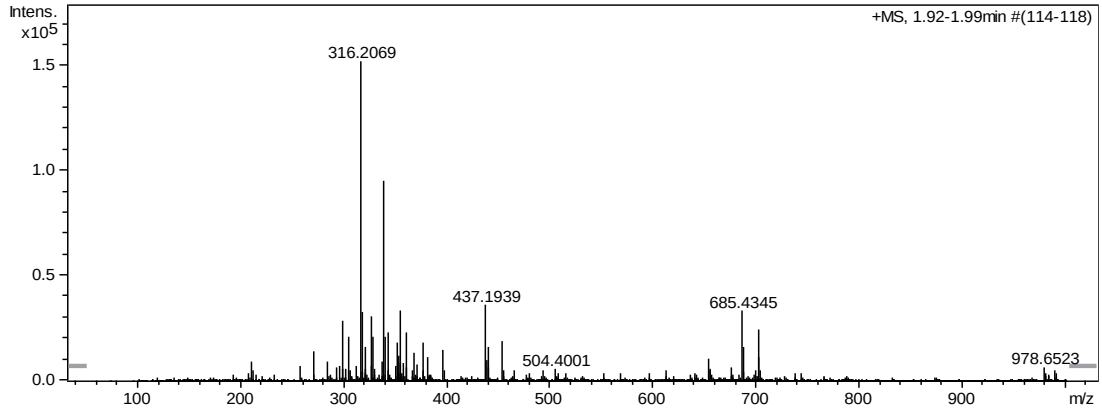
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5j** (86.2 mg, 91% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71-7.67 (m, 2H), 7.07-7.03 (m, 2H), 2.57-2.47 (m, 3H), 2.40 (d, *J* = 16.8 Hz, 1H), 2.19-2.12 (m, 3H), 1.90-1.83 (m, 1H), 1.52-1.45 (m, 2H), 1.39 (s, 3H), 1.38-1.25 (m, 6H), 0.90-0.87 (m, 3H);

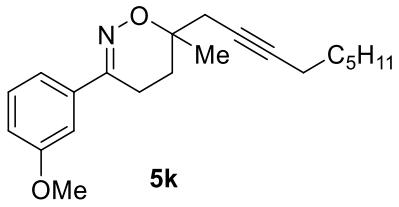
^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.4 (d, *J* = 247.9 Hz), 152.6, 131.9 (d, *J* = 3.3Hz), 127.0 (d, *J* = 8.3 Hz), 115.3 (d, J = 21.5 Hz), 83.0, 75.0, 74.9, 31.3, 28.9, 28.5, 28.2, 26.5, 23.6, 22.5, 19.2, 18.7, 14.0;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.0;

HRMS Calcd (ESI) m/z for $C_{20}H_{27}FNO$ $[M + H]^+$: 316.2071, found: 316.2069.



3-(3-Methoxyphenyl)-6-methyl-6-(non-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5k)



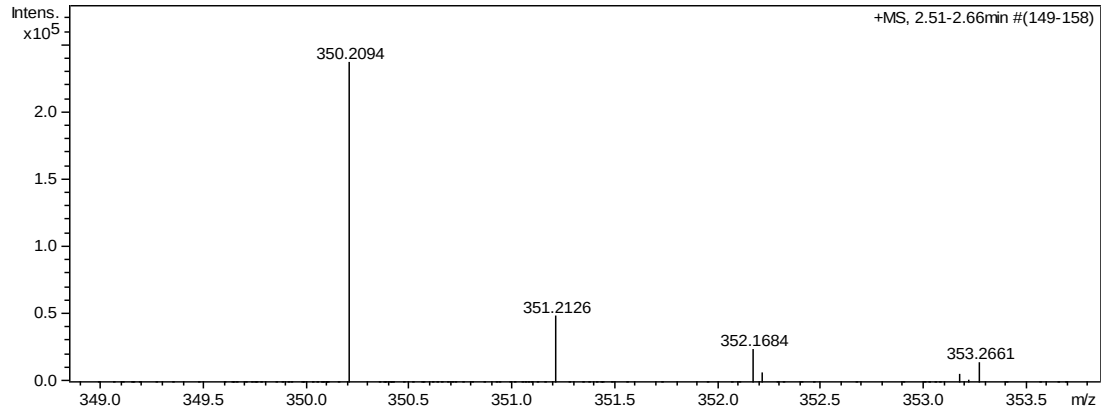
5k

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5k** (81.5 mg, 83% yield) as a yellow oil.

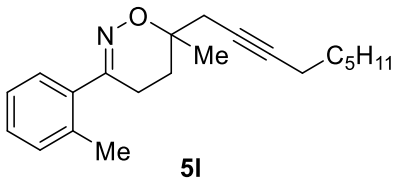
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (s, 1H), 7.22-7.15 (m, 2H), 6.85 (d, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 2.52-2.48 (m, 2H), 2.43 (d, *J* = 16.4 Hz, 1H), 2.34 (d, *J* = 16.4 Hz, 1H), 2.11-2.04 (m, 3H), 1.83-1.76 (m, 1H), 1.45-1.38 (m, 2H), 1.33-1.29 (m, 5H), 1.25-1.19 (m, 4H), 0.83-0.80 (m, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.6, 153.4, 137.2, 129.3, 117.7, 115.8, 110.0, 83.0, 75.0 (2C), 55.3, 31.3, 28.9, 28.5, 28.3, 26.5, 23.7, 22.5, 19.3, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{21}H_{29}NNaO_2$ $[M + Na]^+$: 350.2091, found: 350.2094.



6-Methyl-6-(non-2-yn-1-yl)-3-(o-tolyl)-5,6-dihydro-4H-1,2-oxazine (5l)



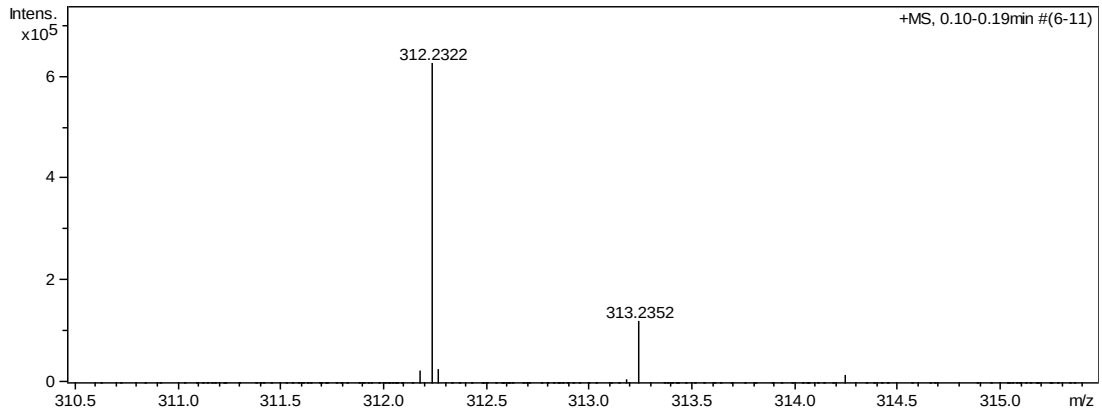
5l

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5l** (70.6 mg, 76% yield) as a yellow oil.

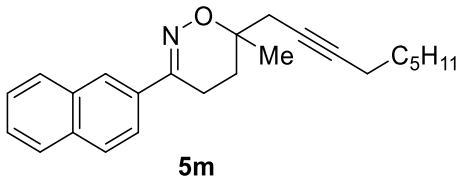
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18-7.10 (m, 4H), 2.50 (d, *J* = 16.4 Hz, 1H), 2.41-2.28 (m, 6H), 2.11-2.03 (m, 3H), 1.84-1.77 (m, 1H), 1.46-1.19 (m, 11H), 0.83-0.80 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.2, 136.7, 135.7, 130.7, 128.5, 127.7, 125.7, 82.9, 75.1, 74.3, 31.3, 28.9, 28.5, 28.4, 26.8, 23.7, 22.9, 22.5, 20.1, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{21}H_{30}NO$ $[M + H]^+$: 312.2322, found: 312.2322.



6-Methyl-3-(naphthalen-2-yl)-6-(non-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5m)



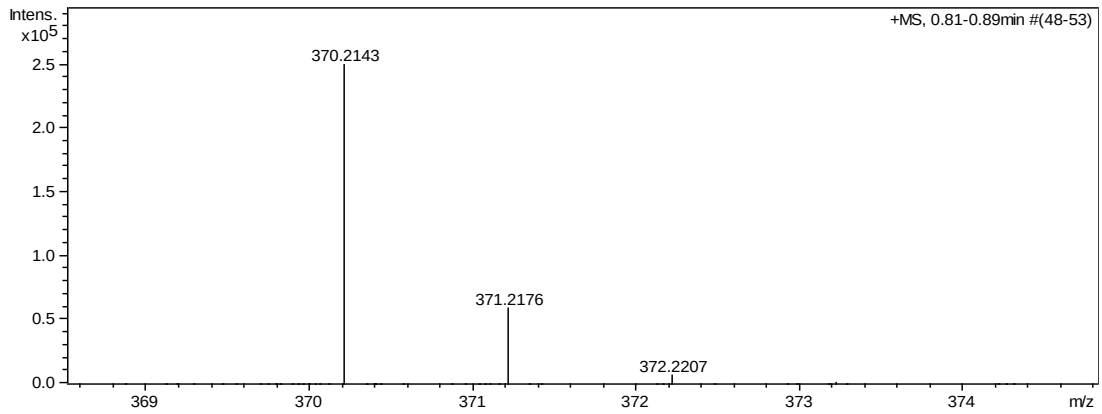
5m

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5m** (98.1 mg, 94% yield) as a brown oil.

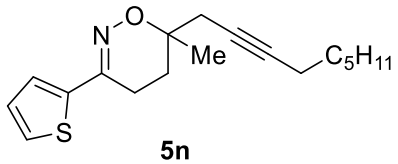
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03-8.01 (m, 2H), 7.86-7.81 (m, 3H), 7.50-7.48 (m, 2H), 2.75-2.71 (m, 2H), 2.57 (d, J = 16.4 Hz, 1H), 2.46 (d, J = 16.4 Hz, 1H), 2.26-2.17 (m, 3H), 1.97-1.90 (m, 1H), 1.55-1.48 (m, 2H), 1.46 (s, 3H), 1.43-1.29 (m, 6H), 0.94-0.90 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 133.7, 133.2, 133.0, 128.4, 128.0, 127.6, 126.6, 126.3, 124.6, 122.7, 82.9, 75.1 (2C), 31.3, 28.9, 28.5, 28.3, 26.6, 23.7, 22.5, 19.1, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{24}H_{29}NNaO$ $[M + Na]^+$: 370.2141, found: 370.2143.



6-Methyl-6-(non-2-yn-1-yl)-3-(thiophen-2-yl)-5,6-dihydro-4H-1,2-oxazine (5n)



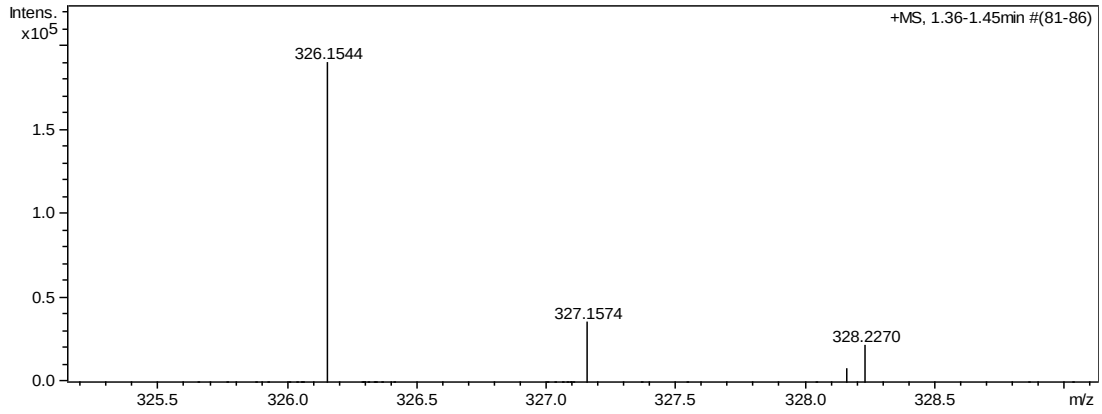
5n

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5n** (67.0 mg, 74% yield) as a brown oil.

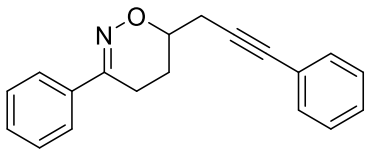
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.27 (m, 1H), 7.22-7.21 (m, 1H), 7.02-7.00 (m, 1H), 2.63-2.59 (m, 2H), 2.51 (d, *J* = 16.8 Hz, 1H), 2.40 (d, *J* = 16.8 Hz, 1H), 2.18-2.11 (m, 3H), 1.90-1.82 (m, 1H), 1.52-1.45 (m, 2H), 1.39-1.26 (m, 9H), 0.91-0.87 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 140.0, 126.9, 126.8, 125.0, 83.0, 75.5, 74.9, 31.3, 28.8, 28.5, 28.2, 26.3, 23.6, 22.5, 19.5, 18.7, 14.0;

HRMS Calcd (ESI) m/z for $C_{18}H_{25}NNaOS$ $[M + Na]^+$: 326.1549, found: 326.1544.



3-Phenyl-6-(3-phenylprop-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5o)



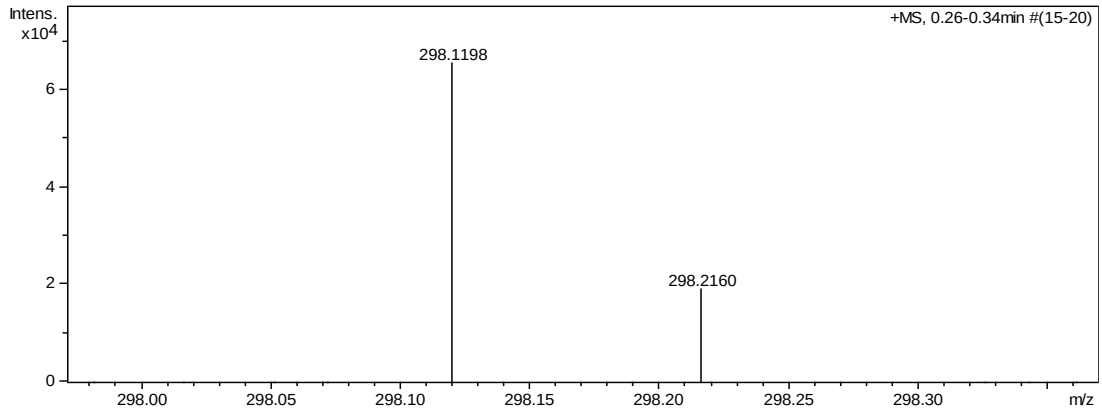
5o

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **5o** (63.1 mg, 76% yield) as a yellow solid; m.p.: 90-92 °C.

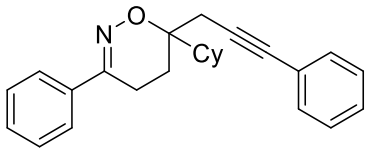
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74-7.70 (m, 2H), 7.44-7.39 (m, 5H), 7.32-7.29 (m, 3H), 4.04-4.01 (m, 1H), 3.01-2.93 (m, 1H), 2.79-2.60 (m, 3H), 2.40-2.32 (m, 1H), 2.01-1.90 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 135.6, 131.6, 129.5, 128.4, 128.2, 127.9, 125.3, 123.3, 84.7, 82.8, 73.2, 24.7, 23.4, 21.6;

HRMS Calcd (ESI) m/z for $C_{19}H_{17}NNaO$ $[M + Na]^+$: 298.1202, found: 298.1198.



6-Cyclohexyl-3-phenyl-6-(3-phenylprop-2-yn-1-yl)-5,6-dihydro-4H-1,2-oxazine (5p)



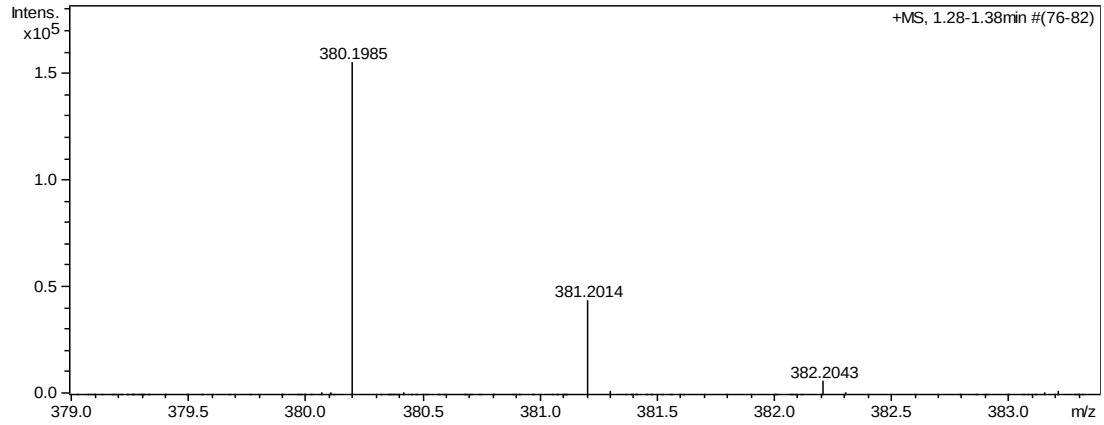
5p

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) gave the product **5p** (75.3 mg, 70% yield) as a white solid; m.p.: 114-116 ºC.

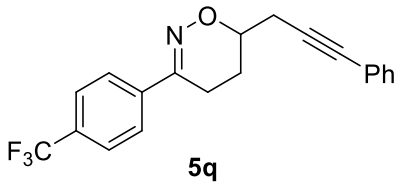
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75-7.74 (m, 2H), 7.39-7.38 (m, 5H), 7.30-7.26 (m, 3H), 2.79 (d, *J* = 16.4 Hz, 1H), 2.72-2.63 (m, 3H), 2.31-2.25 (m, 1H), 2.08-1.99 (m, 2H), 1.96-1.93 (m, 1H), 1.87-1.84 (m, 2H), 1.72-1.69 (m, 1H), 1.37-1.20 (m, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.0, 135.7, 131.5, 129.4, 128.4, 128.2, 127.8, 125.1, 123.6, 85.8, 82.9, 78.6, 44.7, 27.1, 26.9, 26.7, 26.6, 26.5, 23.7, 22.7, 18.9;

HRMS Calcd (ESI) m/z for $C_{25}H_{27}NNaO$ $[M + Na]^+$: 380.1985, found: 380.1985.



6-(3-Phenylprop-2-yn-1-yl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4H-1,2-oxazine (5q)



5q

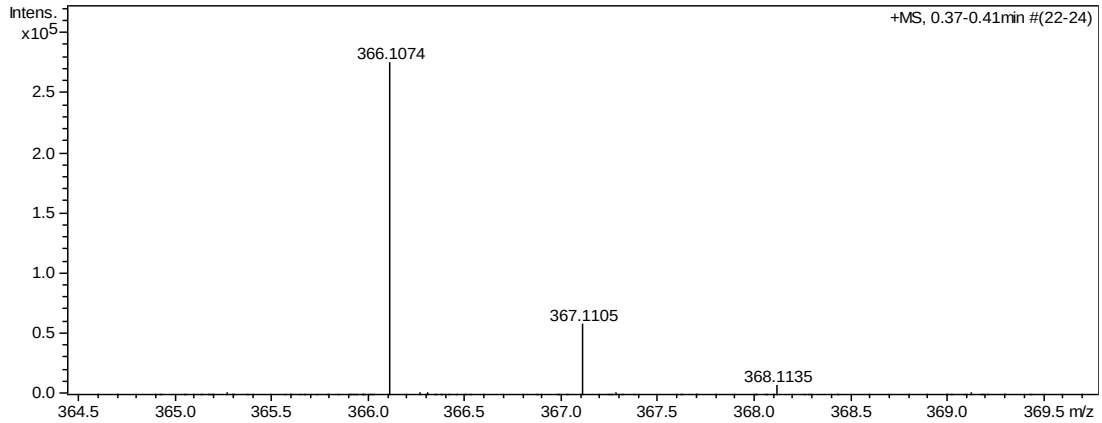
Flash column chromatography on a silica gel (acetone: petroleum ether, 1:22) gave the product **5q** (21.8 mg, 21% yield) as a yellow solid; m.p.: 73-75 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.44-7.42 (m, 2H), 7.31-7.29 (m, 3H), 4.08-4.02 (m, 1H), 3.01-2.95 (m, 1H), 2.80-2.62 (m, 3H), 2.42-2.36 (m, 1H), 2.03-1.94 (m, 1H);

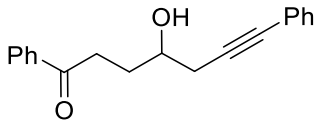
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 134.0, 131.6, 131.3 (q, *J* = 32.4 Hz), 128.2, 128.0, 125.6, 125.4 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 270.6 Hz), 123.2, 84.4, 83.0, 73.5, 24.7, 23.2, 21.6.

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.8.

HRMS Calcd (ESI) m/z for $C_{20}H_{16}F_3NNaO$ $[M + Na]^+$: 366.1076, found: 366.1074.



4-Hydroxy-1,7-diphenylhept-6-yn-1-one (6)



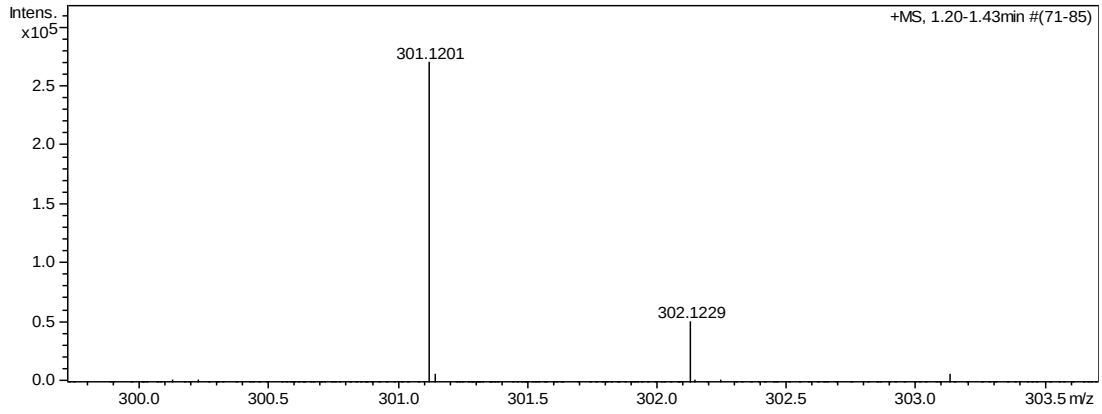
6

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:5) gave the product **6** (21.7 mg, 39% yield) as a yellow solid; m.p.: 63-66 ºC..

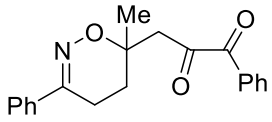
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.50-7.46 (m, 1H), 7.40-7.32 (m, 4H), 7.21-7.18 (m, 3H), 3.87 (s, 1H), 3.16-3.12 (m, 2H), 2.66-2.53 (m, 2H), 2.49 (s, 1H), 2.10-2.03 (m, 1H), 1.97-1.88 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.5, 136.8, 133.1, 131.6, 128.6, 128.2, 128.1, 127.9, 123.2, 85.8, 83.2, 69.7, 34.9, 30.4, 28.6;

HRMS Calcd (ESI) m/z for $C_{19}H_{18}NaO_2$ $[M + Na]^+$: 301.1199, found: 301.1201.



3-(6-Methyl-3-phenyl-5,6-dihydro-4H-1,2-oxazin-6-yl)-1-phenylpropane-1,2-dione (7)



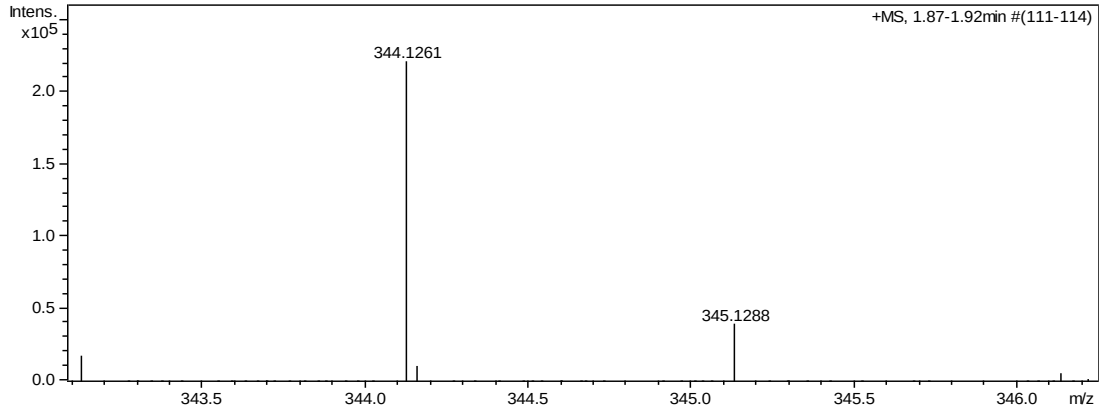
7

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product **7** (31.0 mg, 48% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03-7.99 (m, 2H), 7.67-7.60 (m, 3H), 7.51-7.46 (m, 2H), 7.38-7.35 (m, 3H), 3.32-3.27 (m, 1H), 3.20-3.15 (m, 1H), 2.65-2.61 (m, 2H), 2.21-2.14 (m, 1H), 2.06-2.00 (m, 1H), 1.50 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.6, 191.2, 153.9, 135.4, 134.5, 131.5, 130.4, 129.5, 128.7, 128.4, 125.3, 74.5, 45.5, 27.9, 24.0, 19.0;

HRMS Calcd (ESI) m/z for $C_{20}H_{19}NNaO_3$ $[M + Na]^+$: 344.1257, found: 344.1261.



5. Single Crystal X-Ray Diffraction

Crystals of **3d** were obtained by slow diffusion from a solution of the compounds in $CHCl_3$ layered with petroleum ether at room temperature for several days (Figure S1). Crystal data and details of the structure determination are presented in Table S2.

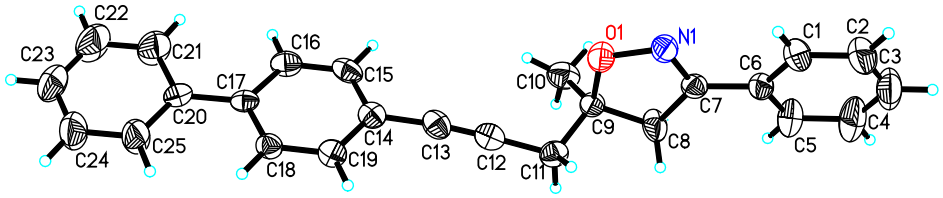


Figure S1. Crystal structure of **3d**

Crystals of **5c** were obtained by slow diffusion from a solution of the compounds in $CHCl_3$ layered with petroleum ether at room temperature for several days (Figure S2). Crystal data and details of the structure determination are presented in Table S2.

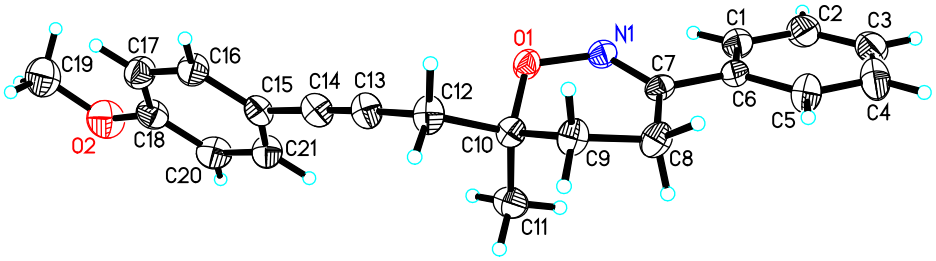


Figure S2. Crystal structure of **5c**

Table S2 The single crystal date of compounds **3b, 5c**

Phase	**3b**	**5c**
Identification code	XSJ20230719	XSJ20231103_a
Empirical formula	$C_{25}H_{21}NO$	$C_{21}H_{21}NO_2$
Formula weight	351.43	319.39
Temperature/K	296(2)	296(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	Cc
a / Å	20.259(6)	20.0023(14)
b / Å	8.444(2)	11.7633(14)
c / Å	11.524(3)	31.100(3)
α (°)	90	90
β (°)	98.245(9)	107.763(4)
γ (°)	90	90
Volume ($Å^3$)	1951.1(10)	6968.7(11)
Z	4	16
Calculated density ($mg·m^{-3}$)	1.196	1.218
Absorption coefficient (mm^{-1})	0.072	0.078
F(000)	744	2720
Crystal size (mm)	0.240 x 0.220 x 0.180	0.240 x 0.220 x 0.180
θ range for data collection	2.617 to 26.000	2.041 to 26.000
Limiting indices	-24<=h<=24, -10<=k<=9, -14<=l<=11	-24<=h<=24, -14<=k<=14, -38<=l<=38
Reflections collected/unique	26292 / 3823 [R(int) = 0.1530]	47862 / 13434 [R(int) = 0.0786]
Completeness to theta	99.8 %	99.9 %
Max. and min. transmission	0.7456 and 0.5849	0.7456 and 0.6689
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3823 / 0 / 245	13434 / 2 / 873
Goodness-of-fit on F^2	1.023	1.005
Final *R* indices[I>2sigma(I)]	R1 = 0.0755, wR2 = 0.1434	R1 = 0.0587, wR2 = 0.1164
R indices (all data)	R1 = 0.2137, wR2 = 0.1922	R1 = 0.1312, wR2 = 0.1406
Largest diff. peak and hole / $Å^{-3}$	0.242 and -0.142	0.156 and -0.174

6. References

1. L. Wang, K. Zhang, Y. Wang, W. Li, M. Chen and J. Zhang, Enantioselective Synthesis of Isoxazolines Enabled by Palladium-Catalyzed Carboetherification of Alkenyl Oximes, *Angew. Chem., Int. Ed.,* 2020, **59**, 4421–4427.

2. S. Wu, S. Zhang, J. Sun, Y. Han, Y. Wang, C.-G. Yan and L. Wang, Synthesis of Multisubstituted Allenes by Palladium-Catalyzed Carboetherification of β,γ-Unsaturated Ketoximes with Propargylic Acetates, *Org. Lett.,* 2023, **25**, 4682–4687.

3. M.-K. Zhu, J.-F. Zhao and T.-P. Loh, Palladium-Catalyzed Oxime Assisted Intramolecular Dioxygenation of Alkenes with 1 atm of Air as the Sole Oxidant, *J. Am. Chem. Soc.,* 2010, **132**, 6284–6285.

4. T. Rouno, T. Niwa, K. Nishibashi, N. Yamamoto, H. Egami and Y. Hamashima, Enantioselective 5-exo-Fluorocyclization of Ene-Oximes, *Molecules.,* 2019, **24**, 3464.

5. L. Xie, Y. Wu, W. Yi, L. Zhu, J. Xiang and W. He, Gold-Catalyzed Hydration of Haloalkynes to α-Halomethyl Ketones, *J. Org. Chem.,* 2013, **78**, 9190–9195.

6. Z.-W. Chen, D.-N. Ye, M. Ye, Z.-G. Zhou, S.-H. Li and L.-X. Liu, AgF/TFA-promoted highly efficient synthesis of α-haloketones from haloalkynes, *Tetrahedron Lett.,* 2014, **55**, 1373-1375.

7. S. Nicolai, R. Sedigh-Zadeh and J. Waser, Pd(0)-Catalyzed Alkene Oxy- and Aminoalkynylation with Aliphatic Bromoacetylenes, *J. Org. Chem.,* 2013, **78**, 3783-3801.

8. K. Yamazaki, S. K. Mahato, Y. Ano and N. Chatani, Double 1,2-Migration of Bromine and Silicon in Directed C-H Alkynylation Reactions with Silyl-Substituted Alkynyl Bromides through an Iridium Vinylidene Intermediate, *Organometallics,* 2022, **41**, 20−28.

9. W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, Investigation of an Efficient Palladium-Catalyzed C(sp)-C(sp) Cross-Coupling Reaction Using Phosphine-Olefin Ligand: Application and Mechanistic Aspects, *J. Am. Chem. Soc.,* 2008, **130**, 14713–14720.

10. X. Bao, Q. Wang and J. Zhu, Palladium-Catalyzed Enantioselective Narasaka–Heck Reaction/ Direct C-H Alkylation of Arenes: Iminoarylation of Alkenes, *Angew. Chem.,*

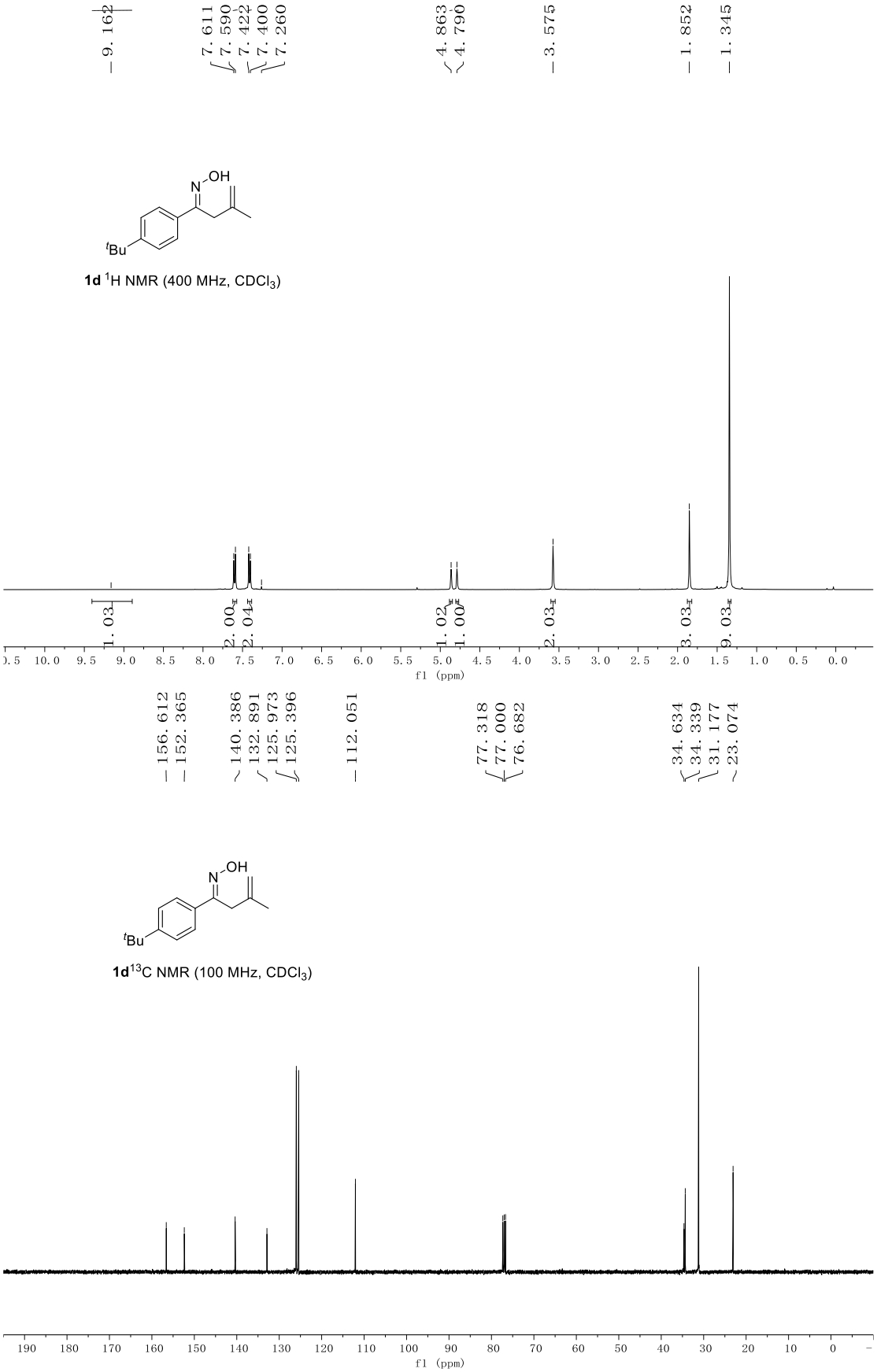
Int. Ed., 2017, **56**, 9577–9581.

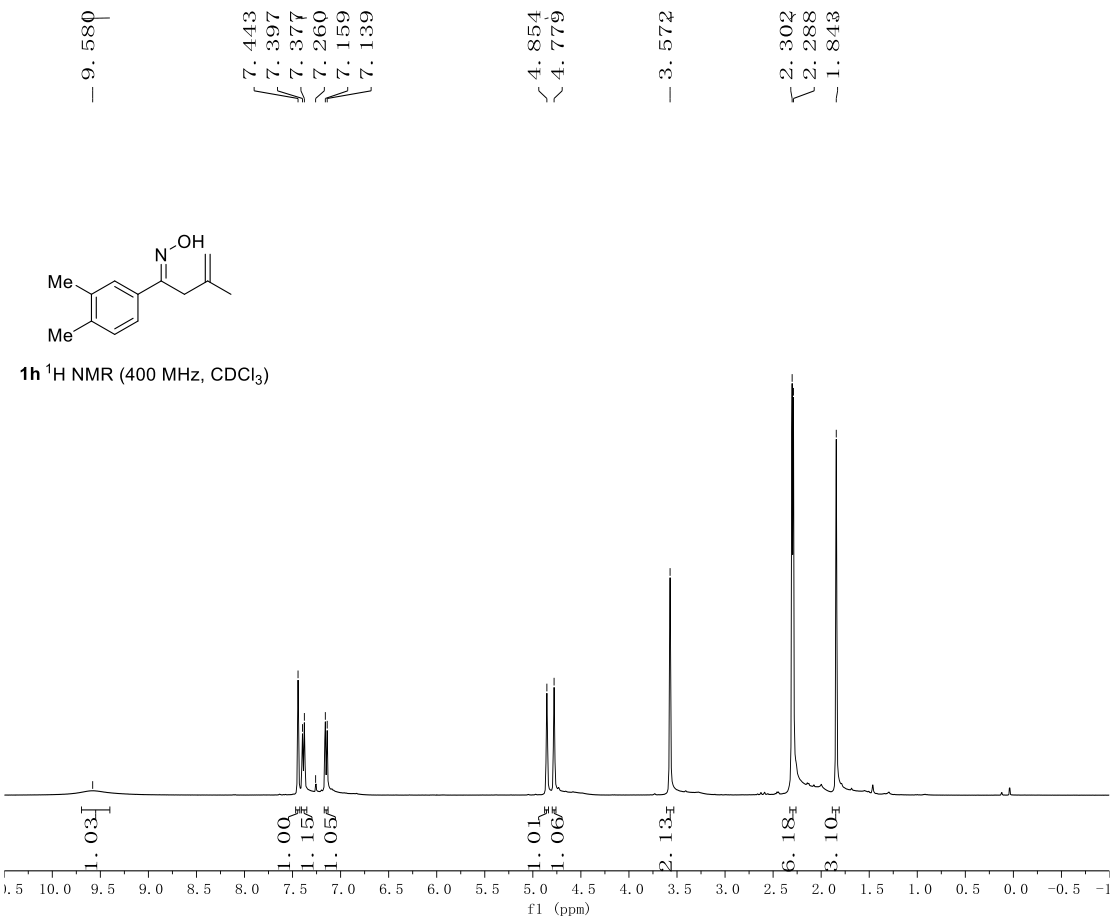
11. R. Suresh, A. K. Simlandy and S. Mukherjee, A Catalytic Enantioselective Iodocyclization Route to Dihydrooxazines, *Org. Lett.,* 2018, **20**, 1300–1303.

12. N. Li, B. Sun, S. Liu, J. Zhao and Q. Zhang, Highly Enantioselective Construction of Dihydrooxazines via Pd-Catalyzed Asymmetric Carboetherification, *Org.Lett.,* 2020, **22**, 190−193.

13. L. Zhou, S. Li, B. Xu, D. Ji, L. Wu, Y. Liu, Z.-M. Zhang and J. Zhang, Enantioselective Difunctionalization of Alkenes by a PalladiumCatalyzed Heck/Sonogashira Sequence, *Angew. Chem. Int. Ed.,* 2020, **59**, 2769 – 2775.

7. Copies of NMR Spectra





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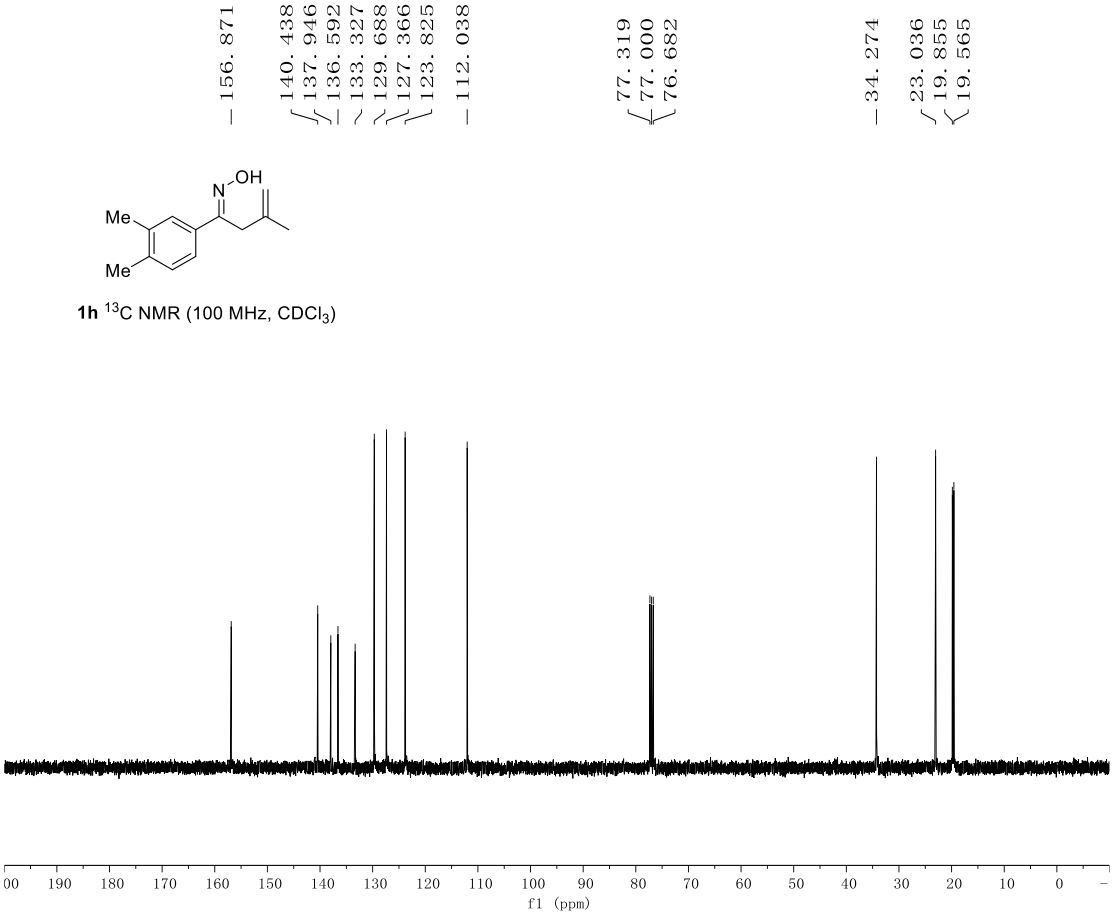

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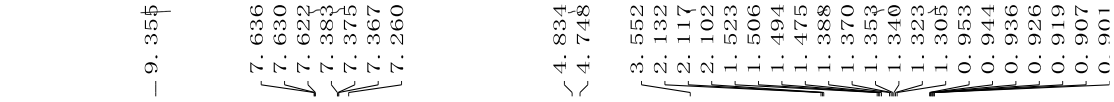

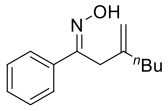

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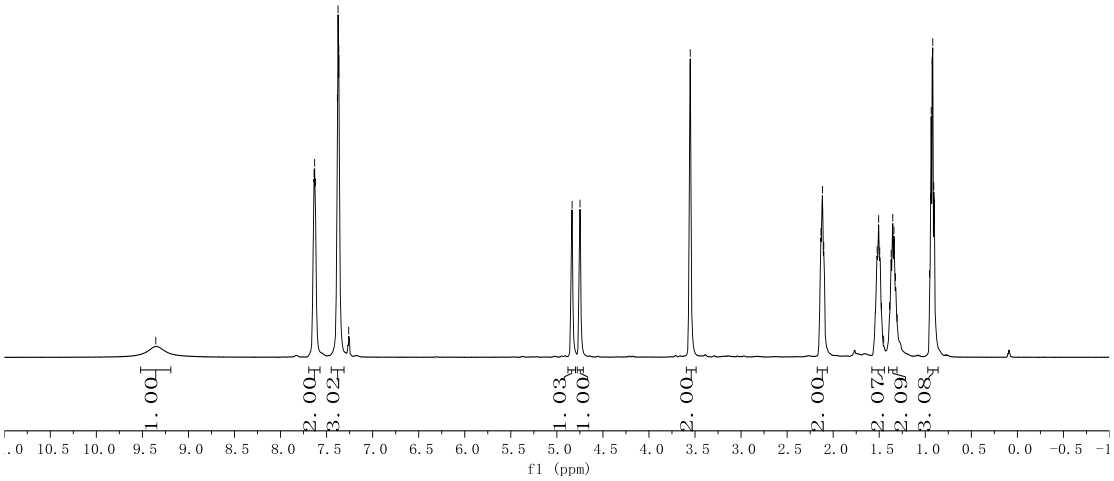

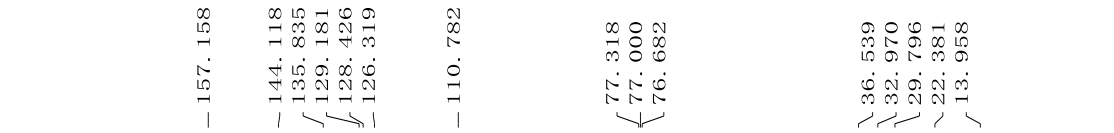

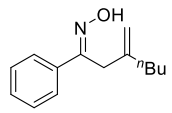

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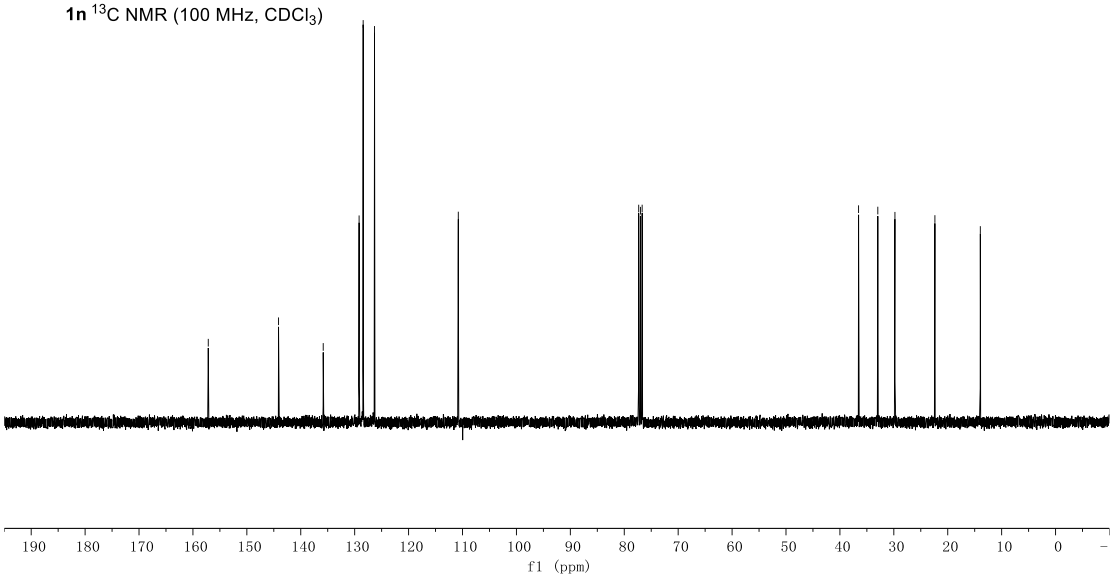

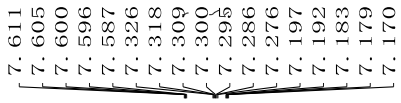

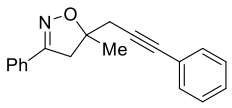

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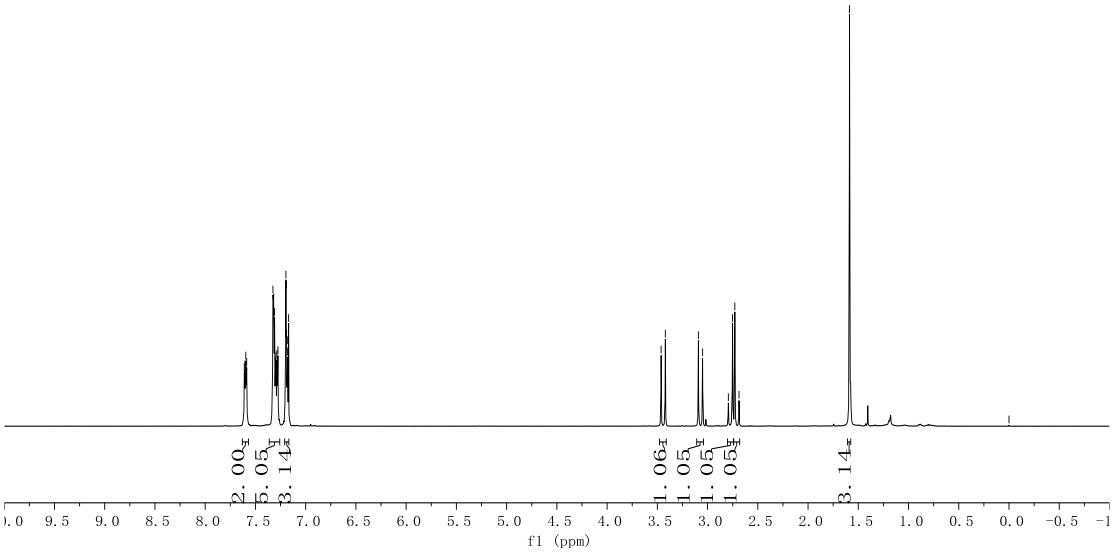

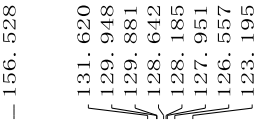

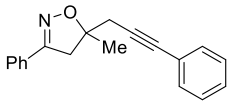

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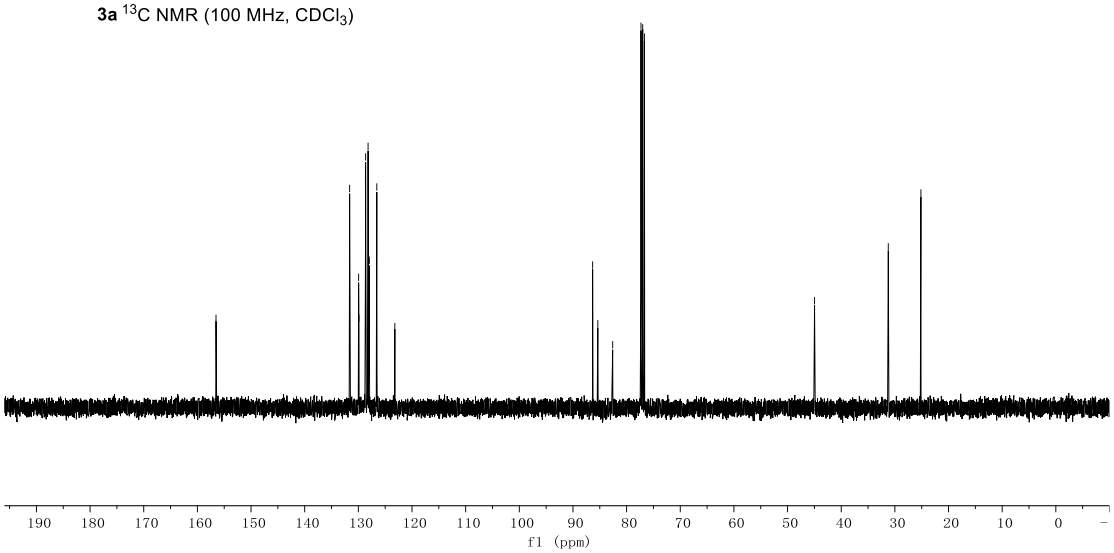

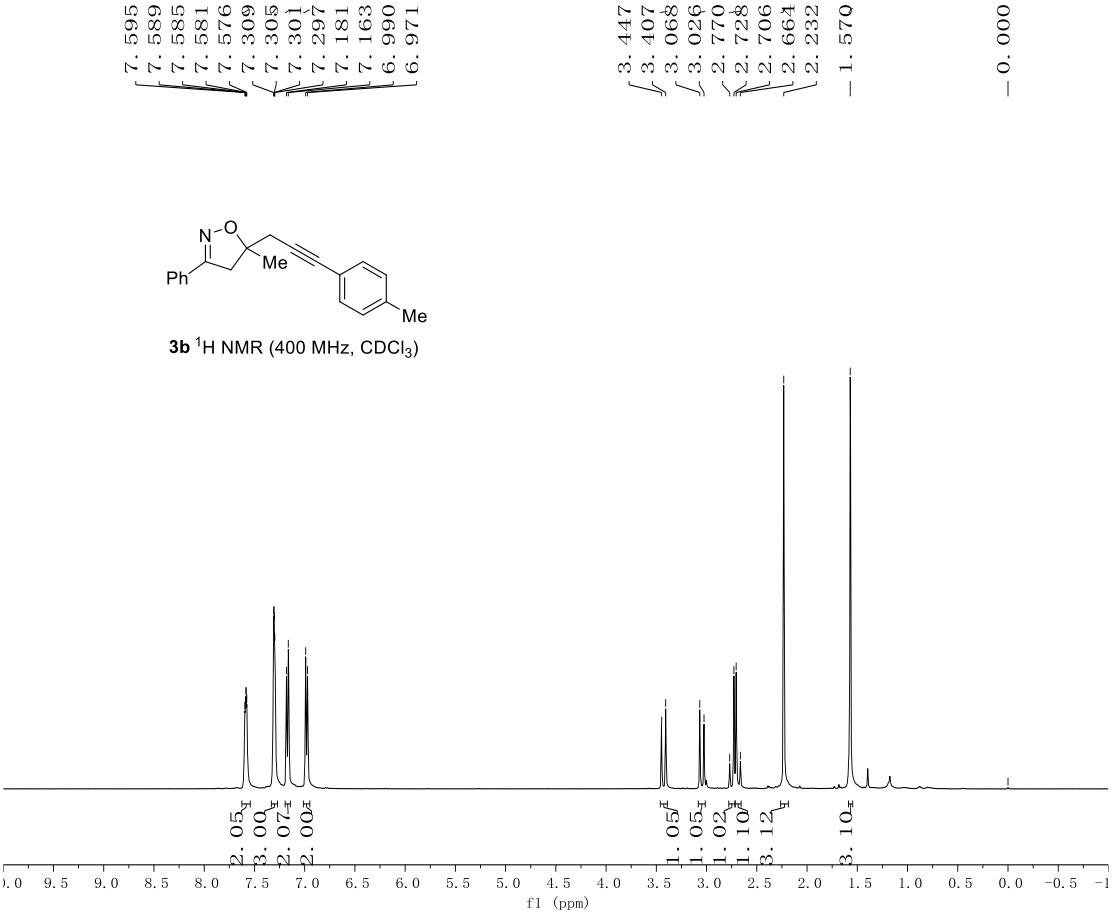

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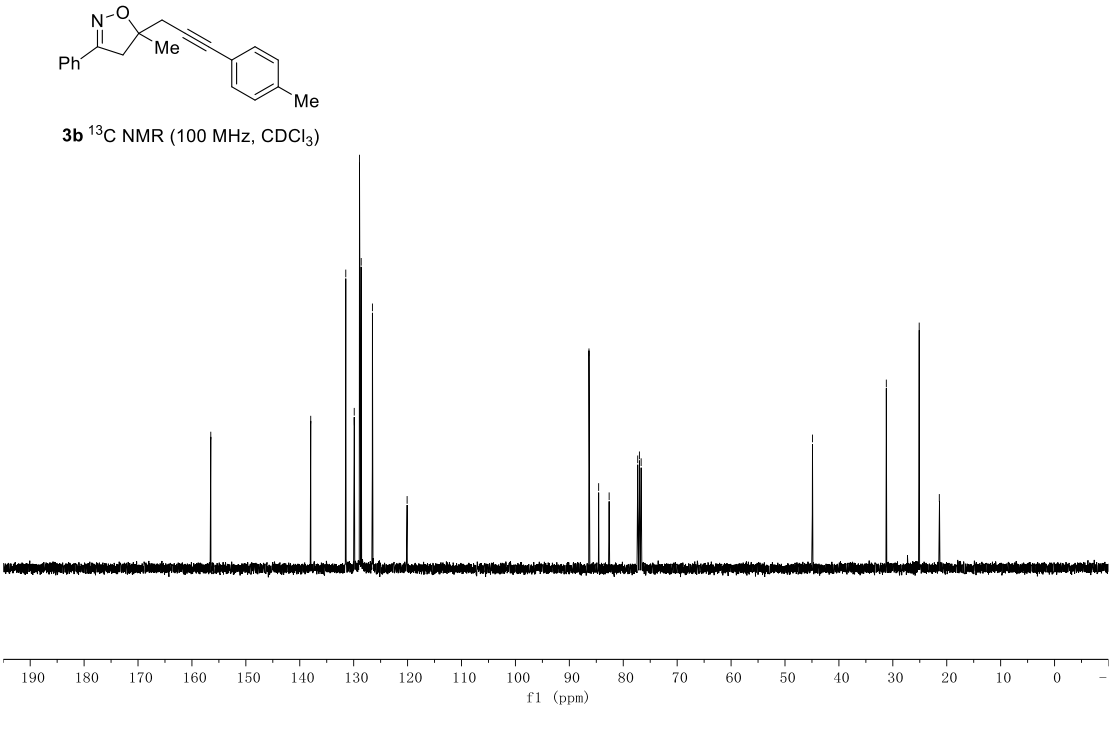

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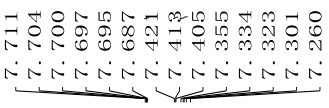

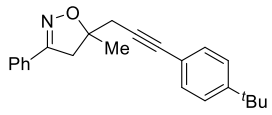

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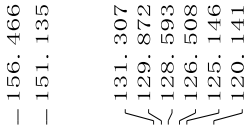

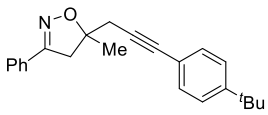

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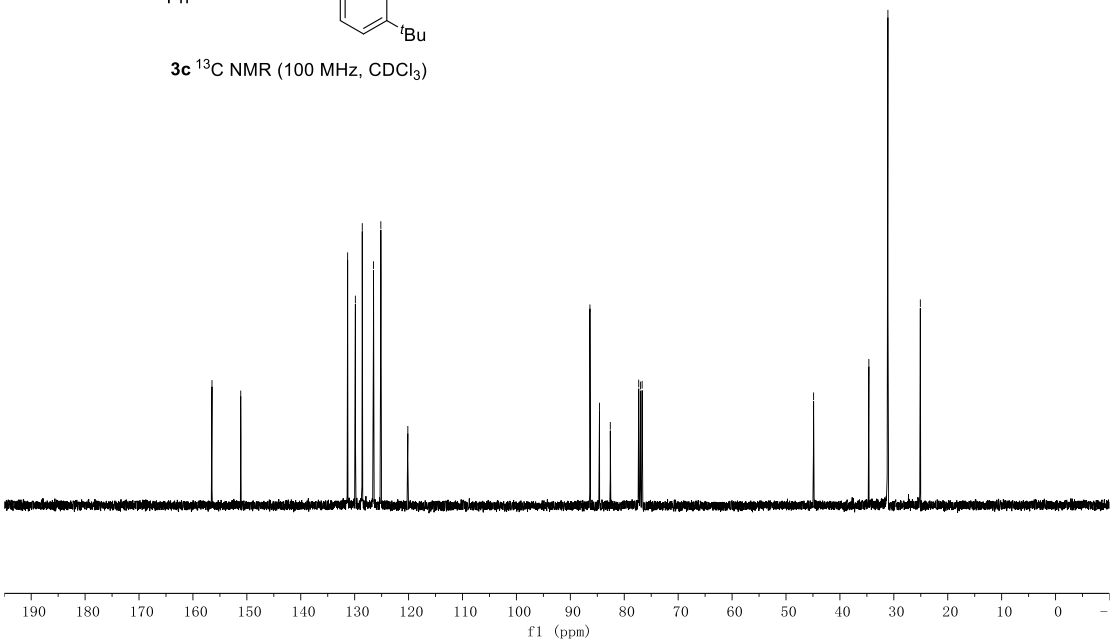

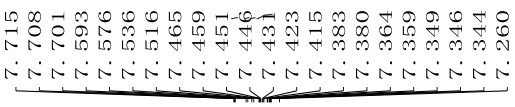

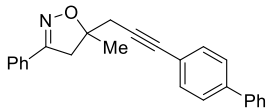

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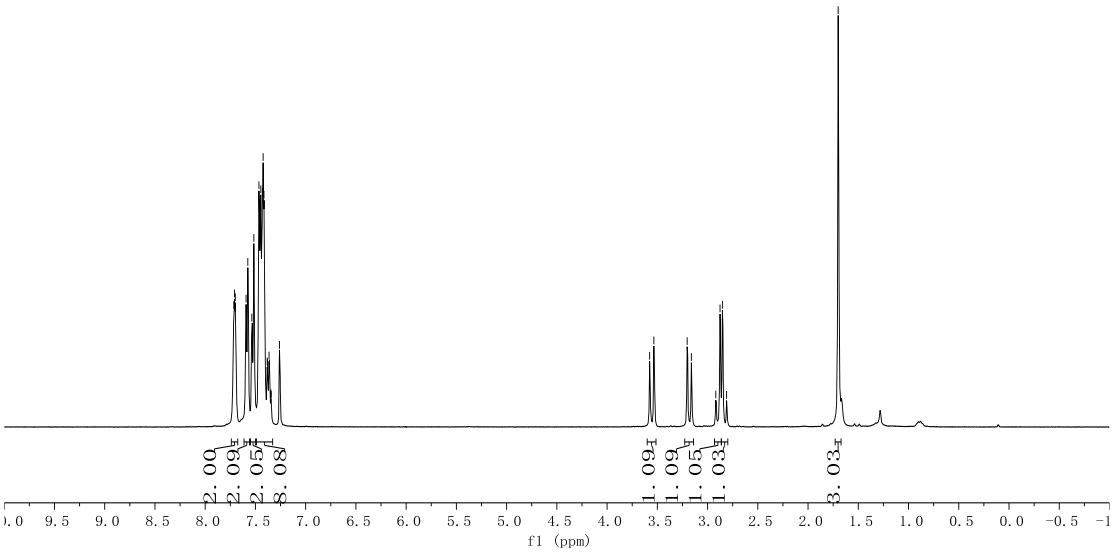

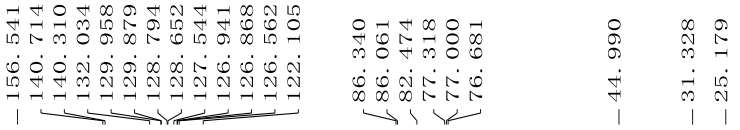

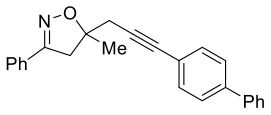

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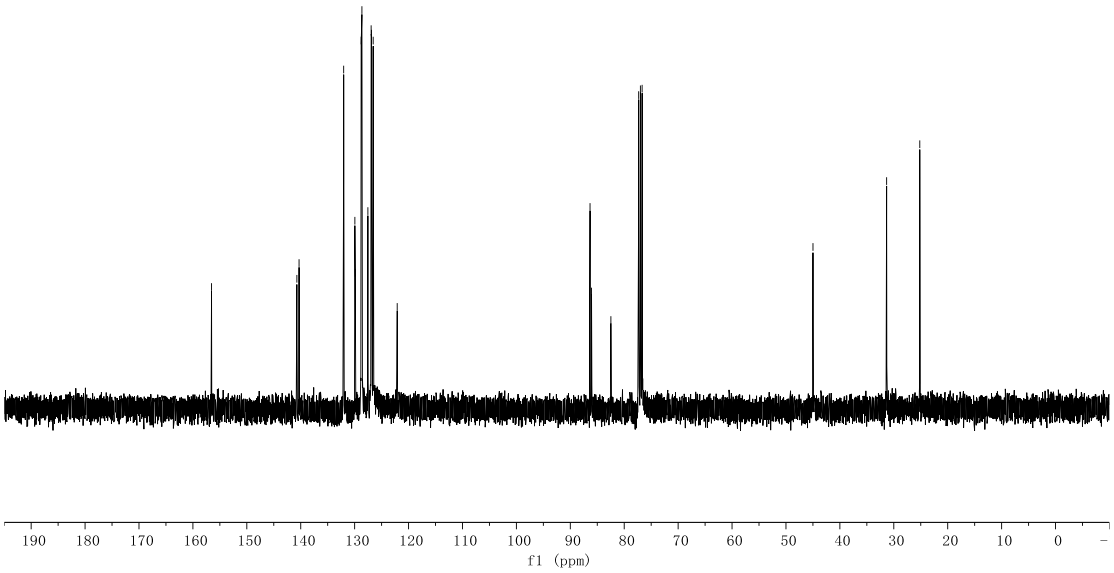

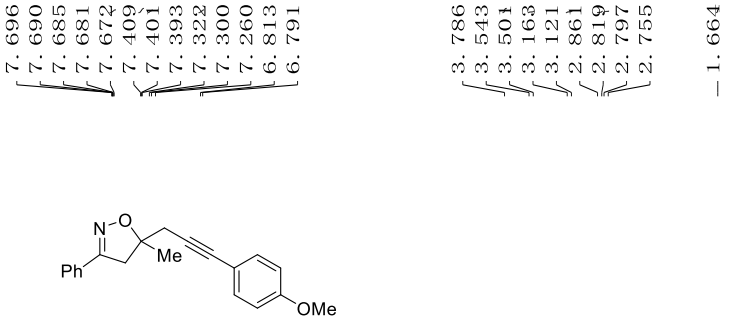

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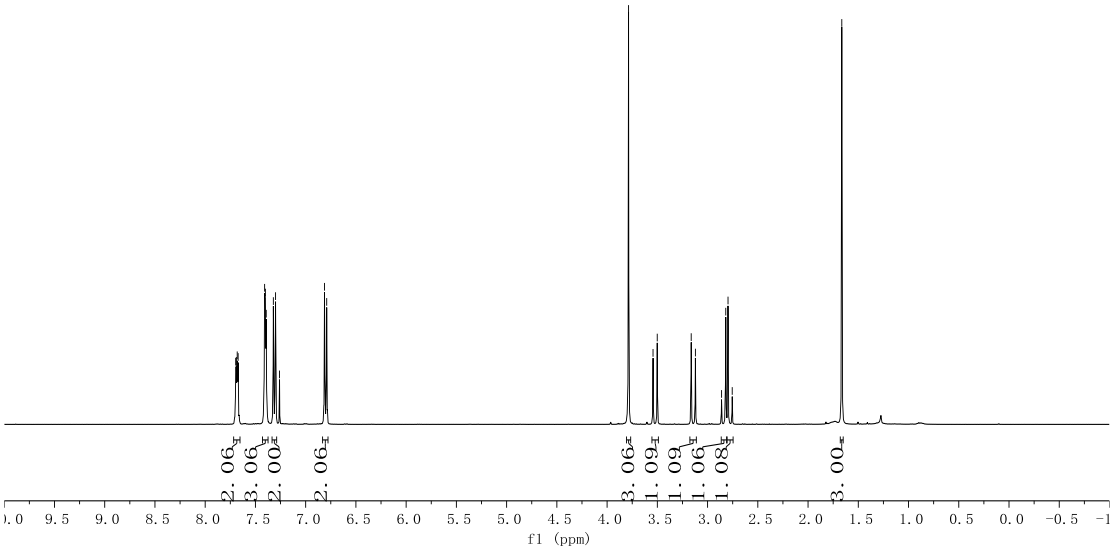

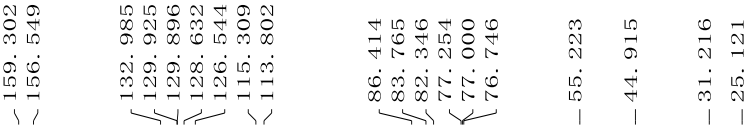

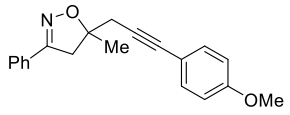

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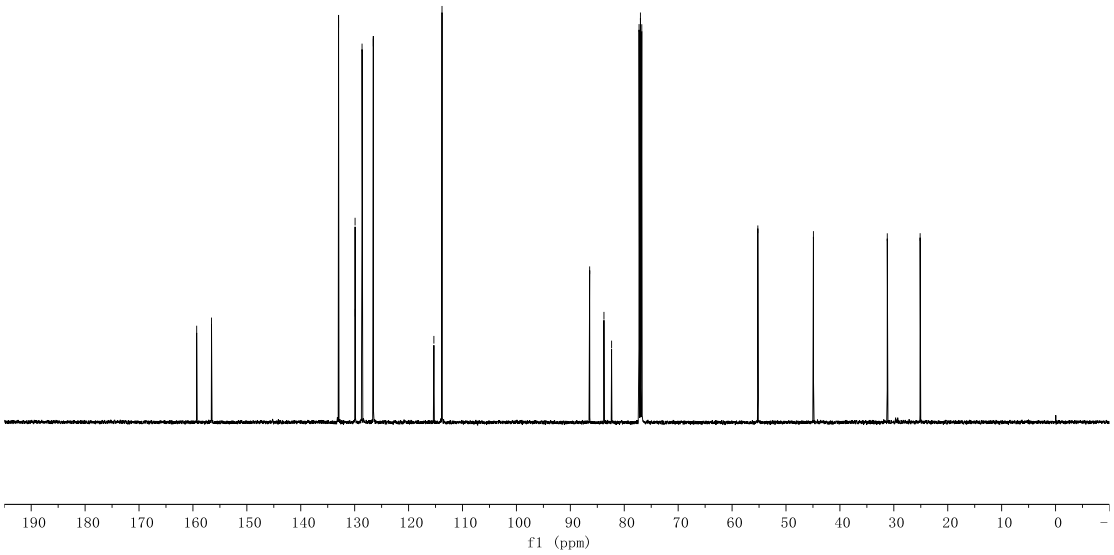
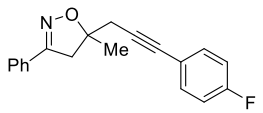
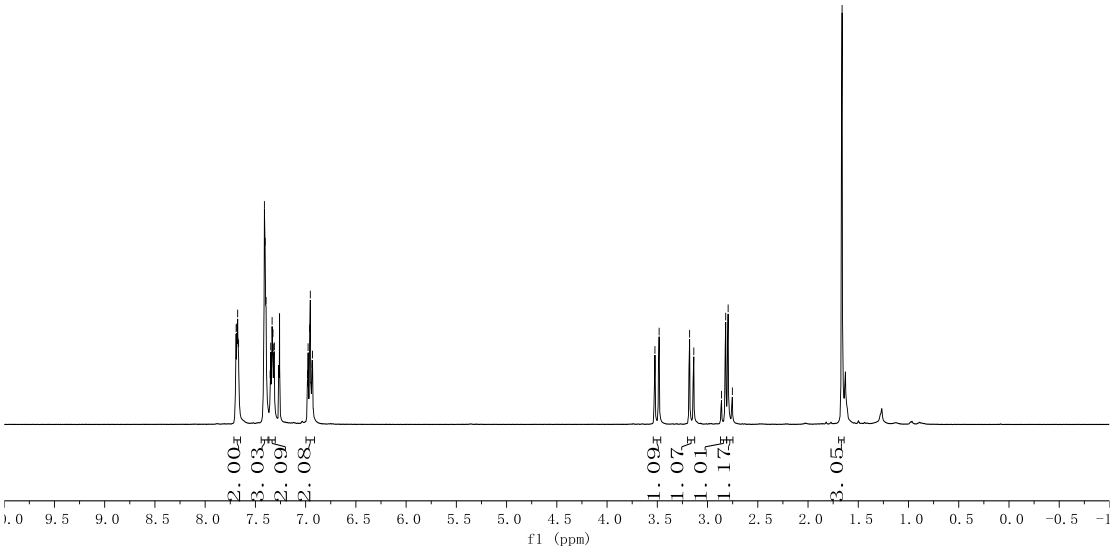
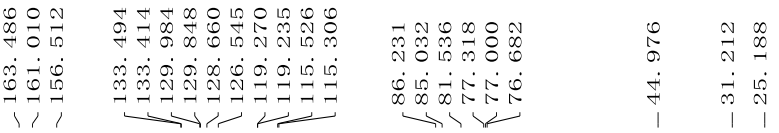
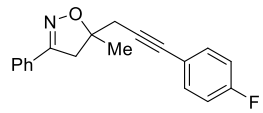




3f ^{1}H NMR (400 MHz, $CDCl_3$)







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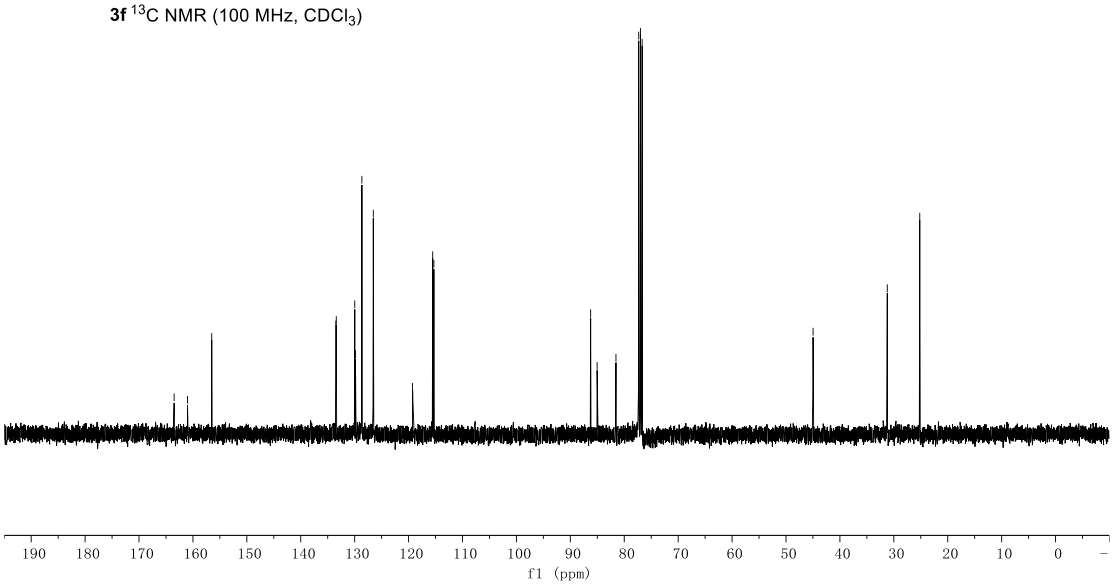
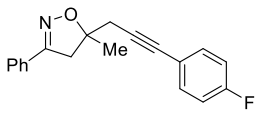
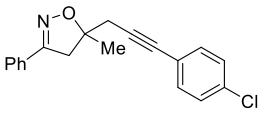
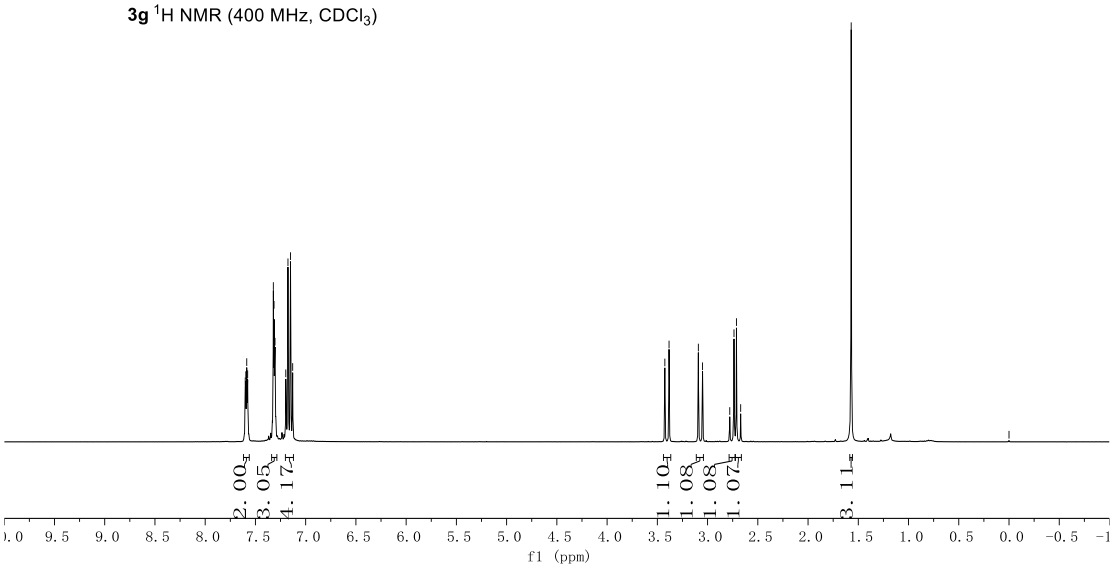


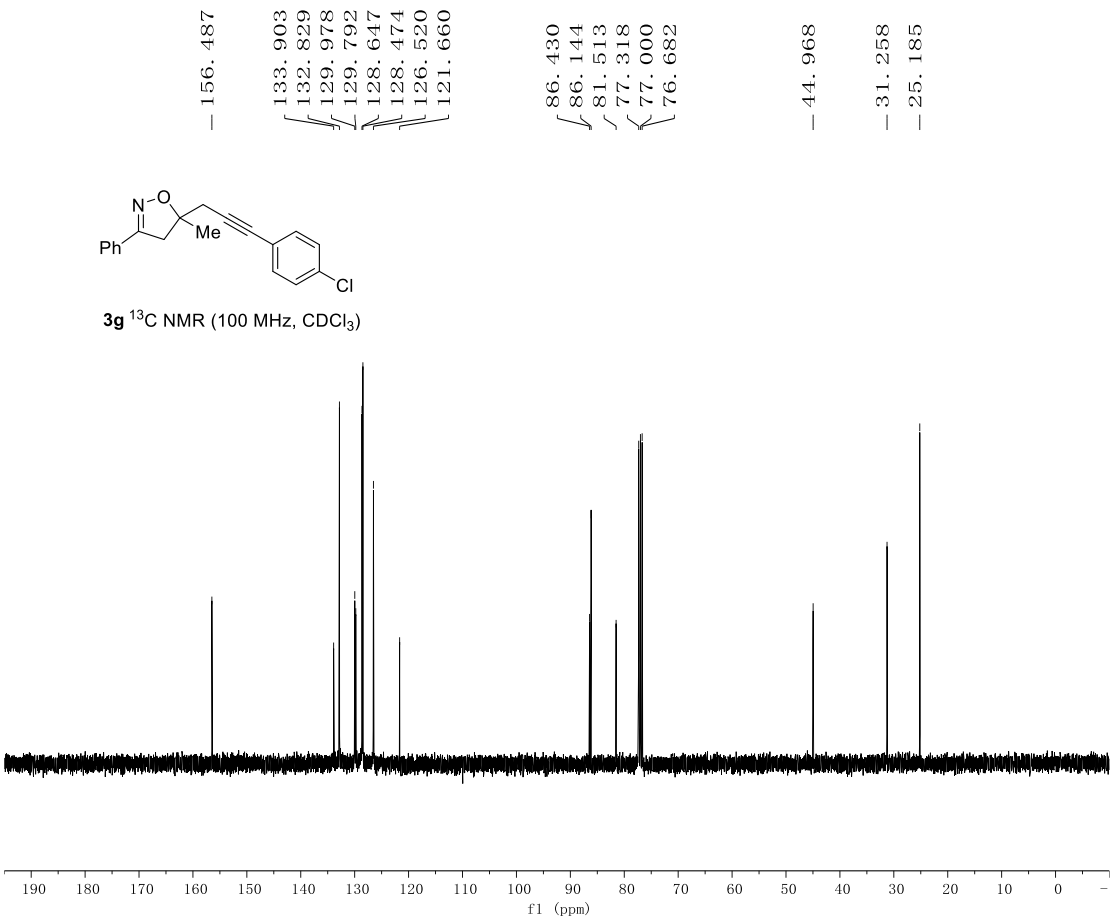


3f ^{19}F NMR (376 MHz, $CDCl_3$)

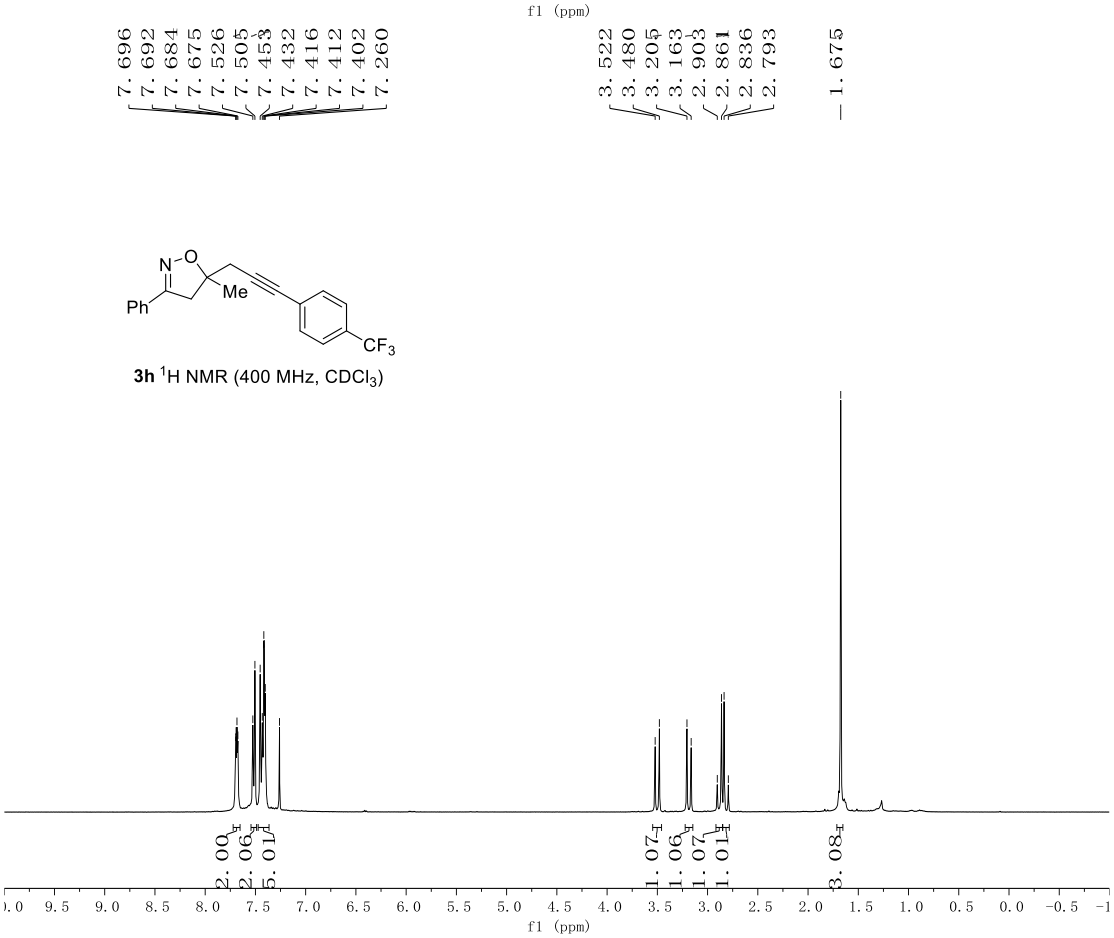


3g ^{1}H NMR (400 MHz, $CDCl_3$)

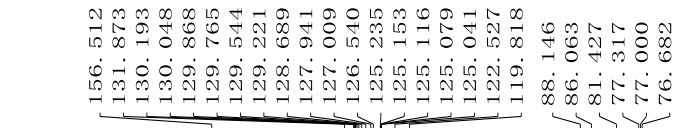


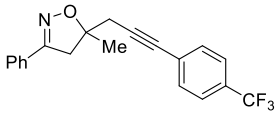


3g ^{13}C NMR (100 MHz, $CDCl_3$)

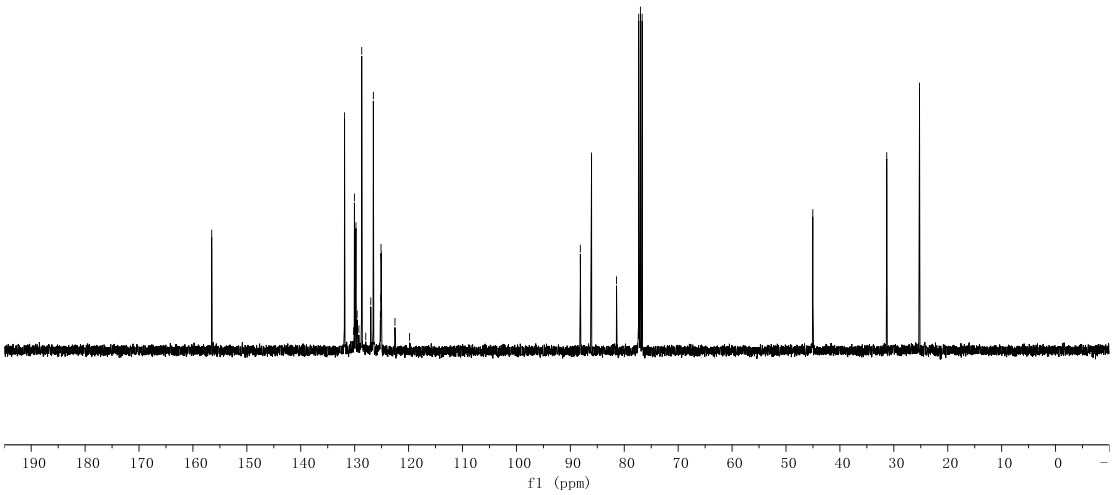


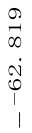
3h ^{1}H NMR (400 MHz, $CDCl_3$)

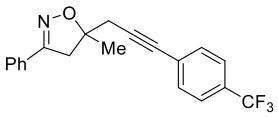




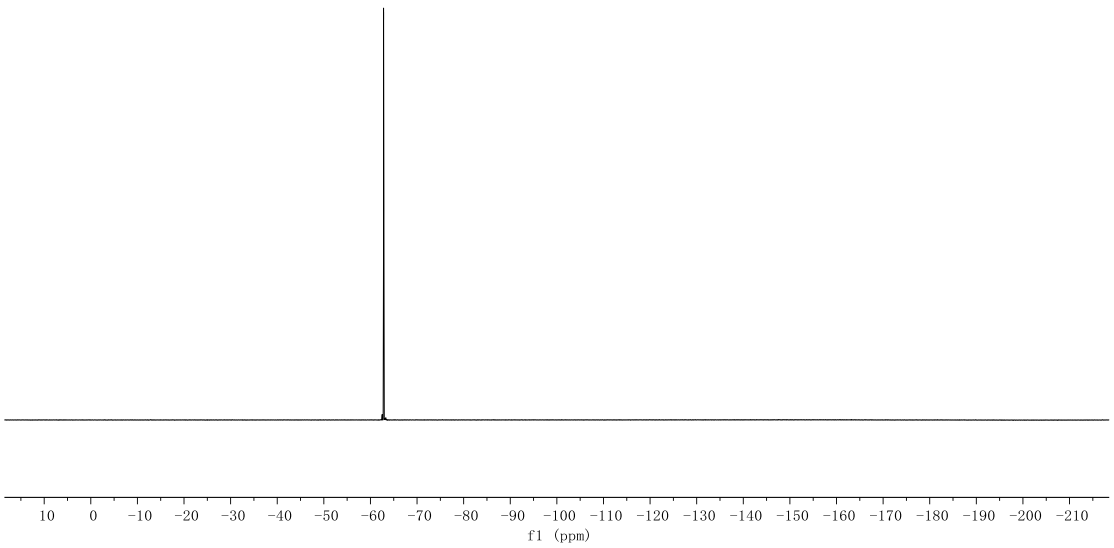
3h ^{13}C NMR (100 MHz, $CDCl_3$)

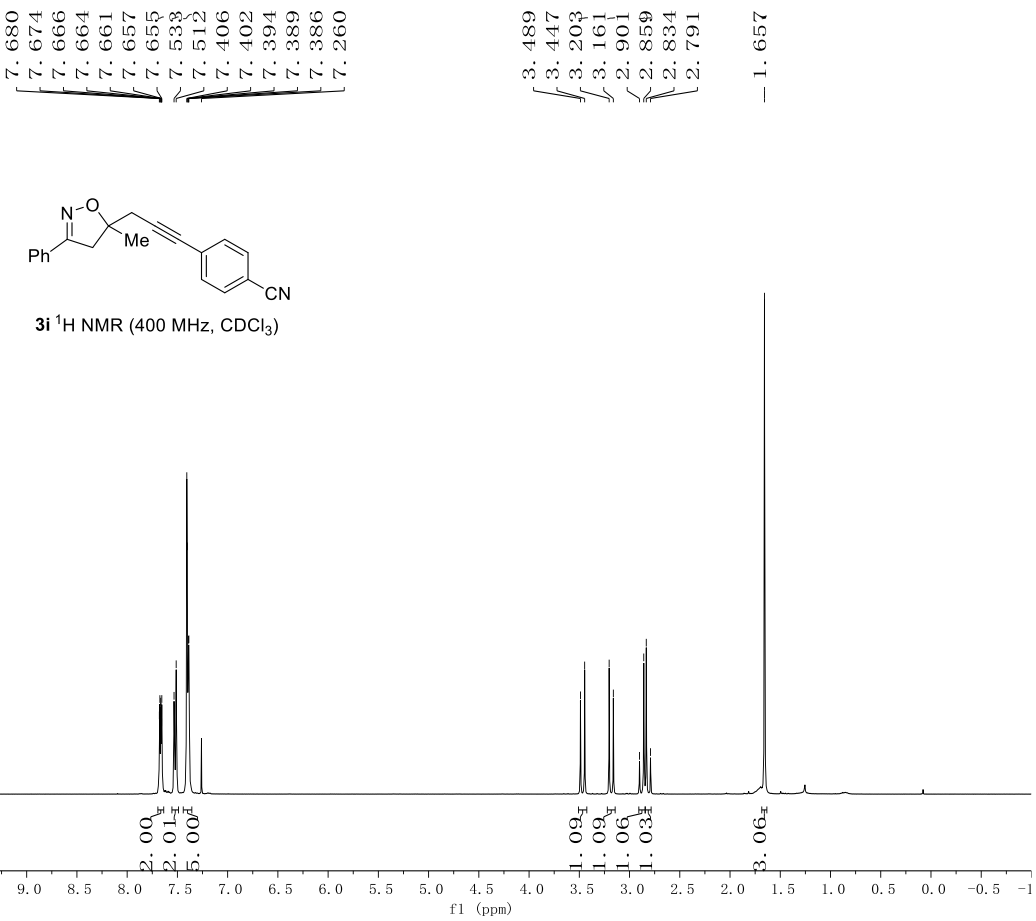




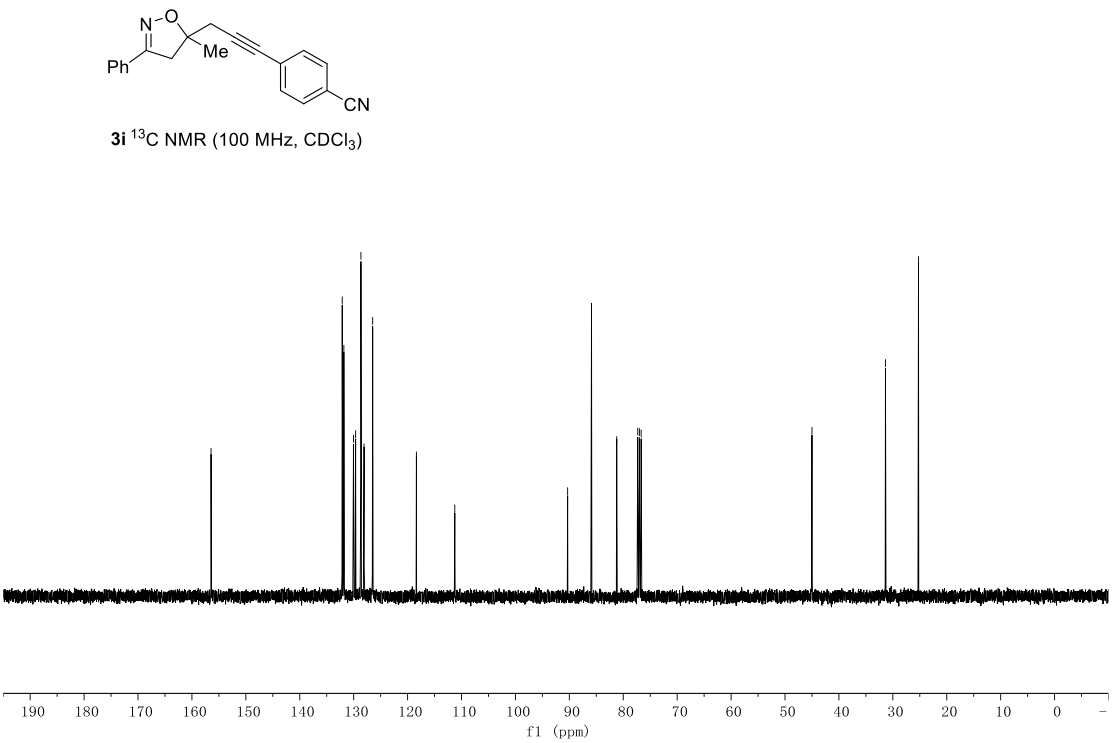


3h ^{19}F NMR (376 MHz, $CDCl_3$)

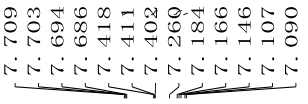


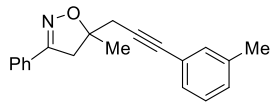


3i ^{1}H NMR (400 MHz, $CDCl_3$)

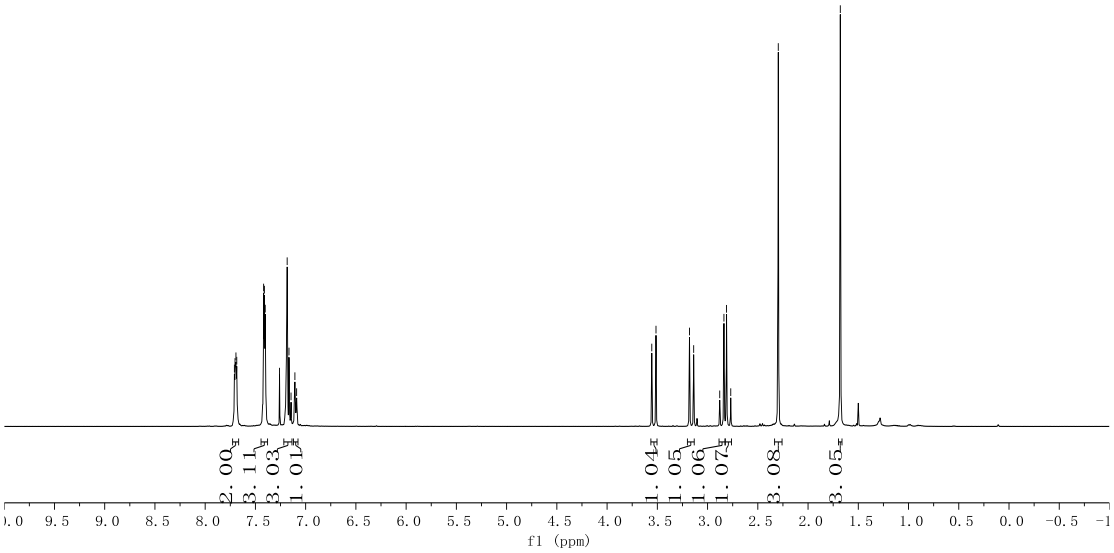


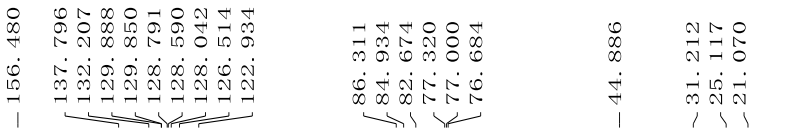
3i ^{13}C NMR (100 MHz, $CDCl_3$)

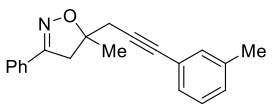




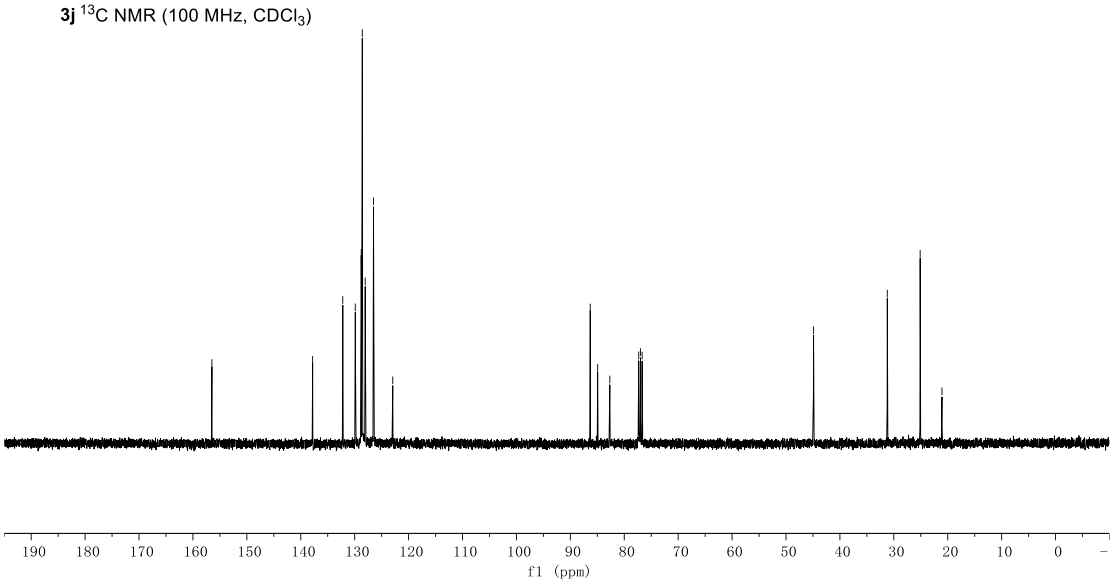
3j ^{1}H NMR (400 MHz, $CDCl_3$)

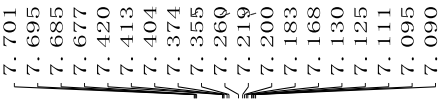


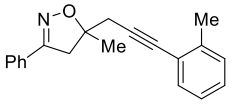




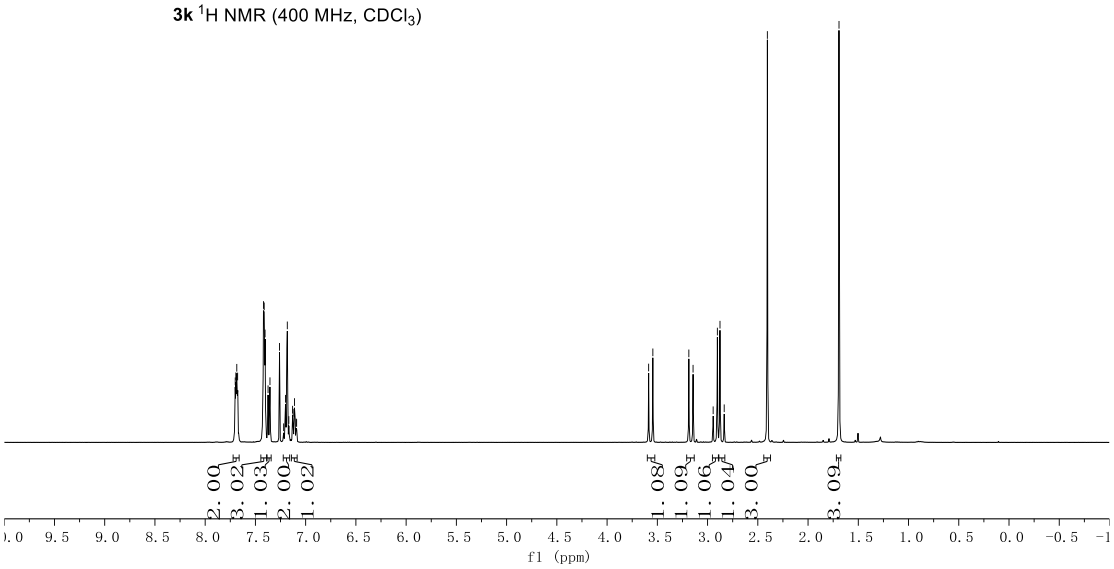
3j ^{13}C NMR (100 MHz, $CDCl_3$)

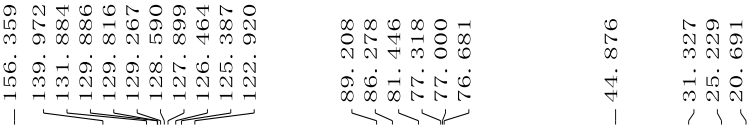


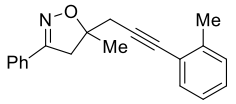




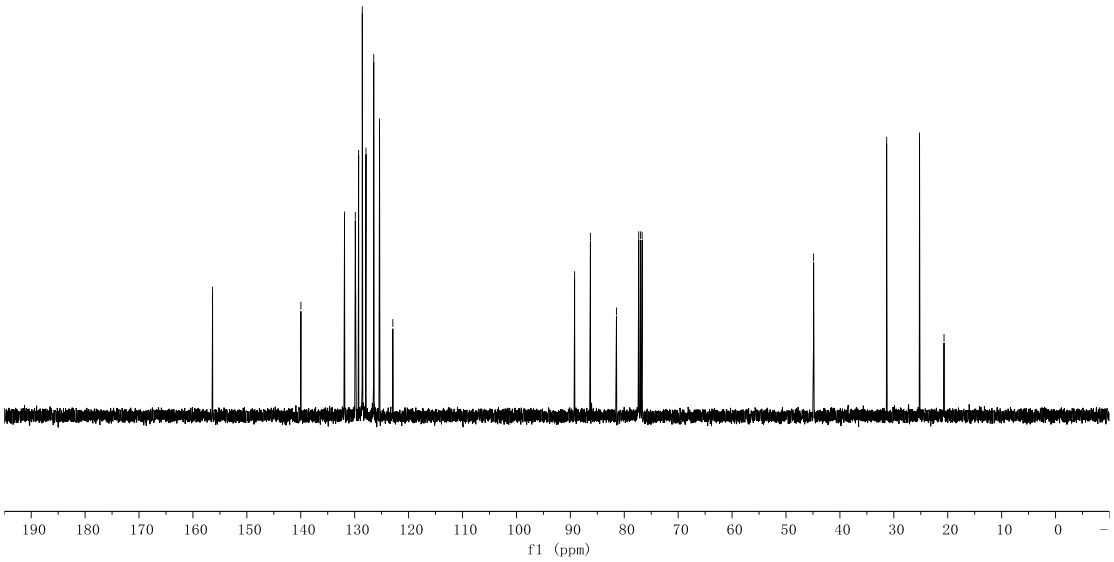
3k ^{1}H NMR (400 MHz, $CDCl_3$)

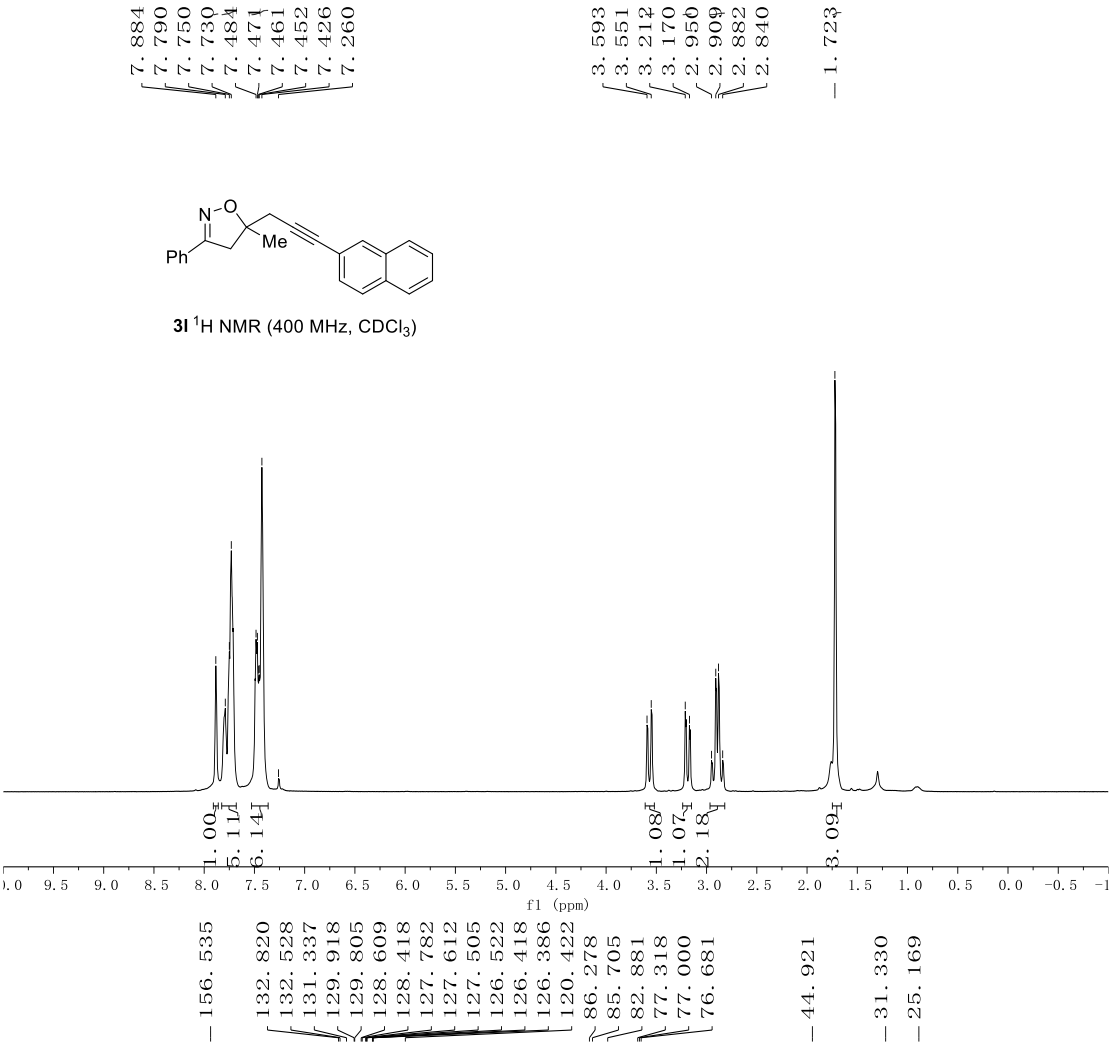




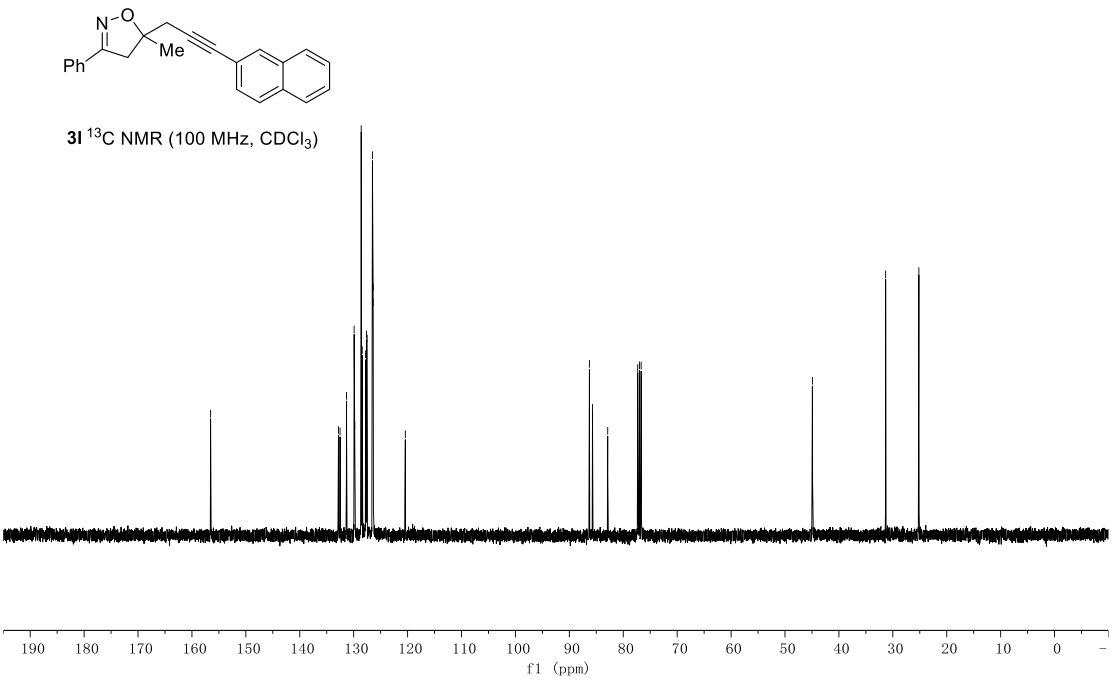


3k ^{13}C NMR (100 MHz, $CDCl_3$)

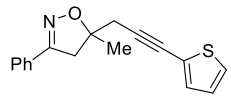




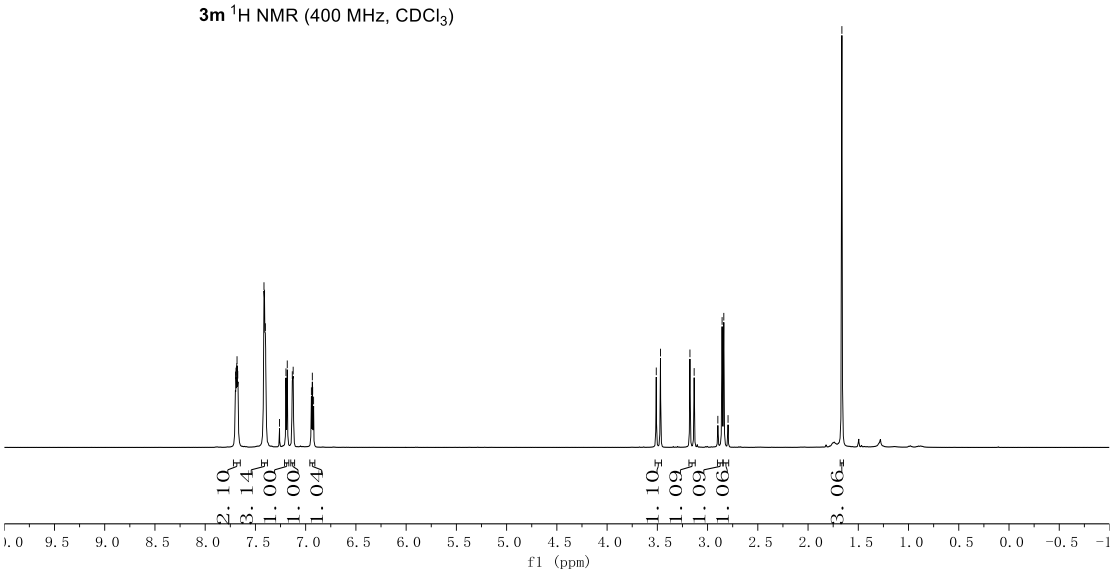
3l ^{1}H NMR (400 MHz, $CDCl_3$)

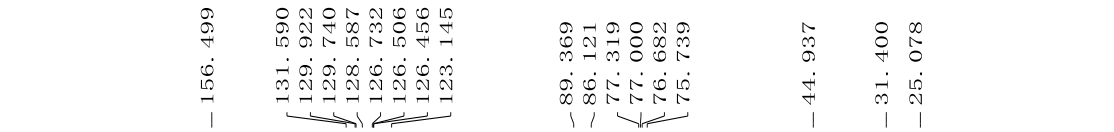


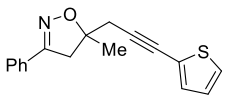
3l ^{13}C NMR (100 MHz, $CDCl_3$)



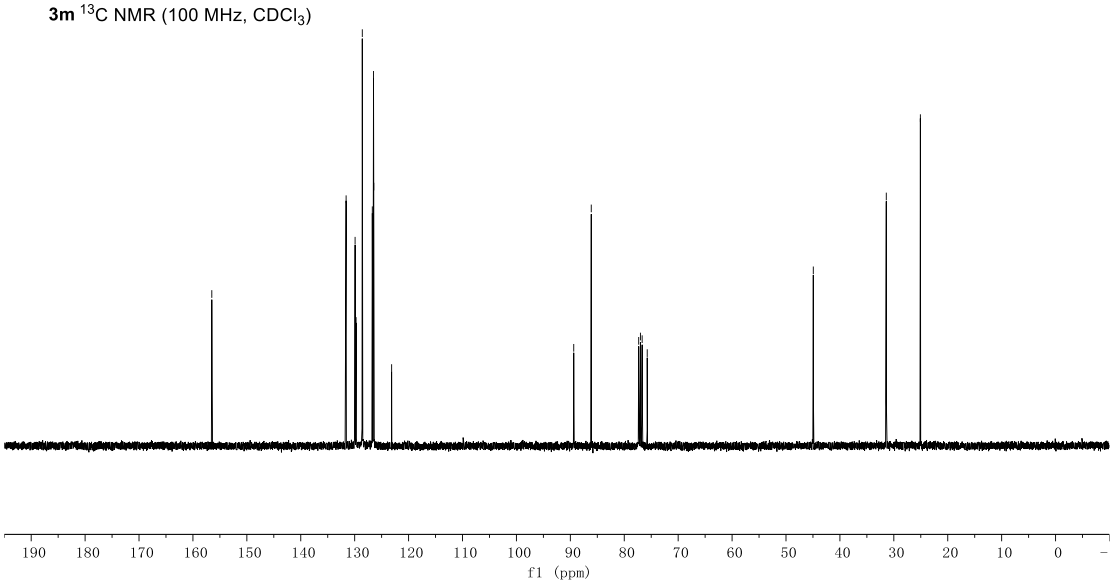
3m ^{1}H NMR (400 MHz, $CDCl_3$)

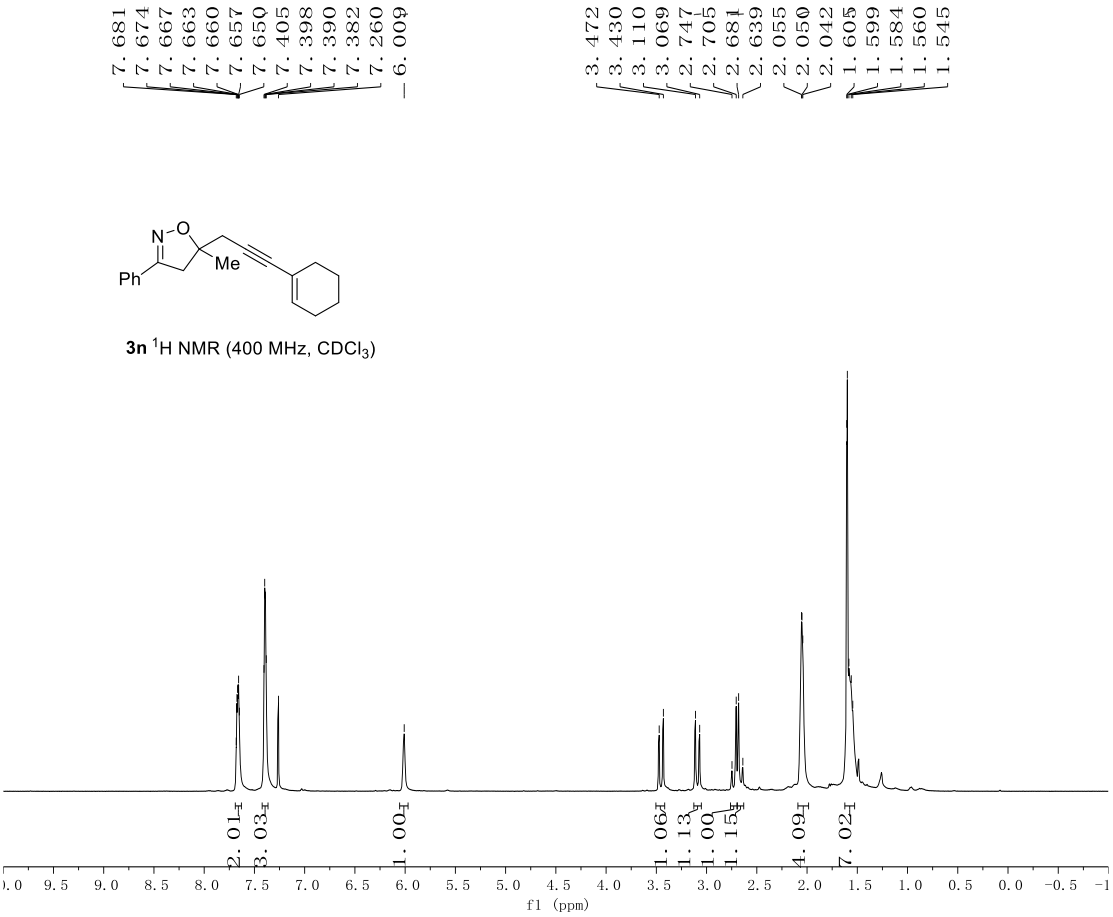




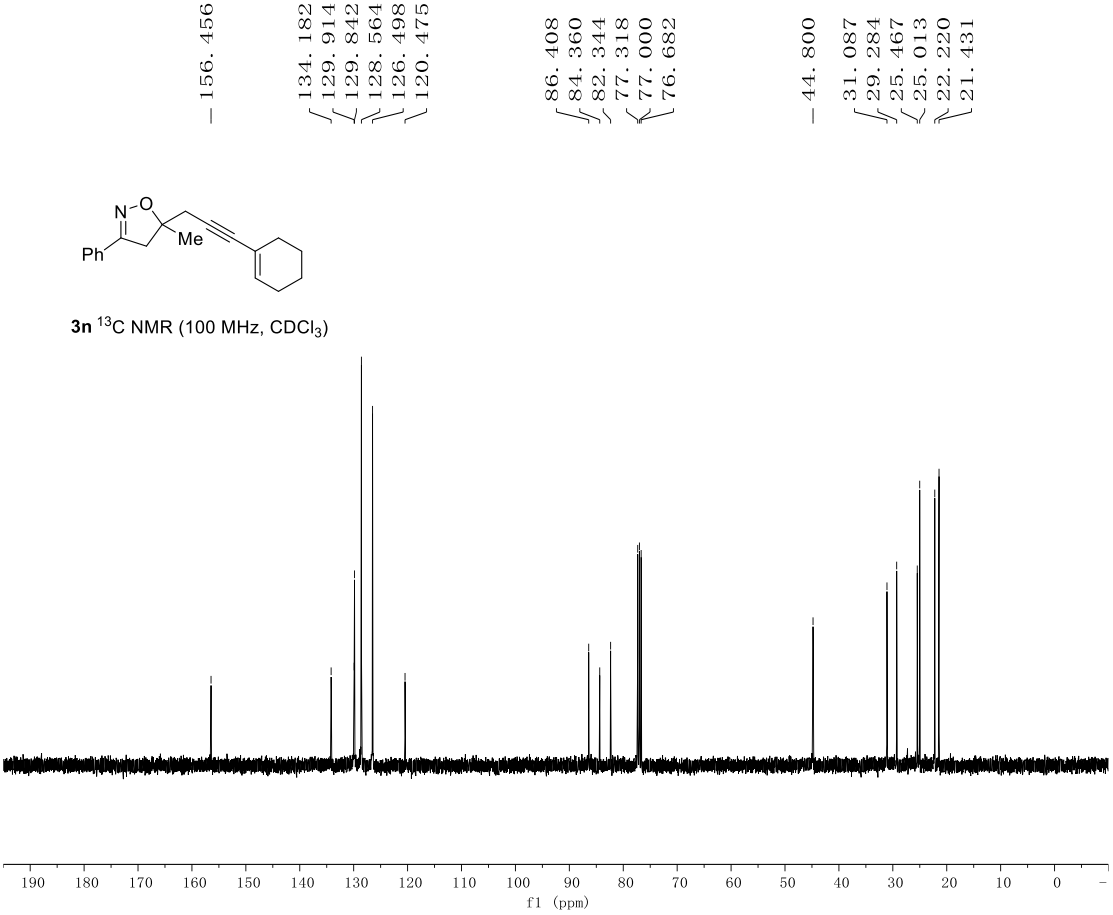


3m ^{13}C NMR (100 MHz, $CDCl_3$)

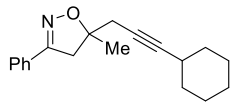




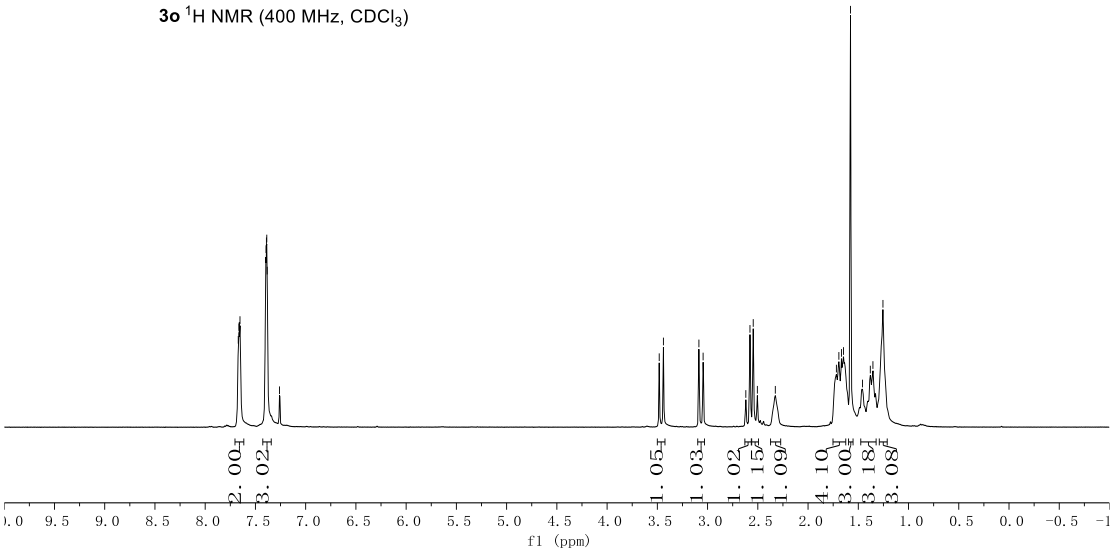
3n ^{1}H NMR (400 MHz, $CDCl_3$)

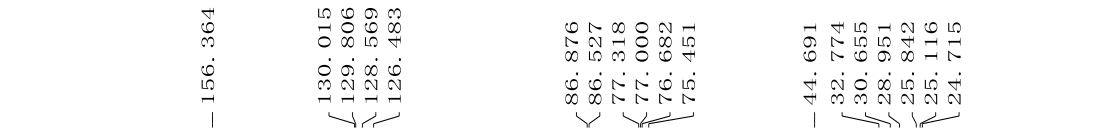


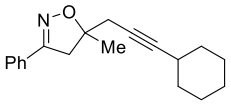
3n ^{13}C NMR (100 MHz, $CDCl_3$)



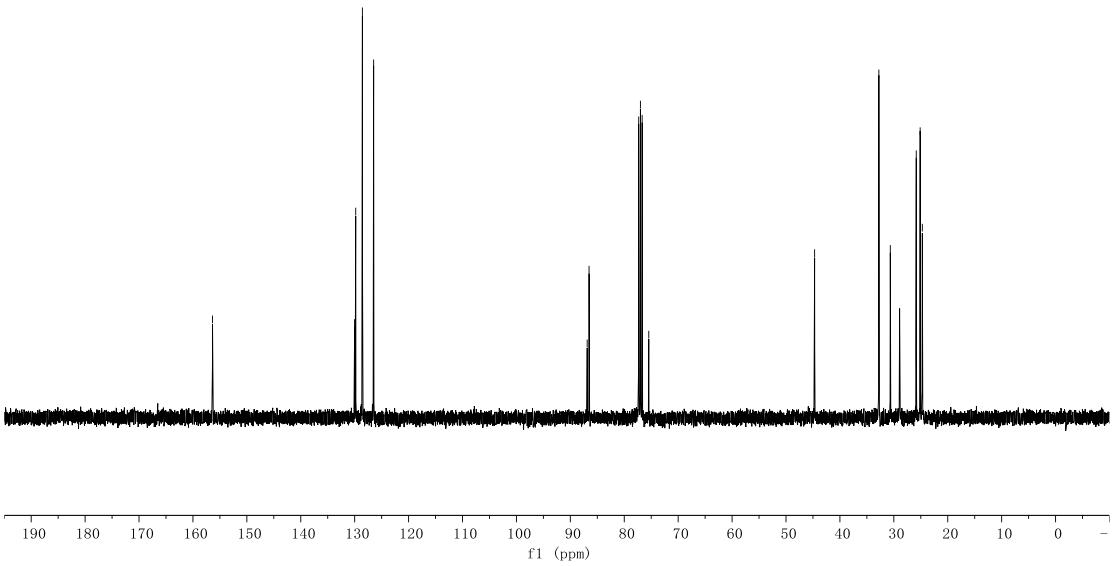
3o ^{1}H NMR (400 MHz, $CDCl_3$)

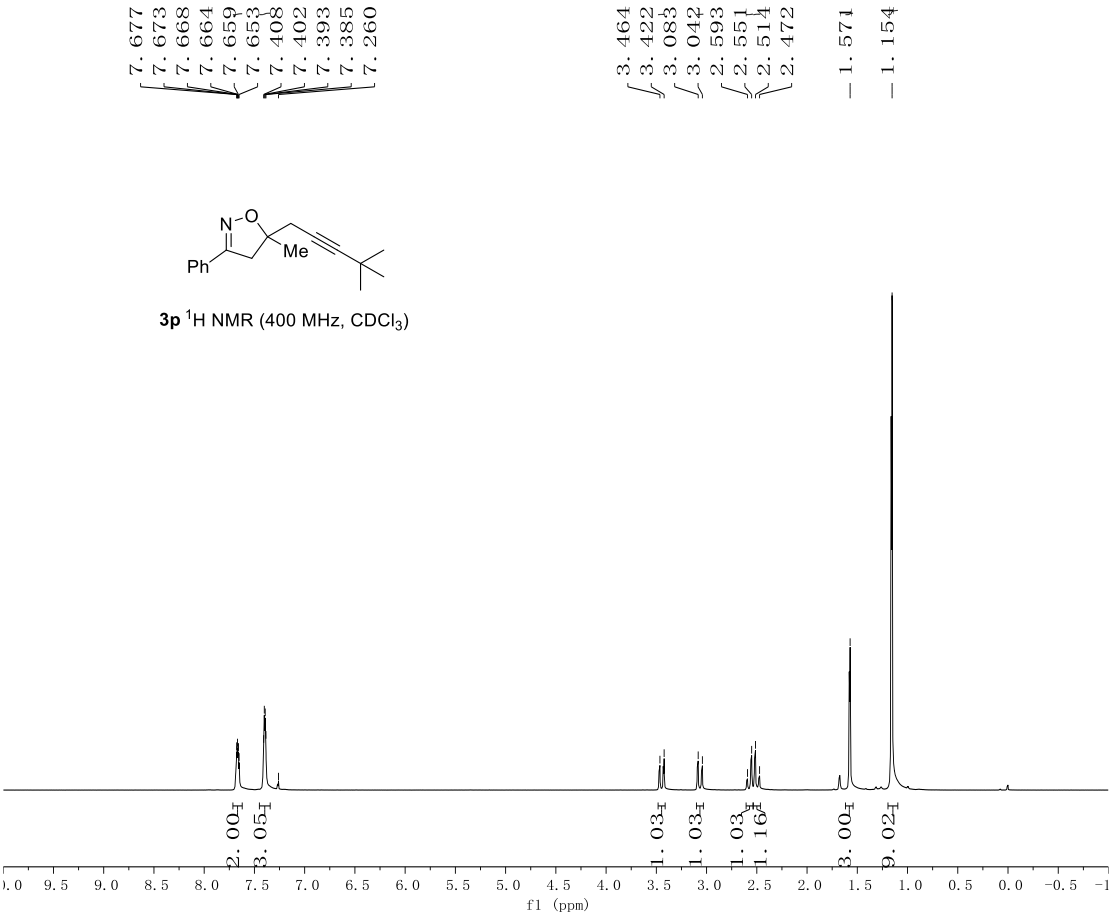




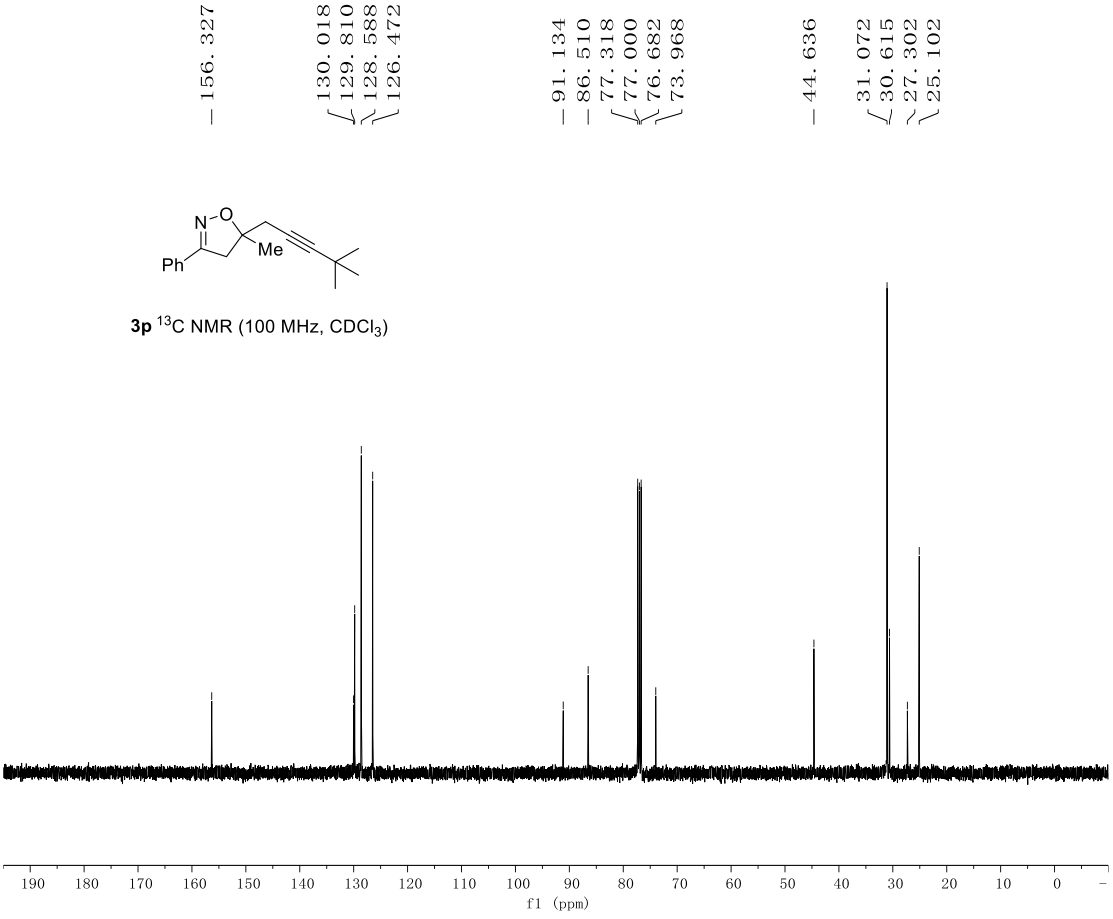


3o ^{13}C NMR (100 MHz, $CDCl_3$)

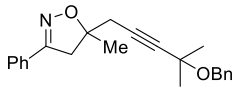




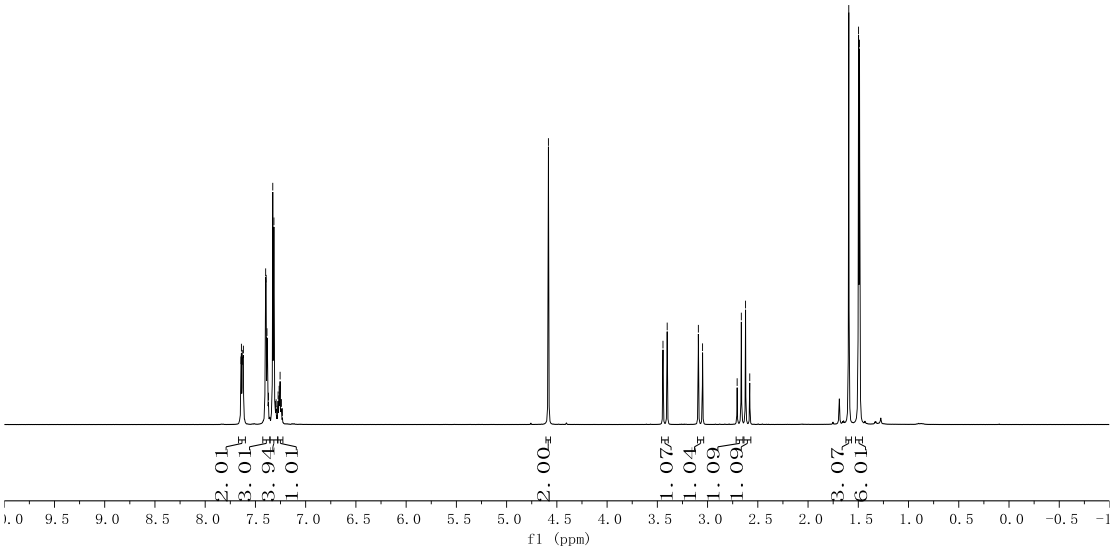
3p ^{1}H NMR (400 MHz, $CDCl_3$)

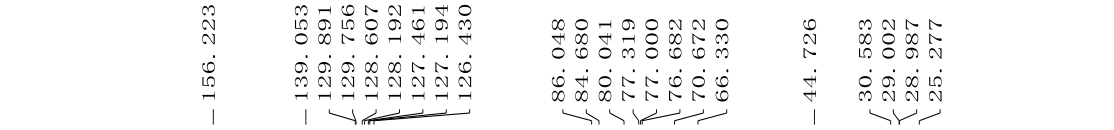


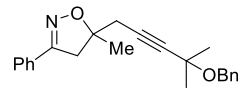
3p ^{13}C NMR (100 MHz, $CDCl_3$)



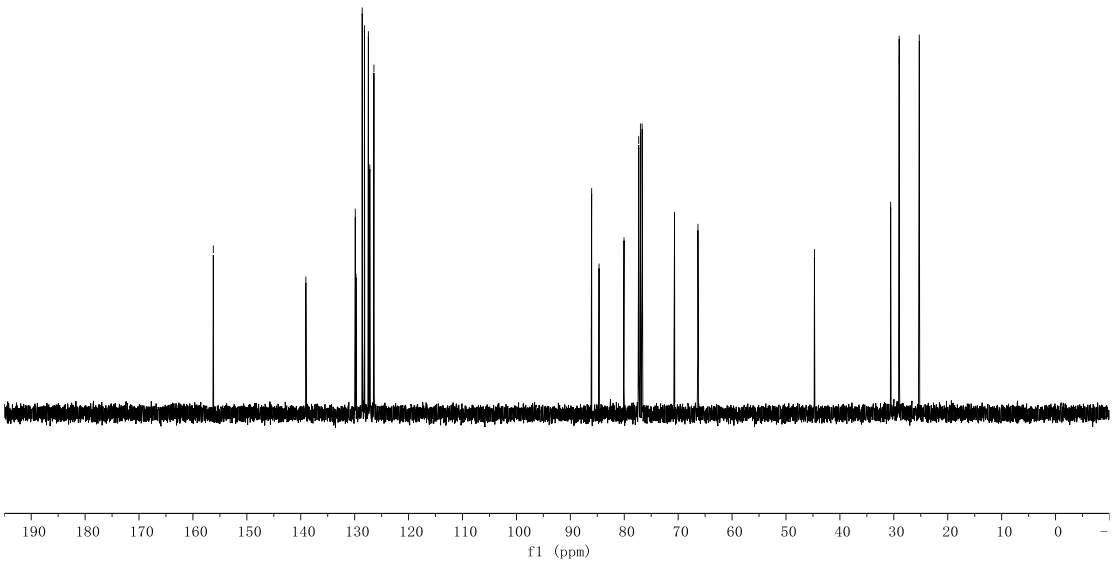
3q ^{1}H NMR (400 MHz, $CDCl_3$)

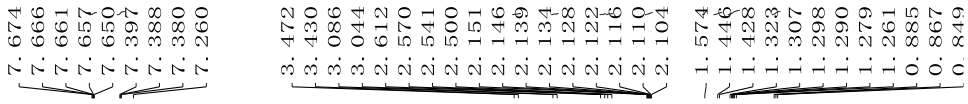


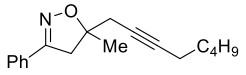




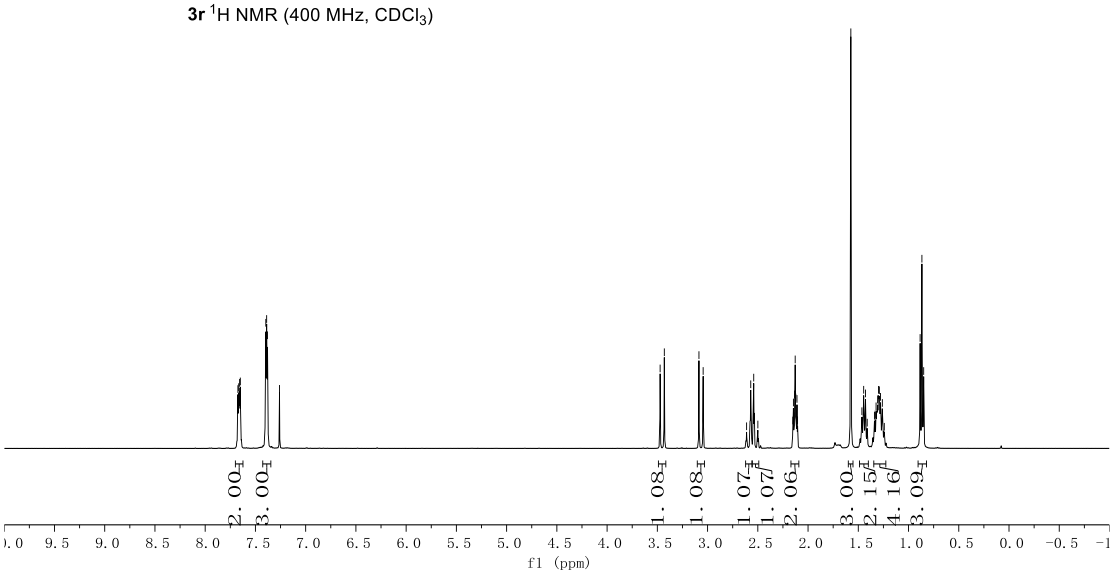
3q ^{13}C NMR (100 MHz, $CDCl_3$)

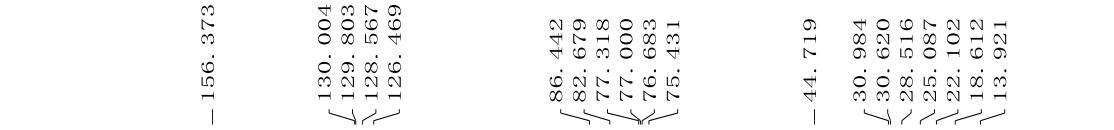


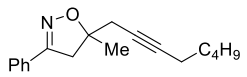




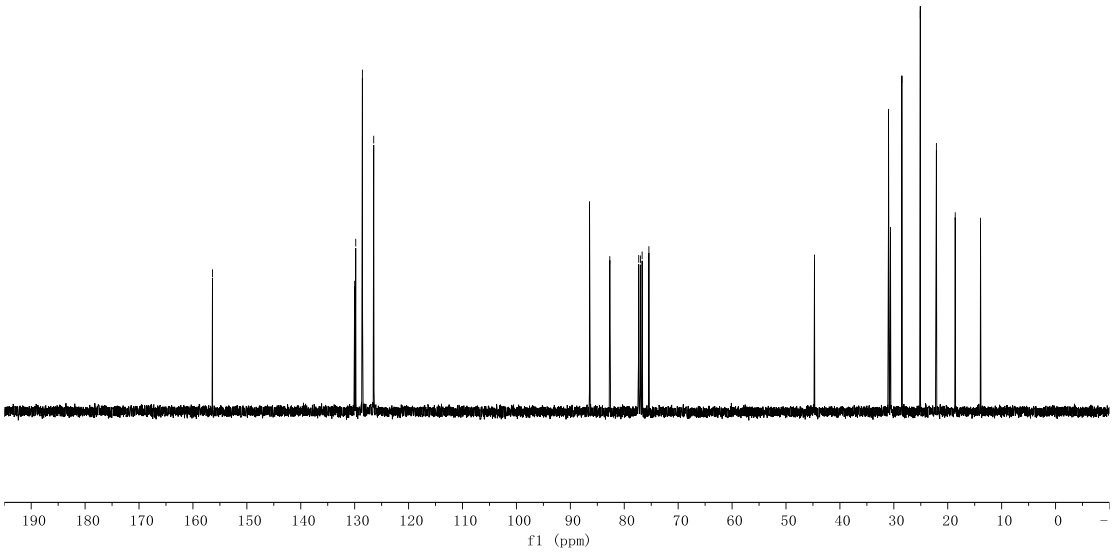
3r ^{1}H NMR (400 MHz, $CDCl_3$)

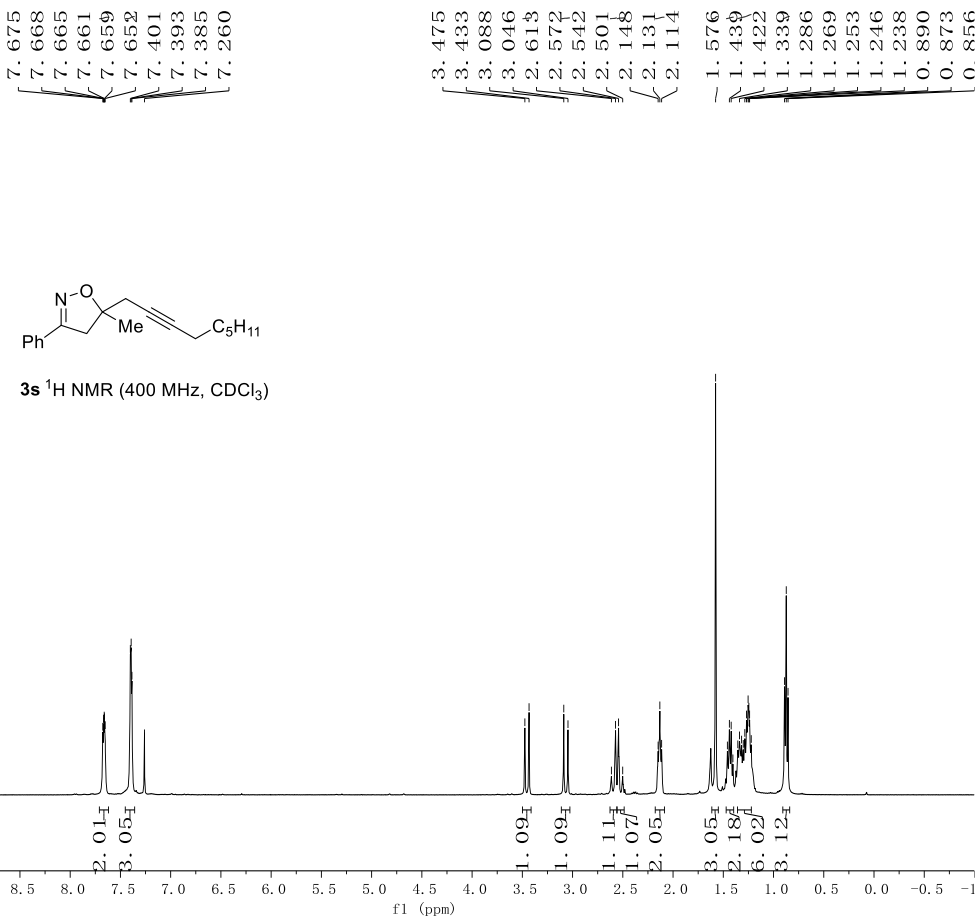




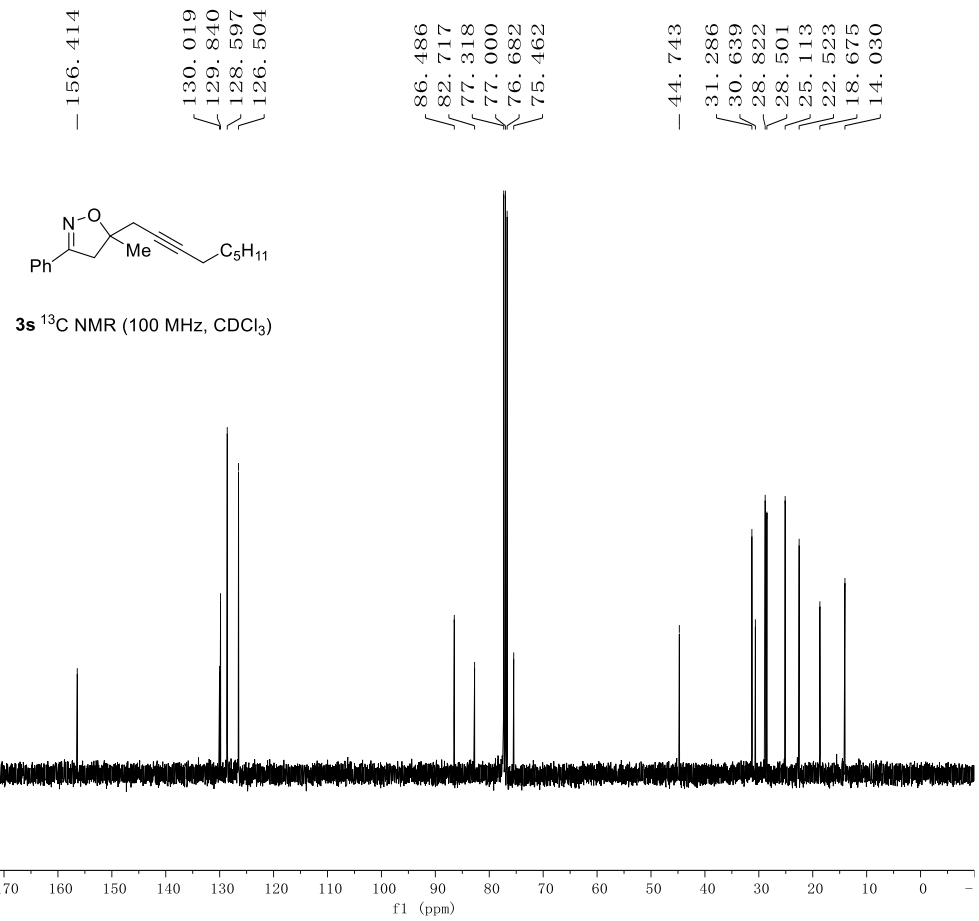


3r ^{13}C NMR (100 MHz, $CDCl_3$)

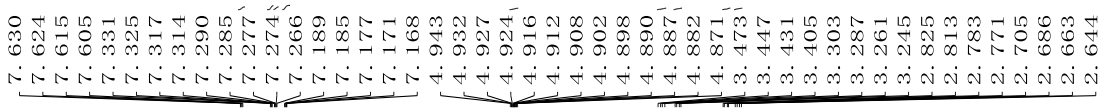


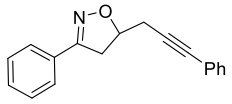


3s ^{1}H NMR (400 MHz, $CDCl_3$)

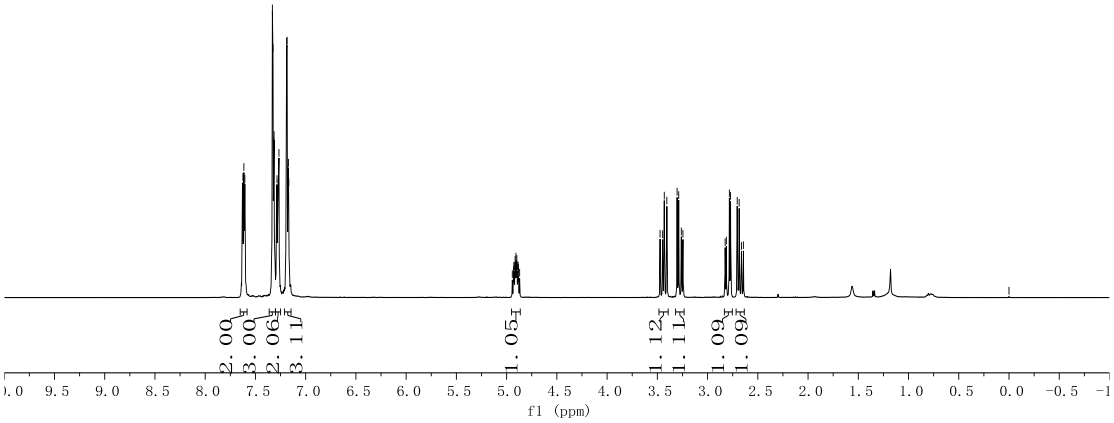


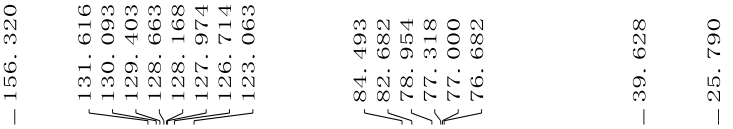
3s ^{13}C NMR (100 MHz, $CDCl_3$)

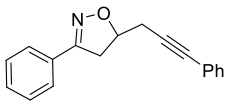




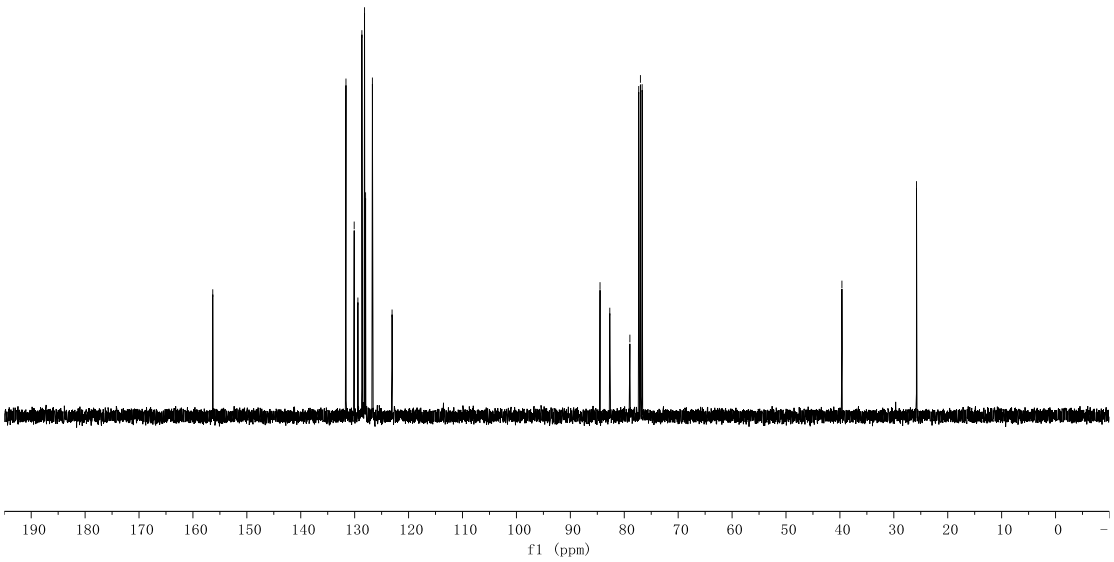
3t ^{1}H NMR (400 MHz, $CDCl_3$)

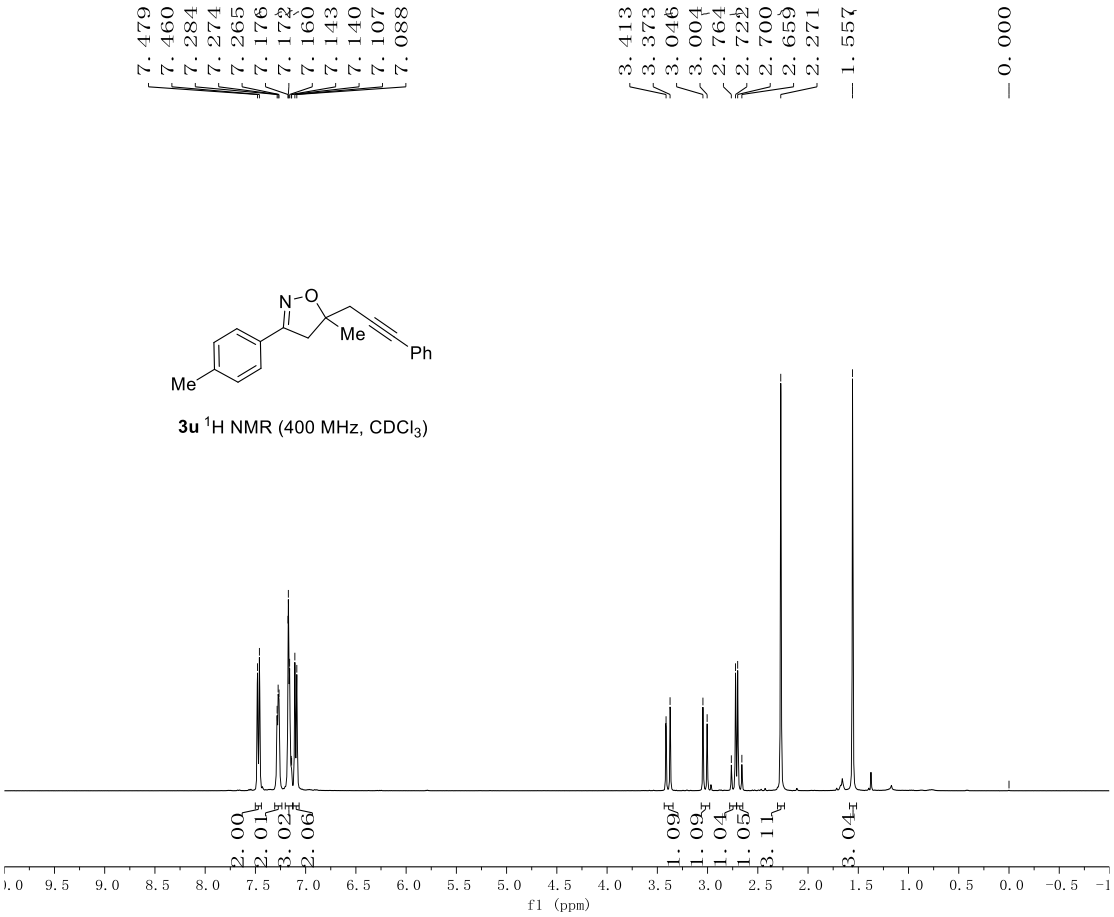




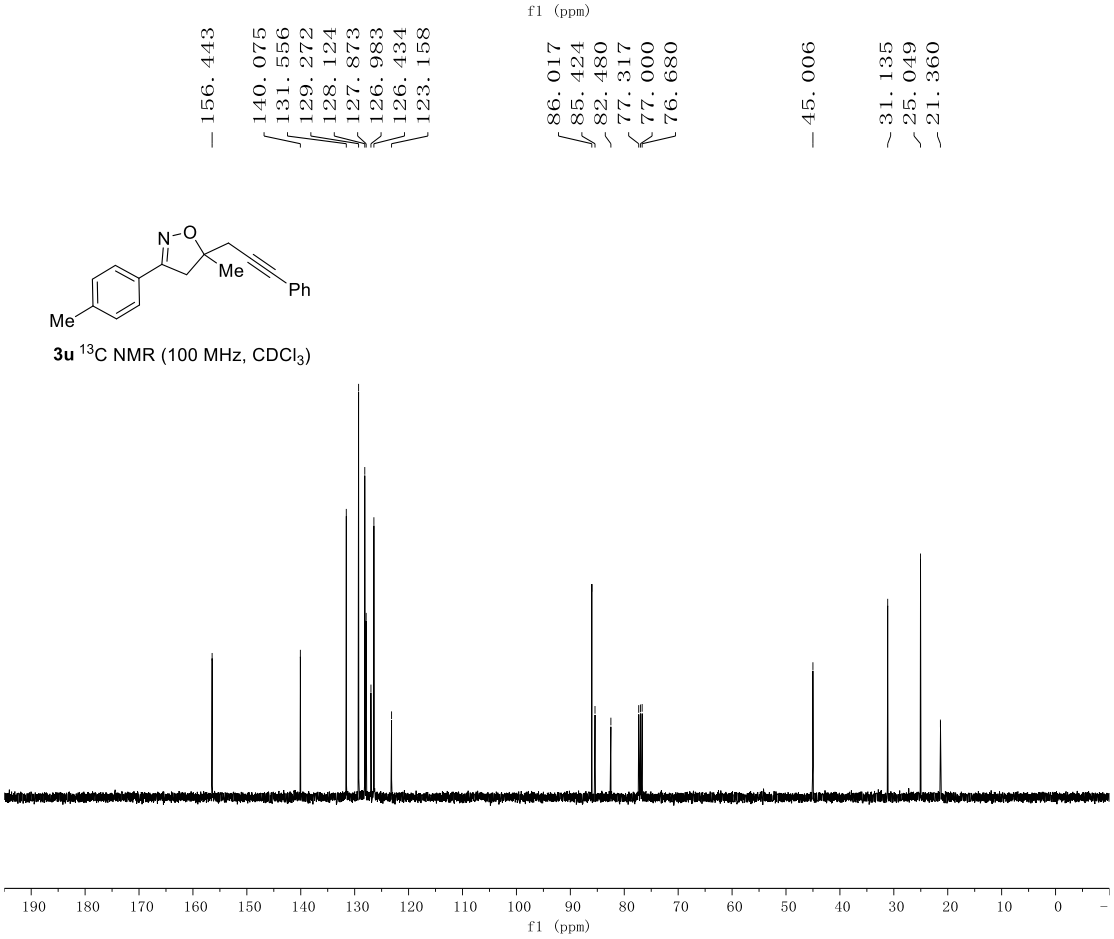


3t ^{13}C NMR (100 MHz, $CDCl_3$)

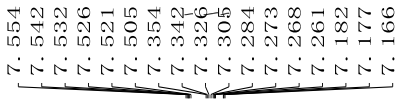


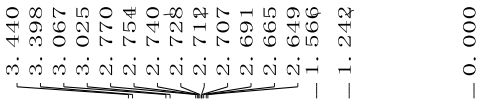


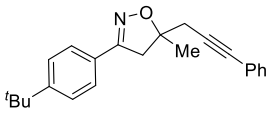
3u ^{1}H NMR (400 MHz, $CDCl_3$)



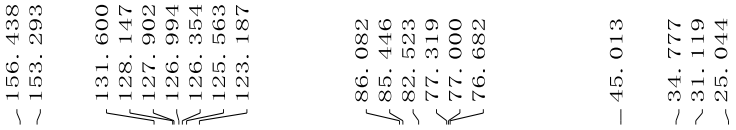
3u ^{13}C NMR (100 MHz, $CDCl_3$)

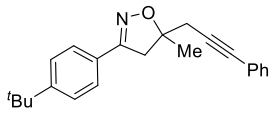




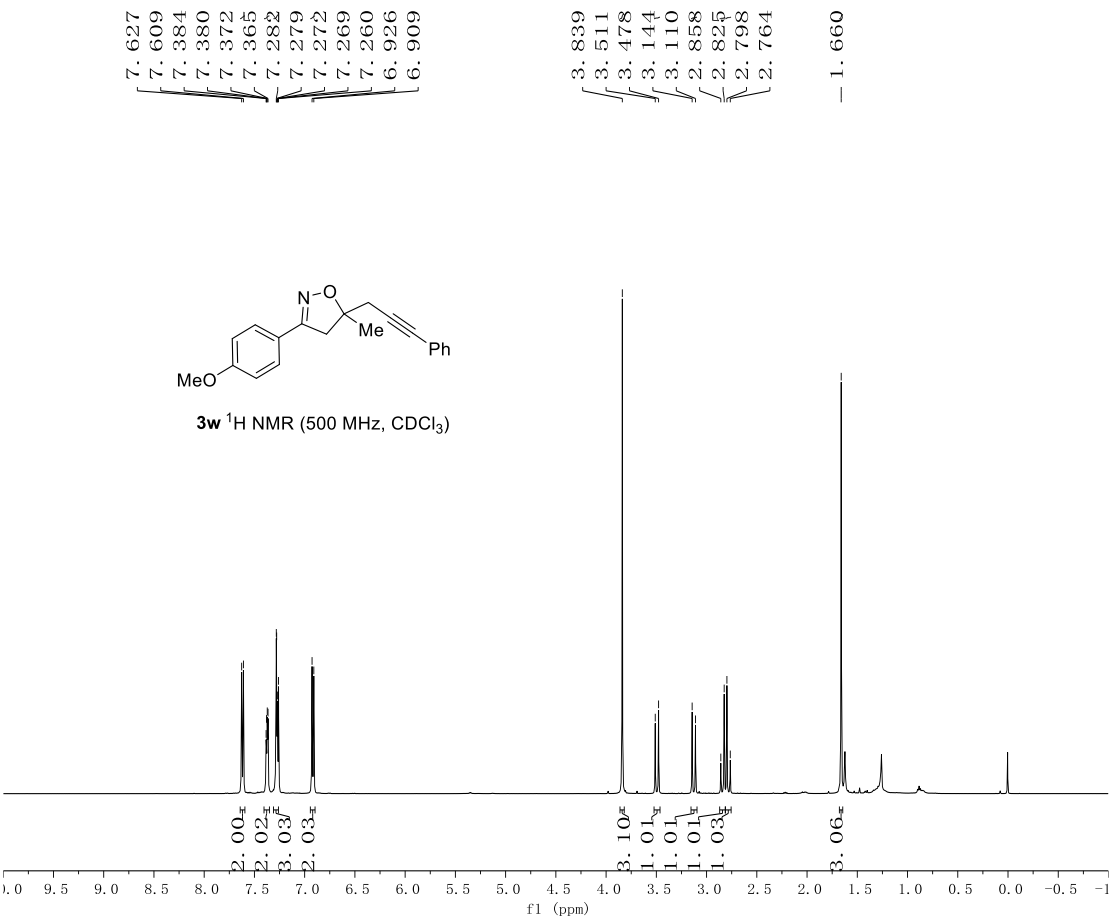


3v ^{1}H NMR (400 MHz, $CDCl_3$)

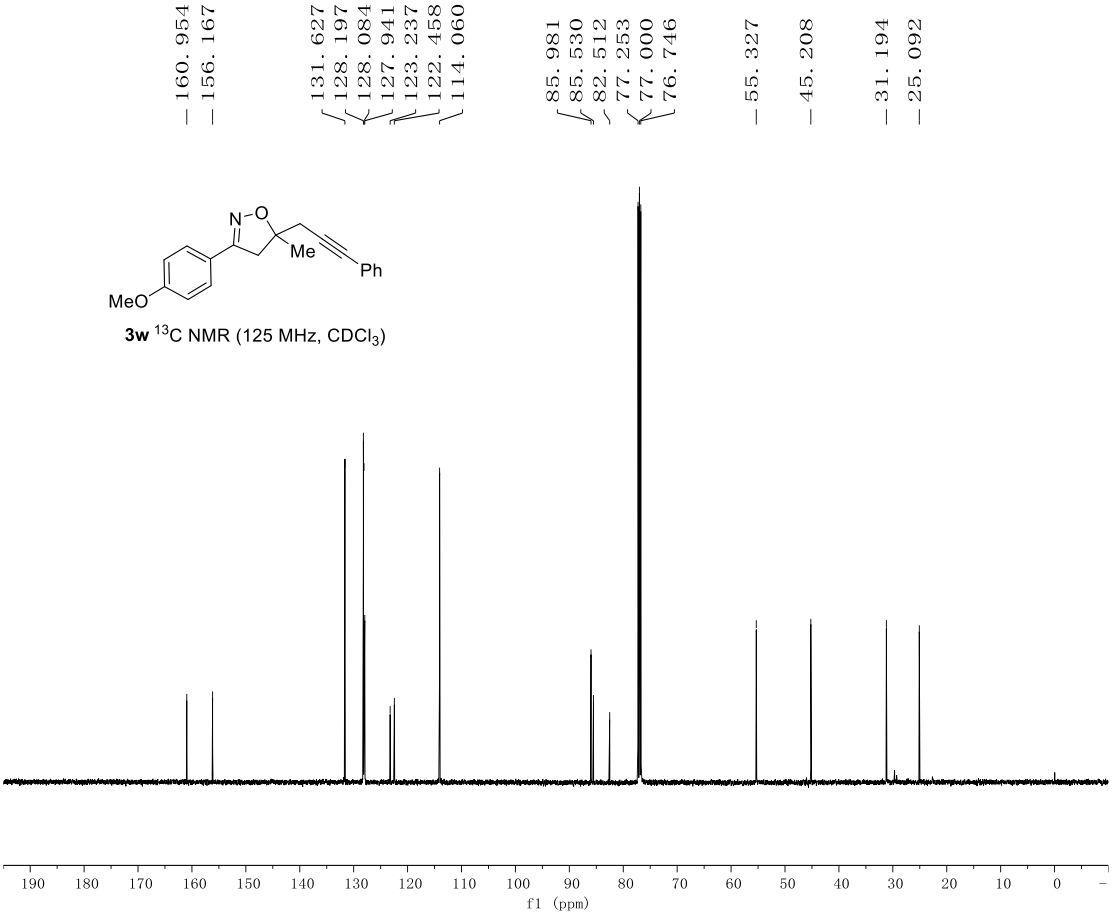




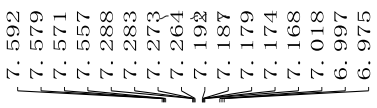
3v ^{13}C NMR (100 MHz, $CDCl_3$)

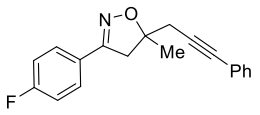


3w ^{1}H NMR (500 MHz, $CDCl_3$)

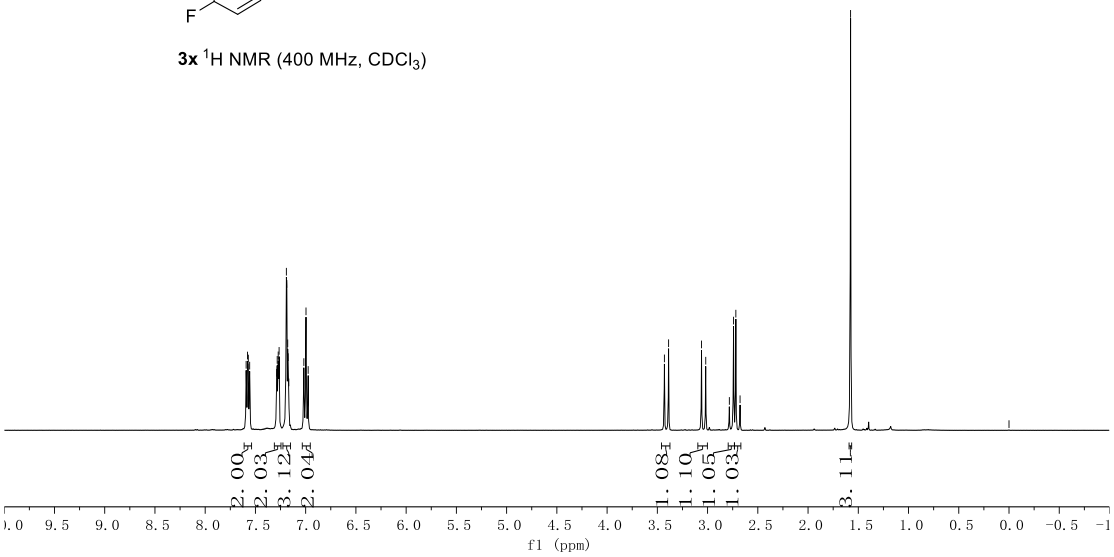


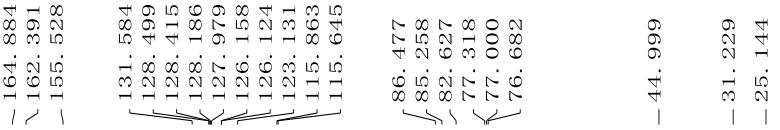
3w ^{13}C NMR (125 MHz, $CDCl_3$)

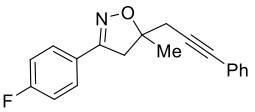




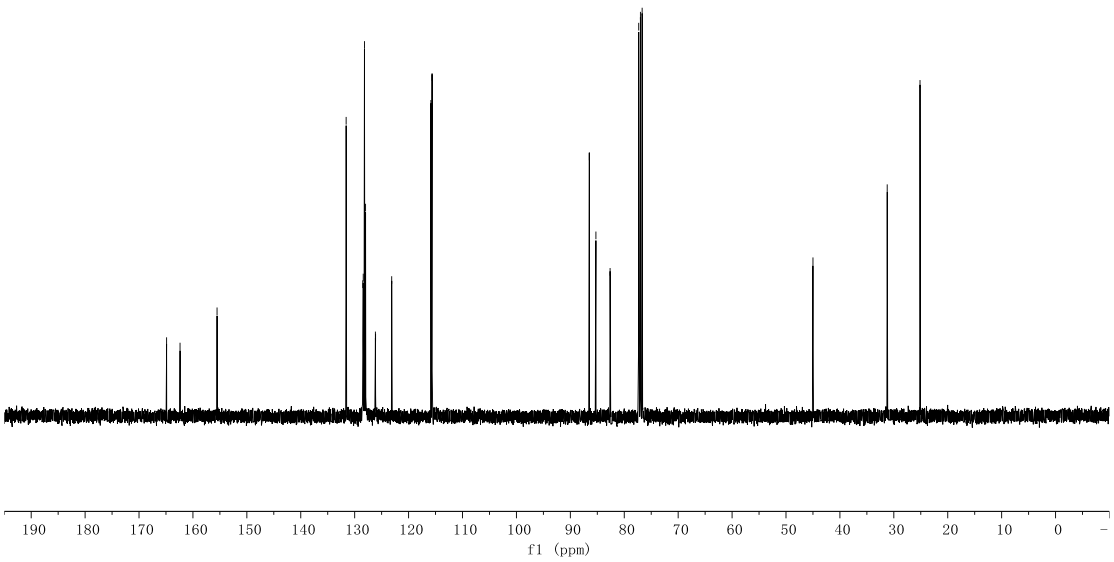
3x ^{1}H NMR (400 MHz, $CDCl_3$)

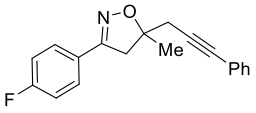




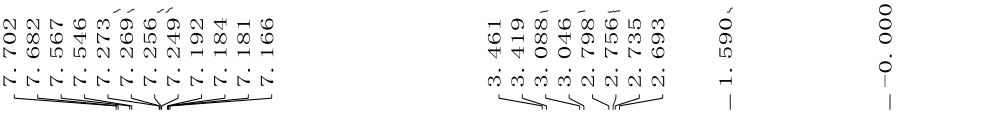


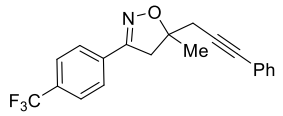
3x ^{13}C NMR (100 MHz, $CDCl_3$)



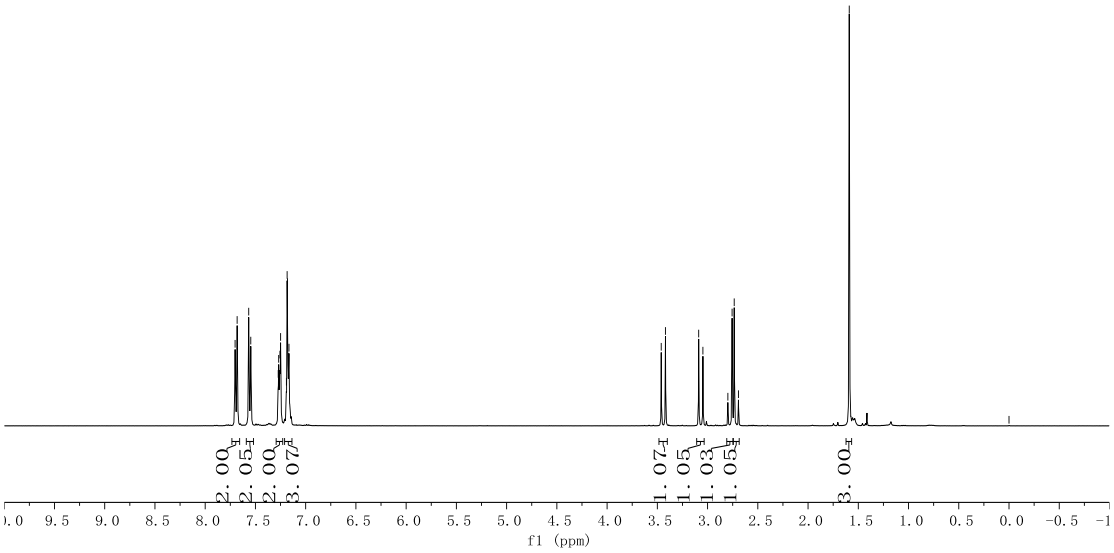


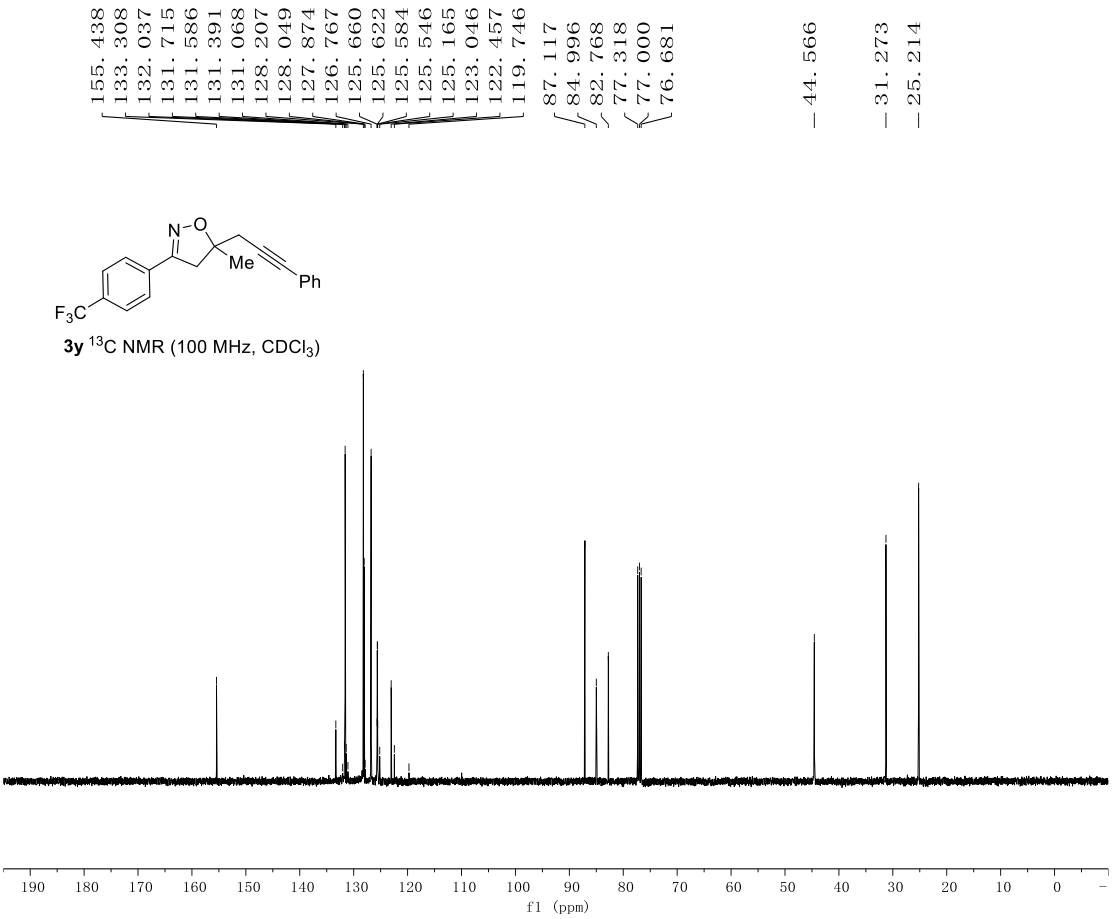
3x ^{19}F NMR (376 MHz, $CDCl_3$)





3y ^{1}H NMR (400 MHz, $CDCl_3$)

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133.308
132.037
131.715
131.586
131.391
131.068
128.207
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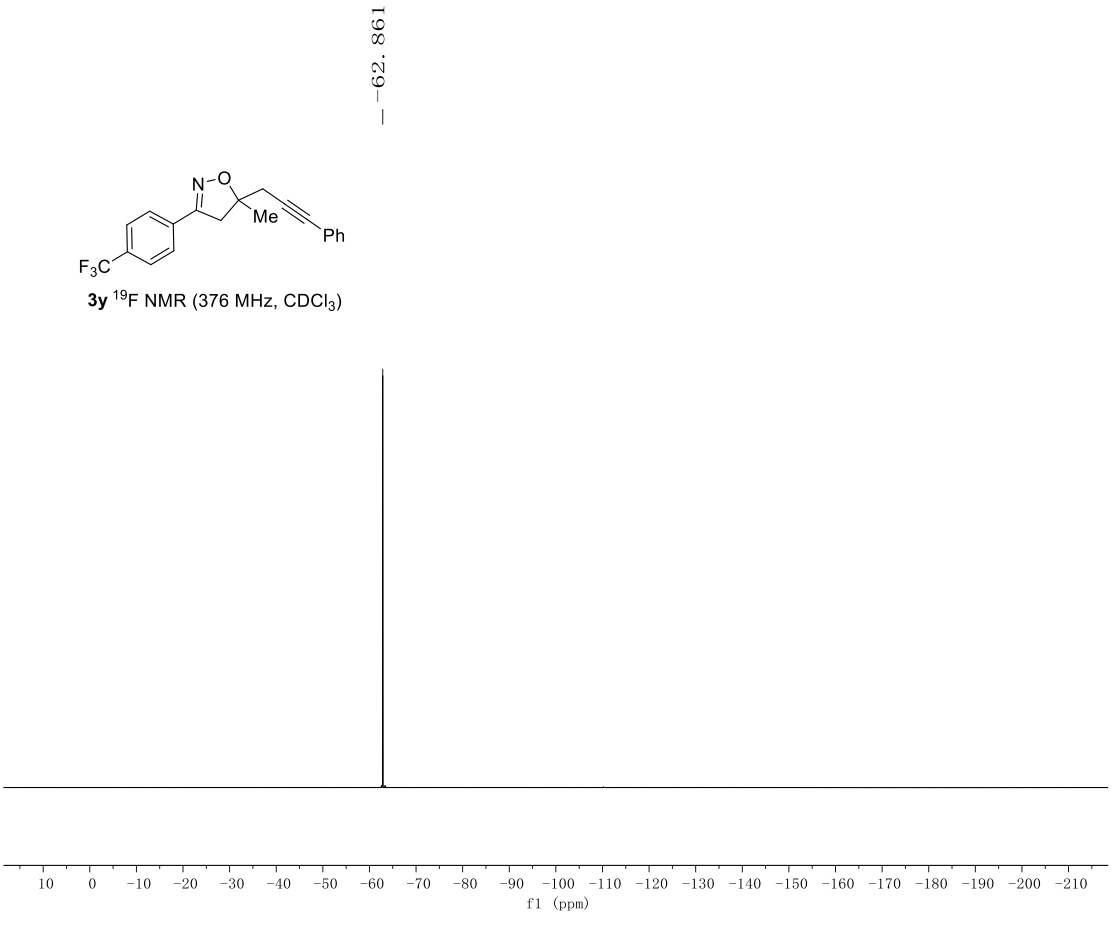
127.874
126.767
125.660
125.622
125.584
125.546
125.165
123.046
122.457
119.746
87.117
84.996
82.768
77.318
77.000
76.681
44.566
31.273
25.214
N
O
Me
Ph
F3C
3y 13C NMR (100 MHz, CDCl3)
f1 (ppm)


−62.861
N
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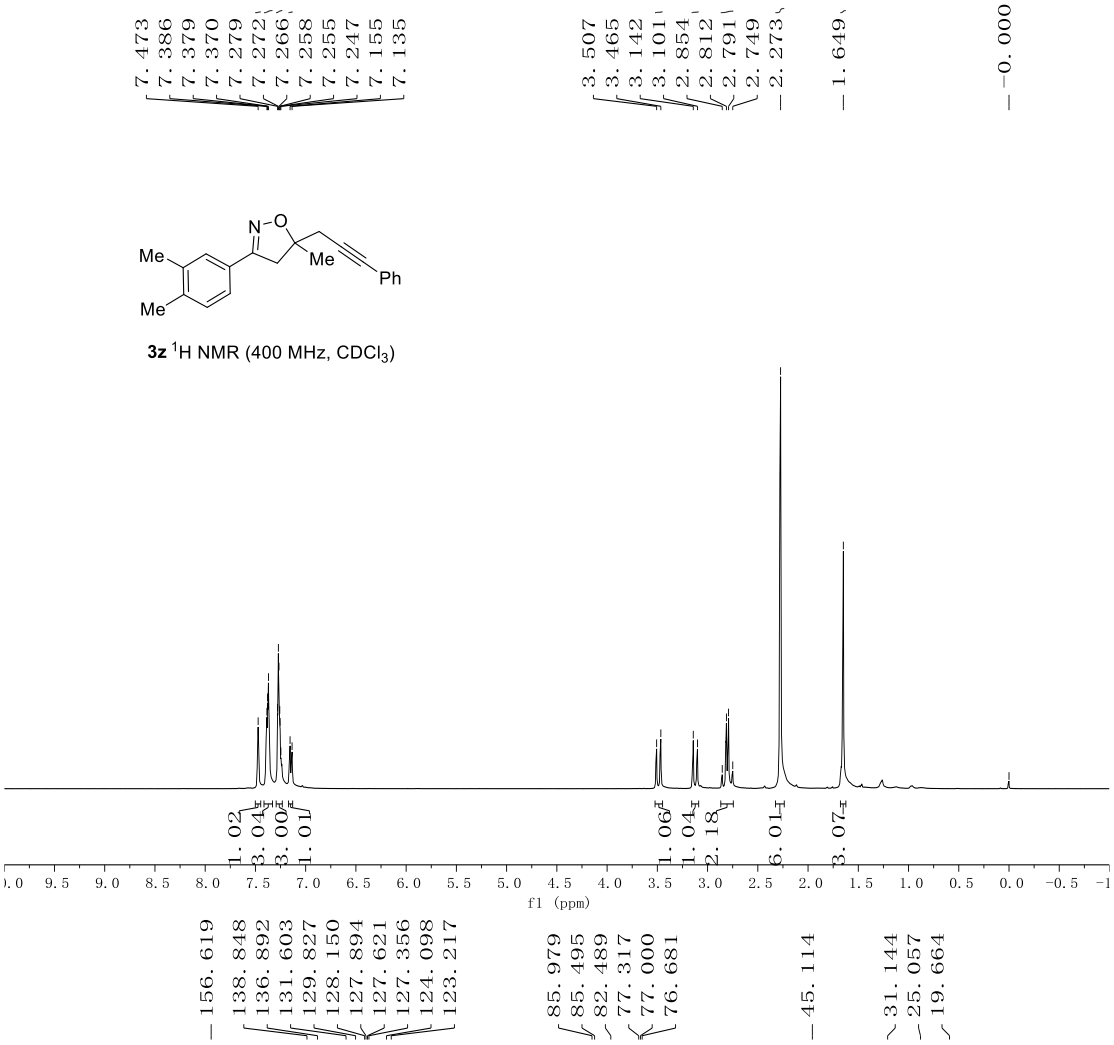
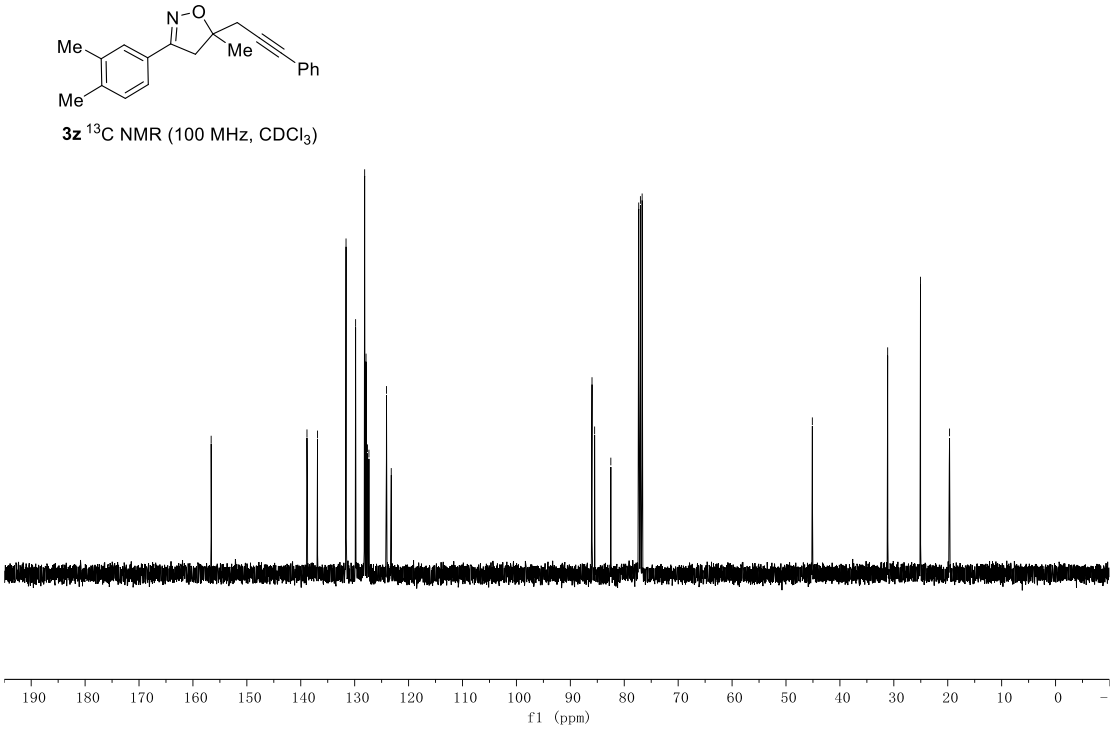
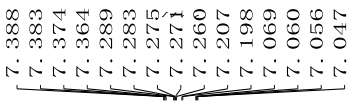
Me
Ph
F3C
3y 19F NMR (376 MHz, CDCl3)
f1 (ppm)

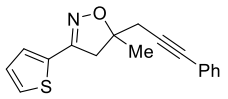


3z ^{1}H NMR (400 MHz, $CDCl_3$)

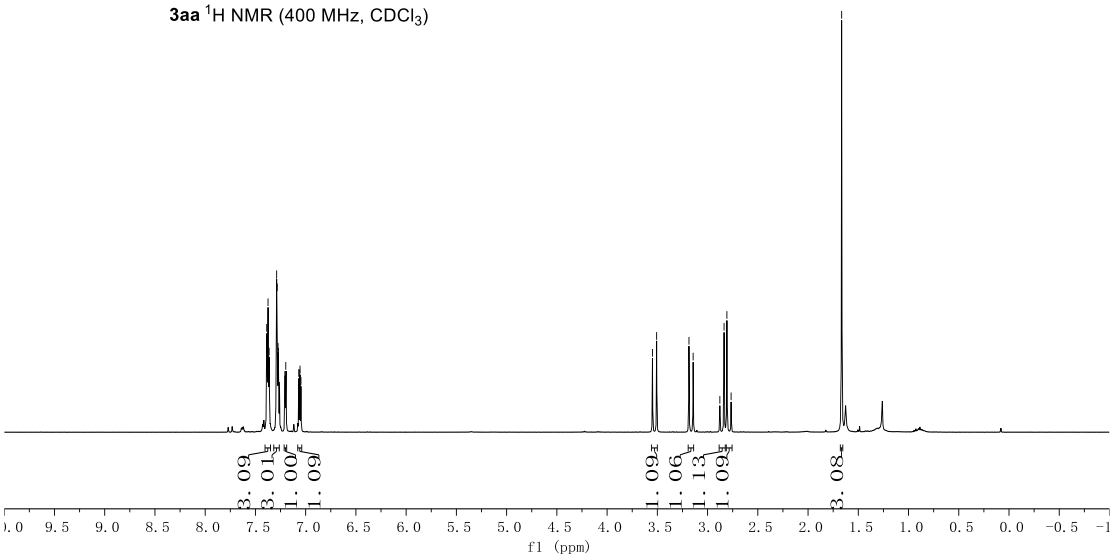


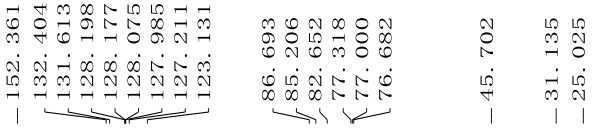
3z ^{13}C NMR (100 MHz, $CDCl_3$)

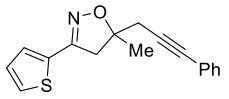




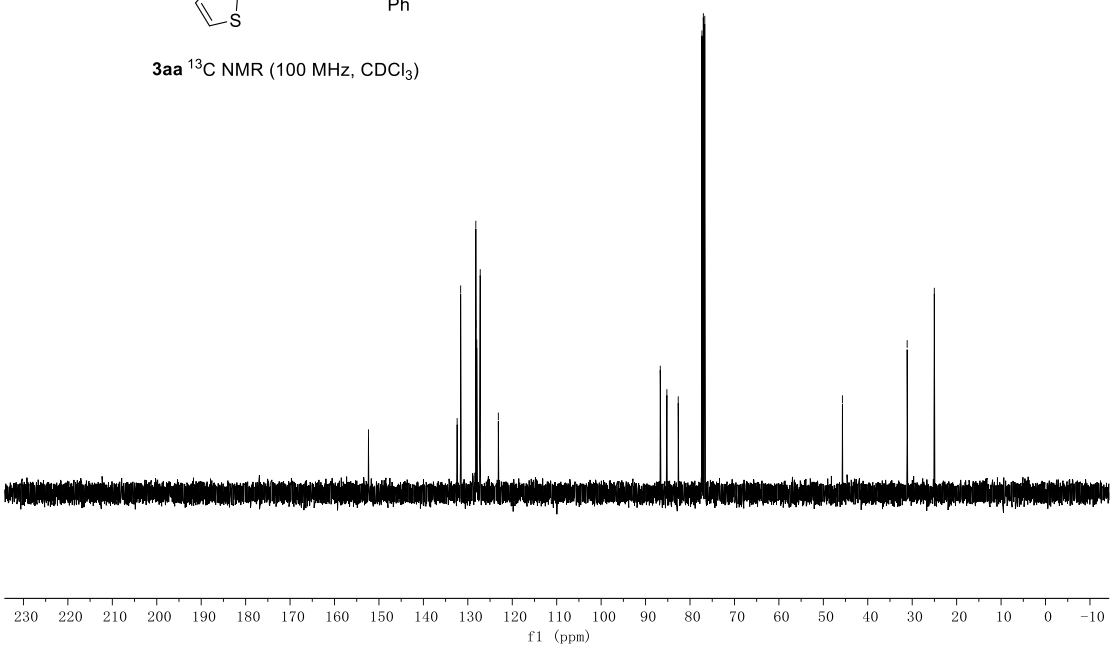
3aa ^{1}H NMR (400 MHz, $CDCl_3$)

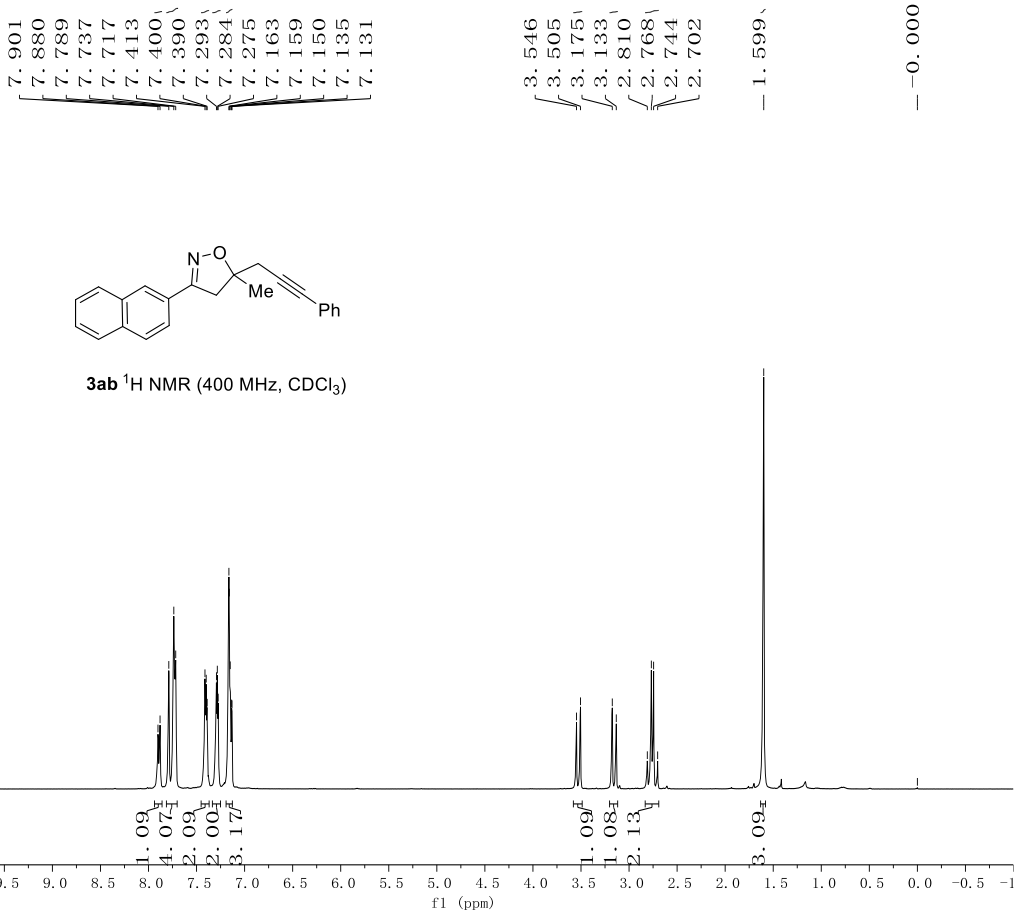




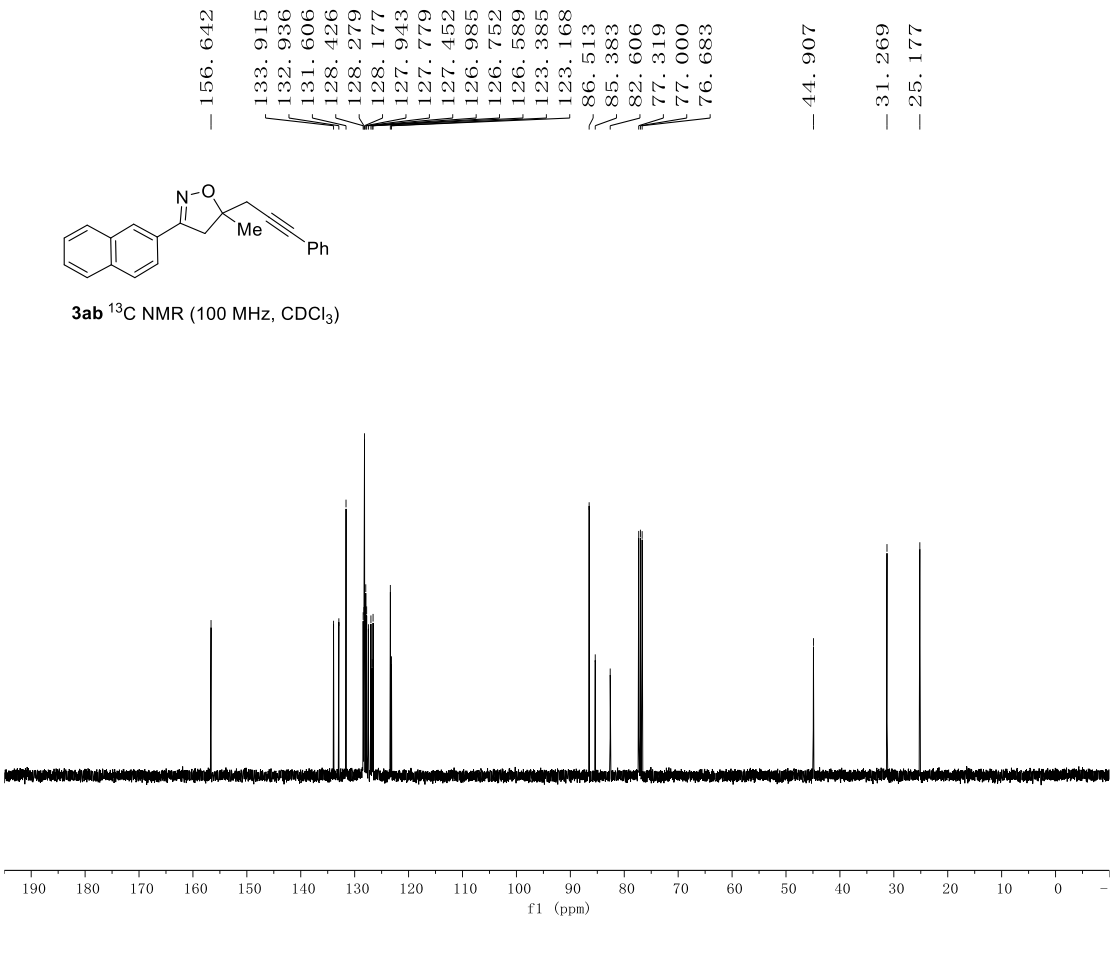


3aa ^{13}C NMR (100 MHz, $CDCl_3$)

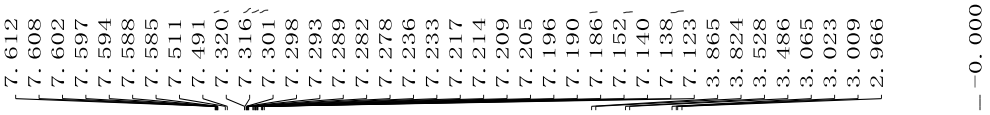


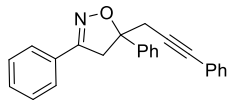


3ab ^{1}H NMR (400 MHz, $CDCl_3$)

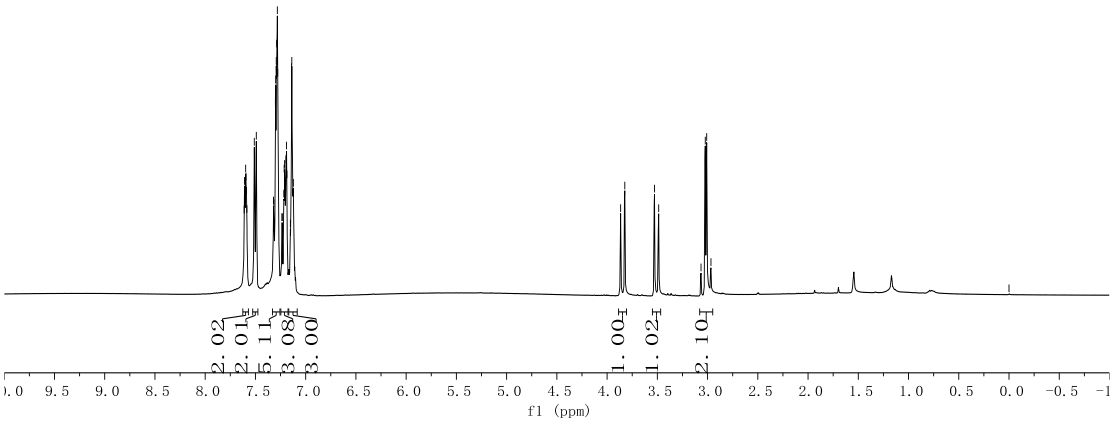


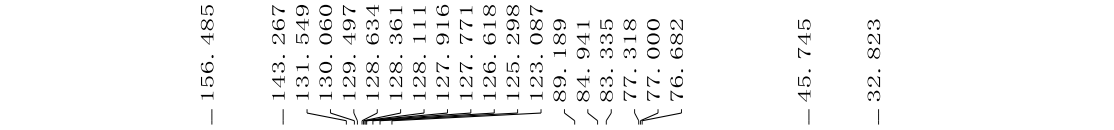
3ab ^{13}C NMR (100 MHz, $CDCl_3$)

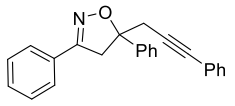




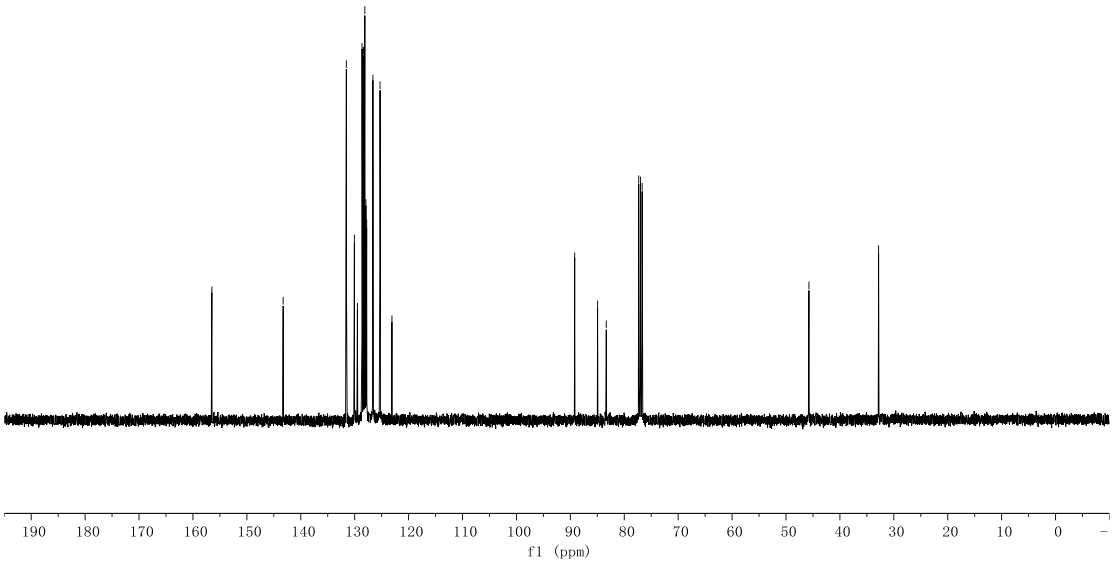
3ac ^{1}H NMR (400 MHz, $CDCl_3$)

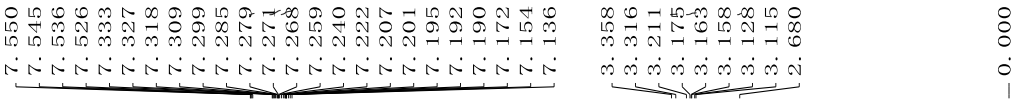


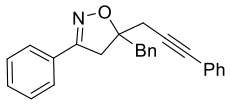




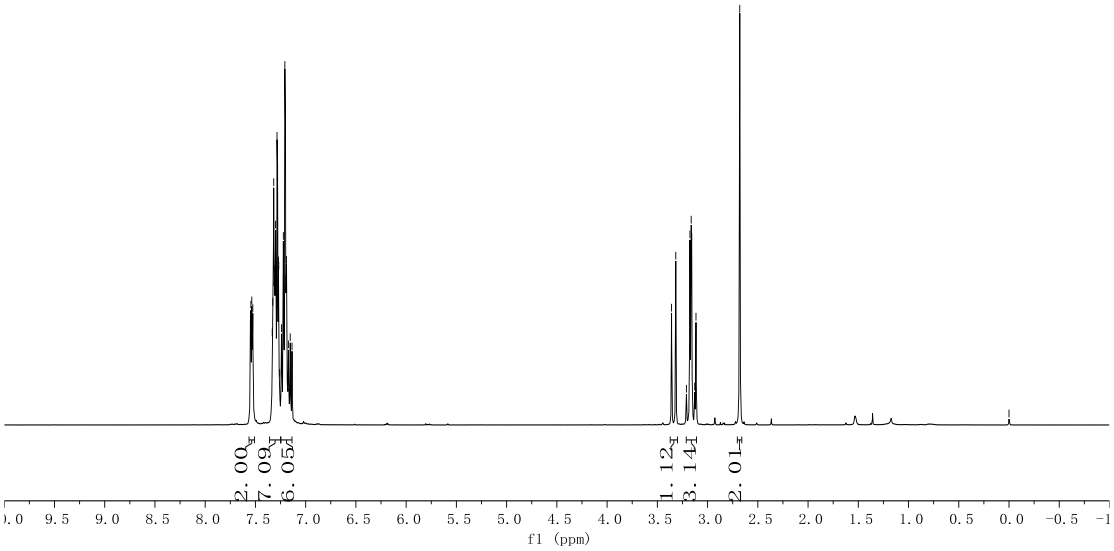
3ac ^{13}C NMR (100 MHz, $CDCl_3$)

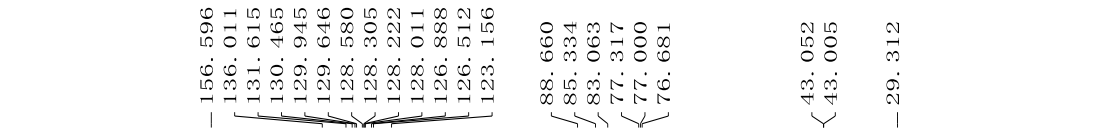


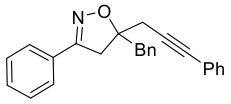




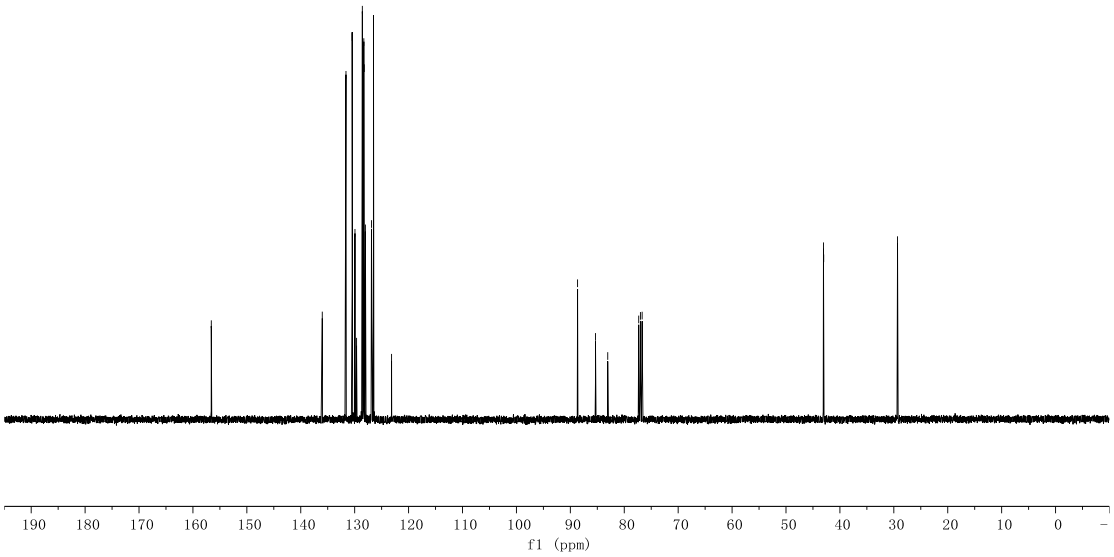
3ad ^{1}H NMR (400 MHz, $CDCl_3$)

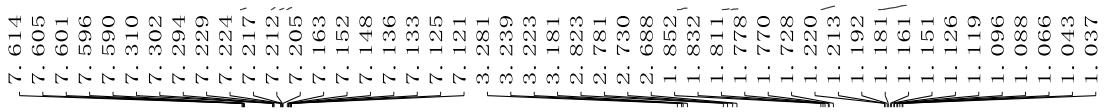


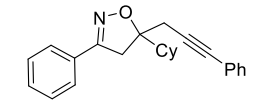




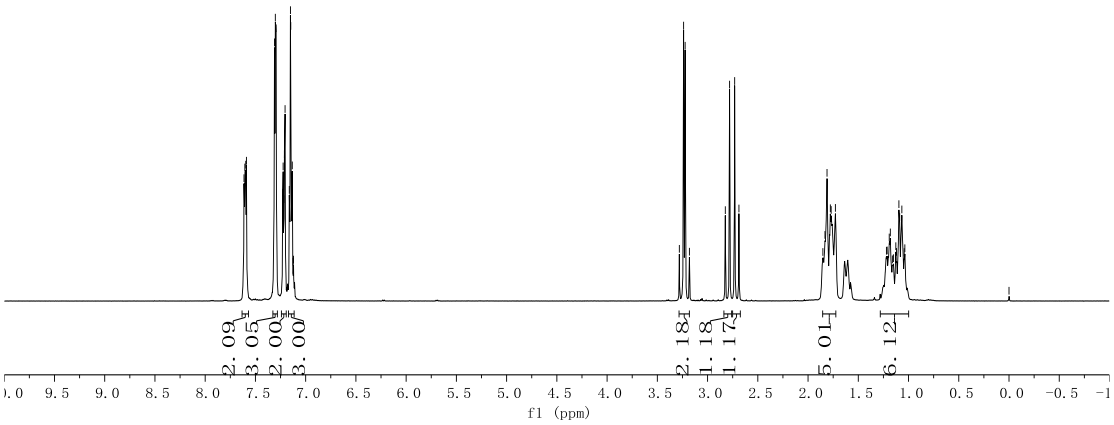
3ad ^{13}C NMR (100 MHz, $CDCl_3$)

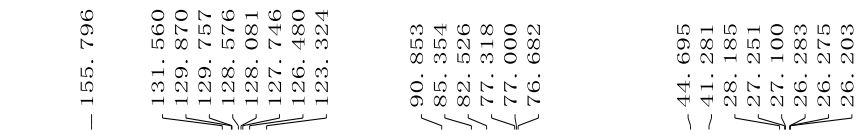


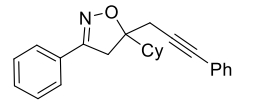




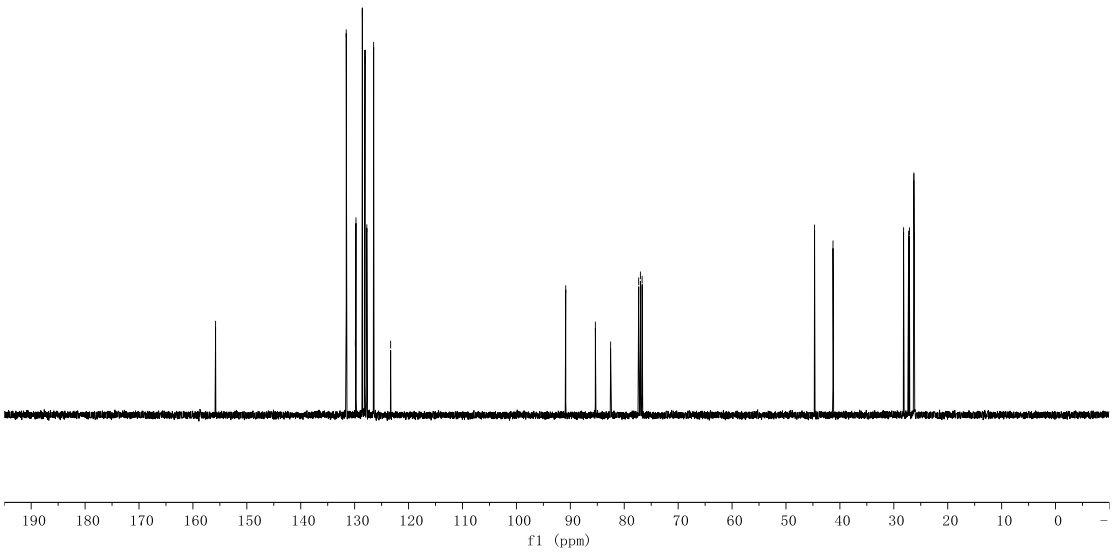
3ae ^{1}H NMR (400 MHz, $CDCl_3$)

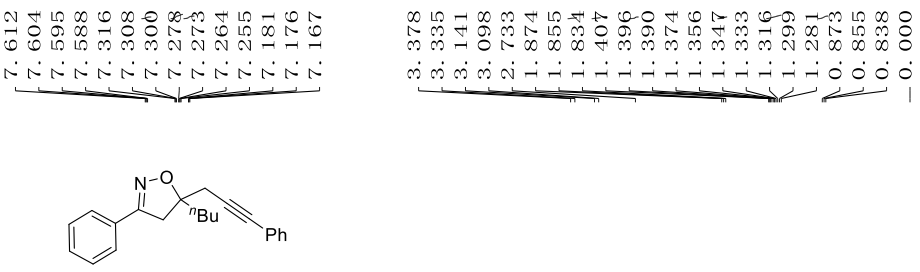




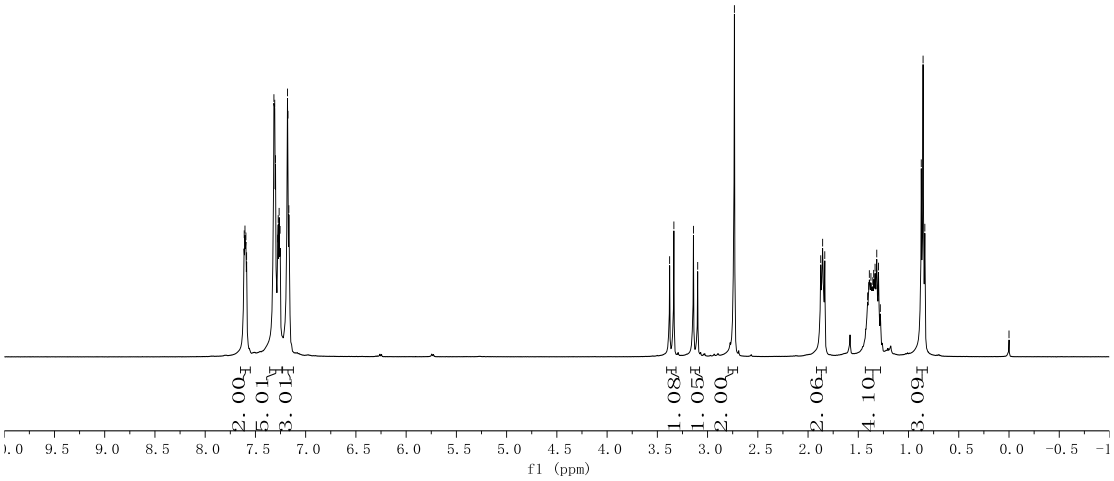


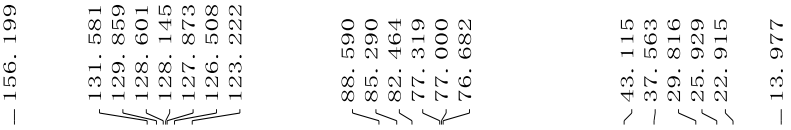
3ae ^{13}C NMR (100 MHz, $CDCl_3$)

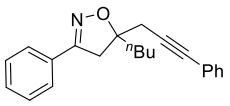




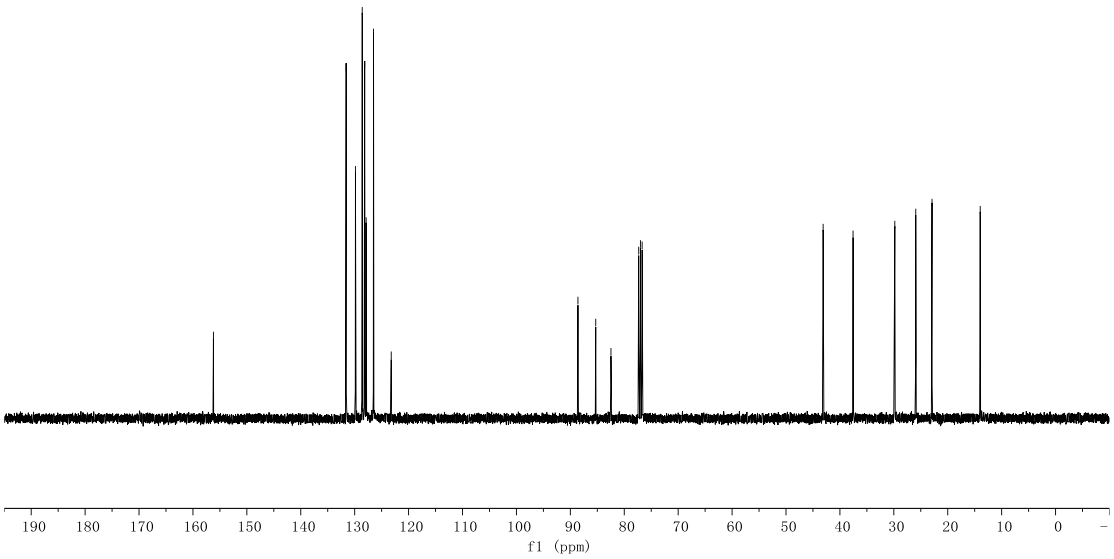
3af ^{1}H NMR (400 MHz, $CDCl_3$)

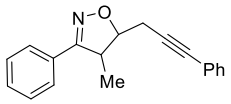




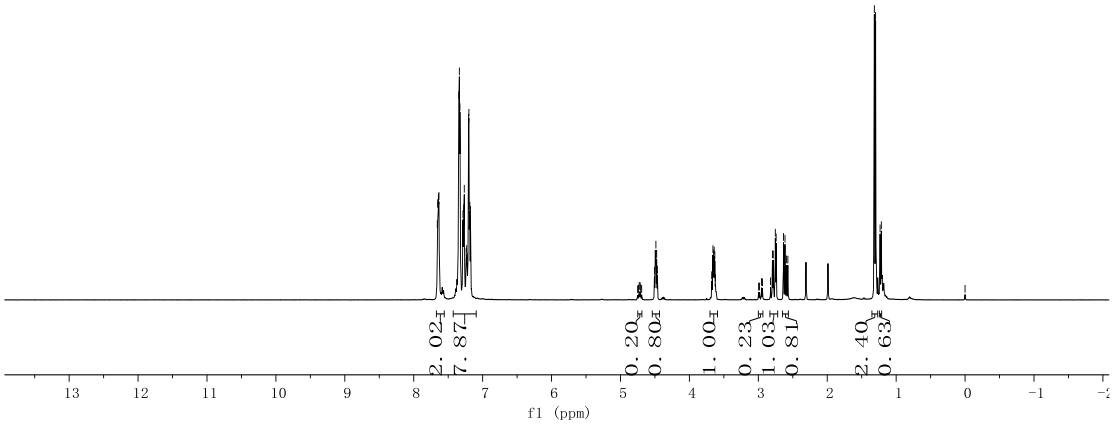


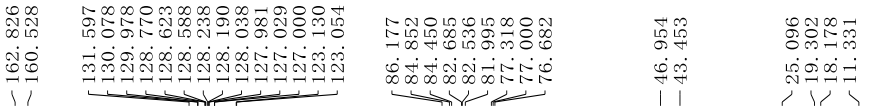
3af ^{13}C NMR (100 MHz, $CDCl_3$)

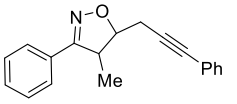




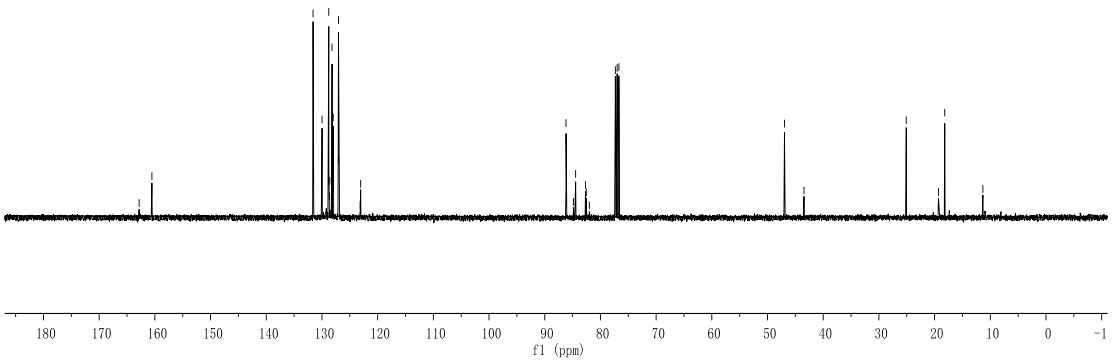
3ag ^{1}H NMR (400 MHz, $CDCl_3$)

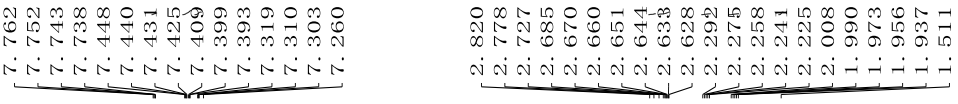


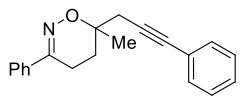




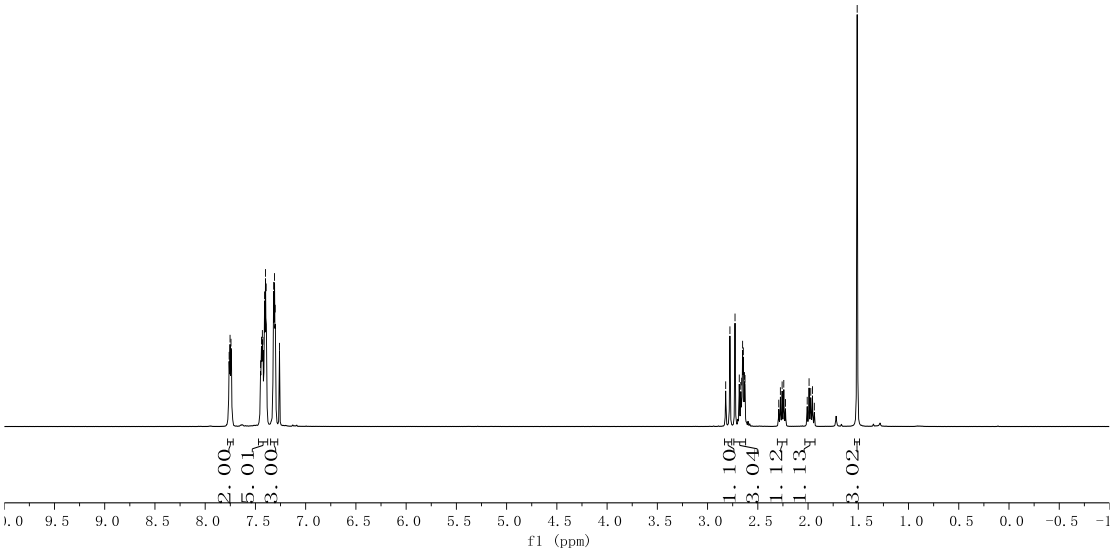
3ag ^{13}C NMR (100 MHz, $CDCl_3$)

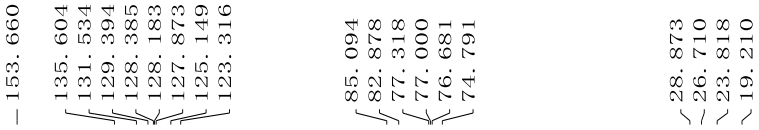


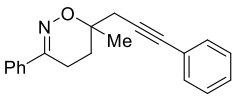




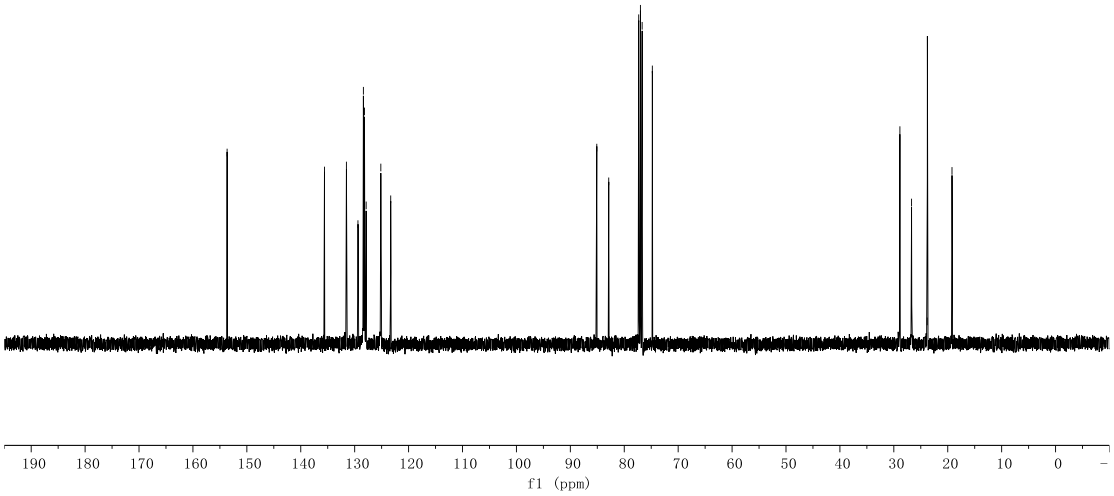
5a ^{1}H NMR (400 MHz, $CDCl_3$)

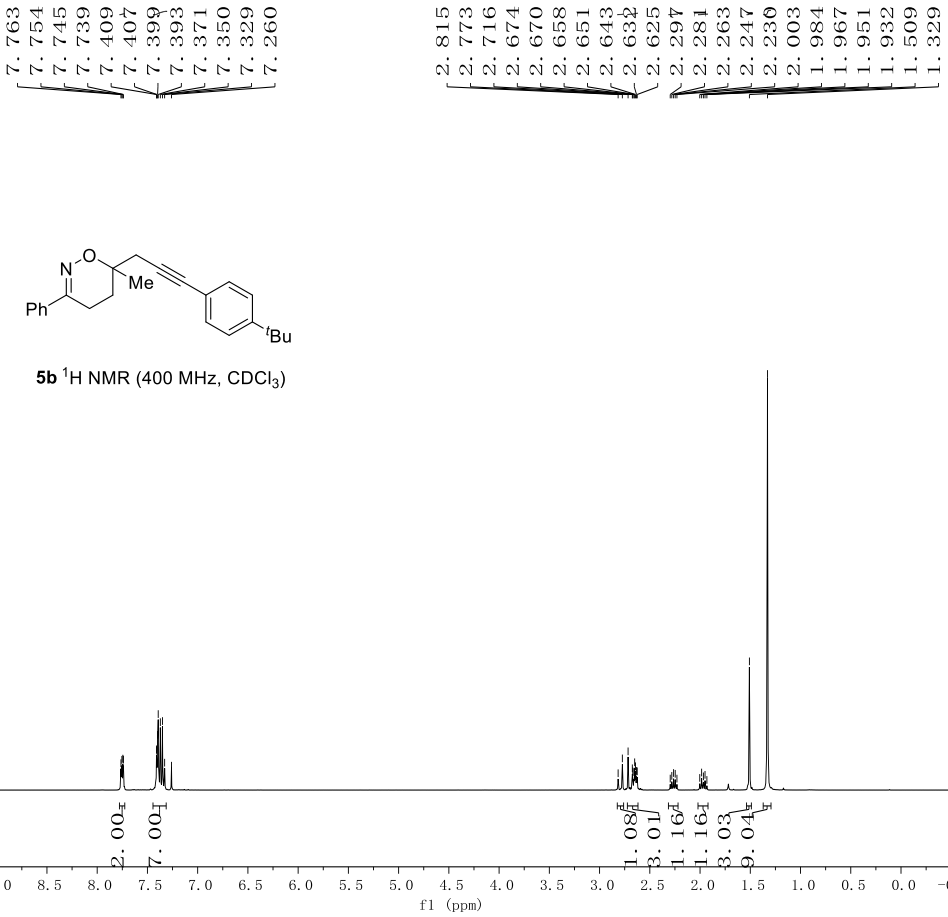






5a ^{13}C NMR (100 MHz, $CDCl_3$)

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7.745
7.739
7.409
7.407
7.399
7.393
7.371
7.350
7.329
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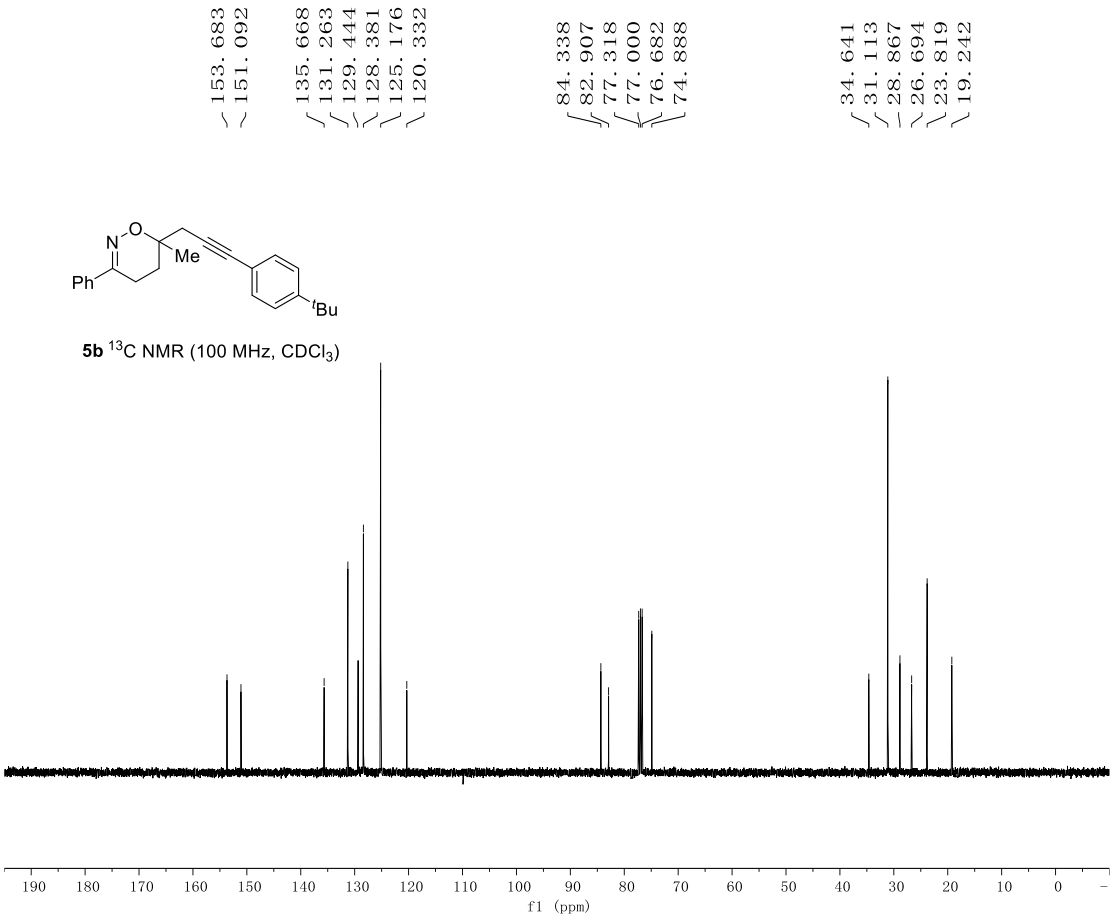
2.815
2.773
2.716
2.674
2.670
2.658
2.651
2.643
2.632
2.625
2.297
2.281
2.263
2.247
2.230
2.003
1.984
1.967
1.951
1.932
1.509
1.329
N
O
Me
Ph
tBu
5b 1H NMR (400 MHz, CDCl3)
2.00
7.00
1.08
3.01
1.16
1.16
3.03
9.04
f1 (ppm)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125.176
120.332
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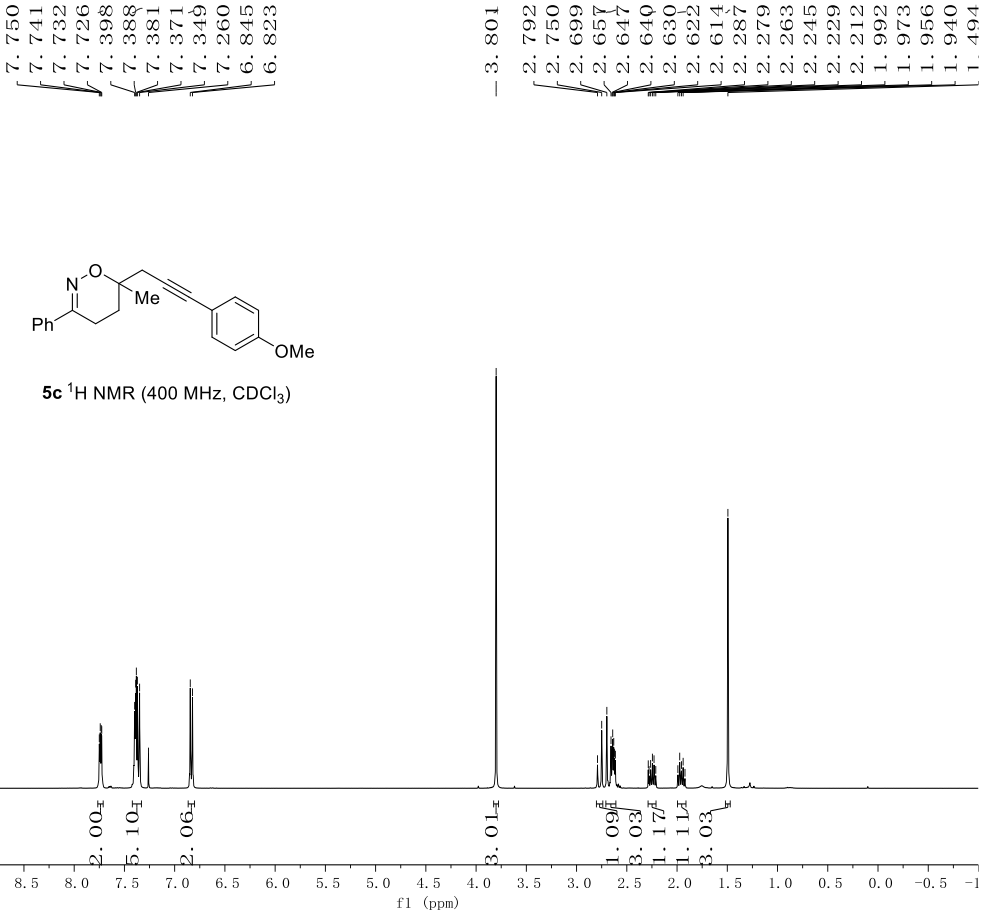
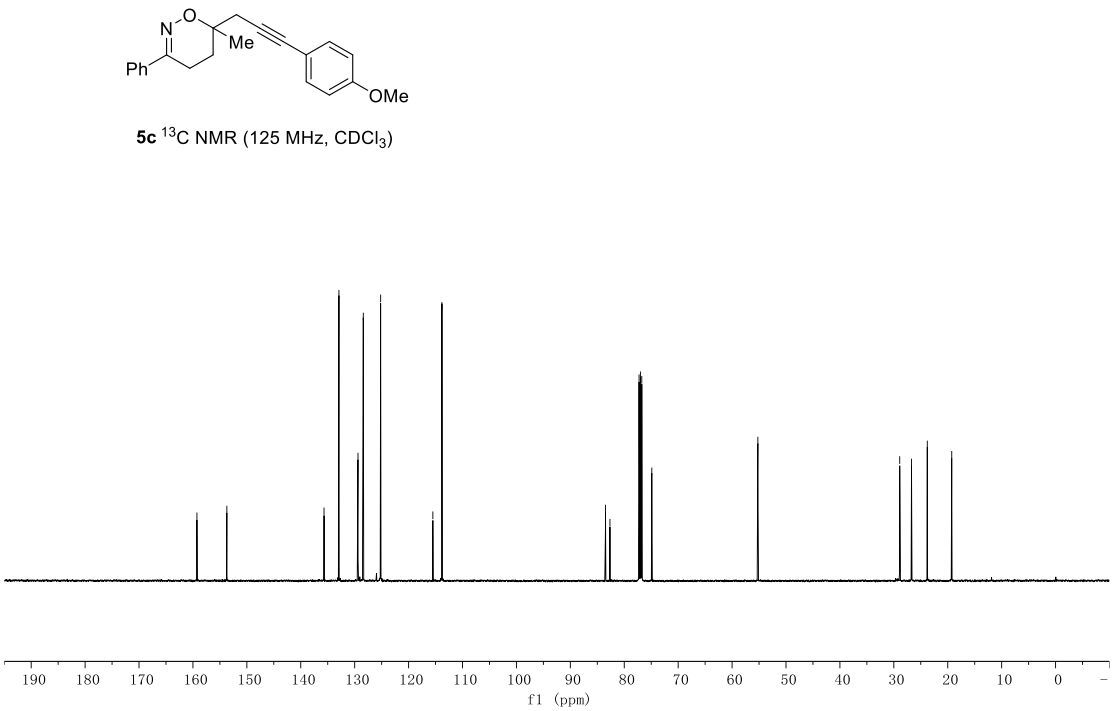
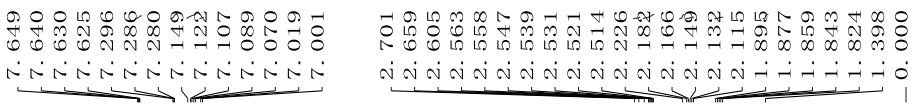
77.000
76.682
74.888
34.641
31.113
28.867
26.694
23.819
19.242
N
O
Me
Ph
tBu
5b 13C NMR (100 MHz, CDCl3)
f1 (ppm)

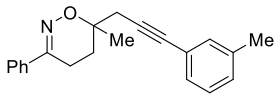


5c ^{1}H NMR (400 MHz, $CDCl_3$)

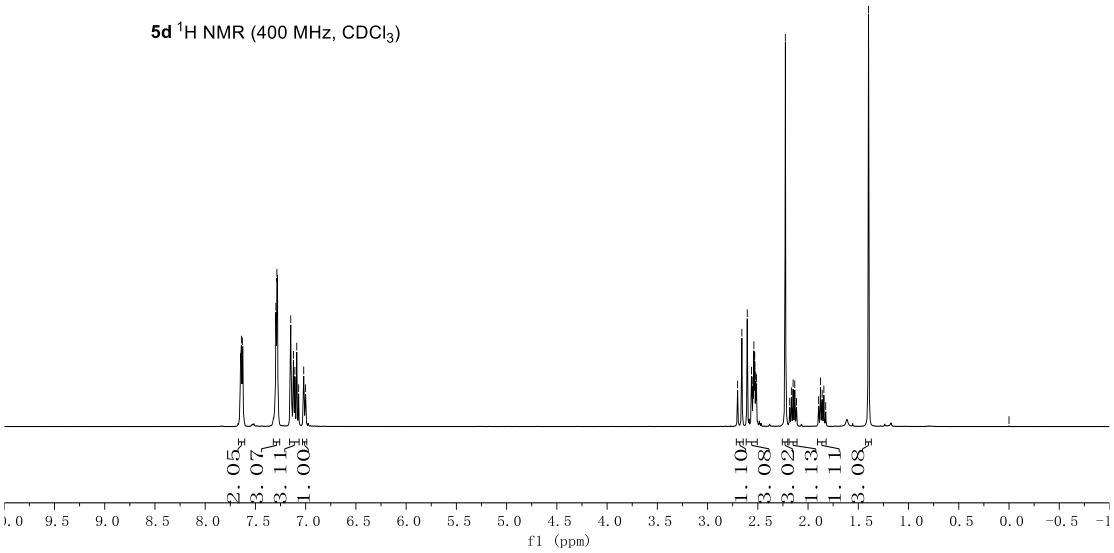


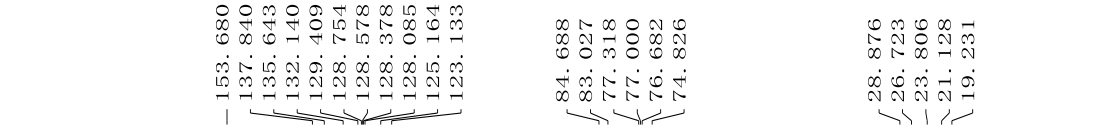
5c ^{13}C NMR (125 MHz, $CDCl_3$)

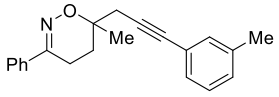




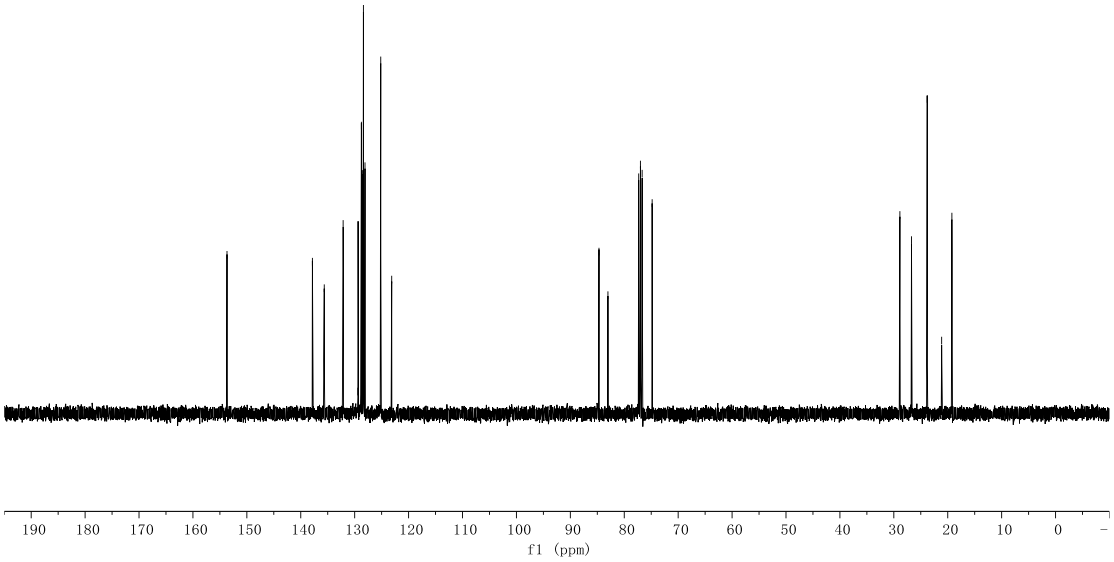
5d ^{1}H NMR (400 MHz, $CDCl_3$)

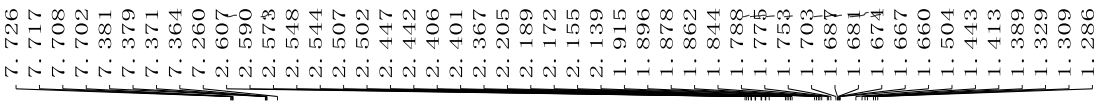


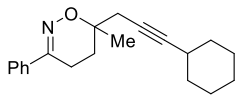




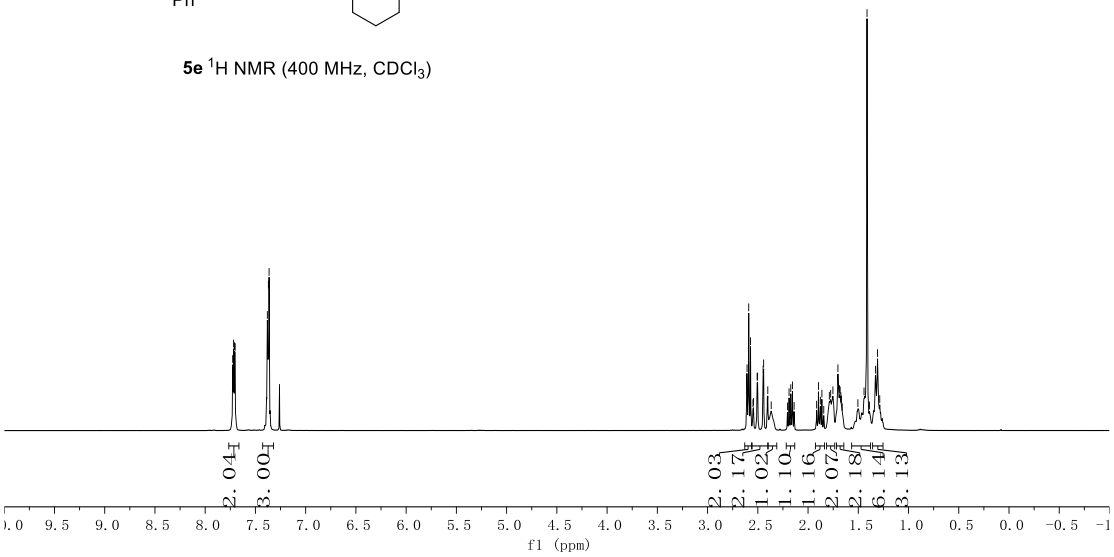
5d ^{13}C NMR (100 MHz, $CDCl_3$)

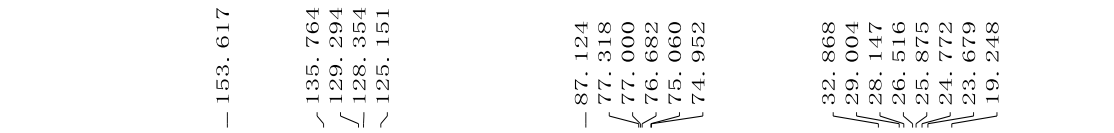


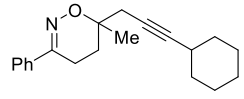




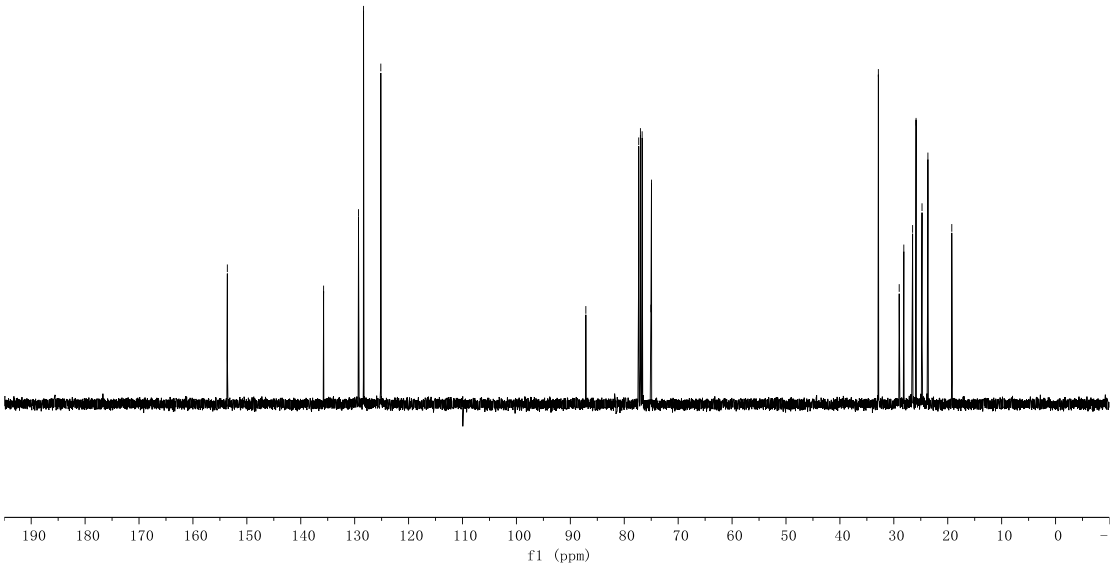
5e ^{1}H NMR (400 MHz, $CDCl_3$)

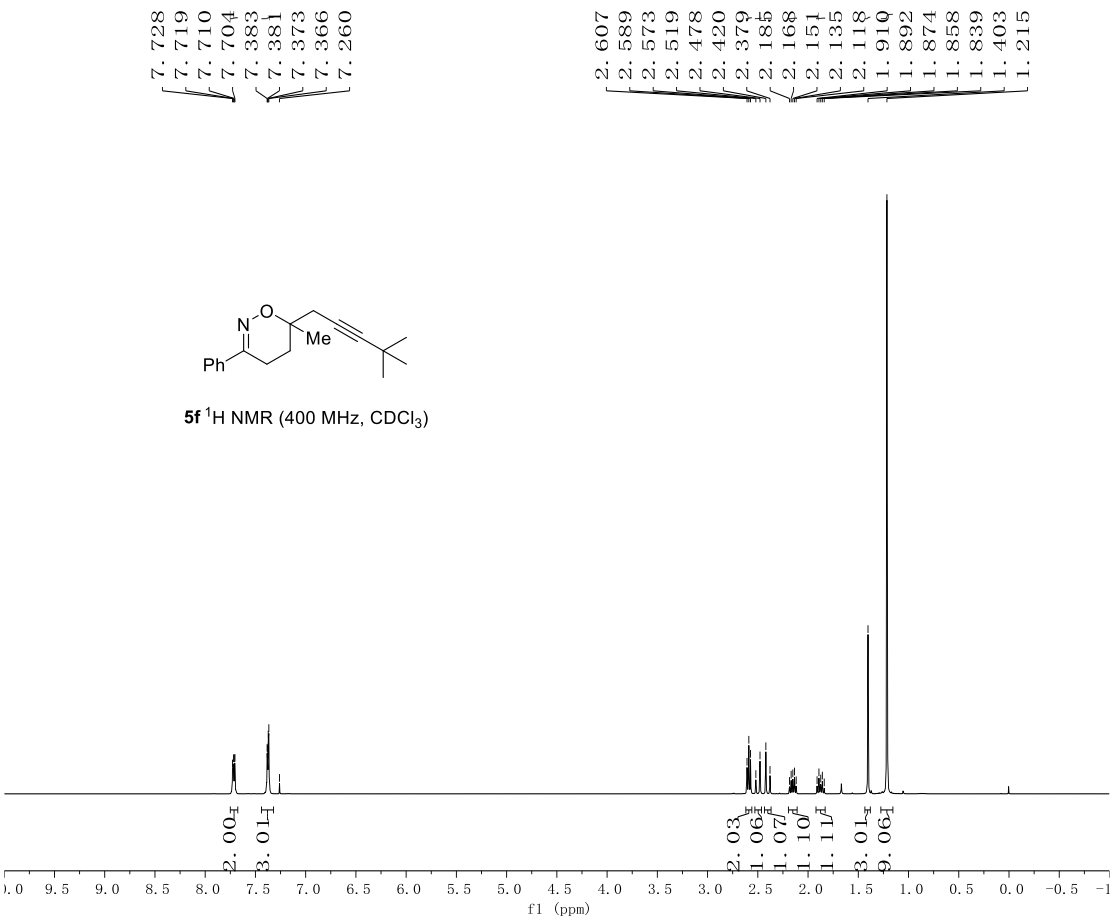




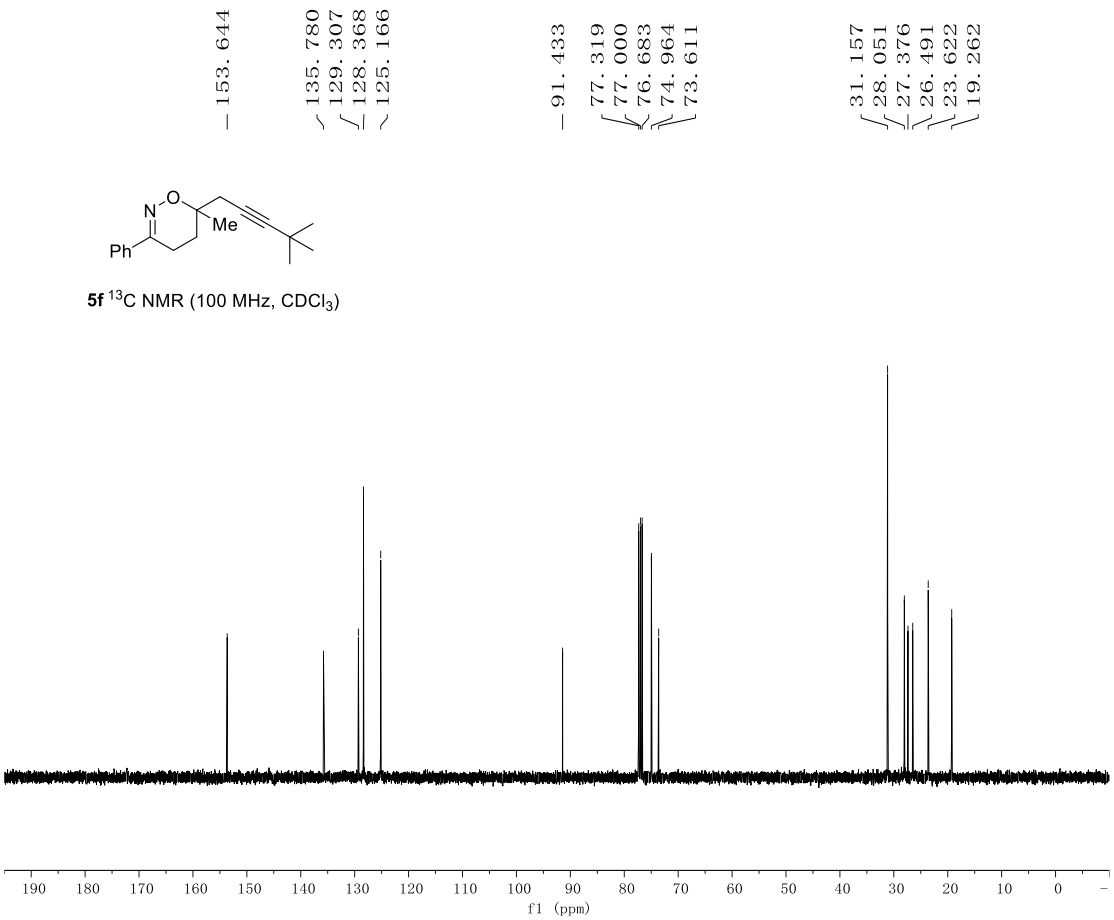


5e ^{13}C NMR (100 MHz, $CDCl_3$)

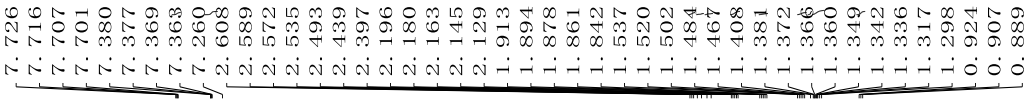


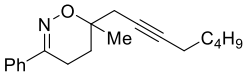


5f ^{1}H NMR (400 MHz, $CDCl_3$)

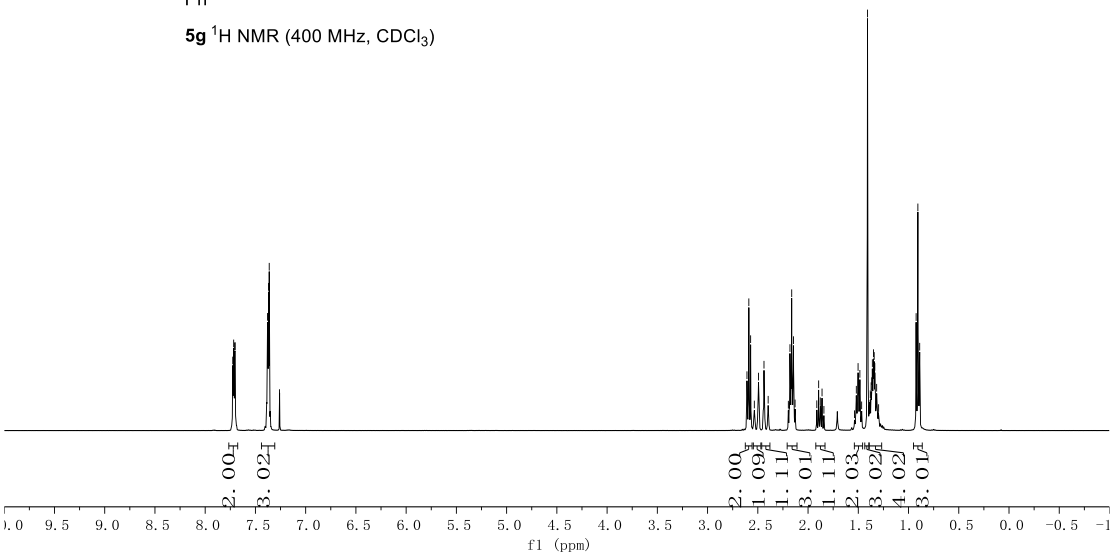


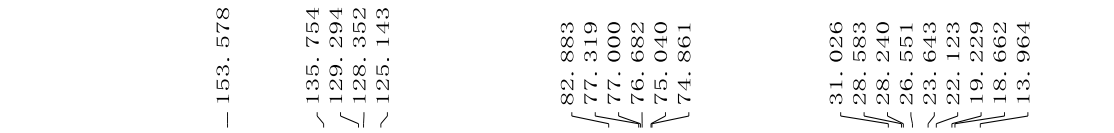
5f ^{13}C NMR (100 MHz, $CDCl_3$)

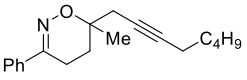




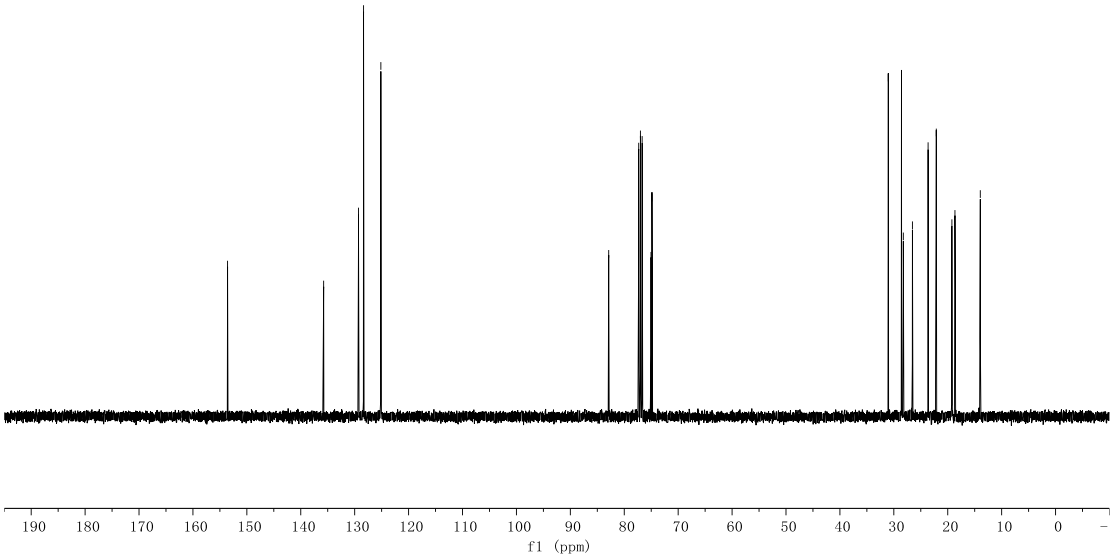
5g ^{1}H NMR (400 MHz, $CDCl_3$)

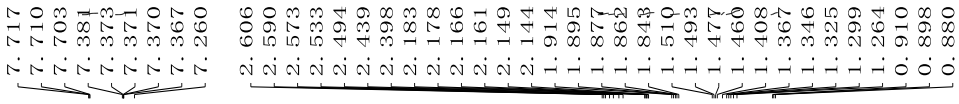


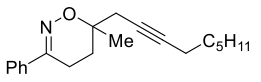




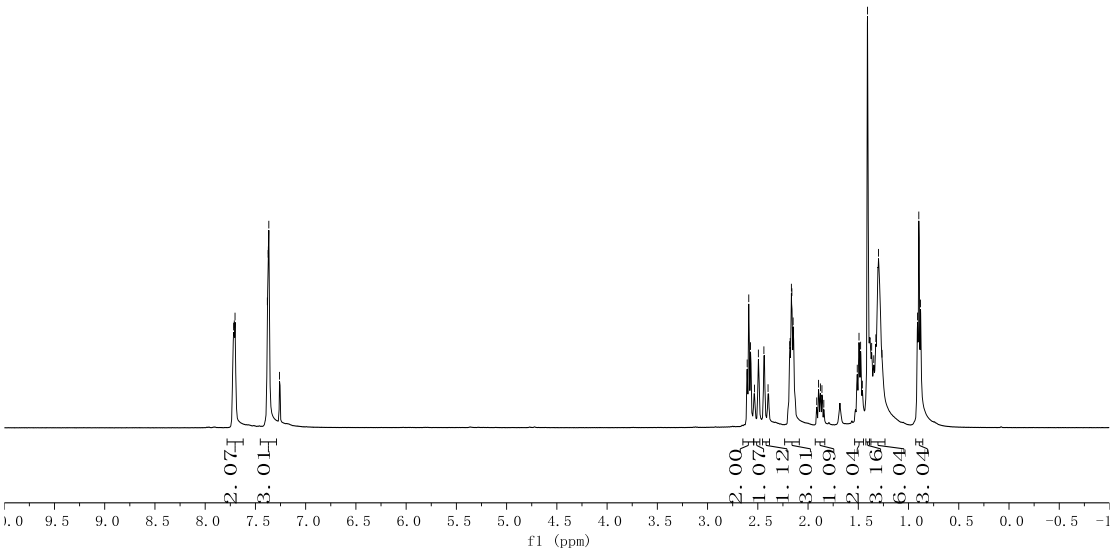
5g ^{13}C NMR (100 MHz, $CDCl_3$)

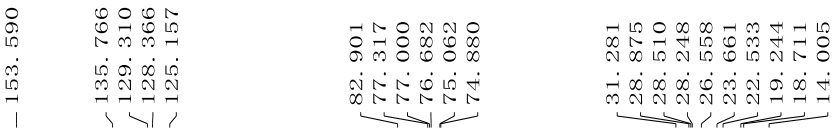


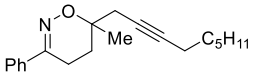




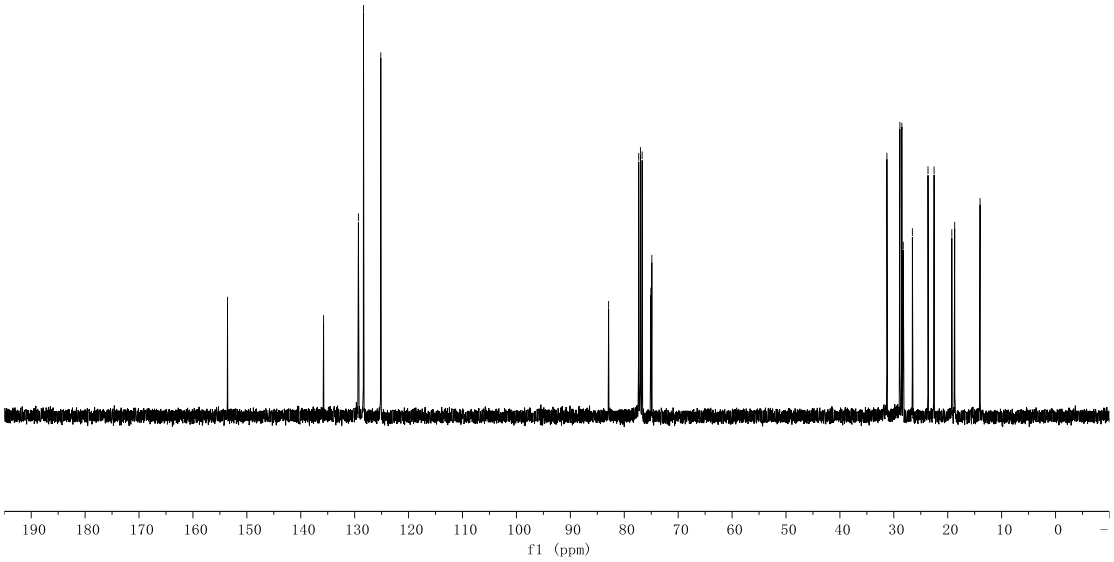
5h ^{1}H NMR (400 MHz, $CDCl_3$)

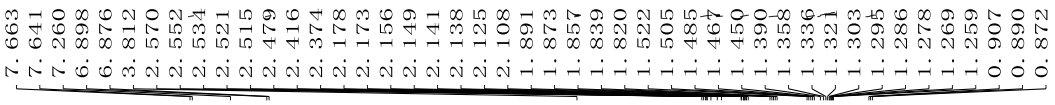


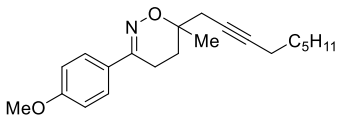




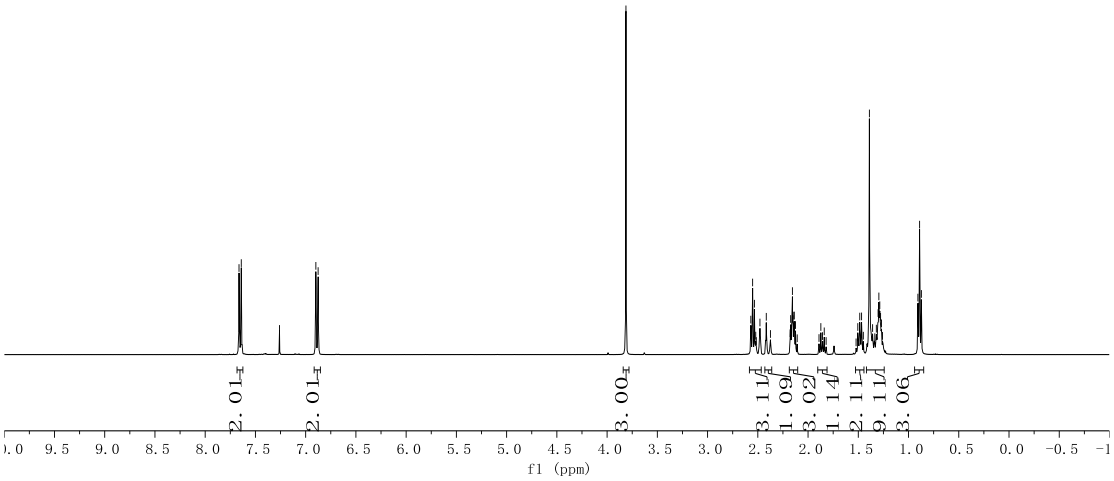
5h ^{13}C NMR (100 MHz, $CDCl_3$)

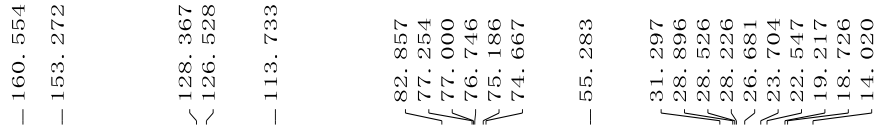


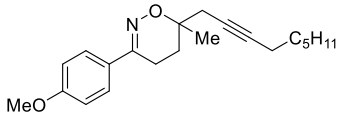




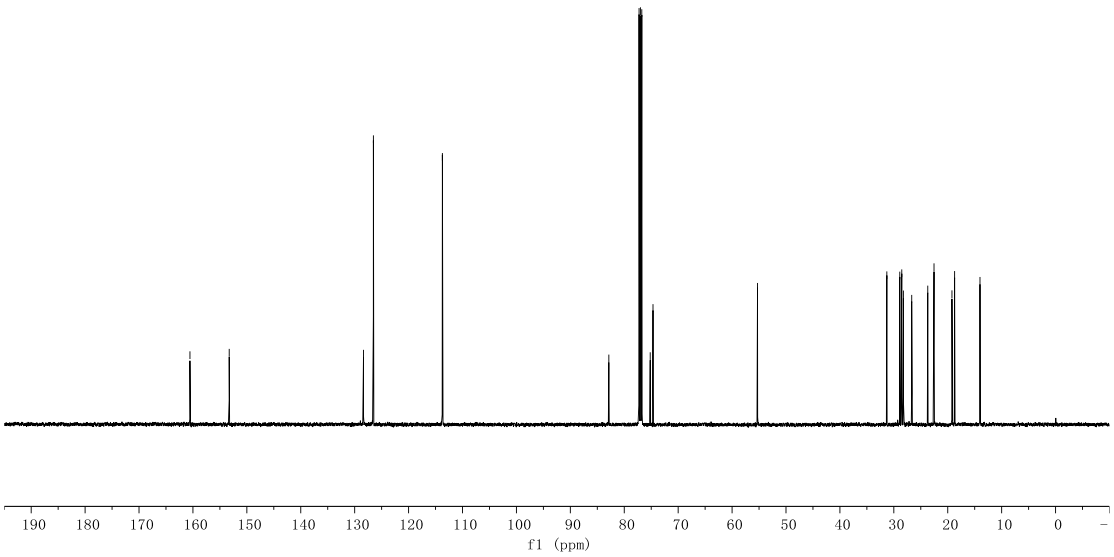
5i ^{1}H NMR (400 MHz, $CDCl_3$)

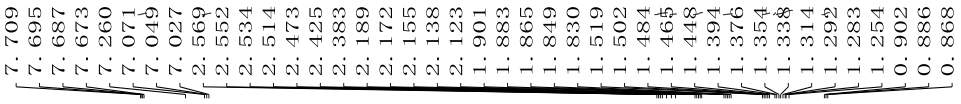


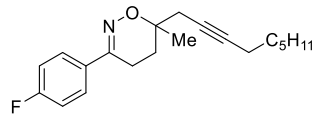




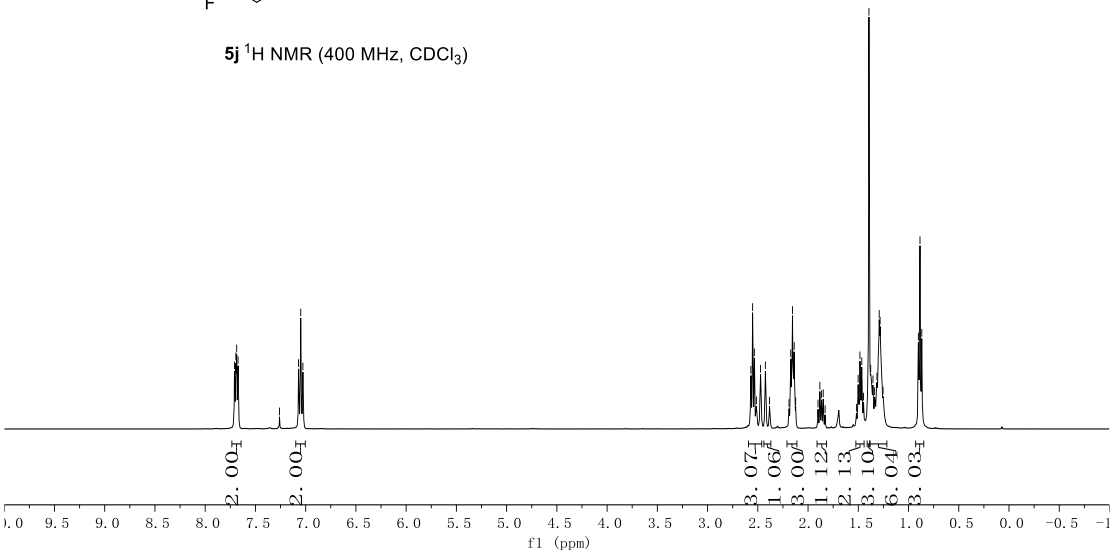
5i ^{13}C NMR (125 MHz, $CDCl_3$)

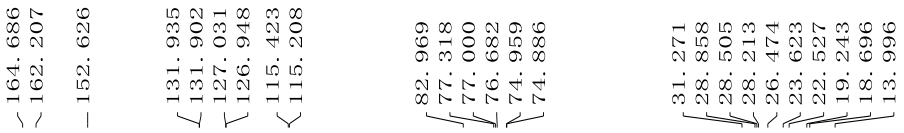


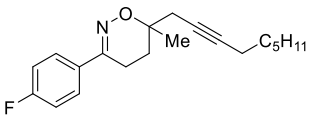




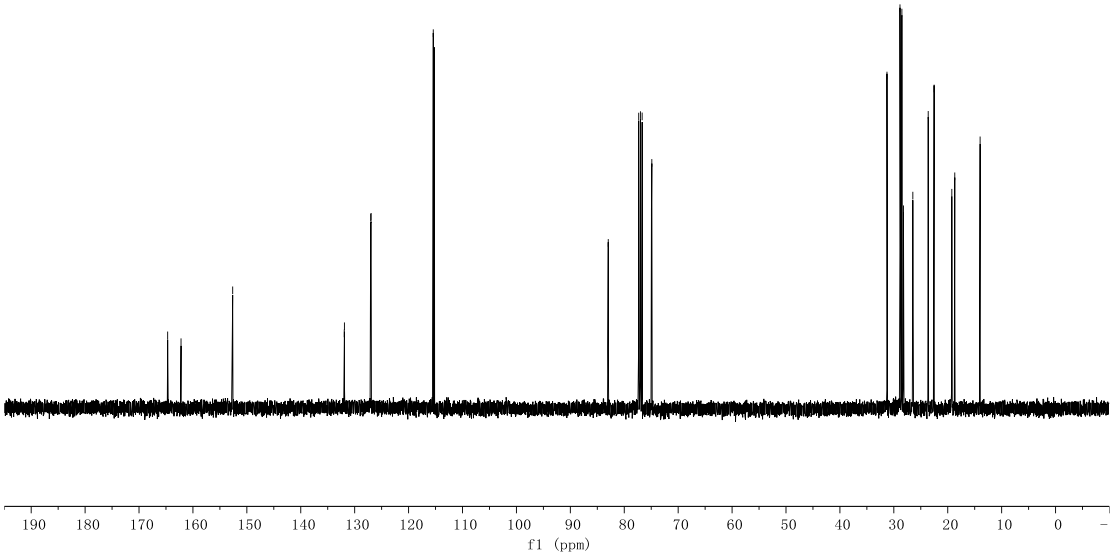
5j ^{1}H NMR (400 MHz, $CDCl_3$)

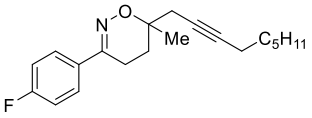




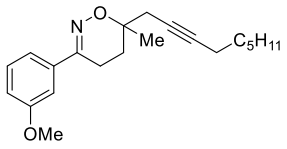


5j ^{13}C NMR (100 MHz, $CDCl_3$)

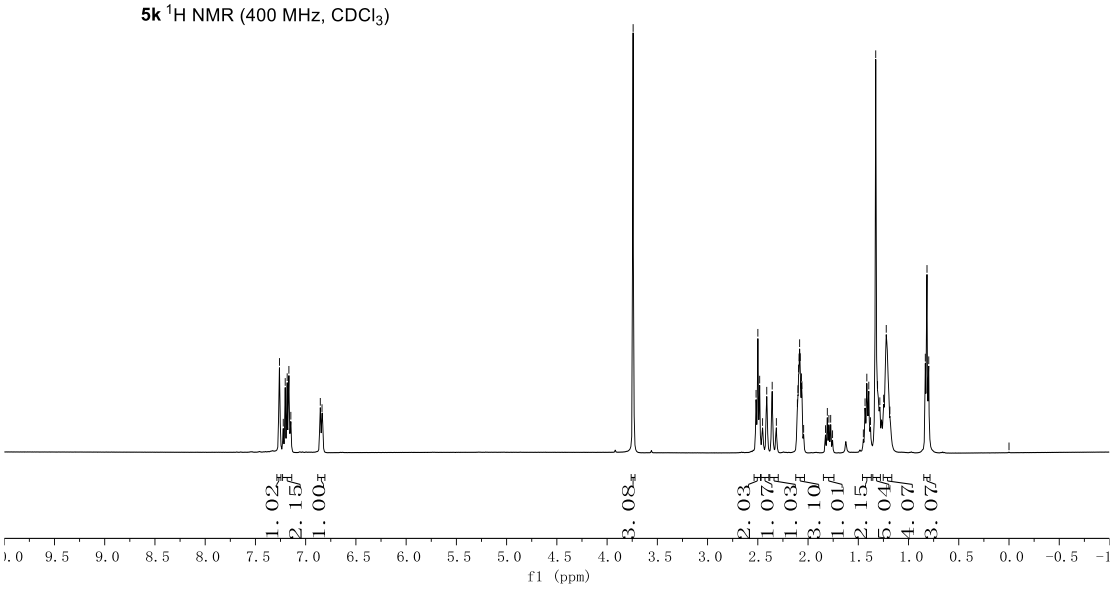


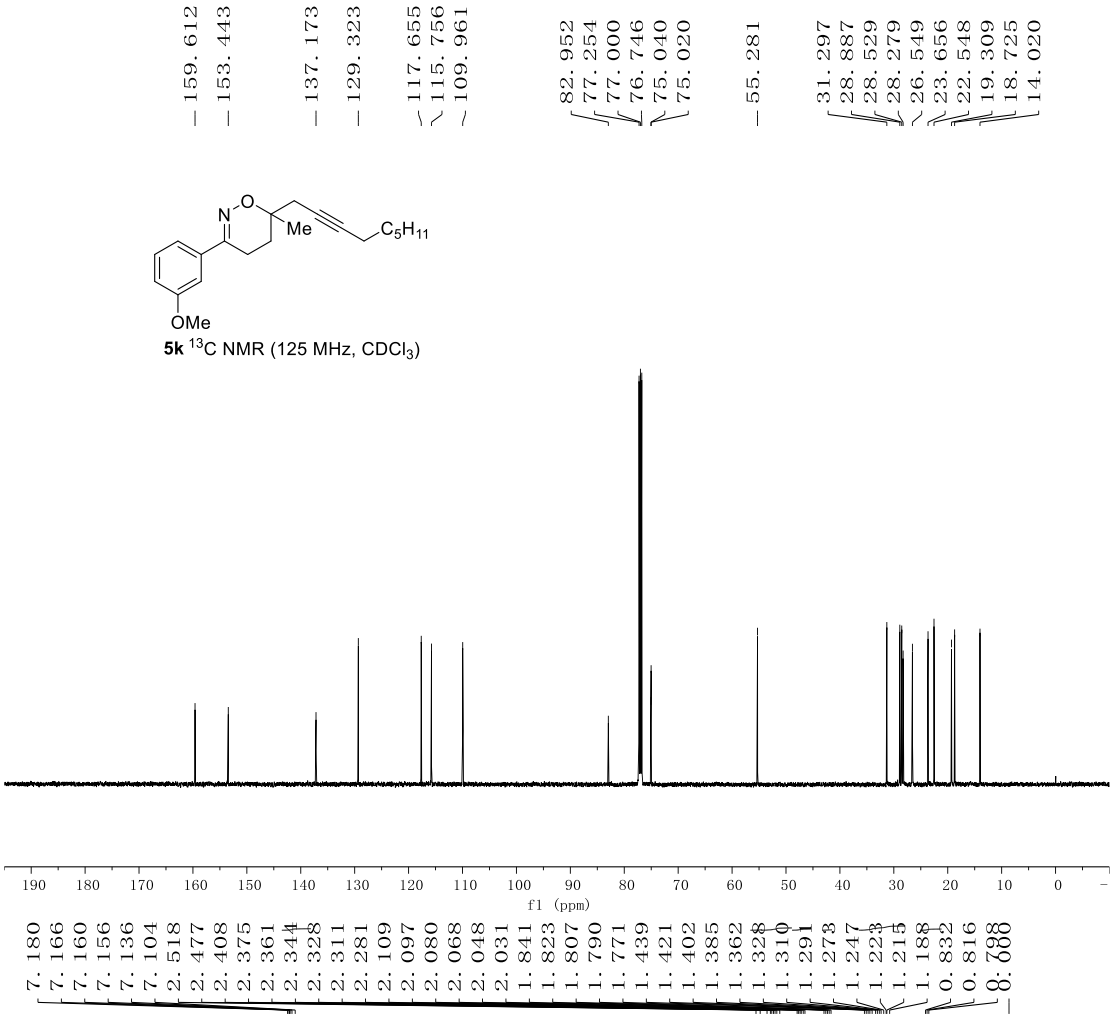


5j ^{19}F NMR (376 MHz, $CDCl_3$)

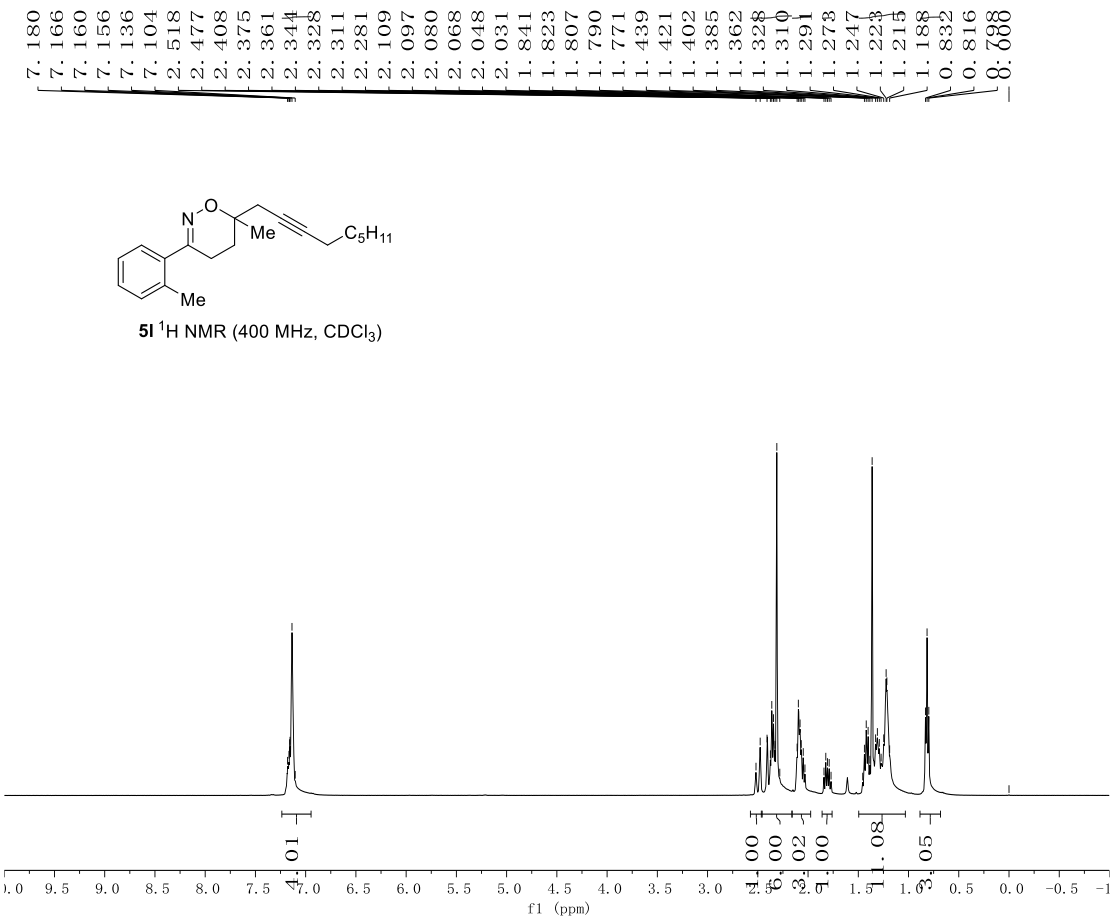


5k ^{1}H NMR (400 MHz, $CDCl_3$)

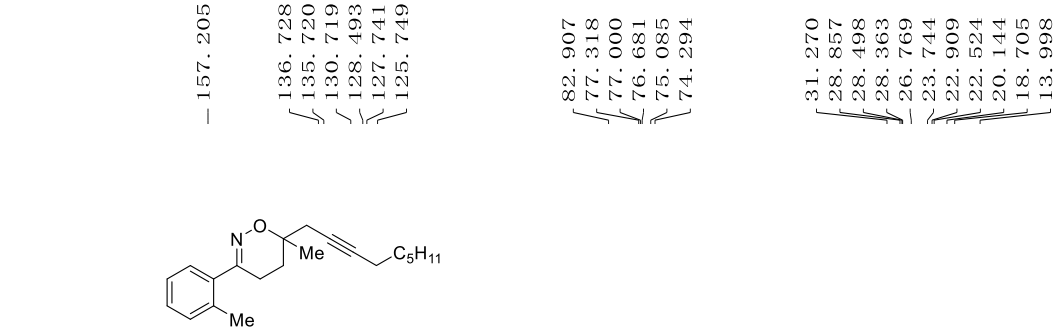




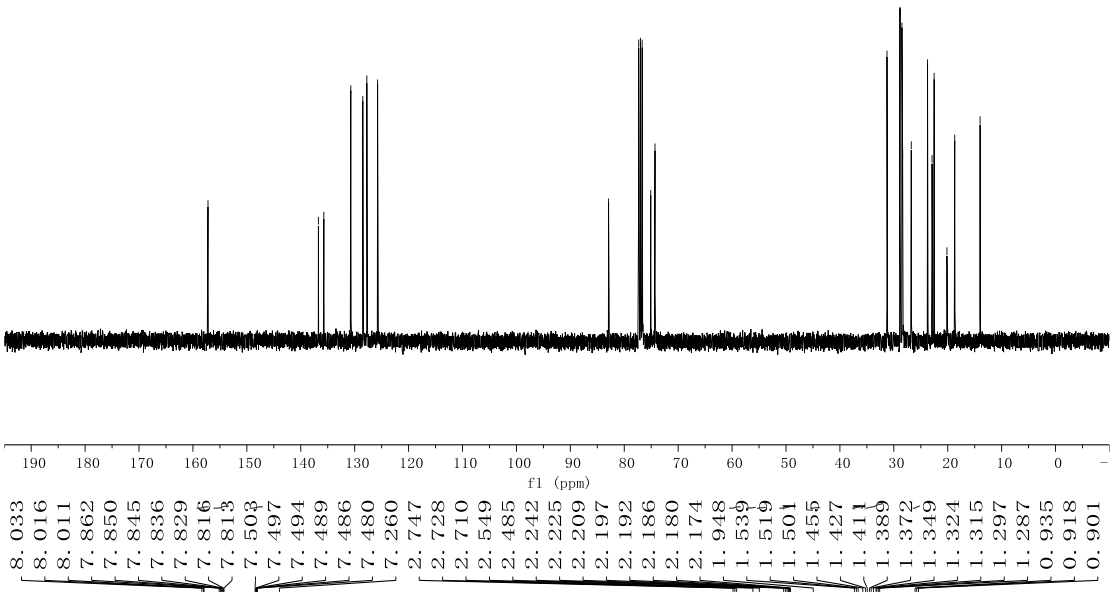
5k ^{13}C NMR (125 MHz, $CDCl_3$)

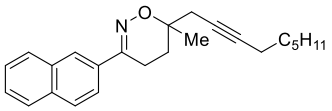


5l ^{1}H NMR (400 MHz, $CDCl_3$)

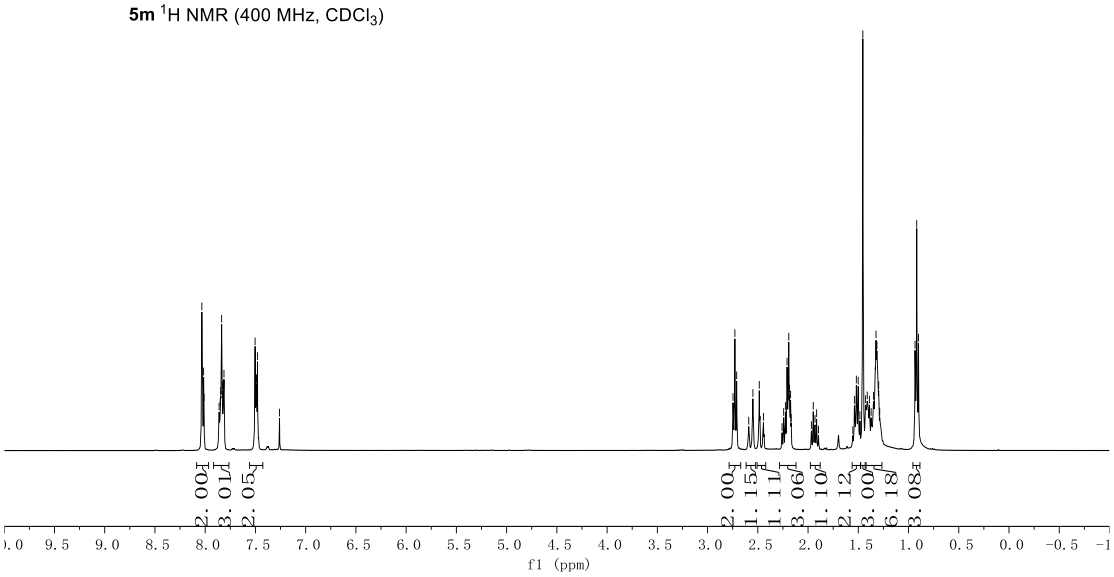


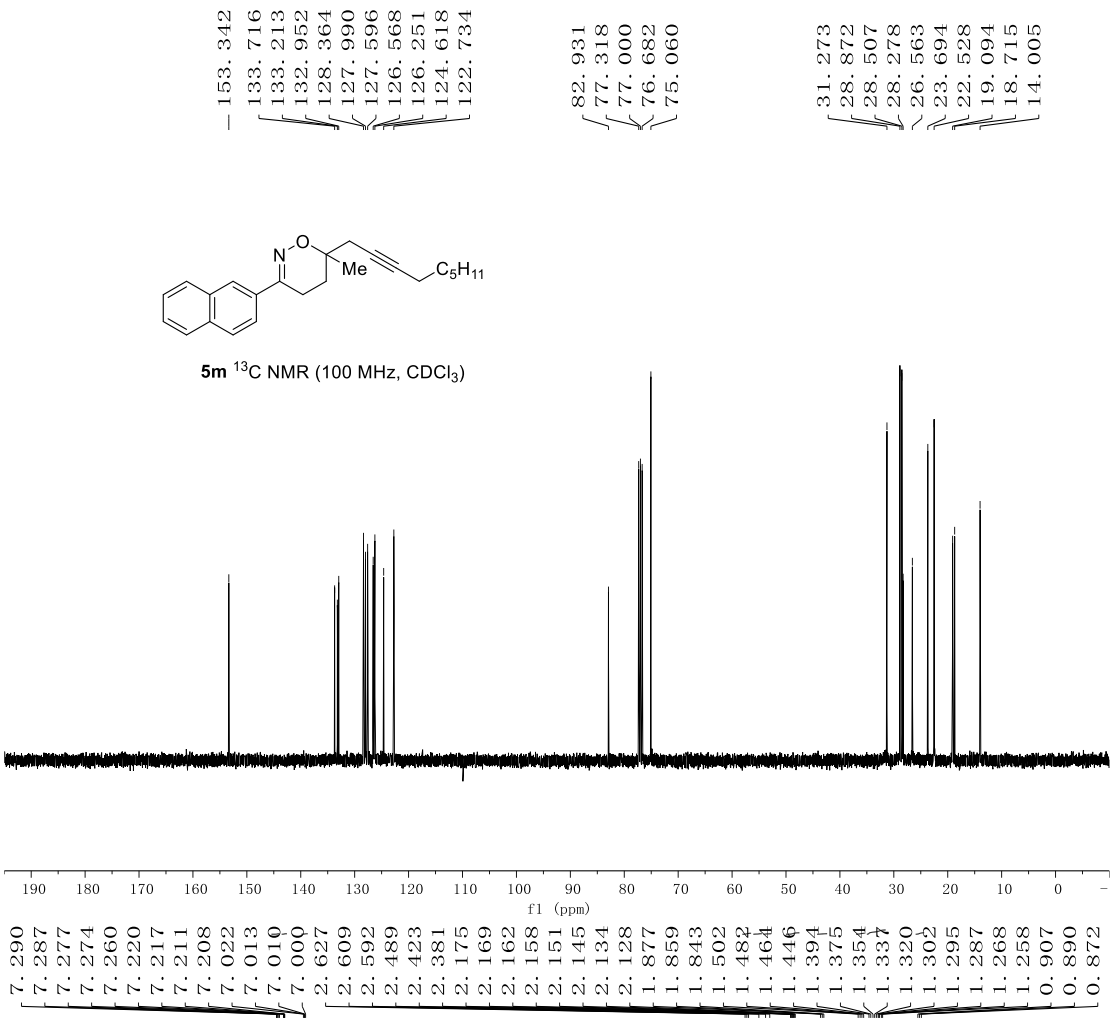
5l ^{13}C NMR (100 MHz, $CDCl_3$)



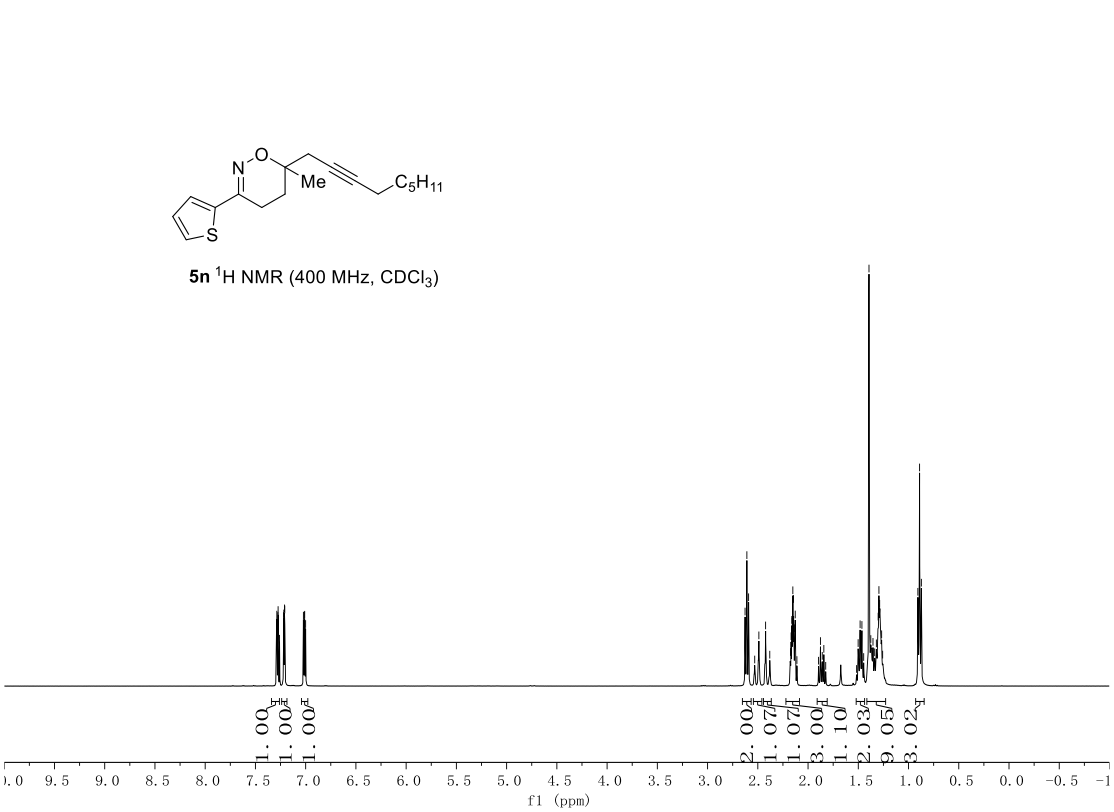


5m ^{1}H NMR (400 MHz, $CDCl_3$)

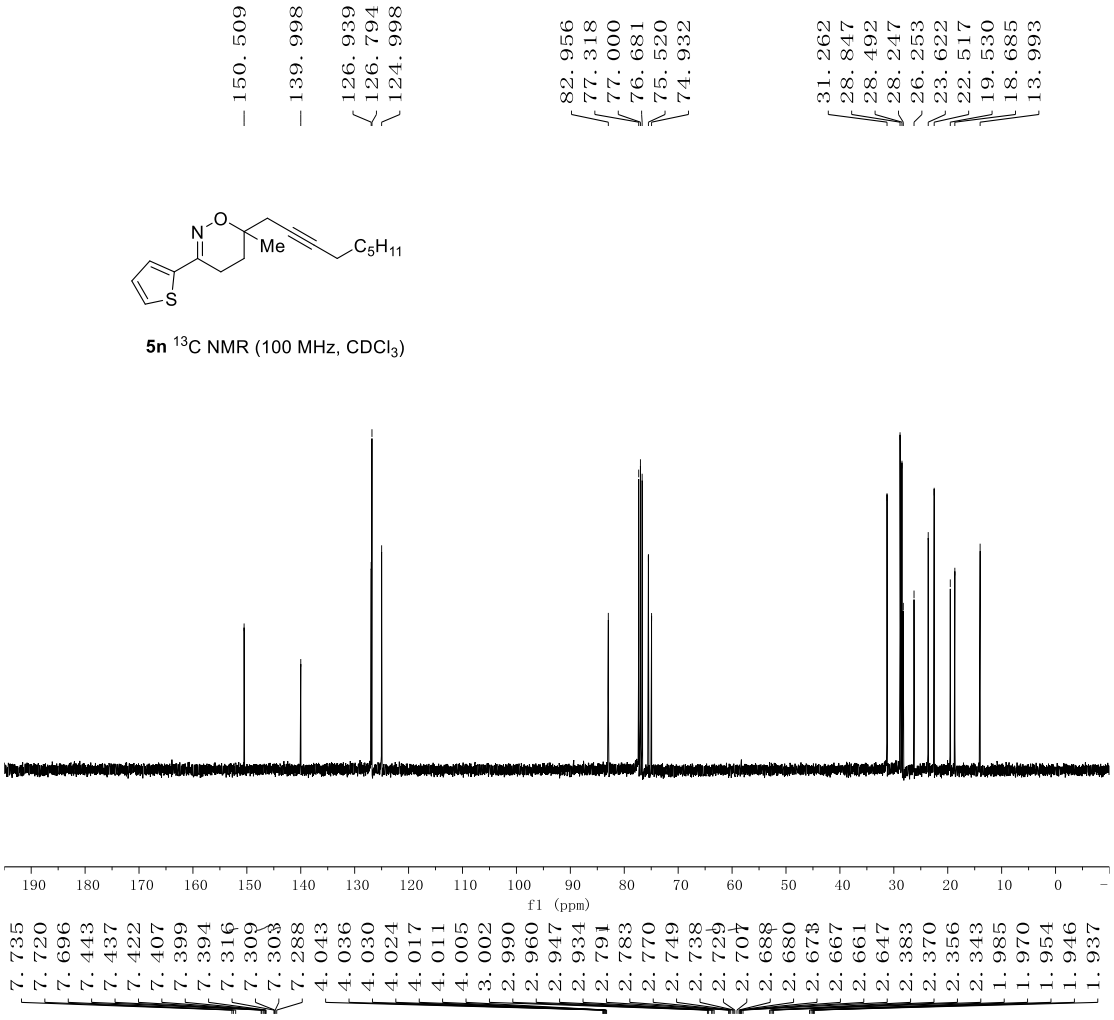




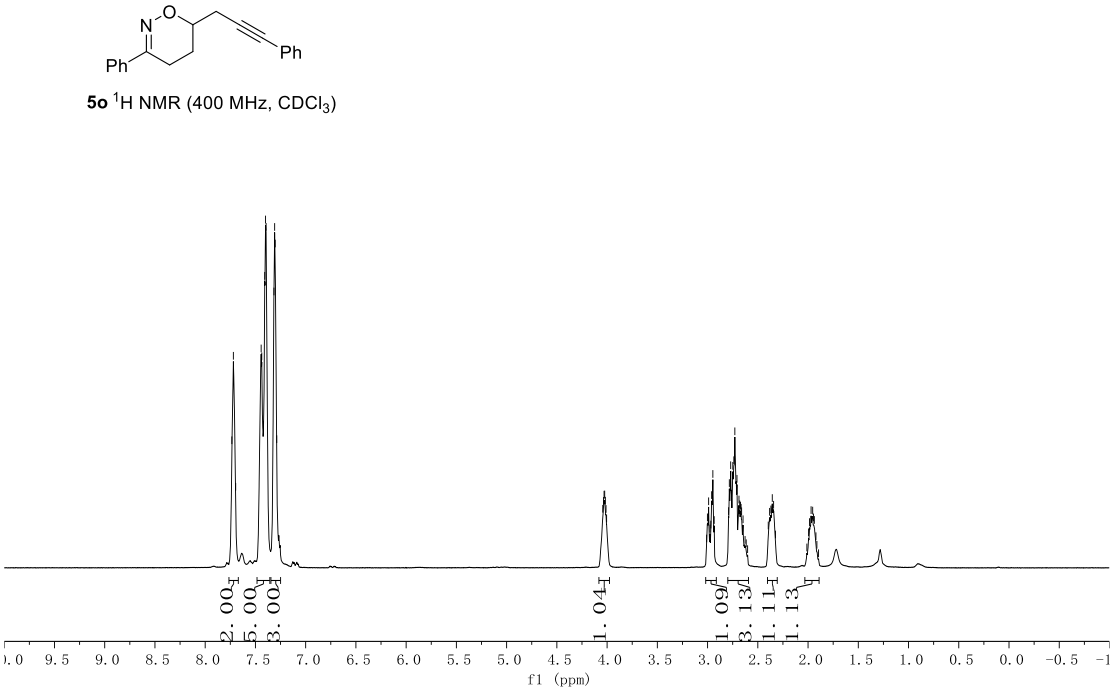
5m ^{13}C NMR (100 MHz, $CDCl_3$)



5n ^{1}H NMR (400 MHz, $CDCl_3$)

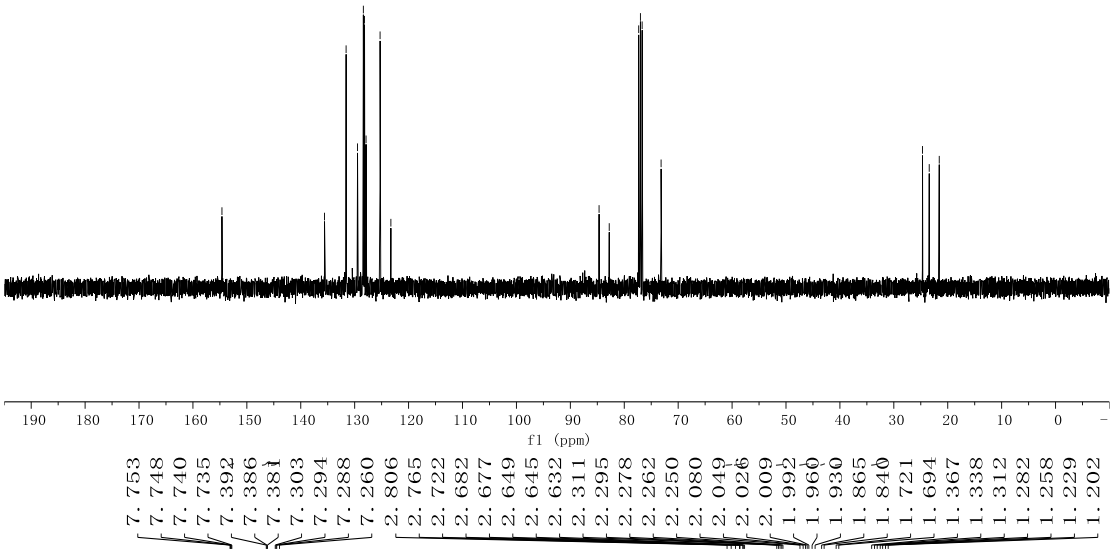


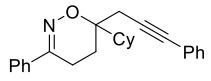
5n ^{13}C NMR (100 MHz, $CDCl_3$)



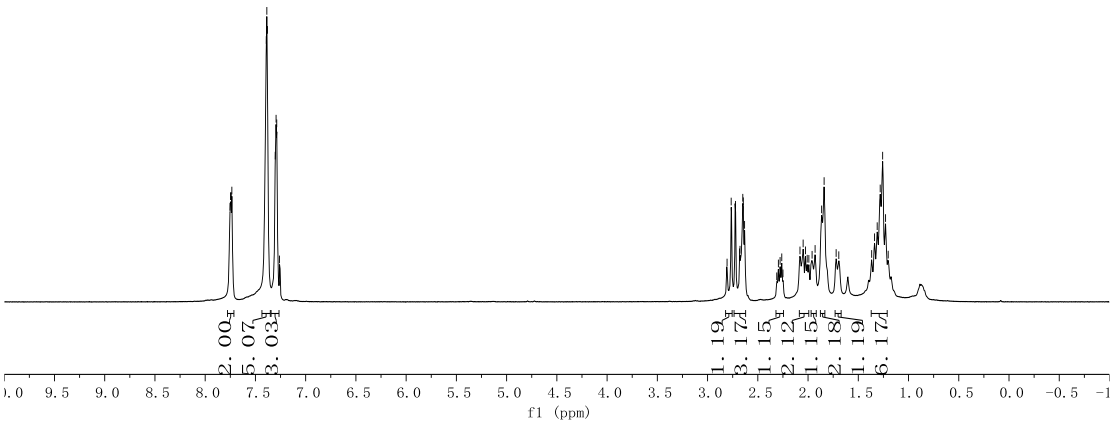
5o ^{1}H NMR (400 MHz, $CDCl_3$)

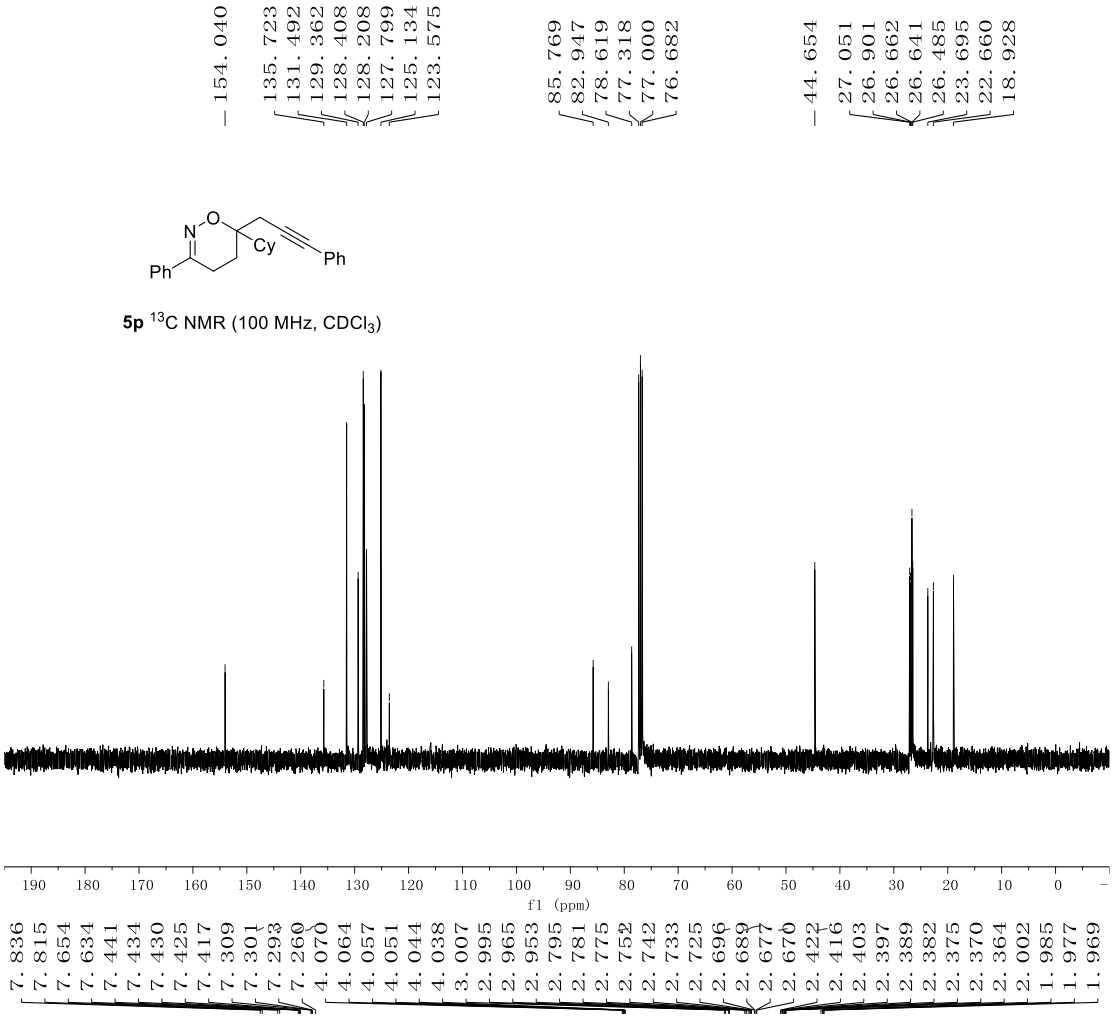
5o ^{13}C NMR (100 MHz, $CDCl_3$)



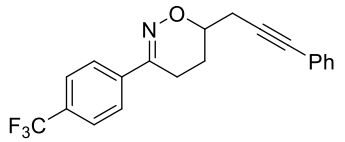


5p ^{1}H NMR (400 MHz, $CDCl_3$)

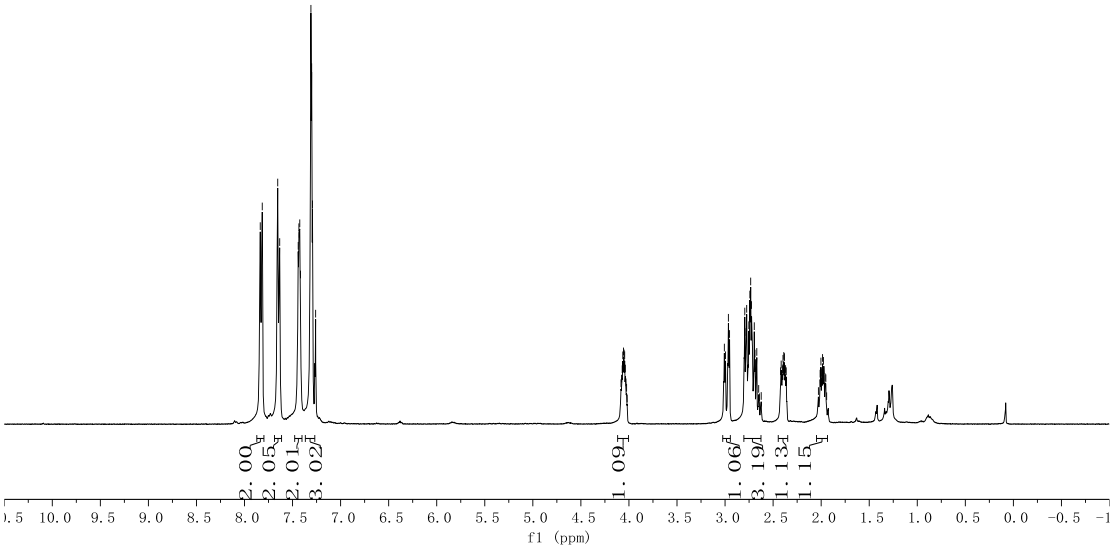


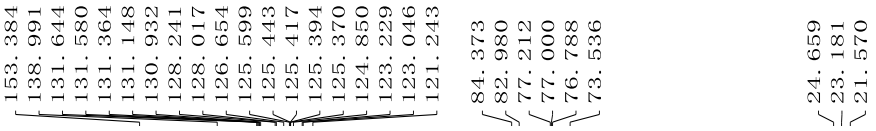


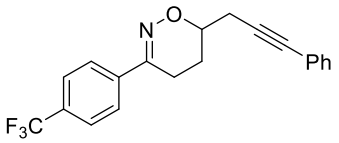
5p ^{13}C NMR (100 MHz, $CDCl_3$)



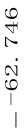
5q ^{1}H NMR (400 MHz, $CDCl_3$)

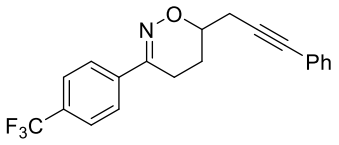




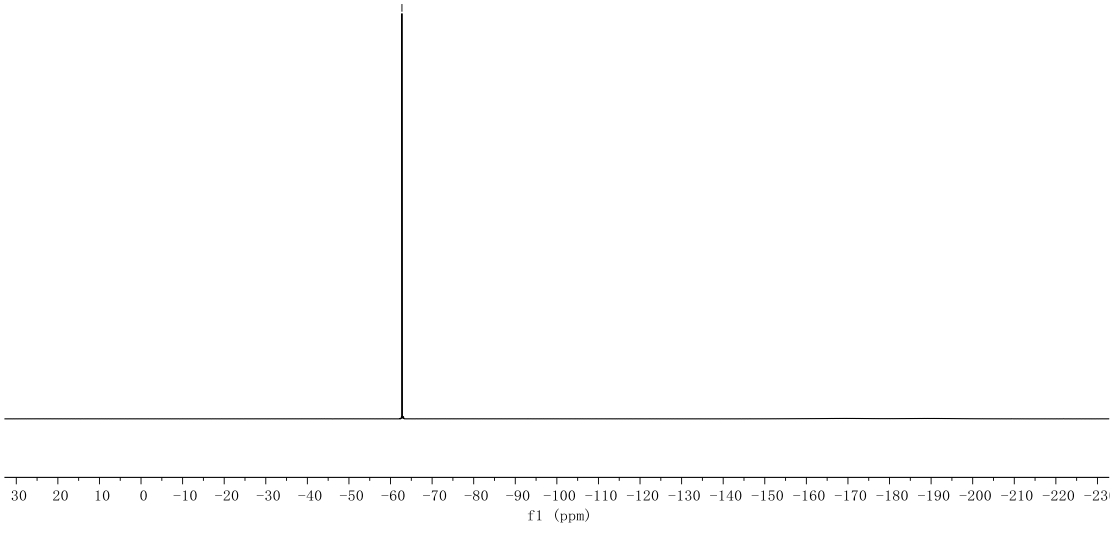


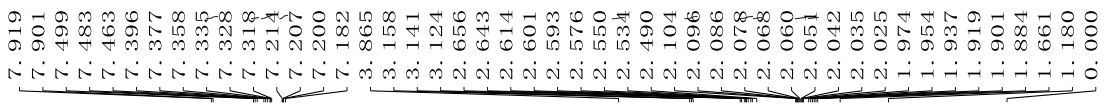
5q ^{13}C NMR (150 MHz, $CDCl_3$)

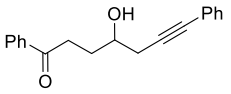




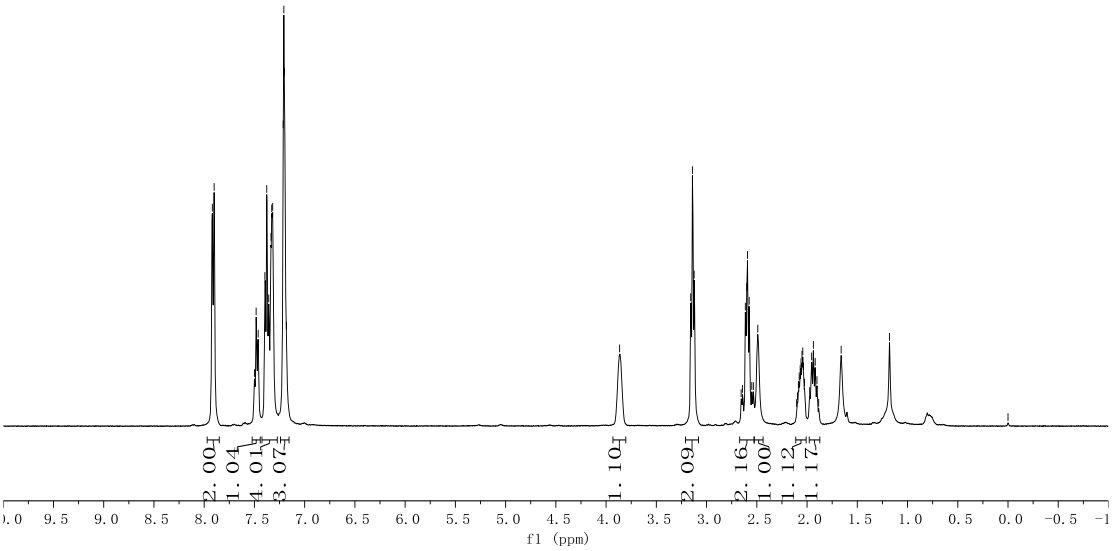
5q ^{19}F NMR (564 MHz, $CDCl_3$)

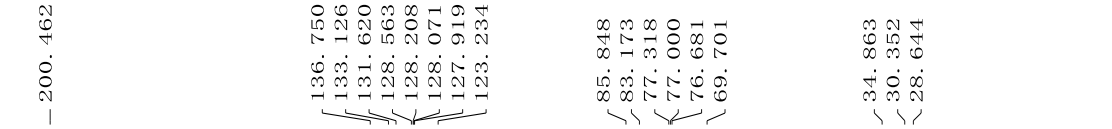


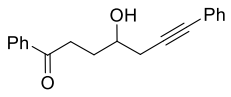




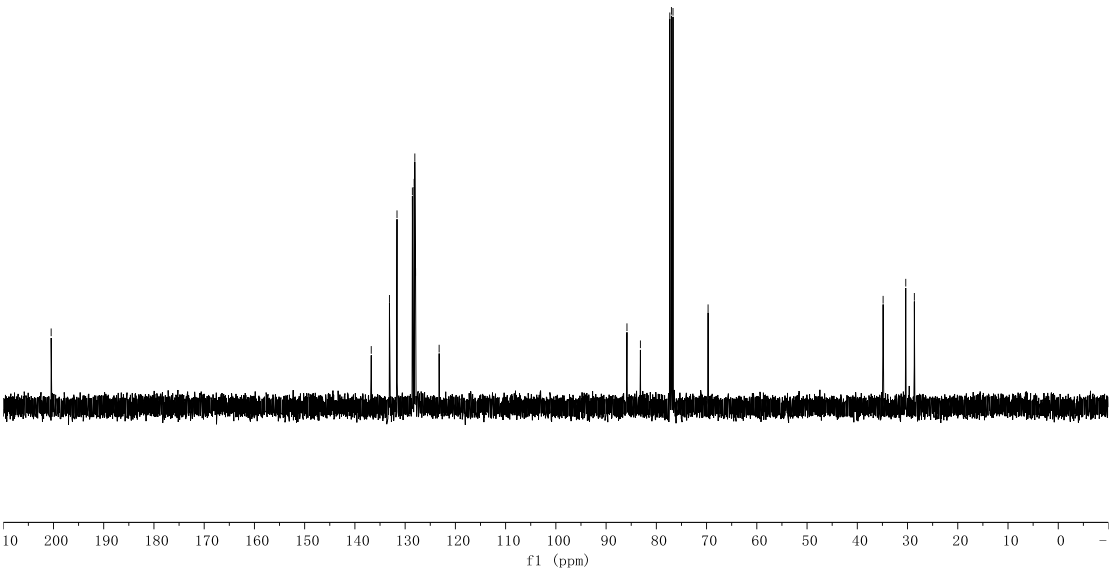
6 ^{1}H NMR (400 MHz, $CDCl_3$)

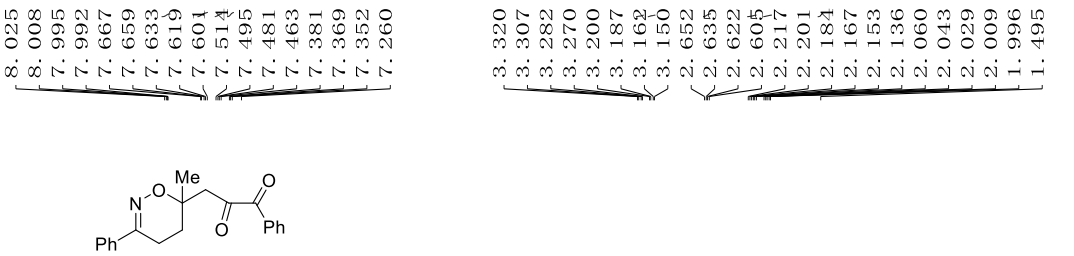




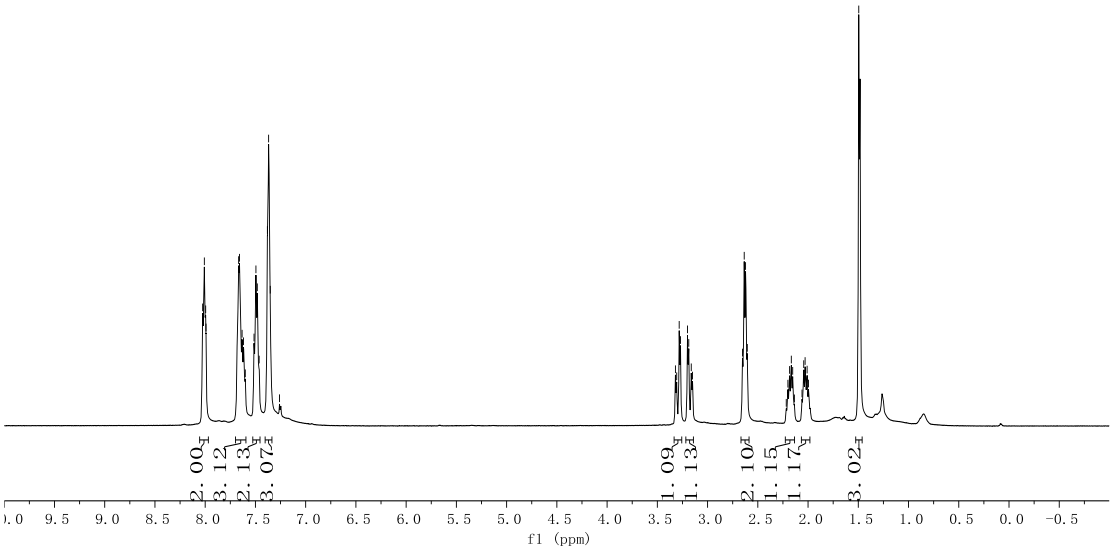


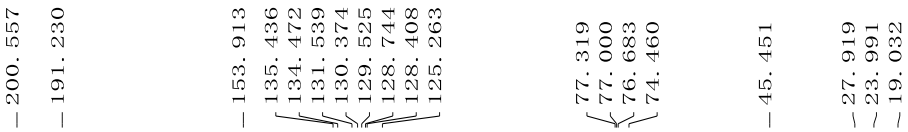
6 ^{13}C NMR (100 MHz, $CDCl_3$)

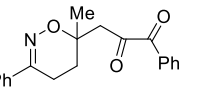




7 ^{1}H NMR (400 MHz, $CDCl_3$)







7 ^{13}C NMR (100 MHz, $CDCl_3$)