Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information

Efficient synthesis of propargylamines from terminal alkynes, dichloromethane and tertiary amines over silver catalysts

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Contents

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1. General remarks

All non-aqueous reactions and manipulations were performed in air atmosphere using standard Schlenk techniques. All solvents before use were dried, degassed by standard methods, and stored under nitrogen. The reactions were monitored by GC and GC-MS. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer at 400 MHz and 100 MHz respectively, and chemical shifts were reported in parts per million (ppm) downfield from TMS using the solvent resonance as internal standard. Flash column chromatography was performed using silica gel 30-60 μm. GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 7820A. Terminal alkynes were purchased from Energy Chemical, Alfa Aesar, Aladdin or Maya Reagent; they were dried and degassed by standard methods and stored under nitrogen before use. The tertiary amines were purchased from Aladdin, dried, and degassed by standard methods before use.

2. General procedure

5 mol% AgOAc, 1.0 mmol terminal alkynes, 15 mmol dichloromethane, 3 mmol tertiary amines were dissolved in 1 mL dioxane under N_2 atmosphere and stirred at 120 ^{o}C in sealed tube (schleck tube which was sealed by a rubber septum). After completion of the reaction, the resulting solution was cooled to room temperature, washed with saturated $NaCO_3$ aqueous solution, and extracted with $CHCl_3$ three times. The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with EtOAc/petroleum ether (1/4−1/100) to afford the desired product.

Caution: We conducted a scale-up experiment (15 mmol phenylacetylene, 45 mmol Et_3N, 125 mmol CH_2Cl_2) (the picture is shown below). It is safe under the adopted conditions. However, it is not sure the potential risks for the synthesis of products in larger scales.

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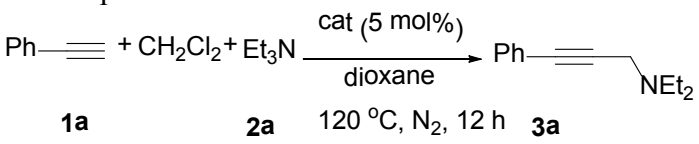
3. Optimization of reaction conditions[a]

SI-Table 1. Optimization of the reaction conditions[a]



Entry	CH_2Cl_2	Et_3N	Catalyst	Yield[b] (%)
1	1	3	AgOAc	trace
2	2	3	AgOAc	10
3	7	3	AgOAc	38
4	15	3	AgOAc	98
5	15	4	AgOAc	98
6	15	2	AgOAc	67
7[c]	15	3	AgOAc	40
8	15	3	$AgNO_3$	88
9	15	3	Ag_2CO_3	80
10	15	3	$AgOSO_2CF_3$	80
11	15	3	$AgBF_4$	90
12	15	3	$AgClO_4$	70
13	15	3	$AgOSO_2C_4F_9$	92
14	15	3	AgCl	85
15	15	3	-	trace

[a] Reaction conditions: phenylacetylene (1.0 mmol), CH_2Cl_2 (1 mmol-15 mmol), Et_3N (2 mmol-4 mmol), dioxane (1mL), N_2, 120 °C, 12 h, sealed tube. [b] Yields were based on phenylacetylene and determined by GC using dodecane as the internal standard.

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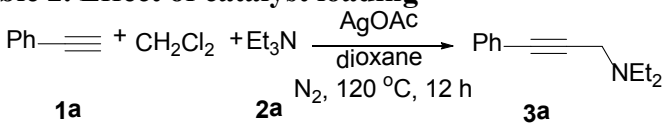
SI-Table 2. Effect of catalyst loading[a]



1a **2a** **3a**

Entry	Catalyst loading (mol%)	Yield[b] (%)
1	1	62
2	3	90
3	5	98
4	7	98
5	10	97

[a] Reaction conditions: phenylacetylene (1.0 mmol), CH_2Cl_2 (15 mmol), Et_3N (3mmol), dioxane (1mL), N_2, 120 °C, 12 h, sealed tube. [b] Yields were based on phenylacetylene and determined by GC using dodecane as the internal standard.

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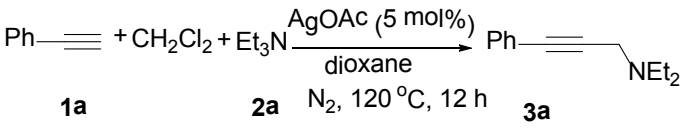
SI-Table 3. Effect of solvent[a]



Entry	Solvent	Yield[b] (%)
1	-	79
2	DMF	87
3	DMSO	80
4	THF	89
5	CH_3CN	43
6	Toluene	33
7[c]	Benzene	72
8	C_2H_5OH	35
9	CH_3OH	16
10	CCl_4	14
11	$C_2H_5OC_2H_5$	36
12	$CH_3COOC_2H_5$	51
13	$CHCl_3$	71
14	Dioxane	98
15	Dioxane (1 mL)+H_2O (0.1 mL)	50
16	Dioxane (1 mL)-air	trace
17	Dioxane (2 mL)	97
18	Dioxane (4 mL)	90

[a] Reaction conditions: phenylacetylene (1.0 mmol), CH_2Cl_2 (15 mmol), Et_3N (3 mmol), solvent (1mL), N_2, 120 °C, 12 h, sealed tube. [b] Yields were based on phenylacetylene and determined by GC using dodecane as the internal standard.

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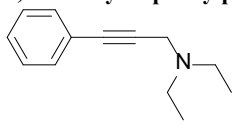
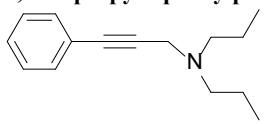
4. ^{1}H NMR and ^{13}C NMR data of products

***N,N*-Diethyl-3-phenylprop-2-yn-1-amine (3a)[1]**



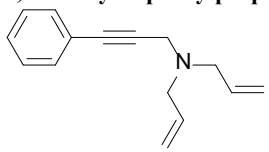
Following the general procedure (EtOAc/petroleum ether 1:4), **3a** was obtained as a pale yellow liquid, isolated yield: 93%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.41–7.44 (m, 2H), 7.28–7.30 (m, 3H), 3.65 (s, 2H), 2.62 (q, 4H, *J* = 7.2 Hz), 1.12 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.6, 128.2, 127.8, 123.3, 85.0, 84.4, 47.3, 41.5, 12.6; GC-MS: m/z=187.

***N,N*-Dipropy-3-phenylprop-2-yn-1-amine (3b)[2]**



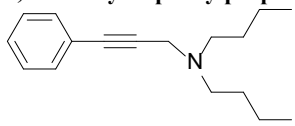
Following the general procedure (EtOAc/petroleum ether 1:6), **3b** was obtained as a faint yellow liquid, isolated yield: 88%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.42–7.44 (m, 2H), 7.29–7.31 (m, 3H), 3.63 (s, 2H), 2.51 (t, 4H, *J* = 6.0 Hz), 1.49-1.58 (m, 4H), 0.93 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.7, 128.2, 127.9, 123.3, 85.0, 84.5, 55.8, 42.7, 20.6, 11.9; GC-MS: m/z=215.

***N,N*-Diallyl-3-phenylprop-2-yn-1-amine (3c)**



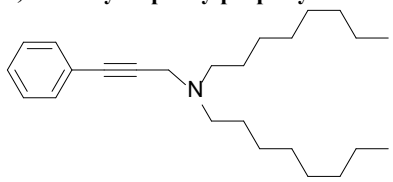
Following the general procedure (EtOAc/petroleum ether 1:4), **3c** was obtained as a colorless liquid, isolated yield: 86%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): *δ* 7.43–7.46 (m, 2H), 7.28–7.31(m, 3H), 5.83-5.92 (m, 2H), 5.29 (q, 1H, *J* = 1.2Hz), 5.25 (q, 1H, *J* = 1.2Hz), 5.19 (t, 1H, *J* = 1.0Hz,), 5.17 (t, 1H, *J* = 1.0Hz), 3.60 (s, 2H), 3.19 (d, 4H, *J* = 2.4Hz); ^{13}C NMR (100 MHz, CDCl3, TMS): δ 135.3, 131.7, 128.2, 127.9, 123.3, 118.2, 85.3, 84.2, 56.5, 42.1. HRMS (EI): calcd for $C_{15}H_{17}N$: 211.1361, found: 211.1378.

***N,N*-Dibutyl-3-phenylprop-2-yn-1-amine (3d)[2]**



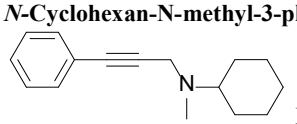
Following the general procedure (EtOAc/petroleum ether 1:6), **3d** was obtained as a faint yellow liquid, isolated yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): *δ* 7.41–7.43 (m, 2H), 7.28–7.30 (m, 3H), 3.61 (s, 2H), 2.53 (q, 4H, *J* = 6.0Hz), 1.45-1.50 (m, 4H), 1.32-1.38 (m, 4H), 0.93 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 131.6, 128.1, 127.8, 123.4, 84.9, 84.7, 53.6, 42.6, 29.7, 20.7, 14.0; GC-MS: m/z=243.

***N,N*-Dioctyl-3-phenylprop-2-yn-1-amine (3e)[2]**



Following the general procedure (EtOAc/petroleum ether 1:100), **3e** was obtained as a colorless liquid, isolated yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): *δ* 7.42–7.45 (m, 2H), 7.28–7.31 (m, 3H), 3.72 (s, 2H), 2.61-2.68 (m, 4H), 1.58 (s, 4H), 1.26-1.32 (m, 20H), 0.88 (t, 6H, *J* = 6.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 131.7, 128.2, 128.2, 128.0, 85.0, 84.7, 53.9, 43.2, 31.8, 29.4, 29.2, 27.4, 26.9, 22.6, 14.1; GC-MS: m/z=355.

***N*-Cyclohexan-N-methyl-3-phenylprop-2-yn-1-amine (3f)[4]**



Following the general procedure (EtOAc/petroleum ether 1:4), **3f** was obtained as a colorless liquid, isolated yield: 89%. ^{1}HNMR ($CDCl_3$, 400 MHz, TMS): *δ* 7.42–7.44 (m, 2H), 7.28–7.31 (m, 3H), 3.65 (s, 2H), 2.45-2.48 (m, 1H), 2.43 (s, 3H), 1.96 (d, 2H, *J* = 10.4Hz), 1.80 (d, 2H, *J* = 2.0Hz), 1.78 (d, 1H, *J* = 2.4Hz), 1.23 (d, 4H, *J* = 1.2Hz), 1.17-1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 131.6, 128.2, 127.9, 123.3, 85.4, 84.9, 61.1, 43.7, 38.5, 29.7, 26.0, 25.5; GC-MS: m/z=227.

1-(3-phenylprop-2-yn-1-yl)piperidine (3g)[2]

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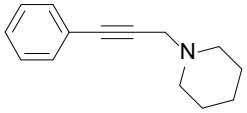
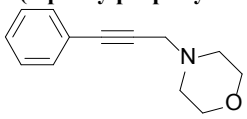


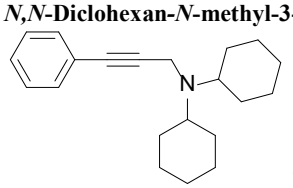
Following the general procedure (EtOAc/petroleum ether 1:4), **3g** was obtained as a colorless liquid, isolated yield: 87%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.42–7.45 (m, 2H), 7.27–7.30 (m, 3H), 3.48 (s, 2H), 2.57 (s, 4H), 1.61-1.67 (m, 4H), 1.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.6, 128.1, 127.9, 123.1, 85.0, 84.8, 53.3, 48.3, 25.8, 23.8; GC-MS: m/z=198.

4-(3-phenylprop-2-yn-1-yl)morpholine (3h)[2]



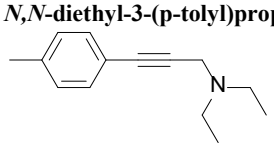
Following the general procedure (EtOAc/petroleum ether 1:1), **3h** was obtained as a colorless liquid, isolate yield: 88%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.43–7.45 (m, 2H), 7.29–7.32 (m, 3H), 3.78 (t, 4H, J = 4.6 Hz), 3.52 (s, 2H), 2.66 (t, 4H, J = 4.6Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.7, 128.3, 128.2, 122.9, 85.6, 83.9, 66.8, 52.4, 48.1; GC-MS: m/z=201.

***N,N*-Diclohexan-*N*-methyl-3-phenylprop-2-yn-1-amine (3i)**



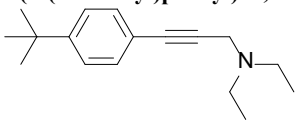
Following the general procedure (EtOAc/petroleum ether 1:10), **3i** was obtained as a colorless liquid, isolated yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.39–7.42 (m, 2H), 7.30–7.32(m, 3H), 3.89 (s, 2H), 3.09 (t, 2H, J = 11.4Hz), 2.02 (d, 4H, J = 11.2Hz), 1.84 (d, 4H, J = 13.2Hz), 1.51-1.66 (m, 6H), 1.15-1.33 (m, 6H); ^{13}C NMR (100 MHz, CDCl3, TMS): δ 131.4, 128.2, 122.7, 85.6, 85.1, 58.4, 35.6, 29.8, 25.8, 25.7; HRMS (EI): calcd for $C_{21}H_{29}N$: 295.2300, found: 295.2306.

***N,N*-diethyl-3-(p-tolyl)prop-2-yn-1-amine (3j)[1]**



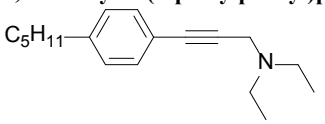
Following the general procedure (EtOAc/petroleum ether 1:4), **3j** was obtained as a faint yellow liquid, isolated yield: 88% ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.31 (d, 2H, J = 8.0 Hz) Ar-H), 7.09 (d, 2H, J = 8.0 Hz), 3.63 (s, 2H), 2.63 (q, 4H, J = 7.2 Hz), 2.33 (s, 3H), 1.11 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 137.9, 131.5, 128.9, 120.2, 85.0, 83.4, 47.2, 41.4, 21.4. 12.6; GC-MS: m/z=201.

3-(4-(tert-butyl)phenyl)-*N,N*-diethylprop-2-yn-1-amine (3k)[6]



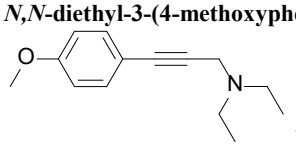
Following the general procedure (EtOAc/petroleum ether 1:4), **3k** was obtained as a colorless liquid, isolated yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.35 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 8.4 Hz), 3.63 (s, 2H), 2.61 (q, 4H, J = 7.2 Hz), 1.30 (s, 9H), 1.11 (t, 6H, J = 7 .2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 151.1, 131.4, 125.2, 120.4, 85.0, 83.6, 47,3, 41.45, 34.7, 31.2, 12.7; GC-MS: m/z=243.

***N,N*-diethyl-3-(4-pentylphenyl)prop-2-yn-1-amine (3l)**



Following the general procedure (EtOAc/petroleum ether 1:5), **3l** was obtained as a faint yellow liquid, isolate yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.32 (d, 2H, J = 8.0 Hz), 7.09 (d, 2H, J = 8.0 Hz,), 3.64 (s, 2H), 2.63 (q, 2H, J = 7.2 Hz), 2.57 (d, 4H, J = 8.0 Hz), 1.55-1.63 (m, 2H), 1.27-1.32 (m, 4H), 1.11 (t, 6H, J = 7.2 Hz), 0.88 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 143.0, 131.5, 128.3, 120.4, 85.1, 83.3, 47.2, 41.3, 35.8, 31.4, 30.9, 22.5, 14.0, 12.5; HRMS (EI): calcd for $C_{18}H_{27}N$: 257.2143, found: 257.2122.

***N,N*-diethyl-3-(4-methoxyphenyl)prop-2-yn-1-amine (3m)[1]**



Following the general procedure (EtOAc/petroleum ether 1:4), **3m** was obtained as a white liquid, isolated yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.34 (d, 2H, J = 8.8 Hz), 6.80 (d, 2H, J =

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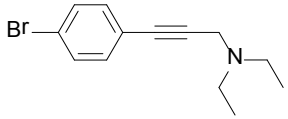
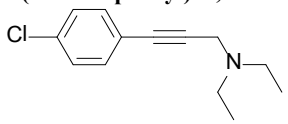
8.8 Hz), 3.79 (s, 3H), 3.62 (s, 2H), 2.60 (q, 4H, *J* = 7.2 Hz), 1.11 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 159.3, 133.1, 115.5, 113.8, 84.7, 82.7, 55.3, 47.3, 41.5, 12.6; GC-MS: m/z=217.

3-(4-bromophenyl)-*N,N*-diethylprop-2-yn-1-amine (3n)



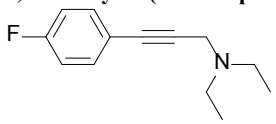
Following the general procedure (EtOAc/petroleum ether 1:4), **3n** was obtained as a faint yellow liquid, isolate yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.40 (d, 2H, *J* = 6.8 Hz), 7.26 (d, 2H, *J* = 6.8 Hz), 3.61 (s, 2H), 2.62 (q, 4H, *J* = 7.2 Hz), 1.11 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 133.2, 131.5, 122.3, 122.1, 85.8, 83.9, 47.3, 41.5, 12.6; GC-MS: m/z=265; HRMS (EI): calcd for $C_{18}H_{27}N$: 265.0466, found: 265.0453.

3-(4-chlorophenyl)-*N,N*-diethylprop-2-yn-1-amine (3o)[1]



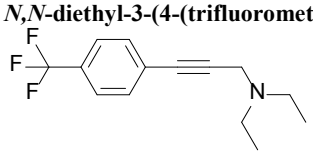
Following the general procedure (EtOAc/petroleum ether 1:4), **3o** was obtained as a faint yellow liquid, isolated yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.28 (d, 2H, *J* = 8.4 Hz), 7.18 (d, 2H, *J* = 8.4 Hz), 3.56 (s, 2H), 2.56 (q, 4H, *J* = 7.2 Hz), 1.04 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 133.9, 132.9, 128.6, 121.8, 85.4, 83.9, 47.3, 41.4, 12.5; GC-MS: m/z=221.

***N,N*-diethyl-3-(4-fluorophenyl)prop-2-yn-1-amine (3p)[4]**



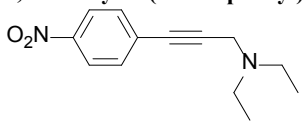
Following the general procedure (EtOAc/petroleum ether 1:4), **3p** was obtained as a faint yellow liquid, isolate yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.38–7.41 (m, 2H), 6.96–7.00 (m, 2H), 3.62 (s, 2H), 2.62 (q, 4H, *J* = 7.2 Hz), 1.11 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 161.0, 133.5, 133.4, 115.5, 115.3, 83.9, 47.2, 41.3, 12.5; GC-MS: m/z=205.

***N,N*-diethyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (3q)[4]**



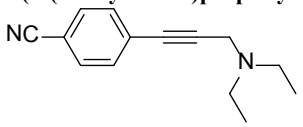
Following the general procedure (EtOAc/petroleum ether 1:4), **3g** was obtained as white liquid, isolated yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.54 (d, 2H, *J* = 8.4 Hz), 7.50 (d, 2H, *J* = 8.4 Hz), 3.64 (s, 2H), 2.62 (q, 4H, *J* = 7.2 Hz), 1.12 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ* 131.9, 129.5, 127.2, 125.2 (q, *J* = 3.7 Hz), 122.6, 87.3, 47.3, 41.4, 12.6; GC-MS: m/z=255.

***N,N*-diethyl-3-(4-nitrophenyl)prop-2-yn-1-amine (3r)**



Following the general procedure (EtOAc/petroleum ether 1:4), **3r** was obtained as a colorless liquid, isolate yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.28 (d, 2H, *J* = 8.4 Hz), 6.96 (d, 2H, *J* = 8.4 Hz), 3.67 (s, 2H), 2.62 (q, 4H, *J* = 7.2 Hz), 1.12 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl3): δ 146.9, 132.4, 130.3, 123.5, 90.8, 83.4, 47.4, 41.6, 12.6. HRMS (EI): calcd for $C_{13}H_{18}N_2O_2$: 232.1212, found: 232.1201

4-(3-(diethylamino)prop-1-yn-1-yl)benzonitrile (3s)[1]



Following the general procedure (EtOAc/petroleum ether 1:4), **3s** was obtained as a colorless yellow liquid, isolated yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ* 7.54 (d, 2H, *J* = 8.0 Hz), 7.45 (d, 2H, *J* = 8.0 Hz), 3.63 (s, 2H), 2.58 (q, 4H, *J* = 7.2 Hz), 1.08 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 132.2, 131.9, 128.3, 118.5, 111.3, 89.6, 83.6, 47.4, 41.5, 12.6; GC-MS: m/z=212.

3,3'-(1,4-phenylene)bis(N,N-diethylprop-2-yn-1-amine) (3t)

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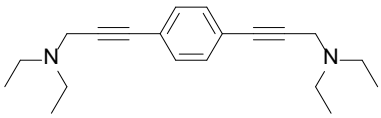
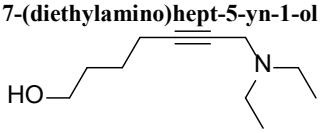


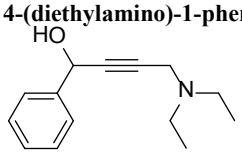
Following the general procedure (EtOAc/Petroleum ether 1:2), **3t** was obtained as a colorless liquid, isolated yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.35 (s, 4H), 3.66 (s, 4H), 2.62 (q, 8H, J = 7.2 Hz), 1.12 (t, 12H, J = 7.2 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.5, 122.8, 85.9, 84.8, 47.3, 41.4, 12.6; GC-MS: m/z=296.

7-(diethylamino)hept-5-yn-1-ol (3u)



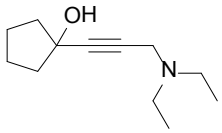
Following the general procedure, **3u** was obtained as a colorless liquid, isolated yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.59 (t, 2H, J = 6.8 Hz), 3.54 (s, 2H), 2.50 (q, 4H, J = 7.2 Hz), 2.14 (t, 2H, J = 7.2 Hz), 1.51-1.58 (m, 4H), 1.01 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 85.6, 84.3, 61.8, 46.9, 40.6, 31.6, 25.1, 18.4, 11.8. HRMS (EI): calcd for $C_{11}H_{21}NO$: 183.1623, found: 183.1617.

4-(diethylamino)-1-phenylbut-2-yn-1-ol (3v)



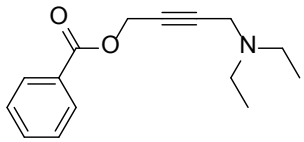
Following the general procedure, **3v** was obtained as a colorless liquid, isolated yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.50 (d, 2H, J = 7.6 Hz), 7.34 (t, 2H, J = 7.2 Hz), 7.28 (d, 1H, J = 8.0 Hz), 5.44 (s, 1H), 3.44 (s, 2H), 2.55 (q, 4H, J = 7.2 Hz), 1.05 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 128.4, 127.9, 126.6, 86.0, 79.9, 63.9, 47.0, 11.8. HRMS (EI): calcd for $C_{14}H_{17}NO$: 217.1467, found: 217.1443.

1-(3-(diethylamino)prop-1-yn-1-yl)cyclopentanol (3w)



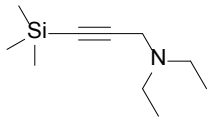
Following the general procedure, **3w** was obtained as a colorless liquid, isolated yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.44 (s, 2H), 2.57 (s, 1H), 2.54 (q, 4H, J = 7.2 Hz), 1.91-1.95 (m, 4H), 1.81-1.83 (m, 2H), 1.72-1.81 (m, 2H), 1.07 (t, 6H, J = 7.2 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 89.2, 77.0, 74.1, 47.0, 42.5, 40.7, 23.3, 12.2. HRMS (EI): calcd for: $C_{12}H_{21}NO$:195.16, found: 195.1615.

4-(diethylamino)but-2-yn-1-yl benzoate (3x)



Following the general procedure (EtOAc/petroleum ether 1:4), **3x** was obtained as a colorless liquid, isolated yield: 91%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.04 (d, 2H, J = 8.0 Hz), 7.53 (t, 1H, J = 7.2 Hz), 7.41 (t, 2H, J = 7.6 Hz), 4.92 (s, 2H), 3.45 (s, 2H), 2.53 (q, 4H, J = 7.2 Hz), 1.04 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.9, 133.2, 129.7, 129.6, 128.4, 81.9, 78.8, 52.9, 47.2, 40.9, 12.4. HRMS (EI): calcd for: $C_{15}H_{19}NO_2$:245.1416, found: 245.1421.

***N,N*-diethyl-3-(trimethylsilyl)prop-2-yn-1-amine (3y)**[6]



Following the general procedure (EtOAc/Petroleum ether 1:4), **3y** was obtained as a colorless liquid, isolated yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.42 (s, 2H), 2.55 (q, 4H, J = 7.2 Hz), 1.07 (t, 6H, J = 7.2 Hz), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 100.8, 89.4, 47.1, 41.6, 12.5, 0.05; GC-MS: m/z=183

***N,N*-diethyldodec-2-yn-1-amine (3z)**[5]

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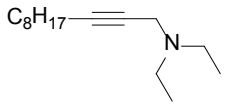
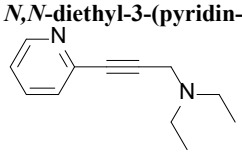


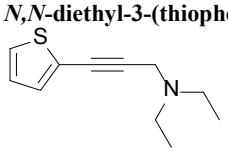
Following the general procedure (EtOAc/Petroleum ether 1:4), **3z** was obtained as a colorless liquid, isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.47 (s, 2H), 2.64 (q, 4H, J = 7.0 Hz), 2.18-2.21 (m, 2H), 1.25-1.50 (m, 12H), 1.13 (t, 6H, J = 7.0 Hz), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 47.2, 40.6, 31.8, 29.7, 29.2, 29.0, 28.8, 28.8, 22.6, 18.7, 14.1, 11.9; GC-MS: m/z=224.

_N,N_-diethyl-3-(pyridin-2-yl)prop-2-yn-1-amine (3z$_1$)[7]



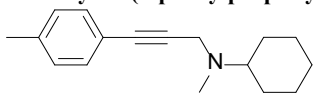
Following the general procedure (EtOAc/Petroleum ether 1:4), **3z$_1$** was obtained as a faint yellow liquid, isolated yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.56 (d, 1H, J = 7.2 Hz), 7.61-7.65 (m, 1H), 7.22-7.42 (m, 1H), 7.20-7.22 (m, 1H), 3.70 (s, 2H), 2.65 (q, 4H, J = 7.2 Hz), 1.12 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz,$CDCl_3$, TMS): δ 149.8, 143.2, 136.0, 127.1, 122.6, 84.6, 84.6, 47.3, 41.2, 12.6; GC-MS: m/z=188.

_N,N_-diethyl-3-(thiophen-2-yl)prop-2-yn-1-amine (3z$_2$)[10]



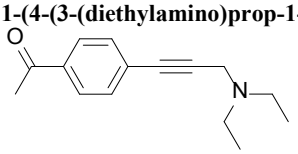
Following the general procedure (EtOAc/Petroleum ether 1:4), **3z$_2$** was obtained as a faint yellow liquid, isolated yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.19-7.21 (m, 1H), 7.16-7.17 (m, 1H), 6.94-6.96 (m, 1H), 3.66 (s, 2H), 2.62 (q, 4H, J = 7.2 Hz), 1.11 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.5, 126.7, 126.4, 123.2, 88.5, 78.0, 47.3, 41.6, 12.6; GC-MS: m/z=193.

_N_-methyl-_N_-(3-phenylprop-2-yn-1-yl)cyclohexanamine (3z$_3$)[4]



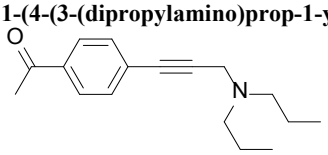
Following the general procedure (EtOAc/Petroleum ether 1:4), **3z$_3$** was obtained as a faint yellow liquid, isolated yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30–7.32 (d, 2H, J = 8.0 Hz), 7.10 (d, 2H, J = 8.0 Hz), 3.62 (s, 2H), 2.44-2.47(m, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.96 (t, J = 5.6 Hz, 2H), 1.79 (t, J = 6.0 Hz, 2H), 1.60 (q, J = 9.6 Hz, 1 H), 1.15-1.28 (m, 4H), 1.09-1.16 (m, 1H); ^{1}3C NMR (100 MHz, $CDCl_3$, TMS): δ 137.9, 131.5, 128.9, 120.3, 84.9, 84.6, 61.0, 43.7, 38.4, 29.7, 26.0, 25.5, 21.4; GC-MS: m/z=242.

1-(4-(3-(diethylamino)prop-1-yn-1-yl)phenyl)ethanone (3z$_4$)[11]



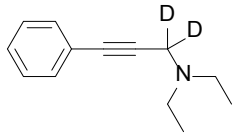
Following the general procedure (EtOAc/petroleum ether 1:4), **3z$_4$** was obtained as a faint yellow liquid, isolated yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.86 (d, 2H, J = 8.4 Hz), 7.47 (d, 2H, J = 8.4 Hz), 3.65 (s, 2H), 2.60 (q, 4H, J = 7.2 Hz), 2.57 (s, 3H), 1.11 (t, 6H, J = 7.2 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 197.3, 136.0, 131.8, 128.2, 88.4, 84.3, 47.4, 41.6, 26.6. 12.6; GC-MS: m/z=229.

1-(4-(3-(dipropylamino)prop-1-yn-1-yl)phenyl)ethanone (3z$_5$)



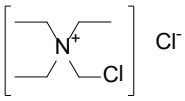
Following the general procedure (EtOAc/petroleum ether 1:4), **3z$_5$** was obtained as a faint yellow liquid, isolated yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.86 (d, 2H, J = 8.4 Hz), 7.47 (d, 2H, J = 8.4 Hz), 3.62 (s, 2H), 2.57 (s, 3H), 2.48 (t, 4H, J = 7.6 Hz), 1.46-1.53 (m, 4H), 0.90 (t, 6H, J = 7.0 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 197.3, 136.0, 131.8, 128.4, 128.2, 88.7, 84.3, 55.9, 42.8, 26.6. 20.7, 11.9; HRMS (EI): calcd for $C_{18}H_{27}N$: 257.1780, found: 257.1762.

_N,N_-Diethyl-3-phenyl-2-deuteriopropyn-1-amine (3a-_d_)[1]



Following the general procedure (EtOAc/petroleum ether 1:4), **3a-*d*** was obtained as a colorless liquid, isolate yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.41–7.43 (m, 2H), 7.27–7.28 (m, 3H), 2.62 (q, 4H, J = 7.2 Hz), 1.11 (t, 6H J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 131.6, 128.2, 127.8, 123.3, 85.0, 84.4, 47.3, 41.5, 12.6; GC-MS: m/z=189.

***N*-(chloromethyl)-*N*,*N*-diethylethanaminium chloride ($4a_1$)[5]**



The product was prepared according to the following procedure: dichloromethane and triethylamine were dissolved in DMF under N_2 atmospheres, stirred at 80 °C for 12 h. The mixture was allowed to cool to room temperature, washed with diethyl ether and dried under reduced pressure to give a colorless solid, isolated yield: 85% ^{1}H NMR (400 MHz, D_2O): δ 4.36 (s, 2H), 3.07 (q, 4H, J = 7.2 Hz), 2.83 (q, 2H, J = 7.2 Hz), 0.97 (t, 6H, J = 7.2 Hz), 0.92 (t, 3H, J = 7.2 Hz).

5. References

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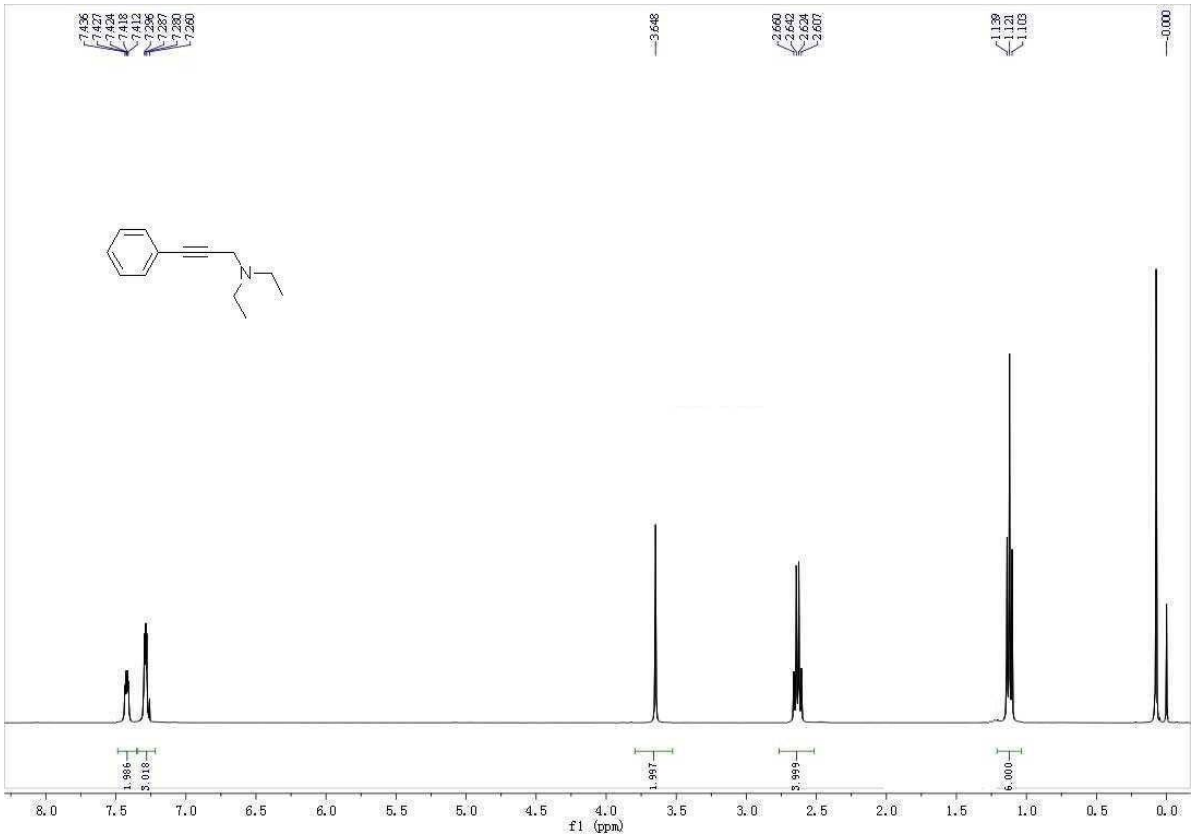
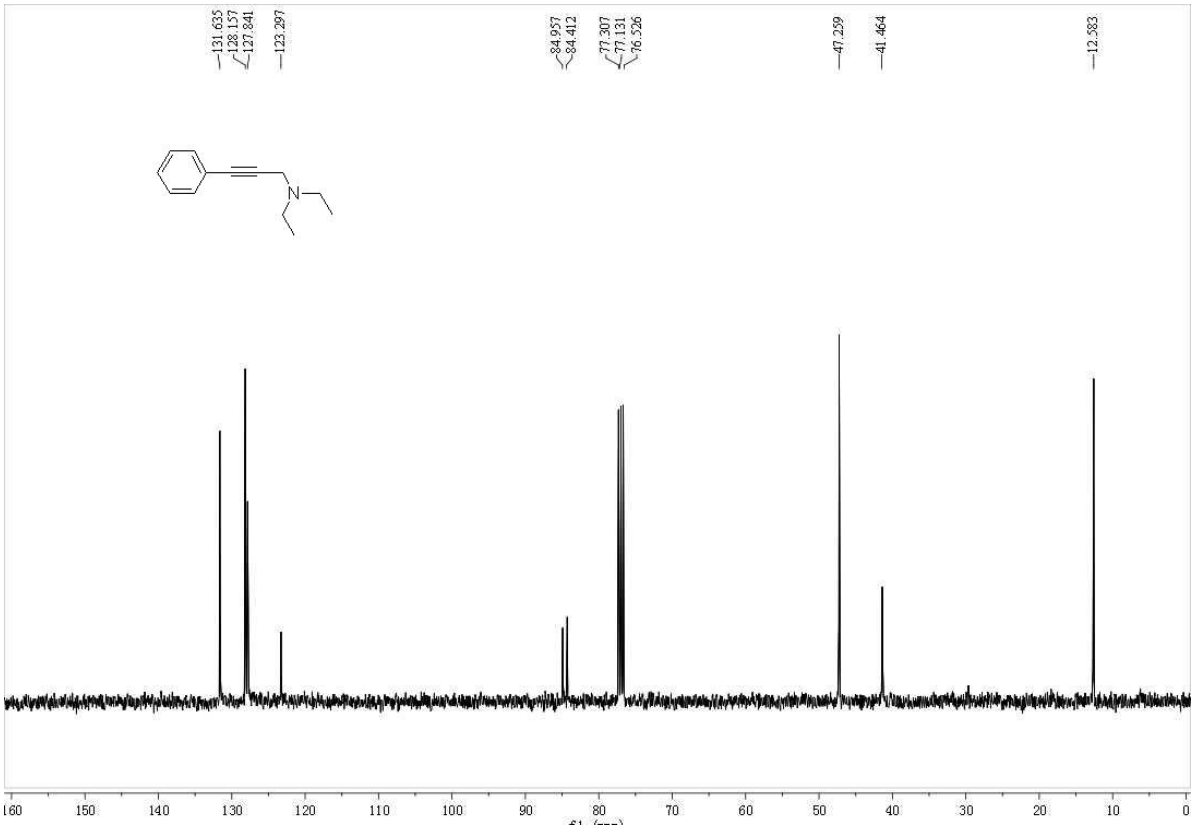
6. Copies of ^{1}H and ^{13}C NMR spectra

^{1}H NMR and ^{13}C NMR of **3a**





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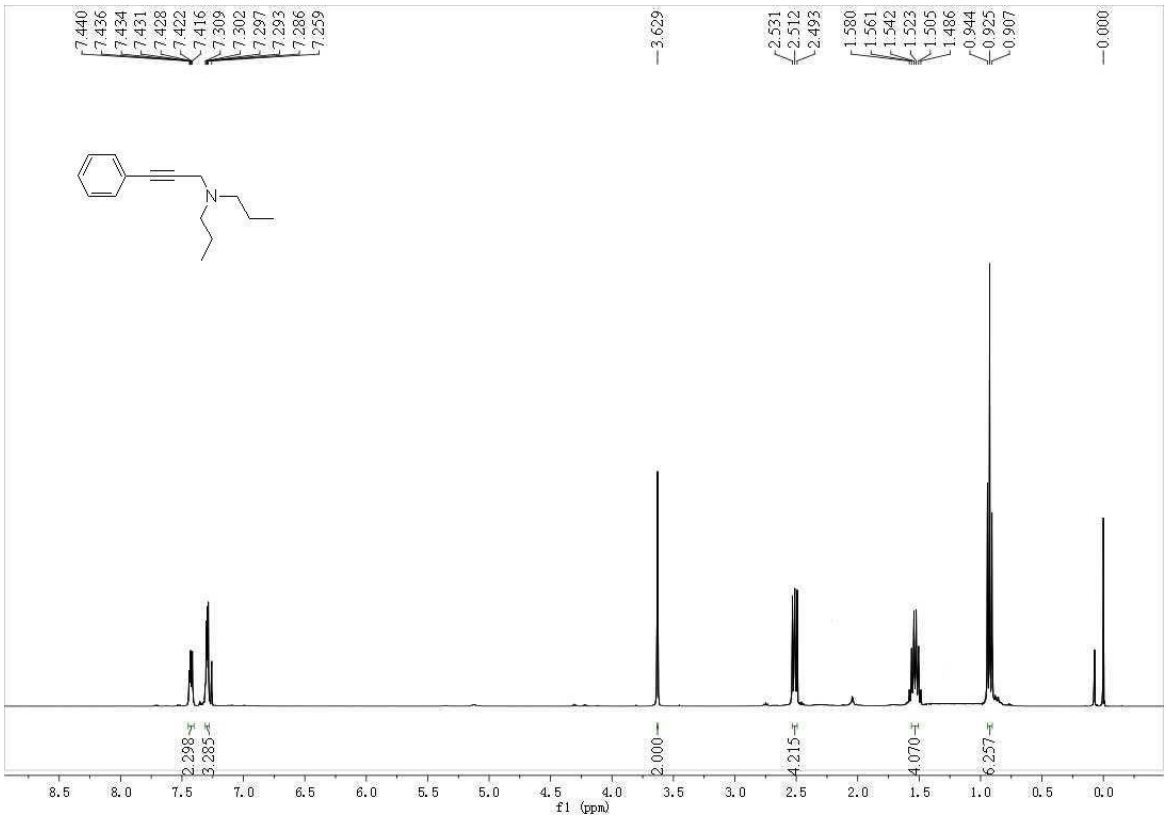
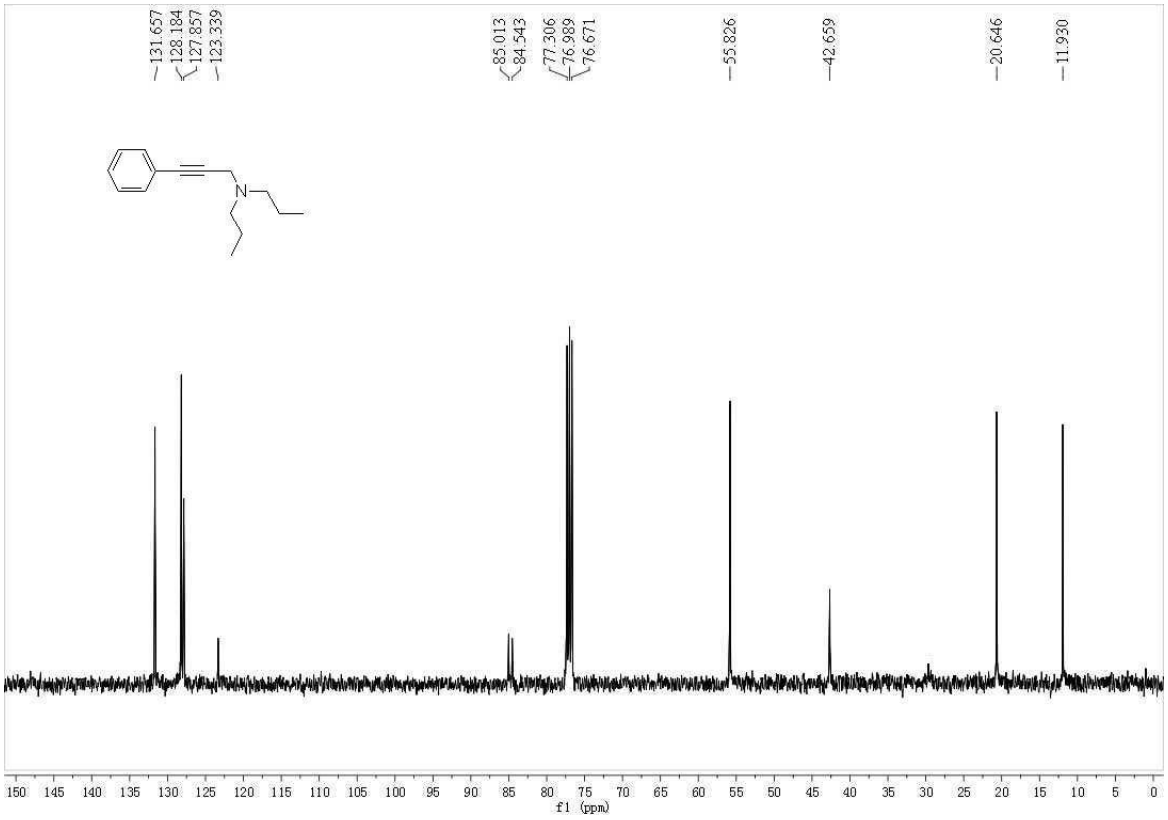
^{1}H NMR and ^{13}C NMR of **3b**





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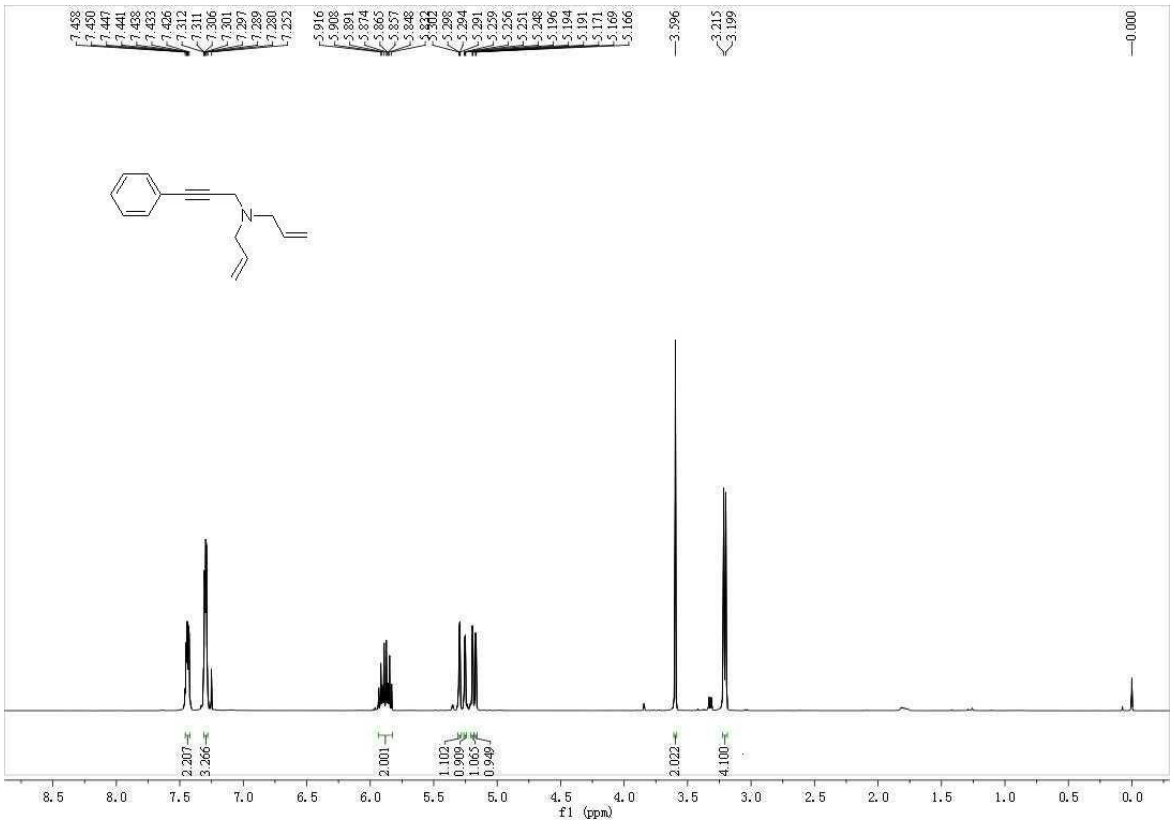
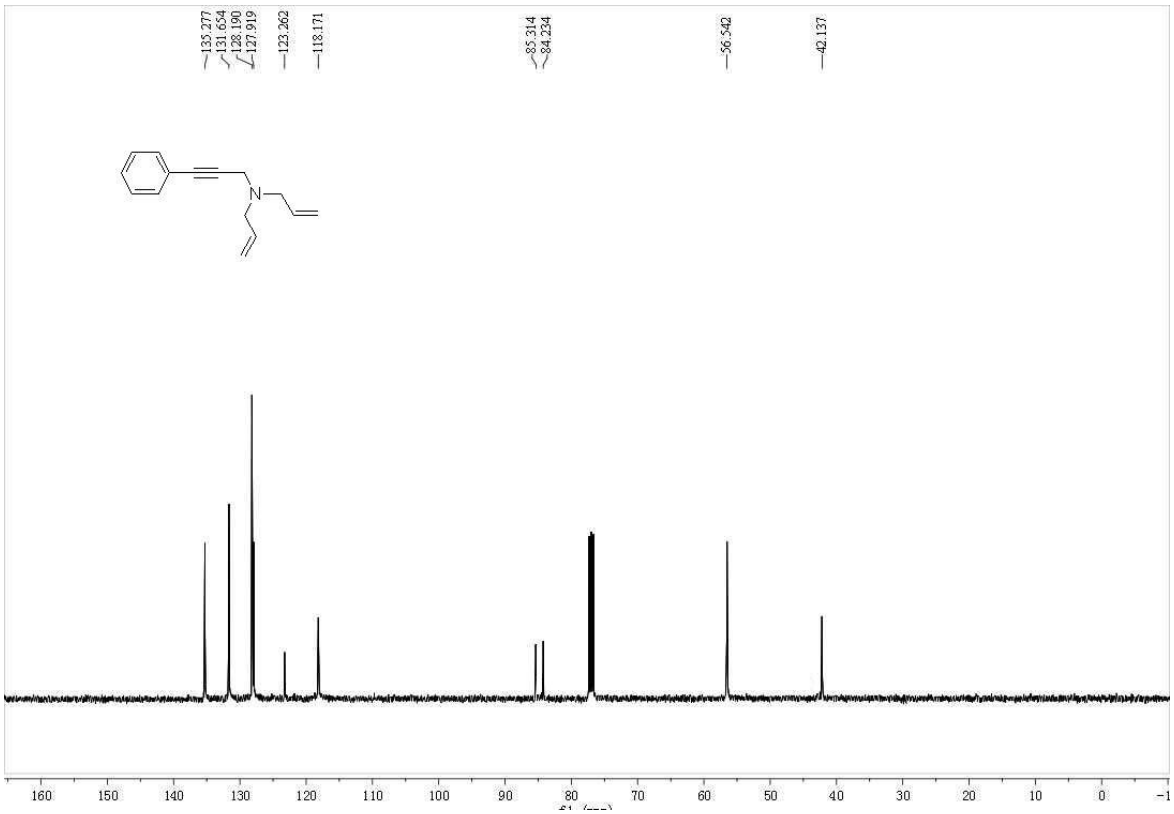
^{1}H NMR and ^{13}C NMR of **3c**





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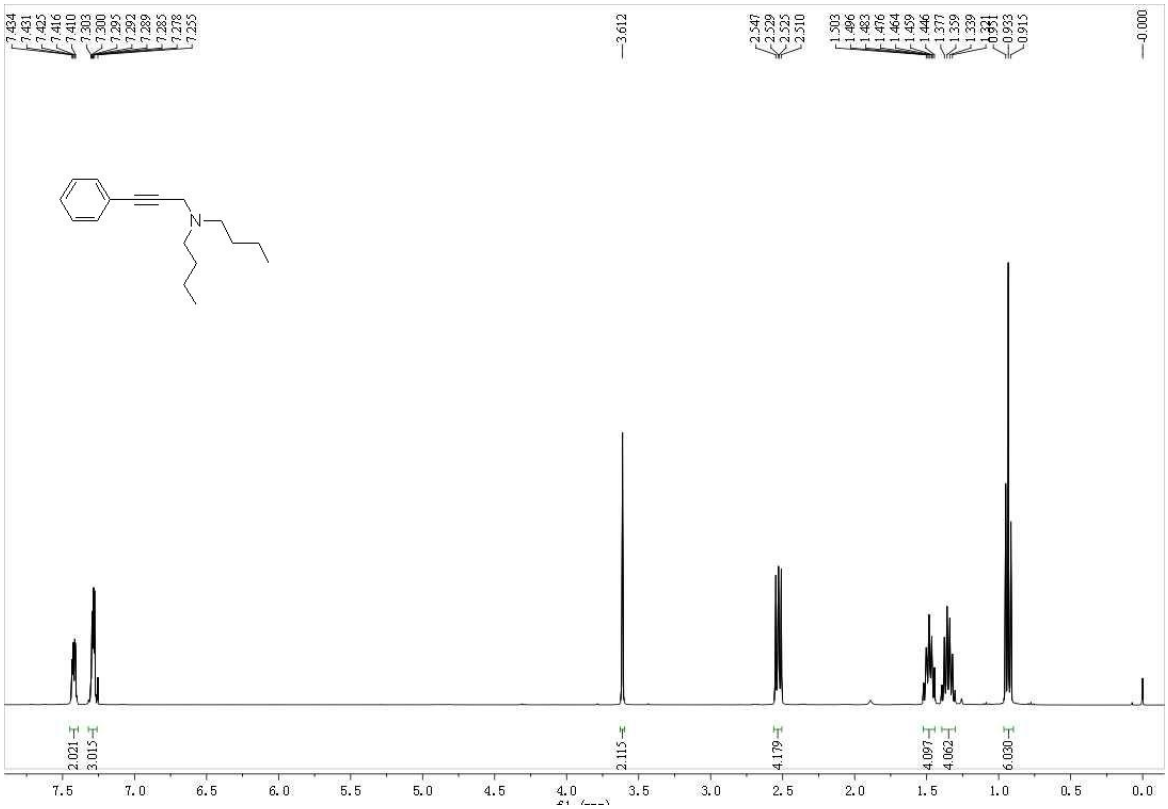
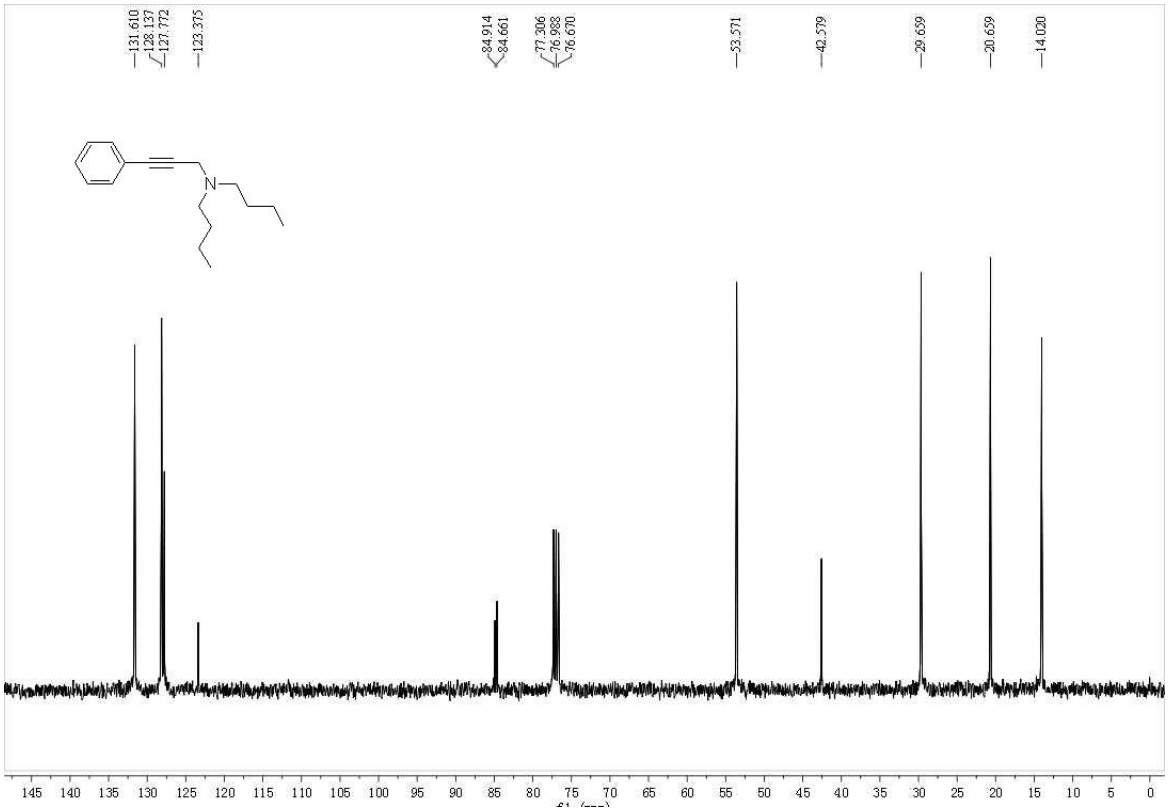
^{1}H NMR and ^{13}C NMR of **3d**





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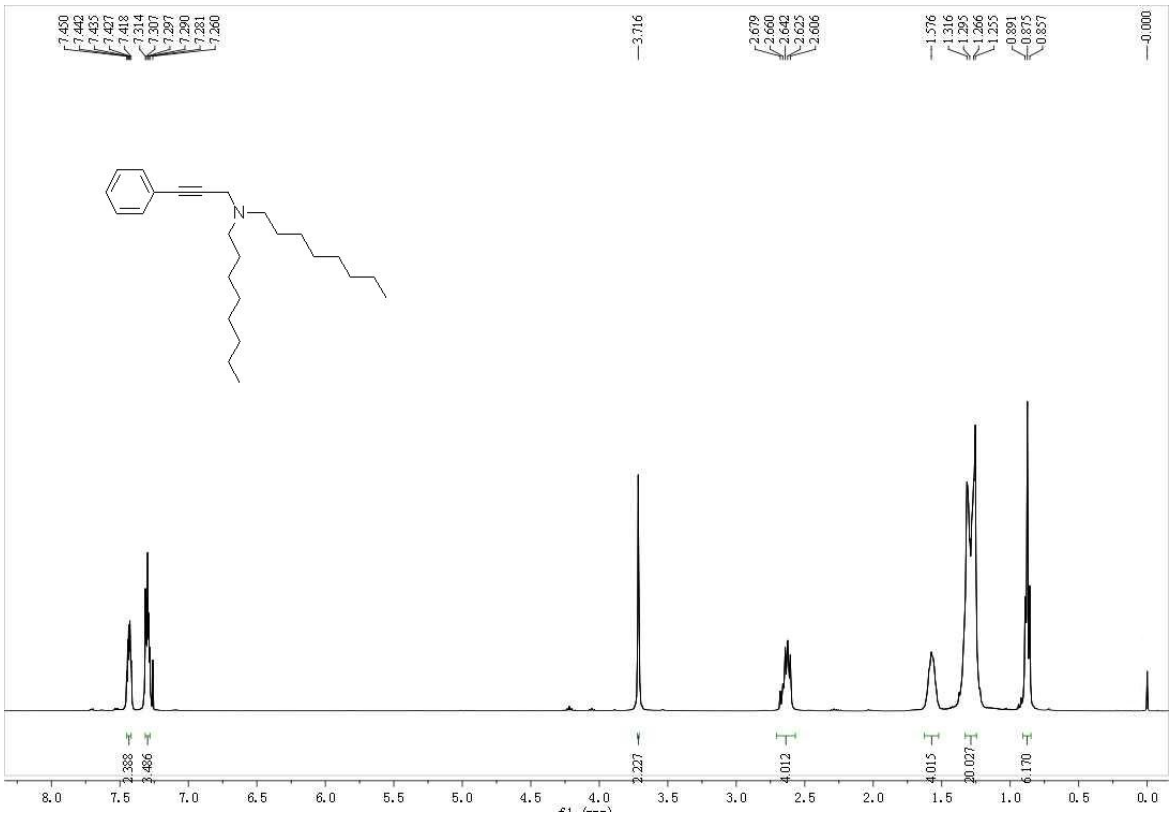
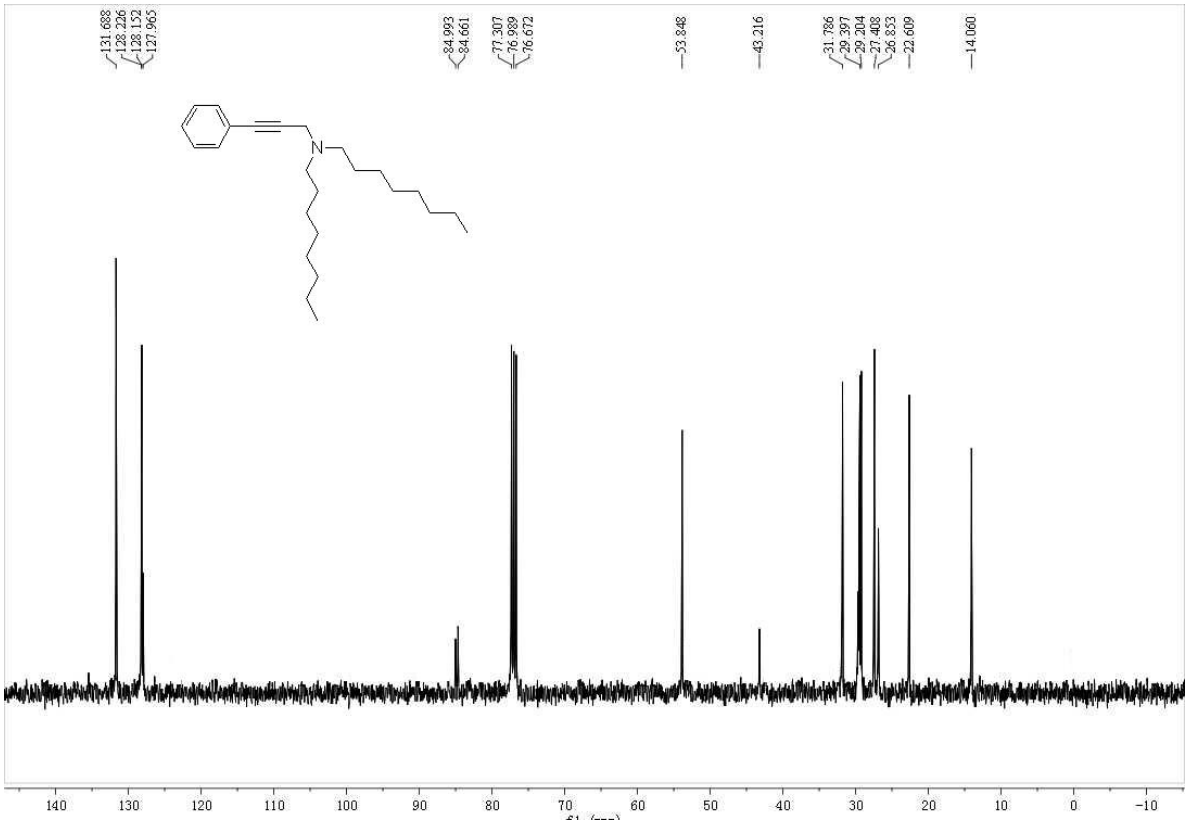
^{1}H NMR and ^{13}C NMR of **3e**





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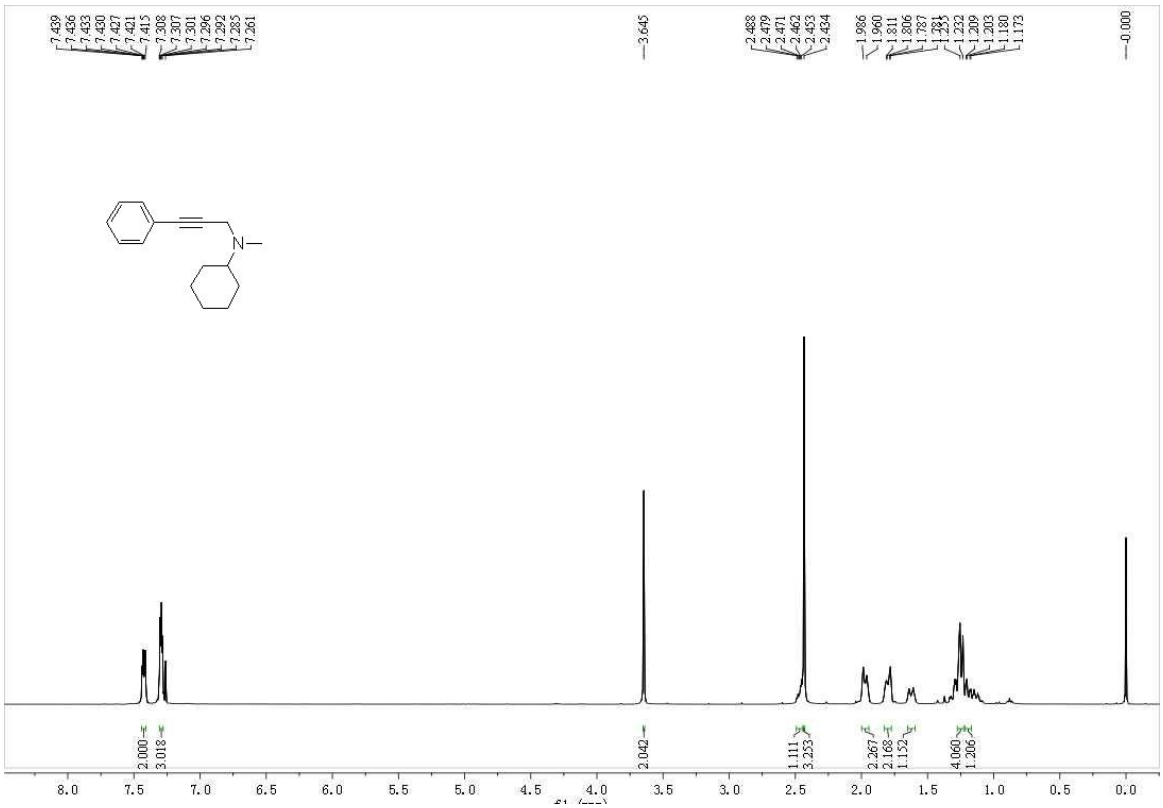
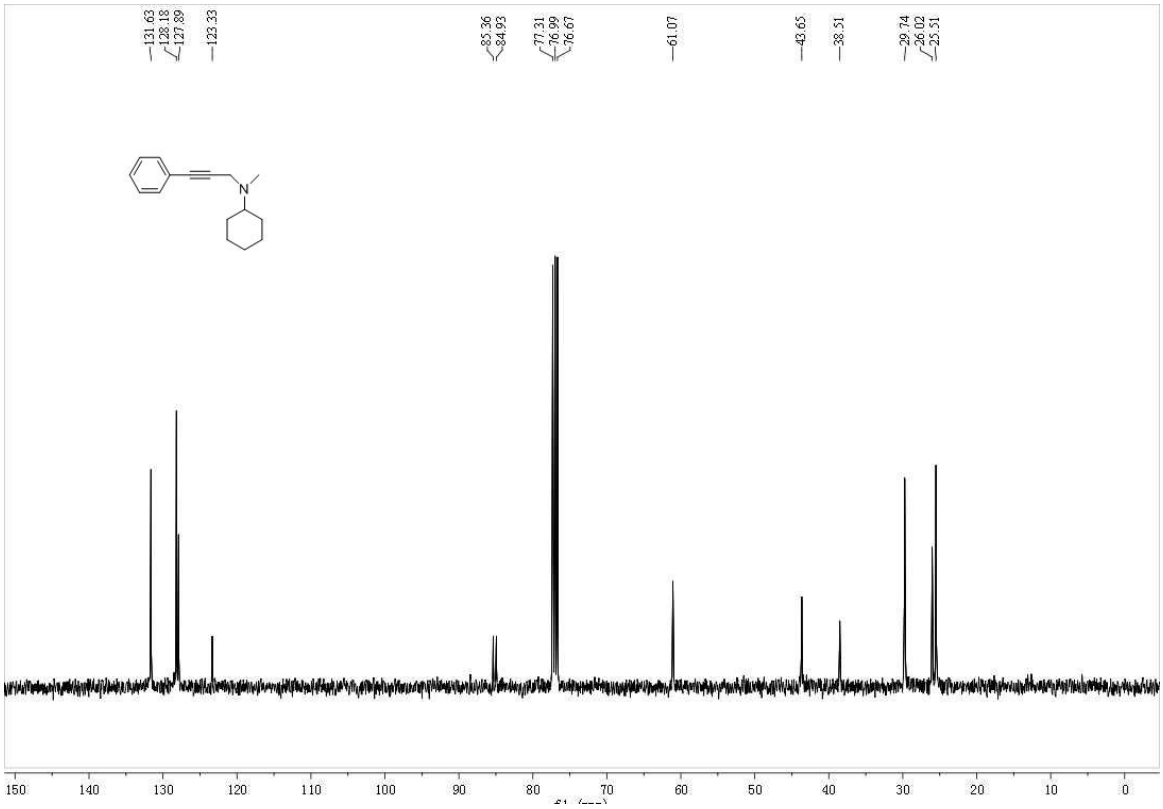
^{1}H NMR and ^{13}C NMR of **3f**





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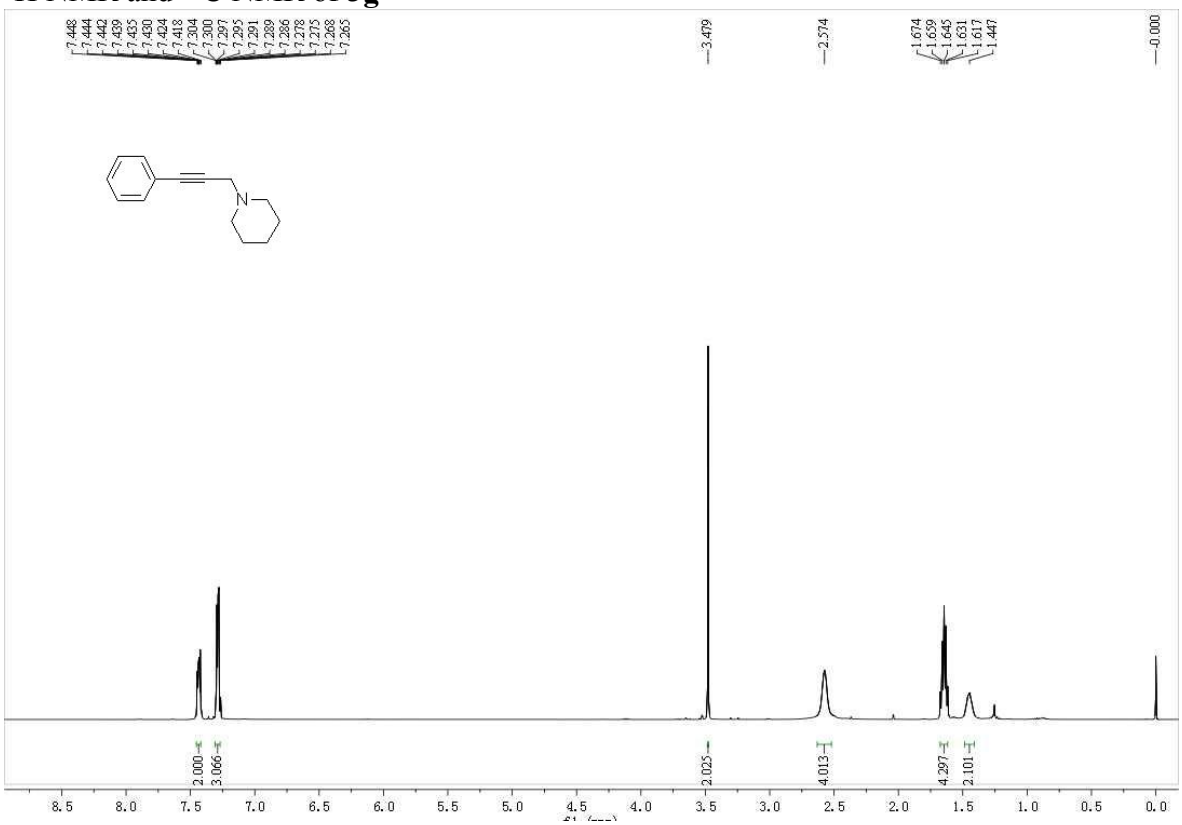
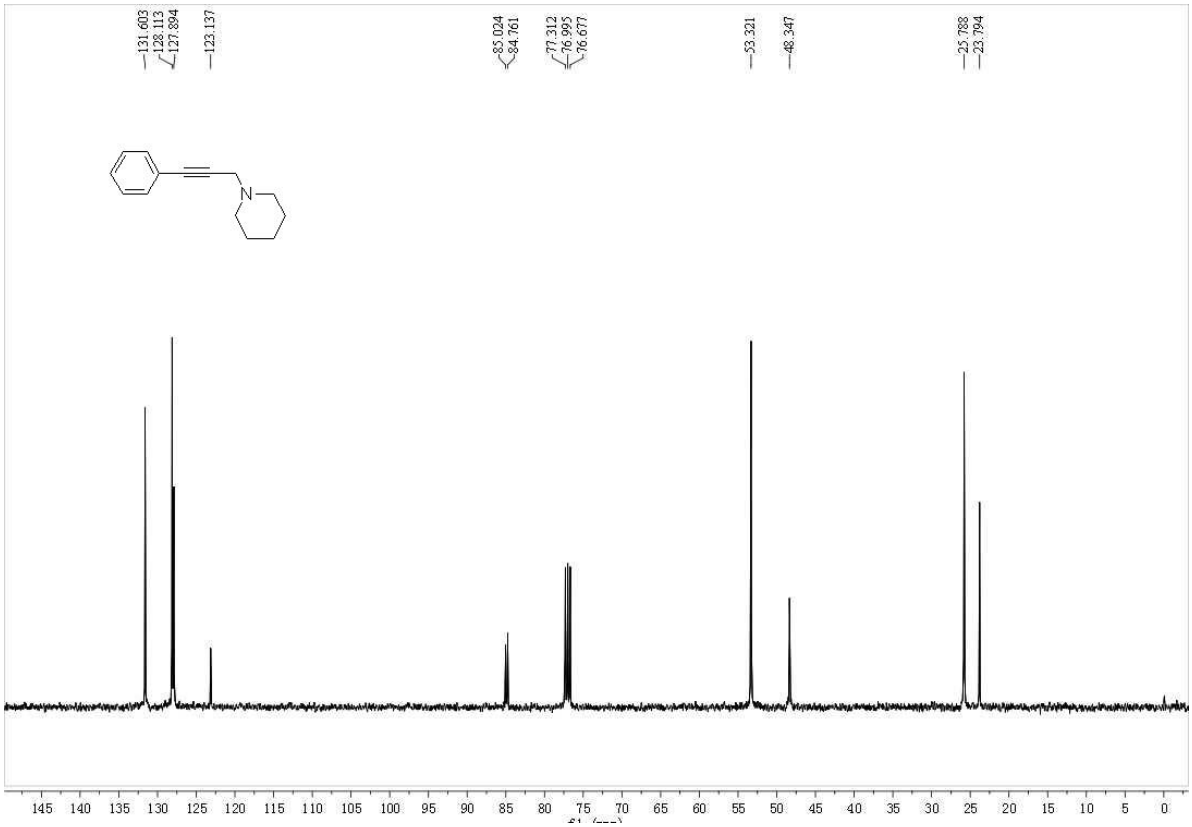
^{1}H NMR and ^{13}C NMR of **3g**





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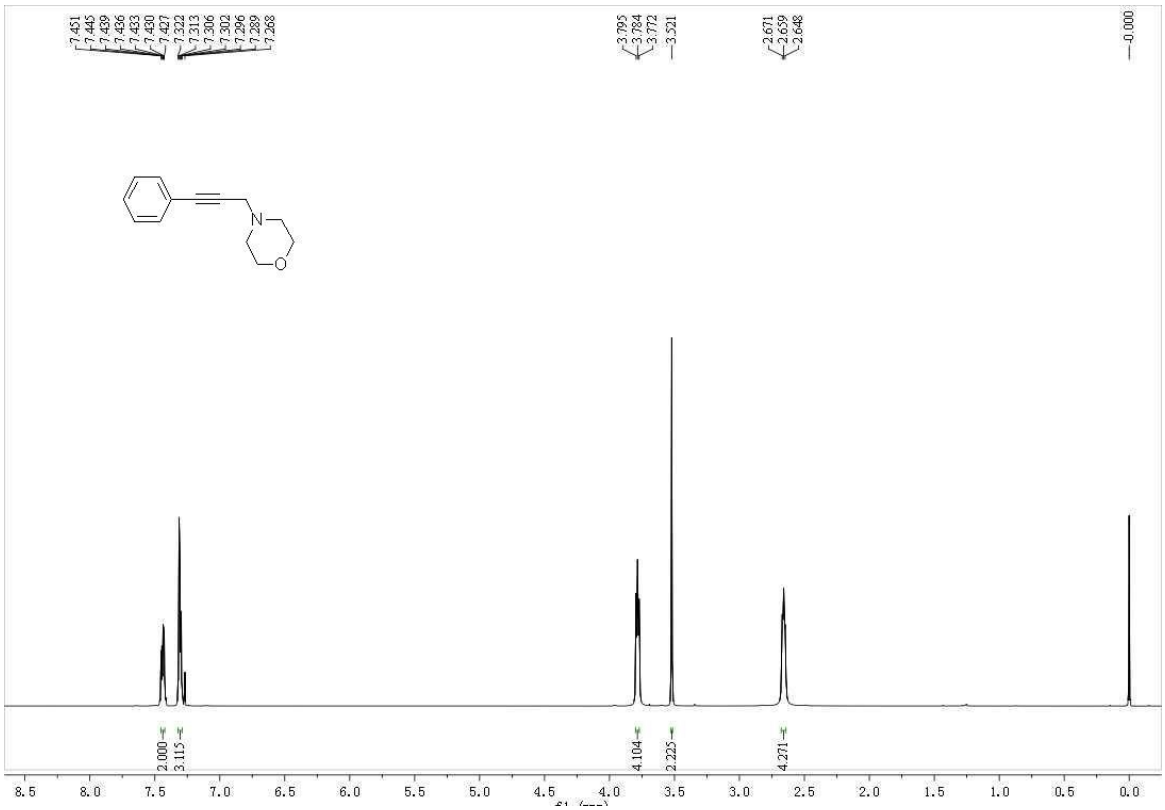
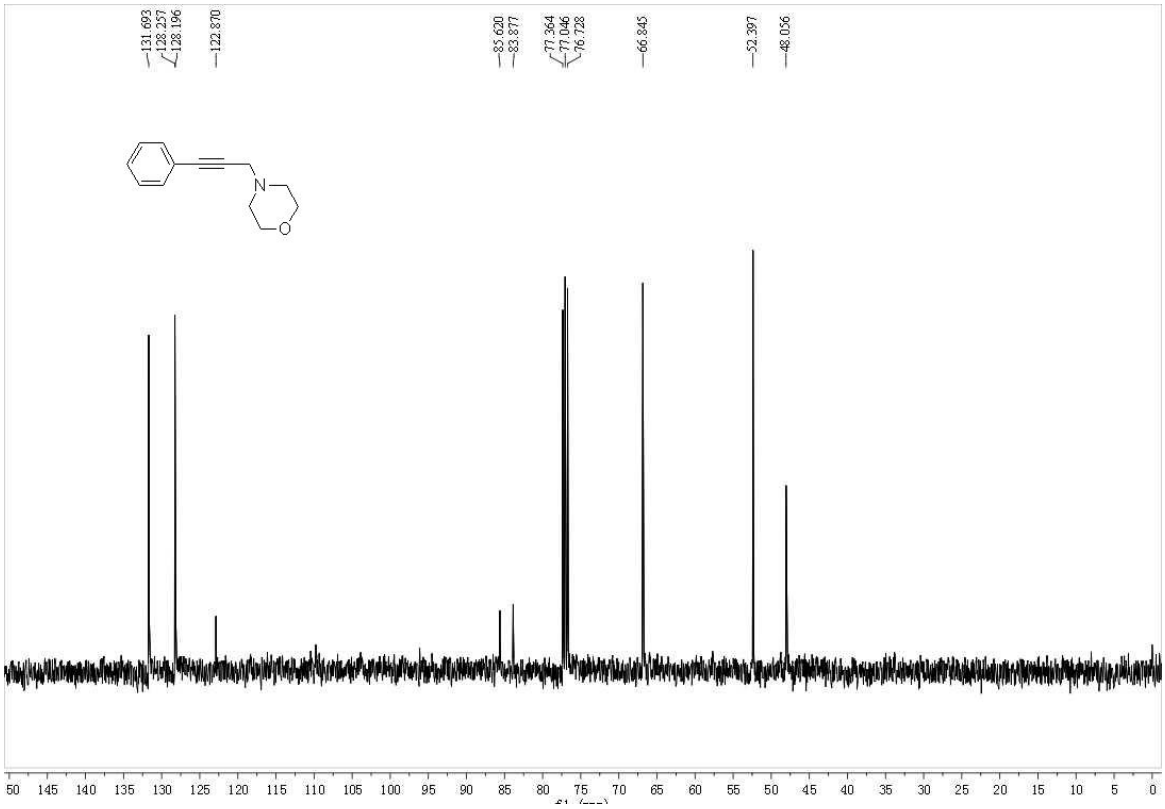
^{1}H NMR and ^{13}C NMR of **3h**





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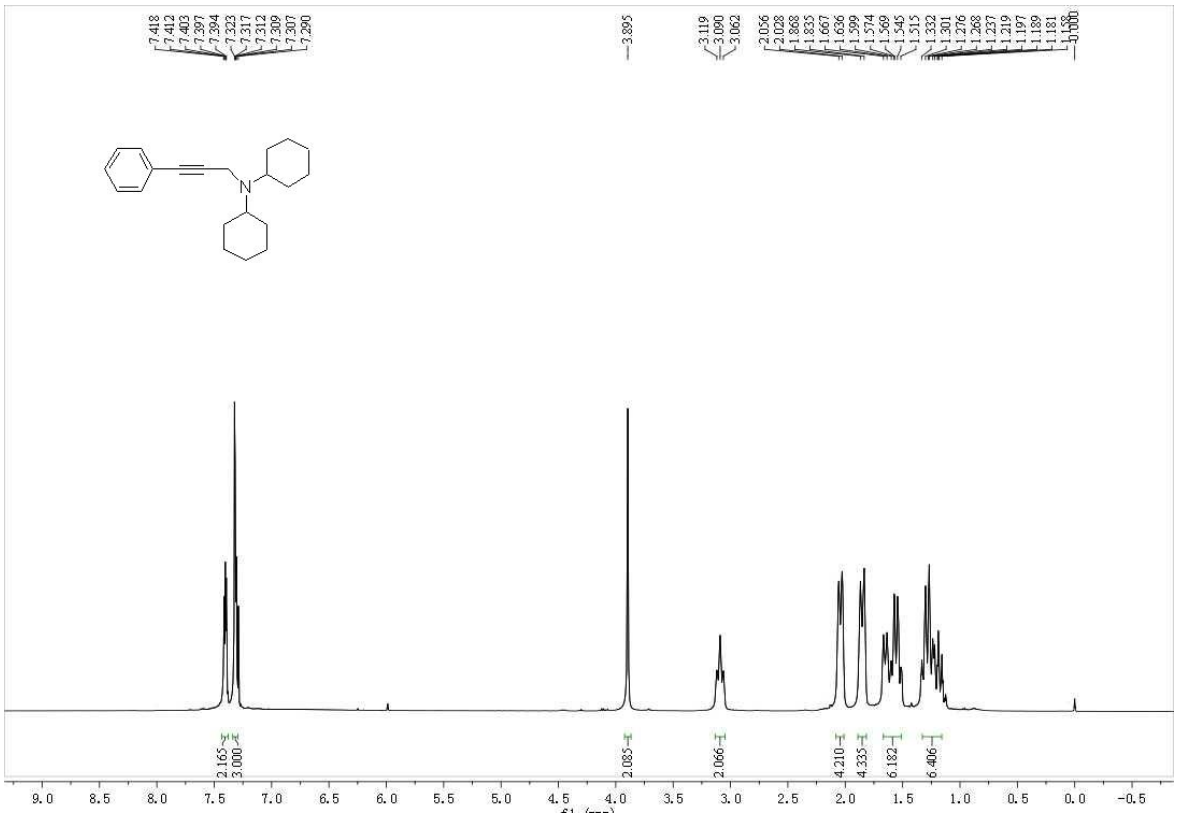
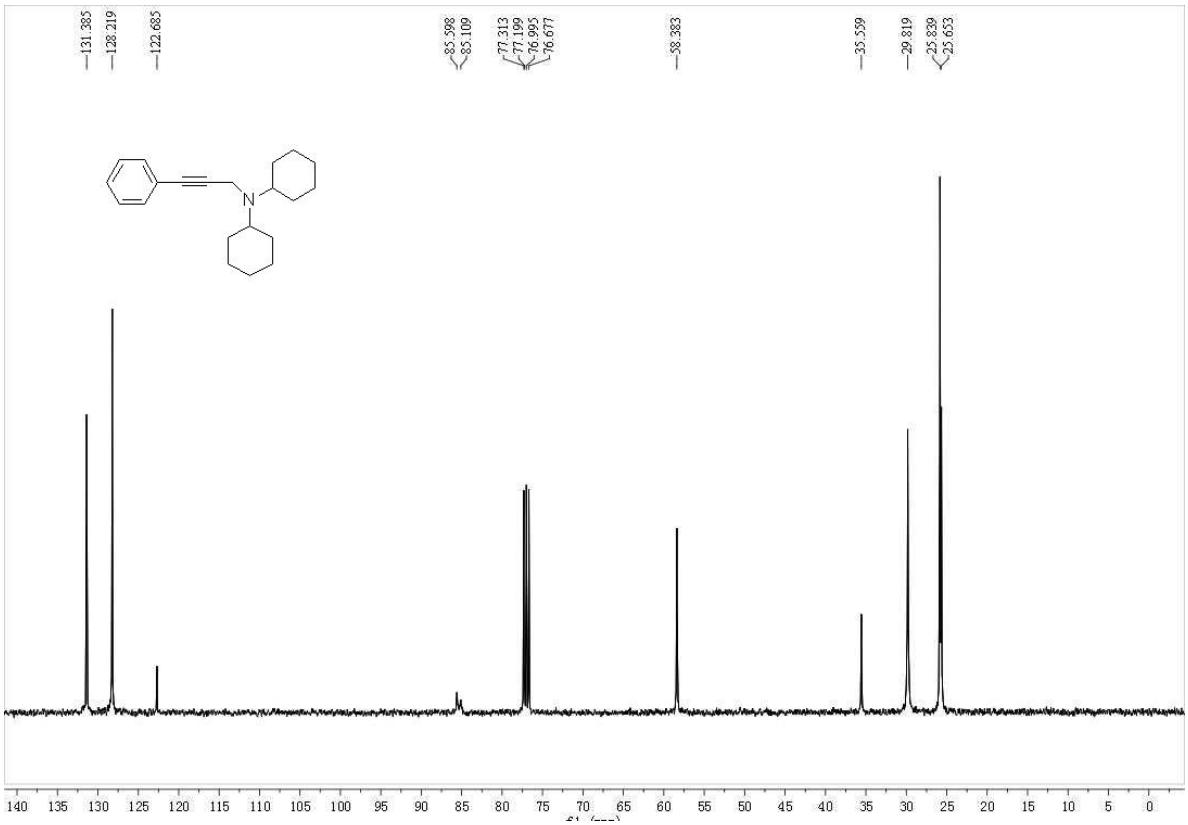
^{1}H NMR and ^{13}C NMR of **3i**





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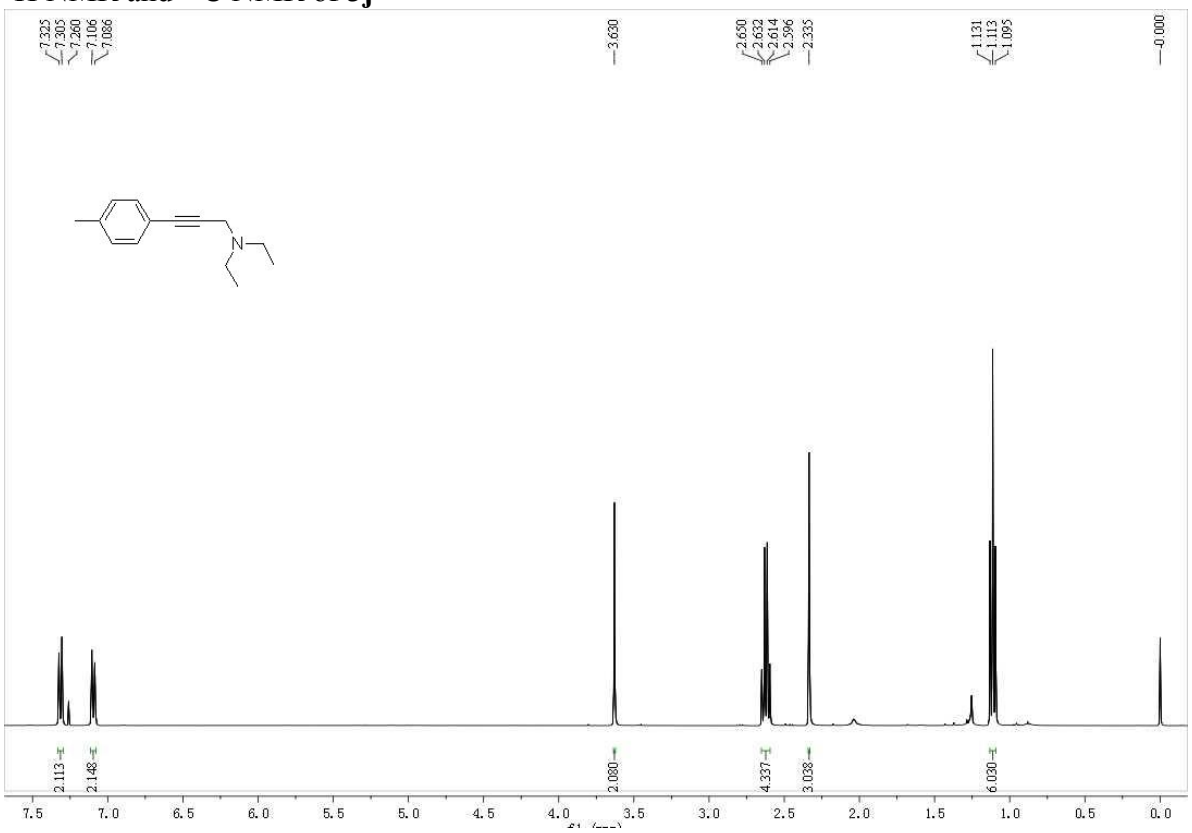
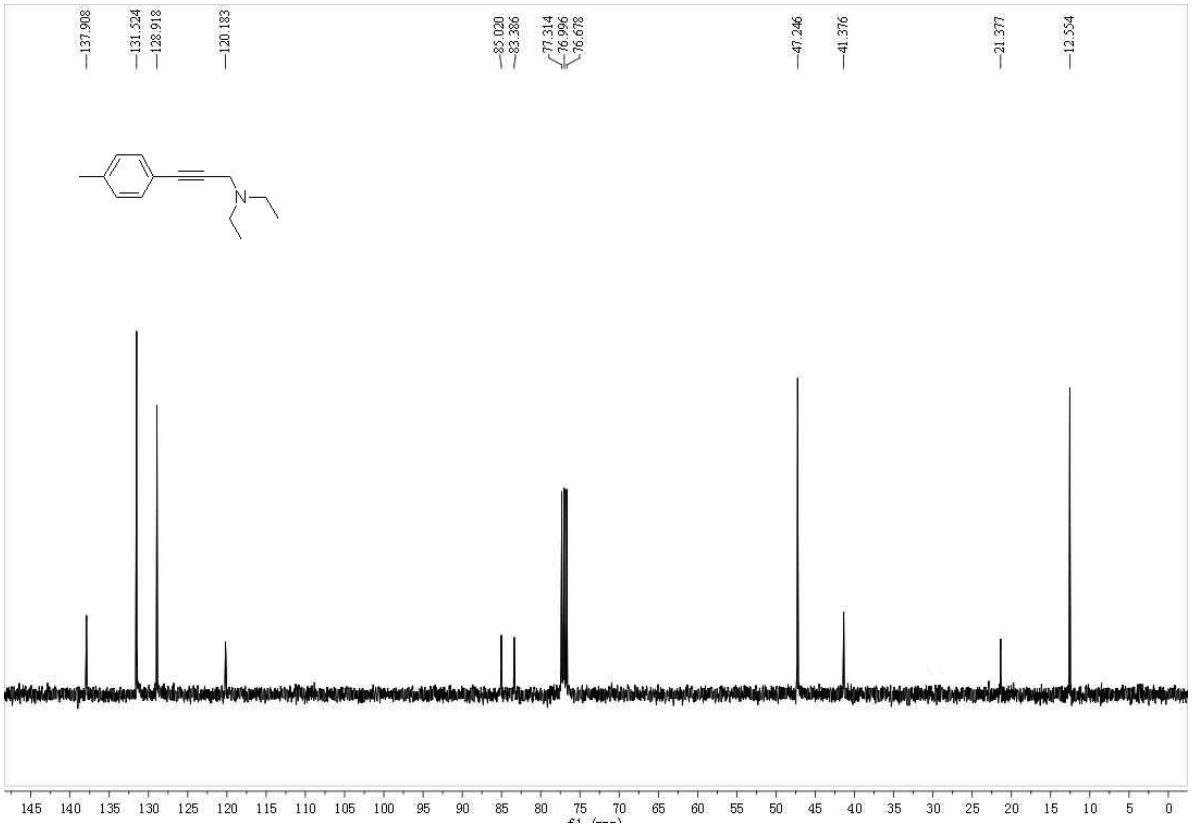
^{1}H NMR and ^{13}C NMR of **3j**





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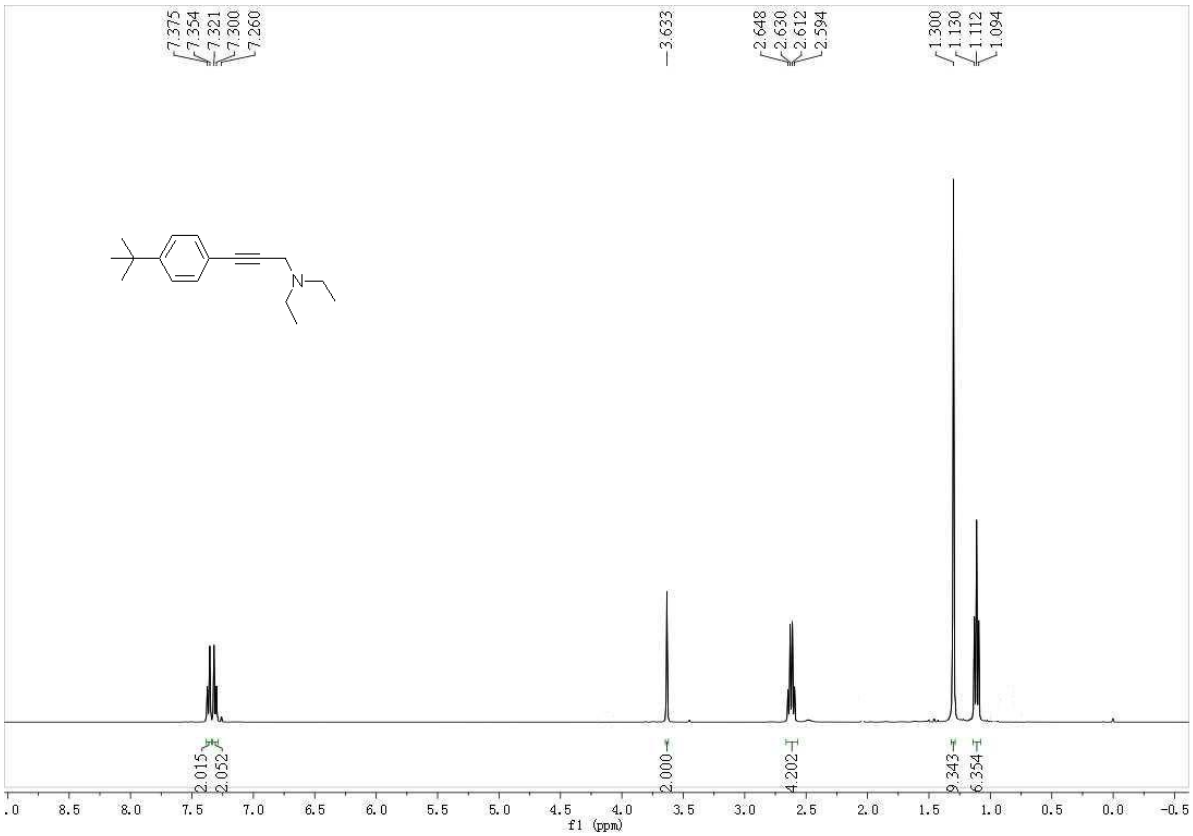
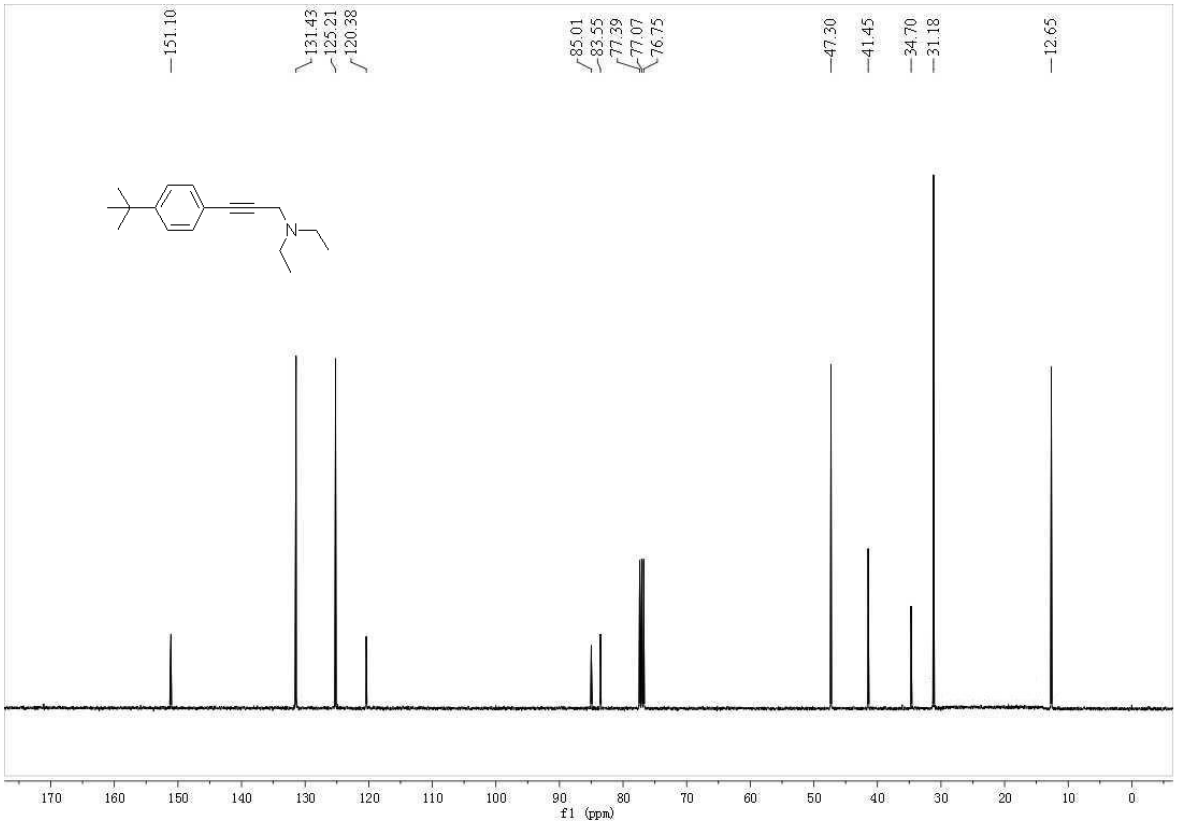
^{1}H NMR and ^{13}C NMR of **3k**





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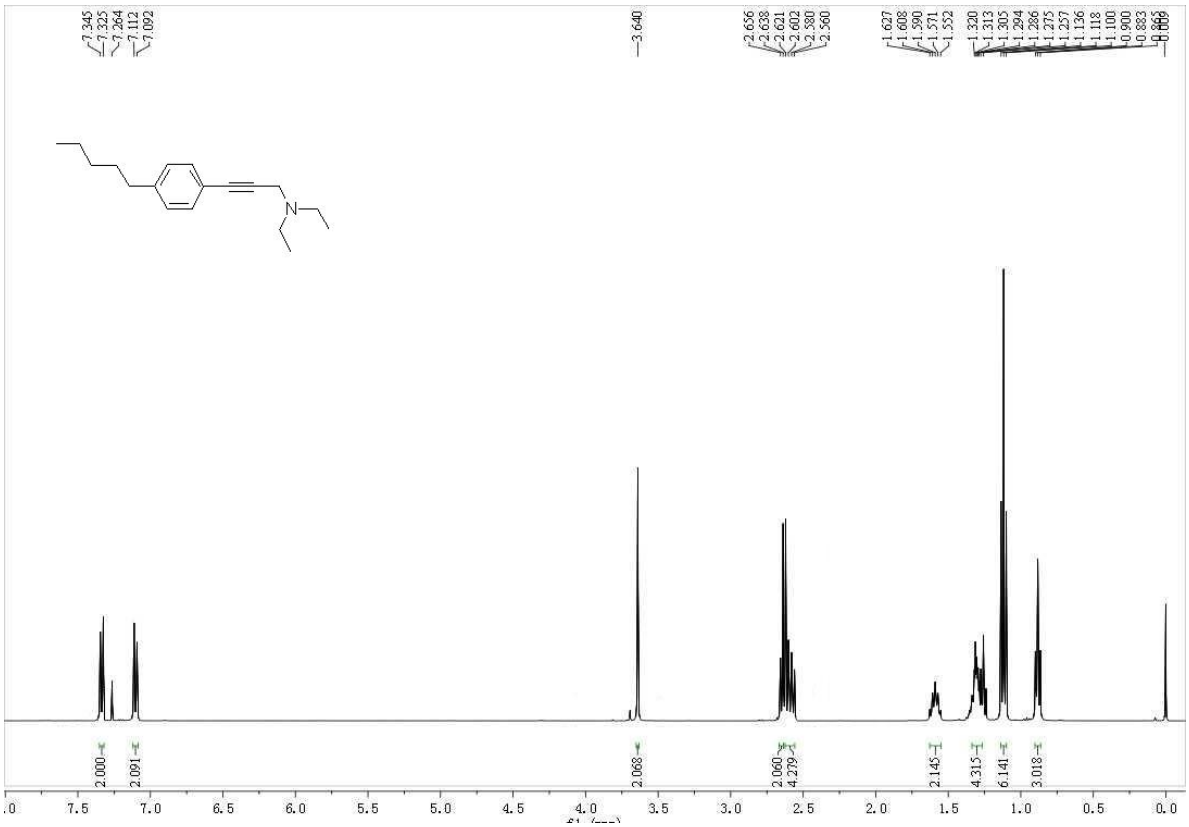
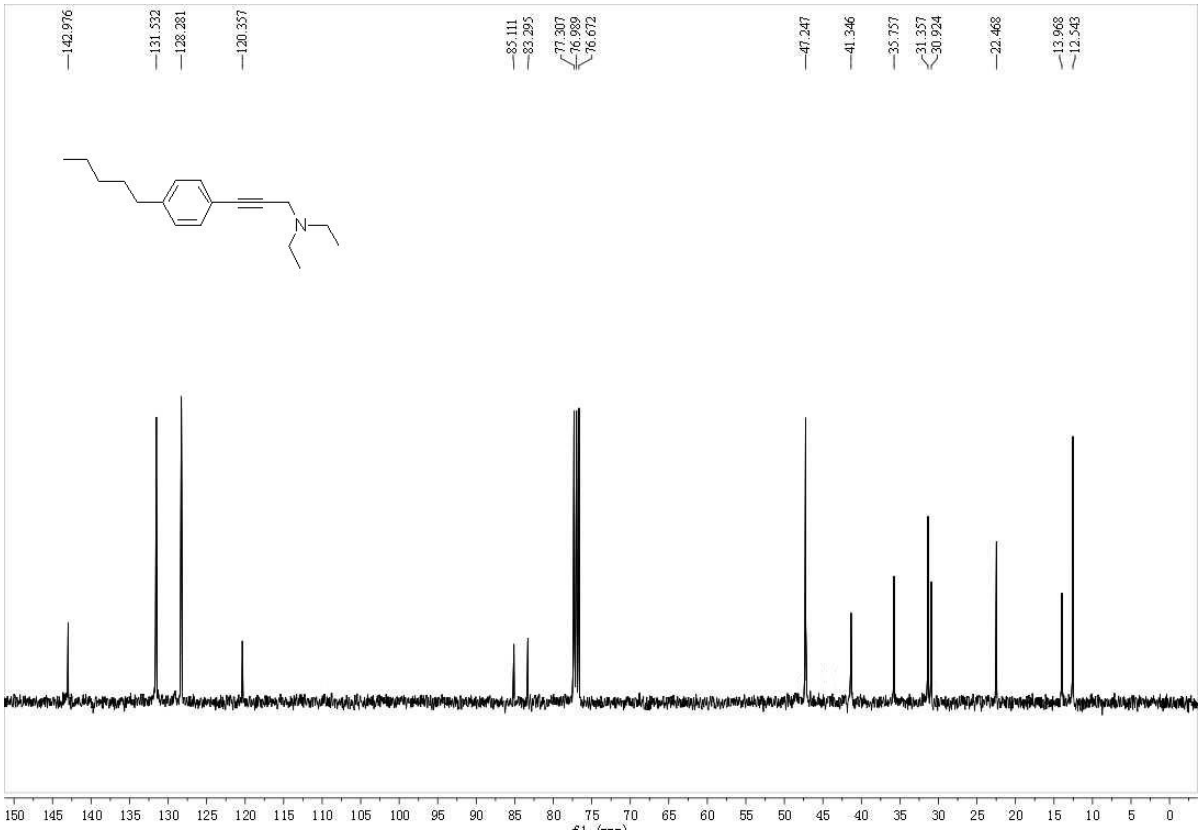
^{1}H NMR and ^{13}C NMR of **3l**





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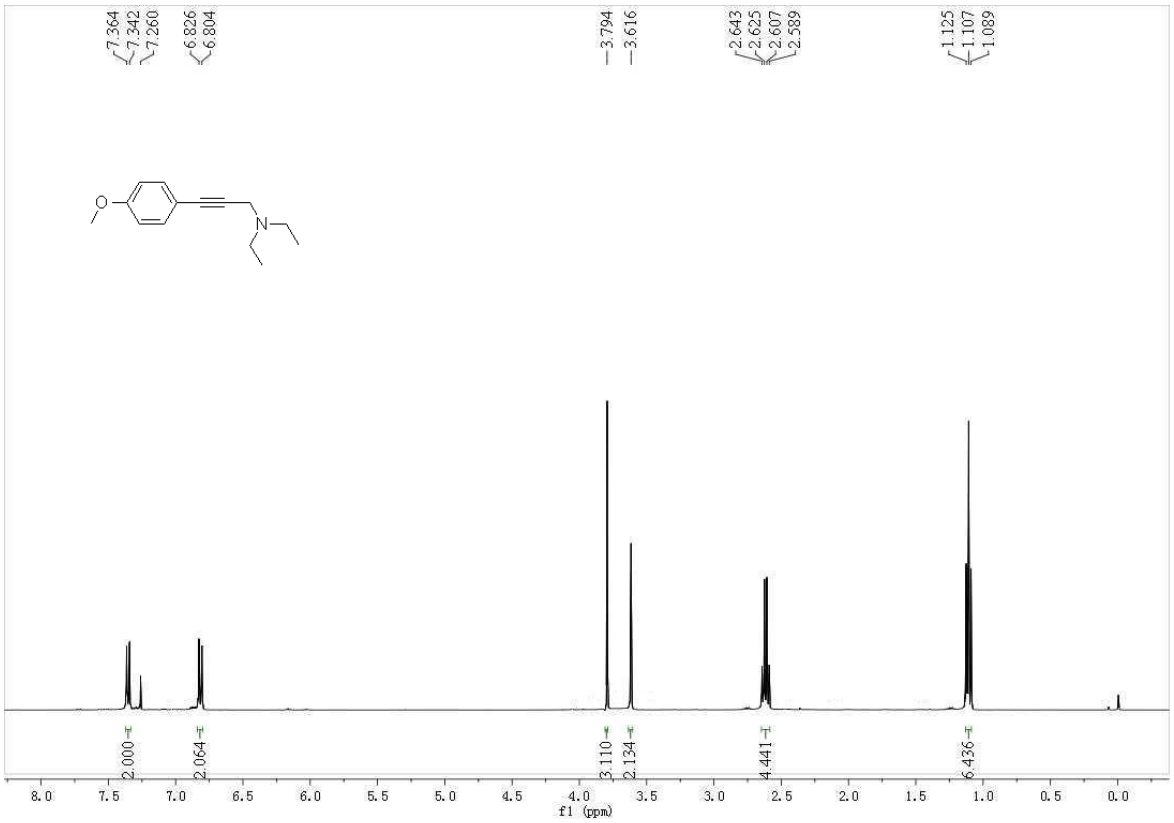
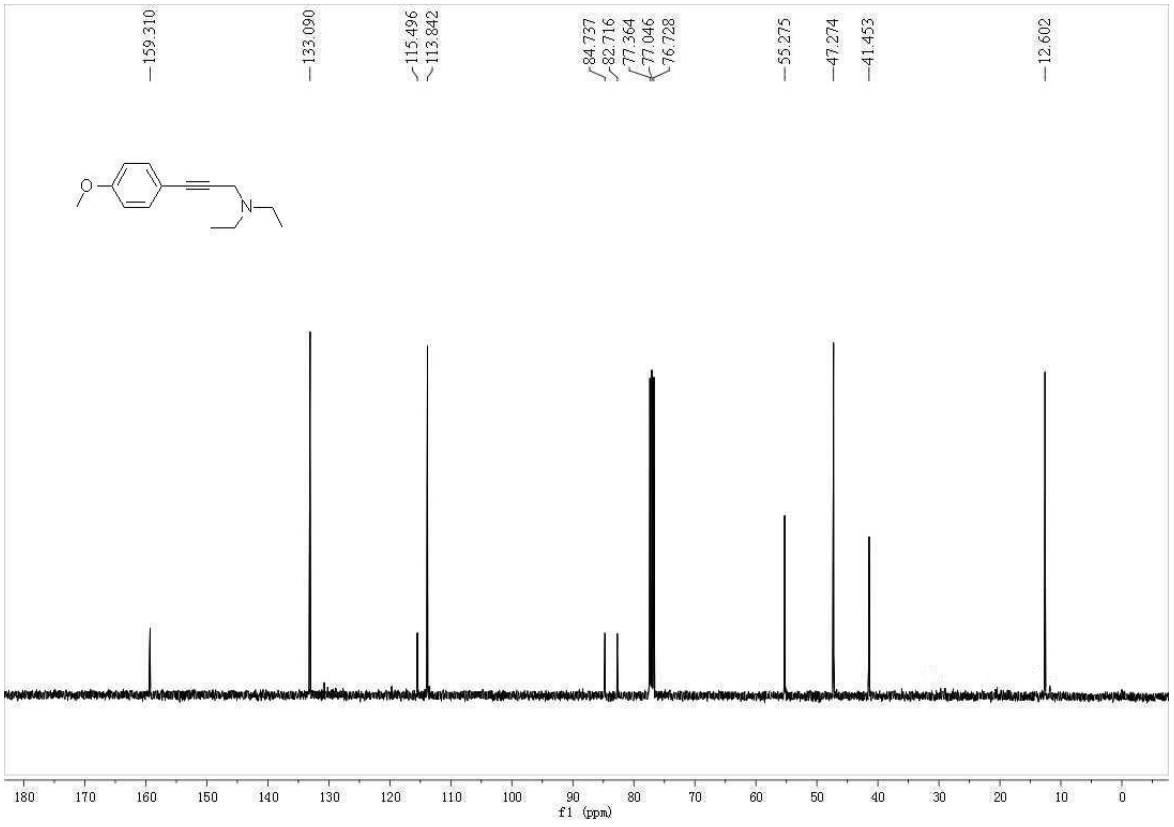
^{1}H NMR and ^{13}C NMR of **3m**





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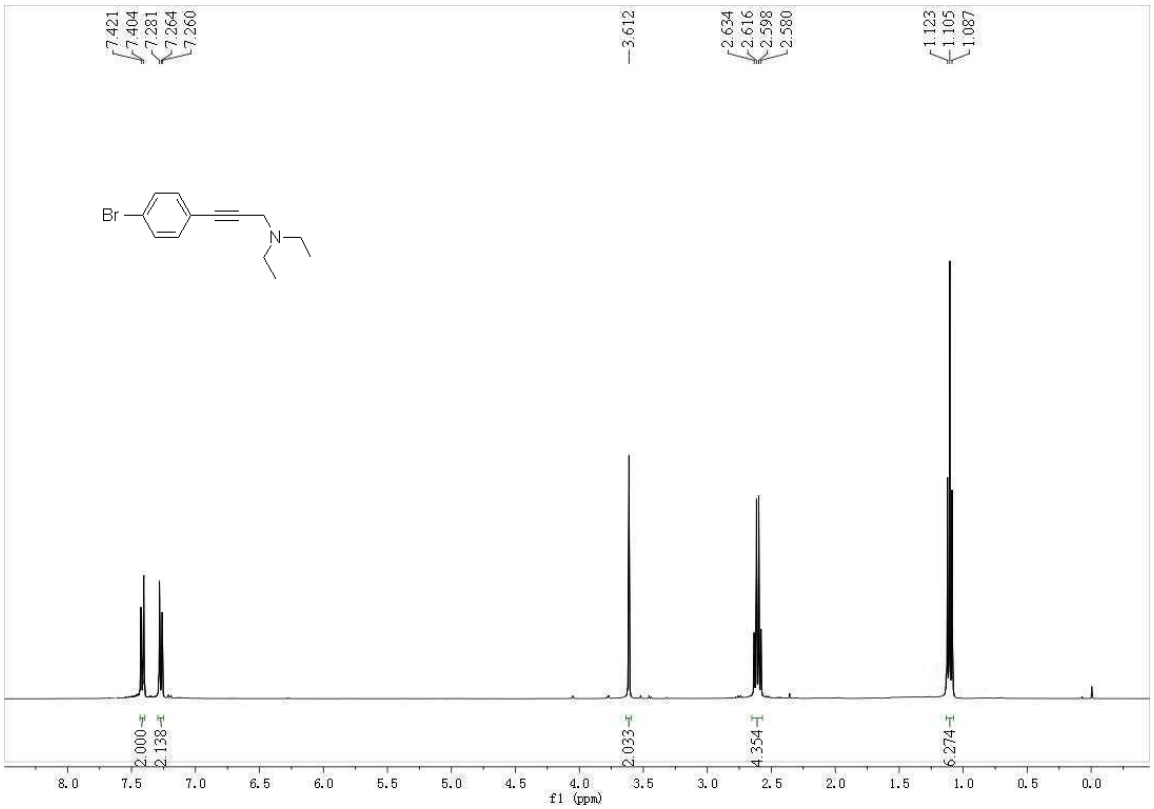
^{1}H NMR and ^{13}C NMR of **3n**



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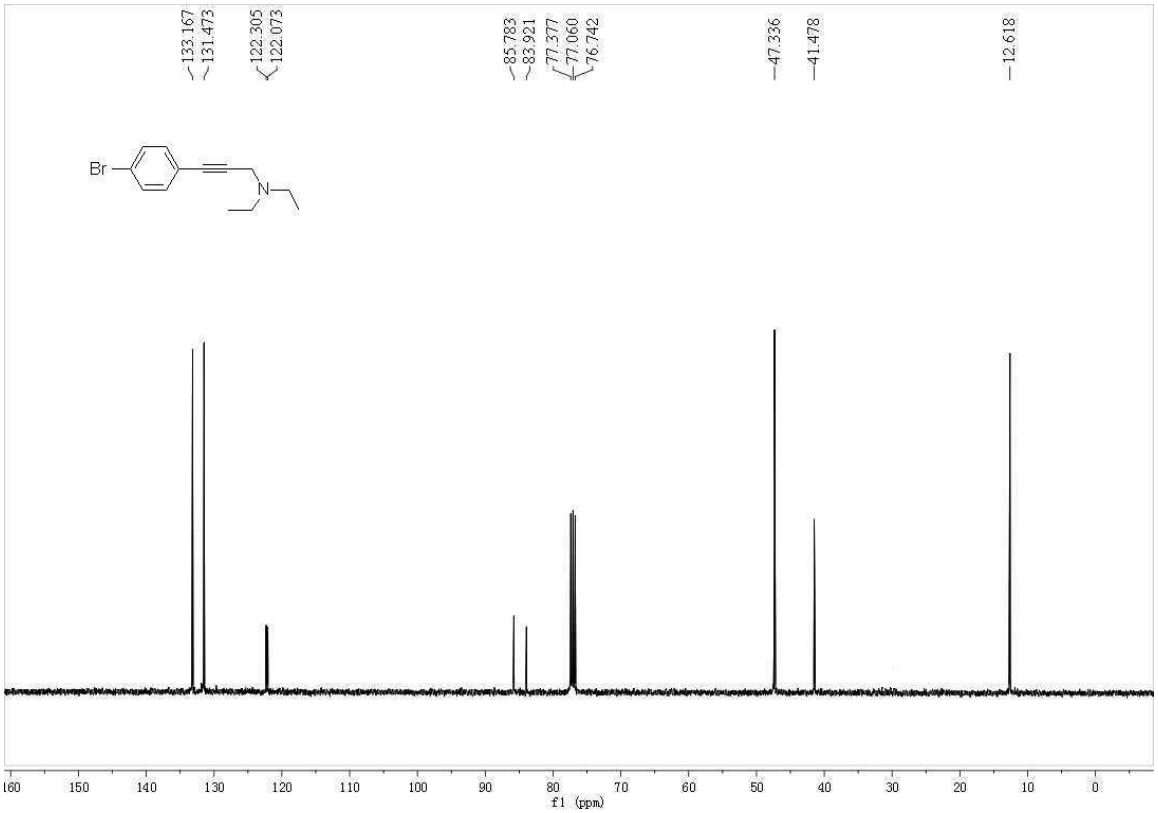

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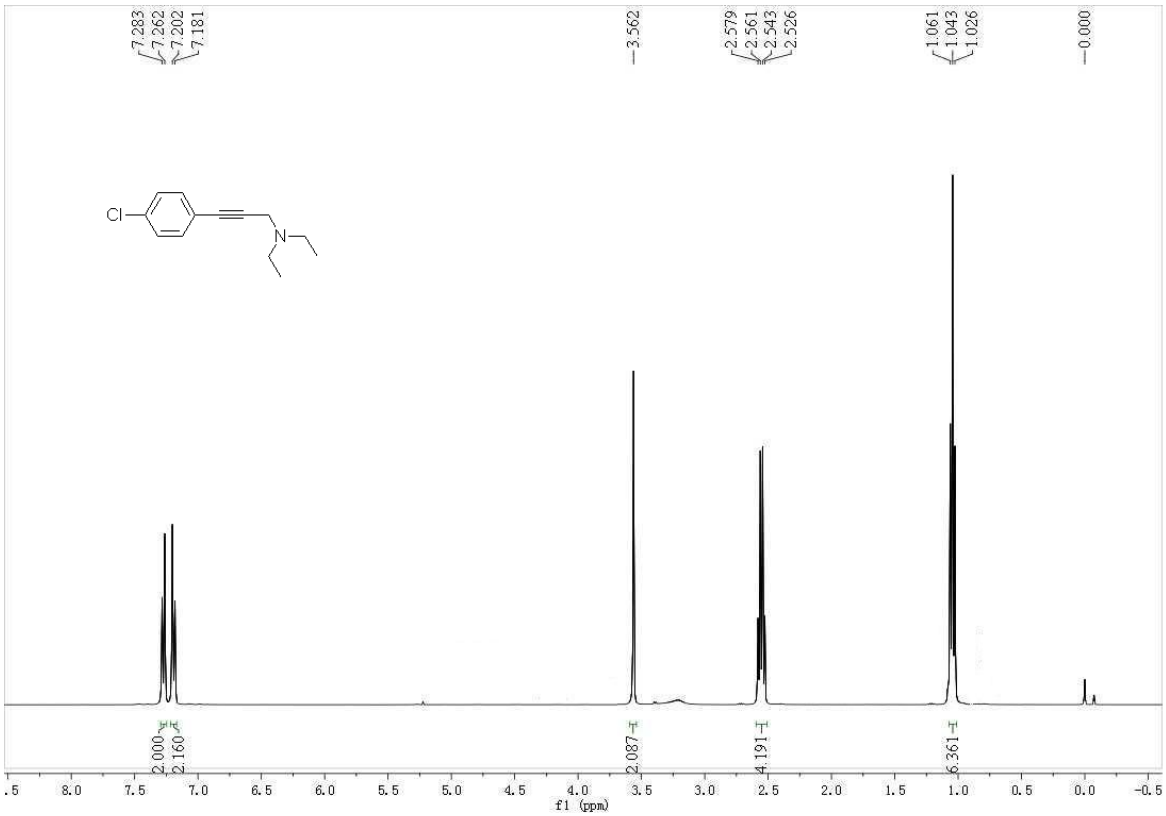
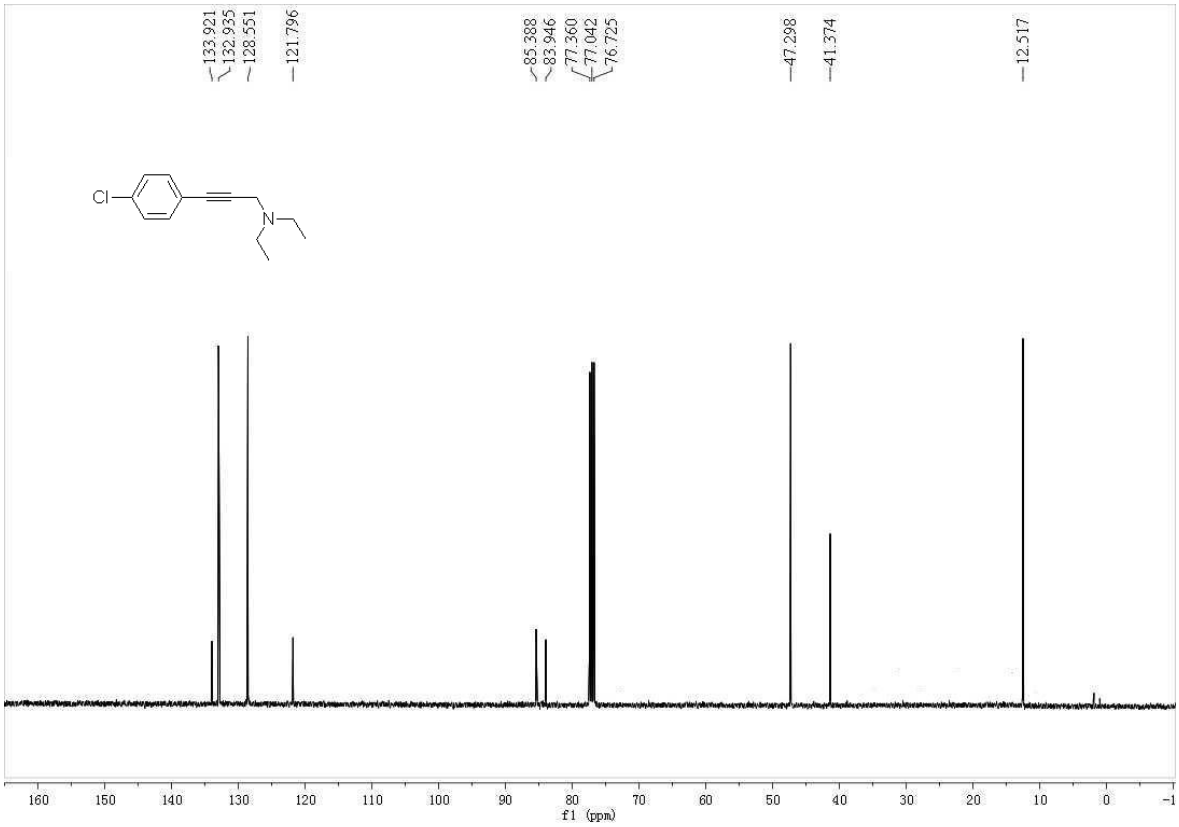
^{1}H NMR and ^{13}C NMR of **3o**





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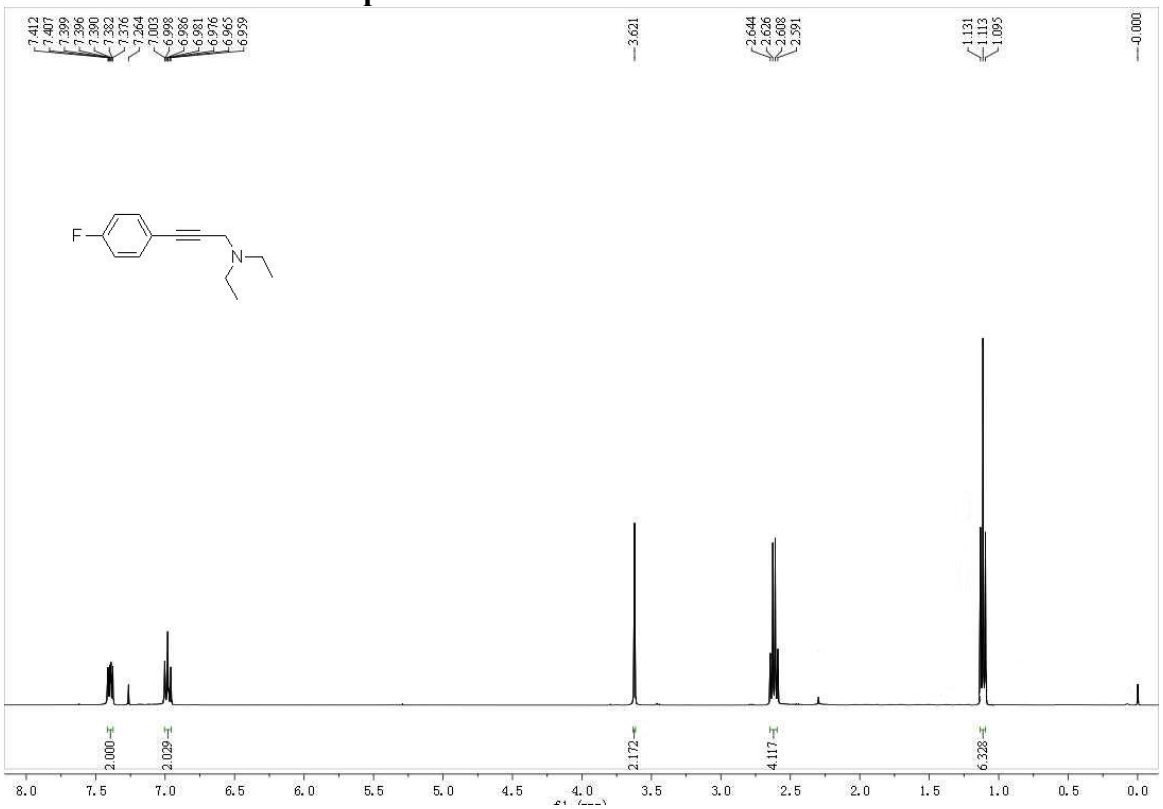
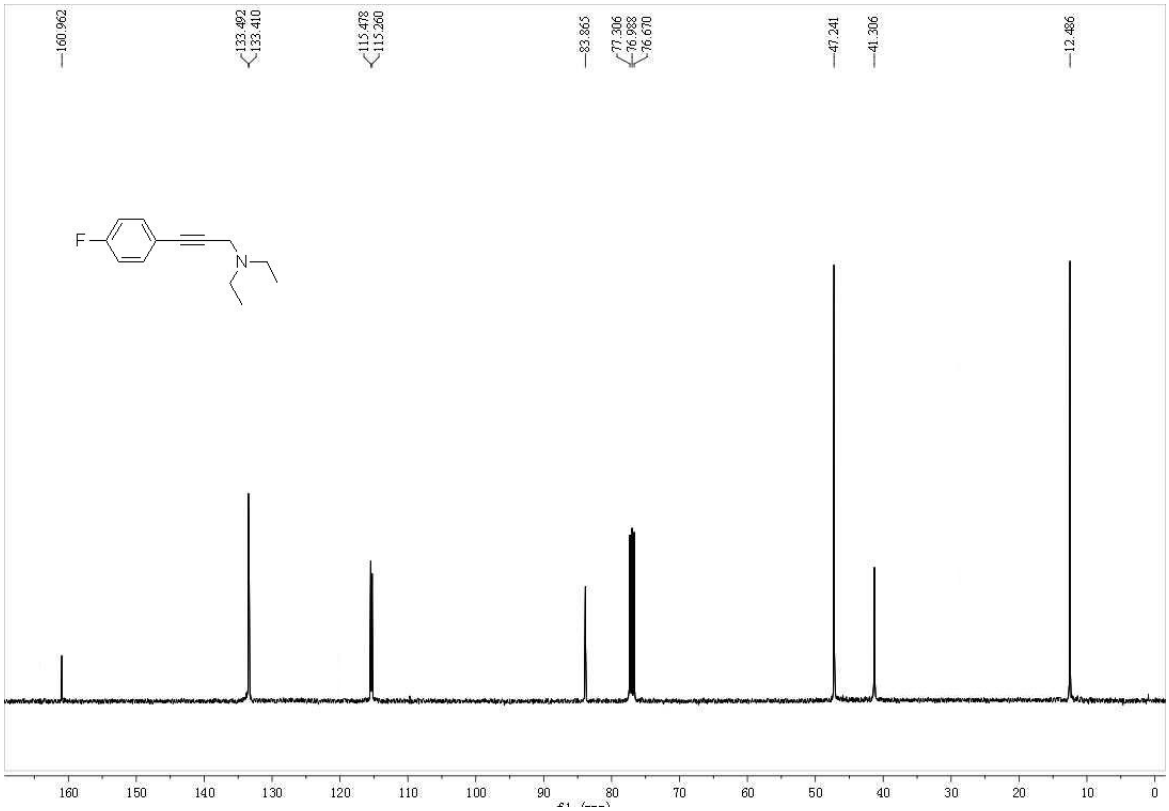
^{1}H NMR and ^{13}C NMR of **3p**





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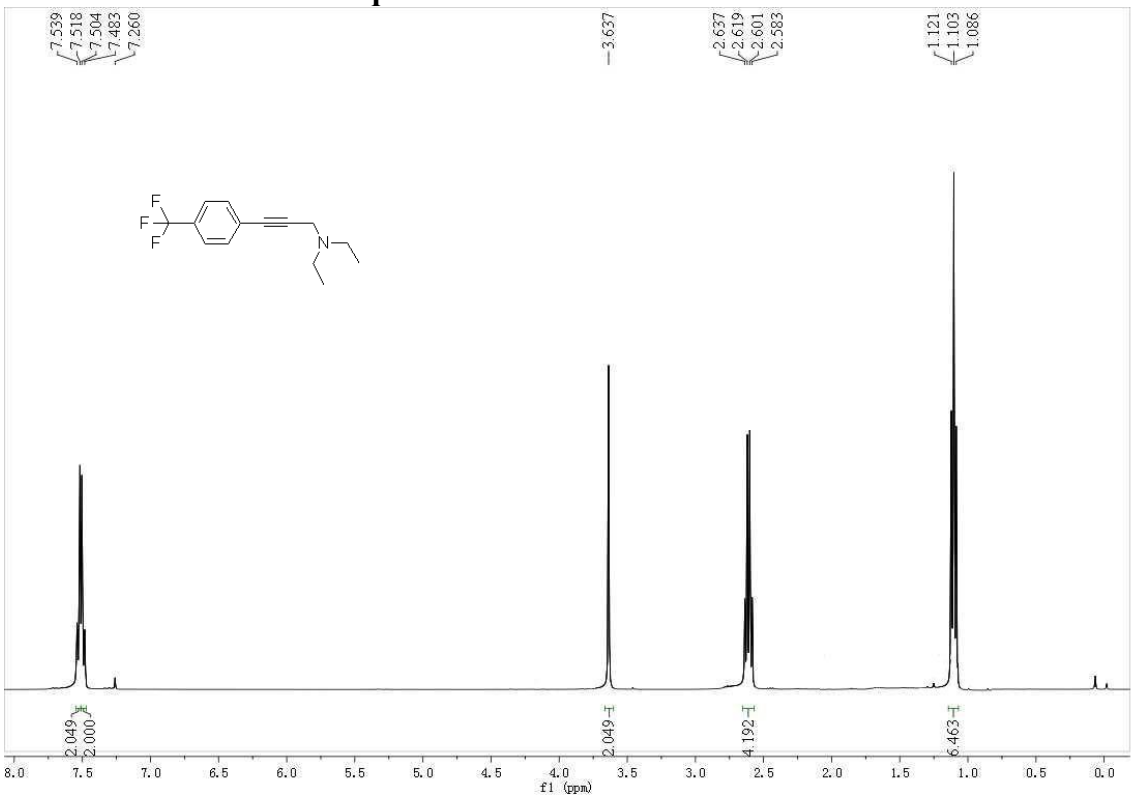
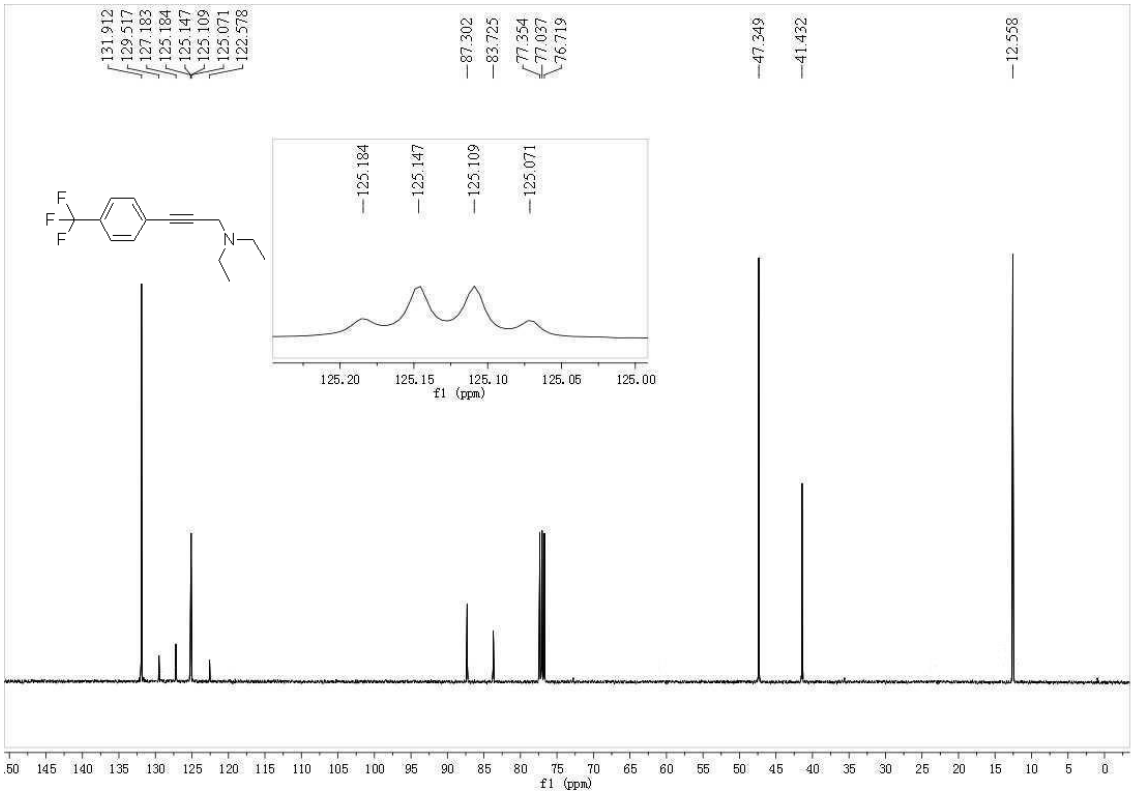
^{1}H NMR and ^{13}C NMR of **3q**





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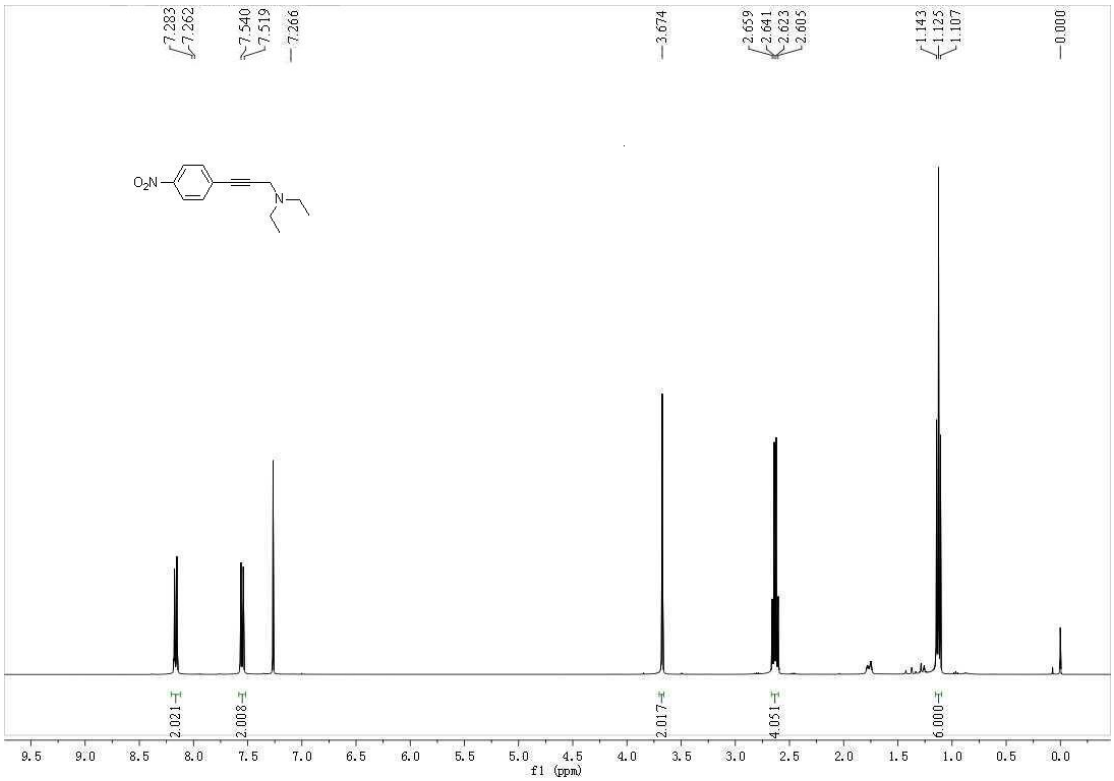
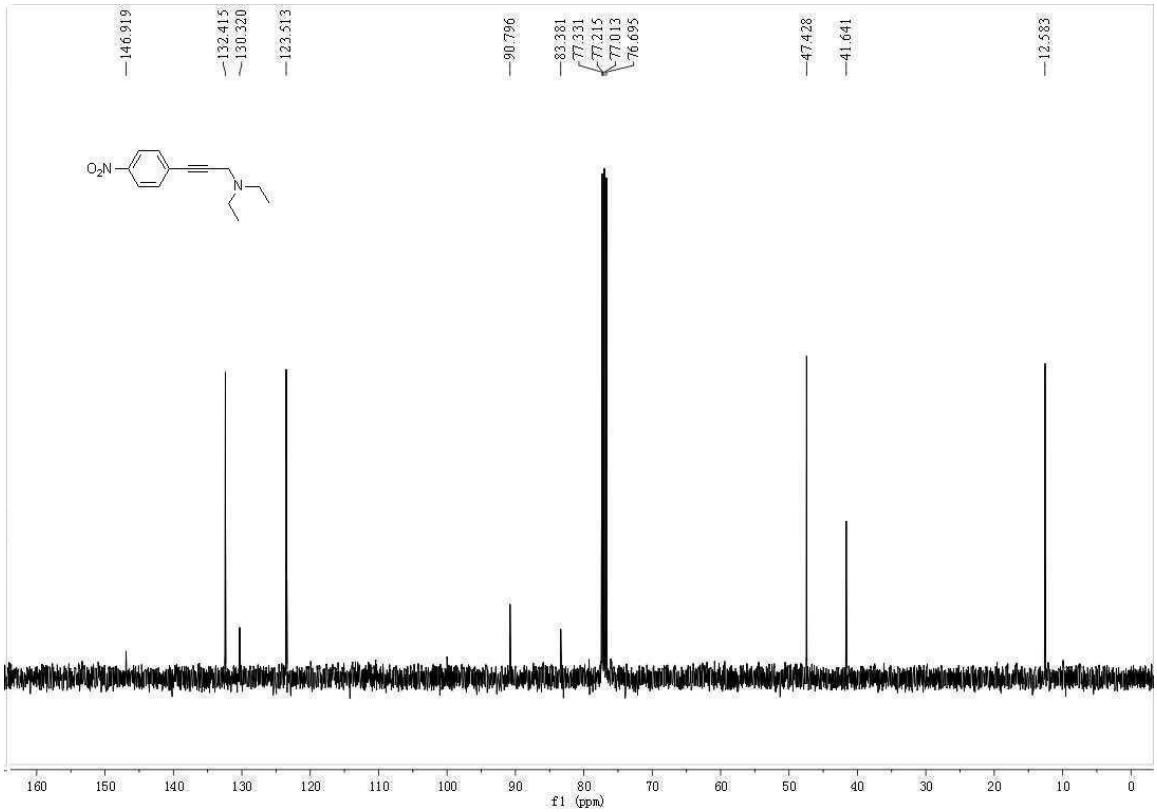
^{1}H NMR and ^{13}C NMR of **3r**





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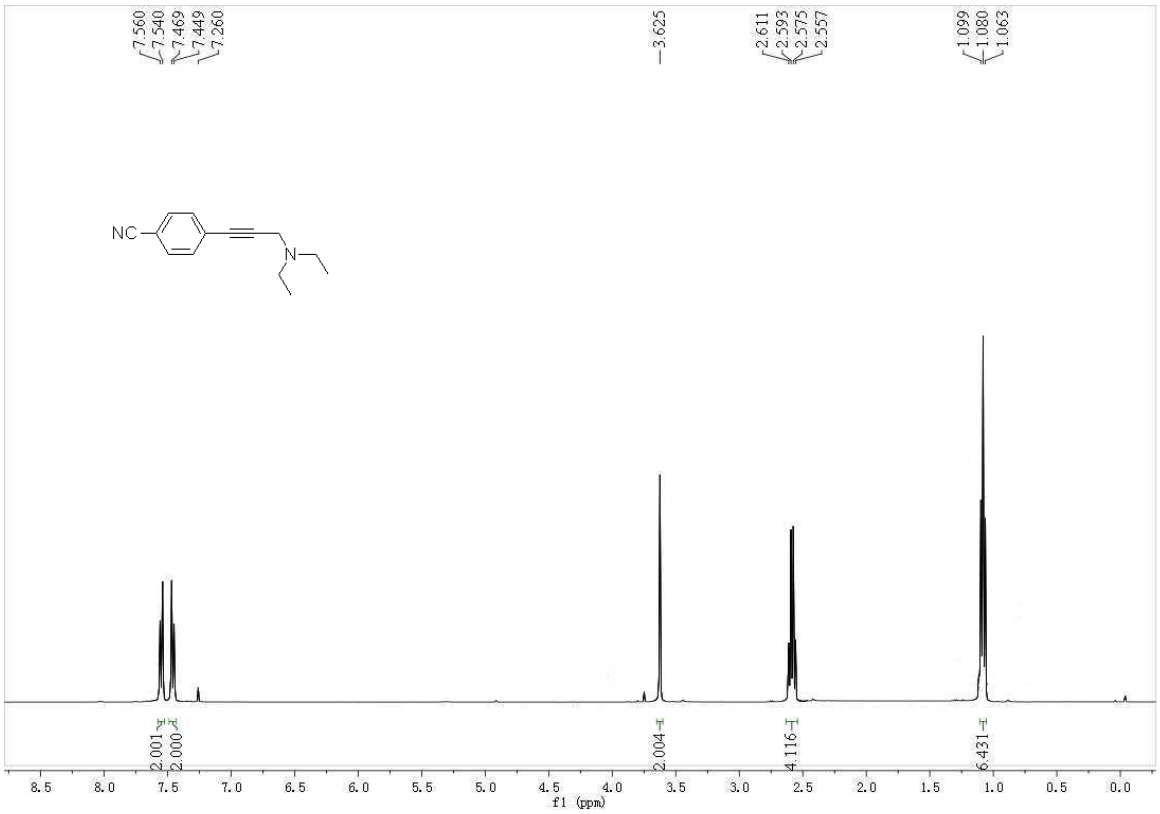
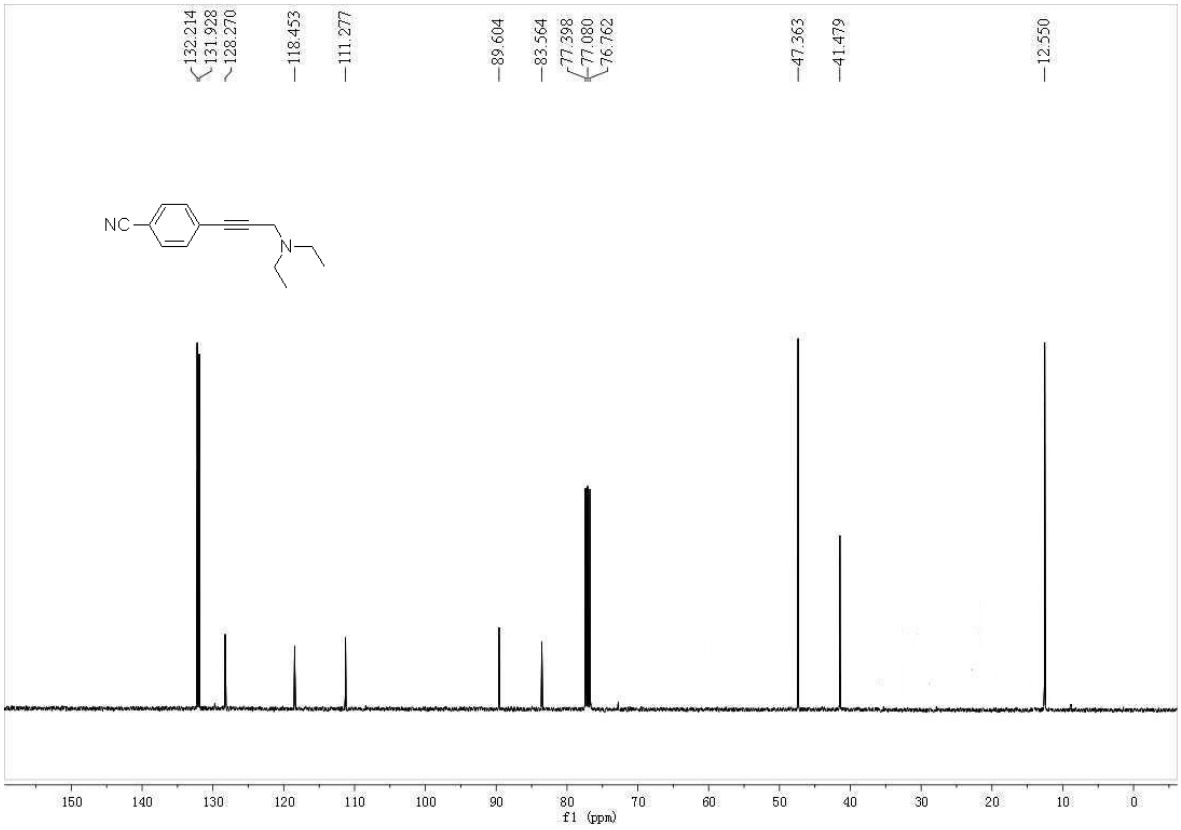
^{1}H NMR and ^{13}C NMR of **3s**





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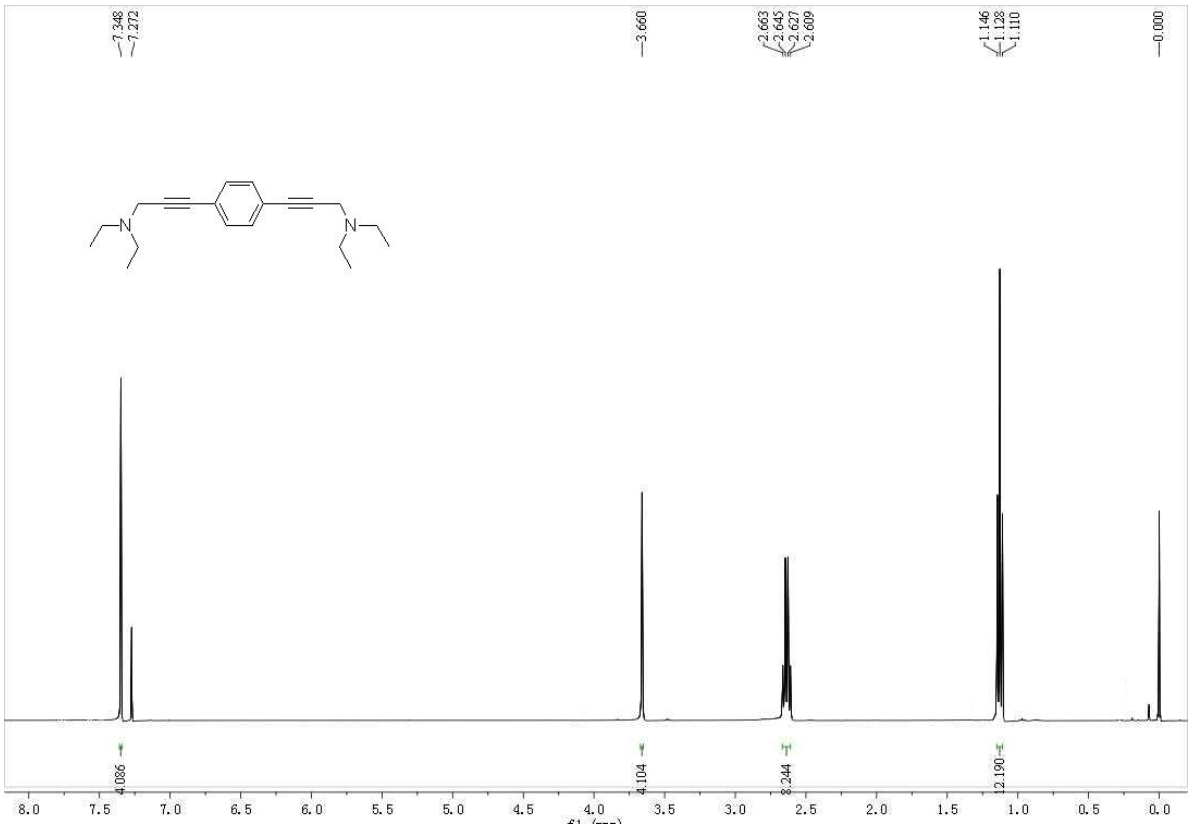
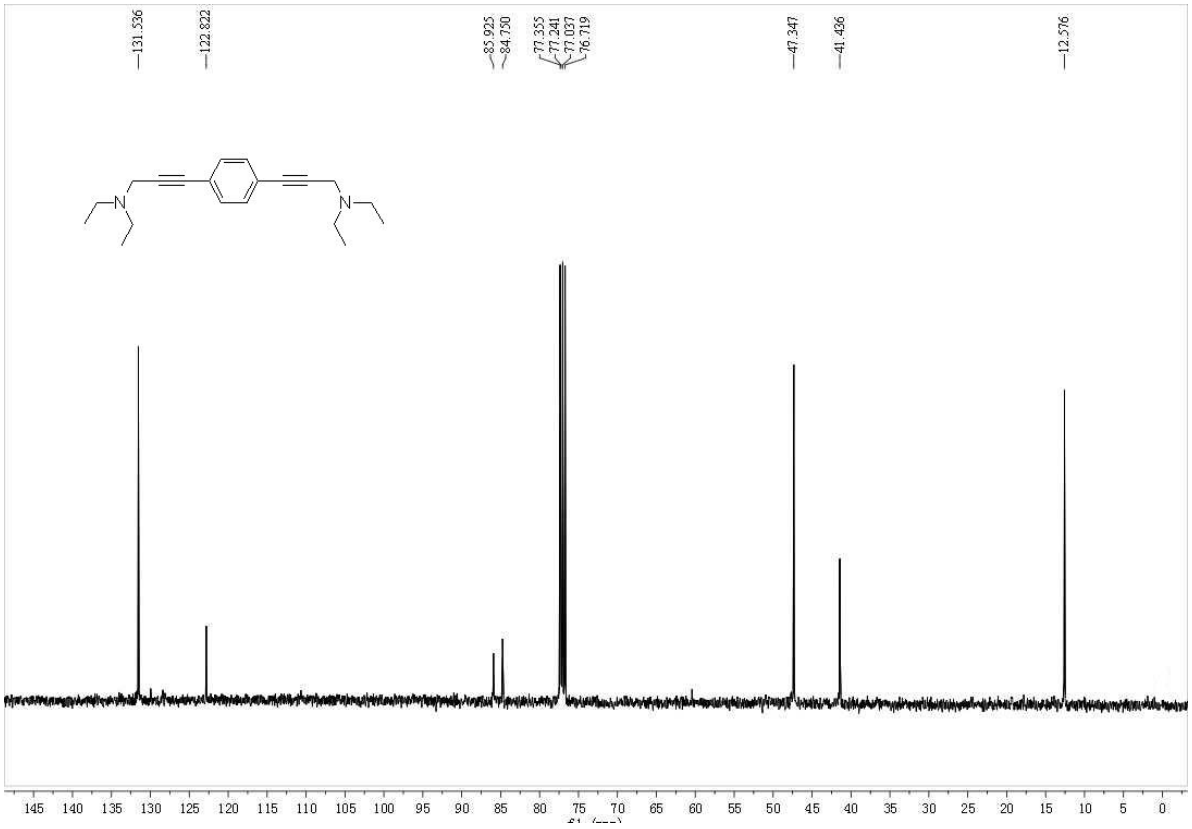
^{1}H NMR and ^{13}C NMR of **3t**





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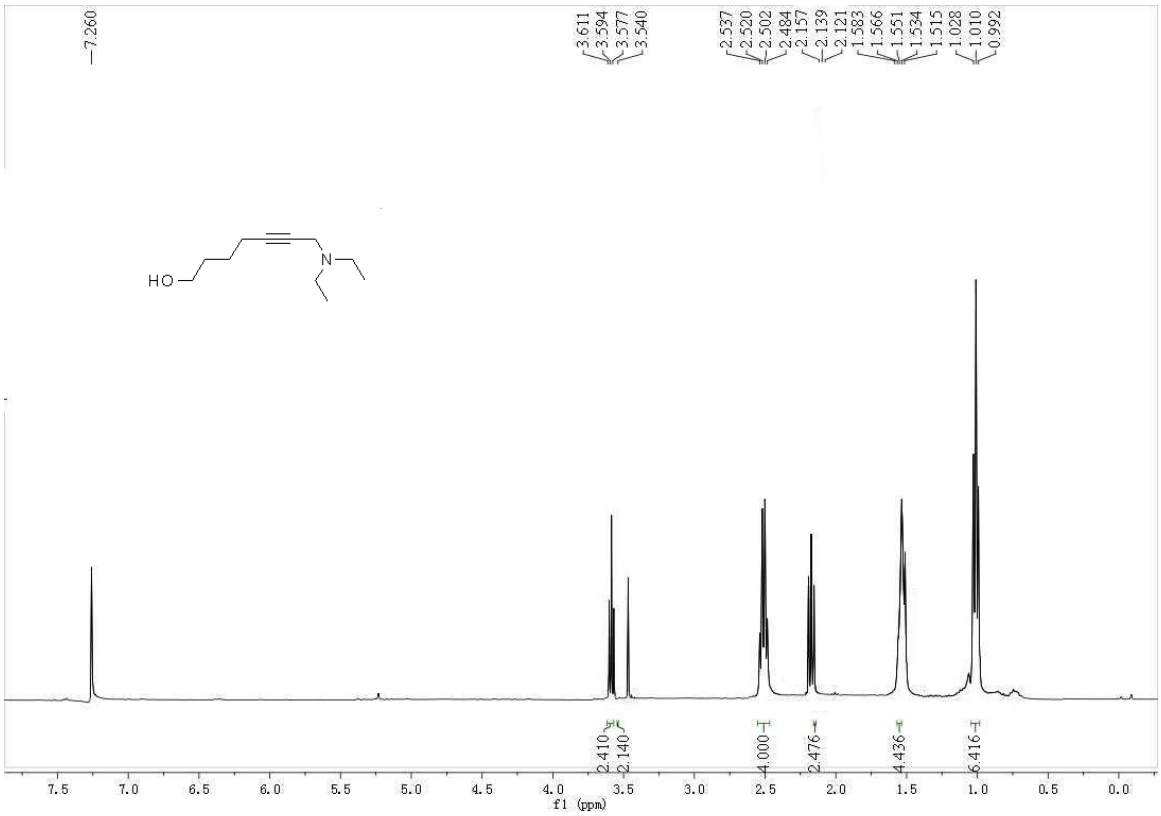
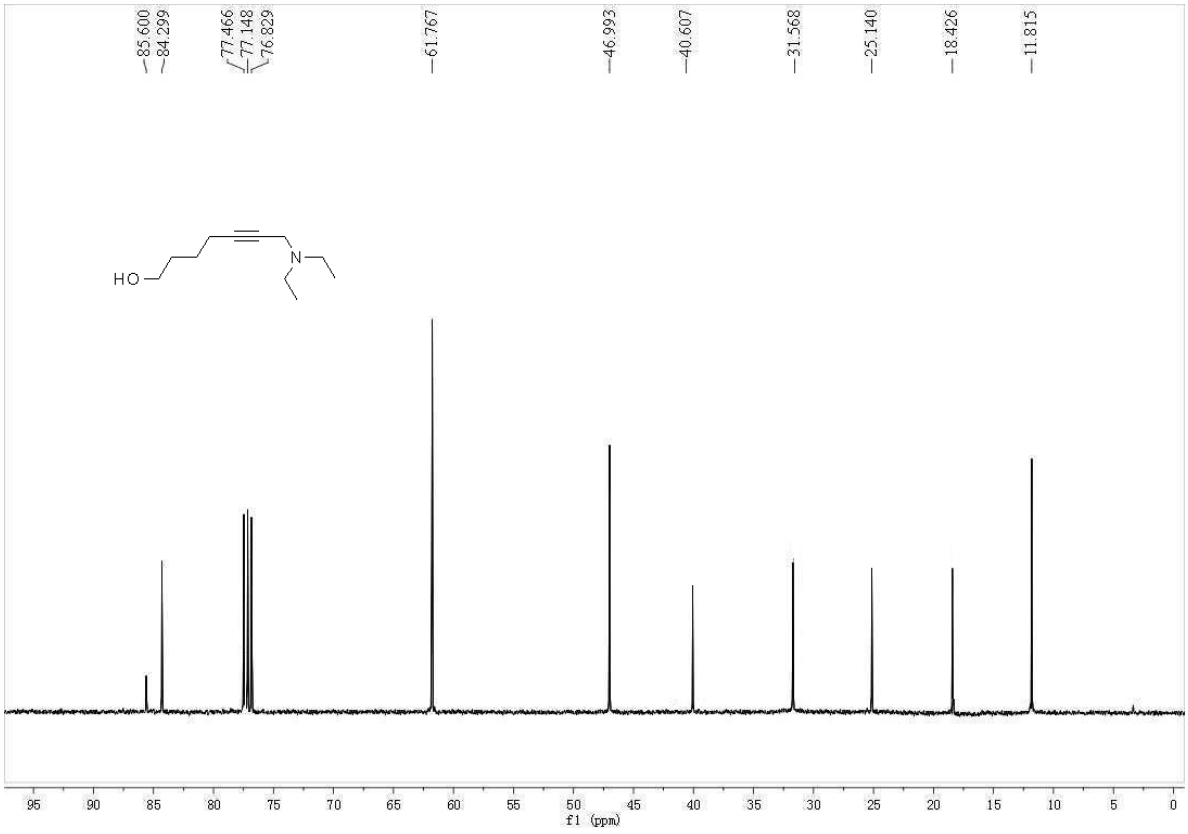
^{1}H NMR and ^{13}C NMR of **3u**





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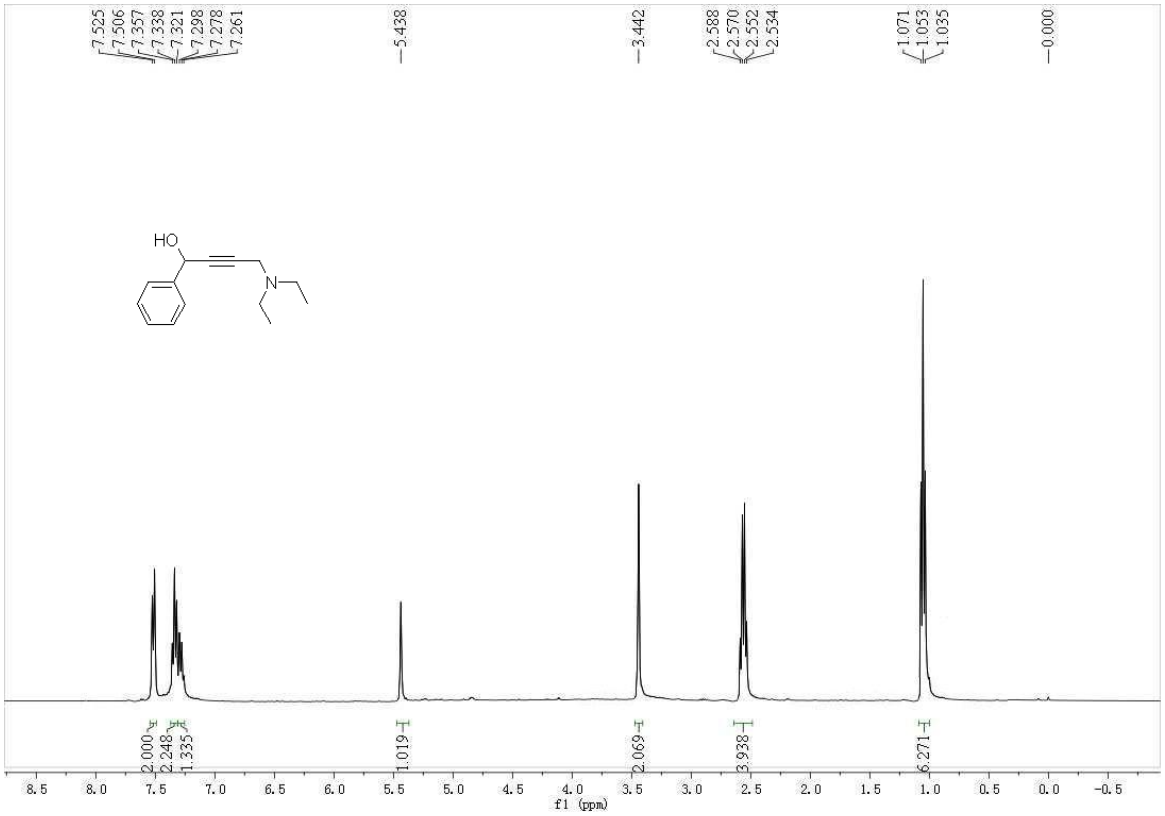
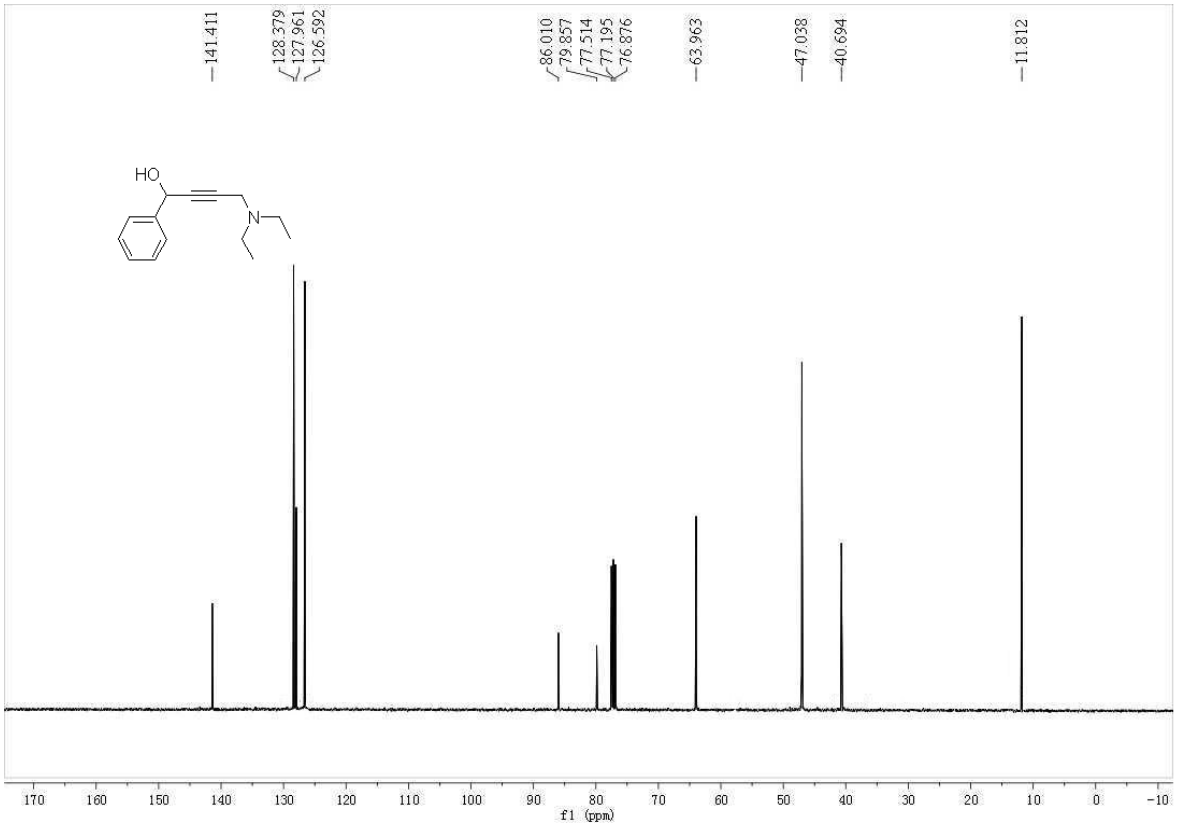
^{1}H NMR and ^{13}C NMR of **3v**





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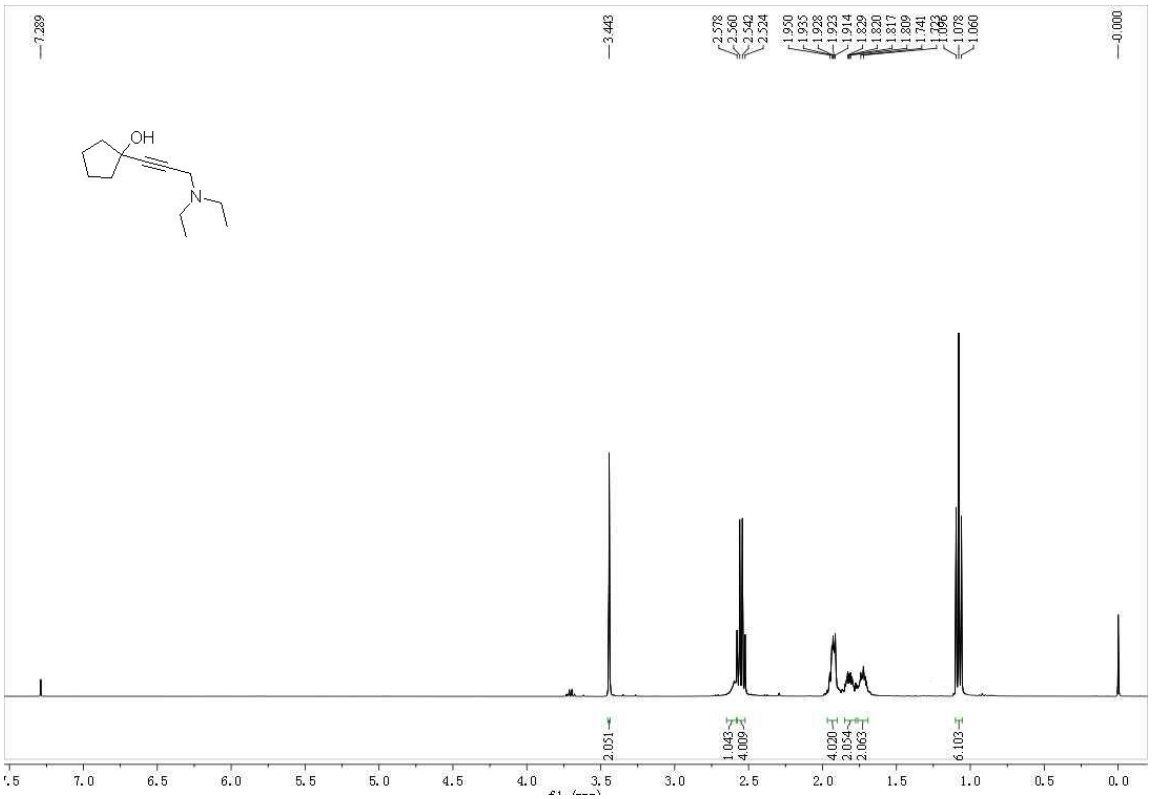
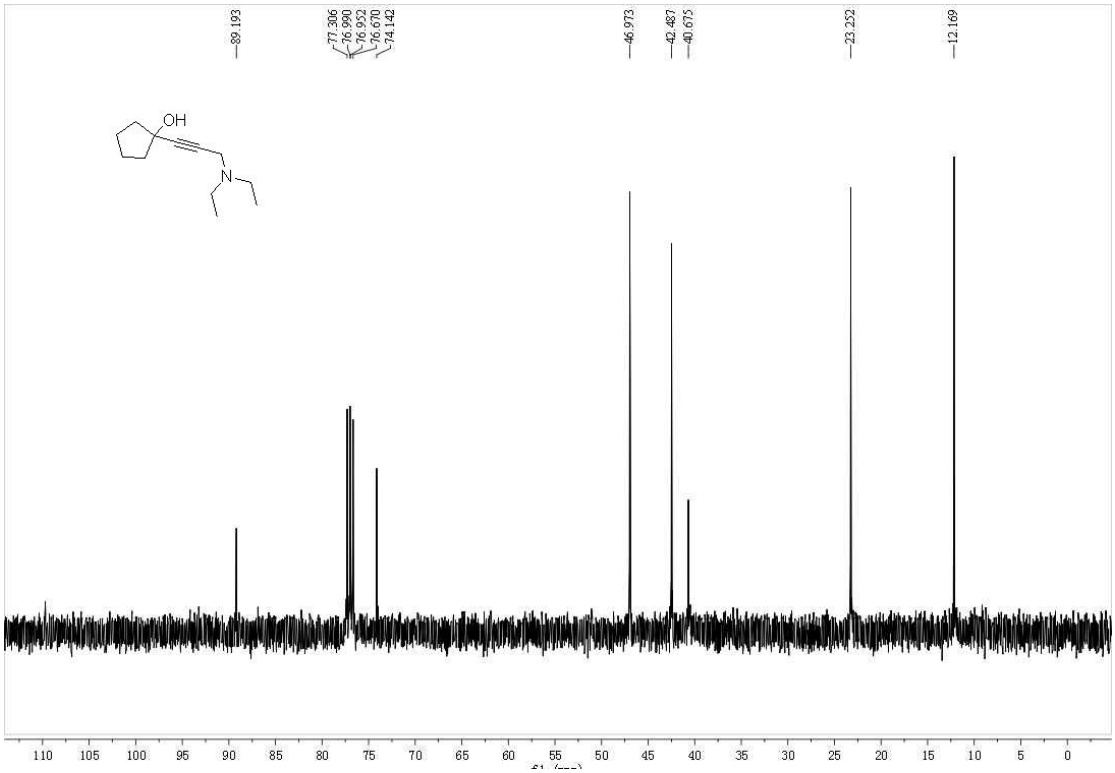
^{1}H NMR and ^{13}C NMR of **3w**





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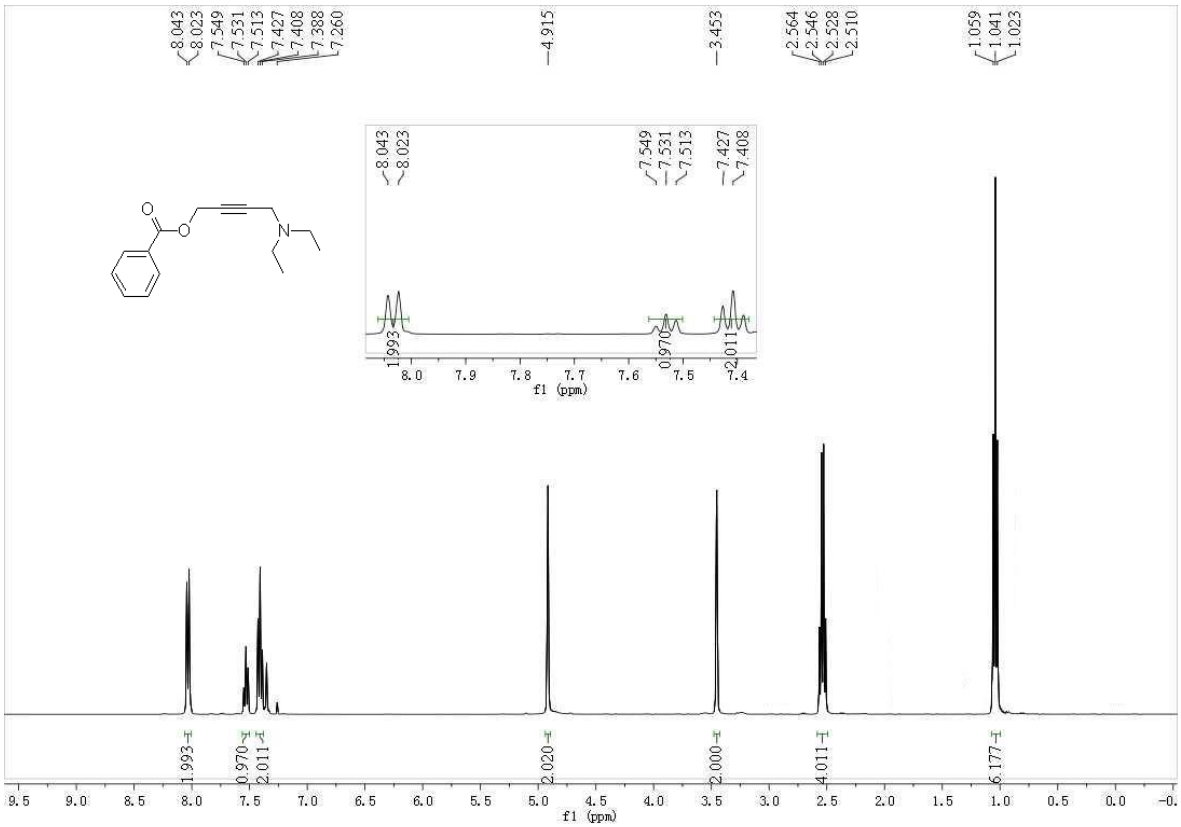
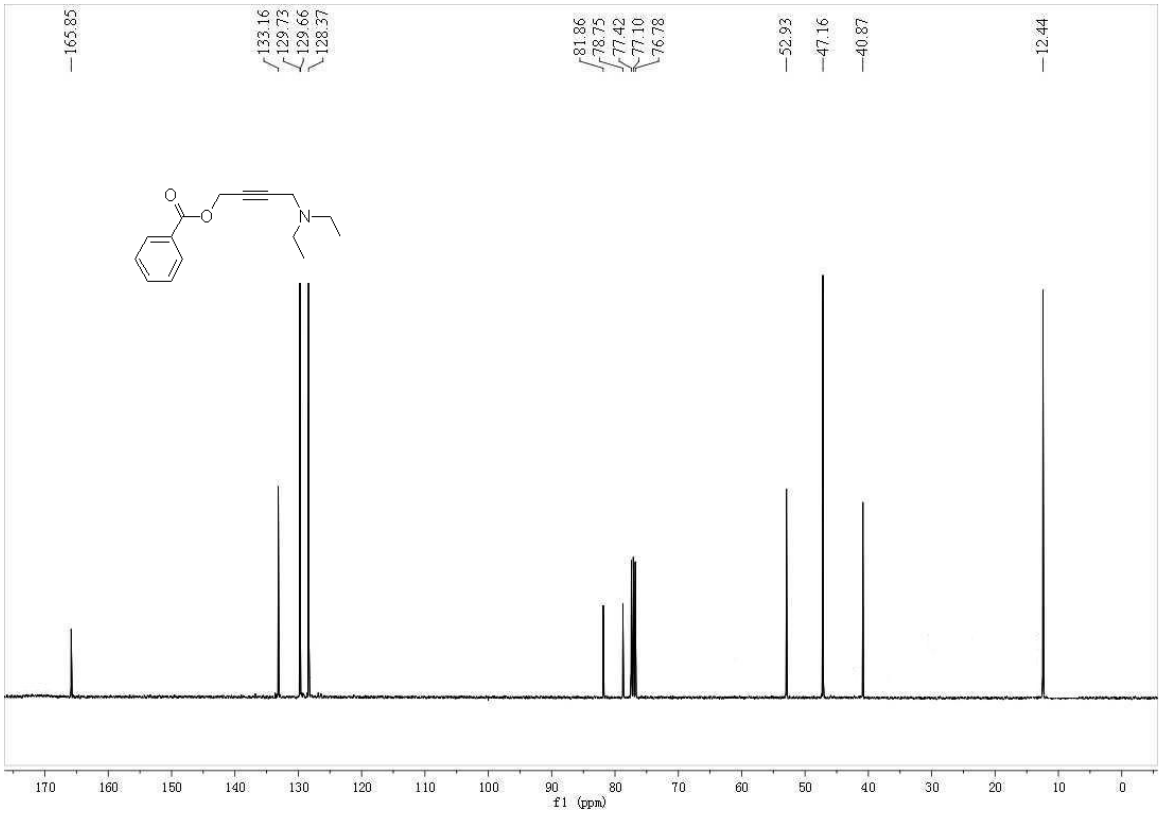
^{1}H NMR and ^{13}C NMR of **3x**





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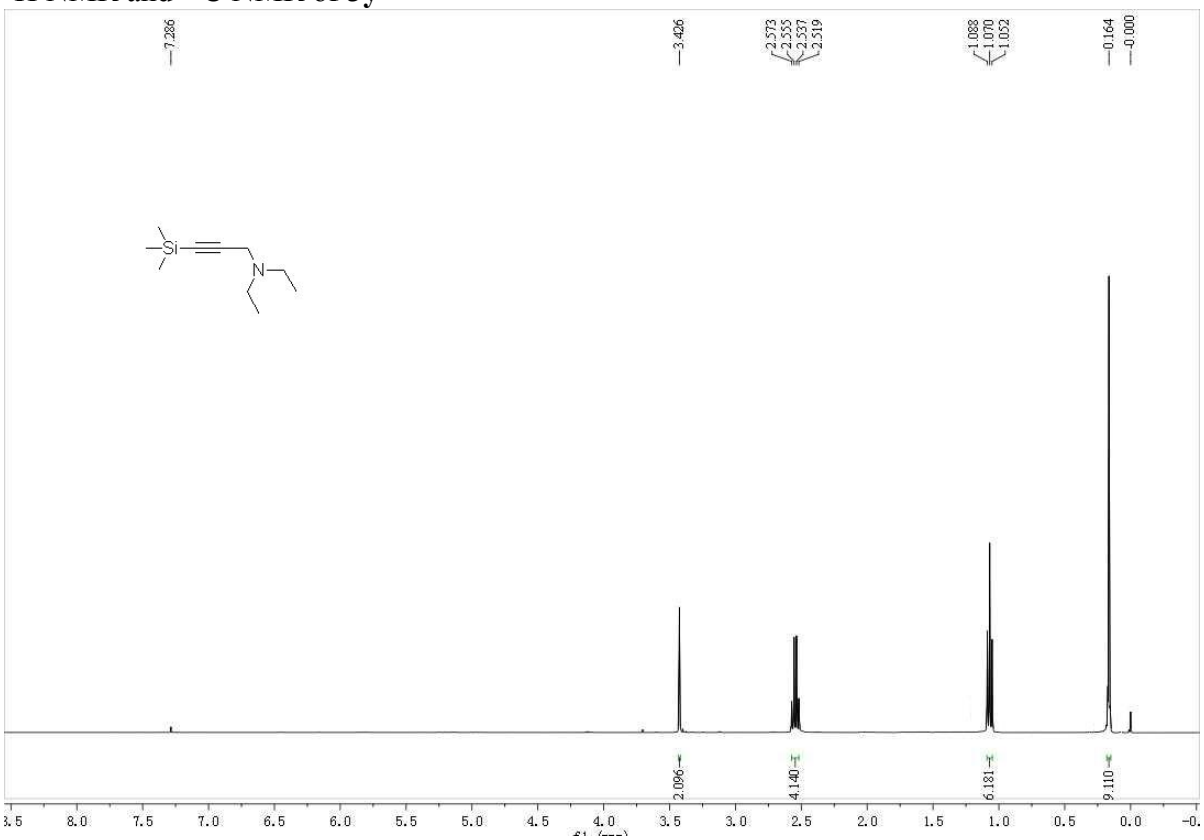
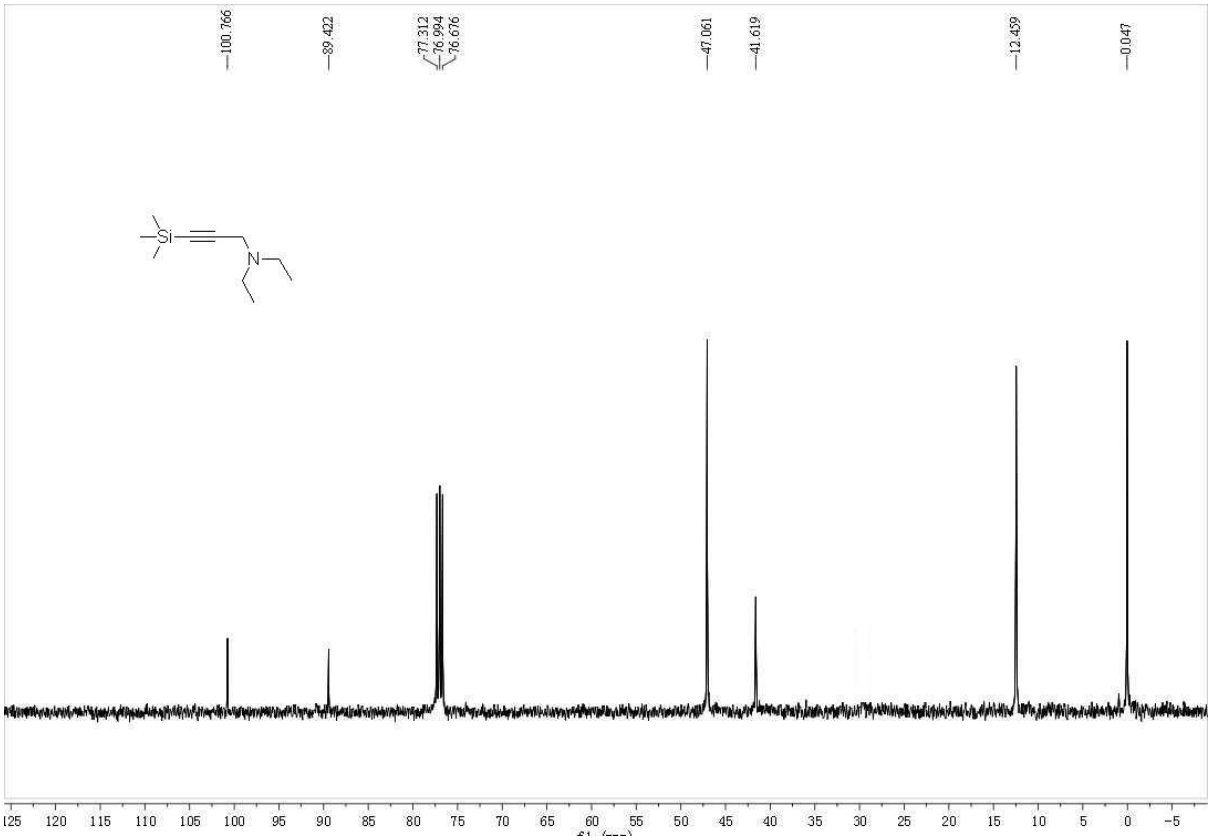
^{1}H NMR and ^{13}C NMR of **3y**





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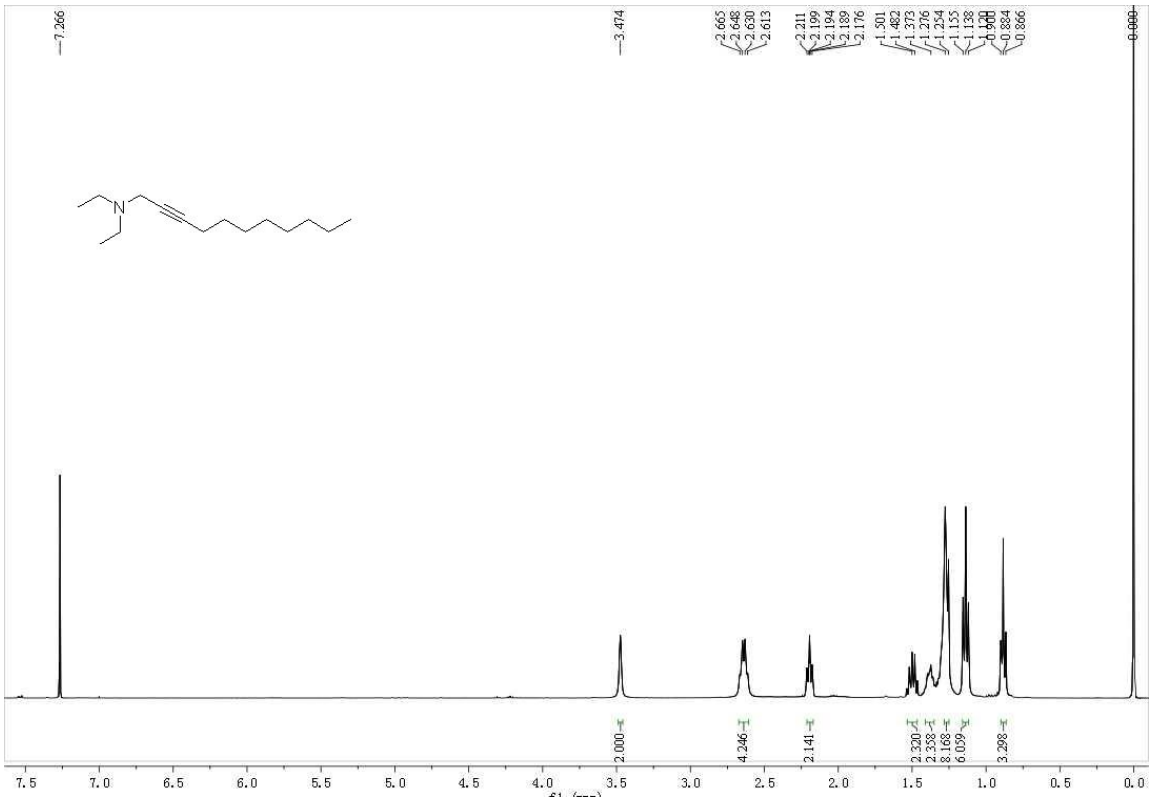
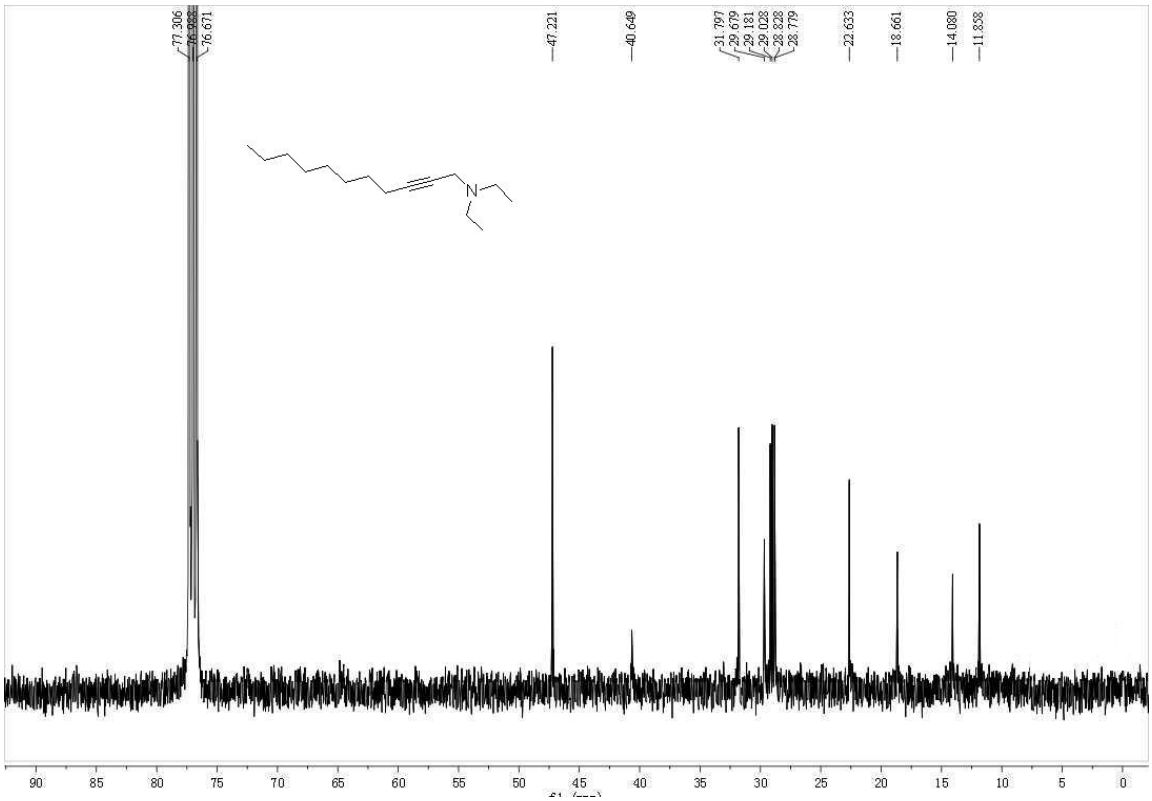
^{1}H NMR and ^{13}C NMR of ***3z***





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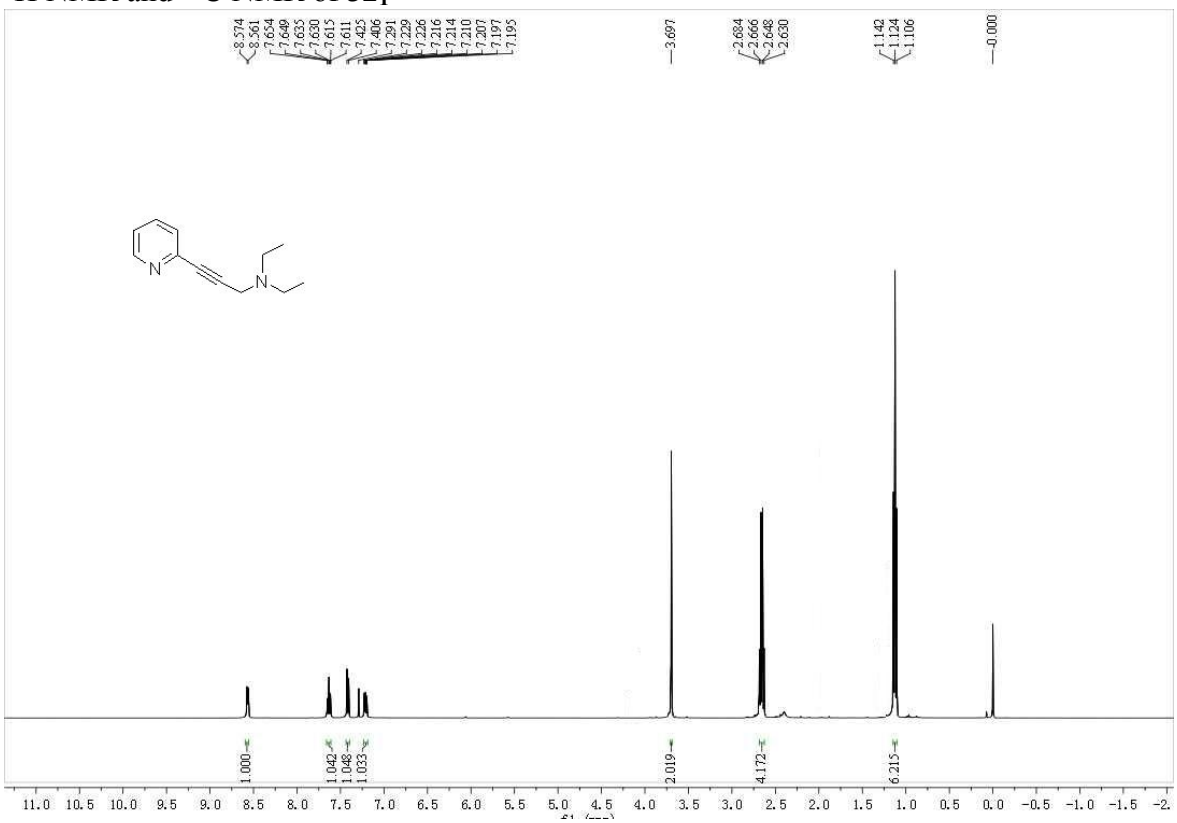
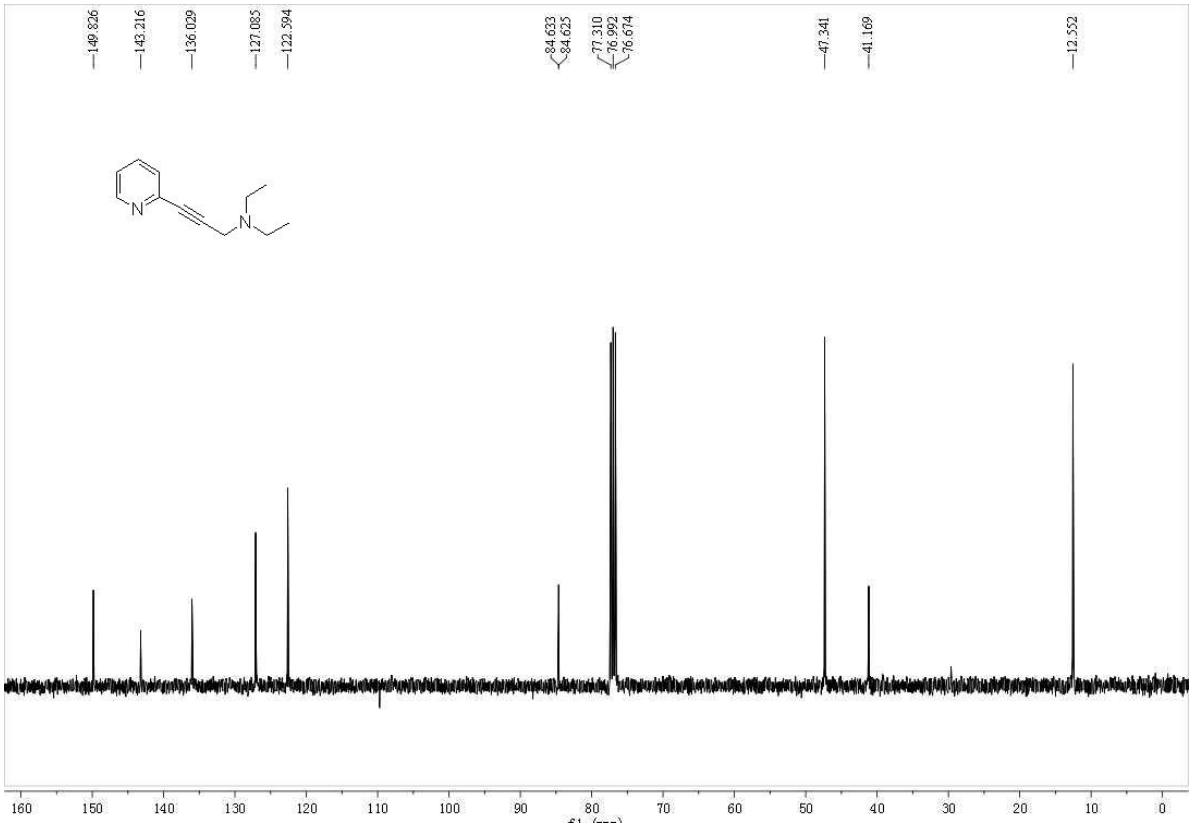
^{1}H NMR and ^{13}C NMR of **3z$_1$**





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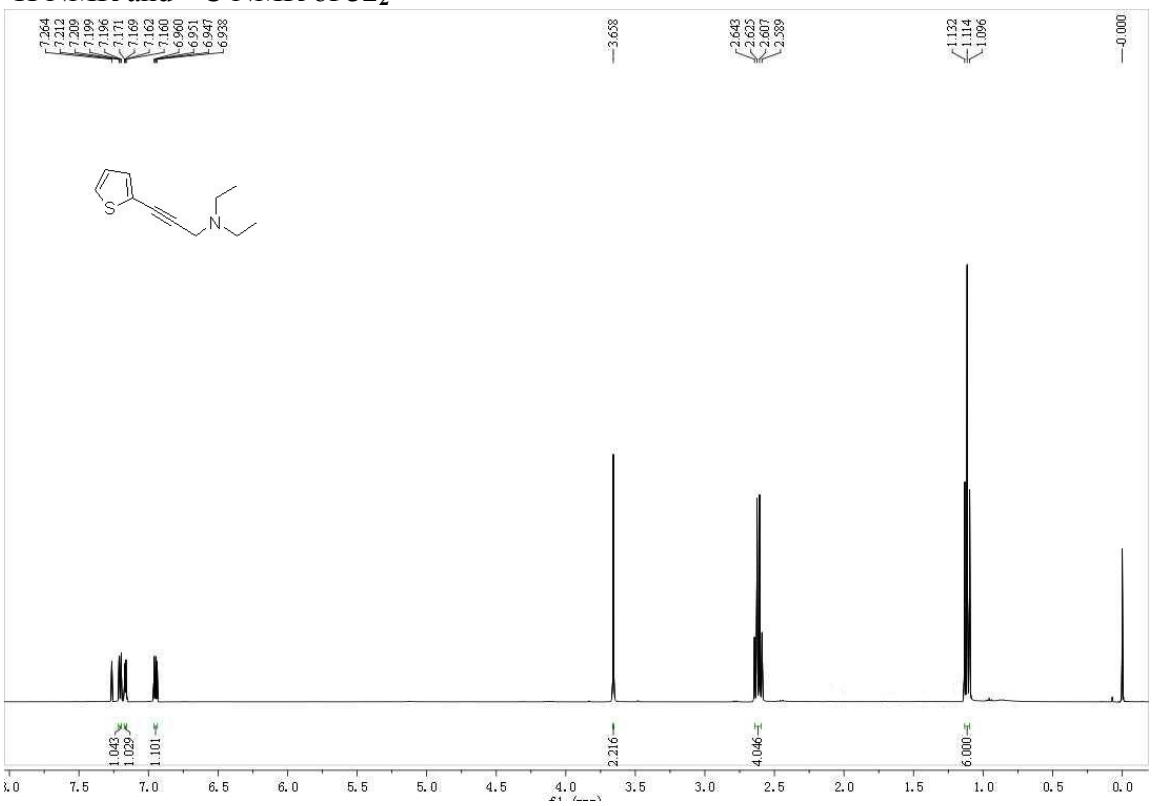
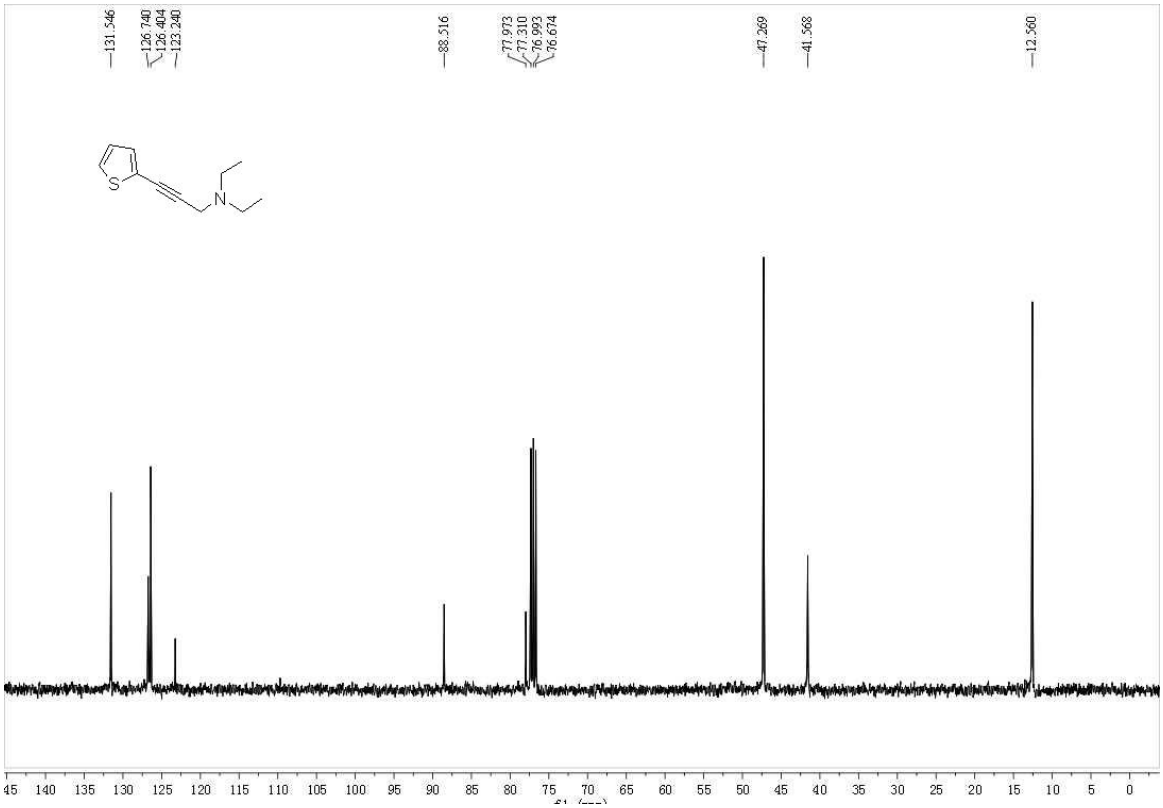
^{1}H NMR and ^{13}C NMR of **3z$_2$**





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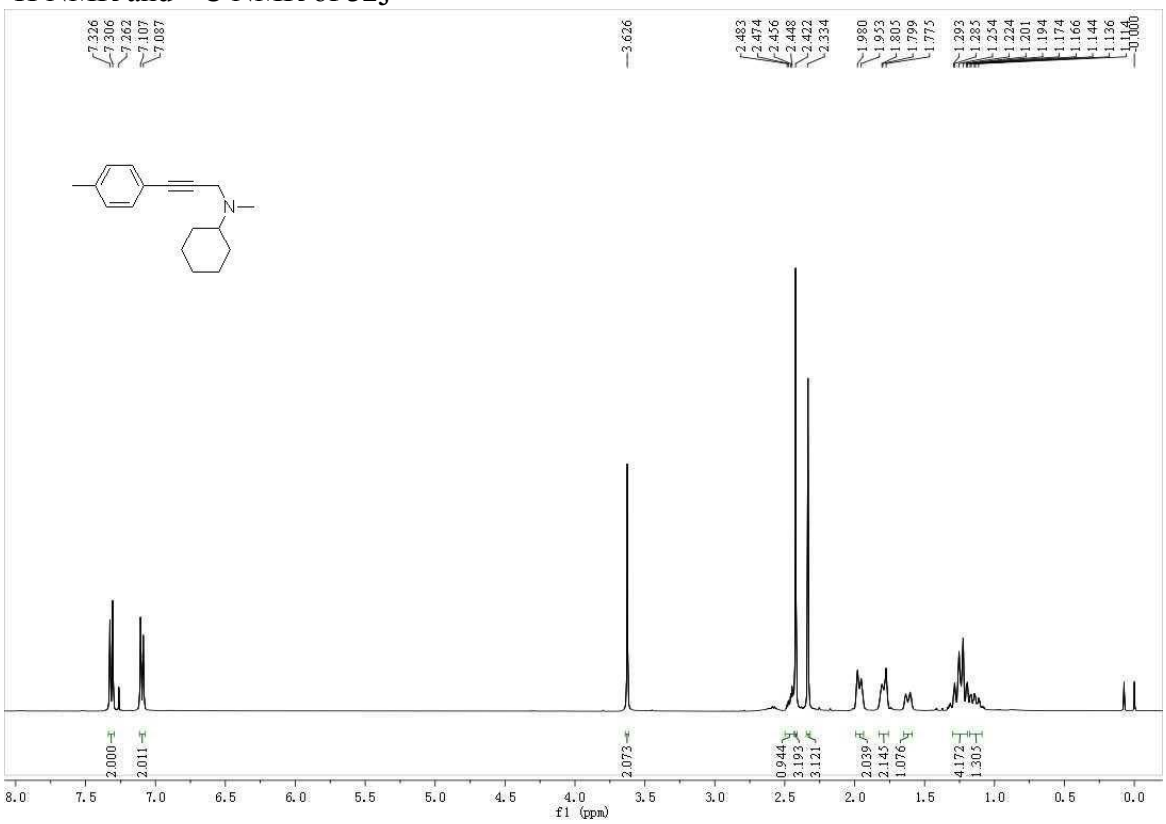
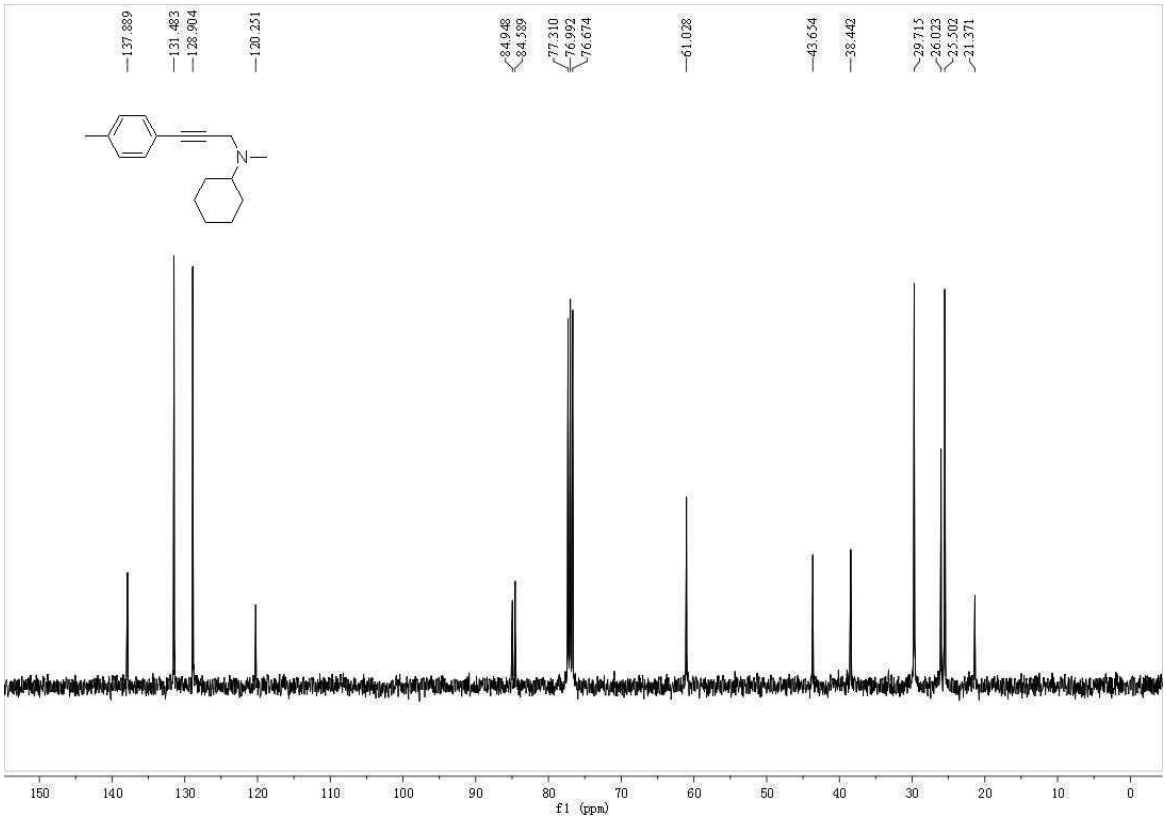
^{1}H NMR and ^{13}C NMR of **3z$_3$**





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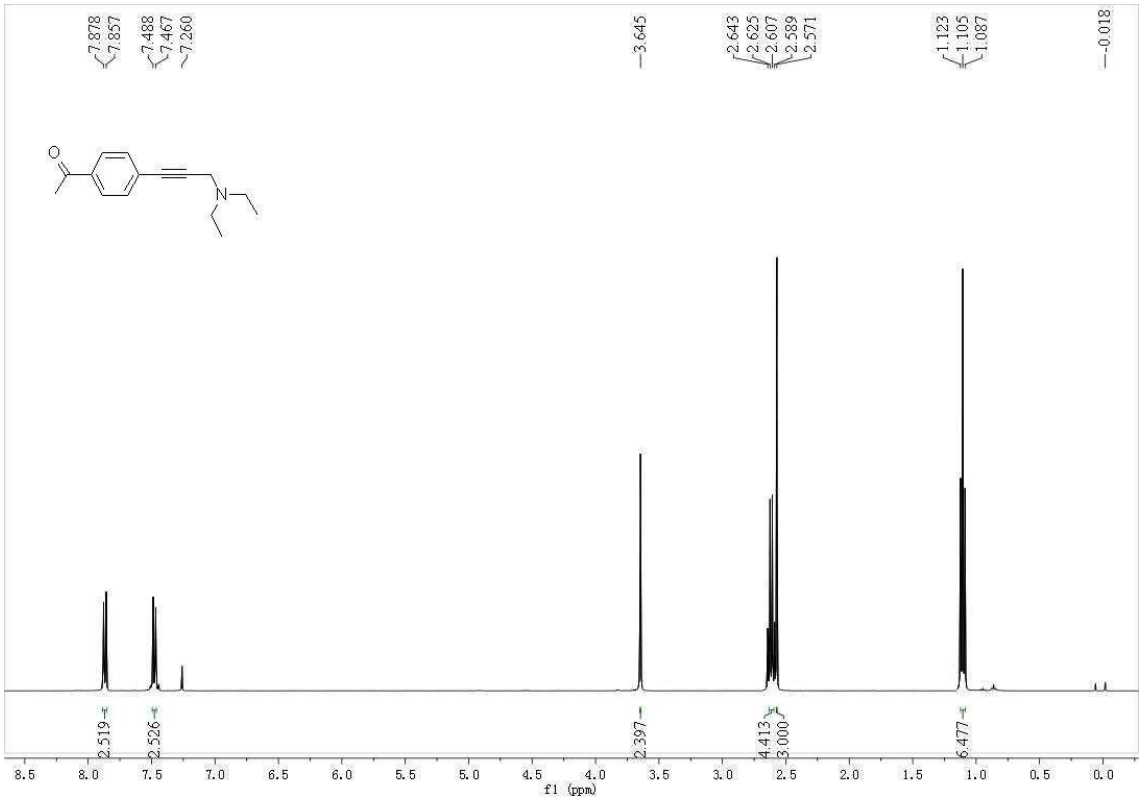
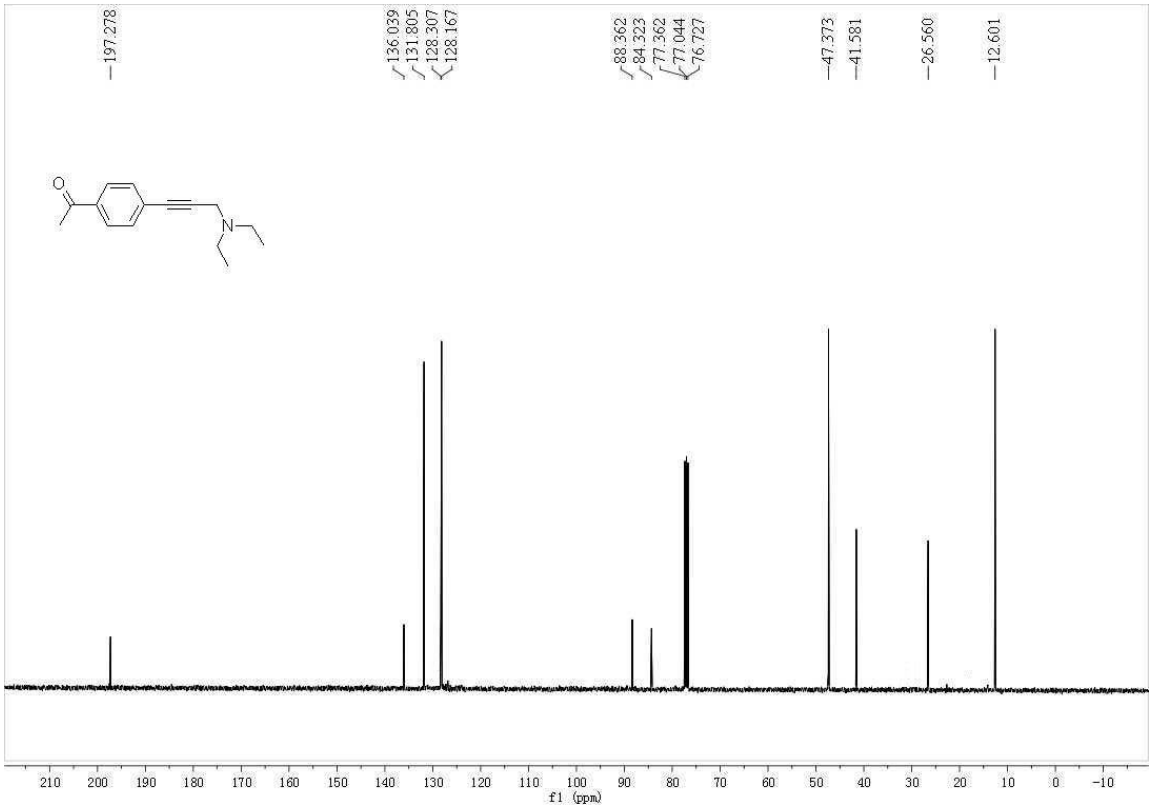
^{1}H NMR and ^{13}C NMR of **3z$_4$**





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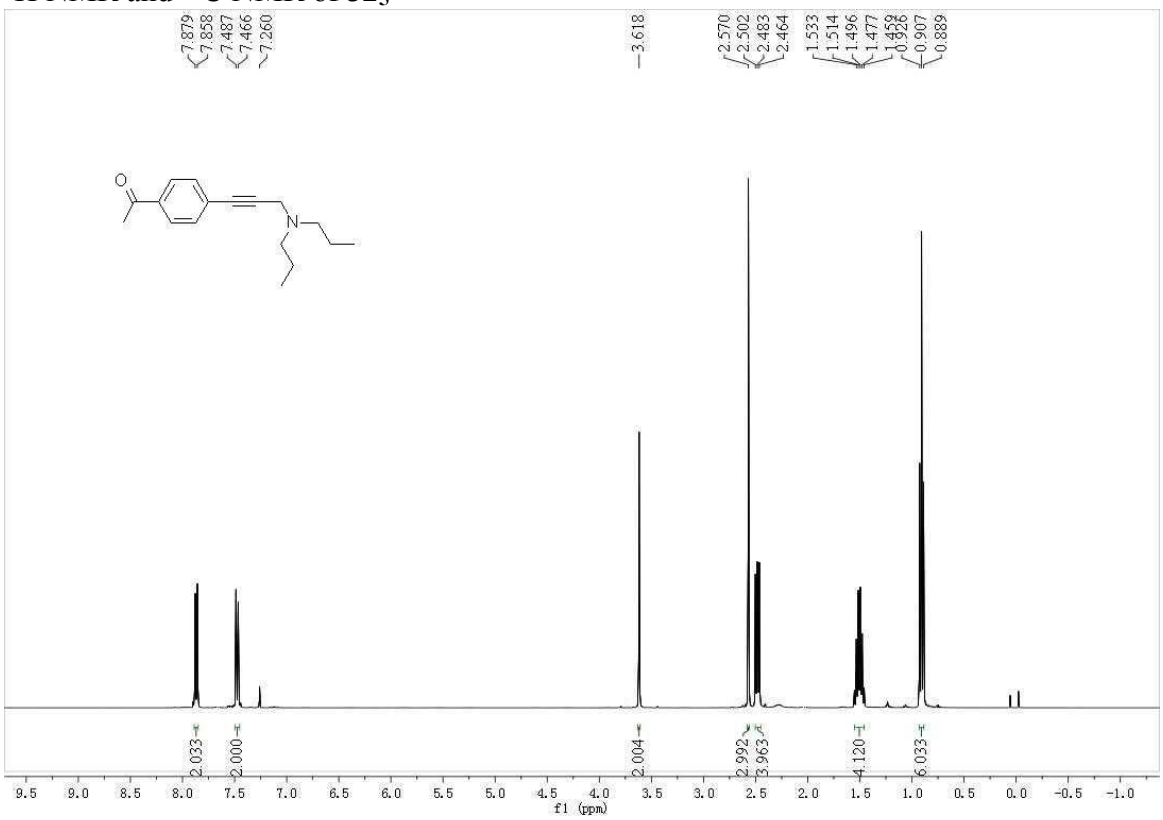
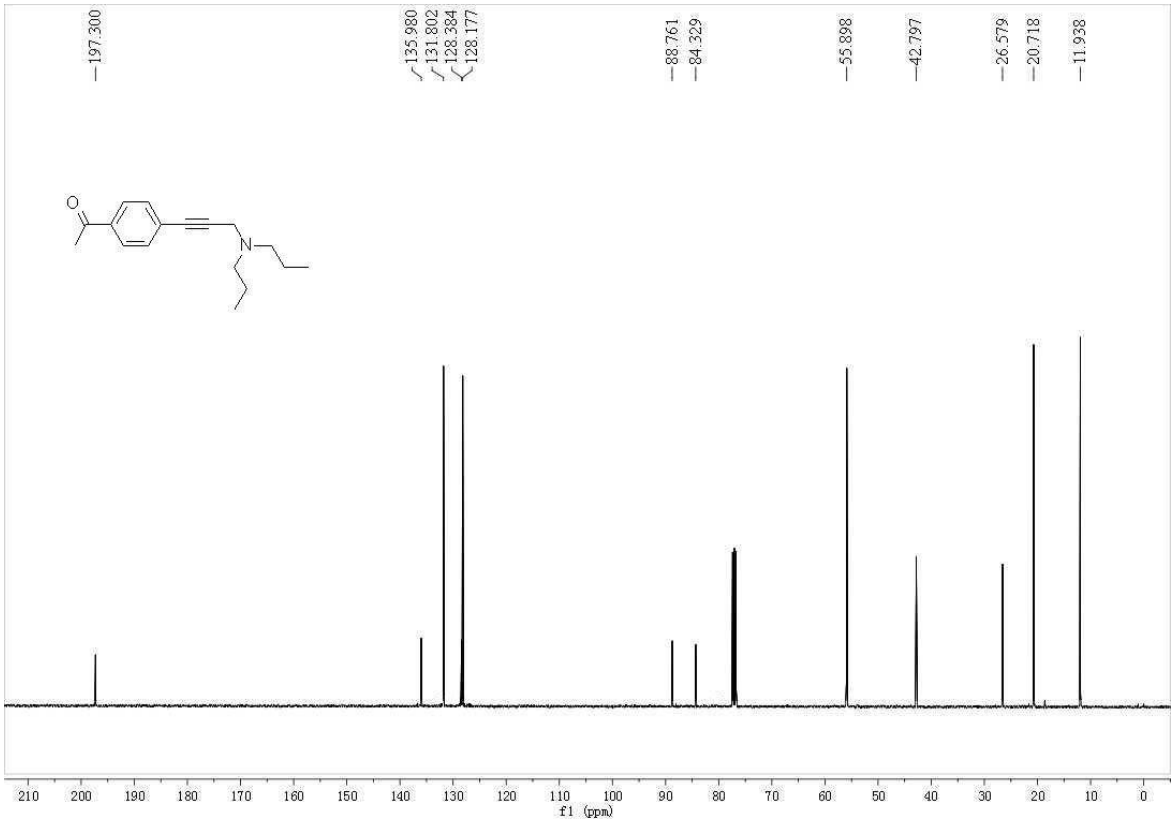
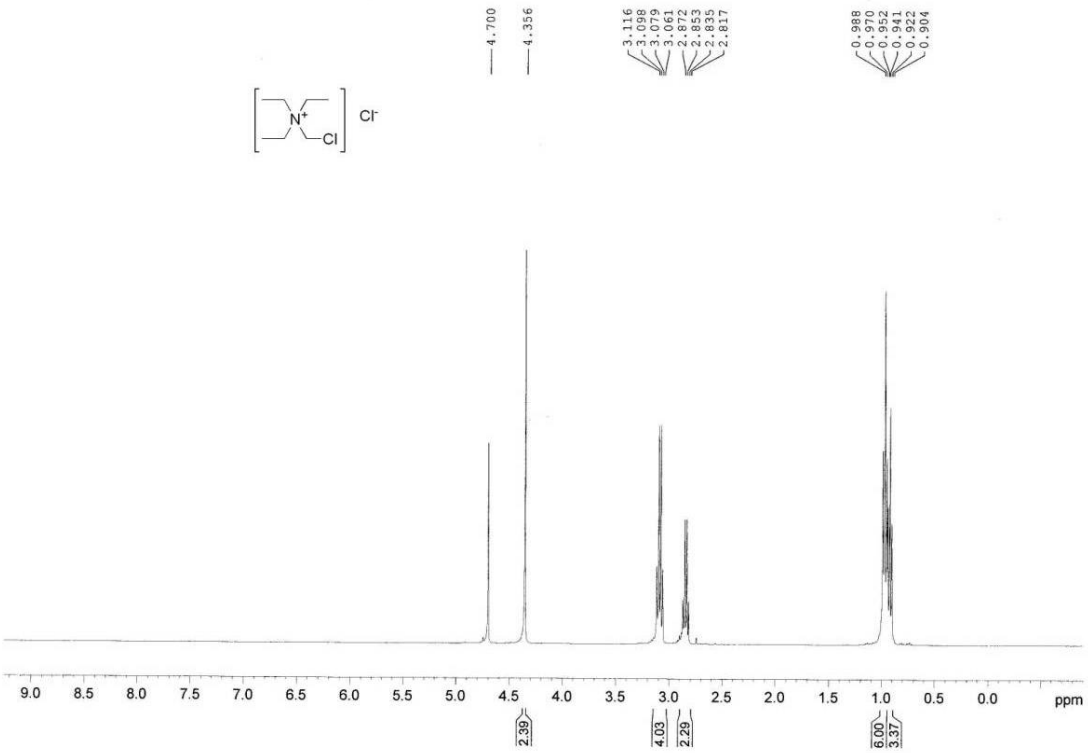
^{1}H NMR and ^{13}C NMR of **3z$_5$**





^{1}H NMR of **4a**


4.700
4.356
3.116
3.098
3.079
3.061
2.872
2.853
2.835
2.817
0.988
0.970
0.952
0.941
0.922
0.904
N+
Cl
Cl-
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.39
4.03
2.29
6.00
3.37

^{1}H NMR and ^{13}C NMR of **3a-*d***