Supporting Information

Copper catalyzed decarboxylative alkynylation of quaternary α-cyano acetate salts

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Part 1. General Information

a. Materials

All the reactions were carried out in oven-dried Schlenk tubes under argon atmosphere. The solvent was bought from commercial suppliers and used without further purification. All alkynyl bromides were synthesized by alkyne or aldehyde. All of the alkynyl chlorides were synthesized by alkyne. Potassium cyanoacetate derivatives were synthesized by saponification of the corresponding ethyl ester according to the literature methods.[1] The ethyl cyanoacetate derivatives were synthesized by treating ethyl cyanoacetate with corresponding alkyl bromides according to the literature methods. [2]

b. Methods

^{1}H-NMR, ^{13}C-NMR spectra were recorded on a Bruker Avance 300 and 600 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System.

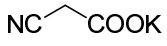
Part 2. Experimental Section

a.Synthesis of potassium cyanoacetate and derivatives

Synthesis of potassium cyanoacetate

According to the literature procedure,[3] to a stirred mixture 2-cyanoacetic acid (1.70 g, 20.0 mmol) in ethanol (20 mL) at room temperature, was added a solution of potassium tert-butoxide (2.24 g, 20 mmol) in ethanol (20 mL) over 30 min. After completion of addition, the reaction mixture was stirred for another 1 hour at room temperature. After removing about 4/5 of the ethanol, 50 mL diethyl ether was added. The resulting solid was collected by filtration, washed sequentially with ethanol (5 mL x 2) and diethyl ether (10 mL x 2), dried under vacuum at 30 °C for 2 h to provide potassium cyanoacetate in 95 % yields.

Potassium 2-cyanoacetate (s1)



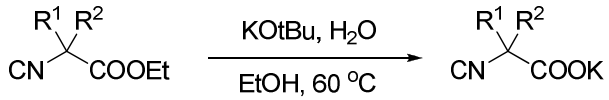
S1

According to the general procedure, compound **s1** was prepared from 2-cyanoacetic acid (20 mmol) yielding **s1** as a white solid (2.34 g, 95 %).

^{1}H NMR (300 MHz, D_2O) δ 3.35 (s, 2H H-D exchange in D_2O).

^{13}C NMR (75 MHz, D_2O) δ 172.61, 120.44, 30.01.

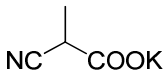
Synthesis of potassium cyanoacetate derivatives



According to the literature procedure,[1] general procedures for the synthesis of potassium cyanoacetate derivatives from ethyl cyanoacetate derivatives (Take potassium 2-cyanopropanoate for example):

To a stirred mixture of ethyl 2-cyanopropanoate (20.0 mmol)and water (21 mmol) in ethanol (40 mL) at 60 °C, was added a solution of potassium tert-butoxide (2.24 g, 20.0 mmol) in ethanol (20 mL) over 30 min. After completion of addition, the reaction mixture was stirred in 60 °C until consumption of the starting material (monitored by GC analysis). After removing of the ethanol, 20 mL diethyl ether was added. The resulting solid was collected by filtration, washed sequentially with 1:1 mixture of diethyl ether and ethanol (5 mL x 2) and diethyl ether (10 mL x 2), dried under vacuum at 30 °C for 2 h to provide Potassium 2-cyanopropanoate in 93 % yields.

Potassium 2-cyanopropanoate (s2)



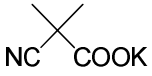
s2

According to the general procedure, compound **s2** was prepared from ethyl 2-cyanopropanoate (20 mmol) yielding **s2** as a white crystal (2.50 g, 93 %).

^{1}H-NMR (300 MHz, D_2O) δ 3.52 (q, 1H, H-D exchange in D_2O), 1.43 (s, 3H).

^{13}C NMR (75 MHz, D_2O) δ 176.53, 124.29, 36.74, 18.05.

Potassium 2-cyano-2-methylpropanoate (s3)



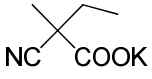
s3

According to the general procedure, compound **s3** was prepared from ethyl 2-cyano-2-methylpropanoate (20 mmol) yielding **s3** as a white solid (2.78 g, 92 %).

^{1}H NMR (300 MHz, D_2O) δ 1.42 (s, 6H).

^{13}C NMR (75 MHz, D_2O) δ 179.39, 127.54, 44.28, 27.02.

Potassium 2-cyano-2-methylbutanoate (s4)



s4

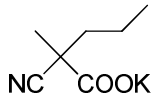
According to the general procedure, compound **s4** was prepared from ethyl 2-cyano-2-methylbutanoate (20 mmol) yielding **s4** as a white solid (2.91g, 88 %).

^{1}H NMR (600 MHz, D_2O) δ 1.84 – 1.62 (m, 2H), 1.44 (s, 3H), 0.96 (t, J = 7.3 Hz,

3H).

^{13}C NMR (151 MHz, D_2O) δ 176.12, 124.20, 48.24, 31.27, 22.97, 9.55.

Potassium 2-cyano-2-methylpentanoate (s5)



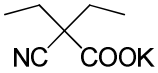
s5

According to the general procedure, compound **s5** was prepared from ethyl 2-cyano-2-methylpentanoate (10 mmol) yielding **s5** as a white solid (1.43 g, 80 %).

^{1}H NMR (600 MHz, D_2O) δ 1.70 – 1.53 (m, 2H), 1.44 – 1.32 (m, 4H), 1.25 – 1.14 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, D_2O) δ 176.24, 124.43, 47.40, 39.97, 23.43, 18.95, 13.19.

Potassium 2-cyano-2-ethylbutanoate (s6)



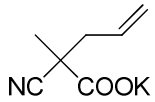
s6

According to the general procedure, compound **s6** was prepared from ethyl 2-cyano-2-ethylbutanoate (10 mmol) yielding **s6** as a white solid (1.61 g, 90 %).

^{1}H NMR (600 MHz, D_2O) δ 1.73 – 1.60 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (151 MHz, D_2O) δ 175.29, 123.57, 55.46, 30.34, 9.57.

Potassium 2-cyano-2-methylpent-4-enoate (s7)



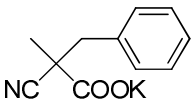
s7

According to the general procedure, compound **s7** was prepared from ethyl 2-cyano-2-methylpent-4-enoate (10 mmol) yielding s7 as a white solid (1.52 g, 86 %).

^{1}H NMR (600 MHz, D_2O) δ 5.73 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.22 – 5.00 (m, 2H), 2.45 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.33 (dd, *J* = 13.9, 7.5 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (151 MHz, D_2O) δ 175.32, 132.46, 123.84, 119.44 47.35, 41.77, 22.75.

Potassium 2-cyano-2-methyl-3-phenylpropanoate (s8)



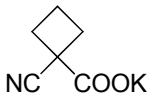
s8

According to the general procedure, compound **s8** was prepared from ethyl 2-cyano-2-methyl-3-phenylpropanoate (10 mmol) yielding **s8** as a white solid (1.95 g, 86 %).

^{1}H NMR (600 MHz, D_2O) δ 7.54 – 7.02 (m, 5H), 3.07 (d, *J* = 13.6 Hz, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 3H).

^{13}C NMR (151 MHz, D_2O) δ 175.13, 136.29, 129.82, 128.47, 127.41, 123.66, 49.07, 43.01, 23.18.

Potassium 1-cyanocyclobutanecarboxylate (s9)



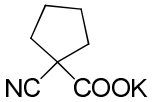
s9

According to the general procedure, compound **s9** was prepared from ethyl 1-cyanocyclobutanecarboxylate (10 mmol) yielding **s9** as white solid (1.47 g, 85 %).

^{1}H NMR (600 MHz, D_2O) δ 2.55 – 2.41 (m, 4H), 2.16 – 2.07 (m, 1H), 2.06 – 1.91 (m, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.50, 124.30, 42.36, 31.08, 16.67.

Potassium 1-cyanocyclopentanecarboxylate (s10)



s10

According to the general procedure, compound **s10** was prepared from ethyl 1-cyanocyclopentanecarboxylate (10 mmol) yielding **s10** as white solid (1.59 g, 90 %).

^{1}H NMR (600 MHz, D_2O) δ 2.17 – 2.01 (m, 4H), 1.82 – 1.63 (m, 4H).

^{13}C NMR (151 MHz, D_2O) δ 176.45, 125.28, 50.92, 37.50, 24.86.

Potassium 1-cyanocyclohexanecarboxylate (s11)

s11

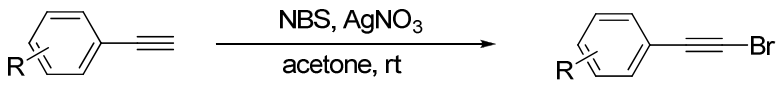
According to the general procedure, compound **s11** was prepared from ethyl 1-cyanocyclohexanecarboxylate (10 mmol) yielding **s11** as a white solid (1.71 g, 89%).

^{1}H NMR (600 MHz, D_2O) δ 2.08 – 1.82 (m, 2H), 1.79 – 1.55 (m, 5H), 1.53 – 1.30 (m, 2H), 1.24 – 1.06 (m, 1H).

^{13}C NMR (151 MHz, D_2O) δ 176.38, 123.50, 49.18, 32.94, 24.42, 22.51.

b.Synthesis of alkynyl bromides

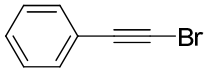
General procedure for preparation of alkynyl bromides from alkyne:



To the mixture of terminal alkyne (10 mmol), NBS (12 mmol) and 30 mL acetone,

$AgNO_3$ (10 mol %) was added and the mixture was stirred at room temperature for five hours. After completion of the reaction, the mixture was filtered. And the filtrate was added 30mL of water, extracted with diethyl ether (30 mL x 3), The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give alkynyl bromides.

(bromoethynyl)benzene (t1)



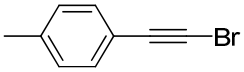
t1

According to the general procedure, compound **t1** was prepared from phenylacetylene (10 mmol) yielding **t1** as a light yellow oil (1.56g, 86 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 2H), 7.35 – 7.25 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 132.02, 128.69, 128.35, 122.74, 80.09, 49.73.

1-(bromoethynyl)-4-methylbenzene (t2)



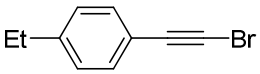
t2

According to the general procedure, compound **t2** was prepared from 4-Ethynyltoluene (10 mmol) yielding **t2** as a light yellow oil (1.62 g, 83 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.88 , 131.89, 129.10, 119.67, 80.19, 48.75, 21.51.

1-(bromoethynyl)-4-ethylbenzene (t3)



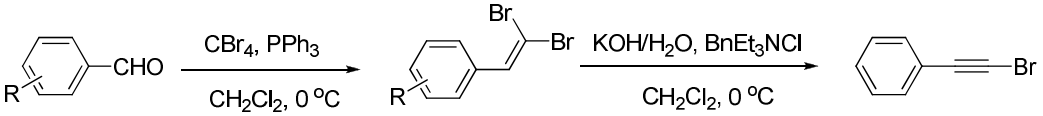
t3

According to the general procedure, compound **t3** was prepared from 4-Ethylphenylacetylene (10 mmol) yielding **t3** as a light yellow oil (1.69 g, 80 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.16, 131.99, 127.90, 119.90, 80.22, 48.73, 28.84, 15.26.

General procedure for preparation of Alkynyl bromides from aldehyde:[4]

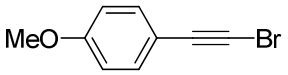


The mixture of aldehyde (10 mmol), carbon tetrabromide (20 mmol) and dichloromethane (25 mL) at 0 °C under nitrogen atmosphere was added triphenyl phosphine (40 mmol) in portions over 15 minutes. And the solution was stirred at

0 °C for 1 h. Reaction mixture was quenched with petroleum ether (100 mL), and filtered through a short silica gel column to remove the majority of the triphenylphosphine oxide. The filtrate was concentrated and purified by column chromatography to afford dibromoalkene.

To a solution of the dibromoalkene (5 mmol) and benzyltriethylammonium chloride (4.4 mmol) in CH_2Cl_2 (25 mL) rapidly stirred at 0 °C was added a solution of KOH (12.9 g) in H_2O (10 mL). The solution was stirred at 0 °C until consumption of the starting material (monitored by GC analysis), and then was extracted with CH_2Cl. The organic phase was washed with brine , dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give alkynyl bromides.

1-(bromoethynyl)-4-methoxybenzene (t4)



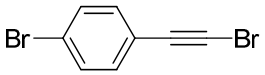
t4

According to the general procedure, compound **t4** was prepared from 4-methoxybenzaldehyde (10 mmol) yielding **t4** as a light yellow solid (1.69 g, 80 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz,2H), 3.80 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.90, 133.44, 114.82, 113.97, 79.95, 55.29, 47.81.

1-(bromoethynyl) -4-bromobenzene (t5)



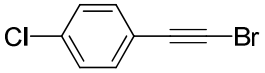
t5

According to the general procedure, compound **t5** was prepared from 4-bromobenzaldehyde (10 mmol) yielding **t5** as a pale solid (1.82 g, 70 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.41, 131.63, 123.02, 121.66, 79.06, 51.20.

1-(bromoethynyl)-4-chlorobenzene (t6)



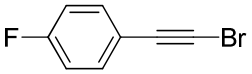
t6

According to the general procedure, compound **t6** was prepared from 4-chlorobenzaldehyde (10 mmol) yielding **t6** as a pale solid (1.72 g, 80 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 134.81, 133.21, 128.71, 121.19, 78.99, 50.99.

1-(bromoethynyl)-4-fluorobenzene (t7)



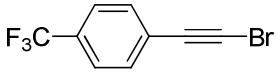
t7

According to the general procedure, compound **t7** was prepared from 4-fluorobenzaldehyde (10 mmol) yielding **t7** as a light yellow solid (1.42 g, 86 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.33 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.71 (d, *J* = 250.1 Hz), 133.93 (d, *J* = 8.5 Hz), 118.80 (d, *J* = 3.6 Hz), 115.66 (d, *J* = 22.2 Hz), 79.02, 49.51.

1-(bromoethynyl)-4-(trifluoromethyl)benzene (t8)



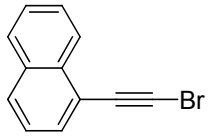
t8

According to the general procedure, compound **t8** was prepared from 4-(trifluoromethyl)benzaldehyde (10 mmol) yielding **t8** as a white solid (1.87 g, 75 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.39 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 132.28, 130.45 (q, *J* = 34.1 Hz), 126.47, 125.29 (q, *J* = 3.8 Hz), 123.78 (q, *J* = 322.8, 50.4 Hz), 78.82, 52.96.

1-(bromoethynyl)naphthalene (t9)



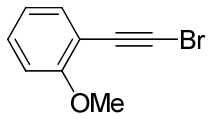
t9

According to the general procedure, compound **t9** was prepared from 1-naphthaldehyde (10 mmol) yielding **t9** as a brown oil (1.64 g, 71 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.66 – 7.48 (m, 2H), 7.47 – 7.37 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.69, 133.16, 131.16, 129.20, 128.37, 127.03, 126.57, 125.98, 125.14, 120.40, 78.52, 54.09.

1-(bromoethynyl)-2-methoxybenzene (t10)



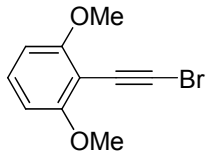
t10

According to the general procedure, compound **t10** was prepared from 2-methoxybenzaldehyde (10 mmol) yielding **t10** as a light yellow solid (1.65 g, 78 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.02 – 6.64 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.62, 134.00, 130.10, 120.40, 111.79 110.61, 76.45, 55.76, 53.04.

2-(bromoethynyl)-1,3-dimethoxybenzene (t11)



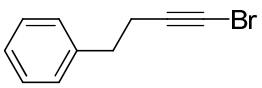
t11

According to the general procedure, compound **t11** was prepared from 2,6-dimethoxybenzaldehyde (10 mmol) yielding **t11** as a light yellow solid (1.76 g, 73 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.17, 130.05, 103.31, 100.79, 72.58, 56.57, 56.07 .

(4-bromobut-3-ynyl)benzene (t12)



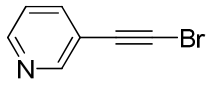
t12

According to the general procedure, compound **t12** was prepared from 3-Phenylpropionaldehyde (10 mmol) yielding **t12** as a white solid (1.25 g, 60 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.21 (m, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.28, 128.45, 128.40, 126.41, 79.63, 38.70, 34.71, 21.87.

3-(bromoethynyl)pyridine (t13)



t13

To mixture of 3-pyridinecarboxaldehyde (10 mmol), carbon tetrabromide (20 mmol) and dichloromethane (25 mL) at 0 °C under nitrogen atmosphere was added triphenyl phosphine (40 mmol) in portions over 15 minutes. And the solution was stirred at 0 °C for 1 h. Reaction mixture was quenched with petroleum ether (100 mL), and filtered through a short silica gel column to remove the majority of the triphenylphosphine oxide. The filtrate was concentrated and purified by column chromatography to afford 3-(2,2-dibromovinyl)pyridine (1.18g, 45%).

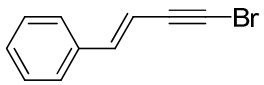
A mixture of 3-(2,2-dibromovinyl)pyridine (1.18 g, 4.5 mmol), potassium tertbutoxide (1.51 g, 13.5 mmol) and toluene (15 mL) were heated at 80 °C for 4 h. After completion of reaction, the reaction mixture was cooled to room temperature, diluted with water (15 mL), and extracted with EtOAc (3 x 30 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduce pressure to obtain

3-(2-bromoethynyl)pyridine**(t13)** as a white solid (0.76g, 95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.56 (d, *J* = 4.2 Hz, 1H), 7.74 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.32 – 7.18 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.62, 148.90, 138.94, 123.01, 119.93, 76.86, 53.79.

(4-bromobut-1-en-3-ynyl)benzene (t14)[5]



t14

To mixture of cinnamaldehyde (10 mmol), carbon tetrabromide (20 mmol) and dichloromethane (25 mL) at 0 °C under nitrogen atmosphere was added triphenyl phosphine (40 mmol) in portions over 15 minutes. And the solution was stirred at 0□ for 1 h. Reaction mixture was quenched with petroleum ether (100 mL), and filtered through a short silica gel column to remove the majority of the triphenylphosphine oxide. The filtrate was concentrated and purified by column chromatography to afford (4,4-dibromobuta-1,3-dienyl)benzene (2.4g, 83%).

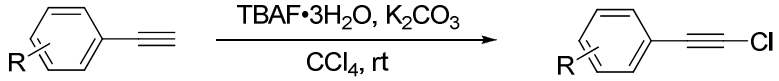
A mixture of (4,4-dibromobuta-1,3-dienyl)benzene (1.15 g, 4 mmol), TBAF·3H_2O (6.3 g, 20 mmol) and DMF (20 mL) were heated at 60 °C for 2 h. After completion of reaction, the mixture was cooled to room temperature and diluted with diethylether (50 mL). The organic phase was washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give (4-bromobut-1-en-3-ynyl)benzene **(t14)** as a yellow oil(0.74g, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.32 (m, 3H), 7.01 (d, *J* = 16.3 Hz, 1H), 6.12 (d, *J* = 16.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.94 , 135.76 , 128.94 , 128.76 , 126.30 , 107.52 , 79.44 , 51.32 .

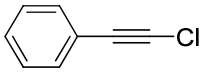
c. Synthesis of alkynyl chlorides

General procedure for preparation of alkynyl chlorides from alkyne:[6]



To the mixture of terminal alkyne (10 mmol), TBAF·3H_2O (1 mmol) and K_2CO_3 (10 mmol), CCl_4 (6 mL) was added and the mixture was stirred at room temperature for two hours. After completion of the reaction, the solution concentrated under reduced pressure. The residue was purified by column chromatography to give alkynyl chlorides.

(chloroethynyl)benzene (t15)



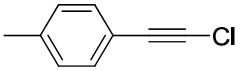
t15

According to the general procedure, compound **t15** was prepared from Phenylacetylene (10 mmol) yielding **t15** as a colorless oil (0.91 g, 66 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.38 – 7.27 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 131.96, 128.60, 128.37, 122.10, 69.35, 68.02.

1-(chloroethynyl)-4-methylbenzene (t16)



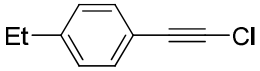
t16

According to the general procedure, compound **t16** was prepared from 4-Ethynyltoluene (10 mmol) yielding **t16** as a colorless oil (0.84 g, 56 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.76, 131.86, 129.12, 119.09, 69.52, 67.17, 21.47.

1-(chloroethynyl)-4-ethylbenzene (t17)



t17

According to the general procedure, compound **t17** was prepared from 4-Ethylphenylacetylene (10 mmol) yielding **t17** as a colorless oil (0.81 g, 49 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).

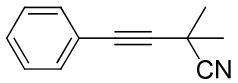
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.04, 131.95, 127.92, 119.32, 69.54, 67.14, 28.81, 15.26.

d.General procedures for the alkynylation decarboxylative of quaternary α-cyanoacetate derivatives.

A 20 mL over-dried Schlenk tube was charged with CuBr (10 % mol, 7.3 mg), 8-hydroxyquinoline (20 mol%, 14.5 mg), Ag_2CO_3 (20 mol%, 27.5 mg), α-cyano acetate derivatives (0.50 mmol) and the corresponding alkyne halides (0.50 mmol) (if solid). The tube was evacuated and filled with argon (this procedure was repeated for three times). Then corresponding alkyne halides (0.50 mmol) (if liquid) and DMAc (1.5 mL) were added with a syringe under a counter flow of argon. The tube was sealed, stirred at room temperature for 15 min (if the mixture was agglomerated，the tube was stirred at 50°C for 15 min). Then the tube stirred in a preheated oil bath (130 °C) for 16 h. Upon completion of the reaction, the mixture was cooled to room temperature. The mixture was diluted with diethyl ether (20 mL), filtered. And the

filtrate was added 20 mL of water, extracted with diethyl ether (20 mL x 2), The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and the product was dried under high vacuum for at least 0.5 h.

1.Compound name: 2,2-dimethyl-4-phenylbut-3-ynenitrile (2a)



2a

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (68.5 mg, 81% yield).

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with (chloroethynyl)benzene (1.5 mmol, 204.9 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (60.1 mg, 71% yield).

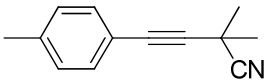
This compound is known.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.36 – 7.29 (m, 3H), 1.74 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 130.76, 127.81, 127.32, 120.78, 120.47, 86.02, 81.66, 27.86, 25.91.

HRMS calcd for $C_{12}H_{11}N$ (M+) 169.0891; found: 169.0896.

2.Compound name: 2,2-dimethyl-4-(p-tolyl)but-3-ynenitrile (2b)



2b

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-4-methylbenzene (1.5 mmol, 292.5 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (72.4 mg, 79% yield).

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(chloroethynyl)-4-methylbenzene (1.5 mmol, 225.9 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (66.9 mg, 73% yield).

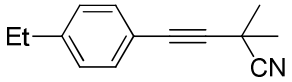
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H), 1.73 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.00, 131.66, 129.09, 121.61, 118.73, 86.35, 82.80, 28.93, 26.94, 21.47.

HRMS calcd for $C_{13}H_{13}N$ (M+) 183.1048; found: 183.1051.

3.Compound name: 4-(4-ethylphenyl)-2,2-dimethylbut-3-ynenitrile (2c)



2c

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-4-ethylbenzene (1.5 mmol, 313.5 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (79.9 mg, 81% yield).

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6 mg) was allowed to react with 1-(chloroethynyl)-4-ethylbenzene (1.5 mmol, 246.9 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (69.2 mg, 70% yield).

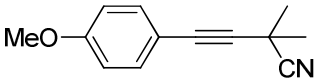
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.73 (s, 6H), 1.22 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.29, 130.74, 126.88, 120.59, 117.95, 85.35, 81.82, 27.93, 27.79, 25.93, 14.27.

HRMS calcd for $C_{14}H_{15}N$ (M+) 197.1204; found: 197.1206.

4.Compound name: 4-(4-methoxyphenyl)-2,2-dimethylbut-3-ynenitrile (2d)



2d

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-4-methoxybenzene (1.5 mmol, 316.5 mg) under 130 ℃ for 16 h. The product was isolated as a light yellow solid (81.7mg, 82% yield).

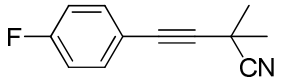
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 3.81 (s, 3H), 1.73 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.00, 134.03, 133.24, 121.69, 113.98, 85.71, 82.60, 55.29, 28.97, 26.95.

HRMS calcd for $C_{13}H_{13}NO$ (M+) 199.0997; found: 199.0994.

5.Compound name: 4-(4-fluorophenyl)-2,2-dimethylbut-3-ynenitrile (2e)



2e

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-4-fluorobenzene (1.5 mmol, 298.5 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (51.5 mg, 55% yield).

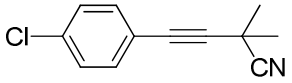
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.33 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 1.73 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.81 (d, *J* = 250.3 Hz), 133.74 (d, *J* = 8.5 Hz), 121.39, 117.85, 115.67 (d, *J* = 22.2 Hz), 86.81, 81.65, 28.82, 26.89.

HRMS calcd for $C_{12}H_{10}FN$ (M+) 187.0797; found: 187.0795.

6.Compound name: 4-(4-chlorophenyl)-2,2-dimethylbut-3-ynenitrile (2f)



2f

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-4-chlorobenzene (1.5 mmol, 323.3 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (50.9 mg, 50% yield).

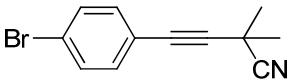
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 1.74 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.97, 132.00, 127.70, 120.26, 119.25, 86.99, 80.59, 27.76, 25.91.

HRMS calcd for $C_{12}H_{10}ClN$ (M+) 203.0502; found: 203.0504.

7.Compound name: 4-(4-bromophenyl)-2,2-dimethylbut-3-ynenitrile (2g)



2g

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl) -4-bromobenzene (1.5 mmol, 390 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (75.6 mg, 61% yield).

This compound is new.

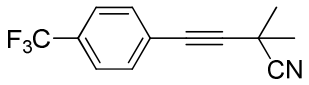
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 1.73

(s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.21, 131.65 , 123.22, 121.24, 120.73, 88.16, 81.68, 28.76, 26.95.

HRMS calcd for $C_{12}H_{10}BrN$ (M+) 246.9997; found: 246.9998.

8.Compound name: 2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)but-3-ynenitrile (2h)



2h

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-4-(trifluoromethyl) -benzene (1.5 mmol, 373.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (47.4 mg, 40% yield).

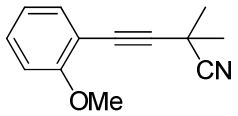
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.4 Hz, 4H), 1.76 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 131.07, 129.65 (q, *J* = 32.8 Hz), 124.58, 124.29 (q, *J* = 3.8 Hz), 120.97, 120.07, 88.40, 80.35, 27.67, 25.93.

HRMS calcd for $C_{13}H_{10}F_3N$ (M+) 237.0765; found: 237.0768.

9.Compound name: 4-(2-methoxyphenyl)-2,2-dimethylbut-3-ynenitrile (2i)



2i

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)-2-methoxybenzene (1.5 mmol, 316.5 mg) under 130 °C for 16 h. The product was isolated as a yellow solid (80.7 mg, 81% yield).

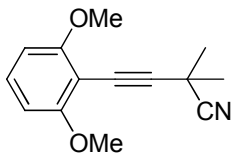
This compound is new.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 1H), 7.33 – 7.26 (m, 1H), 6.96 – 6.74 (m, 2H), 3.86 (s, 3H), 1.75 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.19, 133.72, 130.28, 121.63, 120.35, 110.93, 110.67, 90.86, 79.05, 55.74, 29.70, 28.95.

HRMS calcd for $C_{13}H_{13}NO$ (M+) 199.0997; found: 199.0994.

10.Compound name: 4-(2,6-dimethoxyphenyl)-2,2-dimethylbut-3-ynenitrile (2j)



2j

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 2-(bromoethynyl)-1,3-dimethoxybenzene (1.5 mmol, 361.5 mg) under 130 °C for 16 h. The product was isolated as light yellow solid (94 mg, 82% yield).

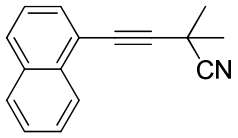
This compound is new.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 6H), 1.78 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.67, 130.23, 121.81, 103.94, 103.39, 95.17, 75.25, 56.04, 29.10, 27.42.

HRMS calcd for $C_{14}H_{15}NO_2$ (M+) 229.1103; found: 229.1101.

11.Compound name: 2,2-dimethyl-4-(naphthalen-1-yl)but-3-ynenitrile (2k)



2k

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 1-(bromoethynyl)naphthalene (1.5 mmol, 346.5 mg) under 130 °C for 16 h. The product was isolated as light yellow solid (86.6 mg, 79% yield).

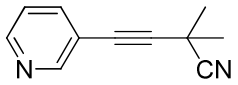
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.62 – 7.47 (m, 2H), 7.46 – 7.35 (m, 1H), 1.84 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.26, 133.14, 130.87, 129.42, 128.41, 127.09, 126.57, 125.74, 125.12, 121.54, 119.32, 91.90, 81.00, 29.08, 27.28.

HRMS calcd for $C_{16}H_{13}N$ (M+) 219.1048; found: 219.1047.

12.Compound name: 2,2-dimethyl-4-(pyridin-3-yl)but-3-ynenitrile (2l)



2l

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with 3-(bromoethynyl)pyridine (1.5 mmol, 273 mg) under 130 °C for 16 h. The product was isolated as light yellow oil (42.6 mg, 50% yield).

This compound is new.

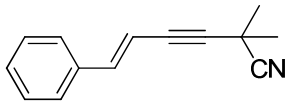
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.57 (d, *J* = 4.1 Hz, 1H), 7.74 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.37 – 7.11 (m, 1H), 1.77 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.31, 149.15, 138.81, 123.05, 121.06, 118.95, 90.37,

79.45, 28.67, 26.94.

HRMS calcd for $C_{11}H_{10}N_2$ (M+) 170.0844; found: 170.0848.

13.Compound name: (*E*)-2,2-dimethyl-6-phenylhex-5-en-3-ynenitrile (2m)



2m

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with (4-bromobut-1-en-3-ynyl)benzene (1.5 mmol, 310.5 mg) under 130 °C for 16 h. The product was isolated as yellow oil (63.4 mg, 65% yield).

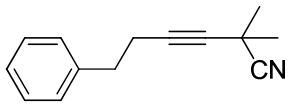
This compound is new.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.35 – 7.28 (m, 3H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.11 (d, *J* = 16.3 Hz, 1H), 1.70 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.67, 135.78, 128.94, 128.75, 126.33, 121.44, 106.65, 88.92, 81.86, 28.83, 27.05.

HRMS calcd for $C_{14}H_{13}N$ (M+) 195.1048; found: 195.1042.

14.Compound name: 2,2-dimethyl-6-phenylhex-3-ynenitrile (2n)



2n

According to the general procedure, potassium 2-cyano-2-methylpropanoate (0.5 mmol, 75.6mg) was allowed to react with (4-bromobut-3-ynyl)benzene (1.5 mmol, 313.5 mg) under 130 °C for 16 h. The product was isolated as yellow oil (34.5 mg, 35% yield).

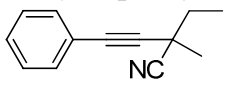
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.02 (m, 5H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.57 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.29, 127.49, 127.35, 125.37, 120.89, 81.57, 78.33, 33.73, 27.97, 25.34, 19.74.

HRMS calcd for $C_{14}H_{15}N$ (M+) 197.1204; found: 197.1201.

15.Compound name: 2-ethyl-2-methyl-4-phenylbut-3-ynenitrile (3a)



3a

According to the general procedure, potassium 2-cyano-2-methylbutanoate (0.5 mmol, 82.6 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (68.7 mg, 75% yield).

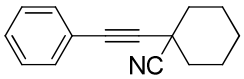
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 2.02 – 1.79 (m, 2H), 1.71 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 131.81, 128.79, 128.34, 121.92, 120.75, 86.05, 83.65, 34.78, 32.85, 26.90, 9.99.

HRMS calcd for $C_{13}H_{13}N$ (M+) 183.1048; found: 183.1049.

16.Compound name: 1-(phenylethynyl)cyclohexanecarbonitrile (3b)



3b

According to the general procedure, potassium 1-cyanocyclohexanecarboxylate (0.5 mmol, 95.8 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (74.3 mg, 71% yield).

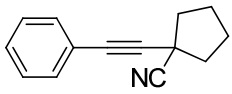
This compound is new.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.35 – 7.30 (m, 3H), 2.16 – 2.07 (m, 2H), 2.02 – 1.92 (m, 2H), 1.82 – 1.74 (m, 2H), 1.72 – 1.64 (m, 2H), 1.57 – 1.51 (m, 1H), 1.50 – 1.41 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 130.79, 127.72, 127.31, 121.02, 119.55, 85.12, 82.82, 35.95, 31.83, 23.69, 21.13.

HRMS calcd for $C_{15}H_{15}N$ (M+) 209.1204; found: 209.1201.

17.Compound name: 1-(phenylethynyl)cyclopentanecarbonitrile (3c)



3c

According to the general procedure, potassium 1-cyanocyclopentanecarboxylate (0.5 mmol, 88.6 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 ℃ for 16 h. The product was isolated as a brown oil (59.5 mg, 61% yield).

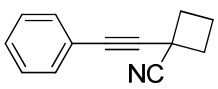
This compound is known.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 2.49 – 2.29 (m, 2H), 2.31 – 2.14 (m, 2H), 1.99 – 1.82 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 131.75, 128.71, 128.33, 122.04, 121.25, 86.23, 83.12, 41.10, 35.46, 23.94.

HRMS calcd for $C_{14}H_{13}N$ (M+) 195.1804; found: 195.1808.

18.Compound name: 1-(phenylethynyl)cyclobutanecarbonitrile (3d)



3d

According to the general procedure, potassium 1-cyanocyclobutanecarboxylate (0.5 mmol, 81.6 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (51.6 mg, 57% yield).

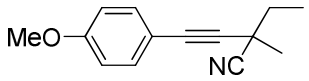
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.35 – 7.30 (m, 3H), 2.87 – 2.73 (m, 2H), 2.73 – 2.59 (m, 2H), 2.40 – 2.13 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 130.75, 127.81, 127.35, 120.94, 119.89, 84.87, 83.19, 34.95, 27.12, 16.67.

HRMS calcd for $C_{13}H_{11}N$ (M+) 181.0891; found: 181.1889.

19.Compound name: 2-ethyl-4-(4-methoxyphenyl)-2-methylbut-3-ynenitrile (3e)



3e

According to the general procedure, potassium 2-cyano-2-methylbutanoate (0.5 mmol, 82.6 mg) was allowed to react with 1-(bromoethynyl)-4-methoxybenzene (1.5 mmol, 316.5 mg) under 130 °C for 16 h. The product was isolated as a yellow solid (81.1 mg, 76% yield).

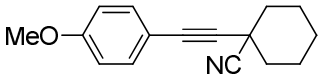
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 2.00 – 1.79 (m, 2H), 1.69 (s, 3H), 1.23 (t, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.98, 133.26, 120.94, 113.98, 113.28, 84.67, 83.57, 55.30, 34.82, 32.86, 26.97, 10.00.

HRMS calcd for $C_{14}H_{15}NO$ (M+) 213.1154; found: 213.1155.

20.Compound name: 1-((4-methoxyphenyl)ethynyl)cyclohexanecarbonitrile (3f)



3f

According to the general procedure, potassium 1-cyanocyclohexanecarboxylate (0.5 mmol, 95.8 mg) was allowed to react with 1-(bromoethynyl)-4-methoxybenzene (1.5 mmol, 316.5 mg) under 130 °C for 16 h. The product was isolated as a light yellow solid (79 mg, 66% yield).

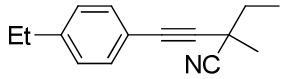
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 2.18 – 2.04 (m, 2H), 2.02 – 1.85 (m, 2H), 1.83 – 1.60 (m, 5H), 1.09 – 0.74 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.93, 133.25, 120.75, 114.10, 113.97, 84.76, 83.73, 55.30, 37.03, 32.86, 24.72, 22.16.

HRMS calcd for $C_{16}H_{17}NO$ (M+) 239.1310; found: 239.1312.

21.Compound name: 2-ethyl-4-(4-ethylphenyl)-2-methylbut-3-ynenitrile (3g)



3g

According to the general procedure, potassium 2-cyano-2-methylbutanoate (0.5 mmol, 82.6 mg) was allowed to react with 1-(bromoethynyl)-4-ethylbenzene (1.5 mmol, 313.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (81.4 mg, 77% yield).

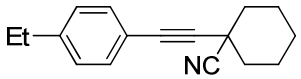
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.99 – 1.81 (m, 2H), 1.70 (s, 3H), 1.23 (td, *J* = 7.5, 3.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.27, 130.77 , 126.88, 119.86, 118.06, 84.32, 82.79, 33.81, 31.85, 27.80, 25.94, 14.30, 8.97.

HRMS calcd for $C_{15}H_{17}N$ (M+) 211.1361; found: 211.1362.

22.Compound name: 1-((4-ethylphenyl)ethynyl)cyclohexanecarbonitrile (3h)



3h

According to the general procedure, potassium 1-cyanocyclohexanecarboxylate (0.5 mmol, 95.8 mg) was allowed to react with 1-(bromoethynyl)-4-ethylbenzene (1.5 mmol, 313.5 mg) under 130 °C for 16 h. The product was isolated as a yellow oil (80.7 mg, 68% yield).

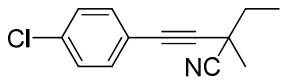
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.24 – 2.03 (m, 2H), 2.04 – 1.87 (m, 2H), 1.85 – 1.59 (m, 4H), 1.59 – 1.40 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.20, 130.77, 126.88, 119.68, 118.17, 84.41, 82.98, 35.99, 31.83, 27.80, 23.70, 21.13, 14.31.

HRMS calcd for $C_{17}H_{19}N$ (M+) 237.1517; found: 237.1514.

23.Compound name: 4-(4-chlorophenyl)-2-ethyl-2-methylbut-3-ynenitrile (3i)



3i

According to the general procedure, potassium 2-cyano-2-methylbutanoate (0.5 mmol, 82.6 mg) was allowed to react with 1-(bromoethynyl)-4-chlorobenzene (1.5 mmol, 323.3 mg) under 130 °C for 16 h. The product was isolated as a brown oil (53.3 mg, 49% yield).

This compound is new.

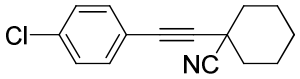
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.07

– 1.82 (m, 2H), 1.71 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.92, 132.02, 127.70, 119.51, 119.35, 86.02, 81.55, 33.67, 31.83, 25.76, 8.97.

HRMS calcd for $C_{13}H_{12}ClN$ (M+) 217.0658; found: 217.0566.

24.Compound name: 1-((4-chlorophenyl)ethynyl)cyclohexanecarbonitrile (3j)



3j

According to the general procedure, potassium 1-cyanocyclohexanecarboxylate (0.5 mmol, 95.8 mg) was allowed to react with 1-(bromoethynyl)-4-chlorobenzene (1.5 mmol, 323.3 mg) under 130 °C for 16 h. The product was isolated as a brown oil (51.1 mg, 42% yield).

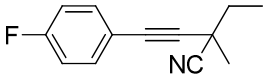
This compound is new.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.19 – 2.05 (m, 2H), 2.01 – 1.89 (m, 2H), 1.81 – 1.73 (m, 2H), 1.72 – 1.65 (m, 2H), 1.59 – 1.52 (m, 1H), 1.49 – 1.41 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.82, 133.01, 128.68, 120.42, 120.36, 87.07, 82.67, 36.81, 32.81, 24.62, 22.11.

HRMS calcd for $C_{15}H_{14}ClN$ (M+) 243.0851; found: 243.0849.

25.Compound name: 2-ethyl-4-(4-fluorophenyl)-2-methylbut-3-ynenitrile (3k)



3k

According to the general procedure, potassium 2-cyano-2-methylbutanoate (0.5 mmol, 82.6 mg) was allowed to react with 1-(bromoethynyl)-4-fluorobenzene (1.5 mmol, 298.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (48.3 mg, 48% yield).

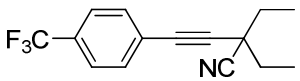
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 2H), 7.02 (t, *J* = 8.5 Hz, 2H), 1.99 – 1.83 (m, 2H), 1.71 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.79 (d, *J* = 250.2 Hz), 133.76 (d, *J* = 8.5 Hz), 120.65, 117.95, 115.66 (d, *J* = 22.2 Hz), 85.79, 82.61, 34.71, 32.81, 26.83, 9.98.

HRMS calcd for $C_{13}H_{12}FN$ (M+) 201.0954; found: 201.0851.

26.Compound name: 2,2-diethyl-4-(4-(trifluoromethyl)phenyl)but-3-ynenitrile (3l)



3l

According to the general procedure, potassium 2-cyano-2-ethylbutanoate (0.5 mmol,

89.6 mg) was allowed to react with 1-(bromoethynyl)-4-(trifluoromethyl)benzene (1.5 mmol, 373.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (46.4 mg, 35% yield).

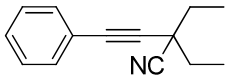
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.5 Hz, 4H), 2.08 – 1.78 (m, 4H), 1.26 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 131.11, 129.60 (q, *J* = 65.5, 32.7 Hz), 124.59, 124.29 (q, *J* = 7.5, 3.7 Hz), 121.62, 120.98, 86.58, 82.26, 38.33, 31.79, 8.90.

HRMS calcd for $C_{15}H_{14}F_3N$ (M+) 265.1078; found: 265.1079.

27.Compound name: 2,2-diethyl-4-phenylbut-3-ynenitrile (3m)



3m

According to the general procedure, potassium 2-cyano-2-ethylbutanoate (0.5 mmol, 89.6 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (66.3 mg, 69% yield).

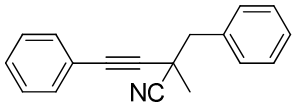
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.38 – 7.29 (m, 3H), 2.16 – 1.68 (m, 4H), 1.25 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 130.79, 127.73, 127.32, 120.99, 118.98, 84.02, 83.59, 38.28, 31.91, 8.91.

HRMS calcd for $C_{14}H_{15}N$ (M+) 197.1204; found: 197.1199.

28.Compound name: 2-benzyl-2-methyl-4-phenylbut-3-ynenitrile (3n)



3n

According to the general procedure, potassium 2-cyano-2-methyl-3-phenylpropanoate (0.5 mmol, 113.7 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 °C for 16 h. The product was isolated as a light brown oil (78.5 mg, 64% yield).

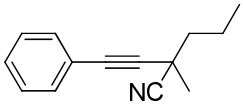
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 10H), 3.17 (s, 2H), 1.74 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 134.50, 131.74, 130.55, 128.92, 128.39, 128.33, 127.86, 121.81, 120.44, 85.92, 84.85, 46.73, 33.26, 26.92.

HRMS calcd for $C_{18}H_{15}N$ (M+) 245.1204; found: 245.1201.

29.Compound name: 2-methyl-2-(phenylethynyl)pentanenitrile (3o)



3o

According to the general procedure, potassium potassium 2-cyano-2-methylpentanoate (0.5 mmol, 89.6 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (67.1 mg, 68% yield).

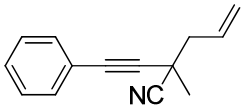
This compound is new.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.36 – 7.29 (m, 3H), 1.96 – 1.58 (m, 7H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 131.80, 128.80, 128.35, 121.93, 120.94, 86.32, 83.55, 43.41, 32.03, 27.40, 19.13, 13.74.

HRMS calcd for $C_{14}H_{15}N$ (M+) 197.1204; found: 197.1209.

30.Compound name: 2-methyl-2-(phenylethynyl)pent-4-enenitrile (3p)



3p

According to the general procedure, potassium 2-cyano-2-methylpent-4-enoate (0.5 mmol, 88.6 mg) was allowed to react with (bromoethynyl)benzene (1.5 mmol, 271.5 mg) under 130 °C for 16 h. The product was isolated as a brown oil (29.3 mg, 30% yield).

This compound is new.

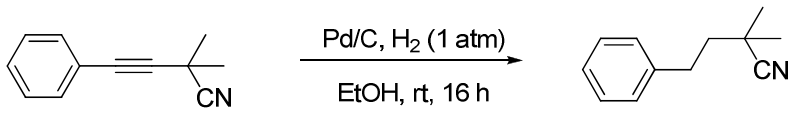
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.39 – 7.28 (m, 3H), 6.16 – 5.73 (m, 1H), 5.48 – 5.10 (m, 2H), 2.63 (d, *J* = 7.2 Hz, 2H), 1.71 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 130.80, 130.19, 127.86, 127.33, 120.76, 119.79, 113.58, 84.74, 83.00, 44.26, 30.71, 25.56.

HRMS calcd for $C_{14}H_{13}N$ (M+) 195.1408; found: 195.1401.

e. Further synthetic transformations of α-cyanoalkynes

General Procedure for selective reduction of α-cyanoalkynes:



2a **I**

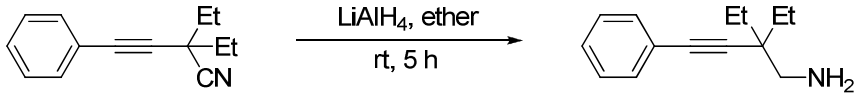
The mixture of 2,2-dimethyl-4-phenylbut-3-ynenitrile (0.4 mmol, 67.7 mg) and Pd/C 10% (40 mg) in EtOH (15 mL) was stirred under H_2 (1 atm) at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography to give 2,2-dimethyl-4-phenylbutanenitrile (52.7 mg, 76% yield) as a light yellow oil.

This compound is known.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 2.85 – 2.73 (m, 2H), 1.87 – 1.75 (m, 2H), 1.41 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.81, 128.58, 128.31, 126.23, 124.85, 43.08, 32.46, 31.80, 26.71.

General Procedure for selective reduction of α-cyanoalkynes:



3m **II**

To an ice-cold suspension of $LiAlH_4$ (62 mg, 1.6 mmol) in Et_2O (3 mL) was added a solution of 2,2-diethyl-4-phenylbut-3-ynenitrile (0.79 mmol, 155 mg) in Et_2O (3 mL). The mixture was stirred for 1 h at 0 °C and for an additional 4.5 h at room temperature. After cooling to 0 °C, a NaOH solution (10 mL, 1 N) was added followed by the addition of water (10 mL). The aqueous layer was extracted with Et_2O (3 x 50 mL), and the combined organic layers was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give 2,2-diethyl-4-phenylbut-3-yn-1-amine (114.5 mg, 72% yield) as light yellow oil.

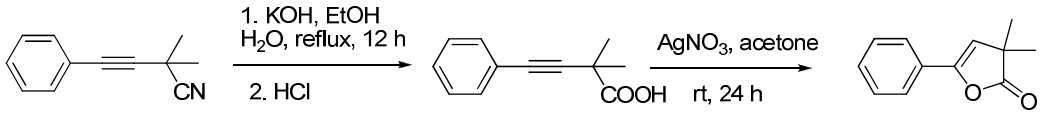
This compound is new.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.30 – 7.22 (m, 3H), 2.70 (s, 2H), 1.95 (s, 2H), 1.64 – 1.36 (m, 4H), 0.97 (t, J = 7.5 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 131.64, 128.17, 127.62, 123.71, 93.72, 83.74, 48.18, 42.45, 28.16, 8.80.

HRMS calcd for $C_{14}H_{19}N$ (M+) 201.1517; found: 201.1512.

General Procedure for hydrolysis and cyclization of α-cyanoalkynes:



2a **III** **IV**

The mixture of 2,2-dimethyl-4-phenylbut-3-ynenitrile (0.75 mmol, 126.5 mg) and KOH (21.4 mmol, 1.2 g) in EtOH/H_2O (5 mL/5 ml), was refluxed at 90 °C for 12 h. After completion of the reaction, the mixture was carefully acidified with 2 N HCl, and extracted with diethyl ether (20 mL x 3). The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to give 2,2-dimethyl-4-phenylbut-3-ynoic acid (120 mg, 85% yield) as a light yellow solid.

This compound is known.

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.38 (s, 1H), 7.46 – 7.40 (m, 2H), 7.35 – 7.27 (m, 3H), 1.62 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 179.88, 131.74, 128.18, 128.16, 122.81, 90.73 82.28, 38.71, 27.09.

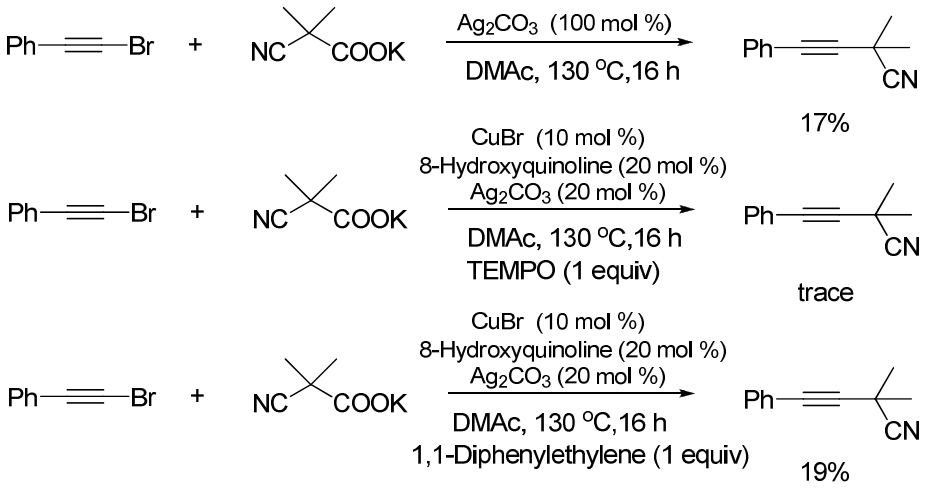
The mixture of 2,2-dimethyl-4-phenylbut-3-ynoic acid (0.52 mmol, 97.7 mg) and $AgNO_3$(0.1 mmol, 18 mg) in acetone (1.5mL) was stirred at room temperature for 24 h. Then, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography to give 3,3-dimethyl-5-phenylfuran -2(*3H*)-one (89.1 mg, 91% yield) as a light yellow solid.

This compound is known.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.47 (m, 2H), 7.44 – 7.32 (m, 3H), 5.82 (s, 1H), 1.40 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 181.98, 150.85, 129.48, 128.65, 128.39, 124.72, 109.69, 45.08, 24.55.

f. Decarboxylative alkynylation under different conditions.



We did some experiments for the study of the mechanism of this reaction. We found that this reaction could react with the yield of 17% by only using the equivalent of Ag_2CO_3. When this reaction was carried out under the standard conditions in the presence of 1 equivalent of TEMPO, a radical trap, we only detected a trace amount of product. When we used another radical trap, 1,1-diphenylethylene, only the yield of 19% was obtained. We suspect that the process of free radicals may be present in the mechanism of this reaction. The detailed mechanism remains to be clarified in our future research.

Part 3. References

[1] Shang, R.; Ji, D. S.; Chu, L.; Fu, Y.; Liu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4470.

[2] Shia, K. S.; Chang, N. Y.; Yip, J.; Liu, H. J. *Tetrahedron Lett.* **1997**, *38*, 7713.

[3] Goossen, L. J.; Rodriguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248.

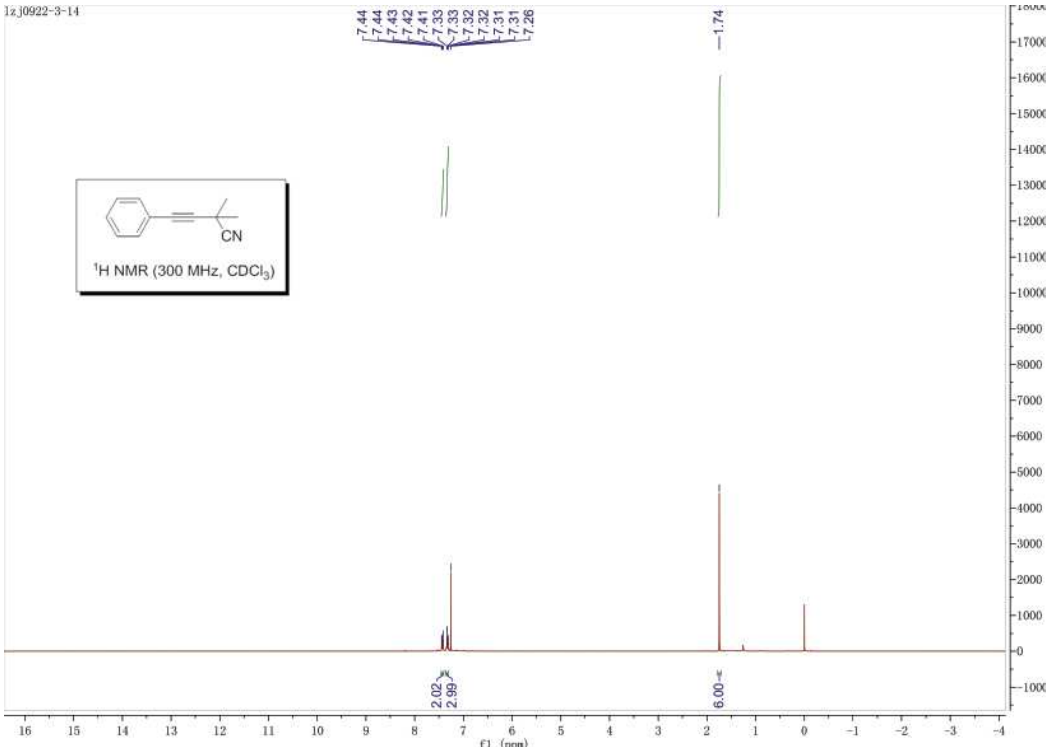
[4] Yao, P. Y.; Zhang, Y.; Hsung, R. P.; Zhao, K. *Org. Lett.* **2008**, *10*, 4275.

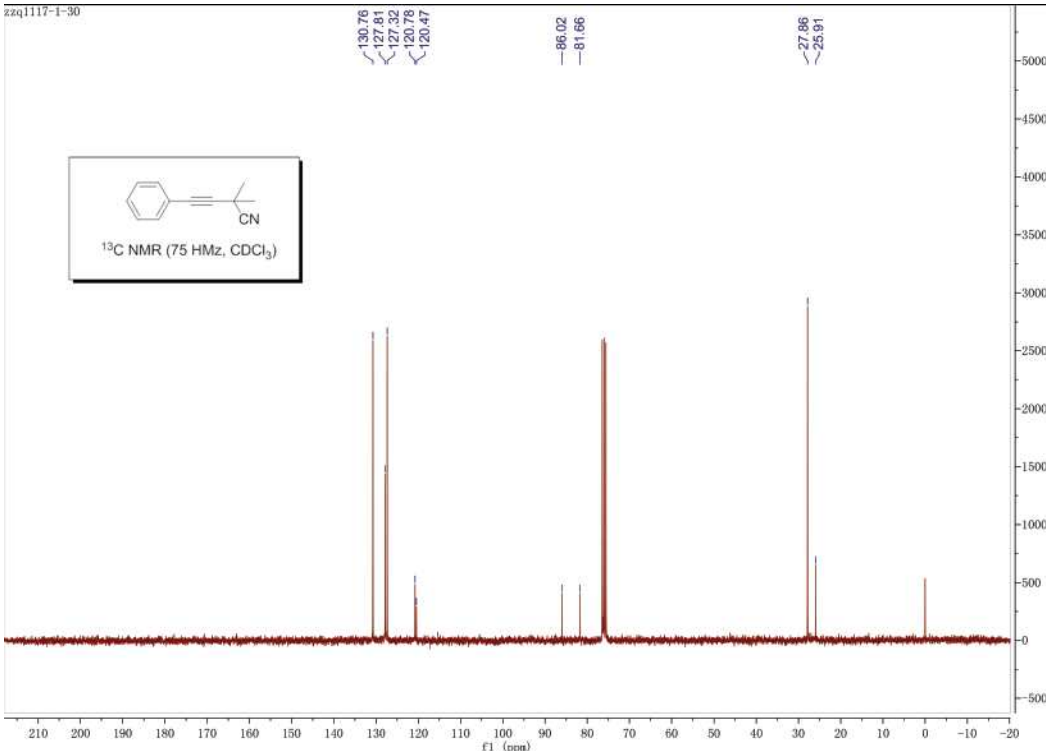
[5] Okutani, M.; Mori, Y. *J. Org. Chem.* **2009**, *74*, 442.

[6] Sasson, Y.; Webster, O. W. *J. Chem. Soc., Chem. Commun.* **1992**, *28*, 1200.

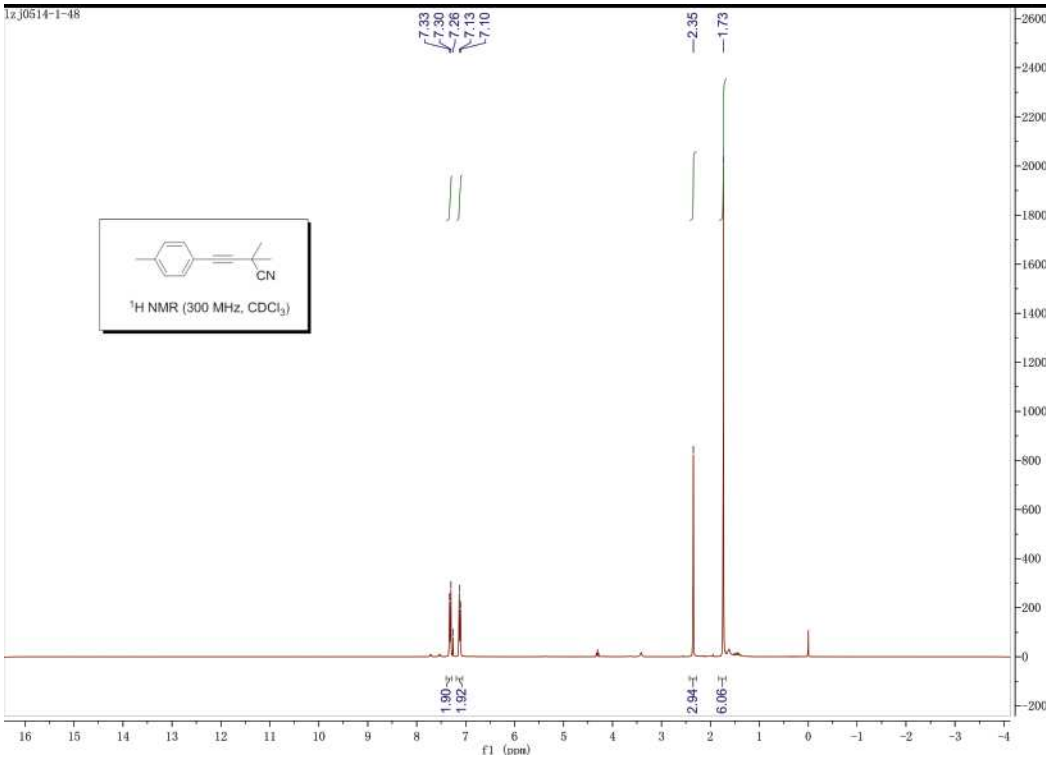
Part 4. Copies of ^{1}H-NMR and ^{13}C-NMR Spectra

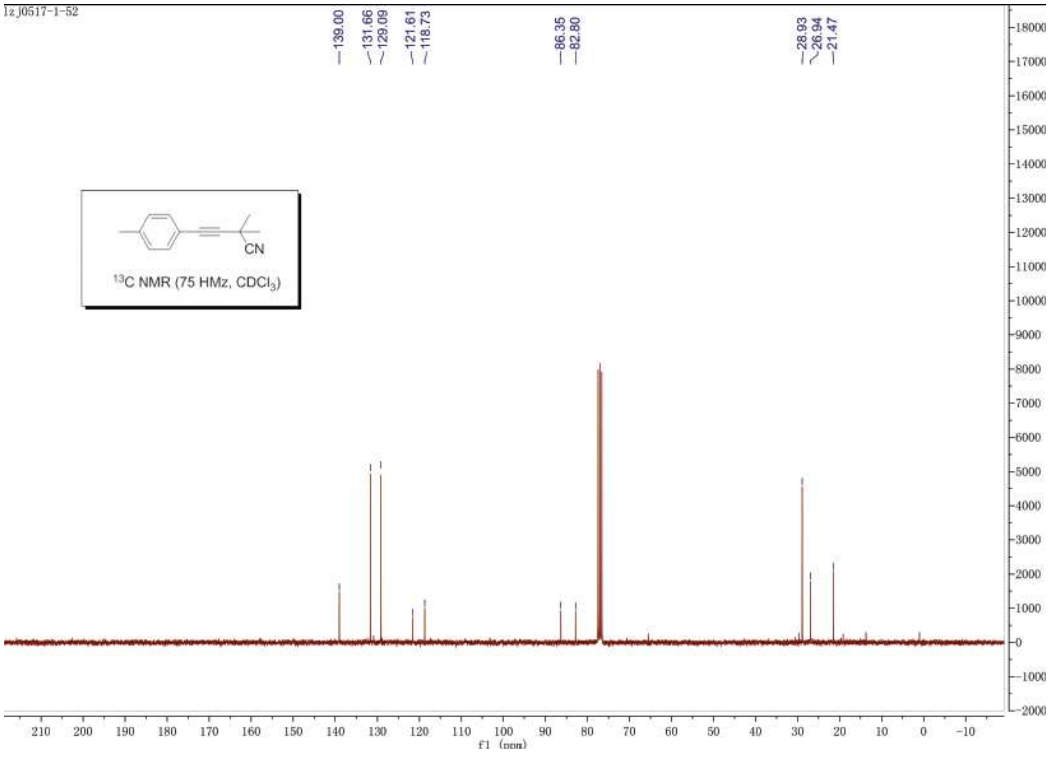
2,2-Dimethyl-4-phenylbut-3-ynenitrile (2a)



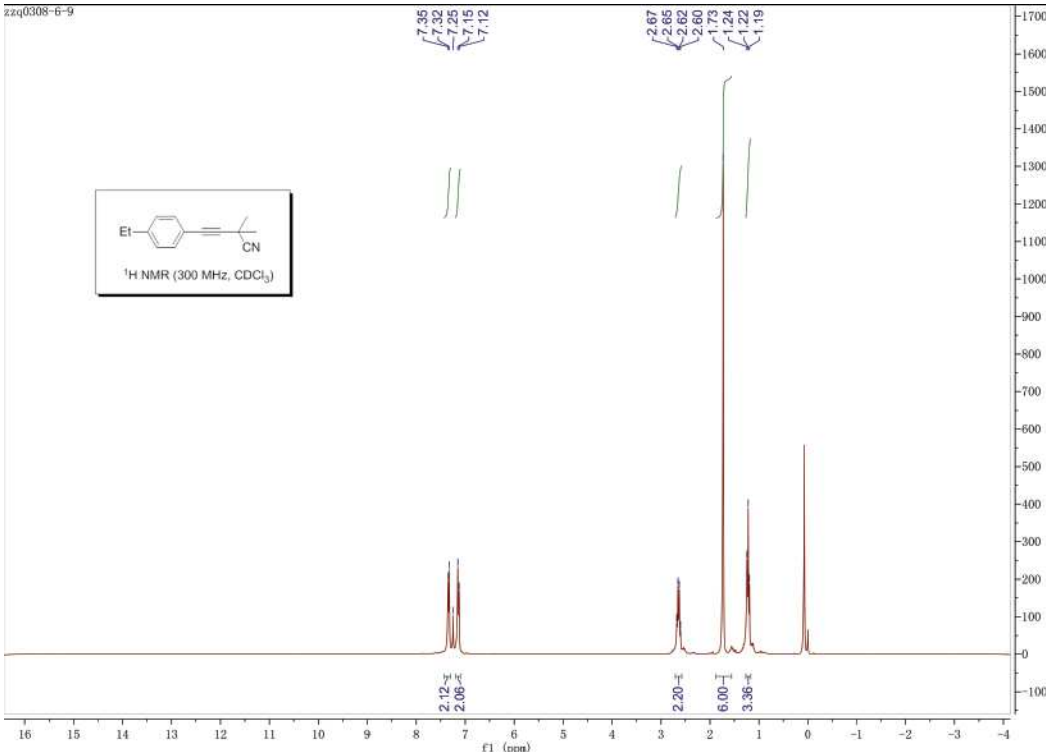


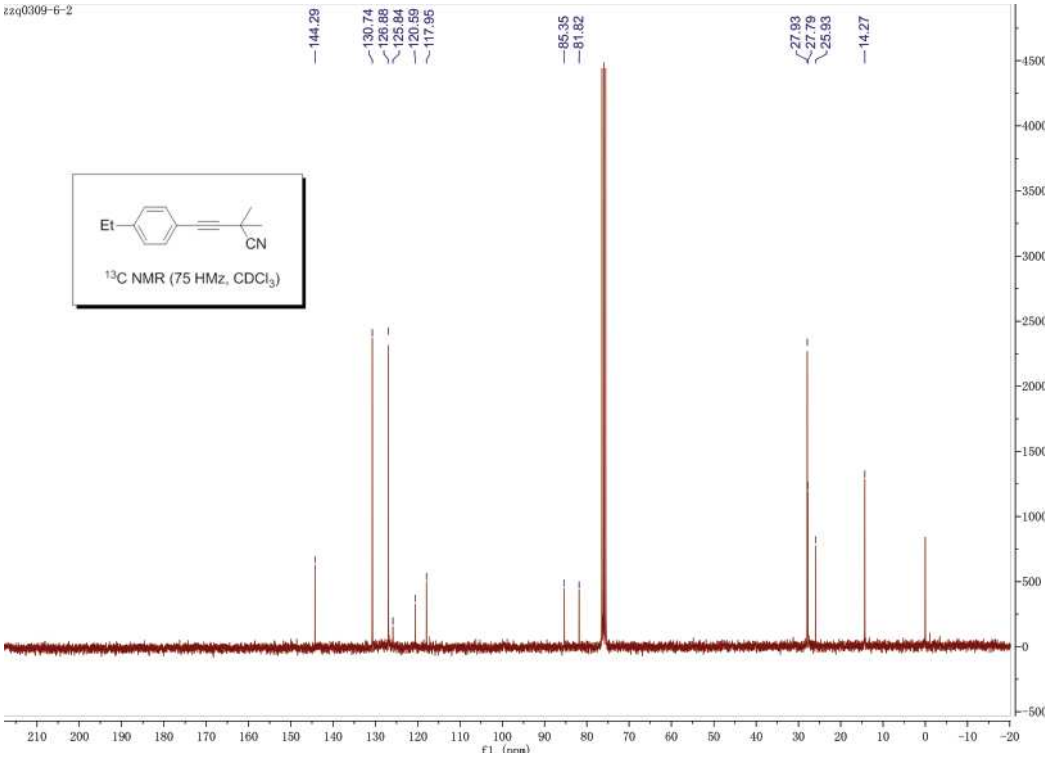
2,2-Dimethyl-4-(p-tolyl)but-3-ynenitrile (2b)



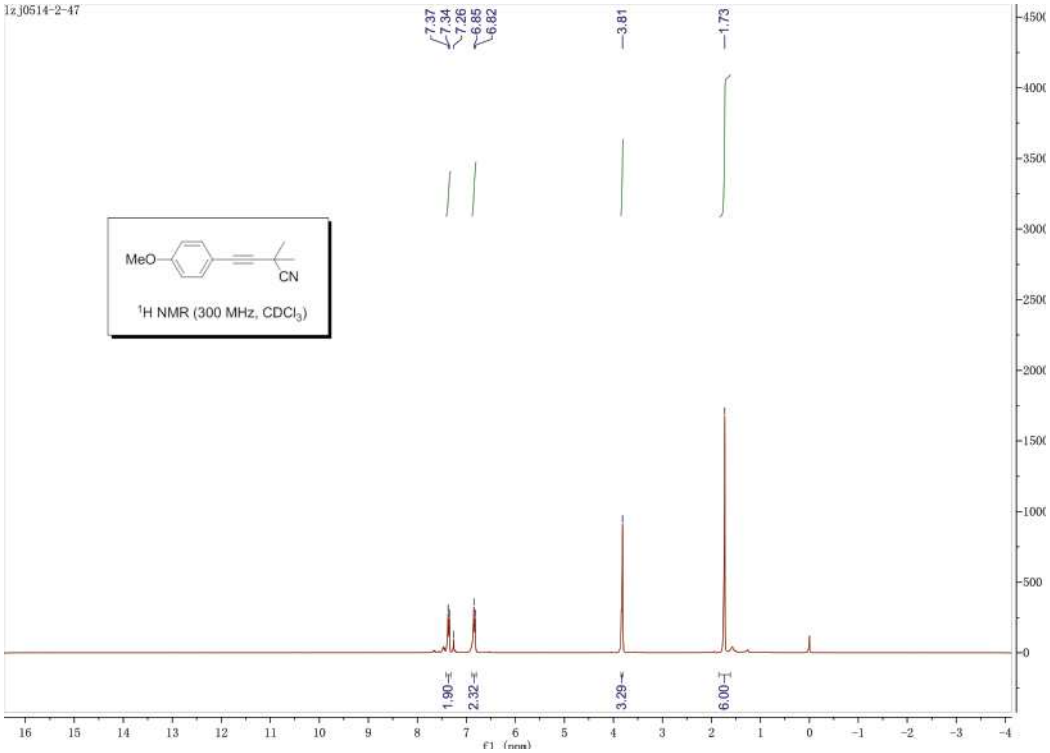


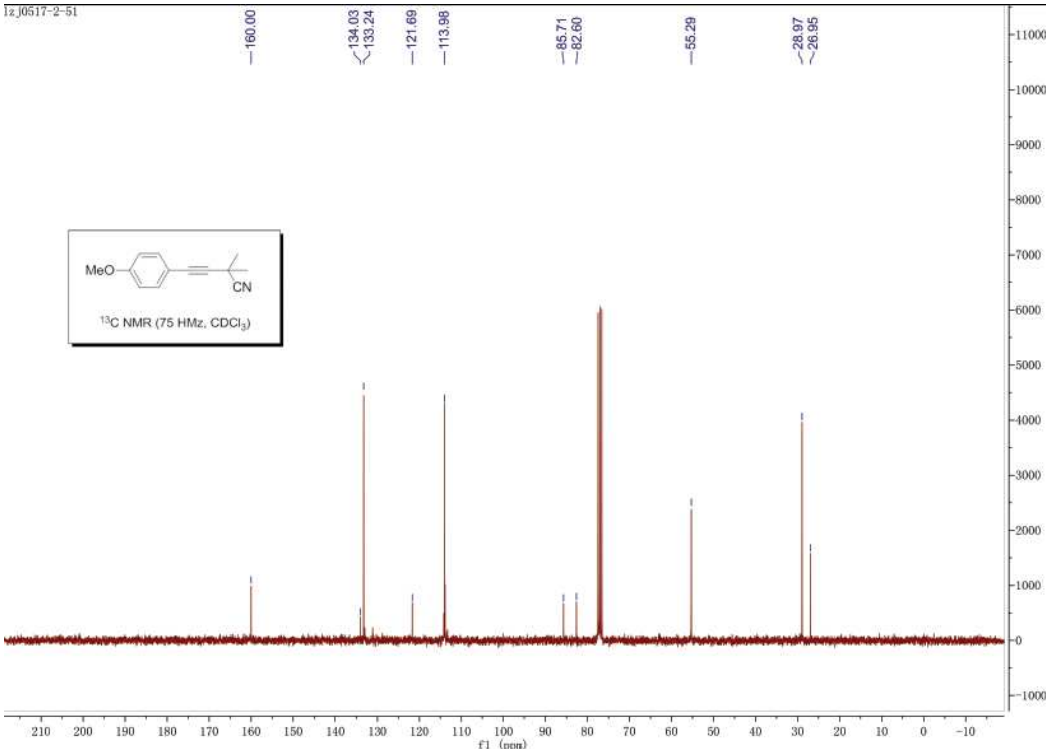
4-(4-Ethylphenyl)-2,2-dimethylbut-3-ynenitrile (2c)



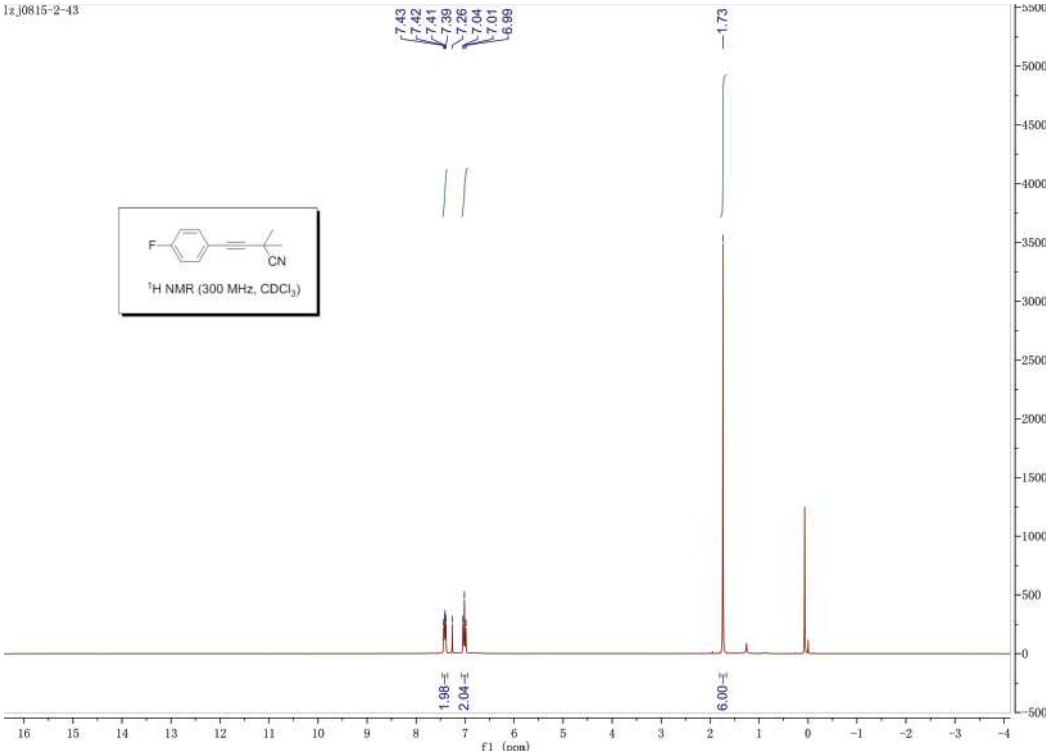


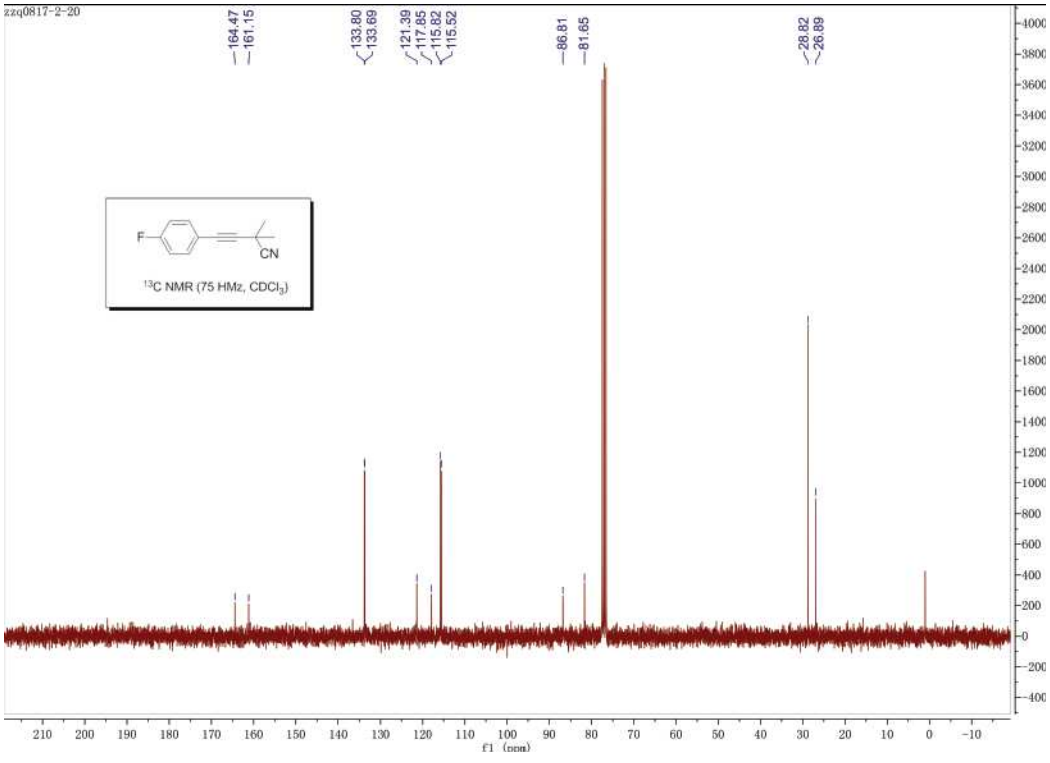
4-(4-Methoxyphenyl)-2,2-dimethylbut-3-ynenitrile (2d)



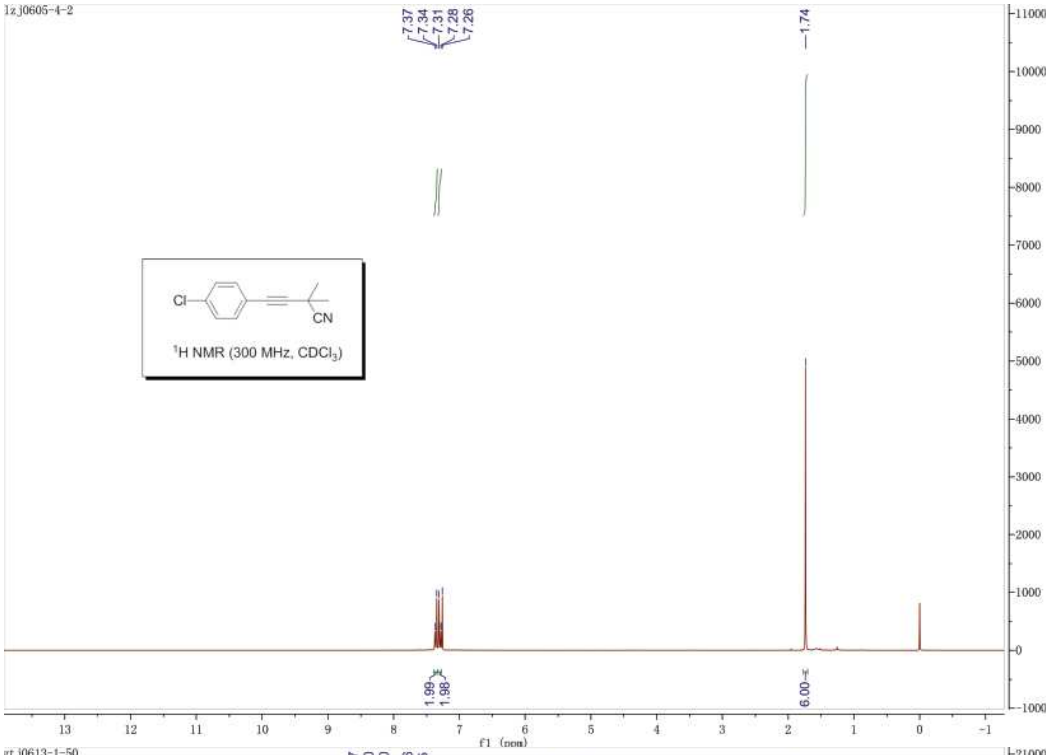


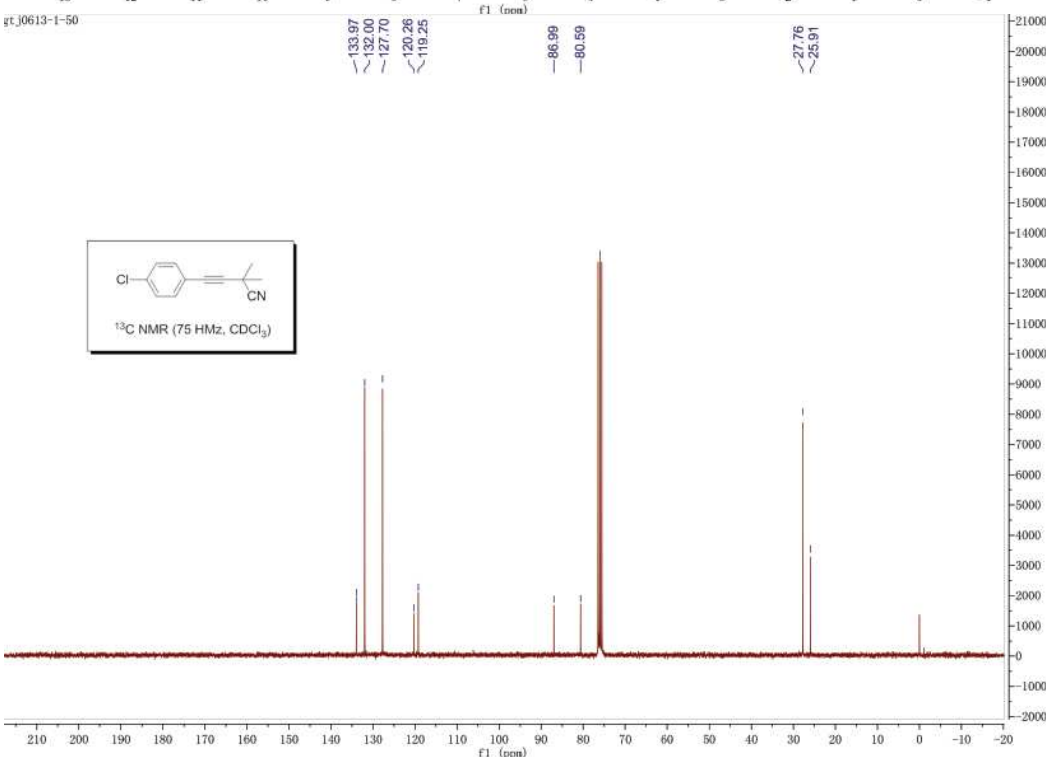
4-(4-Fluorophenyl)-2,2-dimethylbut-3-ynenitrile (2e)



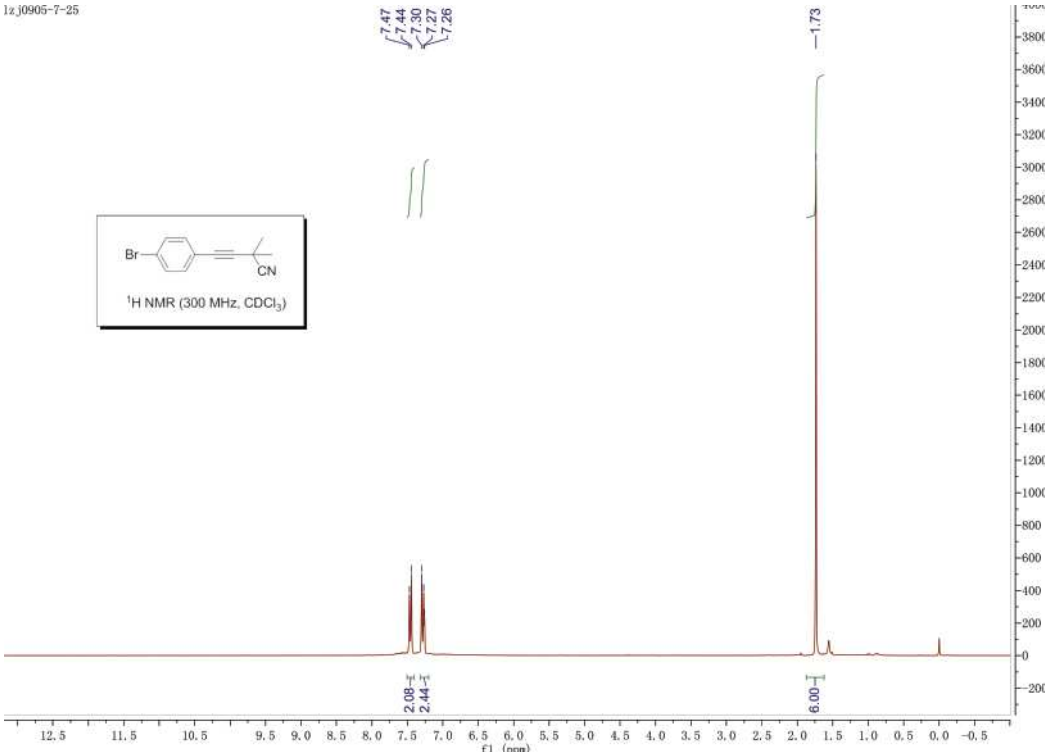


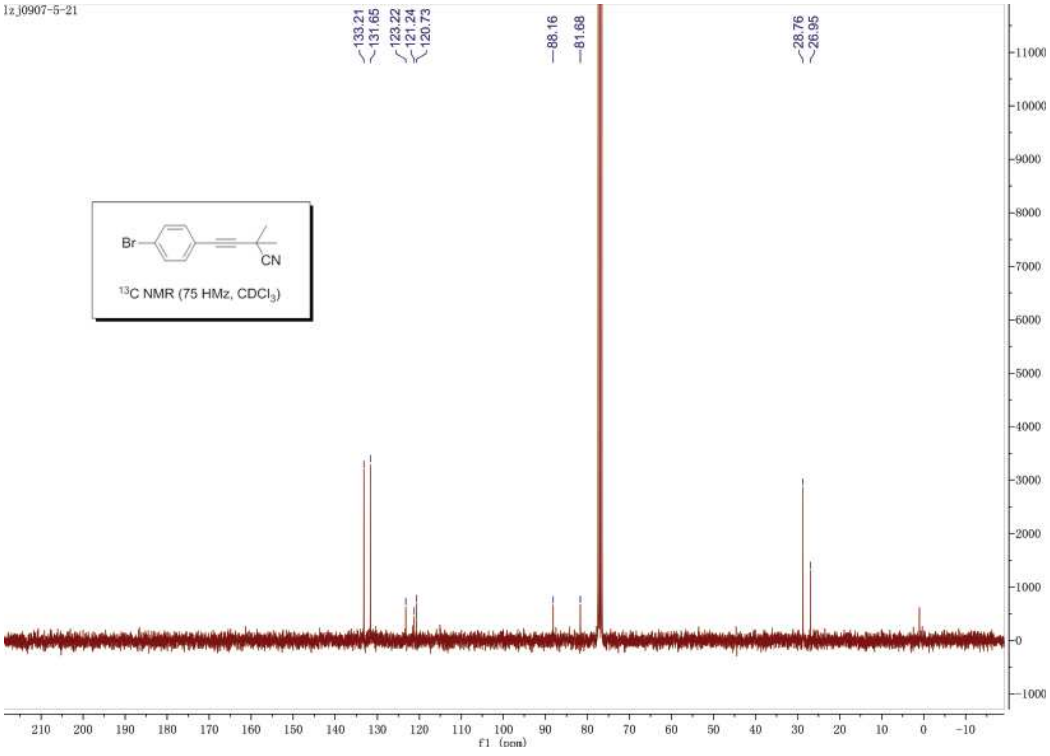
4-(4-Chlorophenyl)-2,2-dimethylbut-3-ynenitrile (2f)



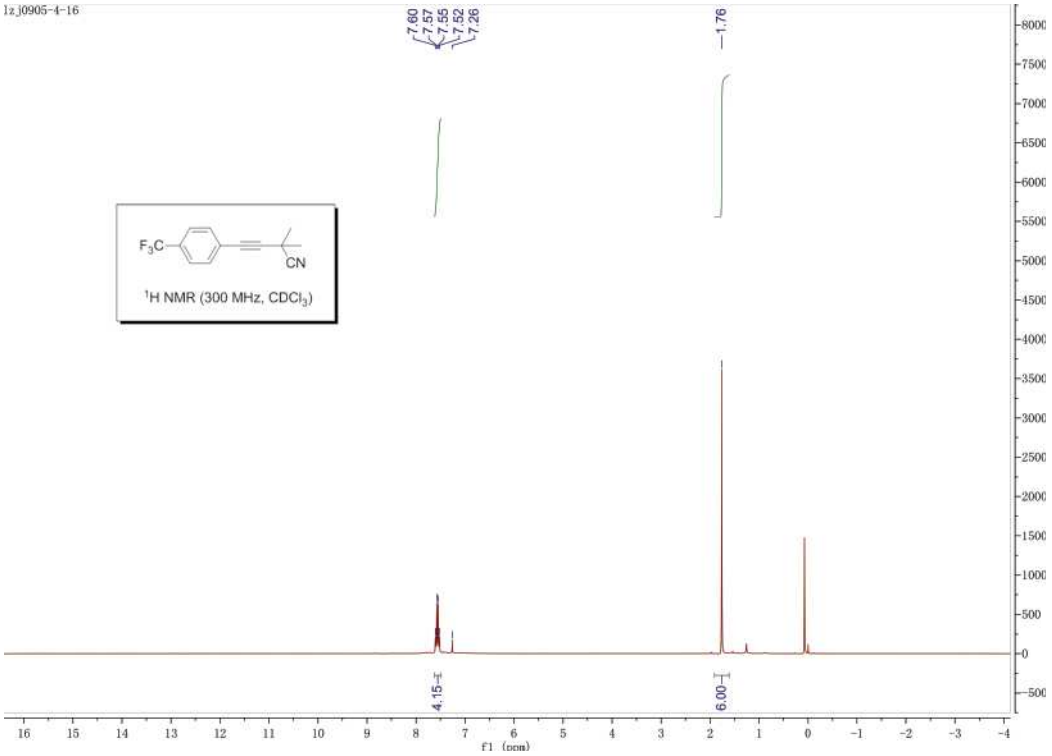


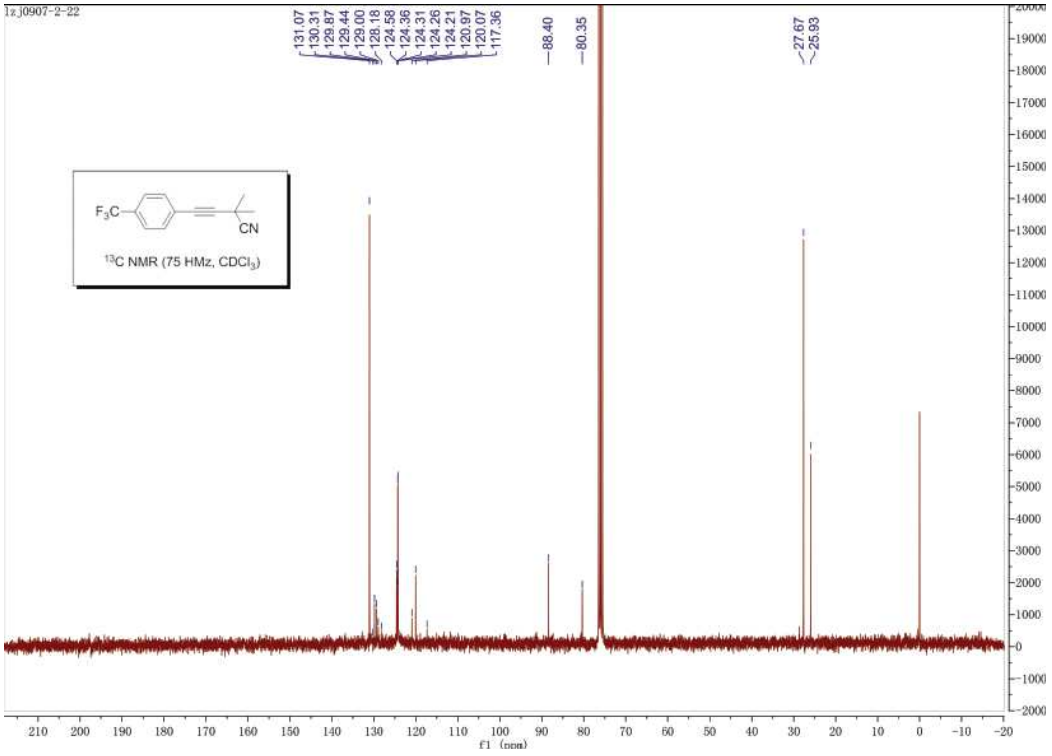
4-(4-Bromophenyl)-2,2-dimethylbut-3-ynenitrile (2g)



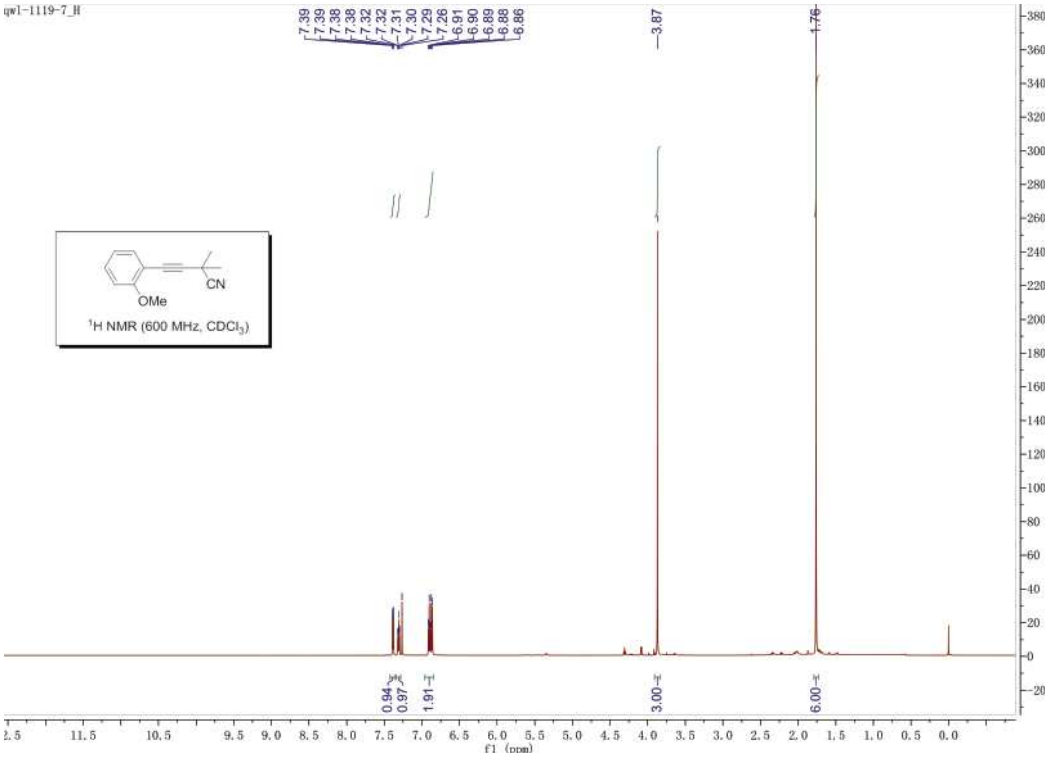


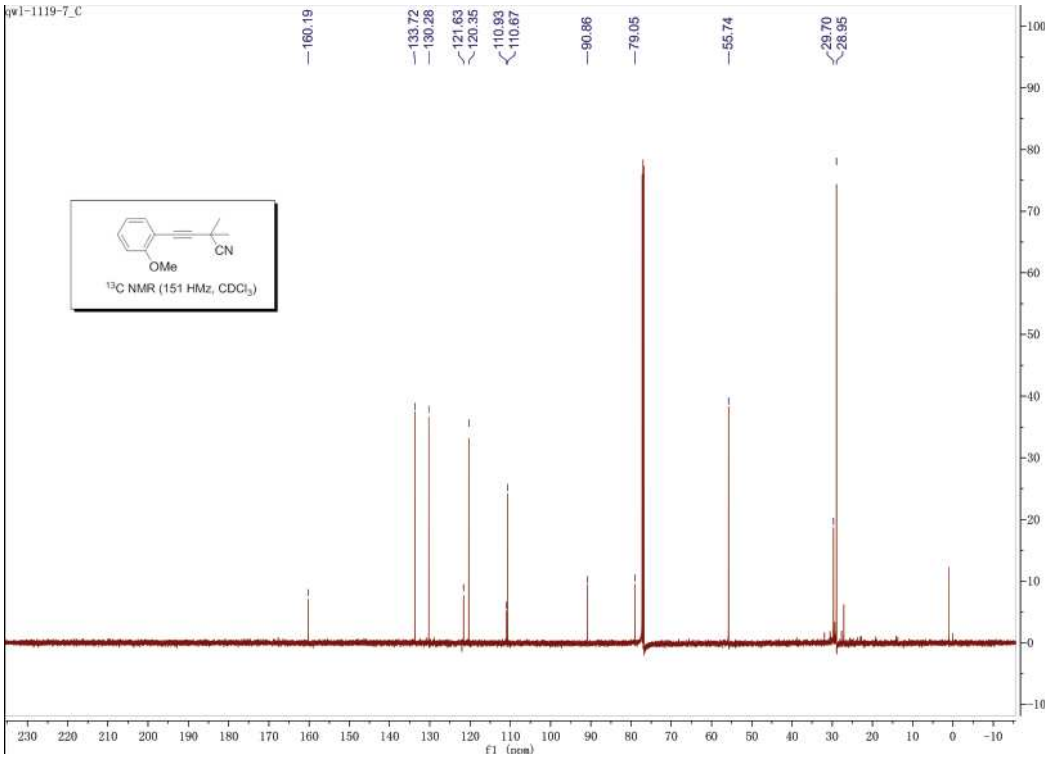
2,2-Dimethyl-4-(4-(trifluoromethyl)phenyl)but-3-ynenitrile (2h)



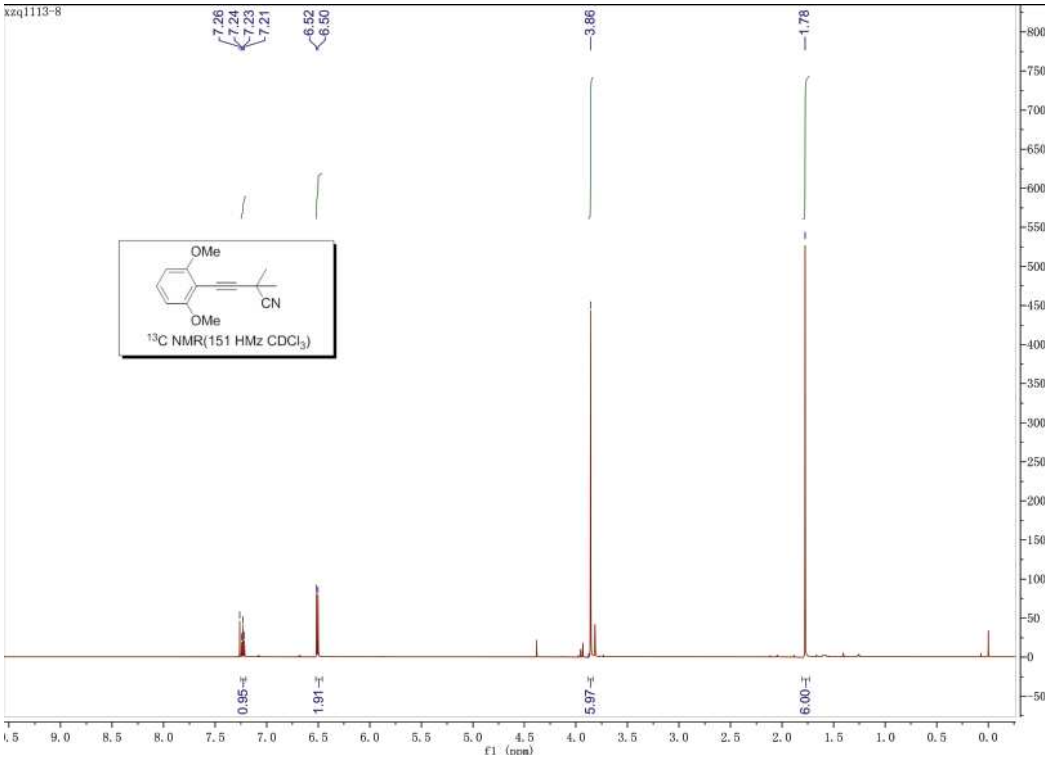


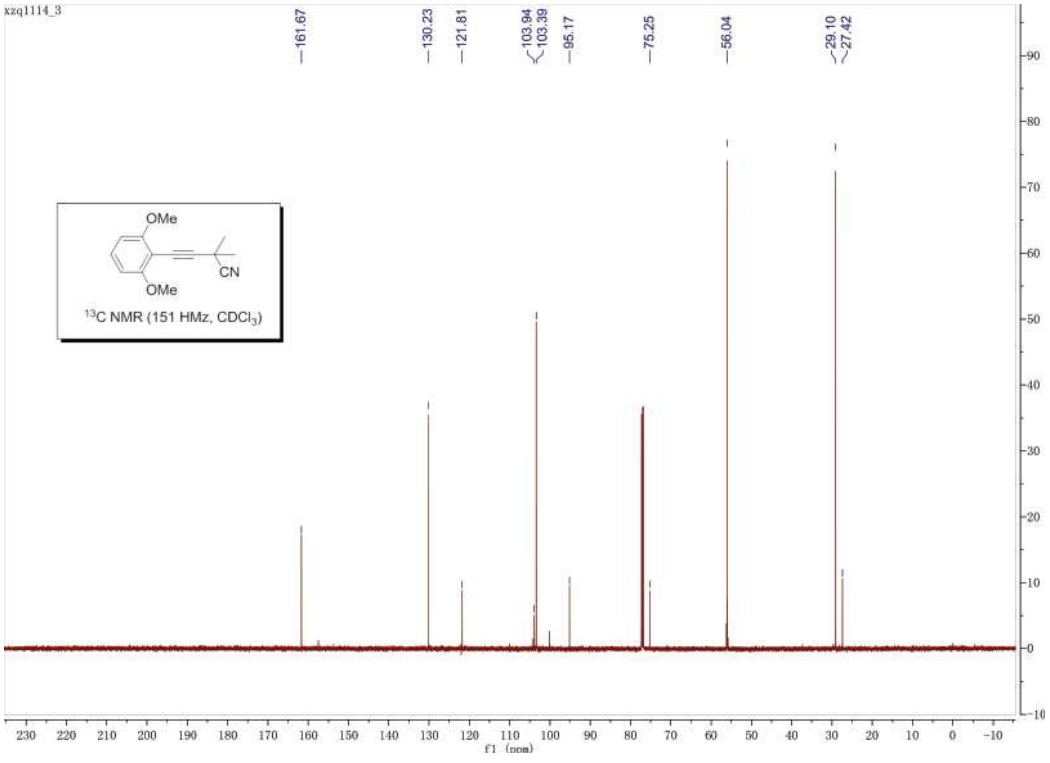
4-(2-Methoxyphenyl)-2,2-dimethylbut-3-ynenitrile (2i)



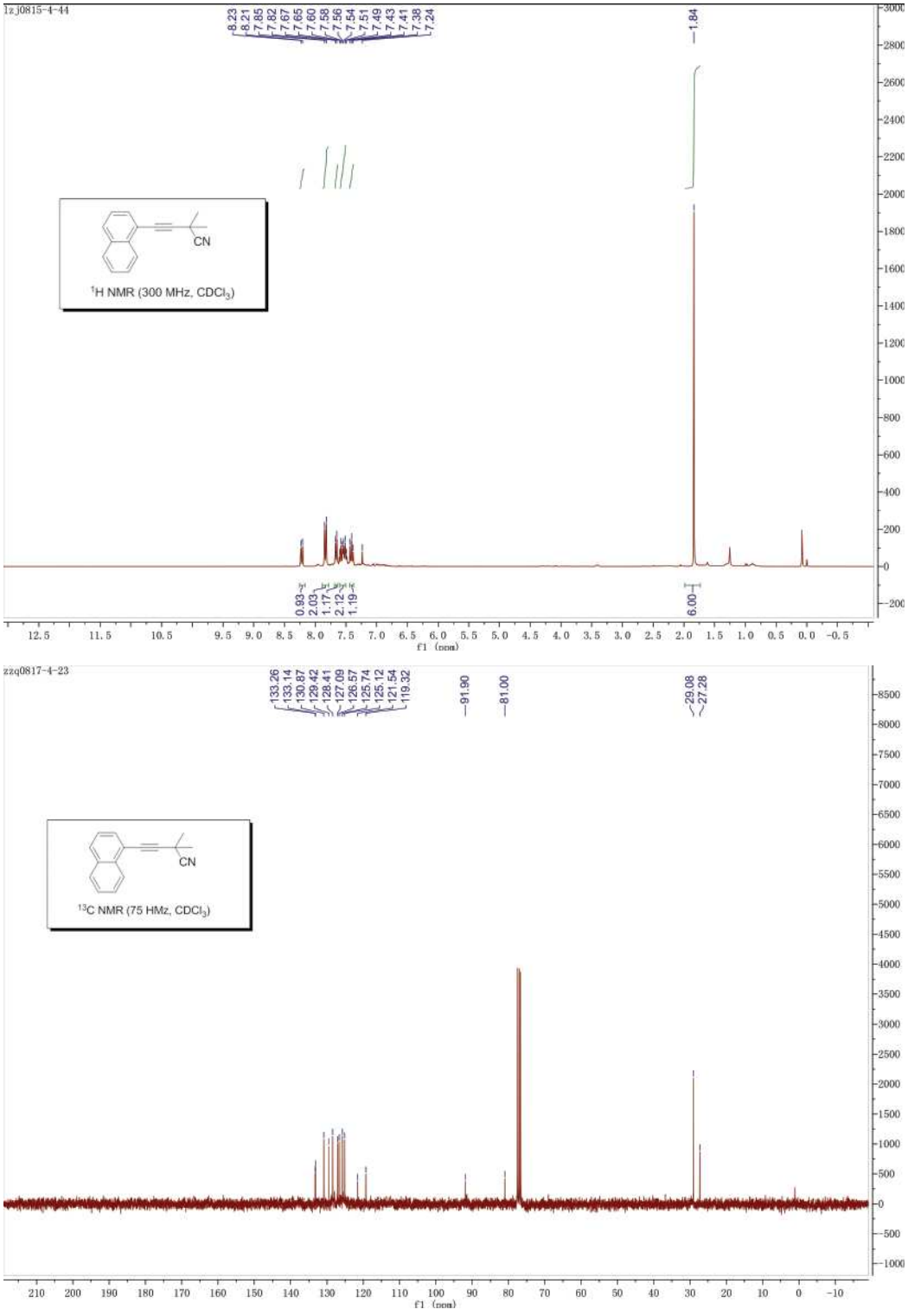


4-(2,6-Dimethoxyphenyl)-2,2-dimethylbut-3-ynenitrile (2j)

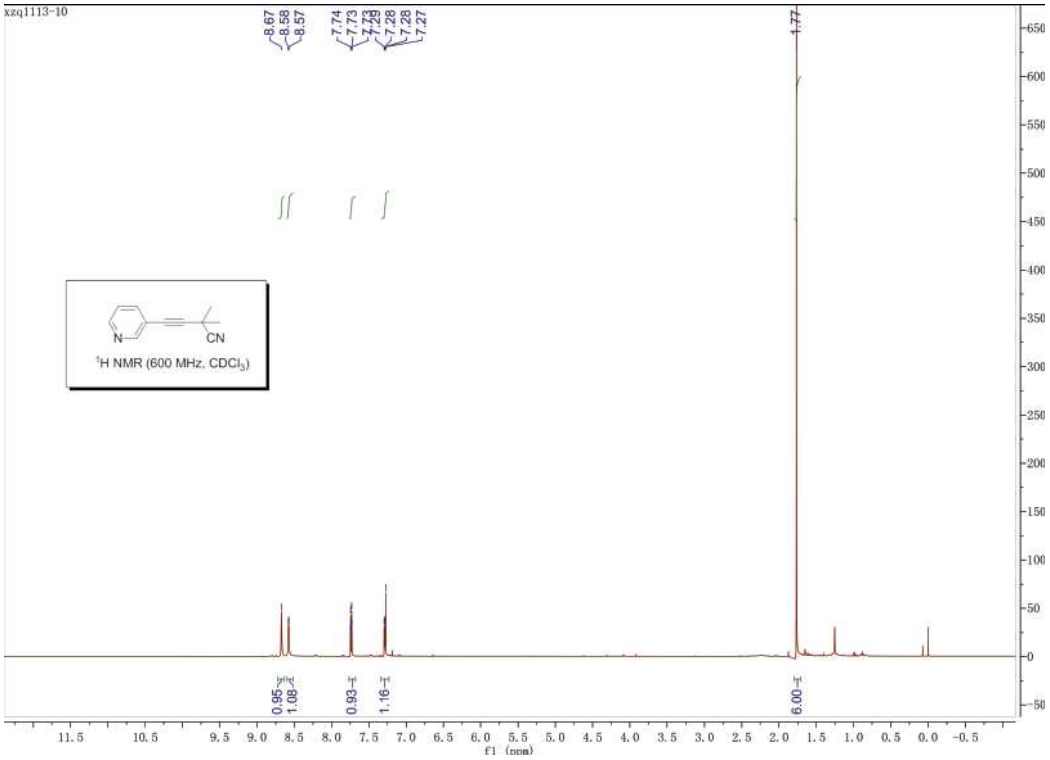


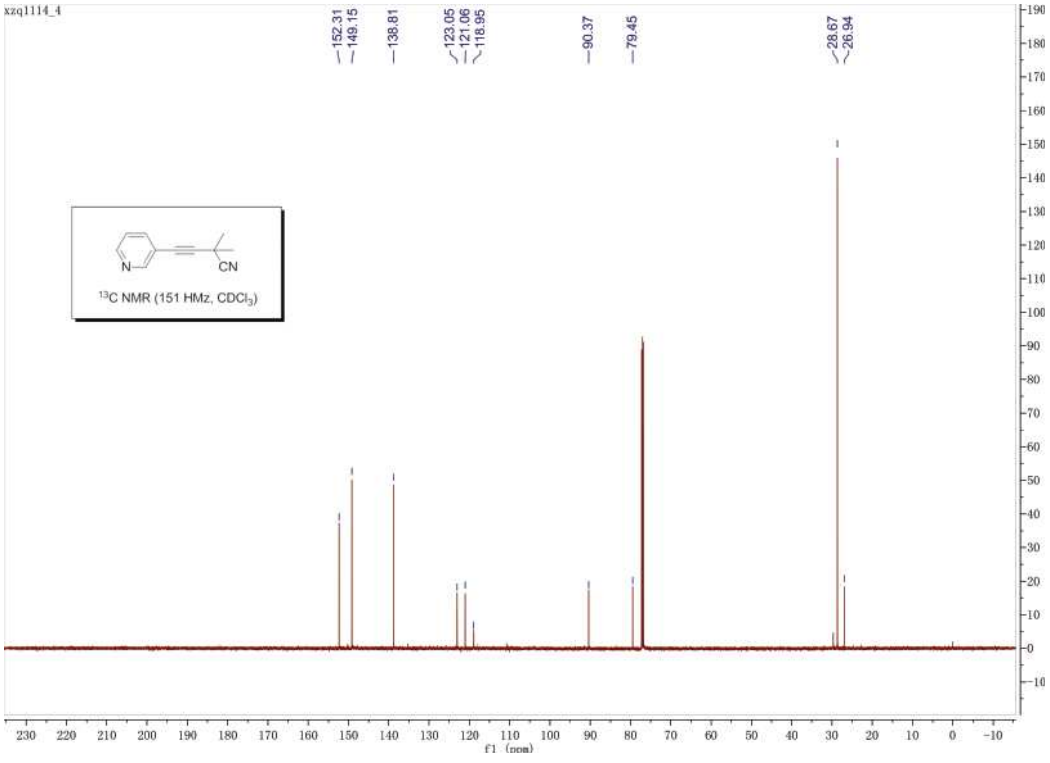


2,2-Dimethyl-4-(naphthalen-1-yl)but-3-ynenitrile (2k)

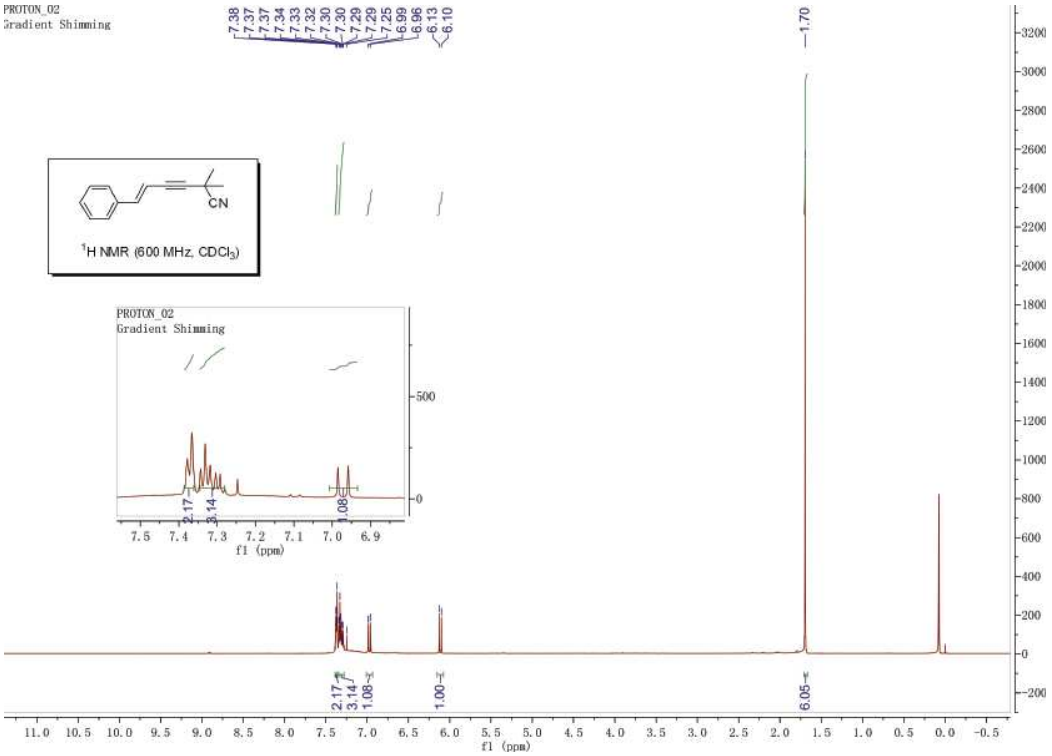


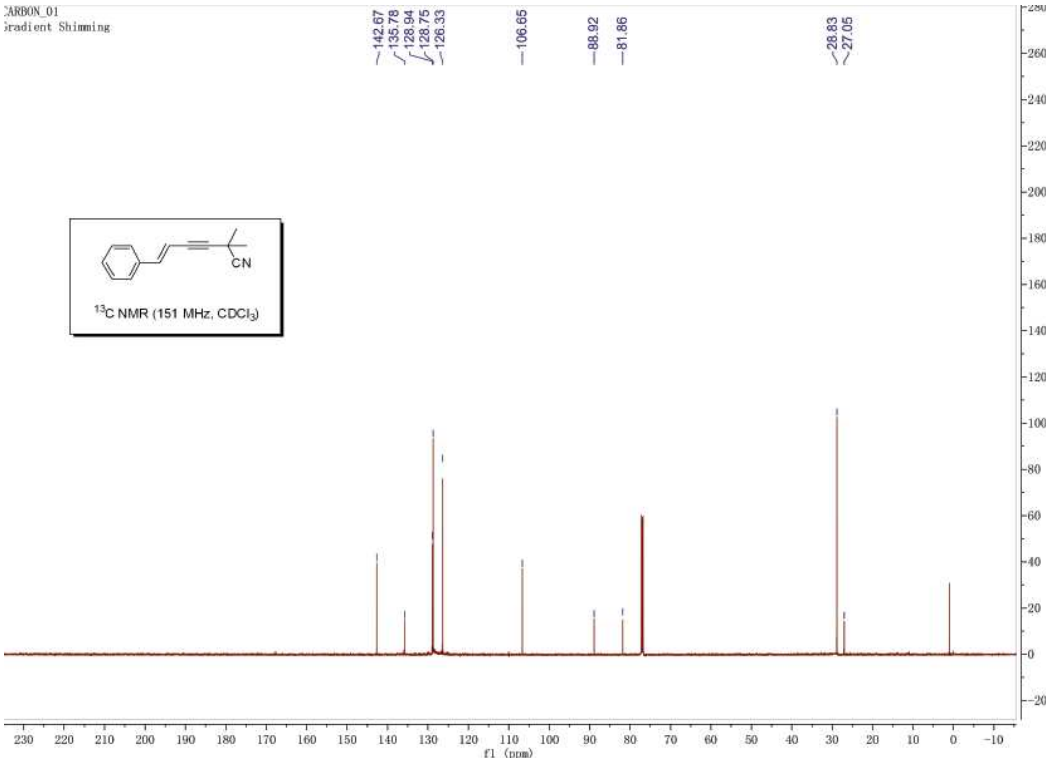
2,2-Dimethyl-4-(pyridin-3-yl)but-3-ynenitrile (2l)



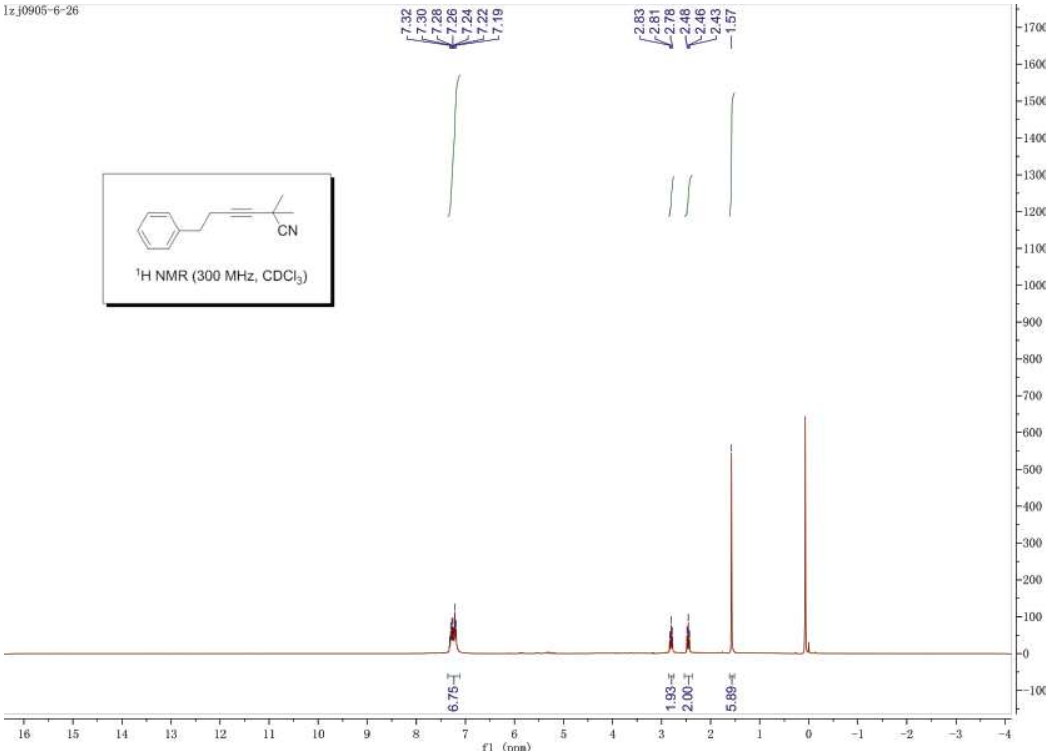


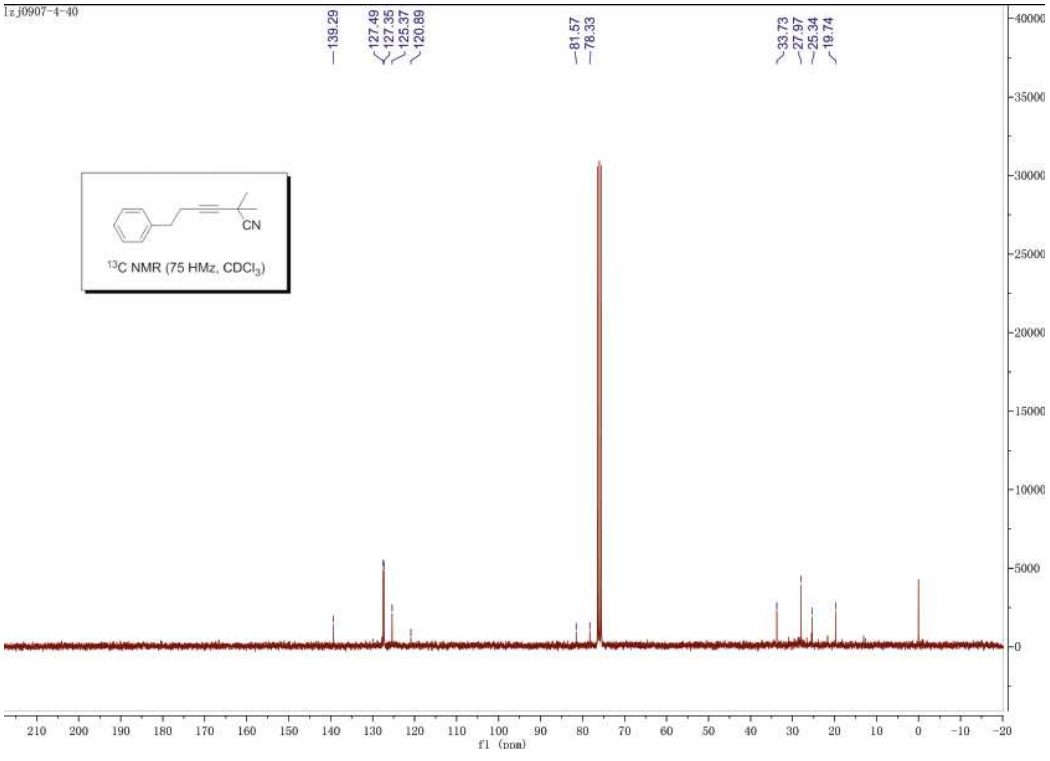
(*E*)-2,2-dimethyl-6-phenylhex-5-en-3-ynenitrile (2m)



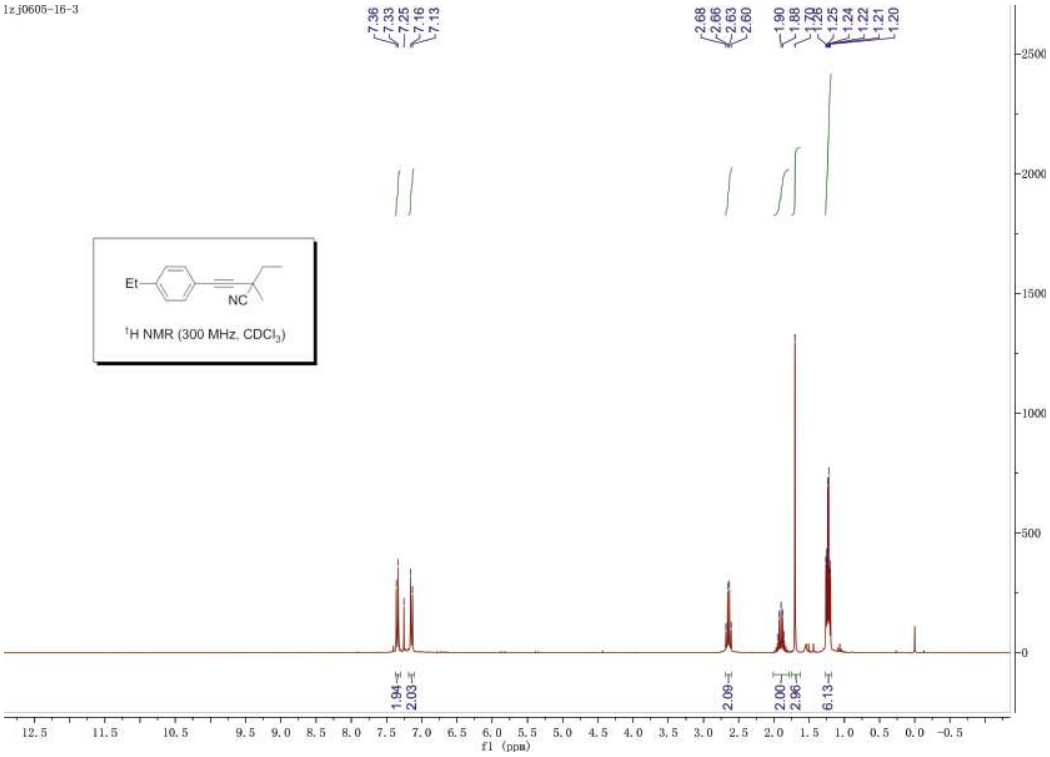


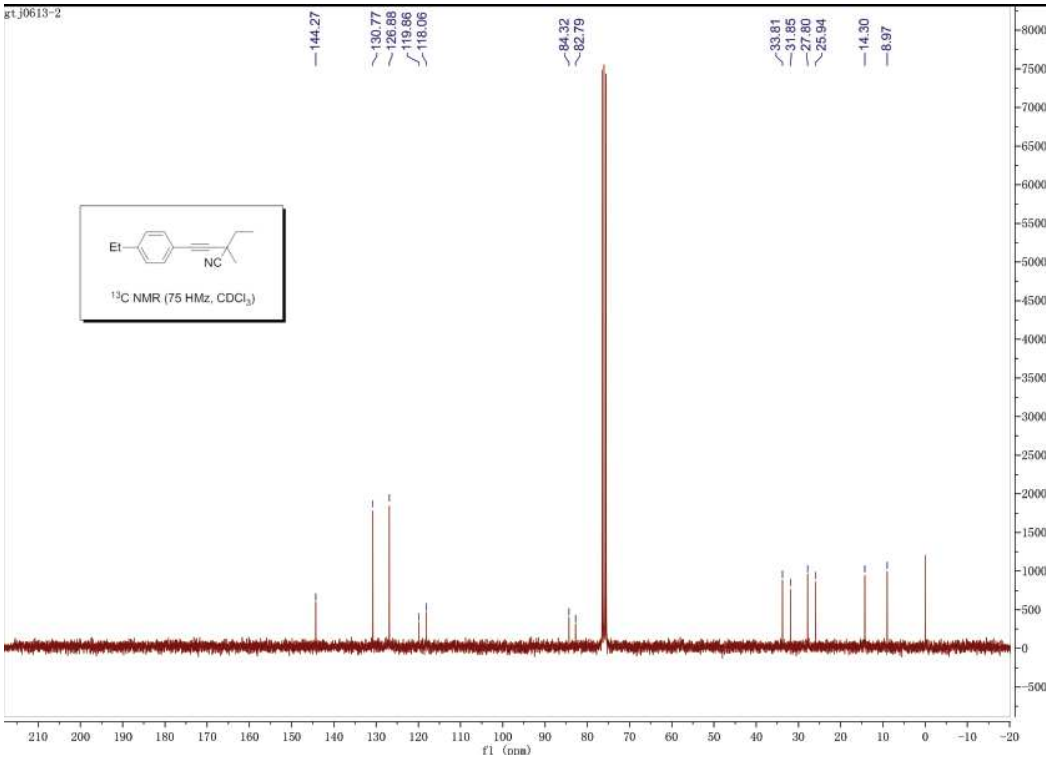
2,2-Dimethyl-6-phenylhex-3-ynenitrile (2n)



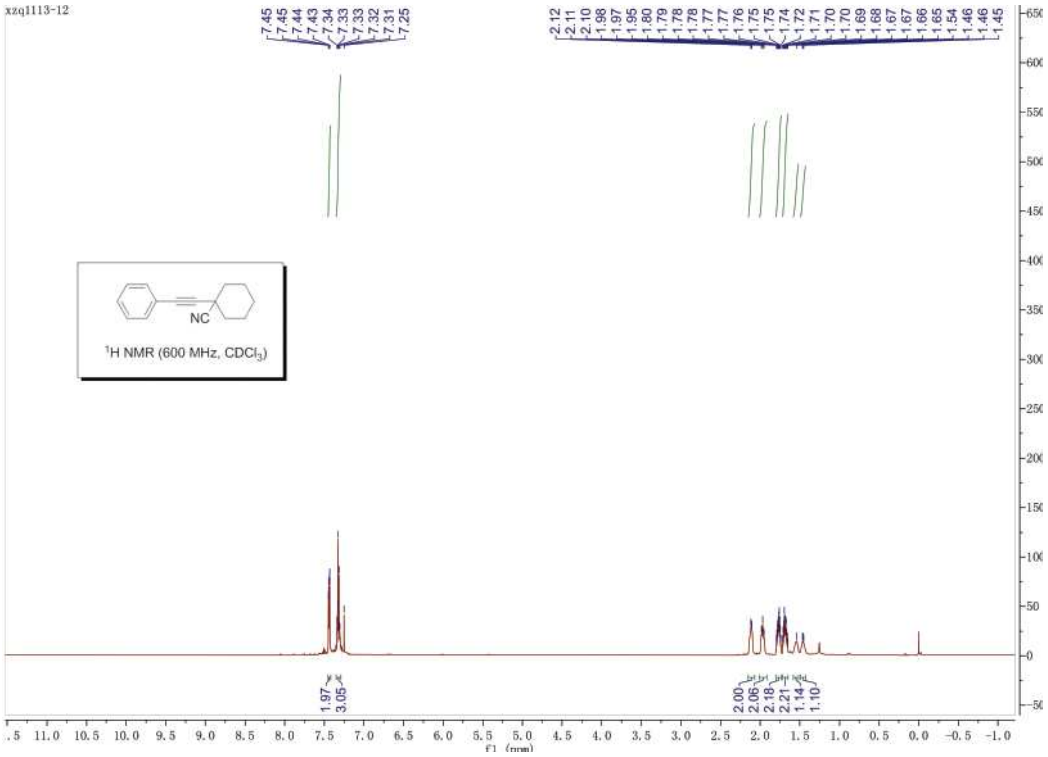


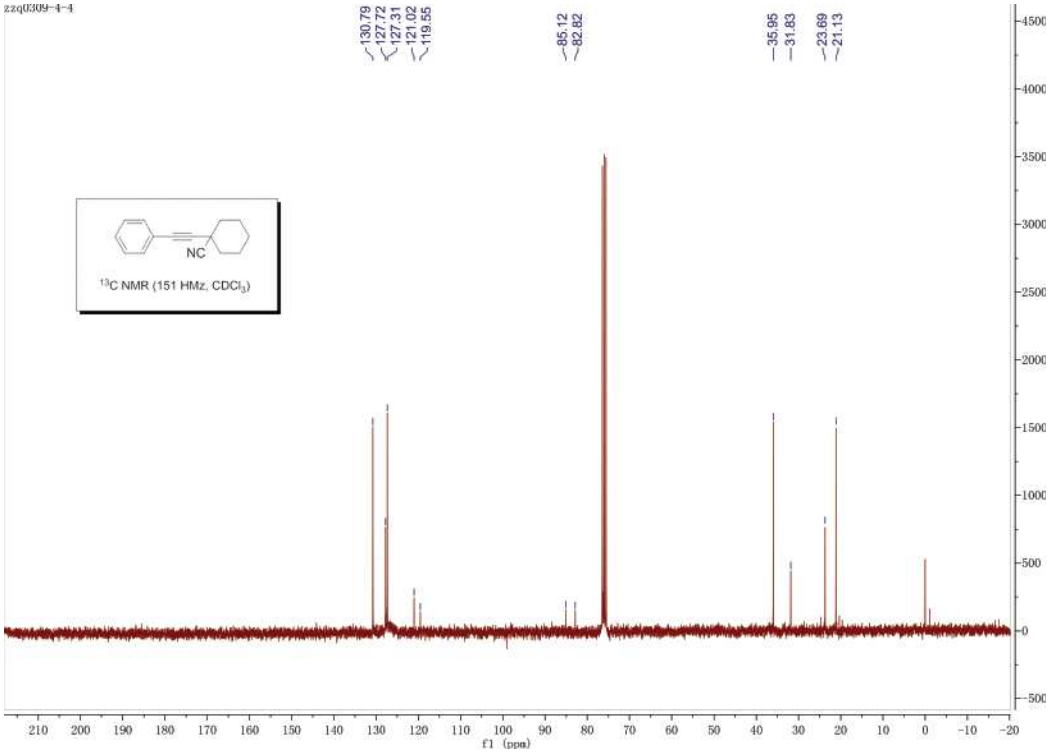
2-Ethyl-2-methyl-4-phenylbut-3-ynenitrile (3a)



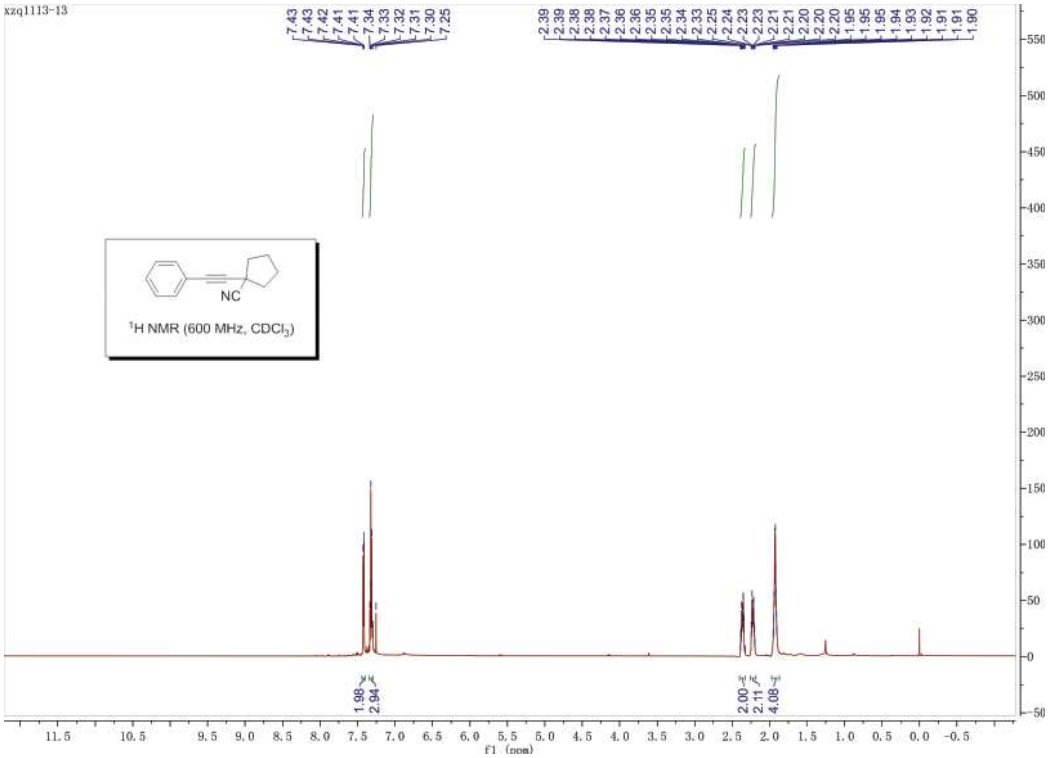


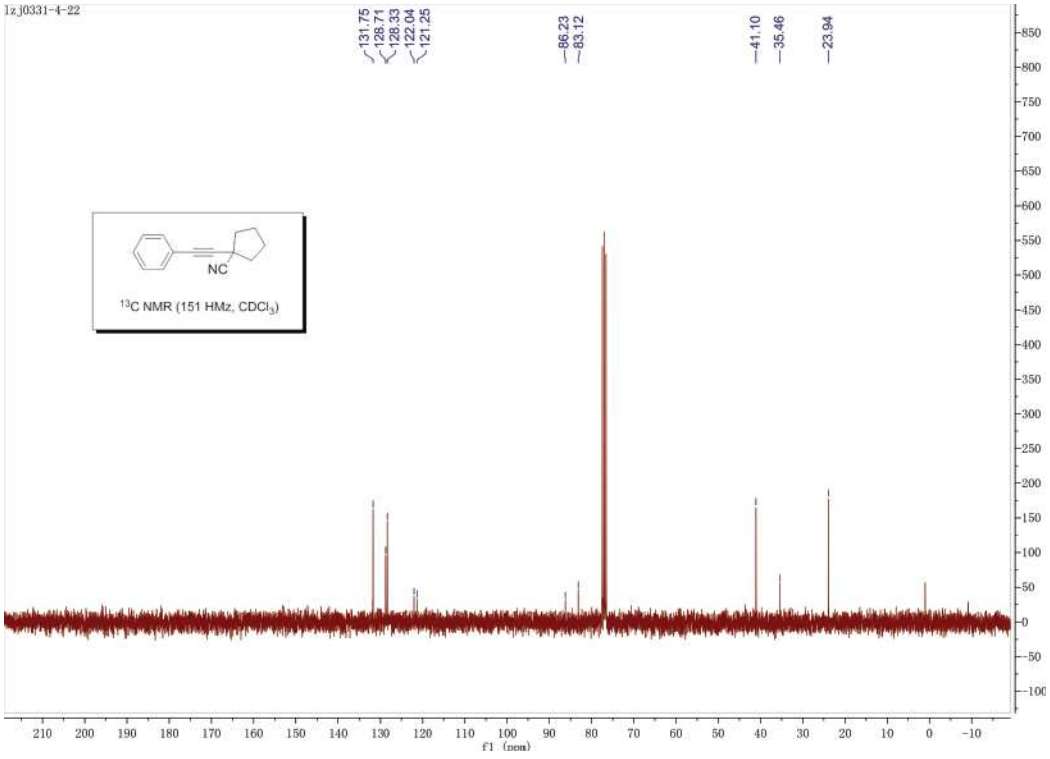
1-(Phenylethynyl)cyclohexanecarbonitrile (3b)



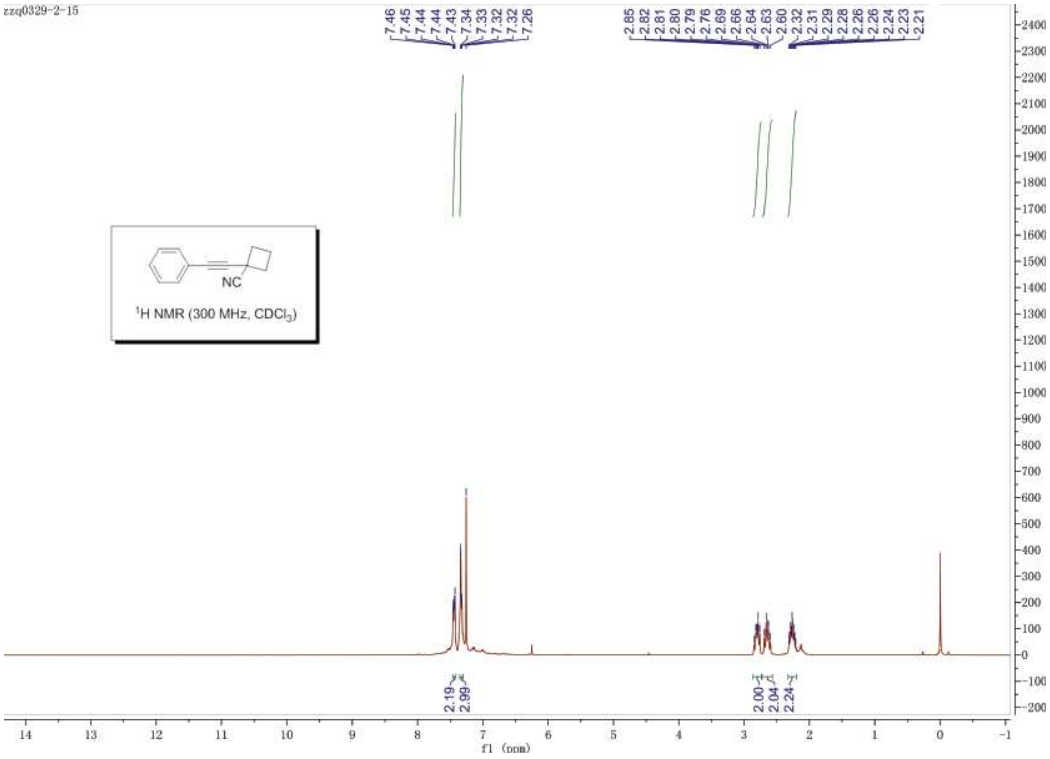


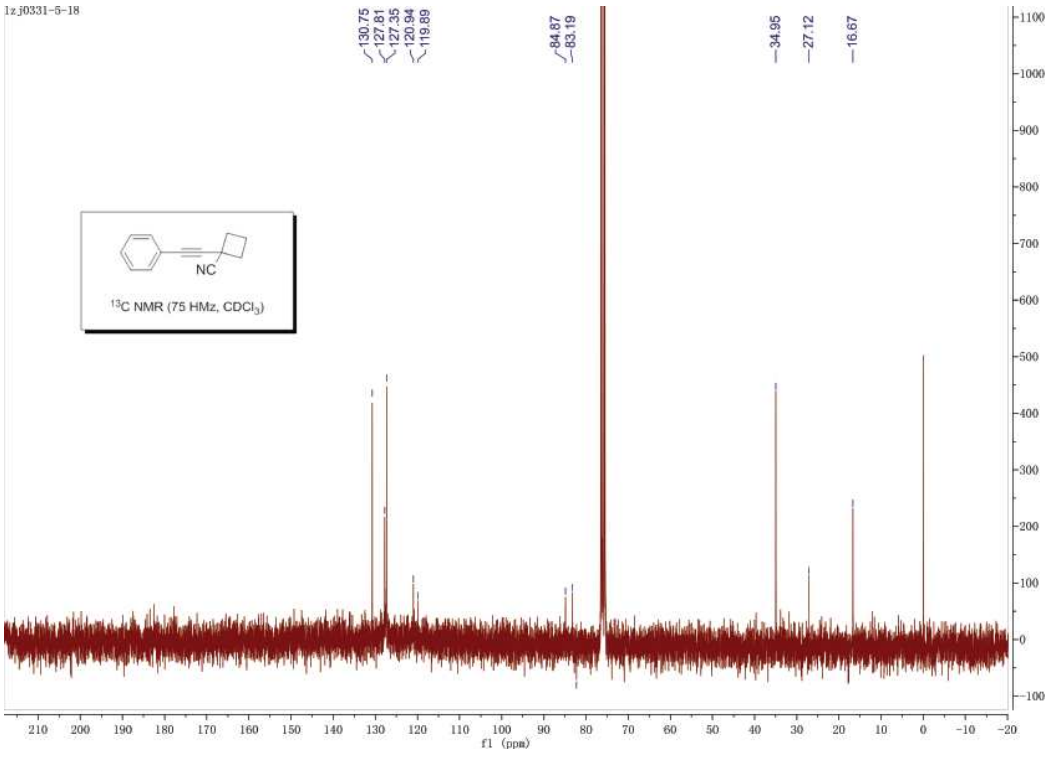
1-(Phenylethynyl)cyclopentanecarbonitrile (3c)



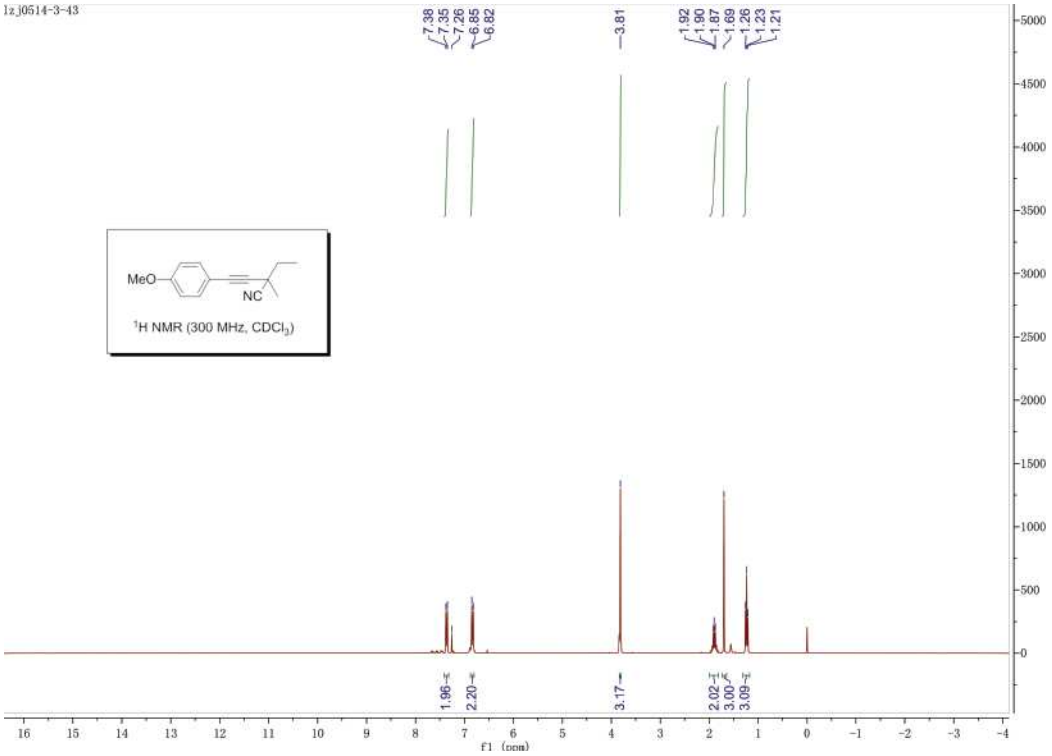


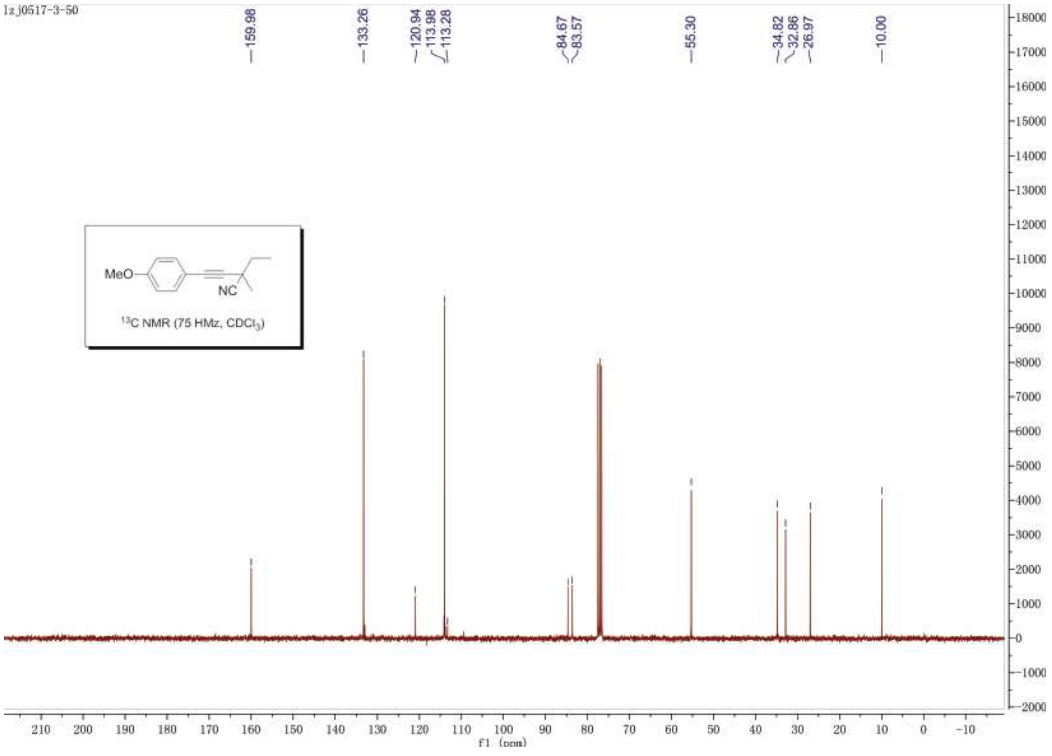
1-(Phenylethynyl)cyclobutanecarbonitrile (3d)



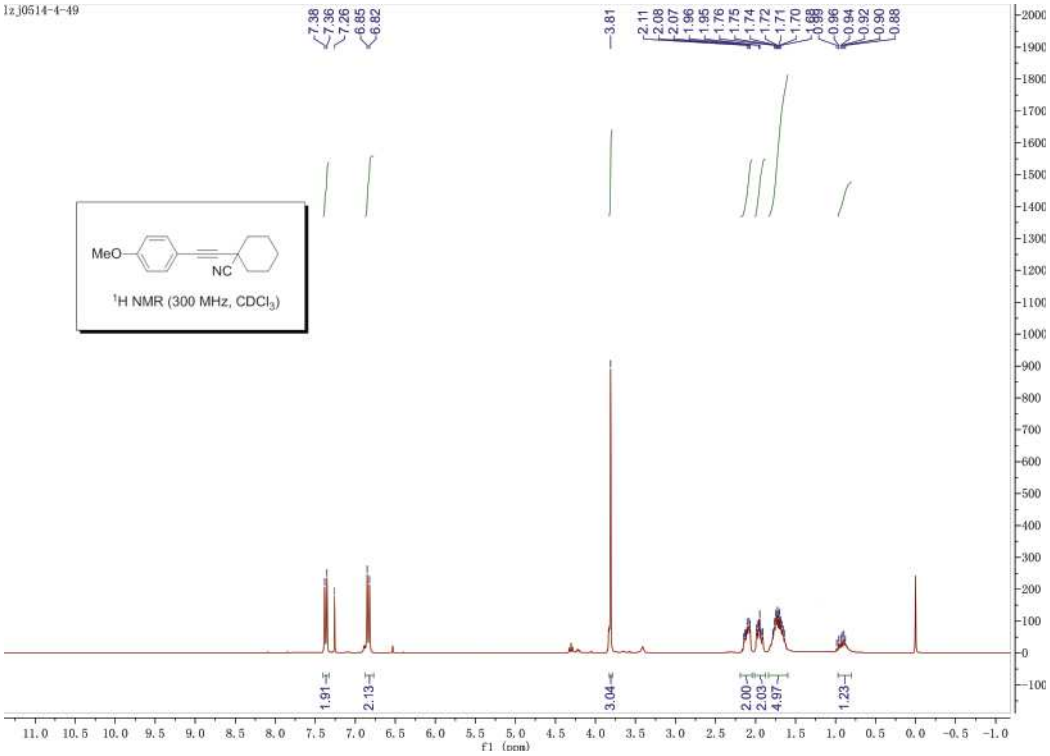


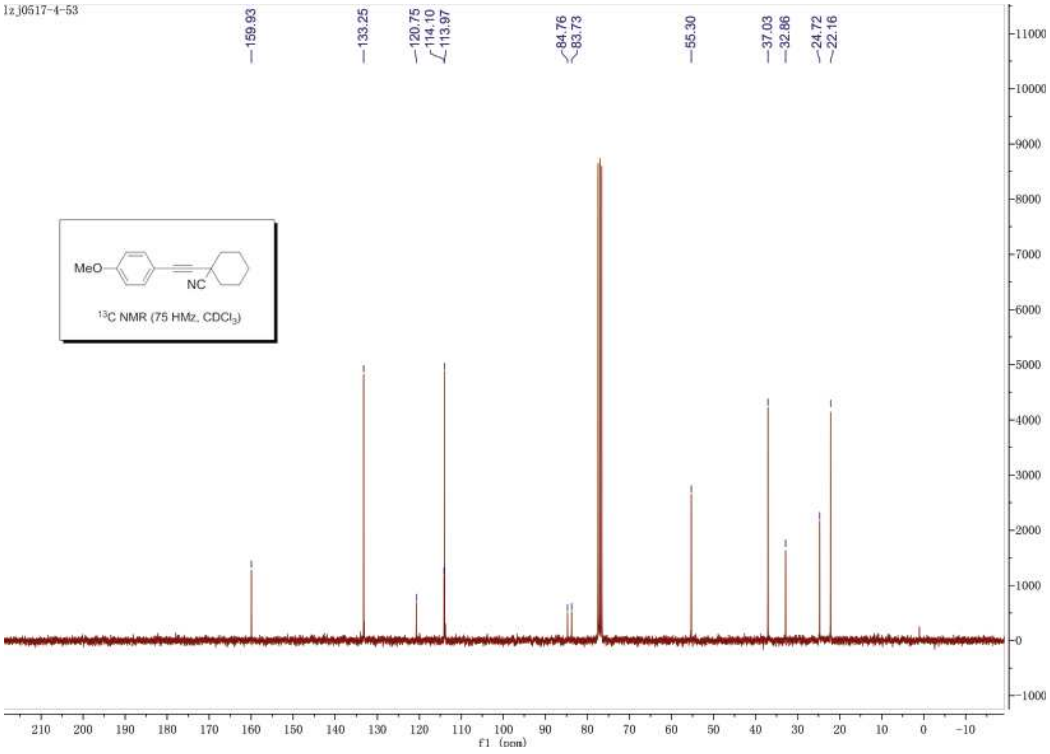
2-Ethyl-4-(4-methoxyphenyl)-2-methylbut-3-ynenitrile (3e)



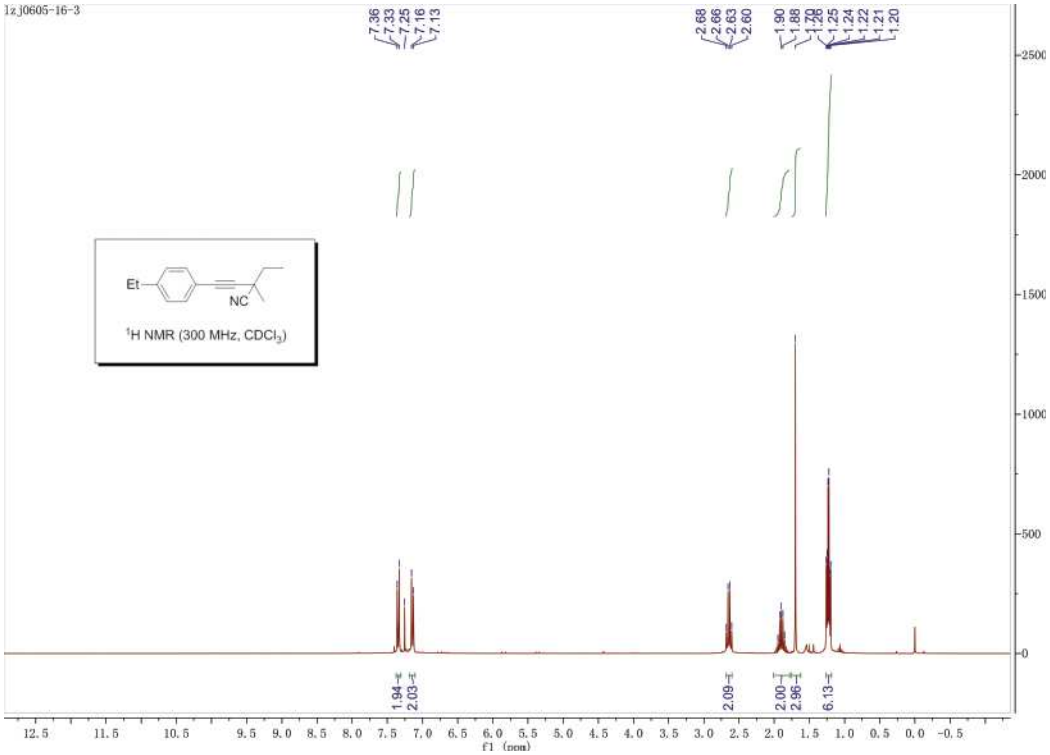


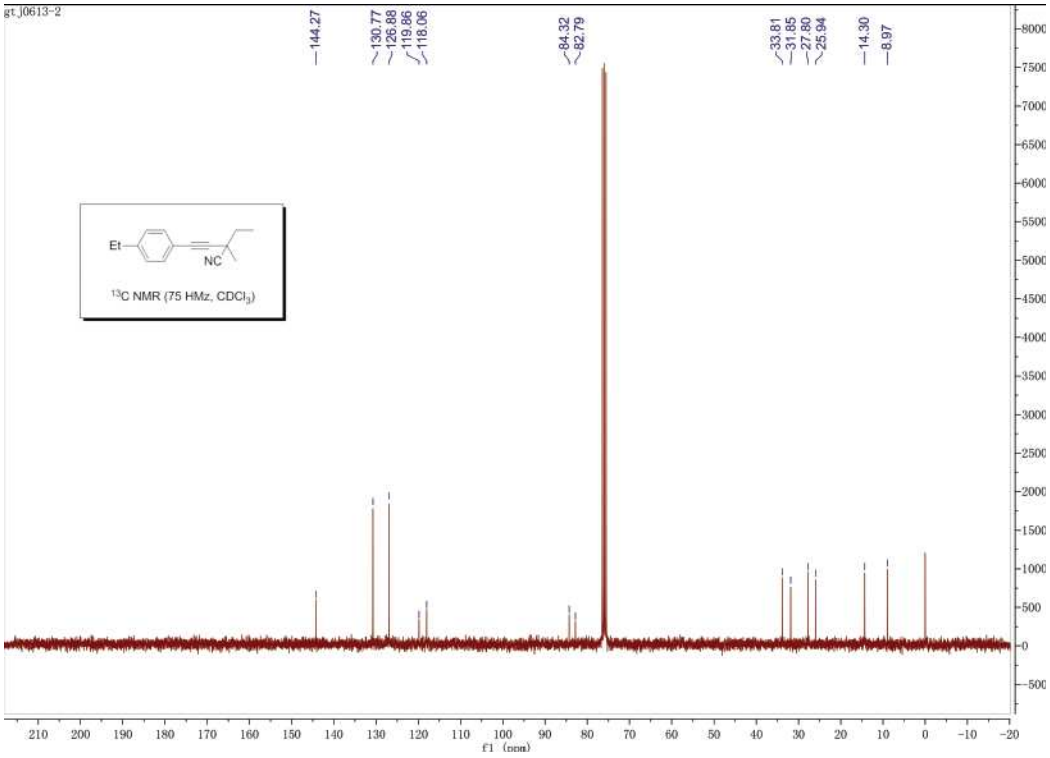
1-((4-Methoxyphenyl)ethynyl)cyclohexanecarbonitrile (3f)



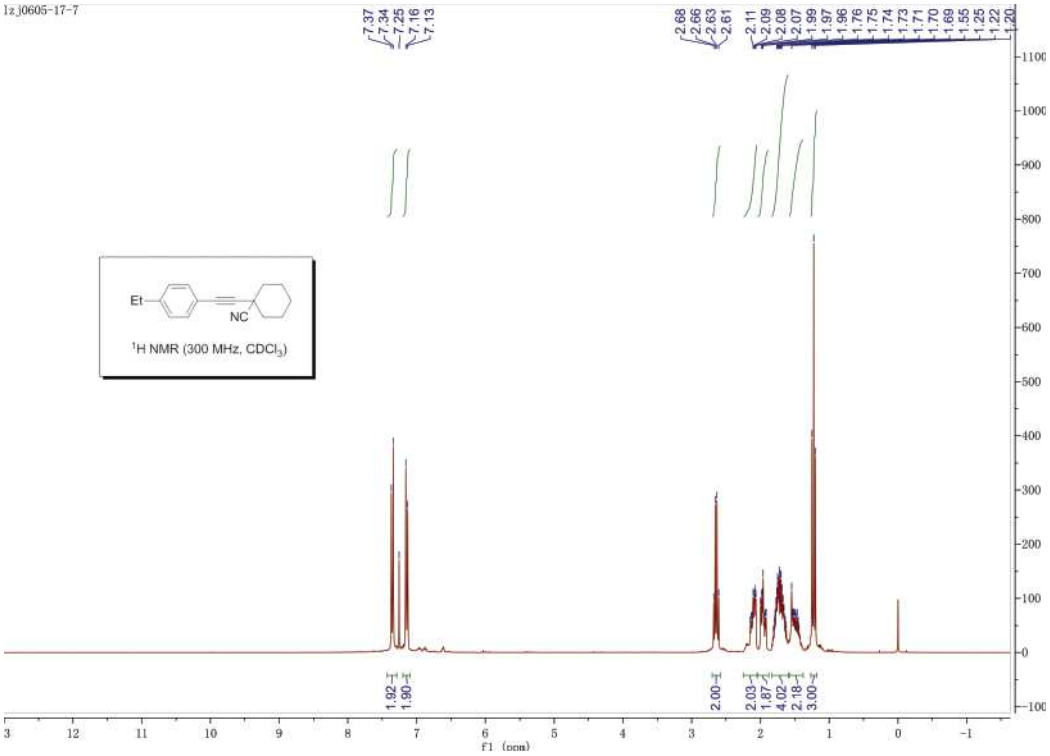


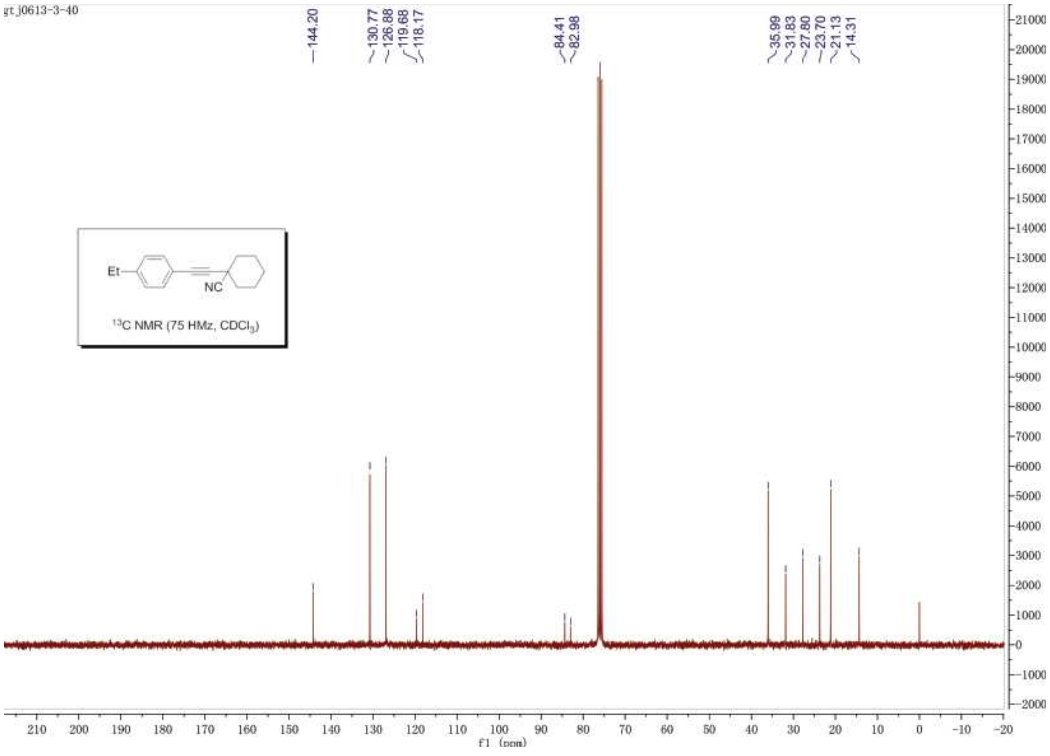
2-Ethyl-4-(4-ethylphenyl)-2-methylbut-3-ynenitrile (3g)



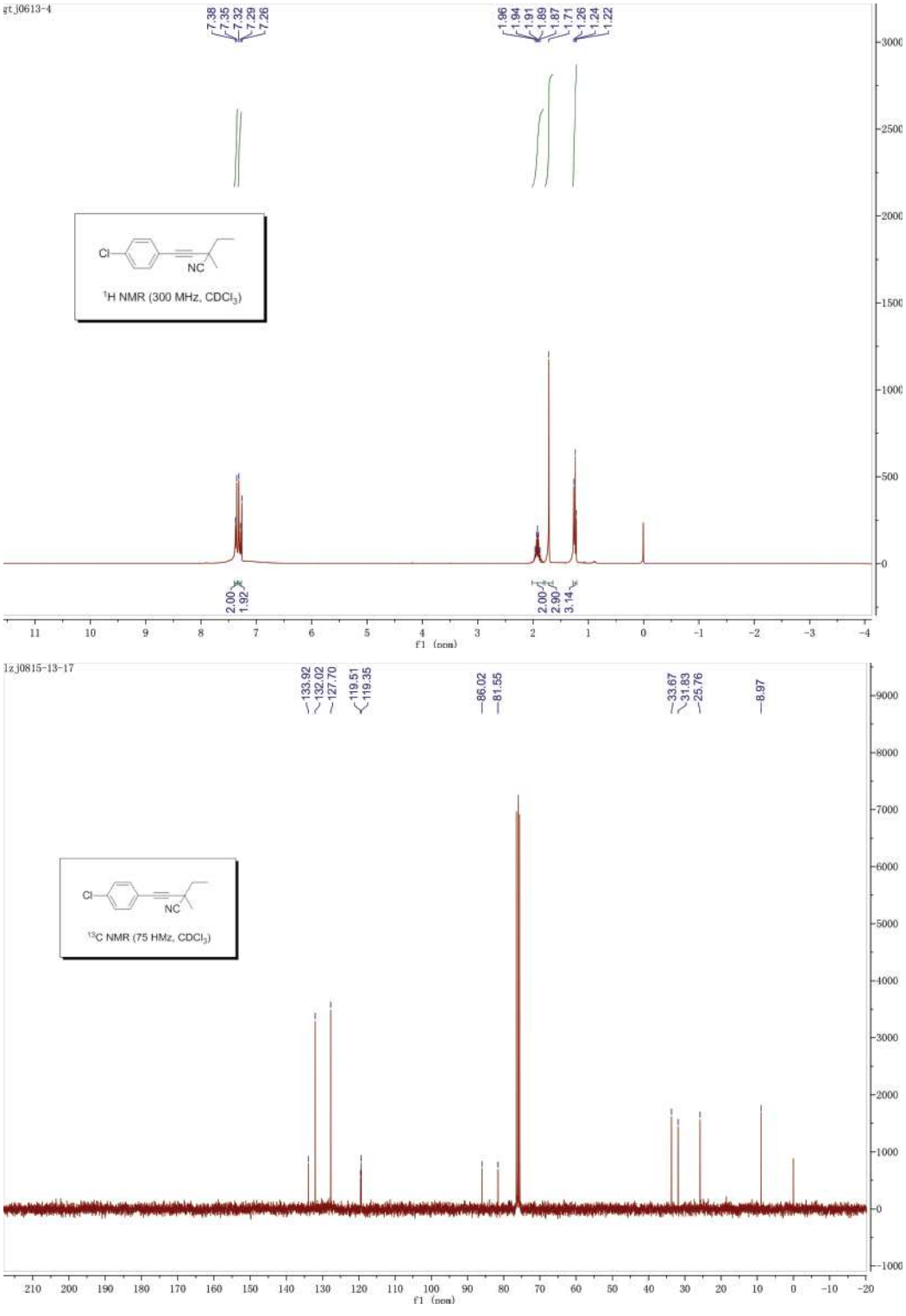


1-((4-Ethylphenyl)ethynyl)cyclohexanecarbonitrile (3h)

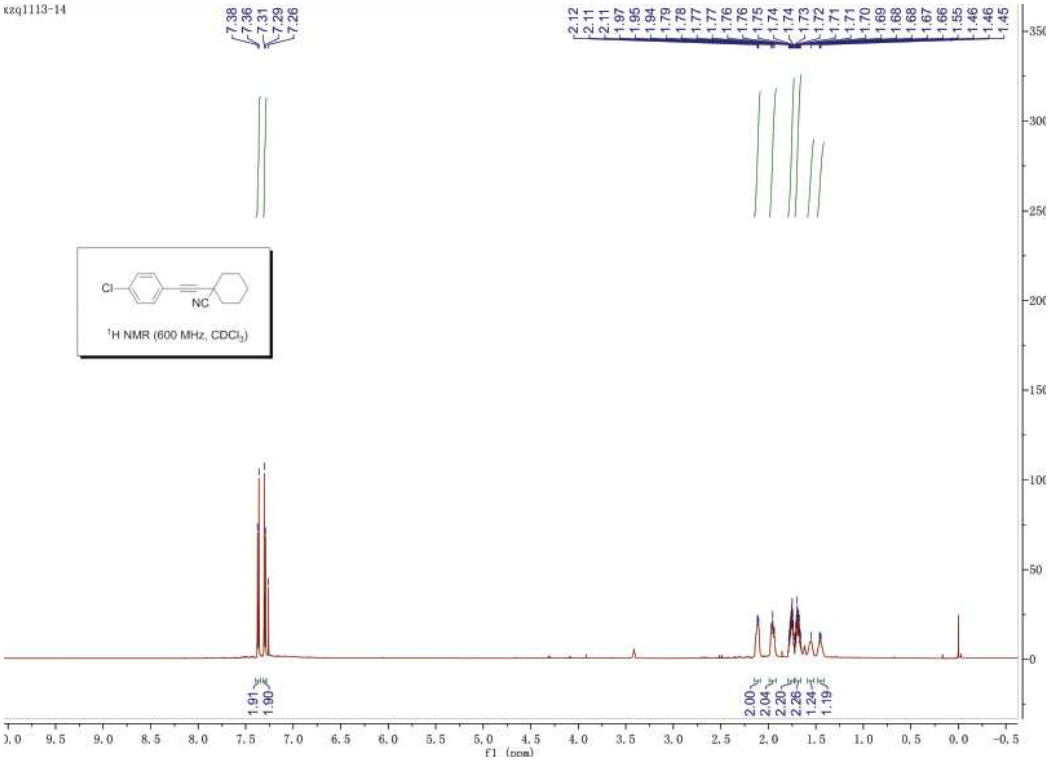


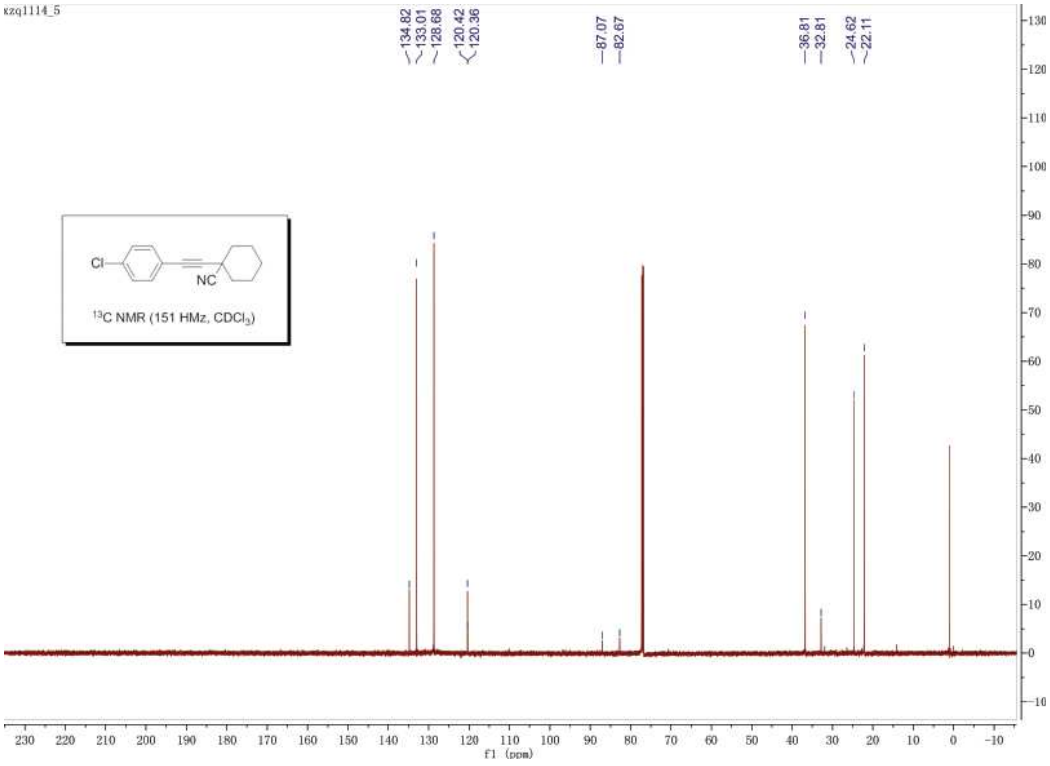


4-(4-Chlorophenyl)-2-ethyl-2-methylbut-3-ynenitrile (3i)

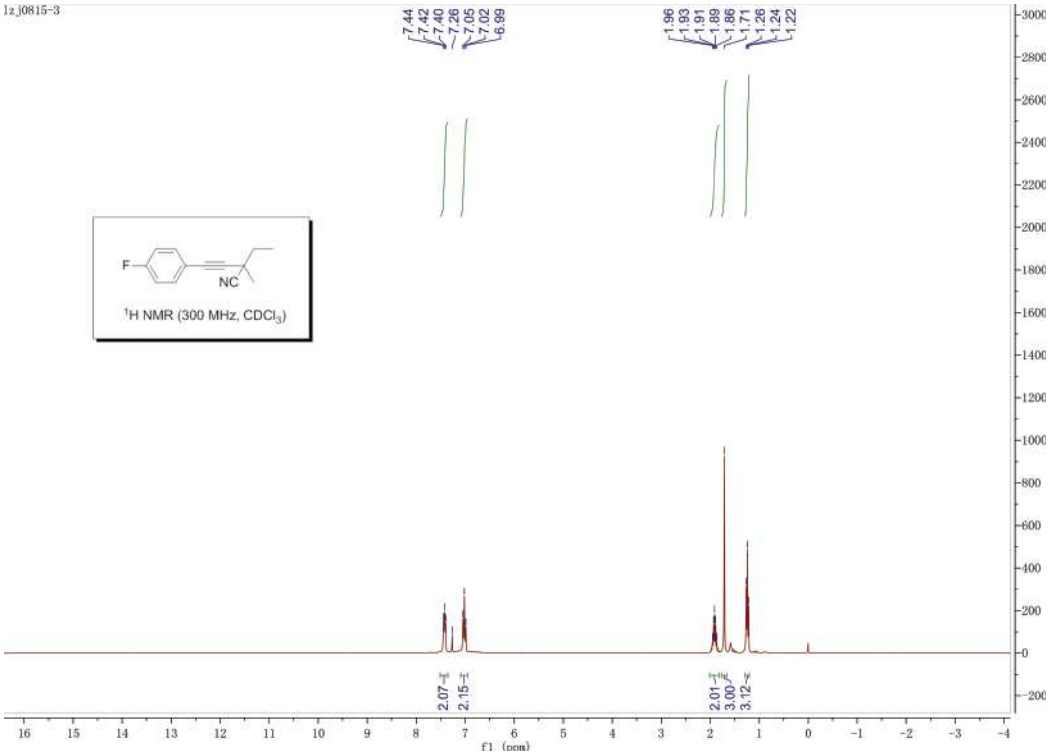


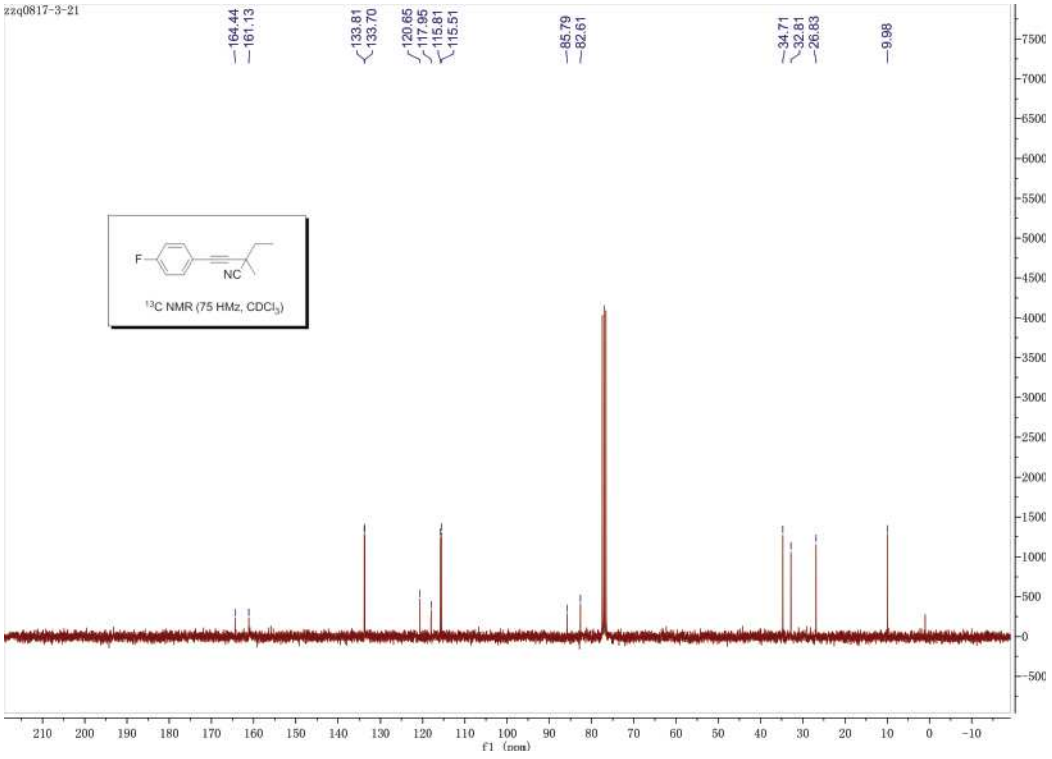
1-((4-Chlorophenyl)ethynyl)cyclohexanecarbonitrile (3j)



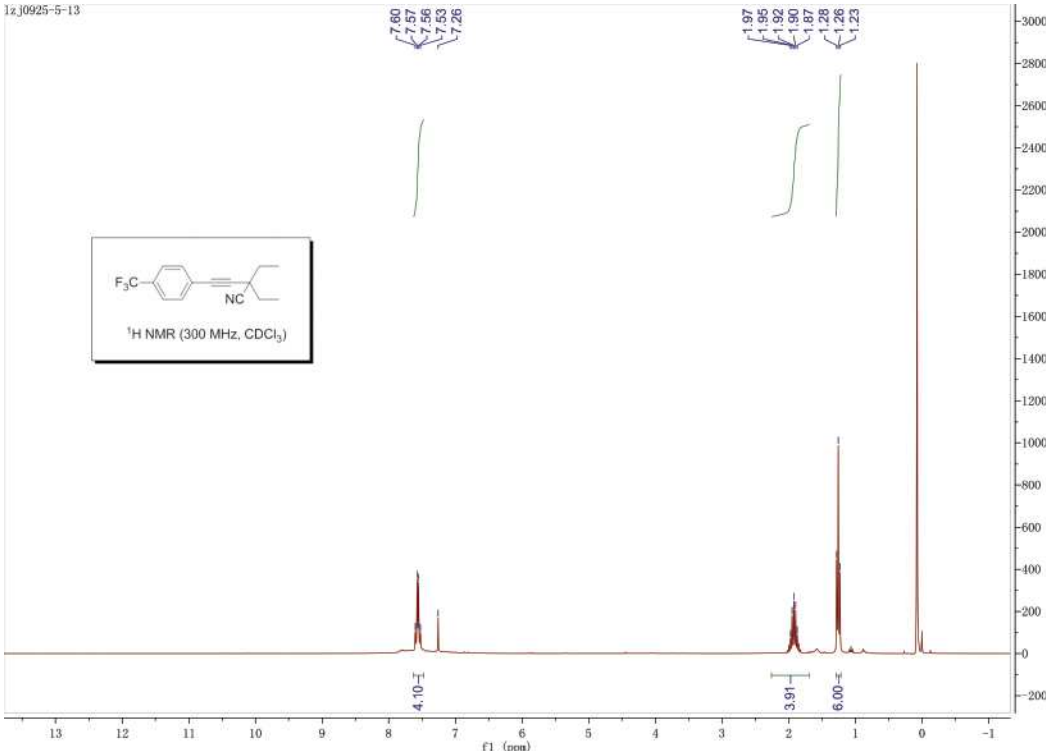


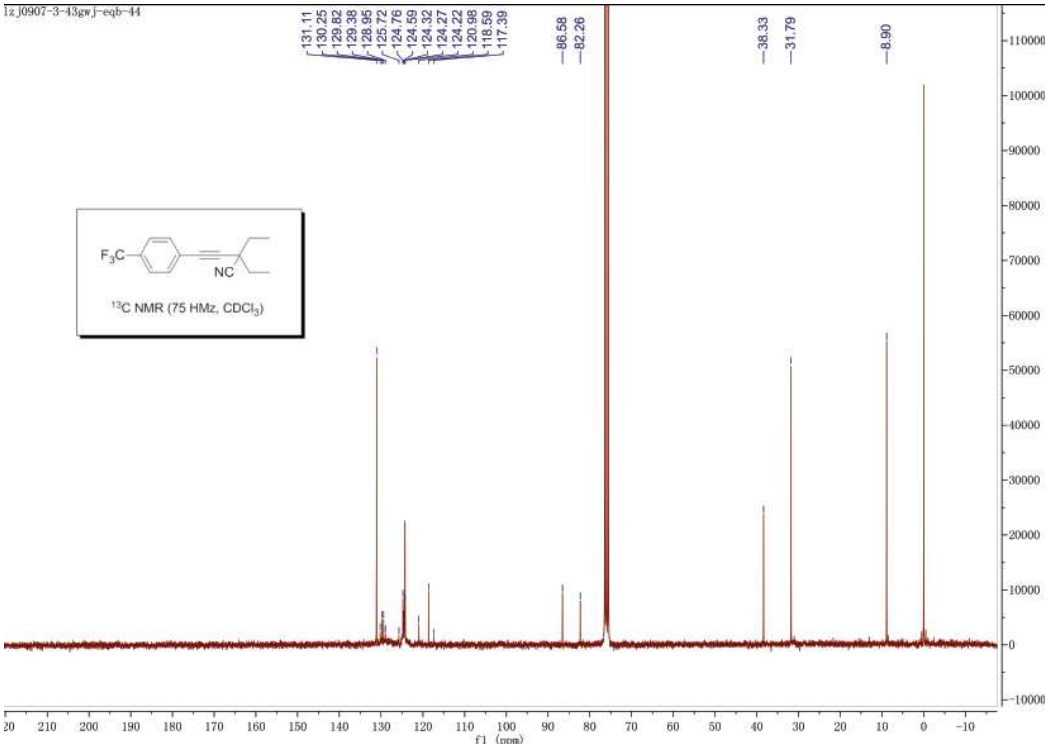
2-Ethyl-4-(4-fluorophenyl)-2-methylbut-3-ynenitrile (3k)



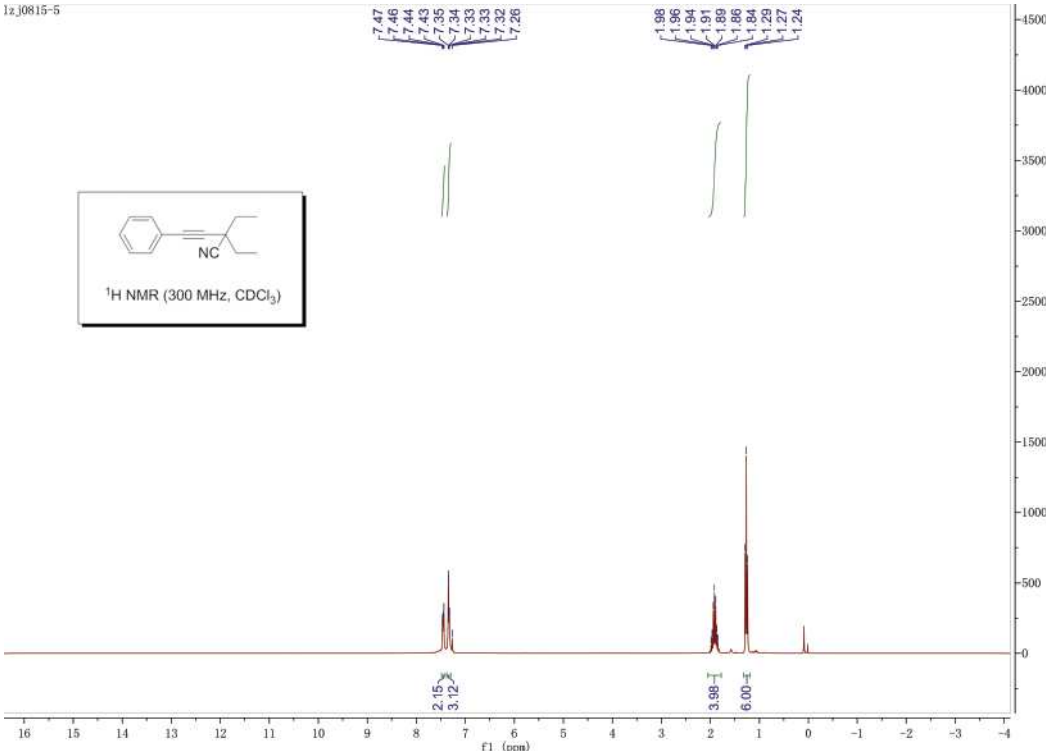


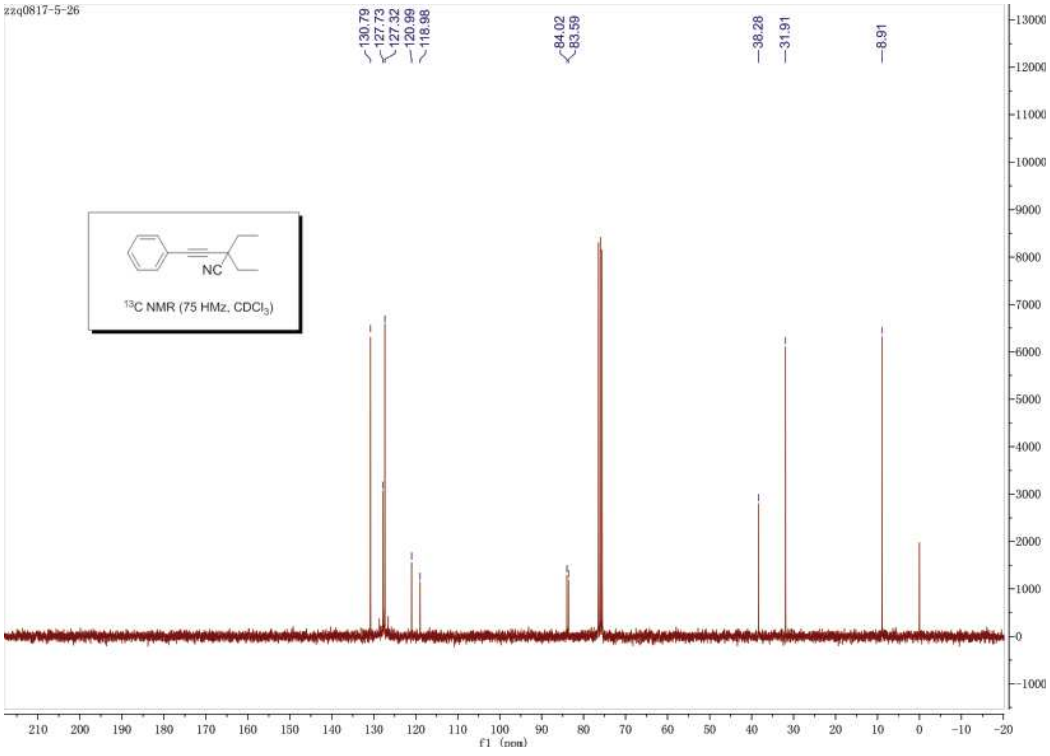
2,2-Diethyl-4-(4-(trifluoromethyl)phenyl)but-3-ynenitrile (3l)



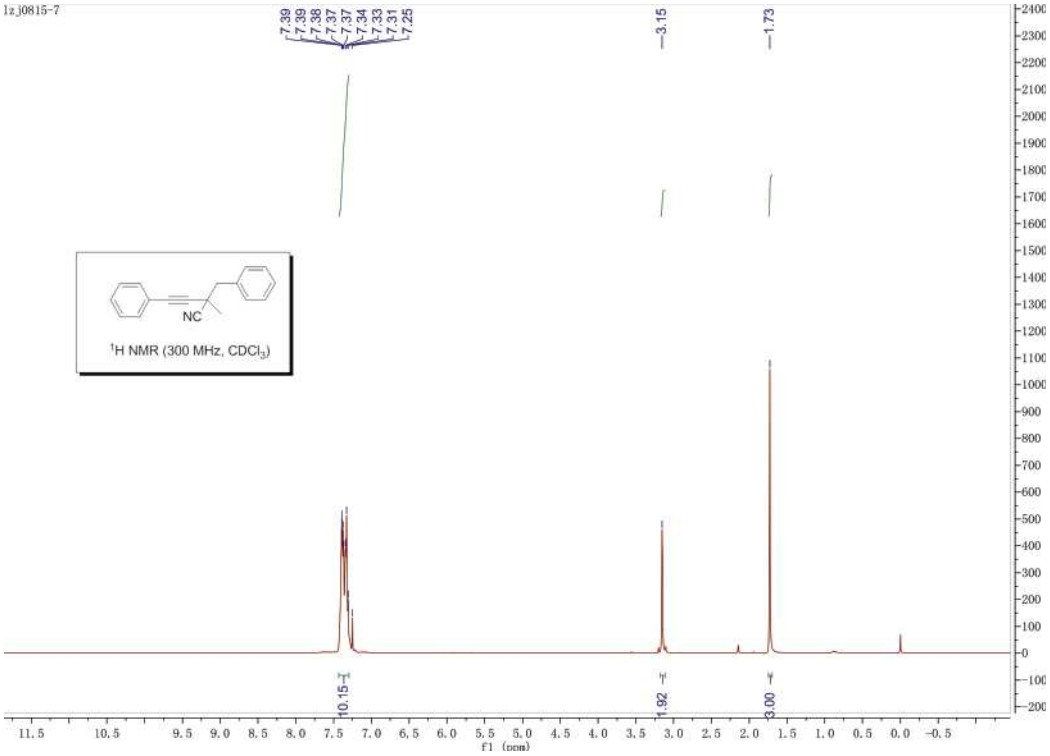


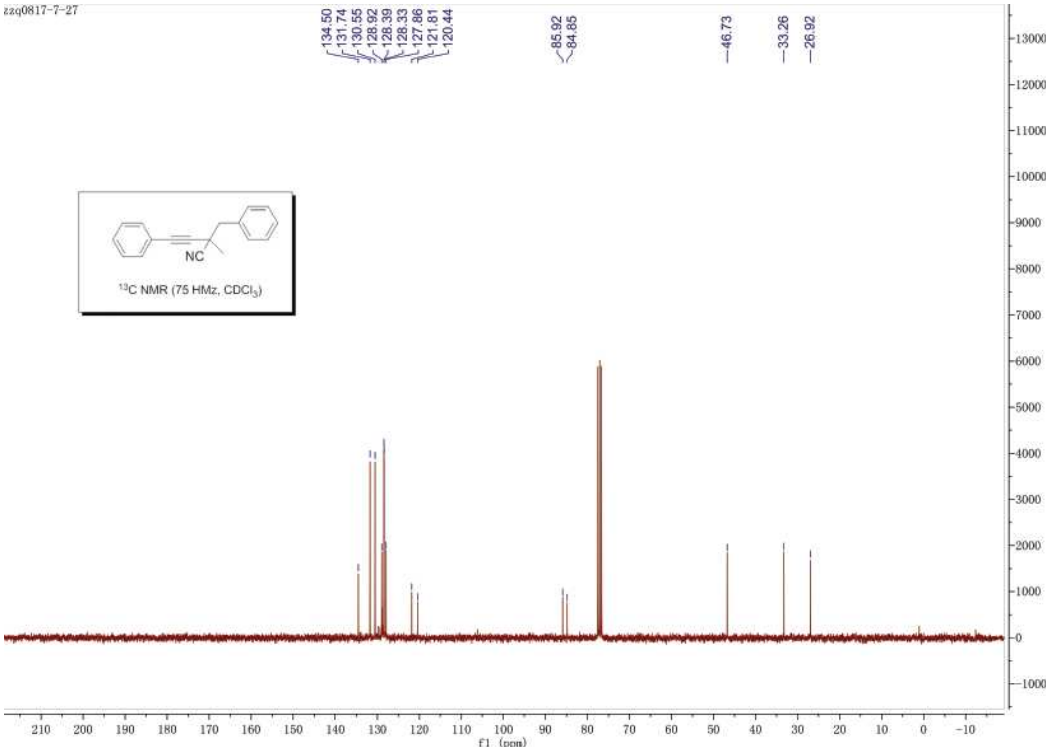
2,2-Diethyl-4-phenylbut-3-ynenitrile (3m)



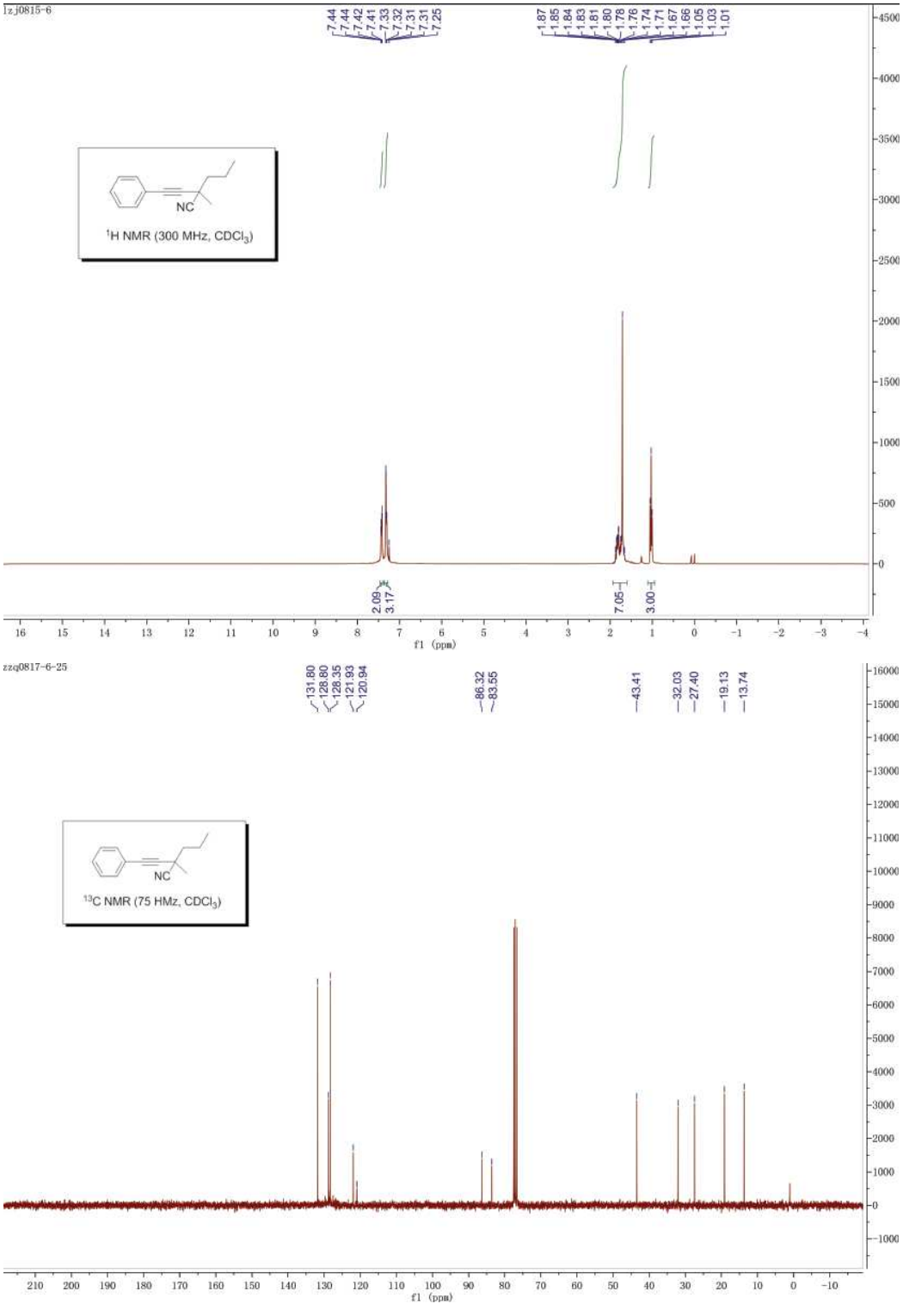


2-Benzyl-2-methyl-4-phenylbut-3-ynenitrile (3n)

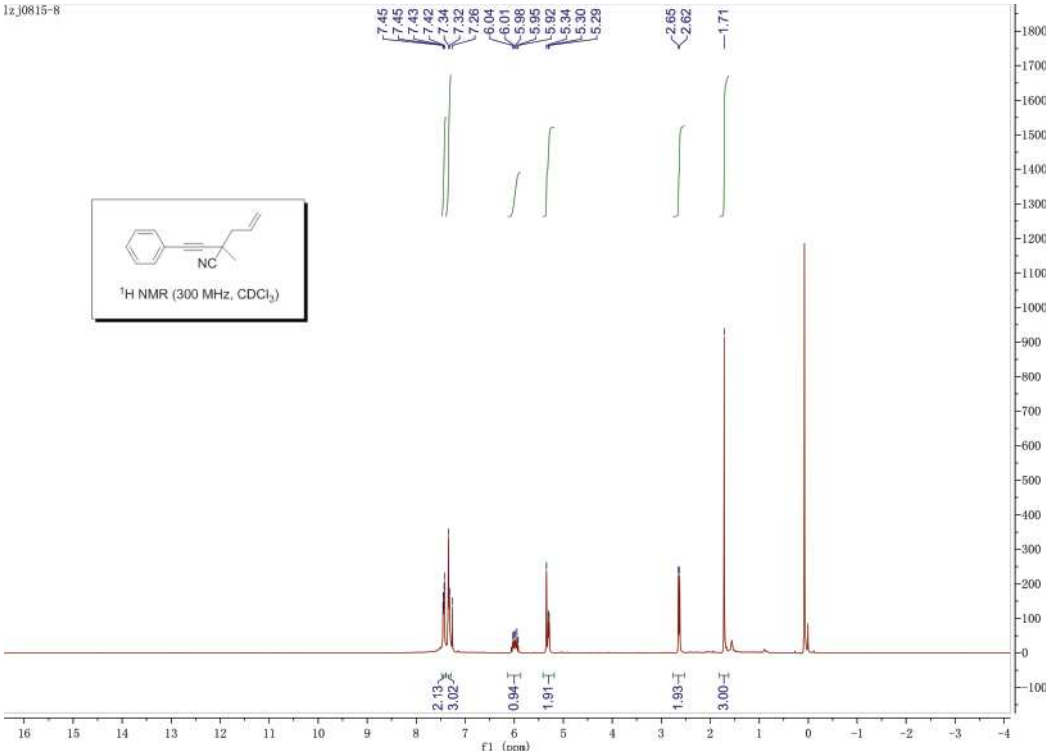


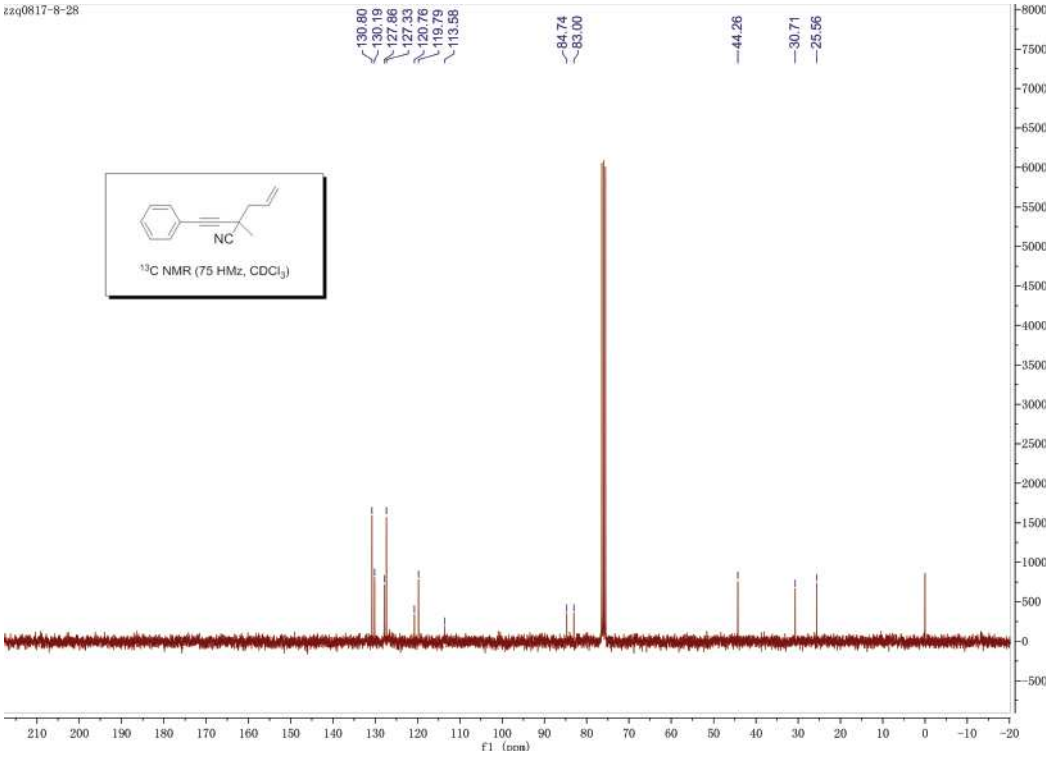


2-Methyl-2-(phenylethynyl)pentanenitrile (3o)

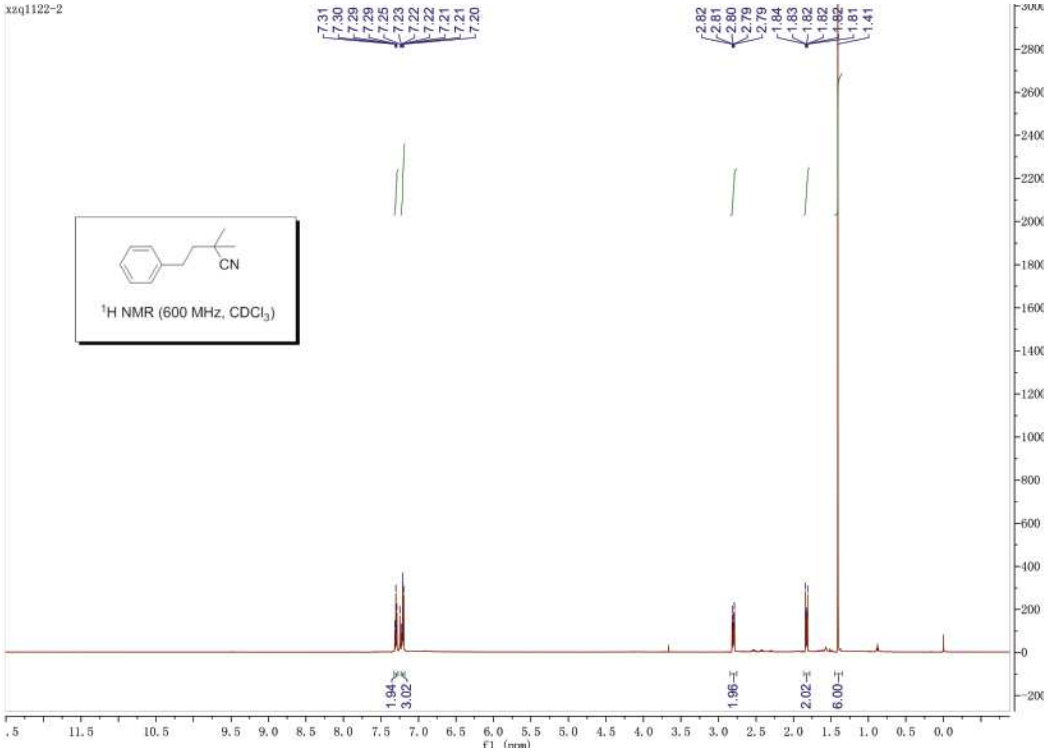


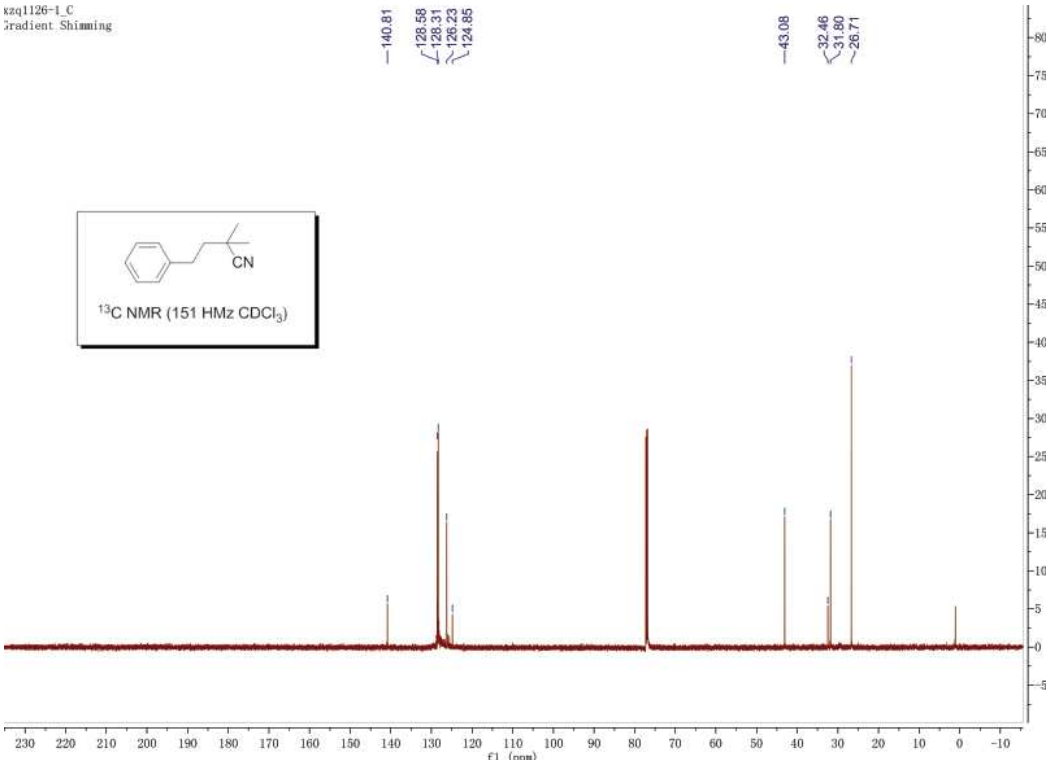
2-Methyl-2-(phenylethynyl)pent-4-enenitrile (3p)



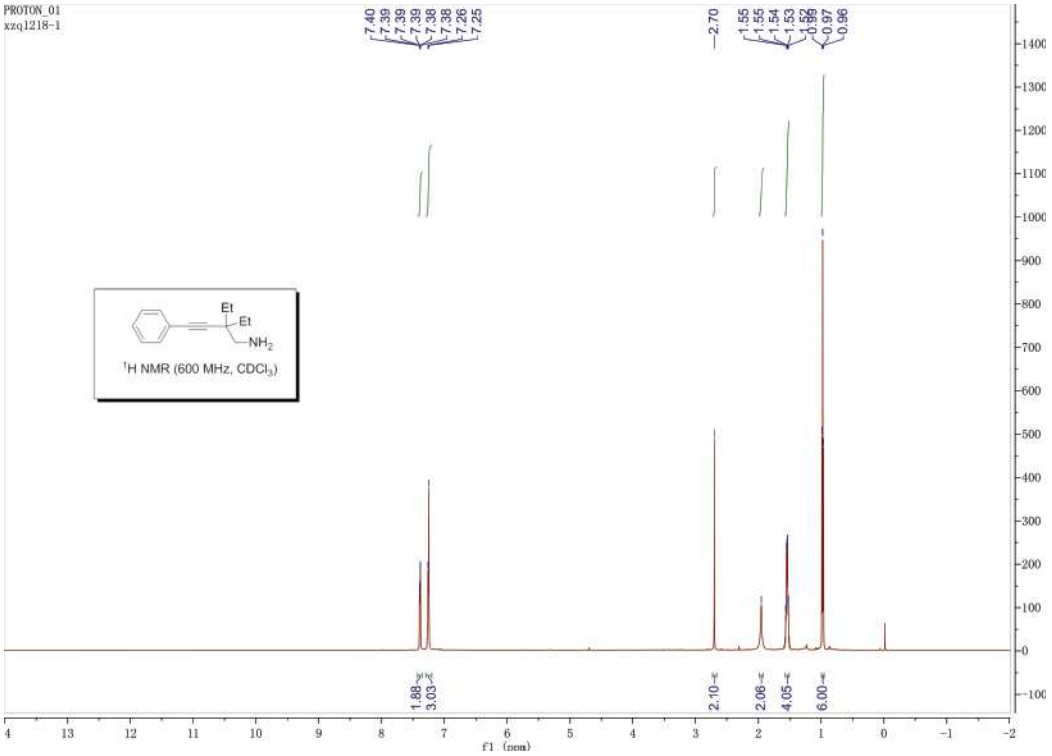


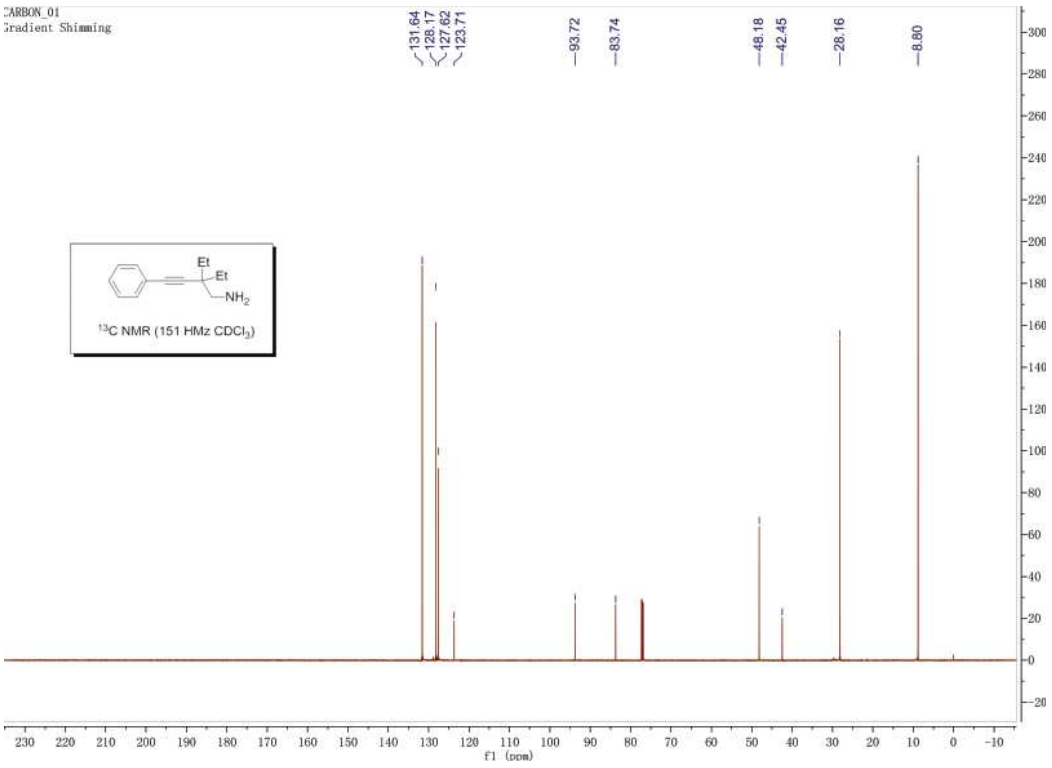
2,2-Dimethyl-4-phenylbutanenitrile (1)



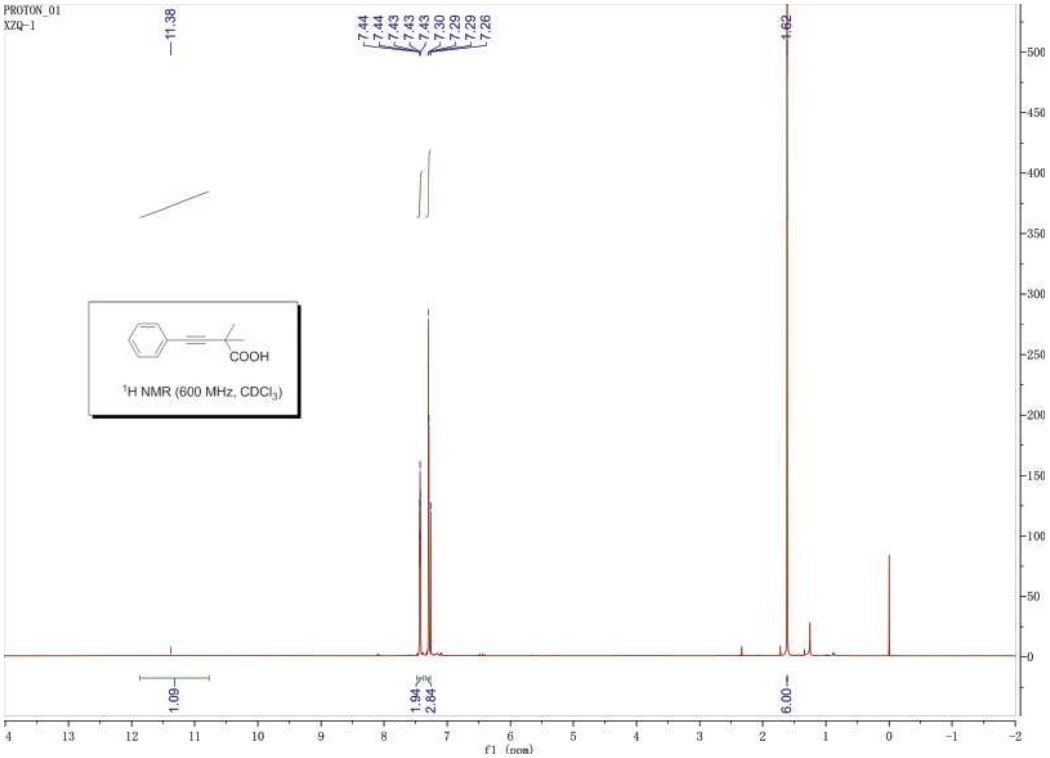


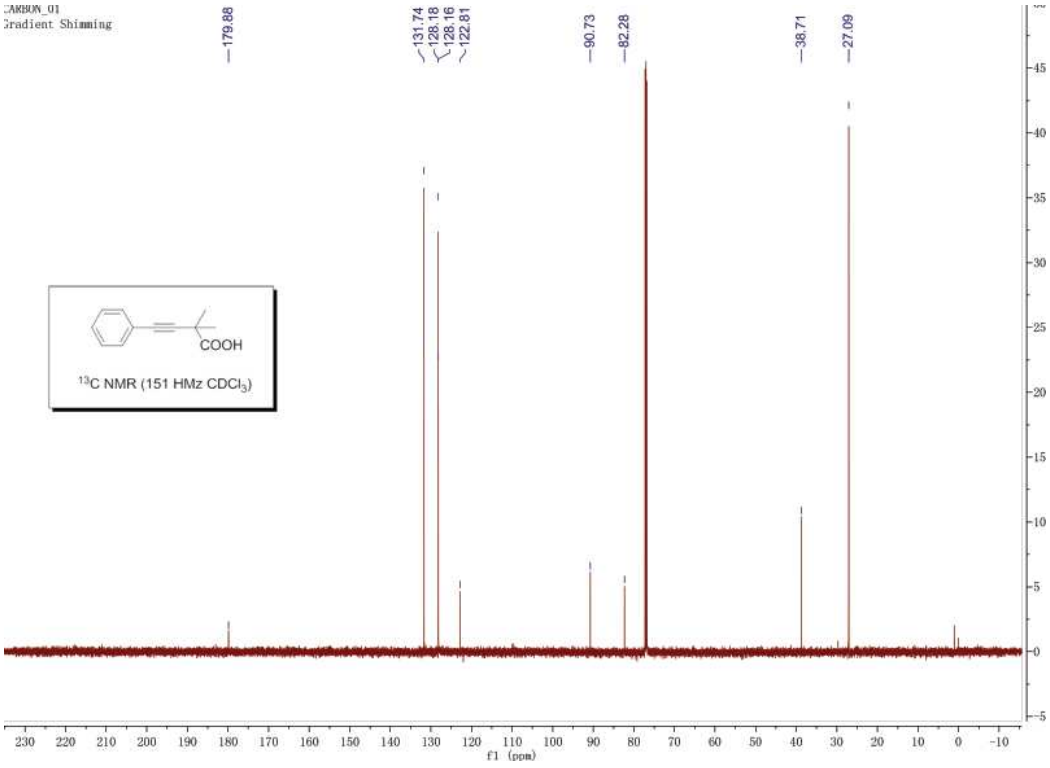
2,2-Diethyl-4-phenylbut-3-yn-1-amine (2)



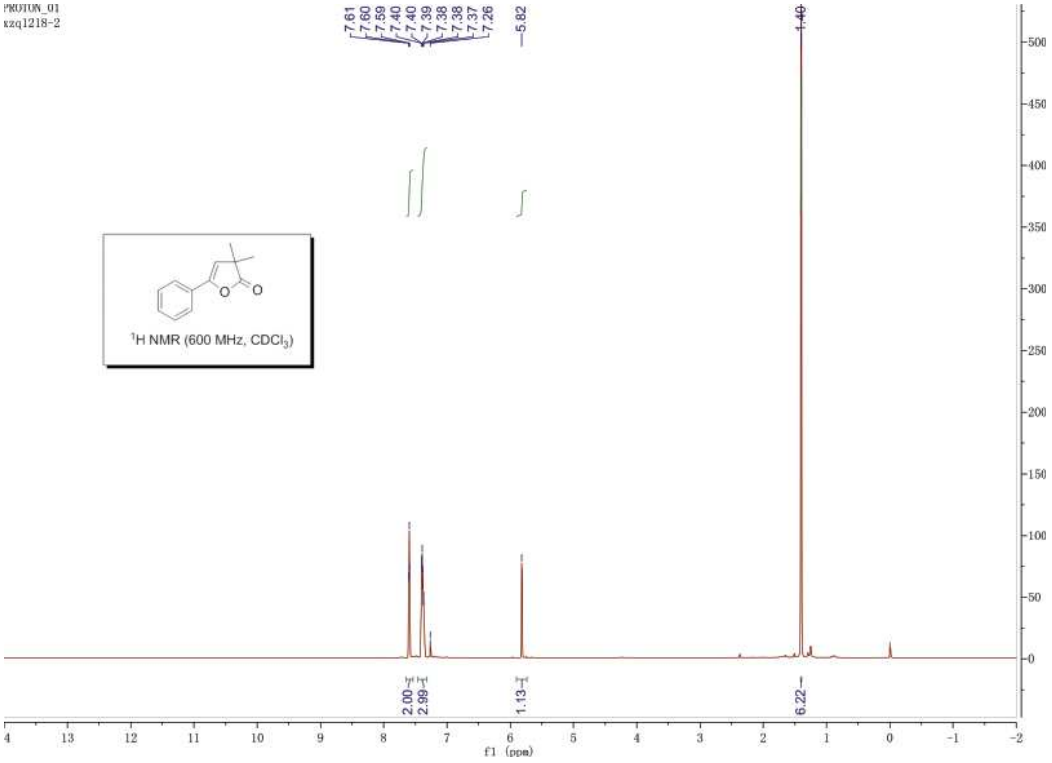


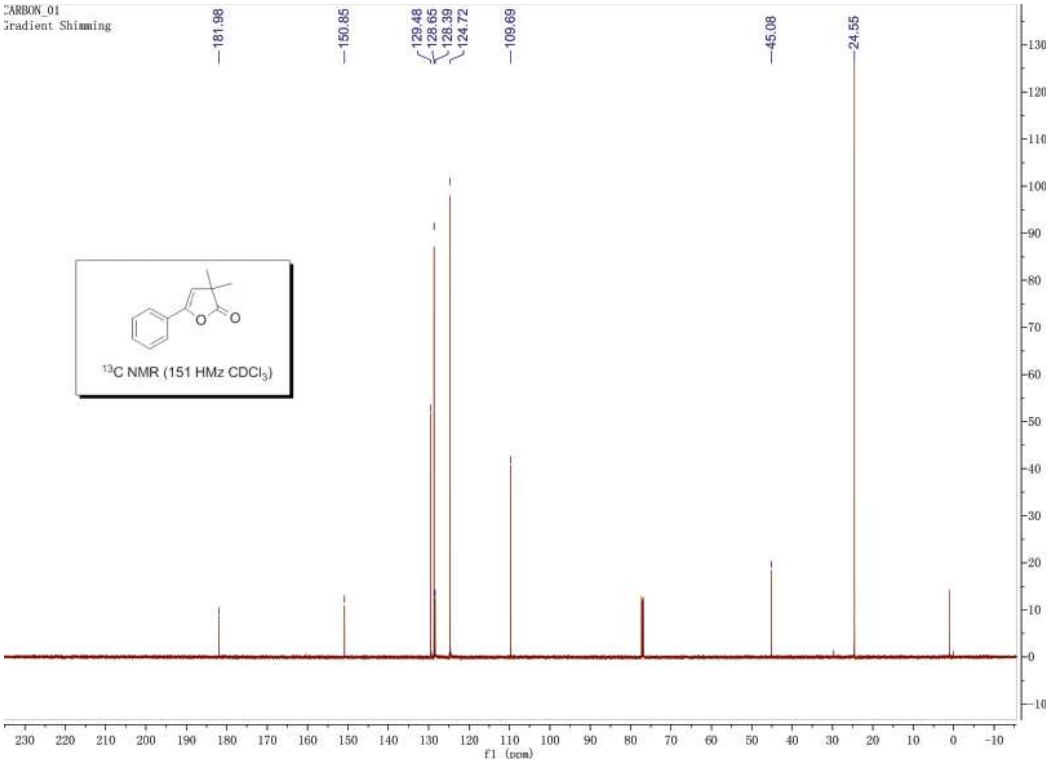
2,2-Dimethyl-4-phenylbut-3-ynoic acid (3)



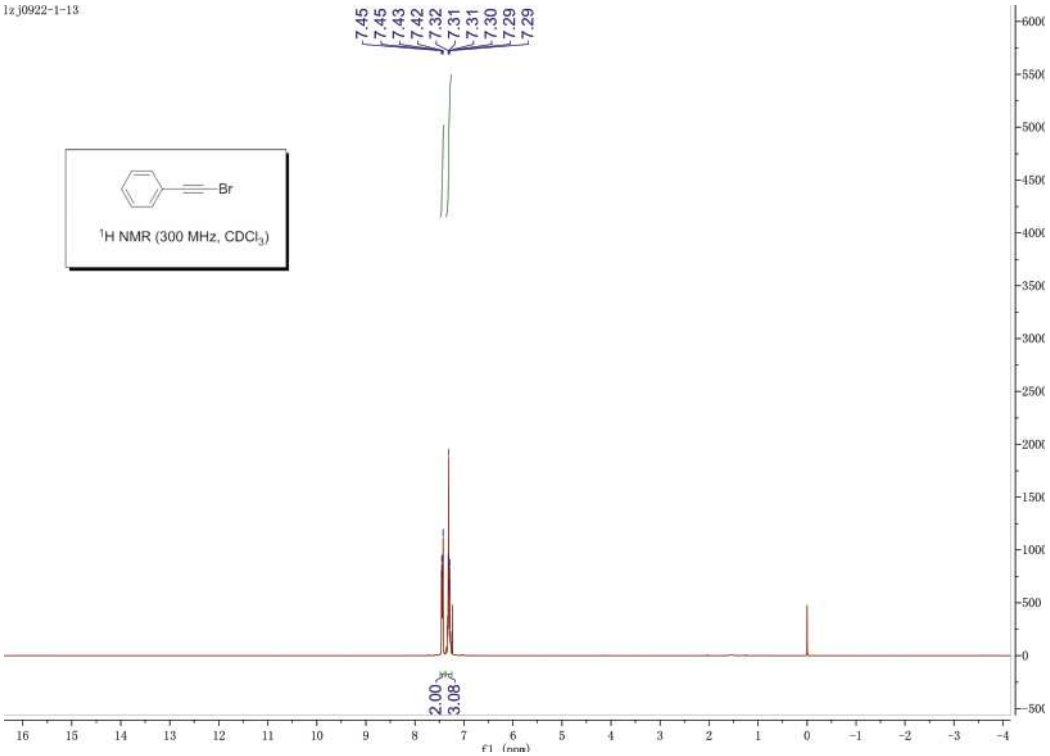


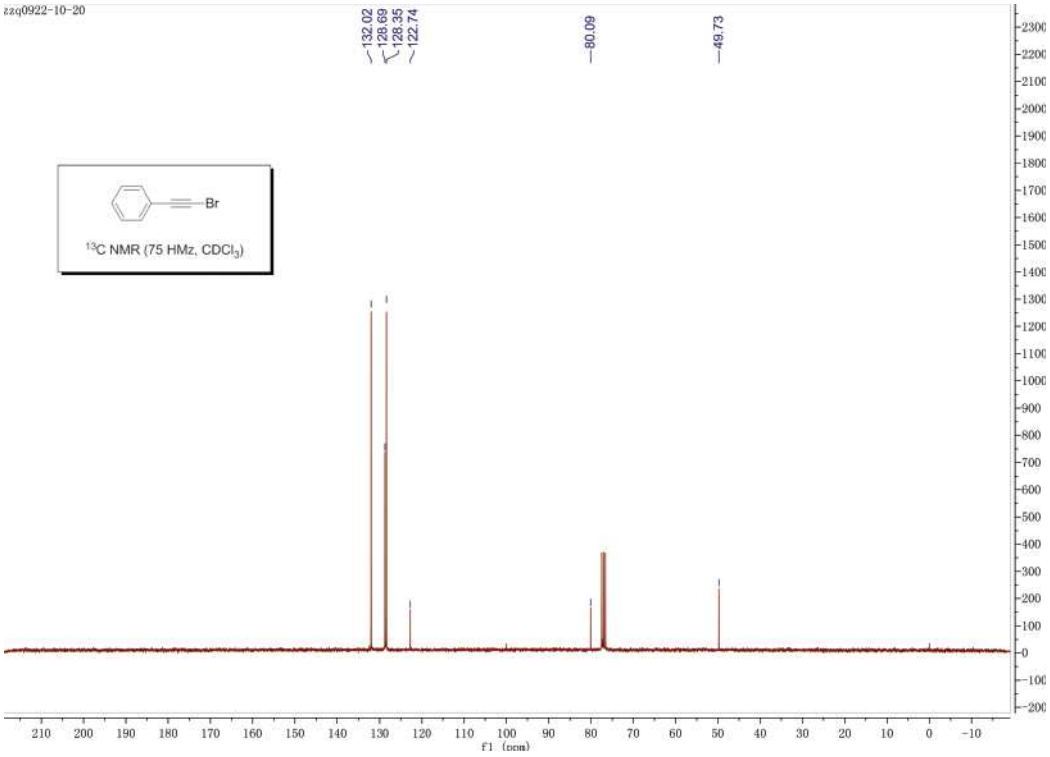
3,3-Dimethyl-5-phenylfuran-2(*3H*)-one (4)



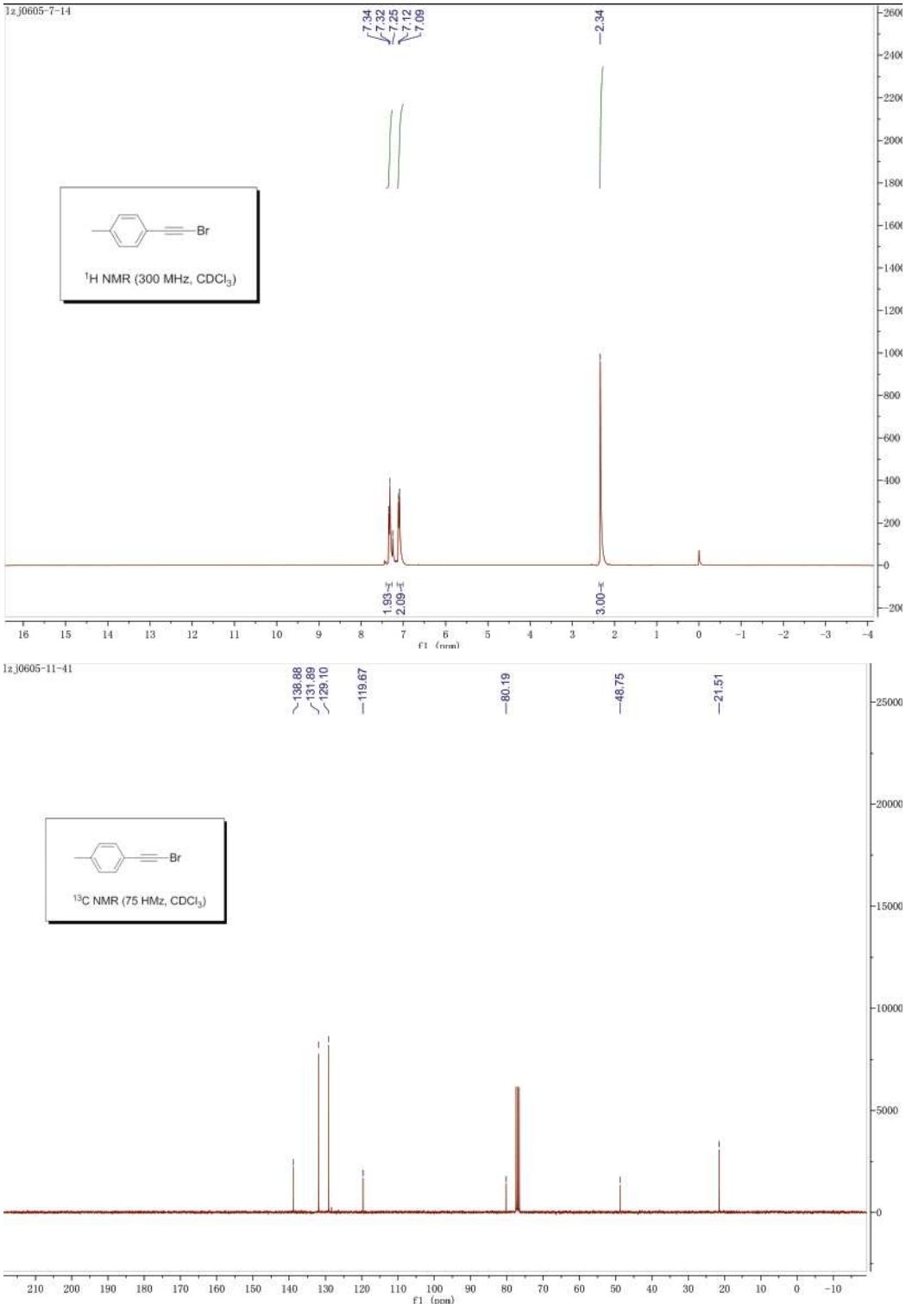


(Bromoethynyl)benzene (t1)

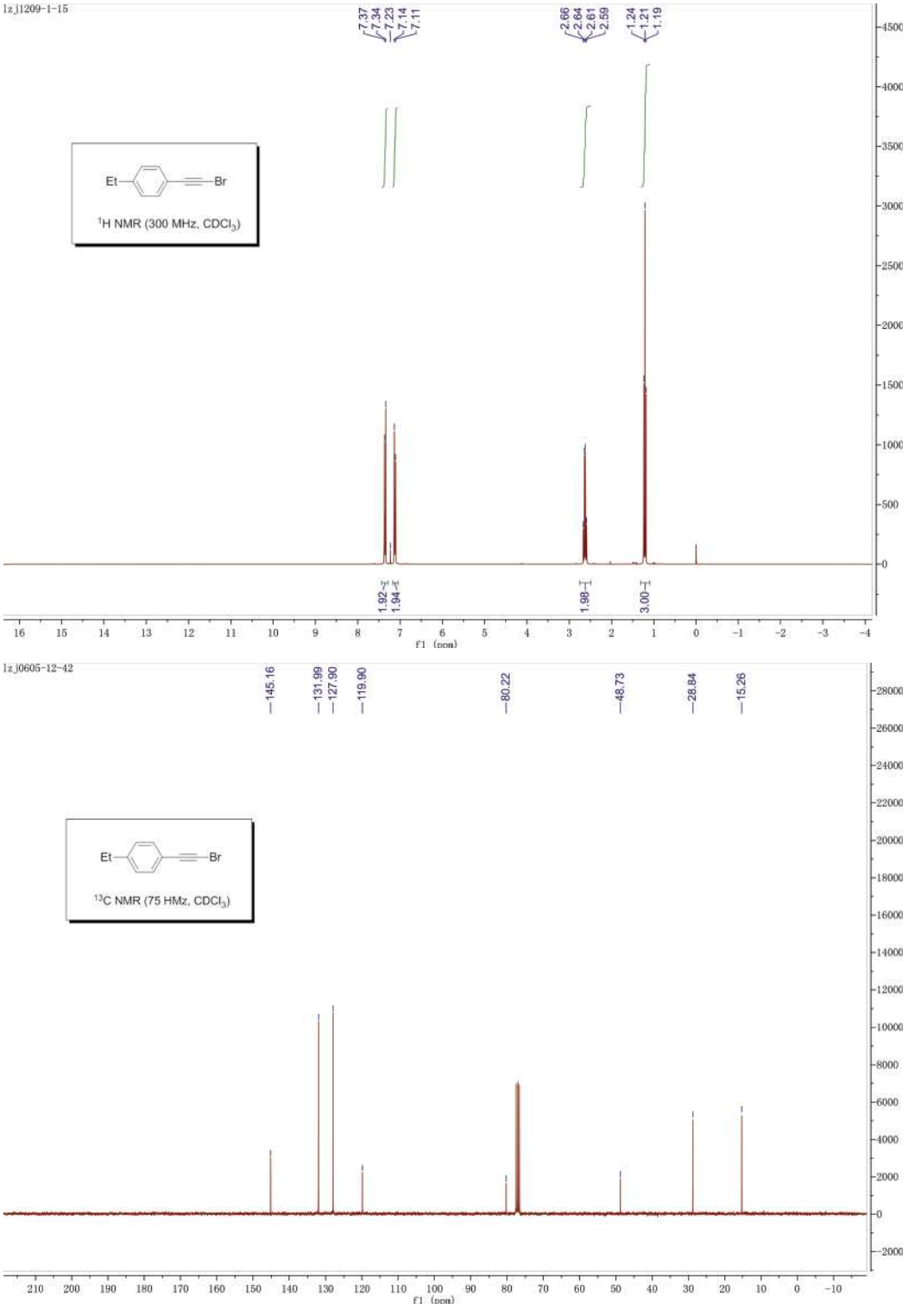




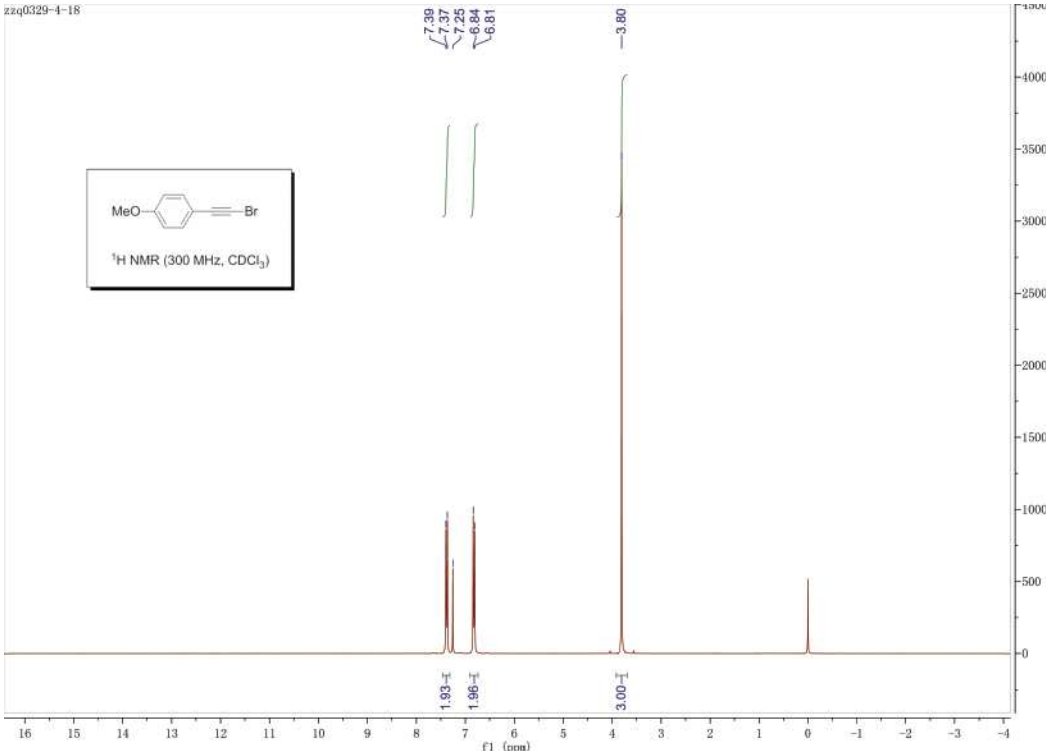
1-(Bromoethynyl)-4-methylbenzene (t2)

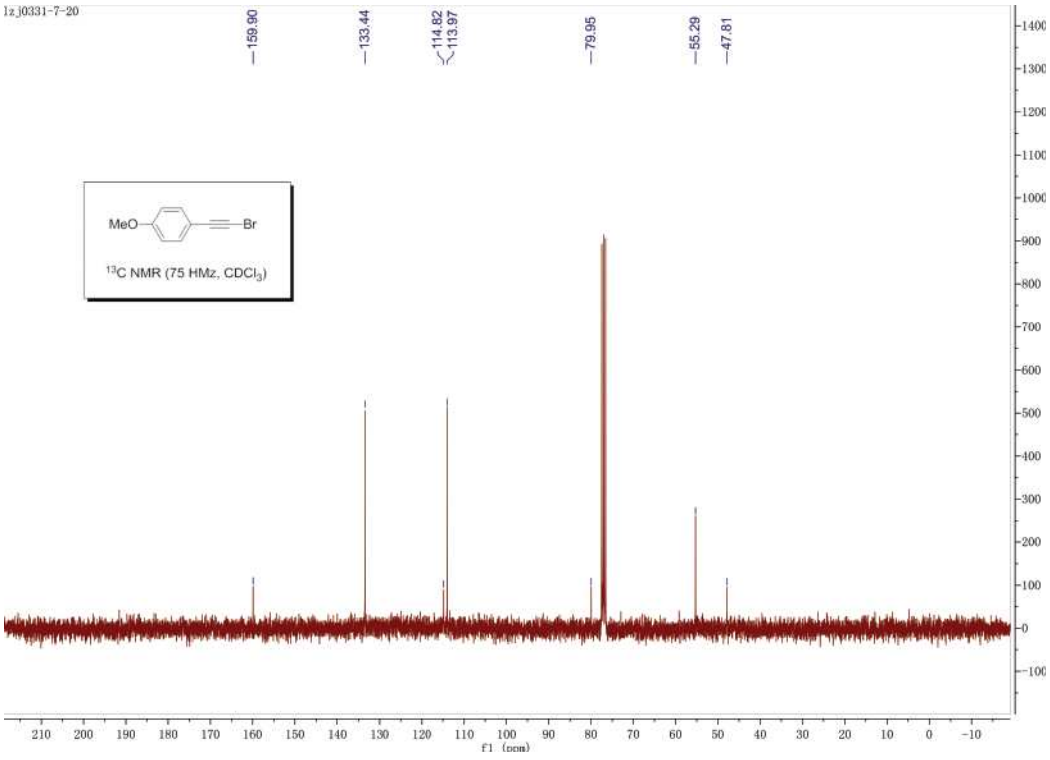


1-(Bromoethynyl)-4-ethylbenzene (t3)

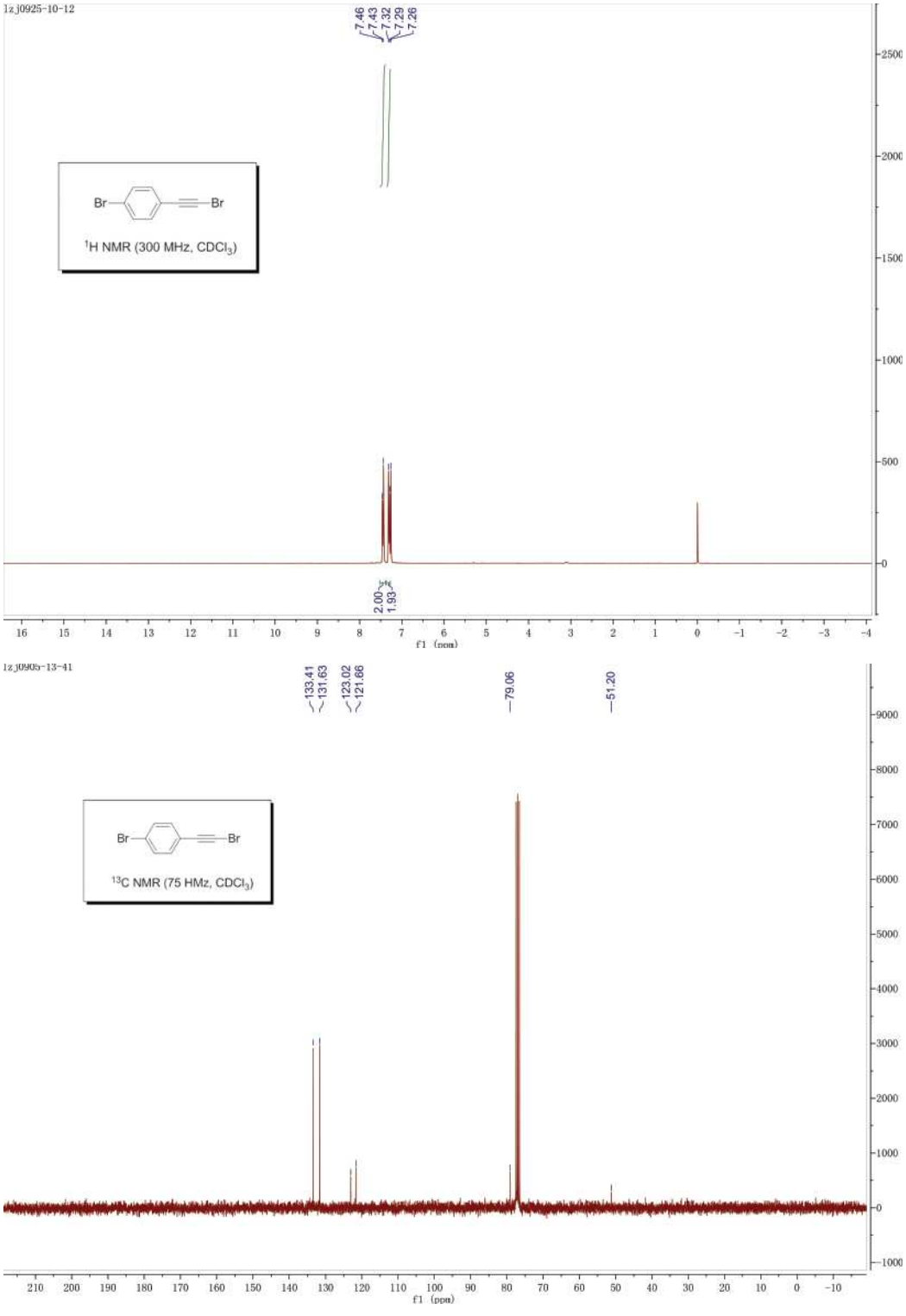


1-(Bromoethynyl)-4-methoxybenzene (t4)

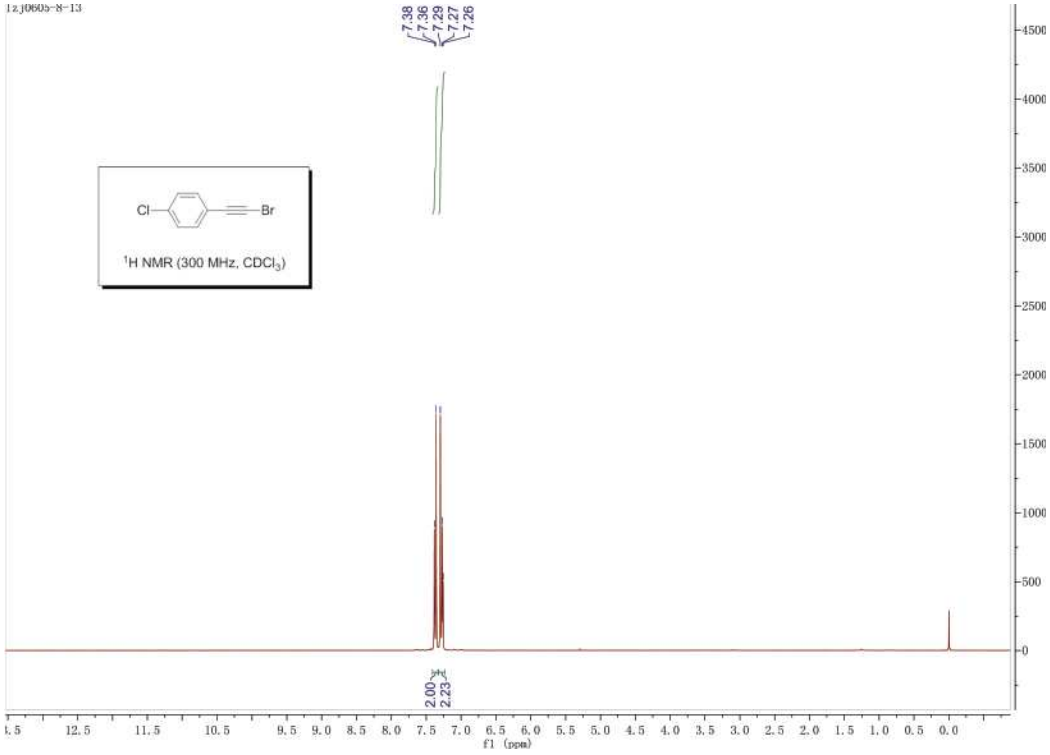


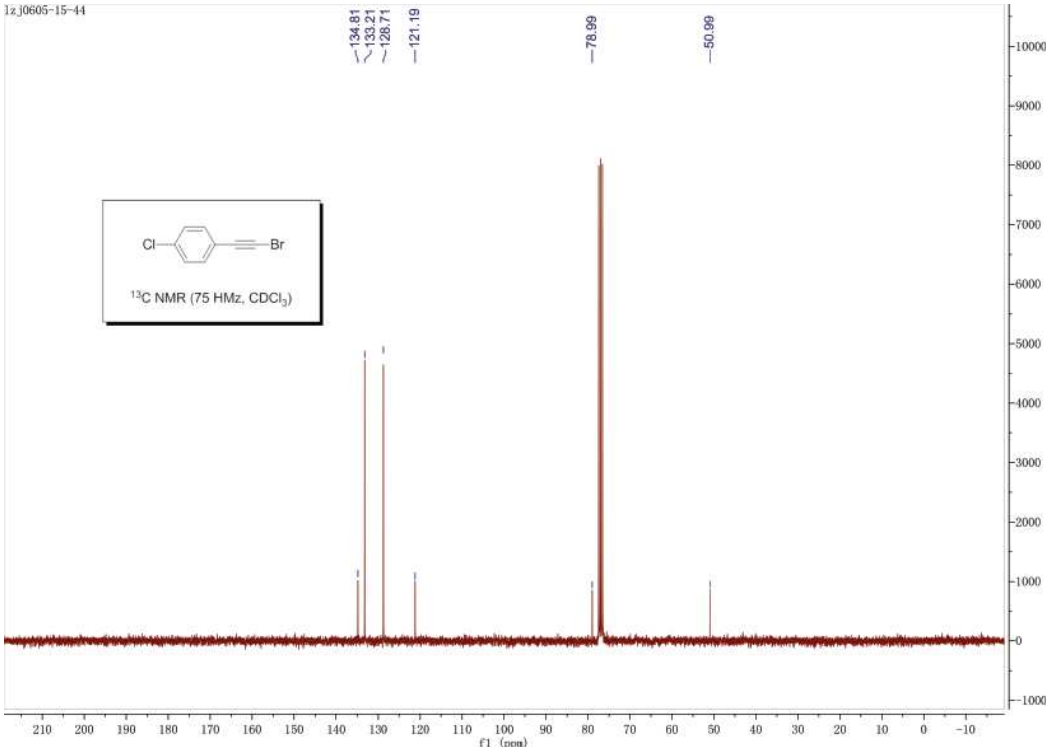


1-(Bromoethynyl) -4-bromobenzene (t5)

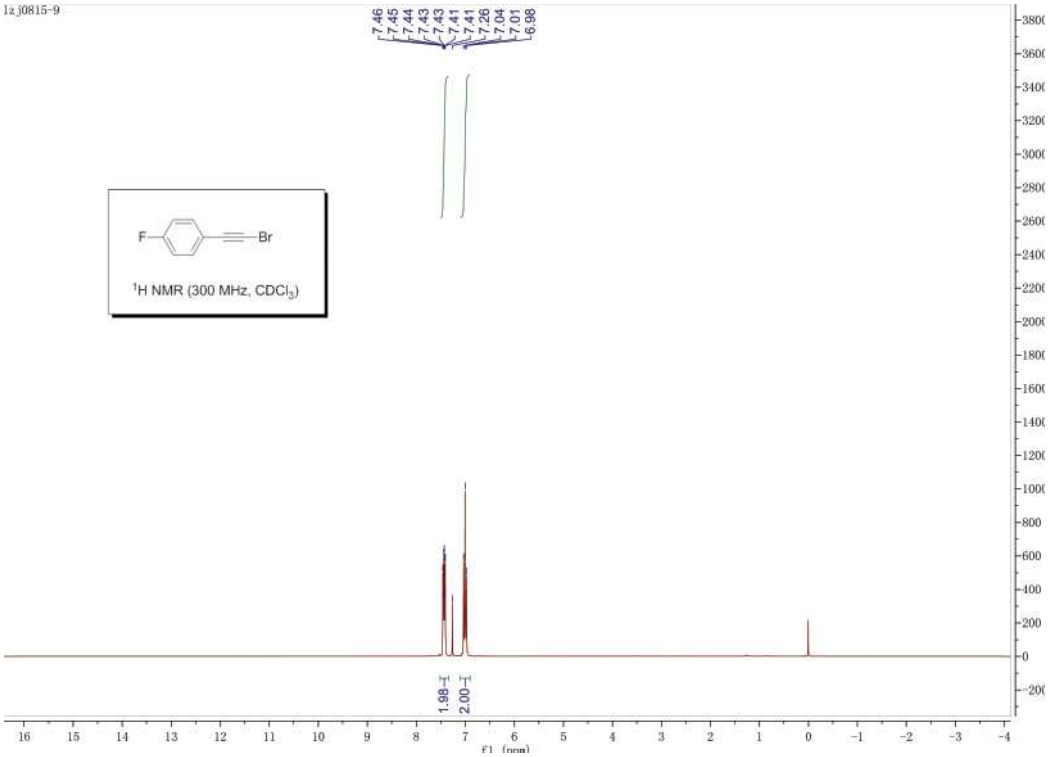


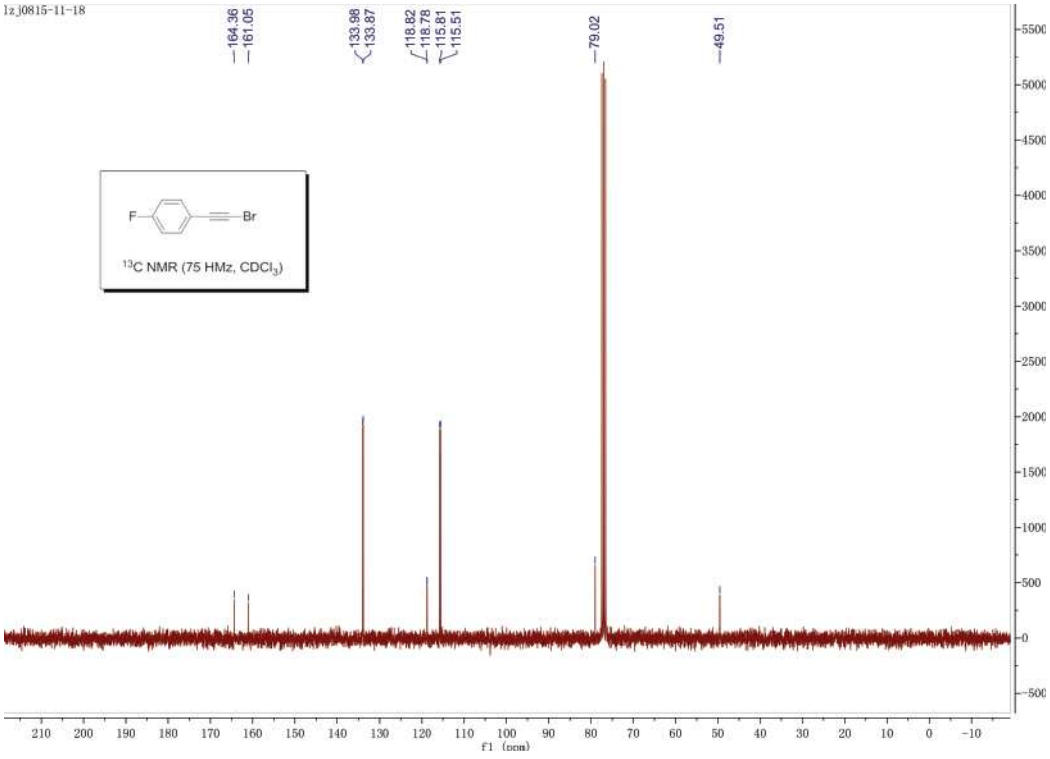
1-(Bromoethynyl)-4-chlorobenzene (t6)



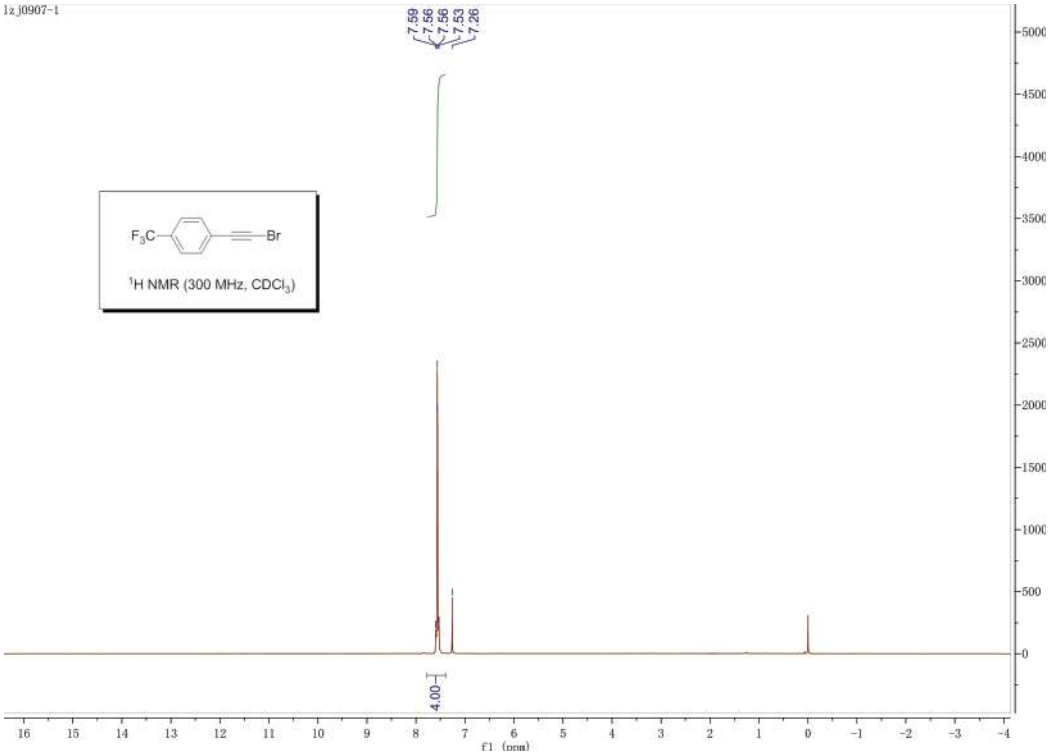


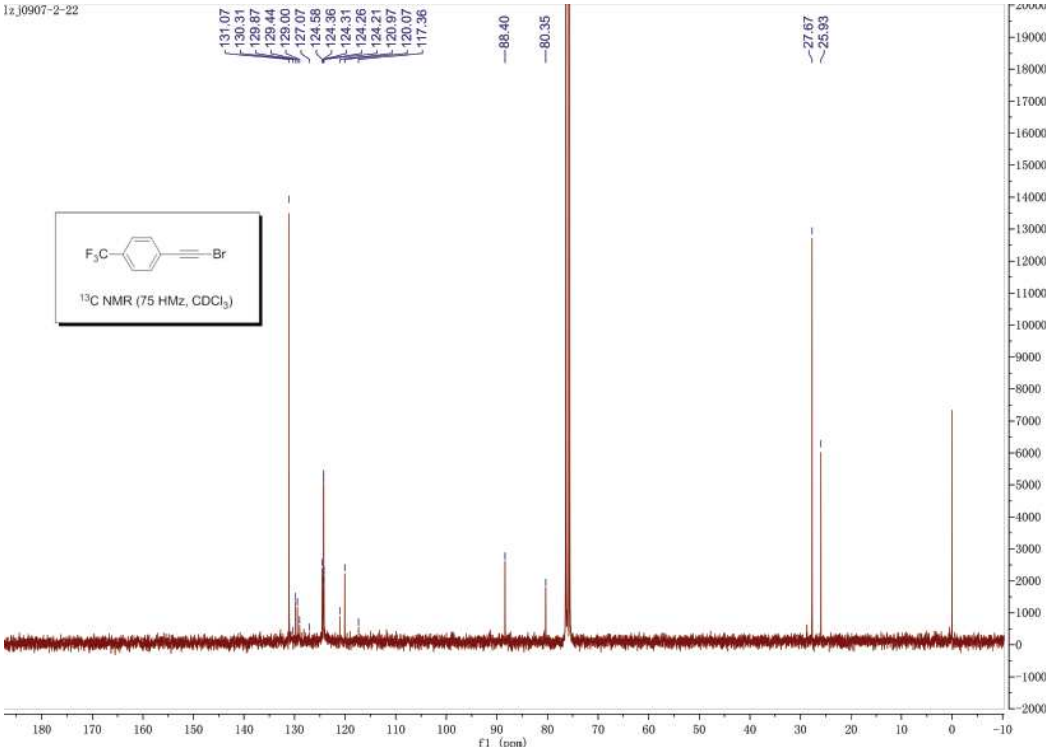
1-(Bromoethynyl)-4-fluorobenzene (t7)



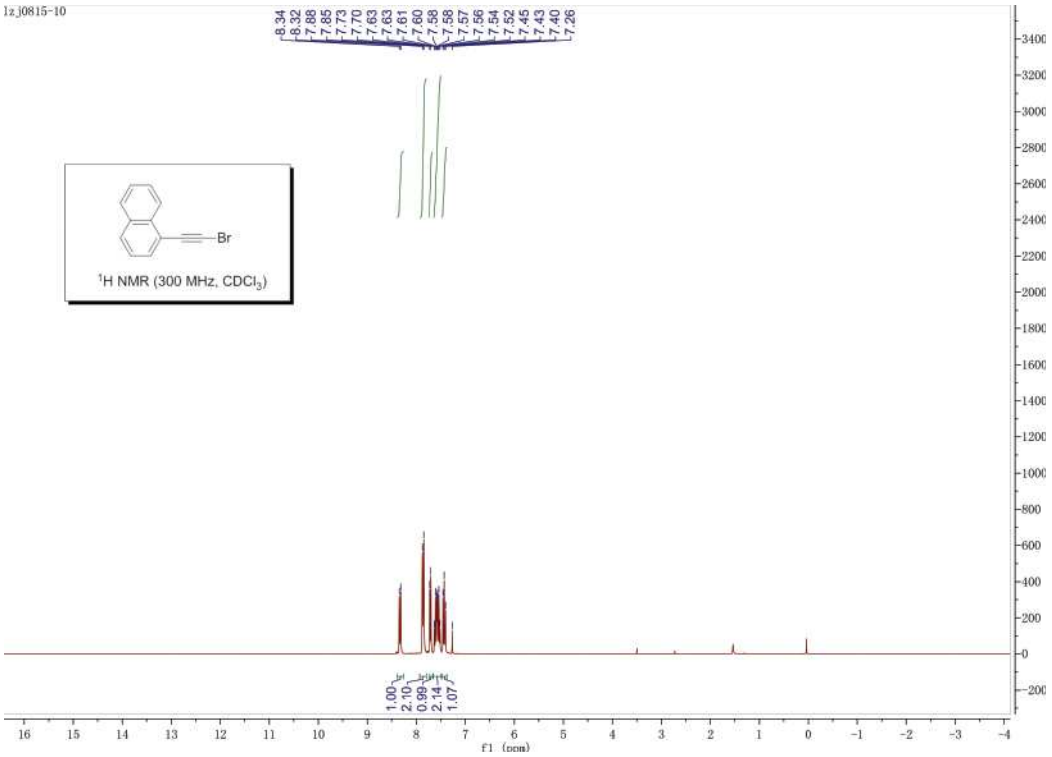


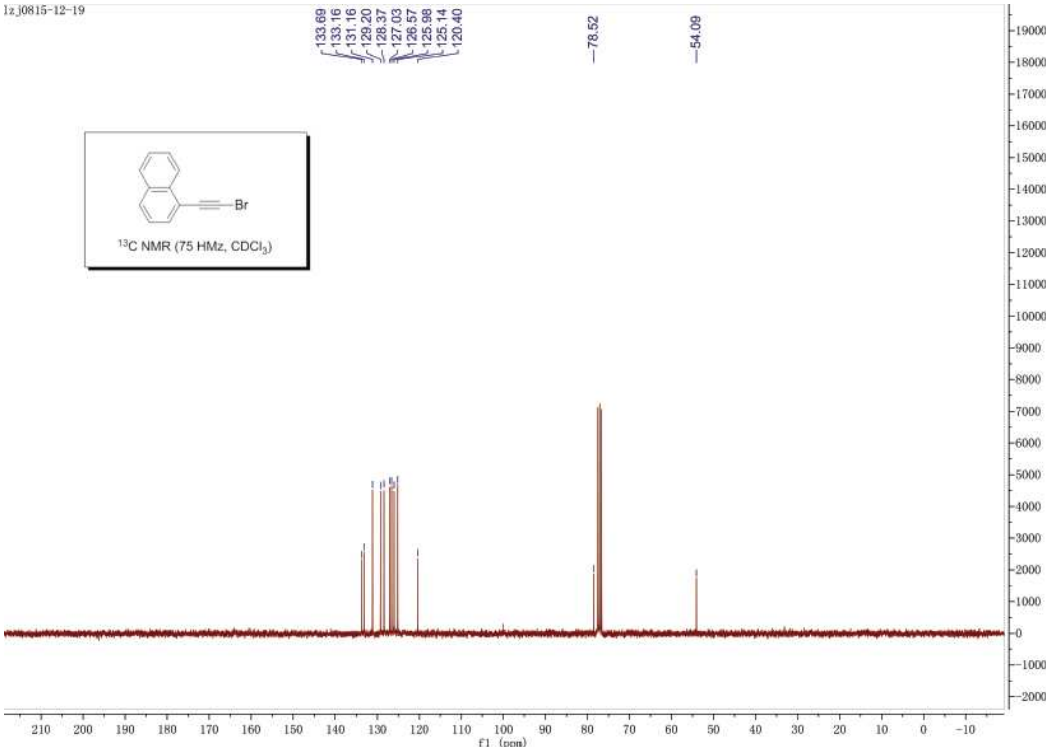
1-(Bromoethynyl)-4-(trifluoromethyl)benzene (t8)



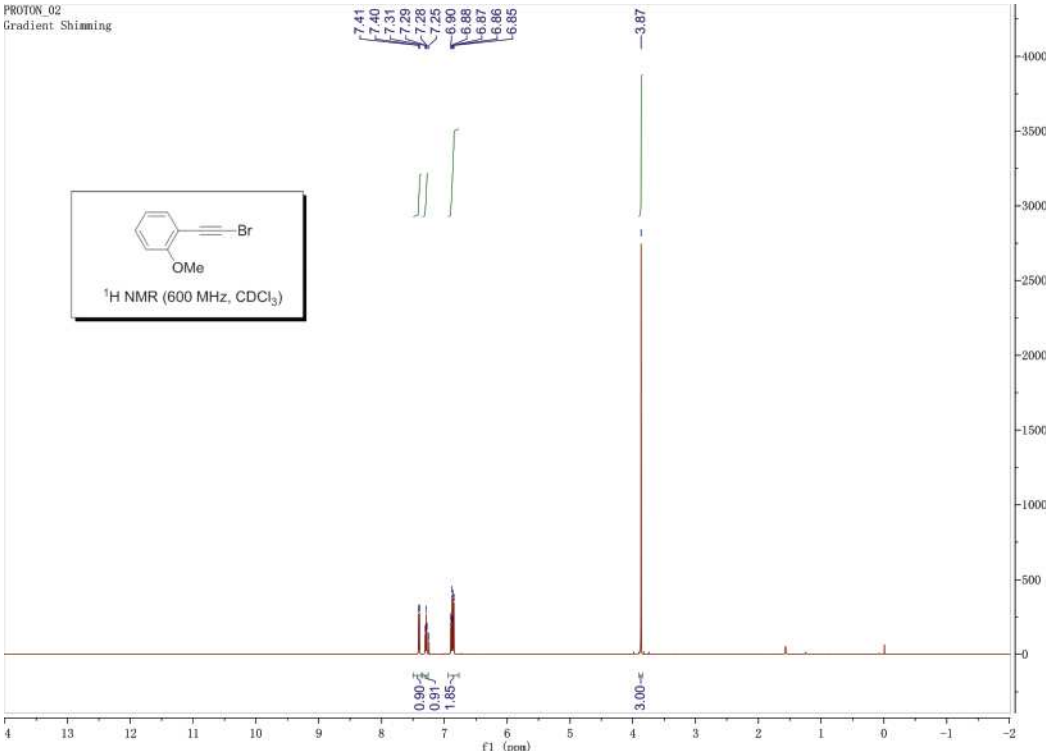


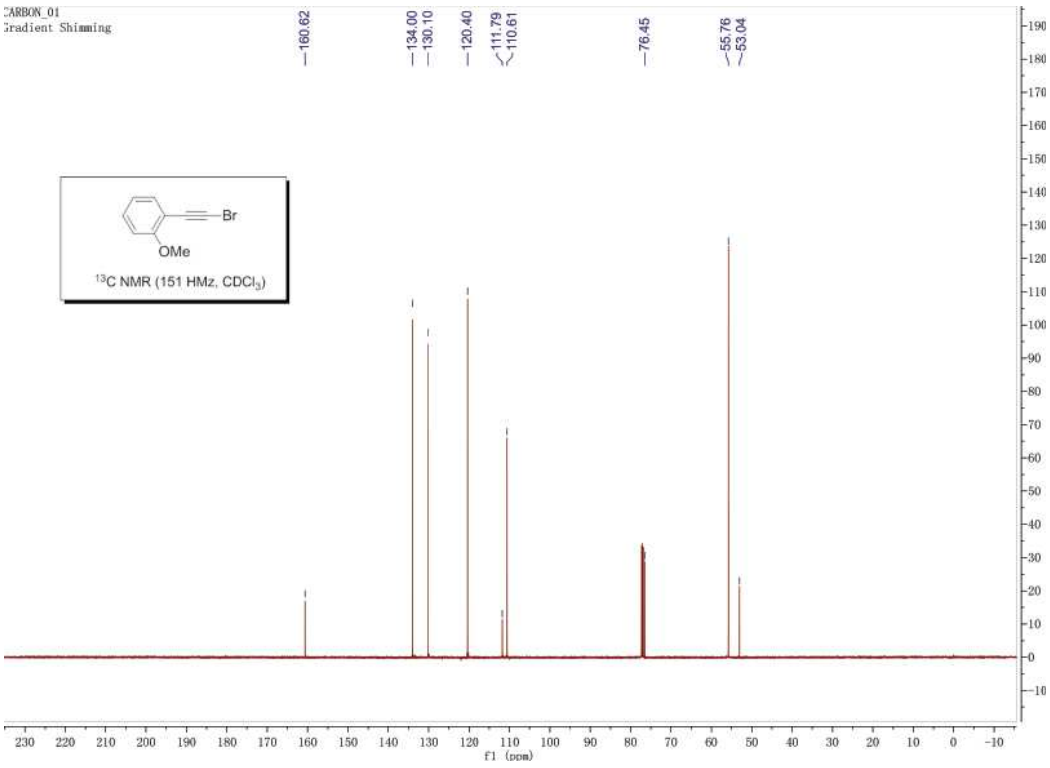
1-(Bromoethynyl)naphthalene (t9)



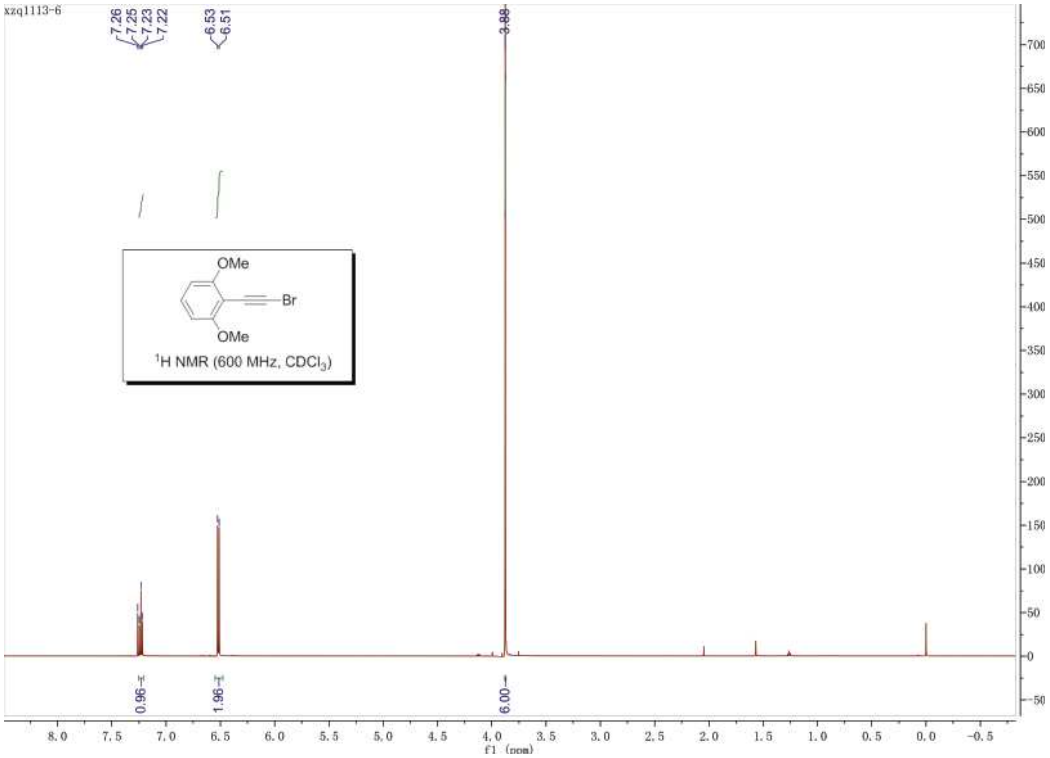


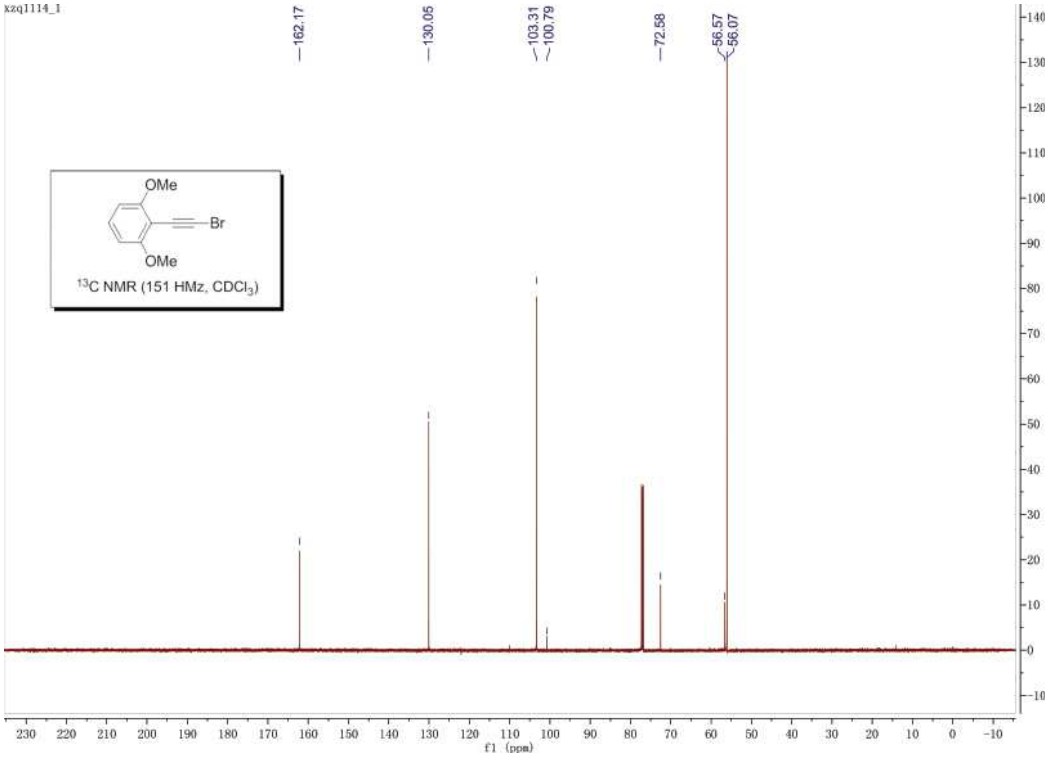
1-(Bromoethynyl)-2-methoxybenzene (t10)



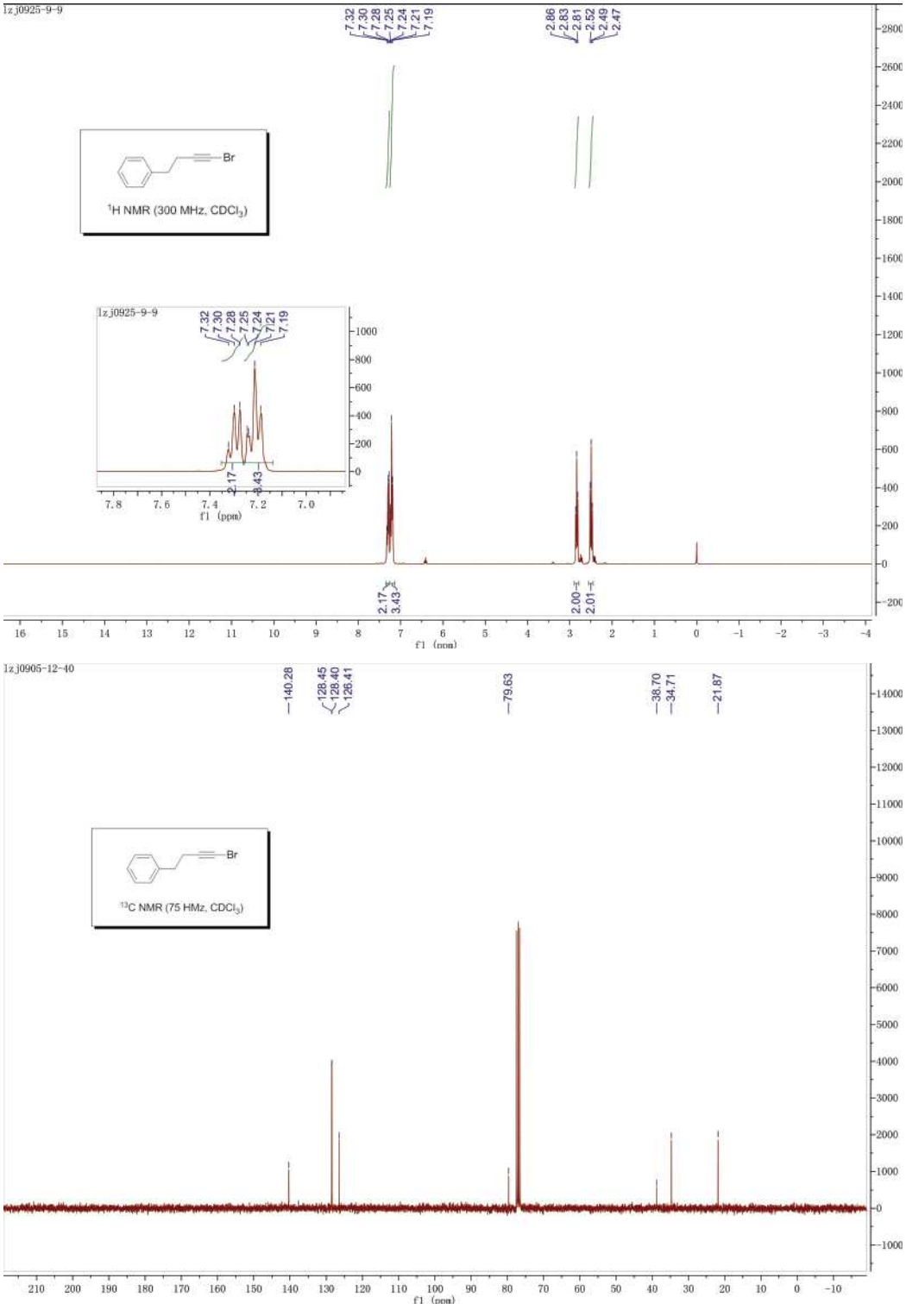


2-(Bromoethynyl)-1,3-dimethoxybenzene (t11)

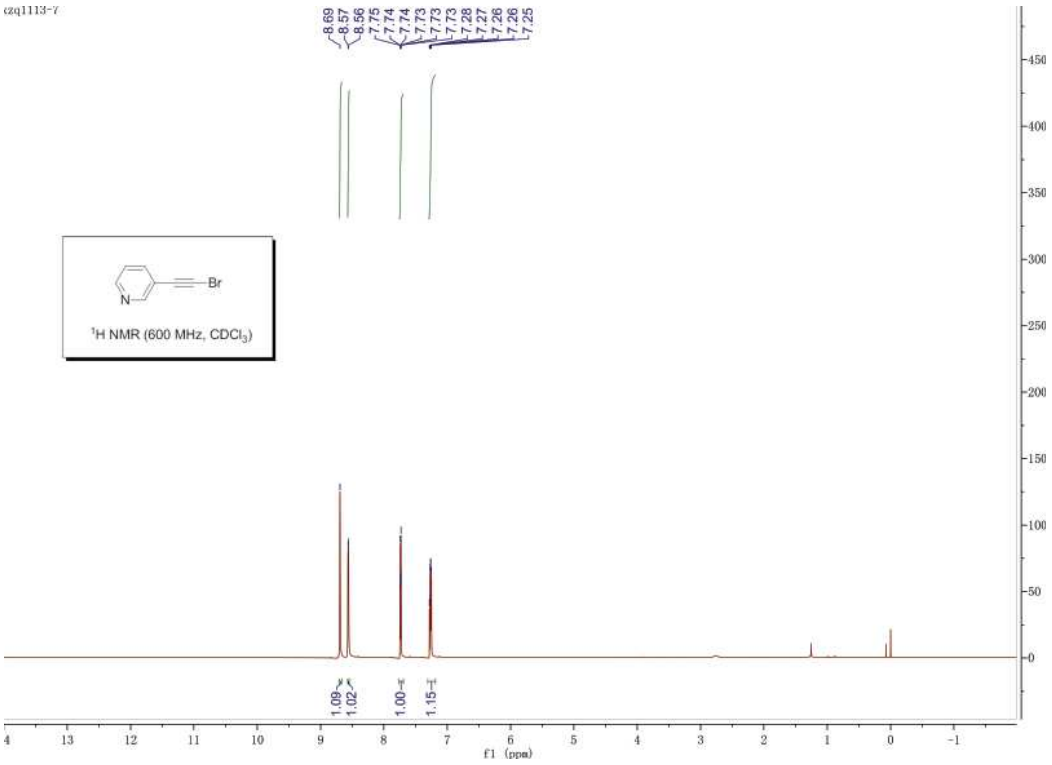


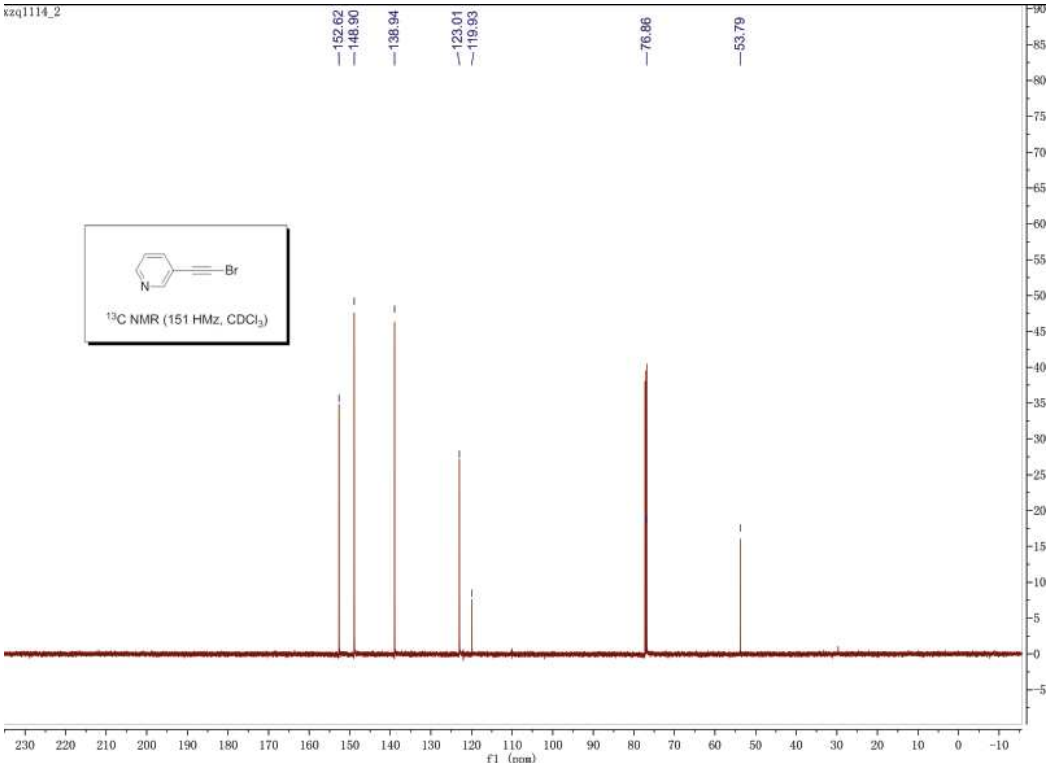


(4-Bromobut-3-ynyl)benzene (t12)

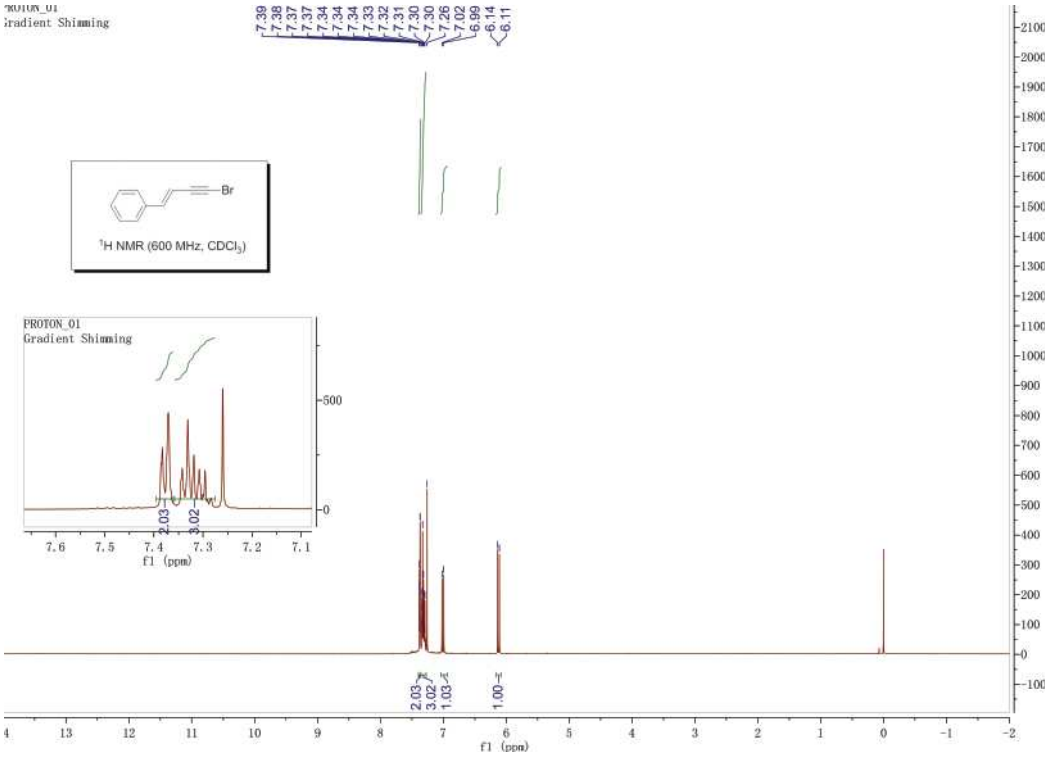


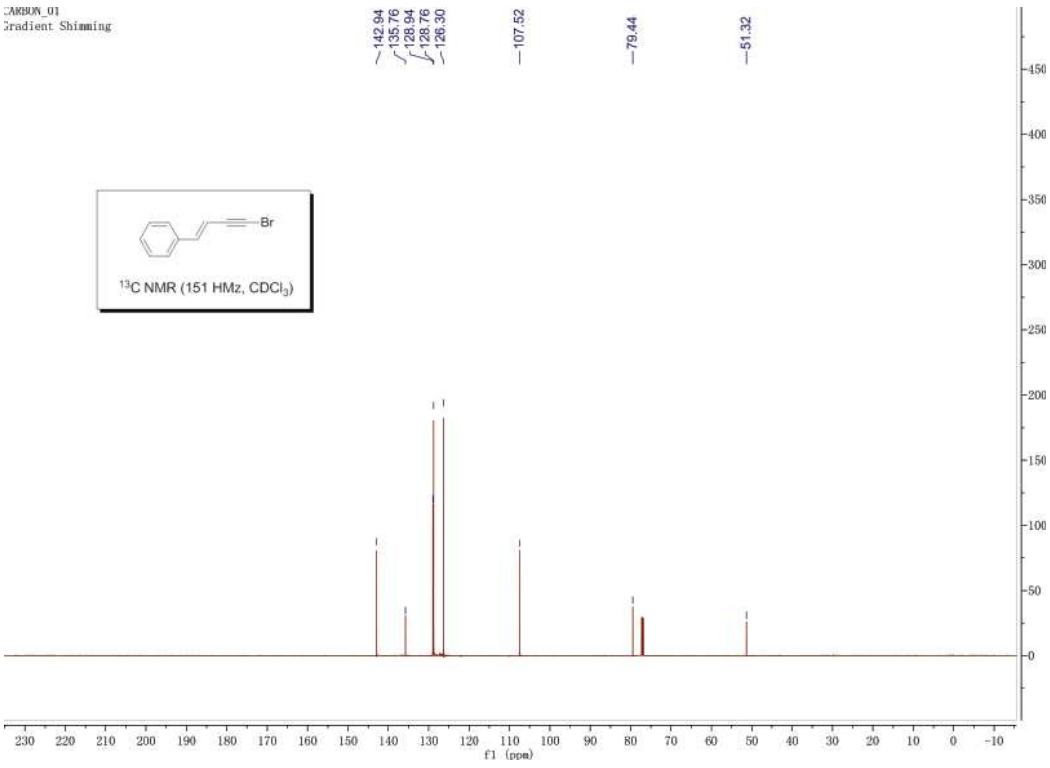
3-(Bromoethynyl)pyridine (t13)



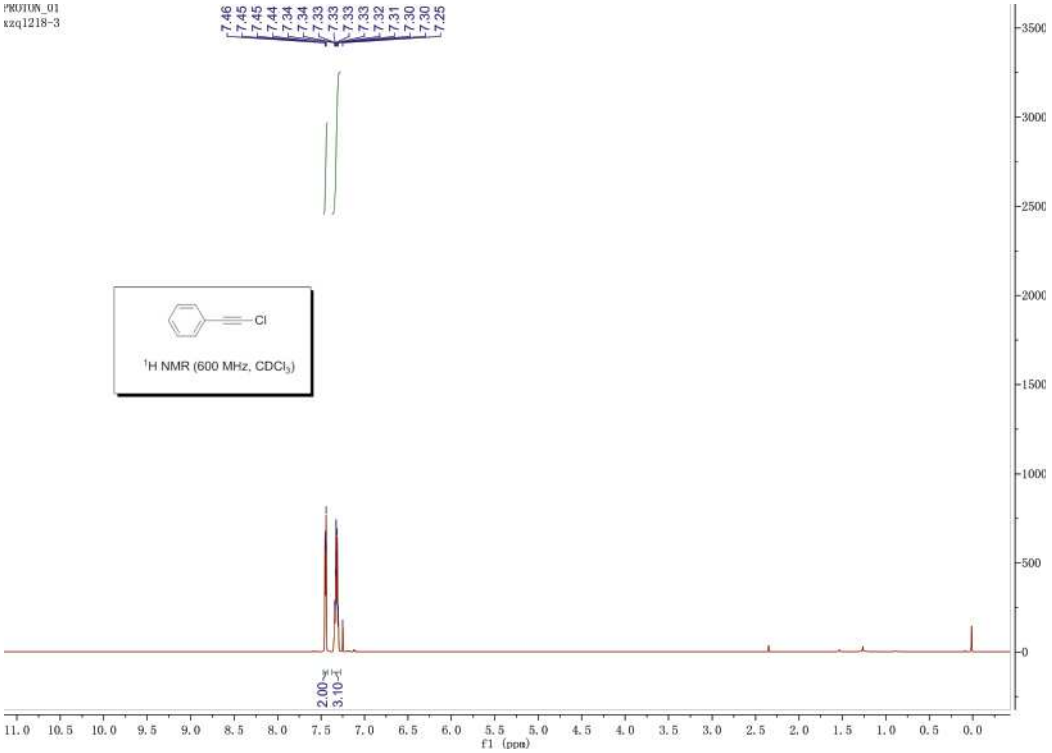


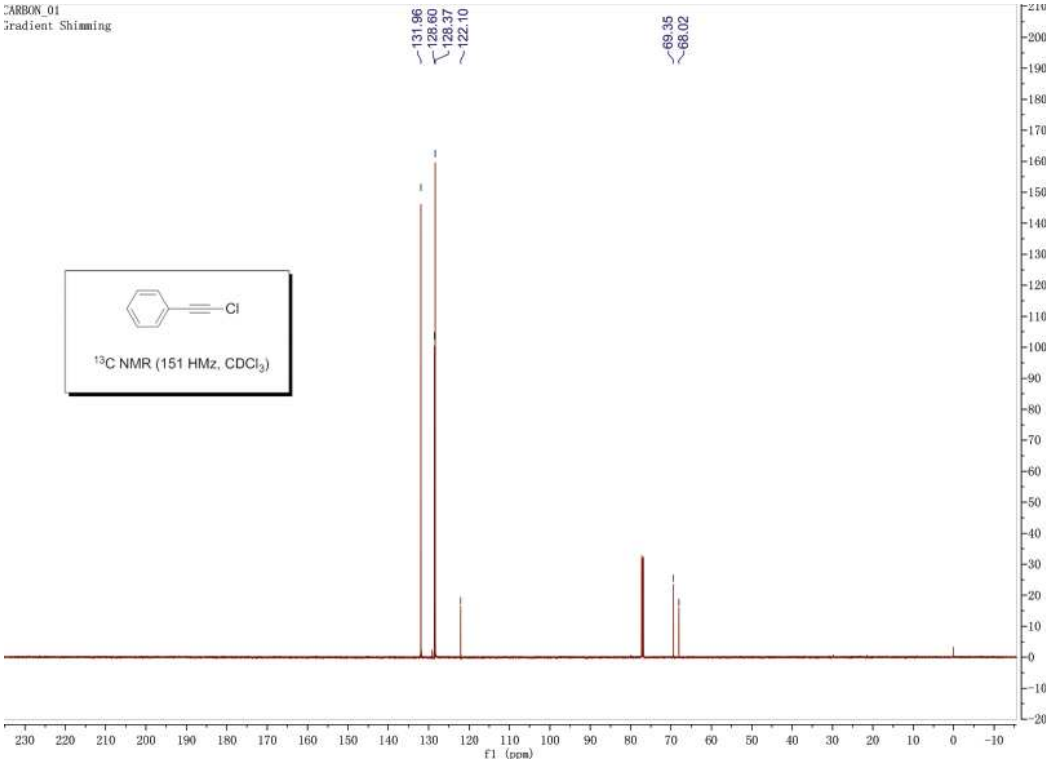
(4-Bromobut-1-en-3-ynyl)benzene (t14)



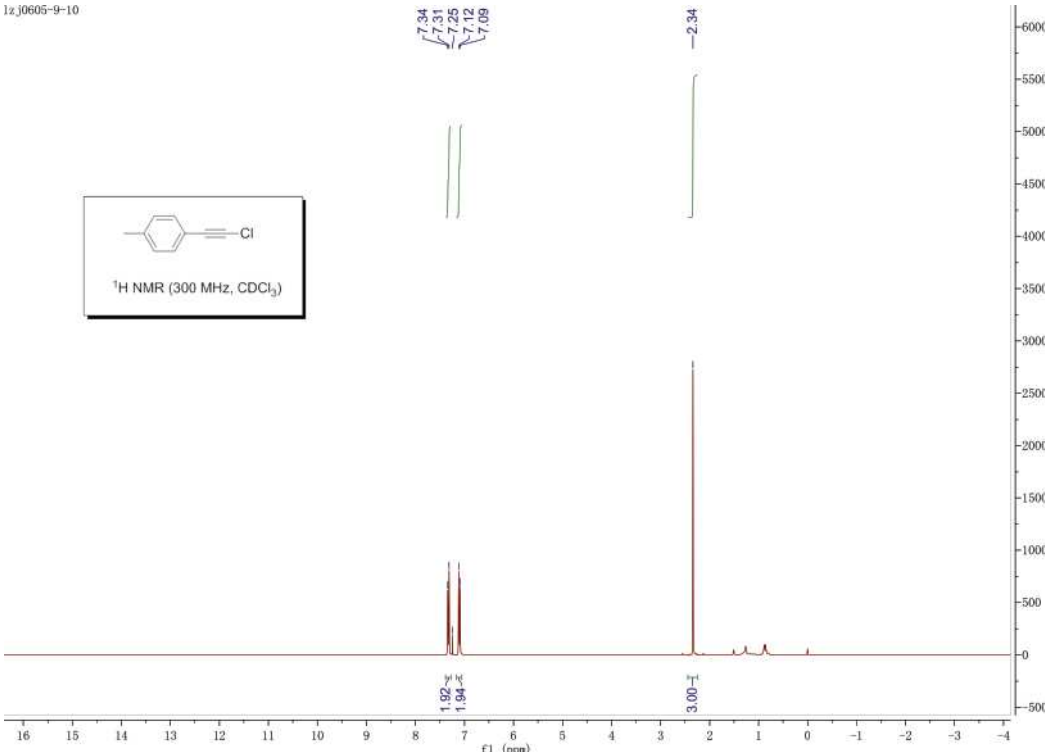


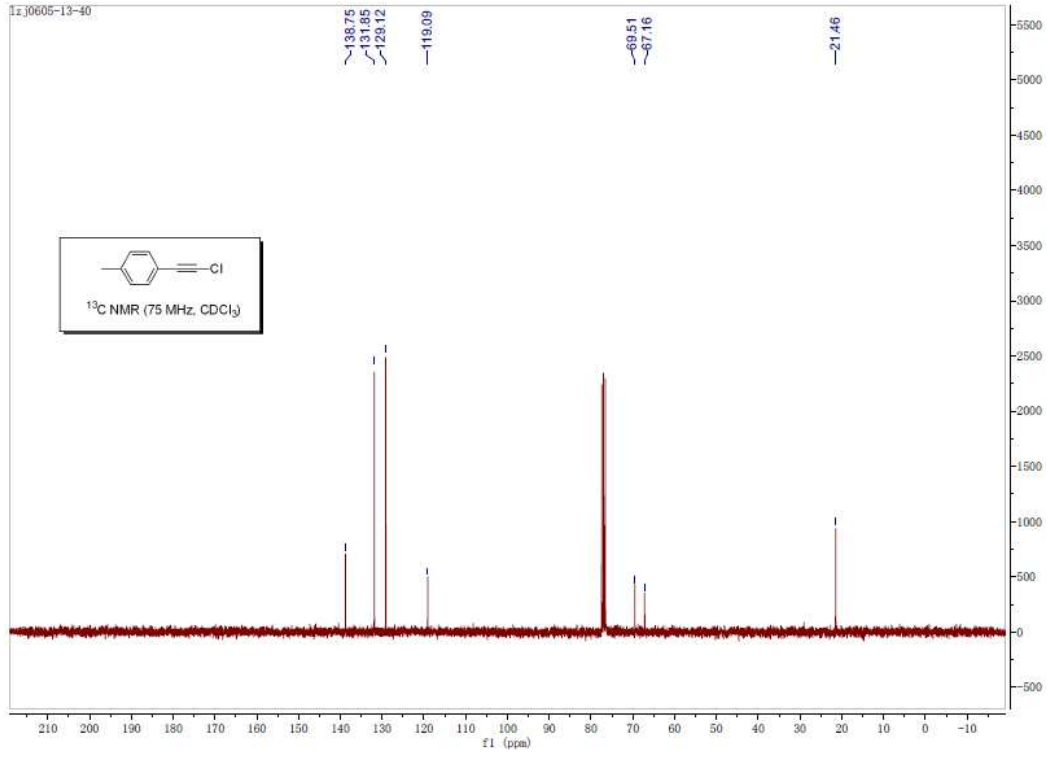
(Chloroethynyl)benzene (t15)



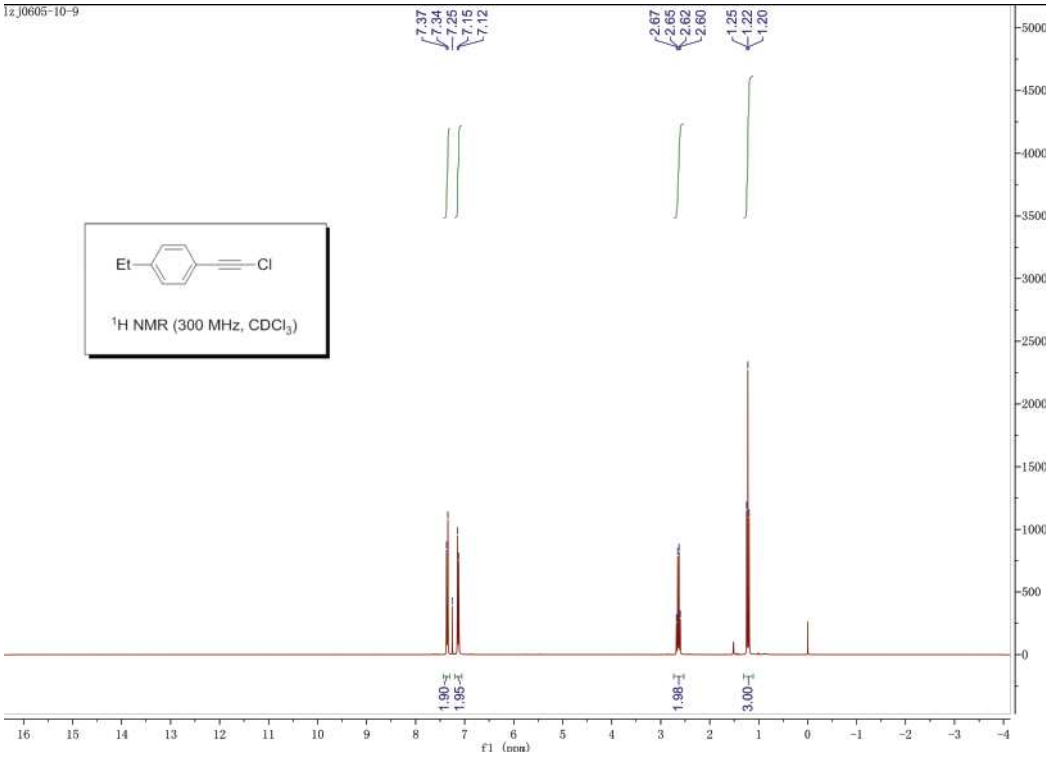


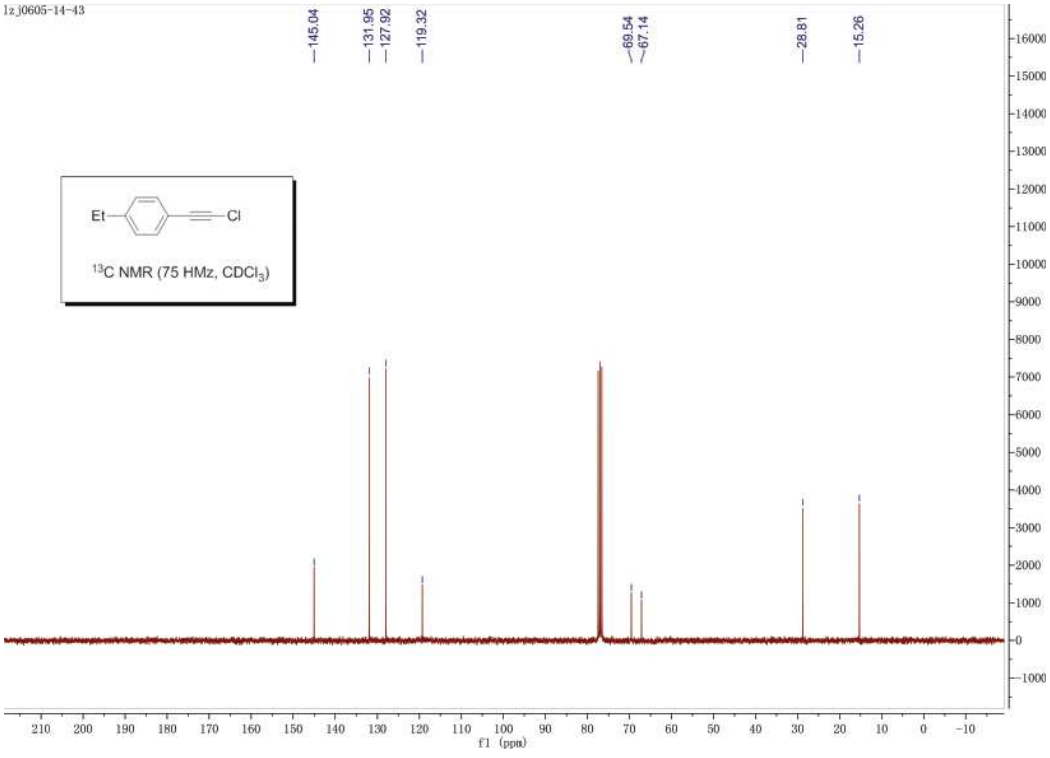
1-(Chloroethynyl)-4-methylbenzene (t16)



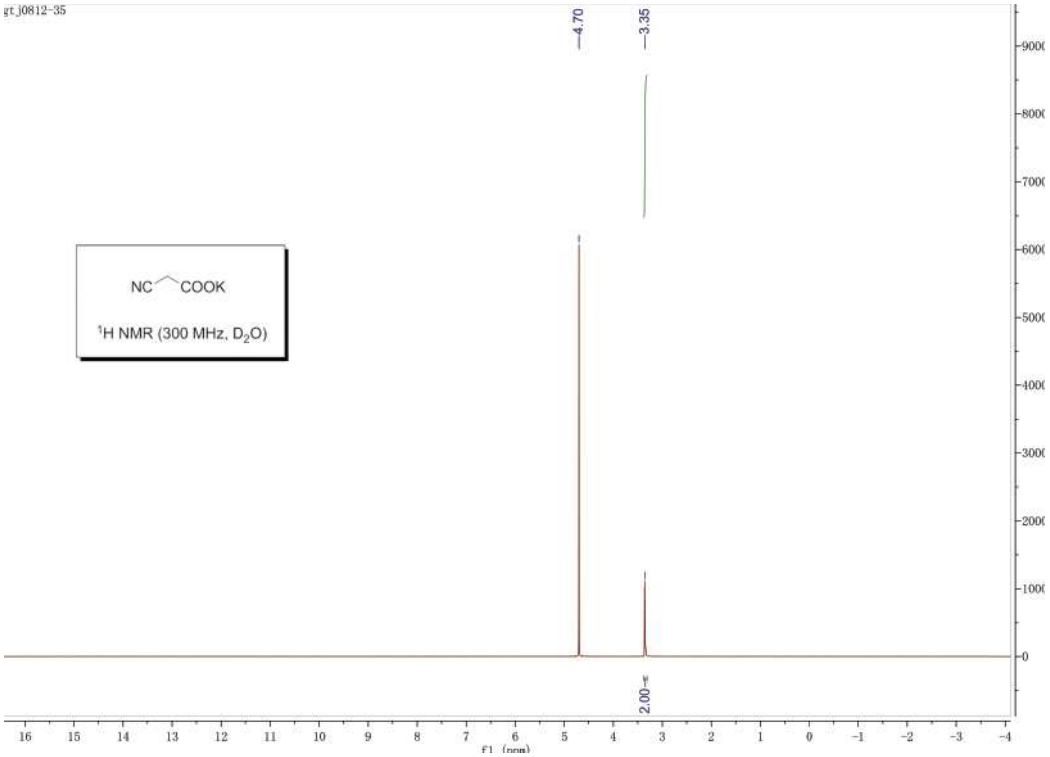


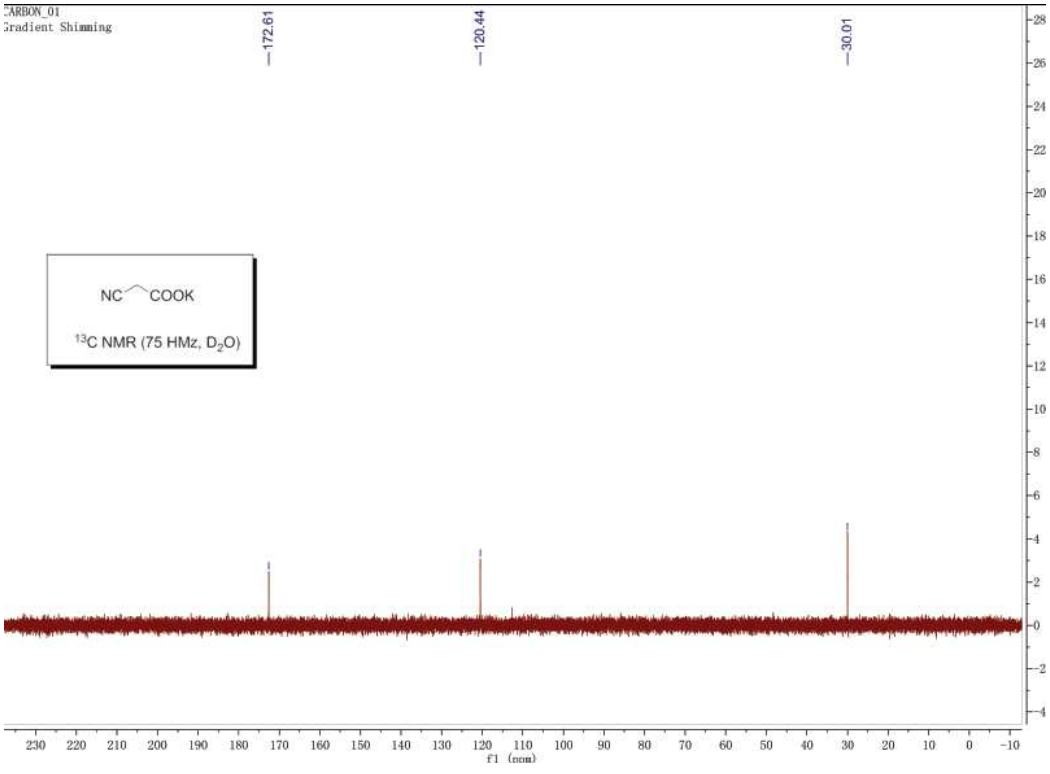
1-(Chloroethynyl)-4-ethylbenzene (t17)



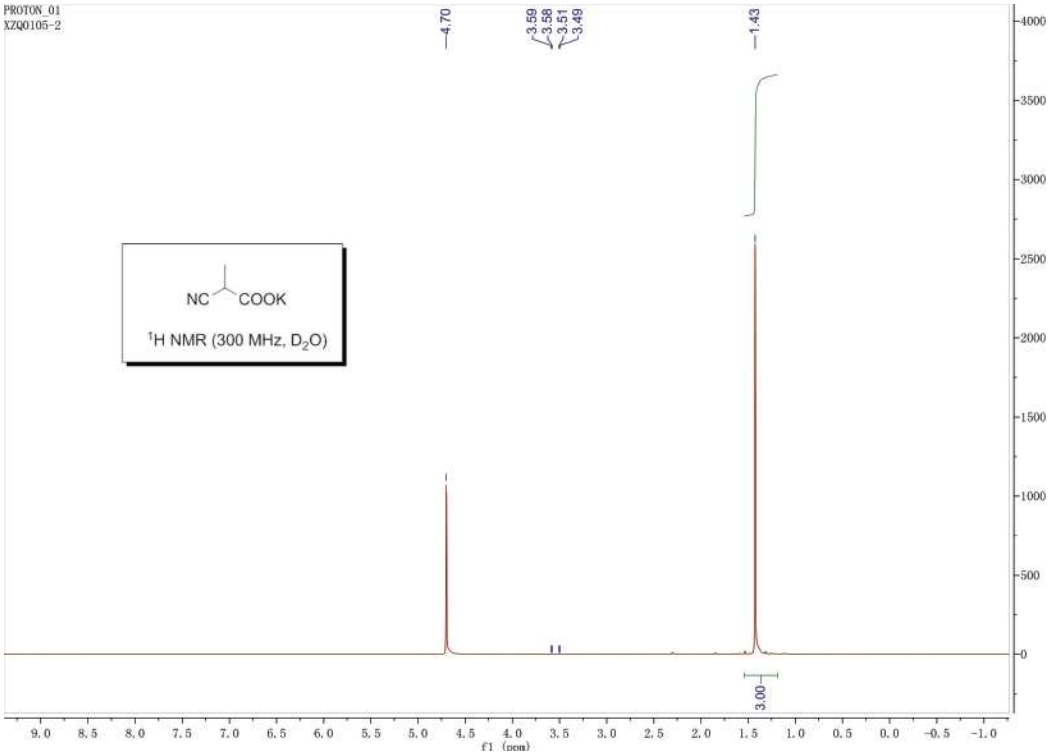


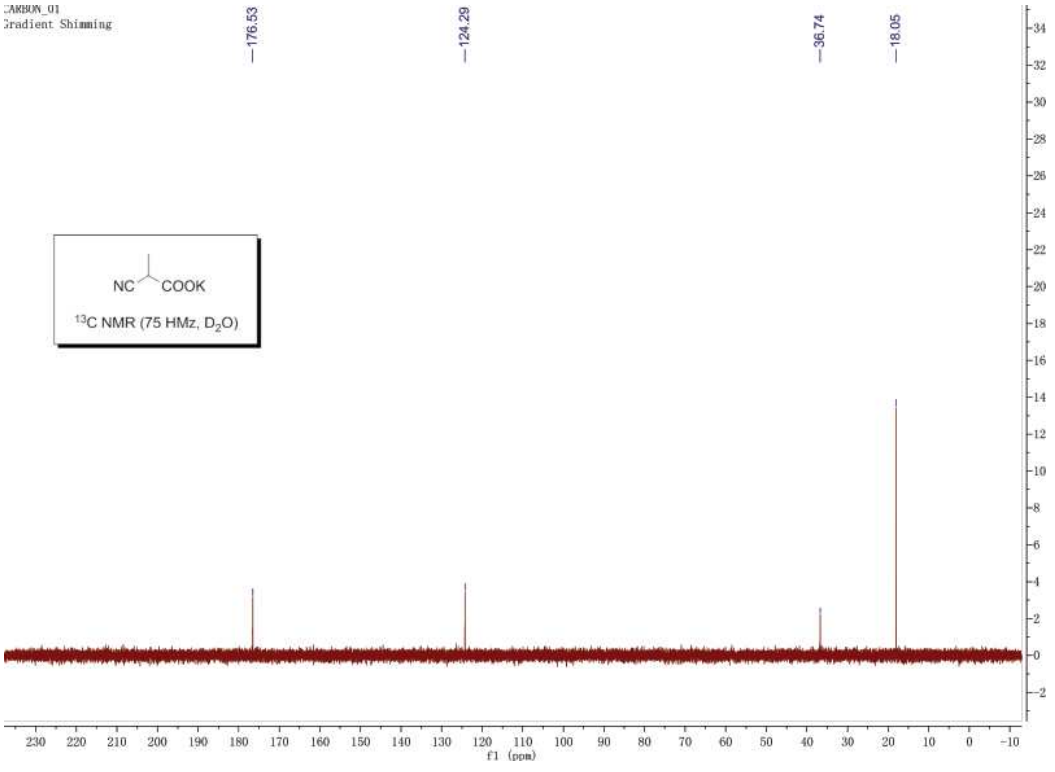
Potassium 2-cyanoacetate (s1)



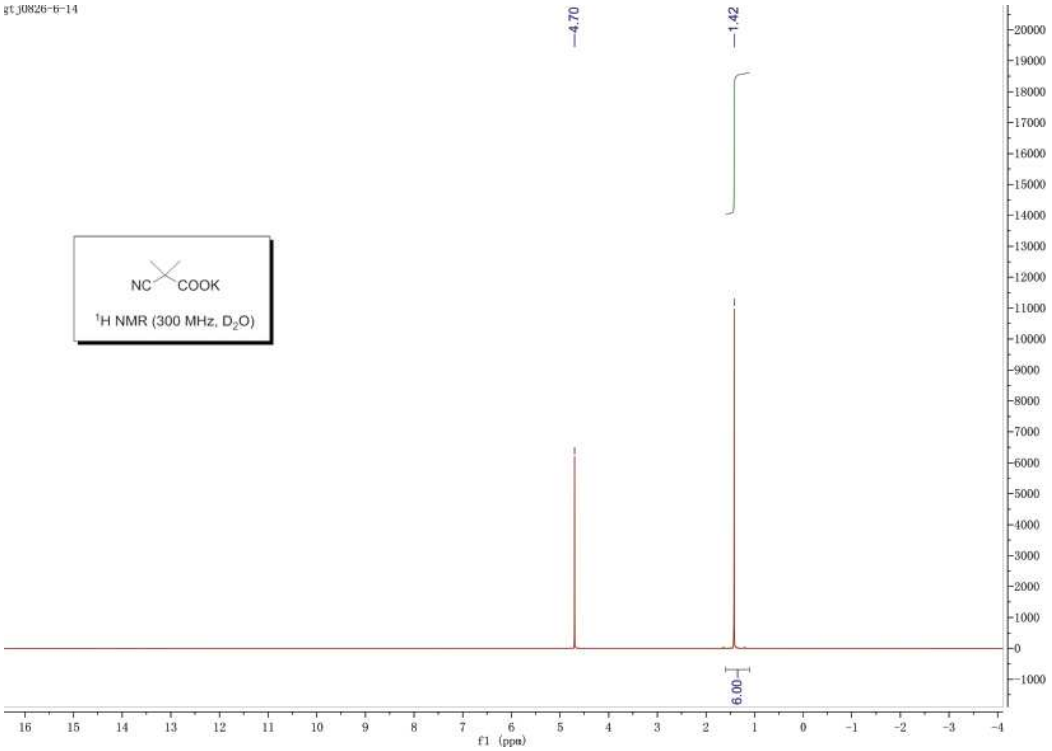


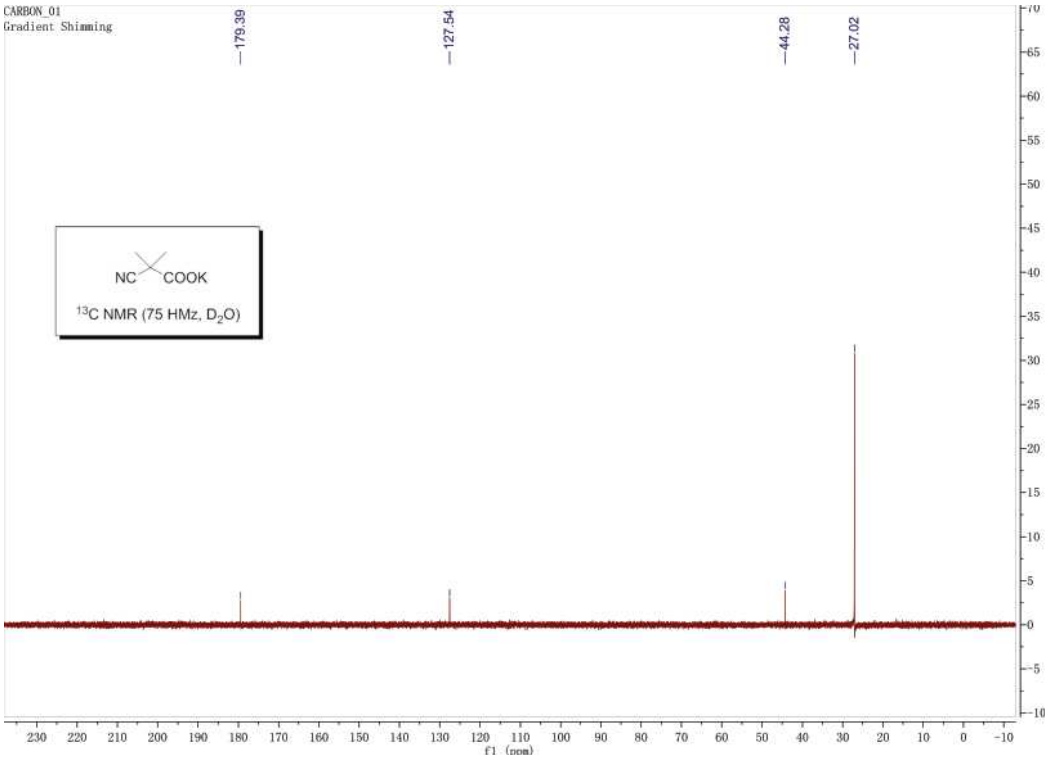
Potassium 2-cyanopropanoate (s2)



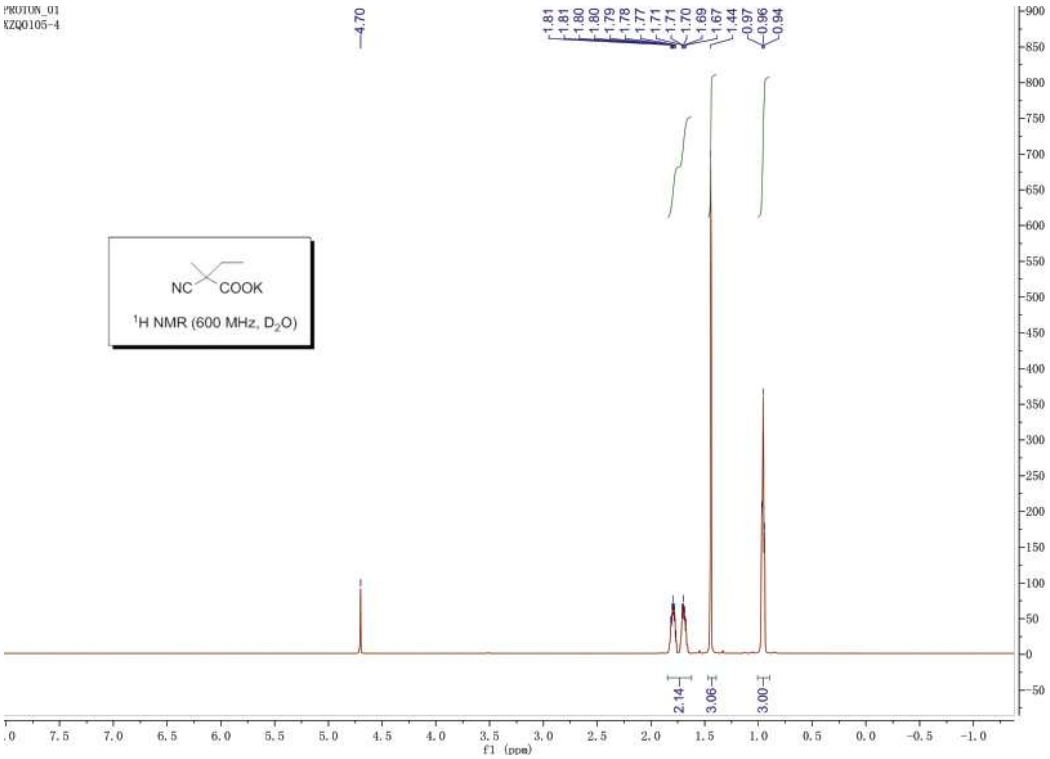


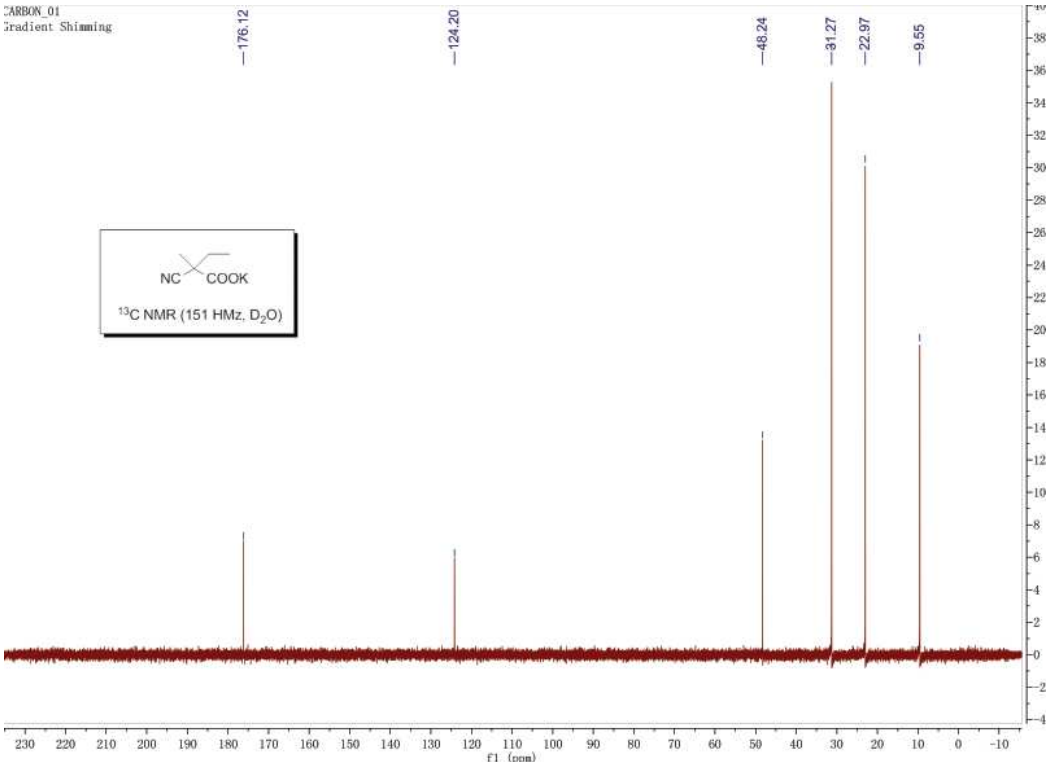
Potassium 2-cyano-2-methylpropanoate (s3)



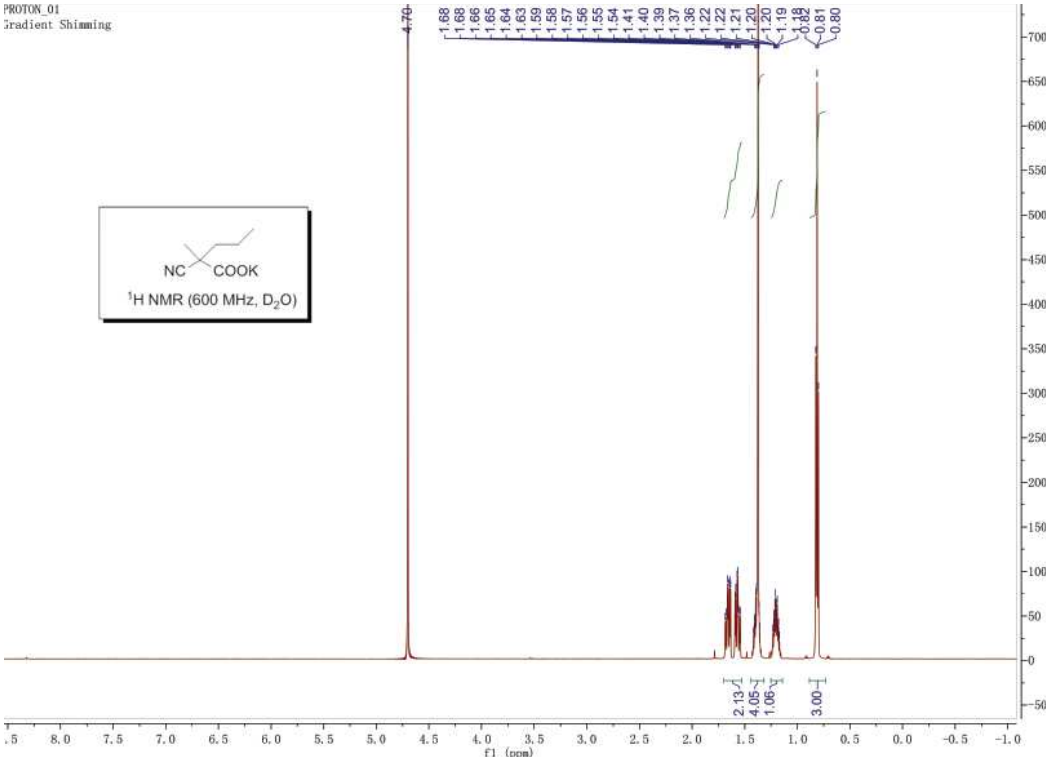


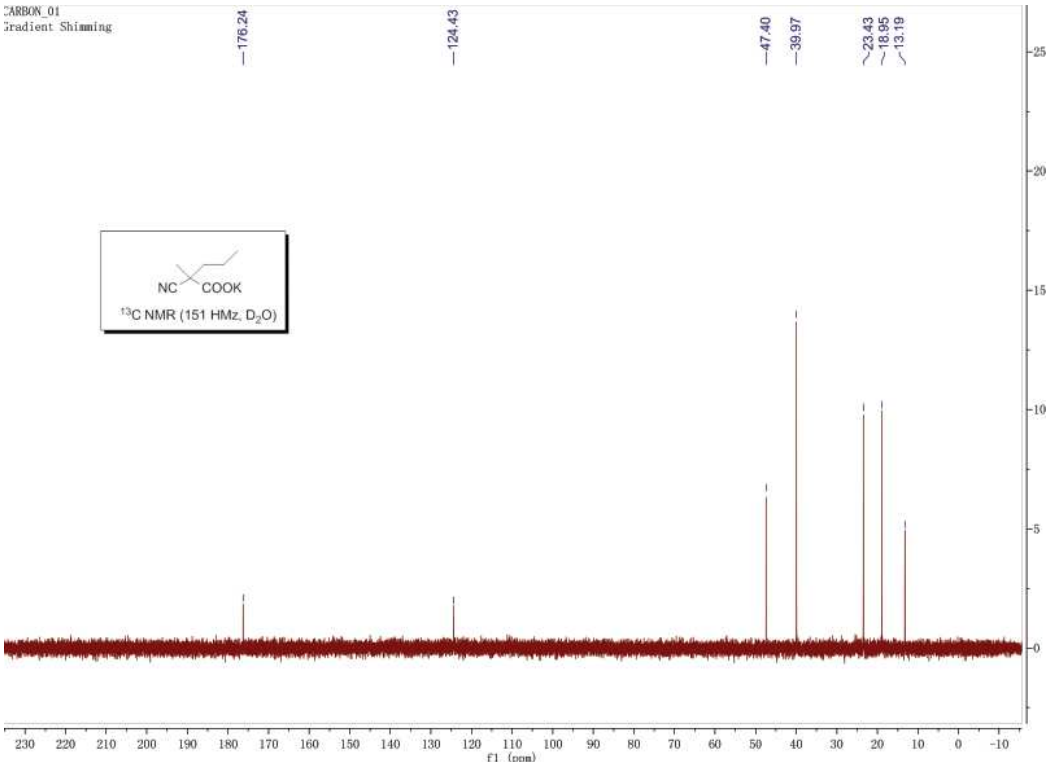
Potassium 2-cyano-2-methylbutanoate (s4)



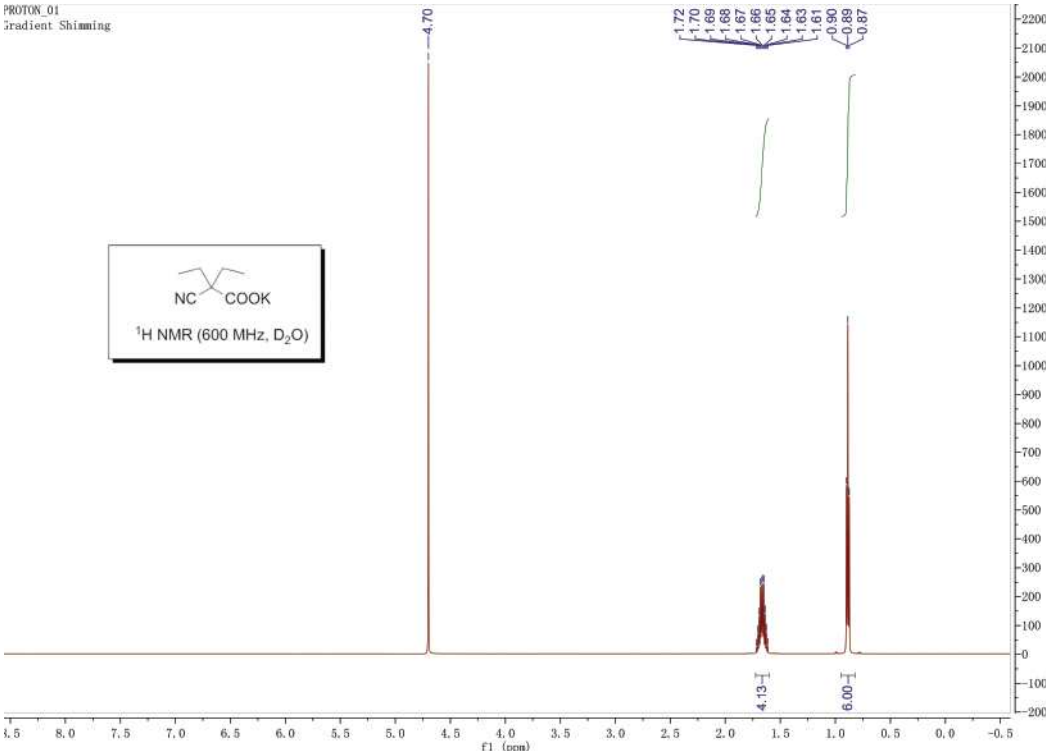


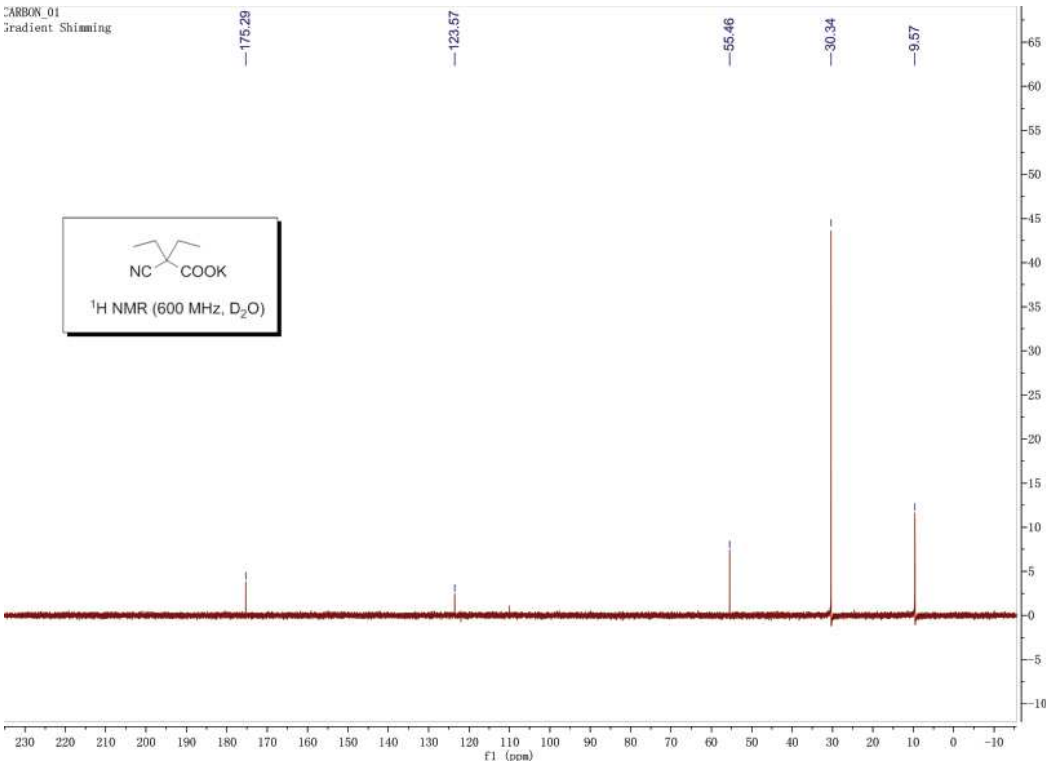
Potassium 2-cyano-2-methylpentanoate (s5)



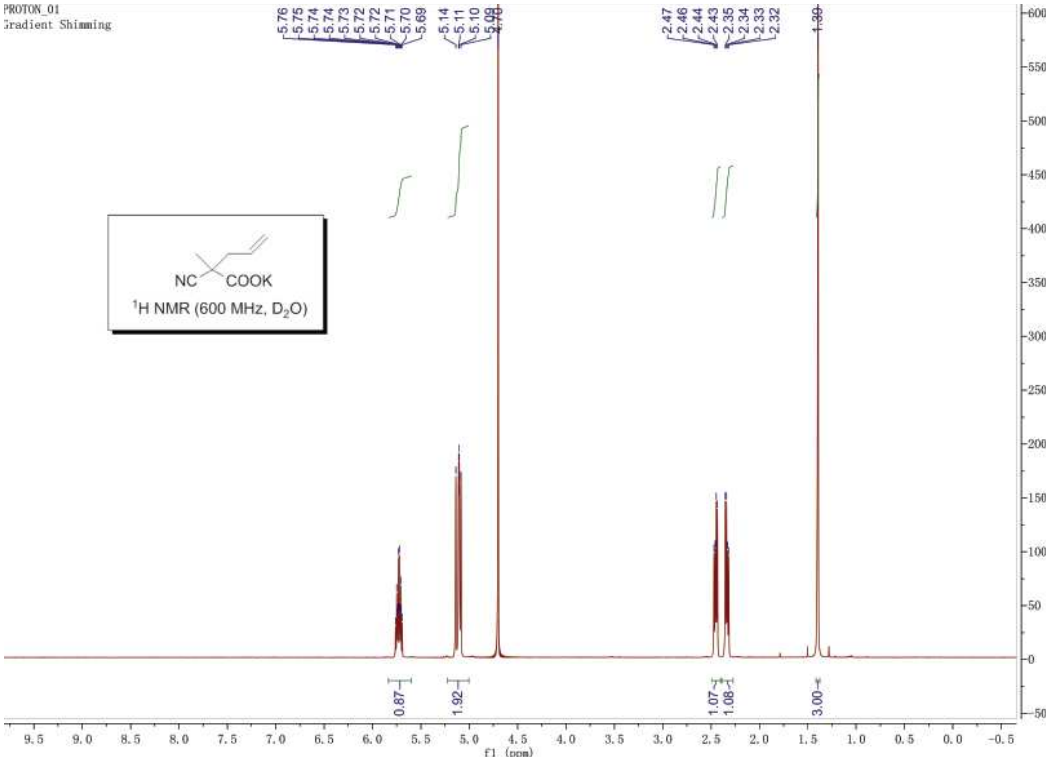


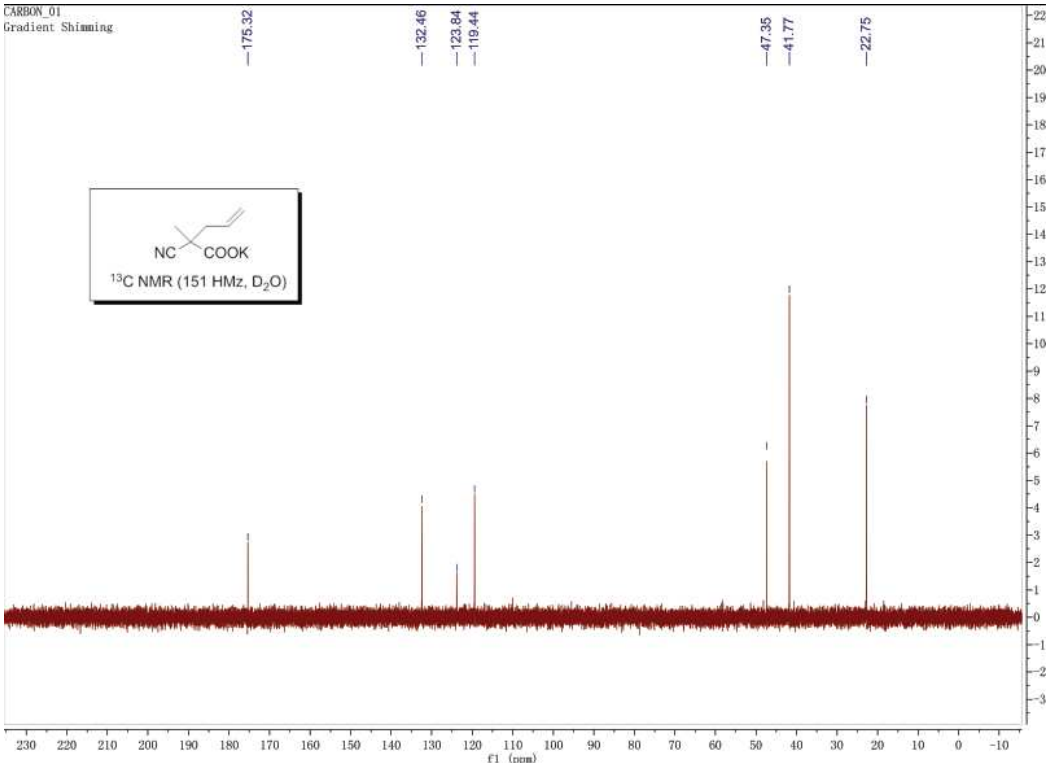
Potassium 2-cyano-2-ethylbutanoate (s6)



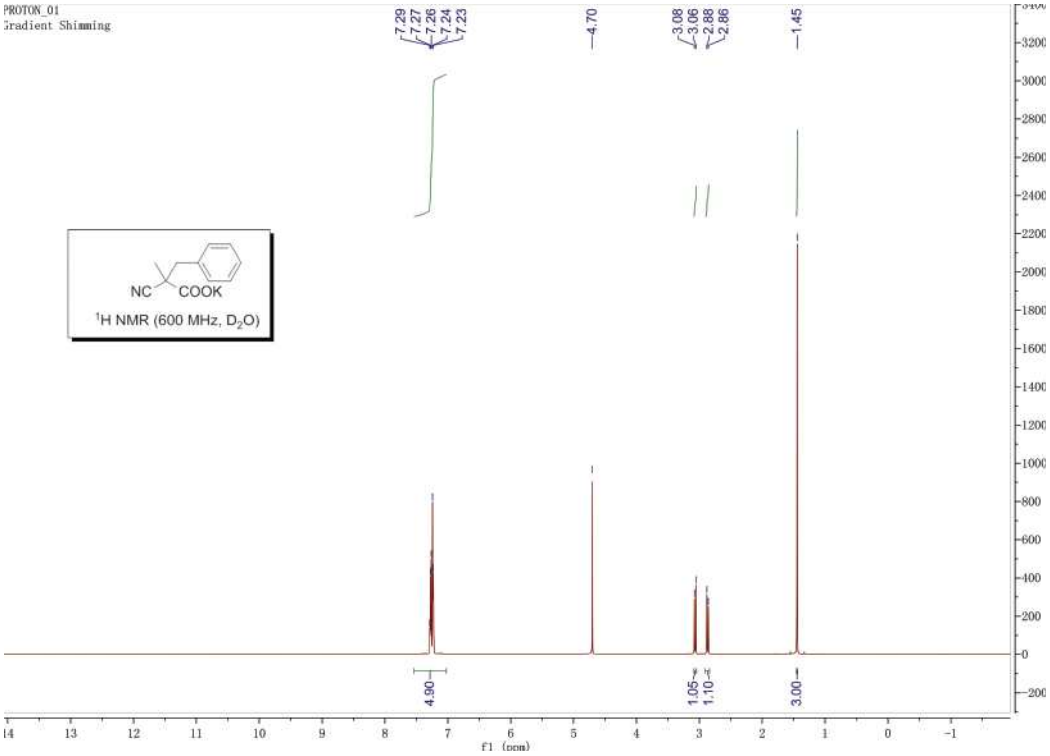


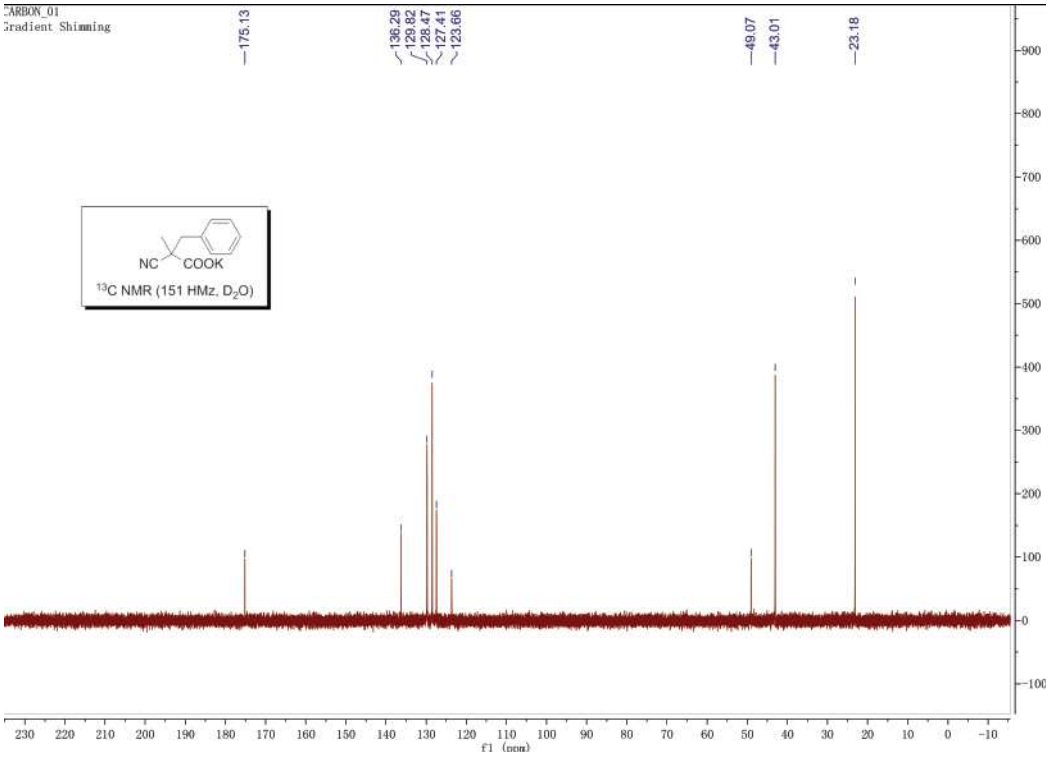
Potassium 2-cyano-2-methylpent-4-enoate (s7)



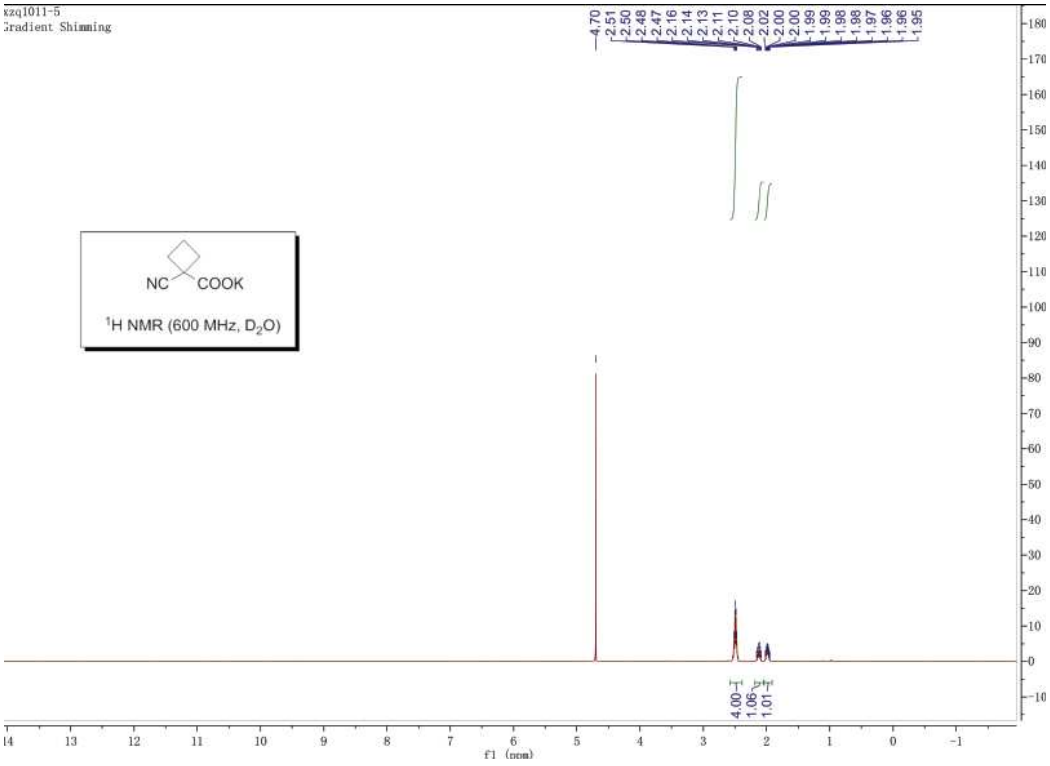


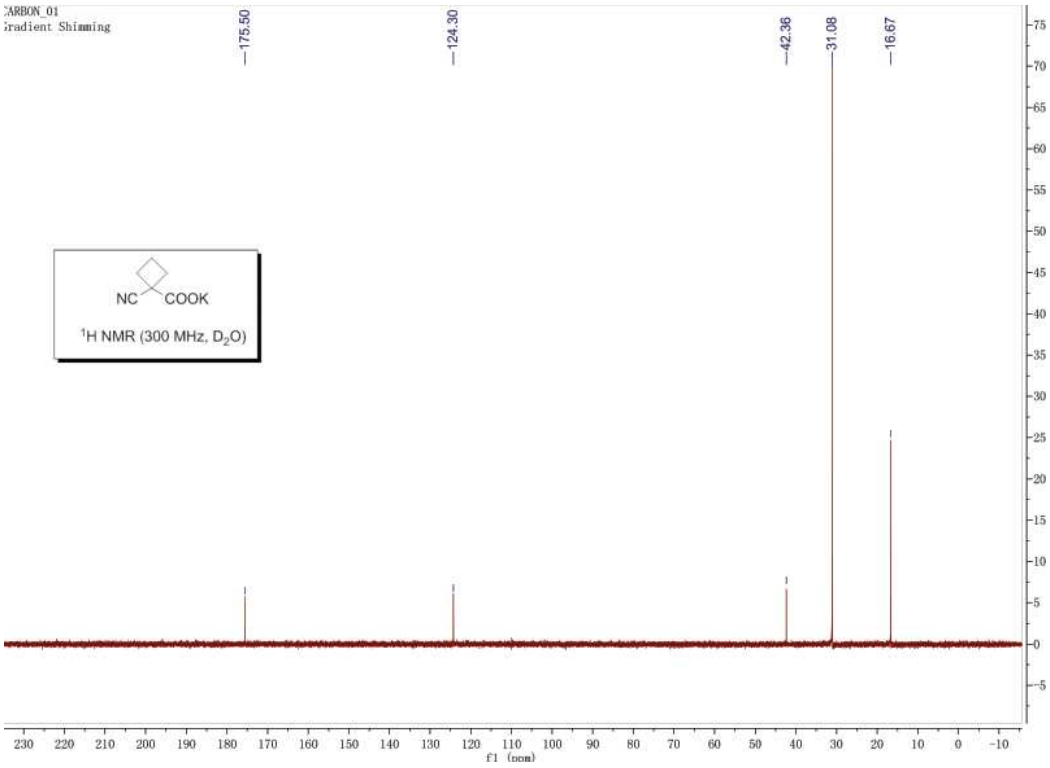
Potassium 2-cyano-2-methyl-3-phenylpropanoate (s8)



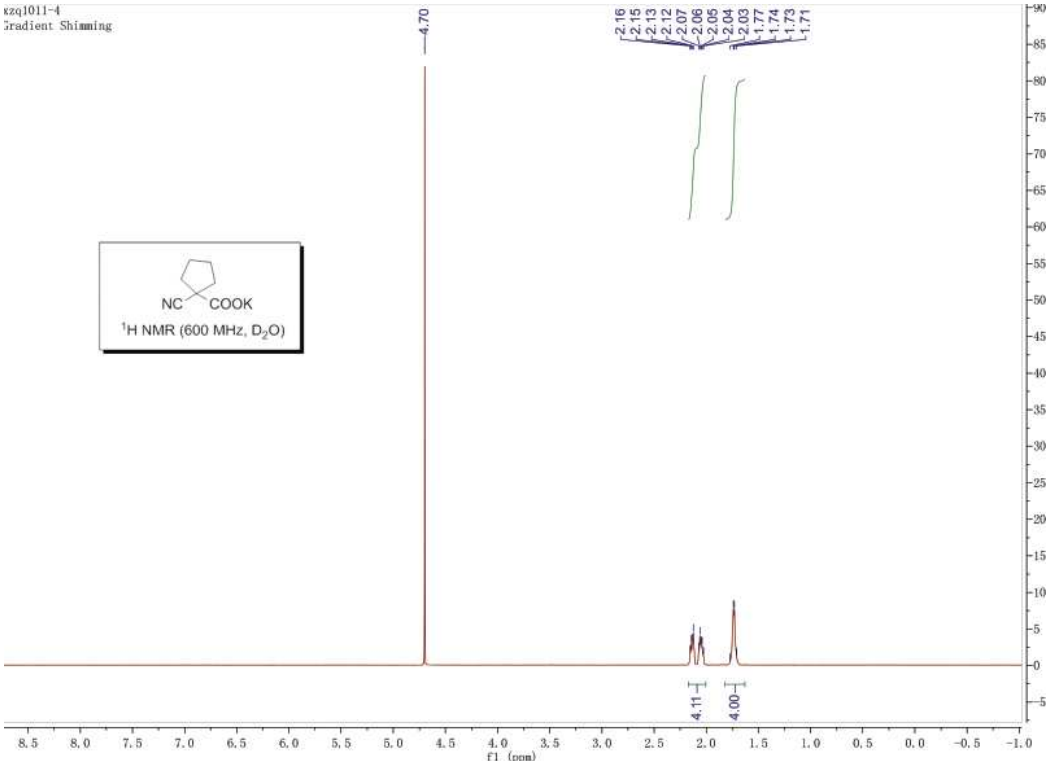


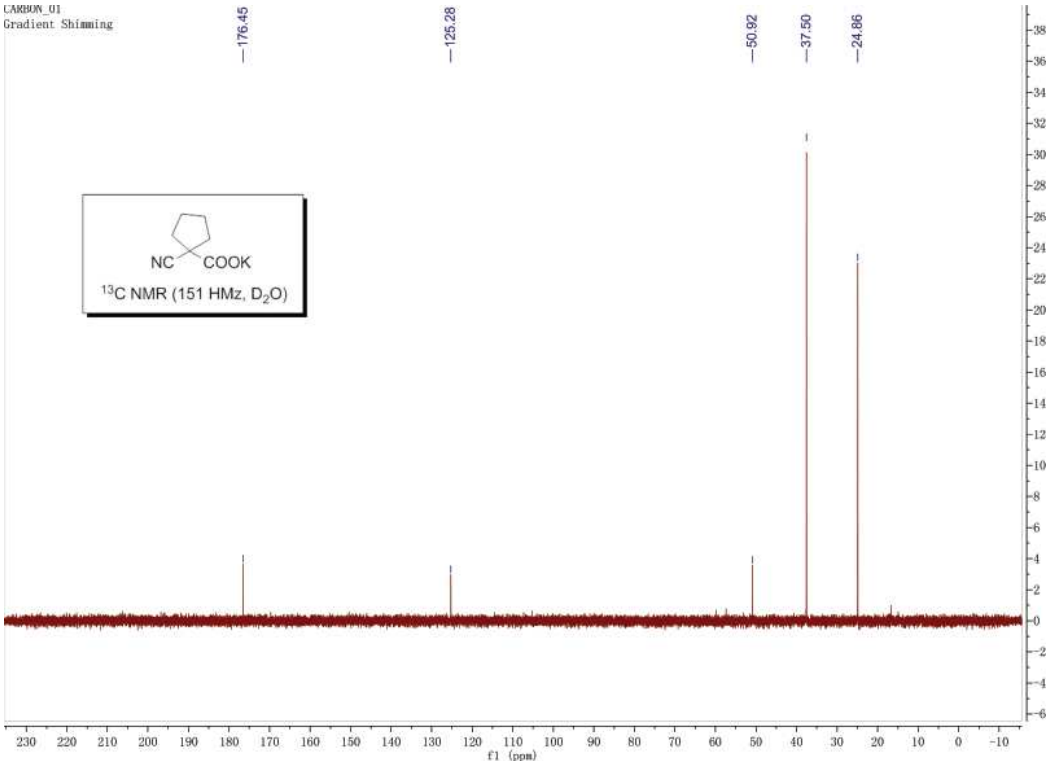
Potassium 1-cyanocyclobutanecarboxylate (s9)





Potassium 1-cyanocyclopentanecarboxylate (s10)





Potassium 1-cyanocyclohexanecarboxylate (s11)