SUPPORTING INFORMATION

Efficient iron(III)-catalyzed three-component coupling reaction of alkyne, CH_2Cl_2 and amine to propargylamine

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1. General experimental methods

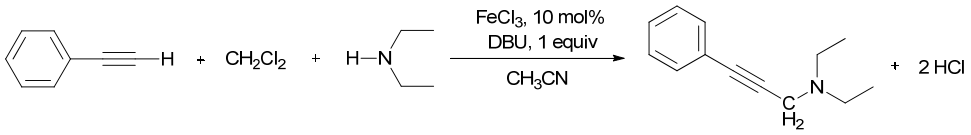
All reactions were carried out without any special precautions against air. All starting materials were commercially available and were used as received, unless otherwise indicated. Various solvents were purified according to the methods mentioned in the book of Purification of Laboratory Chemicals (2009 Version). Dichloromethane was distilled from calcium hydride. ^{1}H NMR spectra was recorded at Bruck 400 in $CDCl_3$ and TMS (0 ppm) was used as internal reference, ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ and $CDCl_3$ (77.0 ppm) was used as internal reference. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. High resolution mass spectrometry was conducted using a Varian 7.0 T FTICR-MS by ESI technique. *In situ* FTIR was collected on a Mettler Toledo React IR ic10, Diamond ATR probe, using ic IR analysis system. ICP was measured on a ICP-9000 (N+M) Inductively coupled plasma emission spectrometer. XPS was measured on a Kratos Axis Ultra DLD multi-technique X-ray photoelectron spectroscopy.

2. General procedure for the iron-catalyzed three-component reaction of alkynes, dichloromethane and amines.

In a typical experiment, a mixture of phenylacetylene (1.0 mmol, 102 mg, 110 μL), dichloromethane (2.0 mmol, 169.9 mg, 128 μL), diethylamine (2.0 mmol, 146.3 mg, 207 μL), TMG (2.0 mmol, 230.4 mg, 254 μL) and $FeCl_3$ catalyst (32.4 mg, 20 mol%) was charged in the reaction tube (10 mL) with 0.5 mL CH_3CN. After stirring at 100 ^{o}C for 12 h, the mixture was diluted with H_2O (10 mL) and the aqueous layers were extracted with diethyl ether (15×6 mL), dried over anhydrous Na_2SO_4 and concentrated to give the crude product which was further purified by column chromatography on neutral aluminium oxide (hexane/ethyl acetate = 20 : 1) to afford the corresponding pure propargylic amine. All products gave satisfactory spectroscopic data. New compounds were characterized with NMR, HRMS.

3. Optimization of reaction conditions

Table S1 Initial study of AHA coupling reaction[a]

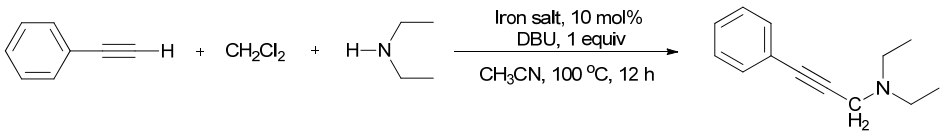


Entry	Solvent	Base	T (^{o}C)	t (h)	Yield (%)[b]
1	CH_3CN	DBU	60	12	0
2	CH_3CN	DBU	80	12	15.5
3	CH_3CN	DBU	100	12	40
4	CH_3CN	DBU	120	12	39
5[c]	CH_3CN	DBU	100	12	50
6[c]	CH_3CN	DBU	100	24	48
7[c,d]	CH_3CN	DBU	100	12	50

[a] Reaction conditions: phenylacetylene (1.0 mmol, 102 mg, 110 μL); dichloromethane (1.1 mmol, 93.5 mg, 70 μL); diethylamine (1.2 mmol, 86.5 mg, 124 μL); DBU (1.0 mmol, 152.0 mg, 149 μL); $FeCl_3$, 10 mol%, 16.2 mg; CH_3CN, 1 mL; [b] NMR yield using $MeNO_2$ as the internal standard; [c] dichloromethane (2.0 mmol, 169.9 mg, 128 μL); diethylamine (2.0 mmol, 146.3 mg, 207 μL); [d] 0.5 mL CH_3CN was used as solvent.

It was found that using stiochiometric amount of DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) as a base, which was supposed to activate the alkyne substrate and to trap the formed HCl by-product, this three-component coupling reaction could afford the desired propargylic amine product in 40% yield at 100 ^{o}C for 12 h (entries 1-3, Table S1). Further elevating the reaction temperature to 120 ^{o}C did not help to increase the yield (entry 4). To our delight, when the amounts of dichloromethane and diethylamine were increased to 2 equivalents related to phenylacetylene, the yield of the desired product reached up to 50% (entry 5). That was because the excessive amount of diethylamine may serve as another equivalent of base to neutralize the acid by-product and to promote the reaction in combination with one equivalent of base DBU. However, there was no benefit to the reaction further prolonging the reaction time to 24 h (entry 6). In addition, it was observed that reducing the amount of solvent to 0.5 mL had no effect on the reaction (entry 7).

Table S2 Screening of iron sources[a]

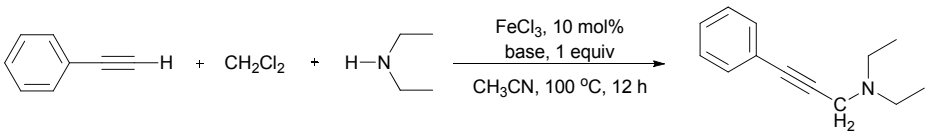


Entry	Iron salts	Yield (%)[b]
1	-	-
2	$FeCl_3$	50
3	$FeCl_3.6H_2O$	7
4	$Fe(NO_3)_3.9H_2O$	3
5	$FeBr_3$	35
6	$Fe(acac)_3$	43
7	$FeBr_2$	30
8	$Fe(acac)_2$	8
9	Fe_2O_3	20
10	nano-Fe_3O_4	3

[a] Reaction conditions: phenylacetylene (1.0 mmol, 102 mg, 110 μL); dichloromethane (2.0 mmol, 169.9 mg, 128 μL); diethylamine (2.0 mmol, 146.3 mg, 207 μL); DBU (1.0 mmol, 152.0 mg, 149 μL); catalyst, 10 mol%; 0.5 mL CH_3CN was used as solvent; 100 °C; 12 h; [b] NMR yield using $MeNO_2$ as the internal standard.

By screening a wide range of iron sources, it was found that the desired propargylic amine product of the AHA coupling reaction could be obtained in yields ranging from 3% to 50% in the presence of a catalytic amount of an iron salt (10 mol%) in any oxidation state (II or III) without any ligand in CH_3CN (entries 2-10, Table S2). Obviously, among the iron sources, $FeCl_3$ led to the best catalyst and afforded the coupling product in a satisfactory 50% yield (entry 2). Of course, a control experiment in the absence of an iron salt could confirm the crucial role which the iron catalyst plays in the described three-component cross coupling reaction as the reaction did not occur (entry 1). Thus $FeCl_3$ was chosen as the catalyst for further investigations.

Table S3 Screening of bases[a]

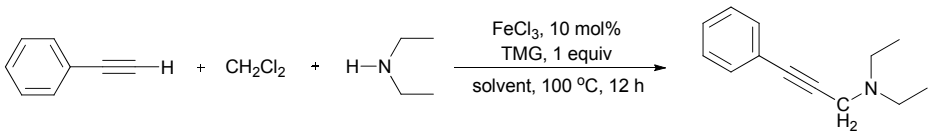


Entry	Base	Yield (%)[b]
1[c]	DBU	50
2[d]	DBN	30
3	Et_3N	29
4[e]	TBD	24
5[f]	TMG	57
6[g]	DIEA	27
7	Na_2CO_3	11
8	K_2CO_3	9
9	Cs_2CO_3	12
10	$NaHCO_3$	20
11	NaOH	13
12	K_3PO_4	7
13	*t*-BuOK	8

[a] Reaction conditions: phenylacetylene (1.0 mmol, 102 mg, 110 μL); dichloromethane (2.0 mmol, 169.9 mg, 128 μL); diethylamine (2.0 mmol, 146.3 mg, 207 μL); base, 1.0 mmol; $FeCl_3$, 10 mol%, 16.2 mg; 0.5 mL CH_3CN was used as solvent; 100 °C; 12 h. [b] NMR yield using $MeNO_2$ as the internal standard. [c] DBU, 1,8-Diazabicyclo[5.4.0]undec-7-ene. [d] DBN, 1,5-Diazabicyclo[4.3.0]non-5-ene. [e] TBD, 1,5,7-triaza-bicyclo [4.4.0]dec-5-ene. [f] TMG, 1,1,3,3-Tetramethylguanidine. [g] DIEA, N,N-diisopropylethylamine.

Generally, organic bases exhibited better performance than the inorganic ones, probably due to their better solubility in CH_3CN. To our delight, it was observed that TMG (1,1,3,3-Tetramethylguanidine), a kind of organic guanidine which are categorized as organic superbases, exhibited the best efficiency for this coupling reaction and the desired propargylic amine product could be obtained with 57% yield, being presumably attributed to influence of basicity and steric effect (entry 5, Table S3).

Table S4 Screening of solvents[a]

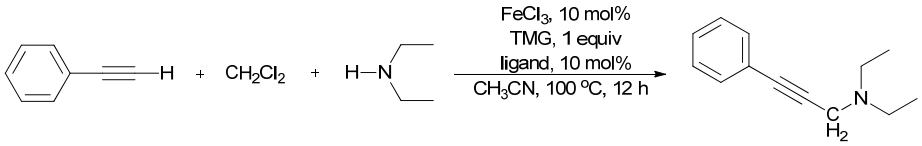


Entry	Solvent	Yield (%)[b]
1	CH_3CN	57
2	CH_2Cl_2	21
3	EtOAc	16
4	DMF	35
5	DMSO	4
6	H_2O	3
7	toluene	0
8	$MeNO_2$	0
9	THF	0
10	EtOH	0
11	neat	12

[a] Reaction conditions: phenylacetylene (1.0 mmol, 102 mg, 110 μL); dichloromethane (2.0 mmol, 169.9 mg, 128 μL); diethylamine (2.0 mmol, 146.3 mg, 207 μL); TMG (1.0 mmol, 115.2 mg, 127 μL); $FeCl_3$, 10 mol%, 16.2 mg; solvent, 0.5 mL; 100 °C; 12 h. [b] NMR yield using $MeNO_2$ as the internal standard.

Among the solvents tested, CH_3CN was the most suitable reaction medium for the AHA coupling reaction (entry 1, Table S4). CH_2Cl_2, EtOAc, DMF, DMSO, H_2O, were inferior and generated the desired product in 21, 16, 35, 4, and 3% yields, respectively (entries 2-6). Unfortunately, no propargylic amine product was obtained when the reactions were carried out in toluene, $MeNO_2$, THF and EtOH (entries 7-10). And under neat condition, only 12% yield was obtained (entry 11). Therefore, CH_3CN was chosen as the reaction medium.

Table S5 Screening of ligands[a]

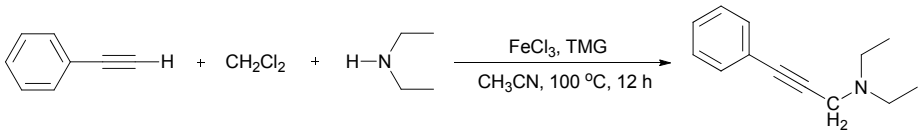


Entry	Ligands	Yield (%)[b]
1	1,10-phenanthroline	20
2	PPh_3	51
3[c]	TMEDA	46

[a] Reaction conditions: phenylacetylene (1.0 mmol, 102 mg, 110 μL); dichloromethane (2.0 mmol, 169.9 mg, 128 μL); diethylamine (2.0 mmol, 146.3 mg, 207 μL); TMG (1.0 mmol, 115.2 mg, 127 μL); $FeCl_3$, 10 mol%, 16.2 mg; CH_3CN, 0.5 mL; ligand, 10 mol%; 100 °C; 12 h. [b] NMR yield using $MeNO_2$ as the internal standard. [c] TMEDA, N,N,N′,N′-Tetramethylethylenediamine.

On testing the effect of the ligand, however, it was found that N-ligands such as 1,10-phenanthroline, TMEDA (N,N,N′,N′-Tetramethylethylenediamine) and P-ligand such as $(C_6H_5)_3P$ did not assist the iron catalyzed three-component coupling reactions of phenylacetylene, dichloromethane and diethylamine, and conversely, restrained the reactivity of the catalyst (entries 1-3, Table S5).

Table S6 Screening of the amounts of starting materials and catalyst[a]



Entry	Catalyst (equiv.)	CH_2Cl_2 (equiv.)	Et_2NH (equiv.)	TMG (equiv.)	Yield (%)[b]
1	$FeCl_3$ (0.1)	2.0	2.0	1.0	57
2	$FeCl_3$ (0.1)	4.0	2.0	1.0	48
3	$FeCl_3$ (0.1)	10.0	2.0	1.0	15
4	$FeCl_3$ (0.1)	2.0	2.0	2.0	60
5	**$FeCl_3$ (0.2)**	**2.0**	**2.0**	**2.0**	**67**
6[c]	**$FeCl_3$ (0.2)**	**2.0**	**2.0**	**2.0**	**95**

[a] Reaction conditions: phenylacetylene (1.0 mmol, 102 mg, 110 μL); CH_3CN, 0.5 mL; 100 °C; 12 h; [b] NMR yield using $MeNO_2$ as the internal standard; [c] 2.0 equiv of piperidine was used as the starting material amine.

Take the quite lower boiling point of CH_2Cl_2 compared with the reaction temperature into account, we envisioned that increasing the amount of CH_2Cl_2 might help enhance the conversion thereby raise the yield of the desired product. Unfortunately, higher amounts of CH_2Cl_2 restrained the AHA coupling reaction which was consistent with the result when using CH_2Cl_2 as the solvent indicating that 2 equiv of CH_2Cl_2 was enough in the reaction system (entries 1-3, Table S6).

Nevertheless, the base, which played a dual roles including activating the alkyne and trapping the formed HCl by-product in the reaction system, might not enough here. Theoretically, at least 2 equiv of base was necessary for the coupling reaction, one for the activation of the alkyne and the other for the trap of formed HCl under the given reaction conditions. However, when 2 equiv of TMG was used, there was only a slight enhancement in the yield (entry 4 *vs* 1). With respect to the catalyst loading, 20 mol% of $FeCl_3$ gave a better result (entry 5). Gratifyingly, it was found that when piperidine, whose boiling point is higher than the reaction temperature, was used as the starting amine material, the corresponding propargylic amine product was obtained in an excellent 95% yield under the identical reaction conditions (entry 6).

Thus, the optimal reaction conditions were defined as following: alkyne, 1.0 mmol; CH_2Cl_2, 2.0 mmol; amine, 2.0 mmol; $FeCl_3$, 20 mol%; TMG, 2.0 mmol; CH_3CN, 0.5 mL; 100 ^oC; 12 h.

4. *In situ* FT-IR Study

(1) The procedure for *in situ* FT-IR study using $FeCl_3$-*method A* (Fig. 1a)

A dried three-neck bottom flask was charged with a stir bar and equipped with Diamond ATR probe on ReactIR. CH_3CN (2.0 mL) was first added and the background measurement was performed. Then the IR scan was started (the spectra were acquired 30 scans per spectrum at a resolution of 8 and the each acquisition was performed by every 15 second) at room temperature. Next, phenylacetylene (10 mmol, 1.1 mL, 1.0 equiv) was added and immediately the C-H stretch signal of a solution of phenylacetylene in acetonitrile was observed at 3277 cm^{-1}. And then to the mixture was added TMG (11 mmol, 1.4 mL, 1.1 equiv). After for a while until the spectrum was stable, $FeCl_3$ (10 mmol, 1.622 g, 1.0 equiv) was added to the mixture in a piecemeal fashion in proportion (8 times, 0.2028 g each time). And then the temperature was increased to 100 ^oC from room temperature. In Figure 1a, the spectrum is shown from 0 min to 240 mins around 3277 cm^{-1}.

(2) The procedure for *in situ* FT-IR study using $FeCl_3$-*method B* (Fig. 1b)

A dried three-neck bottom flask was charged with a stir bar and equipped with Diamond ATR probe on ReactIR. First, the temperature of the system was increased to 100 ^oC. Then, CH_3CN (2.0 mL) was added and the background measurement was

performed. Then the IR scan was started (the spectra were acquired 30 scans per spectrum at a resolution of 8 and the each acquisition was performed by every 15 second). Then TMG (10 mmol, 1.27 mL, 2.0 equiv) was added. After that, $FeCl_3$ (5 mmol, 0.8110 g) was added in four batches. When the mixture was stable, 1.0 equivalent of phenylacetylene (5 mmol, 0.55 mL) was added. At first, the signal at 3277 cm^{-1} corresponding to the C-H stretch of alkyne was observed and this signal disappeared within 50 minutes. When next 1.0 or 2.0 equivalents of phenylacetylene were further added (total 2 or 3 equivalents), the absorbance at 3277 cm^{-1} increased with each addition and remained unchanged with the prolonging of the time. From these results, the activation of terminal alkyne was confirmed and the formation of iron-acetylide species was implied.

5. XPS analysis

XPS (X-ray photoelectron spectroscopy) was used to evaluate the oxidation state of Fe species. Two controlled experiments were conducted: (1) to 0.5 mL CH_3CN, 20 mol% $FeCl_3$ and 2 mmol TMG were added, and the mixture was stirred at room temperature for 12 h; (2) the reaction of phenylacetylene, CH_2Cl_2 and piperidine was performed under the optimal reactions i.e. alkyne (1.0 mmol); dichloromethane (2.0 mmol); amine (2.0 mmol),TMG (2.0 mmol), $FeCl_3$ (32.4 mg, CH_3CN, 0.5 mL; 100 ^oC; 12 h). XPS analysis was performed by taking aliquots of both the aforementioned reaction mixtures. Based on the XPS analytic results (Figure S1, S2), it was found that Fe existed as Fe^{II} species which might be $FeCl_2$ both before and after the reaction. And no Fe(0) species was detected during the XPS analysis. In other words, the initial catalyst $FeCl_3$ could be reduced to Fe^{II} species first in the presence of TMG or amine and no Fe nano-particles were formed.

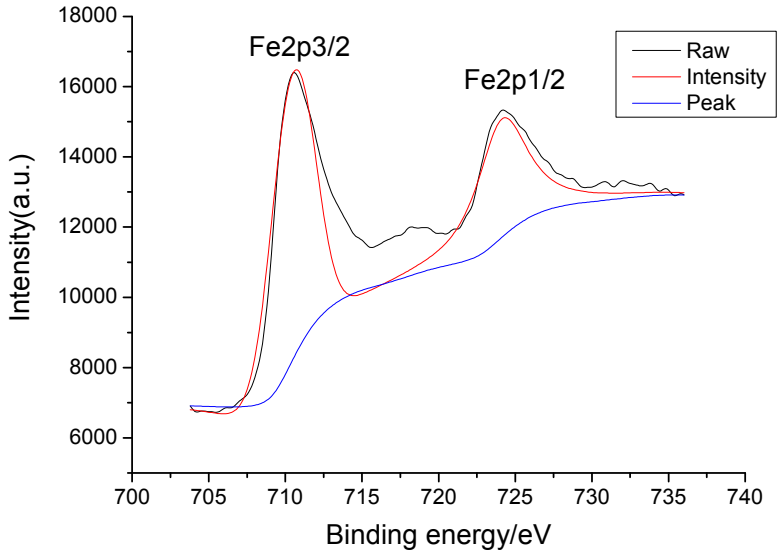


Figure S1 XPS spectrum of controlled experiment (1)

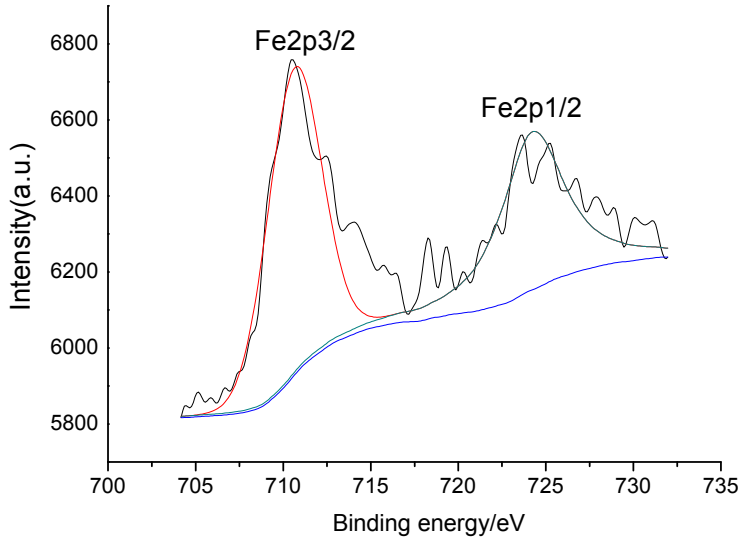
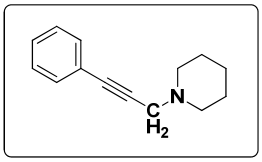


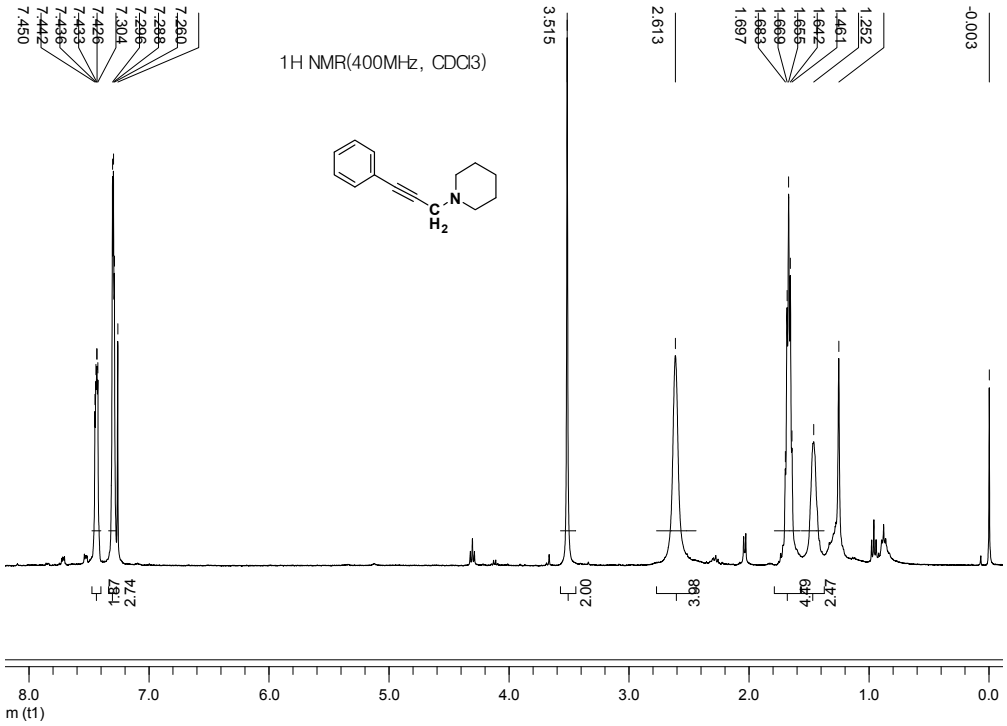
Figure S2 XPS spectrum of controlled experiment (2)

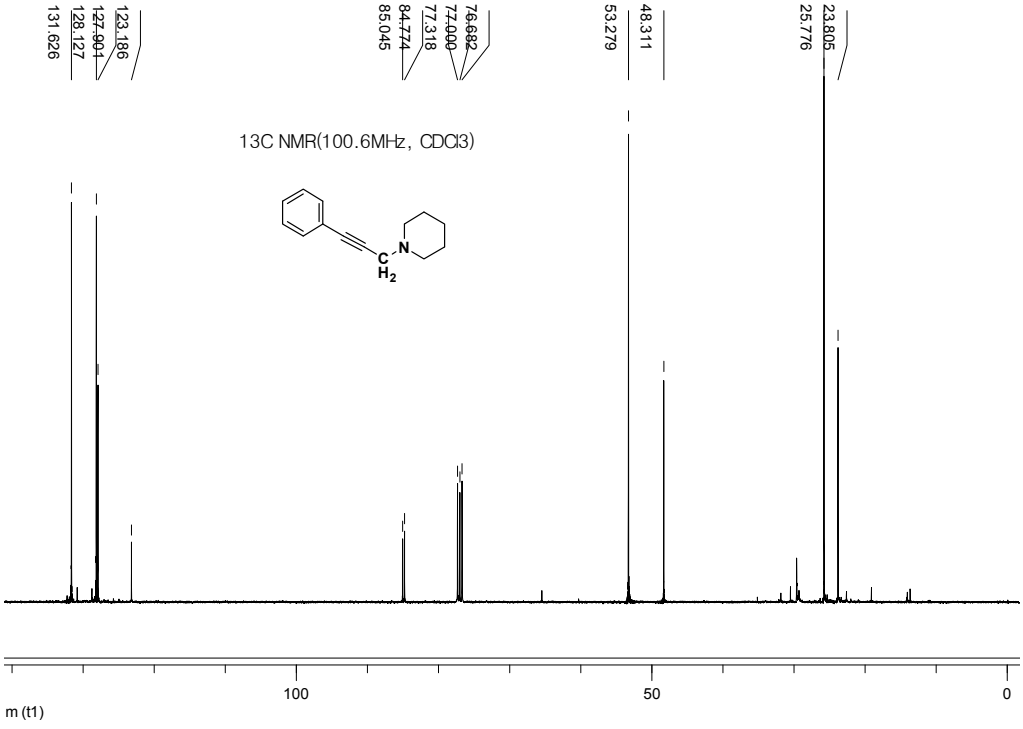
6. The characterization, ^{1}H and ^{13}C NMR charts of the propargylic amine products

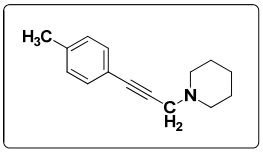


^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3H, CH_3); 3.89-3.93 (dd, $^{3}J_{HH}$ = 8.0 Hz, 8.0 Hz, 1H, CH_2); 4.43-4.47 (t, $^{3}J_{HH}$ = 8.8 Hz, 8.8 Hz, 1H, CH_2); 5.53-5.57 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, CH);

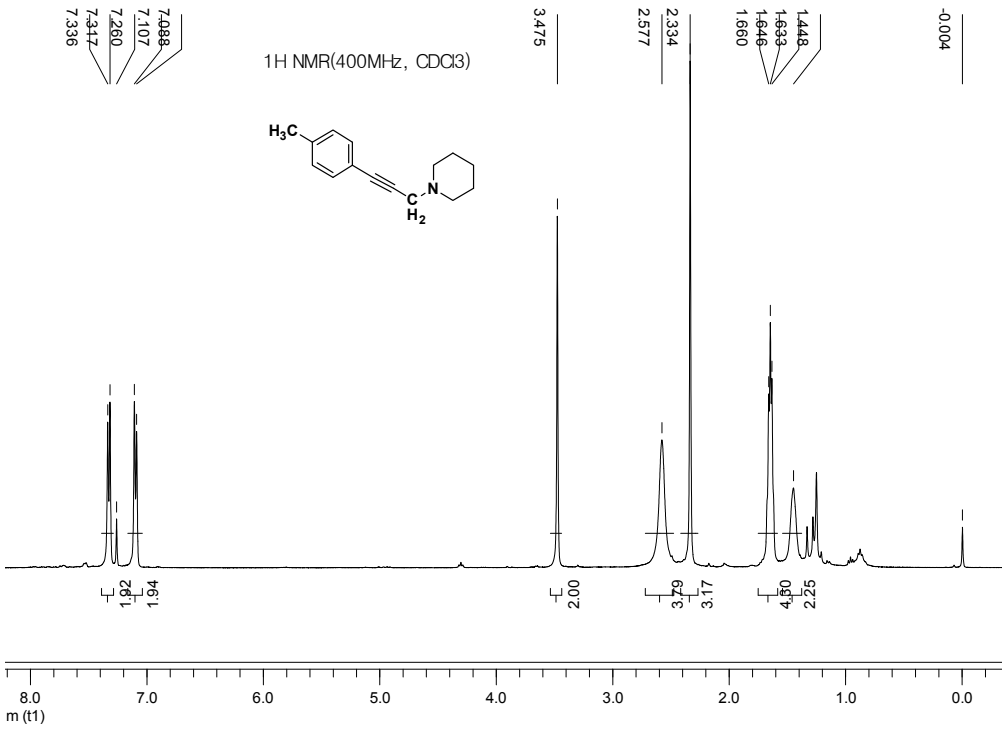
7.27-7.30 (m, 2H, Ar-H); 7.39-7.42 (m, 5H, Ar-H); 7.97-7.99 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.77; 51.65; 75.32; 125.61; 128.36; 129.15; 129.56; 129.98; 133.88; 136.20; 145.89; 151.54 ppm. ESI-MS calcd for $C_{14}H_{17}N$ 199.29, found 200.2 $(M+H)^+$.

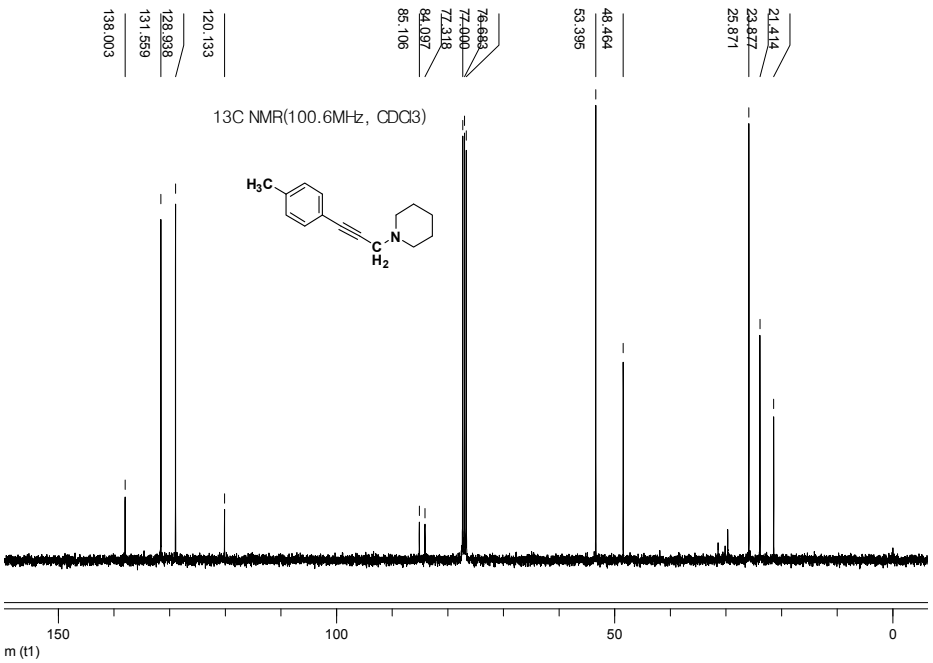


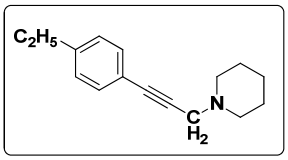




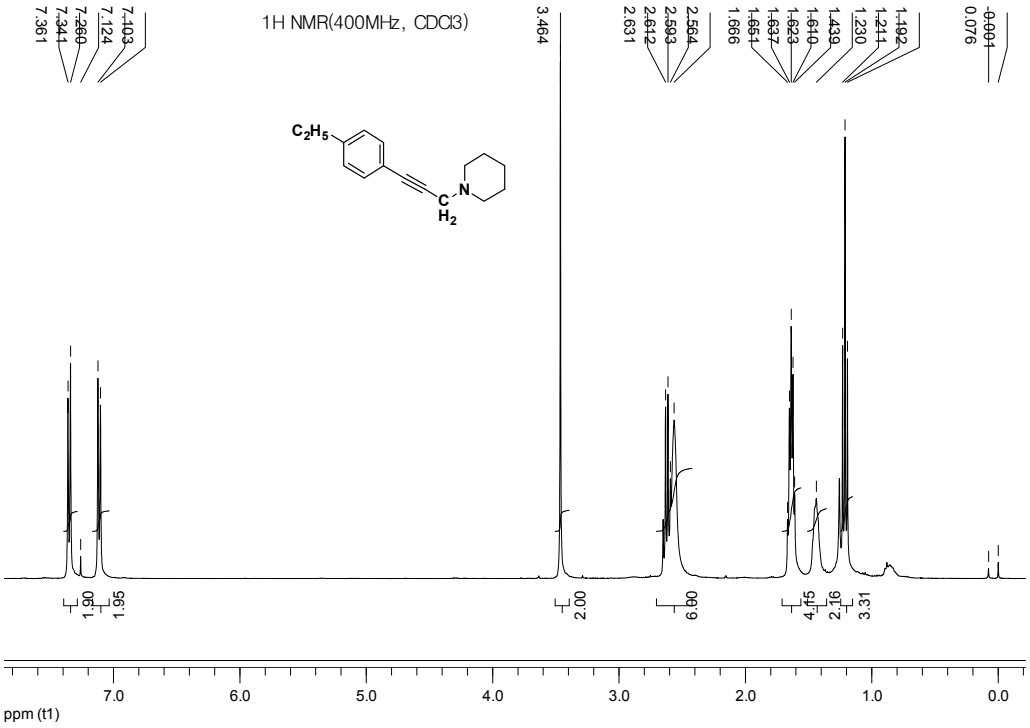
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 2H, CH_2); 1.65 (t, $^{3}J_{HH}$ = 5.4 Hz, 4H, $2CH_2$); 2.33 (s, 3H, CH_3); 2.58 (s, 4H, $2CH_2$); 3.48 (s, 2H, CH_2); 7.10 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar-H); 7.33 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.4; 23.8; 25.8; 48.4; 53.3; 84.0; 85.1; 120.1; 128.9; 131.5; 138.0 ppm. ESI-MS calcd for $C_{15}H_{19}N$ 213.32, found 214.1 $(M+H)^{+}$.

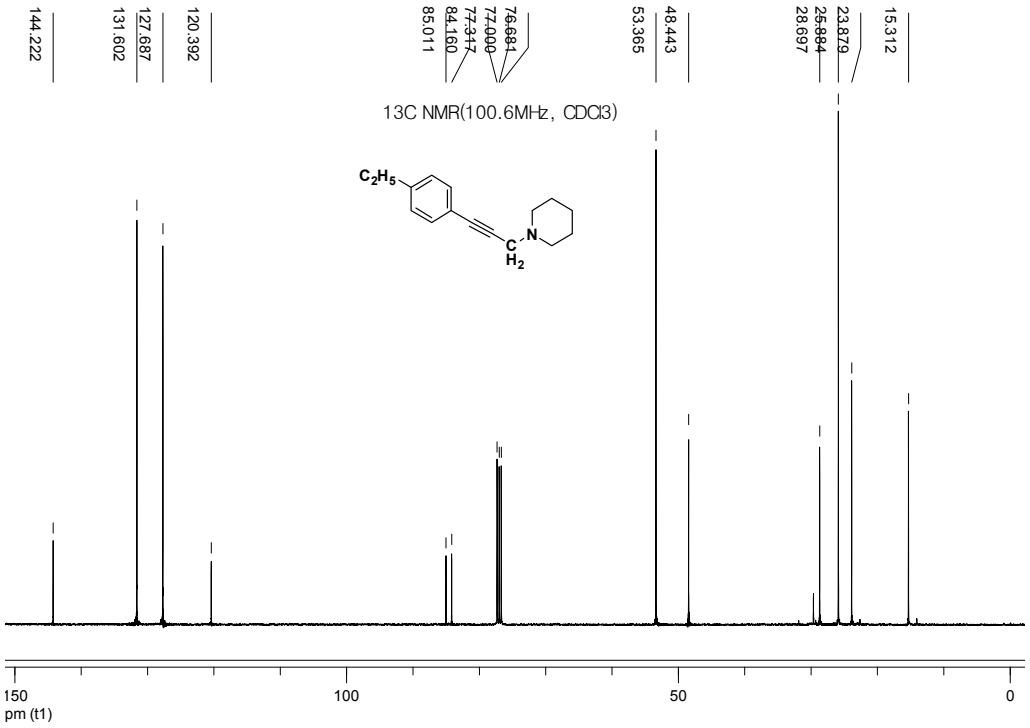


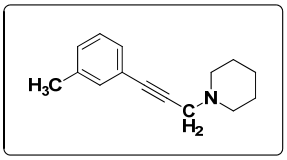




^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H, CH_3); 1.44 (s, 2H, CH_2); 1.61-1.67 (m, 4H, $2CH_2$); 2.56-2.63 (m, 6H, $3CH_2$); 3.46 (s, 2H, CH_2); 7.11 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-H); 7.35 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.3; 23.8; 25.8; 28.6; 48.4; 53.3; 84.1; 85.0; 120.3; 127.6; 131.6; 144.2 ppm. HRMS(ESI): calcd for $C_{14}H_{22}N$ $(M+H)^{+}$ 228.1695, found 228.1745.

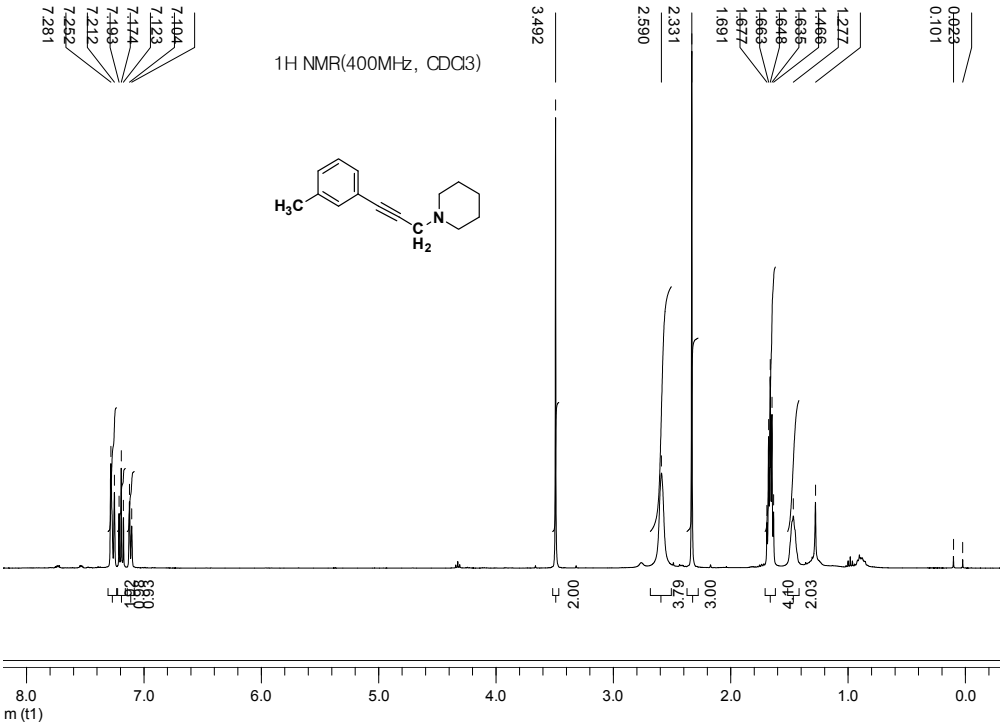


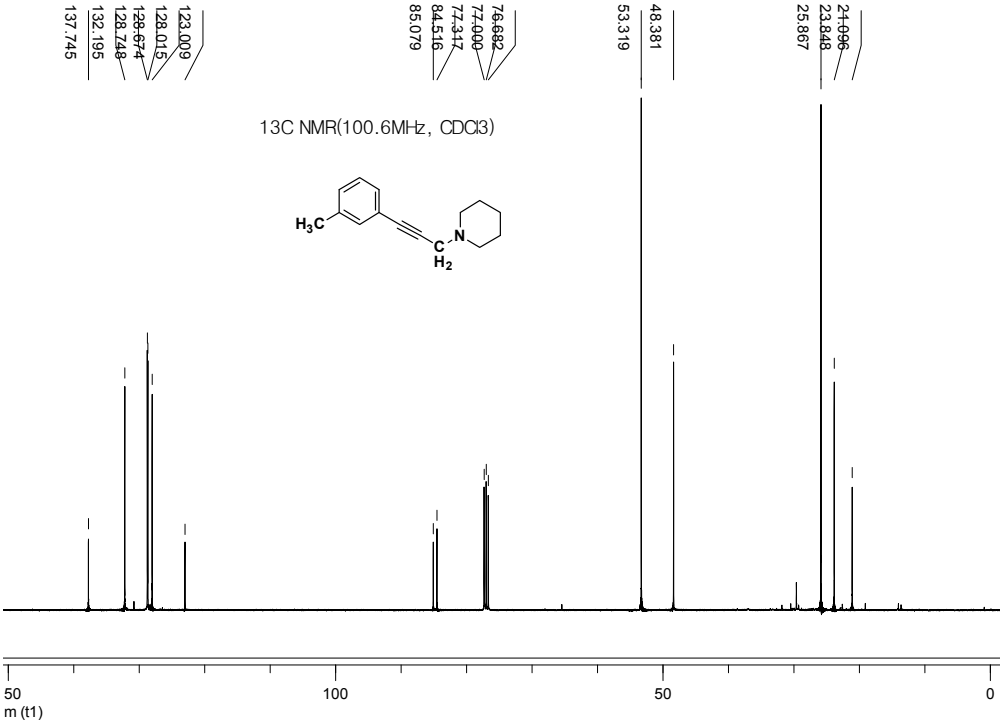


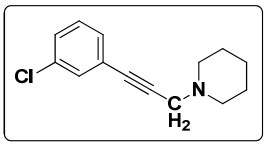


^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 2H, CH_2); 1.64-1.69 (m, 4H, $2CH_2$); 2.33 (s, 3H, CH_3); 2.59 (s, 4H, 2N-CH_2); 3.49 (s, 2H, CH_2); 7.11 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar-H); 7.19 (t, $^{3}J_{HH}$ = 7.6 Hz,

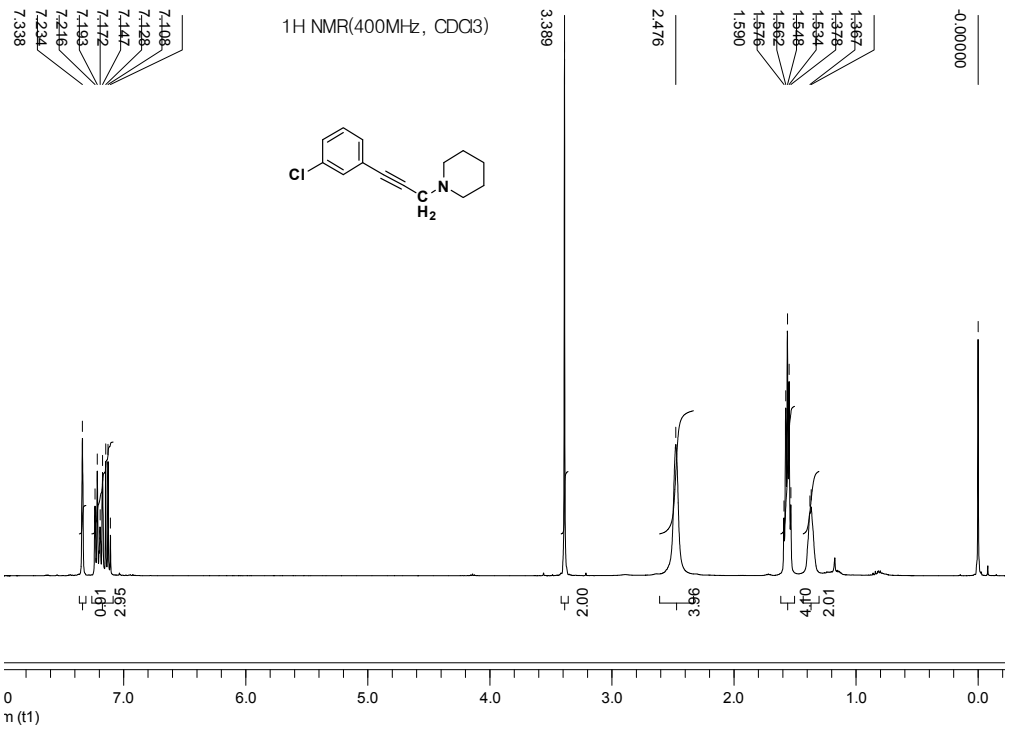
1H, Ar-H); 7.27 (d, $^{3}J_{HH}$ = 11.6 Hz, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.0; 23.8; 25.8; 48.3; 53.3; 84.5; 85.0; 123.0; 128.0; 128.6; 128.7; 132.1; 137.7 ppm. ESI-MS calcd for $C_{15}H_{19}N$ 213.32, found 214.1 $(M+H)^{+}$.

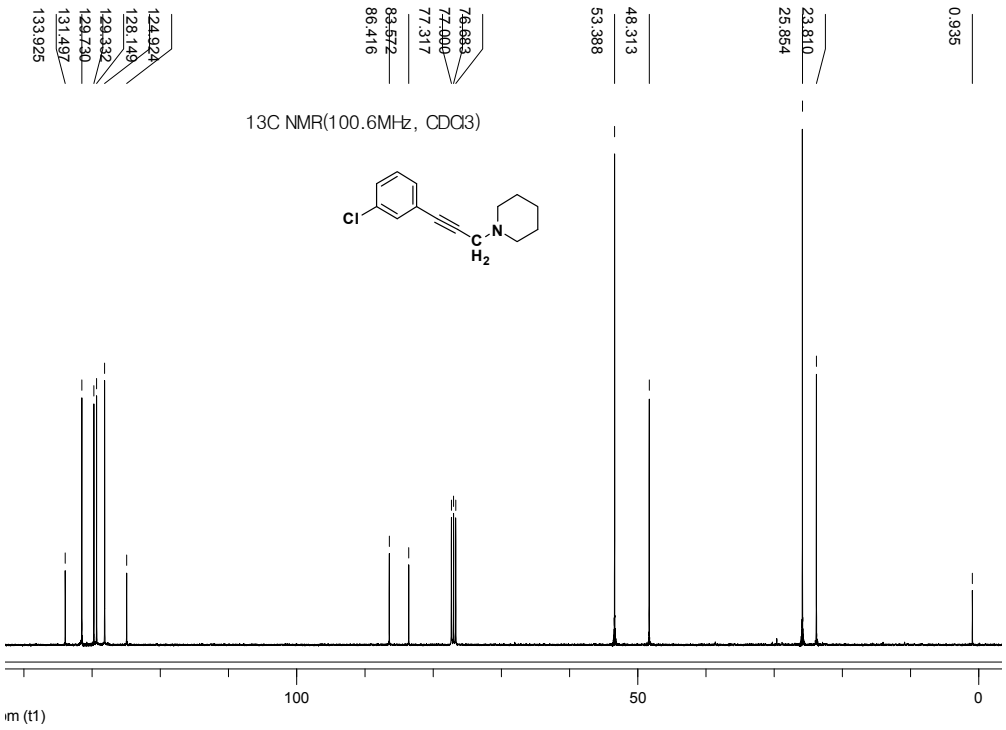


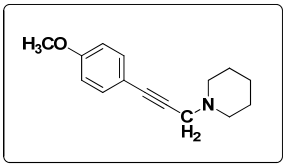




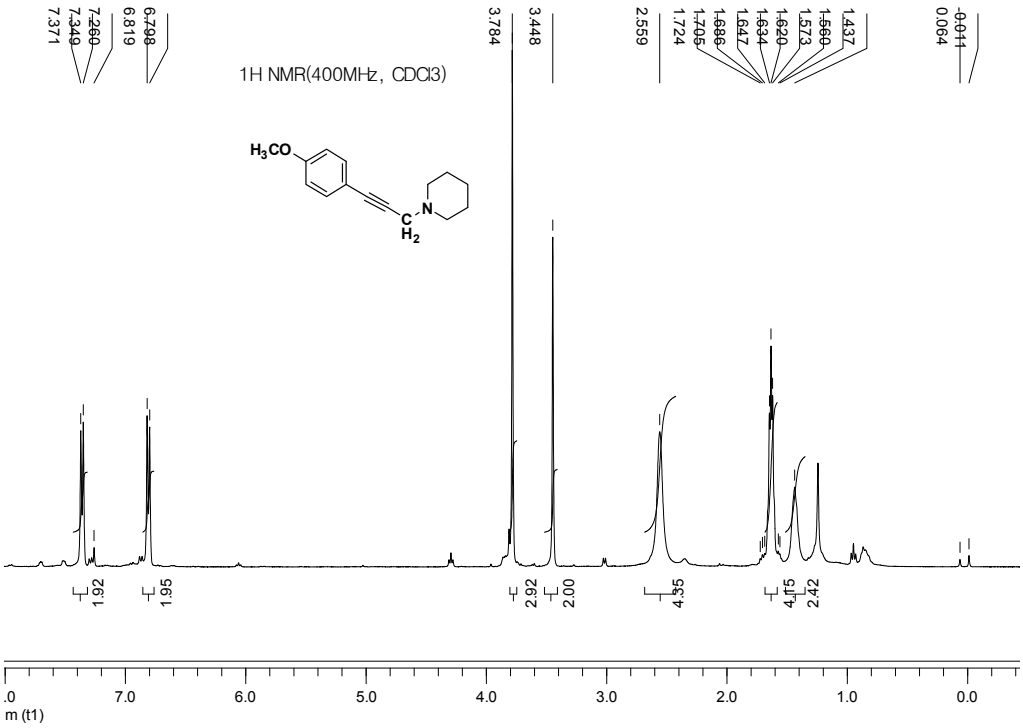
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (d, $^{3}J_{HH}$ = 4.4 Hz, 2H, CH_2); 1.53-1.59 (m, 4H, $2CH_2$); 2.48 (s, 4H, 2N-CH_2); 3.39 (s, 2H, CH_2); 7.11-7.23 (m, 3H, Ar-H); 7.34 (s, 1H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.8; 25.8; 48.3; 53.3; 83.5; 86.4; 124.9; 128.1; 129.3; 129.7; 131.4; 133.9 ppm. HRMS(ESI): calcd for $C_{14}H_{17}ClN$ $(M+H)^{+}$ 234.0995, found 234.1050.

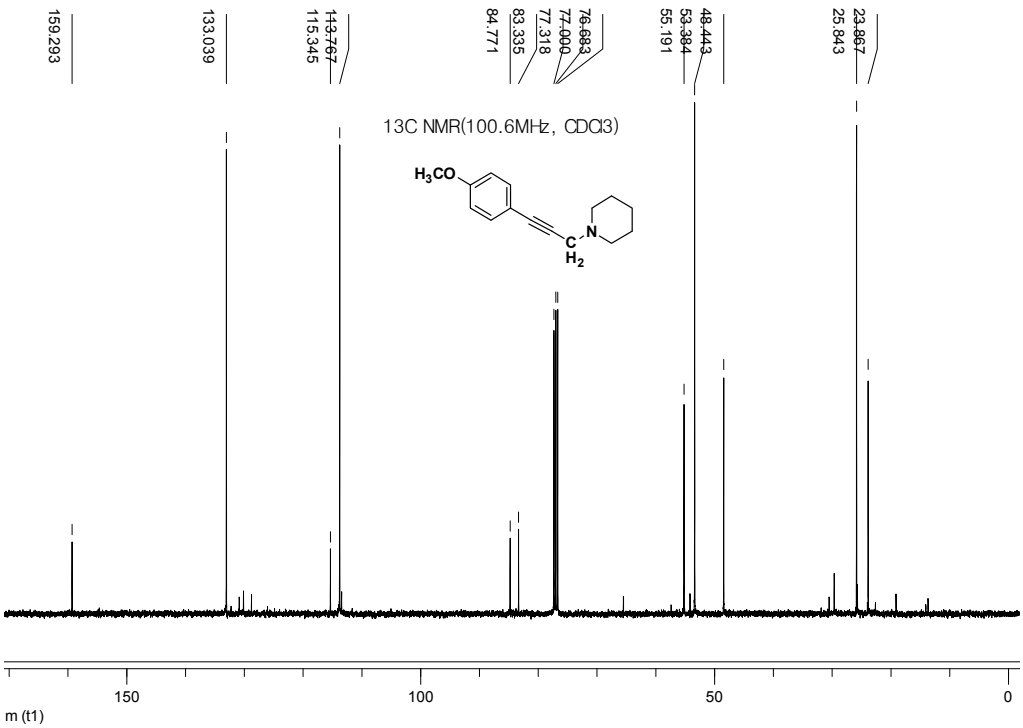


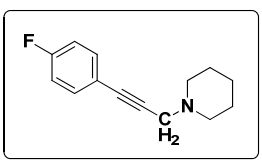




^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 2H, CH_2); 1.56-1.72 (m, 4H, $2CH_2$); 2.56 (s, 4H, $2N\text{-}CH_2$); 3.45 (s, 2H, CH_2); 3.78 (s, 3H, CH_3); 6.81 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-H); 7.36 (t, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.8; 25.8; 48.4; 53.3; 55.1; 83.3; 84.7; 113.7; 115.3; 133.0; 159.2 ppm. ESI-MS calcd for $C_{15}H_{19}NO$ 229.32, found 230.0 $(M+H)^{+}$.

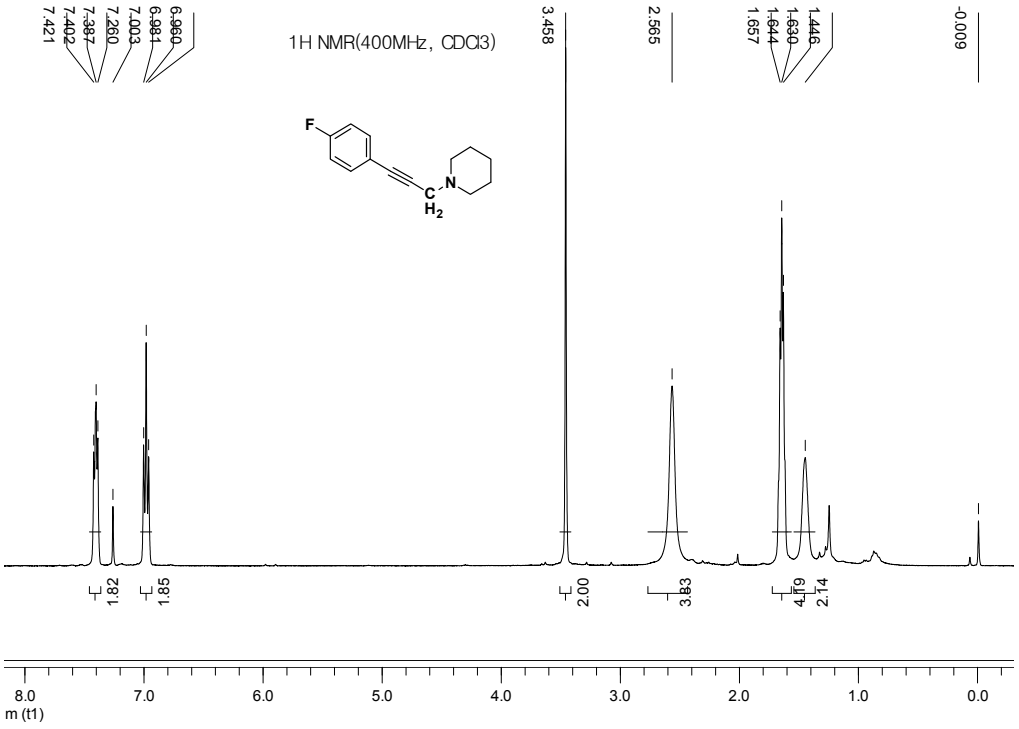


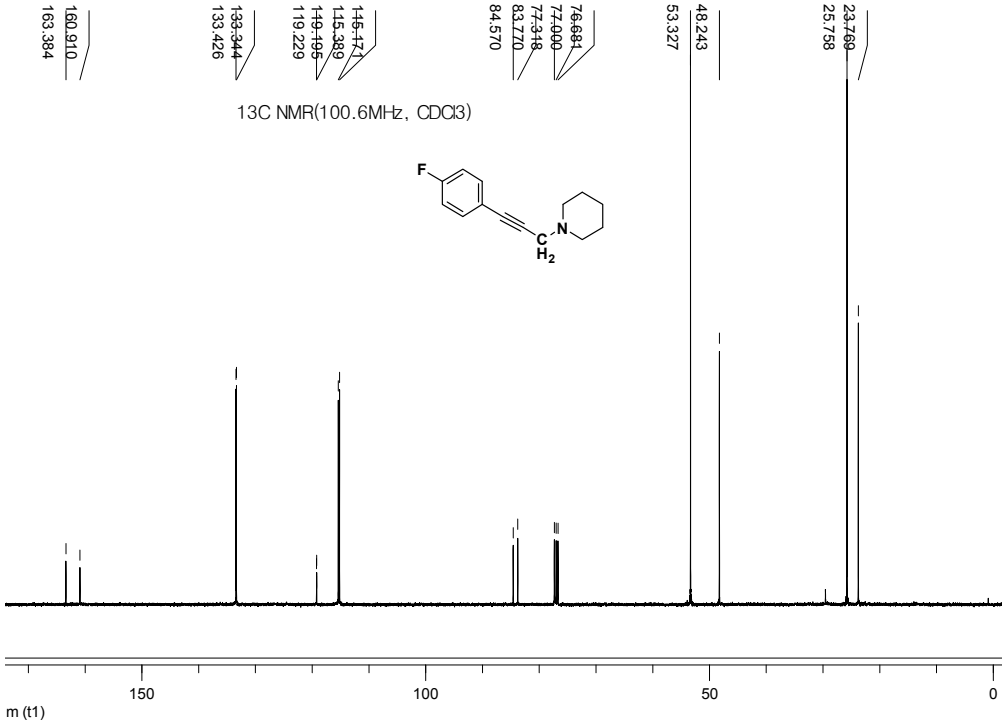


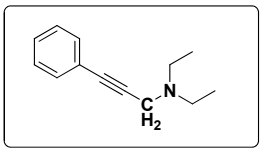


^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 2H, CH_2); 1.64 (t, $^{3}J_{HH}$ = 5.4 Hz, 4H, $2CH_2$); 2.57 (s, 4H, $2CH_2$); 3.46 (s, 2H, CH_2); 6.98 (t, $^{3}J_{HH}$ = 8.6 Hz, 2H, Ar-H); 7.40 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H, Ar-H) ppm.

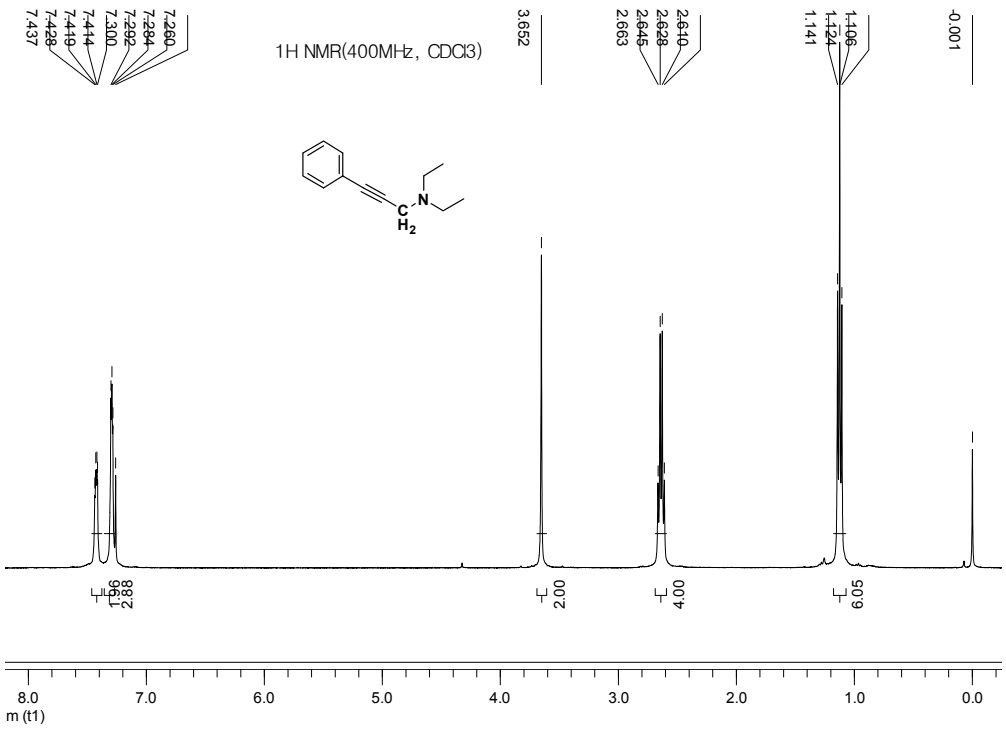
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.7; 25.7; 48.2; 53.3; 83.7; 84.5; (115.1, 115.3); (119.1, 119.2); (133.3, 133.4); (160.9, 163.3) ppm. ESI-MS calcd for $C_{14}H_{16}FN$ 217.28, found 218.0 $(M+H)^+$. HRMS(ESI): calcd for $C_{14}H_{17}FN$ $(M+H)^+$ 218.1295, found 218.1276.

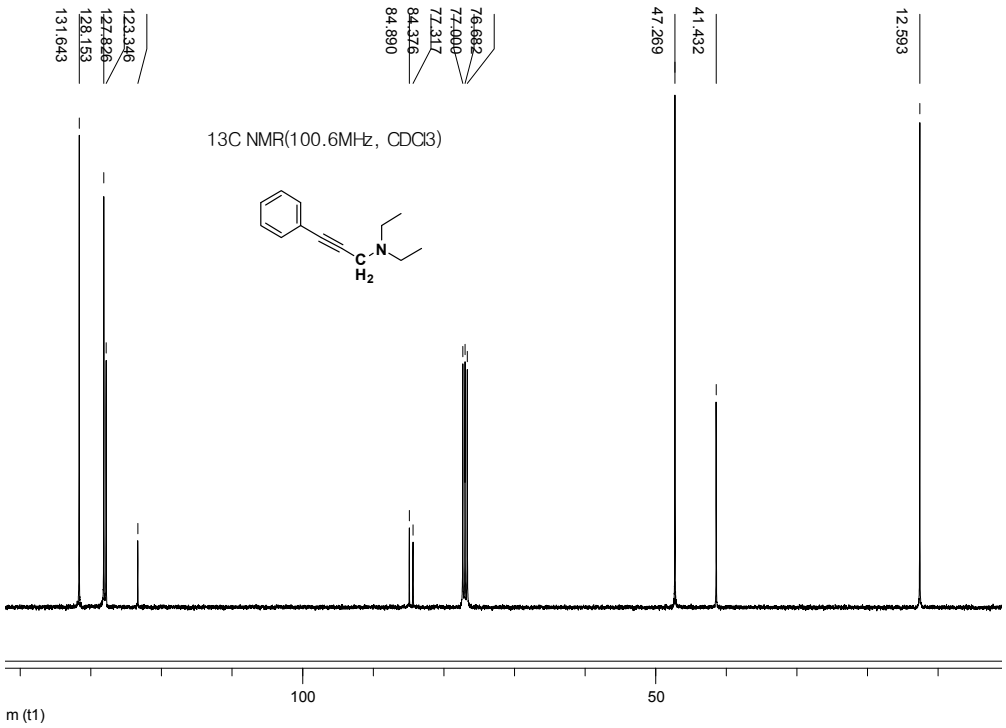


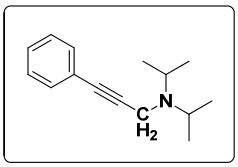




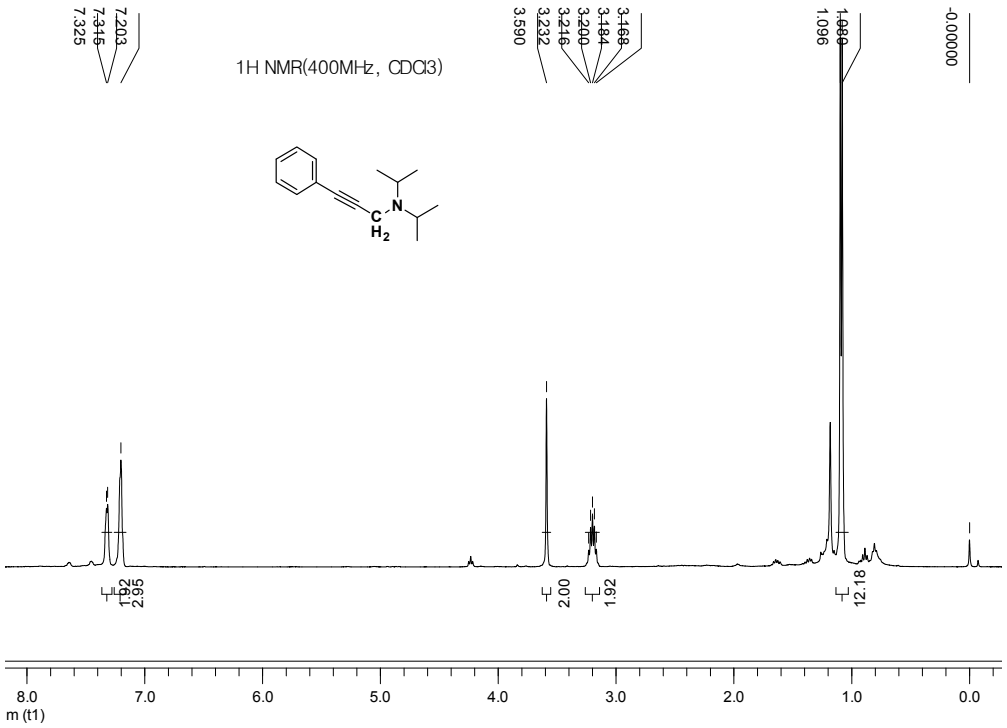
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH_3); 2.64 (q, $^{3}J_{HH}$ = 14.0 Hz, 4H, CH_2); 3.65 (s, 2H, CH_2); 7.28-7.30 (m, 3H, Ar-H); 7.41-7.44 (m, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.59; 41.43; 47.26; 84.37; 84.89; 123.34; 127.82; 128.15; 131.64 ppm. ESI-MS calcd for $C_{13}H_{17}N$ 187.28, found 188.2 $(M+H)^{+}$.

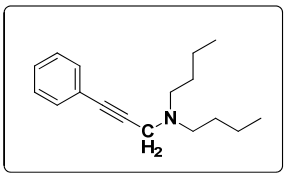




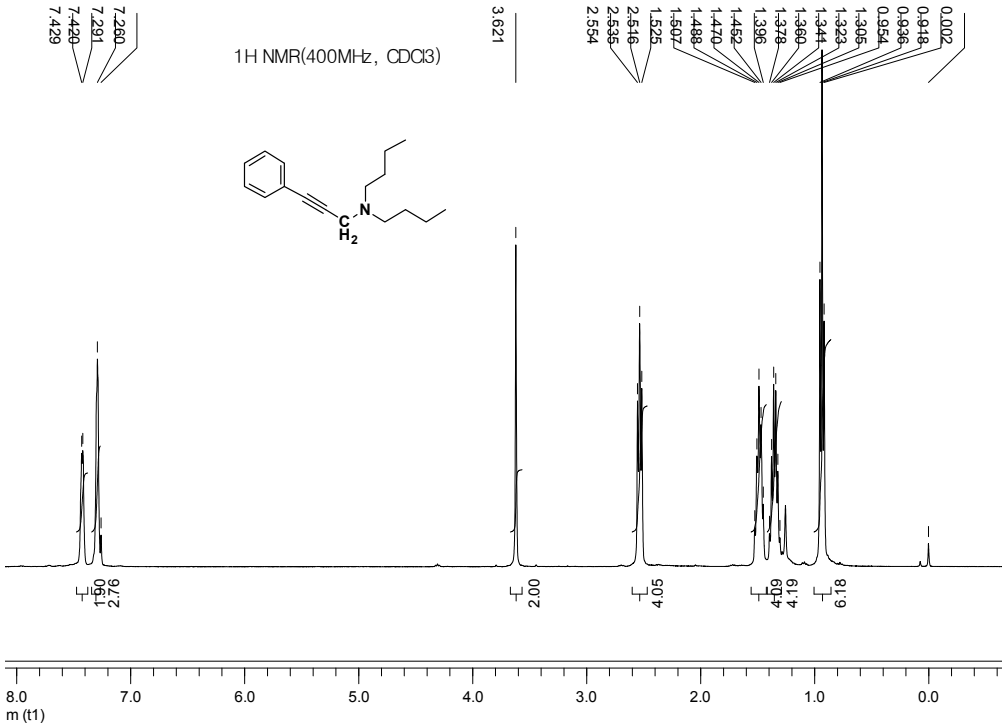


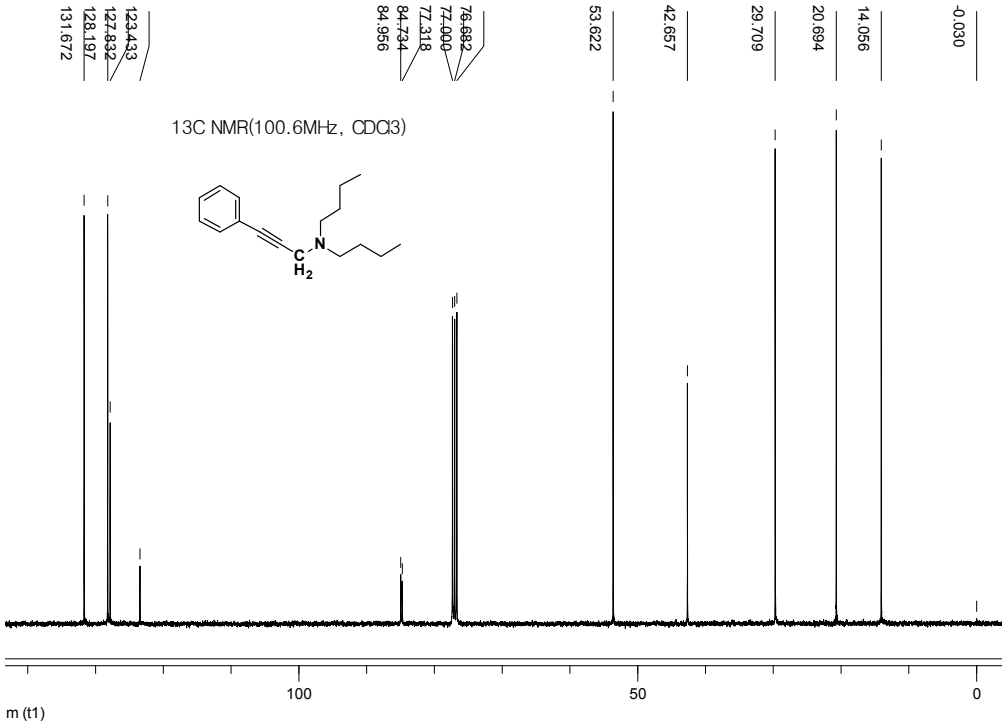
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, $^{3}J_{HH}$ = 6.4 Hz, 12H, $4CH_3$); 3.17-3.23 (m, 2H, 2CH); 3.59 (s, 2H, CH_2); 7.20 (s, 3H, Ar-H); 7.31 (d, $^{3}J_{HH}$ = 4.0 Hz, 2H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.5; 29.6; 34.7; 48.5; 83.5; 88.8; 123.7; 127.6; 128.1; 131.4 ppm. ESI-MS calcd for $C_{15}H_{21}N$ 215.33, found 216.0 $(M+H)^{+}$.

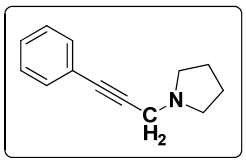




^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, $^{3}J_{HH}$ = 7.2 H，6H, $2CH_3$); 1.31-1.40 (m, 4H, $2CH_2$); 1.45-1.53 (m, 4H, $2CH_2$); 2.54 (t, $^{3}J_{HH}$ = 7.6 H，4H, $2CH_2$); 3.62 (s, 2H, CH_2); 7.29 (s, 3H, Ar-H); 7.42 (d, $^{3}J_{HH}$ = 3.6 Hz, 2H, Ar-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.0; 20.6; 29.7; 42.6; 53.6; 84.7; 84.9; 123.4; 127.8; 128.1; 131.6. ESI-MS calcd for $C_{15}H_{25}N$ 243.39, found 244.1 $(M+H)^{+}$.







^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.81-1.85 (m，4H, $2CH_2$); 2.69 (s, 4H, $2CH_2$); 3.62 (s, 2H, CH_2);

7.28 (t, $^{3}J_{HH}$ = 3.2 Hz, 3H, Ar-H); 7.41-7.44 (m, 2H, Ar-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.7; 43.7; 52.6; 84.3; 85.3; 123.2; 127.8; 128.1; 131.6. ESI-MS calcd for $C_{13}H_{15}N$ 185.26, found 186.1 $(M+H)^{+}$.