Supporting Information

Highly Efficient and Eco-friendly Synthesis of Tertiary Amines by Reductive Alkylation of Aldehydes with Secondary Amines over Pt Nanowires Catalyst

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General Information

All the reactions are heated under an atmosphere of hydrogen at a certain temperature with magnetic stirring. Unless otherwise noted, all materials were used without further purification from commercial suppliers. All solvents were reagent grade. After reaction, the hydrogen atmosphere was removed and the resultant product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. The NMR spectra were measured on a spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ solution with TMS as an internal standard. Chemical shifts (δ) are given in parts per million, and coupling constants (J), in hertz.

Materials:

All chemicals involved in this work were analytical grade and used without further purification. Methanol, ethanol, toluene and hexane were purchased from Shanghai Chemical Industrial Co. Iron pentacarbonyl ($Fe(CO)_5$), oleylamine (OAm), sodium oleate, octadecene, oleic acid and Platinum acetylacetonate were purchased from Sigma-Aldrich. Hydrochloric acid and acetic acid, Water, p-xylene, dioxane, DMF, and n-heptane were purchased from Sinopharm chemical reagent Co. Ltd. Benzaldehyde and its derivatives, piperidine and its derivatives were purchased from Alfa Aesar (China) Chemical Co.,Ltd.

The synthesis of Pt nanowires:

FePt nanowires were synthesized in accordance with the procedure described by S. H. Sun et al.[1] and Gu et al.[2] $Pt(acac)_2$ (200 mg) and OAm (20 mL) were mixed in a 3-neck flask at room temperature under vigorously stirring in argon atmosphere for several minutes. Then, the solution was heated to 60 °C and kept for 10 minutes until the solution became transparent. After that, the solution was rapidly heated to 120 °C and then kept for 15 minutes. After the solution became deep yellow, 150 μL $Fe(CO)_5$ was then injected into the solution, afterwards, the argon atmosphere and the stirring was removed after 30 seconds. And then the temperature was slowly raised to 160 °C. The black solution was cooled to room temperature after the solution was kept at 160 °C for 30 minutes and centrifuged by ethanol. FePt nanowires were obtained after the precipitate was washed in methanol and ethanol for three times.
100 mg FePt NWs were dispersed in 30 mL methanol and subsequently treated by 10 mL HCl/acetic acid (1:1) solution to remove Fe element. The solution was then heated to 60 °C and kept for 1 hour under vigorously stirring, the precipitates were obtained through 10 minutes of centrifugation (3000 rpm). The dark solid was washed with hexane and methanol for three times and finally stored in 30 mL methanol for further use.

Synthesis of Pt nanorods (Pt NRs):

Pt NRs were obtained by acidic etching of FePt NRs. The FePt NRs were synthesized by the following method[2]: $Pt(acac)_2$ (100mg), sodium oleate (75mg) were added to 10 mL oleylamine in a 3-neck flask under argon atmosphere and vigorous stirring. The mixture was then rapidly heated to 120 ^oC and maintained for 15 minutes. As the solution turned lucid yellow, a drop of $Fe(CO)_5$ (~0.005mL) was quickly injected into the solution. The solution turned dark immediately. The temperature was then heated to 250 ^oC and kept the temperature for 30 minutes. The black solution was then cooled to room temperature. The sample was centrifuged in ethanol to get the NRs. The NRs were dispersed in 10 mL toluene and precipitated by adding ethanol. The process was repeated for several times to purify the NRs. The final product was dispersed in 10 mL of methanol.

50 mg FePt NRs (in 20 mL methanol) were treated by 5 mL HCl/acetic acid (1:1) solution. The solution was heated to 60°C and stirred for 1 hour, the resultant precipitates were obtained following 10 minutes of centrifugation (5000 rpm). The dark solid was washed with methanol and stored in methanol.

Synthesis of Pt nanoparticles (Pt NPs):

Pt NPs were achieved by acidic etching of FePt NPs. The FePt NPs were synthesized as follow[2]: $Pt(acac)_2$ (100mg), octadecene (10 mL), oleic acid (1 mL) and oleylamine (1 mL) were mixed in 3-neck flask under argon atmosphere and vigorous stirring. The mixture was then heated to 65 ^oC to dissolve $Pt(acac)_2$. After the solution became transparent, the temperature was then raised to 180 ^oC. A solution of $Fe(CO)_5$ (~0.01mL) in hexane was quickly injected into the solution. The solution was then further heated to 200 ^oC and kept for 1 hour before it was cooled down to room temperature. Appropriate amount of isopropanol was added and then the suspension was centrifuged (8000 rpm) to obtain the NPs. The NPs were dispersed in 10 mL hexane and precipitated by ethanol. The process was repeated for three times to purify the NPs. The final product was dispersed in 10 mL of methanol.

50 mg FePt NPs (in 20 mL methanol) were treated by 10 mL HCl/methanol (1:1) solution. The mixed solution was added into the above suspension. The solution was heated to 60 °C and stirred for 1 hour, the resultant precipitates were obtained after 10 minutes of centrifugation (8000 rpm). The dark solid was washed with methanol for two more times and stored in hexane.

Typical procedure for catalytic hydrogenation of Aldehydes with secondary amines:

Pt NWs (0.005 mmol), benzaldehyde or its derivatives (1 mmol or 1.1mmol), piperidine or its derivatives (1mmol or 1.1mmol), solvent (2 mL) were added in a Schlenk tube and then sealed. The reaction tube was thrice evacuated and flushed with hydrogen and then carried out at a certain temperature under a hydrogen atmosphere. After reaction, the resultant product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. 1-benzylpiperidine and its derivatives were characterized by ^1H NMR and ^{13}C NMR.

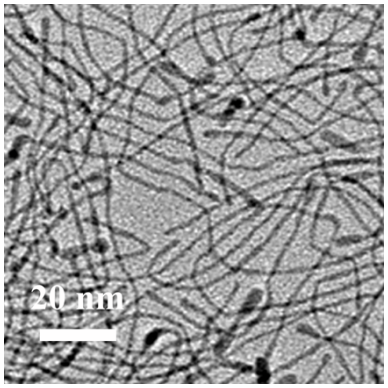


Figure S1. TEM image of Pt nanowires

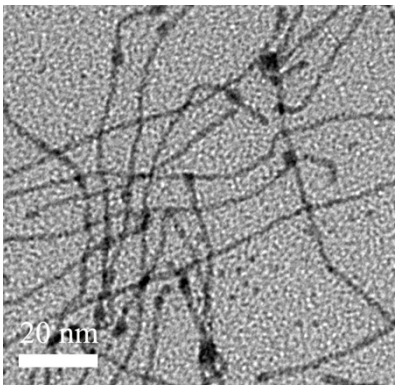


Figure S2. TEM image of Pt nanowires after 10 cycles

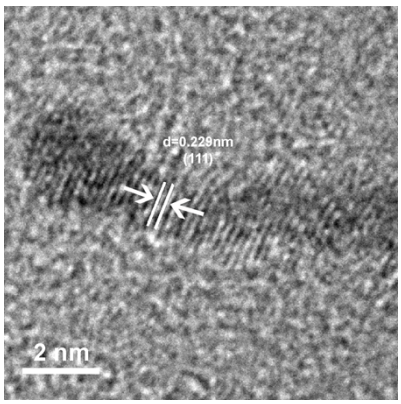


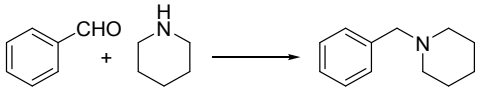
Figure S3. HR-TEM image of Pt nanowire

Table S1. Formation of 1-benzylpiperidine using FePt and Pt nanowires as catalyst[a]

Entry	Catalyst	Solvent	T(°C)	Convention[b](%)	Yield[b](%)
1	FePt Nanowires[c]	ethanol	80	78	52
2	Pt Nanowires	ethanol	80	100	99
[a] Reaction conditions: benzaldehyde (1.0 mmol), piperidine (1.1 mmol) and ethano					

l (2 mL) at 1 bar H_2 with 0.005 mmol Pt NWs for 3 h. [b] GC yield. [c] FePt Nanowires were prepared through the above method.

Table S2. Comparison of the formation of tertiary amine using Pt NWs and Pt/C catalyst



Entry	Catalyst	Solvent	Temperature(°C)	Convension
1[a]	Pt NWs	ethanol	80	99
2[a]	Pt/C	ethanol	80	97
3[b]	Pt NWs	ethanol	80	96
4[b]	Pt/C	ethanol	80	71
Condition: [a] 1mmol benzaldehyde, 1.1mmol piperidine, 2mL ethanol, 0.005mmol Pt NWs and 4.8mg Pt/C (20%). [b] 5mmol benzaldehyde, 5.5 mmol piperidine, 0.025mmol Pt NWs and 24.5mg Pt/C (20%).				

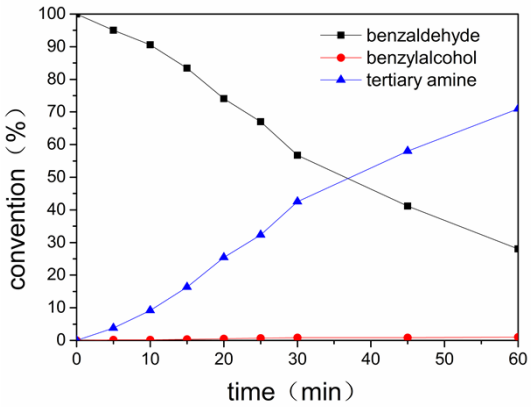
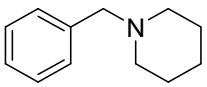


Figure S4. Time-conversion plot for the formation of tertiary amine by interaction of benzaldehyde with secondary amine over Pt/C catalyst (Reaction condition: 5mmol benzaldehyde, 5.5mmol piperidine, 10mL ethanol, 24.5mg Pt/C (20%) catalyst).

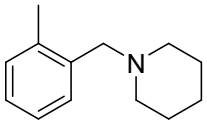
Analytical and spectral data for compounds



1-benzylpiperidine

^{1}H NMR (400 MHz, DMSO): δ =7.32-7.28(m,4H), 7.24-7.20(m,3H), 3.24(s,1H), 2.29(s,1H), 1.49-1.46(m,3H),1.38-1.37(d,2H) ppm;

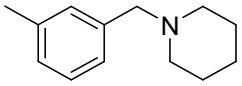
^{13}C NMR (100 MHz, DMSO): δ=138.63, 129.35, 128.19, 126.94, 77.55, 77.23, 76.91, 72.72, 64.02, 54.59, 26.08, 24.51 ppm.



1-(2-methylbenzyl)piperidine

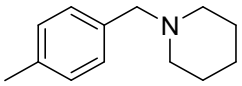
^{1}H NMR (400 MHz, DMSO): δ =7.62-7.55(m,4H), 7.54-7.50(m,4H), 3.76(s,1H), 2.71(s,1H), 1.91-1.88(m,3H), 1.86-1.79(m,4H) ppm;

^{13}C NMR (100 MHz, DMSO): δ=136.93, 136.73, 129.97, 129.40, 126.71, 125.28, 60.93, 54.11, 39.72, 39.51, 39.30, 39.09, 38.88, 25.68, 24.12, 18.81 ppm.



1-(3-methylbenzyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.61-7.58(m,3H), 7.50-7.44(m,4H), 3.77(s,1H), 2.70(s,1H), 1.89-1.88(d,2H), 1.79-1.78(d,2H);

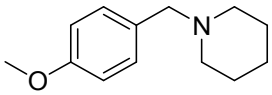
^{13}C NMR (100 MHz, DMSO): δ=138.55, 137.07, 129.37, 127.95, 127.38, 125.85, 62.94, 53.93, 39.93, 39.72, 39.51, 39.30, 39.09, 38.88, 25.57, 24.05, 21.02 ppm.



1-(4-methylbenzyl)piperidine

^{1}H NMR (400 MHz, DMSO): δ =7.57-7.55(d,2H), 7.52-7.50(d,2H), 3.76(s,1H), 2.68(s,1H), 1.89-1.86(m,3H), 1.78-1.77(d,2H) ppm;

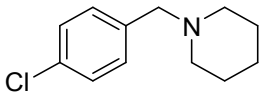
^{13}C NMR (100 MHz, DMSO): δ=135.71, 135.52, 128.71, 128.64, 65.64, 62.68, 53.86, 39.72, 39.30, 38.88, 25.59, 24.09, 20.71 ppm.



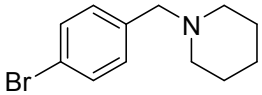
1-(4-methoxybenzyl)piperidine

^{1}H NMR (400 MHz, DMSO): δ =7.60-7.58(d,2H), 7.28-7.26(d,2H), 4.14(s,1H), 3.73(s,1H), 2.68(s,1H), 1.90-1.85(m,5H), 1.78-1.77(d,2H) ppm;

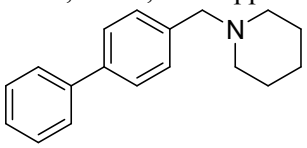
^{13}C NMR (100 MHz, DMSO): δ= 158.14, 130.41, 129.86, 113.39, 62.34, 54.89, 53.78, 39.72, 39.30, 38.88, 25.59, 24.11 ppm.



1-(4-chlorobenzyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.77-7.75(d,2H), 7.71-7.69(d,2H), 3.79(s,1H), 2.69(s,1H), 1.90-1.85(m,5H), 1.78-1.77(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=137.73, 131.25, 130.38, 128.02, 61.95, 53.82, 39.72, 39.30, 38.88, 25.57, 23.98 ppm.

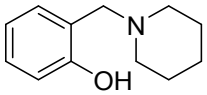


1-(4-bromobenzyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.90-7.88(d,2H), 7.66-7.64(d,2H), 3.78(s,1H), 2.69(s,1H), 1.89-1.86(m,4H), 1.78-1.77(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=138.13, 130.91, 130.74, 119.73, 61.98, 53.80, 39.93, 39.72, 39.51, 39.30, 39.09, 38.88, 25.56, 23.97 ppm.

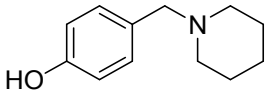


1-(4-phenylbenzyl)piperidine

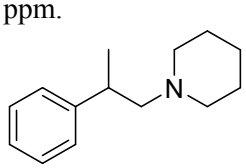
^{1}H NMR (400 MHz, DMSO): δ =7.64-7.57(m,4H), 7.44-7.42(d,2H), 7.36-7.32(d,2H), 3.42(s,1H), 2.31(s,1H), 1.51-1.45(m,5H), 1.37-1.36(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=140.11, 138.75, 137.94, 129.37, 128.92, 127.27, 126.57, 126.43, 62.59, 53.96, 39.72, 39.51, 39.30, 39.09, 38.88, 25.61, 24.06 ppm.



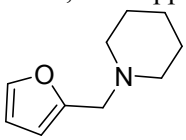
2-((piperidin-1-yl)methyl)phenol
^{1}H NMR (400 MHz, DMSO): δ =7.52-7.44(m,5H), 7.16-7.10(m,4H), 4.02(s,1H), 2.83(s,1H), 1.95-1.93(m,3H), 1.84(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=157.24, 128.85, 127.89, 122.15, 118.63, 115.31, 60.17, 53.26, 39.72, 39.30, 38.88, 25.51, 23.64 ppm.



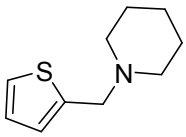
4-((piperidin-1-yl)methyl)phenol
^{1}H NMR (400 MHz, DMSO): δ =7.47-7.45(d,2H), 7.10-7.09(d,2H), 3.68(s,2H), 2.67(s,2H), 1.87(s,2H), 1.78-1.77(m,3H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=156.17, 129.96, 128.59, 114.78, 62.50, 53.77, 39.72, 39.30, 38.89, 25.58, 24.15 ppm.



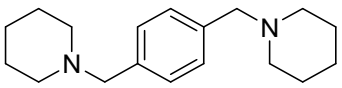
1-(2-phenylpropyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.70-7.66(m,3H), 7.62-7.56(m,3H), 3.37-3.29(m,6H), 2.74(s,1H), 2.69-2.68(d,2H), 1.87(s,1H), 1.77-1.76(d,2H), 1.61-1.59(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=146.09, 128.12, 127.03, 125.82, 66.46, 54.44, 39.93, 39.51, 39.09, 36.62, 25.67, 24.19, 19.85 ppm.



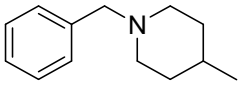
1-((furan-2-yl)methyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.98-7.97(m,4H), 6.80-6.79(m,4H), 3.84(s,1H), 2.73(s,1H), 1.89-1.87(m,3H), 1.76-1.75(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=152.05, 142.21, 110.26, 108.48, 54.74, 53.46, 39.72, 39.51, 39.30, 39.09, 38.89, 25.48, 23.86 ppm.



1-((thiophen-2-yl)methyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.81-7.80(m,5H), 7.37-7.33(m,9H), 4.02(s,1H), 2.75(s,1H), 1.91-1.88(m,3H), 1.79-1.78(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=142.29, 126.39, 125.66, 125.16, 57.15, 53.62, 39.72, 39.51, 39.30, 39.09, 38.88, 25.54, 23.97 ppm.



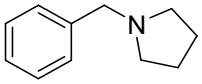
1-(4-((piperidin-1-yl)methyl)benzyl)piperidine
^{1}H NMR (400 MHz, DMSO): δ =7.62(s,1H), 3.79(s,1H), 2.70(s,1H), 1.89-1.87(d,2H), 1.79-1.78(d,2H) ppm;
^{13}C NMR (100 MHz, DMSO): δ=128.55, 79.21, 62.69, 53.93, 39.93, 39.72, 39.51, 39.30, 39.09, 38.88, 25.57, 24.06 ppm.



1-benzyl-4-methylpiperidine

^{1}H NMR (400 MHz, DMSO): δ =7.32-7.22(m,6H), 3.41(s,1H), 2.75-2.73(d,2H), 1.90-1.85(m,3H), 1.52(s,1H), 1.29(s,1H), 1.13(s,1H), 0.88-0.87(d,2H) ppm;

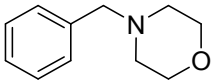
^{13}C NMR (100 MHz, DMSO): δ=138.74, 128.67, 128.05, 126.71, 62.51, 53.29, 39.51, 39.30, 39.09, 38.88, 33.98, 30.33, 21.84 ppm.



1-benzylpyrrolidine

^{1}H NMR (400 MHz, DMSO): δ =7.31-7.29(d,2H), 7.26-7.25(d,2H), 7.24-7.22(m,3H), 3.57(s,1H), 2.42(s,1H), 1.68(s,1H) ppm;

^{13}C NMR (100 MHz, DMSO): δ=139.13, 128.49, 128.09, 126.76, 59.50, 53.38, 39.72, 39.51, 39.30, 39.09, 38.89, 23.08 ppm.



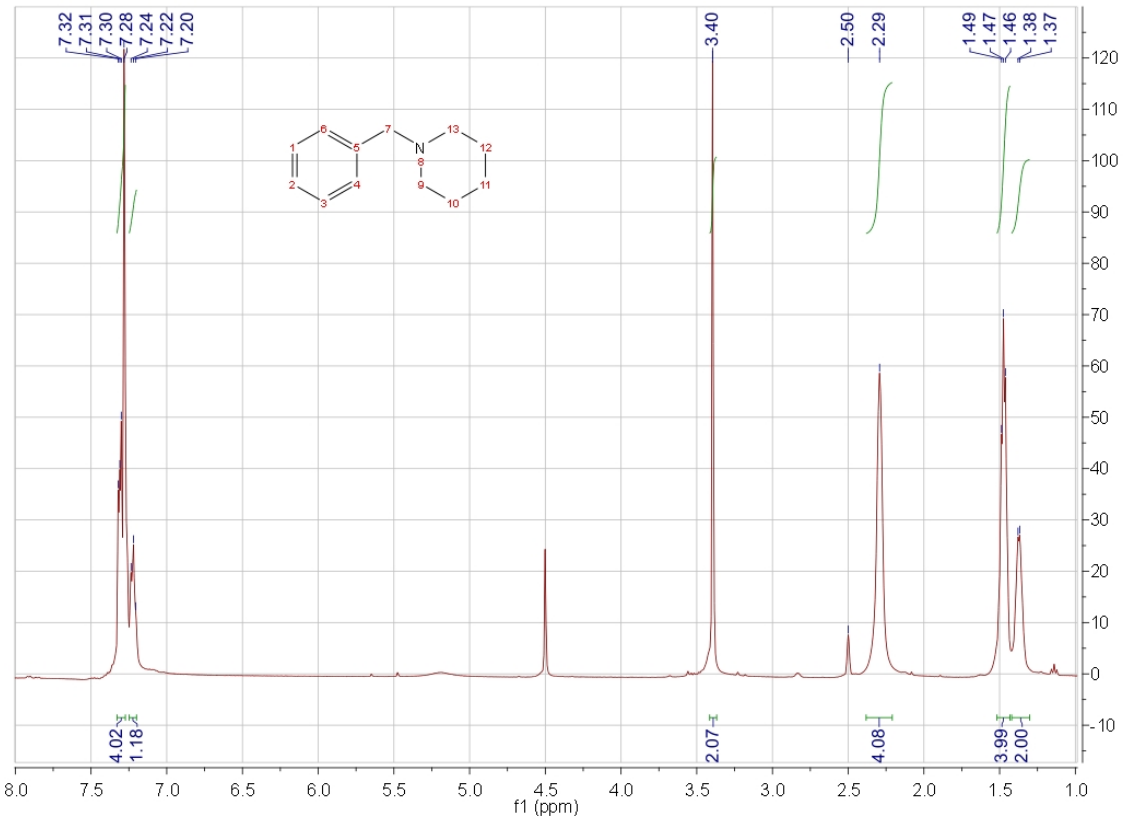
4-benzylmorpholine

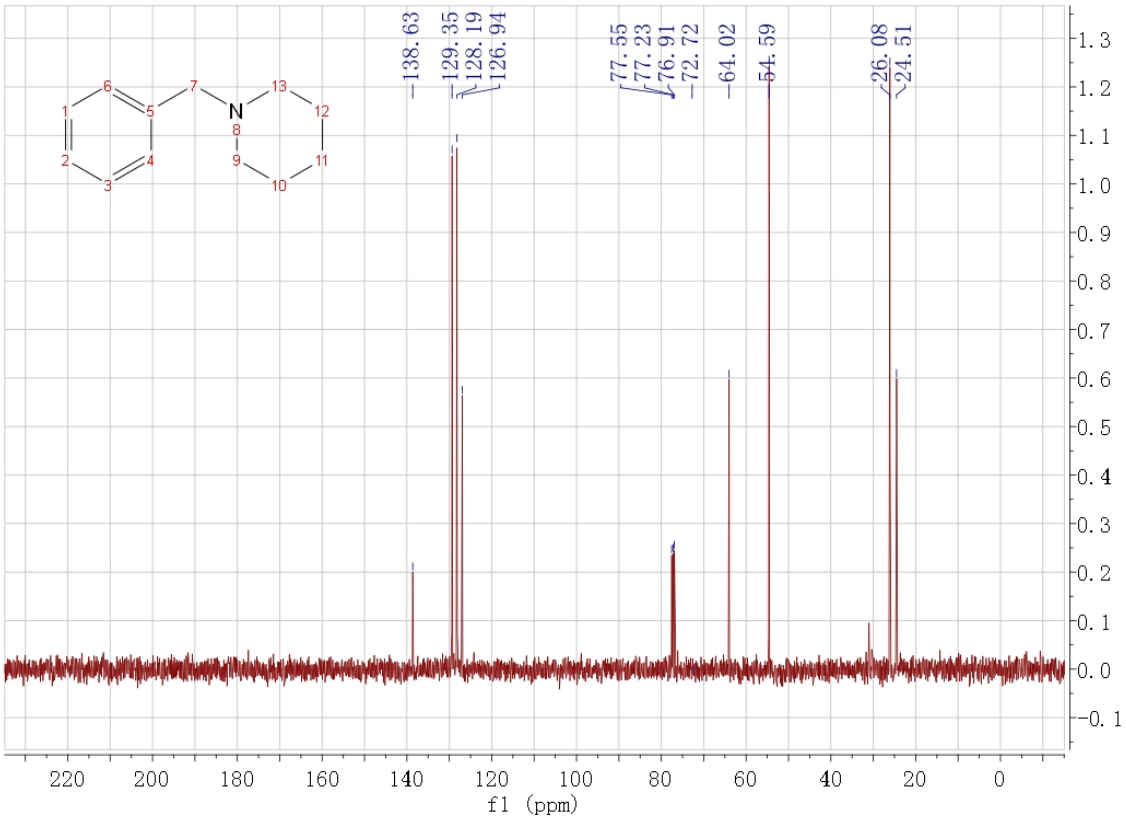
^{1}H NMR (400 MHz, DMSO): δ =7.34-7.29(m,6H), 7.26-7.21(m,6H), 3.57-3.55(m,3H), 3.44(s,1H), 2.33(s,1H) ppm;

^{13}C NMR (100 MHz, DMSO): δ=137.78, 128.86, 128.12, 126.92, 66.19, 62.48, 53.16, 40.13, 39.93, 39.72, 39.51, 39.30, 39.09, 38.88 ppm.

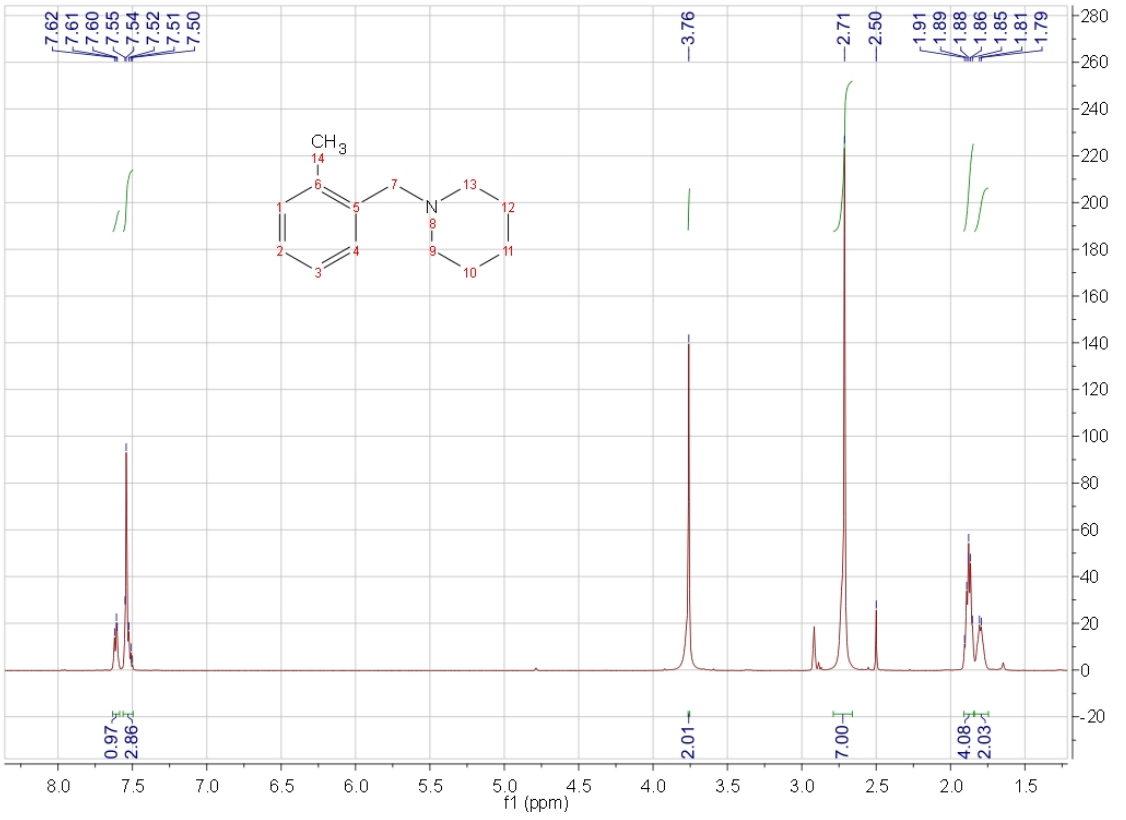
The ^{1}H NMR and ^{13}C NMR charts of products

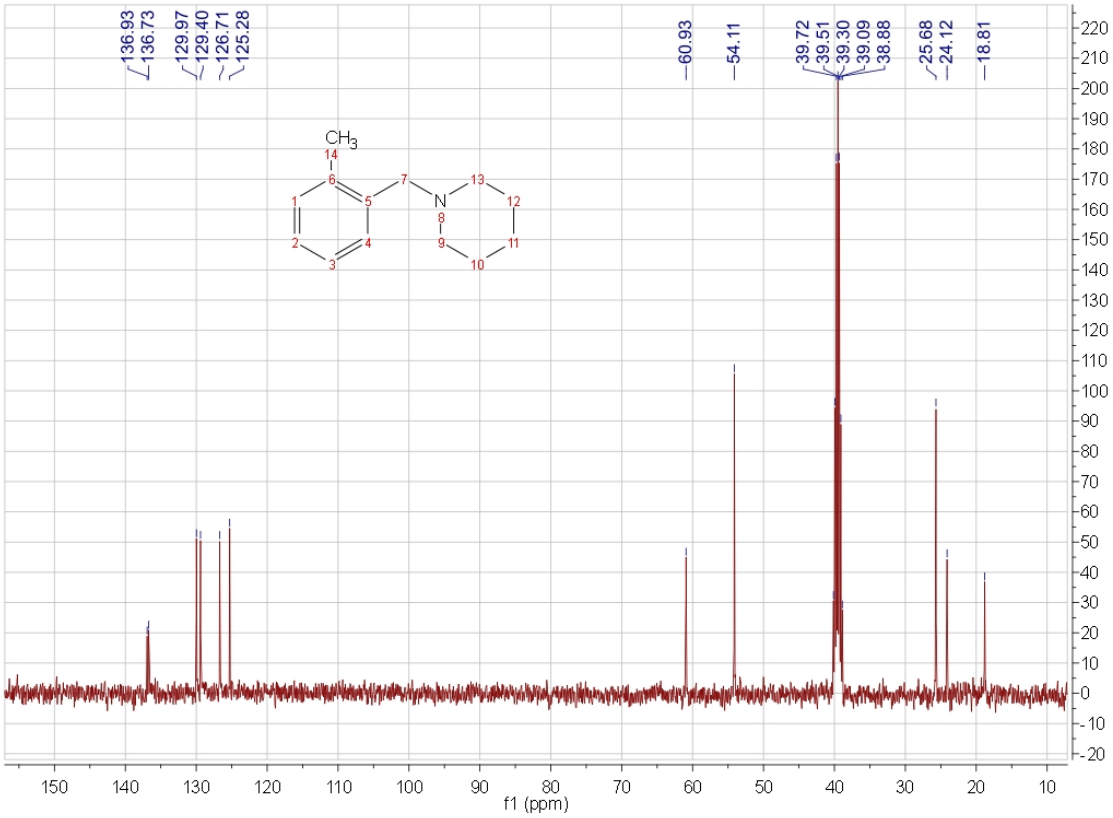
1-benzylpiperidine





1-(2-methylbenzyl)piperidine





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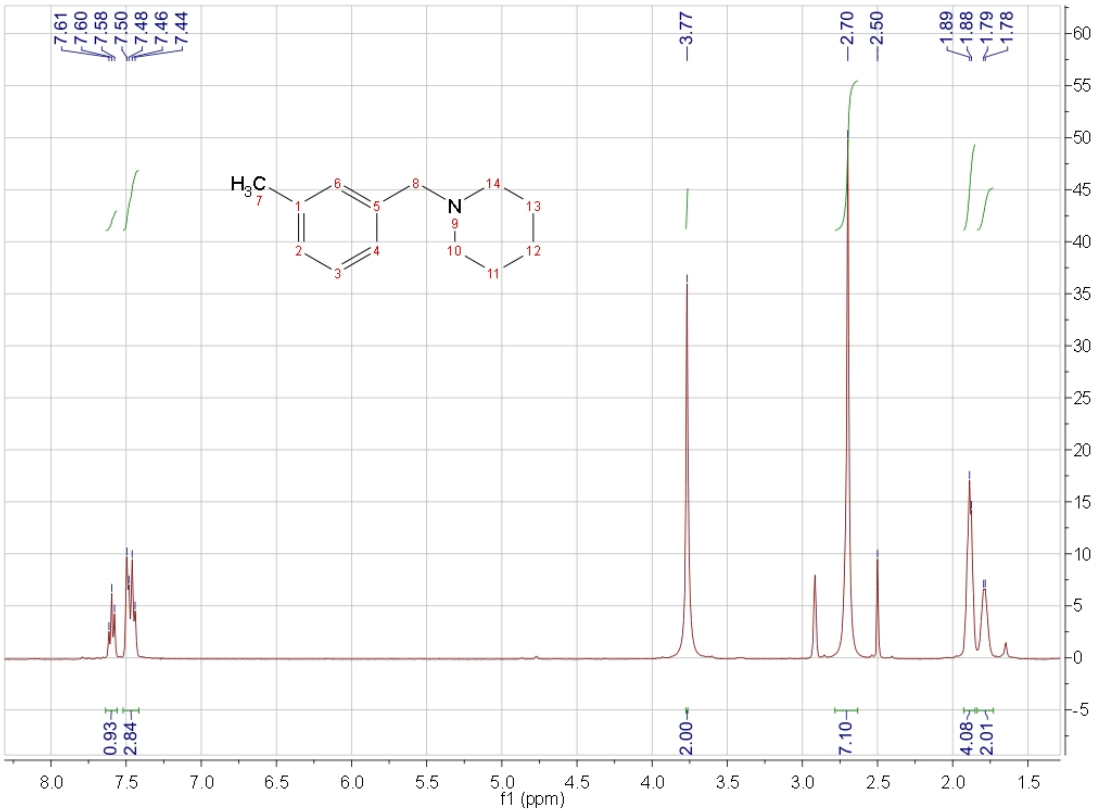

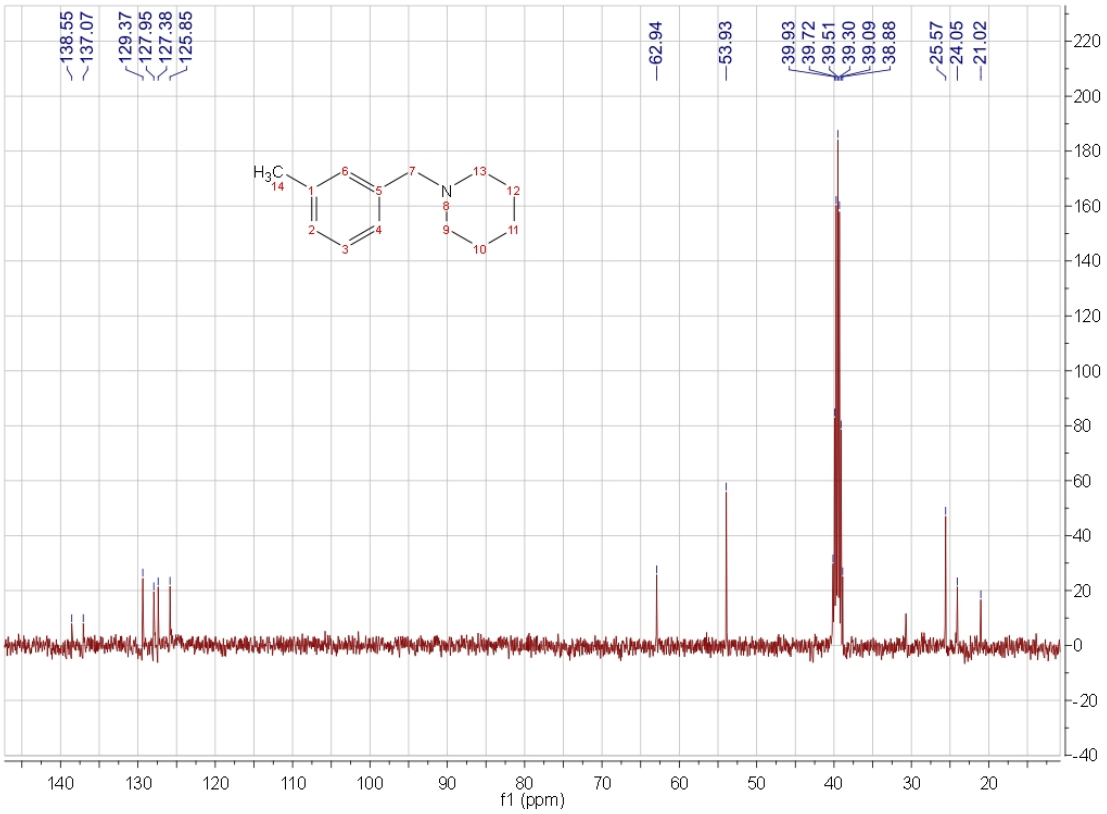
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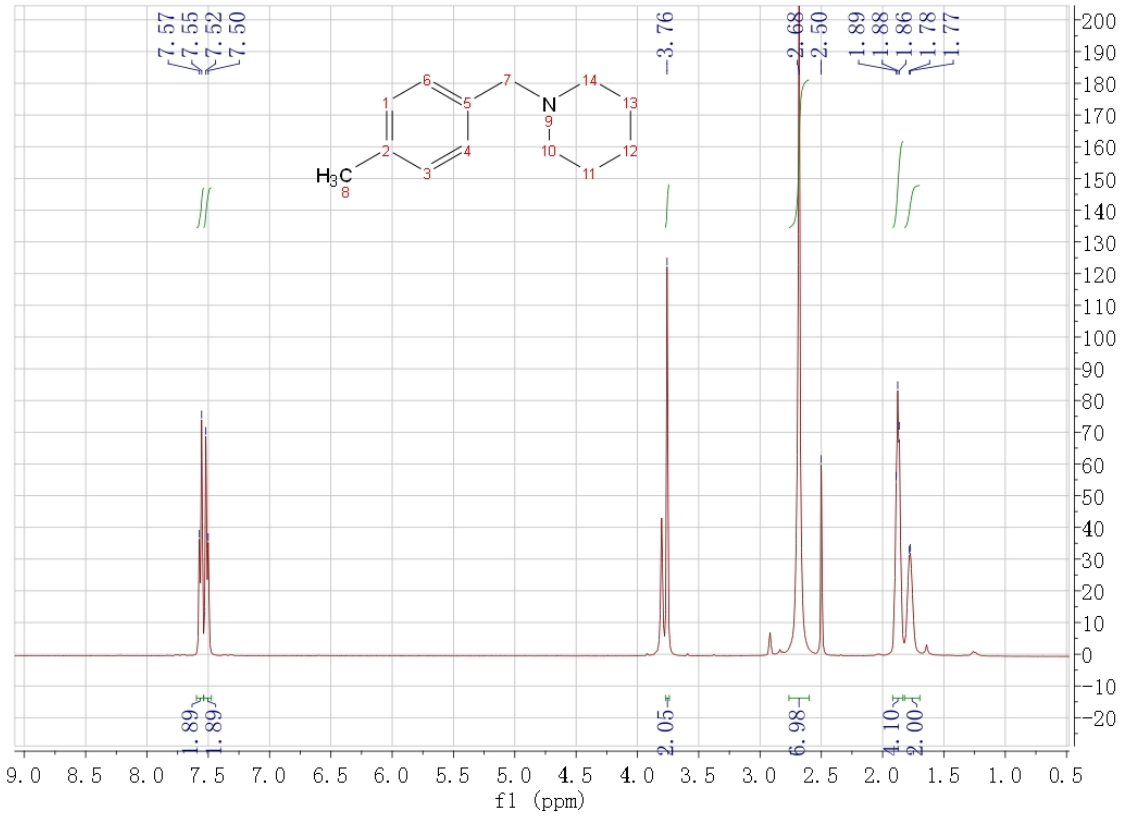
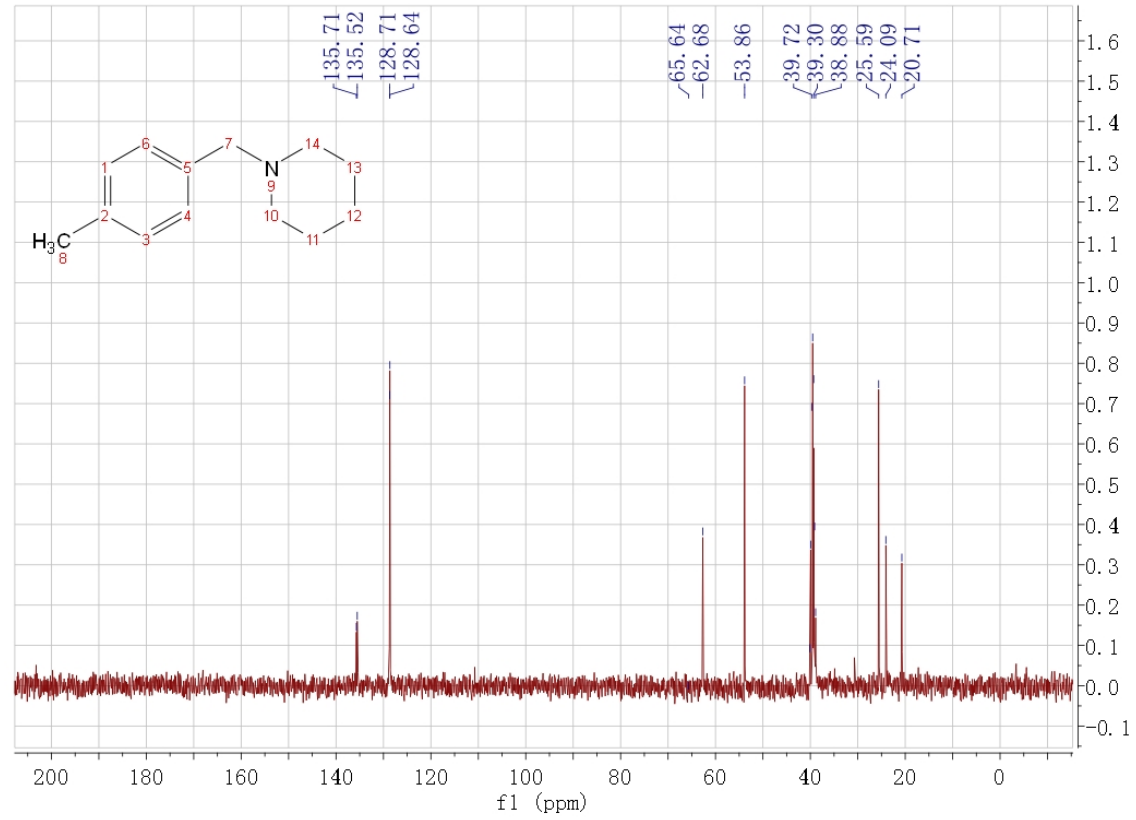
129.37
127.95
127.38
125.85
62.94
53.93
39.93
39.72
39.51
39.30
39.09
38.88
25.57
24.05
21.02
H3C
14
1
2
3
4
5
6
7
N
8
9
10
11
12
13
f1 (ppm)

1-(4-methylbenzyl)piperidine





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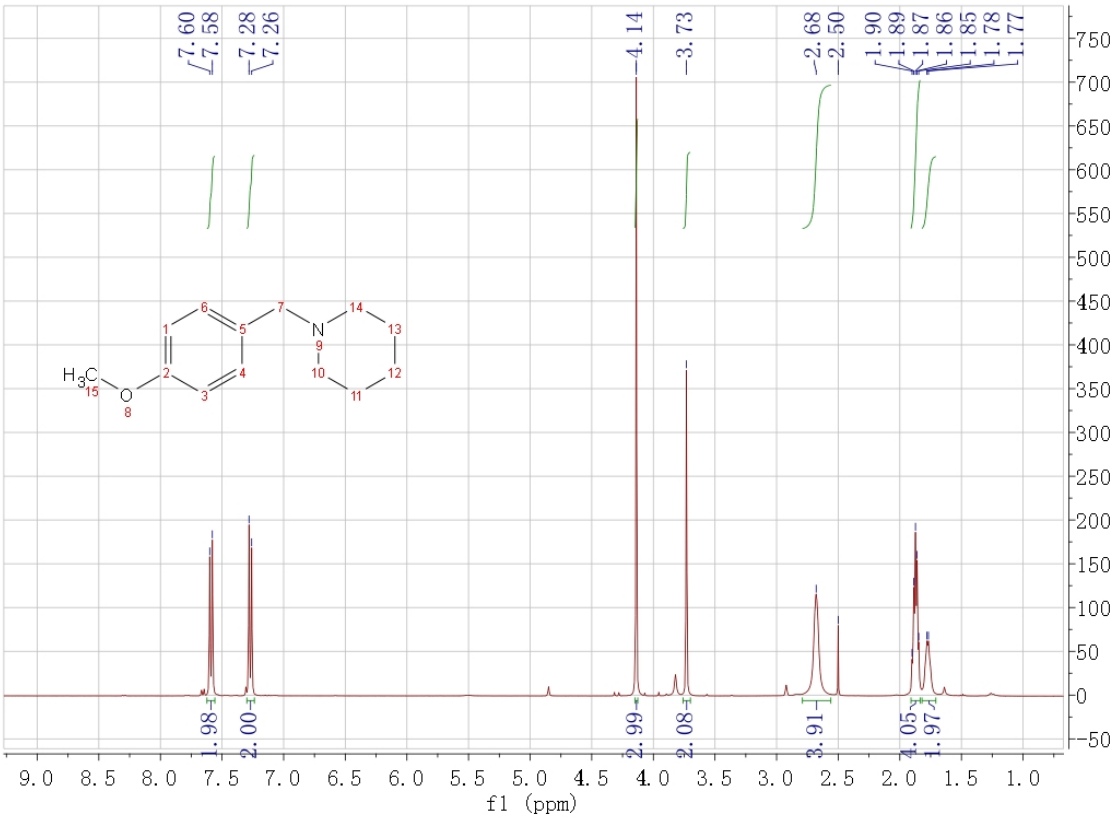
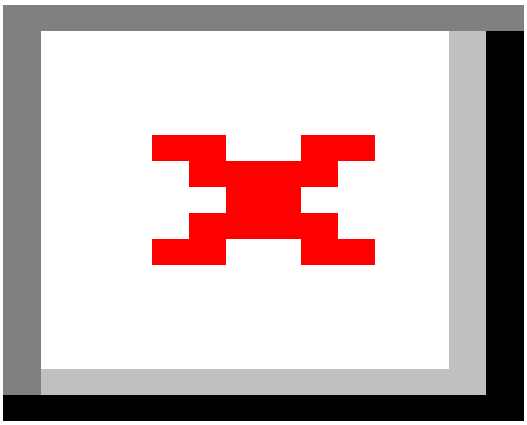
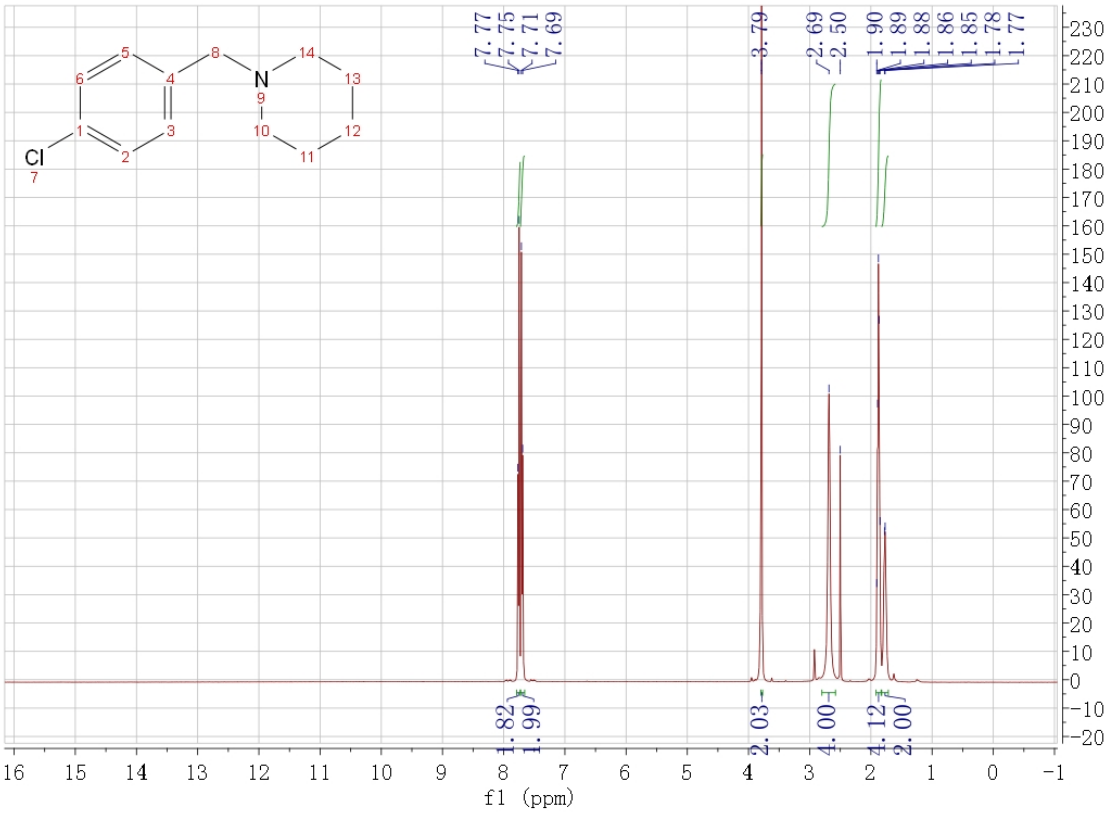
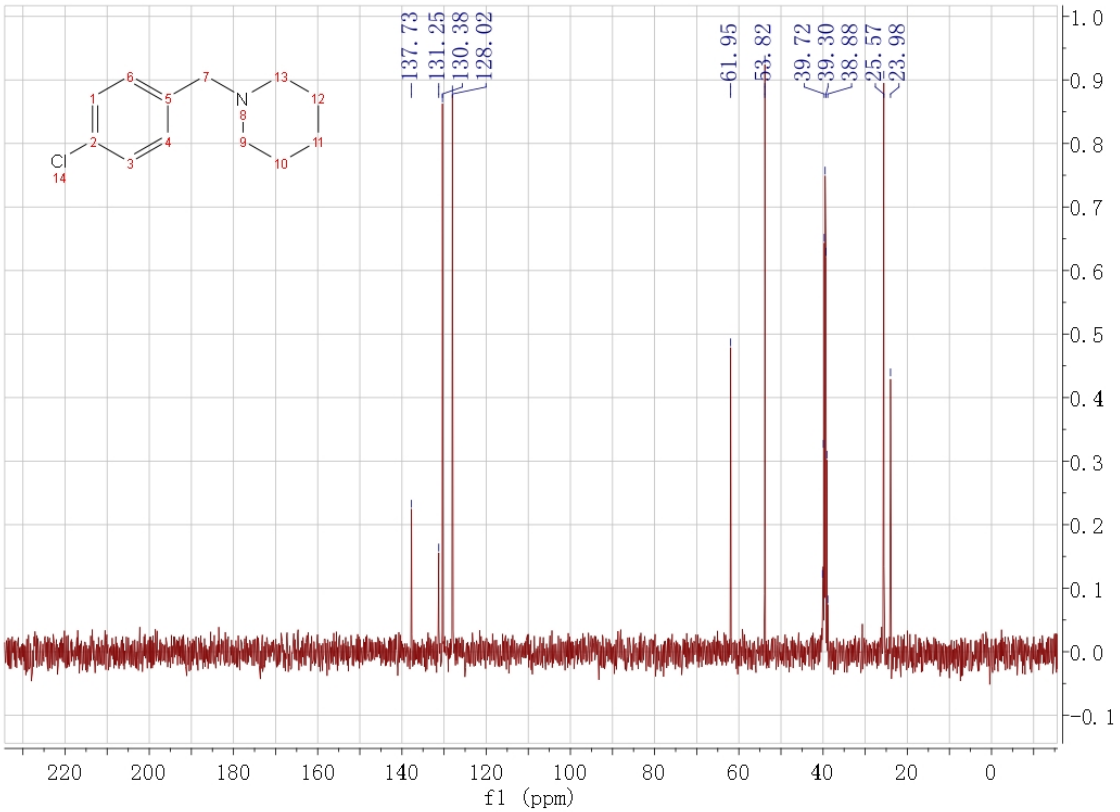


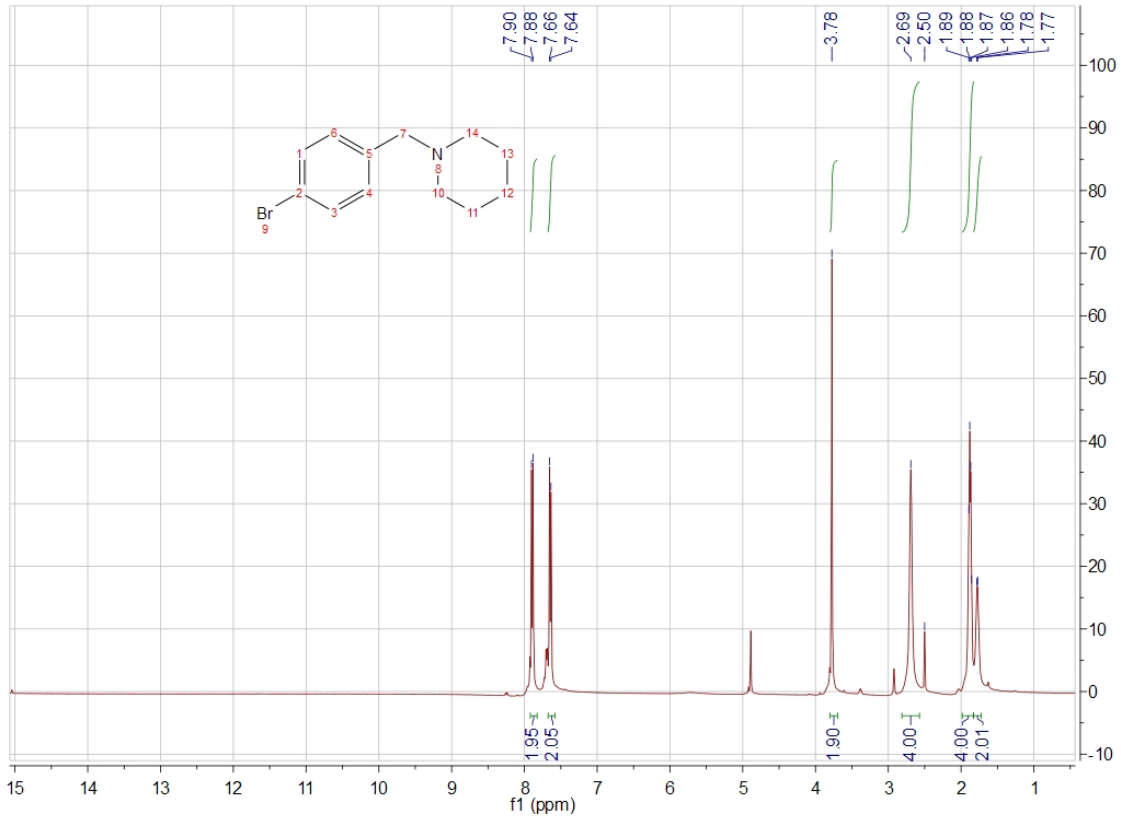


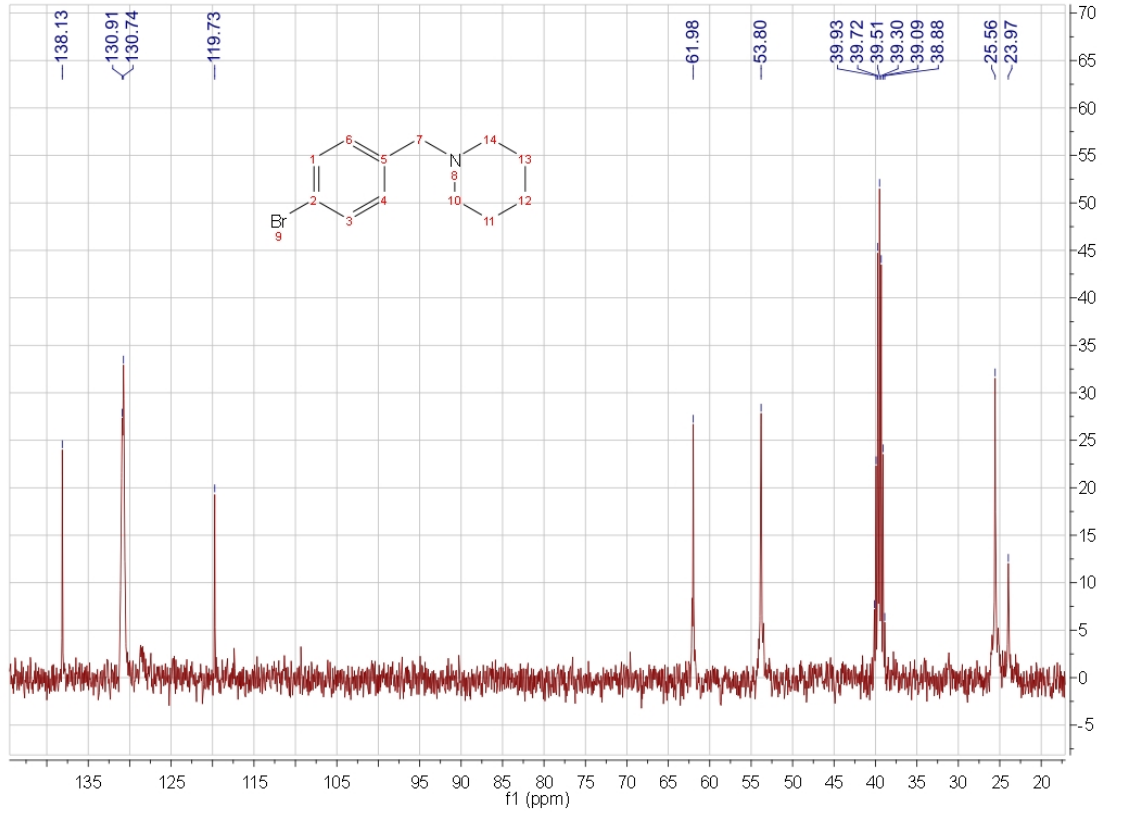
1-(4-chlorobenzyl)piperidine



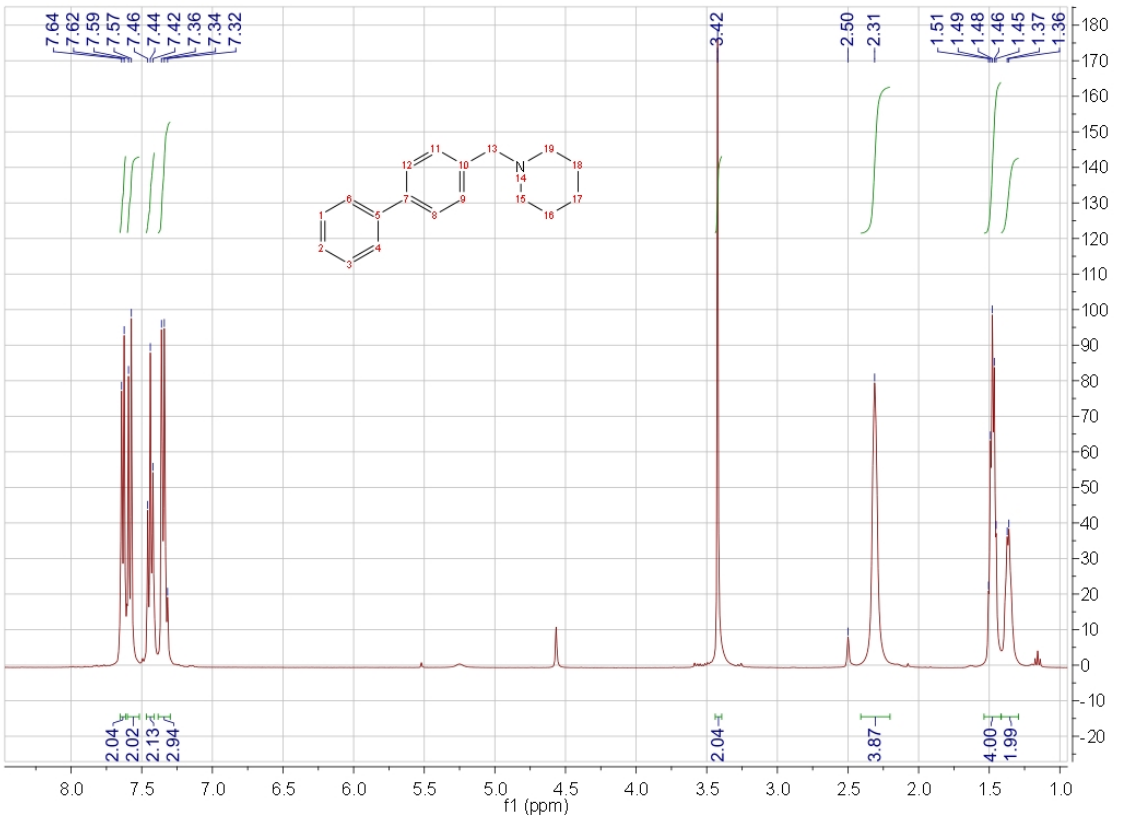


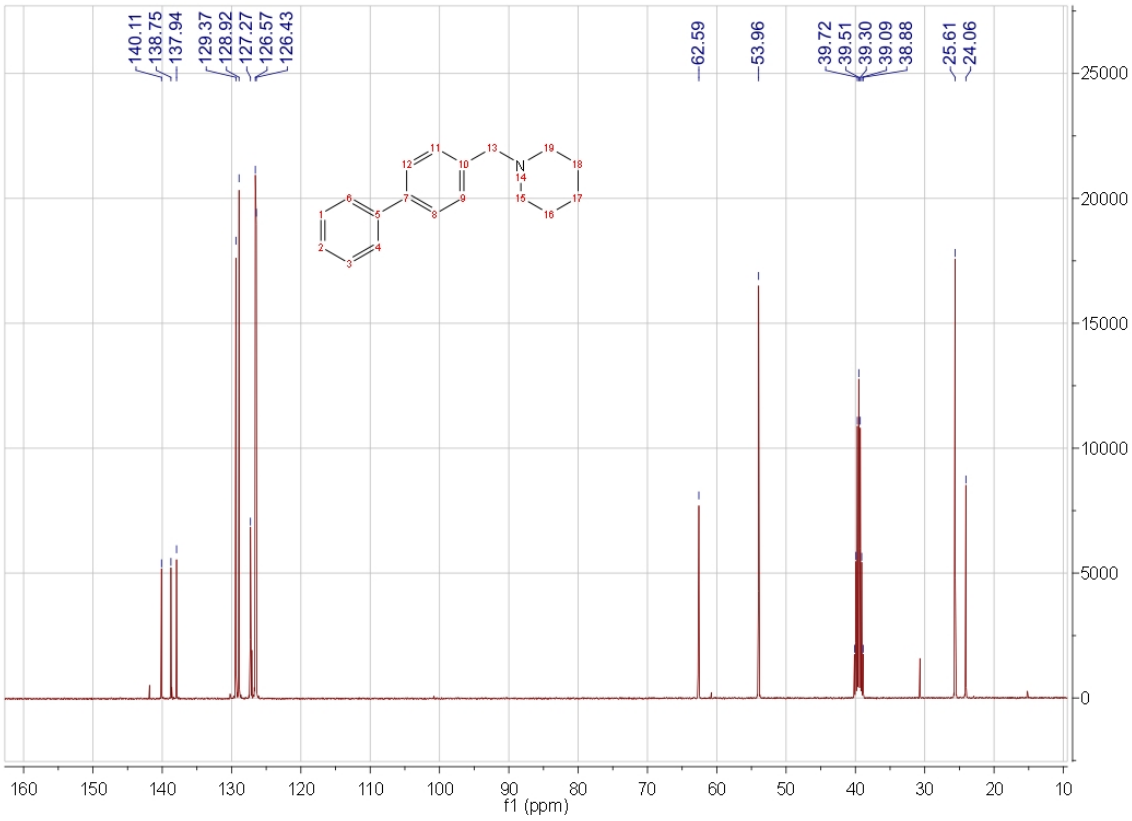
1-(4-bromobenzyl)piperidine



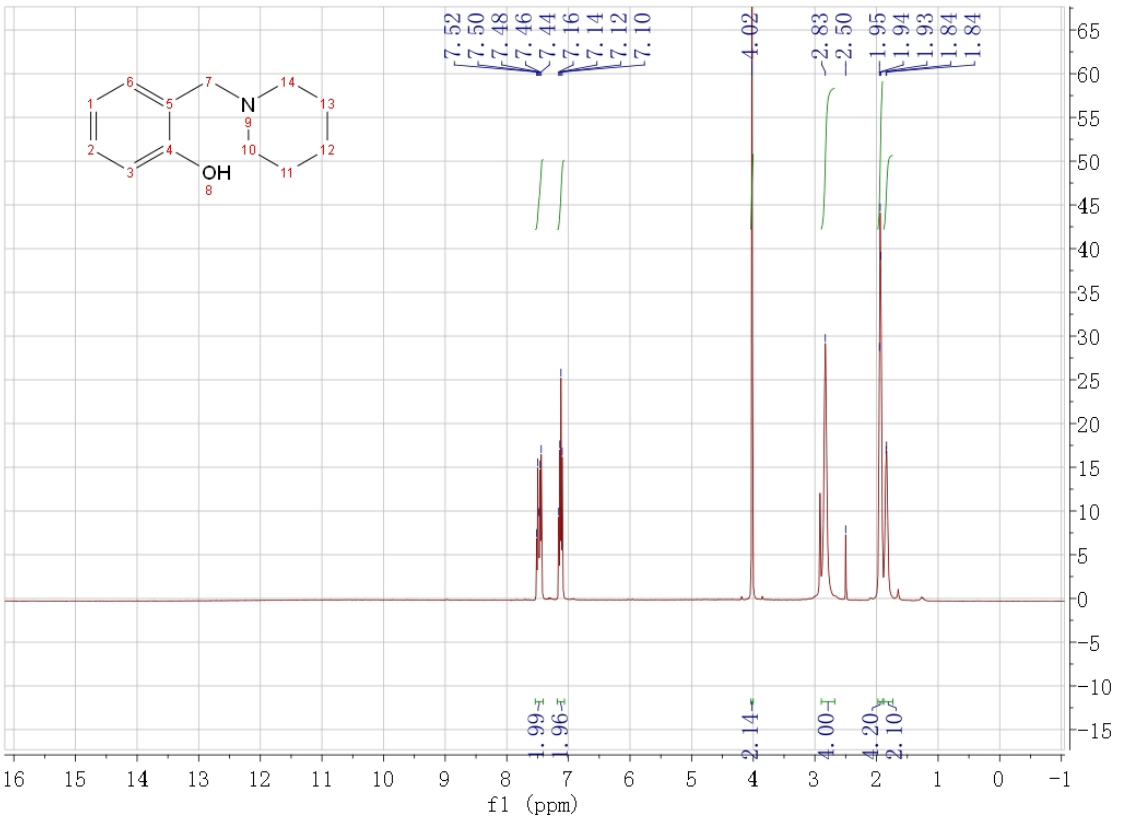


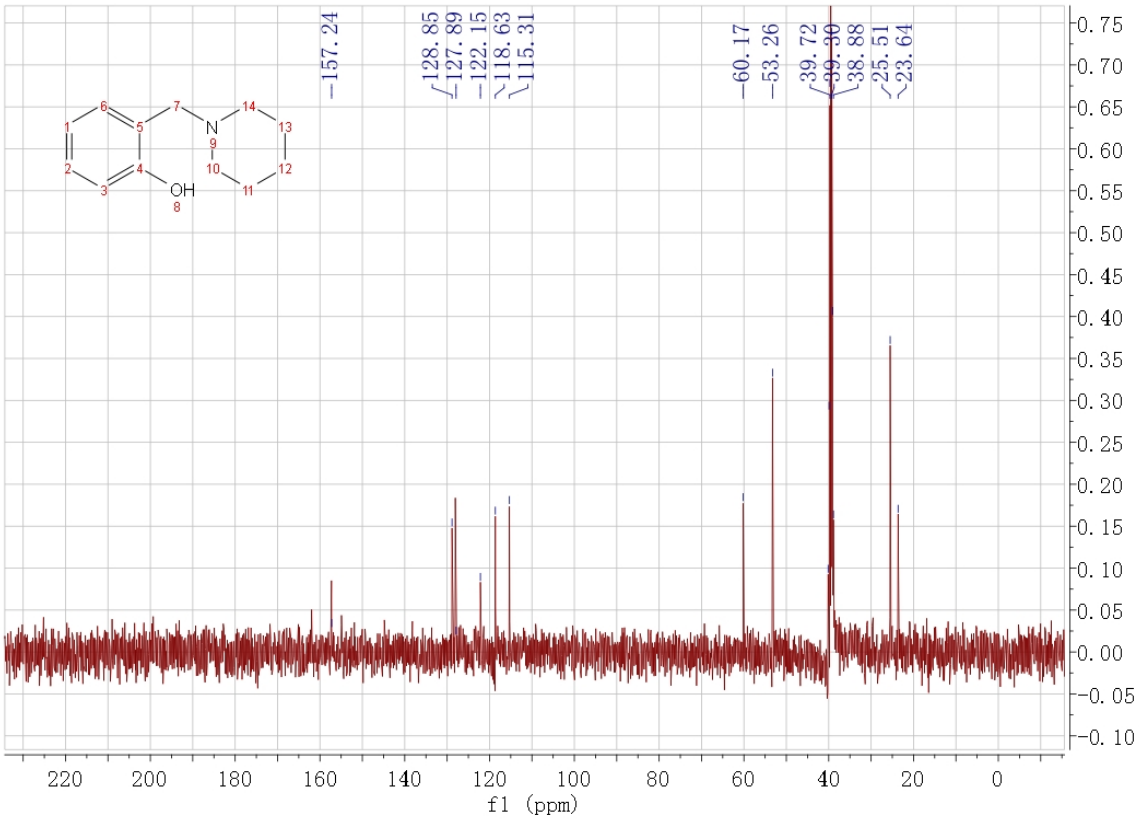
1-(4-phenylbenzyl)piperidine



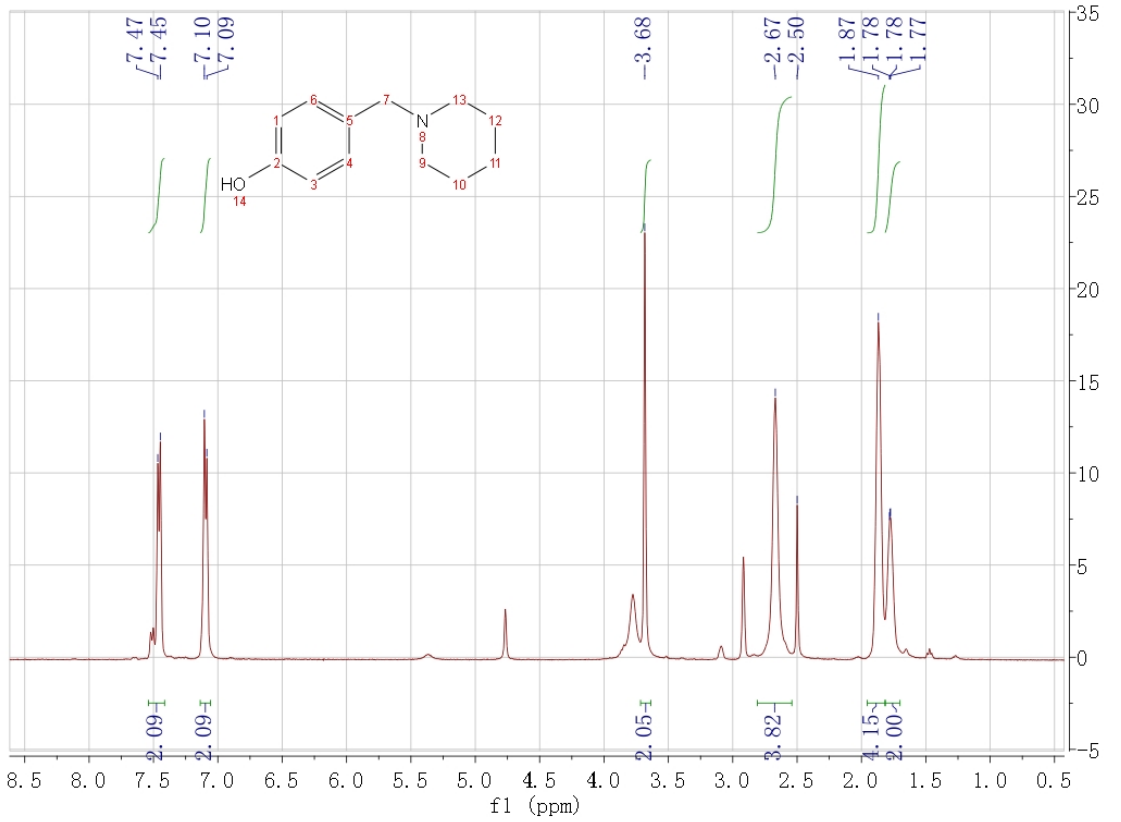


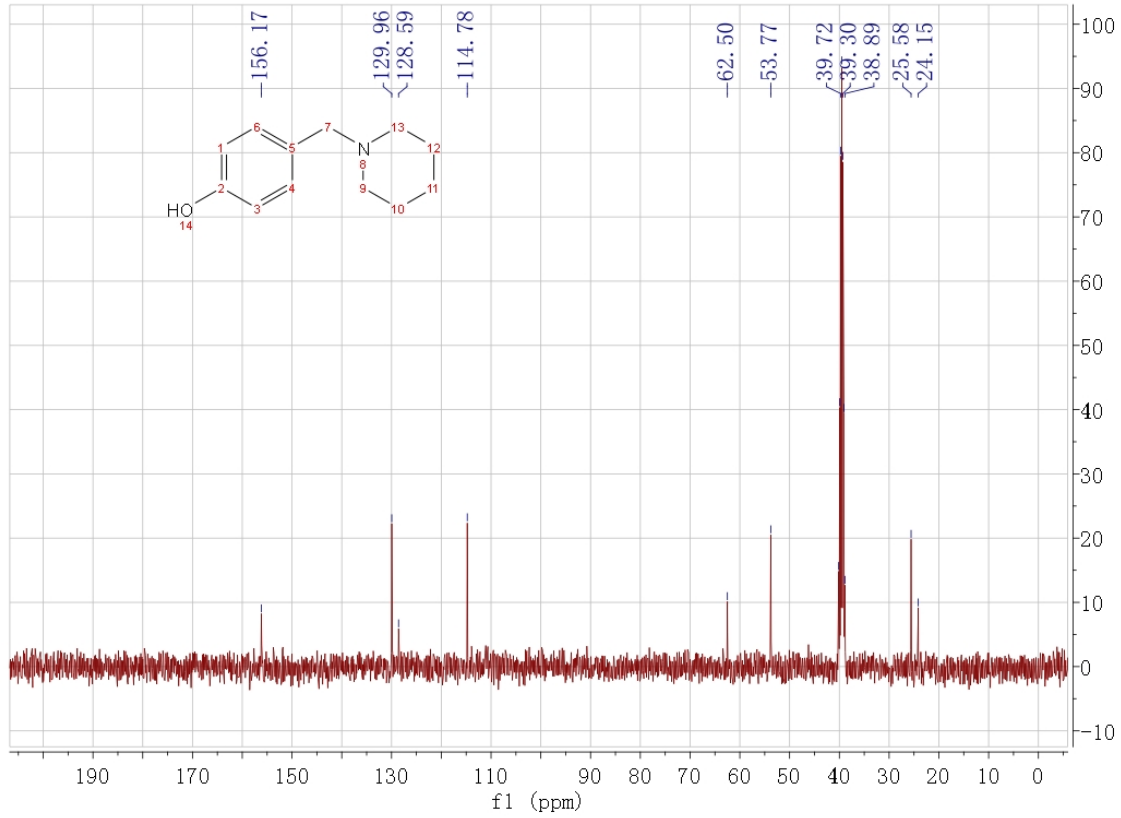
2-((piperidin-1-yl)methyl)phenol



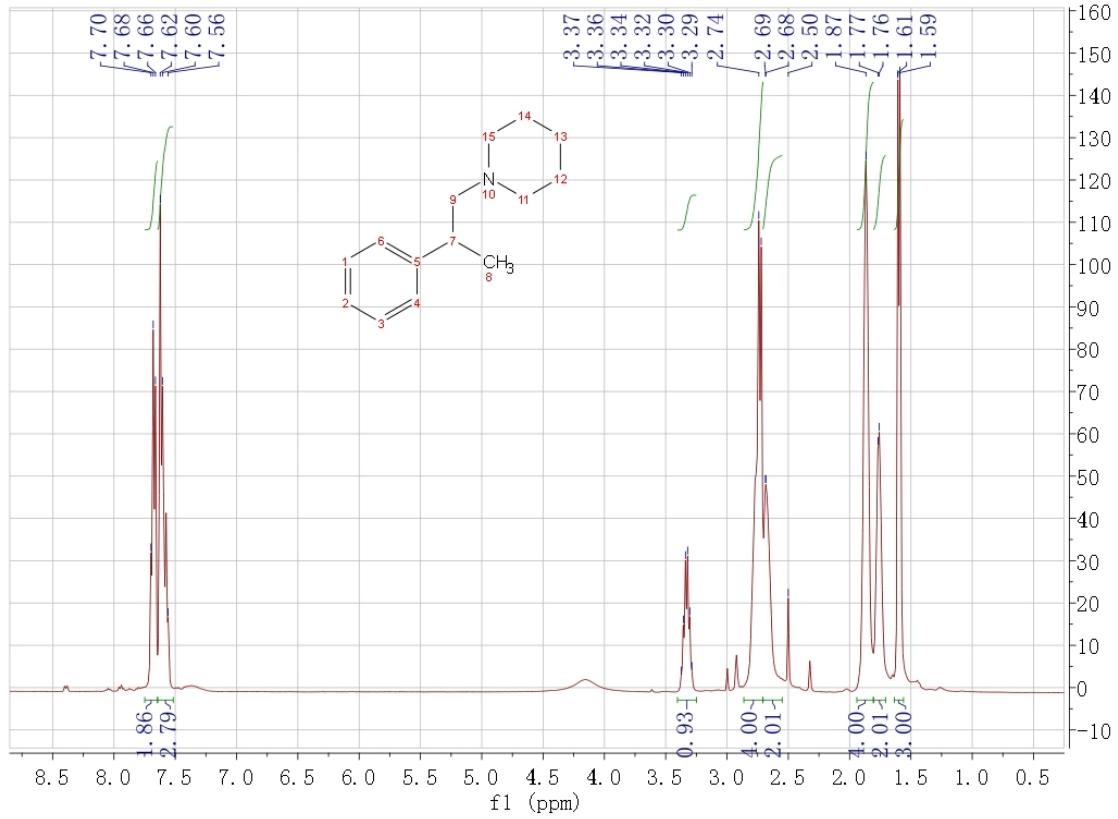


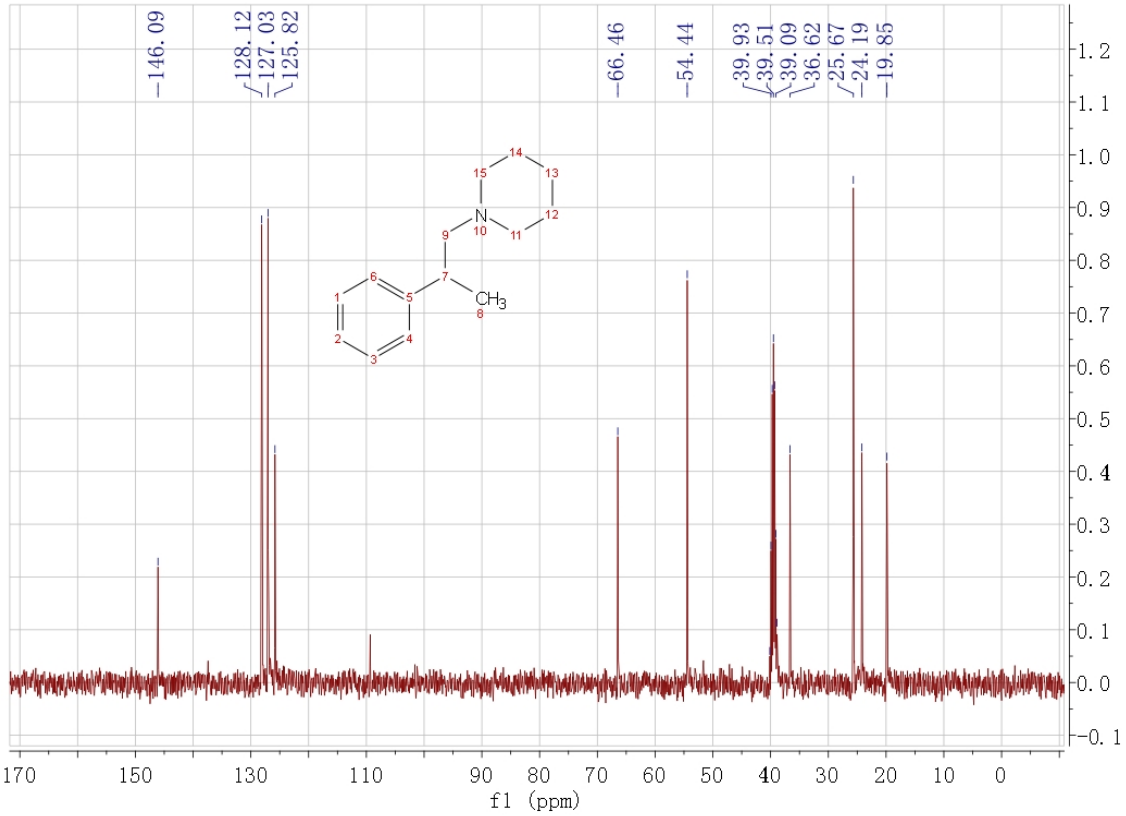
4-((piperidin-1-yl)methyl)phenol



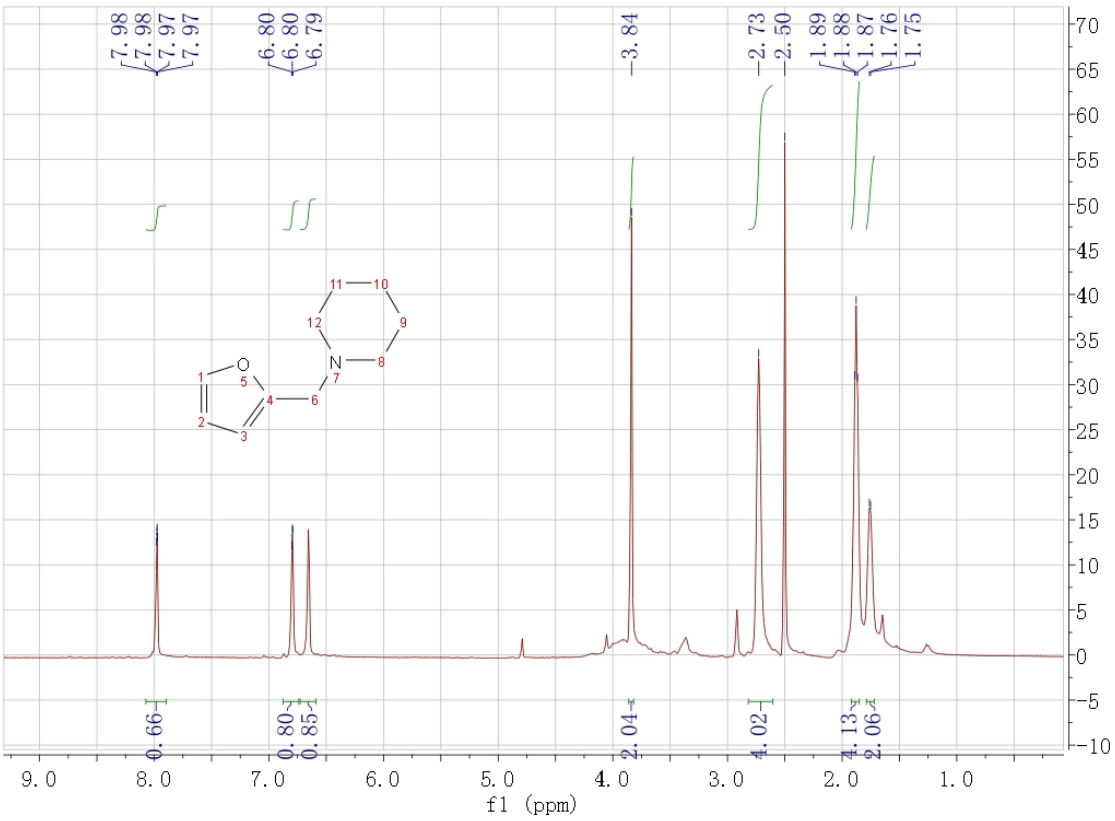


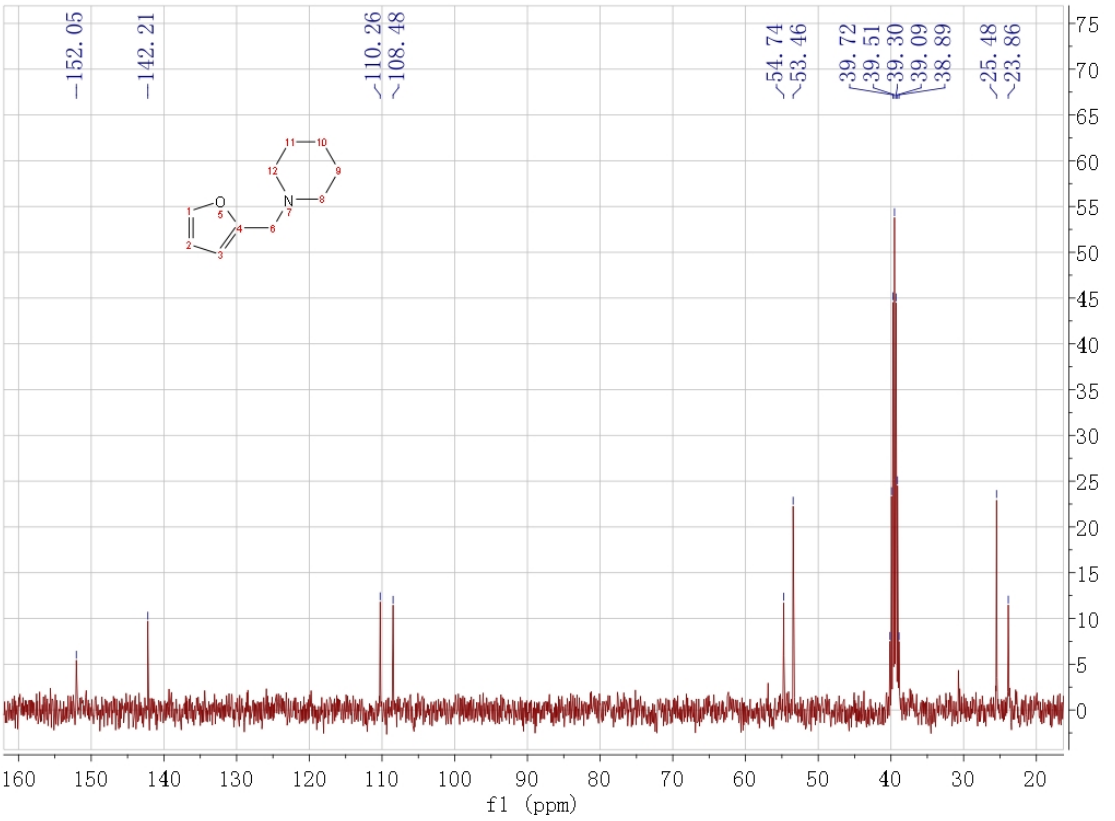
1-(2-phenylpropyl)piperidine



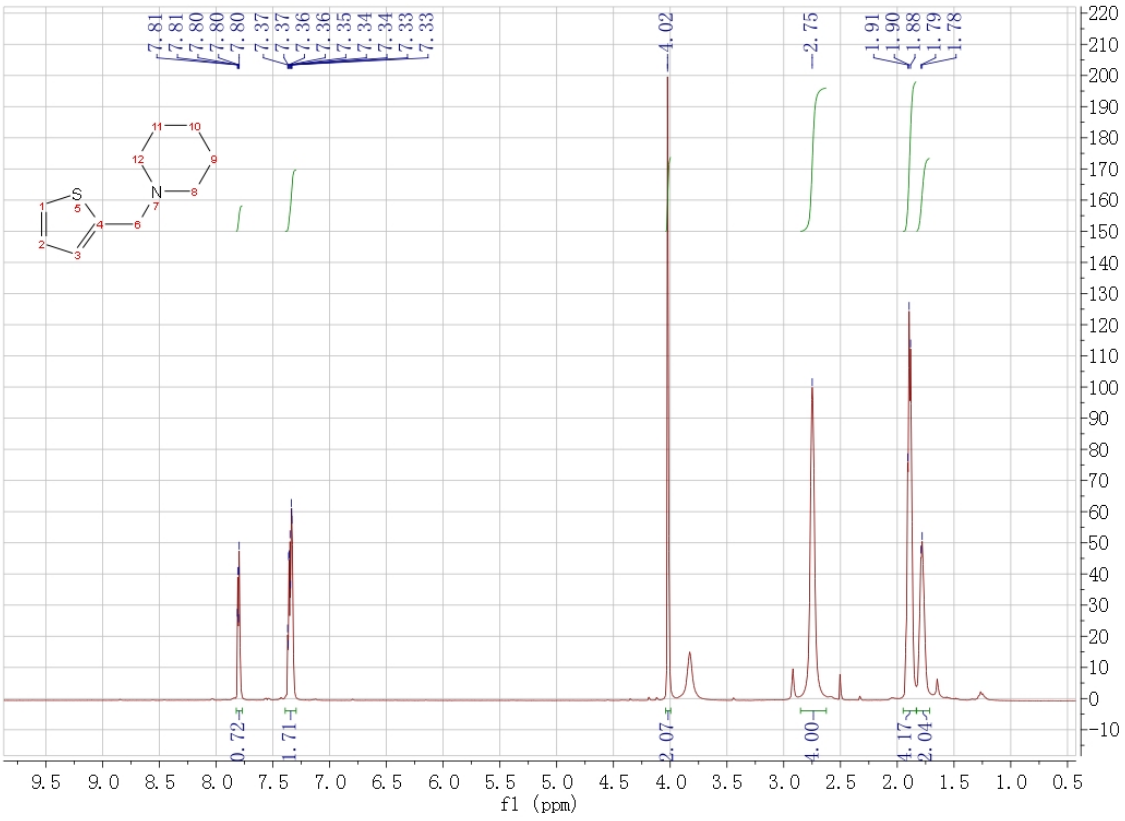


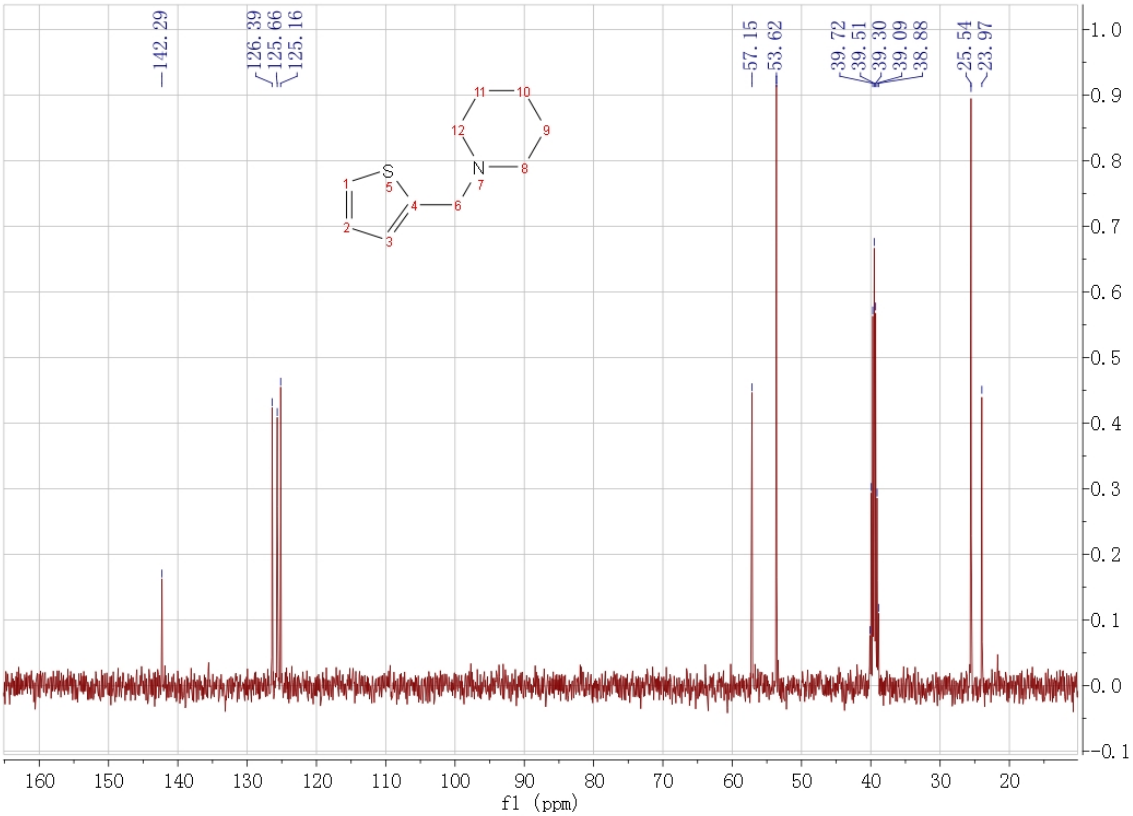
1-((furan-2-yl)methyl)piperidine



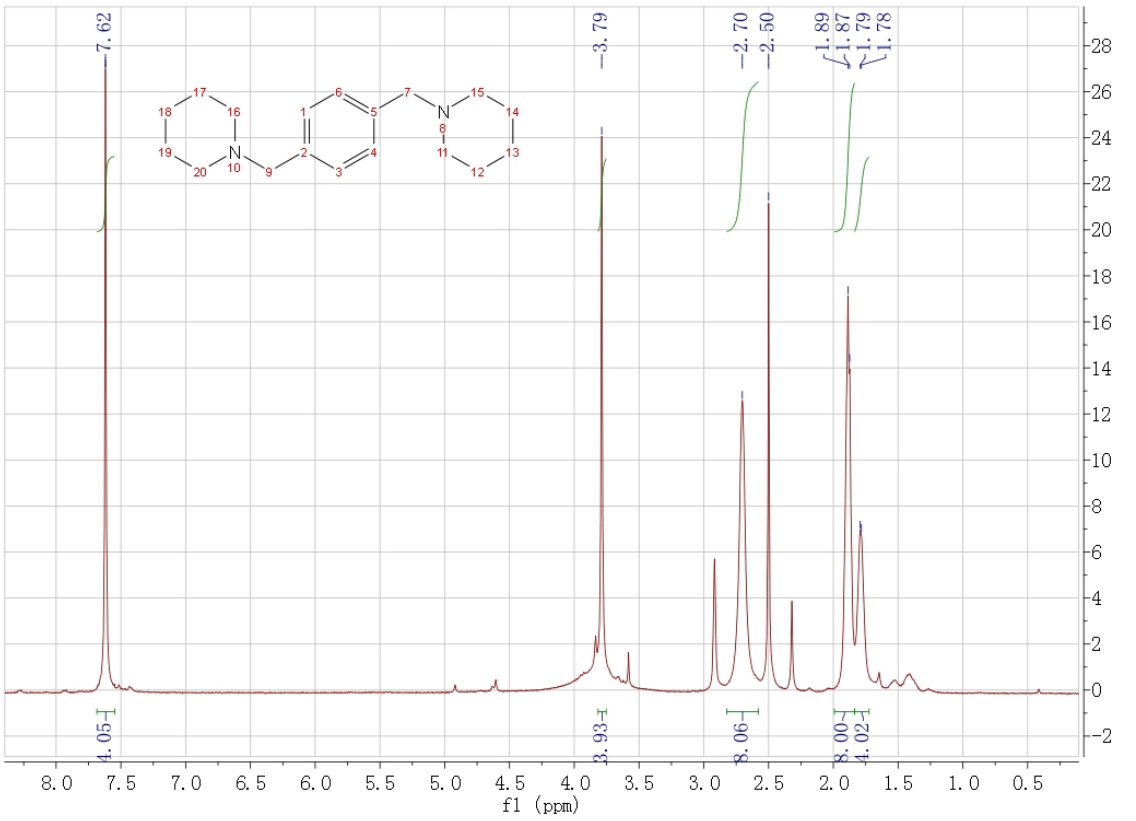


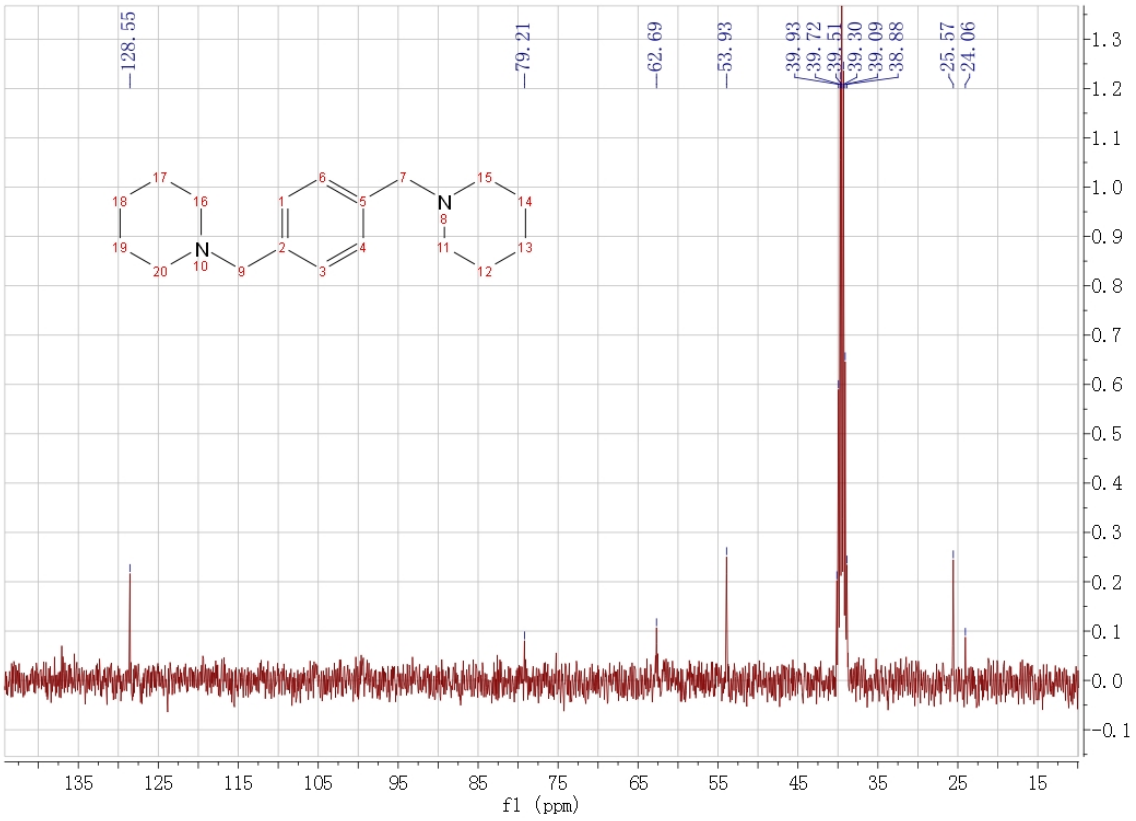
1-((thiophen-2-yl)methyl)piperidine



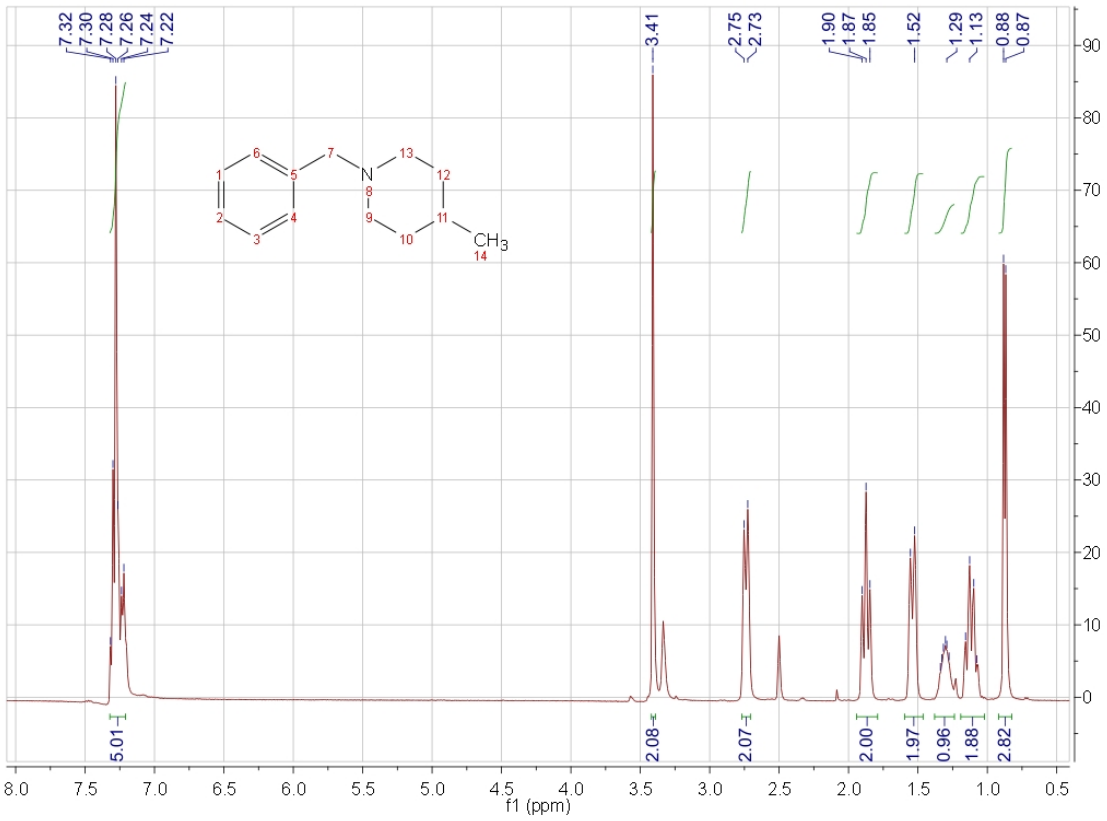


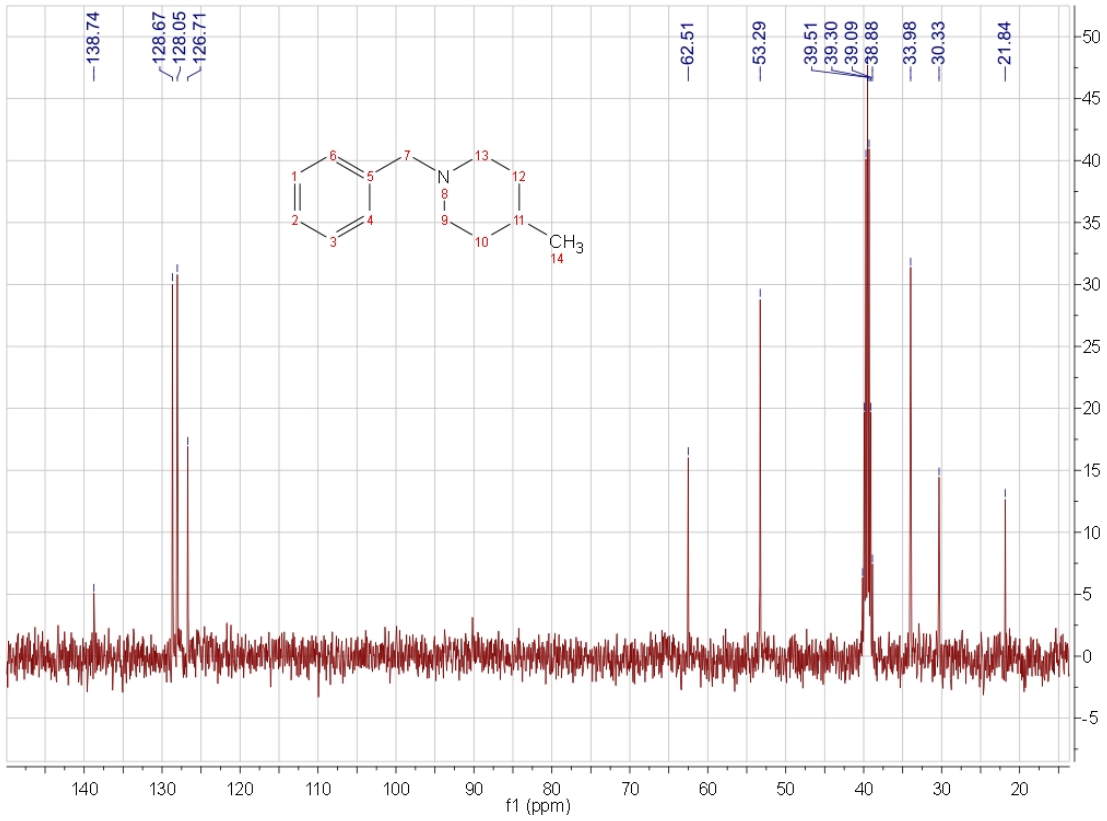
1-(4-((piperidin-1-yl)methyl)benzyl)piperidine



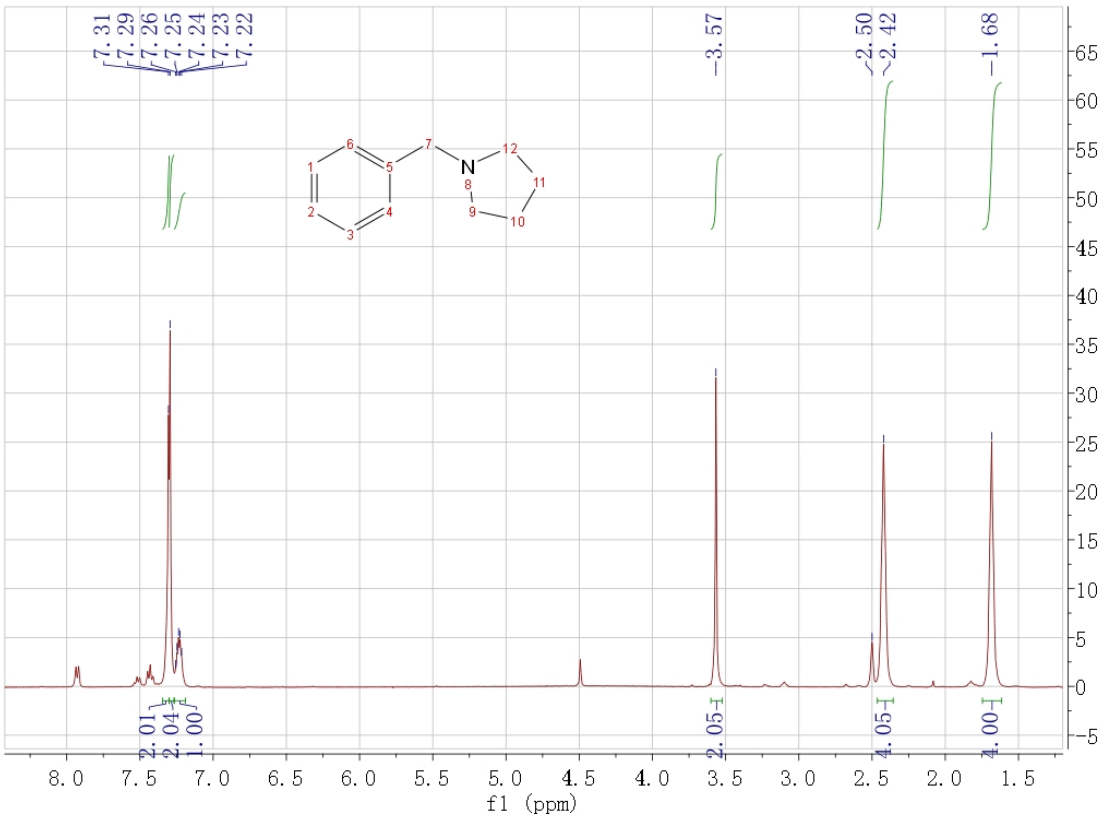


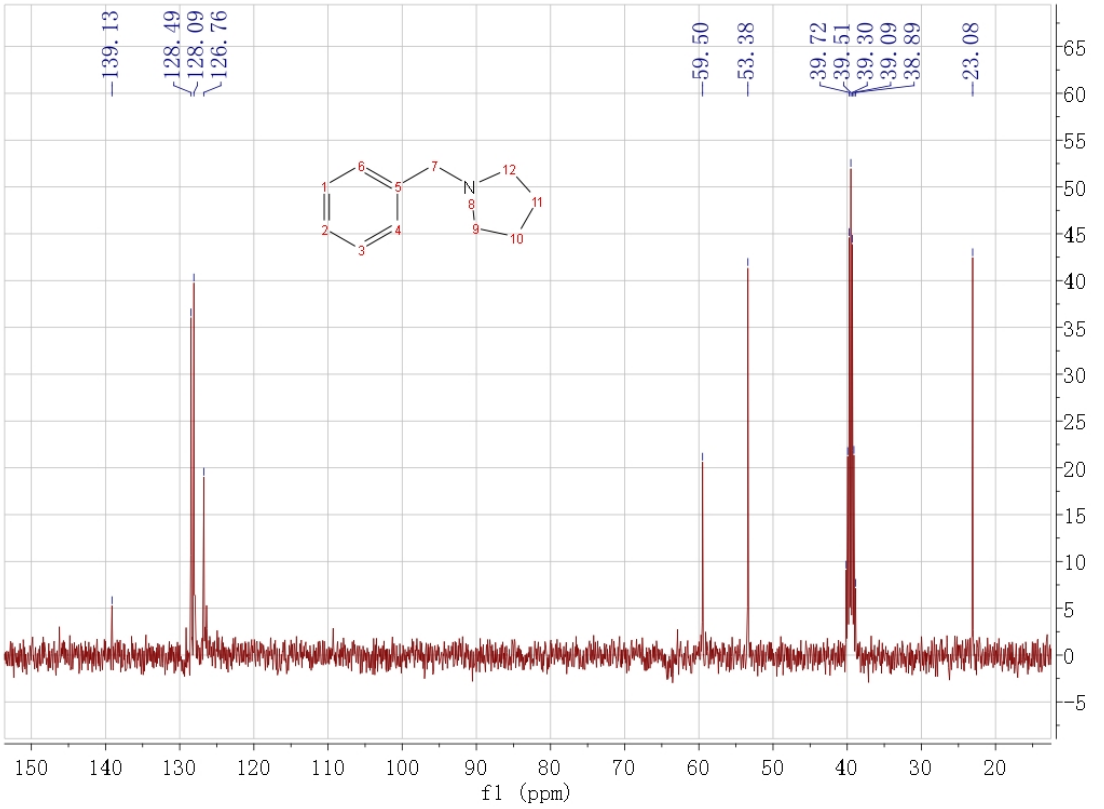
1-benzyl-4-methylpiperidine



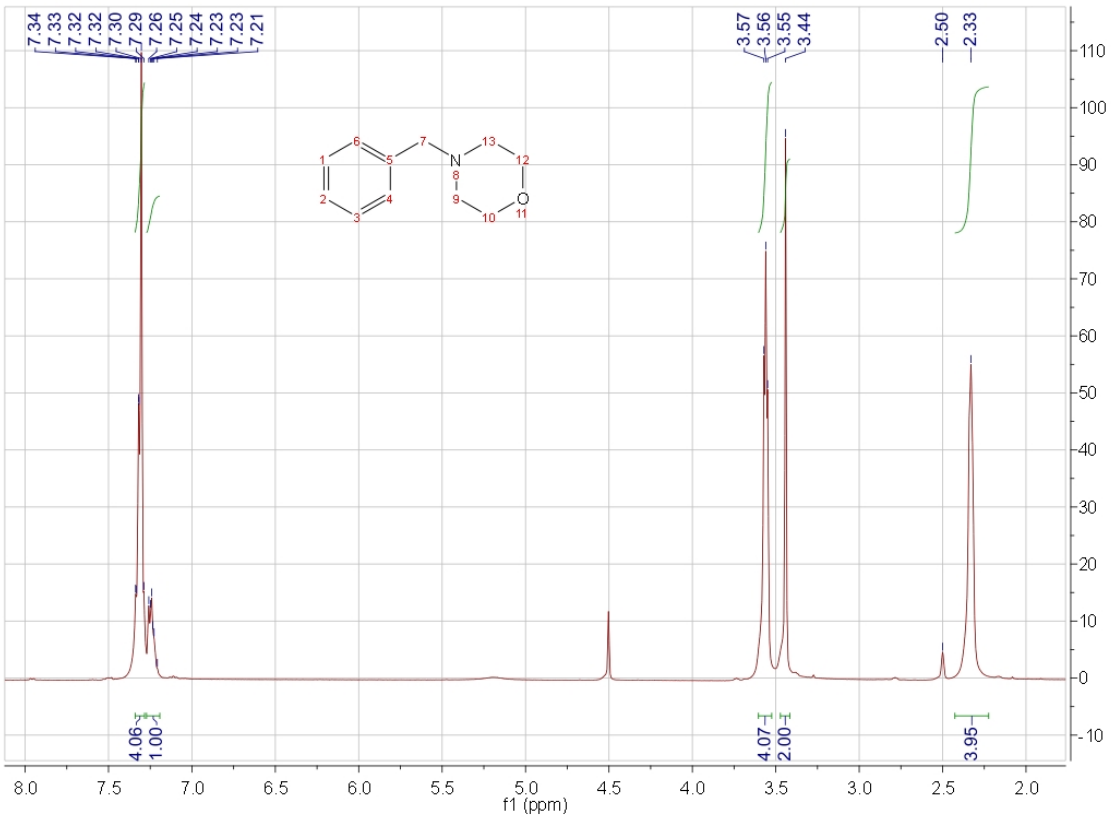


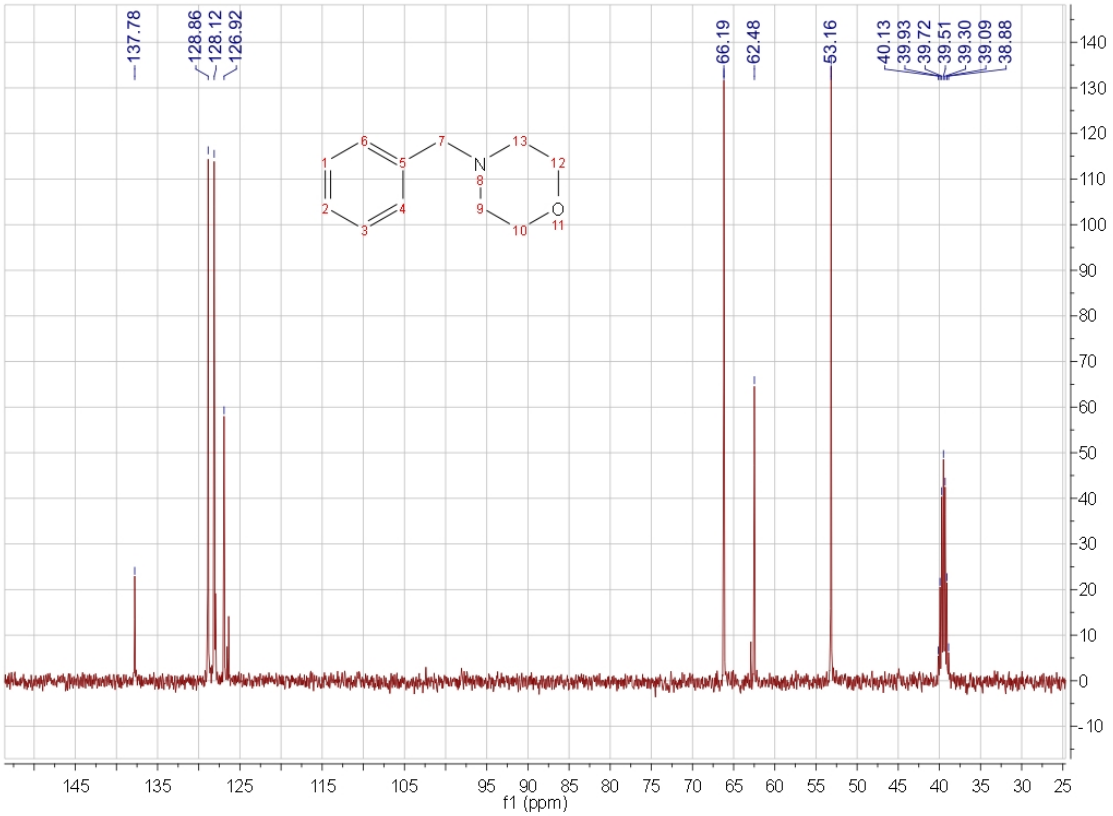
1-benzylpyrrolidine





4-benzylmorpholine





Reference

[1] C. Wang, Y. L. Hou, J. Kim, S. H. Sun, *Angew. Chem. Int. Ed.* **2007**, 46, 6333-6335.
[2] D. H. Ge, L. Hu, X. Q. Cao, J. Q. Wang, F. Q. Qi, J. M. Lu and H. W. Gu, *ChemCatChem.* **2013**, 5, 2183-2186.