# Supporting Information

## Selective interfacial hydrogenation of nitriles to synthesize tertiary amines

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## Experimental Section

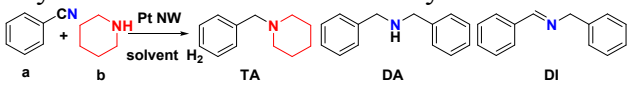
### Preparation of Pt nanowires catalyst:

Ultrathin Pt NWs were achieved through etching of FePt NWs. The mixed 0.2 g $Pt(acac)_2$ and 20 mL oleylamine were heated to 60 $^oC$ under $N_2$ atmosphere to make it dissolved thoroughly. This solution was heated to 120$^oC$ under stirring and then kept for 15 minutes. 0.15 mL $Fe(CO)_5$ was injected into the hot solution and then the temperature was gradually raised up to 160$^oC$. The reaction was kept at this temperature for half an hour without stirring. The black solution was then cooled to room temperature and centrifuged in excess ethanol. The precipitate was redispersed in methanol. The mixture was firstly treated by oxygen bubbling at 100$^oC$, and 10 mL HCl/methanol (1:1) solution was added into the above suspension. The solution was heated and stirred at 70$^oC$ for 1 hour, the resultant precipitates were obtained following 10 minutes of centrifugation (4000 rpm). The dark solid was washed with methanol for at least two times and stored in methanol. Based on the XPS and ICP analysis, no Fe element could be detected at the surface of the catalyst, which indicates the surface is composed by Pt atoms.

### General procedure for the symmetrical secondary amine synthesis using Pt NWs as the catalyst:

Pt NW catalyst in methanol (0.005 mmol) were added in a Schlenk tube and the methanol was evacuated by pressure reducing. Then solvents (either sole solvent or mixed solvent, 2 mL) were added, after which, ultrasonic stirring was used to make the catalyst to disperse uniformly. Nitriles and added secondary amines was injected into the mixture. The reaction tube was thrice evaluated and flushed with hydrogen. The reaction took place 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. All the reactions were performed for at least 5 times till their differences were within an acceptable error range. The products tertiary amines were purified by flash chromatography and characterized by $^1H$ NMR and $^{13}C$ NMR.

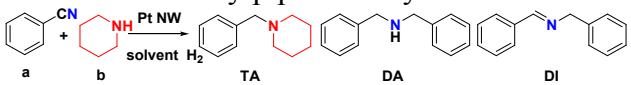
S1. Comparison of the catalytic activities between Pt catalysts with different morphologies [a]




| Entry | Catalyst | Conv. ( % )[b] | Select. ( % )[b] | | |
|---|---|---|---|---|---|
| | | | TA | DA | DI |
| 1 | Pt NPs[1] | 64.1 | 74.1 | 8.7 | 17.2 |
| 2 | Pt NRs[2] | 100 | 81.4 | 6.0 | 12.6 |
| 3 | Pt NWs | 100 | 96.1 | 0.2 | 3.7 |

[a] 0.005 mmol Pt catalyst[3], 1 bar $H_2$ pressure, 100°C, 1 mmol nitrile, 1.1 mmol added secondary amine and mixed solvent 2 mL (1.5 mL water, 0.5 mL 1，4-dioxane); [b] GC yield.

S2. Upscaled process and results of 1-benzylpiperidine synthesis [a]:

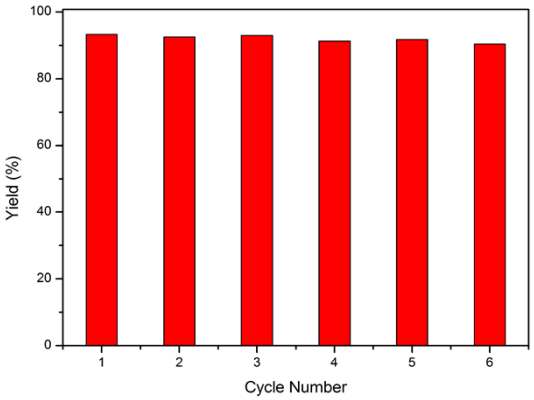



| Entry | Nitrile used | Solvent | $H_2$ (bar) | Temp. (°C) | Time (h) | Yield ( % ) [b] |
|---|---|---|---|---|---|---|
| 1 | 102 μL * 5 | Water&1,4-dioxane(1:3) | 1 | 100 | 24 | 92.0 |
| 2 | 102 μL* 20 | Water&1,4-dioxane(1:3) | 1 | 100 | 24 | 88.0 |

[a] Reaction conditions: the amount of both solvent and catalyst used was corresponding to the magnification times; [b] GC yield.

[1] Wang C., Daimon H., Onodera T., Koda O., Sun S., *Angew. Chem. Int. Ed.*, **2008,** *47*, 3588.
[2] Kim J., Lee Y., Sun S., *J. Am. Chem. Soc.*, **2010**, *132*, 4996.
[3] S. L. Lu, J. Q. Wang, X. Q. Cao, X. M. Li and H. W. Gu, *Chem. Commun*., 2014, **50**, 3512-3515.

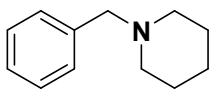
**Figure S1.** The catalytic stability of Pt nanowires in the synthesis of tertiary amines from the reduction of nitriles. (Reaction condition: 0.005 mmol Pt NWs, 1 bar $H_2$ pressure, 100°C, 1 mmol nitrile, 1.1 mmol added secondary amine and mixed solvent 2 mL (1.5 mL water, 0.5 mL 1，4-dioxane), Yields of the product were determined by GC.)




# NMR data of the Secondary Amines:

**Symmetrical secondary amines:**

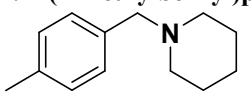
**1. 1-benzylpiperidine**



$^1$H NMR (400 MHz, DMSO-$d_6$): δ =1.37-1.38 (d, 2H), 1.46-1.49 (m, 4H), 2.28-2.30 (m, 4H), 3.40(s, 2H), 7.20-7.24(m, 1H), 7.28-7.32(m, 5H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ =24.51, 26.08, 54.59，64.02，126.94，128.19，129.35，138.63.

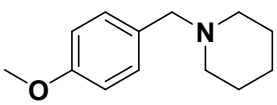
**2. 1-(4-methylbenzyl)piperidine**



$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.77-1.78(d, 2H), 1.86-1.89(m, 4H), 2.67-2.69 (m, 7H), 3.76(s，2H), 7.50-7.52(d，2H), 7.55-7.57 (d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=20.71，24.09，25.59，53.86，62.68，65.64，128.64，128.71，135.52，135.71.

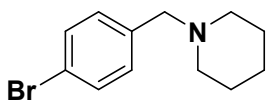
**3. 1-(4-methoxybenzyl)piperidine**



$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.77-1.78 (d, 2H), 1.85-1.90(m, 4H), 2.67-2.69(m, 4H), 3.73(s, 2H), 4.14(s,4H), 7.26-7.28(d,2H), 7.58-7.60(d,2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=24.11, 25.59, 53.78, 54.89, 62.34, 113.39, 129.86, 130.41, 158.14.

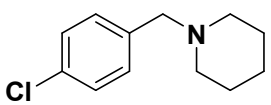
**4. 1-(4-bromobenzyl)piperidine**



$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.77-1.78 (d, 2H), 1.86-1.89 (m, 4H), 2.69 (s, 4H), 3.78 (s, 2H), 7.64-7.66(m, 2H), 7.88-7.90(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.97, 25.56, 61.98, 119,73, 130.74, 130.91, 138.13.

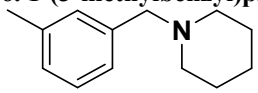
**5. 1-(4-chlorobenzyl)piperidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.77-1.78(d, 2H), 1.85-1.90(m, 4H), 2.68-2.70 (m, 4H), 3.79 (s, 2H), 7.69-7.71(d, 2H), 7.75-7.77(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.98, 25.57, 53.82, 61.95, 128.02, 130.38, 131.25, 137.73.

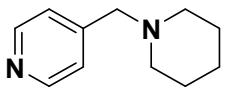
**6. 1-(3-methylbenzyl)piperidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.78-1.79(d, 2H), 1.88-1.89(m, 4H), 2.69-2.71 (m, 7H), 3.77 (s, 2H), 7.44-7.50(m, 3H), 7.58-7.61(m, 1H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=21.02, 24.05, 25.57, 53.93, 62.94, 125.85, 127.38, 127.95, 129.37, 137.07, 138.55.

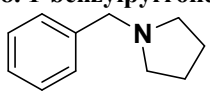
**7. 4-((piperidin-1-yl)methyl)pyridine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.38-1.39(d, 2H), 1.48-1.51(m, 4H), 2.30-2.32 (m, 4H), 7.29-7.30(d, 2H), 8.49-8.51(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.82, 25.52, 53.93, 61.44, 123.65, 147.83, 149.39.

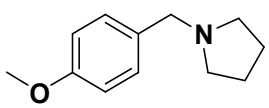
**8. 1-benzylpyrrolidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=167-1.69(m, 4H), 2.41-2.43(m, 4H), 3.57 (s, 2H), 7.22-7.23(m, 1H), 7.24-7.26(m, 2H), 7.26-7.31(m, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.08, 53.38, 59.50, 126.76, 128.09, 128.49, 139.13.

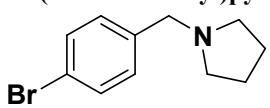
**9. 1-(4-methoxybenzyl)pyrrolidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.67-1.69(m, 4H), 2.36-2.38(m, 4H), 3.47 (s, 2H), 3.72(s, 3H), 6.84-6.86(m, 2H), 7.18-7.20(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.06, 53.34, 54.90, 113.42, 129.54, 131.36, 158.07.

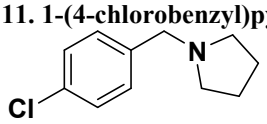
**10. 1-(4-bromobenzyl)pyrrolidine**



$^1$H NMR (400 MHz, DMSO-$d_6$): δ=2.09-2.10(d, 4H), 2.81(s, 4H), 3.93 (s, 2H), 7.66-7.68(d, 2H), 7.89-7.91(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.12, 53.41, 58.75, 119.68, 130.55, 130.98, 138.93.

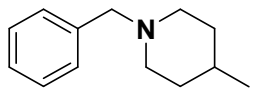
**11. 1-(4-chlorobenzyl)pyrrolidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.65-1.67(d, 4H), 2.38(s, 4H), 3.51(s, 2H), 7.28-7.34(m, 4H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=23.11, 53.40, 58.73, 128.03, 130.11, 131.21, 138.49.

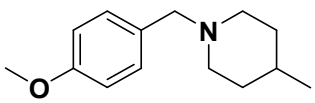
**12. 1-benzyl-4-methylpiperidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=0.87-0.88(d, 3H), 1.07-1.16(m, 2H), 1.28-1.34(m, 1H), 1.52-1.55(d, 2H), 1.85-1.90(m, 2H), 2.73-2.75(d, 2H), 3.41(s, 2H), 7.22-7.32(m, 5H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=21.84, 30.33, 33.98, 53.29, 62.51, 126.71, 128.05, 128.67, 138.74.

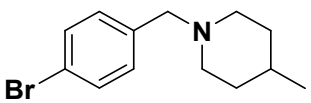
**13. 1-(4-methoxybenzyl)-4-methylpiperidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.27-1.29(d, 3H), 1.46-1.55(m, 2H), 1.67-1.74(m, 1H), 1.93-1.96(d, 2H), 2.22-2.27(m, 2H), 3.12-3.15(d, 2H), 3.75(s, 2H), 4.14(s, 3H), 7.26-7.28(d, 2H), 7.58-7.60(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=21.85, 30.39, 33.99, 53.15, 54.94, 61.91, 113.42, 129.88, 130.51, 158.12.

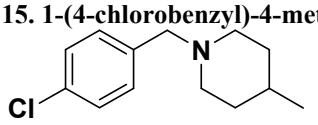
**14. 1-(4-bromobenzyl)-4-methylpiperidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=0.63-0.64(d, 3H), 0.83-0.91(m, 2H), 1.05-1.10(m, 1H), 1.28-1.31(d, 2H), 1.61-1.66(m, 2H), 2.46-2.49(d, 2H), 3.14(s, 2H), 6.99-7.01(d, 2H), 7.24-7.26(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=21.81, 30.25, 33.95, 53.21, 61.58, 128.50, 130.76, 130.94, 138.26.

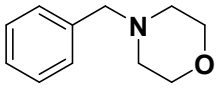
**15. 1-(4-chlorobenzyl)-4-methylpiperidine**




$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.47-1.57(d, 3H), 1.47-1.57(m, 2H), 1.70-1.73(m, 1H), 1.94-1.87(d, 2H), 2.26-2.32(m, 2H), 3.12-3.14(d, 2H), 3.81(s, 2H), 7.70-7.72(d, 2H), 7.76-7.78(d, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=21.83, 30.28, 33.97, 53.22, 61.54, 128.05, 130.42, 131.22, 137.86.

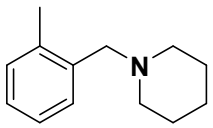
**16. 4-benzylmorpholine**



$^1$H NMR (400 MHz, DMSO-$d_6$): δ=2.33(s, 4H), 3.44(s, 2H), 3.55-3.57(m, 4H), 7.21-7.26(m, 1H), 7.29-7.34(m, 4H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=63.16, 62.48, 66.19, 126.92, 128.12, 128.86, 137.78.

**17. 1-(2-methylbenzyl)piperidine**



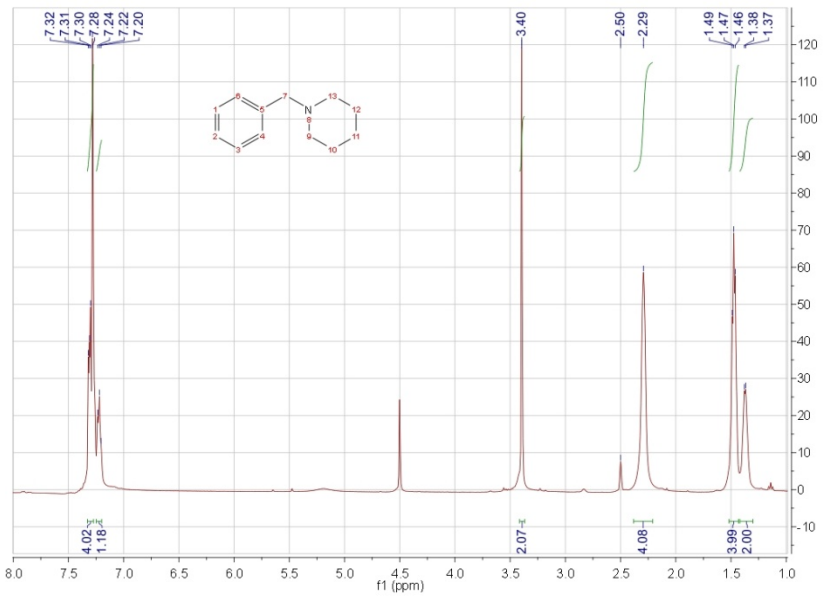
$^1$H NMR (400 MHz, DMSO-$d_6$): δ=1.79-1.81(d, 2H), 1.85-1.91(m, 4H), 2.71-2.73 (m, 7H), 3.76 (s, 2H), 7.50-7.55(m, 3H), 7.60-7.62(m, 1H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ=18.81, 24.12, 25.68, 54.11, 60.93, 125.28, 126.71, 129.40, 129.97, 136.73, 136.93.

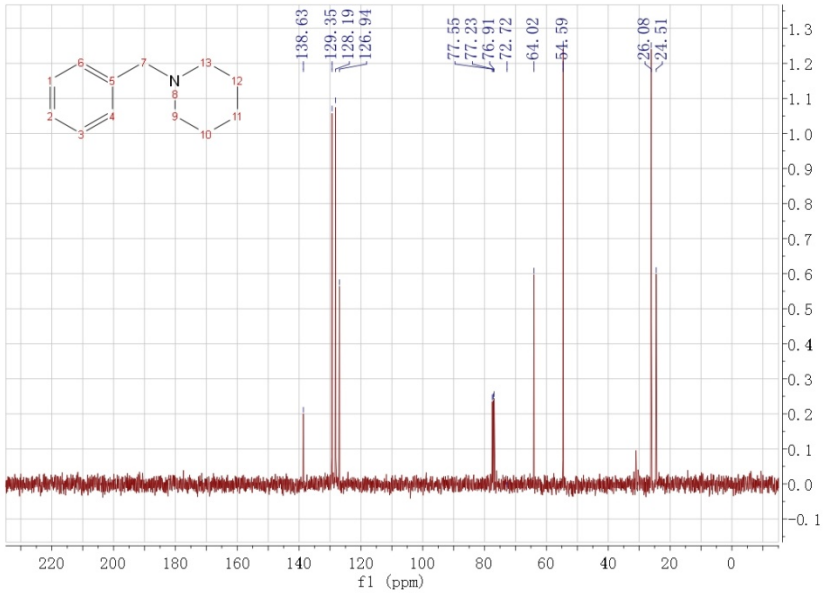
**Symmetrical secondary amines:**

1. **1-benzylpiperidine**

$^1$H NMR

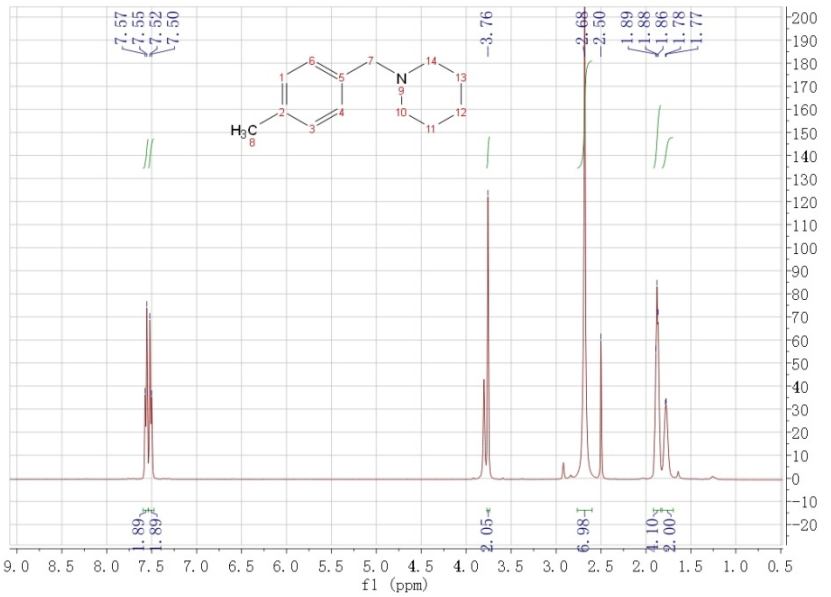



$^{13}$C NMR

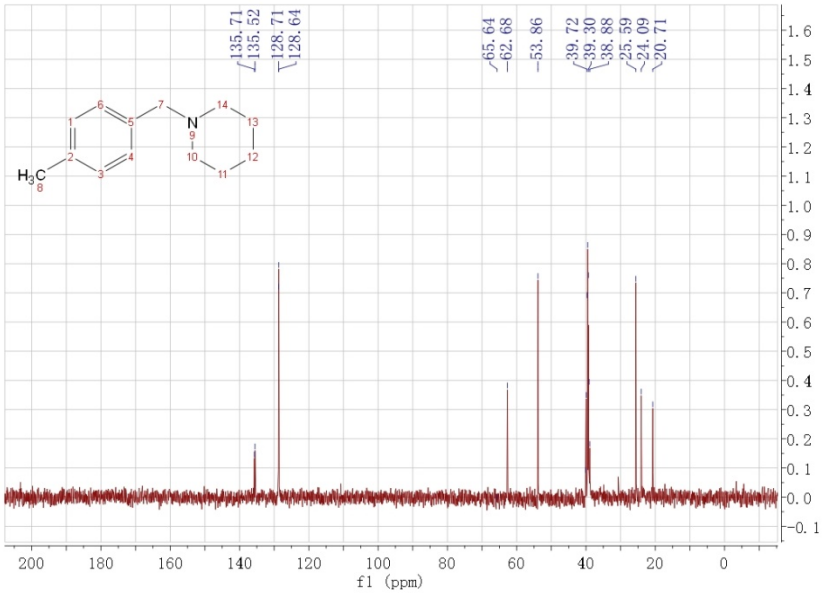



**2. 1-(4-methylbenzyl)piperidine**

$^{1}$H NMR

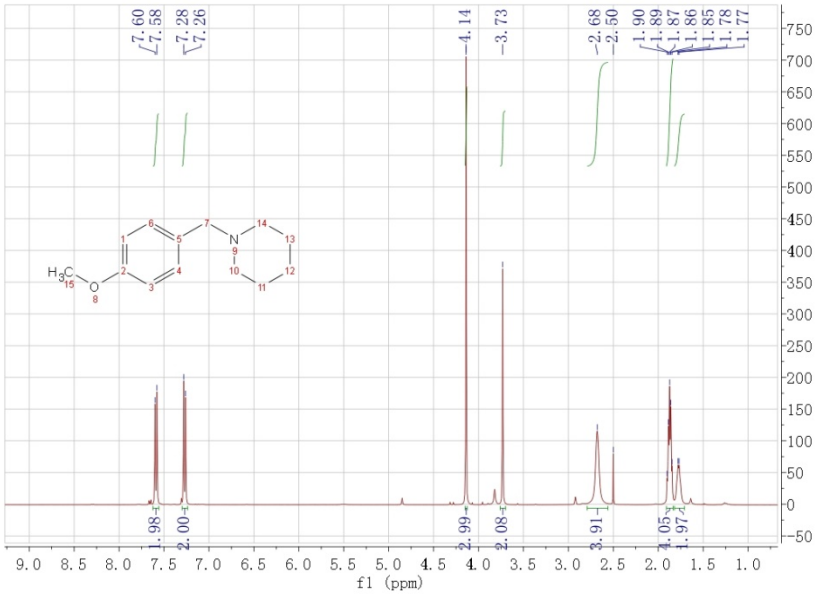



5 $^{13}$C NMR

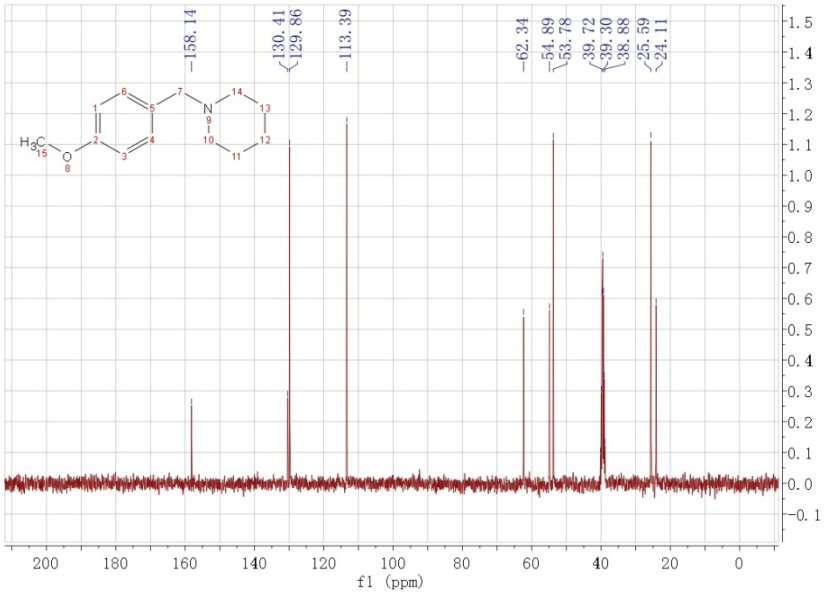



### 3. 1-(4-methoxybenzyl)piperidine

$^{1}$H NMR

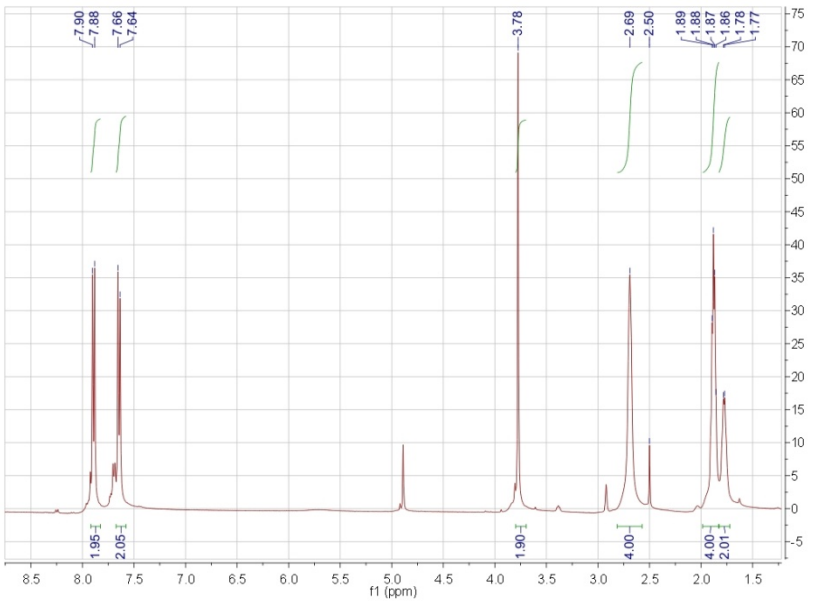



5 $^{13}$C NMR

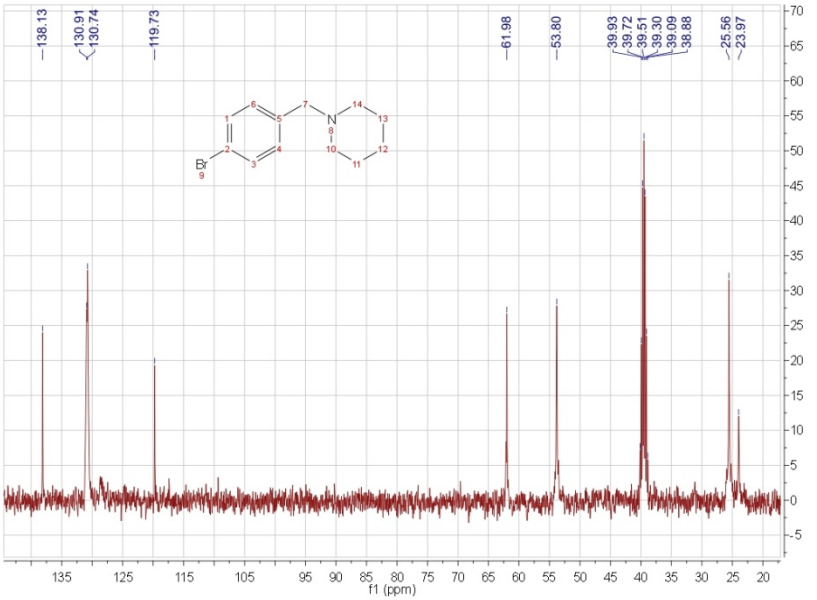



**4. 1-(4-bromobenzyl)piperidine**

$^{1}$H NMR

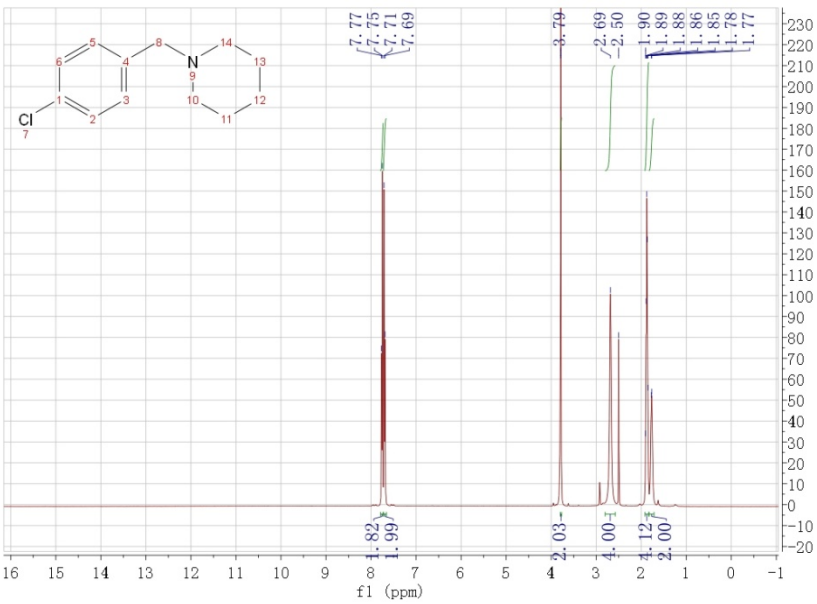



5 $^{13}$C NMR

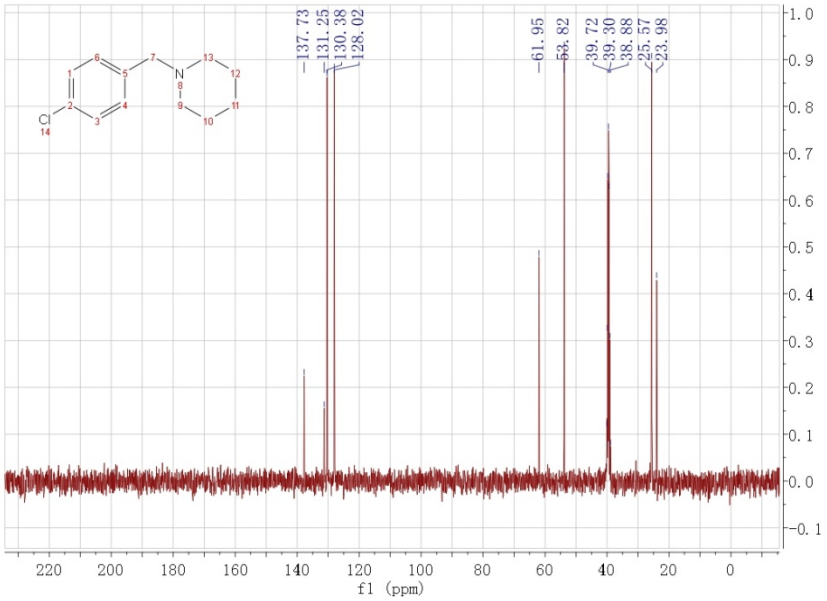



## 5. 1-(4-chlorobenzyl)piperidine

$^{1}$H NMR

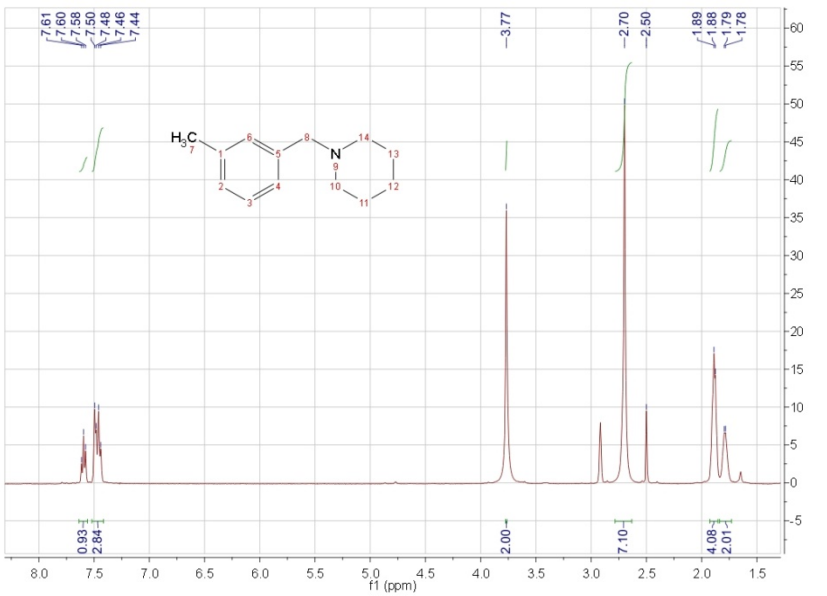



5 $^{13}$C NMR

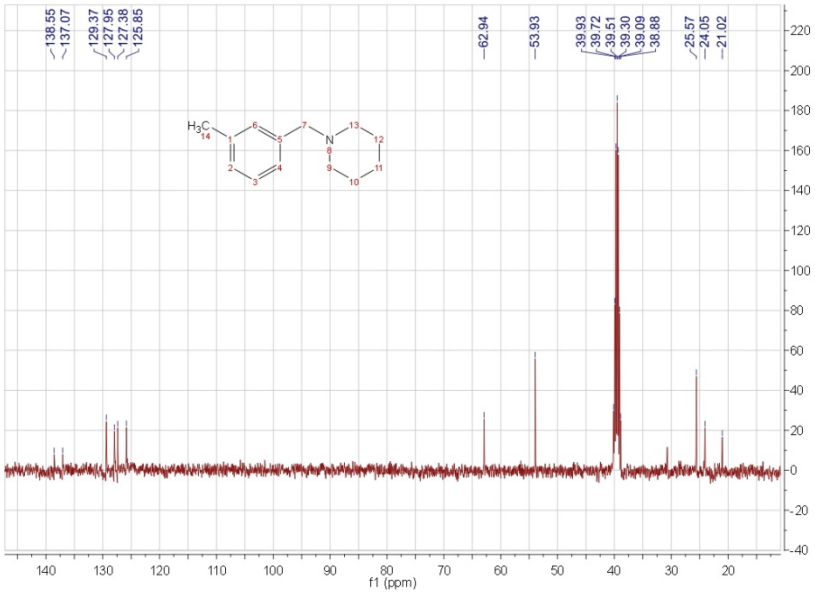



**6. 1-(3-methylbenzyl)piperidine**

$^{1}$H NMR

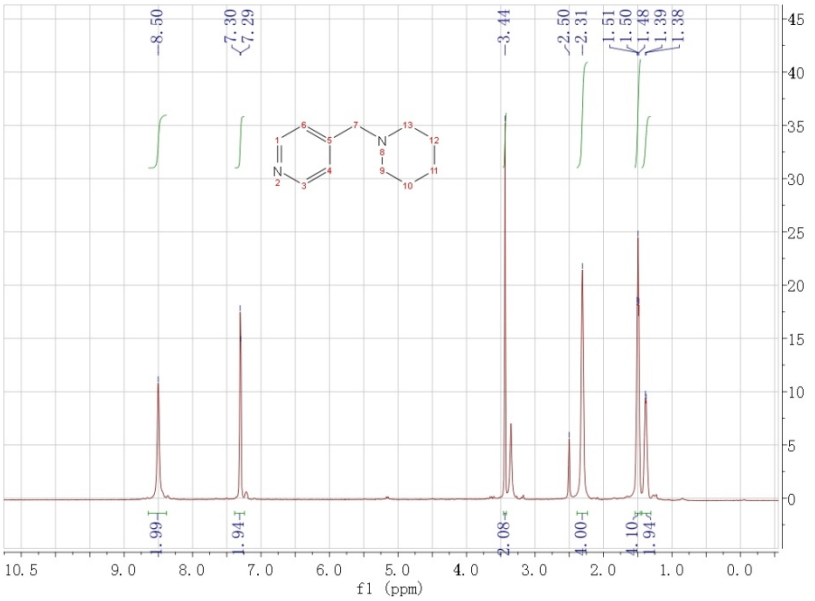



5 $^{13}$C NMR

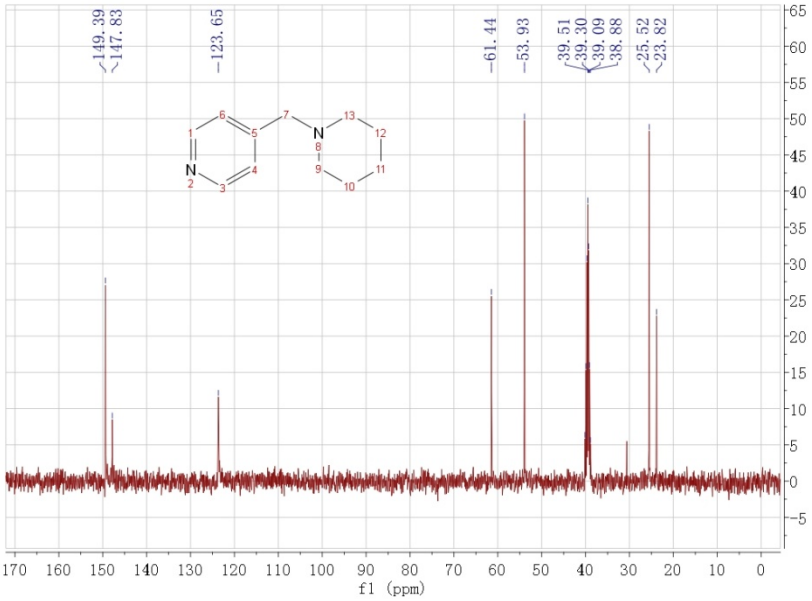



**7. 4-((piperidin-1-yl)methyl)pyridine**

$^{1}$H NMR

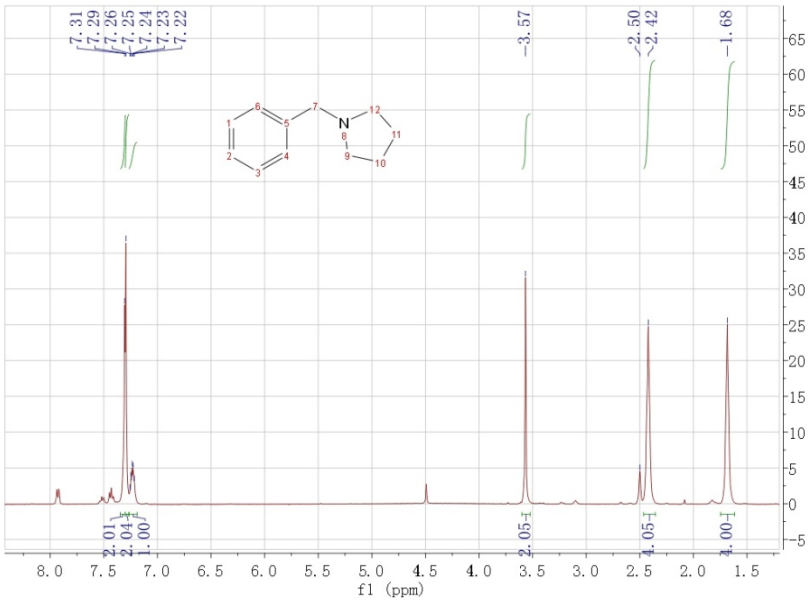



5 $^{13}$C NMR

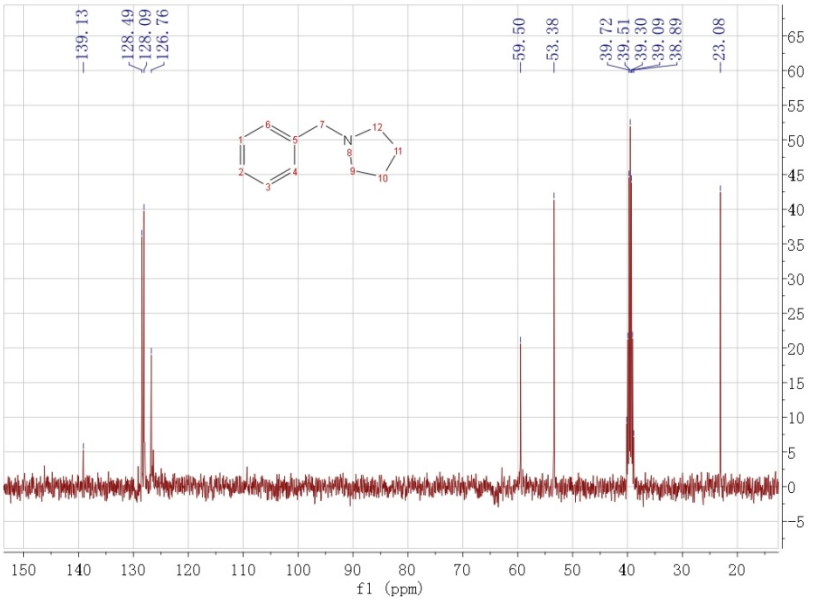



**8. 1-benzylpyrrolidine**

$^{1}$H NMR

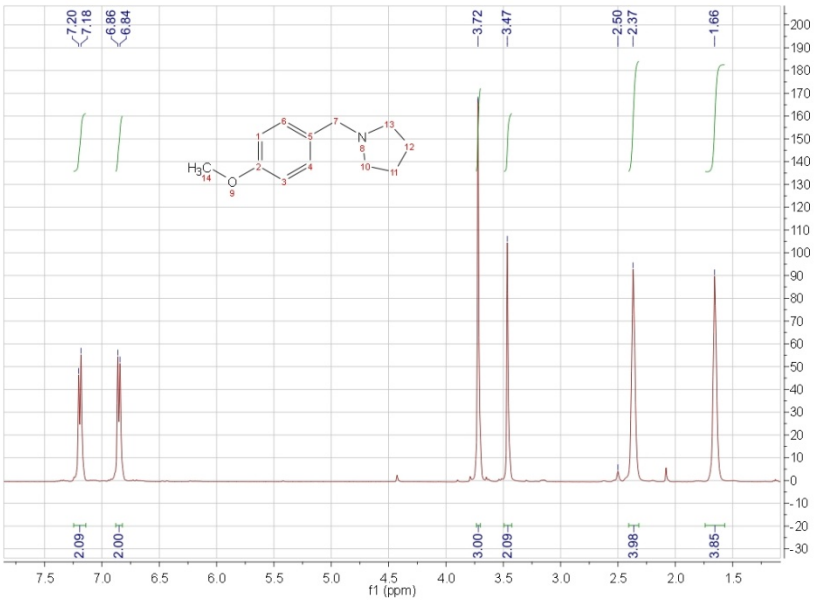



5 $^{13}$C NMR

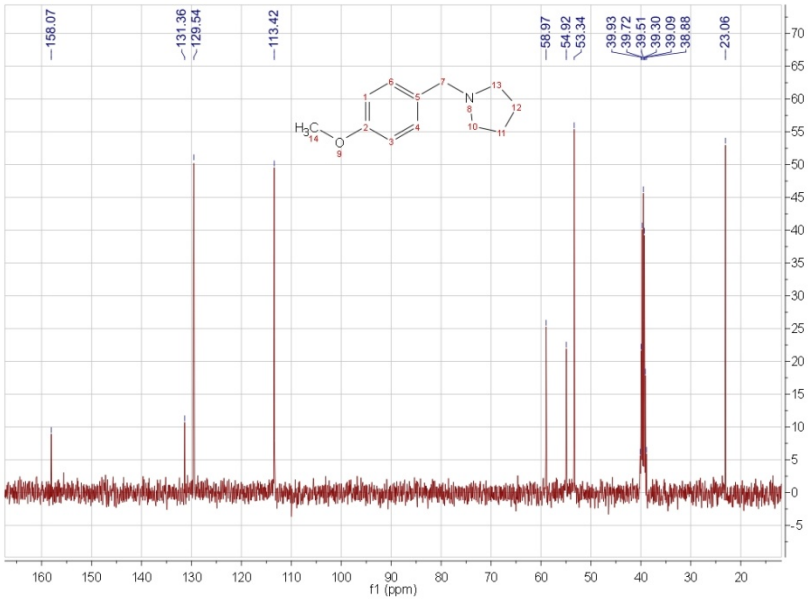



**9. 1-(4-methoxybenzyl)pyrrolidine**

$^{1}$H NMR

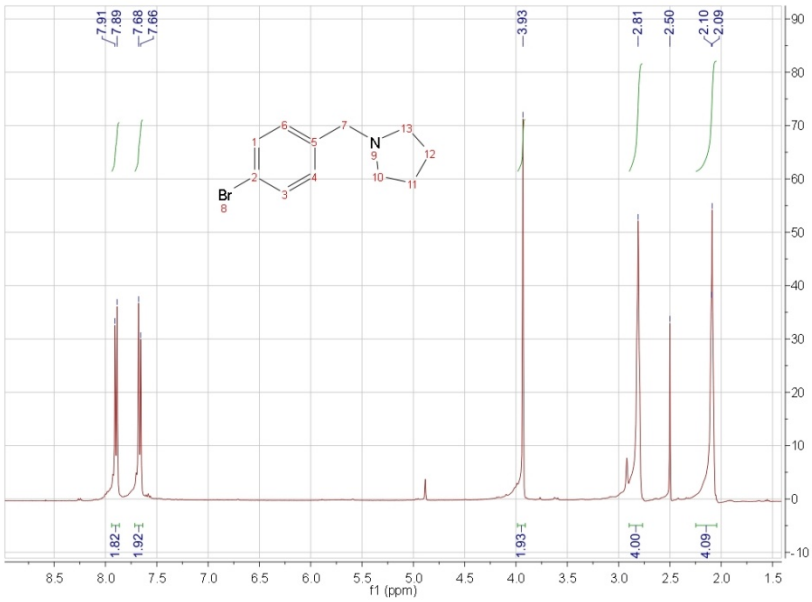



5 $^{13}$C NMR

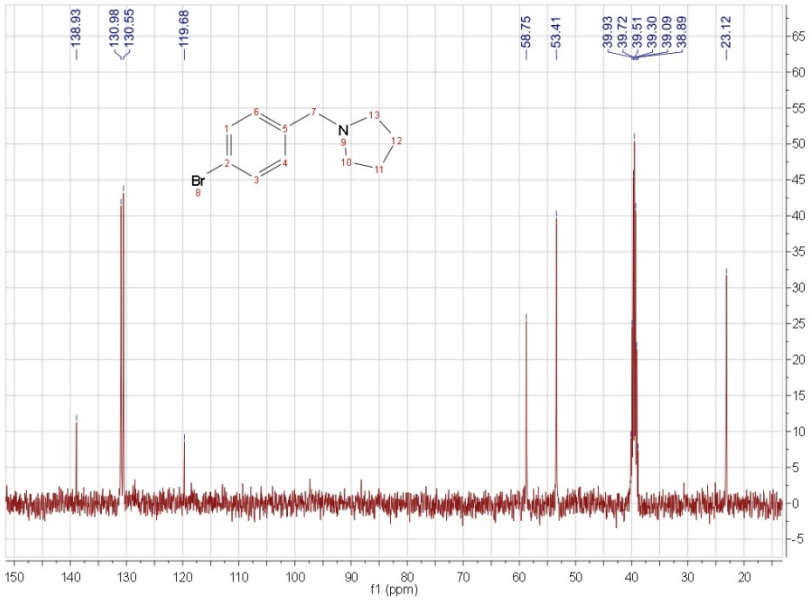



**10. 1-(4-bromobenzyl)pyrrolidine**

$^{1}$H NMR

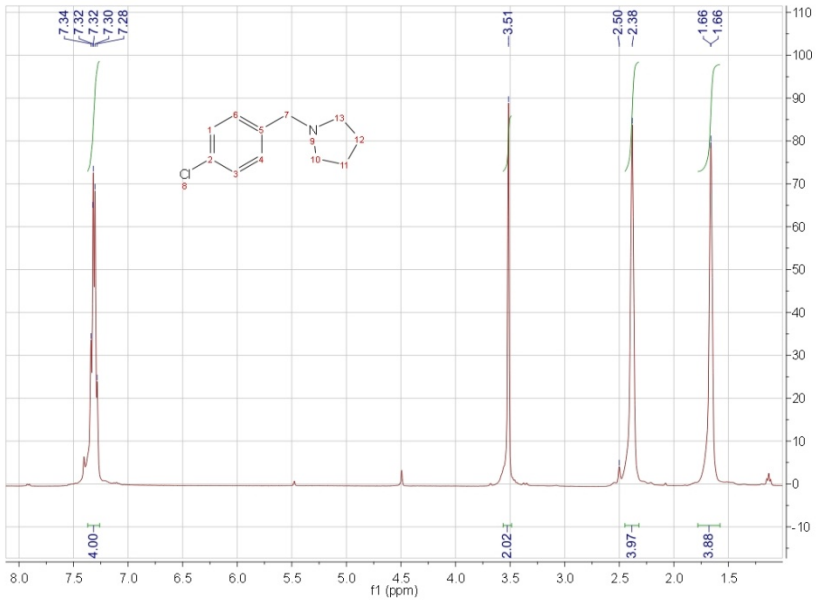



5 $^{13}$C NMR

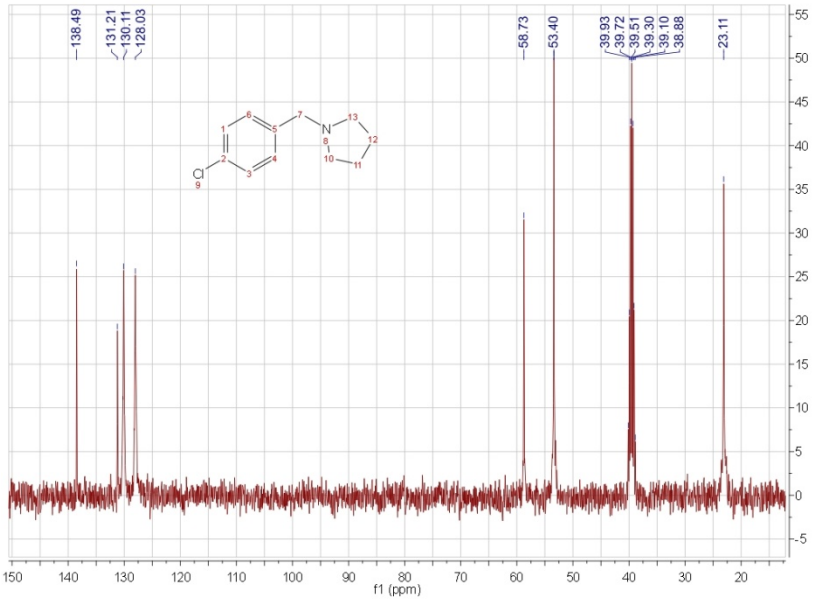



**11. 1-(4-chlorobenzyl)pyrrolidine**

$^{1}$H NMR

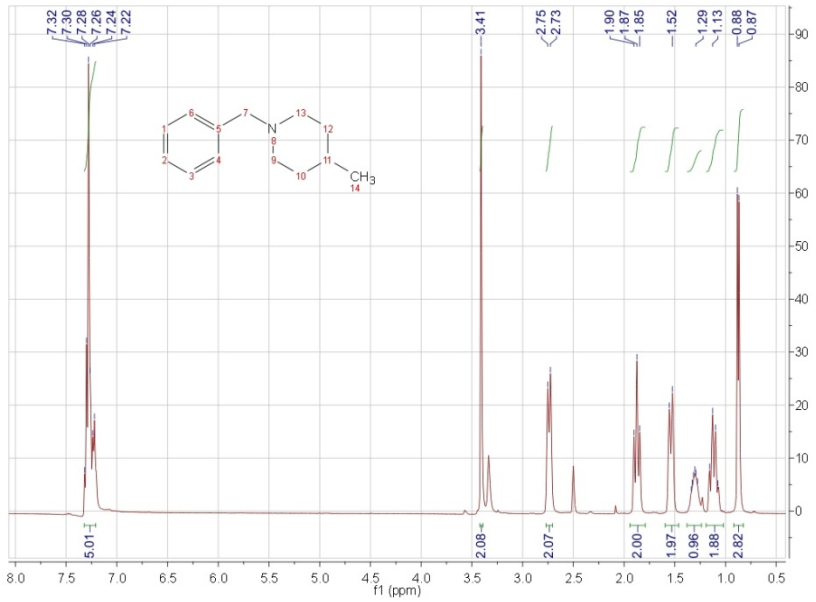



5 $^{13}$C NMR

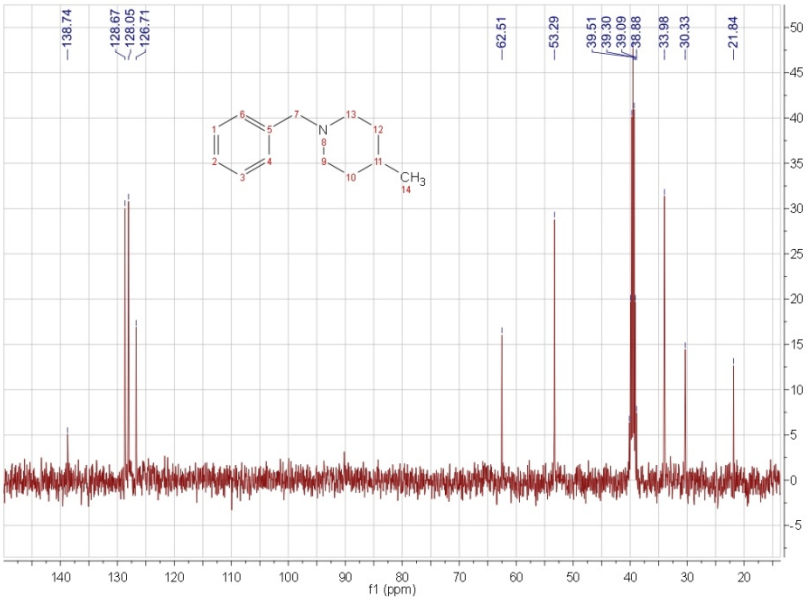



## 12. 1-benzyl-4-methylpiperidine

$^{1}$H NMR

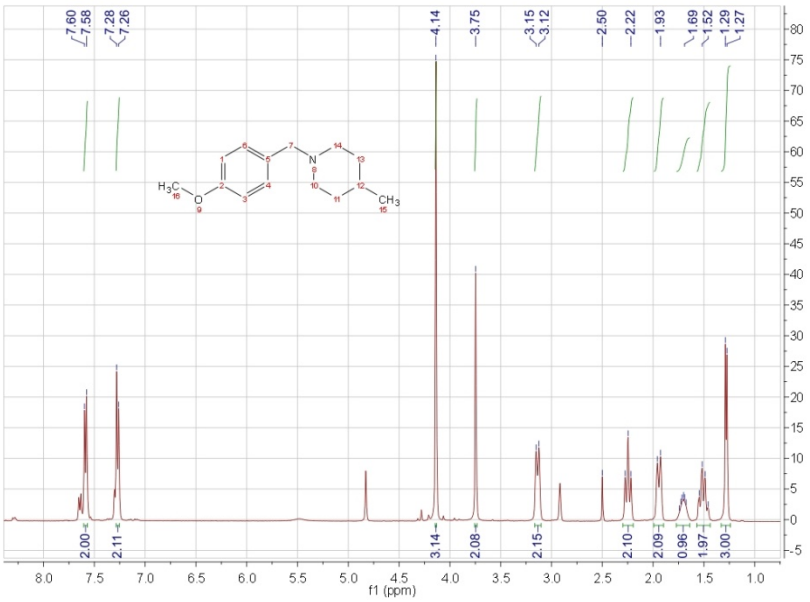



5 $^{13}$C NMR

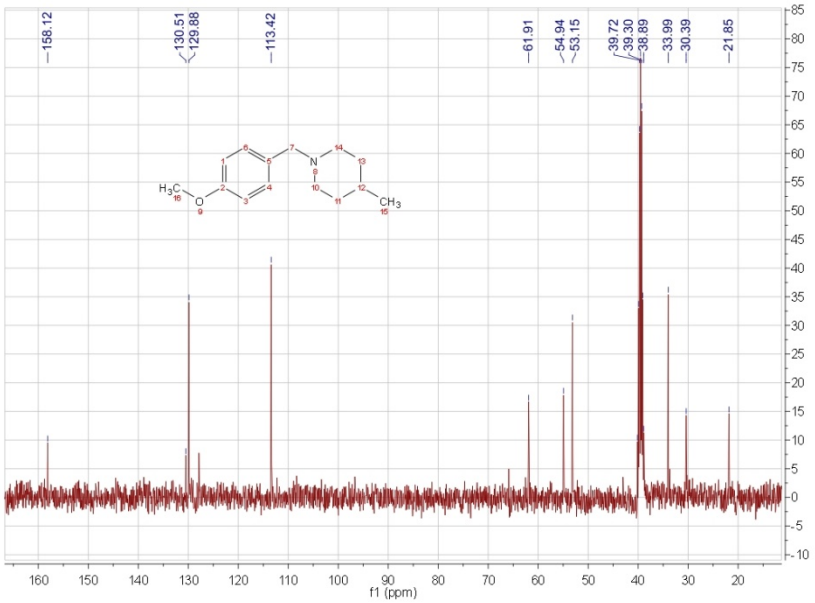



## 13. 1-(4-methoxybenzyl)-4-methylpiperidine

$^{1}$H NMR

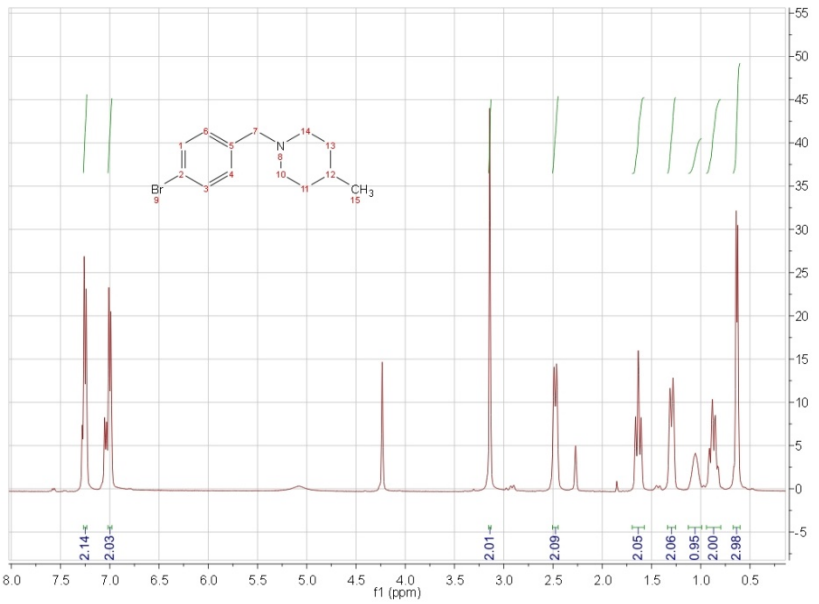



5 $^{13}$C NMR

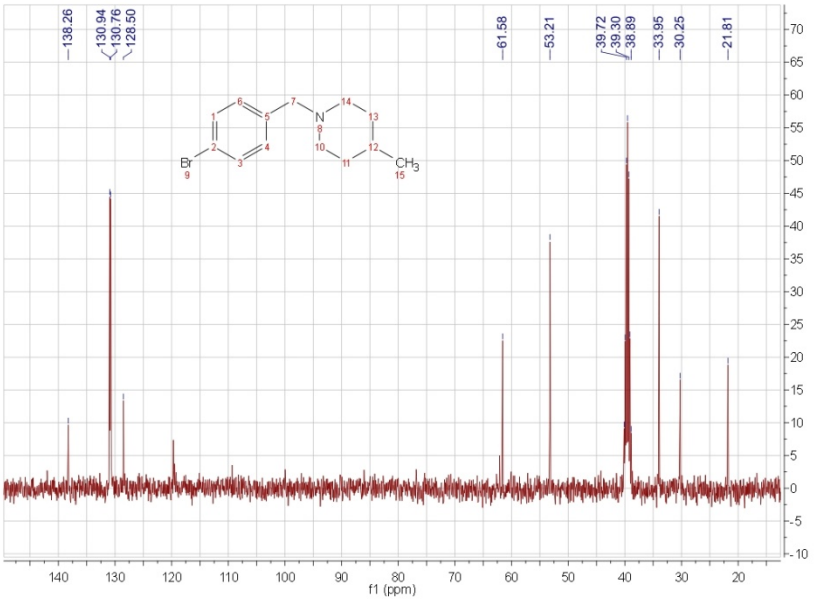



**14. 1-(4-bromobenzyl)-4-methylpiperidine**

$^{1}$H NMR

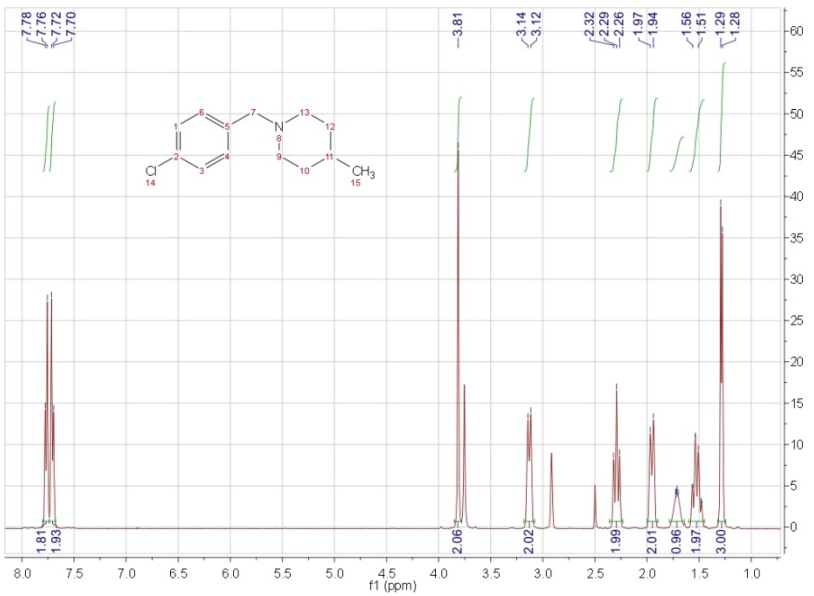



5 $^{13}$C NMR

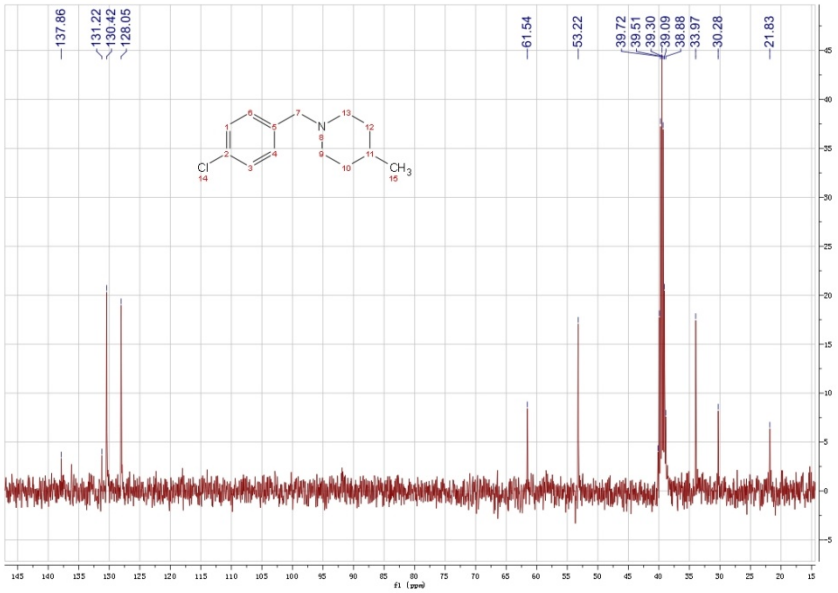



**15. 1-(4-chlorobenzyl)-4-methylpiperidine**

$^{1}$H NMR

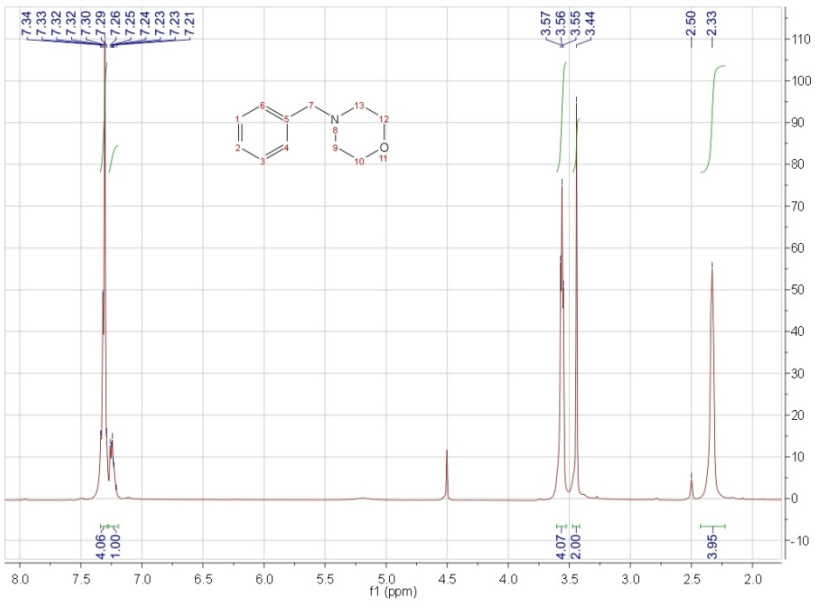



5 $^{13}$C NMR

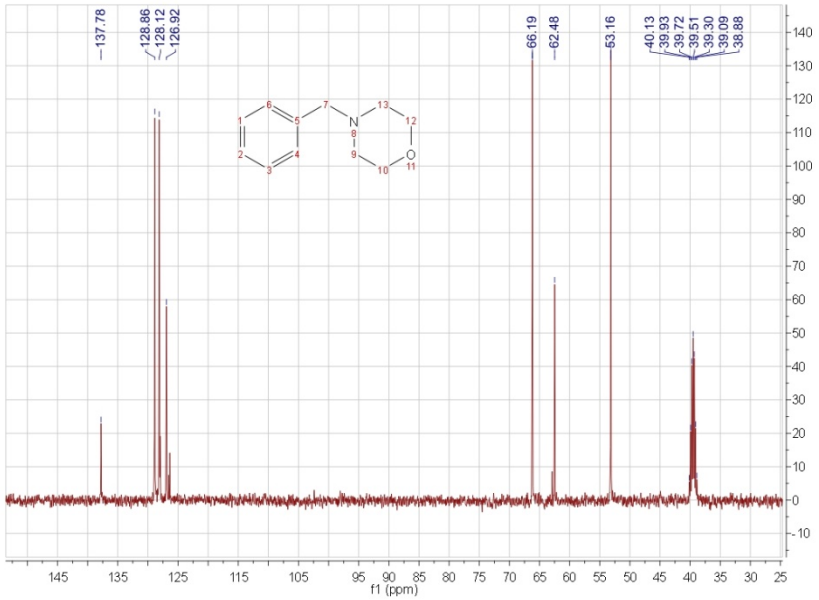



**16. 4-benzylmorpholine**

$^{1}$H NMR

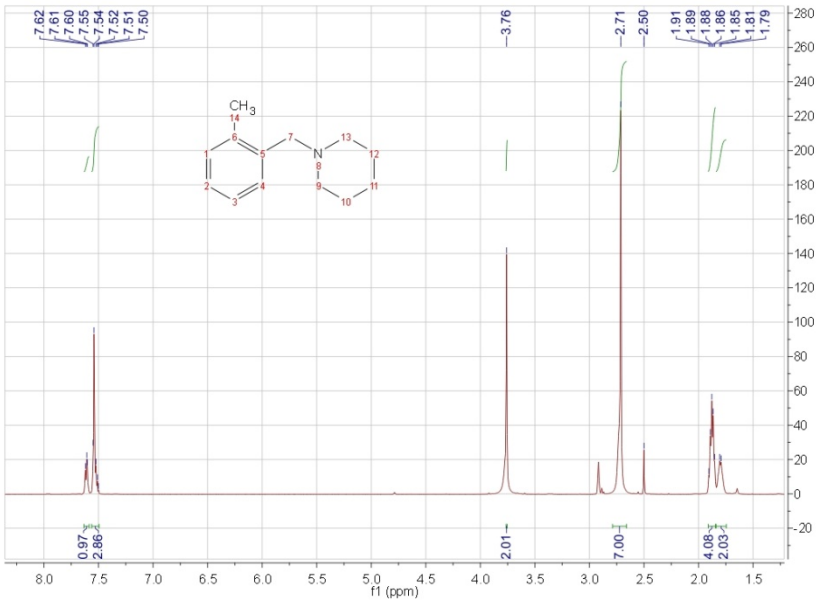



5 $^{13}$C NMR

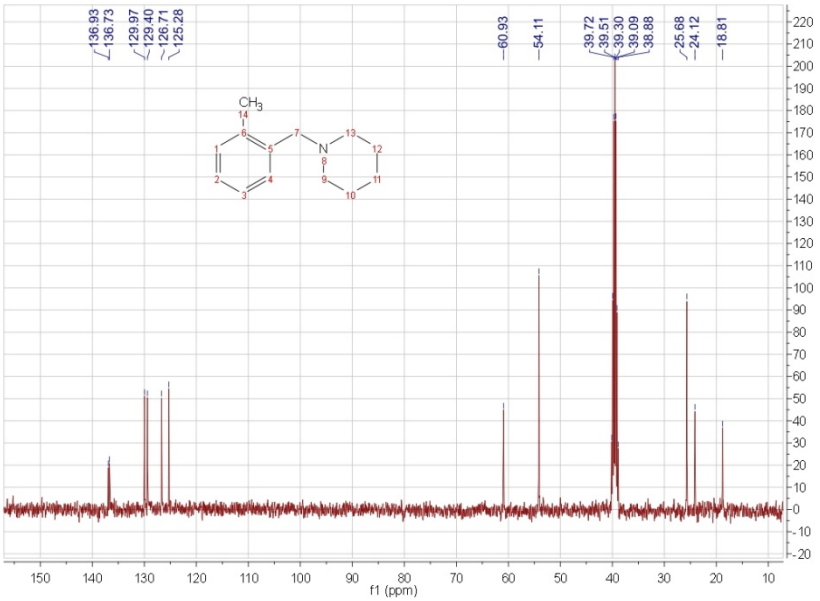



**17. 1-(2-methylbenzyl)piperidine**

$^{1}$H NMR




5 $^{13}$C NMR


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
CH3
14
6
7
13
1
5
N
12
8
2
4
9
11
3
10
f1 (ppm)