Supporting Information

Selective Synthesis of Secondary Amines from Nitriles using Pt Nanowires as a Catalyst

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Experimental Section

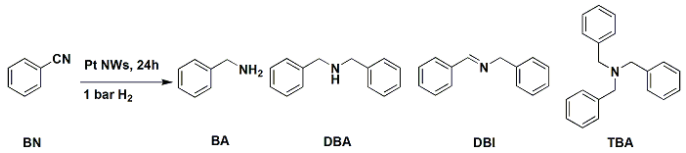
Preparation of Pt nanowires catalyst:

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 were 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.[1]

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

Pt NW catalyst in ethanol (0.005 mmol) was added in a Schlenk tube and the methanol was evacuated by pressure reducing. For the symmetrical secondary amine system, nitrile and solvent were added to the reaction tube and then sealed, while for the asymmetrical secondary amine system, nitrile, solvent and additional primary amine were added. The reaction tube was thrice evaluated and flushed with hydrogen. If higher hydrogen pressure was needed, Schlenk tube is substituted by an autoclave. 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 secondary amines were purified by flash chromatography and characterized by ^1H NMR and ^{13}C NMR.

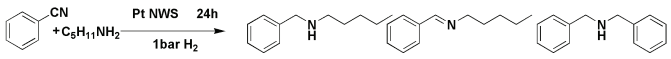
S1. Optimization of the reaction condition of the hygrogenation of benzonitrile [a]



Entry	Solvent	T (^{o}C)	Conv. (%) [b]	Select. (%) [b]			
				BA	DBA	DBI	TBA
1	methanol	40	88.7	-	93.3	6.7	-
2	water	80	100	-	83.7	-	16.3
3	ethanol	80	100	-	95.4	1.6	3.0
4	n-heptane	80	100	1.6	88.2	10.4	-
5	toluene	80	100	1.7	95.7	2.6	-
6	acetic acid	40	100	5.4	85,8	1.2	7.6
7	triethylamine	80	100	3.6	92.5	3.9	-
8	p-xylene	80	100	1.9	88.1	10.0	-
9	dioxane	40	100	2.4	92.1	2.0	3.5
10	ethanol	40	71.2	-	84.9	15.1	-
11	ethanol	60	86.1	-	95.4	1.6	3.0

[a] Reaction conditions: BN (1.0 mmol), solvent (2.0 mL) at 1 bar H_2 with 0.005 mmol Pt NWs catalyst for 24 h; [b] GC yield.

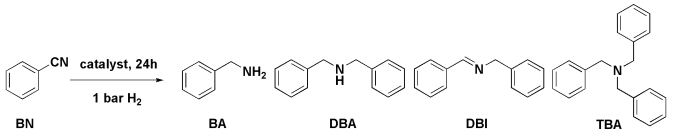
S2. Optimization of the reaction condition between benzonitrile and pentylamine [a]



Entry	Catalyst	H_2 (bar)	Solvent	T (^{o}C)	Conv. (%) [b]	Select. (%) [b]		
						a	b	c
1	-	1	toluene	80	0		N.D.	
2	Pt NWs	-	toluene	80	0		N.D.	
3	Pt NWs	1	water	80	100	81.3	17.4	1.3
4	Pt NWs	1	ethanol	80	100	91.2	5.8	3.0
5	Pt NWs	1	dioxane	80	100	93.9	4.2	1.9
6	Pt NWs	1	ethanol	40	100	87.2	2.0	1.8
7	Pt NWs	1	heptane	80	100	15.0	84.0	0.9
8	Pt NWs	1	*p*-xylene	80	100	69.1	29.4	1.3
9	Pt NWs	1	toluene	40	100	33.5	60.0	6.5
10	Pt NWs	1	toluene	60	100	55.0	41.3	3.7
11	Pt NWs	1	toluene	80	100	94.4	2.4	2.4
12	Pt NWs	1	toluene	90	100	87.3	11.8	0.9
13	Pt NWs	1	toluene	100	100	82.6	2.4	5.0

[a] Reaction conditions: BN (1.0 mmol), nitrile:amine ratio is 1:2, solvent (2.0 mL) at 1 bar H_2 with 0.005 mmol Pt NWs catalyst for 24 h; [b] GC yield.

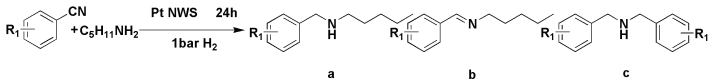
S3. Comparison of the catalytic activities between Pt catalysts with different morphologies [a]

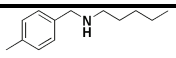
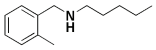
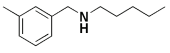
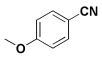
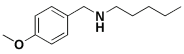
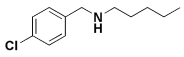
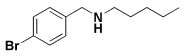
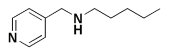


Entry	catalyst	Conv. (%) [b]	Select. (%) [b]			
			BA	DBA	DBI	TBA
1	Pt NPs[1]	88.7	-	74.9	22.0	5.1
2	Pt NRs[2]	100	-	89.0	6.0	5.0
3	Pt NWs	100	-	95.4	1.6	3.0

[a] Reaction conditions: BN (1.0 mmol), ethanol (2.0 mL) at 80 ^oC, 1 bar H_2 with 0.005 mmol Pt NWs catalyst for 24 h; [b] GC yield.

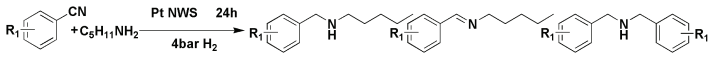
S4. Different nitriles to get asymmetrical secondary amines under atmospheric H2 pressure [a]

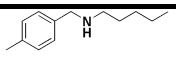
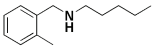
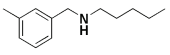
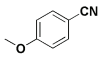
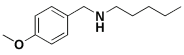
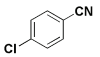
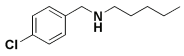
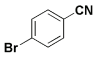
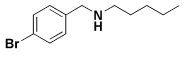
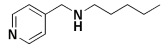


Entry	Nitriles	Products	Conv. (%) [b]	Select. (%) [b]		
				a	b	c
1			100	41.6	57.0	1.4
2			31.5	5.4	94.6	-
3			100	2.9	87.1	-
4			100	81.9	10.3	7.8
5			100	31.4	68.6	-
6			100	60.7	19.1	-
7			100	78.6	11.1	10.3

[a] Reaction Condition：80 ^oC in the atmospheric H_2 pressure, toluene as solvent, ratio of the nitrile and amine is 1：2; [b] GC yield.

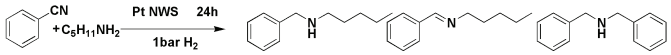
S5. Different nitriles to get unsymmetrical secondary amines under 4bar H2 pressure [a]



Entry	Nitriles	Products	Conv. (%) [b]	Select. (%) [b]		
				a	b	c
1			100	84.2	-	15.8
2			90.6	85.4	2.1	-12.6
3			100	95.0	-	5.0
4			100	85.8	4.6	9.6
5			100	75.5	4.1	20.6
6			100	55.6	6.4	38.0
7			100	90.8	9.2	-

[a] Reaction Condition： 80 ^{o}C in the 4 bar H_2 pressure, toluene as solvent, ratio of the nitrile and amine is 1：2; [b] GC yield.

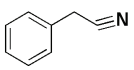
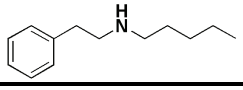
S6. Upscaled process and results of N-benzylbutan-1-amine synthesis [a]



Entry	Nitrile used	Solvent	H_2 (bar)	Temp. (^{o}C)	Time (h)	Yield (%) [b]
1	102 microL × 5	toluene	1	80	24	94.0
2	102 microL × 20	toluene	1	80	24	92.0

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

S7. 2-phenylacetonitrile reacts with pentylamine at the standard temperature (80°C) [a]

Nitrile	Amine	Product	Yield
			75.9%

[a] Reaction condition: 80 °C in 1 bar H_2 pressure for 24 h, toluene (2.0 mL), nitrile:amine ratio of 1:2, GC yield.

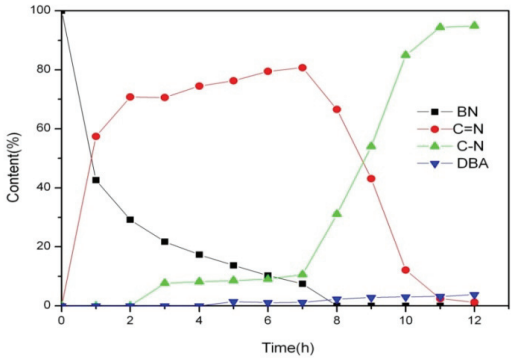


Figure S1. Time-conversion plot for the model reaction that the benzonitrile is hydrogenated with pentylamine to asymmetrical secondary amine with Pt NWs. (80°C, toluene as solvent, atmospheric H_2 pressure)

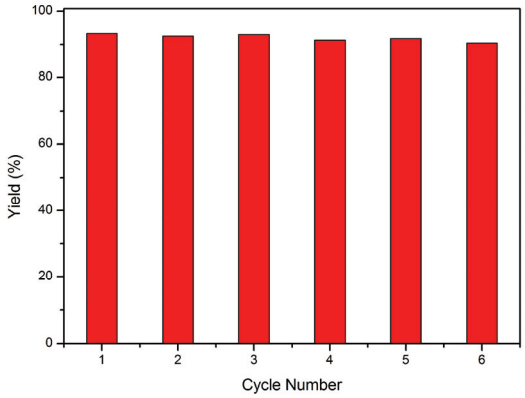


Figure S2. The catalytic stability of Pt nanowires in the synthesis of secondary amines from the reduction of nitriles (Reaction condition: 80 °C in the atmospheric H_2 pressure, 0.005 mmol Pt NWs catalyst, toluene as solvent, ratio of the benzonitrile and pentylamine is 1：2. Yields of the product were determined by GC.)

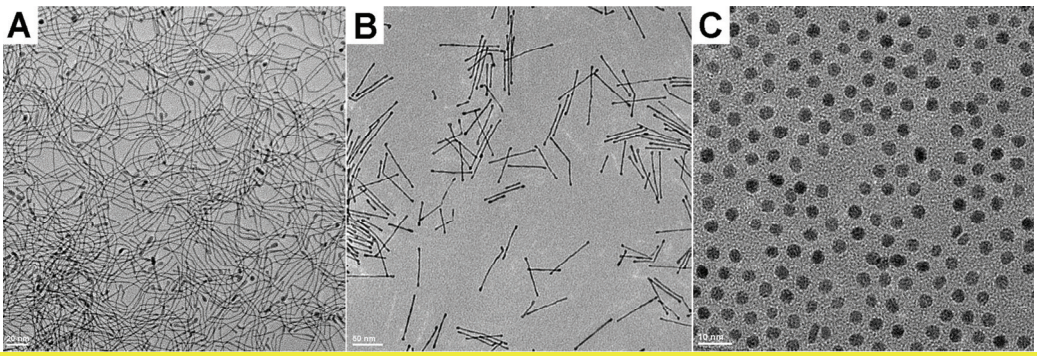


Figure S3. TEM images for different Pt morphologies mentioned in table S3: A (nanoparticles), B (nanorods), C (nanowires).

Reference

[1] L. Hu, X. Q. Cao, D. H. Ge, H. Y. Hong, Z. Q. Guo, L. Chen, X. H. Sun, J. X. Tang, J. W. Zheng, J. M. Lu and H. W. Gu, *Chem. Eur. J.*, **2011**, 17, 14283.

[2]Wang, C.; Hou, Y. L.; Kim, J.; Sun, S. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 6333.

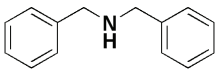
[3] Kim J.; Lee Y.; Sun S. H. *J. Am. Chem. Soc.*, **2010**, 132, 4996.

Analysis.

^{1}H NMR and ^{13}C NMR data were recorded at 400.0 and 100 MHz on a Varian Inova 400 spectrometer. The ^{1}H NMR and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane. All measurements were carried out at 298 K. Abbreviations used in the description of NMR data are as follows: s, singlet; d, dublet; m, multiplet.

Symmetrical secondary amines:

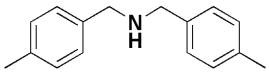
1. Dibenzylamine



^{1}H NMR (400 MHz, DMSO-d_6): δ =3.68 (s, 4H), 7.21-7.24 (m, 2H), 7.30-7.36 (m, 8H).

^{13}C NMR (100 MHz, DMSO-d_6): δ =57.61, 131.90, 133.31, 133.49, 146.22.

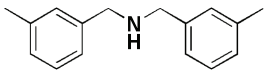
2. Bis(4-methylbenzyl)amine



^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.43 (s, 6H), 3.84(s, 4H), 7.25-7.27 (d, 4H), 7.36-7.38 (d, 4H).

^{13}C NMR (100 MHz, DMSO-d_6): δ =26.05, 50.66, 132.32, 134.00, 140.40, 146.64.

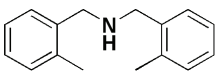
3. Bis(3-methylbenzyl)amine



^{1}H NMR (400 MHz, DMSO-d_6): δ =2.29 (s, 6H), 3.63 (s, 4H), 7.02-7.04 (d, 2H), 7.11-7.21 (m, 6H), ,.

^{13}C NMR (100 MHz, DMSO-d_6): δ =21.08, 52.26, 125.02, 127.16, 128.01, 128.61, 137.10, 140.75.

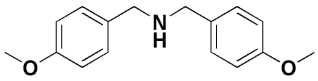
4. Bis(2-methyl)benzylamine



^{1}H NMR (400 MHz, DMSO-d_6): δ =1.40 (s, 6H), 2.83 (s, 4H), 6.26-6.27 (d, 6H), 6.47-6.48 (d, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ =18.56, 50.55, 125.54, 126.50, 128.21, 129.81, 136.03, 138.64.

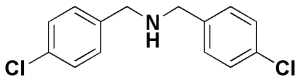
5. Bis(4-methoxybenzyl)amine



^{1}H NMR (400 MHz, DMSO-d_6): δ =3.68 (s, 4H), 3.75(s, 6H), 6.88-6.90 (d, 4H), 7.26-7.28 (d, 4H).

^{13}C NMR (100 MHz, DMSO-d_6): δ =50.52, 60.35, 118.85, 133.49, 141.72, 163.18.

6. Bis(4-chlorobenzyl)amine

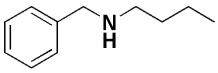


^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.70 (s, 4H), 7.31-7.36 (m, 8H),.

^{13}C NMR (100 MHz, DMSO-d_6): δ =56.69, 133.42, 135.08, 136.45, 145.15.

Unsymmetrical secondary amines:

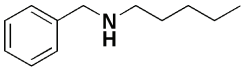
1. N-benzylbutan-1-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.85-0.89 (m, 3H), 1.25-1.34 (m, 2H), 1.44-1.51 (m, 2H), 2.53-2.57 (m, 2H), 3.72 (s, 2H), 7.19-7.23 (m, 1H), 7.28-7.29(m,4H)..

^{13}C NMR (100 MHz, CH_3OD): δ = 22.63, 29.69, 41.36, 58.04, 62.75, 136.05, 137.51, 127.68, 150.74.

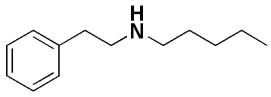
2. N-benzylpentan-1-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.85-0.88 (m, 3H), 1.26 (s, 4H), 1.46-1.50 (m, 2H), 2.48-2.52 (m, 3H), 3.68 (s, 2H), 7.21 (s, 1H), 7.27-7.28 (d, 2H).

^{13}C NMR (100 MHz, CH_3OD): δ = 14.22, 22.78, 29.71, 29.95, 49.66, 54.25, 126.97, 128.24, 128.49, 140.69.

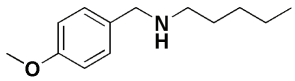
3. N-phenethylpentan-1-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.88-0.92 (m, 3H), 1.26-1.34 (m, 4H), 1.46-1.53 (m, 2H), 2.58-2.62 (m, 2H), 2.80-2.81 (m, 4H), 7.18-7.21 (m, 3H), 7.26-7.29(m, 2H).

^{13}C NMR (100 MHz, CH_3OD): δ = 14.24, 22.78, 29.72, 36.38, 49.99, 51.33, 126.36, 128.67, 128.91, 140.13.

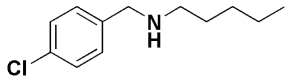
4. N-(4-methoxybenzyl)pentan-1-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.87-0.90 (m, 3H), 1.27-1.34 (m, 4H), 1.46-1.54 (m, 3H), 2.50-2.54 (m, 2H), 3.64 (s, 2H), 3.0 (s, 3H).

^{13}C NMR (100 MHz, CH_3OD): δ = 14.55, 23.79, 30.15, 30.84, 49.96, 53.95, 55.78, 114,93, 130,94, 132.53, 160.48.

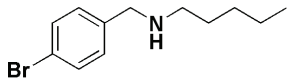
5. N-(4-chlorobenzyl)pentan-1-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.89-0.90 (m, 3H), 1.31-1.32 (m, 4H), 1.52-1.53 (m, 2H), 2.55-2.59 (m, 2H), 3.74(s, 2H), 7.32(s, 4H).

^{13}C NMR (100 MHz, CH_3OD): δ = 14.55, 23.74, 29.96, 30.72, 49.99, 53.62, 129.67, 131.4, 134.21, 138.92.

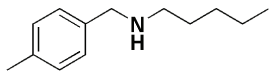
6. N-(4-bromobenzyl)pentan-1-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.88-0.91 (m, 3H), 1.29-1.31 (m, 4H), 1.49-1.56 (m, 2H), 2.54-2.58(m, 2H), 3.72(s, 2H), 7.24-7.26(d, 2H), 7.46-7.47(d, 2H)..

^{13}C NMR (100 MHz, CH_3OD): δ = 14.59, 23.73, 30.02, 30.71, 50.00, 53.70, 122.12, 131.67, 132.64, 139.51.

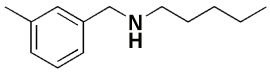
7. (4-Methyl-benzyl)-pentyl-amine



^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05-1.08 (m, 3H), 1.47-1.48 (m, 4H), 1.67-1.72(m, 2H), 2.50 (s, 3H), 2.76-2.80 (m, 2H), 3.91(s, 2H), 7.28-7.30 (d, 2H), 7.37-7.38 (d, 2H)

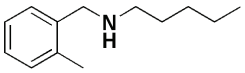
^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.07, 21.11, 22.69, 29.63, 29.75, 49.40, 53.76, 128.17, 129.08, 136.44, 137.28.

8. (3-Methyl-benzyl)-pentyl-amine



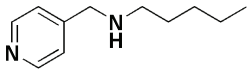
^{1}H NMR (400 MHz, CH_3OD): δ = 0.89-0.92 (m, 3H), 1.31-1.34 (m, 4H), 1.49-1.56 (m, 2H), 2.32 (s, 3H), 2.52-2.56 (m, 2H), 3.68(s, 2H), 7.05-7.07(d, 1H), 7.09-7.11(d, 1H), 7.14(s, 1H), 7.17-7.21(m, 1H).
^{13}C NMR (100 MHz, CH_3OD): δ = 14.56, 21.64, 23.79, 30.20, 30.83, 49.79, 54.58, 128.73, 128.96, 129.48, 130.36, 139.23, 140.58.

9. (2-Methyl-benzyl)-pentyl-amine



^{1}H NMR (400 MHz, CH_3OD): δ = 0.90-0.91 (m, 3H), 1.31-1.33 (m, 4H), 1.55-1.56 (m, 2H), 2.33 (s, 3H), 2.63-2.66 (m, 2H), 3.77(s, 2H), 7.14-7.15(m, 3H), 7.26-7.27(m, 1H).
^{13}C NMR (100 MHz, CH_3OD): δ = 14.60, 19.32, 23.79, 30.27, 30.85, 50.62, 51.85, 127.12, 128.30, 129.75, 131.38, 137.38, 138.75.

10. N-((pyridin-4-yl)methyl)pentan-1-amine



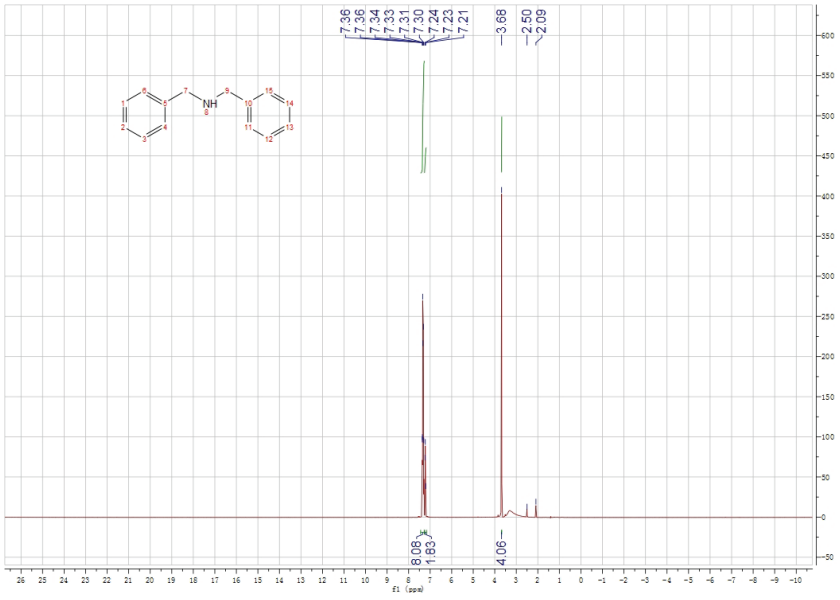
^{1}H NMR (400 MHz, CH_3OD): δ = 0.91 (s, 3H), 1.32-1.34 (m, 4H), 1.53-1.54 (m, 2H), 2.55-2.58 (m, 3H), 3.80 (s, 2H), 7.41(s, 2H), 8.46(s, 1H).
^{13}C NMR (100 MHz, CH_3OD): δ = 14.54, 23.79, 30.35, 30.78, 50.3, 53.30, 125.10, 150.15, 151.73.

All full NMR spectroscopy data :

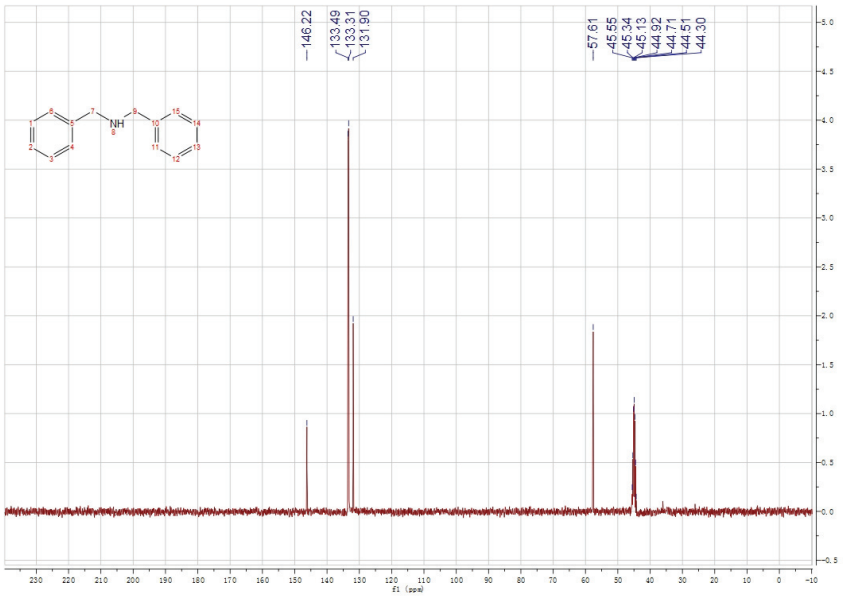
Symmetrical secondary amines:

1. Dibenzylamine

^{1}H NMR

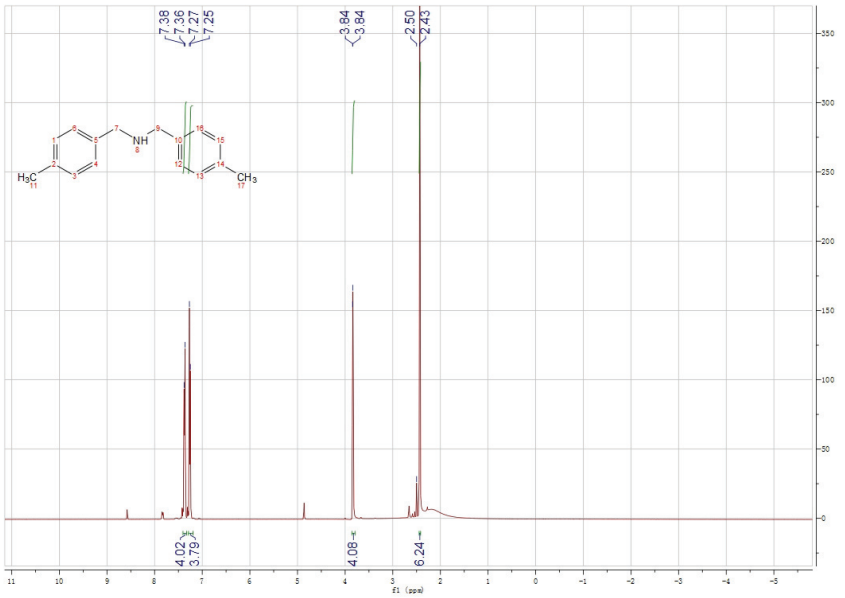


^{13}C NMR

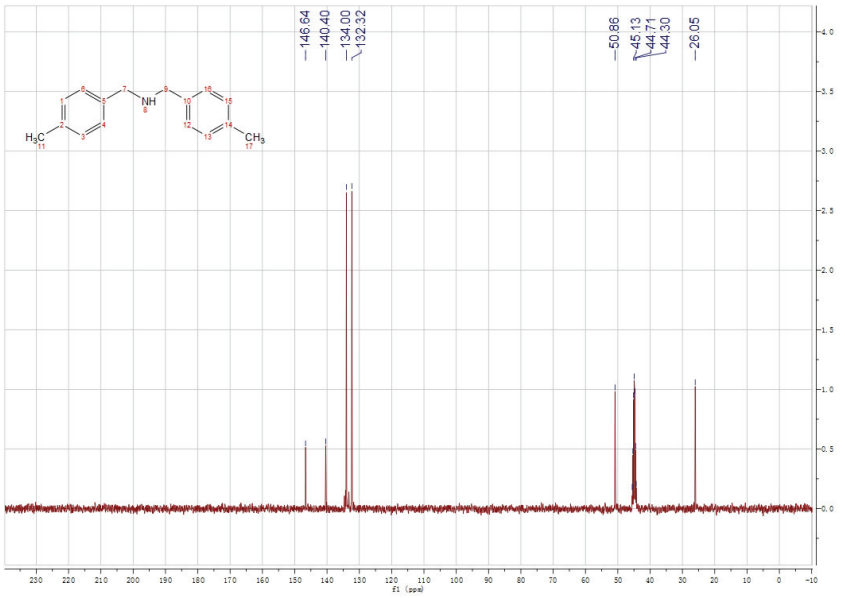


2. Bis(4-methylbenzyl)amine

^{1}H NMR

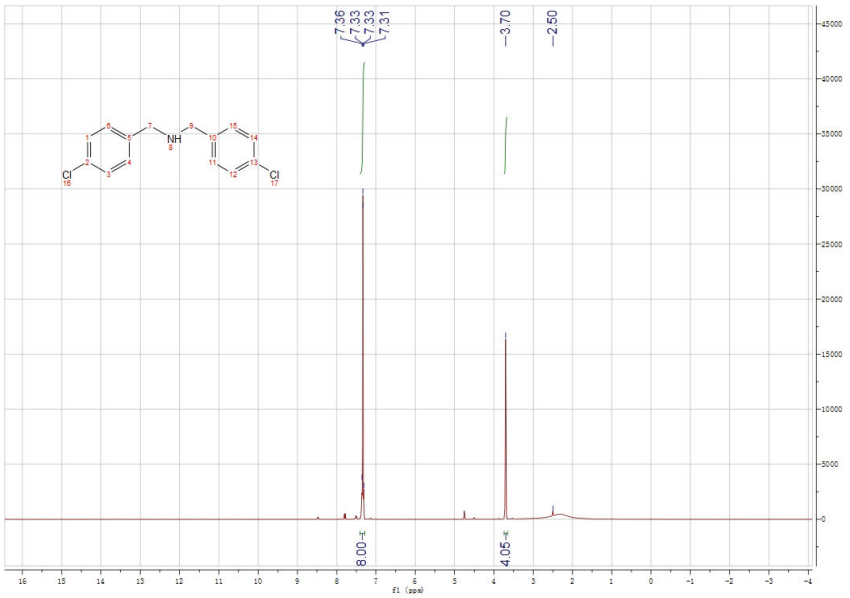


^{13}C NMR

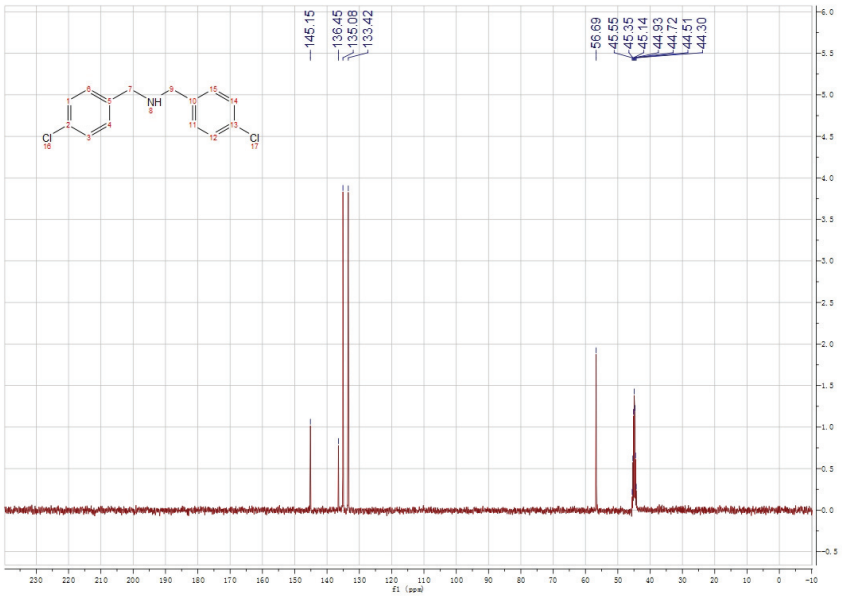


3. Bis(4-chlorobenzyl)amine

^{1}H NMR

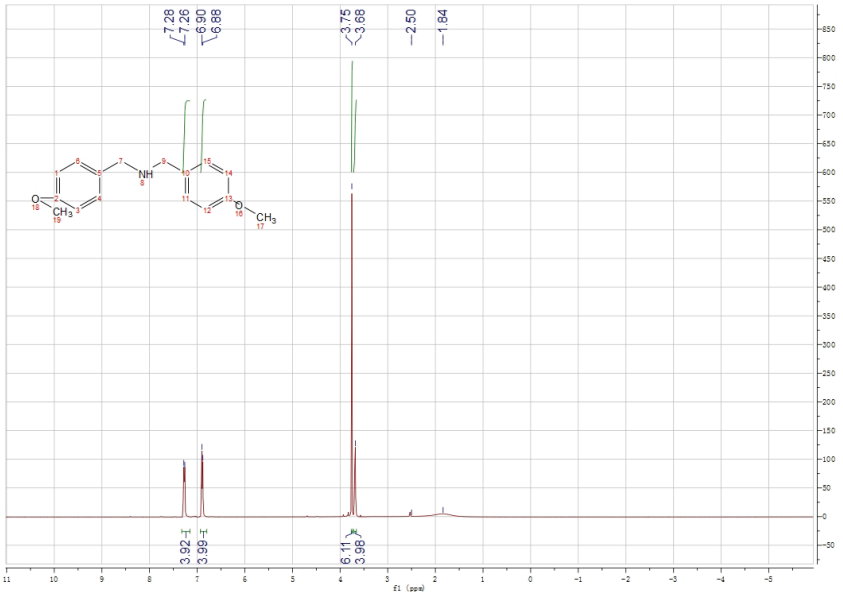


^{13}C NMR

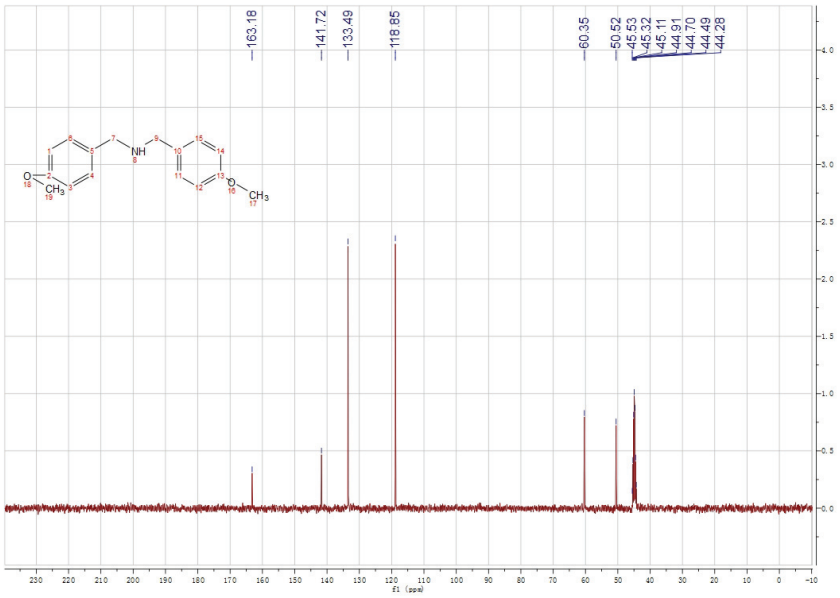


4. Bis(4-methoxybenzyl)amine

^{1}H NMR

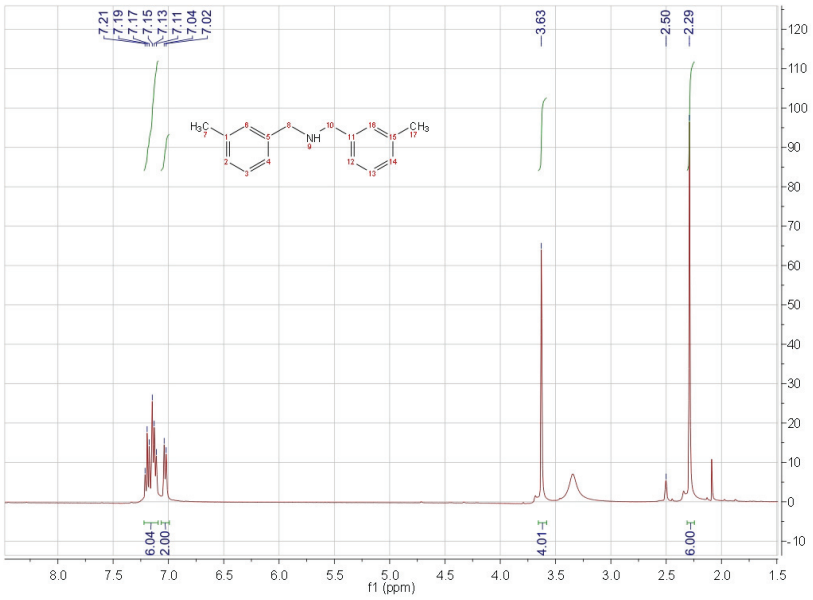


^{13}C NMR

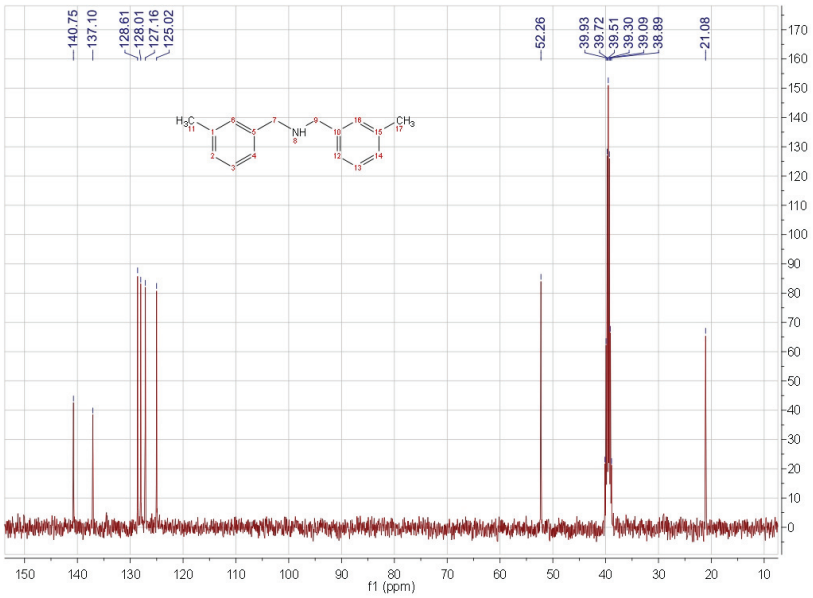


5. Bis(3-methyl)benzylamine

^{1}H NMR

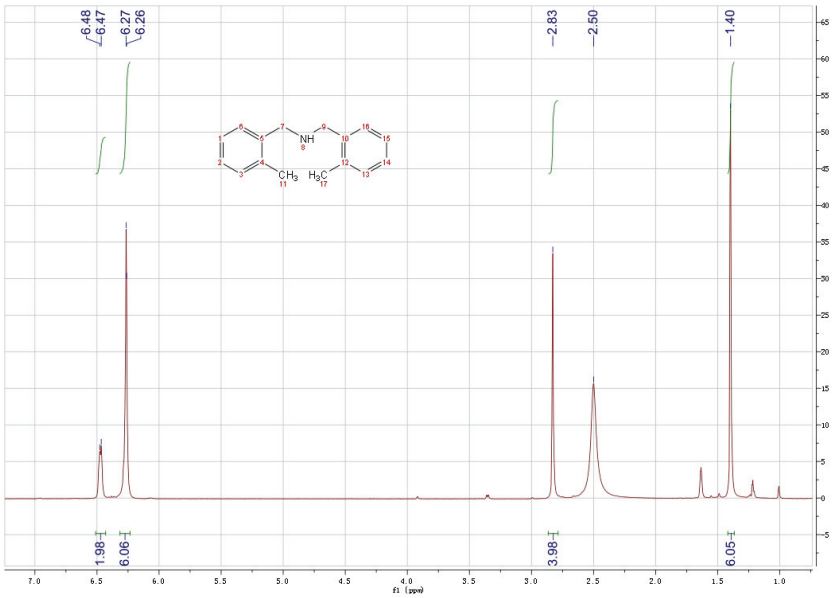


^{13}C NMR

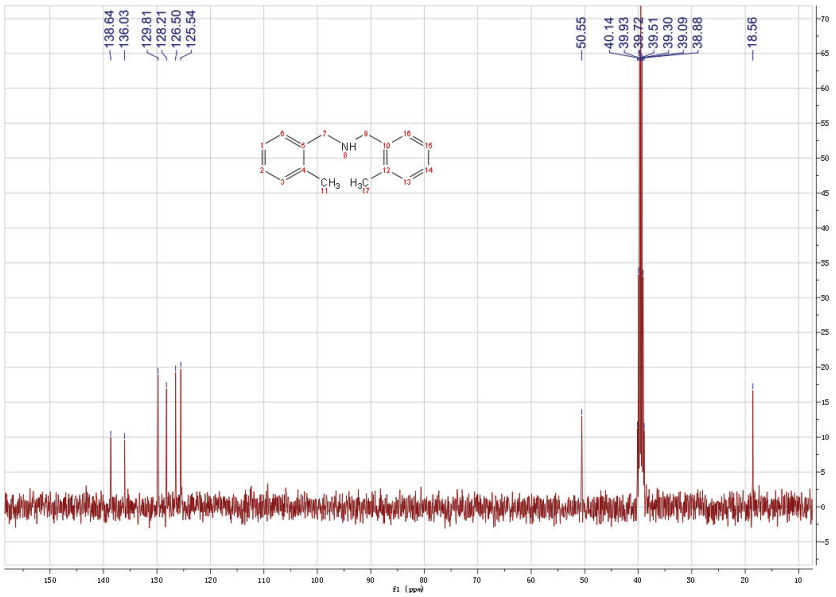


6. Bis(2-methyl)benzylamine

^{1}H NMR



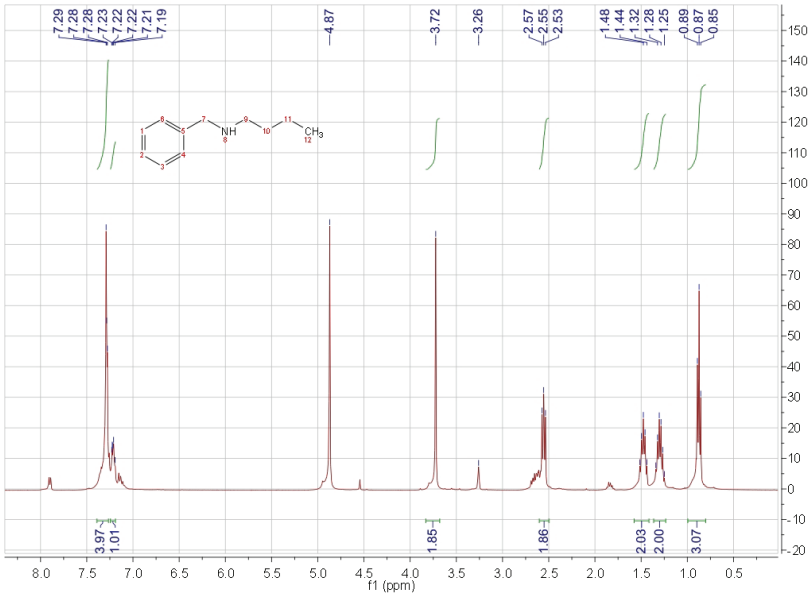
^{13}C NMR



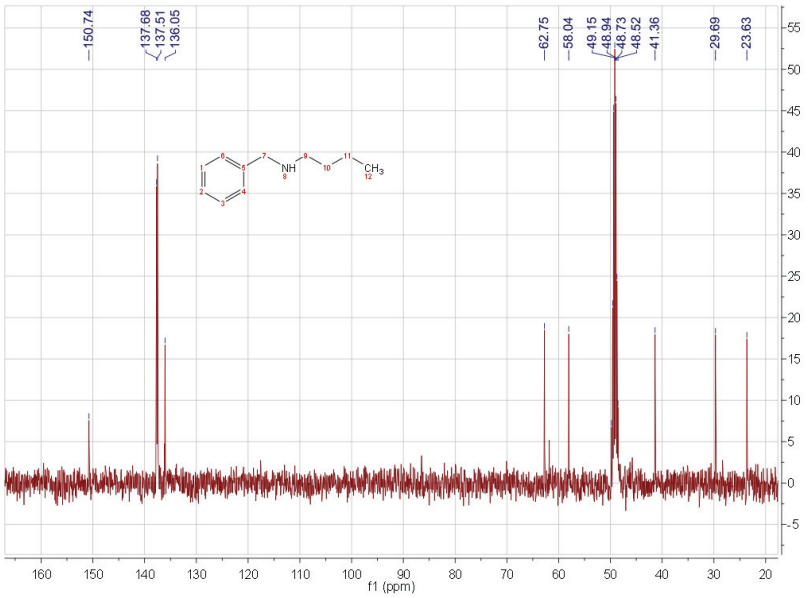
Unsymmetrical secondary amines:

7. N-benzylbutan-1-amine

^{1}H NMR

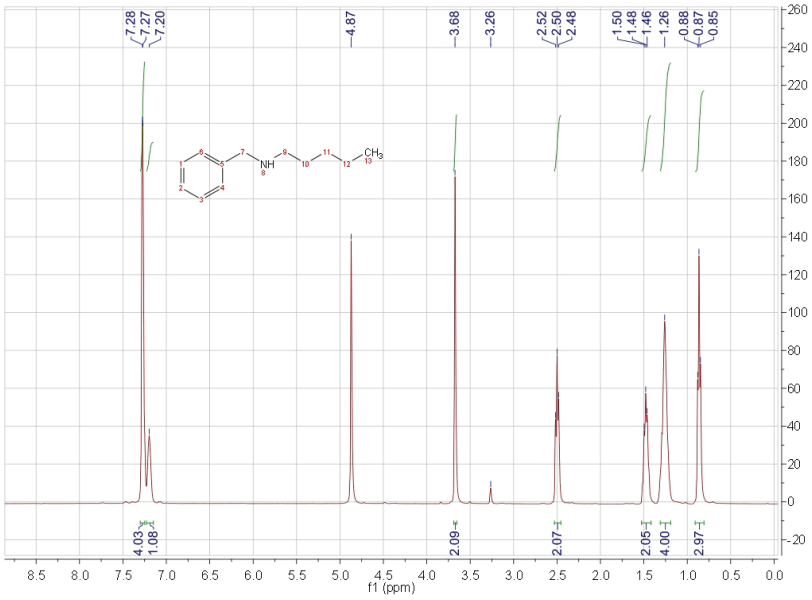


^{13}C NMR

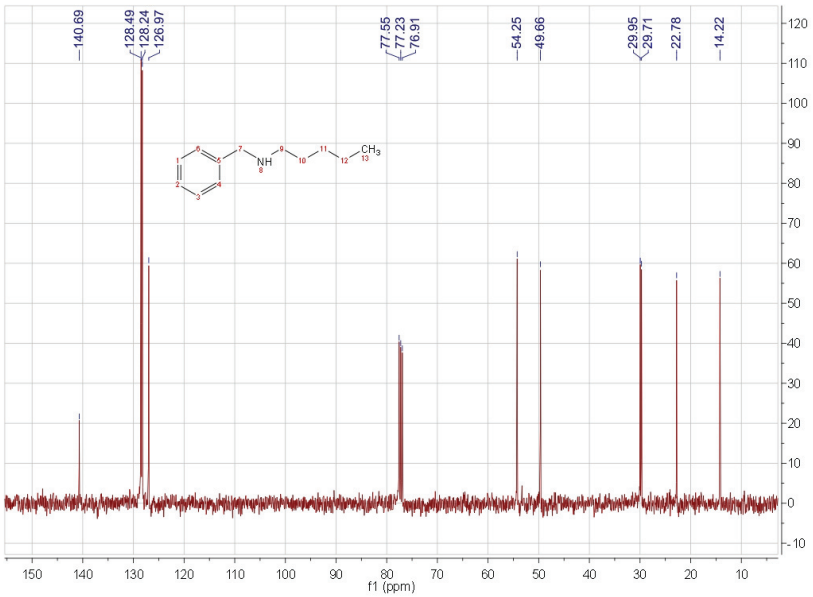


8. N-benzylpentan-1-amine

^{1}H NMR

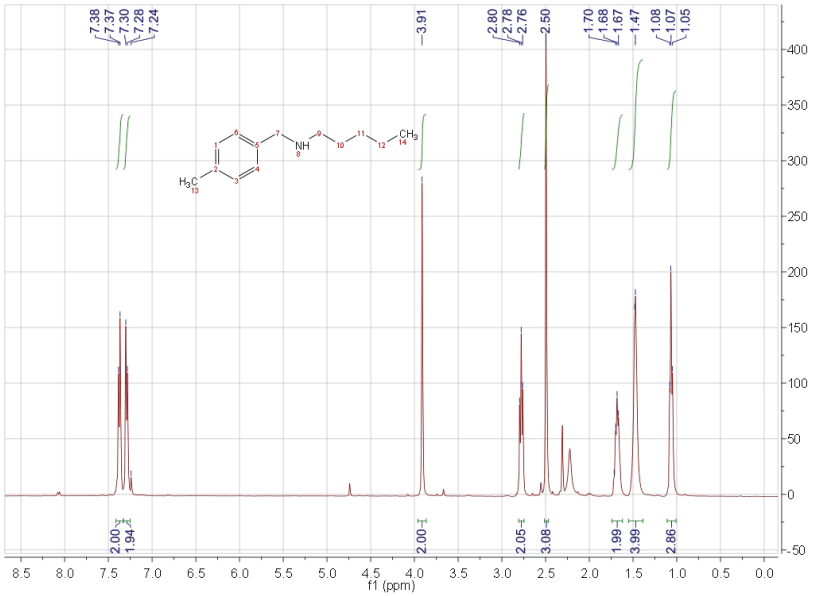


^{13}C NMR

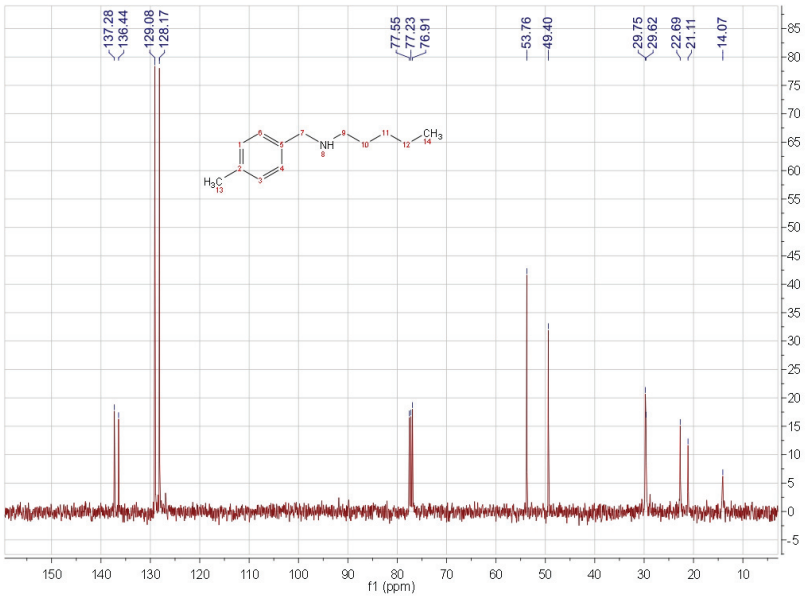


9. (4-Methyl-benzyl)-pentyl-amine

^{1}H NMR

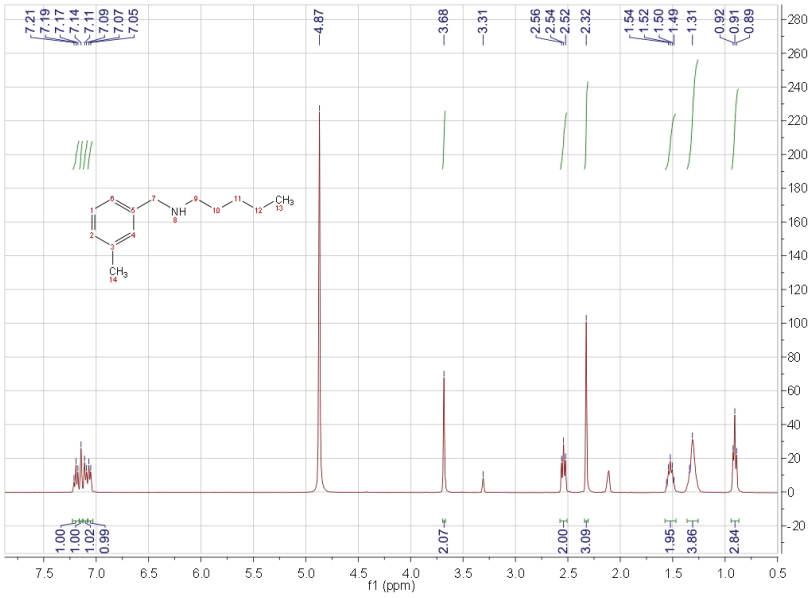


^{13}C NMR

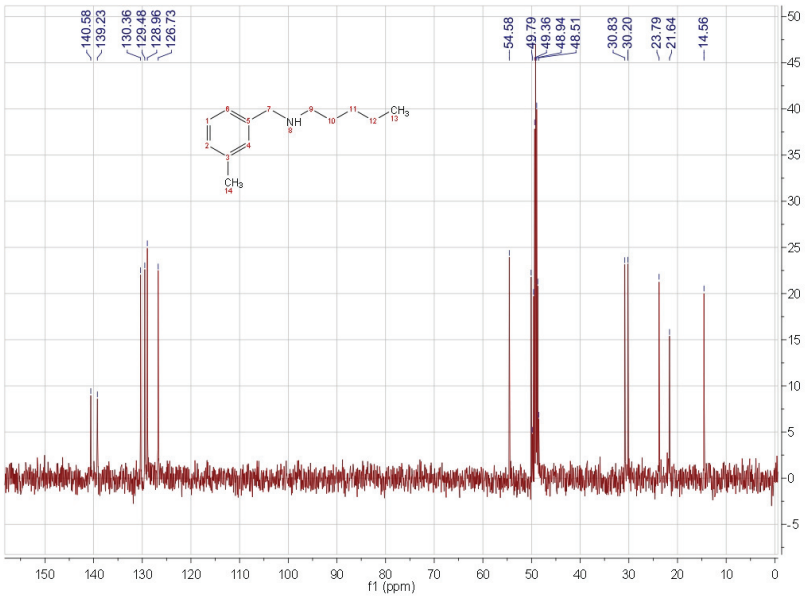


10. (3-Methyl-benzyl)-pentyl-amine

^{1}H NMR

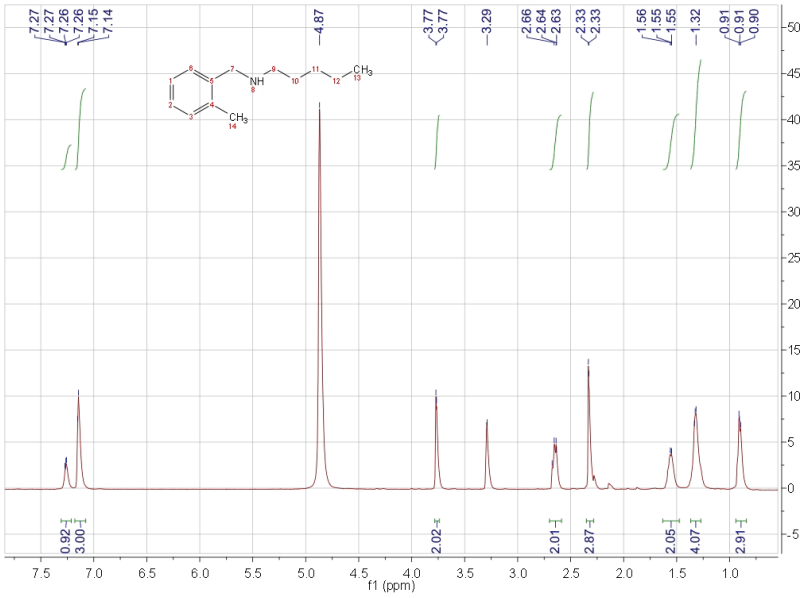


^{13}C NMR

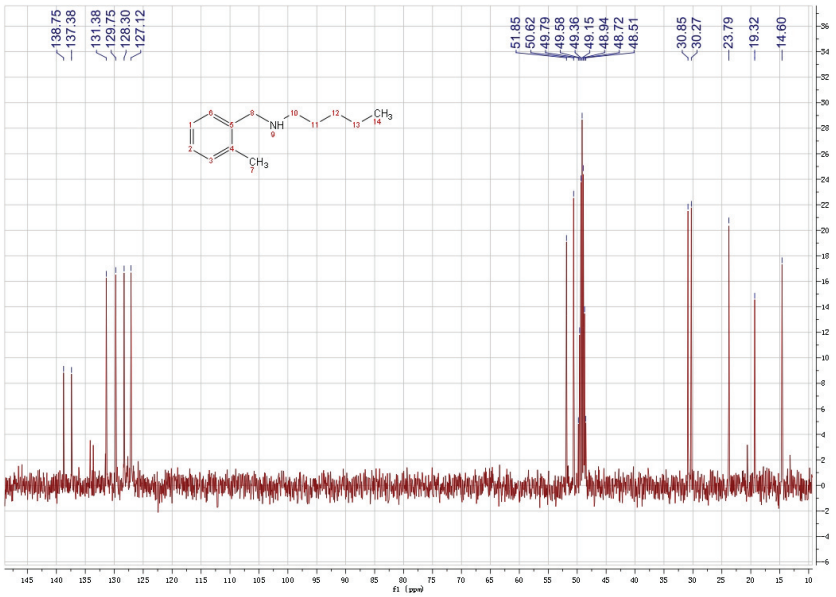


11. (2-Methyl-benzyl)-pentyl-amine

^{1}H NMR

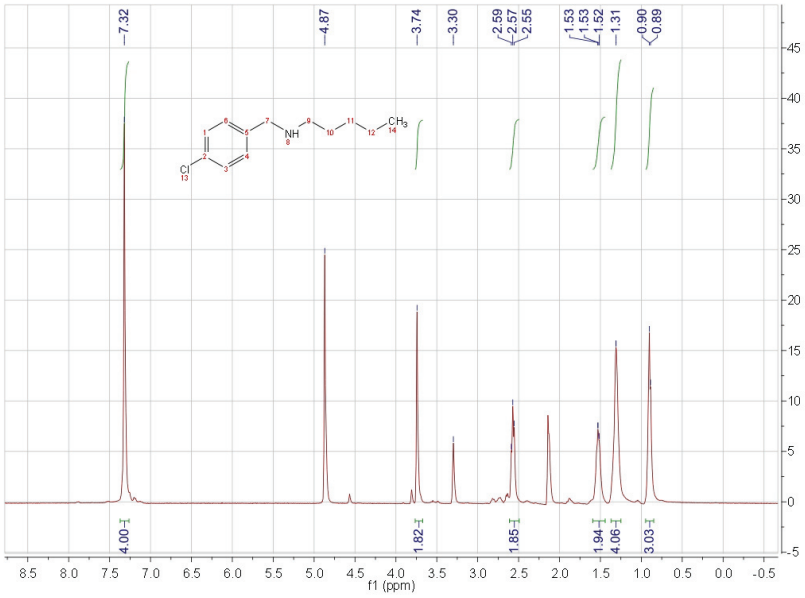


^{13}C NMR

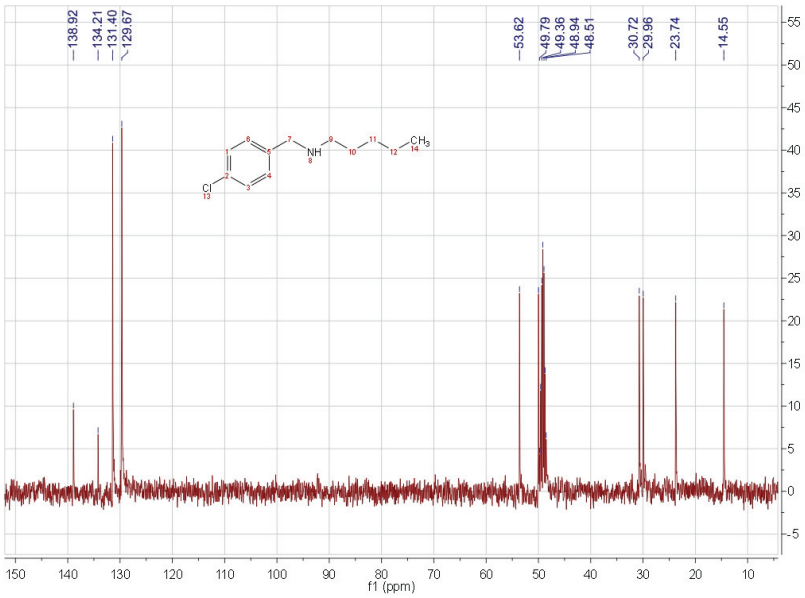


12. N-(4-chlorobenzyl)pentan-1-amine

^{1}H NMR

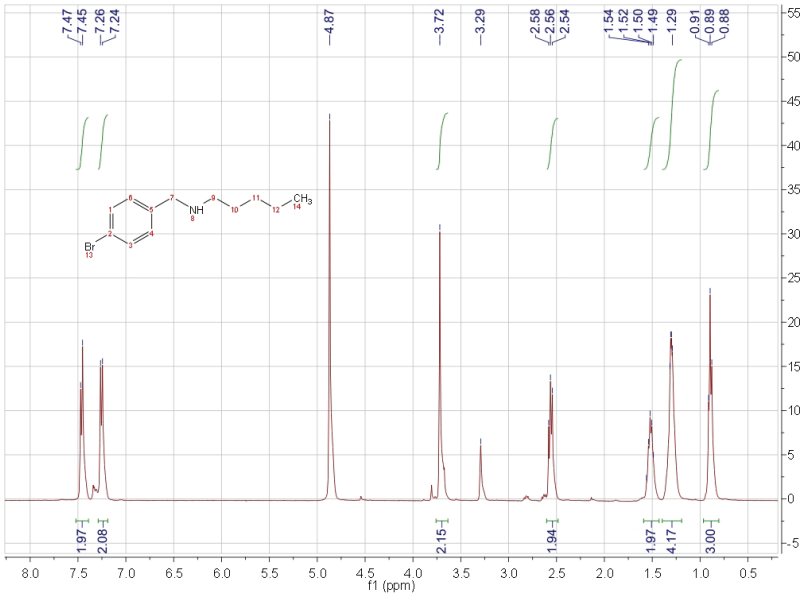


^{13}C NMR

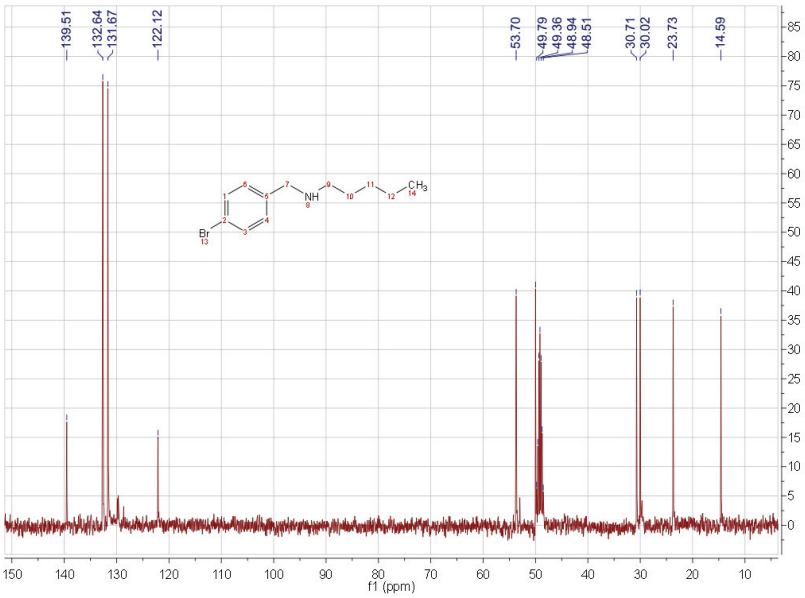


13. N-(4-bromobenzyl)pentan-1-amine

^{1}H NMR

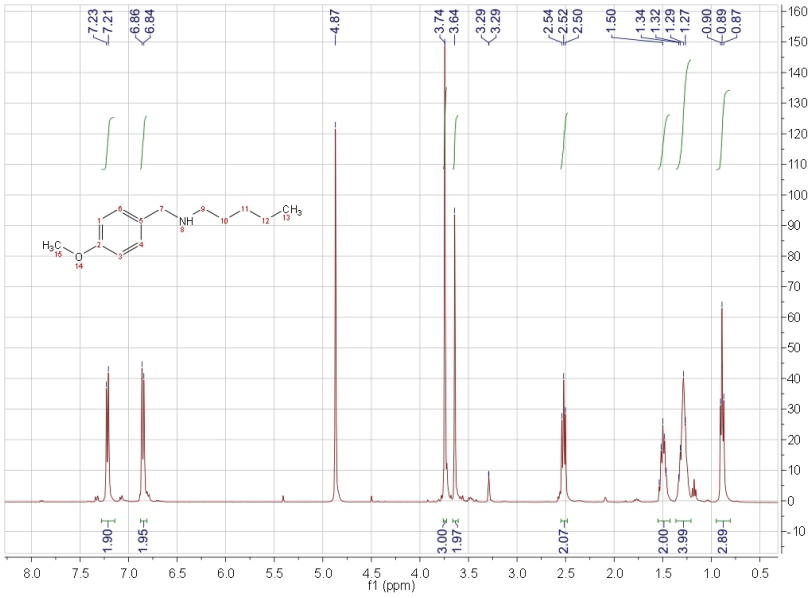


^{13}C NMR

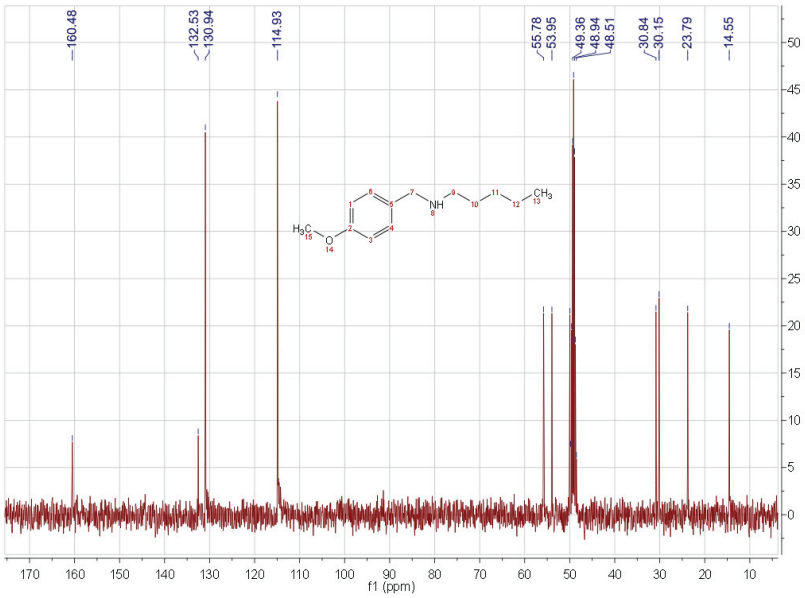


14. N-(4-methoxybenzyl)pentan-1-amine

^{1}H NMR

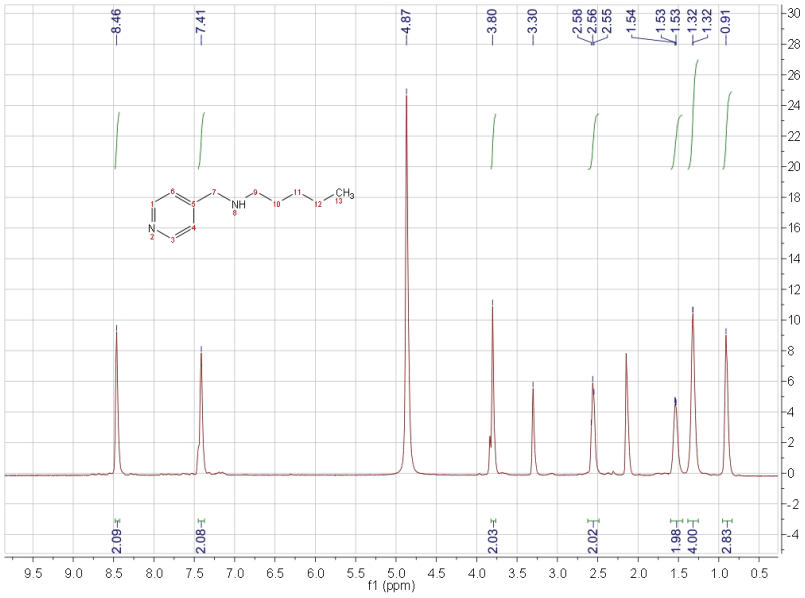


^{13}C NMR

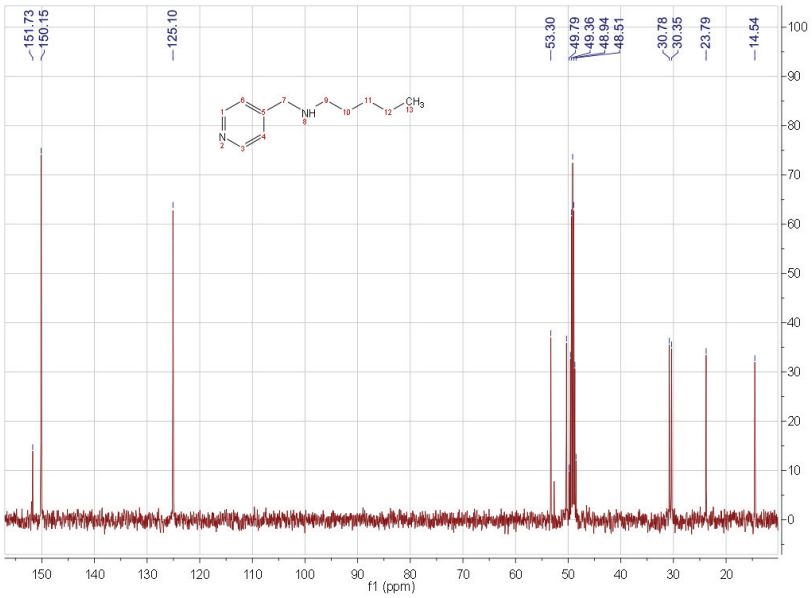


15. N-((pyridin-4-yl)methyl)pentan-1-amine

^{1}H NMR

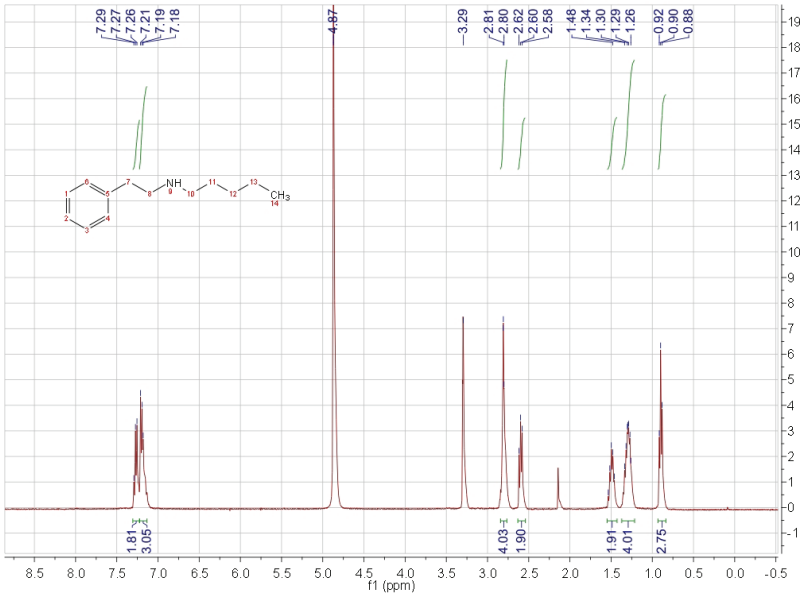


^{13}C NMR

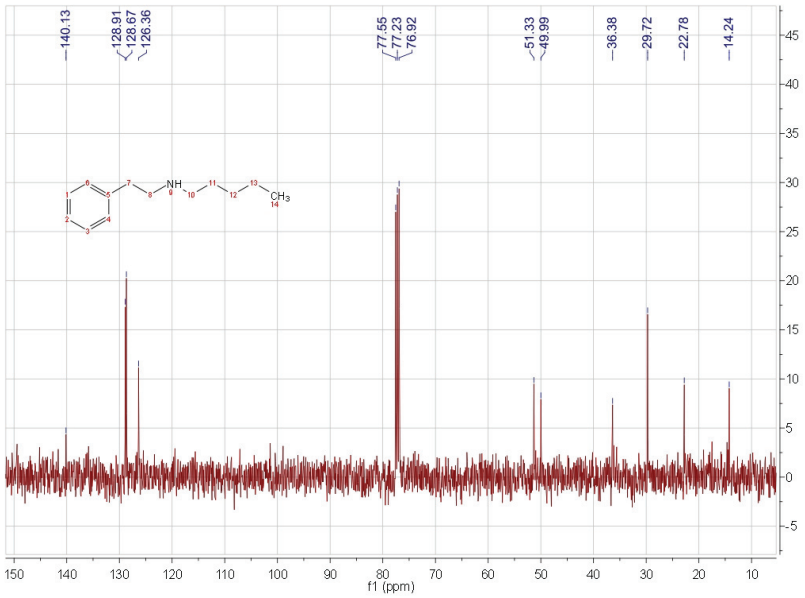


16. N-phenethylpentan-1-amine

^{1}H NMR



^{13}C NMR


140.13
128.91
128.67
126.36
77.55
77.23
76.92
51.33
49.99
36.38
29.72
22.78
14.24
NH
CH3
f1 (ppm)