Supporting Information

Catalyst-free Reductive Amination of Aromatic Aldehydes with Ammonium Formate and Hantzsch Ester

Pan-Pan Zhao,[a] Xin-Feng Zhou,[a] Jian-Jun Dai,*[,a] and Hua-Jian Xu*[,a,b]

[a] *School of Medical Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009*; [b] *Key Laboratory of Advanced Functional Materials and Devices, Anhui Province, P. R. China.*

E-mail: hjxu@hfut.edu.cn

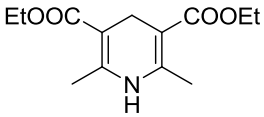
Table of Contents

I. General Information

The chemicals were purchased from commercial suppliers and used without further purification. All reactions were carried out in air. Organic solutions were concentrated under reduced pressure on a rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh). ^{1}H-NMR, ^{13}C-NMR spectra were recorded at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity and coupling constant (Hz). Gas chromatographic (GC) analysis was determined a GC apparatus.

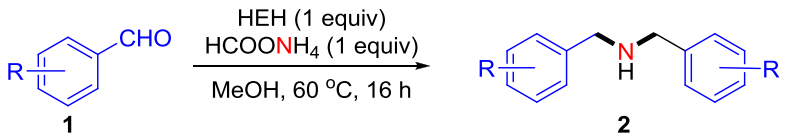
II. Experimental Section

Synthesis of Hantzsch Esters (HEH)[1]



According to general procedure, compound was prepared from formaldehyde (0.1 mol), ethylacetoacetate (0.2 mol), and ammonium acetate (0.1 mol), with PTSA (0.01 mol) as catalyst. They were mixed in methanol (100 mL) and stirred under at room temperature for more than 4 hours. The product was then recrystallized to get pure HEH.

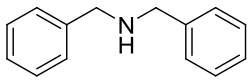
Synthesis of symmetric aromatic secondary amines



Aromatic aldehyde **1** (0.5 mmol) was blended with HEH (127 mg, 0.5mmol) and $HCOONH_4$ (32 mg, 0.5mmol) into a reaction tube, to which 2 mL MeOH was added. The tube was stirred at 60 ^{o}C for 16 hours. Product was separated using flash

chromatography on Silica Gel (200-300 mesh, acetic ether /light petroleum 1:10 or 1:8, and 1% triethylamine). R_f value is 0.3-0.4.

Dibenzylamine (2a)[2]

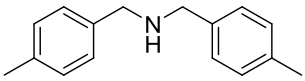


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as colorless oil (46.9 mg, 95% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 8H), 7.25 (t, J = 6.4 Hz, 2H), 3.81 (s, 4H), 1.70 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.26, 128.36, 128.12, 126.91, 53.13.

Bis(4-methylbenzyl)amine (2b)[3]

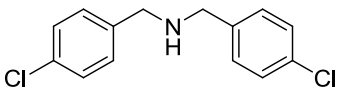


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as light yellow oil (51.3 mg, 91% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, J = 7.8 Hz, 4H), 7.13 (d, J = 7.8 Hz, 4H), 3.75 (s, 4H), 2.33 (s, 6H), 1.70 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.22, 136.40, 129.00, 128.06, 52.74, 21.06.

Bis(4-chlorobenzyl)amine (2c)[2]

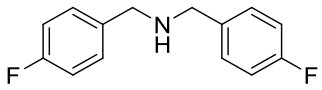


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as light yellow oil (55.2 mg, 83% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, J = 8.5 Hz, 4H), 7.26 (d, J = 8.4 Hz, 4H), 3.74 (s, 4H), 1.60 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.55, 132.65, 129.41, 128.49, 52.28.

Bis(4-fluorobenzyl)amine (2d)[4]

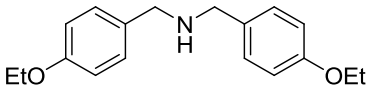


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as colorless oil (45.5 mg, 78% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 5.7 Hz, 2H), 7.28 (d, *J* = 5.6 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 4H), 3.75 (s, 4H), 1.63 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.90 (d, *J* = 244.6 Hz), 135.83 (d, *J* = 3.1 Hz), 129.61 (d, *J* = 7.9 Hz), 115.15 (d, *J* = 21.3 Hz), 52.31.

Bis(4-ethoxybenzyl)amine (2e)



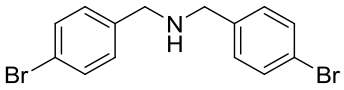
The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (57.1 mg, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 4H), 6.85 (d, *J*= 8.4 Hz, 4H), 4.02 (q, *J*= 7.0 Hz, 4H), 3.72 (s, 4H), 1.90 (s, 1H), 1.41 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.90, 132.22, 129.27, 114.29, 63.36, 52.39, 14.83.

HRMS calcd for $C_{18}H_{23}NO_2$ (M+): 285.1729; found: 285.1732.

Bis(4-bromobenzyl)amine (2f)[2]

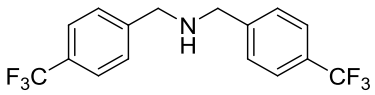


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as yellow oil (66.6 mg, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 4H), 3.72 (s, 4H), 1.64 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.05, 131.45, 129.79, 120.75, 52.31.

Bis(4-(trifluoromethyl)benzyl)amine (2g)[5]

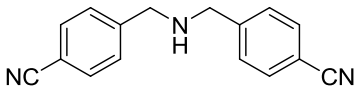


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as yellow oil (60.8 mg, 73% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 4H), 7.46 (d, *J* = 7.9 Hz, 4H), 3.86 (s, 4H), 1.76 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.01, 129.41 (q, *J* = 32.3 Hz), 128.30, 125.36 (q, *J* = 3.8 Hz), 124.22 (q, *J* = 271.8 Hz), 52.54.

4,4'-Azanediylbis(methylene)dibenzonitrile (2h)[6]

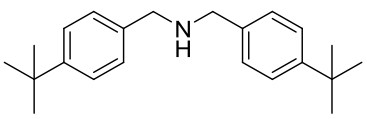


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow solid (46.4 mg, 75% yield). Mp: 101 – 104 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 4H), 7.48 (d, *J* = 8.3 Hz, 4H), 3.87 (s, 4H), 1.62 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.37, 132.21, 128.56, 118.80, 110.89, 52.58.

Bis(4-tert-butylbenzyl)amine (2i)[7]



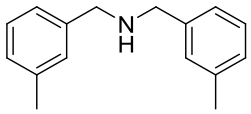
The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as light yellow oil

(34.8 mg, 45% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 4H), 3.80 (s, 4H), 1.85 (s, 1H), 1.33 (s, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.73, 137.21, 127.81, 125.22, 52.78, 34.41, 31.36.

Bis(3-methylbenzyl)amine (2j)[4]

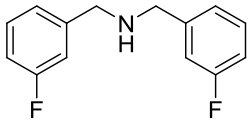


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as light yellow oil (48.4 mg, 86% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (s, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.3 Hz, 2H), 3.77 (s, 4H), 2.35 (s, 6H), 1.79 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.17, 137.95, 128.89, 128.24, 127.63, 125.15, 53.19, 21.37.

Bis(3-fluorobenzyl)amine (2k)



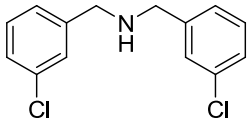
The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as light yellow oil (42.0 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 13.9, 7.8 Hz, 2H), 7.09 (dd, *J* = 14.4, 8.7 Hz, 4H), 6.94 (td, *J* = 8.5, 2.4 Hz, 2H), 3.79 (s, 4H), 1.65 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.03 (d, *J* = 245.8 Hz), 142.87 (d, *J* = 6.9 Hz), 129.81 (d, *J* = 8.1 Hz), 123.54 (d, *J* = 2.8 Hz), 114.83 (d, *J* = 21.3 Hz), 113.84 (d, *J* = 21.2 Hz), 52.53 (d, *J* = 1.5 Hz).

HRMS calcd for $C_{14}H_{13}F_2N$ (M+): 233.1016; found: 233.1021.

Bis(3-chlorobenzyl)amine (2l)[7]

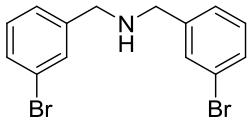


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (54.6 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.28 – 7.17 (m, 6H), 3.76 (s, 4H), 1.62 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.16, 134.25, 129.63, 128.13, 127.15, 126.16, 52.50.

Bis(3-bromobenzyl)amine (2m)[8]

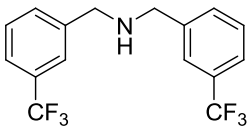


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (66.6 mg, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 2H), 3.76 (s, 4H), 1.64 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.49, 131.12, 130.14, 130.00, 126.70, 122.59, 52.51.

Bis(3-(trifluoromethyl)benzyl)amine (2n)[9]

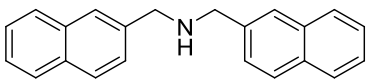


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as yellow oil (58.3 mg, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.55 – 7.50 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.87 (s, 4H), 1.73 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.95, 131.44, 130.75 (q, *J* = 32.2 Hz), 128.86, 124.80 (q, *J* = 3.7 Hz), 124.16 (q, *J* = 272.3 Hz), 123.94 (q, *J* = 3.8 Hz), 52.68.

Bis(naphthalen-2-ylmethyl)amine (2o)[10]

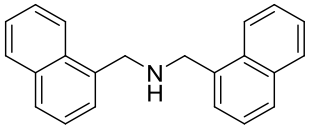


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as white solid (54.3 mg, 73% yield). Mp: 83 – 85 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 8H), 7.50 – 7.41 (m, 6H), 3.98 (s, 4H), 1.77 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.71, 133.41, 132.64, 128.06, 127.66, 127.62, 126.57, 126.50, 125.96, 125.52, 53.19.

Bis(naphthalen-1-ylmethyl)amine (2p)[10]

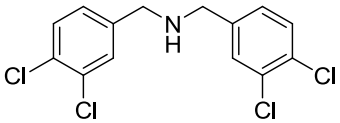


The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as white solid (52.0 mg, 70% yield). Mp: 62 – 64 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.48 – 7.40 (m, 6H), 4.33 (s, 4H), 1.91 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.70, 133.86, 131.83, 128.61, 127.81, 126.25, 125.96, 125.58, 125.30, 123.82, 51.38.

Bis(3,4-dichlorobenzyl)amine (2q)[11]



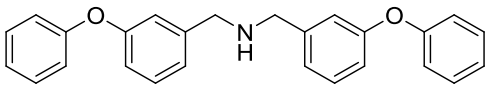
The resulting mixture was purified by flash chromatography (acetic ether /light

petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (62.8 mg, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.4 Hz, 2H), 7.40 (s, 1H), 7.38 (s, 1H), 7.17 (d, *J* = 1.5 Hz, 1H), 7.16 (d, *J* = 1.5 Hz, 1H), 3.74 (s, 4H), 1.61 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.26, 132.48, 130.97, 130.35, 129.94, 127.34, 51.89.

Bis(3-phenoxybenzyl)amine (2r)



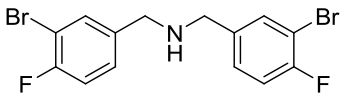
The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (78.2 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.9 Hz, 4H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.10 – 7.05 (m, 4H), 7.00 (d, *J* = 7.5 Hz, 6H), 6.88 (dd, *J* = 8.1, 1.8 Hz, 2H), 3.76 (s, 4H), 1.63 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.41, 157.27, 142.40, 129.70, 129.62, 123.17, 122.93, 118.87, 118.51, 117.38, 52.78.

HRMS calcd for $C_{26}H_{23}NO_2$ (M+): 381.1729; found: 381.1732.

Bis(3-bromo-4-fluorobenzyl)amine (2s)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (66.5 mg, 68% yield).

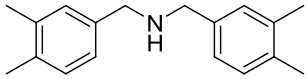
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 3.74 (s, 4H), 1.61 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.19 (d, *J* = 246.6 Hz), 137.43 (d, *J* = 3.6 Hz), 133.01, 128.49 (d, *J* = 7.2 Hz), 116.29 (d, *J* = 22.3 Hz), 108.94 (d, *J* = 20.9 Hz),

51.86.

HRMS calcd for $C_{14}H_{11}Br_2F_2N$ (M+): 388.9226; found: 388.9226.

Bis(3,4-dimethylbenzyl)amine (2t)



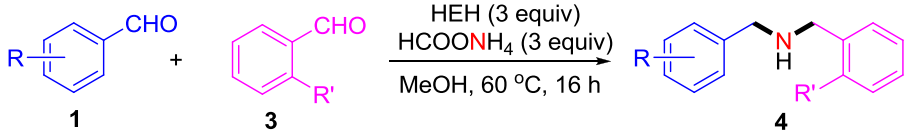
The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:10 and 1% triethylamine) to give the desired product as yellow oil (41.2 mg, 65% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.04 (m, 6H), 3.74 (s, 4H), 2.25 (s, 6H), 2.24 (s, 6H), 1.66 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.63, 136.50, 135.09, 129.57, 129.53, 125.57, 52.84, 19.73, 19.39.

HRMS calcd for $C_{18}H_{23}N$ (M+): 253.1830; found: 253.1827.

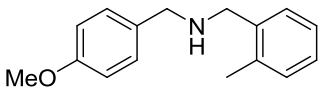
Synthesis of asymmetric aromatic secondary amines



1 3 4

Meta-substituted or para-substituted benzaldehyde **1** (0.25 mmol) and ortho-substituted benzaldehyde **3** (0.5 mmol) were mixed with HEH (191 mg, 0.75 mmol) and $HCOONH_4$ (48 mg, 0.75 mmol) into a reaction tube, to which 2 mL MeOH was added. The reaction carried out at 60 °C for at least 16 hours. Product was separated using forced-flow chromatography on Silica Gel (200-300 mesh, acetic ether /light petroleum 1:8, and 1% triethylamine). R_f value is 0.25-0.4.

N-(4-methoxybenzyl)-1-o-tolylmethanamine (4a)[12]



The resulting mixture was purified by flash chromatography (acetic ether /light

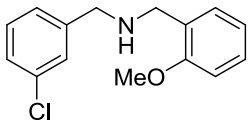
petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (39.2 mg, 65% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.12 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 2H), 3.76 (s, 2H), 2.32 (s, 3H), 1.56 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.58, 138.25, 136.37, 132.52, 130.22, 129.28, 128.36, 126.90, 125.83, 113.72, 55.25, 53.00, 50.83, 18.93.

The yield of self-coupling product of 4-methoxybenzaldehyde was 12% by GC method.

N-(3-chlorobenzyl)-1-(2-methoxyphenyl)methanamine (4b)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (43.2 mg, 66% yield).

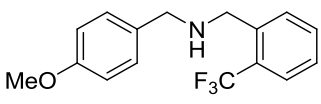
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.28 – 7.18 (m, 5H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 2H), 3.75 (s, 2H), 1.99 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.72, 142.62, 134.20, 129.96, 129.50, 128.36, 128.22, 127.99, 126.95, 126.25, 120.43, 110.32, 55.23, 52.35, 48.63.

HRMS calcd for $C_{15}H_{16}ClNO$ (M+): 261.0920; found: 261.0926.

The yield of self-coupling product of 3-chlorobenzaldehyde was 12% by GC method.

N-(4-methoxybenzyl)-1-(2-(trifluoromethyl)phenyl)methanamine (4c)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (39.1 mg, 53% yield).

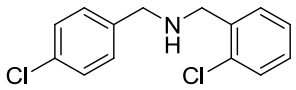
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.97 (s, 2H), 3.80 (s, 3H), 3.77 (s, 2H), 1.67 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.67, 138.90, 132.15, 131.84, 130.33, 129.31, 128.24 (q, *J*= 30.0 Hz), 126.84, 125.83 (q, *J* = 5.8 Hz), 125.44, 123.62, 113.78, 55.25, 52.89, 49.26.

HRMS calcd for $C_{16}H_{16}F_3NO$ (M+): 295.1184; found: 295.1179.

The yield of self-coupling product of 4-methoxybenzaldehyde was 16% by GC method.

N-(2-chlorobenzyl)-1-(4-chlorophenyl)methanamine (4d)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (41.3 mg, 62% yield).

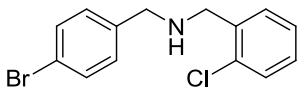
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 11.1, 7.6 Hz, 2H), 7.29 (s, 4H), 7.25 – 7.19 (m, 2H), 3.88 (s, 2H), 3.77 (s, 2H), 1.80 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.61, 137.40, 133.81, 132.70, 130.21, 129.56, 129.47, 128.50, 128.39, 126.79, 52.30, 50.65.

HRMS calcd for $C_{14}H_{13}Cl_2N$ (M+): 265.0425; found: 265.0428.

The yield of self-coupling product of 4-chlorobenzaldehyde was 14% by GC method.

N-(4-bromobenzyl)-1-(2-chlorophenyl)methanamine (4e)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (42.7 mg, 55% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.25 –

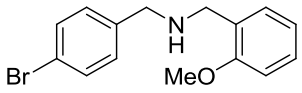
7.19 (m, 4H), 3.88 (s, 2H), 3.75 (s, 2H), 1.79 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.14, 137.39, 133.80, 131.45, 130.20, 129.84, 129.56, 128.39, 126.78, 120.75, 52.33, 50.64.

HRMS calcd for $C_{14}H_{13}BrClN$ (M+): 308.9920; found: 308.9912.

The isolated yield of bis(4-bromobenzyl)amine was 17%.

N-(4-bromobenzyl)-1-(2-methoxyphenyl)methanamine (4f)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (39.0 mg, 51% yield).

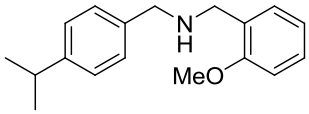
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.21 (m, 3H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 2H), 3.73 (s, 2H), 1.90 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.66, 139.48, 131.33, 129.92, 129.88, 128.32, 127.98, 120.52, 120.37, 110.23, 55.21, 52.22, 48.65.

HRMS calcd for $C_{15}H_{16}BrNO$ (M+): 305.0415; found: 305.0418.

The isolated yield of bis(4-bromobenzyl)amine was 19%.

N-(4-isopropylbenzyl)-1-(2-methoxyphenyl)methanamine (4g)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (38.4 mg, 57% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 2H), 3.82 (s, 3H), 3.75 (s, 2H), 2.93 – 2.85 (m, 1H), 2.00 (s, 1H), 1.24 (d, *J* = 6.9 Hz, 6H).

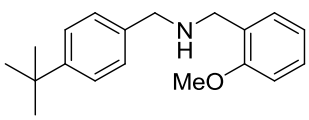
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.70, 147.45, 137.73, 129.92, 128.18, 128.16,

126.33, 120.36, 110.22, 55.31, 52.75, 48.74, 33.77, 24.02.

HRMS calcd for $C_{18}H_{23}NO$ (M+): 269.1780; found: 269.1785.

The yield of self-coupling product of 4-isopropylbenzaldehyde was less than 10% by GC method.

N-(4-tert-butylbenzyl)-1-(2-methoxyphenyl)methanamine (4h)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (33.3 mg, 47% yield).

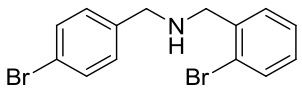
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.22 (m, 4H), 6.92 (t, *J* = 7.0 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 2H), 3.82 (s, 3H), 3.75 (s, 2H), 2.00 (s, 1H), 1.31 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.69, 149.69, 137.39, 129.90, 128.17, 127.87, 125.18, 120.35, 110.21, 55.20, 52.66, 48.79, 34.42, 31.38.

HRMS calcd for $C_{19}H_{25}NO$ (M+): 283.1936; found: 283.1943.

The yield of self-coupling product of 4-tert-butylbenzaldehyde was less than 10% by GC method.

N-(2-bromobenzyl)-1-(4-bromophenyl)methanamine (4i)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (55.9 mg, 63% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 6.9 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 2H), 3.75 (s, 2H), 1.81 (s, 1H).

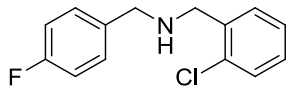
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.01, 138.84, 132.82, 131.42, 130.35, 129.86,

128.69, 127.40, 123.97, 120.73, 53.00, 52.22.

HRMS calcd for $C_{14}H_{13}Br_2N$ (M+): 352.9415; found: 352.9415.

The yield of self-coupling product of 4-tert-butylbenzaldehyde was 12% by GC method.

N-(2-chlorobenzyl)-1-(4-fluorophenyl)methanamine (4j)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (28.1 mg, 45% yield).

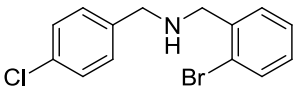
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 5.7 Hz, 1H), 7.31 (d, *J* = 5.6 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 3.89 (s, 2H), 3.77 (s, 2H), 1.79 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.93 (d, *J* = 244.7 Hz), 137.37, 135.72 (d, *J* = 3.0 Hz), 133.77, 130.22, 129.67 (d, *J* = 7.9 Hz), 129.54, 128.38, 126.78, 115.14 (d, *J* = 21.3 Hz), 52.27, 50.63.

HRMS calcd for $C_{14}H_{13}ClFN$ (M+): 249.0721; found: 249.0719.

The isolated yield of bis(4-fluorobenzyl)amine was 20%.

N-(2-bromobenzyl)-1-(4-chlorophenyl)methanamine (4k)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (46.6 mg, 60% yield).

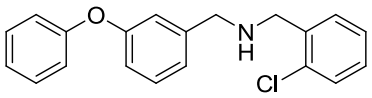
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.27 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 2H), 3.77 (s, 2H), 1.85 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.85, 138.47, 132.84, 132.67, 130.37, 129.51, 128.70, 128.48, 127.41, 124.00, 53.00, 52.19.

HRMS calcd for $C_{14}H_{13}BrClN$ (M+): 308.9920; found: 308.9912.

The yield of self-coupling product of 4-chlorobenzaldehyde was 15% by GC method.

N-(2-chlorobenzyl)-1-(3-phenoxyphenyl)methanamine (4l)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (46.9 mg, 58% yield).

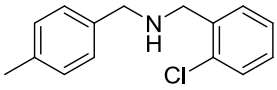
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 7.23 – 7.17 (m, 2H), 7.09 (dd, *J* = 7.3, 4.2 Hz, 2H), 7.05 – 6.98 (m, 3H), 6.90 (d, *J* = 6.3 Hz, 1H), 3.88 (s, 2H), 3.78 (s, 2H), 1.78 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.35, 157.21, 142.22, 137.40, 133.73, 130.20, 129.69, 129.64, 129.48, 128.32, 126.75, 123.14, 122.94, 118.85, 118.51, 117.42, 52.71, 50.60.

HRMS calcd for $C_{20}H_{18}ClNO$ (M+): 323.1077; found: 323.1080.

The isolated yield of bis(3-phenoxybenzyl)amine was 16%.

N-(2-chlorobenzyl)-1-p-tolylmethanamine (4m)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (37.5 mg, 61% yield).

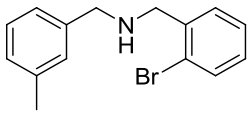
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.2 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 6.8 Hz, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 6.7 Hz, 2H), 3.90 (s, 2H), 3.77 (s, 2H), 2.34 (s, 3H), 1.84 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.43, 136.84, 136.60, 133.75, 130.21, 129.47, 129.07, 128.29, 128.13, 126.74, 52.73, 50.60, 21.09.

HRMS calcd for $C_{15}H_{16}ClN$ (M+): 245.0971; found: 245.0977.

The yield of self-coupling product of 4-methylbenzaldehyde was 14% by GC method.

N-(2-bromobenzyl)-1-m-tolylmethanamine (4n)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (37.0 mg, 51% yield).

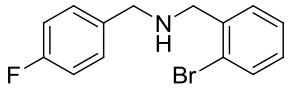
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.33 (td, *J* = 7.6, 1.1 Hz, 1H), 7.24 – 7.11 (m, 5H), 4.26 (s, 2H), 4.21 (s, 2H), 2.37 (s, 3H), 0.88 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.89, 139.07, 138.03, 132.79, 130.39, 128.95, 128.60, 128.29, 127.75, 127.38, 125.22, 124.01, 53.17, 53.01, 21.39.

HRMS calcd for $C_{15}H_{16}BrN$ (M+): 289.0466; found: 289.0468.

The isolated yield of bis(3-methylbenzyl)amine was 19%.

N-(2-bromobenzyl)-1-(4-fluorophenyl)methanamine (4o)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (44.1 mg, 60% yield).

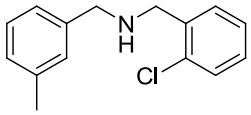
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.14 (t, *J* = 6.8 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 3.87 (s, 2H), 3.77 (s, 2H), 1.82 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.90 (d, *J* = 244.6 Hz), 138.91, 135.70, 132.82, 130.37, 129.70 (d, *J* = 7.9 Hz), 128.67, 127.40, 123.98, 115.14 (d, *J* = 21.3 Hz), 53.03, 52.21.

HRMS calcd for $C_{14}H_{13}BrFN$ (M+): 293.0215; found: 293.0213.

The yield of self-coupling product of 4-fluorobenzaldehyde was 15% by GC method.

N-(2-chlorobenzyl)-1-m-tolylmethanamine (4p)



The resulting mixture was purified by flash chromatography (acetic ether /light petroleum 1:8 and 1% triethylamine) to give the desired product as yellow oil (35.0 mg, 57% yield).

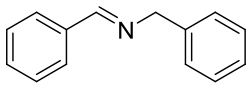
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.18 (s, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 3.91 (s, 2H), 3.77 (s, 2H), 2.35 (s, 3H), 1.80 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.94, 138.00, 137.52, 133.75, 130.20, 129.48, 128.90, 128.28, 128.27, 127.72, 126.73, 125.17, 53.06, 50.77, 21.37.

HRMS calcd for $C_{15}H_{16}ClN$ (M+): 245.0971; found: 245.0977.

The yield of self-coupling product of 3-methylbenzaldehyde was 16% by GC method.

Dibenzylimine[13]



Benzaldehyde (1.02 mL, 10 mmol) and benzylamine (1.09 mL, 10 mmol) were mixed together in toluene (50 mL) and refluxed at 120 ^{o}C for 24 hours. The toluene was evaporated in reduced pressure. 1.9 g of the dibenzylimine was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.81 – 7.73 (m, 2H), 7.40 – 7.18 (m, 8H), 4.78 (s, 2H).

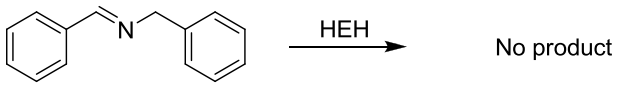
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.80, 139.19, 136.04, 130.61, 128.46, 128.36, 128.15, 127.84, 126.84, 64.88.

Large-Scale Synthesis of Dibenzylamine

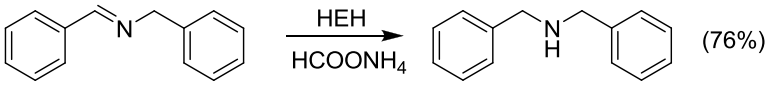
Benzaldehyde (20 mmol, 2.08 g) was blended with HEH (20 mmol, 5.08 g) and $HCOONH_4$ (20 mmol, 1.28 g) into a reaction flask, to which 80 mL MeOH was added. The flask was stirred at 60 ^{o}C for 16 hours. Product was separated using forced-flow

chromatography on Silica Gel (200-300 mesh, acetic ether /light petroleum 1:10 and 1% triethylamine). The product was 1.62 g.

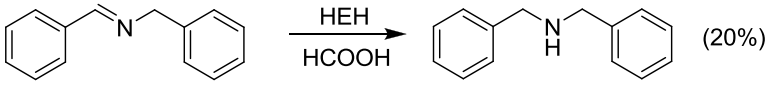
Mechanism



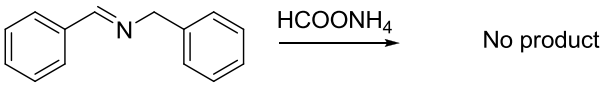
In the reaction, dibenzylimine (0.5 mmol) and HEH (1 equiv) were mixed in MeOH (2 mL), and they were heated at 60 ^{o}C for 16 hours. There was no product.



In the reaction, dibenzylimine (0.5 mmol), $HCOONH_4$ (1 equiv) and HEH (1 equiv) were mixed in MeOH (2 mL), and they were heated at 60^{o}C for 16 hours. The yield was determined by gas chromatography.



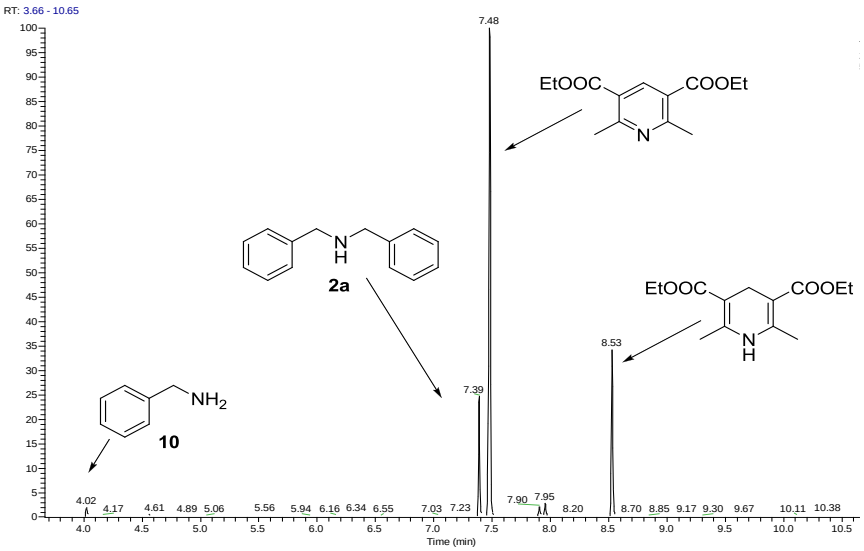
In the reaction, dibenzylimine (0.5 mmol), HCOOH (1 equiv) and HEH (1 equiv) were mixed in MeOH (2 mL), and they were heated at 60 ^{o}C for 16 hours. The yield was determined by gas chromatography.

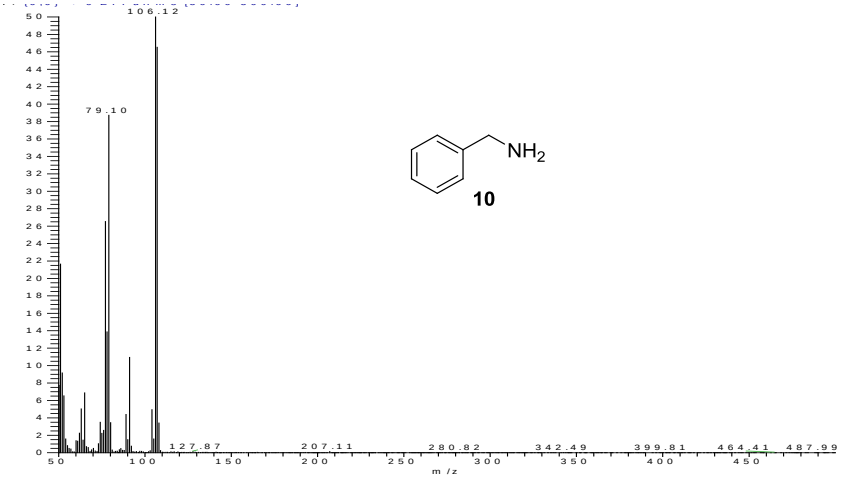


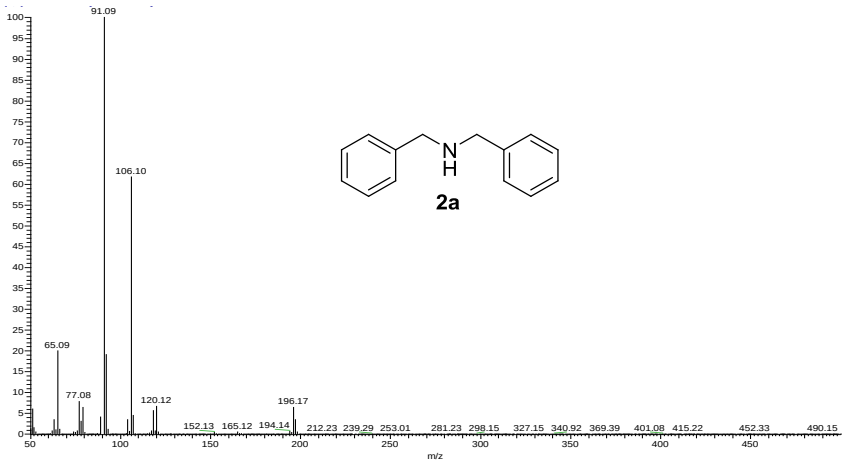
In the reaction, dibenzylimine (0.5 mmol), HCOOH (1 equiv) were mixed in MeOH (2 mL), and they were heated at 60 ^{o}C for 16 hours. There was no product.

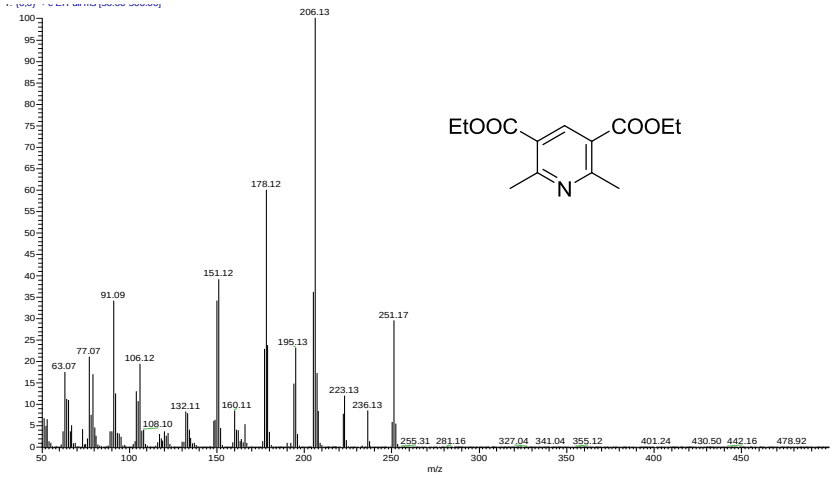
Detection of intermediate 10

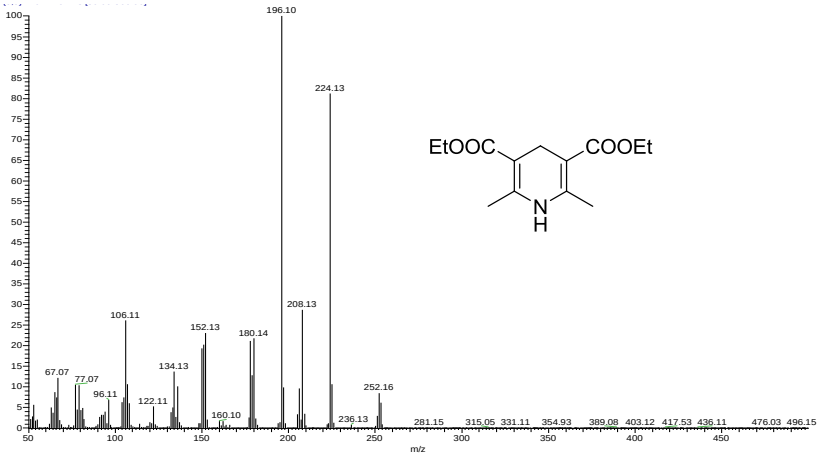
Benzaldehyde (0.5 mmol) was blended with HEH (127 mg, 0.5mmol) and $HCOONH_4$ (96 mg, 3 equiv) into a reaction tube, to which 2 mL MeOH was added. The tube was stirred at 60 ^{o}C for 2 hours. The mixture was detected by GC-MS. A certain amount of benzylamine (intermediate **10)** was detected.


RT: 3.66 - 10.65
7.48
EtOOC
COOEt
N
2a
NH2
10
7.39
8.53
EtOOC
COOEt
N
H
Time (min)

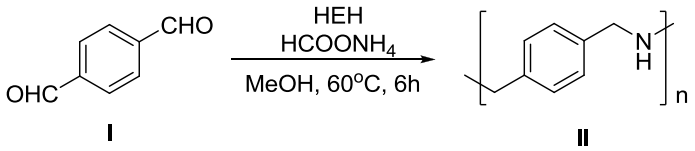

106.12
79.10
NH2
10
m/z


91.09
106.10
65.09
77.08
120.12
196.17
N
H
2a
m/z





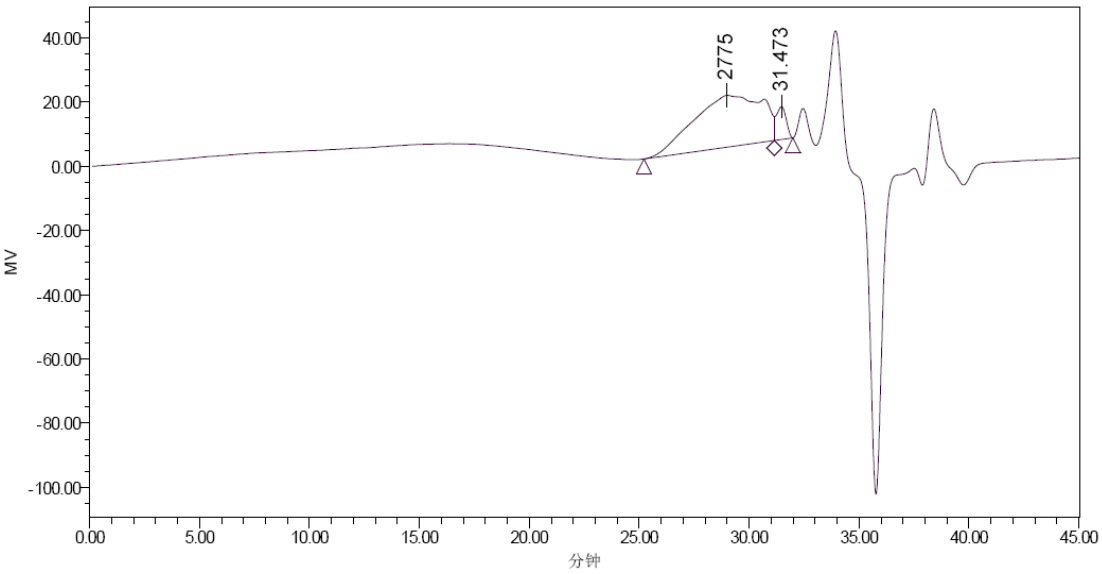
Further research



I II

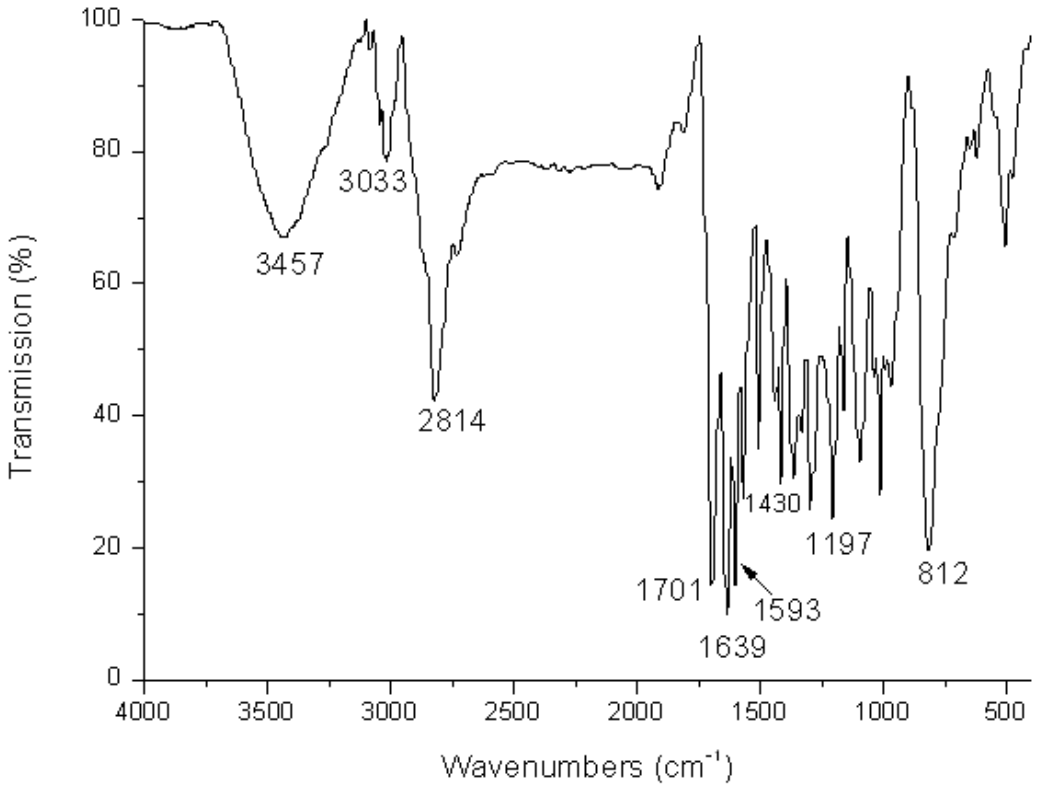
1,4-Phthalaldehyde **I** (0.5 mmol, 67 mg) was heated with $HCOONH_4$ (0.5 mmol, 32 mg) and HEH (0.5mmol, 127 mg) in MeOH (3 mL) at 60 ^oC for about 6 hours. There were pale yellow flocs separated out in the reaction tube. After filtration, the solid was washed by MeOH for 3 times. Then, the solid was dried in vacuum oven for at least 12 hours. Finally, we got polymer **II** about 39 mg.

Gel permeation chromatography was used to detect the relative molecular mass. Polymers were detected as the first broad peak shown in chart below.



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5160	6366	2775	7967	9724	1.233533	1.251525	1.527518

The molecular weight of main product was 5160 as shown in the result form above. So the solid was a polymer really. Then the structure of the polymer was confirmed by infrared spectroscopy (IR).



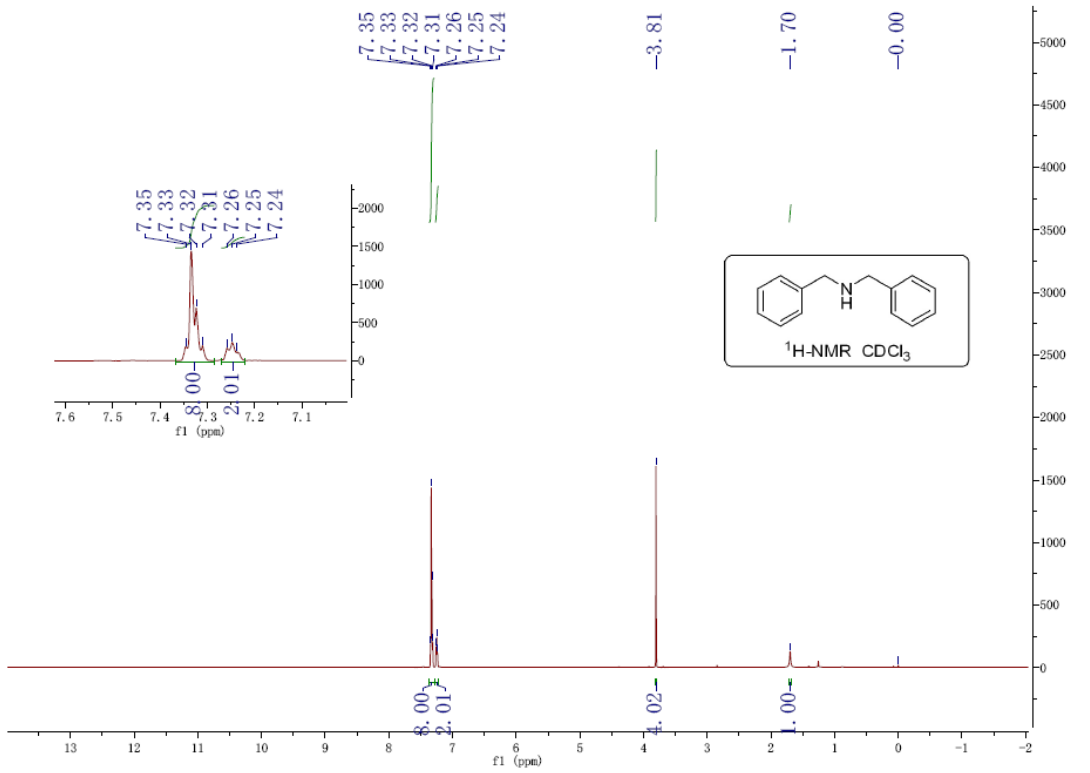
Infrared spectra of polymer **II** was shown above. Methylene group may be certificated

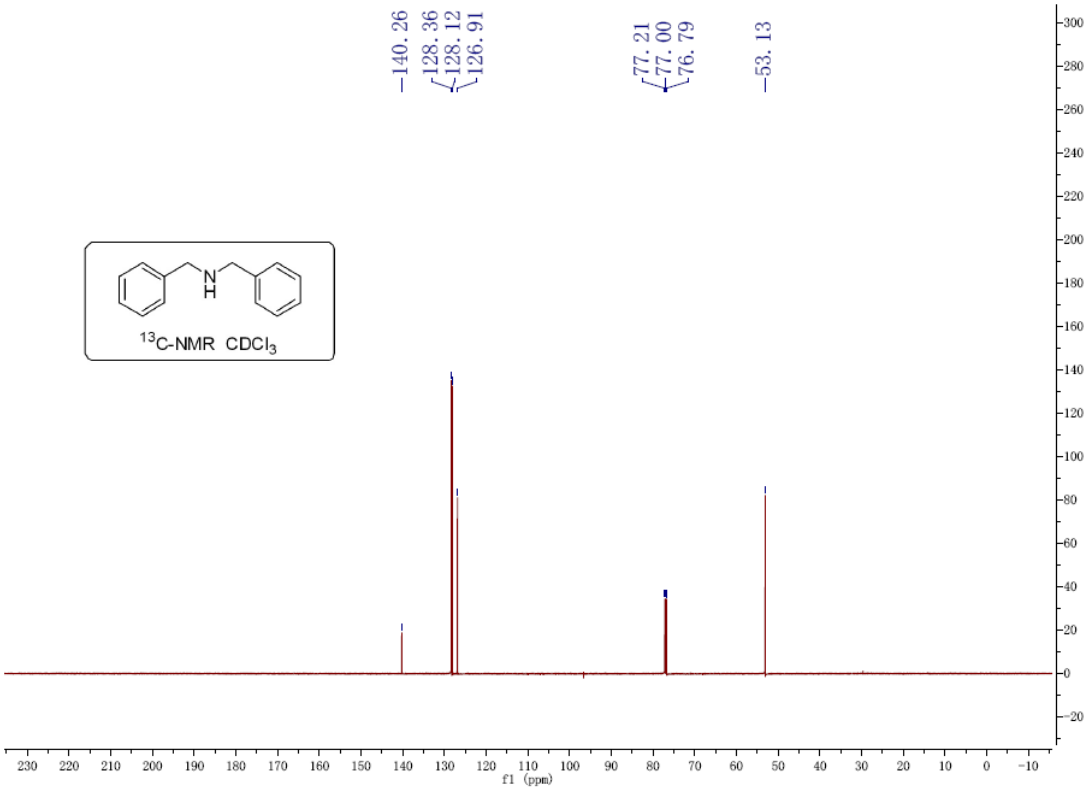
by peaks near 2814 cm^{-1}, 1430 cm^{-1}. The peak at 3033 cm^{-1} may be the stretching vibration of carbon-hydrogen bonds on the benzene ring. The stretching vibration of C=C bonds on the benzene ring may be indicated by peaks at 1593 cm^{-1}, 1639 cm^{-1} and 1701 cm^{-1}. Plane bending vibration peak of carbon-hydrogen bonds on the benzene ring may be represented by peak at 812 cm^{-1}. Peak at 1197 cm^{-1} may imply that nitrogen was connected with methylene. N-H group of the polymer may be indicated by peak near 3457 cm^{-1}.

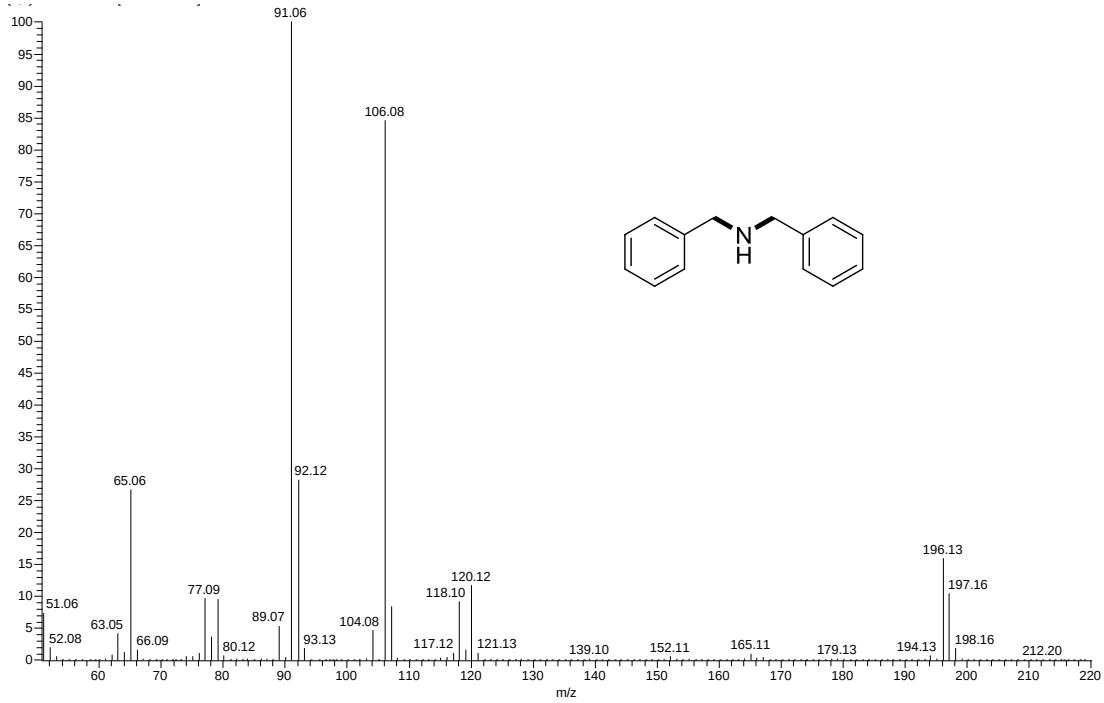
According to the results of gel permeation chromatography and IR, we considered that the polymer **II** was polybenzylamine.

Copies of ^{1}H-NMR, ^{13}C-NMR and MS Spectra

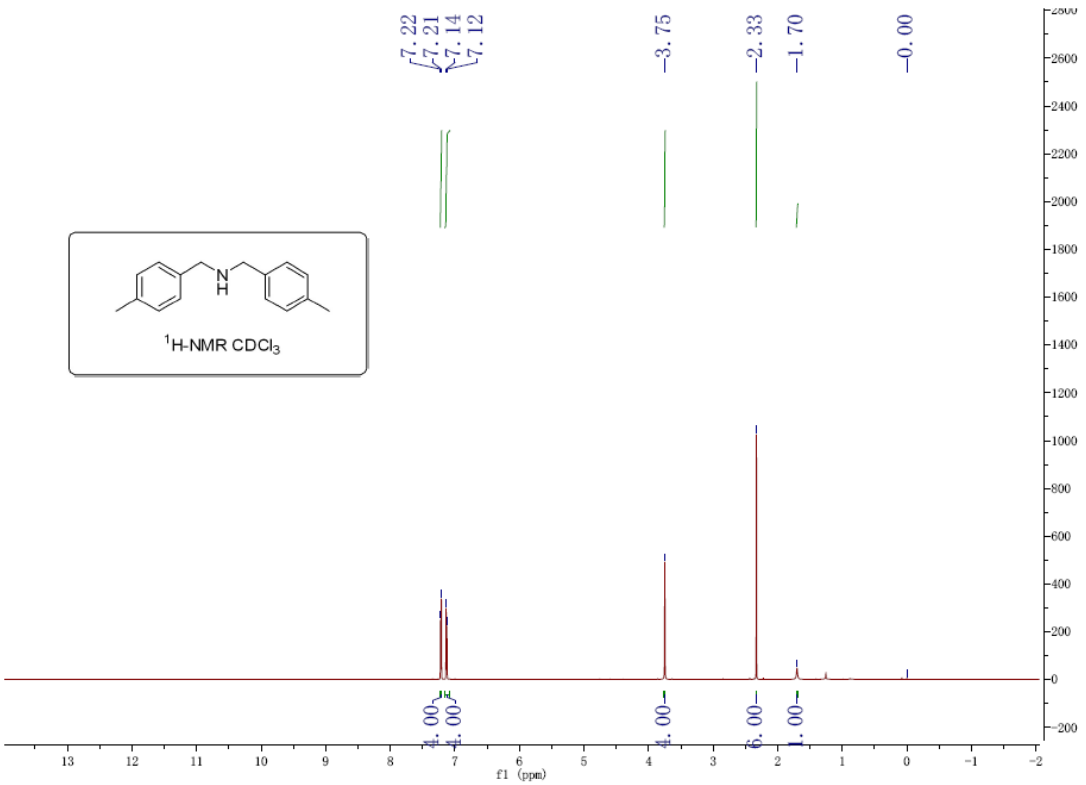
dibenzylamine (2a)

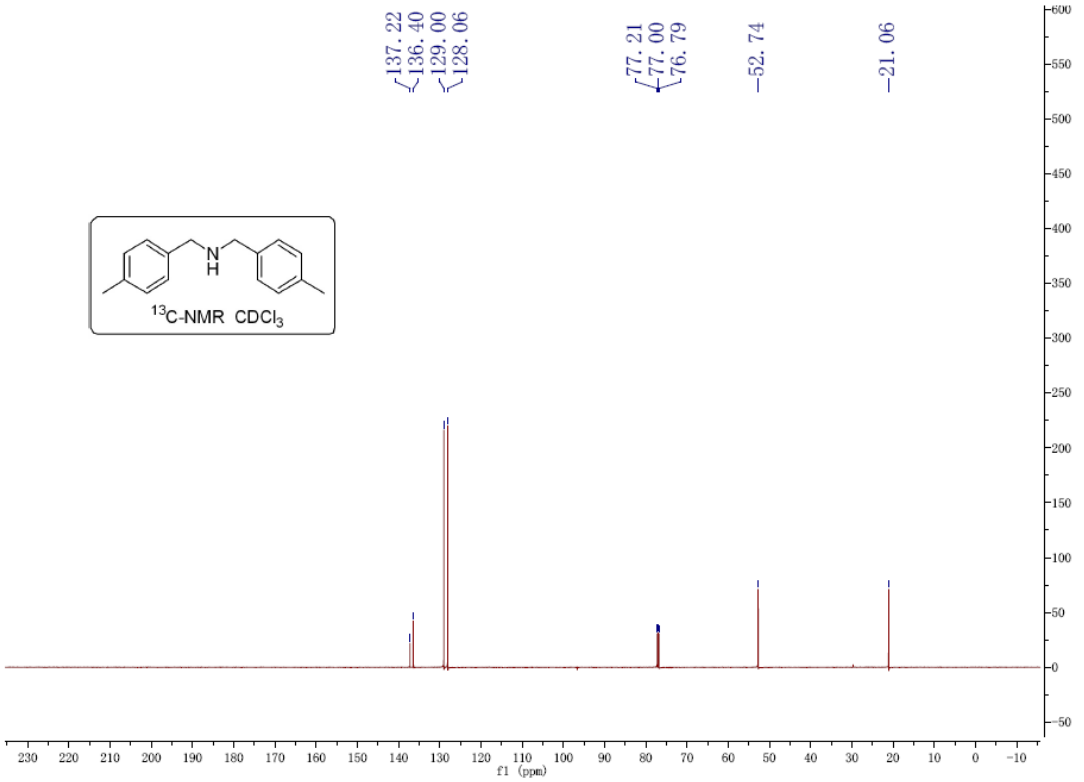


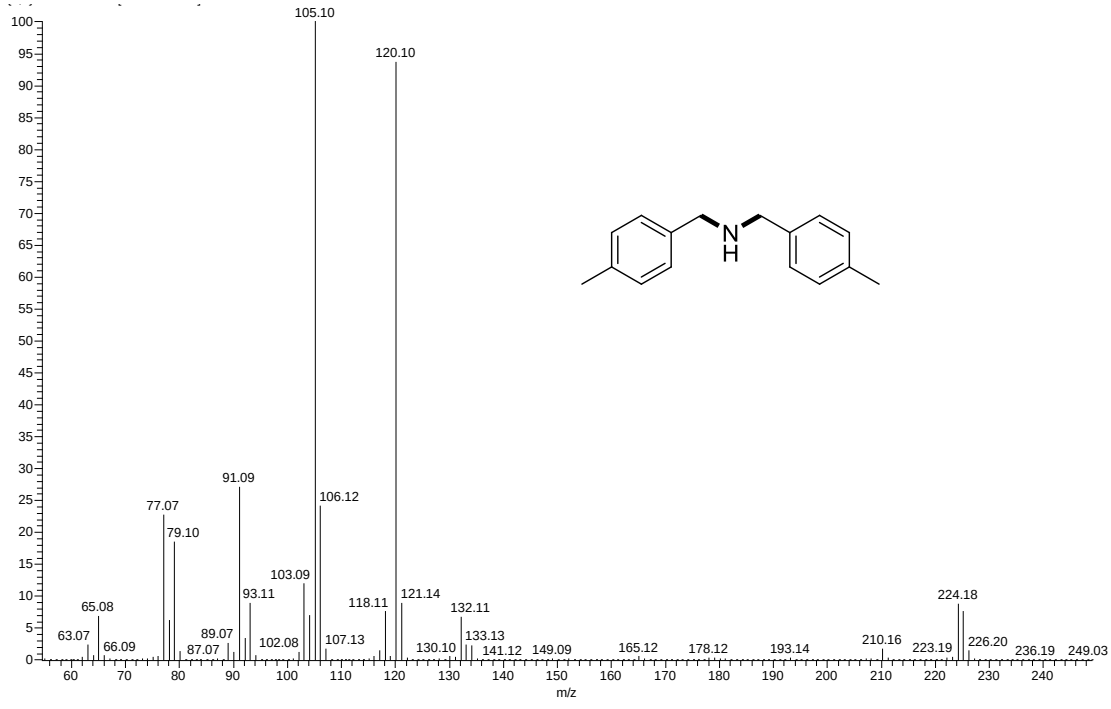




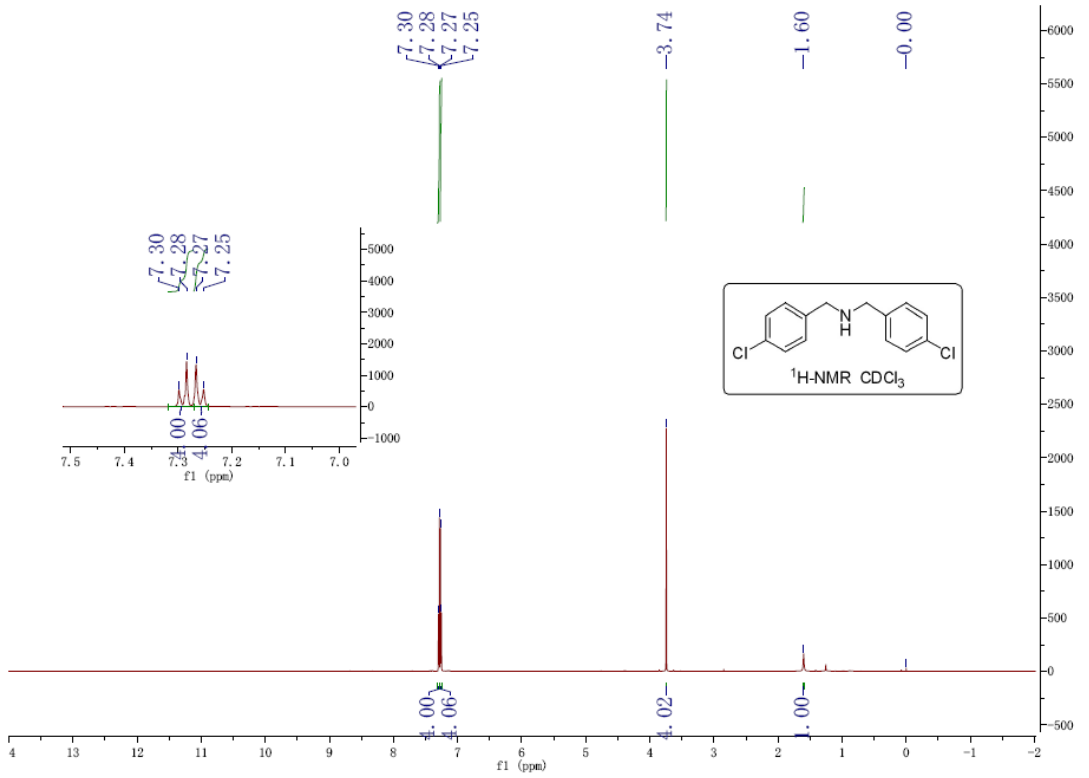
bis(4-methylbenzyl)amine (2b)

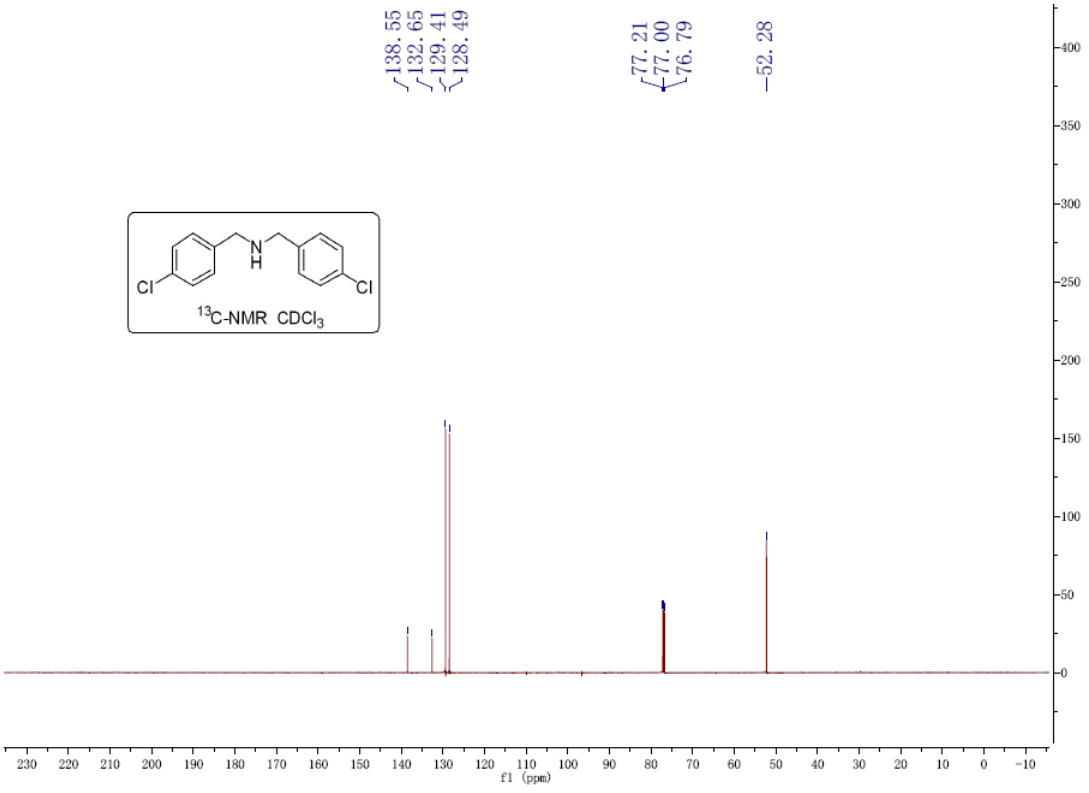


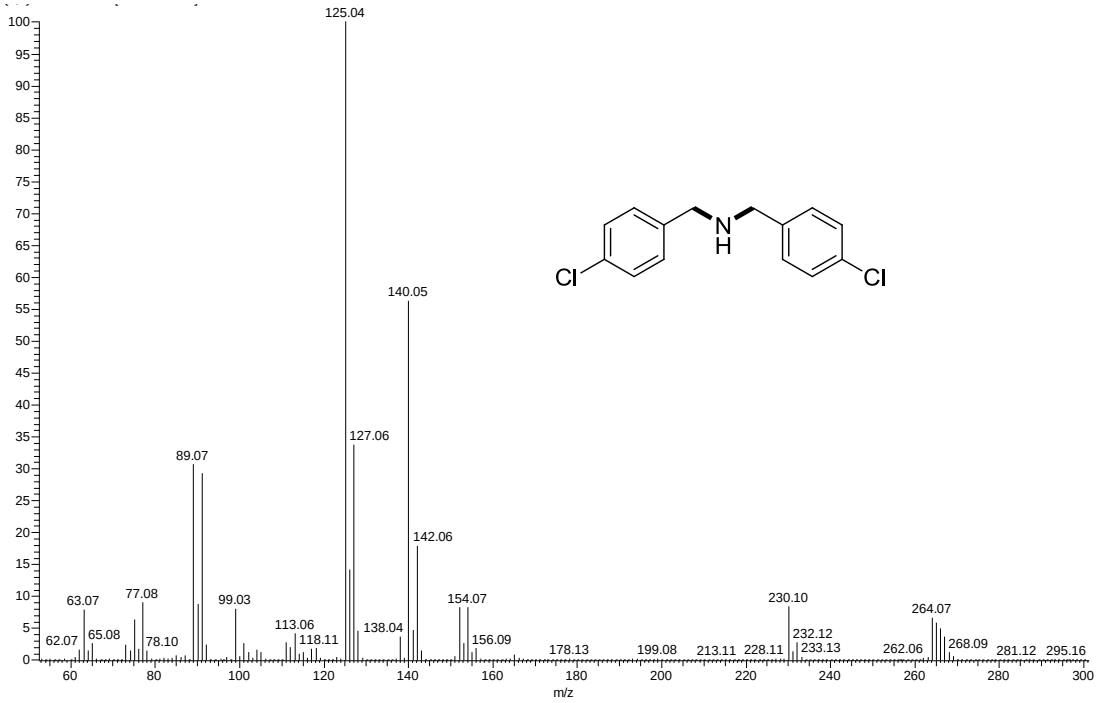

137.22
136.40
129.00
128.06
77.21
77.00
76.79
52.74
21.06
^{13}C-NMR CDCl$_3$
f1 (ppm)


105.10
120.10
91.09
106.12
77.07
79.10
103.09
93.11
65.08
118.11
121.14
132.11
89.07
102.08
107.13
133.13
63.07
66.09
87.07
130.10
141.12
149.09
165.12
178.12
193.14
210.16
223.19
224.18
226.20
236.19
249.03
m/z

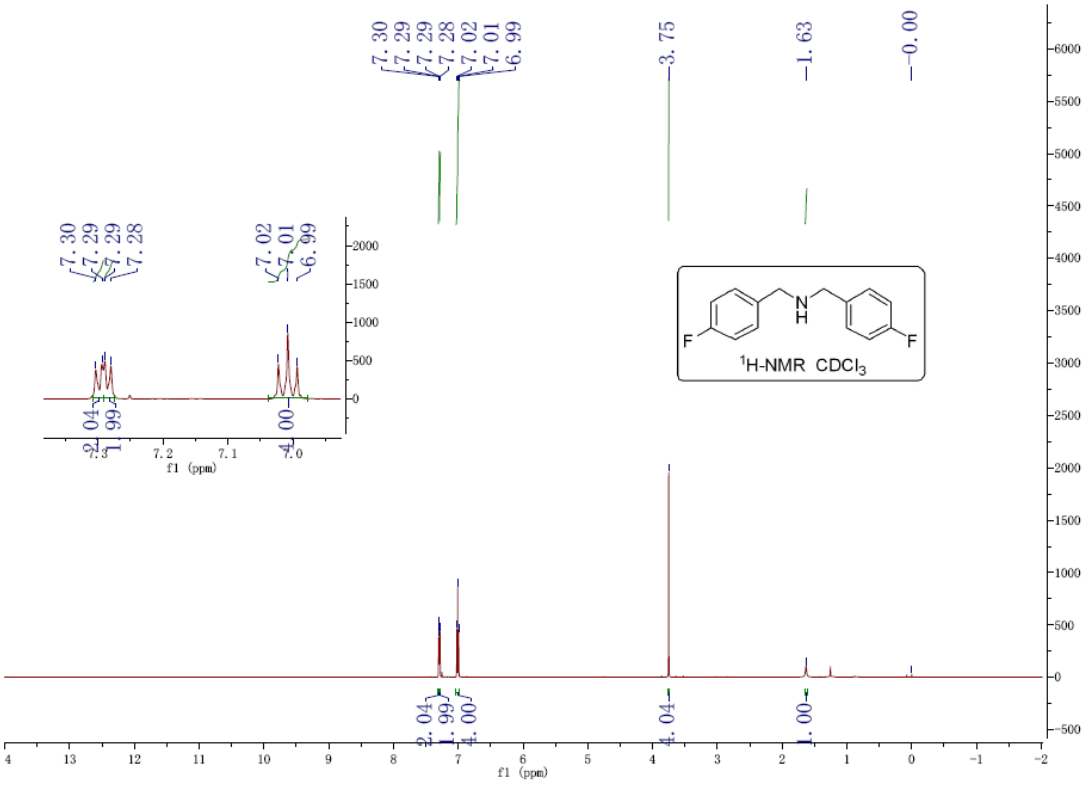
bis(4-chlorobenzyl)amine (2c)

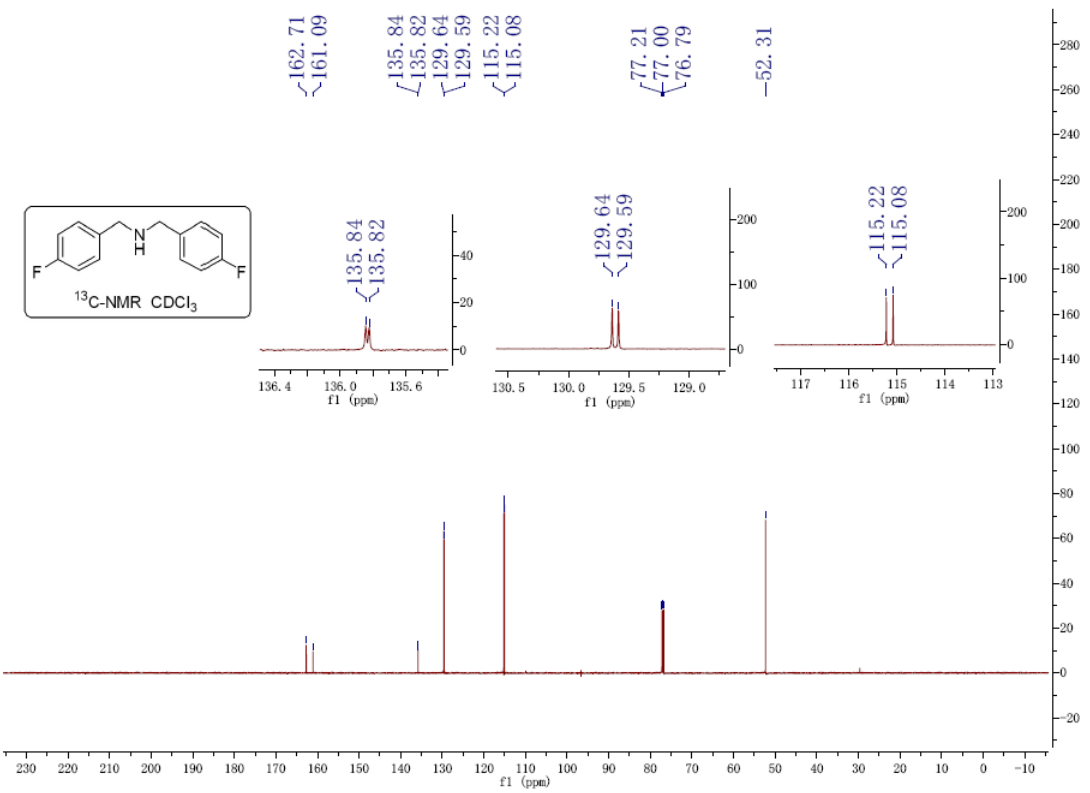


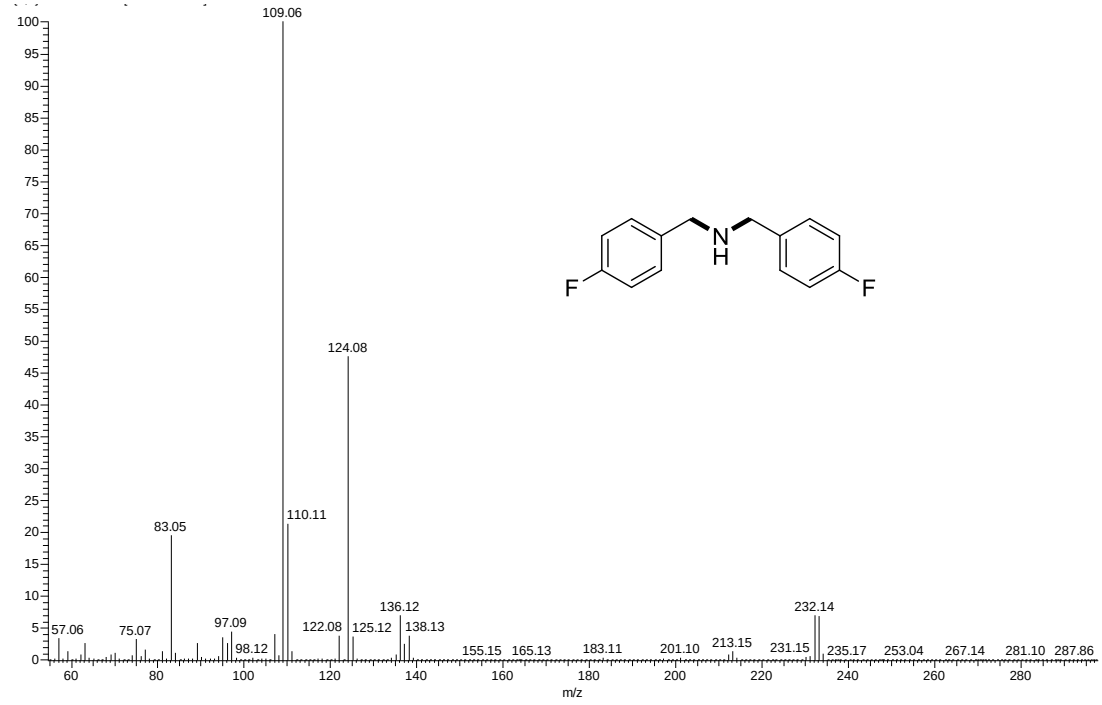




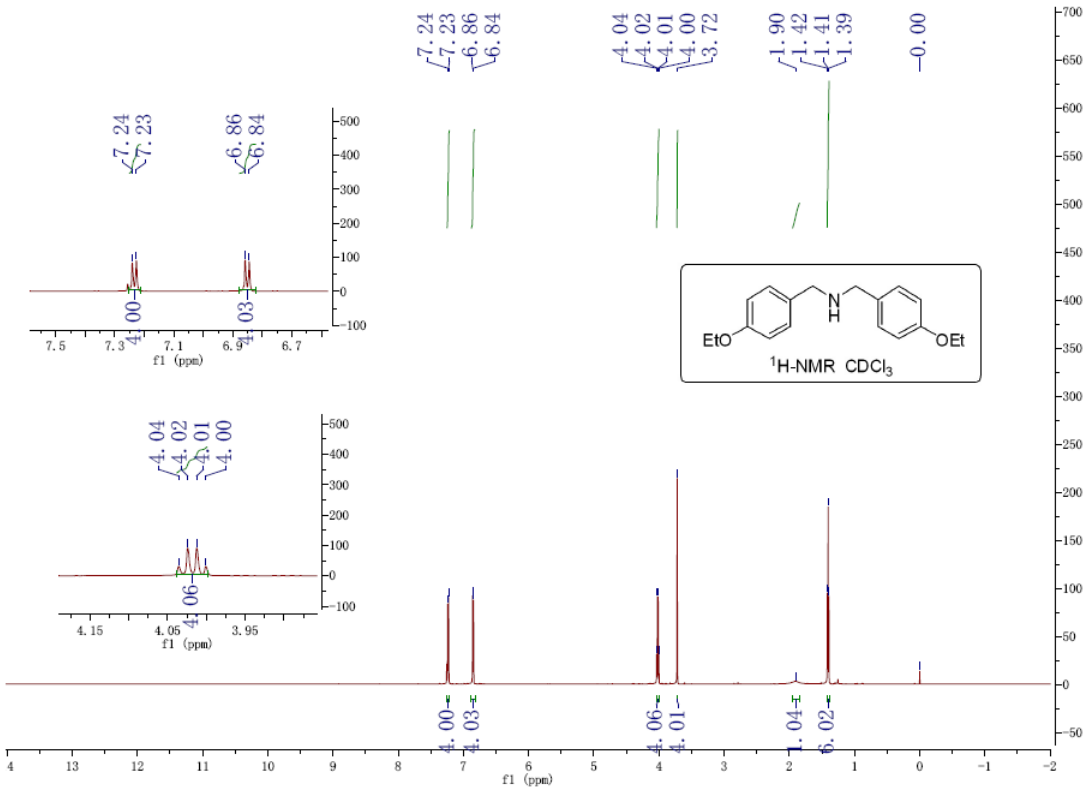
bis(4-fluorobenzyl)amine (2d)

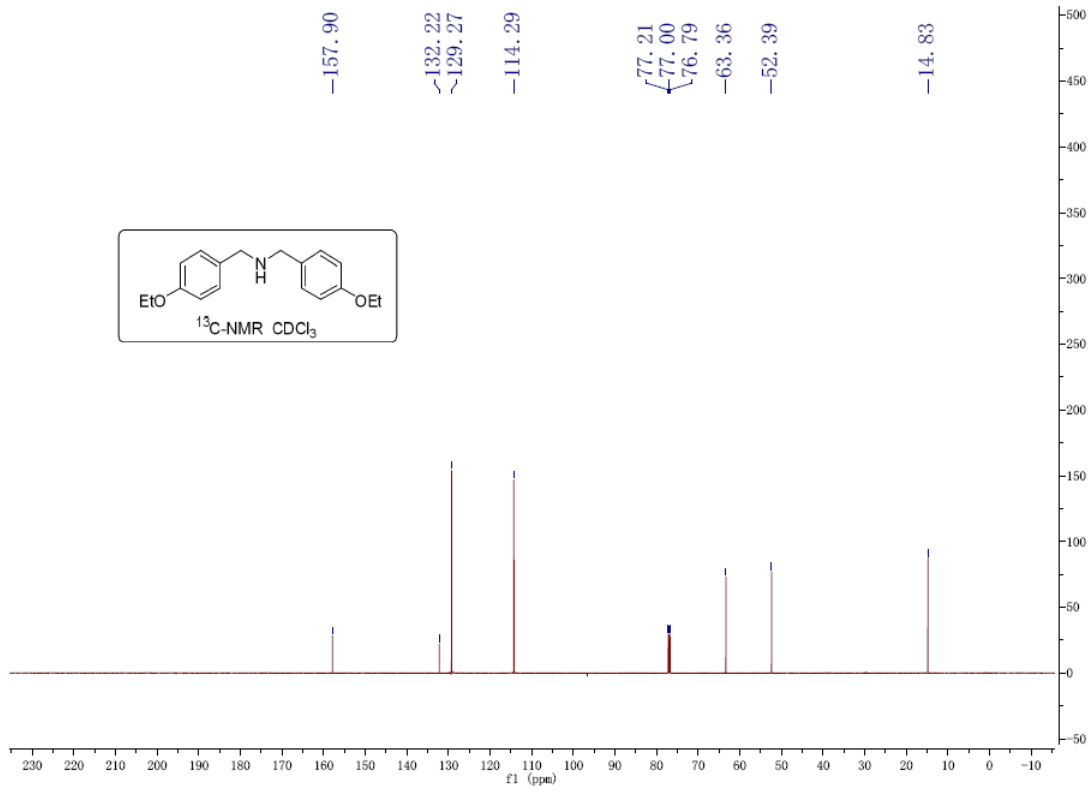



162.71
161.09
135.84
135.82
129.64
129.59
115.22
115.08
77.21
77.00
76.79
52.31
F
N
H
F
13C-NMR CDCl3
f1 (ppm)

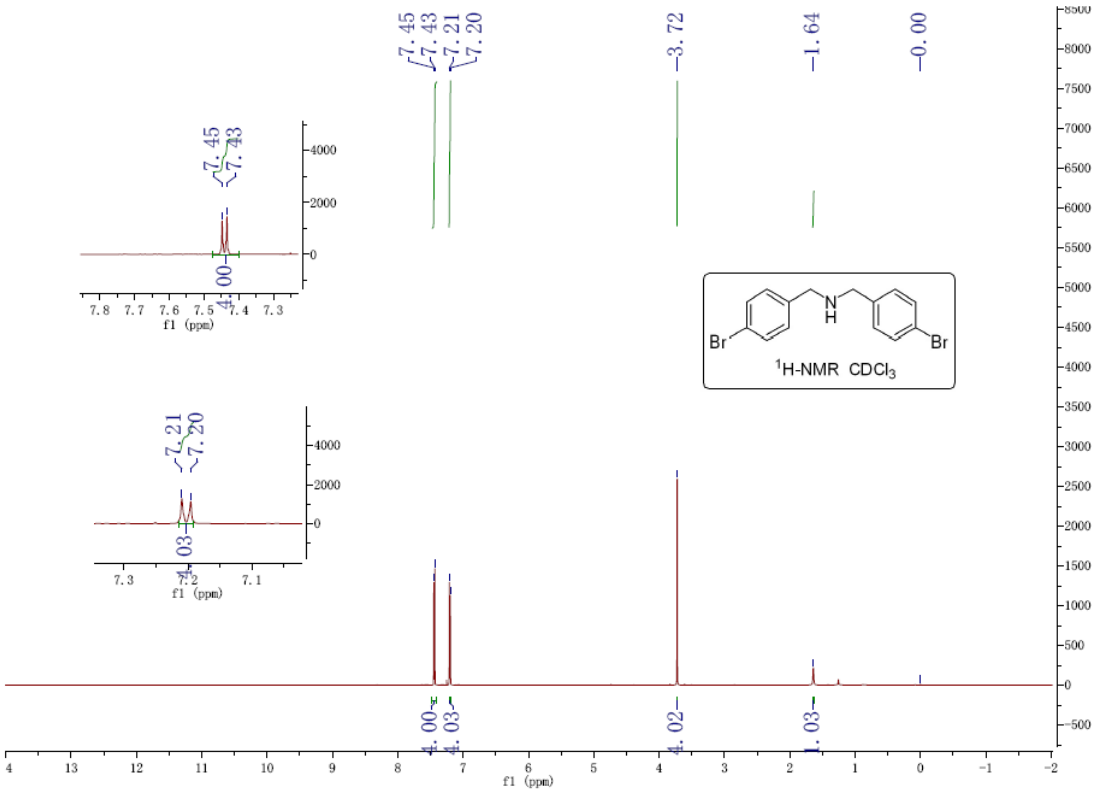

109.06
124.08
110.11
83.05
136.12
232.14
97.09
57.06
75.07
98.12
122.08
125.12
138.13
155.15
165.13
183.11
201.10
213.15
231.15
235.17
253.04
267.14
281.10
287.86
m/z
F
N
H
F

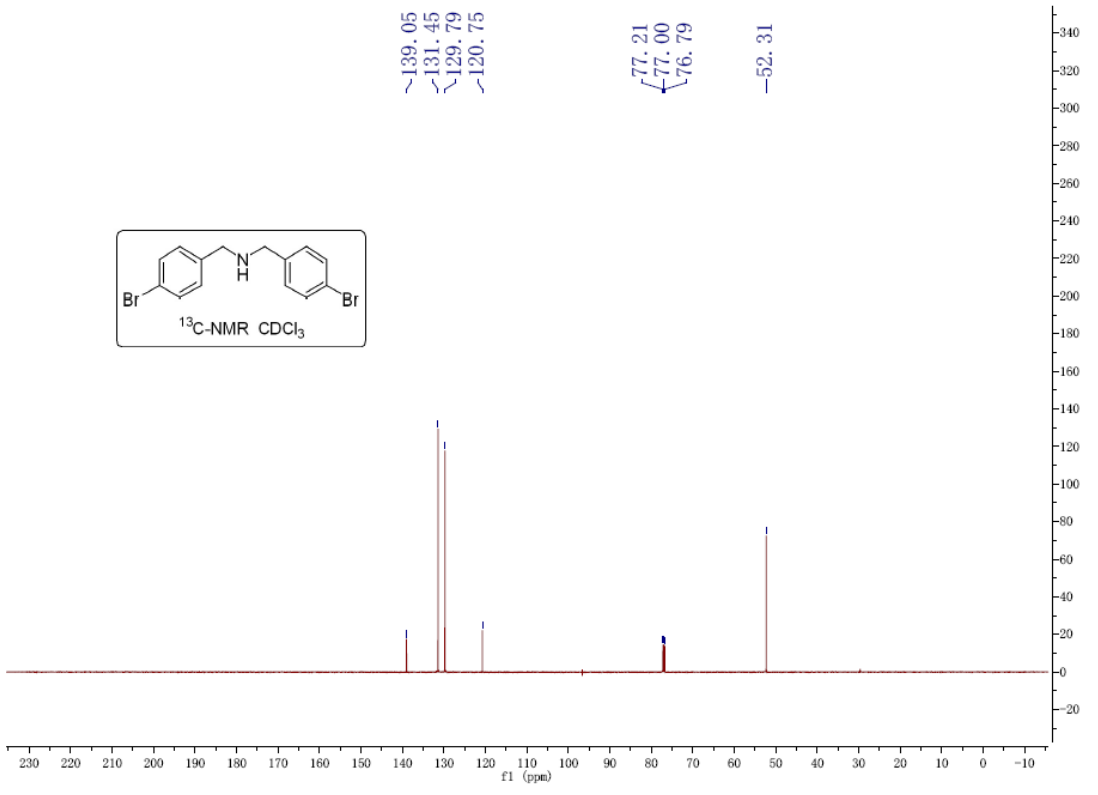
bis(4-ethoxybenzyl)amine (2e)

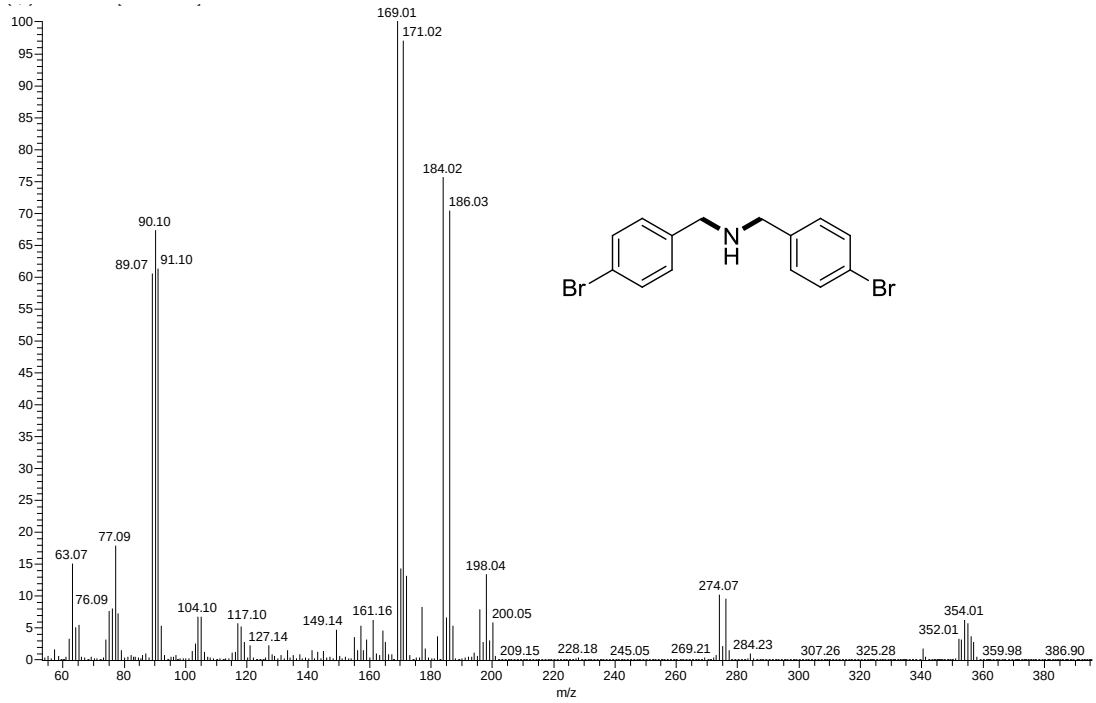




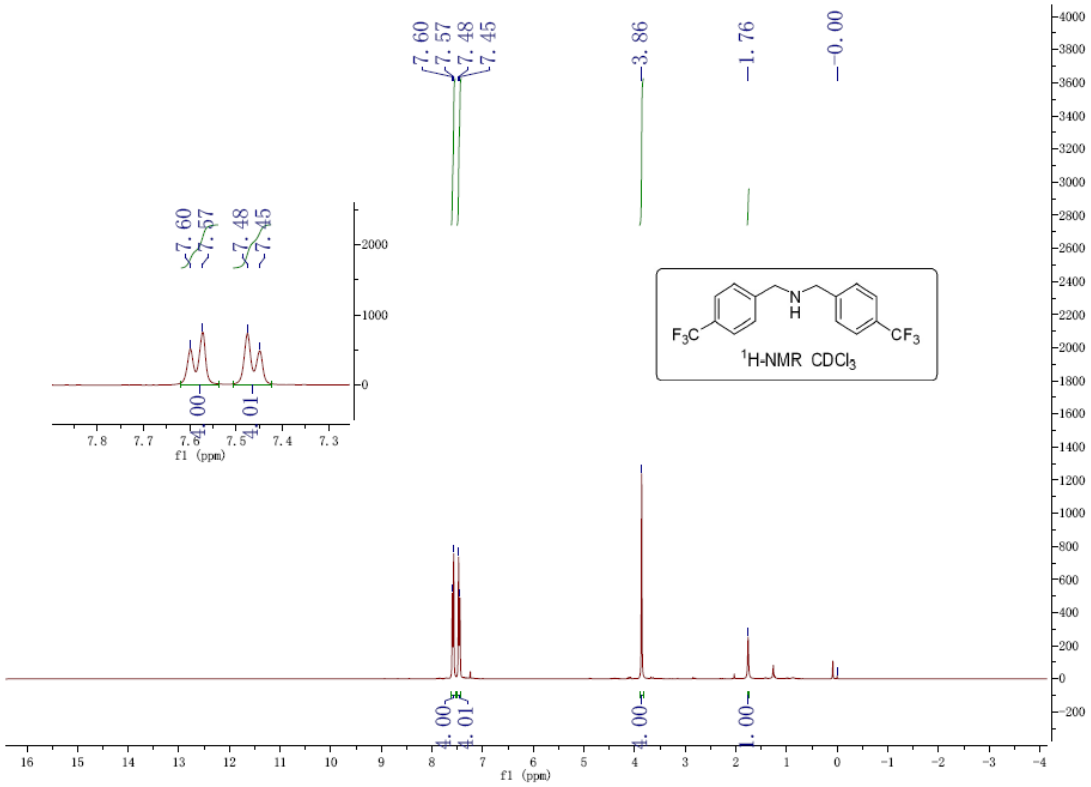
bis(4-bromobenzyl)amine (2f)

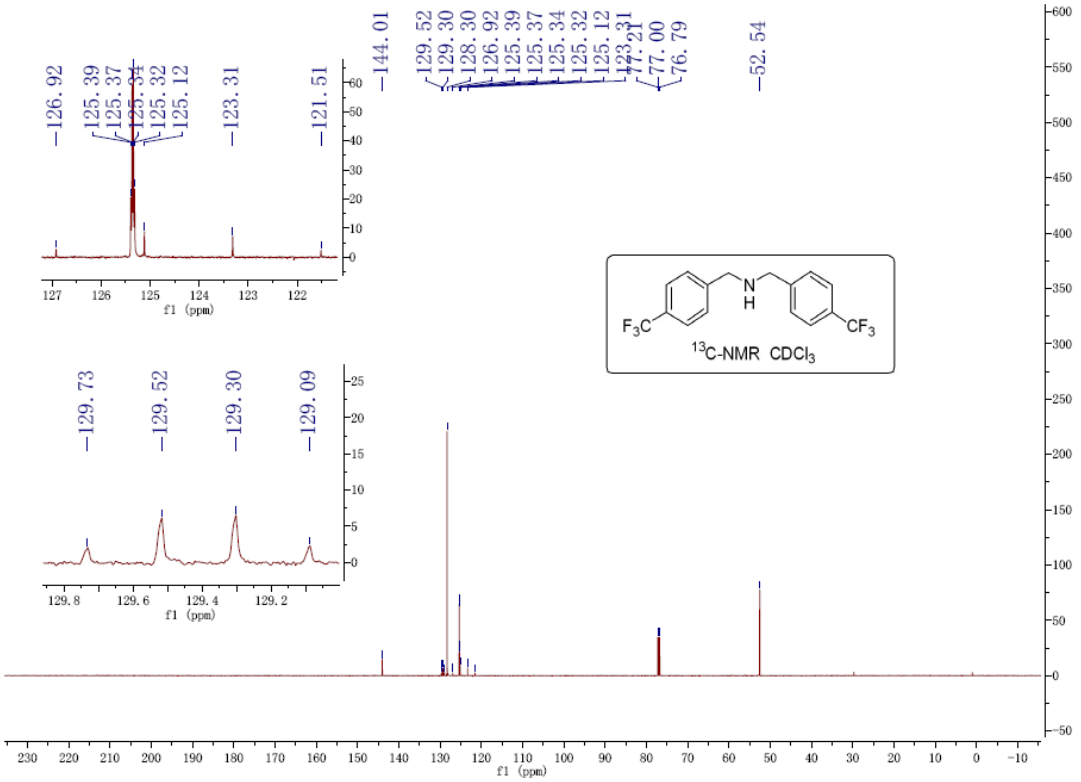


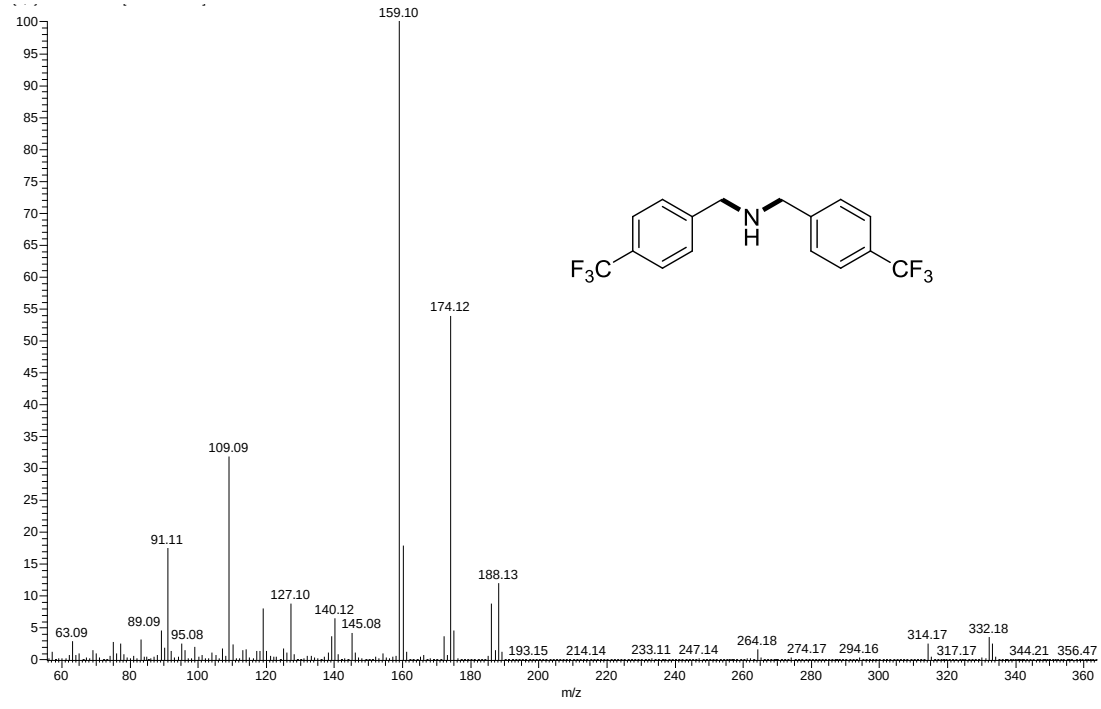




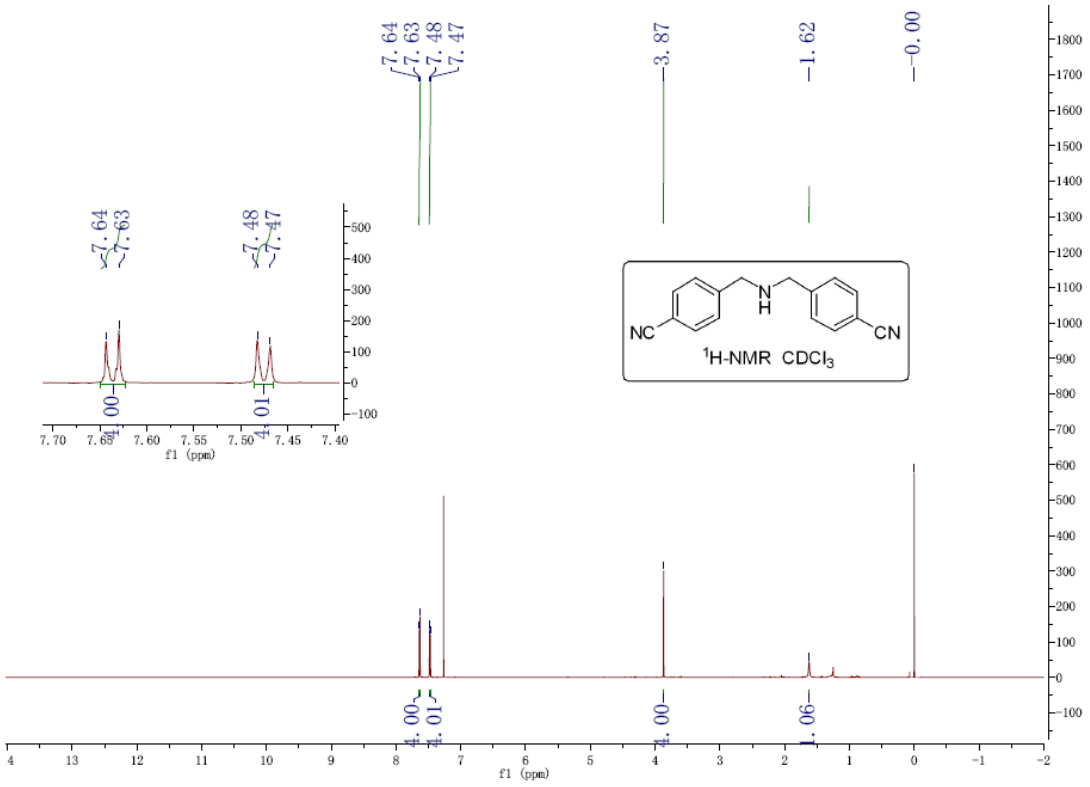
bis(4-(trifluoromethyl)benzyl)amine (2g)

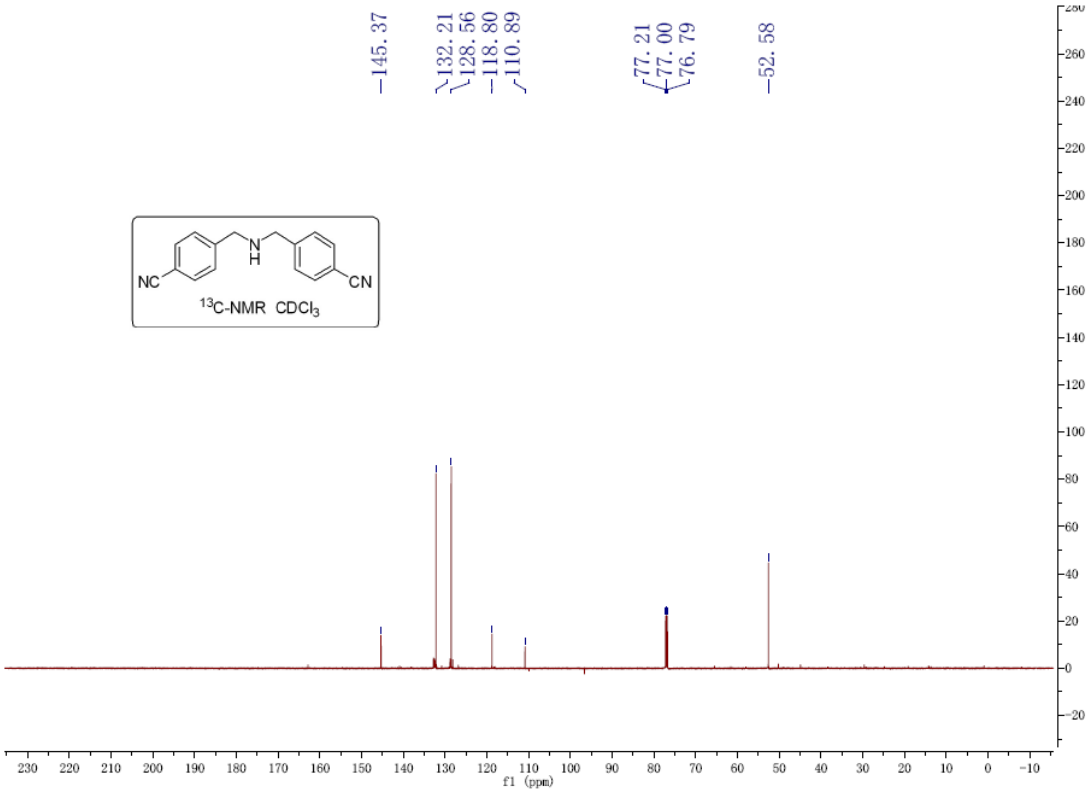


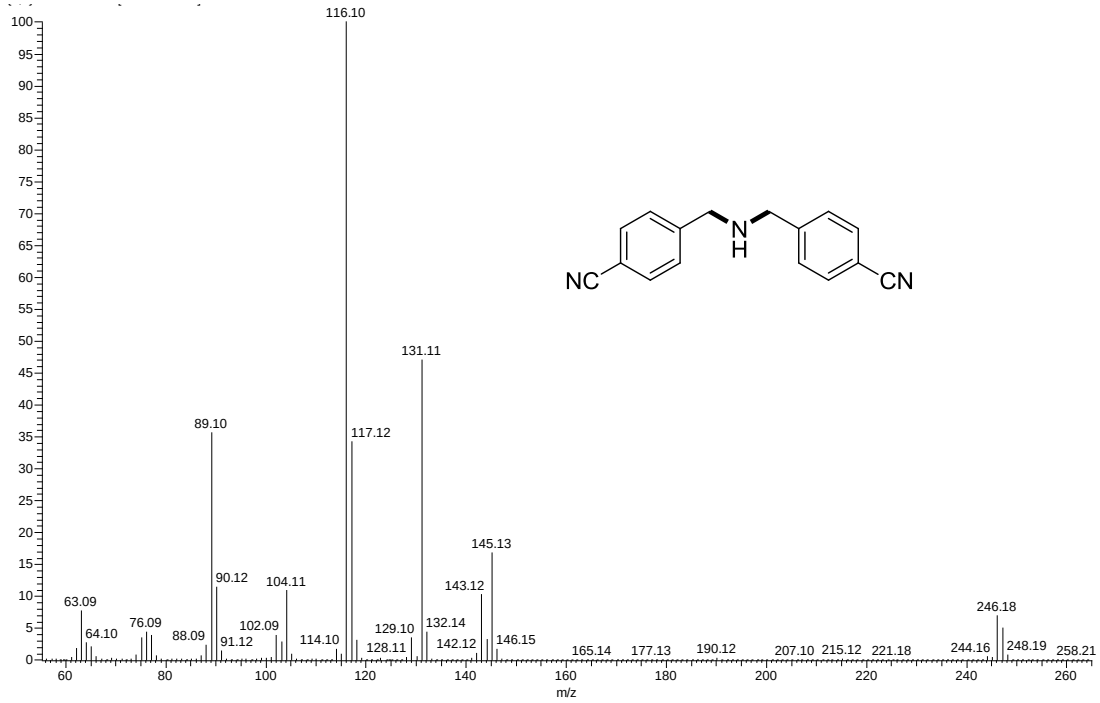

144.01
129.52
129.30
128.30
126.92
125.39
125.37
125.34
125.32
125.12
123.31
77.21
77.00
76.79
52.54
126.92
125.39
125.37
125.34
125.32
125.12
123.31
121.51
f1 (ppm)
129.73
129.52
129.30
129.09
f1 (ppm)
F3C
N
H
CF3
13C-NMR CDCl3
f1 (ppm)


159.10
174.12
109.09
91.11
188.13
127.10
140.12
145.08
89.09
95.08
63.09
193.15
214.14
233.11
247.14
264.18
274.17
294.16
314.17
317.17
332.18
344.21
356.47
m/z
F3C
N
H
CF3

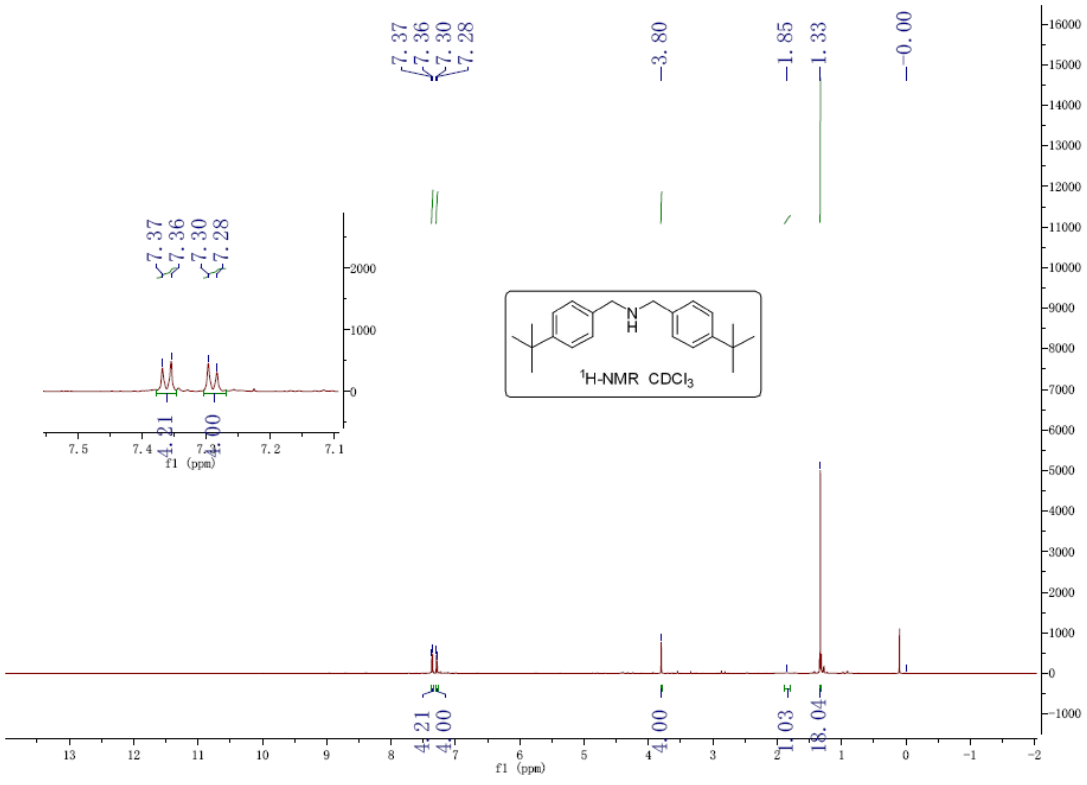
4,4'-azanediylbis(methylene)dibenzonitrile (2h)

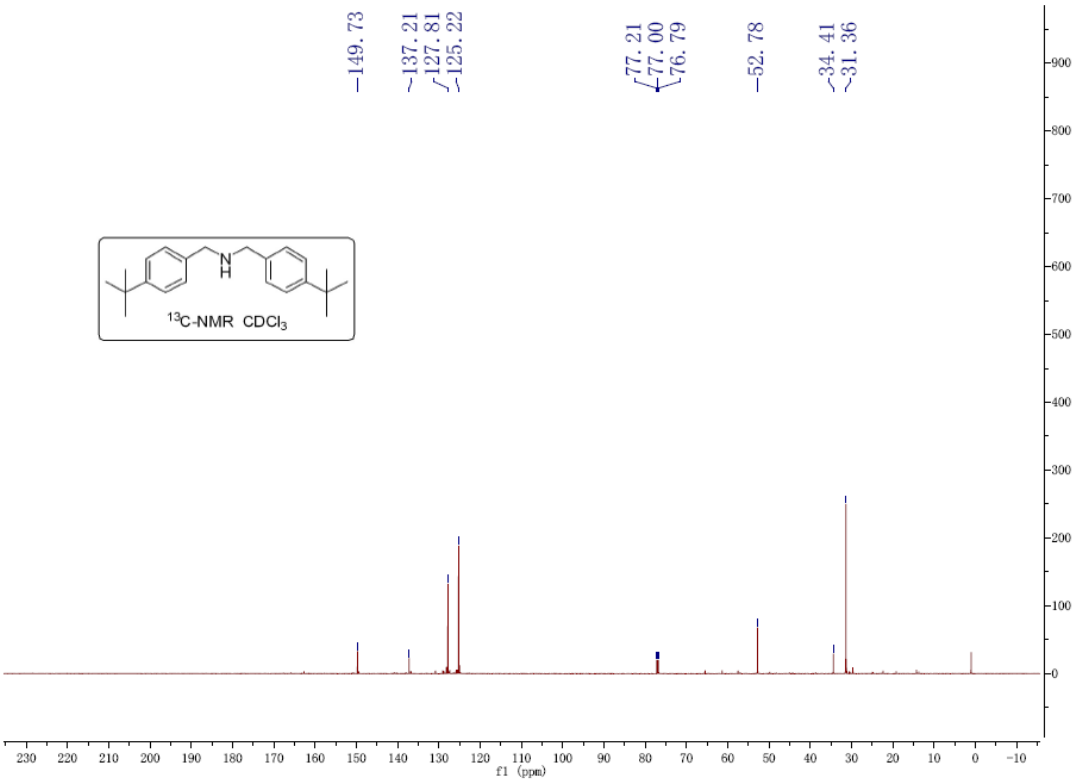


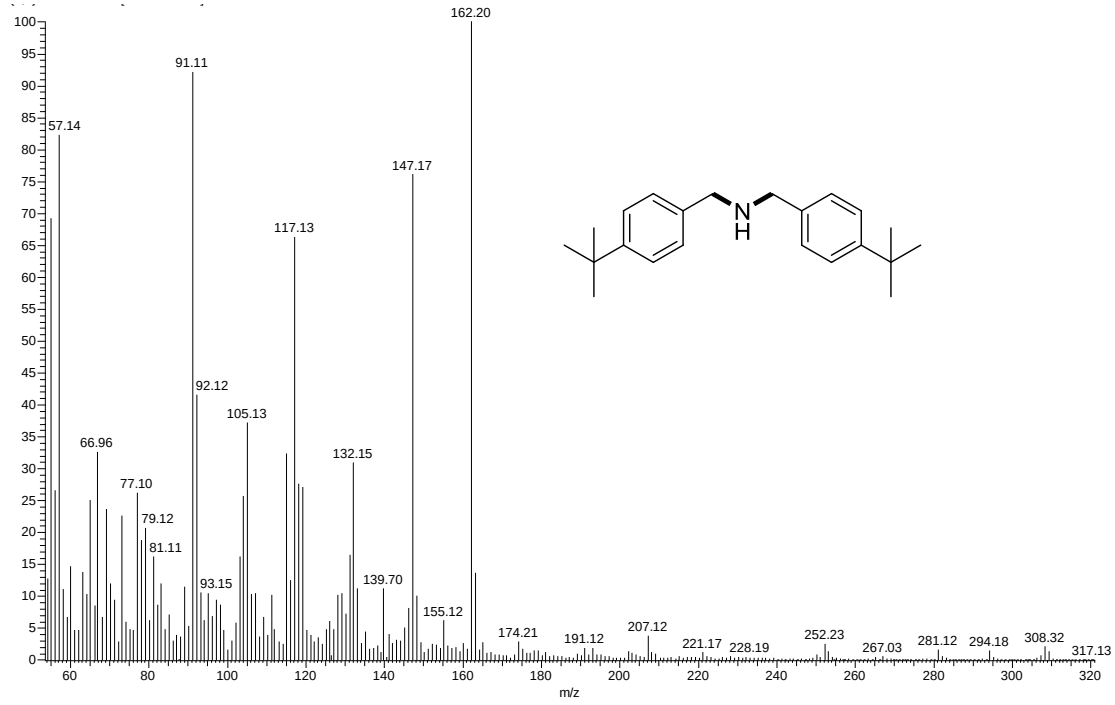




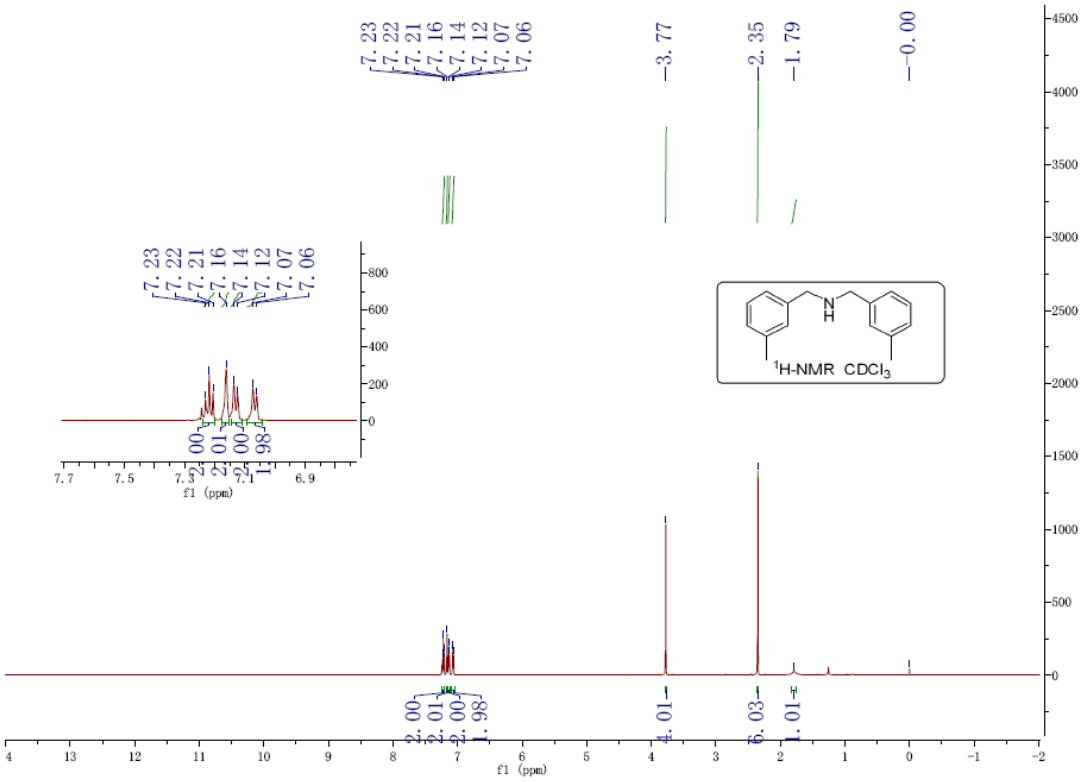
bis(4-tert-butylbenzyl)amine (2i)

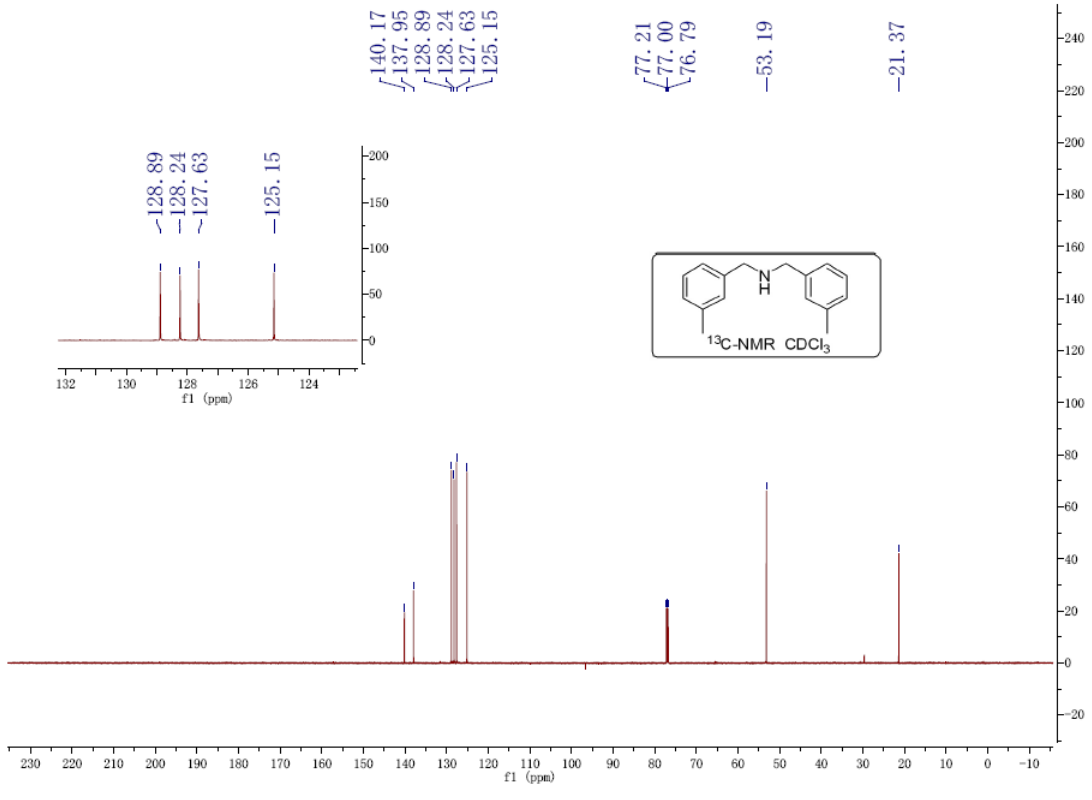


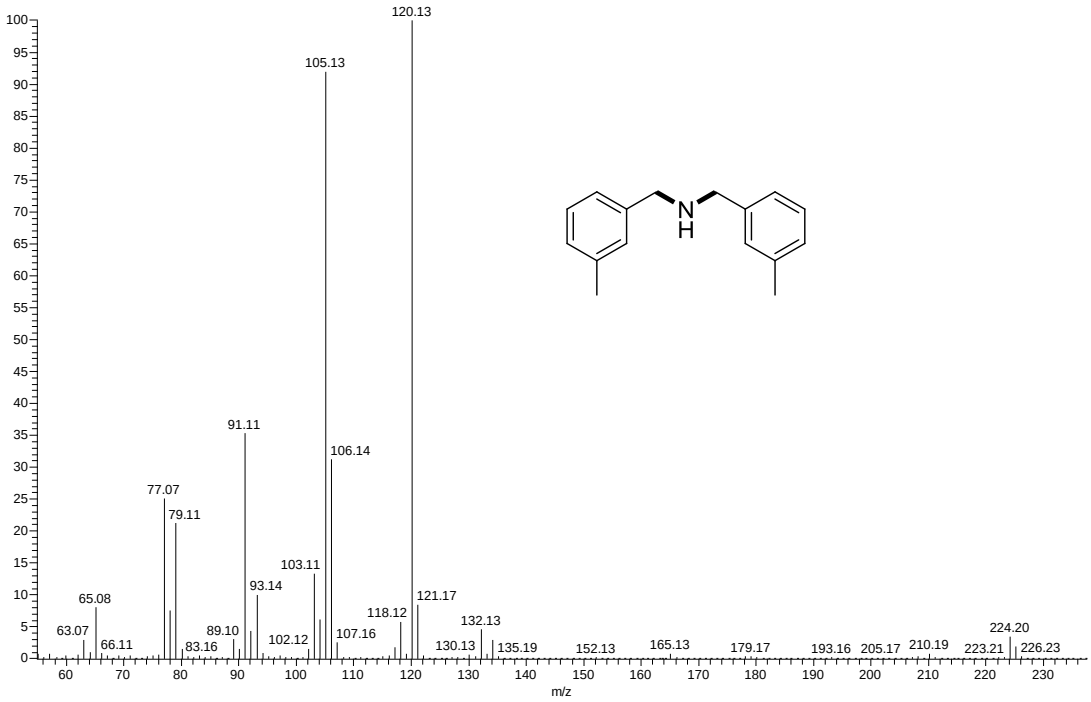

149.73
137.21
127.81
125.22
77.21
77.00
76.79
52.78
34.41
31.36
13C-NMR CDCl3
f1 (ppm)


162.20
91.11
57.14
147.17
117.13
92.12
105.13
66.96
132.15
77.10
79.12
81.11
93.15
139.70
155.12
174.21
191.12
207.12
221.17
228.19
252.23
267.03
281.12
294.18
308.32
317.13
m/z

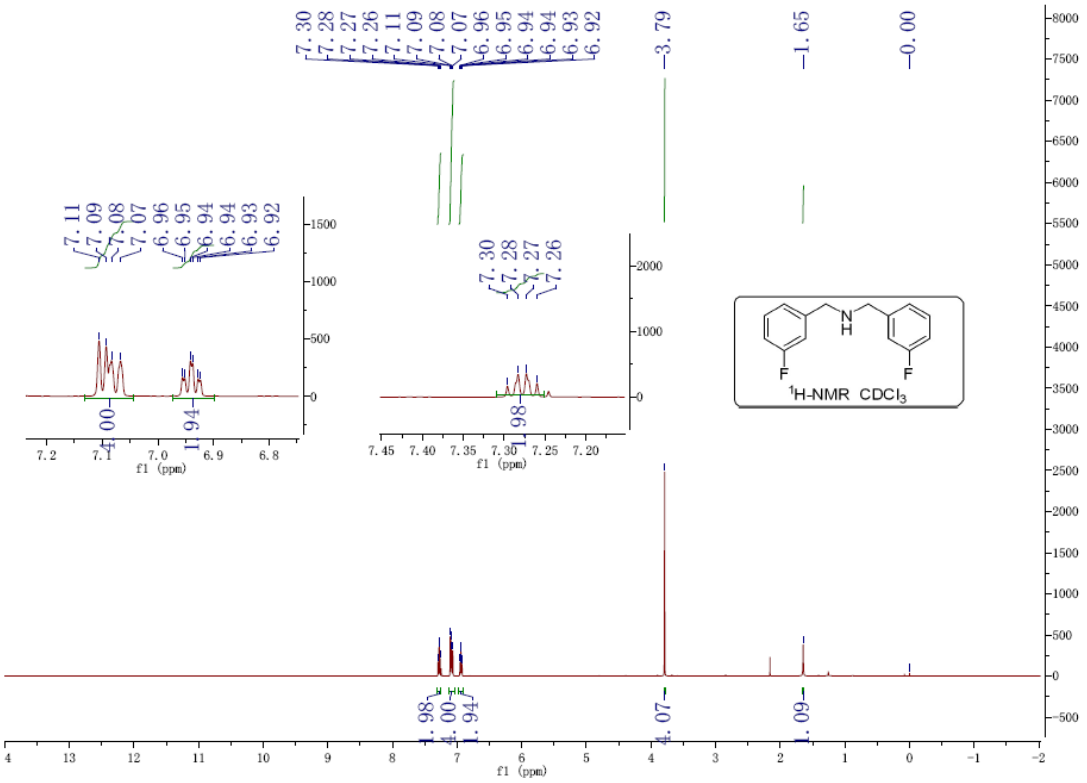
bis(3-methylbenzyl)amine (2j)

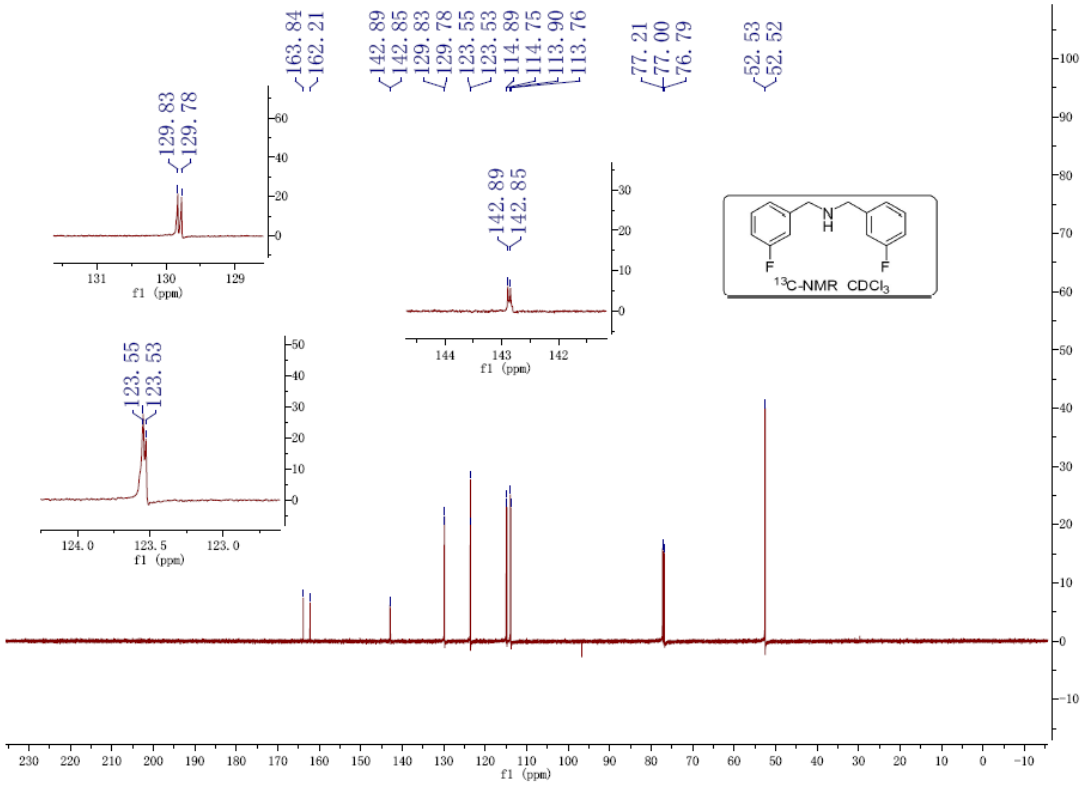




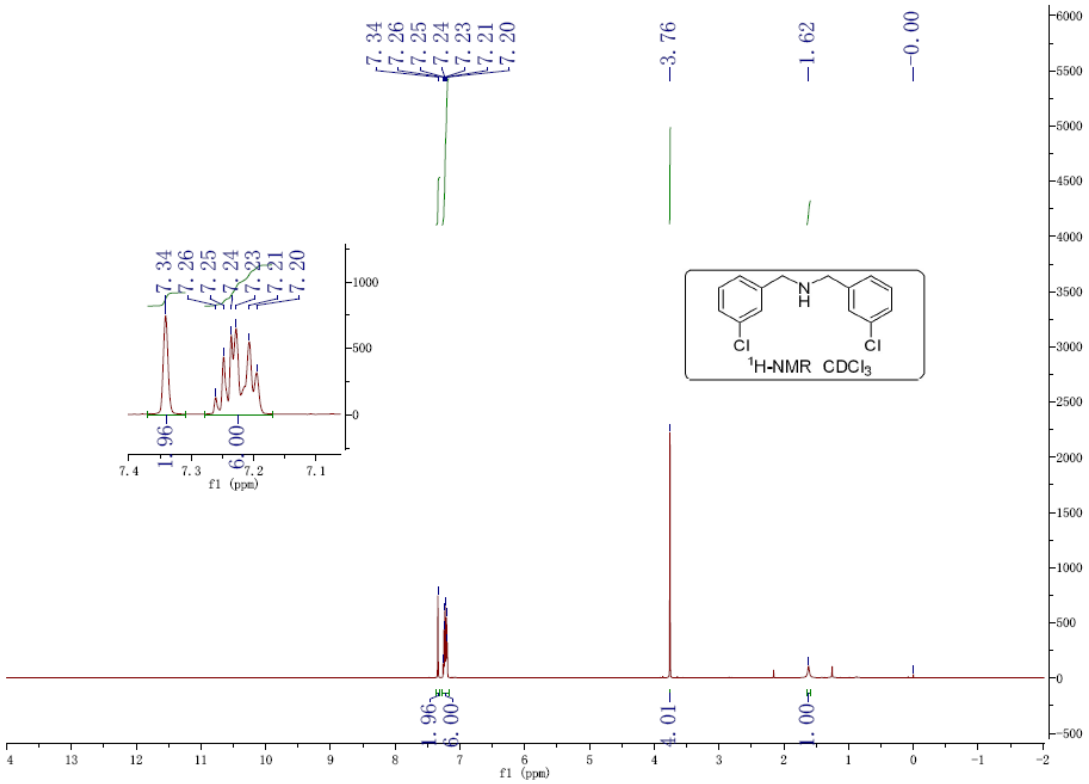


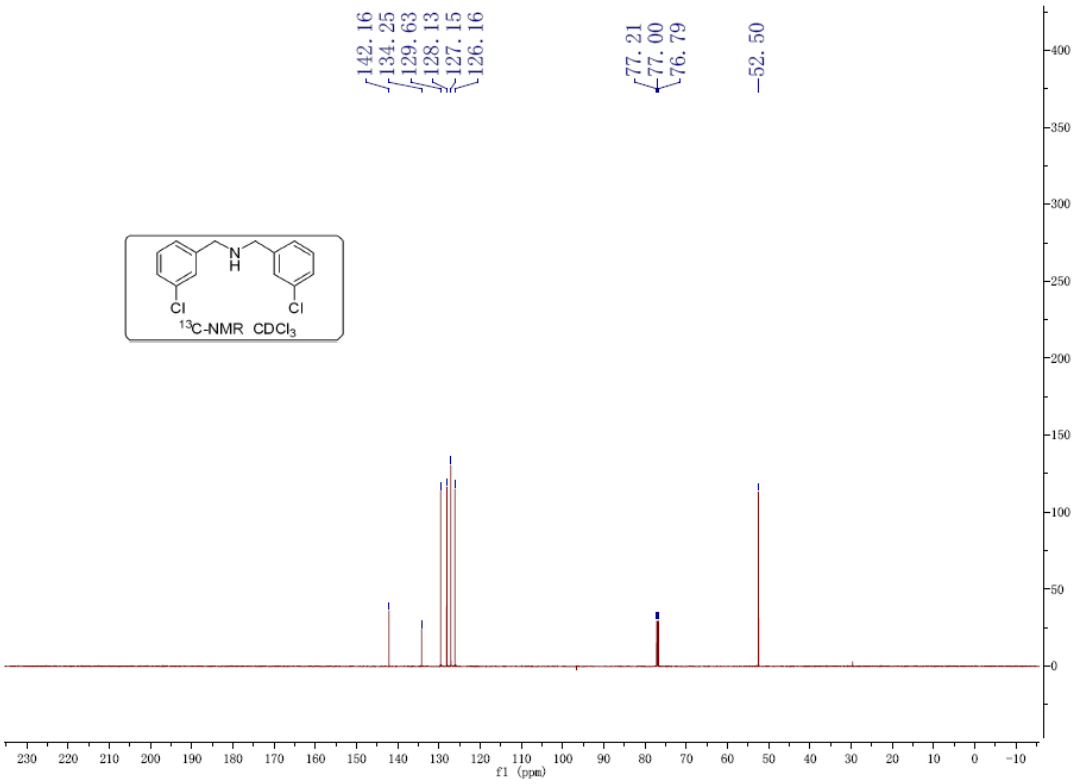
bis(3-fluorobenzyl)amine (2k)

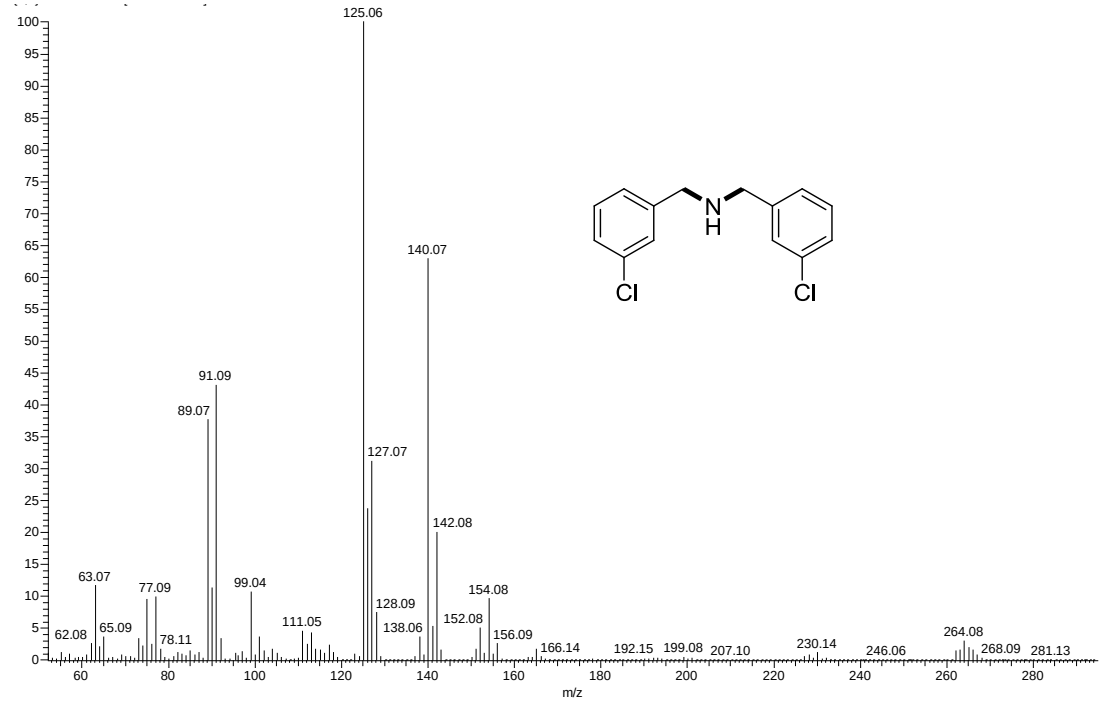




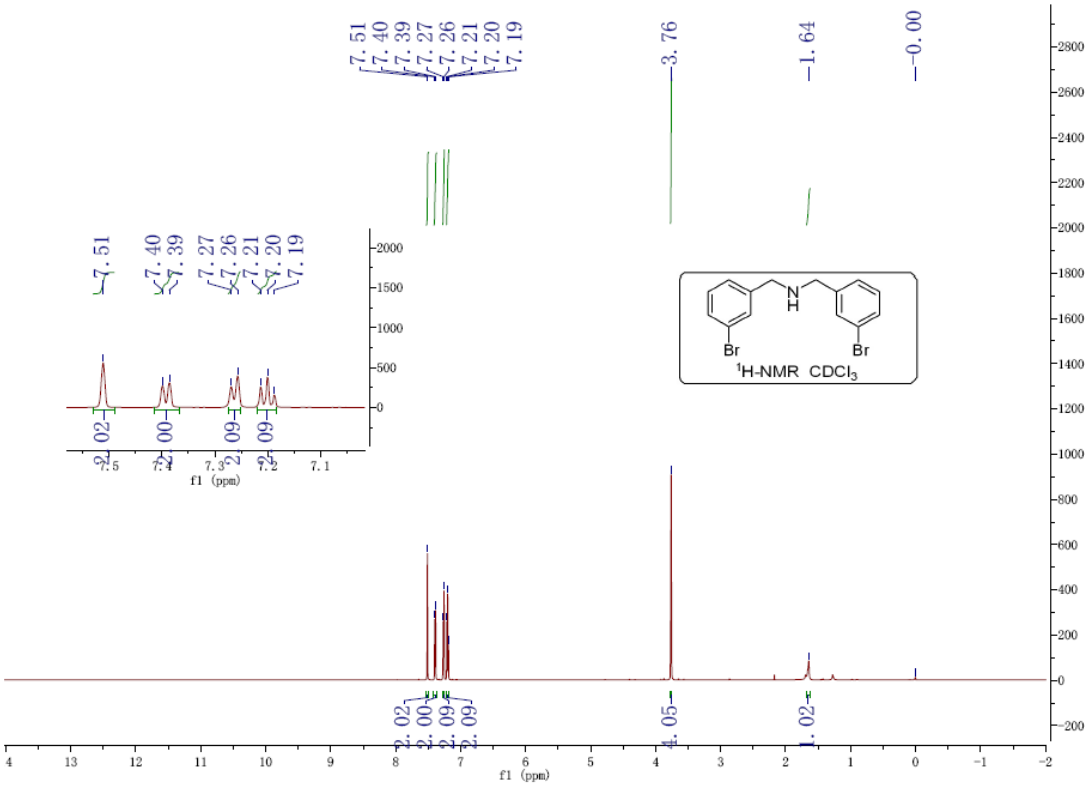
bis(3-chlorobenzyl)amine (2l)

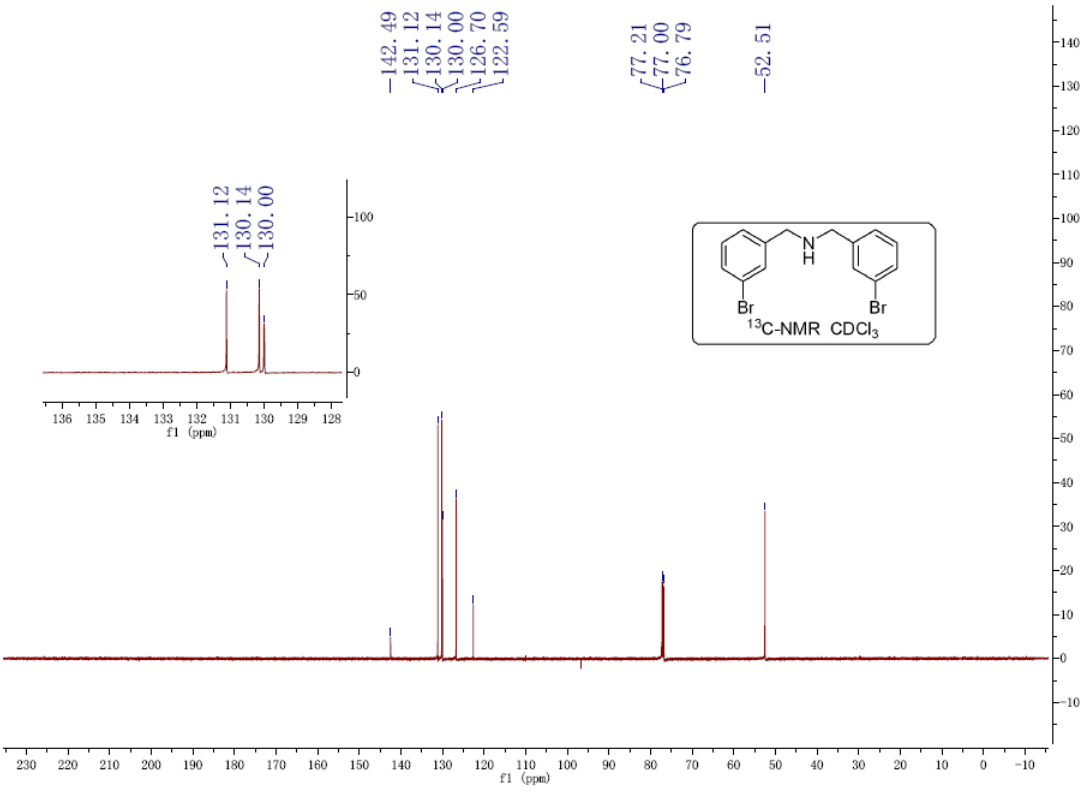


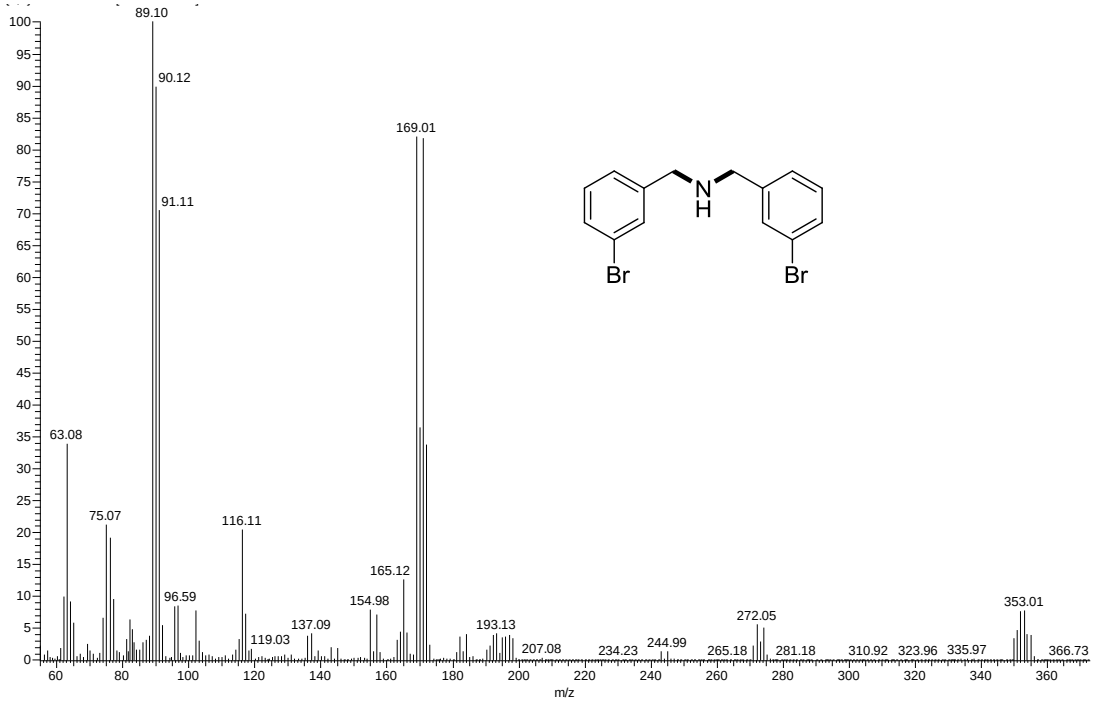

142.16
134.25
129.63
128.13
127.15
126.16
77.21
77.00
76.79
52.50
Cl
Cl
^{13}C-NMR CDCl$_3$
f1 (ppm)


125.06
140.07
91.09
89.07
127.07
142.08
63.07
77.09
99.04
128.09
154.08
62.08
65.09
78.11
111.05
138.06
152.08
156.09
166.14
192.15
199.08
207.10
230.14
246.06
264.08
268.09
281.13
m/z
Cl
Cl

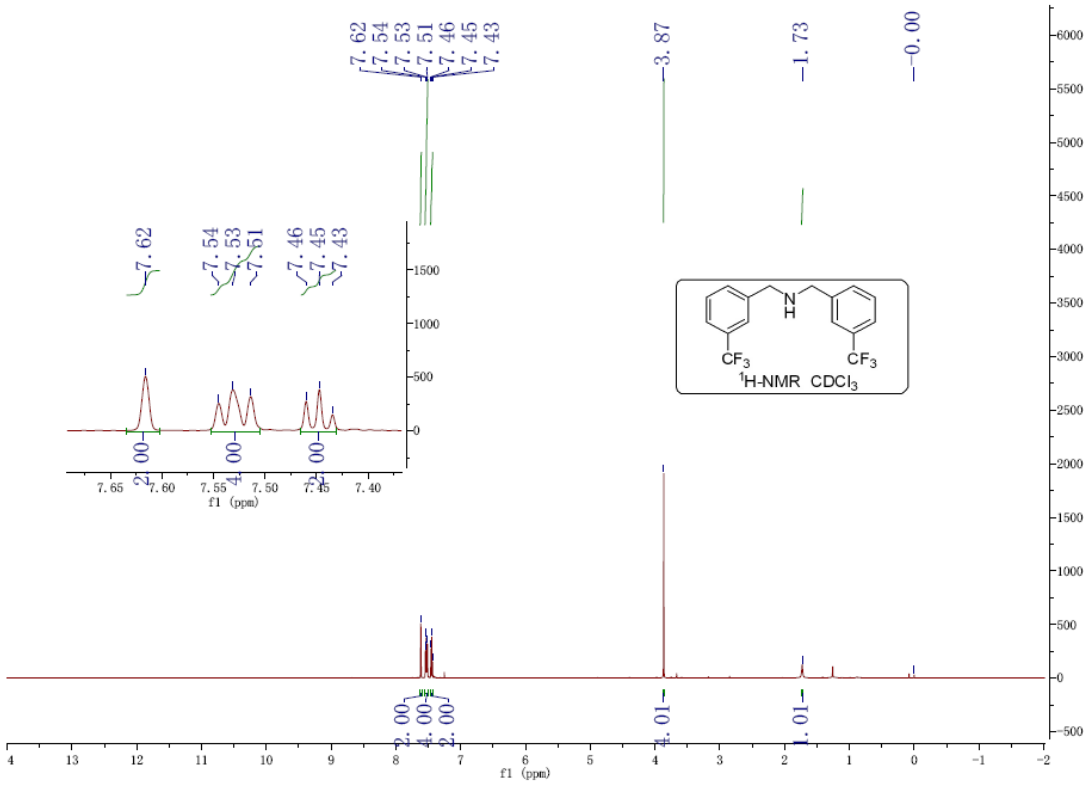
bis(3-bromobenzyl)amine (2m)

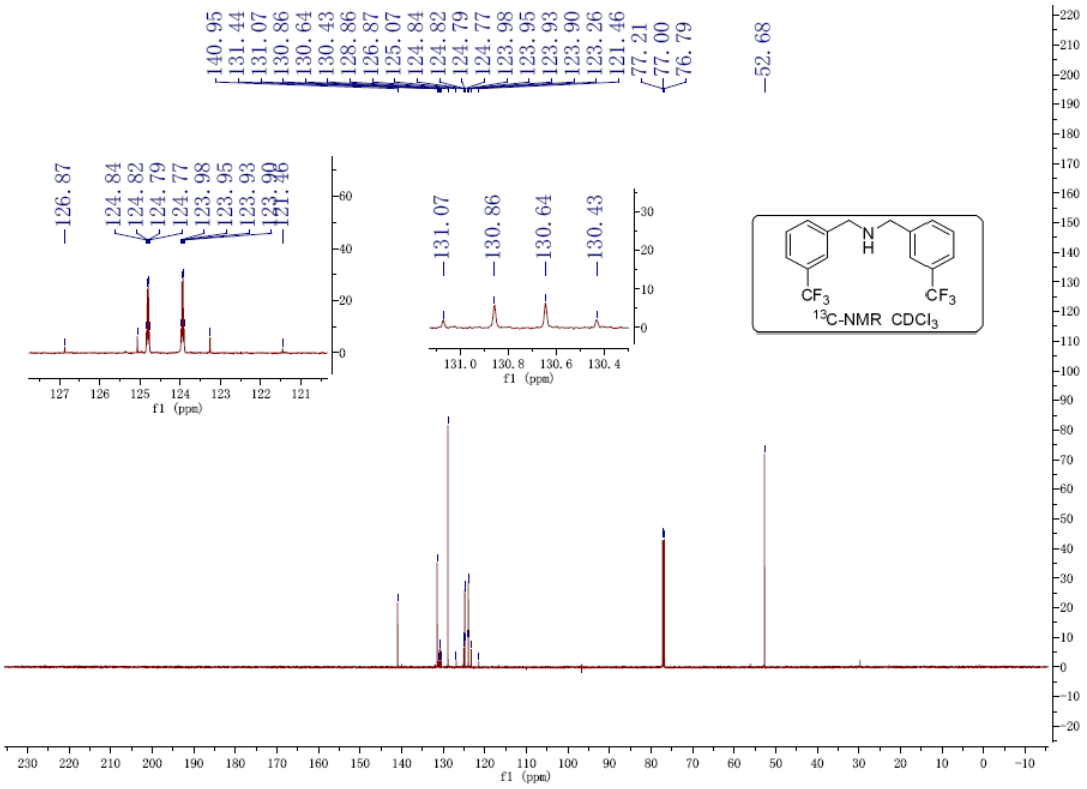


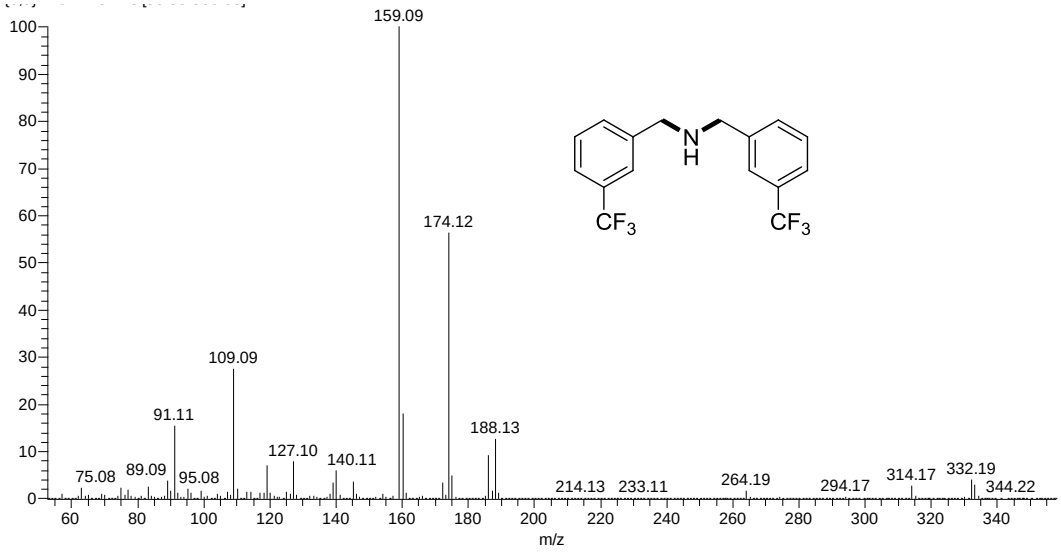




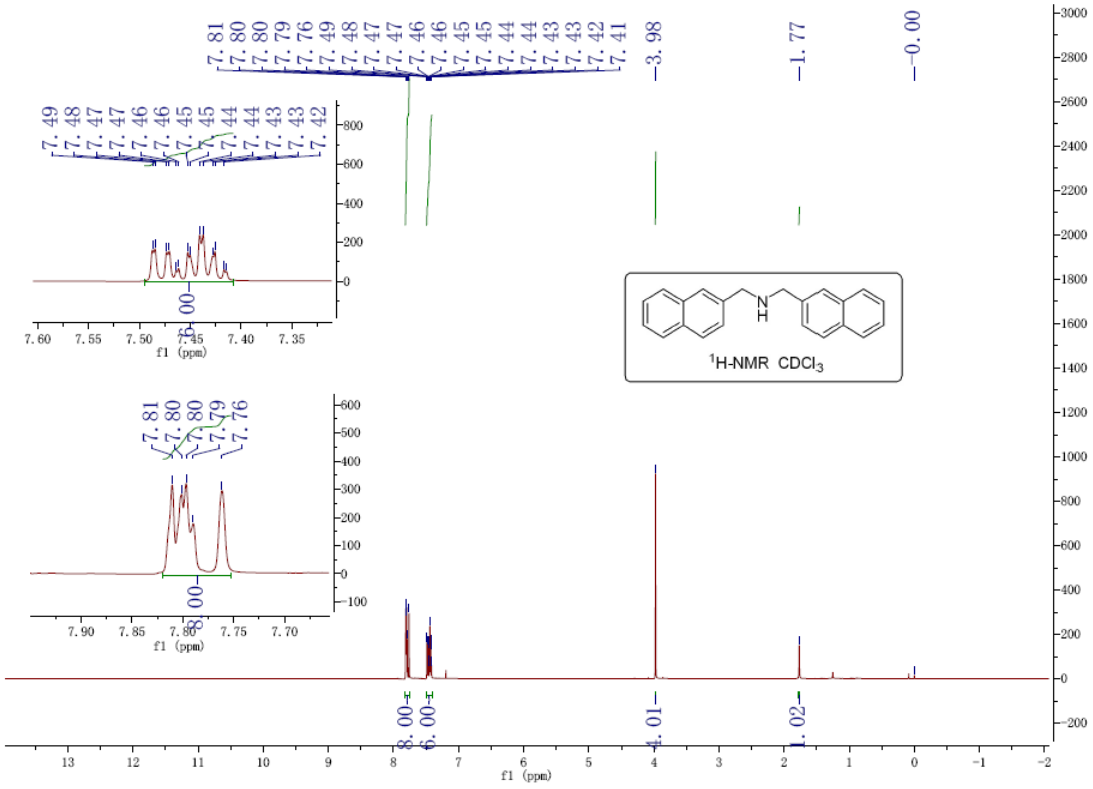
bis(3-(trifluoromethyl)benzyl)amine (2n)

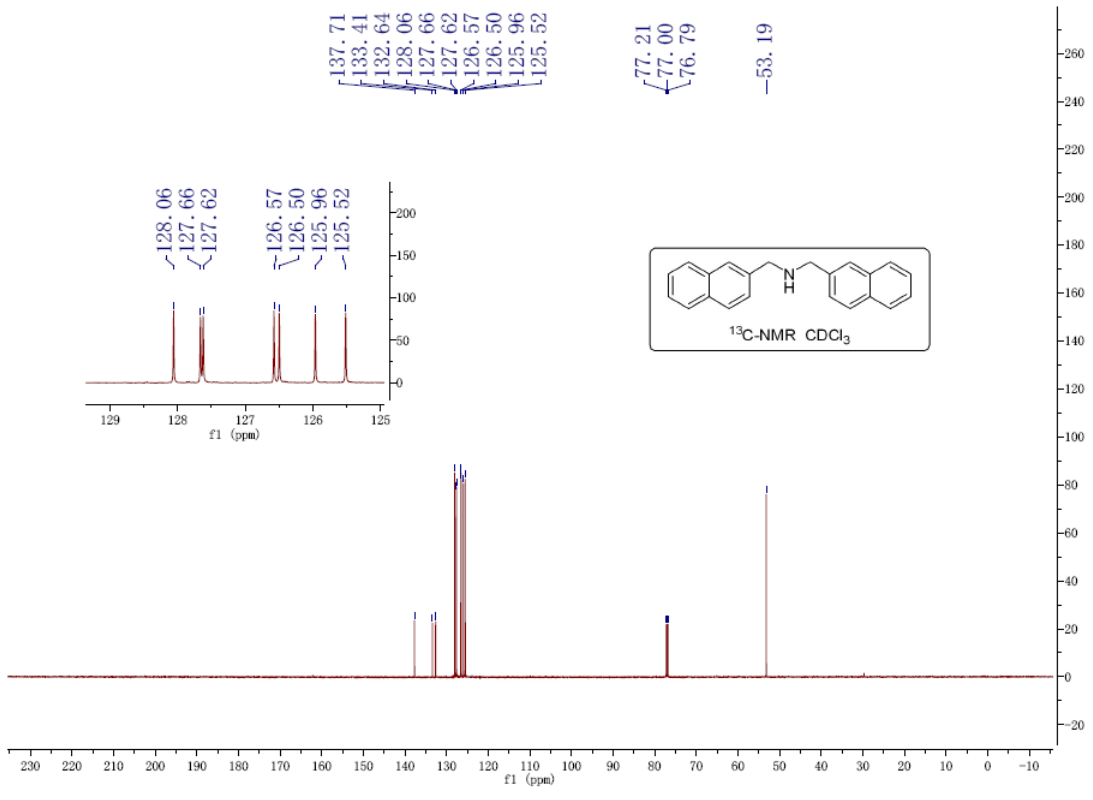


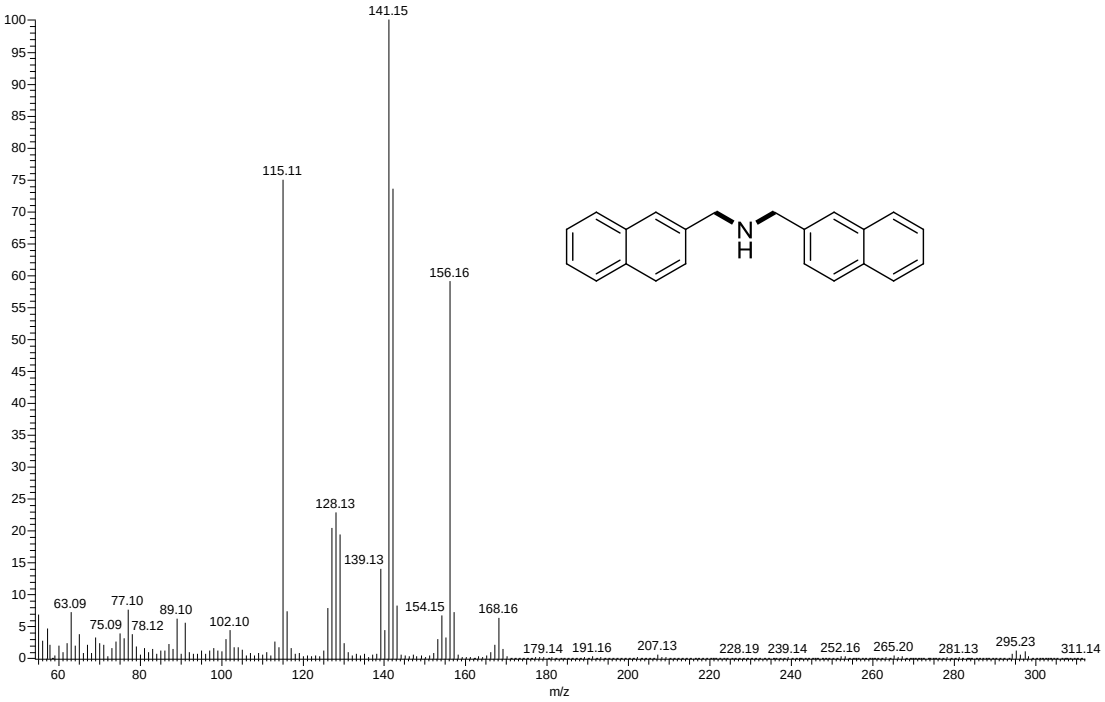

140.95
131.44
131.07
130.86
130.64
130.43
128.86
126.87
125.07
124.84
124.82
124.79
124.77
123.98
123.95
123.93
123.90
123.26
121.46
77.21
77.00
76.79
52.68
126.87
124.84
124.82
124.79
124.77
123.98
123.95
123.93
131.07
130.86
130.64
130.43
f1 (ppm)
CF3
CF3
13C-NMR CDCl3


159.09
174.12
109.09
91.11
188.13
127.10
140.11
75.08
89.09
95.08
214.13
233.11
264.19
294.17
314.17
332.19
344.22
m/z
CF3
CF3

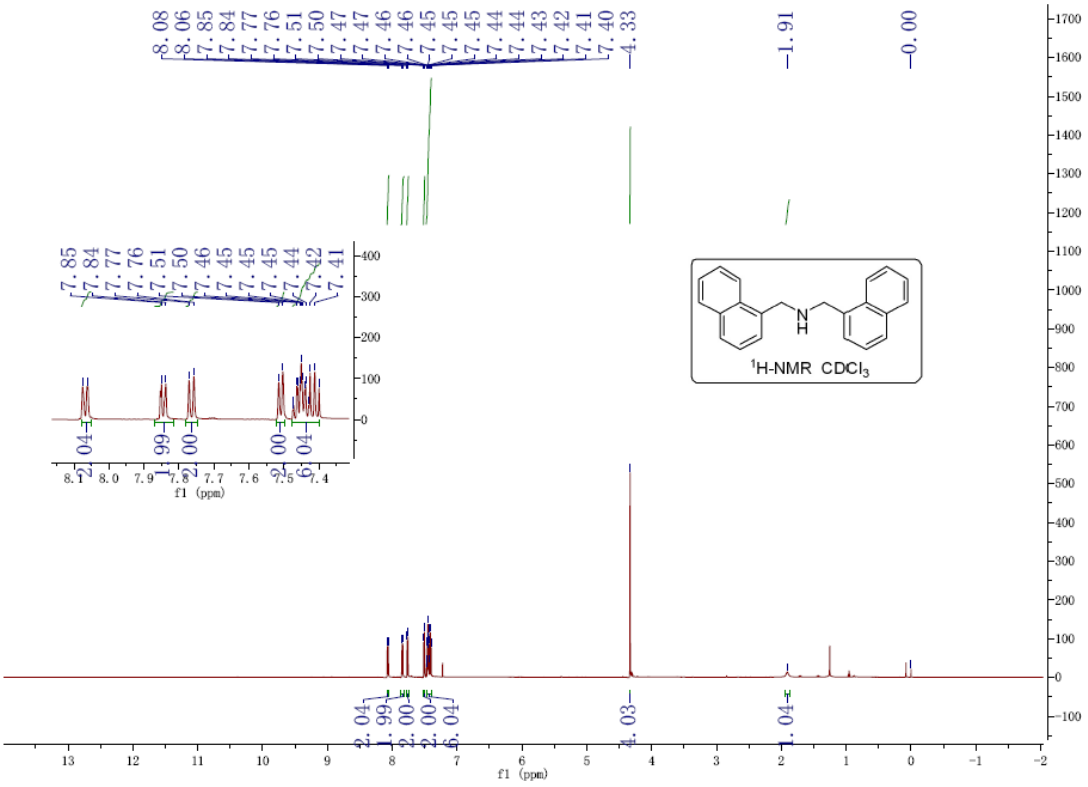
bis(naphthalen-2-ylmethyl)amine (2o)

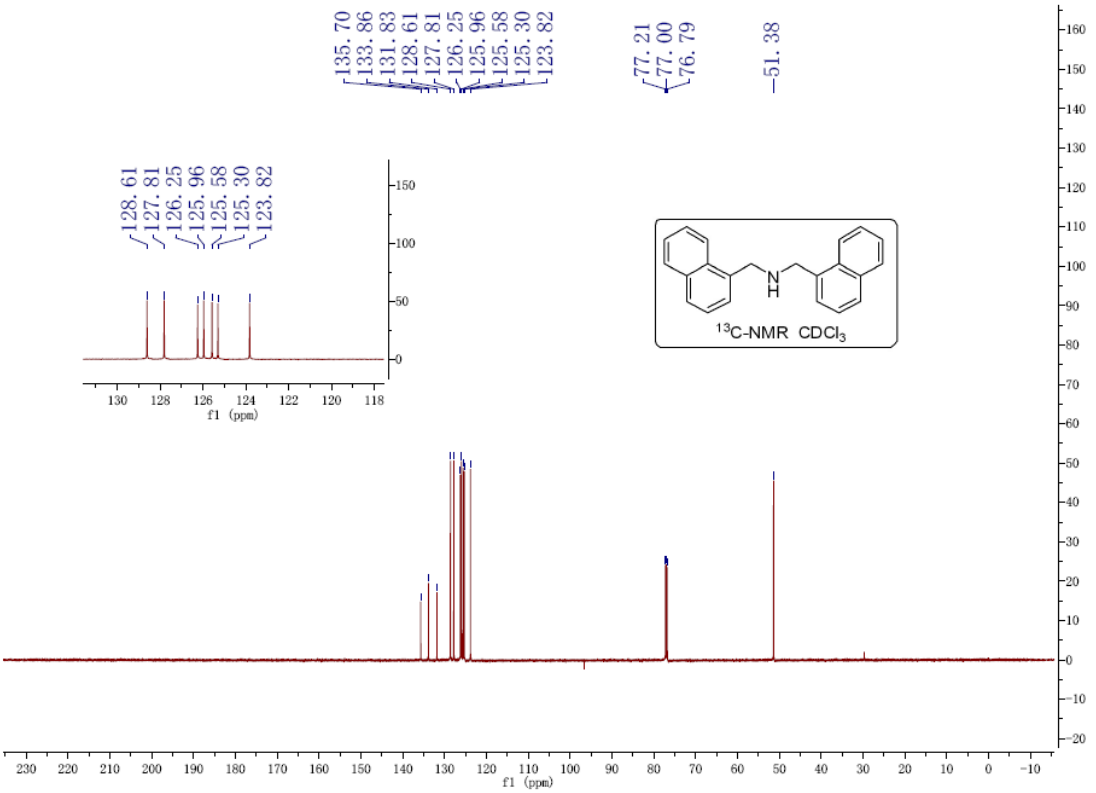


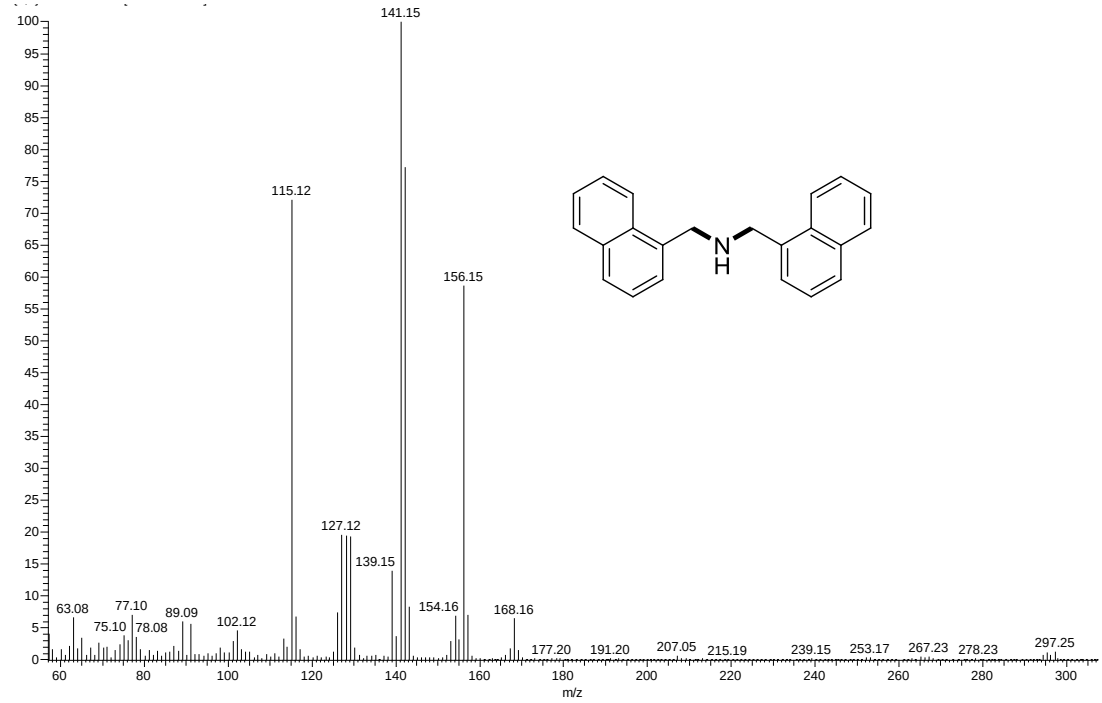




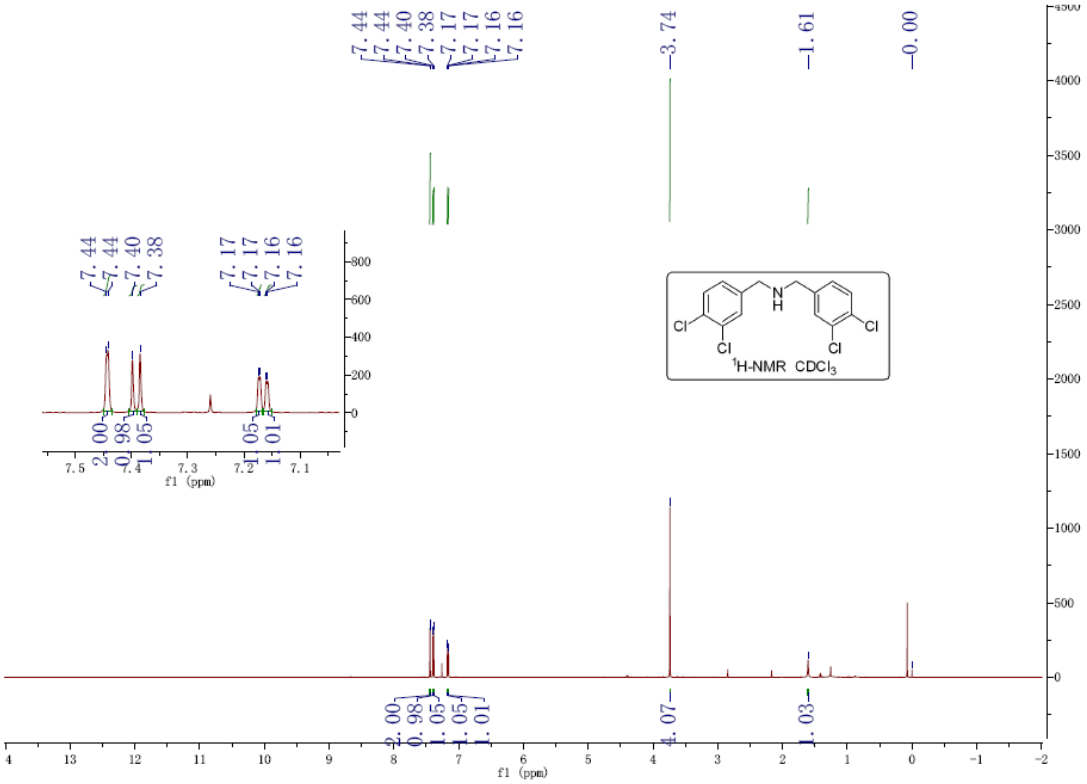
bis(naphthalen-1-ylmethyl)amine (2p)

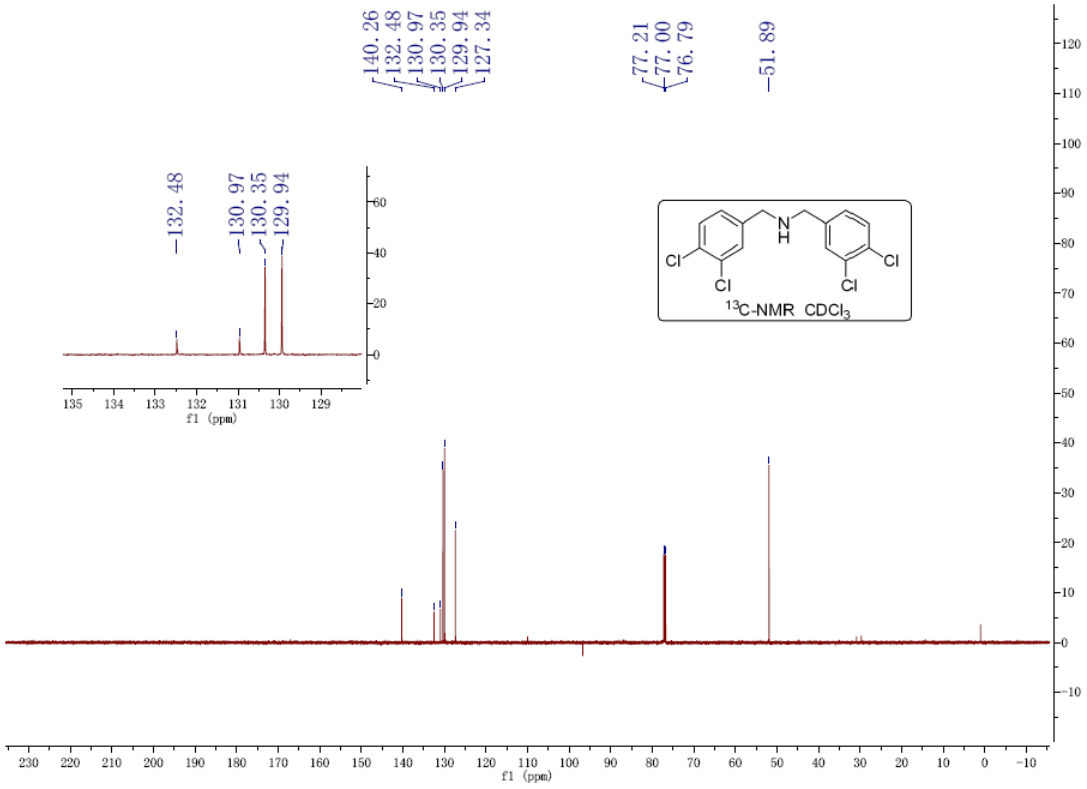


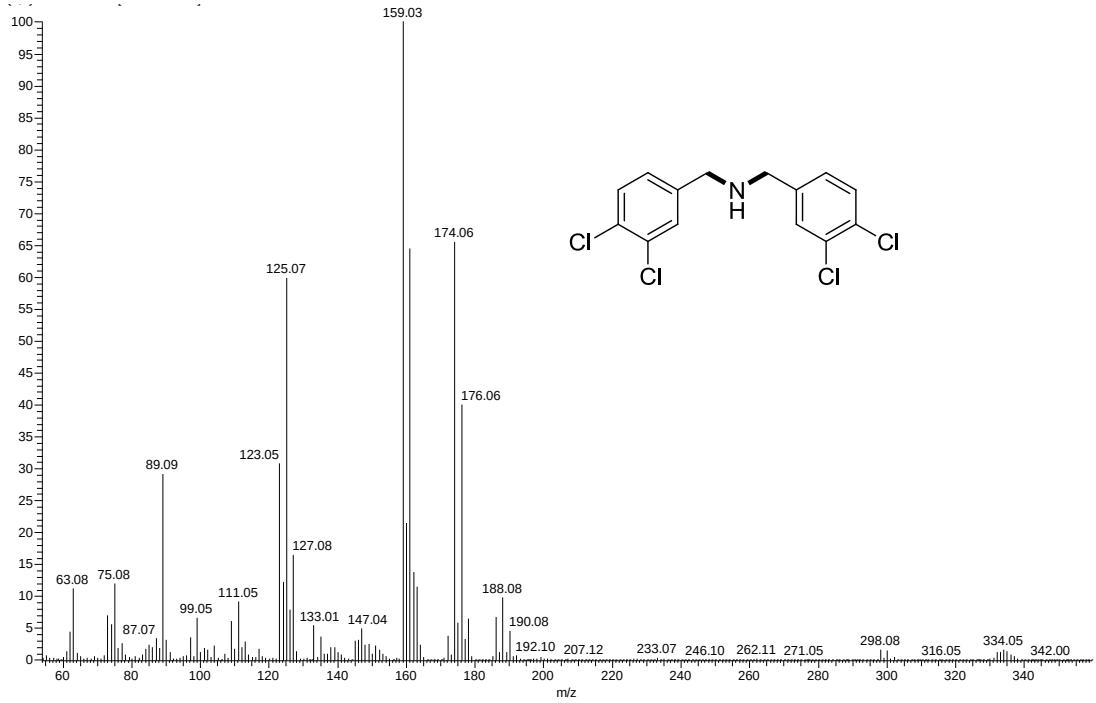

135.70
133.86
131.83
128.61
127.81
126.25
125.96
125.58
125.30
123.82
77.21
77.00
76.79
51.38
128.61
127.81
126.25
125.96
125.58
125.30
123.82
f1 (ppm)
13C-NMR CDCl3
f1 (ppm)


141.15
115.12
156.15
127.12
139.15
154.16
168.16
63.08
77.10
75.10
78.08
89.09
102.12
177.20
191.20
207.05
215.19
239.15
253.17
267.23
278.23
297.25
m/z

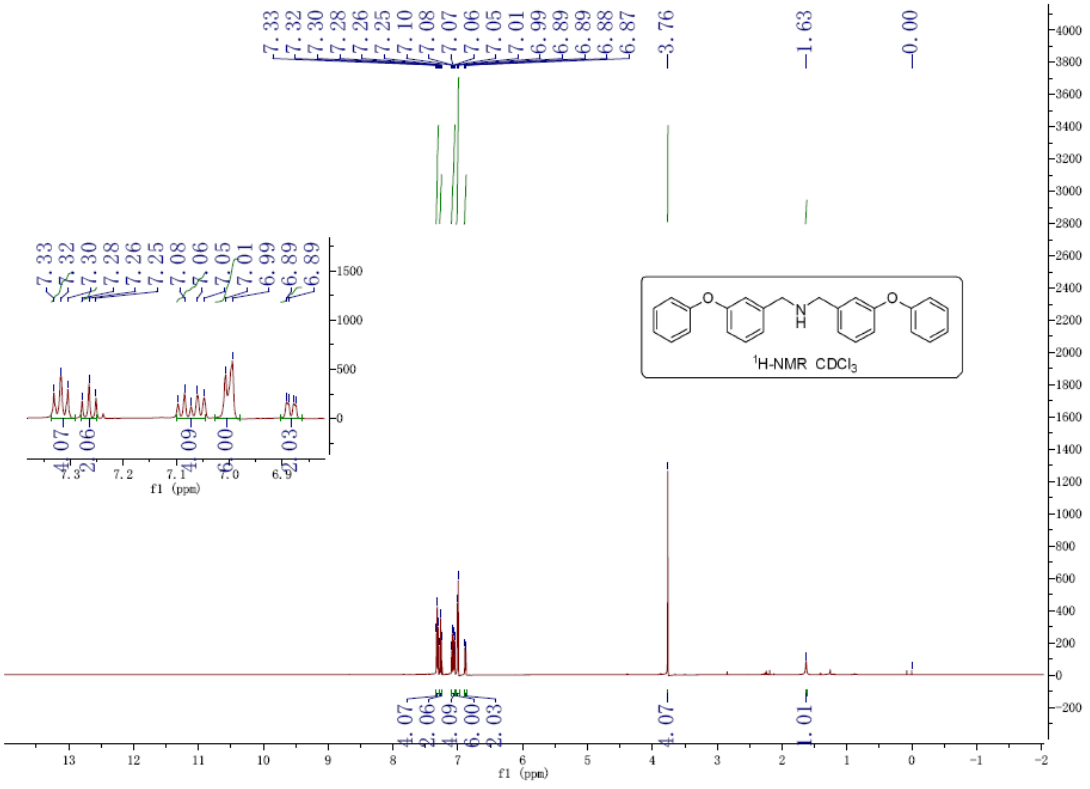
bis(3,4-dichlorobenzyl)amine (2q)

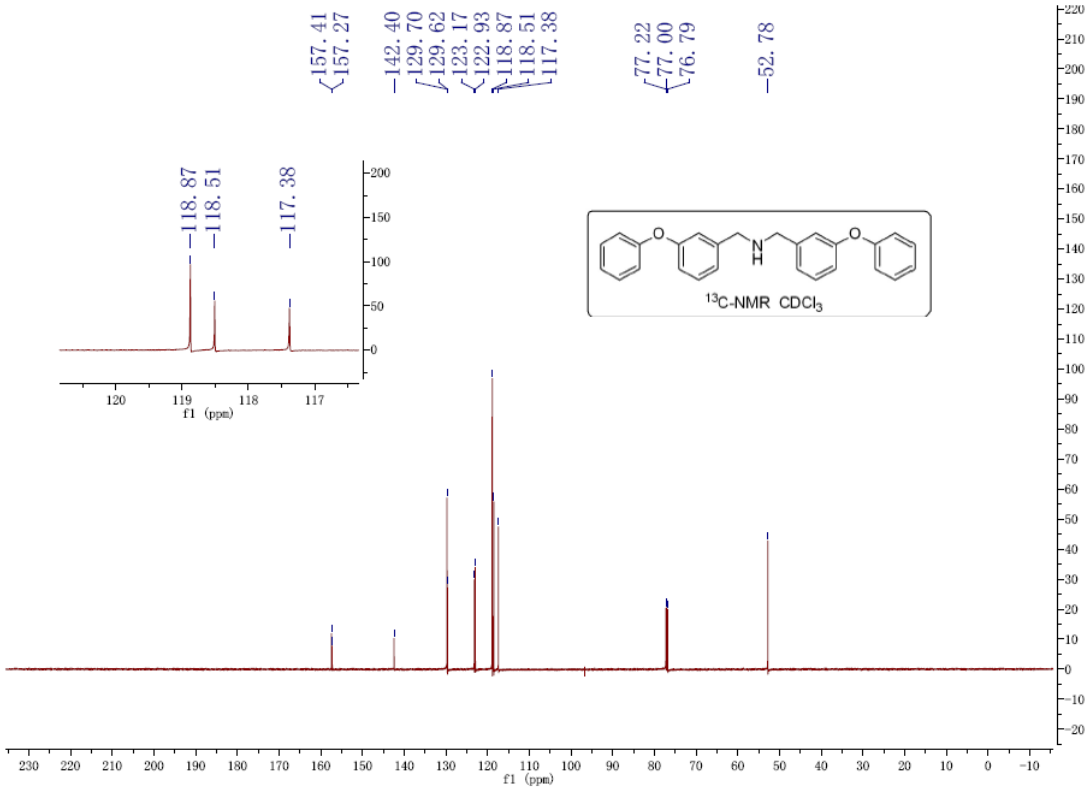




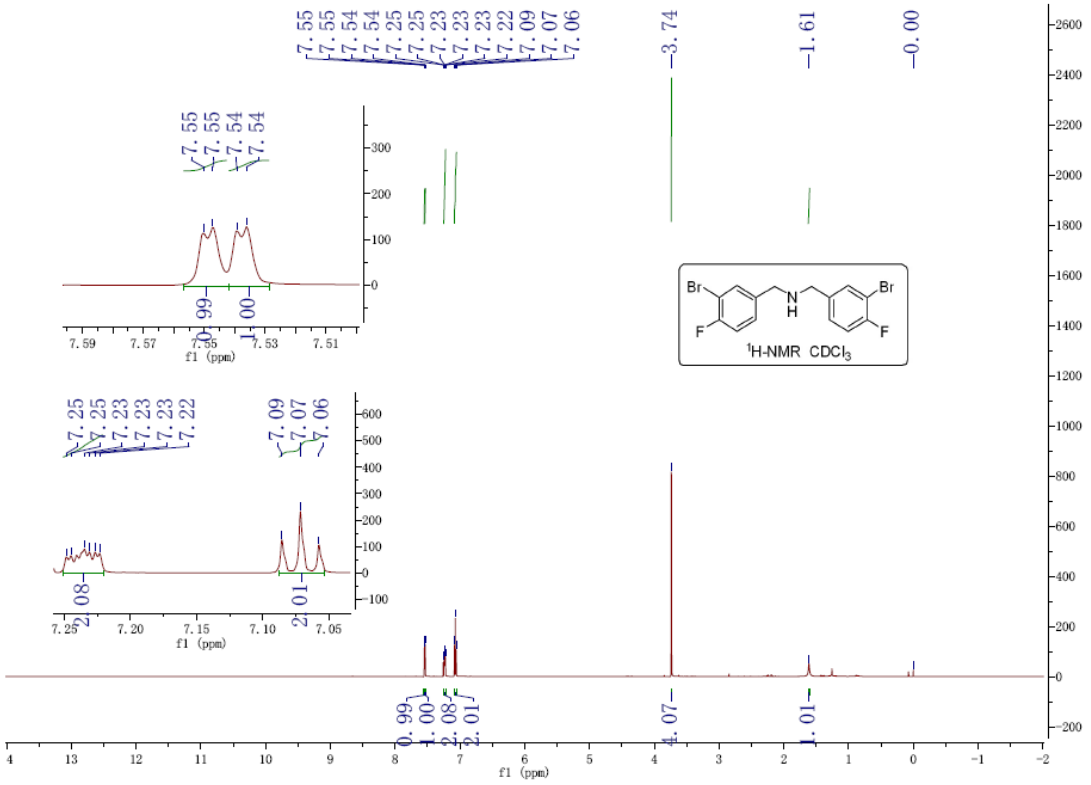


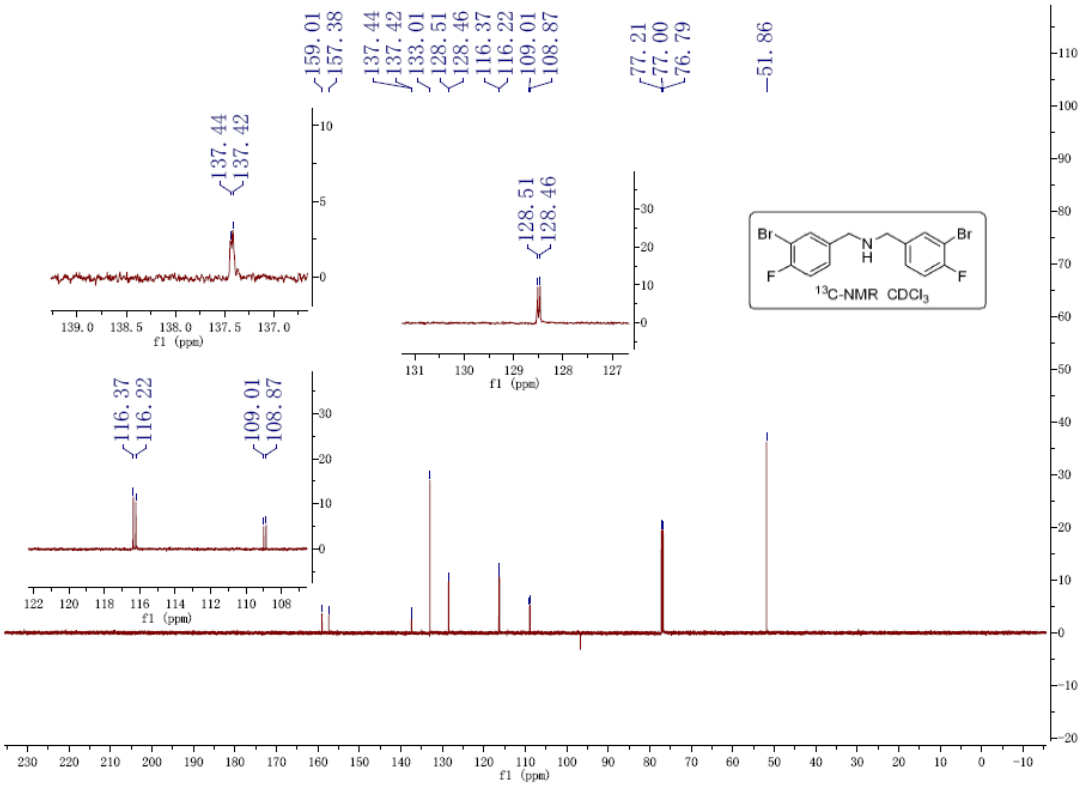
bis(3-phenoxybenzyl)amine (2r)



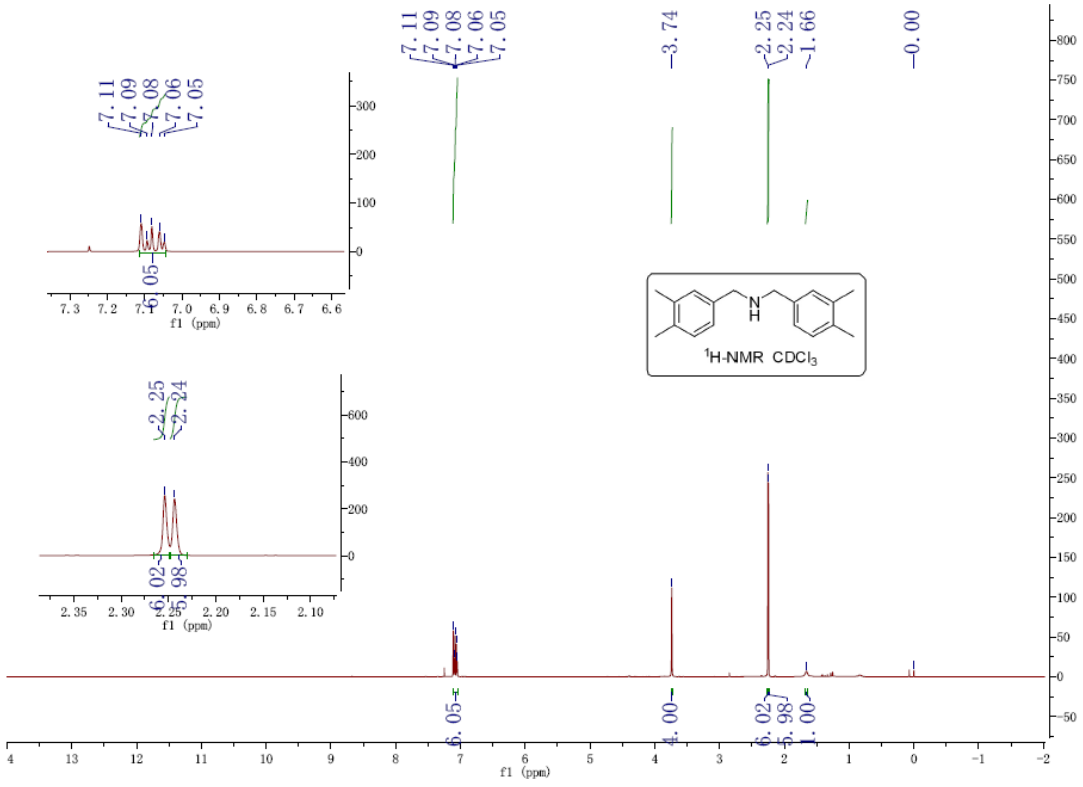


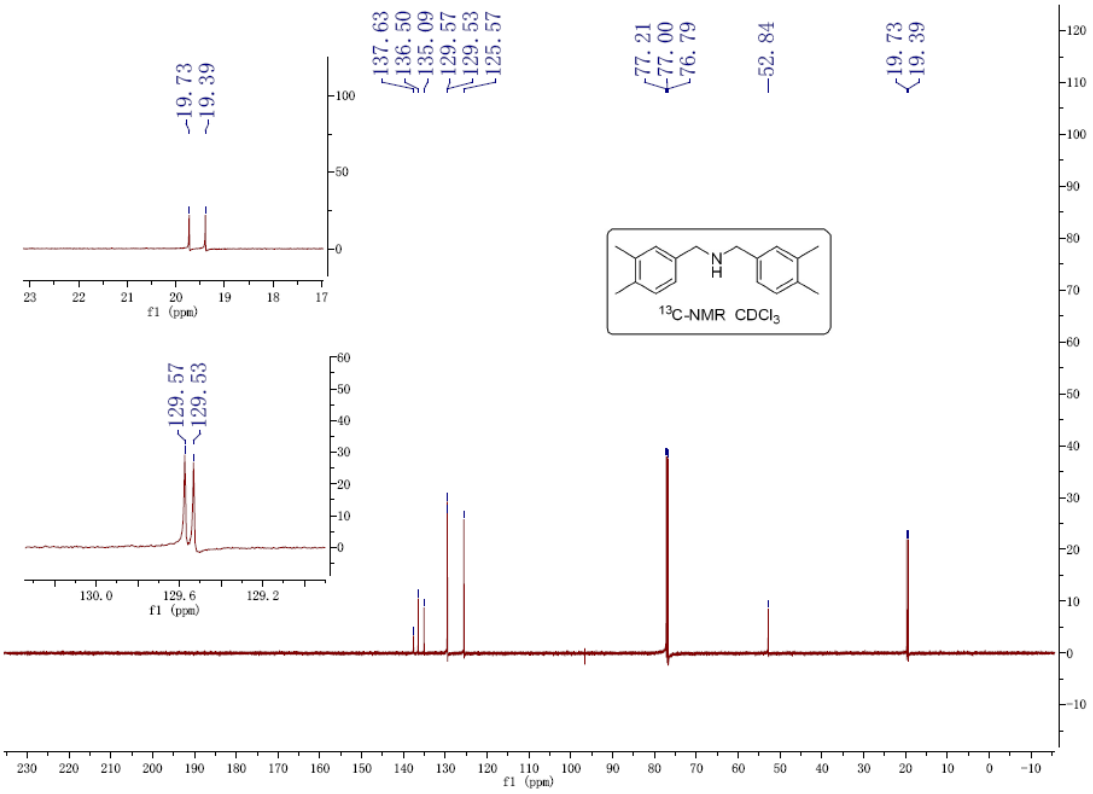
bis(3-bromo-4-fluorobenzyl)amine (2s)



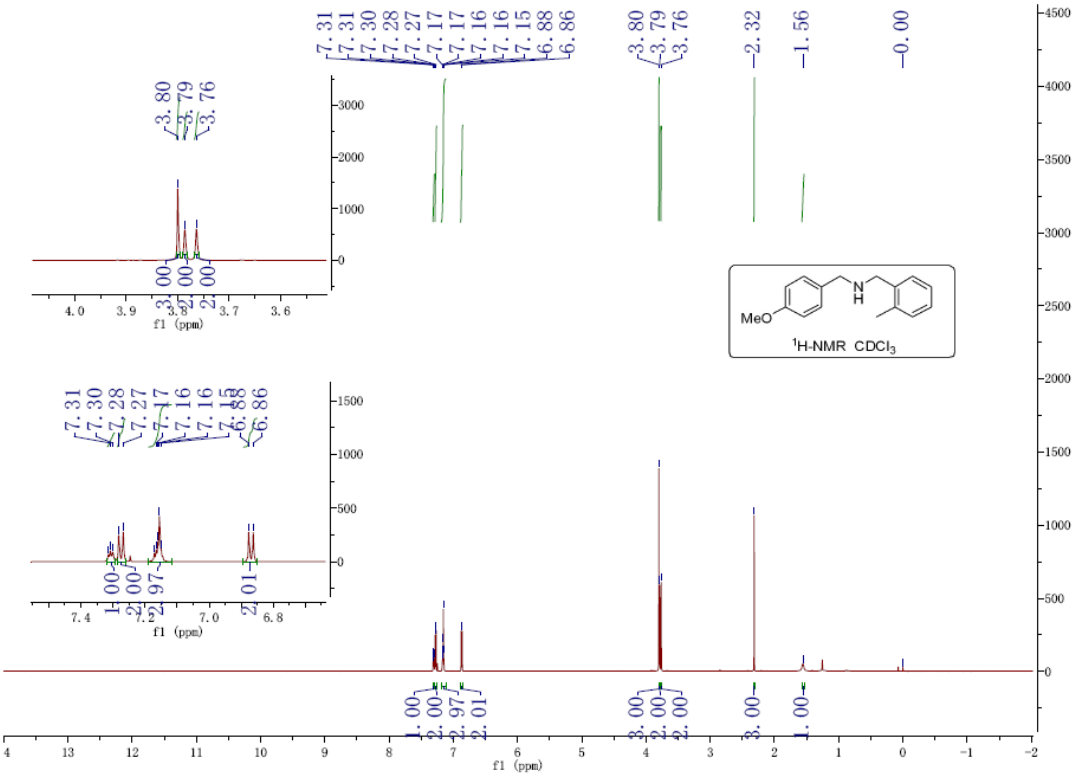


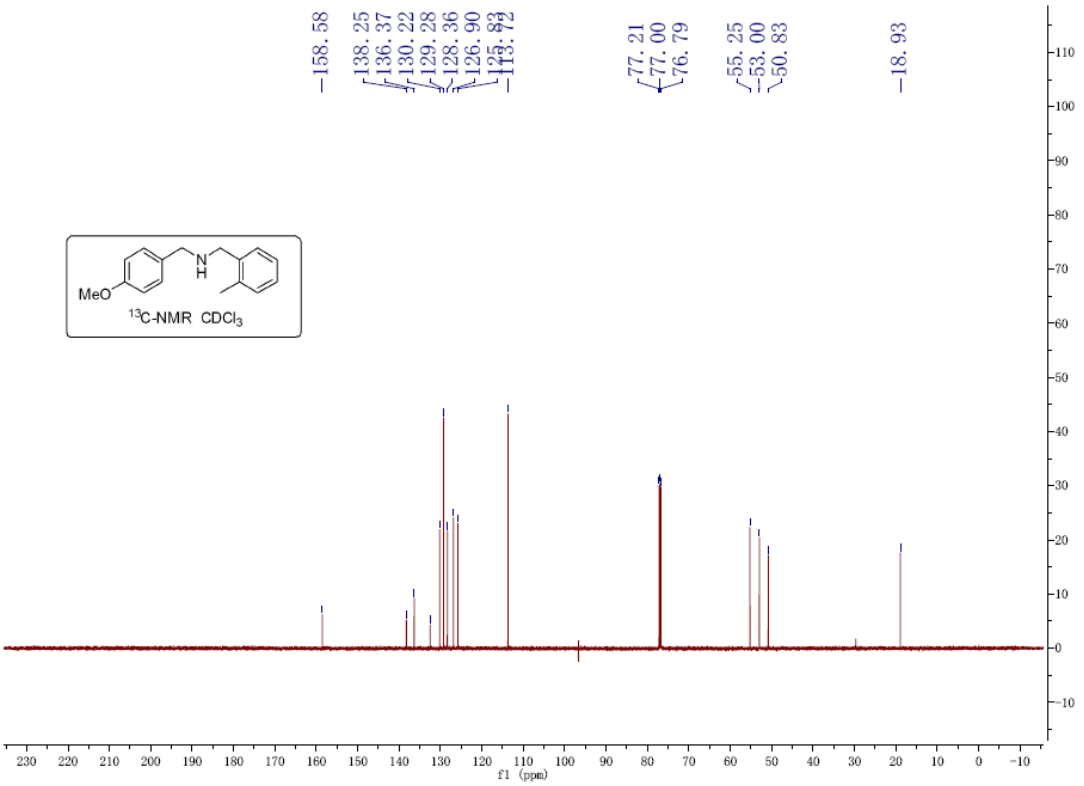
bis(3,4-dimethylbenzyl)amine (2t)

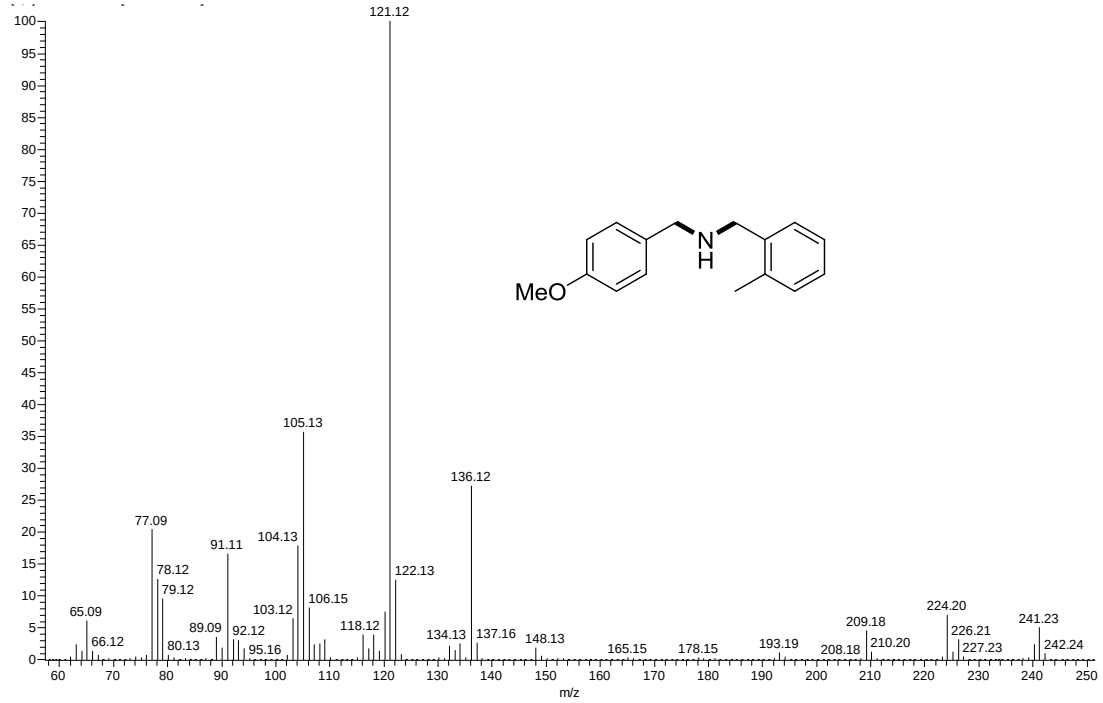




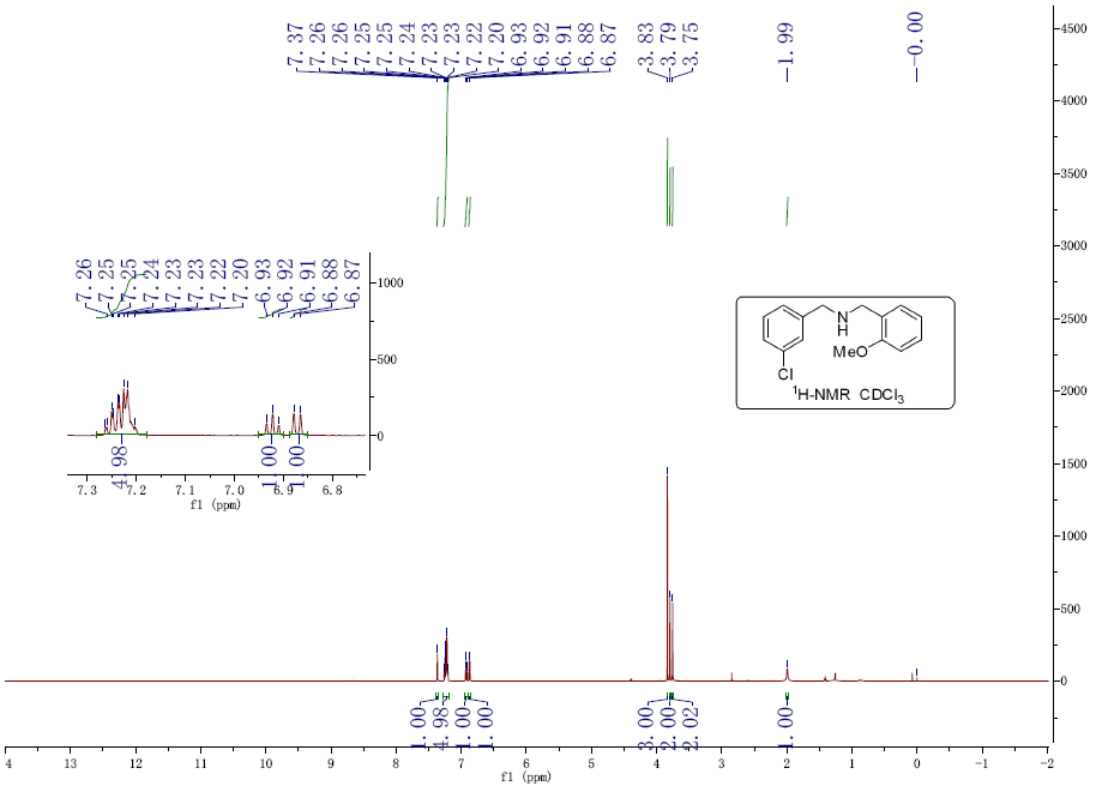
N-(4-methoxybenzyl)-1-o-tolylmethanamine (4a)

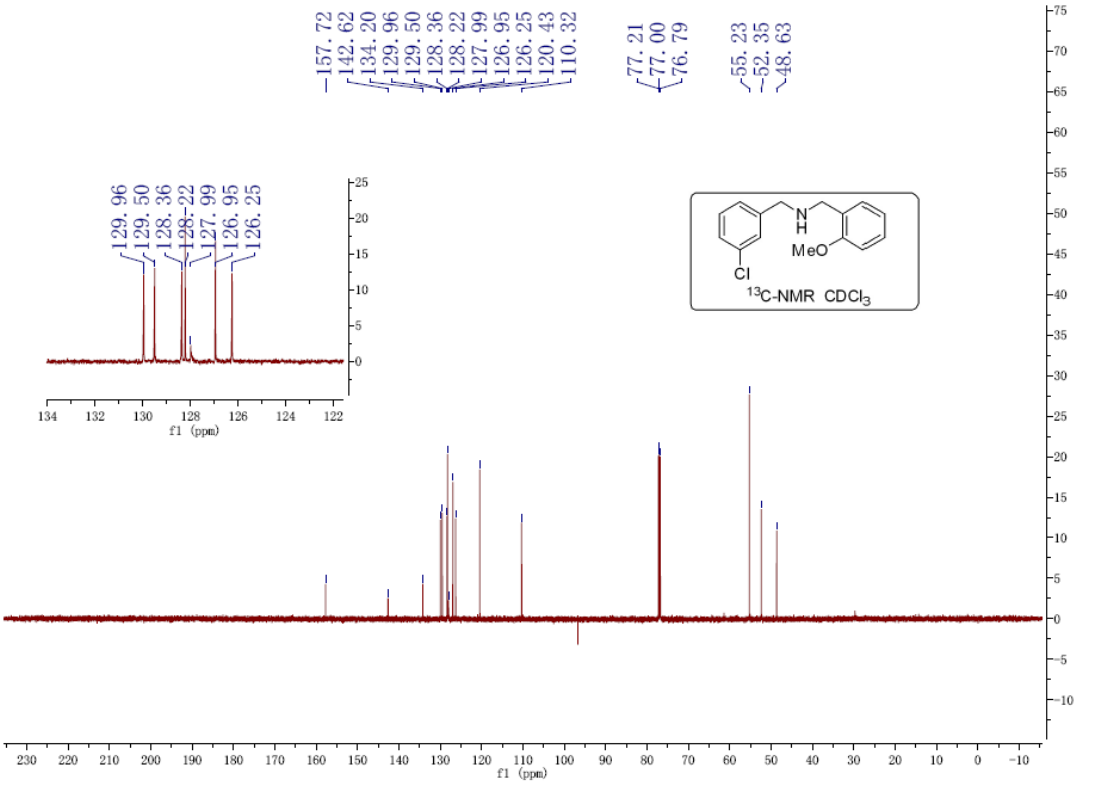



158.58
138.25
136.37
130.22
129.28
128.36
126.90
113.72
77.21
77.00
76.79
55.25
53.00
50.83
18.93
MeO
N
H
13C-NMR CDCl3
f1 (ppm)

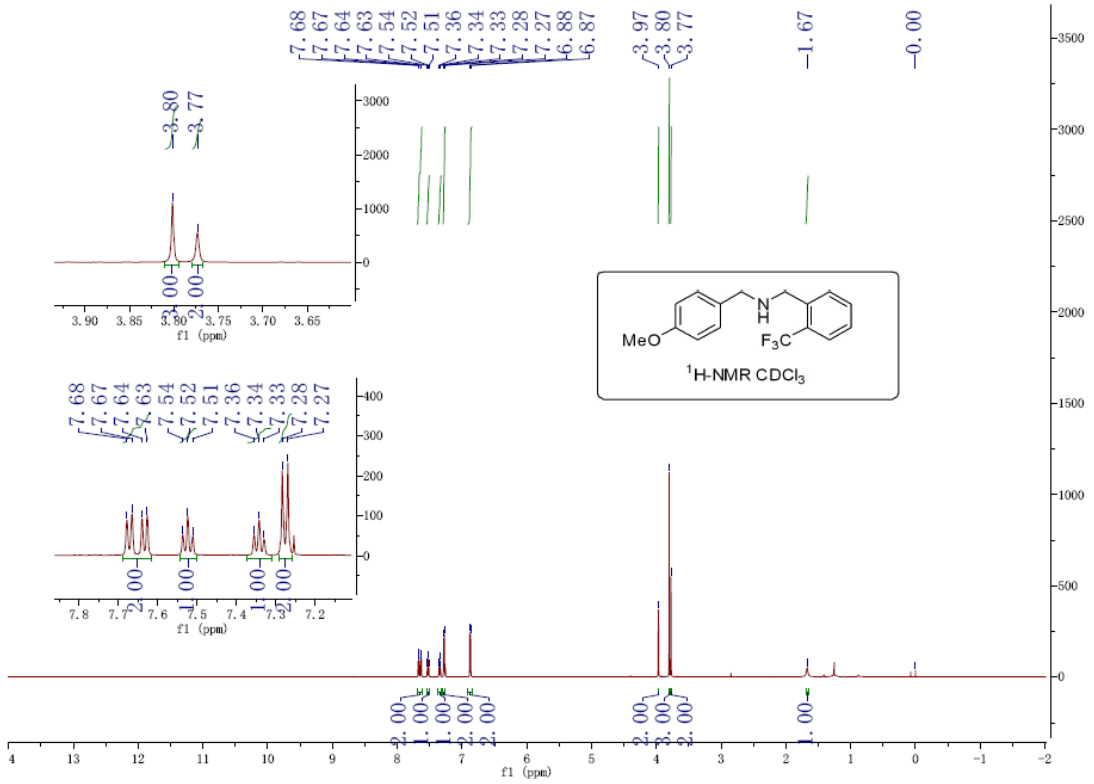

121.12
105.13
136.12
77.09
91.11
104.13
78.12
79.12
122.13
106.15
65.09
103.12
118.12
89.09
92.12
134.13
137.16
148.13
66.12
80.13
95.16
165.15
178.15
193.19
208.18
209.18
210.20
224.20
226.21
227.23
241.23
242.24
MeO
N
H
m/z

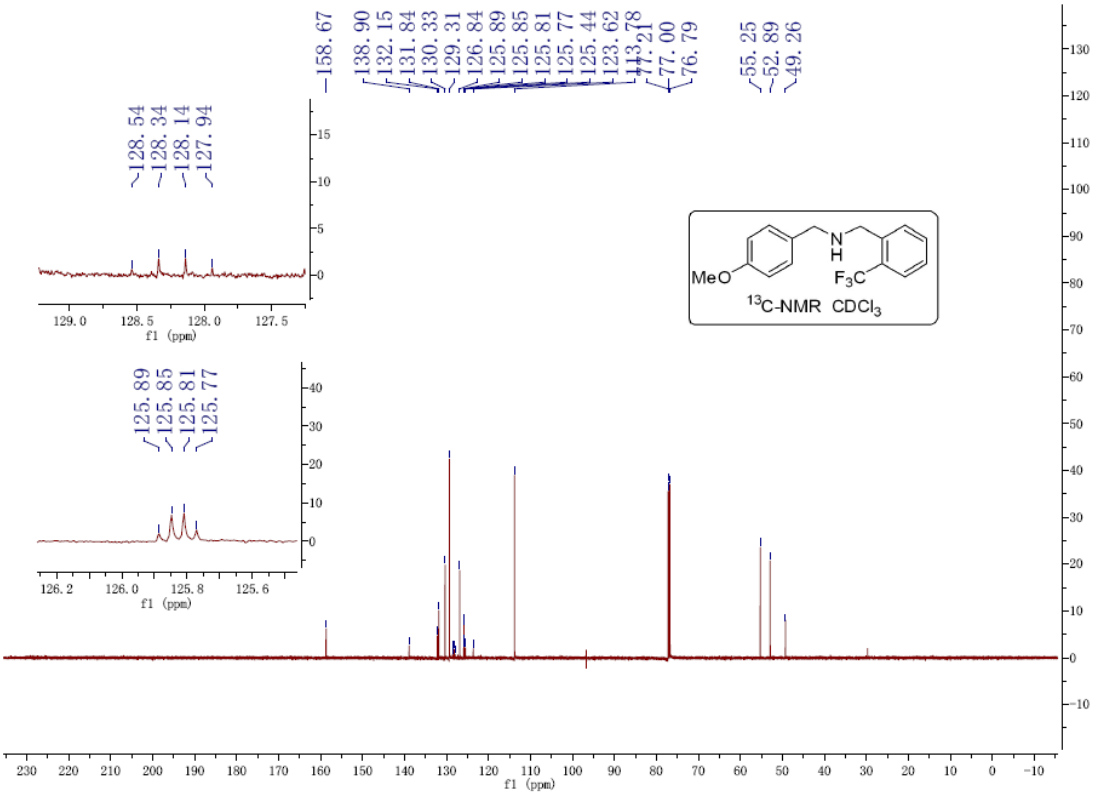
N-(3-chlorobenzyl)-1-(2-methoxyphenyl)methanamine (4b)



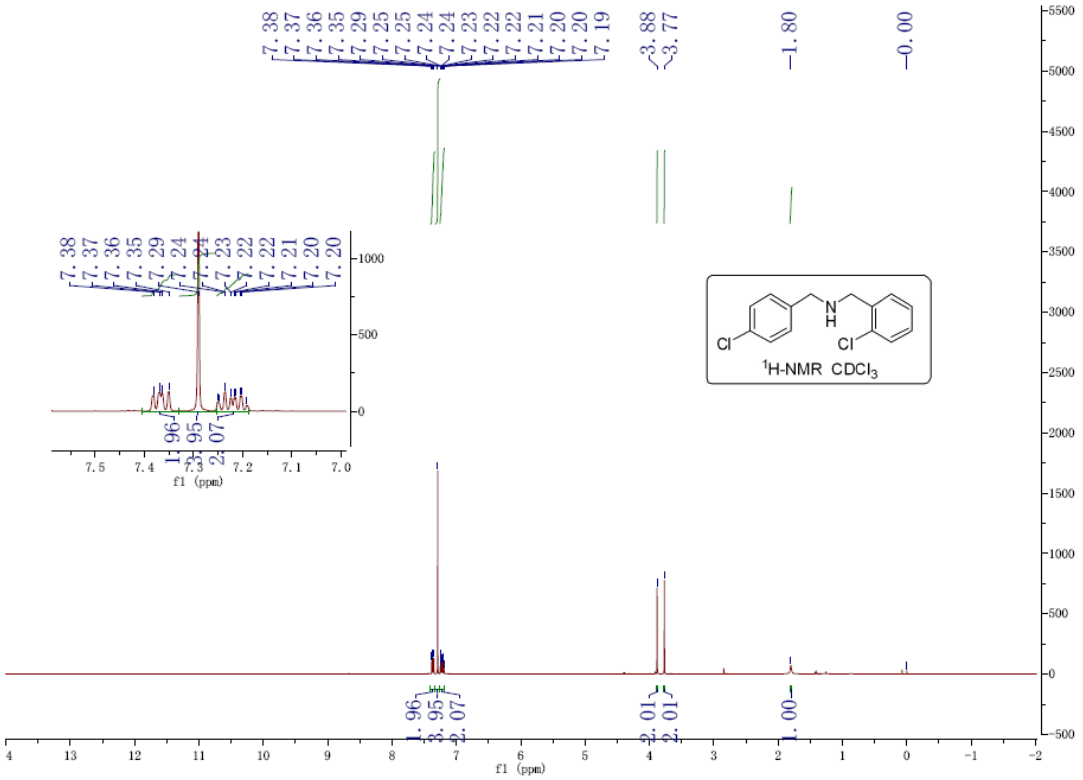


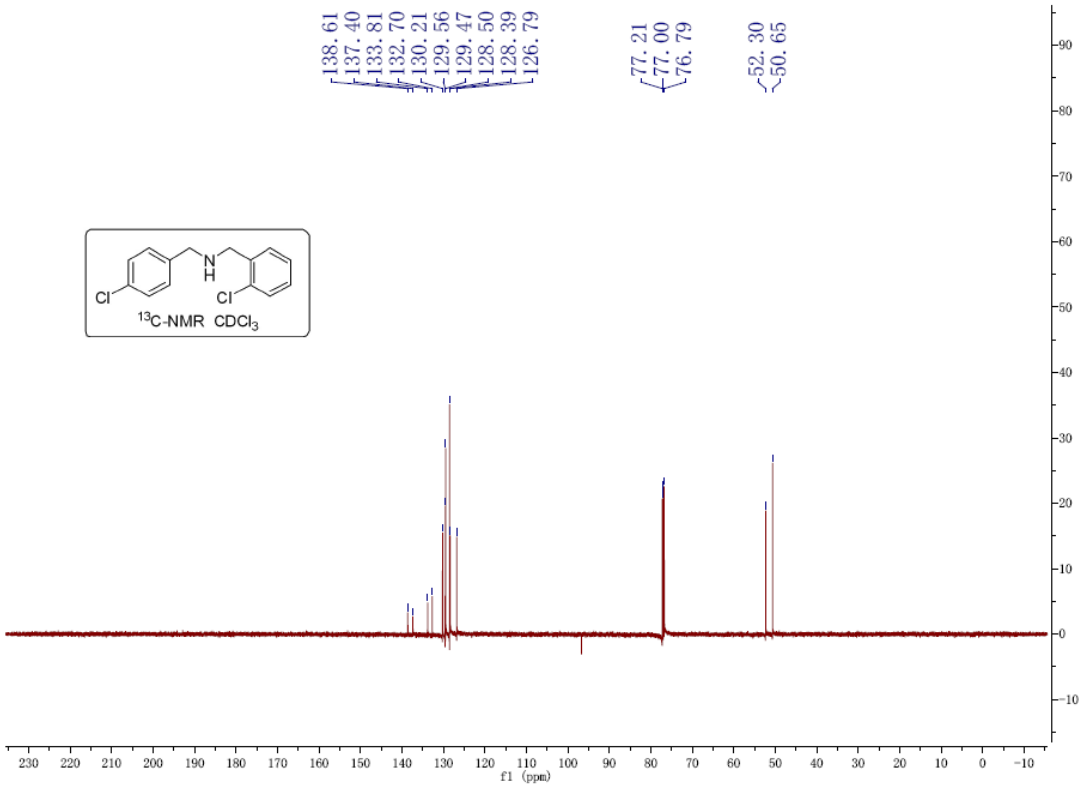
N-(4-methoxybenzyl)-1-(2-(trifluoromethyl)phenyl)methanamine (4c)



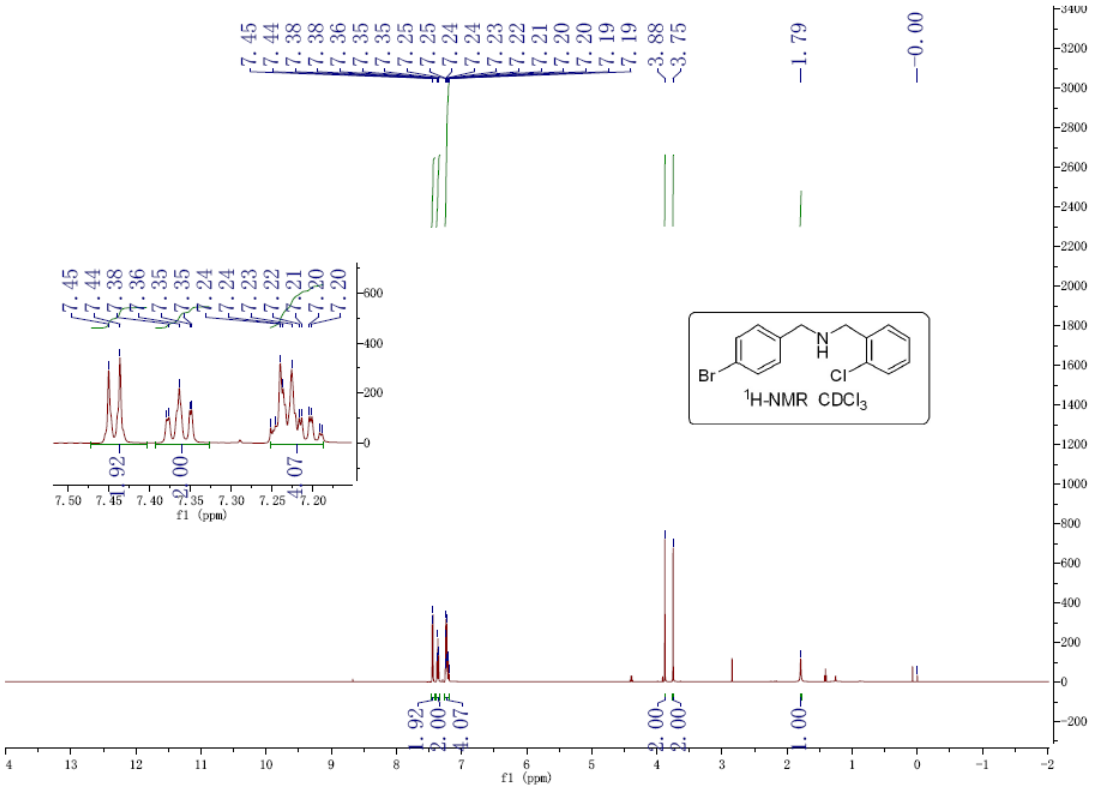


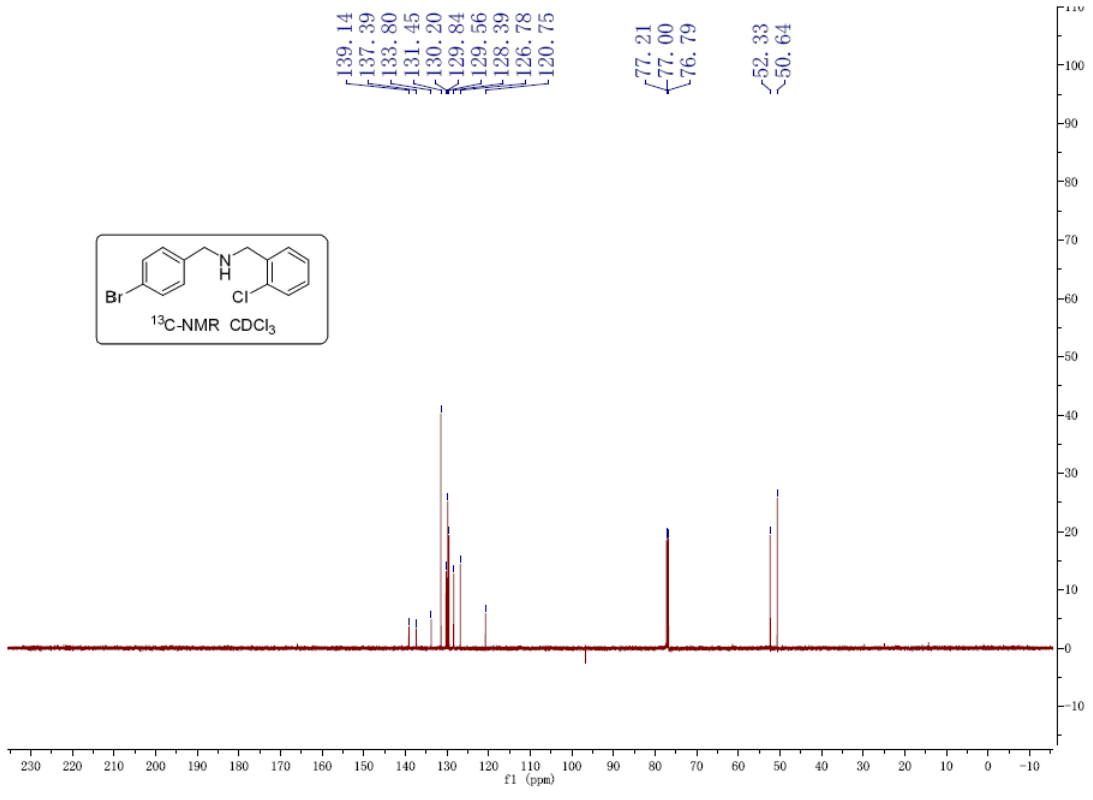
N-(2-chlorobenzyl)-1-(4-chlorophenyl)methanamine (4d)



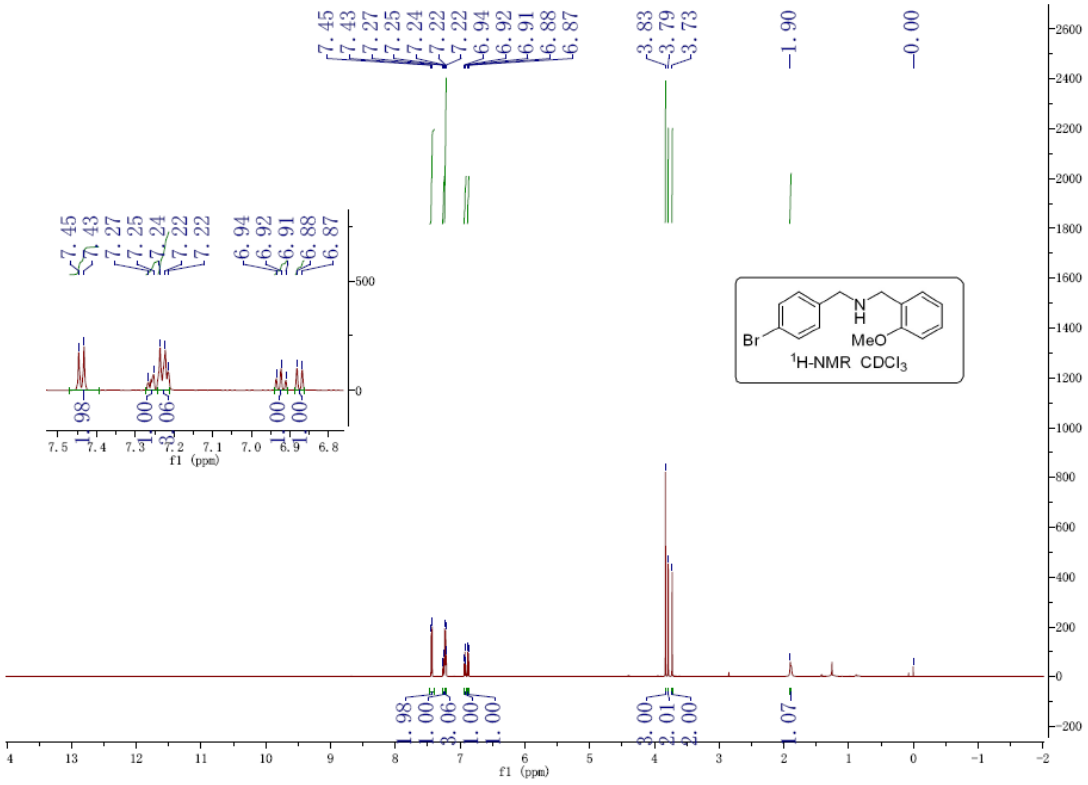


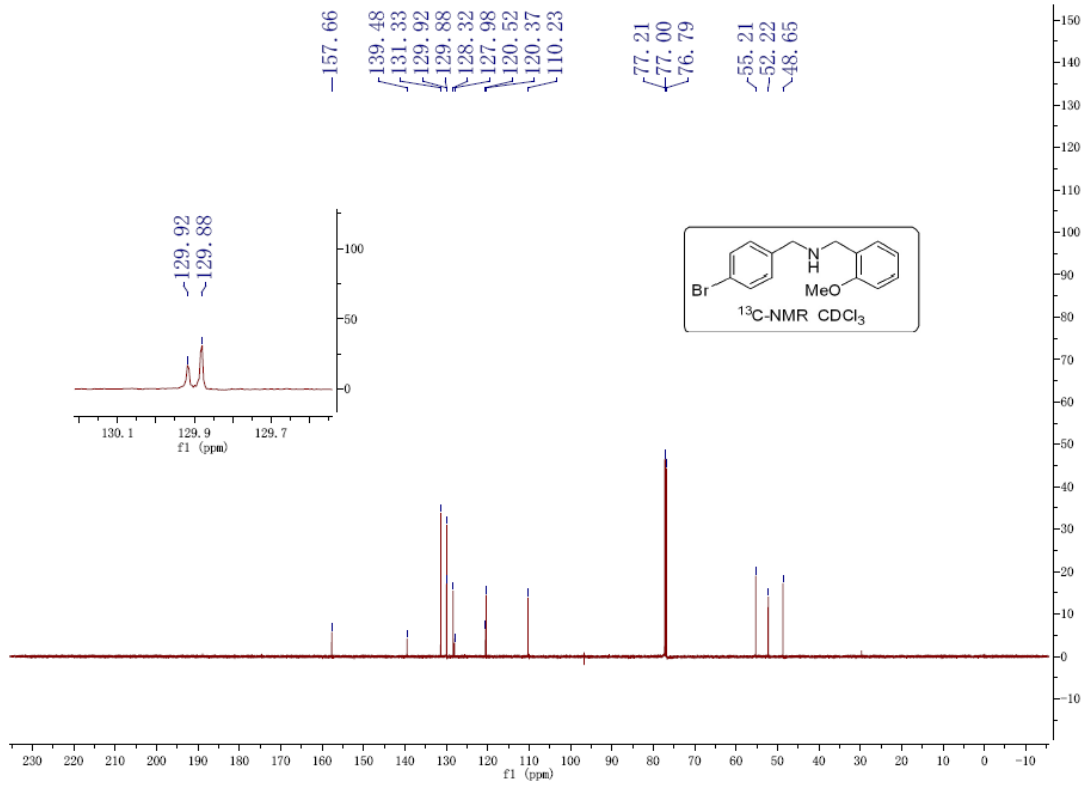
N-(4-bromobenzyl)-1-(2-chlorophenyl)methanamine (4e)



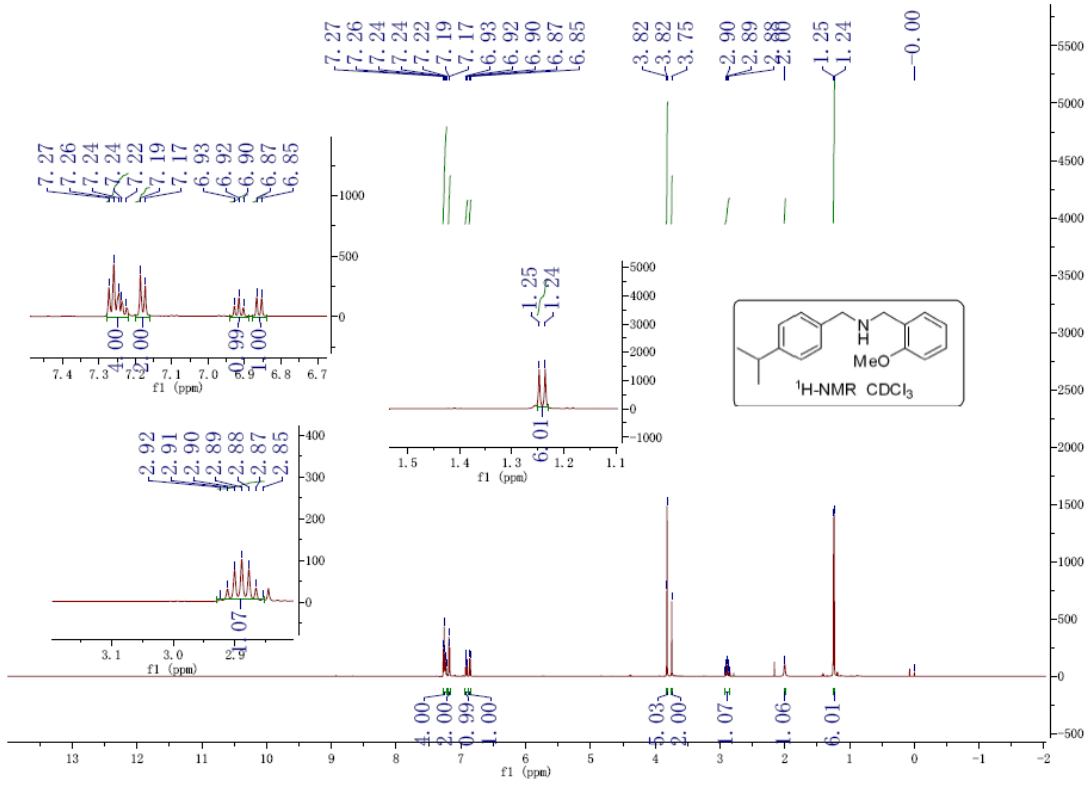


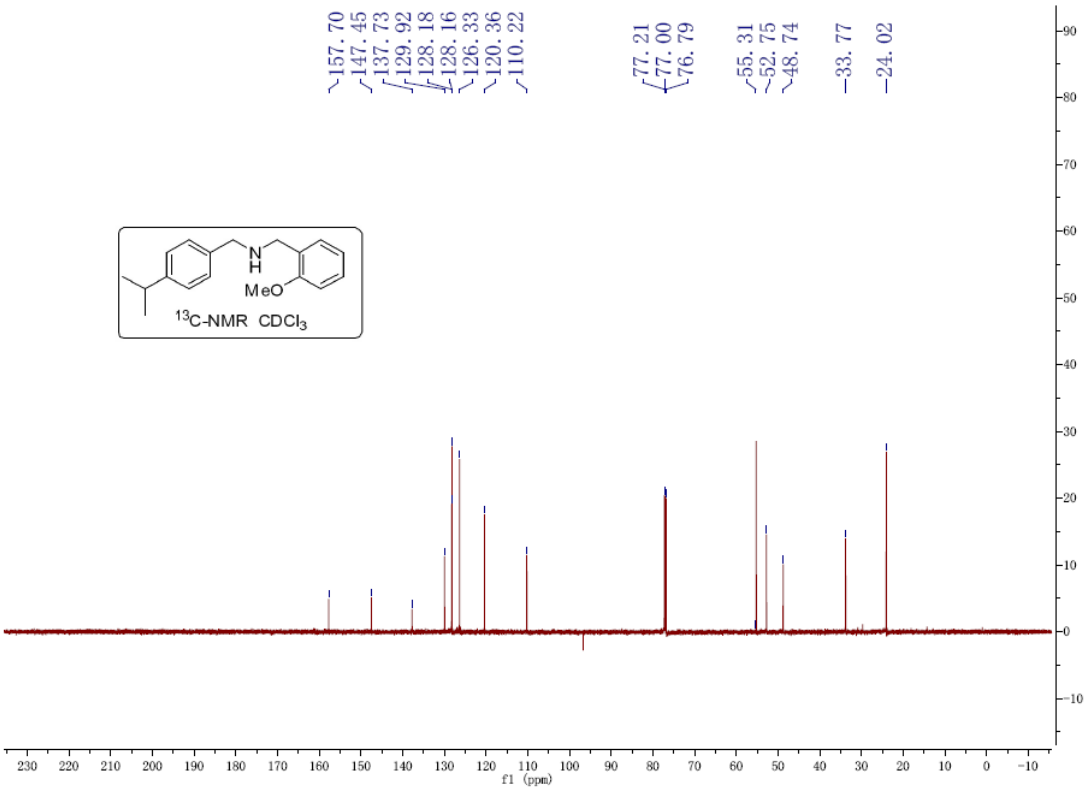
N-(4-bromobenzyl)-1-(2-methoxyphenyl)methanamine (4f)



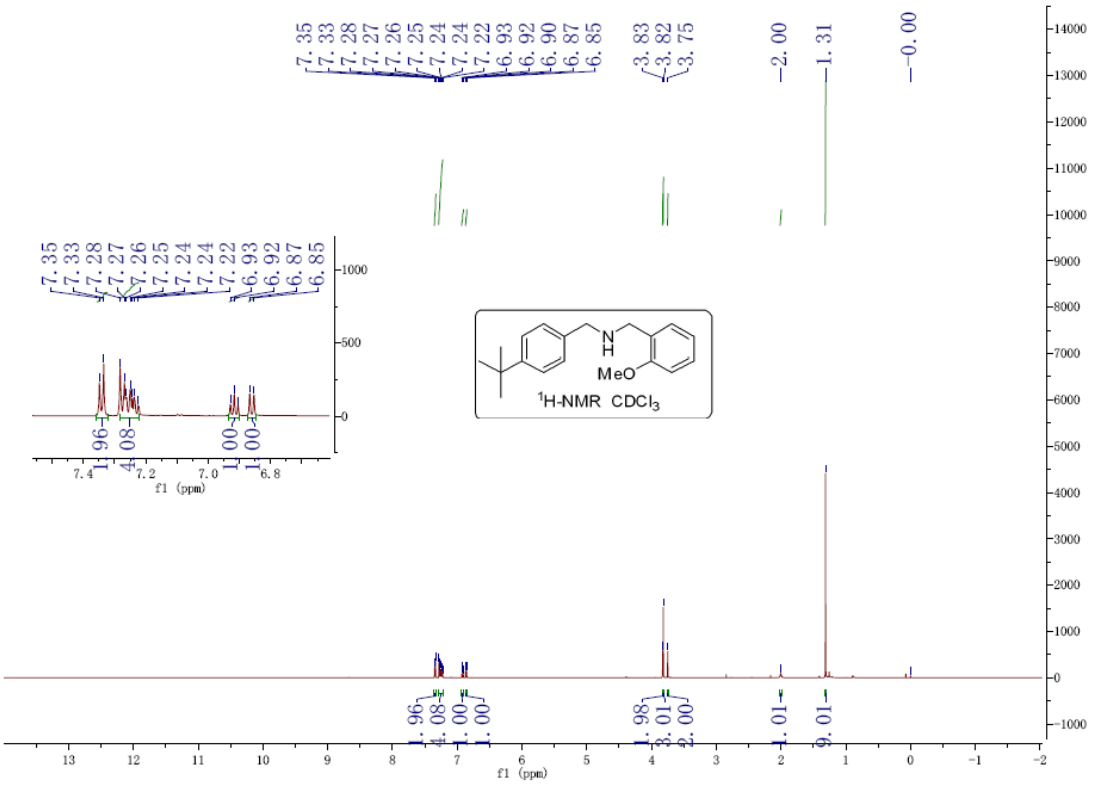


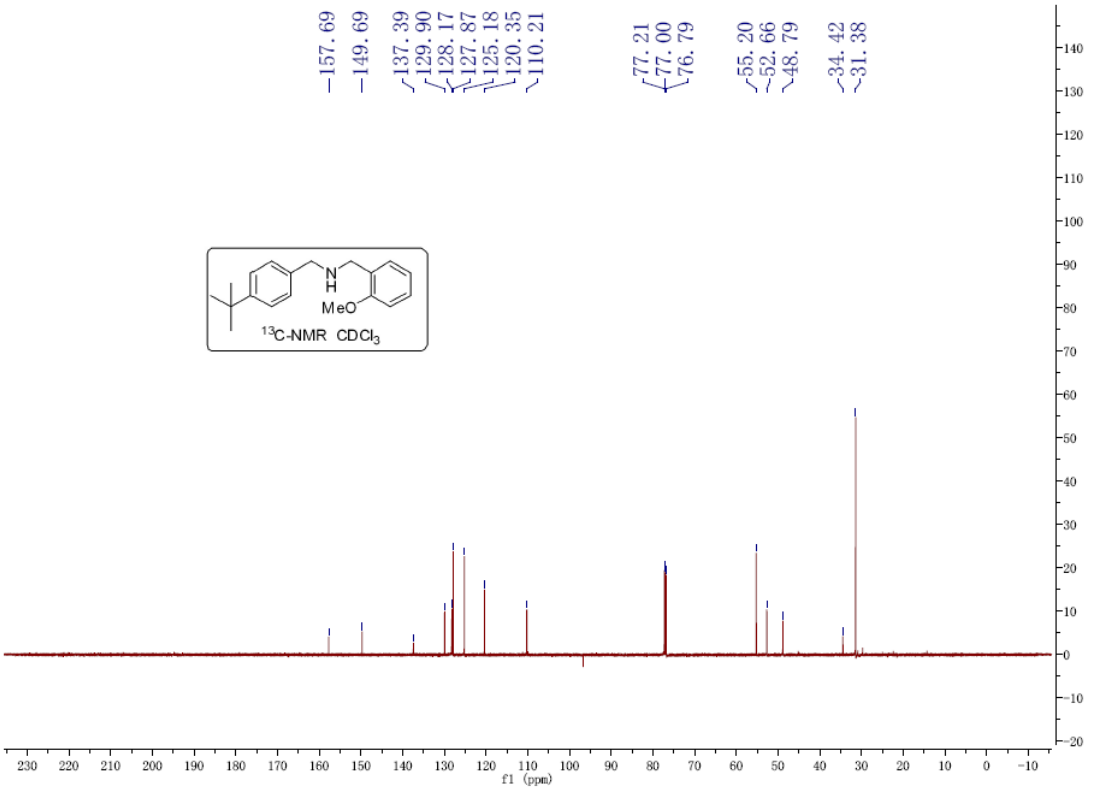
N-(4-isopropylbenzyl)-1-(2-methoxyphenyl)methanamine (4g)



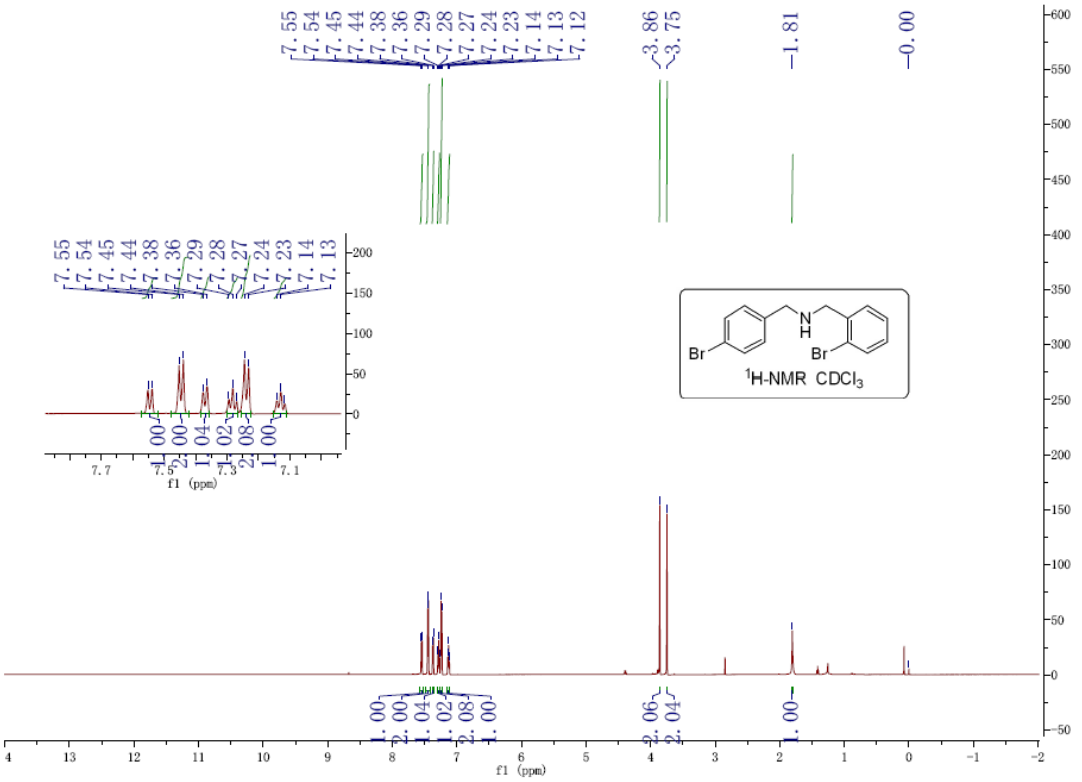


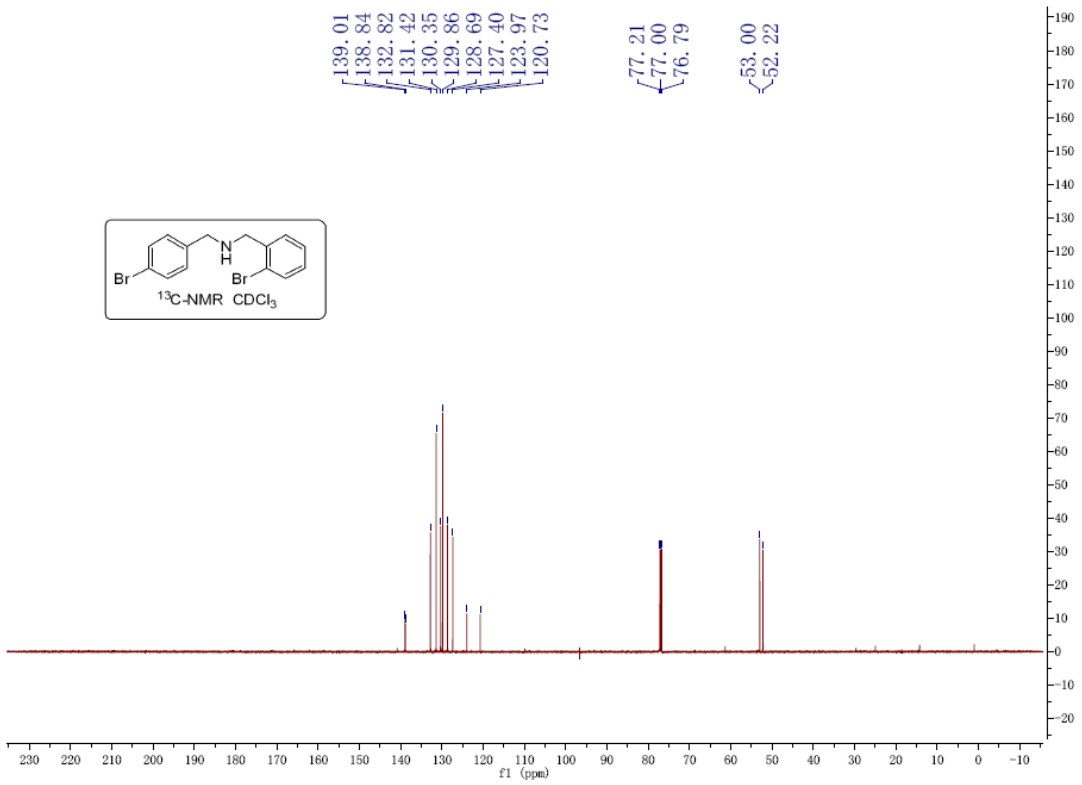
N-(4-tert-butylbenzyl)-1-(2-methoxyphenyl)methanamine (4h)



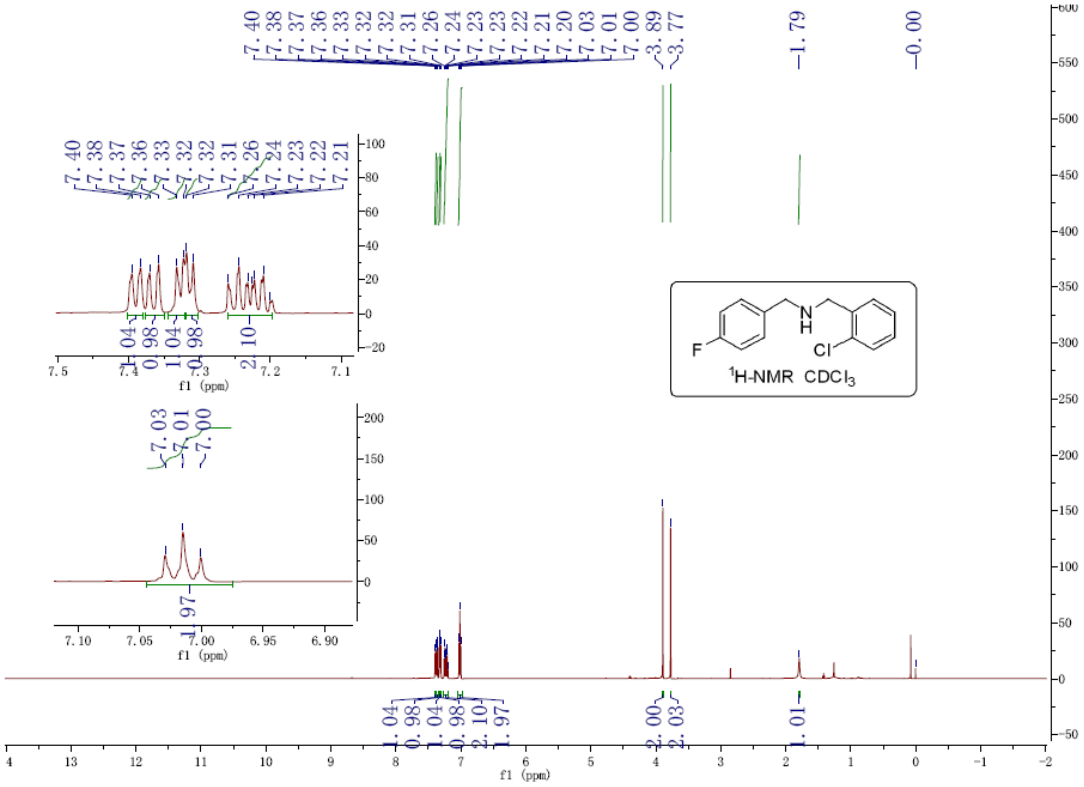


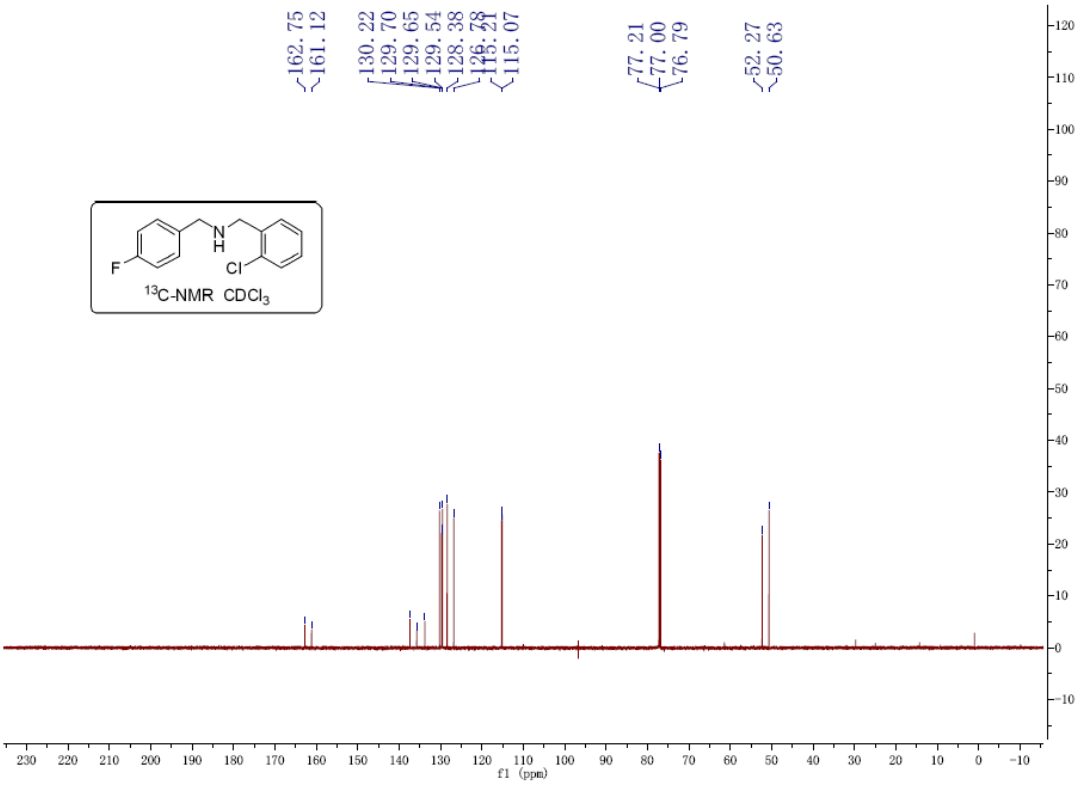
N-(2-bromobenzyl)-1-(4-bromophenyl)methanamine (4i)



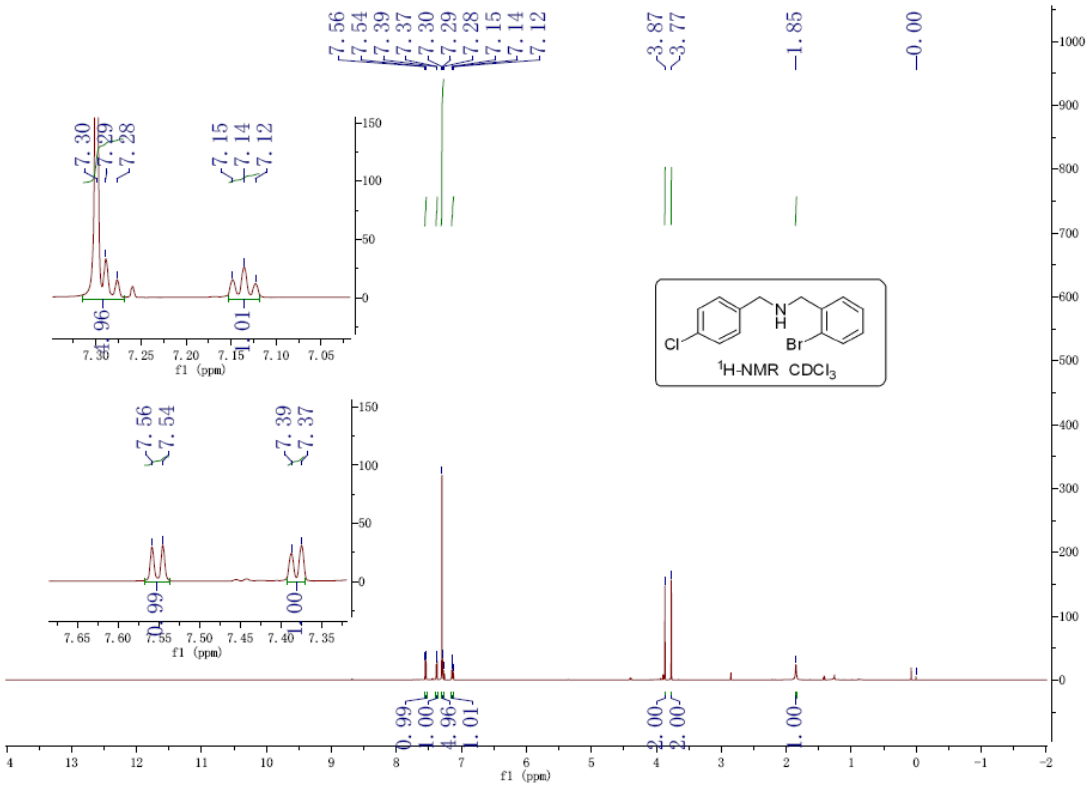


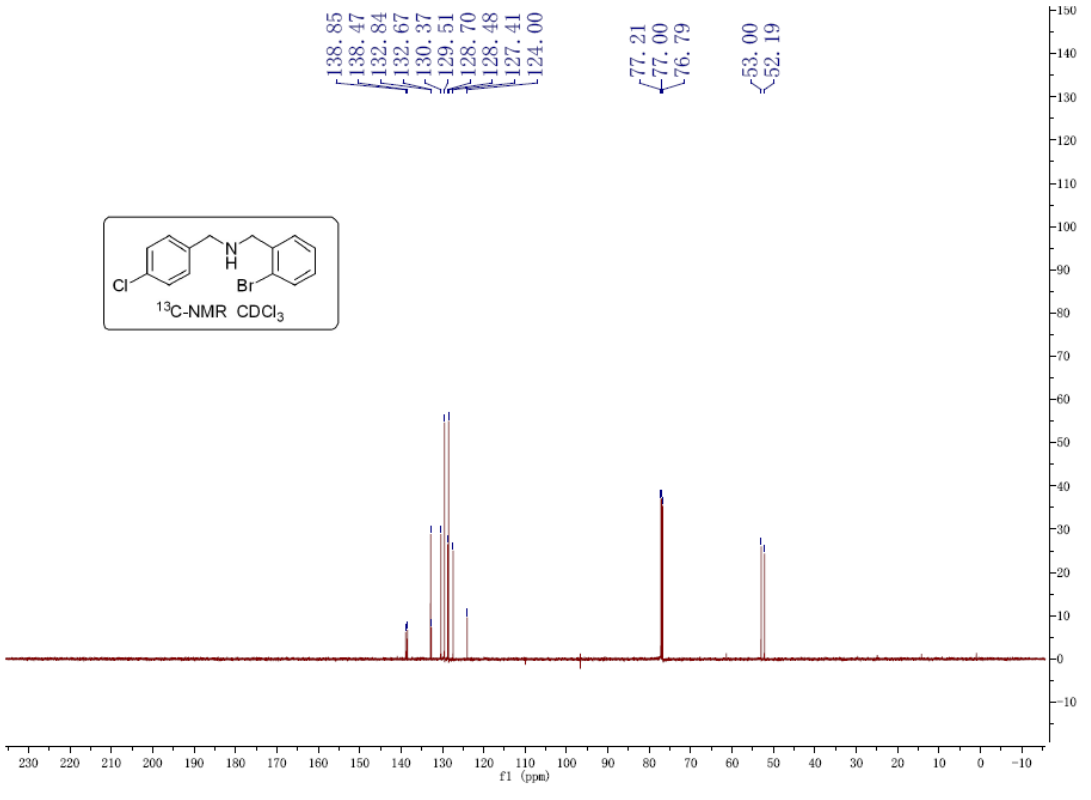
N-(2-chlorobenzyl)-1-(4-fluorophenyl)methanamine (4j)



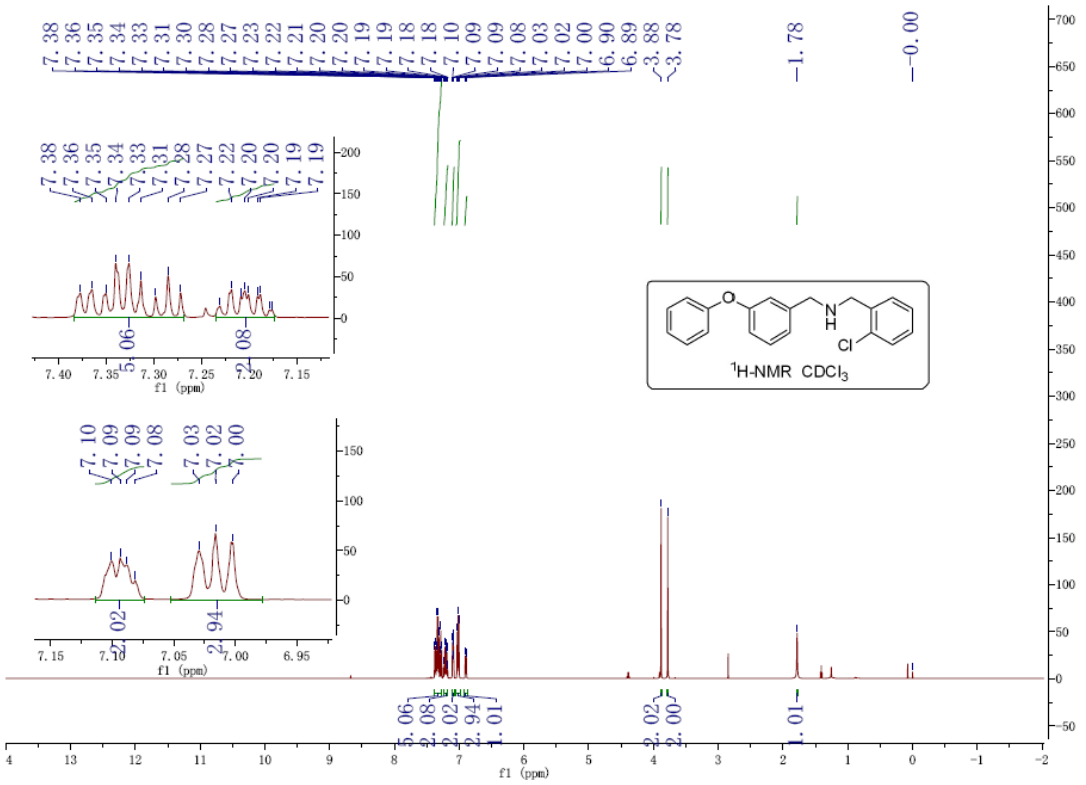


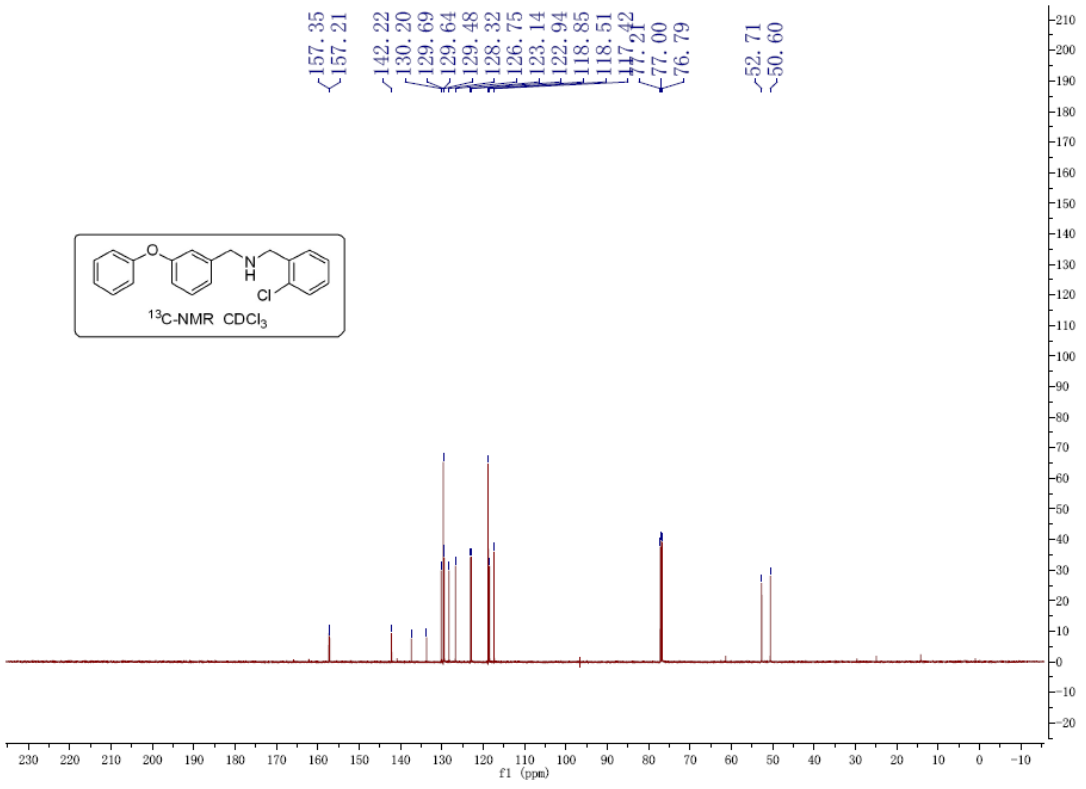
N-(2-bromobenzyl)-1-(4-chlorophenyl)methanamine (4k)



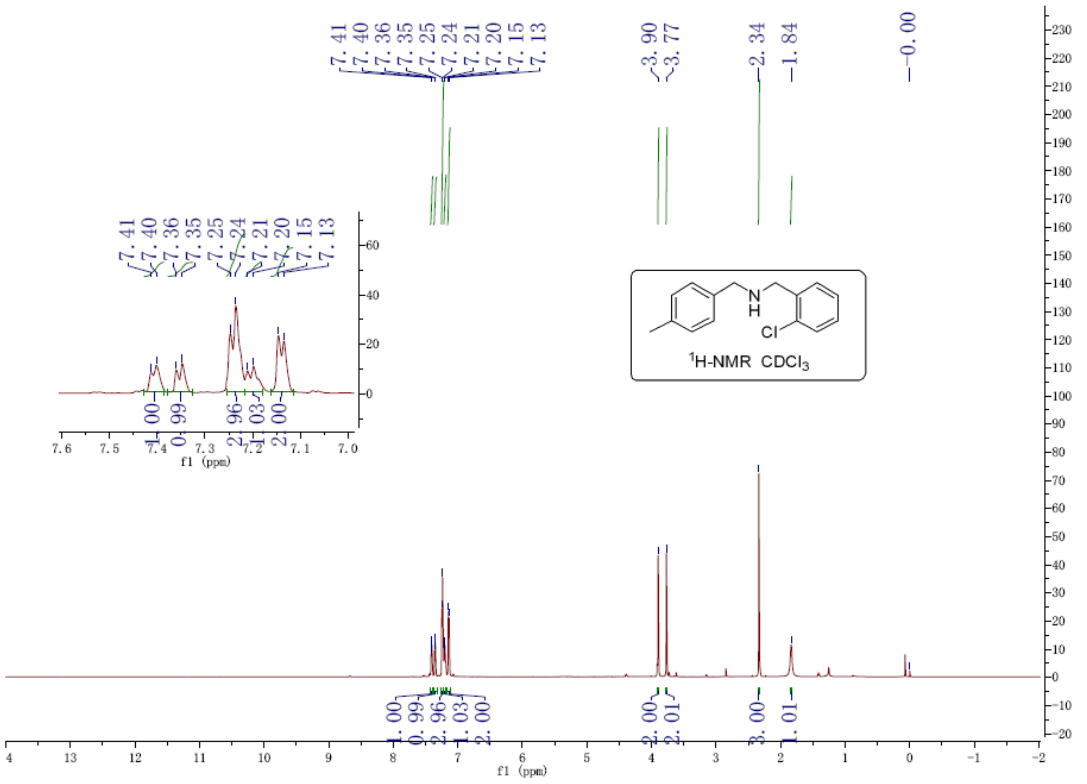


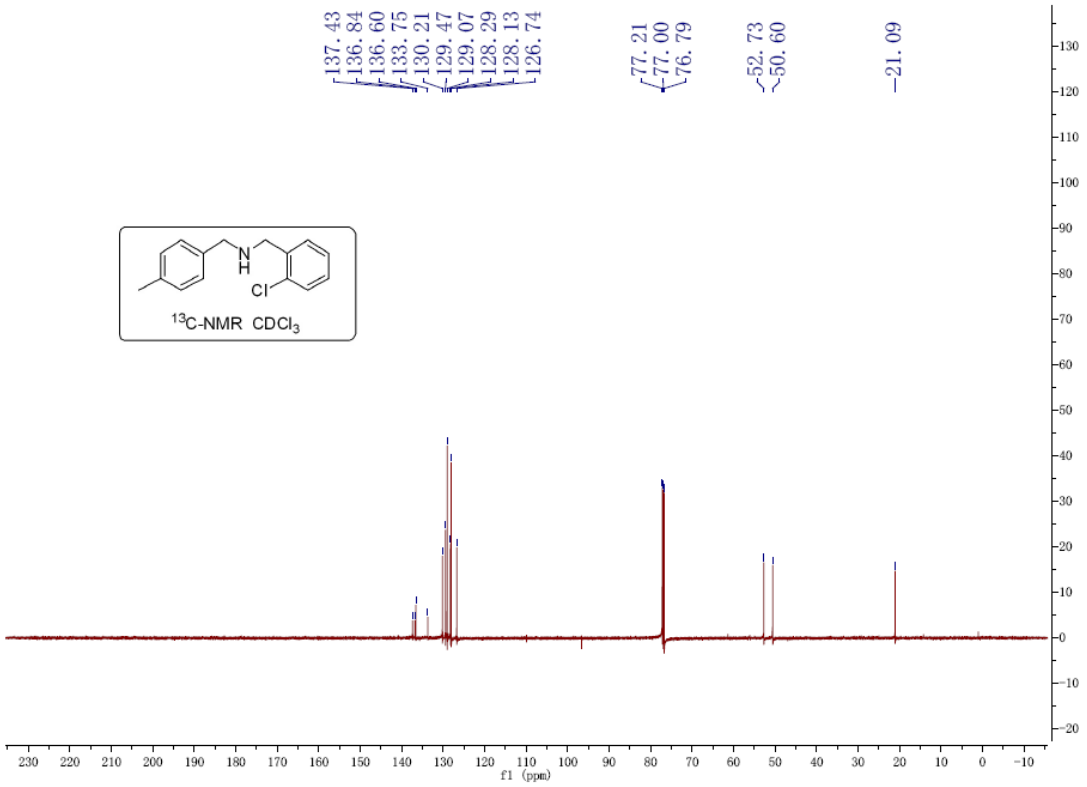
N-(2-chlorobenzyl)-1-(3-phenoxyphenyl)methanamine (4l)



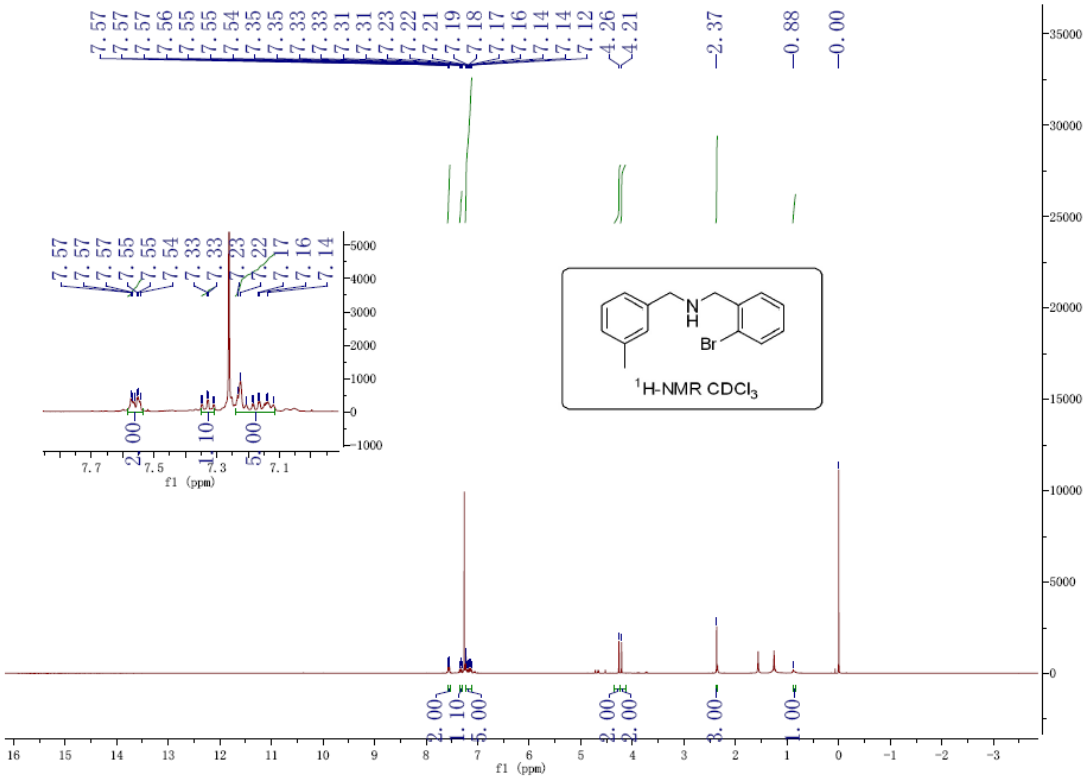


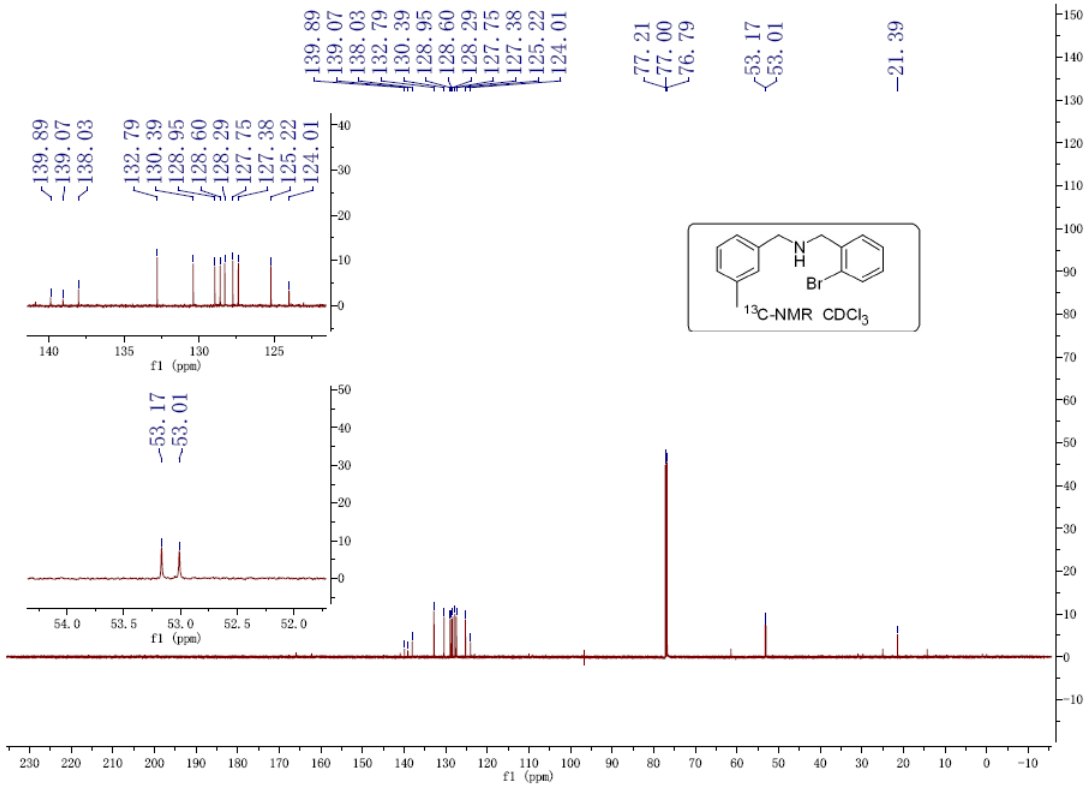
N-(2-chlorobenzyl)-1-p-tolylmethanamine (4m)



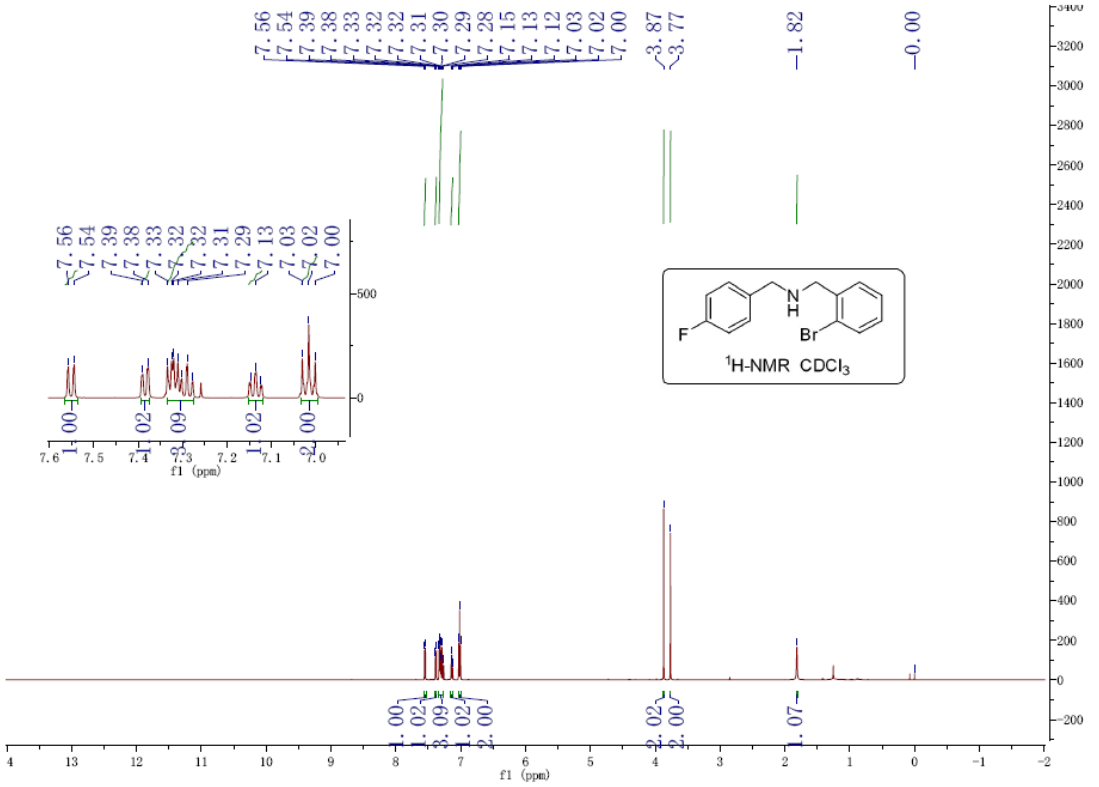


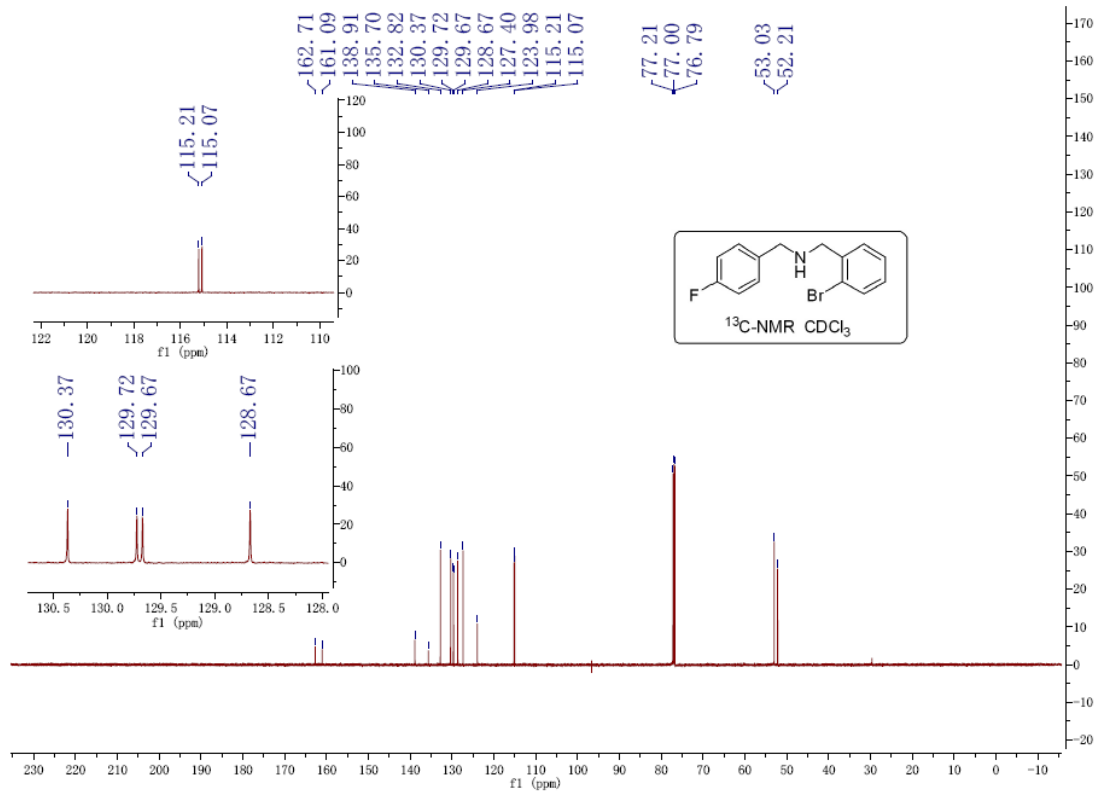
N-(2-bromobenzyl)-1-m-tolylmethanamine (4n)



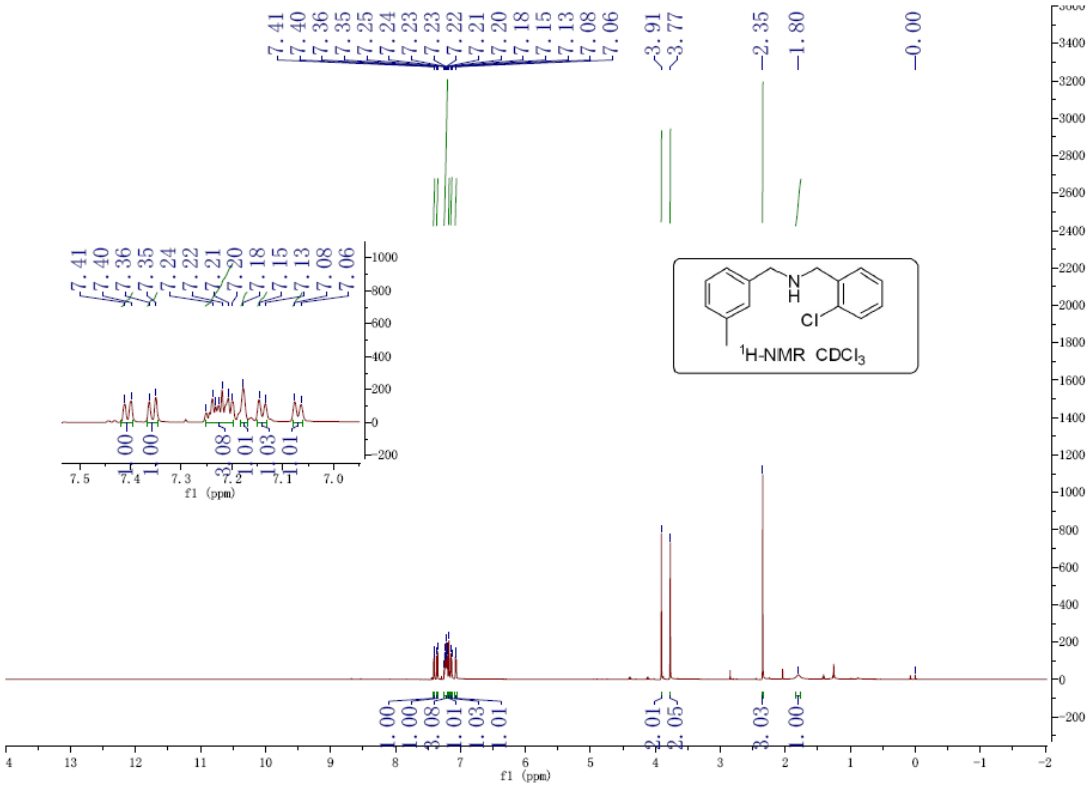


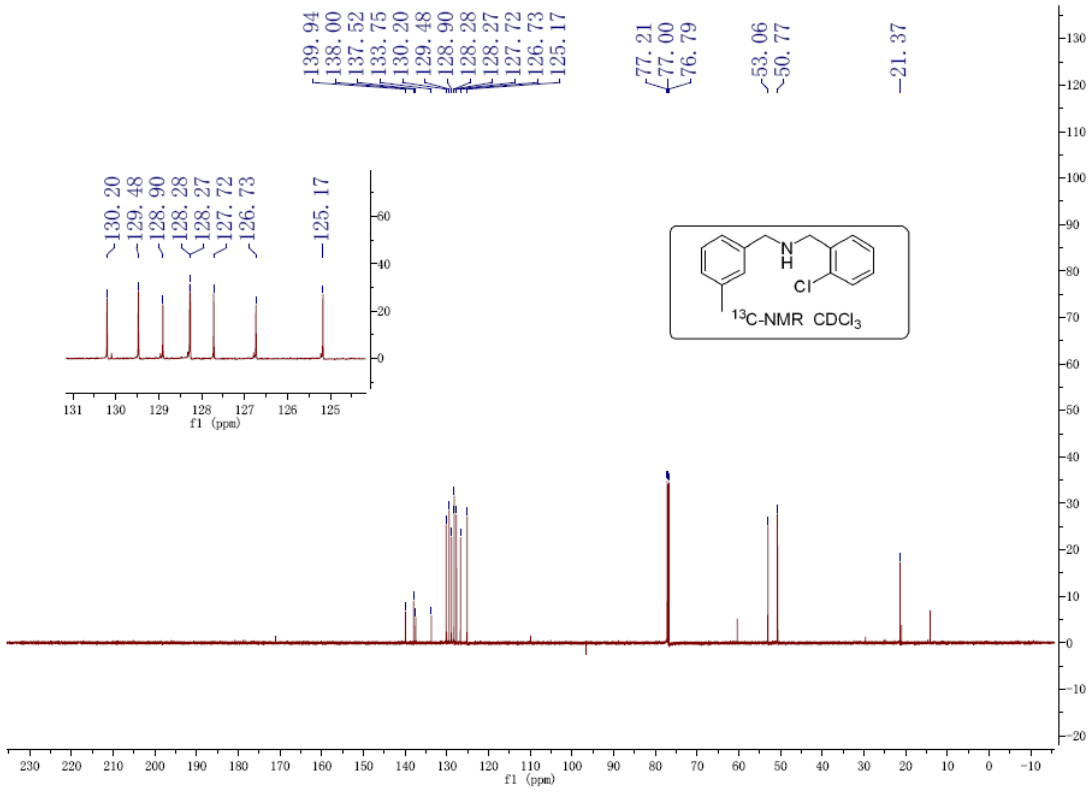
N-(2-bromobenzyl)-1-(4-fluorophenyl)methanamine (4o)



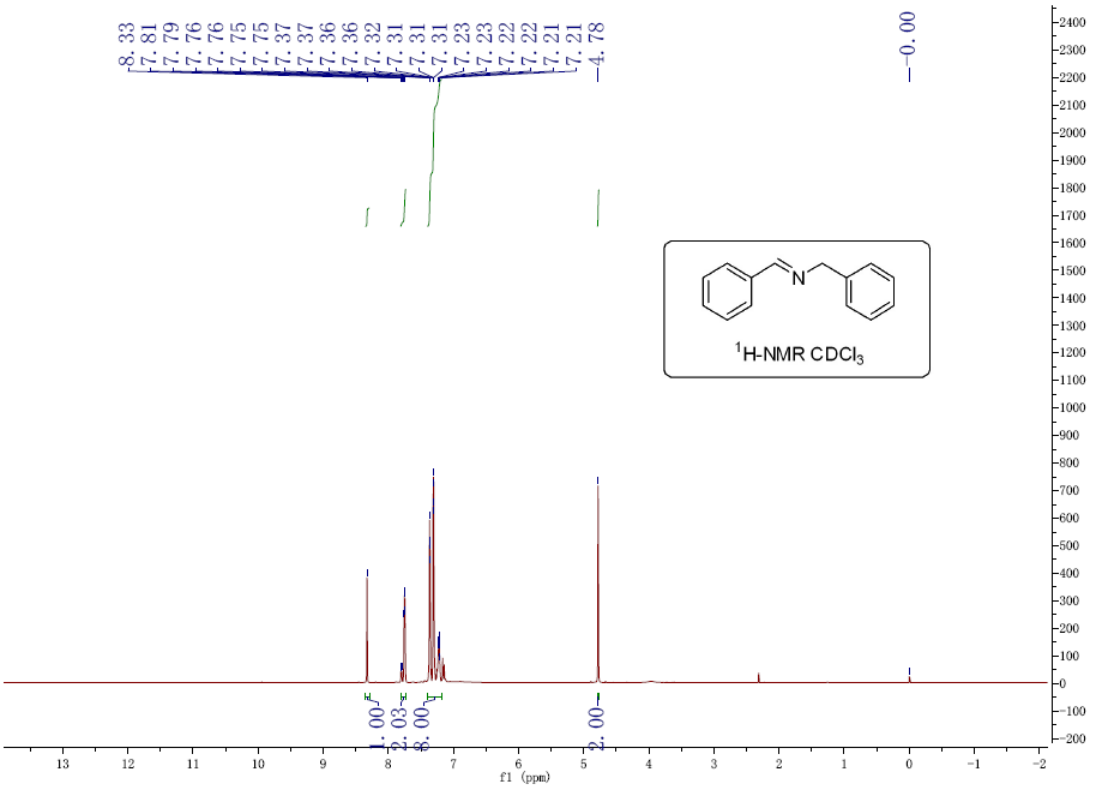


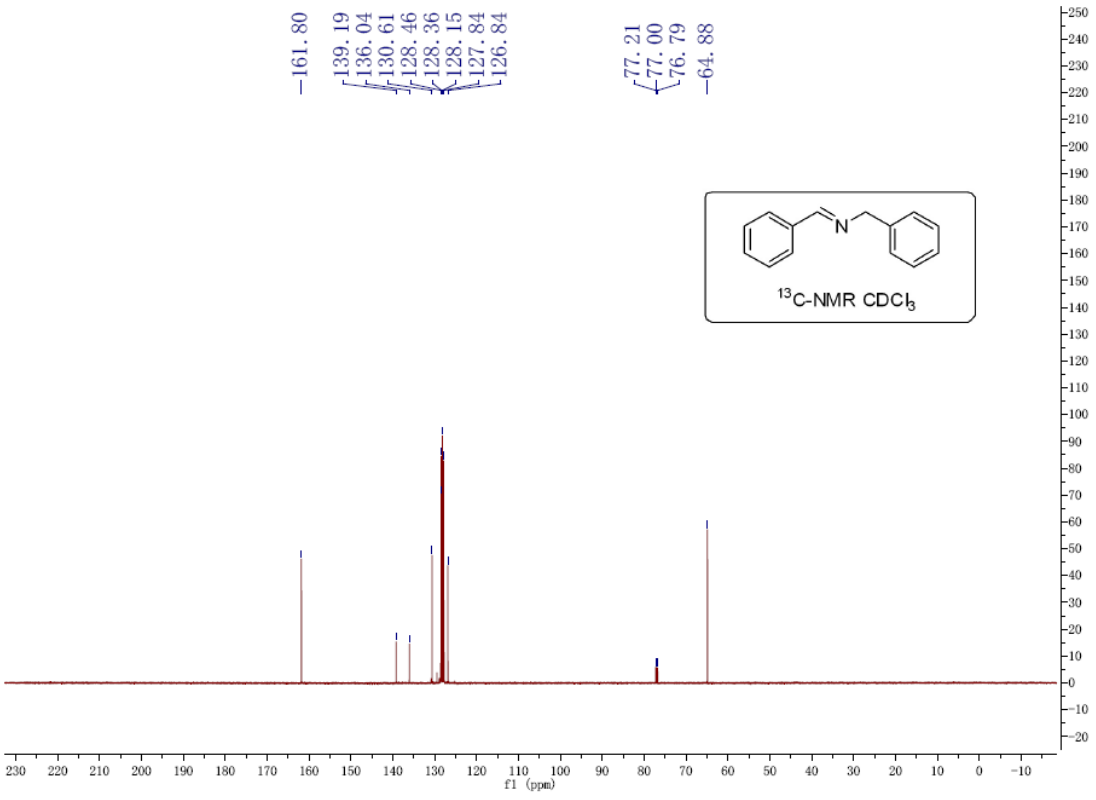
N-(2-chlorobenzyl)-1-m-tolylmethanamine (4p)





dibenzylimine





Reference

[1] A. Kumar and R. A. Maurya, *Synlett*, 2008, **6**, 883.
[2] F.-Q. Qi, L. Hu, S.-L. Lu, X.-Q. Cao and H.-W. Gu, *Chem. Commun*., 2012, **48**, 9631.
[3] B. Li, J. B. Sortais and C. Darcel, *Chem. Commun*., 2013, **49**, 3691.
[4] B. Miriyala, S. Bhattacharyya and J. S. Williamson, *Tetrahedron*, 2004, **60**, 1463.
[5] I. Kim, S. Itagaki, X.-J. Jin, K. Yamaguchi and N. Mizuno, *Catal. Sci. Technol*., 2013, **3**, 2397.
[6] B. R. Henke, A. J. Kouklis and C. H. Heathcock, *J. Org. Chem*., 1992, **57**, 7056.
[7] X.-J. Lang, W.-H. Ma, Y.-B. Zhao, C.-C. Chen, H.-W. Ji and J.-C. Zhao, *Chem. Eur. J*., 2012, **18**, 2624.
[8] J. M. Khurana and G. Kukreja, *Synth. Commun*., 2002, **32**, 1265.
[9] G. Omar and R. Jeff, *PCT Int. Appl*., 2006, WO 2006108149.
[10] X.-W. Wang and B. List, *Angew. Chem. Int. Ed*., 2008, **47**, 1119.
[11] A. F. McKay, D. L. Garmaise, G. Y. Paris, S. Gelblum and R. J. Ranz, *Can. J. Chem*., 1960, **38**, 2042.
[12] H.-R. Wang, M. Wu, H. Yu, S. Long, A. Stevens, D. W. Engers, H. Sackin, J. S. Daniels, E. S. Dawson, C. R. Hopkins, C. W. Lindsley, M. Li and O. B. McManus, *ACS Chem. Biol*. 2011, **6**, 845.
[13] G. E. Keck and E. J. Enholm, *J. Org. Chem*., 1985, **50**, 147.