Supplementary Information

Tuning the selectivity of catalytic nitriles hydrogenation by structure regulation in atomically dispersed Pd catalysts

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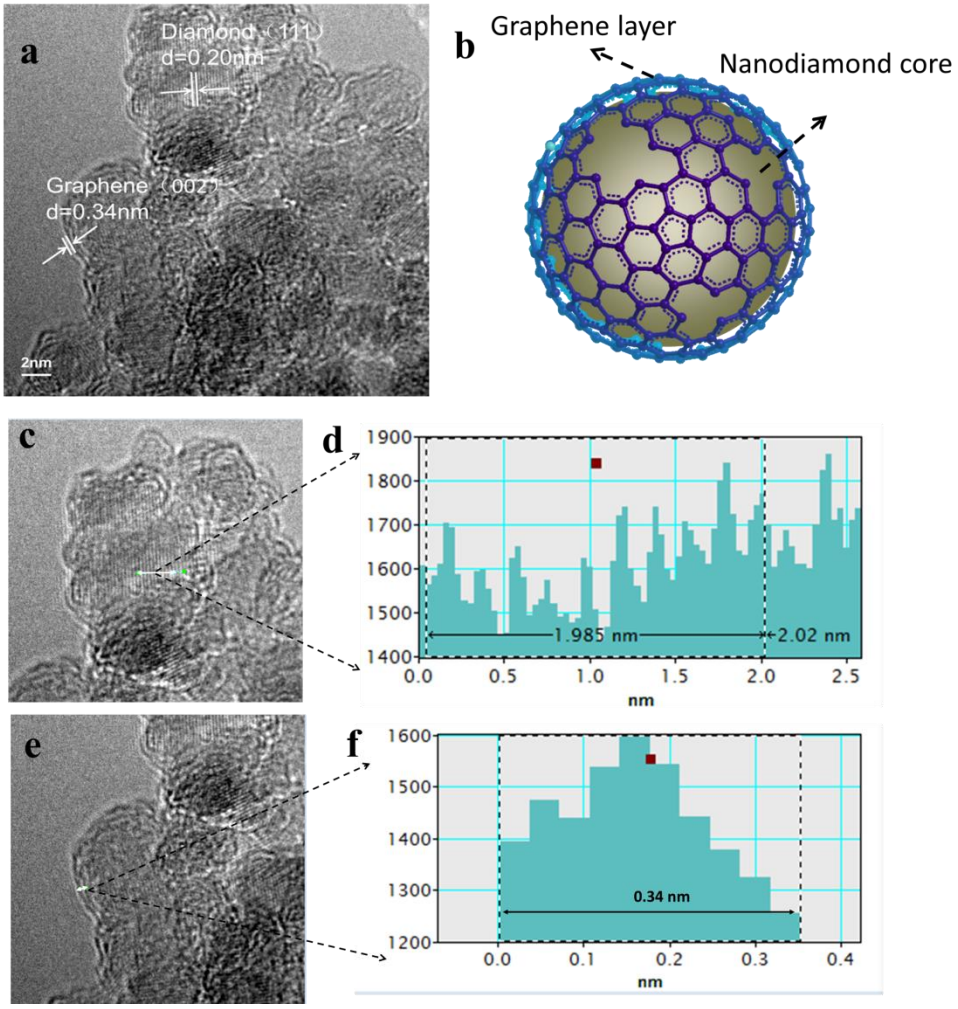
1. Supplementary Figures and Tables

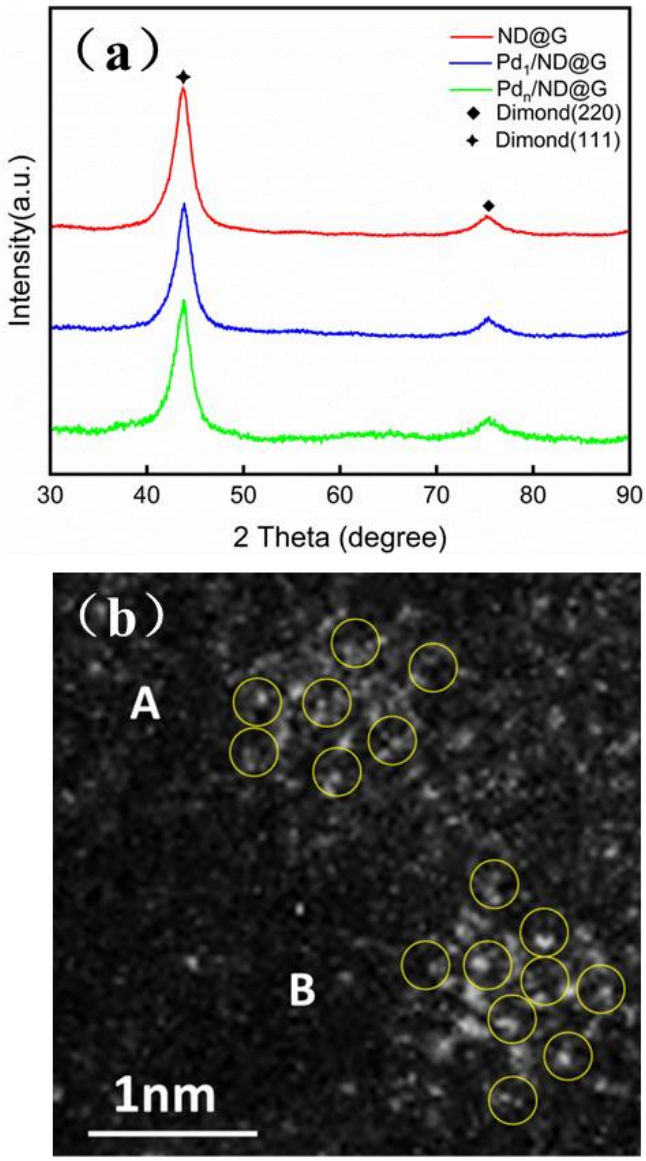
Supplementary Table 1. Physicochemical parameters of different samples.

Sample	Pd[a] [wt%]	S_{BET}[b] [m^2 g^{-1}]	V_{pore}[c] [cm^3 g^{-1}]	Pore size[d] [nm]
ND@G	-	331	1.45	17.5
Pd_1/ND@G	0.11	332	1.50	13.8
Pd_n/ND@G	1.90	345	1.38	15.4

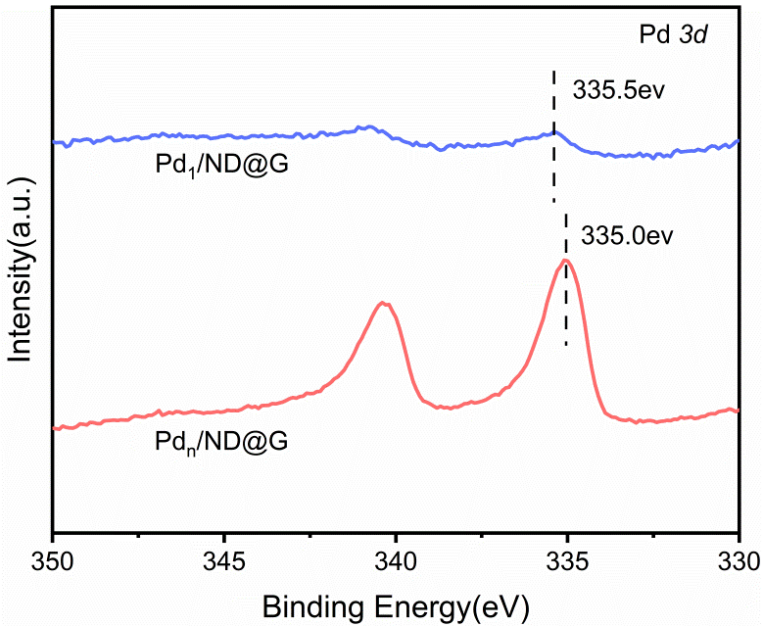
[a] Determined by ICP-AES. [b] BET method. [c] Volume of N_2 at p/p^0 = 0.98. [d] N_2 desorption.



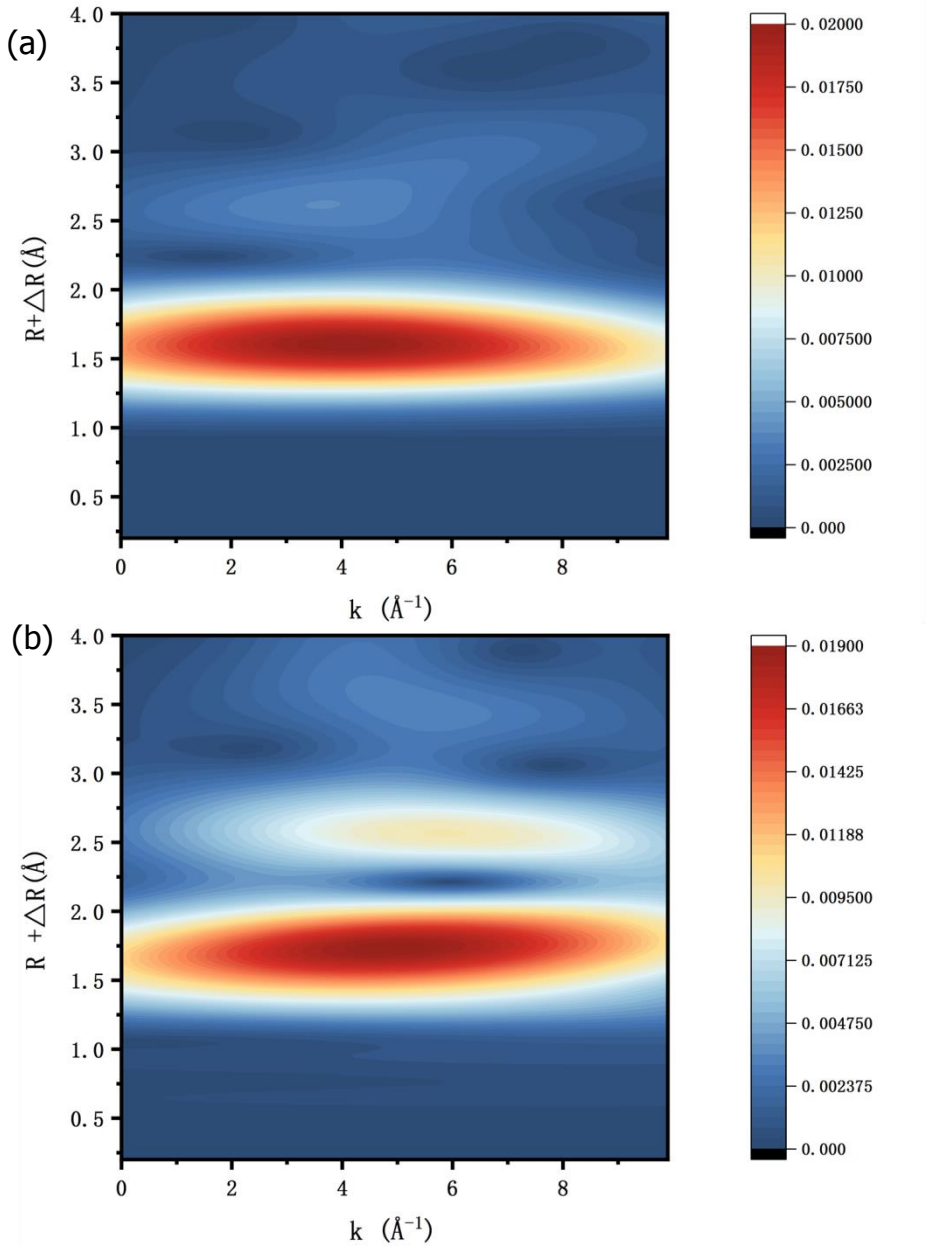
Supplementary Figure 1. (a) HRTEM image of the as-prepared ND@G support with nanodiamond core and defective graphene shell; (b) Structure diagram of ND@G; (c) Partial enlargemen HRTEM image focusing on the nanodiamond core and (e) The corresponding line profile of the nanodiamond core; (e) Partial enlargemen HRTEM image focusing on the defective graphene shell and (f) The corresponding line profile of the defective graphene shell.



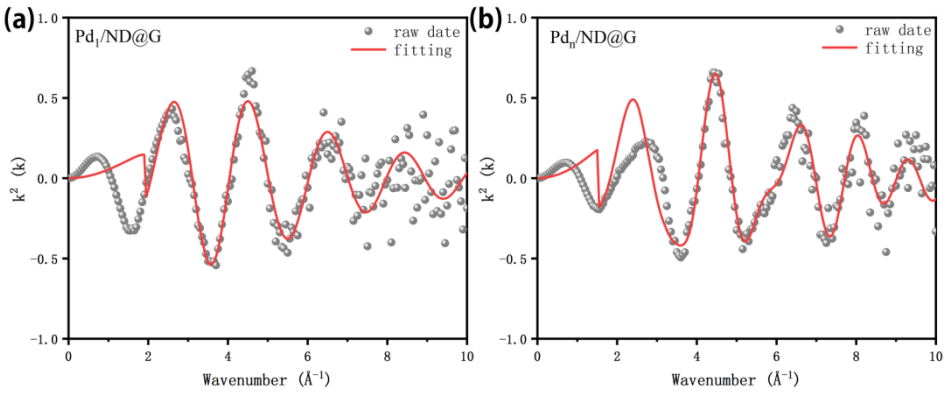
Supplementary Figure 2. (a) XRD profiles of Pd_1/ND@G, Pd_n/ND@G and pure ND@G support. **(**b) The magnified AC-HAADF-STEM images of two clusters in Figure 1d, the separated small Pd clusters were highlighted by yellow circles.



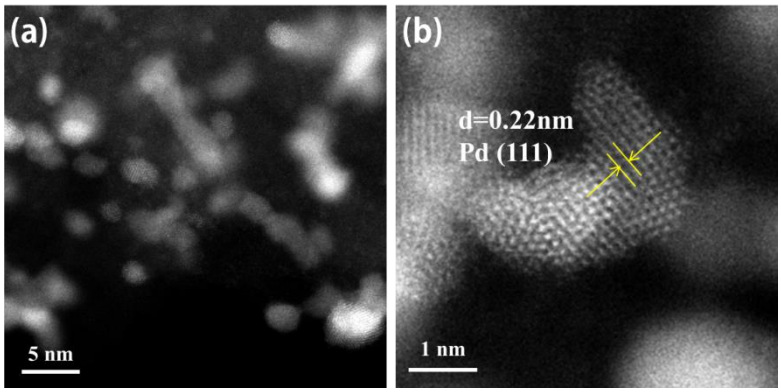
Supplementary Figure 3. XPS spectra of Pd_1/ND@G and Pd_n/ND@G.



Supplementary Figure 4. (a) WT analysis of Pd_1/ND@G. (b) WT analysis of Pd_n/ND@G.



Supplementary Figure 5. Pd K-edge EXAFS fitting results for (a) Pd_1/ND@G and (b) Pd_n/ND@G .



Supplementary Figure 6. (a, b) AC-HAADF-STEM images of the commercial Pd/C catalyst with 5 wt%.

Supplementary Table 2. Structural parameters extracted from quantitative EXAFS curve-fitting (S_0^2= 0.8 – 0.9).

Sample	Shell	C.N.[a]	R(Å)[b]	$\Delta\sigma^2$ ($/10^{-3}$ Å^2) [c]	ΔE_0 (eV) [d]	R factor
Pd foil	Pd-Pd	12.0	2.74	5.86	-6.49	0.001
PdO	Pd-O	4.0	2.01	2.13	-2.62	0.001
Pd_1/ND@G	Pd-Pd	0	-	-	-	0.027
	Pd-C/O	2.6	2.04	1.80	4.660	
Pd_n/ND@G	Pd-Pd	1.9	2.75	5.76	8.603	0.030
	Pd-C/O	2.5	2.02	5.19		

[a] C.N. is the coordination number. [b] R is interatomic distance (the bond length between Pd central atoms and surrounding coordination atoms). [c] σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber scatterer distances).[d] ΔE_0 is edge energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model.

Supplementary Table 3. Reaction conditions optimization of Pd_1/ND@G for selective catalytic transfer hydrogenation of benzonitriles.

Entry	Catalyst (mg)	T (^oC)	AB. (mmol)	Conversion (%)	Selectivity (%)		
					BA	DBA	TOL
1	10	60	4	51	0	68	0
2	20	60	4	90	0	82	0
3	30	60	4	>99	0	>98	0
4	30	50	4	93	0	84	0
5	30	40	4	25	0	36	0
6	30	60	3	54	0	79	0
7	30	60	2	3	0	0	0

Reaction condition: 0.5 mmol Nitriles;10 ml Methanol; 8 h. Toluene (TOL).

Supplementary Table 4. Catalytic performance of the Pd_1/ND@G catalyst in BN hydrogenation with different solvents.

Entry	Solvent	Conversion (%)	Selectivity (%)		
			BA	DBA	TOL
1	EtOH	48	77	23	0
2	MeOH	>99	0	>98	0
3	i-PrOH	4	0	0	0
4	Hexane	5	0	0	0
5	THF	6	0	0	0

Reaction condition:0.5 mmol Nitriles; 8 h; 30 mg Pd_1/ND@G catalyst; 4 mmol ammonia borane; 60 ^{o}C;10ml solvent.

Supplementary Table 5. Reaction conditions optimization of Pd_n/ND@G for selective catalytic transfer hydrogenation of benzonitriles.

Entry	Catalyst (mg)	T (^oC)	AB. (mmol)	Conversion (%)	Selectivity (%)		
					BA	DBA	TOL
1	5	40	3	80	90	10	0
2	10	40	3	>99	>98	trace	0
3	20	40	3	>99	>98	trace	0
4	10	40	2	78	>98	trace	0
5	10	40	4	>99	>98	trace	0
6	10	30	3	95	>98	0	0
7	10	50	3	93	97	3	0
8	10	60	3	98	96	0	4

Reaction condition: 0.5 mmol Nitriles,10 ml Methanol; 0.5 h.

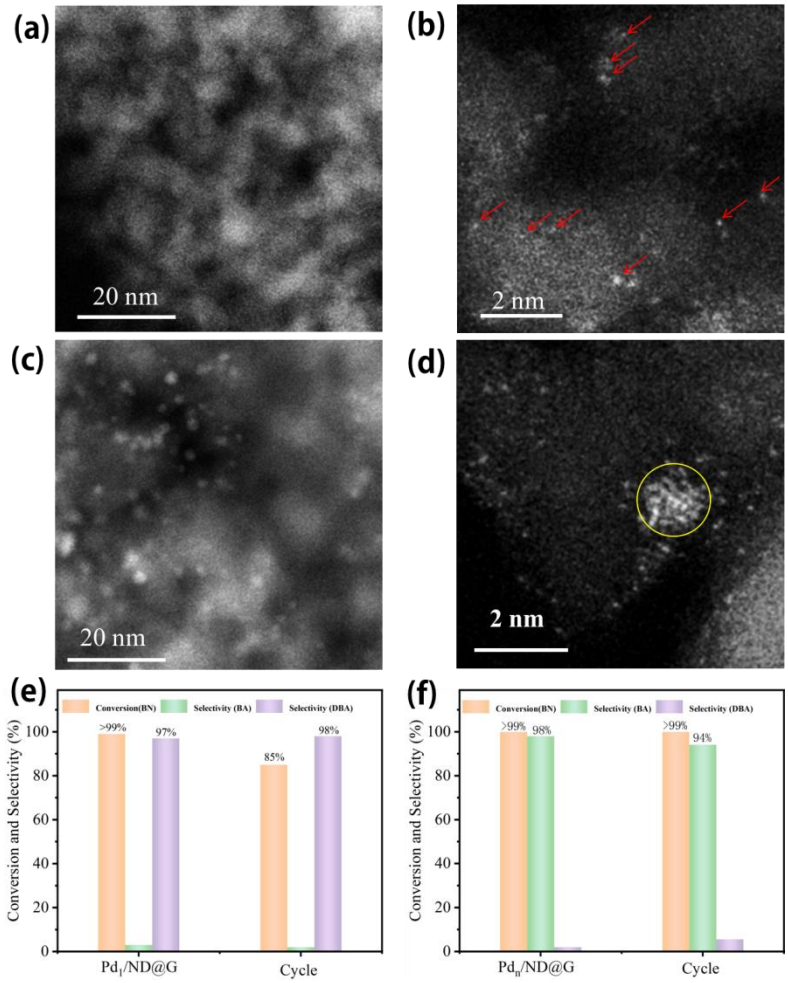
Supplementary Table 6. Catalytic performance of the Pd_nND@G catalyst in BN hydrogenation with different solvents.

Entry	Solvent	Conversion (%)	Selectivity (%)		
			BA	DBA	TOL
1	EtOH	73	79	trace	15
2	MeOH	>99	>98	trace	0
3	i-PrOH	12	0	0	0
4	Hexane	11	0	0	0
5	THF	10	0	0	0

Reaction condition:0.5 mmol Nitriles; 0.5 h; 10mg Pd_n/ND@G catalyst; 3 mmol ammonia borane; 40 ^oC; 10ml solvent.

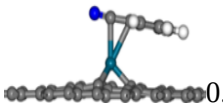
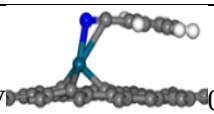
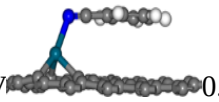
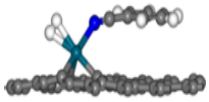
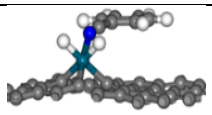
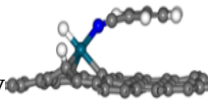
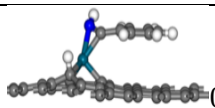
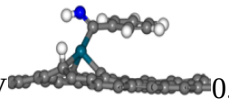
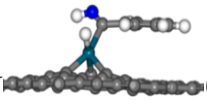
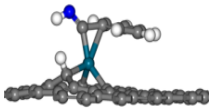
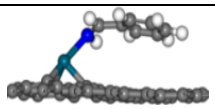
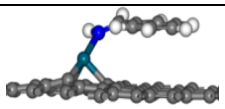
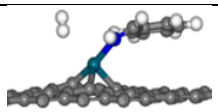
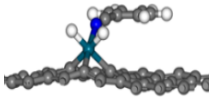
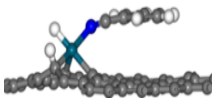
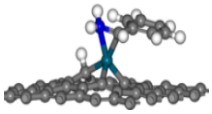
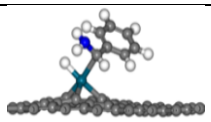
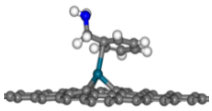
Supplementary Table 7. Catalytic performance of different noble metal catalysts in the hydrogenation and transfer hydrogenation of benzonitriles.

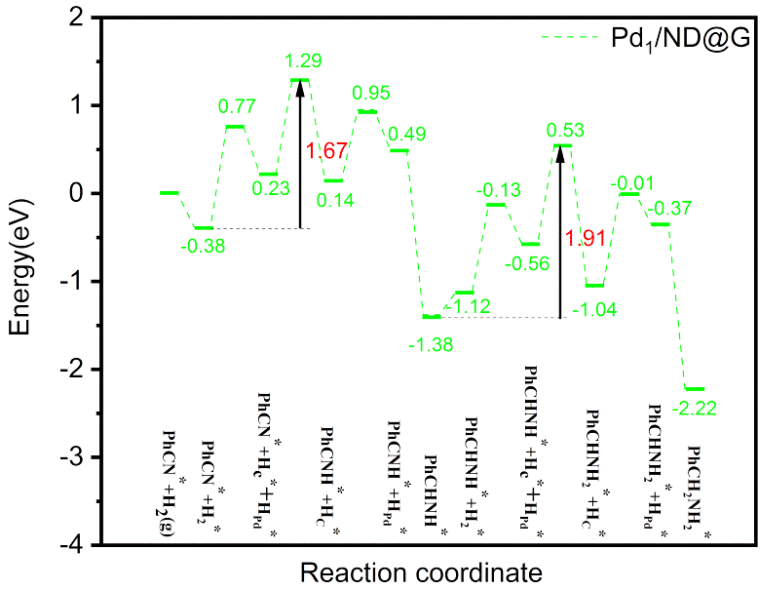
Entry	Reaction conditions	Conversion (%)	Selectivity (%)		TOF (h^{-1})	Reference
			BA	DBA		
Pd/Al_2O_3	70 °C,1.5 MPa H_2, WHSV = 0.5 h^{-1}	96.7	88.9	0	100	[1]
Pd/C	60 °C, 4 MPa H_2, 0.33 h	50	31	0	218	[2]
Pd/C	60 °C, 0.6 MPa H_2, 2.3 h	100	80	0	180	[3]
Pd/TiO_2	30 °C,0.6 MPa H_2,12.5 h	75	94	0	13	
Pd/η-Al_2O_3	90 °C, 1.5 MPa H_2, 4 h	100	91	6	41	[4]
5Pd-Ni/SiO_2	80 °C,0.6 MPa H_2,3 h	100	3.5	96.5	515	[5]
Pd_n/ND@G	**40 °C,3mmol AB.(0.1MPa),0.5 h**	**>99**	**>98**	**trace**	**543**	**This work**
Pd_1/ND@G	**60 °C,4mmol AB.(0.1MPa),8 h**	**>99**	**0**	**>98**	**709**	
Pt /C	105 °C,5.5 MPa H_2,2.5 h	100	0	97	780	[6]
Pt/Al_2O_3	100 °C, 1.5 MPa H_2, 24 h	100	12	0	20	[7]
Pt/C	r.t., 0.34 MPa H_2,4 h	100	0	93	50	[8]
Rh/C	50 °C,2 MPa H_2,10 MPa CO_2,4 h	28.8	25	75	14.4	[9]
Rh/Al_2O_3		21	22.4	77.6	10	
Ru-NPs	290 °C, 6.2 MPa H_2,72 h	100	56.6	0	140	[10]
Ru/K-Al_2O_3	70 °C,0.1 MPa H_2, 82 h	100	93	0	1.2	[11]
Ir/Al_2O_3	100 °C,2.1 MPa H_2	20	36	52	66	[12]



Supplementary Figure 7. The AC-HAADF-STEM images of the Pd_1/ND@G catalyst at low (a) and high (b) magnification after the transfer hydrogenation of benzonitrile. The AC-HAADF-STEM images of the Pd_n/ND@G catalyst at low (c) and high (d) magnification after the transfer hydrogenation of benzonitrile. (e) The recycling experiments of the Pd_1/ND@G catalyst used for the transfer hydrogenation of benzonitrile. Reaction conditions: solvent, methanol, 10 mL; BN, 0.5 mmol; catalyst, 60 mg; AB, 4 mmol; Temperature, 60 ^{o}C; Time, 8 h. (f) The recycling experiments of the Pd_n/ND@G catalyst used for the transfer hydrogenation of benzonitrile. Reaction conditions: solvent, methanol, 10 mL; BN, 0.5 mmol; catalyst, 10 mg; AB, 3mmol; Temperature, 40 ^{o}C; Time, 30 min.

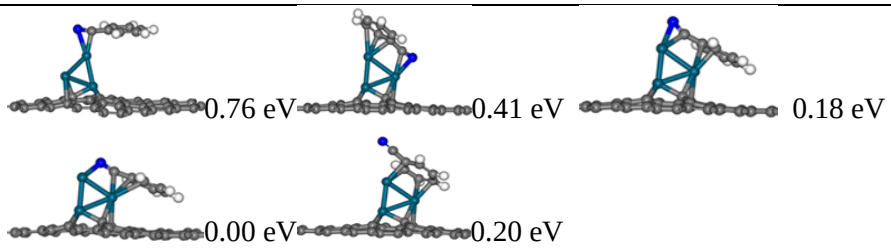
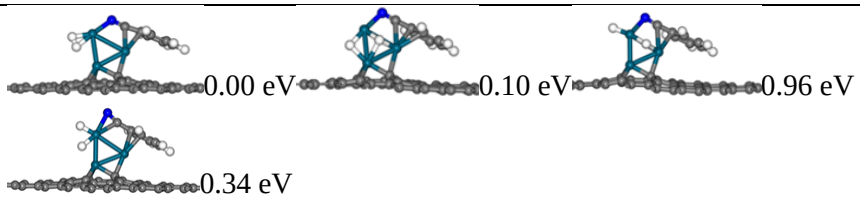
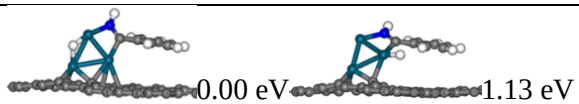
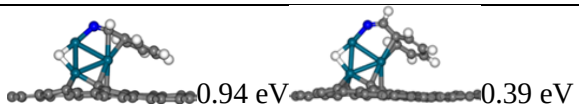
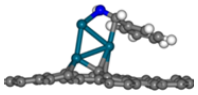
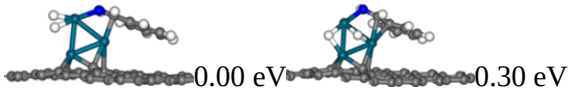
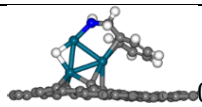
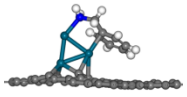
Supplementary Table 8. Relative configurations and energies of different stationary intermediates on Pd_1/ND@G.

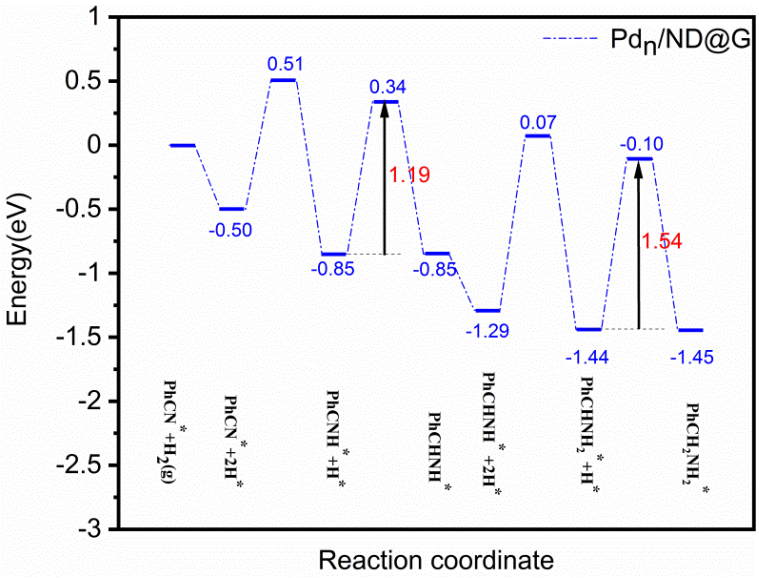
Species	Configurations and Energy
PhCN*	 0.50eV  0.15eV  0.00eV
PhCN*+H_2*	 0.50 eV
PhCN*+2H*	 0.47 eV  0.00 eV
PhCNH*+H*	 0.26eV  0.00eV  0.35eV  0.34 eV
PhCHNH*	 0.26 eV  0.00 eV
PhCHNH*+H_2*	
PhCHNH*+2H*	 0.47 eV  0.00 eV
PhCHNH_2*+H*	 0.00 eV  0.67 eV
PhCH_2NH_2*	



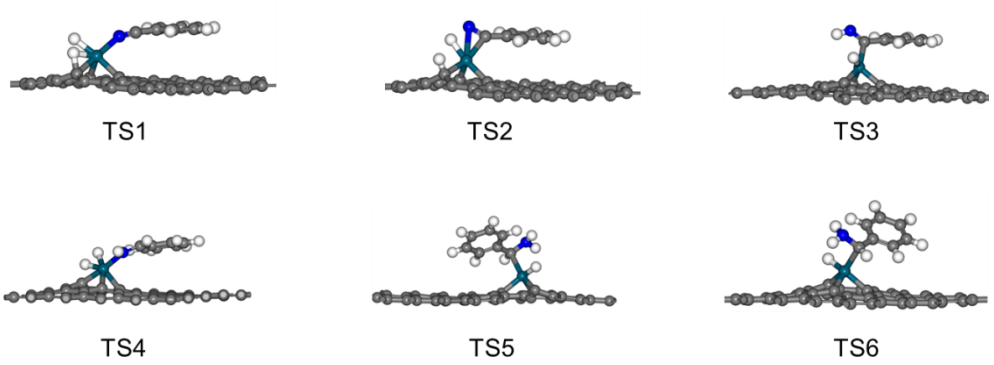
Supplementary Figure 8. The energies of species in the process of hydrogenation reaction from benzonitrile to benzylamine on Pd_1/ND@G.

Supplementary Table 9. Relative configurations and energies of different stationary intermediates on Pd_n/ND@G.

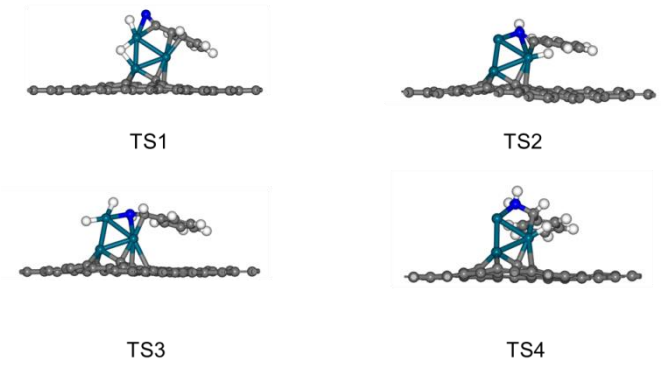
Species	Configurations and Energy
PhCN*	 0.76 eV 0.41 eV 0.18 eV 0.00 eV 0.20 eV
PhCN*+2H	 0.00 eV 0.10 eV 0.96 eV 0.34 eV
PhCNH*+H*	 0.00 eV 1.13 eV
PhCNH*+H*	 0.94 eV 0.39 eV
PhCHNH*	
PhCHNH*+2H	 0.00 eV 0.30 eV
$PhCHNH_2$*+H*	 0.00 eV 1.03 eV
$PhCH_2NH$*+H*	 0.40 eV
$PhCH_2NH_2$*	



Supplementary Figure 9. The energies of species in the process of hydrogenation reaction from benzonitrile to benzylamine on Pd_n/ND@G.



Supplementary Figure 10. Structures of key transition states of benzonitrile hydrogenation on Pd_1/ND@G.



Supplementary Figure 11. Structures of key transition states of benzonitrile hydrogenation on Pd_n/ND@G.

Supplementary Table 10. Step by step barrier (Ea, eV) and enthalpy energy change (ΔE, eV) of benzonitrile to benzylamine on Pd_1-Gr.

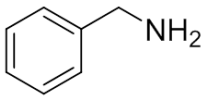
Number	Elementary reactions	E_a (eV)	ΔE (eV)
1	PhCN= PhCN*	-0.77	-
2	H_2(g) + PhCN* = PhCN*+H_2*	-0.77	-
3	PhCN*+H_2* = H*(C)+H*(Pd)+PhCN*	0.61	1.15
4	H*(C)+H*(Pd)+PhCN* = H(C)+PhCNH*	-0.09	1.06
5	H*(C)+PhCNH*= H*(Pd)+PhCNH*	0.35	0.81
6	H*(Pd)+PhCNH*= PhCHNH*	-1.87	-
7	H_2(g) + PhCHNH= H_2*+PhCHNH*	-0.13	-
8	H_2*+PhCHNH* = H*(C)+H*(Pd)+PhCHNH*	0.56	0.99
9	H*(C)+H*(Pd)+PhCHNH* = H*(C)+PhCHNH_2*	-0.48	1.09
10	H*(C)+PhCHNH_2*= H*(Pd)+PhCHNH_2*,	0.67	1.03
11	H*(Pd)+PhCHNH_2* = PhCH_2NH_2*	-1.06	-

Supplementary Table 11. Step by step barrier (Ea, eV) and enthalpy energy change (ΔE, eV) of benzonitrile to benzylamine on Pd_n-Gr.

Number	Elementary reactions	E_a (eV)	ΔE (eV)
1	PhCN= PhCN*	-1.58	-
2	H_2(g) + PhCN* = PhCN*+2H*	-0.89	-
3	PhCN*+2H* = PhCNH*+H*	-0.35	1.01
4	PhCNH*+H* = PhCHNH*	0.00	1.19
5	H_2(g) + PhCHNH* = 2H* + PhCHNH*	-0.83	-
6	2H* + PhCHNH* = PhCHNH_2*+H*	-0.15	1.36
7	PhCHNH_2*+H* = PhCH_2NH_2*	-0.01	1.34

Characterization data of products

Primary amines



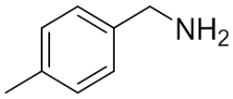
Benzylamine (yellowish liquid)[13]

Isolated yield: 93%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.33-7.26 (m, 5H), 3.83 (s, 2H), 2.03 (s, active H).

^{13}C NMR (151 MHz, Chloroform-d) δ 128.97, 128.77, 128.15, 127.72, 45.34.

GC-MS: *m/z* (%) 107 (60) $[M]^{+}$, 106 (100), 91 (15), 79 (48), 77 (25), 65 (10), 51 (18).



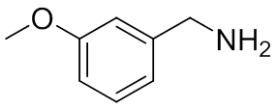
p-tolylmethanamine (colorless liquid)[14]

Isolated yield: 89%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.19 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 3.82 (s, 2H), 2.34 (s, 3H), 1.74 (s, active H).

^{13}C NMR (151 MHz, Chloroform-d) δ 140.17, 136.60, 129.37, 127.23, 46.30, 21.20.

GC-MS: *m/z* (%) 121 (23) $[M]^{+}$, 120 (62), 104 (100), 91 (65), 77 (42), 65 (28), 51 (22).



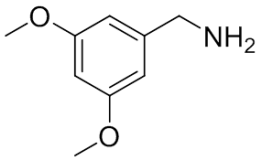
(3-methoxyphenyl)methanamine (yellowish liquid)[14]

Isolated yield: 91%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.28 – 7.20 (m, 1H), 6.86 (d, J = 14.4 Hz, 2H), 6.78 (d, J = 2.2 Hz, 1H), 3.81 (s, 2H), 3.79 (s, 3H), 1.76 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ 159.81, 144.87, 129.52, 119.31, 112.59, 112.20, 55.14, 46.38.

GC-MS: *m/z* (%) 137 (65) $[M]^{+}$, 136 (100), 121 (24), 106 (64), 94 (42), 77 (56), 65 (32), 51 (30).



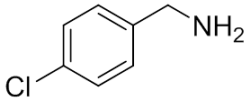
(3,5-dimethoxyphenyl)methanamine (yellowish liquid) (CAS: 1391721-68-8)

Isolated yield: 90%

^{1}H NMR (600 MHz, Chloroform-d) δ 6.45 (s, 2H), 6.32 (s, 1H),3.76（s，2H） 3.75 (s, 6H), 1.94 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ 160.98, 145.60, 104.91, 98.73, 55.23, 46.50.

GC-MS: *m/z* (%) 167 (53) $[M]^{+}$, 166 (65), 146 (63), 136 (30), 105 (100), 77 (50), 65 (27), 51 (25).



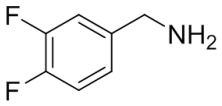
(4-chlorophenyl)methanamine (colorless liquid)[15]

Isolated yield: 83%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.30 (d, J = 9.2 Hz, 2H), 7.25 (d, J = 14.5 Hz, 2H), 3.84 (s, 2H), 1.73 (s, active H).

^{13}C NMR (151 MHz, Chloroform-d) δ 141.61, 132.64, 128.75, 128.61, 45.87.

GC-MS: *m/z* (%) 141 (8) $[M]^{+}$, 140 (35), 106 (100), 89 (15), 77 (45), 63 (12), 51 (25).



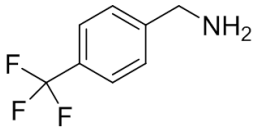
(3,4-difluorophenyl)methanamine (colorless liquid) (CAS: 72235-53-1)

Isolated yield: 81%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.13 (d, J = 2.8 Hz, 1H), 7.05 (d, J = 10.2 Hz, 1H), 7.03 (s, 1H),3.84 (s, 2H)，1.72 (s, active H).

^{13}C NMR (151 MHz, Chloroform-d) δ 150.19 (d, J = 12.8 Hz), 149.65 (d, J = 12.8 Hz), 140.20, 123.21–122.77 (m), 117.25 (d, J = 16.8 Hz), 116.07 (d, J = 17.2 Hz), 45.55.

GC-MS: *m/z* (%) 143 (15) $[M]^{+}$, 142 (60), 123 (100), 95 (17), 75 (22), 63 (45), 51 (10).



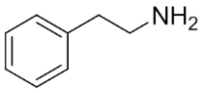
(4-(trifluoromethyl)phenyl)methanamine (brown liquid)[13]

Isolated yield: 94%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.59 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 3.94 (s, 2H), 1.76 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ 147.04, 128.65, 127.47, 125.80, 124.69 (m), 46.06.

GC-MS: *m/z* (%) 175 (46) $[M]^{+}$, 174 (87), 156 (20), 127 (59), 106 (100), 77 (26), 69 (27), 51 (26).



Phenethylamine (yellowish liquid)[13]

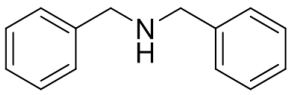
Isolated yield: 85%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.32 (d, J = 12.3 Hz, 2H), 7.28 (s, 2H), 7.21 (s, 1H), 3.52 (dd, J = 14.5, 8.3 Hz, 1H), 2.82 (d, J = 6.2 Hz, 2H), 1.94 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ139.01, 128.84 (d, J = 13.0 Hz), 126.67,40.78，35.76.

GC-MS: *m/z* (%) 121 (21) $[M]^{+}$, 120 (30), 91 (100), 77 (21), 65 (68), 51 (26).

Secondary amines



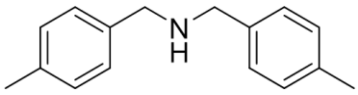
Dibenzylamine (colorless liquid)[16]

Isolated yield: 91%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.29 (d, J = 6.7 Hz, 8H), 7.21 (s, 2H), 3.76 (s, 4H), 1.92 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 140.23, 128.42, 128.19, 126.98, 53.13.

GC-MS:*m/z* (%) 197 (12) $[M]^{+}$, 196 (14), 106 (77), 91 (100), 65 (24), 51 (10).



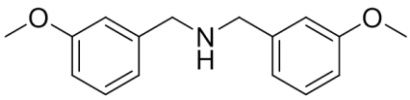
bis(4-methylbenzyl)amine (yellowish liquid)[16]

Isolated yield: 82%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.20 (d, J = 7.9 Hz, 4H), 7.12 (d, J = 7.8 Hz, 4H), 3.73 (s, 4H), 2.32 (s, 6H), 2.11 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 137.13, 136.59, 129.16, 128.25, 52.79, 21.18.

GC-MS: *m/z* (%) 225 (8) $[M]^+$, 120 (65), 105 (100), 91 (30), 77 (26), 65 (12), 51 (10).



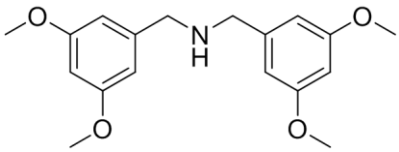
bis(3-methoxybenzyl)amine (yellowish liquid)[17]

Isolated yield: 81%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.22 (t, J = 8.0 Hz, 2H), 6.90 (d, J = 2.1 Hz, 4H), 6.79 (d, J = 8.2 Hz, 2H), 3.78 (s, 6H), 3.76 (s, 4H), 2.16 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 159.82, 141.76 129.44, 120.54, 113.70, 112.60, 55.22, 53.01.

GC-MS: *m/z* (%) 257 (1) $[M]^+$, 136 (83), 122 (100), 121 (75), 91 (39), 77 (27), 65 (23), 51 (10).



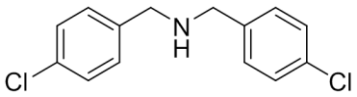
bis(3,5-dimethoxybenzyl)amine (white solid) (CAS:256225-28-2)

Isolated yield: 89%

^{1}H NMR (600 MHz, Chloroform-d) δ 6.50 (s, 4H), 6.36 (s, 2H), 3.77 (s, 12H), 3.73 (s, 4H), 2.12 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 160.79, 142.63, 106.97, 98.92, 55.13, 53.04.

GC-MS: *m/z* (%) 317 (1) $[M]^+$, 166 (28), 152 (100), 91 (5), 77 (15), 65 (10), 51 (3).



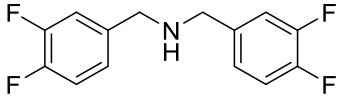
bis(4-chlorobenzyl)amine (colorless liquid)[18]

Isolated yield: 76%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.27 (d, J = 8.4 Hz, 4H), 7.24 (d, J = 8.4 Hz, 4H), 3.72 (s, 4H), 1.90 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 138.53, 132.81, 129.56, 128.62, 52.35.

GC-MS: *m/z* (%) 265 (5) $[M]^+$, 140 (42), 125 (100), 89 (13), 77 (15), 63 (10), 51 (10).



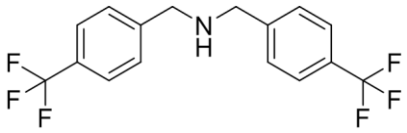
bis(3,4-difluorobenzyl)amine (colorless solid) (CAS: 1284842-52-9)

Isolated yield: 80%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.22 – 7.14 (m, 2H), 7.09 (dt, J = 10.1, 8.2 Hz, 2H), 7.04 (dd, J = 8.0, 4.1 Hz, 2H), 3.74 (s, 4H), 1.82 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 151.27 (d, J = 12.5 Hz), 149.63 (d, J = 12.9 Hz), 148.72 (d, J = 12.8 Hz), 137.18, 123.96, 117.03 (dd, J = 32.0, 17.2 Hz), 52.05.

GC-MS: *m/z* (%) 269 (3) $[M]^{+}$, 136 (100), 121 (24), 106 (64), 94 (42), 77 (56), 65 (32), 51 (30).



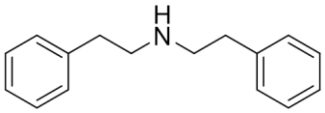
bis(4-(trifluoromethyl)benzyl)amine (colourless liquid)[18]

Isolated yield: 83%

^{1}H NMR (600 MHz, Chloroform-d) δ 7.59 (d, J = 8.2 Hz, 4H), 7.47 (d, J = 8.1 Hz, 4H), 3.86 (s, 4H), 1.95 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 144.11, 129.56 (d, J = 35.9 Hz), 128.47, 126.87 (d, J = 18.5 Hz), 125.51, 52.69.

GC-MS: *m/z* (%) 333 (1) $[M]^{+}$, 142 (32), 127 (100), 101 (15), 77 (5), 63 (8), 51 (2).



Diphenethylamine (yellowish liquid)[18]

Isolated yield: 89%

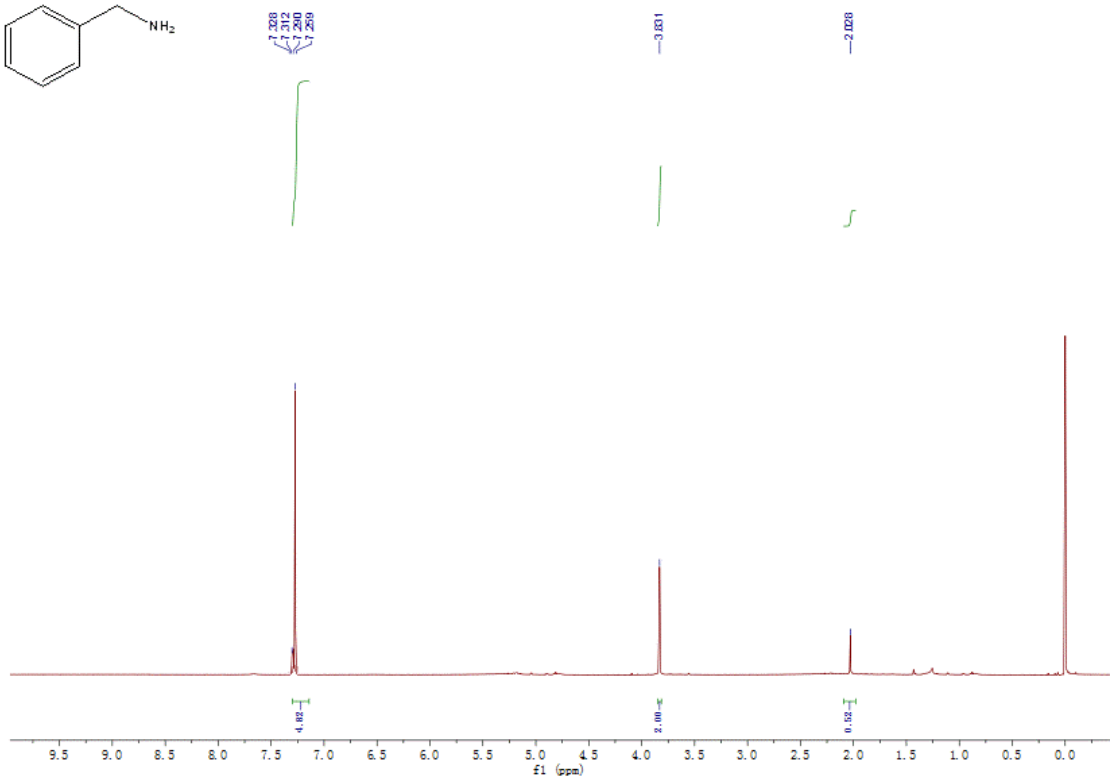
^{1}H NMR (600 MHz, Chloroform-d) δ 7.25 (t, J = 7.5 Hz, 4H), 7.22 – 7.17 (m, 2H), 7.15 (d, J = 8.0 Hz, 4H), 2.93 (s, 4H), 2.77 (t, J = 7.1 Hz, 4H), 1.54 (s, 1H).

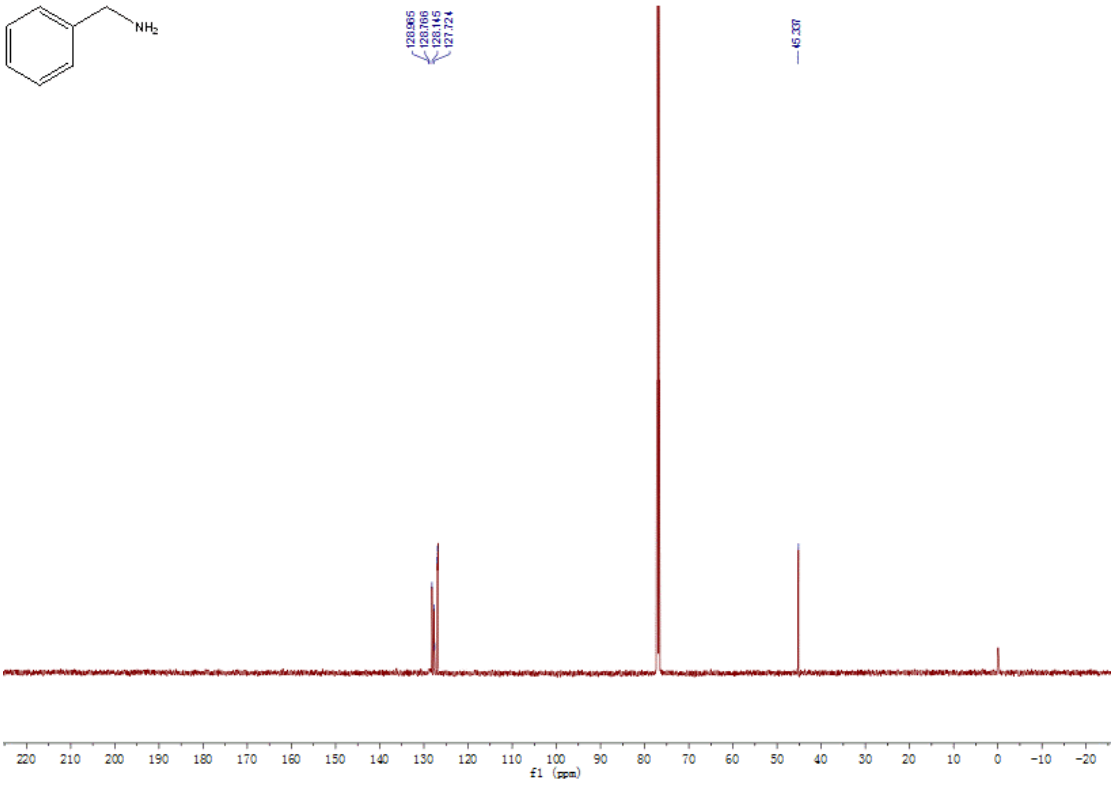
^{13}C NMR (151 MHz, Chloroform-d) δ 140.01, 128.74, 128.52, 126.20, 50.95, 36.46.

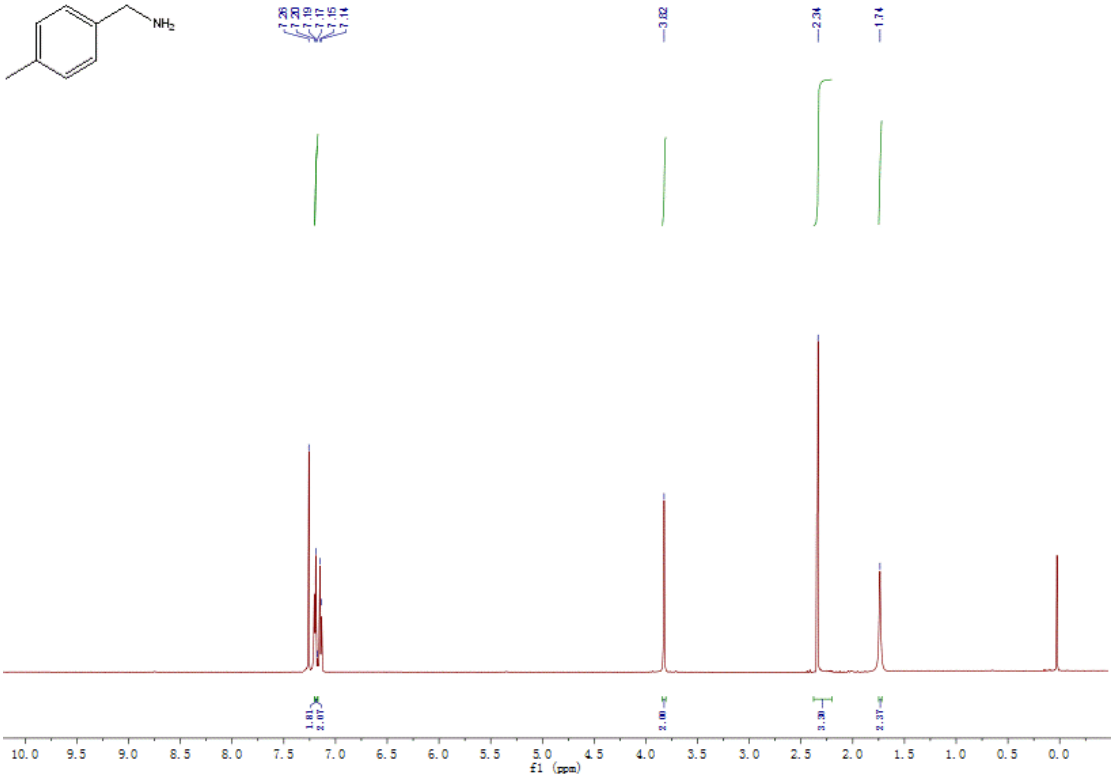
GC-MS: *m/z* (%) 225 (8) $[M]^{+}$, 134 (95), 105 (100), 77 (27), 65 (16), 51 (14).

Copies of ^{1}H and ^{13}C NMR spectrums：

Primary amines



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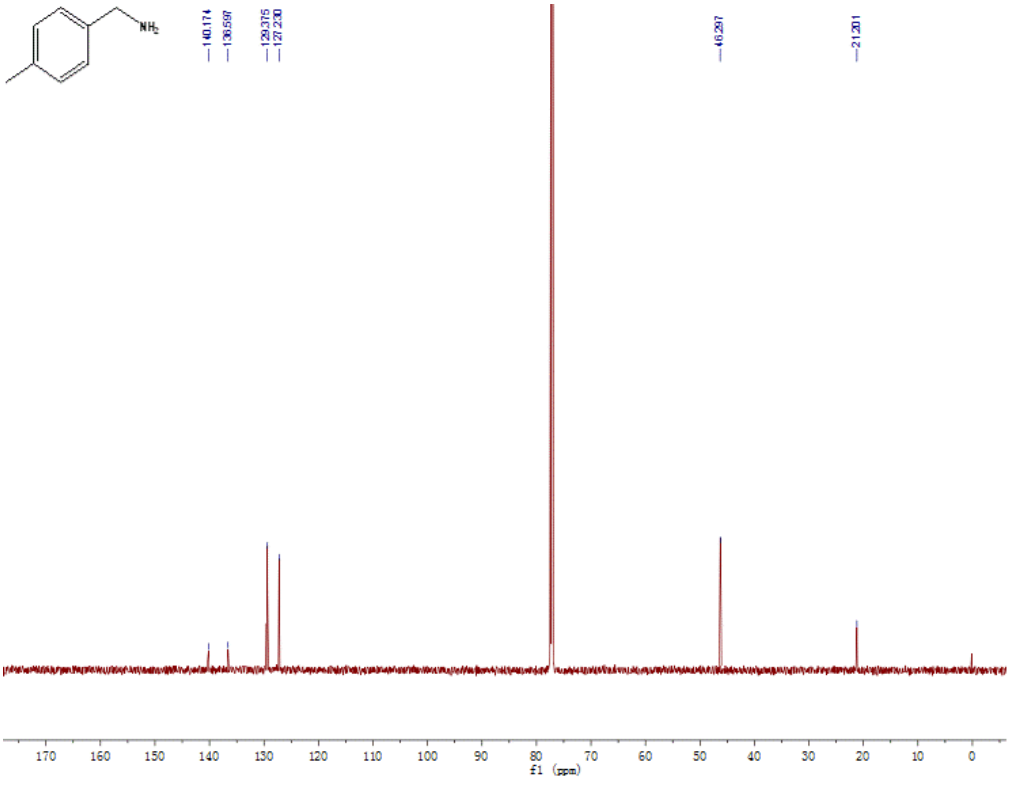
7.20
7.19
7.17
7.15
7.14
3.82
2.34
1.74
1.81
2.07
2.00
3.30
2.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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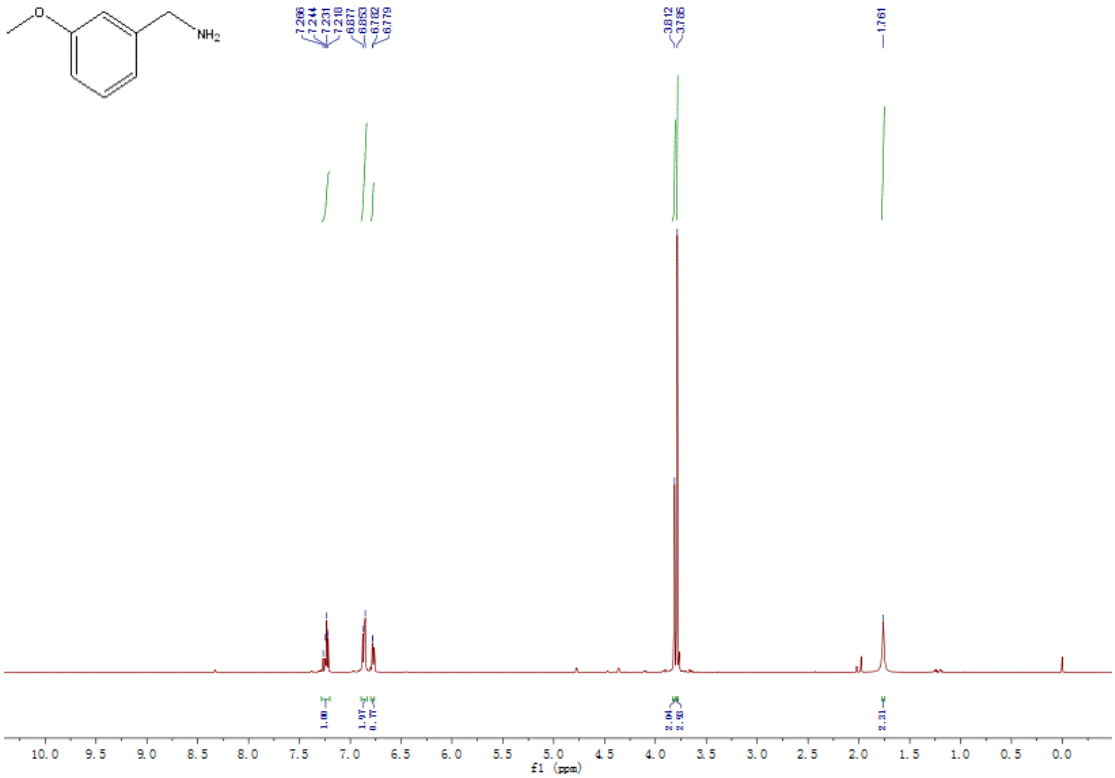
136.597
129.375
127.230
46.297
21.201
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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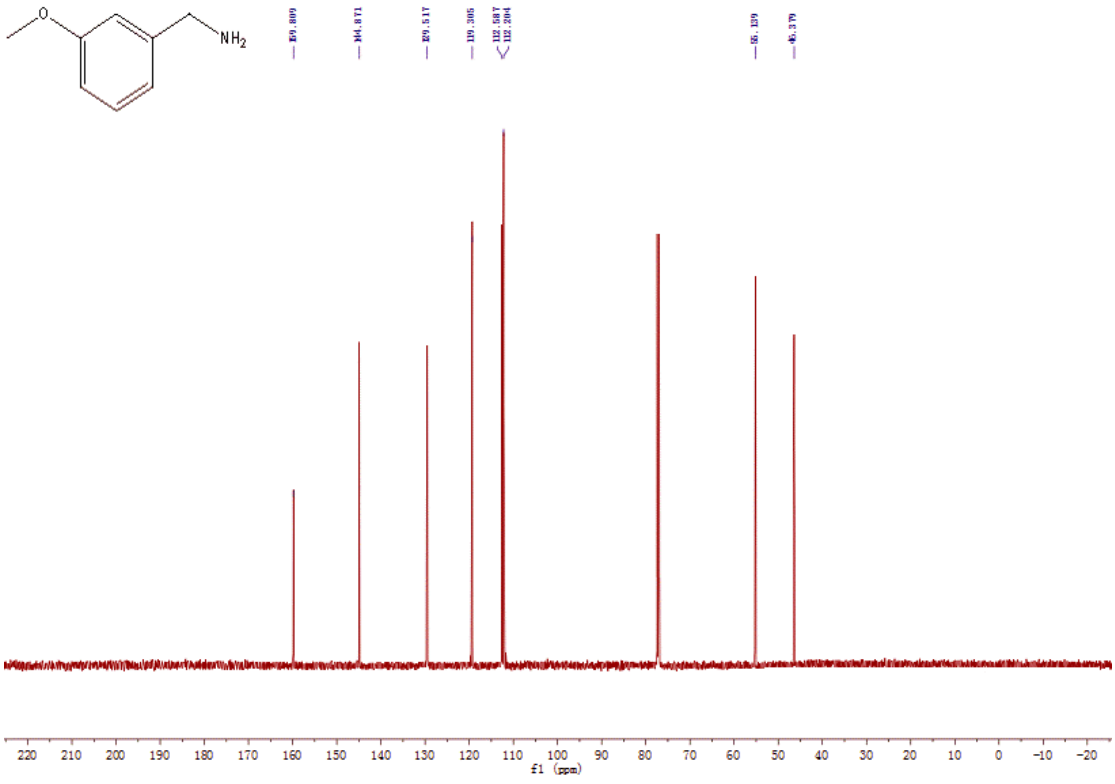
7.244
7.231
7.218
6.857
6.853
6.782
6.779
3.812
3.785
1.761
1.00
1.97
0.77
2.04
2.93
2.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
NH2
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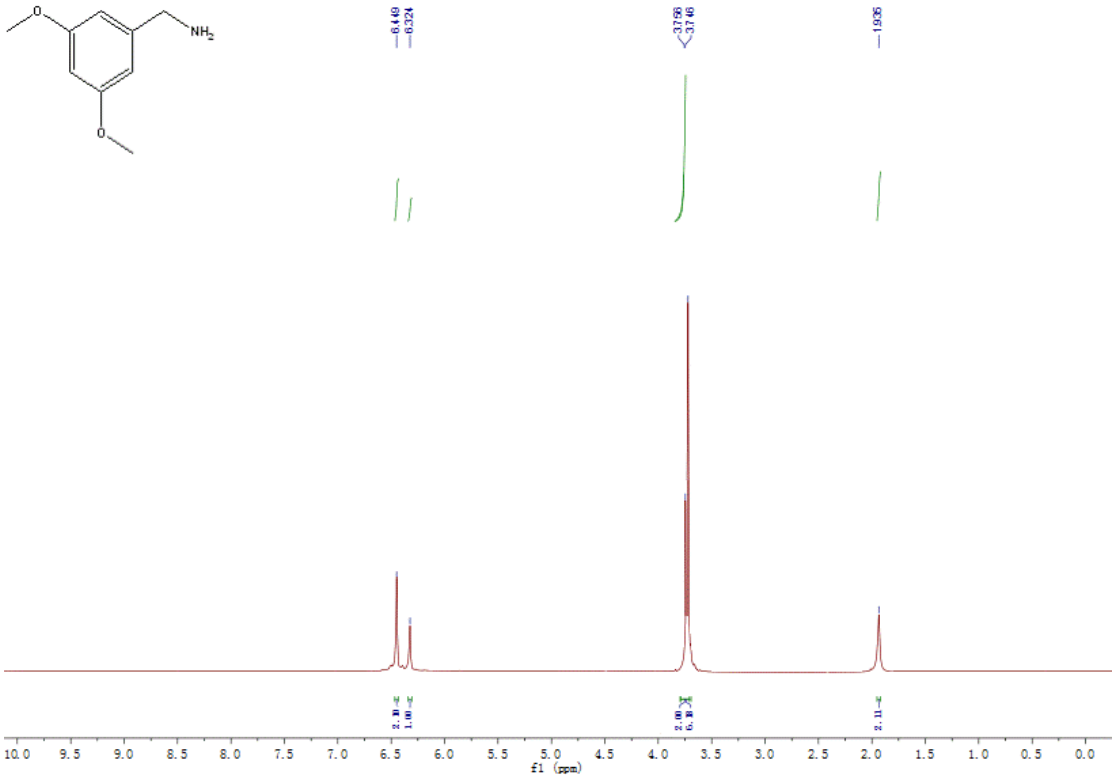
144.871
129.517
119.305
112.587
112.204
66.139
45.379
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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O
O
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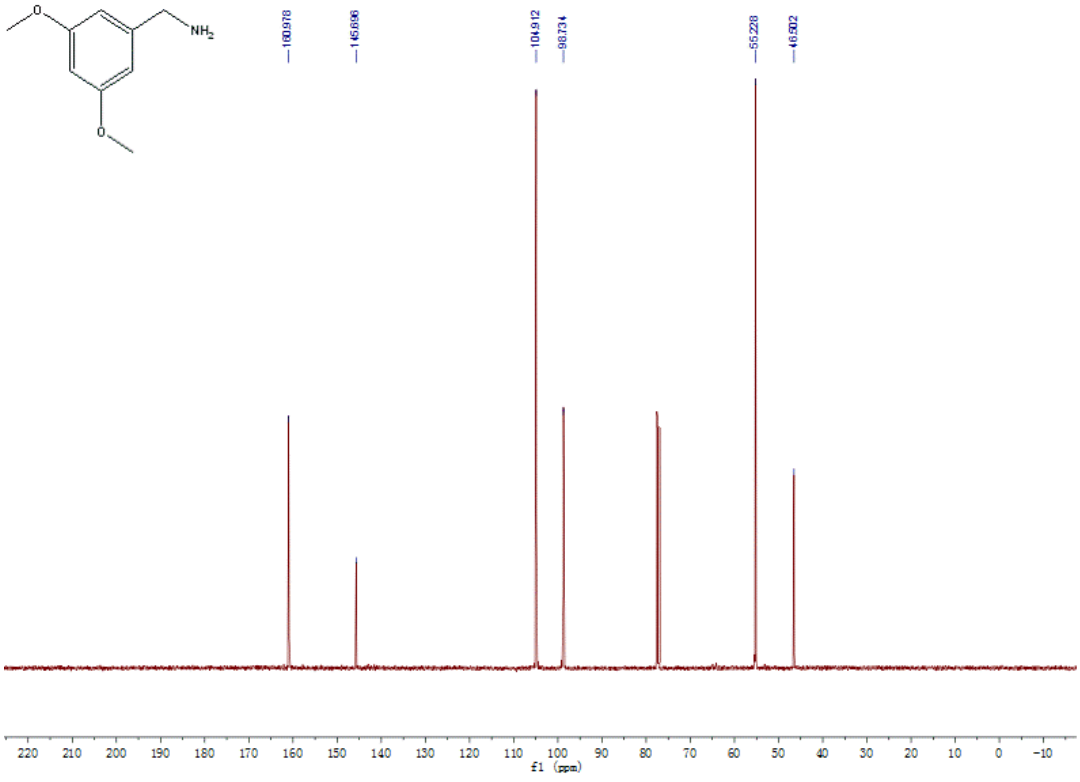
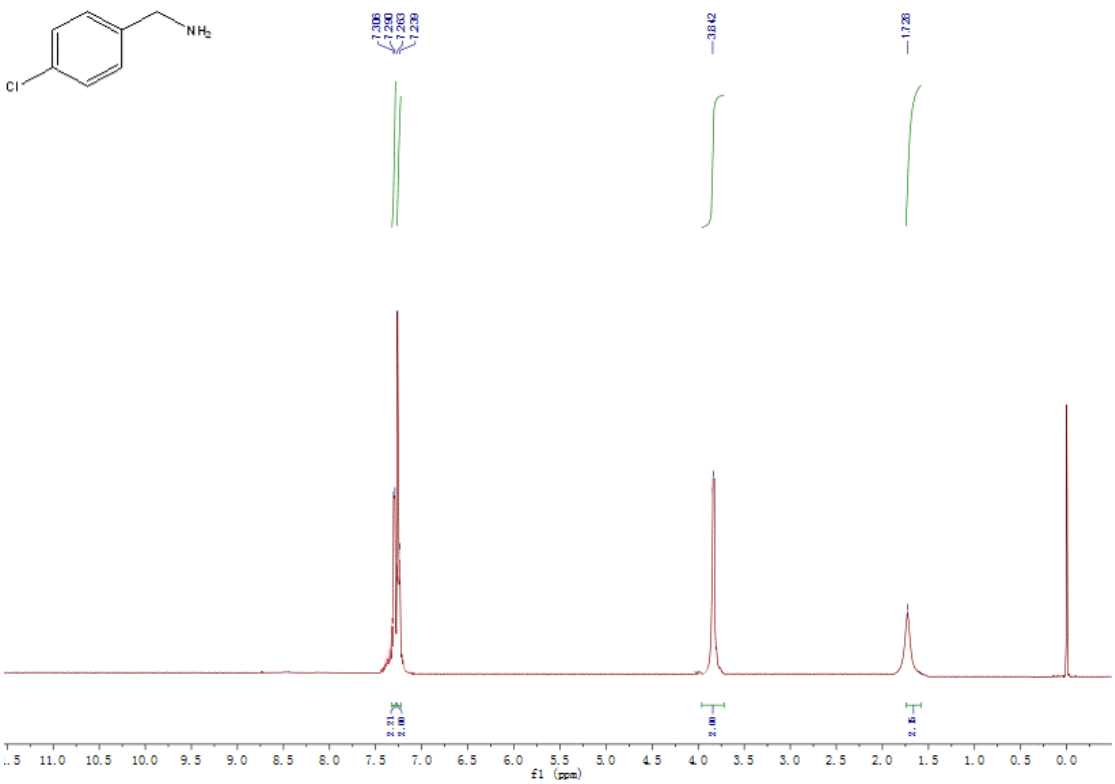
6.324
3.766
3.746
1.935
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NH2
O
O
160.978
145.696
104.912
98.734
55.228
46.502
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH2
Cl
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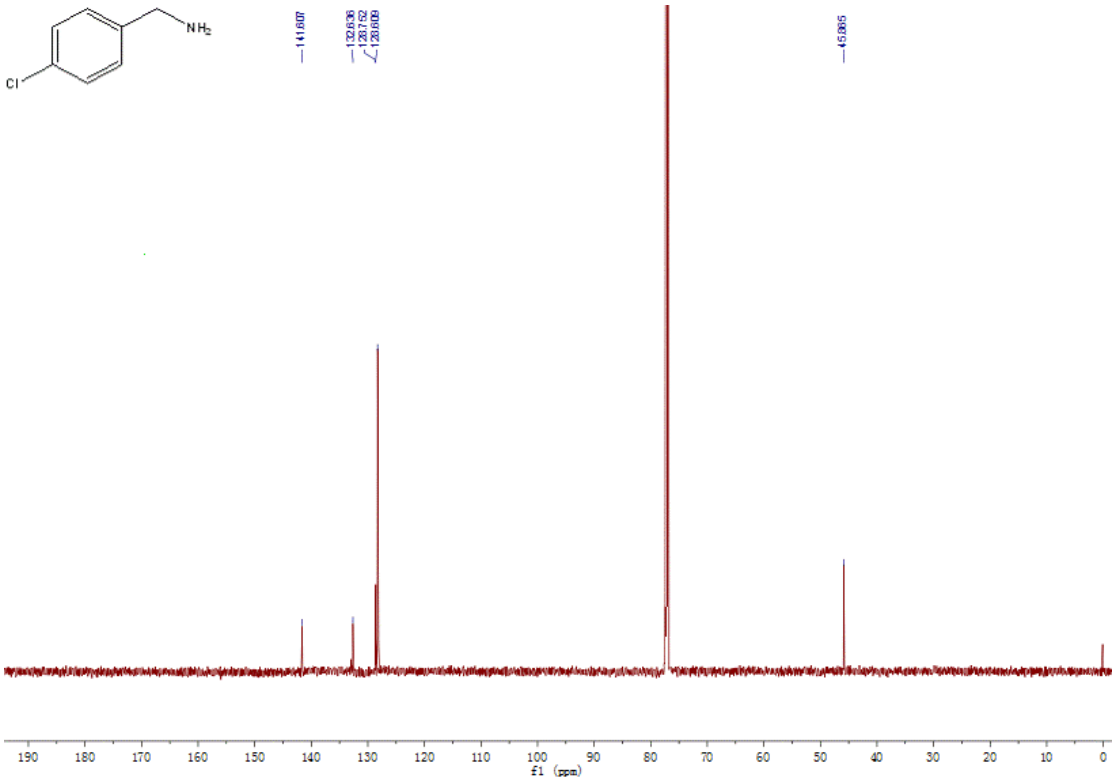
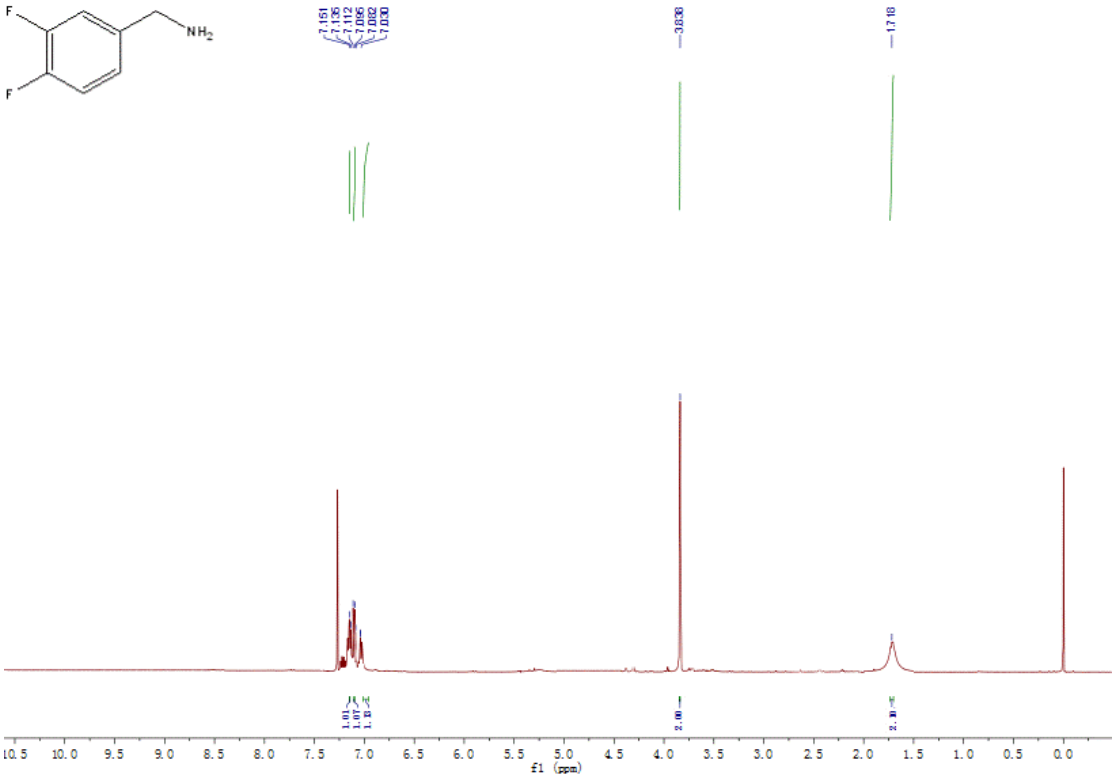
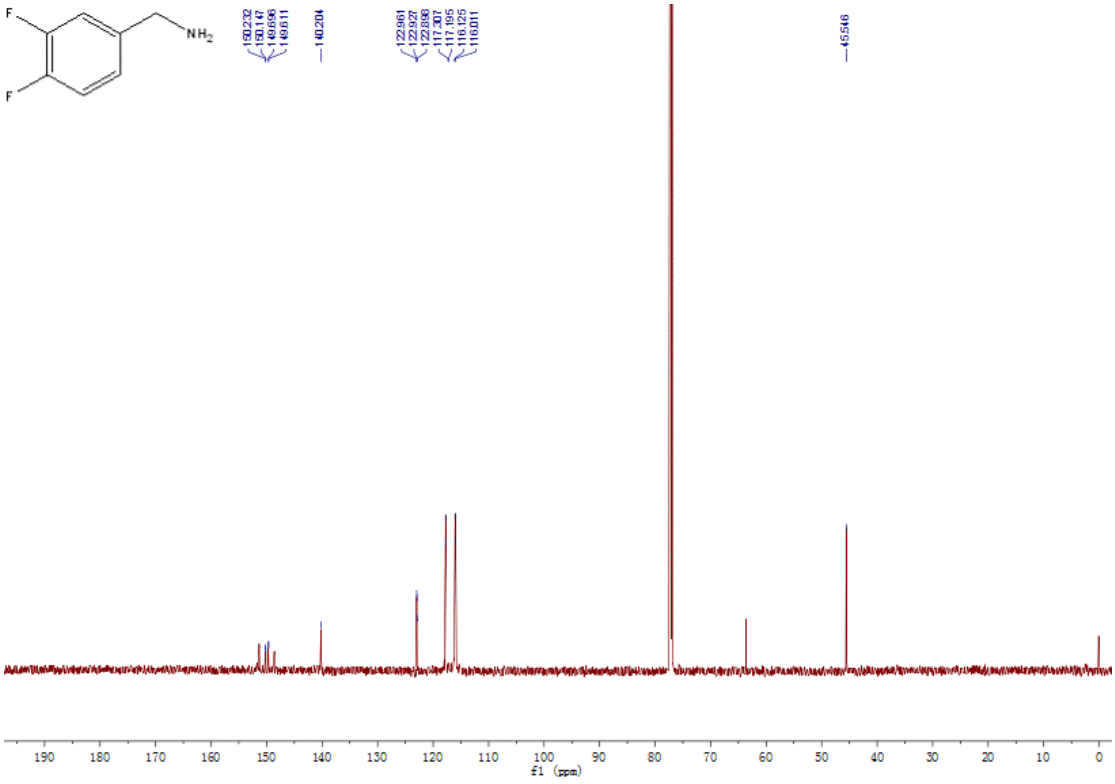
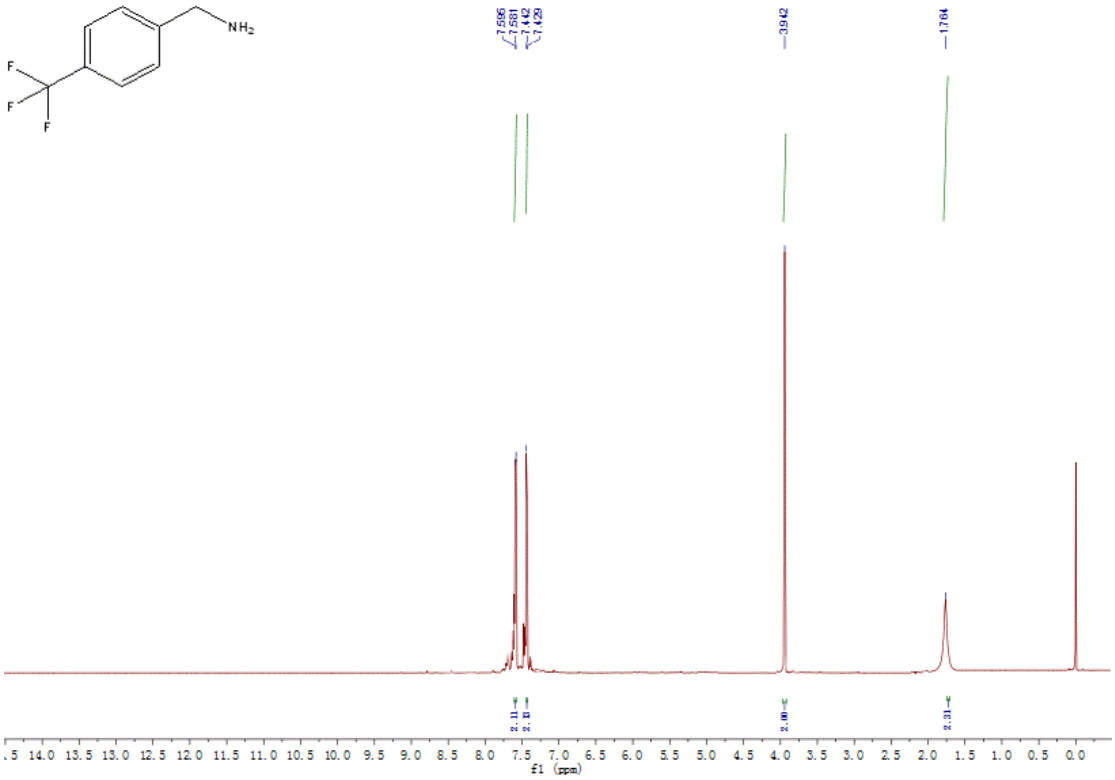
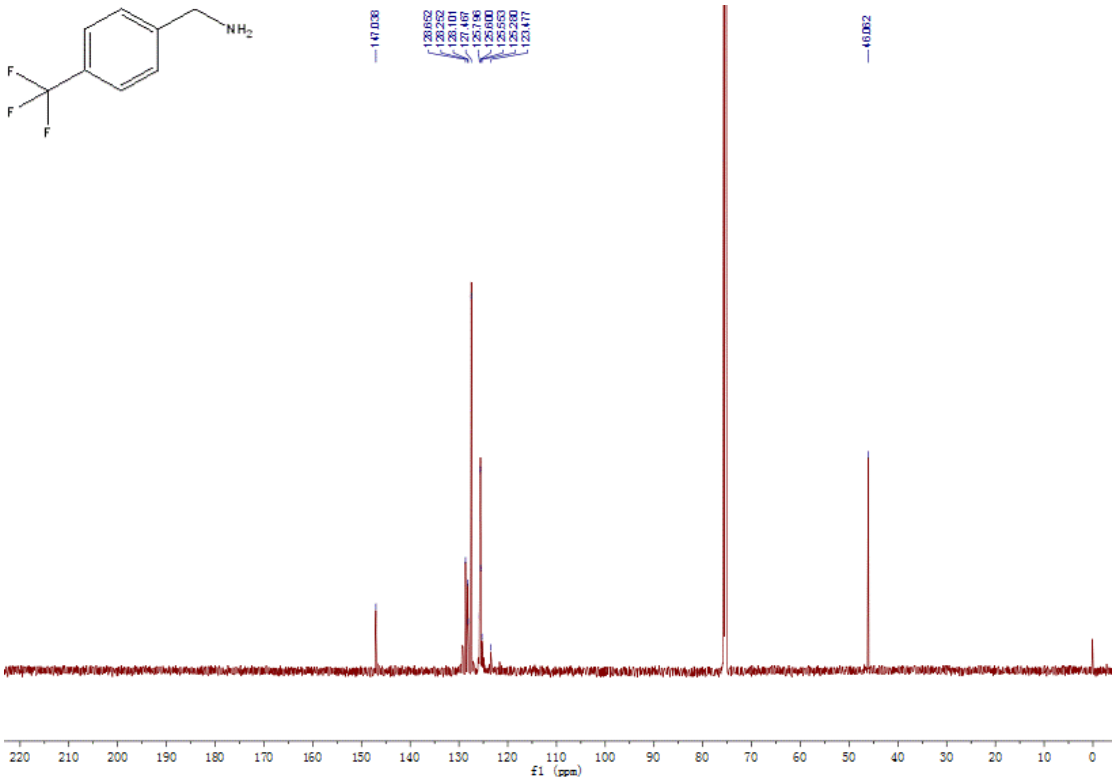
7.290
7.263
7.239
3.842
1.728
2.21
2.00
2.00
2.16
f1 (ppm)

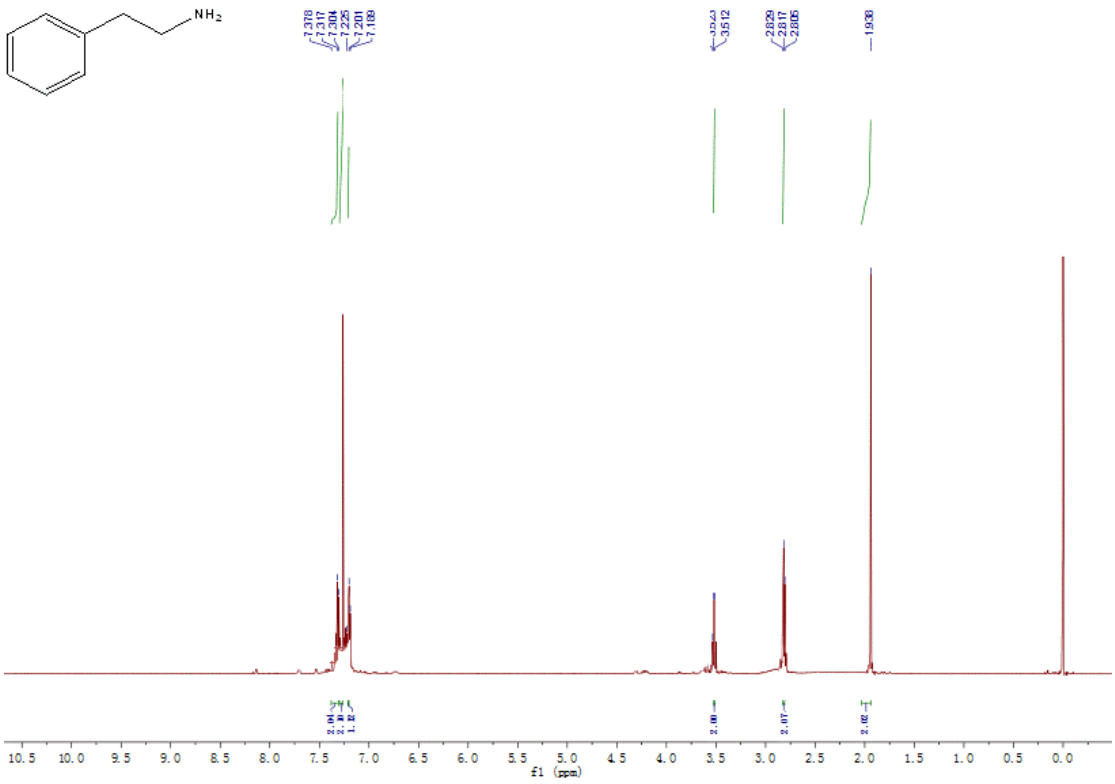

NH2
Cl
141.607
132.636
128.752
128.609
45.865
f1 (ppm)

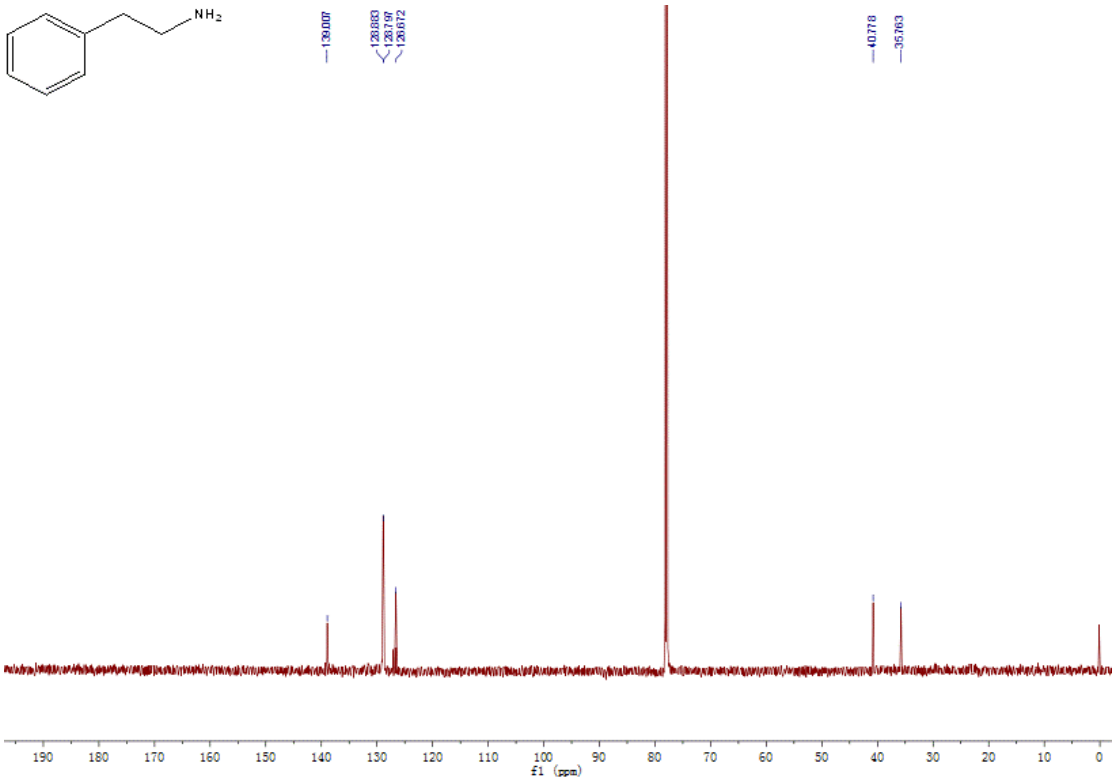

F
NH2
F
7.161
7.135
7.112
7.095
7.082
7.030
3.838
1.718
1.01
1.07
1.13
2.00
2.30
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
NH2
F
150.232
150.147
149.696
149.611
140.204
122.961
122.927
122.890
117.307
117.255
116.125
116.011
45.546
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

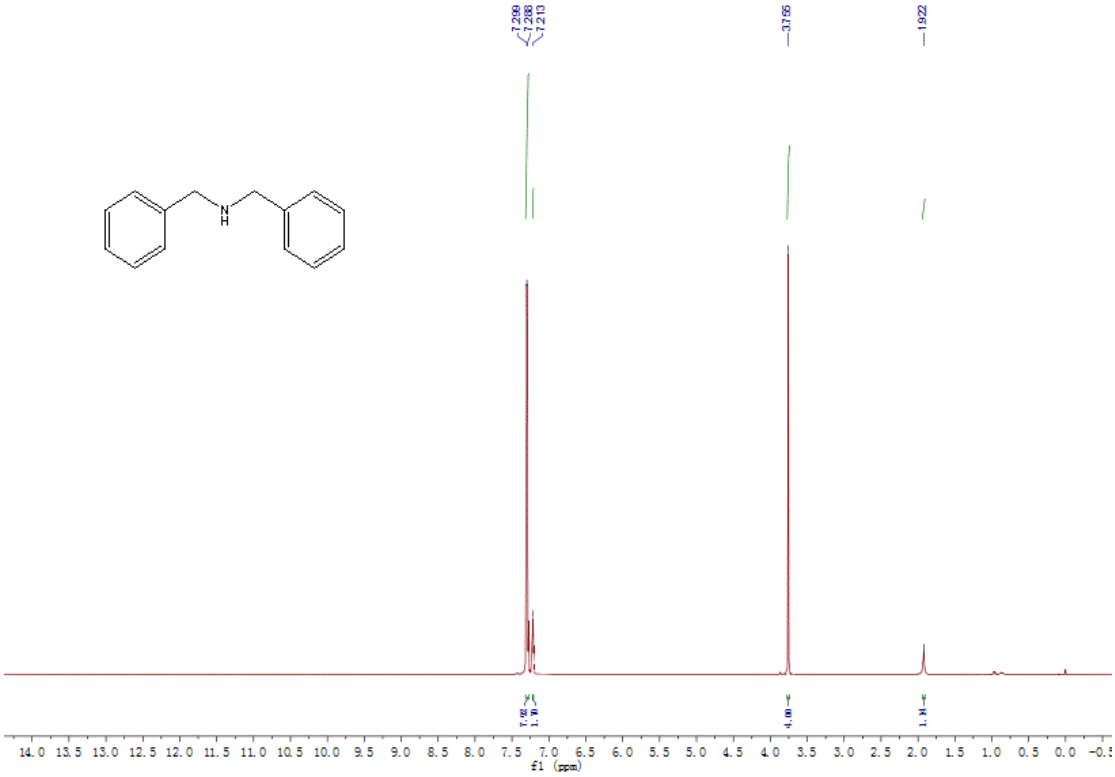

NH2
F
F
F
7.596
7.581
7.442
7.429
3.942
1.764
2.11
2.00
2.31
f1 (ppm)

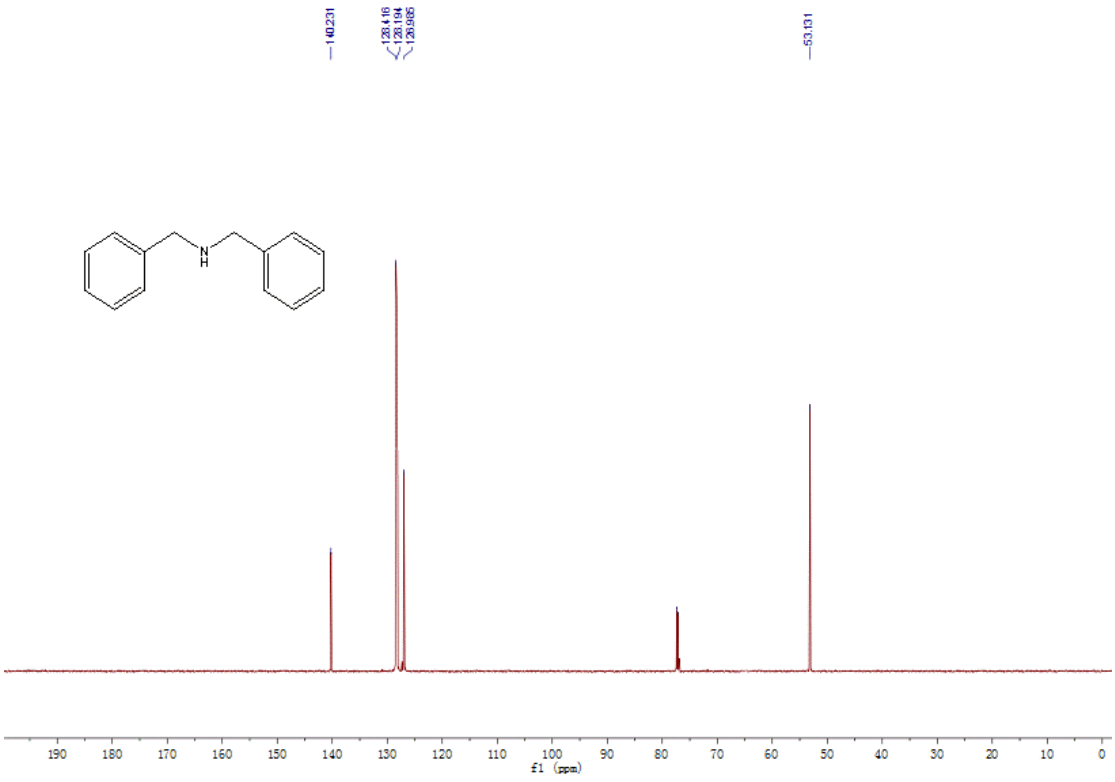

NH2
F
F
F
147.038
46.062
f1 (ppm)

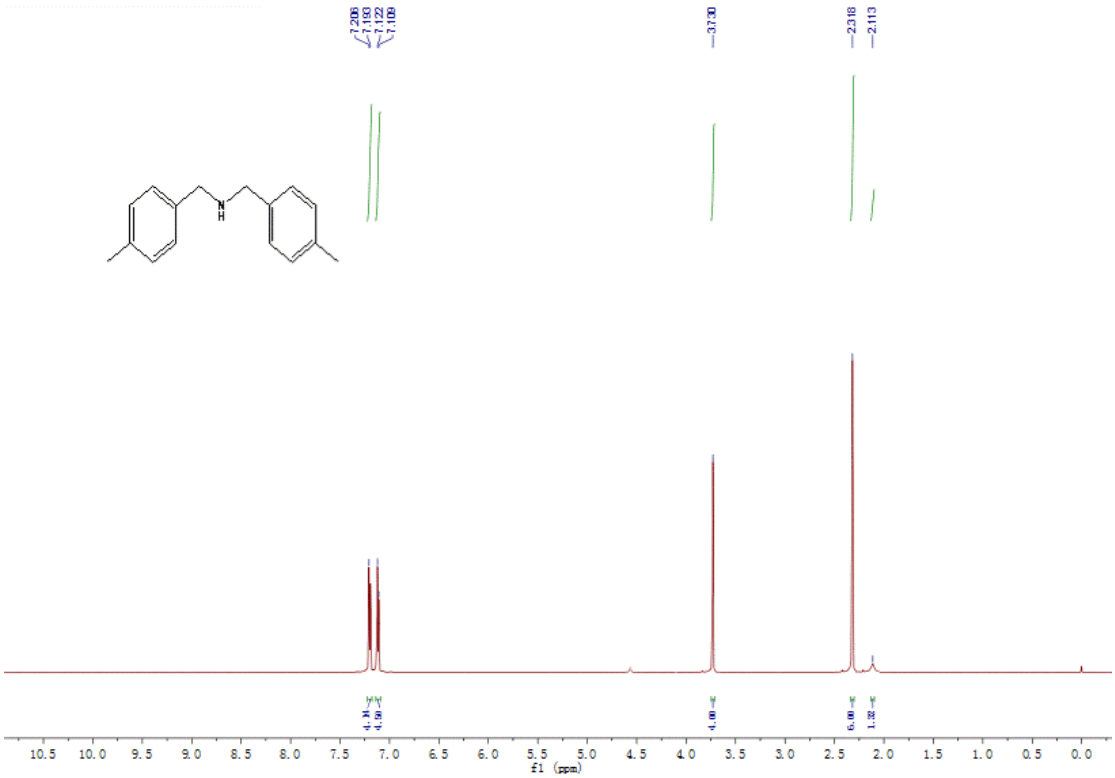

NH2
7.318
7.317
7.304
7.225
7.201
7.189
3.512
2.829
2.817
2.805
1.938
f1 (ppm)

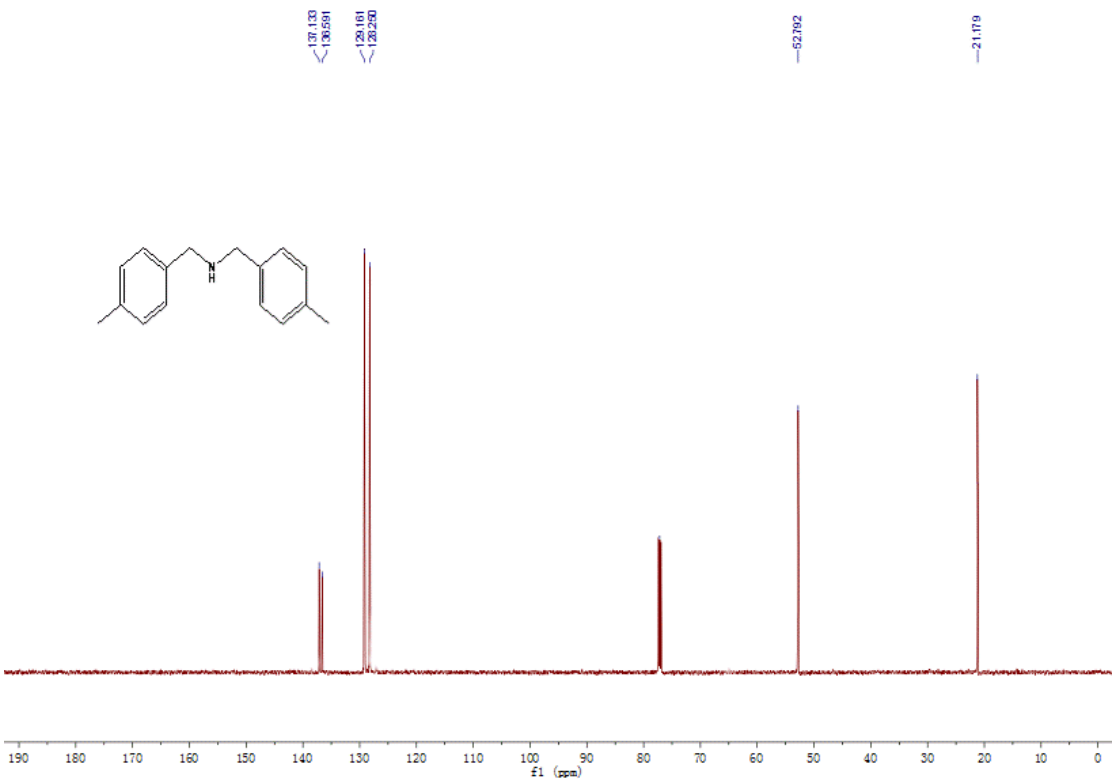

NH2
139.007
126.883
126.797
126.672
40.778
35.163
f1 (ppm)

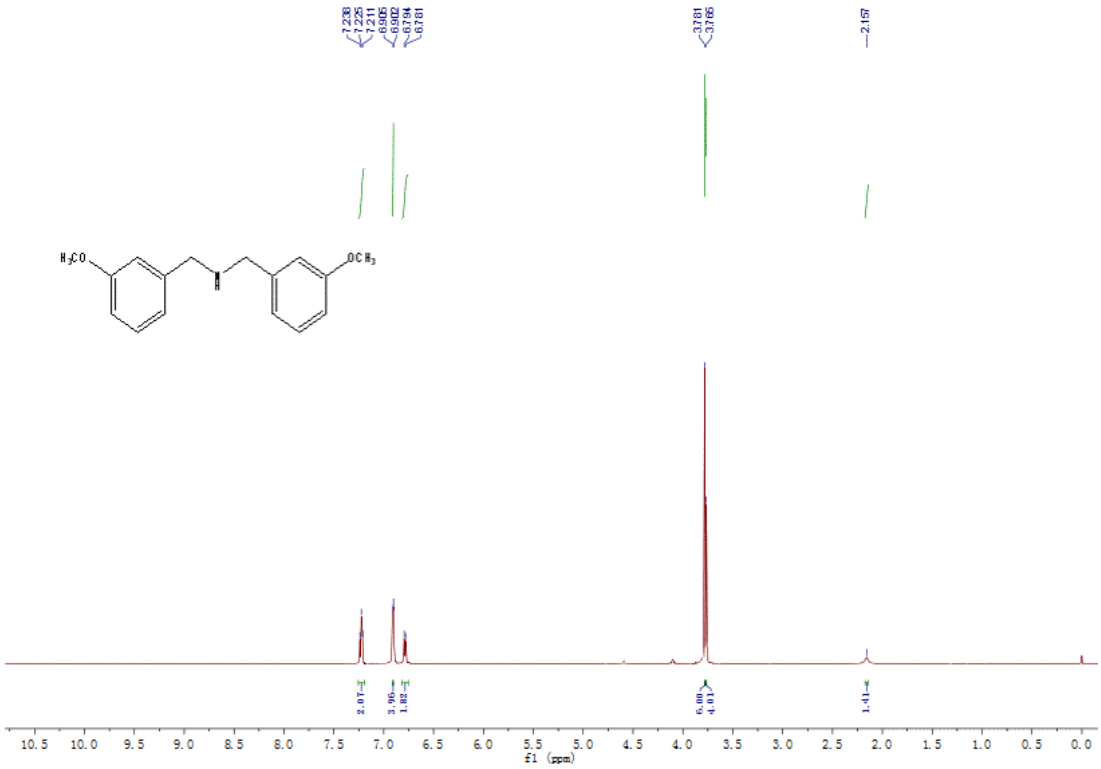
Secondary amines

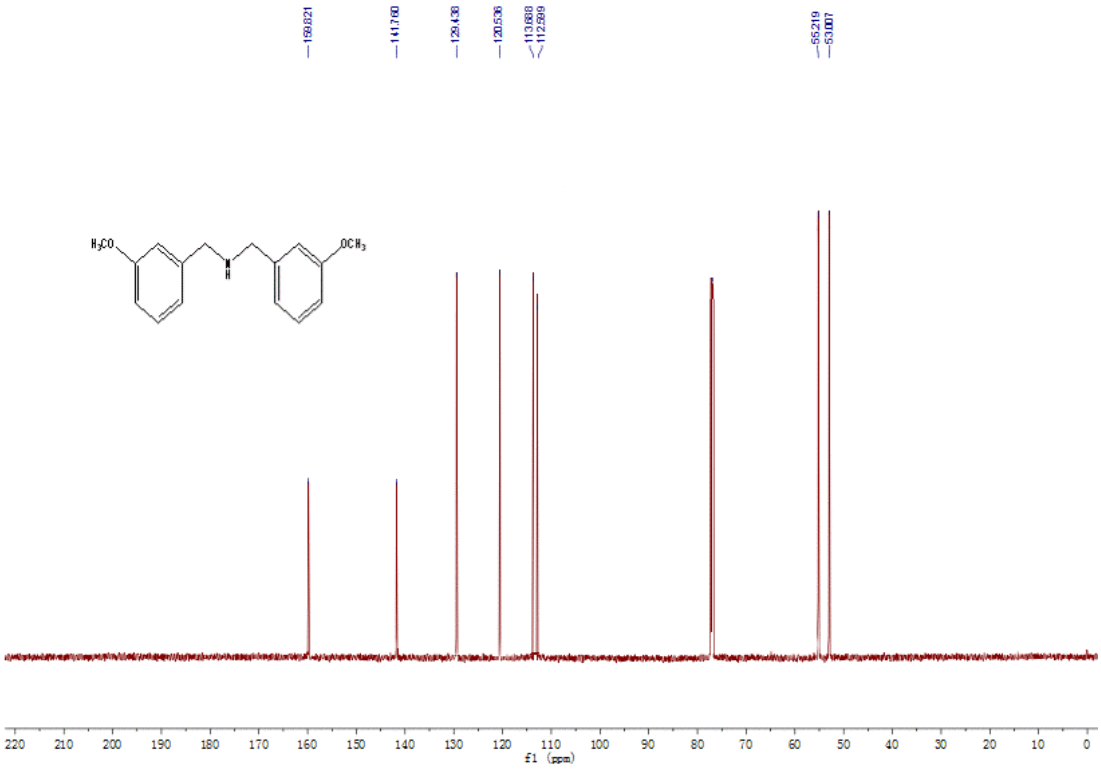


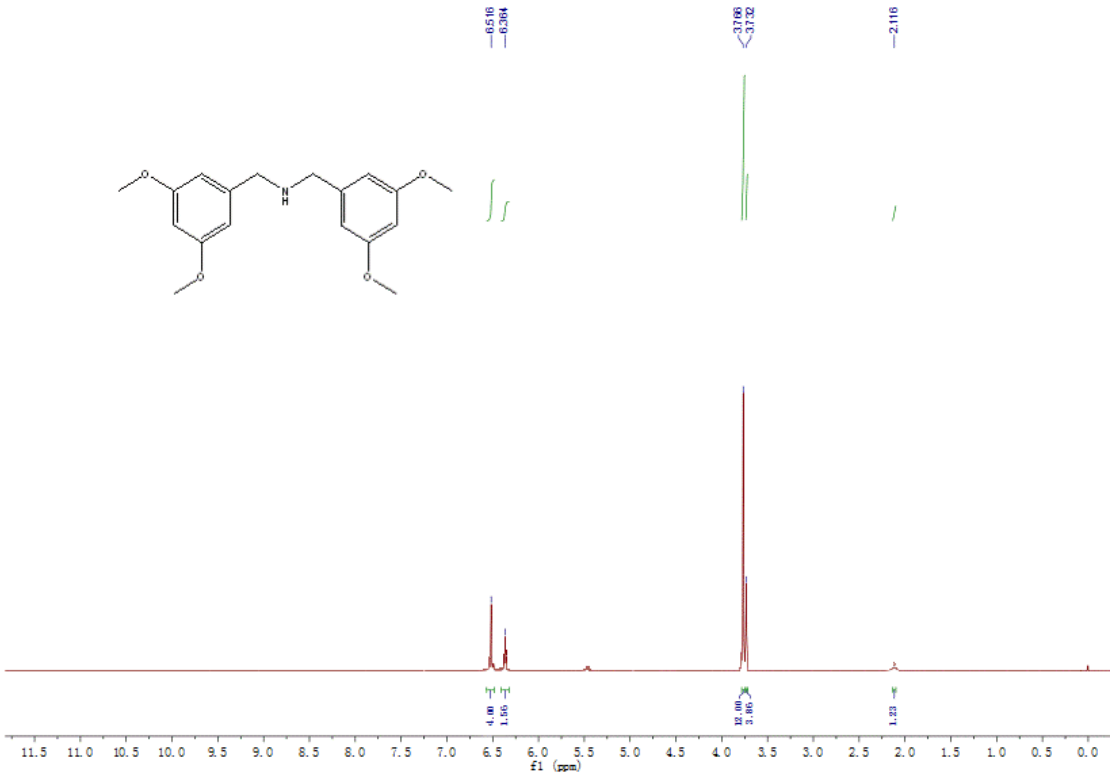


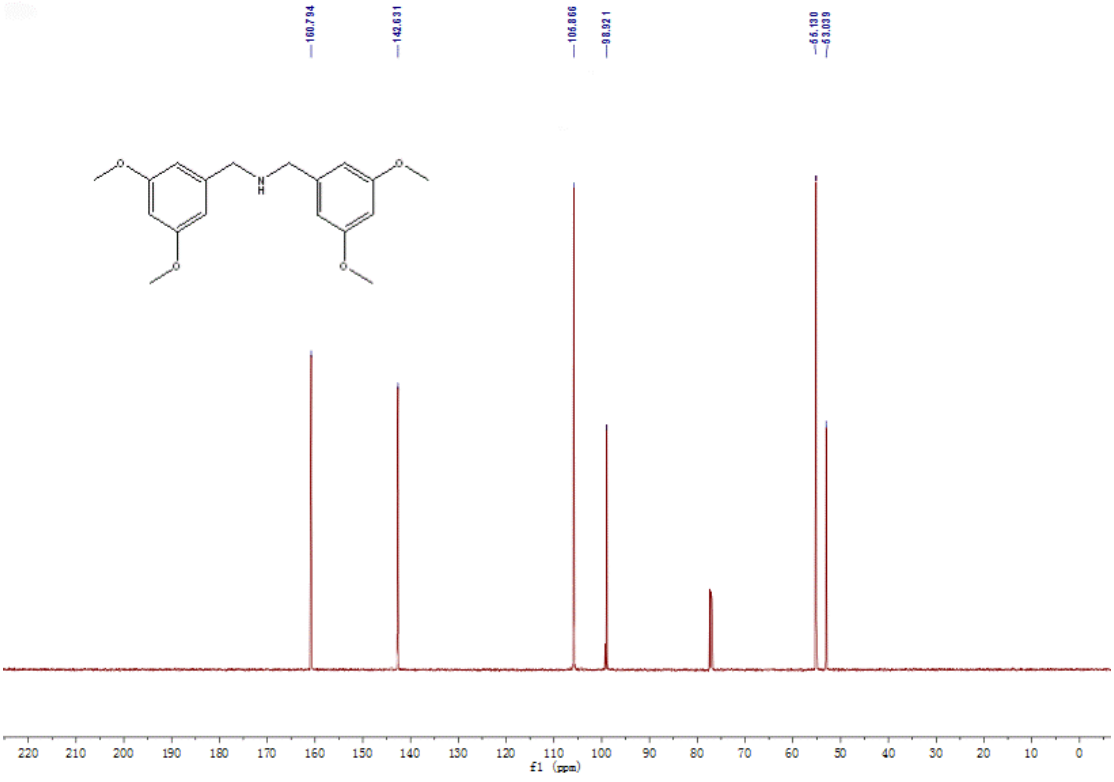

7.200
7.190
7.172
7.108
3.730
2.318
2.113
4.00
4.00
6.00
1.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


137.133
130.591
129.161
128.250
52.792
21.179
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

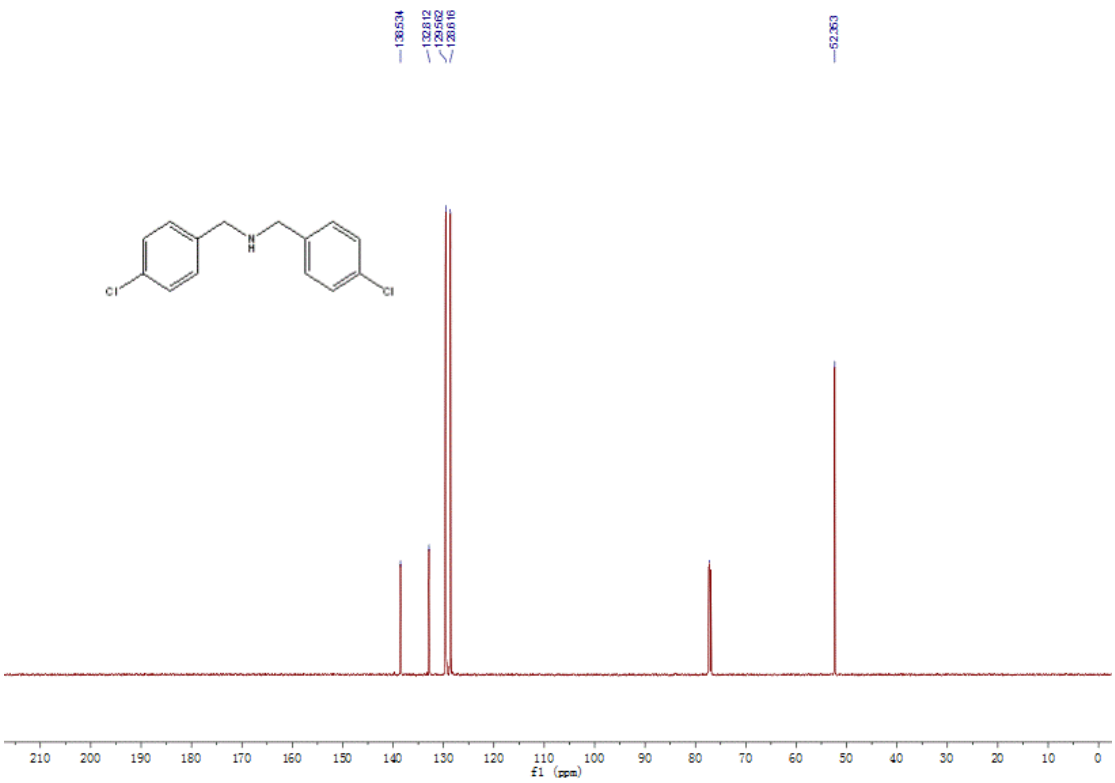

7.238
7.225
7.211
6.805
6.802
6.784
6.781
3.781
3.765
2.157
H3CO
OCH3
2.07
3.96
1.82
6.00
4.01
1.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

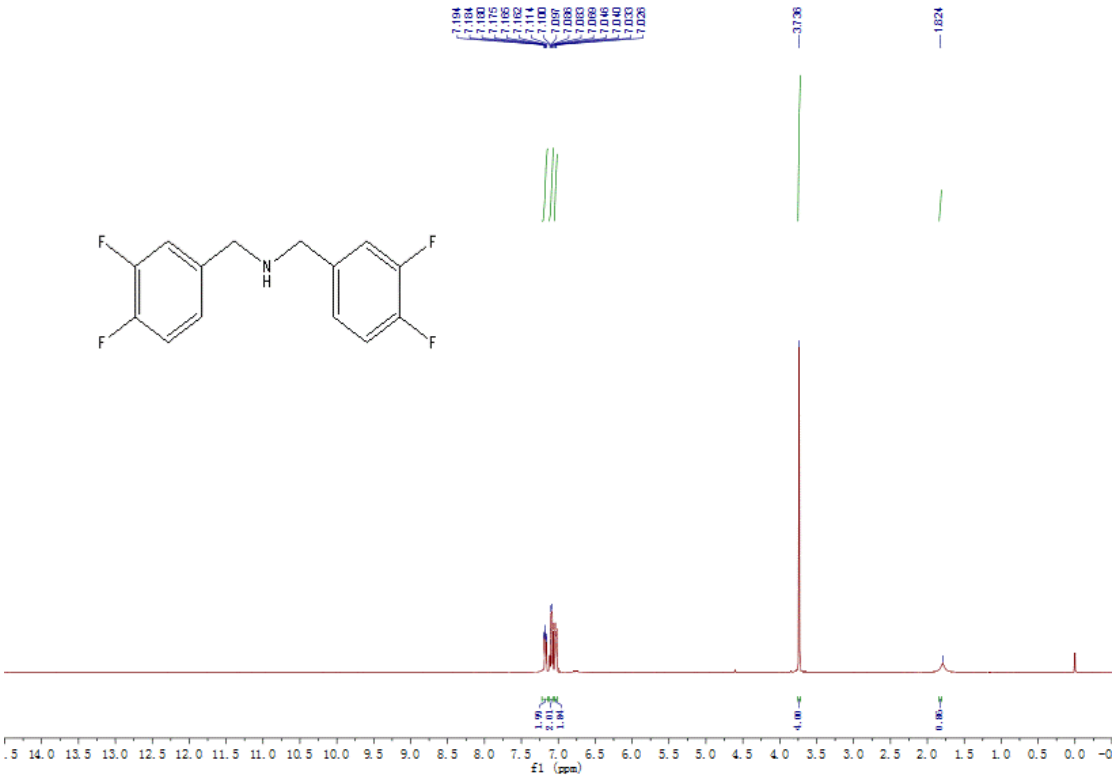

159.821
141.760
129.436
120.536
113.688
112.599
55.219
53.007
H3CO
OCH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

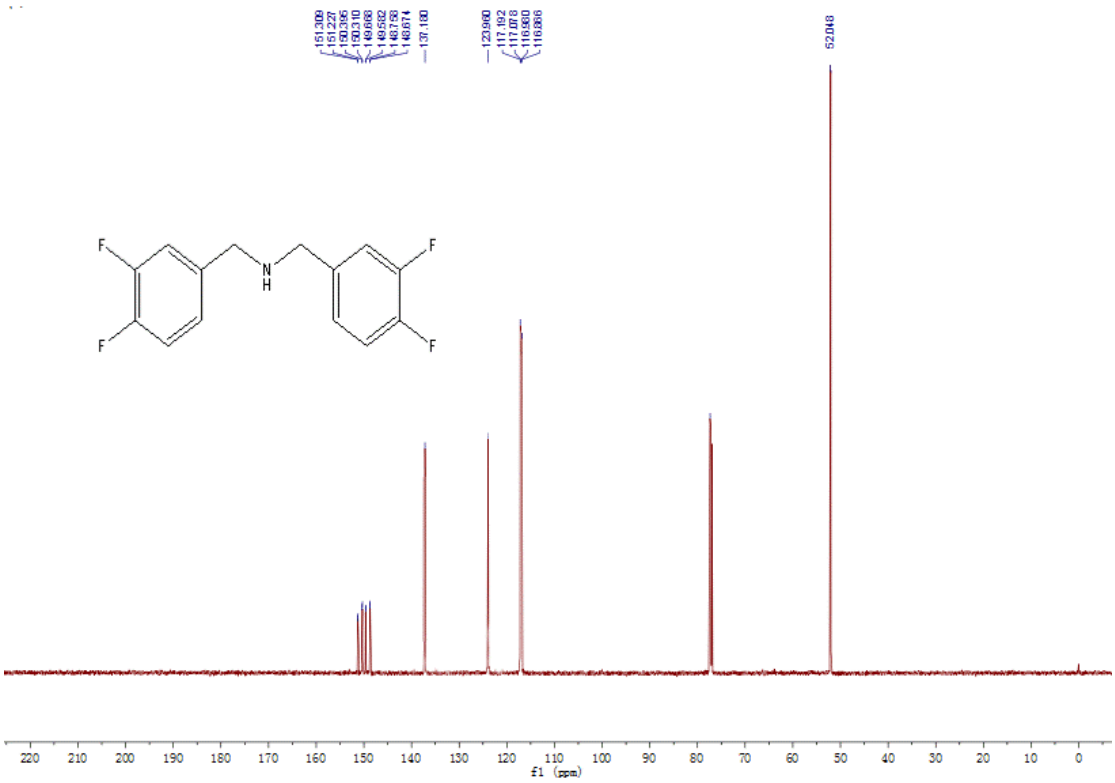

6.516
6.364
3.766
3.732
2.116
4.00
1.56
12.00
3.86
1.23
f1 (ppm)


160.794
142.631
106.866
98.921
55.130
55.039
f1 (ppm)

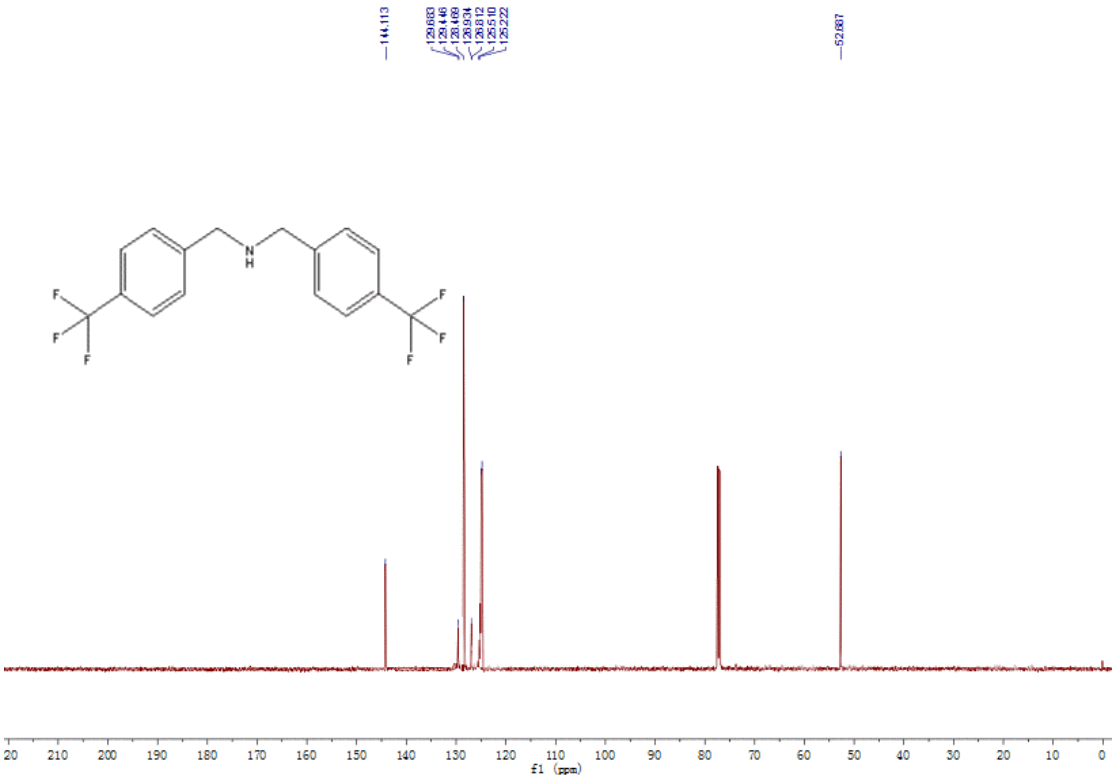

7.281
7.279
7.267
7.249
7.235
7.230
3.723
1.896
Cl
N
H
Cl
3.83
4.38
4.00
1.87
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

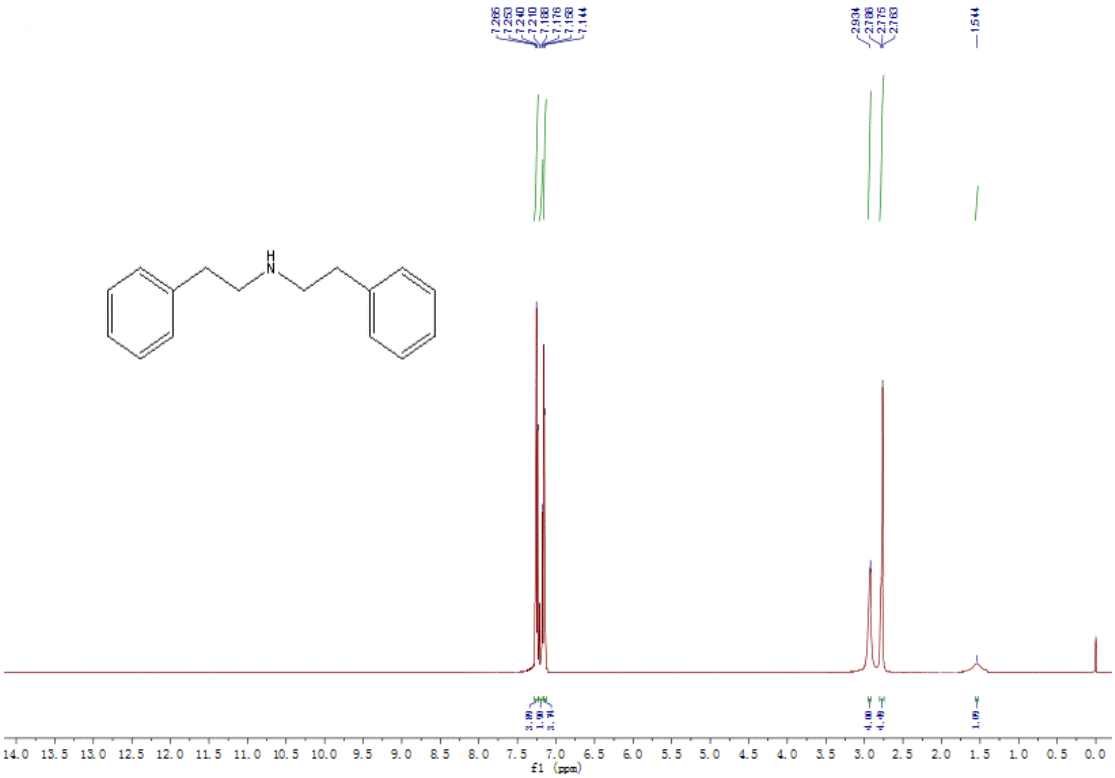

138.534
132.812
129.562
128.616
52.353
Cl
N
H
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

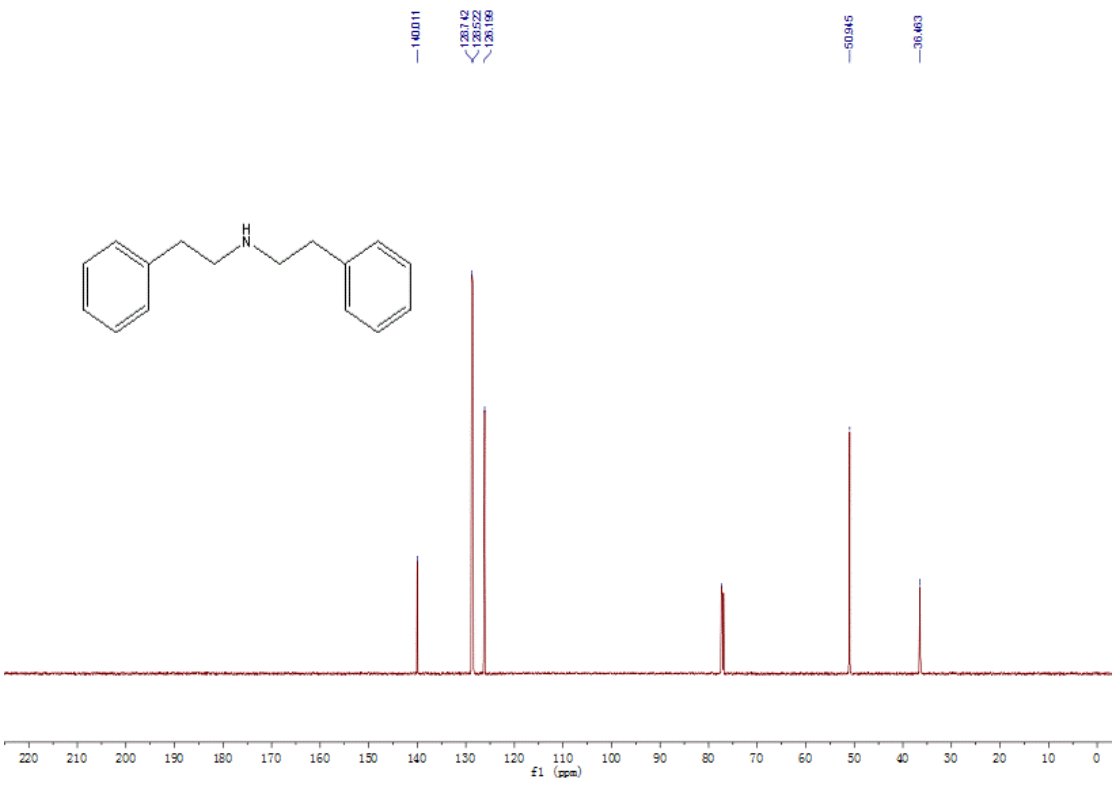

7.194
7.184
7.180
7.175
7.165
7.162
7.114
7.100
7.097
7.088
7.083
7.069
7.046
7.040
7.033
7.026
3.736
1.824
F
F
N
H
F
F
1.99
2.01
1.84
4.00
0.86
f1 (ppm)


151.309
151.227
150.395
150.310
149.668
149.582
148.739
148.674
137.100
123.960
117.192
117.078
116.990
116.886
52.048
F
F
N
H
F
F
f1 (ppm)


7.595
7.581
7.473
7.460
3.883
1.947
3.86
3.96
4.00
1.82
f1 (ppm)


144.113
129.683
129.446
128.469
126.934
126.812
125.510
125.222
52.887
f1 (ppm)


7.265
7.253
7.240
7.210
7.188
7.176
7.158
7.144
2.804
2.788
2.775
2.763
1.544
3.09
1.90
3.94
4.00
4.49
1.09
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.011
128.742
128.522
126.199
50.845
36.463
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Supplementary reference

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