Supporting Information

Efficient and Mild Reductive Amination of Carbonyl Compounds Catalysed by Dual-Function Palladium Nanoparticles

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Total number of pages: 54. Total number of figures: 5. Total number of table: 5.

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1. Generals

All chemicals are commercially available and were purchased from Aladdin (Shanghai, China), and used as received without any further purification. All chemicals used were of analytical grade. ^{1}H NMR and ^{13}C NMR spectrum were recorded on a Bruker Avance-400 instrument, 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, with $CDCl_3$ or DMSO-d_6 or CD_3OD-d_4 as solvent in all cases. All chemical shifts (δ) were quoted in parts per million (ppm) and reported relative to an internal tetramethylsilicane (TMS, δ 0.00) standard. The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet. Yields of some products were measured by HPLC analysis using a SHIMADZU instrument equipped with a Wonda Sil C18-WR column (5 μm). Yields of some other products were measured by GC analysis using FULI 9790II instrument equipped with a DB-624 capillary column (30 m 1.4 μm × 0.25 mm). EI mass spectra were measured on SHIMADZU QP2020 spectrometer.

The High-Resolution Transmission Electron Microscope (HRTEM) measurements were performed using a JEM 2100F microscope. The samples were dispersed in ethanol with ultrasonic for 5 min and then dropped onto a carbon film on copper grid. And the instrument was operated at 200 kV. Inductively coupled plasma-optical emission spectrometer (ICP-OES) from Perkin Elmer Nexion 300 was used to identify the Pd content of the nanoparticles. Samples were prepared by digesting 10 mg of nanoparticles in 2.0 mL of H_2O_2 and 8 ml aqua regia using constant temperature drying oven for 3 hours. The solutions were made up to 50 mL in standard flask and start to detect Pd. X-ray diffraction (XRD) patterms was collected from 5° to 90° with a step of 0.02 on a Bruker D 8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a Lynxeye one-dimensional detector. Elemental analysis (EA) measurement was performed using the Flash 2000. X-Ray photoelectron spectroscopy (XPS) measurements were obtained in ultra-high vacuum (base pressure of 1 × 10-10 mbar) equipped with an Al source (Kα radiation of 1486.6 eV) and an Escalab 250Xi analyser at 53° detection angle. The number of active atoms were determined by chemisorption analysis of hydrogen under 50°C using AutoChem II 2920.

2. General procedure for the synthesis Pd-Ligands

The catalyst Pd-ligands were prepared following the procedure: To a mixed solution of the ligands of 0.1 mmol (**Figure S1**) and HBF_4 (40%, 1 ml), sodium nitrite (0.2 mmol) dissolved in 1 ml ultrapure water was drop wised, stirred at 0°C for 1 h, the generated white solid was filtered and introduced to a

mixed solution by toluene of 1 ml, ultrapure water of 2 ml and K_2PdCl_4 of 0.08 mmol, the resulted mixture was stirred for another 1 h. $NaBH_4$ (0.6 mmol) dissolved in water (1 ml) was dropped at *rt* to the mixture and incubated for 2 h. The solution was centrifuged to remove the aqueous phase, the resulted solid was washed with H_2SO_4 (0.5M) three times and then was mixed with ethanol, sonicated for 5 min, and centrifuged to remove ethanol, the solid was dried to provide Pd-Ligands.

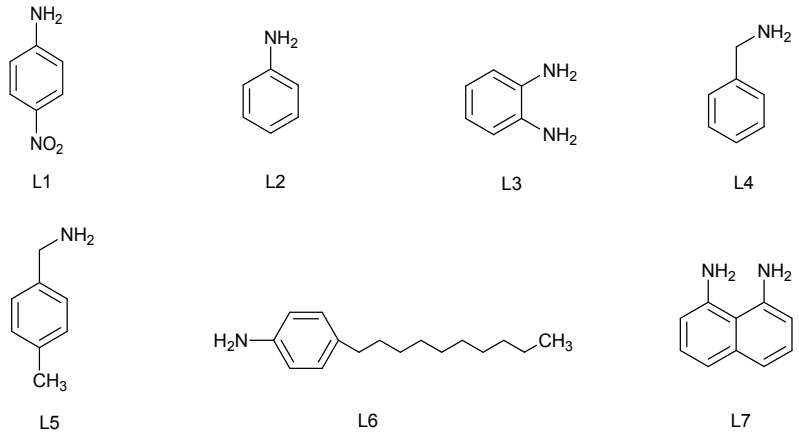


Figure S1. Structure of varied ligands

3. Optimization of conditions for reductive amination of benzaldehyde

Benzaldehyde (0.05 mmol), ammonia water or ammonium salts (0.2 mmol) and catalysts (Pd-(L1-L7)) (2.0 mg) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H_2O (10 ml, different pH varying from 1.0 to 7.0) were added to the reaction tube and the reaction mixture was stirred at room temperature, 60°C, 80°C with H_2 balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC analysis equipped with a C18 reverse column. Among all the tested conditions, the best one is: amine source, ammonia water; catalyst, Pd-L5; pH, 2.0; temperature, *rt*.

4. General procedure for reductive amination of ketones/aldehydes

Ketone or aldehyde (0.05 mmol), ammonia water (0.2 mmol) and Pd-NPs (2.0 mg, 13 mol%) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H_2O (10 ml, pH = 2.0) were added to the reaction tube and the reaction mixture was stirred at room temperature with H_2 balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC

analysis equipped with a C18 reverse column. When the substrate completely consumed, the reaction was stopped and then the solution was extracted with saturated salt water and ethyl acetate (3×10 ml). The organic phase was dried by using Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography using silica gel. The products were characterized with NMR (Due to the small scales of the reactions, we combined the products of several runs to get higher concentration samples).

5. General procedure for the preparation of imines

A round-bottomed flask (25 ml) was charged with a 3M ammonia water in methanol (10 ml) and then ketone or aldehyde (4 mmol) was added dropwise over time increments of 5 minutes at ambient temperature. After the addition was complete, the reaction mixture was left stirring for 24 h at 20 °C. The precipitate formed was filtered and washed with hexane and, finally, dried at room temperature to give imine.[1,2]

6. General procedure for hydrogenation of imines

Crude product of imine (0.05 mmol) and Pd-NPs (2.0 mg, 13 mol%) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H_2O (10 ml, pH = 2.0) were added to the reaction tube and the reaction mixture was stirred at room temperature with H_2 balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC analysis equipped with a C18 reverse column. When the substrate completely consumed, the reaction was stopped and then the solution was extracted with saturated salt water and ethyl acetate (3×10 ml). The organic phase was dried by using Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography using silica gel. The products were characterized with NMR (Due to the small scales of the reactions, we combined the products of several runs to get higher concentration samples).

7. Elemental analysis and ICP-OES of Pd-NPs

Table S1. Elemental analysis and ICP-OES of Pd-L5

Content (wt %)

C[a]	H[a]	N[a]	Pd[b]
30.09	2.76	4.45	35.61

[a] Measured by elemental analysis (EA).

[b] Measured by inductively coupled plasma-optical emission spectrometer (ICP-OES).

8. FT-IR of the Pd-NPs

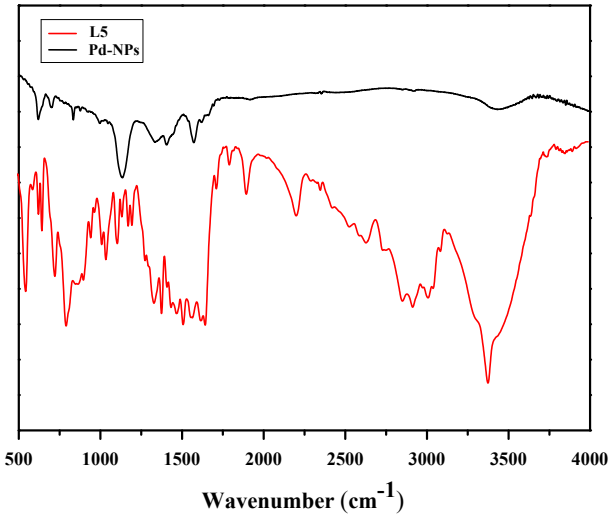


Figure S2. FTIR of Pd-NPs

9. Recycling of Pd-NPs

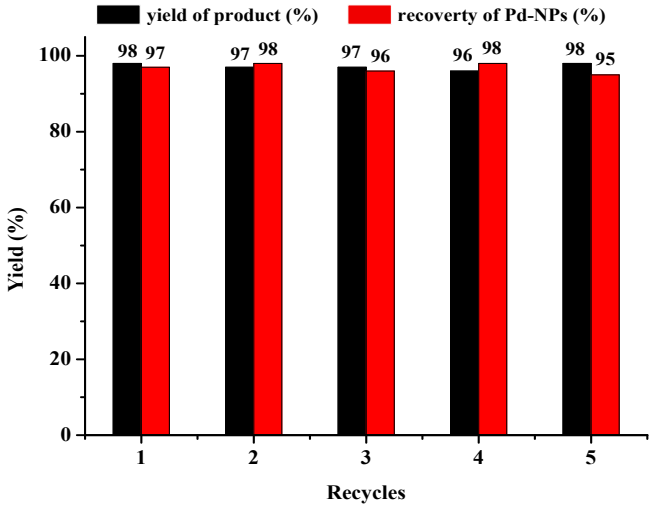


Figure S3. Recycles and reused of Pd-NPs

After the successful utilization of stable Pd-NPs catalyst for the reductive amination of derivatived aldehydes/ketones in water, the recoverability and recyclability of Pd-NPs were investigated on one-pot reductive amination of benzaldehyde and ammonia under optimized reaction condition. After completed the reaction, the reaction mixture was centrifuged, and the solution was removed. The obtained solid was washed with ethanol and dried under vacuum, the catalyst was successfully recovered and reused for the next four cycles with little loss **(Figure S3)**. After the fifth catalytic cycle of reductive amination, the catalyst was analyzed by HRTEM and showed that Pd-NPs was uniform distribution without any apparent agglomeration **(Figure S4)**.

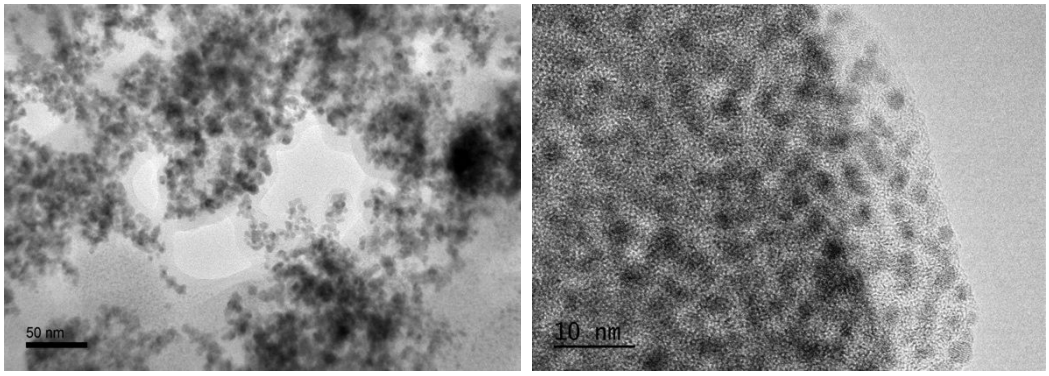
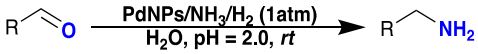
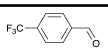
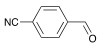
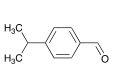
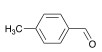
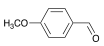
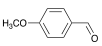


Figure S4. HRTEM image of Pd-NPs after five catalytic cycles

10. Calculation of TOF and TON

Table S2. Reductive amination of aldehydes

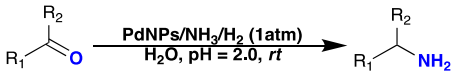


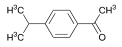
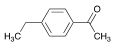
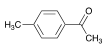
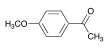
Entry	Aldehyde	Amine source	TON	Entry	Aldehyde	Amine source	TON
1		NH_3	372	15		NH_3	378
2		NH_3	340	16		NH_3	303
3		NH_3	351	17		NH_3	389
4		NH_3	361	18		$C_2H_5NH_2$	497
5		NH_3	319	19		$C_2H_5NH_2$	483
6		NH_3	383	20		$C_2H_5NH_2$	484

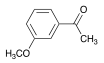
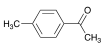
7	R = *p*-Br	NH_3	21	21		$C_2H_5NH_2$	463
8	R = *o*-Cl	NH_3	22	22		$C_2H_5NH_2$	472
9	R = *m*-Br	NH_3	276	23	n-C_3H_7CHO	$PhNH_2$	277
10	R = *o*-Br 	NH_3	319	24	n-C_3H_7CHO	NH_3	290
11	R = *p*-Cl	NH_3	361	25		NH_3	300
12	R = *m*-Cl	NH_3	286	26		NH_3	368
13	R = *o*-I	NH_3	368	27		NH_3	315
14	R = *p*-l	NH_3	376	28		NH_3	301

Reaction conditions: aldehyde, 0.05 mmol; 0.2mmol ammonia in water; Pd-NPs, 2.0mg; H_2O, 10ml, H_2 filled in a balloon; reaction time, 3h; Temperature, rt; pH of the reaction medium was made at 2.0; Yields were determined by HPLC analysis equipped with a C18 reverse column. TOF was calculated by mmol of product formed per mmol of the available active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. TON=TOF*0.5h.

Table S3. Reductive amination of ketones

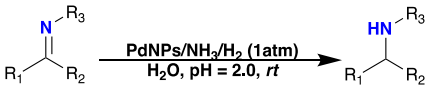


Entry	Ketone	Amine source	TON	Entry	Ketone	Amine source	TON
1		NH_3	318	11	R = *m*-Cl	NH_3	231
2		NH_3	202	12	R = *m*-Br	NH_3	255
3		NH_3	297	13	R = *o*-Cl 	NH_3	248
4		NH_3	308	14	R = *o*-Br	NH_3	250
5		NH_3	276	15	R = *o*-l	NH_3	238
6		NH_3	255	16	R = *p*-l	NH_3	296

7		NH_3	249	17		$C_2H_5NH_2$	335
8	R = H	NH_3	297	18		$C_2H_5NH_2$	320
9	R = *p*-Cl	NH_3	305	19		NH_3	128
10	R = *p*-Br	NH_3	234				

Reaction conditions: Ketone, 0.05 mmol; 0.2mmol ammonia in water; Pd-NPs, 2.0mg; H_2O, 10ml, H_2 filled in a balloon; reaction time, 3h; Temperature, rt; pH of the reaction medium was made at 2.0; Yields were determined by HPLC analysis equipped with a C18 reverse column. TOF was calculated by mmol of product formed per mmol of the available active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. TON=TOF*0.5h.

Table S4. Hydrogenation of imines



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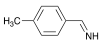
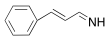
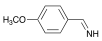
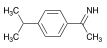
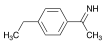
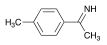
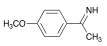
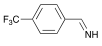
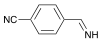
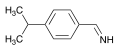
3		1051	27		1054
4		1052	28		1051
5		1060	29	PhCH=NPh	1051
6		1056	30		1052
7	R = *p*-Cl	1051	31		1053
8	R = *p*-Br	1053	32		1054
9	R = *m*-Cl	1055	33		1053
10	R = *m*-Br	1062	34		1049
11	R = *o*-Cl 	1054	35		1051
12	R = *o*-Br	1050	36		1056
13	R = *o*-I	1049	37	R = H	1053
14	R = *p*-I	1055	38	R = *p*-Cl 	1052
15		1057	39	R = *p*-Br	1053
16		1054	40	R = *m*-Cl	1052

17		1049	41	R = *m*-Br	1053
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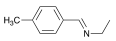
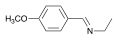
19		1051	43	R = *o*-Br	1052
20		1053	44	R = *o*-l	1050
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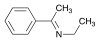
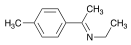
22		1052	46		1062
23	n-C_3H_7CH=NPh	1055	47		1052
24	n-C_3H_7CH=NH	1049	48		1049

Reaction conditions: Imine, 0.05 mmol; Pd-NPs, 2.0 mg; H_2O, 10ml; H_2 filled in a balloon; Reaction time, 1h; Temperature, rt; pH of the reaction medium was set at 2.0; Yields were determined by HPLC analysis equipped with a C18 reverse column. TOF was calculated by mmol of product formed per mmol of the available active sites of Pd (as determined by the chemisorption analysis) for the used catalyst. TON=TOF*1h.

11. Quantum chemical calculations

Density functional theory (DFT) calculations were conducted at the B3LYP level theory (6-31++G* basis sets for H, C, N, and O) using the conductor-like polarizable continuum model (CPCM) with parameters of the universal force field (UFF). The geometries of **1a**, **2a**, and all intermediates and byproducts were optimized, and the vibrational analysis was performed to confirm that they had no imaginary frequency. The Gibbs free energies in H_2O (at 1 atm and 298.15 K) were calculated. All calculations were performed with the Gaussian16 program package.

Table S5. Cartesian coordinates (in Å) of the calculated structures.

Benzaldehyde (1a)

atom	x (Å)	y (Å)	z (Å)
C	-3.388070	0.112541	-0.023724
C	-2.000882	0.082556	0.093863
C	-1.276512	1.287060	0.157718
C	-1.955761	2.515566	0.102582
C	-3.346671	2.543452	-0.015325
C	-4.061091	1.342408	-0.078330
H	-3.950217	-0.815875	-0.073266

H	-1.466128	-0.861639	0.137319
H	-1.391863	3.444380	0.152275
H	-3.871103	3.493807	-0.057891
H	-5.143796	1.361443	-0.170116
C	0.192900	1.291028	0.282345
H	0.657258	2.295796	0.323754
O	0.898999	0.290763	0.340209

Charge = 0; *E* = -345.5171785 hartree

Benzimide (2a)

atom	x (Å)	y (Å)	z (Å)
C	-1.340748	-1.330616	-0.000001
C	0.036520	-1.118677	0.000002
C	0.553071	0.190207	0.000002
C	-0.337442	1.276654	-0.000001
C	-1.718831	1.064189	-0.000004
C	-2.222337	-0.239871	-0.000004
H	-1.732387	-2.344496	-0.000001
H	0.724514	-1.958408	0.000004
H	0.055168	2.291154	0.000000
H	-2.397977	1.912456	-0.000006
H	-3.295944	-0.408998	-0.000006
C	2.004234	0.456186	0.000006
H	2.277022	1.519799	0.000004
N	2.889319	-0.472212	0.000010
H	3.828135	-0.065820	0.000012

Charge = 0; *E* = -325.6246157 hartree

Benzylamine (3a)

atom	x (Å)	y (Å)	z (Å)
C	-1.388510	-1.314178	0.308133
C	-0.024413	-1.100240	0.520785
C	0.558376	0.149479	0.253719
C	-0.259220	1.179811	-0.231260
C	-1.626765	0.970865	-0.448059
C	-2.194886	-0.277359	-0.178494
H	-1.824351	-2.286296	0.525667
H	0.597127	-1.908662	0.899757
H	0.176179	2.155379	-0.438706
H	-2.244953	1.782547	-0.823741
H	-3.256906	-0.442038	-0.342056
N	2.838039	-0.289274	-0.587335
H	2.652546	0.159126	-1.484919
H	3.830597	-0.144358	-0.401420
C	2.041459	0.373027	0.468534

H	2.347326	-0.067331	1.424858
H	2.236336	1.454829	0.532733

Charge = 0; *E* = -326.8152174 hartree

Cyclohexylmethylamine (4a)

atom	x (Å)	y (Å)	z (Å)
C	1.458373	-1.453198	-0.125611
C	0.038797	-1.004363	-0.550038
C	-0.463243	0.161767	0.316421
C	0.433482	1.408462	0.094190
C	1.898518	1.046008	-0.251451
C	2.313394	-0.276801	0.408176
H	1.385975	-2.230280	0.647207
H	0.048161	-0.675498	-1.600332
H	0.011171	2.019790	-0.716765
H	2.012170	0.949523	-1.340492
H	2.186584	-0.185310	1.496348
C	-1.937364	0.514271	0.075050
H	-2.101100	0.661764	-1.001110
N	-2.848244	-0.556142	0.523655
H	-2.806350	-0.633832	1.540361
H	-3.810906	-0.300482	0.306320
H	0.405193	2.033672	0.996944
H	2.568307	1.859440	0.055390
H	3.379433	-0.475732	0.239314
H	1.960712	-1.918167	-0.984479
H	-0.657459	-1.848325	-0.495828
H	-0.371980	-0.142923	1.372105
H	-2.153484	1.479768	0.564726

Charge = 0; *E* = -330.3594992 hartree

4,5-dihydro-2,4,5-triphenyl-1H-imidazole (5a)

atom	x (Å)	y (Å)	z (Å)
C	0.506908	0.746406	-1.071446
C	1.579255	0.914597	-0.190337
C	1.665151	2.052736	0.626382
C	0.646661	3.014239	0.543583
C	-0.425131	2.852371	-0.339269
C	-0.498254	1.715954	-1.151268
H	0.457583	-0.142817	-1.694999
H	2.350055	0.149919	-0.141891
H	0.690922	3.896546	1.178700
H	-1.205259	3.608089	-0.385442
H	-1.333242	1.583680	-1.834437
N	3.315069	1.039154	2.213945

H	2.633496	0.309950	2.397664
C	4.090148	3.617822	-0.306109
C	4.156292	3.021357	-1.573242
C	4.046808	3.795063	-2.732904
C	3.865024	5.179410	-2.642162
C	3.801368	5.784888	-1.382738
C	3.918653	5.007945	-0.226025
H	4.303900	1.948021	-1.648434
H	4.104708	3.316349	-3.707537
H	3.780823	5.781002	-3.543680
H	3.669225	6.860864	-1.299769
H	3.880144	5.488384	0.749928
C	4.190573	2.799785	0.964686
H	4.642903	3.441756	1.735107
N	5.040123	1.602898	0.846528
C	4.500028	0.683275	1.577988
C	5.093812	-0.655841	1.790380
C	6.045025	-1.148016	0.879913
C	4.728174	-1.447730	2.891665
C	6.613445	-2.407994	1.065169
H	6.325956	-0.536587	0.028334
C	5.301083	-2.709100	3.076431
H	4.014335	-1.075333	3.620686
C	6.242912	-3.193204	2.164071
H	7.343673	-2.779851	0.351317
H	5.013875	-3.309158	3.935632
H	6.686541	-4.174900	2.307325
C	2.822688	2.278104	1.586209
H	2.496087	2.984371	2.354052

Charge = 0; *E* = -920.3352138 hartree

N-(phenylmethylene)-benzenemethanamine (6a)

atom	x (Å)	y (Å)	z (Å)
C	3.569159	3.018509	0.024834
C	4.635889	3.936233	0.049989
C	4.511622	5.176581	-0.573321
C	3.321894	5.520770	-1.231029
C	2.256702	4.616039	-1.261582
C	2.380963	3.372134	-0.636631
H	5.555011	3.665084	0.560309
H	5.340704	5.879058	-0.548776
H	3.228763	6.489038	-1.715847
H	1.332239	4.876816	-1.769821
H	1.551866	2.668232	-0.660606
C	3.655199	1.695304	0.670667

H	2.753968	1.068945	0.577945
N	4.686186	1.279235	1.300713
C	5.744723	-0.940502	1.367197
C	5.578518	-1.660131	0.174466
C	6.967681	-1.034692	2.046371
C	6.611606	-2.455644	-0.330340
H	4.633330	-1.600004	-0.361346
C	8.004923	-1.828213	1.544824
H	7.108696	-0.486201	2.975410
C	7.829313	-2.540840	0.354056
H	6.465013	-3.010472	-1.253735
H	8.946064	-1.892642	2.085268
H	8.632724	-3.160768	-0.035560
C	4.625474	-0.058892	1.893684
H	3.650345	-0.537864	1.709615
H	4.740830	0.058609	2.978420

Charge = 0; *E* = -595.8995057 hartree

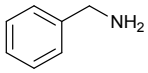
N-(phenylmethyl)-benzenemethanamine (7a)

atom	x (Å)	y (Å)	z (Å)
C	3.186299	2.920446	-0.163554
C	3.528684	3.331259	-1.461997
C	3.601494	4.688139	-1.787313
C	3.332784	5.658909	-0.814376
C	2.989745	5.262304	0.481457
C	2.916865	3.901370	0.801441
H	3.736234	2.580796	-2.221750
H	3.863423	4.988813	-2.798815
H	3.386854	6.714862	-1.066824
H	2.776029	6.008840	1.242392
H	2.644538	3.598635	1.810648
C	5.840428	-1.072724	0.995429
C	6.670695	-1.396064	-0.089954
C	6.337542	-1.244926	2.295139
C	7.965597	-1.877811	0.118382
H	6.296401	-1.271256	-1.103771
C	7.634658	-1.725840	2.509744
H	5.704038	-1.004167	3.146617
C	8.452163	-2.043206	1.421112
H	8.593507	-2.127862	-0.733293
H	8.002637	-1.854352	3.524676
H	9.458610	-2.420096	1.584540
C	4.445975	-0.530143	0.765905
H	3.953419	-1.088666	-0.040448
H	3.838722	-0.679025	1.676438

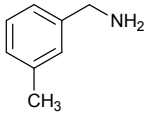
C	3.129916	1.449894	0.191231
H	2.514366	1.313517	1.098145
H	2.639872	0.887567	-0.614009
N	4.481179	0.885473	0.357389
H	4.971400	1.419896	1.076086

Charge = 0; *E* = -597.0859442 hartree

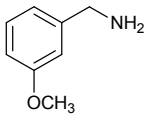
12. Characterization data for all products



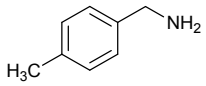
phenylmethanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.18 (m, 5H), 3.79 (s, 2H), 1.43 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.42, 128.53, 127.09, 126.76, 46.51.



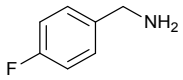
(3-methylphenyl)methanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.20 (m, 1H), 7.12-7.04 (m, 3H), 3.81 (s, 2H), 2.34 (s, 3H), 1.51 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.34, 138.18, 128.48, 127.89, 127.53, 124.11, 46.51, 21.42.



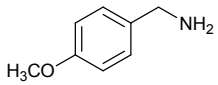
(3-methoxyphenyl)methanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (t, *J* = 16.0 Hz, 1H), 6.89-6.76 (m, 3H), 3.82 (s, 2H), 3.79 (s, 3H), 1.50 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.85, 145.08, 129.55, 119.32, 112.59, 112.21, 55.18, 46.50.



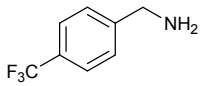
(4-methylphenyl)methanamine: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 2H), 2.27 (s, 3H), 1.72 (brs, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.76, 135.46, 129.08, 127.39, 45.93, 21.12.



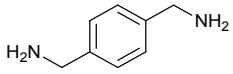
(4-fluorophenyl)methanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.22 (q, *J* = 4.0 Hz, 2H), 6.97 (t, *J* = 20.0 Hz, 2H), 3.78 (s, 2H), 1.55 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.68 (d, *J* = 242.0 Hz), 138.97 (d, *J* = 3.0 Hz), 128.5 7 (d, *J* = 8.0 Hz), 115.10 (d, *J* = 21.0 Hz), 45.61.



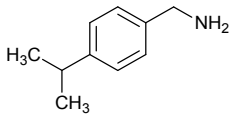
(4-methoxyphenyl)methanamine: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.24 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 3.65 (s, 2H), 1.68 (brs, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.25, 136.82, 128.56, 113.91, 55.41, 45.60.



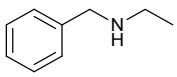
(4-(trifluoromethyl)phenyl)methanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 1.64 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.07, 128.66 (q, *J* = 40.0 Hz), 127.30, 125.41 (q, *J* = 4.0 Hz), 122.91, 45.93.



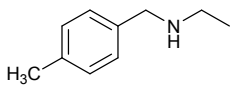
1,4-phenylenedimethanamine: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.25 (s, 4H), 3.68 (s, 4H), 2.21 (brs, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 142.59, 127.24, 45.95.



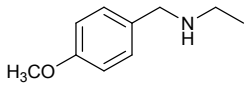
(4-isopropylphenyl)methanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.18 (m, 4H), 3.81 (s, 2H), 2.92-2.85 (m, 1H), 1.51 (s, 2H), 1.24 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.45, 140.85, 127.11, 126.60, 46.29, 33.82, 24.10.



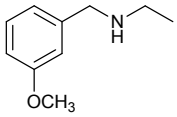
N-ethylbenzylamine: ^{1}H NMR (400 MHz, $CDCl_3$)*:* δ = 7.32-7.23 (m, 5H), 3.79 (s, 2H), 2.71-2.65 (m, 2H), 1.62(s, 1H), 1.13 (t, *J* =16.0 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$)*:* δ = 140.40, 128.39, 128.15, 126.89, 53.93, 43.62, 15.25.



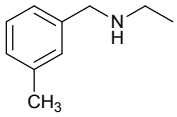
N-ethyl-4-methylbenzylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21-7.12 (m, 4H), 3.75 (s, 2H), 2.68-2.64 (m, 2H), 2.33 (s, 3H), 1.75 (s, 1H), 1.12 (t, *J* = 16.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.32, 136.45, 129.06, 128.11, 53.61, 43.53, 21.07, 15.20.



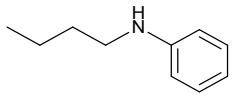
N-ethyl-4-methoxybenzylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.72 (s, 2H), 2.69-2.64 (m, 2H), 1.48 (s, 1H), 1.12 (t, *J* = 16.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.56, 132.64, 129.30, 113.74, 55.24, 53.35, 43.54, 15.25.



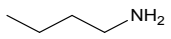
N-ethyl-3-methoxybenzylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.22 (m, 1H), 6.91-6.78 (m, 3H), 3.81 (s, 3H), 3.77 (s, 2H), 2.71-2.66 (m, 2H), 2.18 (s, H), 1.14(t, *J* = 12.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.72, 141.67, 129.39, 120.50, 113.65, 112.51, 55.19, 53.69, 43.46, 15.05.



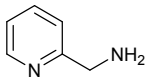
N-ethyl-3-methylbenzylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.05 (m, 4H), 3.75 (s, 2H), 2.71-2.66 (m, 2H), 2.34 (s, 3H), 2.28 (s, 1H), 1.14 (t, *J* = 12.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.95, 138.04, 129.01, 128.30, 127.73, 125.27, 53.76, 43.54, 21.38, 15.06.



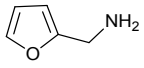
N-butylaniline: ^{1}H NMR (400 MHz, $CDCl_3$)*:* δ = 7.27-7.19 (m, 2H), 6.75-6.63 (m, 3H), 3.57 (brs, H), 3.15 (t, *J* = 12.0 Hz, 2H), 1.68-1.61 (m, 2H), 1.52-1.42 (m, 2H), 1.00 (t, *J* = 16.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)*:* δ = 148.49, 129.21, 117.08, 112.69, 43.68, 31.65, 20.30, 13.92.



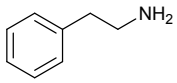
Butan-1-amine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (t, *J* = 12.0 Hz, 2H), 1.44-1.32 (m, 4H), 1.15 (brs, 2H), 0.92 (t, *J* = 16.0 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 41.82, 35.93, 19.85, 13.77.



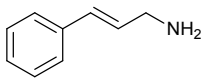
2-(aminomethyl)pyridine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 4.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.13-7.10 (m, 1H), 3.94 (s, 2H), 1.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.91, 149.22, 136.49, 121.73, 121.14, 47.78.



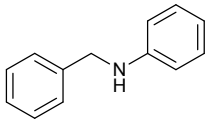
2-furfurylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.35 (m, 1H), 6.33-6.32 (m, 1H), 6.15-6.14 (m, 1H), 3.83 (s, 2H), 1.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.66, 141.53, 110.14, 104.98, 39.31.



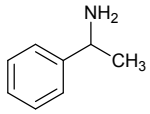
2-phenylethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.30 (m, 2H), 7.27-7.23 (m, 3H), 3.02 (t, *J* = 12.0 Hz, 2H), 2.80 (t, *J* = 12.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.86, 128.84, 128.45, 126.15, 43.60, 40.16.



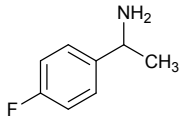
3-phenyl-2-propen-1-amine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.23 (m, 5H), 2.73-2.67 (m, 4H), 1.91-1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.17, 128.38, 128.34, 125.78, 49.51, 33.72, 31.75.



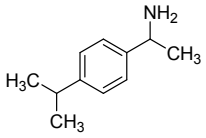
N-benzylaniline: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.15 (m, 7H), 6.73-6.62 (m, 3H), 4.32 (s, 2H), 4.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.17, 139.45, 129.29, 128.66, 127.53, 127.25, 117.58, 112.86, 48.33.



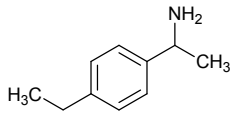
1-phenylethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.17 (m, 5H), 4.06-4.01 (m, 1H), 1.66 (s, 2H), 1.34 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.79, 128.49, 126.81, 125.71, 51.31, 25.70.



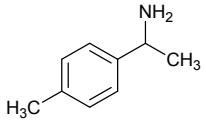
1-(4-fluorophenyl)ethanamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.28 (m, 2H), 7.02-6.97 (m, 2H), 4.13-4.08 (m, 1H), 1.63 (s, 2H), 1.36 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.91 (d, *J* = 243.0 Hz), 143.38 (d, *J* = 3.0 Hz), 127.25 (d, *J* = 7.0 Hz), 115.23 (d, *J* = 21.0 Hz), 50.65, 25.81.



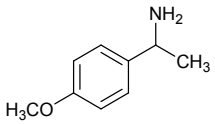
1-(4-isopropylphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.17 (m, 4H), 4.09-4.04 (m, 1H), 2.92-2.85 (m, H), 1.93 (s, 2H), 1.38 (d, *J* = 8.0 Hz, 3H), 1.25 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.44, 145.03, 126.53, 125.65, 51.03, 33.76, 25.50, 24.06.



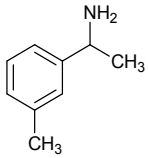
1-(4-ethylphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.08 (q, *J* = 20.0 Hz, 1H), 2.63 (q, *J* = 20.0 Hz, 2H), 1.72 (brs, 2H), 1.38 (d, *J* = 4.0 Hz, 3H), 1.23 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.04, 142.80, 127.98, 125.67, 51.07, 28.49, 25.63, 15.66.



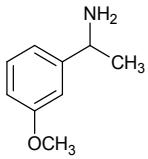
1-(4-methylphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.09 (q, *J* = 20.0Hz, 1H), 2.32 (s, 3H), 1.77 (s, 2H), 1.37(d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.76, 136.37, 129.17, 125.61, 51.04, 25.63, 21.03.



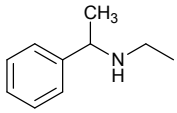
1-(4-methoxyphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 12.0 Hz, 2H), 4.03-3.98 (m, 1H), 3.72 (s, 3H), 1.93 (s, 2H), 1.31 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.49, 139.63, 126.78, 113.84, 55.29, 50.67, 25.55.



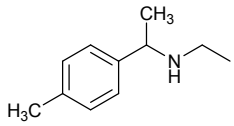
1-(3-methylphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.20 (m, 1H), 7.16-7.12 (t, *J* = 16.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 4.10 (q, *J* = 20.0 Hz, 1H), 2.35 (s, 3H), 1.82 (s, 2H), 1.39 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.61, 138.11, 128.42, 127.59, 126.44, 122.73, 51.30, 25.55, 21.47.



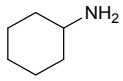
1-(3-methoxyphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 16.0 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 2H), 6.70-6.67 (m, 1H), 4.02-3.97 (m, 1H), 3.72 (d, *J* = 8.0 Hz, 3H), 1.93 (s, 2H), 1.30 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.78, 149.33, 129.52, 118.06, 112.11, 111.42, 55.19, 51.31, 25.47.



N-ethyl-1-phenethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.21 (m, 5H), 3.79-3.74 (m, 1H), 2.56-2.44 (m, 2H), 1.50 (brs, 1H), 1.36 (d, *J* = 4.0 Hz, 3H), 1.09 (t, *J* = 16.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.80, 128.40, 126.83, 126.53, 58.30, 42.01, 24.26, 15.41.



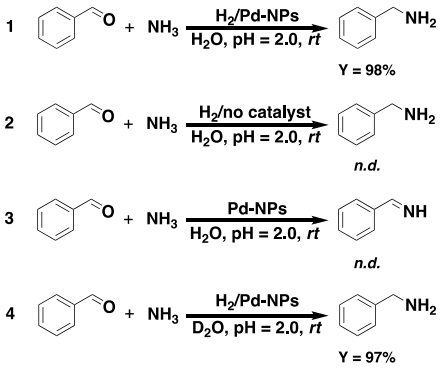
N-ethyl-1-(4-methylphenyl)ethylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.12 (m, 4H), 3.76-3.71 (m, 1H), 2.55-2.44 (m, 2H), 2.33 (s, 3H), 1.57 (s, 1H), 1.35 (d, *J* = 8.0 Hz, 3H), 1.09 (t, *J* = 16.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.73, 136.37, 129.08, 126.43, 57.95, 41.97, 24.25, 21.05, 15.38.



Cyclohexylamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65-2.58 (m, 1H), 1.83-1.56 (m, 5H), 1.32-0.99 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.36, 36.81, 25.59, 25.05.

13. The control reactions and MS spectra

The results from the control experiments showed us that in the presence of H_2 plus Pd-NPs, the formation of benzaldimine was not observed, only the final product benzylamine was generated (**eq 1**). By removing Pd-NPs, neither the formation of benzaldimine nor the generation of benzylamine was detected (**eq 2**), and if we solely use unincubated Pd-NPs in absence of H_2, the proposed benzaldimine was not observed, nor with the product benzylamine (**eq 2**), indicating that in the presence of H_2, the imidization of benzaldehyde into benzaldimine cannot occur without Pd-NPs, or under the condition that in the presence of Pd-NPs without H_2 (**eq 3**). However, the imidization reaction could take place with incubated Pd-NPs even without H_2 (**Scheme S1**). Besides, in order to check the possible H/D exchange, reaction was performed using D_2O and H_2 (**eq 4**), results indicated that the element D of D_2O didn't participate the reductive amination process.



Scheme S1. Control reactions

Input: 2834 Spectra library: NIST17-1. lib Molecular formula: C_7H_9N Molar mass: 107

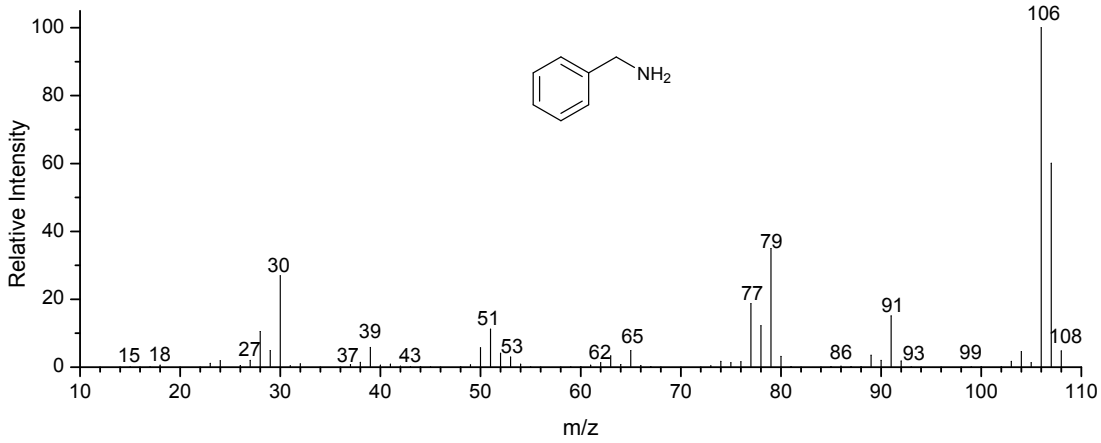
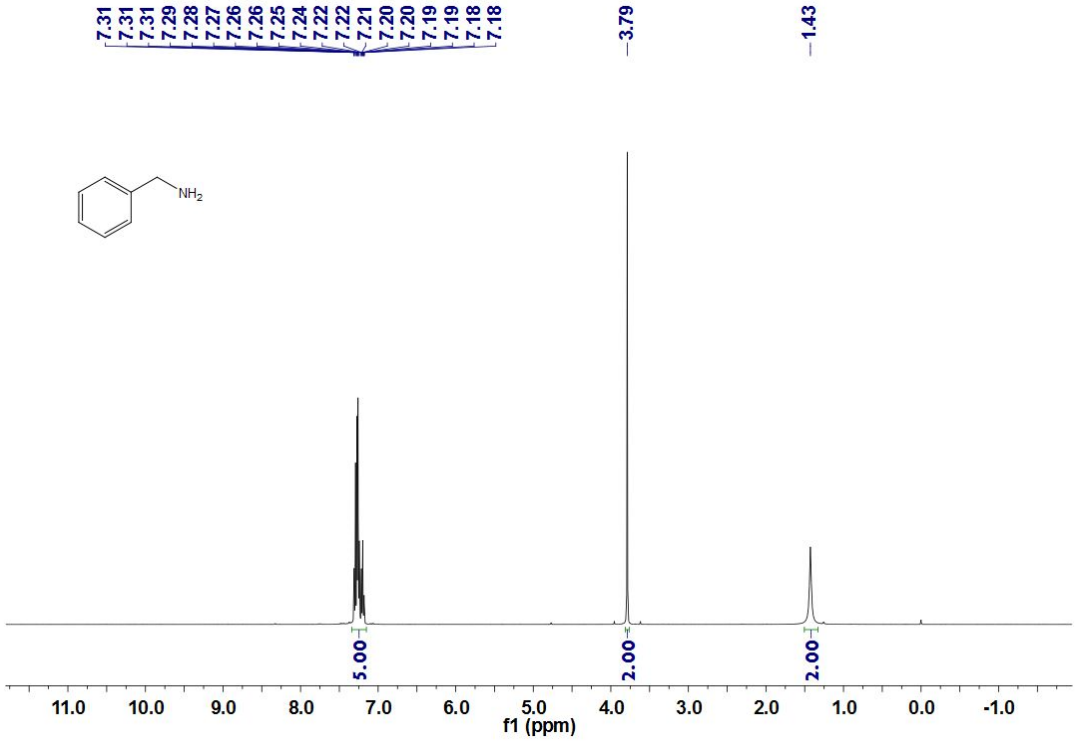


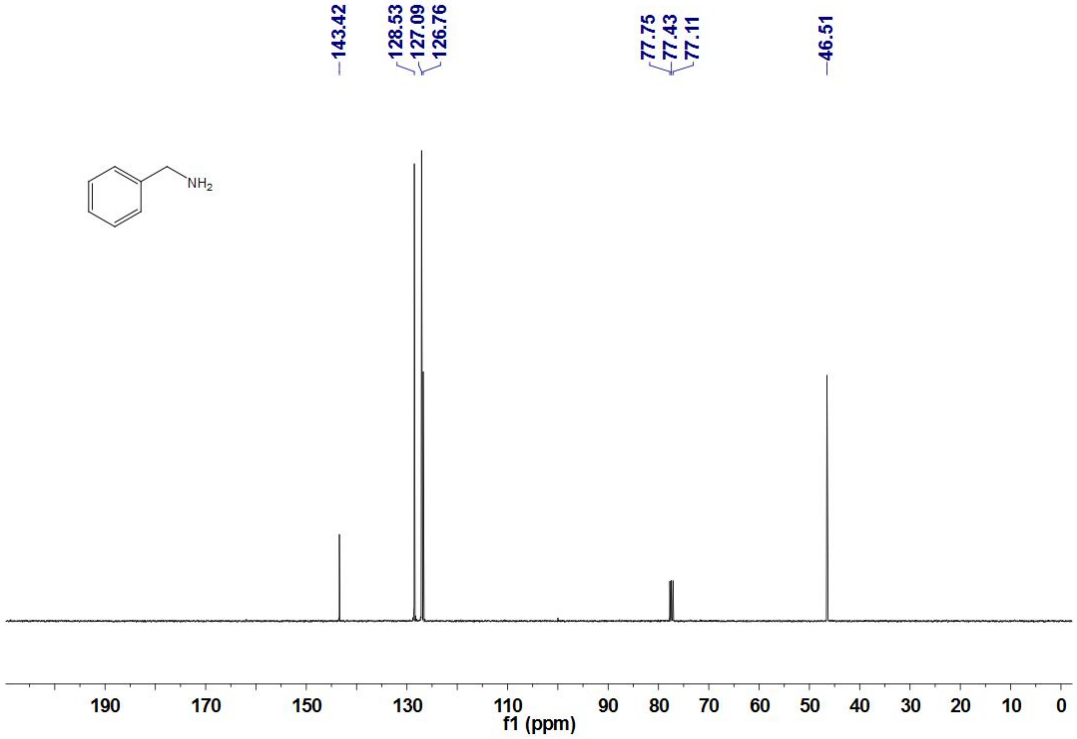
Figure S5. MS spectra of phenylmethanamine

The reductive amination of benzaldehyde proceed in D_2O using H_2 of 1 atm. MS (EI): m/z calculated for product: 106. Obtaining the structure of phenylmethanamine from a library, and fragment peak information also matches the compound, the result shows H/D exchange didn't carried out.

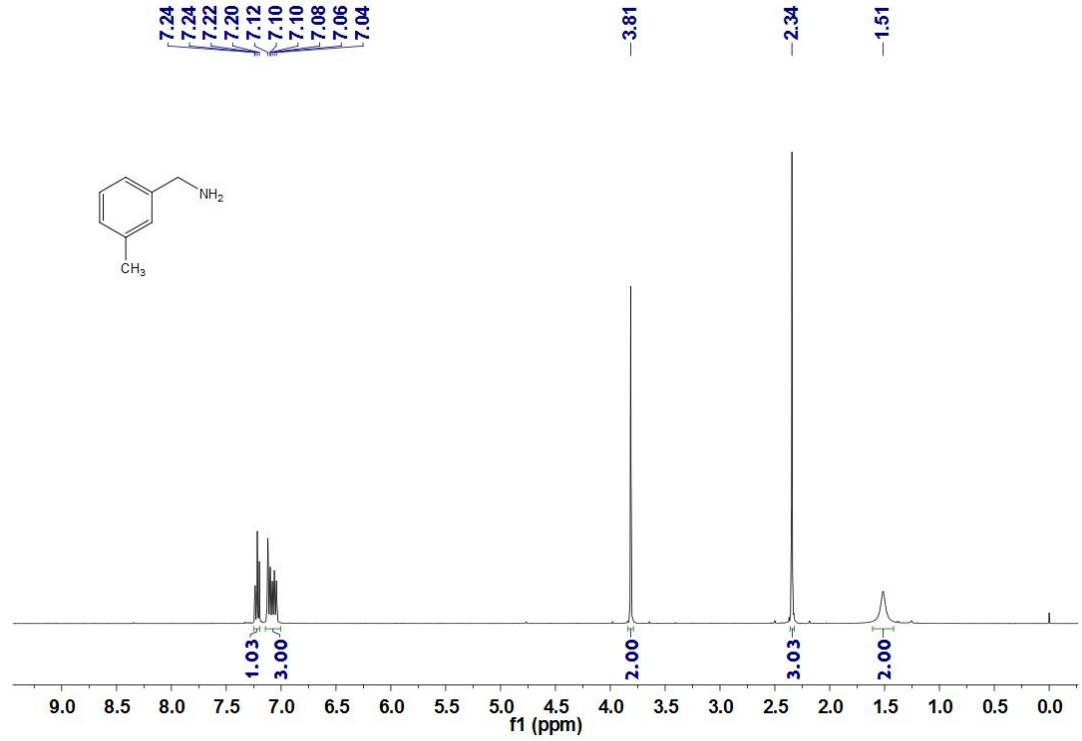
14. ^{1}H NMR and ^{13}C NMR spectra of products



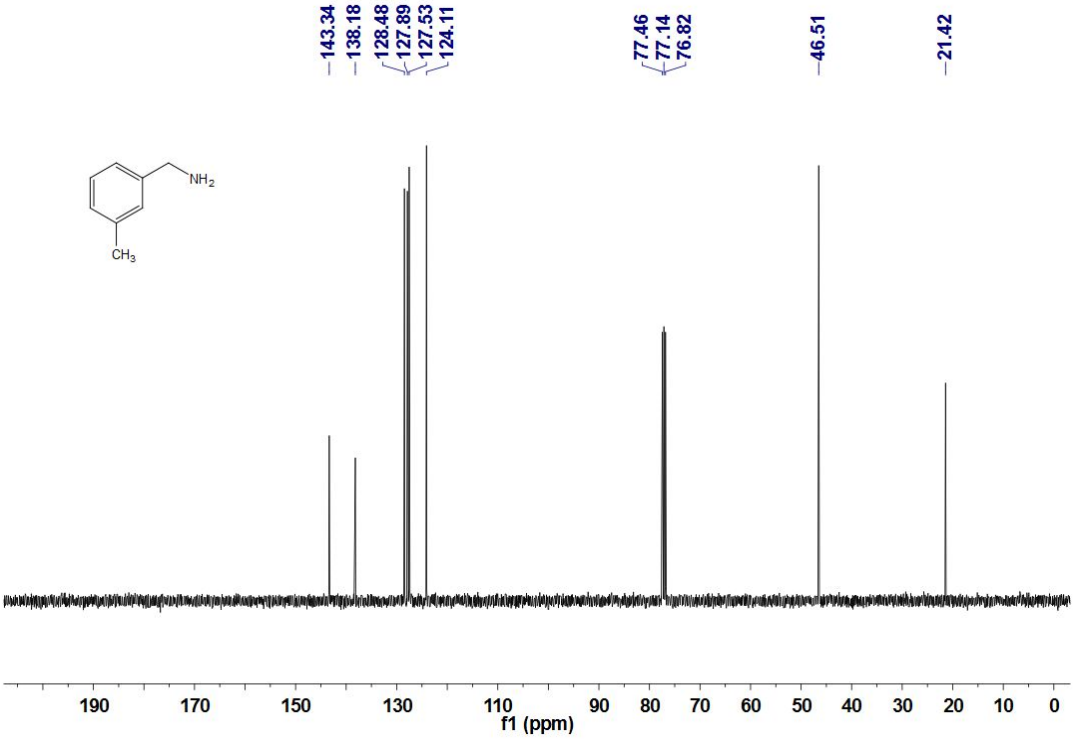
^{1}H NMR of phenylmethanamine



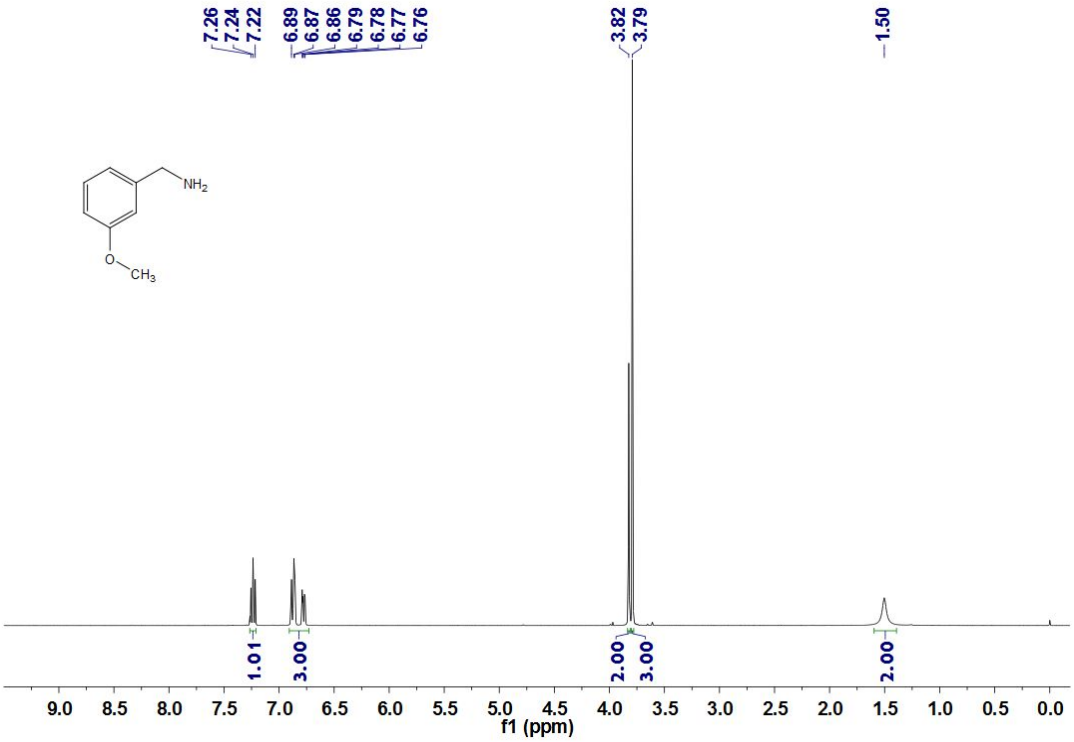
^{13}C NMR of phenylmethanamine



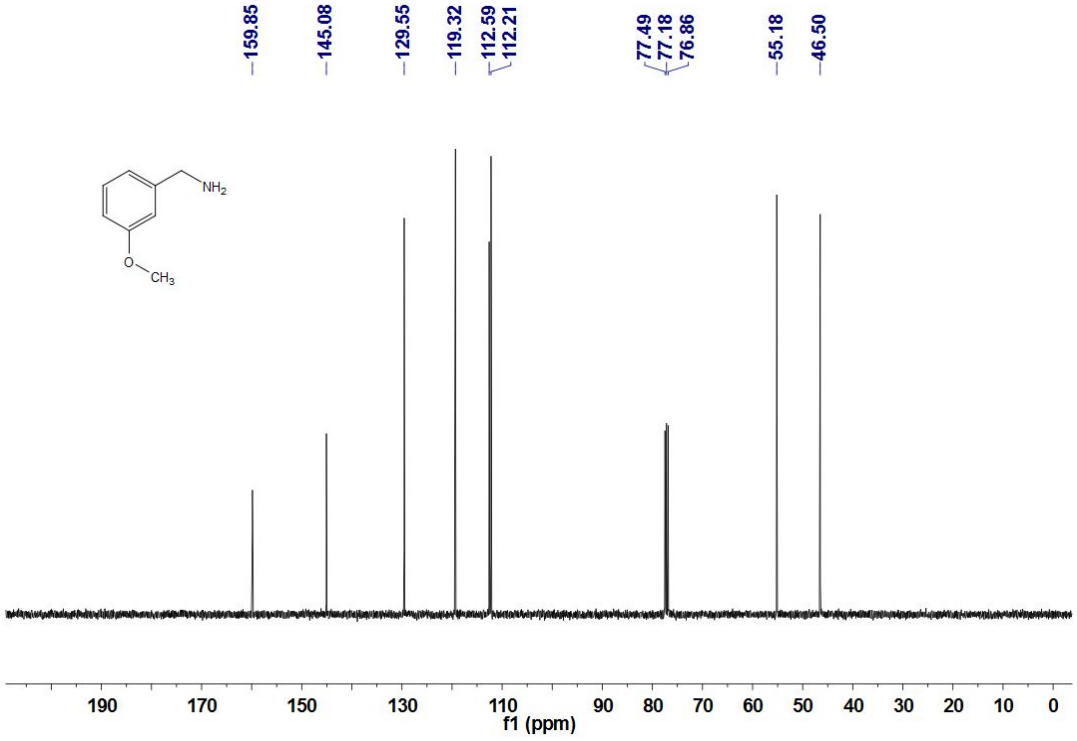
^{1}H NMR of (3-methylphenyl)methanamine



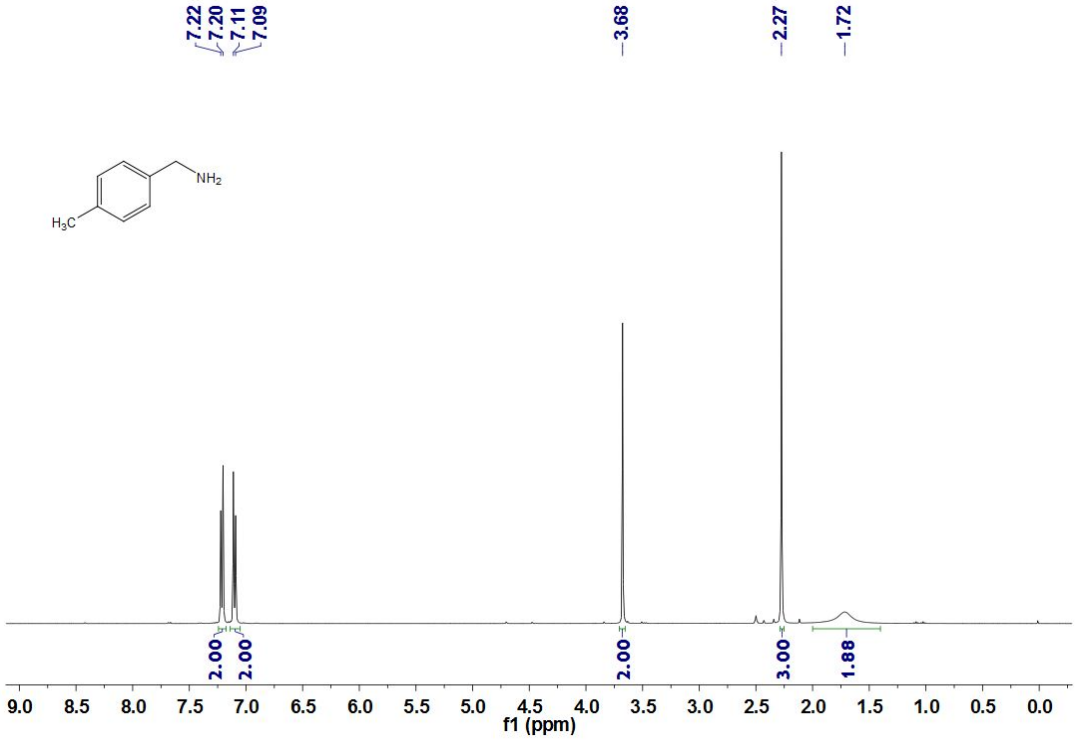
^{13}C NMR of (3-methylphenyl)methanamine



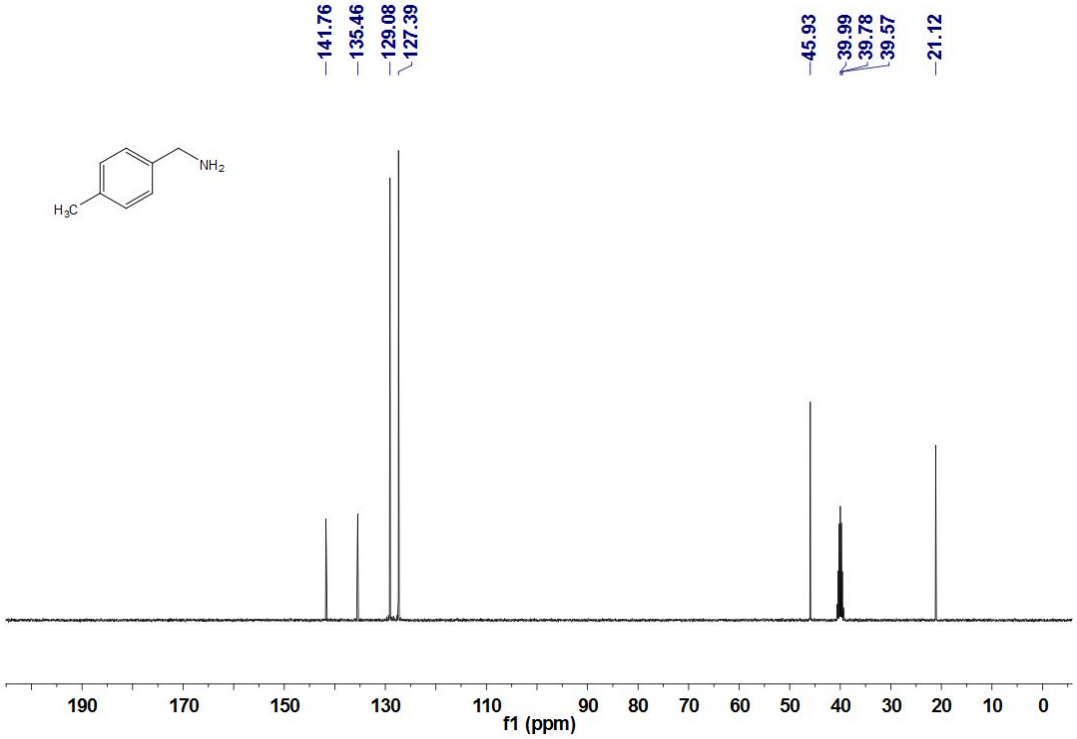
^{1}H NMR of (3-methoxyphenyl)methanamine



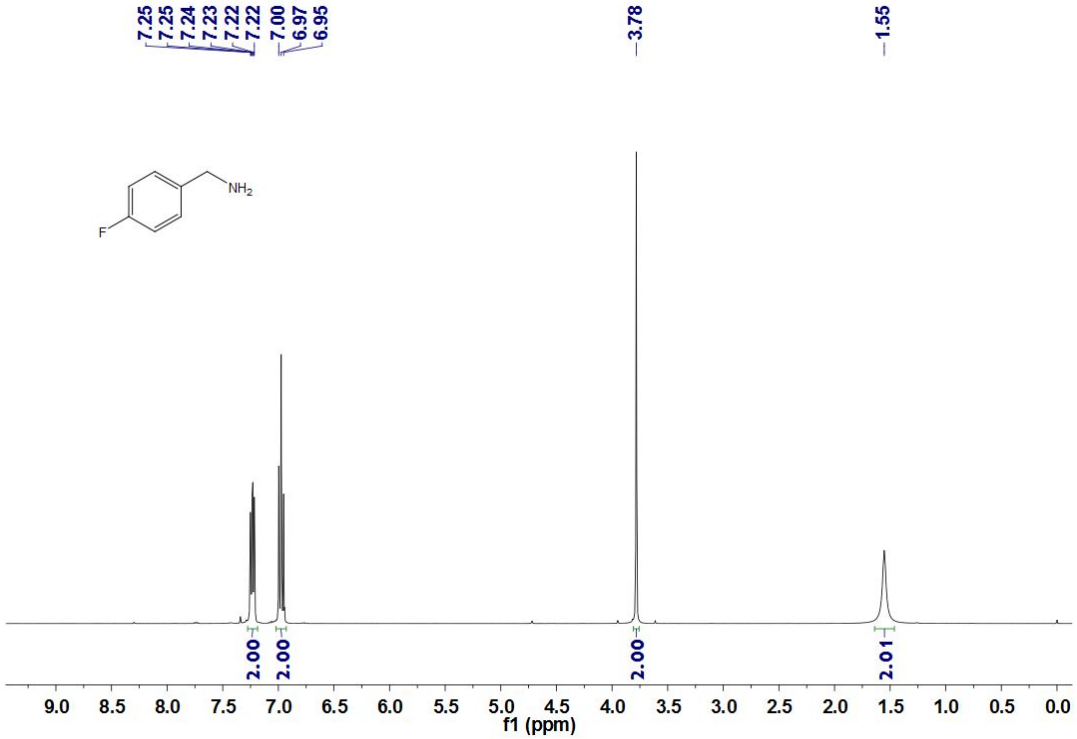
^{13}C NMR of (3-methoxyphenyl)methanamin



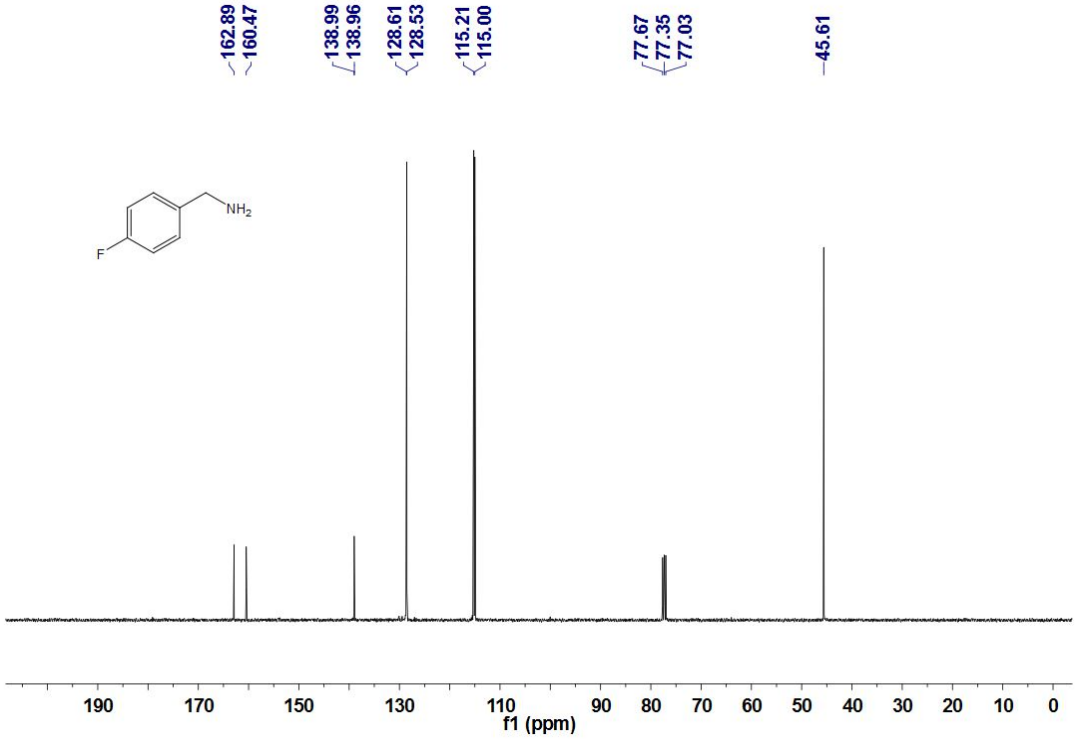
^{1}H NMR of (4-methylphenyl)methanamine



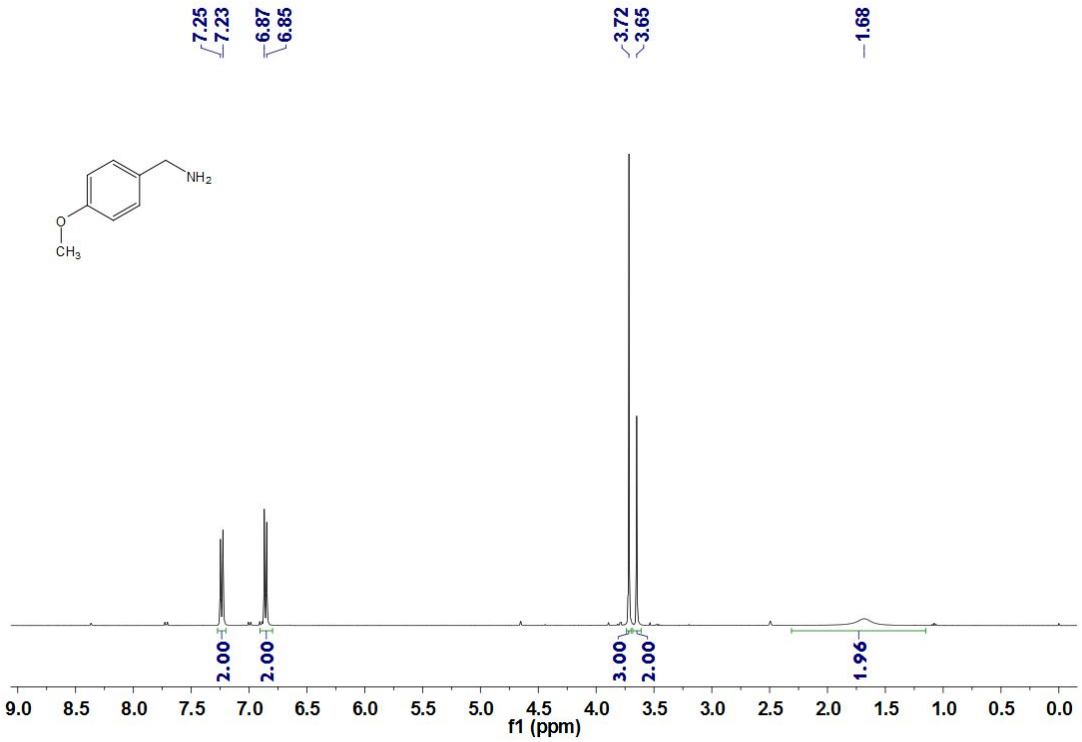
^{13}C NMR of (4-methylphenyl)methanamine



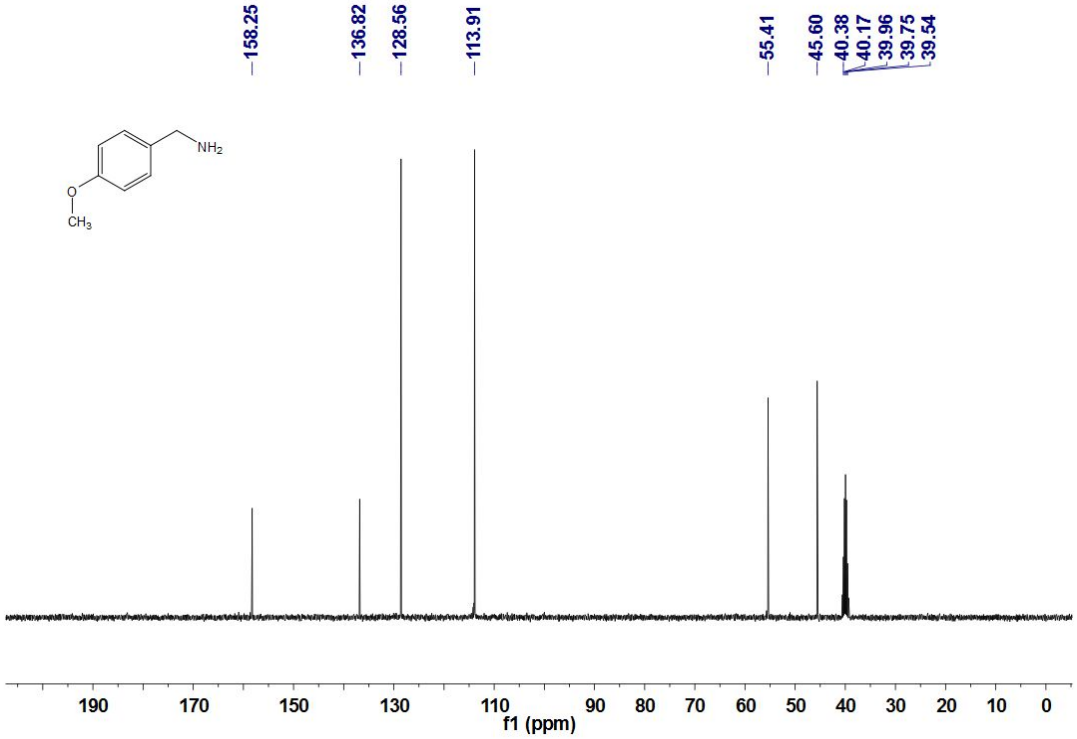
^{1}H NMR of (4-fluorophenyl)methanamine



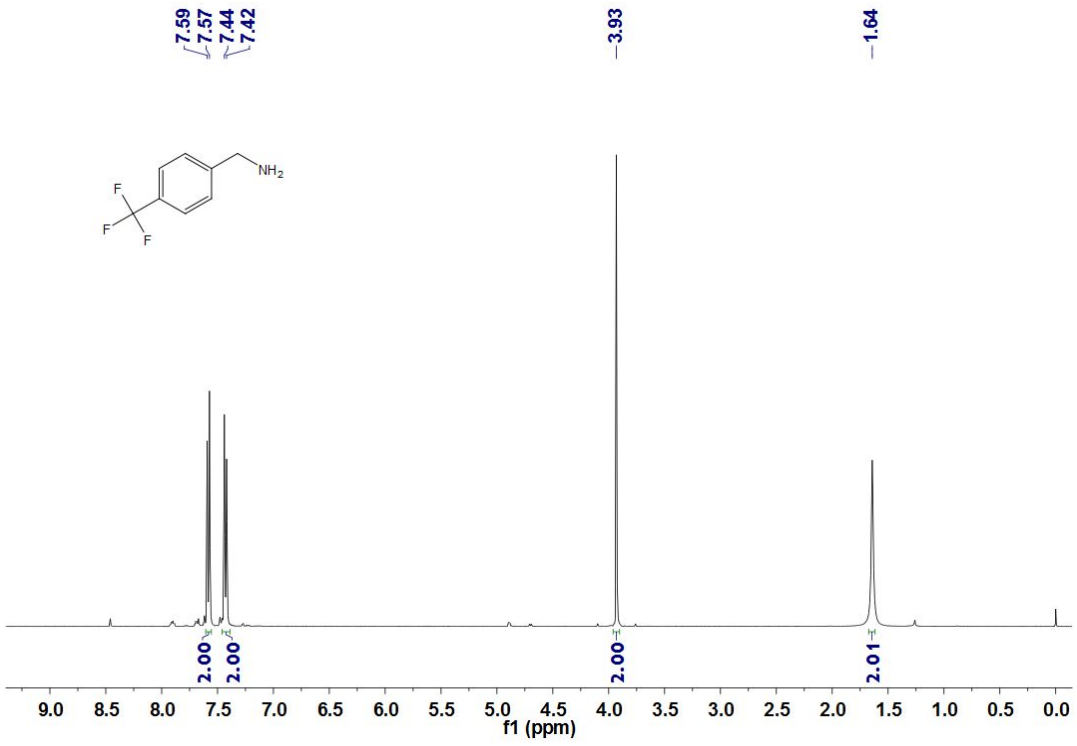
^{13}C NMR of (4-fluorophenyl)methanamine



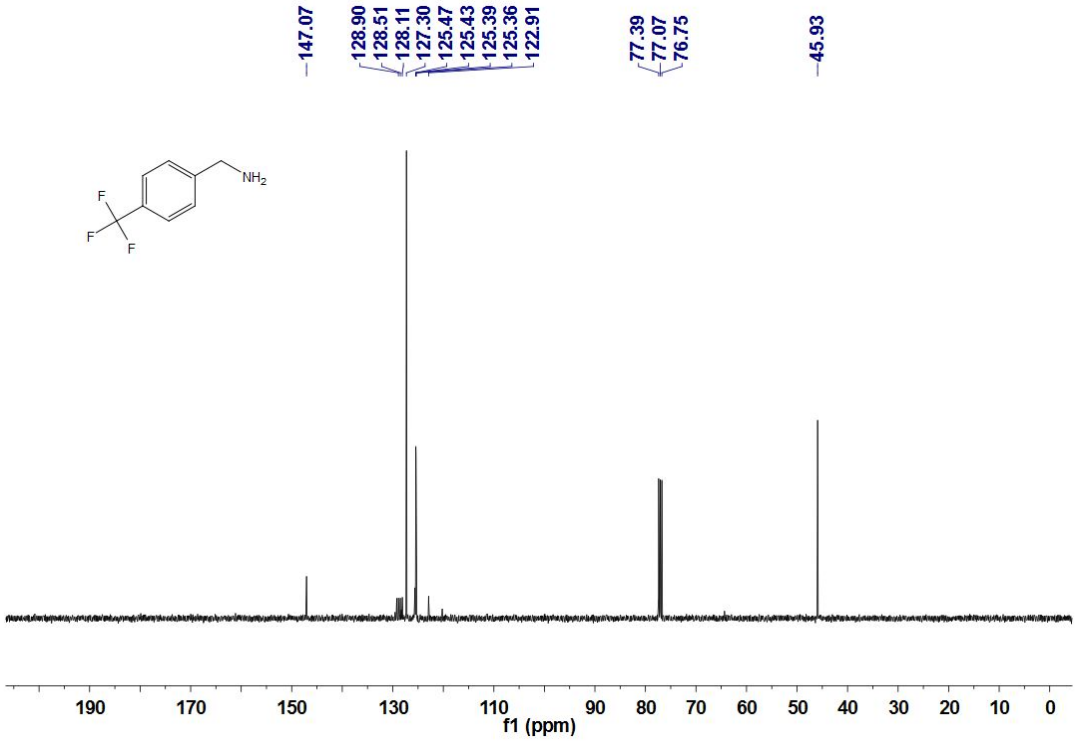
^{1}H NMR of (4-methoxyphenyl)methanamine



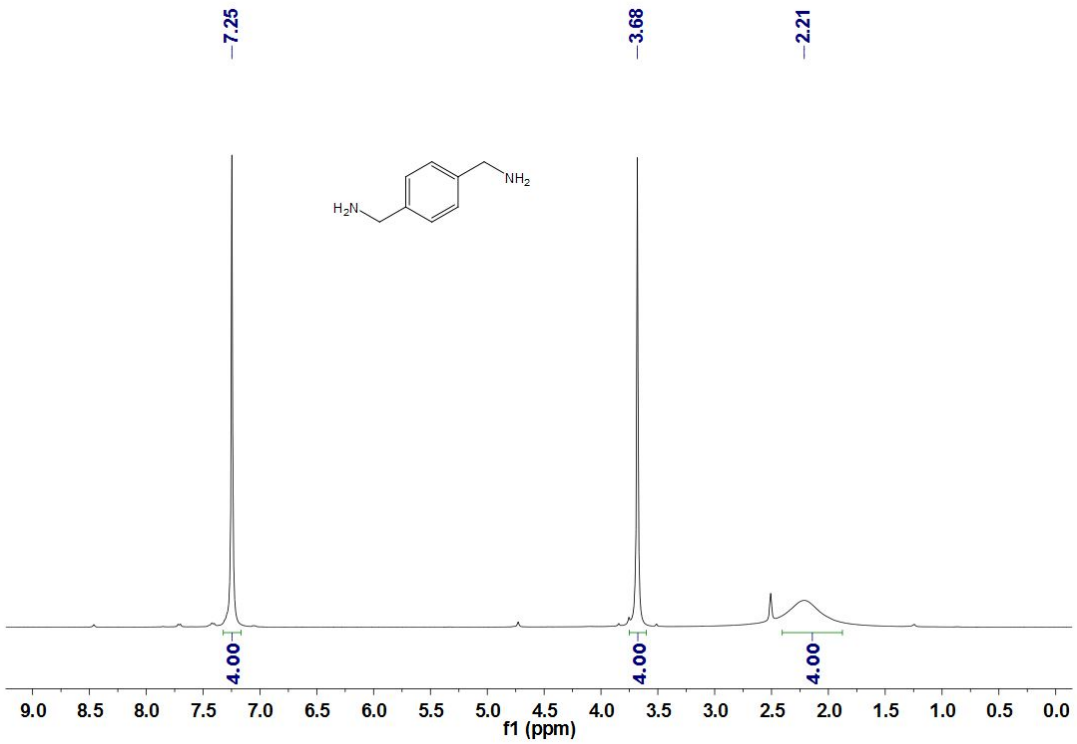
^{13}C NMR of (4-methoxyphenyl)methanamine



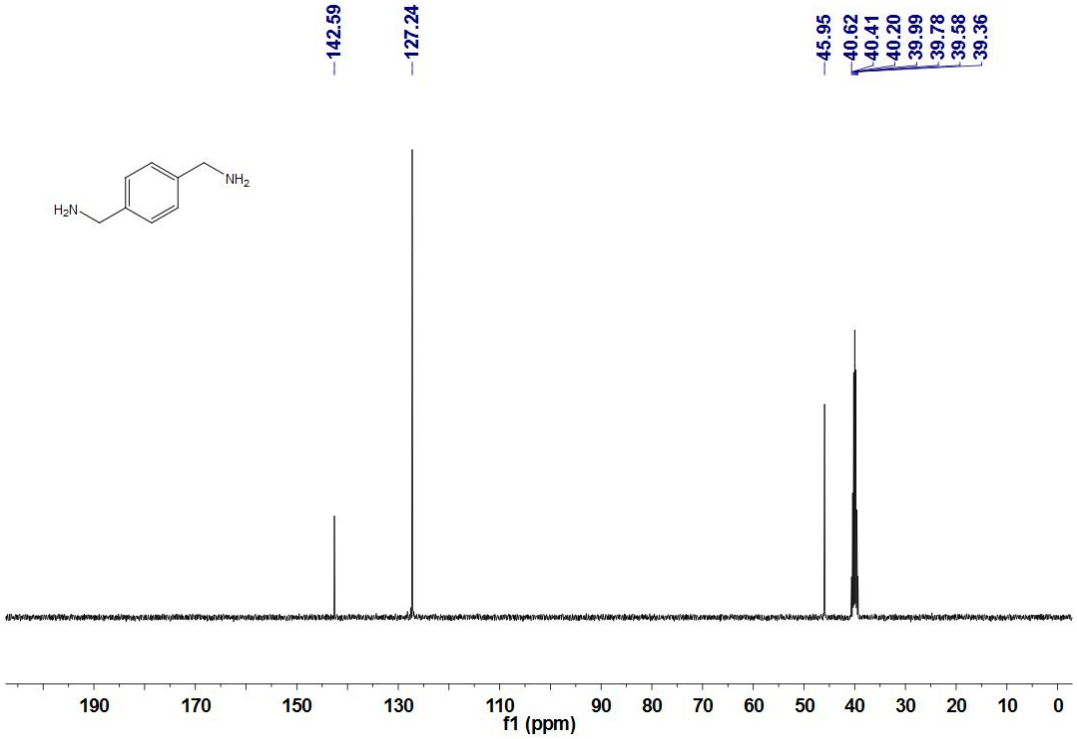
^{1}H NMR of (4-(trifluoromethyl)phenyl)methanamine



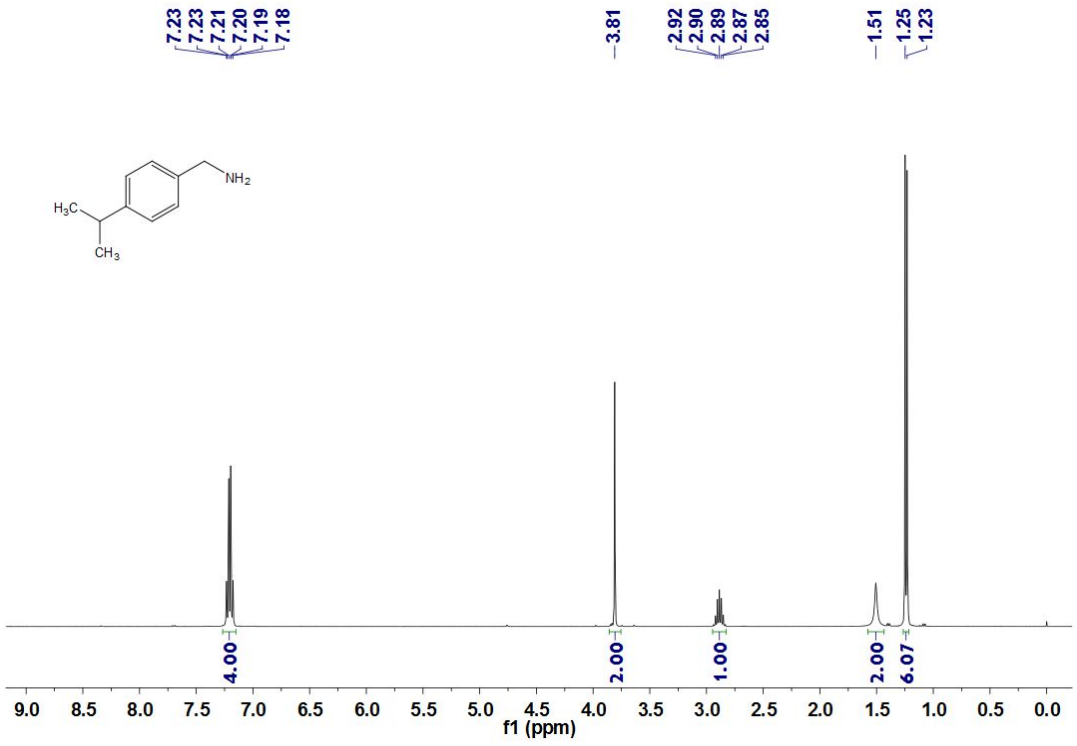
^{13}C NMR of (4-(trifluoromethyl)phenyl)methanamine



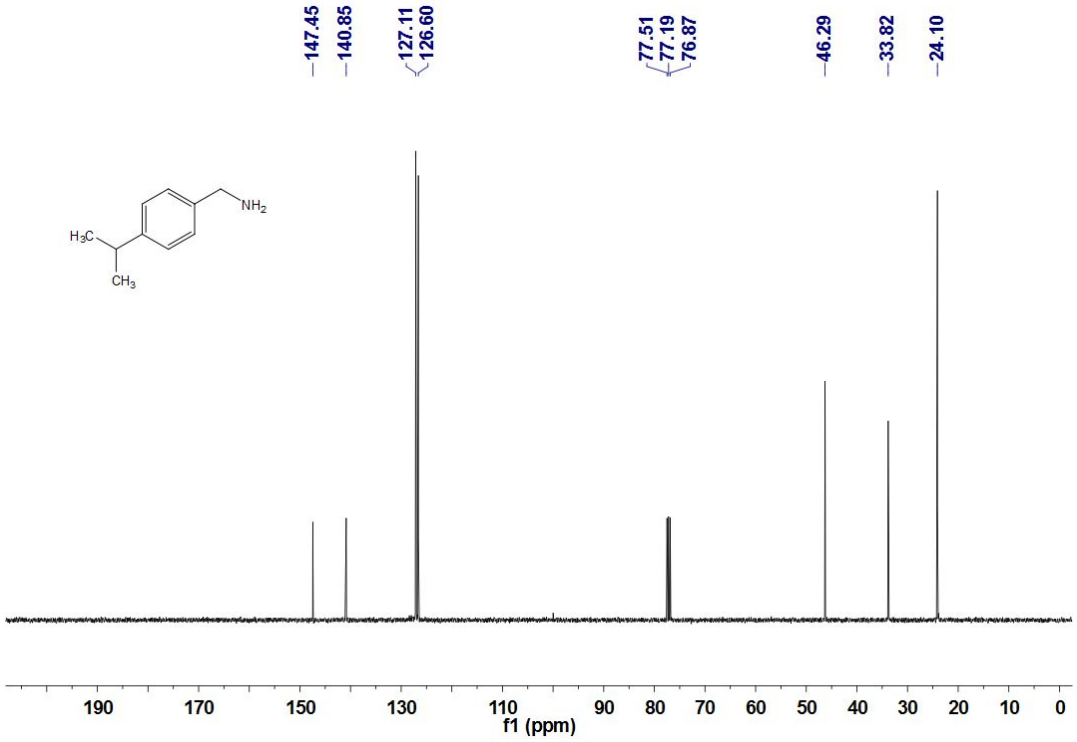
^{1}H NMR of 1,4-phenylenedimethanamine



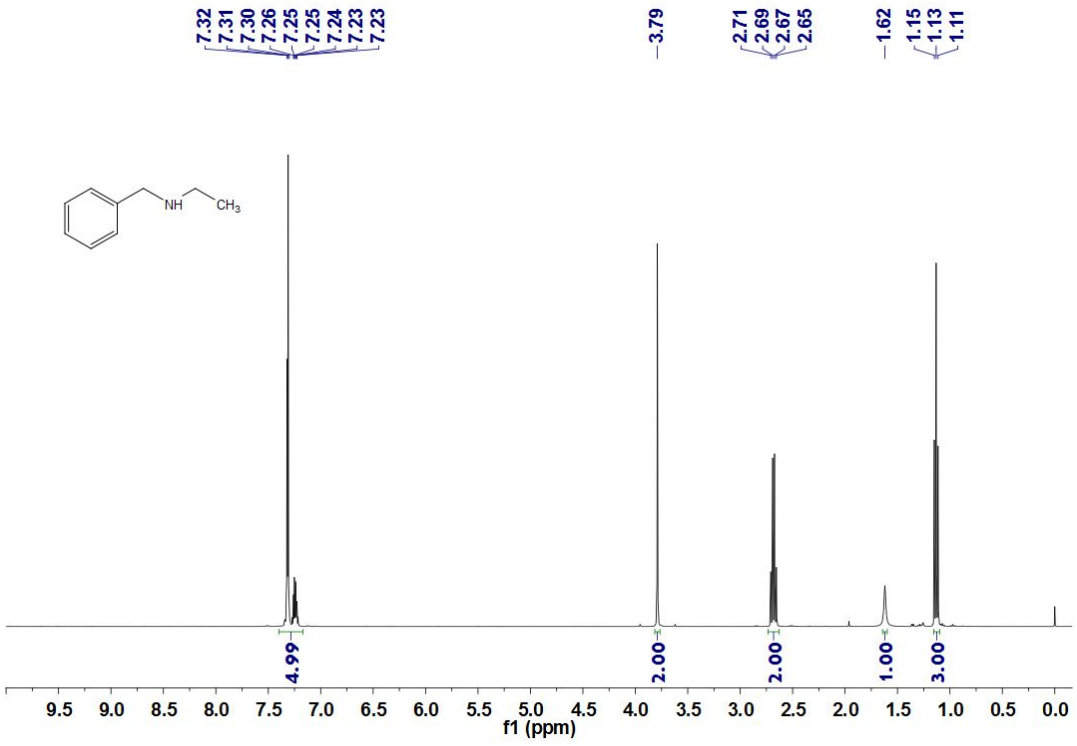
^{13}C NMR of 1,4-phenylenedimethanamine



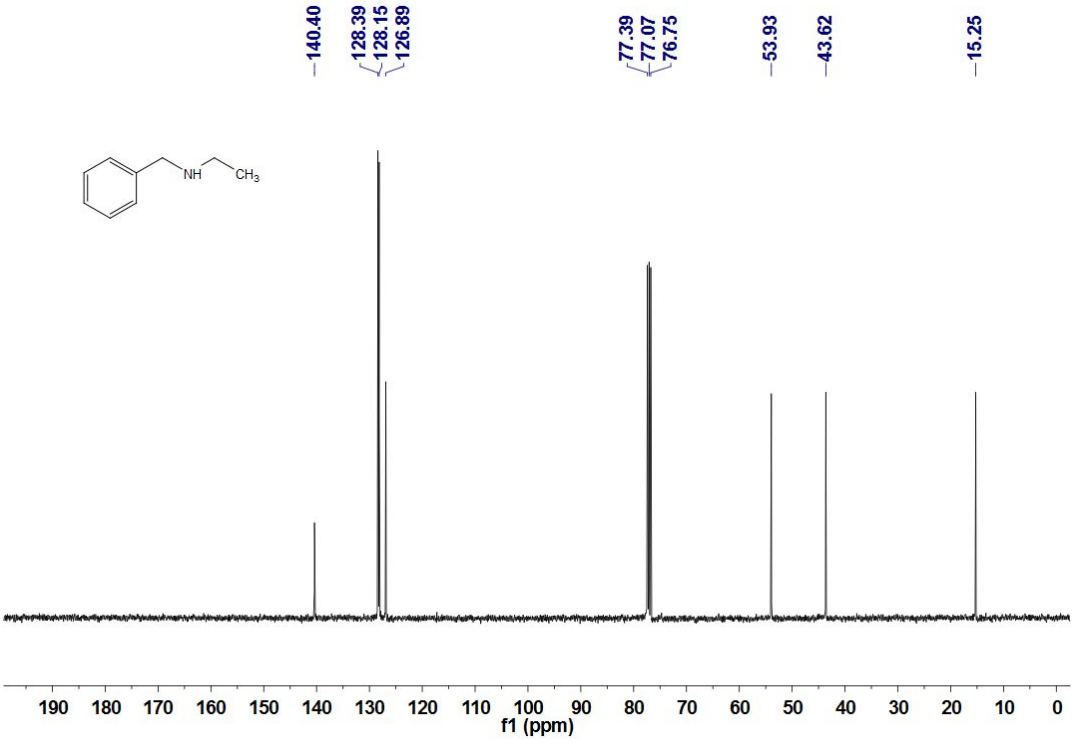
^{1}H NMR of (4-isopropylphenyl)methanamine



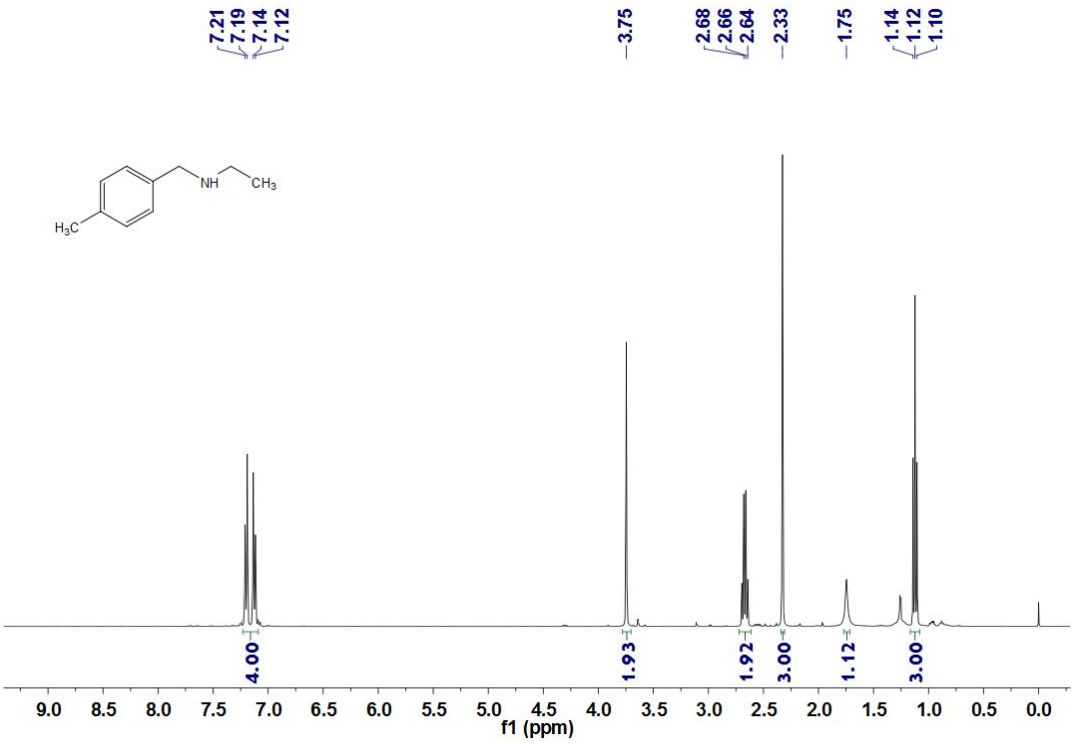
^{13}C NMR of (4-isopropylphenyl)methanamine



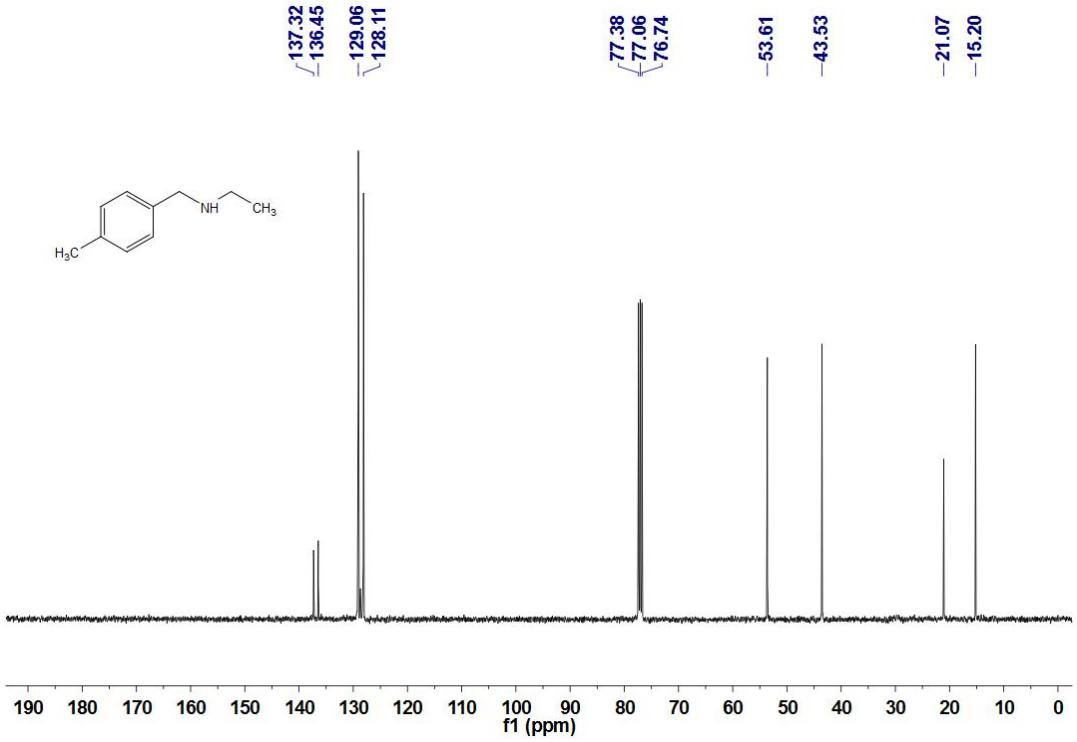
^{1}H NMR of N-ethylbenzylamine



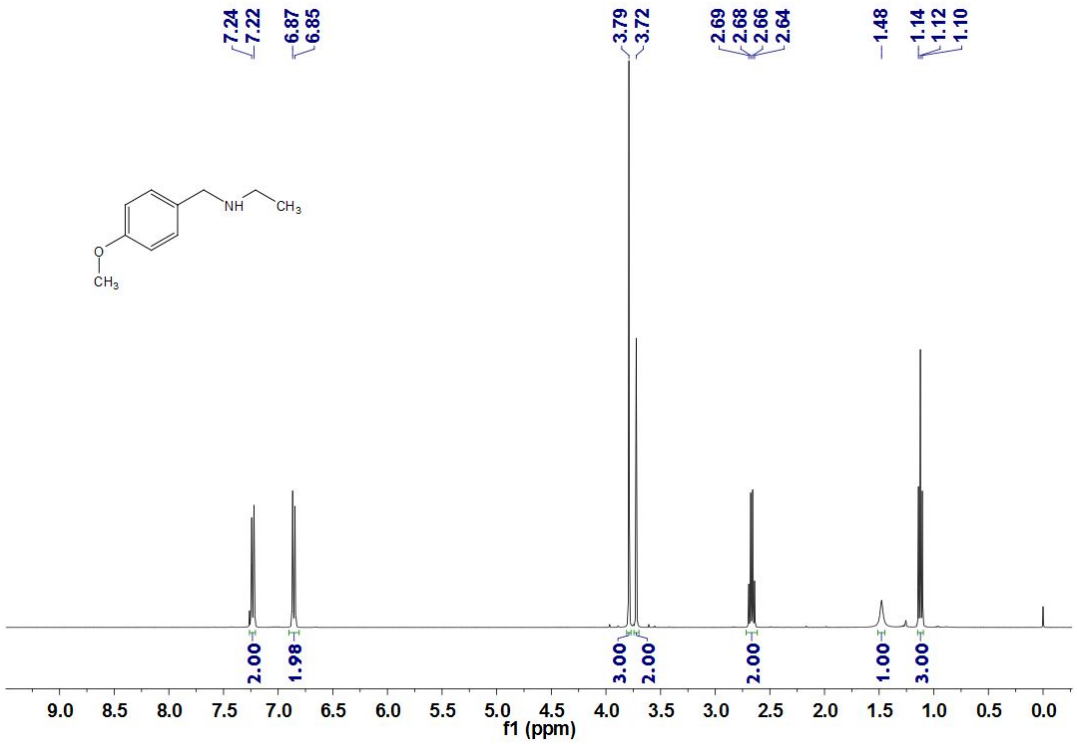
^{13}C NMR of N-ethylbenzylamine



^{1}H NMR of N-ethyl-4-methylbenzylamine



^{13}C NMR of N-ethyl-4-methylbenzylamine



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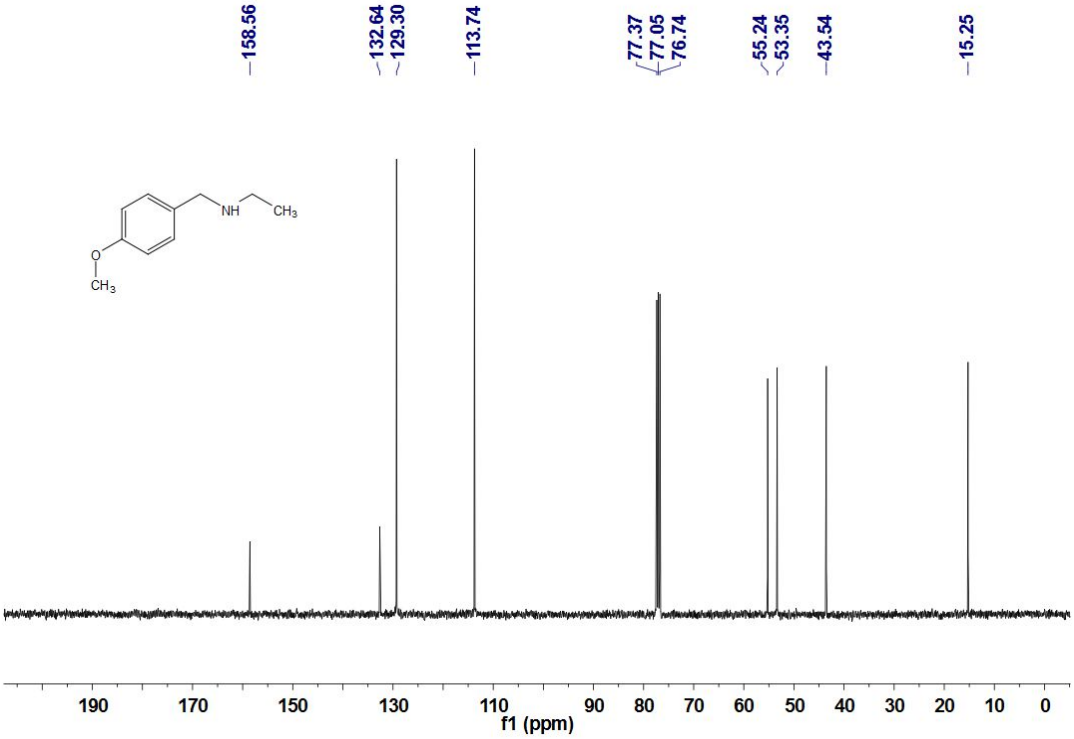

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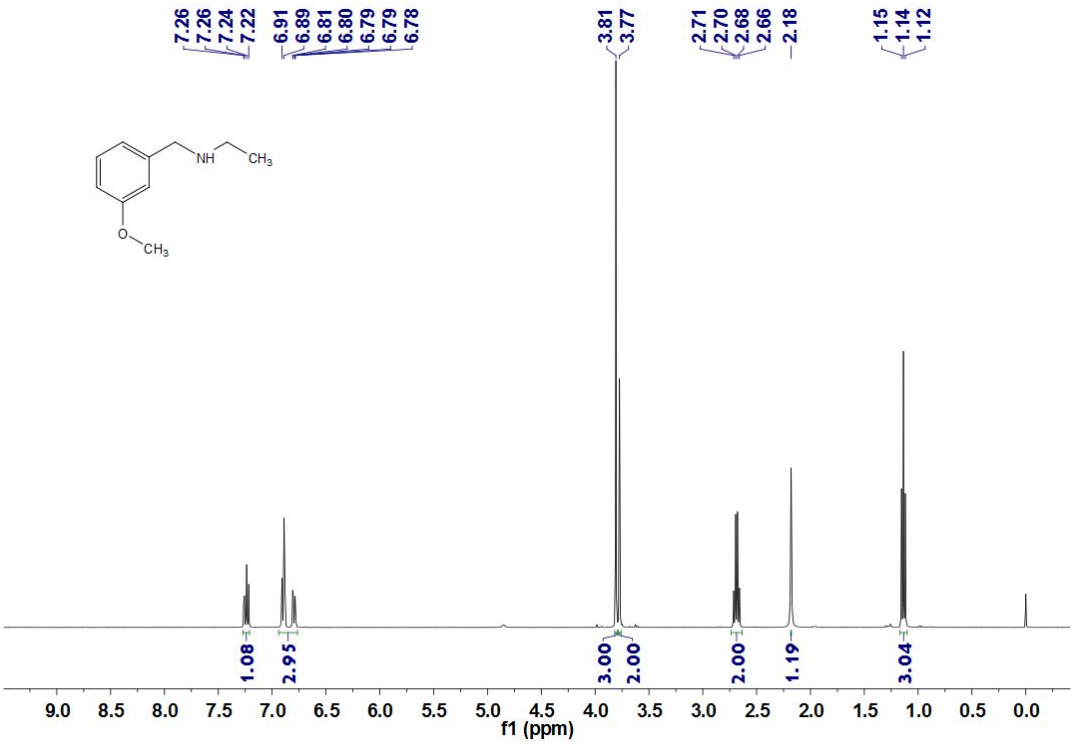

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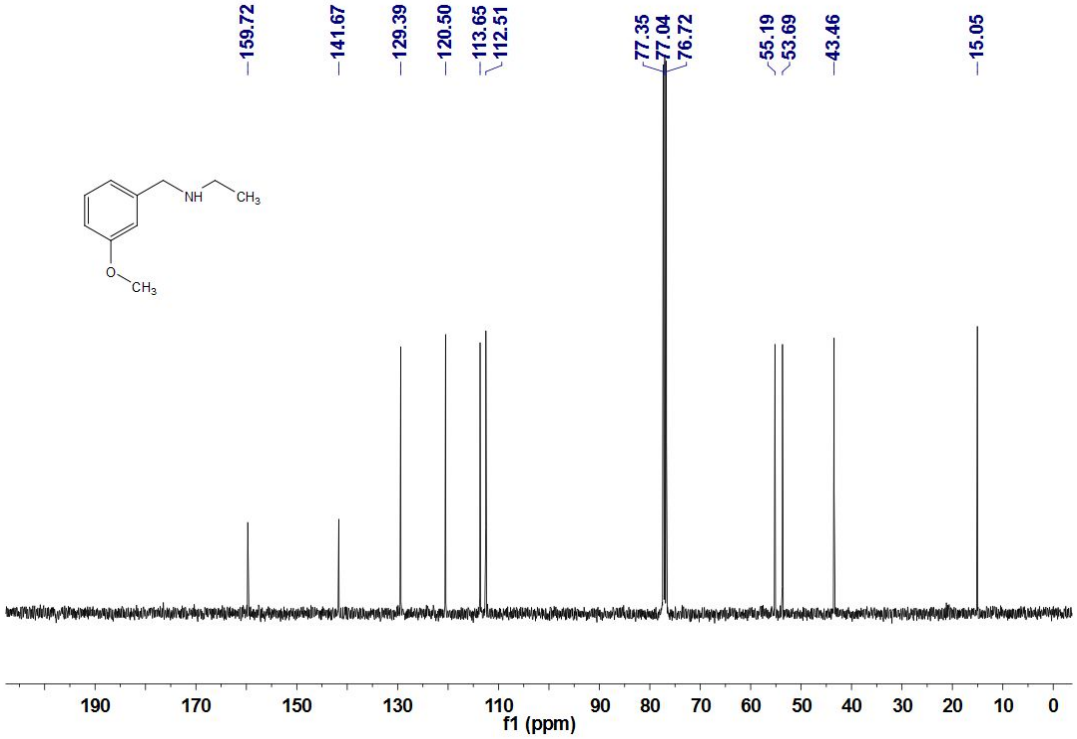

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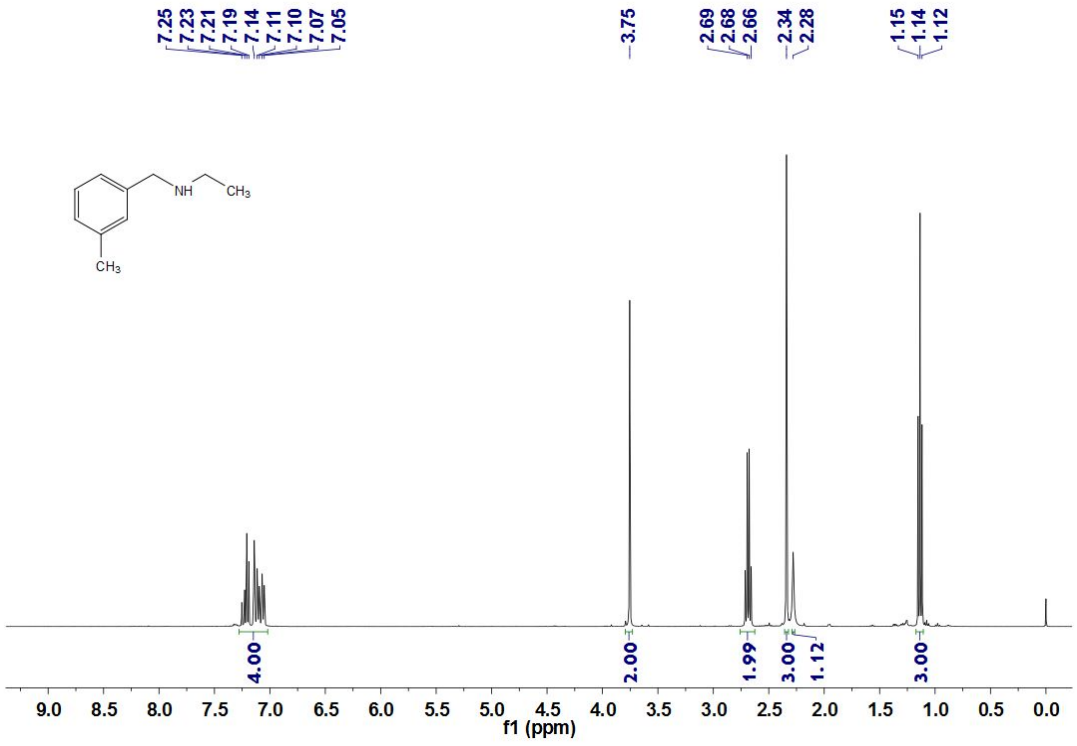

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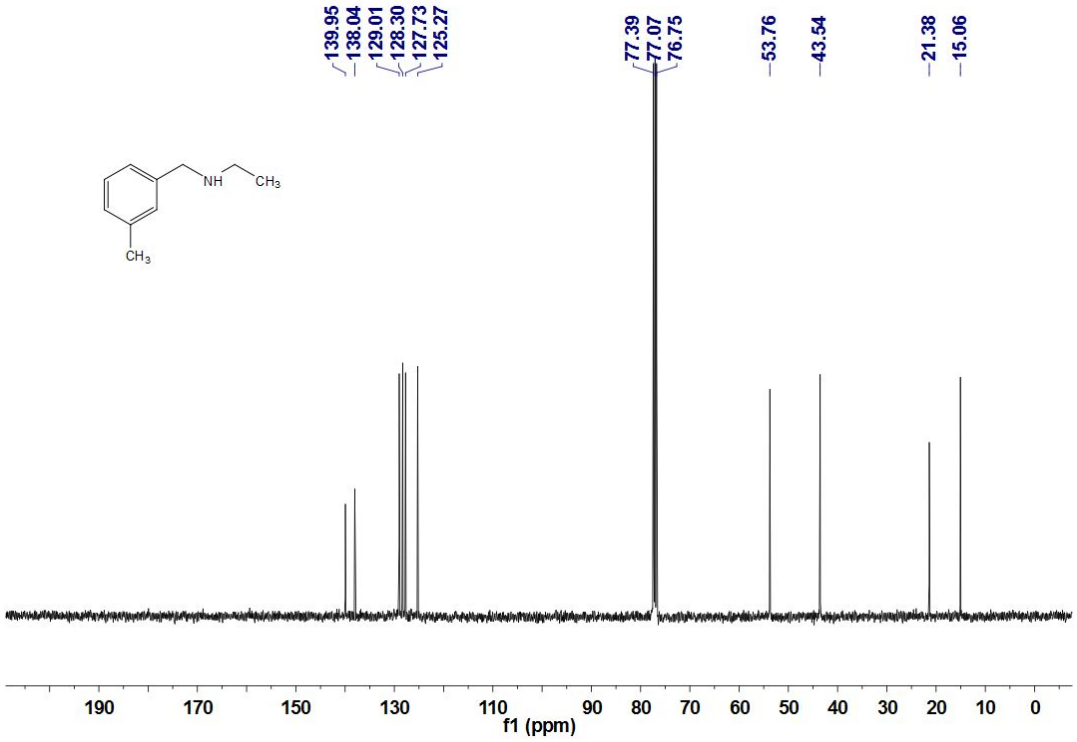

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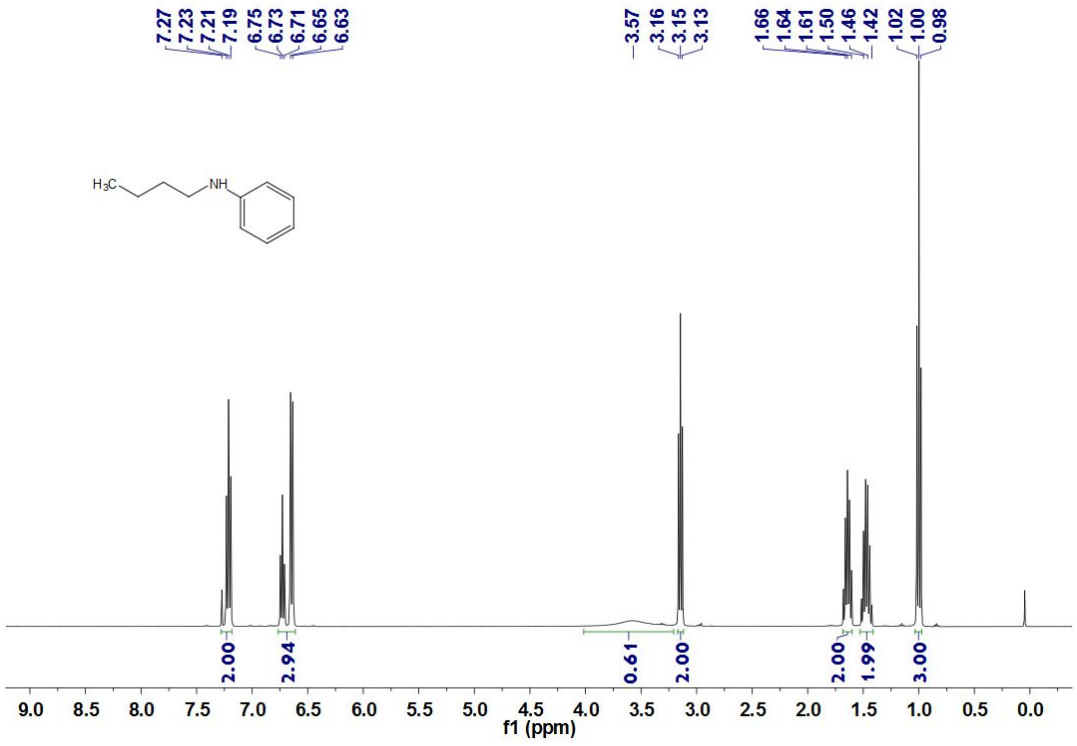
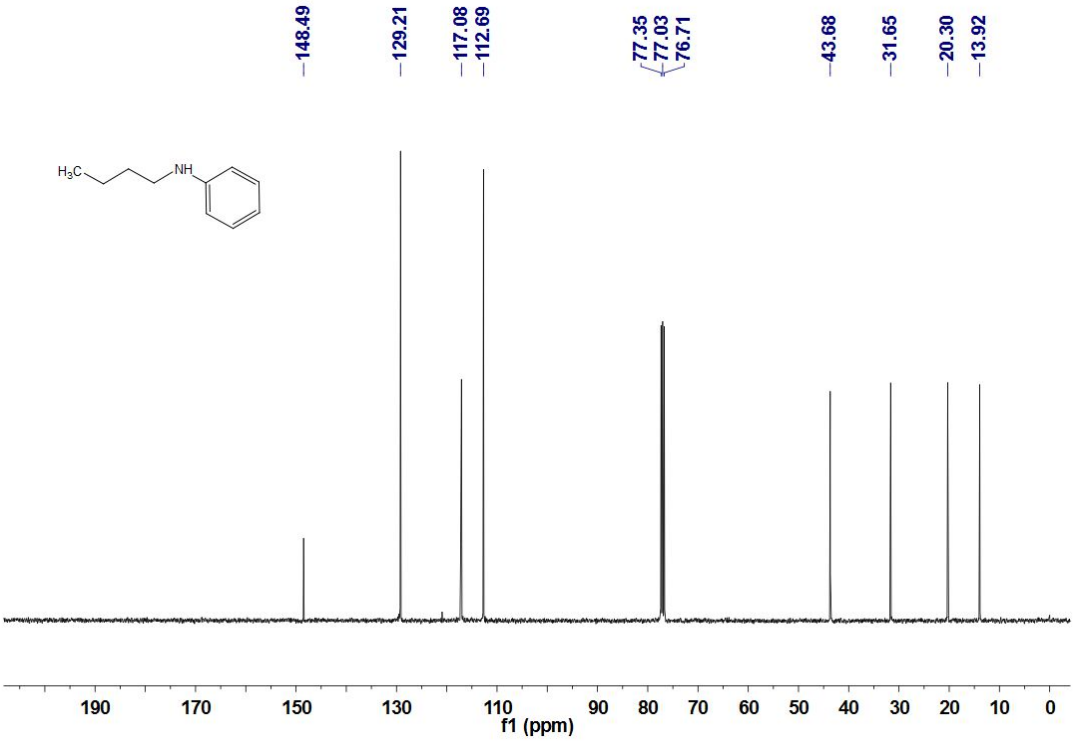
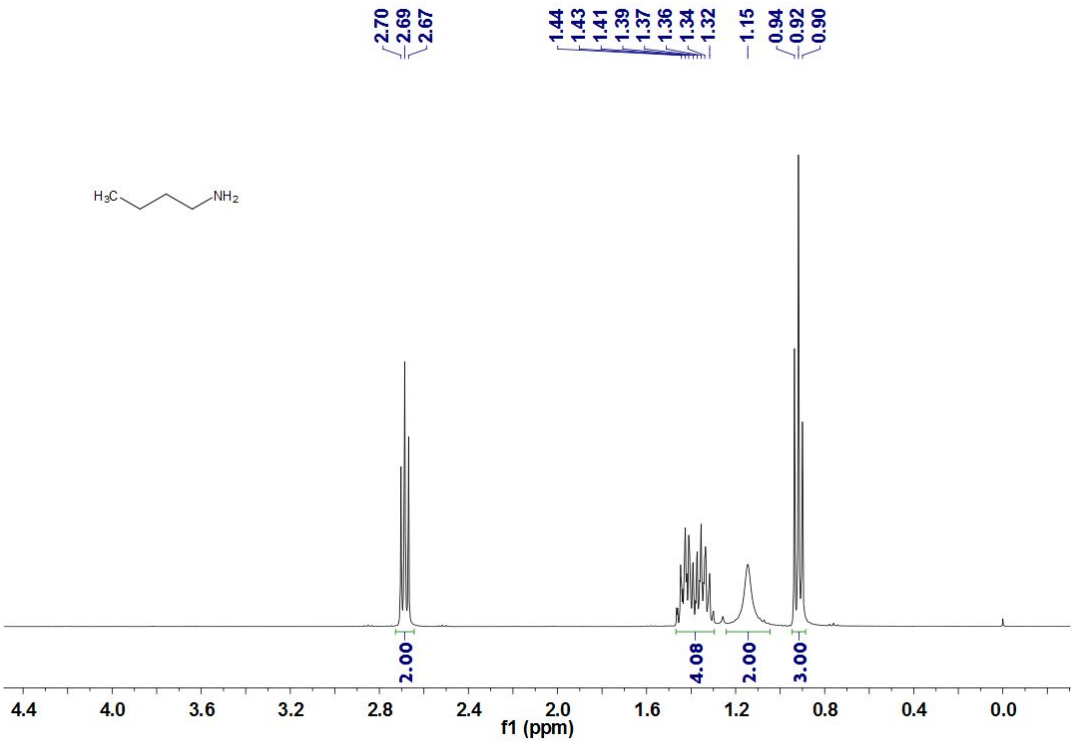


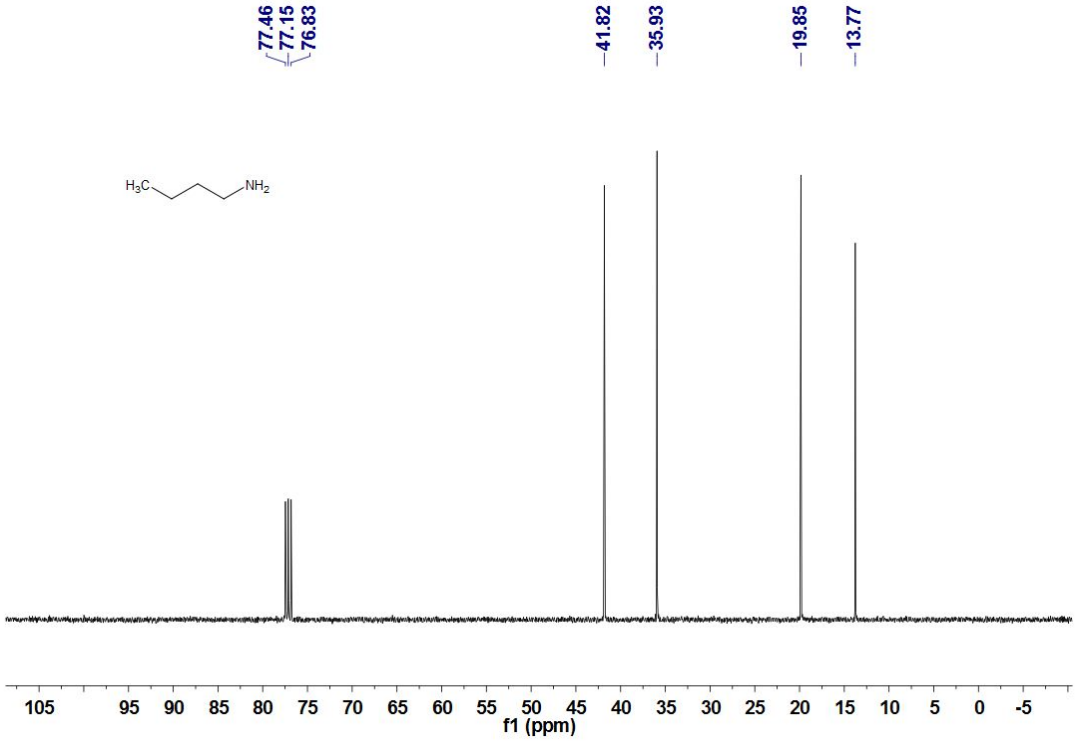
^{1}H NMR of N-butylaniline



^{13}C NMR of N-butylaniline



^{1}H NMR of butan-1-amine



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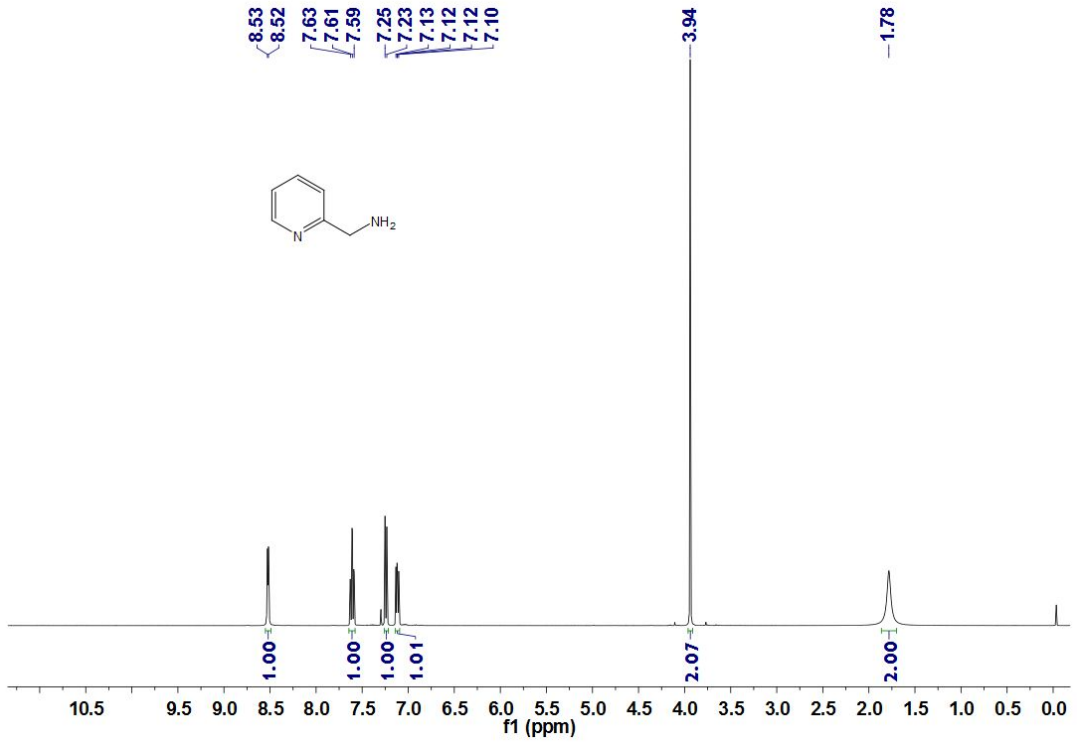
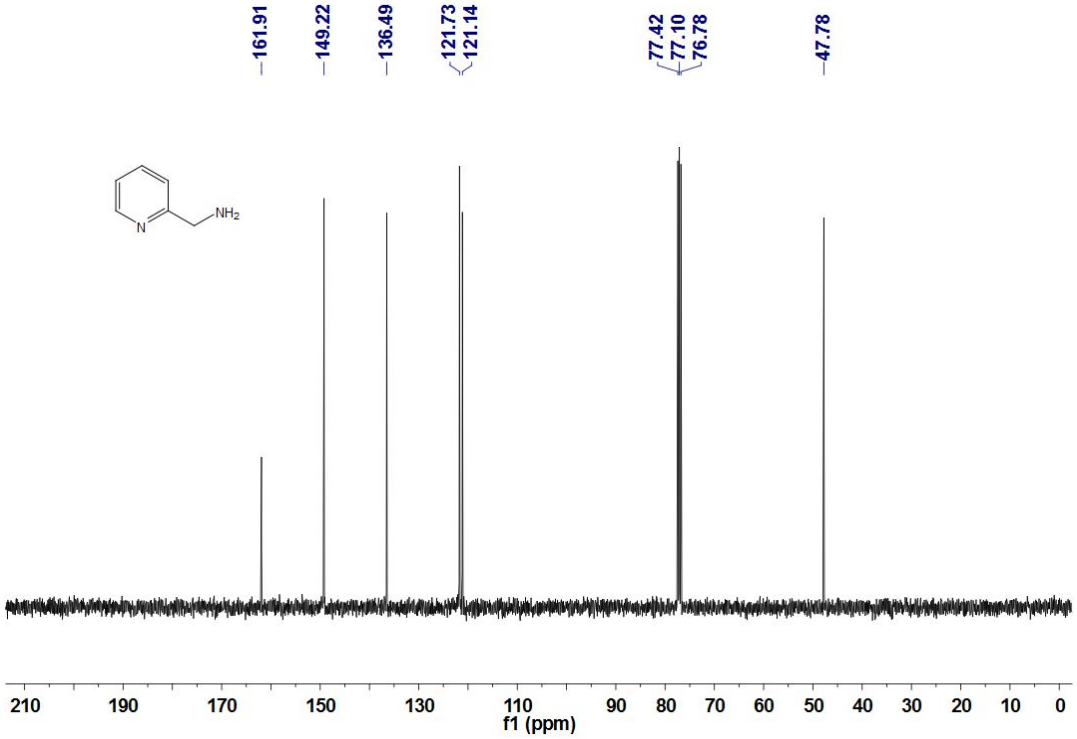
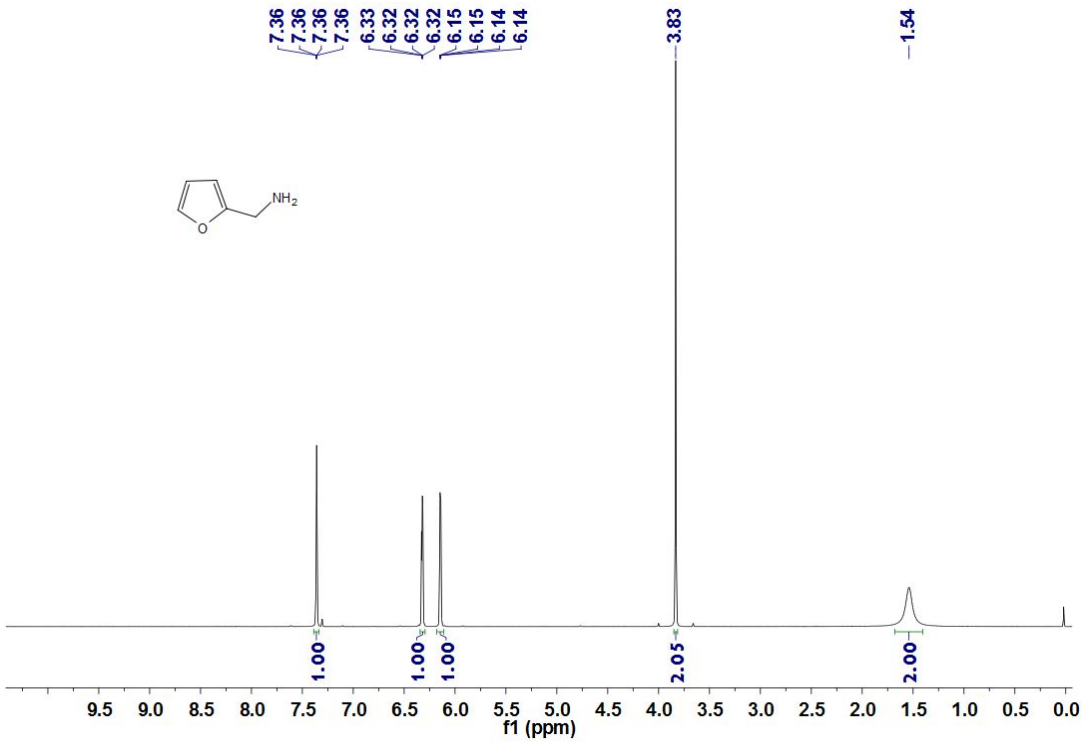


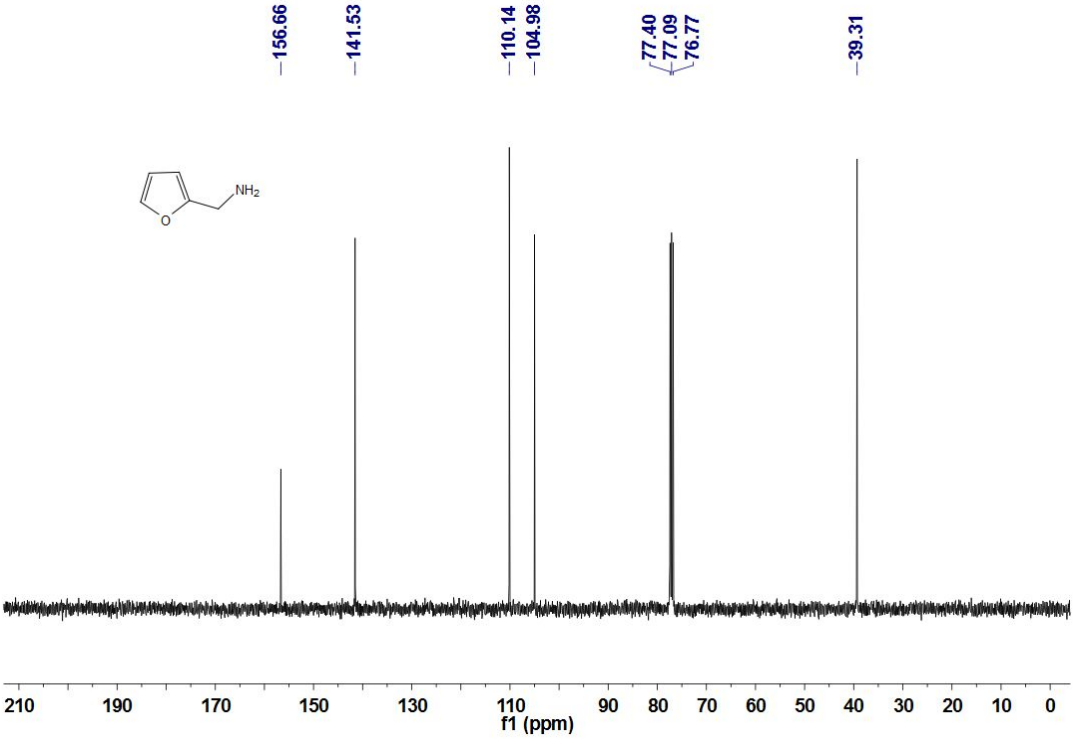
^{1}H NMR of 2-(aminomethyl)pyridine



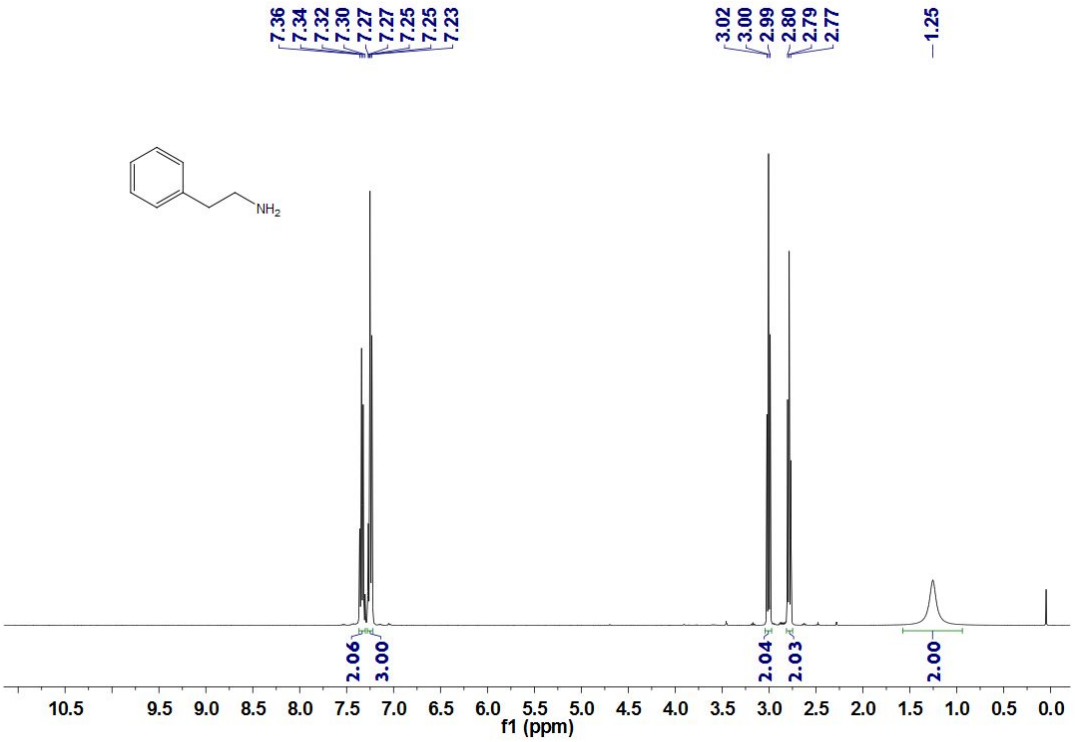
^{13}C NMR of 2-(aminomethyl)pyridine



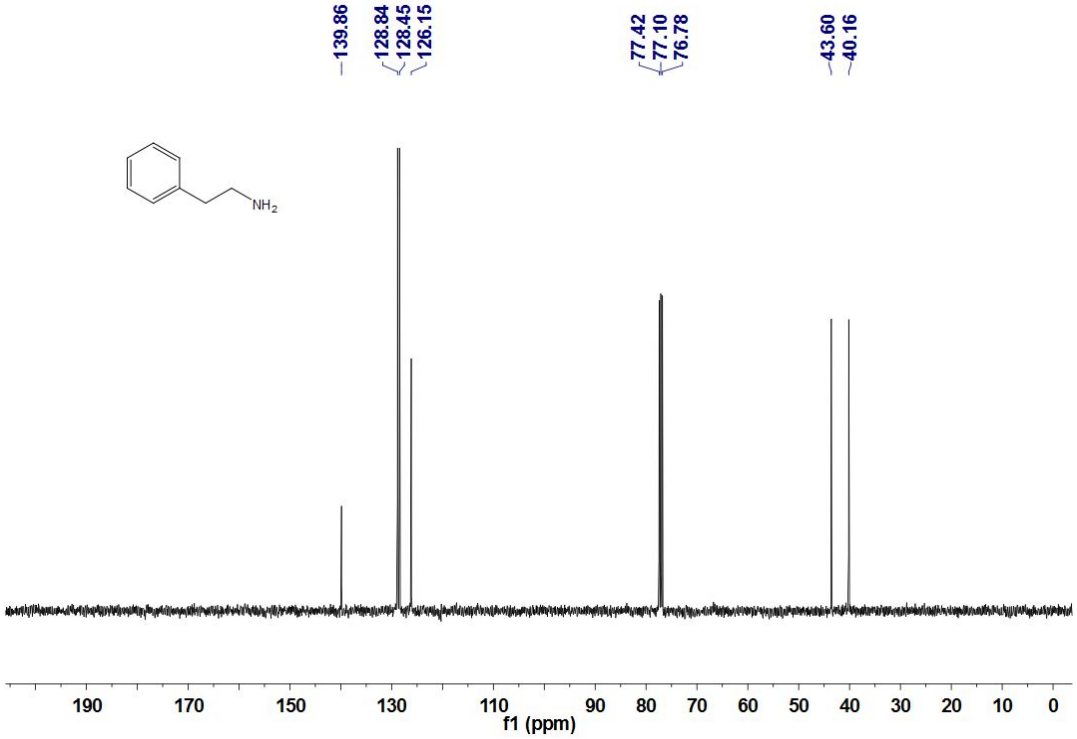
^{1}H NMR of 2-furfurylamine



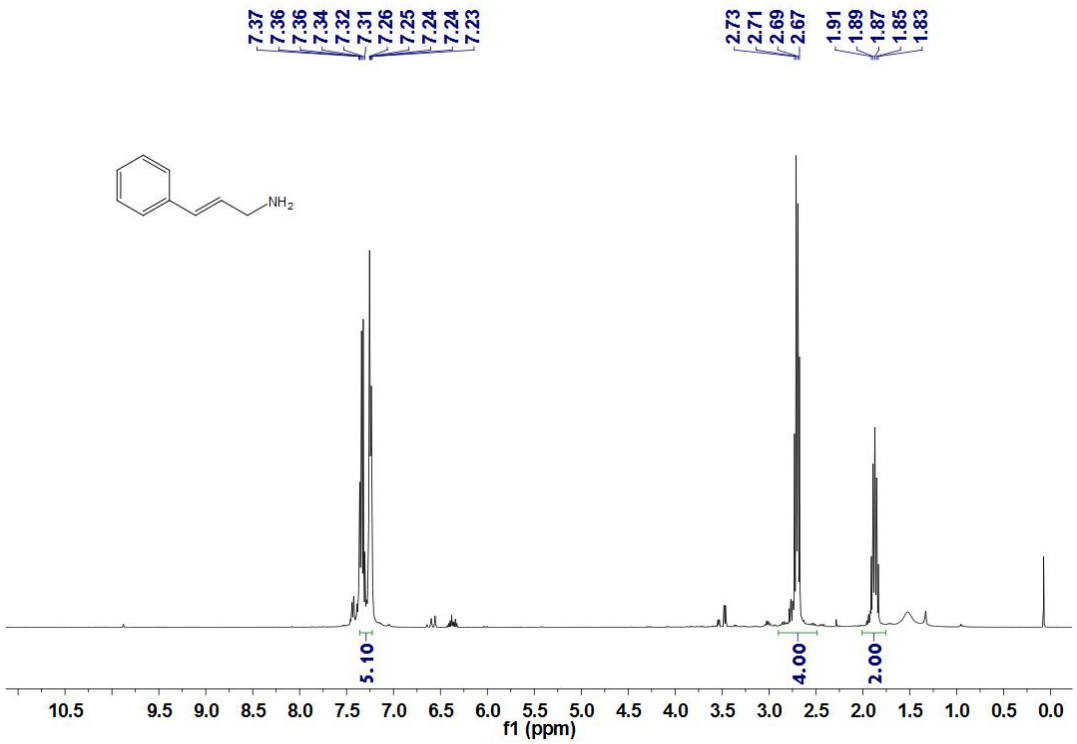
^{13}C NMR of 2-furfurylamine



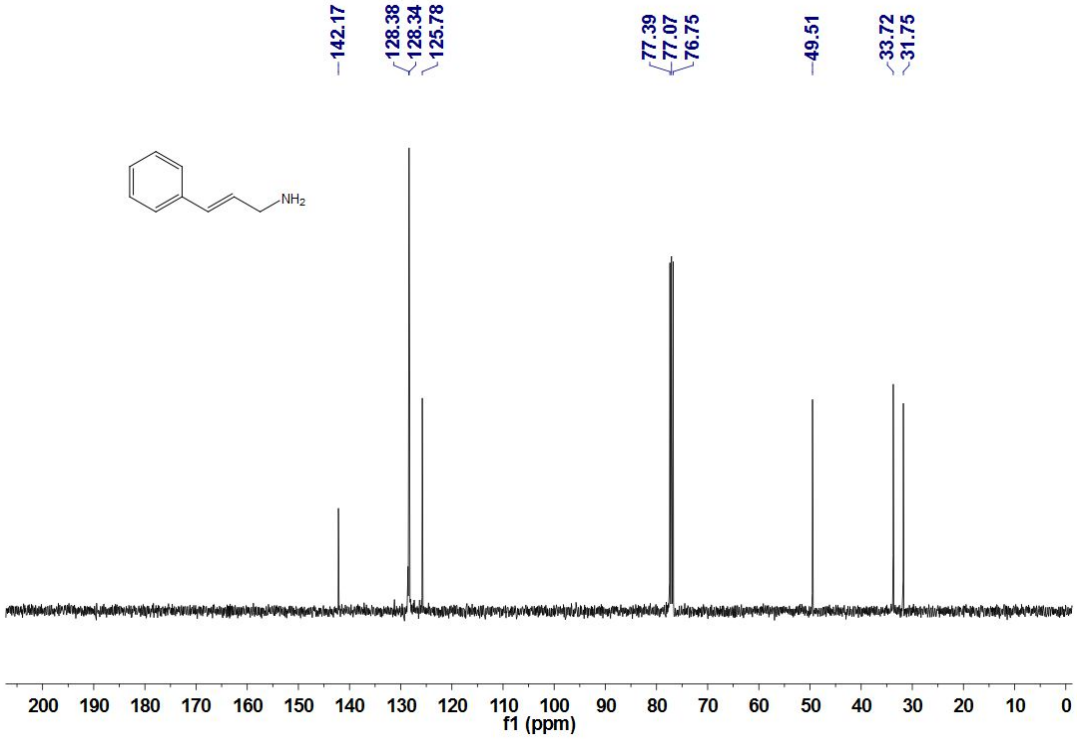
^{1}H NMR of 2-phenylethylamine



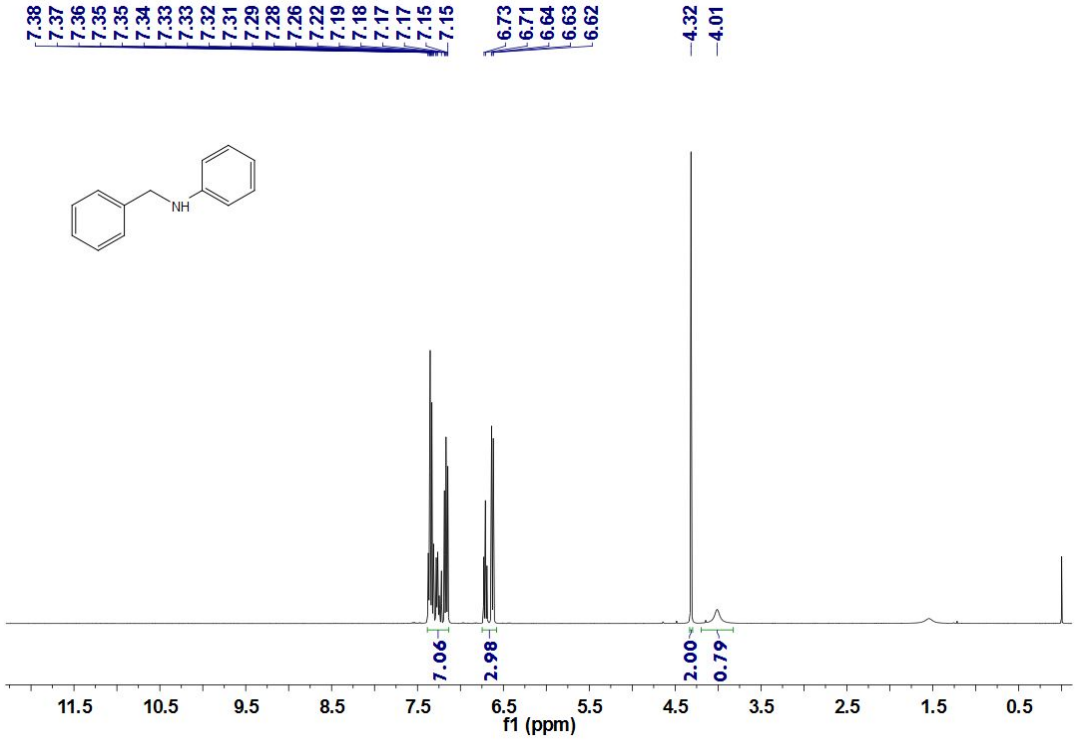
^{13}C NMR of 2-phenylethylamine



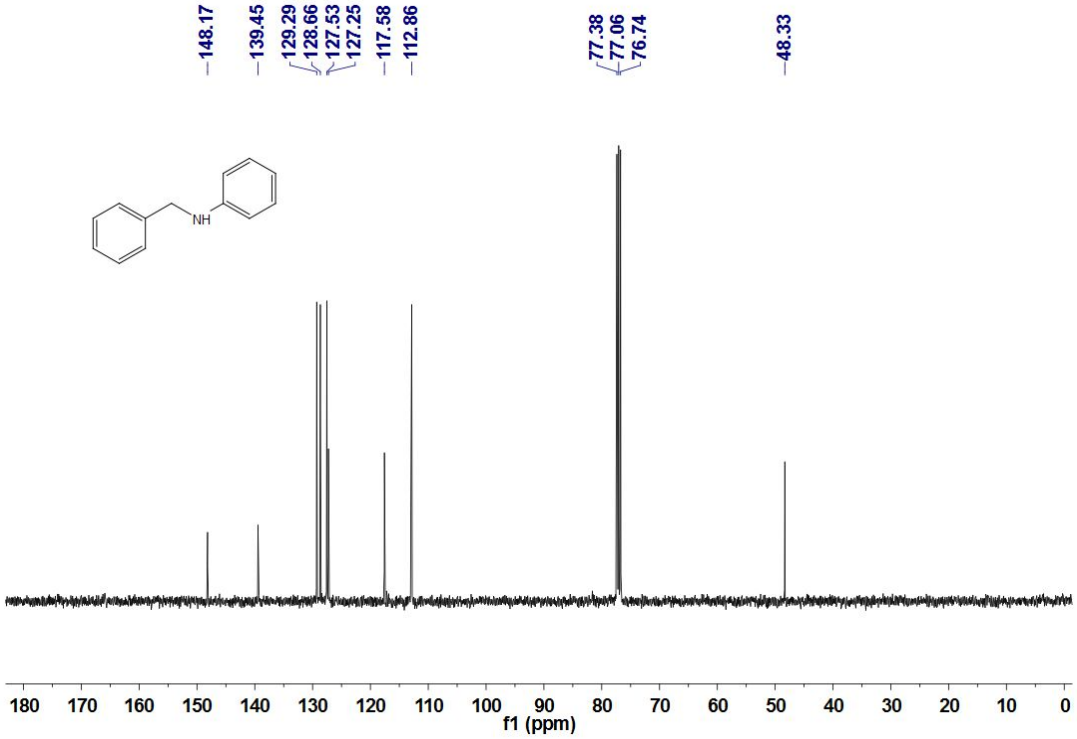
^{1}H NMR of 3-phenyl-2-propen-1-amine



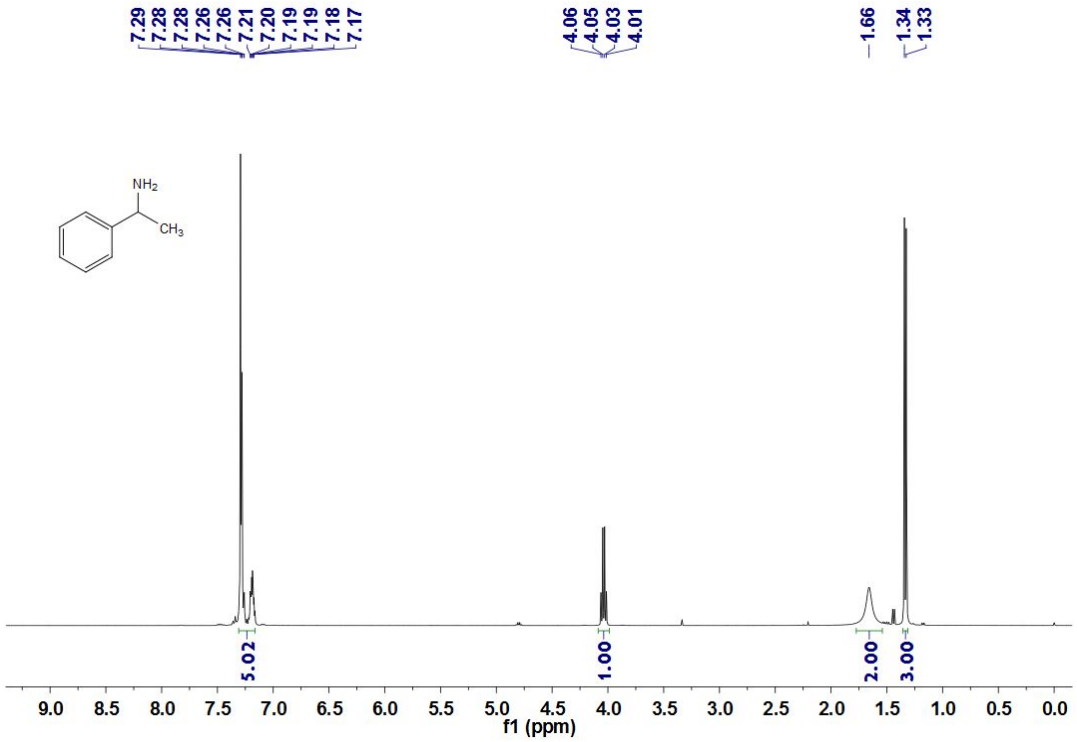
^{13}C NMR of 3-phenyl-2-propen-1-amine



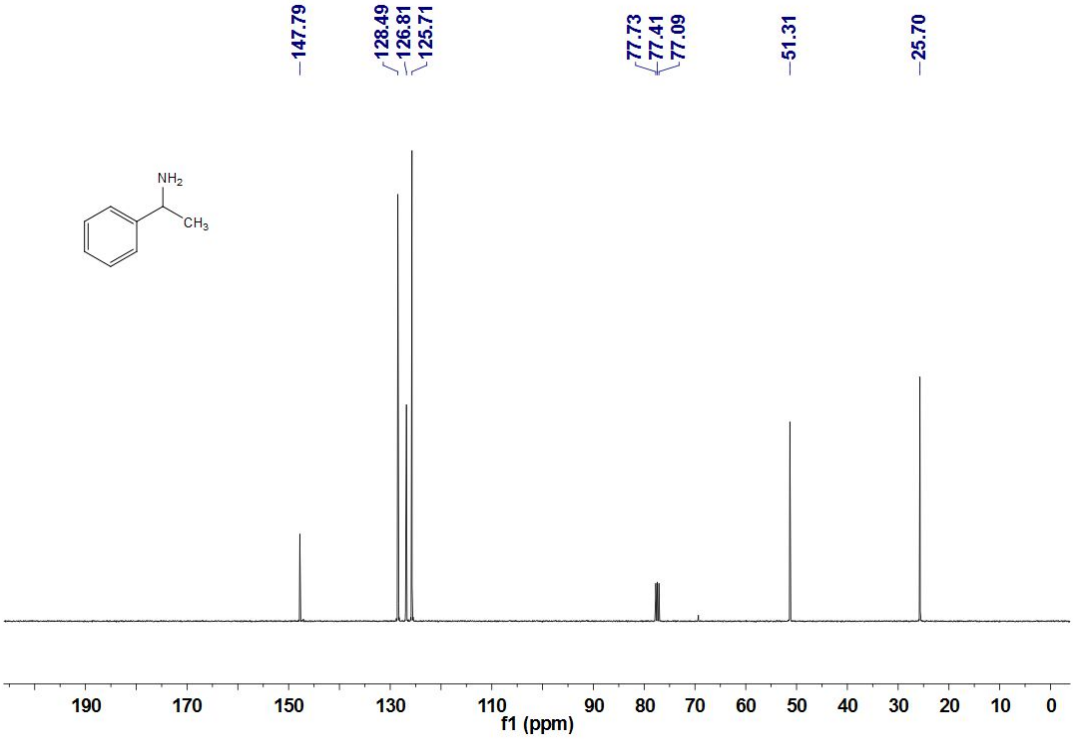
^{1}H NMR of N-benzylaniline



^{13}C NMR of N-benzylaniline



^{1}H NMR of 1-phenylethylamine



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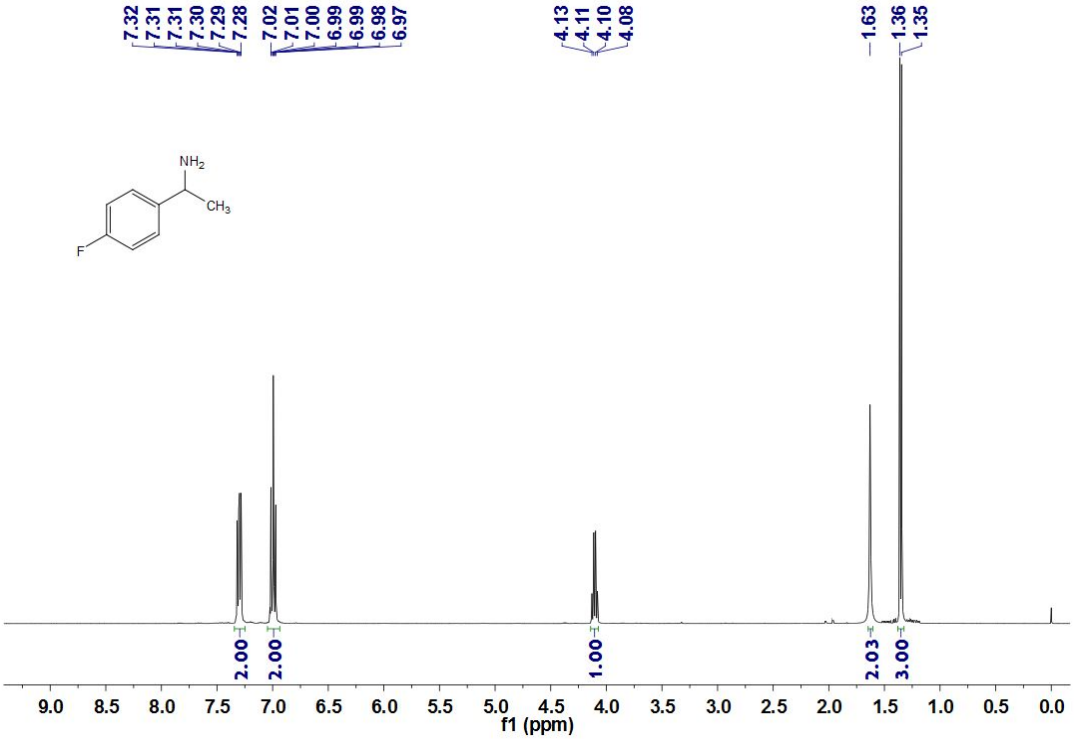
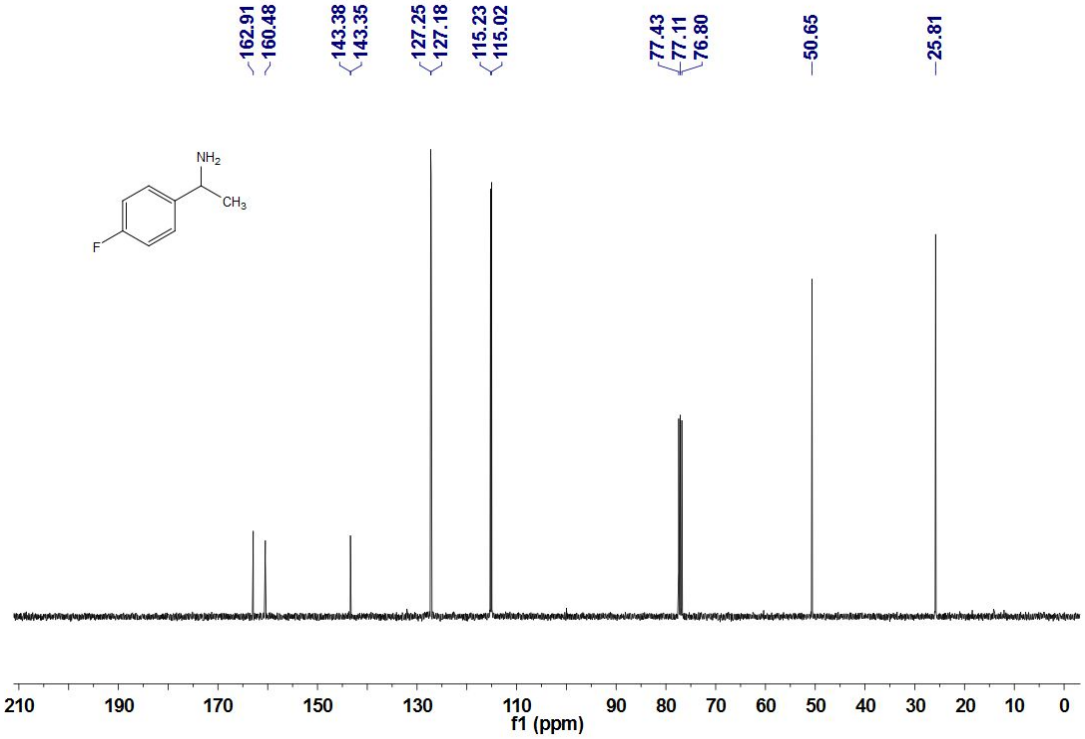


^{1}H NMR of 1-(4-fluorophenyl)ethanamine



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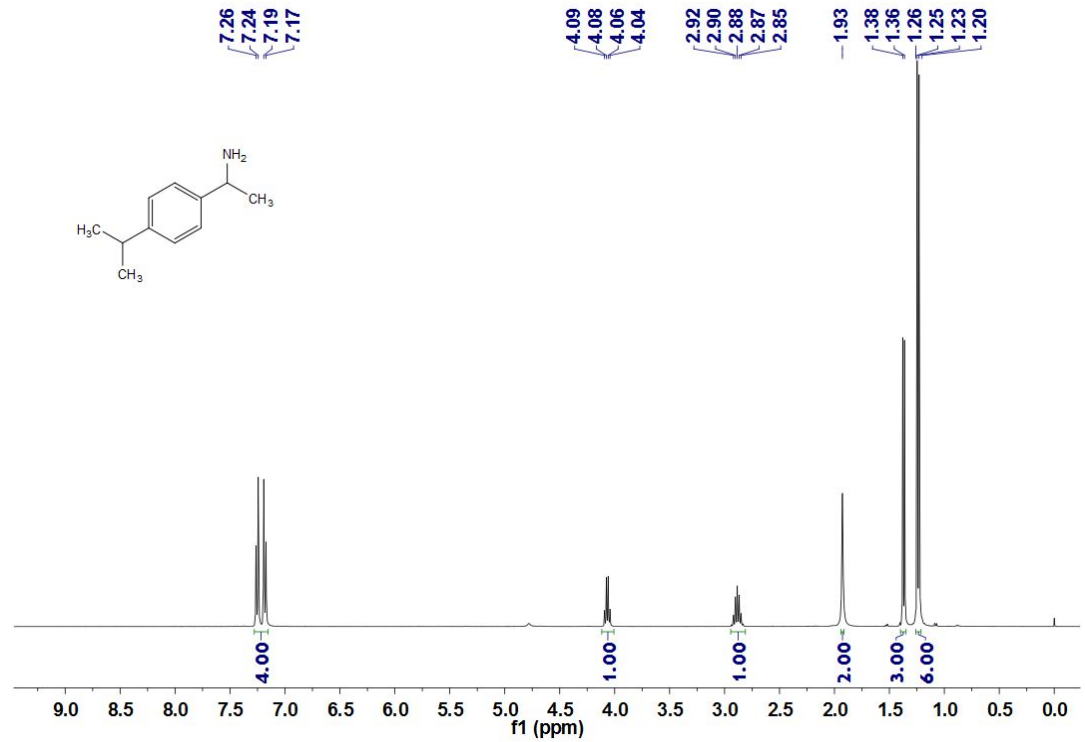
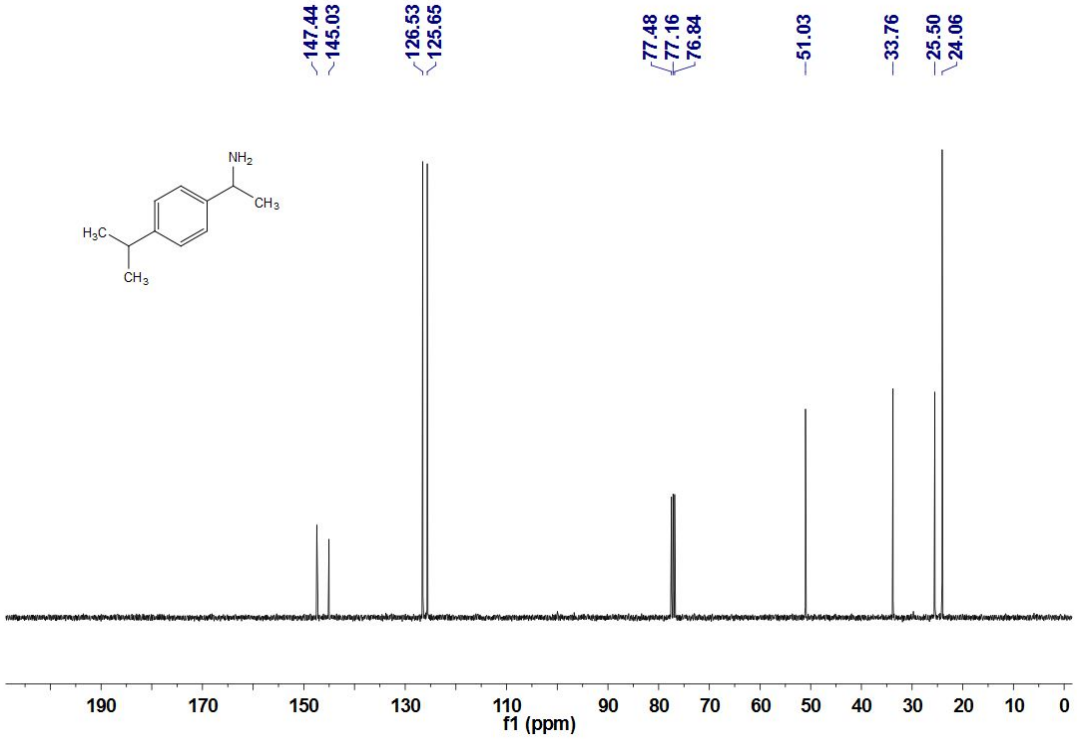
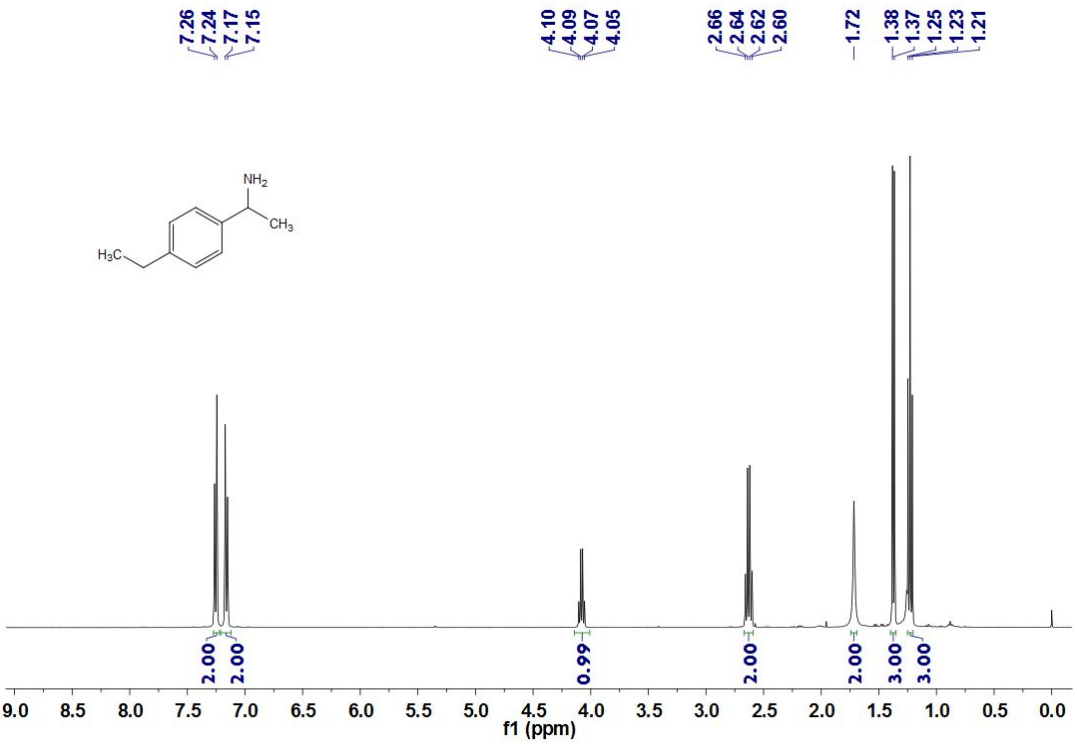


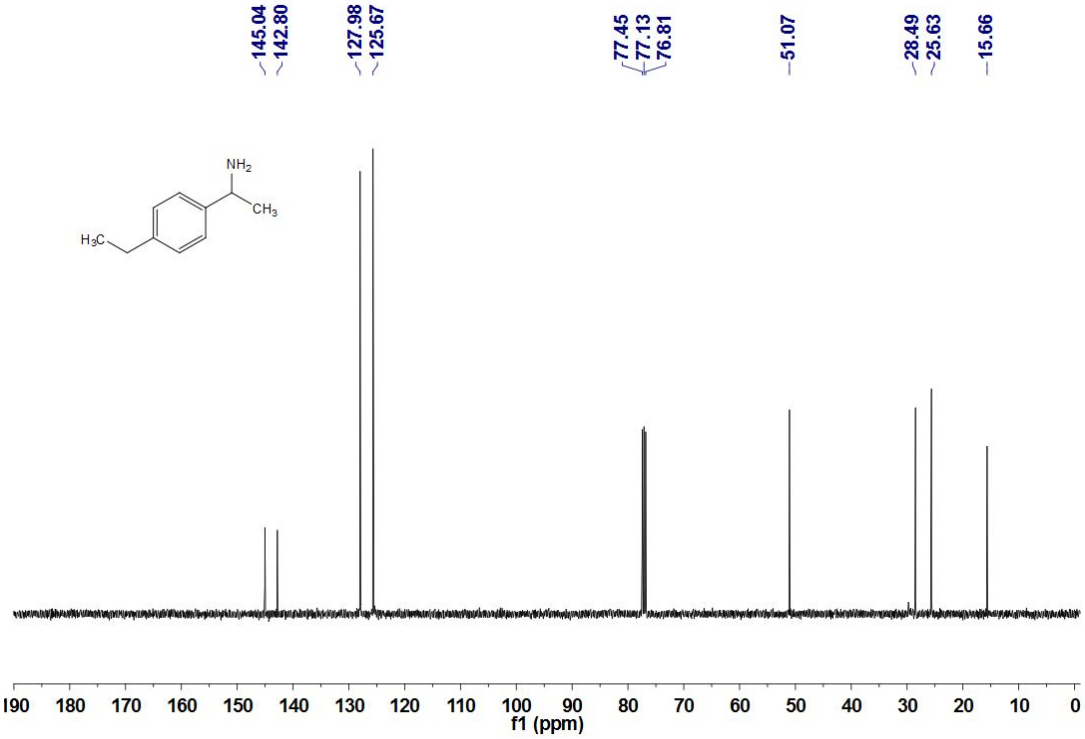
^{1}H NMR of 1-(4-isopropylphenyl)ethylamine



^{13}C NMR of 1-(4-isopropylphenyl)ethylamine



^{1}H NMR of 1-(4-ethylphenyl)ethylamine



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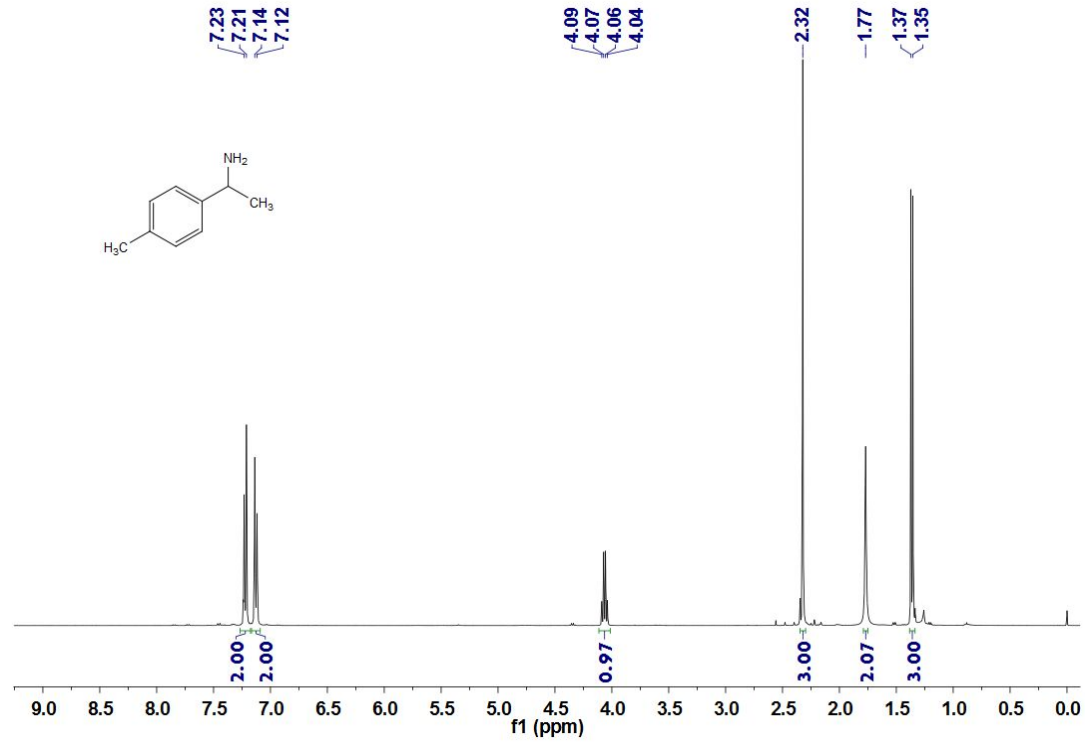
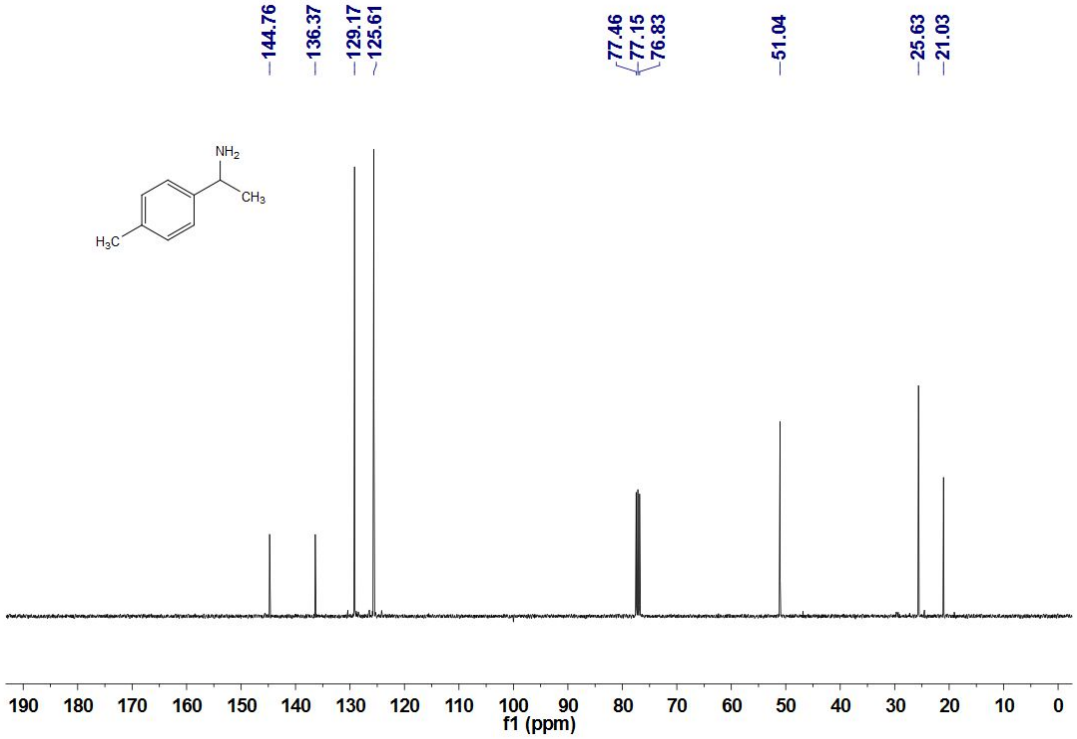


^{1}H NMR of 1-(4-methylphenyl)ethylamine



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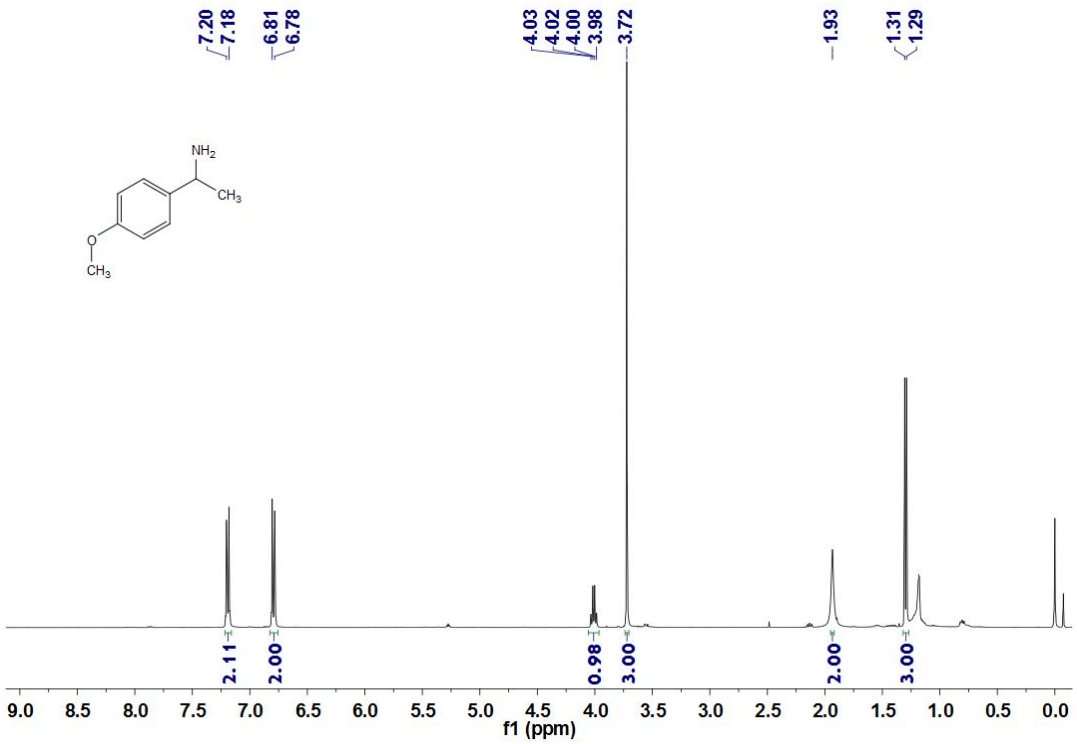
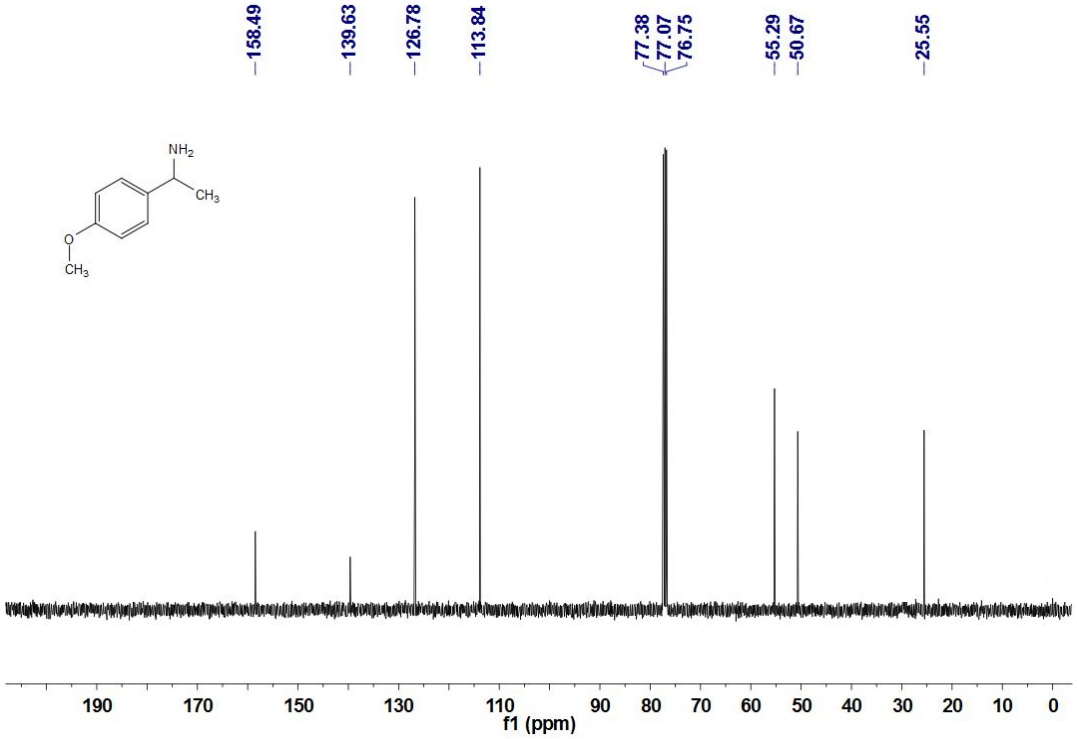
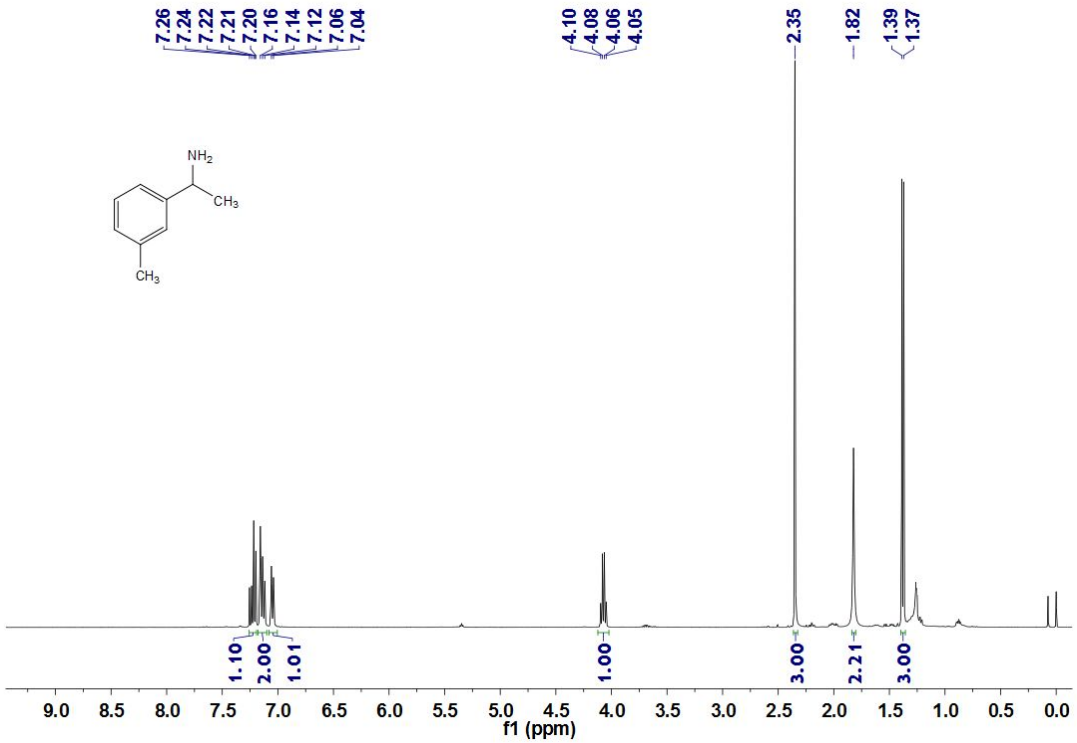


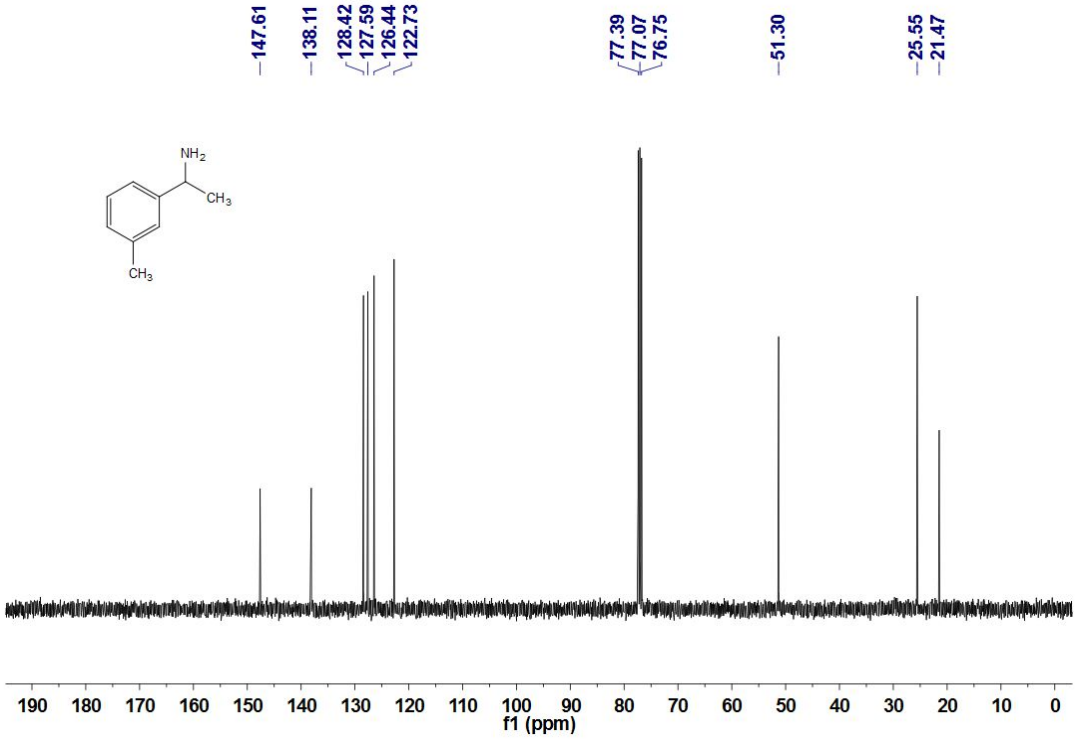
^{1}H NMR of 1-(4-methoxyphenyl)ethylamine



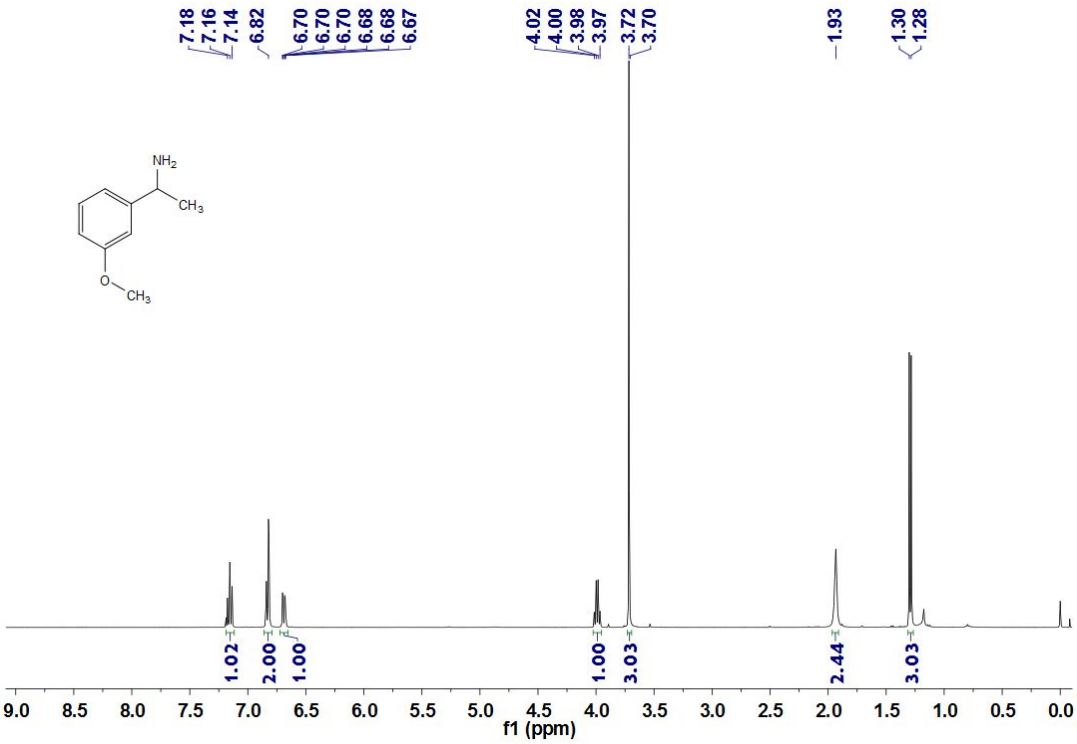
^{13}C NMR of 1-(4-methoxyphenyl)ethylamine



^{1}H NMR of 1-(3-methylphenyl)ethylamine



^{13}C NMR of 1-(3-methylphenyl)ethylamine



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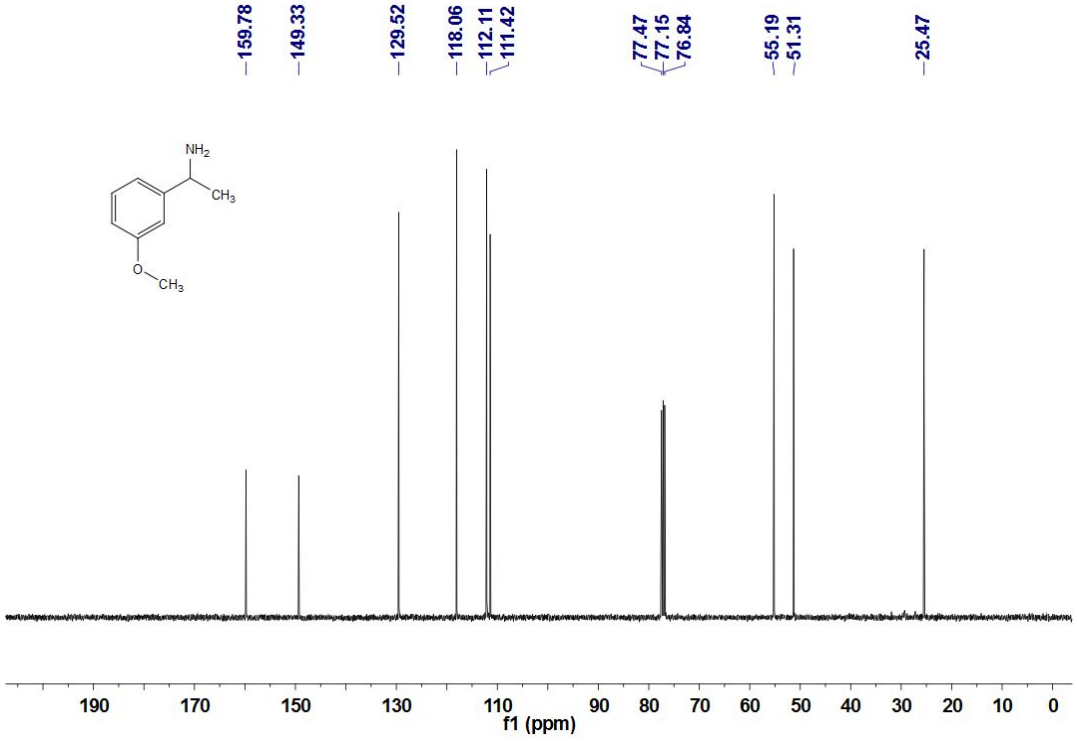

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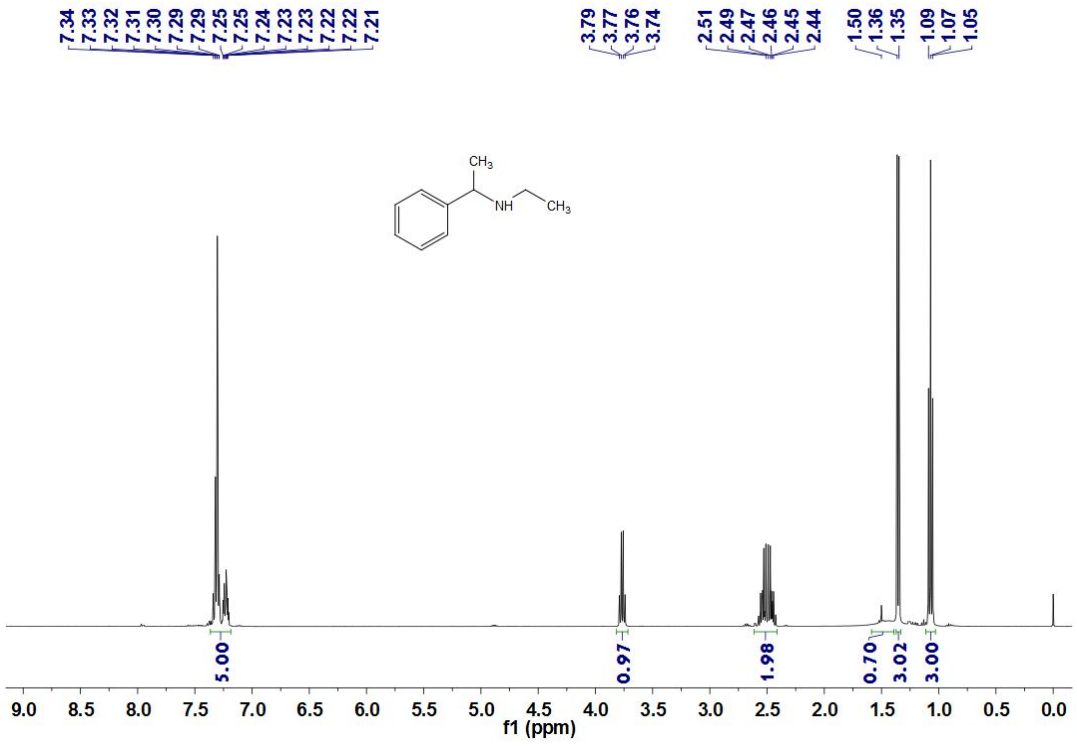
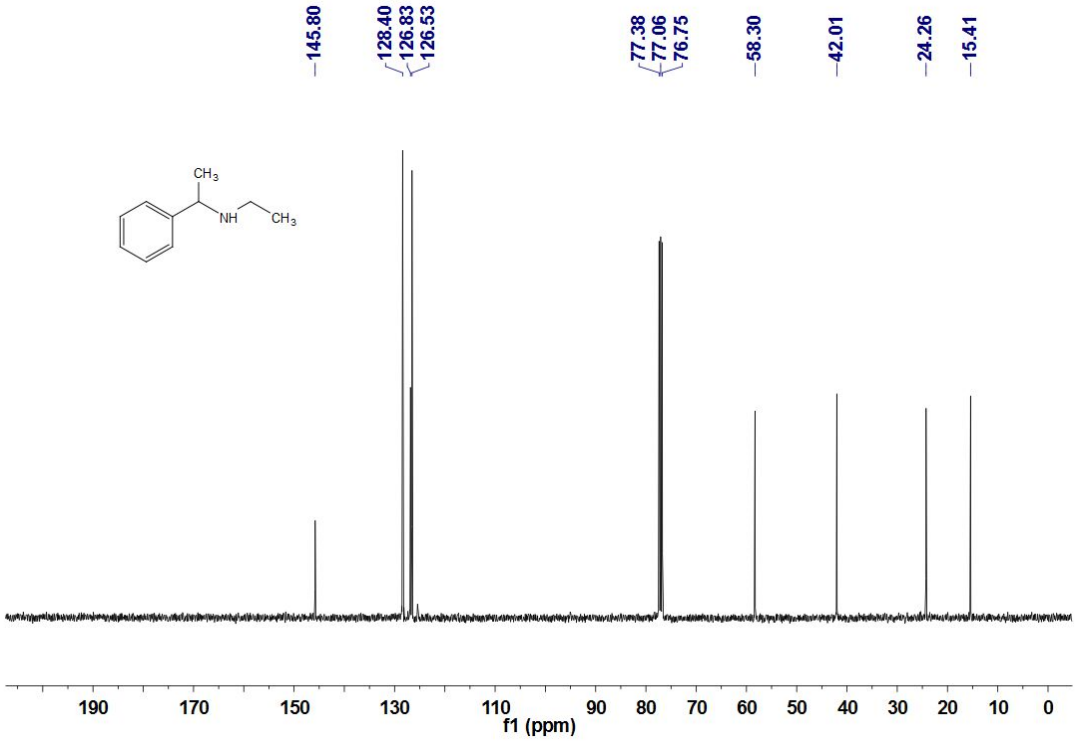
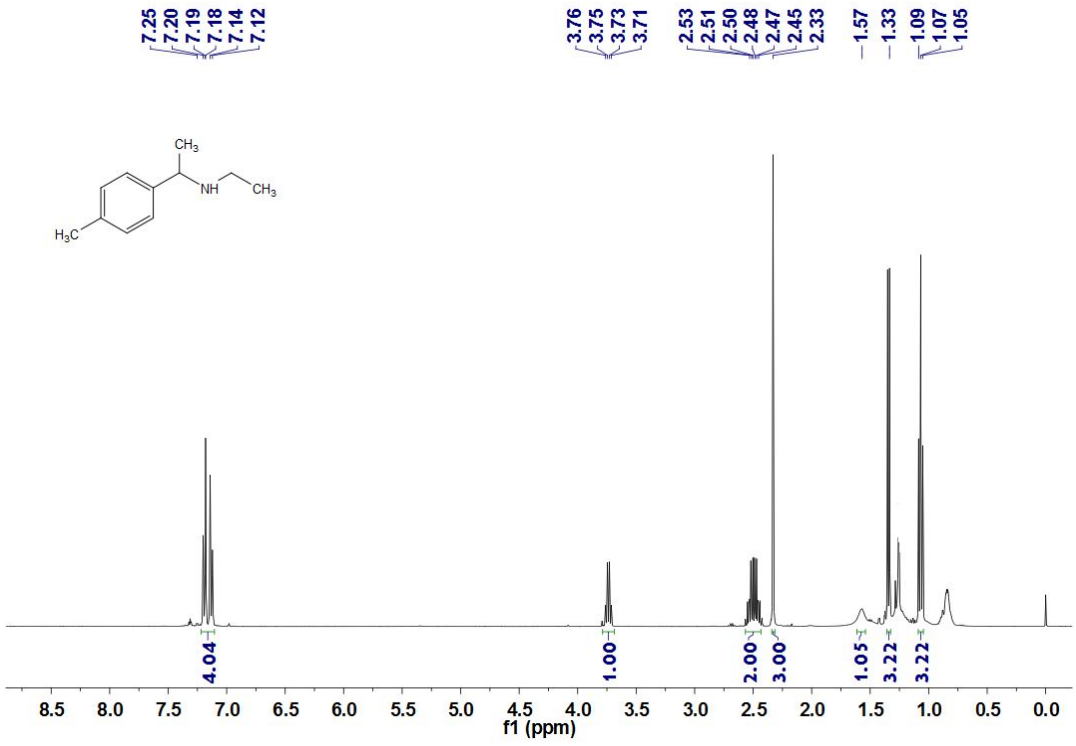


^{1}H NMR of N-ethyl-1-phenethylamine



^{13}C NMR of N-ethyl-1-phenethylamine



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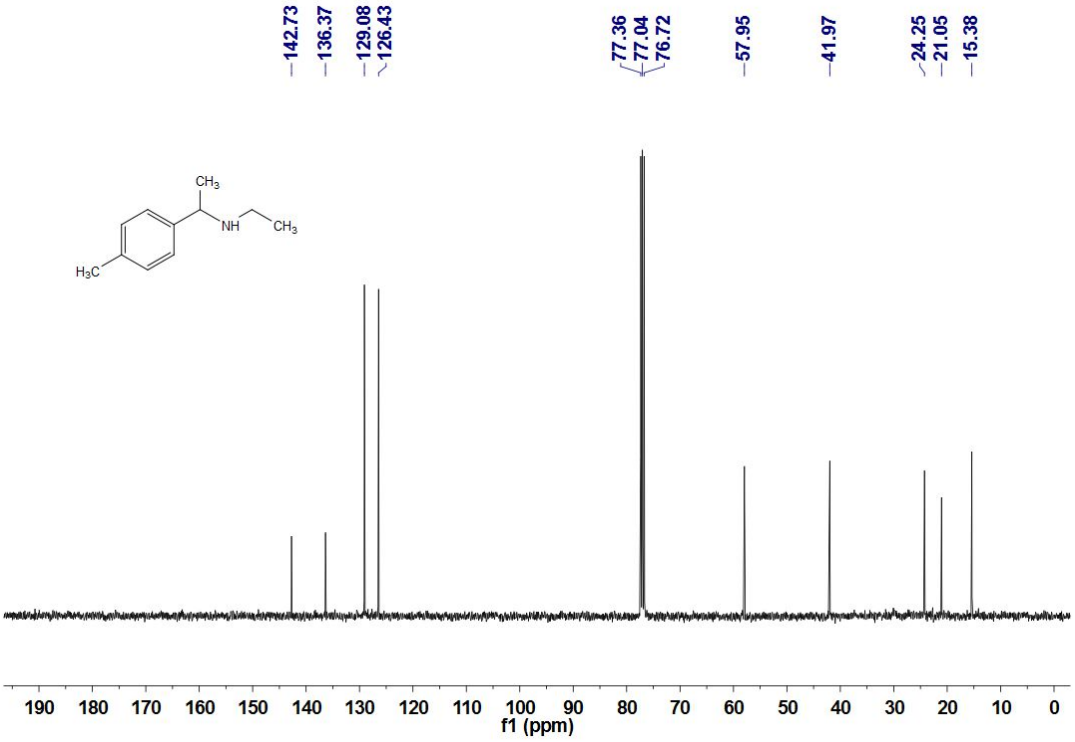

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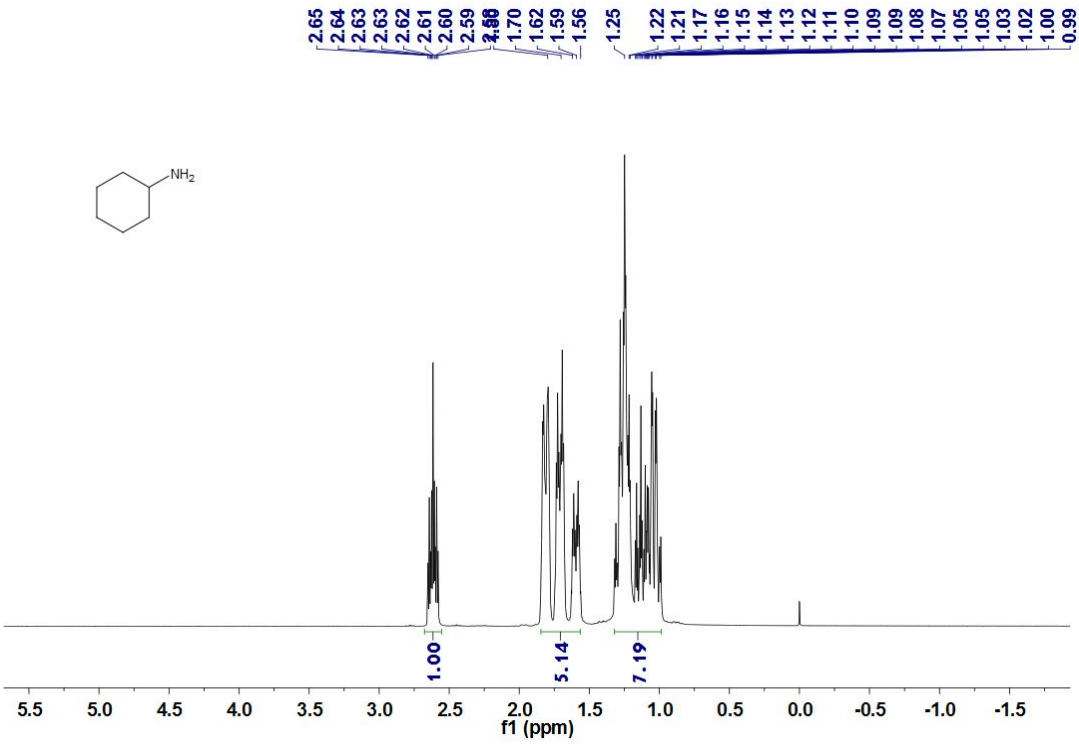
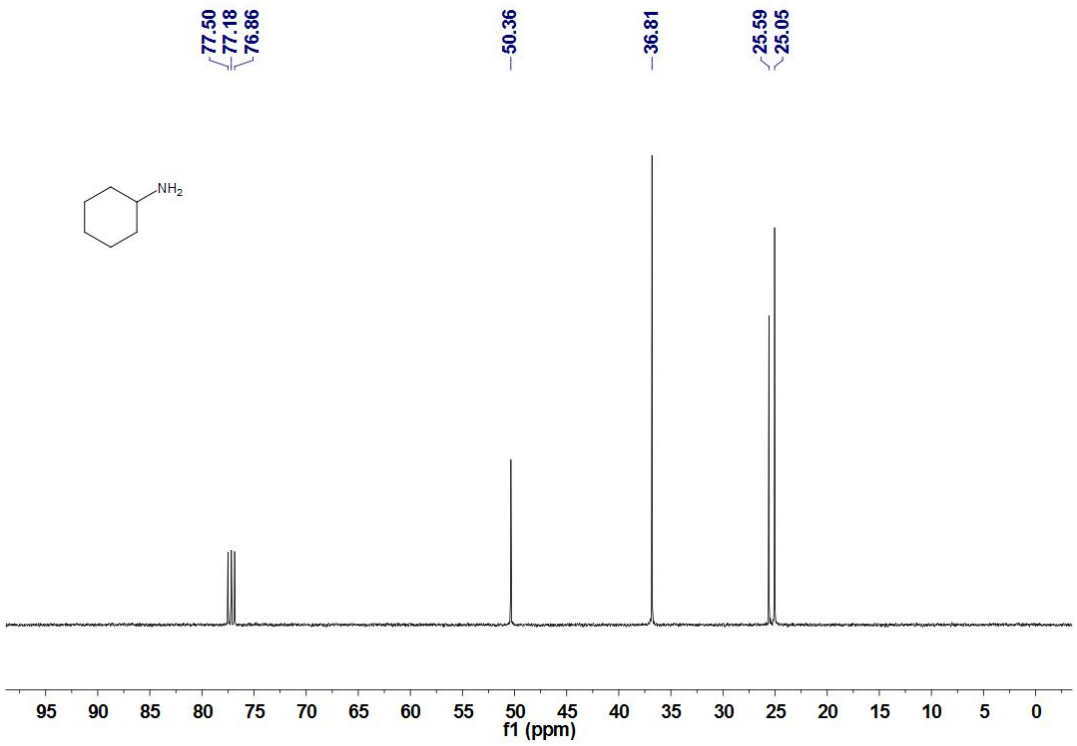


^{1}H NMR of cyclohexylamine



^{13}C NMR of cyclohexylamine

15. References

(1) Pouramiri, B.; Kermani, E. T. Efficient, Three-Component Synthesis of 1-Aryl-2,3-Dihydro-3-Phenyl-1H-Naphth[1,2-e][1,3]Oxazines Derivatives, Using $LaCl_3$/$ClCH_2COOH$ as an Environmentally Benign and Green Catalytic System. *Sci. Iran*. **2014**, 21, 703-707.

(2) Korotaev, V. Y; Sosnovskikh, V. Y.; Kutyashev, I. B.; Barkov, A. Y.; Matochkina, E. G.; Kodess, M. I. A Simple and Convenient Synthesis of 4-Methyl-3-Nitro-2-Trihalomethyl-2H-Chromenes from *N*-Unsubstituted Imines of 2-Hydroxyacetophenones and Trichloro(trifluoro)ethylidene Nitromethanes. *Tetrahedron*. **2008**, 64, 5055-5060, DOI: 10.1016/j.tet.2008.03.065.