Electronic Supplementary Information

Ionic Liquid/H_2O-Mediated Synthesis of Mesoporous Organic Polymers and Their Application in Methylation of Amines

Xiaoxiao Yu,+[a, b] Zhenzhen Yang,+[a] Hongye Zhang,[a] Bo Yu,[a] Yanfei Zhao,[a] Zhenghui Liu,[a, b] Guipeng Ji[a, b] and Zhimin Liu*[a, b]

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China.
E-mail: liuzm@iccas.ac.cn

Table of Contents

1. General experimental methods

Materials

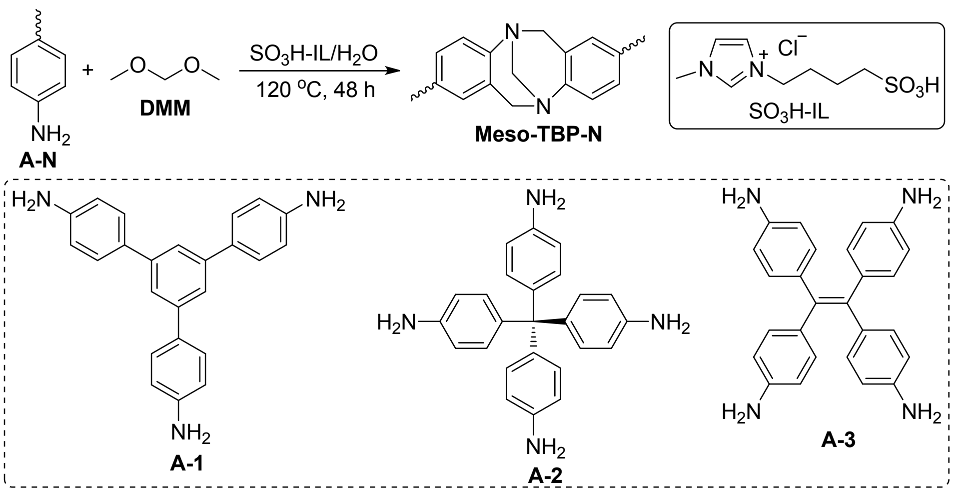
All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise. 1-butylsolfonate-3-methylimidazolium chloride was purchased from Lanzhou Greenchem ILS, LICP. CAS. China.

Instrumentation

Liquid ^{1}H and ^{13}C NMR spectra was recorded on Bruck 400 MHz NMR spectrometer. Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm^{-1}. Gas sorption isotherms were obtained with Micromeritics TriStar II 3020 and Micromeritics ASAP 2020 M+C accelerated surface area and porosimetry analyzers at certain temperature. The samples were outgassed at 140 ^{o}C for 8 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 15.0 kV. (HR) Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 and JEM-2011F instrument operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of ~3×10^{-9} mbar (1 mbar = 100 Pa) using Al Ka as the excitation source (1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the C_{1s} line at 284.8 eV from adventitious carbon. The XRD analysis was performed on a D/MAX-RC diffractometer operating at 30 kV and 100 mA with $Cu_{K\alpha}$ radiation. The reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a nonpolar capillary column (DB-5) (30 m × 0.25 mm × 0.25 μm). The column oven was temperature-programmed with a 2 min initial hold at 323 K, followed by the temperature increase to 538K at a rate of 20 K/min and kept at 538 K for 10 min. High purity nitrogen was used as a carrier gas.

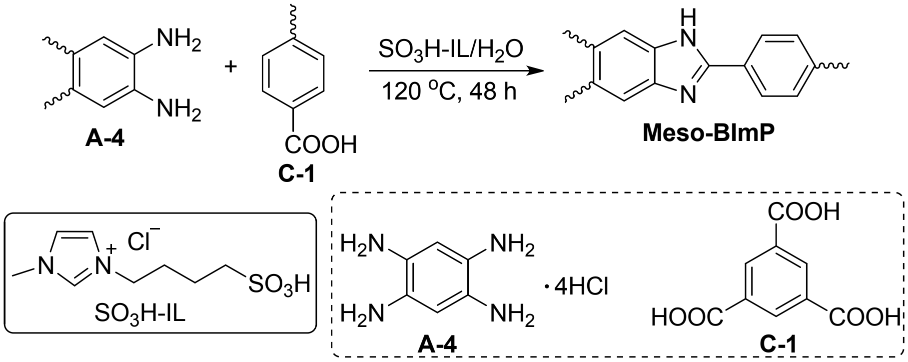
2. Synthetic procedures

(1) Synthetic procedure for Meso-TBP-N (N = 1~3)



SO_3H-IL (4 g), **A-N** (0.6 mmol), DMM (0.6 mL) and desired amount of H_2O were added successively to a 25 mL autoclave with a Teflon inner tube. The mixture was stirred at 25 °C for 2 h and then 120 °C for 48 h. After cooling to room temperature, the mixture was slowly poured into aqueous ammonium hydroxide solution (100 mL) and stirred vigorously for 2 h. The solid was collected by filtration and repeated another two times by washing with aqueous ammonium hydroxide solution (100 mL*2). The collected solid was then washed with distilled water, tetrahydrofuran (THF) and ethanol. After extracted in a Soxhlet extractor with methanol, H_2O and THF for 48 h, the desired polymer was collected and dried in vacuum oven at 140 °C for 24 h as brown solid. The yield was 81%, 79% and 83% for **Meso-TBP-1**, **Meso-TBP-2** and **Meso-TBP-3**, respectively.

(2) Synthetic procedure for Meso-BImP



SO_3H-IL (4 g), **A-4** (1 mmol), **C-1** (0.67 mmol) and H_2O (6 g) were added successively to a 25 mL autoclave with a Teflon inner tube. The mixture was stirred at 25 °C for 2 h and then 120 °C for 48 h. After cooling to room temperature, the mixture was slowly poured into aqueous ammonium hydroxide solution (100 mL) and stirred vigorously for 2 h. The solid was collected by filtration and repeated another two times by washing with aqueous ammonium hydroxide solution (100 mL*2). The collected solid was then washed with distilled water, tetrahydrofuran (THF) and ethanol. After extracted in a Soxhlet extractor with methanol, H_2O and THF for 48 h, the desired polymer was collected and dried in vacuum oven at 140 °C for 24 h as brown solid with 87% yield.

(3) Synthetic procedure for Meso-TBP-1@Ir

To a dichloromethane solution (10 mL) of **Meso-TBP-1** (0.15 g), iridium precursor-$[IrCp^*Cl_2]_2$ (0.10 g, 0.01 mmol) was added under N_2 atmosphere and refluxed for 24 h. Filtered the solid at room temperature, washed with dichloromethane (10*25 mL), extracted in a Soxhlet extractor with dichloromethane for 24 h, and dried under vacuum at 60 °C for 24 h.

(4) Typical procedure for the methylation of amines with MeOH catalyzed by Meso-TBP-1@Ir

To a stainless steel autoclave with a Teflon tube (25 mL inner volume), **Meso-TBP-1@Ir** (0.075 g), amine (1 mmol) and MeOH (4 mL) was added under air atmosphere successively. The autoclave was sealed and stirred at 110 °C for 24 h. After reaction, the autoclave was cooled down to room temperature. Product yields of **2a-2d**, and **2l-2n** were determined by GC using dodecane as an internal standard. Products **2e-2k** were isolated by column chromatography on silica gel using petroleum ether/ethyl acetate/ethanol/small amount of triethylamine as eluent and identified by NMR spectra. For catalyst (**Meso-TBP-1@Ir**) recycling, the catalyst was filtrated, washed with dichloromethane (10*25 mL) and then dried under vacuum at 60 °C for 24 h. The recycled catalyst was reused for the next run without further purification. For each recyclability test, three parallel experiments have been done, and the yield was taken the average.

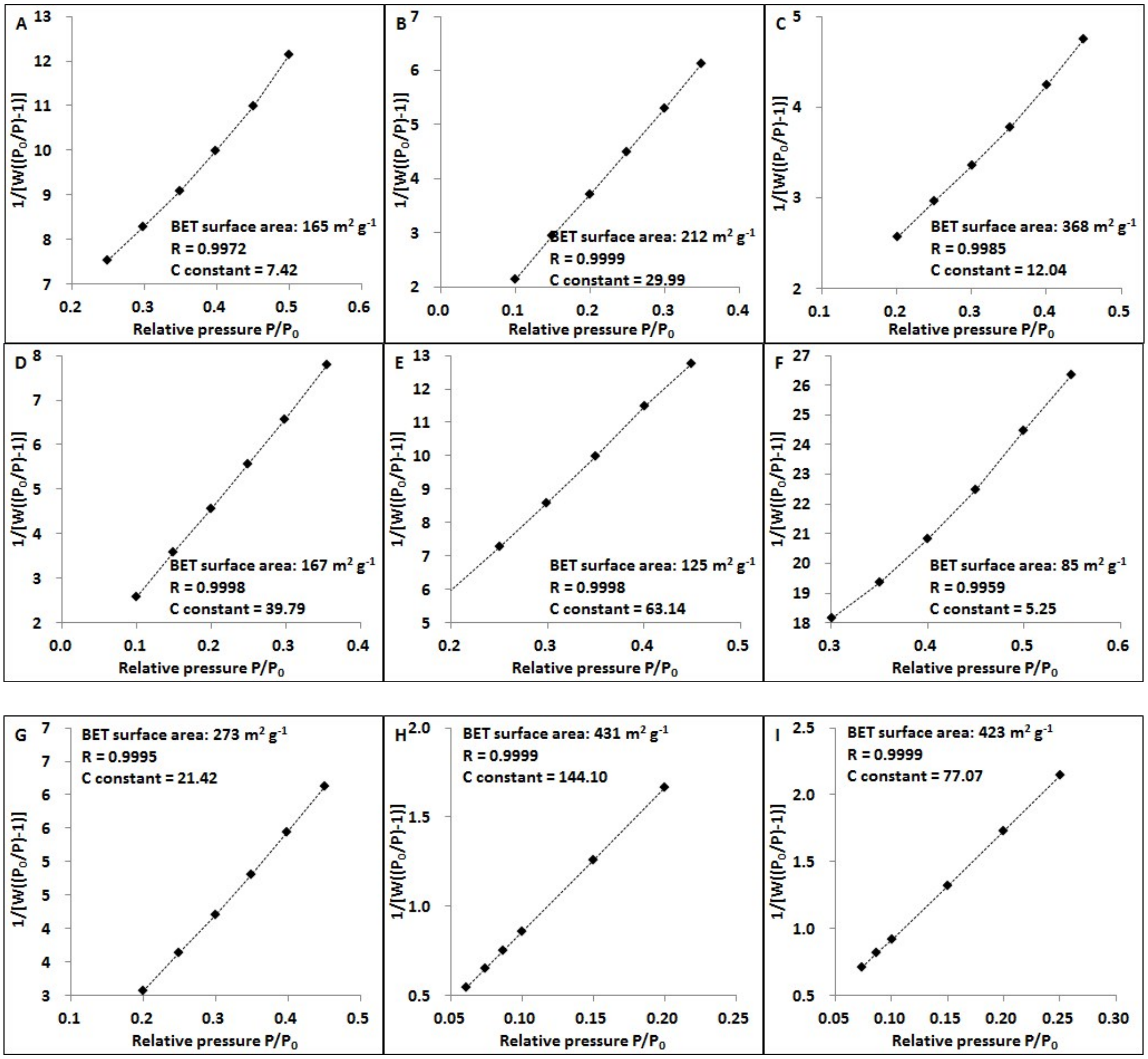


Figure S1 BET plot of **Meso-TBP-1-r** obtained in SO_3H-IL/H_2O mixture with a mass ratio of (A) 0.5, (B) 1.0, (C) 1.5, (D) 2.0, (E) 2.5 and (F) 3.0. (G) BET plot of **Meso-TBP-2**. (H) BET plot of **Meso-TBP-3**. (I) BET plot of **Meso-BImP**.

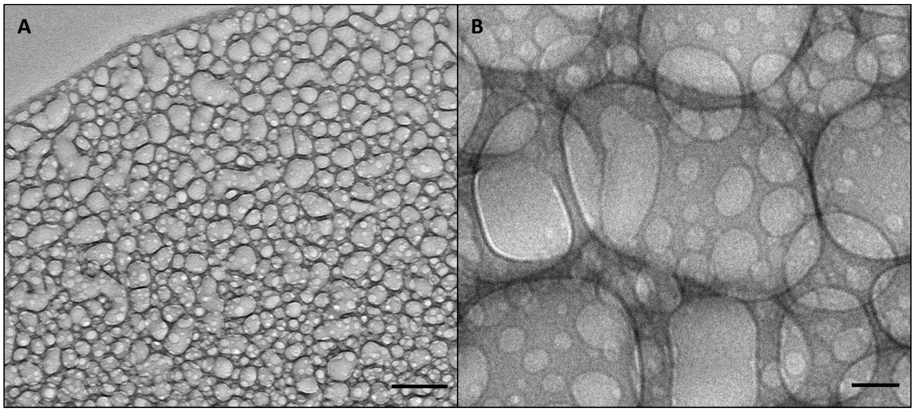


Figure S2 Cyro-TEM images of H_2O/SO_3H-IL mixture with a mass ratio of 1.5. Scale bars for A and B was 100 nm and 25 nm, respectively.

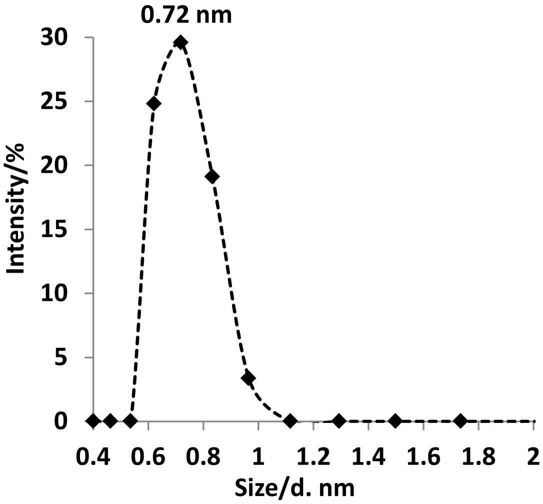


Figure S3 Hydrodynamic diameter distribution of the micelles in the mixture of H_2O/SO_3H-IL with mass ratio of 1.5, detected by the dynamic light scattering (DLS) method at room temperature.

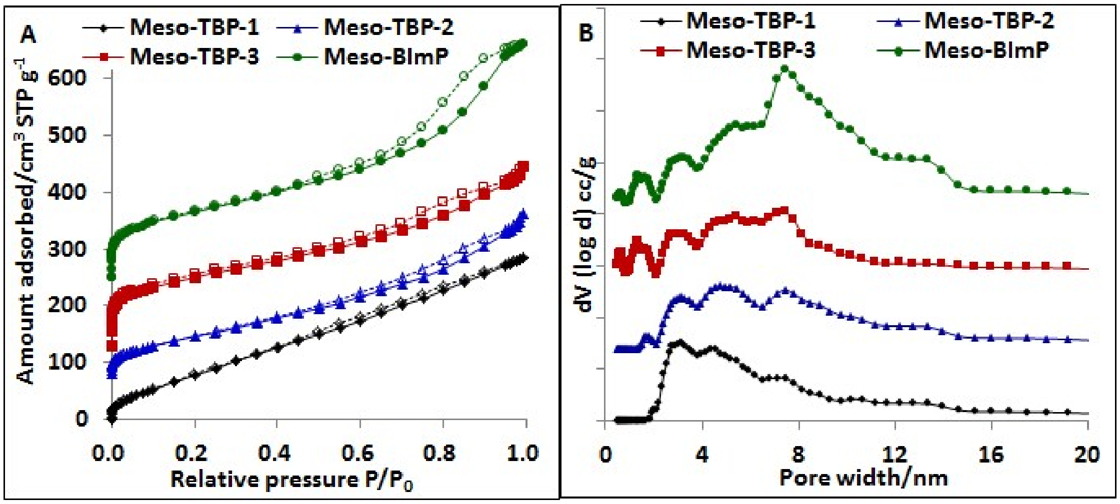


Figure S4 (A) Adsorption (filled) and desorption (empty) isotherms of N_2 at 77 k for **Meso-TBP-1/2/3** and **Meso-BImP** obtained in H_2O/SO_3H-IL with a mass ratio of 1.5. (B) Pore size distributions of **Meso-TBP-1/2/3** and **Meso-BImP** based on the calculation results of the NLDFT method.

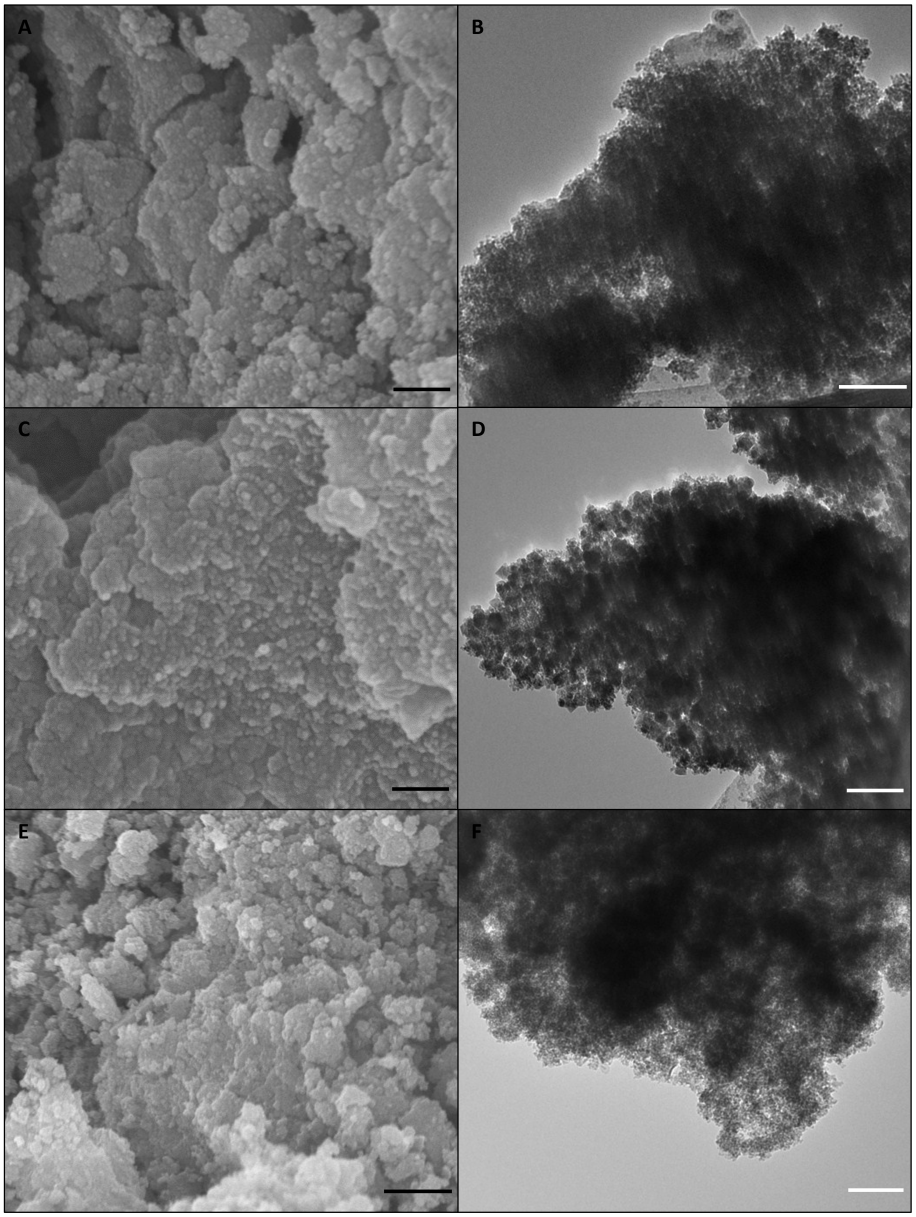


Figure S5 (A) SEM and (B) TEM image of **Meso-TBP-2**. (C) SEM and (D) TEM image of **Meso-TBP-3**. (E) SEM and (F) TEM image of **Meso-BImP**. Scale bar, (A) 125 nm, (B) 100 nm, (C) 125 nm, (D) 100 nm, (E) 500 nm, (F) 50 nm.

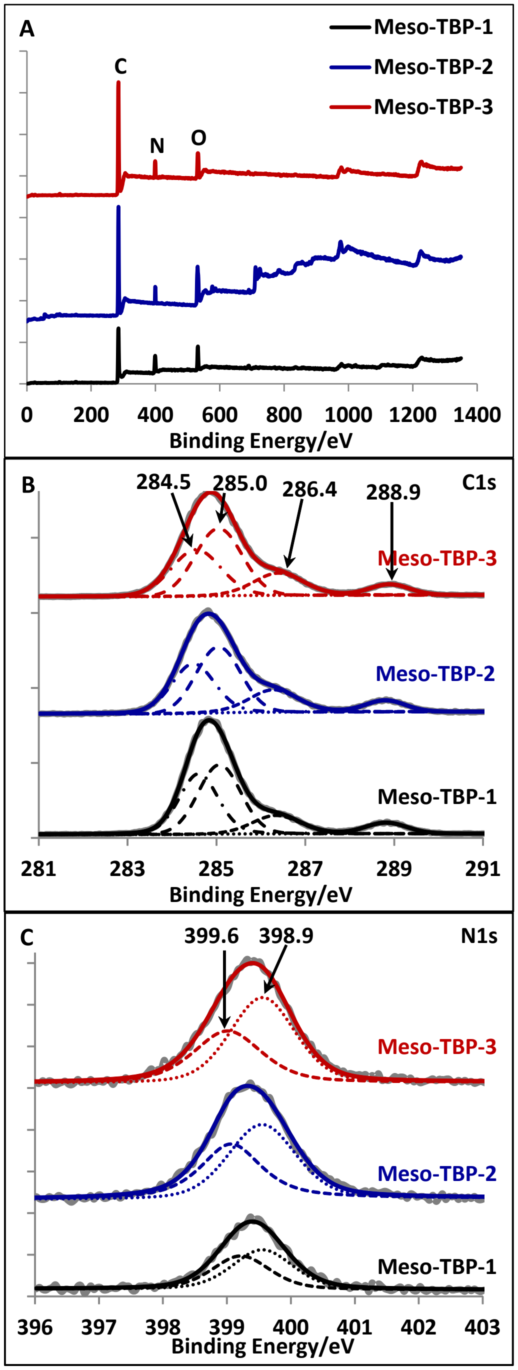


Figure S6 (A) XPS spectra with binding energy range of 0~1400 eV, (B) C1s and (C) N1s for **Meso-TBP-N** (N = 1, 2, 3).

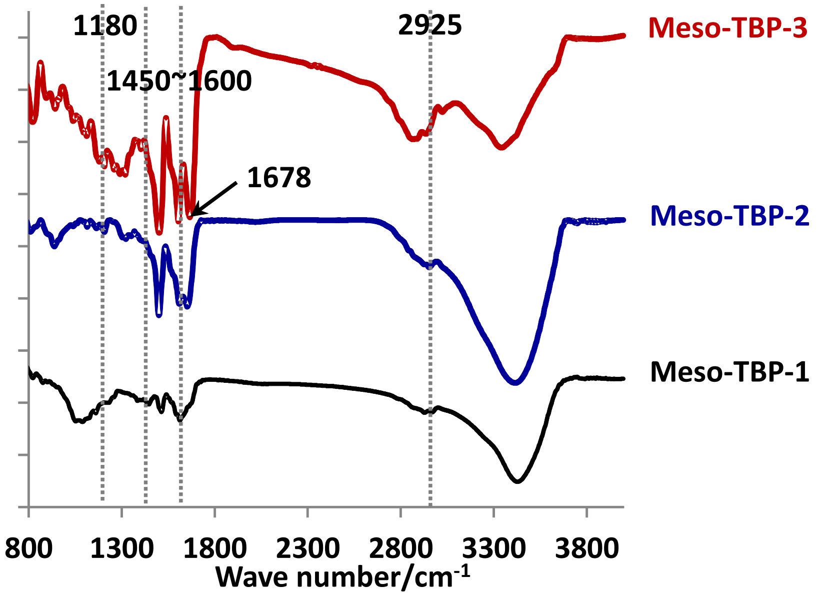


Figure S7 FTIR spectra of **Meso-TBP-N** (N = 1, 2, 3). The spectra were recorded as KBr pellets.

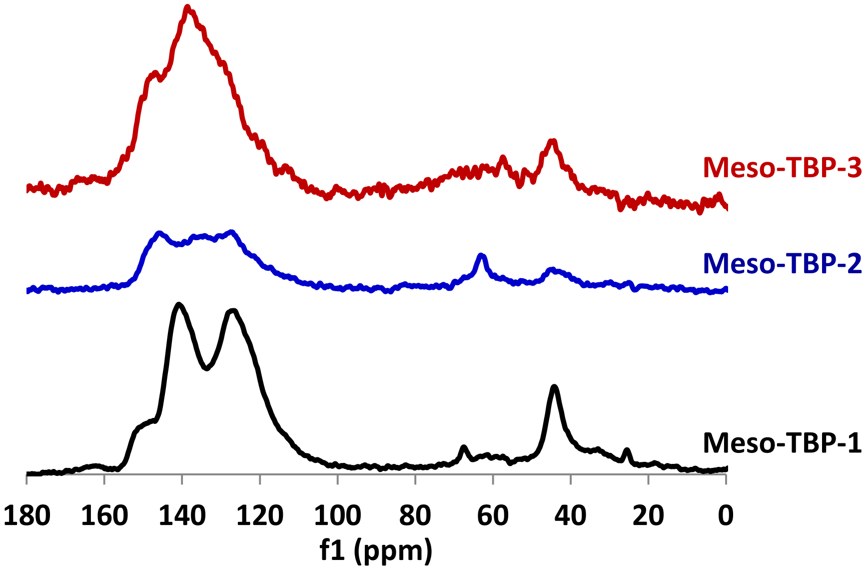


Figure S8 CP/MAS ^{13}C NMR spectra for **Meso-TBP-N** (N = 1, 2, 3).

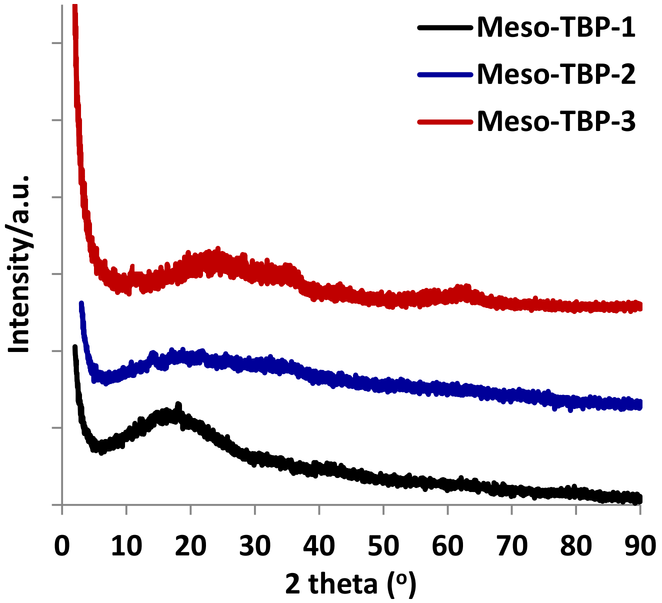


Figure S9 PXRD-pattern of for **Meso-TBP-N** (N = 1, 2, 3).

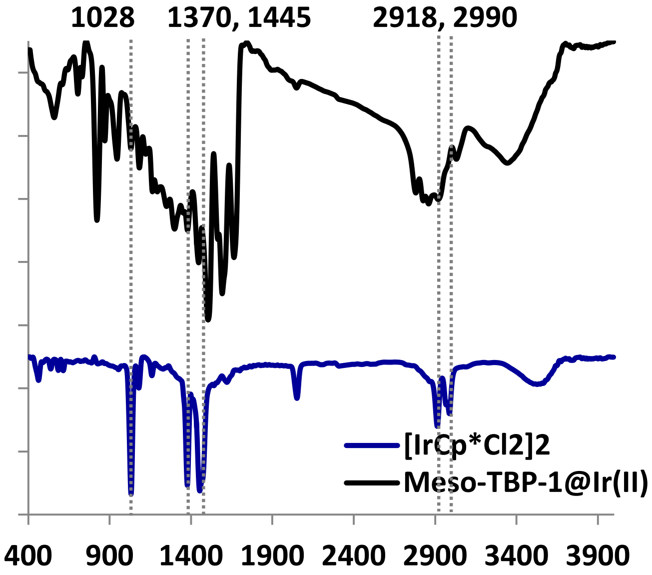


Figure S10 FTIR spectra of **Meso-TBP-1@Ir**. 1028 cm^{-1} (C=C), 1370, 1445 cm^{-1} (CH_3), 2918, 2990 cm^{-1} (C-H in CH_3).

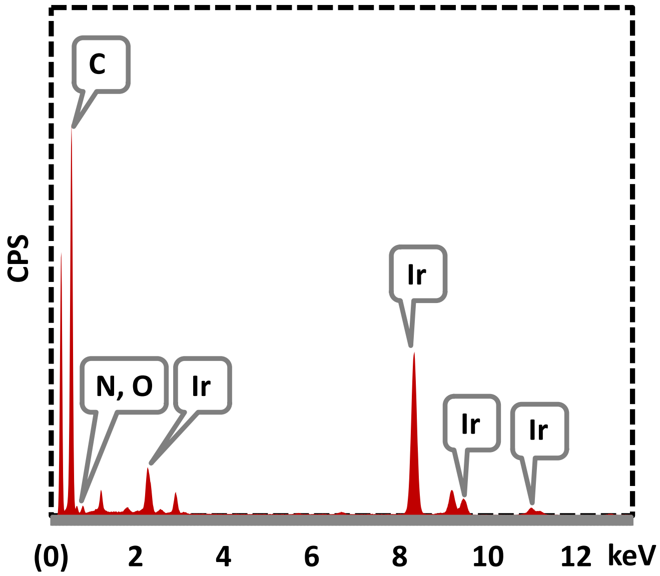


Figure S11 EDS profile of **Meso-TBP-1@Ir^{II}**.

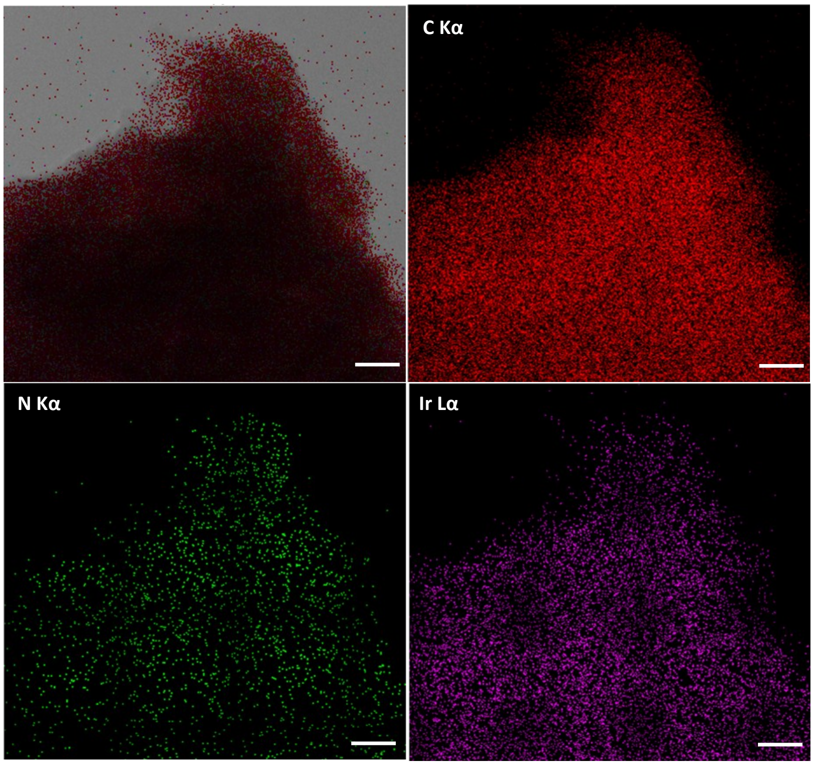


Figure S12 Compositional EDS mapping of **Meso-TBP-1@Ir^{II}** using scanning transmission electron microscopy. Scale bar 50 nm.

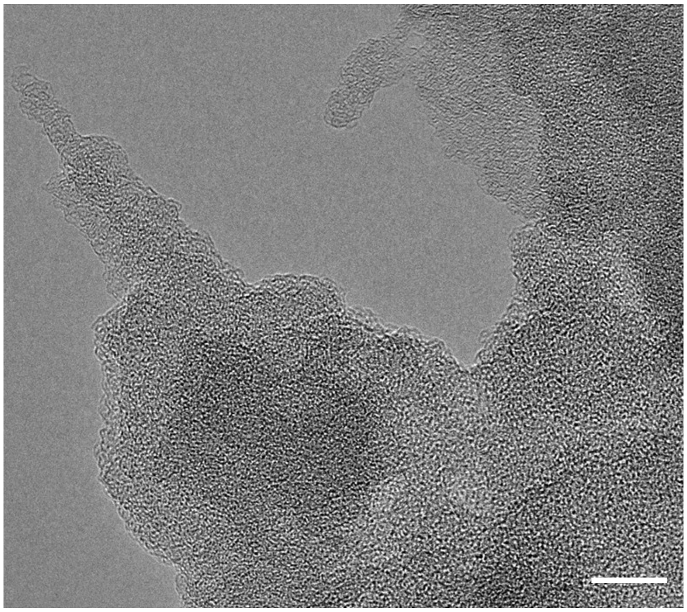


Figure S13 (HR)TEM image of **Meso-TBP-1@Ir^{II}**. Scale bar 10 nm.

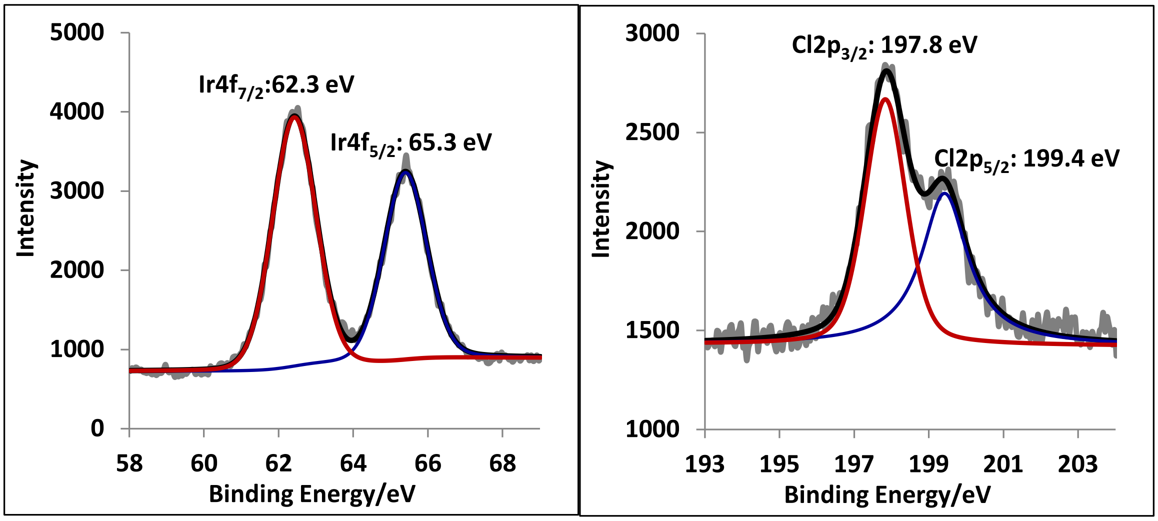
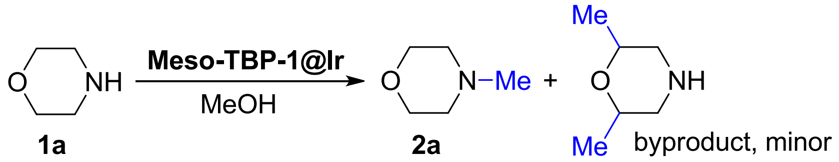


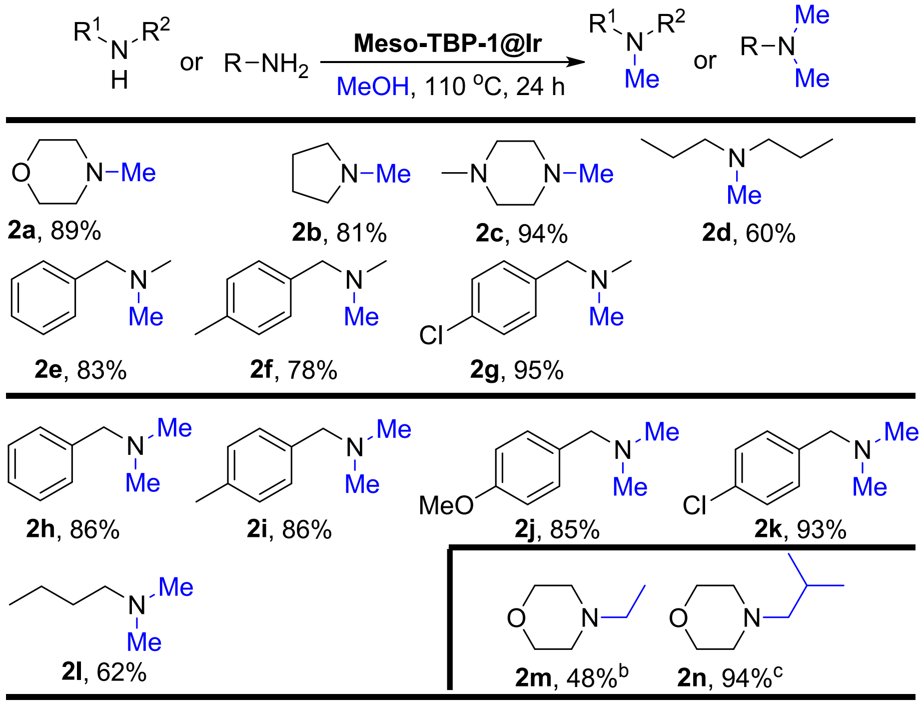
Figure S14 XPS spectra of Ir and Cl in **Meso-TBP-1@Ir**.

Table S1 Methylation of morpholine with methanol catalyzed by **Meso-TBP-1@Ir**.[a]

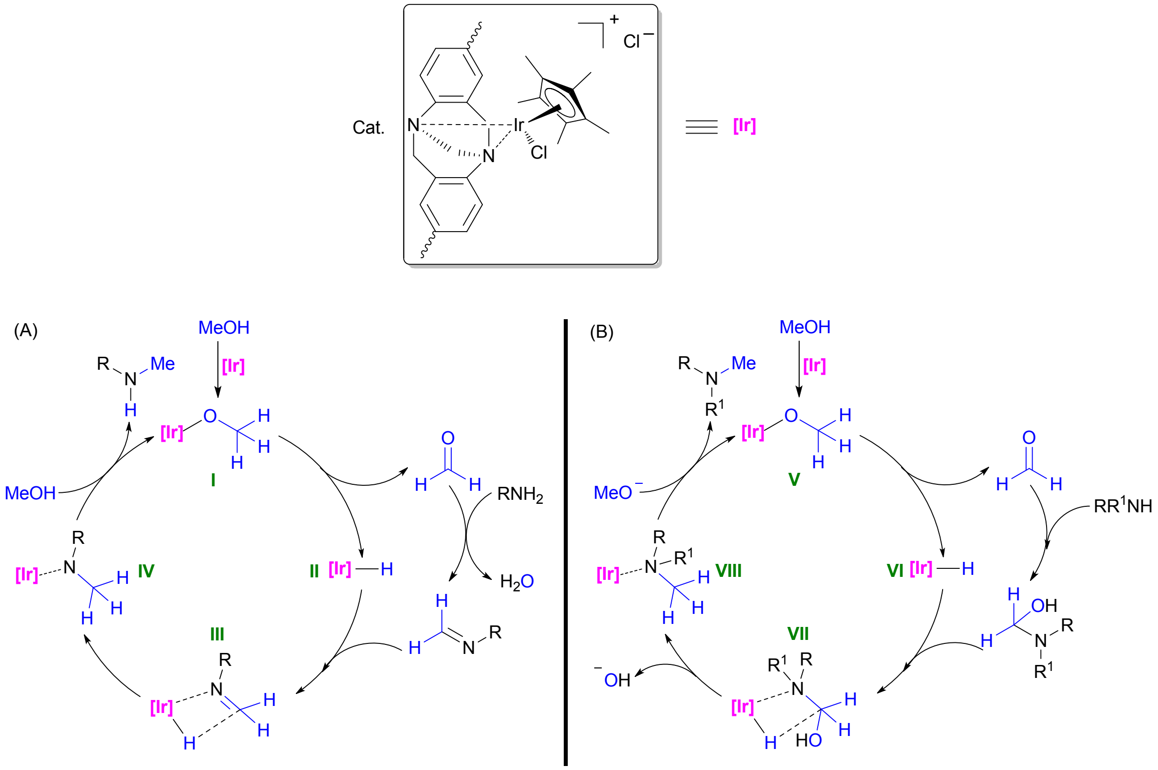


Entry	MeOH/mL	Temperature/°C	Cat. loading/mol%	Time/h	Conv./%[b]	Yield/%[b]
1	4	140	No	24	<1	<1
2	2	140	3	24	83	79
3	3	140	3	24	90	85
4	4	140	3	24	93	89
5	4	120	3	24	93	88
6	4	110	3	24	97	89
7	4	100	3	24	80	75
8	4	80	3	24	49	46
9	4	60	3	24	37	30
10	4	110	4	24	97	90
11	4	110	2	24	75	61
12	4	110	3	48	>99	90
13	4	110	3	12	88	80
14	4	110	3	6	79	69

[a] Reaction conditions: Morpholine (**1a**) 1 mmol, **Meso-TBP-1@Ir** 0.075 g (3 mol% Ir based on **1a**).
[b] Determined by GC using dodecane as an internal standard.



Scheme S1 Methylation of amines with methanol. a Reaction conditions: amine 1 mmol, **Meso-TBP-1@Ir** 3 mol%, MeOH (unless otherwise stated) 4 mL, 110 °C, 24 h. b Ethanol and c Isobutanol was added in stand of MeOH. The yields of **2a-2d**, and **2l-2n** were determined by GC using dodecane as the internal standard. The yields of **2e-2k** were isolated yields.



Scheme S2 Possible reaction mechanism for the **Meso-TBP-1@Ir** catalyzed methylation of amines with methanol. (A) Primary amines as substrate; (B) Secondary amines as sbustrate. Taking primary amines as an example, firstly, a Ir-methoxy complex (**I**) is formed in the presence of supported Ir complex and methanol, which then transforms into Ir-hydride (**II**) intermediate through β-hydride abstraction, releasing formaldehyde. The reaction of formaldehyde with the amine produces imine, which further coordinates with Ir-hydride (**II**) and forms intermediate III. Hydrogen transfer within **III** leads to formation of the Ir-methylamine complex (**IV**), which releases the methyl amine product through re-coordination of Ir complex with methoxide.

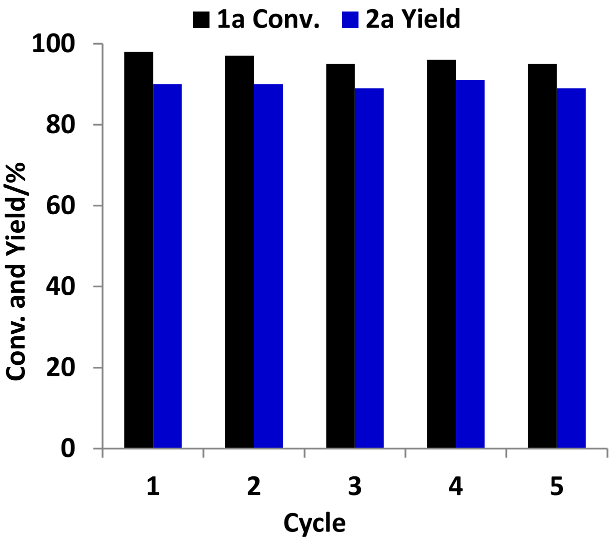


Figure S15 Recyclability test of **Meso-TBP-1@Ir**. Reaction conditions: Morpholine 1 mmol,

Meso-TBP-1@Ir 3 mol%, MeOH 4 mL, 110 ºC, 24 h. Conversion and yield were determined by GC using dodecane as an internal standard. Three parallel experiments were conducted for each cycle and the average results were given.

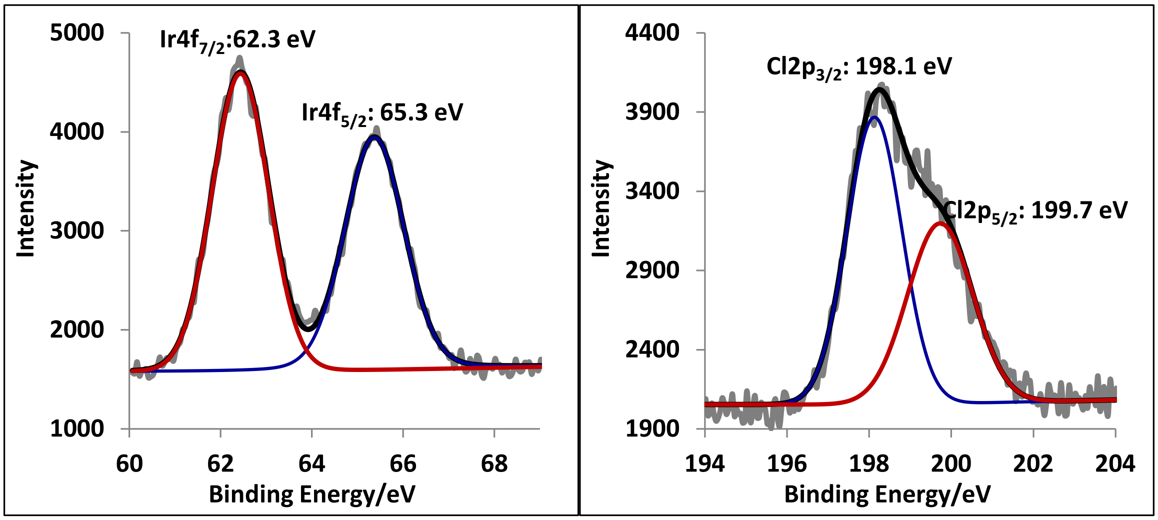
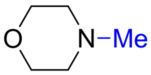


Figure S16 XPS spectra of Ir and Cl in recycled **Meso-TBP-1@Ir** after being reused for five times.

3. Determination of the product yields

For product **2a-2d** and **2m-2o**, the structures of the products were characterized by comparing the retention time with the authentic compound and GC-MS. The yields of the products for each reaction were determined by GC using dodecane as the internal standard and calculated through the calibartion curves as shown below. For **2e-2l**, isolated yields were given. The products were isolated by column chromatography on silica gel using petroleum ether/ethyl acetate/ethanol/small amount of triethylamine as eluent and identified by NMR spectra.



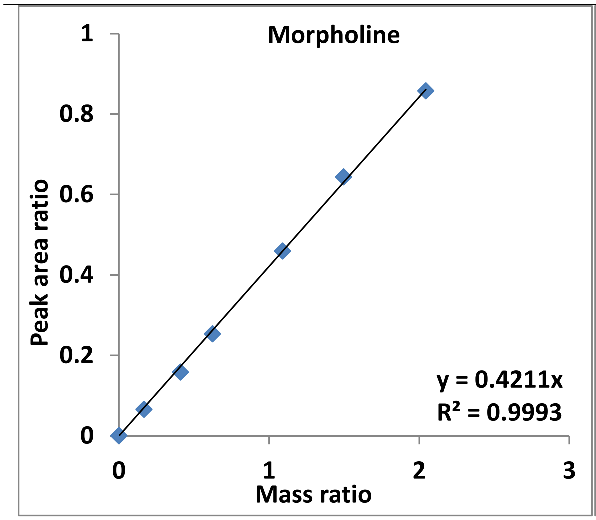
2a

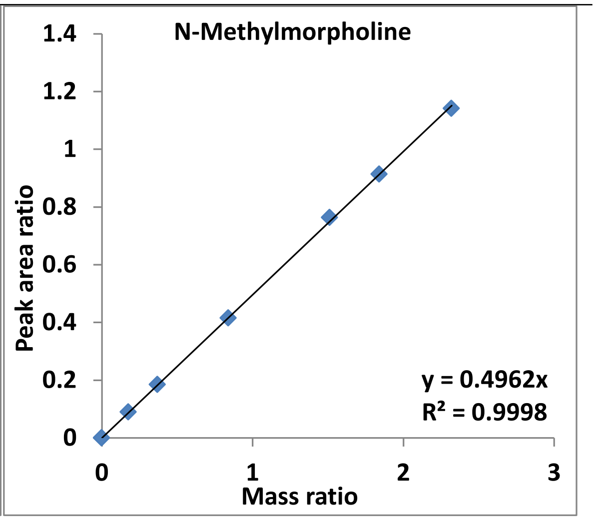
Calibration Curve

Standard Solution	Morpholine/g	dodecane/g
1	0.1063	0.052
2	0.0808	0.054
3	0.0574	0.0526
4	0.0357	0.0572
5	0.0215	0.0525
6	0.0089	0.0528

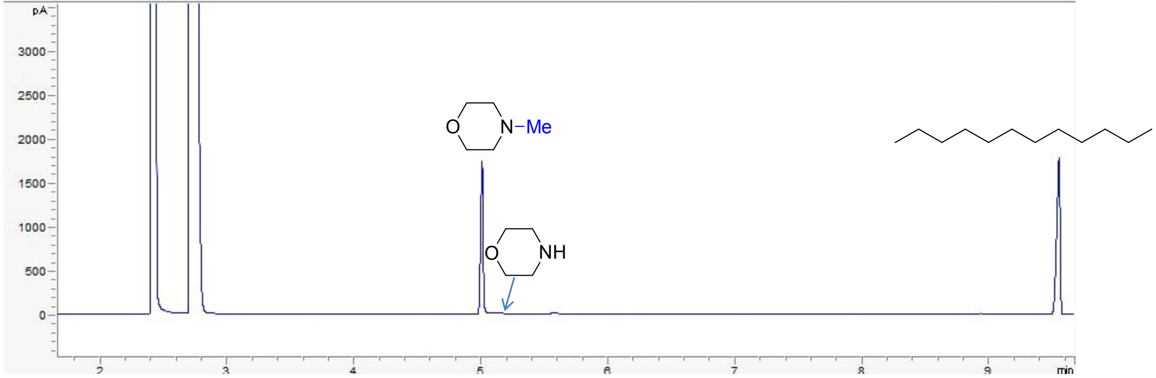
Standard Solution	N-Methylmorpholine/g	dodecane/g
1	0.0094	0.0532
2	0.0192	0.052
3	0.0452	0.0538

4	0.0795	0.0526
5	0.1053	0.0572
6	0.1218	0.0525

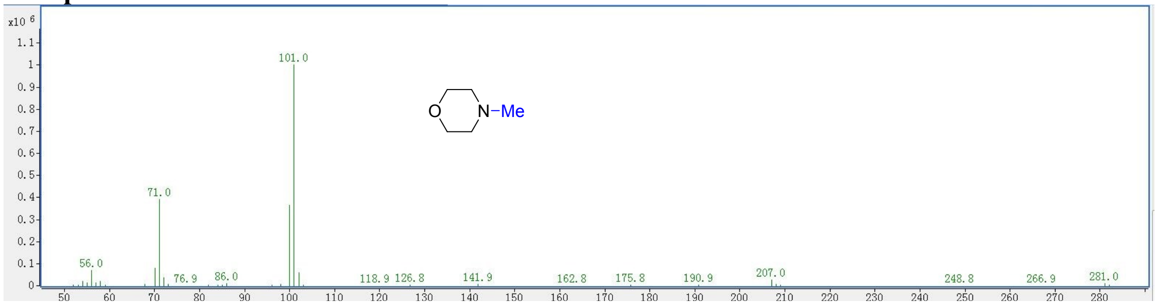


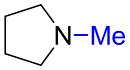


GC spectra



MS spectra



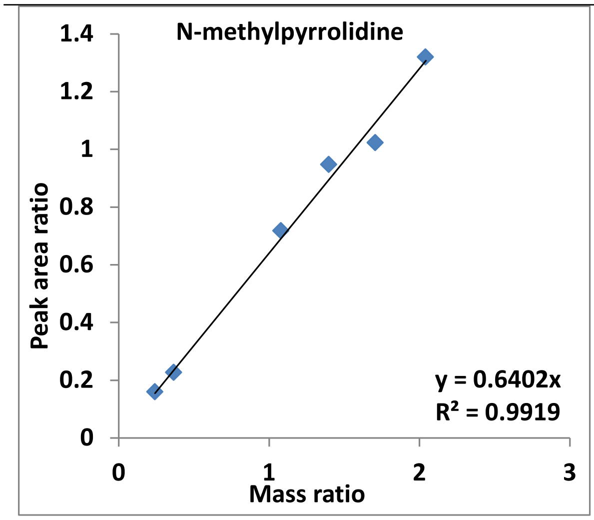


2b

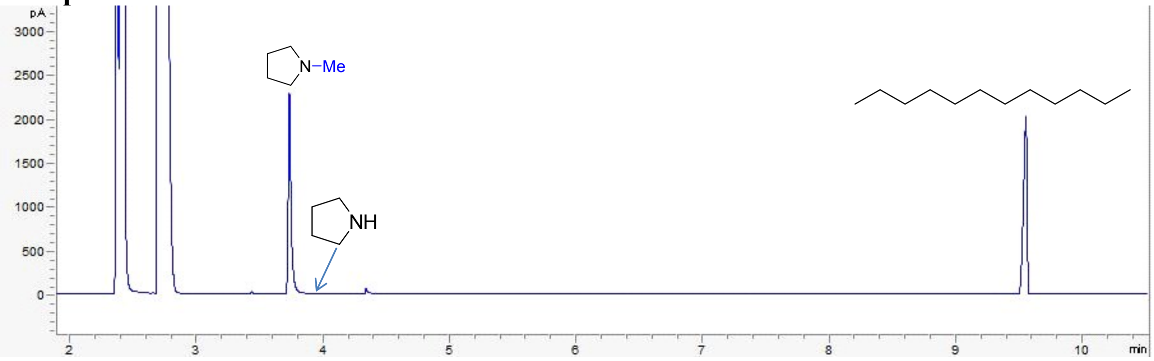
Calibration Curve

Standard Solution	N-methylpyrrolidine/g	dodecane/g
1	0.0114	0.0472
2	0.016	0.0435

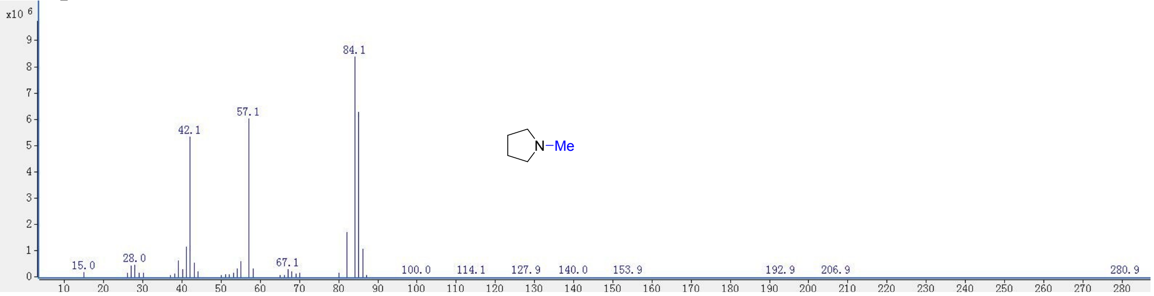
3	0.0535	0.0495
4	0.0689	0.0493
5	0.0874	0.0512
6	0.1009	0.0494

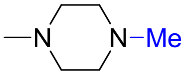


GC spectra



MS spectra



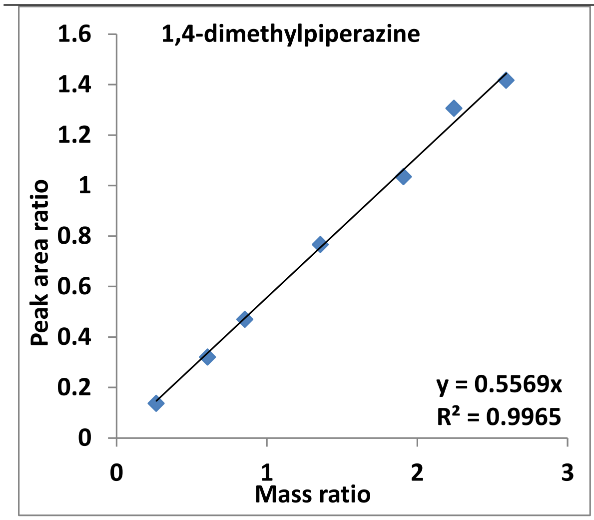


2c

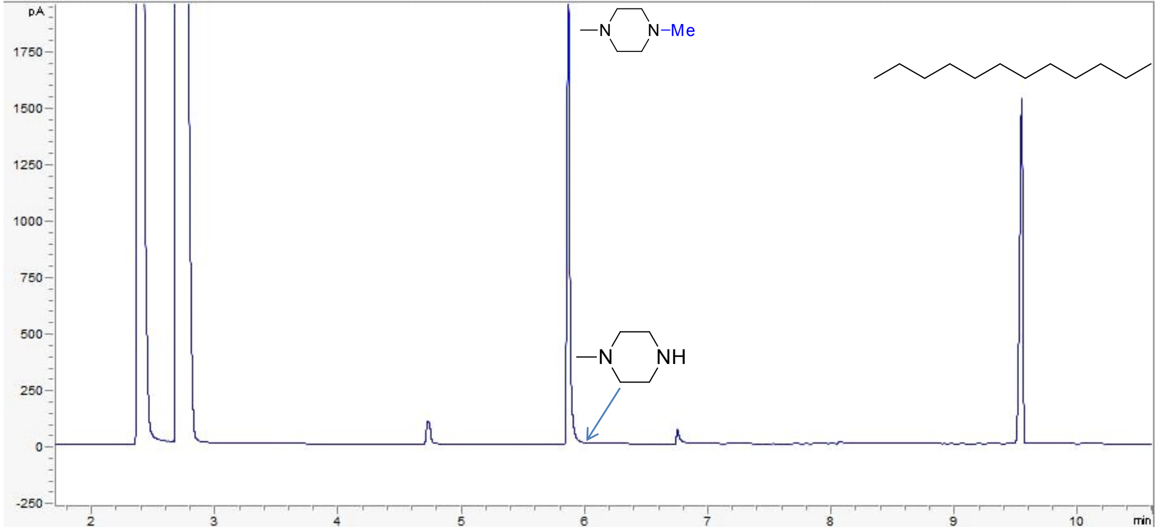
Calibration Curve

Standard Solution	1,4-dimethylpiperazine/g	dodecane/g
1	0.0131	0.0495
2	0.0306	0.0506

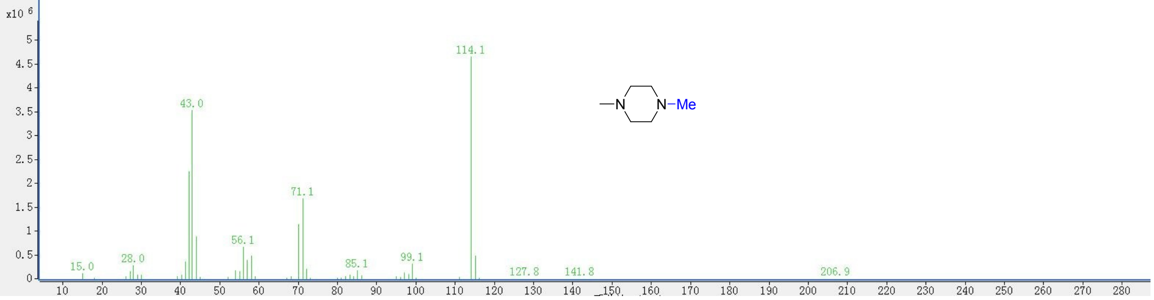
3	0.0429	0.0502
4	0.0692	0.051
5	0.0924	0.0484
6	0.1124	0.0501
7	0.1314	0.0507

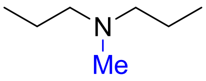


GC spectra



MS spectra

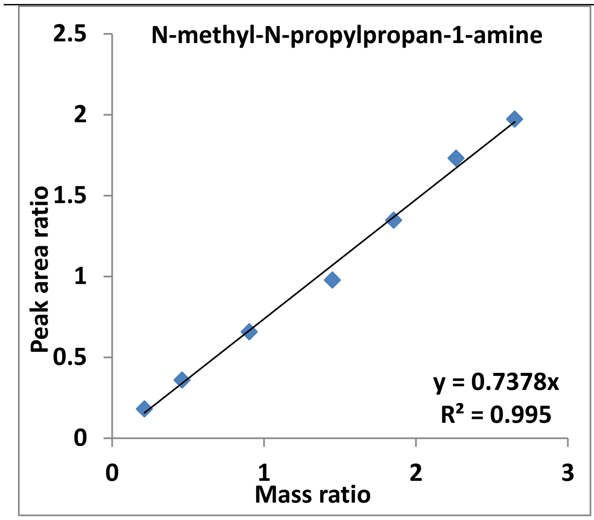




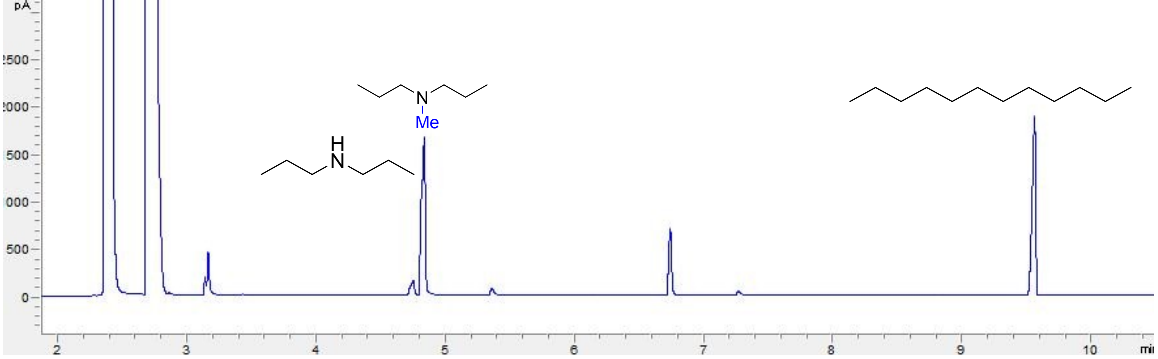
2d

Calibration Curve

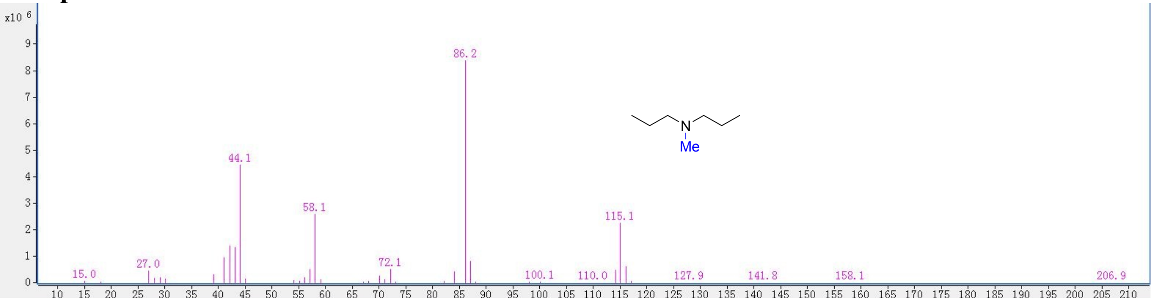
Standard Solution	N-methyl-N-propylpropan-1-amine/g	dodecane/g
1	0.0109	0.0512
2	0.023	0.05
3	0.0445	0.0493
4	0.0718	0.0495
5	0.0932	0.0503
6	0.1157	0.0511
7	0.1328	0.0501

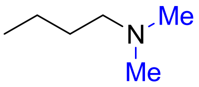


GC spectra



MS spectra

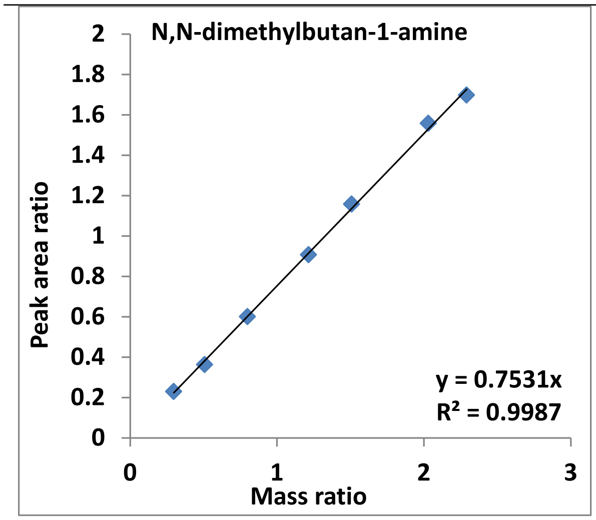




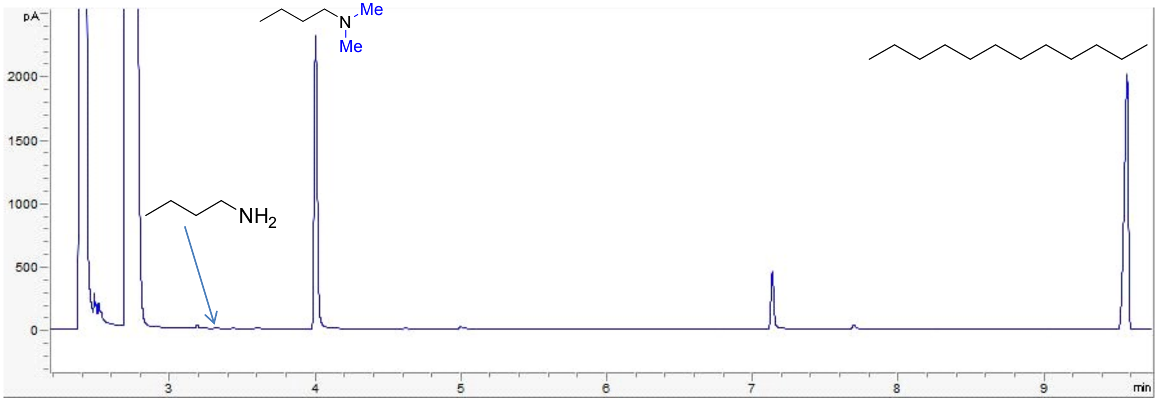
2l

Calibration Curve

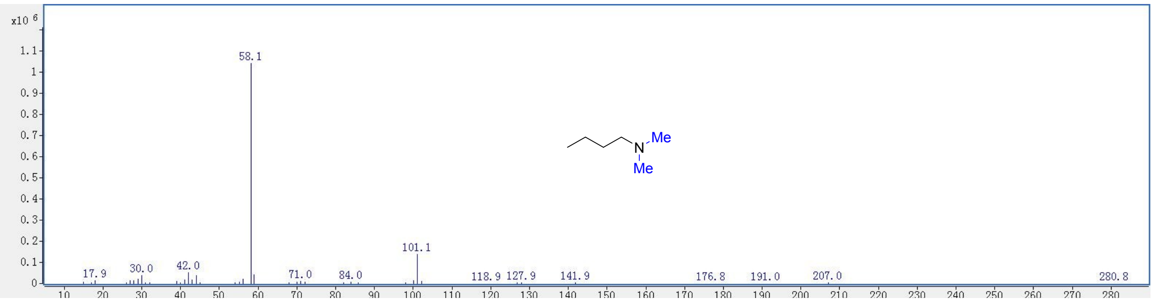
Standard Solution	N,N-dimethylbutan-1-amine/g	dodecane/g
1	0.0152	0.0511
2	0.0267	0.0524
3	0.0407	0.0508
4	0.0653	0.0537
5	0.0802	0.0531
6	0.102	0.0502
7	0.121	0.0528

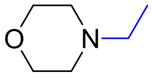


GC spectra



MS spectra

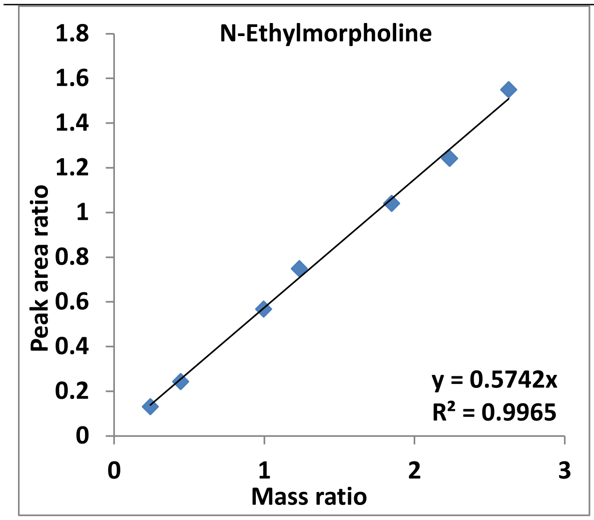




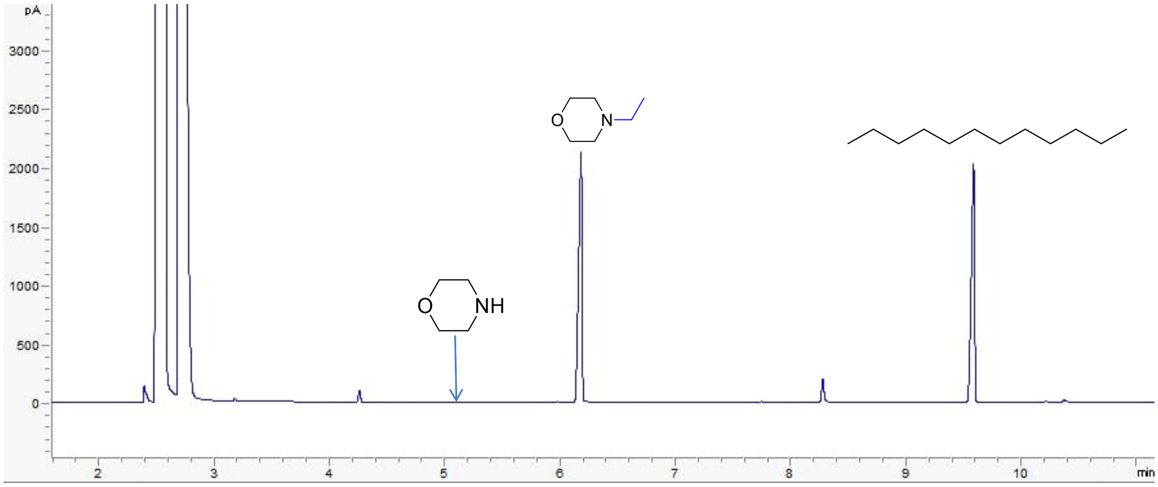
2m

Calibration Curve

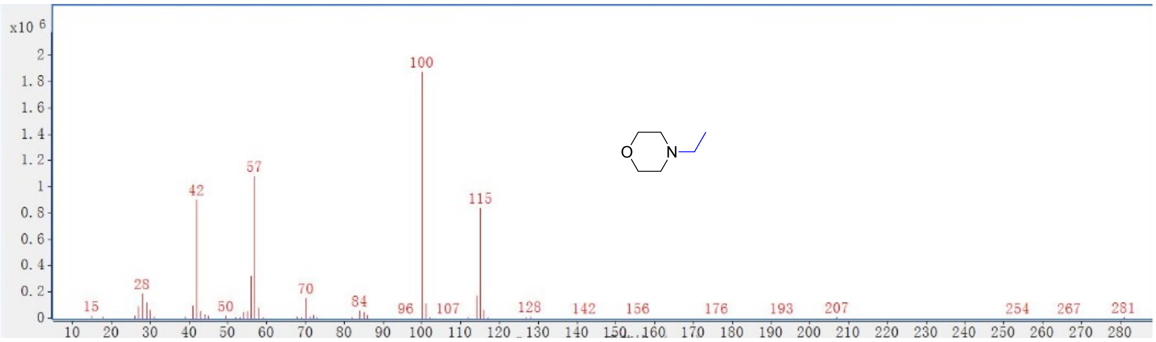
Standard Solution	N-Ethylmorpholine/g	dodecane/g
1	0.1332	0.0507
2	0.12	0.0537
3	0.0959	0.0519
4	0.0664	0.0538
5	0.0513	0.0515
6	0.0228	0.0515
7	0.0134	0.0557

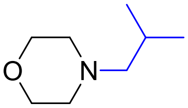


GC spectra



MS spectra

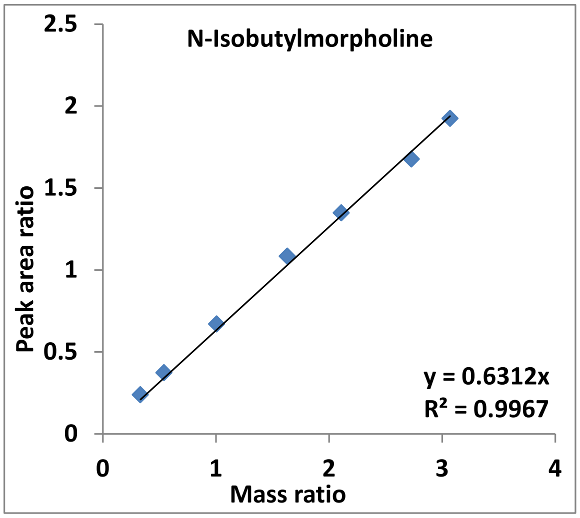




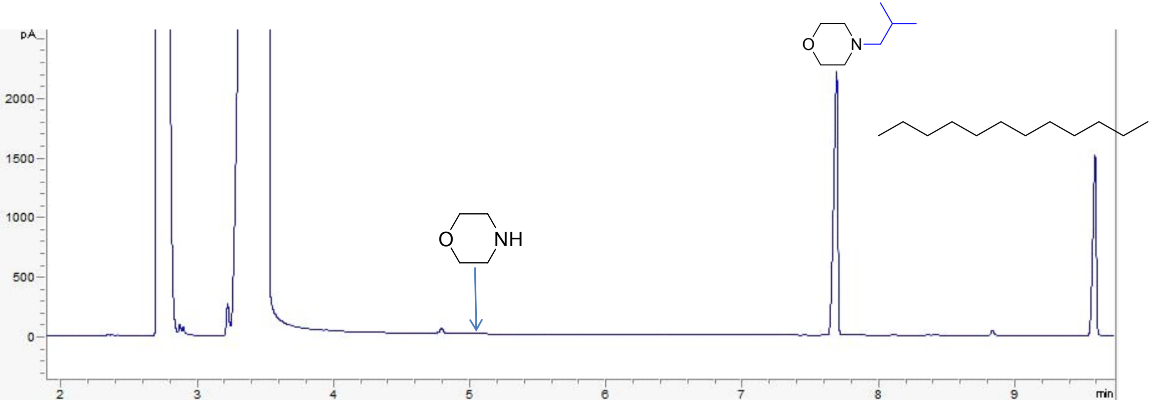
2n

Calibration Curve

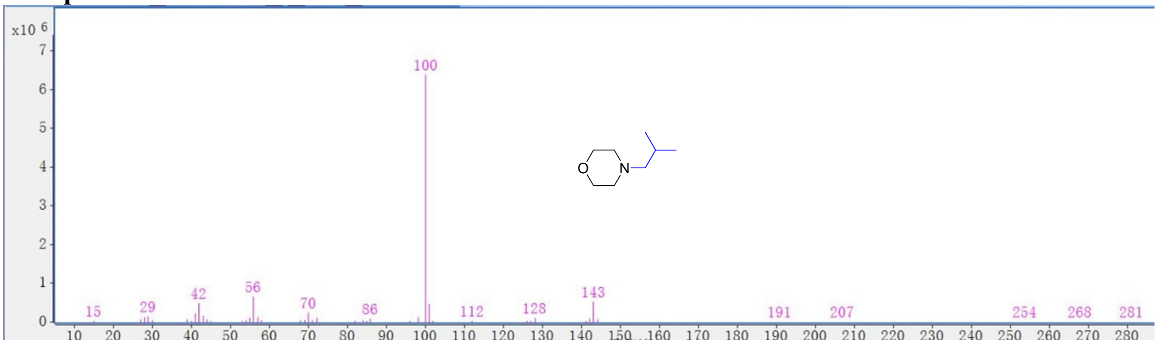
Standard Solution	N-Isobutylmorpholine/g	dodecane/g
1	0.0169	0.0507
2	0.029	0.0537
3	0.0523	0.0519
4	0.0878	0.0538
5	0.1086	0.0515
6	0.1405	0.0515
7	0.171	0.0557

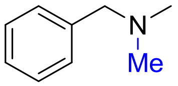


GC spectra



MS spectra

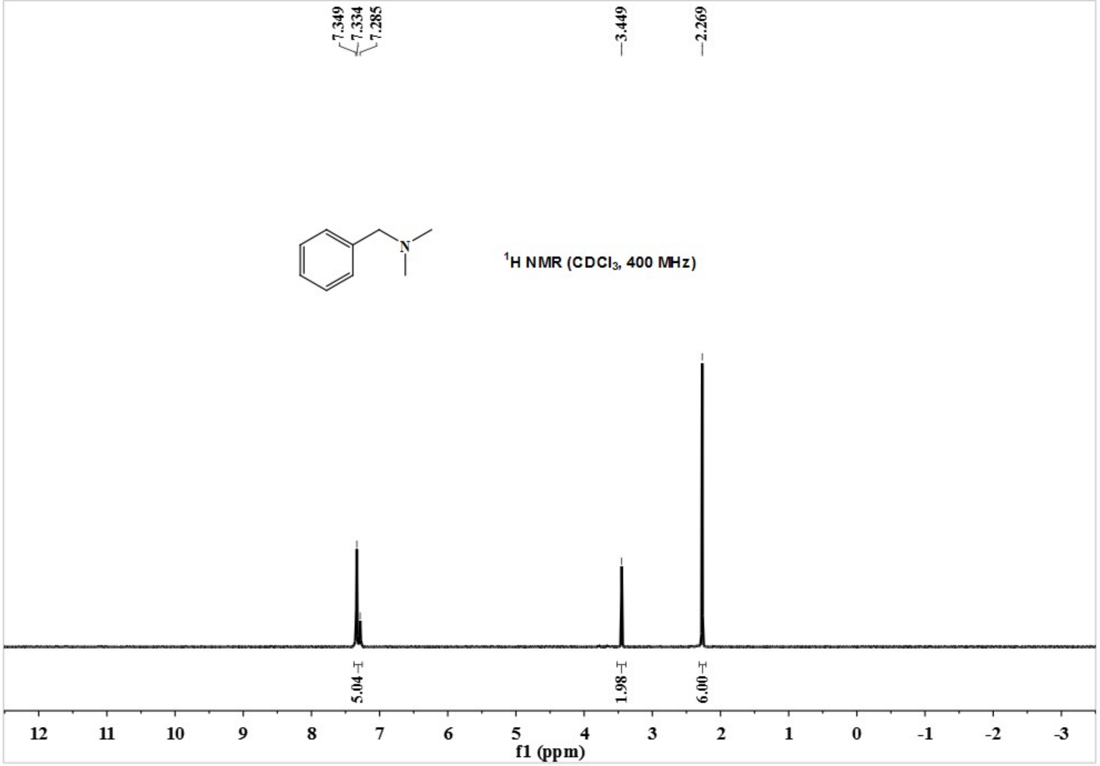


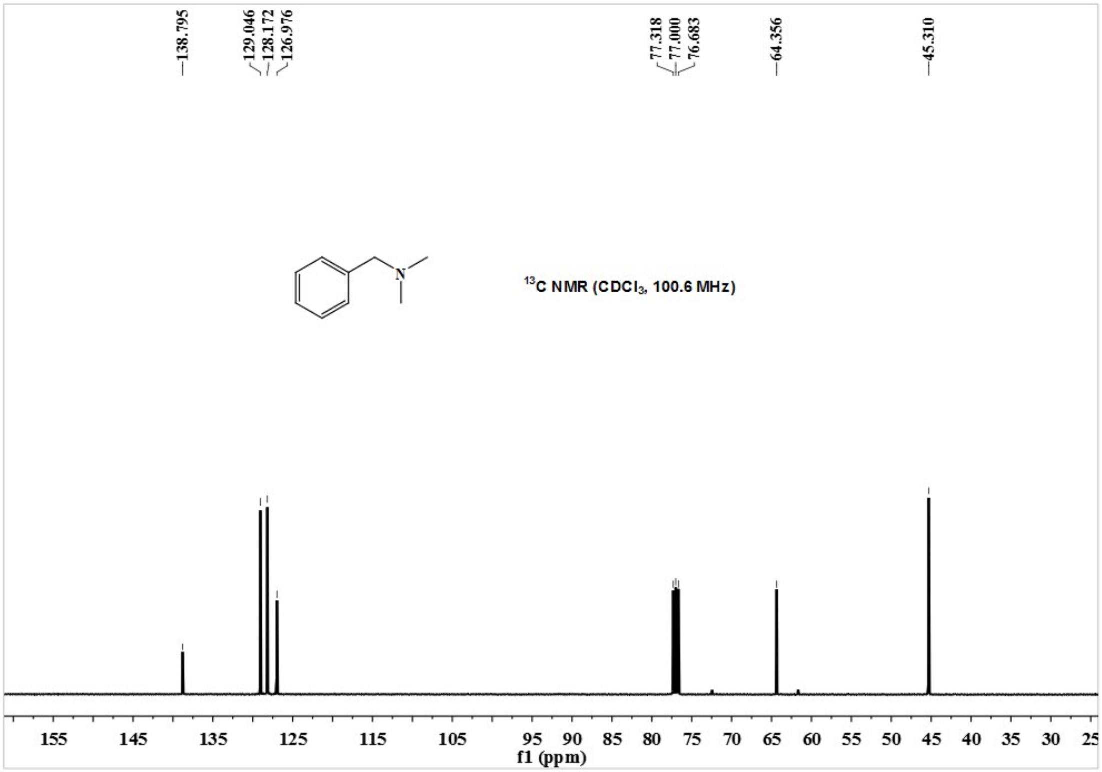


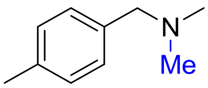
and

2e **2h**

^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.27 (s, 6H), 3.45 (s, 2H), 7.29-7.35 (m, 5H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 45.31, 64.36, 126.98, 128.17, 129.05, 138.80.

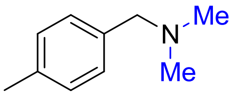

^{1}H NMR (CDCl$_3$, 400 MHz)


^{13}C NMR (CDCl$_3$, 100.6 MHz)



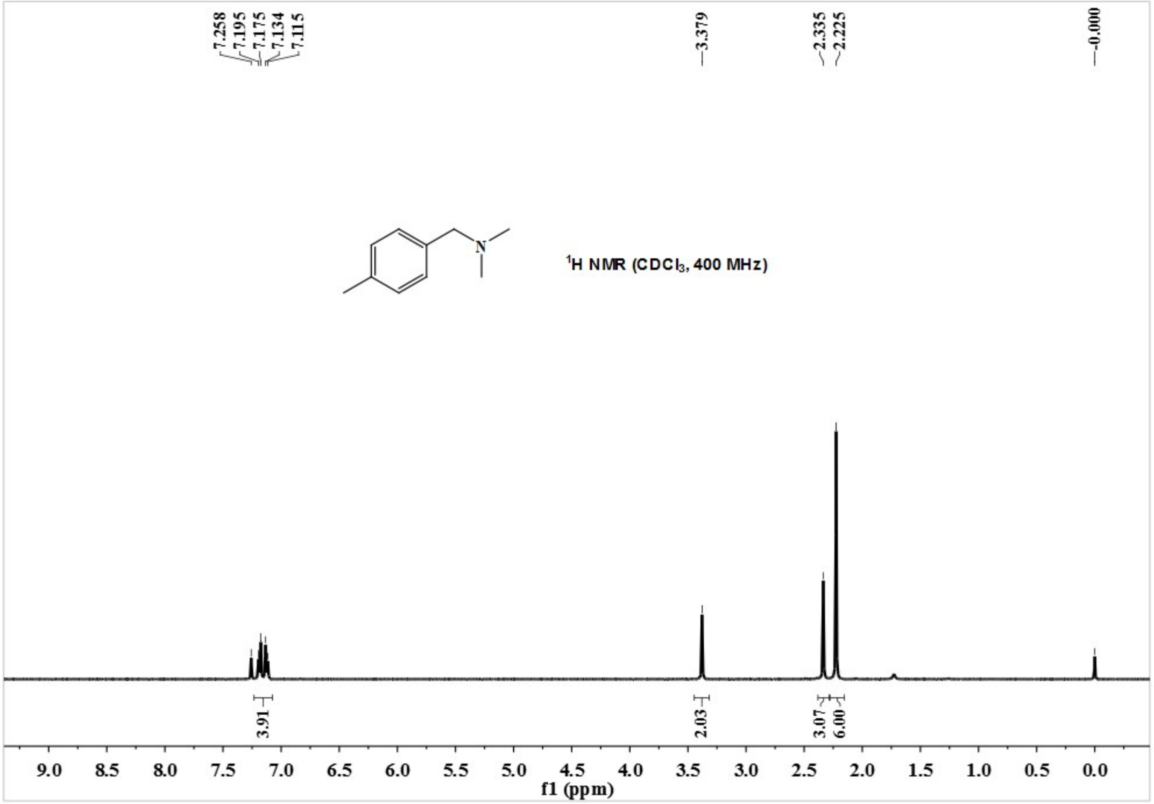
2f

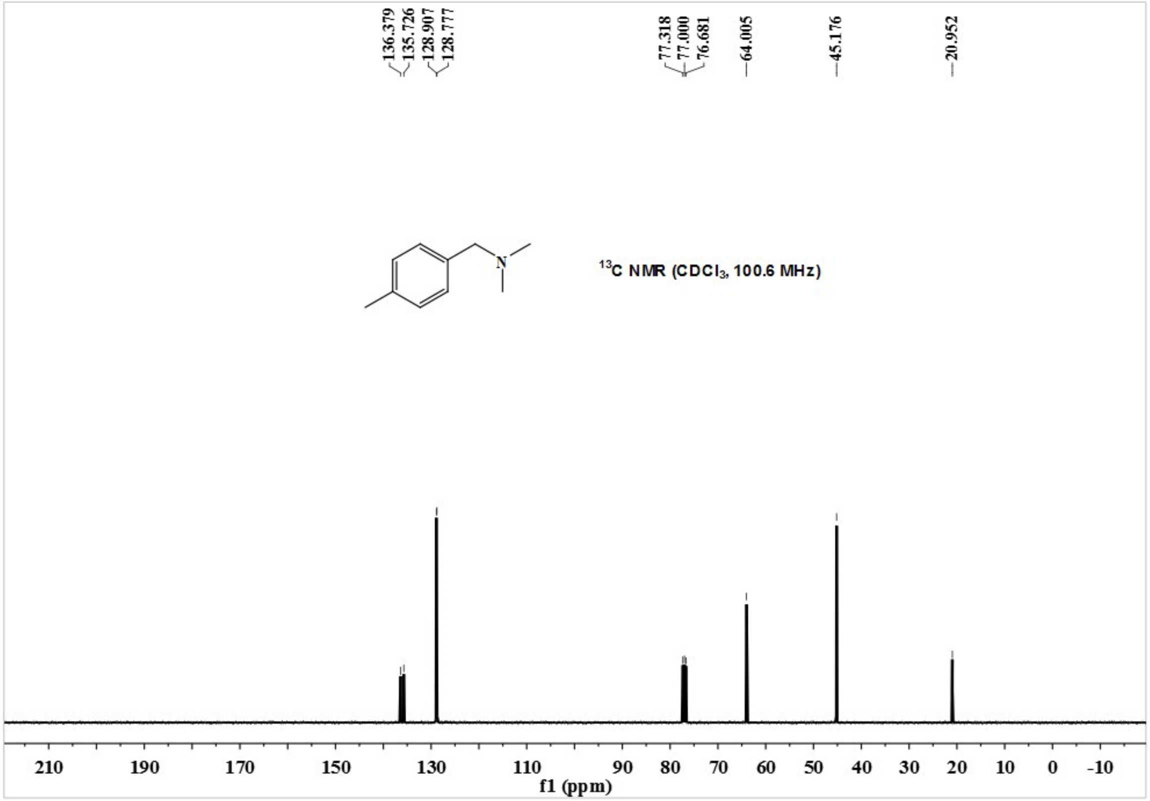
and

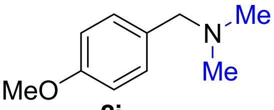


2i

^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.22 (s, 6H), 2.33 (s, 3H), 3.38 (s, 2H), 7.11-7.19 (m, 4H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 20.95, 45.18, 64.00, 128.78, 128.91, 135.73, 136.38.

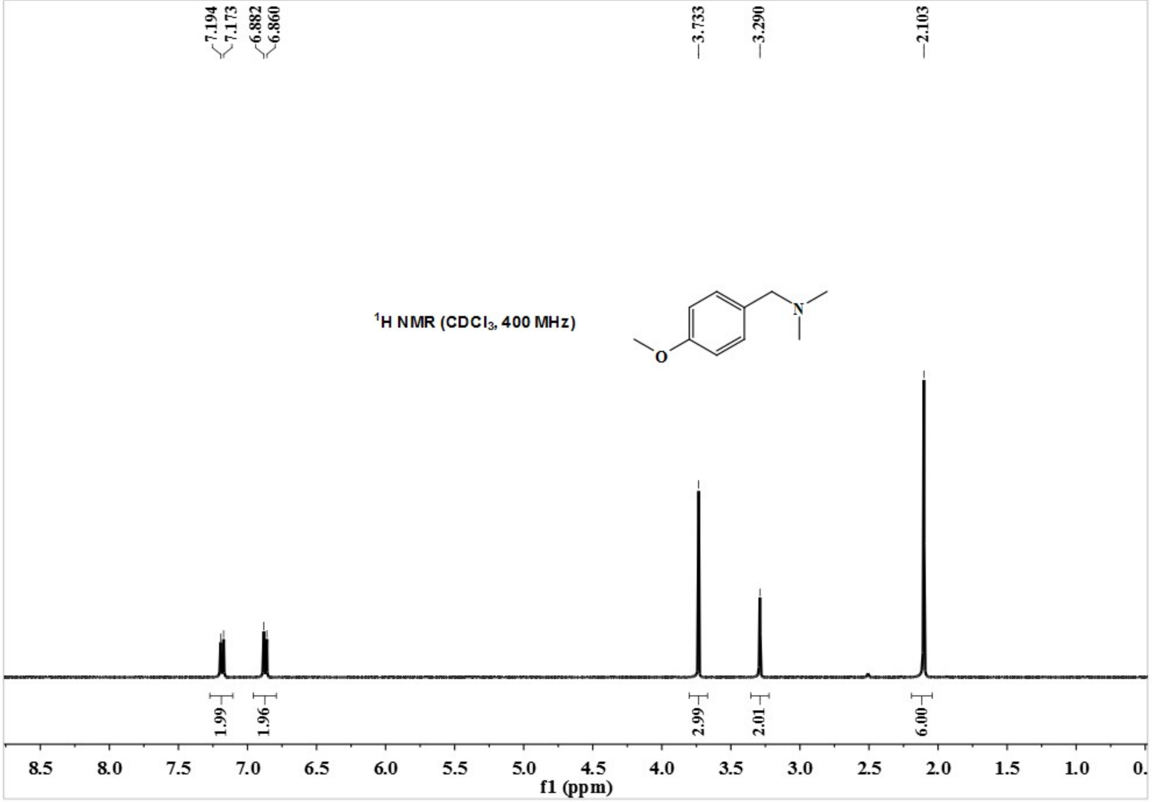


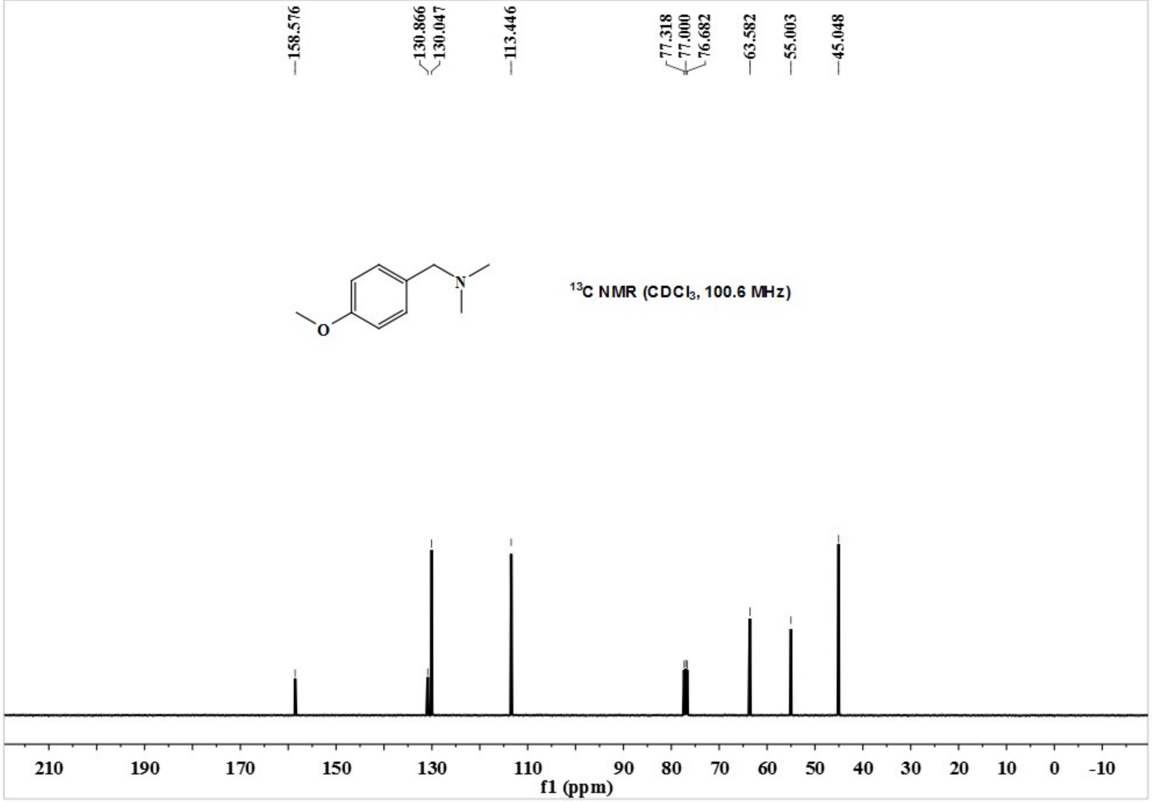


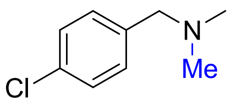


2j

^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.10 (s, 6H), 3.29 (s, 2H), 3.73 (s, 3H), 6.87 (d, ^3J = 8.8 Hz, 2H), 7.18 (d, ^3J = 8.4 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 45.05, 55.00, 63.58, 113.45, 130.05, 130.87, 158.58.

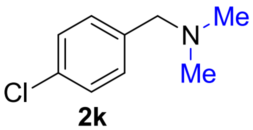

7.194
7.173
6.882
6.860
3.733
3.290
2.103
1H NMR (CDCl3, 400 MHz)
O
N
1.99
1.96
2.99
2.01
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.
f1 (ppm)


158.576
130.866
130.047
113.446
77.318
77.000
76.682
63.582
55.003
45.048
O
N
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



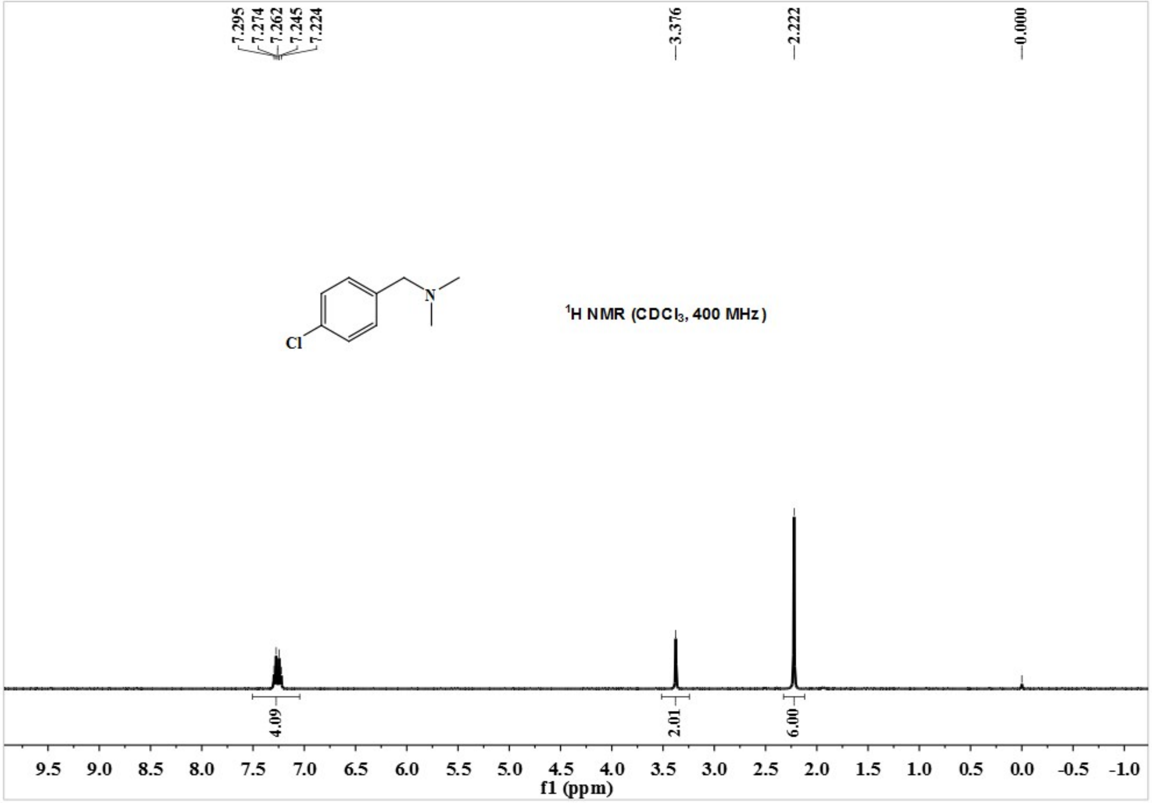
2g

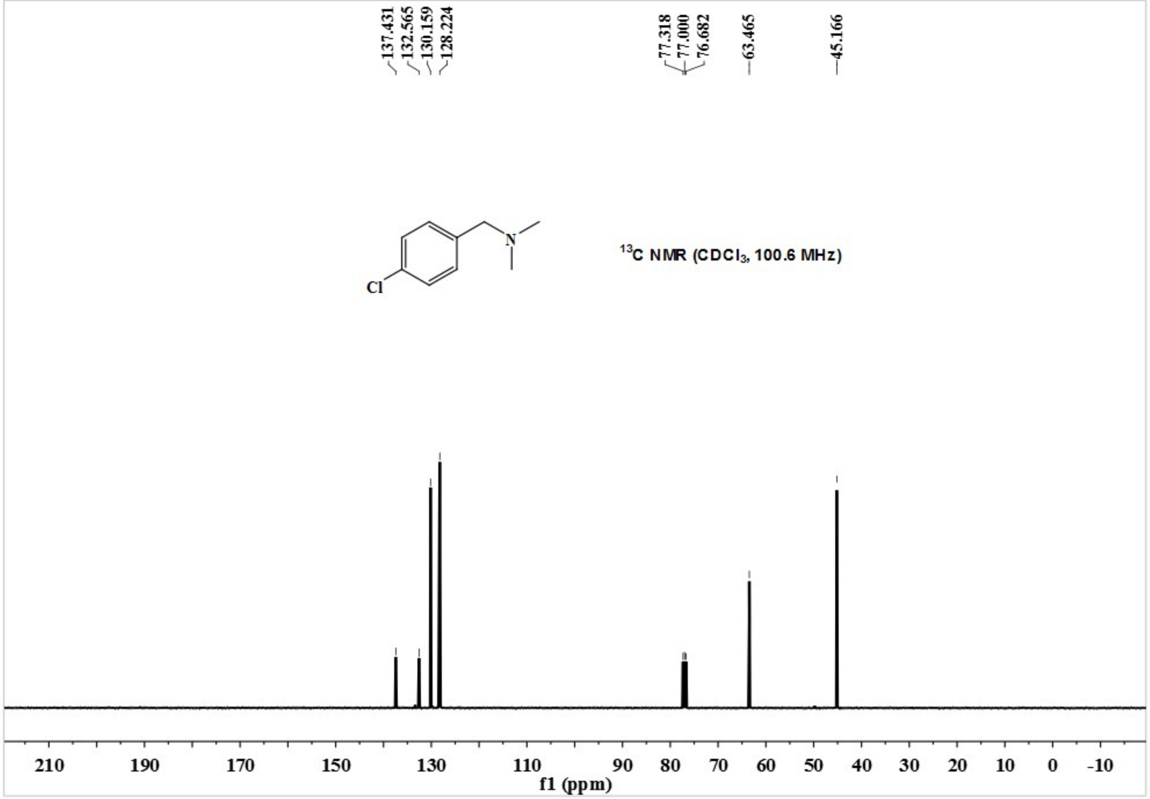
and



2k

^{1}H NMR (CDCl$_3$, 400 MHz) δ2.22 (s, 6H), 3.38 (s, 2H), 7.22-7.29 (m, 4H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 45.17, 63.46, 128.22, 130.16, 132.56, 137.43.




137.431
132.565
130.159
128.224
77.318
77.000
76.682
63.465
45.166
N
Cl
^{13}C NMR (CDCl$_3$, 100.6 MHz)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)