Supporting Information

N-monomethylation of amines using paraformaldehyde and H₂

Hongli Wang, Yongji Huang, Xingchao Dai and Feng Shi*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.
Contents

I. General Information and Experimental Section ..................S3
II. Characterization results of catalysts ..............................S6
III. Characterization data for products ..............................S10
IV. NMR spectra of the products ......................................S16
I. General Information and Experimental Section

General Information:

XRD measurements were conducted by using a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator with CuKa1 radiation and current of 40 kV and 150 mA, respectively. The XRD patterns were scanned in the 2 Theta range of 10-85°. XPS were obtained using a VG ES-CALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar⁺ iron gun. The electron binding energy was referenced to the C1s peak at 284.8 eV. The background pressure in the chamber was less than 10⁻⁷ Pa. The peaks were fitted by Gaussian–Lorentzian curves after a Shirley background subtraction. For quantitative analysis, the peak area was divided by the element-specific Scofield factor and the transmission function of the analyzer. The BET surface area measurements were performed on a Quantachrome IQ₂ at the temperature of 77 K. The pore size distribution was calculated from the desorption isotherm by using the Barrett, Joyner, and Halenda (BJH) method. Prior to measurements, the samples were degassed at 200 °C for 10 h, at a rate of 10 °C/min. TEM was carried out by using a Tecnai G2 F30 S-Twin transmission electron microscope operating at 300 kV. Single-particle EDX analysis was performed by using a Tecnai G2 F30 S-Twin Field Emission TEM in STEM mode. For TEM investigations, the catalysts were dispersed in ethanol by ultrasonication and deposited on carbon-coated copper grids. Extended X-ray absorption fine structure (EXAFS) experiments were performed at the Beijing Synchrotron Radiation Facility (BSRF) in Beijing Institute of High Energy Physics, Chinese Academy of Sciences with storage ring energy of 2.5 GeV and a beam current between 150 and 250 mA. The Cu K edge absorbance of powder catalysts was measured in transmission geometry at room temperature. The energy was scanned from -200 eV below to 800 eV above the Cu K edge (8979 eV). EXAFS data analysis was carried out using ifeffit analysis programs (http://cars9.uchicago.edu/ifeffit/). NMR spectra were measured by using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (¹H) and 100 MHz (¹³C). Chemical shifts were reported in parts per
million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants ($J$) were reported in Hz and refered to apparent peak multiplications.

**Experimental Section:**

All solvents and chemicals were obtained commercially and were used as received.

**Typical procedure for catalyst preparation:**

Cu(NO$_3$)$_2$·3H$_2$O (4.356g, 18 mmol) and Al(NO$_3$)$_3$·9H$_2$O (6.750 g, 18 mmol) were added to deionized water (60 mL) at rt and agitated until complete dissolution. Then, aqueous Na$_2$CO$_3$ (75 mL, 0.9 M) was added dropwise and the mixture was stirred for a further 5 h at 80 °C. The reaction mixture was centrifuged and washed with water to remove the base until the pH value of the aqueous solution was ≈ 7. Subsequently, the solid was dried at 100 °C in air for 5 h, calcined at 400 °C for 4 h, and then reduced under a hydrogen flow at 450 °C for 2.0 h. The resulting catalyst samples were denoted as CuAlOx(5 : 5).

**Typical procedure for N-monomethylation of amines with (HCHO)$_n$ and H$_2$**

A mixture of aniline 1a (97 mg, 1.0 mmol), paraformaldehyde (36 mg, 1.2 mmol), CuAlO$_x$(5:5) (20 mg ) and THF (3 mL) were added a glass tube which was placed in an 100 mL autoclave. Then the autoclave was purged and charged with H$_2$ (0.5 MPa) three times. The reaction mixture was stirred at 120 °C for 9 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with 5 mL of methanol for quantitative analysis by GC-FID (Agilent 7890A). The crude reaction mixture was concentrated by rotary evaporator and purified by column chromatography on a silica gel column. The isolated product was treated with HCl to give the desired products 3a.
Typical procedure for N-monomethylation of benzylamine with formaldehyde and H₂

A mixture of benzylamine \textbf{1m} (128 mg, 1.2 mmol), 37% formaldehyde (81 mg, 1.0 mmol), and THF (3 mL) were added to a glass tube which was placed in a 100 mL autoclave. The reaction mixture was stirred at 120 °C for 9 h. Then, the autoclave was cooled to room temperature and purged and charged with H₂ (0.5 MPa) three times. The reaction mixture was stirred at 140 °C for 9 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, biphenyl was added to the reaction mixture which was diluted with 7 mL of methanol for quantitative analysis by GC-FID (Agilent 7890A).

Typical procedure for N-monomethylation of cyclohexylamine with formaldehyde and H₂

A mixture of cyclohexylamine \textbf{1n} (120 mg, 1.2 mmol), 37% formaldehyde (81 mg, 1.0 mmol), and THF (3 mL) were added to a glass tube which was placed in an 100 mL autoclave. The reaction mixture was stirred at 120 °C for 9 h. Then, the autoclave was cooled to room temperature and purged and charged with H₂ (0.5 MPa) three times. The reaction mixture was stirred at 140 °C for 9 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The crude reaction mixture was filtered and filtrate was concentrated by rotary evaporator. MeNO₂ was added to mixture for quantitative analysis by \textsuperscript{1}H NMR.
II. Characterization results of catalysts

1. Table S1. Reaction conditions optimization for N-methylation of aniline

\[ \text{CuAlO}_x, \text{H}_2 (\text{X MPa}), \text{THF}, 120^\circ\text{C} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>CuAlO\text{x}</th>
<th>H\text{2} (x MPa)</th>
<th>solvent</th>
<th>Conv.\text{b} (%)</th>
<th>Sel.\text{c} (%)</th>
<th>3a</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>7a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2 : 8) 50 mg</td>
<td>1.0</td>
<td>THF</td>
<td>80</td>
<td>76</td>
<td>10</td>
<td>13</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>(3 : 7) 50 mg</td>
<td>1.0</td>
<td>THF</td>
<td>78</td>
<td>87</td>
<td>1</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>(5 : 5) 50 mg</td>
<td>1.0</td>
<td>THF</td>
<td>94</td>
<td>97</td>
<td>3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>(7 : 3) 50 mg</td>
<td>1.0</td>
<td>THF</td>
<td>90</td>
<td>91</td>
<td>9</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>(8 : 2) 50 mg</td>
<td>1.0</td>
<td>THF</td>
<td>90</td>
<td>91</td>
<td>8</td>
<td>--</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>(5 : 5) 50 mg</td>
<td>1.0</td>
<td>toluene</td>
<td>75</td>
<td>44</td>
<td>48</td>
<td>--</td>
<td>2</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>(5 : 5) 50 mg</td>
<td>1.0</td>
<td>1,4-dioxane</td>
<td>90</td>
<td>98</td>
<td>2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>(5 : 5) 50 mg</td>
<td>1.0</td>
<td>cyclohexane</td>
<td>86</td>
<td>94</td>
<td>6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>(5 : 5) 30 mg</td>
<td>1.0</td>
<td>THF</td>
<td>91</td>
<td>98</td>
<td>2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>(5 : 5) 20 mg</td>
<td>1.0</td>
<td>THF</td>
<td>96</td>
<td>96</td>
<td>4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>11</td>
<td>(5 : 5) 10 mg</td>
<td>1.0</td>
<td>THF</td>
<td>94</td>
<td>89</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>12</td>
<td>(5 : 5) 5 mg</td>
<td>1.0</td>
<td>THF</td>
<td>93</td>
<td>77</td>
<td>2</td>
<td>13</td>
<td>6</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>13</td>
<td>(5 : 5) 20 mg</td>
<td>0.5</td>
<td>THF</td>
<td>89</td>
<td>94</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>14</td>
<td>(5 : 5) 20 mg</td>
<td>0.2</td>
<td>THF</td>
<td>83</td>
<td>95</td>
<td>--</td>
<td>3</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>15\text{d}</td>
<td>(5 : 5) 20 mg</td>
<td>0.5</td>
<td>THF</td>
<td>80</td>
<td>96</td>
<td>1</td>
<td>--</td>
<td>3</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>16\text{e}</td>
<td>(5 : 5) 20 mg</td>
<td>0.5</td>
<td>THF</td>
<td>56</td>
<td>--</td>
<td>97</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>17\text{f}</td>
<td>(5 : 5) 20 mg</td>
<td>0.5</td>
<td>THF</td>
<td>97\text{(98\text{g})}</td>
<td>93\text{(91\text{h})}</td>
<td>7\text{(9\text{i})}</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

\text{a}1a (1.0 mmol), paraformaldehyde (1.2 mmol), CuAlO\text{x} (5 : 5) (20 mg), H\text{2} (1.0 Mpa), THF (3.0 mL), 120 °C, 5 h; \text{b}Conversion of aniline was determined by GC-MC; \text{c}Selectivity by GC-MS analysis based on the aniline consumed; \text{d}100 °C; \text{e}80 °C; \text{f}9 h. \text{g}The catalyst was recovered and reused at the 3rd run.
2. Table S2. The physical properties of catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Cu wt%</th>
<th>SA (m²/g)</th>
<th>PV (cm³/g)</th>
<th>APS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuAlOx (2:8)</td>
<td>17</td>
<td>59.2</td>
<td>0.46</td>
<td>15.4</td>
</tr>
<tr>
<td>2</td>
<td>CuAlOx (3:7)</td>
<td>27</td>
<td>85.9</td>
<td>0.30</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>CuAlOx (5:5)</td>
<td>57</td>
<td>58.7</td>
<td>0.28</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>CuAlOx (7:3)</td>
<td>82</td>
<td>52.4</td>
<td>0.27</td>
<td>10.0</td>
</tr>
<tr>
<td>5</td>
<td>CuAlOx (8:2)</td>
<td>83</td>
<td>36.3</td>
<td>0.26</td>
<td>15.5</td>
</tr>
</tbody>
</table>

\(^a\) Determined by ICP-AES. \(^b\) Determined by an IQ2 automated gas sorption analyser. SA: Surface area; PV: Pore volume; APS: Average pore size

3. Fig. S1 BJH Desorption patterns of prepared CuAlOx catalysts
4. Fig. S2 XPS diffraction patterns of prepared CuAlOx(5:5)
5. Fig. S3 XRD diffraction patterns for (a) CuAlOx (2:8), (b) CuAlOx (3:7), (c) CuAlOx (5:5), (d) CuAlOx (7:3), (e) CuAlOx (8:2), (f) CuAlOx (5:5) used three times.

6. Fig. S4 TEM (a), HR-TEM (b), HAADF (c) and the line-scan EDS analysis (d) images of the fresh catalyst CuAlOx(5:5)
7. Fig. S5 TEM (a), HR-TEM (b), HAADF (c) and the line-scan EDS analysis (d) images of the used three times catalyst CuAlOx(5:5)
III. Characterization data for products

N-methylaniline hydrochloride (3a): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (30 : 1 to 10 : 1) to give the desired product which was treated with HCl to give a brown solid. 127 mg, 89% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.03 (s, 3H), 7.40-7.48 (m, 3H), 7.64-7.66 (m, 2H), 11.55 (brs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 37.9, 122.6, 129.5, 130.2, 137.0.

N,4-dimethylaniline hydrochloride (3b): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (40 : 1 to 10 : 1) to give the desired product which was treated with HCl to give a red-brown solid. 134 mg, 85% yield. $^1$H NMR (400 MHz, D$_2$O) $\delta$ 2.33 (s, 3H), 3.02 (s, 3H), 7.31-7.36 (m, 4H); $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 20.1, 36.8, 121.5, 130.7, 133.5, 140.4.

N, 2-dimethylaniline hydrochloride (3c): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (50 : 1 to 30 : 1) to give the desired product which was treated with HCl to give a red-brown solid. 132 mg, 84% yield. $^1$H NMR (400 MHz, D$_2$O) $\delta$ 2.39 (s, 3H), 3.04 (s, 3H), 7.37-7.39 (m, 4H); $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 16.0, 35.8, 121.8, 127.8, 129.8, 131.0, 132.3, 134.6.

N, 3, 5-trimethylaniline hydrochloride (3d): The title compound was prepared according to the general procedure and purified by column chromatography using
petroleum ether /diethyl ether (30 : 1 to 10 : 1) to give the desired product which was treated with HCl to give a red-brown solid. 142 mg, 83% yield. $^1$H NMR (400 MHz, D$_2$O) δ 2.30 (s, 6H), 3.00 (s, 3H), 7.07 (s, 2H), 7.16 (s, 1H); $^{13}$C NMR (100 MHz, D$_2$O) δ 20.2, 36.8, 119.1, 131.1, 136.1, 140.9.

![4-(tert-butyl)-N-methylaniline hydrochloride (3e)](image)

4-(tert-butyl)-N-methylaniline hydrochloride (3e)$^5$: The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (30 : 1 to 10 : 1) to give the desired product which was treated with HCl to give red-brown solid. 160 mg, 80% yield. The product was treated with HCl to give a red-brown solid. $^1$H NMR (400 MHz, D$_2$O) δ 1.29 (s, 9H), 3.06 (s, 3H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 30.4 34.2, 37.0, 121.5, 127.4, 133.6, 153.6.

![4-methoxy-N-methylaniline (3f)](image)

4-methoxy-N-methylaniline (3f)$^6$: The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (10 : 1 to 6 : 1) to give a brown solid. 104 mg, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.81 (s, 3H), 3.25 (brs, 1H), 3.76 (s, 3H), 6.58-6.62 (m, 2H), 6.79-6.83 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 31.6, 55.8, 113.6, 114.9, 143.6, 152.1.

![4-fluoro-N-methylaniline hydrochloride (3g)](image)

4-fluoro-N-methylaniline hydrochloride (3g)$^7$: The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (30 : 1 to 10 : 1) to give the desired product which was treated with HCl to give a purple solid. 113 mg, 70% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.98 (s, 3H), 7.08-7.13 (m, 2H), 6.63-7.66 (m, 2H), 11.50 (brs, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -110.34; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 38.2, 117.2 ($J = 23.1$ Hz), 124.6 ($J = 8.7$ Hz), 132.91 ($J = 3.1$ Hz), 162.6 ($J = 249.1$ Hz).
4-chloro-N-methylaniline (3h): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (40 : 1 to 10 : 1) to give yellow oil. 105 mg, 74% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.82 (s, 3H), 3.72 (brs, 1H), 6.53 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 30.8, 113.4, 121.8, 129.0, 147.8.

4-bromo-N-methylaniline hydrochloride (3i): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (10 : 1 to 6 : 1) to give the desired product which was treated with HCl to give a red-brown solid. 154 mg, 69% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.98 (s, 3H), 7.51-7.57 (m, 4H), 11.55 (brs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 37.9, 123.7, 124.4, 133.4, 136.0.

Ethyl 4-(methylamino)benzoate (3j): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (8 : 1 to 4 : 1) to give a white solid. 141 mg, 79% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.36 (t, $J = 7.0$ Hz, 3H), 2.88 (s, 3H), 4.29 (brs, 1H), 4.32 (t, $J = 7.0$ Hz, 2H), 6.55 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.4, 30.1, 60.1, 111.1, 118.6, 131.4, 152.8, 166.9.

4-(methylamino)benzonitrile (3k): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (3 : 1) to give white solid. 81 mg, 61% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.87 (s,
3H), 4.33 (brs, 1H), 6.55 (d, \(J = 8.8\) Hz, 2H), 7.42 (d, \(J = 8.4\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 29.9, 98.4, 111.8, 120.5, 133.6, 152.2.

**N-methylnaphthalen-2-amine (3l)**: The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether /diethyl ether (50 : 1 to 10 : 1) to give yellow oil. 127 mg, 81% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.01 (s, 3H), 4.54 (brs, 1H), 6.61 (d, \(J = 7.6\) Hz, 1H), 7.25 (d, \(J = 8.0\) Hz, 1H), 7.37 (t, \(J = 8.0\) Hz, 1H), 7.41-7.47 (m, 2H), 7.76-7.80 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 31.1, 103.9, 117.4, 119.8, 123.4, 124.7, 125.7, 126.6, 128.6, 134.2, 144.4.

**4-methylmorpholine hydrochloride (3p)**: The title compound was prepared according to the general procedure and purified by column chromatography using DCM / MeOH (30 : 1 to 10 : 1) to give the desired product which was treated with HCl to give a white solid. 109 mg, 79% yield. \(^1\)H NMR (400 MHz, D\(_2\)O) 2.92 (s, 3H), 3.20 (td, \(J_1 = 12.4\) Hz, \(J_2 = 3.6\) Hz, 2H), 3.47-3.50 (m, 2H), 3.80 (td, \(J_1 = 12.6\) Hz, \(J_2 = 2.0\) Hz, 2H), 4.2 (dd, \(J_1 = 13.2\) Hz, \(J_2 = 3.2\) Hz, 2H); \(^{13}\)C NMR (100 MHz, D\(_2\)O) \(\delta\) 43.3, 53.2, 63.9.

**1-ethyl-4-methylpiperazine hydrochloride (3q)**: The title compound was prepared according to the general procedure and purified by column chromatography using DCM / MeOH (10 : 1 to 6 : 1) to give the desired product which was treated with HCl to give white solid. 199 mg, 99% yield. \(^1\)H NMR (400 MHz, D\(_2\)O) 1.33 (t, \(J = 7.4\) Hz, 3H), 3.01 (s, 3H), 3.34 (q, \(J = 7.2\) Hz, 2H), 3.43 (brs, 2H), 3.89 (brs, 2H); \(^{13}\)C NMR (100 MHz, D\(_2\)O) \(\delta\) 8.6, 42.9, 48.1, 50.3, 52.4.
N-methyl-N-octyl-1-amino hydrochloride (3r): The title compound was prepared according to the general procedure and purified by column chromatography petroleum ether / ethyl acetate (6:1 to 4:1) to give the desired product which was treated with HCl to give a white solid. 256.5 mg, 88% yield. $^1$H NMR (400 MHz, CDCl$_3$) 0.85 (t, $J$ = 6.8 Hz, 6H), 1.22-1.29 (m, 20H), 1.79 (brs, 4H), 2.70 (s, 3H), 2.91 (brs, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 22.5, 23.6, 26.7, 28.9, 31.6, 39.76, 55.66.

N-benzyl-N-methyl-1-phenylmethanamine (3s): The title compound was prepared according to the general procedure and purified by column chromatography using petroleum ether / diethyl ether (30:1 to 10:1) to give yellow oil. 158 mg, 75% yield. $^1$H NMR (400 MHz, CDCl$_3$) 2.18-2.19 (m, 3H), 3.52 (s, 4H), 7.23-7.26 (m, 2H), 7.30-7.38 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 42.2, 61.9, 126.9, 128.2, 128.9, 139.3.

N-benzyl-N-methylethanamine hydrochloride (3t): The title compound was prepared according to the general procedure and purified by column chromatography petroleum ether / ethyl acetate (4:1 to 2:1) to give the desired product which was treated with HCl to give a white solid. 183 mg, 99% yield. $^1$H NMR (400 MHz, D$_2$O) 1.28 (t, $J$ = 7.4 Hz, 3H), 2.71 (s, 3H), 3.04-3.13 (m, 1H), 3.22-3.31 (m, 1H), 4.16 (d, $J$ = 13.2 Hz, 1H), 4.36 (d, $J$ = 13.2 Hz, 1H), 7.42-7.48 (m, 5H); $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 8.7, 38.5, 50.9, 59.2, 129.2, 129.3, 130.1, 130.9.

N-ethyl-N-methylcyclohexanamine hydrochloride (3u): The title compound was prepared according to the general procedure and purified by column chromatography using DCM / MeOH (10:1 to 8:1) to give the desired product which was treated with HCl to give a
white solid. 175 mg, 99% yield. **H NMR** (400 MHz, D$_2$O) 1.02-1.12 (m, 1H), 1.20-1.47 (m, 7H), 1.58 (d, $J$ = 6.2 Hz, 1H), 1.80 (d, $J$ = 6.2 Hz, 2H), 1.90 (brs, 2H), 2.68 (s, 3H), 2.99-3.08 (m, 1H), 3.15-3.25 (m, 2H); **C NMR** (100 MHz, D$_2$O) δ 9.2, 24.3, 24.5, 24.5, 25.3, 27.2, 35.2, 48.9, 64.2.

**N,N-dimethylaniline hydrochloride (3v)**: The title compound was prepared according to the general procedure and purified by column chromatography petroleum ether/diethyl ether (50 : 1 to 30 : 1) to give the desired product which was treated with HCl to give a white solid. 106 mg, 67% yield. **H NMR** (400 MHz, D$_2$O) 3.26-3.27 (m, 6H), 7.57-7.58 (m, 5H); **C NMR** (100 MHz, D$_2$O) δ 46.3, 120.2, 130.4, 130.6, 141.9.

**References:**

IV. NMR spectra of all products

![NMR spectra diagram]

- **NMR spectra of all products**
- **Diagram showing NMR spectra with peak assignments**